THE UNIVERSITY OF MANITOBA

STUDIES ON HETEROCYCLIC SULFUR COMPOUNDS

by

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TO MY PARENTS

ABSTRACT

4,5-Diphenyl-1,2-dithiole-3-thione reacts with dimethyl acetylenedicarboxylate, ethyl propiolate and ethyl phenylpropiolate via a (3 +2) cycloaddition to provide the corresponding mono-adducts, formulated as 2-(2-thioacylmethylene)-1,3-dithioles. Further reaction provides di-adducts, formulated as thiopyranspiro-1,3-dithioles, via a (4 +2) cycloaddition of the initially formed mono-adducts with the respective acetylenic esters, only in the case of dimethyl acetylenedicarboxylate and ethyl propiolate. The mono-adducts, formed from the unsymmetrical acetylenic esters, are found to consist of two 2-(2-thioacylmethylene) -1,3-dithioles (as indicated by n.m.r.) which are probably *s-cis* geometrical isomers (with respect to the exocyclic double bond). N.m.r. studies indicate that the two *s-cis* isomers may possibly be formed during the reaction and may not be interconvertible. The (4 + 2) cycloaddition of 2-(2-thioacylmethylene)-1,3-dithioles with ethyl propiolate occurs in only one direction, as indicated by n.m.r.

1,2-Dithiole-3-thione and 4-phenyl-1,2-dithiole-3-thione both react with dimethyl acetylenedicarboxylate and dibenzoylacetylene to give, in each case, an unstable 2-thioformylmethylene-1,3-dithiole which forms a bis-dithiolylidene-2-butene probably by extrusion of a sulfur atom from two 2-thioformylmethylene-1,3-dithioles. Further reaction of the 2-thioformylmethylene-1,3-dithioles (from 4-phenyl-1,2-dithiole-3-thione only) with the acetylenes provides the corresponding thiopyranspiro-1,3-dithioles. These same 2-thioformylmethylene-1,3-dithioles form the corresponding 2-formylmethylene-1,3-dithioles, possibly either by oxidation or by hydrolysis.

4,5-Diphenyl-1,2-dithiole-3-thione and 5-phenyl-1,2-dithiole-3-thione both do not react with *trans*-dibenzoylethylene but react with dibenzoylacetylene to give the corresponding 2-(2-thioacylmethylene)-1,3-dithioles and the corresponding thiopyranspiro-1,3-dithioles. Sulfurization of these thioacylmethylene-1,3-dithioles with phosphorus pentasulfide does not yield the expected thieno [3,4,d]-1,3-dithiole, but gives the corresponding 1,2-dithiole-3-thiones. However, sulfurization of 4,5-dibenzoyl-1,3-dithiole-2-spiro-4-(2-phenyl-5,6-dibenzoylthiopyran) with phosphorus pentasulfide gives the expected thienothiopyranspirothieno [3,4,d]-1,3-dithiole. To permit the preparation of thieno-[3,4,d]-1,3-dithioles without the 2-thioacylmethylene side chain, attempts were made to obtain 4,5-dibenzoyl-1,3-dithiole-2-thione by reaction of dibenzoylacetylene with 1,3-dithiolane-2-thione and with 4,5-diphenyl-1,3-dithiole-2-thione. Both attempts failed.

Reaction of 3-phenylimino-5-phenyl-1,2-dithiole and 4,5-diphenyl-3-phenylimino-1,2-dithiole with dimethyl acetylenedicarboxylate gives, in both cases, only a thiopyranspirothiazole. 3-Phenylimino-5-phenyl-1,2-dithiole reacts with ethyl propiolate and ethyl phenylpropiolate to give, in each case, only one 2-(2-thioacylmethylene) thiazole, as indicated by n.m.r. 4,5-Diphenyl-3-phenylimino-1,2-dithiole does not react with either ethyl propiolate or ethyl phenylpropiolate.

3-Benzylidene-5-phenyl-1,2-dithiole reacts with dimethyl acetylenedicarboxylate to give products which could not be purified satisfactorily. Reaction of N-phenyl-5-phenylisothiazolium perchlorate with sulfur in pyridine does not give the expected Δ^4-isothiazolin-3-thione but gives 3-phenylimino-5-phenyl-1,2-dithiole. The synthesis

of an isothiaphospholium salt by reaction of a 1,2-dithiolium salt with phenyl phosphine and the synthesis of a Δ^3-isothiaphospholin-5-thione were unsuccessful.

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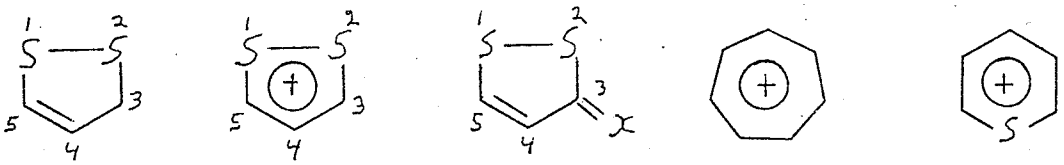
The symbols, units, nomenclature and numbering of compounds conform with those used in Canadian Journal of Chemistry, e.g., 4,5-diphenyl-1,2-dithiole-3-thione (27) or the 1,2-dithiole-3-thione 27.

INTRODUCTION

General

The 1,2-dithiole system 1 is a heterocyclic ring consisting of three carbon atoms and two sulfur atoms. Two examples of this system were of interest: the aromatic 1,2-dithiolium cationic system 2 and the 1,2-dithioles 3 in which the five-membered ring contains one double bond while the other double bond is exocyclic.

The concept of isosterism [1] requires that a $-\ddot{S}-$ atom replaces a $-CH=CH-$ group in an aromatic system. Since the sulfur atom, through the participation of *d* orbitals, is capable of accommodating a decet of electrons in its outer shell, it is also possible to regard the replacement as one of $=\ddot{S}=$ for $=CH-CH=$. Thus, by successive replacements, the tropylium cationic system 4 gives rise, first to the thiopyrylium cationic system 5 and then to the dithiolium cationic system 2. Thus dithiolium salts are isosteres of tropylium and thiopyrylium salts, and in accordance with this isosterism, the properties of the dithiolium salts should parallel, to some extent, those of the tropylium salts [2-4] and those of the thiopyrylium salts [5,6].

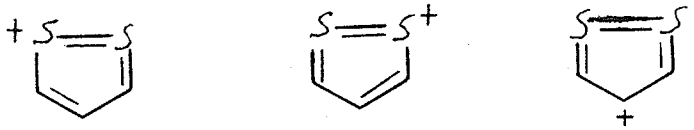


1 2 3 4 5

The resonance forms 2 a,b, c and d are the contributing structures of the 1,2-dithiolium system not utilizing sulfur 3 *d* orbitals, while the resonance forms 2 e,f and g are contributing structures using *d* orbitals. From consideration of these resonance forms, it would be expected that positions -3 and -5 in 2c and 2d respectively, should be activated

towards nucleophilic attack. If the decet forms 2 e, f and g have any significant influence, position -4, 2 g, should also be susceptible to nucleophilic attack. Although nucleophilic attack does take place preferentially at positions -3 and -5, very "thiophilic" groups must also be expected to attack one of the sulfur atoms, leading either to cleavage of the disulfide bridge or less likely, to occupation of a *d* orbital of the sulfur[7,8]. No evidence has been presented for nucleophilic attack at postion -4.

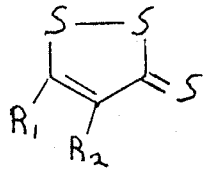
2 a b c d



2 e f g

The dithioles 3 are potentially aromatic structures. Compounds containing this type of structure are the 1,2-dithiole-3-thiones 6, the 3-alkylidene-1,2-dithioles 7 and the 3-imino-1,2-dithioles 8. All possibilities of aromaticity in these compounds require charge-separated polar structures. If the compounds 6, 7 and 8 are not resonance stabilized they would react only as α-β unsaturated thiones, 1,3-dienes and α-β unsaturated imines, respectively. Of the possible polar canonical forms of the dithioles 3, the structures 3 e,f and g utilize the *d* orbitals of the sulfur atoms. It would be expected that positions -3 and -5 in 3a and 3d, respectively, should be activated towards nucleophilic attack

as is the case with dithiolium salts. Similarly, if the decet forms 3 e,f and g have any significant contributions to the resonance hybrid, nucleophilic attack might also occur in position -4, 3g. Analogously with the reactions of dithiolium salts, only positions -3 and -5 are found to be sites for nucleophilic attack.



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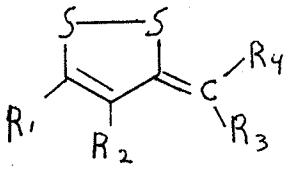

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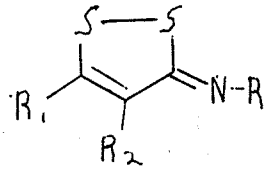

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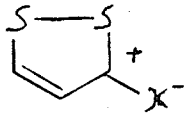
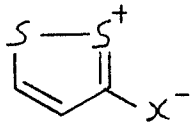
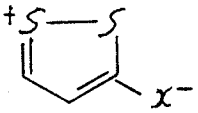


3 a



b



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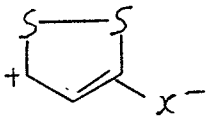
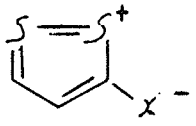
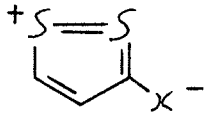


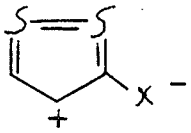
d



3 e



f



g

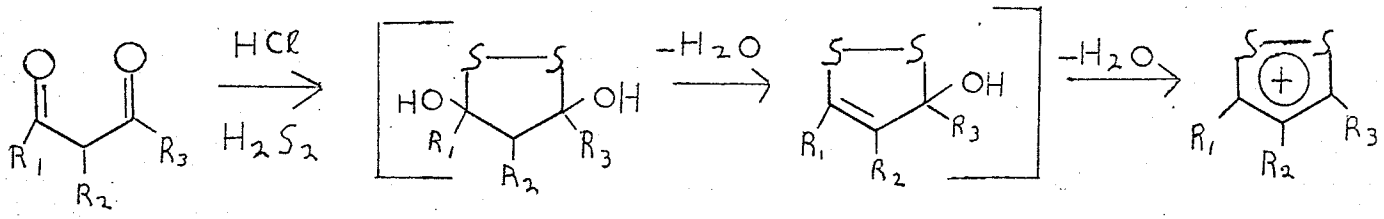
PART I: 1,2-Dithiolium Salts

Section A: Preparation of 1,2-Dithiolium Salts

The synthesis of 1,2-dithiolium salts containing only alkyl and aryl substituents will be discussed in this section.

1. From 1,3-Diketones and 1,3-Ketothiones.

Leaver[9] reported the synthesis of dithiolium salts by the action of hydrogen disulfide on 1,3-diketones in ether solutions saturated with hydrogen chloride. Although no intermediates have been isolated, the formation of the dithiole 10 has been postulated as an unstable intermediate in this reaction. The salts 11 a,b, and c, isolated as the perchlorate salts, were obtained in good yields. Schmidt and Schulz[10] have also prepared these salts and the salt 11 d using hydrogen disulfide, hydrogen trisulfide and hydrogen polysulfide (S∿5) in various solvents saturated with hydrogen chloride. Various alkyl and aryl dithiolium salts have also been prepared by Dingwall, McKenzie and Reid by the treatment of 1,3-diketones with hydrogen disulfide either in a solution of perchloric acid and acetic acid or in acetic acid saturated with hydrogen bromide[11].



9 10 11

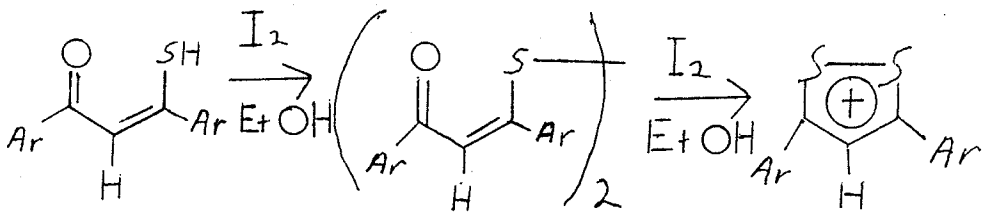
11 a) $R_1 = R_3 = Ph$, $R_2 = H$

b) $R_1 = Ph$, $R_2 = H$, $R_3 = CH_3$

c) $R_1 = R_3 = CH_3$, $R_2 = H$

d) $R_1 = R_3 = CH_3$, $R_2 = Ph$

Various 3,5-diaryl-1,2-dithiolium salts 14, isolated as the triiodides, have been obtained by the oxidation of 1,3-diaryl-3-mercapto-prop-2-ene-1-ones 12 using iodine in ethanol[12]. It has been shown that the disulfides 13 are the initial products formed in the oxidation and further oxidation leads to the dithiolium salts 14[12].



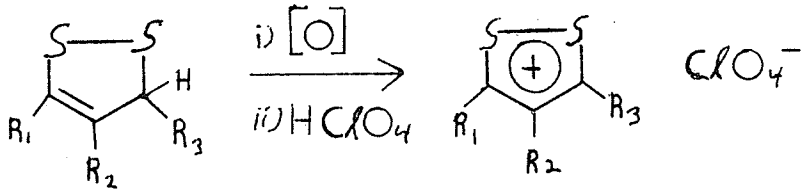
12 13 14

A variation of the above procedures involves the action of phosphorus pentasulfide on 1,3-diketones or 1,3-ketothiones followed by treatment with acid[13]. Only 3,5-disubstituted-1,2-dithiolium salts with at least one aryl substituent have been prepared.

2. From 1,2-Dithiole Derivatives.

(a) Oxidation.

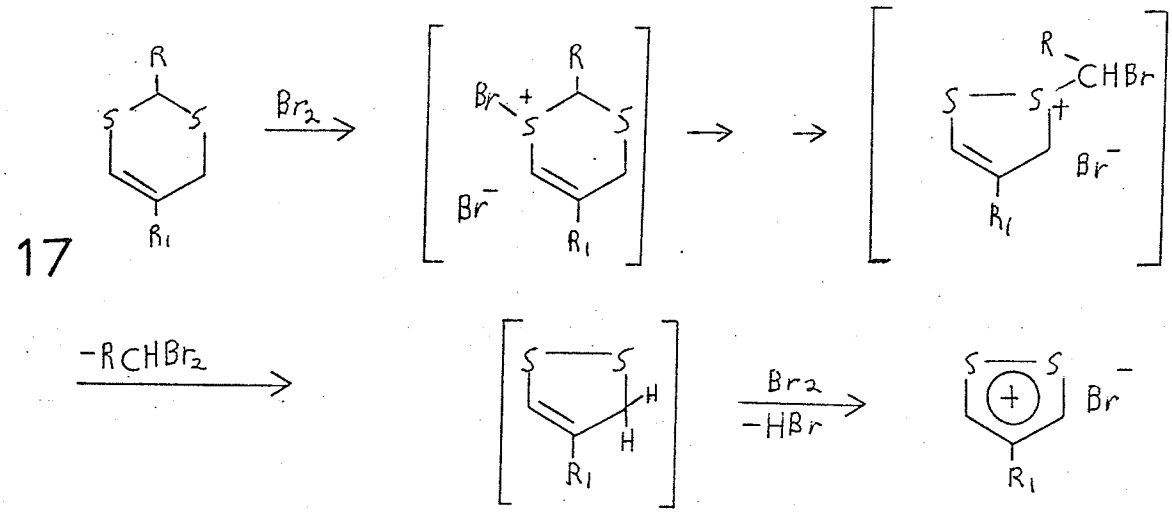
Oxidation of the dithiole 15 a by potassium persulfate gives the 1,2-dithiolium salt 16 a, isolated as the perchlorate salt[14]. This synthetic route has not been extended because of the thermal instability of most 1,2-dithioles of the general type 15. It has been shown that 1,2-dithiole derivatives 15 can be isolated only if the ring is stabilized by several aryl substituents[15].



15 16

a) $R_1 = H, R_2 = Ph, R_3 = p\text{-}(CH_3)_2N\text{-}C_6H_4$

An unusual route to 1,2-dithiolium salts involves oxidative ring contraction of 1,3-dithio-cyclohexenes 17[5]. Treatment of the cyclohexenes 17 with bromine yield the 4-substituted-1,2-dithiolium bromides 19. The dithiole 18 has been postulated as an unstable intermediate in this reaction. Sulfuryl chloride has also been used as the oxidizing agent.

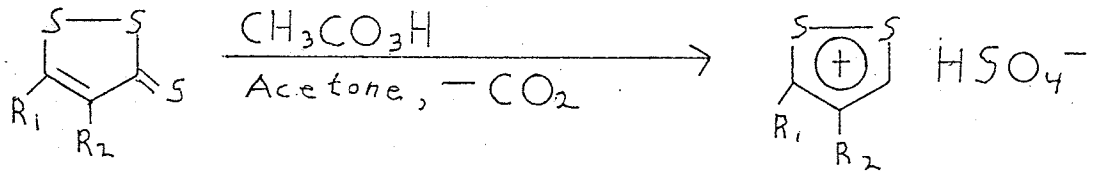


17 18 19

(b) Reduction.

The reduction of 4,5-substituted-1,2-dithiole-3-thiones 20 to the corresponding 3,4-substituted-1,2-dithiolium salts 21 with 40% peracetic acid in acetone generally gives the salts 21 in good yields[3,16]. The thione sulfur is eliminated as the hydrogen sulfate anion. In this manner, 3-thio-1,2-dithiole-4-carboxylic acid (20a) upon oxidation of the thione function gives 1,2-dithiolium hydrogen sulfate (21 a) with spontaneous decarboxylation of the acid function[3]. The success of this reaction has been attributed to the relative insolubility of the hydrogen sulfate salts 21 in acetone[16]. An analogy has been drawn with the preparation of thiazoles[17], imidazoles[18,19], 1,3-dithiolium salts[20,21] and thiopyrylium salts[22] from the corresponding 2-thione derivatives. Most 3- and 4- monosubstituted and 3,4-disubstituted alkyl and aryl

salts have been prepared using this procedure.



20a

$R_1 = CO_2H$, $R_2 = H$

21a

$R_1 = R_2 = H$

Variations of the Klingsberg method[3] involve oxidation with 30% hydrogen peroxide in glacial acetic acid[21] or in a methanol-sulfuric acid medium[23]. Oxidation with chlorine in glacial acetic acid is more complex and gives the salts 21 in poor yields[24].

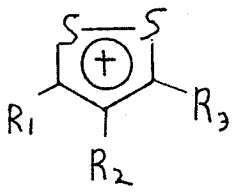
Section B: Reactions of 1,2-Dithiolium Salts

It is expected that 1,2-dithiolium salts would be susceptible to nucleophilic reagents and not to electrophilic reagents. Accordingly, under nitration conditions, the dithiole ring is resistant to attack e.g., the 4-phenyl-1,2-dithiolium cation 22a is nitrated in the *p*-position of the phenyl group while the 3-phenyl isomer 22b (R_1=Ph) is nitrated in the *p*- and *m*- positions[3]. The reactions of some nucleophilic nitrogen reagents with aryl and alkyl substituted 1,2-dithiolium salts will be discussed in this Section.

1. With Ammonia.

1,2-Dithiolium salts 22a and b react with ammonia in ethanol or with ammonium acetate in acetic acid to give the isothiazoles 25a and b, respectively[9,25]. Here as in the reaction of pyrylium[26,27] and thiopyrylium salts[28] with ammonia, a ring heteroatom is replaced by nitrogen. Nucleophilic attack occurs at position -3 for 4-phenyl-1,2-dithiolium perchlorate (22a), but at either position -3 or -5 for 5-aryl-1,2-dithiolium perchlorates 22b. However, under a variety of conditions, the 5-arylisothiazole 25b is the major product and in many cases, the only product when the salt 22b is used[25]. The mechanism was shown to be one of addition-elimination followed by ring closure via displacement of sulfhydride ion by the nucleophilic nitrogen present in either of the open-chain compounds 23 or 24[25]. (See next page.)

A different mechanism is operative when 4-phenyl-1,2-dithiolium perchlorate (22a) is treated with ammonia in dry benzene[15]. 4-Phenylisothiazole (25a) is found only as a minor product, the bisdithioylsulfide 26 being the major fraction found. The sulfide 26 is probably formed from two dithiolium cations and hydrogen sulfide which would be eliminated during the formation of the isothiazole 25a. The tropylium cation reacts with hydrogen sulfide in a similar manner to form



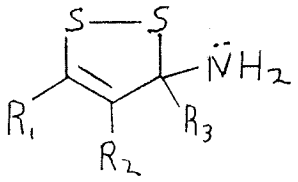
ClO_4^-

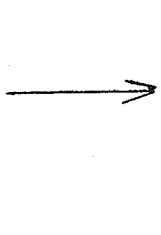
22

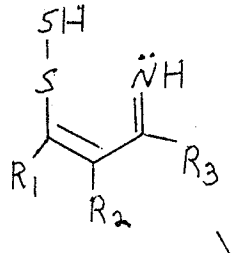
a) $R_1 = R_3 = H$, $R_2 = Ph$

b) $R_1 = Ar$, $R_2 = R_3 = H$

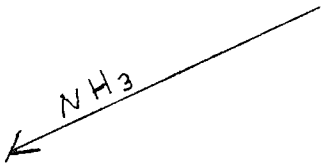
c) $R_1 = R_2 = Ph$, $R_3 = H$

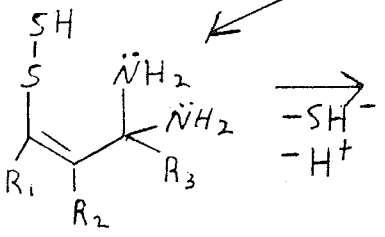


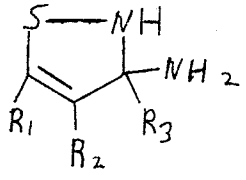


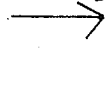


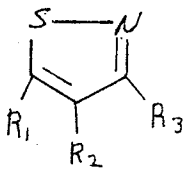
23











24

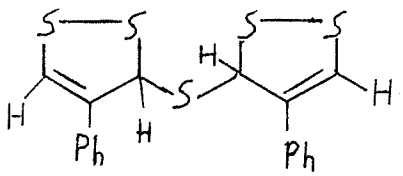
25

a) $R_1 = R_3 = H$, $R_2 = Ph$

b) $R_1 = Ar$, $R_2 = R_3 = H$

c) $R_1 = R_2 = Ph$, $R_3 = H$

ditropyl sulfide[29].



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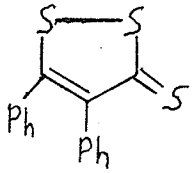
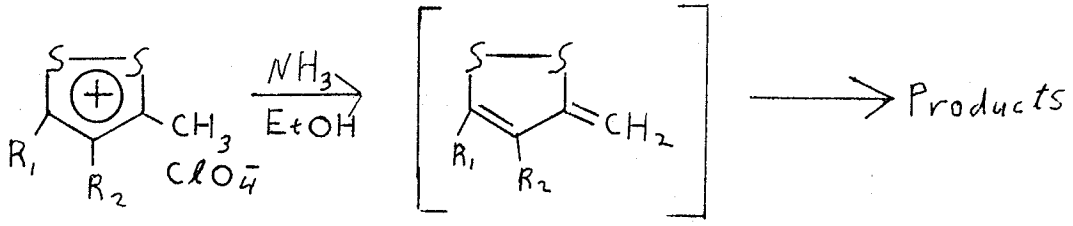


27

It is also reported that the products of the reaction of 3,4-diphenyl-1,2-dithiolium perchlorate (22c) and ammonia in ethanol contained 4,5-diphenyl-1,2-dithiole-3-thione (27) and not the corresponding isothiazole 25c[30].

The abstraction of a methyl proton from 3-methyl salts 28 by ammonia in ethanol and the subsequent decomposition of the unstable 3-methylene-1,2-dithiole 29, formed, proceed faster than the addition of ammonia to the dithiolium ring and no isothiazole is found[9].

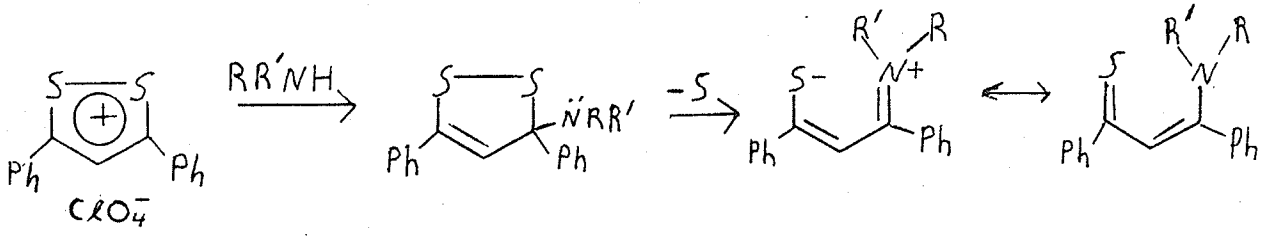


28 29

2. With Primary and Secondary Amines.

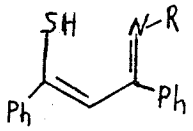
The behaviour of 3-aryl substituted-1,2-dithiolium salts such as 3,5-diphenyl-1,2-dithiolium perchlorate (30), towards primary amines[15,31], such as methylamine and aniline and secondary amines[15] such as piperidine and N-methylaniline is initially similar to their behaviour towards ammonia, but the initially formed dithiole 31 undergoes ring opening with the elimination of sulfur to form the 1-amino-propene-3-thione 32. Ring closure, in the case of primary amines, to form isothiazolium salts 36 does not occur because the nucleophilic character of these amines is

lower than that of ammonia. On the basis of spectroscopic evidence, the product of the reaction with primary amines has been assigned the thione structure 32a and not the tautomeric anil structure 33[15].



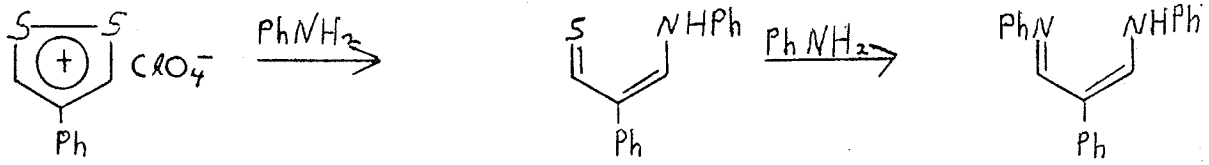
30 31 32

a) R′=H



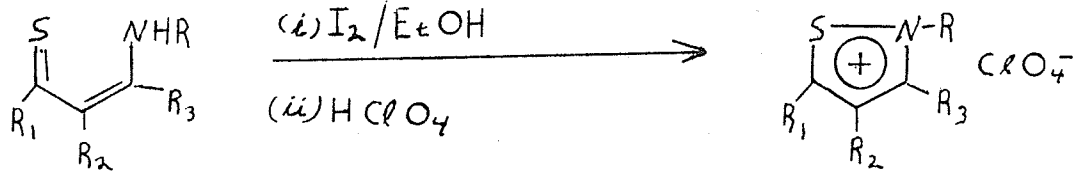
33

This cis isomer of malonic dialdehyde dianil 35 has been obtained from the reaction of 4-phenyl-1,2-dithiolium perchlorate (22a) with aniline. It seems probable that the anilinothial 34 is formed initially and would be sufficiently reactive to form the dianil 35 with more aniline[15].



22a 34 35

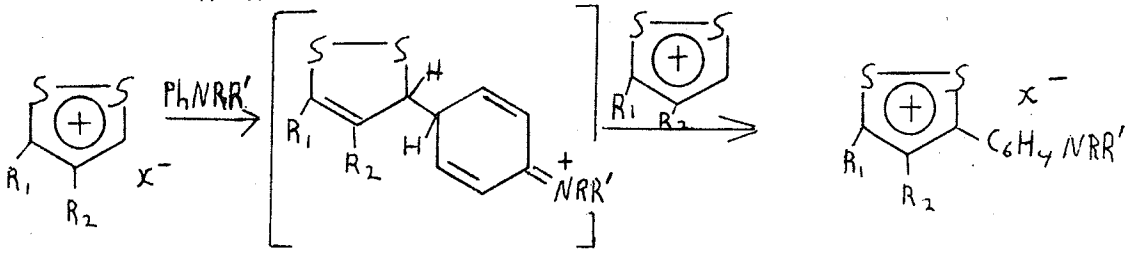
The isothiazolium cations, isolated as the perchlorate salts 37 may be formed by the oxidative ring closure of aminothiones 36 using iodine in ethanol[31].



36 37

3. With Tertiary Amines.

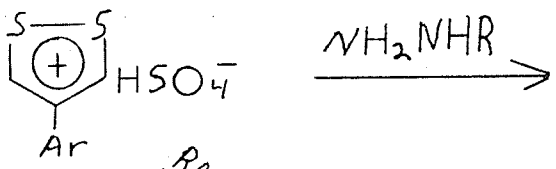
1,2-Dithiolium salts 21 with no substituent in position -3 combine with tertiary aromatic amines to form violet dyes[14,15]. Electrophilic attack by the cation on the *p*-position of the aromatic amine forms the unstable dithiole 38 which is converted into the dye 39 by the oxidative loss of hydride ion. Here the cation 21 acts as the oxidizing agent.



21 38 39

4. With Hydrazines.

The formation of pyrazoles 41a and b and pyrazolium salts 42 from hydrazines and dithiolium salts is similar to the formation of isothiazoles from ammonia and dithiolium salts. Thus with 85% hydrazine hydrate and monosubstituted hydrazines, 4-aryl-1,2-dithiolium salts 40 react to give the pyrazoles 41a and 41b respectively[3]. 3-Substituted unsymmetrical salts are reported to undergo nucleophilic attack at both positions -3 and -5 of the dithiole ring to give a mixture of isomers which are difficult to separate[32]. N,N'-disubstituted hydrazines afford N,N'-disubstituted pyrazolium salts 42 at temperatures below -20°C[33]. Along with the salts 42, the corresponding 1,2-dithiole-3-thiones 43 are found as minor products. The sulfur required for the formation of the thiones 43 may arise by decomposition of more of the dithiolium salts 40.



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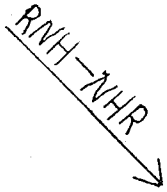
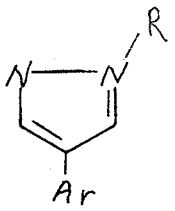
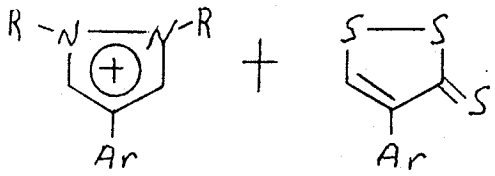




41

a) R = H

b) R = alkyl, aryl



42

R = alkyl, aryl

43

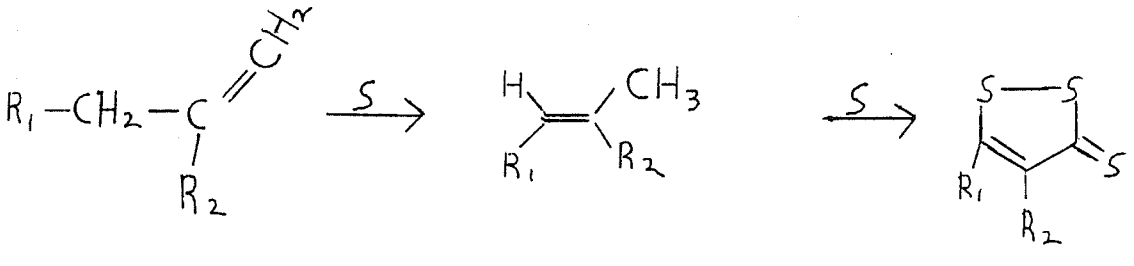
PART II: 1,2-Dithiole-3-thiones

Section A: Preparation of 1,2-Dithiole-3-thiones

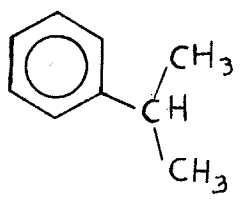
Most of the preparations of 1,2-dithiole-3-thiones 6 make use of elemental sulfur or phosphorus pentasulfide or a mixture of both. Only the synthesis of alkyl and aryl substituted thiones 6 will be discussed in this section.

1. From Olefins.

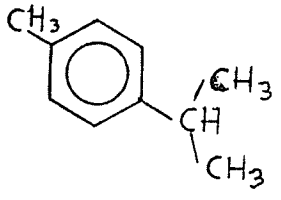
Alkenes when submitted to the action of sulfur or phosphorus pentasulfide, or a mixture of both, give 1,2-dithiole-3-thiones 6. This preparative method has been the subject of extensive investigations over the past twenty-five years. The majority of this work has been compiled in reviews by Landis[34] and Lozac'h and Vialle[35]. Many aryl and alkyl mono- and disubstituted thiones 6 have been made in this fashion. When sulfur is used as the sulfurizing agent, the temperature of the reaction is maintained between 160 and 220°C. Olefins 45 with an allylic methyl group or olefins 44 which readily isomerize to methyl substituted derivatives 45 are used as starting materials.



44 45 6



46

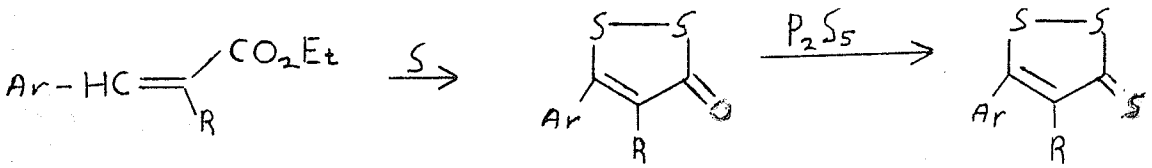


47

Olefins of the type 45 are thought to be intermediates in the reaction of cumene (46) and *p*-cymene (47) with sulfur in the presence of a basic catalyst[36]. Also, compounds which can lose water[37] or hydrogen sulfide[38,39] to yield the olefins 45 react with sulfur to give the thiones 6.

2. From Esters.

5-Aryl-1,2-dithiole-3-ones 49[40-44] formed from the reaction of 3-aryl-α-β unsaturated esters 48 and sulfur are easily converted into the corresponding thiones 50 using phosphorus pentasulfide[43]. When the α-alkyl ester 48a is used, the thione 50a is formed directly[44], but the α-aryl ester 48b gives 4,5-diphenyl-1,2-dithiole-3-one (49)[44]. The thione 50b can be made directly from the ester 48c if a mixture of sulfur and phosphorus pentasulfide is used[45].



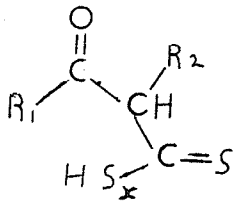
48 49 50

a) Ar = Ph, R = CH_3 a) Ar = R = Ph a) Ar = Ph, R = CO_2Et

b) Ar = R = Ph b) Ar = Ph, R = H

c) Ar = Ph

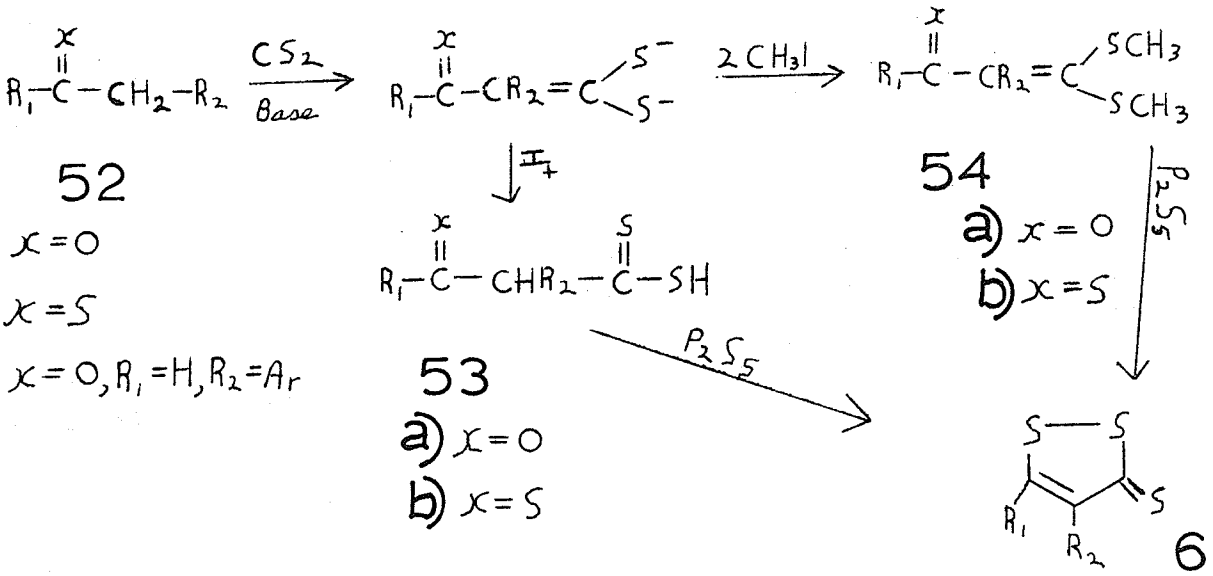
Phosphorus pentasulfide converts β-ketoesters into aryl and alkyl mono- and disubstituted thiones 6. Sulfur is sometimes employed in conjunction with phosphorus pentasulfide, but is not necessary[37,39,45-54]. A β-ketodithiocarboxylic acid 51 is believed to be an intermediate in this reaction.



51

3. From Ketones and Thiones.

β-Ketodithiocarboxylic acids 53, prepared by the base catalyzed reaction of enolizable ketones 52a with carbon disulfide, or the dimethyl derivatives 54, when treated with phosphorus pentasulfide, both give mono- and disubstituted aryl and alkyl thiones 6[39,54-57]. This reaction also occurs when enolizable thioketones 52b are used[58]. 4-Aryl-1,2-dithiole-3-thiones 43 are obtained when the aldehydes 52c are employed.



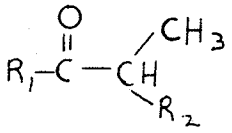
52
a) X = O
b) X = S
c) X = O, R1 = H, R2 = Ar

53
a) X = O
b) X = S

54
a) X = O
b) X = S

6

The ketones 55, on direct treatment with a mixture of sulfur and phosphorus pentasulfide produce the 1,2-dithiole-3-thiones 6[60-62]. Alphatic ketones 55a give lower yields of the thiones 6 than do aromatic ketones 55b.



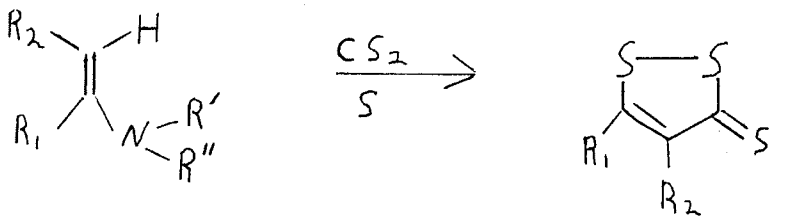
55

a) R_1 = alkyl

b) R_2 = aryl

4. From Enamines.

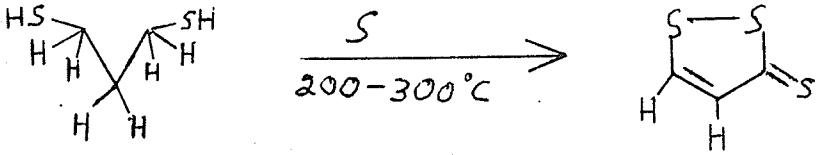
The action of carbon disulfide and sulfur on enamines 56 at room temperature in a polar solvent also leads to the formation of 1,2-dithiole-3-thiones 6 with the evolution of heat[63-65].



56 6

5. From 1,3-Disulfides.

1,3-Dimercaptopropanes have been dehydrogenated and sulfurized to give 1,2-dithiole-3-thiones 6[66,67]. Thus, the passage of 1,3-dimercaptopropane (57) through molten sulfur at temperatures between 200-300°C gives 1,2-dithiole-3-thione (58)[67].

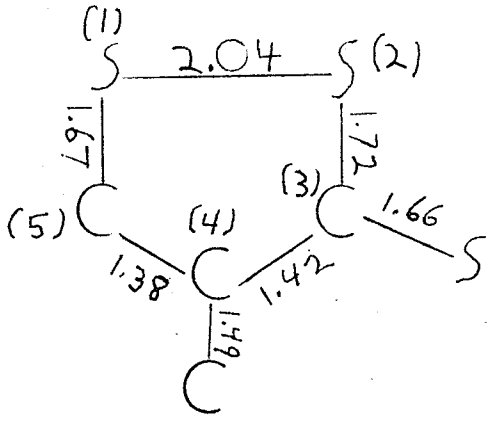


57 58

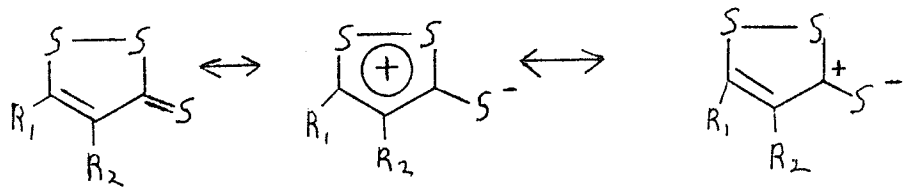
Section B: Cycloaddition Reactions of 1,2-Dithiole-3-thiones

The structure and bond lengths of 4-methyl-1,2-dithiole -3-thione (59) has been established by x-ray analysis[68,69]. The C(3)-C(4) and C(4)-C(5) bonds have lengths similar to those of C-C aromatic bonds. Although the C(4)-C(5) bond has more double bond character, the C(3)-C(4) bond also has a significant amount of double bond character. The thiocarbonyl double bond is slightly longer than that which would be predicted for C=S bond (1.61°A). All these facts are consistent with a considerable contribution from the dipolar forms 6a-e. (See next page.)

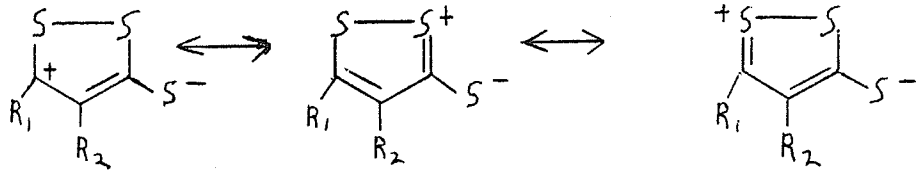
Dipole moment measurements[70] and infrared studies[71] also confirm the polar nature of 1,2-dithiole-3-thiones. In this Section, reactions of 1,2-dithiole-3-thiones involving a significant contribution from the dipolar forms 6b-e in cycloadditions will be discussed. It should be noted that the dipolar form 6b is analogous to the dipolar form of a



59



6 6a 6b



6c 6d 6e

thioketone and the dipolar form 6c is analogous to one of the dipolar forms of an α-β unsaturated thioketone.

Over the years, the term 'cycloaddition' has been used to describe all reactions in which a new ring is formed. This definition is too general and a new definition with the following criteria has been proposed by R. Huisgen[72,73].

The product of a cycloaddition corresponds to the sum of the components and cycloadditions are not accompanied by the elimination of small molecules or ions. Cycloadditions do not involve the breaking of σ bonds and the number of σ bonds is increased. Cycloadditions can be intramolecular if one molecule contains the necessary functional groups. When more than two components combine, only the reaction step leading to a ring is a cycloaddition. The products of the cycloaddition need not be stable or isolable, but the cycloadducts must occur at least as intermediates.

Cycloaddition reactions, obeying the above criteria, have been classified according to the number of π bonds involved in the cycloaddition. Thus a general reaction of a π-electron system of m electrons with a π-electron system of n electrons would be classified as a (m + n) cycloaddition reaction. This classification does not adequately describe the size of the ring which is formed or the number of ring atoms which each reactant contributes.

The classification, most widely accepted and employed in this thesis, is based upon the assumption that the criteria outlined above are obeyed and incorporates into its description the size of the ring formed and the number of ring atoms contributed by each reaction partner. Thus, cycloaddition reactions leading to a three-membered ring system

may be described as (1 + 2 = 3) cycloadditions and leading to a four-membered ring system as (1 + 3 = 4), (2 + 2 = 4) or (3 + 1 = 4) cycloadditions. Commonly in the primary literature, this description is simplified and a cycloaddition leading to a four-membered ring may be referred to as a (1 + 3), (2 + 2) or a (3 + 1) cycloaddition. It must be emphasized that this definition is not restricted only to a multi-centred process with a cyclic electron shift, commonly referred to as concerted process, but encompasses cycloadditions involving different types of mechanisms.

All the cycloadditions to be described in this section conform to the criteria outlined previously and can be classified in the following manner:

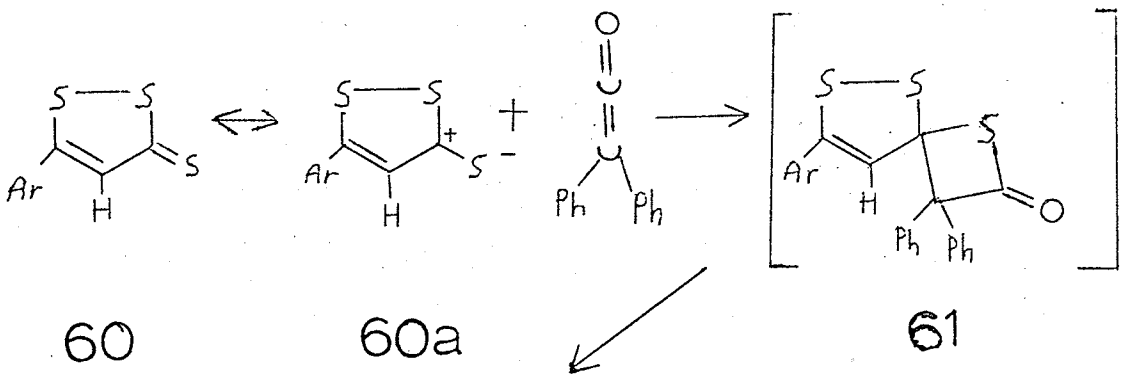
1. As (2 + 2) cycloadditions in which 1,2-dithiole-3-thiones behave as thioketones.
2. As (3 + 2) cycloadditions -
   (i) in which 1,2-dithiole-3-thiones behave as thioketones and contribute two atoms to the five-membered ring,
   (ii) in which 1,2-dithiole-3-thiones contribute three atoms to the five-membered ring.

Examples of these will be discussed below.

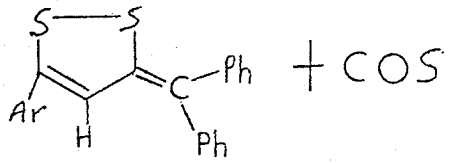
1. (2 + 2) Cycloadditions.

5-Aryl-1,2-dithiole-3-thiones 60, possibly in the dipolar form 60a react with diphenylketene in boiling xylene to give the corresponding 3-(diphenylmethylene)-1,2-dithioles 62 and carbonyl sulfide in good to moderate yields[74]. A poor yield is obtained when 5-methyl-1,2-dithiole-3-thione (63) is used and no reaction occurs for 5-unsubstituted-1,2-dithiole-3-thiones 64. The authors postulated, as the intermediates formed

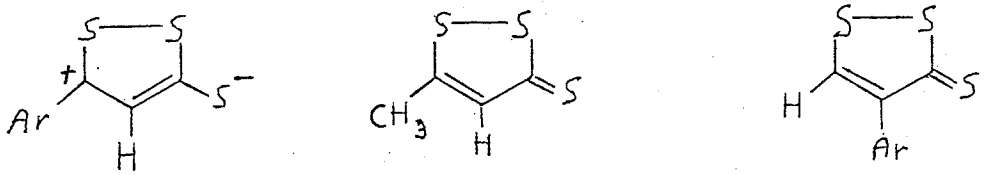
from the (2 + 2) cycloaddition of the thiones 60 and diphenylketene, the thietan-2-ones 61 which on rearrangement of the thietane ring give the 3-methylene-1,2-dithioles 62 and carbonyl sulfide. Since only 5-aryl substituted thiones 60 react appreciably, the dipolar form 60b which can effectively stabilize the positive charge must have a significant role in determining the course of the reaction.



60 60a 61



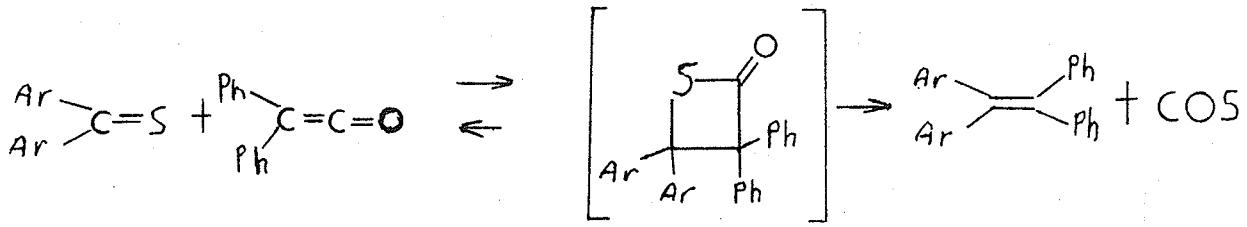
62



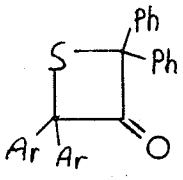
60b 63 64

Similar behaviour has been reported for acyclic thioketones. A thietan-2-one 67 has also been postulated by Staudinger as an intermediate in the reaction of diaryl thioketones 65 and diphenylketene[75]. He found that at high temperatures, the products isolated were the olefins 68 and carbonyl sulfide. He also reported that the diaryl thioketones 65 and diphenylketene at room temperature form stable 1:1 adducts[75]. Due to the fact that regeneration of the starting materials occurred

upon heating the 1:1 adducts above their melting point and recombination was evident on subsequent cooling, Staudinger proposed that the thietan-3-ones 66 were the 1:1 adducts. This assignment has been confirmed spectroscopically by Rioult and Vialle[74]. This behaviour has also been observed for various carbonyl compounds in their reactions with ketenes[76,77].

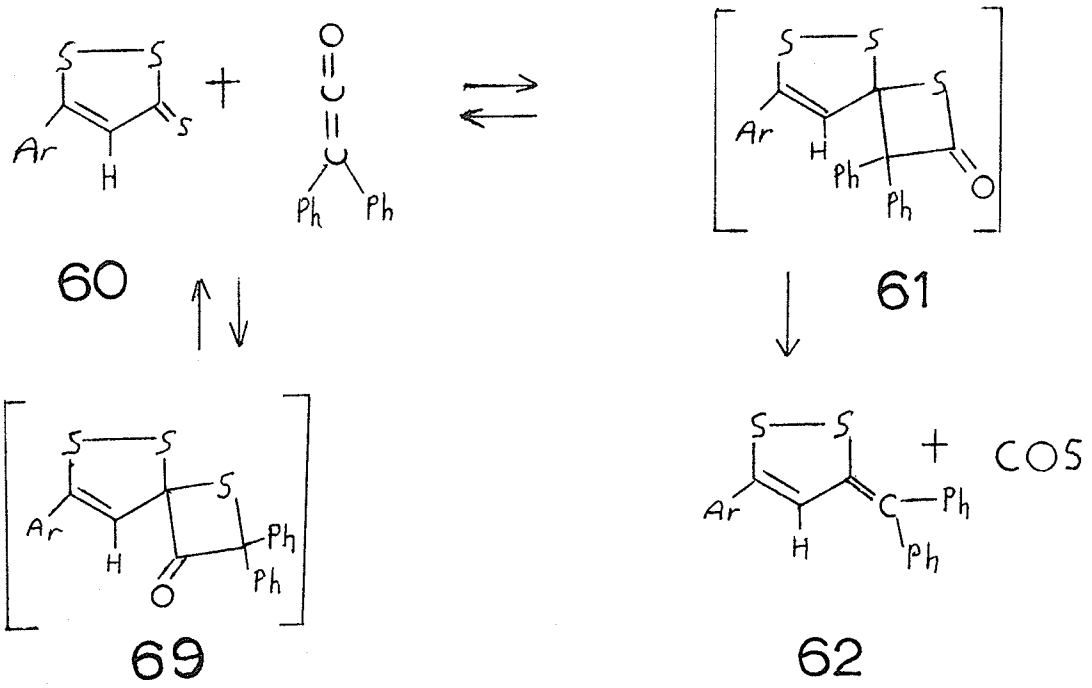


65 67 68

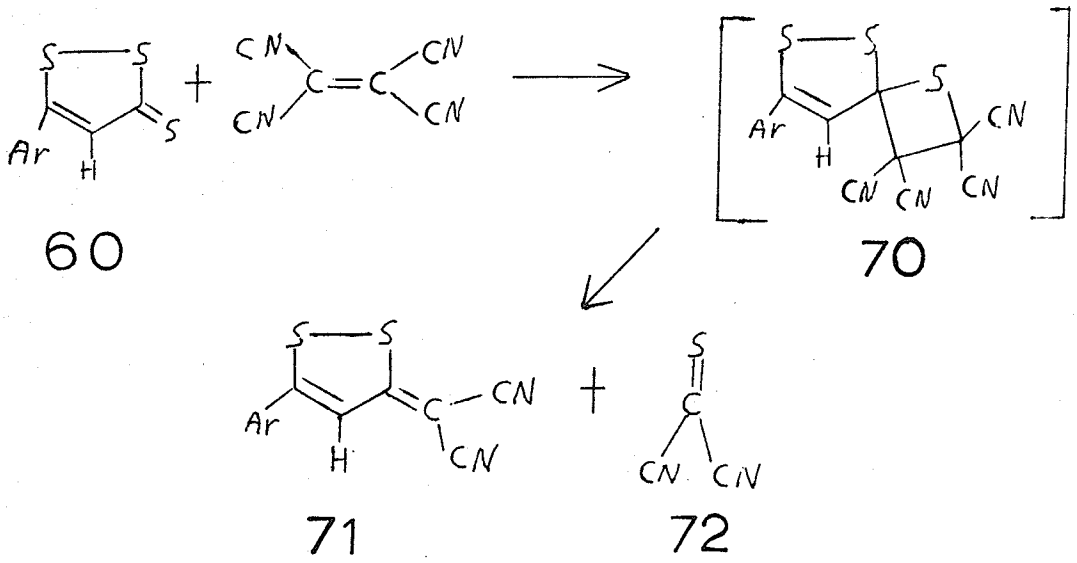


66

Thus it is possible that in the reaction of the 1,2-dithiole-3-thiones 60 with diphenylketene, two reversible competitive (2 + 2) cycloadditions leading to the thietan-2-ones 61 and the thietan-3-ones 69 may be occurring. At high temperatures, the thietan-2-ones 61 could irreversibly decompose to give the olefins 62 and carbonyl sulfide. No thietan-3-one 69 is reported to be found when the reaction is carried out at room temperature, only a small amount of the 3-methylene-1,2-dithioles 62 and the unchanged 1,2-dithiole-3-thiones were isolated. However, the thietan-3-ones 69 may be unstable even at room temperature or they may have decomposed to give the starting materials during the isolation procedures.



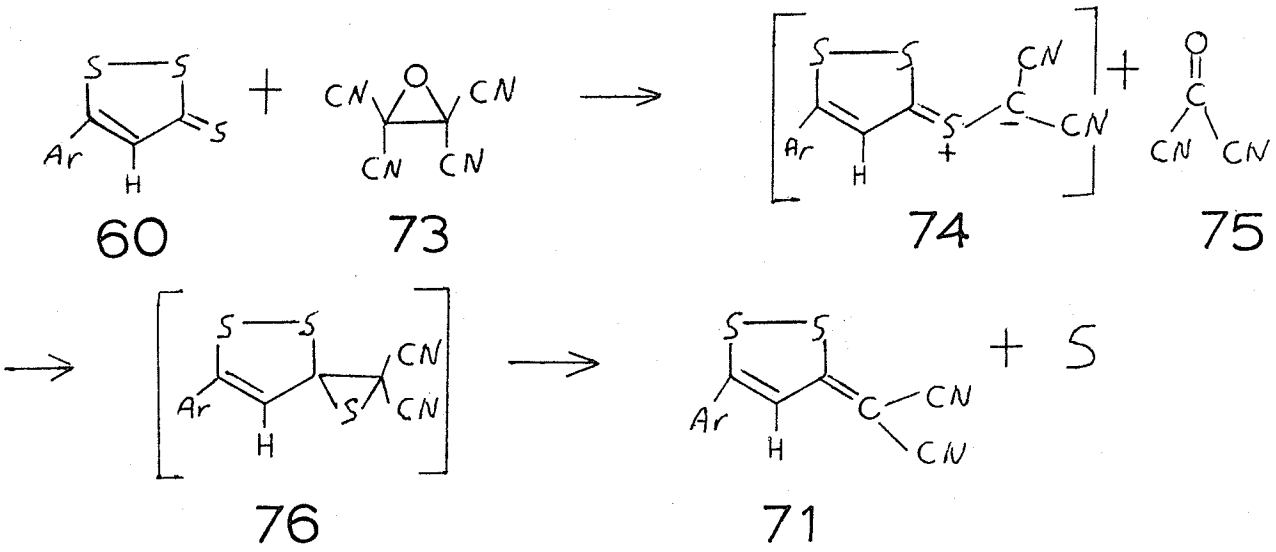
The intermediacy of a thietane has also been invoked in the reaction of 5-aryl-1,2-dithiole-3-thiones 60 with tetracyanoethylene[78]. The authors postulate that the thietanes 70 resulting from a (2 + 2) cycloaddition of tetracyanoethylene and the thione 60 could decompose to give the α-(5-aryl-1,2-dithiole-3-ylidene) malononitriles 71 and 2-thioketomalononitrile (72).



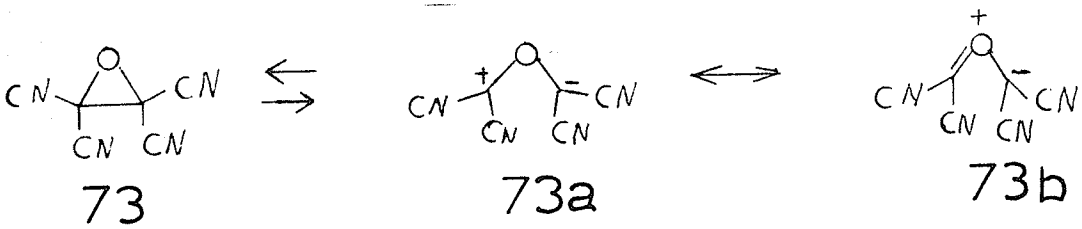
2.(i) (3 + 2) Cycloadditions.

The malononitriles 71 can also be made, quantitatively at low temperatures, from the 5-aryl-1,2-dithiole-3-thiones 60 and tetracyanoethylene

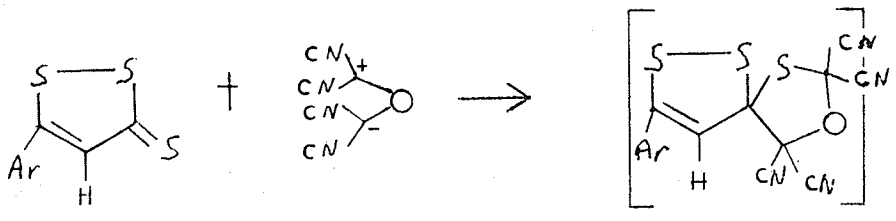
oxide (73)[78]. It is postulated by the authors that the sulforium ylide 74, as an intermediate in the reaction, could cyclize to form the episulfide 76. The spontaneous elimination of sulfur, favoured by the presence of two electron-withdrawing groups, could then give the malononitriles 71.



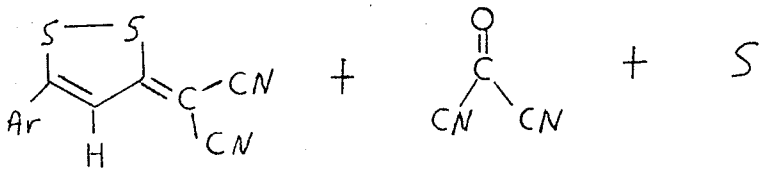
However, recent studies of the reaction of tetracyanoethylene oxide with olefins show that the oxide 73 can be considered to react in the form of a carbonyl ylide which is a 1,3-dipole possessing the sextet and octet forms 73a and 73b, respectively[79-82]. Carbonyl ylides are known to be involved in 1,3-dipolar cycloadditions, a special class of (3 + 2) cycloadditions[83]. The 1,3-dipolar cycloaddition will be discussed in detail in the next section. Thus, the reaction of these 1,2-dithiole-3-thiones 60 with tetracyanoethylene oxide may possibly be described as a 1,3-dipolar cycloaddition in which the thione 60, possibly in the dipolar form 60a is the dipolarophile. The 1,3-oxothiolane 77, as the cyclic intermediate formed, could then decompose to give the 3-methylene-1,2-dithioles 71, 2-ketomalononitrile (75) and elemental sulfur.



73 73a 73b

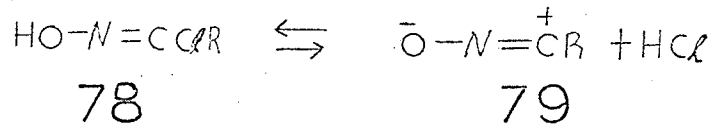


60 73a 77

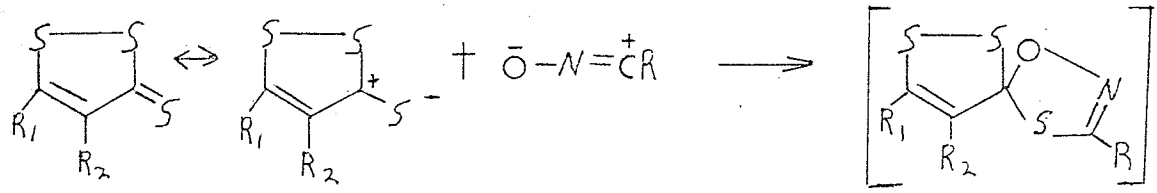


71 75

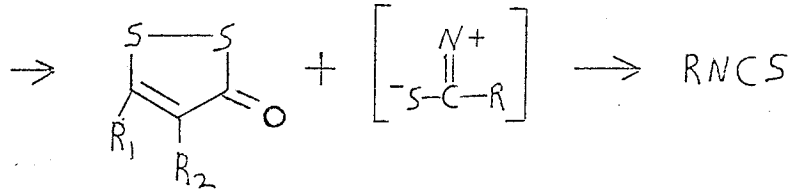
It has been reported by Boberg and Knoop that 4- and 5-monosubstituted and 4,5-disubstituted-1,2-dithiole-3-thiones react with hydroximoyl chlorides 78, at elevated temperatures to give the corresponding 1,2-dithiole-3-ones 81 and the isothiocyanates 83[84]. Hydroximoyl chlorides 78 at high temperatures[84,85] or in the presence of a base[103] are known to be converted into nitrile oxides 79 which are known to function as 1,3-dipoles in 1,3-dipolar cycloadditions[83]. Boberg and Knoop have proposed that the 1,4,2-oxathiazoles 80 as the adducts formed from the 1,3-dipolar cycloaddition of the nitrile oxides 79 and the thiones 6, possibly in the dipolar form 6b, could thermally decompose to give the corresponding 1,2-dithiole-3-ones 81 and the reactive thioketoazenes 82. The latter could undergo molecular rearrangement to yield the isothiocyanates 83. 1,3-Dipolar cycloadditions of this type have been proposed for the addition of aromatic and aliphatic nitrile oxides to compounds containing various thiocarbonyl functional groups[86].



78 79

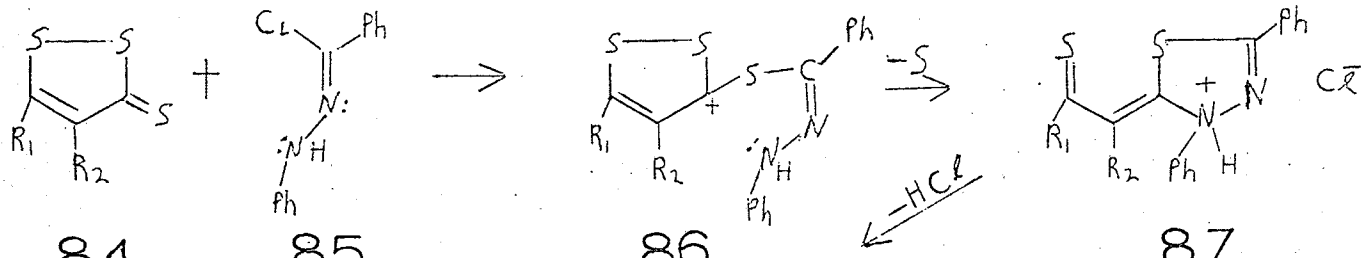


6 6b 79 80



81 82 83

The 1,2-dithiole-3-thiones 84 a, b and c combine with N-(α-chlorobenzylidene)-N'-phenylhydrazine (85) in boiling xylene to give the 2-(2-thioacylmethylene)-1,3,4-thiadiazoles 88 a,b and c[87]. The authors postulate that the thiadiazoles 88 are produced in a non-concerted fashion. The dithiolium salts 86, produced from the thiones 84 and the phenylhydrazone 85 could lose sulfur, after an intramolecular attack of the terminal nitrogen on the electron deficient carbon -3 of the dithiole ring, to gve the 1,3,4-thiadiazolium salts 87. By further loss of hydrogen chloride, the salts 87 would yield the 1,3,4-thiadiazoles 88.



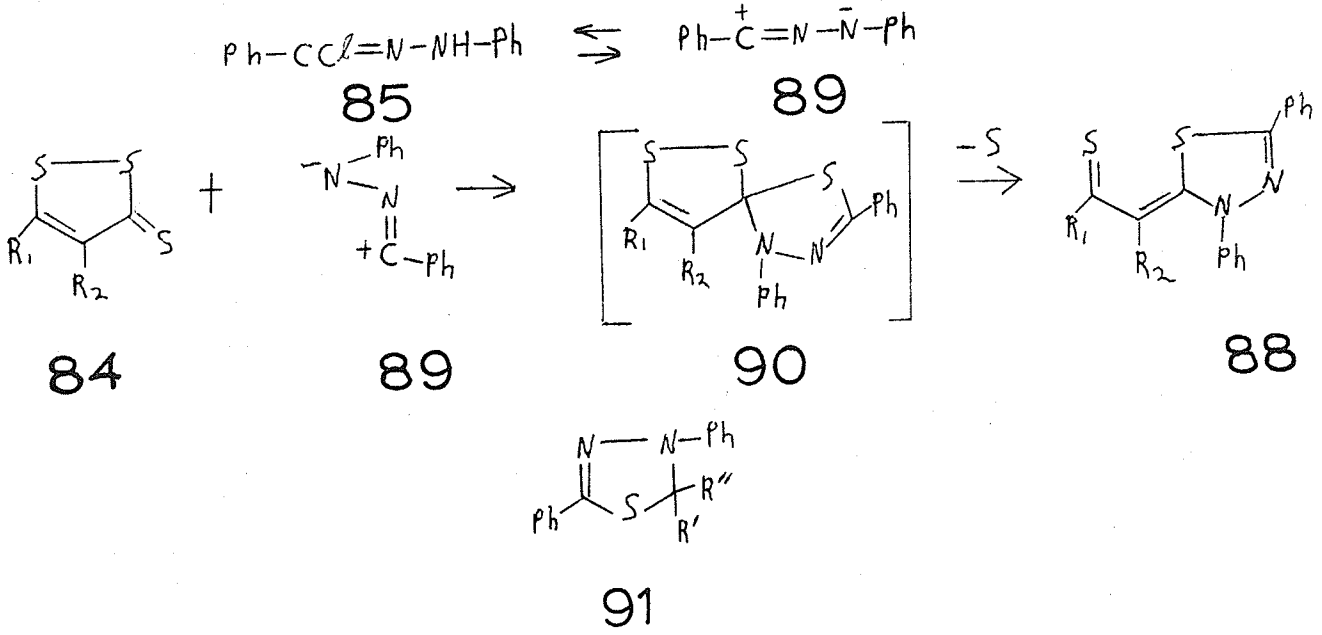
84 85 86 87

a) $R_1=Ar, R_2=H$
b) $R_1=H, R_2=Ar$
c) $R_1=Ar, R_2=CH_3$

88

a) $R_1=Ar, R_2=H$
b) $R_1=H, R_2=Ar$
c) $R_1=Ar, R_2=CH_3$

The nitrile imine 89 formed from N-(α-chlorobenzylidene)-N'-phenylhydrazine (85) in the presence of a tertiary base is known to combine with acyclic thioketones via a 1,3-dipolar cycloaddition to give Δ^2-1,3,4-thiadiazolines 91[88]. Thus in the reaction with the 1,2-dithiole-3-thiones 84, the phenylhydrazone 85, at high temperatures could possibly lose hydrogen chloride to give the nitrile imine 89 in a manner similar to the loss of hydrogen chloride from hydroximoyl chlorides to form nitrile oxides[84,85]. The spiran compound 90, formed from the 1,3-dipolar cycloaddition of the thiones 84 and the nitrile imine 89 could then lose sulfur to give the 1,3,4-dithiazole 88.

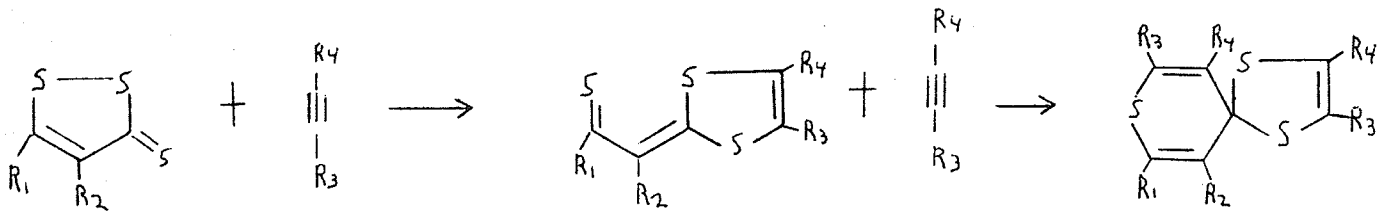


91

2. (ii) (3 + 2) Cycloadditions.

1,2-Dithiole-3-thiones and activated acetylenes react by a (3 + 2) cycloaddition to form 1:1 adducts 93[89-92], formulated as 2-(2-thioacylmethylene)-1,3-dithioles. In contrast to the cycloadditions discussed previously, the thiones 92 contribute three atoms to the new

five-membered ring. Subsequent reaction[89], in some cases, provides 2:1 adducts, the spiran compounds 94, by a further (2 + 4) cycloaddition of the activated acetylenes and the initially formed adducts 93. On the basis of desulfurization experiments, the structure 93 and 94 were assigned to the 1:1[90,91] and the 2:1 adducts[89], respectively. Supplementary confirmation of the assignment of the 1:1 adducts was provided by the independent synthesis of the 2- (2-thioacylmethylene)-1,3-dithioles 98 from the corresponding 2- (2-acylmethylene)-1,3-dithioles 97[91]. The condensation[93] of phenacyl bromide (95) and the dithiocarboxylic acids 96a gave the ketones 97. The acetylenes used in this reaction were dimethyl acetylenedicarboxylate[89,90], diethyl acetylenedicarboxylate[90], propynal[90], various monoarylacetylenes[90,91], benzyne[89] and methylthioacetylene[92]. 5-Aryl-[89,91] 4,5-dialkyl-[89] and 5-methylthio-4-alkyl or aryl[92]-1,2-dithiole-3-thiones 92a, 92b and 92c respectively, have been reported to give the 1:1 adducts. A 1:1 adduct could not be isolated from the reaction of benzo-1,2-dithiole-3-thione (99) with dimethyl acetylenedicarboxylate[89,90], only the 2:1 adduct 101 was found[89]. It is postulated that the *o*-quinonoid structure 100 of the expected 1:1 adduct would be very reactive and would quickly react with more acetylene to form the spiran 101. When unsymmetrical acetylenes are employed two structural isomers, 93 and 102 are possible. No evidence for the existence of these isomers was found[90-92]. It has been suggested that, by rapid *cis-trans* isomerization at the exocyclic double bond, these isomers become identical[90].

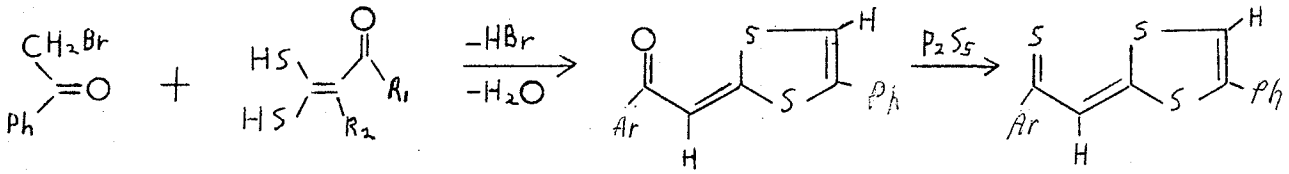


92 93 94

a) $R_1 = Ar$, $R_2 = H$

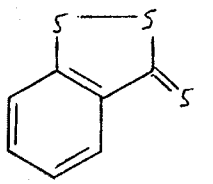
b) $R_1 = Et$, $R_2 = CH_3$; $R_1, R_2 = -[CH_2]_3-$; $R_1, R_2 = -[CH_2]_4-$

c) $R_1 = SCH_3$, R_2 = alkyl or aryl

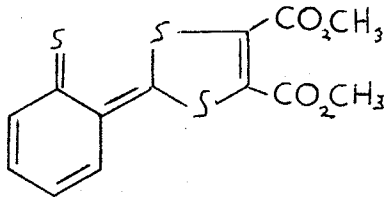


95 96 97 98

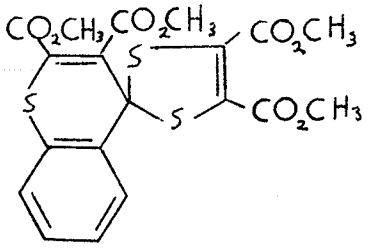
a) $R_1 = Ar$, $R_2 = H$



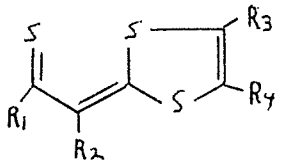
99



100

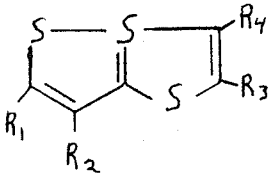


101

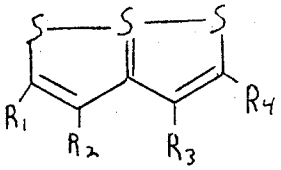


102

Behringer[90] has suggested that the tetravalent sulfur structure 103 is a significant resonance contributor to the overall bonding of the 1:1 adducts. This suggestion was prompted by the similarity in chemical behaviour and in ultraviolet spectra of the 1:1 adducts to the thiothiophthenes, a class of compounds in which the tetravalent sulfur structure 104[94] is thought to be a significant resonance contributor. However, it should be noted that the instability of the 1:1 adduct 100 and the formation of the spirans 94 are not consistent with the isothiothiophthene 103, but with the thione form 93.



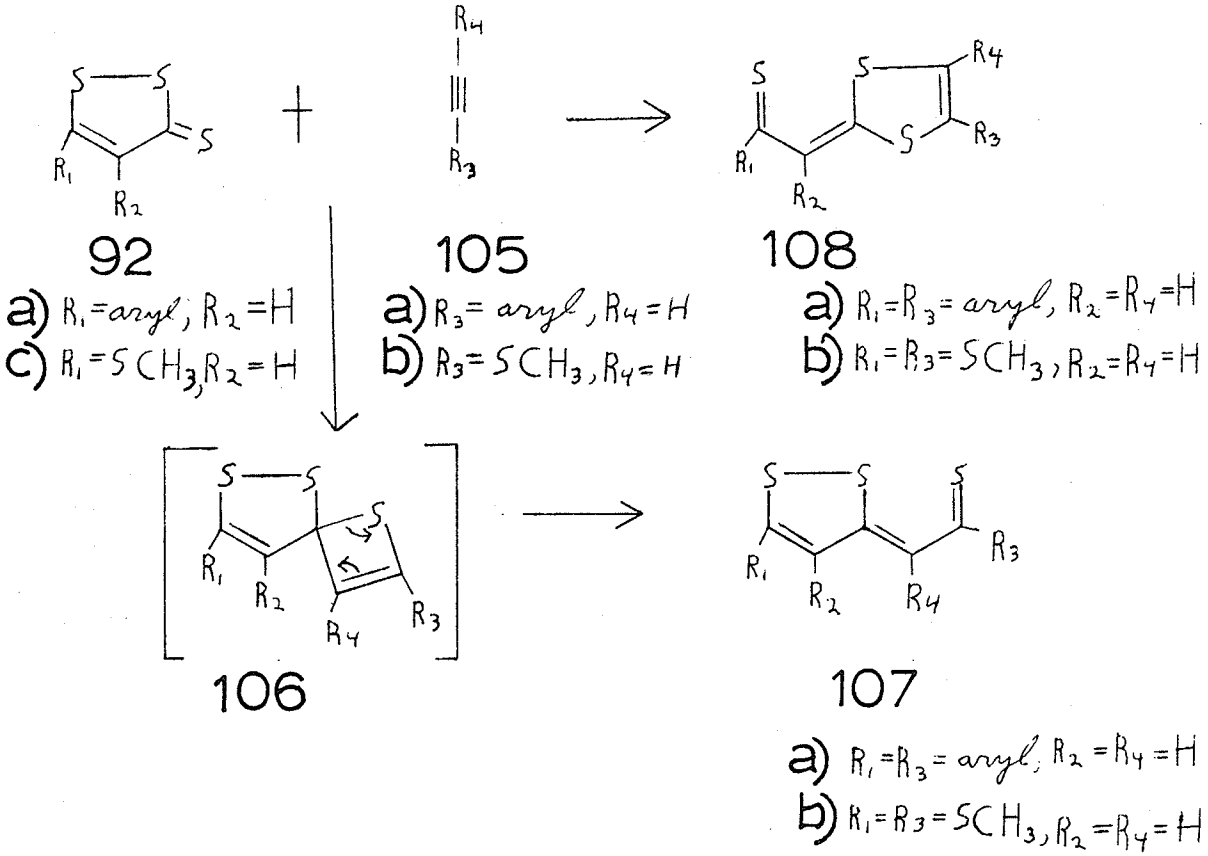
103



104

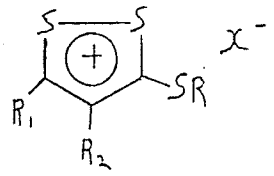
The monoarylacetylenes 105a[91] and methylthioacetylene 105b[92] reacted with thiones 92a and 92c, respectively to give the thiothiophthenes 107a and 107b, respectively, and the 2-(2-thioacylmethylene)-1,3-dithioles 108a and 108b, respectively. The relative proportion of both was dependent on the experimental conditions. In dry refluxing xylene, the 1,3-dithioles 108 were the major products and in some cases, the only product. In refluxing xylene saturated with hydrogen chloride, the reverse was found. The 1,3-dithioles 108 on treatment with phosphorus pentasulfide were converted into the thiothiophthenes 107. The authors[91,92] postulated that two competing cycloaddition reactions are occurring. The (3 + 2) cycloaddition described earlier and a (2 + 2) cycloaddition of the reactants best explain the products found. A thietene 106 which could be formed by the (2 + 2) cycloaddtion, could then rearrange to the

thiothiophthenes 107.



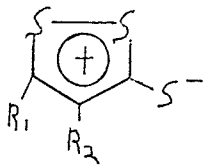
1,2-Dithiole-3-ones of the type 81 are reported not to react with activated acetylenes[90]. This is possibly due to the decreased nucleophilicity of the exocyclic oxygen atom. For 1,2-dithiole-3-thiones, the nucleophilicity of the exocyclic sulfur atom is shown by the ease of alkylation[34] and acylation[95-99] of the exocyclic sulfur to form the dithiolium salts 120a and 120b, respectively. In contrast, for the ketones 81, alkylation can only be achieved with the use of triethyloxonium tetrafluoroborate[100], a powerful alkylating agent[101]. It has been proposed by Behringer that the increased nucleophilicity of the exocylcic sulfur of 1,2-dithiole-3-thiones stems from the

the stability of the quasi-aromatic dithiolium ring 6a[90].



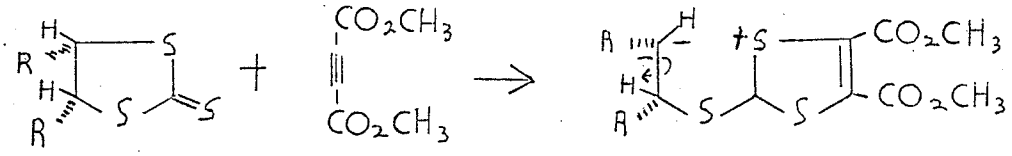
109

a) R = alkyl
b) R = aryl



6a

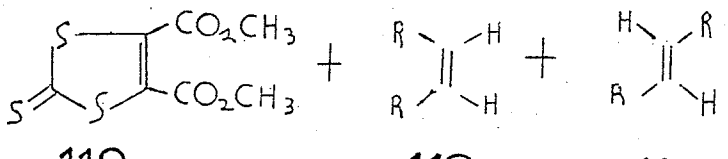
Similarly to 1,2-dithiole-3-thiones, 1,3-dithiolane-2-thiones 110 react with activated acetylenes in a (3 + 2 = 5) cycloaddition[84]. Thus, 1,3-dithiolane-2-thione (110a) reacts rapidly at 140°C with dimethyl acetylenedicarboxylate to give the 1,3-dithiole-2-thione 112 together with ethylene. *cis*-4,5-Diphenyl-1,3-dithioane-2-thione (110b) gives *cis*- and *trans*-stilbene (113b) and (114b) respectively, in the ratio 42:58, together with the thione 112. It was found that *cis*-stilbene does not isomerize under the reaction conditions. The non-stereospecificity of this reaction, as indicated by the isolation of *cis*- and *trans*-stilbene suggests that an intermediate such as the zwitterion 111 may be involved. This zwitterion 111 could lead to the mixture of *cis*- and *trans*-stilbene.



110

a) R = H
b) R = Ph

111



112

113

a) R = H
b) R = Ph

114

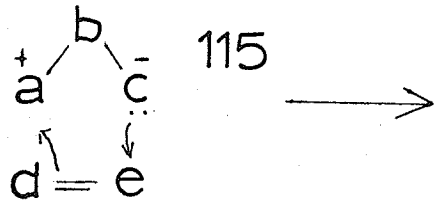
a) R = H
b) R = Ph

The participation of dipolar forms of the type 6d and 6e in the (3 + 2) cycloaddition of 1,2-dithiole-3-thiones and acetylenes and the mechanism of this (3 + 2) cycloaddition will not be dealt with here, but will be dealt with in the Discussion of Results. This cycloaddition has tentatively been referred to as a 1,3-dipolar cycloaddition. In the next section, the special class of (3 + 2) cycloadditions, the 1,3-dipolar cycloadditions, will be discussed.

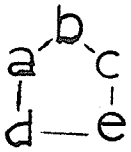
Section C: 1,3-Dipolar Cycloadditions

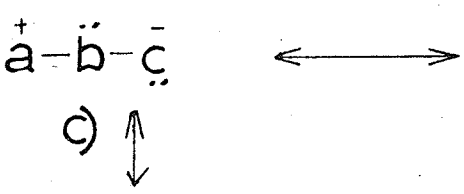
The term 1,3-dipolar cycloaddition has been applied to cycloadditions of the type (3 + 2 = 5) by R. Huisgen[83,102]. Huisgen has found that a (3 + 2) cycloaddition, leading to an uncharged five-membered ring, cannot possibly occur with octet-stabilized reactants which have no formal charge. A dipole[83] 115 has been defined such that atom 'a' possesses an electron sextet, i.e., an incomplete valence shell combined with a formal positive charge, and that atom 'c', the negatively charged centre has an unshared pair of electrons. (See next page.) The 1,3-dipole, so defined, does not have to be isolated. If it is isolated, the sextet structure 115 would only be a resonance contributor. Compounds which contain such a 1,3-dipole must be ambivalent in positions -1 and -3 of the dipole. The combination of a 1,3-dipole which has internal octet stabilization with a multiple bond system, termed the dipolarophile, is referred to as a 1,3-dipolar cycloaddition[83]. Internal octet stabilization can occur if 'b' possesses an unshared pair of electrons. In this case, the mesomerism of the octet structure 116a,b and 117a,b and the sextet structures 116c,d and 117c,d results in partial charge compensation and exchange of formal charges respectively. (See next page.) 1,3-Dipoles which contain internal octet stabilization may, or may not, contain a double bond in the sextet formulation. Atom 'b' of 1,3-dipoles which do not contain a bond in the sextet structure can be either N-R, O or S.

Examples of 1,3-dipoles possessing internal octet stabilization are shown in Tables I and II. Extensive investigations of the 1,3-dipolar cycloadditions of different types of compounds containing the dipoles listed in Tables I and II have been reviewed by R. Huisgen[83]. Huisgen[103-105] has proposed a concerted mechanism for 1,3-dipolar cycloadditions, in accordance with the conservation of orbital symmetry[106], since the thermal cycloaddition involves (4 + 2) π electrons. He has shown[103,104] that the stereoselectivity observed with *cis* and *trans*

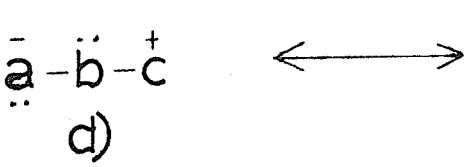


115

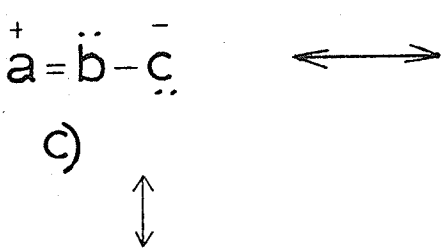




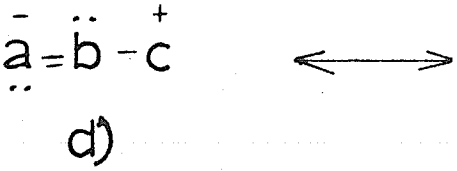
116



116



117



117

TABLE I

1,3-Dipoles with a Double Bond and Internal Octet Stabilization

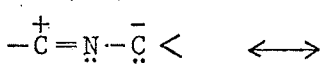
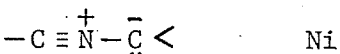
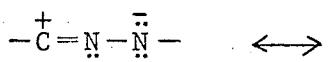
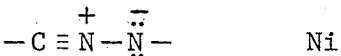
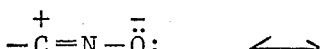
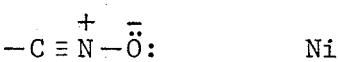
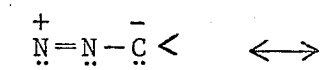
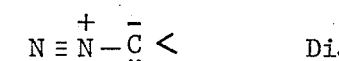
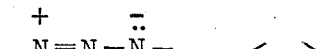
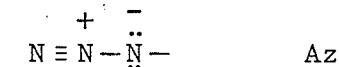
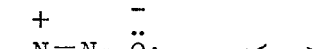
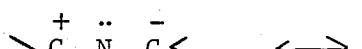
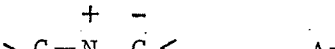
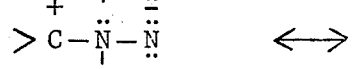
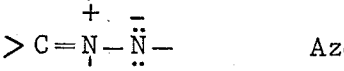
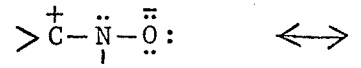
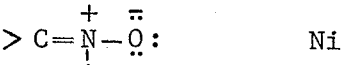
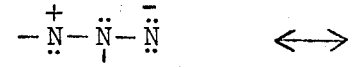
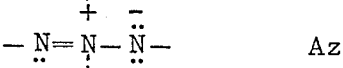
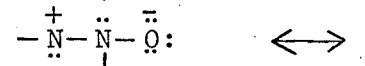
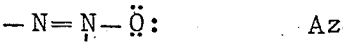
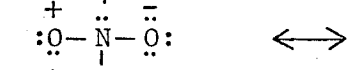
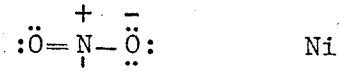
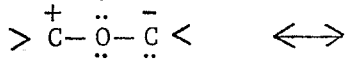
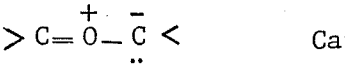
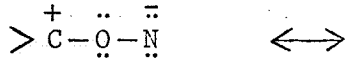
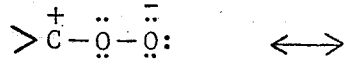
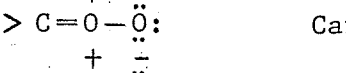
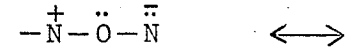
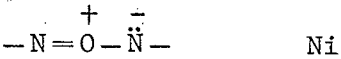
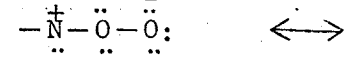
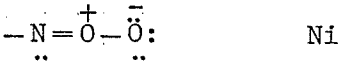
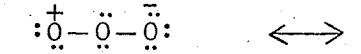
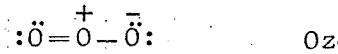
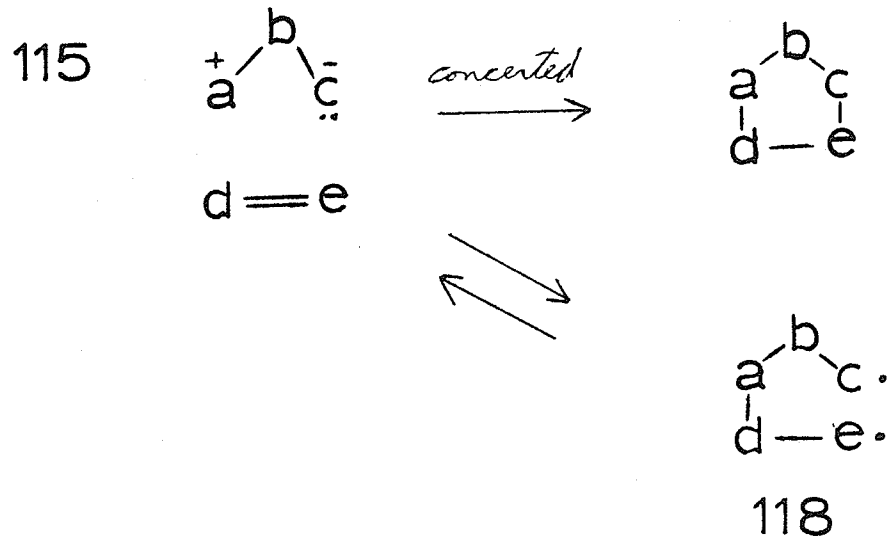
Sextet Structures		Octet Structures	
	⟷		Nitrile ylides
	⟷		Nitrile imines
	⟷		Nitrile oxides
	⟷		Diazoalkanes
	⟷		Azides
	⟷		Nitrous oxide

TABLE II

1,3-Dipoles Without a Double Bond but with Internal Octet Stabilization

Sextet Structures		Octet Structures	
	⟷		Azomethine ylides
	⟷		Azomethine imines
	⟷		Nitrone
	⟷		Azimines
	⟷		Azoxy compounds
	⟷		Nitro compounds
	⟷		Carbonyl ylides
	⟷		Carbonyl imines
	⟷		Carbonyl oxides
	⟷		Nitrosimines
	⟷		Nitroso oxide
	⟷		Ozone

isomeric dipolarophiles, the effect of solvent and substitutents on the rate constants and the large negative entropy of activation are all consistent with a concerted addition in which two new σ bonds are formed simultaneously although not necessarily at equal rates. R. Firestone[107] has suggested that a two-step mechanism with a discrete intermediate, a spin-paired diradical 118 would also be consistent with the evidence presented. He postulates that the energy barrier for rotation about the d-e bond is greater than the activation energy for ring closure or for reconversion back to reactants. This hypothesis is not consistent with other evidence presented for spin-paired diradicals in which rotation competes favourably with ring closure[108,109]. Also, a low activation barrier for reconversion is not consistent with the energetics involved in the retrograde step of diradical 118 to reactants. This activation barrier has been estimated by Huisgen to be less than 1.3 kcal./mole[105].

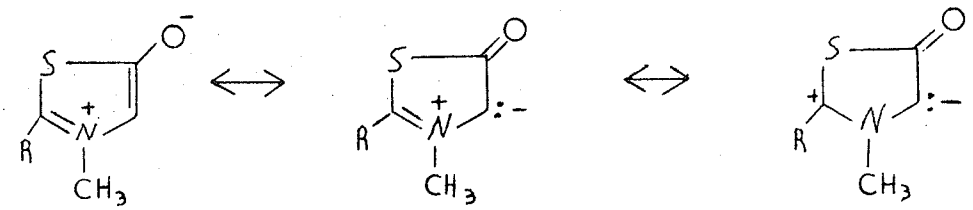


From the study of the mechanism of 1,3-dipolar cycloadditions, Huisgen[103,104] has found that in all reactions studied, changes in solvent polarity had no appreciable effect on the rates of addition and that dipolarophilic character of an acetylenic triple bond is measured by

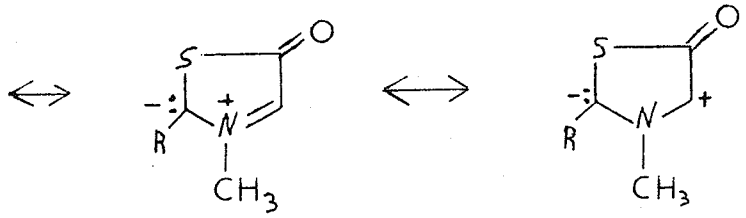
competitive rate experiments is similar in magnitude to that of a comparable ethylenic double bond. Thus reactions leading to aromatic rings do not proceed at a faster rate. It was shown from molecular orbital considerations of the concerted attack that the transition state is geometrically closer to the orientated complex of the components and thus does not profit from the aromatic resonance of the product. In many of the reactions studied, unsymmetrically bonded dipolarophiles add to the 1,3-dipole in two directions. This dual addition is consistent with the ambivalent nature of 1,3-dipoles in which positions -1 and -3 can be both positive and negative centres.

Anydro-5-hydroxy-3-methyl-thiazolium hydroxides 119[110] and anydro-5-hydroxy-1,3-dithiolium hydroxides 120[111], are reported to participate in 1,3-dipolar cycloadditions with acetylenes. The resonance forms 119 b,c and d of the meso-ionic thiazole 119 indicate that the 1,3-dipole inherent in the ring is an azomethine ylide. Similarly for the meso-ionic 1,3-dithiole-5-one 120, the resonance structures 120 b,c,d and e depict a thiocarbonyl ylide. This is the first report of 1,3-dipolar cycloadditions of the thiocarbonyl ylides. In fact, this is the first reported case of 1,3-dipoles with internal octet stabilization which contain a sulfur atom in the central position of the dipole. The meso-ionic 1,3-dithiole-5-one 120 also is found to add stereo-specifically to olefins[112]. The expression "meso-ionic" compounds refers to compounds which do not possess a formal charge but can be only represented by zwitterionic resonance forms[113]. However, the 1,3-dithiole derivatives 120 may also be represented by the neutral tetravalent resonance structure 120f. Thus it is also possible that other known

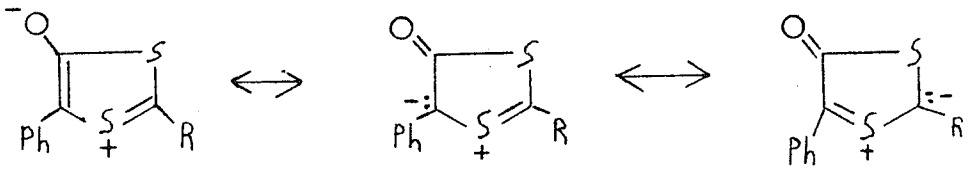
tetravalent sulfur compounds[113-118], in their reactions with acetylenes and olefins, may be considered to be thiocarbonyl ylides.



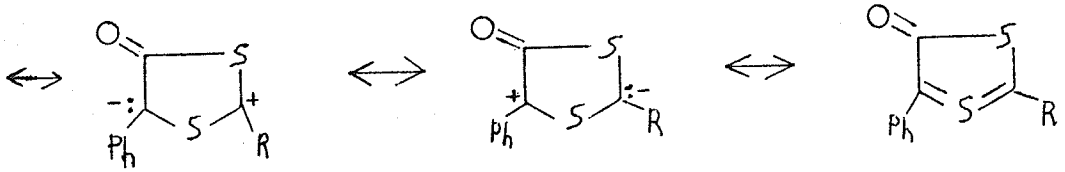
119 a b c



119 d e



120 a b c

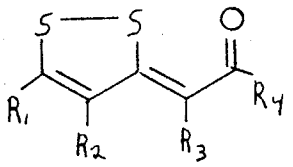


120 d e f

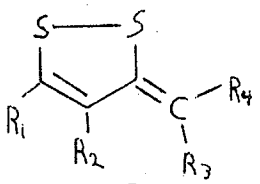
PART III: 3-Alkylidene-1,2-dithioles

Section A: Preparations of 3-Alkylidene-1,2-dithioles

Extensive investigations have been made over the past decade on the synthesis of various 3-ylidene-1,2-dithioles 7. Most of the interest has been in the field of thiothiophthenes 107 and their oxygen analogues, the 3-(2-acylmethylene)-1,2-dithioles 121. These two classes of 3-alkylidene-1,2-dithioles 7 which exhibit unique chemical properties have been the subject of numerous reviews[35,94,120-122], and will not be discussed in this section. Only the 3-alkylidene compounds possessing the structure 122 will be discussed. The stereochemistry of many of these dithioles 122 has not been thoroughly investigated.



121

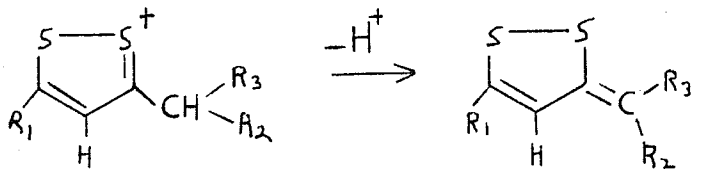


122

$R_3, R_4 = H$, aryl, alkyl or CN

1. From 1,2-Dithiolium Salts.

1,2-Dithiolium salts 123 a,b and c which contain an α-hydrogen in the substituent at position -3 of the dithiole ring, on treatment with weak bases, readily form the 3-alkylidene-1,2-dithioles 124 a, b and c, respectively[74,123].



123 124

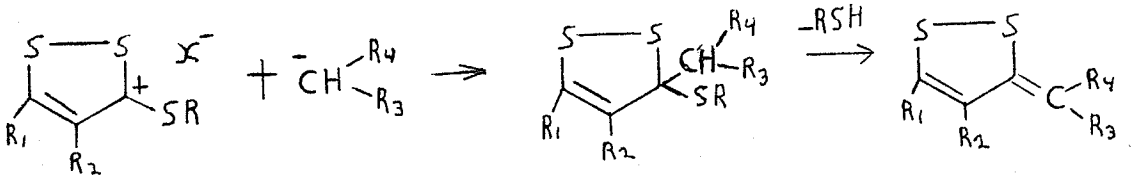
a) $R_1 = R_2 = Ph$, $R_3 = H$

b) $R_1 = R_2 = R_3 = Ph$

c) $R_1 = p\text{-}CH_3OC_6H_4$, $R_2 = R_3 = Ph$

2. From 3-Alkylthio-1,2-dithiolium Salts.

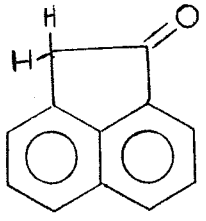
The general route to 3-alkylidene-1,2-dithioles utilizes 3-alkylthio-1,2-dithiolium salts 125 and compounds containing an activated methylene group in the presence of a base. The methylene compound as the carbanion and the dithiolium salt, possibly in the resonance form 125, combine to form the dithiole 126 which, in a basic medium, could readily lose alkyl mercaptan to give the appropriate 3-alkylidene-1,2-dithiole 7.



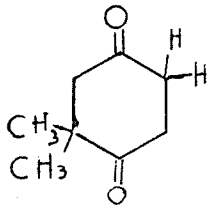
125 126 7

a) R_1=Ar, R_2=H, R=alkyl
b) R_1=Ar, R_2=Ar, alkyl, R=alkyl
c) $R_1 \neq Ar$, R=alkyl

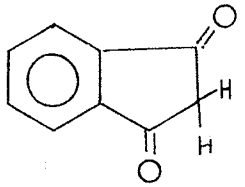
1-Acenaphthenone (127)[127,128], 5,5-dimethyl-1,3-cyclohexanedione (128)[125], 1,3-indanedione (129)[125], 1,3-phenalanedione (130)[125], barbituric acid (2,4,6-pyrimidinetriol) (131)[125], rhodanines (2-thiothiazolidine-2,4-diones) 132[124,125], malononitrile (133)[126], N-methyl-2-methylenebenzothiazoline (134)[124], fluorene (135)[126], substituted cyclopentadienes 136[126] and 4,5-diphenylimidazole (137)[129] have been used as sources of an activated methylene group. These compounds also give the 3-alkylidene-1,2-dithioles 7 with the corresponding 1,2-dithiole-3-thiones in the presence of a base.



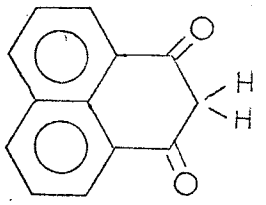
127



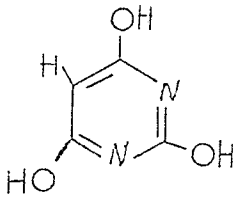
128



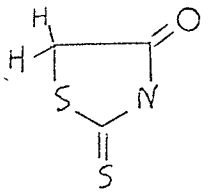
129



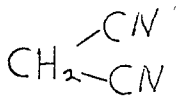
130



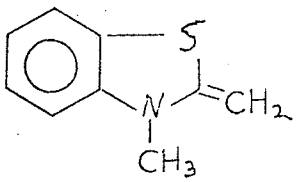
131



132



133



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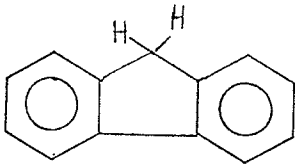

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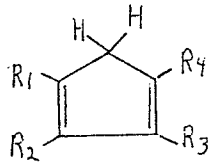

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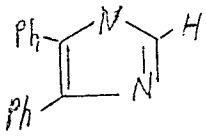
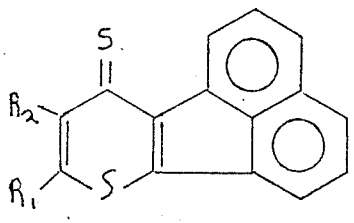


137

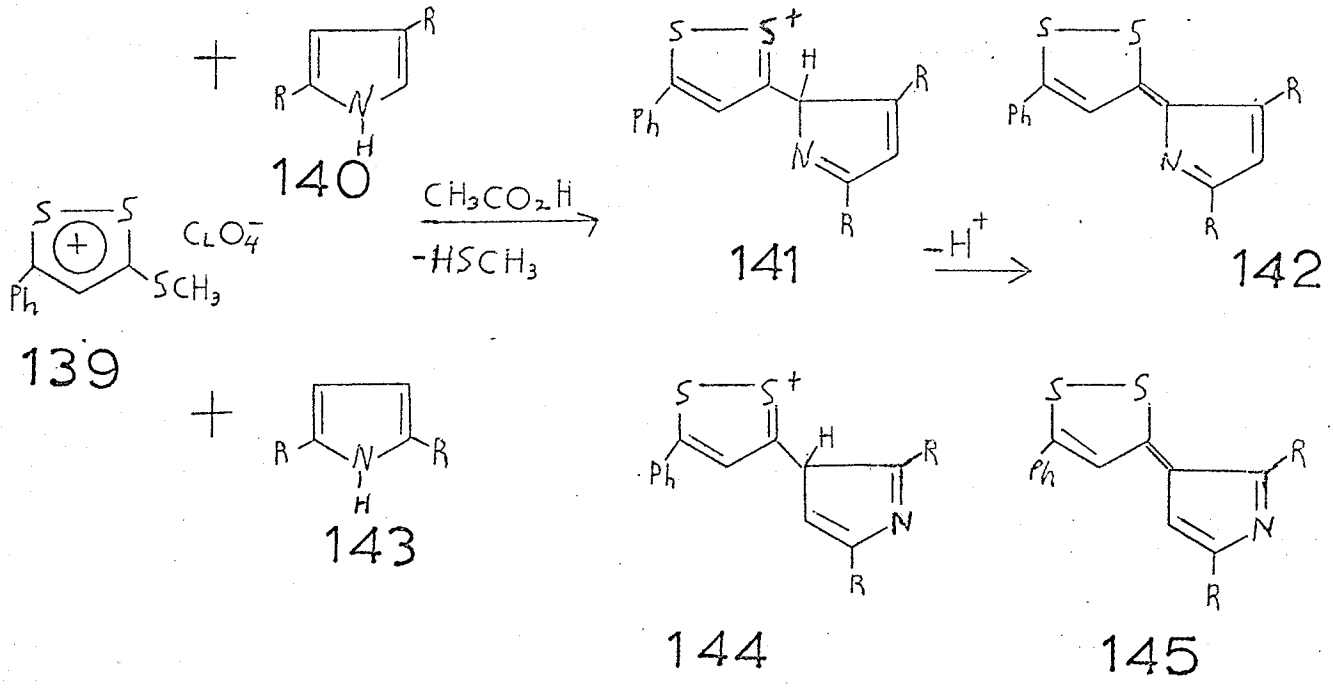
Good yields are obtained from the 5-aryl salts 125a, whereas for the more sterically hindered 4,5-disubstituted salts 125b the yield decreases. In the reaction of acenaphthenone (127) with dithiolium salts 125c which do not have an aryl substituent at position -5, acenaphtho-(1,2-b)-thiopyran-10-thiones 138 are the only products isolated[127].



138

$R_1 \neq Ar$

3-Alkylthio-1,2-dithiolium salts are also reported to give 3-alkylidene-1,2-dithioles on treatment with glacial acetic acid[129]. Thus the dithiolium salts 141 and 144 which are formed by the reaction of 2,4-disubstituted and 2-5-disubstituted pyrroles, 140 and 143, respectively, and 3-methylthio-5-phenyl-1,2-dithiolium perchlorate (139) in glacial acetic acid, on the addition of base, produce the azadithiofulvalenes 142 and 145, respectively.

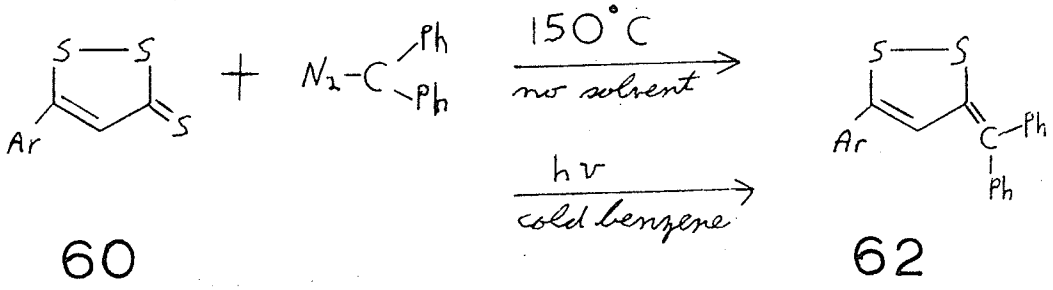


3. From 1,2-Dithiole-3-thiones.

The synthesis of (5-aryl-1,2-dithiole-3-ylidene)malononitrile 71 [75] prepared from 1,2-dithiole-3-thiones and tetracyanoethylene or tetracyanoethylene oxide and the synthesis of 3-diphenylmethylene-1,2-dithioles 62[74] prepared from 1,2-dithiole-3-thiones and diphenylketene have been discussed previously (Part II, Section B).

3-Diphenylmethylene-1,2-dithioles 62 have also been obtained in

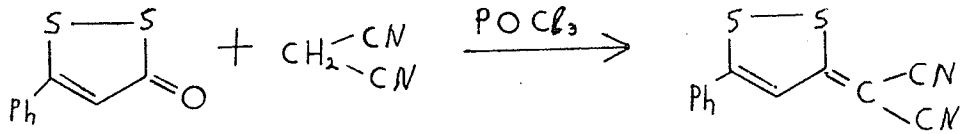
the reaction of 5-aryl-1,2-dithiole-3-thiones 60 and diphenyldiazomethane[130].



60 62

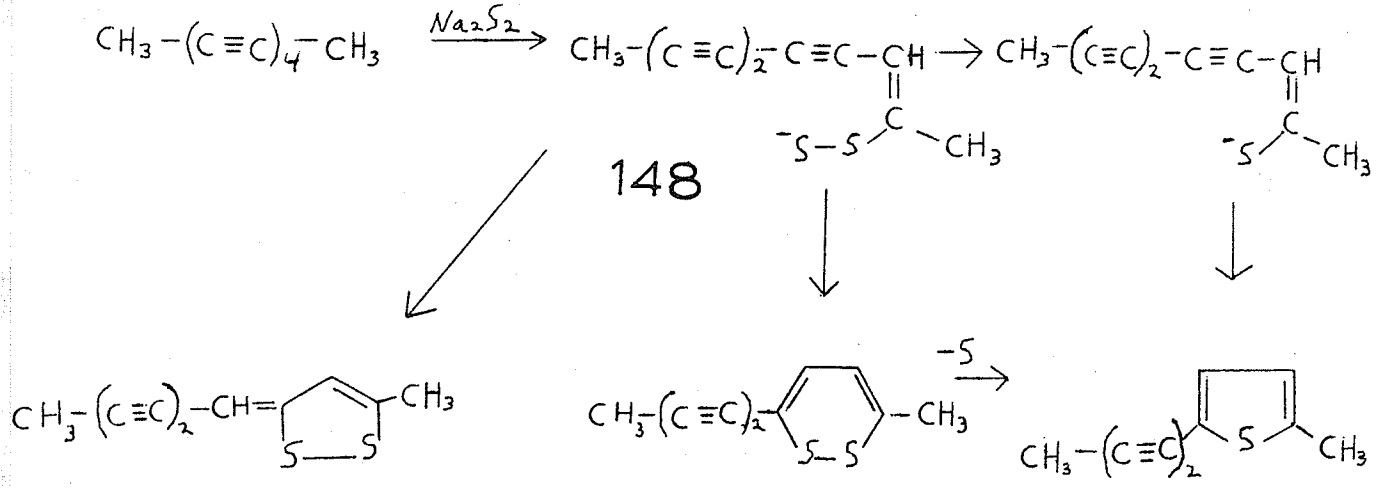
4. Miscellaneous Preparations.

Condensation of 5-phenyl-1,2-dithiole-3-one (146) and malononitrile in the presence of phosphorus oxychloride is reported to give the dinitrile 147[131].



146 147

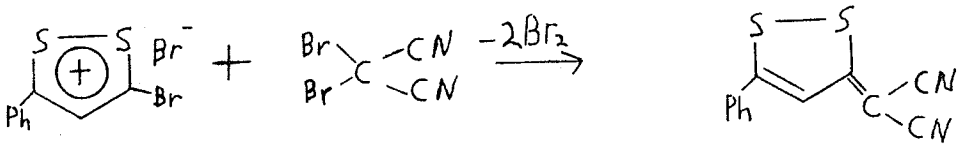
A 3-alkylidene-1,2-dithiole has been prepared by the treatment of a polyacetylene with sodium disulfide[132]. Thus 5-(hexa-2,4-diyne-1-ylidene)-5-methyl-1,2-dithiole (149) has been obtained from deca-2,4,6,8-tetrayne, along with 2-methyl-5-(penta-1,3-diynyl)thiophene (151). It has been suggested by the authors that the anion 148, formed by the addition of the disulfide anion to the polyacetylene, could cyclize to give the 3-alkylidene-1,2-dithiole 149 and the dithiin 150 or could lose sulfur and then cyclize to yield the thiophene 151. The dithiin 150 could also lose sulfur to give the thiophene 151.



148

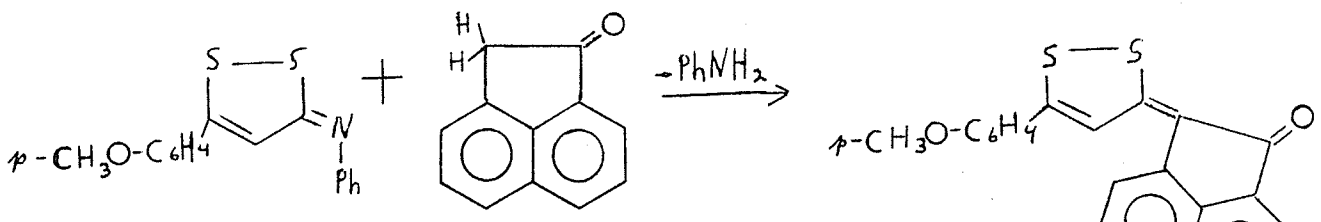
149 150 151

Boberg and Wiedermann have also made the malononitrile 147 by the reaction of 3-bromo-5-phenyl-1,2-dithiolium bromide (152) and dibromomalononitrile[133].



152 147

A 2-(1,2-dithiole-3-ylidene)-1-acenaphthenone 154 has been prepared by the reaction of acenaphthenone (127) and 3-phenylimino-5-*p*-methoxyphenyl-1,2-dithiole (153) in the presence of pyridine[128].

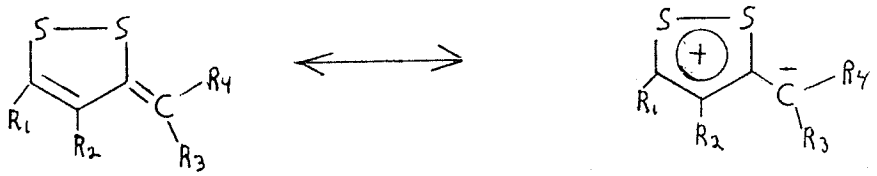


153 127

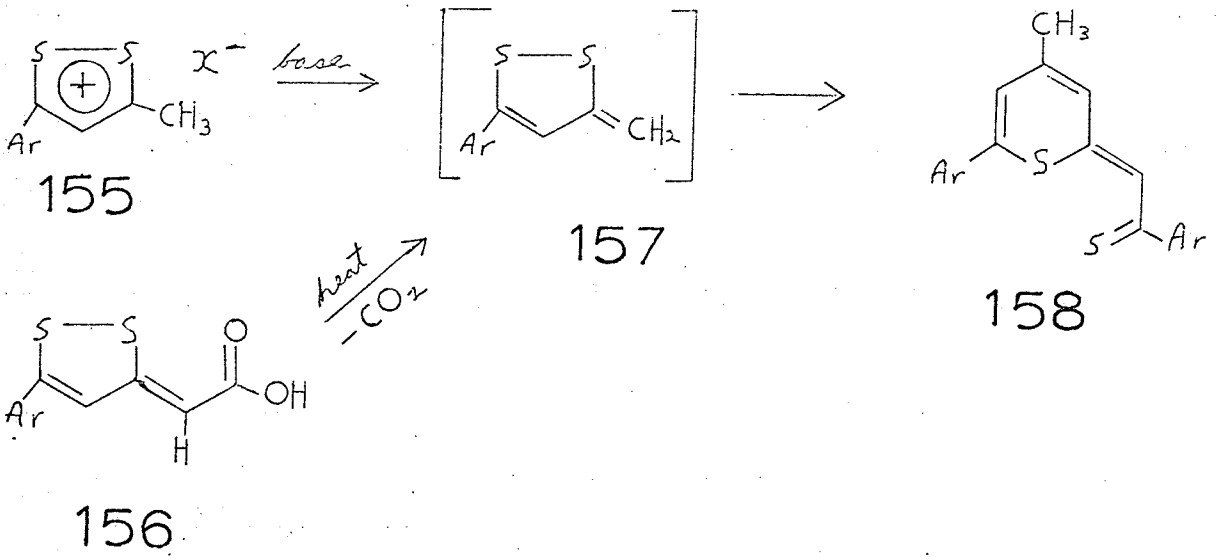
154

Section B: Reactions of 3-Alkylidene-1,2-dithioles

Few reactions of 3-alkylidene-1,2-dithioles of the type 122 have been reported. In fact, few of these dithioles 122 have been synthesized. Resonance stabilization of 3-alkylidene-1,2-dithioles can be achieved through the quasi-aromatic resonance form 7a, only if the negative charge at the exocyclic carbon atom can be effectively stabilized. Thus 3-alkylidene-1,2-dithioles of the type 122 with electron withdrawing substituents at the exocyclic carbon atom should be stable. This is found to be the case[125,126,134]. It has been reported that 3-alkylidene-1,2-dithioles with alkyl substituents at the exocyclic carbon atom are too unstable to be isolated[134]. Also, attempts to isolate 3-methylene-1,2-dithioles 157 only give the thiopyrans 158. The 3-methylene-1,2-dithioles 157 have been generated by the treatment of 5-aryl-3-methyl-1,2-dithiolium salts 155 with base[135] and by decarboxylation of the acid function of the dithioles 156[136]. Nucleophilic attack of the exocyclic carbon atom of a methylene dithiole 157 upon another molecule of the dithiole 157 is probably involved in the formation of the thiopyrans 158.

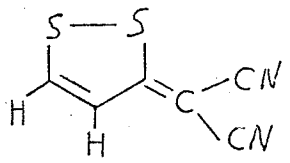


7 7a



155 157 158 156

The protonation of 3-alkylidene-1,2-dithioles containing alkyl or aryl substituents at the exocyclic carbon atom is achieved with relatively mild protonating agents[123,137]. However, when electron withdrawing groups, such as nitriles, are at the exocyclic carbon atom, the basicity is lowered to such an extent that the dinitrile 159 is reported not to be appreciably protonated, even in trifluoroacetic acid[138].

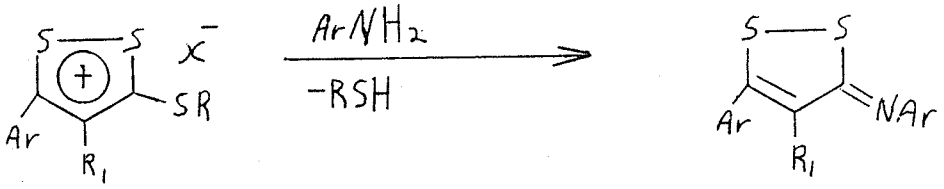


159

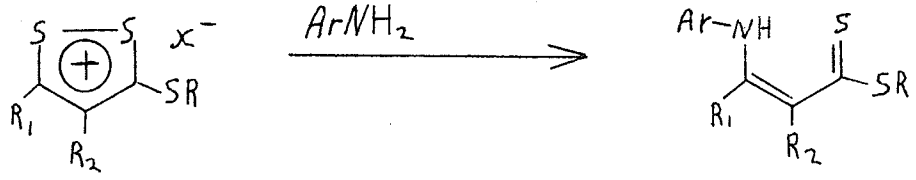
PART IV: 3-Imino-1,2-dithioles.

Section A: Preparations of 3-Imino-1,2-dithioles

Rather analogously to the preparation of 3-alkylidene-1,2-dithioles from 3-alkylthio-1,2-dithiolium salts, previously mentioned (Part III, Section A-2), 3-arylimino-5-aryl-1,2-dithioles have been prepared by the reaction of 3-alkylthio-5-aryl-1,2-dithiolium salts 160 with primary aromatic amines[97,124,128,139,140]. In contrast, 5-unsubstituted[140] and 5-alkyl[97,140] dithiolium salts 162a and 162b give the corresponding alkyl esters of 3-arylamino-dithiopropenoic acids 163a and 163b, respectively, by nucleophilic attack of the amine at C-5 of the dithiole ring and subsequent ring opening and loss of sulfur.



160 (R = alkyl) 161



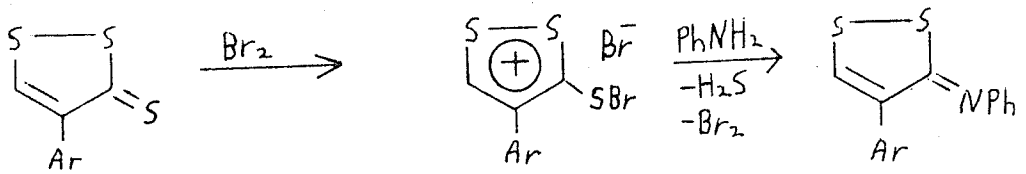
162 163

a) R_1 = H, R = alkyl
b) R_1 = R = alkyl

a) R_1 = H, R = alkyl
b) R_1 = R = alkyl

An 3-arylimino-4-aryl-1,2-dithiole 166 has been prepared by the treatment of a 4-aryl-1,2-dithiole-3-thione 164 with bromine and then by

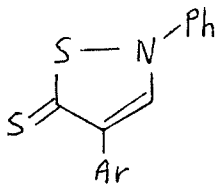
subsequent reaction with aniline[141]. The 3-bromothio-1,2-dithiolium bromide 165 is believed to be the intermediate which reacts with aniline to form the imine 166. However, other work indicates that the product of this reaction may be, in fact, the Δ^3-isothiazolin-5-thione 167[142].



164 $Ar = p\text{-}CH_3C_6H_4$

165

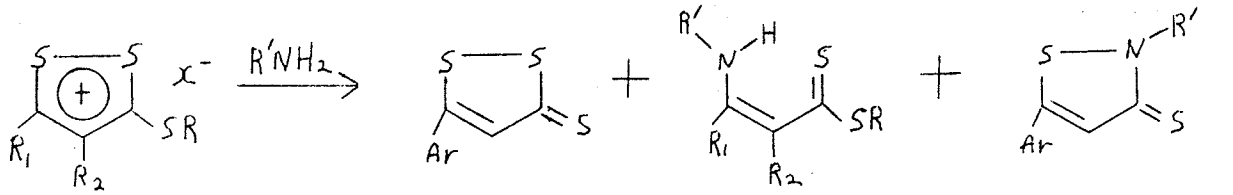
166 $Ar = p\text{-}CH_3C_6H_4$



167

In an analogous manner, 3-arylimino-5-aryl-1,2-dithioles 161 have been prepared by the treatment of 5-aryl-1,2-dithiole-3-thiones 60 with chlorine and primary aromatic amines[143].

The action of primary alkyl amines on 3-alkylthio-5-aryl-1,2-dithiolium salts 168a has been reported not to give the corresponding 3-alkylimino-5-aryl-1,2-dithioles 172 but to give the corresponding 5-aryl-1,2-dithiole-3-thiones 169, alkyl esters of 3-alkylaminodithiopropenoic acids 170a and 2-alkyl-5-aryl-Δ^4-isothiazolin-3-thiones 171 in variable yields[144]. The reaction of the isomeric 3-alkylthio-4-aryl-1,2-dithiolium salts 168b and primary alkyl amines gives only the 3-alkylamino-dithiopropenoates 170b[144].



168 169 170 171

a) R_1=Ar, R_2=H, R= alkyl

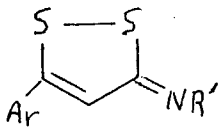
b) R_1=H, R_2=Ar, R= alkyl

R′=alkyl

170

a) R_1=Ar, R_2=H, R=R′= alkyl

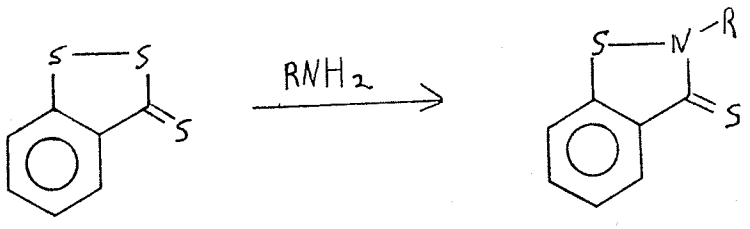
b) R_1=H, R_2=Ar, R=R′= alkyl



172

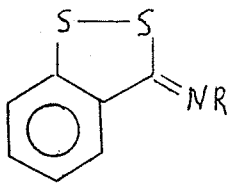
R′=alkyl

The Δ^4-isothiazolin-3-thiones 173 have also been reported to be the products formed in the reaction of benzo-1,2-dithiole-3 thione (99) with primary alkyl amines and aniline[145,146]. However, some of the reactions of these Δ^4-isothiazolin-3-thiones 173 have been shown to be better explained by the use of the 3-imino-1,2-dithiole formula 174. Further studies of this system are necessary before any definite conclusions can be reached.



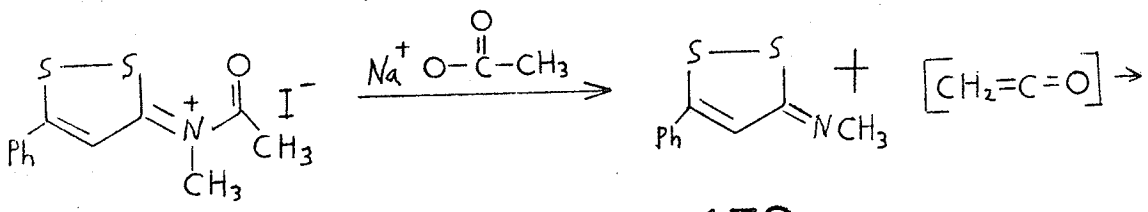
99 173

R=Ph or alkyl



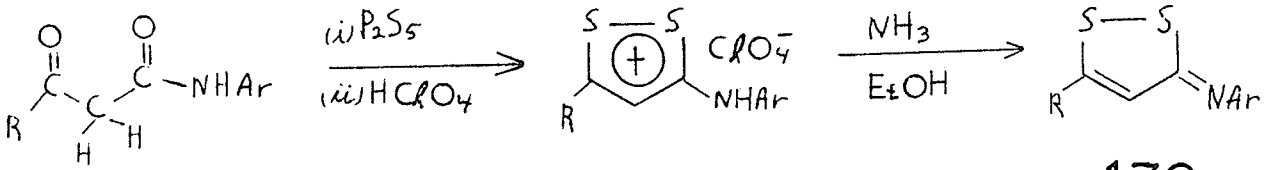
174
R = Ph or alkyl

3-Methylimino-5-phenyl-1,2-dithiole (176) has been obtained by the treatment of 3-(N-methyl-N-acetyl)-5-phenyl-1,2-dithiolium iodide (175) with sodium acetate[147].



175 176

The sulfurization of the N-aryl-β-ketopropanamides 177a and 177b, followed by treatment with perchloric acid gives the iminium salts 178a and 178b, respectively, which, in a solution of ammonia in ethanol, are converted into the imines 179a and 179b, respectively[143]. The imine 179b is the first 3-arylimino-5-alkyl-1,2-dithiole to be prepared.



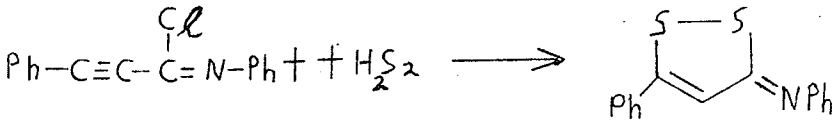
177 178 179

a) R = Ph
b) R = CH_3

a) R = Ph
b) R = CH_3

3-Phenylimino-5-phenyl-1,2-dithiole (181) has been prepared by

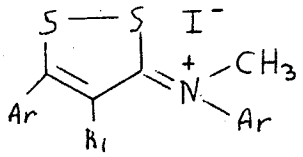
the reaction of N-phenyl-5-phenyl-propiolimidoyl chloride (180) and hydrogen disulfide.



180 181

Section B: Reactions of 3-Imino-1,2-dithioles

Few studies of the reactions of 3-imino-1,2-dithioles have been reported. 3-Arylimino-5-aryl-1,2-dithiole 153 has been found to participate in typical imine reactions[128]. The nitrogen atom of 5-aryl-substituted imines 161 is sufficiently nucleophilic to be alkylated by methyl iodide to give the iminium salts 182[128,140].



182

Analogously to the preparation of 3-alkylidene-1,2-dithioles by the reaction of 1,2-dithiole-3-thiones and compounds containing an activated methylene group, the 3-imino-1,2-dithiole 153 reacts with acenaphthenone in the presence of a base to give the 2-(1,2-dithiole-3-ylidene)-1-acenaphthenone 154[128]. This reaction has been mentioned previously (Part III, Section A-4).

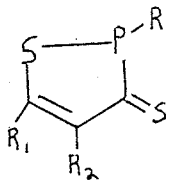
DISCUSSION

Object of Research

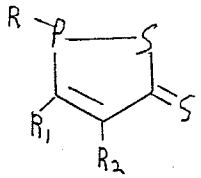
A. To investigate the reactions of 5-substituted and 5-unsubstituted-1,2-dithiole-3-thiones with activated acetylenes and olefins in order to determine the stereochemistry of the products and the mechanism by which they are formed.

B. To investigate the reactions of 3-imino-1,2-dithioles 8 and 3-alkylidene-1,2-dithioles 7 and activated acetylenes in order to determine if these dithiole derivatives react with acetylenes via a (3 + 2) cycloaddition.

C. To investigate the reactions of Δ^4-isothiazolin-3-thiones of the type 171, Δ^4-isothiaphospholin-3-thiones 183 and Δ^3-isothiaphospholin-5-thiones 184 and activated acetylenes in order to determine if these heterocyclic compounds react with acetylenes via a (3 + 2) cycloaddition.



183



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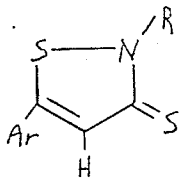


171

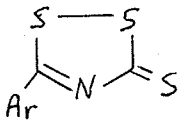
D. To investigate the use of 2-(2-thioacylmethylene)-1,3-dithioles 93 as precursors to new and interesting heterocyclic compounds.

Chapter I. Reactions of 1,2-Dithiole-3-thione with Acetylenic Esters and Olefins

1,2-Dithiole-3-thiones and activated acetylenes have been reported to react via a (3 + 2) cycloaddition to form 2-(2-thioacylmethylene)-1,3-dithioles 93 (mono-adducts)[89-92]. Mono-adducts 93 prepared by the reaction of thiones 6 and dimethyl acetylenedicarboxylate react further with the acetylenic ester to give thiopyranspiro-1,3-dithioles 94 (di-adducts)[89] via a (4 + 2) cycloaddition. The reaction of 1,2-dithiole-3-thiones with the less reactive arylacetylenes gives thiothiophthenes of the type 107 along with the corresponding mono-adducts 93 which can be converted into the thiothiophthenes 107 by treatment with phosphorus pentasulfide[91]. These reactions have been previously discussed in the Introduction [Part II, Section B-2(ii)]. During the course of this research, further reports dealing with the (3 + 2) cycloaddition of 1,2-dithiole-3-thiones and activated acetylenes have been published[149-154]. Two of these reports[153,154] are expanded versions of earlier communications of Vialle and co-workers[91] and Behringer and Wiedenmann[90], respectively. Some of the results from these papers will be discussed throughout the remainder of this Chapter. From these new reports, one change in the reaction scheme, illustrated on the next page has been proposed. Vialle who earlier[91] had postulated that the formation of the thiothiophthenes 107 was achieved by the rearrangement of the thietenes 106 which were formed by a competing (2 + 2) cycloaddition of the thiones 6 and arylacetylenes, now states[152] that he has obtained experimental proof that the thiothiophthenes 107 are formed from the mono-adducts 93 and not from the thietenes 106 and

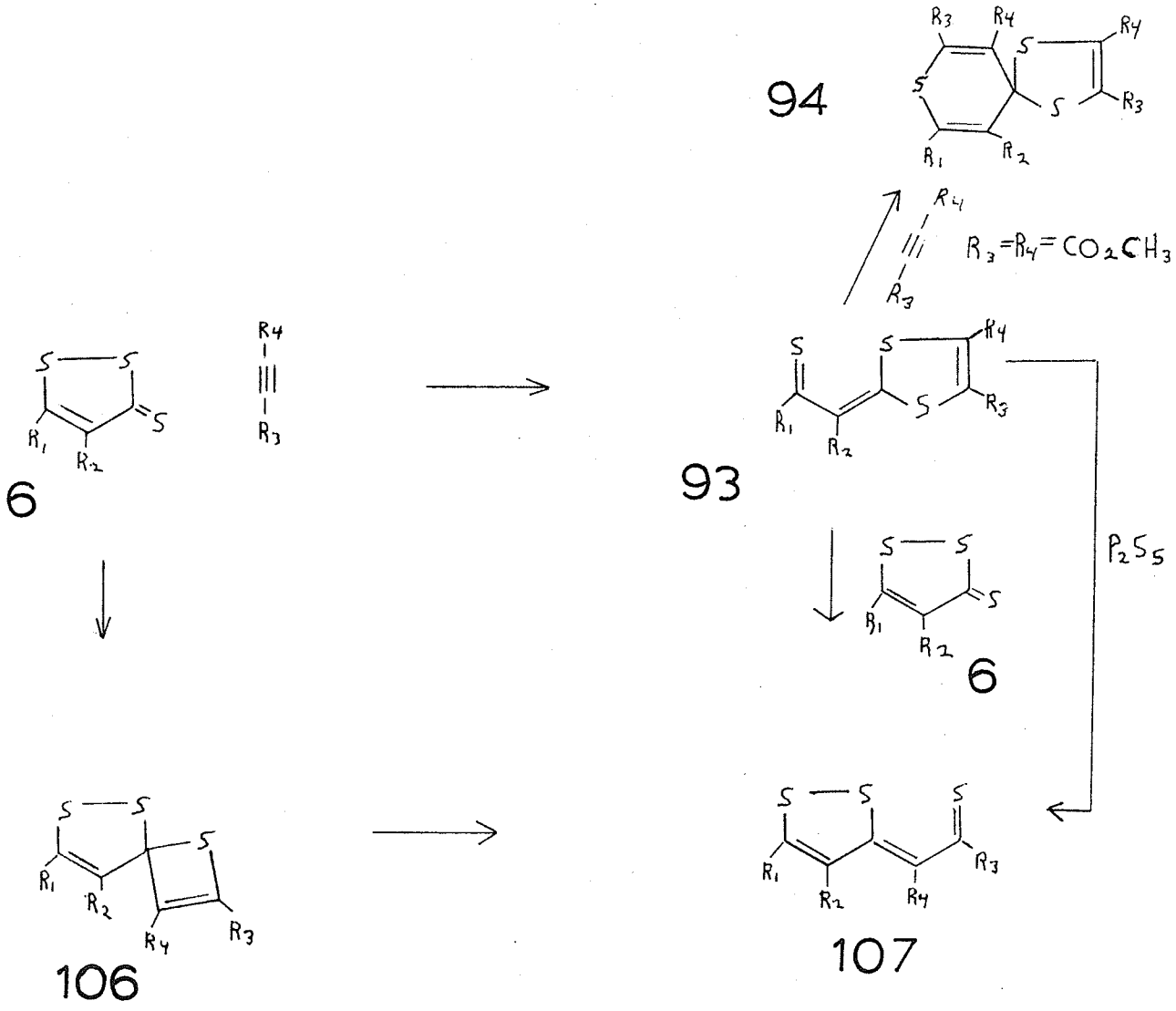
that the unchanged 1,2-dithiole-3-thiones 6, remaining in solution, are catalysts for these transformations. A more complete report with experimental details concerning this new mechanism is still forthcoming.

Similar results to those mentioned above for the reaction of 1,2-dithiole-3-thiones and activated acetylenes have been obtained for the reaction of 1,2,4-dithiazole-3-thiones 185 and activated acetylenes [154-159]. Some of these results will be discussed throughout the remainder of this Chapter.



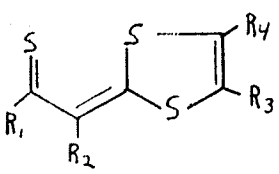
185

a) Ar = Ph

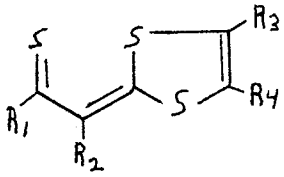


Section A: Reactions of 4,5-Diphenyl-1,2-dithiole-3-thione with Dimethyl Acetylenedicarboxylate, Ethyl Propiolate and Ethyl Phenylpropiolate

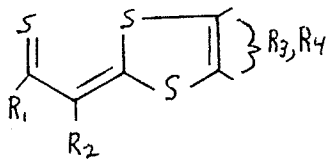
Although many studies of the reactions of 1,2-dithiole-3-thiones and activated acetylenes have been undertaken prior to this research, little has been reported concerning the products of these reactions, namely, thioacylmethylene-1,3-dithioles 93 and thiopyranspiro-1,3-dithioles 94. When an unsymmetrical acetylene is employed, two possible thioacylmethylene-1,3-dithioles, formulated as 93 and 102 are possible. For simplicity, a mixture of mono-adducts of the types 93 and 102 will be designated as the mono-adduct 93' throughout the remainder of this thesis and will denote the interchangeability of the substituents R_3 and R_4.



93

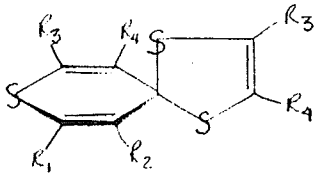


102

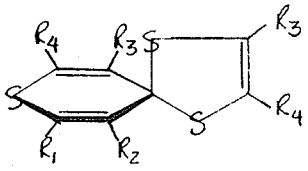


93'

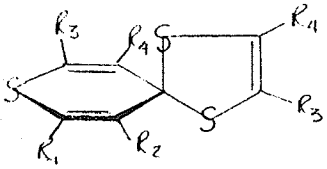
For the formation of thiopyranspiro-1,3-dithioles of the type 94 from thioacylmethylene-1,3-dithioles 93', four di-adducts 94, 186, 187 and 188 are possible since there are two possible modes of addition of the thioketonic side chain of the mono-adduct 93' to the unsymmetrical acetylene, although nucleophilic addition is usually β to the ester function of acetylenic esters[104]. However, the di-adducts 94 and 186 are enantiomers as are the di-adducts 187 and 188.



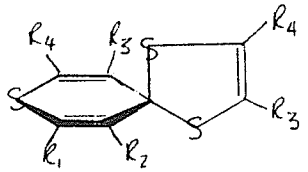
186



187

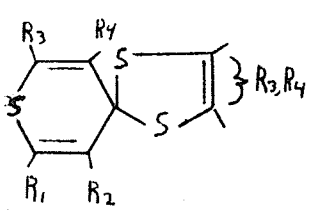


94

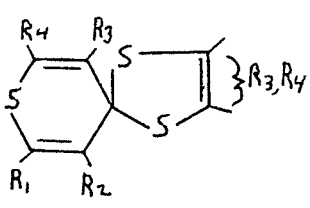


188

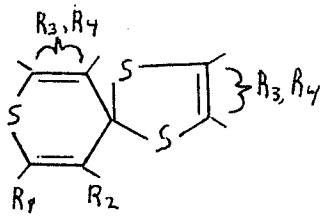
Again for simplicity, the enantiomeric pair 94 and 186 and the enantiomeric pair 187 and 188 will be designated 94' and 187', respectively and will denote the interchangeability of the substituents R_3 and R_4 on the dithiole ring. A mixture of the enantiomeric pairs 94' and 187' will be designated as 94" and will denote the interchangeability of the substituents R_3 and R_4 on both the 1,3-dithiole and thiopyran rings.



94'



187'

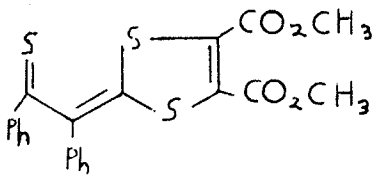


94"

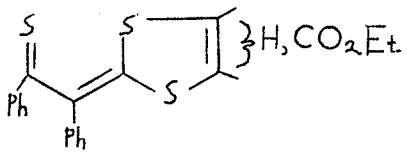
From the elucidation of the stereochemistry of the mono- and di-adducts 93 and 94, respectively, information about the mechanism of the (3 + 2) and the (4 + 2) cycloadditions by which these adducts are formed, may possibly be ascertained. Thus it seemed desirable to investigate the reaction of 1,2-dithiole-3-thiones and activated acetylenes in order to determine the stereochemistry of 2-(2-thioacylmethylene)-1,3-dithioles 93 and thiopyranspiro-1,3-dithioles 94. The acetylenic ester dimethyl acetylenedicarboxylate and the two unsymmetrical acetylenic esters ethyl propiolate and ethyl phenylpropiolate were employed as the activated acetylenes because di-adducts 94 have only been prepared by the reaction of 1,2-dithiole-3-thiones and dimethyl acetylenedicarboxylate[89]. 4,5-Diphenyl-1,2-dithiole-3-thione (27) was chosen as the thione to determine if a phenyl group in position -4 of the 1,2-dithiole ring has any effect on the (3 + 2) cycloaddition of the thione 27 and acetylenes. Few studies of the reaction of 4,5-disubstituted-1,2-dithiole-3-thiones and acetylenes have been undertaken [Introduction, Part II, Section 2 (ii)]. 4,5-Diphenyl-1,2-dithiole-3-thione (27) was prepared by the reaction of α-methyl stilbene and sulfur.

1. Discussion of the Reactions:

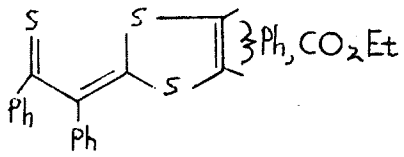
4,5-Diphenyl-1,2-dithiole-3-thione (27) reacted with the three acetylenic esters to give, in each case, one greenish-black mono-adduct 93a, 93a' and 93b', respectively. Analysis of the nuclear magnetic resonance (n.m.r.) spectra of the mono-adducts 93a' and 93b' indicated that each mono-adduct was a mixture of two thioacylmethylene-1,3-dithioles of the type 93 and 102. The n.m.r. spectra will be discussed later in this section.



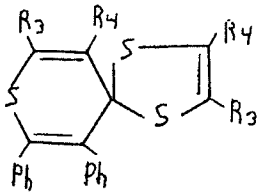
93a



93a'

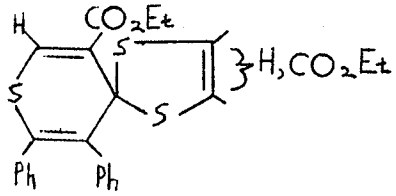


93b'

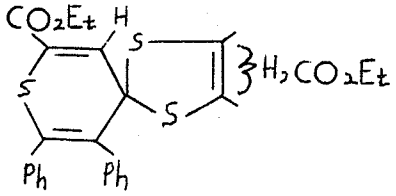


94a

$R_3 = R_4 = CO_2CH_3$



94a'



187a'

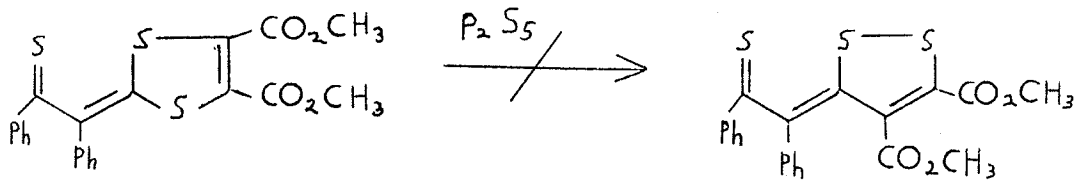
Dimethyl acetylenedicarboxylate and ethyl propiolate reacted further with the mono-adducts 93a and 93a', respectively to give in each case one yellow di-adduct 94a and either 94a' or 187a' respectively. An analysis of the n.m.r. spectrum of the latter di-adduct revealed that only one of the enantiomeric pairs of the type 94' and 187' was present, and therefore, the thioketonic side chain of the mono-adduct 93a' adds to ethyl propiolate in only one direction. Since nucleophilic attack usually occurs β to the ester function of acetylenic esters[104], the di-adduct formed probably is the thiopyranspiro-1,3-dithiole94a' and will be designated as such throughout

the remainder of this thesis. The mode of addition of thioacylmethylene-1,3-dithioles of the type 93 to acetylenic esters will be discussed more fully in Section D of this Chapter. A di-adduct of the type 94 was not found from the reaction of the thione 27 and two equivalents of ethyl phenylpropiolate or from the reaction of the mono-adduct 93b' and ethyl phenylpropiolate. Possibly steric hindrance or reduced reactivity of the acetylene made formation of a di-adduct more difficult.

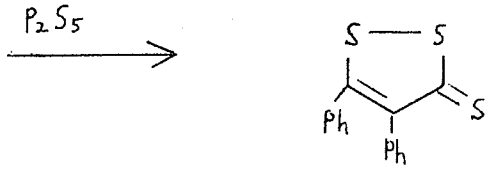
The reduced reactivity, mentioned above, is evident from the reaction conditions needed to obtain the mono- and di-adducts. The difference in reactivity of acetylenic esters towards 1,3-dipoles has been measured by R. Huisgen[104] and has been found to be substantial. Dimethyl acetylenedicarboxylate was found to be the most reactive acetylene studied, and then in decreasing order methyl propiolate and ethyl phenyl-propiolate. In the same study, phenylacetylene was found to be less reactive than ethyl phenylpropiolate and thus also would not be expected to form di-adducts 94. No di-adducts 94 have been reported for the reaction of 1,2-dithiole-3-thiones and arylacetylenes.

The thione 27 reacted with dimethyl acetylenedicarboxylate at room temperature to give the mono-adduct 93a as the major product and the di-adduct 94a in small amounts. Easton and Leaver also report similar behaviour for the reactions of various 1,2-dithiole-3-thiones with dimethyl acetylenedicarboxylate[89]. The di-adduct 94a became the major product when the thione 27 and two equivalents of dimethyl acetylene-dicarboxylate reacted in boiling benzene. A violet powder ($\sim$ 10 mg.) was a minor product of this reaction. It was first thought that this compound might be the thiothiophthene 107a since thiothiophthenes containing carboethoxy groups are purple in colour[11]. In an attempt to

obtain a sizeable amount of the violet compound, the mono-adduct 93a was treated with phosphorus pentasulfide in boiling tetralin. This method is used to convert mono-adducts of the type 93 which contain only aryl substituents into the corresponding thiothiophthenes 107[153]. No thiothiophthene 107a could be found, but 4,5-diphenyl-1,2-dithiole-3-thione (27) was recovered. A possible mechanism for this 'retro' step will be discussed in Section D of this Chapter.



93a 107a



27

The violet compound is formed by the reaction of the mono-adduct 93a, the thione 27 and the dimethyl acetylenedicarboxylate since it was found not to be formed by the reaction of the mono-adduct 93a and the ester. The violet compound also is not formed when the di-adduct 94a alone or in the presence of the thione 27 are heated under the reaction conditions. The infrared (i.r.) spectrum of the violet compound showed the presence of ester groups and the mass spectrum contained a molecular ion at M^+/e 518. A minor peak at M^+/e 428 corresponding to the molecular weight of the thiothiophthene 107a was also found. However, lacking any analytical data, it is not known if the compound is pure and thus no structure

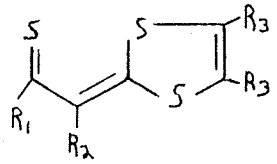
can be assigned to this compound.

The thione 27 and ethyl propiolate at room temperature reacted very slowly to give the mono-adduct 93a' in small yields along with a small amount of the di-adduct 94a' which becomes the major product when the reaction proceeds in boiling benzene. At elevated temperatures, the reaction of the mono-adduct 93a' probably proceeds faster than the initial reaction of the thione 27 with ethyl propiolate. Five other products in trace amounts that were not present when the reaction was performed at room temperature, were isolated along with the mono-adduct 93a'. Possibly, these trace products are formed by the reaction of the mono-adduct 93a' with both the thione 27 and ethyl propiolate.

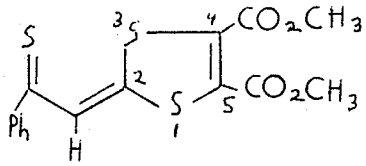
2. Discussion of n.m.r. Spectra:

The n.m.r. spectra of the various 2-(2-thioacylmethylene)-1,3-dithioles 93 and the various thiopyranspiro-1,3-dithioles 94 which have been prepared are summarized in Tables III and IV, respectively. The n.m.r. spectrum of the mono-adduct 93a showed two singlets (6.19, 6.07 τ) assigned to the methyl protons of the carbomethoxy groups which are not equivalent in this molecule. Analogous 2-(2-thioacylmethylene-1,3-dithioles 93b ($R_3 = R_4$) have been reported to have equivalent substituents as indicated by n.m.r.[154]. This equivalence is probably fortuitous since the n.m.r. spectrum (Table III) of the mono-adduct 93c prepared by the reaction of 5-phenyl-1,2-dithiole-3-thione (50b) with dimethyl acetylene-dicarboxylate in hexadeuteriobenzene (because of its solvent shift effects [161]) indicated that the methyl ester groups are not equivalent (6.78, 6.75 τ). This mono-adduct 93c was first prepared by Behringer who reported that the n.m.r. spectrum in carbon disulfide (Table III)

indicated that the carbomethoxy groups were equivalent (singlet 6.1 τ)[154]. In deuteriochloroform (Table III), the methyl protons of the two ester groups also were not equivalent (6.10,6.12 τ) but the Δτ was smaller (∿0.02 τ) and the proton on the side chain absorbed at lower fields (1.92 τ) than the protons of the phenyl group. In carbon disulfide and hexadeuteriobenzene, this proton absorbed in the region of the aromatic protons (C_6D_6, 2.32τ).



93b



93c

The detection of the non-equivalence of the substituents on the 1,3-dithiole ring of the mono-adducts of the type 93b, as indicated by n.m.r., seems to be related to the presence of a phenyl substituent α to the thiocarbonyl group in the thioacylmethylene-1,3-dithioles 93 (originally a 4-substituent on the starting 1,2-dithiole-3-thione). The mono-adducts of the type 93b which are reported to have equivalent substituents on the 1,3-dithiole ring[154] do not have a phenyl or an aryl substituent at the position α to the thiocarbonyl group. The detection of the non-equivalence could possibly be due to a steric or a ring current effect of the phenyl group α to the thiocarbonyl group, e.g., Δτ between the methyl protons of the two ester groups of 93a is 0.12τ ($CDCl_3$) and between the methyl protons of the same two ester groups of 93c is ∿0.02τ. Thus the substituent at position-5 of the 1,3-dithiole ring would be in a different chemical environment than the same substituent

at position -4.

The two carbomethoxy groups on the 1,3-dithiole ring of the thiopyranspiro-1,3-dithiole 94a would be expected to be equivalent. This is found to be the case as indicated by n.m.r. The methyl protons of the two carbomethoxy groups on the thiopyran ring which are not equivalent (6.19, 6.13 τ) absorb at lower fields than the methyl protons of the same ester groups on the 1,3-dithiole ring (6.38τ).

A complex splitting pattern (Figure I, see next page) was observed in the n.m.r. spectrum of the mono-adduct 93a' obtained by the reaction of the thione 27 with ethyl propiolate at room temperature and in boiling benzene. This pattern is interpreted as resulting from a mixture of thioacylmethylene-1,3-dithioles. The absorptions have been assigned in the following manner: two singlets (2.26,2.13τ) due to two different protons on the dithiole ring, two broad singlets (2.98,2.80τ) due to the protons of the two phenyl groups on the side chain and two overlapping quartets [5.67τ(J=7.2 Hz), 5.57τ(J=7.2 Hz)] and two overlapping triplets [8.72τ(J=7.2 Hz), 8.62τ(J=7.2Hz)] due to two carboethoxy groups on the dithiole ring in the ratio of 1:1:10:10:2:2:3:3, respectively. Vialle has observed the similar phenomena in the n.m.r. spectra of various acylmethylene-1,3-dithioles 189a' prepared by the treatment of the corresponding aryl substituted thioacylmethylene-1,3-dithioles 108a' with mercuric acetate[153] (illustrated on page 68). The thioacylmethylene-1,3-dithioles were prepared by the reaction of 1,2-dithiole-3-thiones with arylacetylenes[153]. These same acylmethylene-1,3-dithioles 189a' were also prepared by the dehydration of hydroxy -1,3-dithiolanes of the

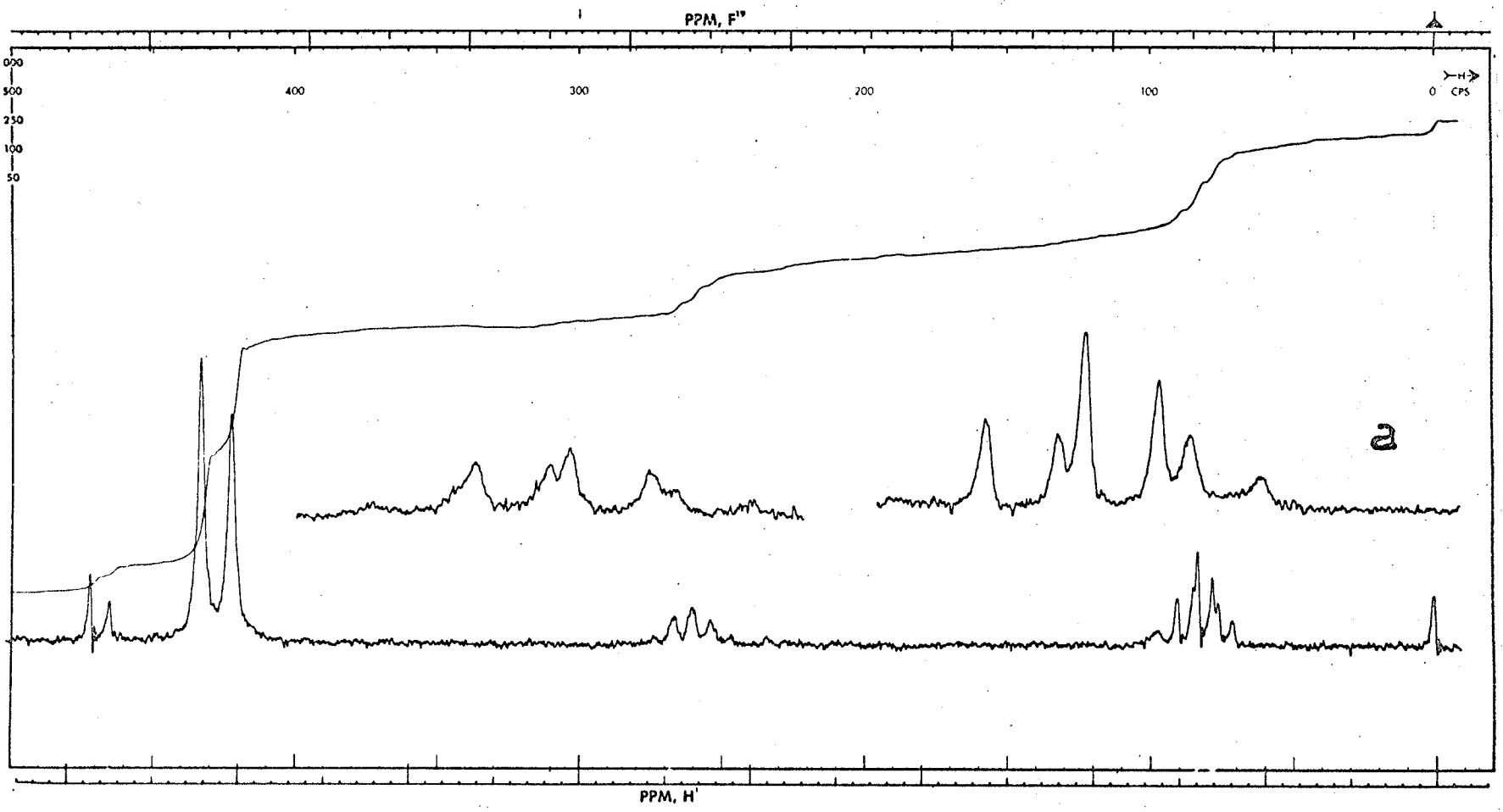
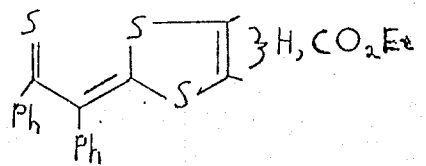
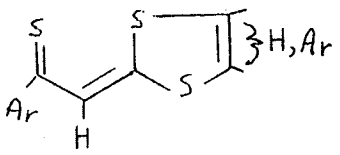


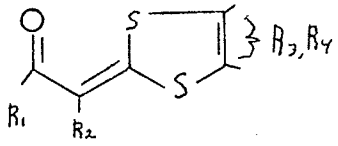
FIG. I: N.M.R. Spectrum of Ethyl 2-(α-Phenylthiophenacylidene)-1,3-dithiole-4-carboxylate (93a'); Sweep Width 500 hz.
a : Sweep Width 100 Hz.



192



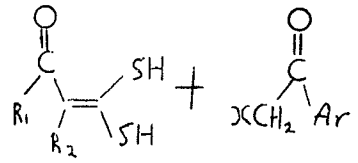
108a'



189'

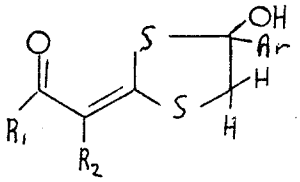
a) $R_1 = Ar, R_2 = H; R_3, R_4 = H, Ar$

b) $R_1 = Ph, R_2 = H; R_3, R_4 = H, Ph$



96

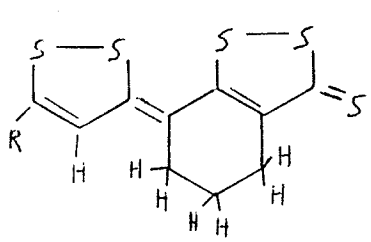
a) $R_1 = Ar, R_2 = H$



190

a) $R_1 = Ar, R_2 = H$

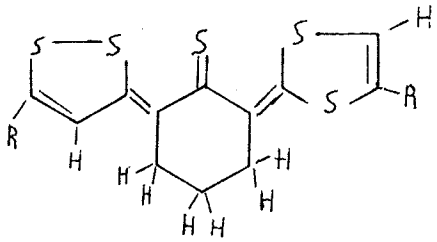
$-H_2O$



191

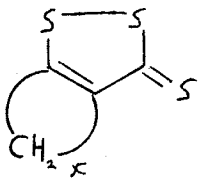
$R = (CH_3)_3C-$

$R-\equiv-H$



193

$R = (CH_3)_3C-$



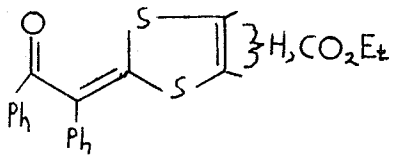
194

type 190 which were formed by the reaction of dithiocarboxylic acids 96a with the appropriate α-halo-ketone. The n.m.r. spectra of the acylmethylene-1,3-dithioles 189a', prepared by both methods, were identical[153]. Campaigne and Haaf[93] also have prepared various ketones of the type 189' which also show the presence of two acylmethylene-1,3-dithioles, as indicated by n.m.r., by the latter method and the acylmethylene-1,3-dithiole 189b' by the reaction of the 2-methylthio-4-phenyl-1,3-dithiolium salt 192 with ethyl benzoylacetate in the presence of pyridine[93].

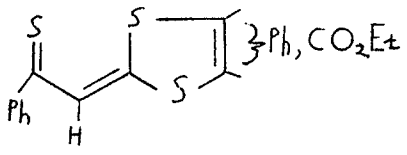
Presumably the thioacylmethylene-1,3-dithioles 108a' mentioned above, also exhibit similar patterns in their n.m.r. spectra. However, for many thioacylmethylene-1,3-dithioles made by the reaction of 1,2-dithiole-3-thiones with unsymmetrical acetylenes, little n.m.r. data has been published. Behringer has mentioned that from the n.m.r. spectra of various mono-adducts of the type 108a' two different thioacylmethylene-1,3-dithioles were evident, but no n.m.r. data was presented[154]. Stavaux and Lozac'h[150] have reported the n.m.r. spectrum of the mono-adduct 193 prepared by reaction of the bicyclothione 191 with *t*-butylacetylene (illustrated on the previous page). It showed singlets for the *t*-butyl protons and for the proton on the dithiole ring, thus indicating the presence of one thioacylmethylene-1,3-dithiole. The appearance of singlets for these substitutents may be fortuitous since the authors state that they had difficulty in analyzing the spectrum. Further n.m.r. studies of mono-adducts of the type 193 and of other mono-adducts derived by the reaction of bicyclo-1,2-dithiole-3-thiones of the type 194 with unsymmetrical acetylenes are needed before any definite conclusions can be made. The scarcity of

n.m.r. data may be due either to the low solubility of mono-adducts in common organic solvents or to the use of 1,2-dithiole-3-thiones which have no aryl substituent at position -4 of the 1,2-dithiole ring. In both cases, the interpretation of the resulting complex spectra might be difficult. Difficulty was encountered in dissolving the mono-adducts, discussed in this Chapter, in common organic solvents at room temperature in sufficient quantities to provide proper spectra.

The acylmethylene-1,3-dithiole 189c' (discussed below) prepared by the treatment of the mono-adduct 93a' with mercuric acetate also displayed a complex n.m.r. spectrum (Table III) which has been interpreted as showing the presence of two acylmethylene-1,3-dithioles. Similarly, the n.m.r. spectrum of the mono-adduct 93b' can be interpreted as a mixture of mono-adducts in which $\Delta\tau$ between the overlapping quartets and between the overlapping triplets of the carboethoxy group is equal to the J value (0.12τ). The n.m.r. spectrum of the mono-adduct 93c' (Table III) which was prepared by the reaction of 5-phenyl-1,2-dithiole-3-thione (50b) with ethyl phenylpropiolate[162] (discussed in Section D of this Chapter) also showed the presence of two mono-adducts in which the small $\Delta\tau$ (0.04τ) between the two overlapping quartets and the two overlapping triplets is probably due to the absence of a phenyl substituent α to the thiocarbonyl group.

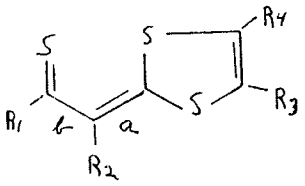


189c'

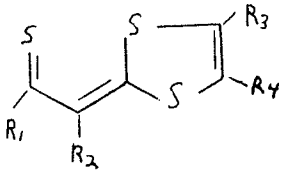


93c'

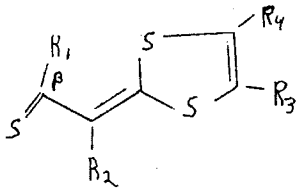
In the n.m.r. of mono-adducts of the type 93', the two conformers, i.e., the *s-cis* form 93 and the *s-trans* form 195 (see below) and the geometrical isomers, i.e., the two *s-cis* forms 93 and 102 (93') could both give rise to two different signals for each substituent since each substituent would be in a different chemical environment. However, if the pattern was caused by the two conformers of the type 93 and 195, there should be more than two signals for the protons of the two phenyl groups of the mono-adduct 93a' (see Figure I). The expected multiplet might be due to the increased anisotropy of the protons of the phenyl group which is at the β-position of the side chain of the *s-trans* conformer 195a caused by the proximity of this phenyl group to a sulfur atom of the 1,3-dithiole ring.



93



102

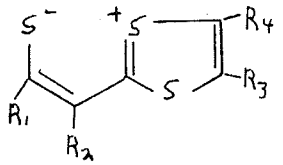


195

a) $R_1=R_2=Ph$, $R_3=H$, $R_4=CO_2Et$

Also, the conversion of one conformer into the other should be temperature dependent, but high temperature n.m.r. studies (40 - 95°C) on the mono-adduct 93a' and its oxygen analogue, the acylmethylene-1,3-dithiole 189c' have shown that there was no interconversion. In the case of the mono-adduct 93a', a higher resolution n.m.r. spectrum was obtained. Similar studies (40 - 130°C) conducted by Campaigne and Haaf[93] on acylmethylene-1,3-dithioles of the type 189' were also unsuccessful. Thus it is probable that thioacylmethylene-1,3-dithioles 93' exist

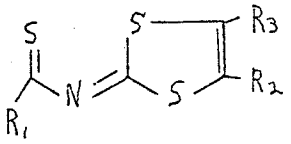
mainly in the *s-cis* conformation which may possibly be stabilized by a contribution from the dipolar form 196a.



196a

The two *s-cis* isomers 93 and 102 could possibly occur by conversion of the initially formed isomer 93 into the other isomer 102, by rotation about the 'a' bond of the side chain. Also both might be formed in the reaction and not be interconvertible. If the former mechanism is operative, this *cis-trans* isomerization about the exocyclic double bond should be temperature dependent, and as discussed above, no interconversion was found between 40 - 130°C . Also there should be an equal amount of each of the two *s-cis* isomers. But the n.m.r. spectrum of the mono-adduct 93a' (Figure I) indicates that the isomers are found in different proportions, i.e., the heights and area of the two singlets and of the two triplets due to the proton and the methyl protons of the carboethoxy group on the 1,3-dithiole ring respectively, are not equal. These two observations suggest that the two *s-cis* isomers are formed during the reaction of 1,2-dithiole-3-thiones and acetylenic esters. This may also be the case for the mono-adducts 108a' formed by reaction of 1,2-dithiole-3-thiones and arylacetylenes. The non-equivalence of the carbomethoxy groups on the mono-adducts 93a and c (discussed above) is consistent with the presence of two *s-cis* isomers. Mechanisms by which both isomers can be formed in the reaction will be discussed in Section C of this Chapter.

2-(2-Thiobenzimino)-1,3-dithiole-5-dicarboxylate (197b) prepared by reaction of 5-phenyl-1,2,4-dithiazole-3-thiones (185a) with ethyl propiolate is reported to consist of only one isomer, as indicated by n.m.r.[155]. Similarly, the n.m.r. spectrum of the dimethyl ester 197a indicated that the two carbomethoxy groups on the 1,3-dithiole ring are equivalent[155], but this may only be fortuitous. It is possible that only one isomer is formed and is not interconvertible or that due to the greater electronegativity of the side chain nitrogen in the compounds 197 a,b compared to the side chain carbon in the thioacymethylene-1,3-dithioles 93, the exocyclic double bond may acquire more single bond character, permitting free rotation and thus only one signal for each substituent will be detected by n.m.r. Such free rotation should be temperature dependent, but even at -60°C the n.m.r. spectrum of the ethyl ester 197b is reported to indicate that only one compound is present[158]. Further investigations are required to determine which of the two possibilities, mentioned above, is responsible for the detection of one of the two possible isomers, as indicated by n.m.r.



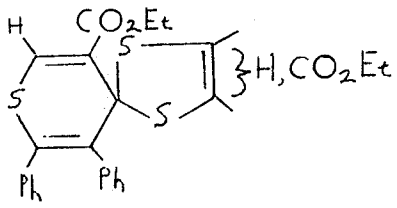
197

a) $R_1 = Ph$, $R_2 = R_3 = CO_2CH_3$

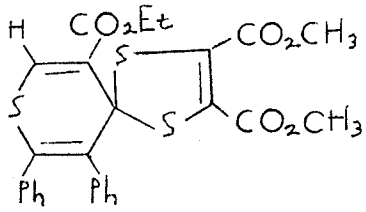
b) $R_1 = Ph$, $R_2 = H$, $R_3 = CO_2Et$

The n.m.r. of the di-adduct 94a' is consistent with the presence of one enantiomeric pair since only a singlet (2.49τ) for the proton

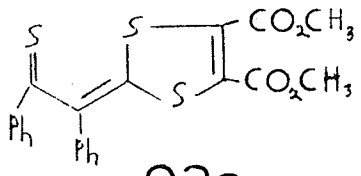
on the thiopyran ring is apparent. The two protons on the 1,3-dithiole ring absorbed at 3.5τ and are equivalent in the enantiomers. A mixed di-adduct assigned the structure 94b was prepared by reaction of the mono-adduct 93a with ethyl propiolate to allow proper assignment of the protons in the different rings of the di-adduct 94a'. It demonstrated that protons (2.45τ) on the thiopyran ring absorb at lower fields than those on the 1,3-dithiole ring. The enantiomeric pair comprising the di-adduct 94a' probably is formed by β- addition of the thione sulfur of the mono-adduct 93a' to the acetylenic ester (discussed earlier in this Section).



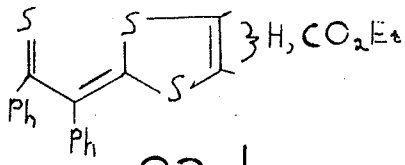
94a'



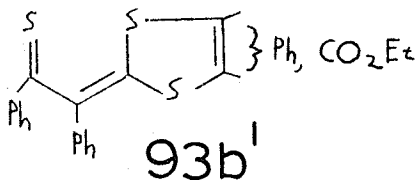
94b



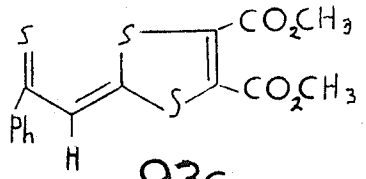
93a



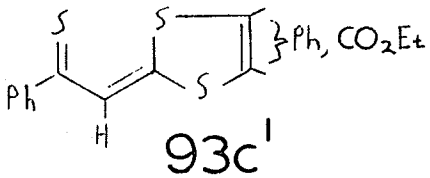
93a'



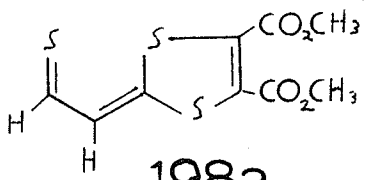
93b'



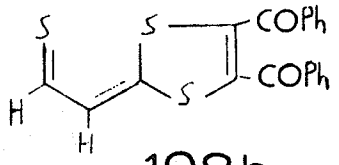
93c



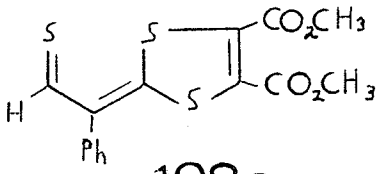
93c'



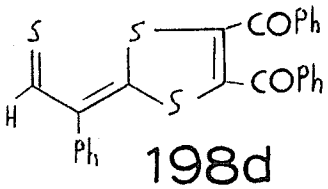
198a



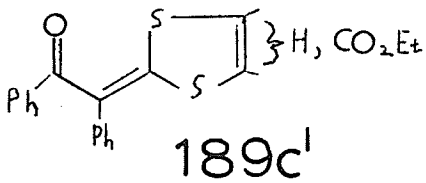
198b



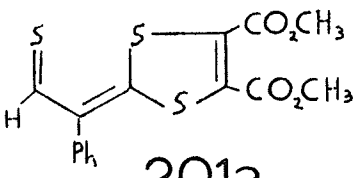
198c



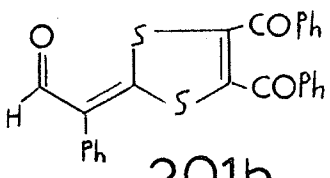
198d



189c'



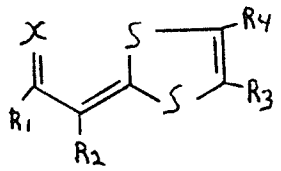
201a



201b

TABLE III

N.M.R. Spectral Data of 1,3-Dithiole-2-ylidene Derivatives of the Type 93, 93', 189', 198 and 201[a]



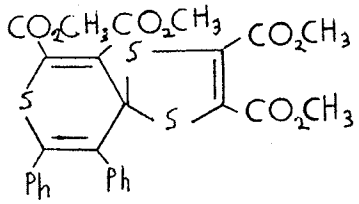
			N.m.r. (J,Hz.)[n][b] proton signals of substituents at			
Compound[c]	Fig.	X	R_1	R_2	R_3[d]	R_4[d]
93a	XXXVIII	S	2.79[5][e,f]	2.95[5][f]	6.07[3][f]	6.19[3][f]
93a'	I	S	2.80[5][e,f]	2.98[5][e,f]	2.13 / 2.26 } [1]	5.57q(7.2) / 5.67q(7.2) }[2], 8.62t(7.2) / 8.72t(7.2) }[3]
93b'	XLIV	S	2.53-3.05m[15]			5.78q(7.2) / 5.90q(7.2) }[2], 8.80t(7.2) / 8.92t(7.2) }[3]
93c	XLV	S	2.32-2.83m[5]	1.92[1]	6.10[3][f]	6.12[3][f]
93c[g]	XLVI	S	2.25-3.05m[5]	2.32[1]	6.75[3][f]	6.78[3][f]
93c[h]	-	S	2.4-2.9[6]		6.1[6]	
93c'	XLVII	S	2.15-2.79m[5]	1.92 / 1.96 }[1]	2.67[5]	5.83q(7.0) / 5.86q(7.0) }[2], 8.82t(7.0) / 8.86t(7.0) }[3]
198a	XLVIII	S	- 1.65d(7.5)[1]	1.55d(7.5)[1]	5.78[6]	
198b	XLI	S	- 0.78d(7.5)[1]	2.17d(7.5)[1]	2.45-3.03m[10]	

TABLE III (Cont'd)

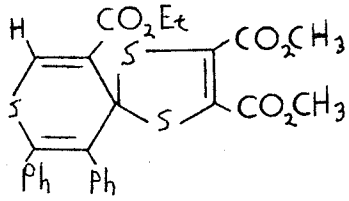
N.M.R. Spectral Data of 1,3-Dithiole-2-ylidene Derivatives of the Type 93, 93', 189', 198 and 201[a]

Compound[c]	Fig.	X	N.m.r. (J,Hz.)[n] proton signals of substituents at R_1	R_2	R_3[d]	R_4[d]
198c	LIII	S	— 0.35[1]	2.73[5]	6.17[3][f]	6.25[3][f]
198d	LVII	S	— 0.65[1]		2.50-2.99m[15]	
189c'	XLII	O	2.27-3.07m[10]		2.27 2.43 }[1]	5.71q(7.0) 5.78q(7.0) }[2], 8.66t(7.0) 8.73t(7.0) }[3]
201a	LV	O	0.75[1]	2.73[5]	6.18[3][f]	6.23[3][f]
201b	LX	O	0.72[1]		2.33-3.07m[15]	

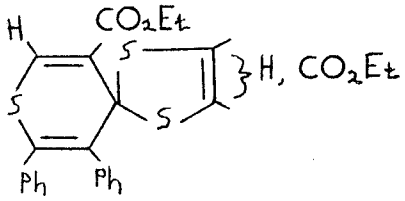
[a]Measurements were made in saturated deuteriochloroform solutions at 40°C, using a Varian A 56-60 A spectrometer at 60 MHz. Chemical shifts are recorded on the frequency independent τ-scale relative to internal tetramethylsilane. Spin-spin coupling values (J) are in Hz., measured on the 500 Hz. scale: d = doublet, t = triplet, q = quartet, m = multiplet. [b]Number of protons by integration in brackets. [c]Compounds are illustrated on opposite page. [d]Assignment based upon β-addition to acetylenic ester function. [e]Broadened singlet. [f]Assignment of signal(s) to substituent (R) is arbitrary. [g]Hexadeuteriobenzene (C_6D_6) used as solvent. [h]See Ref. 154 (carbon disulfide used as solvent).



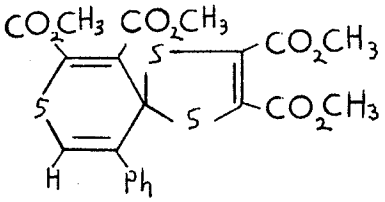
94a



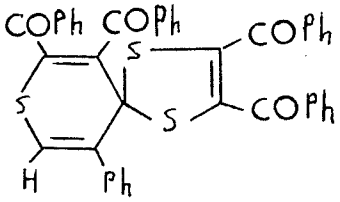
94b



94a'



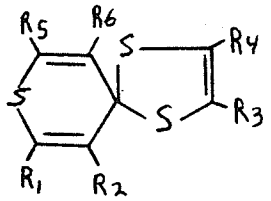
199a



199b

TABLE IV

N.M.R. Spectral Data of Thiopyranspiro-1,3-dithiole Derivatives of the Type 94, 94' and 199[a]



		N.m.r. (J, Hz.) [n][b] proton signals of substituents at					
Compound[c]	Fig.	R_1	R_2	R_3[d]	R_4[d]	R_5[d]	R_6[d]
94a	XXXIX	2.7-3.03m[5]	2.77[5]	6.32[6H]		6.13[3]	6.19[3]
94b	XLV	2.50-3.02m[10]		6.38[6H]		2.45[1]	5.63q(7.0)[2], 8.77t(7.0)[3]
94a'	XLI	2.93[10]		3.50[H]	5.90q(7.0)[2], 8.79t(7.0)[3]	2.49[1]	5.67q(7.0)[2], 8.69t(7.0)[3]
199a	LVI	3.67[1]	2.50-2.78m[5]	6.32[6]		6.13[3]	6.18[3]
199b	LVIII	3.58[1]	2.20-3.32m[25]				

[a]Measurements made in saturated deuteriochloroform solutions at 40°C, using a Varian A 56-60 A spectrometer at 60 MHz. Chemical shifts are recorded on the frequency independent τ-scale relative to internal tetramethylsilane. Spin-spin coupling values (J) are in Hz., measured on the 500 Hz. scale; t = triplet, q = quartet, m = multiplet. [b]Number of protons by integration in brackets. [c]Compounds are illustrated on the opposite page. [d]Assignment based upon β-addition to acetylenic ester function.

Section B: Reactions of 1,2-Dithiole-3-thione (58) and 4-Phenyl-1,2-dithiole-3-thione (164a) with Dimethyl Acetylene Dicarboxylate and Dibenzoylacetylene.

While the reactions of various activated acetylenes with 1,2-dithiole-3-thiones 6 have been studied extensively, most of the reactions have involved the use of 5-substituted 1,2-dithiole-3-thiones of the type 60. The initial products of the reaction are then 2-(2-thioacylmethylene)-1,3-dithioles 93. Likewise, the reactions of 5-unsubstituted-1,2-dithiole-3-thiones 64 would provide 2-thioformylmethylene-1,3-dithioles 198. These being thials, would be expected to be less stable than the thiones 93[163]. Little is reported on this type of reaction, but 4-phenyl-1,2-dithiole-3-thione (164a) reacted with ethyl phenylpropiolate to give a product[162] which, on the basis of desulfurization experiments[164] proved to be a bisdithiolylidene-2-butene of the type 200. It seemed desirable to investigate these reactions to identify intermediates and products. It was also interesting to determine if the initial adducts reacted with more activated acetylene to form spiran di-adducts 199 of the type reported for 4,5-diphenyl-1,2-dithiole-3-thione (27), discussed in Section A of this Chapter.

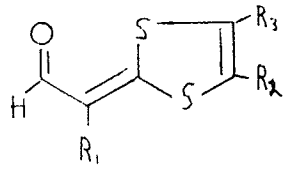
The 5-unsubstituted thiones 64 used in these studies were 1,2-dithiole-3-thione (58) prepared by reaction of 1,3-dimercapto-propane (57) with sulfur[67] (see Introduction, Part II, Section A-5) and 4-phenyl-1,2-dithiole-3-thione (164a) prepared by reaction of cumene with sulfur[36] (see Introduction, Part II, Section A-1). Dimethyl acetylenedicarboxylate and dibenzoylacetylene were used as the acetylenes because it was found that these acetylenes reacted with 4,5-diphenyl-1,2-dithiole-3-thione (58)

rapidly at room temerpature to give mono-adducts of the type 93. Thus it was hoped that a thial 198 which is heat sensitive could be isolated and characterized.

1. Discussion of Reactions:

A reaction scheme illustrating the products found in these reactions is shown on the next page. The two thiones 58 and 164a and the two acetylenes reacted rapidly to give a brown pasty solid as the major product in each case. These solids were insufficiently stable to permit proper isolation but were assigned the structure of the thial mono-adduct 198 by analysis of the n.m.r. spectra. The appearance of the thial protons in each case (-0.35 to -1.65τ) is within the accepted range for thials[11]. The n.m.r. spectra will be discussed later in this Section. Also, in each case, heating of the thials 198a-d produced stable bis-dithiolylidene-2-butenes 200a-d in varying yields, possibly by extrusion of two sulfur atoms from the thials 198a-d, along with other minor products. A possible reaction scheme for the formation of the butene 200 from the thial 198 will be discussed later in this Section. The geometry of these butenes 200 could not be established. Further reaction of the thials 198a-d with the acetylenes produced di-adducts 199a,b only from the thials 198c,d [from 4-phenyl-1,2-dithiole-3-thione (164a)]. Also the formylmethylene-1,3-dithioles 201a,b (aldehydes) were isolated in varying amounts from the reactions involving 4-phenyl-1,2-dithiole-3-thione (164a) or its thial mono-adducts 198c,d.

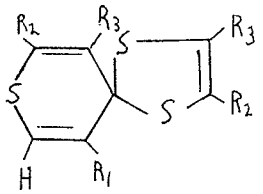
From the above products and examination of the reactions by which they are obtained (discussed below), a sequence of reactions may be seen. Reaction of the initial 1,2-dithiole-3-thione 58 or 164a



201

a) $R_1 = Ph, R_2 = R_3 = CO_2CH_3$

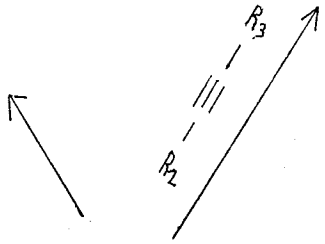
b) $R_1 = Ph, R_2 = R_3 = COPh$

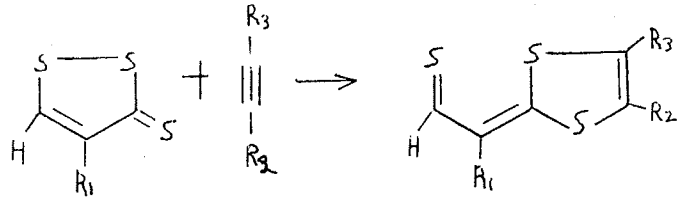


199

a) $R_1 = Ph, R_2 = R_3 = CO_2CH_3$

b) $R_1 = Ph, R_2 = R_3 = COPh$





64

58 : $R_1 = H$

164a : $R_1 = Ph$

-25

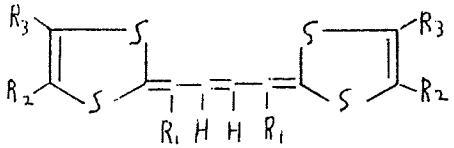
198

a) $R_1 = H, R_2 = R_3 = CO_2CH_3$

b) $R_1 = H, R_2 = R_3 = COPh$

c) $R_1 = Ph, R_2 = R_3 = CO_2CH_3$

d) $R_1 = Ph, R_2 = R_3 = COPh$



200

a) $R_1 = H, R_2 = R_3 = CO_2CH_3$

b) $R_1 = H, R_2 = R_3 = COPh$

c) $R_1 = Ph, R_2 = R_3 = CO_2CH_3$

d) $R_1 = Ph, R_2 = R_3 = COPh$

with the activated acetylene first produces a thial mono-adduct 198 which may react in three ways. One reaction common to all studied is that producing the butenediylidenedithioles 200. However, when the thial is stabilized by conjugation to a phenyl group as in 198c,d, this reaction becomes slower and other reactions may compete effectively with it, i.e., the thial may react with a suitably activated acetylene to form a di-adduct 199 or it may form the corresponding aldehyde 201, possibly by oxidation or hydrolysis of the corresponding thial.

When 1,2-dithiole-3-thione (58) reacted with one equivalent of dimethyl acetylenedicarboxylate at room temperature, and after a short reaction time (3h.) five fractions were separated by thin layer chromatography (t.l.c.). Two of these fractions were obtained in trace amounts and were not identified. The other three fractions were identified as the unchanged thione 58 (10%), the thial 198a (76%) and the butene 200a in trace amounts. This butene 200a (40%) was the only product identified when the reaction was allowed to proceed for one day in boiling benzene, although of the six other fractions separated, two were obtained in a sizeable amount (∿30mg.) as uncrystallizable glasses. The i.r. and n.m.r. spectra (see Experimental) indicated that they were methyl esters of carboxylic acids. Since it is not known if these glasses were pure and lacking any analytical data, no satisfactory structure can be advanced, but it is probable that they were formed either by reaction of the thial 198a with the acetylene (with or without the thione 58) or by the decomposition of the unstable thial 198a. Heating the thial 198a in benzene gave the butene 200a (41%) along with five other fractions in trace amounts none of which was the thial 198a.

Treatment of the thione 68 or the thial 198a with dimethyl acetylenedicarboxylate gave rather similar results and none of the minor fractions could be identified as a di-adduct of the type 199. In the separation of all the reaction mixtures, described above, (t.l.c.), a considerable amount of orange material (up to 30% of the starting materials) could not be separated using the typical developing solvents (benzene and chloroform), but was partially separated using methanol-chloroform mixtures and was found to contain many fractions. This was also found to be the case for the reactions involving the thione 58 and dibenzoylacetylene, discussed below. Also sulfur was isolated in all reactions involving the application of heat (found for all reactions of the thiones 58 and 164a with both acetylenes).

Very similar results were obtained by treatment of the thione 58 with dibenzoylacetylene. Reaction over a short period of time provided the thial 198b (74%), the unchanged thione 58 (10%) and five other fractions in trace amounts, none of which was the butene 200b which was obtained as the major product (38%) when the reactants were heated in boiling benzene for one day. The thial 198b (∿4%) and ten other fractions in trace amounts were also separated by t.l.c. The thial 198b gave the butene 200b (43%) along with twelve other fractions, none of which was the thial 198b. The butene 200b (39%), the unchanged thial 198b (11%) and twelve other fractions were found in trace amounts when the thial 198b reacted with one equivalent of dibenzoylacetylene. When the thial 198b reacted with dimethyl acetylenedicarboxylate, the butene 200b was obtained along with other fractions, one of which, an orange glass, showed the presence of ester carbonyls (1735, 1715 cm^{-1}) and ketone carbonyl (1660 cm^{-1}) in the i.r. spectrum. This glass

could possibly be a di-adduct of the type 199.

4-Phenyl-1,2-dithiole-3-thione (164a) reacted with dimethyl acetylenedicarboxylate to give the thial 198c (85%), the thione 164a (8%) and minute amount of the aldehyde 201a which was also obtained by treatment of the thial 198c with mercuric acetate. In boiling benzene, the thial 198c gave the butene 200c (43%) and the aldehyde 201a (∿3%) along with the unchanged thial 198c (43%). However, in boiling xylene, the yield of the butene 200c was increased substantially (80%) and the thial 198c and the aldehyde 201a were found in trace amounts. Further reaction of the thial 198c and dimethyl acetylenedicarboxylate in boiling benzene gave the di-adduct 199a (46%) as an orange oil, the aldehyde 201a (∿7%) the unchanged thial 198c (∿3%) and many other fractions in trace amounts. The n.m.r. of the orange oil (Table IV) was consistent with the structure 199a and the mass spectrum showed a parent ion at M^+/e 494 (molecular weight of the di-adduct 199a is 494). The aldehydes 201a,b were obtained even when the reactions were performed under dry nitrogen and in dry solvents. It appears that they are formed from unreacted thial by aerial oxidation or by hydrolysis on the t.l.c. plates prior to developing. When the thial 198c was subjected to ultraviolet (u.v.) radiation or intense visible light at room temperature, the aldehyde 201a was obtained as the major product (38%) along with eight other fractions none of which was the thial 198c or the butene 200c.

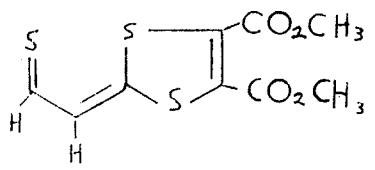
4-Phenyl-1,2-dithiole-3-thione (164a) reacted with dibenzoylacetylene at room temperature to give the thial 198d (71%), the di-adduct 199b (14%) and the unchanged thione 164a (13%). In boiling benzene,

the butene 200d was obtained in a low yield (11%) along with the aldehyde 201b (11%) and the unchanged thial 198d (67%) from the thial 198d. However, in boiling xylene the butene 200d was obtained in a more satisfactory yield 51% from the thial 198d along with the aldehyde 201b (16%) and the unchanged thial 198d (11%). The aldehyde 201b, an uncrystallizable oil, was also obtained by treatment of the thial 198d with mercuric acetate. The n.m.r. spectrum (Table III) and the mass spectrum of the oil were consistent with the structure of the aldehyde 201b. The di-adduct 199b (70%), the butene 200d (∿7%), the unchanged thial 198d (∿3%) and an orange powder were separated when the thial 198d and dibenzoylacetylene reacted in boiling benzene. The n.m.r. spectrum of this orange powder showed only phenyl protons, the i.r. spectrum showed the presence of ketone carbonyls and the mass spectrum did not give a parent peak (last peak at M^+/e 573). Also a satisfactory elemental analysis could not be obtained. Lacking meaningful spectroscopic data and a satisfactory elemental analysis, no structure for this powder can be advanced.

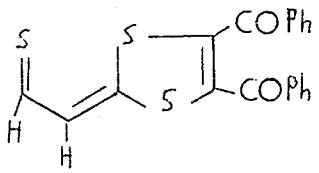
2. Discussion of N.M.R. Spectra:

The n.m.r. spectra of the thials 198a-d, of the di-adducts 199a,b and of the butenes 200a-d are summarized in Tables III, IV and V respectively. The n.m.r. spectra of the aldehydes 201a,b are also summarized in Table III. The n.m.r. of the thial 198a showed a doublet (-1.65τ, J = 7.5 Hz.) due to the thial proton, a doublet (1.55τ, J = 7.5 Hz.) due to the ring proton on the side chain and a singlet (5.78τ) due to the methyl protons of the two carbomethoxy groups which is probably fortuitous (see Section A-2 of this Chapter).

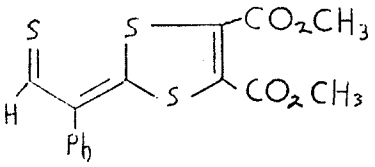
Unfortunately, the thial 198a was insufficiently soluble in cold benzene to obtain a spectrum in hexadeuteriobenzene and heating caused rapid formation of the butene 200a. However, the four carbomethyoxy groups of the butene 200a which are equivalent (6.20τ) as indicated by n.m.r. ($CDCl_3$) are evident as two singlets (6.77, 6.75τ) in the n.m.r. spectrum using hexadeuteriobenzene as the solvent. The magnitude of the spin-spin coupling constant J , (7.5 Hz.) is more indicative of a *S-cis* conformation, i.e., structure 198 than of a *S-trans* conformation of the type 195 for the thial 198a since the magnitude of J due to the coupling between the two *cis* protons in the ring of 1,2-dithiole-3-thione (58) is 6 Hz. (see Experimental). The J value of the thial 198b is also 7.5 Hz. The non-equivalence of the ester functions of the thial 198c and the aldehyde 201a (6.25, 6.17τ)(6.23, 6.18τ) respectively, as indicated by n.m.r. is as expected for mono-adducts which possess a phenyl substituent α to the thiocarbonyl (in this case a thial) group of the side chain (see Section A-2 of this Chapter).



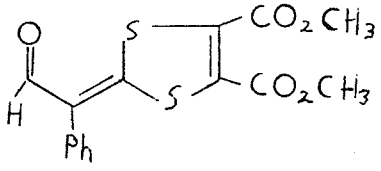
198a



198b



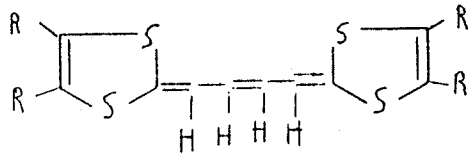
198c



201a

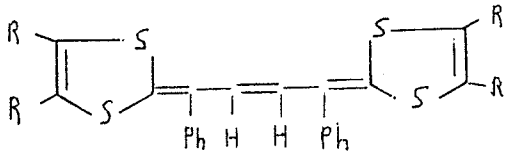
Also as expected, the ester functions on the 1,3-dithiole ring of the

di-adduct 199a are shown to be equivalent (6.32τ) while those on the thiopyran ring are not equivalent (6.18, 6.13τ) as indicated by n.m.r. (see Section A-2 of this Chapter). The four vinyl protons of both the bisdithiolylidene-2-butenes 200a,b constitute an AA'XX' system whose spectrum is not easily analysed. A complex symmetrical multiplet which could not readily be interpreted was found in each case for the butenes 200a,b. Singlets (4.23 and 4.10τ) were apparent for the two vinyl protons of each of the butenes 200c,d, respectively, thus indicating that either a *cis* or a *trans* isomer is formed. The vinyl protons of *cis* olefins which possess a two-fold plane of symmetry and of *trans* olefins which possess a centre of inversion are evident as a singlet, e.g., the vinyl protons of both *cis* and *trans* stilbene appear as singlets in the n.m.r.[165]. Thus it cannot be determined if the bisdithiolylidene-2-butenes 200 so formed are the *cis* or the *trans* isomers although the *trans* isomers are more likely.



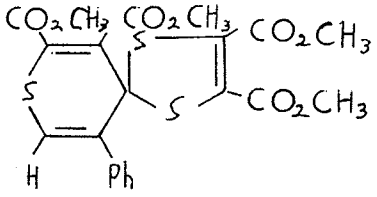
200

a) R = CO_2CH_3
b) R = COPh

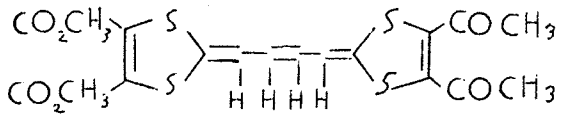


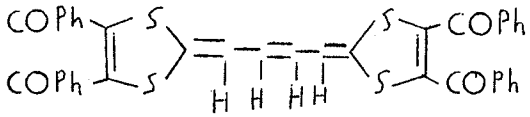
200

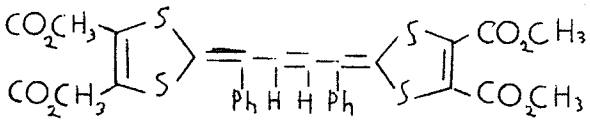
c) R = CO_2CH_3
d) R = COPh



199a

200a 

200b 

200c 

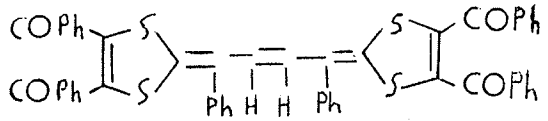
200d 

TABLE V

N.M.R. Spectral Data of Dithiolylidene-2-butene Derivatives 200[a]

Compound[c]	Fig.	N.m.r. (J,Hz.)[n][b] proton signals of substituents at R_1	R_2	R_3	R_4
200a	XLIX	3.92-4.27m[4]		6.20[12]	
200a[d]	L	4.33-4.75m[4][e]		6.75[6][f]	6.77[6][f]
200b	LII	3.7-4.3m[4]		2.4-2.9m[20]	
200c	LIV	4.23[2]	2.42-2.92m[10]	6.22[6][f]	6.27[6][f]
200d	LIX	4.10[2]	2.35-3.00m[30]		

[a]Measurements were made in saturated deuteriochloroform solutions at 40°C, using a Varian A56-60 A spectrometer at 60MHz. Chemical shifts are recorded on the frequency independent τ-scale relative to tetramethylsilane; m = multiplet. [b]Number of protons by integration in brackets. [c]Compounds are illustrated on opposite page. [d]Hexadeuteriobenzene (C_6D_6) used as solvent. [e]Approximate assignment due to small signal/noise ratio caused by relative insolubility of sample in C_6D_6. [f]Assignment of signal to substituent (R) is arbitrary.

3. Reaction Scheme for the Formation of Bisdithiolylidene-2-butenes 200:

Thiones and thials are known to lose sulfur under the influence of heat to form ethylene derivatives[166]. Although this reaction does not occur with all thiocarbonyl compounds, it seems to occur for all thiones and thials that do react when subjected to heat[166], e.g., stilbene and tetraphenylthiophene are formed from the dry distillation of thiobenzaldehyde[166]. Tetraphenylthiophene probably is formed by the reaction of stilbene with the sulfur liberated during its formation. Also, pyrylenes 203a and dithiopyrylenes 203b, respectively, are formed when the corresponding thiopyrones 202a and dithiopyrones 202b are subjected to heat[167].

202

a) X = O

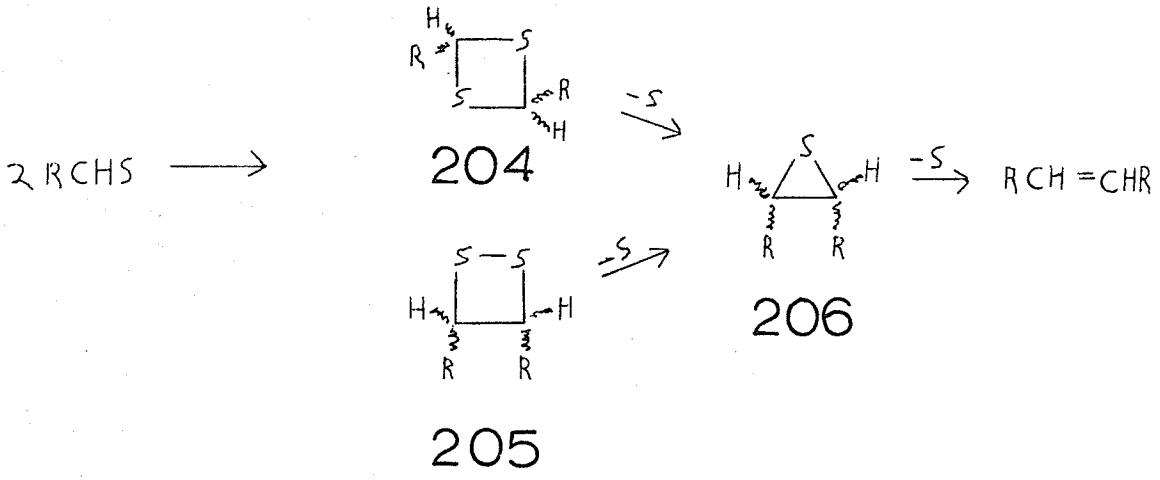
b) X = S

203

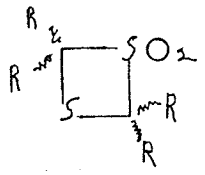
a) X = O

b) X = S

Presumably all thiones and thials which decompose under the influence of heat form ethylene derivatives in a similar manner. The ethylene derivatives could possibly be formed by the stepwise extrusion of two sulfur atoms from either of the initially formed dithiacyclobutanes 204 or 205 (illustrated on the next page).



Although the 1,2-dithiacyclobutane 205 cannot be excluded, the dithiacyclobutane 204 appears more likely to be the structure of the dimer on the basis of results with various thiocarbonyl compounds. Such dimers of the type 204, as well as trimers are known to be formed from various thiones and thials[166,168]. Also thiophosgene[169-171] and fluorinated thioketones[171,172] form 1,3-dithiacyclobutanes of the type 204 and recently such intermediates have been proposed in the reaction of carbon disulfide and dimethyl acetylenedicarboxylate[173]. No direct evidence appears to be available for the loss of sulfur from a 1,3-dithiacyclobutane 204 to form the episulfide 206, but certain thiones under the influence of acetylides form both 1,3-dithiacyclobutanes 204 and episulfides 206[174]. Possibly the former are precursors of the latter. Also a dithiacyclobutanedioxide of the type 207 loses sulfur dioxide to form an episulfide 206[175].



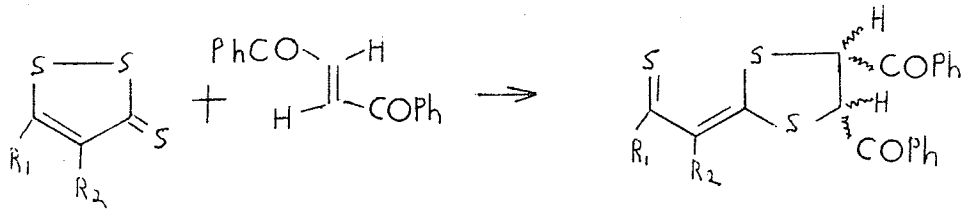
207

The last step in the proposed scheme, the loss of sulfur from the episulfide 206 to form the olefin is a well-known reaction[176,177]. The geometry of the olefin would be determined by that of the initially formed dithiacyclobutane 204 (or possibly 205) only if loss of sulfur from the dimer 204 and from the episulfide 206 is a concerted process in both steps. The thial in a dipolar form[11] or as diradicals may undergo a (2 + 2) cycloaddition to form the dithiacyclobutane 204 (or possible 205). Thials and aliphatic thiones are believed to behave as diradicals in some of their reactions, e.g., polymerization[166].

Section C: Reactions of 1,2-Dithiole-3-thiones with Olefins and Comments on the (3 + 2) Cycloadditions of 1,2-Dithioles-3-thiones and Activated Acetylenes.

If the two new σ bonds are closed simultaneously during a cycloaddition, the result must be a stereospecific addition[103]. However, if the two σ bonds are closed one after the other and an intermediate is formed, the result usually is a non-stereospecific addition[178]. Thus in order to determine if the (3 + 2) cycloaddition of 1,2-dithiole-3-thiones and acetylenes is a concerted process, the reactions of 5-phenyl-1,2-dithiole-3-thione (50b) and 4,5-diphenyl-1,2-dithiole-3-thione (27) with *trans*-dibenzoylethylene were investigated. *trans*-Dibenzoylethylene, a symmetrical olefin, was chosen as the olefin to eliminate the possibility of two modes of addition of the thiones 27 and 50b to the olefin and because in its reactivity with 1,3-dipoles[104] it is comparable to the acetylenic ester, methyl propiolate.

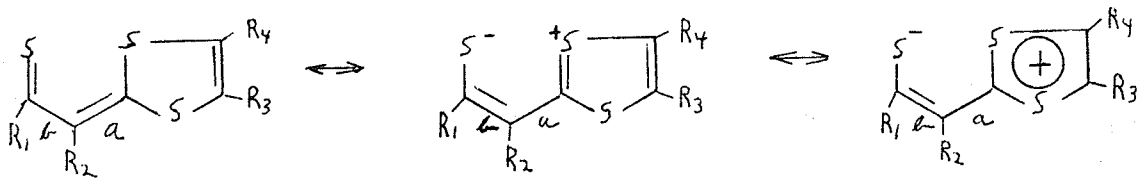
When both thiones 27 and 50b and the olefin were heated in boiling benzene or xylene, no colour change was observed and the starting materials were recovered. Similar results have been obtained when 5-phenyl-1,2-dithiole-3-thione (50b)[179] and various 1,2,4-dithiazole-3-thiones 185[159] were treated with dimethyl azodicarboxylate. The expected products, 2-(2-thioacylmethylene)-1,3-dithiolane of the type 208 are not potentially aromatic and thus it is possible that the formation of these mono-adducts 208 would involve the loss of aromatic stability which is not lost when thioacylmethylene-1,3-dithioles 93 are formed from reaction of the same thiones 27 and 50b with acetylenes.



27 : $R_1 = R_2 = Ph$

50b: $R_1 = Ph, R_2 = H$

208



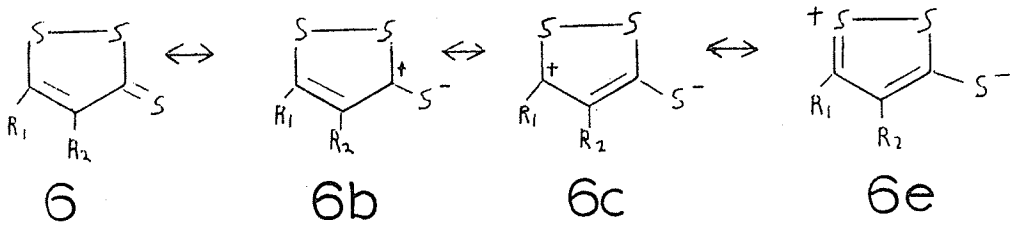
93 196a

Since no product could be obtained from reaction of the thiones 27 and 50b with *trans*-dibenzoylethylene, it cannot be determined if the (3 + 2) cycloaddition of 1,2-dithiole-3-thiones and acetylenes is a concerted process. However, from the results of the reactions of 4,5-diphenyl-1,2-dithiole-3-thione (27) with acetylenic esters, discussed in Section A of this Chapter, possible reaction schemes for this (3 + 2) cycloaddition which may depend on a concerted (3 + 2) cycloaddition (scheme A) and which do not depend on whether the cycloaddition is a concerted process (schemes B and C) can be postulated. The analysis of the n.m.r. spectra of the mono-adducts of the type 93' indicated that they contained two thioacylmethylene-1,3-dithioles of the type 93 and 102 which were formed during the reaction and were not interconvertible, e.g., by rotation about the 'a' bond of the dipolar structure 196a. Until further n.m.r. studies of mono-adducts prepared by reaction

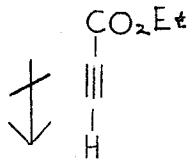
of various 1,2-dithiole-3-thiones, including the bicyclothiones 194 with unsymmetrical acetylenes have been undertaken, the possibility of interconversion of thioacylmethylene-1,3-dithioles cannot be totally excluded. Possible reaction schemes in which two thioacylmethylene-1,3-dithioles are formed during the reaction are discussed below.

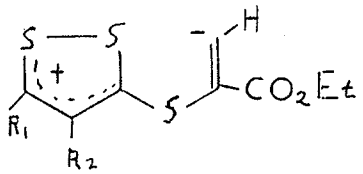
1. Scheme A:

This reaction scheme essentially involves the addition of the thiones 6 to both acetylenic carbon atoms of unsymmetrical acetylenes. For unsymmetrical acetylenic esters such as ethyl propiolate, this necessitates that the exocyclic sulfur atom of the thiones 6 must possess sufficient nucleophilic activity to attack the ester at the acetylenic carbon atom which is the least susceptible to nucleophilic attack, i.e., the carbon atom α to the ester function. Attack by the neutral form 6 of 1,2-dithiole-3-thiones or by the dipolar forms 6b,c, and e on the carbon atom α to the ester function of acetylenic esters also necessitates the absence of an intermediate of the type 209 during the cycloaddition since the resulting negative charge on the carbon atom β to the ester function cannot be effectively stabilized. However, the intermediate 209a resulting from attack of the dipolar form 6d may be more effectively stabilized by the proximity of the opposing charges in the intermediate 209a.

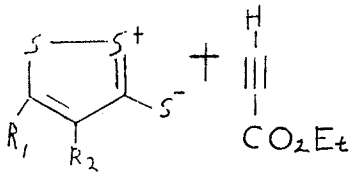


6 6b 6c 6e

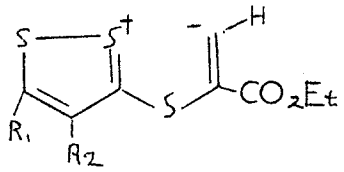




209

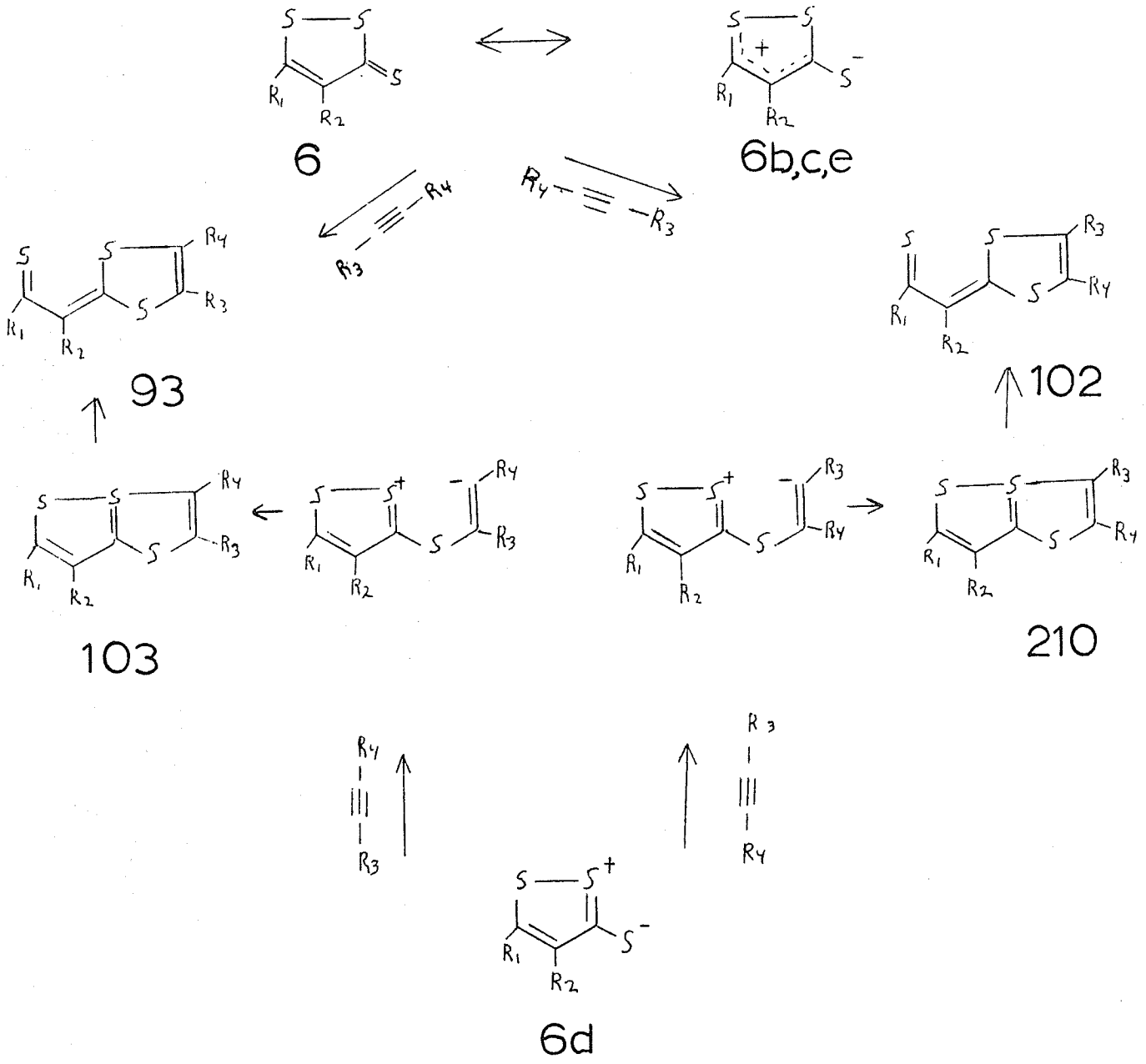


6d



209a

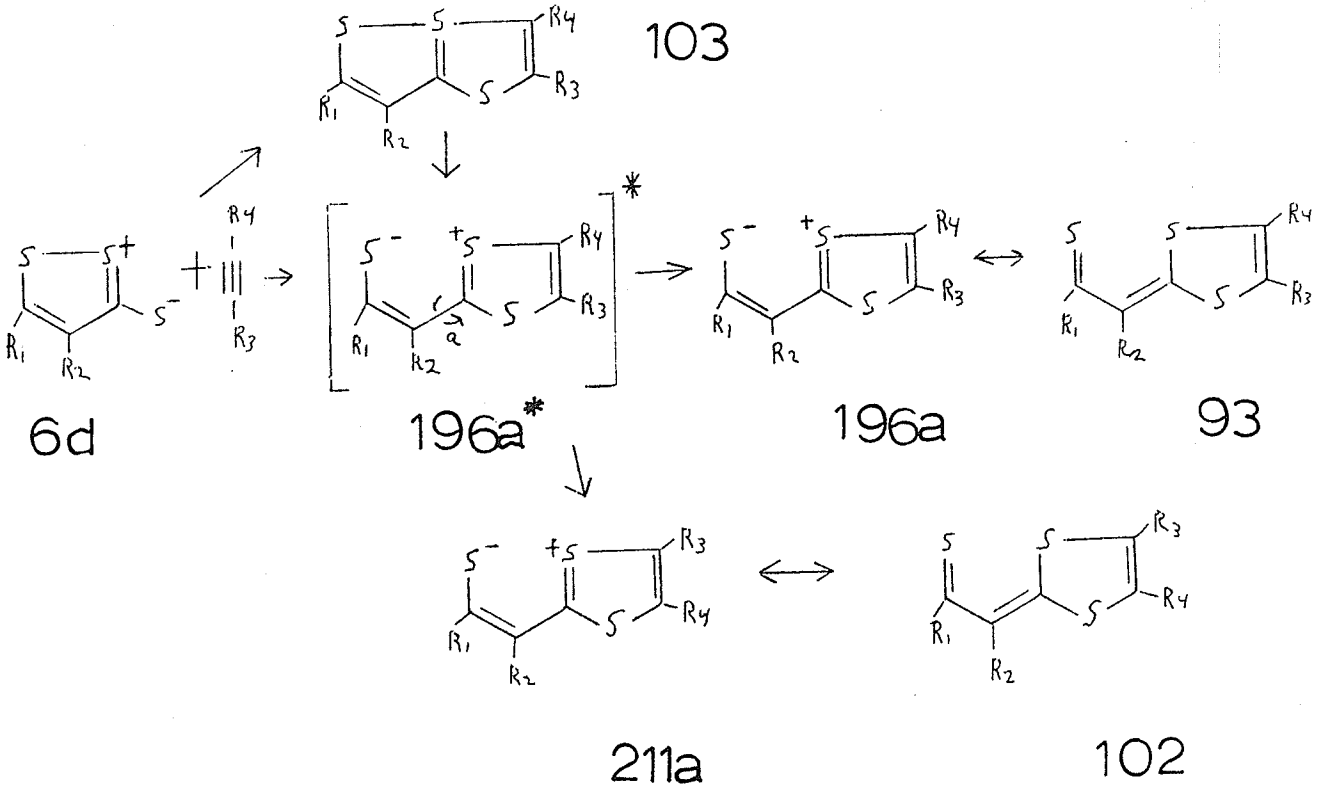
Similar arguments can be put forward for attack by thiones 6 on unsymmetrical arylacetylenes. A concerted (3 + 2) cycloaddition involving both modes of addition of the neutral form 6 or the dipolar forms 6b,c and e to unsymmetrical acetylenes probably would lead to simultaneous cleavage of the disulfide bond of the dithiole ring. A stepwise cycloaddition involving both modes of addition of the dipolar form 6d to unsymmetrical acetylenes could possibly lead to tetravalent sulfur structures 103 and 210 which by cleavage of the disulfide bond could then give the mono-adducts 93 and 102.



2. Scheme B:

The first step in this scheme involves the addition of the thione 6, e.g., the dipolar form 6d to unsymmetrical acetylenes in one direction only in one or two steps. However, the resulting cleavage of disulfide bond of the 1,2-dithiole ring (or less likely of the tetravalent sulfur structure 103 in the case of the dipolar form 6d) might result

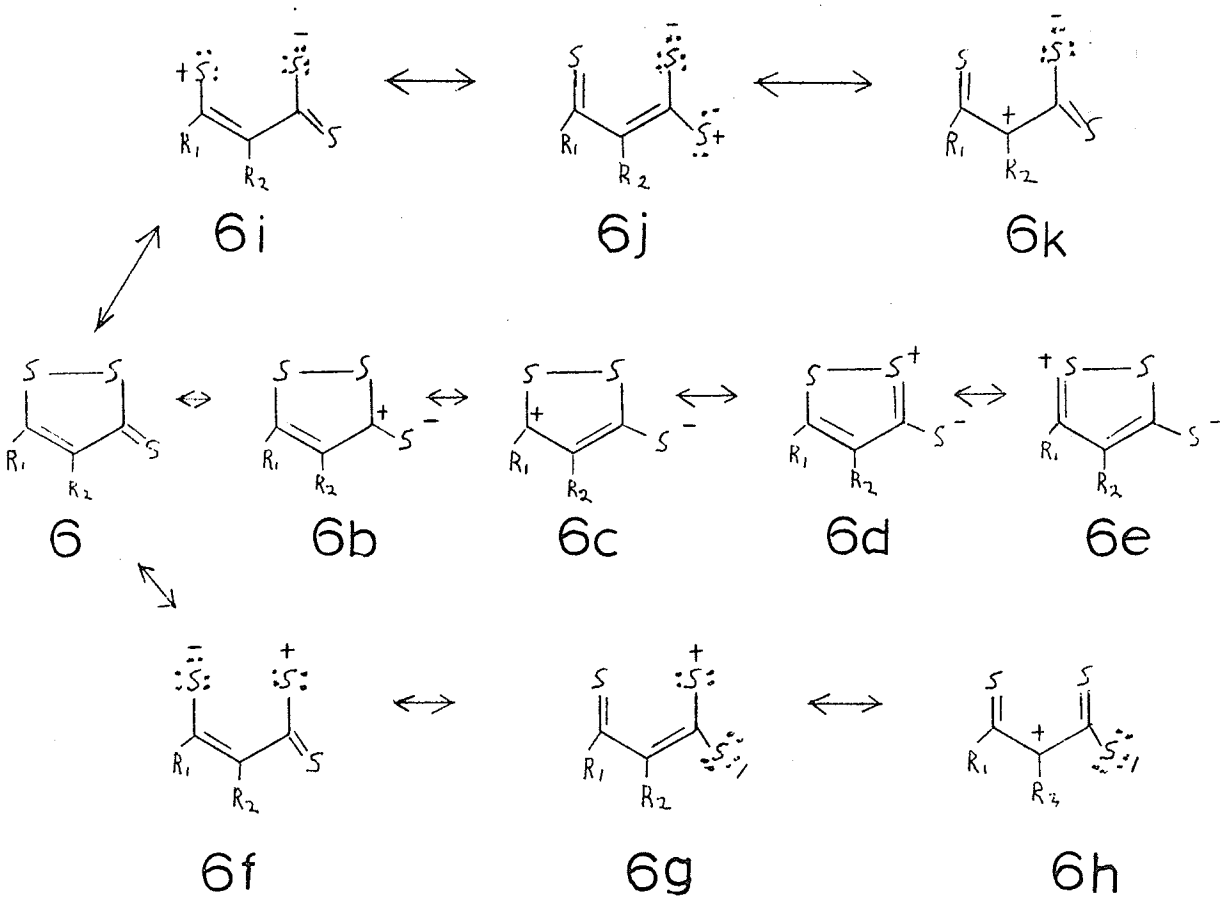
in the formation of high energy intermediates of the type 196* (196a* in the case of 6d) which could lose their excess energy either by forming the dipolar resonance form of the type 196 (196a* in the case of 6d) or by rotating about the exocyclic 'a' bond and forming the dipolar resonance form of the type 211 (211a for 6d) of the thioacylmethylene-1,3-dithiole 102.



3. Scheme C:

Thioacylmethylene-1,3-dithioles 93 and 102 can be formed if 1,2-dithiole-3-thiones 6 react as 1,3-dipoles, i.e., $\bar{S} - \underset{|}{C} - \overset{+}{S}$, in which the charges on the sulfur atoms of the 1,3-dipole are ambivalent, i.e., interchangeable. Thus, in the case of acetylenic

esters, addition of the thiones 6, acting as 1,3-dipoles, β to the ester function of unsymmetrical acetylenes would result in the formation of two mono-adducts of the type 93 and 102. The acyclic resonance forms 6g and 6j are the two sextet forms of the 1,3-dipole inherent in 1,2-dithiole-3-thiones 6 in which the formal charges are interchangeable. The definition of a 1,3-dipole and of a 1,3-dipolar cycloaddition are found in the Introduction (Part II, Section C).



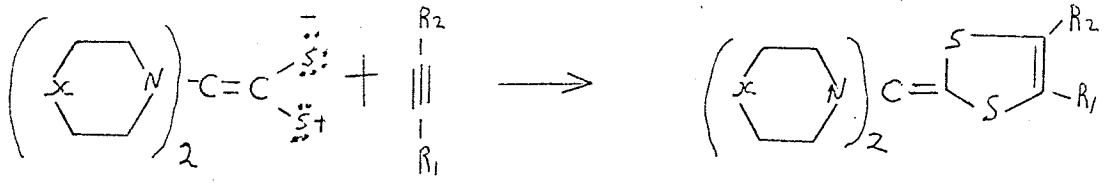
Behringer[90] had considered the possibility that the acyclic resonance forms 6f-k might participate in the (3 + 2) cycloaddition of 1,2-dithiole-3-thiones and activated acetylenes. Also acyclic resonance forms have

been considered for 1,2-dithiolium cations 2[94].

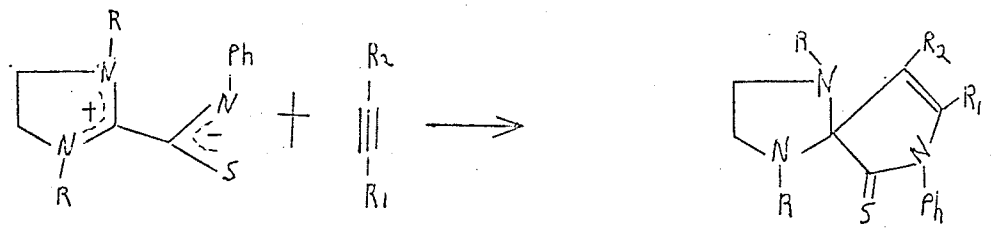
It should be noted that 1,2-dithiole-3-thiones, if they can be considered as 1,3-dipoles, are 1,3-dipoles in which the central atom, i.e., a carbon atom, is not capable of stabilizing the 1,3-dipole by internal octet stabilization. However, stabilization of the 1,3-dipole by the neutral octet resonance form 6 and the dipolar resonance forms 6d,e can occur and results in partial charge compensation in the 1,3-dipoles. 1,3-Dipoles with this type of octet stabilization have been classified as 1,3-dipoles with external octet stabilization by R. Huisgen[83]. Little is known about this type of 1,3-dipole. Since the term 1,3-dipolar cycloaddition has been defined by R. Huisgen[83] as referring to (3 + 2) cycloadditions of 1,3-dipoles with internal octet stabilization and dipolarophiles, the description of the (3 + 2) cycloaddition of 1,2-dithiole-3-thiones and activated acetylenes as a 1,3-dipolar cycloaddition is inappropriate, e.g., the lack of reactivity of the thiones 27 and 50b towards *trans*-dibenzoylethylene, described above, is in contrast to the comparable reactivity displayed by 1,3-dipoles which are involved in 1,3-dipolar cycloadditions towards olefins and acetylenes[83].

It should also be noted that the dipolar octet resonance form 6c and the sextet resonance forms 6f,h,i and k permit further partial charge compensation via the 'exo' double bond of the middle carbon atom of the S - C - S dipole. Zwitterionic formamidiniumdithiocarboxylates 212 prepared either by reaction of tetraaminoethylenes with carbon disulfide[180] or by the reaction of enediamines with sulfur[181] are reported to add to dipolarophilic acetylenes as S - C - S dipoles to

give the 2-ylidene-1,3-dithioles 213[182]. These zwitterionic dithiocarboxylates 212 permit partial charge via the 'exo' double bond at the carbon atom of the 1,3-dipole. In contrast, the imidazolinium betaine 214 prepared by reaction of tetraaminoethylenes with phenylisothiocyanate forms the spiran heterocyclics 215 by addition of a C - C - N dipole to acetylenes[182]. The betaine 214 also reacts with alkenes, isocyanates and isothiocyanates. This C - C - N dipole is an example of a 1,3-dipole with external octet stabilization.



212 213

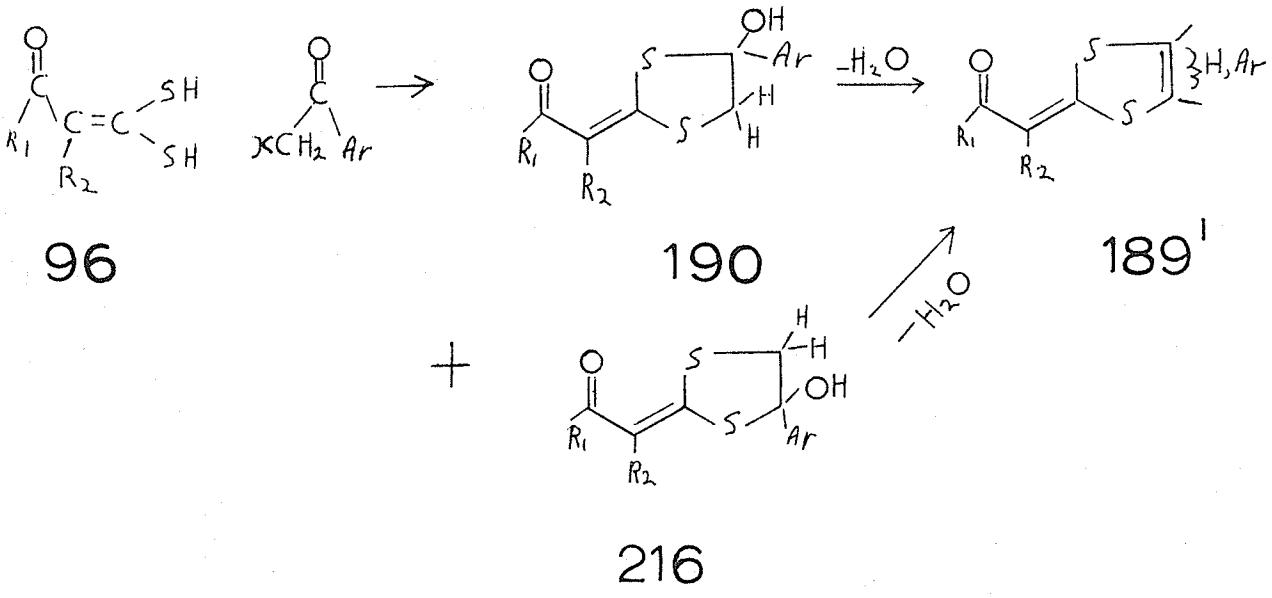


214 215

A S - C - S dipole which can be stabilized via double bond at the carbon atom has been postulated as an intermediate in the reaction of carbon disulfide with dimethyl acetylenedicarboxylate[173] and hexafluoro-2-butyne[183].

The formation of acylmethylene-1,3-dithioles 189' (see Section A of this Chapter) by a reaction of dithiocarboxylic acids 96 with α-

halo-ketones may result from the dehydration of two hydroxy-acyl-methylene-1,3-dithiolanes 190 and 216. These dithiolanes 190 and 216 could be formed by nucleophilic attack of the *trans* and the *cis* sulfur atoms (with respect to the acyl group), respectively, of the dithiocarboxylic acids 96 at the α carbon of the α-halo-ketones.



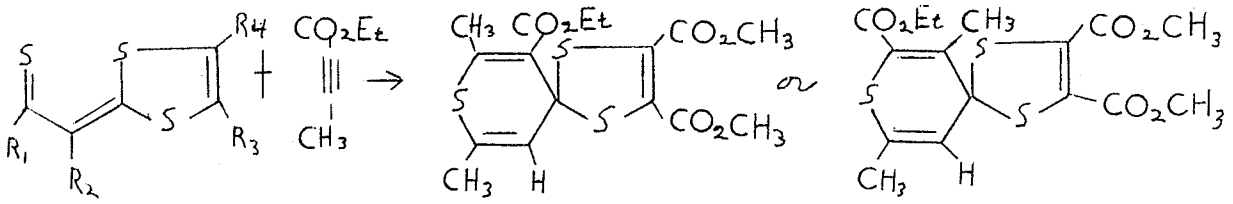
96 190 189'

+

216

Section D: Mode of Addition of 2-(2-Thioacylmethylene) -1,3-dithioles to Acetylenic Esters and Comments on this (4 + 2) Cycloaddition.

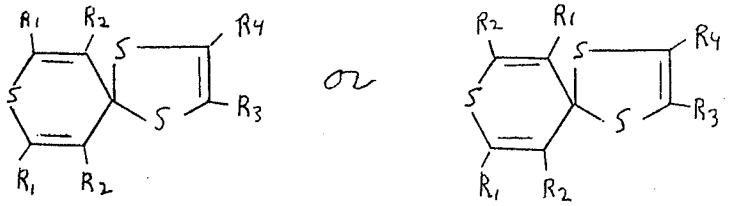
The n.m.r. spectrum of the thiopyranspiro-1,3-dithiole 94a' (Table IV, also see Section A-2 of this Chapter) indicated that the mono-adduct 93a' adds to ethyl propiolate in only one direction which is probably β to the ester function. If a thiopyranspiro-1,3-dithiole in which the thiopyran ring contains only two substituents, i.e., the spiran compound 219 or 220 could be derived in some way by reaction of a mono-adduct 93 with an acetylenic ester, an n.m.r. analysis of this thiopyranspiro-1,3-dithiole would reveal if it were the spiran compound 219 or 220. Thus the mode of addition of mono-adducts 93 would easily be established. The mono-adduct 93d, prepared by reaction of 5-methyl-1,2-dithiole-3-thione (63) with dimethyl acetylene-dicarboxylate, was the mono-adduct chosen for this study. Reaction of this mono-adduct 93d with ethyl tetrolate (105c) would give either the di-adduct 217 or 218 which on hydrolysis of the ester functions and subsequent decarboxylation of the resulting acid functions would yield the desired thiopyranspiro-1,3-dithiole 219a or 220a.



93 105c 217 218

d) $R_1 = CH_3, R_2 = H, R_3 = R_4 = CO_2CH_3$

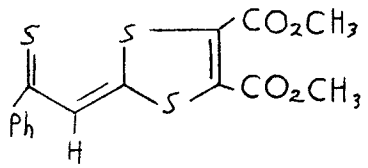
(i) hydrolysis
(ii) decarboxylation



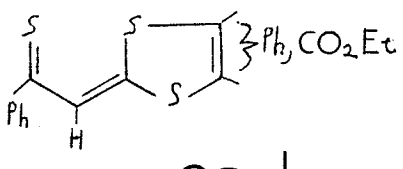
219 220

a) $R_1 = CH_3, R_2 = R_3 = R_4 = H$ a) $R_1 = CH_3, R_2 = R_3 = R_4 = H$

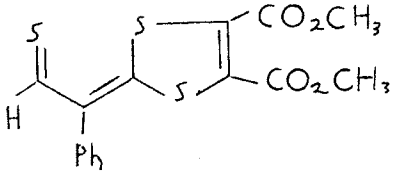
5-Methyl-1,2-dithiole-3-thione (63) was prepared by the method of Thuillier and Vialle[56] (see Introduction, Part II, Section A-3). The starting materials were recovered when the mono-adduct 93d and ethyltetrolate (105c) were heated in boiling benzene or in boiling xylene. Thus the mode of addition of mono-adducts 93 to acetylenic esters could not be established using this approach. Similar results were obtained using the mono-adducts 93c and 93c' with ethyl phenylpropiolate. Heating the thial 198c and ethyl phenylpropiolate in boiling benzene gave the bisdithiolylidene-2-butene 200c.



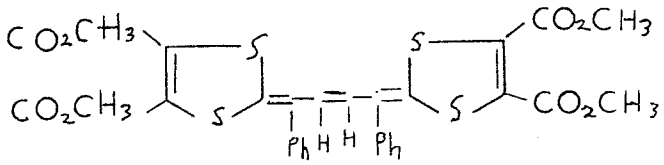
93c



93c'



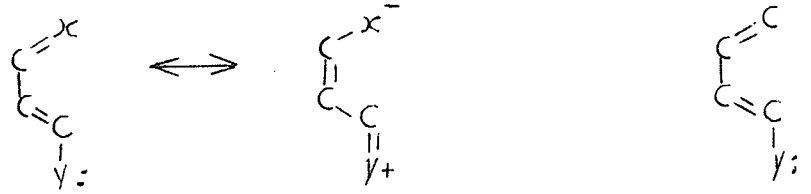
198c



200c

Probably ethyl tetrolate is not sufficiently activated to react further with the mono-adduct 93d. Also variations of the substituents on the side chain or on the 1,3-dithiole ring of thioacylmethylene-1,3-dithiole 93 (i.e. 93c, 93c', and 198c) did not seem to affect the reactivity of thioacylmethylene-1,3-dithioles towards ethyl phenylpropiolate (i.e. no reaction).

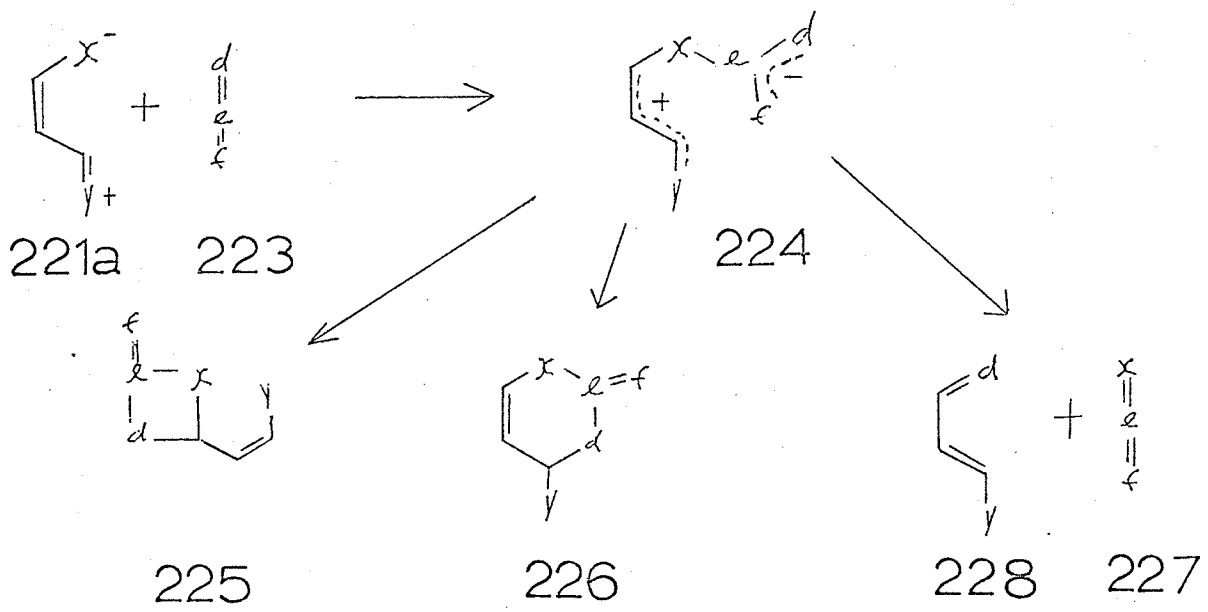
The (4 + 2) cycloaddition of thioacylmethylylene-1,3-dithioles 93 and acetylenic esters might be a concerted process, i.e., a type of Diels Alder reaction or it might proceed in two steps. The thioketonic side chain of thioacylmethylene-1,3-dithioles 93 are hetero-1,3-dienes of the type 221 in which the neighbouring atom Y has an unshared pair of electrons, i.e., in this case X = Y = S. For hetero-1,3-dienes of this type 221, the dipolar form 221a is believed to be the reactive species[178].



221 221a 222

It also has been postulated that hetero-1,3-dienes 221 in the dipolar

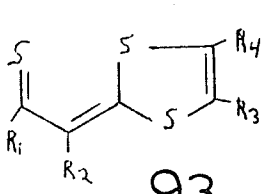
form 221a and polar 1,3-dienes of the type 222 react with hetero-cumulenes 223 to form dipolar intermediates which can be signified by the structure 224 (in the case of hetero-1,3-dienes)[178]. These dipolar intermediates 224 might then cyclize to form four-membered rings 225 or six-membered rings 226. They might also eliminate a new heterocumulene 227 to give a new hetero-1,3-diene 228.



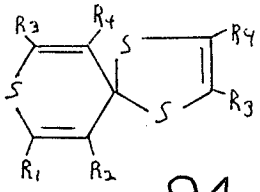
The reaction scheme illustrated above has been proposed by Gompper[178] to account for the products obtained by reaction of hetero-1,3-dienes 221 with heterocumulenes 223. Polar 1,3-dienes 222 react similarly with heterocumulenes[178]. It is possible that thioacyl-methylene-1,3-dithioles 93 also react similarly with acetylenic esters to produce thiopyranspiro-1,3-dithioles 94, with 1,2-dithiole-3-thiones 6 to form the corresponding thiothiophthenes 107 (see Intro-duction to this Chapter) and with phosphorus pentasulfide to form

either the 1,2-dithiole precursor (see Section A-1 of this Chapter) or the corresponding thiothiophthenes 107 (see Introduction to this Chapter). The dipolarophilic nature of the thiones 6 has been well established [see Introduction, Part II, Section B-1 and 2(i)].

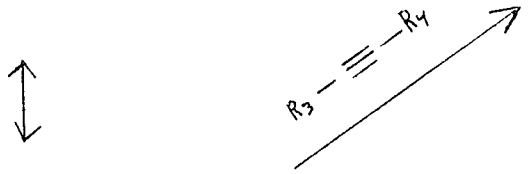
Some possible schemes for the above reactions are illustrated on the next page. Also the mono-adduct 93a may react similarly with 4,5-diphenyl-1,2-dithiole-3-thione (27) and then with dimethyl acetylene-dicarboxylate to give the unknown violet powder described in Section A-1 of this Chapter.

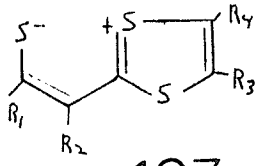


93

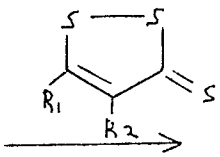


94





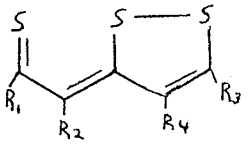
197a



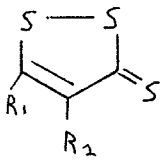
6

P_2S_5

P_2S_5

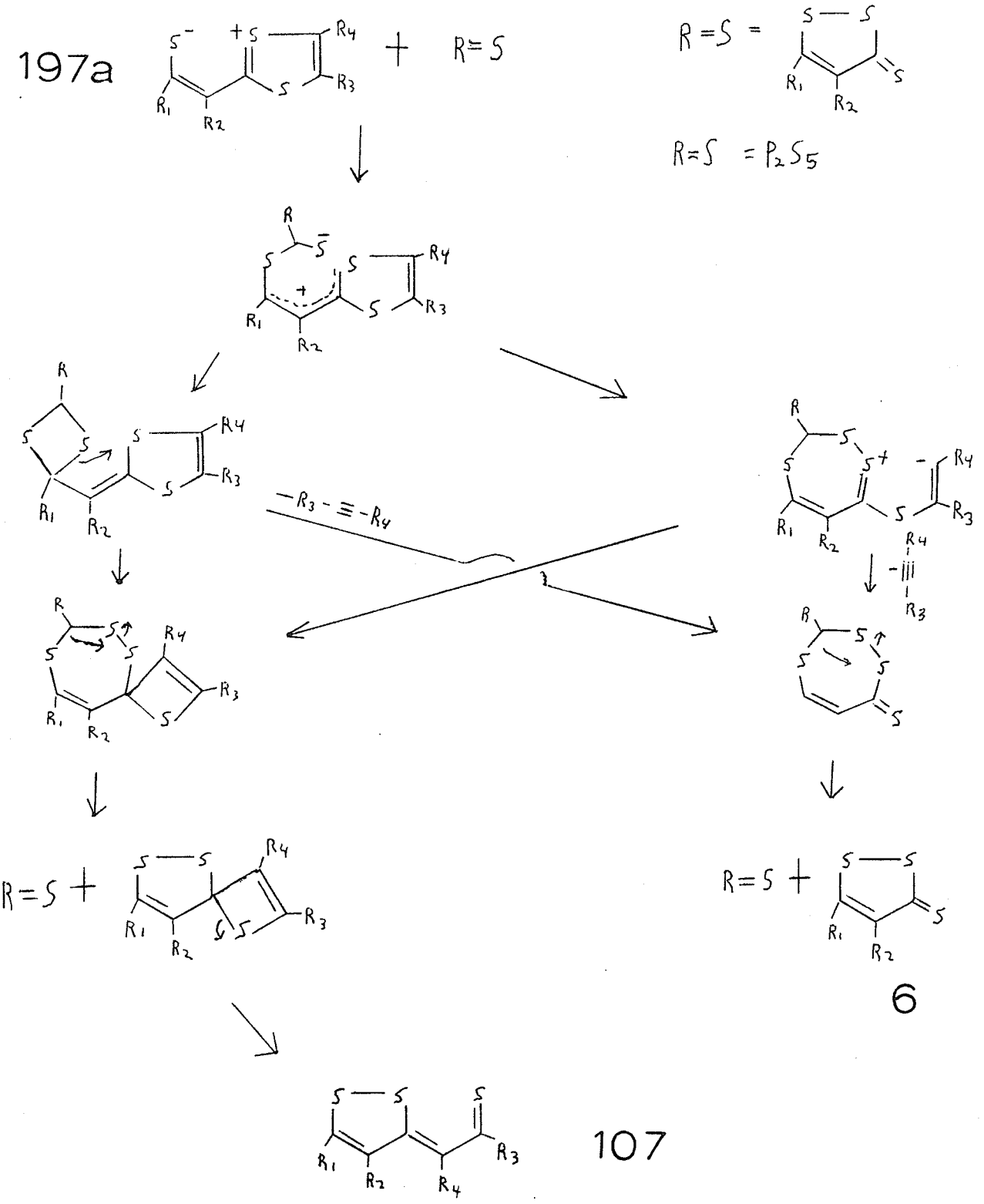


107



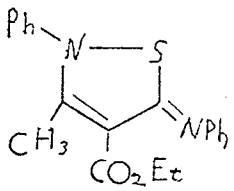
27

$R_1 = R_2 = Ph$

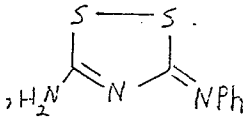

197a
R=S
R=S = P2S5
−R3 − ≡ −R4
R=S +
R=S +
6
107

Chapter II. Reactions of 3-Imino-1,2-dithioles and 3-Alkylidene-1,2-dithioles with Acetylenic Esters.

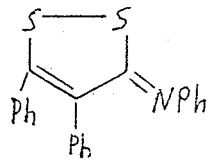
Since similar partial ionic structures can be written for 1,2-dithiole-3-thiones 6, 3-alkylidene-1,2-dithioles 7 and 3-imino-1,2-dithioles 8 (see General Introduction), it might be expected that the 3-alkylidene-1,2-dithioles 7 and the imines 8 could undergo reactions with activated acetylenes similarly to the thiones 6. Behringer reports obtaining an adduct by reaction of the Δ^3-5-imino-isothiazolin 229 with dimethyl acetylenedicarboxylate[184]. Probably the reaction of a 3-imino-1,2,4-dithiazole 230 with dimethyl acetylenedicarboxylate proceeds similarly[154].



229



230

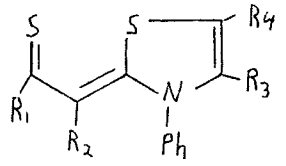


231

1. Reaction of 3-Phenylimino-5-phenyl-1,2-dithiole (181) and 3-Phenylimino-4,5-diphenyl-1,2-dithiole (231) with Dimethyl acetylene dicarboxylate, Ethyl Propiolate and Ethyl Phenylpropiolate.

3-Phenylimino-5-phenyl-1,2-dithiole (181) and 3-phenylimino 4,5-diphenyl-1,2-dithiole (231) were chosen as the imines to be studied and were prepared by reaction of the appropriate 3-methylthio-1,2-dithiolium salts of the type 125 with aniline[140]. Neither imine 181 or 231 reacted with the acetylenic esters at room temperature. At elevated temperatures reaction of the imines 181 and 231 with

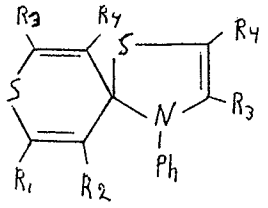
dimethyl acetylenedicarboxylate did not give the expected mono-adducts of the type 232, 2-(2-thioacylmethylene)-thiazoles. Instead the di-adducts, the thiopyranspirothiazoles 233a,b, respectively, were obtained.



232

a) $R_1 = Ph$, $R_2 = R_3 = H$, $R_4 = CO_2Et$

b) $R_1 = R_3 = Ph$, $R_2 = H$, $R_4 = CO_2Et$

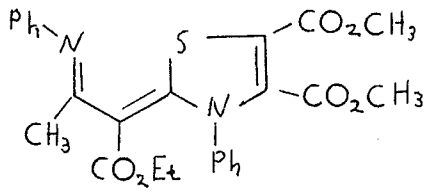


233

a) $R_1 = Ph$, $R_2 = H$, $R_3 = R_4 = CO_2CH_3$

b) $R_1 = R_2 = Ph$, $R_3 = R_4 = CO_2CH_3$

Presumably mono-adducts of the type 232 reacted more rapidly than the starting material with the acetylenic ester. However, Behringer reports obtaining the mono-adduct 234 by reaction of Δ^3-5-imino-isothiazolin 229 with dimethyl acetylenedicarboxylate[184]. In this case, steric interference by the phenyl group on the nitrogen atom of the side chain of the mono-adduct 234 may hinder reaction with more acetylenic ester.

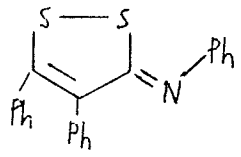


234

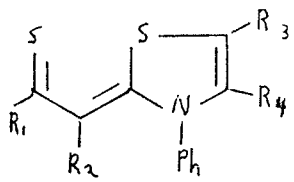
The n.m.r. spectrum of the di-adduct 233a (see Experimental Section) showed four singlets (6,42,6.32,6.20,6.12τ) for the expected non-equivalent carbomethoxy methyl groups. However, for the di-adduct 233b, the four non-

equivalent carbomethoxy methyl groups appeared as two main peaks which could not properly be resolved (6.57 - 6.37τ) as indicated by n.m.r.

The imine 181 reacted with the less reactive ethyl propiolate and ethyl phenylpropiolate to give the mono-adducts 232a,b, respectively. In contrast, the imine 231 failed to react with these esters, probably due to steric interference. In the imines 181 and 231 the N-phenyl group may be *cis* or *trans* to the sulfur atoms. In the imine 231, however, steric hindrance by the 4-phenyl group makes the *cis* form 231a more likely and this form 231a would in turn be less susceptible to approach by the acetylenic esters. The lack of reactivity of the imine 231 is also evident by the reaction conditions, employed, to obtain the di-adducts 233a,b. The imine 181 reacted with dimethyl acetylenedicarboxylate in boiling benzene while the imine 231 reacted with the same ester in boiling xylene.



231a



235a

$R_4 = CO_2Et$

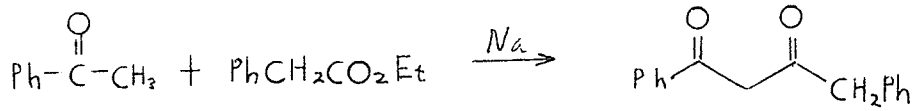
The n.m.r. spectra (see Experimental section) of the mono-adducts 232a,b indicated that they both were single compounds. Only one triplet and one quartet for the ethyl protons of the carboethoxy group was evident for each of the mono-adducts 232a,b. The possibility that they are a mixture of geometrical isomers and that the ester groups are equivalent is not likely since in one of the isomers the ester function is at the carbon atom adjacent to the sulfur atom of

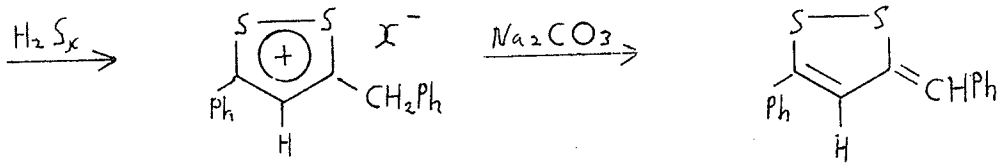
the thiazole ring, i.e., of the type 232. In the other isomer, the ester function is at the carbon atom adjacent to the N-phenyl group of the thiazole ring, i.e., 235a. Thus the chemical environment of the ester groups in these isomers would be substantially different. Also, it is possible that the exocyclic nitrogen atom of the imine 181 does not have sufficient nucleophilic activity to add α to the ester function of ethyl propiolate or ethyl phenylpropiolate (see Scheme A of Section C of the previous Chapter). The mono-adducts 232a,b formed may be either thiazole-4- or -5-carboxylic esters. They are forumulated as the latter since these would be the expected products of initial β-addition to the acetylenic esters. In the n.m.r. of the mono-adduct 232a only one singlet (2.25τ) is evident for either the proton on the thiazole ring or for the proton on the side chain. No proper assignment can be made. In a paper published previously[158], the n.m.r. spectral data given for the mono-adducts 232a,b are inaccurate due to difficulties in calibration, especially in the aromatic region of the spectrum.

2. Reaction of 3-Benzylidene-5-phenyl-1,2-dithiole (124a) with Dimethyl Acetylenedicarboxylate.

3-Benzylidene-5-phenyl-1,2-dithiole (124a) was the 3-alkylidene-1,2-dithiole 7 chosen to react with dimethyl acetylenedicarboxylate. The dithiole 124a was prepared by treatment of the dithiolium salt 123a with sodium carbonate[123] (see Introduction, Part III, Section A-1). The dithiolium salt 123a was prepared by reaction of benzoylphenylacetone with hydrogen polysulfide using a procedure outlined by Schmidt and Schultz[10] (see Introduction, Part I, Section A-1).

Benzoylphenylacetone was prepared by the reaction of acetophenone with ethyl phenylacetate in the presence of sodium[123].

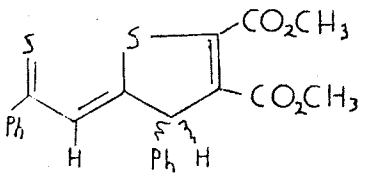




123a 124a

No colour change was observed when the dithiole 124a (0.6 m.moles) and dimethyl acetylenedicarboxylate (0.6 m.moles) in benzene were stirred at room temperature. T.l.c. analysis of the solution revealed that only the starting materials were present. However, in boiling benzene, the colour of the solution changed from the original reddish-orange to yellow over 18 hours. Twelve main fractions (each containing between 10-20 mg.) were found when the reaction mixture was separated by t.l.c., on silica. Other fractions in trace amounts were also found. There was insufficient material for each fraction to properly characterize the products of the reaction. However, an n.m.r. of the combined fractions revealed the presence of carbomethoxy groups and the dithiole 124a was found not to decompose under the reaction conditions. Thus 3-benzylidene-5-phenyl-1,2-dithiole (124a) reacted with dimethyl acetylenedicarboxylate to give the many fractions described above. It is possible that the expected mono-adduct, a 2,3-dihydrothiophene 236 and the expected di-adduct, a thiopyranspiro-2,3-

dihydrothiophene 237 are two of the fractions isolated.



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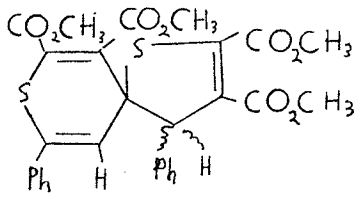
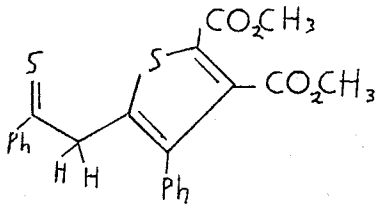


237

Some of the products found may be due to the tautomerism of the proton on the 2,3-dihydrothiophene ring of the expected mono-adduct 236. One possible product of this tautomerism could be the thiophene 238.

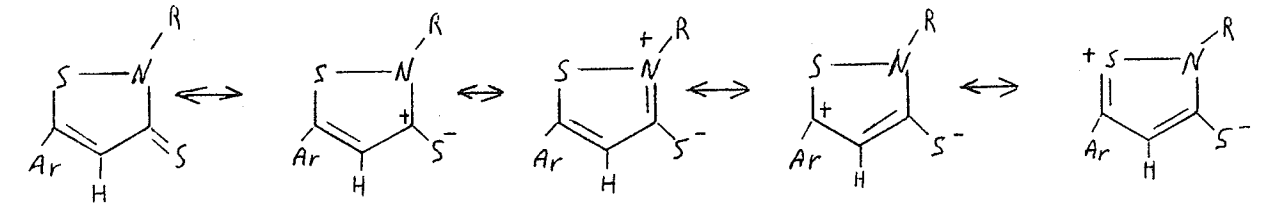


238

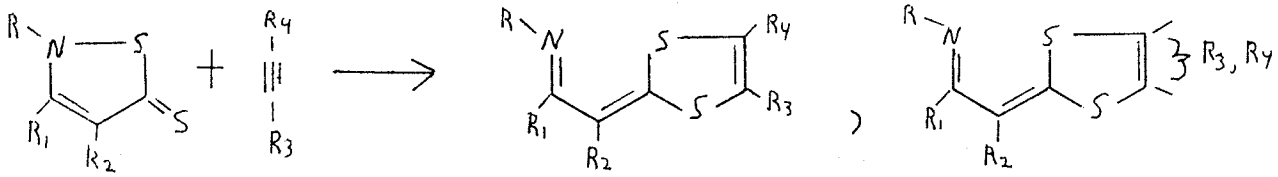
Chapter III. Studies on the Synthesis of Δ^4-Isothiazolin-3-thiones, Δ^4-Isothiaphospholin-3-thiones and Δ^3-Isothiaphospholin-5-thiones.

Section A: Studies on the Synthesis of Δ^4-Isothiazolin-3-thiones of the Type 171

Since similar partial ionic structures can be written for 1,2-dithiole-3-thiones 6 and Δ^4-isothiazolin-3-thiones of the type 171 (illustrated below), it might be expected that Δ^4-isothiazolin-3-thiones of the type 171 may react with activated acetylenes in a similar manner. Behringer has reported obtaining adducts of the type 240 by reaction of the isomeric Δ^3-isothiazolin-5-thiones 239 with activated acetylenes and that the adducts 240 prepared by reaction of the thiones 239 with unsymmetrical acetylenes are a mixture of *S-cis* isomers, i.e., 240', as indicated by n.m.r.[184].

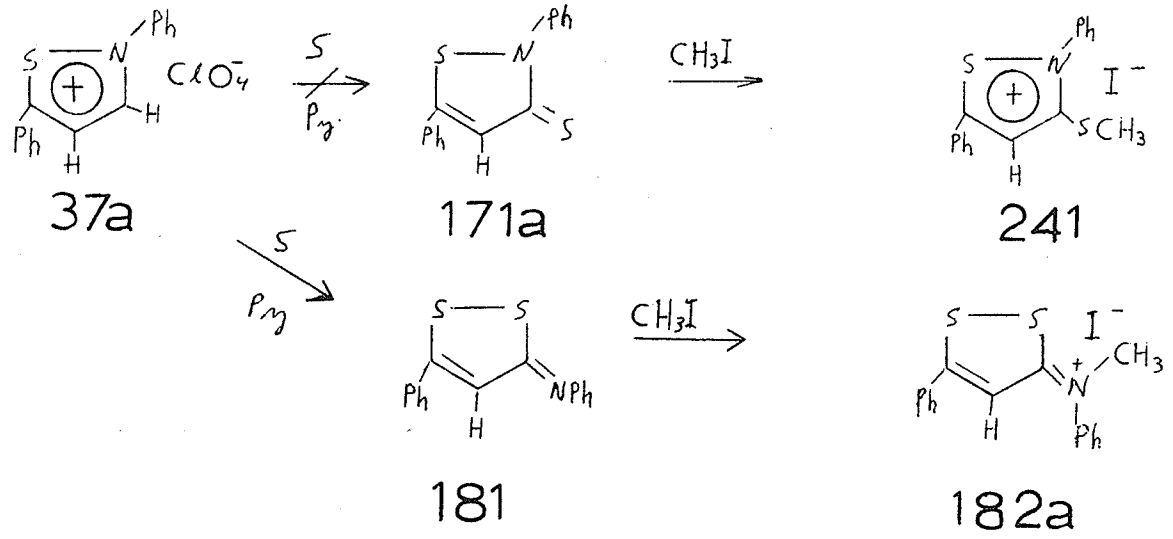


171



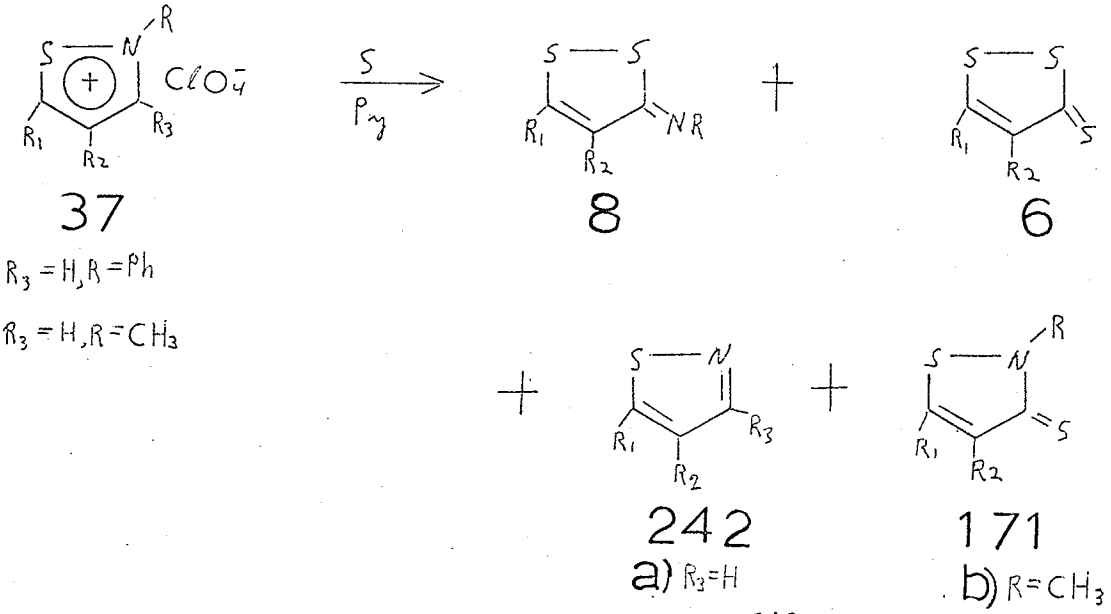
239 240 240'

McKinnon and Robak[31] have reported obtaining the Δ^4-isothiazolin-3-thione 171a, isolated as its methiodide salt 241, by reaction of the corresponding isothiazolium salt 37a with sulfur in pyridine, Thus using the method of McKinnon and Robak[31] the synthesis of N-phenyl-5-phenyl-Δ^4-isothiazolin-3-thione (171a) from N-phenyl-5-phenylisothiazolium perchlorate (37a) was attempted.

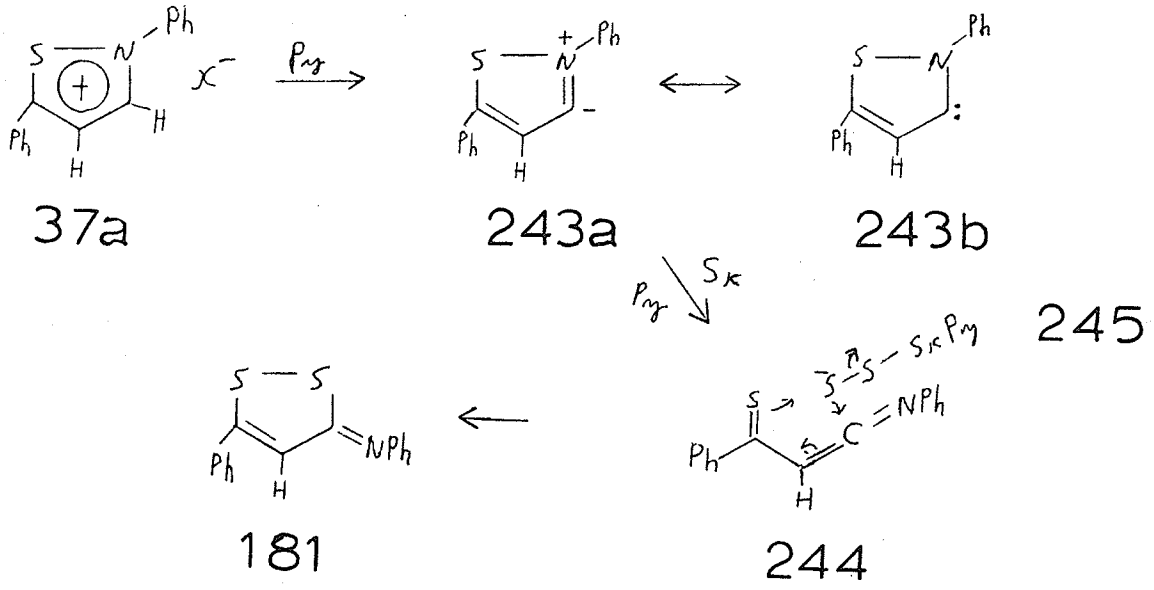


3-Phenylimino-5-phenyl-1,2-dithiole (181) was isolated by reaction of the isothiazolium salt 37a with sulfur in boiling pyridine. The i.r. spectrum of a methiodide salt isolated from the treatment of the reaction mixture with methyl iodide was identical to the i.r. spectrum of an authentic sample[179] of the methiodide salt 182a of 3-phenylimino-5-phenyl-1,2-dithiole (181). Further investigations of the reactions of 3-unsubstituted isothiazolium salts 37b with sulfur in boiling pyridine by Bachers and McKinnon[142] revealed that the products formed in this reaction were dependent on the substituents at carbon atoms -4 and -5 and at the nitrogen atom of the isothiazole ring. The products formed were 1,2-dithiole-3-thiones 6, 3-imino-1,2-dithioles 8,

isothiazoles 242a and Δ^4-isothiazolin-3-thiones of the type 171b (when N-methylisothiazolium salts 37c were used). A Δ^4-isothiazolin-3-thione of the type 171b was also obtained by reaction of a N-methylisothiazolium salt of the type 37c with sulfur in boiling pyridine by Le Coustumer and Mollier[144].



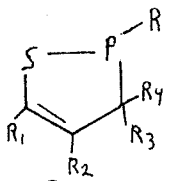
The investigations of Bachers and McKinnon[142] indicate that 3-phenylimino-5-phenyl-1,2-dithiole (181) may be formed by the following reaction scheme (illustrated below). The scheme would first involve formation of a carbene 243b (a resonance form of the dipolar structure 243a) by the loss of a proton from position -3 of the isothiazolium salt 37a. The carbene 243b could then rearrange to form the thioketimine 244 which on nucleophilic attack by the activated polysulfide anion 245 and on subsequent ring closure could yield 3-phenylimino-5-phenyl-1,2-dithiole (181).



Certain thiazolium salts lose a proton on treatment with a base to produce a carbene[185] and it has been shown that isoxazolium salts produce ketoketimines when treated with tertiary amines[186]. Activated polysulfide anions of the type 245 are known to be formed by attack of nucleophilic agents on elemental sulfur[187].

Section B: Studies on the Synthesis of Δ^4-Isothiaphospholin-3-thiones 183 and Δ^3-Isothiaphospholin-5-thiones 184.

No derivatives of the isothiaphosphole system of the type 246 have been prepared. The isothiaphospholium salts 247 are of particular interest since they may possess aromatic character. They are isoelectronic with isothiazolium salts 37 and 1,2-dithiolium salts 6 and thus may have properties similar to these salts. Δ^4-isothiaphospholin-3-thiones 183 and Δ^3-isophospholin-5-thiones 184 for which partial ionic structures can be written (illustrated below) may react with activated acetylenes via a (3 + 2) cycloaddition.



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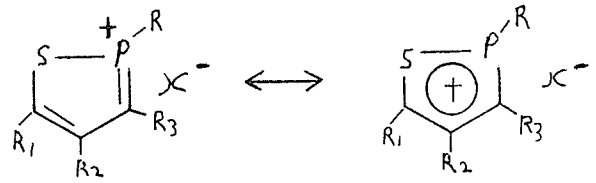
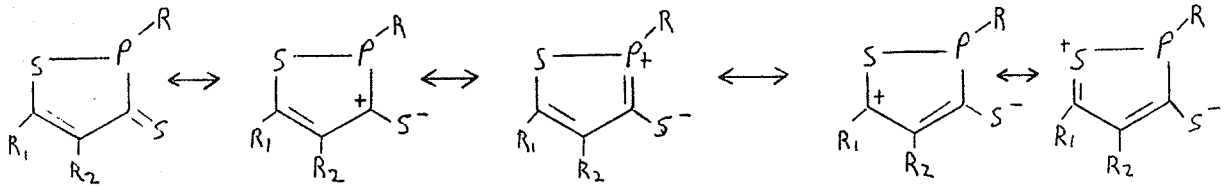
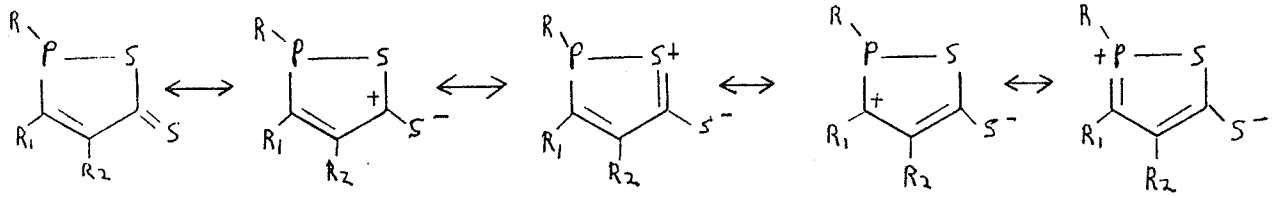


247



183

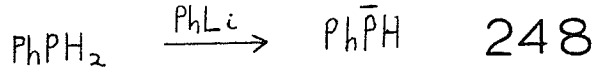


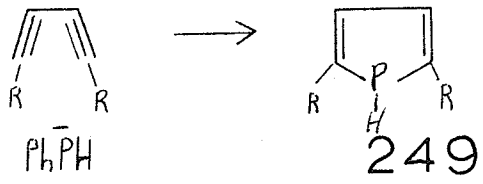
184

1. Reaction of Phenyl Phosphine with 3-Phenyl-1,2-dithiolium Perchlorate (22b).

Phenyl phosphine, a primary aromatic phosphine, in some instances displays the same chemical behaviour as aniline, a primary aromatic amine. This similarity is evident in their behaviour as nucleophiles.

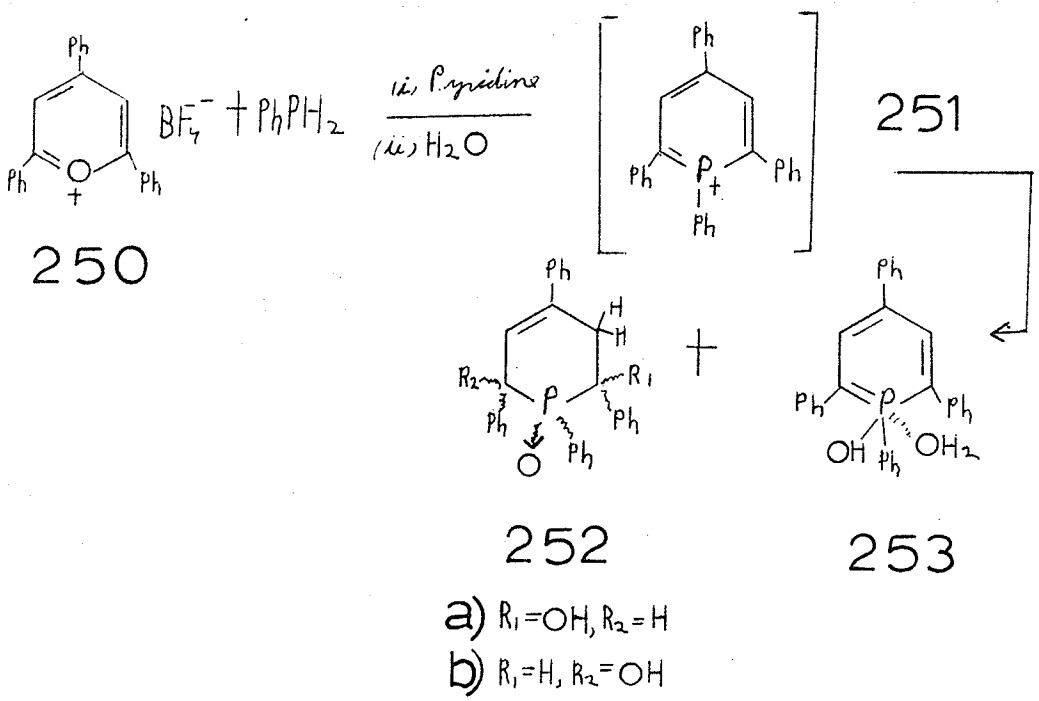
Phenyl phosphine, in the form of its phosphide anion 248, adds smoothly to butadiynes at room temperature to yield the corresponding phospholes 249[188]. Phosphide anions similar to the anion 248 which is formed from phenyl phosphine and a catalytic amount of phenyl lithium are known to be strong nucleophiles[189]. In a similar manner, ammonia or aniline and butadiynes form pyrroles[190].





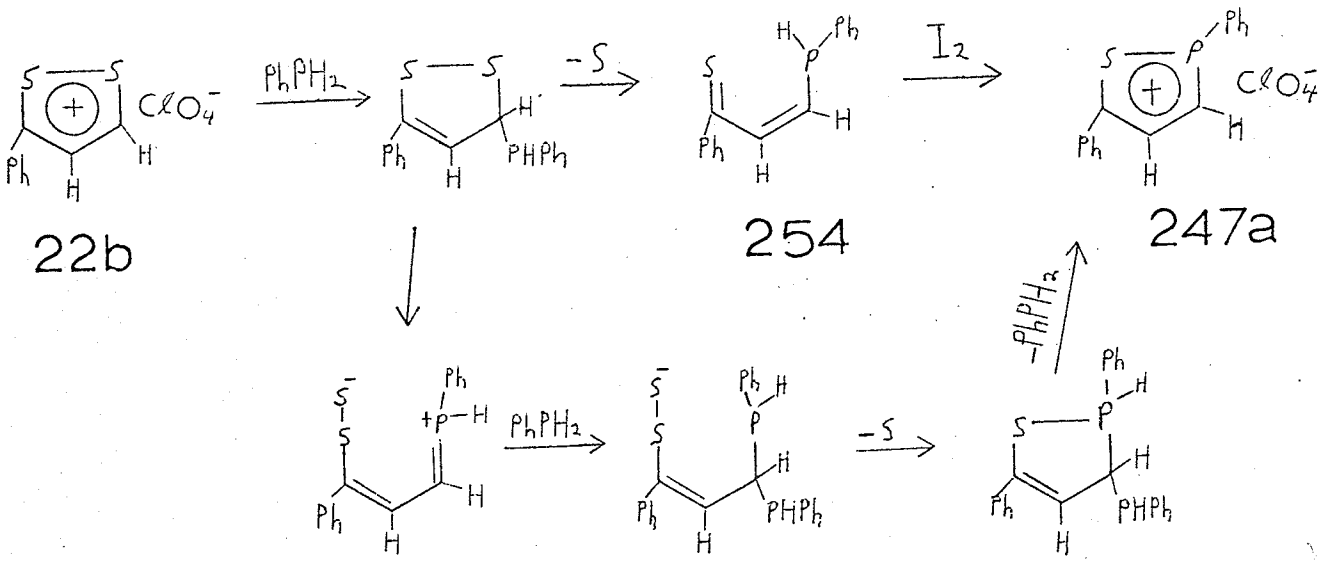
248 $Ph\bar{P}H$ 249

However, in the reaction of phenyl phosphine with 2,4,6-triphenylpyrylium tetrafluoroborate 250, the phosphine itself has sufficient nucleophilic activity to form the phosphorinium salt 251 which cannot be isolated but on treatment with water affords the phosphapyran oxides 252a and 252b and the phosphorabenzene mono-hydrate 253[191]. The formation of the salt 251 parallels the formation of pyridinium and thiopyrylium salts from the treatment of pyrylium salts with substituted amines[26] and sulfide ions[28], respectively.



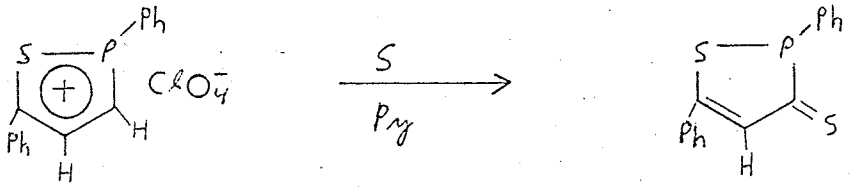
Thus, in analogy with the reaction of aniline with 1,2-dithiolium salts (see Introduction, Part I, Section B-2), phenyl phosphine similarly might be involved in a nucleophilic attack at position -5 [in the case of 3-phenyl-1,2-dithiolium perchlorate (22b)] of 1,2-dithiolium salts to give the corresponding 1-phenylphosphino-propene-3-thione 254 (in the case of the dithiolium salt 22b) which on treatment with iodine might give the isothiaphospholium salt 247a (illustrated below). 1-Arylaminopropenethiones 36 on treatment with iodine give the corresponding isothiazolium salts 37[31] (see Introduction, Part I, Section B-2). Formation of the isothiaphospholium salt 247a from the propenethione 254, a secondary phosphine may have to take place 'in situ' since secondary phosphines, like primary phosphines[192], are likely to be very reactive in air and form pentavalent phosphorus structures. Also, it is possible that isothiaphospholium salts, e.g., 247a, may be obtained in one step from 1,2-dithiolium salts, e.g. 22b

and phenyl phosphine (illustrated below) in a manner similar to the preparation of isothiazoles by reaction of 1,2-dithiolium salts with ammonia[25] (see Introduction, Part I, Section B-1).



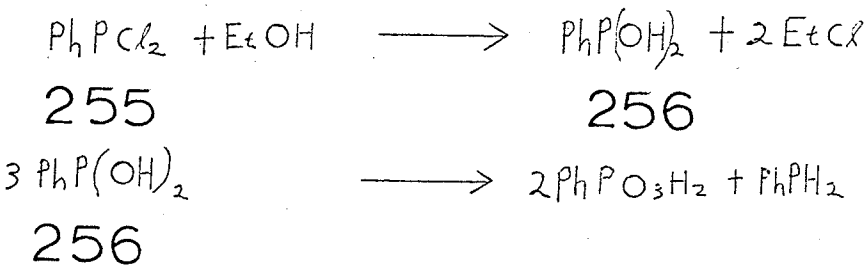
22b 254 247a

The isothiaphospholium salt 247a, on treatment with sulfur in pyridine might give the corresponding Δ^4-isothiaphospholin-3-thione 183a (illustrated below) since similar 1,2-dithiolium salts, e.g., 22b have been reported to undergo oxidation with sulfur in pyridine to provide the corresponding thiones, e.g., 5-phenyl-1,2-dithiole-3-thione (50b)[33].



247a 183a

3-Phenyl-1,2-dithiolium perchlorate (22b), the salt used in this study, was prepared from 5-phenyl-1,2-dithiole-3-thione (50b) using the method of Klingsberg[3] [see Introduction, Part I, Section A-2 (b)]. Phenyl phosphine was prepared using the method of Mann and Millar[192], which involved the formation of phenylphosphonous acid (256) from the reaction of phenyldichlorophosphine (255) with ethanol. Thermal decomposition of phenylphosphonous acid (256) produced phenyl phosphine.



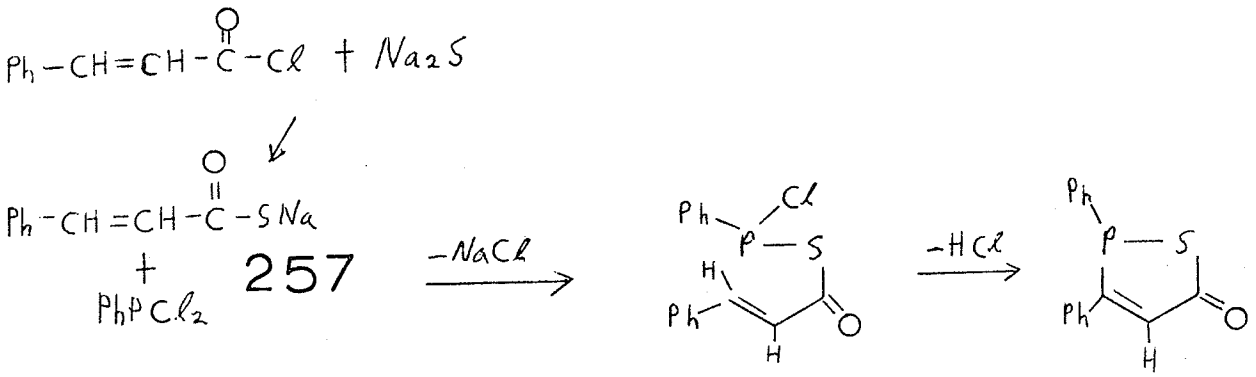
All attempts to make 5-phenylisothiaphospholium perchlorate (247a) were unsuccessful. Immediately after addition of phenyl phosphine to a solution of 3-phenyl-1,2-dithiolium perchlorate (22b) in ethanol at room temperature (under nitrogen), the colour of the solution changed from brown to green. The green colour persisted for 3-6 seconds, then changed to orange and after 1-2 minutes an amorphous yellow powder was precipitated which was found to be soluble in benzene and chloroform but relatively insoluble in petroleum ether, ethanol and methanol. The ethanol solution remaining was found to contain more of this amorphous powder. Over a period of weeks, the powder turned from yellow to grey. Further purification of the yellow powder by column chromatography, using neutral alumina, led to decomposition products. Also, no separation resulted when the powder was subjected to purification by t.l.c. using silica. An elemental analysis of the

amorphous powder was not consistent with the propenethione 254 or the isothiaphospholium salt 247a but corresponded closely to the formula $C_{19}H_{18}PO_2S_2$. It is possible that the powder was impure propenethione 254 but on treatment with iodine in benzene, the yellow powder was recovered. It is also possible that the propenethione 254 might be the cause of the colour changes observed, therefore, in another series of experiments, iodine in ethanol was added to the reaction solution at the two colour stages. In both cases, the yellow powder was recovered. No structure can be advanced for the yellow powder since its purity has not been established.

It has been assumed that initial attack of phenyl phosphine would be at a carbon atom but it is known that for many sulfur-containing compounds, phosphines preferentially attack the sulfur atom[193]. Thus the yellow powder may have resulted from an initial attack at one of the sulfur atoms of the 1,2-dithiolium salt 22b.

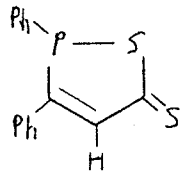
2. Attempted Synthesis of Phenylphosphino-3-phenyl-Δ^3-isothiaphospholin-5-thione (184a).

The following series of reactions were undertaken in an attempt to synthesize phenylphosphino-3-phenyl-Δ^3-isothiaphospholin-5-thione (184a) (illustrated below). It is possible that on heating sodium thiocinnamate (257) which was prepared by reaction of *trans*-cinnamoyl chloride with anhydrous sodium sulfide, with phenyldichlorophosphine (255), phenylphosphino-3-phenyl-Δ^3-isothiaphospholin-5-one (259) could be prepared. The thione 184a could then be prepared by treatment of the ketone 259 with phosphorus pentasulfide.



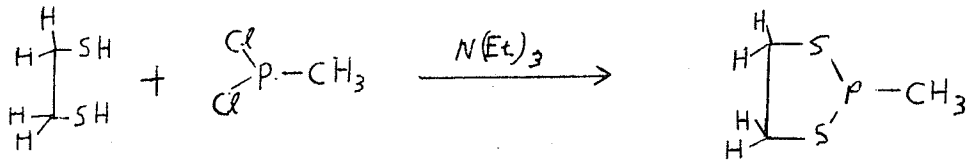
255

258 259



184a

It was hoped that sodium thiocinnamate (257) would initially combine with phenyldichlorophosphine (255) to form the phosphinothioester 258 which by intramolecular nucleophilic attack of the phosphorus atom at the olefinic bond would then cyclize and yield the ketone 259. Reaction of methyldichlorophosphine with various dimercapto compounds in the presence of a base gives heterocyclic compounds containing two sulfur and one phosphorus atoms[194] [illustrated below for the reaction of dimercaptoethane with methyldichlorophosphine].

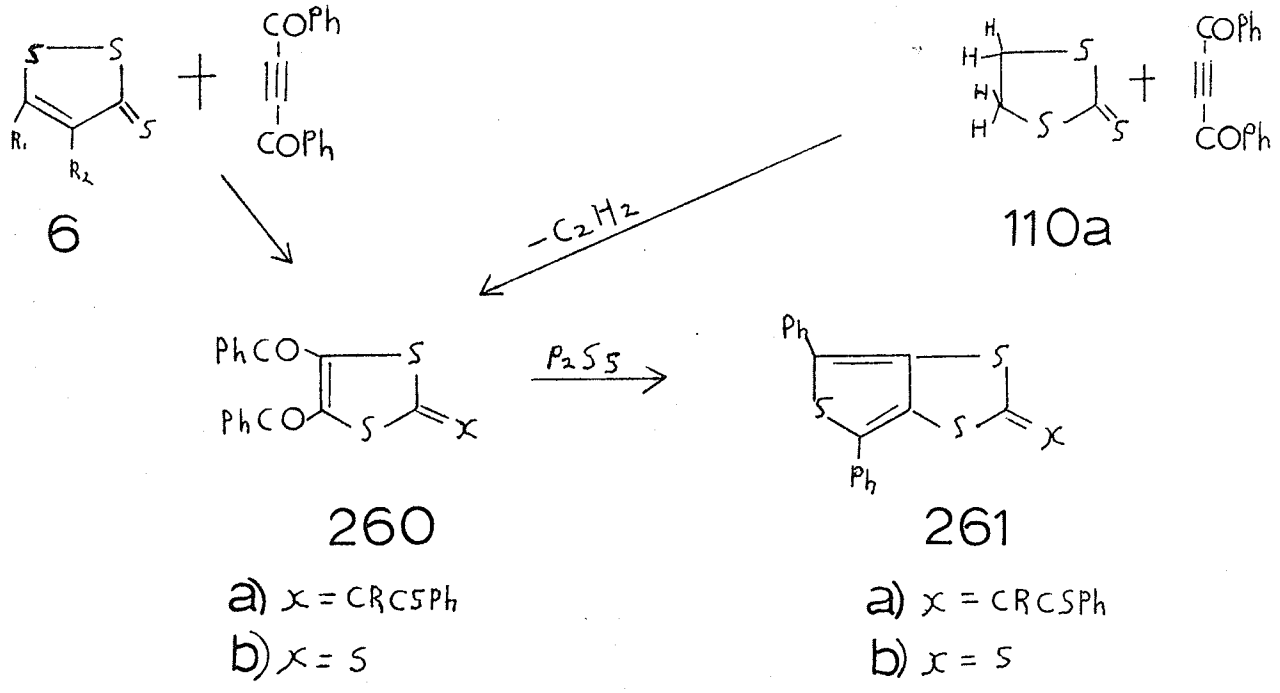


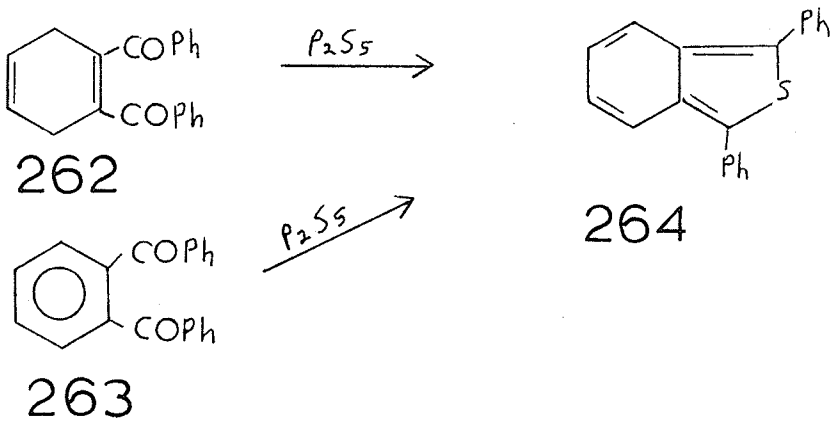
Reaction of phosphonous dihalides such as phenyldichlorophosphine (255) with olefins, especially in cycloadditions is well known[195].

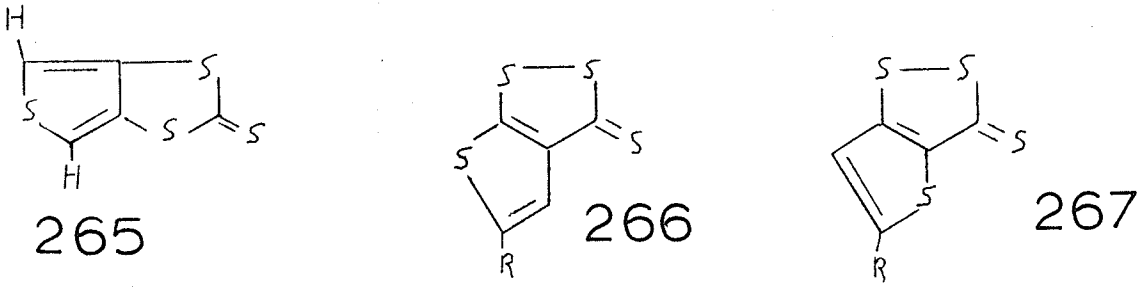
Hydrogen chloride was given off when a mixture of sodium thiocinnamate (257) and phenyldichlorophosphine was heated in boiling dioxane. A greenish-yellow oily paste was recovered. The paste was found to consist of many fractions, as indicated by t.l.c. and an i.r. spectrum indicated that the paste still contained a carbonyl function. The greenish-yellow paste, without further purification, was treated with phosphorus pentasulfide in boiling benzene to give an orange paste whose i.r. spectrum revealed the absence of a carbonyl group. It is possible that this orange paste contained phenylphosphino-3-phenyl-Δ^3-isothiaphospholin-5-thione (184a) but an attempt to isolate this thione 184a as the methiodide salt was unsuccessful.

Chapter IV. Studies on Some 4,5-Dibenzoyl-1,3-dithioles.

Treatment of 4,5-dibenzoyl-1,3-dithioles 260 with phosphorus pentasulfide could yield derivatives of the thieno [3,4,d]-1,3-dithiole system 261. The dibenzoyl-1,3-dithioles 260 are substituted dibenzoylethylenes and, as such, might be expected to give thiophenes on sulfurization, similar to the preparation of isobenzothiophenes 264 from diacyldihydrobenzenes 262[196] or diacylbenzenes 263[197]. Thieno [3,4,d]-1,3-dithiole-2-thione (265) is already known[198] and examples of isomeric thieno-1,2-dithioles 266 and 267 have also been prepared[199], but apart from these few examples no other derivatives of this system 261 have been reported, and it seemed desirable to prepare some derivatives of the thieno [3,4,d]-1,3-dithiole system 261. One approach to 4,5-dibenzoyl-1,3-dithioles 260a and b would be by the (3 + 2) cycloaddition of 1,2-dithiole-3-thiones 6 or 1,3-dithiolane-2-thione (110a), respectively, with dibenzoylacetylene [see Introduction, Part II, Section B-2(ii)].



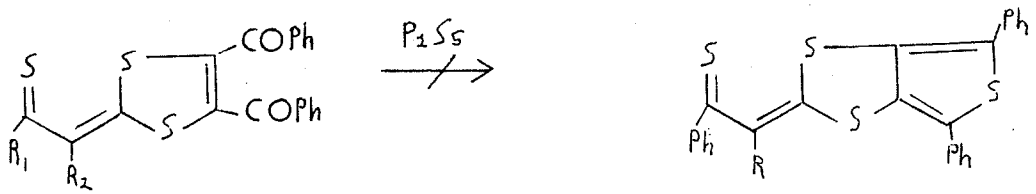




1. Reaction of 5-Phenyl-1,2-dithiole-3-thione (50b) and 4,5-Diphenyl-1,2-dithiole-3-thione (27) with Dibenzoylacetylene.

Dibenzoylacetylene is readily prepared from dibenzoylethylene using the method of Lutz and Smithey[200] which involves the treatment of dibenzoyldibromoethane with triethylamine. Dibenzoylacetylene reacted rapidly at room temperature with both thiones 50b and 27 to give the mono-adducts 93e and f, respectively, as the main products and the thiopyranspiro-1,3-dithioles 94c and d, respectively, as minor products which became the only products formed when the thiones 50b and 27 and two equivalents of the acetylene were heated in boiling benzene. Treatment of the dibenzoyl-2-thioacylmethylene-1,3-dithioles 93e and f with phosphorus pentasulfide gave the corresponding 1,2-dithiole-3-thiones 50b and 27, respectively, instead of the expected thieno-[3,4,d]-1,3-dithioles of the type 261a. 4,5-Diphenyl-1,2-dithiole-

3-thione (27) was also obtained when the mono-adduct 93a was treated with phosphorus pentasulfide (see Chapter I, Section A-1). Presumably, the reaction of these mono-adducts 93e and f with phosphorus pentasulfide proceeds similarly. A mechanism for this reaction has previously been proposed (see Chapter I, Section D). The sulfurization of the thiopyranspiro-1,3-dithiole 94c, using phosphorus pentasulfide was successful and a product of the presumed thienothiopyranspirothieno-1,3-dithiole structure 268 was obtained.

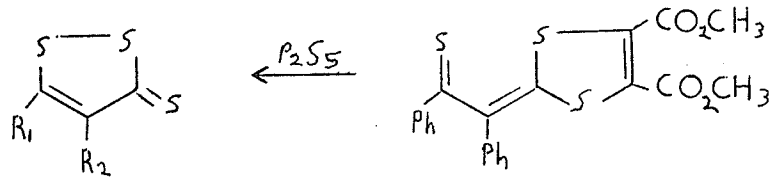


93

e) $R_1 = Ph, R_2 = H$

f) $R_1 = R_2 = Ph$

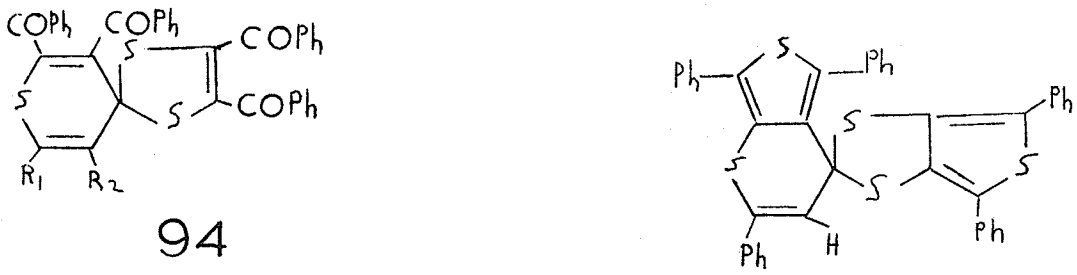
261a



50b: $R_1 = Ph, R_2 = H$

27: $R_1 = R_2 = Ph$

93a



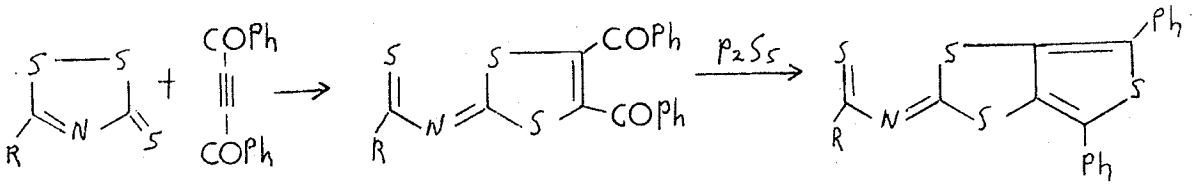
94

c) $R_1 = Ph, R_2 = H$

d) $R_1 = R_2 = Ph$

268

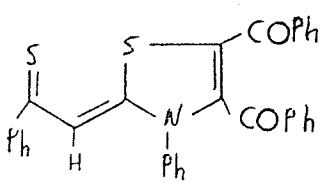
Several 2-thioacylimino-4,5-dibenzoyl-1,3-dithioles 197c which were prepared by reaction of various 1,2,4-dithiazole-3-thiones 185 with dibenzoylacetylene, on treatment with phosphorus pentasulfide give the corresponding 2,5-diphenylthieno[3,4,d]-2-thioacylimino-1,3-dithioles 269[159,201]. Probably the substitution of a nitrogen atom for a carbon atom on the side chain is the determining factor in the successful sulfurization of thioacylimino-1,3-dithioles 197c.



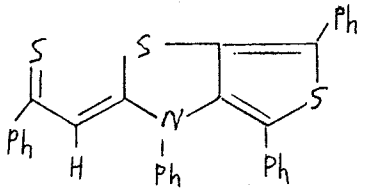
185 197c 269

2. Reaction of 3-Phenylimino-5-phenyl-1,2-dithiole (181) with Dibenzoylacetylene.

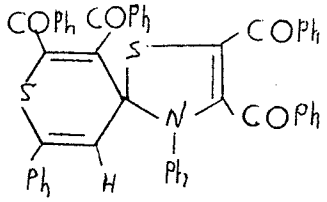
The sulfurization of the 2-thioacylmethylene-4,5-dibenzoylthiazole 232c may provide the thieno[3,4,d] thiazole 270. However, reaction of 3-phenylimino-5-phenyl-1,2-dithiole (181) with dibenzoylacetylene in boiling benzene gave an orange powder whose elemental analysis was not consistent with the structure of the mono-adduct 232c. The elemental analysis corresponded more closely with the structure of the thiopyranspirothiazole 233c, i.e., the di-adduct. Reaction of the imine 181 with dimethylacetylenedicarboxylate, which is observed to be comparable in reactivity to dibenzoylacetylene also gives the thiopyranspirothiazole 233a (see Chapter II-1).



232c



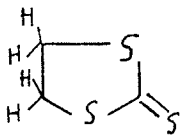
270



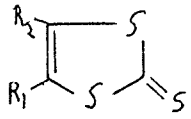
233c

3. Reaction of 1,3-Dithiolane-2-thione (110a) with Dibenzoylacetylene.

No reaction occurred at room temperature or in boiling benzene. In boiling xylene, the solution turned dark but the only identifiable product was unchanged 1,3-dithiolane-2-thione (110a). Dibenzoylacetylene was found to decompose under the reaction conditions. Possibly the exocyclic sulfur atom of the dithiolane 110a does not have sufficient nucleophilic activity to react with the highly reactive acetylene at lower temperatures and at higher temperatures, dibenzoylacetylene decomposed. Easton and Leaver[89] have reported that the thione 110a and dimethyl acetylenedicarboxylate react in boiling xylene [see Introduction, Part II, Section B-2(ii)]. This decreased reactivity possibly may be due to lack of sufficient dipole character in the thione 110a since it does not have resonance forms comparable to 1,3-dithiole-2-thiones 271.



110a



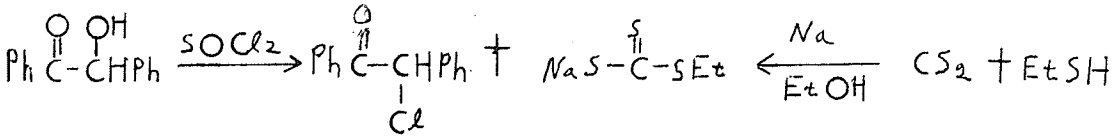
271

a) $R_1 = R_2 = Ph$

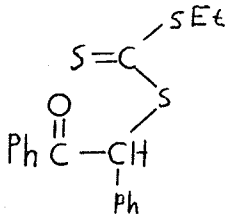
To test this latter hypothesis, 4,5-diphenyl-1,3-dithiole-2-thione (271a) was prepared by acid-catalysized cyclization of α-phenylphenacyl ethyl trithiocarbonate (274) to the 4,5-diphenyl-2-ethylthio-1,3-dithiolium salt 275, similar to known methods[202,203] followed by treatment with sodium hydrogen sulfide. This thione 271a did react with dibenzoylacetylene in boiling benzene, but the products, although they possessed benzoyl groups, as indicated by i.r., could not be purified satisfactorily.

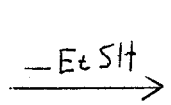
α-Phenylphenacyl ethyl trithiocarbonate (274) was obtained by reaction of desyl chloride[204] with sodium ethyl trithiocarbonate (273) similar to known methods[21]. Also from this reaction a colourless compound which turned green on exposure to light was also recovered. This compound was identified as 4,5-diphenyl-1,3-thiaoxole-2-thione (277). This thione 277 has previously been prepared by treatment of α-phenylphenacyl ethyl xanthate (276) with base in aequeous dioxane[205]. The melting point and mass spectrum corresponded to those reported for the thione 277[205] and also an elemental analysis was consistent with the assignment. The reaction scheme of the preparation of 4,5-diphenyl-1,3-dithiole-2-thione (271a) and 4,5-diphenyl-1,3-thiaoxole-2-thione (277) is illustrated on the next page.

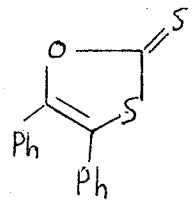
The reactivity of 4,5-diphenyl-1,3-dithiole-2-thione (271a) towards dibenzoylacetylene is less than that for the isomeric 4,5-diphenyl-1,2-dithiole-3-thione (27), e.g., reaction occurred in boiling benzene for the thione 271a and at room temperature for the thione 27, both with dibenzoylacetylene. This decreased reactivity for the thione 271a since both have similar resonance forms, may be due to the



272 | 273

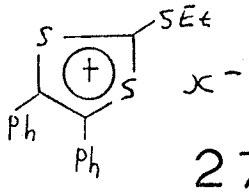




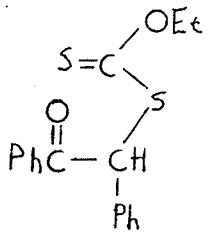


274

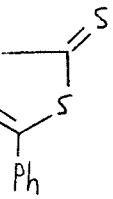
277



275

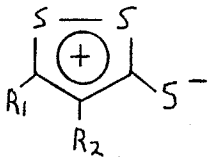


276



271a

difference in the nucleophilicity of the exocyclic sulfur atom of the 1,3- and 1,2-dithiolethiones, i.e., 171a and 27. Behringer reports that 1,3-dithiole-2-thiones of the type 171 do not react with dimethyl acetylenedicarboxylate[154]. Mayer[163] has conducted studies on 1,2-dithiole-3-thiones 6 and 1,3-dithiole-2-thiones 171 and has shown that the basicity, ease of alkylation and acylation and nucleophilicity of the thiocarbonyl group of 1,2-dithiole-3-thiones 6 is greater than those of the thiocarbonyl group of 1,3-dithiole-2-thiones 171. Mayer[163] attributed this difference to the increased delocalization of the positive charge over the 1,2-dithiole ring of 1,2-dithiole-3-thiones 6 as compared to 1,3-dithiole-2-thiones 171. For 1,2-dithiole-3-thiones 6 this would mean an increased contribution from the resonance form 6a [see Introduction, Part II, Section B-2(ii)].



6a

Conclusions and Suggestions for Future Research

Although the mechanism of the (3 + 2) cycloaddition of 1,2-dithiole-3-thiones and acetylenic esters or arylacetylenes has not been determined, the initial product (193a', 193b') of the reaction of 4,5-diphenyl-1,2-dithiole (27) with ethyl propiolate and ethyl phenylpropiolate, respectively, has been found to contain, in each case, two thioacylmethylene-1,3-dithioles of type 93 and 102 (as indicated by n.m.r.) which are *S-cis* geometrical isomers. This is also the case for the mono-adduct 93c' formed by reaction of 5-phenyl-1,2-dithiole-3-thione (50b) with ethyl phenylpropiolate. Presumably, reaction of 1,2-dithiole-3-thiones 6 with acetylenic esters or arylacetylenes proceeds similarly and the mono-adducts 93', so formed by the use of unsymmetrical acetylenes, consist of two *S-cis* geometrical isomers. An analysis of the n.m.r. spectrum of the mono-adduct 93a' indicated that the two isomers were formed during the reaction and were not interconvertible. Until further n.m.r. studies of mono-adducts 93' prepared by reaction of various 1,2-dithiole-3-thiones 6, including the bicyclo-1,2-dithiole-3-thiones 194, with unsymmetrical acetylenes have been undertaken, the possibility of interconversion of the two *S-cis* isomers cannot be totally excluded.

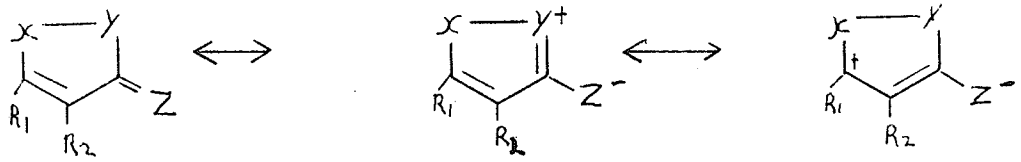
A kinetic study of the formation of the mono-adducts 93 might be useful in determining the mechanism of the (3 + 2) cycloaddition. Dimethyl acetylenedicarboxylate would be an ideal acetylene for such a study since its reactivity is such that the reaction will proceed rapidly at room temperature.

Reaction of the 5-unsubstituted-1,2-dithiole-3-thiones 58 and 164a with activated acetylenes (dimethyl acetylenedicarboxylate and dibenzoylacetylene) gives the expected thioformylmethylene-1,3-dithioles 198a,b,c and d. But since these mono-adducts 198 are thials, other products are also obtained. Bis-dithiolylidene-2-butenes 200 were obtained in all cases from the decomposition of the thials 198, probably by extrusion of two sulfur atoms from the thials 198. When the thial 198 is stabilized by conjugation to a phenyl group, i.e., 198c and d [4-phenyl-1,2-dithiole-3-thione (164a) is the starting thione] the reaction to produce the butene 200 becomes slower and other reactions compete effectively with it, i.e., the thial 198 may react with a suitably activated acetylene to form a thiopyranspiro-1,3-dithiole 199 or it may form the corresponding aldehyde 201, possibly by oxidation or hydrolysis of the corresponding thial 199.

Reaction of 3-phenylimino-5-phenyl-1,2-dithiole (181) with dimethyl acetylenedicarboxylate, ethyl propiolate and ethyl phenylpropiolate gave, in the case of dimethyl acetylenedicarboxylate, the thiopyranspirothiazole 233a and, in the case of ethyl propiolate and ethyl phenylpropiolate, the thioacylmethylenethiazoles 232a and b, respectively, which were found to consist of one of the two possible isomers (as indicated by n.m.r.). 3-Phenylimino-4,5-diphenyl-1,2-dithiole (231) only reacted with dimethyl acetylenedicarboxylate and also produced a di-adduct 233b. 3-Benzylidene-5-phenyl-1,2-dithiole (124a) and 4,5-diphenyl-1,3-dithiole-2-thione (271a) reacted with dimethyl acetylenedicarboxylate and dibenzoylacetylene, respectively to give products which could not be purified satisfactorily. Successful (3 + 2) cycloadditions with activated acetylenes have been reported for 1,3-

dithiolane-2-thiones 110[89], 1,2,4-dithiazole-3-thiones 185[154-159], the 3-imino-1,2,4-dithiazole 230[154], Δ^3-isothiazolin-5-thiones 239[184] and the Δ^3-5-imino-isothiazolin 229[184]. 1,2-Dithiole-3-ones 81 are reported not to react with activated acetylenes[90] [see Introduction, Part II, Section B-2(ii)].

All the compounds mentioned above which react with activated acetylenes via a (3 + 2) cycloaddition are five-membered heterocyclic systems of the type 278 in which Y and Z are always atoms which possess an unshared pair of electrons and for which the dipolar resonance forms 278a and b are possible. A (3 + 2) cycloaddition of this type commonly occurs when the exocylcic atom Z is a sulfur atom. It would be interesting to see if a heterocyclic system of the type 278 in which Z is a selenium atom, e.g., 278c could undergo a (3 + 2) cycloaddition with activated acetylenes.

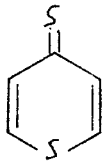


278 278a 278b

c) X = Y = S, Z = Se

The reactivity of 1,2-dithiole-3-thiones 6 towards acetylenes is much greater than that displayed by the 1,3-dithiole-2-thione 271a or that reported for 1,3-dithiolanes-2-thiones 110[89]. A correlation between this reactivity and basicity, ease of alkylation and acylation and

nucleophilicity of the thiocarbonyl group of the thiones 6, 271a and 110 can be seen (see Discussion, Chapter IV-3). Since these same properties of the thiocarbonyl group of thiopyran-4-thiones 279 and thiopyran-2-thiones 280 are more pronounced than those for the thiocarbonyl group of 1,2-dithiole-3-thiones 6, it would seem likely that these thiones 279 and 280 would also react with acetylenes, although not especially via a (3 + 2) cycloaddition.



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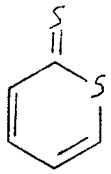


280

Thioacylmethylene-1,3-dithioles 93, hetero-1,3-dienes of the type 221, which react further with suitably activated acetylenes (dimethyl acetylenedicarboxylate, ethyl propiolate and dibenzoylacetylene) to give thiopyranspiro-1,3-dithioles 94 may also react with heterocumulenes 223 to possibly give a variety of compounds (see Discussion, Chapter I, Section D). With ethyl propiolate, only one mode of addition of the mono-adducts 94b and 94a' to the acetylenic ester is found to occur.

EXPERIMENTAL

Infrared (i.r.) spectra were recorded on a Perkin-Elmer model 137 spectrophotometer in liquid paraffin mulls, unless otherwise stated. Nuclear magnetic resonance spectra were recorded on a Varian A-56/60 A spectrometer using deuteriochloroform ($CDCl_3$) as solvent, unless otherwise stated, and give in τ units and the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, J = coupling constant. The mass spectra were obtained on a Finnegan 1015 quadrupole mass spectrometer. Melting points (m.p.) were measured on a Fisher-Johns melting point apparatus and are uncorrected. Microanalyses were performed by Alfred Bernhardt, 5251 Elbach über Engelskirchen, West Germany. The alumina used in column chromatography was "Camag" band 507C and the silical gel used in thin layer chromatography (t.l.c.) was "Camag" type D.S.F. 5, both supplied by Mondray Ltd. The t.l.c. separations were carried out using glass plates coated with 1 mm. layer of adsorbent and were achieved by multiple developments of the plates using solvents or mixture of solvents of increasing polarity. 100-150 mg. of material were separated on each plate.

The compounds which are characterized in a reaction are indicated in square brackets after the title of that reaction.

PART I: Reactions Involving 1,2-Dithiole-3-thiones

Acetylenic Esters

Dimethyl acetylenedicarboxylate, ethyl propiolate and ethyl phenylpropiolate were obtained from Aldrich Chemical Company. Ethyl tetrolate (105c) was obtained from J.T. Baker Chemical Company. These esters were stored in the cold prior to use.

Dibenzoylacetylene

Dibenzoylacetylene was prepared from *trans*-Dibenzoylethylene using the method of Lutz and Smithey[200], m.p. 109-111°C. *trans*-Dibenzoylethylene was obtained from Aldrich Chemical Company.

General Procedure for Separation of Reaction Mixtures

The work-up used in all the reactions described in Part I of the Experimental was the same. The following is a general description of the work-up.

After completion of reaction, the solvent was flash evaporated and the reaction mixture was separated by t.l.c., using multiple development of the plates. Where bands were not completely separated, each fraction was re-chromatographed using the same developing mixtures but with only a maximum of 50 mg. on each plate.

Also the methods used in identification of compounds that are isolated in these reactions which have previously been prepared, i.e., starting materials, or which have been characterized in a reaction described elsewhere in the Experimental will be indicated in square brackets after the compound. The methods used were either a comparison of i.r. spectra, n.m.r. spectra or m.p. with those of an authentic sample (or a combination of any of the three).

Section A: Reactions Involving 4,5-Diphenyl-1,2-dithiole-3-thione (27).

Preparation of 4,5-Diphenyl-1,2-dithiole-3-thione (27)

The thione 27 was prepared by reaction of α-methyl stilbene with sulfur[160] and was purified by column chromatography using petroleum (pet.) ether : benzene (1/1) as the eluent. The thione 27 was then recrystallized from ethanol, m.p. = 159-161°C. [Lit. m.p. = 160°C][160].

Reaction of 4,5-Diphenyl-1,2-dithiole-3-thione (27) with Dimethyl Acetylenedicarboxylate to form the Mono-adduct [93a].

The thione 27 (381 mg., 1.33 m.mole) and the acetylenic ester (185 mg., 1.33 m.mole) in benzene (60 ml.) were stirred together at room temperature for 18h. The solution quickly turned from reddish-orange to dark green. The solution was evaporated to give a dark-green solid which was separated by t.l.c. (petroleum (pet.) ether/ C_6H_6 = 1/3, C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1). Three bands were found. The brown main band (b) had the medium R_f value.

a) The orange band (highest R_f value) was found to be unchanged thione 27 [I.R., M.P.], (80 mg.).

Mono-adduct 93a

b) Elution of the brown main band gave a dark-green powder (370 mg., 66%) which on recrystallization from ethanol gave the product 93a as dark-green needles, m.p. = 158.5-160.5°C.

Infrared spectrum [Fig. II]: absorptions (cm^{-1}) at 1725, 1750 (ester C=O).

Nuclear Magnetic Resonance Spectrum [Fig. XXXVIII]: see Table III.

Analysis:

Calculated for $C_{21}H_{16}O_4S_3$: C, 58.88; H, 3.74; S, 22.43;

Found: C, 58.84; H, 3.72; S, 22.24.

c) Elution of the third band (yellow) gave the di-adduct 94a [I.R., N.M.R.], (60 mg., 16%). Characterization of this compound is described below.

Reaction of 4,5-Dipheny-1,2-dithiole-3-thione (27) with Dimethyl Acetylenedicarboxylate to form the Di-adduct [94a]

The thione 27 (285 mg., 1 m.mole) and the ester (282 mg., 2 m.mole) in benzene (30 ml.) were refluxed together for 15h. The reddish-brown product obtained on evaporation was separated by t.l.c. (C_6,H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1, $CHCl_3$). Four main bands were found along with one other which contained a trace of material (∿1-2 mg.). The major band had the second lowest R_f value.

a) The orange band (highest R_f value) on elution was found to be the unchanged thione 27 [I.R., M.P.], (50 mg.).

b) The brown band (second highest R_f value) on elution was found to be the mono-adduct [I.R., N.M.R.], (40 mg., 9%).

Di-adduct 94a

c) The yellow major band on elution gave a light yellow powder which on recrystallization from ethanol gave the product 94a as yellow prisms, m.p. = 111-113°C.

Infrared spectrum [Fig. III]: absorptions (cm^{-1}) at 1700, 1725, 1740 (ester C=O).

Nuclear Magnetic Resonance Spectrum [Fig. XXXIX]: see Table IV.

Analysis:

Calculated for $C_{27}H_{22}O_8S_3$: C, 56.84; H, 3.86; S, 16.86;

Found: C, 56.96; H, 3.75; S, 16.80.

d) The purple fourth band on elution gave a violet oil (10 mg.) which crystallized from ethanol, m.p. 161-163°C.

Infrared spectrum [Fig. IV]: absorptions (cm^{-1}) at 1700-1740 (unresolved, ester, C=O).

Mass spectrum: M^+/e (% of base peak last twelve peaks are given, >100 peaks are evident in the spectrum) 518(40%), 487(13%), 460(<4%), 455(13%), 430(<1%), 429(10%), 428(<1%), 427(11%), 415(<3%), 403(<1%), 396(20%), 395(100%, base peak).

Reaction of Dimethyl 2-(α-Phenylthiophenacylidene-1,3-dithiole-4,5-dicarboxylate (93a) with 4,5-Diphenyl-1,2-dithiole-3-thione (27) and Dimethyl Acetylenedicarboxylate

The mono-adduct 93a (85 mg.,0.2 m.mole), the thione 27 (28 mg., 0.1 m.mole) and the ester (28 mg., 0.2 m.mole) in benzene were refluxed together for 15h. Separation of the reddish-orange paste, remaining after evaporation of the solvent, by t.l.c. ($CHCl_3$, MeOH/$CHCl_3$ = 1/99) gave three bands. These were found to be the unchanged thione 27 [I.R., M.P.] (23 mg.), the di-adduct 94a [I.R., N.M.R.] (95 mg., 84%) and the violet powder, described in the previous experiment [I.R.] (∿4 mg.).

The mono-adduct 93a (43 mg., 0.1 m.mole) in benzene (10 ml.) was heated for 15h. and examination of the reaction mixture by t.l.c. (MeOH/$CHCl_3$ = 1/99) revealed that the mono-adduct 93a was unchanged.

The mono-adduct 93a (43 mg., 0.1 m.mole) and the thione 27 (14 mg., 0.05 m.mole) were heated in boiling benzene for 15h. and examination

of the reaction mixture by t.l.c. ($MeOH/CHCl_3$ = 1/99) revealed that both the mono-adduct 93a and the thione 27 were unchanged.

The mono-adduct 93a (43 mg., 0.1 m.mole) and dimethyl acetylene-dicarboxylate (14 mg., 0.1 m.mole) in benzene (10 ml.) were refluxed together for 15h. The di-adduct 94a [I.R., N.M.R.] (50 mg., 88%) was recovered by t.l.c. separation ($CH_3OH/CHCl_3$ = 1/99).

Treatment of Dimethyl 2-(α-Phenylthiophenacylidene)-1,3-dithiole-4,5-dicarboxylate (93a) with Phosphorus Pentasulfide

The mono-adduct 93a (120 mg., 0.28 m.mole) and phosphorus pentasulfide (80 mg.) in tetralin (10 ml.) were refluxed for 1h. After cooling, the brown solution was poured into benzene (30 ml.). The black solid, remaining in the flask was washed with benzene (20 ml.). The combined benzene extracts were washed with water (20 ml.), 10% sodium hydroxide (20 ml.), water (20 ml.), dried (Na_2SO_4) and the solvent was removed under reduced pressure. The black paste remaining was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3). One main band was found and on elution gave 4,5-diphenyl-1,2-dithiole-3-thione (27) [I.R., M.P.], (40 mg., 50%). Four other bands were found to contain trace amounts of material (∿1-5 mg.).

Reaction of Dimethyl 2-(α-Phenylthiophenacylidene)-1,3-dithiole-4,5-dicarboxylate (93a) with Ethyl Propiolate [94b]

The mono-adduct 93a (151 mg., 0.35 m.mole) and ethyl propiolate (51 mg., 0.52 m.mole) in benzene (40 ml.) were refluxed together for 4 days. Five bands were obtained from a t.l.c. separation (C_6H_6, $CHCl_3/C_6H_6$ = 1/3, $CHCl_3/C_6H_6$ = 1/1). The band with the highest R_f value on elution gave unchanged mono-adduct 93a [I.R.] (10 mg.).

Di-adduct 94b

The major band (yellow, 2nd lowest R_f value) on elution gave a yellow powder (115 mg., 62%) which on recrystallization from ethanol gave the mixed di-adduct 94b as yellow needles, m.p. = 148-50°C.

Infrared spectrum [Fig. V]: absorptions (cm^{-1}) at 1680, 1700, 1725 (ester, C=O)

N.M.R. Spectrum [Fig. XL]: see Table IV

Analysis:

Calculated for $C_{26}H_{22}O_6S_3$: C, 59.32; H, 4.18; S, 18.25;

Found: C, 59.12; H, 4.04; S, 18.17.

The other three bands were found to contain 3-6 mg. of material each.

Reaction of 4,5-Diphenyl-1,2-dithiole-3-thione (27) with Ethyl Propiolate [93a'] and [94a']

The thione 27 (213 mg., 0.75 m.mole) and the ester (74 mg., 0.75 m.mole) in benzene (50 ml.) were refluxed 24h. After evaporation, the crude mixture was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1). Of the eight bands found, five contained trace amounts of material.

a) The band with the highest R_f value on elution gave unchanged thione 27 [I.R., M.P.] (4o mg.).

b) Mono-adduct 93a'

The band with the third highest R_f value on elution gave a brown pasty solid (77 mg., 29%) which on recrystallization from ethanol:benzene (1/1) gave the mono-adduct 93a' as greenish-brown needles, m.p. = 175-178°C.

Infrared Spectrum [Fig. VI]; absorption (cm^{-1}) at 1740 (ester, C=O).

N.M.R. Spectrum [Fig. I]: see Table III.

Analysis:

Calculated for $C_{20}H_{16}O_2S_3$: C, 62.50; H, 4.17; S, 25.00;

Found: C, 62.38; H, 4.33; S, 24.90.

c) Di-adduct 94a'

The band with the third lowest R_f value on elution gave a yellow powder (127 mg., 70%) which on recrystillization from ethanol gave the di-adduct 94a' (100% theoretical yield = 181 mg.) as yellow prisms, m.p. = 149-151°C.

Infrared Spectrum [Fig. VII]: absorptions (cm^{-1}) at 1710, 1730 (ester, C=O).

N.M.R. Spectrum [Fig. XLI]: see Table IV.

Analysis:

Calculated for $C_{25}H_{22}O_4S_3$: C, 62.24; H, 4.56; S, 19.92;

Found: C, 61.98; H, 4.61; S, 19.83.

When the thione 27 (286 mg., 1.0 m.mole) and the ester (98 mg., 1.0 m.mole) in benzene (40 ml.) were stirred together at room temperature for 24h. the colour of the solution slowly darkened. After removal of the solvent and separation of the resulting dark orange residue by t.l.c. ($CHCl_3/C_6H_6$ = 1/1) three bands were found. They were found to be unchanged thione 27 [M.P.] (340 mg.), the mono-adduct 93a' [I.R., N.M.R.] (35 mg., 9%) and the di-adduct 94a' [I.R.] (∿5 mg., 3%).

Preparation of the 2-(α-Phenylphenacylidene)-1,3-dithiole [189c']

A hot solution of excess mecuric oxide (red) in glacial acetic acid (20 ml.) was added to the mono-adduct 93a' (149 mg., 0.39 m.mole). The dark colour of the mono-adduct 93a' disappeared almost instantaneously The resulting mixture was diluted with water (100 ml.) and extracted with benzene (3 X 50 ml.). The yellow oil remaining after removal of the benzene crystallized after one day (116 mg., 85%). Recrystallization from ethanol:benzene (1/1) gave the ketone 189c' as yellow plates, m.p. = 170-172°C.

Infrared spectrum [Fig. VIII]: absorptions (cm^{-1}) at 1725 (ester, C=O), 1590 (ketone, C=O).

N.M.R. Spectrum [Fig. XLII]: see Table III.

Analysis:

Calculated for $C_{20}H_{16}O_3S_2$: C, 65.21; H, 4.35; S, 17.39;

Found: C, 65.18; H, 4.79; S, 17.41.

High Temperature Nuclear Magnetic Resonance Study of Ethyl 2-(α-Phenylthiophenacylidene)-1,3-dithiole-4 or 5-carboxylate (93a') and Ethyl 2-(α-Phenylphenacylidene)-1,3-dithiole-4 or 5-carboxylate (189c')

The mono-adduct 93a' and the oxygen analogue 189c' in saturated deuteriochloroform solution were examined at temperatures between 40°C and 95°C. No change in the spectrum was observed. In the case of the mono-adduct 93a', a higher resolution spectrum was obtained [Fig. XLIII].

Reaction of 4,5-Diphenyl-1,2-dithiole-3-thione (27) with Ethyl Phenyl-Propiolate [93b']

The thione 27 (325 mg., 1.13 m.mole) and the ester (195 mg., 1.12 m.moles) in xylene (25 ml.) were refluxed for 24h. The solvent was removed under reduced pressure, and the residue was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1). Two main bands were found. The band with the highest R_f value was found to be the thione 27 [I.R., M.P.] (85 mg.). The other band on elution gave a black powder (287 mg., 56%) which on recrystallization from ethanol gave the mono-adduct 93b' as greenish-black plates, m.p. = 183-185°C.

Infrared spectrum [Fig. IX]: absorption (cm^{-1}) at 1725 (ester, C=O).

N.M.R. Spectrum [Fig. XLIV]: see Table III.

Analysis:

Calculated for $C_{26}H_{20}O_2S_3$: C, 67.82; H, 4.35; S, 20.87;

Found: C, 67.62; H, 4.30; S, 20,85.

When the reaction was carried out in boiling benzene for 2 days, a small yield of the mono-adduct 93b' (18%) was obtained.

When the reaction of the thione 27 (143 mg., 0.5 m.mole) and two equivalents of ethyl phenylpropiolate (174 mg., 1.0 m.mole) was carried out in boiling xylene (10 ml.) for 24h., again only the mono-adduct 93b' (168 mg., 53%) and the thione 27 (25 mg.) were obtained in sizeable amounts.

Attempted Reaction of the Mono-adduct 93b' with Ethyl Phenylpropiolate

The mono-adduct 93b' (200 mg., 0.435 m.mole) and the ester (76 mg., 0.435 m.mole) in xylene (15 ml.) were refluxed for 24h. No colour change was observed and on separation of the crude mixture by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3), the starting materials were recovered.

Reaction of 4,5-Diphenyl-1,2-dithiole-3-thione (27) with Dibenzoylacetylene [93f] and [94d]

The thione 27 (171 mg., 0.60 m.mole) and the acetylene (139 mg., 0.60 m.mole) in benzene (10 ml.) were stirred together at room temperature for 2h. The solution rapidly became dark. After the solvent was removed, the residue was separated by t.l.c. ($CHCl_3/C_6H_6$ = 1/3, 1/1). Three bands were found. The band with the highest R_f value on elution gave the thione 27 [I.R., M.P.] (10 mg.).

2-(α-Phenylthiophenacylidene)-4,5-dibenzoyl-1,3-dithiole (93f)

The band with the second highest R_f value on elution gave a brown powder (254 mg., 83%) which on recrystallization from nitromethane gave the mono-adduct 93f as greenish-brown plates, m.p. = 209-210°C.

Infrared spectrum [Fig. X]: absorptions (cm^{-1}) at 1680, 1660 (ketone C=O).

N.M.R. Spectrum: 2.09-2.40τ (20 H, m.).

Analysis:

Calculated for $C_{31}H_{20}O_2S_3$: C, 70.98; H, 3.92; S, 18.82;

Found: C, 70.76; H, 3.96; S, 18.75.

Di-adduct 94d

The last band on elution gave a yellow powder (35 mg., 13%) which on recrystallization from ethanol gave the di-adduct 94d as yellow needles, m.p. = 106-108°C.

Infrared spectrum [Fig. XI]: absorptions (cm^{-1}) at 1660, broad, 1645, shoulder, (ketone, C=O).

N.M.R. Spectrum: 1.93-1.41τ (30 H, m.).

Analysis:

Calculated for $C_{47}H_{30}O_4S_3$: C, 74.80; H, 3.98; S, 12.73;

Found: C, 75.03; H, 3.88; S, 12.68.

When the reaction was carried out in boiling benzene with two equivalents of the acetylene, only the di-adduct 94d was found, i.e., the thione 27 (179 mg., 0.62 m.mole) and the acetylene (300 mg., 1.28 m.mole) in benzene (20 ml.) were refluxed together for 9h. After evaporation of the solvent the yellow powder, remaining, was recrystallized from ethanol, m.p. 106-108°C (353 mg., 76%). The mother liquor did not

contain any mono-adduct 93f as indicated by t.l.c. examination of the residue of the mother liquor.

Attempted Sulfurization of 2-(α-Phenylthiophenacylidene)-4,5-dibenzoyl-1,3-dithiole (93f)

Two sulfurizations were attempted by the treatment of the mono-adduct 93f with phosphorus pentasulfide in boiling pyridine. In both cases, two main fractions were found and identified as 4,5-diphenyl-1,2-dithiole-3-thione (27) [I.R., M.P.] and unchanged mono-adduct 93f [I.R.]. Many fractions in trace amounts were also found. The procedure used in both cases is described below.

The thione 27 (105 mg., 0.21 m.mole) and phosphorus pentasulfide (43 mg.) in pyridine (1.5 ml.) were refluxed for 3h. The mixture was thrown into water (20 ml.) and extracted with benzene (4 X 10 ml.). The dried benzene extracts (Na_2SO_4) were evaporated, and the residue was separated by t.l.c. (pet. ether/C_6H_6 = 1/1, 1/3 and C_6H_6). The thione 27 (30 mg., 50%) and the mono-adduct 93f (25 mg.) were recovered.

When the reaction was allowed to proceed for 5h. using the same amount of starting material, the yield of the thione 27 increased (36 mg., 60%) while the amount of the mono-adduct 93f, recovered, decreased (15 mg.).

Attempted Reaction of 4,5-Diphenyl-1,2-dithiole-3-thione (27) with *trans*-Dibenzoylethylene

The thione 27 (286 mg., 1.0 m.mole) and the olefin (230 mg., 1.0 m.mole) in benzene (30 ml.) were refluxed for 4 days. The evaporated mixture was examined by t.l.c. Only the starting materials were recovered.

Similar results were obtained when equimolar quantities of the thione 27 and the olefin in xylene were refluxed for 2 days.

Section B: Reactions Involving 5-Phenyl-1,2-dithiole-3-thione (50b)

Preparation of 5-Phenyl-1,2-dithiole-3-thione (50b)

The thione 50b was prepared by the method of Klingsberg[3] and was further purified by column chromatography using pet. ether: benzene (1/1) as eluent. The thione 50b was recrystallized from ethanol as orange needles, m.p. = 123-125°C. [Lit. m.p. = 125-127°C][3]

Reaction of 5-Phenyl-1,2-dithiole-3-thione (50b) with Dimethyl Acetylene-dicarboxylate to form Dimethyl 2-Thiophenacylidene-1,3-dithiole-4,5-dicarboxylate (93c)

The thione 50b (210 mg., 1.0 m.mole) and the ester (142 mg., 1.0 m.mole) in benzene (40 ml.) were stirred together for 24h. After evaporation of solvent, the crude mono-adduct 93c was purified by t.l.c. and then recrystallized from ethanol:benzene (1/1), dark-green needles, m.p. = 149-151°C (264 mg., 74%). [Lit. m.p. = 152-153°C][154]

Infrared spectrum: absorptions (cm^{-1}) at 1740, 1710 (ester, C=O)

N.M.R. Spectra ($CDCl_3$ and C_6D_6): see Table III, [Fig. ($CDCl_3$) XLV], [Fig. (C_6D_6) XLVI]

Attempted Reaction of Dimethyl 2-Thiophenacylidene-1,3-dithiole-4,5-dicarboxylate (93c) with Ethyl Phenylpropiolate

The mono-adduct 93c (176 mg., 0.5 m.mole) and the ester (87 mg., 0.5 m.mole) in xylene (10 ml.) were refluxed for 10 h. After removal of the solvent under reduced pressure, the starting materials were recovered.

Reaction of 5-Phenyl-1,2-dithiole-3-thione (50b) with Ethyl Phenylpropiolate to form Ethyl 2-Thiophenacylidene-4 or 5-phenyl-1,3-dithiole-4 or 5-dicarboxylate 93c')

The thione 50b (210 mg., 1.0 m.mole) and the ester (174 mg., 1.0 m.mole) in xylene (20 ml.) were refluxed for 10 h. After the solvent was removed under reduced pressure, the black residue was purified by t.l.c. and then recrystallized from ethanol:benzene (1/1) to give greenish-black needles m.p. = 121-123°C (230 mg., 60%). [Known m.p. = 123-125°C][162]

Infrared spectrum: absorption (cm^{-1}) at 1690 (ester, C=O)

N.M.R. Spectrum [Fig. XLVII]: see Table III

When the thione 50b and two equivalents of the ester in xylene were heated for 2 days, similar results were obtained.

Attempted Reaction of the Mono-adduct 93c' with Ethyl Phenylpropiolate

The mono-adduct 93c' (192 mg., 0.5 m.mole) and the ester (87 mg., 0.5 m.mole) in xylene (20 ml.) were refluxed for 24h. No colour change was observed. After removal of the solvent under reduced pressure, the residue was examined by t.l.c. The starting materials were found.

Reaction of 5-Phenyl-1,2-dithiole-3-thione (50b) with Dibenzoylacetylene [93e]

The thione 50b (1.04 g., 5.0 m.mole) and the acetylene (1.34 g., 5.7 m.mole) in benzene (50 ml.) were stirred together for 18h. The solution rapidly turned dark brown. After the solvent was removed, the crude mono-adduct 93e was recrystallized from nitromethane as a brown powder, m.p. = 141-143°C (1.78 g., 80%).

Infrared spectrum [Fig. XII]: absorptions (cm^{-1}) at 1660, shoulder, 1645 (ketone, C=O)

N.M.R. Spectrum: 2.81 - 2.41τ (15H, m) and 1.71τ (1H,s)

Analysis:

Calculated for $C_{25}H_{16}O_2S_3$: C, 67.57; H, 3.60; S, 21.62;

Found: C, 67.51; H, 3.48; S, 21.57.

The residue from the nitromethane mother liquor was separated by t.l.c. ($CHCl_3/C_6H_6$ = 1/3, 1/1). Three bands were found. The band with the highest R_f value was found to be the thione 50b [I.R., M.P.], (100 mg.). The band with the second highest R_f value was found to be the mono-adduct 93e [I.R.] (50 mg.). The last band on elution gave an orange powder which was found to be the di-adduct 94c [I.R.] (50 mg.). The preparation of this di-adduct 94c is described below.

Reaction of 5-Phenyl-1,2-dithiole-3-thione with Two Equivalents of Dibenzoylacetylene to form 4,5-Dibenzoyl-1,3-dithiole-2-spiro-4-(2-phenyl-5,6-dibenzoylthiopyran) [(94c)]

The thione 50b (520 mg., 2.5 m.mole) and the acetylene (1.34 g., 5.7 m.mole) in benzene (30 ml.) were refluxed together for 9h. The orange solution was evaporated under reduced pressure and the crude product recrystallized from nitromethane as an orange powder, m.p. = 191-193°C (1.6 g., 95%)

Infrared Spectrum [Fig. XIII]: absorption (cm^{-1}) at 1665, broad, (ketone C=O)

N.M.R. Spectrum: 2.99 - 2.16τ (25 H, m) and 3.12τ (1H,)

Analysis:

Calculated for $C_{41}H_{26}O_4S_3$: C, 72.57; H, 3.83; S, 14.22;

Found: C, 72.47; H, 3.93; S, 14.07.

Attempted Sulfurizations of 2-Thiophenacylidene-4,5-dibenzoyl-1,3-dithiole (93e)

The sulfurizations were attempted by treatment of the mono-adduct 93e with phosphorus pentasulfide (freshly recrystallized from carbon disulfide) in a variety of solvents. In all cases, the main and only identifiable product was 5-phenyl-1,2-dithiole-3-thione (50b) in 18-33% yields. Many other fractions in trace amounts were also found. The solvents used were pyridine, benzene, xylene and carbon disulfide (both commercial and anhydrous). Reaction times varied from 1-3h. When carbon disulfide was used as the solvent, the thione 50b (18%) and the mono-adduct 93e (30% recovery) were isolated. A typical reaction is outlined below.

The mono-adduct 93e (222 mg., 0.5 m.mole) and phosphorus pentasulfide (120 mg.) in pyridine (5 ml.) were refluxed for 1.5h. The mixture was diluted with water (25 ml.) and extracted with benzene (3 X 20 ml.). The dried benzene extracts (Na_2SO_4) were evaporated, and the residue was separated by t.l.c. (pet. ether/C_6H_6 = 1/3, C_6H_6). The thione 50b [I.R., M.P.] was obtained (35 mg., 33%).

Sulfurization of 4,5-Dibenzoyl-1,3-dithiole-2-spiro-4-2-phenyl-5,6-dibenzoylthiopyran) (94c)[268]

The di-adduct 94c (240 mg., 0.35 m.moles) and phosphorus pentasulfide (160 mg.) in pyridine (7 ml.) were refluxed for 3h. The pyridine was removed under reduced pressure and the residue was separated by t.l.c. (pet. ether/C_6H_6 = 1/1, 1/3, C_6H_6). The sulfurized di-adduct 268 was recrystallized from ethanol:benzene (2/1) as brown felted needles, m.p. = 219-221°C (80 mg., 33%).

Infrared spectrum [Fig. XIV]: absence of carbonyl absorptions.

Analysis:

Calculated for $C_{41}H_{26}S_5$: C, 72.57; H, 3.83; S, 23.62;

Found: C, 72.92; H, 3.66; S, 23.69.

Attempted Reaction of 5-Phenyl-1,2-dithiole-3-thione (50b) with *trans*-Dibenzoylethylene

The thione 50b (210 mg., 1.0 m.mole) and the olefin (230 mg., 1.0 m.mole) in benzene (25 ml.) were refluxed for 3 days. After removal of the solvent, the residue was separated by t.l.c. Only the starting materials were recovered.

Similar results were obtained when equimolar quantities of the thione 50b and the olefin in xylene were refluxed for 2 days.

Section C: Reactions Involving 1,2-Dithiole-3-thione (58)

The thials 198a and b, isolated, were unstable and decomposed on standing or in solution, as indicated by a t.l.c. examination of the thials. No streaking of the thial bands on thin layer chromatograms was observed, thus this decomposition does not occur while the thials are being separated by t.l.c., but the possibility that some decomposition occurs on the t.l.c. plates prior to developing cannot be excluded. The thials 198a and b, employed in further reactions, were used immediately after separation by t.l.c. In the separation of the reaction mixtures by t.l.c., discussed in this Section, a considerable amount of orange material (up to 30% of the starting materials) could not be separated using benzene:chloroform mixtures as the developing medium, but was partially separated using a methanol:chloroform mixture (1/19), and was found to contain many fractions. In all the experiments, involving the application of heat (described in this Section), sulfur was found in varying amounts on the chromatograms at the solvent front.

The infrared spectra of the thials 198a and b and of the oils or glasses, described in this Section were obtained using methylene chloride solutions of the samples on a Perkin-Elmer model 700 i.r. spectrophotometer (for the thial 198b, the i.r. spectrum was obtained on a Perkin-Elmer 137). The methylene chloride solutions of the thials 198a and b were obtained by eluting the silica gel bands containing these thials with methylene chloride.

Preparation of 1,2-Dithiole-3-thione (58)

The thione 58 was prepared by the method of Wessely and Siegel[67]

and was purified by t.l.c. just prior to use, m.p. = 77-79°C. [Lit. m.p. = 79-81°C][67]

N.M.R. Spectrum: 4.32τ(1H, d, J = 6 Hz.), 3.20τ(1H, d, J = 6 Hz.)

Reaction of 1,2-Dithiole-3-thione (58) with Dimethyl Acetylenedicarboxylate to form Dimethyl 2-Thioformylmethylene-1,3-dithiole-4,5-dicarboxylate [(198a)]

The thione 58 (134 mg., 1 m.mole) and the ester (142 mg., 1 m.mole) in benzene (30 ml.) were stirred at room temperature for 3h. The solution rapidly became dark. The solvent was removed in the cold under reduced pressure and the resulting residue was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_c$ = 1/3, 1/1). Of the five bands found, two contained trace amounts. The band with the highest R_f value, on elution, gave unchanged thione 58 [I.R.], (14 mg.), and the band with the second lowest R_f value, on elution gave the butene 200a as a purple solid [I.R.], (∿5 mg.). The characterization of this butene 200a is described below.

Thial 198a

The band with the second highest R_f value, on elution, gave the thial 198a as a brown paste (209 mg., 76%) which could not be purified further.

Infrared Spectrum [Fig. XV]: absorption (cm^{-1}) at 1725 (broad, ester, C=O).

N.M.R. Spectrum [Fig. XLVIII]: see Table III.

Reaction of 1,2-Dithiole-3-thione (58) with Dimethyl Acetylenedicarboxylate to form Tetramethyl 1,4-Butenediylidene-2,2'-bis(1,3-dithiole-4,5-dicarboxylate [(200a)]

The thione 58 (134 mg., 1 m.mole) and the ester (142 mg., 1 m.mole) in benzene (30 ml.) were refluxed for 18h. After the solvent was removed, the reddish-orange oil was separated by t.l.c. ($CHCl_3/C_6H_6$ = 1, 3, 1/1, 3/1, and $CHCl_3$). Of the five bands found, two were found to contain trace amounts.

a) The band with the highest R_f value, on elution, gave unchanged thione [I.R.], (16 mg.).

Tetramethyl 1,4-Butenediylidene-2,2'-bis(1,3-dithiole-4,5-dicarboxylate (200a)

b) The band with the third highest R_f value, on elution, gave a purple solid (90 mg., 41%) which on recrystallization from nitromethane gave the butene 200a as purple matted needles, m.p. = 195-197°C.

Infrared spectrum [Fig. XVI]: absorptions (cm^{-1}) in the carbonyl region were not properly resolved. They were resolved when the i.r. spectrum was performed on a Perkin-Elmer model 337 i.r. spectrophotometer: 1740, 1725, 1710 (sharp, ester, C=O).

N.M.R. Spectra were taken in $CDCl_3$ [Fig. XLIX] and in C_6D_6 [Fig. L] as solvent. The n.m.r. data is listed in Table V.

Analysis:

Calculated for $C_{18}H_{16}O_8S_4$: C, 44.27; H, 3.28; S, 26.23;

Found: C, 44.54; H, 3.06; S, 26.33.

c) The band with the second lowest R_f value, on elution, gave an orange oil which on further separation by t.l.c. ($CHCl_3/C_6H_6$ = 1/1, 3/1, $CHCl_3$, $CH_3OH/CHCl_3$ = 2/98) gave three bands. Two of these bands gave orange glasses 'a' and 'b' (each 30 mg.) and the third band gave a yellow oil in trace amounts. These three fractions had similar R_f

values ('a' > 'b' > yellow oil).

The infrared spectrum of glass 'a' gave ester carbonyl peaks at 1740 cm^{-1} (strong, broad) and at 1700 cm^{-1} (medium, shoulder), and the n.m.r. spectrum consisted of two singlets 4.72τ and 6.17τ in the ratio of 1/12.

The infrared spectrum of glass 'b' gave ester carbonyl peaks at 1750 cm^{-1} (strong, broad) and at 1700 cm^{-1} (weak) and the n.m.r. spectrum showed absorptions at 3.5τ, 4.28τ, 4.42τ, 4.70τ, 6.17τ and 6.22τ in the ratio of 6/1/1/8/21/21.

Similar results were obtained when the thione was allowed to react with 2 equivalents of the acetylenic ester.

Conversion of Dimethyl 2-Thioformylmethylene-1,3-dithiole-4,5-dicarboxylate (198a) into Tetramethyl 1,4-Butenediylidene-2,2'-bis (1,3-dithiole-4,5-dicarboxylate (200a)

The thial 198a (100 mg., 0.3 m.moles) in benzene (25 ml.) was refluxed for 24h. Separation of the resulting reddish-orange oil by t.l.c. ($CHCl_3/C_6H_6$ = 1/1, 3/1 and $CHCl_3$) gave one main band. Six other bands gave only traces of material. The main band (second highest R_f value), on elution, gave the butene 200a [I.R., N.M.R.], (35 mg., 40%).

Reaction of 1,2-Dithiole-3-thione (58) with Dibenzoylacetylene [198b] and [200b]

The thione 58 (134 mg., 1.0 m.mole) and the acetylene (234 mg., 1.0 m.mole) in benzene were stirred together for 2.5h. The solvent was removed in the cold under reduced pressure, and the residue was separated by t.l.c. ($CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1). Of the seven bands found, five gave traces of material.

a) The band with the highest R_f value, on elution, gave unchanged thione 58 [I.R.], (15 mg.).

Thial 198d

b) The band with the second highest R_f value, on elution, gave the thial 198b as a brown pasty solid, (273 mg., 74%).

Infrared spectrum [Fig. XVII]: absorption (cm^{-1}) at 1660 (broad, ketone C=O)

N.M.R. Spectrum [Fig. LI]: see Table III.

1,4-Butenediylidene-2,2'-bis(4,5-dibenzoyl-1,3-dithiole) (200b)

A repeat of the above reaction for 18h in boiling benzene, using identical isolation procedures gave the thial 198b (15 mg., 4%) and a dark solid (115 mg., 38%) which on recrystallization from nitromethane gave the butene 200b as dark green plates, m.p. = 203-205°C.

Infrared spectrum [Fig. XVIII]: absorptions (cm^{-1}) at 1630, 1655 (strong, ketone, C=O)

N.M.R. Spectrum [Fig. LII]: see Table V.

Analysis:

Calculated for $C_{38}H_{24}O_4S_4$: C, 67.86; H, 3.57; S, 19.04;

Found: C, 68.08; H, 3.67; S, 18.97.

Ten other bands were also separated, but gave only trace amount of products. The thial band had the second highest R_f value while the butene band had the fourth highest R_f value.

Similar results were obtained when the thione 58 was treated with two equivalents of the acetylene.

Conversion of 4,5-Dibenzoyl-2-thioformylmethylene-1,3-dithiole (198b) into 1,4-Butenediylidene-2,2'-bis(4,5-dibenzoyl-1,3-dithiole) (200b)

The thial 198b (150 mg., 0.24 m.mole) in benzene (30 ml.) was

refluxed for 18h. Work up of the mixture using the procedures outlined in the previous experiment gave the butene 200b (53 mg., 43%) and ten other minor fractions. The butene band had the third highest R_f value.

Reaction of 4,5-Dibenzoyl-2-thioformylmethylene-1,3-dithiole (198b) with Dimethyl Acetylenedicarboxylate

The thial 198b (20 mg., 0.055 m.mole) and the ester 7.7 mg., 0.055 m.mole) in benzene (5 ml.) were refluxed for 3h. Work up of the mixture using the procedure outlined in the previous experiment gave the butene 200b (∿6 mg., 33%), unchanged thial (∿4 mg.) and an orange glass (∿10 mg.) along with five other fractions.

The i.r. spectrum of the orange glass (fourth highest R_f value) showed both ester carbonyl absorptions (1735, 1715 cm^{-1}) and a ketone carbonyl absorption (1660 cm^{-1}). This glass could possibly be a di-adduct of the type 199.

Section D: Reactions Involving 4-Phenyl-1,2-dithiole-3-thione (164a)

The thials 198c and d, when isolated, were unstable, but not to the same extent as the thials 198a and b, described in the previous Section. No streaking of the thial bands on thin layer chromatograms was observed, thus decomposition of the thials does not occur while they are being separated by t.l.c., but the possibility that some decomposition occurs on the t.l.c. plates prior to developing cannot be excluded. The thials 198c and d which were employed in further reactions were used immediately after separation by t.l.c. In all the experiments, involving the application of heat, sulfur was found in varying amounts on the chromatograms at the solvent front.

The infrared spectra of the thials 198c and d, and of the oils or glasses, described in this Section were obtained using methylene chloride solutions of the samples on a Perkin-Elmer model 700 i.r. spectrophotometer. The benzene used in these experiments was "Analar", analytical reagent grade benzene, supplied by the British Drug Houses Ltd.

Preparation of 4-Phenyl-1,2-dithiole-3-thione (164a)

The thione 164a was prepared using the method of Fields[36] and was purified by column chromatography using benzene:pet. ether (1/1) as eluent and stored in the dark, prior to use, m.p. = 119-121°C. [Lit. m.p. = 122°C][36]

Reaction of 4-Phenyl-1,2-dithiole-3-thione (164a) with Dimethyl Acetylenedicarboxylate [198c]

The thione 164a (210 mg., 1 m.mole) and the ester (142 mg.,

1 m.mole) in benzene (30 ml.) were stirred together at room temperature for 1.5h. After removal of the solvent, the brown paste was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3). Three bands were found.

Thial 198c

The main band (second highest R_f value) on elution, gave the thial 198c as a brown pasty solid (300 mg., 85%).

Infrared spectrum [Fig. XIX]: absorption (cm^{-1}) at 1740 (broad, ester, C=O)

N.M.R. Spectrum [Fig. LIII]: see Table III.

The band with the highest R_f value, on elution, gave unchanged thione 164a [I.R.], (15 mg.).

The other band, on elution, gave the aldehyde 201a [I.R.] (∿3 mg.).

The characterization of this aldehyde 201a will be described later in this Section.

Conversion of Dimethyl α-Phenylthioformylmethylene-1,3-dithiole-4,5-dicarboxylate (198c) into Tetramethyl 1,4-Diphenyl-1,4-butenediylidene-2,2'-bis(1,3-dithiole-4,5-dicarboxylate [(200c)]

The thial 198c (230 mg., 0.65 m.mole) in benzene (30 ml.) was refluxed for 24h. After removal of solvent, the residue was separated by t.l.c. ($CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1 and $CHCl_3$). Three bands were found.

Tetramethyl 1,4-Diphenyl-1,4-butenediylidene-2,2'-bis (1,3-dithiole-4,5-dicarboxylate) (200c)

The band with the highest R_f value, on elution, gave unchanged thial 198c [I.R., N.M.R.], (105 mg., 43%). The band with the second highest R_f value, on elution, gave the aldehyde 201a [I.R.], (∿8 mg., 3%).

The other band, on elution, gave a purple solid (92 mg., 43%) which on recrystallization from nitromethane gave the butene 200c as reddish-purple needles, m.p. = 212-216°C.

Infrared spectrum [Fig. XX]: absorptions (cm^{-1}) at 1750, 1725 (ester, C=O)

N.M.R. Spectrum [Fig. LIV]: see Table V.

Analysis:

Calculated for $C_{30}H_{24}O_8S_4$: C, 56.25; H, 3.75; S, 20.00;

Found: C, 56.17; H, 3.75; S, 19.82.

When the reaction was performed in boiling xylene, the yield was raised to 80%. A small amount of the thial 198c (∿5 mg.) and of the aldehyde 201a (∿5 mg.) was also obtained. Similar results were obtained when the reaction was carried out in anhydrous benzene or anhydrous xylene under dry nitrogen.

Preparation of Dimethyl α-Phenylformylmethylene-1,3-dithiole-4,5-dicarboxylate [(201a)]

A hot solution of excess mecuric acetate in acetic acid (10 ml.) was added to the thial 198c (120 mg., 0.34 m.mole). The dark colour of the thial disappeared almost instantaneously. The solution was diluted with water (30 ml.), and the aqueous solution was extracted with benzene (3 X 30 ml.). The residue obtained from the benzene extracts was purified by t.l.c. The orange oil, obtained, crystallized in two days (83 mg., 80%) and an recrystillization from ethanol:benzene (1/1) gave the aldehyde 201a as orange prisms, m.p. = 127-129°C.

Infrared spectrum [Fig. XXI]: absorptions (cm^{-1}) at 1770, 1750 (ester, C=O) and 1590 (aldehyde, C=O)

N.M.R. Spectrum [Fig. LV]: see Table III

Analysis:

Calculated for $C_{15}H_{12}O_5S_2$: C, 53.53; H, 3.57; S, 19.04;

Found: C, 53.61; H, 3.56; S, 19.21.

Reaction of Dimethyl α-Phenylthioformylmethylene-1,3-dithiole-4,5-dicarboxylate (198c) with Dimethyl Acetylenedicarboxylate [199a]

The thial 198c (274 mg., 0.78 m.mole) and the ester (122 mg., 0.78 m.mole) in benzene were refluxed for 3h. After the solvent was removed, the orange glass was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1 and $CHCl_3$). Of the seven bands found, five contained trace amounts of material and the band with the highest R_f value was found to be unchanged thial 198c [I.R.] (10 mg.).

The main fraction (third highest R_f value) was rechromatographed using the same developing mixtures, but using only 30 mg./plate. This fraction was found to contain four bands of which two contained trace amounts of material. The band with the highest R_f value was found to contain the aldehyde 201a [I.R.](18 mg.).

Di-adduct 199a

The band with the second highest R_f value, on elution, gave the di-adduct 199a as an uncrystallizable orange glass (180 mg., 46%).

Infrared spectrum [Fig. XXII]: absorption (cm^{-1}) at 1720 (broad, ester, C=O)

N.M.R. Spectrum [Fig. VI]: see Table IV

Mass spectrum showed a parent ion at M^+/e 494, calculated 494. The base peak is at M^+/e 435 (loss of CO_2CH_3).

Attempted Reaction of Dimethyl α-Phenylthioformylmethylene-1,3-dithiole-4,5-dicarboxylate (198c) with Ethyl Phenylpropiolate

The thial 198c (176 mg., 0.5 m.mole) and the ester (87 mg., 0.5 m.mole) in benzene (30 ml.) were refluxed for 24h. The reddish-orange oil remaining after removal of solvent was separated by t.l.c. ($CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1 and $CHCl_3$). Of the more than eight bands found, only two could be identified. They were unchanged thial 198c and the butene 200c. N.m.r. examination of the other fractions indicated none with an ethyl group.

Irradiation of Dimethyl α-Phenylthioformylmethylene-1,3-dithiole-4,5-dicarboxylate (198c) with Visible Light and Ultraviolet Radiation

The thial 198c (106 mg., 0.30 m.mole) in benzene (4 ml.) (in a pyrex flask) was irradiated using a Hanovia Ultraviolet Quartz Lamp type 30620 for 24h. at room temperature. The dark colour slowly disappeared during irradiation. The yellow oil, remaining after removal of the solvent was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1 and $CHCl_3$). The main band, on elution, gave a yellow oil which crystallized on standing for 2 days (39 mg., 38%). The i.r. and n.m.r. spectra of this compound were identical with those of an authentic sample of the aldehyde 201a. Over ten other fractions in trace amounts were also present.

Similar results were obtained when the thial 198c was irradiated with the same source, but in a quartz flask.

Reaction of 4-Phenyl-1,2-dithiole-3-thione (164a) with Dibenzoylacetylene [198d] and [199b]

The thione 164a (420 mg., 2.0 m.mole) and the acetylene (464 mg.,

2.0 m.mole) in benzene (40 ml.) were stirred at room temperature for 2.5h. After removal of solvent, the brown paste was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1). Three bands were found. The band with highest R_f value, on elution, gave unchanged thione 164a [I.R., M.P.], (65 mg.).

Thial 198d

The band with the second highest R_f value, on elution, gave the thial 198d (658 mg., 71%) as a brown pasty solid.

Infrared spectrum [Fig. XXIII]: absorption (cm^{-1}) at 1655 (broad, ketone, C=O)

N.M.R. Spectrum [Fig. LVII]: see Table III

Di-adduct 199b

The other band, on elution, gave the di-adduct 199b (99 mg., 14%) as a yellow oil which crystallized from ethanol as a yellow powder, m.p. = 87-92°C.

Infrared spectrum [Fig. XXIV]: absorptions (cm^{-1}) at 1640, 1675 (ketone, C=O)

N.M.R. spectrum [Fig. LVIII]: see Table IV

Analysis:

Calculated for $C_{41}H_{26}O_4S_3$: C, 72.57; H, 3.83; S, 14.22;

Found: C, 72.47; H, 3.80; S, 14.06.

Conversion of 2-α-Phenylthioformylmethylene-4,5-dibenzoyl-1,3-dithiole (198d) into 1,4-Diphenyl-1,4-butenediylidene-2,2'-bis(4,5-dibenzoyl-1,3-dithiole) [(200d)]

The thial 198d (160 mg., 0.36 m.mole) in xylene (20 ml.) was refluxed for 24h. After removal of the solvent under reduced pressure,

the residue was separated by t.l.c.($CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1 and $CHCl_3$). Of the four bands found, three could be identified. The band with the highest R_f value, on elution, gave unchanged thial 198d [I.R.], (17 mg.).

1,4-Diphenyl-1,4-butenediylidene-2,2'-bis(4,5-dibenzoyl-1,3-dithiole) (200d)

The band with the third highest R_f value, on elution, gave a purple solid (76 mg., 51%) which on recrystallization from nitromethane gave the butene 200d as purple needles, m.p. = 244-246°C.

Infrared spectrum [Fig. XXV]: absorption (cm^{-1}) at 1675, unresolved (ketone, C=O)

N.M.R. Spectrum [Fig. LIX]: see Table V

Analysis:

Calculated for $C_{50}H_{32}O_4S_4$: C, 72.94; H, 3.90; S, 15.54;

Found: C, 72.72; H, 4.04; S, 15.39.

The band with the lowest R_f value, on elution, gave the aldehyde 201b as an uncrystallizable orange oil [I.R.], (24 mg., 16%). The characterization of the aldehyde is described in the next experiment.

When the conversion was carried out in boiling benzene for 24h, the same compounds were isolated but in different proportions, i.e., thial 198d (67%), the butene 200d (11%) and the aldehyde 201b (11%).

Preparation of 2-α-Phenylformylmethylene-4,5-dibenzoyl-1,3-dithiole [(201b)]

Excess mecuric acetate in boiling acetic acid (10 ml.) was added to the thial 198d (200 mg., 0.45 m.mole). The solution turned yellow after 5 minutes of heating, and the resulting mixture was poured into water (50 ml.) and extracted with benzene (3 X 50 ml.) Evaporation of

the benzene extracts gave the aldehyde 201b as an uncrystallizable orange oil.

Infrared spectrum [Fig. XXVI]: absorptions (cm^{-1}) at 1655 (broad, ketone, C=O) and 1625 (shoulder, aldehyde, C=O)

N.M.R. Spectrum [Fig. LX]: see Table III

Mass spectrum contained a parent peak at M^+/e = 428, calculated 428.

Reaction of 2-α-Phenylthioformylmethylene-4,5-dibenzoyl-1,3-dithiole (198d) with Dibenzoylacetylene

The thial 198d (165 mg., 0.47 m.mole) and the acetylene (110 mg., 0.47 m.mole) were refluxed in benzene (20 ml.) for 18h. After the solvent was removed, the residue was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1, $CHCl_3$). Five bands not completely separated, were observed. The material from each band was rechromatographed using the same developing mixtures, but with only a maximum of 35 mg./plate. Of the five fractions, four could be identified. They were unchanged thial 198d [I.R.], (∿5 mg.), the butene 200d [I.R.], (∿8 mg., 6%), the aldehyde 201b [I.R.], (∿8 mg., 6%) and the di-adduct 199b [I.R.], (192 mg., 70%). These compounds had similar R_f values (thial>butene>aldehyde> di-adduct).

The other band (lowest R_f value), on elution, gave an orange oil which crystallized from ethanol, m.p. = 190-193°C.

Infrared spectrum [Fig. XXVII]: absorptions (cm^{-1}) at 1690 (medium, C=O), 1650 (strong, C=O) and 1640 (medium, shoulder, C=O)

N.M.R. Spectrum showed a multiplet 2.33-3.17τ.

Mass spectrum: last peak at M^+/e = 573 and base peak at M^+/e = 385.

Analysis:

Found: C, 71.50; H, 4.32; S, 13.69.

Another analysis was performed because it was found that the sample was not dry.

Found: C, 73.08; H, 3.88; % loss on drying, 1.99%.

Section E: Reactions Involving 5-Methyl-1,2-dithiole-3-thione (63)

Preparation of 5-Methyl-1,2-dithiole-3-thione (63)

The thione 63 was prepared by the method of Thuillier and Vialle[56] and was purified by column chromatography using benzene:pet.ether (1/1), m.p. = 33-34°C. [Lit. m.p. = 33°C][56]

Reaction of 5-Methyl-1,2-dithiole-3-thione (63) with Dimethyl Acetylenedicarboxylate to form Dimethyl 2-Thioacetonylidene-1,3-dithiole-4,5-dicarboxylate [(93d)]

The thione 63 (296 mg., 2.0 m.mole) and dimethyl acetylene-dicarboxylate (284 mg., 2.0 m.mole) in benzene (80 ml.) were stirred together for 24h. After the solvent was removed, the brown solid was recrystallized from ethanol:benzene (1/1) as light brown matted needles, m.p. 108-110°C.

Infrared spectrum [Fig. XXVIII]: absorption (cm^{-1}) at 1725 (ester, C=O)

N.M.R. Spectrum: 2.23τ (1H, s, methine proton on side chain), 6.12τ (6H, s,- CO_2CH_3) and 7.18τ (3H, s, - CH_3 on side chain)

Analysis:

Calculated for $C_{10}H_{10}O_4S_3$: C, 41.38; H, 3.45; S, 33.10;

Found: C, 41.40; H, 3.54; S, 33.06.

Attempted Reaction of Dimethyl 2-Thioacetonylidene-1,3-dithiole-4,5-dicarboxylate (93d) with Ethyl Tetrolate (105c)

The mono-adduct 93d (290 mg., 1.0 m.mole) and ethyl tetrolate (105c) (112 mg., 1.0 m.mole) in xylene (20 ml.) were refluxed for 24h. No colour change was observed and the starting materials were recovered.

Similar results were obtained when the starting materials were heated in boiling benzene or nitromethane.

PART II: Reactions not Involving 1,2-Dithiole-3-thiones

Preparation of 3-phenylimino-5-phenyl-1,2-dithiole (181)

The imine 181 was prepared by the method of Paulmier, Mollier and Lozac'h[140], m.p. = 127-129°C. [Lit. m.p. = 131°C][140]

Reaction of 3-Phenylimino-5-phenyl=1,2-dithiole (181) with Dimethyl Acetylenedicarboxylate [233a]

The imine 181 (120 mg., 0.45 m.mole) and excess ester in benzene (50 ml.) were refluxed for 18h. The colour of the solution, after 20 minutes, changed from yellow to red. The crude product 233a obtained on evaporation was purified by t.l.c. and recrystallized from ethanol as orange prisms, m.p. = 173-175°C, (153 mg., 62%).

Infrared spectrum [Fig. XXIX]; absorptions (cm^{-1}) at 1695, 1725, 1775 (ester, C=O)

N.M.R. Spectrum [Fig. LXI]: 2.73τ (5H, s, due to protons on N-phenyl group); 2.62-2.83τ (5H, m, due to protons on benzene ring on the side chain); 3.75τ (1H, s, proton on the side chain); 6.42τ (3H, s, $-O-CH_3$); 6.32τ (3H, s, $-O-CH_3$); 6.20τ (3H, s, $-O-CH_3$); 6.12τ (3H, s, $-O-CH_3$).

Analysis:

Calculated for $C_{27}H_{23}NO_8S_2$: C, 58.59; H, 4.16; N, 2.53; S, 11.58;

Found: : C, 58.46; H, 4.10; N, 2.68; S, 11.69.

Unchanged imine 181 [R_f > R_f (di-adduct 233a)] was also recovered by t.l.c. (40 mg.).

When the reaction was performed with equimolar quantities of reagents, the product was a mixture of the di-adduct 233a and unchanged imine 181.

Reaction of 3-Phenylimino-5-phenyl-1,2-dithiole (181) with Ethyl Propiolate [232a]

The imine 181 (400 mg., 1.49 m.mole) and the ester (150 mg., 1.53 m.mole) in benzene (20 ml.) were refluxed for 18h. After removal of the solvent, the residue was separated by t.l.c. (pet. ether/C_6H_6 = 1/3, C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1). Of the four bands found, the two with the lowest R_f values contained small amounts of material (∿10 mg., each). The band with the highest R_f value contained unchanged imine 181 (80 mg.). The other band, on elution, gave an orange powder (417 mg., 75%) which on recrystallization from ethanol gave the mono-adduct 232a as dark orange needles, m.p. = 221-223°C.

Infrared spectrum [Fig. XXX]: absorption at 1720 (ester, C=O)

N.M.R. Spectrum [Fig. LXII]: 2.24τ (1H, s, due to either the proton on the side chain or the proton on the thiazole ring); 2.33-2.92τ (11H, m, due to 10 protons on the two benzene rings and one proton either on the side chain or on the thiazole ring); 5.84τ (2H, q, J = 7.0 Hz., $-O-CH_2-$); 8.75τ (3H, t, J = 7.0 Hz., $-O-CH_2-CH_3$).

Analysis:

Calculated for $C_{20}H_{17}NO_2S_2$: C, 65.39; H, 4.63; N, 3.82; S, 17.44;

Found: C, 65.23; H, 4.66; N, 3.95; S, 17.47.

Reaction of 3-Phenylimino-5-phenyl-1,2-dithiole (181) with Ethyl Phenylpropiolate [232b]

The imine 181 (329 mg., 1.22 m.mole) and the ester (200 mg., 1.15 m.mole) in xylene (20 ml.) were refluxed for 14h. The solvent was removed under reduced pressure and the yellowish-orange residue was extracted with boiling ethanol (80 ml.) to remove unchanged imine 181.

The insoluble mono-adduct 232b was collected (140 mg.). Separation by t.l.c. (pet. ether/C_6H_6 = 1/3, C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1) of the residue of the ethanol extract gave two main bands. The band with the highest R_f value contained unchanged imine 181 (120 mg.). The other band contained more of the mono-adduct 232b (188 mg., combined yield = 64%) which on recrystallization from ethanol:benzene (1/1) gave dark orange needles, m.p. = 261-263°C.

Infrared spectrum [Fig. XXXI]: absorption at 1695 (ester, C=0)

N.M.R. Spectrum [Fig. LXIII]: 2.37-3.22τ (16H, m, due to 15 protons on the three benzene rings and one proton on the side chain); 5.84τ (2H, q, J = 7.0 Hz, $-O-CH_2-$); 8.82τ (3H, t, J = 7.0 Hz, $O-CH_2-CH_3$).

Analysis:

Calculated for $C_{26}H_{21}NO_2S_2$: C, 70.43; H, 4.74; N, 3.16; S, 14.45;

Found: C, 70.24; H, 4.86; N, 3.26; S, 14.26.

Reaction of 3-Phenylimino-5-phenyl-1,2-dithiole-3-thione (181) with Dibenzoylacetylene

The imine 181 (268 mg., 1.0 m.mole) and the acetylene (234 mg., 1.0 m.mole) in benzene (20 ml.) were refluxed together for 18h. The solution was evaporated and the residue separated by t.l.c. ($CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1, $CHCl_3$). Of the three main bands, the one with the highest R_f value contained unchanged imine 181 (200 mg.) and the one with the lowest R_f value contained dibenzoylacetylene (110 mg.). The other band, on elution, gave an orange solid (150 mg.) which on recrystallization gave an orange powder, m.p. = 268-272°C. The elemental analysis did not correspond to the structure of the mono-adduct 232c or to the structure of the di-adduct 233c.

	C	H	N	S
Calculated for the mono-adduct 232c:	75.47	4.44	2.84	12.98
$C_{31}H_{21}NO_2S_2$				
Calculated for the di-adduct 233c:	76.54	4.75	1.90	8.68
$C_{47}H_{31}NO_4S_2$				
Found:	78.08	4.34	2.44	5.31

Infrared spectrum [Fig. XXXII]: absorption cm^{-1} at 1660 (ketone, C=O)

Preparation of 3-Phenylimino-4,5-diphenyl-1,2-dithiole (231)

The imine 231 was prepared by the method of Paulmier, Mollier and Lozac'h[140], m.p. = 174-175°C. [Lit.m.p. = 173°C][140]

Reaction of 3-Phenylimino-4,5-diphenyl-1,2-dithiole (231) with Dimethyl Acetylenedicarboxylate [233b]

The imine 231 (330 mg., 0.96 m.mole) and the ester (136 mg., 0.96 m.mole) in xylene (30 ml.) were refluxed for 72h. The solvent was removed under reduced pressure and the orange residue was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1). Of the two main bands found, the one with the highest R_f value contained unchanged imine 231 (205 mg.). The other band, on elution, gave a yellow powder (212 mg., 75%) which on recrystallization from ethanol gave the di-adduct 233b as yellow prism, m.p. = 230-232°C.

Infrared spectrum [Fig. XXXIII]: absorptions (cm^{-1}) at 1740, 1710 (ester, C=O)

N.M.R. Spectrum [Fig. LXIV]: 2.67-3.05τ (15H, m); 6.37-6.57τ (12H, two main peaks but not properly resolved, $-O-CH_3$).

Analysis:

Calculated for $C_{33}H_{27}NO_8S_2$: C, 62.97; H, 4.29; N, 2.23; S, 10.17;

Found: C, 62.73; H, 4.47; N, 2.17; S, 10.21.

Attempted Reaction of 3-Phenylimino-4,5-diphenyl-1,2-dithiole-3-thione (231) with Ethyl Propiolate

The imine 231 was treated with excess ester in boiling xylene for 1 week. A t.l.c. separation of the mixture indicated only starting materials.

Attempted Reaction of 3-Phenylimino-4,5-diphenyl-1,2-dithiole-3-thione (231) with Ethyl Phenylpropiolate

The imine 231 was treated with excess ester in boiling xylene for 1 week. A t.l.c. separation of the mixture indicated only starting materials.

Preparation of Benzoylphenylacetone

Benzoylphenylacetone was prepared using the method of McKinnon[123].

Preparation of 3-Benzylidene-5-phenyl-1,2-dithiole (124a)

Sulfur (48 g., 1.5 mole) was dissolved with warming in a solution of anhydrous sodium sulfide (39 g., 0.5 mole) in water (70 ml.). The resulting red solution was added to cold concentrated hydrochloric acid (1.5 l.) making sure that the temperature did not rise above -10°C. The yellow oil so formed, after decantation of the supernatant liquid was added to a solution of benzoylphenylacetone (24 g., 0.1 mole) in ether:carbon disulfide, (1/1, 100 ml.), saturated with hydrogen chloride. The resulting solution was left standing for 2 weeks. After a few days, a colourless oil was deposited which slowly crystallized. The resulting white solid, after decantation of the supernatant liquid was treated with sodium carbonate solution (5%) and extracted with benzene. From the

benzene extracts, the 3-benzylidene-1,2-dithiole 124a was obtained as golden-brown plates and was purified by column chromatography using pet.ether:benzene (1/1), prior to use, m.p. = 170-172°C, (1.4 g., 5%). [Lit. m.p. = 173-175°C][123]

Reaction of 3-Benzylidene-5-phenyl-1,2-dithiole (124a) with Dimethyl Acetylene dicarboxylate

The dithiole 124a (160 mg., 0.6 m.mole) and the ester (85 mg., 0.6 m.mole) in benzene (25 ml.) were refluxed for 18h. The solution slowly changed from reddish-orange to yellow. After removal of the solvent, the yellow oil was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1, $CHCl_3$). Twelve main bands were found, each containing between 10-20 mg. Other bands (>6) were also found, each containing trace amounts of material. An n.m.r. spectrum of the combined main fractions showed absorptions between 6.1 - 6.9τ (CO_2CH_3)

The dithiole 124a was recovered unchanged after it was heated in boiling benzene for 18h.

Preparation of N-Phenyl-5-phenylisothiazolium Perchlorate (37a)

N-Phenyl-5-phenylisothiazolium perchlorate (37a) was prepared by the method of McKinnon and Robak[31], m.p. = 195-197°C.

Reaction of N-Phenyl-5-phenylisothiazolium perchlorate (37a) with Sulfur in Pyridine

The salt 37a (338 mg., 1.0 m.mole) and excess sulfur in pyridine (5 ml.) were refluxed for 1/2h. The solution turned a dark red. Dilution with water (15 ml.) deposited a red pasty solid which was extracted with ether. The reddish residue, remaining after the removal of the ether, was separated by t.l.c. (C_6H_6/Pet.ether = 1/3,1/1,3/1 C_6H_6, $CHCl_3/C_6H_6$ = 1/3).

One main band (the second lowest R_f value) was found along with three other bands which contained trace amounts. This band, on elution, gave a yellow solid (86 mg., 32%) which on recrystallization from ethanol gave 3-phenylimino-5-phenyl-1,2-dithiole (181) as yellow plates, m.p. = 124-126°C. The infrared spectrum of this compound was identical with that of an authentic sample.

In another experiment, the red pasty solid, first obtained, was dissolved in methyl iodide and left standing for 48h. A reddish-yellow methiodide salt was deposited which turned yellow on washing with ether, m.p. = 213-215°C. The infrared spectrum and m.p. of this salt were identical with those of an authentic sample[179] of the methiodide salt of 3-phenylimino-5-phenyl-1,2-dithiole (181).

Preparation of 3-Phenyl-1,2-dithiolium Perchlorate (22b)

The salt 22b was prepared by the method of Klingsberg[3], m.p. = 177-179°C. [Lit.m.p. = 180-182.5°C][3]

Preparation of Phenyl Phosphine

Phenyl phosphine was prepared by the method of Mann and Millar[192] and was stored under nitrogen, prior to use, B.P. = 153-156°C. [Lit. B.P. = 157-159°C][192]

Reaction of Phenyl Phosphine with 3-Phenyl-1,2-dithiolium Perchlorate (22b)

To a stirred solution of the perchlorate salt 22b (558 mg., 2.0 m. mole) in ethanol (40 ml.) phenyl phosphine (220 mg., 2.0 m.mole) was added rapidly under nitrogen. Immediately, the colour of the solution changed from light brown to green, and, after 3-6 seconds, to orange. After 1-2 minutes, an amorphous yellow powder (650 mg.) was deposited. On evaporation of the ethanol solution to 1/2 volume (under reduced

pressure) more of the yellow powder (100 mg.) was obtained. The colour of the powder changed progressively to grey with exposure to air, over a period of weeks. Attempted purification by column chromatography gave fractions whose i.r. spectra showed carbonyl absorptions which were not present in the i.r. spectrum of the yellow powder [Fig. XXXIV]. The powder adhered to silica gel and could not be separated by t.l.c. A sample reprecipitated from benzene by addition of petroleum ether, m.p. = 155-158°C, gave the following analysis: C, 59.86; H, 4.77; P, 8.41; S, 17.74.

In another series of experiments, a saturated solution of iodine in ethanol was added to the solution of phenyl phosphine and the salt 22b at both the green and orange colour stages. In both cases, the amorphous yellow powder was isolated.

To a stirred solution of the yellow powder (50 mg.) in benzene (5 ml.), excess iodine was added. After 2h. petroleum ether (5 ml.) was added and the yellow powder was redeposited.

Preparation of *trans*-Cinnamoyl Chloride

trans-Cinnamic acid (100 g., 0.68 mole) and thionyl chloride (70 ml.) were refluxed for 1h. After the excess thionyl chloride was removed by distillation, the residue was distilled under reduced pressure and *trans*-cinnamoyl chloride was collected as a light yellow liquid, $B.P._{2mm.}$ = 96-98°C, which solidified on standing. The solid was dried and stored, prior to use, in a vacuum dessicator, m.p. = 37-39°C, (95 g., 85%).

Preparation of Sodium Thiocinnamate (257)

Anhydrous sodium sulfide was prepared in the following manner.

To half of a stirred solution of sodium (1.6 g., 0.07 mole) in anhydrous methanol (55 ml.), hydrogen sulfide was passed through for 3.5h. The other half of the methanol solution was added to the resulting greenish-yellow solution, and the combined solution was evaporated to dryness.

To the resulting white solid, *trans*-cinnamoyl chloride (10 g., 0.06 mole) and sand (10 g.) in anhydrous dioxane (250 ml.) was added. The mixture was stirred magnetically for 20h. and then used in the next stage.

Reaction of Sodium Thiocinnamate (257) with Phenyldichlorophosphine (255)

To the greyish-green mixture of sodium cinnamate (257), sand and dioxane, phenyldichlorophosphine (255), (8.4 ml., 0.06 mole, obtained from Alpha Inorganic Ltd.) was added and the resulting mixture was refluxed 24h. Hydrogen chloride was liberated. After filtration of the mixture and removal of dioxane, a greenish-yellow oily paste remained. A t.l.c. separation of a sample of the paste indicated that it contained 9 main fractions, and an i.r. spectrum of the paste indicated the presence of a carbonyl function. This paste was used directly in the next stage.

Sulfurization of the Product of the Reaction of Sodium Thiocinnamate (257) and Phenyldichlorophosphine (255)

The oily paste (5 g.) and phosphorus pentasulfide (15 g.) in benzene (80 ml.) were refluxed for 3h. After cooling, the mixture was filtered, and the orange filtrate washed with water (2 X 100), dried (sodium sulfate) and the benzene removed. The remaining orange paste was found to contain more than 10 fractions, as indicated by a t.l.c. separation of a sample of the paste.

The orange paste (200 mg.) dissolved in methyl iodide (3 ml.) was left standing for 24h. No solid was found.

Attempted Reaction of 1,3-Dithiolane-2-thione (110a) with Dibenzoylacetylene

The thione 110a (640 mg., 4.7 m.mole obtained from Aldrich Chemical Co.) and dibenzoylacetylene (1.0 g., 4.3 m.mole) in xylene (20 ml.) were refluxed 18h. The dark mixture was separated by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1, 3/1). Many bands were found. Of these bands, the only one (highest R_f value) that could be identified, was found to be unchanged 1,3-dithiolane-2-thione (110a) (500 mg.).

When dibenzoylacetylene was heated in boiling xylene for 18h. the solution turned dark and a t.l.c. examination of the solid, remaining after the removal of xylene, revealed that there was some decomposition of the acetylene.

Preparation of Desyl Chloride (272)

Desyl chloride (272) was prepared by the method of Ward[204].

Preparation of α-Phenylphenacyl Ethyl Trithiocarbonate (274) [277]

Ethanethiol (25 g., 0.4 mole) was added to a solution of sodium (10 g., 0.48 mole) dissolved in ethanol (250 ml.). Carbon disulfide (26.6 ml., 0.5 mole) was added with stirring and after 1/2h. desyl chloride (272) (71 g., 0.3 mole) in ethanol (350 ml.) was added. After 3 minutes, the orange solution turned cloudy and a white solid was deposited. The mixture was allowed to stand for 1h., then filtered. A white solid which turned green on exposure to light was collected. The orange filtrate was poured into water (2 l.) and after 5h. a yellow solid 274 was filtered off (56.5 g., 56%). This was used directly in the next stage.

4,5-Diphenyl-1,3-thiaoxole-3-thione (277)

The light sensitive powder (8.1 g., 10%) which on recrystallization gave the thione 277 as colourless needles, m.p. = 133-134°C. [Lit. m.p. = 132-133°C][205]

Infrared spectrum [Fig. XXXV]: an absence of a carbonyl peak.

Mass spectrum: parent ion M^+/e = 270, calculated 270; other major peaks, M^+/e = 165, 121, 105, 77.

Analysis:

Calculated for $C_{15}H_{10}OS_2$: C, 66.68; H, 3.70; S, 23.70;

Found: C, 66.61; H, 3.60; S, 23.90.

Preparation of 4,5-Diphenyl-2-ethylthio-1,3-dithiolium Perchlorate [(275)]

α-Phenylphenacyl ethyl trithiocarbonate (274) (1g., 3.0 m.mole) in sulfuric acid (10 ml.) was heated at 100°C for 10 minutes. The dark solution was chilled and diluted with water (10 ml.) and ethyl acetate (20 ml.) added. After standing at 0°C for several hours a dark orange paste was obtained which was dissolved in acetic acid (10 ml.) and 70% perchloric acid (0.4 ml.) added. Cooling deposited pale purple crystals of the salt 275, m.p. = 121-123°C (623 mg., 51%).

Infrared spectrum [Fig. XXXVI]: absence of a carbonyl absorption.

Analysis:

Calculated for $C_{17}H_{15}ClO_4S_3$: C, 49.16; H, 3.61; Cl, 8.70; S, 23.13;

Found: C, 49.20; H, 3.72; Cl, 8.70; S, 23.24.

Preparation of 4,5-Diphenyl-1,3-dithiole-2-thione (271a) from 4,5-Diphenyl-2-ethylthio-1,3-dithiolium Perchlorate (275) [271a]

The perchlorate salt 275 (1.0 g., 2.42 m.mole) in ethanol (10 ml.) was treated with a saturated solution of sodium hydrogen sulfide in

ethanol (10 ml.) and heated until solution had occurred. Cooling afforded yellow needles which were recrystallized from ethanol, m.p. = 119-120°C, (660 mg., 96%).

Infrared spectrum [Fig. XXXVII]: absence of absorptions for perchlorate salt.

Analysis:

Calculated for $C_{15}H_{10}S_3$: C, 62.91; H, 3.52; S, 33.59;

Found: C, 62.85; H, 3.61; S, 33.68.

Reaction of 4,5-Diphenyl-1,3-dithiole-2-thione (271a) with Dibenzoylacetylene

The thione 271a (286 mg., 1.0 m.mole) and the acetylene (242 mg., 1.0 m.mole) in benzene (20 ml.) were refluxed for 72h. The evaporated mixture was separated by t.l.c. (Pet. ether, C_6H_6/Pet.ether =1/3, 1/1, 3/1, C_6H_6). Of the three bands found, only the one with the highest R_f value could be identified. It was found to be unchanged thione 271a (180 mg.). The other two bands, on elution, gave uncrystallizable oils. The i.r. spectrum of each showed a carbonyl absorption at 1650 cm^{-1} (broad). One of the oils (130 mg., lowest R_f value) when separated again by t.l.c. (C_6H_6, $CHCl_3/C_6H_6$ = 1/3, 1/1) was found to consist of seven fractions.

SPECTRA

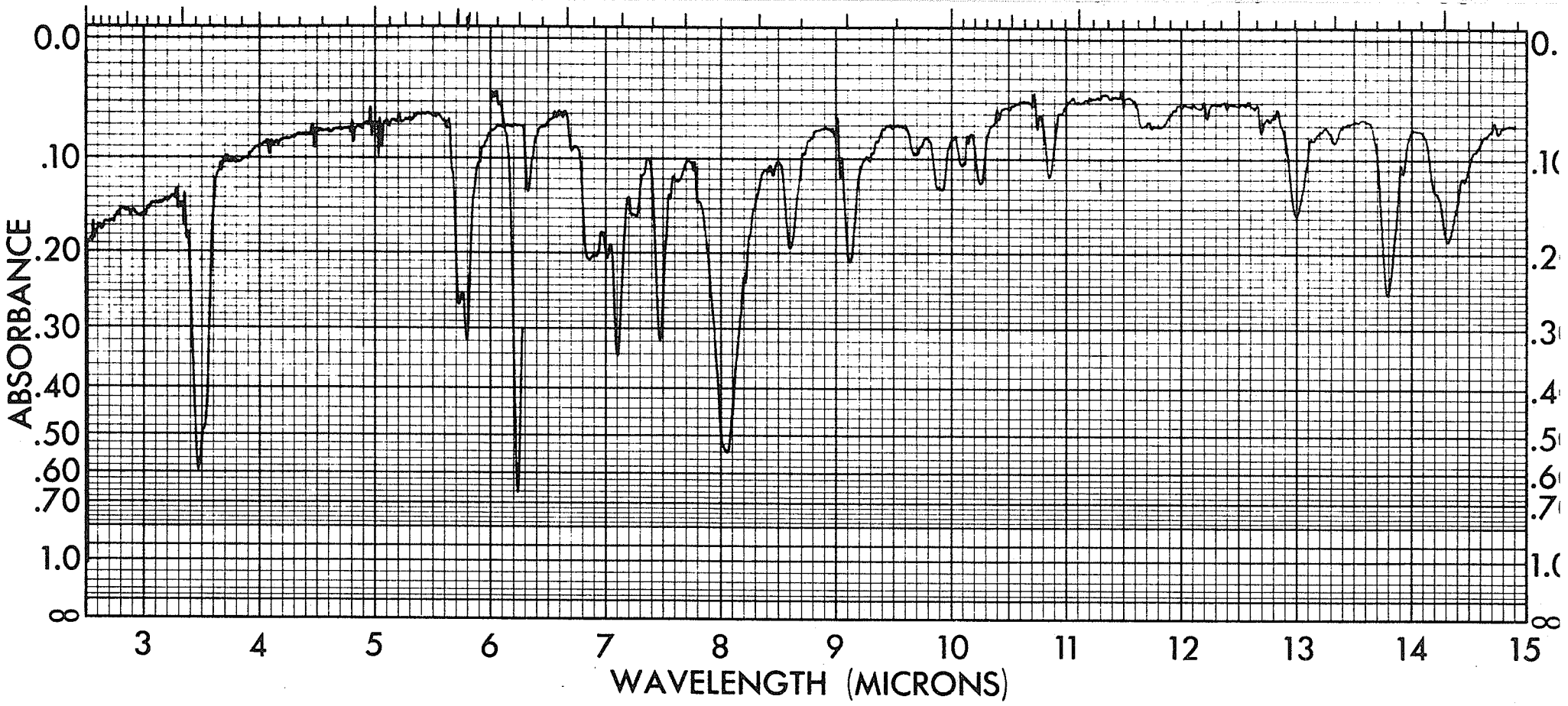
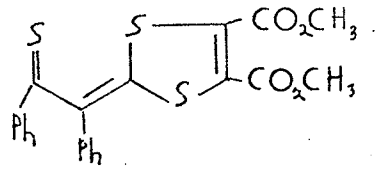


FIG. II: Infrared Spectrum of Dimethyl 2-(α-Phenylthiophenacylidene)-1,3-dithiole-4,5-dicarboxylate (93a).



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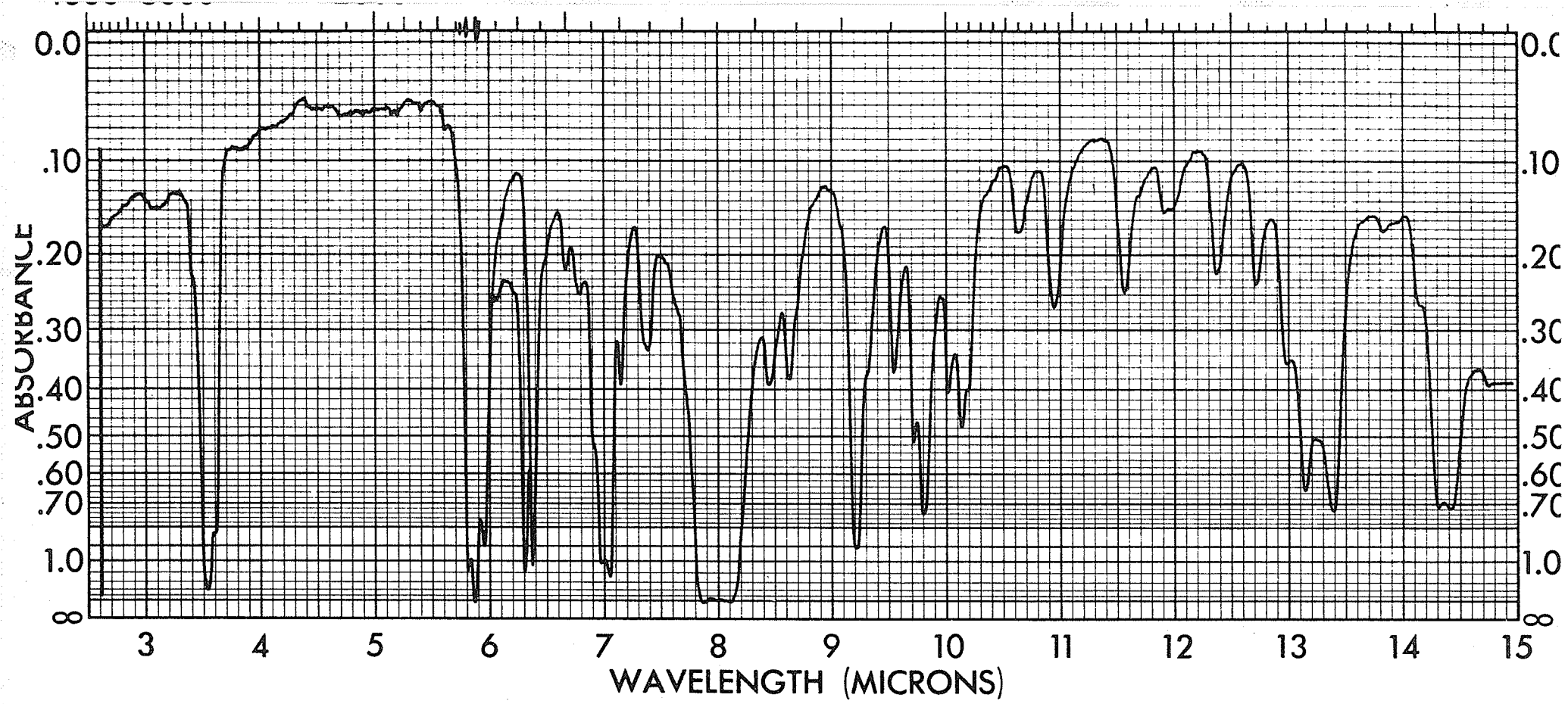
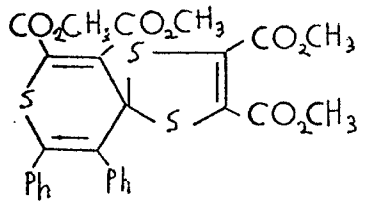


FIG. III: Infrared Spectrum of Tetramethyl 1,3-Dithiole-4,5-dicarboxylate-2-spiro-4-(2,3-diphenylthiopyran-5,6-dicarboxylate) (94a).



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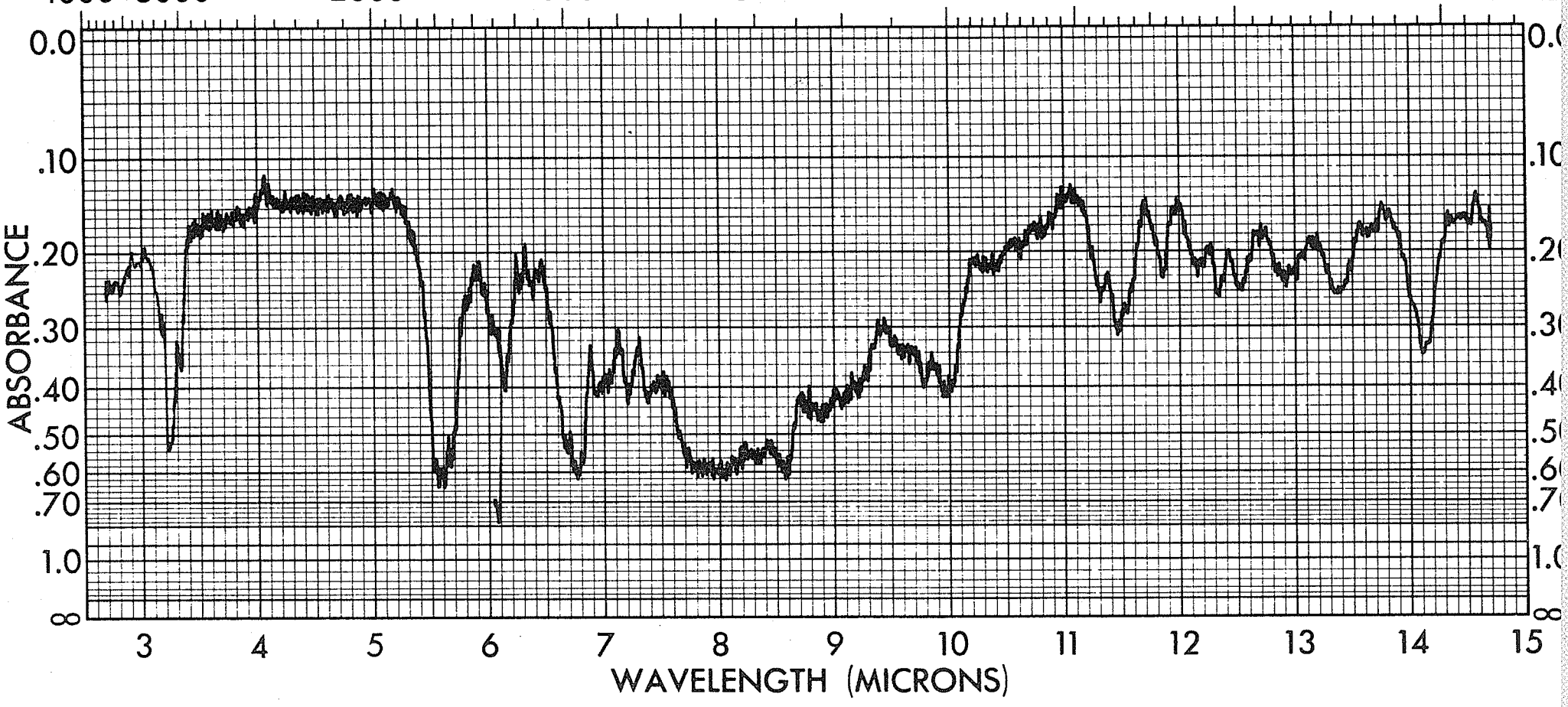


FIG. IV: Infrared Spectrum of Violet Powder Formed by Reaction of 4,5-Diphenyl-1,2-dithiole-3-thione with Two Mole Equivalents of Dimethyl Acetylenedicarboxylate.

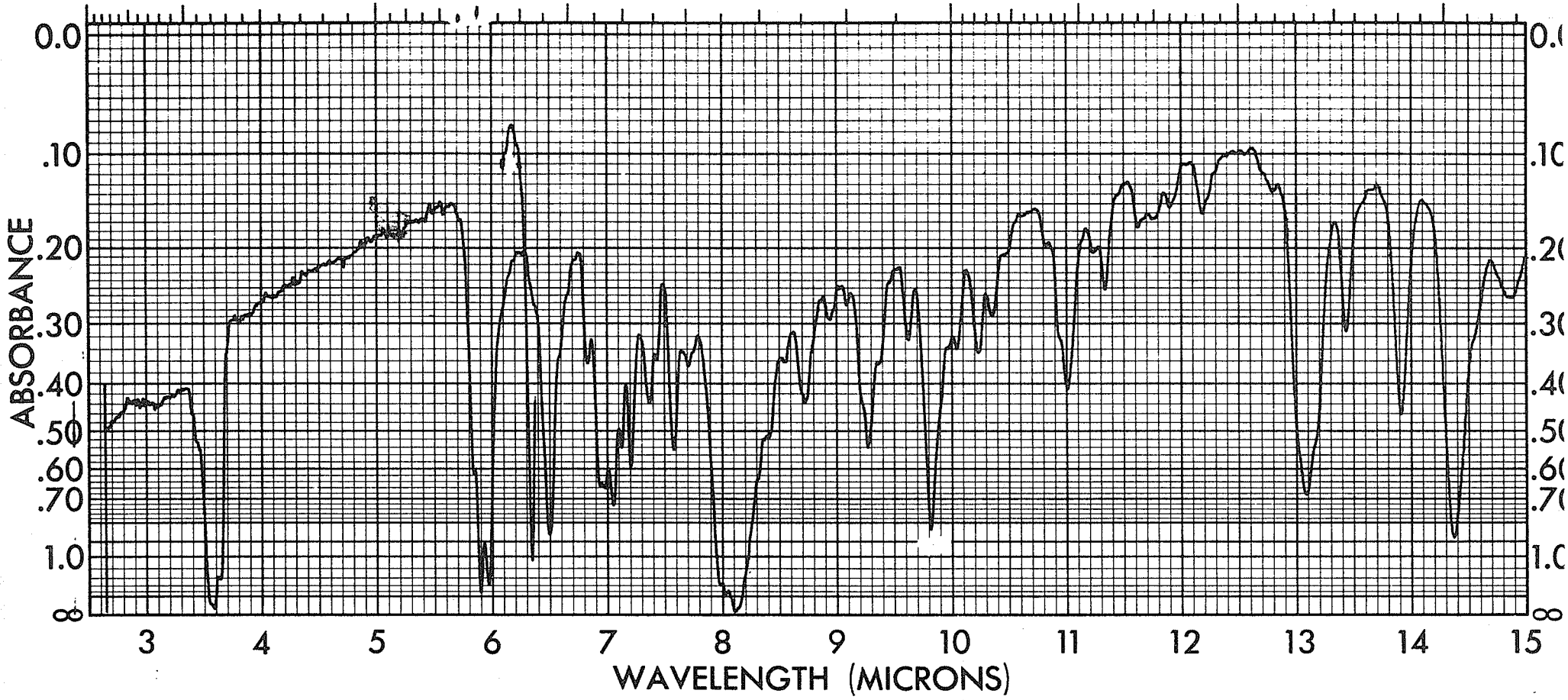
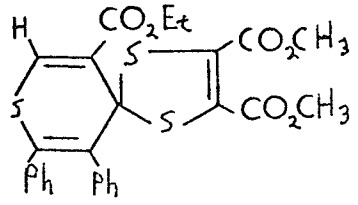


FIG. V: Infrared Spectrum of Dimethyl 1,3-Dithiole-4,5-dicarboxylate-2-spiro-4-(2,3-diphenyl-5-carboethoxythiopyran) (94b).



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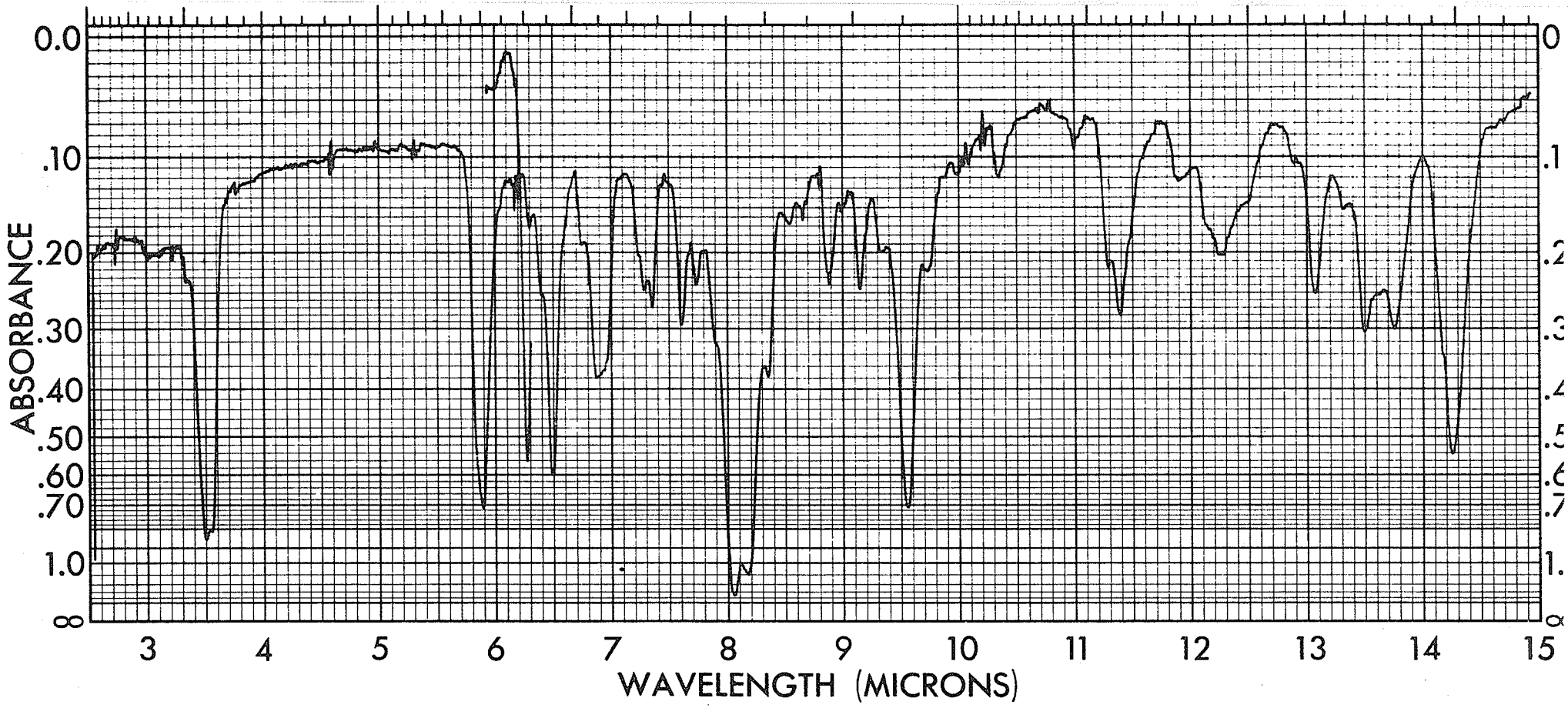
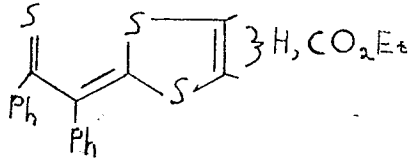


FIG. VI: Infrared Spectrum of Ethyl 2-(α-Phenylthiophenacylidene)-1,3-dithiole-4 or 5-carboxylate (93a').



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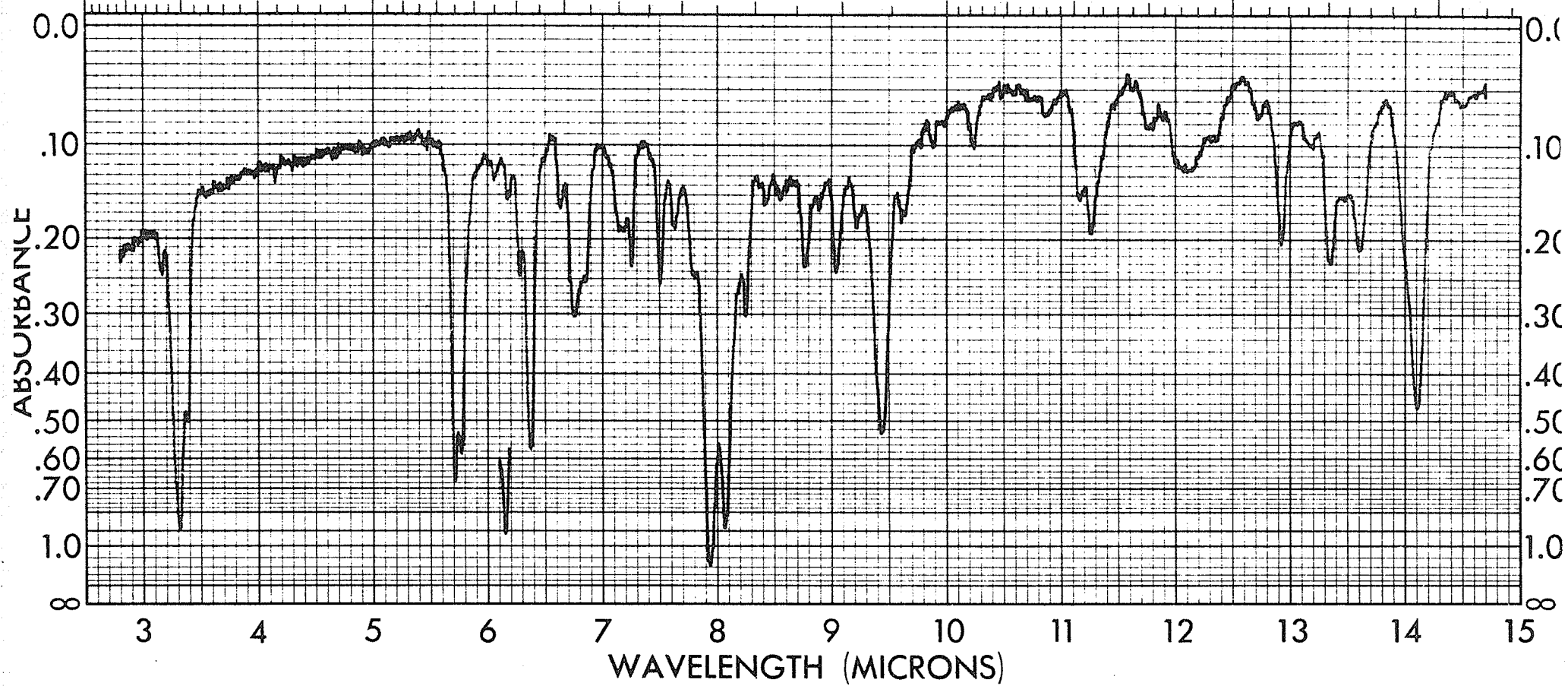
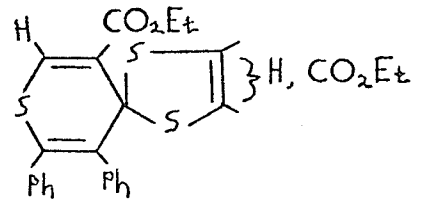


FIG. VII: Infrared Spectrum of Diethyl 1,3-Dithiole-4, or 5-carboxylate-2-spiro-4-(2,3-diphenylthiopyran-5-carboxylate) (94a').



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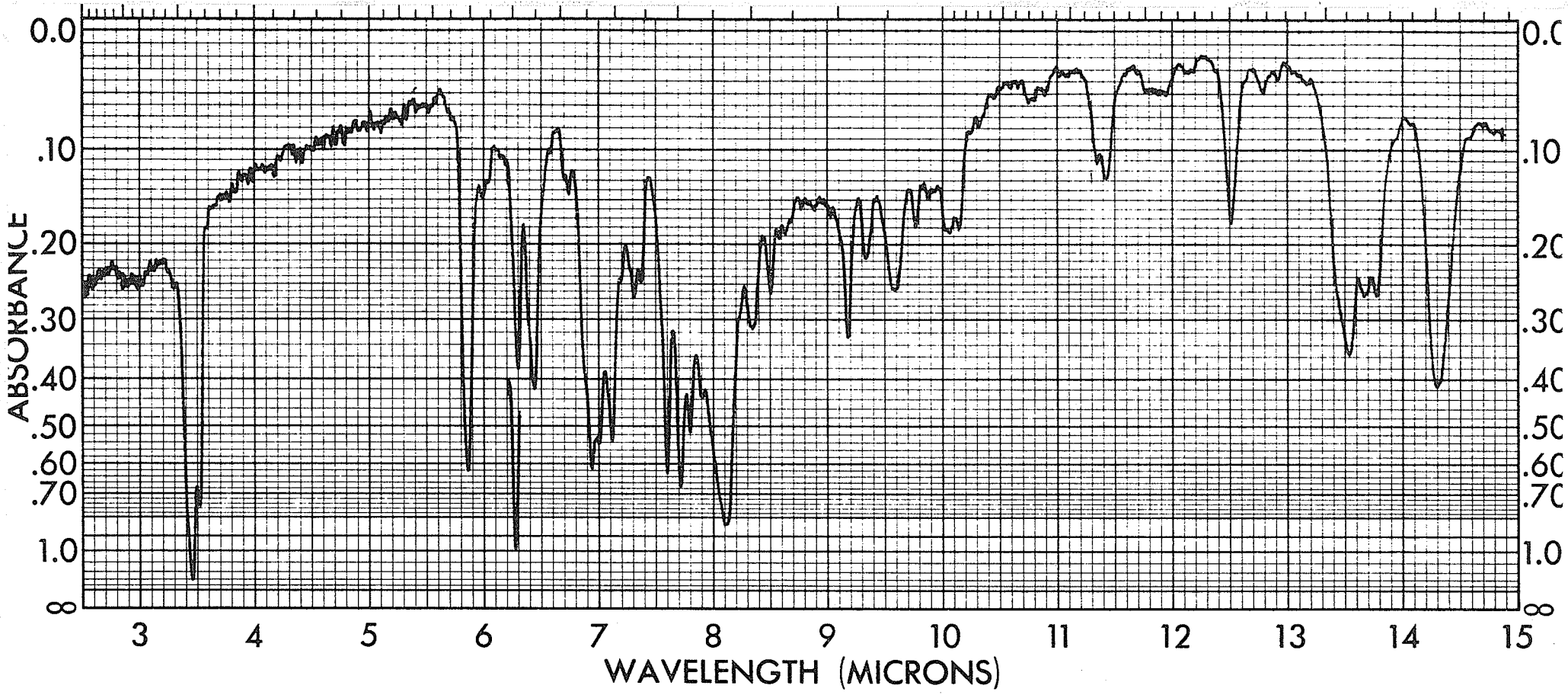
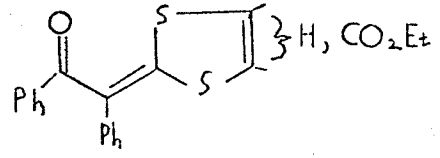


FIG. VIII: Infrared Spectrum of Ethyl 2-(α-Phenylphenacylidene)-1,3-dithiole-4, or 5-carboxylate (189c').



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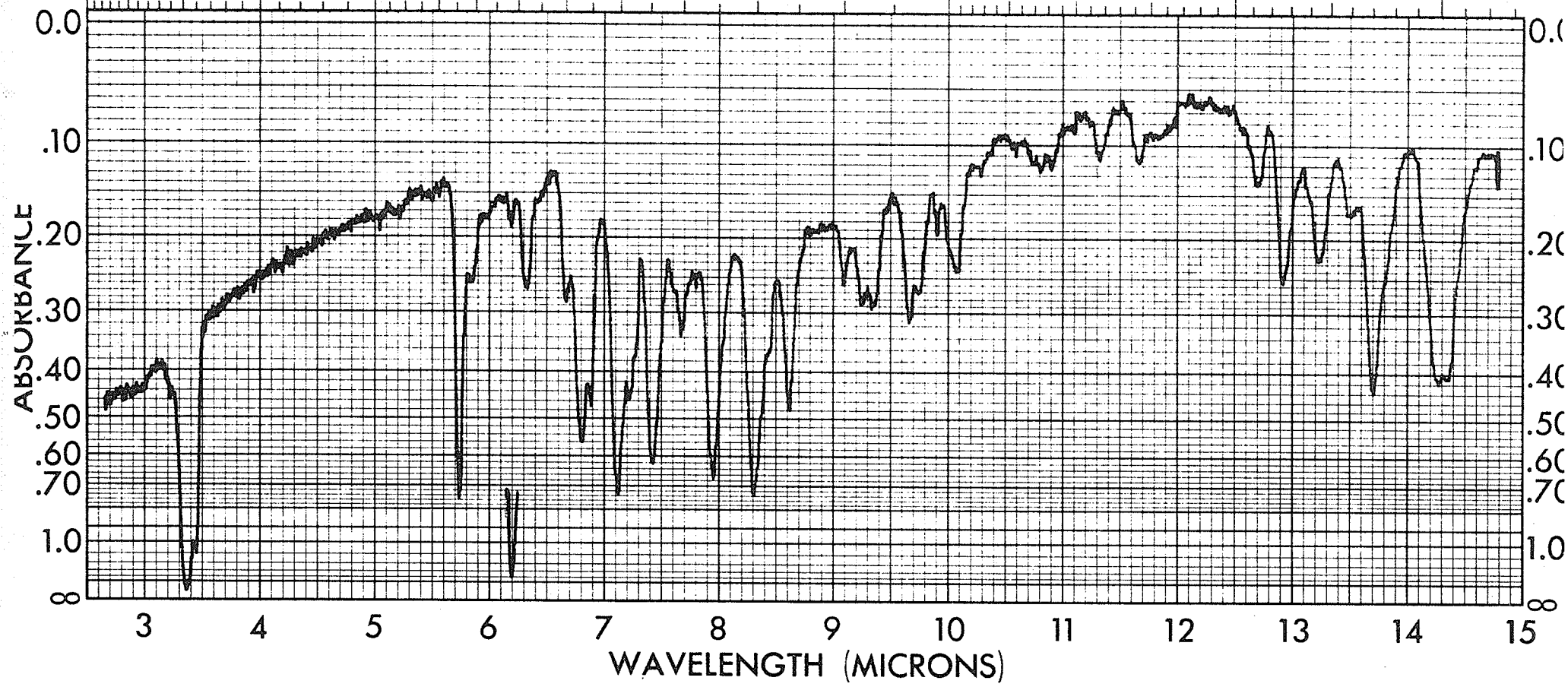
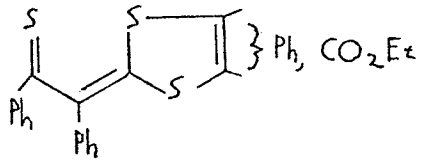


FIG. IX: Infrared Spectrum of Ethyl 2-(α-Phenylthiophenacylidene)-4, or 5-phenyl-1,3-dithiole-4, or 5-carboxylate (93b').



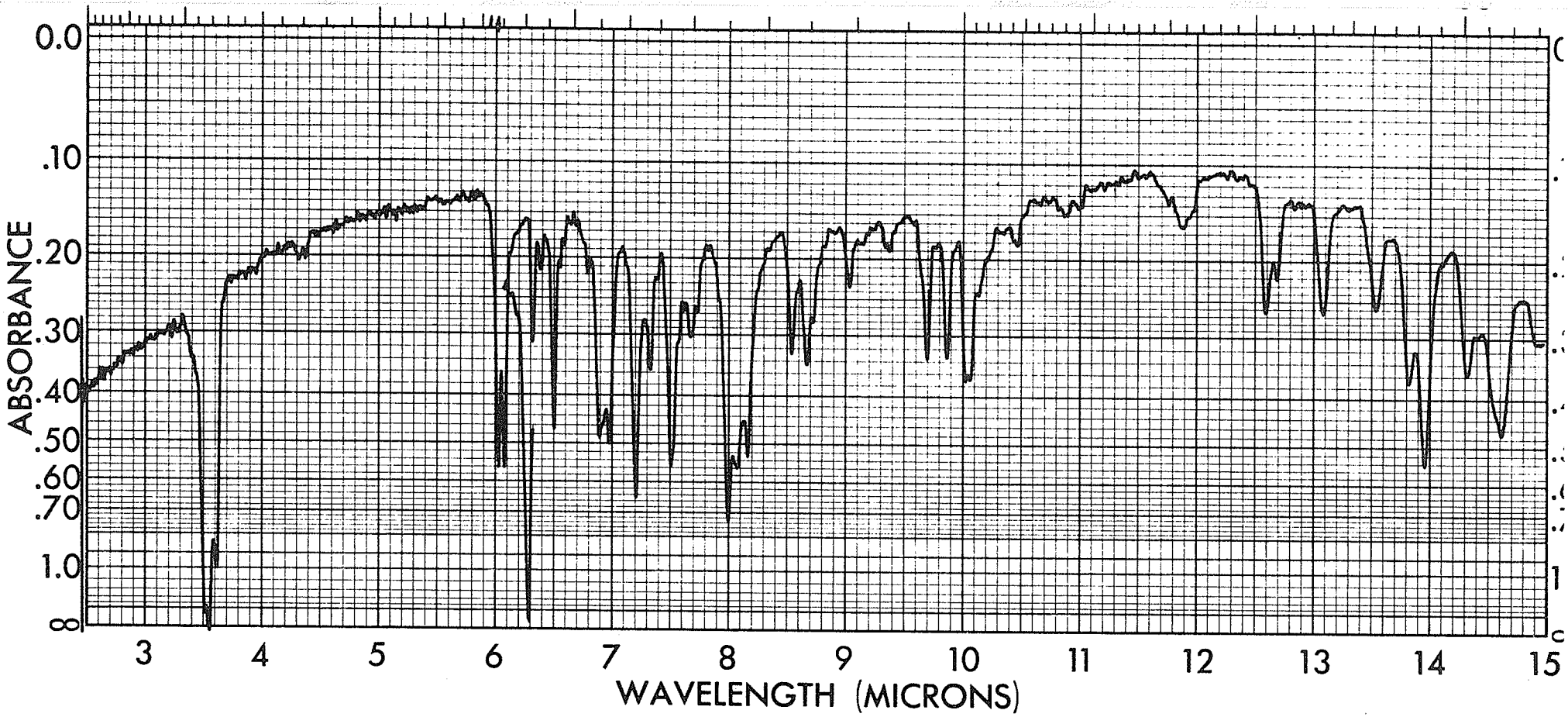
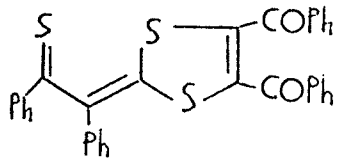


FIG. X: Infrared Spectrum of 2-(α-Phenylthiophenacylidene)-4,5-dibenzoyl-1,3-dithiole (93f).



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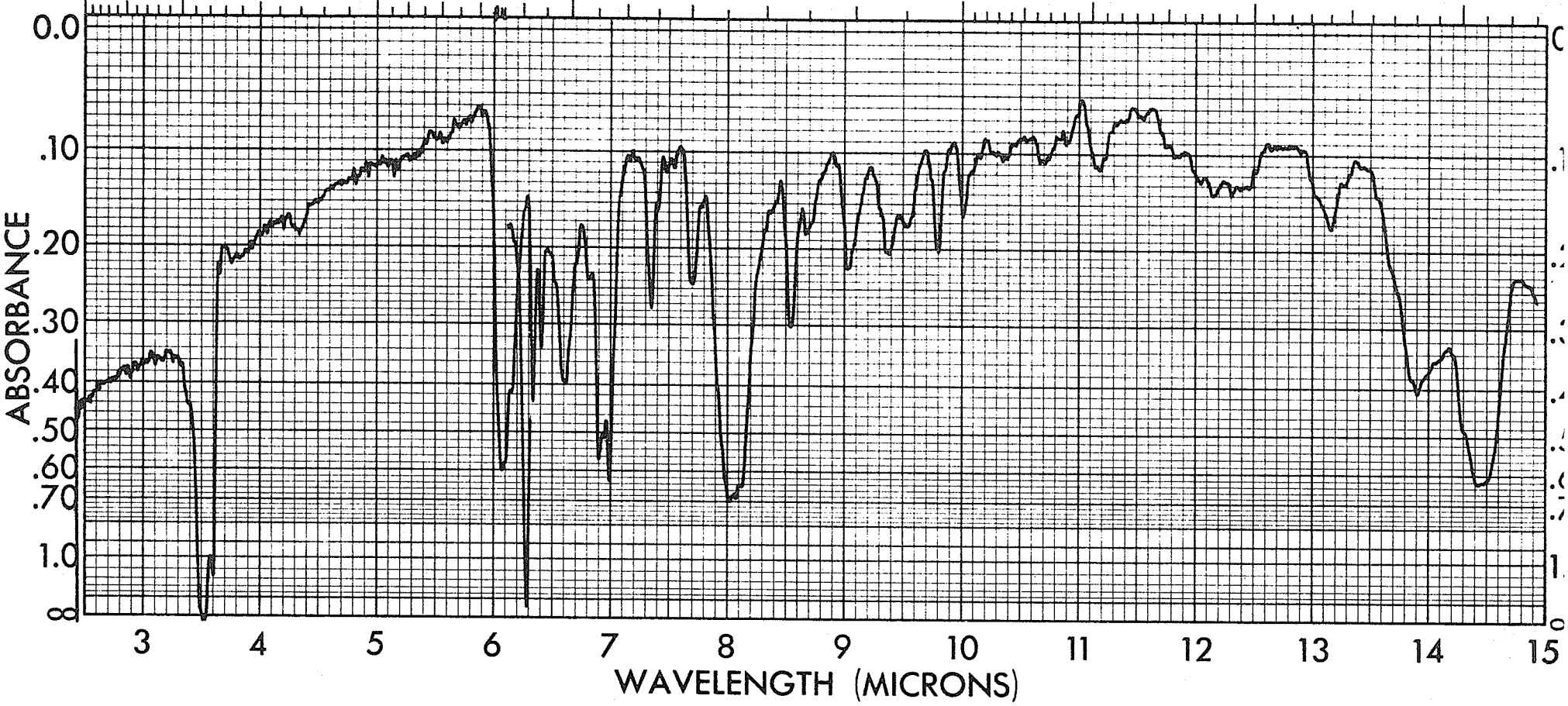
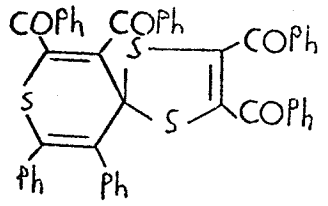


FIG. XI: Infrared Spectrum of 4,5-Dibenzoyl-1,3-dithiole-2-spiro-4-(2,3-diphenyl-5,6-dibenzoylthiopyran) (94d).



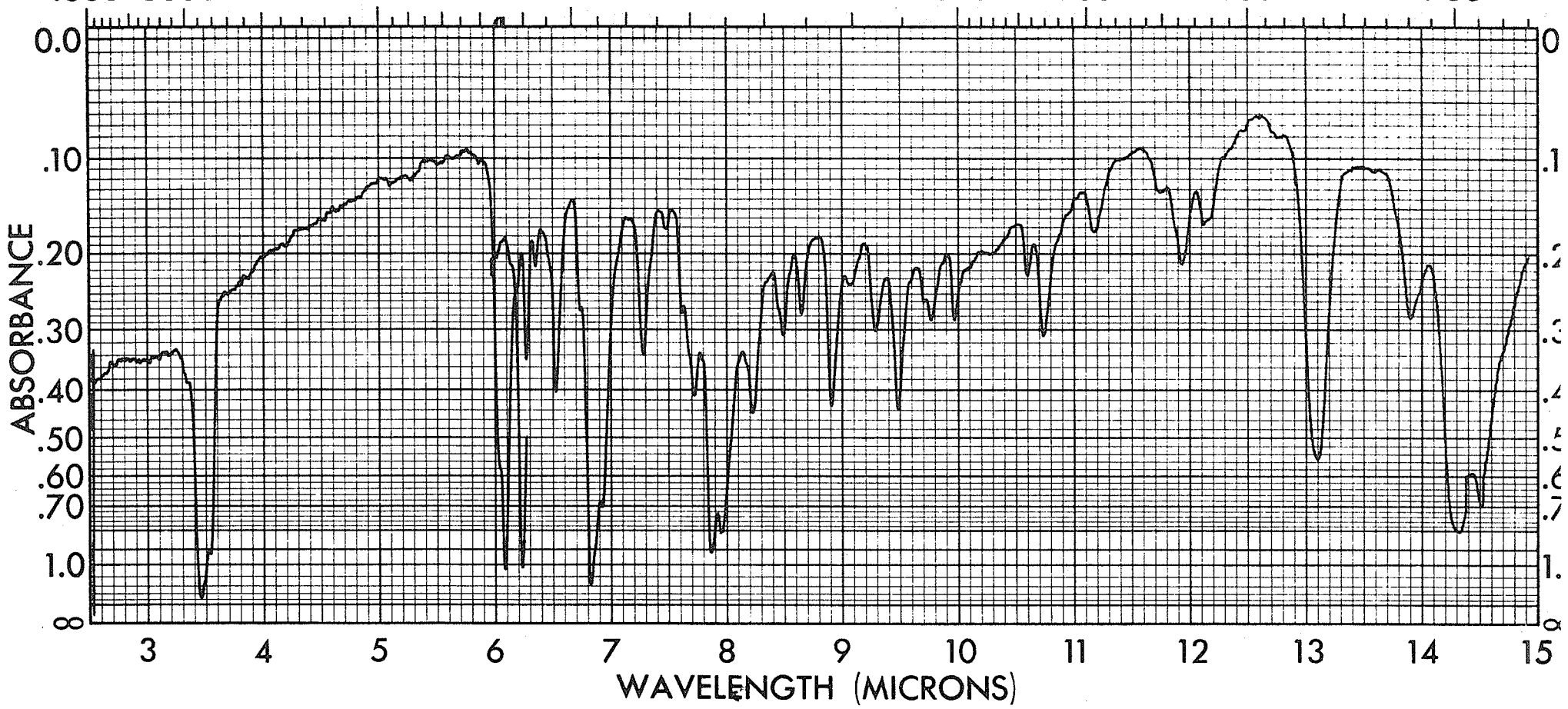
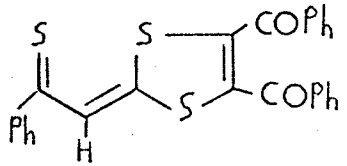


FIG. XII: Infrared Spectrum of 2-Thiophenacylidene-4,5-dibenzoyl-1,3-dithiole (93e).



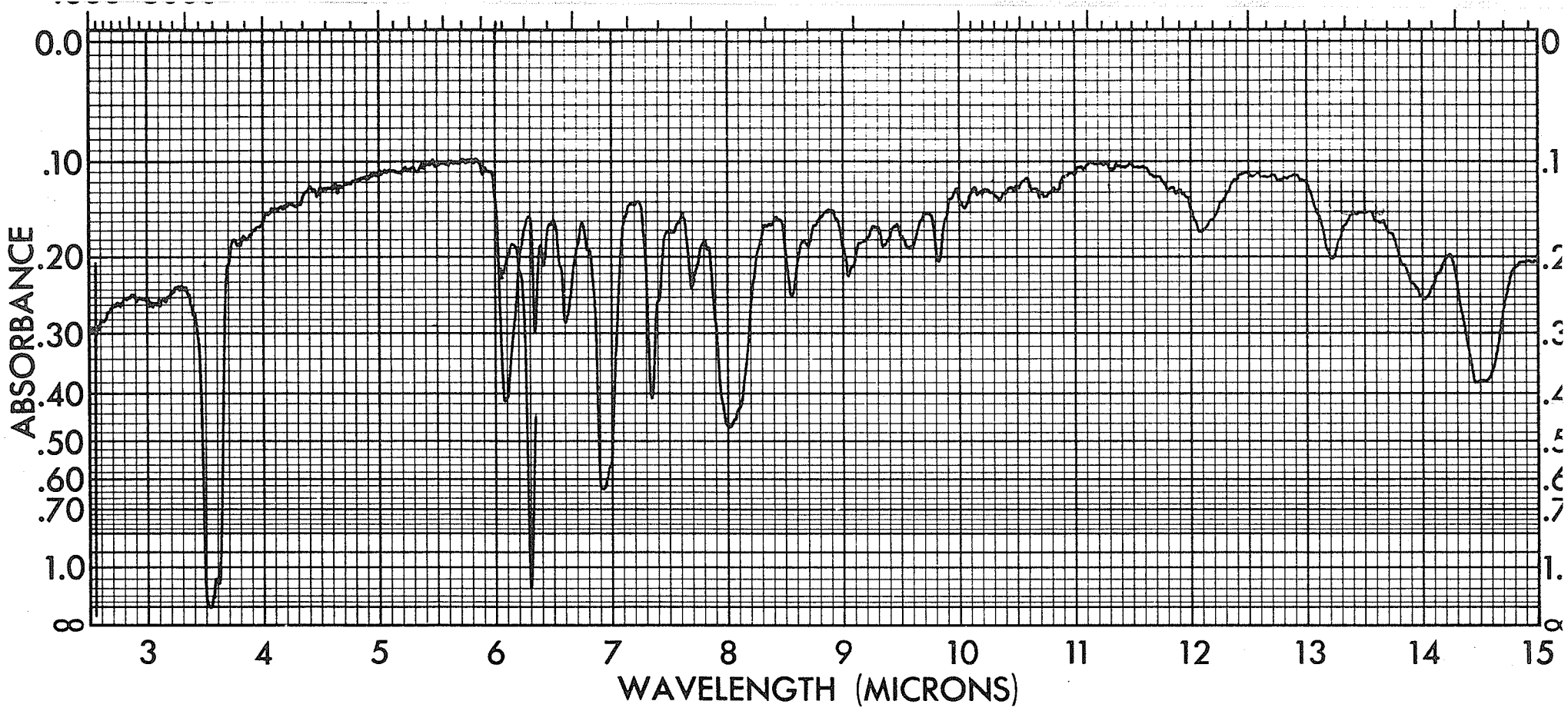
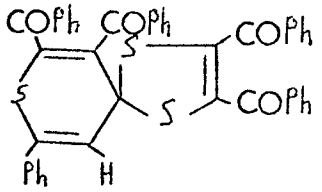


FIG. XIII: Infrared Spectrum of 4,5-Dibenzoyl-1,3-dithiole-2-spiro-4-(2-phenyl-5,6-dibenzoylthiopyran) (94c).



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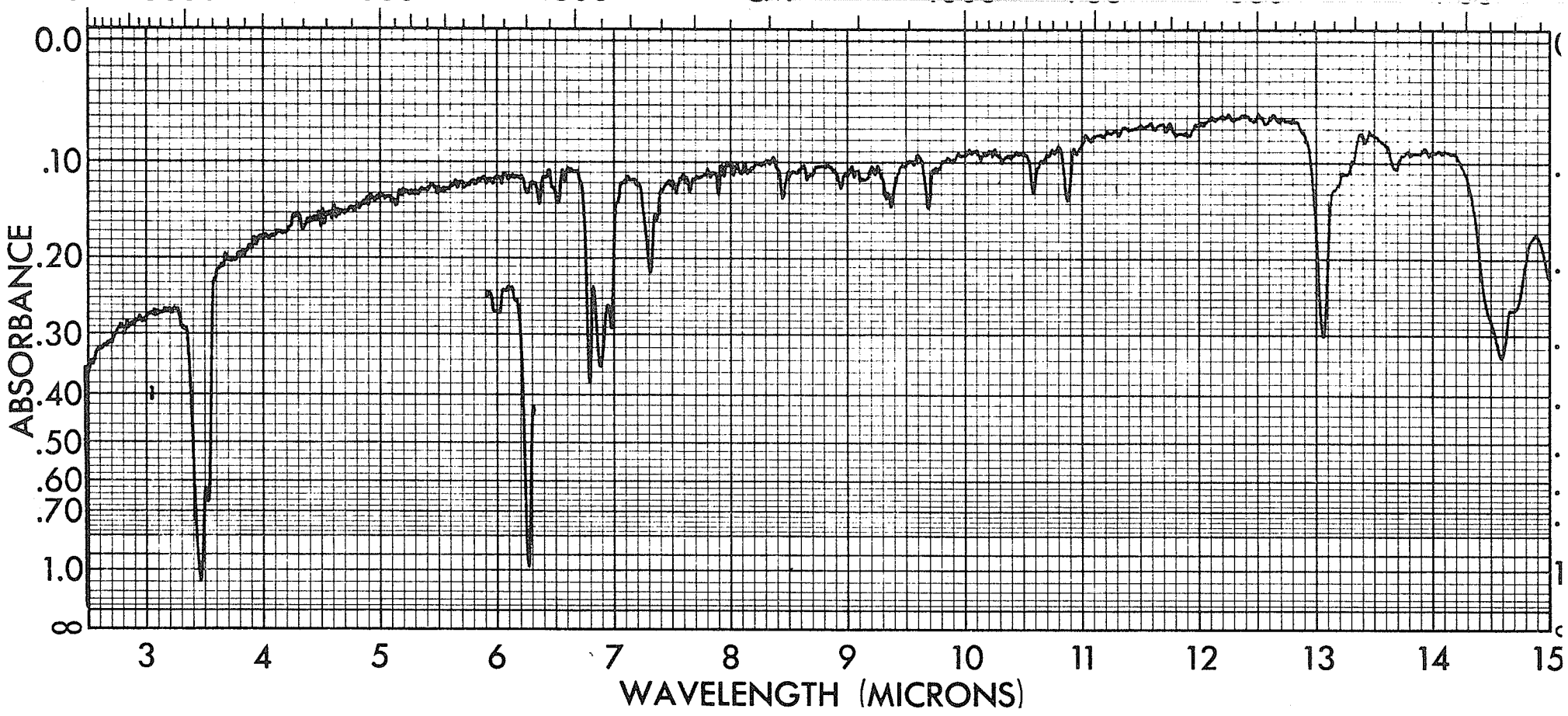


FIG. XIV: Infrared Spectrum of 1',3',5'-Triphenyl-7'-thieno[3,4,b] thiopyranspiro-4,6-diphenyl-2-thieno[3,4,d]-1,3-dithiole (268).

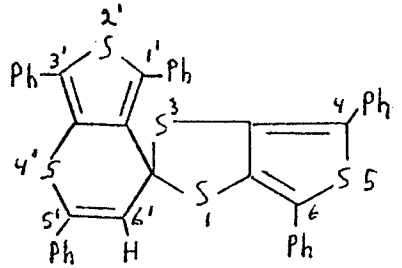
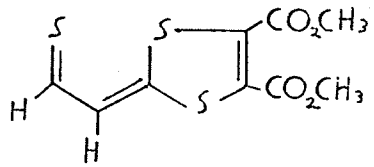
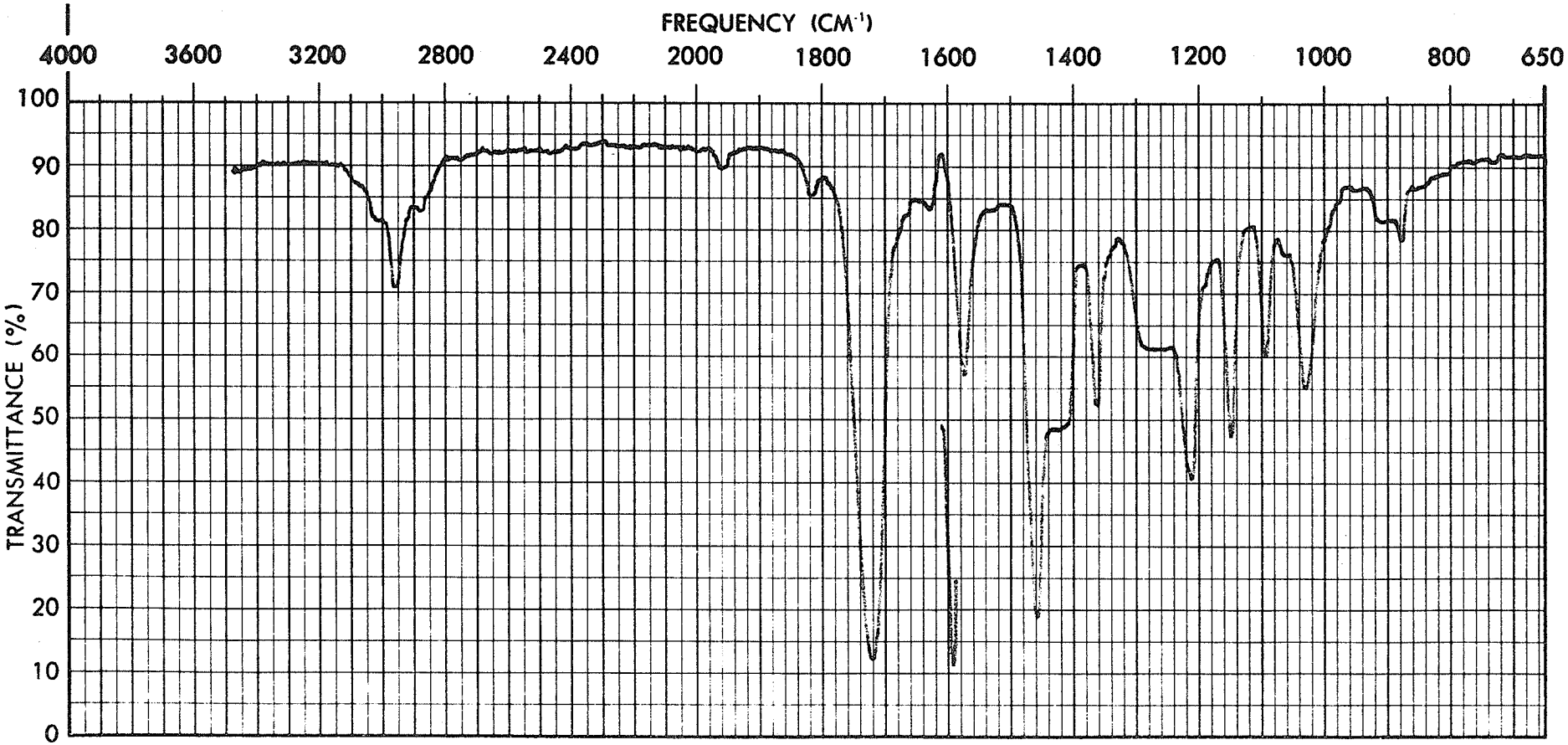


FIG. XV: Infrared Spectrum of Dimethyl Thioformylmethylene-1,3-dithiole-4,5-dicarboxylate (198a); Methylene chloride solution (P.E. Model 700).





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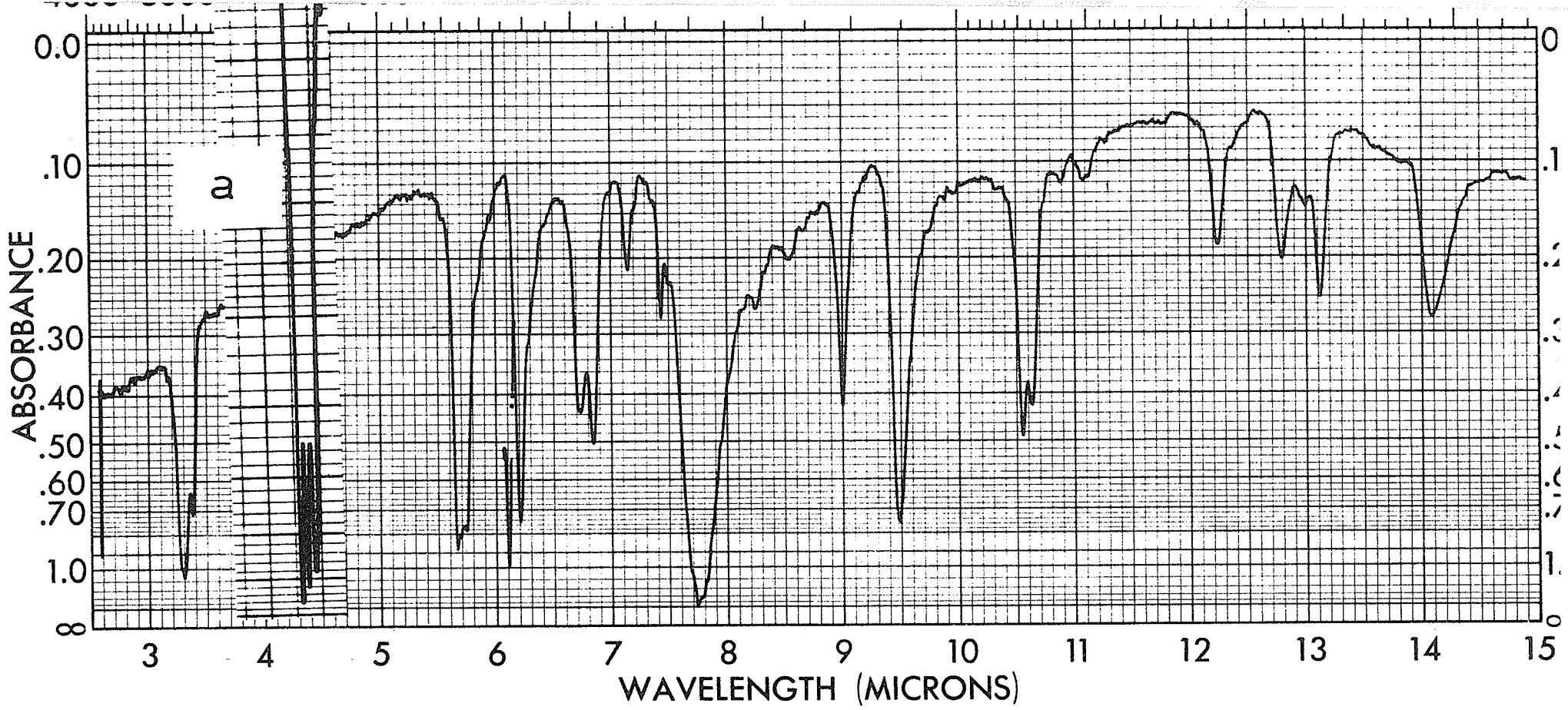
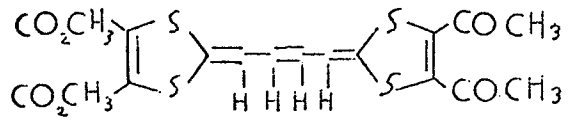


FIG. XVI: Infrared Spectrum of Tetramethyl 1,4-Butenediylidene-2,2'bis - (1,3-dithiole-4,5-dicarboxylate) (200a). *a* : Carbomethoxy carbonyl absorptions (P.E. model 337).



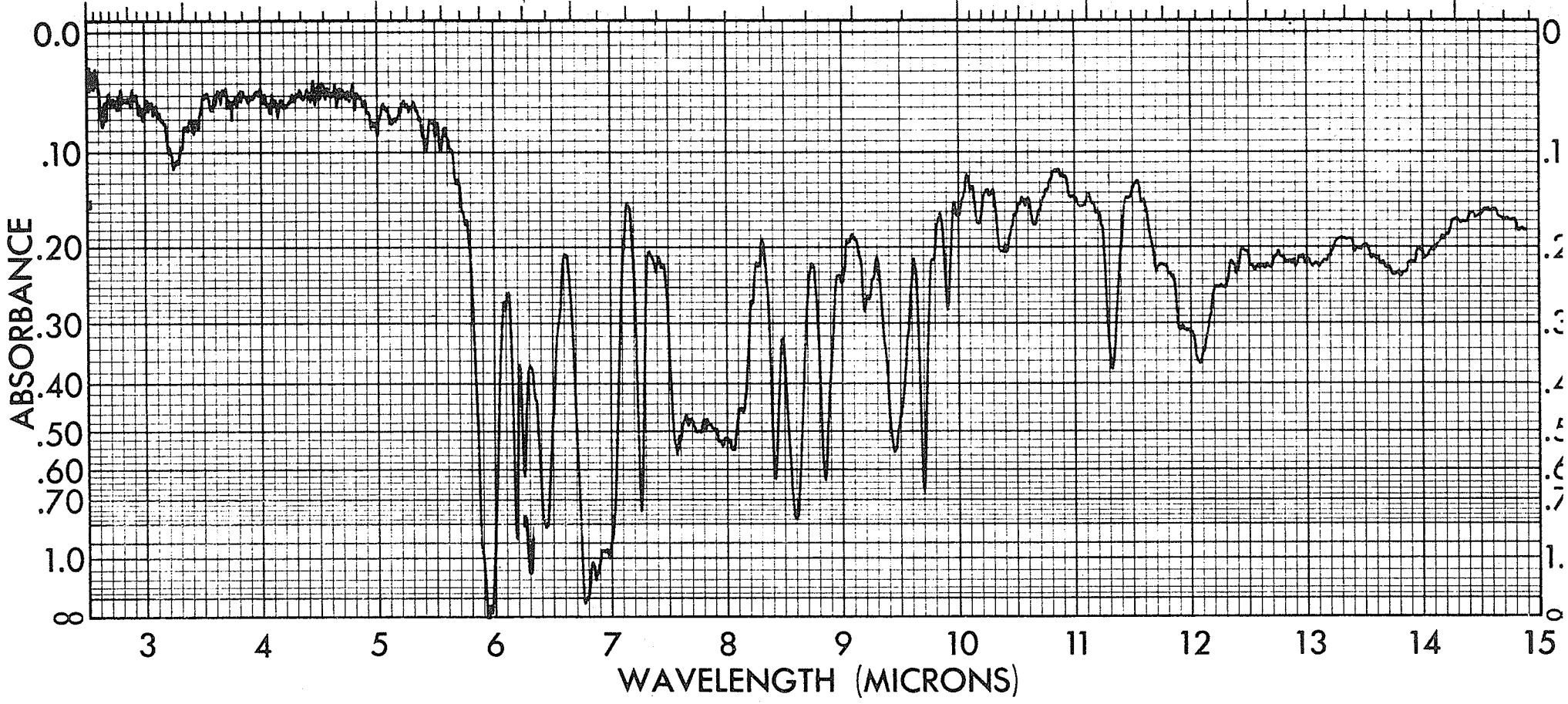
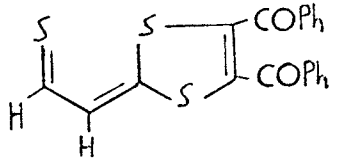


FIG. XVII: Infrared Spectrum of 4,5-Dibenzoyl-2-thioformylmethylene-1,3-dithiole (198b); Methylene chloride solution.



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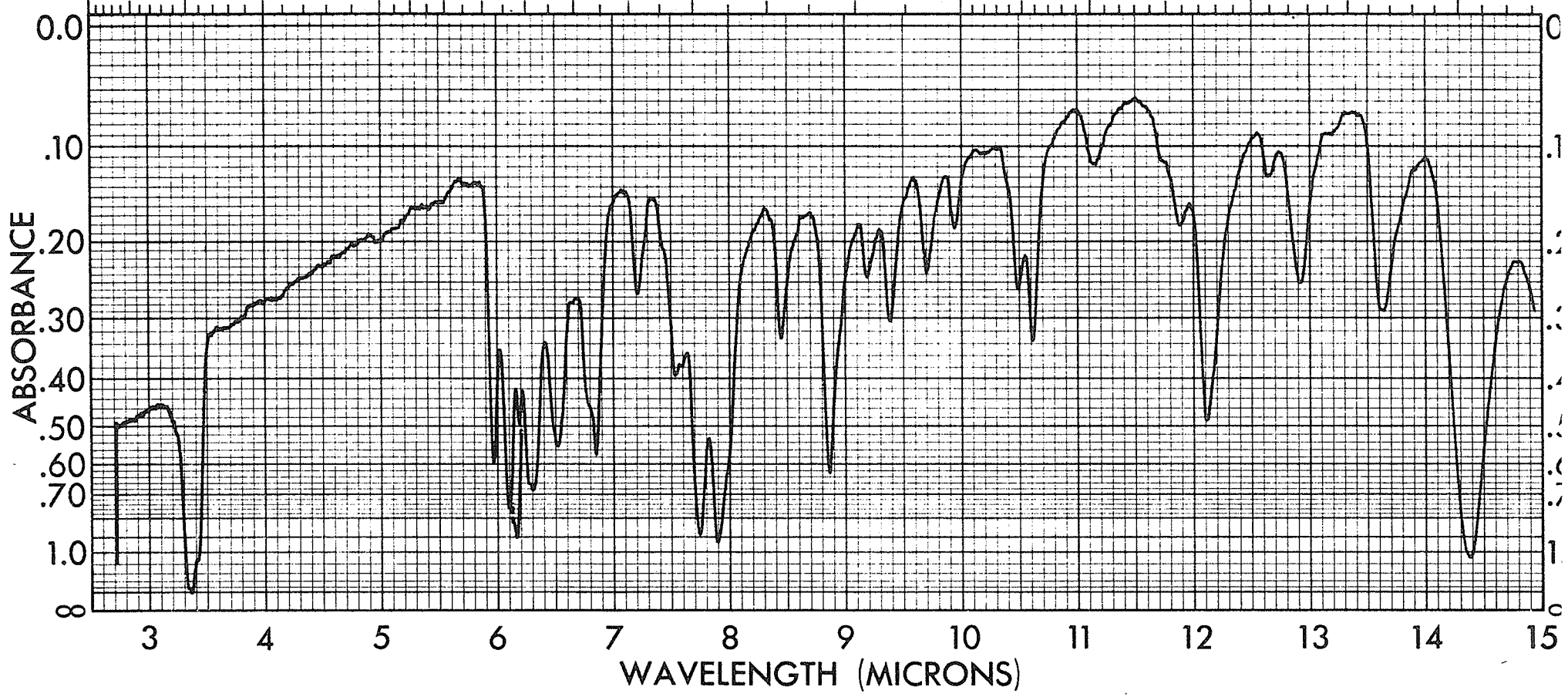

FIG. XVIII: Infrared Spectrum of 1,4-Butenediylidene-2,2'-bis(4,5-dibenzoyl-1,3-dithiole) (200b).

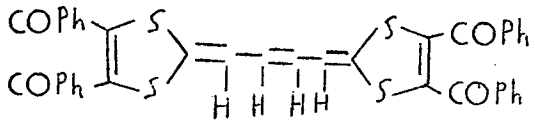

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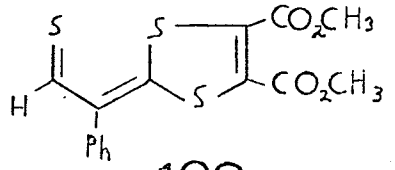
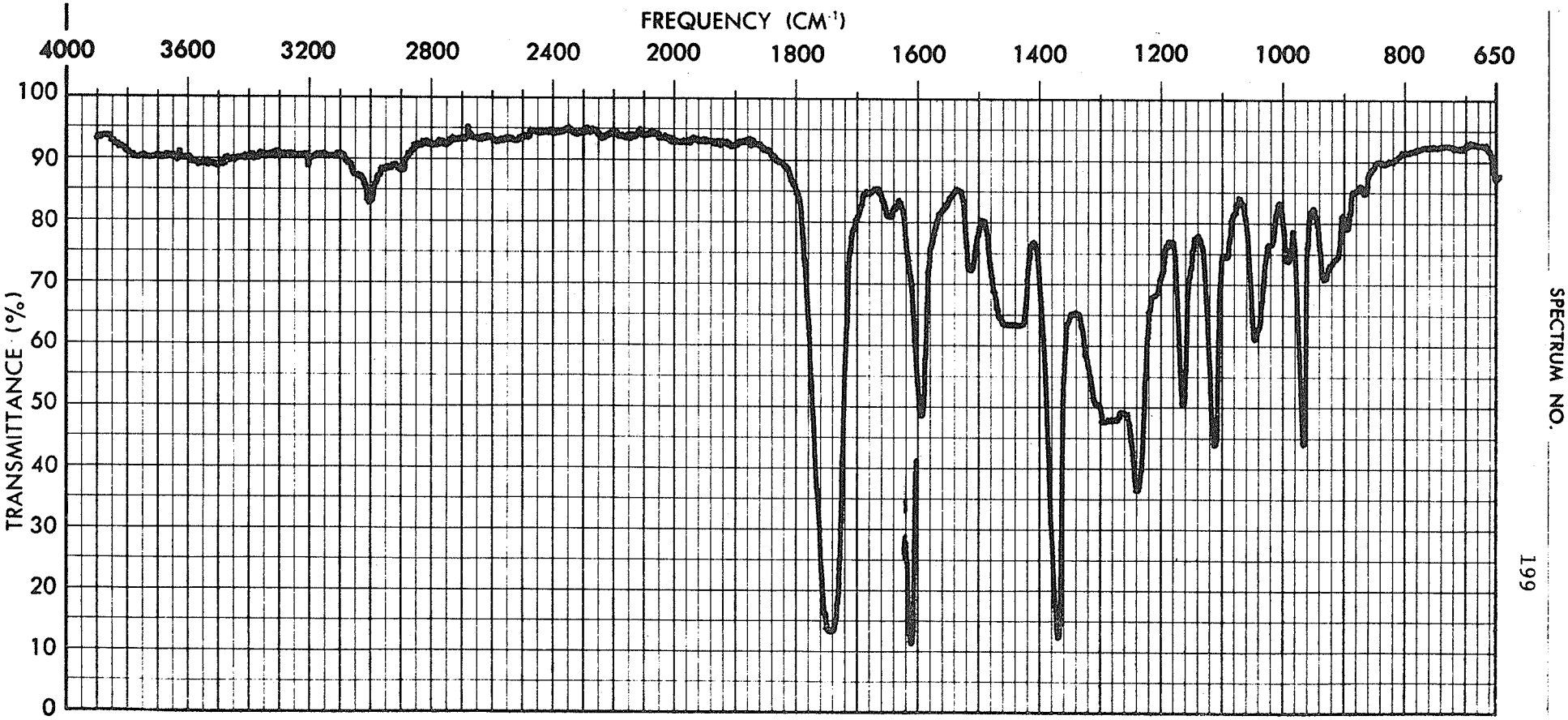
FIG. XIX: Infrared Spectrum of Dimethyl 2-(α-Phenylthioformylmethylene) -1,3-dithiole-4,5-dicarboxylate (198c); Methylene chloride solution (P.E. model 700).



198c



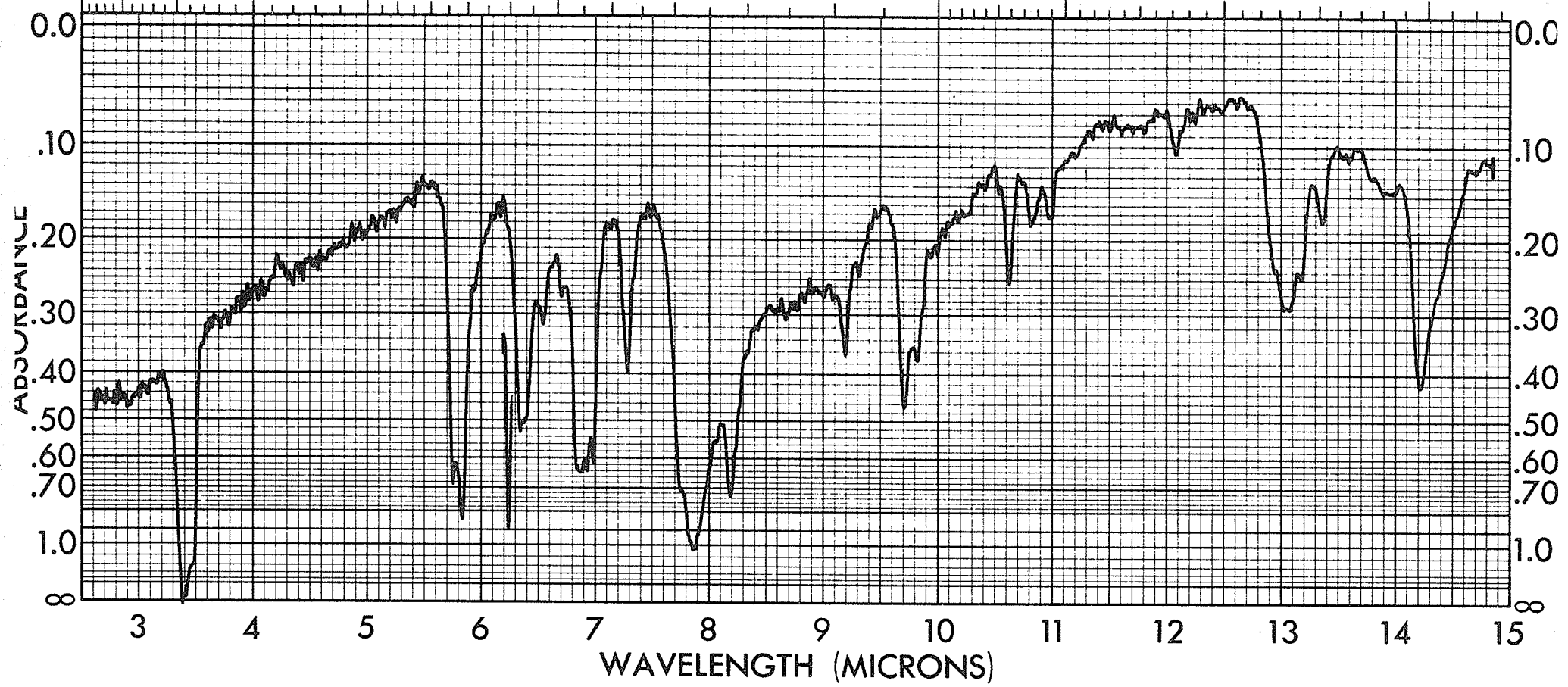
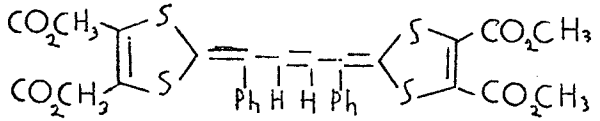


FIG. XX: Infrared Spectrum of Tetramethyl 1,4-Diphenyl-1,4-butenediylidene-2,2'-bis(1,3-dithiole-4,5-dicarboxylate) (200c).



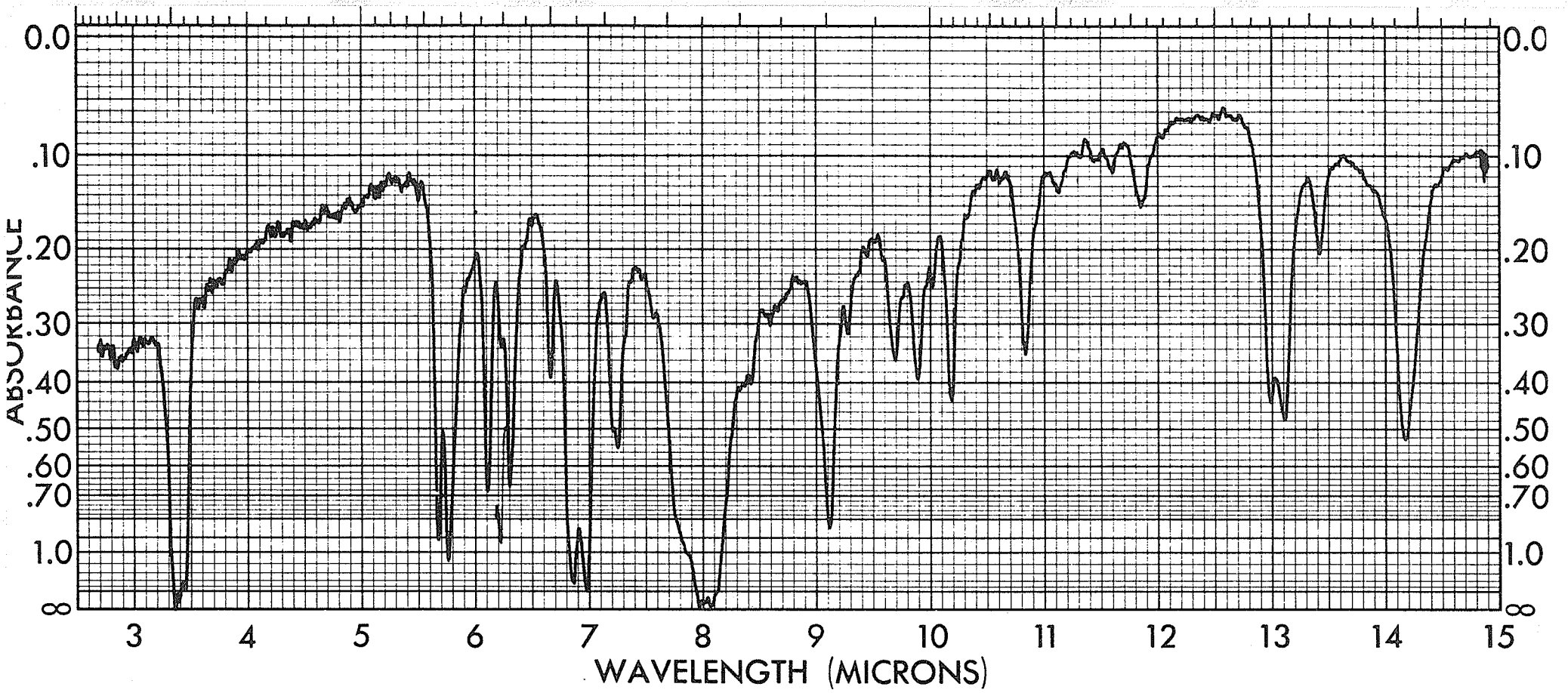
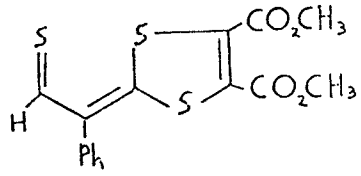
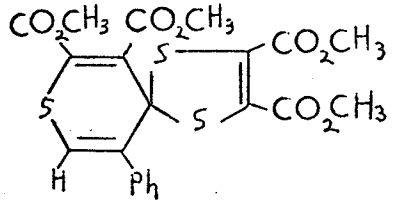


FIG. XXI: Infrared Spectrum of Dimethyl 2-(α-Phenylformylmethylene)-1,3-dithiole-4,5-dicarboxylate (201a).



201

FIG. XXII: Infrared Spectrum of Tetramethyl 1,3-Dithiole-4,5-dicarboxylate-2-spiro-4-(3-phenylthiopyran-5,6-dicarboxylate) (199a); Methylene chloride solution (P.E. model 700).



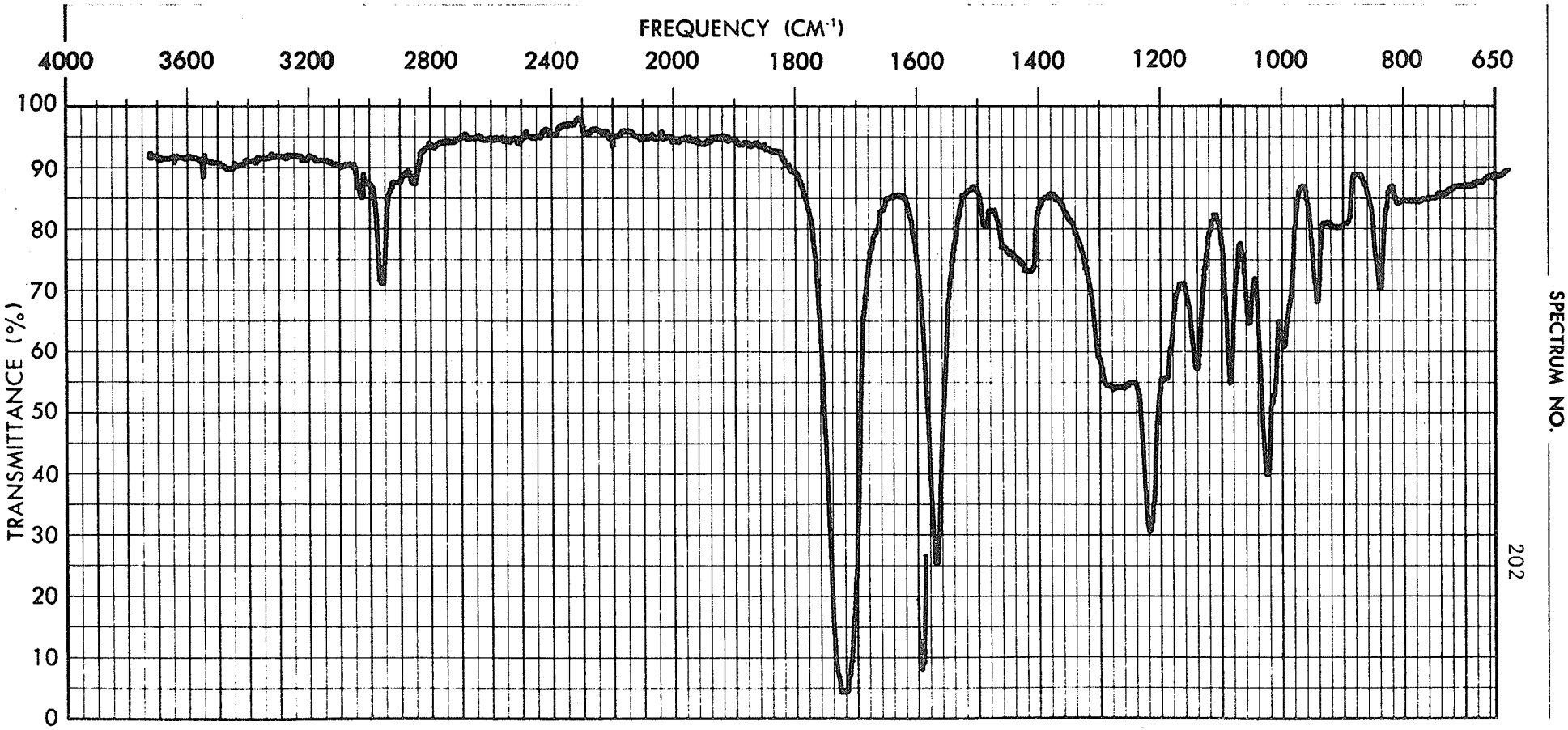
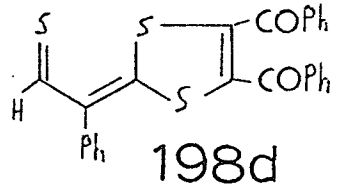
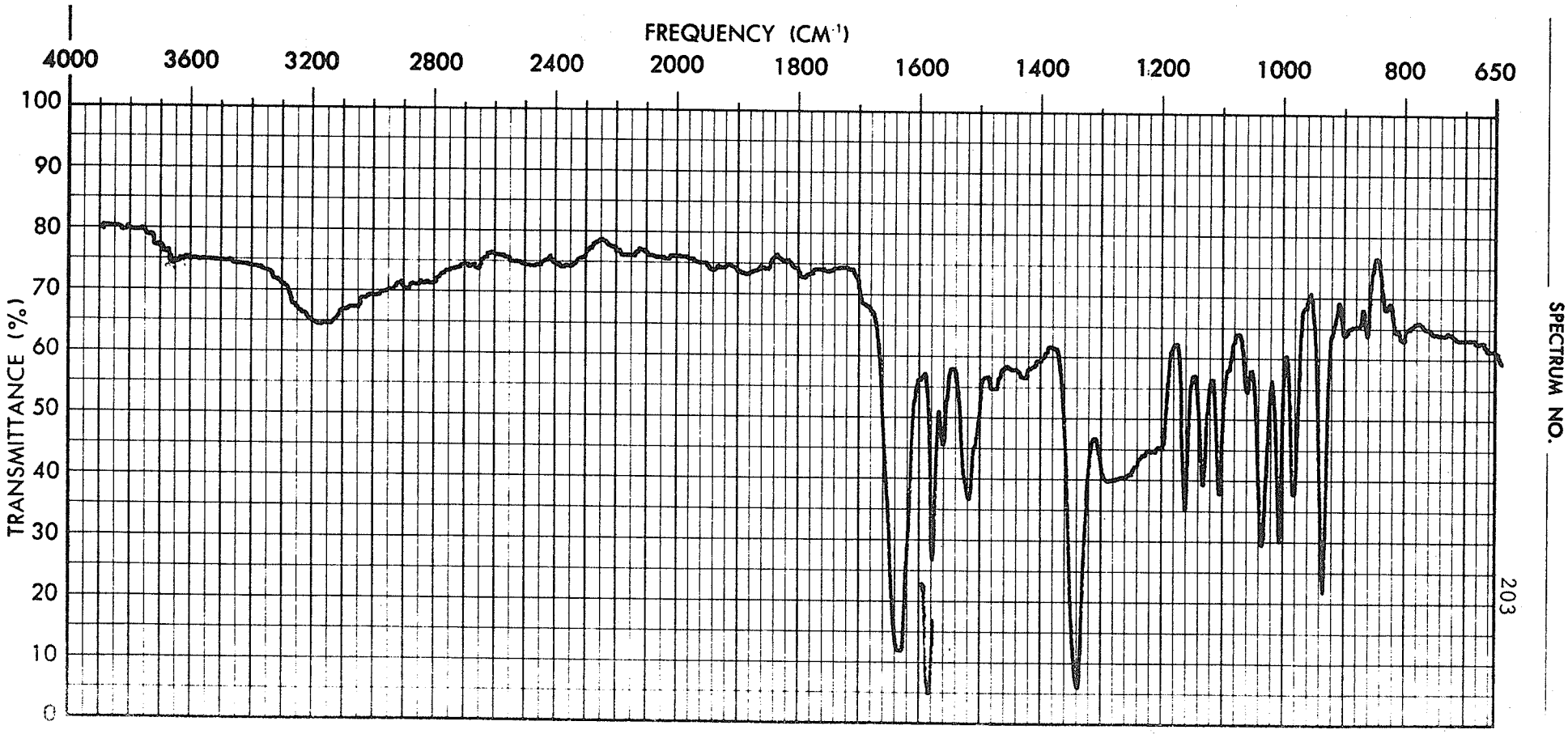


FIG. XXIII: Infrared Spectrum of 2-α-Phenylthioformylmethylene-4,5-dibenzoyl-1,3-dithiole (198d); Methylene chloride solution (P.E. model 700).



198d



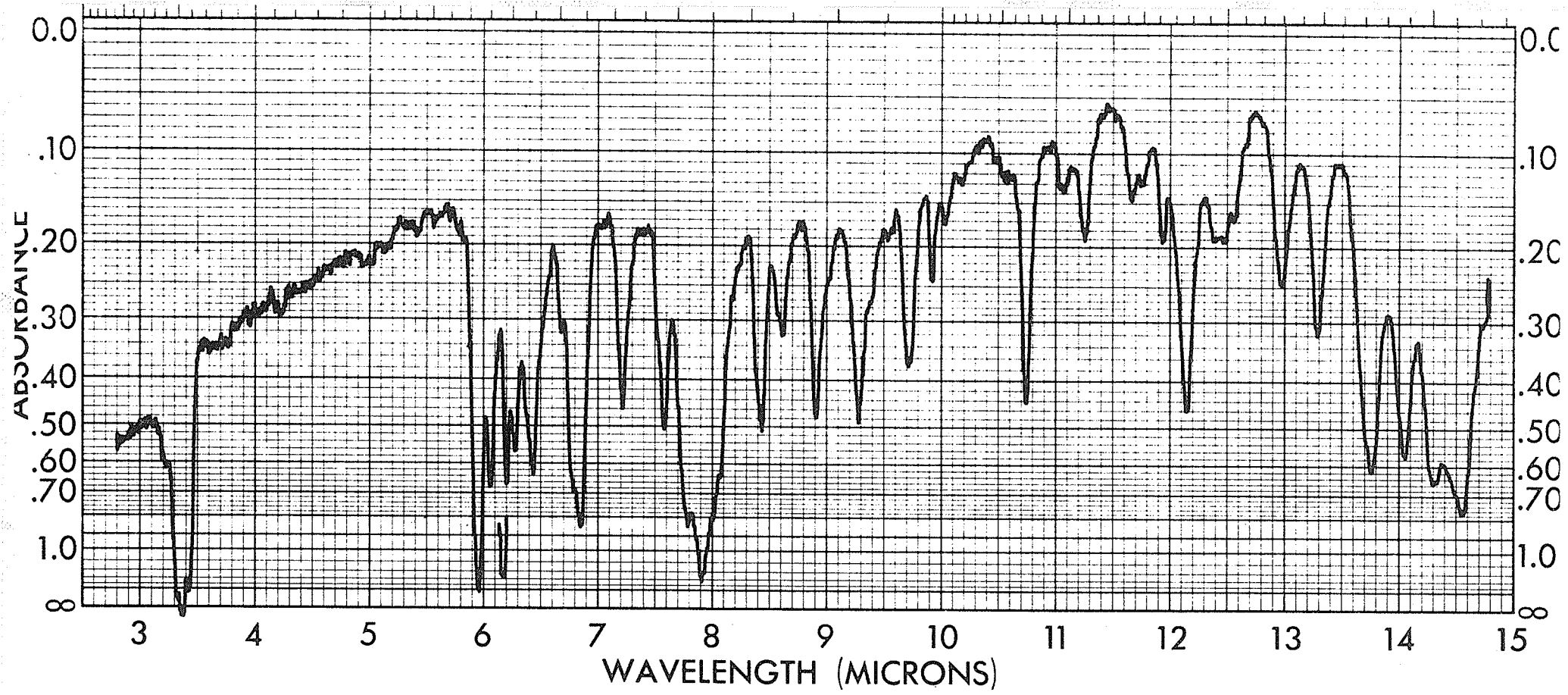
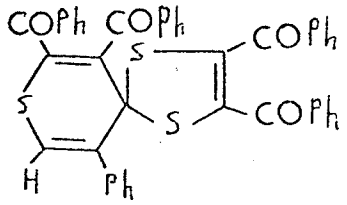


FIG. XXIV: Infrared Spectrum of 4-5-Dibenzoyl-1,3-dithiole-2-spiro-4-(3-phenyl-4,5-dibenzoylthiopyran) (199b).



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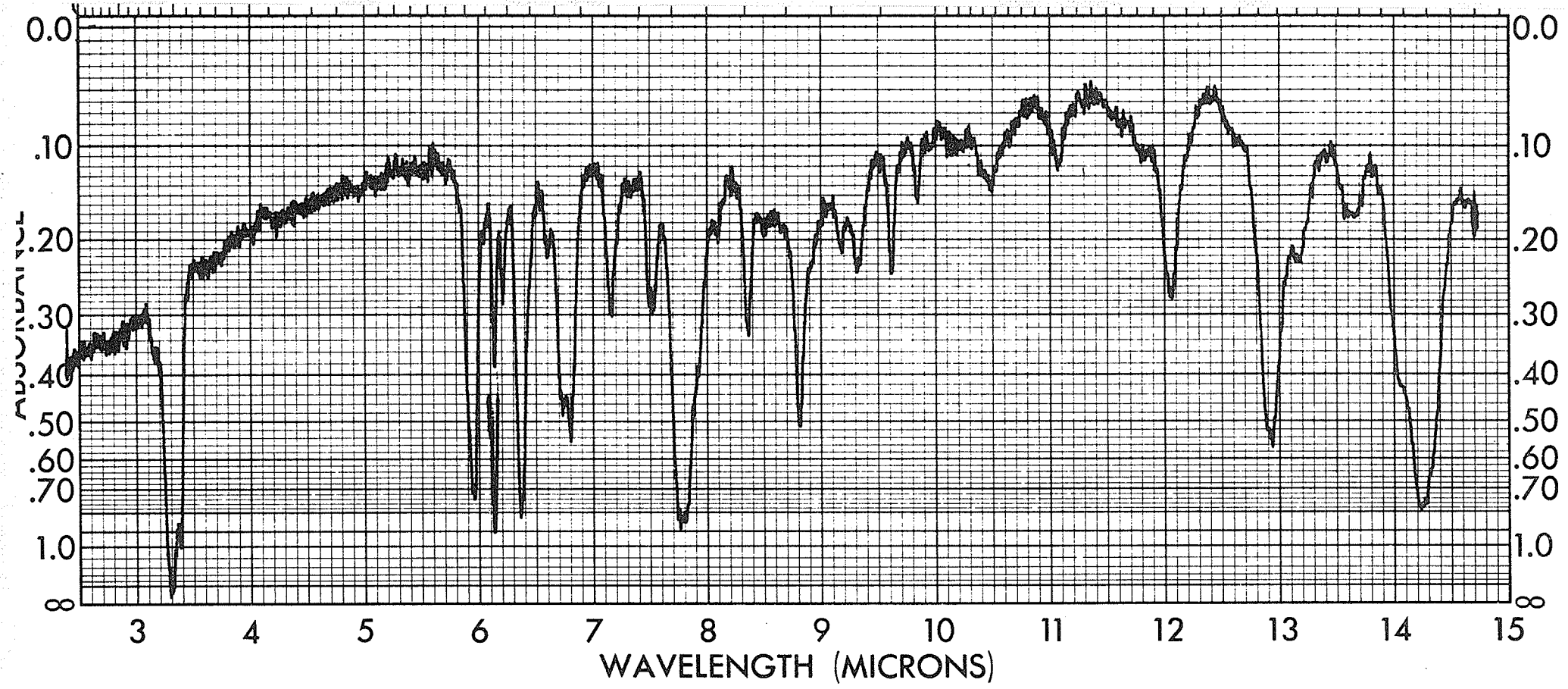

FIG. XXV: Infrared Spectrum of 1,4-Butenediylidene-2,2'-bis(4,5-dibenzoyl-1,3-dithiole) (200d).

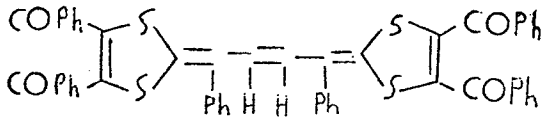

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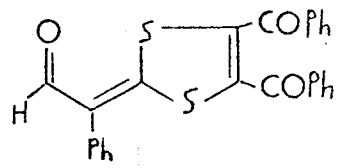
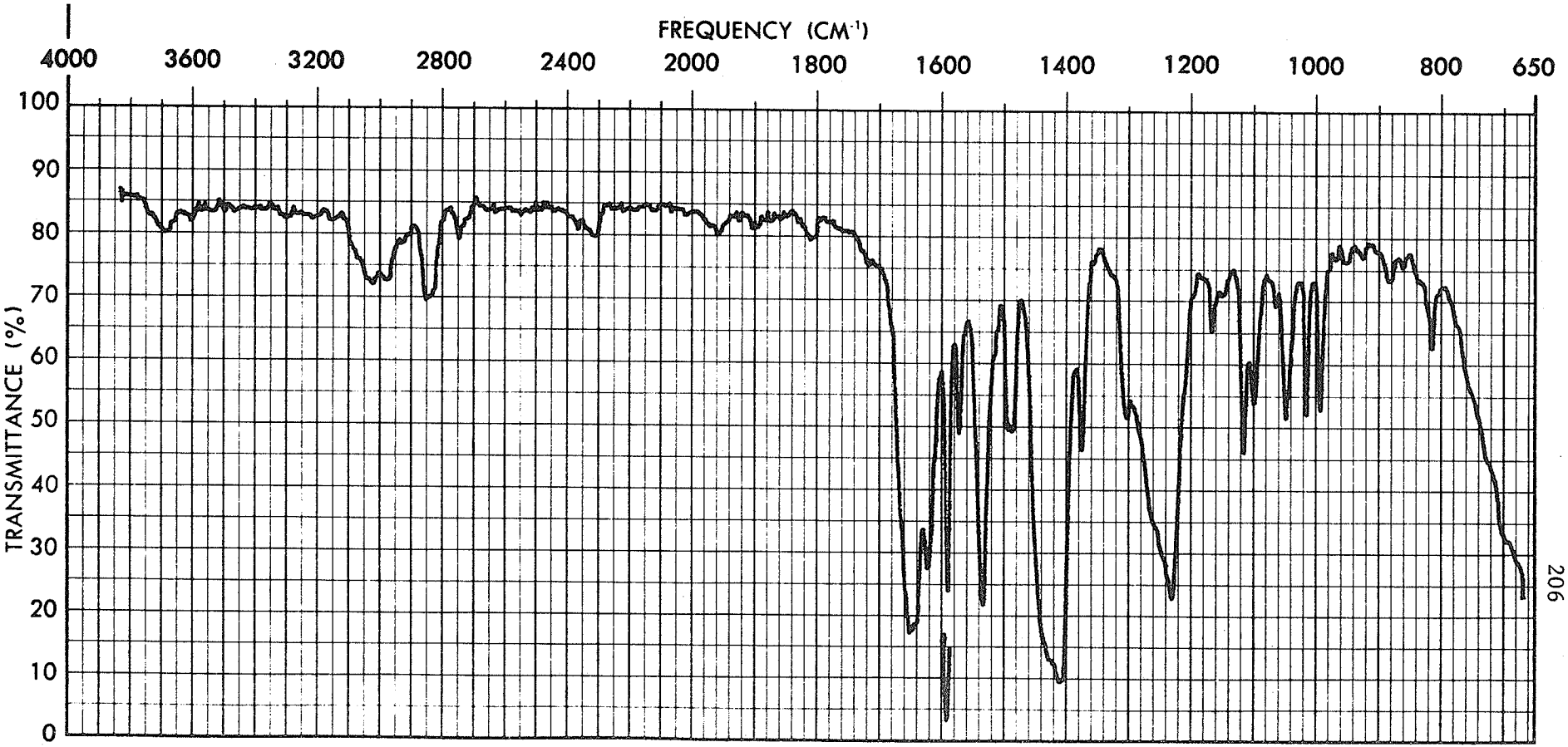
FIG. XXVI: Infrared Spectrum of 4,5-Dibenzoyl-2(α-phenylformylmethylene) -1,3-dithiole (201b); Methylene chloride solution (P.E. model 700).





SAMPLE

SPECTRUM NO. 206

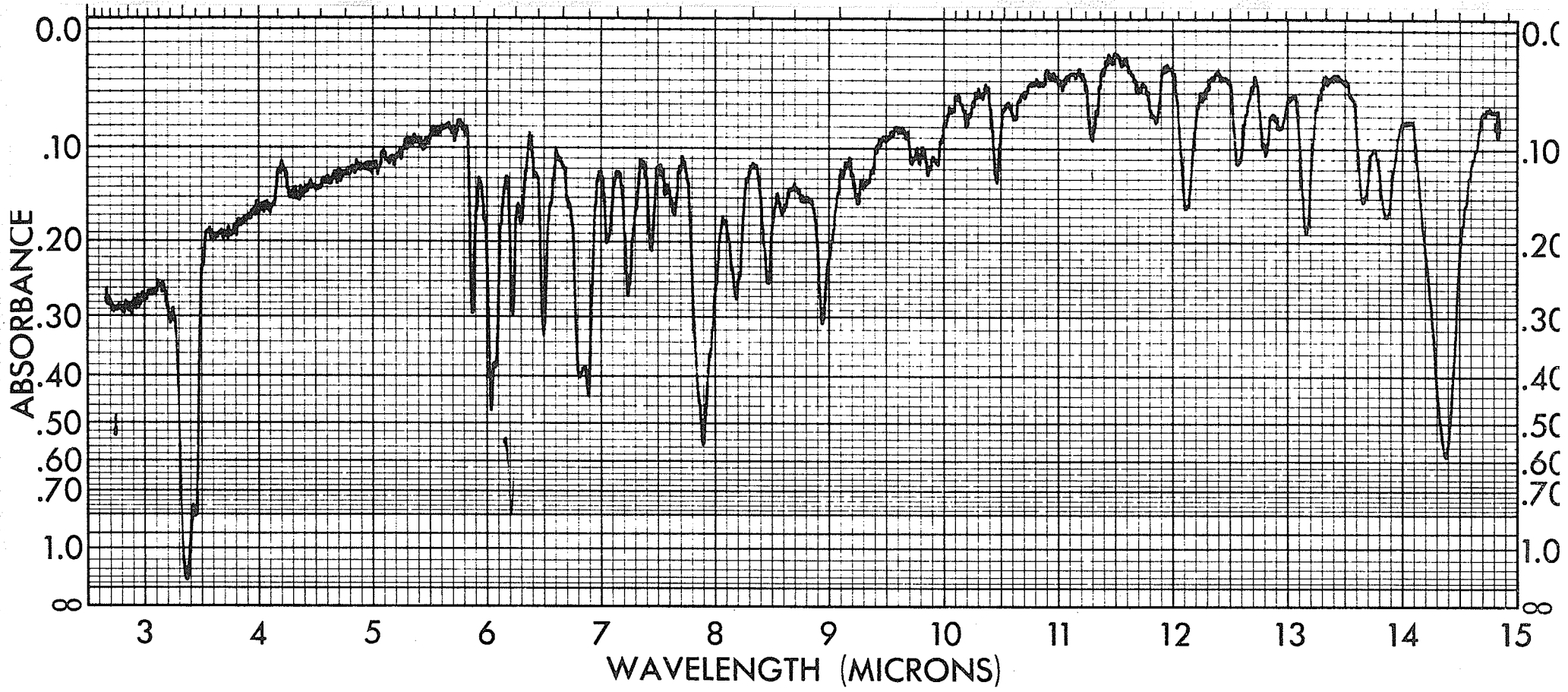


FIG. XXVII: Infrared Spectrum of Orange Solid Formed by Reaction of 4,5-Dibenzoyl-2-(α-phenylthioformylmethylene)-1,3-dithiole (198d) with Dibenzoylacetylene.

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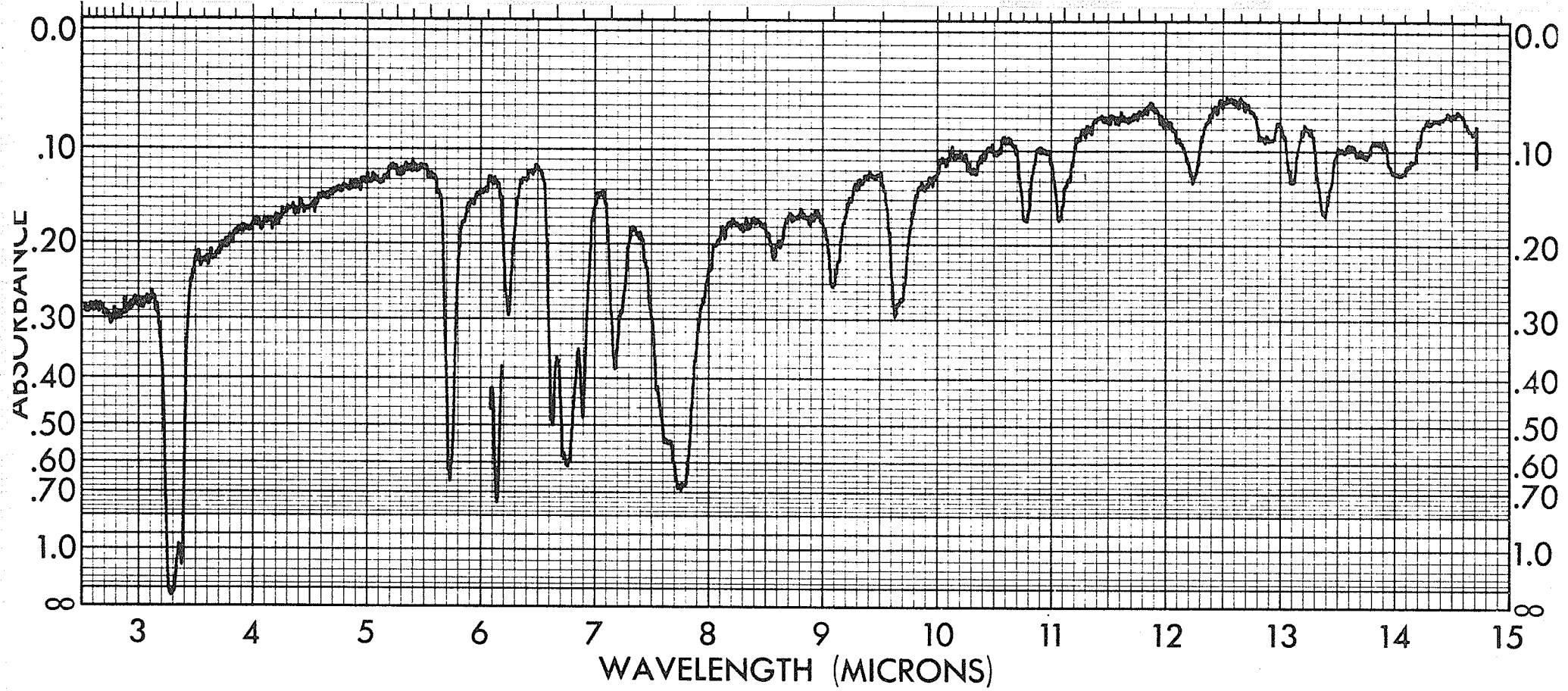
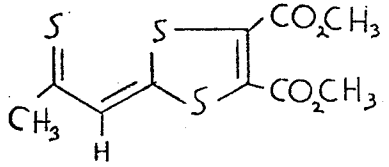


FIG. XXVIII: Infrared Spectrum of Dimethyl 2-Acetonylidene-1,3-dithiole-4,5-dicarboxylate (93d).



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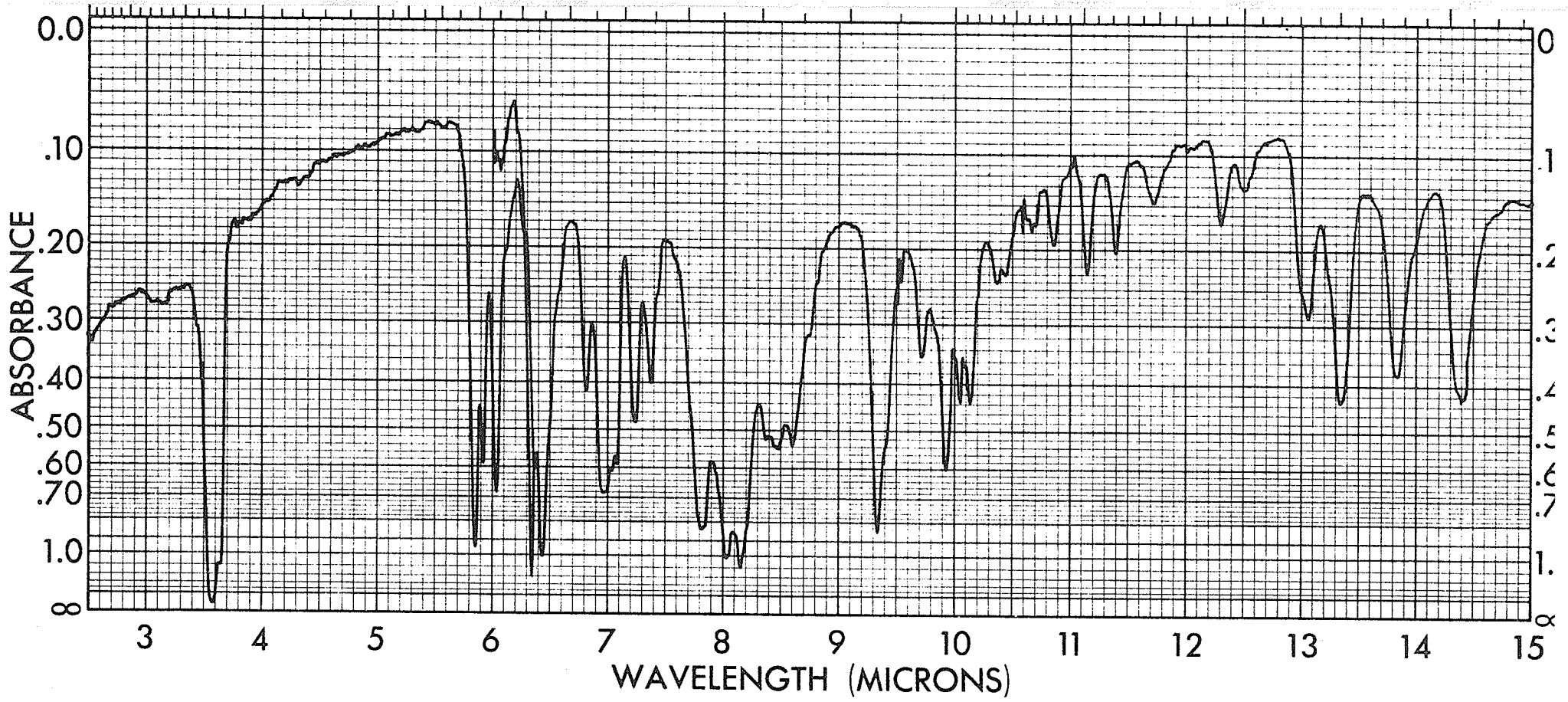
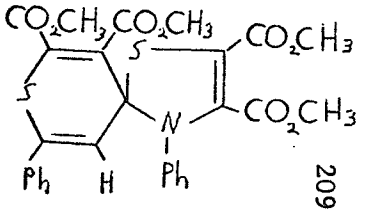


FIG. XXIX: Infrared Spectrum of Tetramethyl N-Phenylthiazole-4,5-dicarboxylate-2-spiro-4-(2-phenylthiopyran-5,6-dicarboxylate) (233a).



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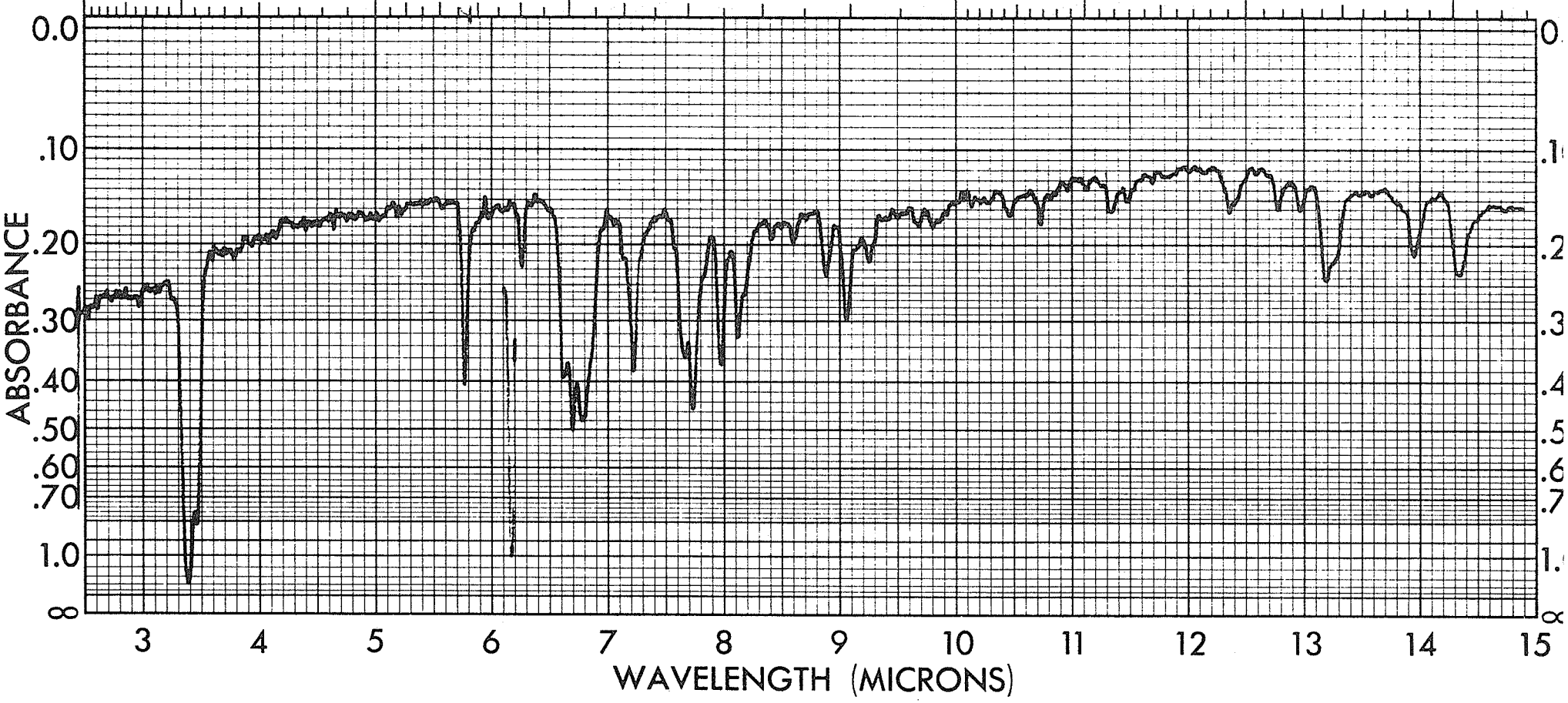
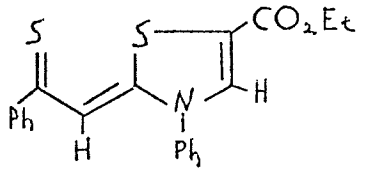


FIG. XXX: Infrared Spectrum of Ethyl N-Phenyl-2-thiophenacylidenethiazole-5-carboxylate (232a).



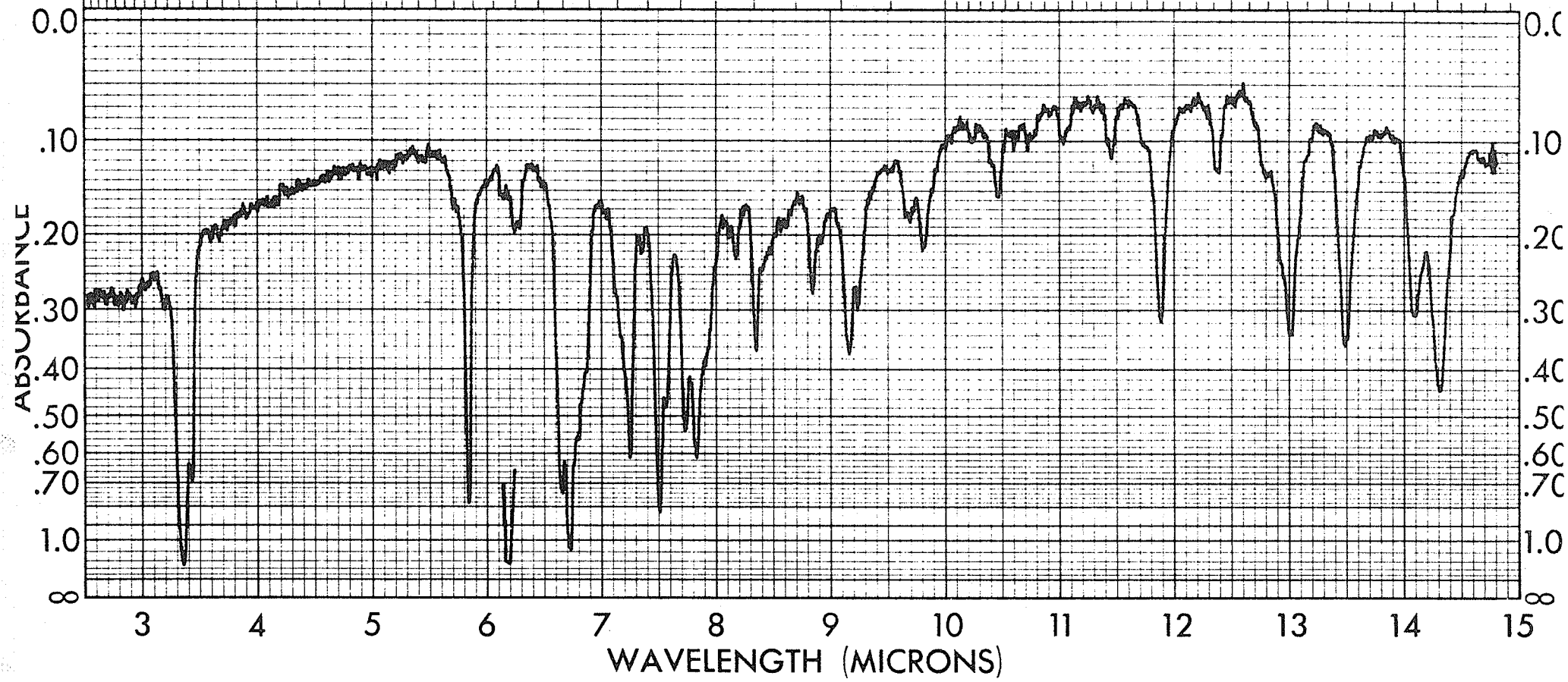
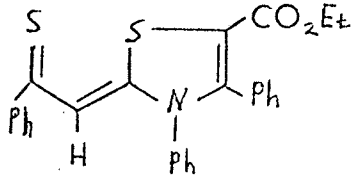


FIG. XXXI: Infrared Spectrum of Ethyl N-Phenyl-4-phenyl-2-thiophenacylidene-thiazole-5-carboxylate (232b).



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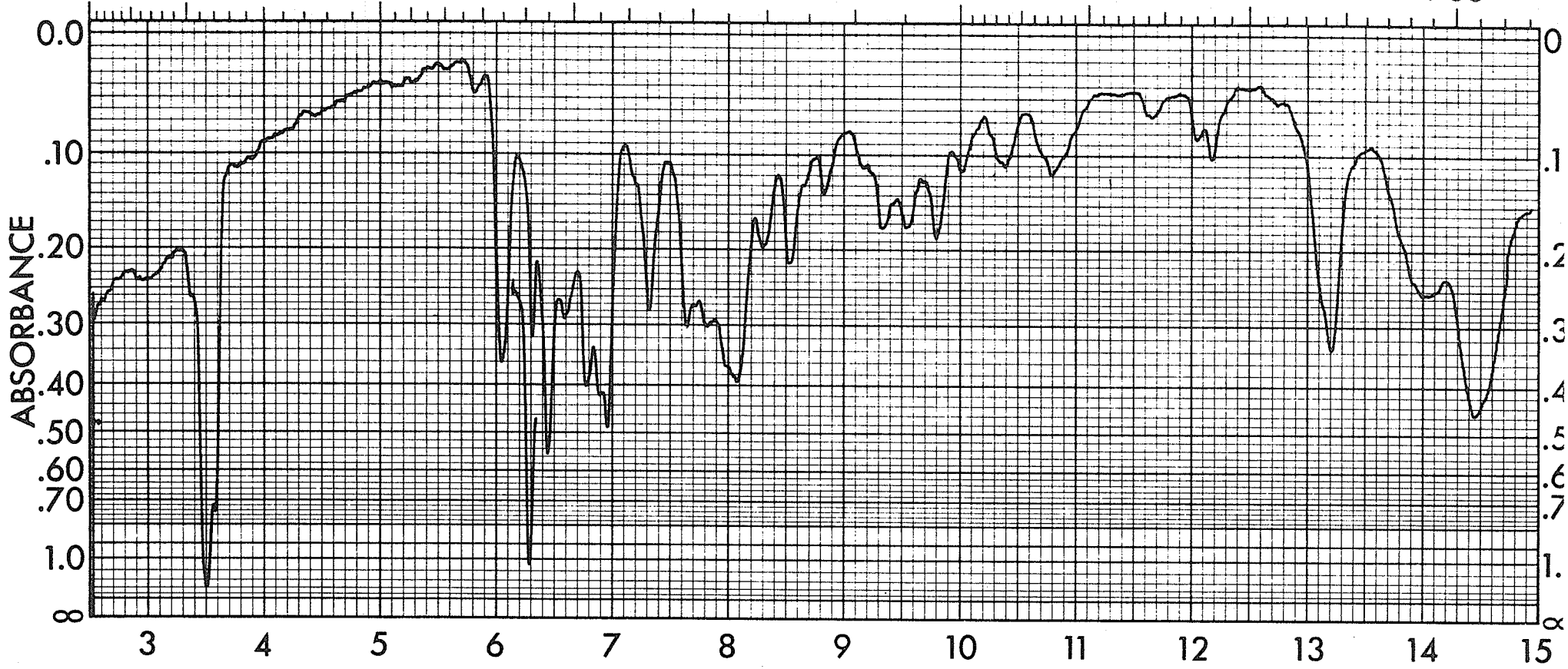


FIG. XXXII: Infrared Spectrum of the Major Product formed from the Reaction of 3-Phenylimino-5-phenyl-1,2-dithiole with Dibenzoylacetylene.

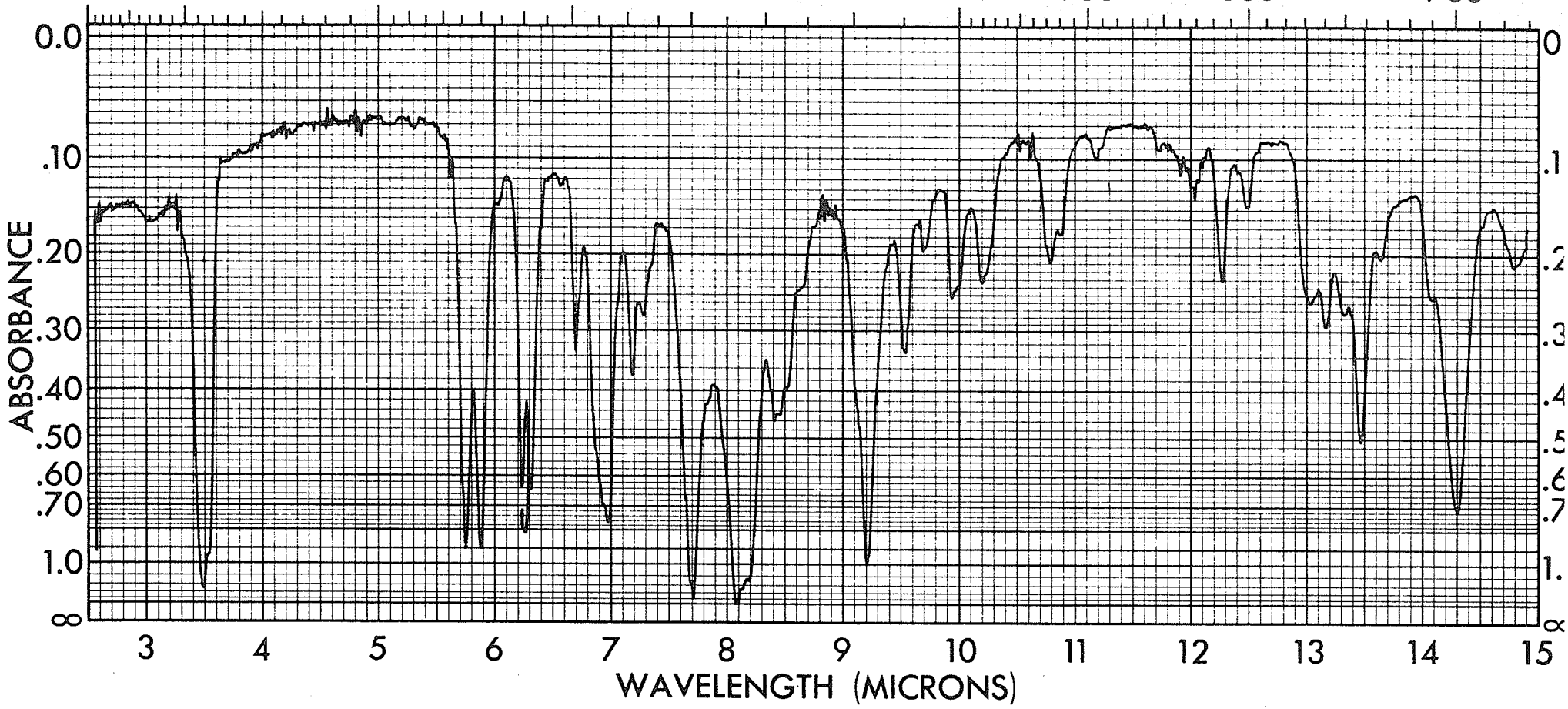
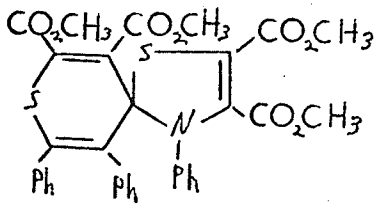


FIG. XXXIII: Infrared Spectrum of Tetramethyl N-Phenylthiazole-4,5-dicarboxylate-2-spiro-4-(2,3-diphenylthiopyran-5,6-dicarboxylate) (233b).



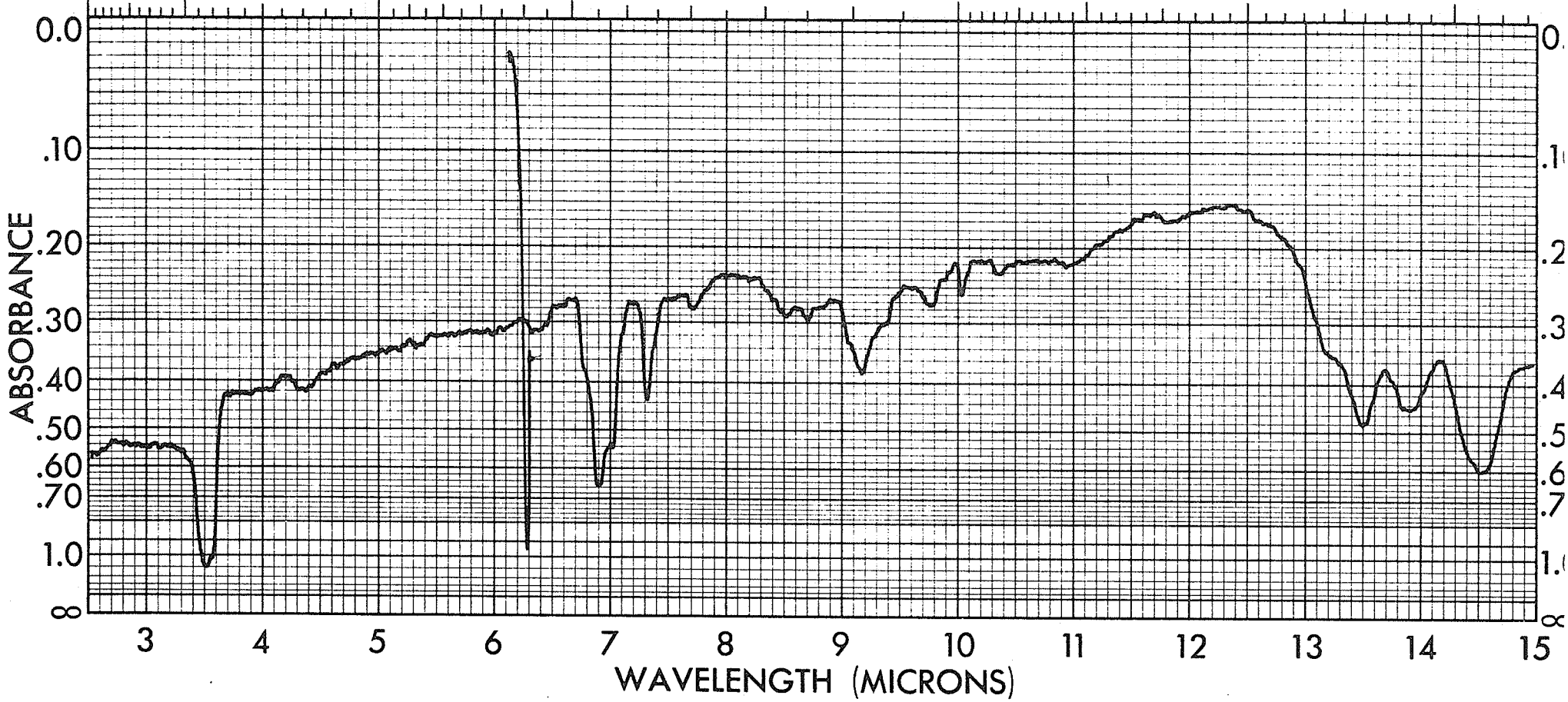


FIG. XXXIV: Infrared Spectrum of Yellow Amorphous Powder Formed by Reaction of 3-Phenyl-1,2-dithiolium Perchlorate with Phenyl Phosphine.

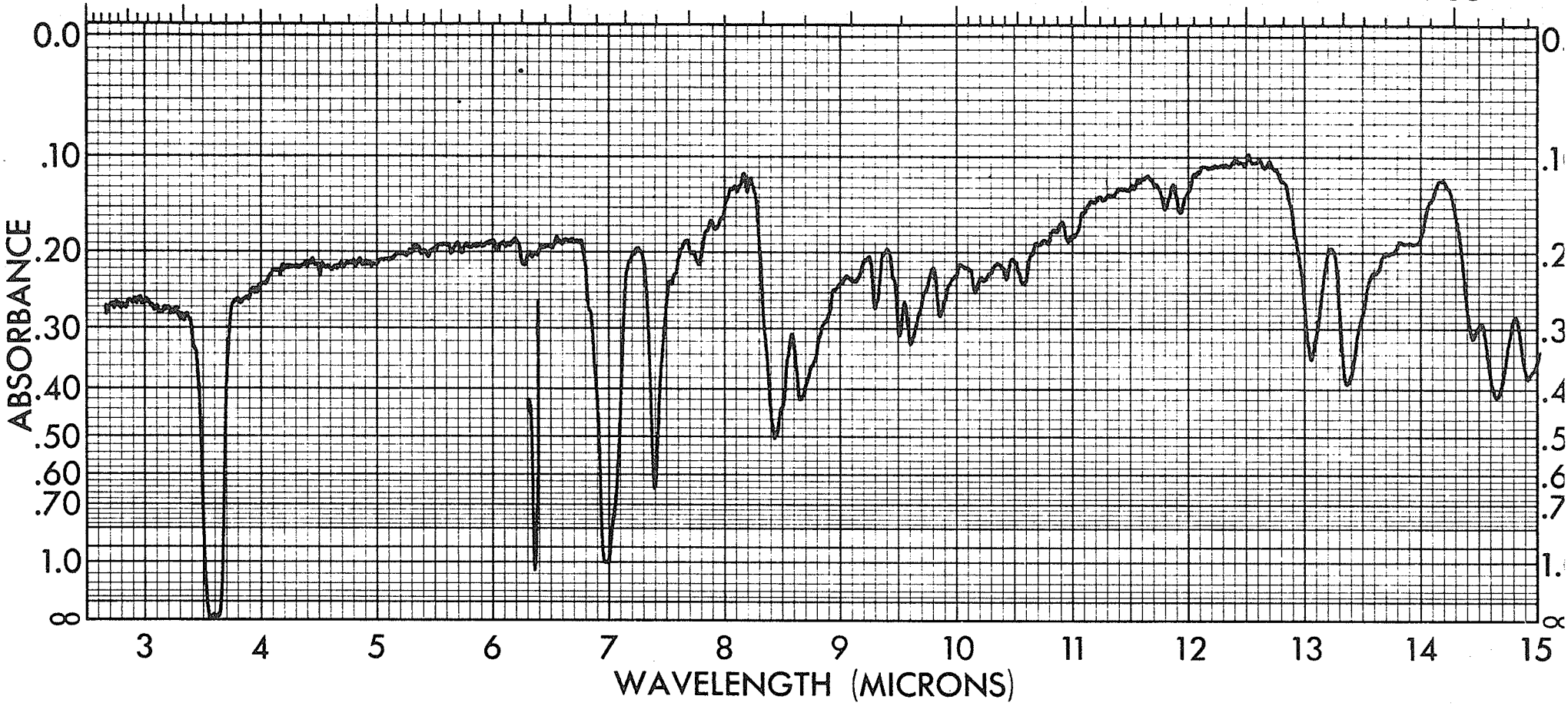
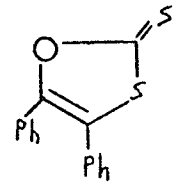


FIG. XXXV: Infrared Spectrum of 4,5-Diphenyl-1,3-thiaoxole-2-thione (277).



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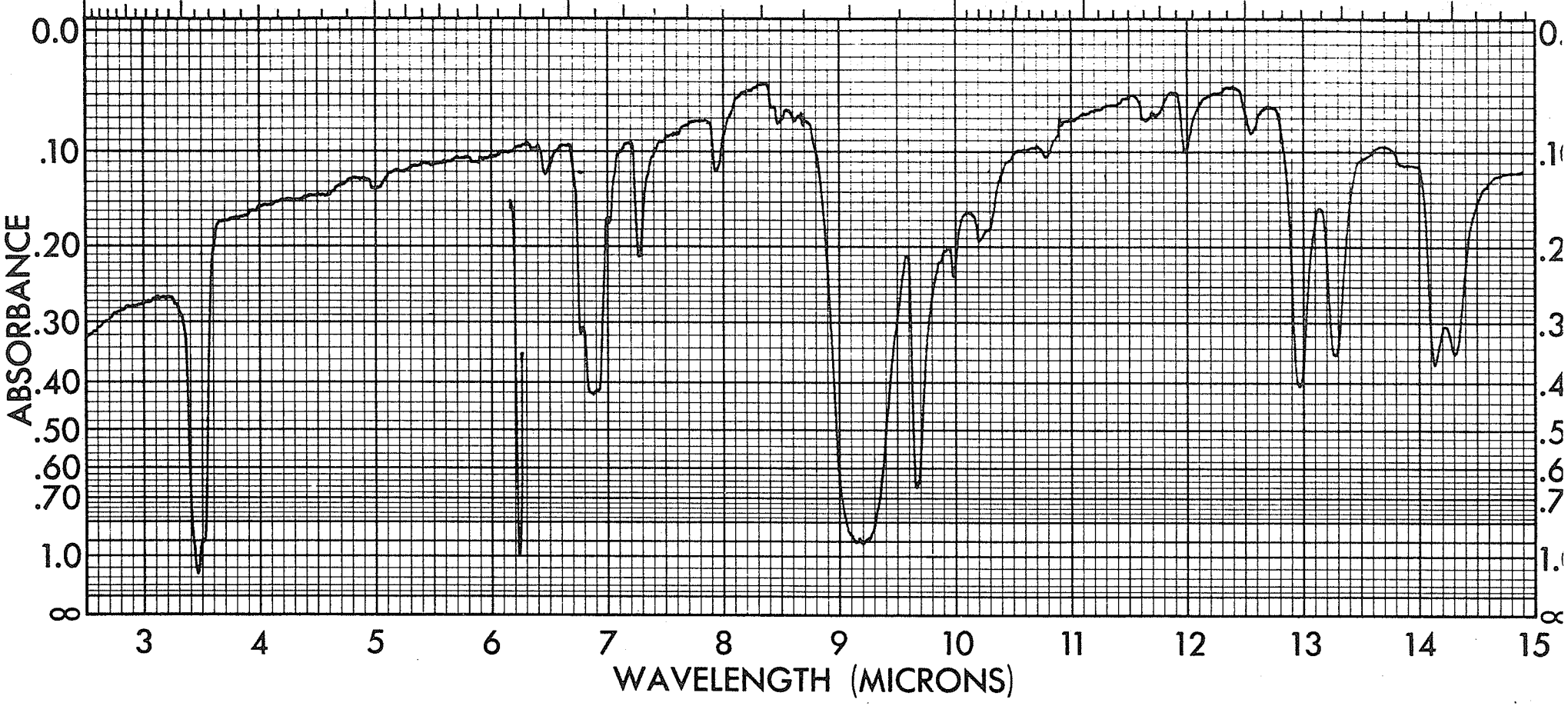
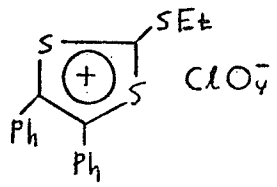


FIG. XXXVI: Infrared Spectrum of 4,5-Diphenyl-2-ethylthio-1,3-dithiolium Perchlorate (275).



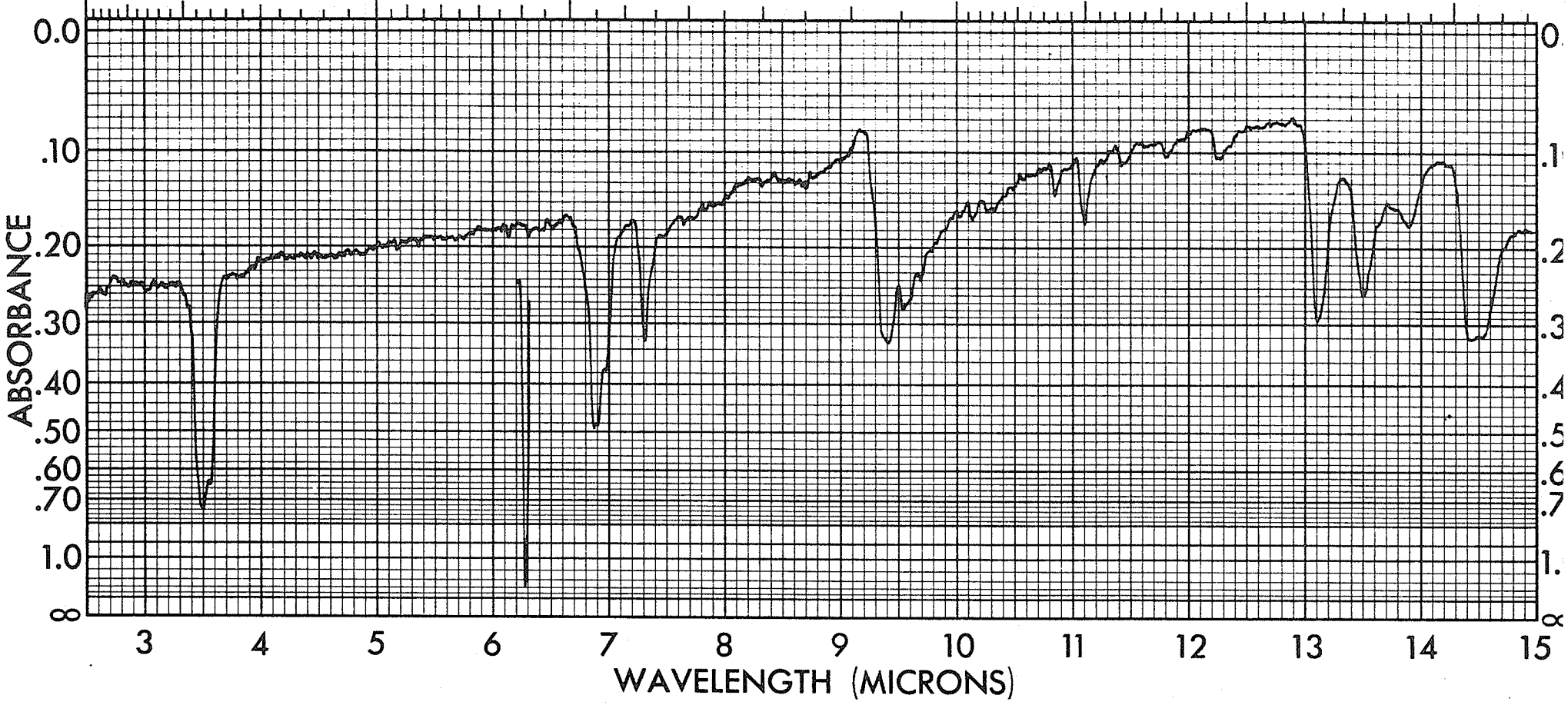
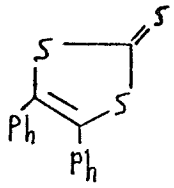


FIG. XXXVII: Infrared Spectrum of 4,5-Diphenyl-1,3-dithiole-2-thione (271a).



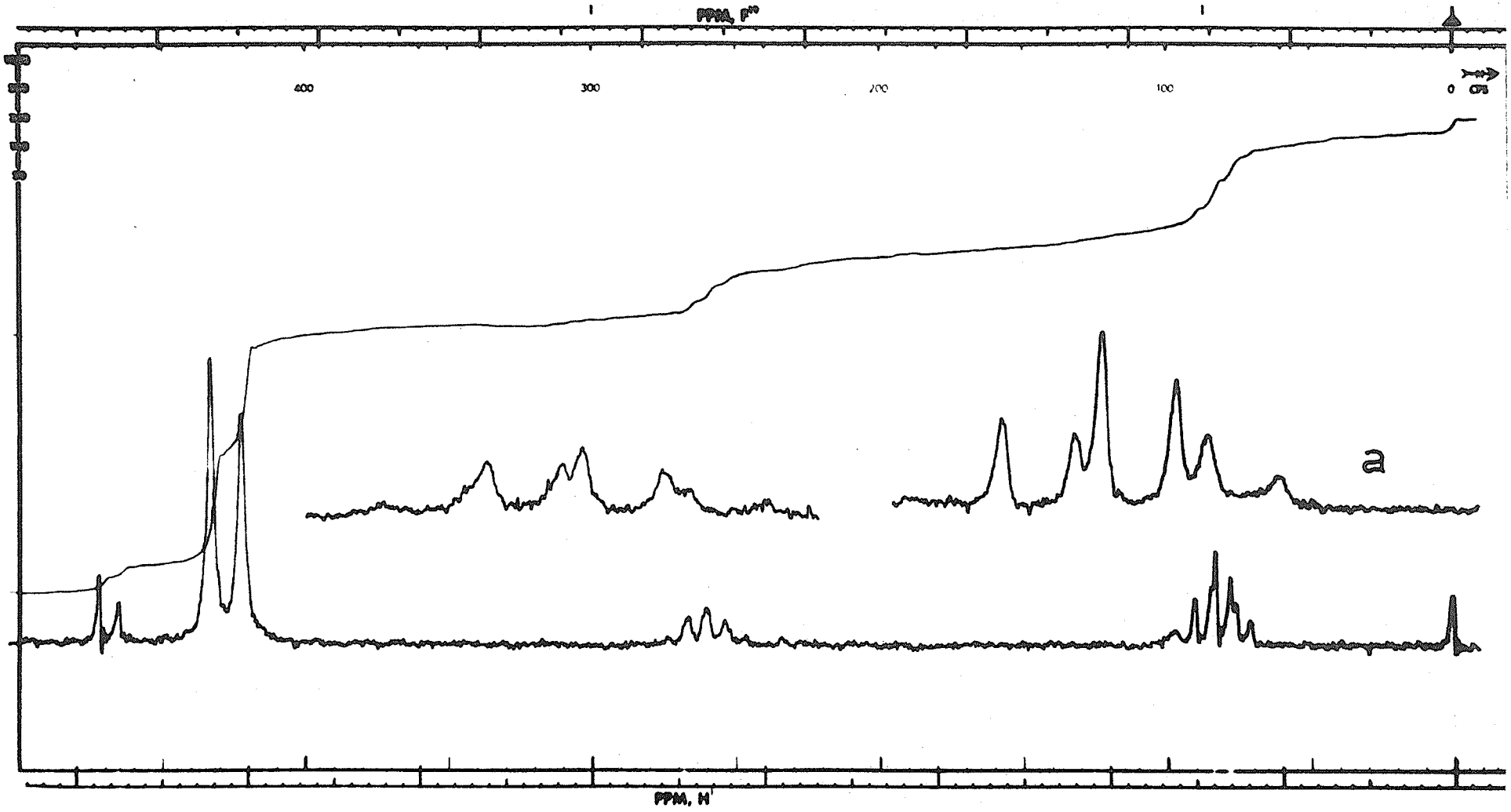
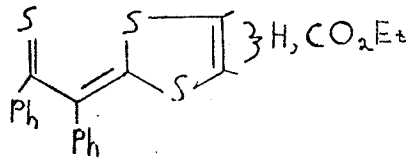


FIG. I: N.M.R. Spectrum of Ethyl 2-(α-Phenylthiophenacylidene)-1,3-dithiole-4, or 5-carboxylate (93a'); Sweep Width 500 Hz. *a* : Sweep Width 100 Hz.



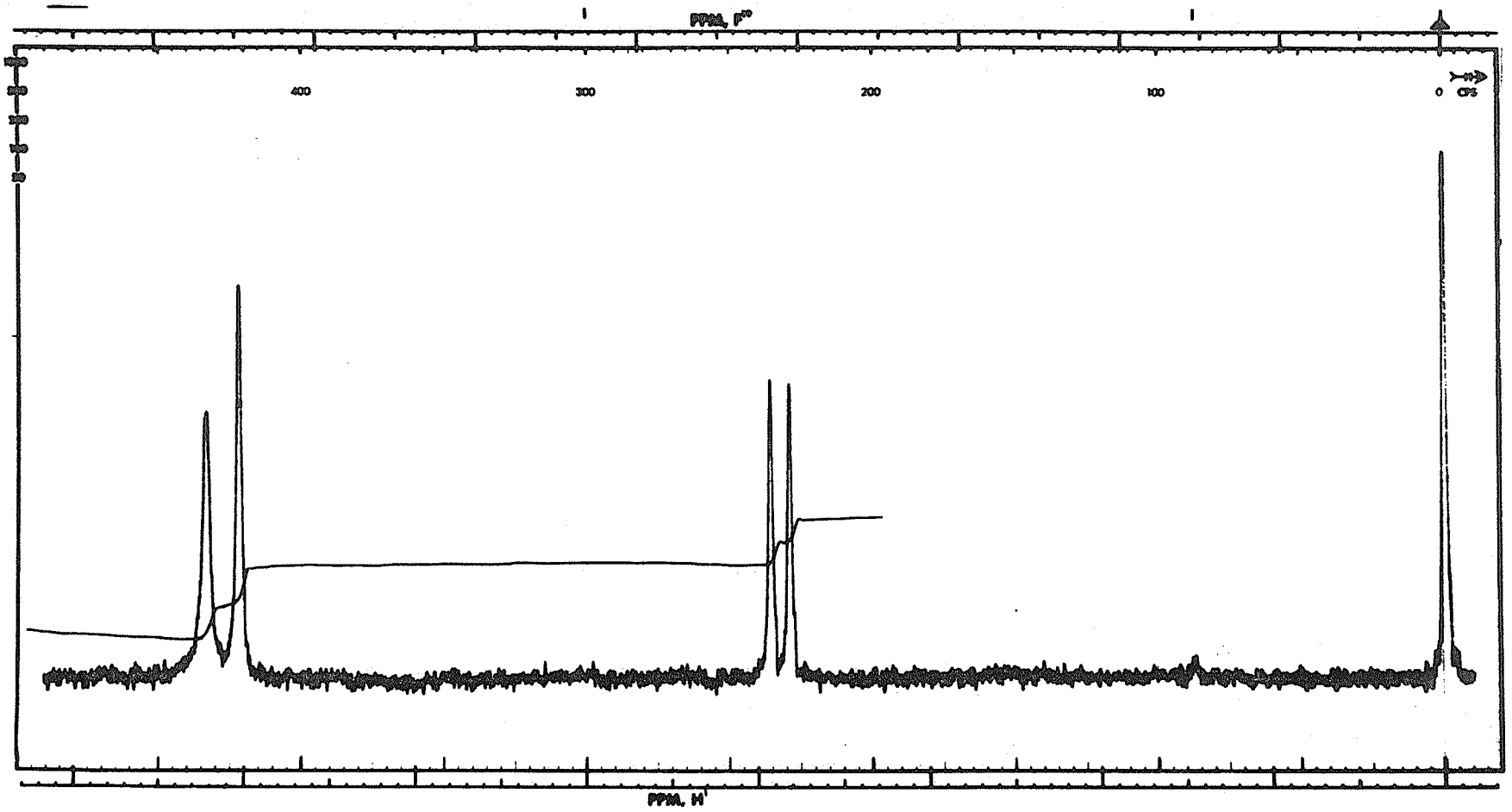
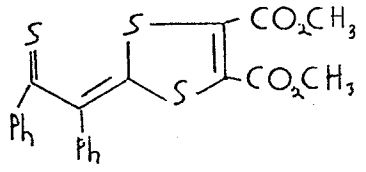
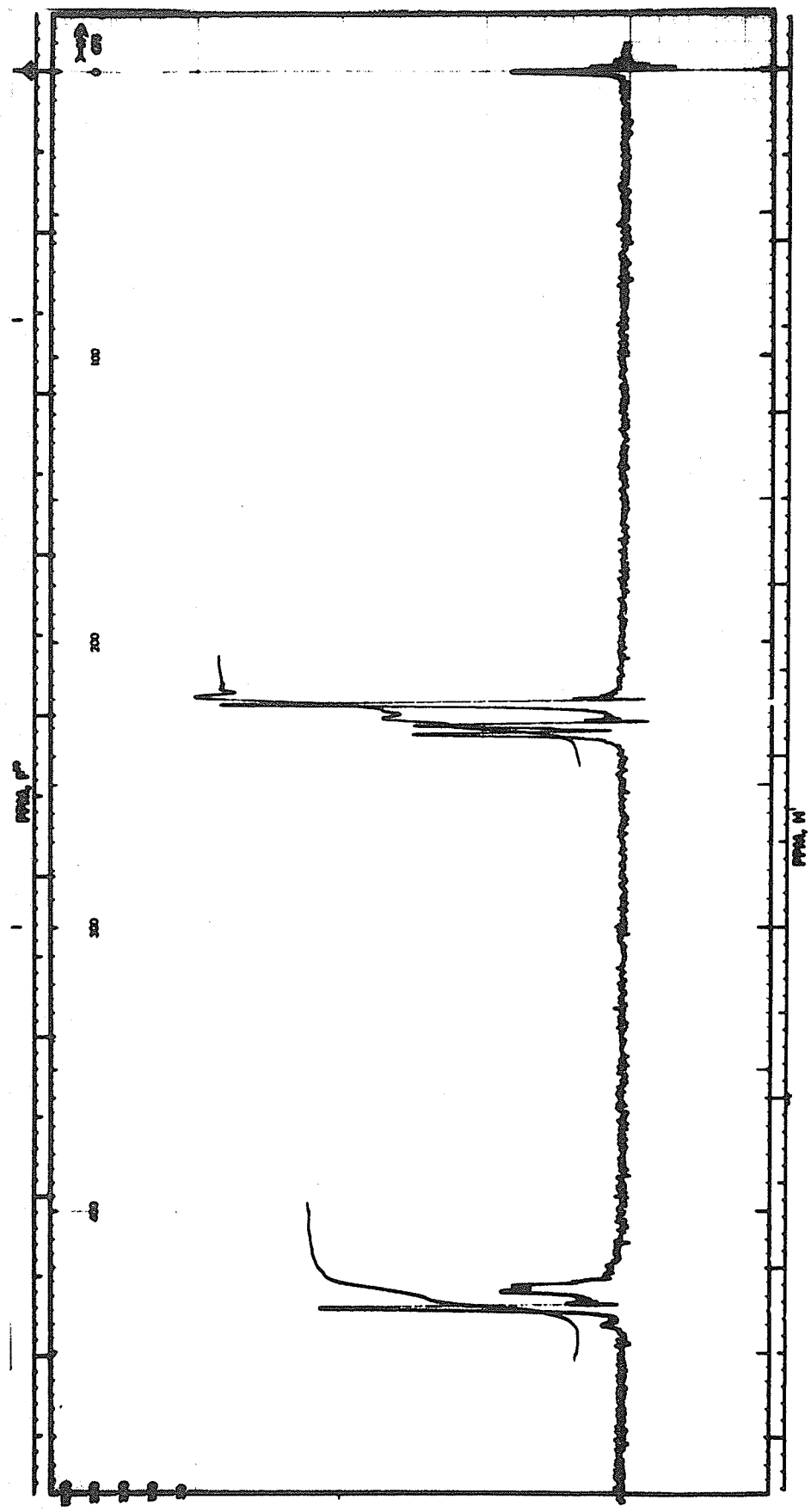


FIG. XXXVIII: N.M.R. Spectrum of Dimethyl 2-(α-Phenylthiophenacylidene)-1,3-dithiole-4,5-dicarboxylate (93a).





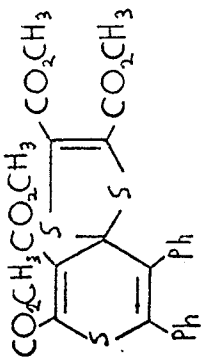
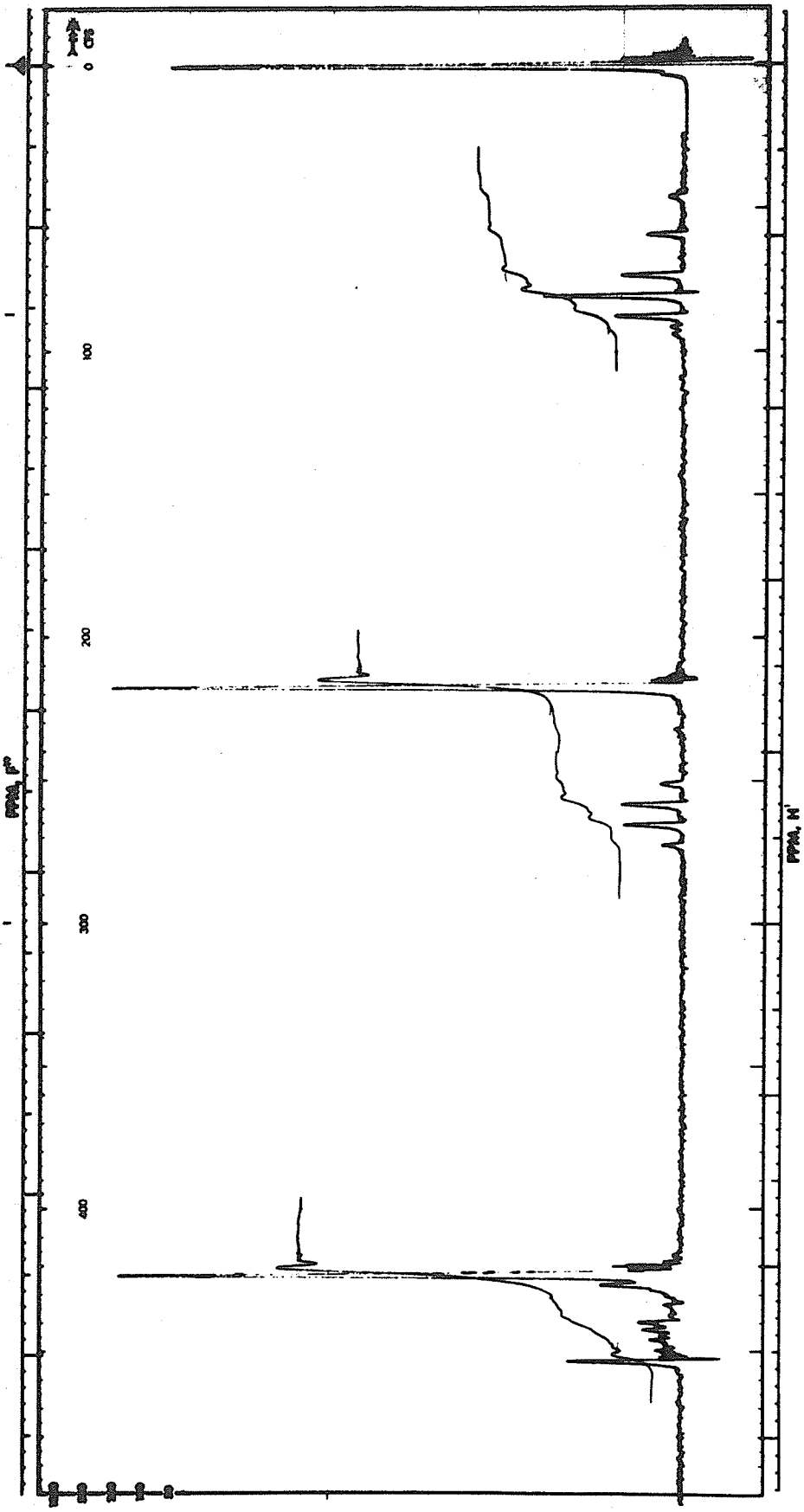


FIG. XXXIX: N.M.R. Spectrum of Tetramethyl 1,3-Dithiole-4,5-dicarboxylate-2-spiro-4-(2,3-diphenylthiopyran-5,6-dicarboxylate)(94a).



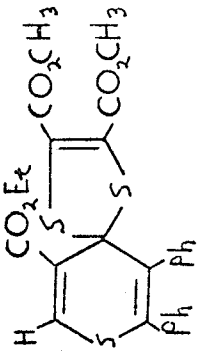


FIG. XL: N.M.R. Spectrum of Dimethyl 1,3-Dithiole-4,5-dicarboxylate-2-spiro-4-(2,3-diphenyl-5-carboethoxythiopyran) (94b); Sweep Width 500 Hz.

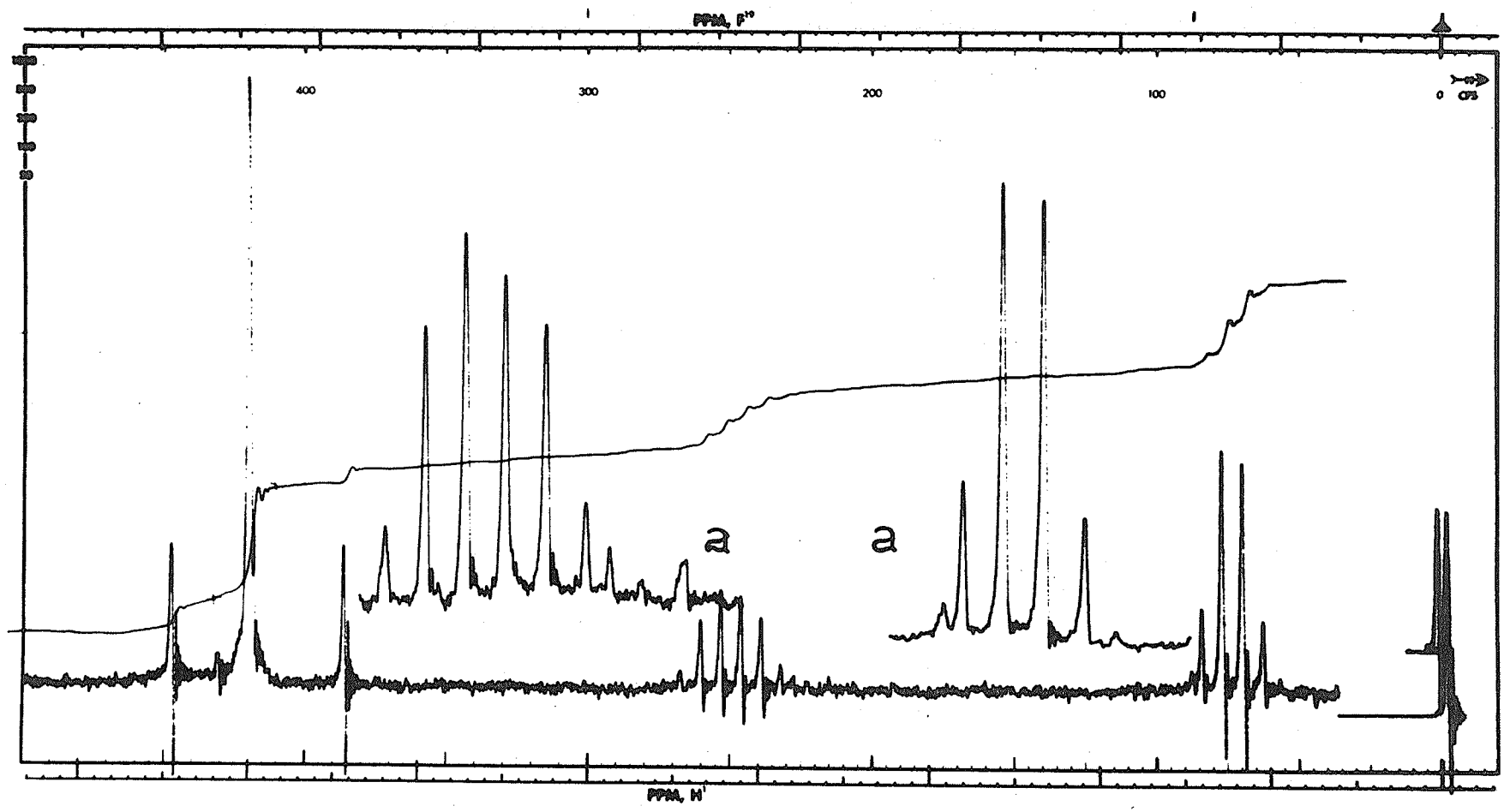
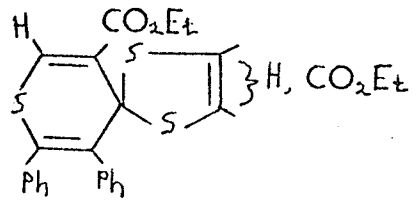


FIG. XLI: N.M.R. Spectrum of Diethyl 1,3-Dithiole-4, or 5-carboxylate-2-spiro-4-(2,3-diphenylthiopyran-5-carboxylate) (94a'); Sweep Width 500 Hz. *a* : Sweep Width 250 Hz.



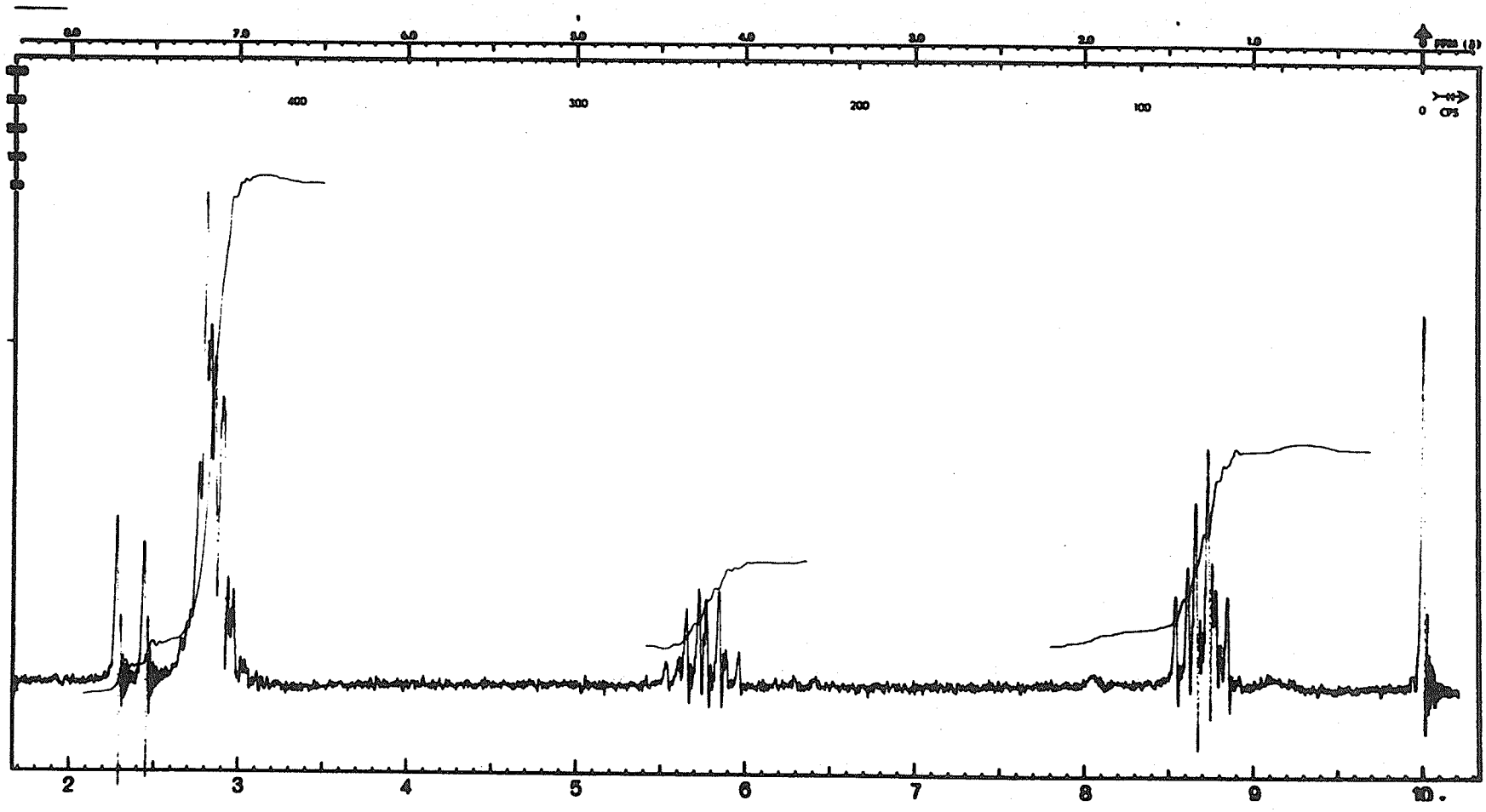
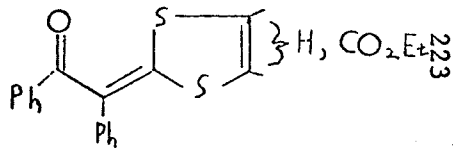


FIG. XLII: N.M.R. Spectrum of Ethyl 2-(α-Phenylphenacylidene)-1,3-dithiole-4, or 5-carboxylate (189c'); Sweep Width 500 hz.



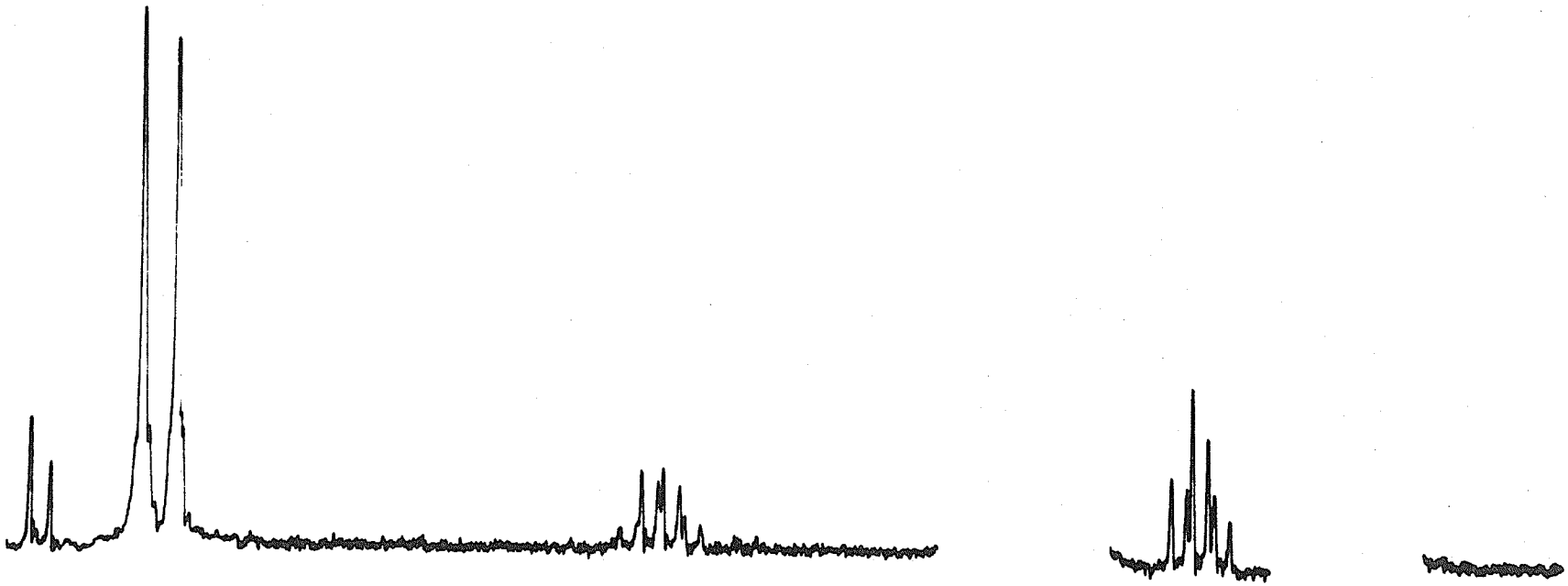
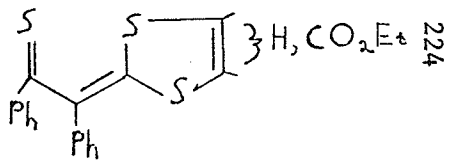


FIG. XLIII: N.M.R. Spectrum of Ethyl 2-(α-Phenylthiophenacylidene-1,3-dithiole-4, or 5-carboxylate (93a'); Sweep Width 500 Hz. (72°C).



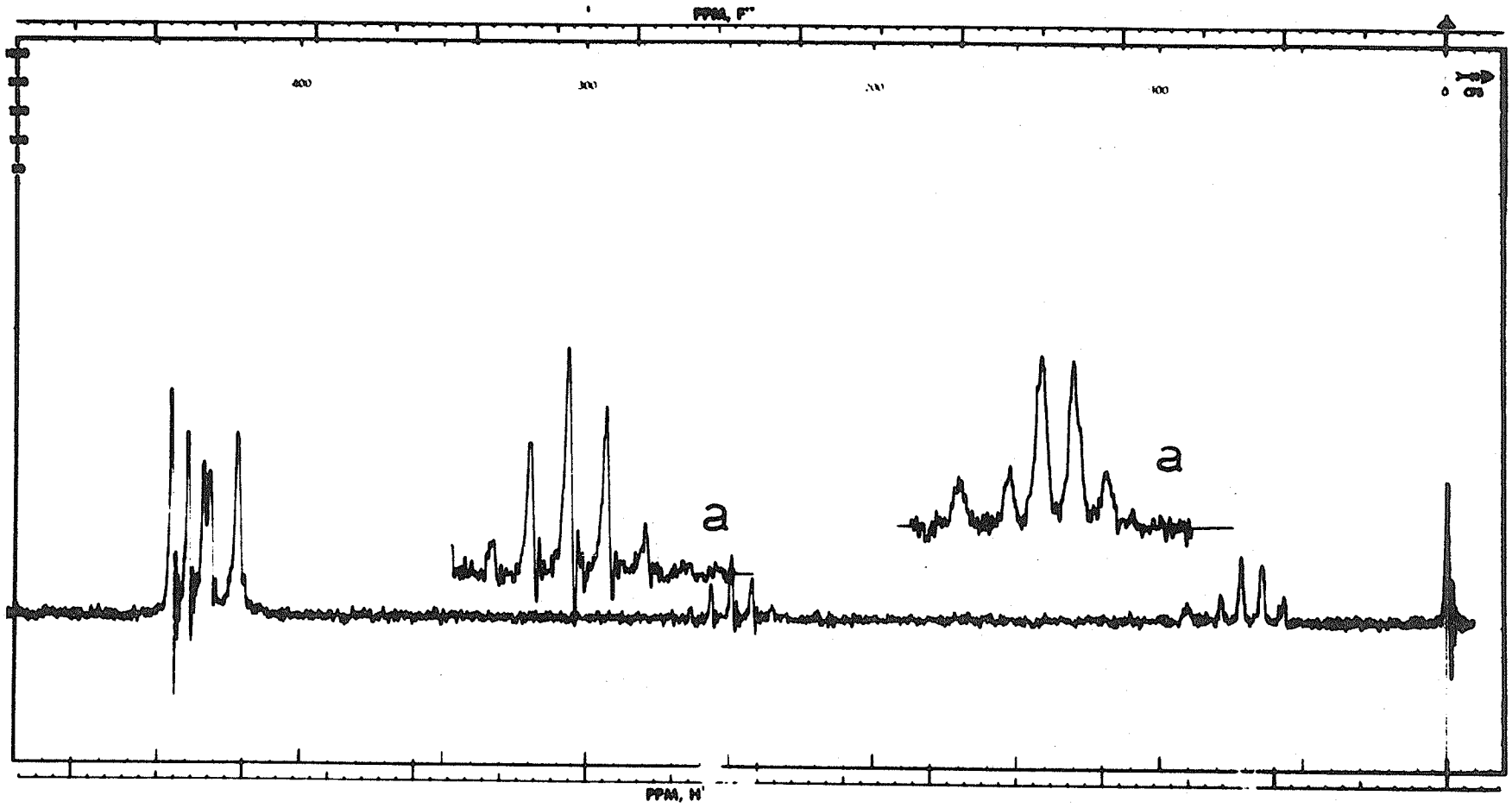
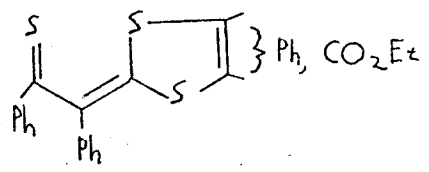
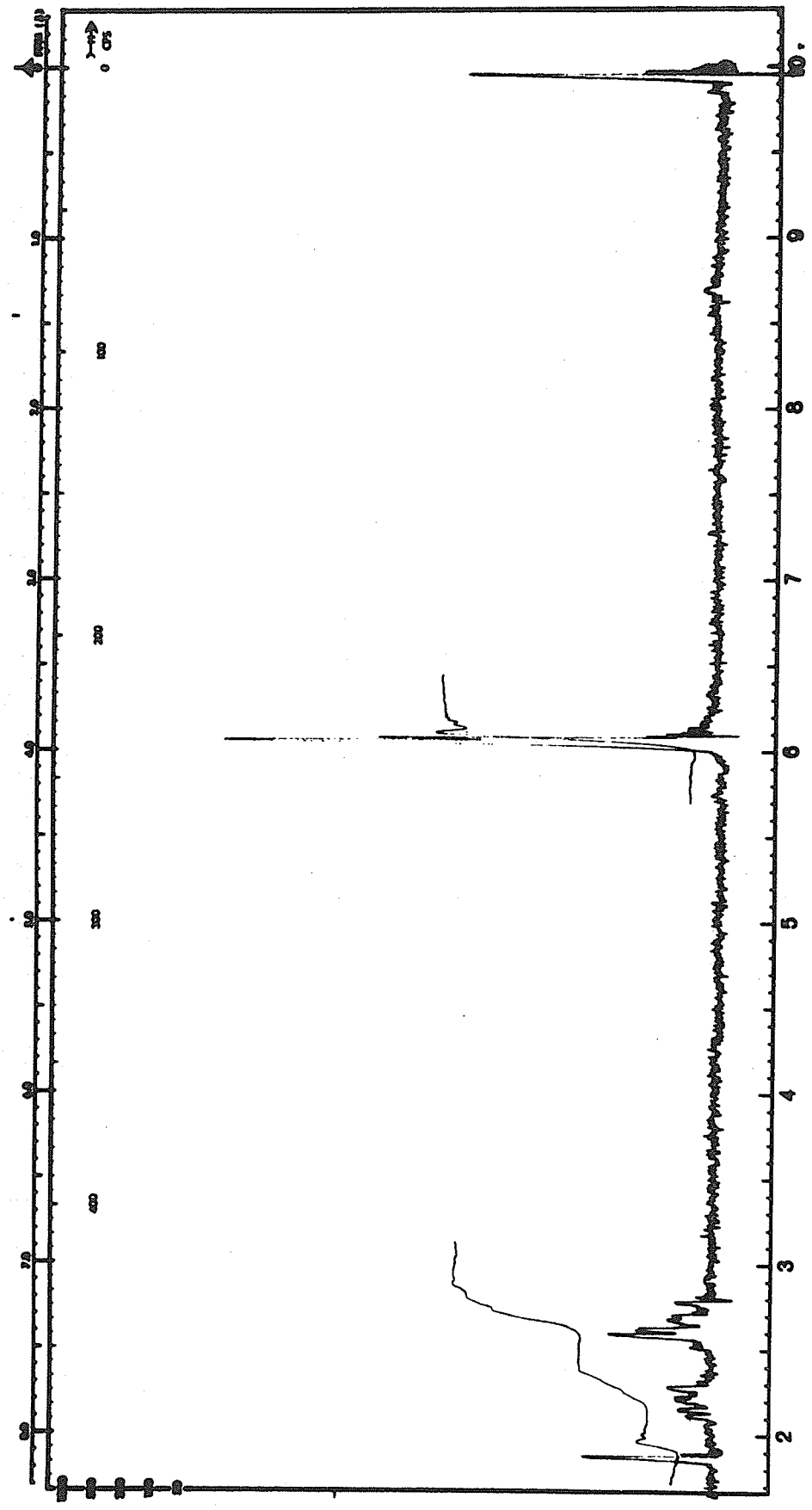


FIG.: XLIV: N.M.R. Spectrum of Ethyl 2-(α-Phenylthiophenacylidene)-4, or 5-phenyl-1,3-dithiole-4, or 5-carboxylate (93b'); Sweep Width 500 Hz., *a* : Sweep Width 250 Hz.





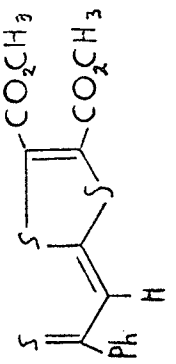


FIG. XLV: N.M.R. Spectrum of Dimethyl 2-Thiophenacylidene-1,3-dithiole-4,5-dicarboxylate (93c); Sweep Width 500 Hz.

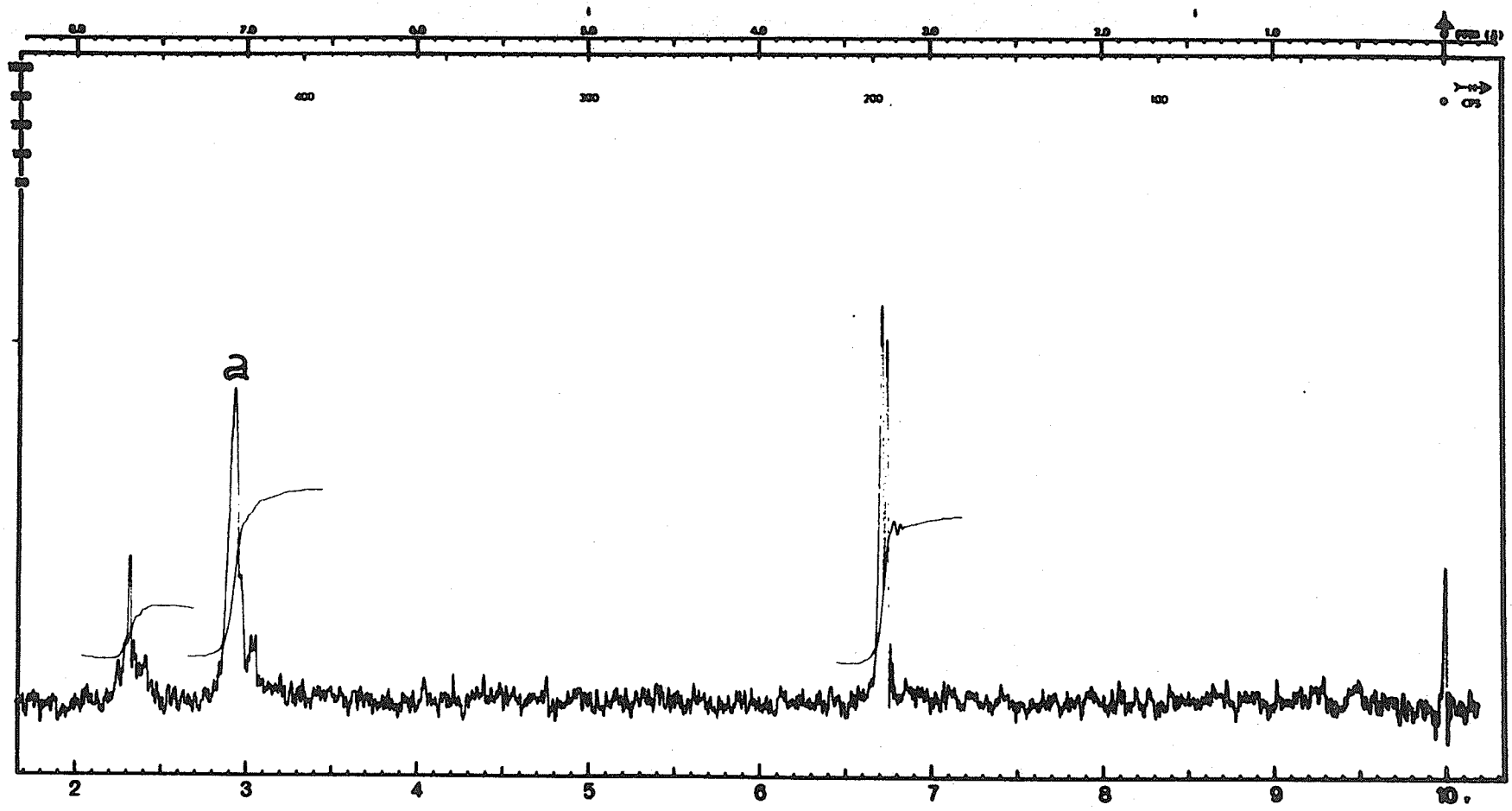
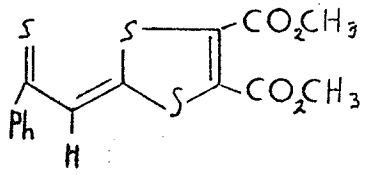
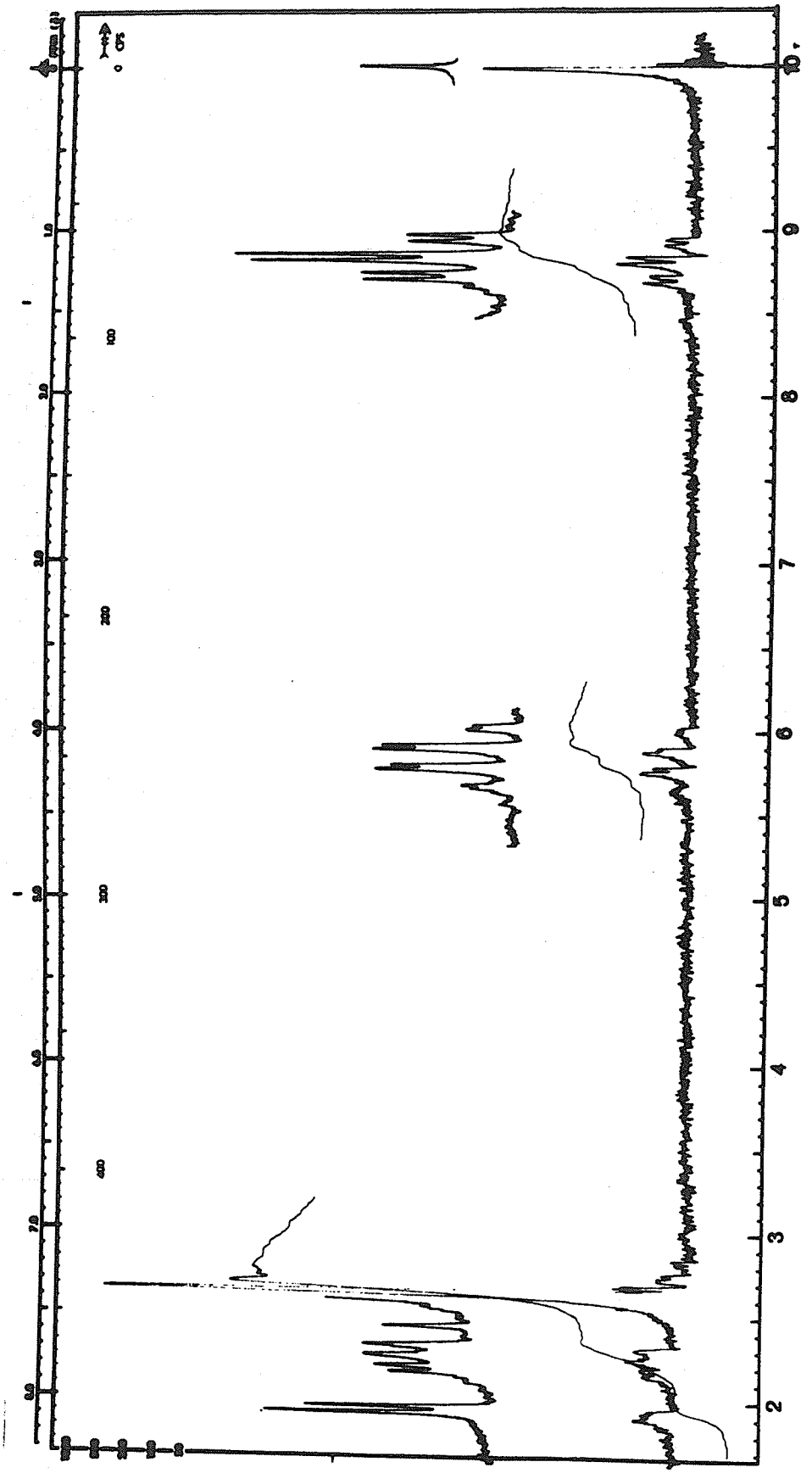


FIG. XLVI: N.M.R. Spectrum of Dimethyl 2-Thiophenacylidene-1,3-dithiole-4,5-dicarboxylate (93c); Sweep Width 500 Hz., Hexadeuteriobenzene (C_6D_6). *a* : benzene.





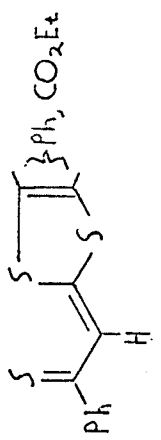
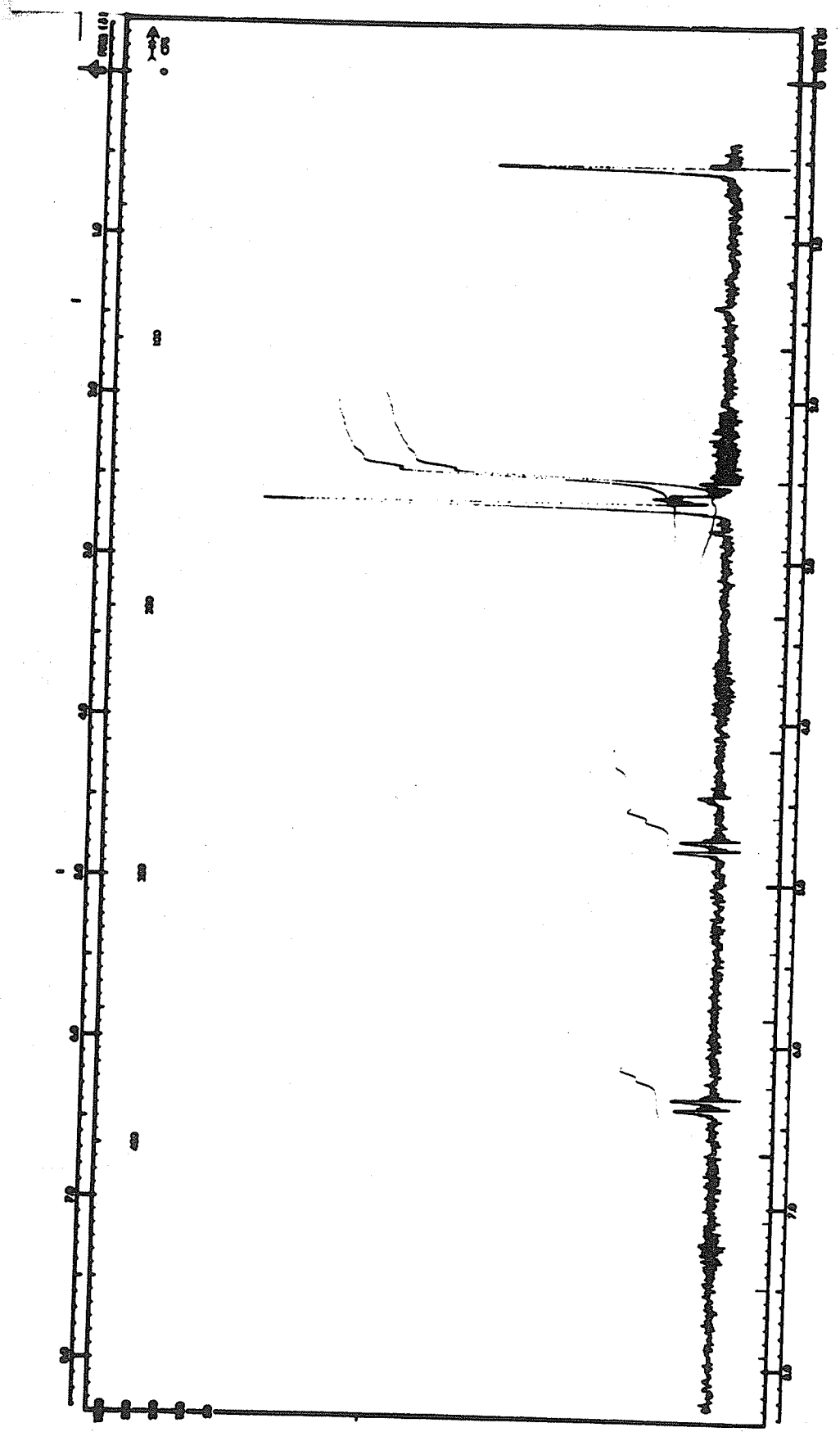


FIG. XLVII: N.M.R. Spectrum of Ethyl 4, or 5-Phenyl-2-thiophenacylidene-1,3-dithiole-4, or 5-carboxylate (93c'); Sweep Width 500 Hz.



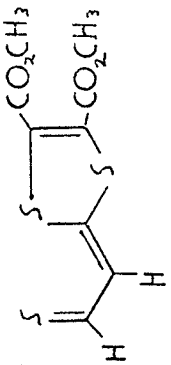


FIG. XLVIII: N.M.R. Spectrum of Dimethyl Thioformylmethylene-1,3-dithiole-4,5-dicarboxylate (198a); Sweep Width 1000 Hz.

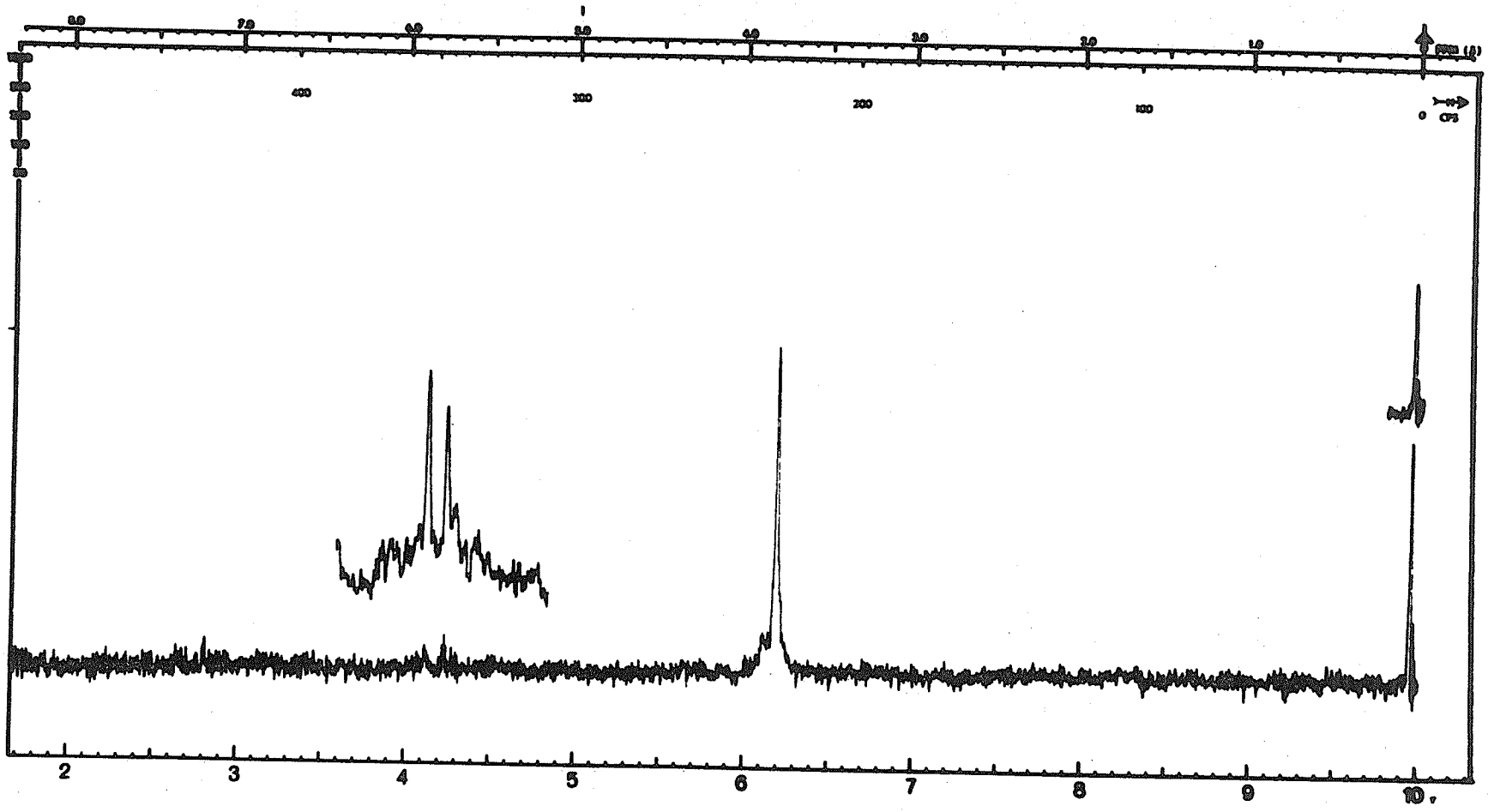
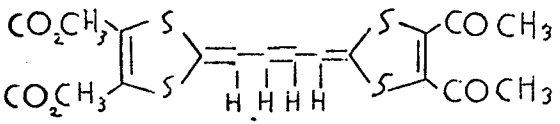


FIG. XLIX: N.M.R. Spectrum of Tetramethyl 1,4-Butenediylidene-2,2'bis-(1,3-dithiole-4,5-dicarboxylate) (200a); Sweep Width 500 Hz.



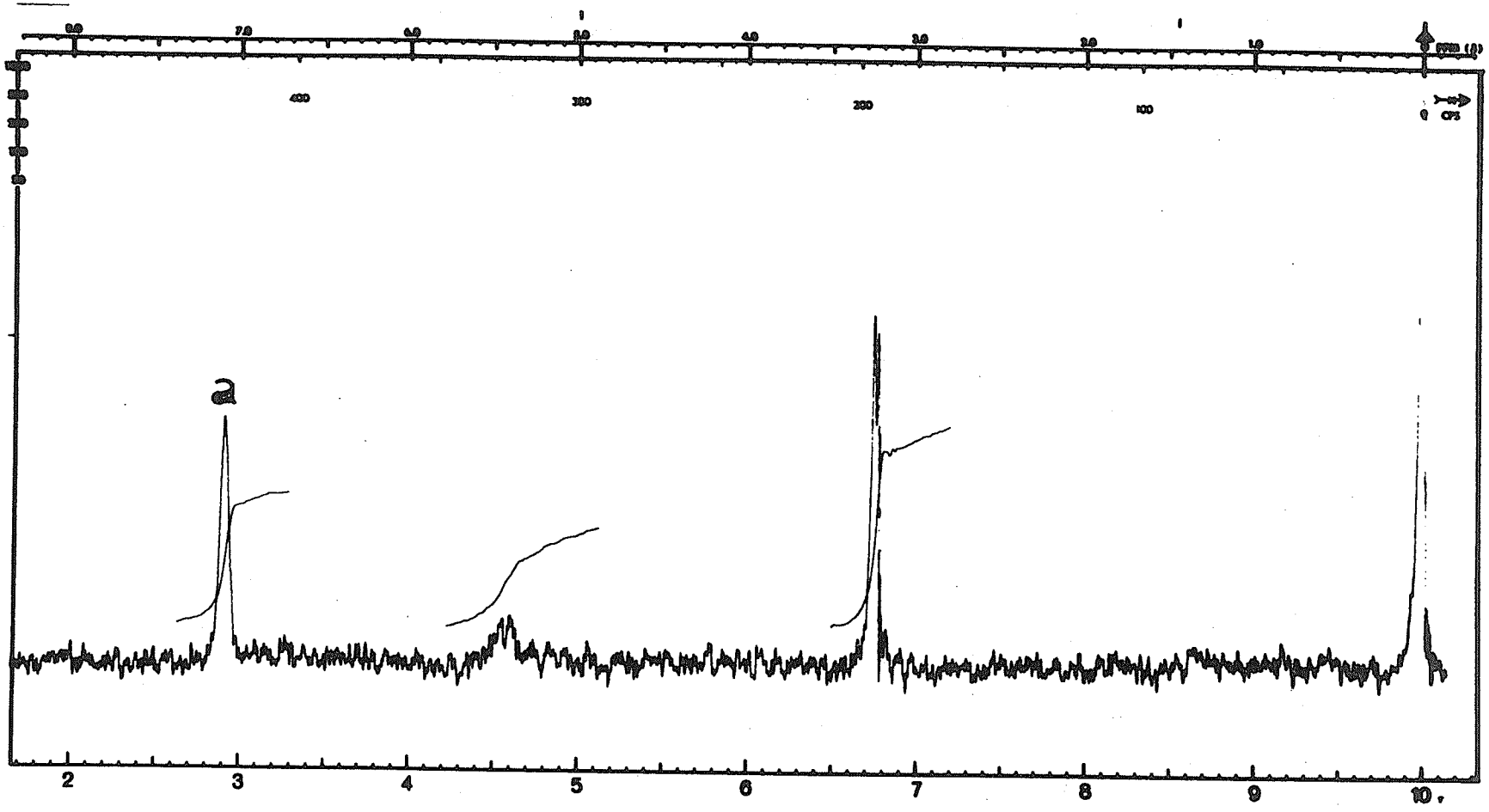
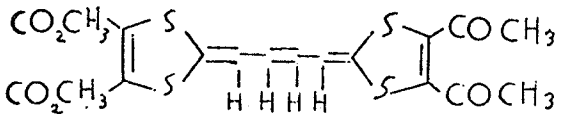
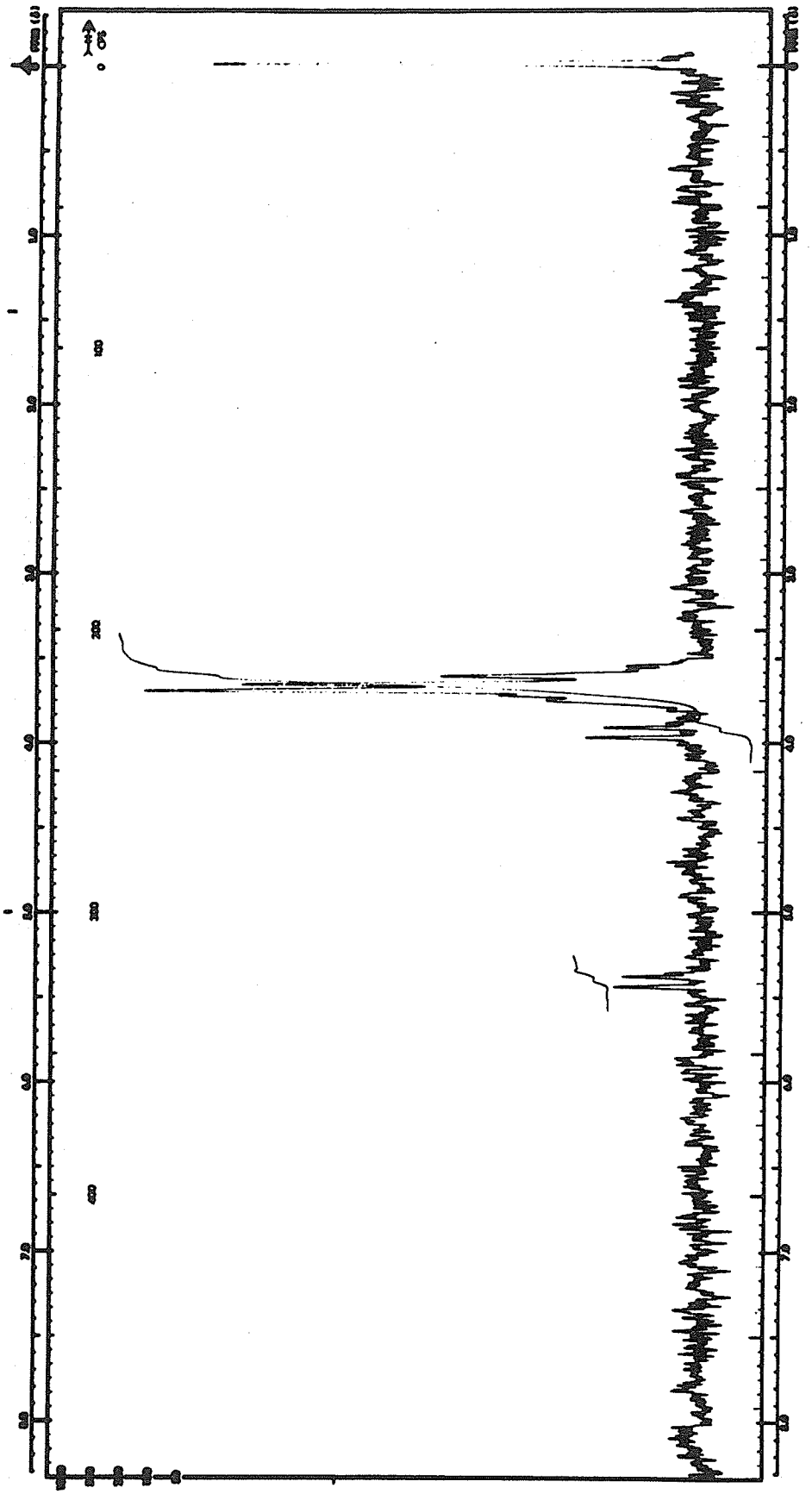


FIG. L: N.M.R. Spectrum of Tetramethyl 1,4-Butenediylidene-2,2'bis-(1,3-dithiole-4,5-dicarboxylate) (200a); Hexadeuteriobenzene (C_6D_6), Sweep Width 500 Hz. *a* : Benzene.





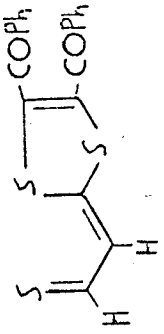
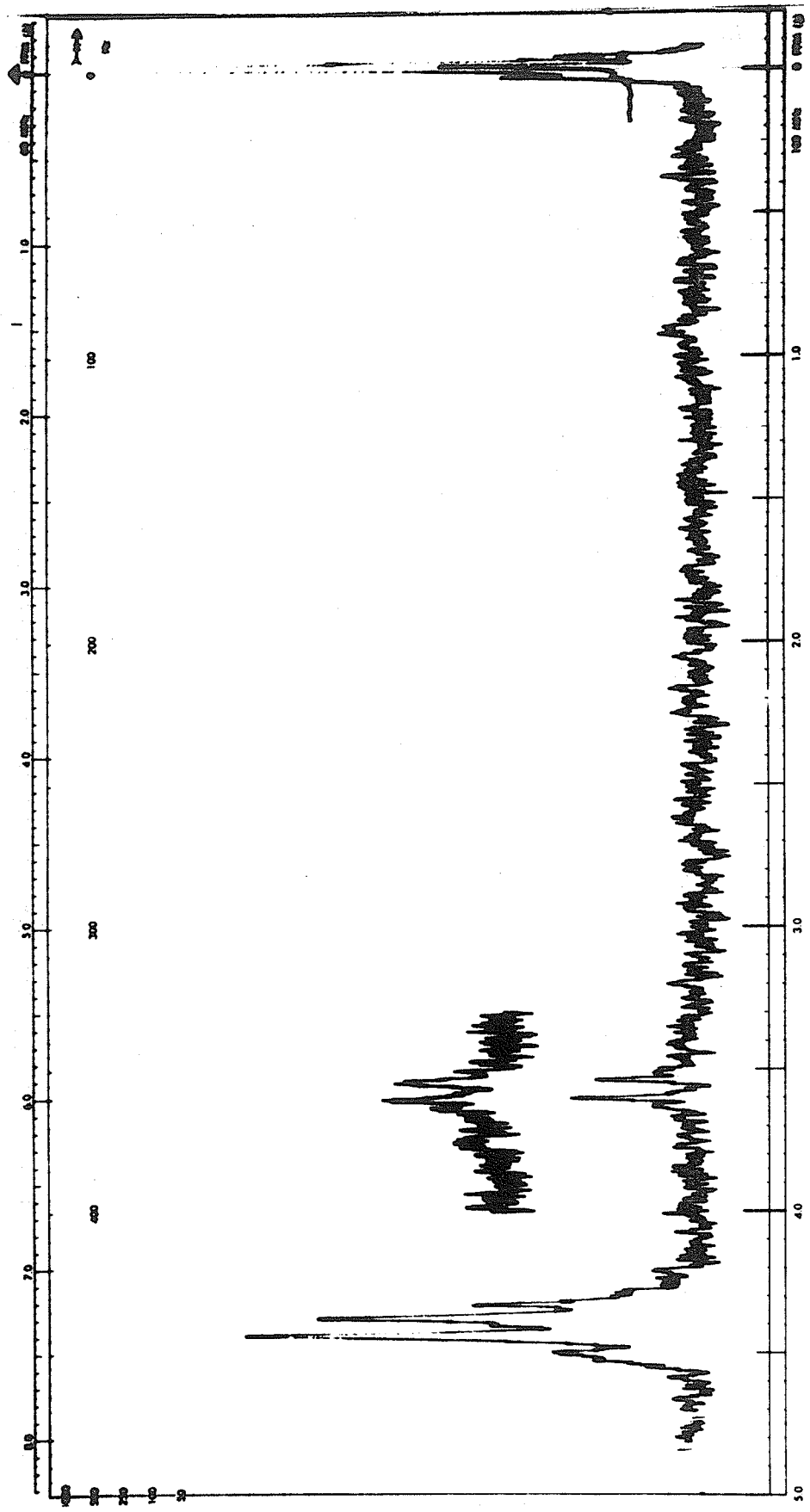


FIG. LI: N.M.R. Spectrum of 4,5-Dibenzoyl-2-thioformylmethylene-1,3-dithiole (198b); Sweep Width 1000 Hz.



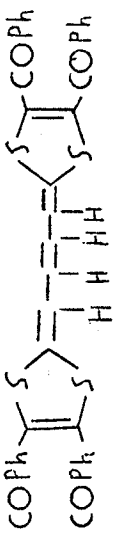


FIG. LII: N.M.R. Spectrum of 1,4-Butenediylidene-2,2'-bis(4,5-dibenzoyl-1,3-dithiole) (200b); Sweep Width 500 Hz.

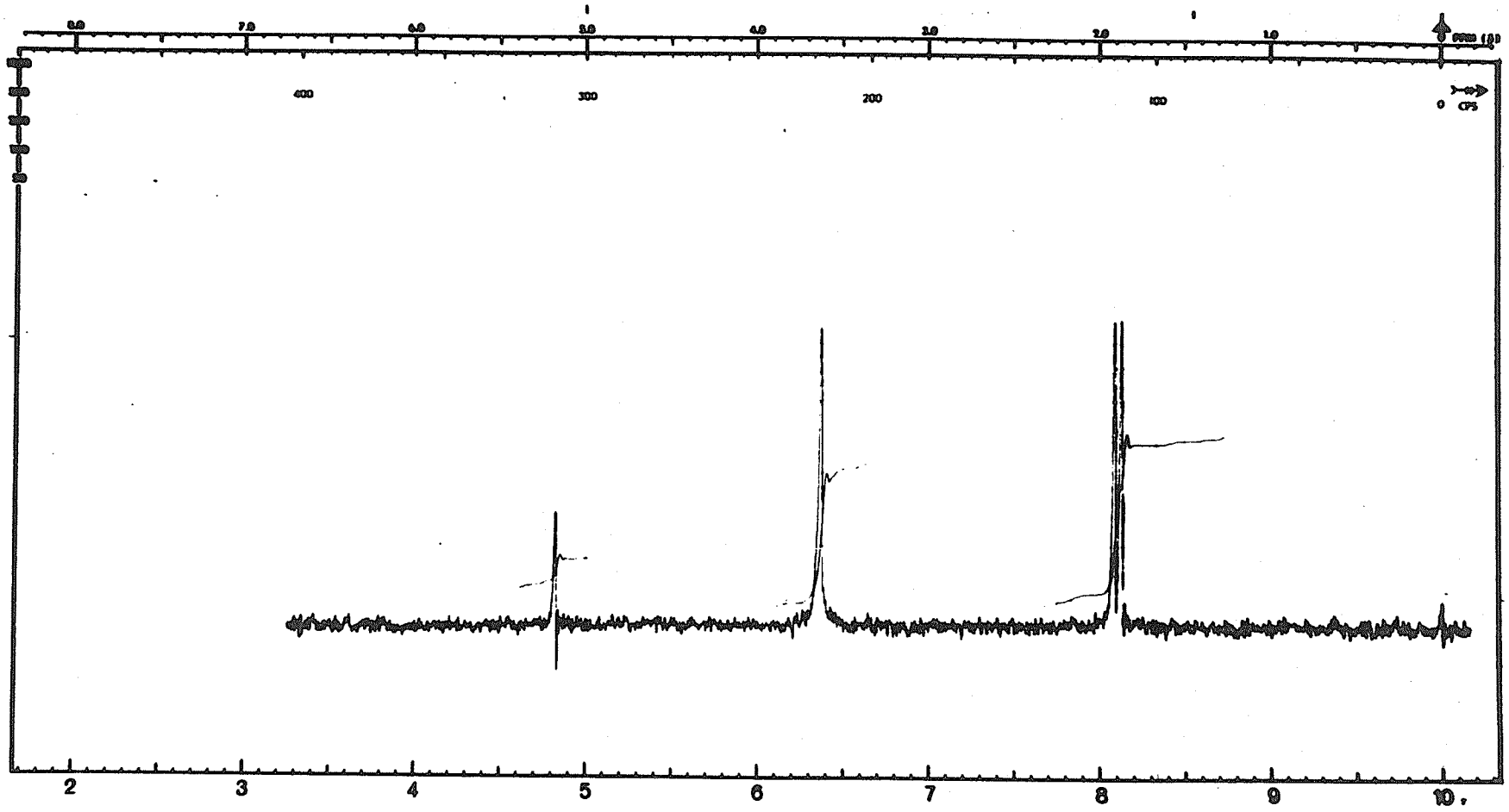
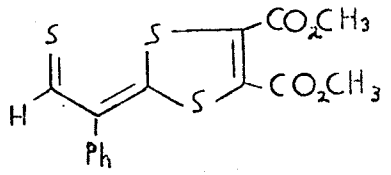


FIG. LIII: N.M.R. Spectrum of Dimethyl 2-(α-Phenylthioformylmethylene) -1,3-dithiole-4,5-dicarboxylate (198c); Sweep Width 1000 Hz.



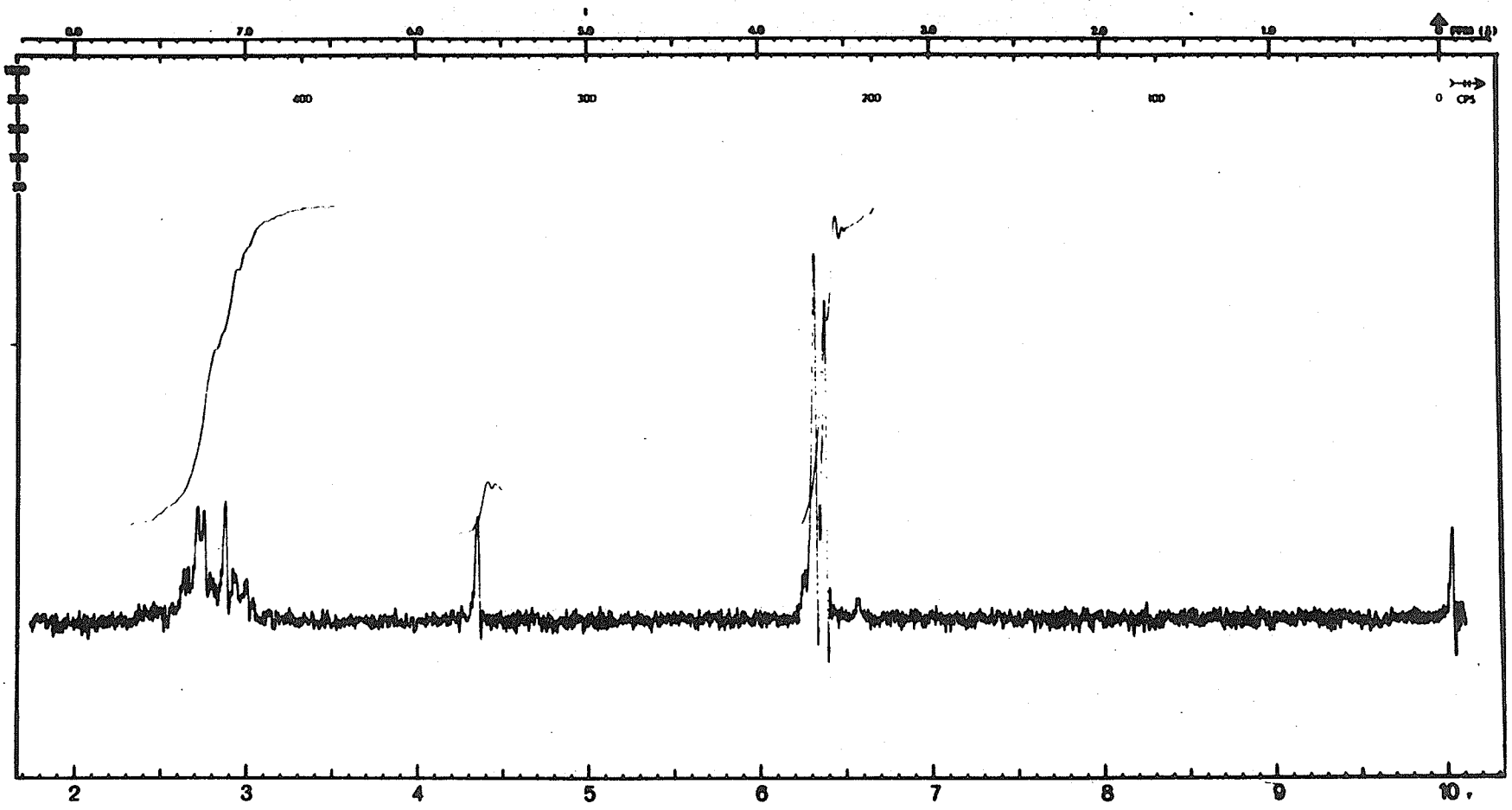
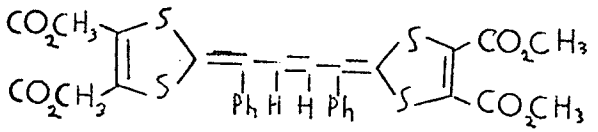


FIG. LIV: N.M.R. Spectrum of Tetramethyl 1,4-Diphenyl-1,4-butenediylidene-2,2¹-bis(1,3-dithiole-4,5-dicarboxylate) (200c); Sweep Width 500 Hz.



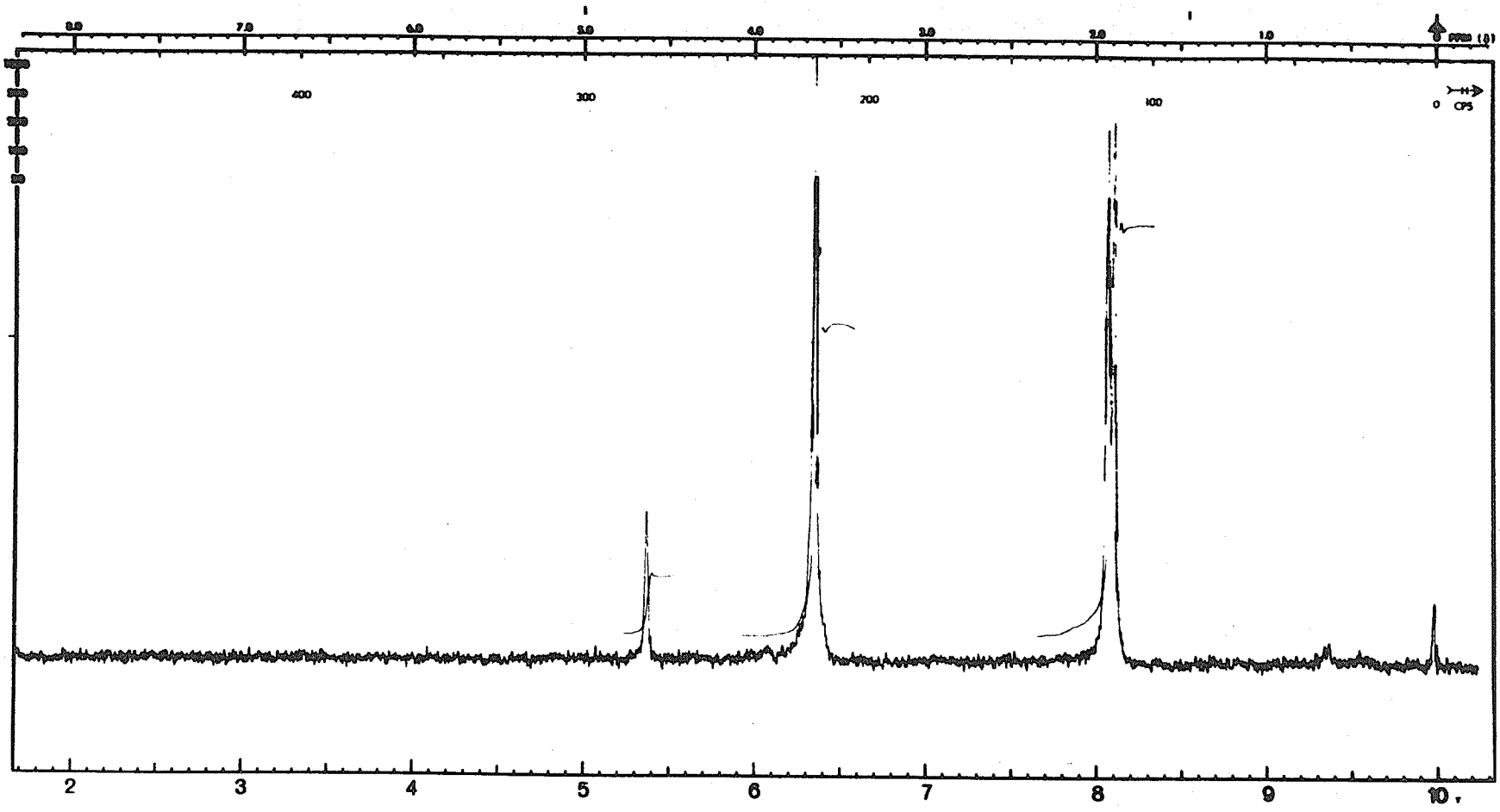
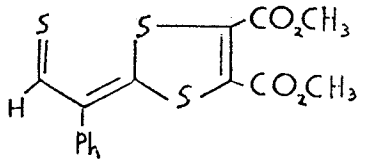
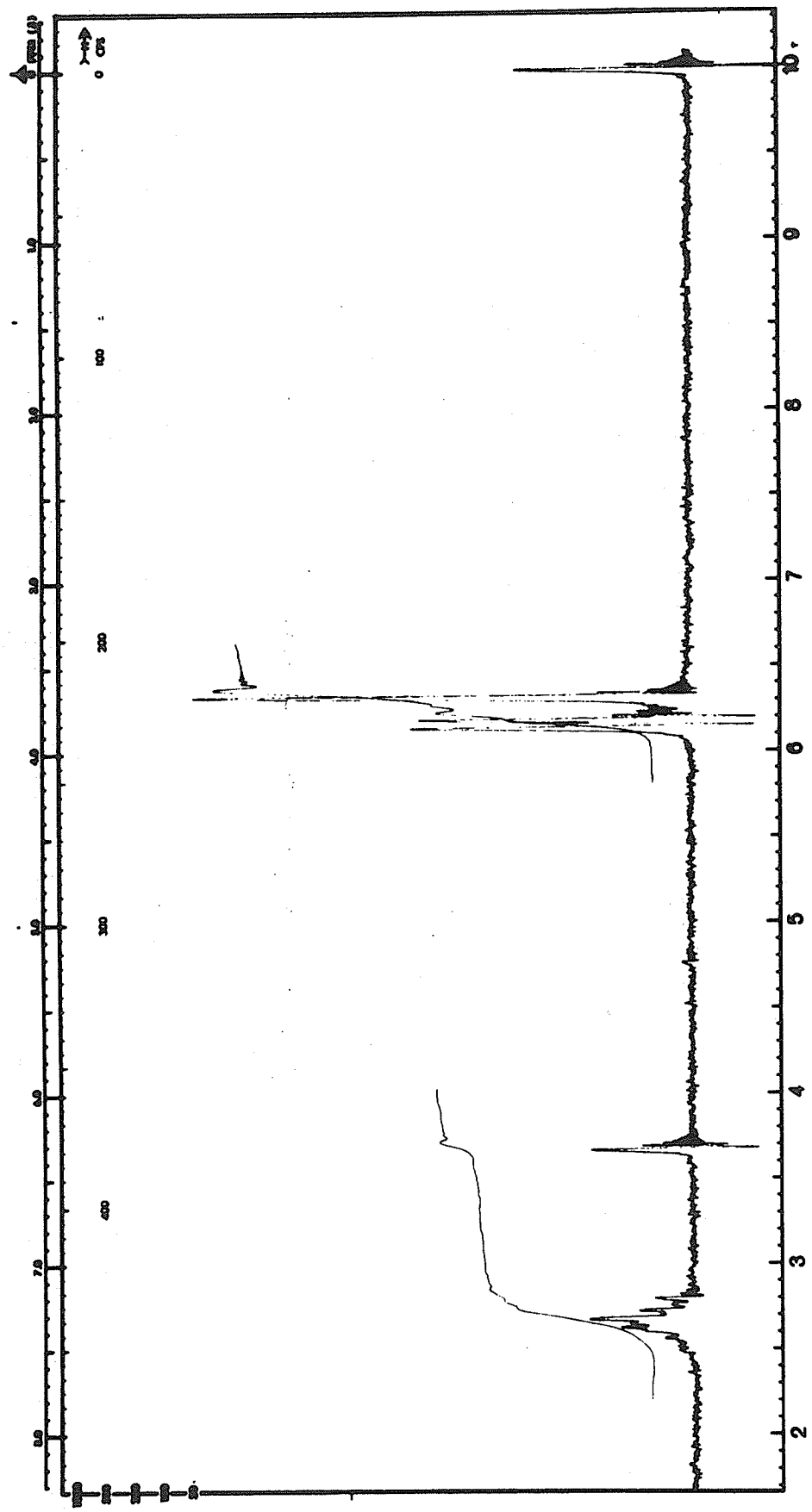


FIG. LV: N.M.R. Spectrum of Dimethyl 2-(α-Phenylformylmethylene)-1,3-dithiole-4,5-dicarboxylate (201a); Sweep Width 1000 Hz.





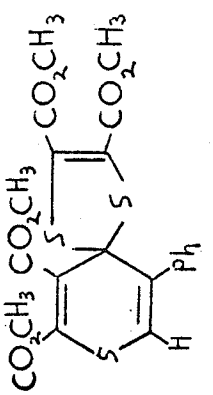


FIG. LVI: N.M.R. Spectrum of Tetramethyl 1,3-Dithiole-4,5-dicarboxylate-2-spiro-4-(3-phenylthiopyran-5,6-dicarboxylate) (199a); Sweep Width 500 Hz.

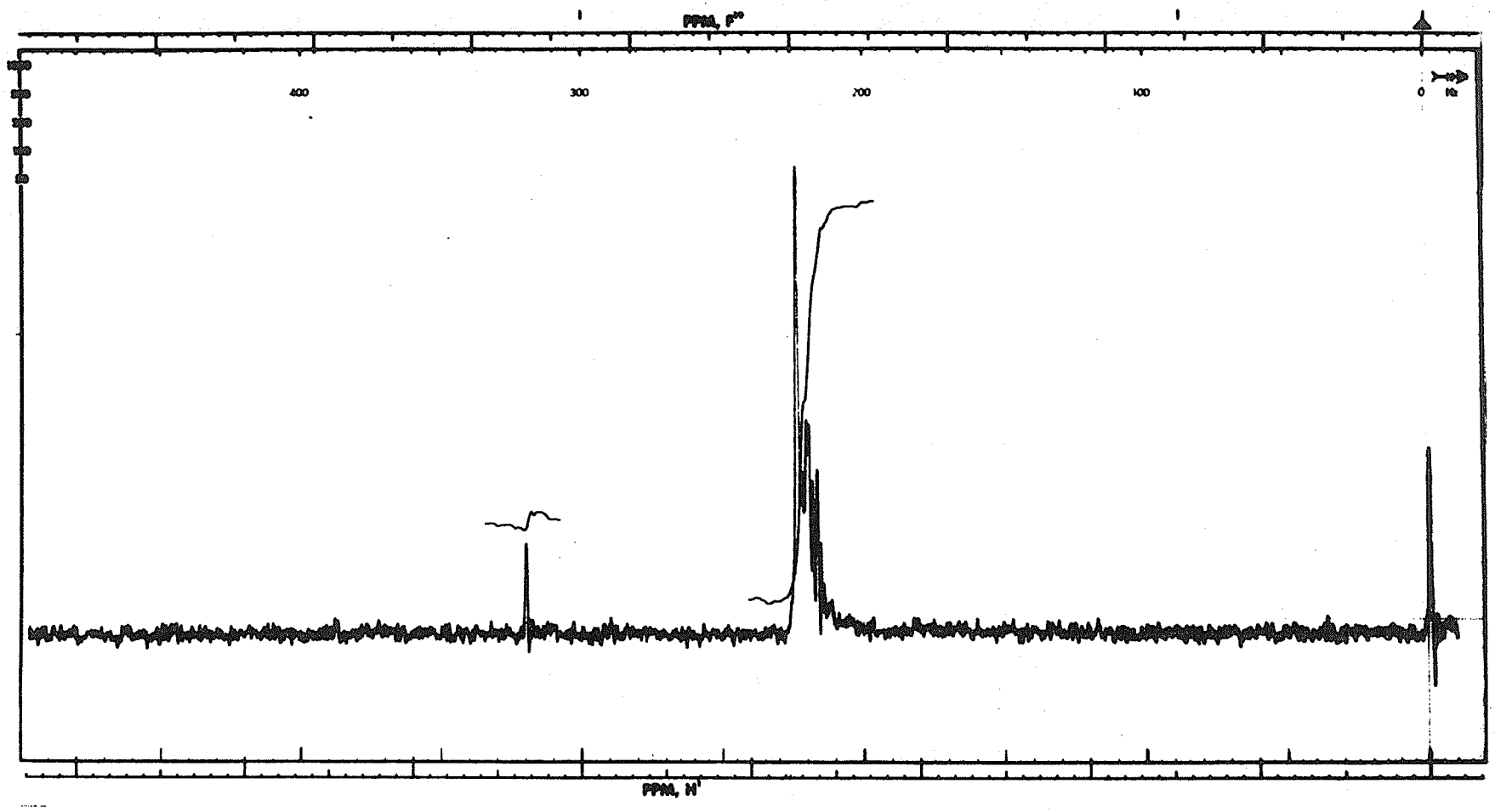
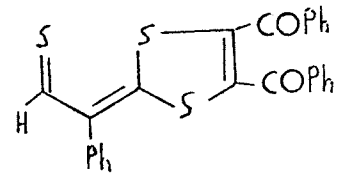


FIG. LVII: N.M.R. Spectrum of 2-α-Phenylthioformylmethylene-4,5-dibenzoyl-1,3-dithiole (198d); Sweep Width 1000 Hz.



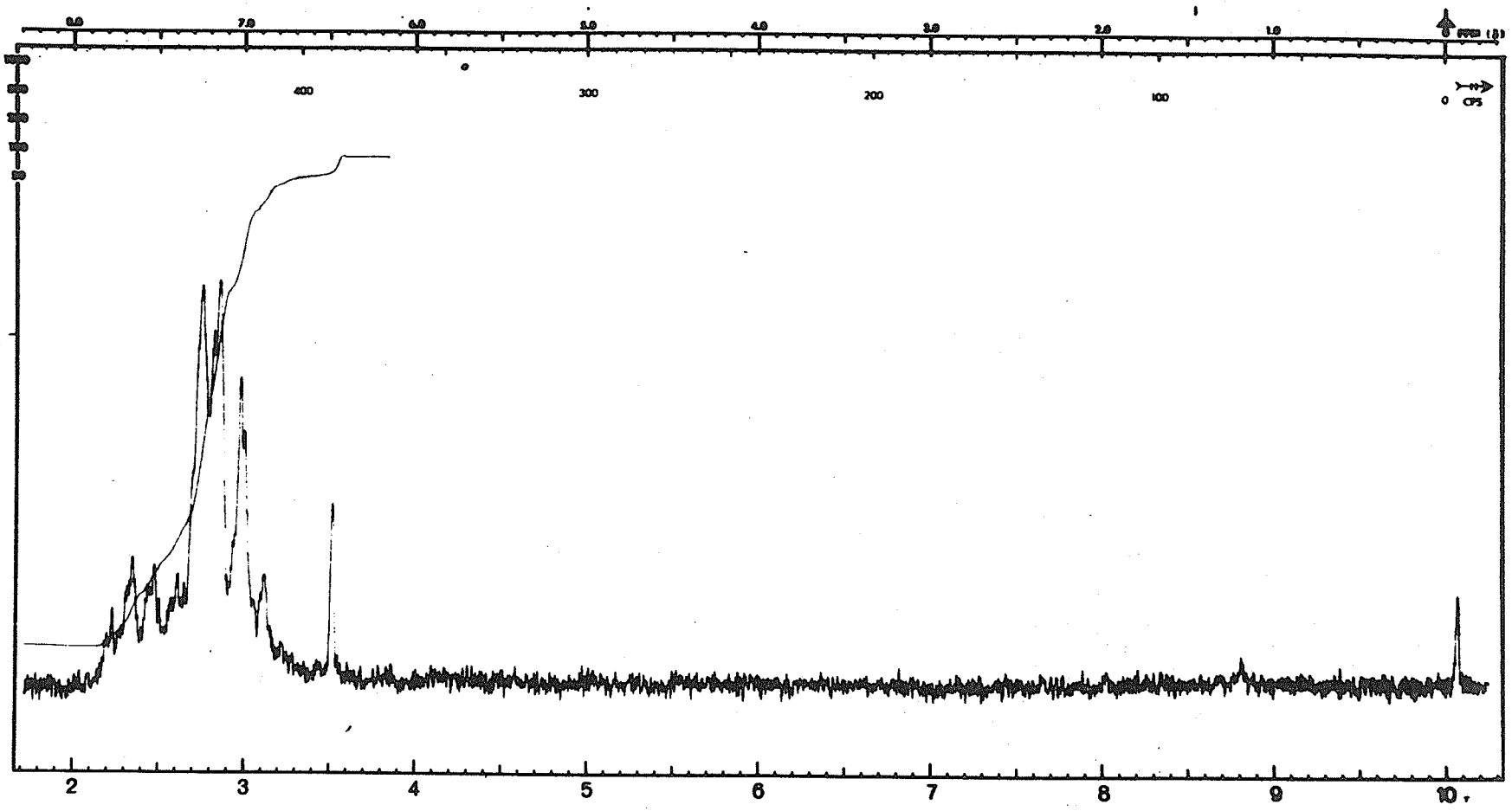
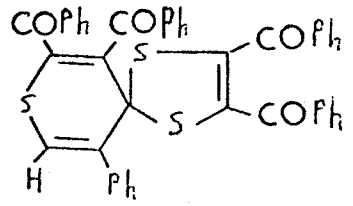


FIG. LVIII: N.M.R. Spectrum of 4-5-Dibenzoyl-1,3-dithiole-2-spiro-4-(3-phenyl-4,5-dibenzoylthiopyran) (199b); Sweep Width 500 Hz.



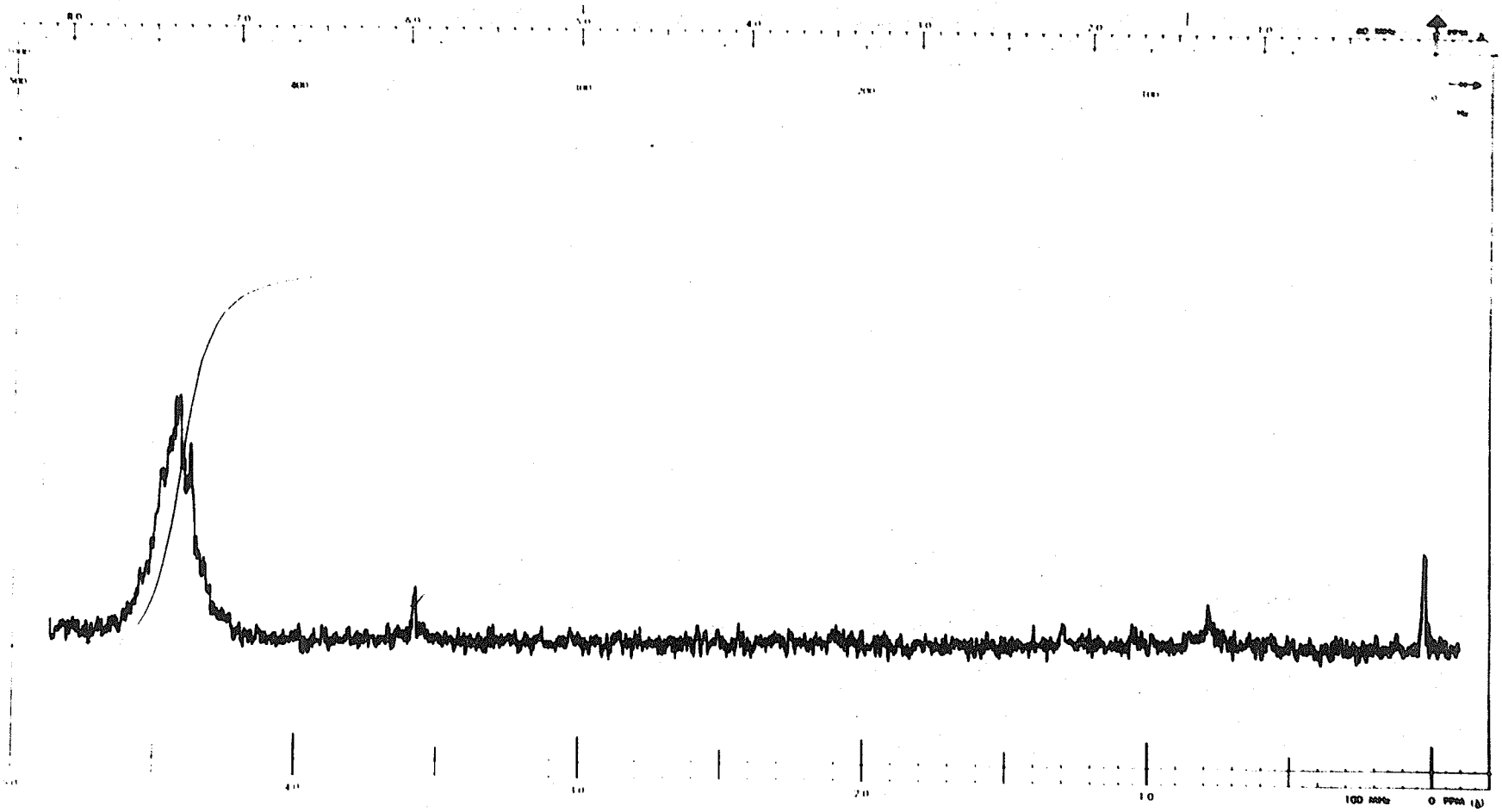
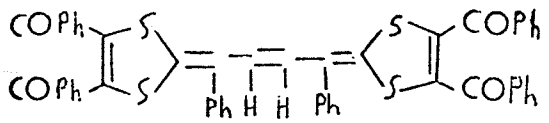
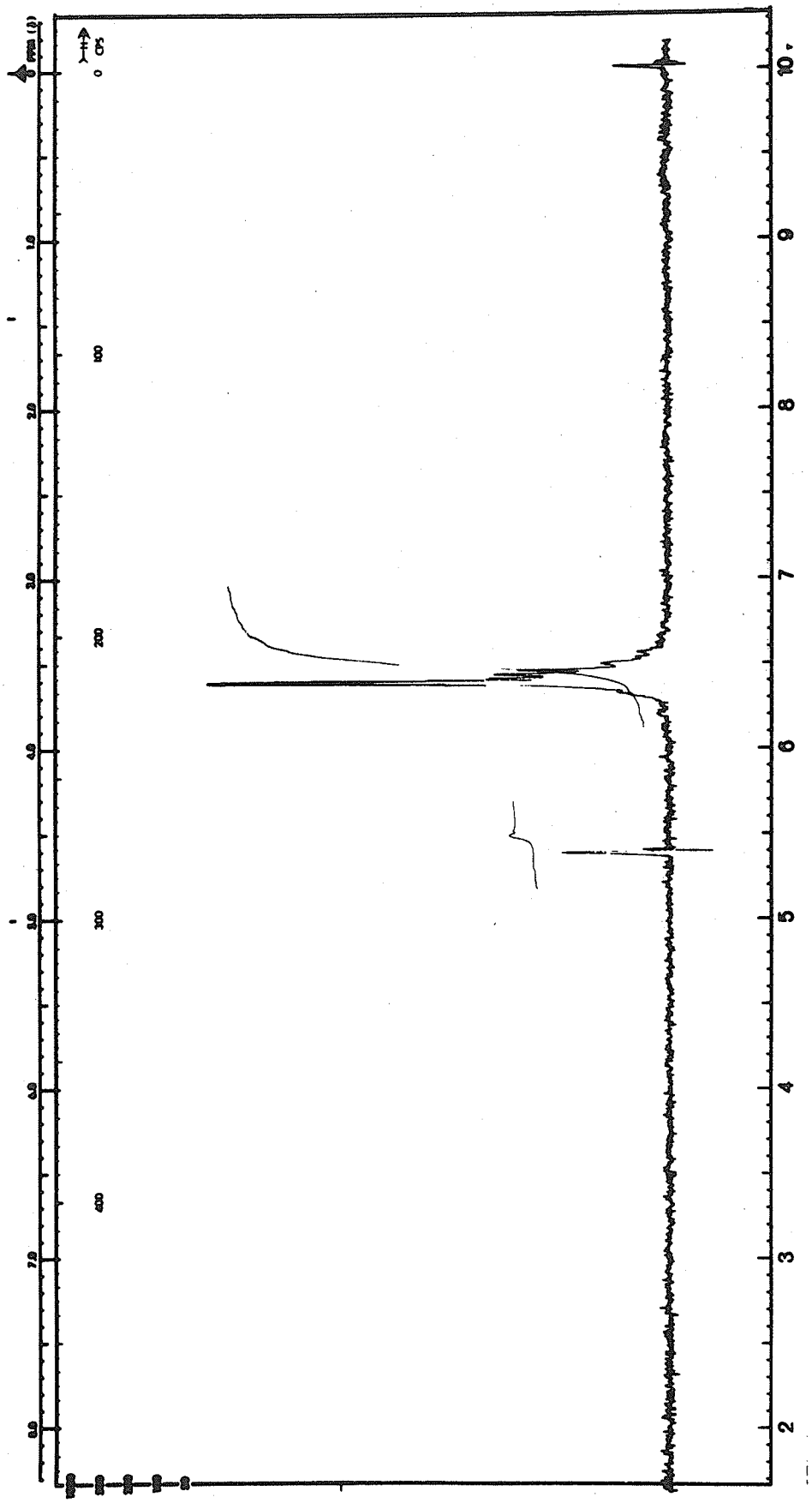


FIG. LIX: N.M.R. Spectrum of 1,4-Butenediylidene-2,2'-bis(4,5-dibenzoyl-1,3-dithiole) (200d); Sweep Width 500 Hz.





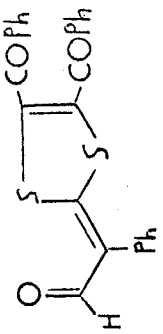
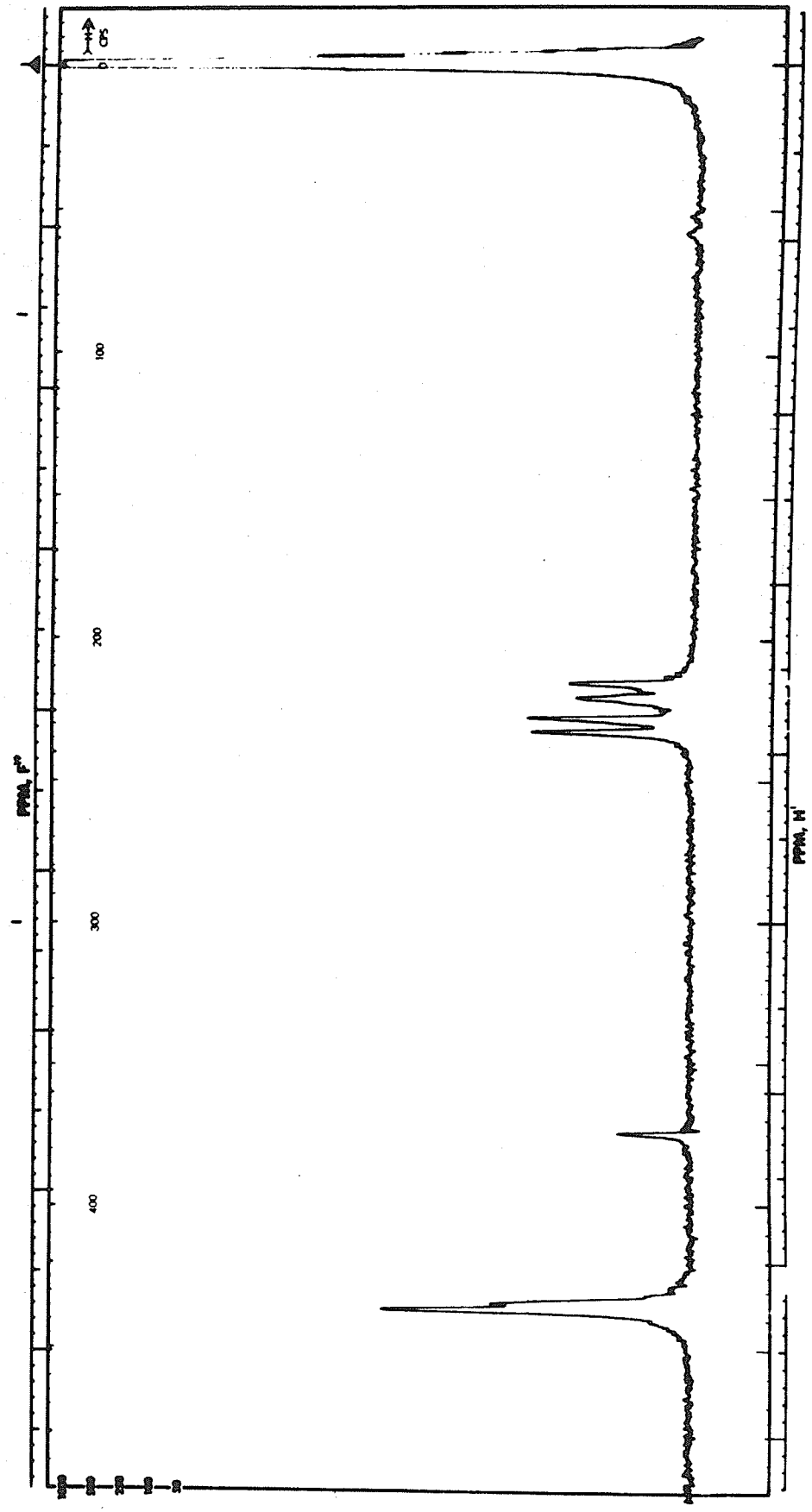


FIG. LX: N.M.R. Spectrum of 4,5-Dibenzoyl-2(α-phenylformylmethylene)-1,3-dithiole (201b); Sweep Width 1000 Hz.



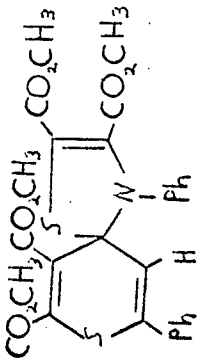
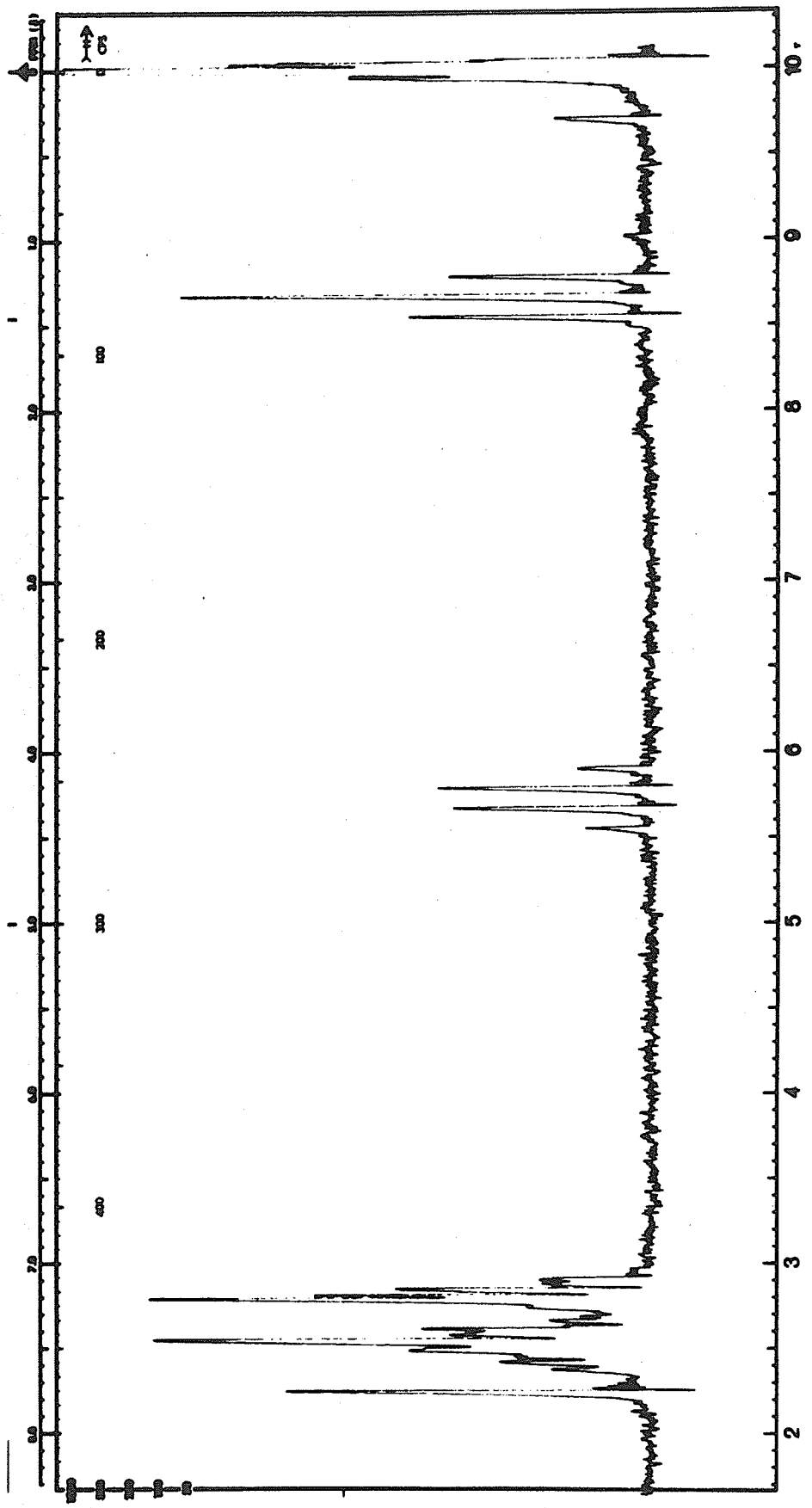


FIG. LXI: N.M.R. Spectrum of Tetramethyl N-Phenylthiazole-4,5-dicarboxylate-2-spiro-4-(2-phenylthiopyran-5,6-dicarboxylate)(233a); Sweep Width 500 Hz.



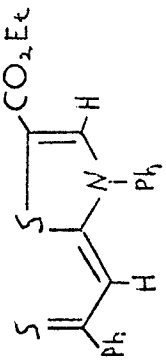
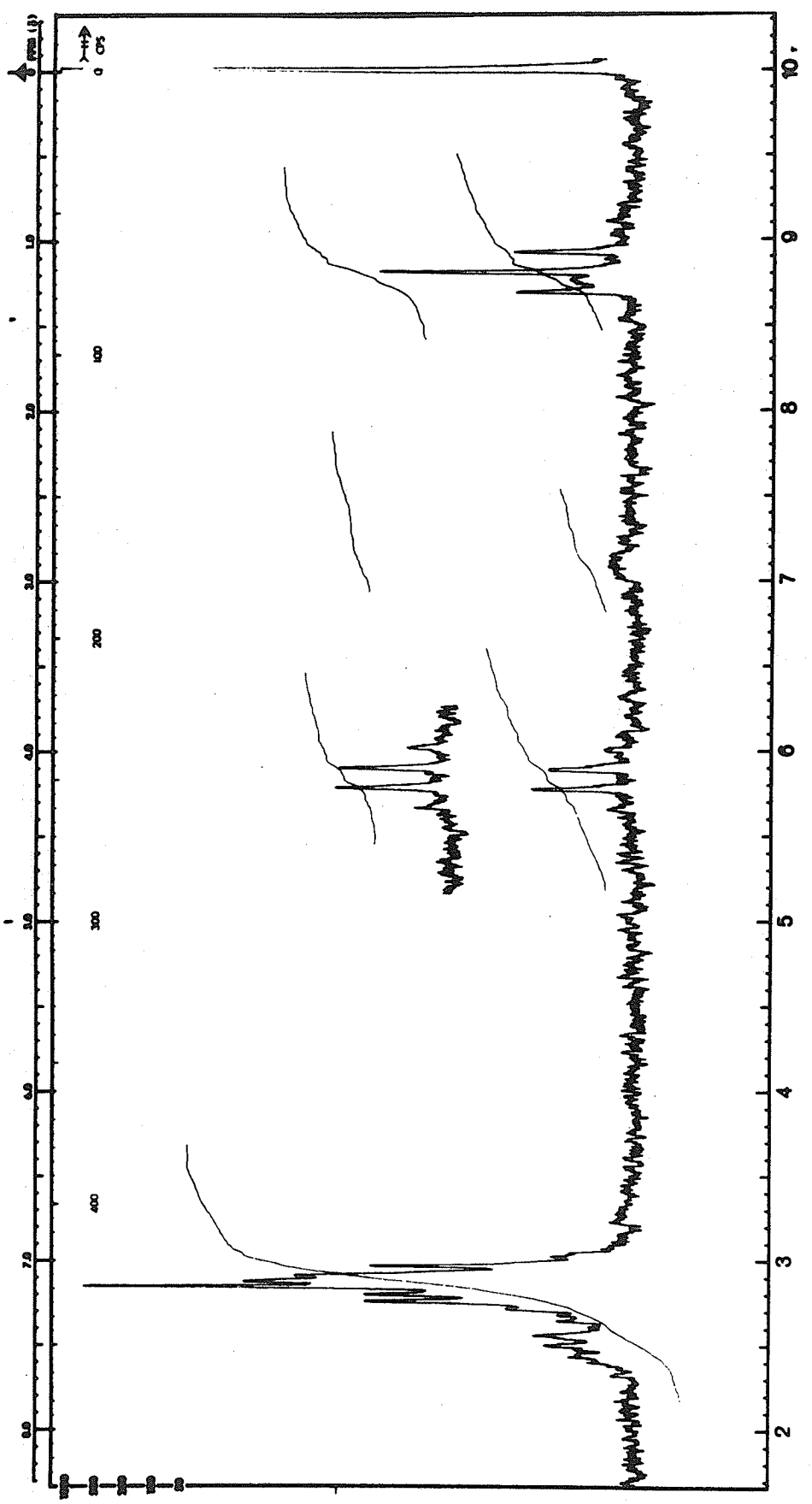


FIG. LXII: N.M.R. Spectrum of Ethyl N-Phenyl-2-thiophenacylidenethiazole-5-carboxylate (232a); Sweep Width 500 Hz.



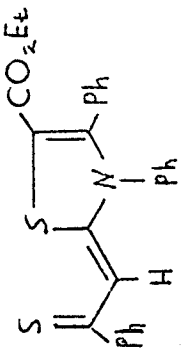
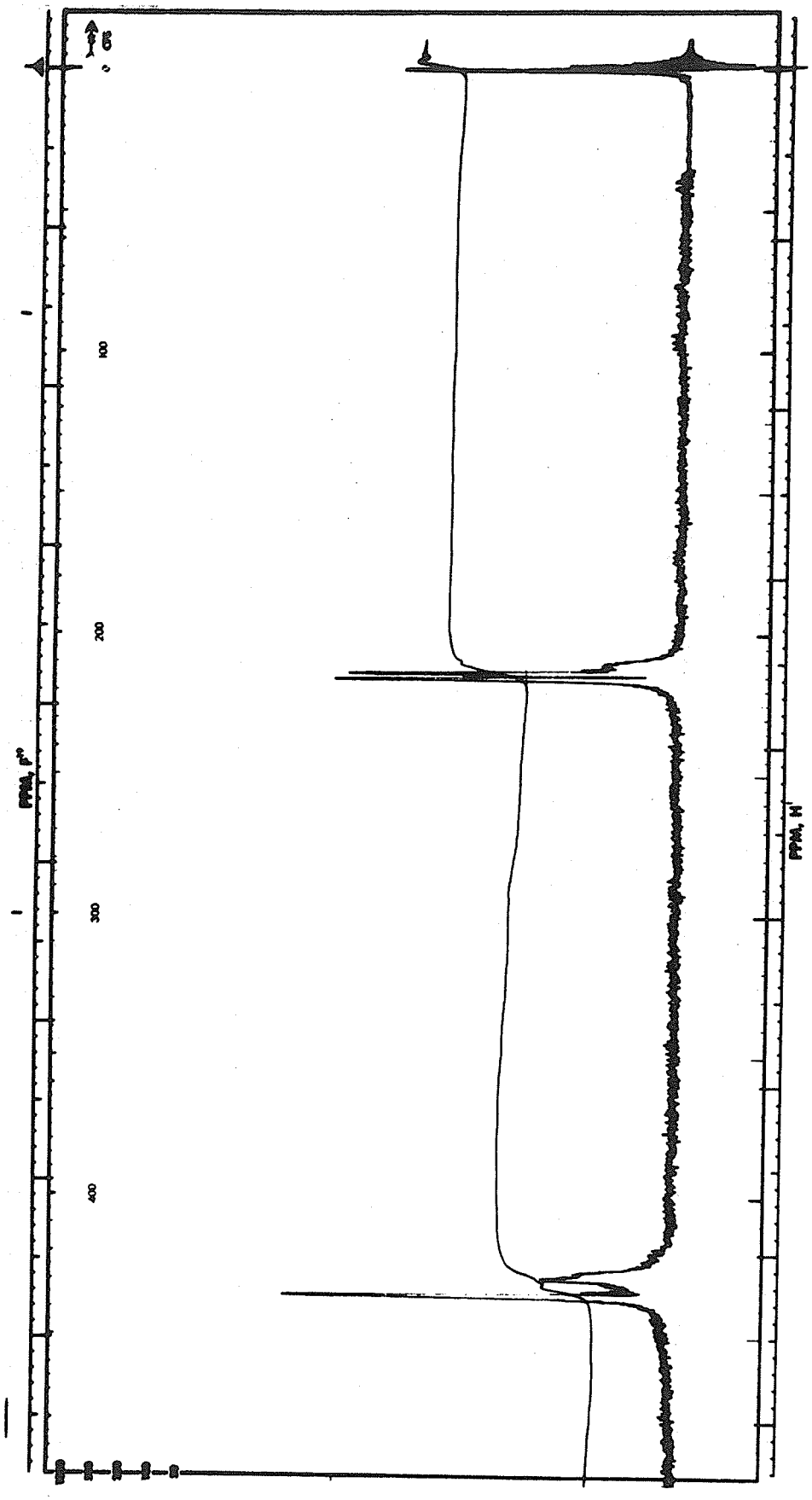


FIG. LXIII: N.M.R. Spectrum of Ethyl N-Phenyl-4-phenyl-2-thiophenacylidene-thiazole-5-carboxylate (232b); Sweep Width 500 Hz.



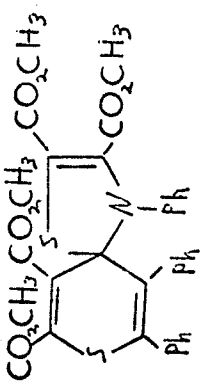


FIG. LXIV: N.M.R. Spectrum of Tetramethyl N-Phenylthiazole-4,5-dicarbozylate-2-spiro-4-(2,3-diphenylthiopyran-5,6-dicarboxylate) (233b); Sweep Width 500 Hz.

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