

THE UNIVERSITY OF MANITOBA

STUDIES IN THE 1,2,4-DITHIAZOLE SYSTEM

presented by

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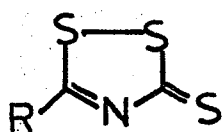
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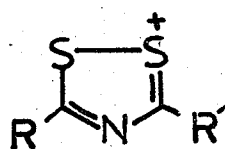
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GENERAL INTRODUCTION

The 1,2,4-dithiazole system is a heterocyclic ring consisting of two sulfur, one nitrogen, and two carbon atoms. Two examples of this system were of interest: the 1,2,4-dithiazole-3-thiones (I) and the 1,2,4-dithiazolium cation (II). Some examples of both of these are known and will be dealt with later.

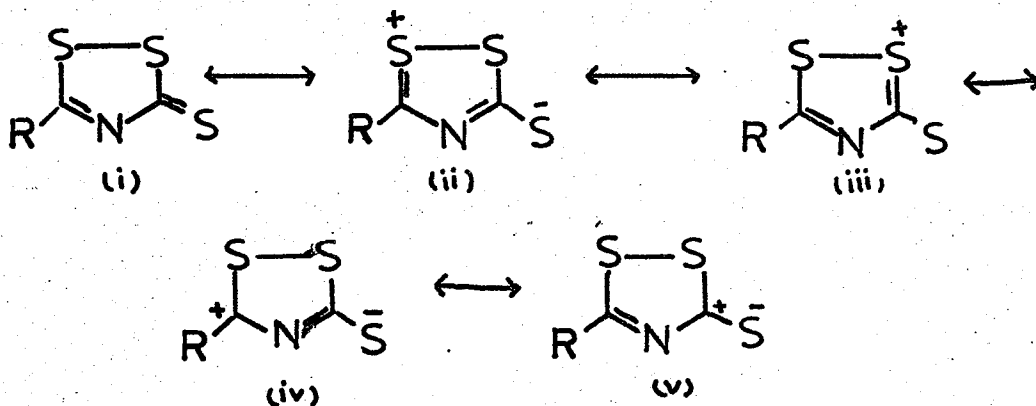


(I)

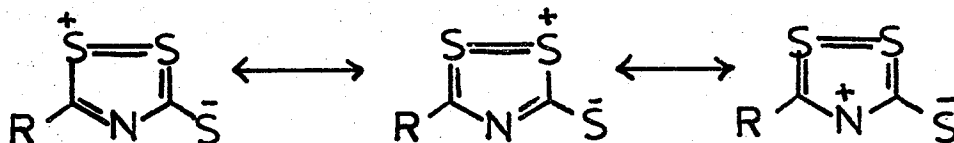


(II)

The thione compound exists as a resonance hybrid of the following contributing structures:



Structures involving sulfur d-orbitals can also be proposed, but they are probably less important.

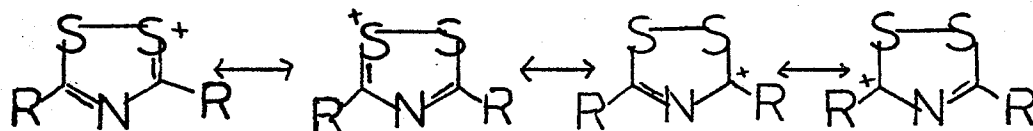


It will be noted that several of these forms indicate that this system will be potentially highly aromatic in character. Also, the exo-

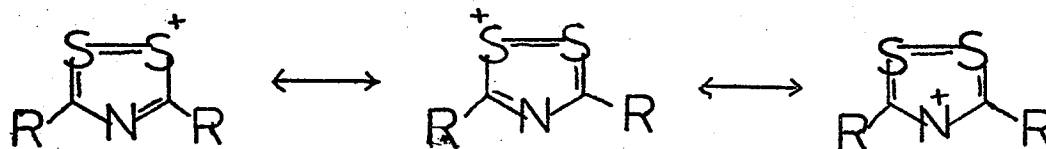
cyclic double bond should have a fairly high polar character, and the sulfur atom may function as a nucleophile in certain reactions.

Calculations of resonance energy of this system have not so far been reported.

The 1,2,4-dithiazolium cation should have four main contributing structures:

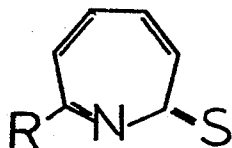


Structures utilizing d-orbitals can also be proposed:

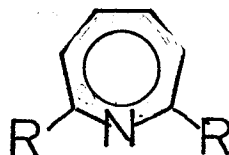


but these are less likely.

In accordance with the Longuet-Higgin theory of isosterism, each sulfur atom in the ring is equivalent to a $-\text{CH}=\text{CH}$ group and therefore the systems (I) and (II) will be isoelectronic with



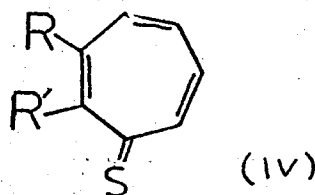
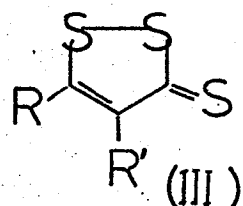
and



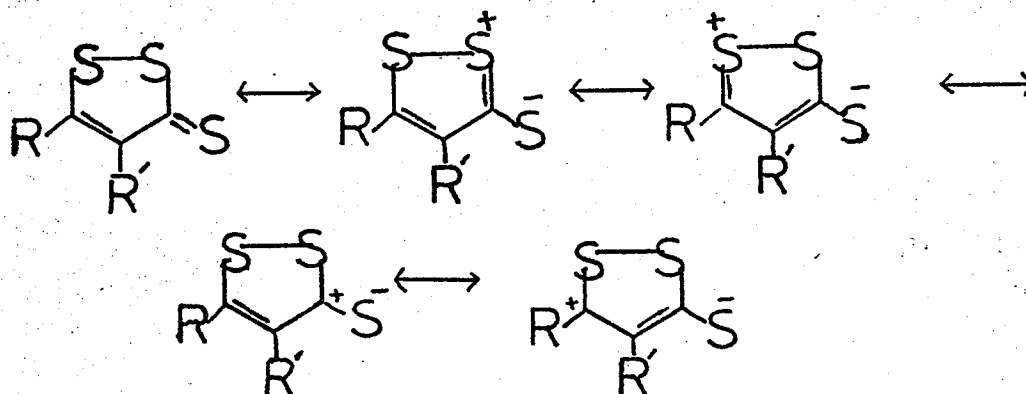
respectively

in the same way that thiophene is isoelectronic with benzene, with

which it has quite a few similar chemical properties. They may also be regarded as 4-aza derivatives of the 1,2-dithiole system (III) which is isoelectronic with the 1,3,5 cyclohepta triene system (IV). This is not confirmed directly, but the suggestion is in conformity with experimental results. It is to be expected therefore, that in many of their reactions these compounds (I & II) will be similar to the corresponding 1,2-dithioles.



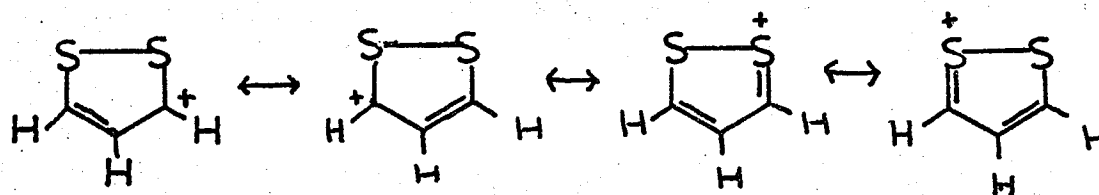
A number of derivatives of the carbon analogue (III) of (I) have long been prepared, and their physical and chemical properties investigated. Kehl and Jeffrey² have made a complete structural analysis of 4-methyl-1,2-dithiole-3-thione (III, R' = CH₃, R = H) determining the bond lengths and the conjugative interactions of the three groups S-S, C=C, and C=S, each of which has pi orbitals perpendicular to the plane of the dithiole ring. The main resonating forms of this compound may be represented as:



This suggests that in the analogous compound (I) pi orbitals of C=S, S-S, and C=N should be perpendicular to the plane of the dithia-

zole ring. On this basis of analogy, it may reasonably be suggested that the first three resonance forms of the 1,2,4-dithiazole thione system (i - iii) contribute most to the structure.

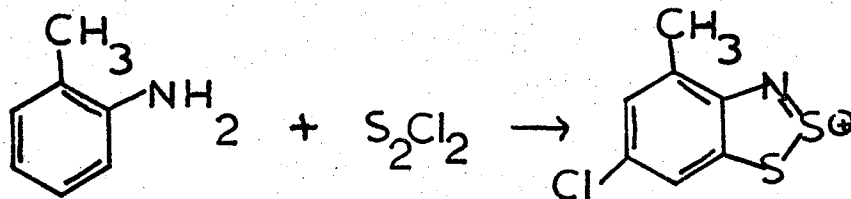
The 1,2-dithiolylium cation, built up with three trigonal carbon atoms and two sulfur atoms has a pronounced aromatic character together with a fair stability. Recently dithiolylium ions without any alkylthio substituents have been described^{3,4,5} which can be represented as the following canonical forms:



The above structure is isosteric with cyclohepta-trienylium ion.

However in the above structures, no canonical form involves positive charge on carbon 4, whereas in the tropylium ion, all the seven atoms of the ring are equivalent.

Only a few derivatives of the 1,2,4-dithiazolium system are known, probably due to lack of suitable preparative methods, rather than instability, since the derivatives of the isomeric isosteric system, the 1,2,3-dithiazolylium cation are known. It is formed in the Herz reaction.

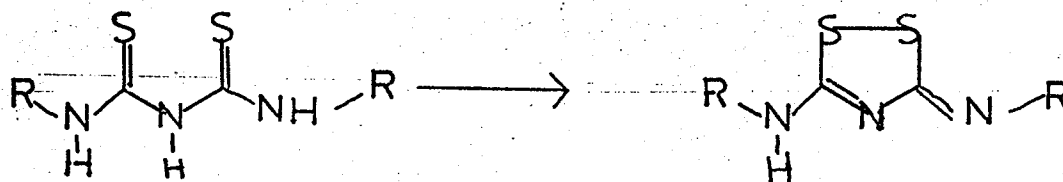


Different aryl amines have been used^{6,7} to obtain several 1,2,3-dithiazolylium cation derivatives.

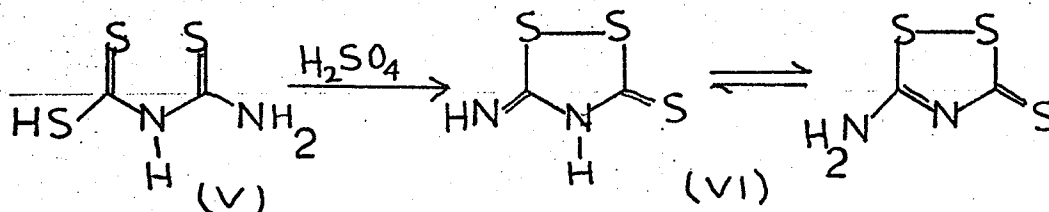
PREPARATION OF 1,2,4-DITHIAZOLE-3-THIONES

Although various derivatives^{9,10} of the system 1,2,4-dithiazole-3-thione have been made during the last two decades, synthesis of the unsubstituted ring itself has not so far been reported.

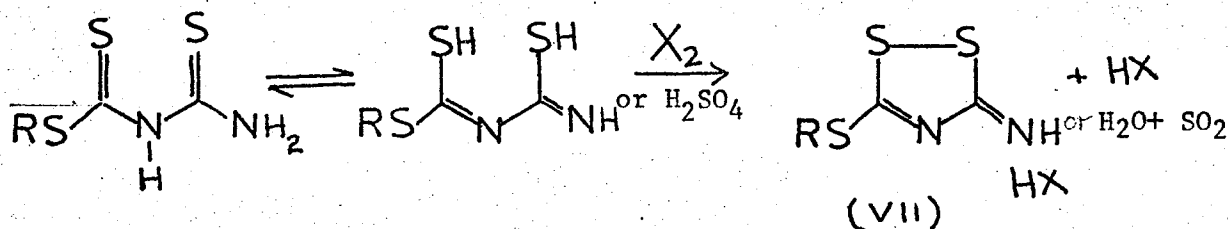
E. Fromm¹¹ reported the synthesis of cyclic disulfides of thiurets by the oxidation of the thiurets with iodine.



Later, Rosenheim et al¹² obtained 5-imino-1,2,4-dithiazolidine-3-thione by treatment of trithioallophanic acid (V) with conc. sulfuric acid:



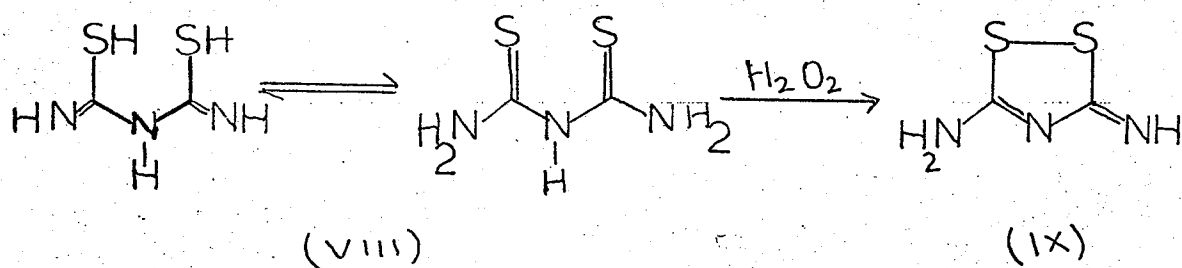
Oxidation of several alkyl esters of trithioallophanic acids with halogens or sulfuric acid gives 3-imino-5-alkylmercapto-1,2,4-dithiazoles¹³ (VII) as their hydrohalides or sulfates.



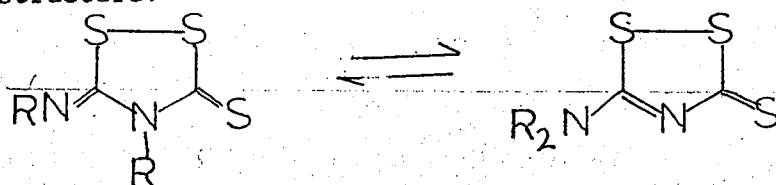
R = CH₃, n-C₃H₇, i-C₃H₇, n-C₄H₉, OH.CH₂.CH₂, C₂H₅

X = Halogen,

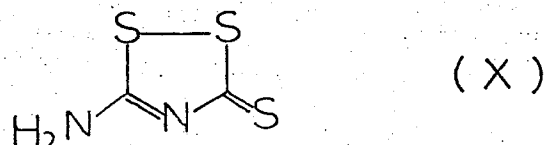
Preisler et al¹⁴ obtained the 3,5-diimino derivative of 1,2,4-dithiazole (IX) as its hydrochloride by suspending the dithiobiuret (VIII) in normal hydrochloric acid and subsequent treatment with hydrogen peroxide. Dithiobiuret may be obtained by the condensation of two moles of thiourea.



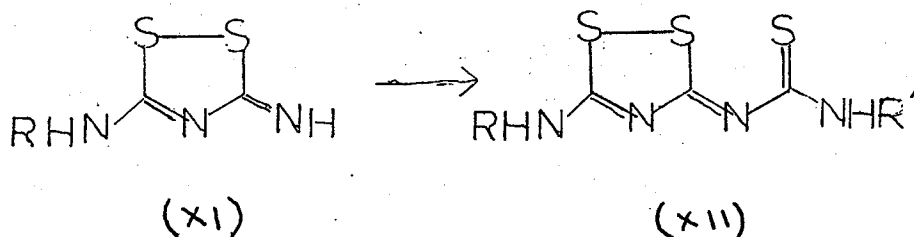
Freund¹⁵ isolated compounds of the type $(\text{RNCS})_2\text{Br}_3$, which on digestion with water or alcohol gave compounds of the type $(\text{RNCS})_2\text{S}$ having structure:



Hantzsch and Wolfenkamp¹⁶ postulated that isoperthiocyanic acid exists as (X), which was confirmed by crystallographic studies by Emelèus et al¹⁰.

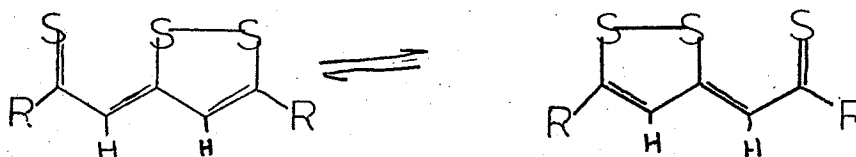


Behringer and Weber¹⁸ reacted N-substituted-5-amino-3-imino-1,2,4-dithiazole (XI) with various isothiocyanates, and obtained the imino derivatives (XII), which may also be considered as 1,2,4-dithiazole derivatives.

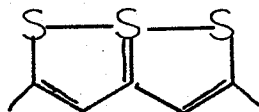


- | | |
|---|-----------------------|
| (a) R = Ph | R' = Ph |
| (b) R = Ph | R' = p-methoxy-phenyl |
| (c) R = p-OMe.C ₆ H ₄ | R' = Ph |

The compound (XII) is an aza analogue of the "thiothiophthene"* system



where the two forms shown may either exist in tautomeric equilibrium¹⁷, or may represent two contributing structures to a resonance hybrid where the sulfur-sulfur bonds exhibit single bond - no-bond resonance⁶². Another possible resonance structure would involve d-orbital participation of the central S atom.

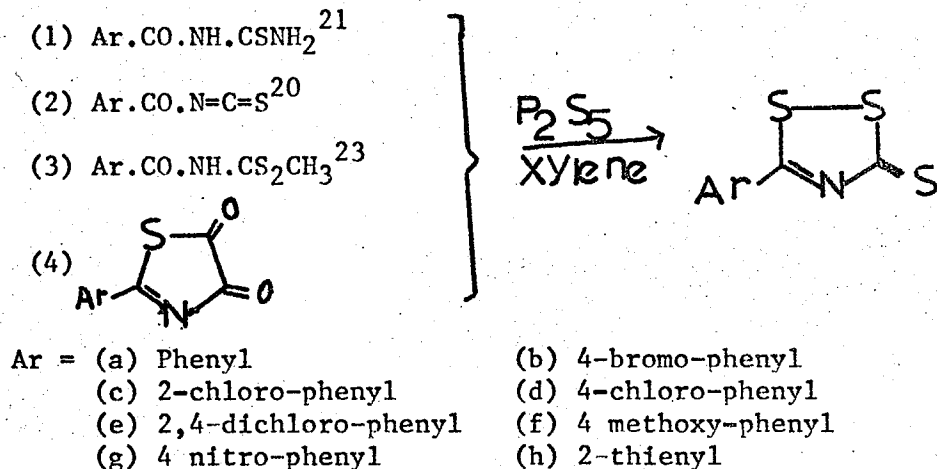


The sulfur-sulfur bonding has been investigated by K. Maeda²⁵ who suggests that it may involve $p_{\sigma} - p_{\sigma}$ bonding.

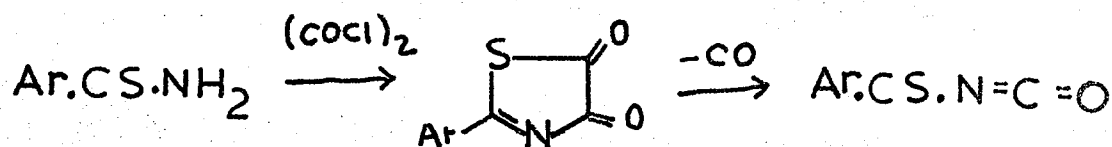
* Some authors call it "thiathiophthene", but in this thesis we will use "thiothiophthene".

However, syntheses of the system 1,2,4-dithiazole-3-thione, containing carbon atom attached directly to the heterocyclic ring have been reported only recently.^{1,19}

Derocque and Vialle¹⁹ used four procedures to obtain the 5-aryl substituted compounds. In the first procedure, they used N-benzoyl thiourea as the starting material and reacted it with phosphorus pentasulfide, but the yield of 5-phenyl-1,2,4-dithiazole-3-thione was very low. In the second method they used N-arylisothiocyanate prepared by the method of Hoggarth²⁰, and reacted it with phosphorus pentasulfide. In the third procedure, they prepared various N-aryldithiocarbamates from the isothiocyanate, and then sulfurized the compound by refluxing it with phosphorus pentasulfide. In the fourth method, an N-thioaroyl isocyanate was sulfurized.

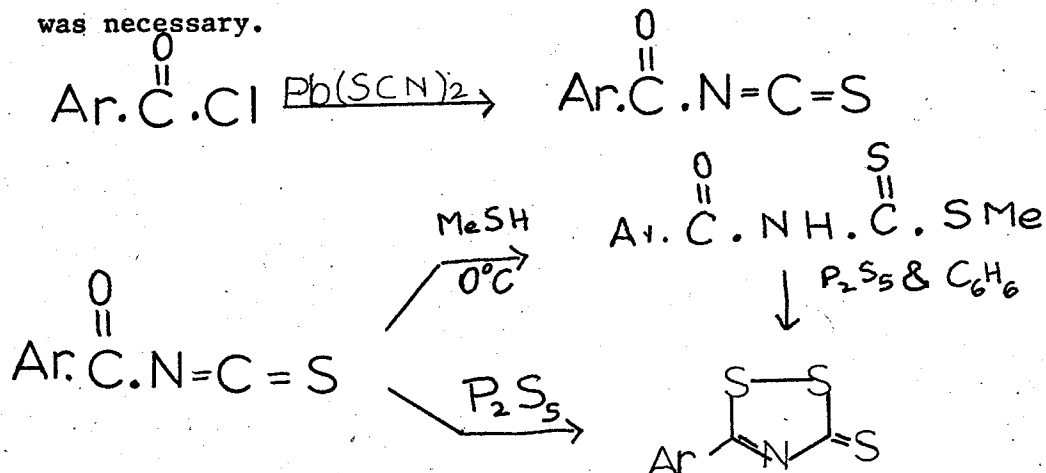


The thioaroylisocyanate was prepared by treatment of an aryl thioamide with oxalylchloride to provide a 5-aryl-thiazoline-4,5-dione, which was pyrolyzed.



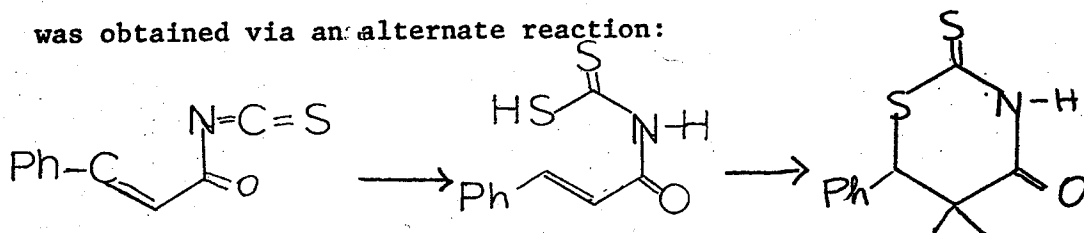
Other solvents besides xylene were used also, e.g. benzene, toluene and pyridine, but the yield was comparatively less.

MacDonald and McKinnon¹ prepared 5-aryl substituted dithiazole-3-thiones by rather similar methods, and also noted that sulfurization of benzoyl thionocarbamates gave 1,2,4-dithiazole-3-thiones but in low yield. They noted that the synthesis failed where the 5-substituent was aliphatic and suggested that a stabilizing aromatic substituent was necessary.



Ar = (a) Ph (b) p-methyl phenyl (c) o-toluyyl, (d) 2,5-dimethyl-phenyl, (e) p-methoxy-phenyl, (f) o-chloro-phenyl, (g) p-chloro-phenyl, (h) 2-furyl, (i) 2-thienyl, (j) 1-naphthyl, (k) 2-naphthyl

When cinnamoyl isothiocyanate was sulfurized, a 1,3-thiazine derivative was obtained via an alternate reaction:



Apart from these papers, which describe synthesis of the heterocyclic system there do not appear to be any reported in which other synthetic methods are used.

PREPARATION OF THE 1,2,4-DITHIAZOLIUM CATION

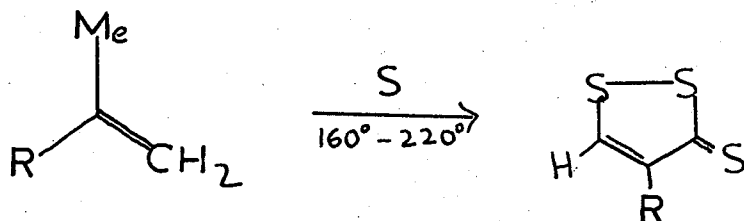
No preparations of this system from acyclic starting materials are reported, and it is hard to envisage syntheses analogous to those used for 1,2-dithiolium salts, e.g. action of hydrogen disulfide on a diacylamide, or oxidation of a dithiodiacylamide, since these precursors are not very well known. Successful methods used start from the corresponding dithiazole-3-thiones and are discussed under the reactions of these.

REACTIONS OF 1,2,4-DITHIAZOLE-3-THIONES:

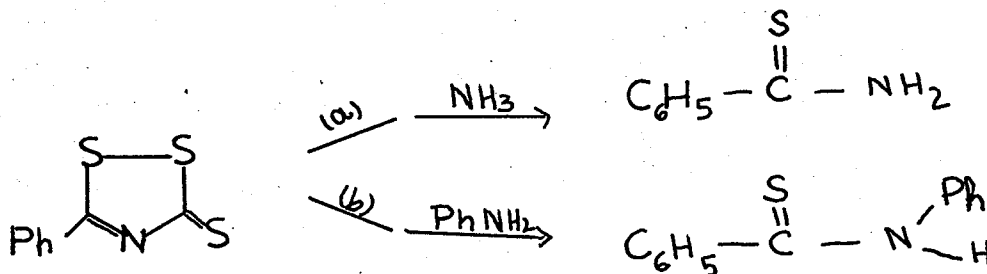
The system appears to be fairly stable, but probably less so than the 1,2-dithioles. Reactions of 1,2,4-dithiazole-3-thione so far reported in literature may be classified as:

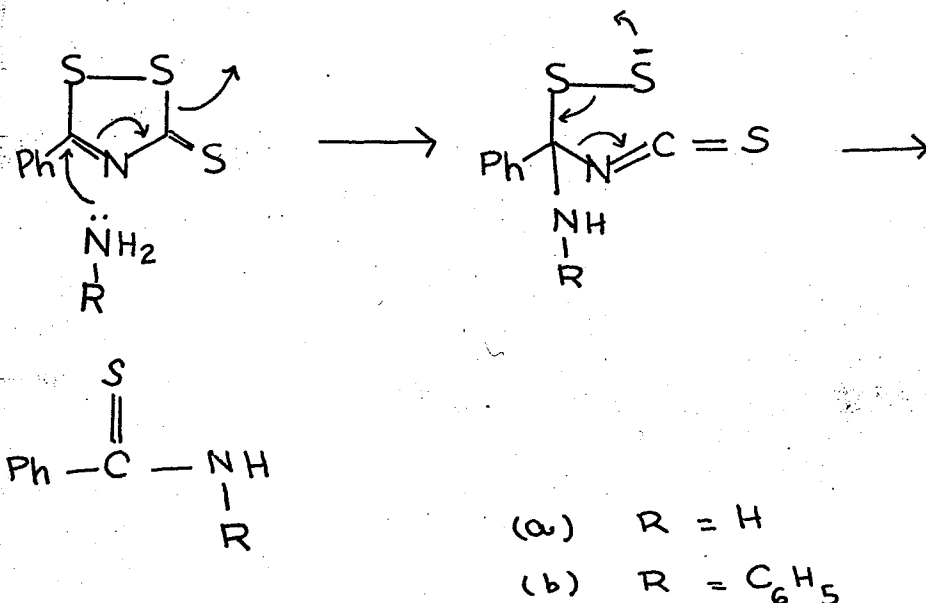
- (a) effect of heat
- (b) reaction with bases, e.g. ammonia and amines,
- (c) reaction with mercuric acetate,
- (d) reaction with acetylenes,
- (e) reaction with alkylating agents.

(a) On heating in a sealed tube. 5-phenyl-1,2,4-dithiazole-3-thione suffers decomposition¹, giving sulfur, carbon disulfide and benzonitrile. This may be contrasted with the dithiole thiones which appear to be fairly stable to heat as may be seen by some of the methods of synthesis⁵³.

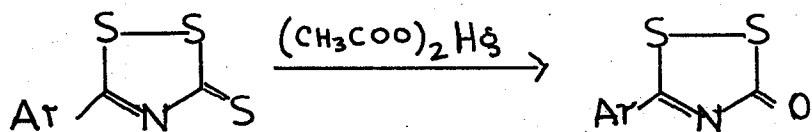


(b) 5-phenyl-1,2,4-dithiazole-3-thione reacts with ammonia and aniline¹ and gives as decomposition products thiobenzamide and N-phenyl thiobenzamide. Presumably they are formed via initial nucleophilic attack at position 5 with ring fission.





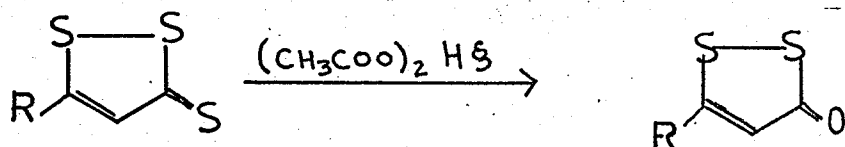
(c) Derocque and Vialle¹⁹ attempted conversion of the exocyclic C=S group of the thione to C=O. 5-aryl-1,2,4-dithiazole-3-thione was treated with mercuric acetate, and the product obtained was the 1,2,4-dithiazole-3-one. The IR spectrum of the compound showed strong absorption bands at 1670 cm^{-1} and 1700 cm^{-1} characteristic of the carbonyl group.



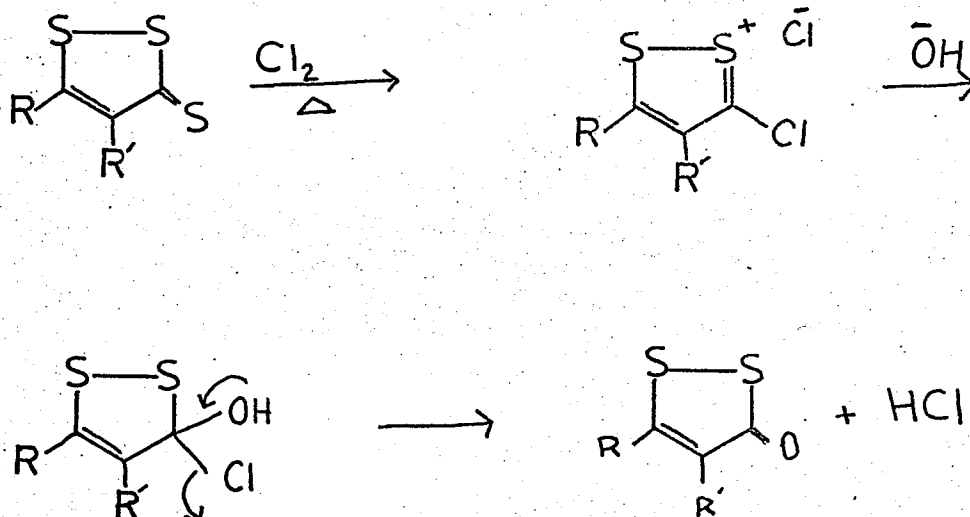
Ar = Phenyl, 4-bromo-phenyl; 2-chloro-phenyl; 4-chlorophenyl
2,4-dichlorophenyl; 4-methoxyphenyl; 4-nitrophenyl;
2-thienyl

This reaction is also found in the 1,2-dithiole-3-thiones, the carbon analog of the thiazole thione system, which have been reported⁷¹,

to undergo conversion to C=O group from C=S using mercuric acetate.



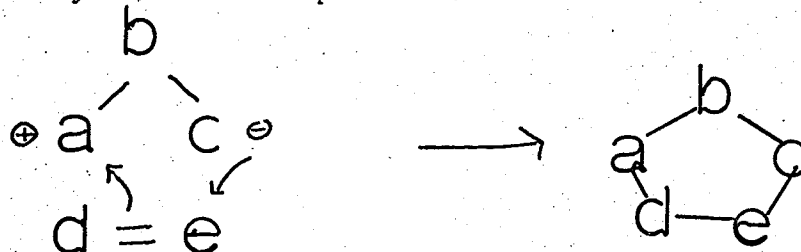
The ketones may also be made from the 1,2-dithiole-3-thiones²⁶ by chlorination followed by hydrolysis:



(d) A very interesting type of reaction which 5-phenyl-1,2,4-dithiazole-3-thione has been reported. This is their 1,3-dipolar cycloaddition reactions with activated acetylenes and benzyne.

1,3 addition reactions of diazoalkanes, azides and ozones have been known for over 50 years, and although they were reviewed²⁷ to a reasonable extent in the past, it is only recently²⁸ that the general concept of 1,3 dipolar cycloadditions has been presented more clearly.

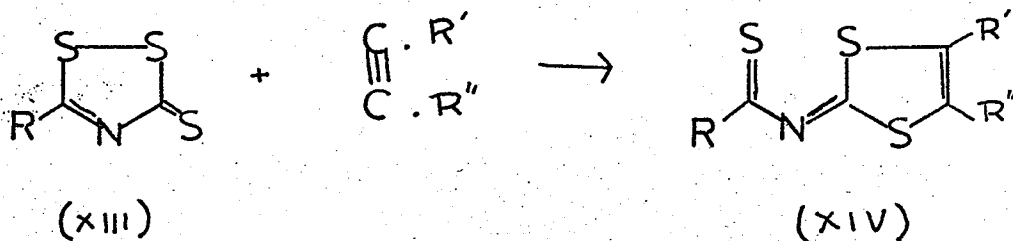
Most frequently in cycloadditions, two reactants unite to form a cyclic compound creating two new sigma bonds at the expense of two pi bonds. In cyclo addition of the type $(3+2 = 5)$, a - b - c is a 1,3 dipole; atom 'a' possessing an electron sextet and 'c' is the negatively charged centre with an unshared pair of electrons. Combination of such a 1,3 dipole with a multiple bond system d = e, called dipolarophile, is referred to as a 1,3 dipolar cycloaddition. The dipolarophile may be any double or triple bond.



A large number of groups acting as dipolarophile, have been reviewed by Huisgen²⁸. Two mechanisms have been suggested for 1,3 dipolar cycloadditions. Huisgen²⁹ suggested that the reaction goes by a concerted rather than stepwise mechanism. According to him, 1,3 dipole is always an ambivalent compound, which displays electrophilic and nucleophilic activity in positions 1 and 3. The mesomerism of the octet and sextet resonance structures of the 1,3 dipole results in charge compensation or charge exchange, respectively, which makes it impossible to identify unequivocally an electrophilic and nucleophilic centre. This eliminates the possibility of the stepwise mechanism. Thus according to him a concerted addition, which can also be described in terms of molecular orbitals and in which the two new sigma bonds are formed simultaneously, offers the best explanation of the experimental

facts. Firestone³⁰ on the other hand suggested a two step mechanism, with a discrete intermediate a spin-paired diradical. Conjugation exerts the promoting effect on the dipolarophilic activity of all multiple bonds, which means that the intermediate, whether dipolar or diradical in nature derives some stabilization through conjugation. Both Huisgen and Firestone have their views substantiated by arguments, and it is not the purpose of this thesis to go into these arguments.

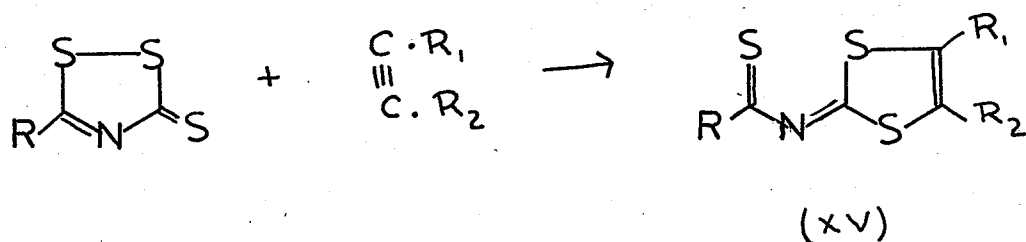
A number of instances have been reported in literature where $C \equiv C$ derivatives act as dipolarophile, and add to the cyclic 1,3 dipole causing ring opening of the initial starting material. Behringer and Deichmann³¹ reported the addition of acetylene derivatives to 5-phenyl-1,2,4-dithiazole 3-thione:



XIV

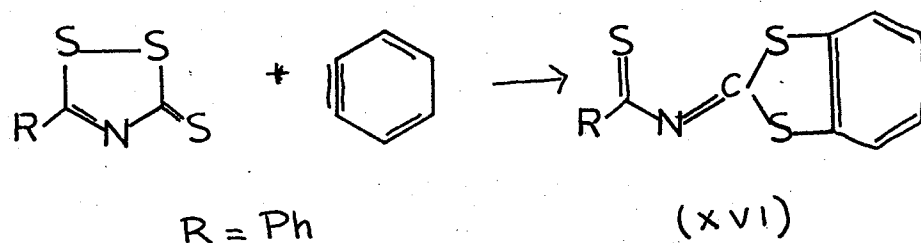
XIII - R=	R=	R'=	R''=
(a) Ph	(a) Ph	COOCH ₃	COOCH ₃
(b) p-Cl C ₆ H ₄	(b) Ph	H	COOH
(c) p-CH ₃ .C ₆ H ₄	(c) Ph	H	H++
(d) p-OCH ₃ .C ₆ H ₄	(d) Ph	H	CHO
	(e) Ph	H	Ph
	(f) p-Cl.C ₆ H ₄	COOCH ₃	COOCH ₃
	(g) p-Cl.C ₆ H ₄	H	CHO
	(h) p-CH ₃ .C ₆ H ₄	COOCH ₃	COOCH ₃
	(i) p-CH ₃ .C ₆ H ₄	H	CHO
	(j) p-CH ₃ O.C ₆ H ₄	COOCH ₃	COOCH ₃
	(k) p-CH ₃ O.C ₆ H ₄	H	CHO

MacDonald and McKinnon¹ have also reported the formation of monoadducts of the type (XV).

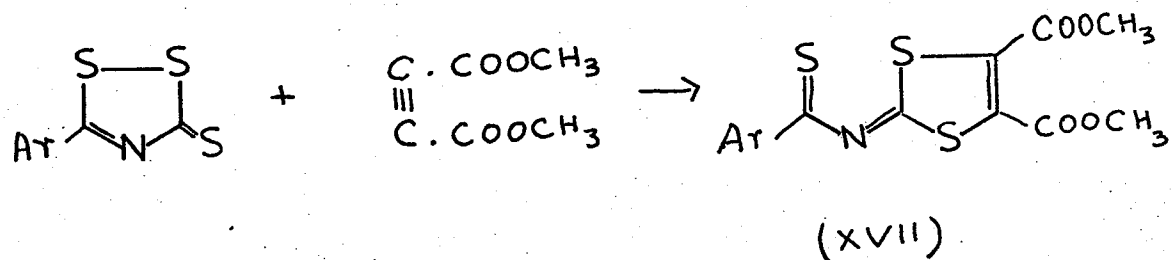


	R	R ₁	R ₂
(a)	Ph	COOEt	H
(b)	Ph	COOEt	Ph
(c)	Ph	COOMe	COOMe
(d)	thienyl	COOEt	H

They also reported the addition of benzyne on the ring in a similar fashion; benzyne acting as a dipolarophile:

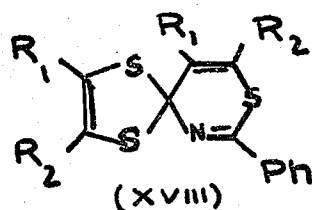
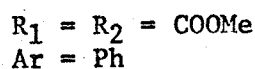
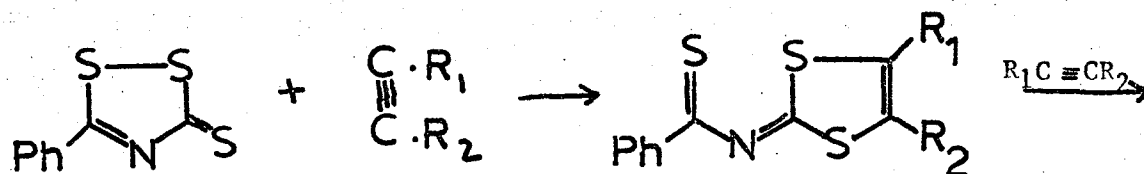


Lang and Vialle³² have also obtained 1,3 monoadduct of the following type:

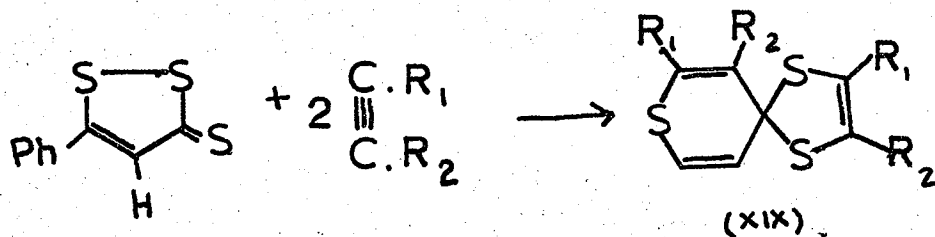


Ar =	(a) Ph
	(b) p-Cl.C ₆ H ₄
	(c) p-OCH ₃ .C ₆ H ₄

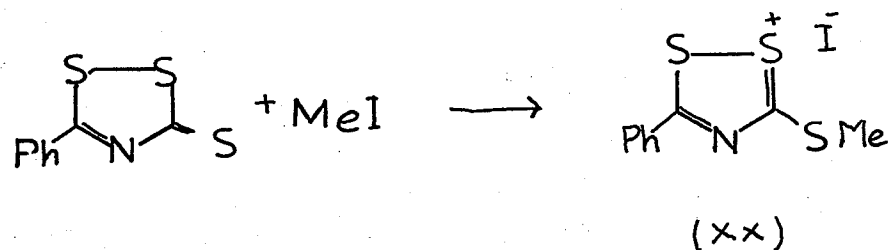
They have also reported the formation of a diadduct with acetylenic compound and 5-phenyl-1,2,4-dithiazole-3-thione:



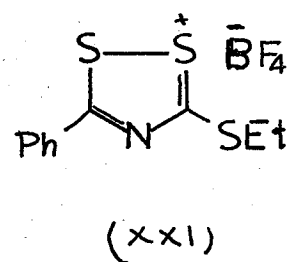
Similar type of addition reactions of activated dipolarophilic acetylenes have been reported for the carbon analogue of the dithiazole substrate.^{33,34,35} They are also reported^{33,34,36} to give a diadduct by the addition of one more acetylene molecule:



(e) Reactions with alkylating agents - Only a few reactions with alkylating reagents have so far been reported. MacDonald and McKinnon¹ obtained the methyl iodide salt of the thione (XIII-a), i.e. 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide (XX), by dissolving the thione in methyl iodide and allowing the mixture to stand for 16 hours.

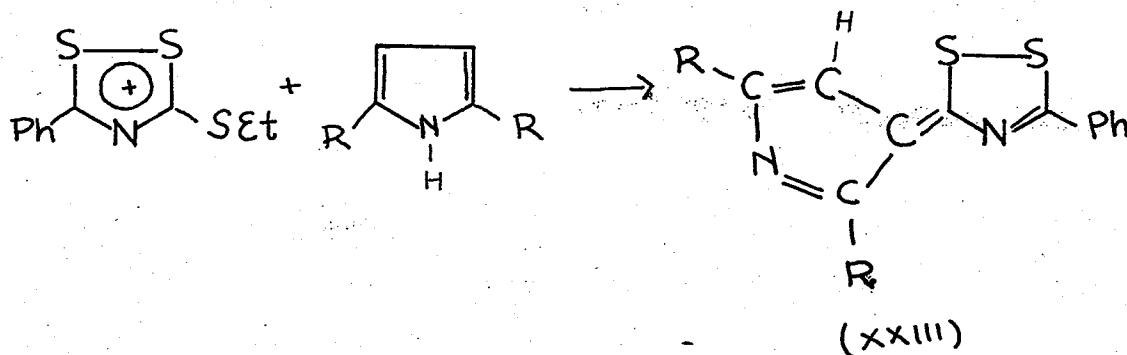
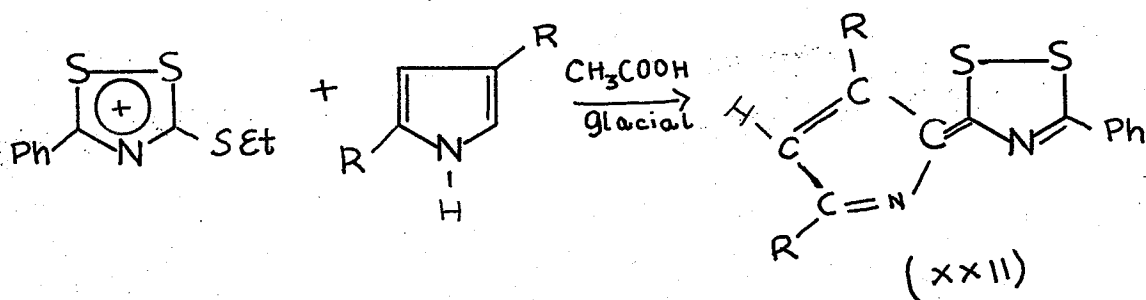


Similarly Gompper and Weiss⁸ prepared 5-phenyl-3-ethylthio-1,2,4-dithiazolium fluoroborate (XXI) by the reaction of triethyl-oxonium fluoroborate with dithiazole thione:



REACTIONS OF 1,2,4-DITHIAZOLIUM CATION

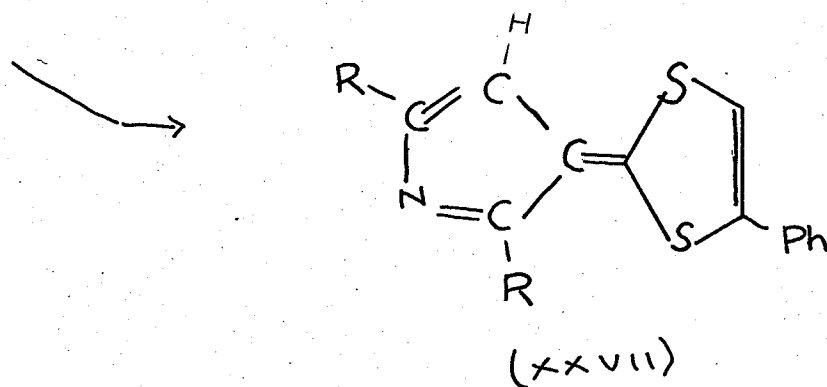
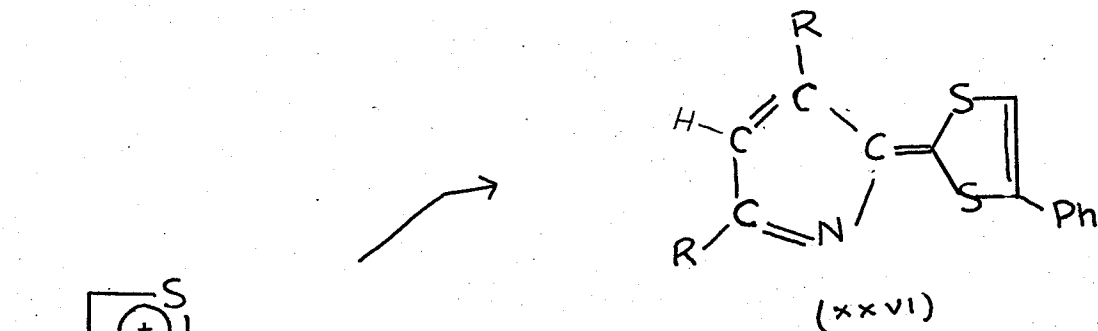
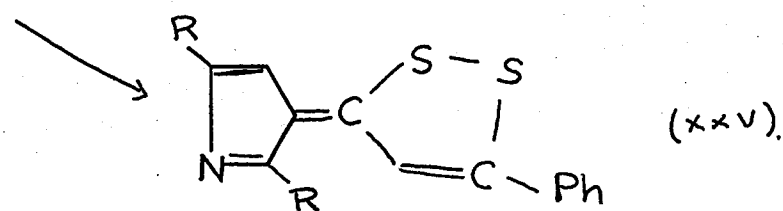
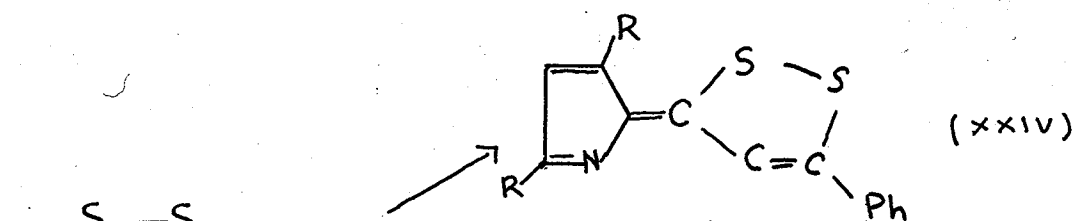
Not much work has been done on the 1,2,4-dithiazolium cation. Gompper and Weiss⁸ have reported the formation of azafulvenes by the action of dimethyl or diphenyl pyrroles with 3-ethylthio-1,2,4-dithiazolium salts (XXI).



These reactions obviously proceed via nucleophilic addition of the pyrroles to the 3 position of the heterocyclic ring, with elimination of ethanethiolate anion.

Analogously, 5-phenyl-3-methylthio-1,2-dithiolium and 4-phenyl-2-methylthio-1,3-dithiolium cations have been made⁸, which also on reaction with dimethyl pyrroles and diphenyl pyrrole in glacial acetic

acid give the corresponding fulvenes:



OBJECT OF RESEARCH

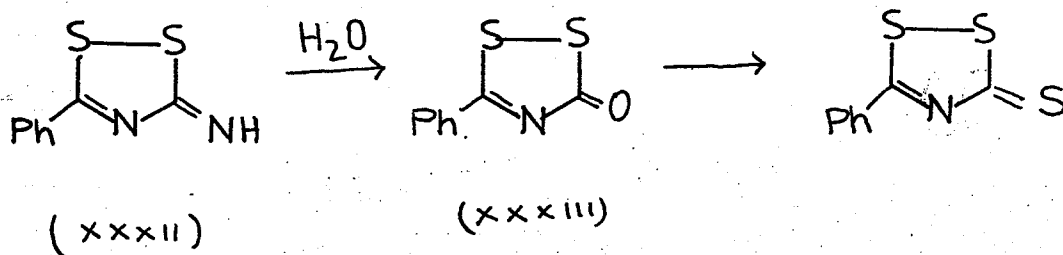
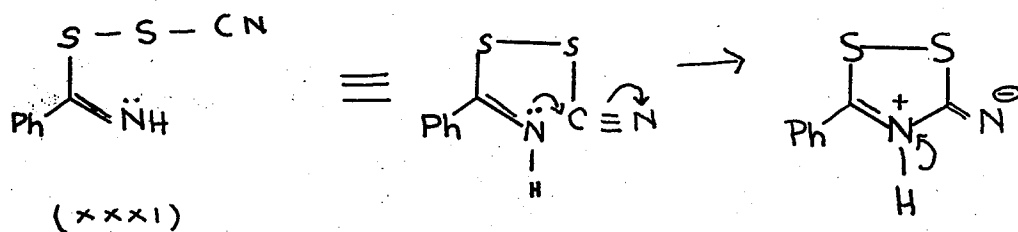
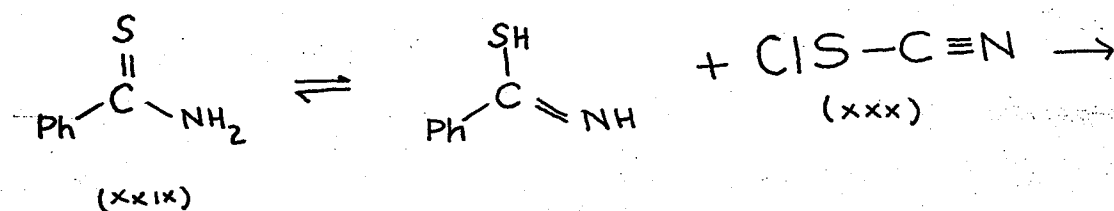
The object of the present study was:

- (A) To extend the previous methods of synthesis of the 1,2,4-dithiazole-3-thione ring;
- (B) To develop new methods of synthesizing the 1,2,4-dithiazole-3-thione system and to attempt to convert it to the 1,2,4-dithiazolium system by methods analogous to those used for 1,2-dithiole-3-thiones;
- (C) To study nucleophilic reactions on the 5-aryl-1,2,4-dithiazole-3-thione system;
- (D) To study the reactions of certain 1,3 dipolarophiles on this system. Once more the formation of mono adducts would be expected. These would be able in certain cases to form diadducts. If these adducts have suitable functional groups, e.g. carbonyls, it might be possible to build up novel heterocyclic systems;
- (E) To study the reactions of the 1,2,4-dithiazolium cation
It is to be expected that the system would behave analogously to the 1,2-dithiolium cation and would be subject to nucleophilic attack at the 1 or 2 position. It would be also expected that certain 2-substituents e.g. Cl or S-alkyl, would be displaced by certain nucleophiles. In addition, the cation should behave as an electrophilic agent, and be able to substitute certain activated aromatic rings.

DISCUSSION

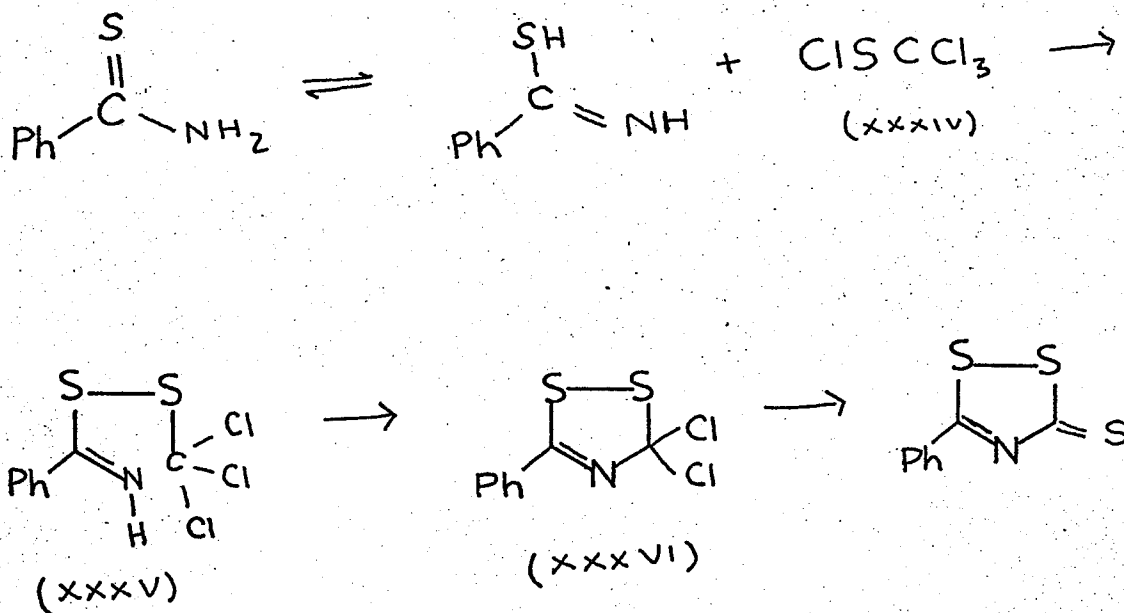
Syntheses of the 1,2,4-dithiazole ring

One scheme devised to develop a new synthesis involved thio-benzamide (XXIX) as the starting material, which on reaction with thiocyanogen chloride (XXX) would give (XXXI), and which by intra-molecular nucleophilic substitution should give a dithiazole ring with imino group on carbon 3. Hydrolysis and subsequent sulfurization would be expected to give 5-phenyl-1,2,4-dithiazole-3-thione.



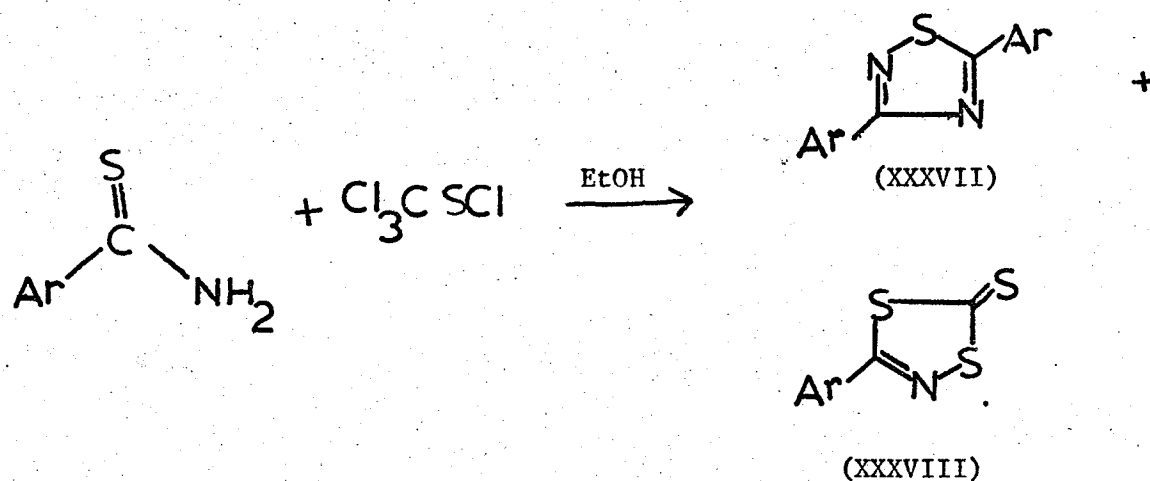
However, when the thiobenzamide and thiocyanogen chloride were allowed to react, the expected product (XXXI) was not obtained. There was no NH peak in the IR, and the elemental analysis did not give the calculated percentage of elements in the compound. It is assumed that $\text{Ph}-\overset{\text{SH}}{\underset{|}{\text{C}}}=\text{NH}$ perhaps is not a sufficiently good nucleophile to replace chlorine of the compound (XXX). The experiment was thus abandoned after several attempts.

A second course of reactions starting with thiobenzamide and trichloromethane sulphenyl chloride was attempted.



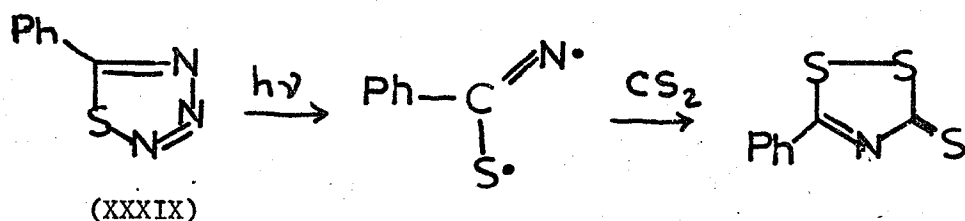
This had to be abandoned since the reaction product of these reagents could not be obtained. In trichloromethane sulphenyl chloride, the sulfur atom is expected to have greater positive charge due to the inductive effect of three methyl chlorine atoms in order to act as a more favourable substrate for the nucleophilic attack by thiobenzamide; but at the same time, it does not facilitate the removal of chlorine atom on sulfur, and therefore not favoring the nucleophilic attack.

Noel and Vialle³⁸ used the same reagents to synthesize a dithiazole thione ring. They effected the reaction in alcohol, and obtained a mixture of a 3,5-diaryl-1,2,4-thiadiazole (XXXVII) and 3-aryl-1,4,2-dithiazole-5-thione (XXXVIII).

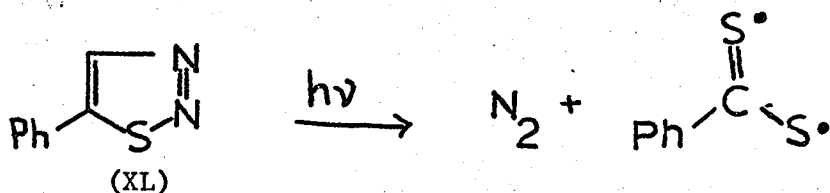


Failure in our experiment may probably be due to wrong choice of solvent. Perhaps the acetone was not a sufficiently polar solvent to help in the formation of ion $+\text{S}-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}-\text{Cl}$ which could then be attacked by the nucleophile sulfur of a thiolic form of thiobenzamide $\text{Ph}-\overset{\text{SH}}{\text{C}}=\text{N}-\text{H}$ to give (XXXV).

The third method attempted for the synthesis of 5-phenyl-1,2,4-dithiazole-3-thione involved 5-phenyl-1,2,3,4-thiatriazole (XXXIX) as the starting material. The 5-phenyl-1,2,3,4-thiatriazole (XXXIX) when subjected to UV light would be expected to homolytically decompose into a diradical in carbon disulfide, which would immediately combine with carbon disulfide to give a dithiazole-3-thione.



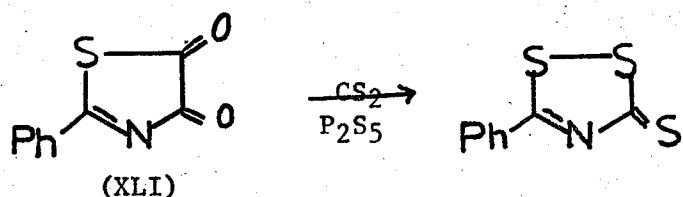
Such photolytic reactions are not uncommon; the 1,2,3-thiadiazole (XL) has been reported to undergo homolytic fission to give a diradical when subjected to ultraviolet light:



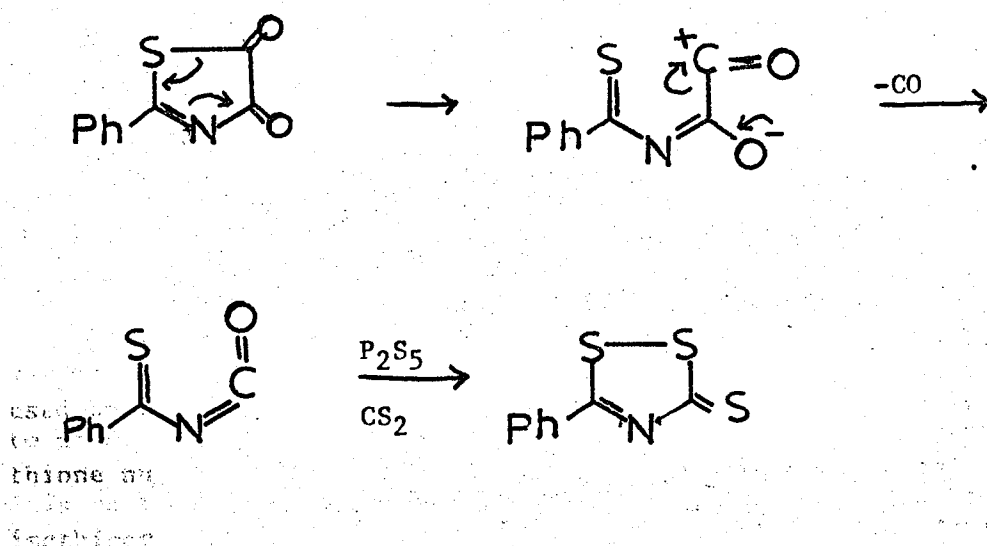
But when (XXXIX) was subjected to the UV light using Fisher UVL.22 lamp for 48 hours, no formation of the product was observed. This may be attributed to unsuitable wave-length. Homolytic fission of (XXXIX) was also attempted by heating it in carbon disulfide under pressure in a sealed tube in water bath, which also was not successful, presumably due to the insufficient amount of energy supplied in heating on the water bath.

A further synthesis of 5-phenyl-1,2,4-dithiazole-3-thione was attempted starting 2-phenylthiazolin-4,5-dione (XLI). Derocque and Vialle¹⁹ have synthesized 5-aryl-1,2,4-dithiazole-3-thione by refluxing (XLI) in xylene with phosphorus pentasulfide. We attempted to obtain the thione by refluxing the dione (XLI) in carbon disulfide and phosphorus pentasulfide and obtained 5-phenyl-1,2,4-dithiazole-3-thione,

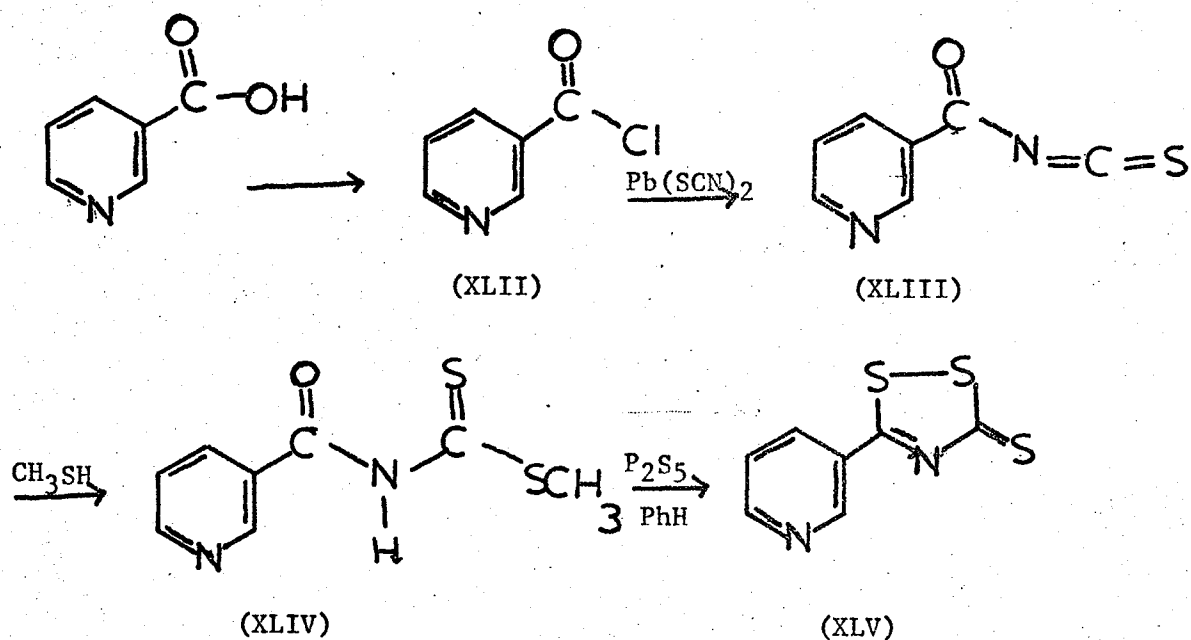
which was identical with the thione made by the previous methods as determined by infrared spectrum.



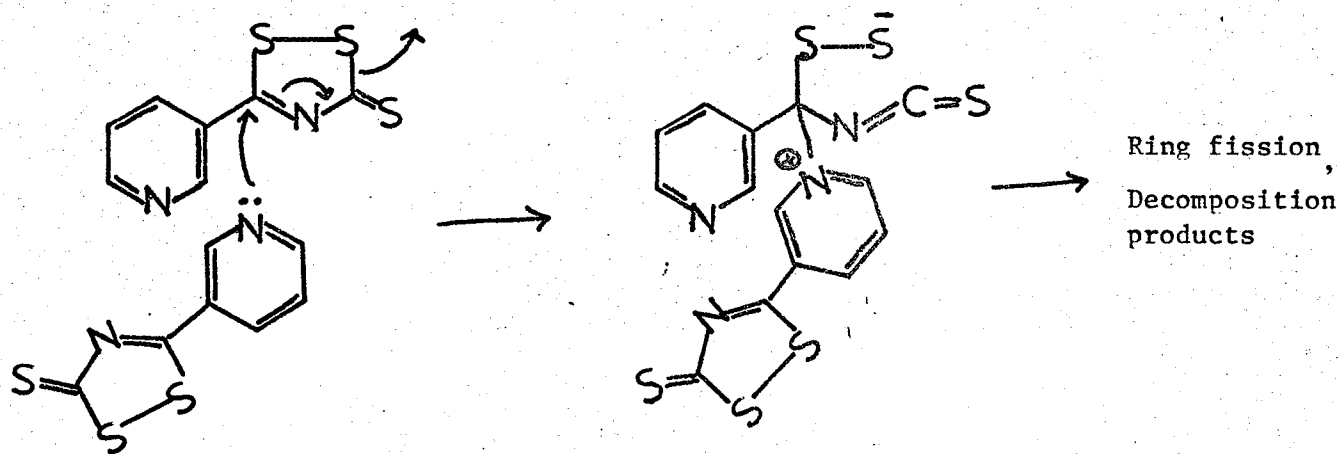
The reaction proceeds probably according to the following mechanism:



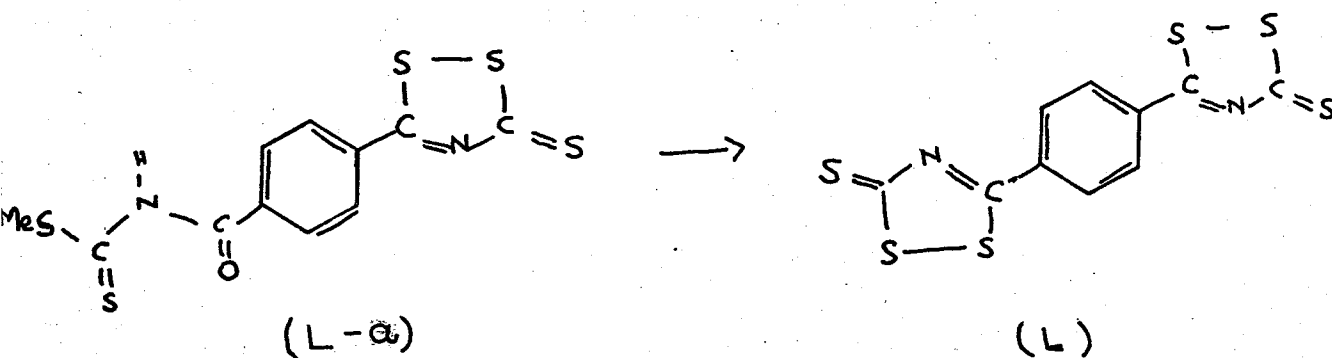
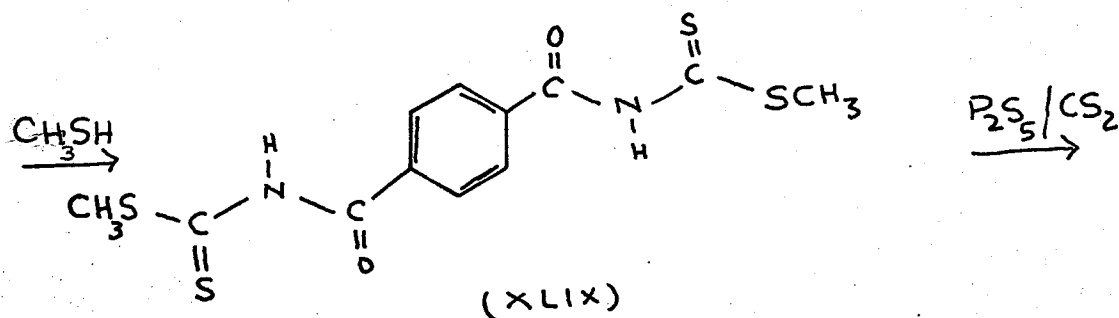
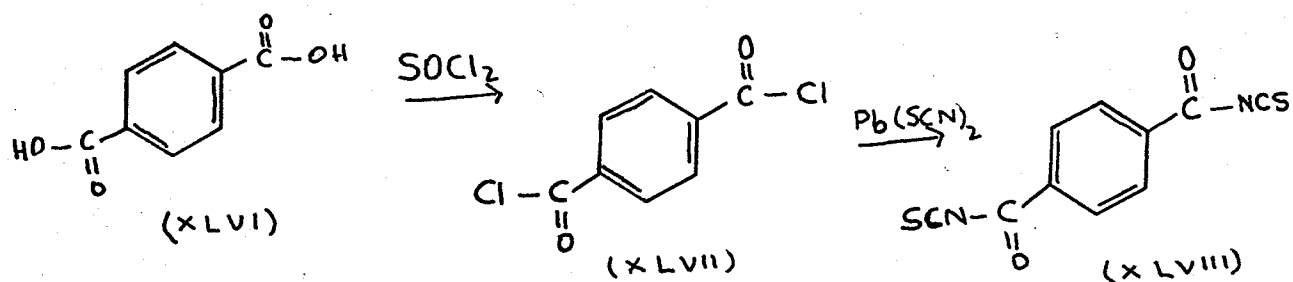
Using methods of the 1,2,4-dithiazole-3-thione ring synthesis used by the previous workers,^{1,19} the synthesis of 1,2,4-dithiazole-3-thione nucleus with different 5-aryl groups, was attempted. Nicotinoyl isothiocyanate (XLIII) was made from nicotinoyl chloride (XLII), which was made by the method of Wingfield et al.³⁹ (XLII) was then converted to give nicotinoyl dithiocarbamate (XLIV) by treating with methyl mercaptan. This on treatment with phosphorus pentasulfide in carbon disulfide was expected to give the corresponding thione.



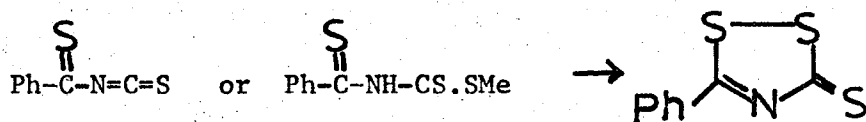
The nicotinoyl isodithiocarbamate (XLIV) was synthesized successfully, but its conversion into the thione (XLV) could not be achieved. The 1,2,4-dithiazole-3-thione system appears to be unstable to bases, e.g. ring fission by attack of aniline. Possibly the failure of the reaction here is caused by nucleophilic attack of alpha pyridine ring on the dithiazole ring. MacDonald and McKinnon¹ have shown that the 1,2,4-dithiazole ring is attacked by base leading to ring fission.



Another synthesis attempted started with terephthalic acid (XLVI); this was converted into terephthaloyl chloride (XLVII), then into terephthaloyl diisothiocyanate (XLVIII), and then into dimethyl terephthaloyl dithiocarbamate (XLIX). Refluxing it with carbon disulfide and phosphorus pentasulfide was expected to give the corresponding thione.



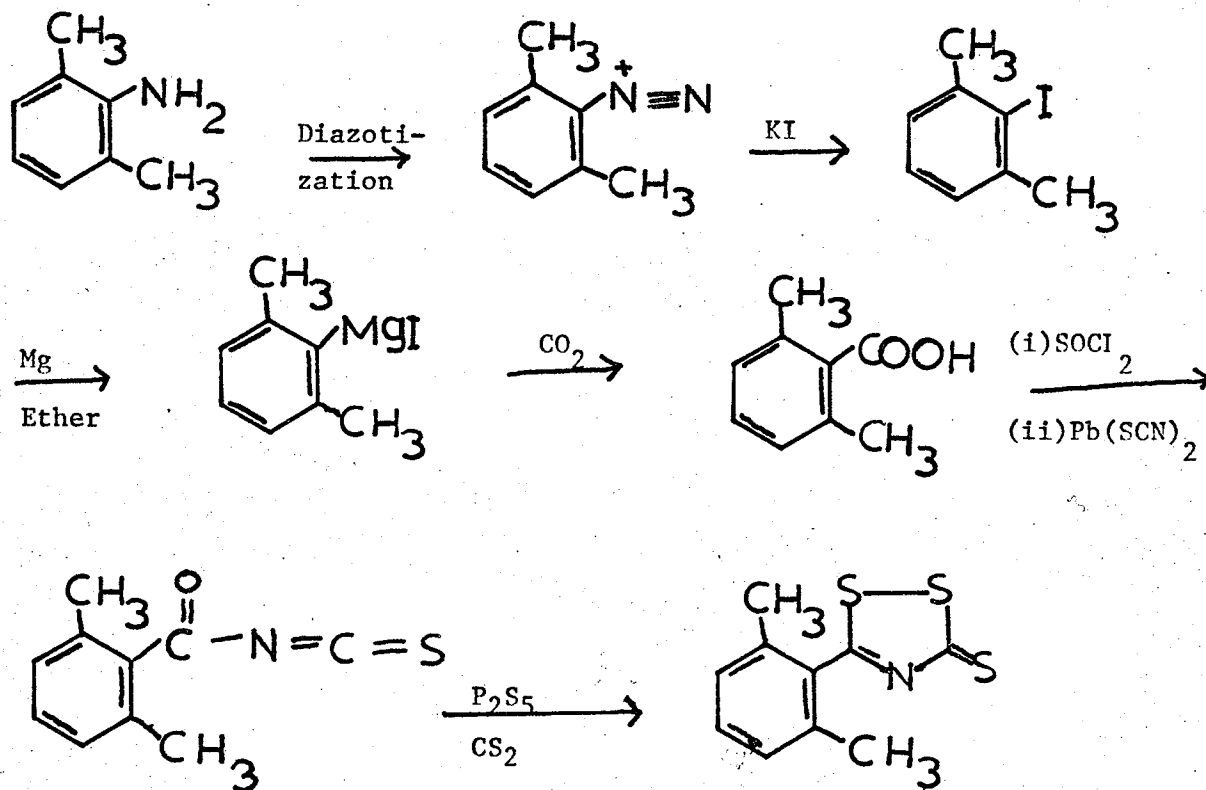
We were able to obtain compound (XLIX) according to the above scheme as was confirmed by the elemental analysis and the infrared spectrum; however, when this was refluxed with phosphorus pentasulfide in (i) carbon disulfide and (ii) xylene, the corresponding thione (L) was not obtained. It could have equally been possible that only one isodithiocarbamate group was converted into thione, but the elemental analysis on the product obtained when (XLIX) was refluxed with phosphorus pentasulfide in carbon disulfide does not substantiate this line of thought also. Failure to obtain the expected product may be attributed to the lack of resonance stabilization. In 5-aryl derivatives made previously¹, it has been suggested that the aryl contributes by way of resonance to the stability of the respective thiones. Lack of this, and also possibly steric interference, or some sort of steric interaction between the two large isodithiocarbamate groups might have led to the failure to synthesize the thione (La) or (L). Another reason may be statistical. For



yield is low, say (x/100)%. Here yield for the double process would be (x²/100²)% - this could be very low!

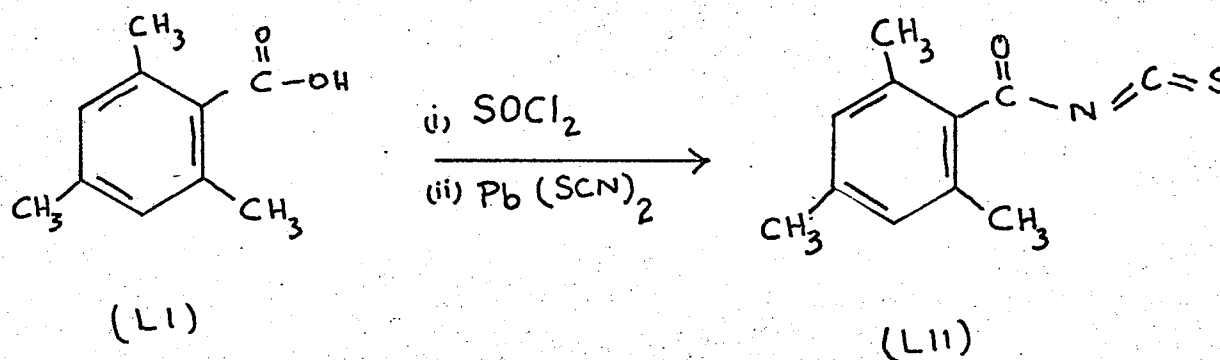
Further attempts were made to synthesise (a) 5-(2,6-dimethylphenyl)-1,2,4-dithiazole-3-thione, (b) 5-(2,4,6-trimethylphenyl)-1,2,4-dithiazole-3-thione, and (c) 5-(2-vinylphenyl)-1,2,4-dithiazole-3-thione.

Starting material for (a) was 2,6-dimethylaniline, which would have given the thione according to the following scheme:



Conversion of 2,6-dimethylaniline into 2,6-dimethylbenzoic acid has though been reported in literature^{40,41,42} by the above method, but our efforts failed to obtain 2,6-dimethylphenyl iodide. A second approach was then adopted which involved conversion of the aniline into 2,6-dimethylphenyl cyanide by the method of Haring⁴³, and subsequent hydrolysis by sulfuric acid.⁴³ The nitrile was obtained in approximately 30% yield, but its conversion into 2,6-dimethyl benzoic acid could not be effected. The more obvious reason for the failure to obtain such a compound is probably that due to the 2,6-dimethyl groups, it was very difficult for the big iodine atoms to substitute for the amino group; again, -COOH group is also a very big group which suffers steric hindrance by the two ortho methyl groups, thus rendering it extremely difficult to obtain such an acid.

In synthesizing (b) again, similar type of difficulties were encountered. Starting material was 2,4,6-trimethylbenzoic acid, which was converted into the isothiocyanate (LII), but the subsequent ring cyclization could not be achieved, again perhaps due to large 2,6-dimethyl groups' steric hindrance. These groups would prevent the coplanarity of the benzene ring with the dithiazole, and hence would prevent conjugation and in turn would prevent stabilization, which has been suggested as being necessary in this type of synthesis¹.



Starting material for the synthesis of compound (c) was o-chlorobenzaldehyde, which was converted into o-chlorovinyl benzene by the method of Overbergers, Saunders and Aleen⁴⁴. Subsequent conversion of o-vinyl chlorobenzene into o-vinyl benzoic acid could not be achieved. This is in accordance with what has been found in literature³⁷.

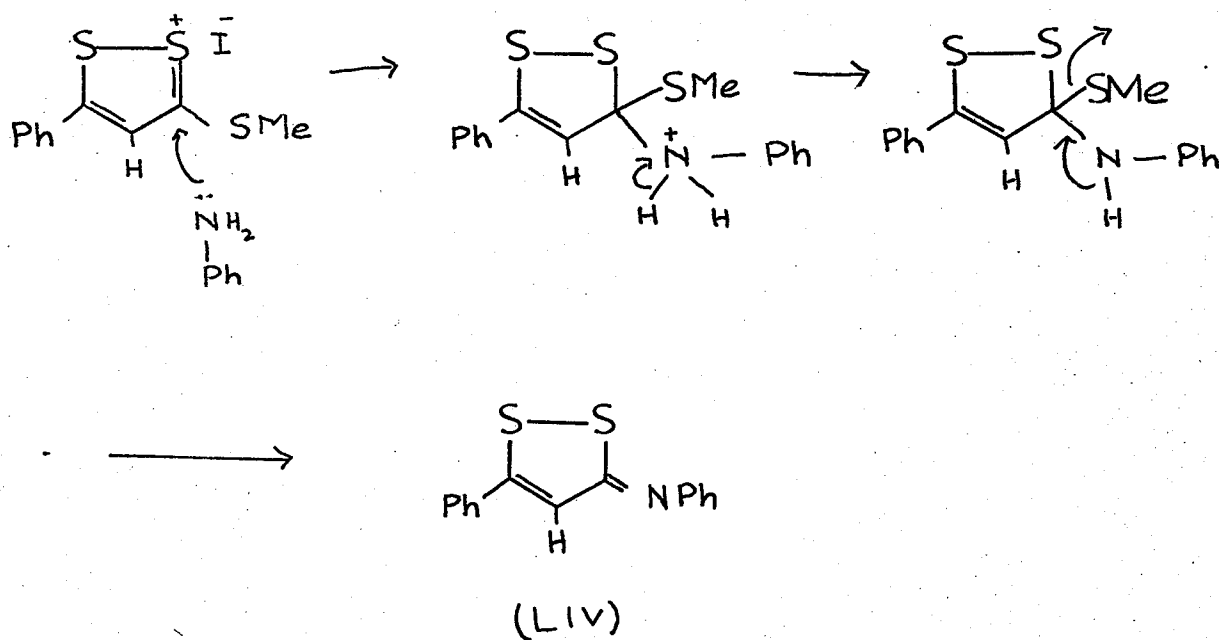
Reactions

The type of reactions carried out may be classified as under:

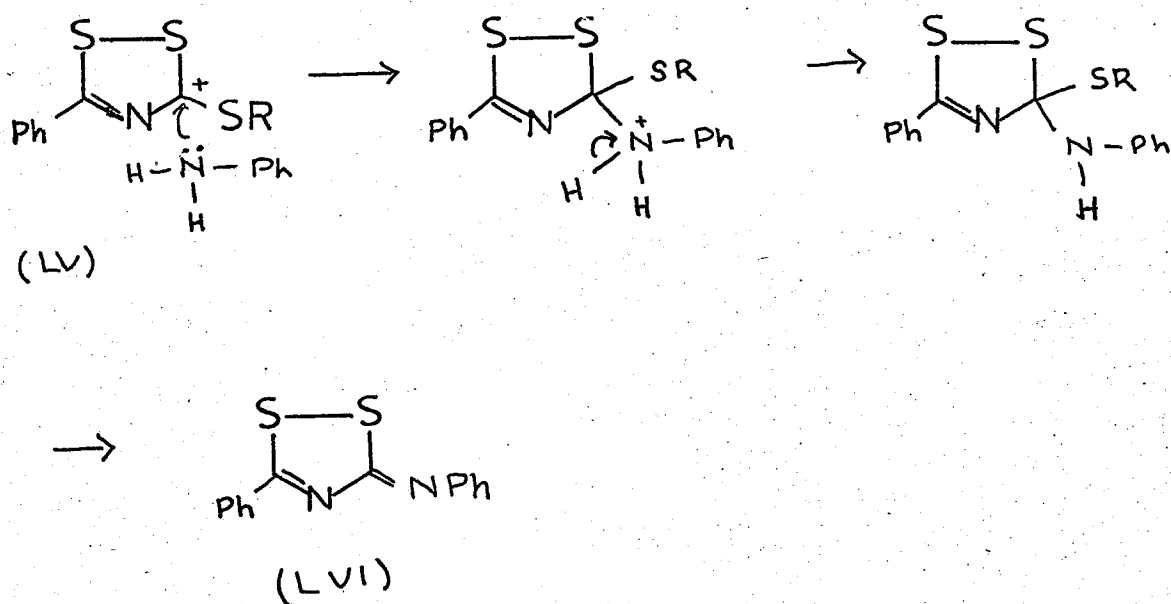
- (1) Reactions of 3-alkylthio-5-phenyl-1,2,4-dithiazolium cation with different nucleophiles.
- (2) Reactions of 5-phenyl-1,2,4-dithiazole-3-thione with:
 - (i) activated acetylenic compound
 - (ii) other reagents.
- (3) Further reactions of the monoadduct with the activated acetylenes prepared in 2(i) and the conversion of some of these monoadduct into novel heterocyclic systems.

(1) Reactions of 5-phenyl-3-alkylthio-1,2,4-dithiazolium cation

(i) Reaction with aniline: It was observed that 5-phenyl-3-methylthio-1,2-dithiolium iodide reacts with aniline^{77,78} to give the product (LIV) by initial nucleophilic attack at the 3 position followed by loss of methane thiol



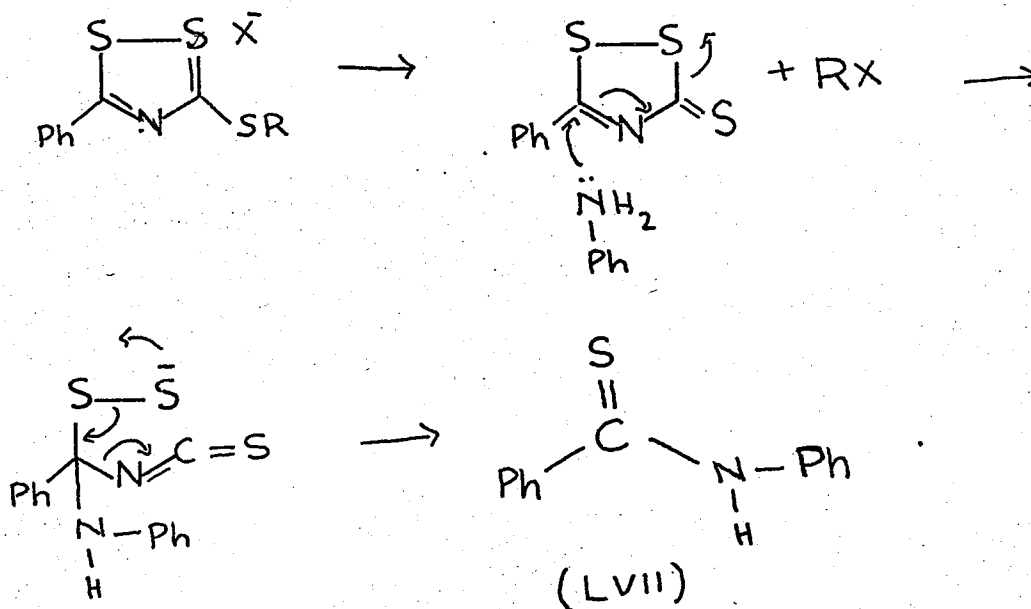
We attempted the similar reaction with 3-methylthio- and 3-ethylthio-5-phenyl-1,2,4-dithiazolium cations. The latter compound was found more soluble in acetic acid than the former. On the basis of analogy, the reaction was expected to take the following course.



- (LV) (a) R= Me
 (b) R= Et

(LV-a) reacted rapidly with aniline in dimethyl sulfoxide, but the IR of the product obtained was not consistent with the formation of the compound (LVI). In compound (LV) C - N bond is shorter than the C-C bond in (LIII). Further, nitrogen being more electronegative than carbon, has a tendency to inductively attract electrons towards itself, thus making carbon 3 more susceptible to nucleophilic attack by aniline which would allow the formation of (LVI). On the other hand, it may also be possible that carbon 5 is a better site for nucleophilic

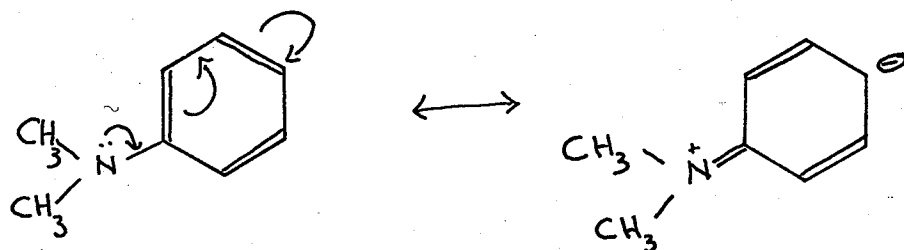
attack by aniline in which case one possible reaction would involve demethylation of the substrate, with the subsequent formation of thio-benzanilide (LVII), according to the following scheme:



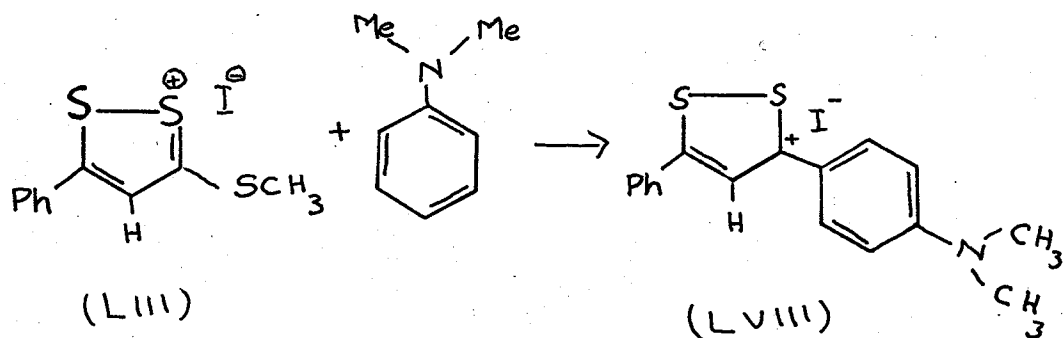
Comparison of the melting points and the respective IRs of the genuine N-phenyl thiobenzanilide and the compound (LVII) showed that the two compounds were not similar; this eliminates the second mechanism also. On repeating the reaction with (LV-a) in ethanol solvent, two products were obtained, one of them was identified to be N-methyl anilinium iodide from its isothiocyanate derivative. However, (LV-b) on reacting with aniline in acetic acid gave a product which on methanol recrystallization gave light yellow needles. Elemental analysis of the compound was done, but on the basis of the results no suitable structure could be assigned.

(ii) Reaction with N,N-dimethyl aniline and N-methyl aniline:

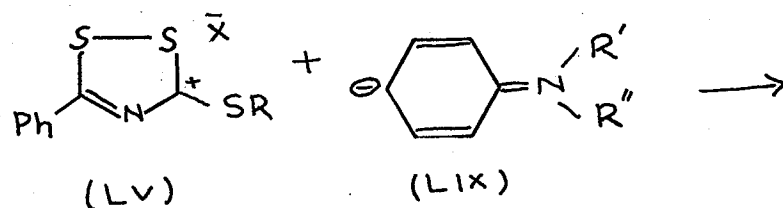
Aniline is a weak base; but the basicity can be increased by replacing N-hydrogens by the methyl groups, which by virtue of their electron releasing property facilitate the delocalization of lone pair of electrons on nitrogen over the benzene ring and make the para position a stronger nucleophile:



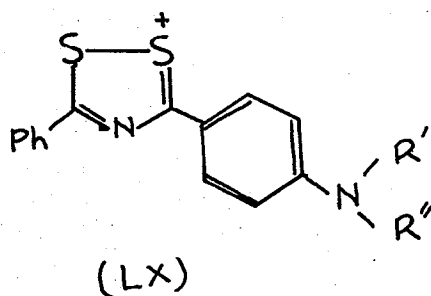
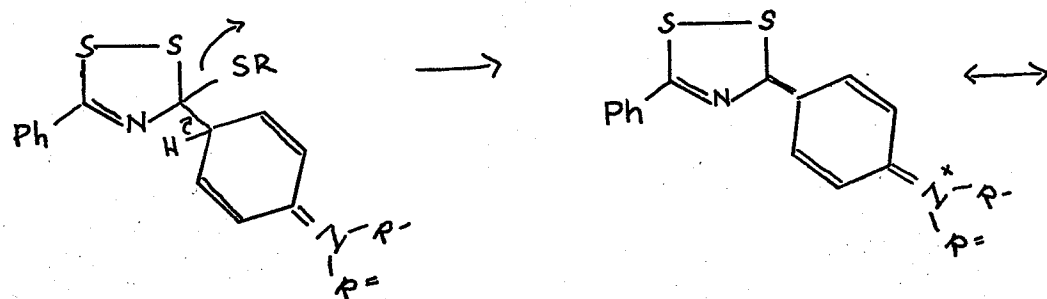
Reaction of such a nucleophile with (LIII) has been observed to give a compound of the type (LVIII). In a similar way, 3-alkylthio-5-phenyl-



1,2,4-dithiazolium cation would be expected to react with N-methyl, and N,N-dimethyl anilines to give (LX).



- a) $R = CH_3, X = I$ (a) $R' = R'' = Me$
 b) $R = C_2H_5, X = ClO_4^-$ (b) $R' = H, R'' = Me$

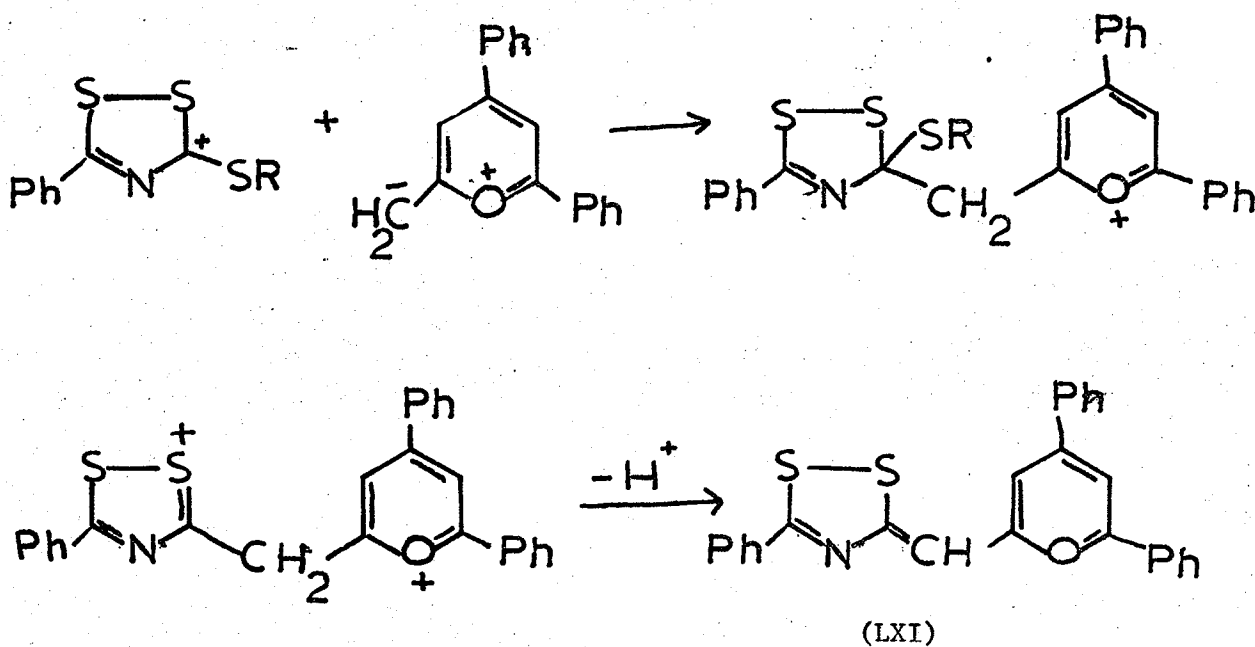


(LV-a), when reacted with N,N-dimethyl aniline gave the triiodide salt of (LX) as shown by the elemental analysis, while (LV-b) on reaction with N,N-dimethyl aniline (LIX-a) rapidly gave product which on recrystallization from acetic acid and washing with ether, gave bright green crystals - the ClO_4^- salt of (LX). Infrared spectrum

and elemental analysis confirmed the formation of the compound (LX). Rapid change of color was also observed when (LV-a) was reacted with (LIX-b) but apparently the product was the cation (LX) as its triiodide salt. N-methyl aniline, (LIX-b) reacted with (LV-b) in acetic acid and gave an oily product which was found soluble in ether, and therefore not a salt of the type (LX). This may not be very unexpected since (LIX-b) is a weaker nucleophile than (LIX-a).

(iii) Reactions with 2-methyl-4,6-diphenyl pyrylium perchlorate.

These reactions in presence of pyridine base are expected to give cyanine dyes according to the following mechanism:

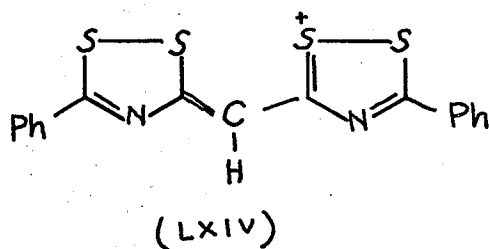
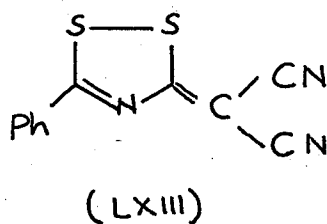
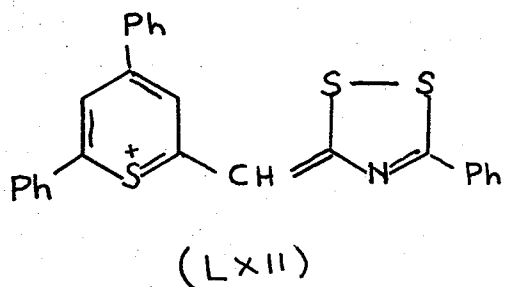


The reaction was observed to give an instantaneous change of color, but the product when recrystallized from acetic acid and purified by ether showed that its IR was not consistent with the product (LXI),

and was very similar to that of the pyrylium perchlorate salt. Probably the 3-alkylthio-dithiazolium salt is unstable in the presence of pyridine base and is decomposed rapidly, preventing the formation of the expected product, (LXI).

The dithiazolium cations (LV-a,b) must have met the same fate when reacted with 2,6-dimethyl-4-phenyl pyrylium perchlorate in presence of pyridine.

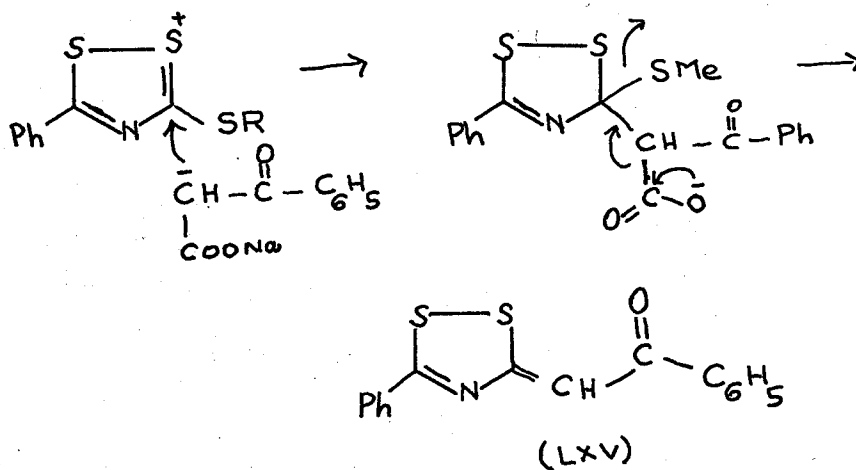
More reactions were attempted to ensure that it was not the nucleophilicity of the attacking reagent but the instability of the dithiazolium cation in strong base which was involved and which prevented the reaction to go to completion. They included the reaction of 3-alkylthio-1,2,4-dithiazolium cation with - (i) 2-methyl-4,6-diphenyl thiopyrylium perchlorate, (ii) malononitrile, and (iii) malonic acid; all in presence of pyridine. They were expected to give products (LXII) (LXIII) and (LXIV) respectively, but in all the three cases the expected products were not obtained.



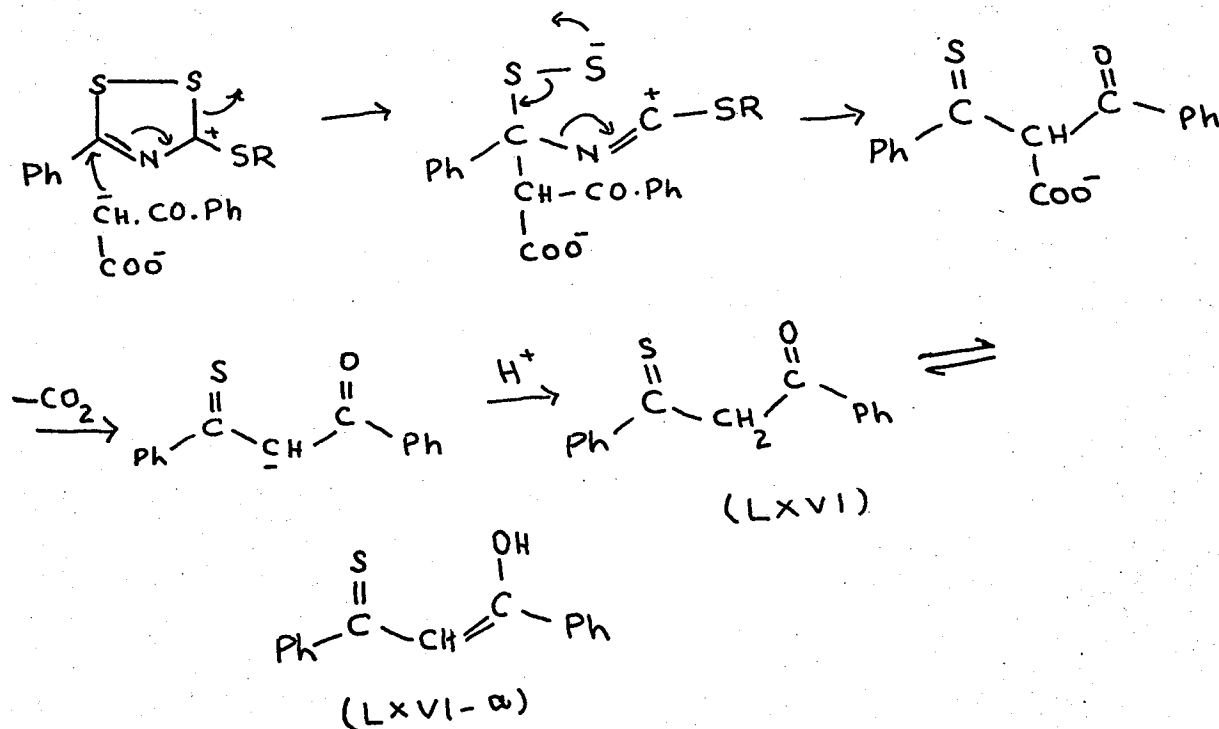
(iv) Reaction with sodium benzoyl acetate:

Sodium benzoylacetate should act as a strong nucleophile in basic medium and should attack either carbon 3 or carbon 5 both of which are susceptible to nucleophilic attack. Corresponding to the two possibilities of the nucleophilic attack, the following two routes of reaction may be postulated:

(a) When attack is on carbon 3:

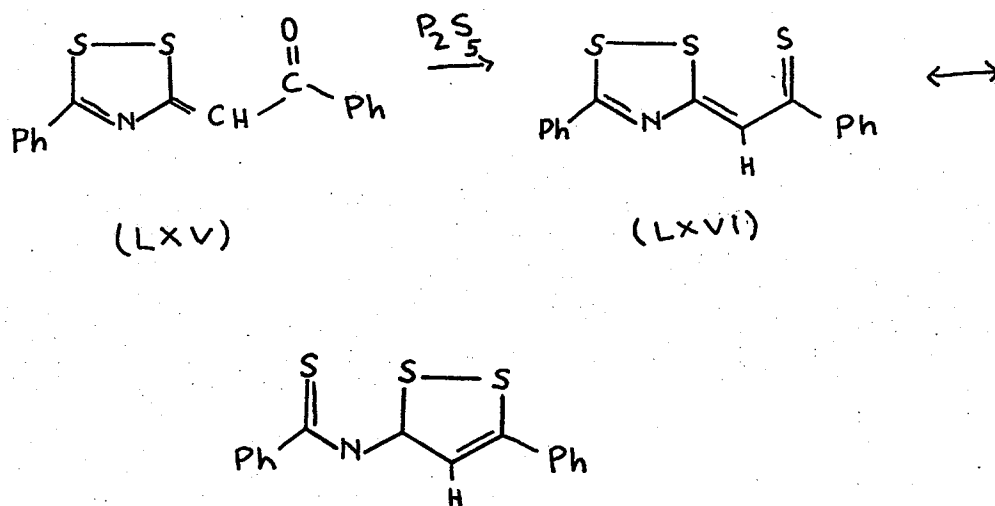


(b) When attack is on carbon 5:

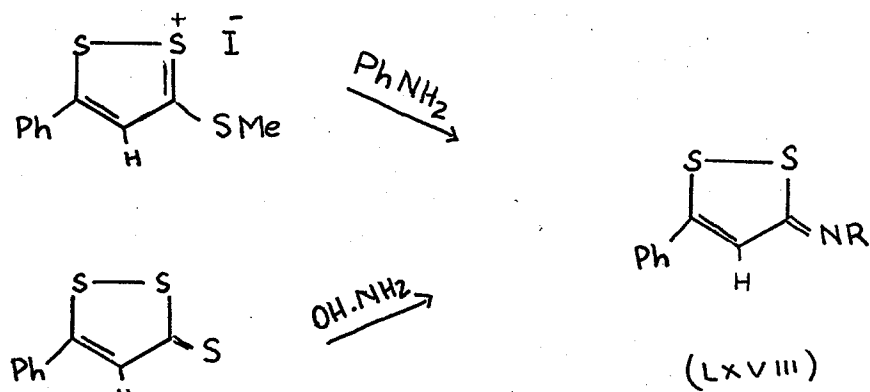


Infra red spectrum of the product obtained showed OH peak at approx. 3200 cm^{-1} and C=O peak at approx. 1700 cm^{-1} . Further, elemental analysis gave negative results for nitrogen. This indicated that nucleophilic attack was not at carbon 3 and that (LXV) was not obtained. It might thus be suspected that nucleophilic attack was at carbon 3 giving the product (LXVI-a), having OH group and a carbonyl group as also shown by the IR. However, the elemental analysis and mass spectrum of the product obtained did not substantiate this view.

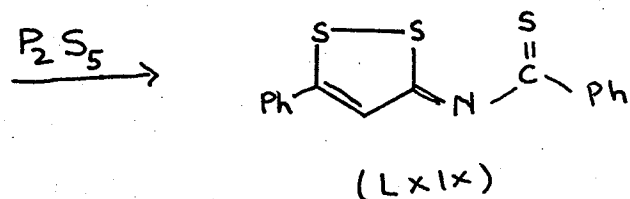
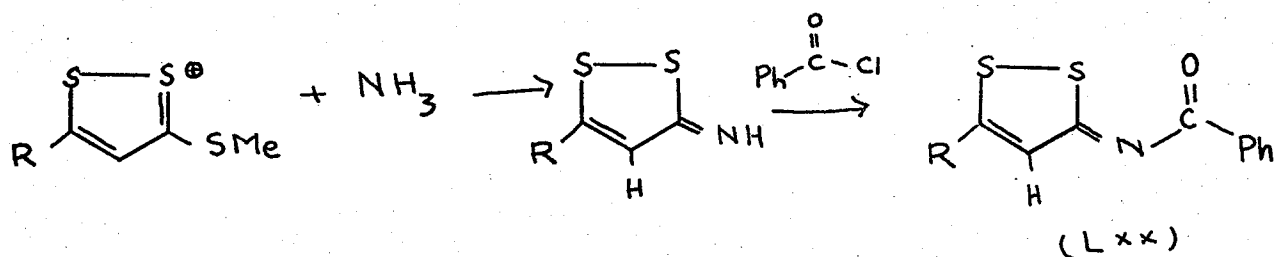
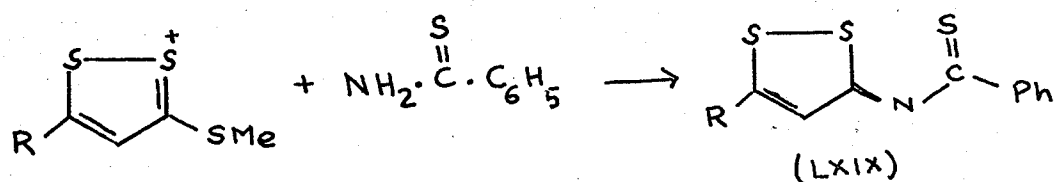
During the course of these reactions, we became interested in synthesizing a system of the type (LXV) which should on sulfurization give a system similar to the "thiothiophthene" system.



It has been noted that (LIII) reacts with aniline^{60,61} and 5-phenyl-1,2-dithiol thione reacts with hydroxylamine^{63,64}, and gives a system (LXVIII)

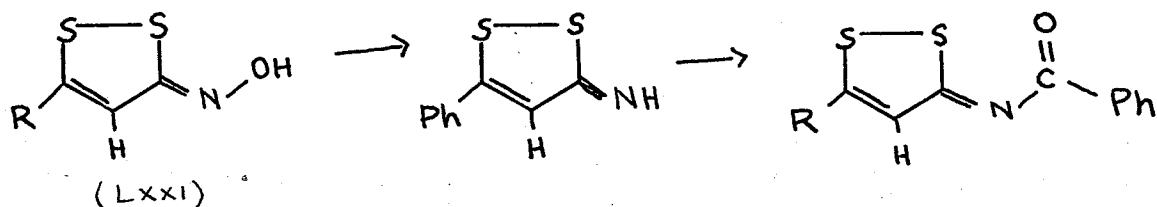


This suggests another possible approach to the meribicyclic system (LXIX), the introduction of a thioacylimino side chain to a dithiole nucleus e.g.



In neither of these cases was the first product obtained. Thiobenzamide failed to react with 3-methylthio-5-phenyl-1,2-dithiolium iodide,

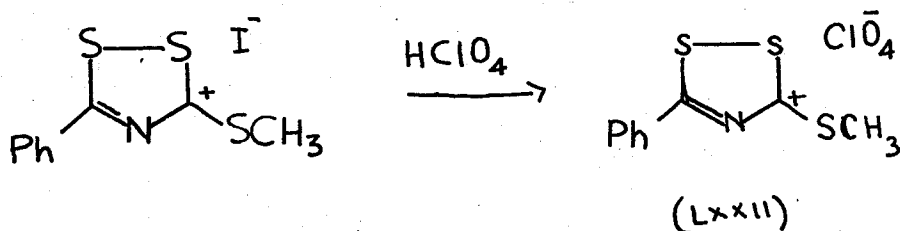
presumably because of its low nucleophilicity, and ammonia gave indefinite products by fission of the dithiole ring. However, other workers have since used this approach with success using an oxime as an intermediate;



Even p-dimethylaminothiobenzamide failed to react with the 3-methylthio-1,2-dithiolium salt. The amino group in this would be expected to be more nucleophilic than in thiobenzamide, but obviously it is still too weak.

(v) Reaction with perchloric acid:

3-methylthio-5-phenyl-1,2,4-dithiazolium iodide was reacted with perchloric acid in nitromethane. IR of the product exhibited a perchlorate peak confirming that iodine in the substrate is attached by ionic bond, and not by a covalent bond; as a result, in strongly polar medium, ion exchange takes place and the perchlorate salt is obtained.



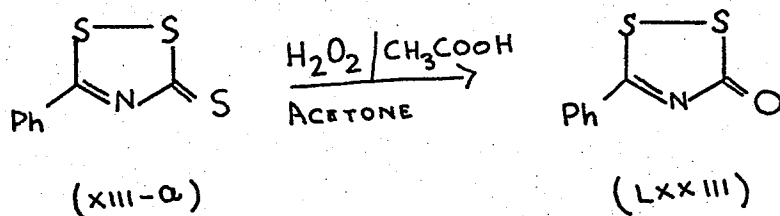
REACTIONS OF 5-PHENYL-1,2,4-DITHIAZOLE-3-THIONE

The reactions of 5-phenyl-1,2,4-dithiazole-3-thione (XIII-a) are classified as: (A) reactions of the exocyclic thione function, (B) reactions in which a nucleophile attacks on the positive carbon 3 and gives the corresponding products, and (C) those in which it reacts with activated dipolarophiles and give 1,3 addition products.

(A) Reactions of the exocyclic thione function:

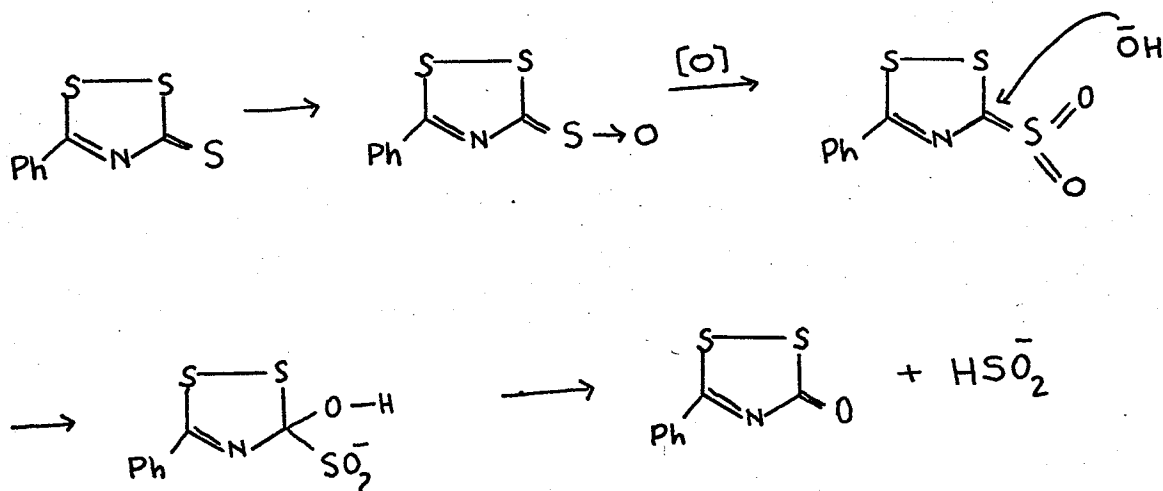
(i) Oxidation of 5-phenyl-1,2,4-dithiazole-3-thione.

Oxidation may be brought about by the action of peracetic acid on the thione (XIII-a). Klingsberg^{45,46} used peracetic acid oxidation of 1,2-dithiol-3-thiones to prepare both aryl derivatives of the system, and the parent 1,2-dithiolium cation itself. We attempted hydrogen peroxide oxidation of (XIII-a) in acetone in presence of an equal volume of acetic acid. Only an ether soluble product was obtained, whose IR showed a carbonyl peak at 1650 cm^{-1} .



The IR of the product (LXXIII) was compared with that of a genuine 5-phenyl-1,2,4-dithiazole-3-one made by the method of Derocque and

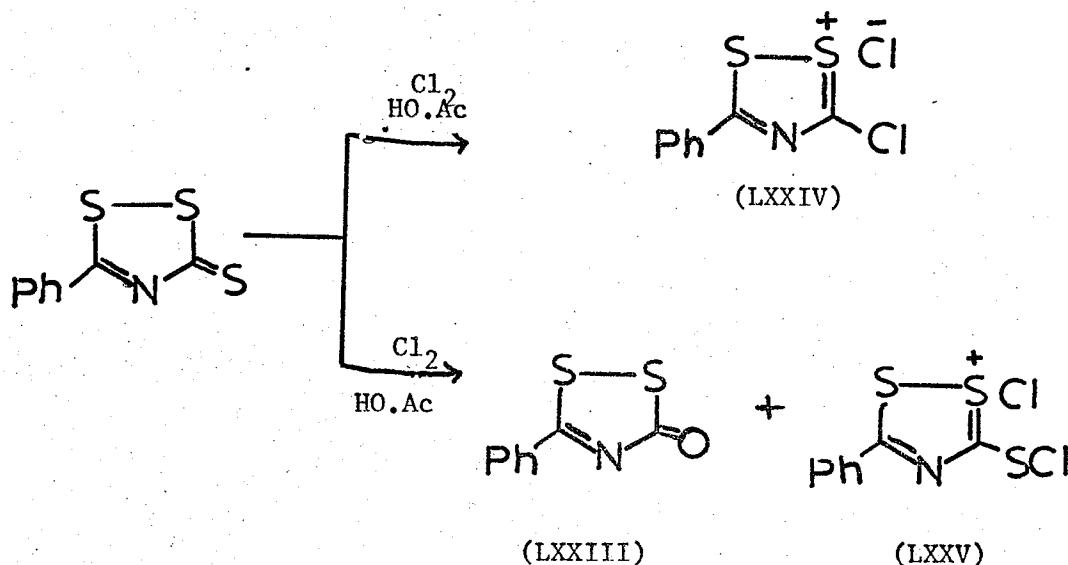
Vialle¹⁹ IRs were found identical thus confirming the formation of (LXXIII). One possible mechanism for the above transformation may be:



(if) Chlorination of 5-phenyl-1,2,4-dithiazole-3-thione.

Chlorination of the thione in glacial acetic acid was attempted in order to obtain a system of the type (LXXIV). It is reported^{65,66} that 1,2-dithiole-3-thiones when reacted with chlorine gave 3-chloro-1,2-dithiolium salts. When the thione in glacial acetic acid was reacted with chlorine, a yellow colored substance was obtained which was only slightly soluble in ether. Ether soluble material gave an IR very much similar to that of the compound (LXXIII) showing the replacement of exocyclic sulfur by oxygen. The ether insoluble product, which was observed to be decomposing quite fast, was probably only an

adduct (LXXV) and not the expected compound (LXXIV).

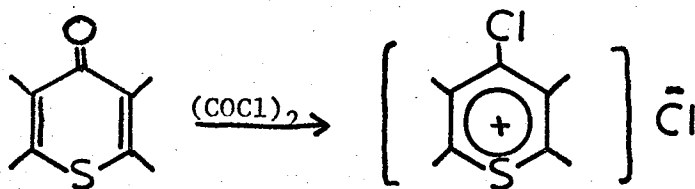


In another approach dithiazole-3-thione was dissolved in carbon tetrachloride, and the chlorine gas was passed through it. Reaction was observed to be instantaneous, but the IR showed that (LXXIV) was not obtained. It may be noted that when chlorination of 5-phenyl-1,2,4-dithiazole-3-thione was attempted in acetic acid, two products, the chlorine adduct of thione, and 5-phenyl-1,2,4-dithiazole-3-one were obtained, while in a medium like benzene or carbon tetrachloride, only the adduct was obtained. Possibly in the hydroxylic solvents the initial adduct was hydrolyzed.

Schonberg and Frese⁴⁷ reported successful conversion of C=O or C=S groups in $\text{>C}(\text{Cl})_2$ by the action of thionyl chloride or oxalyl chloride. We attempted a similar conversion to obtain (LXXIV) using benzene as a solvent. The infrared spectrum of the product obtained

was similar to that of the starting material, showing that the reaction had not worked.

J. Faust⁴⁸ has reported the conversion of C=O group reacting the compound 4H-thiopyranone-(4) with oxalyl chloride to obtain 4-chloro-thiopyrylium chloride:



We tried similar methods to obtain the system (LXXIV). After refluxing for seven hours, it was observed that the expected product was not obtained

Attempts were also made to obtain the system (LXXIV) by refluxing 5-aryl-1,2,4-dithiazole-3-thione in chloroform with equimolar quantity of phosphorus pentachloride. After 7 hours of refluxing it was found that no reaction had occurred.

(B) Reactions in which a nucleophile attacks carbon 3

Alkylation reactions of dithiazole thione by:

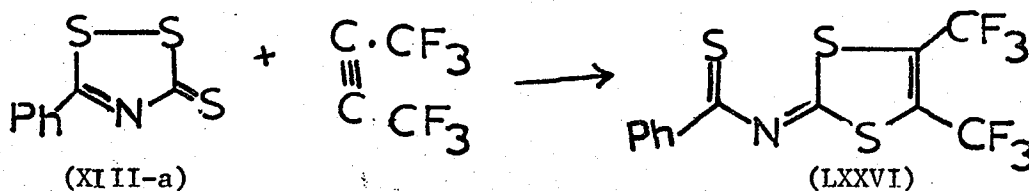
- (a) benzyl bromide
- (b) dimethyl sulfate
- (c) ethyl iodide
- (d) butyl bromide
- (e) benzal chloride
- (f) triphenyl methyl perchlorate
- (g) benzhydryl bromide

Similar to the 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide salt formation from the dithiazole-3-thione and methyl iodide, reported by MacDonald and McKinnon¹, the study of some more 3-alkylthio-1,2,4-dithiazolium salt formation was attempted. The thione was allowed to

react with the reagents (a - g) in methylene chloride solution for several days, and it was found that (b), (d), (e) and (f) did not give any product. Crystalline products obtained with benzyl bromide, ethyl iodide, and benzhydryl bromide gave unsatisfactory elemental analyses. However, the second of these corresponds fairly well to a triiodide.

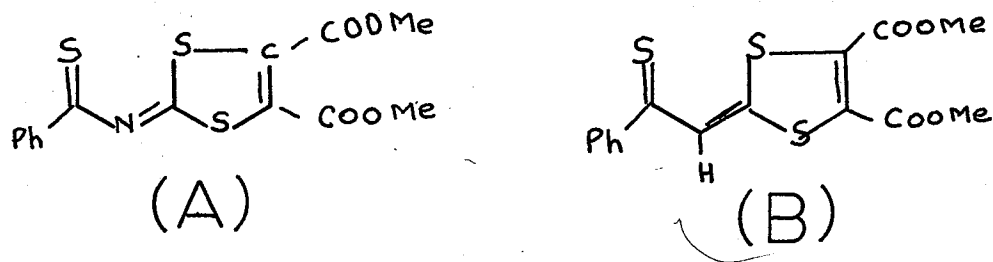
(C) Reactions with activated dipolarophiles - 1,3-cycloaddition reactions

Behringer and Diechmann³¹, MacDonald and McKinnon,¹ and Lang and Vialle³² reported the 1,3-cycloaddition reactions of 5-substituted 1,2,4-dithiazole-3-thiones with acetylenic esters and dehydrobenzene as dipolarophiles. We attempted similar reactions using hexafluoro-2-butyne, dibenzoyl acetylene, dicyanoacetylene and dimethyl azodicarboxylate. When (XIII-a) was reacted with hexafluorobutyne, a compound of the type (LXXVI) was obtained, whose formation was confirmed by infrared, NMR, and elemental analysis data.



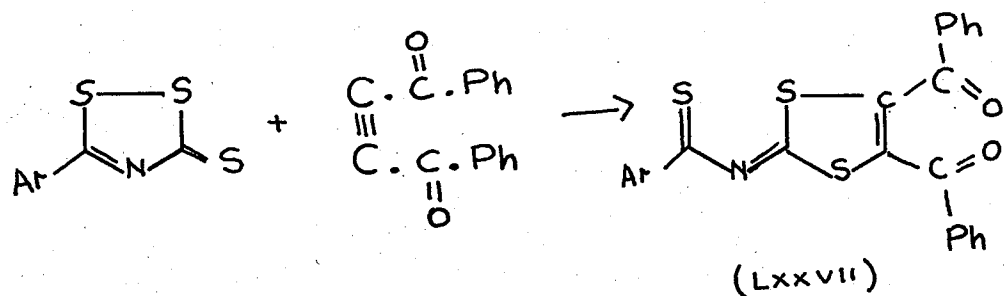
5-phenyl-1,2,4-dithiazole-3-thione acts as a dipole displaying electrophilic activity at position 2 and nucleophilic activity at the exocyclic sulfur. The dipolarophile hexafluoro-2-butyne is activated at the triple bond by the strongly electron attracting trifluoromethyl groups which facilitate the addition reaction.

The fluorine magnetic resonance of this compound indicated that the two trifluoromethyl groups in the compound were equivalent. In the related dicarboxylic ester (A) the two methyl groups are also equivalent, yet in the corresponding carbon compound (B) it appears that they are not equivalent.⁶⁹



It has been suggested that the equivalence in the case of the compound (A) is caused by some form of free rotation of the side chain, possibly because of the electron withdrawing property of the nitrogen⁶⁸.

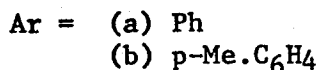
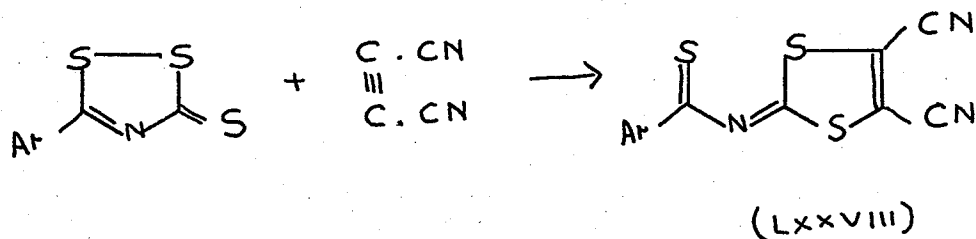
Dibenzoyl acetylene on reaction with the thione readily gave the 1,3 cycloaddition product (LXXVII).



- Ar = (a) Ph
 (b) o-Me.C₆H₄
 (c) p-Me.C₆H₄
 (d) 2-furyl
 (e) 2-thienyl

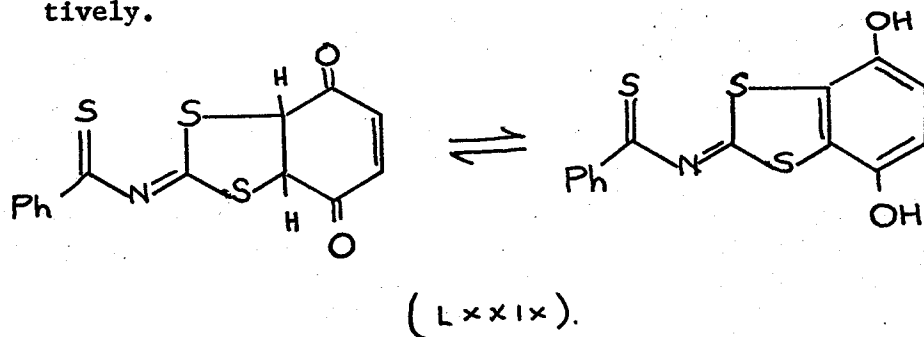
Formation of these compounds was confirmed by infrared and the elemental analysis. In the IR, the carbonyl peaks were shifted to approximately 1650 cm^{-1} due to strong conjugation between these two groups, and also with the phenyl groups. Benzoyl groups of the dipolarophile activated the triple bond due to their conjugative and electron attracting properties.

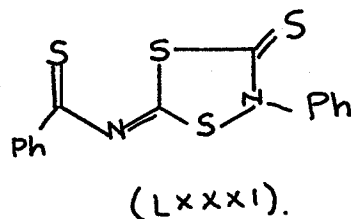
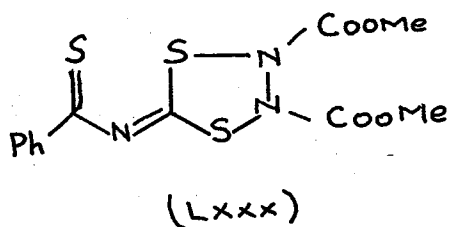
5-aryl-1,2,4-dithiazole-3-thione was found to readily form such a monoadduct also with dicyanoacetylene. The nitrile group, again, functions as an activating group by electron withdrawal and therefore dicyanoacetylene an effective dipolarophile. On reaction, they formed 1,3-cycloaddition products of the type (LXXVIII).



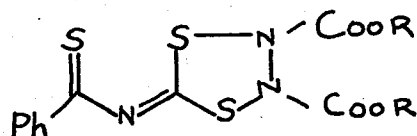
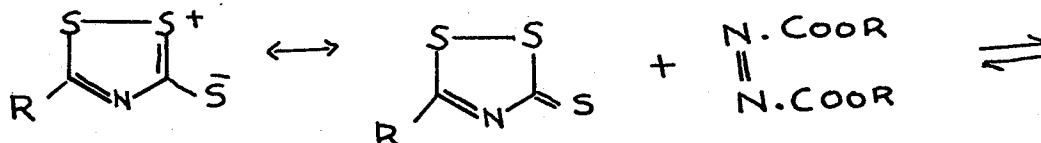
Formation of (LXXVIII) was confirmed by elemental analysis.

We also attempted similar 1,3 cycloaddition reactions with (i) benzoquinone, (ii) dimethyl azodicarboxylate, and (iii) phenyl isothiocyanate hoping to obtain products (LXXIX), (LXXX), and (LXXXI) respectively.

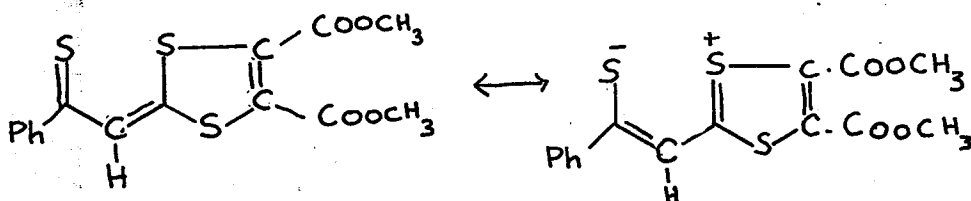




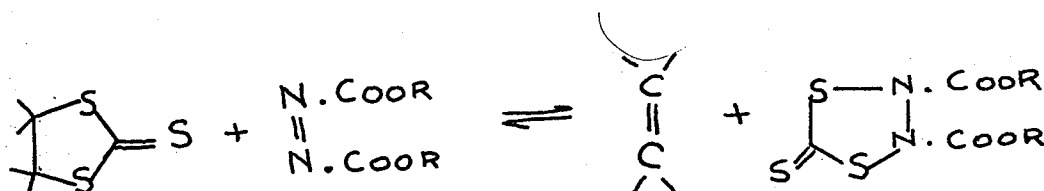
Even after refluxing for above 19 hours in benzene, reactions (i) and (ii) gave back the starting material, the thione. Reaction (iii) was carried out in ethanol and xylene by refluxing for 48 hours, in which case also, the starting material was obtained. The first two of these compounds are not as reactive as the acetylenic compounds, and this is probably the reason for the failure of the first two reactions to form adducts. The failure of the azodicarboxylic ester to form an adduct was rather unexpected, in view of its high reactivity. However, if we postulate an equilibrium in this reaction:



it can be seen that the product would not be potentially aromatic, in contrast to the reaction product of the thione with an acetylenic ester.



Since then in the first case the reaction would involve loss of some aromatic stability, the lack of reaction is more easy to understand. To test this hypothesis the reaction of 1,3-dithiolan-2-thione with the dimethyl azodicarboxylate was tried:

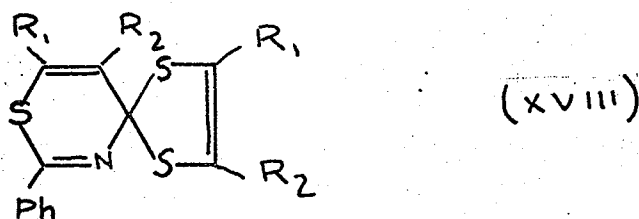


In this case, the reaction would be expected to work more readily, since the dithiolan has no aromatic character. Indeed a product was obtained but this was an oil and was unsatisfactory for analysis.

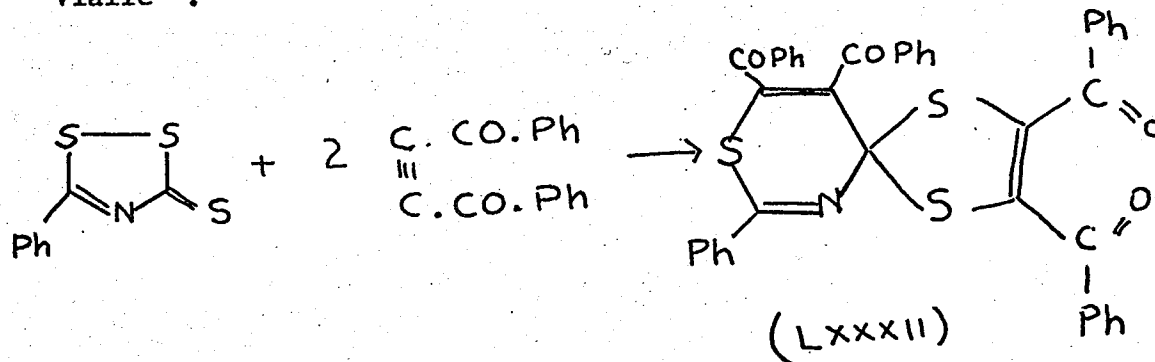
A reaction was tried using propargyl bromide as a dipolarophile. The typical green color of the monoadduct was observed in this reaction but only traces of addition compound were obtained. No reaction took place when 1,4-dichloro-2-butyne was used as a dipolarophile. In these cases, there are no strongly activating electron withdrawing groups. Chlorine and bromine atoms are inductively electron attracting, but the inductive effect is practically nil after the first carbon atom, and therefore these do not activate the triple bond sufficiently for the reactions.

1,4 addition reactions of the monoadducts to give diadducts

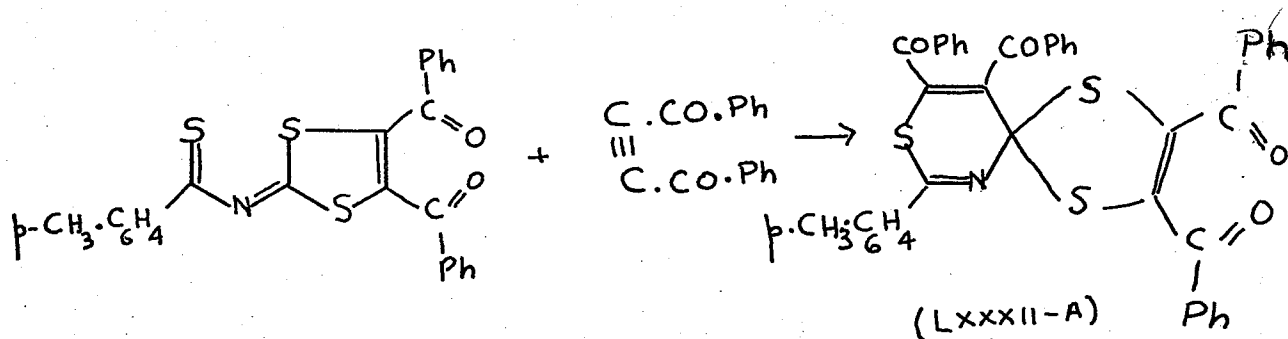
Lang and Vialle³² reported the formation of diadduct (XVIII) from dimethyl acetylene dicarboxylate and 5-phenyl-1,2,4-dithiazole-3-thione:



A similar diadduct with the corresponding carbon analogue, 5-phenyl-1,2-dithiol-3-thione has been reported by Behringer and Wiedenmann Easton and Leaver³⁴ and Behringer et al³⁶. We attempted to prepare diadducts of the above type with 5-phenyl-1,2,4-dithiazole-3-thione and various activated dipolarophiles. When (XIII-a) and dibenzoyl acetylene were refluxed in benzene using equimolar quantities for 1 - 1.5 hours, only monoadduct was formed. When however, they were allowed to reflux for nearly 7 hours, with excess of the dipolarophile, a yellow colored compound was obtained which was identified by infrared and elemental analysis a diadduct of the type obtained by Lang and Vialle³².



This second addition reaction is an example of 1,4 cycloadditions, and a number of 1,4 cycloadditions in different other classes of compounds also have been reported in literature. It is reasonable that (LXXXII) is formed via the monoadduct (LXXVII) in which sulfur of the C = S group exhibits nucleophilic activity and the carbon atom 3 of the ring exhibits electrophilic activity. Similarly, when the monoadduct (LXXVII-c), formed from dibenzoyl acetylene and 5-p-toluy1-1,2,4-dithiazole-3-thione, was refluxed with an equimolar quantity of dibenzoyl acetylene in benzene solvent for 6 hours, a similar yellow product, i.e. the diadduct was obtained. This confirms that the 1,4 cycloaddition is subsequent to the 1,3-addition.

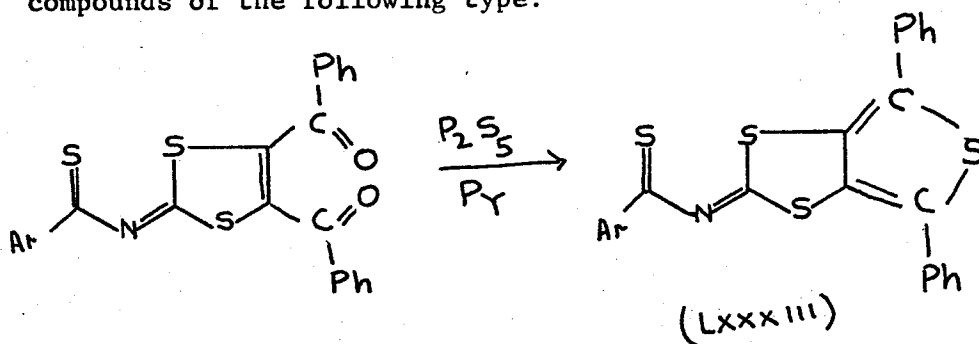


We tried to obtain similar diadducts with (LXXVI) using (i) hexafluoro-2-butyne, (ii) dimethyl azodicarboxylate, and (iii) acetylene dimethyl-dicarboxylate in benzene and xylene. Only the starting material was obtained in each case which might be due to less dipolar activity of the substrate as well as insufficiently active dipolarophile. The monoadduct (XIV) also was reacted with dimethyl azodicarboxylate and hexafluoro-2-butyne in an attempt to obtain a diadduct, but only the

starting material was obtained, again possibly due to insufficiently activated dipolarophiles.

Sulfurization reactions of mono adducts

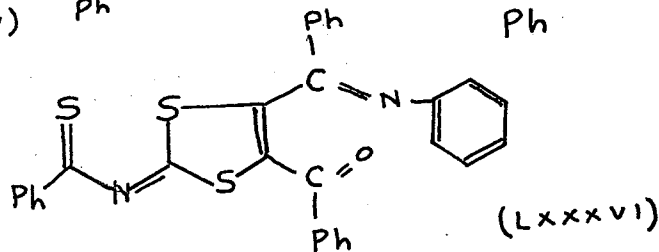
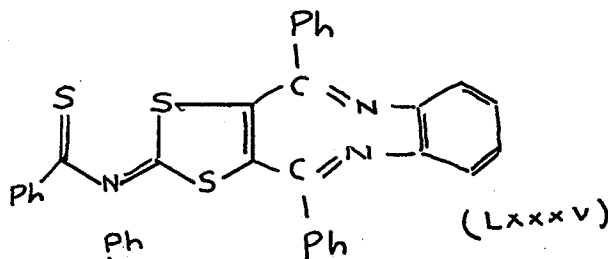
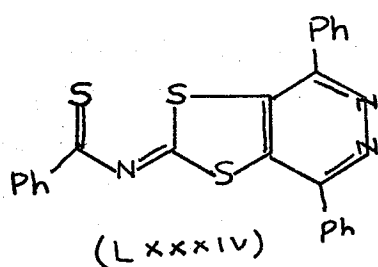
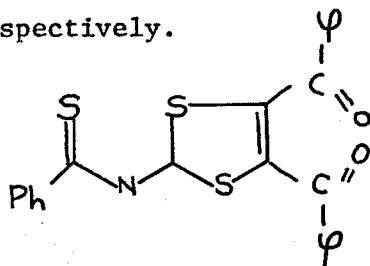
Monoadducts obtained by 5-phenyl-1,2,4-dithiazole-3-thione and dibenzoyl acetylene may be considered as 1,4 dicarbonyl compounds, and therefore should give substituted thiophens on sulfurization by phosphorus pentasulfide similar to known reactions of 1,4 diketones⁷². Sulfurization of these monoadducts was attempted in pyridine using an equimolar quantity of phosphorus pentasulfide and refluxing for about 7 hours. By this way we were able to obtain thieno-1,3-dithiole compounds of the following type:



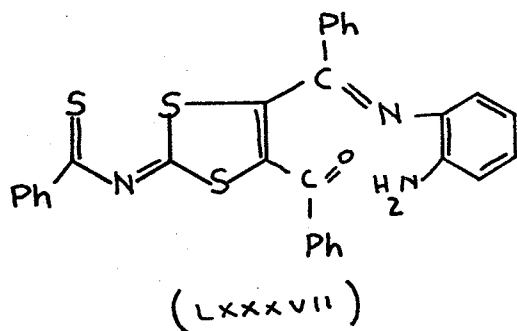
- Ar =
- (a) Ph
 - (b) o-Me.C₆H₄
 - (c) p-Me.C₆H₄
 - (d) 2-furyl

Formation of these compounds was confirmed by the infrared and elemental analyses.

Some more reactions of the carbonyl group of the monoadduct were attempted which included reactions with (i) hydrazine, (ii) *o*-phenylenediamine, and (iii) aniline, hoping to obtain (LXXXIV) (LXXXV), (LXXXVI) respectively.

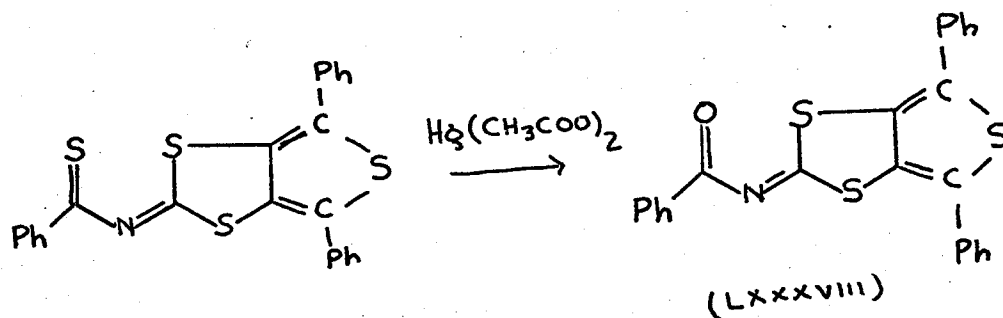


Reaction with hydrazine gave only some decomposition purple colored product. However, when reactions with (ii) and (iii) were carried out, nitromethane and benzene-ethanol mixture recrystallization products were obtained. whose IR showed NH peak and a sharp C=O peak at 1670 cm^{-1} as compared to 1625 cm^{-1} in the starting material. On this basis it was thought that compounds (LXXXVI) and (LXXXVII) were formed, but the elemental analyses did not substantiate this.



Conversion of the C=S group into C=O group

A number of examples are reported in literature where exocyclic C=S group is converted to C=O group. Derocque and Vialle¹⁹ used mercuric acetate for such a conversion. We attempted to react the C=S group in (LXXXVIII) to obtain (LXXXVIII) using mercuric acetate.



Infrared showed carbonyl peak at approximately 1640 cm^{-1} and the elemental analysis confirmed the formation of (LXXXVIII)

Salt formation with triethyloxonium perchlorate

Similar to the nucleophilic salt formation reactions of the thione with methyl iodide and triethyloxonium fluoroborate, we attempted to obtain such a salt with (LXXXVIII), both with methyl iodide and triethyloxonium fluoroborate. Such salts would represent examples of the

thieno-1,3-dithiolylium system, which would be a new aromatic ring, isoelectronic with naphthalene. Methyl iodide after keeping for several days did not give any salt with (LXXXIII). Triethyl oxonium fluoro-borate gave a mixture of two crystalline products when recrystallized from acetic acid with few drops of perchloric acid, which could not be separated. However, the IR showed the perchlorate peak and strong C=O absorption. The amount obtained was insufficient for analysis. No product was obtained when the sulfurized product of (LXXXIII) was allowed to stand in methylene chloride solution of triethyloxonium fluoroborate.

EXPERIMENTAL

All melting points given were determined on a Fischer-Johns melting point apparatus and are uncorrected.

Solutions were dried over anhydrous calcium chloride or anhydrous sodium sulfate

Thin layer chromatography was performed on silica gel DSF-5 made by Camag, obtained from Mondray Ltd., 4180 de Courtraï, Montreal.

Infrared spectra were obtained on a Perkin-Elmer Model 137 Infrared Spectrometer.

The NMR spectra were obtained on a Varian A-56/60A Spectrometer using deuterated chloroform (99.8% D) containing tetramethylsilane as the internal standard.

The mass spectrum was performed by Mr. Charles Reichert on a Hitachi Perkin-Elmer RMU-60 mass spectrometer.

The elemental analyses were done by Alfred Bernhardt Microanalytical Laboratory, 5251, Elbach uber Engelskirchen, West Germany, or by Micro-Tech Labs Inc. Skokie Illinois, USA.

Preparation of thiobenzamide

Made by the method of Gabriel and Heymann⁷⁰. Recrystallized from benzene. m.pt.90-91°C. Yield:55%.

Preparation of thionicotinamide

Nicotinonitrile (1 g), in ethanol (30 ml) saturated with ammonia and hydrogen sulfide was refluxed for 3 hours, using the method of Gabriel and Heymann⁷⁰. Recrystallized from ethanol. m.pt.154-7°C. Yield:40%.

Preparation of thiocyanogen chloride

Thiocyanogen chloride was made by the method of Bacon & Guy⁴⁹.

Reaction of thiocyanogen chloride and thiobenzamide

Thiocyanogen chloride in acetic acid and thiobenzamide were taken in a flask and allowed to react at room temperature. The product was recrystallized from ethanol; m.pt.79°C. Yield:20%. Analysis found: C=67.25%, H=3.88%, S=17.19%, N=11.45%. C_7H_7NS , thiobenzamide, requires: C=61.32%, H=5.11%, N=10.22%, S=23.35%.

Reaction of thiobenzamide and trichloromethane sulphenyl chloride

Equimolar quantities of thiobenzamide and trichloromethane sulphenyl chloride were allowed to react in acetone. The reaction was instantaneous, and white precipitate was obtained. This precipitate was then refluxed in benzene for about 30 minutes. Hydrogen chloride was evolved. IR of the oily product obtained on evaporation showed a nitrile peak.

Preparation of 5-phenyl-1,2,3,4-thiatriazole

The compound was made by the action of carboxy methyl dithiobenzoate and sodium azide using the method of Jensen and Pedersen⁵⁰.

Colorless crystals, m.pt.94.5-95°C. Yield:75%.

Attempted preparation of 5-phenyl-1,2,4-dithiazole-3-thione from thiatriazole

0.5 g of 1,2,3,4-thiatriazole was dissolved in carbon disulfide and heated in oil bath at 125°C for 3 hours in a sealed tube. An infrared spectrum of the compound obtained on evaporation of the solvent showed that no reaction had taken place.

Attempted photosynthesis of 5-phenyl-1,2,4-dithiazole-3-thione from thiatriazole

0.5 g of 1,2,3,4-thiatriazole in carbon disulfide solution was subjected to UV light using Fisher UVL.22 lamp for 48 hours. There was no reaction.

Reaction of 2-phenylthiazolin-4,5-dione with phosphorus pentasulfide in carbon disulfide

2-phenyl thiazolin dione-4,5 made by the method of Goerdeler and Schenk⁵¹, was refluxed with a little excess of phosphorus pentasulfide in carbon disulfide. Product recrystallized from benzene - ethanol mixture. IR corresponded to that of the thione made by the method of MacDonald and McKinnon¹. m.pt.136°C. Color - dark brown.

Preparation of Nicotinoyl isothiocyanate

Nicotinoyl chloride, made by the method of Wingfield et al⁵² was refluxed with calculated amount of lead thiocyanate in benzene for 3 hours. Evaporation of benzene from the filtrate, and subsequent distillation at 1.5 mm pressure and 106-7°C gave the product. Yield:65%.

Preparation of methyl nicotinoyldithiocarbamate

To 15 gms of nicotinoyl isothiocyanate at 0°C was added excess methanethiol. The reagents were kept in ice bath overnight. A light yellow colored product was obtained on evaporation of the excess of thiol. Recrystallized from benzene: m.pt.140-45°C. Yield:80%. Analysis found: C=45.06%, H=3.68%, N=13.3%, S=30.03%, O=7.9%. $C_8H_8N_2S_2O$ requires: C=45.29%, H=3.7% N=13.2%, S=30.2%, O=7.54%.

Attempted preparation of 5(3-pyridyl)-1,2,4-dithiazole-3-thione

1 g. of methyl nicotinoyl dithiocarbamate was refluxed in xylene with excess phosphorus pentasulfide for 5 hours. Expected thione product could not be isolated from the reaction products.

Preparation of methyl terephthaloyl dithiocarbamate

Terephthaloyl chloride was obtained by heating terephthalic acid with phosphorus pentachloride for 12 hours, and extracting the product with benzene. The product was recrystallized from benzene. m.pt.70-72°C. Calculated quantities of terephthaloyl chloride and lead thiocyanate refluxed in benzene for 3 hours gave terephthaloyl diisothiocyanate in benzene as filtrate. The product was isolated by evaporating out benzene and distilling at 2 mm between 119-20°C.

Product solidified immediately on the walls of the condenser. Yield:70%.

It was then treated with excess methyl mercaptan at 0°C which gave bright yellow product, recrystallized from benzene. Yield:85% m.pt.176-80°C.

Analysis found: C=42.01%, H=3.55%, N=8.21%, S=37.04%, O=9.37%. $C_{12}H_{12}S_4N_2O_2$ requires: C=41.86% H=3.5%, N=8.14%, S=37.2%, O=9.4%.

Attempted preparation of 5(3-thio-1,2,4-dithiazole-5-yl-p.phenylene)-1,2,4-dithiazole-3-thione

1 g of methyl terephthaloyl dithiocarbamate was refluxed with excess phosphorus pentasulfide in xylene. Color changed to deep brownish-red in two hours. Product could not be recrystallized from benzene, ethanol, or acetone. Acetone extract of the product gave a red brown substance, recrystallized from nitrobenzene, m.pt.206-7°C. Analysis which did not confirm the formation of the expected product found: C=40.66%, H=2.67%, N=10.93%, S=41.55%. $C_{10}H_4S_6N_2$ requires: C=34.88%, H=1.16%, N=8.14%, S=55.81%.

Preparation of 2,4,6-trimethyl benzoyl chloride:

From 2,4,6-trimethyl benzoic acid, using standard method. Product distilled between 223-5°C. Yield:90%.

Preparation of 2,4,6-trimethyl benzoyl isothiocyanate

This was prepared using the method of Lipp et al⁶⁷. Product distilled between 98-100°C at 0.7 mm pressure. Yield:80%.

Attempted preparation of 2,4,6-trimethyl phenyl-1,2,4-dithiazole-3-thione

2,4,6-trimethyl benzoylisothiocyanate was refluxed with excess phosphorus pentasulfide in carbon disulfide for over 3 hours. A red

oily product was obtained after evaporation of benzene, but it could not be solidified and crystallized.

Attempted preparation of 2,6-dimethyl benzoic acid

2,6-dimethyl benzonitrile was made by the method of Haring.⁴³ However, attempted hydrolysis of this compound by 75% sulfuric acid⁴³ did not give 2,6-dimethyl benzoic acid. Only a black tar was obtained.

Attempted preparation of o-vinyl benzoic acid.

o-Chlorophenylmethyl carbinol was made by the method of Overbergers et al⁴⁴. Dehydration was effected by refluxing in benzene with p-toluenesulfonic acid and traces of phenol to minimize polymerization. The product o-vinylchlorobenzene was distilled over between 60-80°C at 1.5 mm. An attempted synthesis from it of o-vinylbenzoic acid via grignard reagent failed.

Preparation of acetylene dicarboxamide

Made by the method of Saggiomo.⁵⁶ Yield: 85%. m.pt. 192°C.
Color: light tan.

Preparation of dicyanoacetylene

By the method of Blomquist and Winslow⁵⁷. m.pt. 20-21°C. Yield: 13%.
Color: white.

Preparation of dibenzoyl acetylene

47.2 gms dibenzoyl ethylene converted to its dibromide by the usual method. 25 gms of this were then converted to dibenzoyl acetylene

by the method of Lutz and Smithy⁵⁸. m.pt.108-11°C. Yield:25%.

Color: Cream.

Preparation of triethyl oxonium fluoroborate

By the method of Schultz and Jacobs⁵⁹. m.pt.92°C. Yield:quantitative.

5-phenyl-1,2,4-dithiazole-3-thione and its methyl iodide salt

Made by the method of MacDonald and McKinnon¹. Yield of 5-phenyl-1,2,4-dithiazole-3-thione = 15%. m.pt.136°C. Yield of 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide:61%. m.pt.133°C.

Reaction of 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide and aniline

(i) In dimethyl sulfoxide: Equimolar quantities of the salt and aniline in dimethyl sulfoxide were stirred for 15 minutes. A very rapid reaction occurred. A yellow product was obtained by filtration and was recrystallized from carbon tetrachloride. m.pt.86-89°C. Yield: 70%. The IR and the m.pt. of the genuine thiobenzanilide was not identical to that of the product. Analysis found: C=53.8%, H=5.43%, S=25.35%, N=7.48%; $C_{13}H_{11}NS$ requires: C=73.24%, H=5.16%, N=6.5%, S=15.02%.

(ii) In ethanol - Equimolar quantities of the reagents were heated for 5 minutes which on cooling gave elemental sulfur. Addition of benzene to the filtrate and evaporation of ethanol gave a crystalline product, m.pt.215-225°C. Analysis found: C=34.1%, H=3.77%, I=55.8%, N=6.27%. $C_7H_{10}NI$ requires: C=36%, H=3.4%, N=6.1%, I=54.5%. This suggested that compound was N-methylanilinium iodide.

A second component was obtained by evaporating off benzene from the second filtrate and was recrystallized from ethanol, m.pt.126-30°C. Yield:15%. IR in nujol showed sharp peaks at 1645, 1610, 1540, 1340, 1300, 1275 1240, 1175, 775 745 735 and 695 cm^{-1} . Analysis found: C=66%, H=4.67%, N=11.72%, S=17.64%. Calculated on the basis of thiobenzanilide $\text{C}_{13}\text{H}_{11}\text{NS}$: C=73.34%, H=5.16%, S=15.02%, N=6.5%.

Reaction of 5-phenyl-3-ethylthio-1,2,4-dithiazolium perchlorate and aniline

0.5 g of the salt and corresponding quantity of aniline in acetic acid were allowed to react. Product recrystallized from methanol as light yellow needles. m.pt.125-30°C. IR in "Nujol" showed peaks at 1640, 1570, 1525, 1425, 1300, 1275, 1150, 1070, 1060, 1030, 800, 780, 760 and 740 cm^{-1} . Elemental analysis found: C=68.61%, H=4.87%, S=14.20%, N=12.40%. $\text{C}_{14}\text{H}_{10}\text{S}_2\text{N}_2$ requires: C=62.22%, H=3.7%, S=23.7%, N=10.35%. No suitable structure could be assigned to the product.

Reaction of 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide with p-toludine

Equimolar quantities of the reagents in dimethylsulfoxide were allowed to react; product recrystallized from carbon tetrachloride. m.pt.189-94°C. Color: Yellow. Product not identified by the IR. Analysis found: C=51.38%, H=4.44%, S=9.01%, N=8.13%. $\text{C}_{14}\text{H}_{13}\text{NS}$ requires C=73.54%, H=5.82% S=14.34%, N=6.28%.

Reaction of 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide with dimethyl aniline

Equimolar quantities of the reagents were allowed to react in hot acetic acid. Reaction was found to be almost instantaneous. Product recrystallized from nitromethane and washed with ether, m.pt. 240-45°C did not give satisfactory elemental analysis for the monoadduct. Apparently the compound was the triiodide. Analysis found C=29.60%, H=2.49%, N=4.09%, S=9.35%, I=54.89%. $C_{16}H_{15}N_2S_2I$ requires: C=45.07%, H=3.52%, N=6.55%, S=15.02%, I=29.85%. $C_{16}H_{15}N_2S_2I_3$ requires: C=28.25%, H=2.21%, N=4.13%, S=9.42%, I=56.1%.

Reaction of 5-phenyl-3-ethylthio-1,2,4-dithiazolium perchlorate and N,N-dimethyl aniline

Equimolar quantities of the reagents in acetic acid were heated for 15 minutes; product recrystallized from acetic acid and washed with ether. m.pt. 225-26°C. IR in "Nujol" gave perchlorate peak between 1030 and 1050 cm^{-1} and other peaks at 1690, 1600, 1400 1210, 1200, 980, 780 750 cm^{-1} . Yield: 70%. Analysis found: C=47.99%, H=3.86%, N=7.01%, S=16.23%, Cl=9.1%. $C_{16}H_{15}N_2S_2O_4Cl$ requires: C=48.18%, N=7.03%, H=3.76%, S=16.06%, O=16.06% Cl=8.9%.

Reaction of 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide with 2-methyl-4,6-diphenyl pyrylium perchlorate

Equimolar quantities of the reagents in acetic acid were allowed to react in presence of a drop of pyridine. Dark brown product recrystallized from nitromethane. m.pt. 144-45°C. IR indicated that the product was mainly unreacted pyrylium salt.

Reaction of 5-phenyl-3-ethylthio-1,2,4-dithiazolium perchlorate and 2-methyl-4,6-diphenyl pyrylium perchlorate

0.5 g. of the dithiazole salt and about 0.45 g pyrylium salt were heated in acetic acid (10 ml) in presence of pyridine. IR of the product showed that no reaction had occurred.

Reaction of 5-phenyl-3-ethylthio-1,2,4-dithiazolium perchlorate and 2,6-dimethyl-4-phenyl pyrylium perchlorate

Equimolar quantities of the reagents in acetic acid with few drops of pyridine were allowed to react. Although a red color developed, the product could not be purified satisfactorily for analysis.

Reaction of 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide and 2-methyl-4,6-diphenyl thiopyrylium perchlorate

Equimolar quantities of the reagents in acetic acid and few drops of pyridine were allowed to react. Product recrystallized from nitromethane, m.pt. 183-5°C. Analysis found: C=55.07%, H=3.78%, S=10.07%, N=3.78%, Cl=1.91%. $C_{26}H_{18}NC_{10}O_4S_3$ requires: C=57.8%, H=3.3%, N=2.6%, S=17.7%, Cl=8.7%, O=11.85%.

Reaction of 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide and sodium benzoyl acetate

A suspension of sodium benzoylacetate in ethanol (15 ml) was prepared by addition of metallic sodium (0.12 g) to ethanol (15 ml) followed by addition of benzoylacetic acid (0.82 g). To this was added 3-methylthio-5-phenyl-1,2,4-dithiazolium iodide (1.8 g) and the mixture was heated for 5 minutes. The product poured in water to dissolve any sodium iodide formed, and then extracted with ether. Recrystallized from ethanol m.pt. 128-9°C. IR showed OH peak at 3200 and C=O peak at 1670 cm^{-1} . Elemental analysis found: C=75.63%, H=4.31%, S=31.43%, $C_{15}H_{12}OS$ require: C=75%, H=5.00%, S=13.3%, O=6.6%.

Reaction of 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide and malonic acid.

Equimolar quantities of the reagents in acetic acid were allowed to react using traces of pyridine as a catalyst. The crude product was recrystallized from acetic acid with few drops of perchloric acid, but the IR of the product obtained corresponded to that of 5-phenyl-1,2,4-dithiazole-3-thione.

Reaction of 5-phenyl-3-ethylthio-1,2,4-dithiazolium perchlorate and sodium benzoyl acetate

Equimolar quantities of the reagents in ethanol were allowed to react. Reaction products poured in water, and extracted with ether. An oily product obtained was chromatographed. Light yellow compound was obtained whose IR did not suggest the expected product.

Reaction of 5-phenyl-3-ethylthio-1,2,4-dithiazolium perchlorate with malononitrile

Equimolar quantities of the reagents in acetic acid with few drops of pyridine were allowed to react. Reaction products poured in water, and the product extracted with ether. The oily product was separated by TLC, and a large number of bands were obtained. No definite single product could be isolated from this.

HALOGENATION REACTIONS OF 5-PHENYL-1,2,4-DITHIAZOLE-3-THIONE

Bromination of 5-phenyl-1,2,4-dithiazole-3-thione

To 0.5 g of the thione dissolved in 20 ml acetic acid approximately 0.8 g of bromine was added slowly with stirring. The product obtained by filtration gave an IR similar to that of the starting material.

Chlorination of 5-phenyl-1,2,4-dithiazole-3-thione

(a) In acetic acid: 0.5 g of the thione dissolved in 10 ml glacial acetic acid, and chlorine gas passed through it until a yellow colored product was obtained. This was then treated with ether. The ether-soluble product was identified to be 5-phenyl-1,2,4-dithiazole-3-one by IR. m.pt. 87-8°C. The insoluble material was presumed to be the chlorine adduct of the thione since it decomposed rapidly on keeping.

(b) In carbontetrachloride : The thione (0.5 g) dissolved in carbon tetrachloride and chlorine gas passed through it gave a yellow compound, similar to that found in (a).

Chlorination of 5-o-toluy1-1,2,4-dithiazole-3-thione

0.36 g of the thione dissolved in 15 ml of chloroform, and 0.3 g of phosphorus pentachloride added to it. Reagents were refluxed for 6 hours. Ether did not precipitate any salt. Evaporation of the solvents gave an orange-red compound, whose IR corresponded to that of the thione itself showing no reaction had occurred.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with thionyl chloride

0.5 g of the thione dissolved in benzene was refluxed with 0.56 g

of thionyl chloride for 5 hours. Product obtained by filtration was found from its IR to be the starting material. m.pt. 115-35°.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with oxalyl chloride

Equimolar quantities of the reagents in benzene were refluxed for 48 hours. No reaction occurred as only starting material was recovered.

Reaction of 5-phenyl-1,2,4-dithiazole-3-one with oxalyl chloride

0.5 g. of the starting material was prepared by the method of Derocque and Vialle¹⁹ was dissolved in carbon tetrachloride, and refluxed with oxalyl chloride for 7 hours. Evaporation of the solvent, and recrystallization of the product from ethanol gave back the starting material.

Oxidation of 5-phenyl-1,2,4-dithiazole-3-thione by hydrogen peroxide

5-phenyl-1,2,4-dithiazole-3-thione (1 g.) dissolved in 20 ml of acetone and 20 ml acetic acid, treated with 30% hydrogen peroxide (0.5 g); the solution stirred for 10 minutes and kept for 1 hour. It was then filtered, and to the filtrate few drops of perchloric acid were added. Ether did not precipitate any compound. The solution was evaporated under vacuum; product recrystallized from ethanol was found to be 5-phenyl-1,2,4-dithiazole-3-one. m.pt. 84-5°C. Yield: 25%. Identical to an authentic sample.¹⁹

Reaction of 3-methylthio-5-phenyl-1,2-dithiolium iodide^{63,54,22} with thiobenzamide

Equimolar quantities of dithiolium iodide (0.58 g) and thiobenzamide (0.225 g) were refluxed in ethanol for over 30 minutes. Reaction product recrystallized from ethanol, m.pt. 110-5°C was identified as

5-phenyl-1,2-dithiole-3-thione by IR and by mixed melting point.

Reaction of 3-methylthio-5-phenyl-1,2-dithiolium iodide and p-dimethyl amino thiobenzamide⁷⁰

Equimolar quantities of the reagents in ethanol were refluxed for 2 hours. Shining brown crystals obtained were found to be the p-dimethylamino-thiobenzamide from IR.

Reaction of thionicotinamide with 3-methylthio-5-phenyl-1,2-dithiolium iodide

Equimolar quantities of the reagents in ethanol were refluxed for 2 hours. Reaction did not work.

Reaction of 5-phenyl-3-methylthio-1,2,4 dithiazolium iodide with perchloric acid

0.5 g of the 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide was dissolved in 15 ml of nitromethane, and then 5-7 drops of perchloric acid added to it. The reaction was instantaneous. A brownish colored product started precipitating out on addition of ether. IR showed ClO_4^- peak at $110 - 1050 \text{ cm}^{-1}$.

REACTIONS OF 5-PHENYL-1,2,4-DITHIAZOLE-3-THIONE WITH DIPOLAROPHILES

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with dimethyl azodicarboxylate

Equimolar quantities of the reagents were refluxed in ethanol for two days. The precipitate obtained on recrystallization from ethanol was found to be the starting material, m.pt. 125-6°C (low melting point due to contamination). When the reagents were refluxed in xylene for 48 hours, and the product recrystallized from ethanol, only the starting material was obtained (similar IR as that of the genuine thione).

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with hexafluoro-2-butyne

0.5 g. of the thione in benzene contained in a glass tube cooled down to -70° in dry ice-acetone bath, and a slight excess of hexafluoro-2-butyne was allowed to condense into it. The tube was sealed and heated in water bath at 70° for 6-7 hours. Green product obtained on evaporation of the solvent was recrystallized from ethanol. m.pt. 128-9°. Yield: 95%. IR gave -CF₃ peak at 1160 cm⁻¹. NMR gave a single fluorine peak at τ 3133 T (55.54 parts per million). Analysis found: C=38.7%, H=1.53%, F=30.47%, S=25.72%, N=3.81%. C₁₂H₅F₆S₃N requires: C=38.7%, H=1.3%, F=30.3%, S=25.5%, N=3.7%.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with dibenzoyl acetylene

Equimolar quantities of the thione (0.5 g.) and dibenzoyl acetylene (0.6 g.) were refluxed for 2 hours. Solvent evaporated and the product recrystallized from nitromethane which gave brownish needle-like crystals. m.pt. 160-1°C. IR in "Nujol" gave peaks at 1665,

1650, 1590, 1510, 1450, 1360, 1310, 1260, 1160, 1050, 1010, 980, 930, 850, 810, 775, and 725 cm^{-1} . Sharp peaks at 1665 and 1650 showed two carbonyl groups. Yield: 95%, Analysis found C=64.64%, H=3.56%, S=21.4% O=7.15%, N=3.25%. $\text{C}_{24}\text{H}_{15}\text{S}_3\text{O}_2\text{N}$ requires: C=64.71%, H=3.37%, S=21.58%, O=7.19%, N=3.15%.

When 0.5 g. of the thione and excess of dibenzoyl acetylene (1 gm.) were refluxed in benzene for 7 hours, and the solvent evaporated besides the monoadduct, a yellow diadduct was also obtained. Recrystallized from nitromethane, m.pt. $187-8^\circ\text{C}$. Yield: 70%. Analysis found C=70.81%, H=3.86%, N=2.22%, S=14.31%. $\text{C}_{40}\text{H}_{25}\text{NS}_3\text{O}_4$ requires: C=70.68%, H=3.68%, N=2.06%, S=14.15%, O=9.42%.

Reaction of 5-o-toluy1-1,2,4-dithiazole-3-thione with dibenzoyl acetylene

5-o-toluy1-1,2,4-dithiazole-3-thione (0.5 gm), and dibenzoyl acetylene (0.501 g.) refluxed in benzene for 3 hours gave red compound recrystallized from nitromethane. m.pt. $160-1^\circ\text{C}$. IR showed strong C=O peak at 1640 cm^{-1} . Analysis found: C=64.48%, H=3.92%, S=20.65%, N=3.16%. $\text{C}_{25}\text{H}_{17}\text{S}_3\text{NO}_2$ requires: C=64.46%, H=3.79%, S=20.81%, N=3.05%, O=6.9%, Yield: 90%.

Reaction of 5-p-toluy1-1,2,4-dithiazole-3-thione¹ with dibenzoyl acetylene

0.5 g. of 5-p-toluy1-1,2,4-dithiazole-3-thione and 0.51 g. of dibenzoylacetylene refluxed in benzene for 3 hours. Solvent evaporated

and the product recrystallized from nitromethane. m.pt. 167°C . Yield: 90%. IR in "Nujol" showed strong carbonyl absorption at 1625 cm^{-1} , C=S absorption at 1260 cm^{-1} . Other peaks were at: 1560, 1525, 1400, 1370, 1365, 1290, 1200, 1115, 1040, 1025, 1015, 960, 890, 780, 760, and 725 cm^{-1} . Analysis found: C=64.59%, H=3.90%, S=20.95%, N=3.17%. $\text{C}_{25}\text{H}_{17}\text{S}_3\text{NO}_2$ requires: C=64.46%, H=3.8%, S=20.8%, N=3.05%, O=6.91%.

When 0.5 g. of the above monoadduct was refluxed with approx. 0.25 g. of dibenzoylacetylene for $6\frac{1}{2}$ hours in benzene, and the solvent evaporated, a yellow colored diadduct was obtained, recrystallized from nitromethane. m.pt. $185-5.8^{\circ}\text{C}$. Yield: 85%. Analysis found: C=70.82%, H=4.28%, S=13.77%, N=2.16%. $\text{C}_{41}\text{H}_{27}\text{NS}_3\text{O}_4$ requires: C=71.01%, H=3.95%, N=2.02%, S=13.81%, O=9.23%.

Reaction of 5-(2-furyl)-1,2,4-dithiazole-3-thione with dibenzoylacetylene

5-(2-furyl)-1,2,4-dithiazole-3-thione (0.5 g.) and dibenzoylacetylene (0.53 g.) were refluxed in benzene for $3\frac{1}{2}$ hours; solvent evaporated, and the product recrystallized from nitromethane, which gave purple crystalline compound, m.pt. $145-7^{\circ}\text{C}$. Yield: 90%. Analysis found: C=60.81%, H=3.14%, S=22.06%, N=3.33%. $\text{C}_{22}\text{H}_{13}\text{S}_3\text{NO}_3$ requires: C=59.32%, S=21.57%, N=3.14%, O=10.78%, H=3.0%.

Reaction of 5-(2-thienyl)-1,2,4-dithiazole-3-thione with dibenzoylacetylene

5-(2-thienyl)-1,2,4-dithiazole-3-thione (0.5 g) and dibenzoylacetylene (0.515 g) refluxed in benzene for $3\frac{1}{2}$ hours. Solvent evaporated and the product recrystallized from nitromethane. m.pt. $197-8^{\circ}\text{C}$.

Yield: 90%. Analysis found: C=58.58%, H=2.71%, S=28.35%, N=3.17%.

$C_{22}H_{13}S_4NO_2$ requires: C=58.53%, H=2.88%, S=28.38%, N=3.1%, O=7.1%.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione and dicyanoacetylene

0.5 g of the thione and equimolar quantity of dicyanoacetylene were refluxed in benzene for 2 hours. Solvent evaporated, and the dark green product recrystallized from nitromethane-nitrobenzene mixture gave the product. m.pt. $220-1^{\circ}C$. Yield: 95%. Analysis found: C=50.03%, H=1.80%, S=33.56%, N=14.48%, $C_{12}H_5S_3N_3$ requires: C=50.18%, H=1.74%, S=33.45%, N=14.63%. IR showed CN absorption at 2185 cm^{-1} .

Reaction of 5-(p-toluy1)-1,2,4-dithiazole-3-thione and dicyanoacetylene

0.25 g. of the thione and equimolar quantity of dicyanoacetylene were refluxed in benzene for 5 hours. Product recrystallized from nitromethane-nitrobenzene mixture, gave green product, m pt. $213-4^{\circ}C$. Yield: 96%. Analysis found: C=51.71%, H=2.35%, N=13.79%, $C_{13}H_7N_3S_3$ requires: C=51.82%, H=2.22%, N=13.9%, S=31.89%. IR showed CN absorption at 2200 cm^{-1} .

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with 1,4-dichloro-2-butyne

Equimolar quantities of the reagents refluxed in benzene for $2\frac{1}{2}$ hours. solvent evaporated, and the product recrystallized from benzene was found to be the starting material.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with propargyl bromide

Equimolar quantities of the reagents refluxed in benzene for 2 hours. No addition product obtained.

Reaction between 5-phenyl-1,2,4-dithiazole-3-thione and benzoquinone

Equimolar quantities of the reagents refluxed in benzene for 19 hours gave back the thione as shown by the IR of the product obtained.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with phenylisothiocyanate

The thione (0.5 g) and approx 0.5 g of phenyl isothiocyanate in benzene were refluxed for 22 hours. After evaporating the solvent, the product was recrystallized from benzene. It was found to be the starting material.

SULFURIZATION REACTIONS OF THE MONOADDUCTS

Reaction of 2-thiobenzoylimino-4,5-dibenzoyl-1,3-dithiole with phosphorus pentasulfide

0.5 g of 3-thiobenzoylimino-4,5-dibenzoyl-1,3-dithiole with 0.2 g phosphorus pentasulfide refluxed in pyridine for 5 hours. The green product obtained after evaporating pyridine under vacuum, was recrystallized from a mixture of ethanol and benzene, m.pt. 203-3.5°C. IR showed the absence of the carbonyl peak. Yield: 45%. Analysis found: C=64.54%, H=3.56%, S=28.63%, N=3.26%. $C_{24}H_{15}S_4N$ requires: C=64.71%, H=3.37%, S=28.76%, N=3.15%.

Reaction of 2-(o-thiotoluylimino)-4,5-dibenzoyl-1,3-dithiole with phosphorus pentasulfide


0.5 g of the dibenzoyl compound and 0.25 g of phosphorus pentasulfide in pyridine refluxed for 5 hours gave green needles, recrystallized from benzene-ethanol mixture, m.pt. 197-200°C. Yield 47%. Analysis found C=65.35%, H=3.88%, S=27.78%, N=3.24%. $C_{25}H_{17}S_4N$ requires: C=65.35%, H=3.7%, S=27.9%, and N=3.05%. IR showed the absence of carbonyl group.

Reaction of 2-(2-thiofuroylimino)-4,5-dibenzoyl-1,3-dithiole and phosphorus pentasulfide

0.25 g of 2 (2-thiofuroylimino)-4,5-dibenzoyl-1,3-dithiole and 0.15 g of phosphorus pentasulfide in pyridine refluxed for 5 hours. Solvent evaporated under vacuum, and the green product recrystallized from nitrobenzene. m.pt. 218-20°C. Yield: 55%. Analysis found: C=59.35%, H=3.74%, S=27.89%, N=3.92%. $C_{22}H_{13}S_4NO$ requires: C=60.68%, H=3.0%, S=29.43%, N=3.21%, O=3.67%.

Reaction of 2-(p-thiotoluylimino)4,5-dibenzoyl-1,3-dithiole and phosphorus pentasulfide

0.5 g of the dibenzoyl compound and about 0.3 g of phosphorus pentasulfide refluxed in pyridine for 5 hours. Solvent evaporated and the green product recrystallized from nitrobenzene. m.pt. 207-7.5°C. Yield: 50%. Analysis found: C=65.4%, H=3.64%, S=27.64%, N=3.05%. $C_{25}H_{17}S_4N$ requires: C=65.36%, H=3.7%, S=27.90%, N=3.05%.



REACTIONS INVOLVING PREPARATION OF THE 1:4 DIADDS FROM 1:3 MONOADDUCTS

Reaction of 2-thiobenzoylimino-4,5-dicyano-1,3-dithione and hexafluoro-2-butyne

0.5 g of the monoadduct and a slight excess of hexafluoro-2-butyne refluxed in benzene in sealed tube for 6 hours gave back the starting material.

Reaction of 2-thiobenzoylimino-4,5-dicyano-1,3-dithiole and dimethyl acetylenedicarboxylate

Equimolar quantities of the reagents refluxed in benzene for 6 hours gave back the starting material.

Reaction of dimethyl-2-thiobenzoylimino-1,3-dithiole-4,5-dicarboxylate and hexafluoro-2-butyne

Equimolar quantities of the reagents refluxed in benzene in sealed tube for 8 hours gave back the starting material.

Reaction of dimethyl-2-thiobenzimino-1,3-dithiole-4,5-dicarboxylate and dimethyl azodicarboxylate.

Equimolar quantities of the reagents in benzene and in xylene were refluxed for 24 hours. Only the starting material was obtained.

Reaction of 2-thiobenzoylimino-4,5-dicyano-1,3-dithiole and dimethyl azodicarboxylate

Equimolar quantities of the reagents refluxed in benzene and xylene for 24 hours and 48 hours gave back the starting material.

Reaction of 2-thiobenzoylimino-4,5-dibenzoyl-1,3-dithiole and dimethyl azodicarboxylate

Equimolar quantities of the reagents refluxed in ethanol for 8 hours. Product put on TLC. Three bands were obtained on the plate when 5% chloroform and 95% benzene mixture was used. Band I (green) gave unreacted starting material. Band III (orange-yellow) gave a product recrystallized by nitromethane. m.pt. 187-8°C, orange crystalline product. IR gave strong carbonyl peak at 1650 and 1640 cm^{-1} , while the IR of the reagent, dimethyl azodicarboxylate, gave strong carbonyl absorption at 1750 cm^{-1} . Analysis found C=66.70%, H=3.65%, N=3.28%, S=14.96%. $\text{C}_{28}\text{H}_{21}\text{N}_3\text{S}_3\text{O}_6$ requires: C=56.84%, H=3.55%, N=7.1%, S=16.25%, O=16.25%. On repeating the experiment, orange-yellow band could not be obtained on TLC plate and the orange-yellow crystalline product was not obtained; apparently there were some unknown factors working when the experiment was done first.

REACTIONS INVOLVING CARBONYL GROUPS OF 2-THIOBENZOYLIMINO-4,5-DIBENZOYL-1,3-DITHIOLE

Reaction of 2-thiobenzoylimino-4,5-dibenzoyl-1,3-dithiole and hydrazine

0.25 g of 2-thiobenzoylimino-4,5-dibenzoyl-1,3-dithiole and 0.02 g of hydrazine in ethanol were refluxed for 3 hours. The crude product obtained on evaporation of the solvent was separated by TLC which gave a purple band of some decomposition product which was too small to be analysed.

Reaction of 2-thiobenzoylimino-4,5-dibenzoyl-1,3-dithiole and phenylenediamine

Equimolar quantities of the reagents in ethanol refluxed for 6 hours. Orange yellow crystals obtained by recrystallization from nitromethane, m.pt. 222-23°. IR showed N-H peak at 3150 cm^{-1} , and strong carbonyl peak at 1675 cm^{-1} as compared to the carbonyl absorption peak at 1625 cm^{-1} in case of the starting material. Analysis found C=66.95%, H=4.58%, N=8.67%, S=13.35%. $\text{C}_{30}\text{H}_{21}\text{N}_3\text{S}_3\text{O}$ requires: C=67.28%, H=3.9%, N=7.84%, S=17.94%, O=3.0%.

Reaction of 2-thiobenzoylimino-4,5-dibenzoyl-1,3-dithiole and aniline

Equimolar quantities of the reagents in benzene refluxed for 6 hours. Product purified by TLC recrystallized from benzene-ethanol mixture. m.pt. 223-5°C. Yield: 30%. IR showed shifted strong absorption peak at 1675 cm^{-1} . Found: C=73.5%, H=4.62%, S=12.21%, N=5.42%, O=4.25%. $\text{C}_{30}\text{H}_{20}\text{N}_2\text{S}_3\text{O}$ requires: C=69.23%, H=4.84%, S=18.46%, N=5.38%, O=3.07%.

MISCELLANEOUS REACTIONS:

Oxidation of C=S group of 2-thiobenzoylimino-4,5-dibenzoyl-1,3-dithiole

The compound 2-thiobenzoyl-imino-4,5-dibenzoyl-1,3-dithiole (0.5 g) in 15 ml of acetic acid was reacted with mercuric acetate until the color of the solution became milky. The mixture was shaken for 24 hours, and then filtered, to removed unreacted mercuric acetate. The filtrate was treated with water to dissolve any unreacted mercuric acetate, and the product extracted with ether. Evaporation of ether, and recrystallization of the product by nitromethane gave the product, m.pt.169-70°C. Analysis found: C=15.14%, H=2.22%, N=0.08%, S=12.07%. $C_{24}H_{15}NS_2O_3$ requires: C=67.2%, H=3.49%, N=3.26%, S=14.94%, O=11.19%. Obviously the compound analysed was contaminated with some inorganic compound.

Oxidation of C=S group of 2,5-diphenylthieno(3,4-d)2-thiobenzamino-1,3-dithiole

0.25 g of 2,5-diphenylthieno(3,4-d)2-thiobenzamino-1,3-dithiole was taken in 15 ml of acetic acid. Mercuric acetate added to this until the solution became somewhat milky. The mixture shaken for about 48 hours, insoluble mercuric sulfide filtered, and the filtrate treated with water to dissolve any unreacted mercuric acetate; the product extracted with ether, and recrystallized from ethanol-benzene mixture IR showed strong C=O absorption at 1640 cm^{-1} . Analysis found: C=66.91%, H=3.64%, N=3.3%. $C_{24}H_{15}S_3ON$ requires: C=67.13%, H=3.5%, S=22.38%, O=3.73%, N=3.26%. m.pt.214-5°C. Yield: 60%.

Reaction of 2-thiobenzoylimino-4,5-dibenzoyl-1,3-dithiole and triethyloxonium fluoroborate

0.5 gm of the starting material and methylene chloride solution of excess triethyloxonium fluoroborate were allowed to stand for 5 days. Crystals started forming after removing methylene chloride. Recrystallization gave two type of crystals having a large melting range. The product was insufficient for analysis.

Reaction of 2,5-diphenylthieno-(3,4-d)-2-thiobenzamino-1,3-dithiole and triethyloxonium fluoroborate

0.5 g of the starting material allowed to stand for several days in methylene chloride solution of excess triethyloxonium fluoroborate. Only starting material was obtained back.

Sulfurization of 4,5-dibenzoyl-1,3-dithiole-2-spiro-4-(5',6')-dibenzoyl 2'-phenyl-1,3-thiazine

0.5 g of the spiro compound and corresponding amount of phosphorus pentasulfide refluxed in pyridine for 5½ hours. The product was put on TLC. A large number of bands were obtained. The bottom, intense yellow band was scraped out, and the compound extracted with chloroform. IR in methylene chloride was not suitable for interpretation.

ALKYLATION REACTIONS OF DITHIAZOLE-3-THIONE

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with benzyl bromide

0.5 g of the product allowed to stand with excess benzyl bromide for 2 days. Ether insoluble light brown needles slowly formed and were filtered off. m.pt. $95-5.5^{\circ}\text{C}$. Analysis found: C=43.52%, H=3.78%, S=22.46%, N=3.58%; $\text{C}_{15}\text{H}_{12}\text{S}_3\text{BrN}$ requires: C=47.12%, H=3.14%, S=25.12% N=3.67%, Br=20.94%.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with dimethyl sulfate

0.5 g of thione in excess dimethyl sulfate allowed to stand for 5 days. No salt formation occurred.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with ethyl iodide

0.5 g of the thione in excess ethyl iodide gave purple needles after 3 days. m.pt. of ether-washed product: $84-5^{\circ}\text{C}$. Analysis found: C=17.21%, H=1.77%, N=1.46%, S=14.65%. $\text{C}_{10}\text{H}_{10}\text{NS}_3\text{I}$ requires: C=32.7%, H=2.71%, N=3.81%, S=26.14%, I=34.6%. $\text{C}_{10}\text{H}_{10}\text{NS}_3\text{I}_3$ requires: C=19.6%, H=1.63%, N=2.29%, S=15.68%, I=61.35%. Apparently the compound is mostly the triiodide.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione and benzhydryl bromide

0.5 g of the thione in excess benzhydryl bromide allowed to stand for 3 days. A yellow precipitate was formed which was filtered off, washed with ether, m.pt. $120-4^{\circ}\text{C}$. Analysis found: C=44.28%, H=3.5%, N=2.39%, and 2.56% ash. $\text{C}_{21}\text{H}_{16}\text{S}_3\text{NBr}$ requires C=55%, H=3.5%, N=3.05%, S=20.48%, Br= 12.46%.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with butyl bromide

5-phenyl-1,2,4-dithiazole-3-thione (0.25 g) was dissolved in butyl bromide (10 ml) and allowed to stand for 4 days. No reaction was observed.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with benzal chloride

0.25 g of 5-phenyl-1,2,4-dithiazole-3-thione in benzal chloride (10 ml) was allowed to stand for 4 days. No salt formation was observed.

Reaction of 5-phenyl-1,2,4-dithiazole-3-thione with triphenyl methyl perchlorate

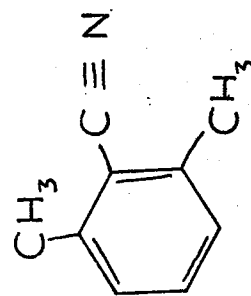
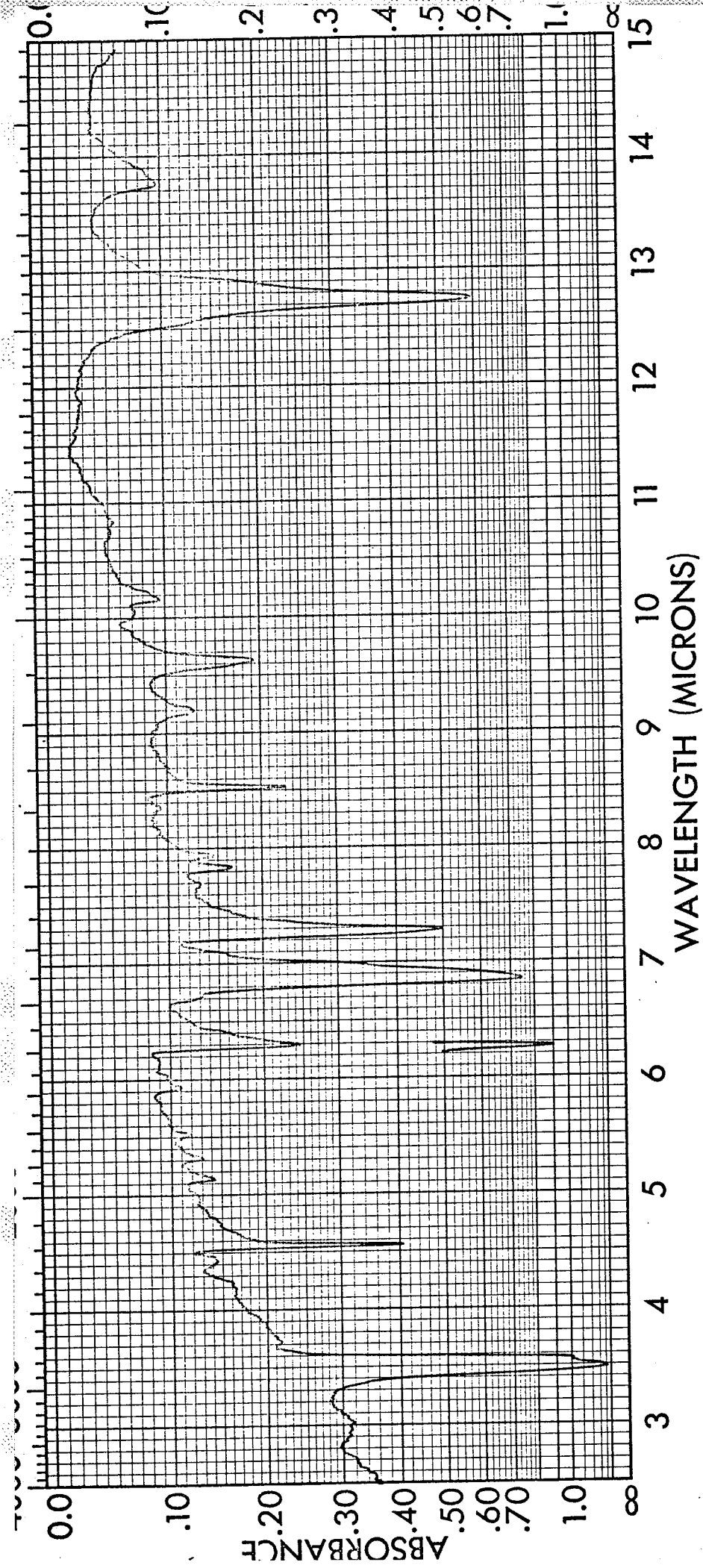
0.25 g of 5-phenyl-1,2,4-dithiazole-3-thione in acetone and a little excess of triphenyl methyl perchlorate were allowed to stand for 4 days. No salt formed.

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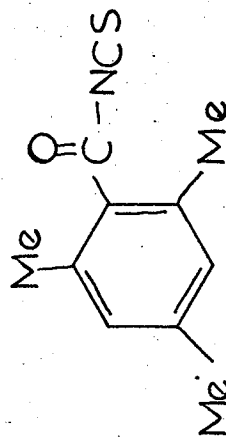
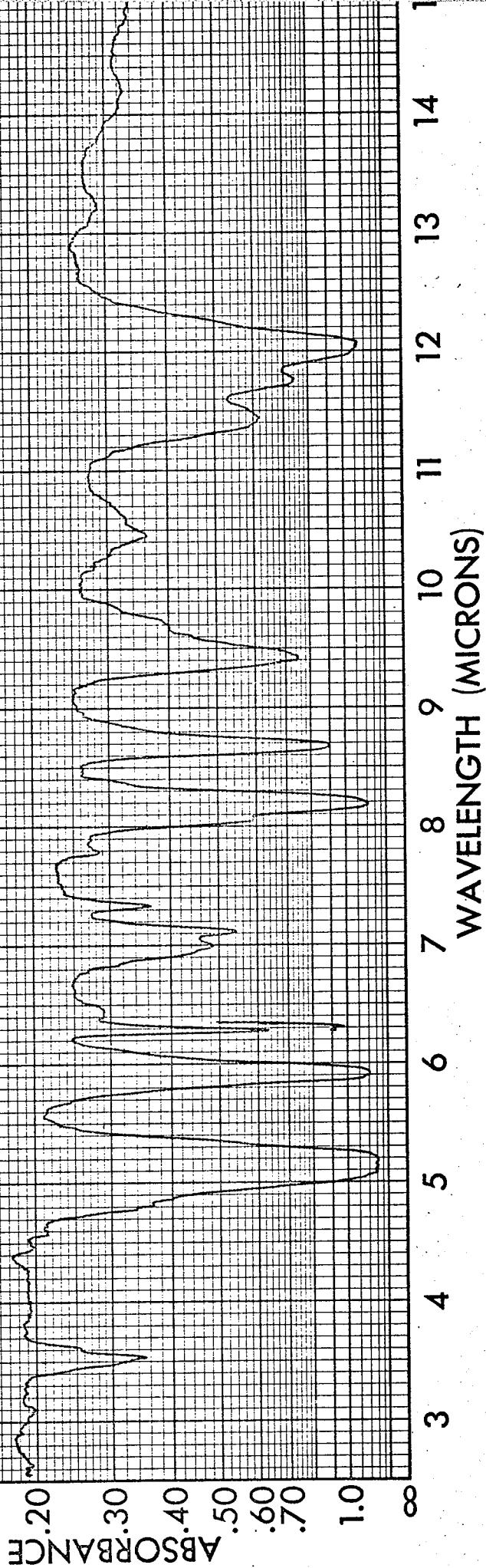
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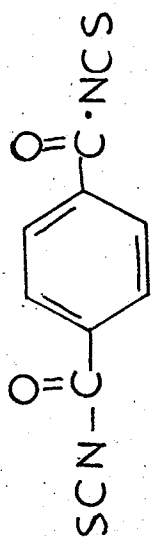
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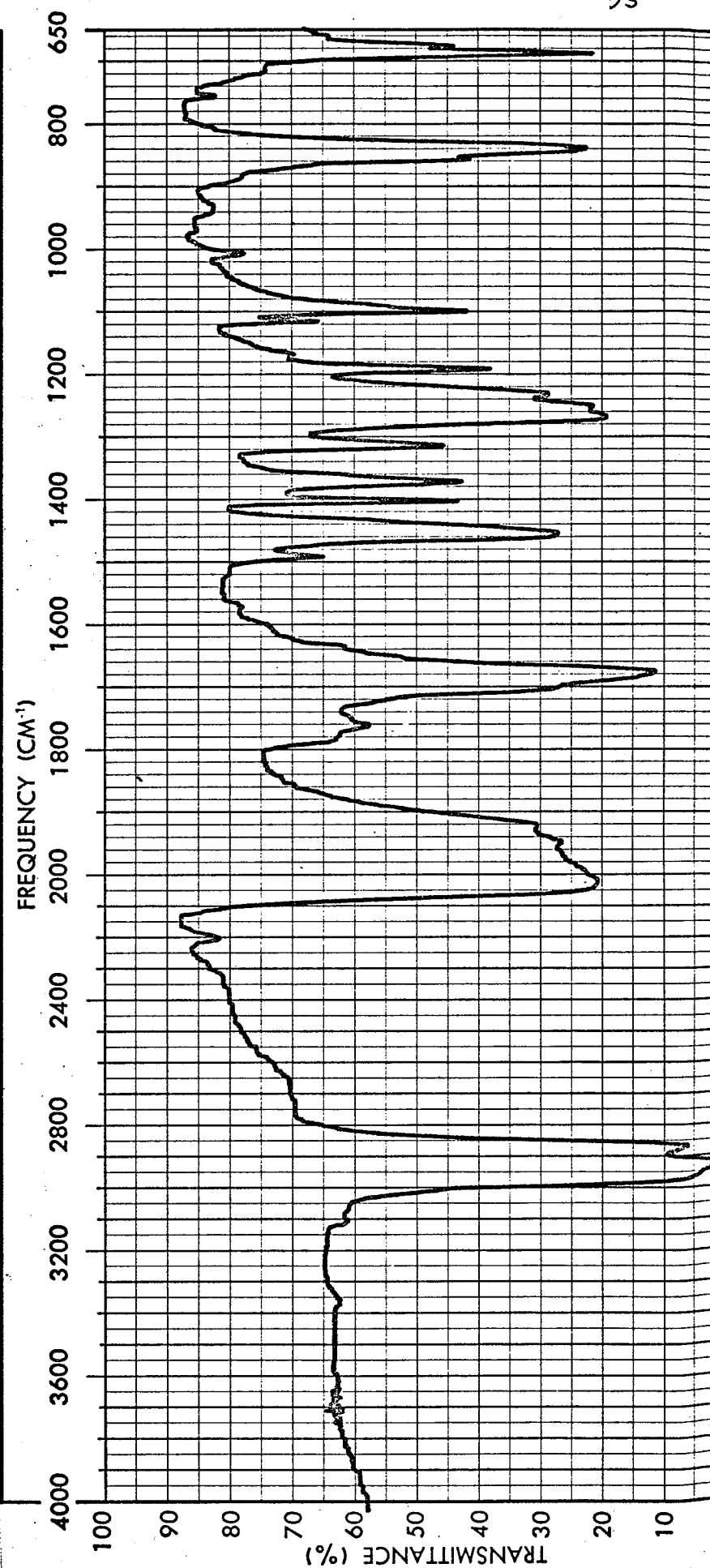
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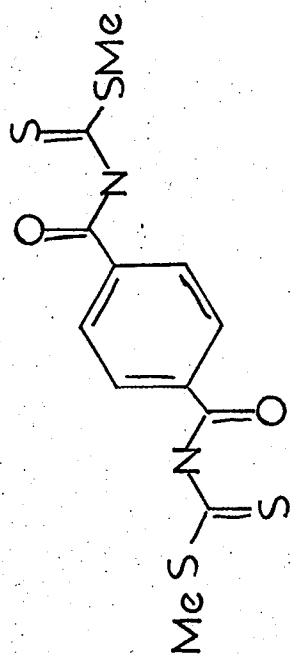


2,4,6-trimethylbenzoyl isothiocyanate

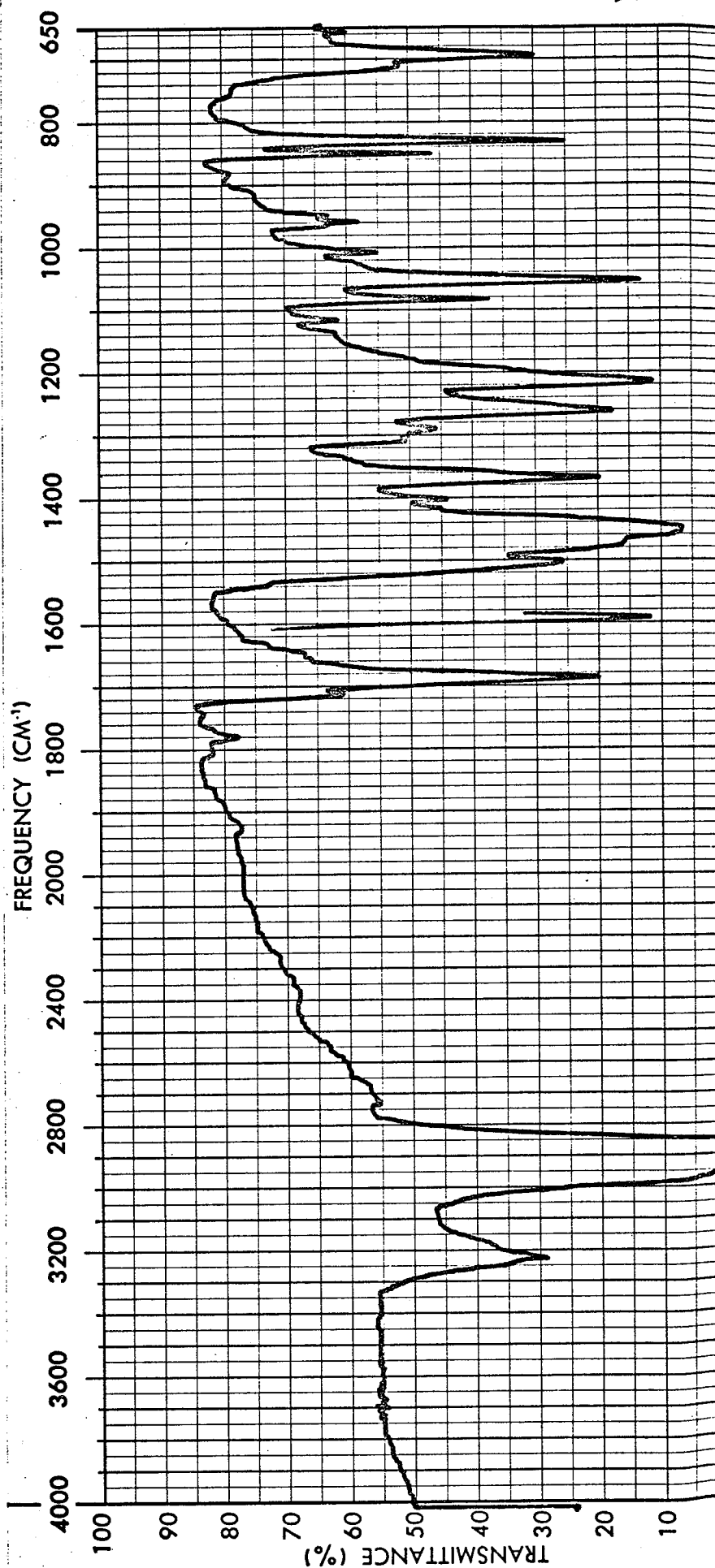


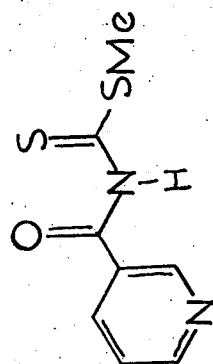
Terephthaloyl diisothiocyanate



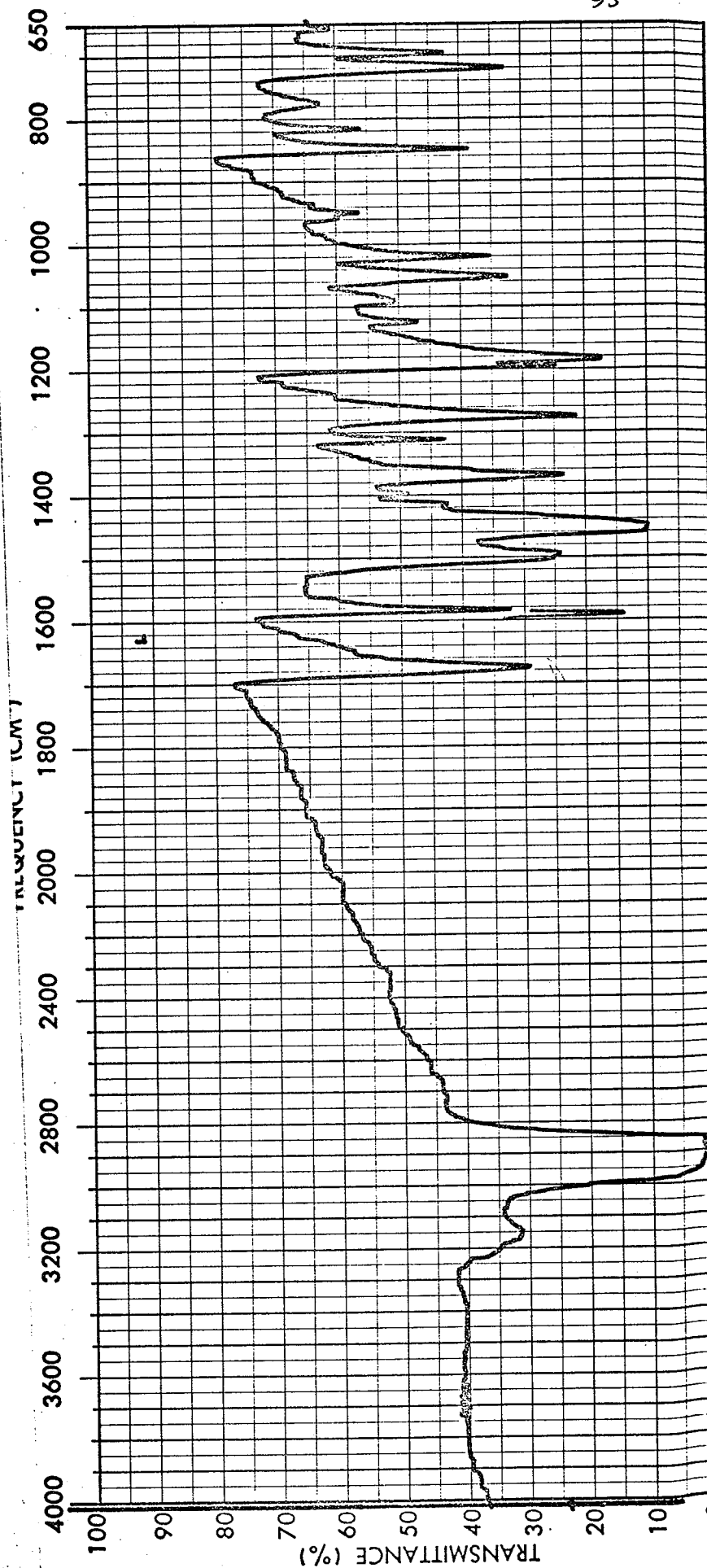


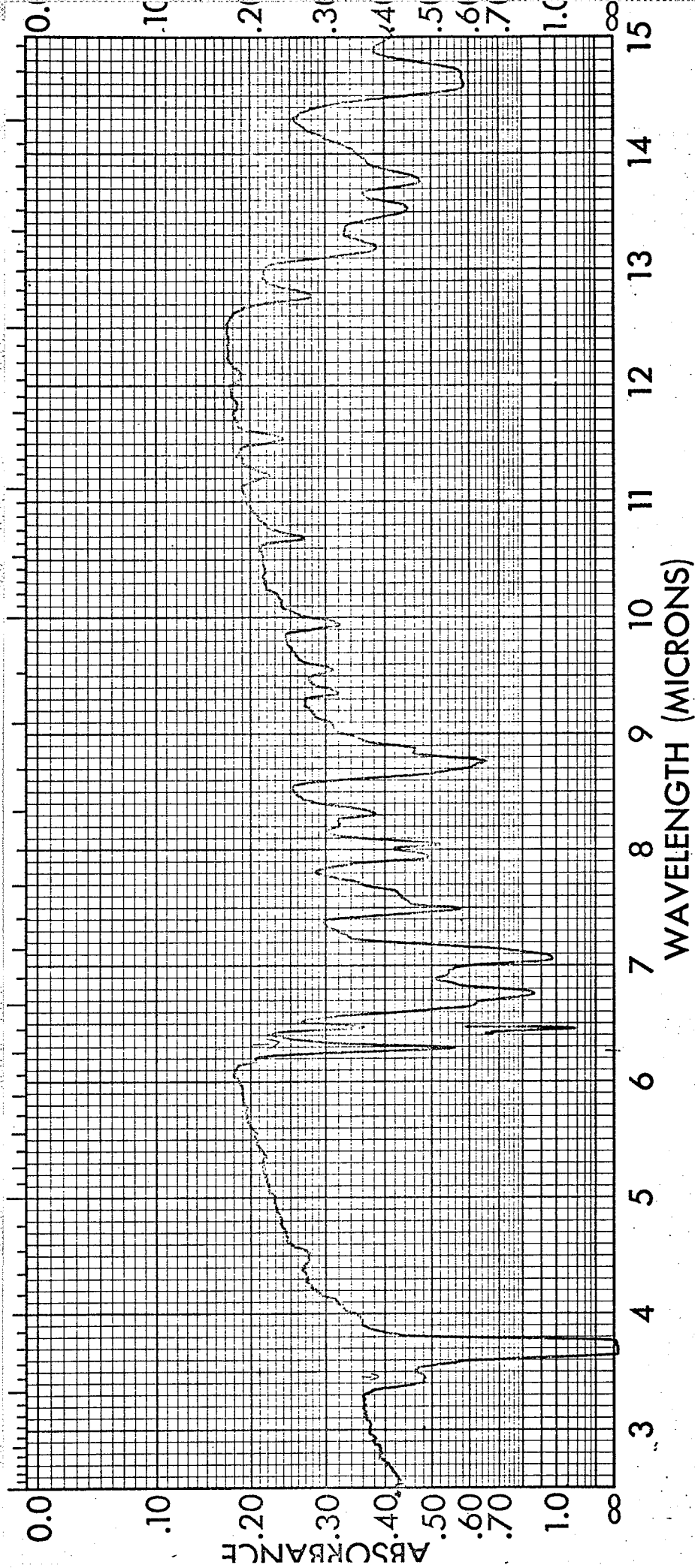
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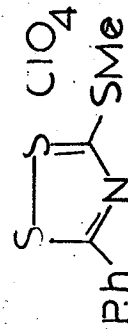
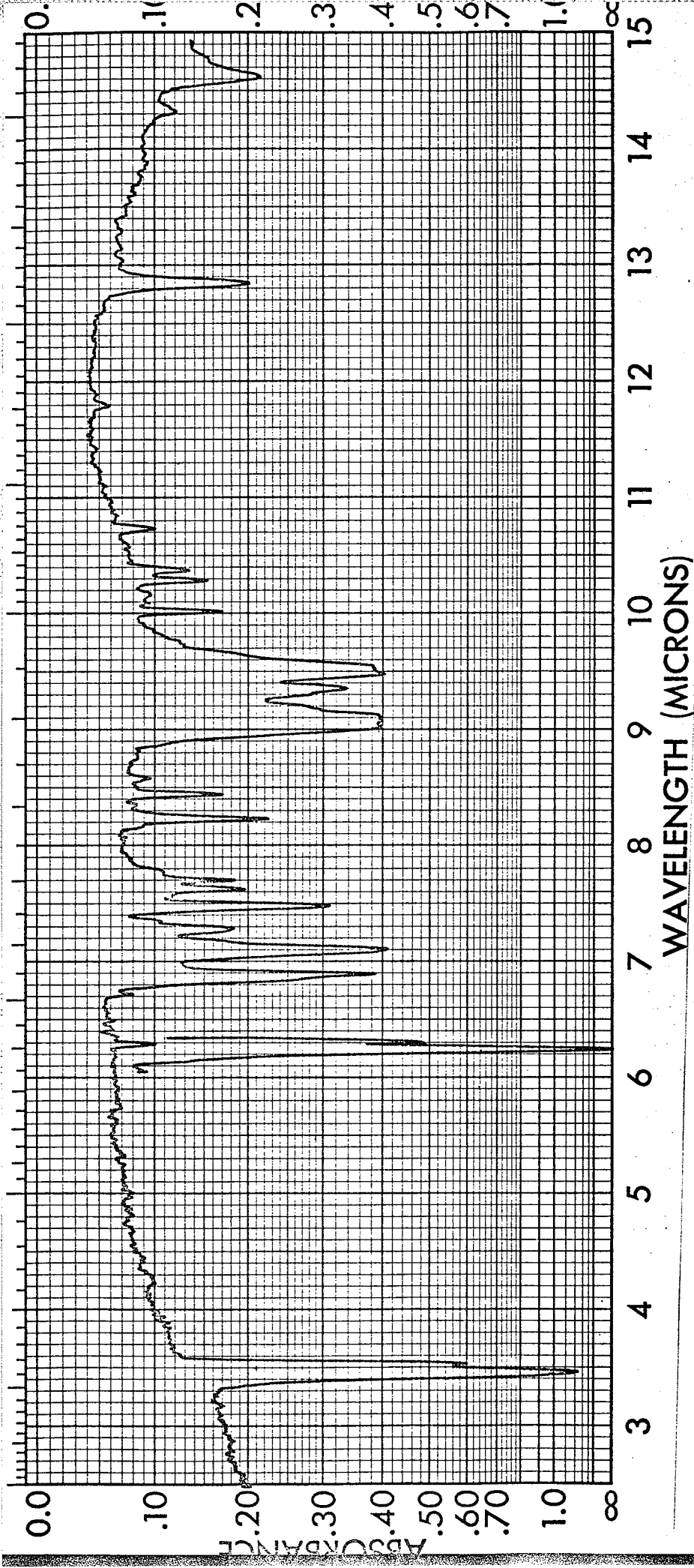


Methyl nicotinoyldithiocarbamate

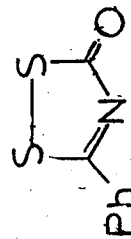
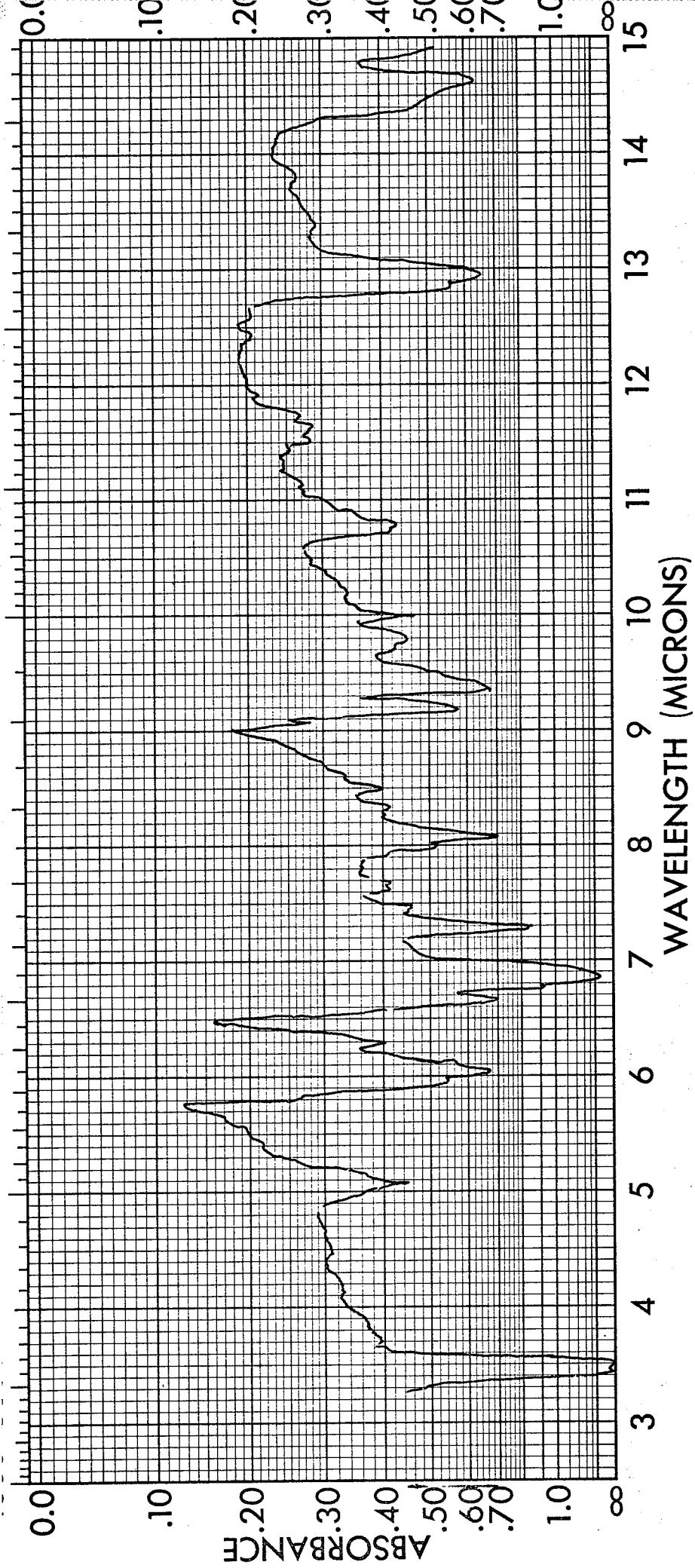




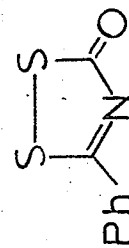
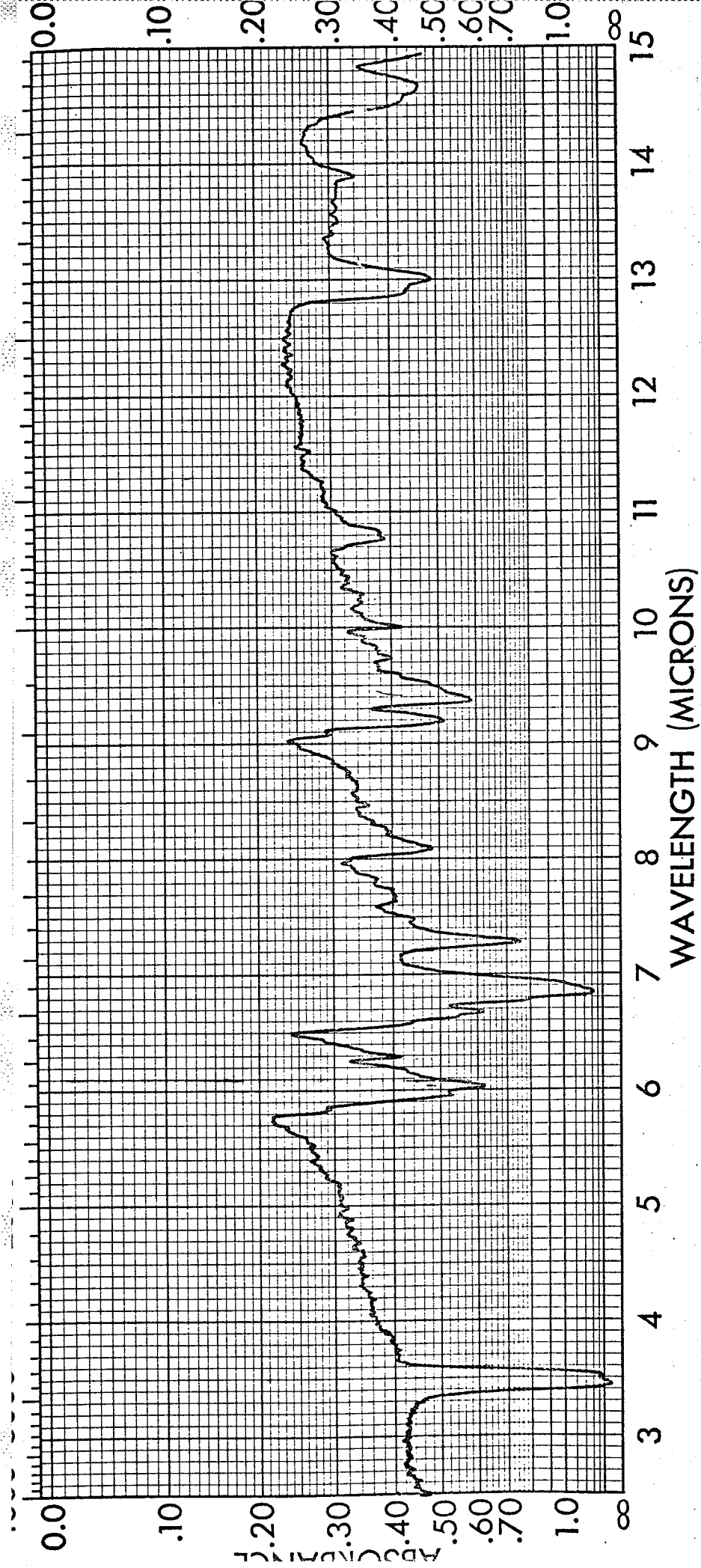
REACTION PRODUCT OF 5-PHENYL-3-THIOETHYL-1,2,4-DITHIAZOLIUM
PERCHLORATE AND ANILINE IN ACETIC ACID
Recrystallized from MeOH



5-Phenyl-3-methylthio-1,2,4-dithiazolylum perchlorate

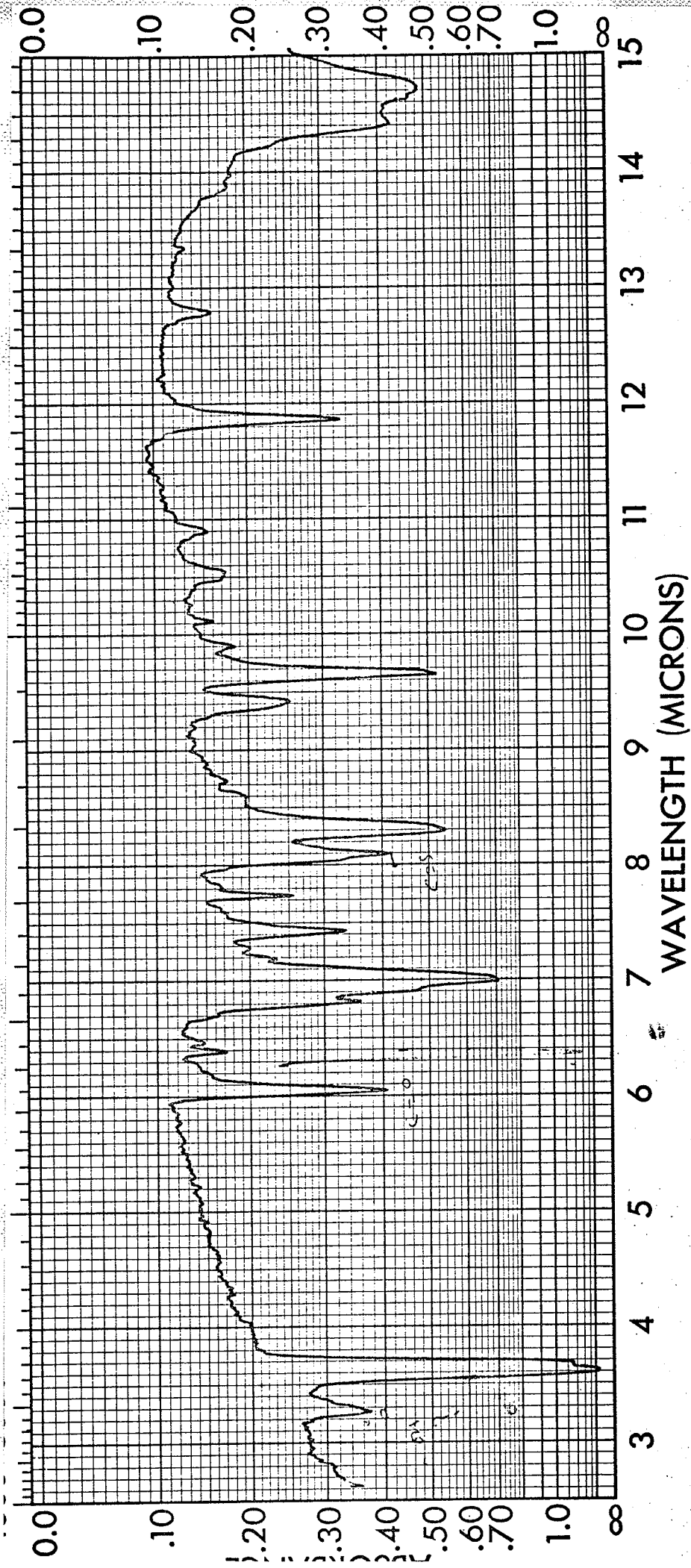


5-Phenyl-1,2,4-dithiazole-3-one
(Ether soluble component of 5-phenyl-1,2,4-dithiazole-3-thione
chlorination product)

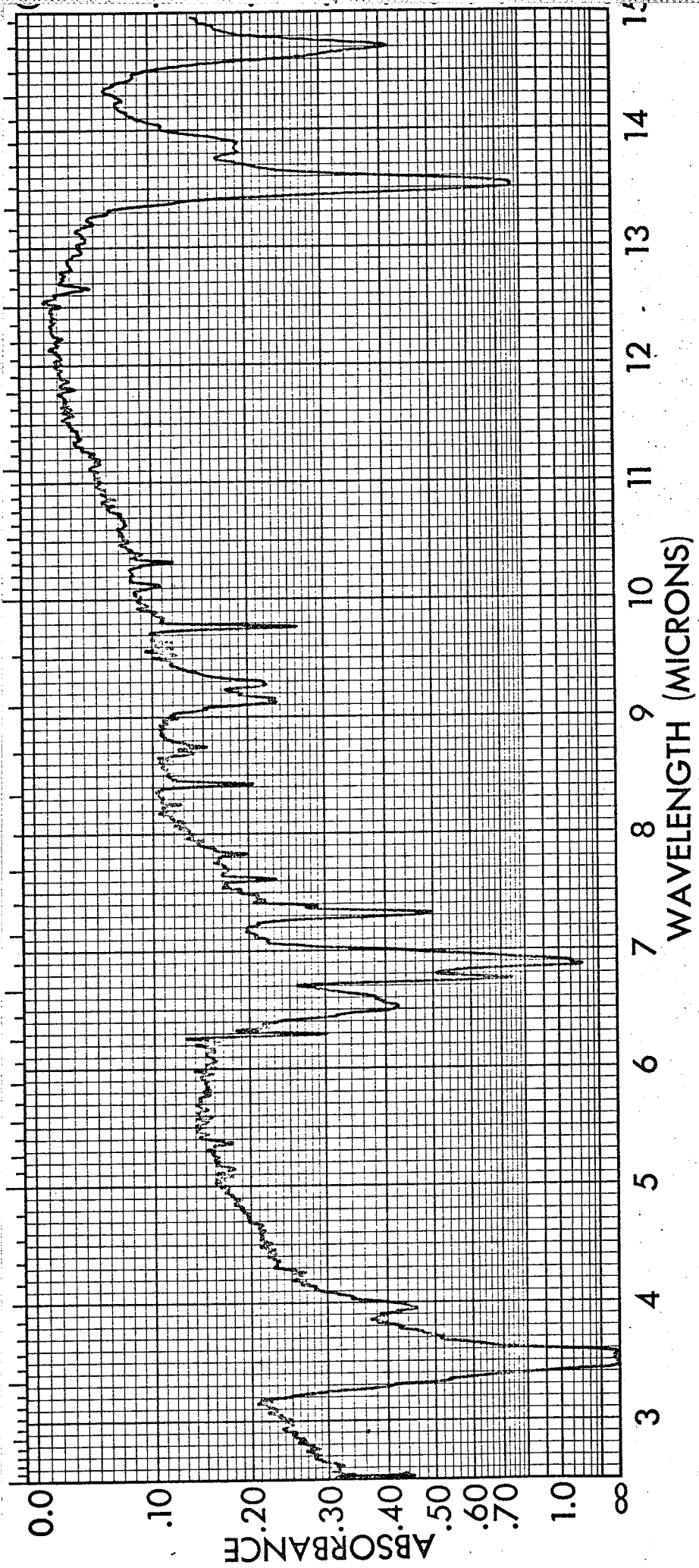


5-phenyl-1,2,4-dithiazole-3-one

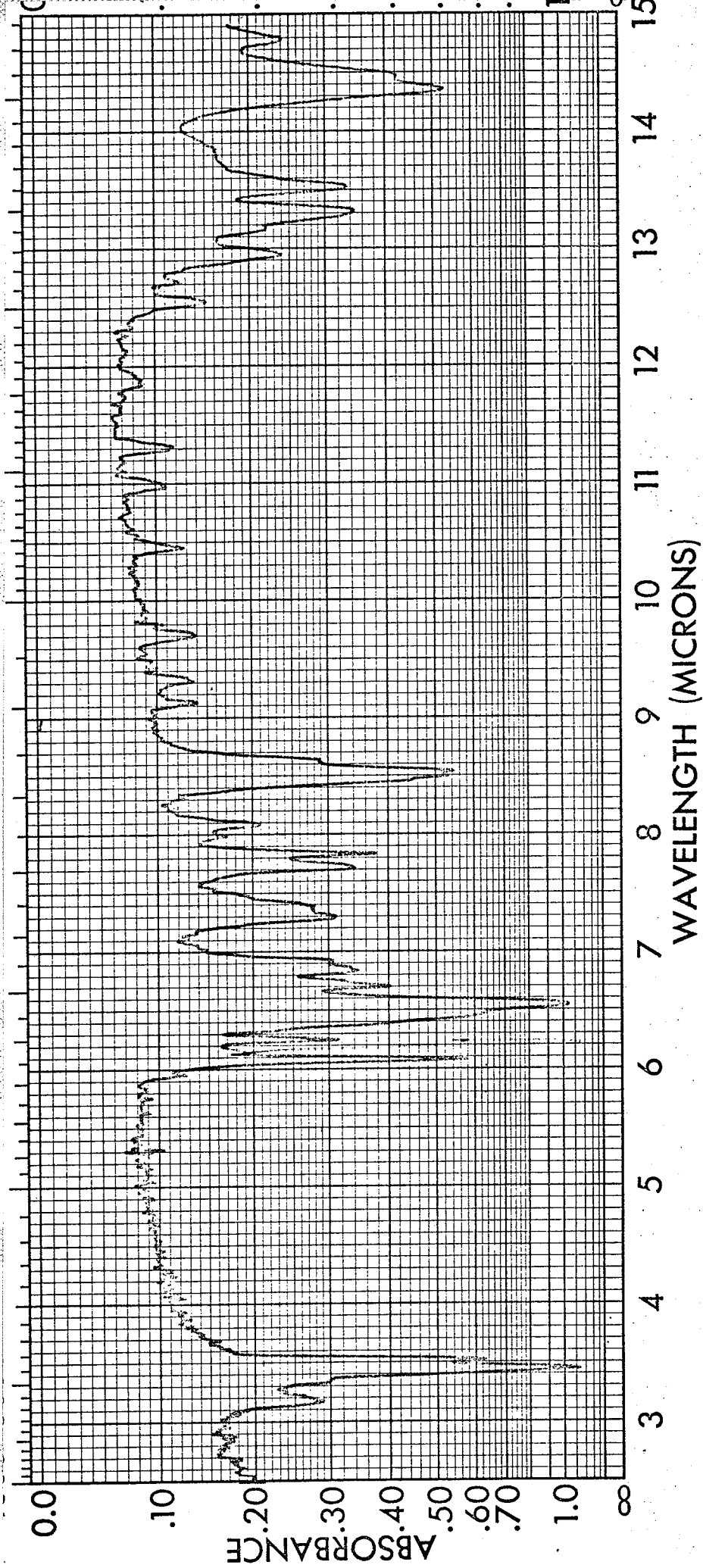
(Hydrogen peroxide oxidation product of 5-phenyl-1,2,4-dithiazole-3-thione)



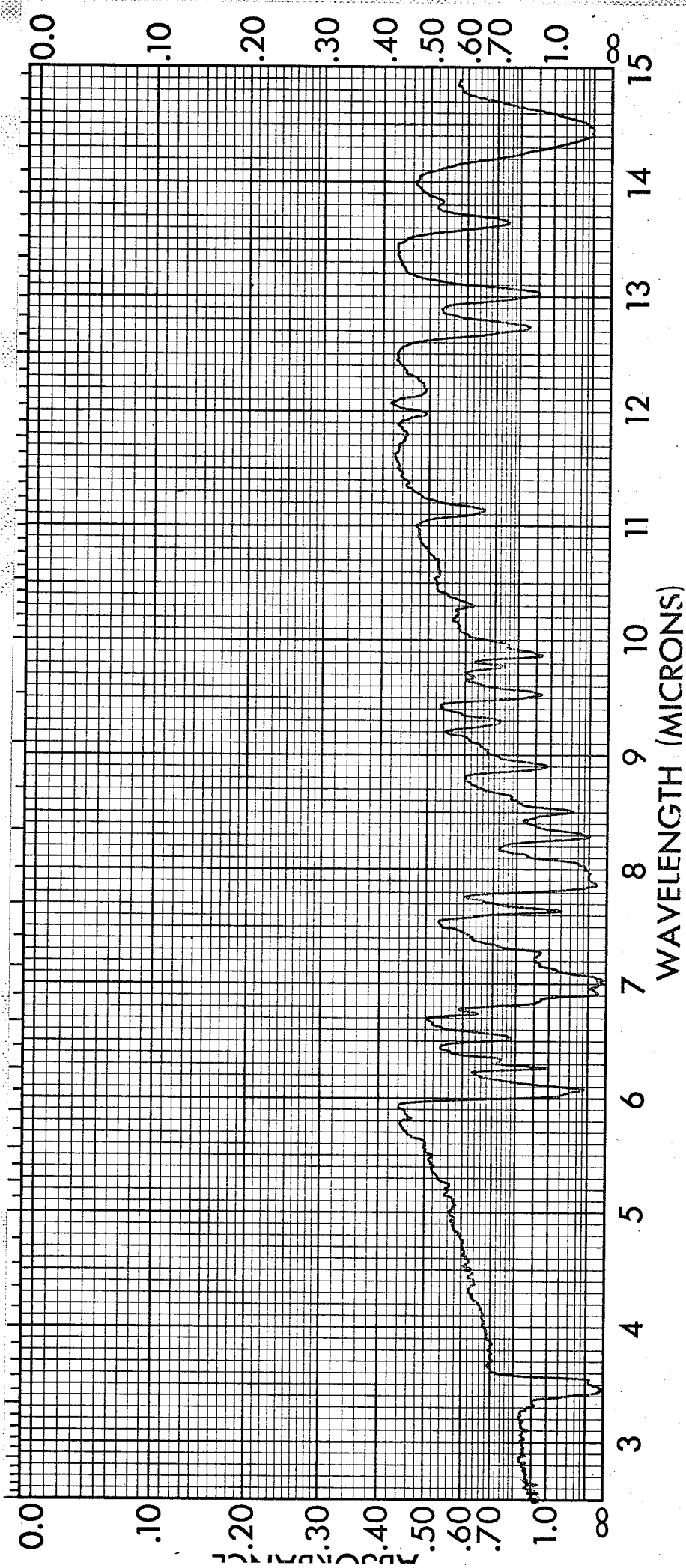
Reaction product of 5-phenyl-3-methylthio-1,2,4-dithiazolium iodide
and sodium benzoacetate
(recrystallized from ethanol, m.pt. 128-9°C)



N-methyl, anilinium iodide

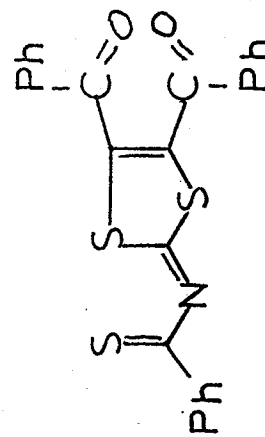


Second component of the product obtained when
5-phenyl-3-methylthio-1,2,4-dithiazolium iodide and aniline were
reacted in ethanol. (First component was N-methyl anilinium iodide)

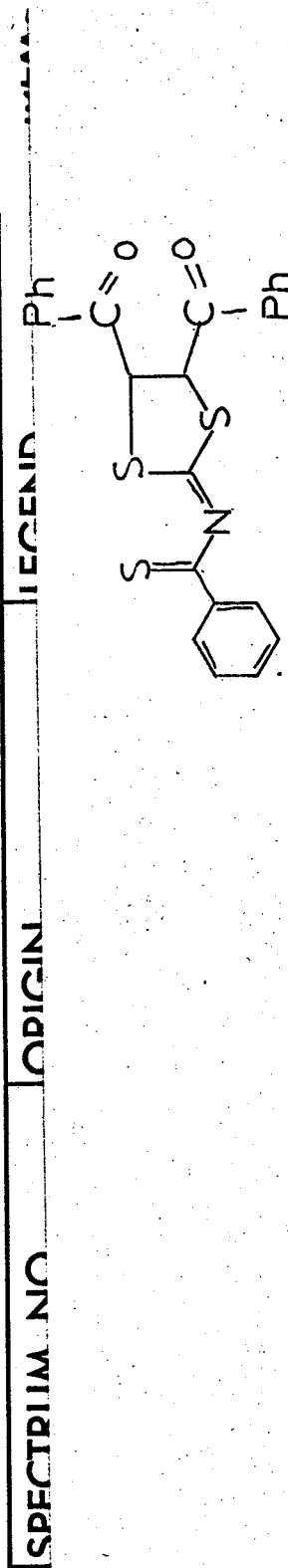
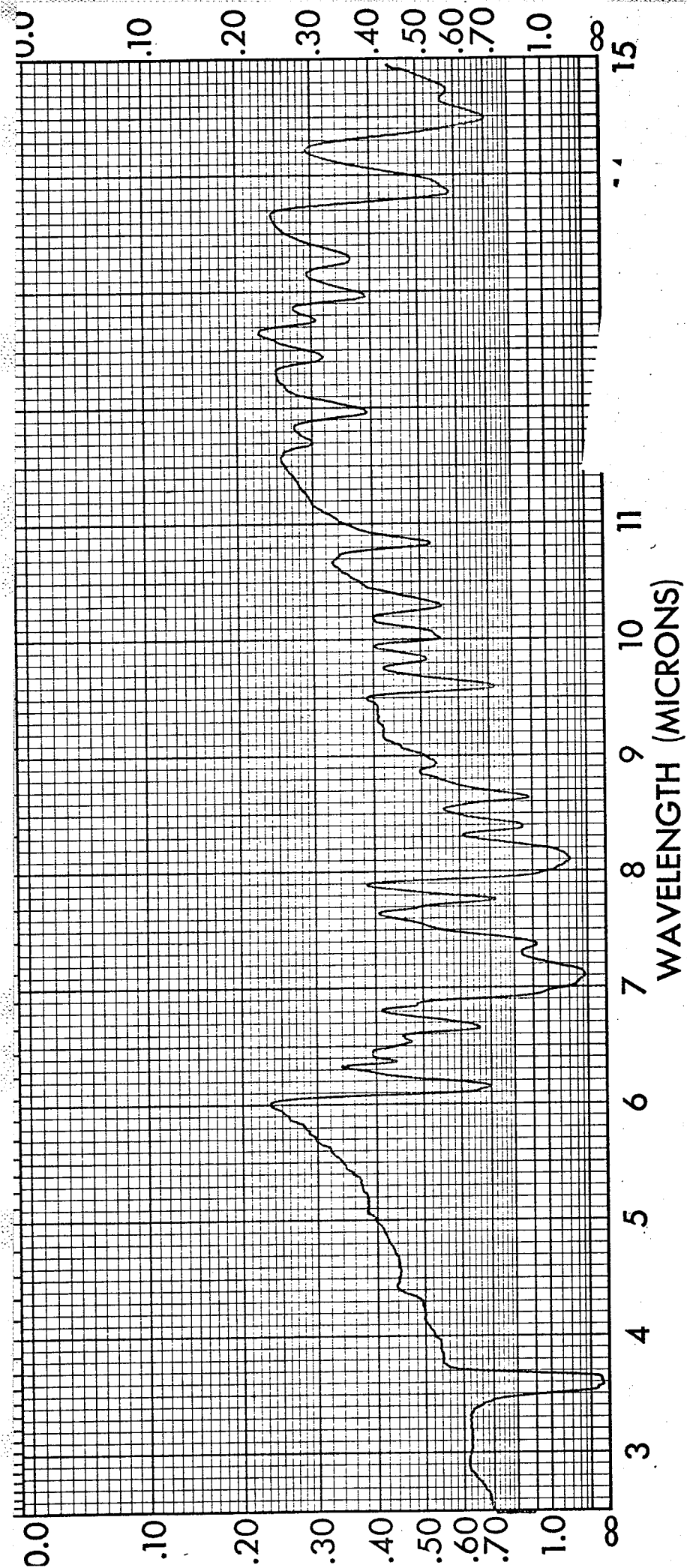


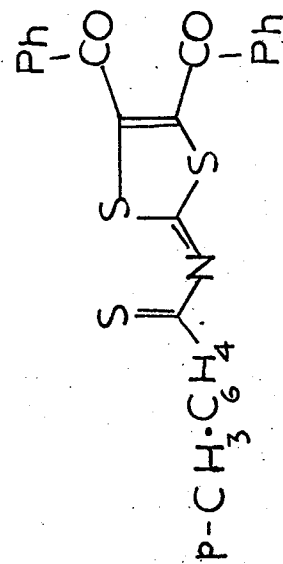
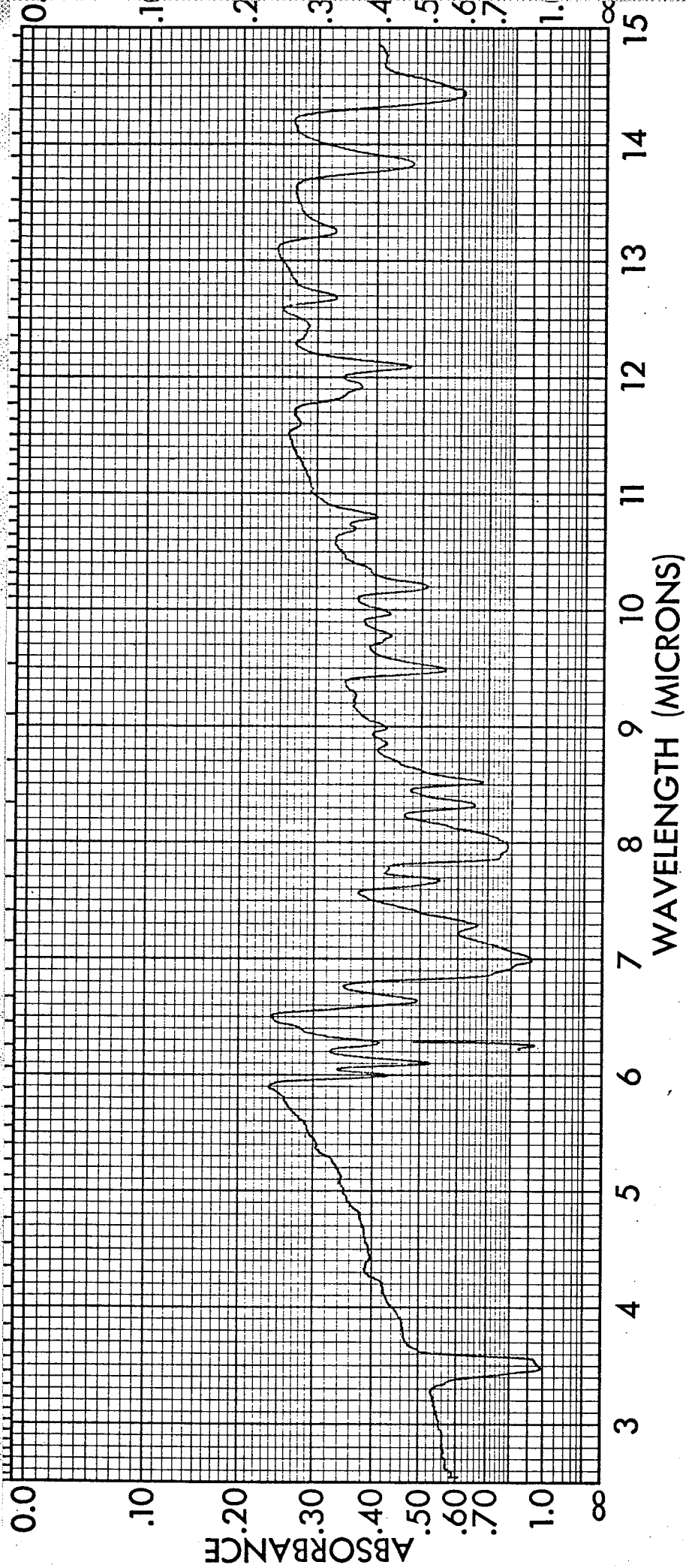
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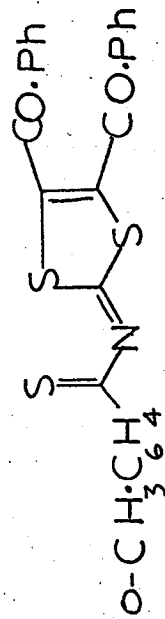
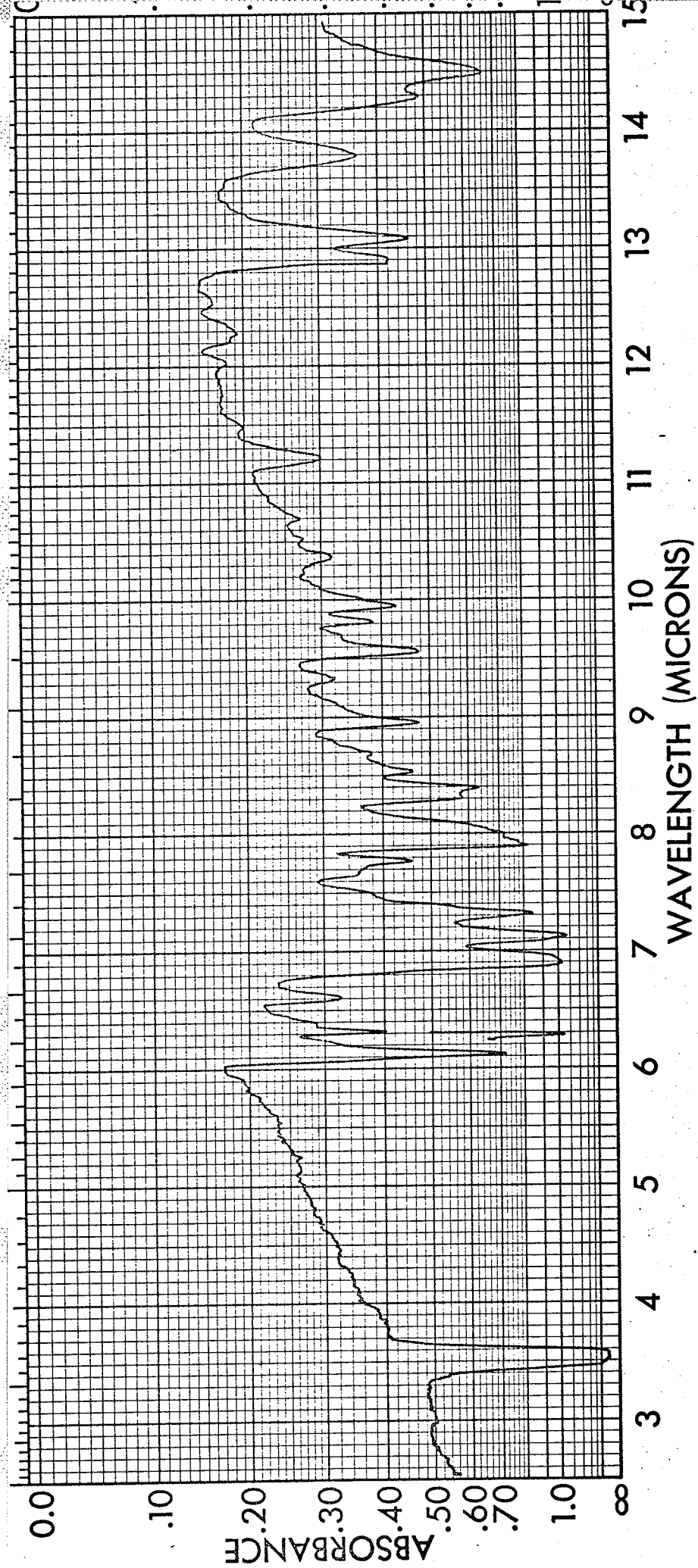


2-thiobenzoylimino-4,5-dibenzoyl-1,3-dithiole
(recrystallized from EtOH-C₆H₆ mix.)

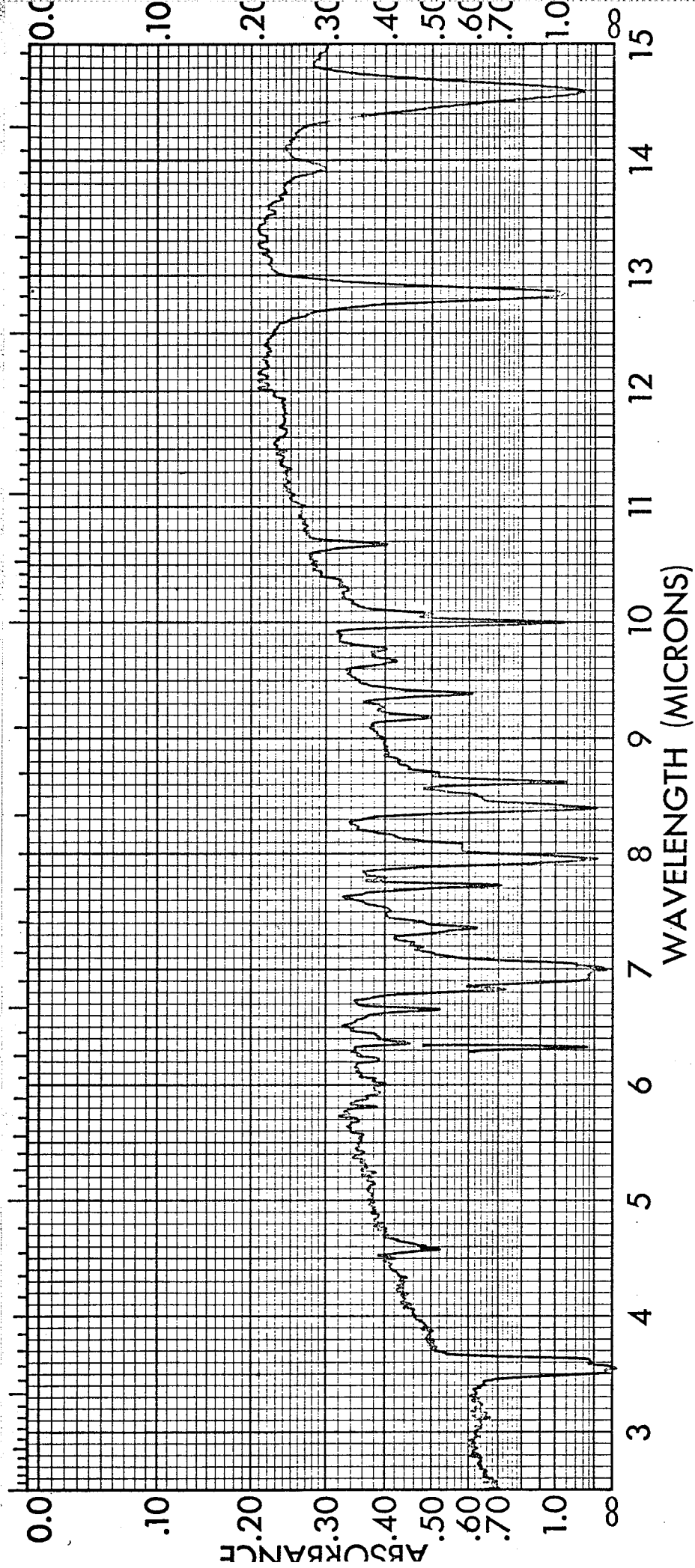




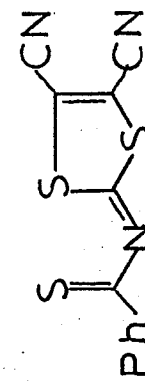
2-(thio-p-toluylyl)imino-4,5-dibenzoyl-1,3-dithiole



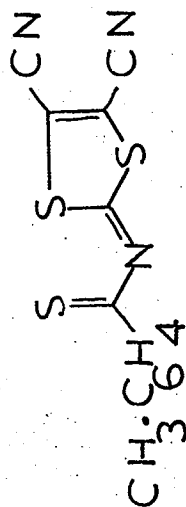
2-(o-thiophenylimino)-4,5-dibenzoyl-1,3-dithiole



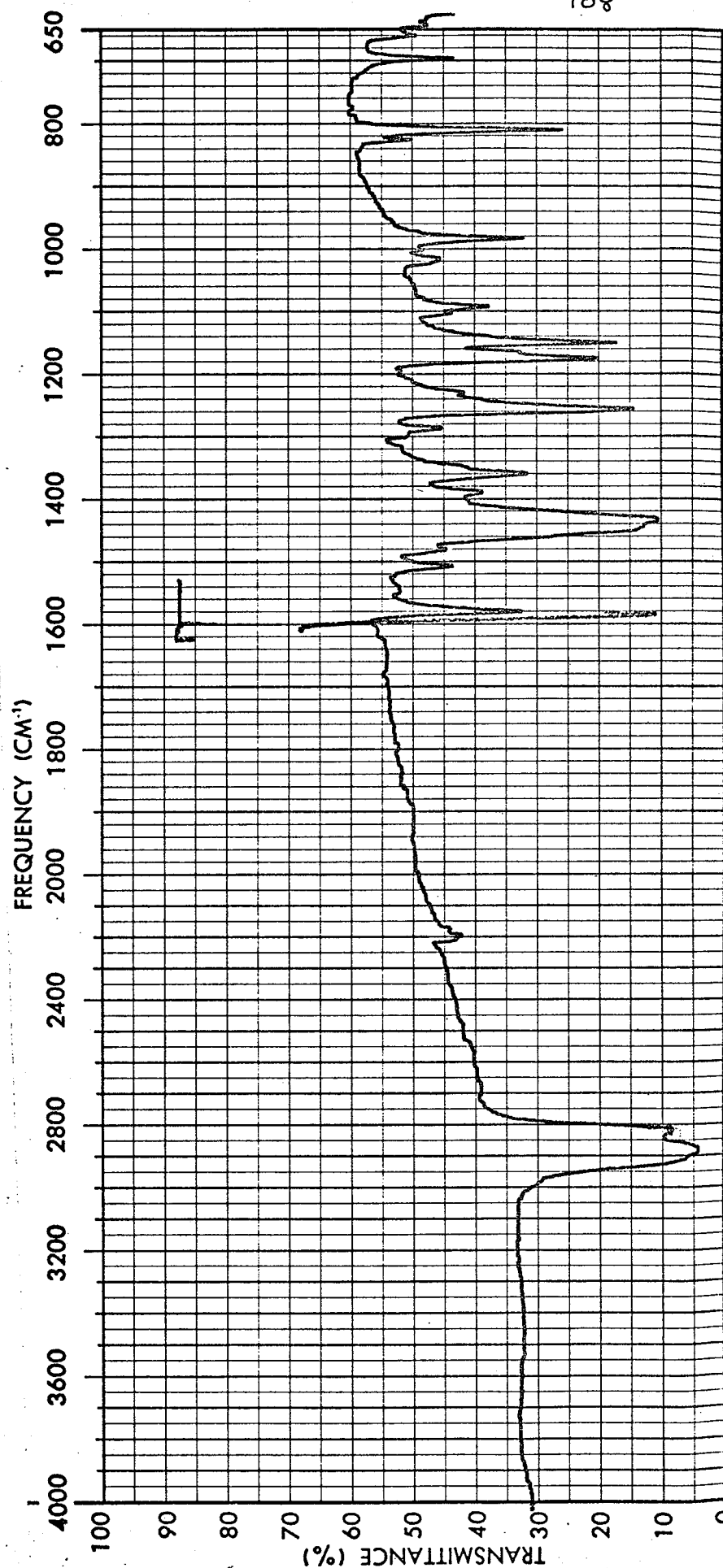
REMARKS

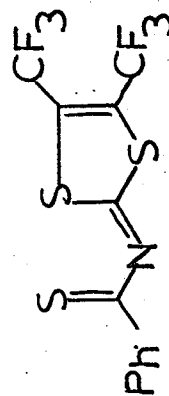
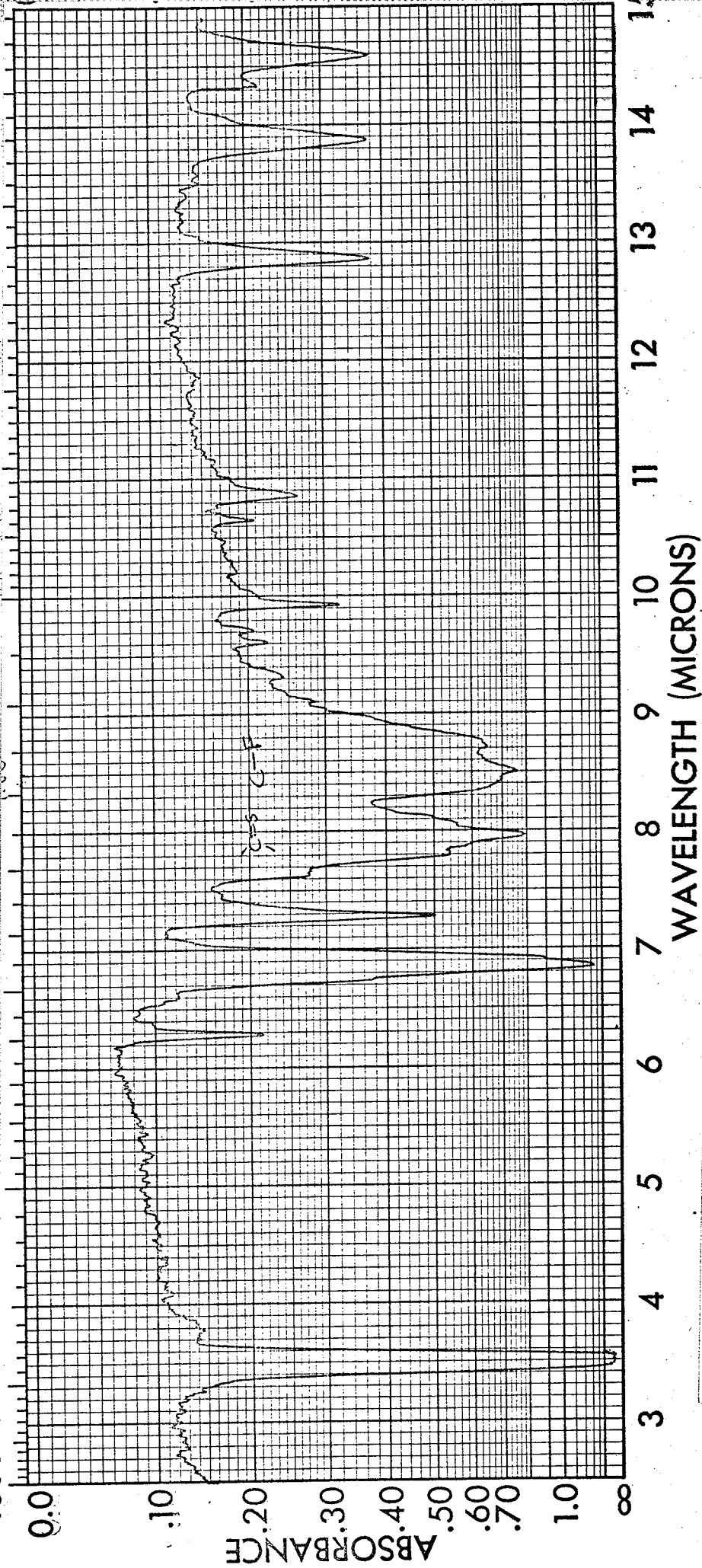


2-thiobenzoylimino-4,5-dicyano-1,3-dithiole

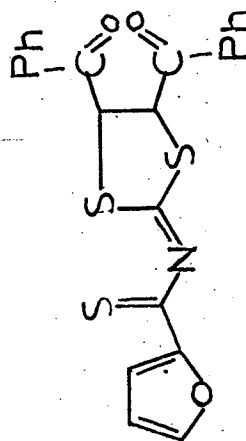
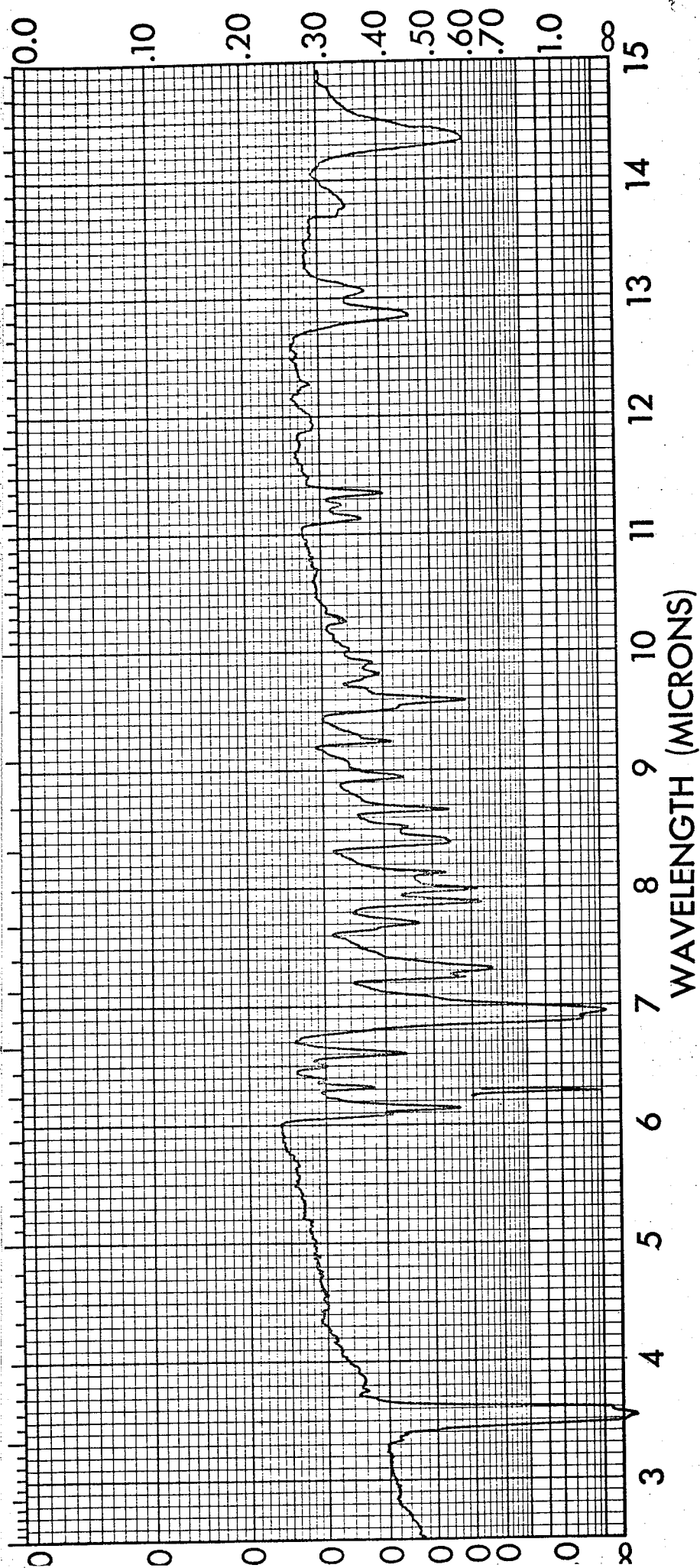


2-thio-(p-toluy1)-imino-4,5-dicyano-1,3-dithiole

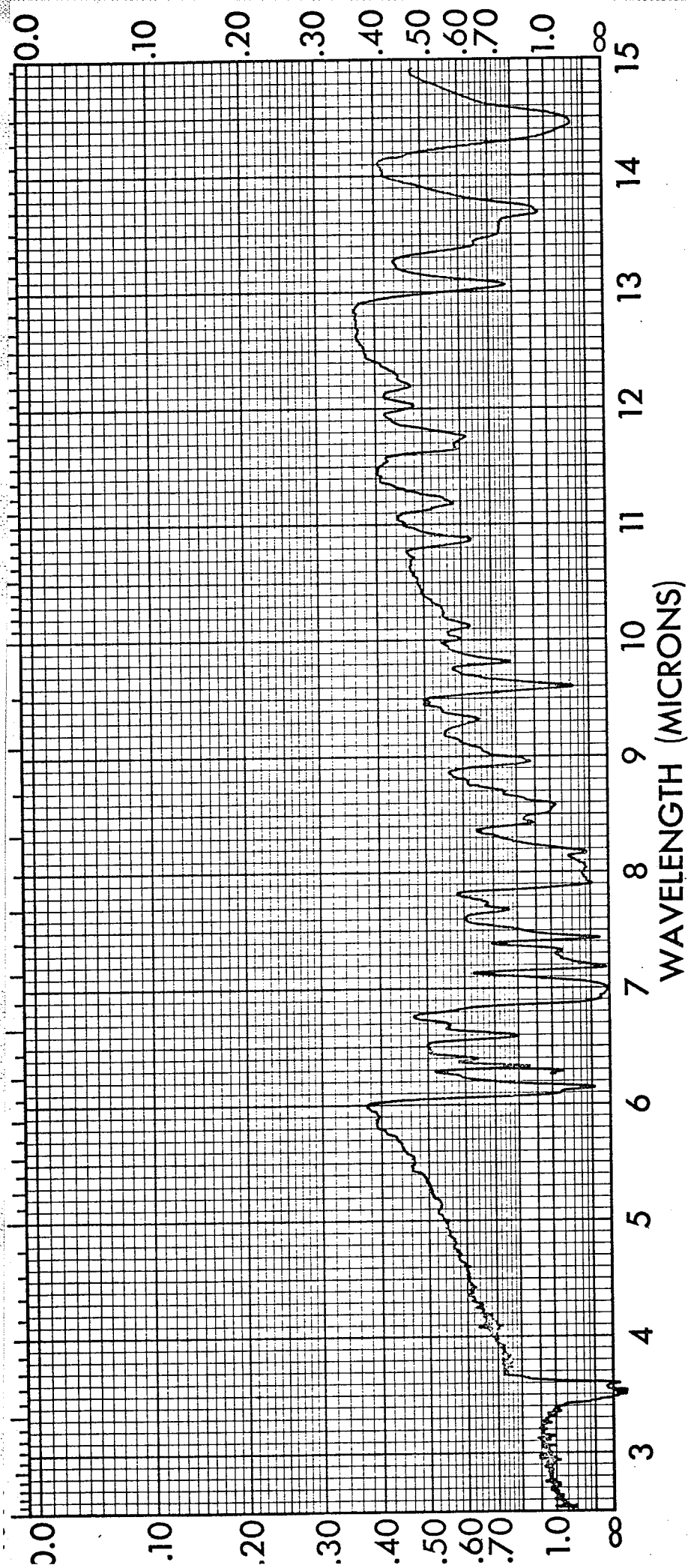




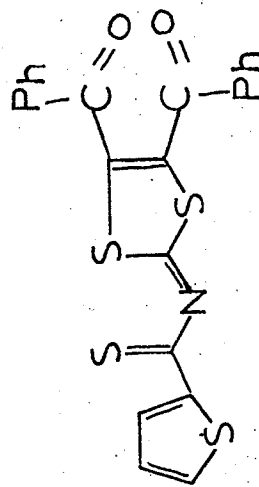
2-thiobenzoylimino-4,5-bis(trifluoromethyl)-1,3-dithiole



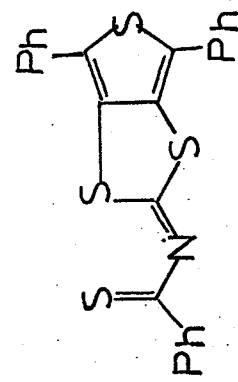
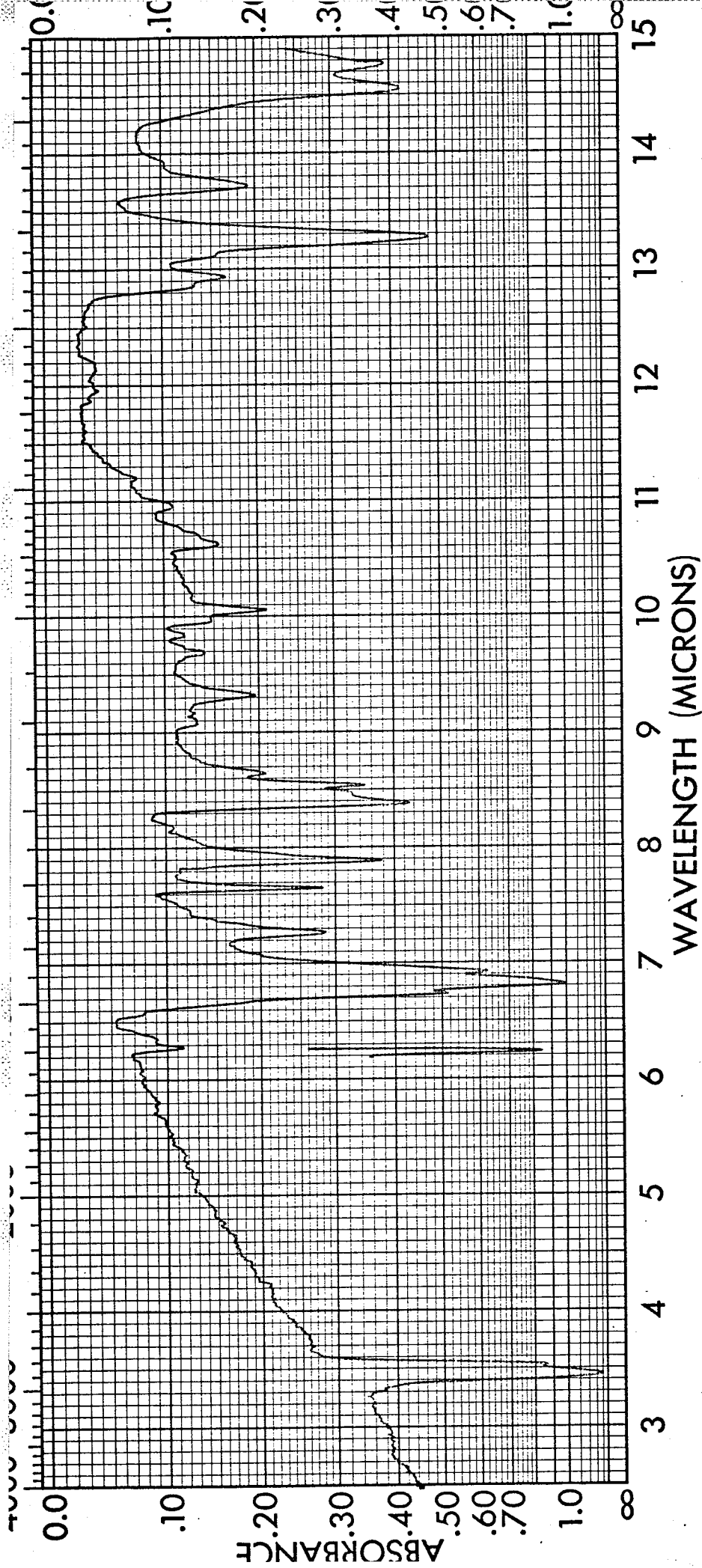
2-(2-thiofuroylimino)-4,5-dibenzoyl-1,3-dithiole



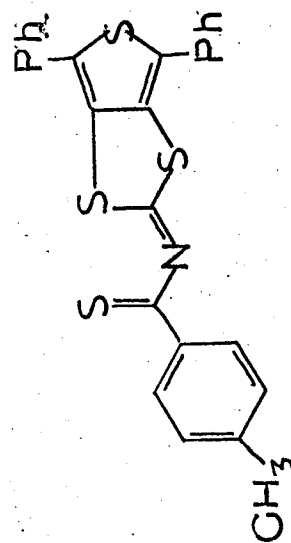
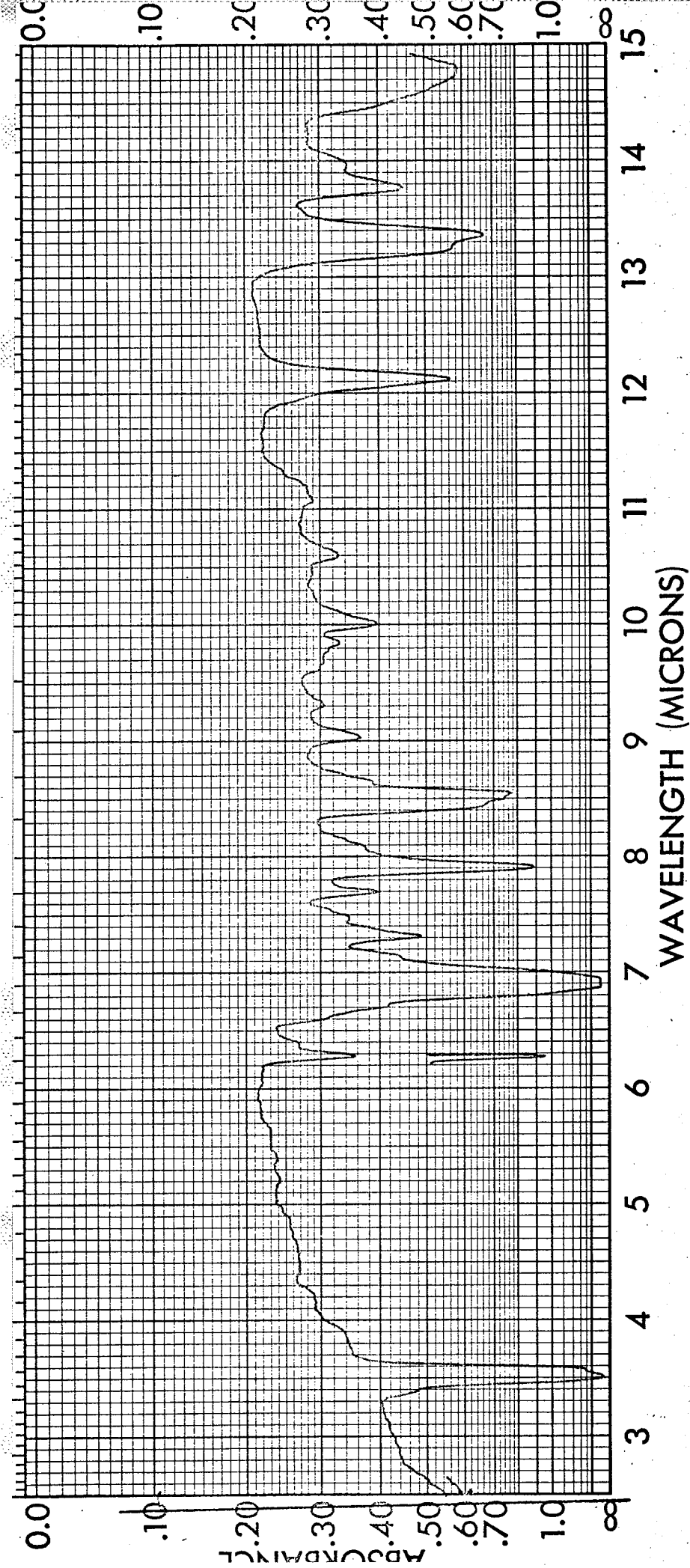
TECHNICAL SERVICES



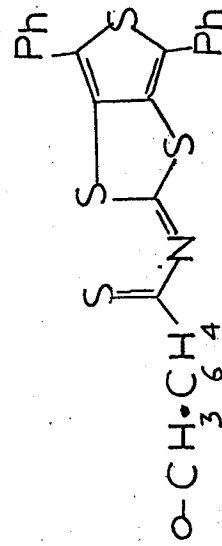
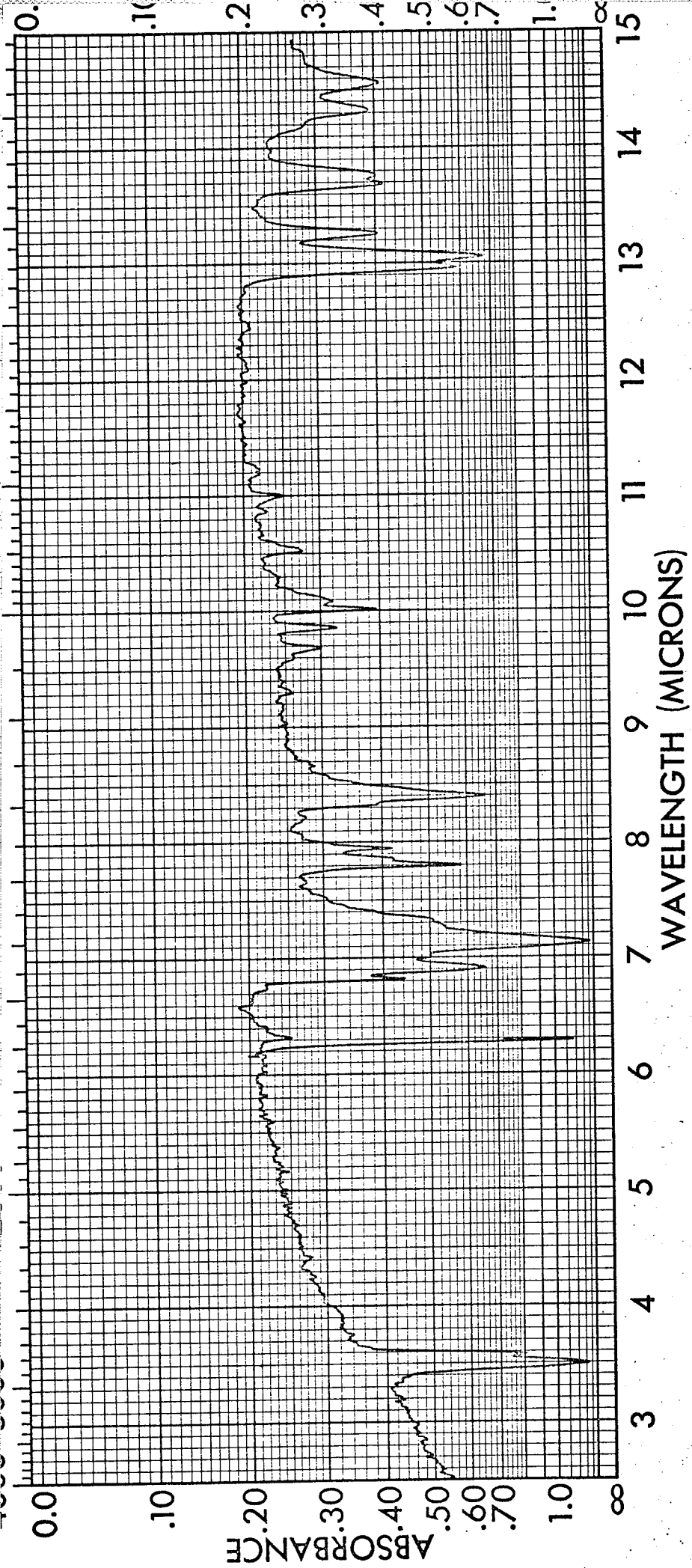
2-(2 thiothienylimino)-4,5-dibenzoyl-1,3-dithiole



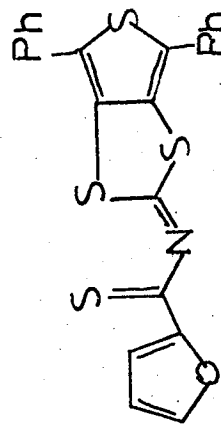
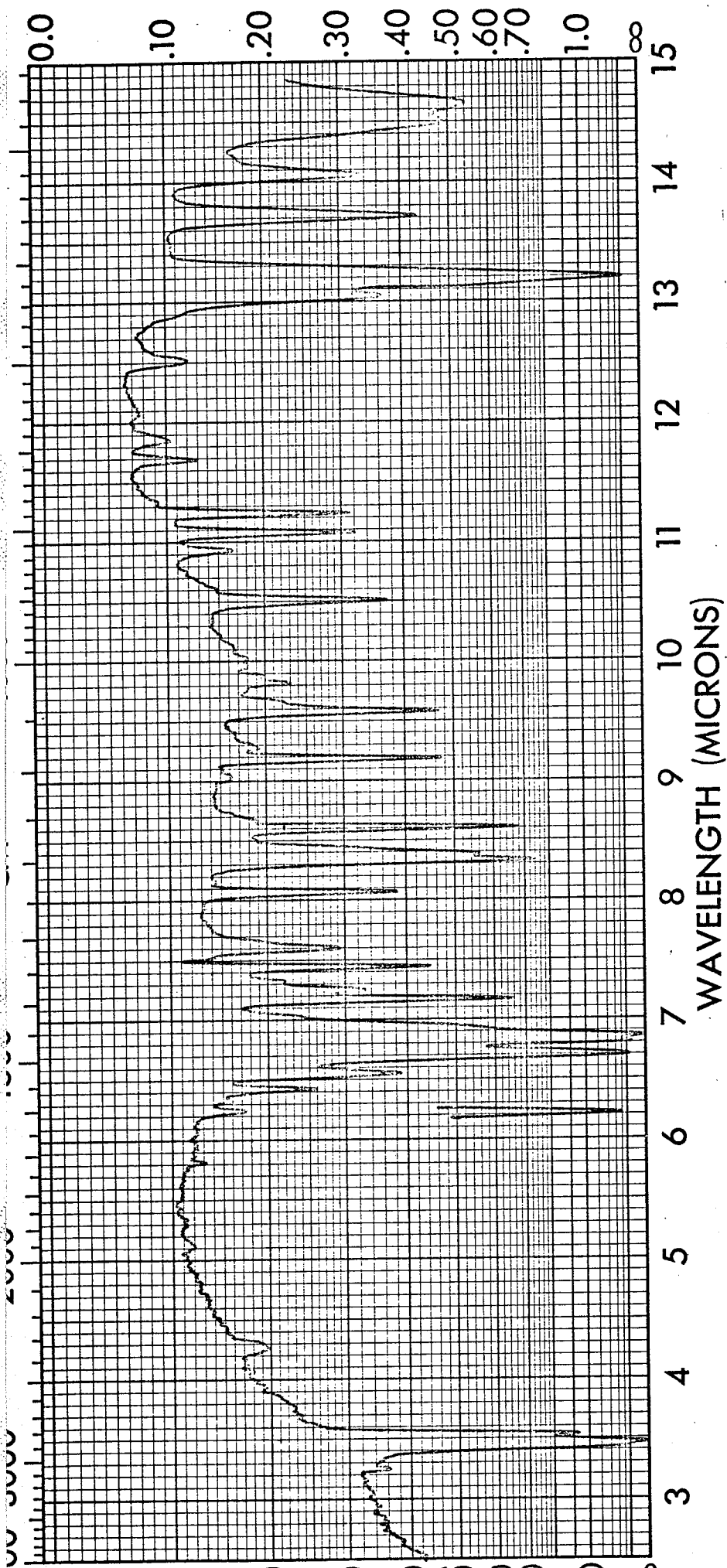
2,5-diphenylthieno-(3,4-d)-2-thiobenzamino-1,3-dithiole



2,5-diphenylthieno-(3,4-d)-2-(thio-p-tolyl)imino-1,3-dithiole



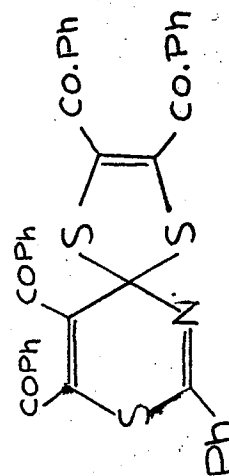
2,5-diphenyl thieno-(3,4-d)-2-(o-thiotoluylimino)-1,3-dithiole



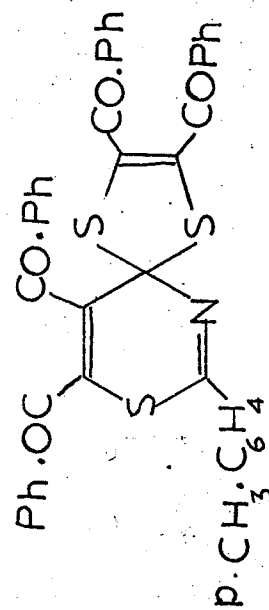
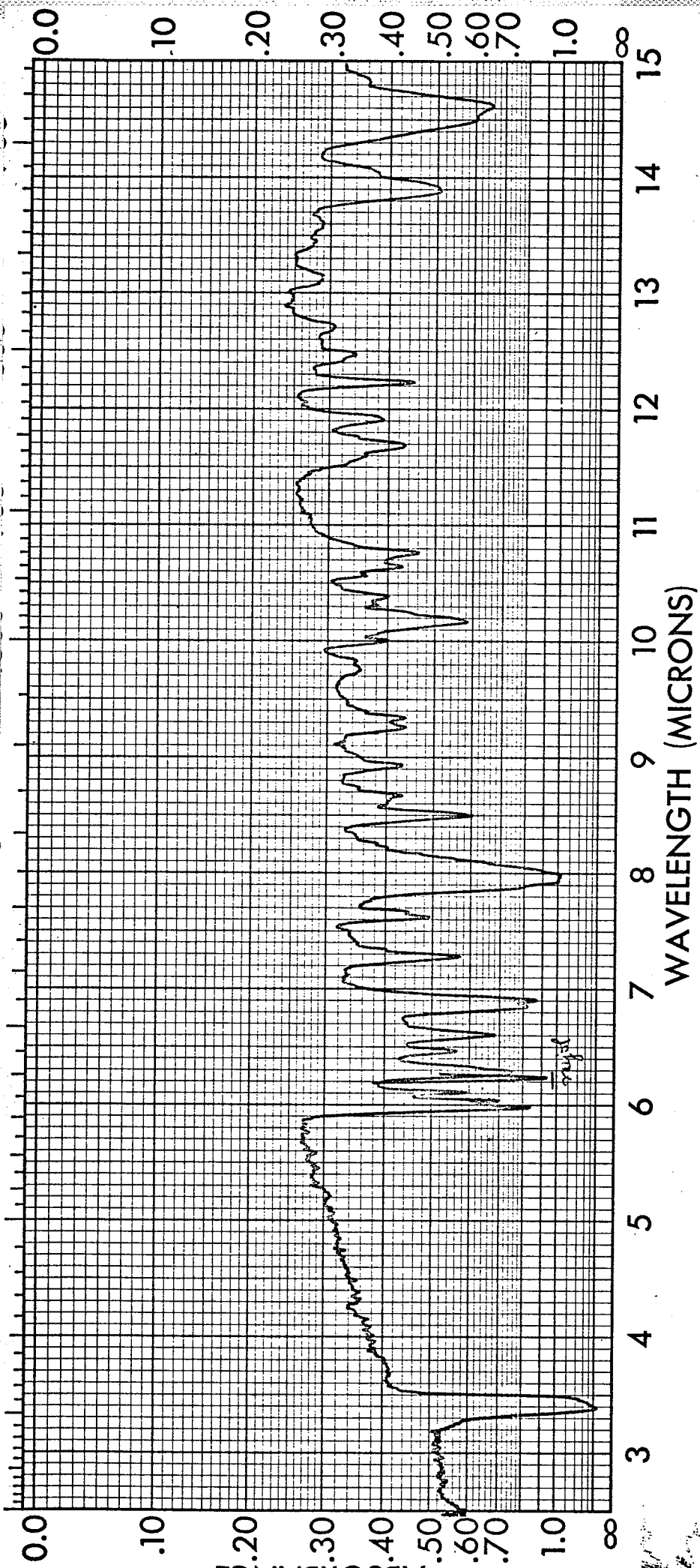
2,5-diphenylthieno-(3,4-d)-2-(2-thiofuroylimino)-1,3-dithiole

ABSORBANCE

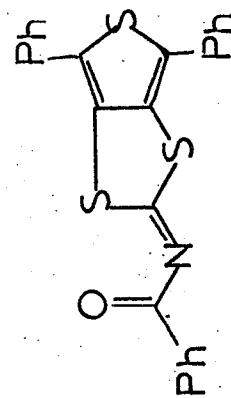
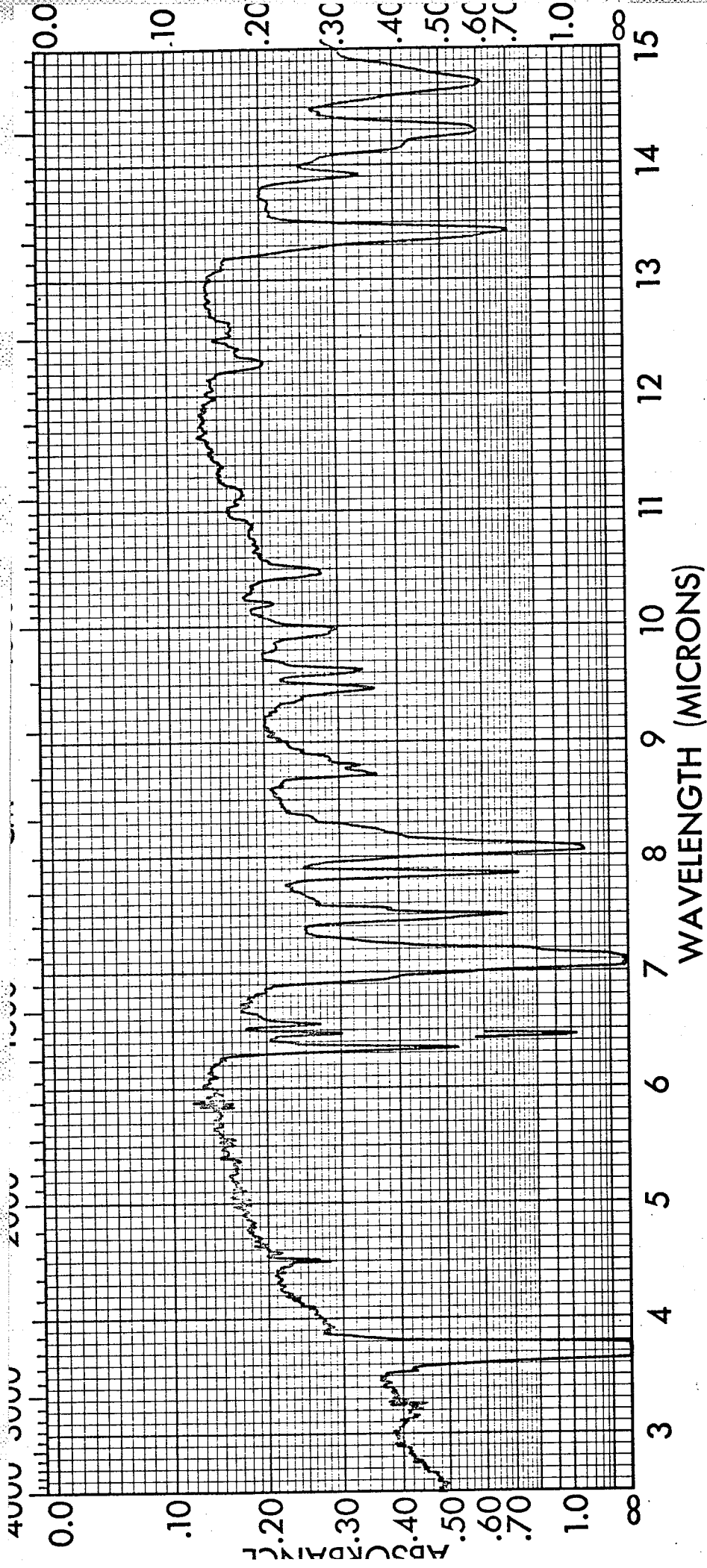
WAVELENGTH (MICRONS)



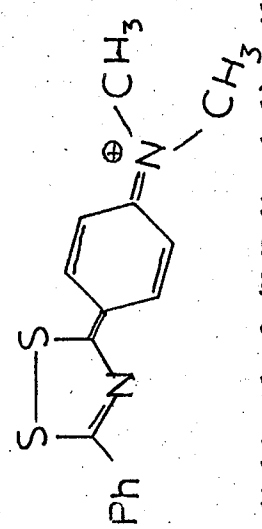
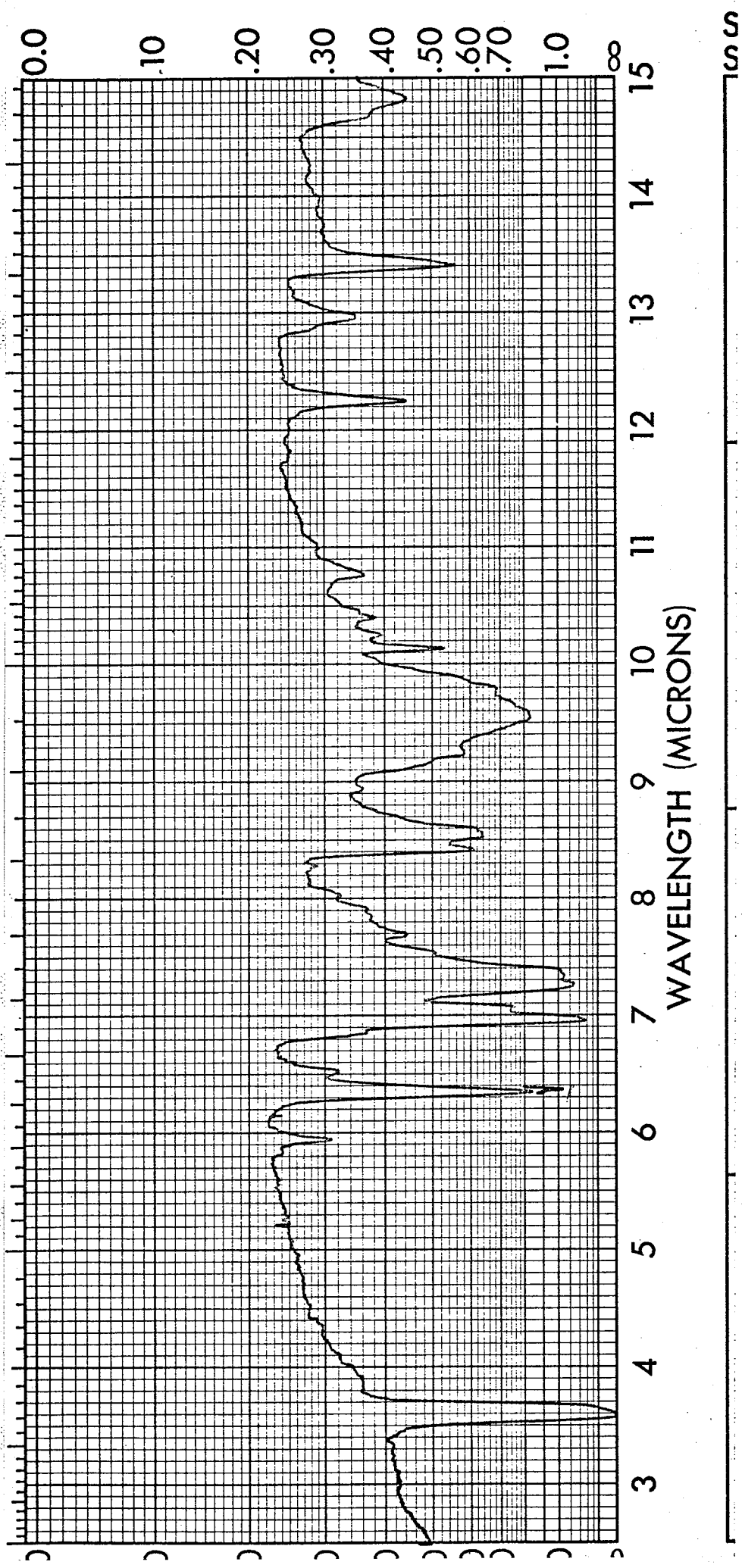
4,5-dibenzoyl-1,3-dithiole-2-spiro-4-(5',6'-dibenzoyl)-2'-phenyl-1,3-thiazine



4,5-dibenzoyl-1,3-dithiole-2-spiro-4-(5'-6'-dibenzoyl)-
2'-p-tolyl-1,3-thiazine



2,5-diphenylthieno-(3,4-d)-2-benzamino-1,3-dithiole



5-phenyl-1,2,4-dithiazole-3-(N,N-dimethyl)-anilinium perchlorate

