THE SYNTHESIS AND ORIENTATION OF SOME COMPOUNDS PREPARED FROM 2 AND 3-SUBSTITUTED FLUORANTHENES

by

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To

Mom, Dad, and Bob

ACKNOWLEDGMENTS

The author wishes to express her appreciation to Dr. E. H. Charlesworth for his kind assistance and encouragement during the course of this work.

Grateful acknowledgments are also extended to the University of Manitoba for the Graduate Student Teaching Assistantship and for the Graduate Student Fellowship and to the National Research Council of Canada for a summer grant-in-aid of research and to Mr. C. Reichert and Dr. J. Westmore for the mass spectra and interpretations.

ABSTRACT

2-Acetamidofluoranthene has been shown to undergo nitration in position 3. It was proved that 3-nitrofluoranthene is nitrated in position 9. The theoretical implications of these results have been discussed. As a result of this work a number of new 2,3 and 3,9-disubstituted fluoranthene derivatives have been prepared, namely, 2-acetamido-3-nitrofluoranthene, 2-amino-3-nitrofluoranthene, 2-acetamido-3-aminofluoranthene, and 3,9-dinitrofluoranthene. The nitration of 2-nitrofluoranthene produced the new compound 2, ( )-dinitrofluoranthene. A discussion of mass spectral evidence for the position of the second nitro-group in this compound is given. The new compound, 3-acetamido-9-bromofluoranthene, has been prepared. A comparison of the compound, 2-acetamido-8-bromofluoranthene, prepared by Kaminska and Mazonski with that previously prepared by Blackburn, in these laboratories, has been made. It was shown that the two samples were the same.

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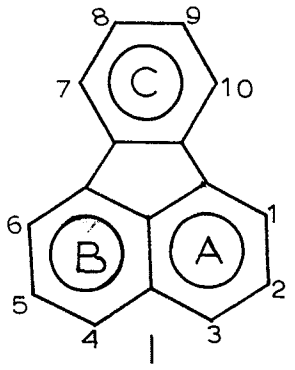
INTRODUCTION

Although the study of fluoranthene chemistry has been carried out for almost fifty years, only within the last fifteen years has research provided information about the directive properties of substituents in the fluoranthene nucleus. This was obtained principally through the study of disubstituted compounds derived from 3-monosubstituted fluoranthenes.



I

In 1955 Campbell and Keir (7) postulated that a deactivating (m-directing) group in ring A of fluoranthene would direct a second substituent to position 9, and that an activating (o-p-directing) group in this same ring would direct a second substituent to position 8. This was found to be an oversimplification since Kloetzel et al. (22) showed that 3-acetamidofluoranthene was nitrated in position 2 rather than in position 8. Charlesworth and Blackburn (8) further substantiated this view by demonstrating that 3-acetamido-and 3-aminofluoranthene were brominated in position 2.

Further study of the directive properties of substituents

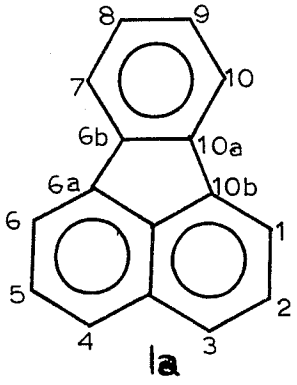
in this and other positions of the fluoranthene nucleus was required to resolve the differences which had arisen. This was partially done by Charlesworth and Dolenko (9). These workers showed that 2-aminofluoranthene was brominated in position 3 and that 2-nitrofluoranthene was brominated in position 9.

The object of the present study was the investigation of the directive properties of the nitro and acetamido groups in positions 2 and 3, under nitrating conditions.

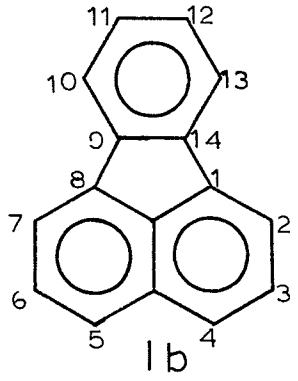
It was thought that the results of such a study would provide experimental proof that the existing orientation rules are applicable to substituents in the 2 and 3 positions which are subjected to nitration. This was also a desirable project since it afforded an opportunity for the preparation of several new 2 and 3 substituted fluoranthene derivatives.

LITERATURE SURVEY [1]

Fluoranthene is a colourless crystalline hydrocarbon of molecular formula $C_{16}H_{10}$. It was discovered independently, in 1877, by Fittig and Gebhard (13) and by Goldschmiedt (16). Fittig and Gebhard isolated fluoranthene from the high boiling fraction of coal tar, whereas Goldschmiedt discovered it after distillation and crystallization of the hydrocarbon fraction of the mercury ores of Idria. This latter hydrocarbon fraction had previously been found by Dumas (11) and Laurent (23). Very little was known of the structure of fluoranthene until 1929 when von Braun and Anton (2) synthesized the hydrocarbon from ethyl 9-fluorenecarboxylate and β-chloroethylpropionate. Thus they proved its structure to be as shown below.



Ia



Ib

The numbering system in formula Ia is that used in Chemical Abstracts and that which will be used throughout this thesis. The numbering system in Ib is in accordance with the Richter system of notation and it is employed by most European chemists.

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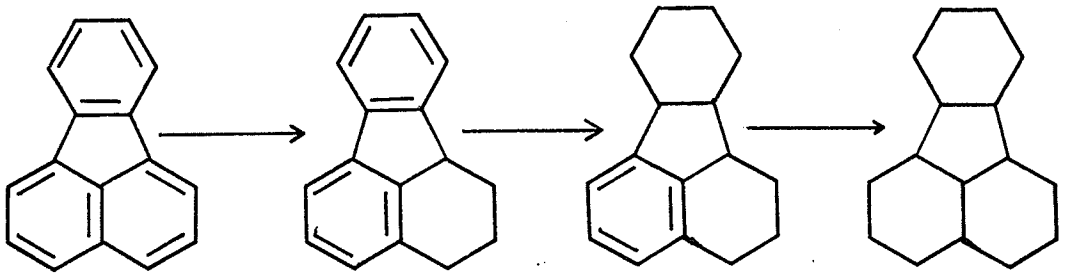
[1] For an excellent review of the chemistry of fluoranthene up to 1951 see reference (26).

Reduction of Fluoranthene

Although Goldschmiedt (17) prepared hydrogenated derivatives of fluoranthene in 1880, he was not able to characterize the products.

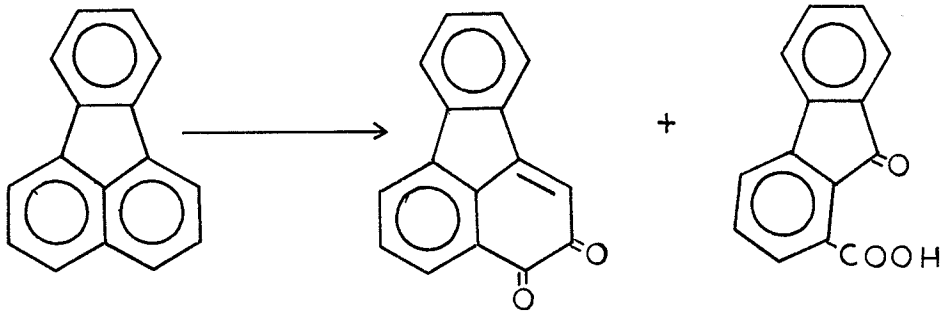
In 1930, von Braun and Manz (3) investigated the products of reduction of fluoranthene. They reported that treatment of the hydrocarbon with sodium amalgam and alcohol or phosphorous and hydriodic acid below 180°C produced an almost quantitative yield of 1,2,3,10b-tetrahydrofluoranthene. Above 200°C, they obtained an inseparable mixture of products.

Catalytic hydrogenation of fluoranthene using 20% palladium-charcoal as catalyst initially gave 1,2,3,10b-tetrahydrofluoranthene. Further hydrogenation produced 1,2,3,6b,7,8,9,10,10a,10b-decahydrofluoranthene and perhydrofluoranthene.



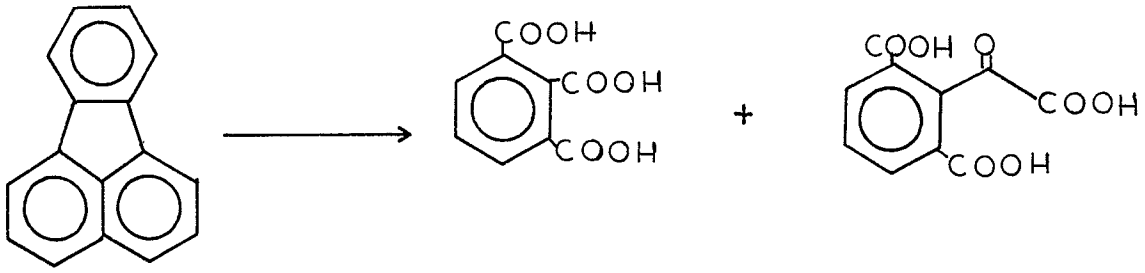
Oxidation of Fluoranthene (26)

By varying the conditions, several different products may be isolated from the oxidation of fluoranthene. Oxidation with potassium chromate in dilute sulfuric acid produces a mixture of 2,3-fluoranthenequinone and 1-fluorenonecarboxylic acid.

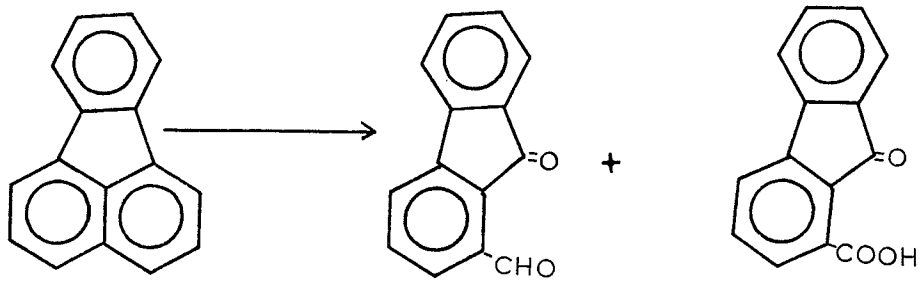


1-Fluorenonecarboxylic acid is also produced in good yield as a result of the oxidation of the hydrocarbon with chromic anhydride in acetic acid.

When fluoranthene is treated with alkaline permanganate, over an extended period, a mixture is obtained in which the principal products are hemimellitic acid and 2,6-dicarboxyphenylglyoxylic acid.



Ozonolysis in glacial acetic acid produces a mixture of 1-fluorenonealdehyde and 1-fluorenonecarboxylic acid.



Monosubstituted Derivatives of Fluoranthene

The 3-position is most readily attacked in substitution reactions. Mono-substitution occurs here, although other positions are also substituted, even under carefully controlled conditions.

The principal product from the controlled bromination of fluoranthene is 3-bromofluoranthene with 8-bromofluoranthene as a minor product. Early chlorination reactions had produced inseparable mixtures of products, however, in 1962, Sieglitz and Troester (24) isolated 3-chlorofluoranthene by passing chlorine through a solution of fluoranthene in propylene oxide at room temperature. Attempts to prepare 3-iodo and 3-fluoro-fluoranthene have produced complex mixtures of polysubstituted products.

Direct sulphonation of fluoranthene by chlorosulphonic acid in an inert solvent (26,12) yields 3-fluoranthenesulphonic acid.

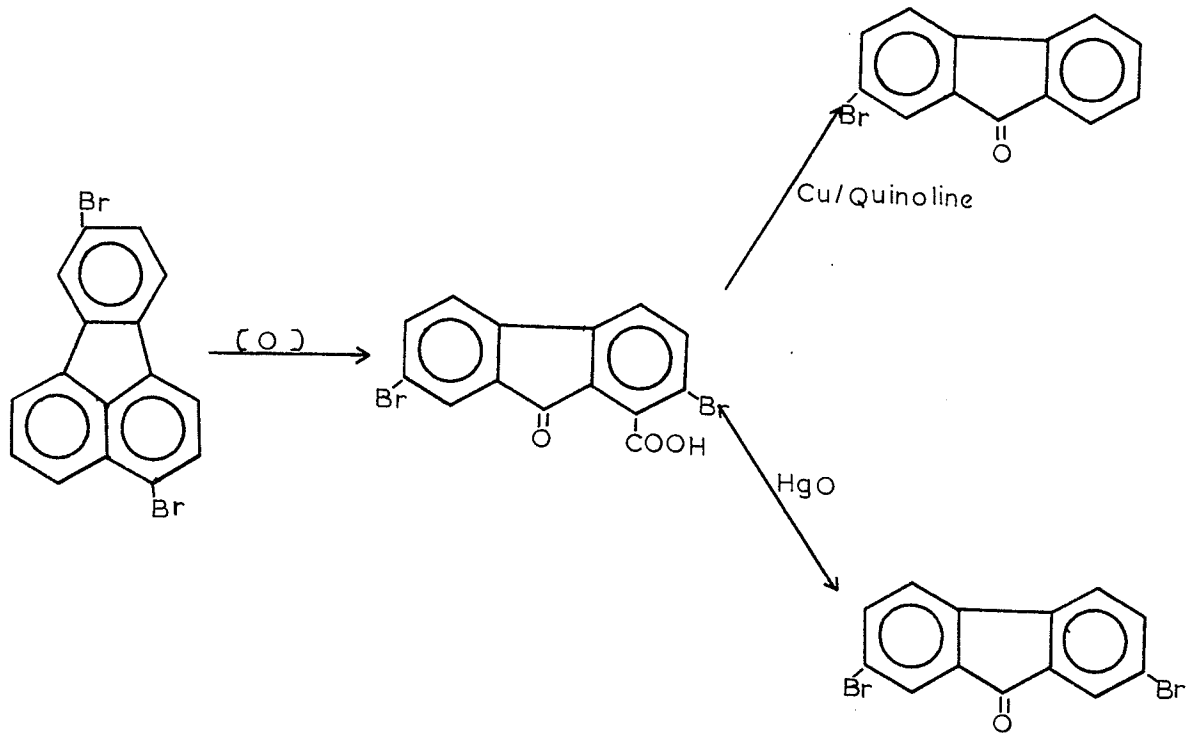
3-Nitrofluoranthene is the principal product obtained from nitration of the hydrocarbon in acetic anhydride at 0° C. or in acetic acid at 50°C. This compound is accompanied by small

amounts of the 1-, the 7-, and the 8-nitrofluoranthene (25).

Treatment of fluoranthene in a Friedel-Crafts reaction with benzoyl chloride in the presence of aluminum chloride gives a mixture 3-benzoyl and 8-benzoylfluoranthene in approximately equal quantities. Acetyl bromide in the presence of aluminum chloride in carbon disulfide acts on fluoranthene to produce a mixture of 3-acetyl, 8-acetyl, and 3,9-diacetylfluoranthene (26).

Disubstituted Derivatives of Fluoranthene

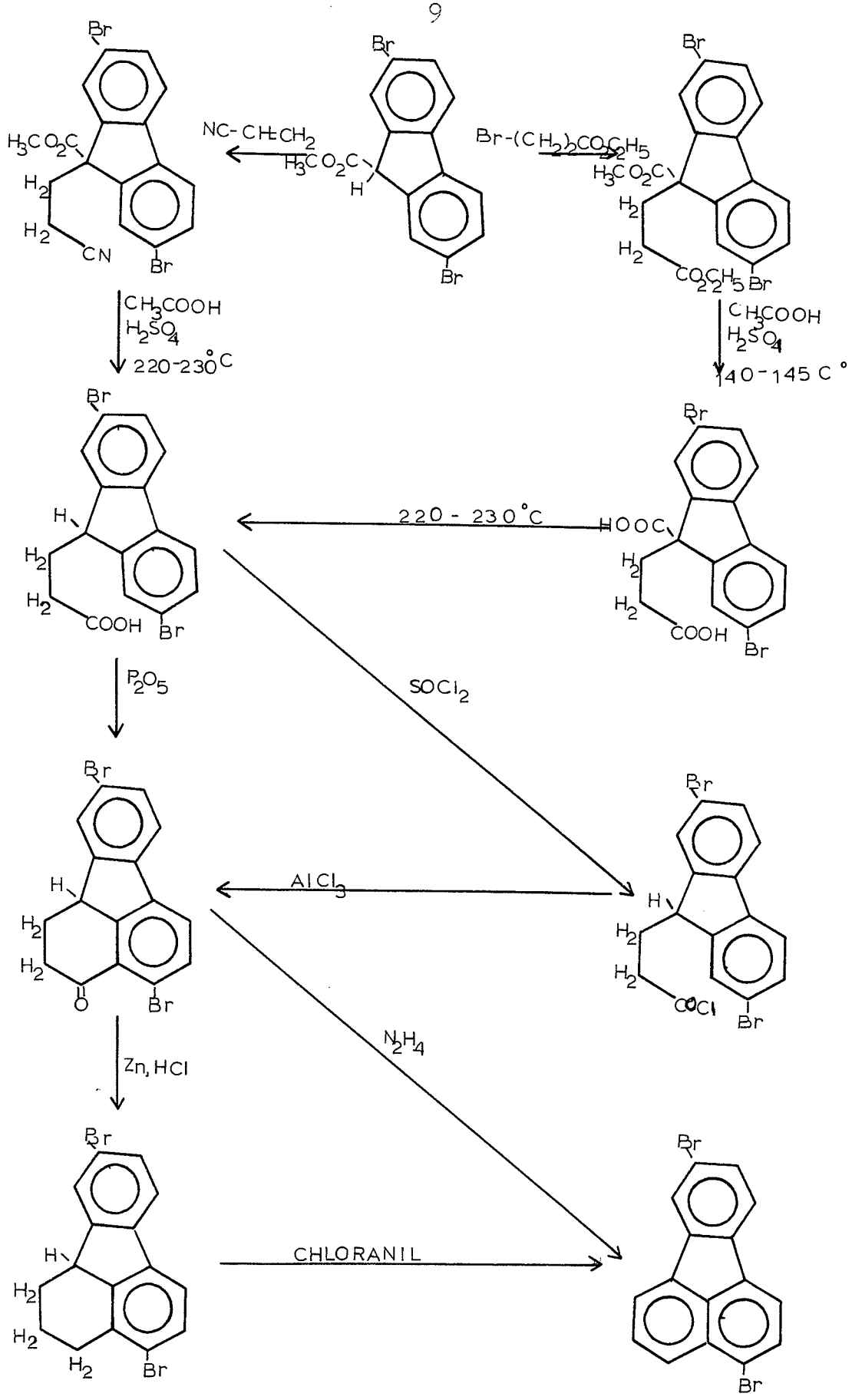
In 1950 Campbell et al. (5) proved the orientation of the bromine atoms in 3,8-dibromofluoranthene which was first prepared in 1880 by Goldschmiedt (17) by direct bromination of the hydrocarbon in nitrobenzene. Prior to 1950 no research had been carried out on disubstituted fluoranthene compounds. Campbell and his co-workers oxidized the dibromo compound with chromic acid to give dibromofluorenone-1-carboxylic acid which gave different results upon decarboxylation, depending upon the catalyst. Using copper and quinoline, they obtained 2-bromofluorenone, whereas when they used mercuric oxide at 180°C, 2,7-dibromofluorenone resulted.



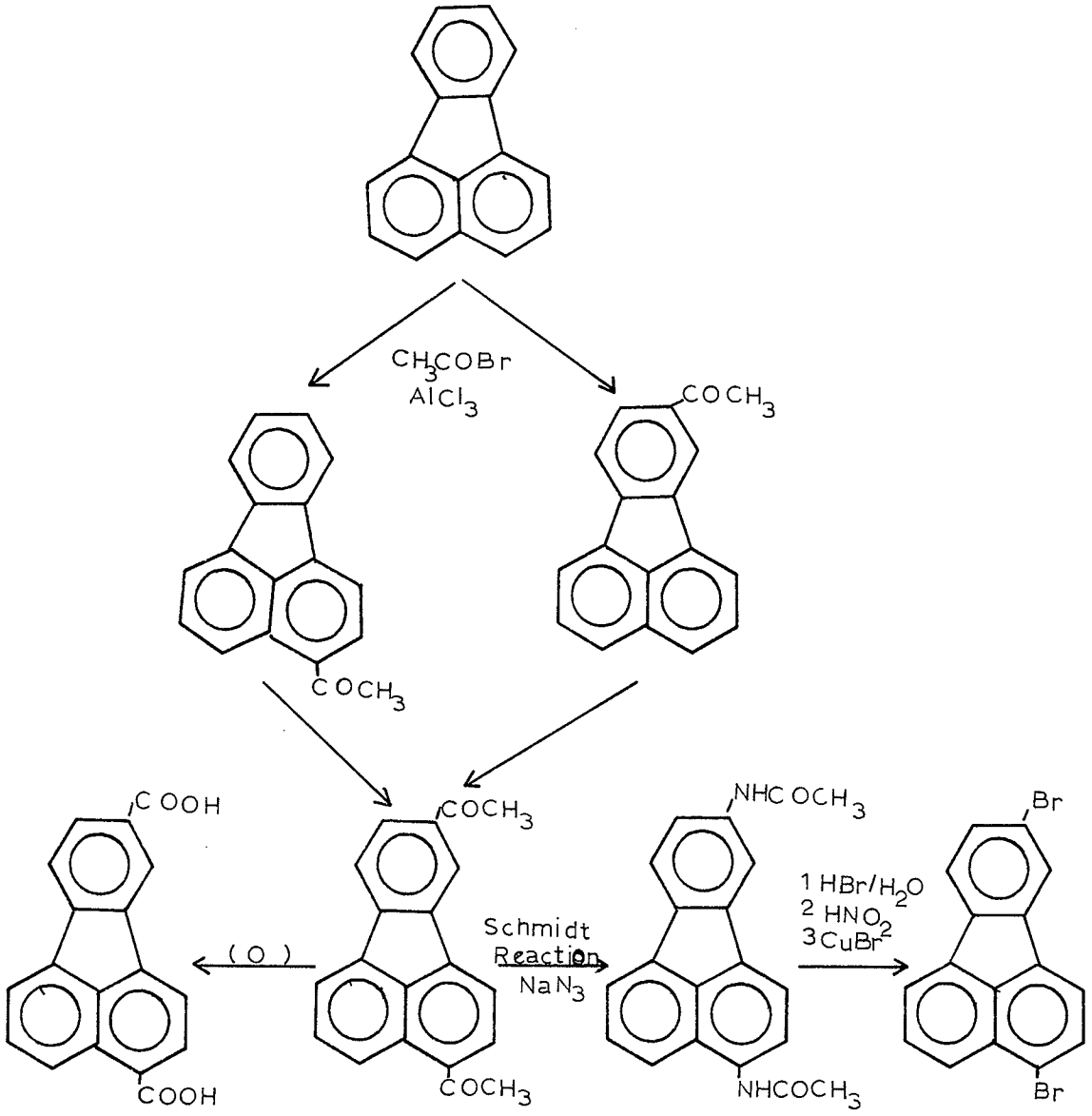
This orientation was independently proved by Holboro and Tagmann (18) who synthesized 3,8-dibromofluoranthene from methyl 2,7-dibromo-9-fluorenecarboxylate as shown on page 9 .

Most recently Kaminska and Mazonski (21) have investigated the bromination of fluoranthene with dioxane-dibromide with respect to the effect of temperature, solvent, and molar ratio of the substrates. They isolated specific percentages of the 3-bromo, 3,8-dibromo, and 3,8,9-tribromo derivatives depending on the molar ratio of the substrates.

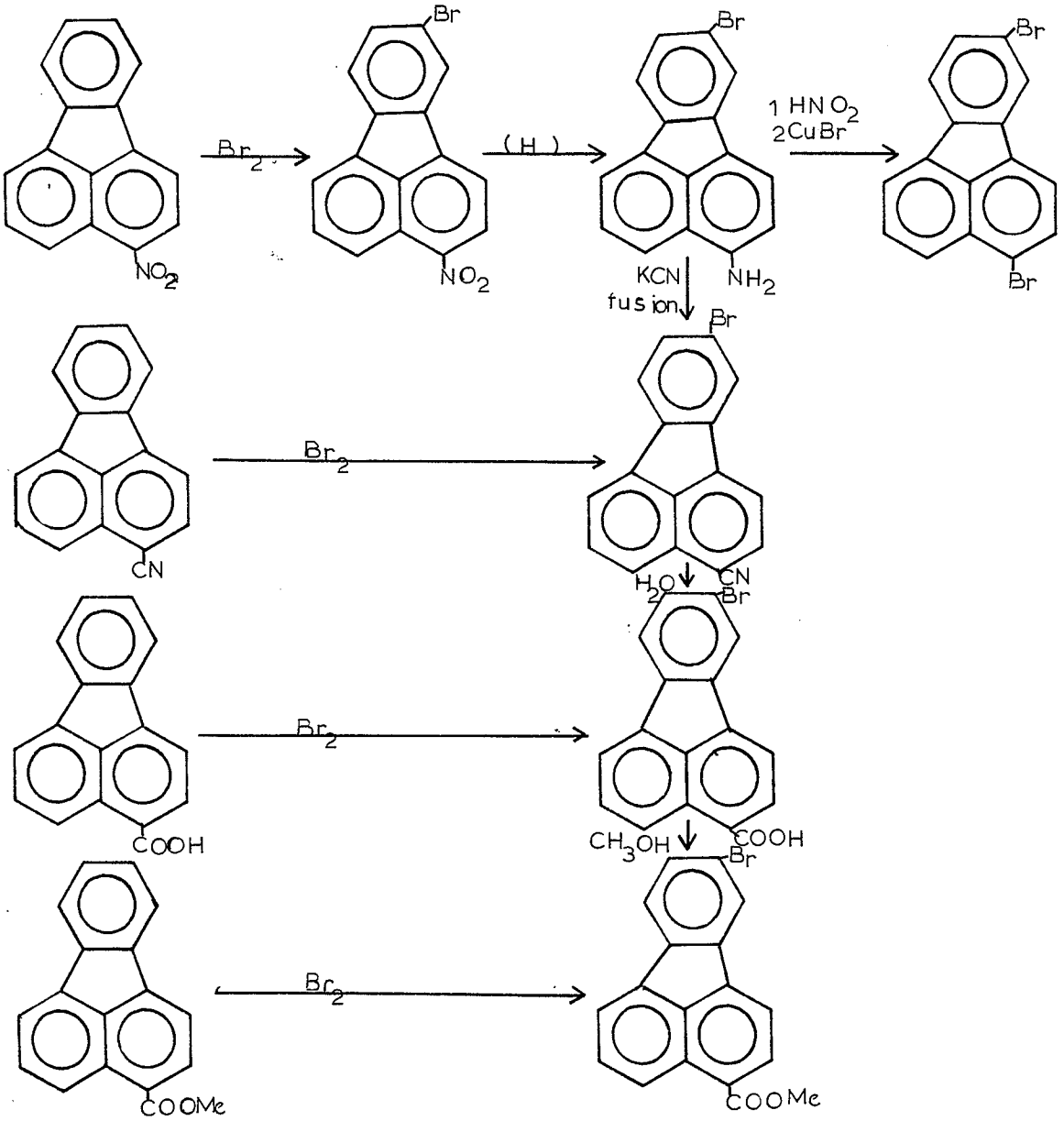
In 1951 Campbell, Leadhill, and Wilshire (6) showed that the product prepared by further acetylation of both 3-acetyl and 8-acetylfluoranthene is 3,9-diacetylfluoranthene. They proved this by oxidizing the diacetyl compound to fluoranthene-dicarboxylic acid. This compound was different from the acid


Br
H3CO2C
H2
H2
CN
NC-CH=CH2
H3CO2C
H
Br-(CH2)2CO2C2H5
CO2C2H5
CH3COOH
H2SO4
220-230°C
140-145°C
COOH
220 - 230°C
HOOC
P2O5
SOCl2
AlCl3
COCl
O
Zn, HCl
N2H4
CHLORANIL

derived from 3,8-dibromofluoranthene via the dinitrile. Further confirmation of this orientation was obtained by converting the diacetylfluoranthene into the diacetamido compound using the Schmidt reaction. They converted this diacetamido compound into a dibromofluoranthene which was found to be different from 3,8-dibromofluoranthene. They concluded that this was 3,9-dibromofluoranthene. This work is shown below.

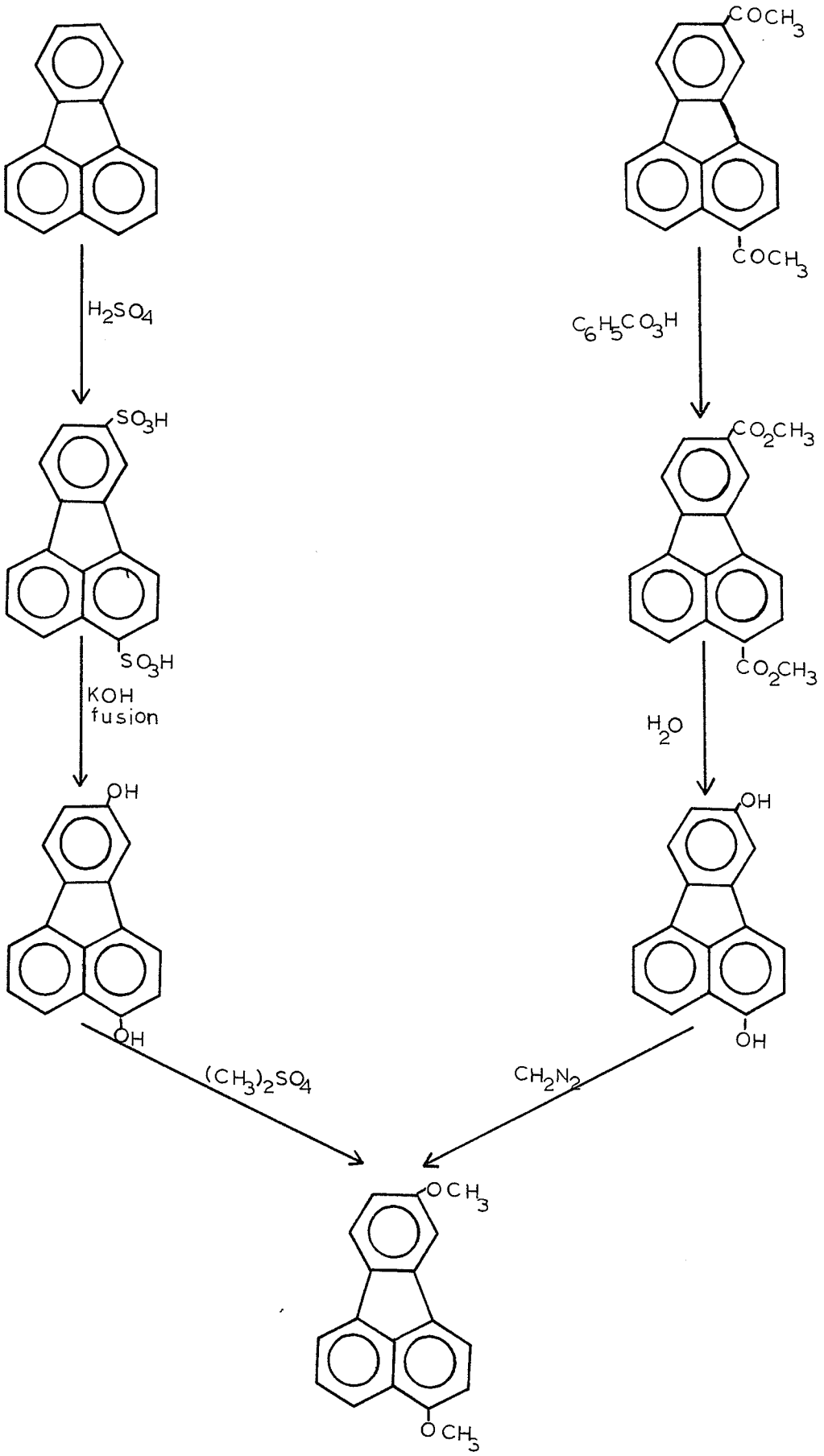


In 1955 Campbell and Keir (7) prepared 3,9-dibromofluoranthene from 3-nitrofluoranthene which was brominated, reduced, diazotized, and treated in a Sandmeyer reaction. This was identical to the product prepared from 3,9-diacetylfluoranthene. At the same time they proved that 3-cyano, 3-carboxy, and 3-carbomethoxyfluoranthene were also brominated in position 9. This work is summarized below.

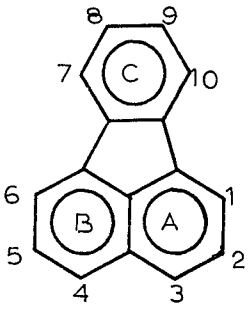


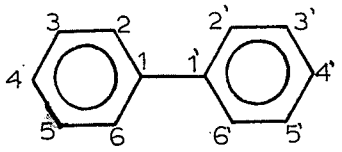
Goldschmiedt prepared fluoranthene disulphonic acid by heating the hydrocarbon in concentrated sulfuric acid. It was suggested that this was the 3,8-disulphonated compound because of the quinhydrone-type of product obtained by fusion with alkali. Campbell and Keir (7) proved that this suggestion was incorrect. Since monosulphonation occurs mainly in the 3-position, the disulphonic acid must contain one sulpho group in that position. The disulphonic acid was fused with potassium hydroxide and the dihydroxy compound was methylated. The product which was obtained was identical to an authentic sample prepared from 3,9-diacetylfluoranthene. This proof is valid only if it is assumed that the alkali fusion of the disulphonic acid was not accompanied by migration of one or both of the sulpho groups. This work is shown on page 13.

As a result of their investigations Campbell and Keir formulated a set of rules regarding the orientation of substituents in fluoranthene. They had shown that 3-substituted fluoranthenes undergo further substitution in the 8 or 9 positions depending on whether the first substituent was activating (ortho/para directing) or deactivating (meta directing). They explained these results by considering fluoranthene as a diphenyl derivative containing the diphenyl nuclei AC and BC. They also pointed out that orientation in the diphenyl series is dominated by the phenyl groups. That is, in most cases substitution occurs in the second ring in the 2' and 4' positions irrespective of the nature and position of the substituent already present in the first ring. An example of this is the three nitrodiphenyls


COCH3
COCH3
H2SO4
C6H5CO3H
SO3H
CO2CH3
SO3H
CO2CH3
KOH
fusion
H2O
OH
OH
OH
OH
(CH3)2SO4
CH2N2
OCH3
OCH3

which undergo substitution in positions 2' and 4' rather than in the 3' (meta)-position.



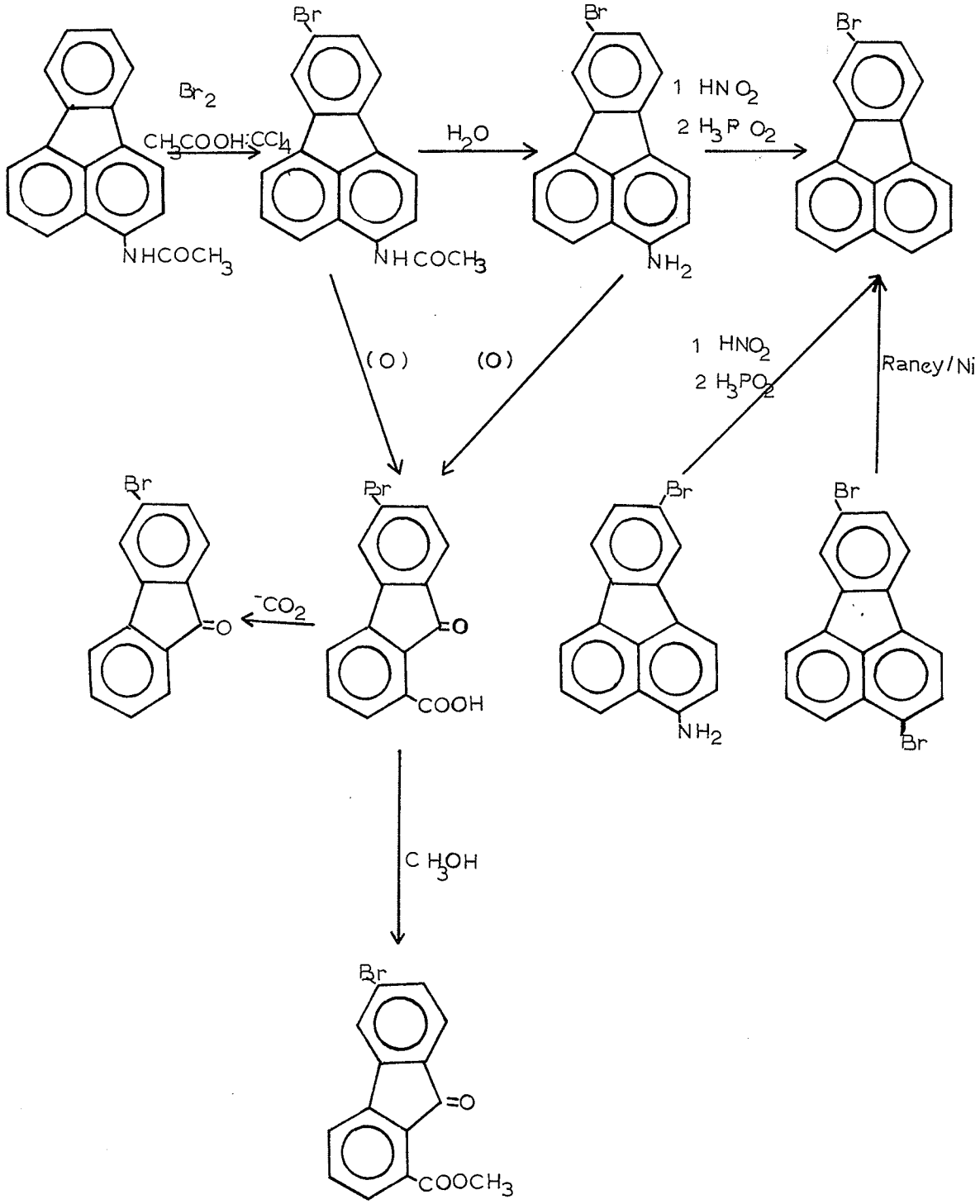


Applying this to fluoranthene, they postulated the following rules regarding orientation of substituents in fluoranthene.

"(1) each of the rings A and B direct substituents predominantly to the para-position in ring C, i.e. to positions 8 and 9 respectively, and (2) an ortho-para directing group in ring A increases the directive power of this ring with consequent substitution at $C_{(8)}$ (and possibly $C_{(10)}$), while meta directing groups decrease the directive power of ring A so that ring B dominates further substitution, which therefore occurs at $C_{(9)}$ (and possibly $C_{(7)}$)."

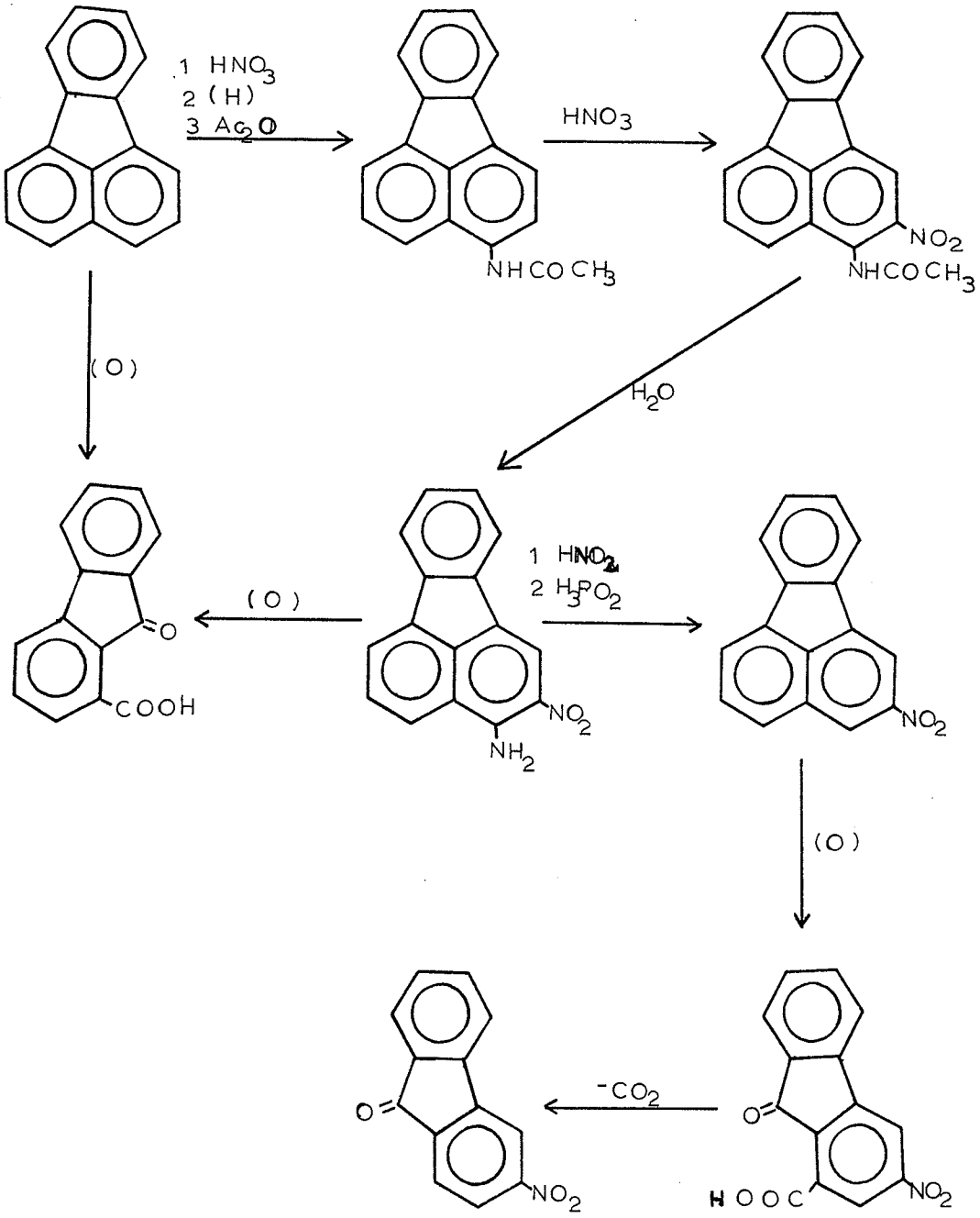
In 1966 Kaminska and Mazonski (20) further substantiated Campbell and Keir's postulates by proving that the bromination of 3-acetamidofluoranthene yields 3-acetamido-8-bromofluoranthene. They showed this by hydrolyzing the brominated product and by oxidizing the bromo-amine. The oxidation produced 6-bromofluorenone-1-carboxylic acid. Deamination of the bromo-amino compound yielded the same bromofluoranthene as that derived from the debromination of 3,8-dibromofluoranthene as well as

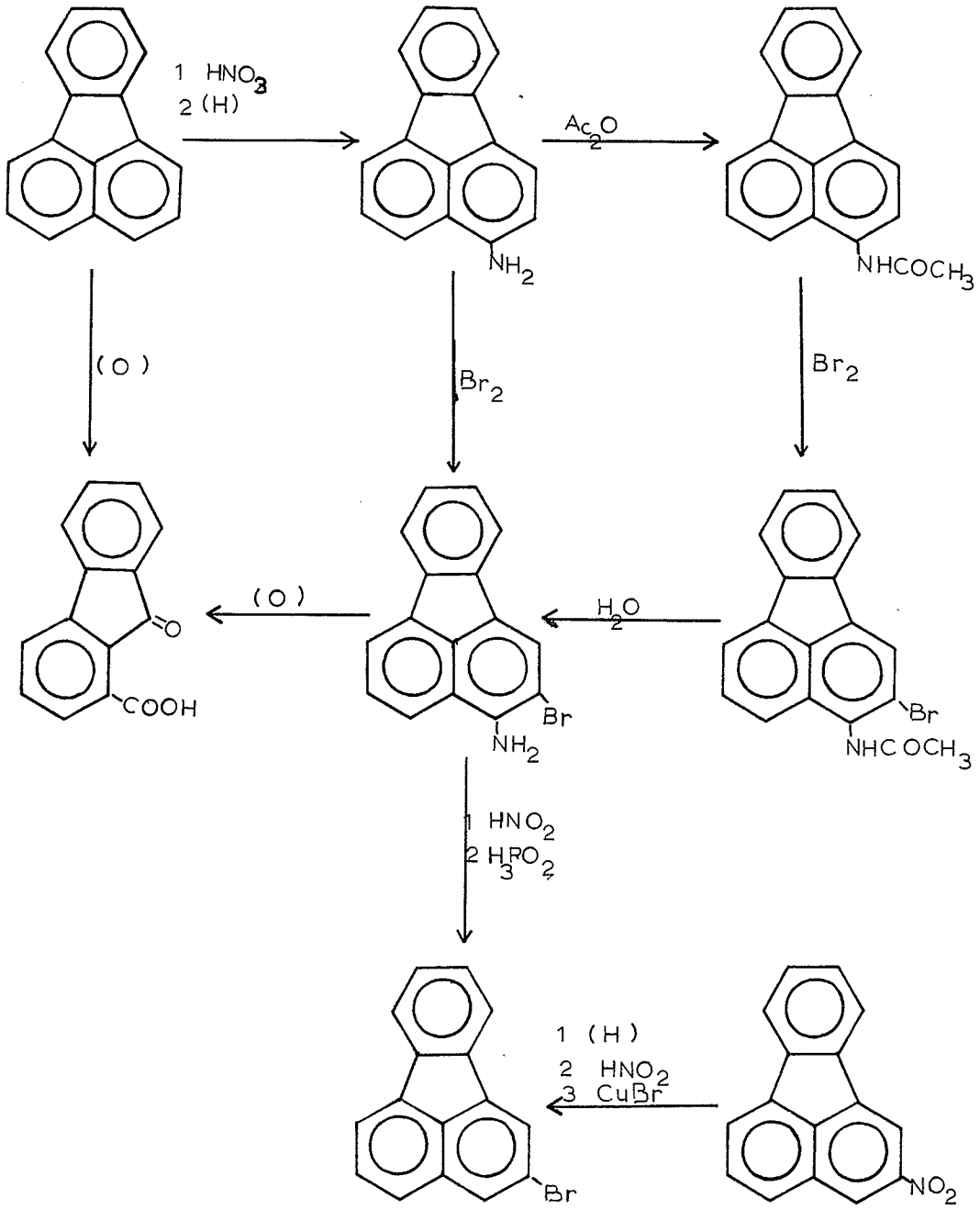
that from the debromination of 3-amino-9-bromofluoranthene. This work is shown below.



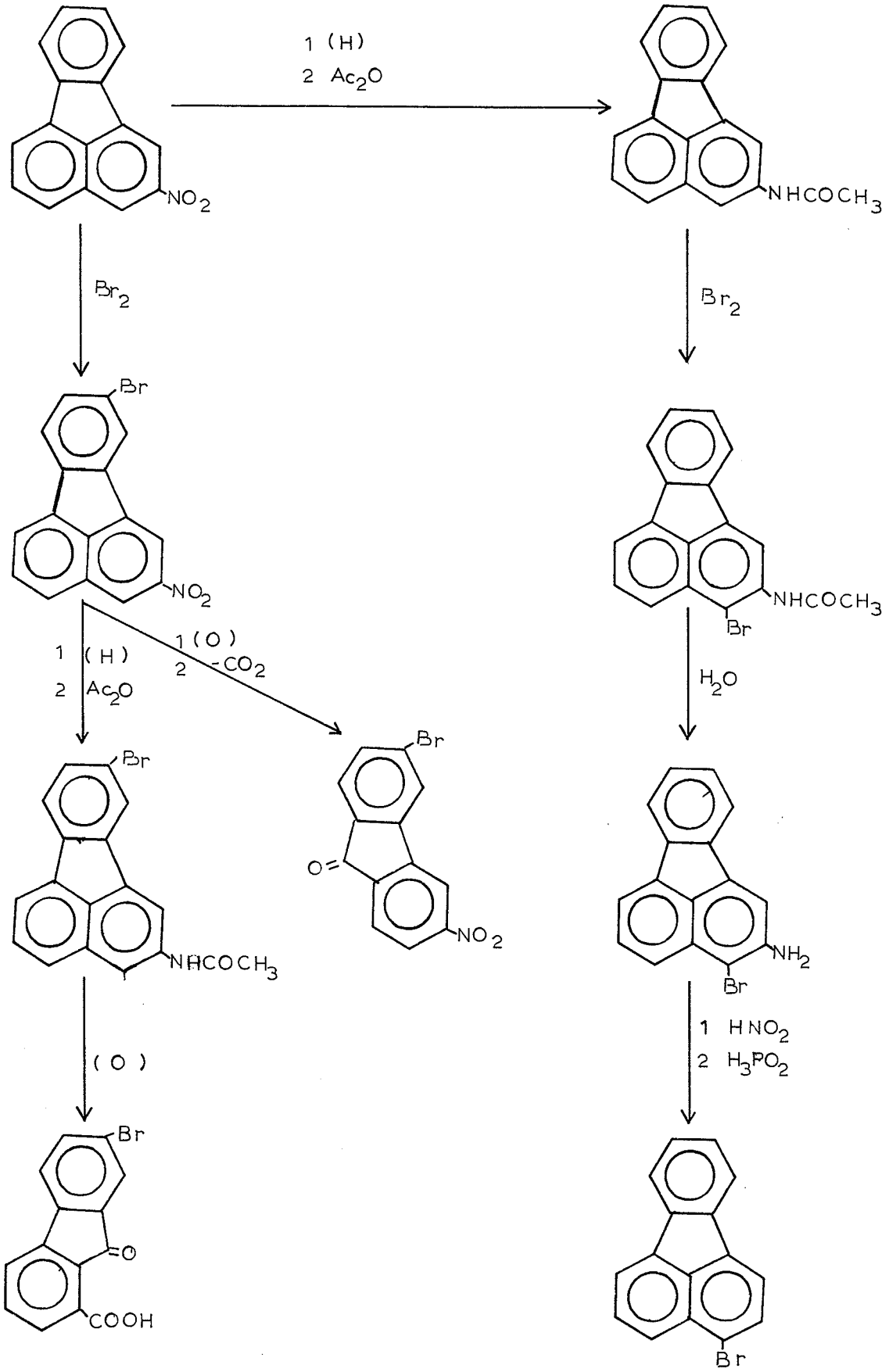
In 1956, Kloetzel, King, and Menkes (22) showed that 3-acetamidofluoranthene was nitrated in position 2 rather than in positions 8 or 10 as was suggested by Campbell's rules. These workers stated that the acetamido group "so intensely activates the ring to which it is attached that the second substituent enters the same ring." They proved the orientation of the acetamido-nitrofluoranthene as follows. They recovered 1-fluorenonecarboxylic acid as the product after oxidation of the nitro-amine. This proves that both of the substituents are in the same ring. Hydrolysis of the acetamido-nitrofluoranthene, deamination and finally oxidation of the resultant nitrofluoranthene gave 3-nitrofluorenone-1-carboxylic acid proving that the nitro group was in position 2. A summary of this is given on page 17.

Charlesworth and Blackburn (8) further confirmed the findings of Kloetzel et al. by proving that both 3-acetamido and 3-aminofluoranthene were brominated in position 2. The product which they obtained from hydrolysis of the acetamido-bromofluoranthene was identical to that produced from the bromination of 3-aminofluoranthene. Thus, the bromine atom must enter the same position in both cases. Oxidation of 3-amino-2-bromofluoranthene gave 1-fluorenonecarboxylic acid proving that both substituents were in the same ring. Deamination of the bromo-amine produced 2-bromofluoranthene, identical with an authentic sample prepared from 2-nitrofluoranthene by reduction, diazotization, and treatment with cuprous bromide in a Sandmeyer reaction. This work is summarized on page 18.


1 HNO3
2 (H)
3 Ac2O
HNO3
NHCOCH3
NO2
NHCOCH3
(O)
H2O
(O)
1 HNO2
2 H3PO2
O
COOH
NO2
NH2
NO2
(O)
-CO2
O
NO2
O
HOOC
NO2


1 HNO3
2 (H)
Ac2O
NH2
NHCOCH3
(O)
Br2
Br2
COOH
O
(O)
H2O
Br
NH2
Br
NHC OCH3
1 HNO2
2 H3PO2
1 (H)
2 HNO2
3 CuBr
Br
NO2

In 1965, Charlesworth and Dolenko (9) studied the influence of strongly activating and deactivating substituents in position 2 of the fluoranthene molecule. These workers proved that 2-acetamidofluoranthene was brominated in position 3 and that 2-nitrofluoranthene underwent bromination in position 9. They established the orientation of these substituents in the following way. Hydrolysis of the acetamido-bromo compound gave a bromo-amine. 3-Bromofluoranthene resulted from the deamination of this latter compound. 9-Bromo-2-nitrofluoranthene was oxidized and decarboxylated. The product of this series of reactions was 3-bromo-6-nitrofluorenone (10). The product obtained from 9-bromo-2-nitrofluoranthene after reduction, acetylation, and oxidation was 7-bromofluorenone-1-carboxylic acid. This was identical with an authentic sample of this material. This work is shown on the following page.


1 (H)
2 Ac2O
NO2
NHCOCH3
Br2
Br2
Br
NO2
NHCOCH3
Br
1 (H)
2 Ac2O
1 (O)
2 -CO2
H2O
Br
NHCOCH3
Br
O=
NO2
NH2
Br
(O)
1 HNO2
2 H3PO2
Br
=O
COOH
Br

DISCUSSION OF RESULTS

As previously stated in the introduction, the purpose of this research was to study the directive properties of strongly activating and strongly deactivating substituents in positions 2 and 3 of fluoranthene, under nitrating conditions.

The compounds chosen for this study were 2-acetamidofluoranthene, 2-nitrofluoranthene and 3-nitrofluoranthene. The first two substances were selected since they are among the few known 2-substituted fluoranthenes. The syntheses of all the starting materials had previously been accomplished. 2-Nitrofluoranthene was chosen because it is readily accessible and although an attempt (27) had been made to nitrate it, the orientation of the resultant product had not been proved. These two substituents represent the extremes on the activity scale, $-NO_2$ being strongly deactivating and $-NHCOCH_3$, being a strongly activating species.

Another aim of this work was to prove that the acetamidobromofluoranthene prepared by Blackburn (1) by the bromination of 3-acetamidofluoranthene in glacial acetic acid and that obtained by Kaminska and Mazonski (20) from the bromination of this compound in glacial acetic acid-carbon tetrachloride are the same product, 3-acetamido-8-bromofluoranthene (XXI). In 1964, Charlesworth and Blackburn (8) proved that bromination of 3-acetamidofluoranthene in pyridine produced 3-acetamido-2-bromofluoranthene. This difference would be accounted for by suggesting that the choice of solvent affects the position

into which a second substituent enters.

2-Acetamidofluoranthene (VII) was prepared from fluoranthene by the ten step procedure outlined by Kloetzel et al. (22). Nitration of 2-acetamidofluoranthene to give 2-acetamido-3-nitrofluoranthene (VIII) was accomplished using a method based on that of Kloetzel et al. for the nitration of 3-acetamidofluoranthene.

The nitro-acetamido compound (VIII) was hydrolyzed to 2-amino-3-nitrofluoranthene (IX). Diazotization and removal of the amino group with 50% hypophosphorous acid produced 3-nitrofluoranthene (II). This proves that the nitro group enters position 3.

Attempted oxidation of 3-acetamido-2-nitrofluoranthene (VIII) produced a tar that could not be purified, however oxidation of 2-amino-3-nitrofluoranthene (IX) gave 1-fluorenonecarboxylic acid (X). This proved that the substituents were in the same ring, otherwise a nitrofluorenonecarboxylic acid would have resulted.

The original 2-acetamido-3-nitrofluoranthene was catalytically reduced to 2-acetamido-3-aminofluoranthene (XI). 2,3-Diacetamidofluoranthene (XIII) was prepared from this compound by acetylation with acetic anhydride in pyridine solution at room temperature. This diacetamido compound had been previously prepared from 3-acetamido-2-nitrofluoranthene (IV) by Kloetzel, King, and Menkes.

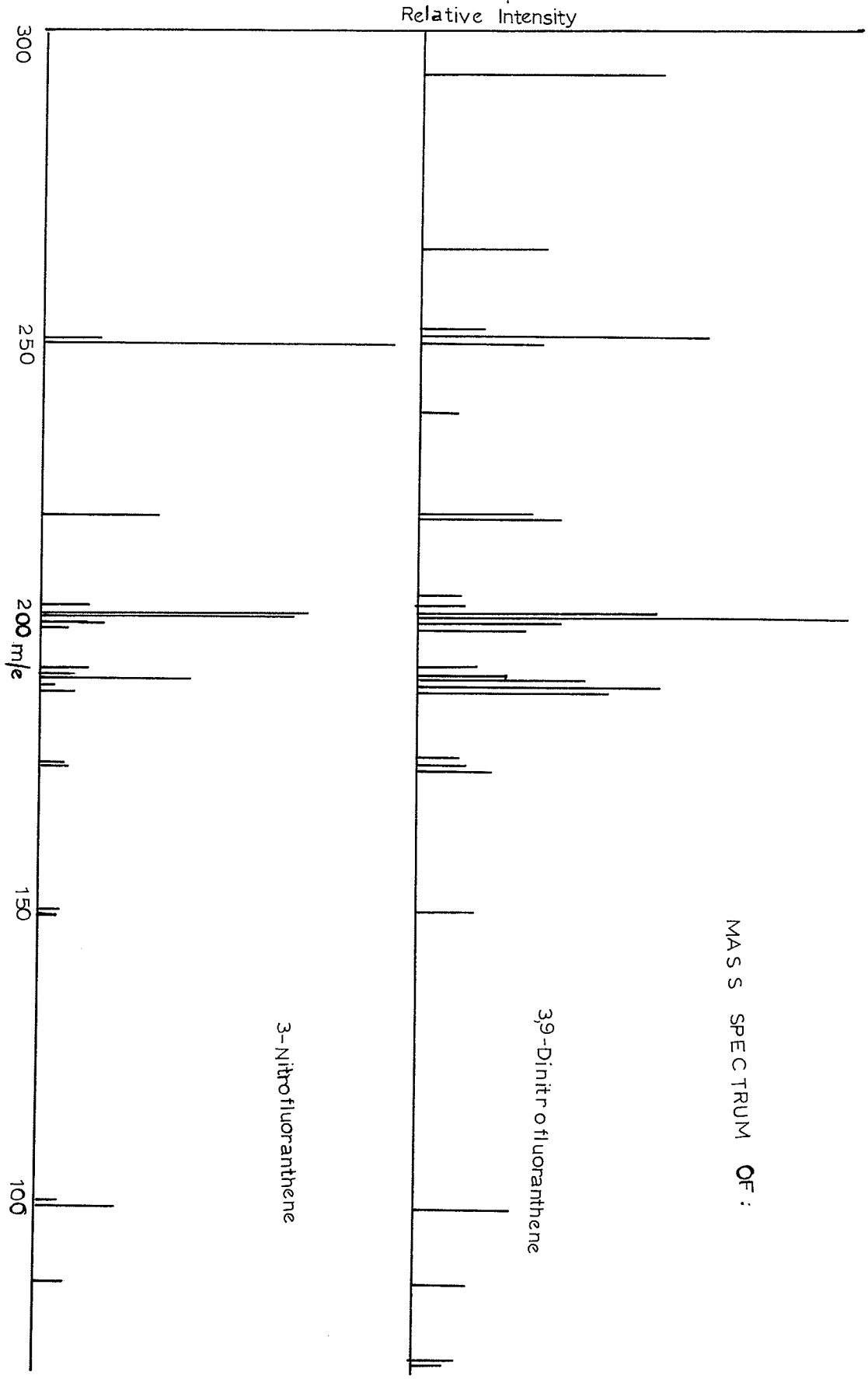
An attempt was made to prepare 2,3-diacetamidofluoranthene (XIII) from o-diaminofluoranthene, however due to the instability

of the latter compound no product was isolated. The diamino compound decomposed very readily and it was not possible to obtain a sample of this product. This is consistent with the tendency of many aminofluoranthenes to decompose readily in light and air.

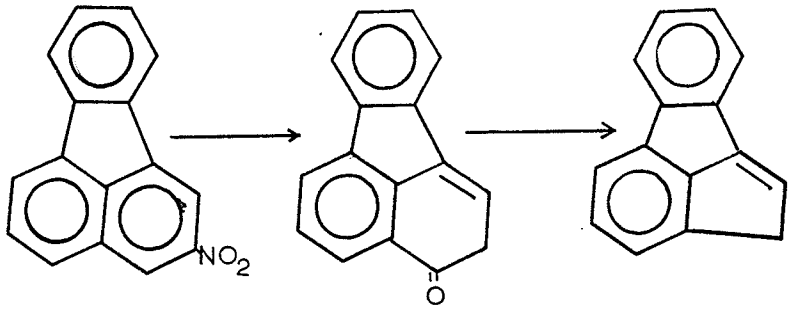
The nitro group is a highly deactivating species. This group has been shown to direct a second substituent to position 9, as predicted by Campbell's rule.

The nitration of 3-nitrofluoranthene (II) was successfully accomplished at 70-80°C. Several recrystallizations of the product from glacial acetic acid gave a pure sample of 3,9-dinitrofluoranthene (XIV). No other dinitro isomers were isolated. Any others would probably be present in very small quantities. This reaction had been attempted earlier by Wilshire (27) but the dinitro compound had not been isolated in a pure state nor had its orientation been proven. This worker only reported the presence of one dinitro compound.

A mass spectrum of our product, shown on page 24, indicated that it was dinitrofluoranthene. The mass spectra of the 1-,2- and 3- mononitro and those of 3,9- and 2,( )-dinitrofluoranthenes showed that preliminary loss of an -NO group occurred with the formation of a -CO bond. This latter bond was probably formed at the adjacent carbon atom. The next step seemed to be the loss of the -CO group and the formation of a five-membered ring.



MASS SPECTRUM OF :



The spectra of each of the dinitro compounds greatly resembled that of the mononitrofluoranthene from which it was derived.

Many attempts to oxidize the dinitrofluoranthene proved unsuccessful since only starting material was isolated after the reactions as shown by comparison infra-red spectra. This may have been due to the strong stability of the dinitro compound.

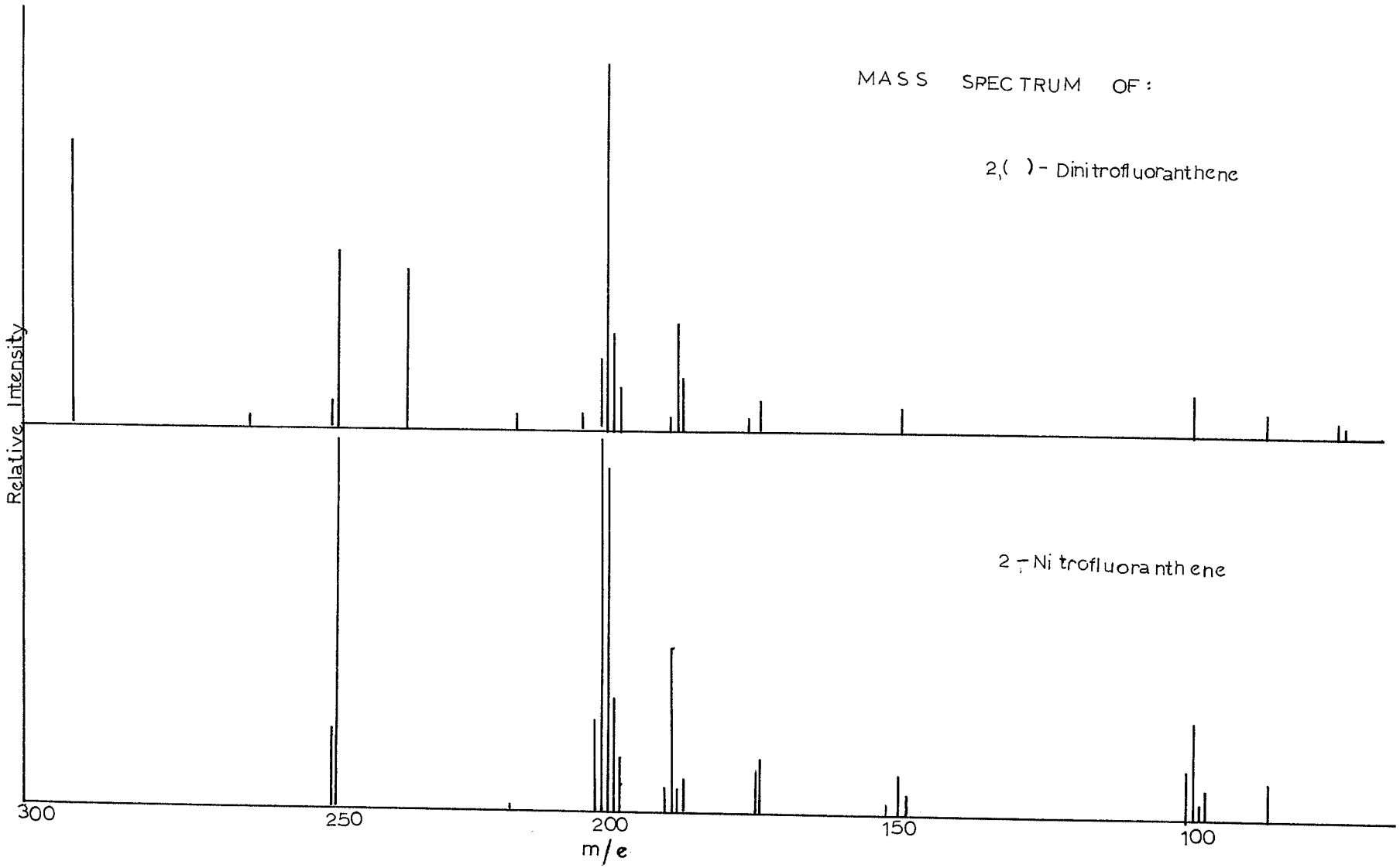
Catalytic hydrogenation of 3,9-dinitrofluoranthene produced 3,9-diaminofluoranthene (XV). This compound was not isolated since it decomposed very readily in light and air. This result was expected since Campbell, Leadhill and Wilshire (6) reported this diamine as its dihydrochloride derivative. Attempts to synthesize 3,9-dibromofluoranthene from 3,9-diaminofluoranthene using the same method as these workers proved unsuccessful. This was possibly because much of the diamine (XV), which was isolated by evaporation of the ethanol under a vacuum, had decomposed before it could be further reacted. A small amount of the diamino-dihydrobomide was successfully prepared by adding fuming hydrobromic acid to an ethanol solution of the diamine (XV) and stirring this mixture at room temperature for several hours, but passage to the dibromo compound through the Sandmeyer reaction was not achieved.

3,9-Diacetamidofluoranthene (XVII) was prepared by acetylation of the diamine (XV) in pyridine solution. This sample of 3,9-diacetamidofluoranthene was compared with an authentic sample of this compound prepared by the diacylation of fluoranthene followed by a Schmidt reaction. These two samples were identical.

2-Nitrofluoranthene (VI) was prepared according to the method of Kloetzel et al, as outlined earlier in this discussion. The nitration of this product was accomplished in acetic anhydride by refluxing the nitrating mixture for three hours. The dinitrofluoranthene (XVIII) was found to be very insoluble in many organic solvents (i.e. benzene, chloroform, methylene-chloride, and acetone). For this reason only very small amounts of material could be chromatographed at a time and much of this chromatographed material remained on the top of the column as tar. It was found that the grade of alumina used affected the product that was obtained on evaporation of the eluate. Using alumina which was not highly activated allowed some of the tar to pass down through the column and to be mixed with the dinitro band. The result of this was that the product was sticky. This problem was eliminated by using more highly activated alumina.

Since it was very difficult to isolate any workable quantities of the dinitro-product (XVIII), the orientation of the second nitro group was not able to be proved by chemical reactions.

The mass spectrum of this compound (XVIII), which appears on page 27, shows a strong similarity to that of the original


MASS SPECTRUM OF :
2,( )- Dinitrofluoranthene
2 - Nitrofluoranthene
Relative Intensity
300
250
200
150
100
m/e

2-nitrofluoranthene (VI). Due to this similarity, several positions in which the second nitro group could exist, may be eliminated. Position 1 may be eliminated since the nitro group is highly deactivating and has never been known to direct to the adjacent carbon in any aromatic system. Position 3 may be eliminated first because nitro is not known to direct ortho to itself and secondly because the peak heights would be expected to be a compromise between that of the 2- and 3-nitrofluoranthenes, i.e. probably equal, whereas the heights are the same as the 2- substituted compound. This same reasoning may be applied to position 4. Position 5 may be eliminated as a possibility for very much the same reason as just given for position 4, i.e. that the peak heights of 3,5- dinitrofluoranthene would be equal since there would be an equal probability of loss of either nitro group. Because fluoranthene is a symmetrical molecule, loss of the nitro from position 3 would result in 2-nitrofluoranthene. Since it is assumed that the second nitro group enters the same position in both dinitro compounds, this position may be eliminated here. The remaining possible positions 6,7,8,9 and 10 may not be eliminated on the basis of mass spectral evidence.

The expected position, analogous to that of 3,9- dinitrofluoranthene (XIV), and according to Campbell's rule is position 9, however in the future some rigorous proof must be developed to show this orientation.

3-Acetamido-9-bromofluoranthene (XX) was very readily prepared from 3-amino-9-bromofluoranthene by acetylation in

benzene solution with acetic anhydride. This compound had not appeared in the literature prior to this work.

In 1966 Kaminska and Mazonski (20) prepared 3-acetamido-8-bromofluoranthene (XXI) by the bromination of 3-acetamido-fluoranthene (III) in a mixture of carbon tetrachloride and glacial acetic acid. This compound (XXI) had previously been isolated in these laboratories by Blackburn (1) however its orientation had not been rigorously proved by this worker. Charlesworth and Blackburn (8) reported that the bromination of 3-acetamidofluoranthene (III) in pyridine gave 3-acetamido-2-bromofluoranthene. Kaminska and Mazonski suggested that the reason for the bromine atom entering into the two different positions was due to a solvent effect. They explained that the bromine-pyridine complex is an active brominating agent and that it cooperates with the acetamido group to accommodate ortho substitution whereas the glacial acetic acid-carbon tetrachloride mixture is a less active solvent and the bromine atoms do not show this cooperation. Comparison of the infra-red spectra of the two products shows that the product prepared in our laboratories is the same, but less pure than that prepared by Kaminska and Mazonski. Thus, this would prove that the directive property is influenced not only by the existing substituent but also by the experimental conditions.

EXPERIMENTAL

Preparation of 3-Nitrofluoranthene (II)

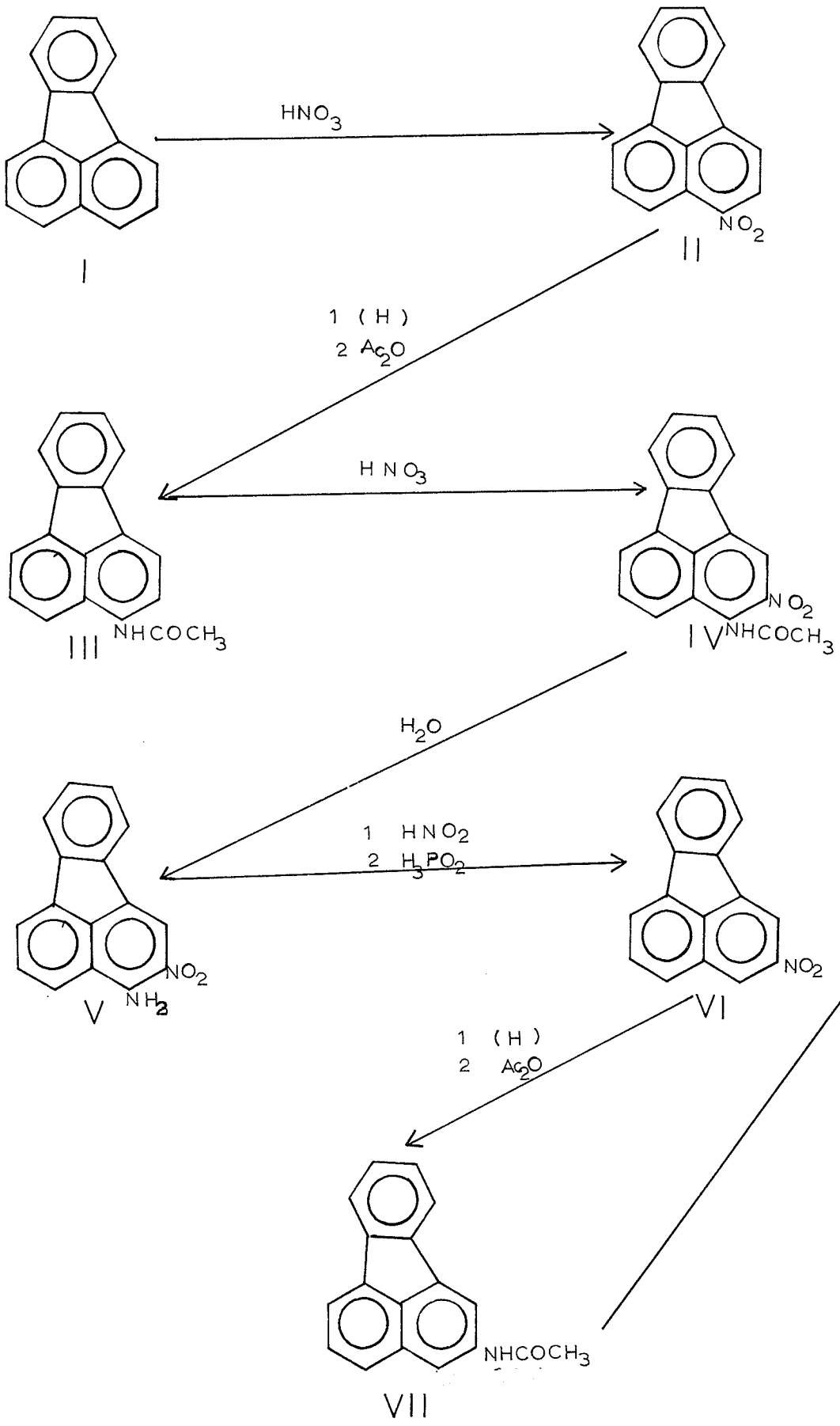
3-Nitrofluoranthene was prepared essentially by the method of Garascia, Fries, and Ching (15).

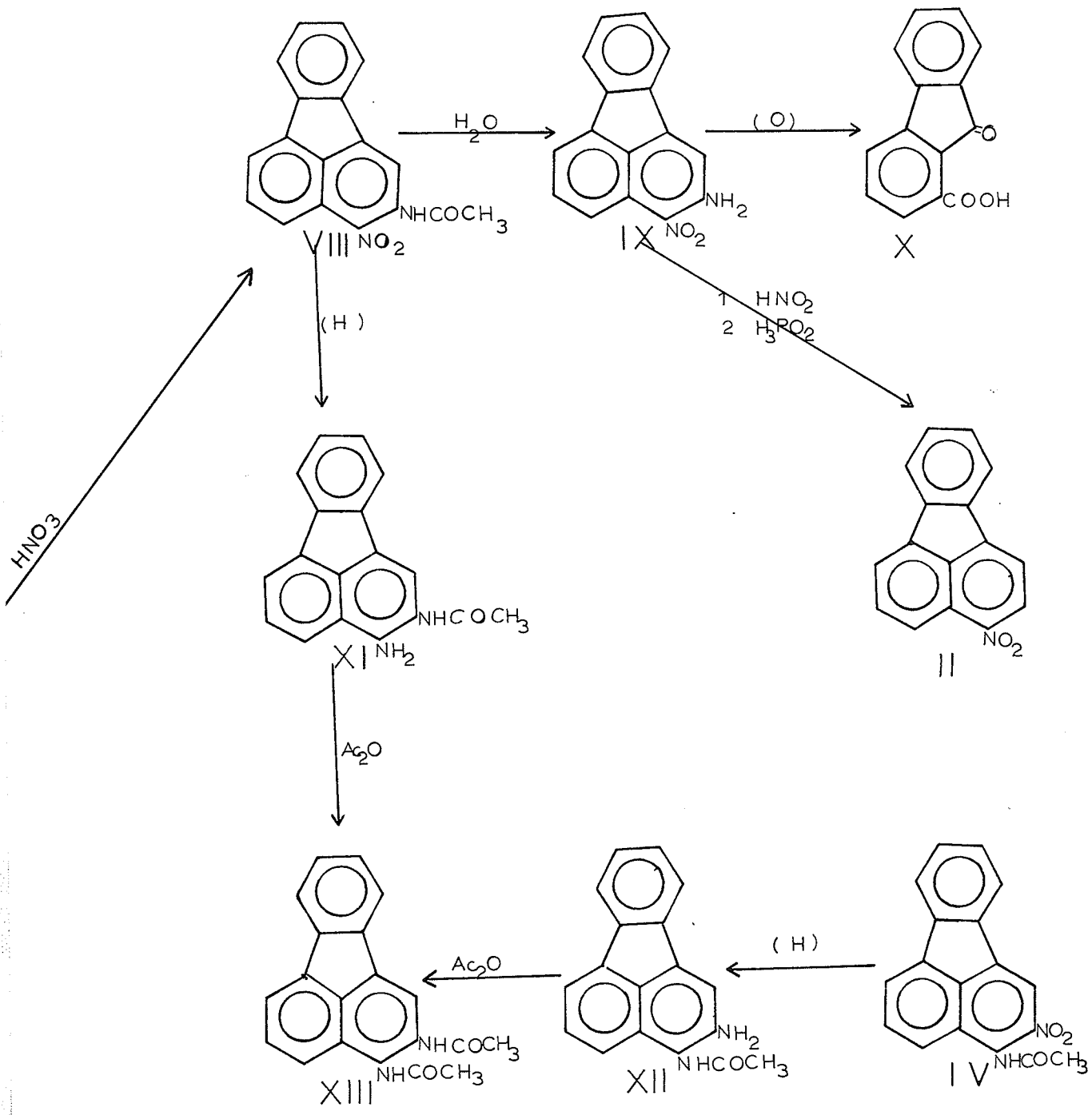
Fluoranthene (40.0 g) was dissolved in glacial acetic acid (300 ml). To this solution, which was maintained at a temperature of 71-75°C., concentrated nitric acid (54 ml) was added dropwise, with stirring, over a period of about fifteen minutes. The orange-yellow precipitate of crude 3-nitrofluoranthene (20.0 g) was filtered from the hot solution, washed with glacial acetic acid, then with water and allowed to dry. Treatment with decolourizing charcoal and recrystallization from glacial acetic acid gave the pure material (13.9 g) which melted at 159-160°C. (lit. 158-160°C).

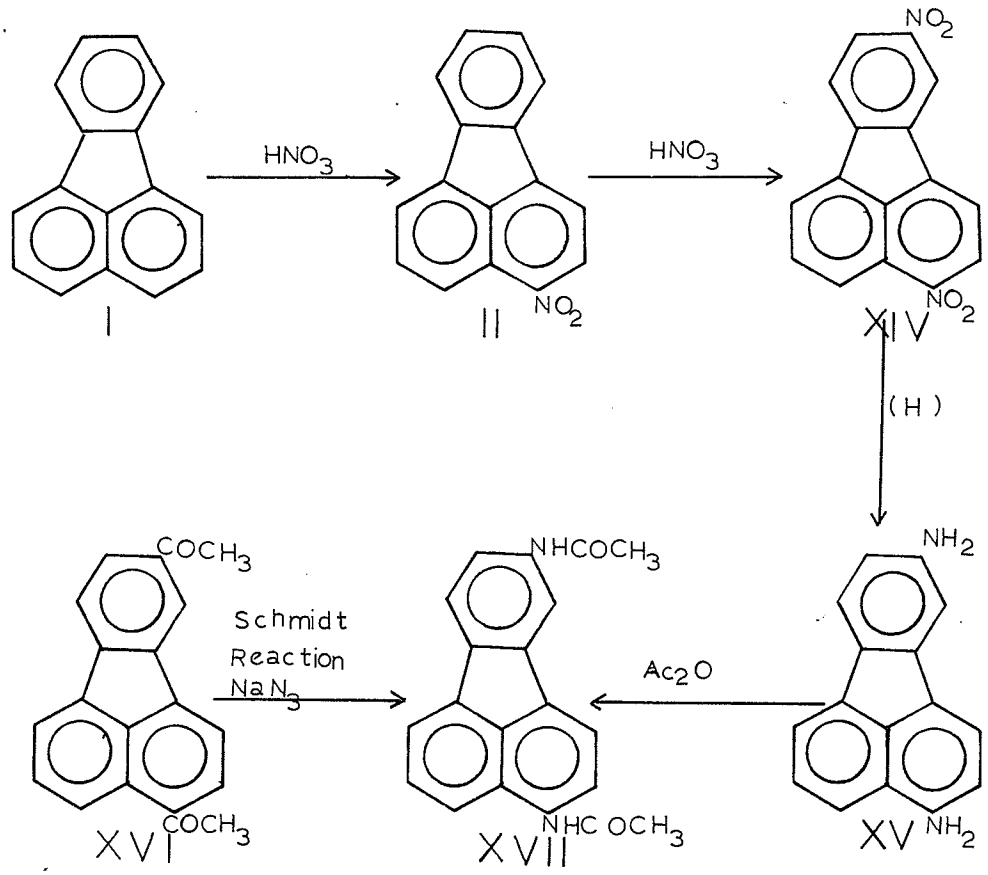
Preparation of 3-Aminofluoranthene

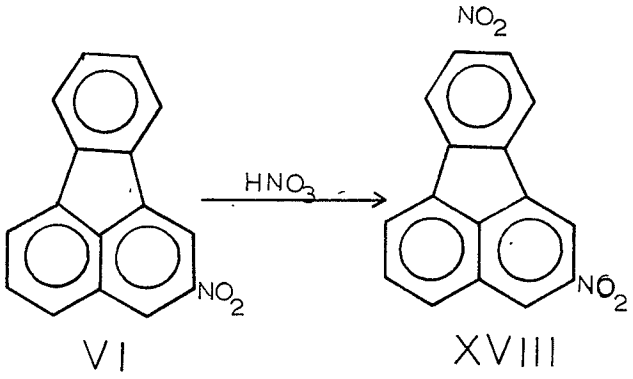
The procedure used for this preparation was that of Kloetzel, King and Menkes (22).

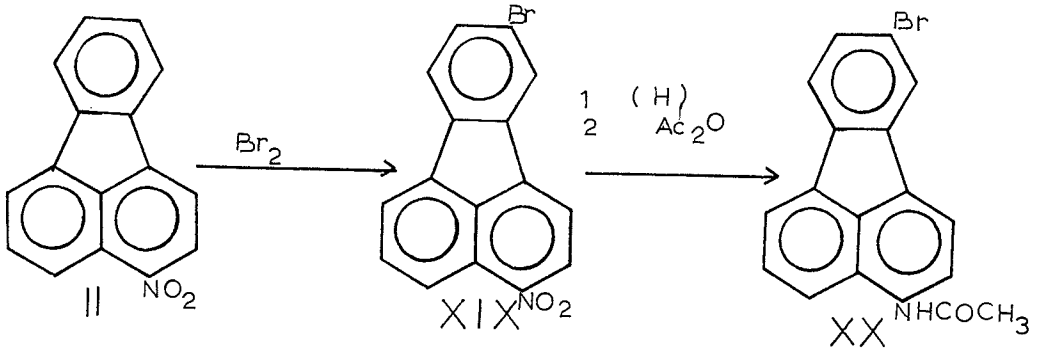
3-Nitrofluoranthene (30.0 g) and platinum oxide (0.39 g) were suspended in absolute ethanol (270 ml). The hydrogenation was carried out in a Parr catalytic hydrogenation apparatus. The reduction was accomplished in one hour during which time the gauge pressure decreased from 43 lbs./sq. in. to 12 lbs./sq. in. The catalyst was filtered off and crude 3-aminofluoranthene (22.9 g) was isolated by dilution of the solvent with water, followed by filtration. This product melted at 111-113°C. (lit. 111-112°C).

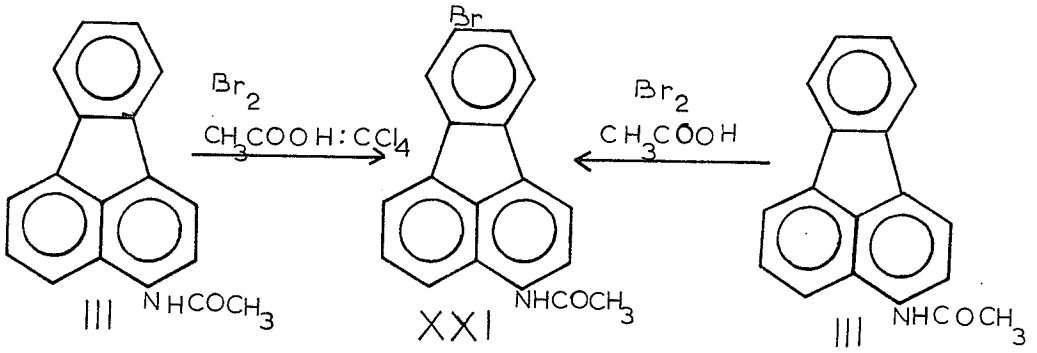

HNO3
NO2
I
II
1 (H)
2 Ac2O
HNO3
NHCOCH3
III
NO2
NHCOCH3
IV
H2O
1 HNO2
2 H3PO2
NO2
NH2
V
NO2
VI
1 (H)
2 Ac2O
NHCOCH3
VII


H2O
(O)
NHCOCH3
NO2
NH2
COOH
VIII
IX
X
(H)
1 HNO2
2 H3PO2
HNO3
NHCOCH3
NH2
XI
NO2
II
Ac2O
Ac2O
(H)
NHCOCH3
NHCOCH3
XIII
NH2
NHCOCH3
XII
NO2
NHCOCH3
IV


HNO3
HNO3
NO2
NO2
NO2
I
II
XIV
(H)
NH2
COCH3
NHCOCH3
Schmidt
Reaction
NaN3
Ac2O
COCH3
NHC OCH3
NH2
XVI
XVII
XV


NO2
HNO3
NO2
NO2
VI
XVIII


Br
Br2
1 (H)
2 Ac2O
Br
II
NO2
XIX
NO2
XX
NHCOCH3


Br2
CH3COOH:CCl4
Br2
CH3COOH
Br
III
NHCOCH3
XXI
NHCOCH3
III
NHCOCH3

Preparation of 3-Acetamidofluoranthene (III)

This preparation was carried out using the method of Kloetzel et al. (22).

3-Aminofluoranthene (15.0 g) was stirred in benzene (900 ml) and a small amount of insoluble material was filtered off. Acetic anhydride (9.5 ml) was added dropwise to the benzene solution and the reaction mixture was stirred at room temperature for thirty-five minutes, during which time a cream-coloured solid precipitated. Filtration of the reaction mixture gave 3-acetamidofluoranthene (15.9 g) of melting point 243-245°C. (lit. 242-245°C).

Preparation of 3-Acetamido-2-Nitrofluoranthene (IV)

The method used for the nitration of 3-acetamidofluoranthene was essentially that of Kloetzel et al. (22).

3-Acetamidofluoranthene was dissolved in glacial acetic acid (1300 ml) and this solution was maintained at a temperature of 80-85°C. Concentrated nitric acid (6.6 ml) was added dropwise, with stirring, and the reaction was allowed to proceed for ninety minutes during which a solid separated out of solution. The reaction mixture was cooled to room temperature and the solid was filtered off and washed with water. The 3-acetamido-2-nitrofluoranthene (7.5 g) was obtained as golden-yellow plates melting at 280-282°C. (lit. 282-283°C).

Preparation of 3-Amino-2-Nitrofluoranthene (V)

3-Amino-2-nitrofluoranthene was prepared by hydrolysis of 3-acetamido-2-nitrofluoranthene according to the method of Kloetzel

and his co-workers (22).

A mixture of 3-acetamido-2-nitrofluoranthene (7.5 g) in 95% ethanol (683 ml) and concentrated hydrochloric acid (683 ml) was heated under reflux for fifteen hours. The cooled reaction mixture was neutralized with 10% sodium hydroxide. After cooling, the mixture was filtered and the crude sample was washed with water and allowed to dry. The impure 3-amino-2-nitrofluoranthene (5.75 g) which was obtained melted at 250-254°C. Treatment with decolourizing charcoal and recrystallization from the pyridine-water mixture gave pure 3-amino-2-nitrofluoranthene (3.4 g) melting at 252-254°C. In another preparation of this product, the impure sample, after recrystallization from chlorobenzene, had a melting point of 234-235°C. This melting point is in accordance with that given by Kloetzel et al. (22). Jemmett et al. (19) reported that this compound softened at 250°C and finally melted at 253°C following recrystallization from ethylene glycol, chlorobenzene and methyl ethyl ketone.

Preparation of 2-Nitrofluoranthene (VI)

Deamination of 3-amino-2-nitrofluoranthene to produce 2-nitrofluoranthene was accomplished using the method of Kloetzel et al. (22).

Powdered sodium nitrite (1.0 g) was dissolved at room temperature by carefully adding it to a stirred solution of water (2.7 ml) and concentrated sulfuric acid (37.0 ml). The solution was then cooled to -5°C., and powdered 3-amino-2-nitrofluoranthene (3.4 g) was slowly added at this temperature.

The resultant mixture was stirred at -5° c for another thirty minutes after which pre-cooled 50% hypophosphorous acid (78.3 ml) was added at such a rate (three hours) that the temperature did not exceed 5°C. The mixture was allowed to stand at 2-3°C for six days after which time it was diluted with three volumes of water. The crude material was filtered off, washed with dilute sodium hydroxide and water, and allowed to dry. Treatment with decolourizing charcoal and recrystallization from glacial acetic acid gave 2-nitrofluoranthene (2.0 g) as yellow needles of melting point 152-154°C (lit. 153-153.5°C).

Preparation of 2-Aminofluoranthene

The hydrogenation of 2-nitrofluoranthene, effected essentially according to the method of Kloetzel et al. (22), produced 2-aminofluoranthene.

2-Nitrofluoranthene (3.2 g), decolourizing charcoal (0.3 g) and platinum oxide (0.3 g) were suspended in absolute alcohol (60 ml). The hydrogenation was completed in three hours during which time the gauge pressure decreased from 43 lbs./sq. in. to 30 lbs./sq. in. The charcoal and the catalyst were filtered out of the solution and the crude amine (2.5 g), of melting point 115-120°C was precipitated with water. Kloetzel et al. found the melting point of the recrystallized product to be 128-129°C. In our case, since the acetyl derivative was required, the amine was not further purified but acetylated directly as in the following preparation.

Preparation of 2-Acetamidofluoranthene (VII)

2-Aminofluoranthene was acetylated in benzene solution

according to the method of Kloetzel et al. (22).

Crude 2-aminofluoranthene (2.5 g) was stirred in benzene (150 ml) and a small amount of insoluble material was filtered off. Acetic anhydride (1.3 ml) was added to the benzene solution and the reaction mixture was stirred at room temperature for one hour during which time a solid precipitated. The solid 2-acetamidofluoranthene (1.9 g), of melting point 226-228°C was filtered off. (lit. 225-226°C).

Preparation of 2-Acetamido-3-Nitrofluoranthene (VIII)

The nitration of 2-acetamidofluoranthene was accomplished using a method similar to that of Kloetzel et al, (22) for the preparation of 3-acetamido-2-nitrofluoranthene.

2-Acetamidofluoranthene (1.3 g) was dissolved at 80-85°C in glacial acetic acid (130 ml) to which acetic anhydride (10 drops) had been added. Concentrated nitric acid (0.66 ml) was added dropwise and the solution was stirred at this temperature for three hours. The reaction mixture was allowed to stand at room temperature for two days in an open vessel. During this time most of the solvent evaporated and black crystals (0.8 g) of melting point 150-153°C were formed. Treatment with decolourizing charcoal and recrystallization from glacial acetic acid gave pure 2-acetamido-3-nitrofluoranthene (0.6 g) as golden-yellow micro-crystals of melting point 190-193°C. This same product was obtained as bright-yellow flocculent needles after recrystallization from ethanol-water. Infra-red peaks of this compound are at 3.02, 5.97, 6.22, 6.57 and 7.27μ.

Analysis Found: N, 9.17%

Calculated for $C_{18}H_{12}N_2O_3$: N, 9.21%

Preparation of 2-Amino-3-Nitrofluoranthene (IX)

2-Acetamido-3-nitrofluoranthene was hydrolyzed using a procedure which was essentially the same as that used by Kloetzel and his co-workers (22) for the hydrolysis of 3-acetamido-2-nitrofluoranthene (0.6 g), 95% ethanol (33 ml) and concentrated hydrochloric acid (33 ml) were heated under reflux for three hours. After the reaction mixture had cooled, it was neutralized with 10% sodium hydroxide, cooled and the crude product (0.5 g) was filtered off.

Infra-red peaks of this compound are at: 2.90, 3.02, 6.00, 6.27, 7.34 and 7.95μ.

Analysis Found: N, 10.97%

Calculated for $C_{16}H_{10}N_2O_2$: N, 10.68%

Deamination of 2-Amino-3-Nitrofluoranthene

The experimental procedure was essentially that which Kloetzel et al. (22) reported for the deamination of 3-amino-2-nitrofluoranthene.

Sodium nitrite (0.09 g) was dissolved at room temperature in a solution of concentrated sulphuric acid (3.1 ml) and water (0.2 ml) by careful addition with stirring. This solution was cooled to -5°C in an ice-salt bath and powdered 2-amino-3-nitrofluoranthene (0.25 g) was added at this temperature. The reaction mixture was stirred at -5°C for thirty minutes. Precooled 50% hypophosphorous acid (6.53 ml) was then added at such a rate (thirty minutes) that the temperature

did not exceed 5°C. The reaction mixture was allowed to stand for six days at 2-3°C after which it was diluted with three volumes of water. The precipitate was filtered, washed with 10% sodium hydroxide and water, and allowed to dry. Treatment with decolourizing charcoal and recrystallization from glacial acetic acid gave pure 3-nitrofluoranthene (0.12 g), m.p. 156-158°C.

A mixed melting point with an authentic sample of 3-nitrofluoranthene, prepared by direct nitration of fluoranthene, showed no depression. Comparison infra-red and ultra-violet spectra, as shown on pages 37 and 38, showed that the deaminated product and an authentic sample were identical.

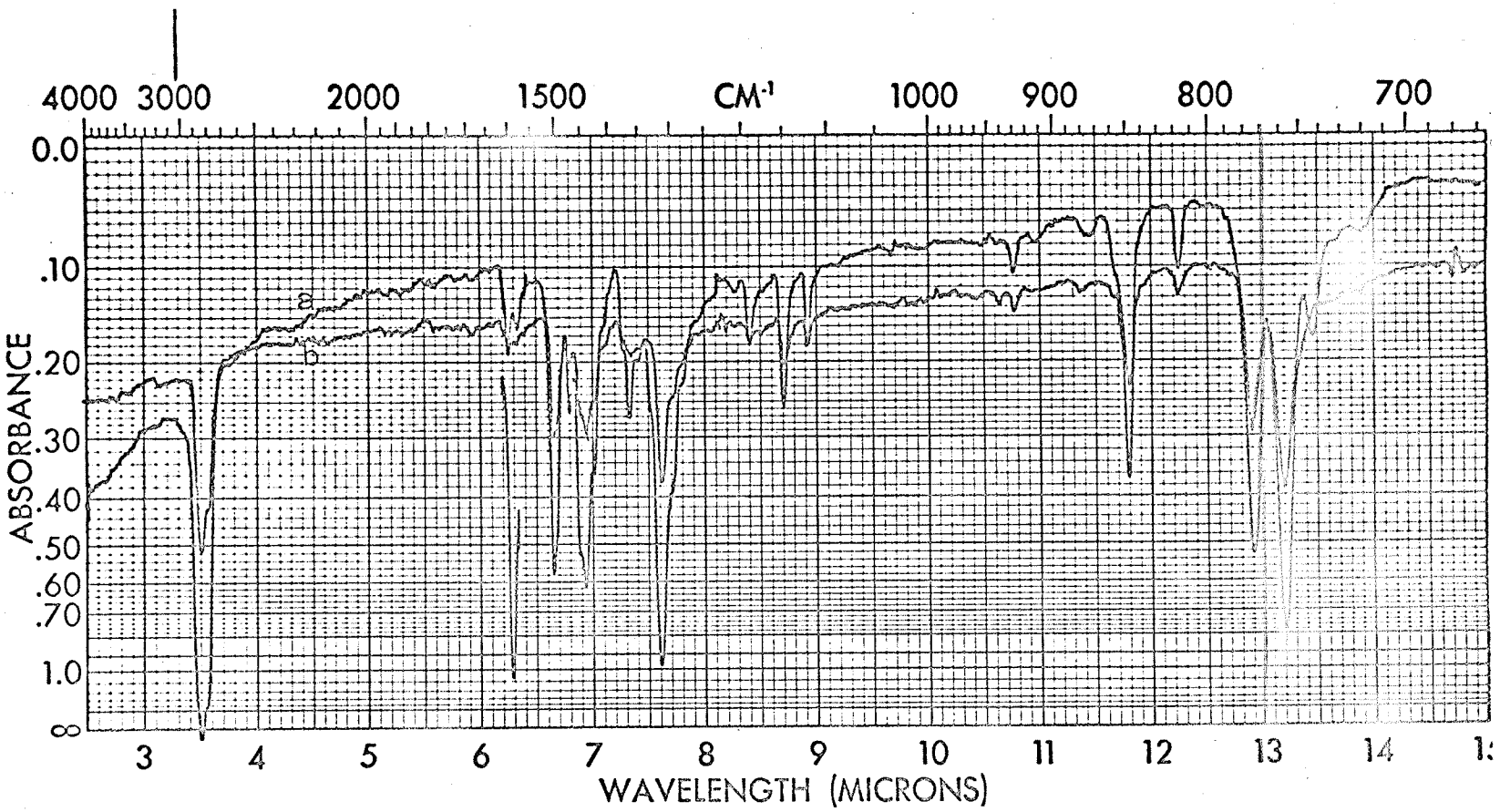
Analysis Found: N, 5.57%

Calculated for $C_{16}H_9NO_2$: N, 5.76%

Oxidation of 2-Amino-3-Nitrofluoranthene

The experimental procedure used was similar to that of Forrest and Tucker (14) in the oxidation of fluoranthene.

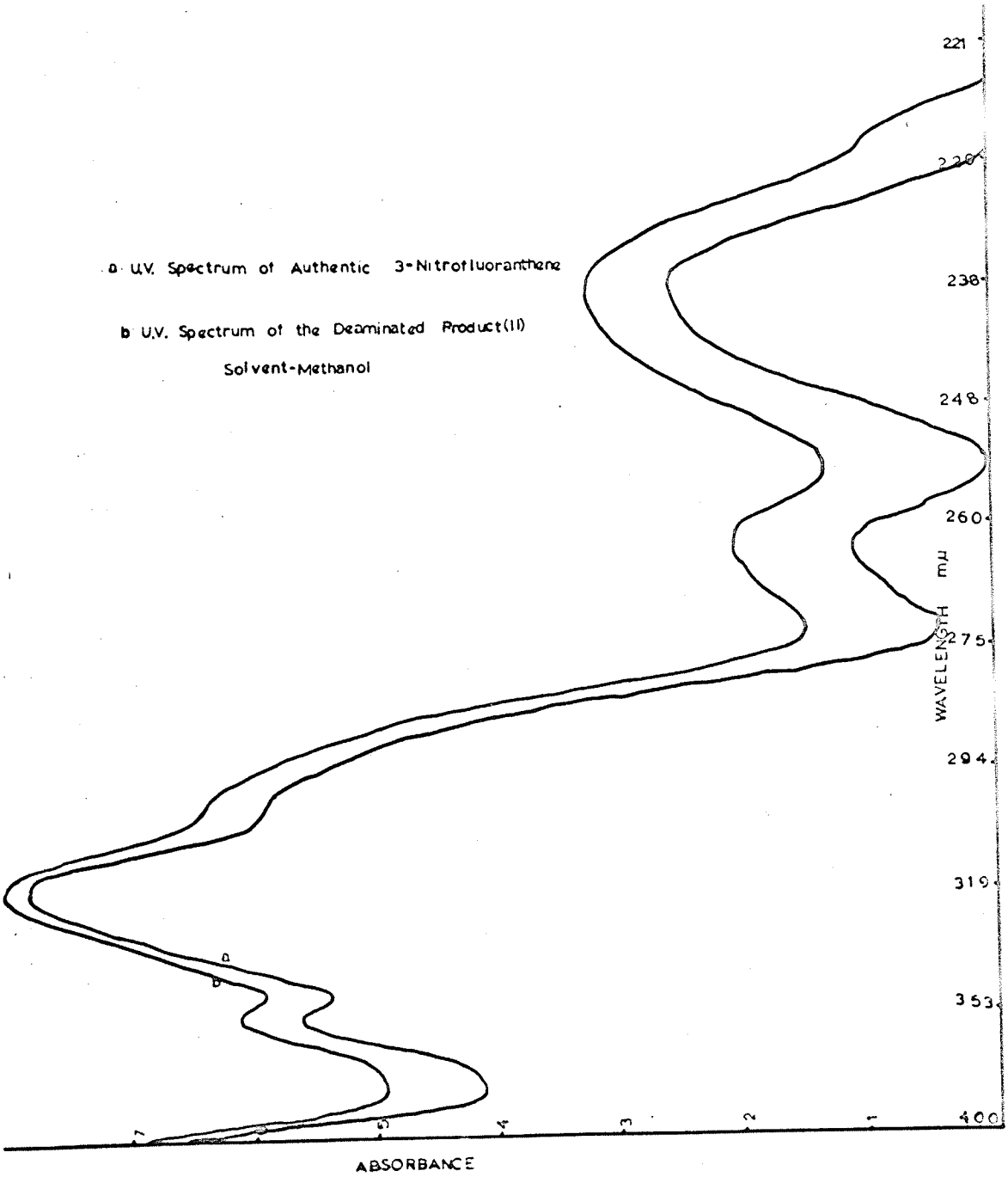
A solution of chromic anhydride (1.5 g) in water (2 ml) and glacial acetic acid (2 ml) was added over a period of ten minutes to a boiling suspension of 2-amino-3-nitrofluoranthene (0.4 g) in glacial acetic acid (20 ml). The remaining oxidation mixture was rinsed into the reaction mixture with a small amount (2 ml) of glacial acetic acid. The mixture was refluxed for four hours and then it was poured into 1:4 v/v sulfuric acid solution (50 ml) and allowed to stand at room temperature overnight. The impure solid was filtered off, washed with dilute acid and distilled water, and allowed to dry. It was purified



a IR Spectrum of Authentic 3-Nitrofluoranthene

b I.R. Spectrum of the Deaminated Product (II)

Phase - Nujol Mull


a U.V. Spectrum of Authentic 3-Nitrofluoranthene
b U.V. Spectrum of the Deaminated Product(II)
Solvent-Methanol
221
238
248
260
275
294
319
353
400
WAVELENGTH mμ
a
b
5
4
3
2
1
ABSORBANCE

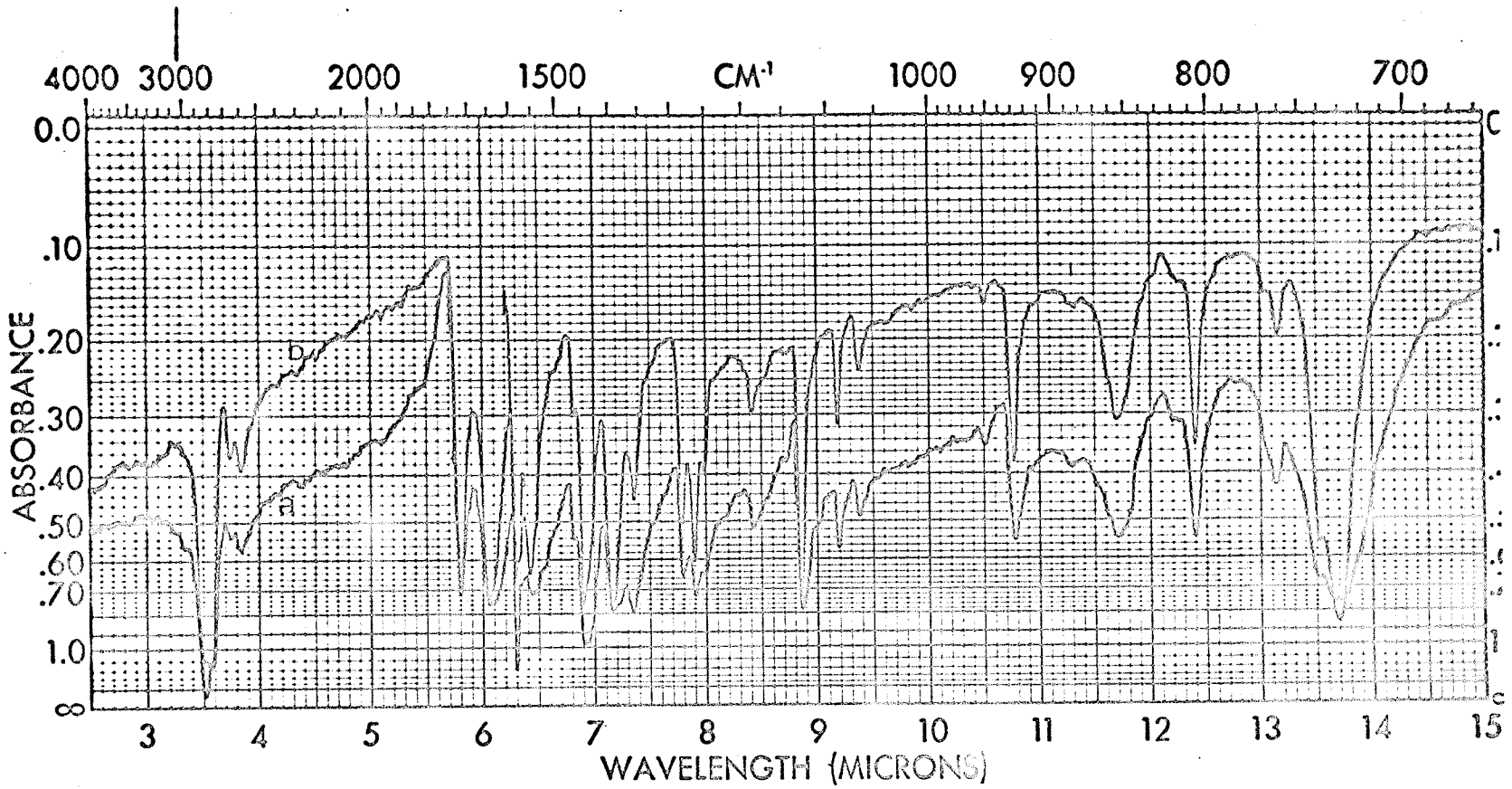
by dissolving it in 5% sodium carbonate solution and filtering out a small amount of insoluble material, and finally by re-precipitating the acid with (1:4 v/v) aqueous sulfuric acid solution. The solid was filtered and allowed to dry. Pure fluorenone-1-carboxylic acid (0.12 g) was obtained as light orange needles, m.p. 190-192°C, after recrystallization from glacial acetic acid (lit. 191-193°C).

Admixture with an authentic sample prepared by the oxidation of fluoranthene caused no depression in the melting point (190-192°C). A comparison infra-red spectrum of this product and of an authentic sample of fluorenone-1-carboxylic acid, shown on page 40 was the same.

Preparation of 2-Acetamido-3-Aminofluoranthene (XI)

The hydrogenation of 2-acetamido-3-nitrofluoranthene was carried out essentially according to the method used by Blackburn (1) for the hydrogenation of 3-acetamido-2-nitrofluoranthene.

2-Acetamido-3-nitrofluoranthene (0.5 g) and palladium-charcoal catalyst (0.056 g) were suspended in absolute ethanol (21 ml). The suspension was hydrogenated for twenty-four hours during which the gauge pressure dropped from 21 lbs./sq. in. to 20 lbs./sq. in. The product was brought into solution by adding pyridine (25 ml) and heating. The catalyst was filtered off and most of the solvent was evaporated under vacuum. Crude 2-acetamido-3-aminofluoranthene (0.38 g) precipitated on dilution of the solvent with water. The impure solid (0.23 g) was recrystallized from pyridine as bright-yellow 2-acetamido-



a IR Spectrum of Authentic Fluorenone-1-Carboxylic Acid

b IR Spectrum of the Oxidation Product from 2-Amino-3-Nitrofluoranthene

Phase - Nujol Mull

3-aminofluoranthene (0.19 g), m.p. 204-206° C.

Infra-red peaks of this compound are at: 2.97, 3.05, 6.07, and 7.77 μ.

Analysis Found: N, 8.85% ''
Calculated for $C_{18}H_{14}N_2O$: N, 10.21%

Acetylation of 2-Acetamido-3-Aminofluoranthene

The acetylation of 2-acetamido-3-aminofluoranthene was accomplished in pyridine solution.

Impure 2-acetamido-3-aminofluoranthene (0.15 g) was dissolved in pyridine (25 ml) and acetic anhydride (4 drops) was added. The solution was stirred at room temperature for ninety minutes and then it was allowed to stand to allow some of the pyridine to evaporate. A bright yellow solid precipitated out of solution. The impure product was recrystallized from glacial acetic acid as cream-coloured micro-crystals of pure 2,3-diacetamidofluoranthene (0.13 g), m.p. 262-263°C. (lit. 268-269°C).

Admixture with an authentic sample, described below, did not depress the melting point (m.p. 262-263°C). Comparison infra-red and ultra-violet spectra, shown on pages 43 and 44 were the same for the two samples.

Preparation of 3-Acetamido-2-Aminofluoranthene (XII)

The method used for the hydrogenation of 3-acetamido-2-nitrofluoranthene was that devised by Blackburn (1).

3-Acetamido-2-nitrofluoranthene (6.5 g) and palladium-charcoal (0.5 g) were suspended in absolute ethanol (300 ml). Hydrogenation was accomplished in fourteen hours during which

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"This result may be due to the partial decomposition of the amino group.

the gauge pressure decreased from 48 lbs./ sq. in. to 41.5 lbs./ sq. in. The product was brought into solution by addition of pyridine (50 ml) and heating. The catalyst was filtered off and most of the solvent was evaporated under vacuum. Dilution of the remaining solvent with water produced 3-acetamido-2-aminofluoranthene (5.0 g) m.p. 197-199°C (lit. 197-199°C).

Preparation of Authentic 2,3-Diacetamidofluoranthene (XIII)

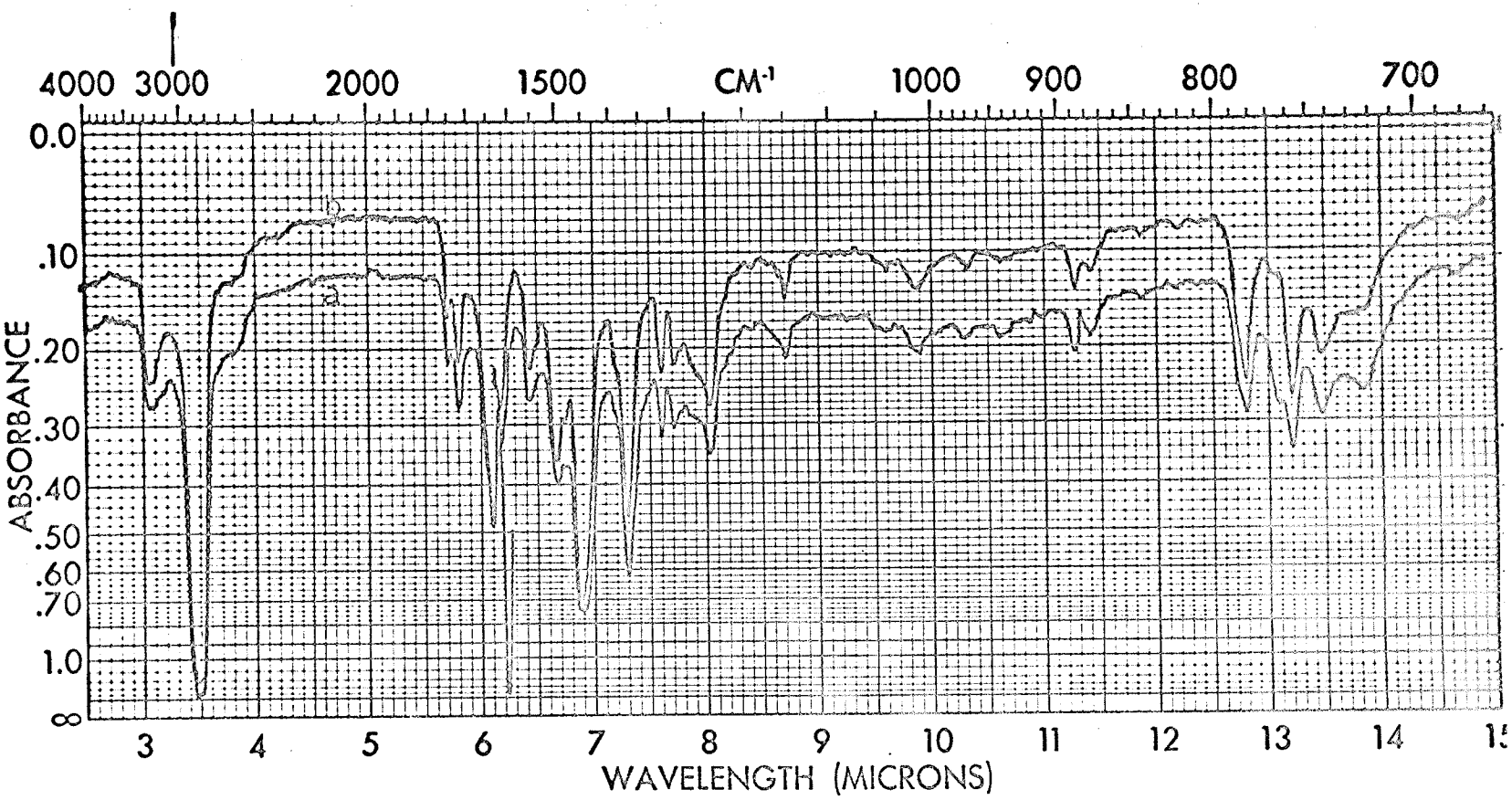
The acetylation of 3-Acetamido-2-aminofluoranthene was performed by Kloetzel, King, and Menkes (22), but these workers did not state full experimental details for this reaction. Pyridine was found to be the best solvent for this reaction.

3-Acetamido-2-aminofluoranthene (1.15 g) was dissolved with stirring at room temperature in pyridine (50 ml). Acetic anhydride (1 ml) was added dropwise. The reaction mixture was stirred at room temperature for sixty minutes during which time a precipitate separated out of solution. The solid was filtered off, washed with water and allowed to dry. Recrystallization from glacial acetic acid gave pure 2,3-diacetamidofluoranthene (0.75 g) as yellow needles with melting point 267-269°C (lit. 268-269°C).

Nitration of 3-Nitrofluoranthene

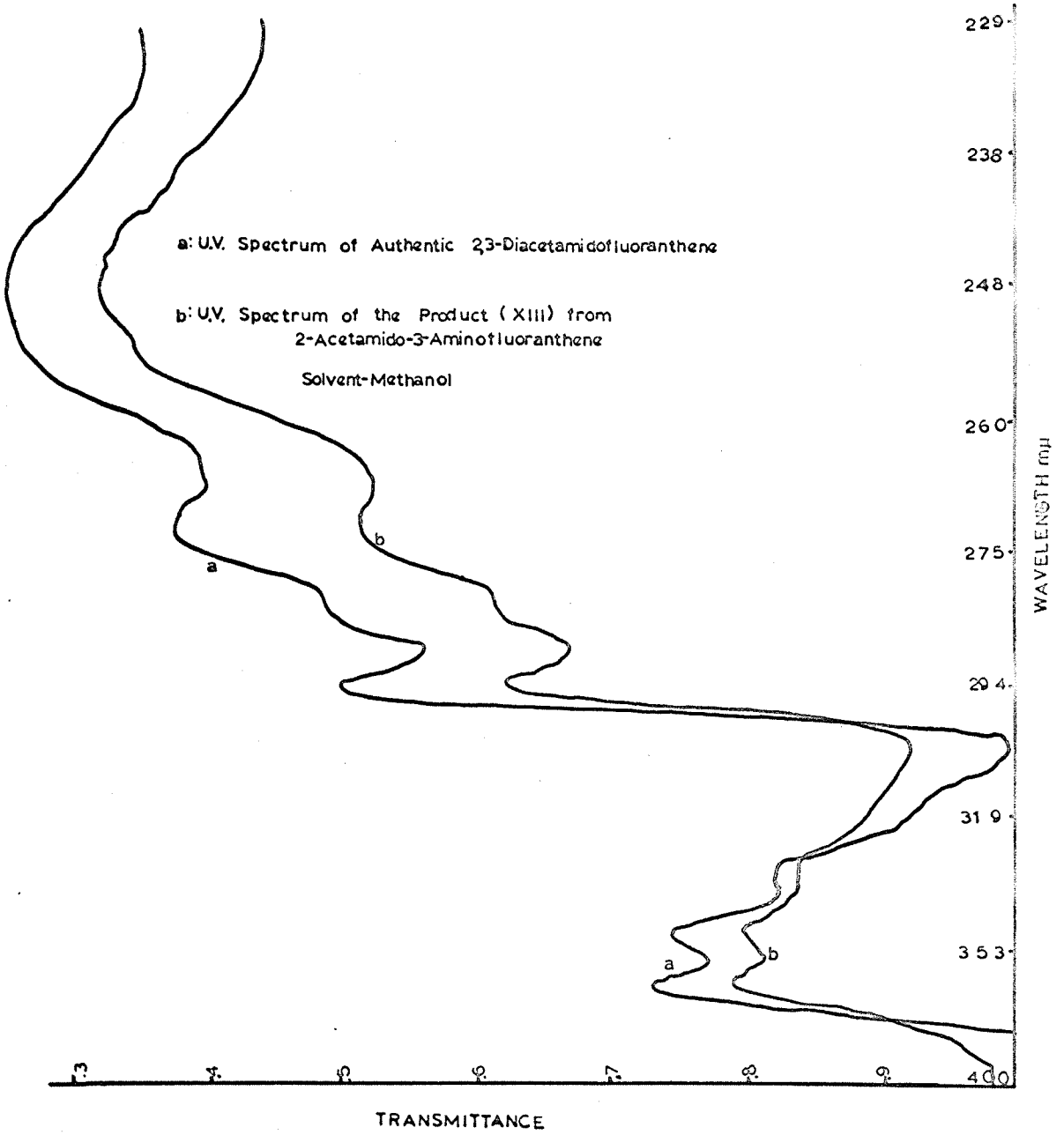
3,9-Dinitrofluoranthene was best obtained by nitration of 3-nitrofluoranthene in acetic anhydride.

Fuming nitric acid (2 ml) was added dropwise, over a period of ten minutes, to a mixture of 3-nitrofluoranthene (2.0 g) in acetic anhydride (60 ml) maintained at 65-71°C. The nitration mixture was stirred at 70-80°C for thirty minutes.



a: I.R. Spectrum of Authentic 2,3-Diacetamidofluoranthene

b. I.R. Spectrum of the Product (XIII) from 2-Acetamido-3-Aminofluoranthene Phase-Nujol Mull


a: U.V. Spectrum of Authentic 2,3-Diacetamidofluoranthene
b: U.V. Spectrum of the Product (XIII) from
2-Acetamido-3-Aminofluoranthene
Solvent-Methanol
a
b
229
238
248
260
275
294
319
353
400
WAVELENGTH mμ
TRANSMITTANCE

It was then allowed to stand at room temperature for a further ninety minutes. The solid (1.5 g) was filtered off and washed with water. Treatment with decolourizing charcoal and several recrystallizations from glacial acetic acid gave pure 3,9-dinitrofluoranthene (0.75 g) as yellow-orange crystals of melting point 275-277°C. A mass spectrum of this compound showed it to be dinitrofluoranthene.

Infra-red peaks of this compound are at: 6.61 and 7.52μ.

Analysis Found: N, 10.26% ''' Calculated for $C_{16}H_8N_2O_4$: N, 9.60%

Attempted oxidation of this product using chromic anhydride regenerated only starting material.

Reduction of 3,9-Dinitrofluoranthene

Catalytic hydrogenation of 3,9-dinitrofluoranthene was effected using palladium-charcoal as the catalyst for the reaction.

3,9-Dinitrofluoranthene (1.5 g) and palladium-charcoal (0.25 g) were suspended in ethanol (100 ml). The dinitro compound was reduced under pressure (26 lbs./sq.in. to 23 lbs./sq.in.) for six hours. The catalyst was filtered off and most of the solvent was evaporated under pressure. The solution of 3,9-diaminofluoranthene was unstable and it darkened quickly. Due to its instability, the diamine was isolated as its acetyl derivative. This preparation is shown below.

Preparation of 3,9-Diacetamidofluoranthene (XVII)

3,9-Diacetamidofluoranthene was prepared by the acetylation of 3,9-diaminofluoranthene, using pyridine as the solvent.

Pyridine (25 ml) was added to the impure 3,9-diaminofluoranthene in ethanol (approximately 10 ml). Acetic anhydride

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''' This result may be due to the presence of some trinitro fluoranthene. This product should be purified by column chromatography rather than by crystallization alone.

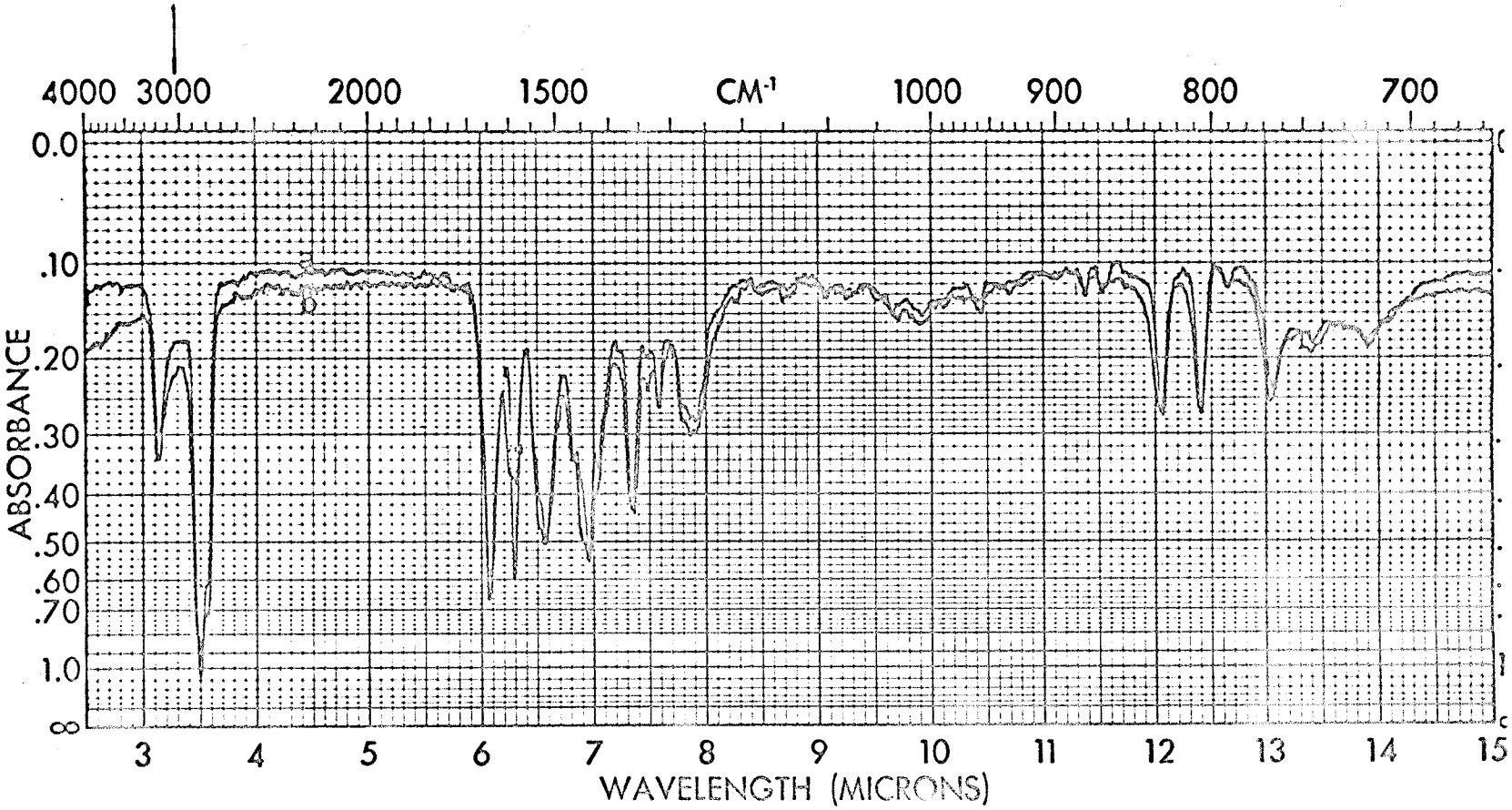
(5 ml) was added to the solution at room temperature. The mixture was stirred for ten hours and then the excess solvent was evaporated off under vacuum. The cream-coloured solid which separated out of solution was filtered off, dried, and finally boiled with benzene. The purified 3,9-diacetamidofluoranthene (0.9 g) was isolated as a light yellow solid of melting point approximately 360°C (lit. ~ 370°C).

Admixture with an authentic sample of 3,9-diacetamidofluoranthene prepared from 3,9-diacetylfluoranthene as shown below, did not depress the melting point. Comparison infrared and ultra-violet spectra of this material, shown on pages 47 and 48 were the same.

Preparation of Authentic 3,9-Diacetamidofluoranthene (XVII)

3,9-Diacetylfluoranthene was prepared from fluoranthene by a Friedel-Crafts reaction using the method of Campbell, Leadhill and Wilshire (6,4). The diacetamido compound was obtained from the diacetyl compound according to the procedure developed by these workers.

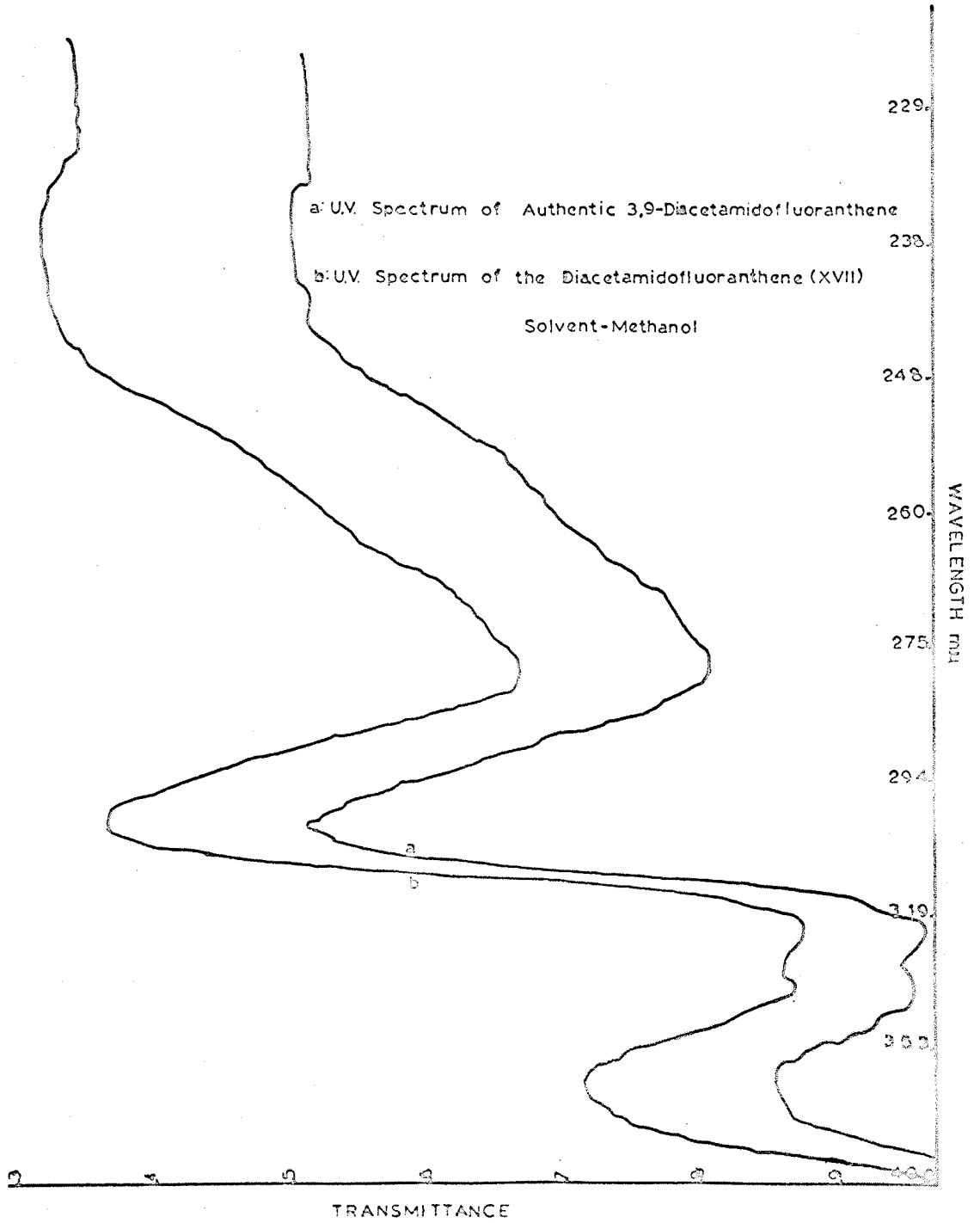
Sodium azide (0.27 g) was added in two portions at an interval of twenty-five minutes to 3,9-diacetylfluoranthene (0.38 g) in trichloroacetic acid (4.2 g) maintained at 60°C. After seven hours at this temperature, the mixture was poured on ice and 3,9-diacetamidofluoranthene precipitated. The product was washed with water and boiled with benzene. 3,9-Diacetamidofluoranthene (0.22 g) of melting point ~ 360°C (lit.~ 370°C) was isolated.



a IR Spectrum of Authentic 3,9-Diacetamidofluoranthene

b IR Spectrum of the Diacetamidofluoranthene (XVII)

Phase - Nujol Mull


a: U.V. Spectrum of Authentic 3,9-Diacetamidofluoranthene
b: U.V. Spectrum of the Diacetamidofluoranthene (XVII)
Solvent-Methanol
229.
238.
248.
260.
275.
294.
319.
363.
WAVELENGTH mμ
a
b
TRANSMITTANCE

Nitration of 2-Nitrofluoranthene

Fuming nitric acid (1 ml) was added dropwise with stirring to a solution of 2-nitrofluoranthene (0.5 g) in freshly distilled acetic anhydride (15 ml). The solution was refluxed for three hours then cooled to room temperature and allowed to stand overnight. The solid (0.15 g) which precipitated out of solution was filtered, washed with water, dried, and dissolved in benzene. The benzene solution was chromatographed on a column (12" x $\frac{1}{2}$") filled with alumina (Brockmann, neutral, Activity 1) and dinitrofluoranthene was eluted in the first portion. The pure 2, ( )-dinitrofluoranthene (0.08 g) was isolated from acetone as bright yellow needles, m.p. 345-347°C (sublimation).

Infra-red peaks of this compound are at: 6.55 and 7.43μ.

Analysis Found: N, 9.59%

Calculated for $C_{16}H_8N_2O_4$: N, 9.60%

Preparation of 3-Acetamido-9-Bromofluoranthene (XX)

The bromination of 3-nitrofluoranthene was accomplished using the method of Campbell and Keir (7). The bromo-nitro compound was hydrogenated essentially by the procedure devised by Charlesworth and Dolenko (9).

3-Amino-9-bromofluoranthene (1.5 ml) was dissolved in benzene (100 ml). Acetic anhydride (1.5 ml) was added to the solution at room temperature. It was stirred for ninety minutes during which time a white solid precipitated. The solid was filtered off, washed with benzene, and allowed to dry. Pure 3-acetamido-9-bromofluoranthene (0.7 g) was obtained as light yellow needles of melting point 280-281°C from chlorobenzene.

Admixture with a sample of 3-acetamido-8-bromofluoranthene prepared as shown below depressed the melting point (m.p. 235-238°C).

Infra-red peaks for this compound are at: 3.23, 6.15, 6.60 and 7.90 μ.

Analysis Found: N, 3.98% Br, 23.89%

Calculated for $C_{18}H_{12}NBrO$: N, 4.1 % Br, 23.6 %

Preparations of 3-Acetamido-8-Bromofluoranthene (XXI)

A. According to the method of Kaminska and Mazonski (20)

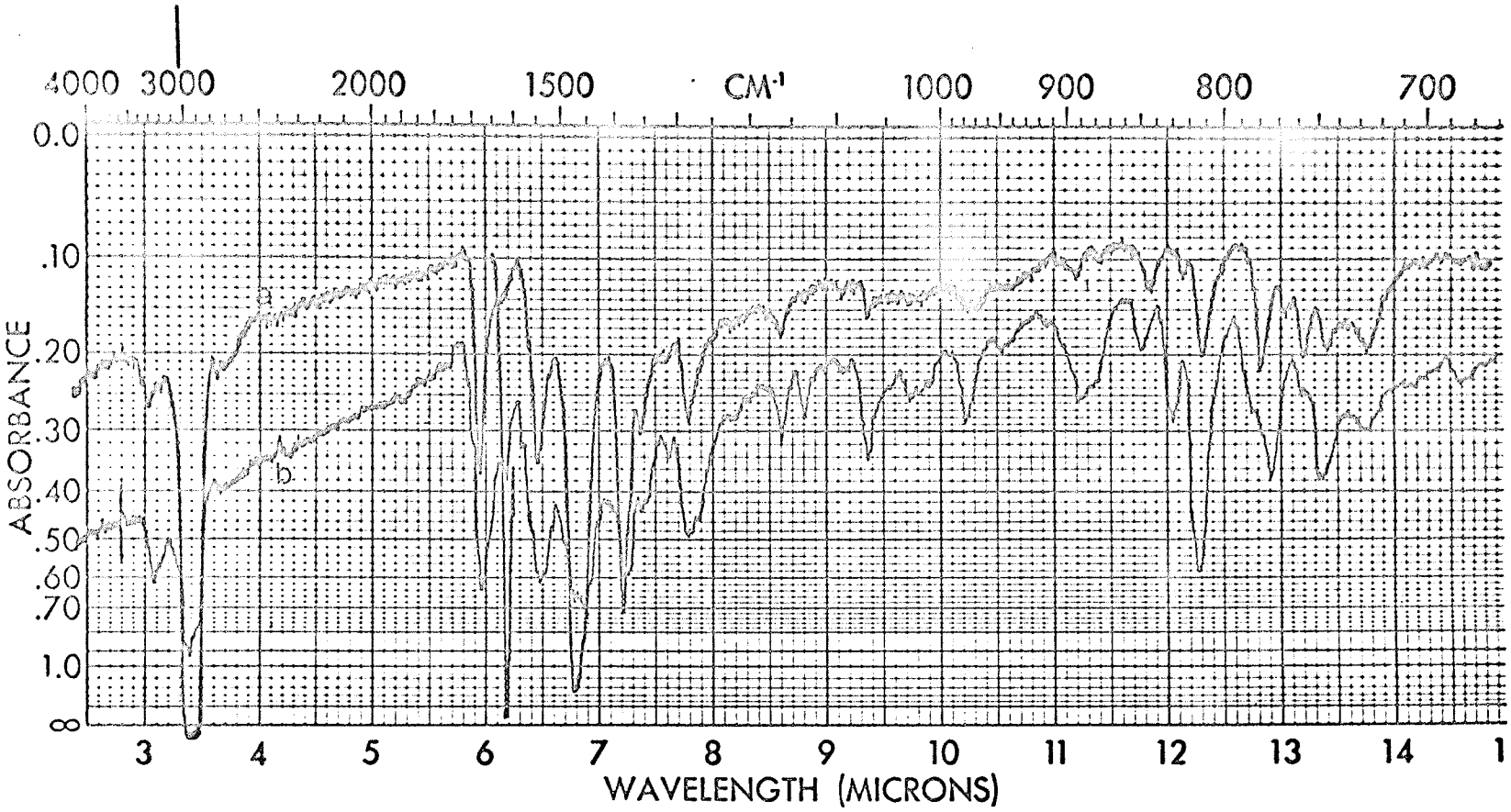
3-Acetamidofluoranthene (2.4g) was dissolved in a hot mixture of glacial acetic acid and carbon tetrachloride (2:1) (150 ml). The solution was cooled to room temperature and bromine (1 ml) in glacial acetic acid (1 ml) was added dropwise with stirring. The resultant mixture was stirred at room temperature for five hours. During this time a solid precipitated out of the solution. This solid was filtered off and washed with sodium bisulfite solution, 10% aqueous sodium hydroxide, and water and then it was dried. Treatment with decolourizing charcoal and recrystallization gave 3-acetamido-8-bromofluoranthene (1.7 g) as yellow micro-crystals, m.p. 248-250°C (lit. 260-262°C).

B. According to the method of Blackburn (1)

Bromine (1 ml) in glacial acetic acid (25 ml) was added dropwise over a period of twenty minutes to a stirred solution of 3-acetamidofluoranthene (2.0 g) in glacial acetic acid (190 ml) at 80°C. The mixture was stirred at 80°C for another thirty-five minutes during which time a small amount of material

precipitated out of solution. The crude product was filtered off, treated with decolourizing charcoal, and recrystallized from chlorobenzene. 3-Acetamido-8-bromofluoranthene (1.1 g) was obtained as yellow micro-crystals of melting point 249-250°C (lit. 265-266°C from pyridine).

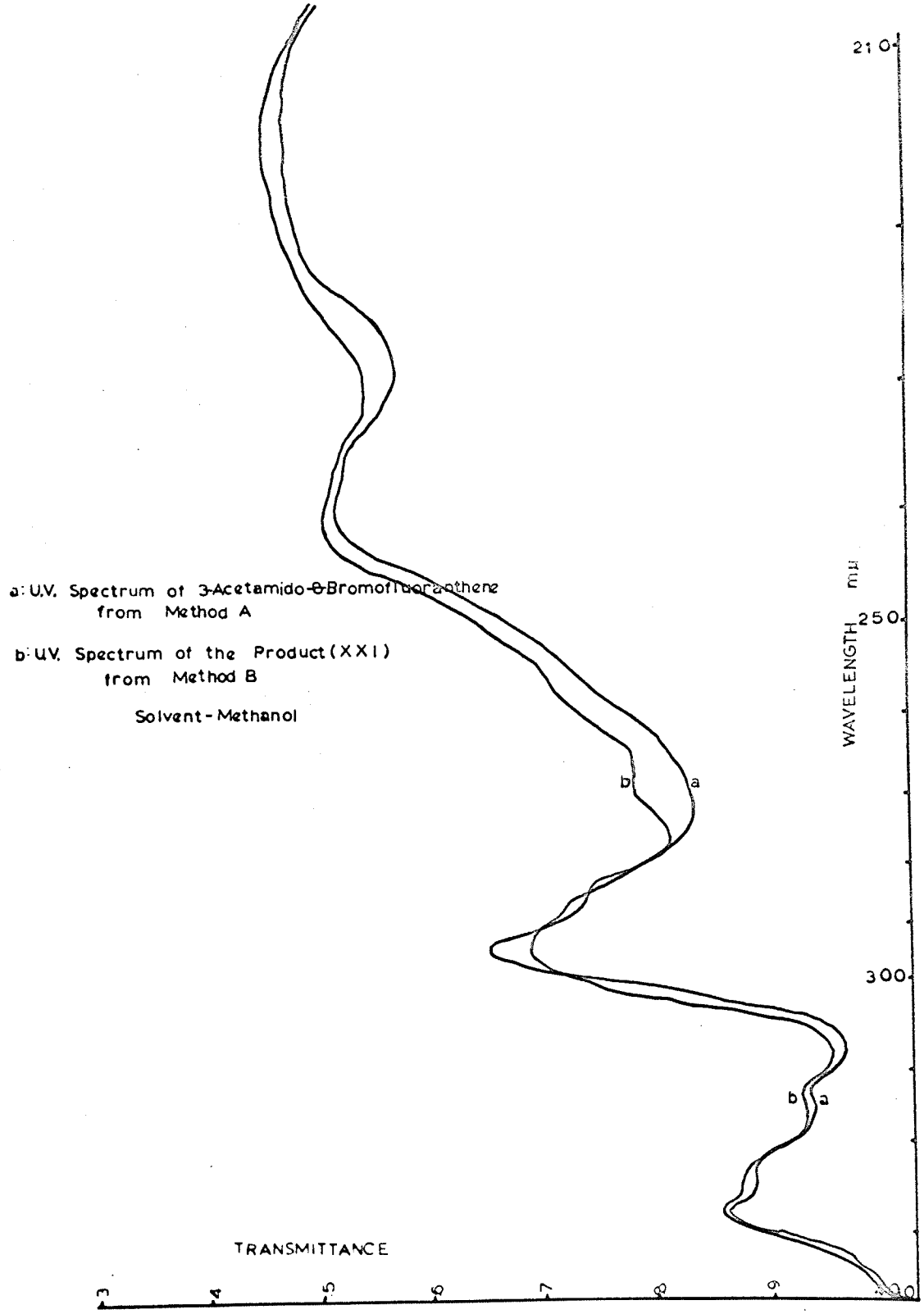
A mixed melting point of the samples from the two methods showed no depression, but the mixed melting point with a sample of 3-acetamido-9-bromofluoranthene was lowered. (m.p. 235-238°C). Comparison infra-red and ultra-violet spectra of samples prepared by methods A and B, on pages 52 and 53 showed no differences.



a IR Spectrum of 3-Acetamido-8-Bromofluoranthene
from Method A

b IR Spectrum of the Product(XXJ)
from Method B

Phase - Nujol Mull


a: U.V. Spectrum of 3-Acetamido-6-Bromofluoranthene from Method A
b: U.V. Spectrum of the Product (XXI) from Method B
Solvent - Methanol
WAVELENGTH mμ
210
250
300
b
a
b
a
TRANSMITTANCE
3
4
5
6
7
8
9
0

SUMMARY

1. Nitration of 2-acetamidofluoranthene in acetic acid gave the previously unknown compound, 2-acetamido-3-nitrofluoranthene.

2. The structure of 2-acetamido-3-nitrofluoranthene was proved in several ways.

(a) The first method was by hydrolysis to the amino-nitro compound and oxidation to 1-fluorenonecarboxylic acid which proved that both groups are in the same ring.

(b) The second way was by deamination of the new compound, 2-amino-3-nitrofluoranthene, to produce the known product, 3-nitrofluoranthene proving that the nitro group entered position 3.

(c) The third way was by hydrogenation of 2-acetamido-3-nitrofluoranthene followed by formation of the o-diacetamido compound. This product was the same as that formed from the known compound 3-acetamido-2-nitrofluoranthene.

3. Nitration of 3-nitrofluoranthene gave the new product, 3,9-dinitrofluoranthene.

4. The orientation of the nitro groups in this dinitro compound was established by reduction and acetylation which gave the known compound, 3,9-diacetamidofluoranthene. This compound was the same as that obtained from 3,9-diacetylfluoranthene through the Schmidt reaction.

5. The nitration of 2-nitrofluoranthene gave a new dinitrofluoranthene. The orientation of this compound was not rigorously proven, however, due to the fact that only very small amounts of this material could be collected.

6. The possible positions for the second nitro group in 2, ( )-dinitrofluoranthene are discussed on the basis of mass spectrophotometric evidence.

7. The previously unknown compound, 3-acetamido-9-bromofluoranthene was prepared by acetylation of the known compound 3-amino-9-bromofluoranthene.

8. A comparison of the products from the bromination of 3-acetamidofluoranthene, prepared according to two methods, was made and it was shown that the product obtained by Blackburn's procedure was the same as that of Kaminska and Mazonski, however it is probably not as pure as that of the latter workers.

9. The position to which the bromine atom enters is determined not only by the substituent present, but also by the solvent which is used.

RECOMMENDATIONS FOR FUTURE WORK

1. More 2, ( )-dinitrofluoranthene should be produced and the orientation of the second nitro group should be proved, possibly by the preparation of the dibromo compound and comparison with that prepared from 2-nitro-9-bromofluoranthene.

2. Another attempt to prepare 3,9-dibromofluoranthene from 3,9-diaminofluoranthene should be made.

3. Another attempt could be made to oxidize both 3,9- and 2, ( )-dinitrofluoranthene to the corresponding dinitrofluorenonecarboxylic acids.

4. 8-Nitrofluoranthene had been isolated by Kloetzel et al. (22) from the nitration mixture remaining after the nitration of fluoranthene. Since no research has been carried out to investigate the direction of substitution caused by substituents in the benzenoid part of the fluoranthene molecule, this compound could be the starting material. Bromination and nitration reactions could be carried out on it.

5. 8-Amino- and 8-acetamidofluoranthene have also been prepared by Kloetzel et al. (22). These compounds could also be subjected to nitration and bromination to find the effect of highly activating species in the benzenoid ring system.

6. The 8-halo substituted series may be prepared using a similar method to that devised by Blackburn (1) for 3-aminofluoranthene.

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