THE SYNTHESIS AND ORIENTATION OF SOME FLUORANTHENE COMPOUNDS

by

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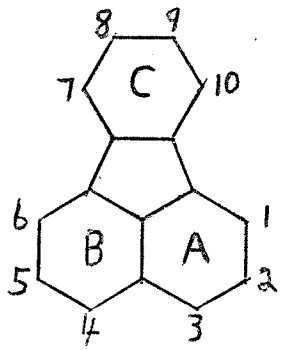
ABSTRACT

It is shown that 3-acetamido-, and 3-aminofluoranthene are brominated in the 2-position. As a result of this work two new fluoranthene derivatives are reported: 3-acetamido-2-bromofluoranthene and 2-bromofluoranthene. The theoretical implications of these results are discussed.

TABLE OF CONTENTS

INTRODUCTION

Very few disubstituted fluoranthene derivatives have been made by reaction on monosubstituted derivatives, and consequently little is known regarding the directive properties of substituents in the fluoranthene nucleus. It is known that 3-carboxy-, 3-carbomethoxy-, 3-cyano-, and 3-nitrofluoranthene are all brominated in the 9-position. Sulfonation of fluoranthene gives 3,9-fluoranthenedisulfonic acid. 3-Bromofluoranthene on further bromination yields 3,8-dibromofluoranthene and 3-acetylfluoranthene on further acetylation yields 3,9-diacetylfluoranthene.



On the basis of the above data, and by drawing an analogy to the disubstitution of diphenyl, Campbell and Keir (4) postulated that a meta-directing substituent in ring A would direct to position 9 and an ortho-para-directing

substituent in the same ring would direct to position 8. Since these rules were postulated, in 1955, one further relevant piece of data has been obtained by Kloetzel, King, and Menkes (17). It has been shown that 3-acetamidofluoranthene nitrates in the 2-position indicating the above postulate is oversimplified. They suggested, that in this case, substitution occurred in the same ring because the acetamido group is a more intensely activating group.

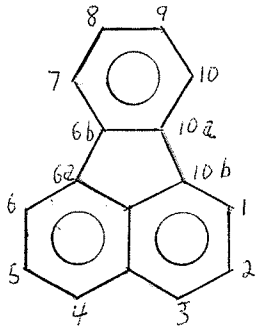
In view of the above work it seemed apparent that further experimentation was necessary on this problem. Nitration of 3-acetamidofluoranthene was the only result inconsistent with the orientation rule of Campbell and Keir. Consequently it seemed logical to see if this compound would brominate in the same position as it nitrated. It was also considered desirable to determine the directive effect of the amino group in the 3-position. If the acetamido group causes substitution in the same ring because it is an intensely activating group as suggested above, then the amino group which is an even more intensely activating group should also cause substitution in the same ring.

LITERATURE SURVEY*

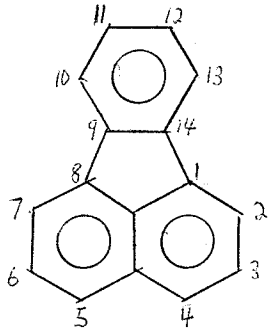
Introduction

Fluoranthene was originally discovered independently by Fittig and Gebhard (10) and by Goldschmiedt (12) in 1877. Goldschmiedt obtained fluoranthene from the mercury ores of Idria. Fittig and Gebhard isolated their sample from the green oil or high-boiling fraction of coal tar. It was not until 1929 that von Braun and Anton (1) proposed and established synthetically the correct structural formula for fluoranthene. Prior to this time little work was done on the chemistry of fluoranthene.

Fluoranthene is a colourless crystalline hydrocarbon melting at 111° C. It has the structure shown below. W



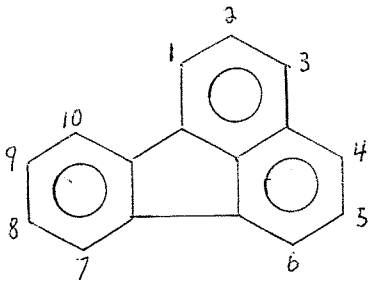
W



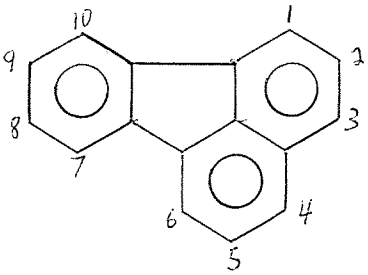
X

*For an excellent review of fluoranthene chemistry up to 1951 see reference (23).

is the numbering system employed by Chemical Abstracts and X is that used by most European chemists. The Chemical Abstracts system will be used exclusively throughout the rest of this thesis. The molecule is also frequently drawn in either of the following ways.

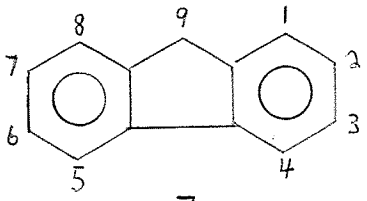


Y



Y'

These latter formulae have some advantages if relationships with the coal tar hydrocarbon fluorene (Z) are being considered.



Z

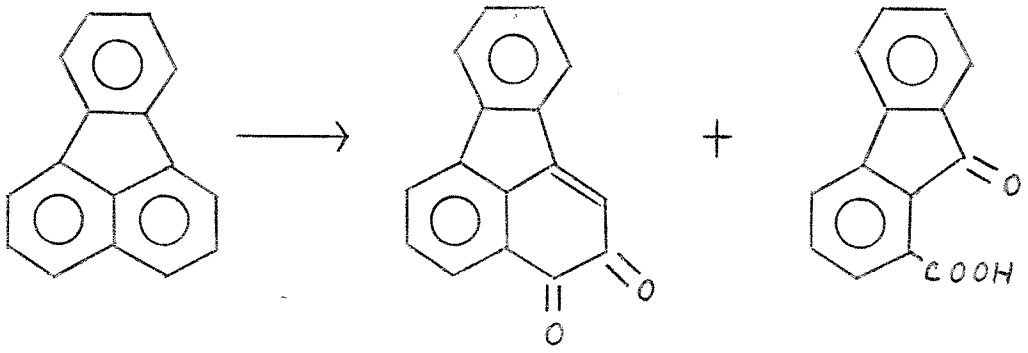
Addition Compounds of Fluoranthene (8, 23)

Like most other aromatic hydrocarbons fluoranthene forms molecular complexes with polynitro compounds. These complexes, often used for characterization, include the

picrate, m.p. 185-186° C.; the 1,3,5-trinitrobenzene complex, m.p. 205-206° C.; the, 1,3-dinitrobenzene complex, m.p. 77° C.; the 2,4-dinitrotoluene complex, m.p. 75.5° C.; the 2,4,7-trinitrofluorenone complex, m.p. 215.4-216.0° C. and several others.

Oxidation of Fluoranthene (23)

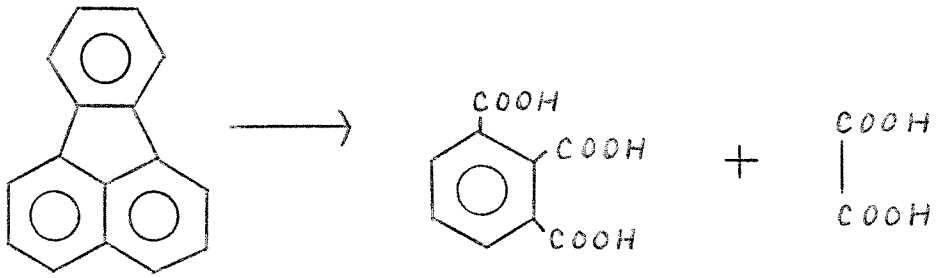
The products of oxidation of fluoranthene vary greatly with the oxidizing conditions. Using potassium chromate in dilute sulfuric acid and chromic anhydride or potassium chromate in acetic acid the principal products isolated are 2,3-fluoranthenequinone (I) and 1-fluorenonecarboxylic acid (II).



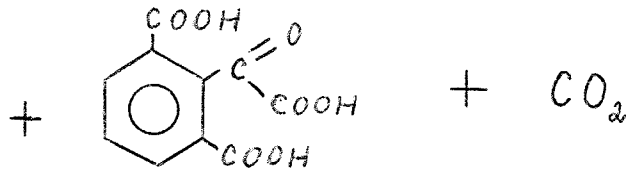
I II

On prolonged alkaline permanganate oxidation the main products are hemimellitic acid (III), oxalic acid, carbon

dioxide, with some 2,6-dicarboxyphenylglyoxylic acid (IV).

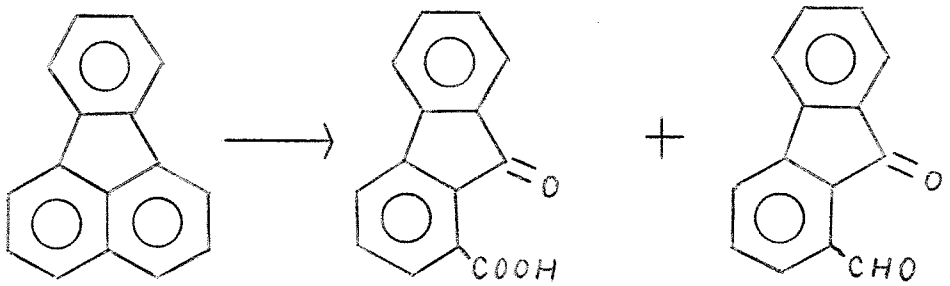


III



IV

Ozonolysis in glacial acetic acid yields a mixture of 1-fluorenonecarboxylic acid (II) and 1-fluorenonealdehyde (V).



II V

Monosubstitution in Fluoranthene (7, 23)

Monosubstitution in fluoranthene occurs predominantly in the 3-position, but even under carefully controlled conditions other products are usually present.

Controlled bromination in carbon disulfide yields mainly 3-bromofluoranthene and some of the 8-isomer. Monochloro- and monoiodo- derivatives have not been obtained by direct halogenation, complex mixtures of polysubstituted products of unknown orientation being obtained instead. Excess of bromine also yields polysubstituted products.

3-Fluoranthenesulfonic acid can be obtained by direct sulfonation of fluoranthene in an inert solvent.

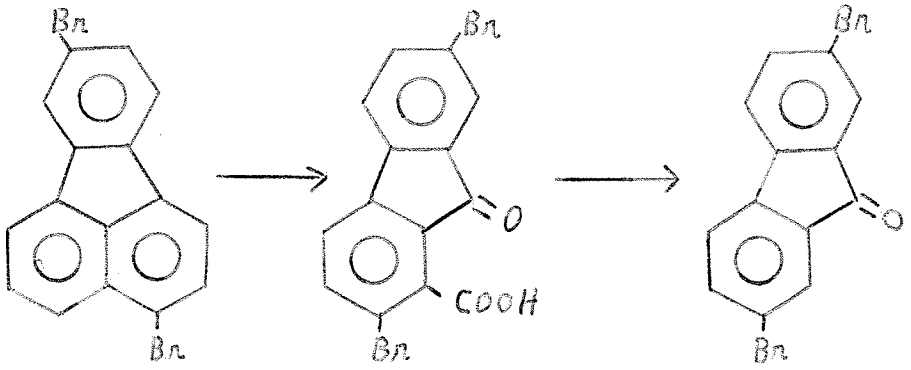
Nitration of fluoranthene in acetic acid yields mainly the 3-nitro isomer and some of the 8-isomer.

A Friedel-Crafts reaction with benzoyl chloride in the presence of aluminum chloride in carbon disulfide gives a mixture of 3- and 8-benzoylfluoranthene in approximately equal quantities. The action of acetyl bromide in the presence of aluminum chloride gives a mixture of 3- and 8-acetylfluoranthene. Either on further treatment yields

3,9-diacetylfluoranthene.

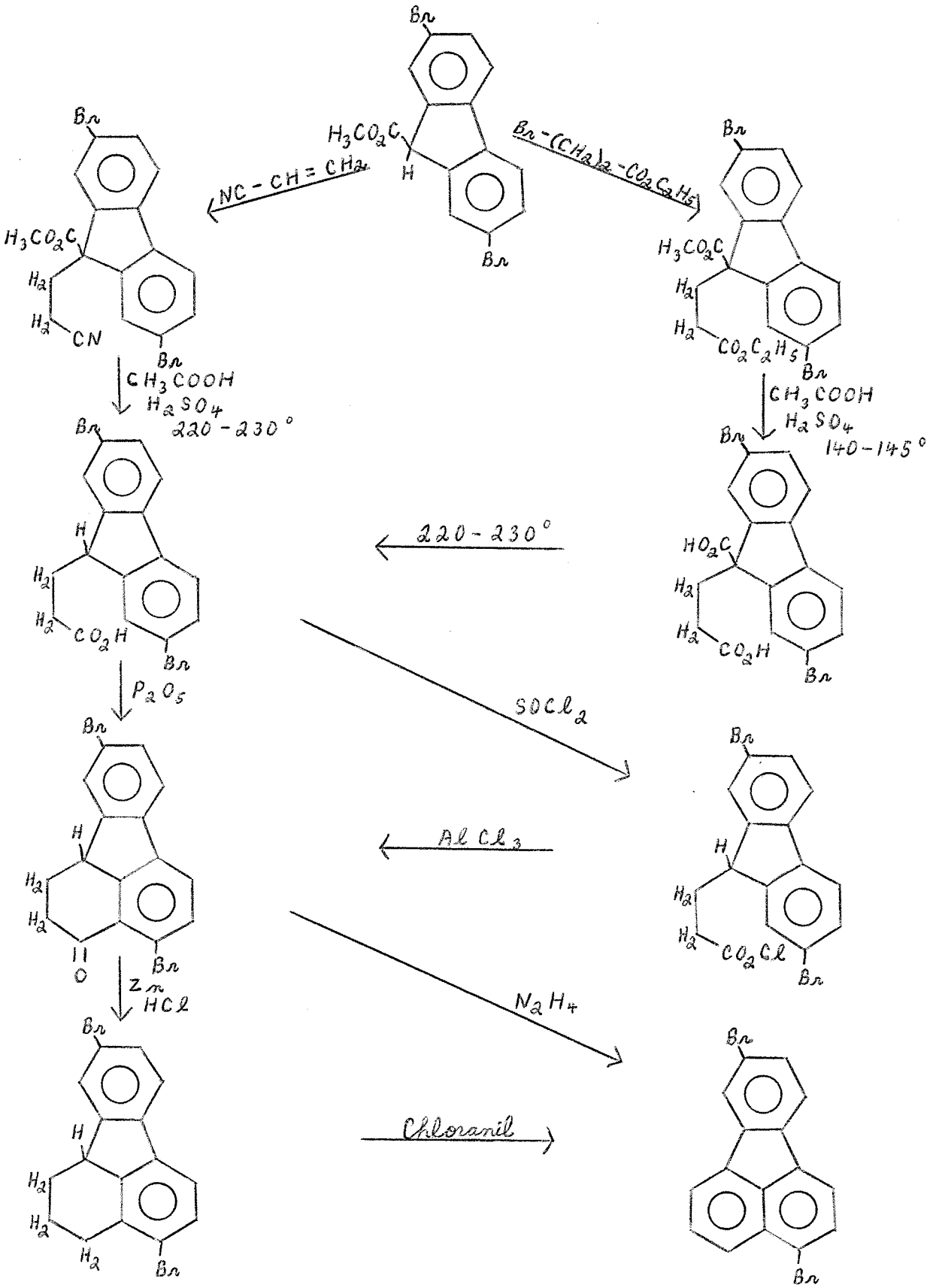
Orientation of Disubstitution in Fluoranthene

The first disubstituted fluoranthene compound whose orientation was determined was 3,8-dibromofluoranthene (VI) in 1950. This compound, most conveniently prepared by bromination in nitrobenzene, has had its structure ascertained by two independent methods. The following proof is by Campbell and his co-workers (3). Chromic acid oxidation of the dibromofluoranthene gave a dibromo-1-fluorenonecarboxylic acid which on decarboxylation with mercuric oxide at 180° C. gave 2,7-dibromofluorenone (VII).

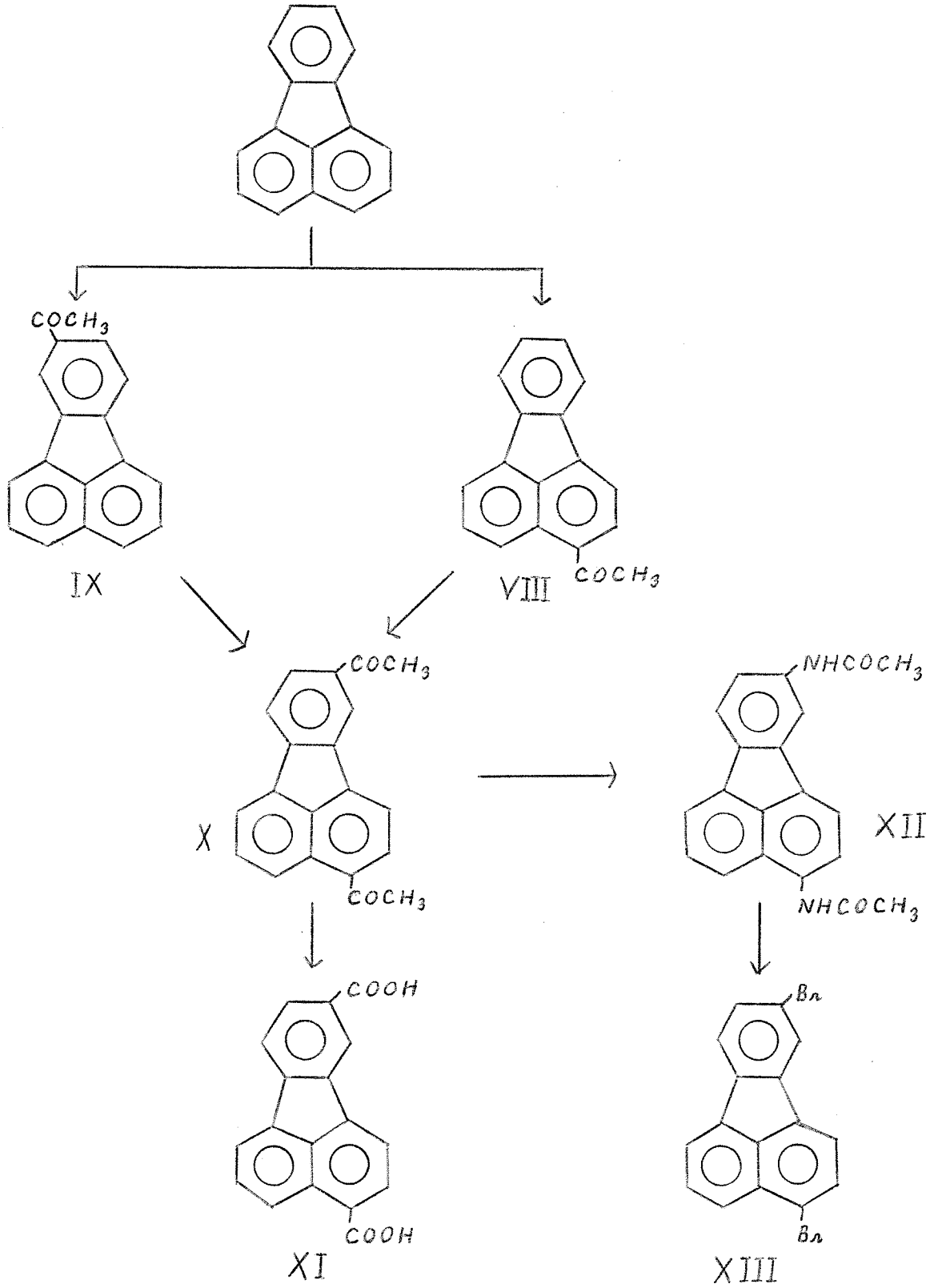


VI VII

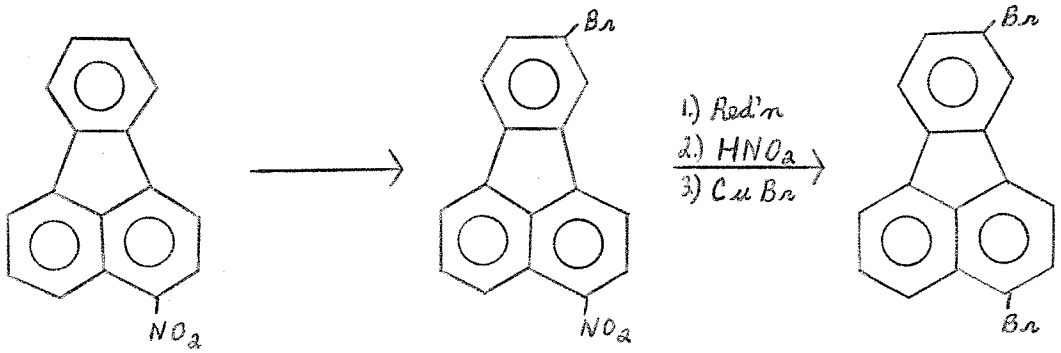
The structure was independently determined by Holbro and Tagmann (15) who synthesized 3,8-dibromofluoranthene from methyl 2,7-dibromo-9-fluorenecarboxylate as shown on page 9.


NC - CH = CH2
Br - (CH2)2 - CO2C2H5
CH3COOH
H2SO4
220 - 230°
CH3COOH
H2SO4
140 - 145°
220 - 230°
P2O5
SOCl2
AlCl3
Zn
HCl
N2H4
Chloranil

In 1951, Campbell et al. (5) were able to show that 3-acetylfluoranthene yielded 3,9-diacetylfluoranthene on further acetylation. They found that the action of acetyl bromide on fluoranthene in the presence of aluminum chloride gave a mixture of 3- (VIII) and 8-acetylfluoranthene (IX) which could be separated chromatographically. Both isomers on further acetylation gave the same diacetyl-fluoranthene (X) which therefore must be either 3,8- or 3,9-diacetylfluoranthene. A decision in favour of the 3,9-isomer was obtained by oxidation to a fluoranthenedicarboxylic acid (XI) which was different from 3,8-fluoranthenedicarboxylic acid prepared from 3,8-dibromofluoranthene via the dinitrile. Further confirmation that this was not the 3,8-isomer was obtained by converting the diacetylfluoranthene into the diacetamido compound (XII) by the Schmidt reaction (using sodium azide in trichloroacetic acid). Hydrolysis of the diacetamido compound, followed by diazotization, and the Sandmeyer reaction gave a dibromofluoranthene (XIII) which was different from 3,8-dibromofluoranthene and therefore must be 3,9-dibromofluoranthene. Their work is summarized as follows.

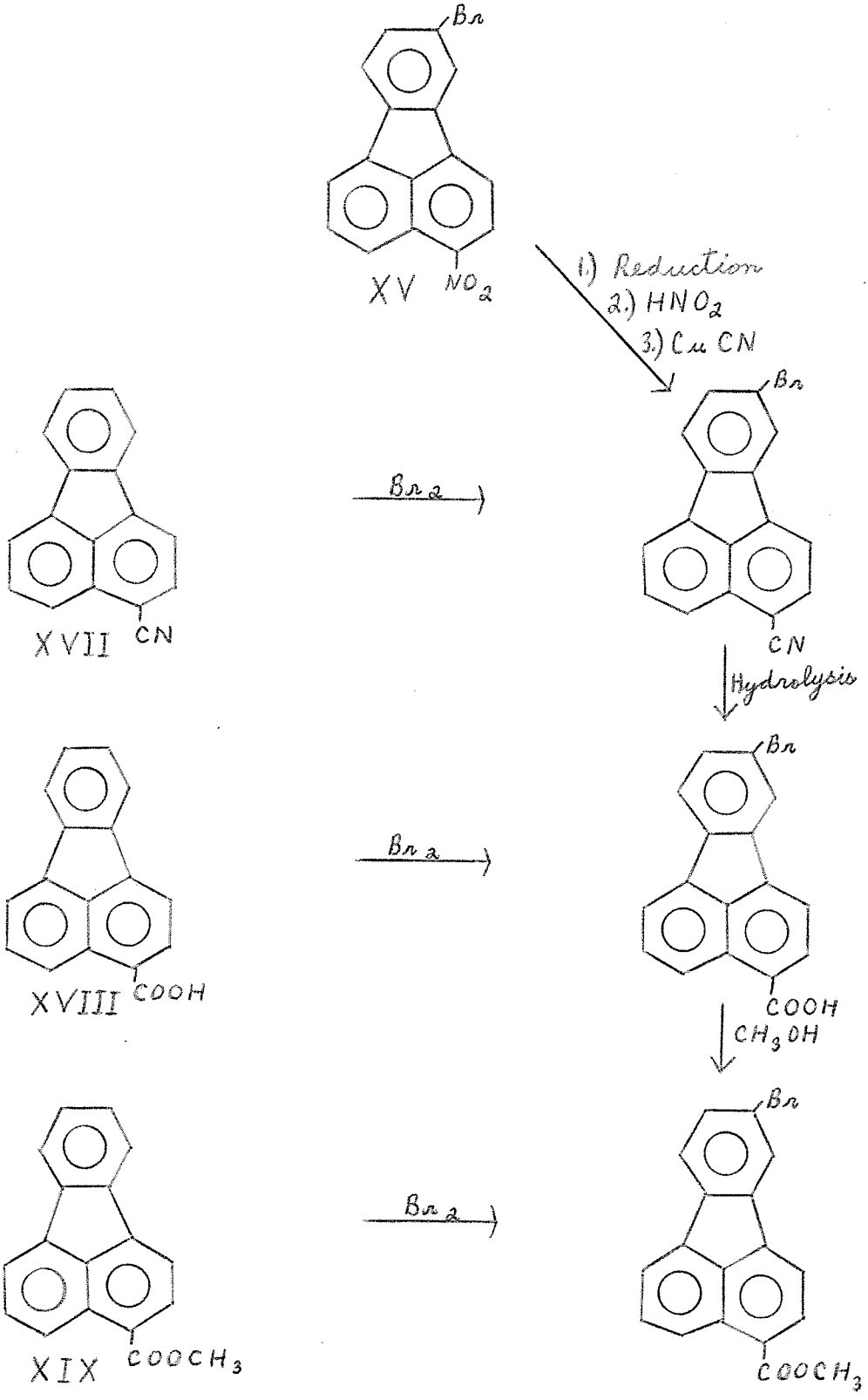

COCH3
IX
VIII
COCH3
COCH3
X
COCH3
NHCOCH3
XII
NHCOCH3
COOH
XI
COOH
Bn
XIII
Bn

In 1955, Campbell and Keir (4) published results on the orientation of five more disubstituted fluoranthene derivatives. Bromination of 3-nitrofluoranthene (XIV) in nitrobenzene gave 9-bromo-3-nitrofluoranthene (XV). This structure was proven by converting it to a sample of dibromofluoranthene (XVI) identical with a sample prepared from 3,9-diacetylfluoranthene. This work can be summarized as follows.



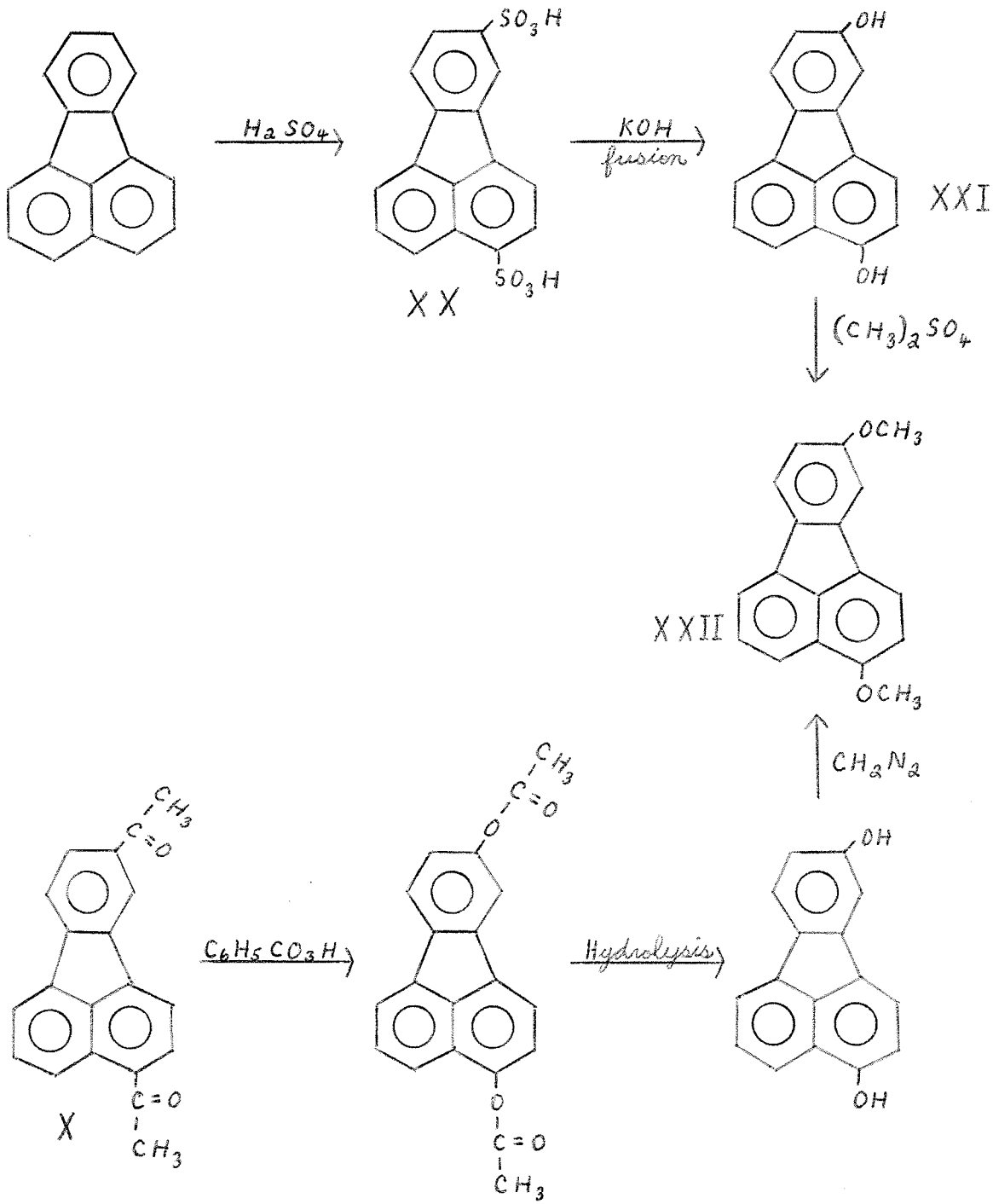
XIV XV XVI

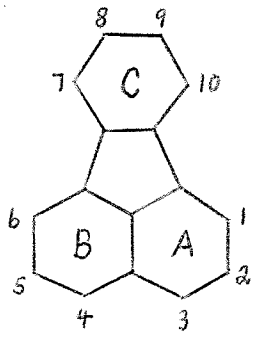
By the following series of reactions it was shown that 3-cyano- (XVII), 3-carboxy- (XVIII), and 3-carbomethoxyfluoranthene (XIX) were all brominated in the 9-position.


Br
XV NO2
1.) Reduction
2.) HNO2
3.) Cu CN
Br
CN
Br2
XVII CN
Hydrolysis
Br
COOH
Br2
XVIII COOH
CH3OH
Br
COOCH3
Br2
XIX COOCH3

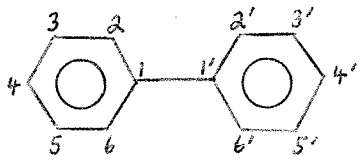
The orientation of the disulfonic acid (XX) obtained by the direct sulfonation of fluoranthene was obtained in the following way. Since monosulfonation occurs mainly in the 3-position the disulfonic acid must contain one sulfo group in that position. The orientation was established by fusing the acid with potassium hydroxide to give a dihydroxy compound (XXI), methylation of which yielded a dimethoxy-fluoranthene (XXII) identical with a specimen prepared from 3,9-diacetylfluoranthene (X). It should be noted that this work rests on the assumption that the fusion of the sulfonic acid with alkali has not been accompanied by the migration of one or both sulfo groups. This work is summarized on the next page.

On the basis of the above work Campbell and Keir (4) in 1955 postulated rules regarding orientation in fluoranthene. They observed that 3-substituted fluoranthenes undergo further substitution mainly in the 8- or 9-position according to whether the first substituent is ortho-para- or meta-directing. To formulate a possible explanation of these results they considered fluoranthene as a diphenyl derivative containing the diphenyl nuclei AC or BC. They pointed out that in the


H_2SO_4
SO_3H
SO_3H
XX
KOH
fusion
OH
OH
XXI
$(CH_3)_2SO_4$
OCH_3
OCH_3
XXII
CH_2N_2
$C_6H_5CO_3H$
Hydrolysis
CH_3
C=O
O
C=O
CH_3
OH
OH
X
C=O
CH_3



diphenyl series orientation is dominated by the phenyl groups. "To be more specific, substitution in most cases 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. The three nitrodiphenyls,

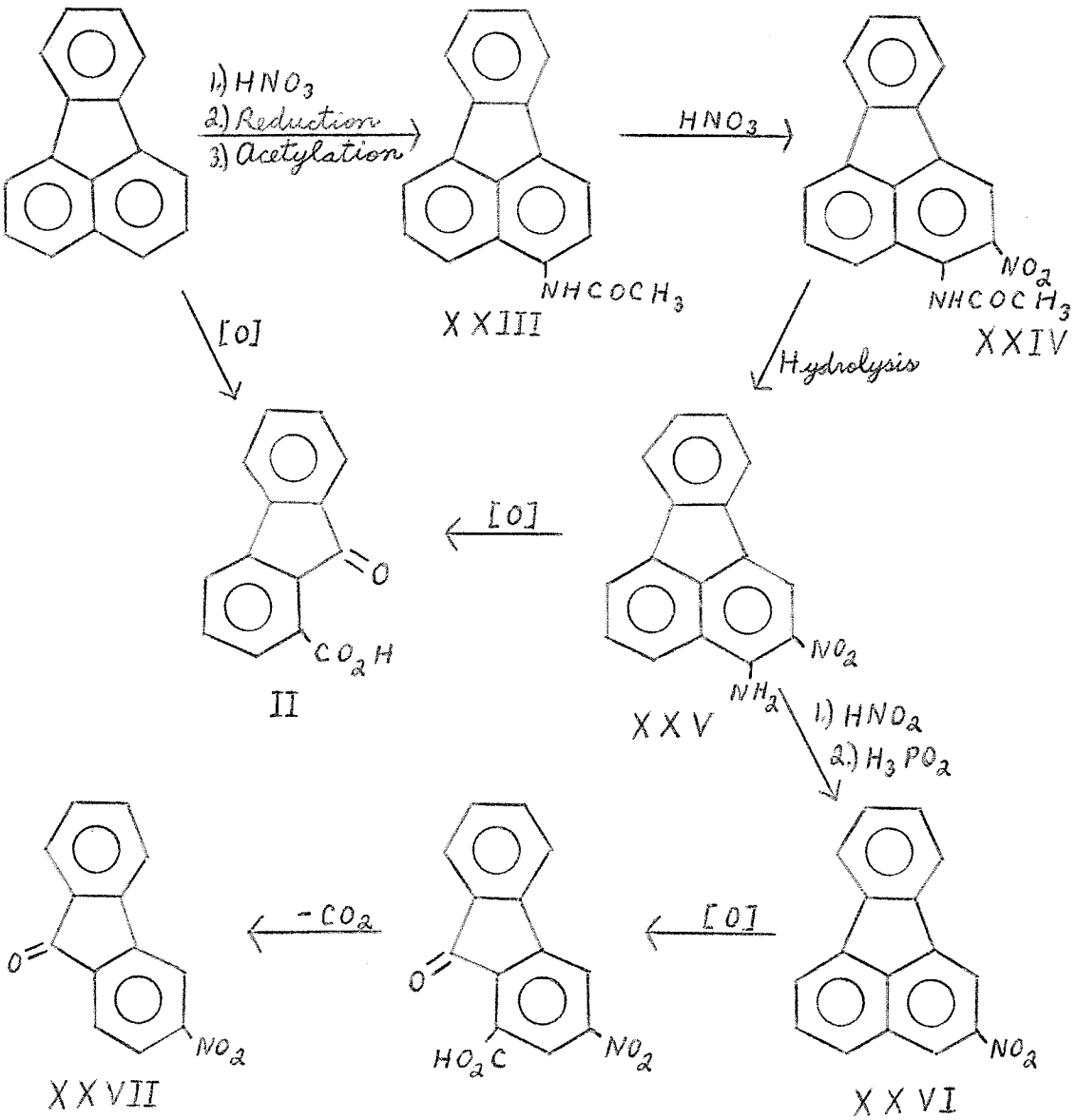


for example, undergo substitution in the 2′- and 4′-positions, but not in the 3′ (meta)-position." They also pointed out that the same regularities are observed in the fluorene molecule. Applying this to fluoranthene they postulated the following, "(1) each of the rings A and B direct substituents predominantly 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 1956, Kloetzel et al. (17) reported a case which did not obey the above rules. They found that 3-acetamido-fluoranthene (XXIII) was nitrated in the 2-position. They accounted for this new type of orientation by postulating that the acetamido group "so intensely activates the ring to which it is attached that the second substituent enters the same ring." They point out that this work "indicates that the orientation rule of Campbell and Keir is over-simplified to the extent that it does not take into account the effects of intensely activating substituents." Kloetzel et al. proved the structure of 3-acetamido-2-nitrofluoranthene (XXIV) in the following manner. Oxidation of 3-amino-2-nitrofluoranthene (XXV) gave 1-fluorenonecarboxylic acid (II) indicating that the nitro group must occupy position 1 or position 2. Deamination of the amino-nitro compound gave a

nitrofluoranthene (XXVI). Oxidation of this followed by decarboxylation gave 3-nitrofluorenone (XXVII) proving the nitro group must be in position 2. This can be summarized as follows.



DISCUSSION OF RESULTS

The purpose of this investigation was to see if 3-acetamidofluoranthene would brominate in the same position as it nitrated, i.e. the 2-position, and to determine the directive effect of the amino group.

3-Nitrofluoranthene was prepared essentially by the method of Garascia, Fries, and Ching (11). The preparation of 3-aminofluoranthene (XXVIII) was accomplished in a manner similar to that described by Kloetzel, King, and Menkes (17) using catalytic reduction of 3-nitrofluoranthene with hydrogen and platinum oxide under slight pressure. 3-Acetamidofluoranthene (XXIII) was also prepared by the method of the above workers by acetylation of 3-aminofluoranthene with acetic anhydride.

Bromination of 3-acetamidofluoranthene to give 3-acetamido-2-bromofluoranthene (XXIX) was successfully accomplished by bromination in pyridine at room temperature for ten hours. Brominations in acetic acid at various temperatures were carried out. Under these conditions we were unable to obtain a satisfactory product, though a small

amount of halogen containing material was obtained which had a melting point close to that of 3-acetamido-2-bromofluoranthene. However the mixed melting point of these compounds gave a large depression. Due to low yield and lack of time, further investigation was not carried out on this compound. Brominations in acetic acid, employing anhydrous aluminum bromide as a catalyst caused extensive decomposition and were therefore unsatisfactory.

At first difficulty was experienced in trying to hydrolyze the 3-acetamido-2-bromofluoranthene due to the extreme insolubility of this compound. However it was found that 3-amino-2-bromofluoranthene (XXX) could be obtained in fairly good yield by refluxing in a pyridine, methanol, sodium hydroxide solution for ten hours.

Oxidation of 3-amino-2-bromofluoranthene was carried out to determine whether the bromine atom and the amino group were on the same ring or not. If these two groups were on the same ring we would expect the ring containing the groups to break and, thus, 1-fluorenonecarboxylic acid (II) would be obtained. If the groups were on different rings we would expect the ring containing the amino group to break and, thus, a bromo-1-fluorenonecarboxylic acid would be

obtained. Oxidations were carried out by refluxing with chromic anhydride or sodium dichromate in glacial acetic acid. In the latter case bromine was evolved copiously indicating the bromine atom and the amino group were on the same ring. Difficulty was met in trying to purify the 1-fluorenonecarboxylic acid that was obtained on oxidation by either method. Crystallization from various solvents and attempts at purification by treatment with barium carbonate and by sublimation failed to bring the melting point up to that of an authentic sample of 1-fluorenone-carboxylic acid prepared by oxidation of fluoranthene. However when the authentic sample was admixed with the sample prepared from the bromo-amino compound it gave no melting point depression. A comparison of the infrared spectra of the two samples also showed they were the same.

The preparation of derivatives of 1-fluorenone-carboxylic acid was attempted in order to give further confirmation to the identity of the above compound. Treatment of the authentic 1-fluorenonecarboxylic acid with phenyl-hydrazine failed to give the compound described by Goldschmiedt (13). The melting point of our compound was

much lower and did not melt with vigorous evolution of gas as did that described by Goldschmiedt. Goldschmiedt states his compound was soluble in alkali. Our compound was also soluble in alkali, but with a very slight amount of insoluble material. The compound obtained on acidification of the alkali solution had a much lower melting point and now appeared to melt with some evolution of gas. It seems the possibility exists that our compound and that of Goldschmiedt could be geometrical isomers. In view of the above, it was apparent that a great deal of work would have to be done to reach any definite conclusion on this problem. As this problem had really nothing to do with the original aims of the research project, this work was abandoned. The treatment of our sample and the authentic sample of 1-fluorenonecarboxylic acid with p-nitrophenylhydrazine gave the same compound, as the products had the same melting point and a mixed melting point gave no depression. However this work was also abandoned as this compound left considerable insoluble material when dissolved in alkali, and had a lower melting point when recovered from the alkali solution.

The synthesis of an authentic sample of 3-acetamido-

2-bromofluoranthene was attempted to determine the structure of our compound. 3-Acetamido-2-aminofluoranthene (XXXI) was prepared by the method of Kloetzel et al. (17) by nitration of 3-acetamidofluoranthene (XXIII), followed by reduction of the nitro group. Attempts to convert 3-acetamido-2-aminofluoranthene into 3-acetamido-2-bromofluoranthene ~~were~~ met with failure. Due to the weakly basic character and insolubility of polycyclic amines high concentrations of sulfuric acid are required for their diazotization. This amine, under these conditions, formed a tarry material. With the hope of avoiding tar formation, it was decided to make the amine salt first and then try to diazotize the salt. The amine salt was precipitated out of ether solution as a white flocculent substance on addition of concentrated sulfuric acid. The salt was filtered out and allowed to dry on the filter paper. As the ether evaporated off the white salt turned to a black tarry material. It is possible that this tar formation is due to some interaction between the acetamido and amino groups. As a result of this no further attempts at diazotization were made as this appeared futile.

Reduction of the diazonium salt of 3-amino-2-bromofluoranthene with hypophosphorous acid gave 2-bromofluoranthene (XXXII). The structure of this compound was determined by comparing it to an authentic sample of 2-bromofluoranthene synthesized from the known 2-amino-fluoranthene (XXXIII). The fact that the amino group and bromine atom were on the same ring plus the fact that 2-bromofluoranthene was obtained on deamination of the bromo-amino compound proves that bromination of 3-acetamido-fluoranthene takes place in the 2-position.

2-Nitrofluoranthene (XXVI) was synthesized by the method of Kloetzel et al. (17) by nitration of 3-acetamidofluoranthene followed by hydrolysis and deamination. Reduction gave the 2-amino compound. Difficulty was met in trying to diazotize this compound. Diazotization by the conventional methods, used for insoluble and weakly basic amines, requires a high concentration of sulfuric acid. Attempts by this procedure resulted in a large amount of decomposition though some diazotization took place as shown by the B-napthol test. This problem was solved by introducing

a modification to the diazotization procedure not previously seen in the literature by this author. In our method the amine sulfate is first prepared by dissolving the amine in an inert solvent such as ether, followed by precipitation of the salt with concentrated sulfuric acid. The amine sulfate is filtered, dried, and finely ground. Then it is dissolved by warming in a solution of equal volumes of concentrated sulfuric acid and glacial acetic acid. An equal volume of ice and water is added to the cooled solution, precipitating out the amine sulfate in a finely divided form which is conducive to going into solution. Diazotization is then effected by addition of an aqueous solution of sodium nitrite. Though this method has only been tried on 2- and 3-aminofluoranthene it is possible that this method might be of general application and prove to be of considerable value in the diazotization of weakly basic, insoluble amines which undergo decomposition in strong sulfuric acid solutions. Diazotization by this method followed by the Sandmeyer reaction gave 2-bromofluoranthene (XXXII).

The bromination of 3-aminofluoranthene was recorded

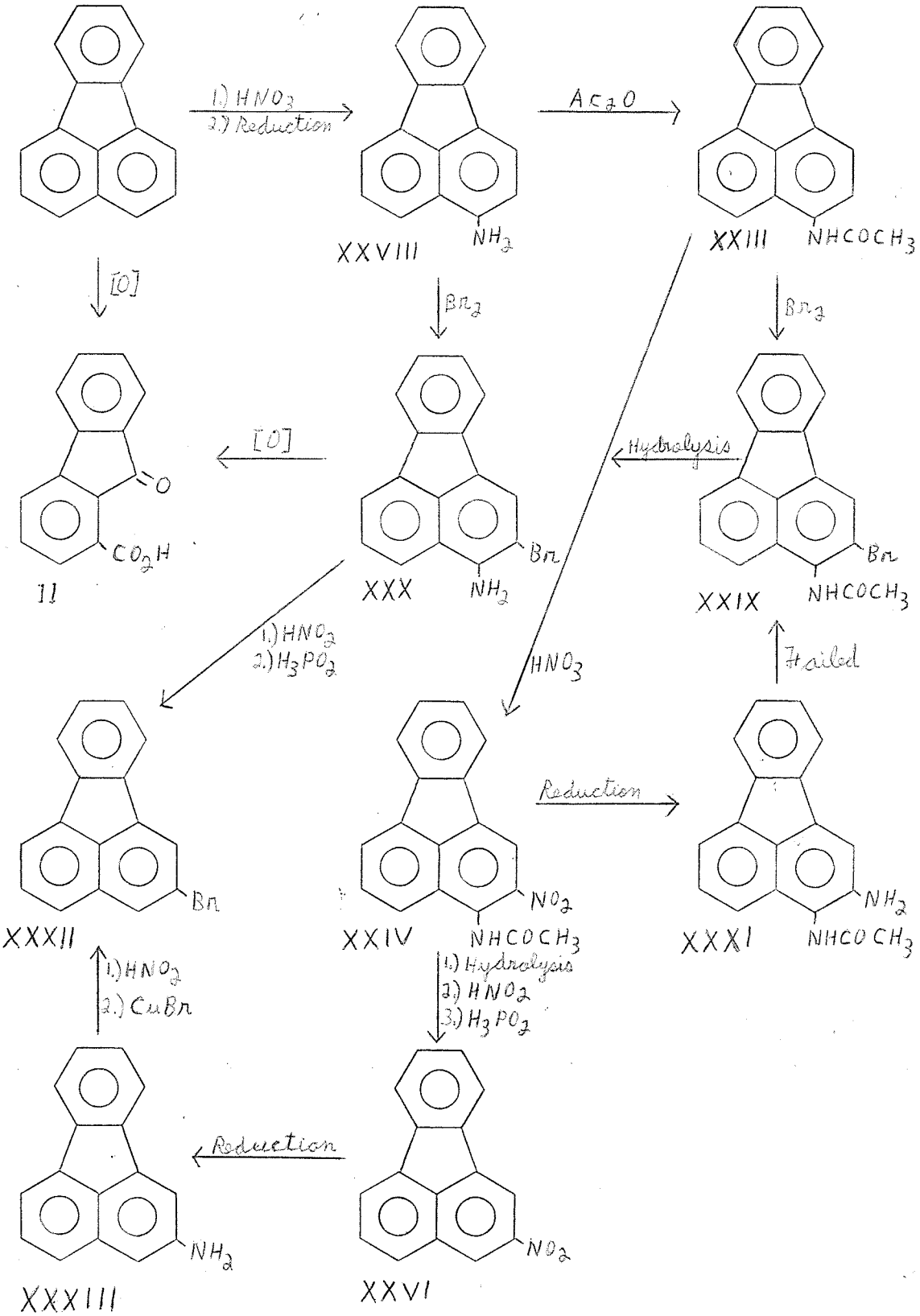
in the patent literature by Meyer and Falta (19); however the orientation of the monobromo derivative had not been determined. Bromination of 3-aminofluoranthene was repeated as described in the patent, but their method of purification failed in our hands. Perhaps this was due to the lack of details given. They reported a melting point of 166-7° C. for this compound, whereas we obtained a melting point of 157-158° C.(decomp.). Several methods were employed in trying to purify this compound, however all attempts were unsuccessful. Both purification by recrystallization and by preparation of the amine salt met with failure. It was hoped that purification of the picrate might be possible, but an attempt to prepare this gave poor results. Sublimation of the compound resulted mainly in the formation of a tarry material. An attempt to purify the compound by acetylation to the 3-acetamido-2-bromo-fluoranthene, followed by hydrolysis back to the amine, failed due to inability to purify the amide. Oxidation of the compound melting at 157-158° C. with sodium dichromate in acetic acid caused copious evolution of bromine, as did oxidation of 3-amino-2-bromofluoranthene, m.p. 176-7° C. This indicated that

this compound must also be 3-amino-2-bromofluoranthene. Comparison of the NMR spectra of the two compounds gave definite confirmation that the compound melting at 157-158° C. was indeed 3-amino-2-bromofluoranthene but that a considerable amount of impurity was present. Thus it is established that 3-aminofluoranthene is brominated mainly in the 2-position.

A literature search disclosed pertinent material that both Campbell et al. and Kloetzel et al. failed to point out. Campbell's statement that substitution in diphenyl usually occurs in the second ring irrespective of the nature of the substituent already present in the first ring does not seem correct. Indications are that further substitution in diphenyl does depend on the nature of the substituent, as strongly activating groups in the 4-position cause substitution in the 3-position. 4-Aminodiphenyl is nitrated in the 3-position (20) and 4-hydroxydiphenyl is nitrated or brominated in the 3-position (21). The acetamido group does not give a uniform result (21). 4-Acetamidodiphenyl nitrates or chlorinates in the 3-position, but brominates

in the 4-position. However this non-uniformity could be due to conditions prevailing during the substitution or to other factors not immediately obvious. It is to be noted that in fluoranthene bromination and nitration of the 3-acetamido derivative do take place at the same position.

In view of the above information the orientation rule of Campbell and Keir should not be relied upon for intensely activating substituents because the rule is based on incorrect information as far as this type of substituent is concerned. Instead it is to be expected that an intensely activating substituent in fluoranthene should cause further substitution in the same ring. This is in agreement with our work and that of Kloetzel et al.


1.) HNO_2
2.) Reduction
Ac_2O
XXVIII
NH_2
XXIII
$NHCOCH_3$
[O]
Br_2
Br_2
11
CO_2H
[O]
XXX
Br
NH_2
Hydrolysis
XXIX
Br
$NHCOCH_3$
1.) HNO_2
2.) H_3PO_2
HNO_3
Hailed
XXXII
Br
XXIV
NO_2
$NHCOCH_3$
Reduction
XXXI
NH_2
$NHCOCH_3$
1.) HNO_2
2.) CuBr
1.) Hydrolysis
2.) HNO_2
3.) H_3PO_2
Reduction
XXXIII
NH_2
XXVI
NO_2

EXPERIMENTAL

Preparation of 3-Nitrofluoranthene

3-Nitrofluoranthene was prepared essentially by the method of Garascia, Fries, and Ching (11).

Fluoranthene (20.0 g) was dissolved in glacial acetic acid (150 ml). With constant stirring, concentrated nitric acid (27 ml) was added dropwise at 71-76° C. over a period of about fifteen minutes. Stirring was continued at 74-75° C. for another fifteen minutes. The orange-yellow precipitate of crude 3-nitrofluoranthene (12.1 g) was filtered from the hot solution. The product was washed with glacial acetic acid, then with water, and allowed to dry. Treatment with charcoal and recrystallization from glacial acetic acid gave pure material (9.4 g) which melted at 158-160° C.

Preparation of 3-Aminofluoranthene

The method of Kloetzel et al. (17) was utilized in this preparation.

3-Nitrofluoranthene (28.0 g) and platinum oxide (0.6 g)

were suspended in absolute ethanol (220 ml). The preparation was carried out in a Parr pressure reaction apparatus. Hydrogenation was accomplished in fifty minutes, during which time the gauge pressure decreased from 53 lbs./sq. in. to 21 lbs./sq. in. The product was isolated by dilution of the solvent with water, followed by filtration. The 3-aminofluoranthene (24.4 g), thus obtained, melted at 111-113° C.

Preparation of 3-Acetamidofluoranthene

This preparation was carried out by the method of Kloetzel, King, and Menkes (17).

Acetic anhydride (9.5 ml) was added to a solution of 3-aminofluoranthene (15.0 g) in benzene (900 ml). The reaction mixture was stirred at room temperature for thirty minutes. During this period a solid precipitated. Filtration of the mixture gave 3-acetamidofluoranthene (16.0 g), m.p. 242-244° C.

Preparation of 3-Acetamido-2-bromofluoranthene

This preparation was accomplished by bromination of

3-acetamidofluoranthene in pyridine.

Bromine (5 ml) was added, with stirring, to a solution of 3-acetamidofluoranthene (10.0 g) in technical grade pyridine (700 ml). The reaction was allowed to proceed at room temperature for ten hours. The crude product was precipitated by addition of water (2 litres). The product was filtered off and washed with a 10% aqueous solution of sodium hydroxide and sodium bisulfite. The resulting material was placed in pyridine (200 ml), and the pyridine was heated to the boiling point. The insoluble material was filtered from the hot pyridine solution and discarded. The filtrate was treated with charcoal, followed by addition of a sufficient amount of water to cause crystallization when the pyridine-water solution cooled. The 3-acetamido-2-bromofluoranthene (7-8 g) was obtained as yellow flakes, m.p. 266-267° C. (decomp.). Found: N, 4.2; Br, 23.3; acetyl, 13.1%. Calc. for $C_{18}H_{12}NBrO$: N, 4.1; Br, 23.6; acetyl, 12.7%.

Bromination of 3-Acetamidofluoranthene in Acetic Acid

The following was the most successful of the many

attempts at bromination in acetic acid.

Bromine (1 ml) in glacial acetic acid (25 ml) was added through a dropping funnel over a period of twenty-five minutes to a stirred solution of 3-acetamidofluoranthene (2.0 g) in glacial acetic acid (190 ml) at 80° C. The reaction was allowed to continue at the same temperature, with stirring, for another thirty-five minutes. A small amount of product which had precipitated out was filtered off from the hot reaction mixture. Treatment with charcoal and recrystallization from pyridine gave a yellow material, m.p. 265-266° C. (decomp.). A mixed melting point with 3-acetamido-2-bromofluoranthene gave a large depression. Treatment of the filtrate from the reaction mixture with water precipitated a larger amount of product, which melted over a wide range even after recrystallization from pyridine. The possibility exists that this compound melting at 265-266° C. is an isomer of 3-acetamido-2-bromofluoranthene.

Preparation of 3-Amino-2-bromofluoranthene

Hydrolysis of 3-acetamido-2-bromofluoranthene gave 3-amino-2-bromofluoranthene.

The reaction was accomplished by heating a mixture of the amide (10.3 g), methanol (600 ml), pyridine (400 ml), and sodium hydroxide (30 g) under reflux for twelve hours. A small amount of insoluble material was filtered off and discarded. The crude product was precipitated by dilution to 4 litres with water. This material was washed with water, dried, and dissolved in boiling pyridine. A small amount of insoluble material was filtered off and the filtrate was treated with charcoal. A sufficient amount of water was added to cause crystallization when the solvent cooled. 3-Amino-2-bromofluoranthene (7.2 g) was thus obtained as beautiful yellow needles, m.p. 176-177° C. (decomp.). Found: N, 4.6; Br, 27.6%. Calc. for $C_{16}H_{10}NBr$: N, 4.7; Br, 27.0%.

Oxidation of 3-Amino-2-bromofluoranthene

Oxidation of 3-amino-2-bromofluoranthene (2.0 g) was accomplished by heating under reflux for five hours with sodium dichromate (20 g) in glacial acetic acid (100 ml). This treatment caused evolution of bromine in gaseous form. The reaction mixture was poured into a solution of

concentrated sulfuric acid (100 ml) in water (700 ml). The solid which precipitated was filtered off and heated in an aqueous solution of sodium carbonate. The insoluble material was filtered out of the carbonate solution and discarded. The filtrate from the diluted reaction mixture was extracted with benzene. The benzene solution was in turn extracted with carbonate solution, and the carbonate solutions were combined. Acidification of the carbonate solution with sulfuric acid produced crude 1-fluorenone-carboxylic acid. The acid was dried and taken up in boiling o-xylene (100 ml), from which the insoluble material was removed. The acid was then recovered by extraction with aqueous carbonate solution, etc. Recrystallization from glacial acetic acid gave 1-fluorenonecarboxylic acid (0.53 g), m.p. 185-189° C. Admixture with an authentic sample caused no depression in melting point. Comparison of the infrared spectra also showed this to be 1-fluorenonecarboxylic acid.

Preparation of Authentic 1-Fluorenonecarboxylic Acid

1-Fluorenonecarboxylic acid was prepared by oxidation of fluoranthene according to the method of Fieser and

Seligman (9), though the purification procedure was altered slightly.

The oxidation was carried out by adding slowly a solution of chromic anhydride (34 g) in water (30 ml) and glacial acetic acid (20 ml) to a solution of fluoranthene (10.0 g) in glacial acetic acid (250 ml), the addition being controlled at such a rate that the mixture was kept just below the boiling point. The reaction mixture was allowed to stand at room temperature for ten hours and then refluxed for one hour. The reaction mixture was then diluted to a total volume of 2 litres with water and the precipitated material was filtered off. This material was extracted with dilute sodium hydroxide solution, the solution was filtered, and the acid precipitated from the filtrate. The acid was then taken up in potassium carbonate solution, filtered, and precipitated again. The dried acid was then re-crystallized from glacial acetic acid to give the orange 1-fluorenonecarboxylic acid (4.3 g), m.p. 191-193° C.

Reaction of Phenylhydrazine with 1-Fluorenonecarboxylic Acid

An attempt was made to repeat the preparation of the phenylhydrazone of 1-fluorenonecarboxylic acid as carried out by Goldschmiedt (13).

A solution of phenylhydrazine (10 drops) in ethanol (3 ml) was added to a hot solution of 1-fluorenonecarboxylic acid (0.1 g) in ethanol (20 ml). The solution was stirred and set aside to cool. The mass of yellow material which was filtered out of the reaction mixture melted at 213-217° C. Recrystallization from glacial acetic acid had a negligible effect on the melting point. The compound reported by Goldschmiedt melted at 230-232° C. without recrystallization. For further comment on this reaction see the "Discussion of Results."

Reaction of p-Nitrophenylhydrazine with 1-Fluorenonecarboxylic Acid

A boiling solution of p-nitrophenylhydrazine (0.13 g) in glacial acetic acid (5 ml) was added to a boiling solution of 1-fluorenonecarboxylic acid (0.1 g) in glacial

acetic acid (20 ml). The mixture was stirred and allowed to cool. The product began to crystallize out almost immediately as fine yellow-orange microcrystals, m.p. 307-308° C. The product obtained from our impure sample of 1-fluorenonecarboxylic acid melted at the same temperature, though not as sharply. A mixed melting point of the two products gave no depression.

Preparation of 3-Acetamido-2-nitrofluoranthene

This preparation was carried out essentially by the method of Kloetzel et al. (17) by nitration of 3-acetamido-fluoranthene.

Concentrated nitric acid (3.3 ml) was added to a solution of 3-acetamidofluoranthene (6.5 g) in glacial acetic acid (650 ml) at a temperature of 80° C. The reaction mixture was kept at 80-85° C., with constant stirring, for one hour and twenty minutes. After the reaction mixture had cooled to room temperature, the solid product that had separated out during the nitration was filtered off and washed with water. The yellow 3-acetamido-2-nitrofluoranthene (6.5 g) thus obtained melted at 280-282° C.

Preparation of 3-Acetamido-2-aminofluoranthene

In this preparation hydrogenation of 3-acetamido-2-nitrofluoranthene was carried out essentially by the method of Kloetzel et al. (17), except that a palladium-charcoal catalyst was used in place of the platinum oxide catalyst.

3-Acetamido-2-nitrofluoranthene (6.5 g) and palladium-charcoal (0.8 g) were suspended in absolute ethanol (300 ml). Hydrogenation was accomplished in less than fourteen hours as the gauge pressure dropped from 52 lbs./sq. in. to 45 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 removed in vacuo. Dilution of the remaining solvent with water gave 3-acetamido-2-aminofluoranthene (5.4 g), m.p. 197-199° C.

Attempted Preparation of the Sulfate Salt of 3-Acetamido-2-aminofluoranthene

The amine (approx. 0.3 g) was dissolved in anhydrous ether (700 ml). Concentrated sulfuric acid (5-6 drops) was

added with stirring. A greyish-white voluminous material precipitated. This was filtered off. As the ether evaporated off, the material shrank in size and turned into a black tar.

Deamination of 3-Amino-2-bromofluoranthene

Information concerning this reaction was obtained from reference (18).

Sodium nitrite (0.75 g) was added slowly with stirring to a solution of concentrated sulfuric acid (60 ml) and water (4.2 ml) at room temperature. Stirring was continued until all the sodium nitrite was in solution. The solution was then cooled to -5° C. Finely ground 3-amino-2-bromofluoranthene (1.16 g) was then added to the above solution, maintained at -5° C., with vigorous stirring over a fifteen minute period. Stirring was continued for another forty-five minutes at the same temperature. Then precooled 50% hypophosphorous acid (85 ml) was added, over a period of two hours and thirty minutes, to the stirred solution at such a rate that the temperature did not exceed 5° C. After standing at 2-3° C. for one week the reaction mixture was

diluted to a total volume of 1 litre with water. The colloidal precipitate was allowed to coagulate and then was filtered off. The dried material was stirred in hot benzene (250 ml) for thirty minutes and the insoluble material was filtered off. The benzene solution was extracted with concentrated sulfuric acid until the benzene solution did not change color on further extraction. The benzene solution was washed with an aqueous carbonate solution and then evaporated to dryness. The material obtained on evaporation was sublimed under high vacuum at approximately 100° C. to yield the pale yellow 2-bromofluoranthene (0.75 g), m.p. 101-103° C. Found: C, 68.3; H, 3.22; Br, 28.8%. Calc. for $C_{16}H_9Br$: C, 68.4; H, 3.23; Br, 28.4%. A mixed melting point with an authentic sample of 2-bromofluoranthene prepared (see below) from 2-aminofluoranthene gave no depression.

Preparation of 3-Amino-2-nitrofluoranthene

Hydrolysis of 3-acetamido-2-nitrofluoranthene by the method of Kloetzel et al. (17) gave 3-amino-2-nitrofluoranthene.

The preparation was carried out by heating under reflux for eleven hours a mixture of the amide (15.3 g), 95% ethanol (1200 ml), and concentrated hydrochloric acid (1200 ml). Then the cooled reaction mixture was neutralized with 10% sodium hydroxide. After cooling, the crude product was filtered off and washed with water. Treatment with charcoal and recrystallization from a mixture of pyridine and water gave beautiful orange-red needles of 3-amino-2-nitrofluoranthene (9.9 g), m.p. 252-254° C. It was found that recrystallization from chlorobenzene gave a slightly lower melting point. Kloetzel et al. reported a melting point of 235-236° C. after recrystallization from chlorobenzene. Jemmett et al. (16) reported that this compound softened at 250° C. and melted at 253° C. after recrystallization from ethylene glycol, then from chlorobenzene, and finally from methyl ethyl ketone.

Preparation of 2-Nitrofluoranthene

Deamination of 3-amino-2-nitrofluoranthene by the method of Kloetzel et al. (17) gave 2-nitrofluoranthene.

Sodium nitrite (3.2 g) was added slowly with stirring

to a solution of concentrated sulfuric acid (110 ml) and water (7.8 ml) at room temperature. Stirring was continued until all the sodium nitrite was in solution. Powdered 3-amino-2-nitrofluoranthene (9.0 g) was added slowly with stirring to the above solution, maintained at -5° C. Stirring was continued at this temperature for another thirty minutes. Cooled 50% hypophosphorous acid (235 ml) was then added to the stirred solution at such a rate (three hours) that the temperature did not exceed 5° C. After standing for five days at 2-3° C. the mixture was diluted with three volumes of water. The crude product was filtered off, washed with dilute aqueous sodium hydroxide and then with water. Treatment with charcoal and recrystallization from glacial acetic acid gave 2-nitrofluoranthene (5.2 g), m.p. 152-154° C.

Preparation of 2-Aminofluoranthene

Hydrogenation of 2-nitrofluoranthene, essentially by the method of Kloetzel et al. (17), gave 2-aminofluoranthene.

2-Nitrofluoranthene (5.6 g), charcoal (0.5 g), and

platinum oxide (0.5 g) were suspended in absolute ethanol (100 ml). Hydrogenation was accomplished in less than one hour and thirty minutes, during which time the gauge pressure dropped from 53 lbs./sq. in. to 42 lbs./sq. in. The catalyst and the charcoal were filtered out of the reaction mixture, and the filtrate was evaporated to dryness under reduced pressure to give crude 2-aminofluoranthene (4.8 g), m.p. 115-120° C. Upon purification, Kloetzel et al. obtained a melting point of 128-129° C. for this compound. Due to lack of time no attempt was made to purify the compound in our case, but it was used directly for the next reaction.

Preparation of Authentic 2-Bromofluoranthene

Diazotization of 2-aminofluoranthene followed by treatment with cuprous bromide gave 2-bromofluoranthene.

Crude 2-aminofluoranthene (2.0 g) was stirred in dry ether (170 ml) and the insoluble material filtered off. Concentrated sulfuric acid (1 ml) was added with stirring to the amine solution. The amine salt was filtered off, allowed to dry, and finely ground. The salt was then

dissolved in a vigorously stirred solution of concentrated sulfuric acid (75 ml) and glacial acetic acid (75 ml) with gentle warming. The solution was cooled and 150 grams of ice and water were added rapidly with stirring to precipitate the amine salt in a finely divided condition. The salt was diazotized at 15-20° C. by addition of sodium nitrite (1.6 g) in water (10 ml). The diazonium solution was poured, with stirring, into a solution of cuprous bromide (15 g) in 48% hydrobromic acid (70 ml) and water (30 ml). The mixture was heated slowly, with stirring, to 95° C. The cooled reaction mixture was diluted with water and the precipitate filtered off. The dried material was stirred in hot benzene and the insoluble material filtered off. The filtrate from above was extracted with benzene. All the benzene extracts were combined and extracted with an aqueous sodium hydroxide and sodium bisulfite solution. The benzene was then extracted with concentrated sulfuric acid until further extraction caused no visible change in the benzene solution. Next, the benzene solution was extracted with an aqueous sodium carbonate solution and, then, evaporated to dryness. Sublimation of the solid residue,

at approximately 100° C. under high vacuum, gave 2-bromofluoranthene (1.1 g), m.p. 102-104° C. Found: C, 67.7; H, 3.39; Br, 27.3; N, 1.17%. Calc. for $C_{16}H_9Br$: C, 68.4; H, 3.23; Br, 28.4%. The analysis indicates some nitrogen containing impurity was present.

Bromination of 3-Aminofluoranthene

The method used is essentially that of Meyer and Falta (19).

Bromine (2.8 ml) in glacial acetic acid (20 ml) was added, with stirring, over a one hour period to a solution of 3-aminofluoranthene (11.0 g) in glacial acetic acid (120 ml) at room temperature. Stirring was continued for another hour. The product was filtered off, washed with dilute alkali solution, and then with water. The amine was taken up in boiling chloroform (1 litre) and the insoluble material was filtered off. Concentrated hydrochloric acid (50 ml) was added with stirring to the cooled chloroform solution. The amine salt was filtered off and hydrolyzed with dilute ammonia solution. The amine was taken up in boiling benzene (500 ml) and the insoluble material was

filtered off. Evaporation to dryness gave crude 3-amino-2-bromofluoranthene (10.3 g), m.p. 157-158° C. (decomp.). For further information regarding this compound see the "Discussion of Results".

SUMMARY

1. Bromination of 3-acetamidofluoranthene in pyridine gave the previously unknown 3-acetamido-2-bromofluoranthene.

2. Hydrolysis of 3-acetamido-2-bromofluoranthene gave 3-amino-2-bromofluoranthene. This is the first time a pure sample of this compound has been prepared.

3. Deamination of 3-amino-2-bromofluoranthene gave the previously unknown 2-bromofluoranthene.

4. A modified diazotization procedure has been introduced which may prove to be of considerable value in the diazotization of weakly basic, insoluble amines which undergo decomposition in strong sulfuric acid solutions.

5. An authentic sample of 2-bromofluoranthene was prepared from the known 2-aminofluoranthene by diazotization and treatment with cuprous bromide in hydrobromic acid.

6. The structure of 3-amino-2-bromofluoranthene was proved by oxidizing it to 1-fluorenonecarboxylic acid, plus the fact that its deamination product was identical with the authentic sample of 2-bromofluoranthene. Establishing the

structure of the amino-bromo compound thereby proved the structure of 3-acetamido-2-bromofluoranthene as the former was obtained by hydrolysis of the latter.

7. The orientation of the bromination product of 3-aminofluoranthene was established by showing it to be the same as our sample of 3-amino-2-bromofluoranthene.

8. The showing that 3-amino-, and 3-acetamido-fluoranthene are brominated in the 2-position gave further indication that the orientation rule of Campbell and Keir (4) is incorrect.

RECOMMENDATIONS FOR FUTURE WORK

1. The compound obtained on bromination of 3-acetamidofluoranthene in acetic acid should be investigated. The possibility exists that this is an isomer of 3-acetamido-2-bromofluoranthene. This would be very interesting as it would show that bromination in pyridine gave a product different from that obtained by bromination in acetic acid.

2. An investigation into the phenylhydrazones of 1-fluorenonecarboxylic acid might prove to be interesting.

3. The modification of the diazotization procedure introduced in this work could be tried on other difficultly soluble and weakly basic amines.

4. To date the work on fluoranthene has only shown how substituents in the 3-position direct. It would certainly be worth while to determine how substituents in the 1-position direct. 1-Nitrofluoranthene, 1-aminofluoranthene, and 1-acetamidofluoranthene (6) have recently been prepared and could be used towards this end.

5. A series of 1-substituted fluoranthene derivatives could be prepared from 1-aminofluoranthene via the

diazonium reaction. This work would be of value in that new compounds would be prepared, and also in that these compounds could be used for disubstitution studies or for further reaction of other types.

6. Iodination of 3-acetamidofluoranthene using the iodination technique of Henne and Zimmer (14) or by using pyridine as a catalyst would be a worthwhile project. Presumably this would give 3-acetamido-2-iodofluoranthene from which 2-iodofluoranthene could be obtained. A use for this compound is given below.

7. An attempt made by von Braun and Anton (2) to prepare a Grignard reagent of 3-bromofluoranthene was unsuccessful. However it might be possible to prepare a Grignard reagent of 3-iodofluoranthene as this compound is more reactive (22). It is possible that the compounds containing halogen in the 1- and 2-positions would be more reactive. Thus it might be worthwhile to attempt to prepare the Grignard reagents of 2-bromo-, 2-iodo-, 1-bromo-, and 1-iodofluoranthene. The last three compounds have never been prepared, but methods of preparing them are suggested above. Once the Grignard reagent is made several new compounds could be obtained.

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