

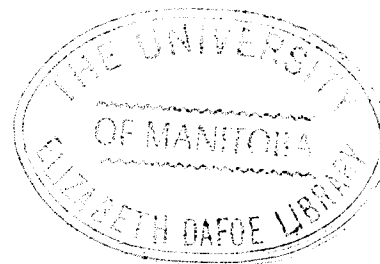
THE SYNTHESIS AND ORIENTATION
OF SOME
FLUORANTHENE COMPOUNDS

by

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A Thesis presented to
the Faculty of Graduate Studies and Research
of the University of Manitoba
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To
My Father

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Grateful acknowledgments are also extended to the University of Manitoba and to the National Research Council of Canada for summer grants-in-aid of research, and to Mr. B. J. Blackburn for his advice and assistance.

ABSTRACT

2-Nitrofluoranthene has been shown to undergo bromination in the 9-position and 2-acetamidofluoranthene in the 3-position. The theoretical implications of these results have been discussed. As a result of this work a number of new 2,9- and 2,3-disubstituted fluoranthene derivatives have been prepared, namely, 9-bromo-2-nitrofluoranthene, 9-bromo-2-acetamidofluoranthene, 3-bromo-2-aminofluoranthene, 3-bromo-2-aminofluoranthene, along with 3-nitro-6-bromofluorenone-1-carboxylic acid and 3-nitro-6-bromofluorenone. The 2-halofluoranthene series has been completed with the preparation of 2-fluoro, 2-chloro and 2-iodofluoranthene.

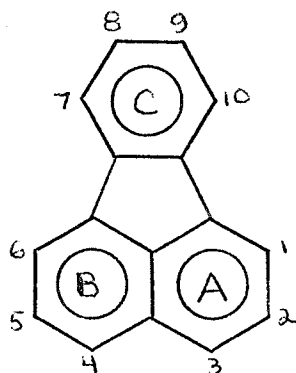
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INTRODUCTION

Only within the last fifteen years have research workers been able to gain some information regarding the directive properties of substituents in the fluoranthene nucleus. For the most part this information has been obtained as a result of the determination of the orientation of a number of disubstituted fluoranthenes, the majority of which had been prepared by further substitution in 3-substituted fluoranthene compounds.



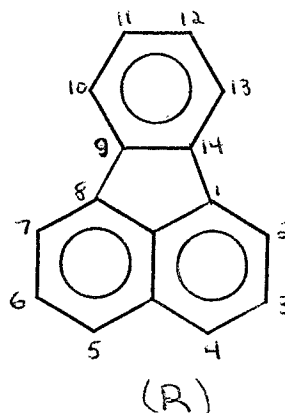
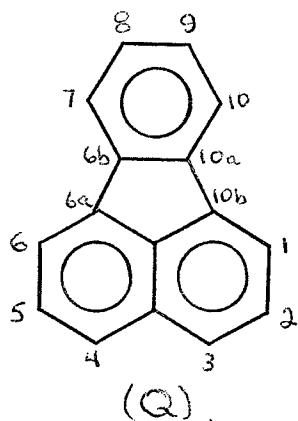
In 1955, Campbell and Keir (6) found that 3-carboxy, 3-carbomethoxy, 3-cyano and 3-nitrofluoranthene were all brominated in the 9-position, and that direct sulfonation of fluoranthene gave 3,9-fluoranthenedisulfonic acid. On the basis of this data coupled with the knowledge that 3-bromofluoranthene gave 3,8-dibromofluoranthene on further bromination, and by drawing an analogy to disubstitution in monosubstituted diphenyl, they postulated that a meta-directing group in ring A of fluoranthene would direct a second substituent to position 9, and that an ortho-para-directing group in the same ring would direct a second

substituent to position 8. In 1956 Kloetzel, King and Menkes (17) found that 3-acetamidofluoranthene was nitrated in the 2-position and suggested that the above postulate was oversimplified in that it did not take into account highly activating substituents, which, they stated, should cause further substitution in the same ring. Their work was later substantiated by that of Charlesworth and Blackburn (7) who showed that not only was 3-acetamidofluoranthene brominated in the same position as it nitrated, but also that 3-aminofluoranthene was brominated in position 2.

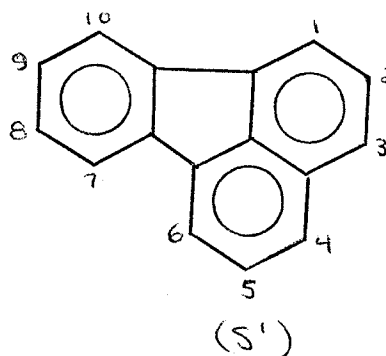
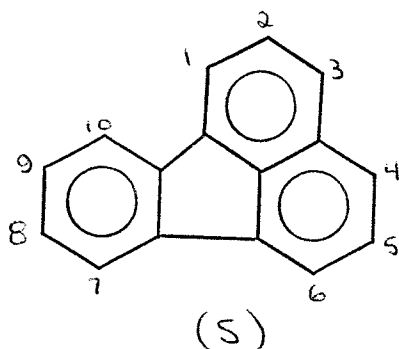
Upon examination of the above work it seemed obvious that additional study was required in this field in order to determine the directive properties of substituents in other positions of the fluoranthene nucleus. Thus, in this investigation, the directive effects of the nitro and acetamido groups in the 2-position were studied under brominating conditions. It was thought that the results of such a study would provide experimental proof that the existing orientation rules, which have been derived on the basis of the directive effects of various substituents in the 3-position, are also applicable to similar substituents in the 2-position. In addition, the fact that very few 2-substituted fluoranthene compounds are known made this investigation seem particularly desirable since it afforded an opportunity for the preparation of a number of new 2-substituted substances.

LITERATURE SURVEY

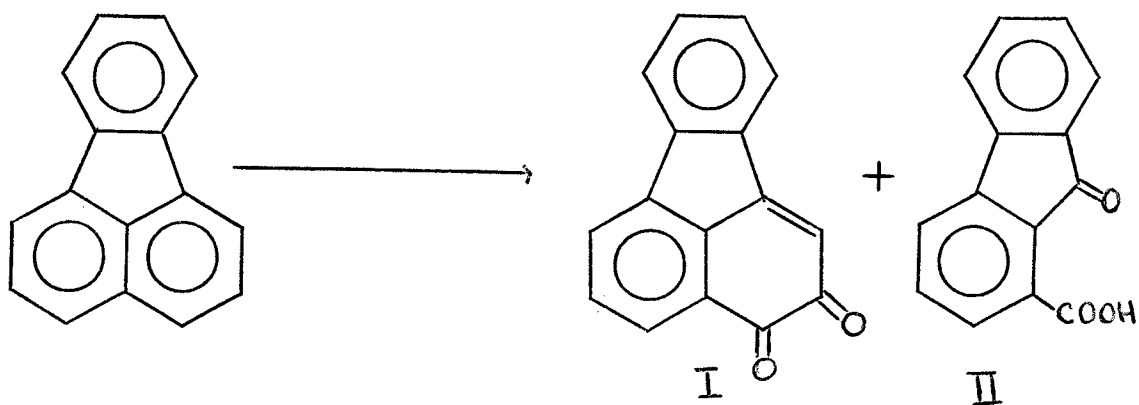
The structure of fluoranthene, a colourless crystalline hydrocarbon, melting at $109.5-110.5^{\circ}$ C. and boiling at 393° C., is depicted graphically below.



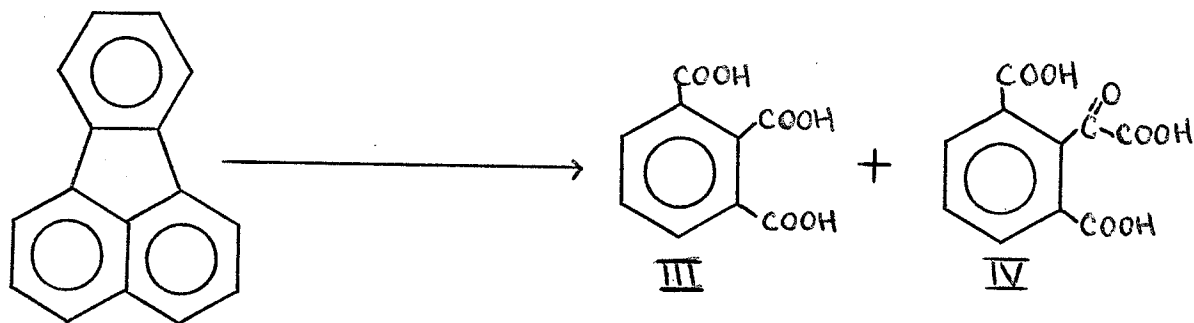
The system of numbering shown in formula (Q) is that employed by Chemical Abstracts. That shown in formula (R) is in accordance with the Richter system of notation and is the system used by most European chemists. The Chemical Abstract system of notation will be used in this thesis. The molecule may also be drawn in either of the following ways.



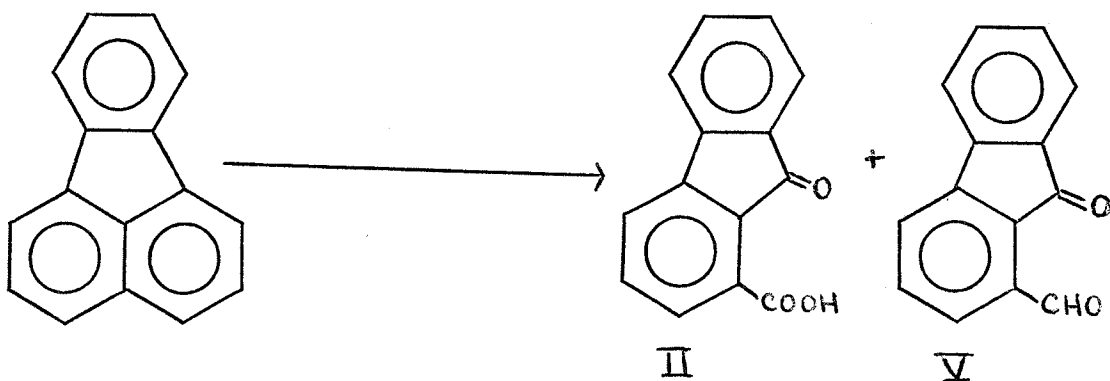
good yield on oxidation with chromic anhydride in acetic acid.



Prolonged treatment with alkaline permanganate yields hemimellitic acid (III) as the main product along with some 2,6-dicarboxyphenylglyoxylic acid (IV).



Finally ozonolysis in glacial acetic acid gives a mixture of II and I-fluorenonealdehyde (V).

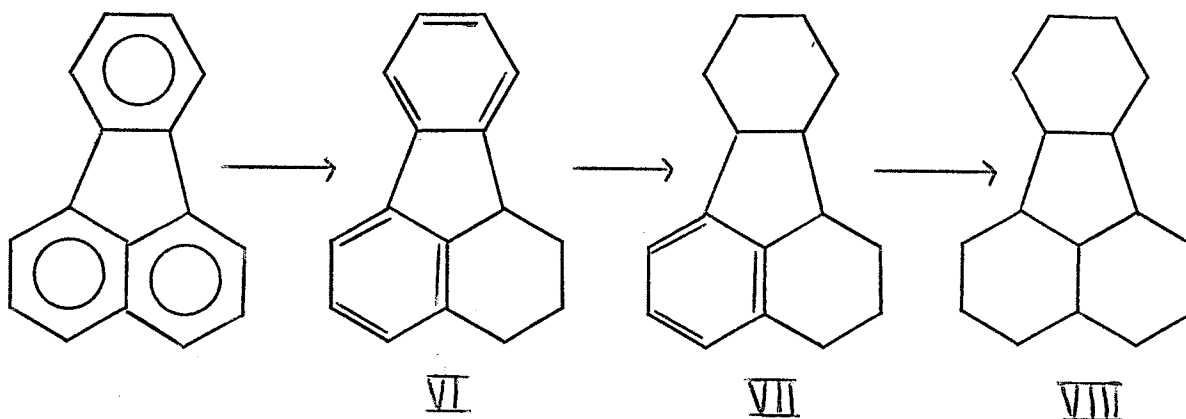


Reduction of Fluoranthene

Goldschmiedt (14) in 1880 was the first to prepare hydrogenated derivatives of fluoranthene. He was not able however, to characterize the products obtained.

In a detailed investigation completed in 1930, von Braun and Manz (3) reported that reduction of the hydrocarbon with sodium amalgam and alcohol, or with phosphorous and hydriodic acid below 180° C., gave almost a quantitative yield of 1,2,3,10b-tetrahydrofluoranthene (VI). Above 200° C. a mixture of hydrogenated products was obtained which could not be separated by distillation.

Catalytic hydrogenation under pressure using 20% palladium-charcoal as catalyst, gave VI as the initial product. 1,2,3,6b,7,8,9,10,10a,10b-Decahydrofluoranthene (VII) and perhydrofluoranthene (VIII) were obtained on further hydrogenation.



Monosubstitution in Fluoranthene

The 3-position in fluoranthene is most susceptible to attack in substitution reactions although in most cases small amounts of other products are also obtained.

3-Fluoranthenesulfonic acid may be prepared by direct sulfonation of the hydrocarbon with chlorosulfonic acid in an inert solvent (23,9).

The nitration of fluoranthene in acetic anhydride at 0° C. and in acetic acid at 50° C., yields 3-nitrofluoranthene as the principal product and small amounts of three additional isomers; the 8-, 7-, and 1-nitrofluoranthenes (22).

Bromination of fluoranthene in carbon disulfide results in the formation of two isomers; 3-bromofluoranthene is the main product and some 8-bromofluoranthene is also formed (23).

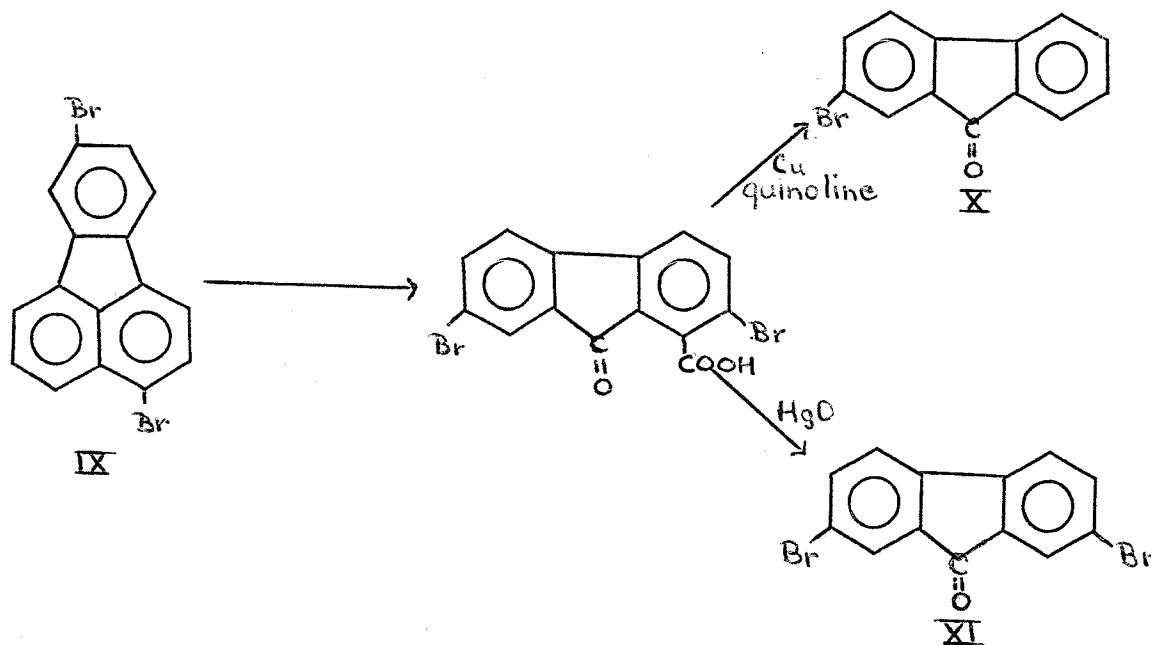
In 1962 Sieglitz and Troester (21) prepared 3-chlorofluoranthene by passing chlorine through a solution of the hydrocarbon in propylene oxide at room temperature. Previous to this, attempts at direct chlorination of fluoranthene had resulted in the formation of complex mixtures of poly-substituted products of unknown orientation.

A Friedel-Crafts reaction with benzoyl chloride in the presence of aluminum chloride and carbon disulfide gives a mixture of 3-benzoyl and 8-benzoylfluoranthene in approximately equal quantities. Acetyl bromide in the presence of aluminum chloride in carbon disulfide acts on fluoranthene

yielding a mixture of 3-acetyl and 8-acetylfluoranthene and 3,9-diacetylfluoranthene (23).

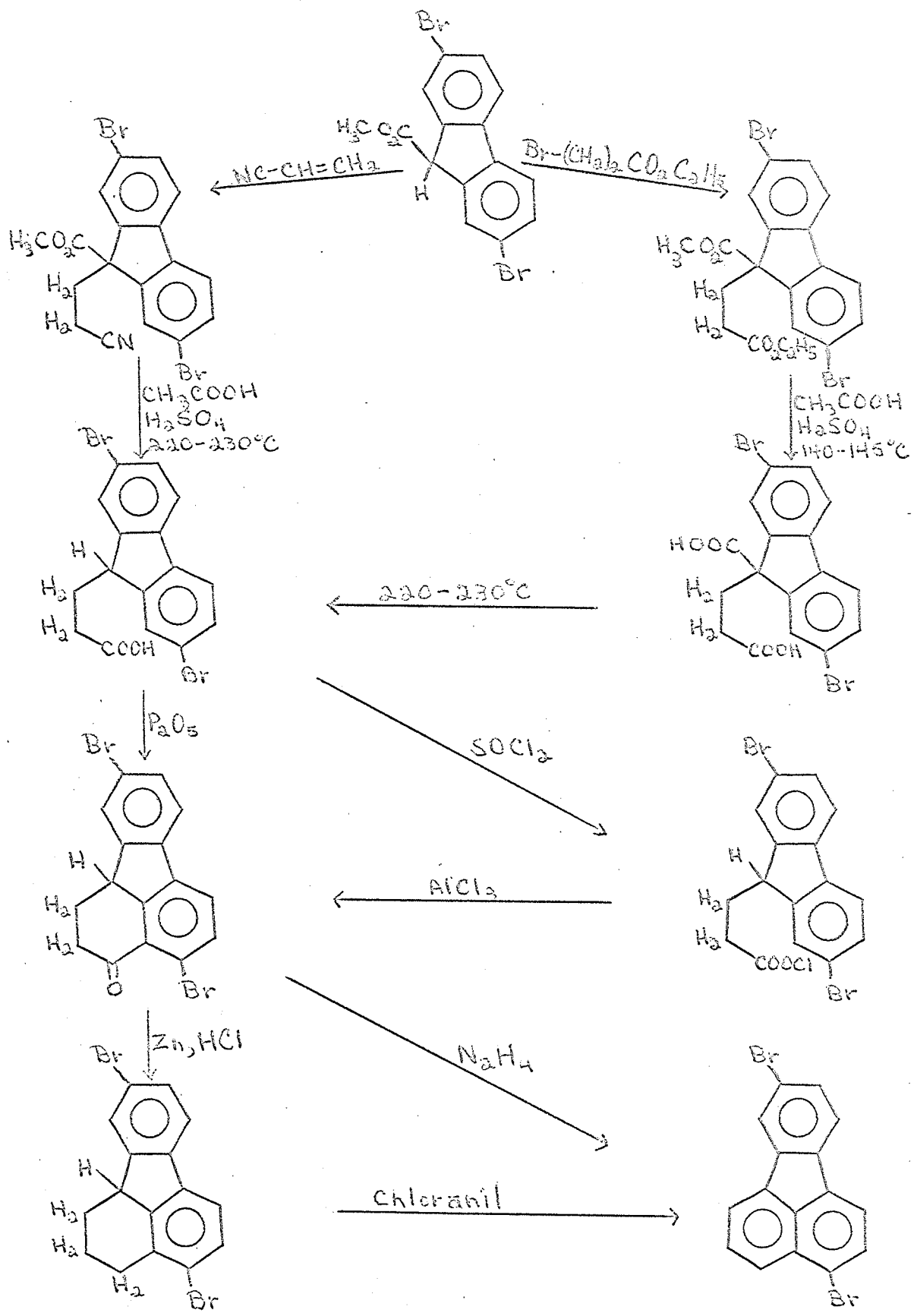
Orientation of Disubstitution in Fluoranthene

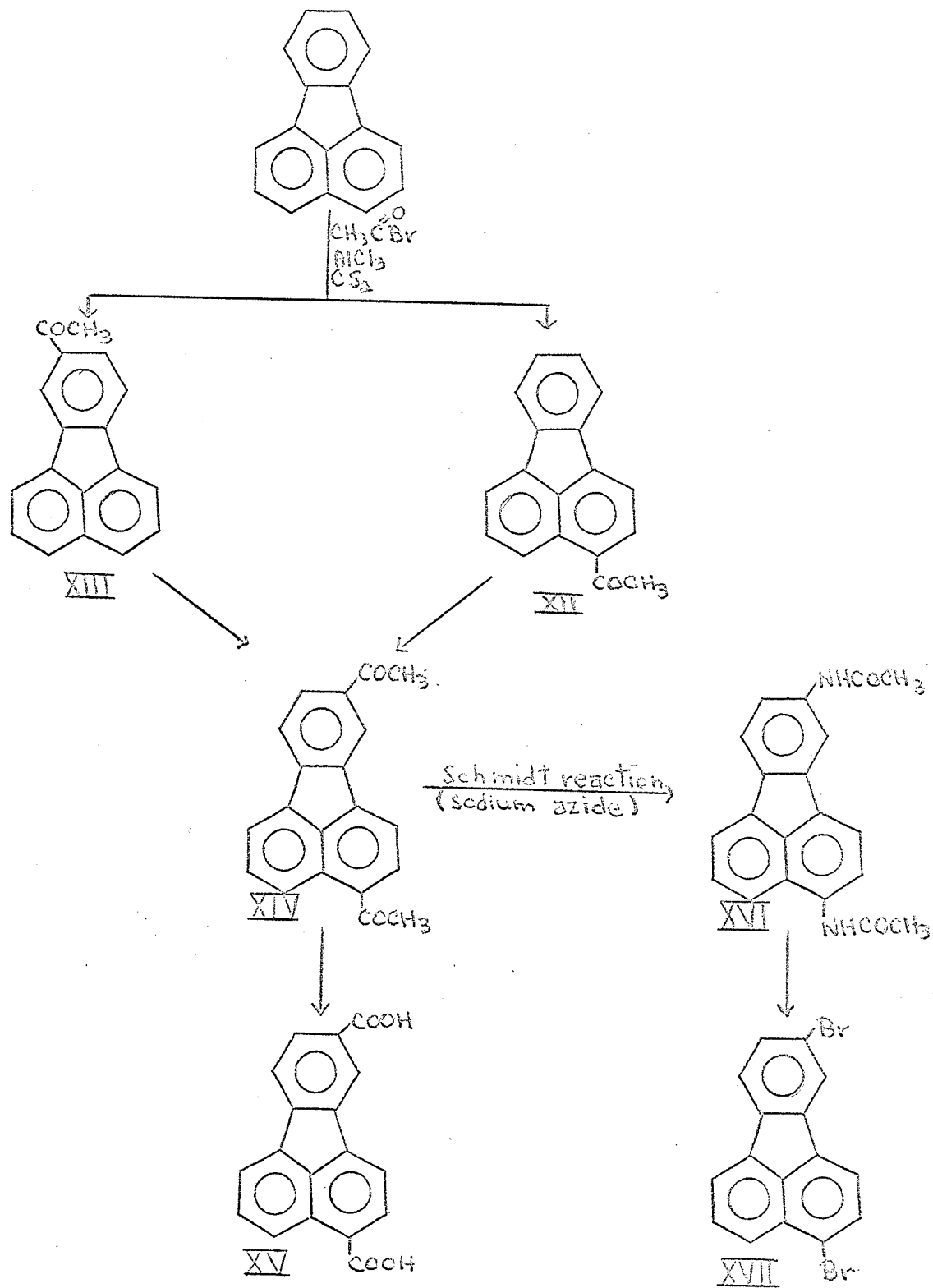
Only quite recently has work been undertaken to determine the orientation of disubstituted fluoranthene compounds. In 1950 the orientation of 3,8-dibromofluoranthene (IX), which was first prepared by Goldschmiedt and by Fittig and Gebhard by direct bromination of fluoranthene (23), was proved by two independent methods. The first method is that of Campbell et al. (4). They oxidized the dibromo compound with chromic acid to give a dibromofluorenone-1-carboxylic acid which on decarboxylation using copper and quinoline yielded 2-bromofluorenone (X). 2,7-Dibromofluorenone (XI) was obtained on decarboxylation of the dibromo acid with mercuric oxide at 180° C.



The second method is that of Holbro and Tagmann (15) who synthesized 3,8-dibromofluoranthene from methyl 2,7-dibromo-9-fluorene-carboxylate as shown on the next page.

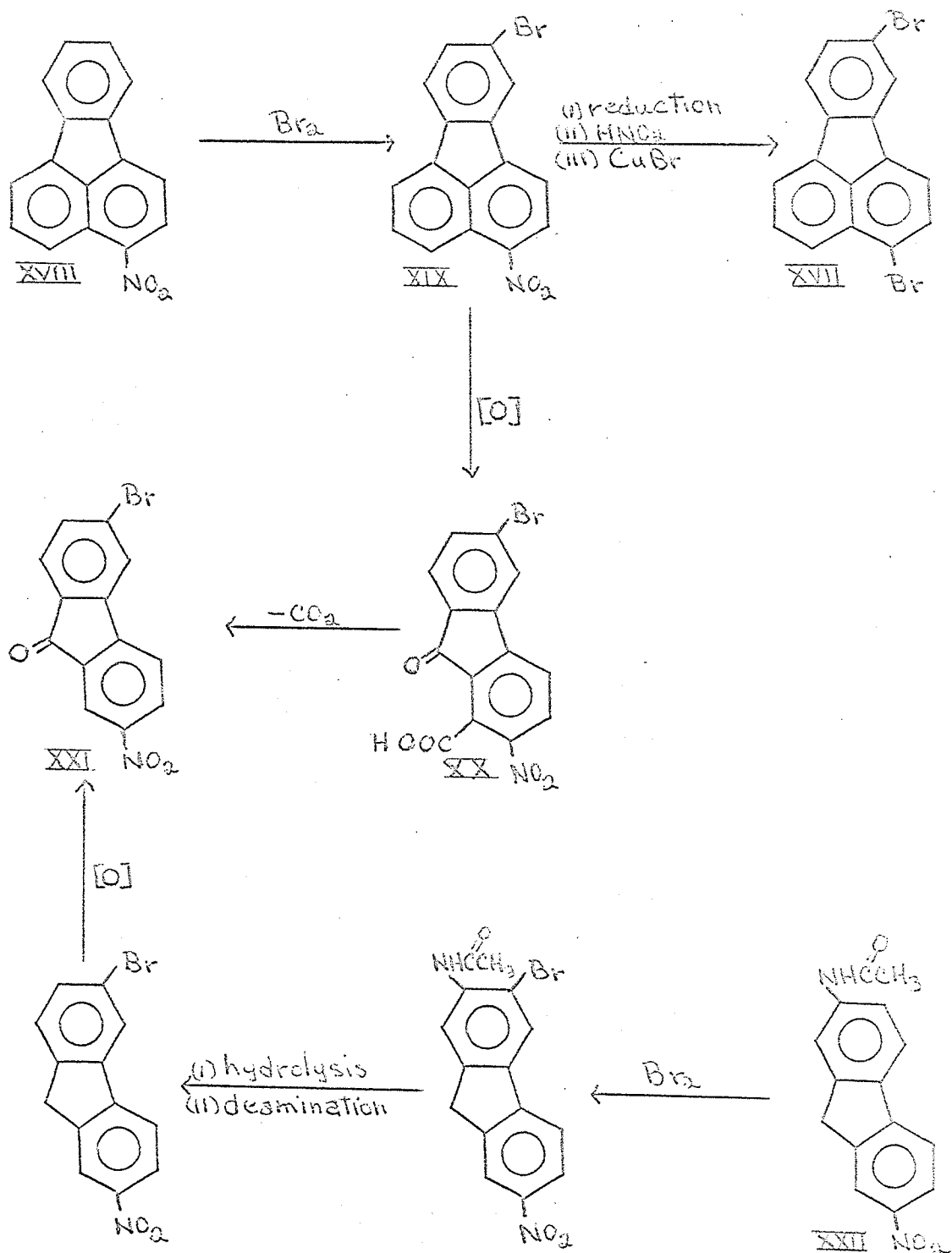
In 1951 Campbell, Leadill and Wilshire (5) prepared the 3- and the 8-acetylfluoranthenes and determined their structure. They also showed that the diacetyl derivative obtained on further acetylation was not 3,8-diacetylfluoranthene as might have been expected by comparison with the result of bromination of fluoranthene, but 3,9-diacetylfluoranthene. Their argument was as follows. The action of acetyl bromide on fluoranthene in the presence of aluminum chloride gave a mixture of 3-(XII) and 8-(XIII) acetylfluoranthene, which were separated chromatographically. On further treatment, both yielded the same diacetylfluoranthene (XIV) which must be the 3,8 or the 3,9 diacetyl compound. Oxidation of this compound yielded a fluoranthene dicarboxylic acid (XV) which was different from the 3,8-dicarboxylic acid prepared from 3,8-dibromofluoranthene via the dinitrile. The diacetylfluoranthene must therefore have been 3,9-diacetylfluoranthene and the derived acid 3,9-fluoranthenedicarboxylic acid. This result was confirmed by converting XIV into the diacetamido compound (XVI) by the Schmidt reaction (using sodium azide in trichloroacetic acid). Hydrolysis of XVI followed by diazotization and the Sandmeyer reaction gave a dibromofluoranthene (XVII) which was shown to be different from 3,8-dibromofluoranthene. Their work is summarized on page 11.



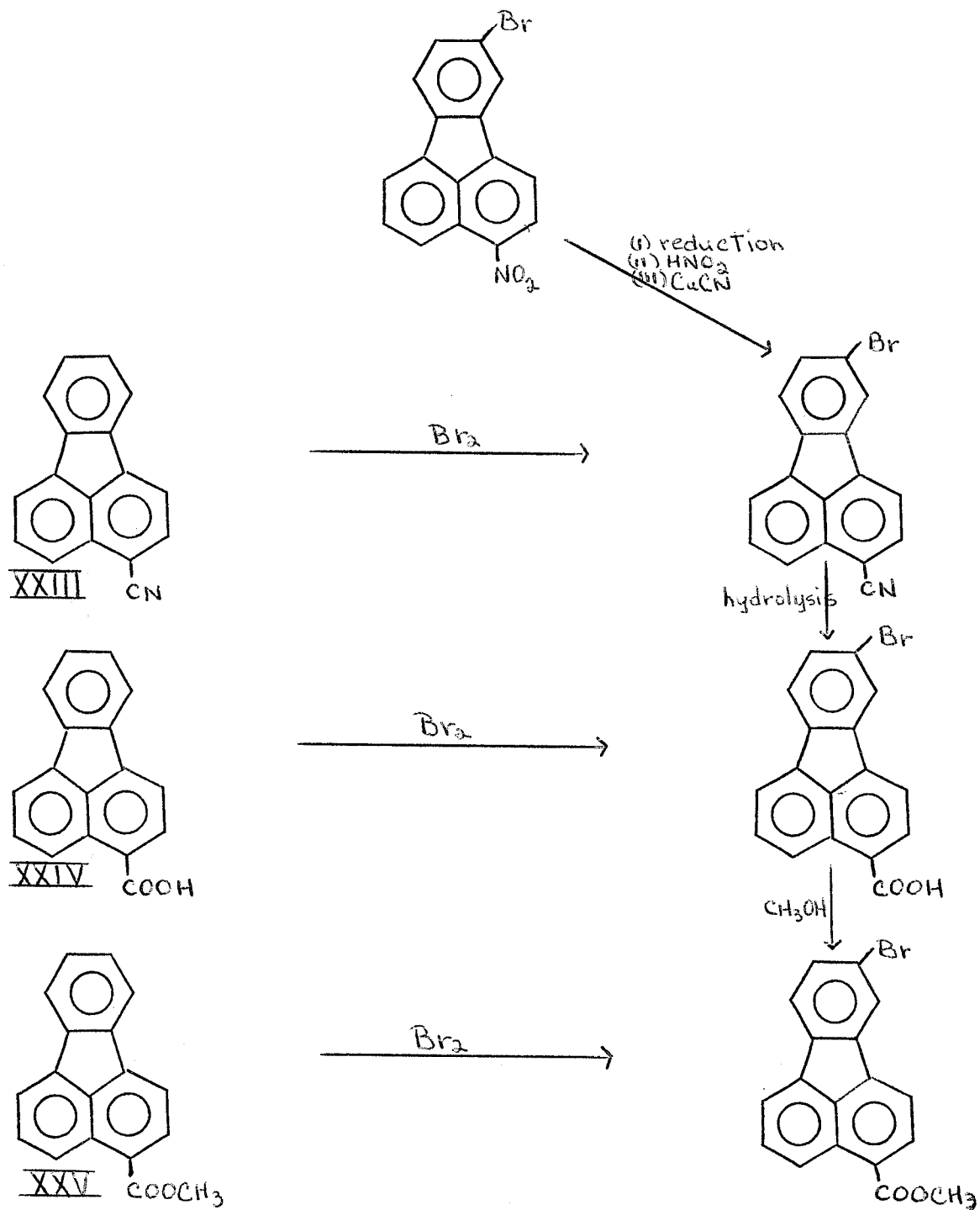


Our knowledge of the orientation in disubstituted fluoranthene compounds was substantially increased when in 1955 Campbell and Keir (6) proved that 3-carboxy-, 3-methoxy-carbonyl-, 3-cyano-, and 3-nitrofluoranthene were all brominated in the 9-position and that sulfonation of fluoranthene gave fluoranthene-3,9-disulfonic acid. Each of these proofs was rigorous except for the disulfonic acid compound.

Bromination of 3-nitrofluoranthene (XVIII) in nitrobenzene afforded 9-bromo-3-nitrofluoranthene (XIX) since on reduction, diazotization and treatment with cuprous bromide XIX yielded a dibromo compound (XVII) identical with a sample prepared from 3,9-diacetylfluoranthene. Also the oxidation of XIX gave 6-bromo-2-nitrofluorenone-1-carboxylic acid (XX) which on decarboxylation in pyridine yielded 6-bromo-2-nitrofluorenone (XXI) identical with a sample synthesized by brominating 2-acetamido-7-nitrofluorenone (XXII). This work is summarized on page 13.

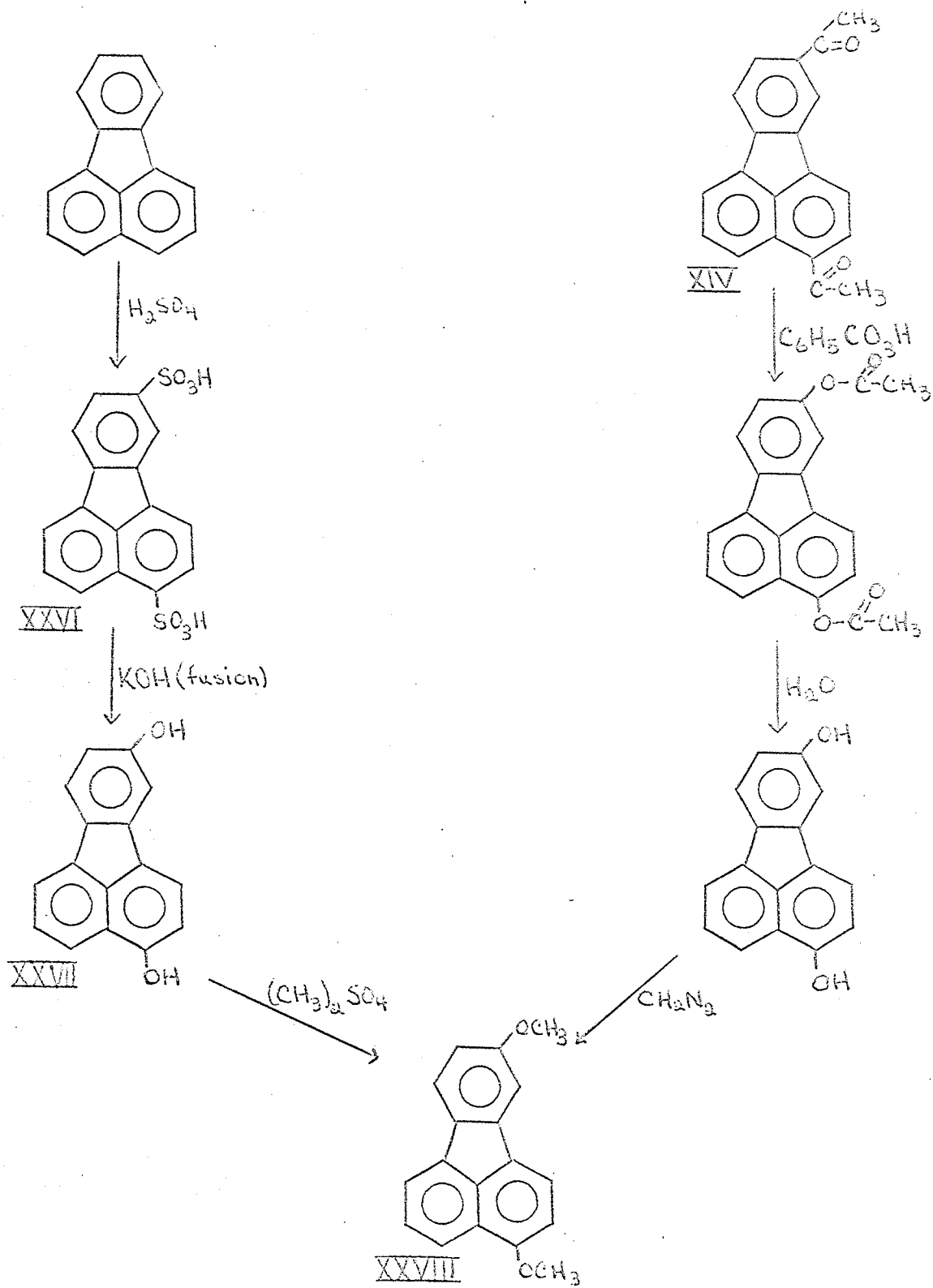


The following series of reactions were required to show that 3-cyano-(XXIII), 3-carboxy-(XXIV), and 3-methoxy-carbonylfluoranthene (XXV) were brominated in the 9-position.

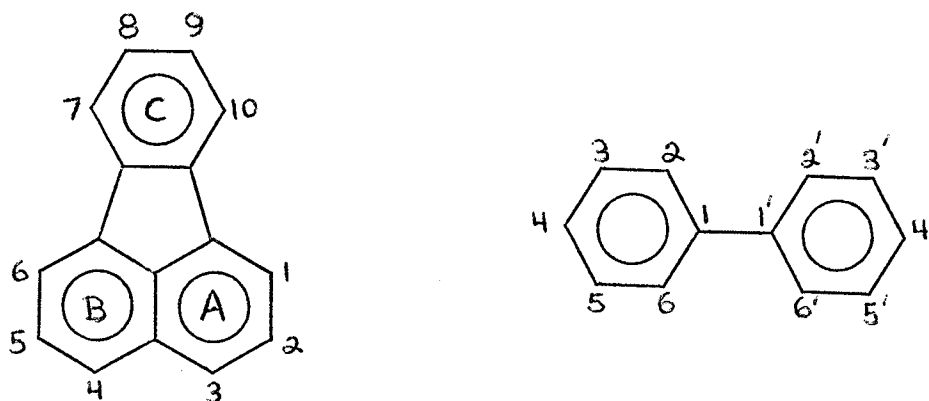


The fluoranthene disulfonic acid (XXVI) first obtained by Goldschmiedt (14) by the direct sulfonation of fluoranthene was at first thought to be the 3,8-derivative because of the quinhydrone-type product obtained by fusion with alkali. After many attempts at converting it to known reference compounds, the orientation was determined in the following way. Since monosulfonation occurs mainly in the 3-position, the disulfonic acid was thought to contain one sulfo group in that position. Fusion with potassium hydroxide produced a dihydroxy compound (XXVII) which on methylation gave a product (XXVIII) identical with a sample prepared from 3,9-diacetylfluoranthene. The validity of this proof is based on the assumption that the fusion of the disulfonic acid with alkali was not accompanied by migration of one or both of the sulfo groups. This work is summarized on page 16.

The results of the orientation work obtained up until that time (1955), indicated that 3-substituted fluoranthene compounds underwent further substitution mainly in the 8 or 9 positions depending on whether the first substituent was ortho-para-~~or~~ meta-directing. As a possible explanation of these results Campbell and Keir considered fluoranthene as a diphenyl derivative containing the diphenyl nuclei AC and BC. They pointed out that orientation in the diphenyl series is dominated by the phenyl groups. That is, in the majority of cases substitution in the second ring of diphenyl occurs



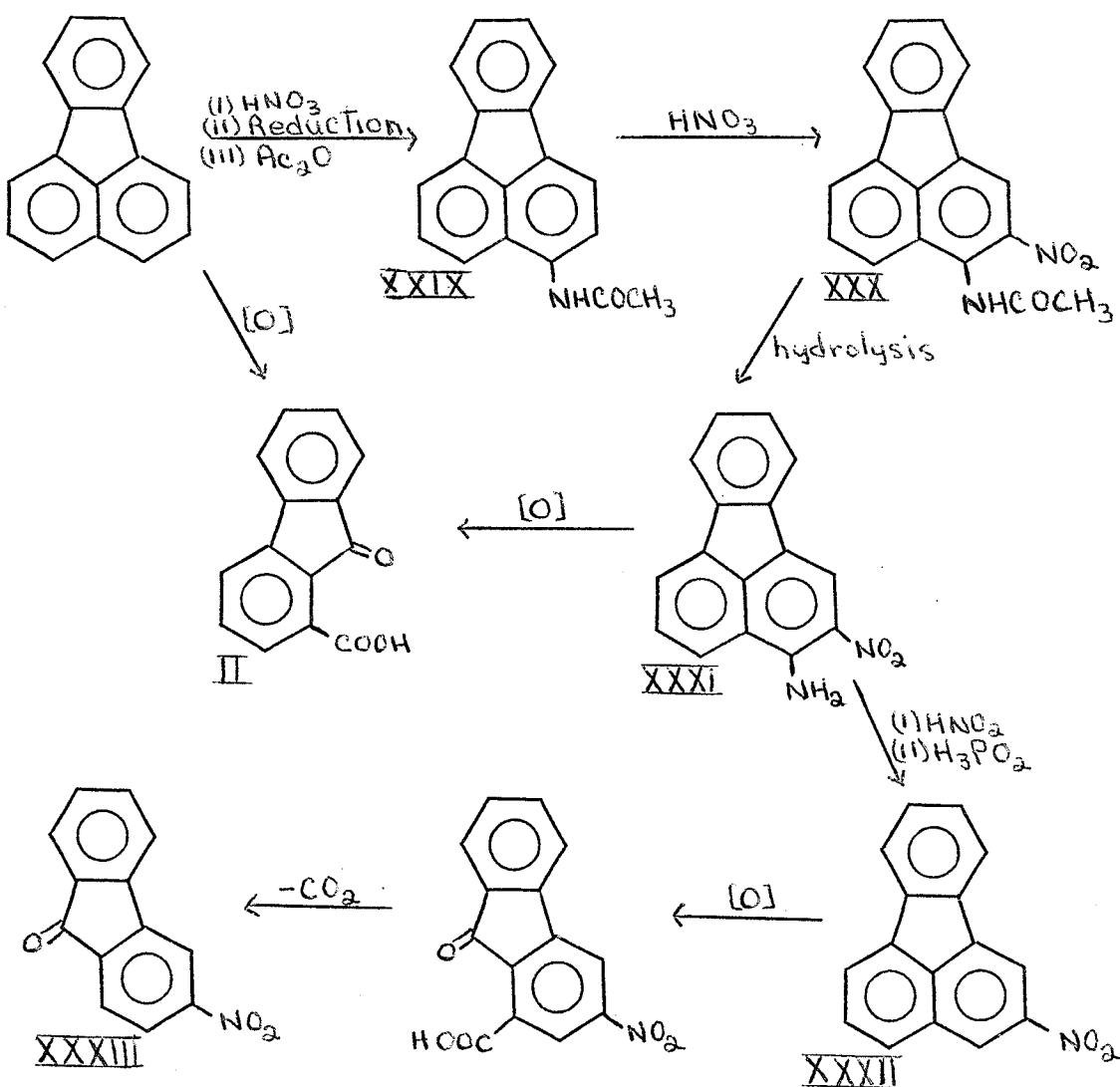
in the 2' and 4' positions regardless of the nature and position of the substituent already present in the first ring. This is exemplified by the fact that the three nitrodiphenyls undergo substitution in the 2' and 4' - positions but not in the 3' (meta)-position.



Thus, using this analogy, they postulated the following rules regarding orientation 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))."

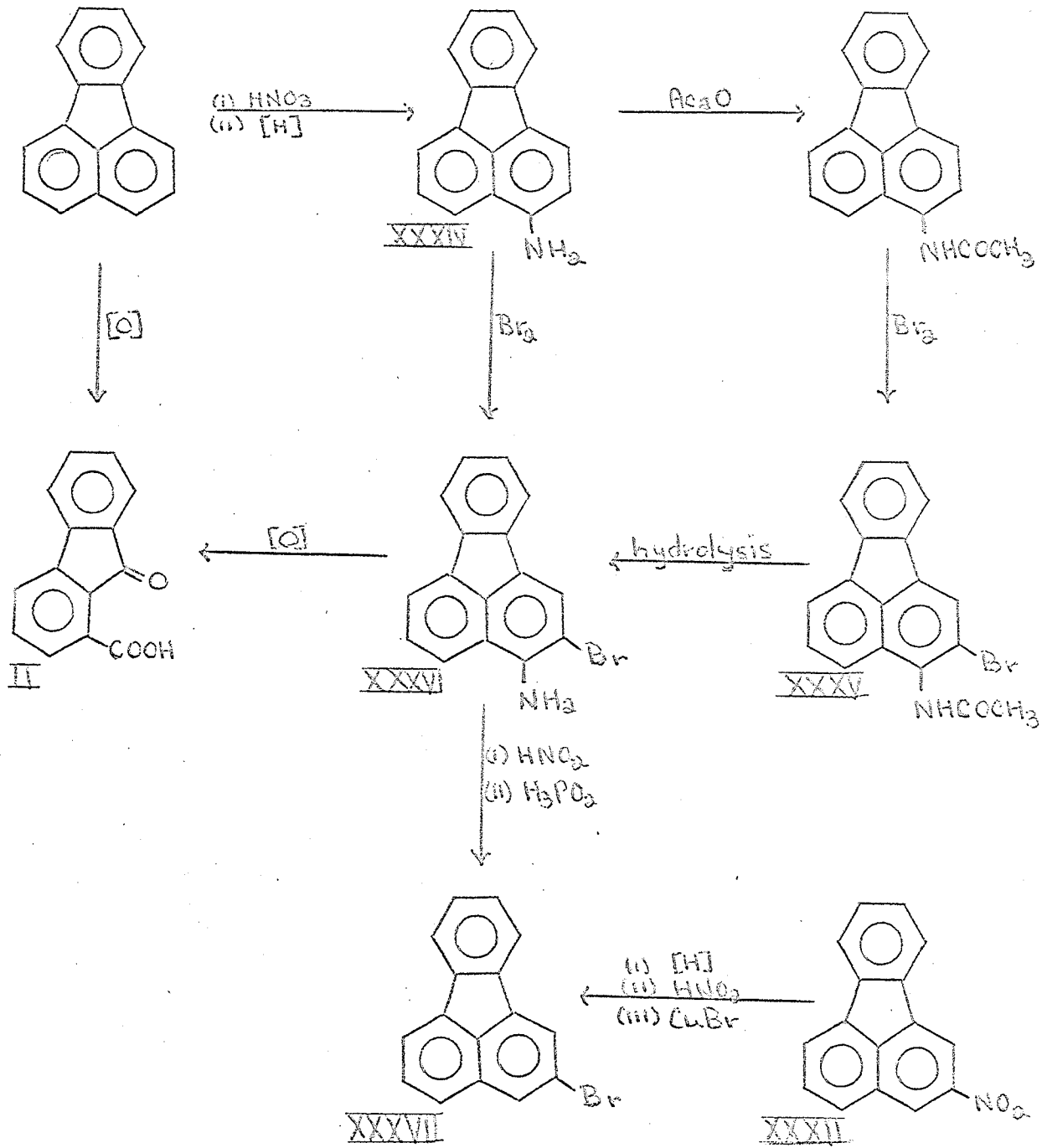
In 1956 Kloetzel, King and Menkes (17) showed that 3-acetamidofluoranthene (XXIX) was nitrated in the 2-position rather than in the 8- or 10-position as was expected from

the above postulates. The structure of the nitration product, 3-acetamido-2-nitrofluoranthene (XXX) was proved in the following manner. Oxidation of 3-amino-2-nitrofluoranthene (XXXI) gave 1-fluorenonecarboxylic acid (II) indicating that the nitro group must have been in the A ring. Deamination of XXXI gave a nitrofluoranthene (XXXII) which upon oxidation followed by decarboxylation gave 3-nitrofluorenone (XXXIII) proving that the nitro group was in position 2. This work may be summarized as follows.



To account for this new type of orientation Kloetzel et al. extended Campbell and Keir's rules, which, they suggested were oversimplified in that they did not take into account "the effects of intensely activating substituents" such as the acetamido group. They postulated that the acetamido group "so intensely activates the ring to which it is attached that the second substituent enters the same ring." This postulate was substantiated in 1964 by Charlesworth and Blackburn (7) who reported that both 3-acetamido and 3-aminofluoranthene (XXXIV) were brominated in the 2-position.

They established the 2-position of the bromine atom in 3-acetamido-2-bromofluoranthene (XXXV) and 3-amino-2-bromofluoranthene (XXXVI) in the following manner. Hydrolysis of XXXV gave a compound which was identical with XXXVI, thus indicating that the bromine atom was in the same position in both of these compounds. Oxidation of XXXVI gave 1-fluorenonecarboxylic acid (II), proving that the amino group and the bromine atom were both in the same ring. Deamination of XXXVI gave a bromofluoranthene (XXXVII) which was identical with the compound obtained from 2-nitrofluoranthene (XXXII) by reduction, diazotization and treatment with cuprous bromide. These results are summarized on page 20.



DISCUSSION OF RESULTS

The purpose of this study was to investigate the directive properties of some 2-substituted fluoranthene compounds under brominating conditions. The specific fluoranthene compounds studied were 2-nitrofluoranthene and 2-acetamidofluoranthene. These were chosen because they are among the few known 2-substituted fluoranthene compounds and their syntheses are relatively well established. Furthermore, the nitro and acetamido groups are representative of opposite ends of the activity scale, i.e., $-\text{NO}_2$ is a strongly deactivating group and $-\text{NHCOCH}_3$ is a strongly activating group.

Directive Properties of the 2-Nitro Group

2-Nitrofluoranthene (XXXII) was prepared essentially by the method of Kloetzel, King and Menkes (17). Direct nitration of fluoranthene according to the method of Garascia, Fries and Ching (12) gave 3-nitrofluoranthene. Catalytic reduction of this compound yielded 3-aminofluoranthene (XXXIV) which was then converted into its acetyl derivative on treatment with acetic anhydride. The directive influence of the acetamido group was subsequently employed to promote nitration in the 2-position. It was this reaction which led Kloetzel et al. (17) to suggest that Campbell and Keir's orientation rules were oversimplified in that they did not take account of intensely

activating substituents. Hydrolysis of 3-acetamido-2-nitrofluoranthene (XXX) gave 3-amino-2-nitrofluoranthene (XXXI) from which the amino group was finally eliminated by reduction of the corresponding diazonium salt with hypophosphorous acid giving 2-nitrofluoranthene.

Bromination of 2-nitrofluoranthene to give 9-bromo-2-nitrofluoranthene (XXXIX) was successfully accomplished by bromination in nitrobenzene at room temperature. The experimental conditions were essentially those used by Campbell and Keir (6) in the bromination of 3-nitrofluoranthene. Brominations in pyridine at various temperatures were carried out with the hope of obtaining a better yield. However, under these conditions no satisfactory product was obtained.

It now remained to determine the position of the bromine atom in XXXIX. Preliminary oxidative evidence coupled with the knowledge that the deactivating nitro group in the 2-position was not likely to direct substituents into the A ring, indicated that the bromine atom was in ring C. Oxidation of the nitrobromofluoranthene yielded an acid which contained both bromine and nitrogen, and which was later shown to be 6-bromo-3-nitrofluorenone-1-carboxylic acid (XL). Thus it was evident that the unsubstituted ring of the naphthelenic nucleus of this compound, i.e., the B ring, had been cleaved on oxidation.

At first the oxidation of XXXIX in a solution of chromic anhydride in glacial acetic acid and water by a method similar to that used by Campbell and Keir (6) in the oxidation of 9-bromo-3-nitrofluoranthene failed to give any product. It was found, however, that by increasing the refluxing time a yellow acidic substance (XL, see page 25) precipitated out of the reaction mixture.

There were two relatively simple sequences of reactions by which the 9-position of the bromine atom could be proven. Both of these reaction series involved oxidative degradation and concluded in the formation of known compounds. Work was undertaken to establish the position of the bromine atom following both these lines of attack.

In the first sequence of reactions 9-bromo-2-nitrofluoranthene (XXXIX) was converted into 9-bromo-2-amino-fluoranthene (XLI) by catalytic reduction of the nitro group using platinum oxide as the catalyst and absolute alcohol as the solvent. However, the product thus obtained was very impure. Several methods of purification were attempted with little success (see Experimental page 35). An analysis of the crude product revealed a non-combustible residue comprising 6.05% of the total weight of sample.

Despite the fact that a pure product could not be obtained, oxidation of the 9-bromo-2-aminofluoranthene was attempted in order to determine whether the bromine atom and the amino group were on the same ring or not.

If these groups were on the same ring, the A ring, it would be expected to break and, thus, 1-fluorenonecarboxylic acid would be obtained. If these 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. Several oxidations were carried out by refluxing the impure amine with chromic anhydride in glacial acetic acid and water. In each case, either no product or a very small amount of impure product was isolated. The failure of this reaction was probably due to the impurity of the starting material. It was thought worthwhile to prepare the acetyl derivative and oxidize it.

9-Bromo-2-acetamidofluoranthene (XLII) was obtained in a relatively pure form by treatment of a benzene solution of the amine with acetic anhydride. It was then successfully oxidized in a manner similar to that described above. The acidic product obtained, contained bromine but no nitrogen. This indicated that the ring containing the acetamido group, the A ring, had cleaved on oxidation as expected (6). It also indicated that the bromine atom was definitely in the C ring since the oxidation product of the original nitrobromo compound (XXXIX) had shown that it was not in the B ring. The oxidation product was found to have the same melting point as 7-bromofluorenone-1-carboxylic acid (XLIII). Admixture with an authentic

sample prepared by the method of Campbell et al. (4) by direct bromination of fluorenone-1-carboxylic acid gave no depression in the melting point. 7-Bromofluorenone-1-carboxylic acid could only have been formed if the bromoacetamidofluoranthene (XLII), and of course the compound from which it was derived, the bromonitrofluoranthene (XXXIX), contained the bromine atom in the 9-position. This proved that 2-nitrofluoranthene underwent bromination in the 9-position, and agreed with Campbell and Keir's rule for non-activating substituents in the A ring. This is the first piece of experimental evidence to show that the rule is applicable to non-activating substituents in the 2-position.

It was hoped that additional proof of this orientation could be obtained by a second line of attack. 9-Bromo-2-nitrofluoranthene was oxidized, as was previously discussed, to give 6-bromo-3-nitrofluorenone-1-carboxylic acid (XL). Decarboxylation of the acid gave 6-bromo-3-nitrofluorenone (XLIV).

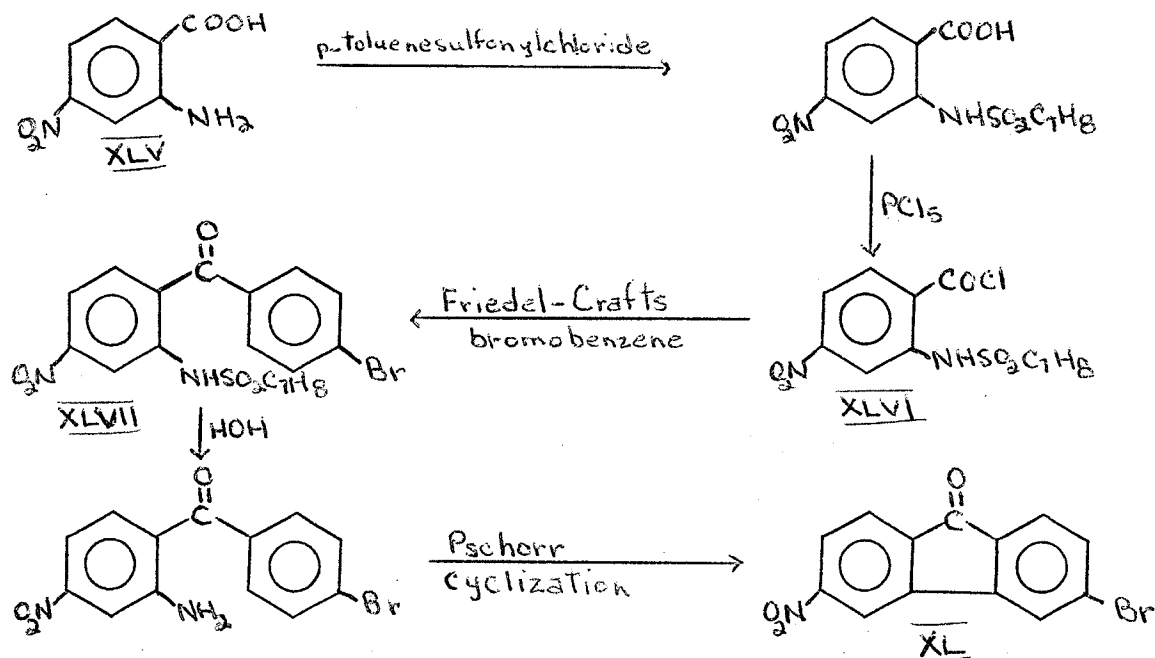
The decarboxylation was carried out essentially by the method used by Campbell and Keir (6) in the decarboxylation of 6-bromo-2-nitrofluorenone-1-carboxylic acid. The acid was refluxed in pyridine with a trace of finely ground copper metal as catalyst. Campbell and Keir used copper bronze as catalyst in their reaction, but since none was available copper metal was used in its place. The decarboxylation

was not done in quinoline because of the possibility of debromination also occurring. On decarboxylating 6-bromo-2-nitrofluorenone-1-carboxylic acid in quinoline the above authors obtained 2-nitrofluorenone. This debromination was not unexpected since the lability of bromine in the 3-position of fluorenone has long been known (20). Even when the decarboxylation was done in boiling pyridine some debromination occurred, although a product of reasonable purity was obtained.

The plan was then to prepare 6-bromo-3-aminofluorenone by catalytic reduction of the nitro compound and to remove the amino group by reduction of the corresponding diazonium salt with hypophosphorous acid. This would have resulted in the formation of 3-bromofluorenone, a known compound. However, because of the low yields in the preceding reactions, especially in the decarboxylation, not enough material was available to carry this plan through, and this line of attack had to be abandoned because of a lack of time.

An attempt is now being made in this laboratory to prepare an authentic sample of 6-bromo-3-nitrofluorenone (XL). The proposed method of synthesis is as follows: 4-nitroanthranilic (XLV) acid is reacted first with p-toluenesulfonylchloride, to protect the amino group, and then with phosphorous pentachloride. The resulting acyl chloride (XLVI) is reacted with bromobenzene in a Friedel-

Crafts reaction to give a substituted benzophenone (XLVII). After hydrolysis of the tosyl group, ring closure is brought about by the Pschorr reaction. These reactions may be summarized as follows.



Directive Properties of the 2-Acetamido Group

2-Acetamidofluoranthene was prepared by the method of Kloetzel et al. (17) by catalytically reducing 2-nitrofluoranthene and acetylating the resulting amine with acetic anhydride.

3-Bromo-2-acetamidofluoranthene (XLVIII) was obtained on bromination of 2-acetamidofluoranthene in pyridine at room temperature according to the method used by Charlesworth and Blackburn (7) in the bromination of 3-acetamidofluoranthene.

The 3-position of the bromine atom was established in the following manner. 3-Bromo-2-acetamidofluoranthene was hydrolyzed on refluxing with a solution of pyridine, methanol and sodium hydroxide to give 3-bromo-2-aminofluoranthene (XLIX). Deamination of this compound gave the 3-bromofluoranthene (I) which, upon admixture with an authentic sample prepared from 3-aminofluoranthene, gave no depression in the melting point.

This result is in agreement with the suggestion made first by Kloetzel, King and Menkes (17) and later confirmed by Charlesworth and Blackburn (7), that an intensely activating substituent in fluoranthene should cause further substitution in the same ring to which it is attached. Now that it has been shown that an intensely activating group in the 2-position also directs substituents into the same ring, and in particular, into the 3-position, the suggestion of these authors appears to be generally applicable to all positions in the A ring.

Authentic 3-bromofluoranthene was prepared by diazotization of 3-aminofluoranthene followed by the Sandmeyer reaction. The method of diazotization used was essentially that developed by Charlesworth and Blackburn (7) for the diazotization of weakly basic and insoluble amines. Their method involved the initial preparation of the amine sulfate. The salt was dissolved in a solution of glacial acetic acid and sulfuric acid, and then precipitated in a finely divided

form. Diazotization was effected by the addition of an aqueous solution of sodium nitrite. This method of diazotization was also used to prepare other halofluoranthenes, namely, 2-chlorofluoranthene, 3-chlorofluoranthene and 2-iodofluoranthene.

It seemed worthwhile to attempt to prepare 2-fluorofluoranthene in order to complete the 2-halofluoranthene series. This was accomplished using a modified Schiemann reaction developed by Fletcher and Namkung (11) in which tetrahydrofuran was used as solvent. In the synthesis of ring-fluorinated 2-acetamidofluoranthenes, these authors found that when the diazonium fluoborate salts were prepared in THF, they "decomposed in inert solvents with little or no tar formation to give fluoro-compounds in better yields and of purer quality than when prepared in the absence of THF." Also they found that 4-aminobenzoic acid and 3-aminofluoranthene, which had hitherto failed to yield any fluoro-compound upon Schiemann decomposition, gave good yields of high quality. However, in applying this method to the preparation of 2-fluorofluoranthene, it was found that some tar formation occurred on decomposition of the diazonium fluoborate salt although a compound of reasonable purity was eventually isolated.

EXPERIMENTAL

Preparation of 3-Nitrofluoranthene (XVIII)

3-Nitrofluoranthene was prepared in a manner similar to that used by Garcia, Fries and Ching (12).

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 twenty minutes. Stirring was continued at 74-75° C. for another fifteen minutes. The orange-yellow precipitate of crude 3-nitrofluoranthene (25.6 g) was filtered from the hot solution, washed with glacial acetic acid, then with water and allowed to dry. Upon treatment with decolorizing charcoal and recrystallization from glacial acetic acid, the pure material (21.2 g) was obtained melting at 159-160° C.

Preparation of 3-Aminofluoranthene (XXXIV)

This compound was prepared essentially by the method of Kloetzel et al. (17).

3-Nitrofluoranthene (30.0 g) together with platinum oxide (0.39 g) was suspended in absolute alcohol (270 ml). The hydrogenation was carried out in a Parr pressure reaction apparatus. Reaction was completed in one hour during which time the gauge pressure decreased from 49 lbs./sq. in. to

19 lbs./sq.in. The platinum oxide catalyst was filtered off and the crude product isolated by dilution of the solvent with water, followed by filtration. The 3-aminofluoranthene (23.0 g) obtained in this manner melted at 111-113° C.

Preparation of 3-Acetamidofluoranthene (XXIX)

This preparation was carried out by acetylation of the amine in benzene solution according to the directions of Kloetzel et al. (17).

3-Aminofluoranthene (15.0 g) was stirred in benzene (900 ml) and a small amount of insoluble material filtered off. Acetic anhydride (9.5 ml) was then added to the benzene solution. The reaction mixture was allowed to stir at room temperature for thirty minutes during which time a cream-coloured solid precipitated. Filtration of the mixture gave 3-acetamidofluoranthene (15.8 g), m.p. 241-242° C.

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

This compound was obtained by the nitration of 3-acetamidofluoranthene according to the method of Kloetzel et al. (17).

Concentrated nitric acid (6.6 ml) was added dropwise, with stirring, to a solution of 3-acetamidofluoranthene (13.0 g) in glacial acetic acid (1300 ml), maintained at a temperature of 80° C. The reaction mixture was kept at 80-85° C., with constant stirring, for ninety minutes. During

this period the product began to precipitate out of solution. After the reaction mixture had cooled to room temperature the precipitate was filtered off, washed with water and allowed to dry. The bright yellow 3-acetamido-2-nitrofluoranthene (12.5 g) thus obtained melted at 280-282° C.

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

3-Acetamido-2-nitrofluoranthene was hydrolyzed by a method similar to that employed by Kloetzel et al. (17).

The hydrolysis was accomplished by refluxing a mixture of the amide (23.5 g), 95% ethanol (2000 ml), and concentrated hydrochloric acid (2000 ml) for fifteen hours. The cooled reaction mixture was neutralized with a 10% solution of sodium hydroxide. Upon cooling, the product was filtered off, washed with water, and allowed to dry. The crude 3-amino-2-nitrofluoranthene (21.5 g) obtained melted at 247-251° C. Treatment with decolourizing charcoal and recrystallization from a mixture of pyridine and water in a manner similar to that described by Blackburn (1) gave the pure product, m.p. 252-254° C. Upon recrystallization from chlorobenzene Kloetzel et al. (17) reported a melting point of 235-236° C. Jemmett et al. (16) recrystallized this compound from ethylene glycol, then from chlorobenzene and finally from methyl ethyl ketone and reported its melting point to be 253° C.

Preparation of 2-Nitrofluoranthene (XXXII)

The deamination of 3-amino-2-nitrofluoranthene to produce 2-nitrofluoranthene was successfully accomplished in a manner similar to that of Kloetzel et al. (17).

Sodium nitrite (3.2 g) was dissolved by carefully adding it, with stirring, to a solution of concentrated sulfuric acid (110 ml) and water (8.0 ml) at room temperature. The solution was then cooled by means of an ice-salt bath to -5° C. Powdered 3-amino-2-nitrofluoranthene (9.0 g) was added slowly keeping the temperature at -5° C. Stirring was continued at this temperature for another thirty minutes. The resulting solution was diluted with precooled 50% hypophosphorous acid (235 ml) at such a rate (three hours and thirty minutes) that the temperature at no time exceeded 5° C. After standing for five days at $2-3^{\circ}$ C. the mixture was diluted with three volumes of water. The crude product was filtered off, washed with dilute aqueous sodium hydroxide, water, and allowed to dry. Treatment with charcoal and recrystallization from glacial acetic acid gave yellow crystals of 2-nitrofluoranthene (6.5 g), m.p. $151.5-153.5^{\circ}$ C.

Preparation of 9-Bromo-2-Nitrofluoranthene (XXXIX)

The method was essentially that used by Campbell and Keir (6) in the bromination of 3-nitrofluoranthene except for the purification.

2-Nitrofluoranthene (3.0 g) was stirred in nitrobenzene (50 ml) and a small amount of insoluble material filtered off. Bromine (1.28 ml) was added dropwise to the above solution at room temperature. Stirring was continued for three hours during which time a solid precipitated. The mixture was filtered and the precipitate was washed with cold 95% ethanol (50 ml) in order to remove some of the nitrobenzene. It was then treated with charcoal and recrystallized from glacial acetic acid. 9-Bromo-2-nitrofluoranthene (2.2 g) was thus obtained as flat yellow plates, m.p. 240-243° C.

| | | |
|-----------------|--|-----------------------------|
| <u>Analysis</u> | Found: | C, 58.56; H, 2.85; N, 4.13; |
| | | Br, 24.80% |
| | Calc. for C ₁₆ H ₈ O ₂ NBr: | C, 58.94; H, 2.45; N, 4.29; |
| | | Br, 24.51% |

Preparation of 9-Bromo-2-Aminofluoranthene (XLI)

9-Bromo-2-aminofluoranthene was best obtained by hydrogenation of 9-bromo-2-nitrofluoranthene (2.2 g) in absolute alcohol (110 ml) in the presence of platinum oxide (0.025 g) at a pressure of 40 lbs./sq.in. for twenty four hours. The catalyst was then filtered off and the amine precipitated with a 10% solution of sodium hydroxide. After standing overnight, the precipitate was filtered off, washed with water and dried. The crude 9-bromo-2-aminofluoranthene (1.8 g) thus obtained had a melting point range of 115-122° C. The following methods of purification were attempted with little success:

1. The amine hydrochloride was prepared by dissolving the amine (0.1 g) in chloroform (30 ml) and precipitating the salt by the addition of a few drops of concentrated hydrochloric acid. Hydrolysis of the salt in a dilute solution of ammonium hydroxide gave a dark brown precipitate which had a wider melting point range than the original crude amine.

2. A benzene solution of the amine (0.25 g) was chromatographed on a short alumina column. Although benzene was not a particularly good solvent to use for amine chromatography, a separation into two distinct bands was obtained. The first band, which was the narrower and less fluorescent of the two was thought to contain the unreacted nitro compound, and the second the amine. On development and evaporation of the solvent under reduced pressure, the second band left a tarry residue.

3. Recrystallizations from solutions of pyridine and water, and benzene and petroleum ether also failed to give a pure product. Solutions of the amine were light sensitive and darkened rapidly upon standing.

| | | |
|-----------------|--|-----------------------------------|
| <u>Analysis</u> | Found: | Br, 18.32; N, 4.36; Residue 6.05% |
| | Calc. for C ₁₆ H ₁₀ NBr: | Br, 26.99; N, 4.73% |

Preparation of 9-Bromo-2-Acetamidofluoranthene (XLII)

Acetic anhydride (0.8 ml) was added to a solution of crude 9-bromo-2-aminofluoranthene (0.6 g) in benzene (60 ml).

The reaction mixture was stirred at room temperature for one hour. During this time a white solid precipitated. The mixture was filtered, washed with benzene and allowed to dry. The crude product (0.49 g) was treated with charcoal and recrystallized from glacial acetic acid. The yellow needles obtained melted at 251-253° C.

| | | | | |
|-----------------|---|------------|----------|----------|
| <u>Analysis</u> | Found: | C, 64.78% | H, 3.84% | N, 4.16% |
| | | Br, 23.71% | | |
| | Calc. for C ₁₈ H ₁₂ NOBr: | C, 64.13% | H, 3.26% | N, 4.15% |
| | | Br, 23.76% | | |

Oxidation of 9-Bromo-2-Acetamidofluoranthene

The experimental details used were similar to those of Campbell and Keir (6) in the oxidation of 9-bromo-3-nitrofluoranthene.

Chromic acid (1.2 g) in water (7.0 ml) and glacial acetic acid (5.0 ml) was added slowly, with stirring, to a mixture of 9-bromo-2-acetamidofluoranthene (0.64 g) in glacial acetic acid (75 ml) at room temperature. The resulting mixture was stirred overnight and then refluxed for two hours. Removal of half the solvent by distillation and precipitation with water gave the crude product (0.41 g). Treatment with decolourizing charcoal and recrystallization from glacial acetic acid yielded pure 7-bromofluorenone-1-carboxylic acid as orange-red needles, m.p. 226-229° C.

| | | |
|-----------------|---|------------|
| <u>Analysis</u> | Found: | Br, 26.35% |
| | Calc. for C ₁₄ H ₇ O ₃ Br: | Br, 26.37% |

Admixture with an authentic sample (see next preparation)

caused no depression in the melting point.

Preparation of Authentic 7-Bromofluorenone-1-Carboxylic Acid

7-Bromofluorenone-1-carboxylic acid was prepared by the bromination of fluorenone-1-carboxylic acid according to the method of Campbell, Easton, Rayment and Wilshire (4).

Fluorenone-1-carboxylic acid (2.0 g) was added to bromine (25.0 ml) and the mixture allowed to stir overnight. The crude product was precipitated on pouring the above mixture into water. The water layer was decanted and the precipitate washed several times with water, and 95% ethanol until the bromine colour was discharged. It was then filtered and allowed to dry. Treatment with charcoal and recrystallization from glacial acetic acid gave pure 7-bromofluorenone-1-carboxylic acid (1.4 g), m.p. 227-229° C.

Oxidation of 9-Bromo-2-Nitrofluoranthene

The method of Campbell and Keir (4) was again utilized in this reaction.

An oxidizing solution was prepared by dissolving chromic acid (2.0 g) in water (12 ml) and glacial acetic acid (8.0 ml). This solution was added slowly, with stirring, to a mixture of 9-bromo-2-nitrofluoranthene (1.0 g) in glacial acetic acid (140 ml). The reaction mixture was stirred at room temperature overnight and then refluxed for eight hours. Upon removal of half the solvent by distillation, and cool-

ing, the solution yielded a bright yellow precipitate of 6-bromo-3-nitrofluorenone-1-carboxylic acid (0.4 g), m.p. 283.5-286° C.

| | | |
|-----------------|--|---|
| <u>Analysis</u> | Found: | C, 48.64; H, 1.69; N, 3.94; Br, 23.39% |
| | Calc. for C ₁₄ H ₆ O ₅ NBr: | C, 48.30; H, 1.74; N, 4.02; Br, 22.95% |

An additional small amount of impure acid was recovered by extraction of the above filtrate with ether which in turn was extracted with a 10% solution of sodium carbonate. Acidification of the carbonate solution with concentrated hydrochloric acid brought about precipitation of the acid (0.052 g) m.p. 265-275° C. As evidenced by the melting point of this compound, it appeared to be quite impure and because of the relatively small amount obtained no attempt was made to purify it. The acid obtained initially was used in subsequent reactions.

Decarboxylation of 6-Bromo-3-Nitrofluorenone-1-Carboxylic Acid

6-Bromo-3-nitrofluorenone-1-carboxylic acid was successfully decarboxylated essentially by the method used by Campbell and Keir (6) in the decarboxylation of 6-bromo-2-nitrofluorenone-1-carboxylic acid except that in this instance copper powder was used as the catalyst instead of copper bronze.

The acid (0.22 g) was refluxed in pyridine (25 ml) with a trace of copper powder for eleven hours. The cooled

reaction mixture was poured into a dilute solution of hydrochloric acid and the precipitate filtered off. The dried material was stirred with hot benzene and a small amount of insoluble material filtered off and discarded. The aqueous filtrate from above was also extracted with benzene. The benzene extracts were combined and washed with a 15% aqueous solution of sodium carbonate until there was no visible change in the carbonate solution, and then with water. The resulting benzene solution was dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and washed colourless with a small amount of benzene. Evaporation of the solvent under reduced pressure left a solid residue which, when treated with decolourizing charcoal and recrystallized from glacial acetic acid gave beautiful golden needles of 6-bromo-3-nitrofluorenone (0.028 g), m.p. 327-330° C.

Analysis

| | |
|-------------------------------|-----------------------------|
| Found: | C, 51.63; H, 2.45; N, 4.34; |
| | Br, 23.39% |
| Calc. for $C_{13}H_6O_3NBr$: | C, 51.35; H, 1.99; N, 4.61; |
| | Br, 26.28% |

It is evident from the analysis, that the decarboxylation was accompanied by some debromination. (see Discussion of Results p.25)

Preparation of 2-Aminofluoranthene

Hydrogenation of 2-nitrofluoranthene in a manner similar to that described by Kloetzel et al. (17) gave 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 dropped from 49.5 lbs./sq. in. to 46.0 lbs./sq.in. The decolourizing charcoal and platinum oxide were filtered out of the reaction mixture. Precipitation with water yielded the crude amine (2.8 g), m.p. 115-121° C. Upon purification Kloetzel et al. obtained a melting point of 128-129° C. for this compound. In this case the amine was required as its acetyl derivative (see next preparation) and therefore was not purified.

Preparation of 2-Acetamidofluoranthene

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

The crude 2-aminofluoranthene (3.0 g) was stirred in benzene (180 ml) and a small amount of insoluble material was filtered off. Acetic anhydride (1.5 ml) was added to the benzene solution and the reaction mixture was stirred at room temperature for one hour. Filtration of the solid which precipitated during this time gave 2-acetamidofluoranthene (2.4 g), m.p. 226-228° C.

Preparation of 3-Bromo-2-Acetamidofluoranthene (XLVIII)

The method was essentially that described by

Charlesworth and Blackburn (7) in the preparation of 3-acetamido-2-bromofluoranthene.

Bromine (1.1 ml) was added slowly with stirring to a solution of 2-acetamidofluoranthene (2.4 g) in pyridine (150 ml). Stirring was continued at room temperature for eleven hours. The crude product was precipitated with water (400 ml), filtered off, and washed successively with 10% solutions of sodium hydroxide and sodium bisulfite and finally with water. It was then dissolved in boiling pyridine (45 ml). A small amount of insoluble material was filtered from the hot pyridine solution and discarded. The filtrate was treated with charcoal and a sufficient amount of water was then added to bring about precipitation when the pyridine-water solution cooled. 3-Bromo-2-acetamidofluoranthene (3.0 g) was then obtained as straw coloured needles, m.p. 223.5-225.5° C.

| | | |
|-----------------|---|---------------------|
| <u>Analysis</u> | Found: | N, 4.15; Br, 23.71% |
| | Calc. for C ₁₈ H ₁₂ ONBr: | N, 4.11; Br, 23.07% |

Preparation of 3-Bromo-2-Aminofluoranthene (XLIX)

The experimental details followed were those of Charlesworth and Blackburn (7) used in the preparation of 3-amino-2-bromofluoranthene.

3-Bromo-2-acetamidofluoranthene (2.3 g) was added to a mixture of methanol (125 ml), pyridine (85 ml) and sodium hydroxide (7.2 g). The resulting solution was heated to the boiling point and the reaction mixture was allowed to



reflux for twelve hours. On dilution to one litre with water a yellow flocculent precipitate was formed. This collected material was washed with water, dried, and dissolved in boiling pyridine. After treatment of this solution with decolourizing charcoal a sufficient amount of water was added to cause crystallization when the solvent cooled. The 3-bromo-2-aminofluoranthene (1.6 g) thus obtained melted at 150.5-152.0° C., with slight decomposition.

| | | |
|-----------------|--|---------------------|
| <u>Analysis</u> | Found: | N, 4.41; Br, 26.88% |
| | Calc. for C ₁₆ H ₁₀ NBr: | N, 4.73; Br, 26.99% |

Deamination of 3-Bromo-2-Aminofluoranthene

Experimental details for this reaction were obtained from reference (18).

Sodium nitrite (0.6 g) was added cautiously with stirring to a solution of concentrated sulfuric acid (45 ml) and water (3.2 ml) at room temperature. When all the sodium nitrite had finally dissolved the solution was cooled to -5° C. by means of an ice-salt bath. Finely ground 3-bromo-2-aminofluoranthene (1.0 g) was added slowly with vigorous stirring to the above solution over a period of fifteen minutes; the temperature being maintained at -5° C. Stirring was continued at approximately the same temperature for one hour. Precooled hydrophosphorous acid (65 ml) was then added to the stirred solution at such a rate (two hours and thirty minutes) that the temperature at no time rose above

5° C. The reaction mixture was then allowed to stand at 2-3° C. for four days after which time the product was precipitated on dilution to one litre with water. The colloidal precipitate was allowed to coagulate and then filtered off. The dried material was stirred in hot benzene and a small amount of insoluble residue was removed. The benzene solution was washed with concentrated sulfuric acid until the acid layer no longer became coloured, then with a 10% sodium carbonate solution and finally with water. It was then dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and washed almost colourless by a small amount of benzene. After removal of the solvent by distillation under reduced pressure, the solid residue which remained was treated with decolourizing charcoal and recrystallized twice from 95% ethanol. 3-Bromofluoranthene (0.3 g) was thus obtained as yellow needles which melted at 104-105.5° C.

| | | |
|-----------------|--|------------|
| <u>Analysis</u> | Found: | Br, 28.12% |
| | Calc. for C ₁₆ H ₉ Br: | Br, 28.43% |

Admixture with an authentic sample of 3-bromofluoranthene obtained from 3-aminofluoranthene (see next preparation) gave no depression in melting point.

Preparation of Authentic 3-Bromofluoranthene (L)

The method employed closely followed that of Charlesworth and Blackburn (7) in their preparation of 2-bromofluoranthene except for some modifications in experimental

details and a change in the purification procedure.

Crude 3-aminofluoranthene (4.0 g) was stirred in absolute ether (200 ml) and the insoluble material filtered off. Concentrated sulfuric acid (3.0 ml) was added with vigorous stirring to the amine solution. The greyish coloured amine salt which precipitated was collected, dried, and finely ground. The salt was partially dissolved in glacial acetic acid (300 ml) by warming the mixture to about 90° C. Enough concentrated sulfuric acid (30 ml) was then added to bring about complete dissolution. 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 form. Diazotization was effected by the addition of sodium nitrite (2.5 g) in water (10 ml) dropwise over a period of about twenty minutes. During the diazotization the temperature of the reaction mixture was kept between 0-5° C. by means of external cooling. Stirring was continued for another thirty minutes after which time urea (2.0 g) was added to destroy any excess nitrous acid. The diazonium salt solution was then filtered through a sintered glass crucible and added, with vigorous stirring, to a precooled solution of cuprous bromide (30.0 g) in 48% hydrobromic acid (100 ml). A light brown flocculent precipitate formed. The mixture was heated slowly, with stirring, to 90° C. and then allowed to stand overnight at room temperature. The precipitate was filtered off and the

dried material stirred with hot benzene. A small amount of insoluble material was removed by filtration. The aqueous filtrate from above was also extracted with benzene. The benzene extracts were combined and washed with 10% solutions of sodium hydroxide and sodium bisulfite. The resulting benzene solution was then extracted with concentrated sulfuric acid until further extraction gave no colouration of the acid layer. Next, the benzene solution was washed with a 10% sodium carbonate solution, then with water, and dried over anhydrous magnesium sulfate. The drying agent was filtered off, and the solvent evaporated under reduced pressure. Upon treatment with decolourizing charcoal and recrystallization from 95% ethanol, the solid brown residue which remained after evaporation yielded pale yellow needles of 3-bromofluoranthene (2.0 g), m.p. 105.5-106.5° C.

Preparation of 3-Chlorofluoranthene and 2-Chlorofluoranthene

These compounds were prepared from the sulfate salts of 3-aminofluoranthene and 2-aminofluoranthene by means of the diazotization procedure described above and a subsequent Sandmeyer reaction.

The diazonium salt solution was poured, with stirring, into a precooled solution of cuprous chloride (20 g) in concentrated hydrochloric acid (150 ml) and water (30 ml). This resulted in the formation of an orange flocculent

precipitate. The mixture was warmed gradually to about 90° C. and then allowed to stand overnight at room temperature. The precipitate was collected and both the filtrate and dried precipitate were extracted with benzene. The combined benzene extracts were washed and dried in the same manner as previously described and the resulting solution evaporated to dryness. Sublimation of the solid residue twice, at approximately 95° C. under high vacuum, gave the desired products.

3-Chlorofluoranthene (2.3 g from 4.0 g. of starting material) was obtained as pale yellow needles, m.p. 97-99° C. (lit. 102-103° C.).

2-Chlorofluoranthene (1.3 g from 4.0 g of starting material) was similarly obtained as pale yellow needles, m.p. 87.5-88.5° C.

| | | |
|-----------------|--|------------|
| <u>Analysis</u> | Found: | Cl, 14.97% |
| | Calc. for C ₁₆ H ₉ Cl: | Cl, 14.98% |

Preparation of 2-Iodofluoranthene

In the preparation of this compound the diazonium salt solution (obtained as described above) was poured into a cold solution of potassium iodide (30.0 g) in water (100 ml). The resulting mixture was allowed to stand overnight and then worked up in the manner already described. The 2-iodofluoranthene which was obtained by treatment of the crude product and decolourizing charcoal and recrystallization from 95% ethanol melted at 124.0-125.5° C.

Analysis Found: I, 37.15%
 Calc. for $C_{16}H_9I$: I, 38.68%

Preparation of 2-Fluorofluoranthene

This compound was prepared via a modified Schiemann reaction first used by Fletcher and Namkung in the preparation of 3-fluorofluoranthene.

48-50% Fluoboric acid (8.0 ml) and water (10 ml) were added to a solution of 2-aminofluoranthene (1.5 g) in tetrahydrofuran (5 ml). A light brown paste of fluoborate salt formed. While stirring and cooling to 5° C. in an ice-salt bath an aqueous solution of sodium nitrite (0.7 g) in water (5 ml) was added dropwise. As the yellow diazonium salt formed, the mixture became more fluid and easier to stir. After stirring for an additional thirty minutes, the mixture was filtered and washed with 5% fluoboric acid, methanol, and ether, and dried. The salt was then mixed with xylene (40 ml) and the mixture boiled. Gradual decomposition took place. When most of the xylene had boiled off, the mixture was removed from the heat and the remaining xylene allowed to evaporate. The dark brown residue which remained was sublimated twice under high vacuum at about 80° C. and then treated with charcoal and recrystallized from 95% ethanol. The 2-fluorofluoranthene (0.2 g) thus obtained melted at 88-89° C.

Analysis Found: F, 8.54% ; C, 87.76% ; H, 4.50%
 Calc. for $C_{16}H_9F$: F, 8.63% ; C, 87.28% ; H, 4.08%

SUMMARY

1. Bromination of 2-nitrofluoranthene in nitrobenzene gave the previously unknown 9-bromo-2-nitrofluoranthene.

2. The structure of 9-bromo-2-nitrofluoranthene was proved by converting it to 9-bromo-2-acetamidofluoranthene which was then oxidized to the known 7-bromofluorenone-1-carboxylic acid.

3. Work was undertaken to prove this structure by another method. 9-Bromo-2-nitrofluoranthene was oxidized to 6-bromo-3-nitrofluorenone-1-carboxylic acid, which was decarboxylated to give a new substituted fluorenone; 6-bromo-3-nitrofluorenone.

4. Bromination of 2-acetamidofluoranthene in pyridine gave a new compound; 3-bromo-2-acetamidofluoranthene.

5. The structure of 3-bromo-2-acetamidofluoranthene was proved by hydrolyzing it to 3-bromo-2-aminofluoranthene which upon deamination gave the known 3-bromofluoranthene.

6. A modified diazotization procedure first introduced by Charlesworth and Blackburn (7) was employed to prepare 3-chloro, 2-chloro and 2-iodofluoranthene; the latter two of which are new compounds.

7. The previously unknown 2-fluorofluoranthene was prepared via a modified Schiemann reaction.

8. The determination of the structure of 9-bromo-2-nitrofluoranthene is the first piece of experimental evidence to show that Campbell and Keir's (6) orientation

rule for deactivating substituents in the 3-position is also applicable to substituents in the 2-position.

9. The proof that 2-acetamidofluoranthene is brominated in the 3-position gives further indication that the orientation rule of Campbell and Keir (6) for activating substituents is incorrect. It also provides the first piece of experimental evidence to show that the orientation rule of Kloetzel et al. (17) for highly activating substituents in the 3-position is also applicable to substituents in the 2-position.

RECOMMENDATIONS FOR FUTURE WORK

1. Now that directive properties of a strongly activating and strongly deactivating substituent in the 2-position have been studied, it might be worthwhile to investigate the directive influence of a weakly activating group, for example, the bromine atom. According to Campbell and Keir's rule a substituent of this type in the 2-position would be expected to direct substituents to position 8. The results of such an investigation could lead to the preparation of many new 2,8-disubstituted fluoranthene compounds.

2. The directive properties of the 2-nitro and 2-acetamido groups could be investigated under nitrating conditions.

3. Another attempt should be made to purify 9-bromo-2-aminofluoranthene.

4. 9-Bromo-2-aminofluoranthene might be used as a starting material for the preparation of a series of 2,9-disubstituted fluoranthene derivatives.

5. Oxidation of some of these new disubstituted fluoranthene compounds followed by decarboxylation would yield a number of new disubstituted fluorenone compounds.

6. Other 2-substituted fluoranthene compounds, such as the 2-cyano, 2-carboxyl, 2-acetyl etc., could be obtained from 2-aminofluoranthene and the directive properties of these groups could be investigated.

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