THE CHEMISTRY OF FLUORANTHENE

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I. INTRODUCTION

The early history of fluoranthene is somewhat obscure. Around 1835 Dumas (61) and Laurent (126) obtained, by extraction of the mercury ores of Idria with oil of turpentine, a hydrocarbon fraction which they called idrialene. In 1844 Boedeker (13) distilled these ores, with production of a similar hydrocarbon which he named idryl. Much later Goldschmiedt (80, 81, 82) showed, by distillation and crystallization, that idryl consisted of anthracene, phenanthrene, chrysene, pyrene, and a hitherto unknown hydrocarbon, $C_{15}H_{10}$, to which he gave the name idryl. Simultaneously with Goldschmiedt's discovery, Fittig and

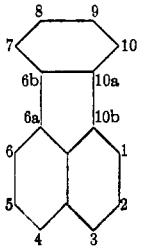
Gebhard (69, 70) isolated from the high-boiling fraction of coal tar a hydrocarbon which was named fluoranthene and was claimed to be identical with Goldschmiedt's idryl.

More recently the presence of fluoranthene has been detected in the high-boiling fractions of pyrogenic acetylenic condensations (133, 134), in carbon black (149), and in the tars produced from coal at low coking temperatures (139).

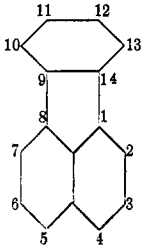
Two principal methods are now available for the extraction of fluoranthene from coal tar on a commercial scale. The pure hydrocarbon may be obtained by the normal processes of distillation and repeated fractional crystallization (103, 109, 120). Alternatively, fusion of the neutral tar-oil fractions with sodium yields a tetrasodium derivative of fluoranthene. The tetrahydrofluoranthene obtained on treatment with water is readily purified by crystallization and converted to fluoranthene by catalytic dehydrogenation (48, 123, 124, 127).

Little interest was displayed in fluoranthene for many years after its discovery, until von Braun and Anton proposed the now universally accepted structure. In the last twenty years many papers concerning fluoranthene have been published.

The numbering of the carbon atoms of fluoranthene first employed by von Braun and Anton and later adopted by *Chemical Abstracts* is shown in formula A. However, von Braun and Anton later adopted the numbering shown in B. This is in accordance with the Richter system of notation and is that used by European chemists. In this review other enumerations have been translated into the *Chemical Abstracts* system.



A



B

II. Physical Properties of Fluoranthene

Fluoranthene crystallizes from its concentrated solution in ethanol as long, thin, colorless needles melting at 109.5–110.5°C. (70, 118). The hydrocarbon is soluble in benzene, carbon disulfide, chloroform, ether, boiling ethanol, and acetic acid (80) but is almost insoluble in water (250 γ per liter) (51). It distils without decomposition at 393°C. in mercury vapor (52) or under reduced pressure (b.p. 250–251°C./60 mm. or 217°C./30 mm.) (72).

The absorption spectrum of fluoranthene resembles that of fluorene (154) and contains three groups of bands: (*i*) log ϵ about 3.5, $\lambda_{max.}$ = 3585, 3420, 3230, 3090 Å.; (*ii*) log ϵ about 4.2, $\lambda_{max.}$ = 2870, 2820, 2716, 2615, 2525, 2450 Å.; (*iii*) log ϵ about 4.5, $\lambda_{max.}$ = 2360 Å. (45). The ultraviolet absorption spectrum is thus very complex (144) and the absorption is more intense when the electric

vector of the light is parallel to the plane of the benzene rings than when it is perpendicular (122). The solutions of many fluoranthenes fluoresce blue or blue-green in ultraviolet light (179).

The addition of fluoranthene or of certain of its derivatives renders plastic materials such as cellulose esters or bakelite opaque to ultraviolet light (21, 93).

Fluoranthene forms the usual addition complexes with the polynitro compounds: fluoranthene picrate, m.p. 185–186°C. (118; *cf.* 70, 80, 88); the 1,3,5-trinitrobenzene complex, m.p. 205–206°C. (118; *cf.* 88, 156); the 2,4,7-trinitrofluorenone complex, m.p. 215.4–216.0°C. (corr.) (144). Sinomiya (156), who prepared these and a number of other complexes, showed that fluoranthene closely resembles naphthalene and pyrene in its propensity for forming molecular complexes with nitro compounds.

Wawzonek and Wang Fan (182) determined the half-wave potential and diffusion current constant for fluoranthene in a 0.175 *M* aqueous dioxane solution of tetrabutylammonium iodide, and deduced that fluoranthene dimerizes by a free-radical mechanism.

Fluoranthene has no interaction, such as is shown by several polycyclic aromatic hydrocarbons, on surface films of cholesterol or cholestanol on water (50).

Auwers and Kraul (4) attributed the observed increase in the optical exaltation of fluoranthene over that of fluorene to the extra double bond in the former; their calculations were, however, based on the erroneous formula for fluoranthene.

III. Pharmacological Reactions of Fluoranthene and Derivatives

Very few pharmacological effects of fluoranthene or of its derivatives have been reported. Fluoranthene and its derivatives have no carcinogenic effect (5, 6, 77) except for 15,16-benzdehydrocholanthrene (67), which has a slight carcinogenic effect; they do not produce long-continued reduction in the rate of growth of young rats, as do compounds such as 1,2,5,6-dibenzanthracene (86). After intravenous injection into fowls, fluoranthene gave a fluorescent derivative with a spectrum similar to that obtained in similar circumstances from 3,4-benzpyrene (39).

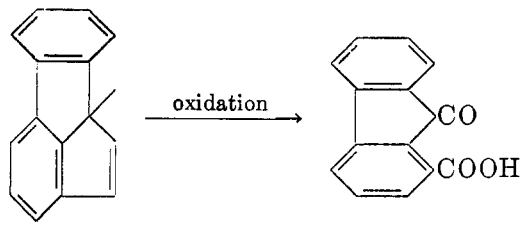
10b-Diethylaminoethyl-1,2,3,10b-tetrahydrofluoranthene phosphate in small doses strengthens the influence of the vagus on respiration in rabbits (23, 89). Some derivatives of 1,2,3,10b-tetrahydrofluoranthene are antispasmodics (40).

When certain types of wheat were treated with fluoranthene for 20 or more days, an increased number of nucleoli was found in the root cells, and some plants produced pollen grains larger than normal (150). Fluoranthene also showed an effect similar to that of retene or acenaphthene in increasing the accumulation of nuclear material in the cells of a strain of yeast (147).

IV. Structure and Synthesis of Fluoranthene

The early formula for fluoranthene (I), suggested by Fittig and Gebhard in 1877 (69), was based on the incorrect formulation $C_{15}H_{10}$ and on an erroneous

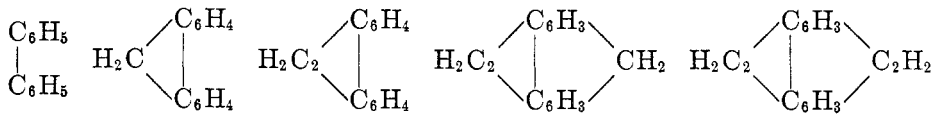
interpretation of oxidative evidence. Treatment of fluoranthene with potassium dichromate and sulfuric acid yielded an acid, $C_{14}H_8O_3$, which on distillation was converted to fluorenone; the acid was later shown to be 1-fluorenone-carboxylic acid (II).



I
Fluoranthene

II
1-Fluorenone-carboxylic acid

This acid (II) on fusion with potassium hydroxide (70) yielded isodiphenic acid, which on oxidation (71, 72) produced isophthalic acid, indicating a structure of type I for fluoranthene on the basis of the $C_{15}H_{10}$ formula. Later, Atterburg (3) regarded fluoranthene as intermediate between phenanthrene and pyrene:



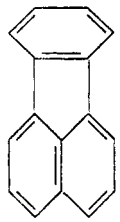
Biphenyl Fluorene Phenanthrene Fluoranthene Pyrene

Further support for formula I was given by Goldschmiedt (83), who showed that fluoranthene did not contain a reactive methylene group since, unlike fluorene, indene, and cyclopentadiene, it failed to condense with benzaldehyde or with ethyl oxalate. This indicated that the fourth ring was attached to C_9 of the fluorene skeleton.

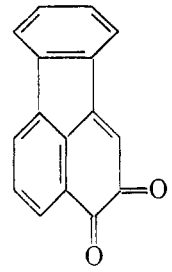
Early work aimed at the synthesis of fluoranthene of structure I was unsuccessful. Thus Mayer in 1913 (130) attempted to prepare the hydrocarbon from 9-fluorenylacetic acid and from 9-fluorenylpropionic acid, whilst Graebe in 1904 (84) obtained phenanthrene instead of the expected fluoranthene by a pyrogenic reaction on 9-ethylfluorene.

The now universally accepted formula for fluoranthene (III) was suggested and established synthetically by von Braun and Anton (15) in 1929. Clearly, according to the Sachse–Mohr concepts of bond strain in organic structures, a compound of formula I would be highly strained or, if it did exist, would be highly unstable. On the other hand III should represent a stable structure. It was also pointed out that the analytical values for carbon and hydrogen for the two compounds represented by formulas I and III, *viz.*, $C_{15}H_{10}$ and $C_{16}H_{10}$, respectively, are nearly the same. Furthermore, the oxidation of fluoranthene

or of fluoranthenequinone to 1-fluorenonecarboxylic acid (II) could be explained if their formulas were III and IV, respectively.

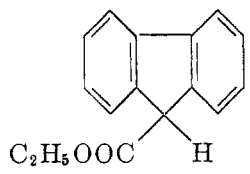


III
Fluoranthene



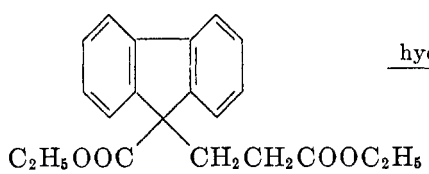
IV
Fluoranthenequinone

That fluoranthene had indeed the structure III was proved by its synthesis by von Braun and Anton (15) from ethyl 9-fluorenecarboxylate (V):

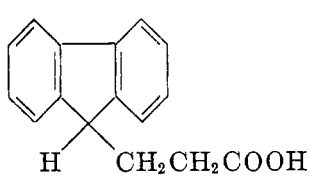


V
Ethyl fluorene-9-carboxylate

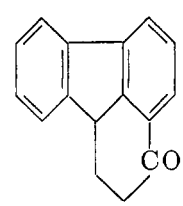
(a) C_2H_5ONa
(b) $ClCH_2CH_2COOC_2H_5$



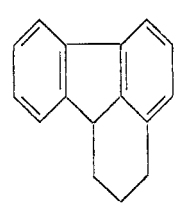
hydrolysis



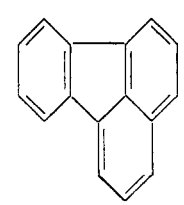
(a) $SOCl_2$
(b) $AlCl_3$



Zn, HCl



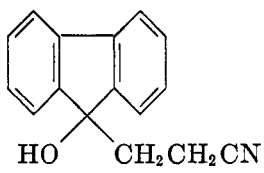
red lead
heat



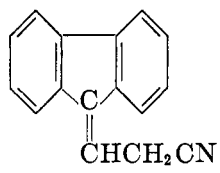
III
Fluoranthene

Bruson's discovery (22) of the reactivity of acrylonitrile with compounds containing reactive hydrogen atoms led to a study of the reaction with fluorene. Acrylonitrile condensed with fluorene to give 9,9-di(2′-cyanoethyl)fluorene; it has not been possible to restrict the condensation to prepare 9-(2′-cyanoethyl)-fluorene, although crotononitrile condensed with fluorene to give the 1:1-adduct, 2-(9′-fluorenyl)propyl cyanide.

Thus, von Braun and Anton's original method of synthesis of fluoranthene *via* β-(9-fluorenyl)propionic acid (15) remained unmodified until 1949, when Campbell and Fairfull (31) condensed acrylonitrile and 9-fluorenol, in the presence of benzyltrimethylammonium hydroxide, to give β-(9-hydroxy-9-fluorenyl)propionitrile (VI), from which β-(9-fluorenylidene)propionitrile (VII) was obtained on treatment with hydrochloric acid. Catalytic hydrogenation of VII gave β-(9-fluorenyl)propionic acid—von Braun and Anton's precursor of fluoranthene.

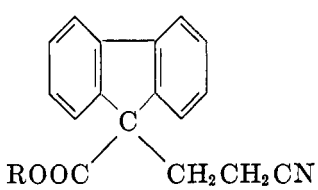


VI

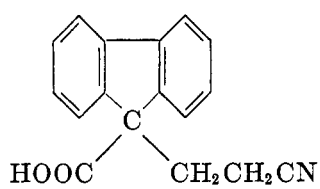


VII

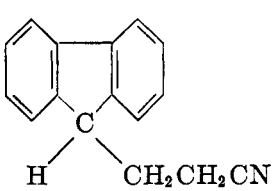
Independently, in the same year, Tucker (175) and A. Campbell and Tucker (27) extended the applicability of this method by using the alkyl 9-fluorenecarboxylates, in which there is only one reactive hydrogen atom in the 9-position, and that a specifically more reactive one than either of those in fluorene. In the synthesis of fluoranthene (27) the 9-fluorenecarboxylate was condensed with acrylonitrile to give 9-carbalkoxy-9-(2′-cyanoethyl)fluorene (VIII), which was hydrolyzed directly or in stages (VIII → IX → X → XI) to β-(9-fluorenyl)-propionic acid (XI).



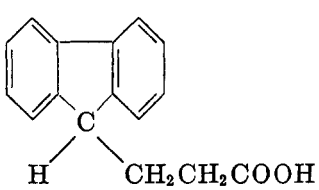
VIII



IX

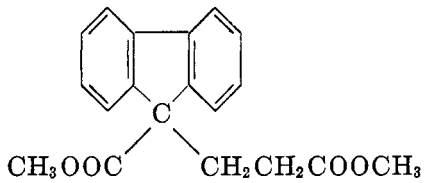


X



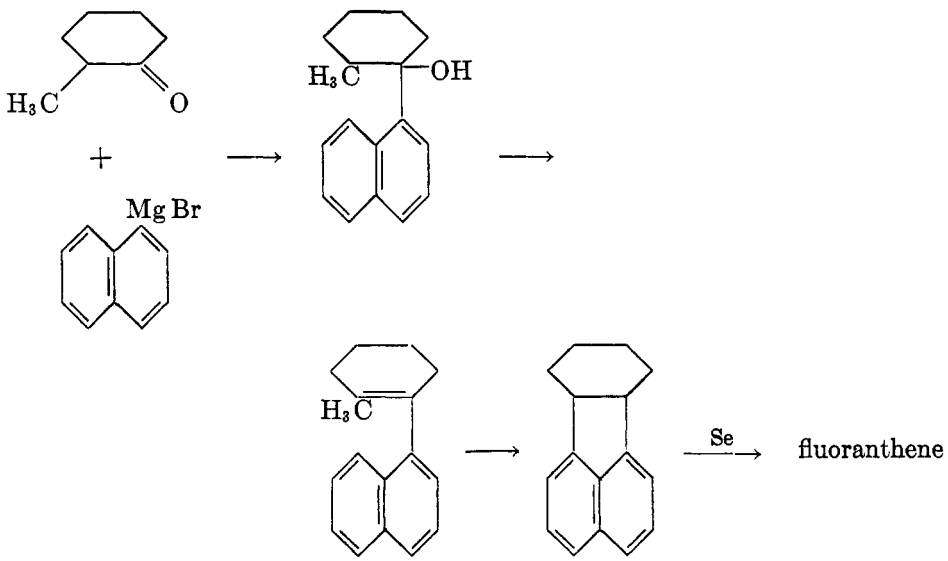
XI

These Michael reactions were brought about by use of potassium hydroxide as the basic catalyst, but it has since been found (176) that better results are obtained by the condensation of 9-fluorenecarboxylic esters with acrylic *esters* in alcoholic solutions of the corresponding sodium alkoxide: the adducts, e.g., methyl β-(9′-carbomethoxy-9′-fluorenyl)propionate (XII), are obtained in high yield, and are rapidly hydrolyzed with potassium hydroxide in 2-methoxyethanol to, for example, β-(9-fluorenyl)propionic acid.



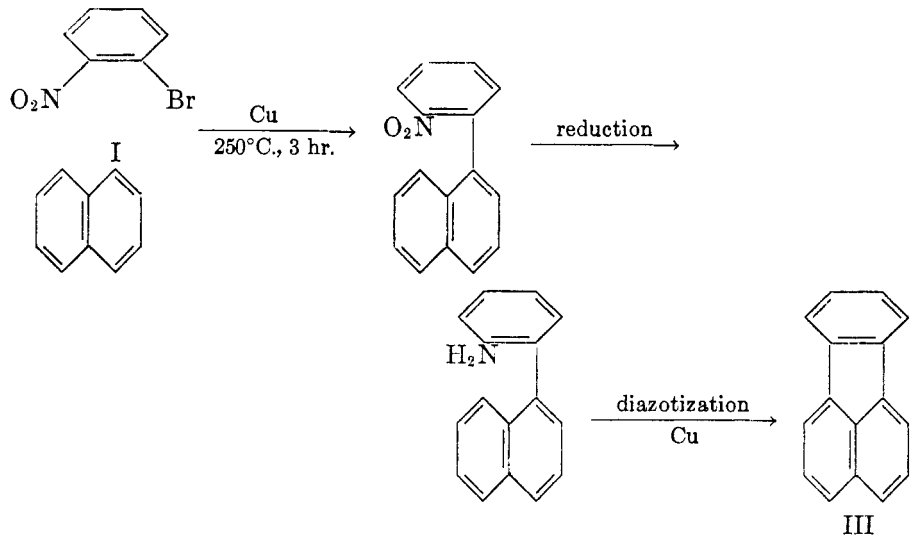
XII

Small quantities of fluoranthene have been obtained by other methods. Cook and Lawrence (46) synthesized it from 2-methylcyclohexanone and α-naphthylmagnesium bromide,



and Orchin and Reggel (140, 142, 143) prepared fluoranthene by the cyclodehydrogenation of α-cyclohexenylnaphthalene with palladium on charcoal or chromia–alumina catalyst. Similar treatment of 2′-hydroxy- and 2′-methoxy-1-phenylnaphthalenes failed to give fluoranthene (140a).

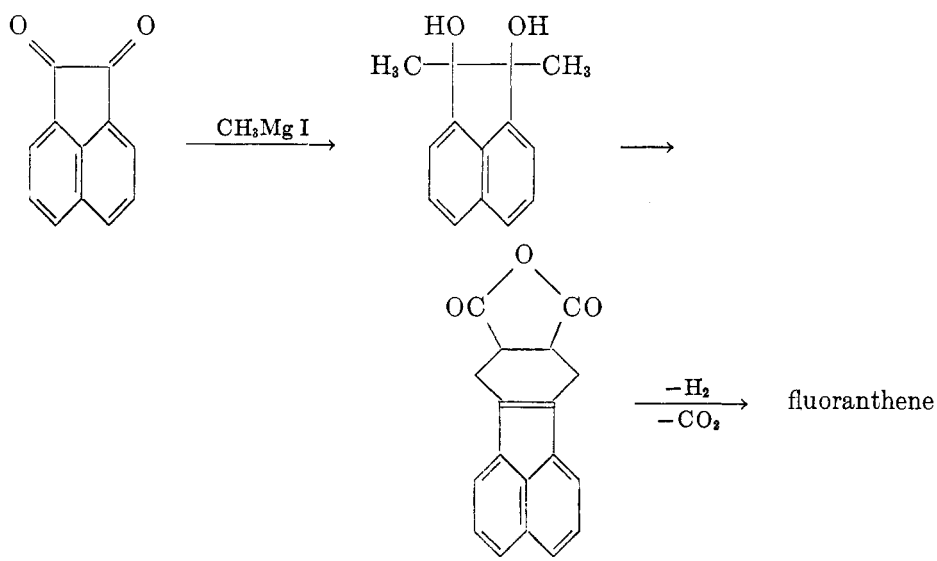
A new type of synthesis of fluoranthene, which established the presence of the naphthalene ring system by starting with α-iodonaphthalene, was devised by Forrest and Tucker (75).



I III

Fluoranthene

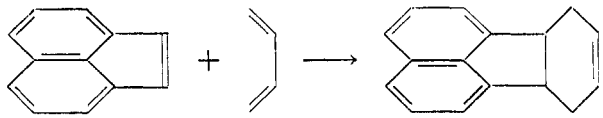
A novel synthesis by Campbell, Gow, and Wang (32, 33) built up the benzene ring of fluoranthene on the acenaphthene skeleton. They condensed *trans*-9,10-dimethylacenaphthene-9,10-diol with maleic anhydride in the presence of acetic anhydride to give XIII, which on dehydrogenation and decarboxylation yielded fluoranthene.



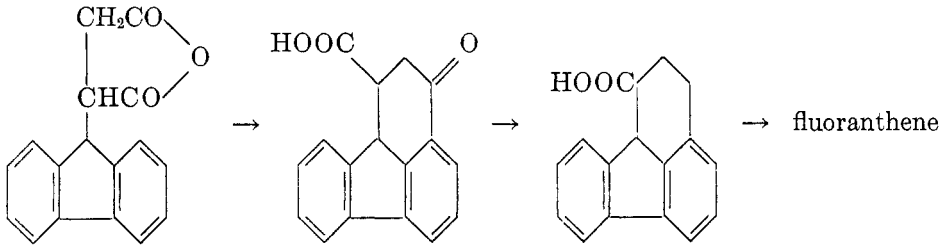
XIII

At about the same time, 1948, Bergmann (11; *cf.* 53, 118) showed that fluoranthene and other polycyclic aromatic hydrocarbons may be formed by diene

syntheses in the high-temperature cracking of petroleum. Thus acenaphthylene reacts readily at 180–200°C. with dienes to give hydrogenated fluoranthenes:



Another synthesis of fluoranthene (12) was accomplished by starting from the addition product of fluorene and maleic anhydride.



The Stobbe condensation of fluorenone with ethyl succinate has also been utilized (31a) to prepare 9-fluorenylsuccinic acid.

V. Oxidation of Fluoranthene

A number of products are obtained under different oxidizing conditions. Using potassium chromate and dilute sulfuric acid Fittig and Gebhard (69, 70, 71, 72) obtained a mixture from which fluoranthenequinone and 1-fluorenonecarboxylic acid were isolated. Under suitable conditions the quinone could be prepared in good yield and was shown to form with fluoranthene a complex consisting of one molecule of quinone to two molecules of the hydrocarbon. 1-Fluorenonecarboxylic acid is produced also in good yield by the oxidation of fluoranthene with chromic anhydride in acetic acid (68, 75, 94).

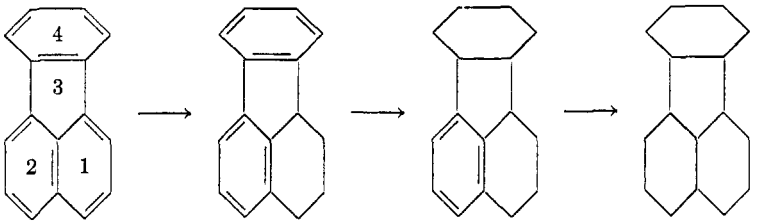
When fluoranthene is treated over a long period with alkaline permanganate (148) the principal product, hemimellitic acid, is accompanied by 2,6-dicarboxyphenylglyoxylic acid. Finally, oxidation with ozone (110, 181) gives a mixture of 1-fluorenonealdehyde and 1-fluorenonecarboxylic acid.

VI. Reduction of Fluoranthene

Goldschmiedt (82) in 1880 first tried to prepare hydrogenated derivatives of fluoranthene. With phosphorus and hydriodic acid or with sodium amalgam and alcohol, two products which were believed to be di- and octahydrofluoranthenes were obtained.

In 1930 von Braun and Manz (17) investigated thoroughly the reduction of the hydrocarbon. Reduction with sodium amalgam and alcohol or with phosphorus and hydriodic acid below 180°C. led to an almost quantitative yield of 1,2,3,10b-tetrahydrofluoranthene (XIV), but above 200°C. there was formed a mixture of hydrogenated products which could not be separated by distillation. It is possible that the dihydro compound (XVIIa or XVIIb) may be a precursor of XIV, but neither has been detected.

The action of sodium in moist ether, or of hydrogen in the presence of palladium or platinum at normal pressure, has no effect on fluoranthene, though with 20 per cent palladium–charcoal as catalyst the tetrahydro compound (XIV) is readily formed. Catalytic hydrogenation under pressure gave 1,2,3,10b-tetrahydrofluoranthene (XIV) as the first-stage hydrogenation product. The nature of the other compounds present varied with the hydrogen absorption. Using rather less than ten atoms of hydrogen per molecule, the main product after XIV was 1,2,3,6b,7,8,9,10,10a,10b-decahydrofluoranthene (XV). When absorption exceeded ten atoms per molecule, perhydrofluoranthene (XVI) was obtained.



XIV XV XVI

The decahydro compound (XV) is also formed by the reduction of 1,2,3,10b-tetrahydrofluoranthene (XIV) with sodium in alcohol, its constitution being established by oxidation to 1,2,3-benzenetricarboxylic acid. Perhydrofluoranthene (XVI) is dehydrogenated at 450°C. with chromia–alumina catalyst (85); fluoranthene is the principal product, though there is evidence that some partially hydrogenated fluoranthenes are formed, e.g., the dihydrofluoranthenes XVIIa and XVIIb.

XVIIa XVIIb

von Braun and Manz (17) did not find it possible to prepare hexahydrofluoranthene (e.g., XVIIIa) either by direct hydrogenation of the parent hydro-

XVIIIa XVIIIb

carbon or by alicyclic bromination of 1,2,3,6b,7,8,9,10a,10b-decahydrofluoranthene (XV) followed by removal of two molecules of hydrogen bromide. The isomeric decahydrofluoranthene (XVIIIb) likewise could not be obtained.

The addition of hydrogen to the fluoranthene nucleus therefore occurs in such a way that ring 1 is hydrogenated first, then ring 4, and finally ring 2.

VII. Substitution in Fluoranthene

A. HALOGENATION

Early workers in the fluoranthene field contributed little to the knowledge of halogeno derivatives. In 1880 Goldschmiedt (82) obtained substances which he believed to be a trichloro- and a tribromofluoranthene, this last substance having been prepared previously by Fittig and Gebhard (70). Gerty (79), repeating Goldschmiedt's work, isolated a tetrachlorofluoranthene. Much later von Braun and Manz (18, 19), while investigating the orientation of substituents in fluoranthene, found that under suitable conditions dibromination may be avoided and two monobromofluoranthenes formed.

A systematic investigation of the products of the bromination of fluoranthene was carried out in 1941 by Tobler, Holbro, Sutter, and Kern (174). Bromination in carbon disulfide confirmed von Braun and Anton's result, 3-bromofluoranthene being the principal product and some 8-bromofluoranthene also being formed. 3-Bromofluoranthene is readily prepared by the dehydrogenation of 4-bromo-1,2,3,10b-tetrahydrofluoranthene with chloranil in boiling xylene (174). Campbell and Gow (33) synthesized 3-bromofluoranthene by an ingenious use of 3-bromoacenaphthenequinone.

A dibromo compound, m.p. 205°C., corresponding to that obtained by Fittig and Gebhard and by Goldschmiedt, was the product of bromination in nitrobenzene (114, 115, 162, 174). This was later shown to be 3,8-dibromofluoranthene (29, 30, 91). The same investigators were unable to confirm Goldschmiedt's report of a tribromofluoranthene, m.p. 345°C., but prepared a tribromo derivative, m.p. 204–205°C., by the bromination of 3,8-dibromofluoranthene in nitrobenzene at 90–95°C., whilst fluoranthene itself in nitrobenzene at 125–130°C. yielded a tetrabromofluoranthene, m.p. 312°C.

3,8-Dibromofluoranthene, the most readily accessible of the bromofluoranthenes, has been used in the dye industry. Dyes producing brown shades on cellulose, silk, or wool are obtained by condensing it with such compounds as 1-amino-4-(benzoylamino)anthraquinone (111, 112, 132, 157, 161, 163, 164, 165, 166, 167). 3,8-Dibromofluoranthene can also be converted into 3,8-dicyanofluoranthene (30), which on hydrolysis yields 3,8-fluoranthenedicarboxylic acid, a valuable dye intermediate (116, 168, 169).

3-Iodofluoranthene has been prepared (172) from 3-aminofluoranthene (18) by the Sandmeyer reaction. Fluoranthene readily undergoes iodination but, as usual in substitution reactions, gives such a mixture of derivatives that isolation of pure 3-iodofluoranthene was not found to be practicable (177). Iodination of 1,2,3,10b-tetrahydrofluoranthene by means of iodine and silver trifluoroacetate (87a), however, gave 1,2,3,10b-tetrahydro-4-iodofluoranthene, which by dehydrogenation with chloranil gave 3-iodofluoranthene (177).

Attempts to fluorinate fluoranthene, using *p*-tolyliododifluoride in chloroform (78), were unsuccessful (a small yield of difluoranthyl was obtained on one occasion), but the use of silver difluoride gave a good yield of perfluorofluoranthene (128).

B. SULFONATION AND NITRATION

Goldschmiedt (82) and later von Braun and coworkers (16, 18) prepared a fluoranthenedisulfonic acid by warming the hydrocarbon with concentrated sulfuric acid. von Braun also prepared two different monosulfonic acids. 3-Fluoranthenesulfonic acid was obtained either from 3-aminofluoranthene or by direct sulfonation of the hydrocarbon with chlorosulfonic acid in an inert solvent (131).

Three nitrofluoranthenes are known. Concentrated nitric acid (69) gave a trinitro compound, and under less vigorous conditions (18) two different mononitrofluoranthenes were isolated.

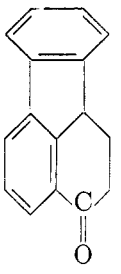
C. ORIENTATION OF SUBSTITUTION

The orientation of monobromination, monosulfonation, and mononitration of fluoranthene was studied by von Braun and Manz (18). That the principal products from these reactions have the substituents attached to the same carbon atom of the fluoranthene nucleus was demonstrated as follows:

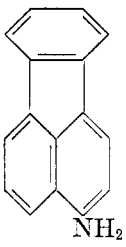
(*1*) Conversion of the bromo compound to the corresponding acid, through the nitrile, gave a product identical with that obtained by fusion of the sulfonic acid with potassium cyanide followed by hydrolysis.

(*2*) The phenol prepared by alkali fusion of the sulfonic acid yielded, on treatment with ammonia, an amine identical with that prepared by reduction of the nitro compound.

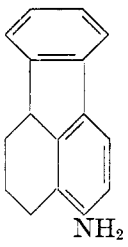
Since it was considered that position 3 in the naphthalene part of the nucleus was likely to be reactive, the known 1,2,3,10b-tetrahydro-3-ketofluoranthene (XIX) was used in an attempt to determine the position of the hydroxyl group in the phenol. The alcohol obtained by reduction of the ketone was similar to that produced by hydrogenation of the phenol and gave the same product with phenyl isocyanate. However, the substances were not identical and were possibly stereoisomers. A more successful method used 3-aminofluoranthene (XX) as starting material.



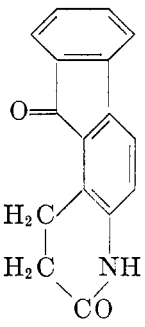
XIX



XX



XXI



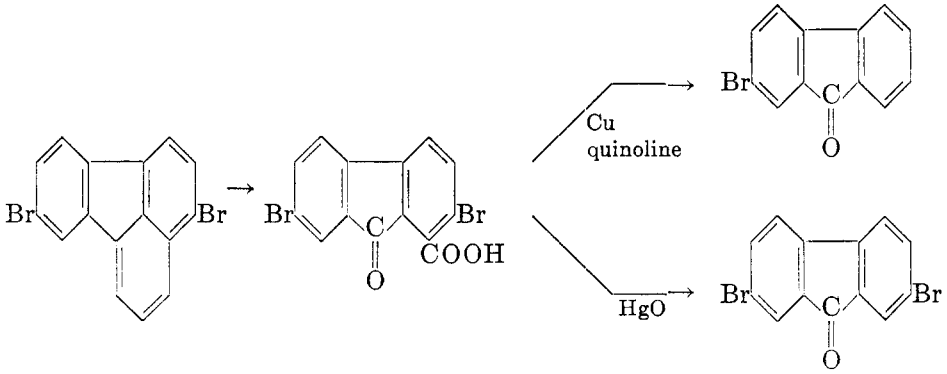
XXII

Like α-naphthylamine, 3-aminofluoranthene hydrogenates in the unsubstituted part of the naphthalene nucleus to give a tetrahydrofluoranthylamine (XXI) which, on acetylation followed by careful oxidation of the tetrahydro ring, gives a ketocarboxylic acid with the same number of carbon atoms. The deacetylated acid spontaneously forms the lactam (XXII),—a reaction which is possible only if the amino group is in the 3-position. 3-Hydroxyfluoranthene was obtained by the usual diazotization process from 3-aminofluoranthene. 3-Aminophthaloylfluoranthene forms a pure blue vat dye (121).

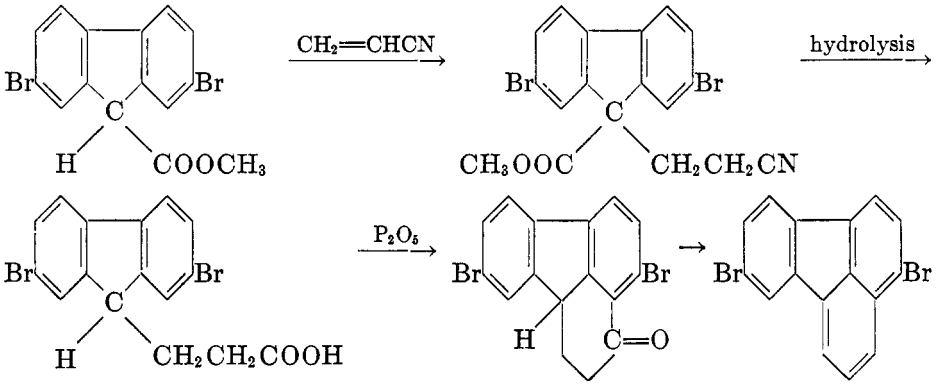
Although bromination, sulfonation, and nitration occur predominantly in the 3-position, von Braun and Anton (16) demonstrated the formation of a small amount of the 8-substituted isomer in each case.

The positions of disubstitution have been established recently. Tobler and coworkers (115, 116, 174), by bromination in nitrobenzene, obtained a dibromo compound, m.p. 203°C., corresponding to that prepared by Goldschmiedt and by Fittig and Gebhard. Conclusive evidence that this is 3,8-dibromofluoranthene was supplied by Campbell (29, 30, 36). Chromic acid oxidation of the dibromofluoranthene gave a dibromofluorenone-1-carboxylic acid which on decarboxylation (copper and quinoline) yielded 2-bromofluorenone. Since 2-bromo- and 2,7-dibromofluorenones are stable to copper in boiling quinoline, the bromine next to the carboxylic acid group must have been removed. Decarboxylation of the dibromo acid with mercuric oxide at 180°C. gave 2,7-dibromofluorenone. This preparation was independently accomplished by Holbro and Tagmann (92) by heating the calcium salt of the acid with mercuric oxide. Heating the dibromofluorenone-1-carboxylic acid with copper in toluene did not effect removal of the bromine atom ortho to the carboxyl group.

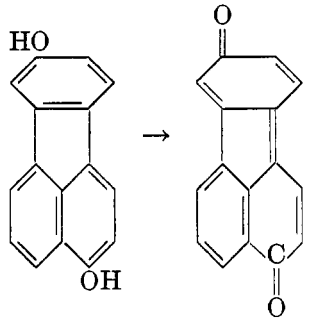
A second oxidation product of 3,8-dibromofluoranthene has been identified as 6-bromofluorenone-1-carboxylic acid (36). The bromine atoms of 3,8-dibromofluoranthene are inert to magnesium but are removed by nickel–aluminum alloy and alkali (30).



3,8-Dibromofluoranthene was synthesized by Holbro and Tagmann (92), and was found to be identical with the compound obtained by direct bromination of fluoranthene. An attempt to reduce the keto group of the dibromoketone, shown below by the Wolff–Kishner–Huang–Minlon method, gave 3,8-dibromofluoranthene directly.



Sulfonation of fluoranthene gives a disulfonic acid which by alkali fusion forms a dihydroxyfluoranthene. Oxidation of this dihydroxy compound yields a green compound of the quinhydrone type. A quinonoid structure may be explained by 3,8-substitution (161):



An *o*-hydroxycarboxylic acid of fluoranthene, believed to be 7-hydroxyfluoranthene-8-carboxylic acid, was prepared by heating a hydroxyfluoranthene under pressure with carbon dioxide. The product is useful as a coupling component for azo dyes (98).

D. SUBSTITUTION BY THE FRIEDEL–CRAFTS REACTION

von Braun and Manz (19) deduced from the results of their experiments that benzoyl chloride in the presence of aluminum chloride and carbon disulfide gave a mixture of 8-benzoyl- and 3-benzoylfluoranthenes, the former being the main product. This is in direct contrast to the effects of bromination, nitration, and sulfonation. 3-Benzoylfluoranthene was characterized by its degradation

$$C_{16}H_9\underset{\displaystyle C_6H_5}{\overset{\displaystyle |}{C}}{=}NOH \xrightarrow[\text{reaction}]{\text{Beckmann}} C_{16}H_9CONHC_6H_5 \rightarrow$$

Oxime of benzoylfluoranthene

$$C_{16}H_9COOH \xrightarrow[\text{degradation}]{\text{Curtius}} C_{16}H_9NH_2$$

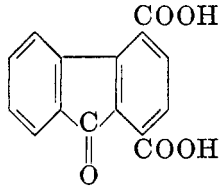
Fluoranthylamine

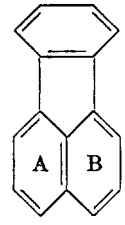
products only. Under similar conditions, substitution in the 8-position with phthalic anhydride and with oxalyl chloride was obtained.

Substitution in the *secondary* products occurs in the same position with both benzoyl chloride and phthalic anhydride, since the oximes, by Beckmann transformation, hydrolysis, and Curtius degradation, yielded the known 3-aminofluoranthene (19) (see page 496).

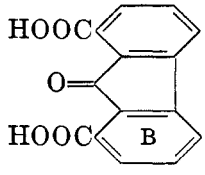
The orientation of the substituent in the *main* product was shown by two methods:

(*1*) The monocarboxylic acid obtained by a Friedel–Crafts reaction with oxalyl chloride gave, on oxidation, a mixture of fluorenonedicarboxylic acids. If the originally introduced carboxyl group were in the 1-, 2-, or 3-position, only *one* fluorenonedicarboxylic acid would be obtainable from *each* fluoranthenemonocarboxylic acid; thus, e.g., 1-fluoranthenecarboxylic acid would give 1,4-fluorenonedicarboxylic acid only.

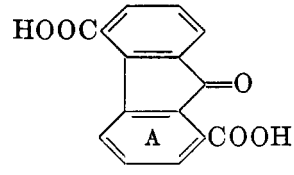




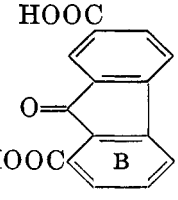
Since *two* acids were obtained, the position of substitution must be 7 or 8, i.e., either ring A or ring B of the fluoranthene nucleus could be ruptured to give:



and



or



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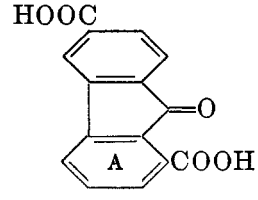
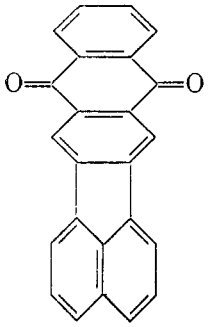
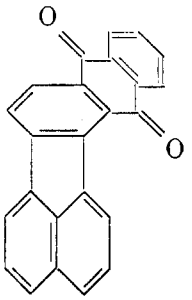


The Friedel–Crafts reaction with fluoranthene was further investigated by Campbell and Easton (28) in 1949. Their experiments showed that 3-benzoylfluoranthene, contrary to the statement of von Braun and Manz, is no mere by-product but is formed in approximately equal quantities with the 8-isomer.

(*2*) Reactions of *o*-carboxybenzoylfluoranthene were also cited by von Braun and Manz (19) in support of 8-substitution. *o*-Carboxybenzoylfluoranthene, on heating in trichlorobenzene, gave two quinones. If the *o*-carboxybenzoyl group were in the 7-position, only one quinone (XXIV) would be possible, whilst a substituent in the 8-position would give two (XXIII and XXIV). von Braun and Manz concluded from their investigations that their red quinone, m.p. 228°C., was XXIII and their yellow quinone, m.p. 332–333°C., was XXIV.

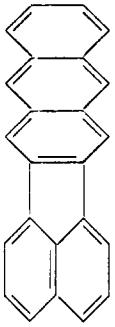


XXIII

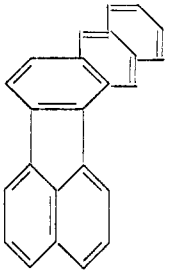


XXIV

Campbell and Gow (33) showed, however, by an unambiguous synthesis, that XXIII is yellow and melts above 310°C. von Braun's assignment of structures must therefore be reversed. Furthermore, the hydrocarbon obtained by von Braun by zinc dust distillation of the yellow quinone must be XXV and not XXVI.



XXV

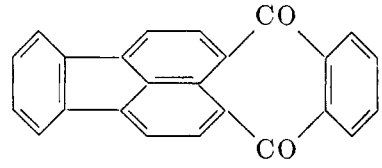


XXVI

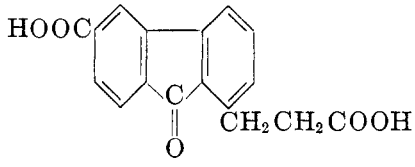
The quinone XXIV has also been synthesized (35, 38) by oxidation of the corresponding hydrocarbon, prepared by the Elbs reaction on 8-*o*-toluoylfluoranthene and (as one of the products) by the ring-closure of 8-*o*-carboxybenzoylfluoranthene. It is a yellow compound melting at 316°C. The identity of the quinone, m.p. 228°C., of von Braun and Manz is unknown, but it must be pointed out that the German workers had not the advantage of chromatography to separate their mixtures. The oxidation studies of von Braun and Manz were unsatisfactory. Of the three oxidation products isolated, two were impure and none was fully identified. It was originally suggested by Campbell that von Braun's product might be 3,4-phthaloylfluoranthene (XXVII) but synthesis of XXVII (35) showed it to be a yellow substance melting at 296°C.

Substitution in the 8-position was compatible with further results of von Braun and Manz (19). 8-Fluoranthenecarboxylic acid[1] was reduced to the 1,2,3,10b-tetrahydrofluoranthene-8-carboxylic acid, which on oxidation gave XXVIII and then 1,6-fluorenonedicarboxylic acid (XXIX).

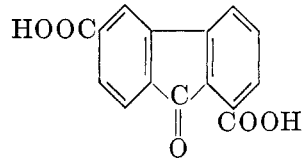
[1] It is worth remembering that von Braun often uses 12- when 11- would be correct: e.g., in Ann. **496**, 181 (1932), "12-Aminofluoranthens" should be "11-Aminofluoranthens," although it is realized that the 11- and 12-positions in a monosubstituted fluoranthene are equivalent (positions 11 and 12 are 8 and 9, respectively, as numbered by *Chemical Abstracts*).



XXVII



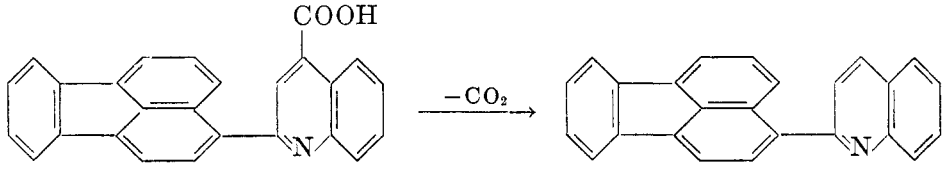
XXVIII



XXIX

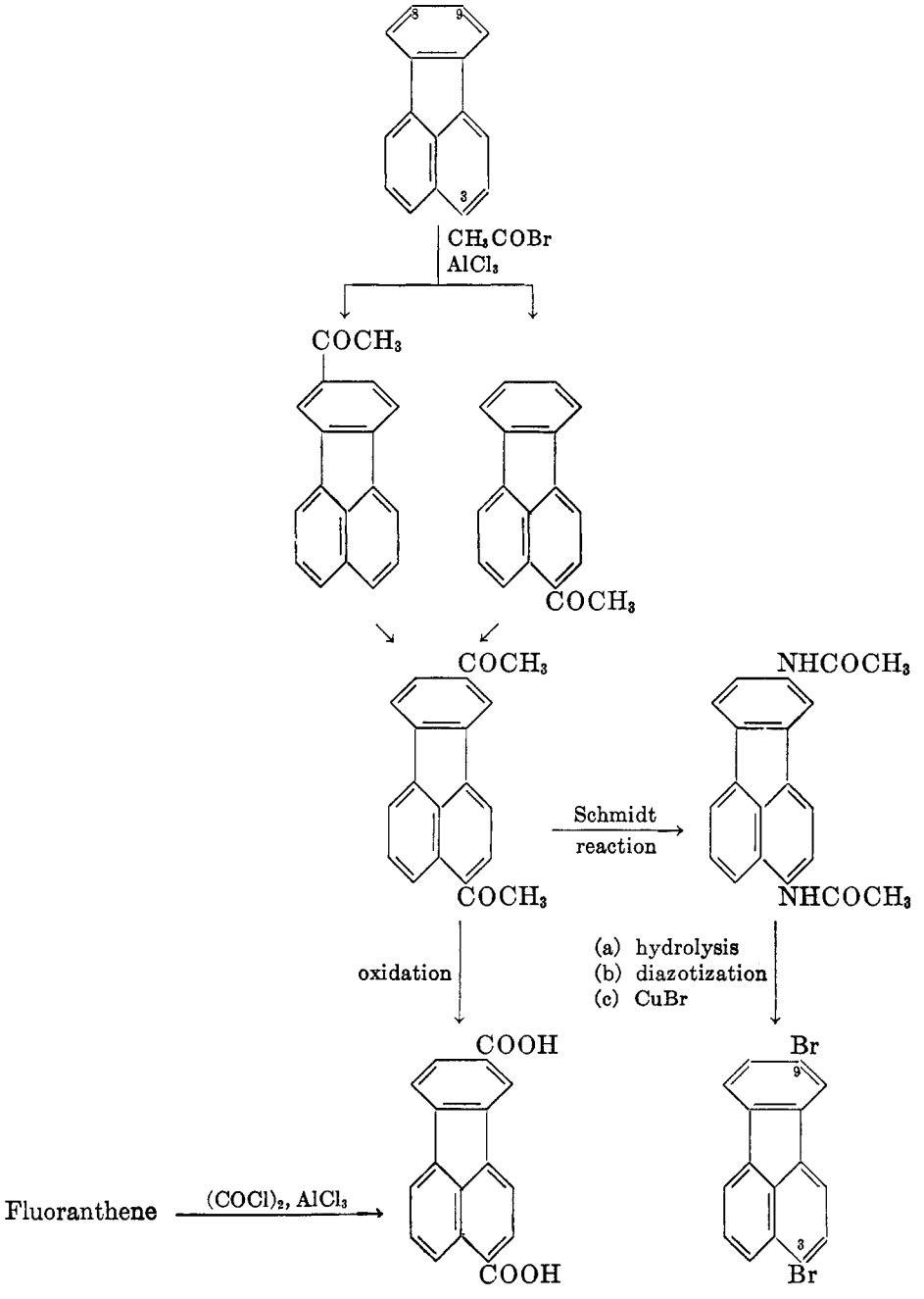
Acetyl derivatives of fluoranthene

Buu-Hoï and Cagniant (24), acting upon fluoranthene with acetyl chloride and aluminum chloride in carbon disulfide, claimed to have isolated 8-acetylfluoranthene in good yield. Its oxime, by a Beckmann transformation, gave, it was alleged, 8-acetylaminofluoranthene, which von Braun and Manz (19) had formerly prepared by the acetylation of 8-aminofluoranthene.[1] Neither a position isomer nor a diacetyl derivative was isolated. The work has been challenged by Campbell and Easton (28), who showed that the supposed 8-acetylfluoranthene was a mixture of fluoranthene, 3-acetylfluoranthene (and an isomer which may be 8-acetylfluoranthene), and a diacetylfluoranthene. In view of these observations, the supposed 8′-fluoranthyl-2-cinchoninic acid, prepared from the acetylfluoranthene by the Pfitzinger reaction with isatin, may in reality be the 3′-derivative, which by the usual decarboxylation would give 3′-fluoranthyl-2-quinoline.

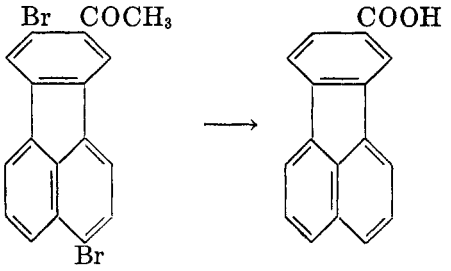


In an excellent research Campbell, Leadill, and Wilshire (34) have prepared 3- and 8-acetylfluoranthenes and settled their constitution. They have shown that the diacetyl derivative also obtained was not the 3,8-derivative, as might have been anticipated by comparison with the result of bromination of fluoranthene, but 3,9-diacetylfluoranthene. Furthermore, this was converted into 3,9-fluoranthenedicarboxylic acid. The argument runs as follows: Fluoranthene, by the action of acetyl bromide in presence of aluminum chloride, gives a mixture of 3- and 8-acetylfluoranthenes. Both on further treatment yield the same diacetylfluoranthene, which accordingly must be the 3,8- or the 3,9-compound. A decision in favor of the latter was obtained by oxidation to a fluoranthenedicarboxylic acid which was different from 3,8-fluoranthenedicarboxylic acid, prepared from 3,8-dibromofluoranthene *via* the dinitrile, but identical with the acid prepared by the action of oxalyl chloride on fluoranthene in the presence of aluminum chloride (28). The Friedel–Crafts product is therefore 3,9-diacetylfluoranthene, and the derived acid is 3,9-fluoranthenedicarboxylic acid. This

was confirmed by conversion of the diacetylfluoranthene into the diacetamido compound by the Schmidt reaction (using sodium azide in trichloroacetic acid). Hydrolysis, diazotization, and the Sandmeyer reaction gave 3,9-dibromofluoranthene, which was shown to be different from 3,8-dibromofluoranthene (29, 30, 92). The work is summarized below:



A trisubstituted fluoranthene has also been prepared (37). 3,8-Dibromofluoranthene with acetyl bromide and aluminum chloride gives 9-acetyl-3,8-dibromofluoranthene, which on oxidation and debromination gives fluoranthene-8(9)-carboxylic acid.



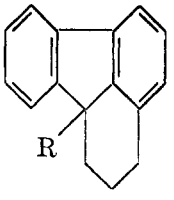
With *tert*-butyl chloride in the presence of aluminum chloride, Buu-Hoï and Cagniant (25) obtained a di-*tert*-butylfluoranthene which may be the 3,8-compound.

p-Quinones (105, 158) and fluoranthenecarboxamide (106), prepared by the Friedel–Crafts reaction, are used as dye intermediates, whilst the Friedel–Crafts reaction with α-olefins and unsaturated esters yields stable lubricating oils of unknown constitution (26).

E. SUBSTITUTION IN TETRAHYDROFLUORANTHENE

1,2,3,10b-Tetrahydrofluoranthene was found by von Braun and Manz (19) to substitute in the 4-position on chlorosulfonation, on bromination, and by the Friedel–Crafts reaction with phthalic anhydride. Small amounts of the 8-isomer were also isolated. It iodinates in the 4-position (177).

1,2,3,10b-Tetrahydrofluoranthene and 1,2,3,10b-tetrahydro-1,1,3-trimethylfluoranthene both contain in the five-membered rings methine groups sufficiently reactive to be alkylated. Thus, Hoffmann and Tagmann (89, 91) obtained various products of the type of XXX by the reaction of these tetrahydrofluoranthenes with tertiary aminoalkyl chlorides, e.g., diethylaminoethyl chloride, in the presence of sodium amide. Some of these compounds show interesting pharmacological effects (see Section III).



XXX

β-(1,2,3,10b-Tetrahydrofluoranthen-10b-yl)propionic acid piperidide may be reduced with hydrogen in the presence of copper–chromium metal catalyst to 1,2,3,10b-tetrahydro-10b-(3-piperidylpropyl)fluoranthene (41).

F. MISCELLANEOUS SUBSTITUTIONS

The patent literature records the preparation of 3,8-dihydroxyfluoranthene (9, 97) and its ethers (101), hydroxysulfonic acids (101, 159, 160), carboxylic

acids (106, 113, 168), 4-aminophthaloylfluoranthene (121), and various other derivatives which, like the above, are used as dyes or as dye intermediates (100, 104, 111, 164, 170).

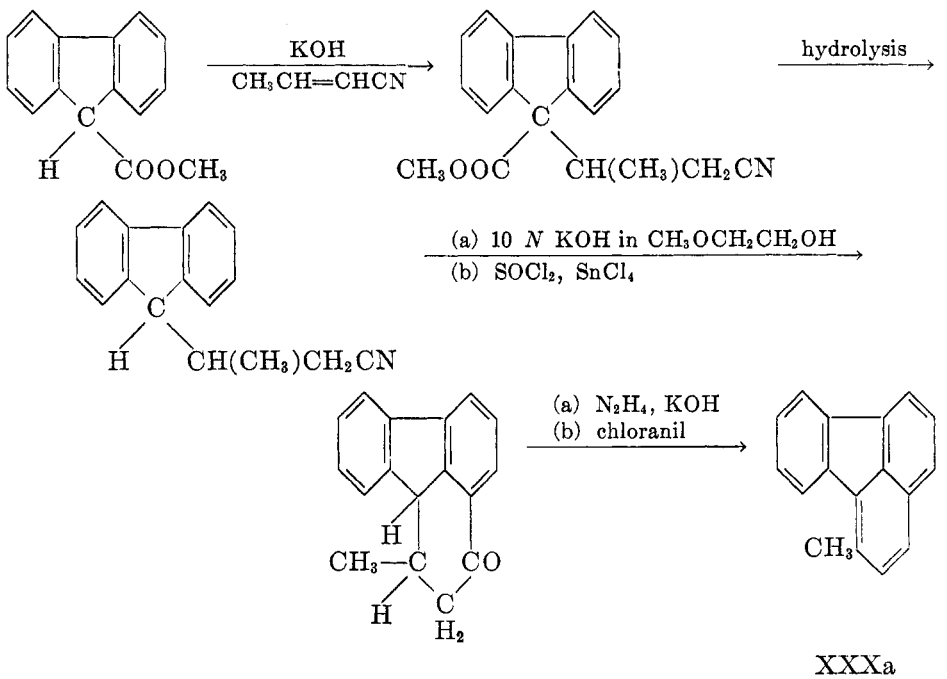
VIII. Alkyl and Aryl Fluoranthenes

A. Monomethylfluoranthenes

This group of fluoranthene derivatives may be conveniently divided into two sections: (*1*) those having substituents attached to the naphthalene skeleton; (*2*) those having substituents in the benzene ring.

1. Monomethylfluoranthenes with the methyl group attached to the naphthalene skeleton

Syntheses of fluoranthene and of its 1-, 2-, and 3-methyl derivatives have been accomplished by the general method introduced by Tucker (175) and elaborated by Campbell and Tucker (27) and by Stubbs and Tucker (171). Thus, 1-methylfluoranthene (XXXa) was synthesized (175) from methyl 9-fluorenecarboxylate and crotononitrile by the following route:

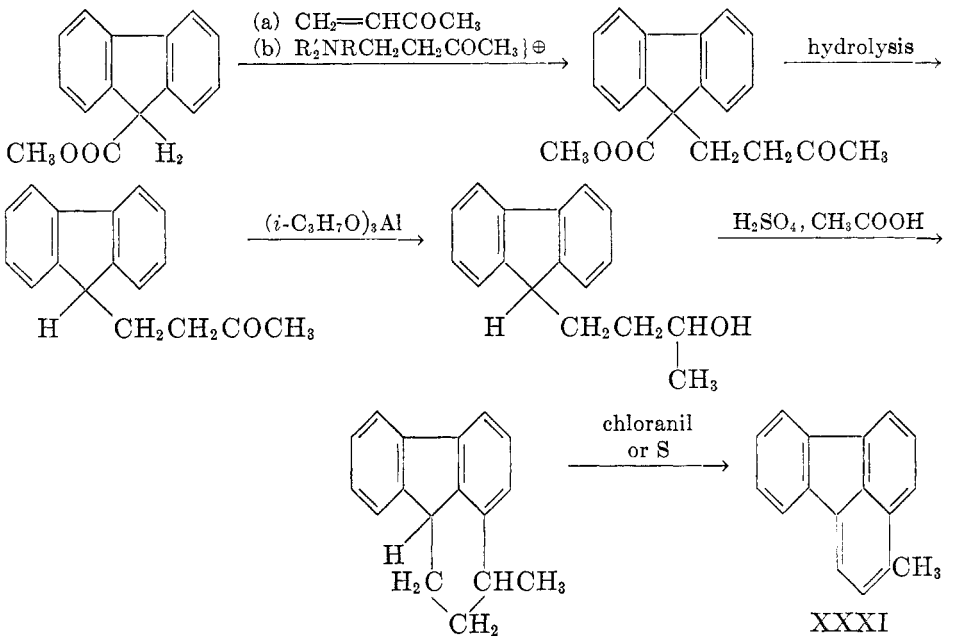


XXXa

2-Methylfluoranthene has been synthesized (176) by the above method, replacing crotononitrile by α-methylacrylonitrile. An improvement in the method has been effected by using methyl α-methylacrylate in place of the above nitrile, and sodium in methanol instead of potassium hydroxide in 2-methoxyethanol or dioxane.

3-Methylfluoranthene (XXXI) was prepared by von Braun and Manz (20)

by the action of methylmagnesium iodide on 1,2,3,10b-tetrahydro-3-keto-fluoranthene followed by dehydration and dehydrogenation. It was more readily synthesized by Stubbs and Tucker (171) from methyl 9-fluorenecarboxylate and methyl vinyl ketone or the corresponding Mannich base:



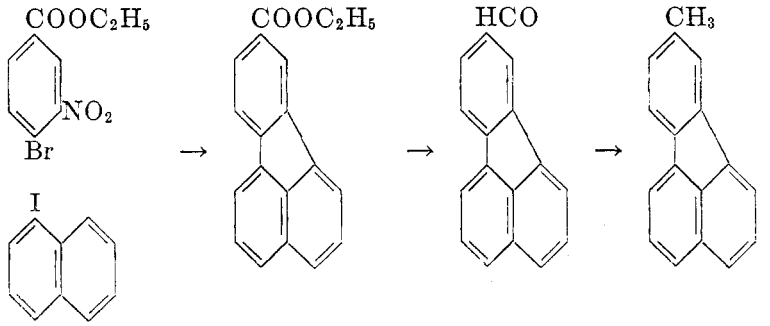
XXXI

Phenyl vinyl ketone (or the Mannich base) similarly gave 3-phenylfluoranthene.

The only other monomethylfluoranthenes (7- and 8-) were prepared as described below (75, 118, 180).

2. Monomethylfluoranthenes with the methyl group attached to the benzene ring

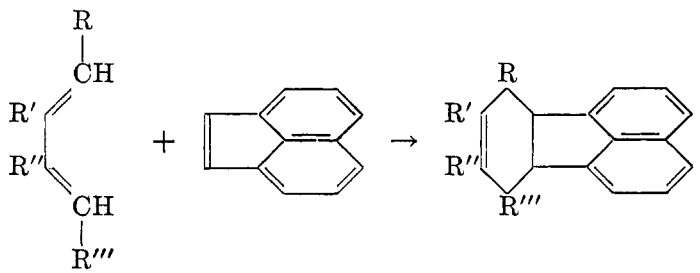
7-Methylfluoranthene was prepared by Tucker and Whalley (180) by the action of copper on a mixture of iodonaphthalene and 2-bromo-3-nitrotoluene, followed by reduction of the nitro compound so produced to the amine. Diazotization of the amine and treatment with copper effected cyclization to 7-methylfluoranthene. The melting point of 7-methylfluoranthene was erroneously given as



105–108°C.; it should be 132–134°C. (Kloetzel and Mertel (118) give 136–137°C.). With ethyl 4-bromo-3-nitrobenzoate and 1-iodonaphthalene as starting materials, ethyl 8-fluoranthenecarboxylate was prepared. This was transformed to 8-fluoranthenealdehyde by the McFadyen–Stevens method and then by reduction to 8-methylfluoranthene (180) (see page 503).

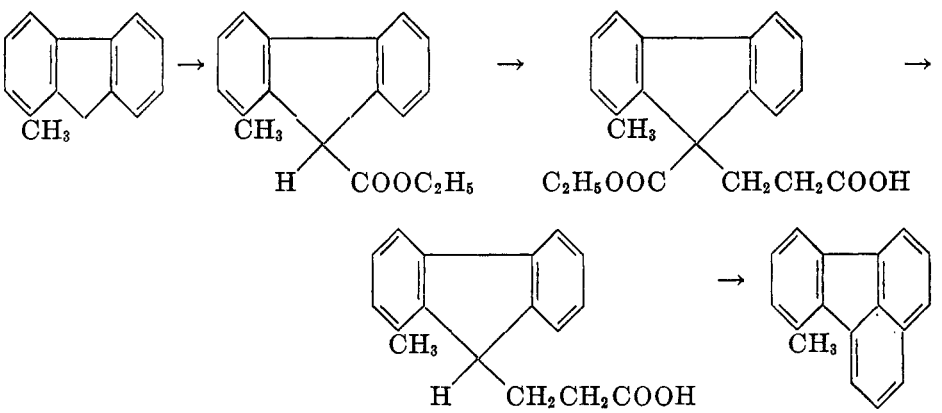
Synthesis of 8-methylfluoranthene from 1-iodonaphthalene and 4-bromo-3-nitrotoluene gave a substance identical with the reduction product of 8-fluoranthenealdehyde. 8-Methoxyfluoranthene also has been synthesized by this method (87).

Kloetzel and Mertel (118) applied Bergmann's diene synthesis (11) of fluoranthene to the preparation of methylated derivatives:

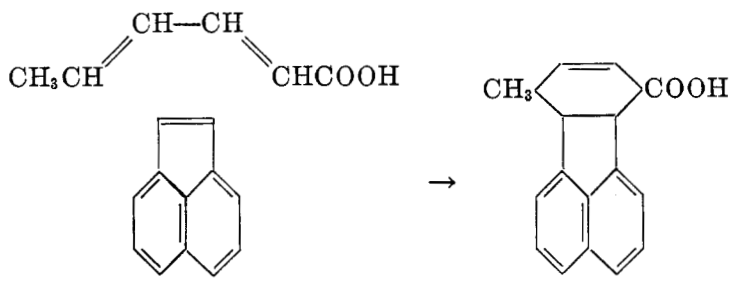


In this manner both 7- and 8-methylfluoranthene were obtained. The identity of 8-methylfluoranthene was confirmed by its preparation from one of the products of a Friedel–Crafts reaction with oxalyl chloride and fluoranthene. Its physical properties agreed with those observed by Tucker and Whalley (180).

The 7-methylfluoranthene synthesized by the diene method was identical with the compound obtained from 1-methylfluorene (118) by the following procedure:

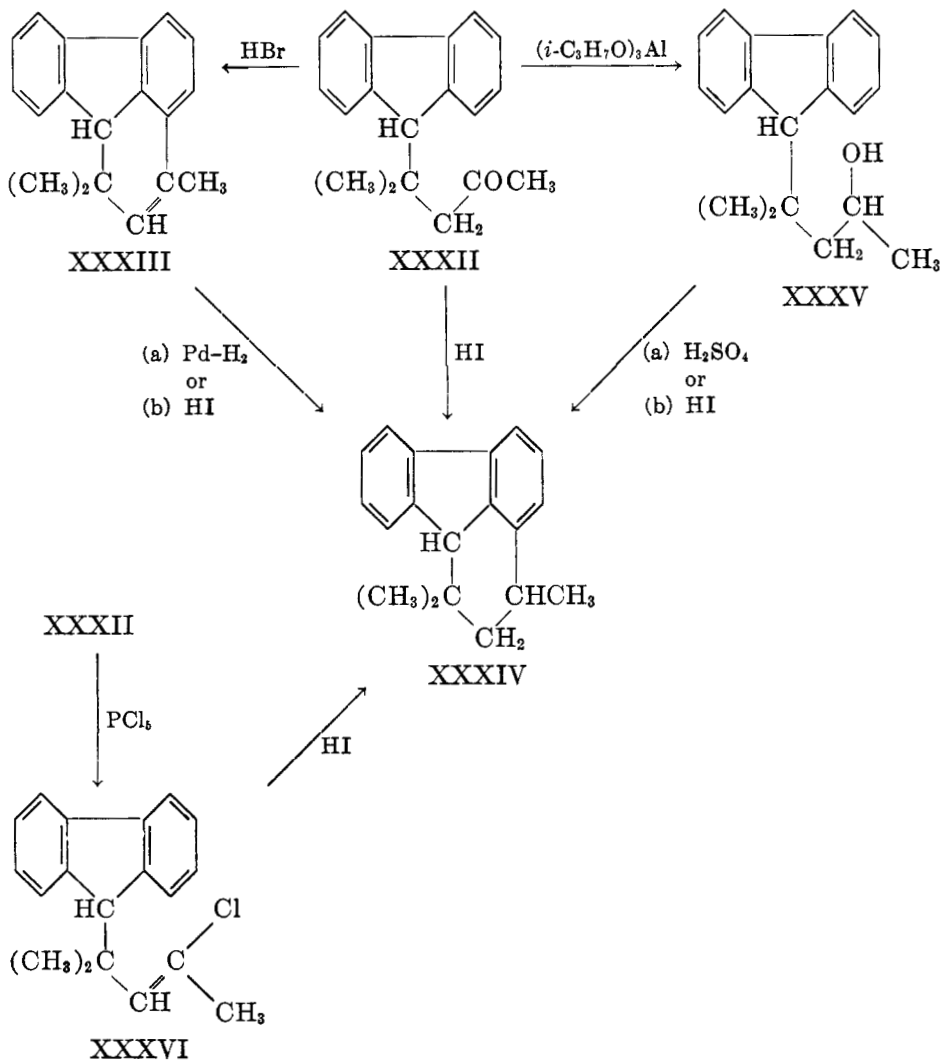


Deno (53) condensed acenaphthylene with sorbic acid, and obtained a tetrahydro-7-methylfluoranthene-10-carboxylic acid. This was not converted into the known 7-methylfluoranthene (180), but the conversion has recently been accomplished (Tucker).



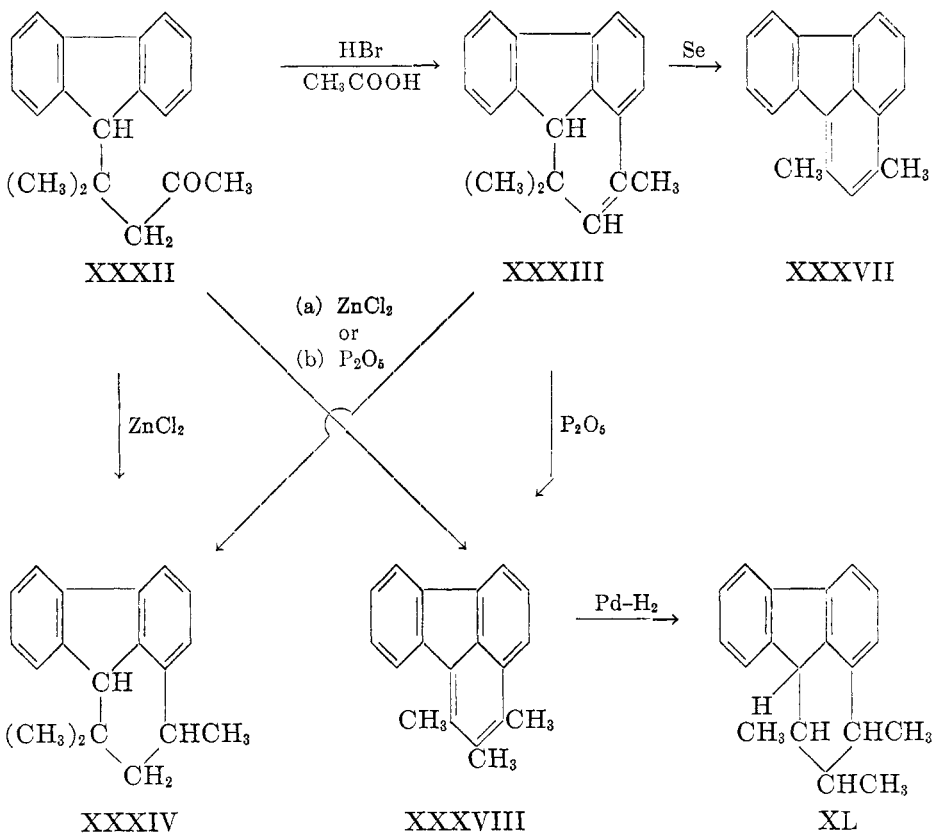
B. POLYMETHYLFLUORANTHENES

In 1937 France, Maitland, and Tucker (76) by reduction of methyl 2-(9-fluorenyl)-2-methylpropyl ketone (XXXII) with zinc and hydrochloric acid,



or with hydriodic acid in glacial acetic acid, obtained a hydrocarbon of the formula $C_{19}H_{20}$. The action of hydrobromic acid on the same ketone gave a substance, $C_{19}H_{18}$, which hydrogenated to the above compound ($C_{19}H_{20}$). The structures of these two hydrocarbons were not elucidated until 1945 (77). Oxidation of the hydrocarbons with sodium dichromate and glacial acetic acid, giving first 1-acetylfluorenone and finally 1-fluorenonecarboxylic acid, showed them to be derivatives of fluoranthene: *viz.*, 1,10b-dihydro-1,1,3-trimethylfluoranthene (XXXIII) ($C_{19}H_{18}$) and 1,2,3,10b-tetrahydro-1,1,3-trimethylfluoranthene (XXXIV) ($C_{19}H_{20}$).

The formation of 1,2,3,10b-tetrahydro-1,1,3-trimethylfluoranthene (XXXIV) by the action of hydriodic acid on the ketone XXXII may follow the sequence XXXII → XXXIII → XXXIV, or alternatively may have been brought about by reduction of XXXII to the carbinol (XXXV) followed by cyclization. The latter is feasible, since reduction of the ketone (XXXII) with aluminum isopropoxide in isopropyl alcohol yielded 4-(9-fluorenyl)-4-methyl-



pentan-2-ol (XXXV) which, either by boiling with hydriodic acid in acetic acid or by the action of concentrated sulfuric acid at room temperature, at once gave XXXIV.

Furthermore, the ketone XXXII also reacted with phosphorus pentachloride

in chloroform to give a chloro derivative (XXXVI) from which the hydrocarbon (XXXIV) was prepared by the action of hydriodic acid in glacial acetic acid.

The reactions of 1,10b-dihydro-1,1,3-trimethylfluoranthene (XXXIII) proved interesting (75). Selenium at 300°C. produced 1,3-dimethylfluoranthene (XXXVII). Migration of a methyl group, with dehydrogenation to 1,2,3-trimethylfluoranthene (XXXVIII), was effected by phosphorus pentoxide at 250°C., the same hydrocarbon being obtained, along with 1,2,3,10b-tetrahydro-1,1,3-trimethylfluoranthene (XXXIV), when the ketone (XXXII) was heated with zinc chloride at 250°C.

1,2,3-Trimethylfluoranthene is unusual in forming a picrate containing two molecules of the hydrocarbon to one of picric acid; it gives a normal complex with 1,3,5-trinitrobenzene.

There is evidence of some fixity of the double bonds in the methylated rings of 1,3-dimethylfluoranthene (XXXVII) and 1,2,3-trimethylfluoranthene (XXXVIII), since in each case the presence of two double bonds is revealed by microhydrogenation. Similarly, on hydrogenation with palladium–charcoal (179) in glacial acetic acid, 1,2,3-trimethylfluoranthene yields 1,2,3,10b-tetrahydro-1,2,3-trimethylfluoranthene (XL), whilst di- and tetrahydro products are obtained from 1,3-dimethylfluoranthene. The olefinic nature of these exo-fluorene-skeleton double bonds is also indicated by the fact that XXXVII and XXXVIII are both oxidized by sodium dichromate in acetic acid to a mixture of 1-acetylfluorenone and 1-fluorenonecarboxylic acid (75). Attempts, however, to form addition products of 1,3-dimethylfluoranthene and of 1,2,3-trimethylfluoranthene with maleic anhydride or sulfur dioxide were unsuccessful.

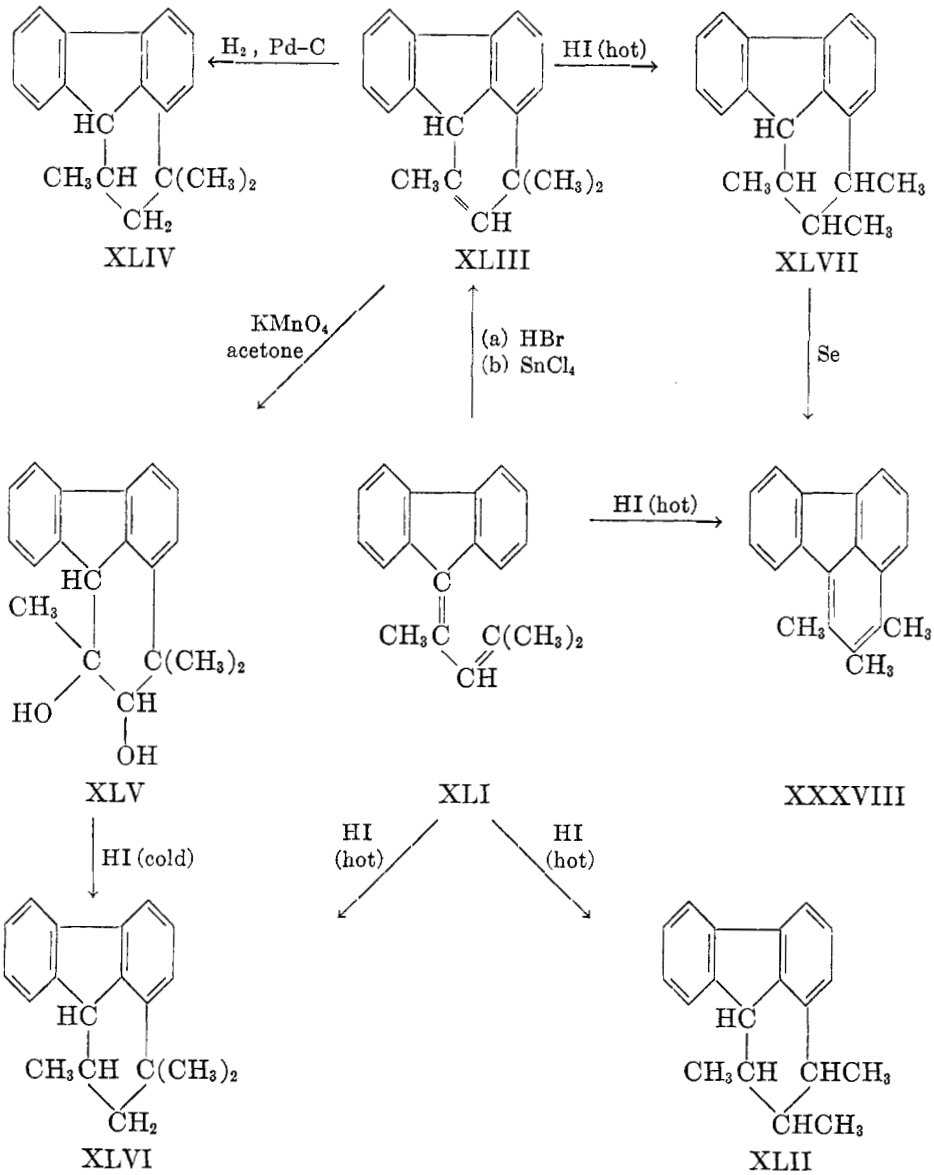
Further derivatives of 1,3-dimethylfluoranthene and 1,2,3-trimethylfluoranthene were prepared by reactions of 1-diphenylene-2,4-dimethylpenta-1,3-diene (XLI), which was obtained by the action of 9-fluorenylmagnesium bromide on mesityl oxide (178).

Maitland and Tucker (129), by treating XLI with hydriodic acid, obtained two compounds: A, m.p. 51–55°C.; B, m.p. 103–104°C. A was later identified as the open-chain hydrogenated compound (XLII) (179). B—shown later to be XLVI—was obtained once only in this later series of experiments (179) in which the principal product was invariably 1,2,3-trimethylfluoranthene (XXXVIII).

Treatment of XLI with hydrogen bromide in glacial acetic acid, followed by stannic chloride in benzene, formed 3,10b(?2,3)-dihydro-1,3,3-trimethylfluoranthene (XLIII). This on catalytic hydrogenation yielded 1,2,3,10b-tetrahydro-1,3,3-trimethylfluoranthene (XLIV).

When XLIII was oxidized with potassium permanganate in acetone at room temperature it gave 1,2(?1,10b)-dihydroxy-1,2,3,10b-tetrahydro-1,3,3-trimethylfluoranthene (XLV), which was reduced with *cold* hydriodic acid to XLVI. This differed from XLIV and was probably an isomer. XLVI was found to be identical with the product (B, above) which is obtained by the action of hydriodic acid on XLI and is therefore 1,2,3,10b-tetrahydro-1,3,3-trimethylfluoranthene.

Reduction of XLIII with *hot* hydriodic acid in glacial acetic acid gave a

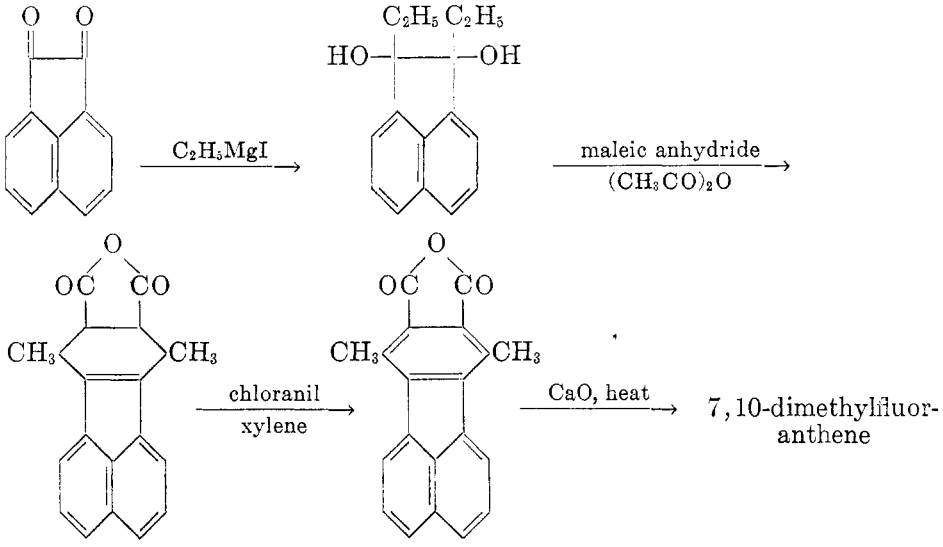


hydrocarbon which must be 1,2,3,10b-tetrahydro-1,2,3-trimethylfluoranthene (XLVII), since on dehydrogenation it yielded 1,2,3-trimethylfluoranthene (XXXVIII) whose structure was established by synthesis from 1,2,3-trimethylnaphthalene. The substance XLVII was, however, different from the product of hydrogenation of XXXVIII: *viz.*, XL (page 506).

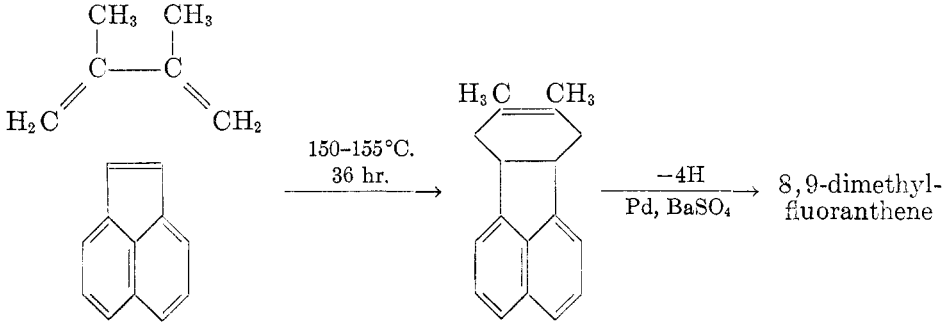
It is interesting to note that whereas, as shown above, XLIII by the action of hot hydriodic acid gives XLVII by migration of the methyl group, the corresponding 1,10b-dihydro-1,1,3-trimethylfluoranthene (XXXIII; page 506) gives, without methyl migration, the normal hydrogenation product, 1,2,3,10b-tetrahydro-1,1,3-trimethylfluoranthene (XXXIV; page 505) (77).

7,10-Dimethyl- and 8,9-dimethylfluoranthenes

7,10-Dimethylfluoranthene was prepared by Campbell and Gow (33) by the following sequence:



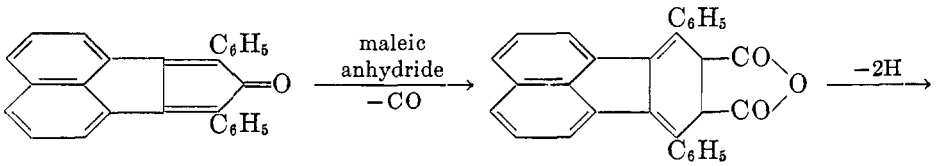
8,9-Dimethylfluoranthene was synthesized by Kloetzel and Mertel (118) by dehydrogenation of the condensation product of acenaphthylene with 2,3-dimethyl-1,3-butadiene:



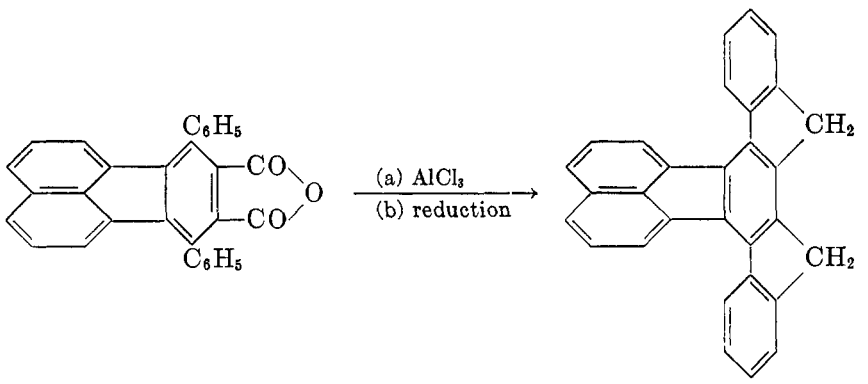
C. PHENYLFLUORANTHENES

Dilthey and Henkels (54) obtained diphenylfluoranthene derivatives by a Diels–Alder reaction between acecyclone (XLVIII) and maleic anhydride; spontaneous evolution of carbon monoxide gave rise to XLIX, which at 150°C. gave L (*cf.* also reference 2a on page 522). L, with aluminum chloride followed by reduction, gave the diindenofluoranthene LI (see page 510).

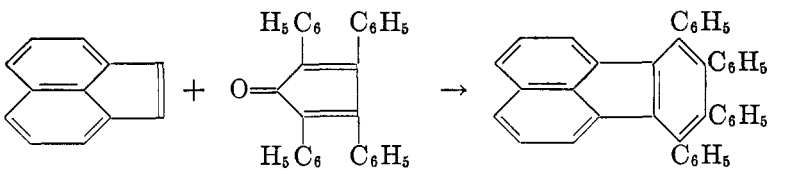
By using acetylene or a substituted acetylene in place of maleic anhydride, Dilthey, Henkels, and Schaefer (55) prepared various phenylfluoranthenes. Thus, the condensation of acecyclone with acetylene in molten phenanthrene yielded 7,10-diphenylfluoranthene. With phenylacetylene, 7,8,10-triphenylfluoranthene was obtained, whilst diphenylacetylene gave 7,8,9,10-tetraphenylfluoranthene. This last compound was also prepared by the condensation of acenaphthylene with tetraphenylfuran (tetracyclone) (see page 510).



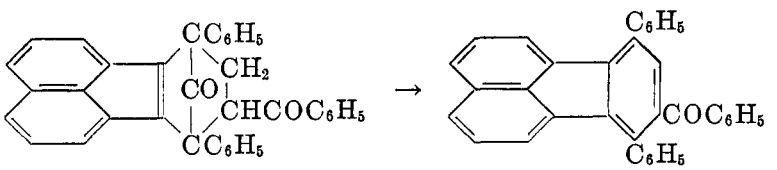
XLVIII XLIX



L LI



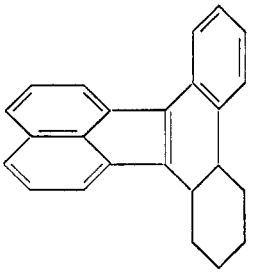
Allen and coworkers (2) condensed acecyclone and β-chloropropiophenone in the presence of toluene and potassium acetate to LII which, on dehydrogenation, gave 8-benzoyl-7,10-diphenylfluoranthene (LIII). Similarly, Abramov and Tsyplenkova (1) found that heating acecyclone in benzene in a sealed tube with vinyl ethyl (or butyl or phenyl) ether or with vinyl formate or bromide gave 7,10-diphenylfluoranthene.



LII LIII

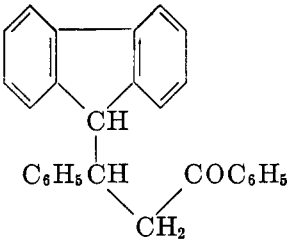
7,10-Diphenylfluoranthene has also been synthesized by Bergmann (11). He suggested that the formation of aromatic compounds in the high-temperature cracking of petroleum may be due to diene synthesis and, in particular, showed that fluoranthene, a typical product of cracking, may be synthesized by a Diels–Alder reaction between acenaphthylene and butadiene. In this way, hydrogenated derivatives of 7-phenylfluoranthene and of 7,10-diphenylfluoranthene were prepared, using the corresponding dienes. When dicyclohexenyl was

used as the diene component, partial *crystallization* seemed to occur, and a substance whose analysis corresponded to that of LIV was obtained.

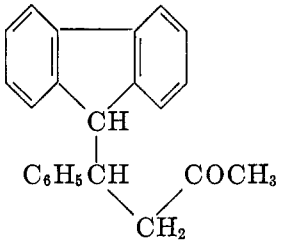


LIV

Two other phenyl-substituted fluoranthenes have been prepared by a method starting with the fluorene skeleton. Tucker and Whalley (178) obtained 1,4-addition products with 9-fluorenyllithium and certain α,β-unsaturated ketones. In particular, benzalacetophenone (chalcone) and benzalacetone gave the ketones LV and LVI, respectively.

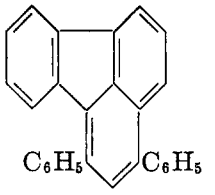


LV

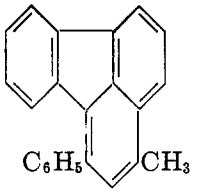


LVI

The alcohols formed on reduction of these ketones were cyclized and dehydrogenated to 1,3-diphenyl- and 1,3-phenylmethylfluoranthene, LVII and LVIII, respectively:



LVII



LVIII

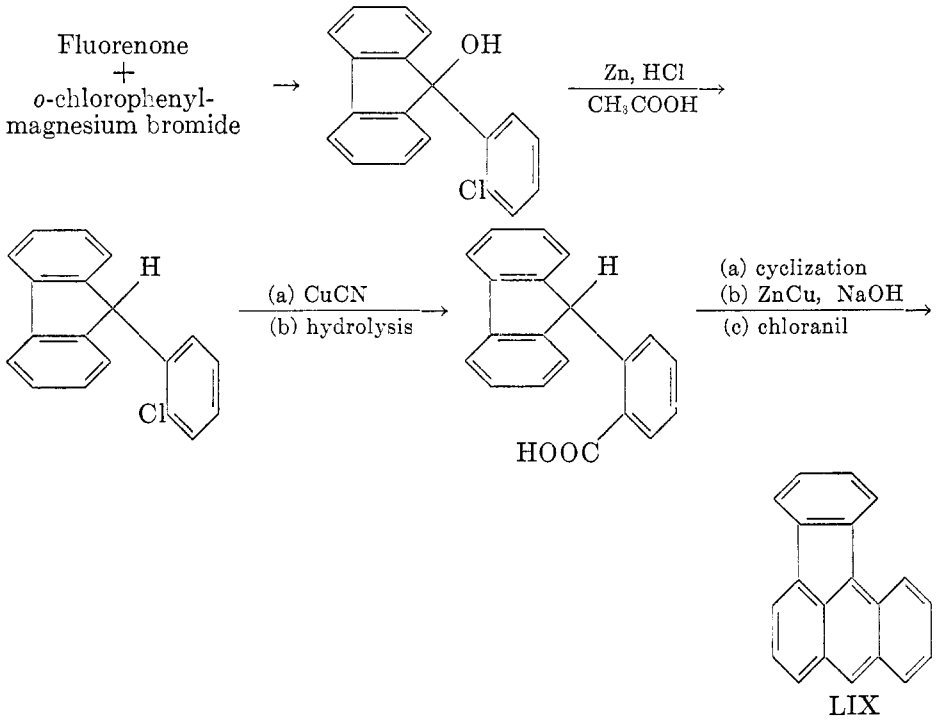
The preparation of a tetraphenylfluoranthene, by condensation of tetraphenylcyclopentadienone (tetracyclone) with unsaturated compounds at high temperatures, is recorded in the patent literature (102, 108).

IX. Benzofluoranthenes and Naphthofluoranthenes

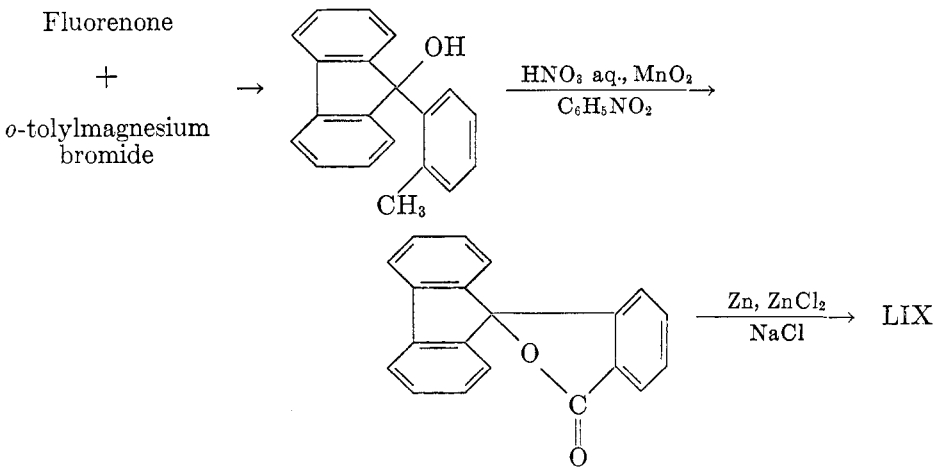
A. Benzofluoranthenes

1,2-Benzofluoranthene (LIX), golden-yellow needles, m.p. 145–146°C., has been synthesized (1951) independently by Campbell and Marks (34a) and by

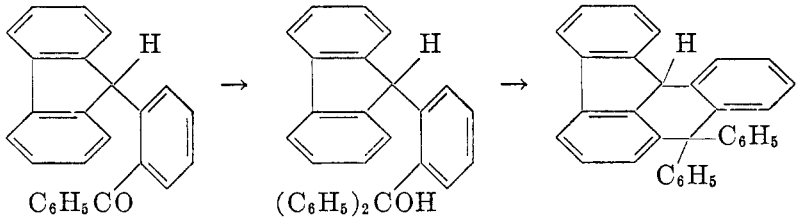
Stubbs and Tucker (173). The former workers used the following method:



Stubbs and Tucker (173) utilized *o*-diphenylenephthalide (119, 183), which by Clar's zinc dust reduction method (44) at 340°C. gave LIX.

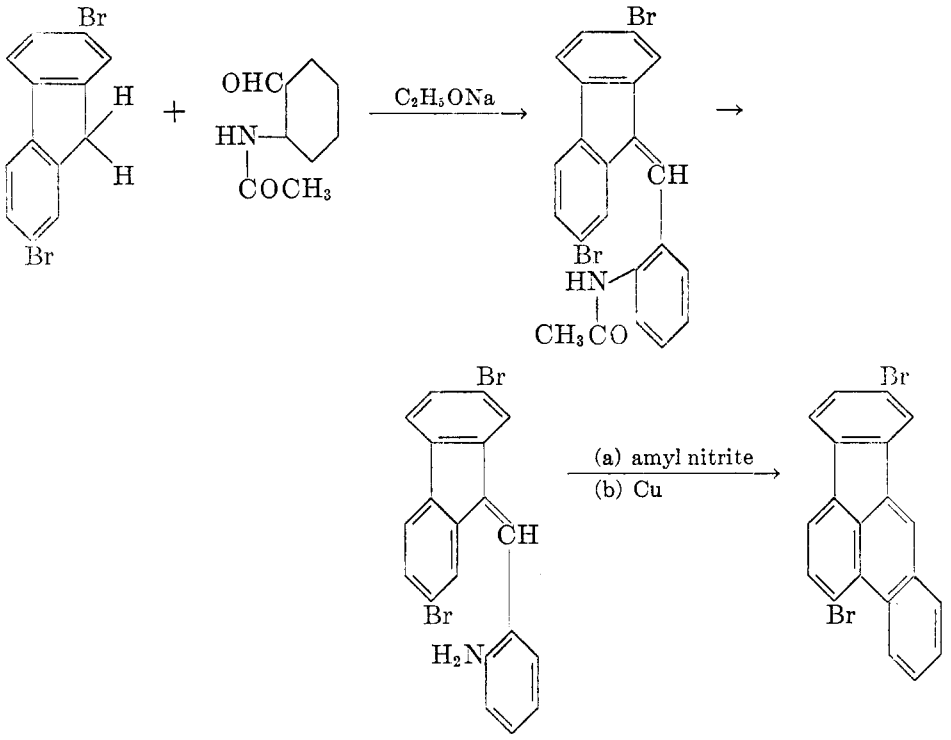


Koelsch (119) synthesized 1,2-benzo-3,10b-dihydro-3,3-diphenylfluoranthene (LX).



LX

Although early attempts by Tobler and coworkers (174) to prepare 3,8-dibromofluoranthene from 2,7-dibromofluorene were unsuccessful, a benzo homolog of 3,8-dibromofluoranthene, *viz.*, 4,9-dibromo-2,3-benzofluoranthene (LXI), was synthesized by the following series of reactions:

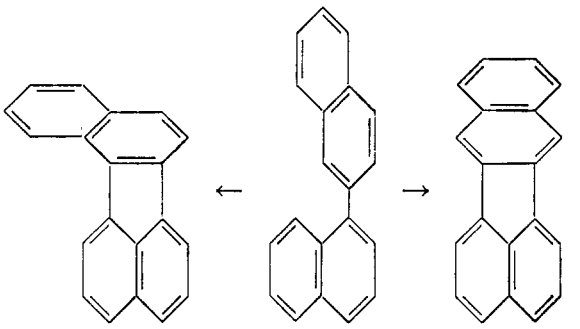


LXI

Treatment of LXI with sodium amalgam in water eliminated the bromine atoms and formed an octahydrobenzofluoranthene which, on dehydrogenation with chloranil in xylene, gave 2,3-benzofluoranthene. This was identical with the previously known benzofluoranthene obtained from 9-(*o*-chlorobenzal)fluorene by ring-closure with alkali (107, 184).

In 1947 Orchin and Reggel (140) found that 1-cyclohexenylnaphthalene may be converted to fluoranthene by cyclic dehydrogenation, using palladium–

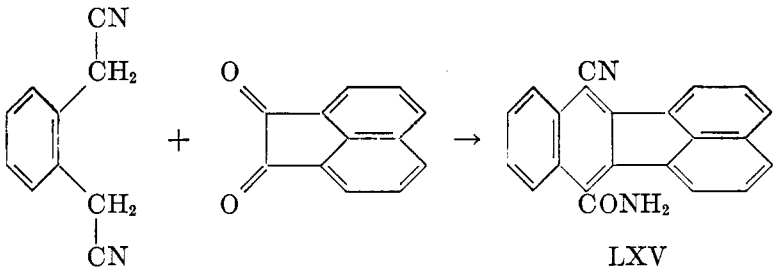
charcoal or chromia–alumina as catalyst. The application of this reaction to 1,2′-binaphthyl (LXII) could lead to two products, since cyclization at the 1′- or 3′-position would give isomeric benzofluoranthenes (LXIII and LXIV).



LXIII LXII LXIV

Two compounds were isolated from the reaction mixture and, though no proof of structure was attempted, it was considered likely that the principal product, m.p. 217°C., was the 7,8-benzofluoranthene LXIII, formed by ring-closure to the more reactive 1′-position of 1,2′-binaphthyl. The second product, m.p. 166°C., was therefore assumed to be 8,9-benzofluoranthene (LXIV).

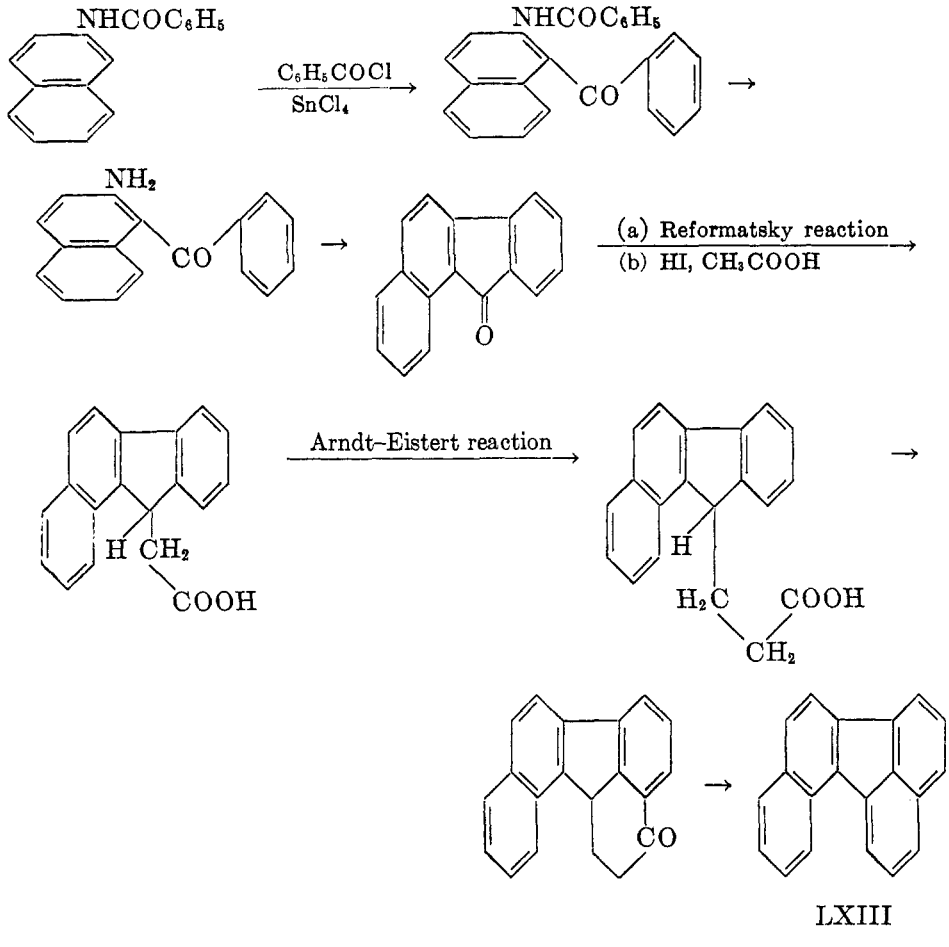
Further information regarding these benzofluoranthenes was obtained by Moureu, Chovin, and Rivoal (135, 136, 137, 138) in 1948. By condensation of the dinitrile of *o*-phenylenediacetic acid with acenaphthenequinone, they obtained the nitrile-amide LXV.



LXV

Like 9,10-dicyanoanthracene, and almost all 2,6-disubstituted benzonitriles, this substance is very resistant to hydrolysis, but with 100 per cent phosphoric acid at 145–155°C. hydrolysis and decarboxylation occurred. Since their product, unambiguously 8,9-benzofluoranthene (LXIV), melted at 217°C., the structures proposed by Orchin and Reggel must be reversed, the principal product therefore being, rather surprisingly, 8,9-benzofluoranthene (LXIV). Proof that this was indeed the case came in 1951 with the synthesis of both hydrocarbons by Orchin

and Reggel (141). Their synthesis of 8,9-benzofluoranthene (LXIV) was essentially that of Moureu, Chovin, and Rivoal, whilst 7,8-benzofluoranthene was obtained by starting with *N*-benzoyl-β-naphthylamine:

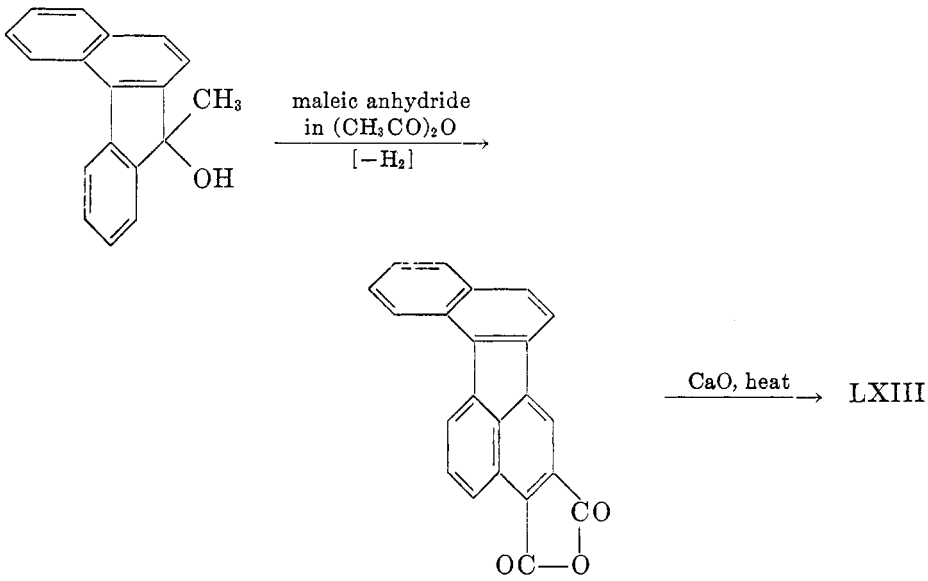


LXIII

The same 7,8-benzofluoranthene (LXIII) was prepared by Zinke and Pack (185) by the action of aluminum chloride on dinaphtho[2,1,1′,2′]furan. The formation of both 7,8- and 8,9-benzofluoranthene was probably observed by Dansi and Reggiani (49) in the dehydrogenation of the products obtained by the action of aluminum chloride and hydrochloric acid on 1,2,3,4-tetrahydronaphthalene or by treatment of 1,2-dihydronaphthalene with sulfuric acid. The correct structures for these benzofluoranthenes were suggested by Bell and Hunter (8).

Finally, Campbell, Khanna, and Marks (33a) have carried out another

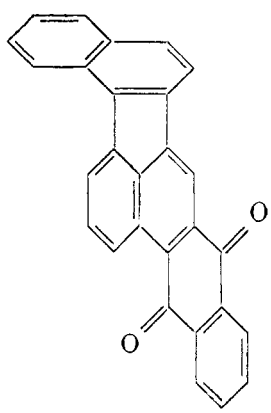
synthesis of 7,8-benzofluoranthene (LXIII) as follows:



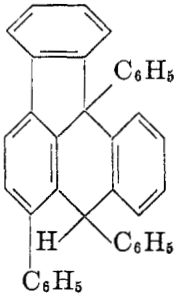
It is worth noting that ring-closure is with the benzene ring and not with the relatively unreactive β-carbon atom of the naphthalene system.

This work is important, since the authors show that the hydrocarbons prepared by Zinke and Pack (185), von Braun and Kirschbaum (16a), and Dansi and Ferri (48a) are 7,8-benzofluoranthene (LXIII). Further, von Braun and Kirschbaum's compound, $C_{20}H_{20}$, is probably 1,2,3,6b,9,10,10a,10b-octahydrofluoranthene.

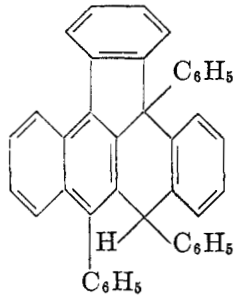
3,4-Benzo-9-methylfluoren-9-ol reacts with 1,4-naphthaquinone to give



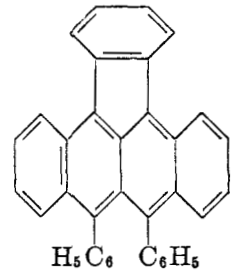
Later, Bergmann (10) and Dufraisse and Amiard (58) confirmed fluoranthene structures for compounds LXVI and LXVII, obtained by the action of metallic chlorides on tetraphenylanthracene and tetraphenyltetracene, respectively.



LXVI

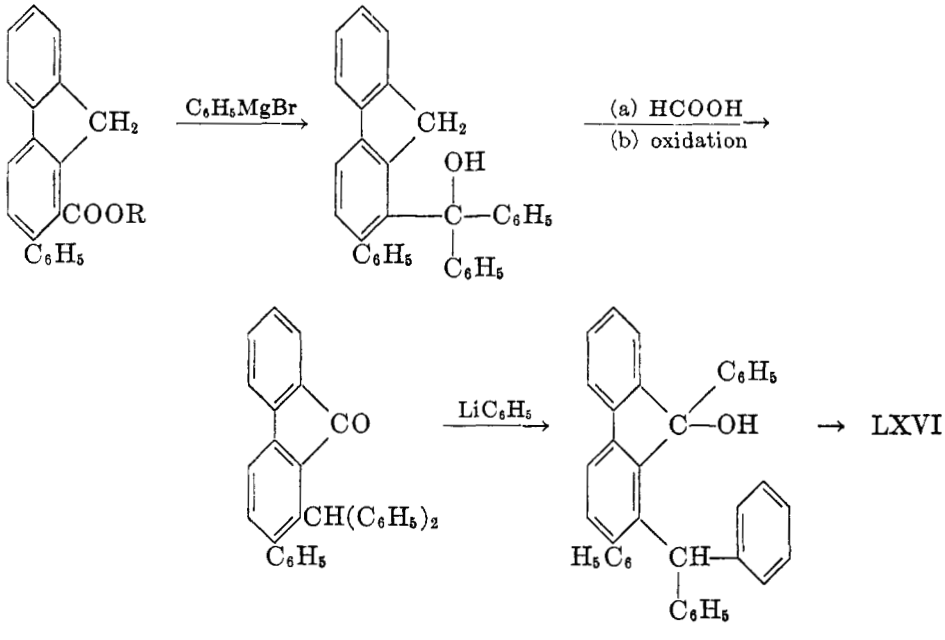


LXVII



LXVIII

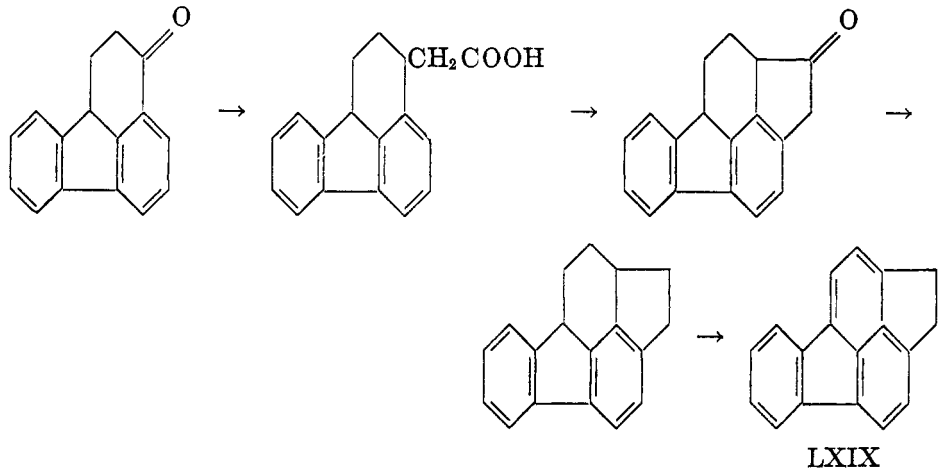
LXVI was synthesized according to the following scheme:



The formula for pseudorubrene (LXVII) was supported by its transformation into 1,2,5,6-dibenzo-3,4-diphenylfluoranthene (LXVIII).

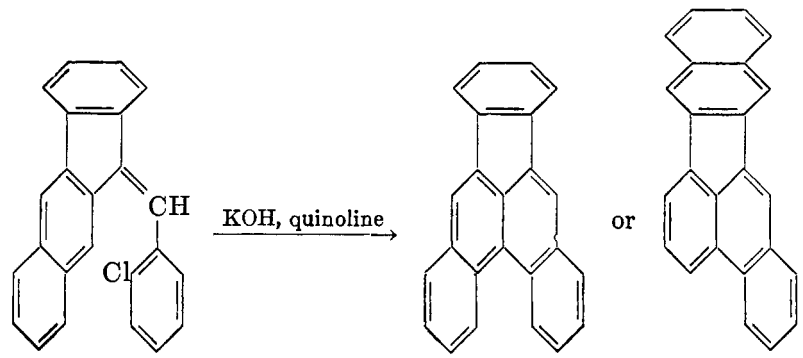
In the course of research on isorubicene, Kloetzel and Chubb (117) prepared a different type of fluoranthene derivative. Starting with 1,2,3,10b-tetrahydro-3-ketofluoranthene and treating it as shown, they obtained 1,2-dihydro-3,4,5-cyclopenta[*cd*]fluoranthene (LXIX), whose absorption spectrum was sufficiently similar to that of fluoranthene to preclude the possibility of skeletal rearrangement during dehydrogenation of the fluoranthene system (see page 518).

2,3-4,5-Dibenzofluoranthene (LXXI) was prepared (107, 184) by cyclization of the condensation product of *o*-chlorobenzaldehyde and 2,3-benzofluorene



LXIX

(LXX) by means of potassium hydroxide in quinoline:

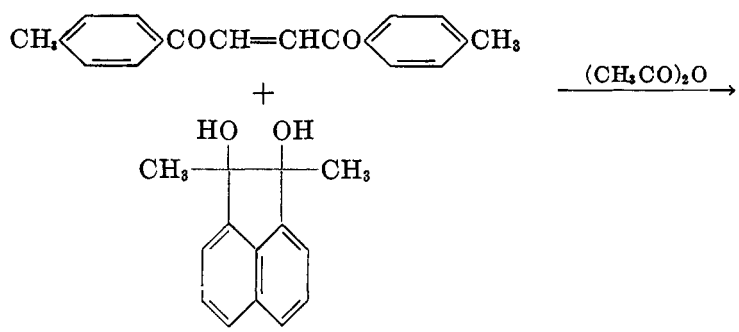


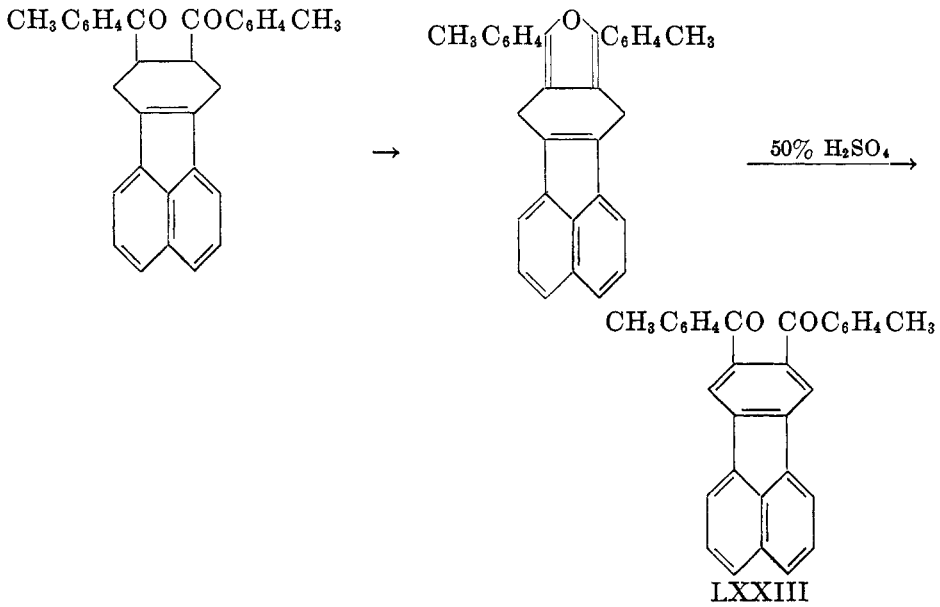
LXX LXXI LXXII

2,3-8,9-Dibenzofluoranthene (LXXII) is also a possible product, but is less likely to be formed, since ring-closure should occur more readily with the naphthalene ring than with the benzene ring of the benzofluorene.

These compounds have no carcinogenic effect (56).

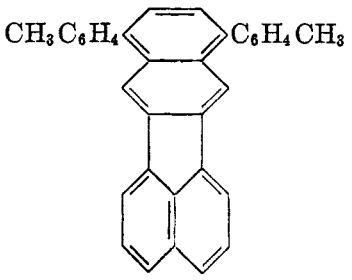
8,9-Di-*p*-toluoylfluoranthene (LXXIII) was prepared by the following series of reactions (33):





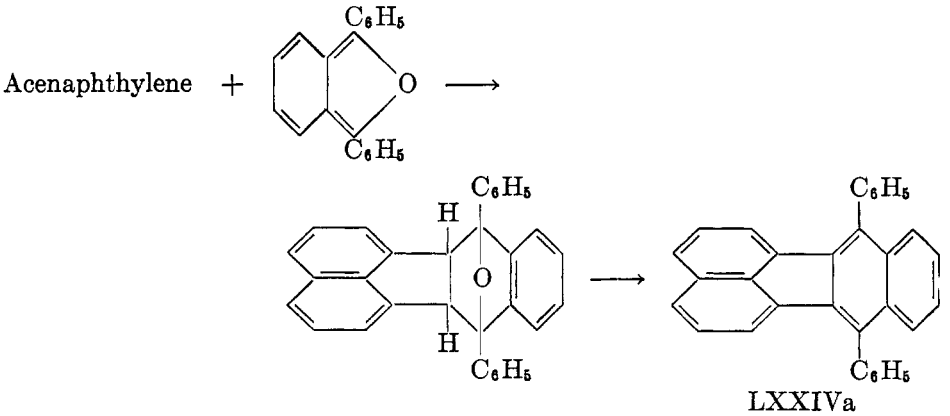
LXXIII

The structure of the furan derivative was confirmed by its combination with maleic anhydride to give an adduct which on hydrolysis and decarboxylation yielded 8,9-benzo-1′,4′-di-*p*-tolylfluoranthene (LXXIV).



LXXIV

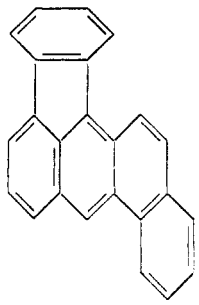
7,12-Diphenylbenzo[*k*]fluoranthene (LXXIVa) has been synthesized by Bergmann (10a) as follows:



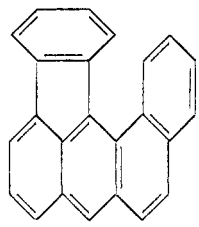
LXXIVa

B. NAPHTHOFLUORANTHENES

The two naphthofluoranthenes, naphtho[2′,1′-1,2]fluoranthene (15,16-benzodehydrocholanthrene) (LXXV) and naphtho[1′,2′-1,2]fluoranthene (LXXVI), were prepared by Fieser and Seligman (68).

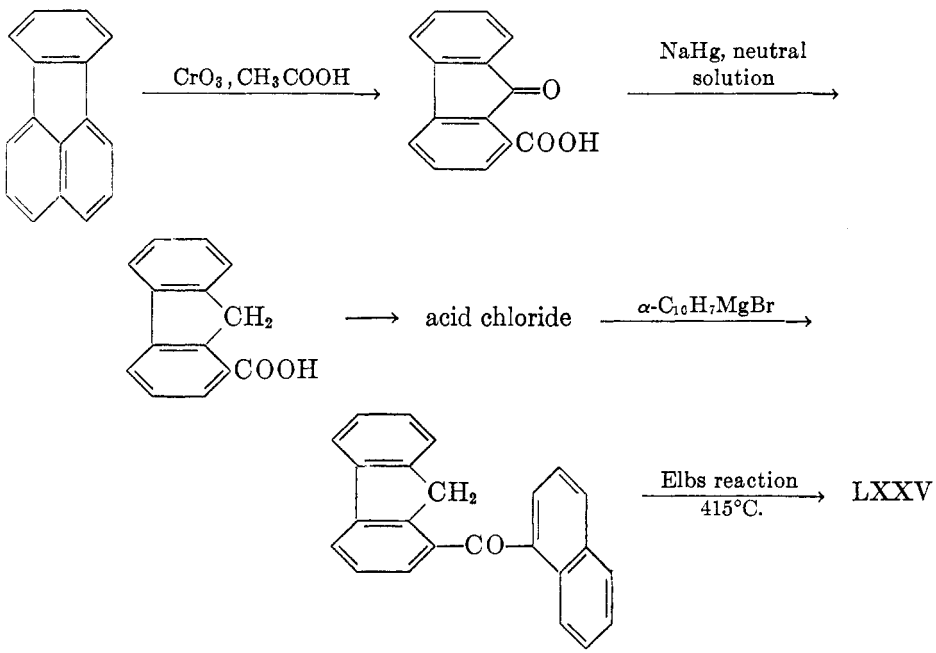


LXXV

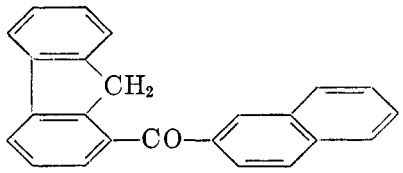


LXXVI

LXXV was prepared from fluoranthene as indicated below:

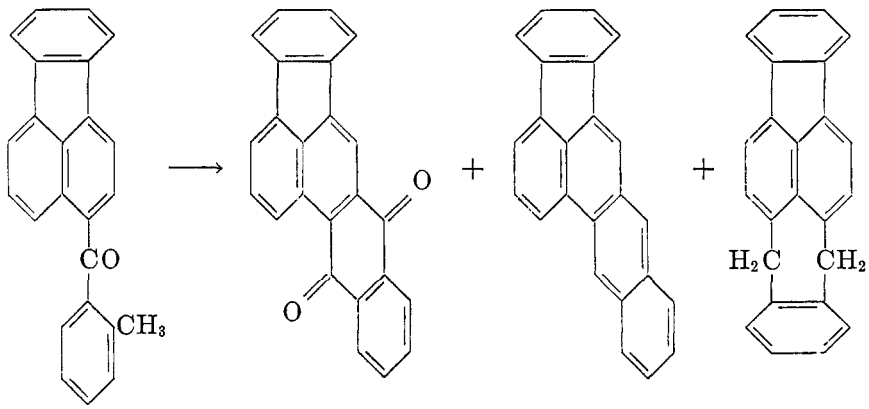


The other naphthofluoranthene (LXXVI) was obtained by the action of the above-mentioned 1-fluorenecarboxylic acid chloride on naphthalene in presence of aluminum chloride in tetrachloroethane, which gave 1-(β-naphthoyl)-fluorene (LXXVII). Pyrolysis of LXXVII gave LXXVI. As was expected from its structural similarity to cholanthrene, LXXV possesses carcinogenic properties but these are only slight (67).



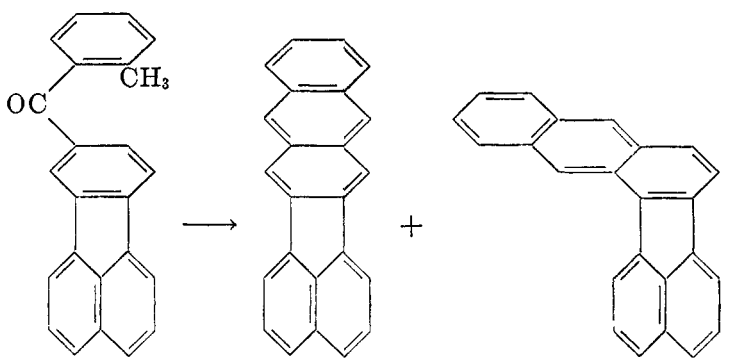
LXXVII

3-*o*-Toluoylfluoranthene under the conditions of the Elbs reaction (35) gave a mixture of the quinone LXXVIII, naphtho[2′,3′-2,3]fluoranthene (LXXIX), and a substance which is probably 3,4-*o*-xylylenefluoranthene (LXXX), since oxidation yielded 3,4-phthaloylfluoranthene.



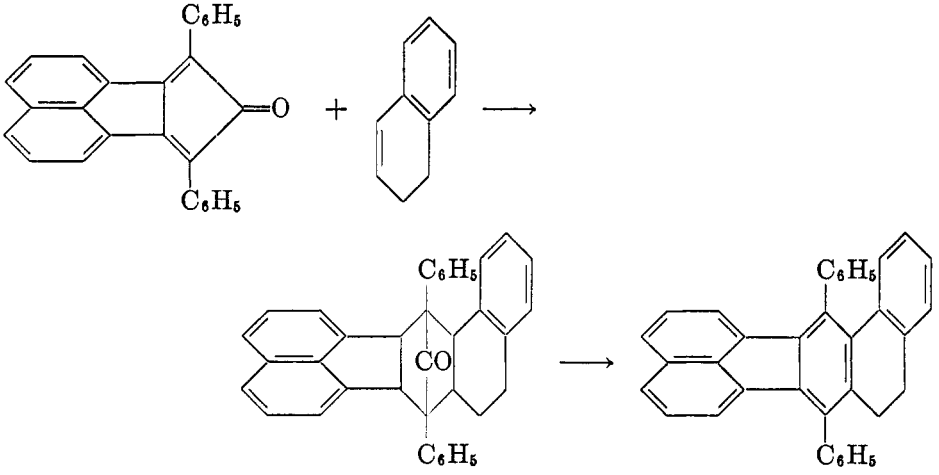
LXXVIII LXXIX LXXX

Pyrolysis of 8-*o*-toluoylfluoranthene (35) gave two isomeric hydrocarbons: one of them was oxidized to the known naphtho[2′,3′-8,9]fluoranthene-1′,4′-quinone, and is therefore naphtho[2′,3′-8,9]fluoranthene (LXXXI); the other was a red substance which by elimination must be naphtho[2′,3′-7,8]fluoranthene (LXXXII).



LXXXI LXXXII

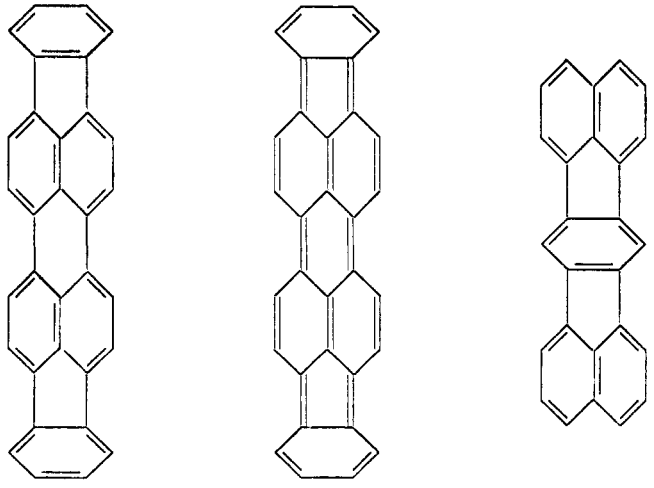
The dihydronaphthofluoranthene (LXXXIIb), 9,10-dihydro-2,3-(1,8-naphthylene)-1,4-diphenylphenanthrene, has been synthesized (2a) from acecyclone and 1,2-dihydronaphthalene, presumably with intermediate formation of LXXXIIa, but this endo-carbonyl compound could not be isolated (*cf.* reference 2 on page 510 and reference 54 on page 509):



LXXXIIa LXXXIIb

X. Condensed Fluoranthene Ring Systems

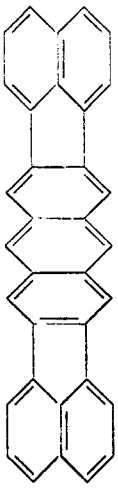
There exist several compounds whose formulas contain more than one fluoranthene skeleton (42) (see formulas LXXXIII–LXXXIX).



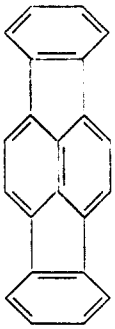
LXXXIIIa LXXXIIIb LXXXIVa

Periflanthene
Diindeno[1,2,3-*cd*,1′,2′,3′-*lm*]perylene

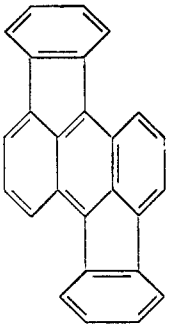
Benzo[1,2-*a*,4,5-*a*′]diacenapthylene



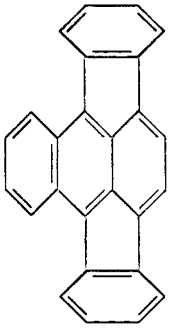
LXXXIVb
Anthraceno[2,3-*b*,6,7-*b*′]-
diacenaphthylene



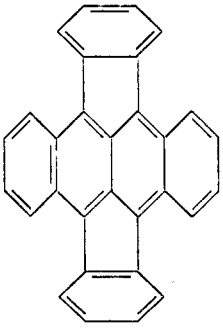
LXXXV
Bisperiphenylenenaphthalene
1,2-5,6-Dibenzopyracylene
Diindeno[1,2,3-*de*,1′,2′,3′-*ij*]-
naphthalene



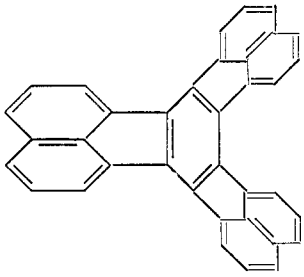
LXXXVI
Rubicene
Diindeno[1,2,3-
de,1′,2′,3′-*kl*]anthracene



LXXXVII
Isorubicene
Diindeno[1,2,3-
de,1′,2′,3′-*mn*]anthracene



LXXXVIII
Diindeno[1,2,3-
fg,1′,2′,3′-*op*]tetracene



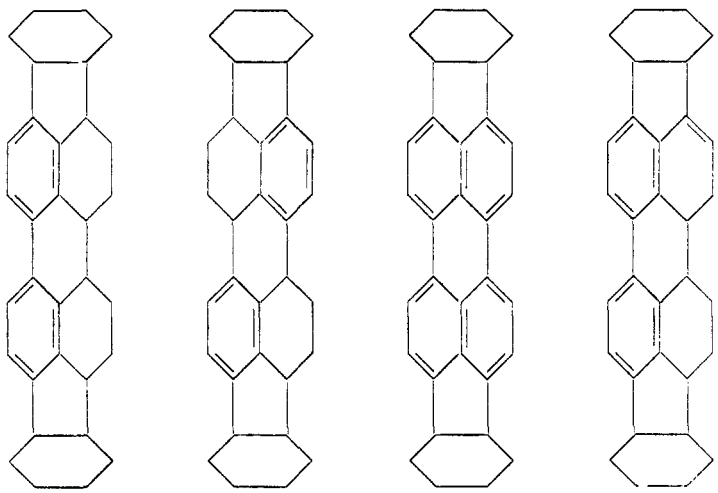
LXXXIX
Decacyclene
Trinaphthylenebenzene
Benzo[1,2-*a*,3,4-a′,5,6-*a*′′]-
triacenaphthylene

A. PERIFLANTHENE

Since naphthalene may be directly aminated with sodium amide, von Braun and Manz (20, 99) attempted to prepare aminofluoranthene by this method. They isolated, in addition to unchanged fluoranthene, a hydrocarbon $C_{32}H_{16}$, of whose constitution there were several indications. 3,3′-Bifluoranthyl, obtained from 3-bromofluoranthene and copper, yielded the same hydrocarbon on treatment with sodium amide. 3-Methyl- and 3-phenylfluoranthenes, which may be synthesized from 3-ketotetrahydrofluoranthene, do not show reactions of this type. Again, linkages at the 8,9- or 1,2-positions are not likely, since they involve the formation of four-membered rings. The name diperifluoranthene or periflanthene with the structure LXXXIIIa or LXXXIIIb was suggested for the hydrocarbon by von Braun and Manz. That it is a perylene derivative is brought out in the systematic name, diindeno[1,2,3-*cd*,1′,2′,3′-*lm*]perylene.

Periflanthene, which has so far been formed in no other way than with sodium amide, is only sparingly soluble in organic solvents. It crystallizes from trichlorobenzene in deep red crystals with a copper reflex and sublimes without melting at 490°C. (186). It is stable toward oxidizing agents.

Hydrogenation of periflanthene with hydrogen and nickel in decalin gave a hydrocarbon, $C_{32}H_{36}$, which did not melt sharply and which appeared to contain



XC XCI XCII XCIII

the two isomers XC and XCI. By less complete hydrogenation there was obtained a substance $C_{32}H_{28}$, corresponding to XCII. The mixture of XC and XCI was changed by repeated crystallization from benzene, in the presence of air, into XCIII, which was stable to aerial oxidation but was dehydrogenated with selenium to XCII.

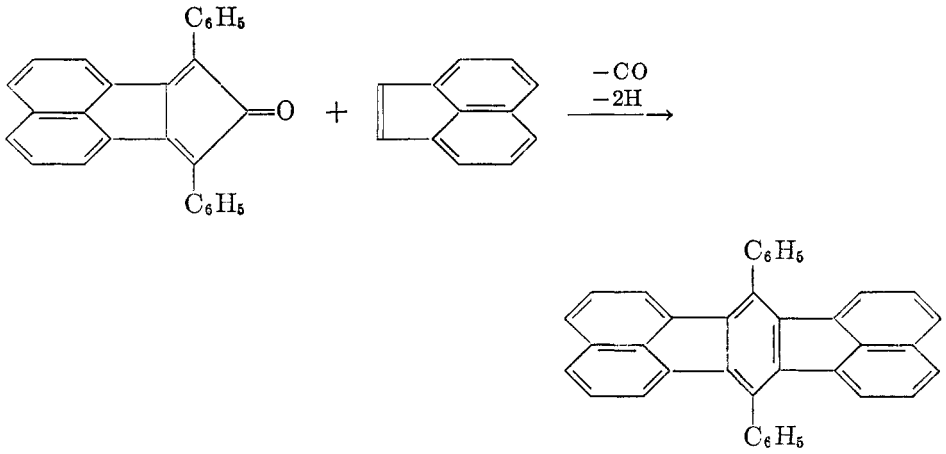
Nitration of periflanthene with concentrated nitric acid gives an amorphous nitro compound, whilst addition of water to its solution in concentrated sulfuric acid precipitates a sulfonic acid. Periflanthene gives no Diels–Alder reaction

with maleic anhydride, but does react with phthalic anhydride in the presence of aluminum chloride and sodium chloride, to give a phthaloyl derivative which can be converted into a vat dye.

B. BENZO[1,2-*a*,4,5-*a*']DIACENAPHTHYLENE

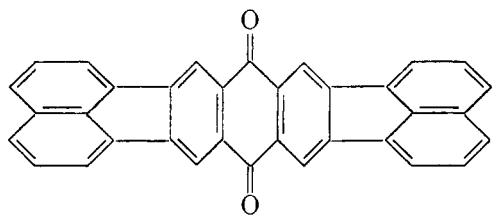
Benzo[1,2-*a*,4,5-*a*']diacenaphthylene (LXXXIVa) has not been synthesized. The general method of fluoranthene syntheses of Forrest and Tucker (75) is being applied, using 1,5-dihalogeno-2,4-dinitrobenzenes and 1-iodonaphthalene.

The diphenyl derivative of LXXXIVa, 3,6-diphenylbenzo[1,2-*a*,4,5-*a*']diacenaphthylene (XCIV) has, however, been synthesized by Dilthey, Henkels, and Schaefer (55) by direct diene addition of acecyclone to acenaphthylene:



XCIV

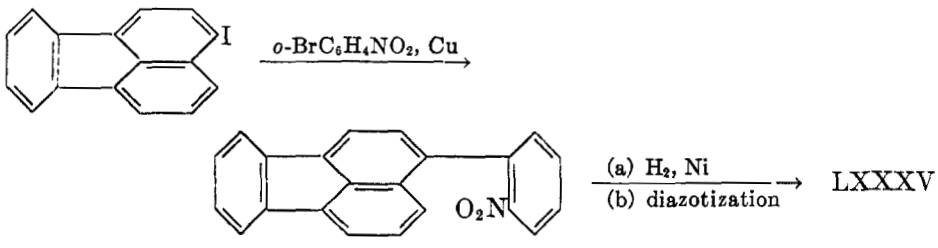
The quinone shown below has been synthesized (33)



but could not be converted into the corresponding hydrocarbon (LXXXIVb).

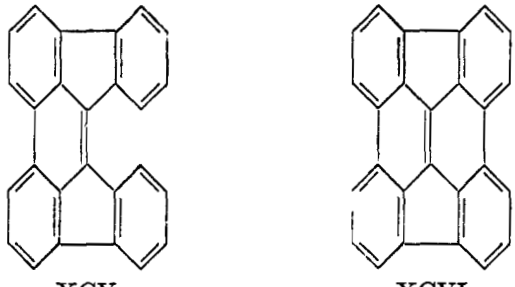
C. BISPERIPHENYLENENAPHTHALENE

Bisperiphenylenenaphthalene, 1,2-5,6-dibenzopyracylene, diindeno[1,2,3-*de*,1',2',3'-*ij*]naphthalene (LXXXV), has been synthesized by Stubbs and Tucker (172) from 3-iodofluoranthene and *o*-bromonitrobenzene by the method of Forrest and Tucker (75), and obtained as orange needles melting at 261–262°C.



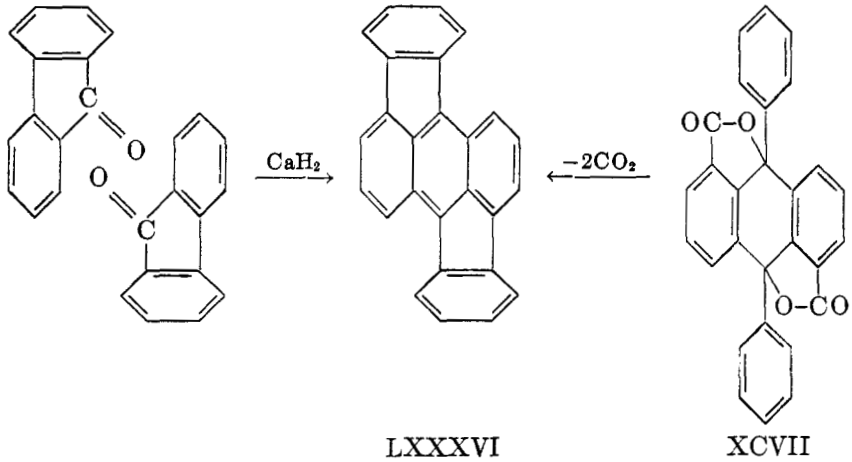
D. RUBICENE

Rubicene, diindeno[1,2,3-*de*,1′,2′,3′-*kl*]anthracene (LXXXVI), was first prepared by Fittig (73, 74) by distillation of diphenic acid with lime. Pummerer (145, 146) called it rubicene, but ascribed to it the incorrect formula XCV, which appeared, however, to be supported by the formation of rubicene by pyrolysis of fluorene (62), and by exposing the vapor of fluorene to contact with a red-hot platinum wire (65). Pummerer (146) quite correctly criticized the formula (XCVI) proposed by Dziewónski and Suszko (64), which does not agree



XCV XCVI

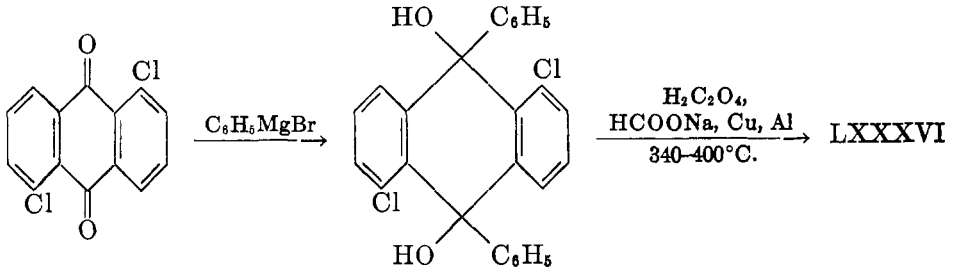
with the formula, $C_{26}H_{14}$, for rubicene. The correct formula (LXXXVI) was suggested by Schlenk and Karplus (151), who obtained rubicene by heating fluorenone with calcium hydride.



LXXXVI XCVII
Rubicene

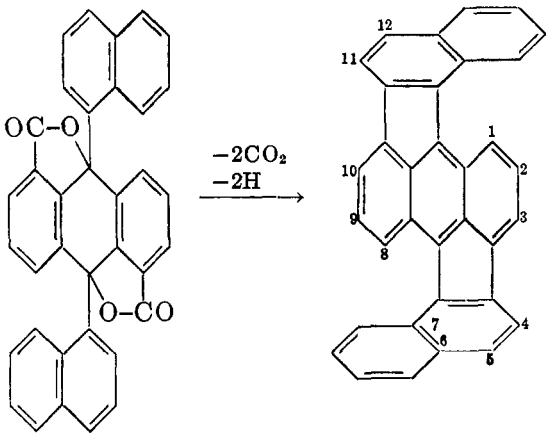
Scholl and Meyer (152) supported the formulation LXXXVI by the synthesis of rubicene from the dilactone of 9,10-dihydro-9,10-dihydroxy-9,10-diphenyl-anthracene-1,5-dicarboxylic acid (XCVII), which by zinc dust distillation gave LXXXVI and 9,10-diphenylanthracene.

Yet another synthesis was accomplished later by Fedorov (66), as indicated below. It is interesting since Fedorov, by the corresponding use of 1,4-dichloro-anthraquinone, similarly synthesized isorubicene (see page 528).



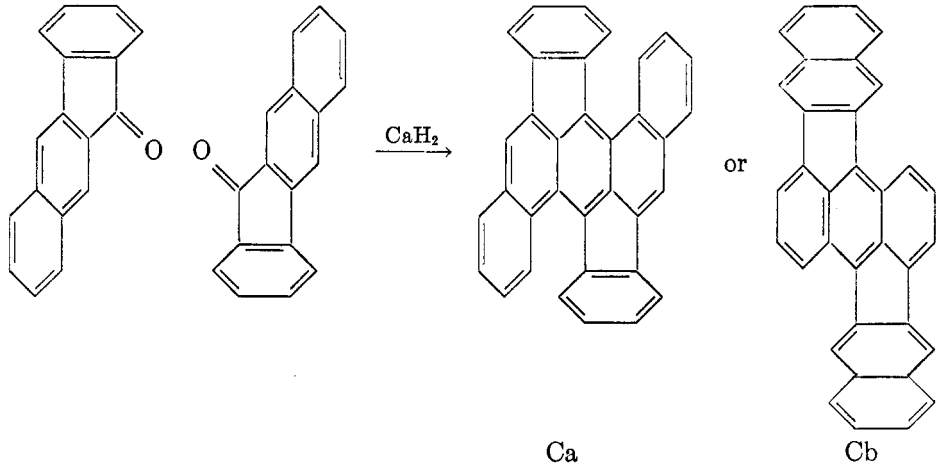
Rubicene crystallizes in red needles melting at 306°C. Sodium and amyl alcohol convert it into perhydrorubicene, $C_{26}H_{40}$ (14, 64), which, on warming in oxygen-containing solvents, gives $C_{26}H_{28}$. Hydrogenation in the presence of nickel gives the above two hydrocarbons and $C_{26}H_{34}$. Derivatives of rubicene have been described (64, 95).

Scholl and Meyer (153), by using the dinaphthyl derivative (XCVIII) corresponding to the above diphenyl-dilactone (XCVII), prepared 6,7-13,14-dibenzorubicene (XCIX).



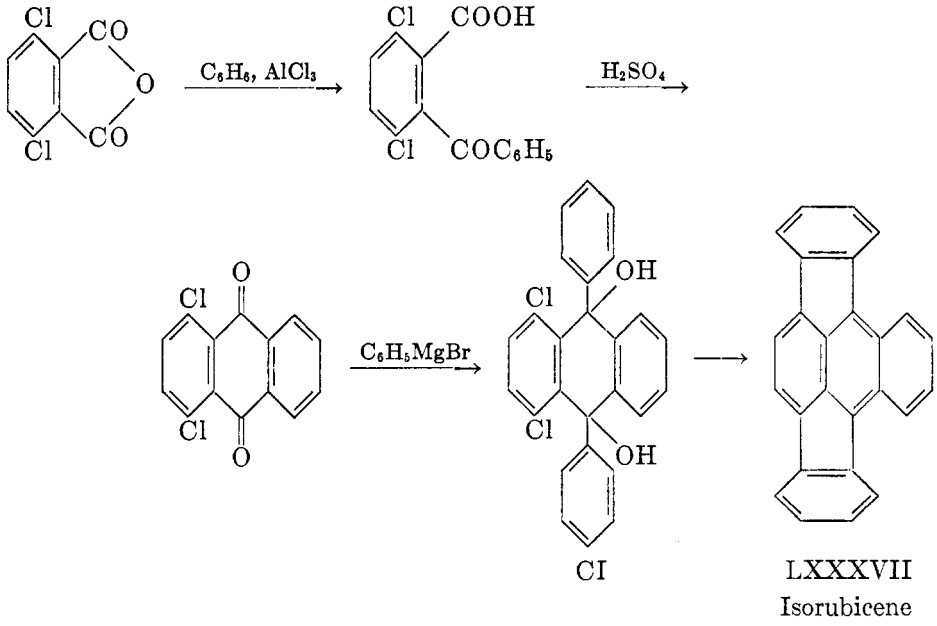
XCVIII XCIX

An isomeric dibenzorubicene was prepared (96) from 2,3-benzofluorenone by heating with calcium hydride, as in the preparation of rubicene from fluorenone (see page 526). It may be either 1,2-8,9-dibenzorubicene (Ca) or 5,6-12,13-dibenzorubicene (Cb), but the greater reactivity of the naphthalene over that of the benzene ring system favors formula Ca.



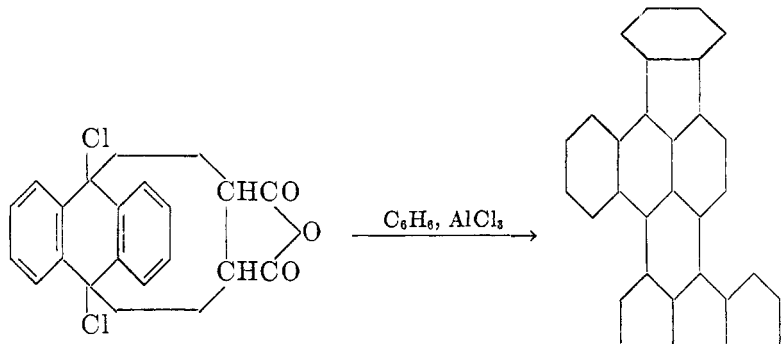
E. ISORUBICENE

Isorubicene, diindeno[1,2,3-*de*,1′,2′,3′-*mn*]anthracene (LXXXVII), was synthesized by Fedorov (66) by heating 1,4-dichloro-9,10-dihydro-9,10-dihydroxy-9,10-diphenylanthracene (CI) with aluminum powder, copper powder, oxalic acid, and sodium formate at 300–365°C. The synthetic route is shown below:



Fedorov supported this formulation by the ultraviolet absorption spectrum, quoting values for the maxima which correspond with those anticipated for the above formula (155). Isorubicene is red-brown and melts at 268–270°C. Fedorov repeated an experiment of Clar's (43), *viz.*, heating the anhydride of 9,10-

dichloroanthracene-9,10-endo-α,β-succinic acid (CII) with aluminum chloride in benzene, and confirmed Clar's finding that deep red needles, melting at 332–333°C. (Clar found a melting point of 335°C.), were thus obtained.[2]

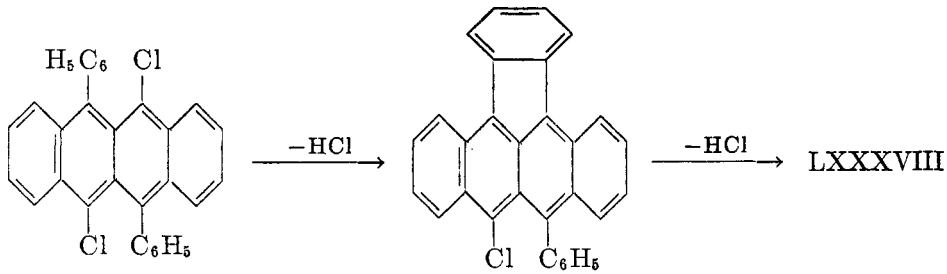


CII CIII

Fedorov (66) similarly synthesized rubicene (LXXXVI) starting with 1,5-dichloroanthraquinone (see page 527).

F. DIINDENO[1,2,3-*fg*,1′,2′,3′-*op*]TETRACENE

Diindeno[1,2,3-*fg*,1′,2′,3′-*op*]tetracene (LXXXVIII) was synthesized by Dufraisse, Buret, and Girard (59) from 6,12-dichloro-5,11-diphenyltetracene (CIV), which when heated to 200°C. lost one molecule of hydrogen chloride and gave 5-chloro-4-phenylindeno[1,2,3-*op*]tetracene (CV). This, in boiling naphthalene or with potassium hydroxide at 325–330°C., lost a second molecule of hydrogen chloride to give LXXXVIII (60).

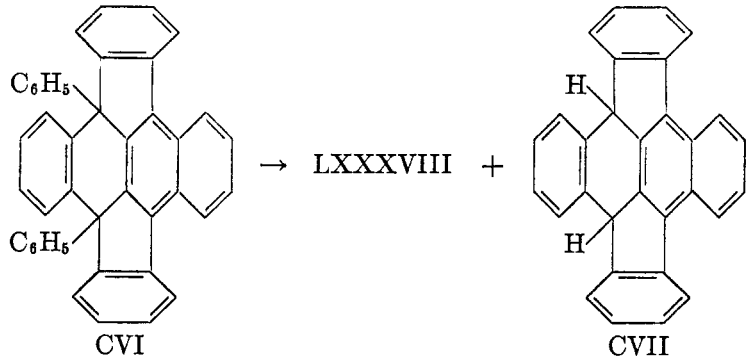


CIV CV

Badoche (7) synthesized LXXXVIII by treatment of CVI, a by-product

[2]Dr. Clar (private communication) suggests that his compound may be 1,2,9,10-dibenzoperiflanthene (CIII, in which the Kekulé double bonds are omitted). The absorption spectrum (42, page 281; 155) is compatible with this formulation.

obtained in the synthesis of rubrene (5,6,11,12-tetraphenyltetracene), with sodium in ether; the dihydro derivative (CVII) was also isolated. LXXXVIII



CVI CVII

crystallizes from xylene in blue needles melting at 465°C.

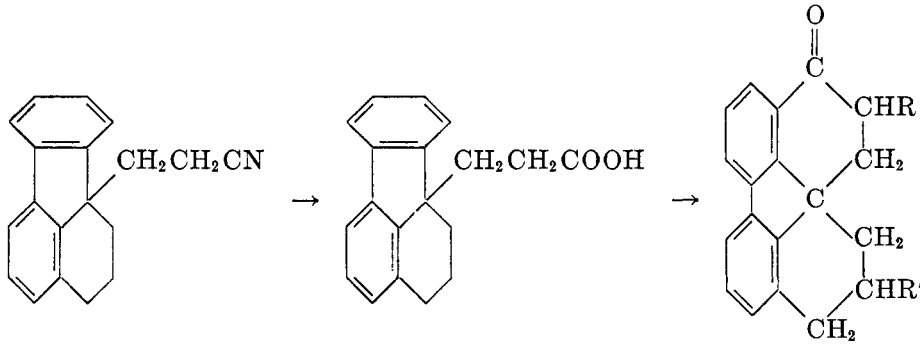
The formulation of the above changes was not at first clear, but was clarified by Dufraisse (57).

G. DECACYCLENE

Decacyclene, trinaphthylenebenzene, benzo[1,2-*a*,3,4-*a'*,5,6-*a''*]triacenaphthylene (LXXXIX), was prepared by heating acenaphthene with sulfur (61a, 148a) or with lead dioxide (63). It has also been obtained by the polymerization of acenaphthylene (62). It exists as yellow needles with a golden reflex, melting at 387°C.

XI. Spirofluoranthenes

Spirofluoranthenes were prepared by Hoffmann and Tagmann (90) in 1949. 1,2,3,10b-Tetrahydrofluoranthene reacted readily with acrylonitrile to give 10b-(2'-cyanoethyl)-1,2,3,10b-tetrahydrofluoranthene (CVIII), which hydrolyzed to β-(1,2,3,10b-tetrahydrofluoranthenyl-10b)propionic acid (CIX). This was cyclized to the spiro compound (CX: R = R' = H).

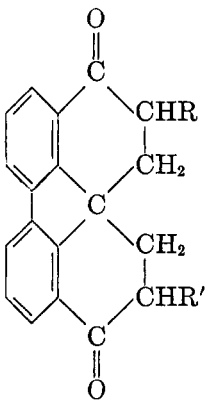


CVIII CIX CX

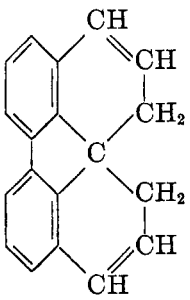
The methyl derivative (CX: R = CH_3; R' = H) was prepared, in a similar

manner, from α-methylacrylonitrole. The parent hydrocarbon may be obtained by Clemmensen reduction of CX (R = R′ = H) or of the diketone CXI (R = R′ = H), which was also prepared. Attempted dehydrogenation of the spirocyclic system, in the hope of obtaining the hydrocarbons CXII and CXIII, was unsuccessful.

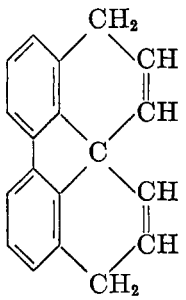
The unsaturated ketone CXIV was prepared by treatment of 1,10b-dihydro-1,1,3-trimethylfluoranthene with acrylonitrile, followed by intramolecular ring-closure (77, 90).



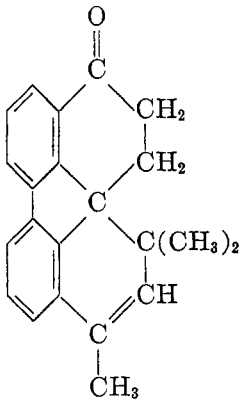
CXI



CXII



CXIII

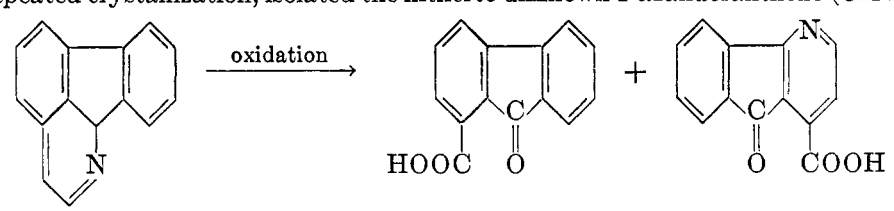


CXIV

The dimethyl derivative (CXI: R = R′ = CH_3) has been isolated by Tucker (176) by the Michael condensation of α-methylacrylonitrile with fluorene dissolved in 2-methoxyethanol in the presence of potassium hydroxide, to give 9,9-di(2′-cyanopropyl)fluorene, followed by hydrolysis to the dicarboxylic acid and cyclization to CXI (R = R′ = CH_3).

XII. Azafluoranthenes

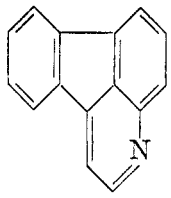
Until recently, the basic constituents of high-boiling fractions of coal tar, except acridine and phenanthridine, had not been carefully investigated. Kruber (125) investigated basic compounds in the fluoranthene–pyrene fraction and, by repeated crystallization, isolated the hitherto unknown 1-azafluoranthene (CXV).



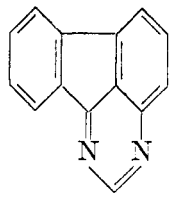
CXV CXVI CXVII

As a derivative of isoquinoline, this azafluoranthene is oxidized in two ways by potassium permanganate, giving either 1-fluorenonecarboxylic acid (CXVI) or 4-azafluorenone-1-carboxylic acid (CXVII), from which 4-azafluorenone is obtained by heating with alkali.

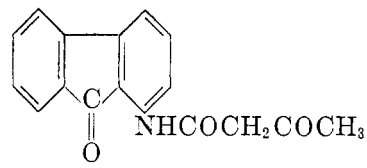
Derivatives of 3-azafluoranthene (CXVIII) and of 1,3-diazafluoranthene (CXIX) were prepared by Cook and Moffatt in 1950 (47). 1-Aminofluorenone



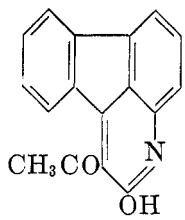
CXVIII



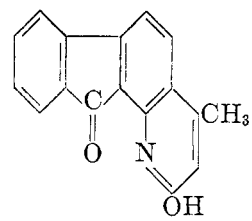
CXIX



CXX



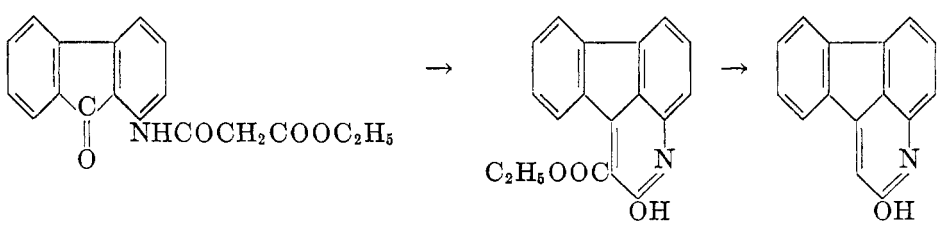
CXXI



CXXII

was condensed with ethyl acetoacetate to give 1-acetoacetamidofluorenone (CXX). This was cyclized in the presence of sodium methoxide in nitrobenzene to a compound which is probably 1-acetyl-2-hydroxy-3-azafluoranthene (CXXI), though ring-closure may have taken place in the alternative direction to form the isomeric lepidone derivative (CXXII). 1-Acetamidofluorenone could not be cyclized.

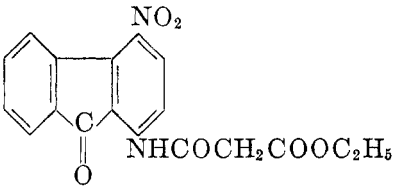
1-Aminofluorenone was, in addition, condensed with diethyl malonate to give CXXIII, which was cyclized with sodium methoxide in nitrobenzene at 140°C. to the ester of 2-hydroxy-3-azafluoranthene-1-carboxylic acid (CXXIV) and hence to CXXV. 2-Chloro-3-azafluoranthene was obtained by the action of phosphoryl chloride. Condensation of the chloro compound with ammonia and a variety of amines gave 3-azafluoranthenes with amino substituents in the 2-position.



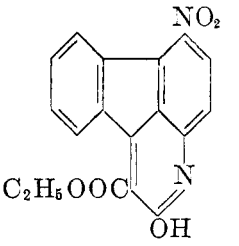
CXXIII CXXIV CXXV

Derivatives of 3-azafluoranthene with amino substituents in the fluorene part of the nucleus were prepared in a similar manner from 1-carbethoxyacetamido-4-nitrofluorenone (CXXVI). The product, 1-carbethoxy-2-hydroxy-6-nitro-3-azafluoranthene (CXXVII), on hydrolysis and decarboxylation yielded 2-hydroxy-6-nitro-3-azafluoranthene (CXXVIII), which was condensed with 3-di-

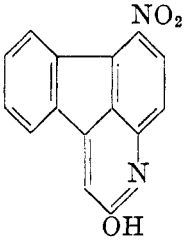
ethylaminopropylamine; the product was reduced to 6-amino-2-[γ-(diethylamino-propyl)amino]-3-azafluoranthene (CXXIX).



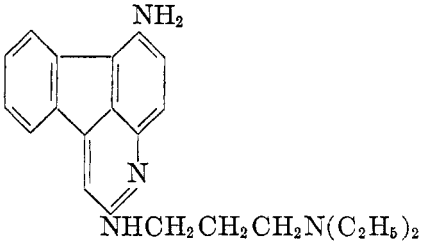
CXXVI



CXXVII

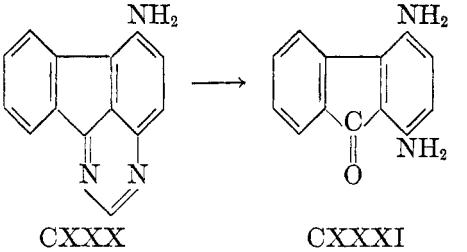


CXXVIII



CXXIX

Several derivatives of 1,3-diazafluoranthene were prepared (47) by methods similar to those employed for 3-azafluoranthenes. 2-Phenyl-1,3-diazafluoranthene was prepared by condensation of 1-aminofluorenone with phenyl cyanide (hydrogen chloride, 190°C.). The *p*-chlorophenyl and *p*-nitrophenyl derivatives were similarly prepared. 1,3-Diazafluoranthene itself was obtained in low yield by interaction of 1-aminofluorenone and boiling formamide. The 1,3-diazafluoranthene ring system was found to be susceptible to hydrolytic fission by mineral acids, hot dilute hydrochloric acid converting 6-amino-1,3-diazafluoranthene (CXX) to 1,4-diaminofluorenone.



CXXX CXXXI

None of the compounds examined showed any chemotherapeutic trypanocidal activity.

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