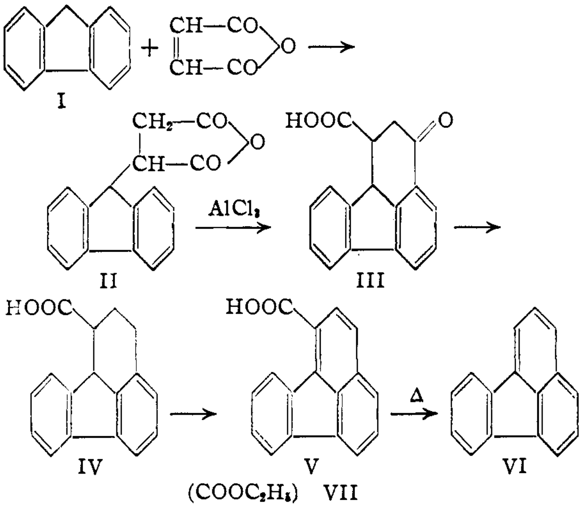
[FROM THE WEIZMANN INSTITUTE OF SCIENCE, REHOVOTH, ISRAEL]

Synthesis of Fluoranthene and its Derivatives

BY E. BERGMANN AND MILTON ORCHIN[1]

Despite the fact that fluoranthene is one of the major constituents of coal tar and therefore readily available, little is known of the geometry and fine structure of this very interesting molecule. As a matter of fact, it had been assigned an incorrect structure until as recently as 1929 when von Braun and Anton[2] established its structure (VI) by an unambiguous synthesis. Since then only two additional syntheses have been reported, one of which[3] gave fluoranthene in insignificant yield. Fluoranthene has been most readily prepared by the second of these methods, *viz.*, cyclodehydrogenation of 1-phenylnaphthalene[4] but the high temperatures essential for the success of this reaction prevent its extension to the preparation of derivatives of fluoranthene in which knowledge of the location of substituents is desirable.[4a] We wish to report here a synthesis of fluoranthene and 1-substituted fluoranthenes which is capable of wide variation. This work is part of a program designed to prepare certain substituted fluoranthenes which are required for a study of the fine structure of the parent hydrocarbon.[4b]

The initial reaction in the synthesis consisted of the known[5] Michael condensation between fluorene, I, and maleic anhydride to give the adduct, II.[6] The adduct was isolated by conversion to fluorenylsuccinic acid and separation of this from the neutral products. The di-acid was then reconverted to the anhydride with acetyl chloride. Cyclization of the anhydride gave the keto acid, III, which was isolated *via* the semicarbazone. After regeneration, III was reduced by the Clemmensen method to the acid IV. The tetrahydro acid, IV, was dehydrogenated easily with sulfur to fluoranthene-1-carboxylic acid, V. Decarboxylation of V gave fluoranthene, VI. Conversion of the acid, V, to the ester VII and Curtius degradation of the latter gave 1-aminofluoranthene, X. The structural relationship of X to 2-aminonaphthalene and to 4-aminofluorene makes X of interest in connection with potential carcinogenic activity.



(COOC$_2$H$_5$) VII
(CONHNH$_2$) VIII
(NHCOOC$_2$H$_5$) IX
(NH$_2$) X

Experimental[7]

9-Fluorenylsuccinic Acid.—A mixture of 8.3 g. of fluorene and 4.9 g. of maleic anhydride was heated in a round-bottom flask fitted with a condenser, for six hours at 190°. The mixture was cooled, digested with sodium carbonate solution, and filtered. The insoluble material (5.42 g.) was unchanged fluorene. Acidification of the filtrate gave 4.64 g. of acid, m. p. 167° with decomposition. After crystallization from dilute (about 20%) acetic acid, the di-acid melted at 186-187°. Calcd.: neut. equiv., 144. Found: neut. equiv., 141. When 61 g. of fluorene and 36 g. of maleic anhydride was heated in a sealed tube at 220° for six hours, 44.3 g. of adduct was obtained.

9-Fluorenylsuccinic Anhydride, II.—A solution of 10.0 g. of the di-acid in 50 cc. of dry ether and 15 cc. of acetyl chloride was refluxed for four hours. Most of the excess chloride and ether was distilled and the mixture taken to dryness in an atmosphere of nitrogen. The residue was taken up in ethyl acetate, the solution treated with norite and filtered. On concentration of the filtrate 7.0 g. of the anhydride, II, m. p. 167.8-168.6° was obtained; reported melting point,[5] 168°.

1-Carboxy-3-keto-1,2,3,10b-tetrahydrofluoranthene, III.—To a solution of 21.7 g. of the anhydride, II, in 200 cc. of nitrobenzene, there was added 23.6 g. of aluminum chloride all at once. The mixture was stirred and heated on the steam-bath for four hours and then decomposed with ice and hydrochloric acid. The precipitate was digested with sodium hydroxide and norite and filtered. The filtrate was acidified and the precipitate filtered and air dried. The dark green material was dissolved in 100 cc. of ethanol and 11.1 g. of semicarbazide hydrochloride and 13.6 of sodium acetate trihydrate in 100 cc. of water added. The aqueous-alcoholic solution was heated under reflux for two hours and the mixture left standing overnight. Filtration gave 15.1 g. of alcohol-insoluble material. This powder was heated with 25 cc. of water and 50 cc. of concentrated hydrochloric acid for five hours. The mixture was filtered and the insoluble material crystallized from acetic acid to give 7.93 g. of yellow crystals, m. p. 197-202°. A pure sample, crystallized from acetic acid, had a melting point of 208.6-210.0°. *Anal.* Calcd. for $C_{17}H_{12}O_3$: C, 77.3; H, 4.6; neut. equiv., 264. Found: C, 77.2; H, 4.7; neut. equiv., 265.

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[2] von Braun and Anton, *Ber.*, **62**, 145 (1929).

[3] Cook and Lawrence, *J. Chem. Soc.*, 1431 (1936).

[4] Orchin and Reggel, THIS JOURNAL, **69**, 505 (1947).

[4a] A recent article by Forrest and Lucker, *J. Chem. Soc.*, 1137 (1948), which appeared after our work was completed, also describes a new synthesis of fluoranthene and some of its methyl homologs.

[4b] For another method, see E. Bergmann, *Nature*, **161**, 889 (1948).

[5] Alder, Pshorr and Vagt, *Ber.*, **75**, 1511 (1942).

[6] For other Michael condensations with fluorene, see Pinck and Hilbert, THIS JOURNAL, **68**, 2014 (1946).

[7] All melting points corrected. Analyses are microanalyses.

1-Carboxy-1,2,3,10b-tetrahydrofluoranthene, IV.—A mixture of 50 g. of zinc, 25 cc. of water, 50 cc. of concentrated hydrochloric acid, 35 cc. of toluene, 5 cc. of acetic acid and 2.64 g. of the keto acid III was refluxed four hours, 25 cc. more of concentrated hydrochloric acid added and refluxing continued twenty-nine hours longer with two more additions of fresh hydrochloric acid. The toluene layer was separated, washed successively with acid, water and saturated sodium chloride solution. The toluene solution was filtered and the filtrate extracted with sodium carbonate solution. The alkaline extract was acidified and the precipitate filtered and dried and crystallized from benzene to give 1.89 g. of pure IV, m. p. 166.8-167.4° as a first crop and 0.42 g. of less pure material, m. p. 154-159°. *Anal.* Calcd. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.9; H, 5.6.

Fluoranthene-1-carboxylic Acid, V.—A mixture of 0.60 g. of IV and 0.154 g. of sulfur was heated at 240° for twenty-five minutes. The melt which solidified on cooling was dissolved in benzene and the benzene solution concentrated to give 0.50 g. of V, yellow needles, m. p. 227-230°. A sample for analysis was crystallized from acetic acid. *Anal.* Calcd. for $C_{17}H_{10}O_2$: C, 82.9; H, 4.1. Found: C, 82.9; H, 3.9

Fluoranthene, VI.—About 20 mg. of V in 2 cc. of dimethylquinoline was refluxed with a pinch of copper powder for about ten minutes. The cooled mixture was taken up in benzene and the benzene solution extracted with acid. The benzene layer was dried and evaporated. The residue was crystallized from alcohol and gave fluoranthene, m. p. 110.4-111.2°; mixed melting point with an authentic sample gave no depression.

Ethyl Fluoranthene-1-carboxylate, VII.—The acid V (1.63 g.) was esterified with ethanol and hydrogen chloride in the usual way. Crystallization from ethanol gave 1.48 g. of the ester VII as tan needles, m. p. 103.2-104.8°. *Anal.* Calcd. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.1. Found: C, 83.1; H, 5.2. The trinitrofluorenone complex was obtained in the usual way[8] and recrystallized from benzene-ethanol to give yellow silky needles, m. p. 140.0-140.4°. *Anal.* Calcd. for $C_{32}H_{19}O_9N_3$: N, 8.0. Found: N, 7.8.

Hydrazide of Fluoranthene-1-carboxylic Acid, VIII.—A mixture of 1.50 g. of the ester VII, 25 cc. of absolute ethanol and 0.7 cc. of hydrazine hydrate was refluxed for seven hours. The solution was concentrated to about 10 cc. and 0.5 cc. more of hydrazine added and refluxing continued an additional sixteen hours. After cooling, the precipitate was filtered to give 1.44 g. of material, m. p. 109-185°. This was recrystallized from benzene to give 0.28 g. of material, m. p. 220-223°. The mother liquor on concentration gave an obvious mixture. It was redissolved in ethanol and the solution treated for fifty hours at reflux with 1 cc. of hydrazine hydrate. After separation of a first crop of hydrazide, the mother liquor was treated once more with hydrazine hydrate. In all, 1.4 g. of the hydrazide, m. p. 224.5-225.5°, was obtained. *Anal.* Calcd. for $C_{17}H_{22}ON_2$: C, 78.4; H, 4.7; N, 10.8. Found: C, 78.2; H, 4.2; N, 11.9. It would probably have been simpler to prepare the hydrazide by using a large excess of hydrazine hydrate originally.

1-Fluoranthenyl Urethan, IX.—To a solution of 1.00 g. of the hydrazide, VIII, in 25 cc. of acetic acid there was added 1 cc. of concentrated hydrochloric acid. The suspension was cooled to 0° with stirring and 0.9 g. of sodium nitrite in 8 cc. of water was added dropwise in the cold with stirring. The mixture was stirred at 0° for one hour, then allowed to come to room temperature. The mixture was diluted with water and filtered. The deep yellow azide was dried in a vacuum desiccator overnight. It melted at 101° with decomposition. It was placed in a flask with 75 cc. absolute ethanol and the mixture warmed gently, then refluxed for three hours. Concentration of the solution gave 0.97 g. of urethan as tan, almost colorless needles, m. p. 171.0-171.8°. *Anal.* Calcd. for $C_{19}H_{15}O_2N$: C, 78.8; H, 5.2. Found: C, 78.6; H, 4.8.

1-Aminofluoranthene, X.—A mixture of 0.82 of the urethan IX, 15 cc. of concentrated hydrochloric acid and 10 cc. of acetic acid was placed in a sealed tube and heated at about 140° for four hours. The tube was cooled in liquid nitrogen and opened. The precipitate was filtered and washed well with water and dried. It weighed 0.70 g. and melted at 234-240°. It was placed in a separatory funnel containing ether-benzene and 10% sodium hydroxide solution. After shaking for about half an hour, the solid phase disappeared. The organic layer was washed well with water and dried. It fluoresced strongly in ordinary light. On concentration, the solution deposited 0.53 g. of yellow needles of X, m. p. 133.0-134.0°. *Anal.* Calcd. for $C_{16}H_{11}N$: N, 6.5. Found: N, 7.3. The trinitrofluorenone complex[8] crystallized from benzene as dark brown crystals, m. p. 254-255° (uncor.). *Anal.* Calcd. for $C_{29}H_{16}N_4O_7$: N, 10.4. Found: N, 11.2.

Summary

A new general synthesis of fluoranthene and its derivatives is reported. The anhydride resulting from the condensation of fluorene and maleic anhydride is cyclized to 1-carboxy-3-keto-1,2,3,10b-tetrahydrofluoranthene which is then reduced and dehydrogenated to fluoranthene-1-carboxylic acid. The carboxyl group is esterified and Curtius degradation of the ester gives 1-aminofluoranthene.

THE DANIEL SIEFF INSTITUTE
REHOVOTH, ISRAEL
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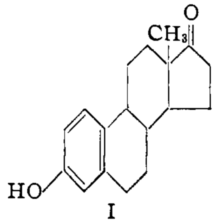
[8] Orchin, Reggel and Woolfolk, THIS JOURNAL, **69**, 1225 (1947).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UPJOHN COMPANY]

Synthetic Sterols. II.[1] An Isomer Technique

BY JOHN A. HOGG

As the first of several model studies directed toward a scheme for the total synthesis[2] of estrone (I), the preparation of 1,2-dimethyl-7-methoxy-1,2,3,4,9,10-hexahydrophenanthrene-2-carboxylic acid (IIIα, β) was described in the first paper of this series.[1]



I

The structure assigned to estrone (I) is capable of sixteen stereochemical variations (eight diastere-

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[1] Previous paper: Hogg, THIS JOURNAL, **70**, 161 (1948).

[2] The total synthesis of estrone was recently achieved by Anner and Miescher [see *Experientia*, **3**, 279 (1947), and *Helv. Chim. Acta*, **31**, 2173 (1948)] through a unique variation of the splendid scheme used by Bachmann, Kushner and Stevenson, THIS JOURNAL, **64**, 974 (1942), in their synthesis of estrone-a, an isomer of estrone.