[Contribution from the Weizmann Institute of Science]

SYNTHETIC EXPERIMENTS IN THE FLUORANTHENE SERIES

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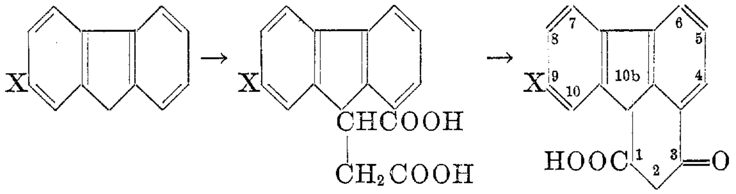
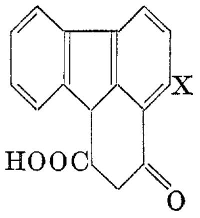
Received July 16, 1951

Bergmann and Orchin (1) have developed a synthesis of fluoranthene based on the cyclodehydration of α-(9-fluorenyl)succinic acid (II, X = H), which in turn is available by a kind of Michael condensation between fluorene and maleic anhydride (2). It seemed interesting to investigate the course this sequence of reactions would take when carried out with an asymmetrically substituted fluorene, *e.g.*, 2-bromofluorene (I, X = Br).



I II III



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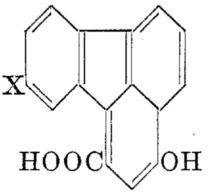
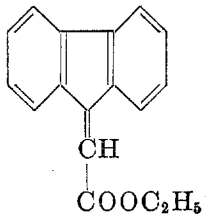


V



VI

The realization of the aim of this investigation was made difficult by the low yield (21%) obtained in the condensation of 2-bromofluorene with maleic anhydride (to II, X = Br). However, it was found that the cyclization of (II, X = Br) led, in variable ratio, to two isomeric products, $C_{17}H_{11}BrO_3$ (m.p. 241–242°, and 230–231°, respectively), which gave both the same ultraviolet absorption spectrum (Fig. 1) and showed the presence of a carboxylic hydroxyl in the infrared spectrum (Fig. 2). Equally, both showed (suspended in paraffin oil) the absorption at 1660 cm^{-1}, which is characteristic for an aromatic ketone (III, IV). It can be assumed that the isomer formed in smaller quantities corresponds to formula (IV), as it is likely that the bromine atom in the 2-position will exert a retarding influence on the cyclization reaction at C_1.

The ultraviolet spectra of III and IV consist of a double band at 2600 and 2730 Å, and of another band at 3270 Å. The first two represent the absorption of the fluorene, the last corresponds to the substituted acetophenone system. Indeed, fluorene shows the following bands (3): 2450, 2620, 2710, 2890, 2930, 3000 Å, whilst acetophenone (4) absorbs at 2415, 2785 and 3186 Å.

In one of the cyclization experiments, a much higher-melting material was isolated as by-product, which was yellow, but still contained the three oxygen atoms; it formed a (yellow) mono-methyl derivative with diazomethane. The ultraviolet absorption spectrum of the latter (Fig. 3) again shows the fluorene bands, but also a band at 3090 Å and a very intense one in the region between 3940 and 3860 Å. It is assumed that this substance has formula (V) of a 3-hydroxy-9-bromofluoranthene-1-carboxylic acid, *i.e.*, is a dehydrogenation product of III. (Obviously, the formula corresponding to IV is not excluded.) The spectrum of V is, indeed, fairly similar to that of fluoranthene (5) (bands at 2360, 2620, 2765, 2820, 2870, 3090, 3220, 3420, 3590 Å); the longest band is shifted towards the red as it would be expected of a hydroxylated fluoranthene. Further-

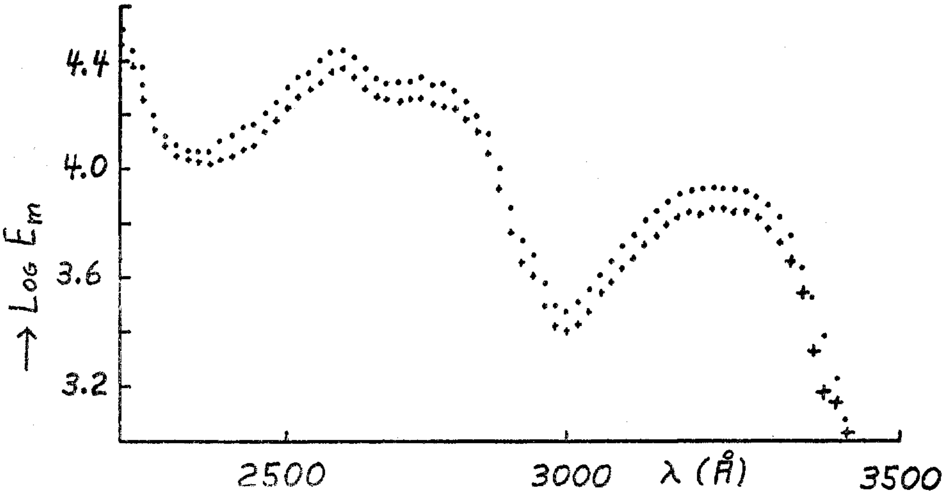


FIGURE 1. ULTRAVIOLET SPECTRA OF THE KETO-ACIDS (IIIa) (........) AND (IIIb) (++++) IN DIOXANE SOLUTION.

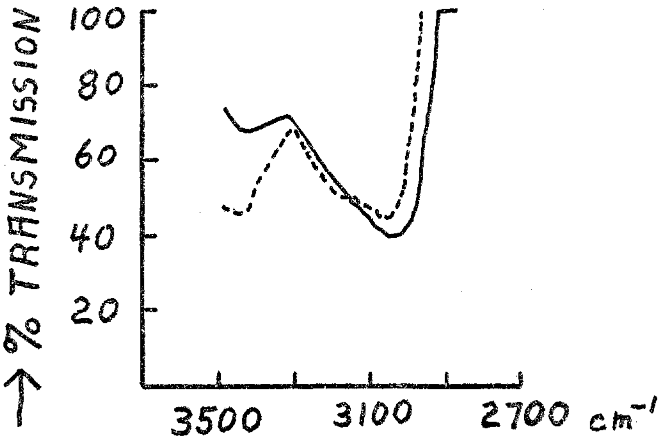


FIGURE 2. INFRARED SPECTRUM (hydroxyl region) OF THE KETO-ACIDS (IIIa) and (IIIb); 10% dioxane solutions; cell thickness 0.1 mm.

more, the analogously constituted ethyl fluorenylideneacetate (VI) has a similar band at 3200 and a weak one around 3800 Å (Fig. 3).

The infrared spectrum of the yellow methyl derivative (0.040 g. in 1 cc. of chloroform; cell thickness, 0.1 mm.) supports formula V. A very intense peak has been observed at 1714 cm^{-1}, about the wave-length characteristic of an α,β-unsaturated carboxylic acid or ester (7). As the substance does not show the infrared absorption of a phenolic hydroxyl (nor of a carbonyl group), the, not wholly satisfactory, conclusion has to be drawn that diazomethane has produced the methylether acid, corresponding to V. Indeed, in the region, in which phenol methylethers absorb, two bands have been observed (at 1104 and 1186 cm^{-1}, respectively).

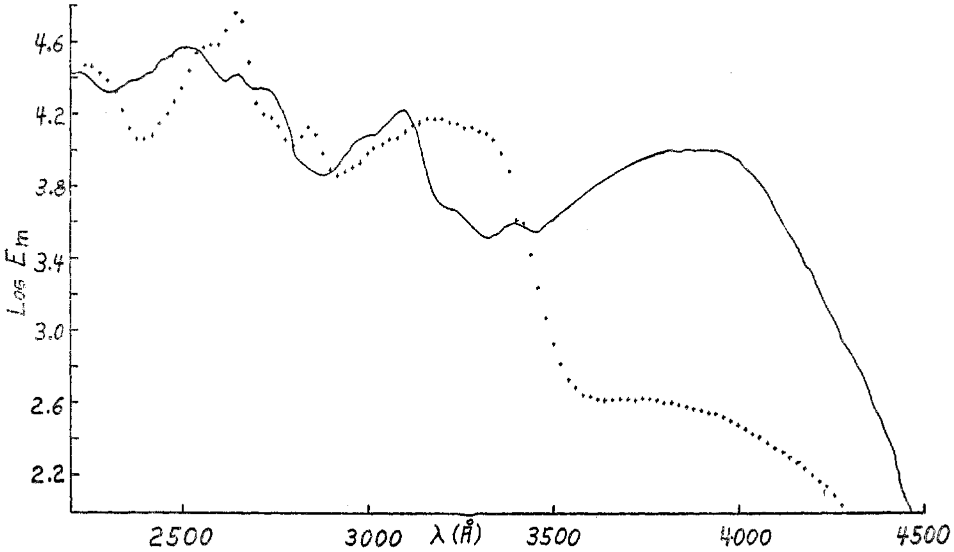
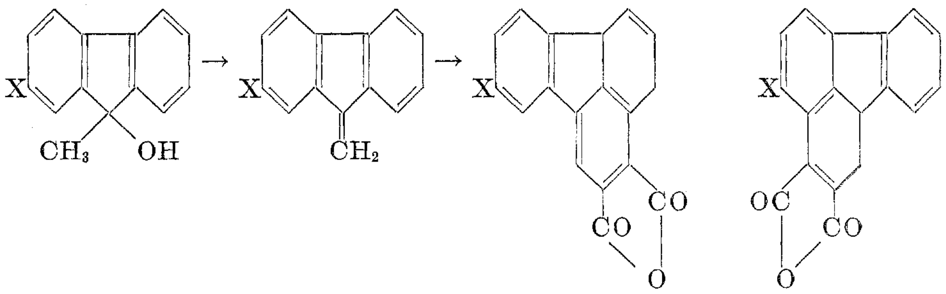


FIGURE 3. ULTRAVIOLET SPECTRA OF THE KETO METHYL ESTER (V) (————) AND ETHYL FLUORENYLIDENE ACETATE (VI) (++++), IN DIOXANE SOLUTION.

A second method for the synthesis of fluoranthene derivatives which has been discovered recently (8), consists in the interaction of maleic anhydride with dibenzofulvene (VIII, X = H), which is employed *in statu nascendi* [methylfluorenol (VII, X = H) plus acetic anhydride].



VII VIII IXa IXb

When this method was applied to 2-bromo-9-methyl-9-fluorenol (VII, X = Br), only one adduct of formula IX (a or b) could be isolated, though in low yield; it could be converted into its well defined dimethyl ester. Decarboxylation proved excessively difficult; under the conditions at which it actually took place (barium hydroxide and copper above 300°), the bromine atom also was eliminated and fluoranthene was obtained.

Acknowledgement: The ultraviolet spectra have been determined by Dr. Y. Hirshberg, the infrared spectra by Dr. S. Pinchas.

EXPERIMENTAL PART

α-(2-Bromo-9-fluorenyl)succinic acid (II, X = Br). A mixture of 36.4 g. of 2-bromofluorene (I, X = Br) (9) (b.p. 158–164°/20 mm., m.p. 114°) and 13 g. of maleic anhydride was heated for eight hours at 245–250° in a glass-lined autoclave. The reaction product was taken up in benzene and, after drying, subjected to fractional distillation. The desired fraction (195–210°/0.1 mm.) (20 g.) was a glassy mass which was recrystallized from 75% acetic acid and had m.p. 217–218°. Yield, 11.5 g. (21%).

Anal. Calc'd for $C_{17}H_{13}BrO_4$: C, 56.5; H, 3.6; Br, 22.2.
Found: C, 56.6; H, 3.7; Br, 22.1.

9-Bromo-3-keto-1,2,3,10b-tetrahydrofluoranthene-1-carboxylic acid (III) *and 4-bromo-3-keto-1,2,3,10b-tetrahydrofluoranthene-1-carboxylic acid* (IV). The preceding acid (5 g.) was converted into its chloride by refluxing it for 4 hours with acetyl chloride (20 cc.) and anhydrous ether (100 cc.). The volatile products were removed *in vacuo* and the residue was digested with some ether and brought to dryness again. The crude chloride (m.p. 162°) was dissolved in 50 cc. of nitrobenzene and, after addition of 7 g. of aluminum chloride, heated on the steam-bath for 4 hours with stirring. From the green mass, the nitrobenzene was removed with steam and the residue treated with hydrochloric acid and re-precipitated from 15% sodium hydroxide solution with acid. Digestion of the product with ether gave a white crystalline powder (1.2 g.), from which by recrystallization from 75% acetic acid, a product of m.p. 241–242° was obtained.

Anal. Calc'd for $C_{17}H_{11}BrO_3$: Br, 23.4. Found: Br, 23.2.

From the mother-liquor, an isomer was isolated by concentration, which after repeated crystallization from the same solvent, had m.p. 230–231°. The mixture with the product of m.p. 241–242° melted at 217–218°.

Anal. Calc'd for $C_{17}H_{11}BrO_3$: C, 59.5; H, 3.1; Br, 23.4.
Found: C, 59.5; H, 3.4; Br, 23.0.

The ratio in which the two isomerides were formed was not always constant; on an average, it was 1:4.

In one experiment, a much higher-melting greenish-yellow product (m.p. 305°, after recrystallization from 80% acetic acid) was isolated instead of the compound of m.p. 241–242°, in addition to the much more easily soluble isomeride of m.p. 230–231°. As pointed out in the introductory paragraphs, this substance is probably *9-bromo-3-hydroxyfluoranthene-1-carboxylic acid* (V). It was characterized as the *methyl derivative*, which was obtained with ethereal diazomethane in the presence of methanol; from benzene as yellow crystals, m.p. 170–171°.

Anal. Calc'd for $C_{18}H_{11}BrO_3$: Br, 22.4; OCH_3, 8.7.
Found: Br, 21.9; 22.1; OCH_3, 8.6.

9-Bromo-1,2,3,10b-tetrahydrofluoranthene-1-carboxylic acid. The substance (III, m.p. 241–242°) was reduced by the method of Wolff-Kishner and gave a crystalline product which after recrystallization from a little alcohol melted at 209°.

Anal. Calc'd for $C_{17}H_{13}BrO_2$: C, 62.0; H, 4.0; Br, 24.3.
Found: C, 62.3; H, 4.0; Br, 24.0.

2-Bromo-9-methyl-9-fluorenol (VII, X = Br). A solution of 13 g. of 2-bromofluorenone (m.p. 142–143°) (10) in dry benzene was added to the Grignard solution from 2.6 g. of magnesium and 14 g. of methyl iodide. After refluxing for 3 hours, the product was decomposed with ice and dilute sulfuric acid and the organic layer separated, dried, and concentrated. From petroleum ether colorless plates, m.p. 148–149°; yield, 10 g.

Anal. Calc'd for $C_{14}H_{11}BrO$: Br, 29.1. Found: Br, 29.7.

9-Bromofluoranthene-2,3-dicarboxylic acid anhydride (*IXa* (*?*)). A mixture of 5.6 g. of the carbinol (VII, X = Br), 10 g. of freshly distilled maleic anhydride, and 40 cc. of acetic anhydride was refluxed for 2 hours. After 12 hours at room temperature, a brick-colored powder had separated, which was recrystallized from acetic anhydride. Orange-colored needles, m.p. 282°; yield 160 mg. From the mother-liquor, nothing definite could be isolated.

Anal. Calc'd for $C_{18}H_7BrO_3$: C, 61.5; H, 2.0; Br, 22.8.
Found: C, 60.0; H, 2.0; Br, 22.3; 22.3.

The corresponding dimethyl ester was obtained by treatment of the suspension of the foregoing anhydride in methanol, with an ethereal diazomethane solution. From a mixture of acetone and methyl alcohol, yellow needles, m.p. 165–166°.

Anal. Calc'd for $C_{20}H_{13}BrO_4$: OCH_3, 15.6; Found: OCH_3, 15.2.

Attempt to decarboxylate IXa. The anhydride (300 mg.) was dissolved in dioxane and after the addition of 1 g. of barium hydroxide the mixture was evaporated to dryness. Copper powder (0.5 g.) was added and the well-mixed product was heated at 300–320° and finally (under 25 mm. pressure) at 340–350°. Yellowish crystals sublimed during the latter operation. Resublimation gave the slightly yellowish platelets of *fluoranthene*, which was identified by its m.p. and mixture m.p. (110°).

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