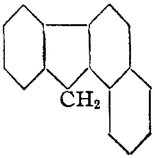
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

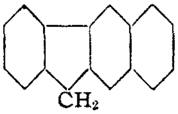
A Synthesis of 2,3-Benzofluorene

BY C. FREDERICK KOELSCH

Since degradation experiments with the hydrocarbon obtained by the action of sodium on 1-diphenylene-3-phenylindene[1] have given results of no value as a structure proof, the problem is being attacked by synthesis. One possible synthesis requires 1,2-benzofluorene (I) as an intermediate. The present paper describes a synthesis which might have led to this hydrocarbon, but which gives its isomer, 2,3-benzofluorene (II), instead.

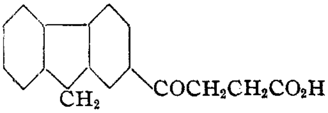


I

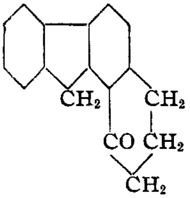


II

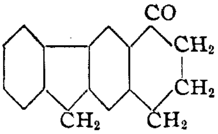
Fluorene and succinic anhydride condense to β-2-fluoroylpropionic acid (III), the orientation of which is shown by oxidation. Reduction of this keto acid gives γ-fluorylbutyric acid. Now although cyclization of this acid by treating its chloride with aluminum chloride may lead to (IV) or (V), actually only one substance is formed.



III



IV



V

The structure of this product is not clearly predictable, since strictly analogous cases have not been investigated previously. γ-2-Naphthylbutyric acid undergoes only angular condensation to form (VI),[2,3] but such a result is occasioned by the known greater reactivity of the α as compared with the β position in the naphthalene nucleus. The more closely related γ-2-tetralylbutyric acid behaves peculiarly, in that it is cyclized by sulfuric acid exclusively to the linear product (VII),[4] while thermal decomposition of its chloride gives a mixture of about equal parts of the linear (VII) and the angular (VIII) products.[5]

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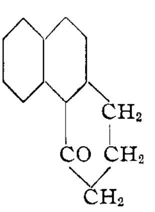
(1) Koelsch, THIS JOURNAL, **55**, 3398 (1933).

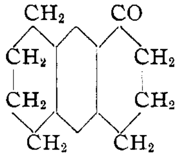
(2) Schroeter, Mueller and Huang, *Ber.*, **62**, 645 (1929).

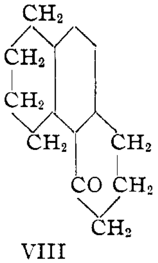
(3) Haworth, *J. Chem. Soc.*, 1126 (1932).

(4) Krollpfeiffer and Schäfer, *Ber.*, **56**, 620 (1923).

(5) Schroeter, *ibid.*, **57**, 2003 (1924).


VI


VII


VIII

The nitration of 2-acetylaminofluorene, which gives the 3-nitro compound[6] and not the 1-nitro compound as was formerly believed,[7] is quite significant as an indication of the greater reactivity of the 3-position in the fluorene nucleus substituted in the 2-position by an *o,p*-directing group.

The further transformations of the cyclization product obtained in the present investigation show it to be the linear (2,3-) compound (V). On reduction it gives tetrahydrobenzofluorene, and this is dehydrogenated to the known 2,3-benzofluorene (II).

Experimental

β-2-Fluoroylpropionic Acid.—To a stirred suspension of 50 g. of succinic anhydride and 85 g. of fluorene in 500 ml. of benzene is added 150 g. of aluminum chloride in portions. The mixture is then heated for one hour on a water-bath with stirring. The reaction mixture is hydrolyzed in the usual way, and the benzene is steam distilled. The solid acid remaining is best purified through its sodium salt, which is easily soluble in hot water and difficultly soluble in cold water. The free acid, obtained in yields of 75–86% after crystallization from acetic acid, forms needles that melt at 210–212°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.6; H, 5.3. Found: C, 76.5; H, 5.3.

On boiling the keto acid (1 g.) for two hours in acetic acid with 2 g. of sodium dichromate, there is obtained *β-fluorenonoylpropionic acid* which crystallizes from acetic acid in yellow plates that melt at 230–234° with previous darkening.

Anal. Calcd. for $C_{17}H_{12}O_4$: C, 72.8; H, 4.3. Found: C, 72.6; H, 4.6.

Fluoroylpropionic acid dissolved in dilute soda solution is rapidly and completely oxidized on boiling with the calculated amount of potassium permanganate to fluorenone-2-carboxylic acid, yellow needles from acetic acid that do not melt at 295° (literature,[8] >275°). This acid, with thionyl chloride and methanol, gives the methyl ester, yellow needles from methanol that melt at 177–181° (literature,[9] 181°).

Methyl β-2-fluoroylpropionate obtained from the keto acid (5 g.), methanol (75 ml.), and concd. sulfuric acid (5 ml.) by refluxing for four hours, forms white plates from methanol that melt at 111–112°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.2; H, 5.7. Found: C, 77.2; H, 5.8.

The methyl ester oxime, recrystallized from benzene–ligroin, forms needles that melt at 129–130°.

Anal. Calcd. for $C_{18}H_{17}O_3N$: C, 73.2; H, 5.8. Found: C, 73.5; H, 5.8.

γ-Fluorylbutyric Acid.—The usual Clemmensen method does not affect the keto

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(6) Eckert and Langecker, *J. prakt. Chem.*, [2] **118**, 263 (1928).

(7) Diels, *Ber.*, **35**, 3285 (1902).

(8) Bamberger and Hooker, *Ann.*, **229**, 158 (1885).

(9) Fortner, *Monatsh.*, **25**, 451 (1904).

acid, but by carrying out the reduction in aqueous alcohol, nearly quantitative yields are obtained.

A mixture of 90 g. of fluoroylpropionic acid, 450 ml. of alcohol, 450 ml. of concd. hydrochloric acid and 180 g. of amalgamated zinc is boiled for one hour, an additional 450 ml. of concd. hydrochloric acid is added, and boiling is continued for eight hours. The mixture is cooled, the solid is separated and boiled with one liter of 5% sodium hydroxide until all of the organic matter is dissolved. The solution is filtered and acidified, giving 85 g. of a product that melts at 142–146°. Recrystallization of a portion from acetic acid and then from benzene–ligroin gives white plates that melt at 151–151.5°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.9; H, 6.4. Found: C, 80.6; H, 6.5.

Ketotetrahydrobenzofluorene.—Distillation of γ-fluorylbutyric acid with phosphorus pentachloride,[2] or heating with 85% sulfuric acid[3] does not cause ring closure. The acid reacts with thionyl chloride to give a black tar which does not have the properties of an acid chloride.

Ring closure is satisfactorily effected as follows: 25 g. of fluorylbutyric acid is refluxed in benzene (250 ml.) with 21 g. of phosphorus pentachloride until the evolution of hydrogen chloride ceases. The solution is cooled and 20 g. of aluminum chloride is added with stirring. After refluxing for thirty minutes, the mixture is poured onto ice and hydrochloric acid, and the benzene is steam distilled. The solid product is dissolved in acetic acid (300 ml.) and boiled with charcoal. The addition of water precipitates 18 g. of light tan colored plates, m. p. 135–140°. Distillation at 20 mm. followed by crystallization from acetic acid is carried out with practically no loss; the ketone forms white plates that melt at 148–149°. It may be distilled without decomposition at atmospheric pressure.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.2; H, 6.0. Found: C, 86.9; H, 6.1.

The semicarbazone, crystallized from acetic acid, forms needles which become brown at 250°, but do not melt at 290°.

Anal. Calcd. for $C_{18}H_{17}ON_3 + CH_3COOH$: C, 68.3; H, 6.0. Found: C, 68.0; H, 6.1.

Tetrahydrobenzofluorene.—Ketotetrahydrobenzofluorene is reduced readily by the usual Clemmensen procedure, four hours boiling sufficing for complete reduction. The crude solid obtained, which is contaminated with a little dimolecular reduction product, is distilled under reduced pressure and crystallized from acetic acid; yield, 60–70%. The hydrocarbon forms white plates that melt at 129°.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.7; H, 7.3. Found: C, 92.8; H, 7.6.

The picrate forms orange-red needles from absolute alcohol that melt at 123–124°.

2,3-Benzofluorene.—Tetrahydrobenzofluorene (3.2 g.) is heated at 250–275° with sulfur (1.6 g.) until the evolution of hydrogen sulfide ceases (about one hour). The violet melt, from which no crystalline substance can be obtained directly, is distilled under reduced pressure. The deeply colored distillate is crystallized from toluene, giving 0.4 g. of benzofluorene that melts at 204–206° (literature,[10] 208°). On oxidation with sodium dichromate in acetic acid, this hydrocarbon gives 2,3-benzofluorenone, yellow needles that melt at 146–148° (literature,[10] 152°).

The analyses reported in this paper were carried out by Mr. P. O. Tawney.

Summary

A synthesis of 2,3-benzofluorene starting with fluorene has been described.

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[10] Thiele and Wanscheidt, *Ann.*, **376**, 276 (1910).