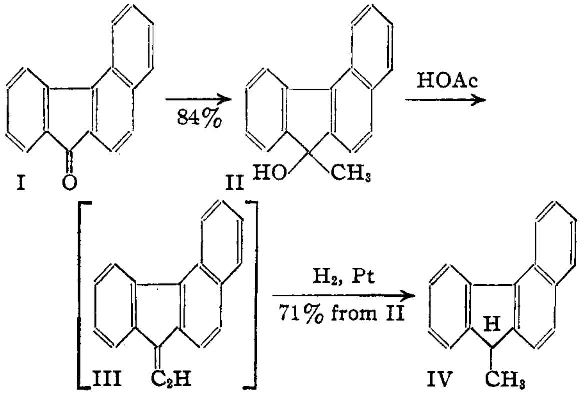
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

9-Methyl-3,4-benzfluorene

BY LOUIS F. FIESER AND LLOYD M. JOSHEL[1]

Because of the marked carcinogenic activity of 10-methyl-1,2-benzanthracene,[2] it seemed of interest to synthesize and test the somewhat analogous 9-methyl-3,4-benzfluorene (IV). 3,4-Benzfluorenone-9 (I) was prepared from 1-phenyl-2,3-naphthalic anhydride by the method of Schaarschmidt[3] but with the introduction of modifications which raised the over-all yield to 83%. Condensation of the ketone with methylmagnesium chloride gave the crystalline carbinol II in good yield, and it was found that this substance is readily dehydrated by short boiling in glacial acetic acid solution. On attempting to isolate the 9-methylene compound III only polymeric material was obtained, for the hydrocarbon appears to be a labile substance resembling 9-methylenefluorene (dibenzofulvene).[4] By heating the carbinol in acetic acid and shaking the resulting solution with hydrogen and Adams catalyst it was possible to obtain the desired hydrocarbon IV without difficulty.



Experimental Part[5]

3,4-Benz-9-fluorenone-1-carboxylic acid[3] was prepared by adding 100 g. of powdered aluminum chloride rapidly (less than five minutes) to a stirred suspension of 91.7 g. of 1-phenyl-2,3-naphthalic anhydride in 500 cc. of dry benzene, refluxing for two hours, and decomposing the cooled mixture with 200 cc. of 20% hydrochloric acid. The solvent was steam distilled and the scarlet red precipitate was washed with hot dilute hydrochloric acid and with hot water, affording 91 g. (99%) of material sintering at 293° and melting at 295–296°. Treatment of the anhydride with hydrogen fluoride at room temperature for twenty-four hours resulted in only partial conversion to the fluorenone derivative.

For decarboxylation to **3,4-benzfluorenone-9** the acid (20 g.) was heated with basic copper carbonate (0.5 g.) in a bath at 310–320°. As soon as the acid melted carbon dioxide was evolved vigorously and the reaction was over in about five minutes. The product was distilled at the pressure of the water pump and crystallized from acetone, giving 13.1 g. of the ketone in the form of orange prisms, m. p. 159–160.5°, and 1.0 g., m. p. 158–160° (84%).

9-Methyl-3,4-benzfluorenol-9 (II).—A solution of 5 g. of the ketone in benzene was treated with excess methylmagnesium chloride in ether and after refluxing for two hours the mixture was decomposed with 25% ammonium chloride solution. The organic layer was washed, dried, and evaporated and the product then crystallized from ether–ligroin in small, colorless needles, m. p. 116–118°; yield 4.5 g. (84%). This material was sufficiently pure for the subsequent steps. A sample recrystallized for analysis melted at 117.8–118.6°.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.72; H, 6.01.

Dehydration.—A solution of the crude carbinol from 1 g. of ketone in 10 cc. of acetic acid was refluxed for one hour, diluted with water and extracted with benzene. Evaporation of the dried solution left an oily residue which when rubbed with alcohol gave an amorphous, almost colorless solid which sintered and darkened at about 200° and completely melted to a deep red liquid at 275–280°; yield 0.7 g. (71%). A similar polymer resulted on distillation of the crude carbinol with a crystal of iodine, followed by passage of a benzene solution of the distillate through a tower of alumina.

Anal. Calcd. for $(C_{18}H_{12})_x$: C, 94.70; H, 5.30. Found: C, 94.40; H, 5.59.

9-Methyl-3,4-benzfluorene (IV).—A solution of 0.60 g. of the carbinol in 25 cc. of acetic acid was refluxed for one hour, cooled, and at once transferred to a hydrogenation flask and shaken with 25 mg. of Adams catalyst and hydrogen. The absorption of one mole of gas was complete in twenty minutes. The product was collected and distilled in vacuum, and crystallization from benzene–ethanol afforded 0.4 g. (71%) of light yellow blades, m. p. 80–81° (a little polymeric material was removed by filtration of the solution). Recrystallization gave material melting constantly at 80.8–82.0°. The color was not removed by treatment with Norite or by passage through a tower of alumina.

Anal. Calcd. for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.63; H, 6.27.

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[1] Fellow of the Finney-Howell Research Foundation.

[2] For summary, see Fieser, *Am. J. Cancer*, **34**, 37 (1937).

[3] Schaarschmidt, *Ber.*, **48**, 1826 (1915); **49**, 1444 (1916); Schaarschmidt and Georgeocopol, *ibid.*, **51**, 1082 (1918).

[4] Sieglitz and Jassoy, *ibid.*, **55**, 2032 (1922); Wieland, Reindel and Ferrer, *ibid.*, **55**, 3313 (1922); Wieland and Probst, *Ann.*, **530**, 274 (1937).

[5] All melting points are corrected. Microanalyses by Lyon Southworth.

In a larger run using a more concentrated solution the yield was poorer and more polymer was encountered. In another experiment the preliminary refluxing was omitted and the solution of the carbinol in acetic acid was shaken with catalyst and hydrogen in a vessel equipped with a sealed-in steam coil. No polymer was formed, but the yield of saturated hydrocarbon was lower.

The **picrate** crystallized from ethanol as reddish-orange needles, m. p. 128–128.5°, with slight previous sintering.

Anal. Calcd. for $C_{24}H_{17}O_7N_3$: N, 9.15. Found: N, 8.72.

Summary

9-Methyl-3,4-benzfluorene has been synthesized for comparison with the actively carcinogenic 10-methyl-1,2-benzanthracene.

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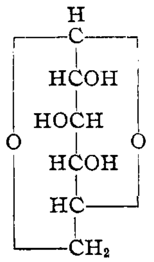
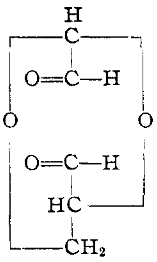
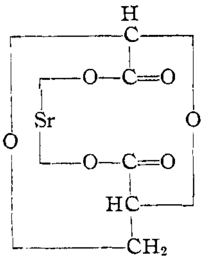
The Cleavage of the Carbon Chain of Levoglucosan by Oxidation with Periodic Acid[1]

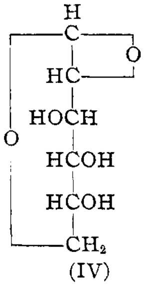
BY ERNEST L. JACKSON AND C. S. HUDSON[1]

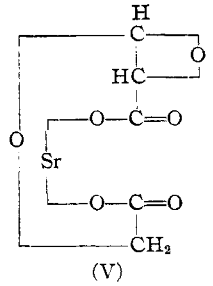
The structure of levoglucosan (I) has been established by methylation methods[2] and by its relationship to the structure of β-methylglucopyranoside.[3] A compound having this structure should be oxidized by periodic acid to produce the dialdehyde (II).


(I)
Levoglucosan


(II)
L′-Oxy-D-methylene-diglycolic aldehyde[4]


(III)
Strontium L′-oxy-D-methylene-diglycolate


(IV)


(V)

The oxidation of levoglucosan with periodic acid or sodium metaperiodate yields a sirupy product which is doubtless L′-oxy-D-methylene-diglycolic aldehyde (II). Oxidation of this product by bromine water kept neutral with strontium carbonate produces in good yield a crystalline strontium salt of a dibasic acid and, under the conditions employed, smaller amounts of strontium oxalate and strontium D-glycerate. The strontium salt of the dibasic acid was proved to be strontium L′-oxy-D-methylene-diglycolate (III) by oxidizing it with bromine water in the presence of strontium carbonate to produce strontium oxalate and strontium D-glycerate. The structure of the dialdehyde (II) follows from that of the strontium salt (III). The formation of strontium oxalate and strontium D-glycerate during the oxidation of the dialdehyde (II) to the strontium salt (III) with bromine water and strontium carbonate evidently is due to the oxidation of some strontium L′-oxy-D-methylene-diglycolate. These results prove levoglucosan to have structure (I); the beta configuration for carbon atom 1 is required by the accepted stereo configurations of the α- and β-forms of D-glucopyranose.[5]

Levoglucosan, upon oxidation by periodic acid or sodium metaperiodate, consumes two moles of the oxidant and produces one mole of formic acid.[6] These figures agree with formula (I). The same data could fit a compound having structure (IV), but (IV) is excluded since the corresponding strontium salt (V) could not yield strontium D-glycerate by oxidation with bromine water and strontium carbonate.

L′-Oxy-D-methylene-diglycolic acid, which is a cyclic acetal having as its two components glyoxylic and D-glyceric acids, could not be hydrolyzed by hot 2.5 *N* hydrochloric acid. This

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(1) Publication authorized by the Surgeon General, U. S. Public Health Service. Presented in part before the Division of Organic Chemistry, at the Boston meeting of the American Chemical Society, Sept. 11–15, 1939. (Not copyrighted.)

(2) Irvine and Oldham, *J. Chem. Soc.*, **119**, 1744 (1921); Charlton, Haworth and Herbert, *ibid.*, 2855 (1931).

(3) Josephson, *Ber.*, **62**, 313 (1929).

(4) The dialdehyde is named according to the plan previously adopted by Jackson and Hudson, THIS JOURNAL, **59**, 994 (1937).

(5) See F. Micheel, "Chemie der Zucker und Polysaccharide," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1939, p. 153.

(6) *Cf.* Jackson and Hudson, THIS JOURNAL, **61**, 1530 (1939).