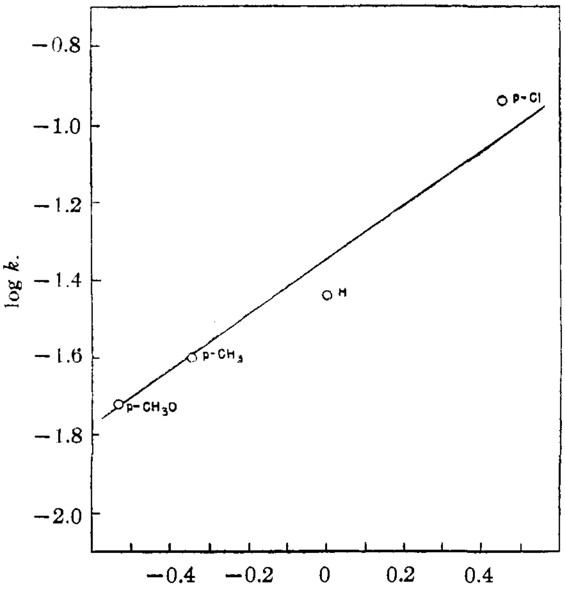


Fig. 1.—Plot of log *k* against the Hammett substituent constant.

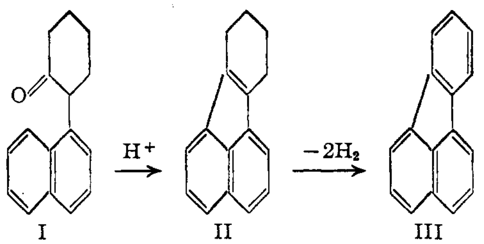
of the selenium–iodine bond by lowering the electron density on the selenium atom.

Los Angeles 24, Calif. Received February 20, 1951

A Synthesis of Fluoranthene by Cyclodehydration

By Milton Orchin and Leslie Reggel

The cyclodehydration[1] of 2-(1-naphthyl)-cyclohexanone (I) followed by dehydrogenation of the intermediate tetrahydrofluoranthene (II) would provide a three-step synthesis of fluoranthene (III). The starting ketone, I, is prepared by condensation of the available[2a,b] *o*-chlorocyclohexanone with 1-naphthylmagnesium bromide.[3] The preparation of fluoranthene (III) by this synthesis was accomplished, but the cyclization of I proceeded so poorly that the method cannot be recommended as a route to this interesting tetracyclic hydrocarbon.



I II III

The cyclized hydrocarbon from I, isolated as the complex with *s*-trinitrobenzene, was at first assumed to have the structure II. However, the ultraviolet spectrum (Fig. 1) showed that it possessed the structure of a substituted acenaphthene rather than that of an acenaphthylene or a vinylnaphthalene. It is possible that the compound originally thought to be II was actually a hexahydrofluoranthene, formed by disproportionation during cyclization. (The amount of material available was too small to permit ready measurement of the hydrogen evolved during the dehydrogenation.) Its analysis, however, is more consistent with a tetrahydro structure; furthermore, fluoranthene should be a product of a disproportionation, but it was absent from the cyclization mixture. It is likely, therefore, that the double bond in the cyclized compound has migrated into a non-conjugated position, possibly because of steric factors.

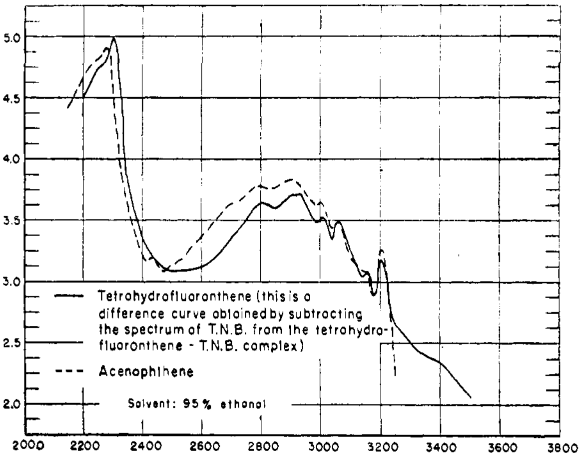


Fig. 1.—Ultraviolet absorption spectra.

Although the fluoranthene nucleus has previously been formed by cyclodehydration,[4] the present synthesis is believed to be the first example in which cyclodehydration has closed the five-membered ring in this system.

Experimental[5]

2-(1-Naphthyl)-cyclohexanone (I).—The following is an improvement of the previously described procedure.[3] To a cooled, vigorously stirred solution of 98.3 g. of *o*-chlorocyclohexanone in 150 ml. of benzene there was added during 35 minutes a solution of 1-naphthylmagnesium bromide (prepared from 155 g. of 1-bromonaphthalene, 20.0 g. of magnesium, 375 ml. of ether and 150 ml. of benzene; titration indicated a yield of 95%). After the reaction had subsided, stirring was continued at room temperature for 17 hours. The mixture was decomposed with dilute hydrochloric acid and then steam distilled. The residual red oil was taken up in benzene, washed, dried, and distilled, giving 90.6 g. of reddish material, b.p. 145–205° (1–3 mm.). Crystallization from benzene–petroleum ether and then from absolute ethanol gave 15.8 g. of I, m.p. 81.5–85.0°. The combined mother liquors in pyridine–ethanol were converted to the semicarbazones; the alcohol-soluble fractions gave 23.8 g. of crude semicarbazone, m.p. 211–216°, which on hydrolysis gave 8.83 g. of I. The total yield was 14.8%.

Cyclodehydration of I.—A mixture of 2.00 g. of I, 15 ml. of 48% hydrobromic acid, and 15 ml. of glacial acetic acid was refluxed for 24 hours. The dark-green product was taken up in benzene, washed with water, sodium bicarbonate solution and saturated sodium chloride solution and dried over sodium sulfate. The resulting oil (2.25 g.) was chromatographed on alumina. The more strongly adsorbed fraction (1.50 g. of orange gum) did not give a Beilstein test for halogen; it was not further investigated but may have consisted of condensation products of I. The less strongly

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(1) C. K. Bradsher, *Chem. Revs.*, **38**, 447 (1946).

(2) (a) M. S. Newman, M. D. Farbman and H. Hipsher, "Organic Syntheses," Vol. 25, John Wiley and Sons, Inc., New York, N. Y., 1945, p. 22. (b) From the Farchan Research Laboratories, 609 East 127 Street, Cleveland 8, Ohio.

(3) M. Orchin, This Journal, **70**, 495 (1948).

(4) H. France, S. H. Tucker and J. Forrest, *J. Chem. Soc.*, 7 (1945).

(5) All melting points corrected. Microanalyses by G. L. Stragand University of Pittsburgh. We wish to thank R. A. Friedel and Marion Springer for the spectral measurements.

adsorbed fraction, which was eluted with Skellysolve B, gave 0.36 g. (20%) of a colorless oil. The oil was treated with 0.39 g. of *s*-trinitrobenzene in alcohol, giving yellow crystals, m.p. 76.2–78.2° (not recrystallized). *Anal.* Calcd. for $C_{16}H_{14}\cdot C_6H_3N_3O_6$: C, 63.0; H, 4.1. Calcd. for $C_{16}H_{16}\cdot C_6H_3N_3O_6$: C, 62.7; H, 4.5. Found: C, 62.4; H, 4.2. A sample of the complex (0.55 g.) was chromatographed on alumina, giving 0.25 g. of a yellow oil (II or isomer) which was dehydrogenated by treatment with 0.06 g. of palladium-on-charcoal.[6] The fluoranthene formed was isolated as the *s*-trinitrobenzene complex, m.p. 208.5–209.4°, mixed m.p. 208.6–209.4°; the identification was confirmed by the ultraviolet absorption spectrum. The yield of III from II was 33%.

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[6] R. P. Linstead and S. L. S. Thomas, *J. Chem. Soc.*, 1172 (1940); catalyst-*d*.

SYNTHETIC LIQUID FUELS BRANCH
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RECEIVED JANUARY 18, 1951

The Preparation of 3,4-Dimethoxy-2,5-dicarbethoxythiophene. 3,4-Dimethoxythiophene

BY C. G. OVERBERGER AND JOGINDER LAL[1]

In connection with other work we had occasion to prepare certain thiophene derivatives for comparison with the corresponding thiophene dioxides. Fager[2] has described the preparation of 3,4-dimethoxythiophene by the reaction of the sodium salt obtained from the condensation of ethyl thiodiacetate and ethyl oxalate with methyl sulfate, subsequent hydrolysis with base to give the 3,4-dimethoxy-2,5-dicarboxythiophene followed by decarboxylation. However, no physical constants except a boiling point and no analysis were reported. Turnbull[3] has reported the preparation of 3,4-dimethoxythiophene by the reaction of diazomethane with 3,4-dihydroxythiophene prepared by the decarboxylation of 3,4-dihydroxy-2,5-dicarboxythiophene and reported a boiling point and correct analytical data. He likewise describes the preparation of 3,4-dimethoxythiophene from 3,4-dimethoxy-2,5-dicarboxythiophene by decarboxylation but he does not compare the product obtained with that from the previous procedure. He does not state how the 3,4-dimethoxy-2,5-dicarboxythiophene was prepared.

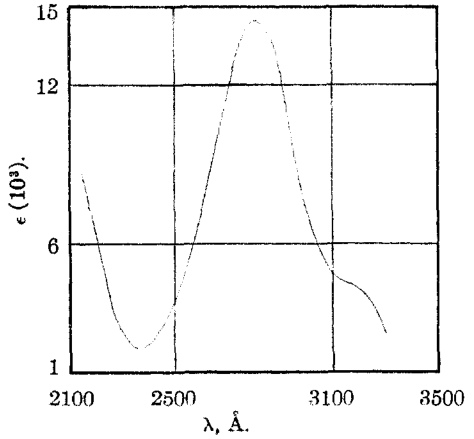

Fig. 1.—Ultraviolet absorption spectrum of 3,4-dimethoxy-2,5-dicarbethoxythiophene in 95% ethanol.

Since the Fager procedure for preparing 3,4-dimethoxythiophene was experimentally more desirable from the viewpoint of quantity, it was necessary for us to establish the authenticity of heretofore non-isolated intermediates and the product. Reaction of the sodium salt obtained from the condensation of ethyl oxalate and ethyl thiodiacetate with methyl sulfate and isolation of the diester directly gave a 51% yield of 3,4-dimethoxy-2,5-dicarbethoxythiophene. This compound was identical with the product obtained by reaction of 3,4-dihydroxy-2,5-dicarbethoxythiophene with diazomethane (95%). This was demonstrated by a mixed melting point and their identical ultraviolet absorption spectra (Fig. 1). This comparison now enabled us to use the general Fager procedure with assurance. Saponification of 3,4-dimethoxy-2,5-dicarbethoxythiophene gave a 92% yield of 3,4-dimethoxy-2,5-dicarboxythiophene. A methoxyl determination demonstrated that two O-methyl groups were present. Decarboxylation of this diacid was effected by heating with copper at 180–190° in vacuum to give an 87.5% yield of pure 3,4-dimethoxythiophene. The 3,4-dimethoxythiophene was further characterized by formation of the 2,5-dinitro derivative.

New derivatives of 3,4-dihydroxy-2,5-dicarbethoxythiophene, the diacetate and dibenzoate are described in the experimental section.

3,4-Dihydroxy-2,5-dicarbethoxythiophene.—This compound was prepared according to the procedure of Hinsberg.[4] From 35 g. (1.52 moles) of sodium in 350 ml. of alcohol, 146 g. (1 mole) of ethyl oxalate and 103 g. (0.5 mole) of ethyl thiodiacetate, there was obtained 102 g., m.p. 134 (78.5%). The sodium salt is isolated in our procedure. Recrystallization from benzene or methanol gave a m.p. 134.5–135° (134°, no yield reported).[4]

(A) **Dibenzoate.**—The reaction of 3,4-dihydroxy-2,5-dicarbethoxythiophene with benzoyl chloride and pyridine[5] gave the dibenzoate. The product was recrystallized twice from hexane to give transparent regular crystals, m.p. 96.5–97.5°.

Anal. Calcd. for $C_{24}H_{20}O_8S$: C, 61.53; H, 4.30. Found: C, 61.34; H, 4.22.

(B) **Diacetate.**—The reaction of 3,4-dihydroxy-2,5-dicarbethoxythiophene with acetic anhydride and sodium acetate gave the diacetate.[6] The product was crystallized from 95% ethanol to give transparent crystals, m.p. 80.5–81.2°.

Anal. Calcd. for $C_{14}H_{16}O_8S$: C, 48.83; H, 4.68. Found: C, 48.64; H, 4.94.

3,4-Dimethoxy-2,5-dicarbethoxythiophene (A).—Methylation of 3,4-dihydroxy-2,5-dicarbethoxythiophene was carried out with diazomethane.[7] To a cold solution of 9 g. (0.0346 mole) of 3,4-dihydroxy-2,5-dicarbethoxythiophene dissolved in 50 ml. of pure dioxane was added with gentle shaking a cold ethereal solution of about 8.5 g. of diazomethane. The reaction mixture was surrounded by ice and allowed to stand for 1–2 hours and then washed with dilute hydrochloric acid to destroy excess diazomethane. The diazomethane-free solution was washed several times with five per cent. sodium carbonate solution to neutralize traces of hydrochloric acid and to remove any unconverted 3,4-dihydroxy-2,5-dicarbethoxythiophene. The ethereal layer

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[1] A portion of a thesis by Joginder Lal submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] E. W. Fager, THIS JOURNAL, **67**, 2217 (1945).

[3] S. G. Turnbull, U. S. Patent 2,453,103, November 2, 1948.

[4] Hinsberg, *Ber.*, **43**, 901 (1910).

[5] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 164.

[6] *Ibid.*, p. 165.

[7] F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., second edition, p. 165.