

4,4'-Dialkylaminoalkyl Dibenzylidicarboxylates.—The hydrochlorides of these compounds were prepared from the diacid chloride of 4,4'-dibenzylidicarboxylic acid¹² by the method indicated in the preparation of the analogous stilbene compounds above. The properties of these compounds prepared are summarized in Table II.

Summary

- Several dialkylaminoalkyl esters of 4,4'-

(12) Fischer and Wolfenstein, *Ber.*, **37**, 3215 (1904).

stilbenedicarboxylic and 4,4'-dibenzylidicarboxylic acid have been prepared.

- Two esters of the stilbene series and one of the dibenzyl series show topical anesthetic properties.

- It is suggested that the activity in the stilbene series is, in part, due to the extensive and continuous conjugation which, if interrupted as in the dibenzyl analogs, results in decreased activity.

CHICAGO, ILLINOIS

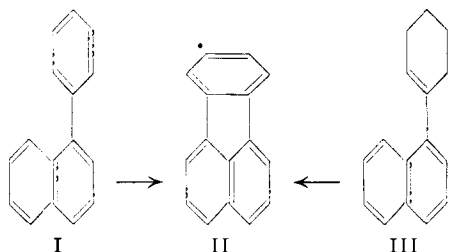
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[CONTRIBUTION FROM THE U. S. BUREAU OF MINES, CENTRAL EXPERIMENT STATION]

Aromatic Cyclodehydrogenation. V. A Synthesis of Fluoranthene¹

BY MILTON ORCHIN² AND LESLIE REGGEL²

In a continuation of the cyclodehydrogenation³ studies in this Laboratory,⁴ we have found that 1-phenylnaphthalene, I, can be readily converted to fluoranthene, II. Since 1-(2',3',4',5'-tetrahydrophenyl)-naphthalene, III, which is an intermediate in the synthesis of I, can be converted directly to II, the isolation of 1-phenylnaphthalene is not required for the successful synthesis of fluoranthene. The tetrahydro compound, III,



can be obtained in good yield in two steps from 1-naphthylmagnesium bromide and cyclohexanone, so that pure synthetic fluoranthene is now readily available by a three-step process.⁵ The cyclodehydrogenations to fluoranthene can be accomplished with a palladium-on-charcoal catalyst,

(1) Published by permission of the Director, U. S. Bureau of Mines. Presented before the Organic Division at the Atlantic City meeting of the American Chemical Society, April 8-12, 1946.

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(3) The word "cyclodehydrogenation" has been used previously, as, for example, by J. W. Cook, *J. Chem. Soc.*, 369 (1934), but has not been precisely defined. We wish to define "aromatic cyclodehydrogenation" as an intramolecular loss of hydrogen from an aromatic or hydroaromatic compound to form a new compound with a greater number of rings. This definition would include the examples cited in Cook's work.

(4) For the previous publication in this series see Orchin and Friedel, *This Journal*, **68**, 573 (1946).

(5) Only two other syntheses of fluoranthene have been reported. Von Braun and Anton, *Ber.*, **62**, 145 (1929), started with 9-sodium-9-carboethoxyfluorene and built up the additional six-membered ring by a series of six reactions. Cook and Lawrence (ref. 7) obtained an unspecified but "very small" yield of fluoranthene by selenium dehydrogenation of the product obtained by aluminum chloride cyclization of 1-(1'-naphthyl)-2-(or 6)-methylcyclohexene-1.

but a pelleted chromia-alumina catalyst⁶ seems to be superior.

Cook and Lawrence⁷ reported that the attempted liquid-phase dehydrogenation of the tetrahydro compound, III, to 1-phenylnaphthalene, I, with a platinum catalyst gave only a small quantity of hydrogen, but the reaction did result in disproportionation into 1-cyclohexylnaphthalene and 1-phenylnaphthalene. We have found that if a palladium-on-charcoal catalyst is used, nearly quantitative evolution of hydrogen occurs, and 1-phenylnaphthalene can be isolated in 94% yield. The formation of 1-cyclohexylnaphthalene can also be avoided by vapor-phase dehydrogenation of III over a palladium-on-charcoal catalyst at 350°, but considerable fluoranthene is formed in this process.

Cook and Lawrence have commented⁷ on the unusual resistance which the tetrahydro compound III displays to hydrogenation under mild conditions with a platinum catalyst. Previously, we have found⁸ that small-scale hydrogenation of polynuclear compounds can be achieved in the absence of a hydrogen atmosphere simply by refluxing an ethanol solution of the compound with Raney nickel.⁹ We have now found that hydrogenation of III proceeds readily under these conditions, and that 1-cyclohexylnaphthalene can be isolated from the products.

(6) The catalyst, designated as Cr-181, was purchased from the Harshaw Chemical Co., Cleveland, Ohio. It is in the form of 3/32" pellets, stated to consist of alumina impregnated with 12% chromia and 2% magnesia. Indications are that this catalyst is superior to palladium-on-charcoal for the cyclodehydrogenations previously reported from this Laboratory.

(7) Cook and Lawrence, *J. Chem. Soc.*, 1431 (1936).

(8) Orchin, *This Journal*, **66**, 535 (1944).

(9) Mazingo, Spencer and Folkers, *ibid.*, **66**, 1859 (1944), state that benzene rings are not reduced by this procedure. Obviously, this does not apply to benzene rings which are part of a fused ring system. In our studies with Raney nickel, we have found that even in the presence of a hydrogen atmosphere, the hydrogen held on the surface of the nickel participates in the reaction. For example, in a quantitative study it was found that the apparent absorption of hydrogen by cyclohexene is always less than theoretical when hydrogenation is done in the presence of Raney nickel, even though no cyclohexene remains unconverted.

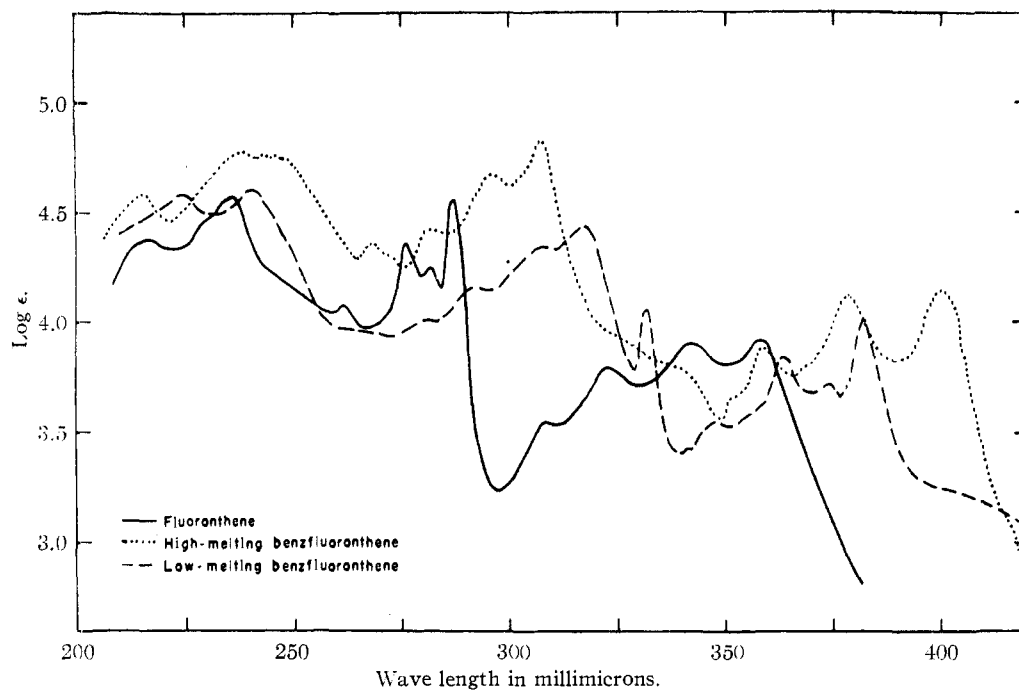
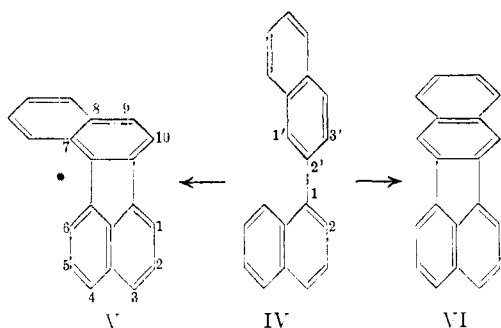


Fig. 1.—Ultraviolet absorption spectra.

In a further study of the formation of the fluoranthene ring system by cyclodehydrogenation, 1,2'-dinaphthyl, IV, was treated with the chromia-alumina catalyst at 500°. Cyclization at the 1'- or 3'-position would give isomeric benzfluoranthenes.¹⁰ Two compounds were indeed



isolated from the reaction mixture. The compound obtained in greater quantity formed, when pure, almost colorless needles, melting point 217.0–217.4°. Although we have not attempted a proof of structure at the present time, it seems likely that this compound is 7,8-benzfluoranthene, V, formed by ring closure at the more reactive 1'-position of 1,2'-dinaphthyl. The second product isolated formed bright yellow crystals, melting point 166.0–166.4°; it is regarded as 8,9-benzfluoranthene, VI. Analyses of the hydrocarbons and of their complexes with 2,4,7-trinitrofluo-

renone¹¹ and *s*-trinitrobenzene were consistent with the benzfluoranthene structure.

The ultraviolet absorption spectra of fluoranthene and the two benzfluoranthenes are shown in Fig. 1¹²; the spectra of the two benzfluoranthenes show considerable similarity to each other and to fluoranthene.

If the two compounds actually are isomeric benzfluoranthenes, as seems probable, their comparative physical properties are quite unusual. The lower melting, more soluble compound is more highly colored than its isomer. When the two compounds are adsorbed on a column of alumina, the yellow compound is eluted from the adsorbent more easily than its isomer; however, sharp separation of the two bands is difficult, and it seems probable that the apparent weaker adsorption of the yellow compound is due to its great solubility. The deep color of the lower melting isomer remains to be satisfactorily explained.^{12a}

(11) Orchin and Woolfolk, *THIS JOURNAL*, **68**, 1727 (1946).

(12) The authors wish to thank Dr. R. A. Friedel and Mrs. H. J. Pierce for the spectra determinations.

(12a) In seeking some theoretical explanation for the color of the lower melting isomer, the nine possible unexcited resonance structures of each isomer were written. It was observed that if one considers the five-membered ring in both isomers, then for 7,8-benzfluoranthene, V, one can write one structure containing no double bonds; four structures containing one double bond; and four structures containing two double bonds, in the five-membered ring. However, for 8,9-benzfluoranthene, VI, one can write two structures with no double bonds; five structures with one double bond; and only two structures with two double bonds, in the five-membered ring. If one assumes that the resonance structures with two double bonds in the five-membered ring make negligible contributions to the molecule (Mills-Nixon effect), then the 8,9-isomer, VI, has more resonance structures than the 7,8-isomer, V. The argument that the compound with the greater number of resonance structures would

(10) Of the four possible monobenzfluoranthenes, only 2,3-benzfluoranthene has previously been reported (Tobler, Holbro. Sutter and Kern, *Helv. Chim. Acta*, **24**, 100 (1941)); see also I. G. Farbenindustrie, British Patent 459,108 [C. A., **31**, 4136 (1937)]; I. G. Farbenindustrie, French Patent 807,704 [C. A., **31**, 5814 (1937)].

The ease with which the tetrahydro compound, III, can be converted to fluoranthene contradicts the implication of Clar¹³ that dehydrogenation of this type of molecule results in aromatization without ring closure. However, our conditions are considerably more drastic than those which have been commonly employed in the past.

The synthesis by cyclodehydrogenation of other compounds containing the fluoranthene nucleus is being investigated.

Experimental¹⁴

1-(2',3',4',5'-Tetrahydrophenyl)-naphthalene, III.—This compound was prepared from 1-naphthylmagnesium bromide and cyclohexanone.¹⁵ The crude distilled carbinol was dehydrated with 90% formic acid, giving a 66% yield of III, b. p. 132–142° (0.9–1.2 mm.). A sample recrystallized from methanol to constant melting point was obtained as small colorless needles, m. p. 47.0–47.5°.

Anal.^c Calcd. for C₁₆H₁₆: C, 92.26; H, 7.74. Found: C, 91.98; H, 8.02.

The complex with 1,3,5-trinitrobenzene formed yellow needles (from alcohol) m. p. 124.7–125.3°.

Anal.^a Calcd. for C₂₂H₁₉N₃O₆: C, 62.70; H, 4.54. Found: C, 62.77; H, 4.50.

The complex with picric acid had melting point 127.5–128.4°.¹⁶

1-Phenylnaphthalene, I.—A mixture of 18.05 g. of III and 1.0 g. of 30% palladium-on-charcoal¹⁷ was heated at 320–360° for three and one-half hours. There was evolved 3680 cc. (N. T. P.) of hydrogen (95%). The product was distilled *in vacuo*, giving 16.70 g. (94%) of pure 1-phenylnaphthalene, colorless oil, b. p. 147–154° (1.0–1.2 mm.), *n*_D²⁰ 1.6646.

Anal.^c Calcd. for C₁₆H₁₂: C, 94.08; H, 5.92. Found: C, 93.90; H, 6.33.

1-Phenylnaphthalene failed to form complexes with picric acid, *s*-trinitrobenzene, or trinitrofluorenone.¹¹

1,2'-Dinaphthyl, IV.—This compound was prepared from 2-naphthylmagnesium bromide and tetralone-1.¹⁸ Careful purification by chromatographic adsorption resulted in the isolation of a small quantity of 2,2'-dinaphthyl, m. p. 184–187°, which was more strongly adsorbed on the alumina than its isomer. The 2,2'-dinaphthyl did not depress the melting point of a pure sample of melting point 186.4–187.4°, synthesized from 2-bromonaphthalene.¹⁸ The 1,2'-dinaphthyl was obtained as colorless crystals, m. p. 76.4–77.4°.

1-Cyclohexylnaphthalene.—A solution of 5.19 g. of the tetrahydro compound, III, in 150 ml. of absolute alcohol

be more highly colored cannot alone be advanced to account for the difference in color, since, as the Referees have pointed out, the energy of the excited state as well as the ground state of a molecule must be considered. Furthermore, the probable geometry of the fluoranthene molecule is such that one cannot count resonance structures only with reference to the five-membered ring. We hope to prove the structures of the benzfluoranthenes by synthesis at some future time.

(13) Clar, "Aromatische Kohlenwasserstoffe," pp. 76–77, Julius Springer Verlag, Berlin, 1941.

(14) All melting points corrected. Microanalyses marked ^a by Dr. T. S. Ma, University of Chicago, and ^b by the Arlington Laboratories, Fairfax, Virginia. Macroanalyses marked ^c by the Coal Analysis Section, U. S. Bureau of Mines, Central Experiment Station, Pittsburgh, Pa.

(15) Weiss and Woidich, *Monatsh.*, **46**, 453 (1926).

(16) Weiss and Woidich, ref. 15, give the melting point of the hydrocarbon as 36°. Cook, Hewett and Lawrence, *J. Chem. Soc.*, 71 (1936), give 46° for the hydrocarbon and 124.5–125.5° for the picrate. Cook and Lawrence, ref. 7, give 121–121.5° for the melting point of the trinitrobenzene complex.

(17) Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940); catalyst-d.

(18) Hooker and Pieser, *THIS JOURNAL*, **58**, 1220 (1936).

was refluxed with about 20 g. of Raney nickel¹⁹ for one hour. The mixture was filtered, the alcohol removed, and the residue distilled, giving 4.06 g. of colorless oil, b. p. 152° (3.5 mm.), *n*_D²⁰ 1.5856.

Anal.^c Calcd. for C₁₆H₁₈: C, 91.37; H, 8.63. Found: C, 90.65; H, 9.21.

The analysis indicated that some hydrogenation of the naphthalene nucleus had taken place.

The picrate prepared from the crude cyclohexylnaphthalene was recrystallized from alcohol; it formed orange needles, m. p. 126.7–127.4°. A mixed melting point with the picrate of the tetrahydro compound was 124.5–126.4°.²⁰

The *s*-trinitrobenzene complex prepared from the crude cyclohexylnaphthalene was recrystallized twice from alcohol; it formed yellow needles, m. p. 119.4–121.0°.

Anal.^a Calcd. for C₂₂H₂₁N₃O₆: C, 62.40; H, 5.00. Found: C, 61.90; H, 4.94.

A mixed melting point with the *s*-trinitrobenzene complex of the tetrahydro compound was 116.0–118.5°.

In view of the slight depressions observed with mixed melting points,²⁰ further evidence for the non-identity of the two *s*-trinitrobenzene complexes was sought in ultraviolet spectra and X-ray diffraction measurements.

The ultraviolet absorption spectra of the *s*-trinitrobenzene complexes of 1-cyclohexylnaphthalene and 1-(2',3',4',5'-tetrahydrophenyl)-naphthalene are shown in Fig. 2.¹² The spectra are very similar to each other. Cyclohexylnaphthalene shows a peak at 313 mμ, which corresponds to the naphthalene peak at 311 mμ; the substitution of the cyclohexyl group on the naphthalene nucleus causes a slight bathochromic shift. Tetrahydrophenylnaphthalene, however, shows no fine structure in the region 300–320 mμ; this can be considered as due to the conjugation effect²¹ of the double bond.

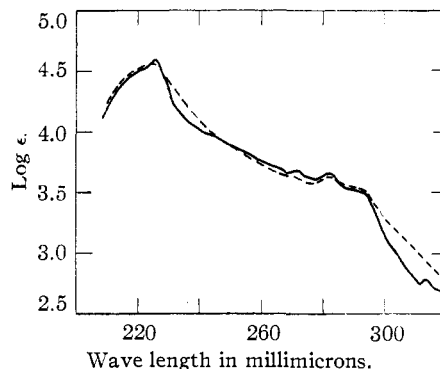


Fig. 2.—Ultraviolet absorption spectra: — 1-cyclohexylnaphthalene-trinitrobenzene, - - - - 1-(2',3',4',5'-tetrahydrophenyl)-naphthalene-trinitrobenzene.

X-Ray diffraction patterns of the two trinitrobenzene complexes were very similar, but showed a few definite differences, which clearly indicated that the two samples were not identical.²²

Cyclodehydrogenation Experiments

The apparatus used in these experiments has been described previously.²³

(19) Mazingo, "Organic Syntheses," **21**, 15 (1941).

(20) Cook and Lawrence, ref. 7, give the melting points of the picrate and *s*-trinitrobenzene complex of 1-cyclohexylnaphthalene as 122–123.5° and 116.5–117.5°, respectively. They state that mixed melting points of the corresponding complexes of 1-cyclohexylnaphthalene and 1-(2',3',4',5'-tetrahydrophenyl)-naphthalene show no depression.

(21) R. N. Jones, *THIS JOURNAL*, **67**, 2127 (1945).

(22) The authors wish to thank Dr. L. J. E. Hofer and Mrs. W. C. Peebles for the diffraction studies, which will be published elsewhere.

(23) Orchin and Woolfolk, *THIS JOURNAL*, **67**, 122 (1945); Orchin, *Ind. Eng. Chem., Anal. Ed.*, **17**, 673 (1945).

TABLE I
SYNTHESIS OF FLUORANTHENE BY CYCLODEHYDROGENATION

Expt.	Starting material	Used, g.	Catalyst	Temp., °C.	Time, hr.	Crude product, g.	Yield of fluoranthene, % ^a	C ₁₆ H ₁₂ ^b recovered, g.
1	C ₁₆ H ₁₆ ^c	12.2	Pd-C	350-365	6.75	10.85	5.6	9.82
2	C ₁₆ H ₁₂ ^b	5.01	Pd-C	450-455	3.25	4.43	7.3	3.98
3	C ₁₆ H ₁₆	2.80	Pd-C	420-430	6.00	2.58	11.0	..
4	C ₁₆ H ₁₆	4.92	Cr ₂ O ₃	475-525	3.25	3.74	31.0	2.18
5	C ₁₆ H ₁₂	5.16	Cr ₂ O ₃	520-530	1.75	3.80	31.1	2.24

^a Represents yield of fluoranthene (based on weight of starting material) obtained in one pass over the catalyst. These values would undoubtedly vary with the rate of passage over the catalyst, which is difficult to control with the apparatus used. ^b 1-Phenylnaphthalene. ^c 1-(2',3',4',5'-Tetrahydrophenyl)-naphthalene.

(A) **Fluoranthene.**—The cyclodehydrogenation experiments to give fluoranthene are summarized in Table I. Experiment 4 will be described in detail, since it illustrates most of the techniques used in separating the products. The product of the dehydrogenation (3.74 g.) which was a mixture of oil and solid, was dissolved in the minimum quantity of boiling methanol and the solution allowed to crystallize, giving 0.78 g. of fluoranthene. This was identified by melting point and mixed melting point with a pure authentic sample, m. p. 110.6-111.0°, and by conversion to the *s*-trinitrobenzene complex, which was compared with a pure authentic sample, m. p. 208.4-209.1°. Treatment of the mother liquor with picric acid gave 1.39 g. of fluoranthene picrate, which did not depress the melting point of a pure authentic sample of melting point 186.8-188.1°. The picrate mother liquors were chromatographed on alumina (without preliminary removal of picric acid) and the adsorbed material selectively eluted with petroleum ether-benzene mixtures. The least strongly adsorbed fraction, which did not fluoresce on the column, gave 2.18 g. of 1-phenylnaphthalene. A more strongly adsorbed fraction, which fluoresced blue-green under ultraviolet light, gave 0.05 g. of fluoranthene, identified as the *s*-trinitrobenzene complex.

Chromatography of the picrate mother liquors in experiment 2 resulted in the isolation of a small fraction (0.04 g.) which was more strongly adsorbed than 1-phenylnaphthalene, but less strongly adsorbed than fluoranthene. This was found from ultraviolet spectrum analysis to consist of 42% 2-phenylnaphthalene and 58% 1-phenylnaphthalene.^{19,24} No 2-phenylnaphthalene was detected in any of the other experiments, but it may have been present in small amounts as an impurity in the recovered 1-phenylnaphthalene.

(B) **7,8- and 8,9-Benzfluoranthenes.**—Cyclodehydrogenation of 1.60 g. of pure 1,2'-dinaphthyl over chromia-alumina at 495-505° during fifteen minutes gave 1.45 g. of a yellow-brown gum. Crystallization from benzene gave 0.22 g. of needles, m. p. 213.5-216.0°. These were chromatographed on alumina, giving almost colorless needles, which were recrystallized to a constant melting point of 217.0-217.4°.

Anal.^a Calcd. for C₂₀H₁₂: C, 95.21; H, 4.79. Found: C, 95.16; H, 4.83.

The complex with trinitrofluorenone¹¹ formed deep orange microcrystals from benzene, which were recrystallized to a constant melting point of 252.0-253.0°.

Anal.^a Calcd. for C₃₃H₁₇N₃O₇: N, 7.40. Found: N, 7.37.

The *s*-trinitrobenzene complex formed yellow needles (from alcohol) m. p. 180.0-182.0°. There was insufficient material for recrystallization.

(24) Mayer and Schiffner, *Ber.*, **67B**, 67 (1934), found that 1-phenylnaphthalene is isomerized to 2-phenylnaphthalene by passage over silica gel at 350°. Since 2-phenylnaphthalene does not form a picrate (Kruber, Marx and Schade, *Ber.*, **71B**, 2478 (1938)), it does not interfere with the separation of fluoranthene picrate as described above. The spectra of our two phenylnaphthalenes will be published in a future paper.

Anal.^b Calcd. for C₂₆H₁₅N₃O₆: N, 9.03. Found: N, 9.49.

The mother liquors from the crystallization of the high-melting benzfluoranthene were chromatographed on alumina, the column eluted, and the yellow band rechromatographed on alumina. There was obtained 0.68 g. 1,2'-dinaphthyl (least strongly adsorbed) and 0.03 g. of yellow needles, m. p. 213-215° (most strongly adsorbed fraction), not depressed by the high-melting benzfluoranthene. The intermediate yellow band was again chromatographed on alumina, eluted, and rechromatographed on 1:1 alumina-supercel. The column was extruded and the yellow section carefully removed from the more strongly adsorbed blue-fluorescent band. The hydrocarbon obtained from this yellow band was crystallized from alcohol, in which it was very soluble, giving bright yellow crystals, m. p. 165.5-166.0°. Recrystallization from methanol gave 18 mg. of bright yellow crystals, m. p. 166.0-166.4°.

Anal.^b Calcd. for C₂₀H₁₂: C, 95.21; H, 4.79. Found: C, 94.92; H, 5.08.

The complex with 2,4,7-trinitrofluorenone¹¹ formed orange-red microcrystals, m. p. 255-256°.

Anal.^b Calcd. for C₃₃H₁₇N₃O₇: N, 7.40. Found: N, 7.72. A mixed melting point with the 2,4,7-trinitrofluorenone complex of the isomeric benzfluoranthene was 248-249°.

The complex with *s*-trinitrobenzene was prepared from the mother liquors of the hydrocarbon and recrystallized from benzene-alcohol; it formed golden-orange needles, m. p. 219.8-220.5°.

Anal.^b Calcd. for C₂₆H₁₅N₃O₆: N, 9.03. Found: N, 9.37.

The mother liquors from the crystallization of the *s*-trinitrobenzene and 2,4,7-trinitrofluorenone complexes of the yellow hydrocarbon were combined, the mixture reduced with tin and hydrochloric acid, and the recovered hydrocarbon treated with picric acid in alcohol. There was obtained a very small amount of orange crystals, m. p. 190.0-193.0°. This compound could not be purified because of insufficient material.²⁵

Summary

Treatment of 1-phenylnaphthalene or 1-(2',3',

(25) Dansi and Ferri, *Gazz. chim. ital.*, **71**, 648 (1941), have reported that selenium dehydrogenation of a compound obtained by treatment of tetralin with aluminum chloride gave a yellow hydrocarbon, C₂₀H₁₂, m. p. 165°, which formed a red picrate, m. p. 195°. They suggest that the hydrocarbon is either cyclobuta[1.2-a,4.3-a']-dinaphthalene or cyclobuta[1.2-a,3.4-a']dinaphthalene. The ultraviolet spectrum is stated to be different from that of naphthalene, but no details are given. Earlier, von Braun and Kirschbaum, *Ber.*, **54B**, 597 (1921), treated 1,2-dihydronaphthalene with sulfuric acid and dehydrogenated the product with lead monoxide or with sulfur; both methods of dehydrogenation gave a yellow hydrocarbon, C₂₀H₁₂, m. p. 165°, which was also regarded as a cyclobutadinaphthalene.

4',5'-tetrahydrophenyl)-naphthalene with a chromia-alumina or palladium-on-charcoal catalyst at 450–525° gives fluoranthene. Similar treatment of 1,2'-dinaphthyl gives a mixture of two

hydrocarbons to which the structures of 7,8- and 8,9-benzfluoranthenes have been tentatively assigned.

PITTSBURGH, PENNSYLVANIA

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[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Synthesis of Some Fluorohydroxybiphenyls

BY ARTHUR ROE AND H. L. FLEISHMAN¹

The preparation and bactericidal properties of several alkyl fluorophenols were reported by Suter, Lawson and Smith²; one other related compound, 1-(2-hydroxy-5-fluorophenyl)-2-pentene, was reported by Deischel³ to have bactericidal properties. No fluorohydroxybiphenyls are reported in the literature; the present synthesis of some of them was undertaken in view of the bactericidal properties shown by the alkyl fluorophenols and by certain 4-halo-4'-hydroxybiphenyls.^{4a,b} This investigation is part of a study of the preparation and properties of aromatic and heterocyclic fluorine compounds under way in this Laboratory.

The new fluorohydroxybiphenyls are shown in the following table; all are white crystalline solids.

TABLE I

Compound	M. p., °C.
I 4-Fluoro-4'-hydroxybiphenyl	167–168
II 2-Fluoro-2'-hydroxybiphenyl	103.5–104.5
III 2-Fluoro-4'-hydroxybiphenyl	131.5–133
IV 4,4'-Difluoro-2-hydroxybiphenyl	93.5–94.5

Fluorine was introduced using the method developed by Balz and Schiemann⁵; the phenolic groups were then introduced by standard methods starting from the corresponding nitro compounds.

A fifth compound was prepared but was not included in the above table because its structure is not known with certainty; available evidence indicates that it is 4,4'-difluoro-2,3'-dihydroxybiphenyl (V). The dinitro-4,4'-difluorobiphenyl from which V was prepared is, according to Shaw and Turner,⁶ probably the 2,3'-dinitro derivative, although it may be 2,2'-dinitro-4,4'-difluorobiphenyl. Further work is being done to clarify the structure of this compound.

The bactericidal properties of these compounds will be reported elsewhere.

(1) The work reported in this paper is taken from the Master's thesis submitted by H. L. Fleishman to the Graduate School of the University of North Carolina.

(2) Suter, Lawson and Smith, *THIS JOURNAL*, **61**, 161–165 (1939).

(3) I. G. Farbenind., A.-G., German Patent 667,063 (November 7, 1938).

(4) (a) Schmidt, Savoy and Abernethy, *THIS JOURNAL*, **66**, 491 (1944); (b) Savoy and Abernethy, *ibid.*, **64**, 2219 (1942).

(5) Balz and Schiemann, *Ber.*, **60B**, 1186 (1927).

(6) Shaw and Turner, *J. Chem. Soc.*, 509 (1932).

Experimental

4-Fluoro-4'-hydroxybiphenyl (I).—The preparation of 4-fluorobiphenyl in 82% yield was carried out essentially as outlined by Schiemann and Roselius,⁷ except that NaBF₄ was used as a source of the fluoborate ion instead of HBF₄. The diazonium sulfate obtained by diazotization of 7 g. of 4-fluoro-4'-biphenylamine⁸ was added slowly to a boiling mixture of 24 cc. of concentrated sulfuric acid and 18 cc. of water. The solution was boiled for five minutes after addition was complete, cooled and the insoluble material filtered off and dissolved in sodium hydroxide. Upon acidification 4 g. of crude (I) was obtained. Repeated crystallization from alcohol and petroleum ether would not remove the yellow color, so the material was refluxed with a small amount of tin and hydrochloric acid, then recrystallized from alcohol; colorless needles, m. p. 167–168°.

*Anal.*⁹ Calcd. for C₁₂H₉OF: F, 10.09. Found: F, 10.36, 10.36.

2-Fluoro-2'-nitrobiphenyl (VI).—Diazotization of 30 g. of 2'-nitro-2-biphenylamine¹⁰ followed by the addition of 30 g. of NaBF₄ dissolved in 40 cc. of water, produced a copious precipitate of 2'-nitro-2-biphenyldiazonium fluoborate (VII). The precipitate was washed with 10 cc. of cold saturated NaBF₄ followed by four 20-cc. portions of ether, the precipitate being sucked as dry as possible after each washing. The orange solid was then spread on a porous paper and allowed to dry overnight; yield 42 g.; m. p. 87° (dec.). In another run 35 g. of the amine hydrochloride was converted to 41 g. of VII.

The thermal decomposition of VII proceeds with great vigor; this rapid and unruly decomposition is characteristic of diazonium fluoborates containing a nitro group. Part of the salt was decomposed by adding it a little at a time to a flask (fitted with a reflux condenser) held at 100°; steam distillation of the black residue gave only a 10% yield of VI. In an attempt to improve the yield, 40 g. of VII was mixed with 80 g. of sodium fluoride in the hope that the boron trifluoride evolved would be absorbed forming NaBF₄, perhaps lessening the violence of the reaction. The mixture was placed in a 2-liter flask fitted with a reflux condenser with a tube leading to a trap containing sodium hydroxide; the reaction was carried out in a hood. Decomposition took place rapidly but with less vigor than before when heat was applied; 4 g. (13%) of pure VI was obtained, m. p. 71–72° (recorded m. p. of VI produced by nitration of 2-fluorobiphenyl,⁸ 71.5°).

2-Fluoro-2'-hydroxybiphenyl (II).—Compound VI was reduced to 2-fluoro-2'-biphenylamine as described by Van Hove.⁸ Conversion of 4.3 g. of this amine to 1.1 g. of pure II was carried out as described for compound I; colorless needles from alcohol, m. p. 103.5–104.5°.

Anal. Calcd. for C₁₂H₉OF: F, 10.09. Found: F, 9.87.

(7) Schiemann and Roselius, *Ber.*, **62B**, 1805 (1929).

(8) Van Hove, *Bull. soc. chim. Belg.*, **32**, 52 (1923).

(9) Fluorine analyses were made by a slight modification of the method of Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

(10) Purdie, *THIS JOURNAL*, **63**, 2276 (1941).