by a Wolff–Kischner reduction.[13] 2,5- and 2,4-dimethylpyrroles were prepared by established procedures.[14] All pyrroles were distilled to obtain center fractions and stored under nitrogen at 5° until used.

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[13] A. I. Vogel, "Practical Organic Chemistry," 3rd. Ed., Longmans, Green and Co., London, 1956, p. 510.

[14] A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 219.

Two Cases of Unexpected Formation of the Fluoranthene System

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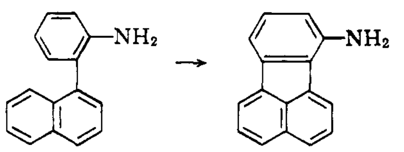
When 1-(2-aminophenyl)naphthalene (I) was treated successively with boron trichloride in boiling benzene and with aluminum chloride at 120°, a boron-free compound, $C_{16}H_{11}N$, was formed. It was a primary amine and was converted by deamination into fluoranthene. Also the spectrum of the nitrogenous compound was practically identical with that of fluoranthene. In accordance with the following equation it can be assumed that the amine is 9-aminofluoranthene (II). The dehydrogenation which takes place is facilitated by the fact that it removes the mutual interference of the hydrogen atoms in the 6-position of the aminophenyl group and the 8-position of the naphthalene system.

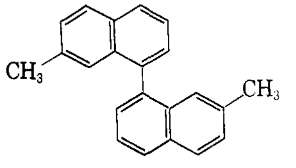


I II

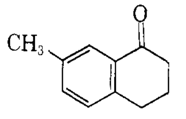
For the synthesis of some complex polycyclic compounds, 7,7′-dimethyl-1,1′-dinaphthyl (III) was required. To this end, 7-methyl-1-tetralone[1] (IV) was reduced with aluminum amalgam to the corresponding pinacol V and the latter, after careful washing, was dehydrated and dehydrogenated. The hydrocarbon (III), $C_{22}H_{18}$, formed colorless needles and absorbed, as expected, at 287 and 296 mμ. When, however, the *crude* (unwashed) pinacol V was dehydrated, a yellow hydrocarbon, $C_{22}H_{16}$, was obtained. Its ultraviolet spectrum was identical, apart from a slight bathochromic shift, with that of benzo[*j*]fluoranthene.[2] It is thus reasonable to assume that the compound is 6,11-dimethylbenzo[*j*]fluoranthene (VI).

Benzo[*j*]fluoranthene had been described originally[3] as colorless, but this was corrected later[4]; the hydrocarbon was yellow.

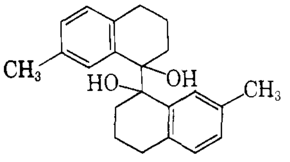
The reaction described could have given an alternative structure, *viz.*, that of perylene derivative (VII); however, the spectrum of perylene is very different from that of our hydrocarbon. Moreover, a similar formation of a fluoranthene system from a 1-phenylnaphthalene derivative had been described before by Cook and Lawrence.[5] The cyclization which is involved in the formation of VI does not take place in the dehydrogenation step. The dehydration products, obtained from pure and crude pinacol V, respectively, are different and have, therefore, probably the structures VIII and IX.[6]



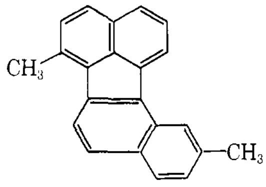
III



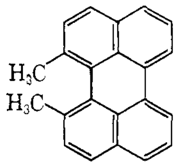
IV



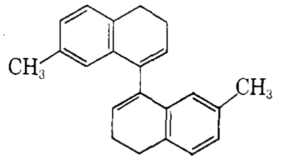
V



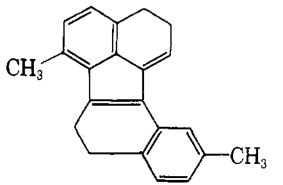
VI



VII



VIII



IX

Experimental

1-Iodonaphthalene[7].—At a temperature not exceeding 5°, a solution of 25.4 g. of 1-naphthylamine in 300 ml. of water and 100 ml. of concentrated hydrochloric acid was diazotized with 7.0 g. of sodium nitrite. A solution of 17 g. of potassium iodide in 50 ml. of water was added and, after 1 hr. at room temperature, the mixture was heated on the water bath for 10 min. and made alkaline. The mass was extracted with benzene and the solvent was evaporated. Distillation of the residue with steam gave a product which was washed with sodium bisulfite solution and water, dried, and distilled: b.p. 168° (2 mm.), yield 18%.

1-(2-Nitrophenyl)naphthalene.—At a temperature of 200°, 12 g. of copper powder was added to a well-stirred mixture of 7 g. of 1-iodonaphthalene and 6 g. of 2-bromonitrobenzene. The temperature was then raised to 250° for a period of 5 hr., and the cooled mixture was extracted repeatedly with 80 ml. of hot benzene. The desired product boiled at 168–173° (2 mm.) and crystallized upon treatment with methanol. Recrystallization from the same solvent gave 2.2 g. (30%) of yellow platelets, m.p. 95° (lit.[8] m.p. 88–90°).

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[1] M. S. Newman, *J. Am. Chem. Soc.*, **62**, 1683 (1940).

[2] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc, New York, N. Y., 1951, No. 542.

[3] M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **69**, 505 (1947).

[4] M. Orchin and L. Reggel, *ibid.*, **73**, 436 (1951).

[5] J. W. Cook and C. H. Lawrence, *J. Chem. Soc.*, 1431 (1936).

[6] A short communication has been published before [E. D. Bergmann and P. Bracha, *Bull. Res. Council Israel*, **11A**, 27 (1962)].

[7] *Cf.* F. Noelting, *Ber.*, **19**, 135 (1886).

[8] J. Forrest and S. H. Tucker, *J. Chem. Soc.*, 1137 (1948).

Anal. Calcd. for $C_{16}H_{11}NO_2$: C, 77.1; H, 4.4; N, 5.6. Found: C, 77.3; H, 4.5; N, 5.6.

The forerun and residue containing 2,2′-dinitrobiphenyl and 1,1′-binaphthyl, respectively, have not been investigated.

1-(2-Aminophenyl)naphthalene (I).—The reduction of the preceding compound caused unexpected difficulties. Tin or titanous chloride in concentrated hydrochloric acid, as well as platinum–charcoal or palladium–charcoal in alcohol with hydrogen, left the nitro compound unaffected; and stannous chloride in concentrated hydrochloric acid, hydrazine hydrochloride with Raney nickel or palladium–charcoal, or hydrogen activated with palladium–charcoal in ethyl acetate or in ethanol containing some hydrochloric acid led to resinous products.

When 0.5 g. of 1-(2-nitrophenyl)naphthalene was hydrogenated in 50 ml. of ethanol containing a few drops of 60% *perchloric acid*, in the presence of 0.1 g. of palladium–charcoal (10%), the reaction was complete in 3 hr., and the amino compound, m.p. 62°, was obtained in 82% yield (lit.[8] m.p. 65°, softening at 61°).

Anal. Calcd. for $C_{16}H_{13}N$: C, 87.7; H, 5.9; N, 6.4. Found: C, 87.7; H, 5.9; N, 6.1.

9-Aminofluoranthene (II).—A solution of 3.12 g. of boron trichloride in 100 ml. of benzene was added, slowly and with stirring, to a solution of 4.5 g. of I in 120 ml. of benzene. The mixture was refluxed for 5 hr. and evaporated *in vacuo*, and the dry residue was heated for 3 hr. at 120° with 0.3 g. of finely powdered aluminum chloride. The product (yield 25%) was extracted repeatedly with anhydrous ether and the concentrated solution was chromatographed on silica. Platelets of m.p. 272° were obtained with $\lambda_{\max}^{\text{EtOH}}$ 262 mμ (log ϵ 4.70), 283 (3.99), 288 (4.30), 294 (3.80), 326 (4.17), 342 (3.63), and 358 (3.77), while we found for fluoranthene 277 (4.51), 283 (4.39), 289 (4.68), 310 (3.64), 326 (3.88), 344 (3.98), and 362 (3.99).

Anal. Calcd. for $C_{16}H_{11}N$: C, 88.5; H, 5.1; N, 6.4. Found: C, 88.3; H, 5.5; N, 6.4.

Diazotization of the product and coupling with an alkaline solution of 2-naphthol gave an azo dye.

Fluoranthene.—A solution of 120 mg. of II in 1 ml. of concentrated hydrochloric acid was diazotized at 5° with 90 mg. of sodium nitrite. The solution was added at 10–15° to a solution of 1.3 g. of anhydrous cupric sulfate in 10 ml. of 32% hypophosphorous acid. After addition of 15 ml. of ethanol, the mixture was brought to a temperature of 55°, cooled, and extracted with ether. The concentrated solution was chromatographed on silica and gave one single compound of m.p. 110°, which was identified by analysis and mixture melting point as fluoranthene.

Anal. Calcd. for $C_{16}H_{10}$: C, 95.0; H, 5.0. Found: C, 94.7; H, 5.2.

7-Methyl-1-tetralone (IV) **and 3,4,3′,4-tetrahydro-7,7′-dimethyl-1,1′-binaphthyl** (VIII), m.p. 115° (from ethanol), were prepared according to Newman[1] who reported a melting point of 110.0–11.6°. The hydrocarbon had $\lambda_{\max}^{\text{EtOH}}$ 255 mμ (log ϵ 4.30).

7,7′-Dimethyl-1,1′-binaphthyl (III).—A mixture of 2 g. of VIII and 0.2 g. of palladium–charcoal (10%) was heated for 3 hr. at 240° and for 2 hr. at 300–320°. The product was extracted with benzene, the solution was evaporated, and the solid residue was recrystallized from ethanol. The hydrocarbon (1.8 g., 90%) formed colorless needles of m.p. 164–165°, $\lambda_{\max}^{\text{EtOH}}$ 287 mμ (log ϵ 4.09) and 296 (4.09).

Anal. Calcd. for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.5; H, 6.5.

2,3,7,8-Tetrahydro-6,11-dimethylbenzo[*j*]fluoranthene (IX).—A mixture of 21 g. of IV in 150 ml. of absolute ethanol and 100 ml. of dry benzene, 6 g. of aluminum foil cut to small pieces, and 0.5 g. of mercuric chloride was refluxed for 18 hr., acidified with dilute hydrochloric acid, and extracted with benzene. The organic layer was washed with 10% hydrochloric acid and a saturated solution of sodium chloride, and concentrated *without* washing with water or drying. The residue was refluxed for 3 hr. with 100 ml. of glacial acetic acid and the acid was removed *in vacuo*. Recrystallization of the residue from ethanol gave crystals of m.p. 118–119°, which depressed the melting point of VIII considerably: $\lambda_{\max}^{\text{EtOH}}$ 318 mμ (log ϵ 4.38) and 334 (4.28).

Anal. Calcd. for $C_{22}H_{20}$: C, 92.9; H, 7.1. Found: C, 92.6; H, 7.2.

6,11-Dimethylbenzo[*j*]fluoranthene (VI).—A mixture of 5 g. of IX and 0.5 g. of palladium–charcoal (10%) was heated at 240° for 3 hr. and at 300–320° for 2 hr. Extraction with benzene gave a solution which exhibited a weak, green fluorescence. The residue of the extract was a yellow compound (4.5 g., 95%) which was chromatographed on neutral alumina (benzene as eluent) and recrystallized from ethanol, m.p. 173–174°. The absorption spectrum (in ethanol) showed the following bands: 244 mμ (log ϵ 4.78), 268 (infl.), 280 (4.23), 291 (3.58), 317 (4.25), 339 (4.00), 370 (3.58), and 390 (3.58).

Anal. Calcd. for $C_{22}H_{16}$: C, 94.3; H, 5.7. Found: C, 94.5; H, 5.9.

Some Nitronium Tetrafluoborate Nitrations

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In connection with other work in our laboratories we have had occasion to examine the competitive rates of nitration of several aromatic compounds with nitronium tetrafluoborate.[1] The nitrations were carried out at room temperature by adding dropwise 0.30 ml. of a 0.67 *M* solution of nitronium tetrafluoborate in tetramethylenesulfone to a solution containing 100 μl. of each of the aromatic compounds dissolved in 20 ml. of tetramethylene sulfone, while maintaining rapid stirring. The solutions were quenched with water and extracted with ether. The ether was washed with water, and dried; the ether was removed on the steam bath. The products were analyzed by gas chromatography on a 12 ft. × 0.25 in. o.d. column of DC-710 silicone fluid on firebrick (2:10) at a 200° temperature.

The relative rate constants obtained from the analyses, assuming the reaction to be first order in aromatic, are reported in Table I.

Table I

Competitive Nitrations with Nitronium Tetrafluoborate

Run	Rate ratio	Binary[a] value	Mixture[b] value	Lit.[c] value
1	Toluene–benzene	1.68 1.74	2.60	1.67
2	Benzene–chlorobenzene	7.6	3.32	7.1
3	Toluene–chlorobenzene	11.2	8.44	(11.8)
4	Benzene–fluorobenzene	1.89 2.08	1.50	2.22
5	Fluorobenzene–chlorobenzene	3.20	2.22	(3.21)
6	Chlorobenzene–bromobenzene	1.08		(1.17)
7	Toluene–fluorobenzene	6.72	3.80	(3.71)

[a] Nitration of a mixture of the two aromatics whose rate ratios are given. [b] Nitration of a mixture of benzene, toluene, fluorobenzene, and chlorobenzene. [c] See ref. 1; values in parentheses are calculated from the rates relative to benzene.

The close agreement of the values which we have obtained for binary mixtures, with the exception of fluorobenzene *vs.* toluene, with those reported by Olah[1] is in contrast with the values obtained from the four-component system.

In every case studied, however, the isomer distributions of the nitrated aromatics are in agreement with the values reported by Olah. With toluene, for example, we obtain *ortho–meta–para* ratios of 63:3:34 in close agreement with Olah's ratios of 65:3:32.

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(1) G. A. Olah, *et al.*, *J. Am. Chem. Soc.*, **83**, 4564, 4571, 4581 (1961).