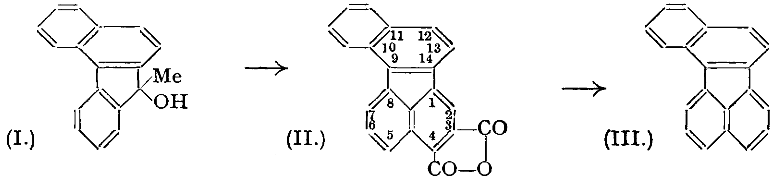
557. *A New Synthesis of* 10 : 11-*Benzofluoranthene.*

By Neil Campbell, N. M. Khanna, and A. Marks.

10 : 11-Benzofluoranthene has been synthesised from 9-methyl-3 : 4-benzofluoren-9-ol and maleic anhydride and found to be identical with products obtained in various ways by Zinke and Pack (*Monatsh.*, 1949, **80**, 213), von Braun and Kirschbaum (*Ber.*, 1921, **54**, 597), and Dansi and Ferri (*Gazzetta*, 1941, **71**, 648).

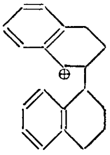
10 : 11-Benzofluoranthene (III) has been synthesised and its structure determined by Orchin and Reggel (*J. Amer. Chem. Soc.*, 1947, **69**, 505; 1951, **73**, 436). We have now prepared it by heating 9-methyl-3 : 4-benzofluoren-9-ol (I) with maleic anhydride and decarboxylating the resulting 10 : 11-benzofluoranthene-3 : 4-dicarboxylic anhydride (II) (cf. Campbell and Wang, *J.*, 1949, 1513). The identity of the hydrocarbon was established by comparison of its trinitrobenzene derivative with an authentic sample kindly supplied by Dr. Reggel. The Diels–Alder reaction results in ring closure on the benzene and not the naphthalene moiety presumably owing to the inactivity of the available β-position of the latter. The product is fully aromatic and not a dihydro-hydrocarbon as might have been expected (cf. Campbell and Wang, *loc. cit.*).

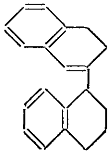


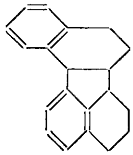
(I.) (II.) (III.)

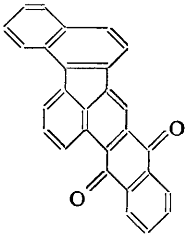
We have proved that three hydrocarbons prepared by other methods are undoubtedly 10 : 11-benzofluoranthene. Zinke and Pack (*Monatsh.*, 1949, **80**, 213) by the zinc dust distillation of a substance previously regarded as 1-hydroxyperylene obtained a yellow hydrocarbon, m. p. 165—167°, which they tentatively regarded as 10 : 11-benzofluoranthene. We have found a sample, which Professor Dr. Zinke was good enough to send us, to be identical with our compound.

Orchin and Reggel (*loc. cit.*, 1947; see also Bell and Hunter, *J.*, 1950, 2904) indicated that two other hydrocarbons might be 10 : 11-benzofluoranthene. von Braun and Kirschbaum (*Ber.*, 1921, **54**, 597) by the action of sulphuric acid on 1 : 2-dihydronaphthalene obtained a product, $C_{20}H_{20}$, which on dehydrogenation gave a hydrocarbon, $C_{20}H_{12}$. Dansi and Ferri (*loc. cit.*) by the action of aluminium chloride on tetralin obtained a substance $C_{20}H_{20}$, which on dehydrogenation gave a hydrocarbon, $C_{20}H_{12}$, identical with that of the German workers (Dansi and Reggiani, *Gazzetta*, 1948, **78**, 801). We have repeated the work of von Braun and Kirschbaum and have found their final product to be identical with 10 : 11-benzofluoranthene. It follows that the hydrocarbon of the Italian workers is likewise 10 : 11-benzofluoranthene. The statement by Bell and Hunter (*loc. cit.*) "that a true dinaphthylene has still to be described" is thereby confirmed. Further since we effected dehydrogenation under mild conditions (chloranil in boiling xylene) von Braun and Kirschbaum's compound $C_{20}H_{20}$ must be an octahydro-10 : 11-benzofluoranthene, and we suggest it is probably 1 : 2 : 3 : 4 : 9 : 12 : 13 : 14-octahydro-10 : 11-benzofluoranthene (VI). Polarisation of the ethylenic double bond in 1 : 2-dihydronaphthalene will give $-\overset{\oplus}{\underset{(1)}{C}}H-\overset{\ominus}{\underset{(2)}{C}}H-$ which will combine with a proton to form a carbonium ion $-\overset{\oplus}{\underset{(1)}{C}}H-\underset{(2)}{CH_2}-$. Interaction of the carbonium ion and the polar compound will afford the dimeric carbonium ion (IV) (cf. Whitmore, *Ind. Eng. Chem.*, 1934, **26**, 94). Passage of (IV) into the octahydrobenzofluoranthene is more open to debate and might be effected by direct attack by the positive centre followed by elimination of a proton, or a proton might first be lost to give the unsaturated hydrocarbon (V). Ring closure would then result from the action of the sulphuric acid on the double bond, followed by interaction with the other "half" of the molecule. If the second alternative is indeed the mode of action it would add to the very few known instances of vinyl compounds undergoing cycloisomerisation (Bergmann, *Chem. Reviews*, 1941, **29**, 529; Cook and Lawrence, *J.*, 1936, 1431). The ultra-violet absorption spectrum of the octahydrobenzofluoranthene resembles that of tetralin and is thus in harmony with formula (VI) and clearly shows the absence of a double bond conjugated with a benzene ring.


(IV.)


(V.)


(VI.)


(VII.)

Heating 9-methyl-3 : 4-benzofluoren-9-ol with 1 : 4-naphthaquinone and acetic anhydride gives an adduct which is probably 10 : 11-benzonaphtho(2′ : 3′-3 : 4)fluoranthene-1′ : 4′-quinone (VII). It is assumed that the ring-closure takes the same course as outlined above and does not involve the naphthalene part of the molecule.

We have dehydrogenated Schroeter's octahydroanthracene, m. p. 73—74° (*Ber.*, 1924, **57**, 1990), to anthracene.

EXPERIMENTAL.

All chromatographic experiments were done on alumina (Brockmann), and fluorescence observations were made with a Hanovia ultra-violet lamp. A Hilger medium quartz spectrophotometer was used for the spectroscopic measurements.

10 : 11-*Benzofluoranthene from* 1 : 2-*Dihydronaphthalene.*—Crude "bisdialin" (von Braun and Kirschbaum, *loc. cit*), b. p. 135—141°/0·03 mm., was further purified chromatographically with benzene as solvent and developer. A pale yellow viscous oil was obtained which on trituration with ethanol yielded 1 : 2 : 3 : 4 : 9 : 12 : 13 : 14-octahydro-10 : 11-benzofluoranthene, colourless crystals (from ethanol), m. p. 90—92° (lit., 93°) (Found : C, 92·3; H, 7·7. Calc. for $C_{20}H_{20}$: C, 92·3; H, 7·7%). Light absorption in *n*-hexane : Max. 268 (log ε = 3·08) and 277 mμ. (log ε = 3·13) and min. 245 (log ε = 2·58) and 273 mμ. (log ε = 2·98). The substance (1·0 g.) with chloranil (3·8 g.) in boiling sulphur-free xylene (20 ml.) (15 hours) (cf. Barclay and Campbell, *J.*, 1945, 530) was dehydrogenated to 10 : 11-benzofluoranthene, which after chromatographic purification crystallised from ethanol in yellow needles, m. p. 162—163°, showing no depression when admixed with an authentic sample (see below) (Found : C, 94·7; H, 5·0. Calc. for $C_{20}H_{12}$: C, 95·2; H, 4·8). The ultra-violet absorption spectrum in *n*-hexane closely resembles that obtained by Orchin and Reggel (*loc. cit.*, 1947) and Dansi and Reggiani (*loc. cit.*). 10 : 11-Benzofluoranthene forms a picrate, orange-red needles m. p. 190—192°, and a *s*-trinitrobenzene derivative, orange needles (from ethanol), m. p. 216—218° (lit., 219·8—220·5°).

Synthesis of 10 : 11-*Benzofluoranthene.*—9-Methyl-3 : 4-benzofluoren-9-ol (1·0 g.), maleic anhydride (3·0 g.), and acetic anhydride (10 ml.) were boiled for 4 hours. The cooled solution deposited 10 : 11-*benzofluoranthene*-3 : 4-*dicarboxylic anhydride* (0·2 g.) which crystallised from 1-methylnaphthalene in orange-red needles, m. p. > 330° (Found : C, 81·5; H, 2·9. $C_{22}H_{10}O_3$ requires C, 82·0; H, 3·1%). Failure to undergo decarboxylation when heated with alkaline potassium ferricyanide confirmed that the substance is fully aromatic (cf. Campbell and Gow, *J.*, 1949, 1555). The anhydride and methanol with sulphuric acid gave the *dimethyl* ester, yellow needles (from methanol–benzene), m. p. 203—204° (Found : C, 76·0; H, 4·7. $C_{24}H_{16}O_4,CH_3{\cdot}OH$ requires C, 75·0; H, 5·0%). The anhydride (100 mg.) was intimately mixed with a large excess of calcium oxide and strongly heated. The yellow sublimate which rapidly separated was chromatographed in benzene. Development with light petroleum (b. p. 100—120°) gave a yellow zone which yielded 10 : 11-benzofluoranthene (70 mg.), compact prisms (from light petroleum), m. p. 163—164° (Found : C, 94·5; H, 5·1. Calc. for $C_{20}H_{12}$: C, 95·2; H, 4·8%). The substance in solution shows a bright green fluorescence and gives in warm concentrated sulphuric acid an olive-green solution.

10 : 11-*Benzonaphtho*(2′ : 3′-3 : 4)*fluoranthene*-1′ : 4′-*quinone.*—9-Methyl-3 : 4-benzofluoren-9-ol (1·0 g.), 1 : 4-naphthaquinone (4 g.), and acetic anhydride (20 ml.) were boiled for 2 hours. The *adduct* (50 mg.) separated and on sublimation gave scarlet prisms, m. p. >330° (Found : C, 87·5; H, 3·9. $C_{28}H_{14}O_2$ requires C, 87·5; H, 3·7%). It gives a greenish-brown colour with concentrated sulphuric acid and a deep blue vat with alkaline dithionite (hydrosulphite).

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