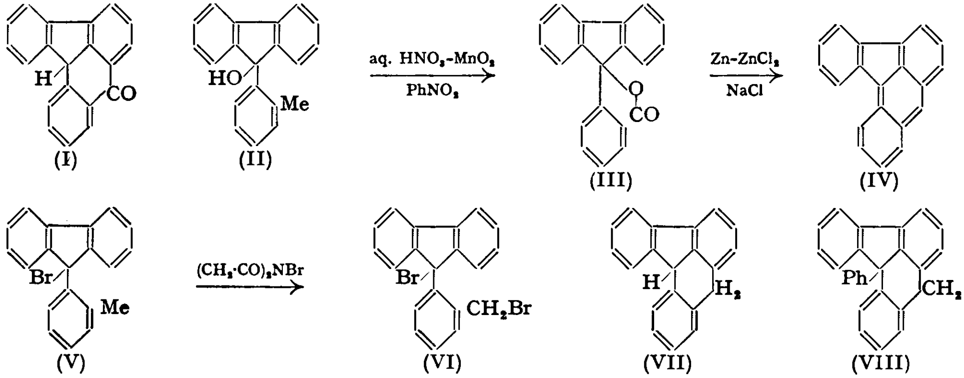
652. *Synthesis of Fluoranthenes. Part VIII.** *2 : 3-Benzofluoranthene.*

By H. W. D. Stubbs and S. Horwood Tucker.

2 : 3-Benzofluoranthene has been synthesised from *o*-diphenylenephthalide (III) by Clar's zinc-dust reduction method. An attempt to prepare the hydrocarbon from 9-bromo-9-(ω-bromo-*o*-tolyl)fluorene (VI) by the action of aluminium chloride in benzene gave chiefly a green hydrocarbon which may be 1 : 9-diphenylanthracene.

Although Weiss and Knapp [*Sitz. Wien. Akad., Kl.* II B (*Chemie*), 1932, **141**, 432] synthesised 1 : 9-phenylene-10-anthrone (1 : 4-dihydro-4-keto-2 : 3-benzofluoranthene) (I), they did not convert it into 2 : 3-benzofluoranthene (IV). We have synthesised (IV) from 9-hydroxy-9-*o*-tolylfluorene (II) (Weiss and Knapp, *loc. cit.*; Adams and Campbell, *J. Amer. Chem. Soc.*, 1950, **72**, 154) by oxidation to *o*-diphenylenephthalide (III), which was converted by the zinc-dust reduction method (Clar, *Ber.*, 1939, **72**, 1645) into 2 : 3-benzofluoranthene (IV).

Another attempt to synthesise 2 : 3-benzofluoranthene was made by treatment of the alcohol (II) with hydrobromic acid in glacial acetic acid, to give 9-bromo-9-*o*-tolylfluorene (V), which, by bromination with *N*-bromosuccinimide gave 9-bromo-9-(ω-bromo-*o*-tolyl)fluorene (VI). Aluminium chloride in boiling benzene reacted with (VI) to give a small amount of what was probably (IV); but the greater part was a pale green, strongly-fluorescent hydrocarbon, m. p. 135—138°, whose analytical results for carbon and hydrogen agree closely with those required for dihydrobenzofluoranthene, or, phenyl- or diphenyl-anthracene; but molecular-weight determinations indicated diphenylanthracene. Formation of an anthracene derivative is understandable if, after cyclisation involving the bromomethyl group and the 1-position of the fluorene skeleton, fission of the 5-membered ring occurs. The green hydrocarbon cannot be 1-phenylanthracene (m. p. 110°); and 9-phenylanthracene (synthesised as by Krollpfeiffer and Branscheid, *Ber.*, 1923, **56**, 1617) is excluded both by its melting point (155—157°) and by its different ultra-violet absorption (see figure).



(I) (II) (III) (IV)
(V) (VI) (VII) (VIII)

Absorption maxima (in Å) of the green hydrocarbon, of 9-phenylanthracene, and of anthracene are compared in the Table. It will be seen that with the green hydrocarbon there

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* Part VII, preceding paper.

is a bathochromic shift of the main absorption bands, relative to 9-phenylanthracene; this is approximately what would be expected for addition of one aryl substituent to 9-phenylanthracene.

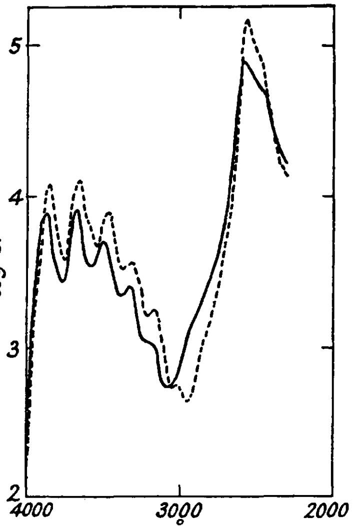
Green hydrocarbon (m. p. 135—138°)	3870	3670	3490	3320	3170	2580
9-Phenylanthracene	3840	3645	3465	3305	3160	2555
Anthracene	3745	3545	3380	3230	3080	2515

Formation of 1 : 9-diphenylanthracene could arise from reaction of the solvent, benzene, with the 9-bromine atom in (VI), to give 9-phenyl-9-(ω-bromo-*o*-tolyl)fluorene (VI; Ph instead of 9-Br); this then, by cyclisation, would give 1 : 4-dihydro-1-phenyl-2 : 3-benzofluoranthene (VIII), which, owing to molecular overcrowding round the 9-carbon atom of the fluorene nucleus, might rearrange to form 1 : 9-diphenylanthracene. The green hydrocarbon cannot be (VIII) since a compound of this formula would have a spectrum resembling that of fluorene and not of anthracene.

An attempt to prepare 1 : 4-dihydro-2 : 3-benzofluoranthene by reduction of *o*-diphenylenephthalide (III) failed.

EXPERIMENTAL.

o-Diphenylenephthalide (III).—9-Hydroxy-9-*o*-tolylfluorene (II) (10 g.), manganese dioxide (0·25 g.), concentrated nitric acid (170 ml.), water (340 ml.), and enough nitrobenzene to render the organic layer readily mobile were boiled together for 70 hours. The nitrobenzene was removed by steam-distillation, and the residue cooled, filtered, and dissolved in alcoholic sodium hydroxide. After dilution with four times its volume of water, and filtration, the filtrate was acidified. The precipitate was filtered off, washed, and dried, giving the phthalide (III) (5·5 g., 53%), m. p. 216—220°. Crystallisation from acetic acid raised the m. p. to 226°, with considerable loss of material (cf. Koelsch, *J. Amer. Chem. Soc.*, 1933, **55**, 3394, who gives 219—220°). The use of vanadium pentoxide (Rieve and Myers, *J. Amer. Chem. Soc.*, 1951, **73**, 1371) in place of manganese dioxide was of no advantage. Heating at 210° for 9 hours with 30% nitric acid alone gave a low-melting compound, apparently with breakdown of the molecule. Potassium permanganate in acetone had no effect on (II) (cf. Weiss and Knapp, *loc. cit.*); chromium trioxide in glacial acetic acid gave fluorenone (cf. Koelsch, *J. Amer. Chem. Soc.*, 1932, **54**, 3389; 1933, *loc. cit.*).



——— *The green hydrocarbon (m. p. 135—138°).*

- - - - - 9-*Phenylanthracene.*

2 : 3-*Benzofluoranthene.*—The phthalide (III) (3 g.) and pure zinc dust (6 g.) were ground together very thoroughly and mixed with powdered sodium chloride (6 g.). To this were added powdered zinc chloride (30 g.) and ten drops of water, and the temperature raised to 270° with vigorous stirring. During 8 minutes the temperature was allowed to rise to 340°, with stirring, the mass was cooled, decomposed with boiling water and a little acetic acid, and filtered, the residue washed well with, successively, hot water, dilute ammonia, and water, dried, and extracted with light petroleum (b. p. 60—80°), and this solution chromatographed (alumina, heated strongly in a vacuum, and cooled under carbon dioxide). A mixture of benzene and light petroleum (1 : 1 v/v) gave a yellow eluate (green fluorescence in ultra-violet light), which gave on evaporation a yellow residue, crystallising from light petroleum (b. p. 60—80°) in long golden-yellow needles of 2 : 3-*benzofluoranthene*, m. p. 145—146° (evacuated, sealed capillary) (Found: C, 95·15; H, 4·9. $C_{20}H_{12}$ requires C, 95·2; H, 4·8%). A mixed m. p. with a sample provided by Dr. Neil Campbell was the same (see following paper). The substance dissolves at once in concentrated sulphuric acid, giving a yellow solution which changes rapidly to violet; there is no further change on warming. A solution in light petroleum (b. p. 60—80°), exposed to light and air, rapidly deposited pale yellow crystals, m. p. 208—211° (without decomp.).

Synthesis of the Green Hydrocarbon, m. p. 135—138°.—9-*Bromo*-9-o-*tolylfluorene* (V). 9-Hydroxy-9-*o*-tolylfluorene (10 g.) was dissolved in glacial acetic acid (200 ml.), the solution cooled to room temperature, and saturated with dry hydrogen bromide (from bromine and tetralin; purified by red phosphorus and then phosphoric oxide). The product (9·7 g., 79%) gave (from glacial acetic acid) yellow platelets of 9-*bromo*-9-o-*tolylfluorene* (V), m. p. 142° (softening at 120°) (Found: C, 71·8; H, 4·4. $C_{20}H_{15}Br$ requires C, 71·7; H, 4·5%).

9-*Bromo*-9-(ω-*bromo*-o-*tolyl*)*fluorene* (VI). 9-Bromo-9-*o*-tolylfluorene (V) (1 g., 1·05 mols.) was dissolved in carbon tetrachloride (10 ml.), *N*-bromosuccinimide (0·5 g., 1 mol.) and benzoyl peroxide (trace) were added, and the mixture was boiled (irradiation by light) till all the *N*-bromosuccinimide had reacted (several hours). After filtration whilst hot, and extraction of the succinimide residue with boiling carbon tetrachloride, the combined filtrates were evaporated and the residue was crystallised from acetic acid (crude yield, 1 g., 86%). Recrystallisation from methyl cyanide or acetic acid slowly raised the m. p. to 158—161° (softening at 140°), giving yellow prisms of, essentially, 9-bromo-9-(ω-bromo-*o*-tolyl)fluorene (VI), contaminated with a little more-highly brominated impurity (Found: C, 54·1; H, 3·45. Calc. for $C_{20}H_{14}Br_2$: C, 58·0; H, 3·4%).

Attempted cyclisation of (VI). The compound (VI) (2 g.) was dissolved in dry benzene (50 ml.), and finely-powdered aluminium chloride (10 g.) was added. A purple complex formed, and the mixture was boiled until evolution of hydrogen halide ceased (20 minutes). After decomposition of the complex in the usual way, the benzene solution was evaporated, and the residue dissolved in light petroleum (b. p. 60—80°) and chromatographed (alumina). The first colourless eluate (blue fluorescence in ultra-violet light) gave, on evaporation, a residue which crystallised from ethanol in pale green needles (0·3 g.), m. p. 135—138° [Found: C, 94·3; H, 5·5%; *M*, (Rast, camphor) 311, 313, (ebullioscopic, benzene) 341. Calc. for $C_{10}H_{14}$: C, 94·45; H, 5·55%; *M*, 254. Calc. for $C_{26}H_{18}$: C, 94·5; H, 5·5%; *M*, 330]. Further treatment of the column with a mixture of light petroleum and benzene (1 : 1 v/v) gave a yellow eluate with a green fluorescence, probably a very small quantity of 2 : 3-benzofluoranthene.

Reduction of o-*Diphenylenephthalide* (III) *with Hydriodic Acid and Phosphorus.*—The phthalide (III) (1·9 g.), constant-boiling hydriodic acid (50 ml.), red phosphorus (7 g.), and xylene (20 ml.) were boiled for 72 hours. After filtration, the residue was extracted well with hot dilute sodium hydroxide solution, and the organic layer of the filtrate washed with water and then dilute sodium hydroxide solution. The combined alkaline solutions gave, on acidification, 9-*o*-carboxyphenylfluorene (Weiss and Knapp, *loc. cit.*; Koelsch, *loc. cit.*). The residue from evaporation of the organic layer gave, on chromatography in the usual manner, a very small amount of 2 : 3-benzofluoranthene.

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