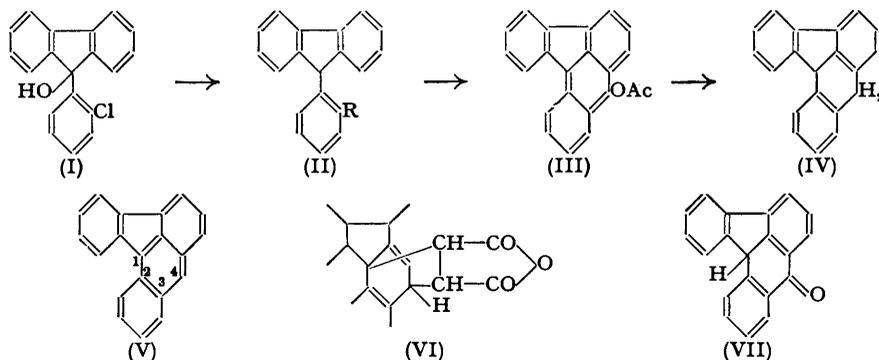


653. Synthesis of 2 : 3-Benzofluoranthene.

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Two syntheses of 2 : 3-benzofluoranthene are described.

THE only simple 2 : 3-benzofluoranthene derivative described in the literature is 1 : 9-phenylene-10-anthrone (1 : 4-dihydro-4-keto-2 : 3-benzofluoranthene) (VII) described by Weiss and Knapp (*Monatsh.*, 1932, **61**, 61). We have now synthesised 2 : 3-benzofluoranthene (V) and find it to be identical with the hydrocarbon synthesised by Stubbs and Tucker (see preceding paper). Fluorenone was condensed with *o*-chlorophenylmagnesium bromide to give 9-*o*-chlorophenylfluorene-9-ol (I) which with amalgamated zinc and hydrochloric acid yielded 9-*o*-chlorophenylfluorene (II; R = Cl). Replacement of the halogen atom by the cyano-group and hydrolysis of the nitrile gave *o*-9-fluorenylbenzoic acid (II; R = CO₂H) which was cyclised to 1 : 9-phenyleneanthranil acetate (III) by the method of Fieser and Hershberg (*J. Amer.*



Chem. Soc., 1937, **59**, 1028). Reductive hydrolysis with zinc and sodium hydroxide yielded a hydrogenated product, probably (IV), which on dehydrogenation gave 2 : 3-benzofluoranthene (V). This dehydrogenation also occurs when the dihydro-product is passed through a column of alumina. 9 : 10-Dihydroanthracene similarly is partly converted into anthracene.

Ring-closure of the acid chloride of *o*-9-fluorenylbenzoic acid by stannic chloride yielded an orange product, m. p. 280—282°, which seemed by analysis to be 1 : 9-phenylene-10-anthrone (VII). The melting point differs considerably from that of Weiss and Knapp (*loc. cit.*), and the cause of this discrepancy is being investigated.

Elbs pyrolysis of 1-benzoylfluorene also gave 2 : 3-benzofluoranthene, but the yield was poor and the product was contaminated with an oxygenated compound, C₄₀H₂₄O, possibly an

ether containing two benzofluoranthene residues. Attempts to prepare the benzoylfluorene from fluorene-1-carboxyl chloride and benzene were unsuccessful, and there were indications that the chloride had condensed with fluorene nuclei in preference to benzene. The failure seems to be due to the inactivity of the benzene since the chloride readily condenses with naphthalene (Fieser and Seligman, *J. Amer. Chem. Soc.*, 1935, 57, 2174) and with anisole. Fluorenone-1-carboxyl chloride reacts readily with benzene, presumably because the latter competes successfully with the deactivated fluorenone molecule. 1-Benzoylfluorene, however, was prepared in good yield from the acid chloride and excess of diphenylcadmium (Cason, *Chem. Reviews*, 1947, 40, 15).

2 : 3-Benzofluoranthene is obtained in golden-yellow crystals and gives with maleic anhydride a colourless adduct, presumably (VI).

Attempts were made to synthesise 2 : 3-benzofluoranthene by converting aceanthraquinone into the dimethyl glycol and heating the latter with maleic anhydride and acetic anhydride (cf. Campbell and Gow, *J.*, 1949, 1555). The quinone and methylmagnesium iodide gave only one dimethyl glycol, which failed to react with maleic anhydride. This is a strong indication that the glycol is the *cis*-compound (cf. Campbell and Gow, *loc. cit.*) and is in harmony with the formation of the *cis*-dimethyl glycol from phenanthraquinone and methylmagnesium iodide (Criegee *et al.*, *Ber.*, 1940, 73, 571).

Unsuccessful efforts were made to extend the work of Campbell and Gow (*loc. cit.*) by heating *trans*-7 : 8-dimethylacenaphthene-7 : 8-diol with citraconic anhydride and β -benzoylacrylic acid. The only product isolated from the last-named substance was the so-called "Pechmann dye" (von Pechmann, *Ber.*, 1882, 15, 885) formed by the self-condensation of the β -benzoylacrylic acid.

Reductive ring-closures of carboxylic acids have been effected by a mixture of potassium iodide and hydriodic acid (Miescher and Billeter, *Helv. Chim. Acta*, 1939, 22, 601). The method proved very convenient for converting 1-*o*-carboxybenzoylnaphthalene into a reduced product which on dehydrogenation gave 1 : 2-benzanthracene, but failed with 4- and 11-*o*-carboxybenzoylfluoranthene and 3-*o*-carboxybenzoylacenaphthene.

Some other methods for synthesising benzofluoranthenes were explored, without success. In an attempt to prepare 9-2'-ketocyclohexylanthracene, 2-chlorocyclohexanone was condensed with 9-anthrylmagnesium bromide (cf. Newman and Booth, *J. Org. Chem.*, 1947, 12, 737), but the only product isolated was anthracene, presumably owing to "enolisation" (cf. Bachmann and Kloetzel, *ibid.*, 1939, 3, 55).

Anthrone and Grignard reagents are known to yield the expected carbinols (Krollpfeiffer and Branschied, *Ber.*, 1923, 56, 1617; Sieglitz and Marx, *Ber.*, 1923, 56, 1619). We were, therefore, surprised to obtain from *o*-chlorophenylmagnesium bromide and anthrone, not a carbinol, but anthraquinone.

Like previous workers (*e.g.*, Pfeiffer and Blank, *J. pr. Chem.*, 1939, 153, 249; Tucker, Whalley, and Forrest, *J.*, 1949, 3194) we found in several instances that ketones reacted with Grignard reagents only when an excess of the latter (2—3 mols.) was used.

EXPERIMENTAL.

All chromatographic experiments were carried out with B.D.H. alumina (Brockmann), and fluorescence observations were made under a Hanovia lamp. New substances were analysed by Drs. Weiler and Strauss (Oxford).

Synthesis of 2 : 3-Benzofluoranthene from Fluorenone.—*o*-Bromochlorobenzene (29.3 g.) in dry ether (80 ml.) was added dropwise with stirring to magnesium (3.2 g.) in dry ether (20 ml.). Fluorenone (9 g.) was dissolved in benzene, dry ether (50 ml.) was added, and the solution was stirred into the Grignard solution. The mixture was boiled for an hour and was then worked up in the usual way, to give an oil which on trituration with light petroleum gave solid 9-*o*-chlorophenylfluoren-9-ol, plates (from methanol), m. p. 140—141° (yield, 75—82%) (Found: C, 78.6; H, 4.4; Cl, 11.6. $C_{18}H_{13}OCl$ requires C, 77.9; H, 4.4; Cl, 12.0%). The alcohol shows a pale heliotrope fluorescence and gives a wine-red colour in concentrated sulphuric acid. With acetyl chloride it forms the *acetate*, prisms (from ethanol-acetic acid), m. p. 145° depressed to 120° when admixed with the alcohol (Found: Cl, 11.3. $C_{21}H_{15}O_2Cl$ requires Cl, 10.5%). The alcohol (17.8 g.) was boiled for 3 hours with lightly amalgamated zinc dust (9 g.), granulated zinc (18 g.), acetic acid (500 ml.), and concentrated hydrochloric acid (100 ml.). Filtration and concentration of the solution gave an oil which crystallised when cooled and scratched. 9-*o*-Chlorophenylfluorene crystallised in prisms (from methanol), m. p. 76—77° (14.5 g., 85%) (Found: C, 82.0; H, 4.8. $C_{18}H_{13}Cl$ requires C, 82.4; H, 4.7%). The chloro-compound (12.3 g.) was converted into the cyano-compound by heating it in a sealed tube for 24 hours at 240° with cuprous cyanide (6 g.), pyridine (15 ml.), and acetonitrile (1.5 ml.). The mixture was poured into dilute acid and was extracted with benzene. The extract was washed successively with ammonia, water, acid, and water, and the volume was then reduced. The concentrate was passed through a column which was developed with benzene. A zone with a weak violet fluorescence at the foot of the

column yielded on elution *o*-9-fluorenylbenzonitrile, compact prisms [from light petroleum (b. p. 80—100°)], m. p. 115—116° (7.5 g.) (Found : C, 90.0; H, 4.9; N, 5.2. $C_{20}H_{13}N$ requires C, 89.9; H, 4.9; N, 5.2%). A deep-violet-fluorescing zone on the column gave unchanged chloro-compound, and a violet-fluorescing zone at the top gave the *amide*, elongated prisms (from light petroleum-benzene), m. p. 142—143° (0.2 g.) (Found : C, 84.5; H, 5.3; N, 4.9. $C_{20}H_{13}ON$ requires C, 84.2; H, 5.3; N, 5.0%). Carrying out the Rosenmund reaction in the presence of copper sulphate and tolunitrile gave a higher percentage of the amide at the expense of the nitrile (cf. Koelsch and Whitney, *J. Org. Chem.*, 1941, 6, 794).

The nitrile (0.3 g.), sodium hydroxide (3.6 g.), water (9 ml.), and ethylene glycol (36 ml.) were boiled for 24 hours. Acidification gave *o*-9-fluorenylbenzoic acid, plates (from acetic acid), m. p. 241—242° (8.8 g., 88%) (Found : C, 82.7; H, 4.9. Calc. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9%). The acid gives a red colour with concentrated sulphuric acid.

The acid (1 g.), acetic acid (6 ml.), acetic anhydride (5 ml.), and a trace of zinc chloride were boiled for 2 hours. Water was added to the hot solution until crystallisation occurred. The crude acetate (0.9 g.) was boiled for 22 hours with sodium hydroxide (30 ml.), toluene (10 ml.), and zinc dust (1.5 g.) which had been shaken with 0.1% copper sulphate solution. Benzene was added and the organic layer, after separation, was washed and passed through a column. A greenish-yellow band separated and on elution gave a product (0.25 g.) which was crystallised from light petroleum. Some of the crystals were separated mechanically into the orange-yellow 2 : 3-benzofluoranthene, m. p. 145—146°, identical with a sample prepared as below and with one kindly supplied by Dr. S. H. Tucker, and a colourless material, m. p. 139—140°, which was assumed to be the dihydro-compound (IV). The mixture of crystals (0.2 g.) was quantitatively dehydrogenated to 2 : 3-benzofluoranthene by boiling them for 13 hours with chloranil (0.2 g.) in sulphur-free xylene. 2 : 3-Benzofluoranthene crystallises from light petroleum in plates and forms a *picrate*, crimson prisms (from benzene), m. p. 215° (Found : N, 8.9. $C_{22}H_{15}O_7N_3$ requires N, 8.7%); and with maleic anhydride it gives an *adduct*, prisms, m. p. 220—235° (decomp.) (Found : C, 81.5; H, 4.1. $C_{24}H_{14}O_3$ requires C, 82.2; H, 4.0%).

o-9-Fluorenylbenzoic acid (0.5 g.) in dry benzene (5 ml.) and phosphorus pentachloride (0.45 g.) were gently warmed and after 15 minutes stannic chloride (0.2 ml.) in dry benzene (3 ml.) was added. 30 Minutes later the mixture was decomposed with ice and hydrochloric acid, and the product (0.22 g.) crystallised from xylene. 1 : 9-*o*-Phenylene-10-anthrone (1 : 4-dihydro-4-keto-2 : 3-benzofluoranthene) (?) was obtained in bright orange prisms, m. p. 280—282° (decomp.) (Found : C, 89.6; H, 4.3. Calc. for $C_{30}H_{18}O$: C, 89.6; H, 4.5%).

Synthesis of 2 : 3-Benzofluoranthene from 1-Benzoylfluorene.—The acid chloride of fluorene-1-carboxylic acid reacted with anisole at room temperature in the presence of aluminium chloride, to give a good yield of 1-*p*-anisoylfluorene, prisms (from ethanol), m. p. 104—105° (Found : C, 82.7; H, 5.6. $C_{31}H_{18}O_2$ requires C, 84.0; H, 5.3%).

Anhydrous cadmium chloride (7 g.) was added in portions to the Grignard reagent prepared from magnesium (1.8 g.), bromobenzene (10 ml.), and ether (50 ml.). When the Michler ketone test showed the absence of Grignard reagent, the ether was distilled off and replaced by benzene (20 ml.). A benzene solution of fluorene-1-carboxyl chloride (2 g.) was added dropwise to the solution, and the mixture was boiled for 4 hours, and then kept overnight. Decomposition with ice and mineral acid gave a benzene extract which was washed with carbonate, then water, and dried. Removal of the solvent yielded an oil, which on trituration with light petroleum gave 1-*benzoylfluorene*, plates (from methanol), m. p. 90—91° (Found : C, 88.4; H, 5.1. $C_{20}H_{14}O$ requires C, 88.9; H, 5.2%).

1-Benzoylfluorene (3.0 g.) was pyrolysed for 15 minutes at 420° in carbon dioxide, and the residue was dissolved in benzene and chromatographed on a column 36" × 1". Development with benzene gave a bright yellow band from which a mixture of yellow and colourless prisms (0.75 g.), m. p. 140—220°, was obtained. The yellow crystals were separated by dissolution in boiling light petroleum and were converted into a picrate, decomposition of which gave 2 : 3-benzofluoranthene, yellow prisms (from aqueous methanol), m. p. 144—145°, in poor yield (Found : C, 94.8; H, 4.9. $C_{20}H_{12}$ requires C, 95.2; H, 4.8%).

Reactions of 1 : 2-Benzacenaphthene-7 : 8-quinone.—The quinone (Liebermann, *Ber.*, 1911, 44, 208) crystallised from chlorobenzene in crimson prisms, m. p. 268—270° (lit., 270°), and gave a green colour with sulphuric acid. Crystallisation from "aged" tetralin yielded pale orange prisms, m. p. 285—286°, which gave a red colour with sulphuric acid and proved to be anthracene-1 : 9-dicarboxylic anhydride (Found : C, 76.4; H, 3.4. Calc. for $C_{18}H_8O_3$: C, 77.4; H, 3.2%).

The quinone (2.0 g.) was added in portions to a Grignard solution prepared from magnesium (0.84 g.), ether (30 ml.), and methyl iodide (5.0 g.). The mixture was boiled and kept over-night. Decomposition with ice and hydrochloric acid gave 7 : 8-dimethyl-1 : 2-benzacenaphthene-7 : 8-diol, pale yellow needles (from ethanol), m. p. 230—231°, showing both in the solid state and in solution a violet fluorescence (Found : C, 81.1; H, 5.9. $C_{18}H_{16}O_2$ requires C, 81.8; H, 6.1%). The glycol (0.5 g.) was suspended in dry benzene (100 ml.) and dry lead tetra-acetate (1.0 g.) was added. After 15 minutes' shaking the mixture was treated with a few drops of ethylene glycol. The clear solution was washed and dried. Evaporation gave 1 : 9-diacetylanthracene, yellow needles (from aqueous acetone), m. p. 156—157° (Found : C, 81.6; H, 5.5. $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.3%).

"Pechmann Dye."—*trans*-7 : 8-Dimethylacenaphthene-7 : 8-diol (0.1 g.), and β -benzoylacrylic acid (0.4 g.) were boiled in acetic anhydride (2 ml.) for 30 minutes. Cooling yielded the "Pechmann dye," elongated crimson prisms (0.04 g.) (Found : C, 76.1; H, 3.8. Calc. for $C_{20}H_{12}O_4$: C, 76.0; H, 4.0%).

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