627. *Syntheses of Benzo*[mno]*fluoranthene and Dibenzo*[k, mno]-*fluoranthene.**

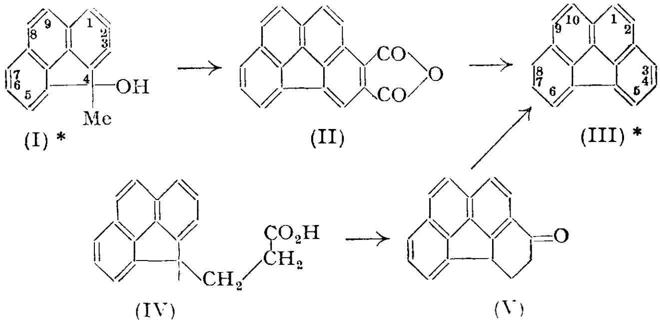
By Neil Campbell and David H. Reid.

The syntheses of benzo[*mno*]fluoranthene (III) and dibenzo[*k*, *mno*]fluoranthene (VIII) are described. These are the first examples known of hydrocarbons having four aromatic nuclei fused directly to a *cyclo*pentane ring.

So far as we are aware no hydrocarbon with four aromatic nuclei annealed directly to a *cyclo*pentane ring has hitherto been synthesised. We have synthesised two hydrocarbons of this type, namely, benzo[*mno*]fluoranthene * (2 methods) and dibenzo[*k*, *mno*]fluoranthene.*

4-Keto*cyclo*penta[*def*]phenanthrene * and methylmagnesium iodide gave the carbinol (I) which, when heated with maleic anhydride and acetic anhydride, underwent a Diels–Alder reaction to form benzo[*mno*]fluoranthene-3 : 4-dicarboxylic acid anhydride (II) (cf. Campbell and Wang, *J.*, 1949, 1513; Campbell and Gow, *J.*, 1949, 1555). The yield of anhydride was poor owing partly at least to extensive polymerisation. It is noteworthy that the tetrahydro-product initially formed was not isolated, but had been transformed into the more stable, fully aromatic compound. Decarboxylation of the anhydride gave benzo[*mno*]fluoranthene (III).

In the second synthesis reaction of vinyl cyanide with methyl 4-*cyclo*penta[*def*]phenanthrene-4-carboxylate (cf. Tucker and Campbell, *J.*, 1949, 2623) gave a nitrile which was hydrolysed to 4-2′-carboxyethyl-4-*cyclo*penta[*def*]phenanthrene (IV). This was cyclised to 3 : 4 : 5 : 5*a*-tetrahydro-3-ketobenzo[*mno*]fluoranthene (V), the cyclisation proceeding as easily as that of β-9-fluorenylpropionic acid (Campbell and Tucker, *loc. cit.*). Reduction of the ketone to the tetrahydrobenzofluoranthene and subsequent dehydrogenation gave benzo[*mno*]fluoranthene (III), identical with the product of the first synthesis.



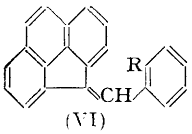
4-*cyclo*Penta[*def*]phenanthrene-4-carboxylic acid was prepared by condensing 4-*cyclo*penta[*def*]phenanthrene with methyl oxalate, followed by hydrolysis and oxidation of the resulting methyl 4-*cyclo*penta[*def*]phenanthrene-4-glyoxylate. The acid had the same m. p. as that prepared in a different way by Kruber (*Ber.*, 1934, **67**, 1000). The methyl ester was obtained in tautomeric forms : the keto-form, formed very pale yellow needles, m. p. 129°, and the enolic form bright yellow needles, m. p. 122°. The tautomerism was established by the preparation of a 2 : 4-dinitrophenylhydrazone and a benzoate. Analogous instances of tautomerism are found in ethyl 9-fluorenylglyoxylate (Kuhn and Levy, 1928, **61**, 2240) and ethyl *o*-fluorenylformylbenzoate (Wislicenus and Neber, *Annalen*, 1919, **418**, 274).

A related hydrocarbon, dibenzo[*k*, *mno*]fluoranthene * (VIII) was also synthesised. 4-*cyclo*Penta[*def*]phenanthrene condensed with *o*-chlorobenzaldehyde to give two products : the *o*-chlorobenzylidene derivative (VI, R = Cl) and a deep yellow substance. The latter is probably a diene (VII, R = Cl) formed from acetaldehyde which is obtained from the

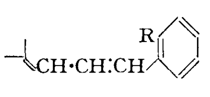
---

* (I), (III), and (VIII), and their derivatives, are named and numbered in accordance with Ring Index principles; (I), cf. R.I. 2570.

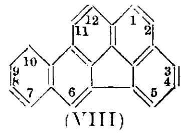
sodium ethoxide used as condensing agent (cf. De Fazi, *Gazzetta*, 1921, **51**, 328; Bergmann, *Ber.*, 1930, **63**, 1617, 2598; Rieveschl and Ray, *Chem. Reviews*, 1938, **23**, 314). Cyclisation of (VI) with a boiling concentrated solution of potassium hydroxide in quinoline gave the dibenzofluoranthene (VIII). A better yield was obtained when the bromobenzylidene compound (VI, R = Br) was used.



(VI)



(VII)



(VIII)

EXPERIMENTAL

Adsorptions were effected on alumina (Brockmann) and, unless otherwise stated, fluorescence observations were made in ultra-violet light from a Hanovia lamp. Analyses were by Drs. Weiler and Strauss, Oxford.

First Synthesis of Benzo[mno]*fluoranthene*.—4-Keto*cyclo*penta[*def*]phenanthrene (0·75 g.) in ether (4 c.c.) and benzene (6 c.c.) was added to the Grignard reagent prepared from magnesium (0·13 g.) and methyl iodide (0·768 g.) in ether (3 c.c.). The solution was boiled for 40 minutes and was then poured on crushed ice (2·0 g.). Working up the mixture in the usual manner gave *4-hydroxy-4-methyl*cyclo*penta*[def]*phenanthrene* (I) (0·615 g.) as prisms (from benzene or by sublimation) (Found: C, 86·9; H, 5·7. $C_{16}H_{12}O$ requires C, 87·2; H, 5·5%). The carbinol has a blue fluorescence both in the solid state and in benzene. With concentrated sulphuric acid it gives a green colour.

The carbinol (0·812 g.), maleic anhydride (3·6 g.), and acetic anhydride (12 c.c.) were boiled for 1 hour. The cooled solution overnight deposited *benzo*[mno]*fluoranthene-3 : 4-dicarboxylic acid anhydride* (II) (39 mg.), which on sublimation gave orange-yellow needles, m. p. 335—340° (decomp.) on slow heating (Found: C, 81·1; H, 2·9. $C_{20}H_8O_3$ requires C, 81·1; H, 2·7%). The anhydride gives a green colour in concentrated sulphuric acid and has an intense yellowish-green fluorescence in benzene or ethanol. The anhydride (19 mg.) was intimately mixed with lime (4·0 g.) and heated strongly. *Benzo*[mno]*fluoranthene* (III) distilled off and was obtained in yellow needles (4 mg.), m. p. 147—149°, from light petroleum (b. p. 60—80°), after purification on a column (0·6 × 20 cm.) with light petroleum (b. p. 60—80°) as solvent and developer (Found: C, 95·2; H, 4·7. $C_{18}H_{10}$ requires C, 95·5; H, 4·5%). It forms a *dipicrate* as golden-yellow needles (from ethanol), m. p. 205—210° (decomp.) (Found: N, 12·3. $C_{18}H_{10},2C_6H_3O_7N_3$ requires N, 12·3%). The hydrocarbon has a greenish-yellow and a blue fluorescence in the solid state and in solution, respectively. It gives a green colour with warm concentrated sulphuric acid, and with benzylidene dichloride and sulphuric acid affords a heliotrope colour which changes to a deep purple (cf. Levy and Campbell, *J.*, 1939, 1442).

Second Synthesis of Benzo[mno]*fluoranthene*.—4-*cyclo*Penta[*def*]phenanthrene (5·7 g.) and methyl oxalate (7·09 g.) were added to a methanolic solution of potassium methoxide [from potassium (2·35 g.) and anhydrous methanol (24 c.c.)], and the mixture was warmed until a homogeneous solution was obtained. The bulk of the methanol was slowly distilled off, and the remaining methanol and methyl oxalate were removed by distillation at 100°/10 mm. The residual methyl 4-*cyclo*penta[*def*]phenanthrene-4-glyoxylate was hydrolysed with boiling glacial acetic acid (40 c.c.), concentrated sulphuric acid (5 c.c.), and water (20 c.c.) for 60 minutes. The solution was poured into water (200 c.c.) and gave the *glyoxylic acid* (8·6 g.) as greenish-yellow needles (from acetic acid), m. p. 231—234° (decomp.) (Found: C, 71·1; H, 4·4. $C_{17}H_{10}O_3,C_2H_4O_2$ requires C, 70·8; H, 4·4%). 30% Hydrogen peroxide (1 c.c.) was added to the keto-acid (0·2 g.) in glacial acetic acid (2 c.c.) and the mixture kept for 120 hours. The yellow precipitate became straw-coloured, and on crystallisation from ethanol gave 4-*cyclo*-penta[*def*]phenanthrene-4-carboxylic acid as needles, m. p. 251—252° (decomp.).

Dry hydrogen chloride was passed into a suspension of the acid (1·10 g.) in absolute methanol (80 c.c.) until the weight of the mixture had increased by 3 g. The clear solution was boiled (12 hours) and methanol (50 c.c.) then removed by distillation. The residual liquid was poured into water (100 c.c.), and the resulting emulsion was extracted several times with benzene until the aqueous layer was clear. The combined benzene extracts were washed first with dilute aqueous sodium carbonate and then with water, and were finally dried (Na_2SO_4). Removal of the benzene yielded an oil which was dissolved in boiling light petroleum (b. p. 80—100°). The solution was cooled and immediately it became turbid it was placed in a bath of acetone–solid carbon dioxide. The *methyl* ester (0·8 g.) was deposited as needles, m. p. 61—62° (Found : C, 81·5; H, 5·1. $C_{17}H_{12}O_2$ requires C, 82·2; H, 4·9%). The sodium carbonate solution on acidification deposited unchanged acid (90 mg.).

Vinyl cyanide (0·22 c.c.) was added to the ester (0·79 g.) in 2-ethoxyethanol (3 c.c.) containing potassium hydroxide (11·2 g./litre of solution). After 1 hour 2-ethoxyethanol (2 c.c.) and 10N-potassium hydroxide (4·5 c.c.) were added and the mixture boiled for 1 hour. The mixture was then added to water (50 c.c.), and the solution boiled with charcoal and filtered. Acidification gave *4-2′-carboxyethyl-*4-cyclo*penta*[def]*phenanthrene* (IV) (0·75 g.), as needles (from benzene–acetone; 4 : 1 by vol.), m. p. 149—153° (Found : C, 80·9; H, 5·6. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·4%).

The acid (0·72 g.) was converted into the chloride by dissolving it in anhydrous benzene (4 c.c.) and adding phosphorus pentachloride (0·63 g., 10% excess). After 30 minutes the solution was boiled for 5 minutes and then cooled, and stannic chloride (0·64 c.c.; 100% excess) added. The mixture was kept for 40 minutes and then poured into concentrated hydrochloric acid (30 c.c.); the resultant mixture was extracted with benzene (40 c.c.) and chloroform (10 c.c.), and the extract washed twice with dilute sodium carbonate solution and then evaporated. The oily residue was dissolved in light petroleum (b. p. 80—100°) containing a little benzene. Evaporation to a small volume gave 3 : 4 : 5 : 5a-*tetrahydro-*3*-ketobenzo*[mno]*fluoranthene* (V) (52%), as pale yellow plates (from light petroleum–benzene; 3 : 1 by vol.), m. p. 159—161° (Found : C, 87·7; H, 5·0. $C_{18}H_{12}O$ requires C, 88·5; H, 5·0%). It affords a 2 : 4-*dinitrophenylhydrazone*, as orange-red needles (from glacial acetic acid), m. p. 293—296° (sublimes and decomp.) (Found : N, 13·4. $C_{24}H_{16}O_4N_4$ requires N, 13·2%). With concentrated sulphuric acid the ketone gives a bright yellow solution with a greenish-yellow fluorescence. The ketone (0·33 g.) in toluene (4 c.c.) was boiled for 60 hours with concentrated hydrochloric acid (4 c.c.), water (6 c.c.), acetic acid (2 c.c.), and 10% zinc amalgam (2 g.), concentrated hydrochloric acid (2 c.c. portions) being added after 6 and 18 hours. The toluene layer was washed with dilute sodium carbonate solution and then with water. The dried extract (Na_2SO_4) gave on evaporation 3 : 4 : 5 :5a-*tetrahydrobenzo*[mno]*fluoranthene* as plates (from ethanol), m. p. 78—79·5° (Found : C, 93·6; H, 6·1. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%). The hydrocarbon was heated for 90 minutes at 300° with 20% palladium–charcoal, and the product extracted with chloroform. Evaporation of the solvent gave benzo[*mno*]fluoranthene (113 mg.) as yellow needles (from light petroleum), m. p. 145—148°, showing no depression in melting point when mixed with the hydrocarbon prepared as above.

Properties of Methyl 4-cyclo*Penta*[def]*phenanthrene-*4*-glyoxylate*.—The crude ester from 4-*cyclo*penta[*def*]phenanthrene (1·90 g.) and methyl oxalate (2·36 g.) was dissolved in warm acetic acid (12 c.c.) and precipitated with concentrated sulphuric acid (2 c.c.) in water (8 c.c.). The precipitate was washed with water (100 c.c.), dried, and crystallised from light petroleum (b. p. 60—80°), giving *methyl* 4-cyclo*penta*[def]*phenanthrene-*4*-glyoxylate* (73%), as bright yellow plates which partially melt at 122°, then giving almost colourless needles which completely melted by 129° (Found : C, 78·3; H, 4·4. $C_{18}H_{12}O_3$ requires C, 78·3; H, 4·4%). In one experiment crystallisation from light petroleum–acetone gave very pale yellow needles, m. p. 129° (sharp). The ester forms a 2 : 4-*dinitrophenylhydrazone*, as yellow needles (from acetic acid), m. p. 240—243° (Found : N, 12·2. $C_{24}H_{16}O_6N_4$ requires N, 12·3%), and with sodium ethoxide in ethanol and subsequent addition of benzoyl chloride yields a *benzoate*, as yellow plates (from ethanol), m. p. 167—168° (Found : C, 78·5; H, 4·3. $C_{25}H_{16}O_4$ requires C, 79·0; H, 4·3%).

The acid (0·40 g.) was boiled with toluene (10 c.c.), concentrated hydrochloric acid (6 c.c.), water (2 c.c.), glacial acetic acid (3 c.c.), and 10% zinc amalgam (2 g.) for 60 hours, hydrochloric acid (2 c.c. portions) being added after 6 and 18 hours. The toluene layer was washed free from mineral acid with water, and the organic acid was then extracted with dilute sodium hydroxide solution (3 × 25 c.c.). Precipitation with hydrochloric acid afforded 4-(*carboxyhydroxymethyl*)-4-cyclo*penta*[def]*phenanthrene* (0·32 g.) as needles (from benzene), m. p. 211—212° (sublimes) (Found : C, 77·3; H, 4·3. $C_{17}H_{12}O_3$ requires C, 77·3; H, 4·6%).

Synthesis of Dibenzo[k, mno]*fluoranthene*.—4-*cyclo*Penta[*def*]phenanthrene (0·452 g.) was added to an ethanolic solution of sodium ethoxide [from sodium (0·081 g.) and absolute ethanol (5 c.c.)], and the temperature was raised to 75°. This temperature was maintained while a solution of *o*-chlorobenzaldehyde (0·335 g.) in absolute ethanol (2 c.c.) was added dropwise. The solution was boiled for 30 minutes, cooled, and poured into water (50 c.c.). The mixture was extracted with benzene (50 c.c.), and the dried extract (Na_2SO_4) on evaporation gave 4-o-*chlorobenzylidene*cyclo*penta*[def]*phenanthrene* (VI, R = Cl), as pale lime-green needles [from light petroleum (b. p. 60—80°)], m. p. 136—137° (Found: C, 84·2; H, 4·3; Cl, 11·4. $C_{22}H_{13}Cl$ requires C, 84·5; H, 4·2; Cl, 11·3%). The presence of a double bond was shown by the usual tests. The combined filtrates were passed through a column (20 × 2·2 cm.). Development with light petroleum gave 2 bands; a lower lime-green band with a yellow fluorescence, which yielded the above chlorobenzylidene compound (0·614 g.), m. p. 136—137°, and a upper, bright yellow zone with a yellow fluorescence which afforded 4-3′-o-*chlorophenylallylidene*cyclo*penta*[def]*phenanthrene* (VII, R = Cl) (51 mg.), m. p. 182—184° (Found: C, 84·4; H, 4·4; Cl, 11·2. $C_{24}H_{15}Cl$ requires C, 85·1; H, 4·5; Cl, 10·5%). It gives a green colour with sulphuric acid.

The *o*-chlorobenzylidene compound (0·27 g.) was boiled for 90 minutes in quinoline (2 c.c.) with potassium hydroxide (0·78 g.), and the mixture poured into concentrated hydrochloric acid (50 c.c.). The acid mixture was extracted with benzene (5 × 100 c.c.), and the extract washed successively with water, dilute sodium carbonate, and water. The dried solution (Na_2SO_4) was concentrated to 40 c.c. and passed through a column (20 × 2·1 cm.). Development with light petroleum (b. p. 60—80°) gave a pale yellow zone with a purple fluorescence from which *dibenzo*[k, mno]*fluoranthene* (35%), m. p. 147—149°, was obtained as pale green needles (from light petroleum) (Found: C, 95·0; H, 4·8. $C_{22}H_{12}$ requires C, 95·6; H, 4·4%). The *picrate* dissociates easily and could not be obtained pure; it was obtained as orange-red needles, m. p. 165—175° (decomp.) (Found: N, 9·8. $C_{28}H_{15}O_7N_3$ requires N, 8·3%). The *trinitrobenzene* compound separated from ethanol in yellow needles, m. p. 170—175° (decomp.) (Found: N, 8·8. $C_{28}H_{15}O_6N_3$ requires N, 8·6%). The hydrocarbon in solution has a strong purple fluorescence both in daylight and in ultra-violet light. With warm concentrated sulphuric acid it gives a green colour which changes to olive-green and finally to brown. Benzylidene dichloride, when added to a suspension of the hydrocarbon in concentrated sulphuric acid, gives a blue colour. The hydrocarbon does not form an adduct with maleic anhydride.

A similar series of reactions gave the following compounds: 4-o-*Bromobenzylidene*cyclo*penta*[def]*phenanthrene* (VI, R = Br) (66%) as lime-green needles (from light petroleum), m. p. 147—149° (Found: C, 73·7; H, 3·5; Br, 21·8. $C_{22}H_{13}Br$ requires C, 74·0; H, 3·7; Br, 22·4%), which in the solid state has a yellow-green and in solution a bluish-green fluorescence. 4-3′-o-*Bromophenylallylidene*cyclo*penta*[def]*phenanthrene* (VII, R = Br) as yellow prisms (from light petroleum), m. p. 198—200° (Found: C, 75·1; H, 3·6; Br, 20·8. $C_{24}H_{15}Br$ requires C, 75·2; H, 4·0; Br, 20·8%); this has a yellow fluorescence in the solid state and an intense yellowish-green fluorescence in solution. The bromobenzylidene compound with potassium hydroxide and quinoline gave dibenzo[*k*, *mno*]fluoranthene in 50% yield.

Thanks are expressed to the Carnegie Trust for the Universities of Scotland for the award of a scholarship to one of us (D. H. R.) and to the Anglo-Iranian Oil Co., Ltd., for a grant.

UNIVERSITY OF EDINBURGH. [*Received, April 24th*, 1952.]