The Rapson Triphenylene Synthesis and its Application to 1 : 2-3 : 4-Dibenzophenanthrene.

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[Reprint Order No. 6652.]

The structure of the intermediate in Rapson's triphenylene synthesis (*J.*, 1941, 15) has been confirmed as octahydrotriphenylene, formed by oxidative cyclodehydration; the same intermediate is obtained when cyclisation is effected with polyphosphoric acid or anhydrous hydrogen fluoride. An extension of the synthesis to 1 : 2-3 : 4-dibenzophenanthrene is described.

RAPSON (*J.*, 1941, 15) showed that treatment of 2-*cyclo*hex-1′-enyl-1-phenyl*cyclo*hexanol (I; R = Ph) with aluminium chloride gave a hydrocarbon which was dehydrogenated smoothly to triphenylene. On the basis of this reaction, and analysis of the hydrocarbon and its picrate, the hydrocarbon was formulated as 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrotriphenylene (II).

We have found that the alcohol (I) gives the same hydrocarbon on treatment with polyphosphoric acid or anhydrous hydrogen fluoride. This is surprising, if the hydrocarbon is indeed an octahydrotriphenylene, for such a compound could be formed from the alcohol (I) only by loss of hydrogen as well as water, and dehydrogenation accompanying cyclodehydration by the latter reagent is rare (cf. Cook, Ludwiczak, and Schoental, *J.*, 1950, 1112; Burr, Riefel, Kubico, and Gold, *J. Amer. Chem. Soc.*, 1948, **70**, 1073). However, the ultraviolet spectrum of the hydrocarbon (Fig. 1) confirms the structure assigned by Rapson; and it is certainly formed from the alcohol (I), and not from an impurity, since we have now obtained the alcohol crystalline and converted the pure material into the same hydrocarbon.

FIG. 1. *Ultraviolet spectra of Rapson's hydrocarbon* (*c*), *naphthalene* (*a*), *and* 1 : 2 : 3 : 4-*tetrahydrophenanthrene* (*b*), *in* 95% *ethanol.*

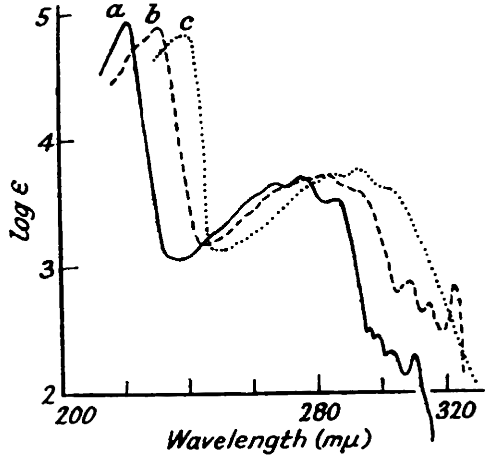


FIG. 4. *Ultraviolet spectra of phenanthrene* (*a*) *and the phenanthrene derivative* (VI), *in* cyclo*hexane.*

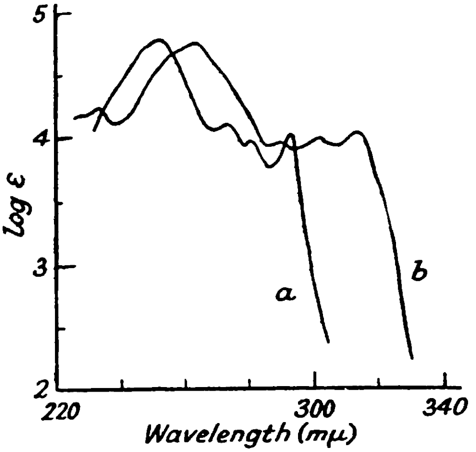


FIG. 2. *Ultraviolet spectra of the spiran* (III) (*a*) *and perinaphthene* (*b*), *in* cyclo*hexane.*

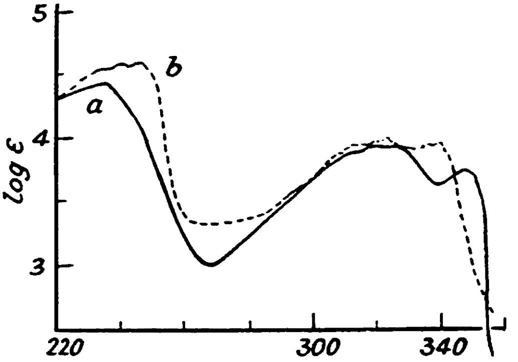
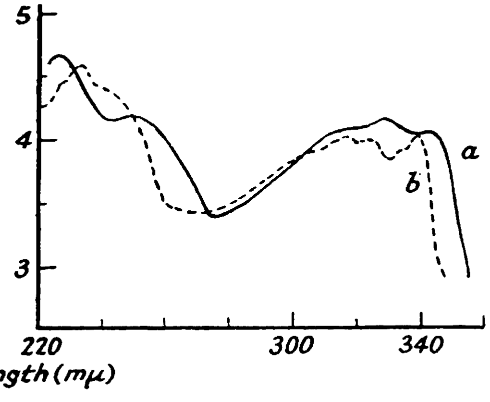
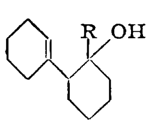


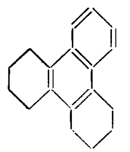
FIG. 3. *Ultraviolet spectra of the spiran* (IV) (*a*) *and benzanthrene* (*b*), *in* cyclo*hexane.*



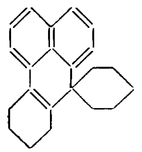
Polyphosphoric acid also catalysed the cyclodehydration of *cyclo*hexanone to dodecahydrotriphenylene (cf. Mannich, *Ber.*, 1907, **40**, 163) and, although the yield was poor, this provides a convenient route to triphenylene.



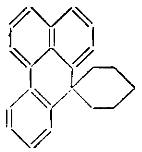
(I)



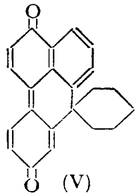
(II)



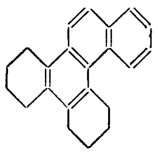
(III)



(IV)



(V)



(VI)

We then attempted to apply the Rapson synthesis to the preparation of 1 : 2-3 : 4-dibenzophenanthrene, by cyclisation of 2-*cyclo*hex-1'-enyl-1-1'-naphthyl*cyclo*hexanol

(I; R = 1-naphthyl). Ring closure with aluminium chloride or anhydrous hydrogen fluoride gave a hydrocarbon formed by loss of water only; but this appeared to be the spiran (III) since its ultraviolet spectrum closely resembled that of perinaphthene (Fig. 2). Dehydrogenation of the spiran gave, as expected, a hydrocarbon with an empirical formula corresponding to that of *cyclo*hexane*spiro*-7-benzanthrene (IV) and an ultraviolet spectrum very similar to that of benzanthrene (Fig. 3). Oxidation of the spiran (IV) gave a crimson quinone for which the structure (V) seems the most probable.

Cyclisation of 2-*cyclo*hex-1′-enyl-1-2′-naphthyl*cyclo*hexanol (I; R = 2-naphthyl) with aluminium chloride gave a small yield of the octahydro-1 : 2-3 : 4-di*cyclo*hexenophenanthrene (VI) which was smoothly dehydrogenated to the known 1 : 2-3 : 4-dibenzophenanthrene. The structure of the precursor (VI) follows from the resemblance of its spectrum to that of phenanthrene (Fig. 4).

EXPERIMENTAL

2-cyclo*Hex-1′-enyl-1-phenyl*cyclo*hexanol.*—The alcohol prepared by Rapson's method (*loc. cit.*) was fractionated. The fraction, b. p. 158—161°/1·25 mm., solidified during five weeks and then crystallised from light petroleum (b. p. 40—60°) in prisms, m. p. 59—60° (Found: C, 84·3; H, 9·5. Calc. for $C_{18}H_{24}O$: C, 84·3; H, 9·4%).

Octahydrotriphenylene.—(a) *With anhydrous hydrogen fluoride.* The preceding alcohol (22·5 g.) was dissolved in anhydrous hydrogen fluoride and left overnight. The residue after evaporation of the hydrogen fluoride was treated with picric acid (10 g.) in ethanol, giving octahydrotriphenylene picrate (6 g.), m. p. 196—197°, raised to 198° by recrystallisation from benzene (Rapson, *loc. cit.*, gives m. p. 185°). Octahydrotriphenylene was isolated by passing a solution of the picrate in benzene through an alumina column; it crystallised from ethanol, acetic acid, or light petroleum in needles, m. p. 125·5° (Rapson, *loc. cit.*, gives m. p. 129—130°; Bachmann and Struve, *J. Org. Chem.*, 1939, **4**, 472, give m. p. 120·5—122°) [Found: C, 91·4; H, 8·6. Calc. for $C_{18}H_{22}$: C, 90·7; H, 9·3. Calc. for $C_{18}H_{20}$ (II) : C, 91·6; H, 8·5%].

(b) *With polyphosphoric acid.* The alcohol (10 g.) was added to a stirred solution of phosphoric oxide (25 g.) in syrupy phosphoric acid (60 ml.) at 110—120°. After 1 hr., water was added, and the octahydrotriphenylene isolated as its picrate (1·4 g.), m. p. 193—196°.

Modified Mannich Synthesis of Triphenylene.—*cyclo*Hexanone (100 ml.) and polyphosphoric acid (400 ml.) were heated together at 160° for 12 hr. The mixture was cooled and poured on ice. The dark, very viscous oil which separated was isolated with chloroform and fractionated. The fraction, b. p. 180—210°/1·5 mm. (27 g.), partly solidified, and after crystallisation from ethanol formed needles, m. p. 210—220°. This impure dodecahydrotriphenylene was dehydrogenated over palladised charcoal at 340—360°; the product crystallised from toluene, to give triphenylene as brownish needles (1·2 g.), m. p. 194—197°. Purification by vacuum-sublimation or chromatography, followed by a further crystallisation, then gave colourless needles, m. p. 199°.

2-cyclo*Hex-1′-enyl-1-1′-naphthyl*cyclo*hexanol.*—Prepared in the same manner as the phenyl analogue (Rapson, *loc. cit.*), the alcohol was collected at 168—172°/0·4 mm. as an uncrystallisable gum (Found: C, 87·8; H, 8·65. Calc. for $C_{22}H_{26}O$: C, 86·2; H, 8·55%) and apparently contained a hydrocarbon impurity, formed by dehydration, judging by analysis of a fraction, b. p. 180—182°/0·4 mm. (Found: C, 91·0; H, 8·4. Calc. for $C_{22}H_{24}$: C, 91·6; H, 8·4%).

8 : 9 : 10 : 11-*Tetrahydro*cyclo*hexane*spiro-7-*benzanthrene.*—Cyclisation of the foregoing alcohol (61 g.) with aluminium chloride (55 g.) in carbon disulphide (100 ml.) following Rapson's procedure (*loc. cit.*), gave a series of fractions, b. p. 200° to 265° at 5 mm., all of which formed the same derivatives. The *trinitrobenzene adduct* of the spiran (III) crystallised from ethanol in red needles, m. p. 176° (Found: C, 67·1; H, 5·4; N, 8·3. $C_{28}H_{25}O_6N_3$ requires C, 67·3; H, 5·05; N, 8·4. $C_{28}H_{27}O_6N_3$ requires C, 67·1; H, 5·4; N, 8·4%). The *picrate* crystallised from ethanol in purple-brown needles, m. p. 163—164° (Found: C, 65·2; H, 5·5; N, 8·2. $C_{28}H_{25}O_7N_3$ requires C, 65·2; H, 4·9; N, 8·15. $C_{28}H_{27}O_7N_3$ requires C, 65·0; H, 5·3; N, 8·1%). Decomposition of the picrate with alkali gave the *spiran* (III) which crystallised from light petroleum in colourless prisms, m. p. 98° (Found: C, 91·5; H, 8·5. $C_{22}H_{24}$ requires C, 91·6; H, 8·4%). The same product was formed when the alcohol was treated with anhydrous hydrogen fluoride.

cyclo*Hexane*spiro-7-*benzanthrene* (IV).—The foregoing tetrahydro-compound (1·5 g.) was dehydrogenated over palladised charcoal at 320°. Crystallisation of the product from light petroleum (b. p. 100—120°) gave the *spiran* (IV) as prisms, m. p. 88—89° (1·2 g.), raised to

89—90° by recrystallisation from ethanol (Found: C, 93·0; H, 7·3. $C_{22}H_{20}$ requires C, 92·9; H, 7·1%). The *picrate* crystallised from ethanol in bright red needles, m. p. 141—142° (Found: C, 65·3; H, 4·9; N, 8·0. $C_{28}H_{23}O_7N_3$ requires C, 65·5; H, 4·5; N, 8·2%).

cyclo*Hexane*spiro-*7-benzanthrene-3* : *9-quinone* (V).—The hydrocarbon (IV) (0·5 g.) was boiled with acetic acid (10 ml.) and potassium dichromate (2 g.) for 10 min. The solution was poured into ice-water, and the precipitate collected, washed, and dried (0·4 g.). The *quinone* (0·4 g.) crystallised from acetic acid in crimson plates, m. p. 221—222° (Found: C, 83·6; H, 5·9; $C_{22}H_{18}O_2$ requires C, 84·05; H, 5·8%); it did not form an azine with *o*-phenylenediamine.

2-cyclo*Hex-1′-enyl-1-2′-naphthyl*cyclo*hexanol*.—2-Naphthylmagnesium bromide was prepared from 2-bromonaphthalene (40·4 g.) and magnesium turnings (6 g.) in anhydrous ether (200 ml.). Dry benzene (300 ml.) was then added, followed by *cyclo*hexenyl*cyclo*hexanone (35 g.). The mixture was left overnight and the product then decomposed by the addition of ice and ammonium chloride. The ether layer was distilled, giving the *alcohol* (20·6 g.), b. p. 200—202°/0·4 mm. (Found: C, 87·4; H, 8·3. $C_{22}H_{26}O$ requires C, 86·2; H, 8·55%).

1 : 2-3 : *4-Di*cyclo*hexenophenanthrene* (VI).—The foregoing alcohol (20·6 g.) in carbon disulphide (50 ml.) was added with shaking to powdered aluminium chloride (18·5 g.) in carbon disulphide (50 ml.). After 12 hr. at room temperature ice and hydrochloric acid were added, the carbon disulphide distilled off, di*cyclo*hexenophenanthrene isolated with chloroform, distilled under reduced pressure, and converted into the *picrate* which crystallised from ethanol, benzene, or light petroleum in dark red needles, m. p. 172°, depressed to 144—150° on admixture with the picrate of tetrahydro*cyclo*hexane*spiro*-7-benzanthrene (Found: C, 65·2; H, 4·5; N, 8·0. $C_{28}H_{25}O_7N_3$ requires C, 65·2; H, 4·9; N, 8·15%). The *hydrocarbon*, isolated by passing a solution of the picrate in benzene through an alumina column, crystallised from light petroleum in white prisms, m. p. 115—116° (Found: C, 92·7; H, 7·3. $C_{22}H_{22}$ requires C, 92·3; H, 7·7%). The trinitrobenzene adduct crystallised from light petroleum in orange needles, m. p. 173°.

1 : 2-3 : *4-Dibenzophenanthrene*.—Dehydrogenation of the di*cyclo*hexeno-compound gave 1 : 2-3 : 4-dibenzophenanthrene which crystallised from light petroleum in colourless needles, m. p. 115—116° (lit., 115—116°). The picrate crystallised from light petroleum in orange needles, m. p. 139—139·5° (lit., 140—140·5°). The trinitrobenzene adduct crystallised from benzene in yellow needles, m. p. 167°. Oxidation with chromic acid gave the quinone, crystallising from acetic acid in crimson needles, m. p. 232—236° (lit., 237—238°; 238—240°).

We are very grateful to the University of London for a research grant, and one of us (P. M. G. B.) to the Department of Scientific and Industrial Research for a Maintenance grant.

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[*Received, July 28th*, 1955.]