214. *Triphenylene: an Examination of Modified Mannich Syntheses, and an Improvement of the Rapson Synthesis.*

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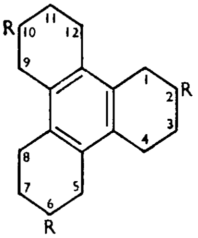
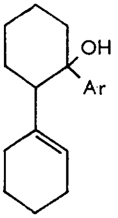
The cyclodehydration of *cyclo*hexanone and its 2-, 3-, and 4-methyl derivative to dodecahydrotriphenylene (I; R = H) and its methyl derivatives, respectively, has been examined.

Rapson's triphenylene synthesis is improved by converting the 1-aryl-2-*cyclo*hexenyl*cyclo*hexanols (II) into the epoxy-derivatives (III) and cyclodehydrating these with hydrobromic–acetic acid. Triphenylene, 1- and 2-methyltriphenylene, and 1 : 2-benzochrysene are thus prepared.

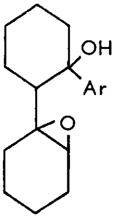
The simplest method of obtaining small quantities of triphenylene is by dehydrogenation of dodecahydrotriphenylene (I; R = H) prepared by cyclodehydration of *cyclo*hexanone with methanolic sulphuric acid.[1] Although the dodecahydrotriphenylene is obtained in a yield of only 6·5%, its isolation is simple and its dehydrogenation with palladised charcoal is almost quantitative. Attempts to improve this yield by means of alternative condensing agents have included the use of zinc chloride (3% yield),[2] thorium oxide at 300° (6·4% yield),[3] polyphosphoric acid (2% yield),[4] aluminium oxide at 320° (23% yield),[5] and a mixture of calcium and aluminium oxides with cerium oxide or thorium oxide at 290° (32% yield).[6] The last two processes are attractive and were investigated by us, but our best yield of dodecahydrotriphenylene amounted to only 13% and was obtained by heating purified *cyclo*hexanone with 13% of its weight of aluminium oxide containing 4·5% of thorium oxide at 280°/57 atm. for 32 hours. The presence of calcium oxide in this catalyst depressed the yield and quality of the product.



(I)



(II)



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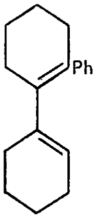

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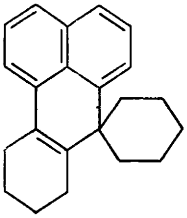
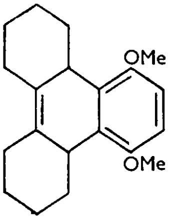


(V)



(VI)

Similarly, cyclodehydration of 4-methyl*cyclo*hexanone by mixed aluminium and thorium oxides at 285°, or by boiling methanolic sulphuric acid, gave dodecahydro-2 : 6 : 10-trimethyltriphenylene (I; R = Me), which was easily dehydrogenated to 2 : 6 : 10-trimethyltriphenylene. The structure of the latter hydrocarbon follows from its method of preparation, and is supported by a comparison of its electronic absorption spectrum with the spectra of triphenylene [7] and its 1- and 2-methyl derivative (see Table). 2-Methyltriphenylene shows a bathochromic shift of 20 Å without change in intensity, whereas the

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[1] Mannich, *Ber.*, 1907, **40**, 153.

[2] Kunze, *Ber.*, 1926, **59**, 2085.

[3] Komatsu and Masumoto, *Mem. Coll. Sci., Kyoto Univ.*, 1925, **19**, *A*, 15.

[4] Bavin and Dewar, *J.*, 1955, 4479.

[5] Petrov, *Bull. Soc. chim. France*, 1928, **43**, 1272; *J. Russ. Phys. Chem. Soc.*, 1928, **60**, 1435.

[6] B.P. 440,285/1935.

[7] Clar and Lombardi, *Ber.*, 1932, **65**, 1414.

1-isomer shows a bathochromic shift of 40 Å and a reduction in intensity. By analogy with similar compounds,[8] the spectroscopic effect of the 1-methyl group indicates that it is forced out of the plane of the remainder of the molecule. 2 : 6 : 10-Trimethyltriphenylene shows a bathochromic shift of 55 Å.

Attempted cyclodehydration of 2-methyl*cyclo*hexanone in the presence of oxides of aluminium and thorium at 285° gave none of the expected dodecahydro-1 : 5 : 9-trimethyltriphenylene, but large amounts of unchanged ketone were recovered and it is likely that steric hindrance by the methyl group prevented reaction. This suggested that 3-methyl*cyclo*hexanone should give 2 : 6 : 10-trimethyltriphenylene, rather than the 1 : 7 : 11-, 1 : 7 : 9-, or 1 : 5 : 9-trimethyl isomer, but no crystalline substance was isolated after refluxing of the ketone with methanolic sulphuric acid.

Ultraviolet absorption maxima (*m*μ) *in* EtOH ($10^{-5}\varepsilon$ in parentheses).

Triphenylene derivative	λ	λ	λ	λ
Unsubst.	284 (0·17)	273 (0·19)	257 (1·51)	248·5 (0·87)
1-Methyl	288 (0·14)	279 (0·16)	261 (1·05)	253·5 (0·74)
2-Methyl	285·5 (0·16)	275 (0·18)	259 (1·51)	250·5 (0·84)
2 : 6 : 10-Trimethyl	288·5 (0·17)	277·5 (0·20)	262·5 (1·50)	253·5 (0·87)

The self-condensation of *cyclo*hexanone is also used in the first stage of Rapson's triphenylene synthesis,[9] in which 2-*cyclo*hex-1′-enyl*cyclo*hexanone is treated with an arylmagnesium halide to give an alcohol (II) which undergoes oxidative [4] cyclisation with aluminium chloride. The resultant 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrotriphenylene is dehydrogenated with palladised charcoal. Triphenylene and its 2-methyl, and 1- and 2-methoxy-derivative were prepared thus, but the yields on cyclisation are low and the products need careful purification. Bavin and Dewar [4] recently modified this stage by using anhydrous hydrofluoric acid as the cyclisation agent.

A modification of this synthesis was suggested by Bradsher's cyclodehydration of 2-(1 : 2-epoxy*cyclo*hexyl)diphenyl to 1 : 2 : 3 : 4-tetrahydrotriphenylene by means of a mixture of hydrobromic and acetic acid.[10] 2-*cyclo*Hex-1′-enyl-1-phenyl*cyclo*hexanol (II; Ar = Ph) with monoperphthalic acid gave a crystalline epoxide (III; Ar = Ph) which was readily cyclodehydrated to 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrotriphenylene in 50% overall yield; dehydrogenation of the crude cyclisation product gave triphenylene in 50% yield (based on the *cyclo*hexanol derivative). Attempts to use 2-*cyclo*hex-1′-enyl-1-phenyl*cyclo*hexene (IV), formed as a by-product in the preparation of the corresponding alcohol, gave only 17% of triphenylene.

The preparation of 2-hydroxytriphenylene from 2-*cyclo*hex-1′-enyl-1-*p*-methoxyphenyl*cyclo*hexanol (II; Ar = *p*-methoxyphenyl) has been described previously by us,[11] and 2-methyltriphenylene was readily obtained from the analogous alcohol (II; Ar = *p*-tolyl). Similarly, 1 : 2-benzochrysene was obtained from 2-*cyclo*hex-1′-enyl-1-α-naphthyl*cyclo*hexanol (II; R = α-naphthyl); cyclisation of this alcohol with aluminium chloride, or anhydrous hydrofluoric acid, is known [4] to give only the spiran (V).

The method was less successful when applied to the preparation of 1-substituted triphenylenes. Thus 1-methyltriphenylene was obtained from the appropriate *cyclo*hexanol (II; Ar = *o*-tolyl), but with greater difficulty; and although attempts to prepare 1 : 4-dimethyltriphenylene by cyclisation of 2-*cyclo*hex-1′-enyl-1-*p*-xylyl*cyclo*hexanol gave small amounts of crystalline material whose analysis was correct for 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-9 : 12-dimethyltriphenylene, dehydrogenation of the crude cyclisation product gave a hydrocarbon, m. p. 176·5—177°; Fieser and Joshel [12] give m. p. 108·4—109·2° for 1 : 4-dimethyltriphenylene. Further, 1-hydroxytriphenylene could not be obtained from

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[8] Peters, *J.*, 1957, 646.

[9] Rapson, *J.*, 1941, 15.

[10] Bradsher, *J. Amer. Chem. Soc.*, 1939, **61**, 3131.

[11] Barker, Emmerson, and Periam, *J.*, 1955, 4482.

[12] Fieser and Joshel, *J. Amer. Chem. Soc.*, 1939, **61**, 2960.

2-*cyclo*hex-1′-enyl-*o*-methoxyphenyl*cyclo*hexanol (II; Ar = *o*-methoxyphenyl); instead, a small amount of triphenylene was obtained as end-product. This loss of a hydroxy(or methoxy)-group in the 1-position from a fully aromatic ring is consistent with our failure to isolate any product other than triphenylene after dehydrogenation of the decahydrodimethoxytriphenylene (VI), but it is not consistent with the smooth dehydrogenation of 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-9-methoxytriphenylene reported by Rapson.[9] Repetition of Rapson's work gave a mixture of triphenylene and 1-methoxytriphenylene which could be separated only by chromatography on alumina.

The use of *meta*-substituted Grignard reagents yields substituted *cyclo*hexanols which can cyclise in two ways. Thus, *cyclo*hex-1′-enyl-1-*m*-tolyl*cyclo*hexanol (II; Ar = *m*-tolyl) can give rise to 1- and 2-methyltriphenylene, but only the latter was isolated, although it is possible that some of the 1-isomer was formed. From *cyclo*hex-1′-enyl-1-β-naphthyl*cyclo*hexanol (II; Ar = β-naphthyl), however, small amounts of 1 : 2 : 3 : 4-dibenzanthracene were isolated, together with a major yield of 1 : 2-benzochrysene.

EXPERIMENTAL

Cyclisation of 2-cyclo*Hex-1′-enyl-1-phenyl*cyclo*hexanol*.—Monoperphthalic acid (4·3 g.) in ether (60 c.c.) was added to 2-*cyclo*hex-1′-enyl-1-phenyl*cyclo*hexanol (5·0 g.) in ether (50 c.c.) at 0°. The mixture was kept at 0° for 16 hr., then shaken with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and evaporated, giving 2-(1 : 2-*epoxy*cyclo*hexyl*)-1-*phenyl*cyclo*hexanol* (5·2 g.), m. p. 140° [from light petroleum (b. p. 60—80°)] (Found: C, 79·6; H, 8·6. $C_{18}H_{24}O_2$ requires C, 79·5; H, 8·8%).

The unpurified epoxide (5·1 g.) was refluxed with acetic acid (51 c.c.) and hydrobromic acid (34% w/w; 36 c.c.) for 12 hr. The brown solid which separated on cooling was dissolved in benzene, the solution was washed with aqueous sodium hydrogen carbonate and dried (Na_2SO_4), and the benzene was removed. Sublimation of the residue at 160—180° (bath)/10^{-2} mm., followed by two crystallisations of the sublimate from ethanol gave 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrotriphenylene (1·9 g.), m. p. 123° (Bavin and Dewar[4] give m. p. 125·5°) (Found: C, 91·6; H, 8·4. Calc. for $C_{18}H_{20}$: C, 91·5; H, 8·5%).

Dehydrogenation of the unpurified hydrocarbon with 30% palladised charcoal at 300° for 3 hr. and purification of the product by sublimation and crystallisation from benzene gave triphenylene, m. p. 198° (50%, based on the *cyclo*hexanol derivative).

2-*Methyltriphenylene*.—(*a*) *p*-Tolylmagnesium bromide with 2-*cyclo*hex-1′-enyl*cyclo*hexanone in ether gave 2-cyclo*hex-1′-enyl-1-*p*-tolyl*cyclo*hexanol* (50%), b. p. 135—136°/10^{-2} mm. (Found: C, 84·5; H, 9·7. $C_{19}H_{26}O$ requires C, 84·5; H, 9·6%). This alcohol was converted into 2-methyltriphenylene, m. p. 103° (from ethanol), in 32% yield without purification of the intermediate epoxide or its cyclisation product; Fieser and Joshel[12] gave m. p. 102·6—103·6°.

(*b*) Formed in an analogous manner, 2-cyclo*hex-1′-enyl-1-*m*-tolyl*cyclo*hexano* (53% yield) boiled at 130—135°/10^{-2} mm. (Found: C, 84·7; H, 9·9. $C_{19}H_{26}O$ requires C, 84·5; H, 9·6%) and gave the *epoxide* (90%), m. p. 104·5—106° (from ether) (Found: C, 80·1; H, 9·1. $C_{19}H_{26}O_2$ requires C, 79·7; H, 9·1%), which was cyclised to a yellow solid. This was dehydrogenated without purification. The product was sublimed (10^{-2} mm.) and twice crystallised from ethanol, giving 2-methyltriphenylene (35%), m. p. 102—103°.

1-*Methyltriphenylene*.—*o*-Tolylmagnesium bromide and 2-*cyclo*hex-1′-enyl*cyclo*hexanone in ether gave 2-cyclo*hex-1′-enyl-1-*o*-tolyl*cyclo*hexanol* (28%), b. p. 132—134°/10^{-2} mm. (Found: C, 83·6; H, 9·7%), whose *epoxide*, m. p. 172° (from ether) (Found: C, 80·2; H, 8·9%), was cyclised, the resultant hydrocarbon being distilled (10^{-2} mm.) and fractionally eluted from alumina with 3 : 7 benzene–light petroleum (b. p. 60—80°), to give 1-methyltriphenylene (15%), m. p. 93—94° (from ethanol) (Fieser and Joshel[12] give m. p. 93·4—94·2°) (Found: C, 93·4; H, 5·8. Calc. for $C_{19}H_{14}$: C, 94·2; H, 5·8%).

Cyclisation of 2-cyclo*Hex-1′-enyl-1-*p*-xylyl*cyclo*hexanol*.—*p*-Xylylmagnesium bromide and 2-*cyclo*hex-1′-enyl*cyclo*hexanone gave 2-*cyclo*hex-1′-enyl-1-*p*-xylyl*cyclo*hexanol (19%) as a viscous liquid yielding a crystalline *epoxide*, m. p. 133—134° (Found: C, 80·3; H, 9·2. $C_{20}H_{28}O_2$ requires C, 80·0; H, 9·3%). Cyclisation of this epoxide gave a gum which, when crystallised from glacial acetic acid, sublimed (10^{-2} mm.), and then twice crystallised from ethanol, gave 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydro*-9 : 12-*dimethyltriphenylene* (50%), m. p. 123—124 (Found: C, 90·5; H, 9·5. $C_{20}H_{24}$ requires C, 90·9; H, 9·1%). Dehydrogenation of this material gave a hydrocarbon (5%), m. p. 176·5—177° (Found: C, 92·3; H, 7·7%).

1 : 2-*Benzochrysene*.—(*a*) The Grignard reagent from 1-bromonaphthalene (36 g.) and 2-*cyclo*hex-1′-enyl*cyclo*hexanone (31 g.), after reaction together and working up in the usual way, gave naphthalene (22·5 g.) and 2-cyclo*hex-1′-enyl*-1-α-*naphthyl*cyclo*hexanol* (17 g.), b. p. 160—161°/10^{-2} mm., which very slowly solidified (Found: C, 86·1; H, 8·6. $C_{22}H_{26}O$ requires C, 86·3; H, 8·5%), m. p. 104—104·5° (from light petroleum). The crystalline *epoxide*, m. p. 159·5—160° (from ether–benzene) (Found: C, 82·0; H, 8·2. $C_{22}H_{26}O_2$ requires C, 82·0; H, 8·1%), was cyclised and the product was dehydrogenated. The resultant hydrocarbon was sublimed (10^{-2} mm.) and crystallised from acetic acid, giving 1 : 2-benzochrysene, m. p. 115—115·5°; Bradsher and Rapoport [13] give m. p. 115—116°.

(*b*) An analogous experiment with 2-naphthylmagnesium bromide gave 2-cyclo*hex-1′-enyl*-1-β-*naphthyl*cyclo*hexanol* as a viscous oil (Found: C, 87·5; H, 8·4%) which yielded a crystalline *epoxide*, m. p. 164—164·5° (from ether–benzene) (Found: C, 82·0; H, 8·1%). This epoxide was cyclised, the product was dehydrogenated, and the resultant material was sublimed, giving a solid, m. p. 103—107°, which was readily separated by elution with benzene–light petroleum ether from an alumina column into 1 : 2-benzochrysene, m. p. 115°, and 1 : 2 : 3 : 4-dibenzanthracene, m. p. 205°; Clar [14] gives m. p. 205° for the latter compound.

Cyclisation of 2-(1 : 2-*Epoxy*cyclo*hexyl*)-1-o-*methoxy*cyclo*hexanol*.—*o*-Methoxyphenylmagnesium bromide and 2-*cyclo*hex-1′-enyl*cyclo*hexanone gave 2-cyclo*hex-1′-enyl*-1-o-*methoxyphenyl*cyclo*hexanol*, b. p. 140—141°/10^{-2} mm., prisms, m. p. 68—70° (Found: C, 79·5; H, 9·0. $C_{19}H_{26}O_2$ requires C, 79·7; H, 9·1%); Rapson [9] obtained this material in semisolid form and gave no analytical data. The derived *epoxide* had m. p. 137° (from ether–benzene) (Found: C, 75·2; H, 8·4. $C_{19}H_{26}O_3$ requires C, 75·5; H, 8·6%) and gave traces of triphenylene as the only crystalline product after cyclisation followed by dehydrogenation.

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[13] Bradsher and Rapoport, *J. Amer. Chem. Soc.*, 1943, **65**, 1646.

[14] Clar, *Ber.*, 1929, **62**, 1574.