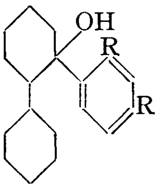
4. *1-Methoxy- and 2-Methoxy-triphenylene.*

By W. S. Rapson.

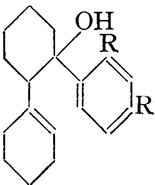
A convenient synthesis of triphenylene derivatives is described. 2-*cyclo*Hexenyl*cyclo*hexanone is condensed with an arylmagnesium halide, and the product cyclised by the action of stannic chloride or aluminium chloride. Disproportionation accompanies cyclisation, since an octahydrotriphenylene, which can be separated as its picrate, is the best-defined product of the reaction. The corresponding triphenylene is produced from the octahydrotriphenylene by dehydrogenation. Triphenylene itself, 2-methyltriphenylene, and 1- and 2-*methoxytriphenylenes* have been prepared by this method—the last substances to act as reference compounds in the orientation of other substituted triphenylenes.

Relatively few modes of entry into the triphenylene series have been worked out, and apart from 1- and 2-methyltriphenylenes (Fieser and Joshel, *J. Amer. Chem. Soc.*, 1939, **61**, 2958; Bachmann and Struve, *J. Org. Chem.*, 1939, **4**, 472) no reference substances are available for the orientation of substituted triphenylenes. The syntheses of 1-*methoxytriphenylene* and 2-*methoxytriphenylene* described here began from the observation by Nenitzescu and Curcaneanu (*Ber.*, 1937, **70**, 346) that 1-phenyl-2-*cyclo*hexyl*cyclo*hexanol (I; R = R′ = H) could be dehydrogenated by selenium in a sealed tube to yield triphenylene. The experiments of these authors have been repeated, but it has only been possible to confirm the small yields recorded by them. Under similar conditions no characterisable products could be obtained from 1-*p*-methoxyphenyl-2-*cyclo*hexyl*cyclo*hexanol (I; R = H, R′ = OMe) or from 1-*o*-methoxyphenyl-2-*cyclo*hexyl*cyclo*hexanol (I; R = OMe, R′ = H).

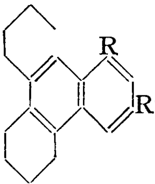
The dehydrogenation of 1-phenyl-2-*cyclo*hexenyl*cyclo*hexanol (II; R = R′ = H), prepared by the interaction of phenylmagnesium bromide and 2-*cyclo*hexenyl*cyclo*hexanone, was therefore explored. This could be made to yield triphenylene in small amounts only, and when the similar dehydrogenation of 1-*p*-methoxyphenyl-2-*cyclo*hexenyl*cyclo*hexanol (II; R = H, R′ = OMe) was carried out, the only product isolated was a trace of 2-*hydroxytriphenylene*. The cyclisation of (II, R = R′ = H) was therefore attempted as a preliminary to its dehydrogenation. Sulphuric acid in acetic acid effected only its dehydration—presumably to *1-phenyl-2-*cyclo*hexenyl*cyclo*hexene*—since only small yields of triphenylene were formed from the product on dehydrogenation. Both stannic chloride and aluminium chloride, however, gave rise to a mixture of products from which much greater yields of triphenylene were obtained on dehydrogenation. The mixture could



(I.)



(II)



(III.)

be separated with the aid of picric acid into a crystalline substance, formulated as 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrotriphenylene* (III ; R = R′ = H), and a liquid material, from which triphenylene was formed in appreciable amount on dehydrogenation but nothing homogeneous could be isolated.

A similar series of reactions beginning with 1-*p*-tolyl-2-*cyclo*hexenyl*cyclo*hexanol (II ; R = H, R′ = Me) led to 2-methyltriphenylene, and from the appropriate starting materials (II ; R = H, R′ = OMe) and (II ; R = OMe, R′ = H), 2-methoxytriphenylene and 1-methoxytriphenylene were prepared. In the latter syntheses aluminium chloride was preferable to stannic chloride as cyclising agent, since the latter effected slight chlorination. 2-Methoxytriphenylene has been demethylated to yield 2-hydroxytriphenylene, but 1-methoxytriphenylene offered considerable resistance to demethylation.

EXPERIMENTAL.

2-cyclo*Hexenyl*cyclo*hexanone*.—The following procedure is an improvement on the methods described by Mannich (*Ber.*, 1907, **40**, 154) and by Wallach (*ibid.*, p. 70; *Annalen*, 1911, **381**, 97). *cyclo*Hexanone was saturated with dry hydrogen chloride at room temperature (water cooling) and left overnight. The mixture, which solidified owing to the formation of the hydrochloride of 2-*cyclo*hexenyl*cyclo*hexanone, was warmed and shaken vigorously after addition of sodium hydroxide or pyridine in excess. After 2 hours the upper layer was separated, washed with water, dried, and distilled in a vacuum, giving an almost quantitative yield of 2-*cyclo*hexenyl*cyclo*hexanone, b. p. 142—145°/15 mm.

2-cyclo*Hexyl*cyclo*hexanone* (compare Wallach, *Annalen*, 1911, **381**, 95).—A palladium–strontium carbonate catalyst (10 g.) was added to a mixture of 2-*cyclo*hexenyl*cyclo*hexanone (40 g.) and alcohol (40 c.c.), which was then shaken with hydrogen at 1·5 atms.; reaction was complete in 15 minutes. The alcohol was evaporated from the filtered solution, and the residue distilled in a vacuum, giving 2-*cyclo*hexyl*cyclo*hexanone, b. p. 136—140°/11 mm.

The Action of Anisylmagnesium Bromide on 2-cyclo*Hexyl*cyclo*hexanone*.—Anisylmagnesium bromide (from 20 g. of *p*-bromoanisole), reacting with 2-*cyclo*hexyl*cyclo*hexanone (18 g.) in the usual way, gave a viscous oil (10 g.), which distilled at 205—210°/5 mm., some decomposition (dehydration) occurring. It crystallised slowly, but was not obtained analytically pure. When it was heated with selenium (17 g.) at 300—320° for 36 hours, dehydration and evolution of hydrogen selenide occurred, but no crystalline material could be isolated from the product obtained by vacuum distillation.

1-*Phenyl*-2-cyclo*hexenyl*cyclo*hexanol* (II; R = R′ = H).—2-*cyclo*Hexenyl*cyclo*hexanone (59 g.) was added to an ethereal solution of phenylmagnesium bromide prepared from bromobenzene (53 g.). Reaction was completed by warming on the water-bath for 1 hour, and after addition of dilute sulphuric acid and ice the ethereal layer was separated. It yielded a product (57 g.), b. p. 170—175°/3 mm., $n_D^{26°}$ 1·5485 (Found : C, 84·4; H, 9·7. Calc. for $C_{18}H_{24}O$: C, 84·4; H, 9·4%), which did not react with 2 : 4-dinitrophenylhydrazine. In an attempted dehydrogenation it was mixed (7 g.) with selenium (10 g.) and heated at 320—340° for 36 hours. On distillation a product (5 g.) was obtained which crystallised partly on cooling. The crystals were separated by the addition of methyl alcohol and filtration, and were identified as triphenylene (0·3 g.). The filtrate was returned to the dehydrogenation flask, the solvent evaporated, and the heating with selenium continued for 24 hours. After working up as before, a further small yield of triphenylene was isolated. No improvement in yield was effected in experiments at higher temperatures in a sealed tube. The use of sulphur led to extensive resinification and no triphenylene was isolated.

Attempts to cyclise 1-*Phenyl*-2-cyclo*hexenyl*cyclo*hexanol*.—(a) To a cold solution of the alcohol (20 g.) in acetic acid was added a solution of sulphuric acid (15 c.c.) in acetic acid (150 c.c.). A turbidity appeared suddenly after 5 minutes' shaking, and an oil separated. This was extracted from the diluted reaction mixture with benzene, washed, and dried, and the benzene distilled. The residue on distillation in a vacuum yielded an oil (16·5 g.), b. p. 155—160°/4 mm., $n_D^{26°}$ 1·5670 (Found : C, 90·6; H, 9·4. $C_{18}H_{22}$ requires C, 90·8; H, 9·2%). The yield was rapidly diminished if the treatment with the sulphuric acid was prolonged or if the reaction mixture was heated. This oil (13 g.) yielded triphenylene (1·5 g.) after repeated treatment with selenium.

(b) The alcohol (25 g.) was dissolved in carbon disulphide (75 c.c.) and added to aluminium chloride (26 g.) suspended in carbon disulphide (75 c.c.) and cooled in ice. A bright viole complex formed gradually as the mixture was shaken and allowed to come to room temperature.

After 5 hours, ice and dilute hydrochloric acid were added and, when the complex had decomposed, the carbon disulphide layer was separated, the carbon disulphide evaporated, and the residue distilled in a vacuum. A distillate (15 g.) was collected, b. p. 180—250°/4 mm., the later portions of which crystallised. It was dissolved in the minimum quantity of acetic acid, and a hot solution of picric acid (9 g.) in acetic acid added. A red picrate separated (9 g.), which, recrystallised from acetic acid, formed needles, m. p. 185°. It was decomposed with ammonia, yielding a white crystalline hydrocarbon, which formed prisms, m. p. 129—130°, after recrystallisation from acetic acid (Found : C, 91·2; H, 8·3. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%). It is formulated as 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydrotriphenylene,* since on heating at 300° for 2 hours with a palladium–charcoal catalyst it gave an almost quantitative yield of triphenylene. Dehydrogenation with sulphur also gave good yields of triphenylene, but in a crude form difficult to purify. The same difficulty has been observed with the products of other sulphur dehydrogenations in this series.

The filtrate from the picrate above was diluted with water and extracted with ether; the extracts, after being washed free from picric acid with alkali, yielded a liquid product (9 g.), b. p. 175—185°/4 mm. Nothing homogeneous could be separated from it, but it yielded triphenylene (2·5 g.) and oily by-products on catalytic dehydrogenation.

(c) Similar results were obtained when stannic chloride was used in place of aluminium chloride in the experiments above.

2-*Methyltriphenylene* (with E. Rollnick).—This was prepared in exactly the same way as triphenylene itself, the initial materials being *p*-tolylmagnesium bromide and 2-*cyclo*hexenyl*cyclo*hexanone. 2-*Methyl*-5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-*octahydrotriphenylene* was recrystallised from aqueous alcohol, forming plates, m. p. 93—94° (Found : C, 91·5; H, 8·4. $C_{19}H_{22}$ requires C, 91·2; H, 8·8%). Its picrate, recrystallised from acetic acid, formed red needles, which melted after slight sintering at 195·5°. It yielded 2-methyltriphenylene, m. p. 102°, on dehydrogenation with a palladium–charcoal catalyst.

1-*Methoxytriphenylene*.—Reaction between 2-*cyclo*hexenyl*cyclo*hexanone and *o*-methoxyphenylmagnesium bromide (from 40 g. of *o*-bromoanisole) was effected in the usual way, and the product worked up by vacuum distillation. The product (35 g.), b. p. 188—192°/6 mm., crystallised with extreme slowness and was so difficult to recrystallise that it was not obtained in an analytically pure condition. It failed to react with ketonic reagents, and after treatment with selenium at 320—340° for 48 hours no characteristic product was obtained. It was dissolved (30 g.) in carbon disulphide (100 c.c.) and added with shaking to an ice-cooled suspension of aluminium chloride (25 g.) in carbon disulphide (100 c.c.). The mixture was allowed to warm to room temperature; after 4 hours, dilute hydrochloric acid and ice were added and, when the solid red complex had been decomposed, the carbon disulphide layer was separated, and dried, and the carbon disulphide evaporated. On distillation of the residue in a vacuum a product was obtained (23 g.), b. p. 190—260°/4 mm., the greater part at 194—200°, which partly crystallised, especially the higher-boiling fractions. The deep brown picrate, prepared from an acetic acid solution, was decomposed by solution in pyridine, followed by addition of water, giving 1-*methoxy*-5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-*octahydrotriphenylene,* which, recrystallised from acetic acid, formed flat rhombohedral prisms (8 g.), m. p. 96—97° (Found : C, 85·2; H, 8·1. $C_{19}H_{22}O$ requires C, 85·7; H, 8·3%). Its picrate crystallised from acetic acid in deep brown needles, m. p. 204—205°. 1-*Methoxytriphenylene* was formed almost quantitatively when the above substance (2 g.) was mixed with a 20% palladium–charcoal catalyst (0·2 g.) and heated at 300° for 2 hours; it was sparingly soluble in the majority of solvents, and was recrystallised from aqueous pyridine or from dioxan, separating in plates, m. p. 172° (Found : C, 88·2; H, 5·5. $C_{19}H_{14}O$ requires C, 88·4; H, 5·4%). Its picrate dissociated with great ease, but separated when a saturated solution of 1-methoxytriphenylene in methyl alcohol was treated with picric acid, forming orange needles, m. p. 196—198°. 1-Methoxytriphenylene was unaffected after boiling for 10 hours with hydriodic acid (*d* 1·7), and even after addition of acetic acid to the reaction mixture and further prolonged boiling, only traces of phenolic material could be isolated.

The mother-liquor from the picrate of (III; $R = OMe$, $R' = H$) was diluted with water and extracted with ether, and the extracts freed from picric acid by shaking with sodium hydroxide solution. The ether was then evaporated and on distillation of the residue in a vacuum a fraction, b. p. 190—200°, was collected. It yielded further small amounts of 1-methoxytriphenylene on dehydrogenation, along with non-crystalline material which was not identified.

2-*Methoxytriphenylene*.—Anisylmagnesium bromide and 2-*cyclo*hexenyl*cyclo*hexanone yielded in the usual way a non-ketonic product, b. p. 193—197°/7 mm. It was a viscous oil which showed signs of decomposition during distillation and did not crystallise even after long standing. No characterisable products were obtained from it by treatment with selenium at 320—350°, but after 12 hours' heating in a sealed tube at 340° a trace of crystalline material was isolated by treating the viscous oil which constituted the bulk of the product with ether–light petroleum. This separated from aqueous methyl alcohol in white needles, m. p. 214° after sintering at 212°. It was later identified as slightly impure 2-*hydroxytriphenylene* (Found : C, 89·1; H, 4·7. $C_{18}H_{12}O$ requires C, 88·5; H, 4·9%).

The distilled product of the Grignard reaction above (25 g.) was dissolved in carbon disulphide (50 c.c.) and added to an ice-cooled suspension of aluminium chloride (25 g.) in carbon disulphide (50 c.c.). The procedure described under 1-methoxytriphenylene was then followed and the distillate, b. p. 190—260°/4 mm., obtained from the material in the carbon disulphide layer was converted into a bright red picrate. This was decomposed, giving 2-*methoxy*-5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-*octahydrotriphenylene*, which, recrystallised from slightly aqueous acetic acid, formed flat elongated prisms (8 g.), m. p. 120—121° (Found : C, 85·3; H, 8·0. $C_{19}H_{22}O$ requires C, 85·7; H, 8·3%). Its picrate was recrystallised from acetic acid, forming brick-red needles, m. p. 193—194°.

2-Methoxy-5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-octahydrotriphenylene (2 g.) was heated with a 30% palladium–charcoal catalyst at 300°. After 3 hours the evolution of hydrogen had ceased, and the 2-*methoxytriphenylene* was taken up in acetone, decolorised with charcoal, and precipitated by the addition of water. It was recrystallised by solution in acetone or pyridine, followed by addition of water; the emulsion initially formed rapidly set to a felted mass of needles, m. p. 97—98° (Found : C, 88·4; H, 5·6. $C_{19}H_{14}O$ requires C, 88·4; H, 5·4%).

2-*Hydroxytriphenylene*.—2-Methoxytriphenylene (2 g.) was boiled with a mixture of hydriodic acid (*d* 1·7, 8 c.c.) and acetic acid (4 c.c.) for 3 hours. The reaction mixture was poured into sodium sulphite solution, and ether added. 2-Hydroxytriphenylene was extracted from the ethereal layer with N-sodium hydroxide and precipitated from this solution with acid. It was recrystallised by solution in hot alcohol, followed by the judicious addition of water; it separated, on cooling, in small slender prisms, m. p. 213—215° (after previous sintering) (Found : C, 88·2; H, 5·1. Calc. for $C_{18}H_{12}O$: C, 88·5; H, 4·9%).

2-*Acetoxytriphenylene*, recrystallised from acetic acid, formed long slender prisms of rectangular outline, m. p. 129° (Found : C, 83·8; H, 4·9. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%).

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