58. *Overcrowded Polyalkylated Cyclohexane-1,3,5-triols, Their Dehydration Products, and Bi- and Tri-cyclic Derivatives.**

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The *cis*- and *trans*-isomers of 2,2,4,4,6,6-hexamethyl- and nonamethylcyclohexane-1,3,5-triol have been prepared and separated through selective sodium-borate complex formation with the *cis*-isomers. The *cis*-isomers also give cage-like phosphite esters. Dehydration of the nonamethylcyclohexane-1,3,5-triols proceeds stepwise. The diaxial *cis*-mono-olefindiol is formed with extreme ease and gives a cyclic sulphite and a cyclic borate; the diolefin-mono-ol is also formed cleanly but less readily, whereas further dehydration is more difficult and accompanied by drastic rearrangements.

OF the two stereoisomeric cyclohexane-1,3,5-triols only the higher-melting *cis*-isomer (m. p. 185°) gives a stable cage complex with sodium metaborate [1] and can therefore be easily separated from the lower-melting *trans*-isomer (m. p. 145°). It was of interest to explore the possibilities of this selective complex formation in isomer sets of alkylated cyclohexane-1,3,5-triols, perhaps less readily separable by other means, hoping to arrive at a general method of separation and assignment of configuration to the isomers.

In order to limit the number of possible stereomers, it was necessary to substitute all six hydrogen atoms in the positions 2, 4, and 6 with one and the same alkyl groups, and/or replace all three hydrogen atoms in positions 1, 3, and 5 with the same or another alkyl group. However, such molecules would become seriously overcrowded, having three substituents axial on one or both sides of the ring. The strain introduced would be enormous, considering that already a single OH · · · OH diaxial interaction represents an instability (ΔF) of 1·9 kcal./mole; [2] one OH · · · CH_3 diaxial interaction (ΔF) 2·4 kcal./mole; [3] and one single CH_3 · · · CH_3 diaxial interaction (ΔH) 3·7 kcal./mole.[4] Flattening of the ring by partial eclipsing and angle-widening may therefore occur [4] to relieve the interaction in the ideal conformation. Formation of adamantane-like cage-complexes with metaborates would therefore be expected to become more difficult than with *cis*-cyclohexane-1,3,5-triol itself.

The compounds selected for the present study were the simplest possible ones obtained by reduction and by a Grignard reaction with methylmagnesium iodide, respectively, from hexamethylcyclohexane-1,3,5-trione, which was recently shown [5] to avoid the axial methyl interaction by adopting a non-chair conformation (I).

Catalytic hydrogenation of hexamethylcyclohexane-1,3,5-trione on copper chromite at 200° and 200 atm. has been reported [6] to yield a triol, m. p. 251°, without statement of the stereochemistry. On Raney nickel we find that the hydrogenation is very incomplete even after 19 hours at 100° and 100 atm. The partially reduced product could be completely reduced with sodium borohydride to give a mixture of a high-melting triol (66%, m. p. 255°) and a low-melting triol (8%, m. p. 155°). During the reduction the higher-melting isomer formed directly a borate complex (III) from which it could be liberated with acids; the lower-melting formed no complex. For this reason we assume the former to have the *cis*-configuration, and the fact that it melts higher than the *trans*-isomer, as is also the case with the cyclohexane-1,3,5-triols themselves,[1] is taken as an indication of a conformation (IV) with all three hydroxyl groups in equatorial positions well placed for efficient intermolecular hydrogen-bonding. The *trans*-isomer (II) must have at least one axial hydroxyl

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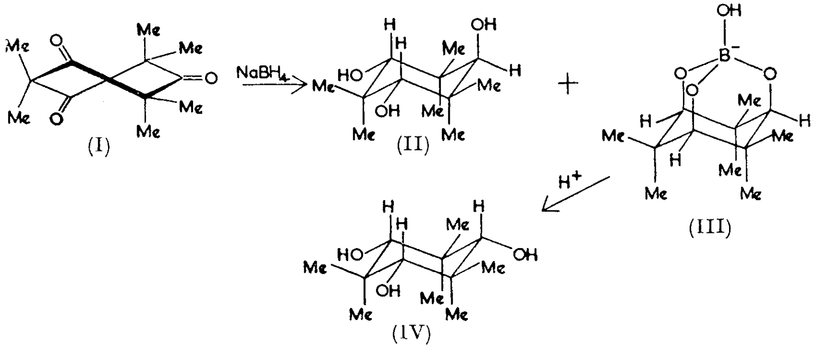
[1] Dale, *J.*, 1961, 922.
[2] Angyal and McHugh, *Chem. and Ind.*, 1956, 1147.
[3] Eliel and Haubenstock, *J. Org. Chem.*, 1961, **26**, 3504.
[4] Allinger and Miller, *J. Amer. Chem. Soc.*, 1961, **83**, 2145.
[5] Dale, *J.*, 1965, in the press.
[6] Ayres and Hauser, *J. Amer. Chem. Soc.*, 1942, **64**, 2461.

group. Direct reduction of the trione (I) with sodium borohydride gave only the *cis*-isomer (84%) and no *trans*-isomer. The conclusion that all three carbonyl groups are attacked by the same borohydride anion forming directly the cage complex may seem natural, but it is not easy to formulate a mechanism for such a reaction.

It should be noted that the borate complex (III) of the *cis*-hexamethylcyclohexane-1,3,5-triol did not form quantitatively, probably because of the expected deviation from the normal chair-conformation, or/and difficulty in inverting the tri-equatorial to the tri-axial form. A little of the free *cis*-isomer was always extracted with the *trans*-isomer, requiring repetition of the process. As the two isomers are also separable by fractional crystallization, the borate-complex formation has in this case only a limited interest as a separation method, but is of course useful for the assignment of configuration. With phosphorus trichloride this triequatorial *cis*-triol gave only a small yield of a cage-like phosphite,[7] analogous to the borate (III). This may be compared with the better yield of (VI) obtained with the tri-axial triol (IX) (see below).



(I) (II) (III) (IV)

The reaction of hexamethylcyclohexane-1,3,5-trione (I) with methylmagnesium iodide has been reported [8] to give after one hour's refluxing the nonamethylcyclohexane-1,3,5-triol of m. p. 258—260°, but no attempt was made to separate the isomers or to determine the configuration. We find that the reaction is very slow and complete only after 17 hours; after shorter reaction times the crude product could be fractionally crystallized to yield 5-hydroxyheptamethylcyclohexane-1,3-dione, m. p. 100°; a 3,5-dihydroxyoctamethylcyclohexanone of unknown (probably *cis*-) configuration, m. p. 210°; and a mixture of isomeric nonamethylcyclohexane-1,3,5-triols, m. p. 240°, inseparable by crystallization. By treating this mixture with sodium metaborate, a non-complexed triol, m. p. 275°, could be extracted (1%), but the major part of the mixture formed a very stable borate-complex (VII) from which the triol, m. p. 222°, could only be liberated (92%) by refluxing with dilute aqueous sulphuric acid.* From this behaviour with borate the former must have the *trans*-configuration (VIII) and the latter, although lower-melting, the *cis*-configuration (IX). The reason for the anomalous melting-point relation is probably that the hydroxyl groups occupy as much as possible the axial positions leaving the larger methyl groups equatorial. Thus, the *cis*-isomer, having three axial hydroxyl groups (IX), may be more internally hydrogen-bonded than the *trans*-isomer, which has one equatorial hydroxyl group (VIII) better placed for external hydrogen-bonding.

When the displacement of the triol (IX) from the complex (VII) with a strong borate-complexing agent like mannitol in very concentrated alkaline solution was attempted, the singly dehydrated compound (XII) was formed. The same crystalline mono-olefindiol

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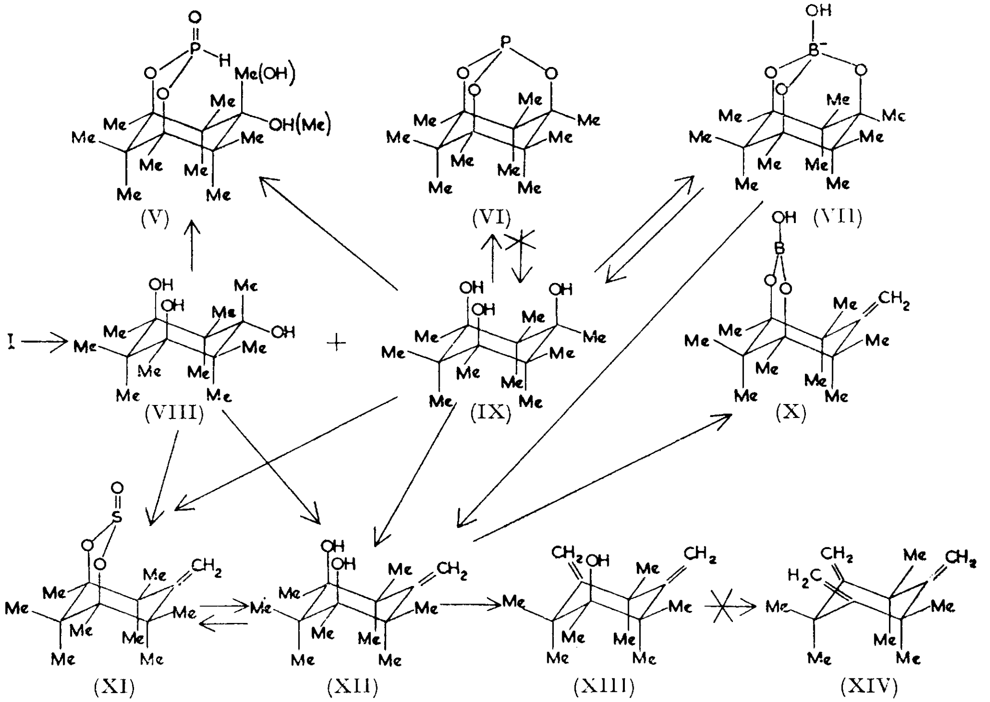
* It is noteworthy that the triol is not dehydrated in this purely aqueous medium, in which it is insoluble, although it is extremely acid-sensitive in anhydrous organic solvents.

[7] Stetter and Steinacker, *Chem. Ber.*, 1952, **85**, 451.

[8] Herzig and Erthal, *Monatsh.*, 1911, **32**, 505.

was obtained from both isomeric triols by dehydration with anhydrous acids under very gentle conditions. As the *trans*-isomer should in principle give rise to two different mono-olefindiols, it seems reasonable to postulate that the selectivity is due to a preferential elimination of the equatorial hydroxyl group in the conformation (VIII) whereby the larger methyl group can bend away from the axial position to form finally a methylene-group. Elimination of an axial hydroxyl group would be less profitable. On this basis the selectivity observed in the dehydration is almost a proof for the preferred axial positions of the hydroxyl groups in these compounds. A further indication is the ease with which the mono-olefin diol (XII) forms a cyclic ester (X) with boric acid; *cis*-cyclohexane-1,3-diol, which has preferentially the hydroxyl groups in equatorial positions, forms an unstable ester only under forcing conditions.[1]



Having the nonamethylcyclohexane-1,3,5-triols in hand, it appeared tempting to try a transformation *via* the trichloride (and subsequent reaction with methylmagnesium halide or dimethylzinc) to the unknown dodecamethylcyclohexane. However, treatment with phosphorus trichloride gave no chlorine-containing substance, but the very stable cage-like phosphite ester (VI) already mentioned of the *cis*-triol, and unstable cyclic phosphonates (V) of both isomers. In fact, when a mixture of these phosphorus compounds was heated with alkali, the phosphonates were destroyed, leaving the phosphite in very high purity. It is puzzling, however, that the *cis*-isomer forms only in part the stable phosphite. Maybe the three axial methyl groups flatten the ring so much that the phosphorus atom in compound (V) is too far away from the axial hydroxyl group. With thionyl chloride an extremely unstable unsaturated cyclic sulphite (XI) was obtained from both triols; it is derived from the same mono-olefindiol (XII) described above, which is also the product obtained with hydrogen chloride in ether at 40°. By heating the triol in ether solution, previously saturated at 20° with hydrogen chloride, to 70° in a sealed tube, some chlorine could be introduced, but rearrangements occur (see below).

A second possible route might have been to prepare the triolefin (XIV) and convert it into a spiro-linked triscyclopropyl derivative by the Simmons-Smith reaction,[9] as hydrogenation is known [10] to open the cyclopropane ring by rupturing the bond opposite to a geminal-disubstituted carbon atom

The first two dehydration steps are effected easily and cleanly. The mono-olefindiol (XII) is formed (cf. above) even in ether with a trace of acid; apparently a substantial part of the strain in the triol is relieved, although the product is still quite strained as evidenced by the abnormal position of the infrared band due to the hydrogen out-of-plane vibration of the double bond (11·1 against the normal value of 11·25 μ) and by the easy loss of just another mole of water with toluenesulphonic acid in refluxing benzene to produce the crystalline diolefinmono-ol (XIII), which now absorbs more normally in the infrared (11·3 μ). The last dehydration step could best be effected in refluxing acetyl chloride, but the liquid product obtained was proved by gas chromatography to be a complex mixture of rearranged hydrocarbons although there were strong infrared bands corresponding to the expected $\gt C=CH_2$ group. A hydrocarbon mixture obtained by treatment with strong acids in refluxing xylene showed no olefinic hydrogen absorption at all; as the substance remained volatile, this must mean rearrangement to give tetrasubstituted double bonds or formation of polycyclic isomers.

A study of Dreiding models [11] gives an idea of the reason for the stepwise dehydration. In fact, in the chair-form of a ring having only tetrahedral carbon atoms, such as structure (IX), all three axial methyl groups are 2·55 Å apart, while by the successive introduction of trigonal carbon atoms a progressive flattening of the ring occurs, whereby the methyl groups bend away from each other. Thus the mono-olefin (XII) has the two axial methyl groups next to the double bond 3·25 Å apart and the other two distances are 2·65 Å; the diolefin (XIII) has two distances of 3·15 Å and one of 2·70 Å; while the triolefin (XVI) has all distances increased to 3·25 Å. Of course, the increasing bond eclipsing which accompanies the ring-flattening [5] is not felt as a tension in Dreiding models, but the resulting Pitzer-strain may not be too important at this degree of flattening and in view of the smaller rotational barrier in single bonds next to double bonds (2·0 kcal./mole [12]) as compared with saturated compounds (~3 kcal./mole [12]). For the same reason,[5] non-chair conformations cannot of course be excluded in these olefinic compounds.

It is improbable from the above that the triolefin should be particularly unstable; the almost " isostructural " triketone (I) is in fact quite stable. The rearrangements that occur may be ascribed to carbonium ion rearrangements occurring under the sharp conditions necessary to take out the last hydroxyl group, as there is little more strain-relief available as a driving-force. To avoid carbonium ion formation, it was finally tried to convert the triketone (I) directly into the triolefin (XIV) by a Wittig reaction,[13] but without success.

EXPERIMENTAL

Reduction of Hexamethylcyclohexane-1,3,5-*trione* (I).—(*a*) *On Raney nickel.* The trione [5] was hydrogenated in ethanol at 100° and 100 atm. for 19 hr. in the presence of Raney nickel (Fluka). After removal of the ethanol and recrystallization from benzene–petrol, a solid, m. p. 59°, was obtained which showed both hydroxyl (2·85 μ) and two different carbonyl bands in the infrared spectrum. At 125° and 75 atm. for 5 hr. a closely similar solid, m. p. 52—63°, was obtained. A third experiment with the trione (20 g.) in ethanol (150 ml.) at 150° and a starting pressure of 100 atm. gave after 3 hr. a constant pressure of 88 atm. which did not change for another 7 hr. This pressure decrease was about half that expected, in excellent accord with the analysis (Found: C, 67·6; H, 9·6%) of the obtained solid, m. p. 45—60°, and its ultraviolet absorption

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[9] Simmons and Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 4256; Shank and Shechter, *J. Org. Chem.*, 1959, **24**, 1825.

[10] Shortridge, Craig, Greenlee, Derfer, and Boord, *J. Amer. Chem. Soc.*, 1948, **70**, 946.

[11] Dreiding, *Helv. Chim. Acta*, 1959, **42**, 1339.

[12] Wilson, *Proc. Nat. Acad. Sci. U.S.A.*, 1957, **43**, 816.

[13] Wittig and Schöllkopf, *Chem. Ber.*, 1954, **87**, 1318.

intensity (in cyclohexane) at 300 mμ (ε 40). Infrared bands were found at 2·85 (sharp, free OH), 5·79, 5·92 (C=O), and several strong bands from 9·4 to 10·1 μ (C–O).

(*b*) *With sodium borohydride.* The above-mentioned partially reduced trione (20 g.) was dissolved in methanol, and a solution of sodium borohydride (7 g.) in methanol, to which a little sodium hydroxide had been added, was dropped in slowly. The solution was then refluxed for 1 hr. After evaporation of the methanol, the white residue was ground in a mortar with five portions of benzene. These benzene extracts yielded a solid, m. p. 230°, which was a mixture of the *trans*-triol with some uncomplexed *cis*-triol. When re-treated with sodium borate and extracted as above it yielded the pure trans-2,2,4,4,6,6-*hexamethylcyclohexane*-1,3,5-*triol* (II) (8%) which, after recrystallization from hexane containing a little benzene, melted at 155° and showed no infrared carbonyl bands, but bands at 2·92 and 9·9 μ (Found: C, 66·4; H, 11·1. $C_{12}H_{24}O_3$ requires C, 66·6; H, 11·2%). A small first fraction melted at 250° (non-complexed *cis*-isomer).

The remaining solid complex (III) was heated with 2N-sulphuric acid to boiling for 15 min. The solid cis-2,2,4,4,6,6-*hexamethylcyclohexane*-1,3,5-*triol* (IV) (66%) was filtered off, washed with water, and recrystallized from acetone; it had m. p. 255°; λ 2·89, 2·95, and 9·85 μ (Found: C, 66·6; H, 11·1%).

When the trione (2·4 g.) was reduced directly with borohydride (0·7 g.), no *trans*-triol, but about 5% of *cis*-triol, was extracted with benzene. The total yield of *cis*-triol was 84%.

Reaction of cis-*Hexamethylcyclohexane*-1,3,5-*triol* (IV) *with Phosphorus Trichloride.*—A solution of phosphorus trichloride (2·6 g.) in benzene was added to a suspension of the triol (1·0 g.) in refluxing benzene. The reaction was slow. When no more hydrogen chloride was evolved, water was added and the two layers separated. The ether extracts of the aqueous layer, together with the benzene layer, yielded a yellowish paste from which a crystalline solid (0·1 g.) could be separated. It melted above 275° and showed no infrared band at 4·2 μ (no PH) and only a very weak band at 7·85 (trace of P=O), but a strong band at 9·7 (C–O–P) together with other strong bands at 10—12 μ; it was undoubtedly the cage-like *phosphite ester* of the *cis*-triol (Found: P, 11·2. $C_{12}H_{21}PO_3$ requires P, 12·7%). The paste showed a band at 4·1 and broad absorption at ~8 and 9·5—10·5 μ indicating phosphonate structures.

Methylation of Hexamethylcyclohexane-1,3,5-*trione* (I).—To a solution of methylmagnesium iodide, prepared from magnesium (7 g.) and methyl iodide (41 g.) in dry ether (200 ml.), was added a solution of the trione (18 g.) in dry ether (100 ml.). After the mixture had been refluxed for 17 hr., a solution of ammonium chloride in water was added slowly, the temperature being kept below 5°. After removal of solids by filtration, the ether layer was separated and the aqueous phase extracted with ether. The crude product (20 g. = 91%) was recrystallized from benzene; it then melted at 240°. No separation into *cis*- and *trans*-triol could be achieved by fractional crystallization; for the separation by borate complexing, see the next section.

When the reaction time was short (1 hr.), intermediate products could be isolated by fractional crystallization as follows. From benzene a first crop (5·5 g.), m. p. 230°, was obtained which contained (see below) a mixture of triols and an incompletely methylated dihydroxy-ketone, and a second crop (7·85 g.) which recrystallized from petrol as needles melting sharply at 100°. This latter compound showed infrared bands at 2·85 (OH) and 5·90 μ (C=O) and was undoubtedly the singly methylated compound 5-*hydroxy*-2,2,4,4,5,6,6-*heptamethylcyclohexane*-1,3-*dione* (Found: C, 68·9; H, 9·9. $C_{13}H_{22}O_3$ requires C, 69·0; H, 9·8%).

The first crop (above) was recrystallized from ethyl acetate and gave a first solid fraction consisting of an isomer mixture of *nonamethylcyclohexane*-1,3,5-*triols*, m. p. 240°. The mother-liquor deposited slowly another fraction which, after recrystallization from benzene, melted at 210°. It showed the infrared bands at 3·10 (OH), 5·89 (C=O), 9·04, and 9·25 μ (C–O) expected for the 3,5-*dihydroxy*-2,2,3,4,4,5,6,6-*octamethylcyclohexanone* (Found: C, 69·5; H, 10·9. $C_{14}H_{26}O_3$ requires C, 69·4; H, 10·8%).

Separation of cis- *and* trans-1,2,2,3,4,4,5,6,6-*Nonamethylcyclohexane*-1,3,5-*triol.*—The triol mixture, m. p. 240° (7 g.) was dissolved in methanol and added to a solution of boric acid (1·7 g.) and sodium hydroxide (1·5 g.) in a little water. If necessary, methanol should be added until complete dissolution is achieved. After 4 hours' refluxing the methanol was evaporated *in vacuo*. The residue was then ground with four portions of benzene. The benzene extracts yielded the *trans*-triol together with a little *cis*-triol. Re-treatment with borate and crystallization from petrol gave the pure trans-*triol* (VIII) (1%), m. p. 275° (Found: C, 69·4; H, 11·3. $C_{15}H_{30}O_3$ requires C, 69·7; H, 11·7%); $\lambda_{max.}$ 2·95, 3·07 (OH), and 9·20 μ (C–O).

The remaining solid was the very stable borate-complex (VII) of the other isomer and had to be boiled for 1 hr. with 2N-sulphuric acid. The insoluble cis-*triol* (IX) (92%) was filtered off, washed with water until neutral, dried, and recrystallized from benzene; it had m. p. 222° (Found: C, 69·6; H, 11·3%); $\lambda_{max.}$ 2·79, 3·10 (OH), 9·05, 9·28, and 9·43 μ (C–O).

An attempt was also made to liberate the *cis*-triol with a strong borate-complexing agent, mannitol. The *cis*-triol borate (VII) was dissolved in methanol, and a very concentrated solution of mannitol in water, containing some sodium hydroxide, was added; the mixture was refluxed for 15 hr. The methanol was then evaporated and the solid dissolved in water and extracted with carbon tetrachloride. A crystalline compound, m. p. 178°, was obtained, the infrared spectrum (3·05 (OH), 9·05, 9·25 (C–O), 6·15, 11·1 μ ($C{=}CH_2$)) and analysis of which showed it to be the cis-1-*methylene*-2,2,3,4,4,5,6,6-*octamethylcyclohexane*-3,5-*diol* (XII) obtained also (see below) by dehydration with acids (Found: C, 74·7; H, 11·6. $C_{15}H_{28}O_2$ requires C, 74·9; H, 11·7%).

Boric Ester (X) *of* cis-1-*Methylene*-2,2,3,4,4,5,6,6-*octamethylcyclohexane*-3,5-*diol*.—The olefinic diol (XII) (0·5 g.) and boric acid (4·0 g.) were refluxed in methanol for 5 hr. The methanol was evaporated and the residue extracted with benzene. On concentration, crystals of the *cyclic boric ester* (X), m. p. 260°, precipitated (Found: C, 67·8; H, 10·1. $C_{15}H_{27}BO_3$ requires C, 67·7; H, 10·2%); $\lambda_{max.}$ 2·93 (OH), 6·15, 11·12 ($>C{=}CH_2$), 7·0—7·4 (B–O), 9·08, and 9·25 μ (C–O).

Reaction of the Nonamethylcyclohexane-1,3,5-*triols with Phosphorus Trichloride*.—In an attempt to prepare nonamethyl-1,3,5-trichlorocyclohexane, a solution of phosphorus trichloride (5·2 g.; 400% excess) in benzene was added slowly to a solution of the mixed triols (2·0 g.) also in dry benzene. The mixture was heated; a strong evolution of hydrogen chloride was observed. When this was finished, the solution was cooled, water added, and the two layers separated. The aqueous phase was extracted with ether, the combined benzene–ether solutions washed with water, then sodium hydrogen carbonate, and dried. After removal of the solvents, a yellow oil was obtained. Addition of pentane precipitated colourless crystals (1·1 g.), m. p. 194°, which after recrystallization from benzene–pentane melted at 204°. The substance contained no chlorine and undoubtedly consisted of the cyclic phosphonate (V) or phosphite (VI) of the triol(s) (Found: C, 59·3; H, 9·0; P, 10·5. $C_{15}H_{29}O_4P$ requires C, 59·2; H, 9·6; P, 10·2%). In accordance with the phosphonate structure there were infrared bands at 4·15 (P–H) and 7·86 μ (P=O), but there were also bands at 7·70, 9·2, 9·35, 10·05, 10·9, 11·55, 11·85, and 12·7 μ.

In order to liberate the triol, the above phosphorus complex was heated with sodium hydroxide in refluxing methanol for 3 hr. The methanol was evaporated and water added. Extraction with cyclohexane gave a small yield of a crystalline compound, m. p. 275°, the infrared spectrum of which showed that the bands at 4·15, 7·70, 7·86, 10·05, 10·9 μ, to be assigned to the phosphonate (V), had disappeared. It was therefore the *phosphite ester* of the *cis*-triol (VI) (Found: C, 63·5; H, 9·6; P, 11·2. $C_{15}H_{27}O_3P$ requires C, 63·0; H, 9·5; P, 10·8%). Typical infrared bands were at 9·2, 9·35, 10·45, 11·55, 11·85, and 12·7 μ; judging from the intensities, the original mixture must have contained about equal quantities of phosphite and phosphonate.

Reaction of the Nonamethylcyclohexane-1,3,5-*triols with Thionyl Chloride, etc.*—When the triols were treated with thionyl chloride in pyridine, an exothermic reaction took place, but only a tarry material could be isolated. In refluxing benzene the evolution of hydrogen chloride and sulphur dioxide, lasting for 3 hr., indicated dehydration, but subsequent polymerization and destruction took place. In the cold the reaction also occurred with both isomers taken separately, yielding after evaporation an ill-defined chlorine-free oil from which very little of a crystalline substance precipitated in the cold. It was pressed off on a porous plate and melted at 182°; it could only be the *cyclic sulphite* (XI) of the olefinic diol (XII). Infrared bands (in KBr) were at 6·16 (C=C), 8·25 (S=O), 9·15 (C–O), 9·36 (S–O), 11·1 ($C{=}CH_2$), 11·33, and 13·4 μ. The S=O band was sharp in the solid but broad and displaced to 8·18 μ in carbon tetrachloride solution. Attempts to sublime the solid at 230°/1 mm. caused destruction; the sublimate contained always an oil. In water the sulphite hydrolysed to give the olefinic diol (XII) already described. When this olefinic diol was re-treated with thionyl chloride in cold benzene, the sulphite re-formed.

Similarly, no chlorine-containing products were obtained either with sulphuryl chloride, with hydrogen chloride–zinc chloride in benzene, or (see below) with hydrogen chloride in ether at 40°. Heating the triol in ether, previously saturated with hydrogen chloride at 20°, in a sealed tube at 70° for 8 hr., gave a liquid which contained no hydroxyl group, but double bonds (infrared spectrum) and only traces of chlorine. Gas chromatography proved it to be a complex mixture; skeletal rearrangements must have occurred. When this olefin was saturated with hydrogen chloride in ether solution at $-20°$ and the product worked up at room temperature, the resulting oil contained about 2 atoms of chlorine per molecule (Found: Cl, 22·9%). However, the infrared spectrum showed both olefin and carbonyl absorption.

Dehydration of Nonamethylcyclohexane-1,3,5-*triols*.—(*a*) Heating the *cis*-triol at 40° in ether containing some hydrogen chloride for 1 hr. produced the same crystalline *cis*-1-methylene-2,2,3,4,4,5,6,6-octamethylcyclohexane-3,5-diol (XII), m. p. 178°, described earlier. The *trans*-isomer did not react even at 50°.

(*b*) Heating either of the triols in methanol containing a little hydrogen chloride at 50° for one hour gave after evaporation a solid which was partially soluble in pentane. The insoluble part was again the olefinic diol (XII), while the concentrated pentane solution on being cooled deposited another crystalline compound, m. p. 89°. Its infrared spectrum showed bands at 2·95 (OH), 6·01, 6·13 (C=C), 9·17 (C–O), and 11·3 μ ($>$C=CH$_2$), and it was therefore 1,3-*bis-methylene*-2,2,4,4,5,6,6-*heptamethylcyclohexane*-5-*ol* (XIII) (Found: C, 81·0; H, 11·6. $C_{15}H_{26}O$ requires C, 81·0; H, 11·8%).

(*c*) Heating the triols for 10 hr. in refluxing benzene containing 3% of toluene-*p*-sulphonic acid gave the same diolefinic alcohol (XIII) as above as the main product.

(*d*) Dehydration over activated alumina at 350° at reduced pressure gave finally a hydroxyl-free liquid showing strong olefinic infrared absorption at 3·25, 6·08, 6·15, 11·2, and 11·3 μ (C=CH$_2$). After filtration through alumina and distillation, its composition approached that of the triolefin (Found: C, 87·7; H, 11·3. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%). However, g.l.c. showed that the liquid consisted of a complex mixture * (at least 8 different hydrocarbons).

(*e*) Heating with toluene-*p*-sulphonic acid in refluxing toluene or xylene, with subsequent chromatography on alumina, gave a liquid hydrocarbon mixture which did not even contain the infrared bands for the $>$C=CH$_2$ groups. It is not a dimer or a polymer, as judged from the volatility, but it must have undergone drastic rearrangements to a very wide variety of hydrocarbons, as shown by the complex gas-chromatogram * (2 main peaks with up to 12 minor peaks).

(*f*) The most gentle conditions for full dehydration were produced by heating the triol (10 g.) in refluxing acetyl chloride (50 ml.). There was a vigorous gas evolution and the reaction was finished after 3 hr. The deep red mixture was poured on ice and the acids neutralized with sodium hydrogen carbonate. Extraction with pentane and filtering through alumina gave a liquid showing the expected infrared bands for $>$C=CH$_2$ at 3·25, 6·09, 6·14, 11·17, and 11·26 μ. However, g.l.c.* revealed again that it was a mixture containing two main peaks together with at least five others; it was not possible to concentrate the main products by distillation.

(*g*) Attempts to prepare tosylates by reaction with toluene-*p*-sulphonyl chloride gave solids, m. p.s from 182 to 192°, which proved to be mixtures of the starting material, the triols (VIII) and (IX), and the olefinic diol (XII).

Attempts to Convert Hexamethylcyclohexane-1,3,5-*trione Directly into* 1,3,5-*Trimethylenehexamethylcyclohexane* (XIV).—Methylenetriphenylphosphine [13] was prepared in ether or glyme (1,2-dimethoxyethane) solution and allowed to react with the trione under various conditions of temperature and time. Although the reaction product showed in some cases a weak infrared band at 6·13 μ, no band appeared at 11·0—11·5 μ; strong absorption occurred at 9 μ.

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* Note to paragraphs (*d*)–(*f*): These chromatograms were obtained on Silicone Gum Rubber or Apiezon L on Embacel in a temperature-programmed F & M apparatus, Model 500. When Silicone Gum Rubber on silanized Embacel was used, even the " main " peaks were split into several peaks.