

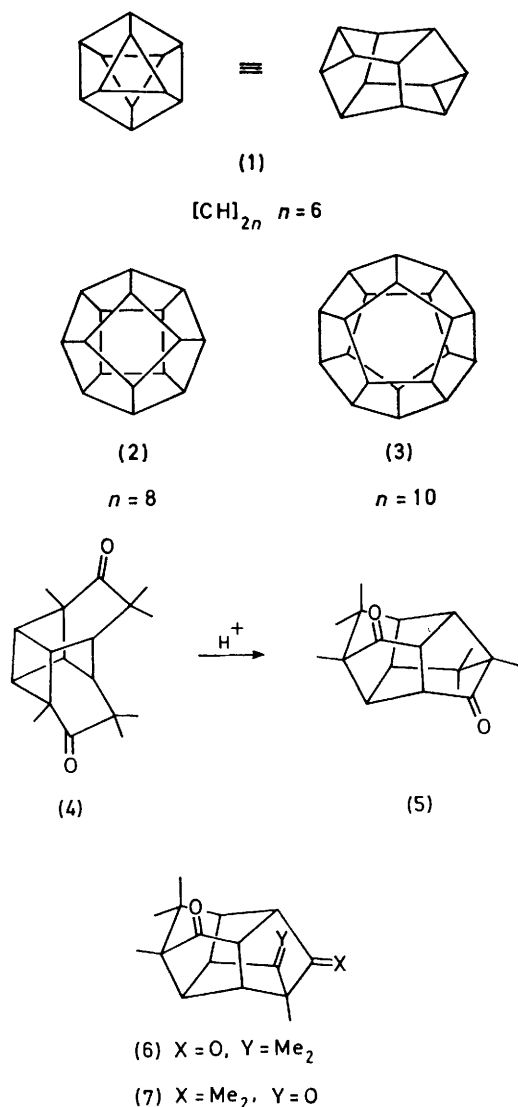
Synthesis of 2,9-Dimethylditriaxane (2,9-Dimethylheptacyclo-[6.4.0.0.0^{2,4}.0^{3,7}.0^{5,12}.0^{6,10}.0^{9,11}]dodecane)

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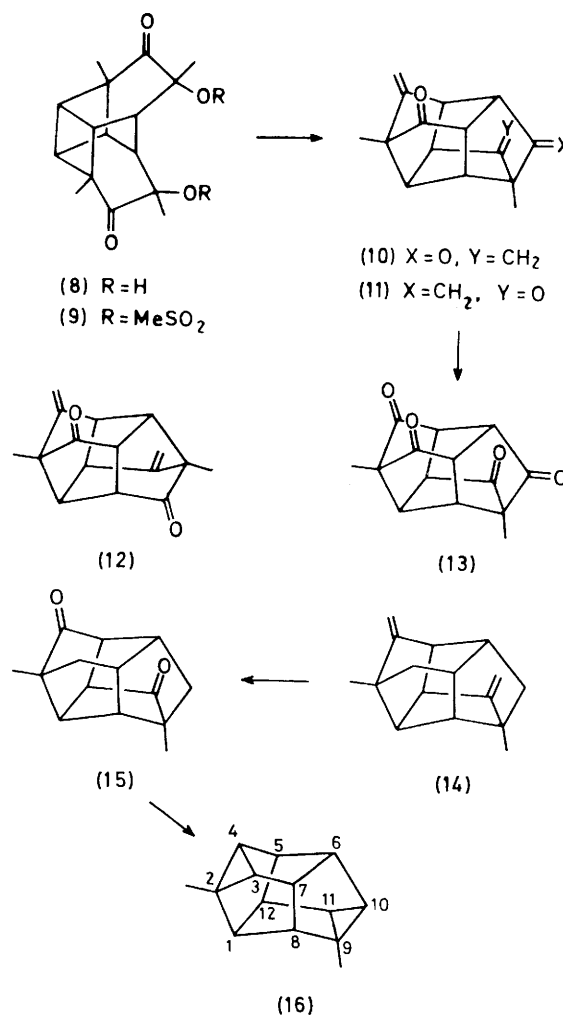
A dimethyl derivative of [6]-ditriaxane, a new polycyclic saturated $[\text{CH}]_{2n}$ hydrocarbon, has been synthesized from a pentacyclic cage compound, derived from 2,6-dimethylphenol, by acid-catalysed rearrangement, the Bamford–Stevens reaction, and subsequent transformations.

Garratt has recently pointed out that a series of polycyclic saturated $[\text{CH}]_{2n}$ hydrocarbons composed of a central n -membered ring connected by alternate carbon atoms to two $n/2$ membered rings (1, 2, 3, etc.) are important from a topological point of view.¹ Among these compounds, however, only dodecahedrane (3), the third member of this series, has received much attention as a synthetic target and recently Paquette has succeeded in synthesising 1,16-dimethyldodecahedrane.² We report here the first synthesis of a dimethyl analogue of [6]-ditriaxane (1),† the first member of the series, which has two triaxane⁴ units with six common carbon atoms.



When the pentacyclic diketone (4) was treated with *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}$ or $\text{CF}_3\text{CO}_2\text{H}$, a completely stereospecific acid-catalysed rearrangement occurred to give quantitatively the dinordiamantane derivative (5) of the three possible isomers (5)–(7).⁵ This rearrangement has now been applied to the synthesis of the title compound from the bismethanesulphonated diketone (9) (m.p. 113–114 °C), which has C_2 symmetry. Compound (9) was prepared (95% yield) from the hydroxy-compound (8)⁶, derived from 2,6-dimethylphenol, with methanesulphonyl chloride.‡

When (9) was treated with a benzene solution of $\text{BF}_3\text{-Et}_2\text{O}$ containing a small amount of 2,6-di-*t*-butylpyridine overnight at room temperature, two dienediones (10) (47%; m.p. 183–184 °C) and (11) (10%; m.p. 149–151 °C) were obtained.§



‡ Satisfactory elemental analyses were obtained for all new compounds.

§ Treatment with a variety of acid catalysts such as *p*- $\text{MeC}_6\text{H}_4\text{-SO}_3\text{H}$, $\text{CF}_3\text{CO}_2\text{H}$, H_2SO_4 , and $\text{BF}_3\text{-Et}_2\text{O}$ gave a complex product mixture.

† According to the proposed nomenclature,³ (1) is named [6]-ditriaxane.

On the basis of their common mass (M^+ 240) and i.r. (1740 and 1660 cm^{-1}) spectroscopic features, (10) and (11) are isomeric olefinic five-membered ring ketones. N.m.r. spectra clearly show that the minor product (11) [$\delta(\text{CDCl}_3)$ 1.31 (6H, s), 4.81 (2H, s), and 4.93 (2H, s)] retained C_2 symmetry, whereas the major product (10) [$\delta(\text{CDCl}_3)$ 1.30 (3H, s), 1.32 (3H, s), 4.77 (1H, s), 4.84 (1H, s), 4.89 (1H, s), and 5.00 (1H, s)] had lost this symmetry. If the reaction followed the same mechanism as in the conversion of (4) into (5), another symmetrical structure (12) instead of (11) appeared more likely. However, this possibility was ruled out because both (10) and (11) gave the same tetraketone (13) [m.p. 289°C (decomp.)] on ozonolysis. The loss of the high stereospecificity observed in the rearrangement of (4) can be ascribed to the steric hindrance of the methanesulphonyl groups to the bulky Lewis acid catalyst.[¶]

When the disemicarbazone [87%; m.p. 256°C (decomp.)] of (10) was heated at 220°C with powdered KOH under N_2 , the diolefin (14) [89%; b.p. $89\text{--}102^\circ\text{C}$ (bath temp.) at 96 mmHg; $\nu(\text{neat})$ 3050, 1660, and 880 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.19 (3H, s), 1.21 (3H, s), 4.41 (1H, s), 4.42 (1H, s), 4.50 (1H, s), and 4.51 (1H, s)] was obtained. Ozonolysis of (14) in EtOH at -70°C , followed by treatment with dimethyl sulphide gave the diketone (15) [76%; m.p. $87\text{--}88^\circ\text{C}$; $\nu(\text{Nujol})$ 1730 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.21 (3H, s) and 1.22 (3H, s)].

[¶] Detailed discussion of this reaction mechanism will be presented in a full paper.

The diketone (15) was converted into its ditosylhydrazone [84%; m.p. 256°C (decomp.)], which was heated with Bu^tOK in diglyme at 130°C . A smooth Bamford–Stevens reaction took place and the resultant crude oil (93% pure by g.l.c.) of the title compound (16) was purified by preparative g.l.c. (3% OV-17 on Chromosorb W at 110°C). On the basis of physical data [$\nu(\text{CCl}_4)$ 3025, 1300, 880, and 840 cm^{-1} ; ^1H n.m.r. $\delta(\text{CDCl}_3)$ 1.10 (6H, s), 1.38 (4H, s), 2.79 (2H, m), and 3.01 (4H, s); ^{13}C n.m.r. $\delta(\text{CDCl}_3)$ 18.52 (q), 40.04 (d), 40.39 (d), 62.06 (d), 63.64 (d), 66.34 (d), and 96.31 p.p.m. (s); m/z 184 (M^+ ; 31%), 169 (16), 119 (63), and 105 (100)], the structure of (16) with C_2 symmetry and containing two cyclopropane rings was established.

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