Chemical Studies of Caged Compounds. The Synthesis of Hexacyclo[5,4,0,0^{2,6},0^{3,10},0^{5,9},0^{8,11}]undecane, "Homopentaprismane"

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Summary A simple synthesis is reported for the caged polycyclic hydrocarbon hexacyclo[5,4,0,0^{2,6},0^{3,10},0^{5,9},0^{8,11}]-undecane and the properties of the precursors are also described.

THE recent interest in polycyclic bridged hydrocarbons[1] prompts us to report the synthesis, in high yield, of hexacyclo[5,4,0,0,^{2,6}0,^{3,10}0,^{5,9}0,^{8,11}]undecane (I) for which the trivial name homopentaprismane is suggested.

Cyclopentadiene and *p*-benzoquinone yielded the dienedione (II), m.p. 75—76° (lit.[2] 76—78°) which upon irradiation underwent cyclization to the diketone (III), m.p. 238—240°(lit.[3] 245°). Reduction of (III) with lithium aluminium hydride gave the diol (IV), m.p. 266—268°(lit.[3] 276°) (70%). The stereochemistry of (IV) was assigned on the basis that it could be converted into a cyclic sulphite, m.p. 188—189°, *m/e* 222, a cyclic ether (IX) m.p. 190—191° (sealed tube), *m/e* 180, and a cyclic thionocarbonate, m.p. 297—299° (sealed tube), *m/e* 218.

The diol (IV) was converted into the dibromide (V) (60%) by PBr_3. Compound (V) was a colourless liquid b.p. 130—131° which upon hydrolysis could be converted into the cyclic ether (IX). Debromination of (V) was effected smoothly by treatment with zinc powder in refluxing ethanol for 2 hr. The products of this reaction were homopentaprismane (I; 62%), (VI; 1%) and two unsaturated compounds (*ca.* 40%) for which spectral evidence suggests the structures (VII) and (VIII).

Homopentaprismane (I) is a white volatile solid m.p. 98—100° (sealed tube) which is unaffected by Br_2 in CCl_4 and has the following spectral characteristics: i.r._{max} (CCl_4) 2958s, 2854w, 1549s, 1308s, 1296s, 1250w, 1208w, 1006w, and 931 cm^{-1}; n.m.r.: no absorption below τ 6·8, complex absorptions centred at 7·2 and 7·9 and a triplet ($J = 1{\cdot}5$ Hz) at $8{\cdot}57_5$ (2H); *m/e* (%): 144 (39), 129 (36), 79 (100), 78 (75), and 66 (91).†

We are studying reactions involving radicals and ions derived from homopentaprismane and a similar synthetic route to the compound with the methylene bridge replaced by a simple bond, for which the trivial name pentaprismane has been suggested.[4]

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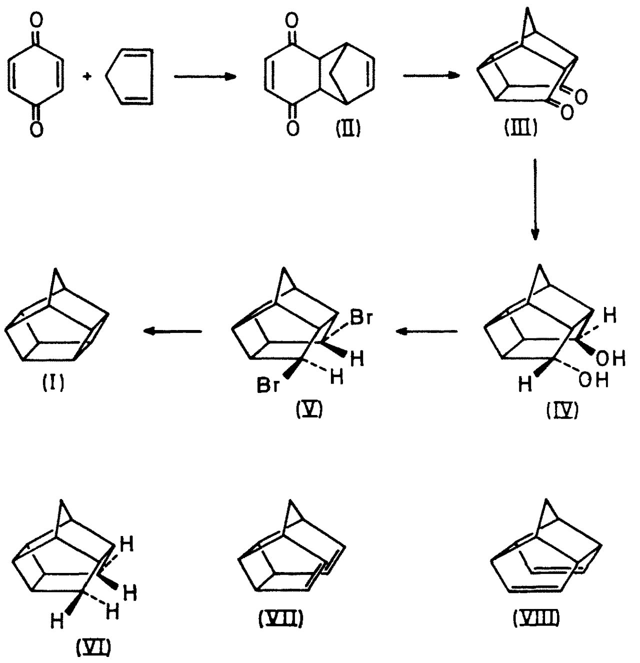

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† Satisfactory elemental analyses were obtained for all new compounds.

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