

1,2,2,4,4-PENTAMETHYLBICYCLO[1.1.0]BUTANE: THE FORMATION OF A BICYCLOBUTANE BY INTRA-
MOLECULAR DISPLACEMENT OF ALKOXIDE ION

D.P.G. Hamon

(The Organic Chemistry Department, The University of Adelaide,
Adelaide, S.A. 5001. Australia)

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It is well known (1) that bicyclo[1.1.0]butanes can be prepared by the intra-molecular displacement of good leaving groups such as halide ions or arylsulphonate ions. It is also known (2) that cyclopropanes can be formed by the 1,3 displacement of the much poorer leaving groups, alkoxide ions. It was therefore of interest to determine whether the bicyclobutane system could be formed by a 1,3 displacement of an alkoxide ion.

3-Methylene-2,2,4,4-tetramethylcyclobutanol 1 (3) was converted to the methyl ether 2 (60% b.p. 142°) by boiling it under reflux in 1,2-dimethoxyethane with sodium hydride and methyl iodide. When dissolved in liquid hydrogen bromide the methyl ether 2 was converted to a mixture of the bromo compounds 3. They were rather unstable, but the mixture could be characterised by its n.m.r. spectrum. [$\delta = 3.25$ ($-\text{OCH}_3$), 3.25 and 3.07 ($-\text{CH}-\text{OMe}$), 1.78 and 1.74 ($-\text{CBrCH}_3$), 1.35, 1.23, 1.09, 1.01 ($-\text{C}(\text{CH}_3)_2$).] It was an approximately 2:3 mixture of isomers. The fragmentation pattern in the mass spectrum was also consistent with the structure 3. Treatment of this mixture of isomers in *n*-decane with sodium/potassium alloy at 60° for 15 hrs yielded a solution of the title compound 4. Separation of the compound 4 from the solvent was effected by preparative GLPC using 10% SE30 on fluropak in a 4 ft glass column. It was however contaminated by a small amount ($\approx 10\%$ by n.m.r.) of isomeric pyrolysis products. The n.m.r. spectrum of the compound in carbon tetrachloride is shown in figure 1. The doublet at $\delta = 1.36$ ($J \approx 0.7$ c/s) is assigned to the angular methyl group. The splitting is due to long-range coupling with

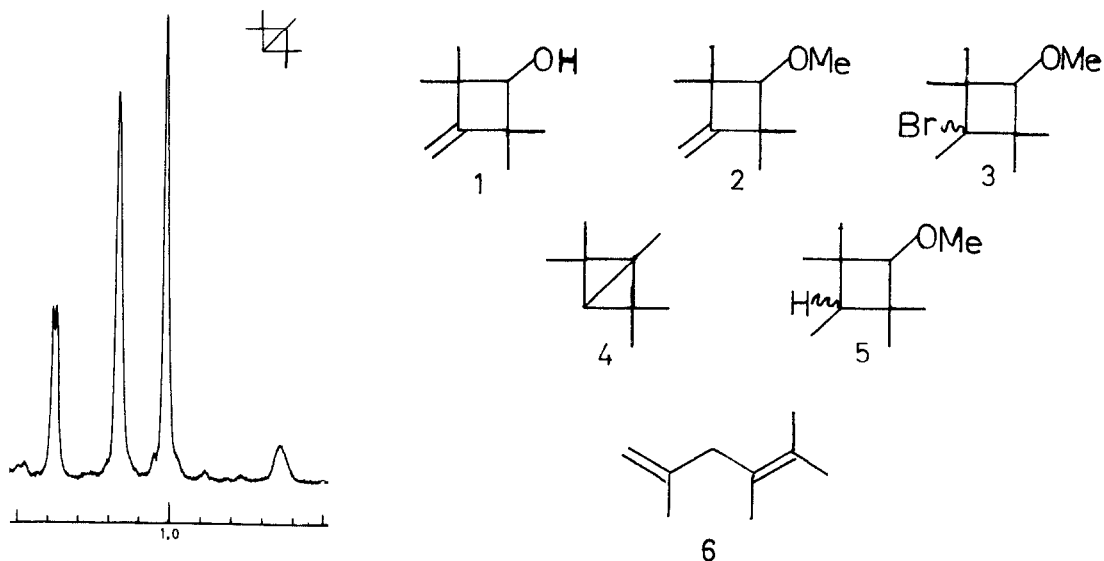


Figure 1

Scheme

the angular hydrogen atom. The broadened peak at $\delta = 0.64$ is assigned to this hydrogen atom. This resonance is considerably upfield from that reported for the angular hydrogen atom in bicyclo[1.1.0]butane ($\delta = 1.37$). (1). The shift can be accounted for by assuming *cis* alkyl-group effects similar to those observed in cyclopropane derivatives. (4). In this instance there are three *cis* alkyl groups to consider. The two peaks at $\delta = 1.01$ and 1.16 are assigned to the remaining methyl groups.

If the reaction between the bromo compounds 3 and the sodium/potassium alloy occurs in benzene as the solvent, and an n.m.r. spectrum is obtained on the filtered solution after reaction, then no pyrolysis products are detected. The spectrum shows, however, that a mixture of the desired bicyclobutane and the isomers 5 are obtained in a ratio of about 4:1. (7) Of interest is the relatively large solvent shift, for a saturated hydrocarbon compound, of 0.11 ppm to lower field of the absorption which occurs at $\delta = 1.16$ in figure 1. We have also observed this effect ($\Delta 0.14$ ppm) on the resonance tentatively assigned to the endo methyl groups in hexamethylbicyclobutane (3) and assume that this is related to the dipolar nature of the structure (5). This would imply that the peak at $\delta = 1.16$ in figure 1 is due to the endo methyl groups. This assignment is not inconsistent with the argument developed previously (3).

Attempts to separate compound 4 on the more conventional, diatomaceous earth or firebrick, supports, led only to products of pyrolysis (3). The mass spectrum of these products showed the same fragmentation pattern as that of the bicyclobutane but with differing ratios of intensities. Both mass spectra showed a molecular ion at m/e 124 and a base peak at M-15. The major product from preparative GLPC, using 20% SE30 on Chromosorb P, was collected. It had a molecular weight of 124 (mass spec.) and its n.m.r. spectrum was consistent with the structure 6. [δ = 4.6 broad (vinylic H), 2.65 broad (allylic H), 1.63 broad (=C-CH₃)]. This ring opening of the compound (and of its homologue (3)) is unusual (6) and is being investigated further.

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