

CAGE COMPOUNDS. 3. ^{13}C AND ^1H N.M.R. TO CHARACTERISE SYMMETRICAL REARRANGEMENT PRODUCTS OF 3,6-EPOXY PENTACYCLO[6,2,2,0^{2,7},0^{4,10},0^{5,9}]DODECANE WITH SULPHURIC ACID.

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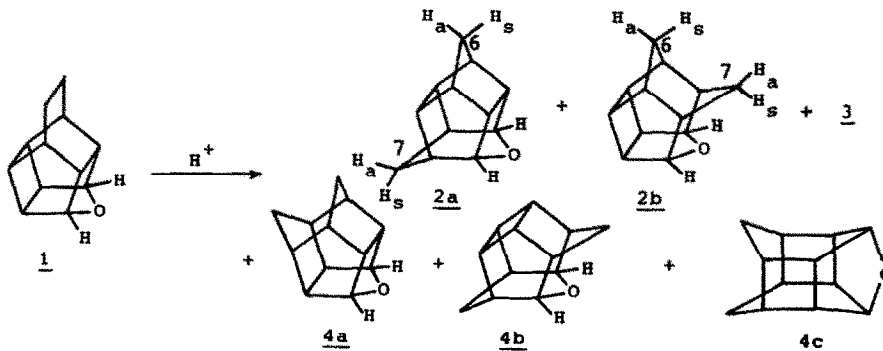
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(Received in UK 16 March 1976; accepted for publication 29 March 1976)

Various skeletal rearrangements of strained bird-cage compounds to less strained isomers have been reported¹ in recent years. We now wish to report that the title compound (1)² rearranges on treatment with 95% sulphuric acid (neat) at room temperature for 24 hrs. Three isomeric ethers (2, 3 and 4), which were separated by gas chromatography³, were formed in the ratio 27:3:1. The IR spectra were free from carbonyl and alcohol absorptions. The absence of olefinic bonds in 2, 3 and 4 was shown by ^1H and ^{13}C nmr.



The proton noise-decoupled ^{13}C nmr spectrum of 2 displayed 7 signals [CDCl_3 : 82.6(2C), 53.9(2C), 52.1(2C), 44.9(1C), 44.4(2C), 41.0(2C) and 29.2(1C) ppm downfield from TMS]. In the undecoupled spectrum the signals at 44.9 and 29.2 ppm were split respectively into a triplet ($J = 131.1$ Hz) and a doublet of doublets ($J = 130.6$ and 134.0 Hz), thus representing two non-identical methylene carbons. The remaining signals were essentially split into doublets. These results point to a symmetrical structure (2a or 2b). The ^{13}C LIS experiments [$\text{Yb}(\text{fod})_3$] indicated the methylene carbon at 29.2 ppm to be closer to the oxygen atom than the methylene carbon at 44.9 ppm. The same result was obtained from the ^1H LIS experiments [$\text{Eu}(\text{fod})_3$], enabling us to identify the methylene protons $\text{H}_{7\text{s}}$, $\text{H}_{7\text{a}}$, $\text{H}_{6\text{s}}$ and $\text{H}_{6\text{a}}$. Since no NOE effect on $\text{H}_{6\text{s}}$ or $\text{H}_{6\text{a}}$ was observed upon irradiation⁴ of $\text{H}_{7\text{a}}$, one is inclined to favour structure 2a rather than 2b for this isomer. This seems reasonable, since 2a is expected to be less strained than 2b.

The proton noise-decoupled ^{13}C nmr spectrum of 4 exhibited only four signals [CDCl_3 : 81.9(4C), 55.2(4C), 40.5(4C) and 32.0(2C) ppm downfield from TMS] indicating a highly symmetrical structure. The undecoupled spectrum of 4 showed that the peak at 32.0 ppm corresponds to two identical methylene carbons. The ^1H nmr spectrum of 4 displayed two different pairs of methylene protons at 1.26 and 1.76 ppm ($J_{\text{gem}} = 11.7$ Hz). Since the ^1H LIS [$\text{Eu}(\text{fod})_3$] of these two signals are small and correspond to those of protons $\text{H}_{6\text{s}}$ and $\text{H}_{6\text{a}}$ of 2, little doubt exists that 4 should have structure 4a rather than 4b. The alternative symmetrical structure 4c is highly improbable due to its expected high internal strain.

Compound 3 is totally dissymmetric, as shown by its ^{13}C proton noise-decoupled spectrum [CDCl_3 : 85.5, 77.2, 56.2, 50.4, 48.6, 47.4, 47.0, 46.6, 45.8, 42.1, 40.1 and 27.9 ppm downfield from TMS]. From this data it is impossible, at this stage, to assign a structure to 3.

We are presently studying the details of this novel rearrangement.

Acknowledgement

We are indebted to the C.S.I.R. for financial support.

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