Skeletal Rearrangements during Lithium Aluminium Hydride Reductions of Bicyclo[2,2,2]octenyl Toluene-*p*-sulphonates

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DURING work on the acid-catalysed rearrangement of bicyclo-octenes we attempted to prepare bicyclo[2,2,2]octene (I) from the *syn*-toluene-*p*-sulphonate (II), m.p. 65–66°,[1] with lithium aluminium hydride in refluxing diethyl ether. Unexpectedly, the major product was (by n.m.r. and g.l.c.) bicyclo[3,2,1]oct-2-ene (III),[2] the overall product distribution (see Table) being determined directly from g.l.c. peak areas.

TABLE

Product distribution (%)

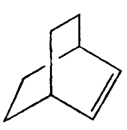
	(I)[3]	(III)	(IV)[4]	(V)[5]
syn-Tosylate (II) ..	9	85	0	6
anti-Tosylate (VI) ..	5	0	2	93

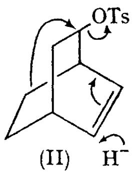
The oily *anti*-toluene-*p*-sulphonate (VI),[6,7] under identical conditions, also gave a major product with a modified skeleton, namely tricyclo[3,2,1,$0^{2,7}$]octane (V) (see Table).

Such product distributions might be expected if the esters were to ionise and the resultant carbonium ions undergo attack with hydride ion from the reagent[8] (II and VI; arrows). Indeed, these product mixtures are analogous in composition to those obtained by acetolysis of the esters (II) and (VI).[7]

Reduction of the deuterio-ester (VII) furnished [1-^{2}H$_{1}$]bicyclo[3,2,1]oct-2-ene (VIII), thus eliminating the possibility of a reaction mechanism involving attack by hydride ion at the methine group adjacent to the ester function as shown (VIIa; arrows).

To establish the structure of (VIII), the trideuterio-olefin (IX) was prepared from [2,2′,4,4′-^{2}H$_{4}$]bicyclo[3,2,1]octan-3-one. This olefin showed a singlet at τ 4·63 and allowed assignment of the protons at C-2 and C-3 in the n.m.r. of the parent olefin (III). The diffuse triplet at τ 4·12 in (III) is collapsed to a diffuse doublet in the monodeuterio-olefin (VIII), indicating that the deuterium is at least substantially in the bridgehead position


(I)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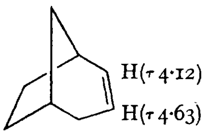
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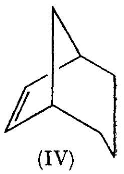
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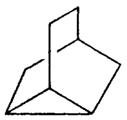
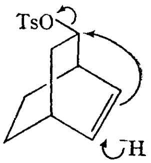
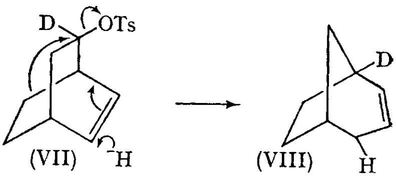
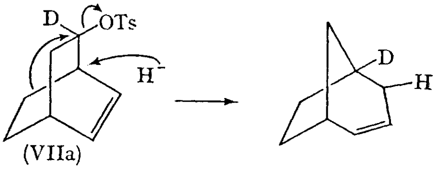
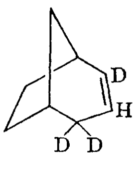

(V)


(VI)


(VII) (VIII)


(VIIa)


(IX)

shown and that there is little, if any, double-bond isomerisation under the conditions used.

Analogous rearrangements have been reported in the bicycloheptyl series.[9]

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[1] H. L. Goering, R. W. Greiner, and M. F. Sloan, *J. Amer. Chem. Soc.*, 1961, **83**, 1391.
[2] R. C. De Selms and C. M. Combs, *J. Org. Chem.*, 1963, **28**, 2206.
[3] C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, 1958, **41**, 1191.
[4] To be published.
[5] C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, 1963, **46**, 1676.
[6] R. R. Fraser and S. O'Farrell, *Tetrahedron Letters*, 1962, 1143.
[7] N. A. LeBel and J. E. Huber, *J. Amer. Chem. Soc.*, 1963, **85**, 3193.
[8] H. C. Brown and H. M. Bell, *J. Org. Chem.*, 1962, **27**, 1928.
[9] For leading refs., see: B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, 1963, **85**, 3902.