

## 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°,<sup>1</sup> 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),<sup>2</sup> the overall product distribution (see Table) being determined directly from g.l.c. peak areas.

TABLE  
Product distribution (%)

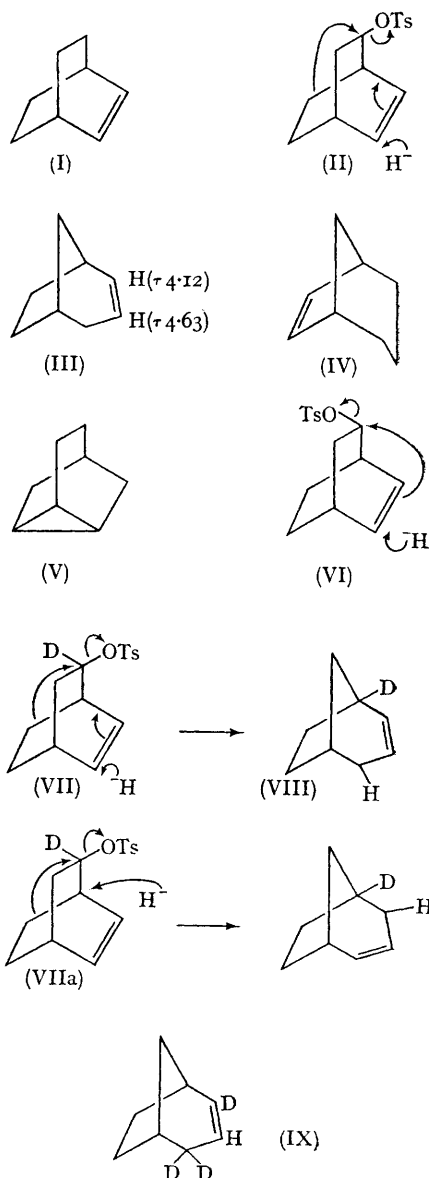
	(I) <sup>3</sup>	(III)	(IV) <sup>4</sup>	(V) <sup>5</sup>
<i>syn</i> -Tosylate (II)	.. 9	85	0	6
<i>anti</i> -Tosylate (VI)	.. 5	0	2	93

The oily *anti*-toluene-*p*-sulphonate (VI),<sup>6,7</sup> under identical conditions, also gave a major product with a modified skeleton, namely tricyclo[3,2,1,0<sup>2,7</sup>]-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<sup>8</sup> (II and VI; arrows). Indeed, these product mixtures are analogous in composition to those obtained by acetolysis of the esters (II) and (VI).<sup>7</sup>

Reduction of the deuterio-ester (VII) furnished [1-<sup>2</sup>H<sub>1</sub>]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 tri-deuterio-olefin (IX) was prepared from [2,2',4,4'-<sup>3</sup>H<sub>4</sub>]bicyclo[3,2,1]octan-3-one. This olefin showed a singlet at  $\tau$  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  $\tau$  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



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

Analogous rearrangements have been reported in the bicycloheptyl series.<sup>9</sup>

(Received, June 1st, 1967; Com. 550.)

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<sup>9</sup> For leading refs., see: B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, 1963, **85**, 3902.