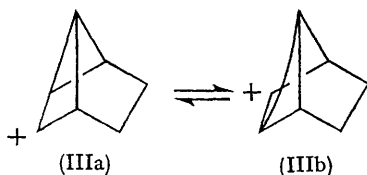
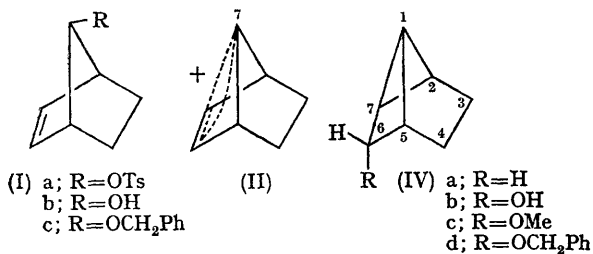


endo-6-Hydroxytricyclo[3,2,0,0^{2,7}]heptane

By JOSEPH J. TUFARIELLO,* THOMAS F. MICH, and ROBERT J. LORENCE

(Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214)

HYDROLYSIS of *anti*-7-norbornenyl toluene-*p*-sulphonate (Ia) has been variously described as proceeding through a nonclassical ion (II)¹ or equilibrating classical ions (*i.e.*, IIIa \rightleftharpoons IIIb).² Isolation of tricyclo[3,2,0,0^{2,7}]heptane (IVa) from the solvolysis of (Ia) in aqueous Diglyme containing sodium borohydride has been reported^{1,2} and the suggestion made that this hydrocarbon resulted from borohydride attack on a tricyclic classical ion (*i.e.*, III). This suggested² that *endo*-7-hydroxytricyclo[4,1,0,0^{2,7}]heptane (IVb), resulting from a similar attack by water on the carbonium ion, might be an unstable intermediate in the hydrolysis which rearranges rapidly to the observed product, *anti*-7-norbornenol (Ib).



We report the synthesis and chemical behaviour of the tricyclic alcohol (IVb). The reaction of *anti*-7-chloronorbornene with sodium benzoate in benzyl alcohol, a method similar to that used for the synthesis of *endo*-7-methoxytricyclo[3,2,0,0^{2,7}]heptane (IVc),^{3,4} afforded a 60:40 mixture of *endo*-6-benzyloxytricyclo[3,2,0,0^{2,7}]heptane (IVd) and *anti*-7-benzyloxynorbornene (Ic), respectively. The tricyclic benzyl ether (b.p. 85° at 0.02 mm.), readily separated from its bicyclic isomer by distillation, was identified by the quartet ($J_{6,7}$ 3.5; $J_{5,6}$ 7.7 Hz.) at δ 3.86 in its n.m.r. spectrum (CCl₄, Me₄Si) characteristic⁴ of the tricyclic ethers and its ready acid-catalyzed conversion into (Ic)†. The benzyl blocking group was removed from (IVd) with sodium in liquid ammonia to afford the tricyclic alcohol (IVb), identified by the quartet at δ 4.18 ($J_{6,7}$ 3.4; $J_{5,6}$ 7.6 Hz.) in its n.m.r. spectrum [(CD₃)₂CO-D₂O; Me₄Si].

Moreover, when a small drop of trifluoroacetic acid was added to the n.m.r. sample, the tricyclic alcohol was spectacularly and completely transformed into the *anti*-7-alcohol (Ib), in less than twenty seconds. However, when the tricyclic alcohol was placed in a 33:67 D₂O-(CD₃)₂CO solvent system, it was not detectably isomerized to (Ib) even after 3 days at room temperature at pH 7. Furthermore, the tricyclic alcohol (IVb) was not detected as a product from the solvolysis^{1,2} of (Ia) in 50% aqueous acetone containing sodium hydrogen carbonate. In a separate experiment, (IVb) which was added to the hydrolysis mixture at the start could be recovered

† It has been shown that *endo*-7-methoxytricyclo[3,2,0,0^{2,7}]heptane undergoes a similar acid-catalyzed rearrangement. See ref. 4.

unchanged. Therefore, (IVb) is *not* an intermediate in the hydrolysis of (Ia) under weakly alkaline conditions.

It should be emphasized that our findings do not reflect on the nature of the cationic intermediates involved in the hydrolysis, since it is quite conceivable that either the nonclassical

ion (II) or a tricyclic classical ion (III) might react with water selectively at the 7-position.^{5,6}

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