Hydride Induced Conversion of an *ent*-Beyer-15-ene 12-*p*-Tosylhydrazone into the Novel *ent*-16*S*-Atis-13-ene System

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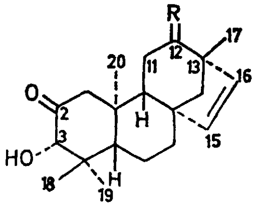
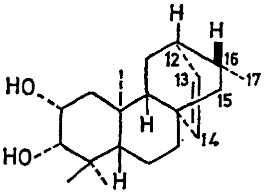
Summary The hydride induced shift of an *ent*-beyer-15-ene 12-*p*-tosylhydrazone, a bicyclo[3,2,1]octene system, to the hitherto undescribed *ent*-16*S*-atis-13-ene, a bicyclo-[2,2,2]octene system, is discussed; the extreme unreactivity of the double bond in the product is reported.

SKELETAL rearrangements induced by basic decomposition of *p*-tosylhydrazones are well known,[1] whereas reaction with complex hydrides usually accomplishes the reductive elimination of a carbonyl function to the methylene group.[2] We report a stereospecific alkyl group migration during the sodium borohydride decomposition of a *p*-tosylhydrazone.

Treatment of the α-ketol (**1a**)[3] with *p*-tosylhydrazine in acetic acid at room temperature gave *ent*-3β-hydroxybeyer-15-en-2-one 12-*p*-tosylhydrazone (**1b**). Reaction of (**1b**) with $NaBH_4$ in ethanol–dioxan at 0° or reflux temperatures gave as the sole isolable product the novel diol *ent*-16*S*-2β,-3β-dihydroxyatis-13-ene (**2**), m.p. 190—192°, in 73% overall yield from (**1a**). The double bond in the atisane compound (**2**) is in the 13(14)-position instead of the usual 15(16)- or 16(17)-positions as found in natural or synthetic atisane diterpenes formally derived from a kaurane system. Confirmation of this was obtained from the mass spectrum of (**2**) where the base peak at 262 ($M - 42$) arises from the retro-Diels–Alder loss of C_3H_6 eliminating C-15, C-16, C-17, and their hydrogen atoms. The stereochemistry at C-16 in the atisane product (**2**) was deduced from its ^{1}H n.m.r. spectrum. The C-17 methyl resonance which in beyeranes is usually[4] one of the downfield methyl group signals now appears as the highest field signal as the expected doublet suggesting that it lies in the shielding region of the double bond and that the configuration at C-16 is therefore *ent*-16*S*.



a; R = O (1)
b; R = NNHTs



(2)

The observed alkyl group migration suggested a mechanism involving formation of an incipient positive charge at C-12 with a concerted rearrangement of C-16 from C-13 to C-12, similar to the first step in the previously reported[5] isomerisation of the beyer-15-en-12-one system.

Similar $NaBH_4$ treatment of the 15,16-dihydro-12-tosylhydrazone analogue of (**1b**) failed to bring about the rearrangement, but gave instead the known *ent*-2β,3β-dihydroxybeyerane.[6] The failure to rearrange may be due in part to the large steric compression that would be incurred by the angular C-20 methyl group and the **13**-*endo*- and 14-*endo*-atisane hydrogens[7] in the transition state.

Although the atisene 13(14)-double bond underwent hydrogenation quite readily it was otherwise inert to bromination, acetoxymercuration (*cis* or *trans*),[8] and neutral permanganate oxidation. Attempted epoxidation with *m*-chloroperbenzoic acid gave an as yet unresolved mixture of aromatic acid esters. This inertness of the *ent*-16*S*-atis-13-ene system must be due to steric crowding of the double bond by the C-20 and C-17 α-oriented methyl groups.

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