Cationic Cyclization Involving a Remote Allene Function in the Trifluoroethanolysis of Hepta-5,6-dienyl Toluene-p-sulphonate

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Summary The remote allene function participates efficiently in the trifluoroethanolysis of hepta-5,6-dienyl toluene-p-sulphonate, leading to the cyclized 2-methylencyclohexyl cation.

CATIONIC cyclization reactions of general type (1) → (2) play a central role in the biogenesis of cholesterol and other steroidal compounds, and are also useful in syntheses of mono- and poly-cyclic molecules. Recently it has been discovered that remote triple bonds can participate in olefinic cyclizations [(3) → (4) + (5)], and this reaction has also been found to be synthetically useful. Since allenes are quite reactive in electrophilic additions, and cyclization involving an allylic function [e.g. (6)] should lead to a relatively stable allylic cation (7), it is surprising that no examples of this transformation are in the literature. We report that, under appropriate conditions, the reaction (6) → (7) takes place.

Scheme

The tosylate (6; X = p-MeC6H4SO3) was prepared from hex-5-en-1-ol. Solvolysis of (6) in acetic acid at 60° gave mainly starting alcohol, but solvolysis in the weakly nucleophilic 2,2,2-trifluoroethanol led to > 90% cyclization. The mixture of trifluoroethyl ethers obtained (ca. 65% yield) consisted of uncyclized material (6; X = OCH3, CF3, 5%), the two allylic isomers (8) (45%) and (9) (45%), and unidentified material (5%). The structures of the cyclized products were inferred from spectral data, and confirmed by independent syntheses.
(60°; trifluoroethanol) showed that the rate constant for ionization of (6) was $8.15 \times 10^{-9} \text{s}^{-1}$, which compares with $k = 4.0 \times 10^{-9} \text{s}^{-1}$ for n-heptyl tosylate.

Despite major structural differences in starting materials and generated cations, the cyclization behaviour of (6) is strikingly similar to that of a number of other substrates. Sulphonates (1; R = H, X = p-NO$_2$C$_6$H$_4$SO$_3$), (3; R = H, X = p-MeC$_6$H$_4$SO$_3$), and (10) all give low proportions of cyclization products in acetic acid but greater amounts in solvents of lower nucleophilicity, such as trifluoroethanol and trifluoroacetic acid; all show borderline participation of the remote unsaturation (Scheme) in the transition state for ionization.$^{3a,4,5,10}$

From a synthetic point of view, cyclization involving a remote allene function should complement other cyclization systems. It also raises the possibility of generating selective enantiomerism at the asymmetric centres on the new C-C bond using optically active allenic substrates. Mechanistically, this study appears to support Peterson's suggestion$^{3a}$ that the transition states for cyclizations bear little resemblance to the final cations generated. In the allene case, most of the charge probably still resides at C-1 as this atom interacts with the remote $\pi$ system, and little C-6-C-7 rotation takes place until the reaction is well past the transition state.$^{1}$

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$^1$ H. T. Hall and W. S. Johnson (personal communication; see H. T. Hall, Ph.D. Dissertation, Stanford University, 1973), have observed the formation of trans-fused bicyclic allylic alcohols on treatment of trans-3-isopropylidene-2,6-dimethyldodeca-6,10,11-trien-2-ol with, e.g., trifluoroacetic acid in CH$_2$Cl$_2$ at $-78^\circ$. The results of this study are entirely analogous to our own findings.

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