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

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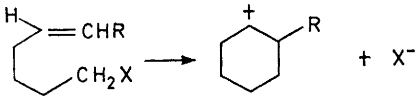
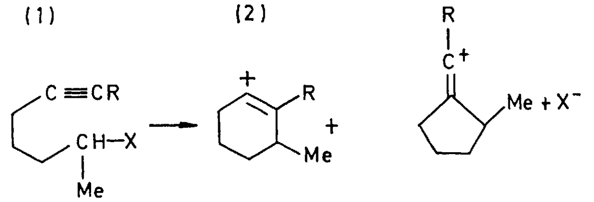
Summary The remote allene function participates efficiently in the trifluoroethanolysis of hepta-5,6-dienyl toluene-*p*-sulphonate, leading to the cyclized 2-methylenecyclohexyl cation.

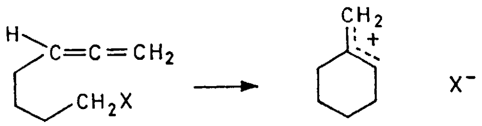
Cationic cyclization reactions of general type (**1**) → (**2**) play a central role in the biogenesis of cholesterol and other steroidal compounds,[1] and are also useful in syntheses of mono- and poly-cyclic molecules.[2] Recently it has been discovered[3] that remote triple bonds can participate in olefinic cyclizations[4] [(**3**) → (**4**) + (**5**)], and this reaction has also been found to be synthetically useful.[4] Since allenes are quite reactive in electrophilic additions,[5] and cyclization involving an allenic 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.



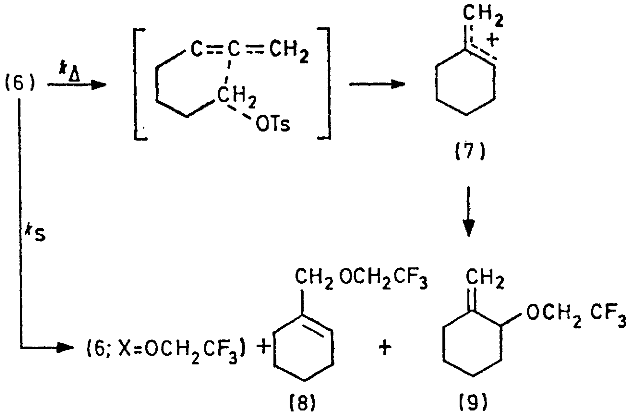
(1) (2)



(3) (4) (5)



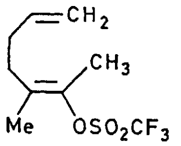
(6) (7)



Scheme

The tosylate (**6**; X = $p\text{-MeC}_6\text{H}_4\cdot\text{SO}_2$) was prepared from hex-5-en-1-ol.[6] Solvolysis of (**6**) in acetic acid at 60° gave mainly starting alcohol, but solvolysis in the weakly nucleophilic 2,2,2-trifluoroethanol[7] led to > 90% cyclization. The mixture of trifluoroethyl ethers obtained (*ca.* 65% yield) consisted of uncyclized material (**6**; X = OCH_2CF_3, 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.[8] Kinetic studies

(60°; trifluoroethanol) showed that the rate constant for ionization of (**6**) was $8{\cdot}15 \times 10^{-7}\,s^{-1}$, which compares with $k = 4{\cdot}0 \times 10^{-7}\,s^{-1}$ for n-heptyl tosylate.



(**10**)

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-$NO_2{\cdot}C_6H_4{\cdot}SO_2$), (**3**; R = H, X = p-$MeC_6H_4{\cdot}SO_2$), 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,6,9,10]

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 π system, and little C-6–C-7 rotation takes place until the reaction is well past the transition state.†

We thank the National Institutes of Health, the Alfred P. Sloan Foundation, and the Camille and Henry Dreyfus Foundation for support.

(*Received*, 26*th June* 1973; *Com.* 919.)

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† 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_2Cl_2 at −78°. The results of this study are entirely analogous to our own findings.

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