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# MEDIUM EFFECTS. II. CYCLIZATION OF 6-HEPTENYL p-NITROBENZENESULFONATE DURING SOLVOLYSIS IN 2,2,2-TRIFLUOROETHANOL (1)

Walter S. Trahanovsky and Michael P. Doyle*
Department of Chemistry, Iowa State University
Ames, Iowa 50010

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Solvolysis of 5-hexenyl arenesulfonates can be viewed as two competing nucleophilic reactions: a) external nucleophilic attack by the hydroxylic solvent to give 5-hexenyl products and b) internal nucleophilic attack by the olefin to give cyclic products (1). It is possible that the ratio of open to cyclic products may be a measure of the relative solvent nucleophilicity of a solvent mixture towards attack on alkyl arenesulfonates or halides. In order for this ratio of open to cyclic products to be a measure of solvent nucleophilicity, ground state changes must be more important than transition state changes (1). Our initial study of the solvolysis of 5-hexenyl p-nitrobenzenesulfonate in various solvent mixtures composed of 20% acetic acid and 80% non-hydroxylic solvent in the presence of urea showed that transition state changes may or may not be as important as ground state changes and thus the ratio of open to cyclic products may or may not measure solvent nucleophilicity (1). Additional studies should eventually show whether or not this ratio is a good measure of solvent nucleophilicity. In this communication, we wish to report that if we assume that this ratio does measure solvent nucleophilicity, then

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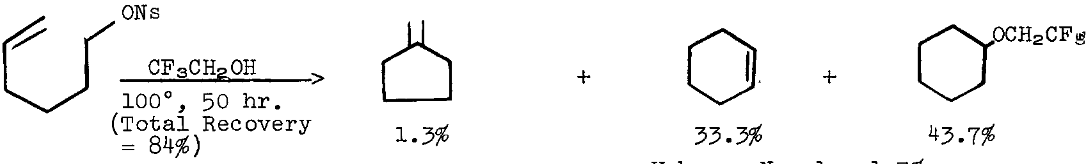
* U. S. Public Health Service Fellow, 1966-1967

2,2,2-trifluoroethanol** is the least nucleophilic ionizing solvent*** (2) that we have used so far. Moreover, the low nucleophilicity of 2,2,2-trifluoroethanol permits olefin participation to give a fair yield of cyclic products even with 6-heptenyl p-nitrobenzenesulfonate. Previous solvolytic studies of 6-heptenyl derivatives have always led completely to open products (acetolysis (3)) or to very low yields (1% from formolysis (4)) of cyclic products.

The yields of products from the solvolysis of 5-hexenyl p-nitrobenzenesulfonate in 2,2,2-trifluoroethanol containing urea[†,††] are as indicated. It is seen that the absolute yield of the three cyclic products methylenecyclo-



Unknown No. 1 - 1.7%
Unknown No. 2 - 1.2%
Unknown No. 3 - 1.7%
Unknown No. 4 - 1.5%

pentane, cyclohexene, and cyclohexyl 2,2,2-trifluoroethyl ether is 78% (relative yield based on all recovered products is 93%). The other products obtained were all unknown and may, in fact, all be cyclic products. The highest previously reported yield of cyclic products obtained from the solvolysis of 5-hexenyl derivatives is 73% (relative yield) from the formolysis of 5-hexenyl p-nitrobenzenesulfonate (4). The highest previously reported yield

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** 2,2,2-Trifluoroethanol was obtained from Halocarbon Products Corporation and was used without further purification.

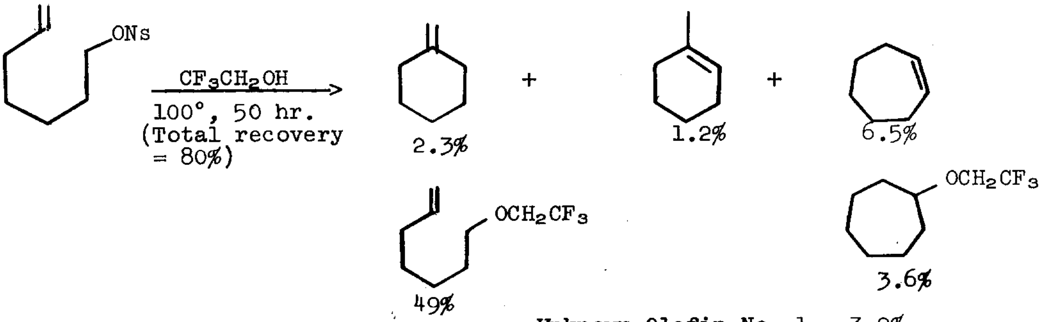
*** Scott (2) has noted the low nucleophilicity of 2,2,2-trifluoroethanol and its conjugate base.

[†] See ref. 1 for experimental details. [RONs] = 0.1 M, [urea] = 0.2 M.

[††] Average absolute yields of the products are reported based on glpc analysis of 3 runs on a carbowax 20 M column with pentyl acetate as the internal standard. The mean deviations of the reported yields are < 8%. The identity of the products was confirmed by glpc peak enhancement with authentic samples, and an nmr spectrum of the product cyclohexyl 2,2,2-trifluoroethyl ether.

of cyclic products obtained from the solvolysis of a 5-hexenyl derivative in a less acidic medium than formic acid is 62% (relative yield) from the acetolysis of 5-hexenyl p-nitrobenzenesulfonate in 20% acetic acid- 80% vinyl sulfone (1).

The yields of products from the solvolysis of 6-heptenyl p-nitrobenzenesulfonate in 2,2,2-trifluoroethanol containing urea[†,†††] are as indicated. The absolute yield of the cyclic products methylenecyclohexane, 1-methylcyclohexene, cycloheptene, and cycloheptyl 2,2,2-trifluoroethyl ether is 14% (17% relative yield). A quantity of 49% of the open product 6-heptenyl 2,2,2-trifluoroethyl ether was obtained. Again, some of the unknown products could be cyclic. An interesting observation is that the major portion of the cyclic products contain 7-membered instead of 6-membered rings. This is unexpected if one considers the additional strain of 7-membered rings compared to 6-membered rings. However, formally the 7-membered rings arise from a secondary cation whereas the 6-membered rings arise from a primary cation.



Unknown Olefin No. 1 - 3.9%
Unknown Olefins Nos. 2 and 3 - 10.7%
Unknown ether No. 1 - 2.3%

Olefinic cationic cyclizations to 7-membered rings have recently been reported by Marshall and Anderson (5) and Goldsmith and Clark (6). These

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[†††] Average absolute yields of the products are reported based on glpc analysis of 2 runs on carbowax 20 M and didecyl phthalate column with pentyl acetate as the internal standard. The mean deviations of the reported yields are < 6%. The identity of the products was confirmed by glpc peak enhancement with authentic samples on both columns except for the 6-heptenyl 2,2,2-trifluroethyl ether which was confirmed by its nmr spectrum.

workers treated unsaturated aldehydes or epoxides with Lewis acids in benzene. In these cases, cyclization to a 7-membered ring was favored by the presence of a 6-methyl group which resulted in a tertiary carbonium ion during cyclization to a 7-membered ring. The almost quantitative yields of 7-membered ring products observed by Marshall and Anderson (5) must be a consequence of the conformational rigidity of their starting materials; the 7-membered chains which cyclized were fused to 5-membered rings.

The use of 2,2,2-trifluoroethanol as a very nonucleophilic ionizing solvent is clearly supported by the data reported in this communication. Moreover, these results support the assumption that the ratio of open to cyclic products from the solvolysis of 5-hexenyl _p_-nitrobenzenesulfonate measures solvent nucleophilicity since other types of experiments have indicated that 2,2,2-trifluoroethanol is nonucleophilic.***

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## References

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