Methyl Loss from Carbocations in Superacid

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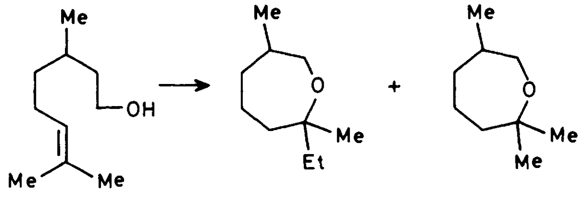
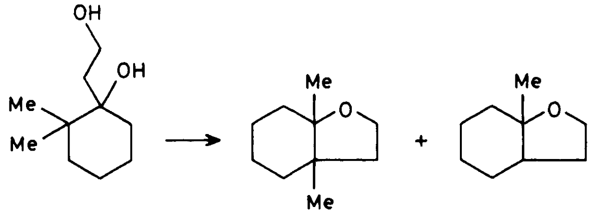
A study of cyclic ether formation in superacidic conditions has revealed two further examples of the loss of a methyl group from a carbocation, throwing new light on the mechanism of the reaction.

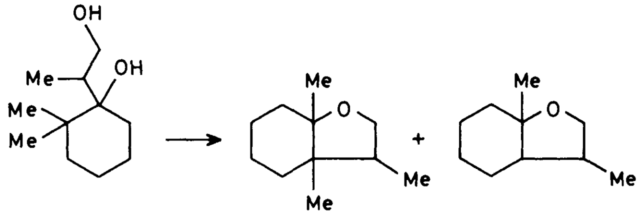
Cleavage of carbon–carbon bonds, leading to loss of an alkyl group, has been observed by several authors[1] during formation of carbocations from alkanes. These reactions usually take place at room temperature or above, and are believed to involve protonation of the alkane, followed by loss of the alkyl group as a neutral hydrocarbon, leaving a carbocation. At lower temperatures (−30 °C) only hydrogen loss is observed.[2] This reaction differs from loss of an alkyl group from a carbocation in superacidic conditions, of which only one example is known,[3] having been observed during the cyclisation of citronellol (**1**) in fluorosulphuric acid–sulphur dioxide at −78 °C. The reaction yielded a mixture of (**2**) and (**3**), in



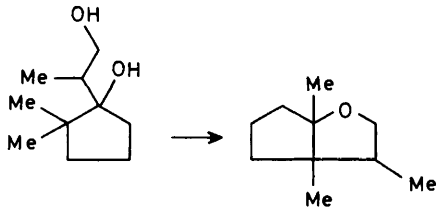
(1) (2) (3)



(4) (5) (6)



(7) (8) (9)



(10) (11)

which (3) had lost a methyl group. The authors were able to detect methyl fluorosulphonate in the reaction mixture, consistent with loss of the methyl group as CH_3^+.

We now report two further examples of loss of a methyl group from a carbocation, both occurring during ether formation. Reaction of (**4**) in $FSO_3H–SO_2$ at −60 °C yields (**5**) and (**6**) in the ratio of 12 : 1, with an overall yield of 75% of ethers; reaction of (**7**) in $FSO_3H–SO_2$ at −50 °C yields (**8**) and (**9**) in the ratio of 4 : 1, overall yield 80%. In both cases, loss of a methyl group competes with methyl migration. Methyl loss is favoured in (**7**), which has more steric crowding around the reaction site than has (**4**). The diols corresponding to (**7**) and (**4**), but differing in having only a single methyl substituent on C-2 rather than a *gem* dimethyl substituent, cyclise after hydride shift without loss or shift of the methyl group, with yields of 68% and 65% respectively. However, the diol (**10**), the cyclopentyl version of (**7**) reacts in $FSO_3H–SO_2$ at −50 °C to give only (**11**) *via* a methyl shift. Methyl loss is not observed in this system. A study of models shows that in the relatively flat five-membered ring, one methyl can undergo a 1,2-shift unhindered by neighbouring groups, whereas the chair shaped cyclohexyl ring places both of the *gem*-dimethyl groups in hindered situations.

All three examples to date involve loss of a methyl group from a *gem*-dimethyl group during cyclic ether formation. Examples of methyl shifts from *gem*-dimethyl groups are well-known,[4] and the stability of ethers in superacid[5] makes direct involvement of the primary hydroxy group in methyl removal seem unlikely. Methyl loss appears to be favoured by steric crowding of the methyl shift transition state, suggesting spontaneous loss of CH_3^+ rather than attack by fluorosulphonate ion. The mechanism of this reaction is as yet unknown, but an elimination process to give CH_3^+ and an alkene, similar to loss of H^+ from a carbocation, seems most likely. In superacid conditions, protonation of the alkene would be very rapid.

Formation of CH_3^+ in solution is unexpected, even from a long lived, highly stabilised carbocation. However, the decomposition process is favoured by steric hindrance, so is presumably unimolecular, and the ion, heavily stabilised, has only a short life before capture by the fluorosulphonate ion to give the methyl fluorosulphonate detected spectroscopically by Banthorpe and Boullier.[3] Although CH_3^+ has not been observed in the reaction, its formation appears likely.

Observation of the ethers spectroscopically was confirmed by quenching the superacid solutions, and recovery of the ether. Methyl loss was demonstrated by comparison with authentic samples of the ethers involved, and was confirmed by mass spectroscopic study of the ethers recovered from the quenching experiment.

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References

1 G. A. Olah and J. Lukas, *J. Am. Chem. Soc.*, 1967, **89**, 2227, 4739; A. F. Bickel, C. J. Gaasbeek, H. Hogeveen, J. M. Oelderik, and J. C. Platteeuw, *J. Chem. Soc., Chem. Commun.*, 1967, 634; D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, 1972, **9**, 179.
2 G. A. Olah and R. H. Schlosberg, *J. Am. Chem. Soc.*, 1968, **90**, 2726.
3 D. V. Banthorpe and P. A. Boullier, *J. Chem. Soc., Perkin Trans. 1*, 1977, 114.
4 T. S. Sorensen, *Acc. Chem. Res.*, 1976, **9**, 257.
5 G. Carr, unpublished data.