An Unusual Case of Proton Removal from an Oxocarbenium Ion[1]

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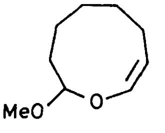
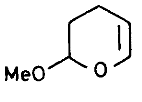
Proton loss from an oxocarbenium moiety of ionic bicyclobutane is found to compete appreciably with the capture of the oxocarbenium by alcohol molecules.

Vinyl ether hydrolysis provides one of the major pathways for the investigation of oxocarbenium ions.[2] In practically all cases the reaction mechanism involves an irreversible protonation on carbon. The sole exception to this behaviour was demonstrated by the hydrolysis of 9-methoxy-2,3-didehydro-oxonane (**1**).[3] In this reaction the rate constant for deprotonation of the intermediate by acetate ion was found to exceed the hydration rate constant by a factor of *ca.* 400 mol^{-1} dm^3. Even though hydration is not expected to be overwhelmingly preferred over proton removal from an oxocarbenium ion,[4] this behaviour is unique to (**1**). In contrast, the analogue 2-methoxy-3,4-dihydro-2*H*-pyran (**2**) represents 'normal' reaction behaviour[5] (*i.e.* hydration of the derived oxocarbenium is faster than proton removal from the α-carbon).

In this communication we report the second example of deprotonation of an oxocarbenium ion.



(**1**)



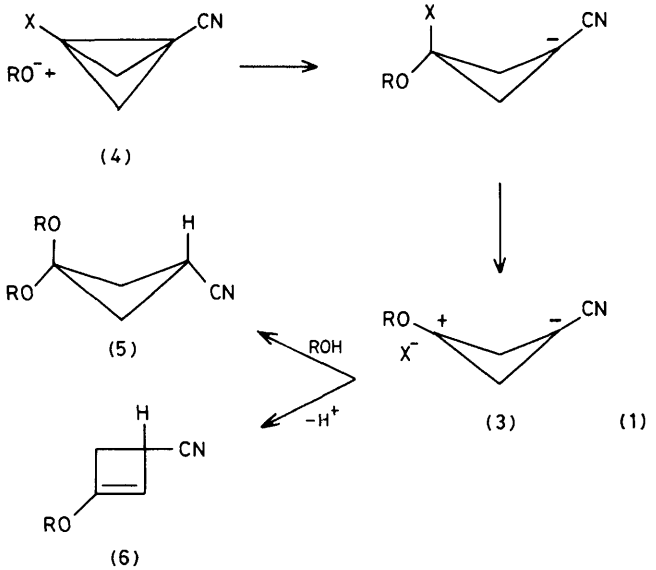
(**2**)

We have recently reported[1] the formation of the ionic bicyclobutane derivative (**3**) as an intermediate in the course of nucleophilic attack of alkoxides on 3-halogenobicyclobutanecarbonitrile (**4**), equation (1). The major product of these reactions is the acetal (**5**) formed by addition of alcohol to (**3**). The addition across the central ionic bond takes place in a manner similar to that of a normal Michael addition reaction, in which the trapping of the oxocarbenium ion is followed by the protonation of the cyano stabilized carbanion.

Table 1. Yields[a] of (**6**) obtained in the reaction of 3-chlorobicyclobutanecarbonitrile (**4**) with alkoxides.[b]

Nucleophile	Solvent	%(**6**)	Nucleophile	Solvent	%(**6**)
MeO^-	MeOH	5	$CF_3CH_2O^-$	Pr^iOH–CF_3CH_2OH(1 : 1)	10
EtO^-	EtOH	4			
Pr^iO^-	Pr^iOH	10—13 (0—5[c])	$CF_3CH_2O^-$	Bu^tOH + CF_3CH_2OH (0.1 M)	42(32[c])
Bu^tO^-	Bu^tOH	0[d]	MeO^-	THF	12[e]
$CF_3CH_2O^-$	CF_3CH_2OH	20	Pr^iO^-	THF	20[e]
MeO^-	Bu^tOH	18	Pr^iO^-	DME	20[e]

[a] Based on g.c. analysis. [b] [Substrate] 0.05—0.002 M, [alkoxide] 0.1—0.7 M. [c] Obtained with the bromo derivative of (**4**). [d] Only nucleophilic attack (on Cl atom and cyano group) was observed. [e] Heterogeneous conditions.



(1)

An accompanying product in these reactions is the vinyl ether (**6**) which is formed by a proton loss from the oxocarbenium intermediate. The reaction was studied in a variety of nucleophile–solvent combinations as shown in Table 1.

The nucleophile–solvent effects on the observed amount of (**6**) exclude the possibility of an *E*2 reaction (on either starting material or any of the intermediates) as the mechanism responsible for the vinyl ether formation. Highly supportive of this conclusion is the Cl/Br element effect on the percentage of (**6**). Such an element effect was observed also for the substitution–elimination ratio in the reaction of 2,3,3-trimethylbut-2-yl cation paired with halide anions.[6]

Thus, this study provides the second example of a deprotonation of an oxocarbenium ion which competes to an appreciable extent with nucleophilic attack on the cationic centre. The reason for the observed behaviour of this system apparently lies in the formation of an extended conjugated system (allyl anion) as well as in the variation of the relative nucleophilicities and basicities of the involved species.

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References

1 For part 5 in the series 'Cyclobutane–Bicyclobutane System' see: S. Hoz and D. Aurbach, *J. Am. Chem. Soc.*, 1983, **105**, 7685.
2 Y. Chiang, W. K. Chwang, A. J. Kresge, and S. Szilagyi, *Can. J. Chem.*, 1980, **58**, 124, and references therein; W. P. Jencks and P. R. Young, *J. Am. Chem. Soc.*, 1977, **99**, 8238.
3 J. D. Cooper, V. P. Vitullo, and D. L. Whalen, *J. Am. Chem. Soc.*, 1971, **93**, 6294.
4 A. J. Kresge and W. K. Chwang, *J. Am. Chem. Soc.*, 1978, **100**, 1249; Y. Chiang, A. J. Kresge, and C. I. Young, *Can. J. Chem.*, 1978, **56**, 461; A. J. Kresge and H. J. Chen, *ibid.*, 1972, **94**, 2818.
5 R. A. Burt, Y. Chiang, and A. J. Kresge, *Can. J. Chem.*, 1980, **58**, 2199.
6 J. F. Bunnett and D. L. Eck, *J. Org. Chem.*, 1971, **36**, 897.