Hydrolysis of Oxiranylmethyl Tosylates

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Summary The participation of the oxiran carbon–carbon bond during hydrolysis of oxiranylmethyl tosylates gives rise to a 2-oxocyclobutyl cation which is further hydrolysed to a ketol.

One interesting aspect of studies of the participation of the oxiranyl group is in determining if the stabilisation of the electron-deficient carbon is due to the unshared, lone pair of the oxygen, or to a conjugation of the oxiran ring,[1] or to both these effects.[2]

We present here results on the hydrolysis of oxiranylmethyl tosylates in the presence of a buffer [$CaCO_3$ for preparative scale, and (—)-nicotine for kinetic results]. Whereas the tosylate (**1**) gives only the α-ketol (**2**), the tosylates (**3t**), (**3e**), (**4t**), and (**4e**) give mainly β-ketols

The structure of the ketols (**9**) and (**10**) was determined by reduction with $LiAlH_4$ to 3-methylpentane-2,4-diol[3] and comparison of its n.m.r. spectra with those of the four known isomers.[4] β-Ketols result from participation of the C–C bond of the oxiran yielding the oxetan-2-yl cation (**11**). The behaviour of this cation is inferred from that of alkoxy-cations occurring in the acid-catalysed hydrolysis of acetals.[5]

The stereochemistry of the ketol (**10**) obtained from (**4t**) shows that hydrolysis occurs with inversion of configuration of the functional carbon [this result is only partially observed for (**4e**), where a mixture of (**9**) and (**10**) is obtained]. This stereospecificity requires the C–OTs and C–C bonds to be antiperiplanar in the conformation leading to the transition state. In this case the interactions between non-bonded atoms are more important for the *erythro*-isomers (**3e**) and (**4e**) (R^2 = Me) where the C–O

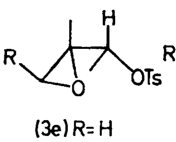
Table. Rates of hydrolysis[a]

Tosylates	10^4k, first order, 80·8 °C
(**3e**)	4·3 ± 0·1
(**3t**)	5·1 ± 0·15
(**4e**)	6·7 ± 0·18[b]
(**4t**)	13·8 ± 0·35[b]
(**12**)[c]	31·5 ± 0·8[b]

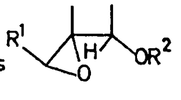
[a] Solvent dioxan–water (50:50 v/v), 0·035M-tosylate, buffer (—)-nicotine. The formation of (+)-nicotine–H^+ was followed polarimetrically at 436 nm. [b] Values extrapolated from 60 and 70 °C. [c] (**12**) = 2,2,3-trimethylpropyl tosylate.

bond of the oxiran and the C–Me bond are almost eclipsed. This observation can explain the existence of a non-stereospecific process in that case.

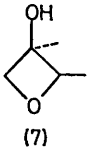
(1) (2)



(3e) R=H
(4e) R=Me



(3t) R^1=H, R^2=Ts
(4t) R^1=Me, R^2=Ts
(5) R^1=R^2=H
(6) R^1=Me, R^2=H



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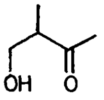

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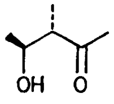

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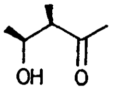
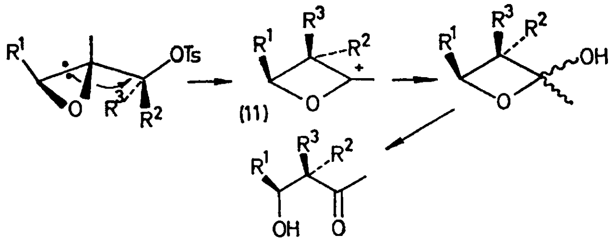


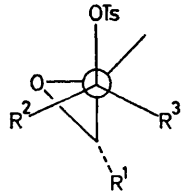
(10)

(**3e**) ⟶ (**5**) (5%) + (**7**) (13%) + (**8**) (82%)
(**3t**) ⟶ (**8**)
(**4e**) ⟶ (**6**) (12·5%) + (**9**) (59%) + (**10**) (28·5%)
(**4t**) ⟶ (**10**)

The kinetic results are in agreement with this: (a) the *threo*-isomers are hydrolysed faster than the *erythro* ones [*k*(**3t**)/*k*(**3e**) = 1·18, *k*(**4t**)/*k*(**4e**) = 2·06 at 80·8 °C]; (b) a methyl group β to the functional carbon (R^1 = Me), in each diastereoisomer, increases the rate of hydrolysis [*k*(**4e**)/*k*(**3e**) = 1·55, *k*(**4t**)/*k*(**3t**) = 2·7 at 80·8 °C].



(8) R^1 = R^3 = H, R^2=Me
(9) R^1 = R^2 = Me, R^3=H
(10) R^1 = R^3 = Me, R^2=H



(3e) R^1=R^3=H, R^2=Me
(3t) R^1=R^2=H, R^3=Me
(4e) R^1=R^2=Me, R^3=H
(4t) R^1=R^3=Me, R^2=H

We conclude from these observations that the oxiranyl group shows in participation reactions a reactivity analogous to that of the cyclopropane ring. It is well known that derivatives of (1-methylcyclopropyl)methyl are solvolysed to yield as major product the 1-methylcyclobutyl cation.[6] Similarly, we obtained the 2-methyl-2-oxetanyl cation from oxiranyl derivatives.

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