Rearrangement, Participation, or Fragmentation in the Solvolysis of β-Substituted Alkyl Tosylates

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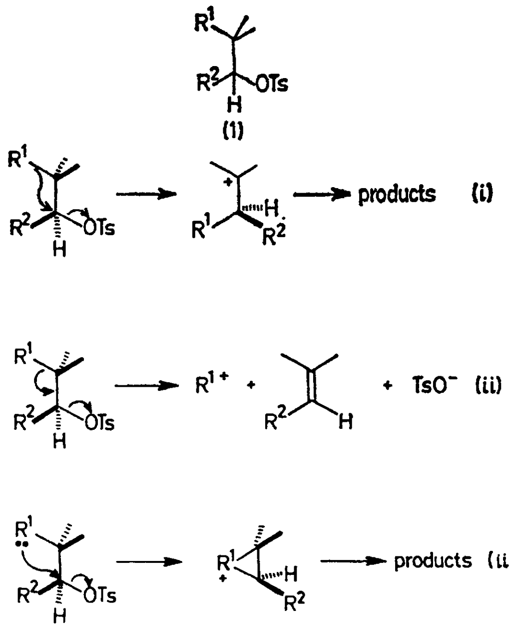
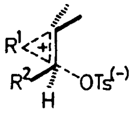
Summary In the solvolysis of compounds analogous to neopentyl tosylate, sulphonyl and sulphinyl groups rearrange, carbonyl groups participate or rearrange according to the conformation of the carbonyl oxygen atom, while nitro and phosphoryl groups lead to fragmentation.

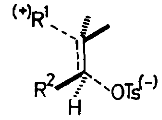
Three closely related solvolysis pathways are open to alkyl tosylates carrying a substituent (R^1) in the β-position (**1**); (i) rearrangement of the substituent (or of one of the methyl groups) (ii) fragmentation with loss of $R^{1}+$, or (iii) participation by some nucleophilic atom in the substituent (Scheme 1). These reactions are closely related because all three require the same anti–peri–planar conformation of substitutent R^1 and leaving group OTs in the reagent, participation may lead to rearrangement, and the transition states for rearrangement (**2**) and fragmentation (**3**) are only slightly different.



Scheme 1



(2)



(3)

What factors decide which pathway shall be followed? At which point do the pathways diverge? These are intriguing questions which we have attempted to answer by studying the solvolysis of compounds (**1**) with electron-withdrawing functional groups as R^1. Compounds with alkyl or aryl groups as R^1 in (**1**) have been widely studied and the reaction usually observed is rearrangement, as in the pinacolyl derivative (**1**; $R^1 = R^2 = Me$).[1]

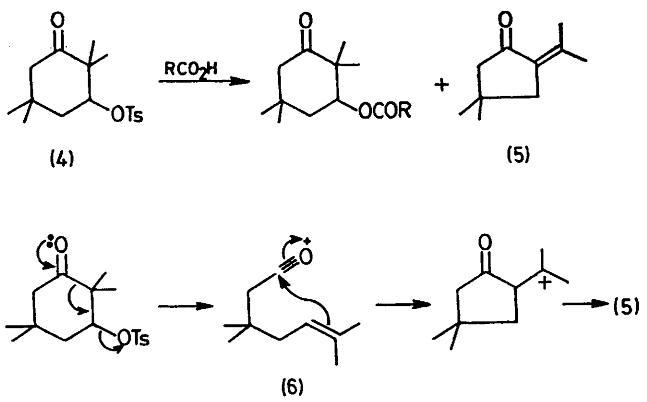
Table

Reaction pathways in the solvolysis of β-substituted alkyl tosylates (**1**)

Functional group, R^1	R^2	Reaction	Ref.
$Ph_2P(O)$[b], Ph(Me)P(O)	H,Me[c]	Rearrangement; R^1 migrates	2,3
$(RO)_2P(O)$	H	Fragmentation	5
Ph(MeO)P(O)	H	”	a
Ph(HO)P(O)	H,Me	”	a
O_2N[d]	Me	”	a
$PhSO_2$[b,c]	Me	Rearrangement; R^1 migrates	a
PhSO[b,c]	Me	”	a
MeO	H	”	6
MeCO, PhCO	H,Me	1,4-Participation; unrearranged products	4

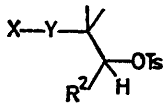
[a] This work. [b] Rates of rearrangement: PhSO > Ph_2PO > $PhSO_2$. [c] Products are olefins: $R^1CHMe{\cdot}C(=CH_2)Me$. [d] Product (NO_2+) trapped by anisole to give *p*-nitroanisole.

We have already described the reactions of some phosphine oxides[2,3] and ketones[4] and we now report the reactions of compounds containing other electron-withdrawing functional groups based on phosphorus, sulphur, carbon, and nitrogen atoms. All these results are summarised in the Table.



Scheme 2

The cyclic ketone (**4**) cannot react by the usual 1,4-carbonyl participation[4] because of the conformation of the carbonyl group. Solvolysis gives a mixture of rearranged (**5**) and unrearranged products (Scheme 2). The rearranged product, cycloartemesia ketone (**5**),[7] could be formed either by an acyl rearrangement or by fragmentation to the acylium ion (**6**) and cyclisation.



(**7**) X—Y = R^1

Except in this last case, each molecule follows one pathway only. Though it would be foolish to attempt to 'explain' these reactions, some firm conclusions can be drawn: 1, if rearrangement occurs, it is always the electronegative group, and never a methyl group which migrates; 2, however, the more electronegative the group, the slower the migration (*e.g.* $PhSO_2$ *vs.* Ph_2PO); 3, if 1,3-participation is possible, it occurs (PhSO, MeO[6]); 4, high electron density on atom X in R^1 (**7**) encourages fragmentation or 1,4-participation at the expense of rearrangement [NO_2,RCO; $(RO)_2PO$ *vs* R_2PO]; 5, electronegative groups based on second-row elements (S, P) migrate more readily than those based on first-row elements (N, C).

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