1,4-Carbonyl Participation in the Solvolysis of 3-Oxo-tosylates

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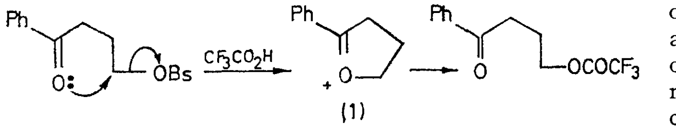
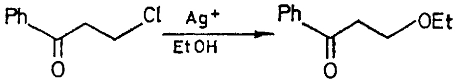
Summary Solvolysis of 3-oxo-tosylates in trifluoroacetic acid occurs by 1,4-carbonyl participation.

Participation by the carbonyl group in solvolysis reactions *via* five- (**1**) or six-membered cyclic intermediates is well established: the intermediate (**1**) is formed extremely rapidly and is stable indefinitely at room temperature.[1] Participation to form a four-membered ring is expected to be less effective and the intermediate to be much less stable.



(1)



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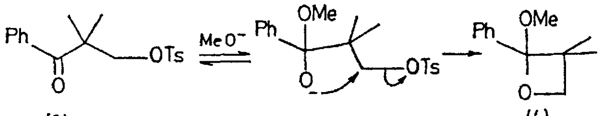
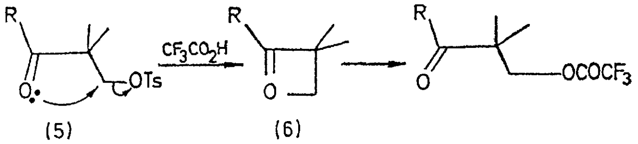
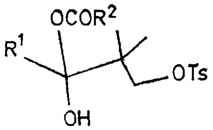


(3) (4)

The 3-oxo-chloride (**2**) shows a small (×8) rate acceleration over n-butyl chloride when treated with $AgNO_3$ in aqueous ethanol but the evidence for participation is ambiguous.[2] The most clear cut examples of 1,4-carbonyl participation occur in the extensive studies of Nerdel and Weyerstahl[3] on the reactions of compounds such as (**3**) with nucleophiles, but in these cases it is the adduct of the nucleophile and the carbonyl group which reacts, and not the carbonyl group itself.[4]



(5) (6)



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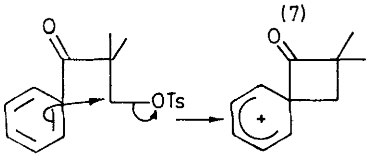

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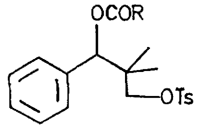
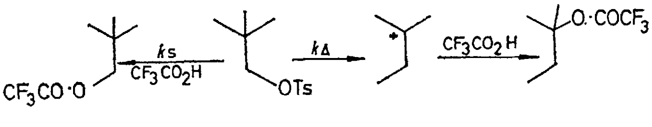


(9)

We now report that in the highly ionising solvent trifluoroacetic acid, compounds of this type (**5**; R = Me, Ar) react by direct 1,4-carbonyl participation through cationic intermediates (**6**). The evidence is briefly: (i) The products are unrearranged trifluoroacetates but the reaction cannot be a direct substitution as it occurs very much faster (*ca.* 10^7) than the unobserved direct substitution (k_s) reaction on neopentyl tosylate (Table). Direct substitution on (**5**) ought to be even slower than on neopentyl tosylate as steric hindrance is greater. In fact, the rates for (**5**) are of the same order of magnitude as that of the observed rearrangement (k_Δ) of neopentyl tosylate to a tertiary cation.



(ii) The order of reactivities (R = p-$MeOC_6H_4$ > Ph > p-$NO_2C_6H_4$ > Me, see Table) is that expected for carbonyl participation to give the cation (**6**), and the reverse of that expected for formation of a carbonyl adduct (**7**).

Table

Solvolysis of compound:	k_{obs} (s^{-1}, 75°) In CF_3CO_2H	In HCO_2H
(5; R = Ph)	$1\cdot8 \times 10^{-4}$	$4\cdot0 \times 10^{-5}$
(5; R = p-$MeOC_6H_4$) ..	$5\cdot4 \times 10^{-4}$	$3\cdot5 \times 10^{-4}$
(5; R = p-$NO_2C_6H_4$)	$7\cdot6 \times 10^{-6}$	$>4 \times 10^{-3}$
(5; R = Me)	$1\cdot1 \times 10^{-6}$	—
Neopentyl tosylate, k_Δ^5 ..	$1\cdot1 \times 10^{-4}$	—
Neopentyl tosylate, k_s^a ..	$2\cdot3 \times 10^{-11}$	—

[a] Estimated from data in ref. 5.

(iii) In the more nucleophilic solvent formic acid, a simple substitution again occurs, but this time the order of reactivities (R = p-$NO_2C_6H_4$ > p-$MeOC_6H_4$ > Ph) suggests that the carbonyl adduct (**7**; R^1 = p-$NO_2C_6H_4$, R^2 = H) is an intermediate in the solvolysis of the p-NO_2 compound in this solvent.

(iv) The same product is formed under the same conditions from the oxetan acetal (**4**) but at a much greater rate. Presumably the cation (**6**; R = Ph) is an intermediate.

(v) The activation parameters compare reasonably with those for the formation of the five-membered ring (**1**):

Formation of (**6**; R = Ph) from (**5**; R = Ph) in
CF_3CO_2H: $\Delta H^\ddagger = 21$ kcal/mol, $\Delta S^\ddagger = -15$ e.u.
Formation[1] of (**1**) $\Delta H^\ddagger = 19$ $\Delta S^\ddagger = -11$

The alternative 1,4-aryl participation we feel is unlikely as the intermediate (**8**) would surely undergo a dienol–benzene type of rearrangement. In any case, the esters (**9**) which could solvolyse by aryl participation, can be recovered after four half-lives of (**5**; R = Ph) under the same conditions.

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