Acid Catalysed Stereomutations about the C(2)–C(3) Bond of 3-Aryl-1-methoxyallyl Cations. Dication Formation by Oxygen Protonation

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The thermally induced *cis* to *trans* isomerization of 3-aryl-1-methoxyallyl cations in superacid media is shown to occur by formation of an intermediate O-protonated dication.

Recently we have shown that one of the pathways for *cis* to *trans* isomerization of unsaturated iminium salts involves protonation at nitrogen to form an intermediate dication.[1] The question arises as to whether a comparable mechanism could operate with the corresponding oxygen substituted analogues. Such a mechanism would be unprecedented in the chemistry of protonated carbonyl compounds and their related *O*-alkyl derivatives.

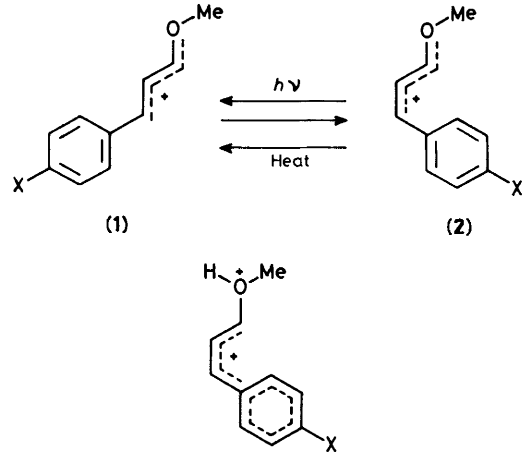
The cations (**1a**—**d**) were prepared by dissolution of the dimethyl acetals of the corresponding aldehydes in FSO_3H, CF_3SO_3H, and FSO_3H–SbF_5. The ions were fully characterized by ^1H n.m.r. and u.v. spectroscopy. Irradiation of solutions of the cations at −60 °C led in each case to the production of photostationary states consisting of (**1**) and the corresponding C(2)–C(3) *Z* isomers (**2**).[2] The latter isomers were identified by the characteristic 9—11 Hz proton–proton coupling constant across the C(2)–C(3) bond.

The *Z* isomers (**2**) underwent an irreversible thermal isomerization to the corresponding *E* isomers when the FSO_3H solutions of the mixture of these ions were heated. The rates of these stereomutations were followed by ^1H n.m.r. spectroscopy. Good first order kinetics were observed and the rate constants are given in Table 1.

It is obvious from the data presented in Table 1 that the rate constants for these stereomutations are markedly dependent on the aryl substituent with electron donating groups accelerating the reaction. A good correlation with σ^+ ($r = 0.9992$) was observed with a large negative slope ($\rho = -5.6$ at −5 °C). It is clear that the conversion of (**2**) → (**1**) in this series involves a single mechanism in which the positive charge on the aryl ring is substantially increased in the transition state as compared to that of the starting cations (**2**).

The rates of conversion of (**2**) into (**1**) are dependent on the acid medium used, Table 1. In the stronger acid FSO_3H–SbF_5 (4 : 1),[3] the isomerizations of (**2b**), (**2c**), and (**2d**) are all much more rapid than in FSO_3H. In CF_3SO_3H, a weaker acid,[4] the isomerization of (**2b**) to (**2c**) is slower than in FSO_3H. The magnitude of the acid strength dependence is large and clearly indicates that the stereomutations involve protonation of (**2**).

Similar large acid strength dependencies have been observed in the rearrangements of protonated cyclohexenones[5] and the isomerization of protonic *cis*-cinnamic acid.[6] It was suggested in the former case that protonation took place at C(2) to form a dication. To test for such a possibility in the present case the isomerizations of (**2a**) to (**1a**) and (**2b**) to (**1b**) were examined in $FSO_3(^2H)$. No deuterium incorporation was detected during the course of these reactions nor when the cation (**1a**) was kept in the same medium at 4 °C for 80 half lives. In the strongest acid [$FSO_3(^2H)$–SbF_5] exchange of the aryl protons could be detected in several of the ions. The rate of this exchange depended on the aryl substituent, it being slowest when X is electron withdrawing. In the case of the isomerization of (**2c**) to (**1c**) in $FSO_3(^2H)$–SbF_5 deuterium exchange on the aryl ring was substantially slower than the rate of the stereomutation. No deuterium exchange could be detected at any site during the isomerization of (**2d**) → (**1d**) in $FSO_3(^2H)$–SbF_5. The deuteriations of the aryl rings would thus seem to be an independent reaction and not associated with the stereomutation of the C(2)–C(3) bond.



(**1**) (**2**)

(**3**)

a; X = Me
b; X = H
c; X = Cl
d; X = CF_3

Table 1. Rate constants for stereomutation.

Reaction	Medium	Rate const. (s^{-1})	Temp. (°C)	$\Delta G^\ddagger$ (kcal mol^{-1})[a]
(**2a**) → (**1a**)	FSO_3H	4.0×10^{-4}	−29	18.0
		1.2×10^{-2} [b]	−5	
(**2b**) → (**1b**)	FSO_3H	2.0×10^{-4}	−5	20.2
	FSO_3–SbF_5	1.9×10^{-4}	−30	18.2
		6.9×10^{-3}	−5[b]	
	CF_3SO_3H	2.4×10^{-4}	+9	21.2
		3.0×10^{-5}	−5[b]	
(**2c**) → (**1c**)	FSO_3H	3.0×10^{-4}	+11	21.2
		3.0×10^{-5} [b]	−5	
	$FSO_3(^2H)$–SbF_5	5.7×10^{-4}	+5	20.4
(**2d**) → (**1d**)	FSO_3H	1.5×10^{-4}	+45.5	24.3
		8.5×10^{-8}	−5[b]	
	FSO_3H–SbF_5	1.0×10^{-3}	+45.5	23.1

[a] $\Delta G^\ddagger$ values were calculated using the Eyring equation and assumed to be temperature independent for the purpose of extrapolation. 1 kcal = 4.18 kJ. [b] Extrapolated value.

Clearly the mechanisms of the isomerizations of (**2**) to (**1**) do not involve protonation at C(2). In the case of (**2c**) and (**2d**) it is also clear that the stereomutations do not involve protonation at any other carbon site in the cations. It would appear that these stereomutations must involve protonation at oxygen to form the dication (**3**). Such a mechanism is fully consistent with the substituent effects noted above.

At first glance such a mechanism seems to be unreasonable, however, let us point out three things. First, the dication (**3**) is in effect only an aryl substituted allyl cation with an inductively withdrawing group at C(1). Second, the dication (**3**) is likely to be the most stable of all possible dications formed for these systems. Third, in the protonation of conjugated systems it is usual to add the proton to one of the ends of the ribbon. Far from being an outrageous suggestion or chemical curiosity, it is likely that oxygen protonation will be found to be a common process in the chemistry of protonated carbonyl compounds.

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