

Eliminative Cleavage of Cyclopropanes: Leaving Group Stabilisation and Transition-state Structure

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In eliminative ring fission of cyclopropanes, the extent of ring fission in the transition state is sensitive to the function stabilising the leaving group; it is small when the stabilising group is phenylsulphonyl, but substantial when it is cyano.

In the preceding communication,¹ acceleration of alkene-forming elimination by straining the connection to a carbon leaving group in a small ring was reported. Comparison with an acyclic unstrained analogue showed acceleration by a factor of at least $10^{11.7}$. We now report on the effect of structure on reactivity for such strained leaving groups and upon the information thereby obtained about transition states for ring fission.

Substrates (Table 1) were obtained by routes similar to those used for (1)¹ and rates of formation of the dienes (7) in the standard² base-solvent system, ethanolic sodium ethoxide, were measured. For substrates (1)–(3), values of $(k_H/k_D)_\beta$ are all close to unity showing that the rate-determining step in formation of the ions (6) is cleavage of the ions (5) (k_2) and the mechanism therefore is $(E1cB)_R$. For substrate (4), incorporation of deuterium from EtONa–EtOD occurred at a rate comparable with that of elimination and the mechanism of ring fission cannot be confidently assigned for this borderline case.

Comparison of the results for substrates (1) and (2) shows that attachment of a phenyl group to the leaving group produces little acceleration of ring fission and as the rank²

(= nucleofugality) data show, all this small effect can be accounted for by inductive acceleration of deprotonation.³ α -Phenyl substitution has a substantial effect on the stability of sulphonyl-stabilised carbanions (Table 1), yet none of this stabilisation is reflected in acceleration of ring fission. In addition, the activation parameters for (1) and (2) are strikingly similar.

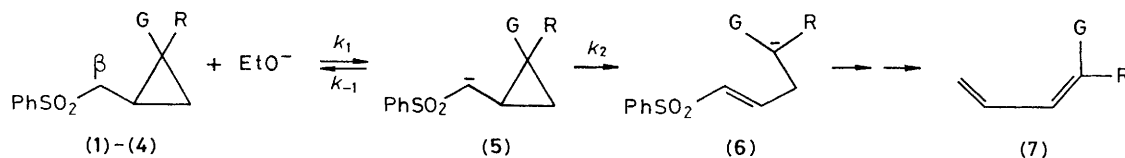
Activated alkene-forming elimination is rather insensitive to leaving group stability within a closely related series. Thus for β -aryloxyethyl sulphones, $\text{PhSO}_2\text{CH}_2\text{CH}_2\text{OAr}$, elimination of aryloxide shows $\beta_{\text{L.G.}} = 0.40$ ⁴ Nevertheless, the miniscule effect of attachment of a phenyl group to the leaving group as in (2) suggests a very small extent of cleavage of the bond to the leaving group (= ring opening). This small extent of ring opening is, however, associated with release of about 60% of the ring strain energy.¹ Evidently, strain in a cyclopropane diminishes very steeply with extension of a ring bond.

The nitriles (3) and (4) reveal a different situation. The cyano-group is less effective than the phenylsulphonyl group in carbanion stabilisation (Table 1) and the rank of (3) is lower than that of (1) or (2). Ring fission is evidently more

Table 1. Eliminative ring fission of cyclopropanes.

Substrate	$k_{\text{obs}}^{\text{a,b}}$	$(k_H/k_D)_\beta^{\text{c}}$	Rank ^{d,e}	$\text{p}K_{\text{a}}^{\text{f}}$ (Me ₂ SO) of MeCHRG	$\Delta H^{\ddagger\text{g}}$	$\Delta S^{\ddagger\text{h}}$
(1; R = H; G = PhSO ₂)	4.7×10^{-3}	0.97	+8.8 ¹	31.1	17.7	-10
(2; R = Ph; G = PhSO ₂)	1.9×10^{-2}	1.00	+8.8	25.4	18.0	-6
(3; R = H; G = CN)	1.9×10^{-3}	1.02	+8.4 ¹	32.6	24.9	+12
(4; R = Ph; G = CN)	2.4	1.03 ^k	+10.9 ¹	23.0	17.0	0

^a Determined spectroscopically for reactions at $25 \pm 0.1^\circ\text{C}$ in ethanolic sodium ethoxide. ^b Units: l mol^{-1} . ^c Mean of three determinations. ^d $\log k_{\text{obs}} - \log k_{\text{deprotonation}} + 11$. ^e Values of $k_{\text{deprotonation}}$ either derived from $k_{\text{deprotonation}}$ and $k_H/k_T = 7.1$ (ref. 3) or calculated from data in ref. 3. ^f Estimated from data in ref. 5. ^g Units: kcal mol^{-1} (1 cal = 4.184 J). ^h Units: $\text{cal mol}^{-1} \text{K}^{-1}$. ⁱ $k_{\text{deprotonation}} = 1.2 \times 10^{-1} \text{l mol}^{-1} \text{s}^{-1}$. ^j $k_{\text{deprotonation}} = 1.1 \times 10^{-1} \text{l mol}^{-1} \text{s}^{-1}$. ^k Value uncertain as only partially deuterated substrate could be obtained. ¹ Rank = 11 = $(E1cB)_T$ mechanism.



advanced at the transition state; ΔH^\ddagger and ΔS^\ddagger are both more positive for (3) than for (1). This is consistent with the greater mesomeric component of the stabilisation of carbanions by cyano than by sulphonyl groups;⁵ a greater degree of transfer of charge to the leaving group is required to benefit from cyano-stabilisation.

Attachment of a phenyl group to the cyano-stabilised leaving group as in (4) accelerates ring fission by a factor of 10^3 . This makes the rate of ring fission comparable with that of deprotonation,† as shown also by the calculated rank for the phenyl-cyano leaving group of 10.9. This is clearly due to the very large additional stabilisation conferred by an α -phenyl group on a cyano-stabilised carbanion (pK_a data in Table 1). Uncertainty about the mechanism of elimination in (4) does not, however, allow much significance to be attached to the rank of this leaving group.

† This substrate was recovered after 2 s from 10^{-3} M $\text{EtO}^- \text{Na}^+ - \text{EtOD}$ in a *ca.* 50:50 mixture with product. The substrate showed about 30% of replacement of β -protonium by deuterium.

Activation entropies suggest, as expected, a smaller degree of ring fission in the transition state for (4) than for (3). The compromise between charge delocalisation in the leaving group and ring fission is achieved earlier in the bond cleavage process.

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