The Feeble Nucleofugality of a Nitronate Leaving Group and its Enhancement by Ring Strain

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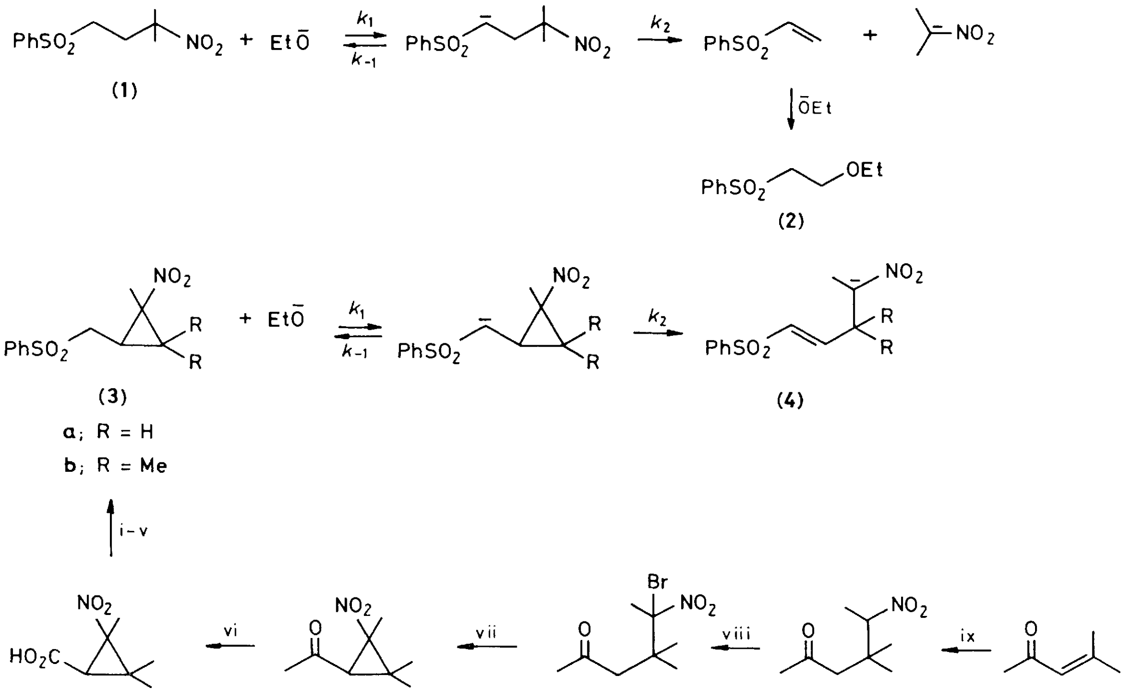
The rank of a nitronate ion in activated alkene-forming elimination is low (+2.6); incorporation of the leaving group in a cyclopropane accelerates elimination so much that the $(E1cB)_R$–$(E1cB)_I$ borderline is traversed but the *retro*-Thorpe–Ingold effect nevertheless operates.

Carbon leaving groups in alkene-forming eliminations have exceptionally low ranks[1,2] (= nucleofugalities) which bear no relation to the $\mathrm{p}K_a$ of the conjugate acid of the leaving group (Z).[2] Within a group of three carbon leaving groups of closely similar $\mathrm{p}K_a^{ZH}$ values, the nitronate ion, $\mathrm{Me_2\bar{C}NO_2}$, came midway in rank between $\mathrm{PhCH_2\bar{C}(CN)_2}$ and $\mathrm{\bar{C}N}$ for 1,2-elimination activated by a benzoyl group.[2] We have now measured the rank of this group in sulphonyl-activated 1,2-elimination and studied the enhancement of its nucleofugality on incorporation in a strained ring.



Scheme 1. i, $EtOH-H_2SO_4$; ii, $LiAlH_4-Et_2O$; iii, *p*-$MeC_6H_4SO_3Cl$–pyridine, 0 °C; iv, PhSNa–EtOH; v, $H_2O_2-MeOH-(NH_4)_2MoO_7$; vi, Br_2-NaOH; vii, $MeCO_2K-EtOH$; viii, $NaOMe-MeOH-Br_2-CHCl_3$; ix, $NaOEt-EtNO_2$.

Table 1. Eliminations in ethanolic sodium ethoxide.[a]

Substrate	k_{obs}[b]	k_1[b,c]	Rank
(1)	1.5×10^{-9}[d]	0.33	+ 2.6
(3a)	61.7	3.5	+12.2[e]
(3b)	5.3	1.6	+11.5[e]

[a] At 25 °C. [b] Units $dm^3 mol^{-1} s^{-1}$. [c] Calculated from $\rho^* \sigma^*$ plots (ref. 3). [d] Estimated from reactions at 80 and 90 °C. [e] *N.B.* a rank >11 shows *E*2 or, within limits, $(E1cB)_I$ mechanisms.

Substrate (**1**) (Table 1) obtained by addition of 2-nitropropane to phenyl vinyl sulphone slowly eliminates 2-nitropropane in ethanolic sodium ethoxide at *ca.* 90 °C. Determination by g.l.c. of the ethoxy-sulphone (**2**) and 2-nitropropane formed allows estimation of the rate constant at 25 °C (Table 1). Calculation of the deprotonation rate constant, k_1[3] allows assignment of rank (+2.6) from the relation[4] Rank = $k_{obs} - k_1 + 11$.

When $k_1 \geqslant k_{obs}$ the mechanistic borderline between $(E1cB)_R$ processes ($k_{obs} \ll k_1$) on the one hand, and $(E1cB)_I$($k_{obs} = k_1$) and $E2$($k_{obs} > k_1$) on the other, is traversed. Such a situation is revealed when the same nitronate leaving group is incorporated in a strained ring as in (**3**) (Scheme 1).

The effect of straining the bond to a leaving group on its nucleofugality has recently been quantified[5] and very large enhancements have been reported. The cyclopropanes (**3a**) and (**3b**) have been synthesised (Scheme 1), the routes being modelled on earlier work.[6] Treatment with ethanolic sodium ethoxide initially gives the alkene (**4**), the reaction being followed by the u.v. spectral change. The rate constants in Table 1 show once again[5] the very large enhancement of k_{obs}, in this case by a factor of 4×10^{10}. Calculation of the rank value from k_{obs} and the calculated deprotonation rate shows that for (**3a**) the value of 11 is greatly exceeded. This points to the *E*2 mechanism for this substrate, a mechanism associated with excellent leaving groups such as halide. The effect of strain, therefore, is to convert a very poor into an excellent leaving group. The mechanistic borderline between the $(E1cB)_R$ and $(E1cB)_I$ mechanisms is traversed as k_2 exceeds k_{-1}, and evidently the very large enhancement of nucleofugality caused by strain calls the *E*2 mechanism into play.

For substrate (**3b**), *gem*-dimethyl substitution produces a small but significant decrease in k_{obs}, of which only a small part can be accounted for by the electronic effect of the methyl groups. Table 1 shows the calculated effect on k_1 were the mechanism a stepwise one. The calculated rank is, however, also above that (11) for the $(E1cB)_I$ process and the lower reactivity of this substrate is consistent with the operation of the *retro*-Thorpe–Ingold effect on the concerted processes of deprotonation and ring cleavage. This is in contrast with the effect of *gem*-dimethyl substitution on concerted eliminative ring-fission of oxirans.[7]

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