Ranks of Carbon Leaving Groups in Alkene-forming Elimination
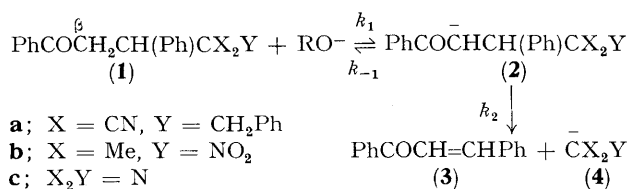
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Summary Carbon leaving groups in alkene-forming eliminations are exceptionally poor and their ranks show no correlation with the pK_a of the conjugate carbon acid; the extent of bond cleavage in the transition state is evidently critical in determining rank.

Ranks of leaving groups ($\equiv$ nucleofugalities) in alkene-forming eliminations are not related to the pK_a of the conjugate acid of the leaving group despite widespread belief that such correlations exist.[1] A particularly striking comparison is that between CN and $\overset{+}{N}Me_3$ with closely similar $pK_a^{Z-H}(H_2O)$ but with ranks differing by at least 12 (log) units.[2] Correlation of rank with pK_a^{Z-H} is,

however, seen when the atom connection to the leaving group is kept constant and the variation in remote functionality is small as for aryloxy-leaving groups in alkene-forming eliminations activated by β-arylsulphonyl and cyano-groups.[3] In such cases the variation in structure of the eliminated *ion* is small. We now report on a comparison of three *carbon* leaving groups in which it may be presumed that the structures of the eliminated ions are considerably different. The chalcone adducts (1a), (1b),[4] and (1c)[5] (Scheme) react on treatment with alcoholic alkoxides. Adducts (1a) and (1b) eliminate the carbanions (4) with formation of chalcone (3) whose rate of formation is measured by u.v. spectrometry. The rate constants vary slightly with [RO⁻] at low [RO⁻] and all reactions have therefore been compared at the same base strengths.

$$\text{PhCO}\overset{\beta}{\text{C}}\text{H}_2\text{CH(Ph)CX}_2\text{Y} + \text{RO}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{PhCO}\overset{-}{\text{C}}\text{HCH(Ph)CX}_2\text{Y}$$

$$\textbf{(1)} \qquad\qquad\qquad\qquad\qquad \textbf{(2)}$$

$$\downarrow k_2$$

a; X = CN, Y = CH$_2$Ph

b; X = Me, Y = NO$_2$ PhCOCH=CHPh + $\overset{-}{\text{C}}$X$_2$Y

c; X$_2$Y = N   **(3)**   **(4)**

SCHEME

The rate constants, k_{obs}, are much smaller than for deprotonation of similar ketones[4] and for (**1b**), for example, the primary kinetic deuterium isotope effect $(k_{H/D})_\beta = 1\cdot03$. We, therefore, assign the $(E1cB)_R$ mechanism with k_2 rate-determining (Scheme). For this mechanism $k_{obs} = k_1.k_2/k_{-1}$ [BH] and values of $\Delta\log k_2$ ($\equiv$ rank differences) are obtained (Table) using Δk_1 values derived from detritiation

small. The present results become interpretable against this background. If the extent of cleavage of the bond to the leaving group is small, delocalisation of the electron pair must *ipso facto* also be small. It is however to such delocalisation that the nitronate ion (**4b**) overwhelmingly, but the bis-cyano-stabilised ion (**4a**) much less crucially, owes its stability.[7] The cyanide ion (**4c**) is particularly intriguing in this respect. We and others[8] have been unable to observe elimination of this ion in protic solvents and the reasons for its very low rank remain mysterious. The comment has been made[9] that its low (calculated) displaceability in methyl transfer reactions is a consequence of the strong carbon–carbon bond in nitriles. In alkene-forming eliminations, however, bond strength does not appear to be a very important factor in determining nucleofugality.[1] Our results are consistent with a general concept

TABLE. Alkene-forming eliminations with carbon leaving groups.

Substrate	k_{obs}(MeO$^-$/MeOH)[a]	$\Delta\log k_2 = \Delta$Rank Z[b]	pK_a^{Z-H}(MeOH)
(**1a**)	10·5[c]	0	14·3[d]
(**1b**)	3·4 × 10^{-4} [e]	−3·9	13·5[f]
(**1c**)	[g]	> −7·9	13·3[f]

[a] Units: dm^3 mol^{-1} s^{-1} at 25 °C, [MeO$^-$] = 0·5 M. [b] Derivations assume that Δk detritiation (ref. 6) is the same for MeO$^-$/MeOH as for EtO$^-$/EtOH, and that σ^*(CH$_2$Z) values are additive and attenuated by a factor of 2·8 for an intervening methylene group. [c] Determined by stopped-flow spectrometry. [d] Determined spectroscopically using H$_-$(MeOH) values (C. H. Rochester, *J. Chem. Soc. B*, 1966, 121). [e] $(k_{H/D})_\beta = 1\cdot03$. [f] Determined spectroscopically using phenol as indicator, pK_a(MeOH) = 14·34 (C. H. Rochester, *Trans. Faraday Soc.*, 1966, **62**, 355). [g] No cyanide ion detectable during lifetime of the substrate in the reaction conditions. $t_\frac{1}{2}$ = *ca.* 48 h in molar MeO$\overset{-}{\text{N}}\overset{+}{\text{a}}$–MeOH.

measurements.[6] It is assumed, as before,[3] that k_{-1} is insensitive to the nature of Z. The Table shows no correlation of rank with pK_a^{Z-H}; indeed the comparison of (**1a**) and (**1b**) shows an out-of-match of 10^4 and of (**1a**) and (**1c**) one of at least 10^8.

All of the evidence so far available about alkene-forming reactions with the $(E1cB)_R$ mechanism suggests that the extent of cleavage of the connection to the leaving group is

that the nucleofugality of nucleofuges depends very much upon the extent of bond cleavage to the leaving group in the transition state. The less this is, the less good will be the correlation between rank and pK_a^{Z-H}.

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