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KINETICS OF DEPROTONATION OF TRIPHENYL(2-SUBSTITUTED-9-FLUORENYL)PHOSPHONIUM IONS IN 50% DIMETHYL SULFOXIDE–50% WATER. INTRINSIC RATE CONSTANTS, IMBALANCES AND EVIDENCE FOR CHANGES IN TRANSITION STATE STRUCTURE

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Rate constants (k_1^B and k_{-1}^{BH}) for the reversible deprotonation of triphenyl(2-Z-9-fluorenyl)phosphonium ions (Z = H, Br, NO_2) by piperidine, morpholine, *n*-butylamine, 2-methoxyethylamine, glycine ethyl ester, cyanomethylamine, OH^- and water were determined in 50% Me_2SO–50% (v/v) water at 20 °C. Brønsted α_{CH} (variation of carbon acid) and β_B values (variation of amine), and intrinsic rate constants [$\log k_0 = \log k_1^B/q$ when $pK_a^{BH} - pK_a^{CH} + \log(p/q) = 0$] were obtained. α_{CH} decreases with increasing basicity of the amine whereas β_B decreases with increasing acidity of the carbon acid. These trends, which imply changes in the transition-state structure with reactivity, can be described by the interaction coefficient $p_{XY} = \partial\beta_B/\partial pK_a^{CH} = \partial\alpha_{CH}/-\partial pK_a^{BH} = 0{\cdot}03$ (primary amines) and 0·01 (piperidine/morpholine). α_{CH} is smaller than β_B, indicating an imbalance due to a lag in the delocalization of the negative charge into the fluorenyl moiety at the transition state. The influence of the Ph_3P^+ group on the intrinsic rate constant is analyzed in terms of possible contributions by inductive/field (I), resonance (R), polarizability (P) and steric (S) effects. Using 9-carbomethoxyfluorene as a reference, it is shown that the stronger electron-withdrawing I effect of the Ph_3P^+ group relative to the COOMe group enhances $\log k_0$ substantially; the fact that the R effect of Ph_3P^+ is weaker than that of COOMe also contributes to an increase in k_0, and so does the P effect of the phosphorus. All these increases are virtually completely offset by the rate-retarding S effect of the bulky Ph_3P^+ group. A similar analysis for the Me_2S^+ derivative studied by Murray and Jencks [*J. Am. Chem. Soc.* 112, 1880 (1990)] leads to similar conclusions except that the still smaller R effect is probably one of the main reasons why k_0 for the Me_2S^+ derivative is more than ten times higher than for the Ph_3P^+ derivative; another potential reason is a difference in the steric effect.

INTRODUCTION

In contrast to proton transfers between electronegative atoms[1,2] which show little variation of the intrinsic barrier ($\Delta G_0^\ddagger$) or intrinsic rate constant (k_0) (For a reaction with forward and reverse rate constants k_1 and k_{-1}, $\Delta G_0^\ddagger$ is defined as $\Delta G_0^\ddagger = \Delta G_1^\ddagger = \Delta G_{-1}^\ddagger$ when $\Delta G^0 = 0$ and k_0 is defined as $k_0 = k_1 = k_{-1}$ when $K_1 = 1$; in proton transfers, statistical factors[3b] are usually included.) with structure, the intrinsic barriers of proton transfer to or from carbon are very sensitive to structural variations in the carbon acid or carbanion.[3] A recent compilation[4] of about 40 examples shows variations in $\log k_0$ from *ca* 9·0 for the reaction of **1** with carboxylate ions in water[5] to −1·22 and −2·10 for the reaction in the same solvent of phenylnitromethane with secondary alicyclic amines and carboxylate ions,[6] respectively.

The most important factor that affects these intrinsic rate constants is the ability or inability of the carbanion to delocalize the negative charge and have this charge solvated (for recent reviews, see Refs 4 and 7). The more effective this delocalization and solvation and the stronger the resulting stabilization, the lower is the intrinsic rate constant. This is because at the transition state the resonance and solvation is weak. This means that in the forward direction the rate is slow because the transition state benefits very little from the resonance and solvational stabilization of the developing carbanion, and in the reverse direction it is slow because most of the resonance stabilization and solvation of the carbanion are lost on reaching the transition state.

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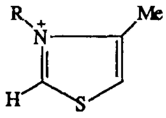

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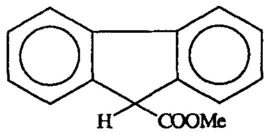

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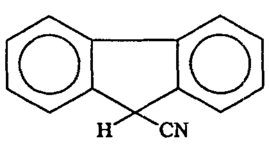

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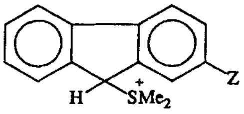
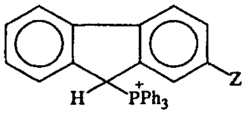
The intrinsic rate constants for the deprotonation of fluorene derivatives lie roughly midway between the extremes for **1** and $PhCH_2NO_2$. For example, log k_0 for the deprotonation of 9-carbomethoxyfluorene (**2**) by primary amines is 2·84 in 50% Me_2SO–50% water, and 3·09 in 90% Me_2SO–10% water;[8] for the deprotonation of 9-cyanofluorene (**3**) by the same amines log $k_0 = 3{\cdot}62$ in 10% Me_2SO–90% water, 3·76 in 50% Me_2SO–50% water and 3·57 in 90% Me_2SO–10% water;[8] for the deprotonation of the dimethyl (9-fluorenyl)sulfonium ion (**4-H**) by primary amines and oxyanions (mainly $RCOO^-$) in water, log $k_0 \approx 4{\cdot}0$ and $\approx 5{\cdot}0$, respectively.[9] These results indicate that the resonance stabilization of the fluorenyl anion is substantial but not nearly as strong as in the phenylnitronate ion.



4-Z (Z = H, Br, NO_2)



5-Z (Z = H, Br, NO_2)

The data on **2**, **3** and **4-H** also suggest that the 9-substituent may affect k_0 in a significant way. A study of the deprotonation of the triphenylphosphonium ions **5-Z** should therefore help in further unraveling the possible interaction mechanisms by which the 9-substituent influences k_0 and this will be a major focus of this investigation. The main possibilities are inductive/field (I) effects, resonance (R) effects, steric (S) effects and, in the case of **4-Z** and **5-Z**, polarizability (P) effects that can stabilize the negative charge of the ylide.[10,11] Electron-withdrawing I effects should increase k_0 and S and R effects should decrease k_0.[4,7] P effects have not been considered before but it will be shown that they should increase k_0. Murray and Jencks[9] concluded that the resonance effect of π-backbonding from carbon to d-orbitals of the sulfur in the ylide derived from **4-H** affects k_0 only in a minor way, if at all; whether resonance effects contribute to the stabilization of the ylide is an unresolved issue.[12] The deprotonation of **5-H** may, however, show a more pronounced R effect on k_0; *ab initio* calculations by Gassman and co-workers[12c,d] suggested that π-backbonding in the phosphonium ylides is stronger than in the sulfonium ylides.

A second point of interest is the degree of transition-state imbalance[7,13] that arises from the lag in the resonance development behind proton transfer. This imbalance can be investigated by comparing Brønsted β_B values determined from the dependence of the deprotonation rates on the pK_a^{BH} of the base with the Brønsted α_{CH} values obtained by varying the pK_a^{CH} of the carbon acid (**5-Z** with Z = H, Br and NO_2).

A third question we wish to examine is the extent by which the transition-state structure changes with the reactivity of the carbon acid and the base. Such changes can be described by the interaction coefficient $p_{xy} = \partial\beta_B/\partial pK_a^{CH} = \partial\alpha_{CH}/-\partial pK_a^{BH}$.[13] In proton transfers with very high intrinsic barriers, such as the deprotonation of nitroalkanes, there is essentially no change in transition-state structure, i.e. $p_{xy} \approx 0$, but with lower intrinsic barriers such changes can be substantial, e.g. $p_{xy} = 0{\cdot}04$ and 0·07 for the reaction of **4-Z** with primary amines and oxyanions, respectively.[9] Our results show similar but smaller changes in transition-state structure for the deprotonation of **5-Z** by primary amines.

RESULTS

All measurements were made in 50% Me_2SO–50% (v/v) water at 20 °C and an ionic strength of 0·5 M maintained with KCl. The pK_a^{CH} values of **5-H**, **5-Br** and **5-NO₂** were determined by standard spectrophotometric procedures, exploiting the large difference in the UV spectra of the triphenyl(2-substituted-9-fluorenyl)phosphonium bromides and their respective ylides. Typically the pK_a^{CH} was obtained as the average of nine determinations according to the equation

$$pK_a^{CH} = pH + \log\left(\frac{A_{C^-} - A}{A - A_{CH}}\right) \qquad (1)$$

where A_{C^-}, A_{CH} and A are the absorbances at $pH \gg pK_a^{CH}$, $pH \ll pK_a^{CH}$ and $pH \approx pK_a^{CH}$, respectively. The measurements were carried out in 2-methoxyethylamine (**5-H**), cacodylate (**5-Br**) and acetate buffers (**5-NO₂**). The pK_a^{CH} values are reported in Table 1; they have an estimated uncertainty of ±0·03 pK_a units.

All rates were measured in a stopped-flow spectrophotometer. The reactions can be described by

$$\mathbf{5\text{-}Z} \underset{k_{-1}^{H}a_{H^+} + k_{-1}^{H_2O} + k_{-1}^{BH}[BH]}{\overset{k_1^{H_2O} + k_1^{OH}a_{OH} + k_1^{B}[B]}{\rightleftharpoons}} \mathbf{5\text{-}Z}^- \qquad (2)$$

Table 1. Summary of rate constants and pK_a values for reaction (2) in 50% Me_2SO-50% water at 20 °C[a]

		5-H ($pK_a^{CH} = 9\cdot38$)		**5-Br** ($pK_a^{CH} = 7\cdot47$)		**5-NO₂** ($pK_a^{CH} = 5\cdot62$)	
B	pK_a^{BH}	k_1^B ($l\ mol^{-1}\ s^{-1}$)	k_{-1}^{BH} ($l\ mol^{-1}\ s^{-1}$)	k_1^B ($l\ mol^{-1}\ s^{-1}$)	k_{-1}^{BH} ($l\ mol^{-1}\ s^{-1}$)	k_1^B ($l\ mol^{-1}\ s^{-1}$)	k_{-1}^{BH} ($l\ mol^{-1}\ s^{-1}$)
OH^-	$17\cdot34$	$2\cdot59 \times 10^{6}$	$7\cdot83 \times 10^{-1}$[b]	$9\cdot06 \times 10^{6}$	$3\cdot37 \times 10^{-2}$[b]	$2\cdot27 \times 10^{7}$	$1\cdot19 \times 10^{-3}$[b]
Piperidine	$11\cdot05$	$2\cdot28 \times 10^{4}$	$4\cdot88 \times 10^{2}$	$9\cdot31 \times 10^{4}$	$2\cdot45 \times 10^{1}$	$2\cdot33 \times 10^{5}$	$8\cdot67 \times 10^{-1}$
Morpholine	$8\cdot70$	$1\cdot61 \times 10^{3}$	$7\cdot71 \times 10^{3}$	$6\cdot98 \times 10^{3}$	$4\cdot11 \times 10^{2}$	$2\cdot01 \times 10^{4}$	$1\cdot67 \times 10^{1}$
n-$BuNH_2$	$10\cdot68$	$1\cdot19 \times 10^{4}$	$5\cdot95 \times 10^{2}$	$5\cdot86 \times 10^{4}$	$3\cdot62 \times 10^{1}$	$1\cdot63 \times 10^{5}$	$1\cdot42$
$MeOCH_2CH_2NH_2$	$9\cdot63$	$1\cdot72 \times 10^{3}$	$9\cdot67 \times 10^{2}$	$1\cdot03 \times 10^{4}$	$7\cdot09 \times 10^{1}$	$3\cdot12 \times 10^{4}$	$3\cdot05$
$EtOOCCH_2NH_2$	$7\cdot87$	$3\cdot79 \times 10^{2}$	$1\cdot20 \times 10^{4}$	$3\cdot10 \times 10^{3}$	$1\cdot38 \times 10^{3}$	$1\cdot26 \times 10^{4}$	$6\cdot94 \times 10^{1}$
$NCCH_2NH_2$	$5\cdot39$	$5\cdot26$	$5\cdot14 \times 10^{4}$	$4\cdot21 \times 10^{1}$	$5\cdot06 \times 10^{3}$	$2\cdot94 \times 10^{2}$	$5\cdot00 \times 10^{2}$
H_2O	$-1\cdot44$	$6\cdot40 \times 10^{-3}$[b]	$1\cdot54 \times 10^{7}$	$1\cdot39 \times 10^{-1}$[b]	$4\cdot10 \times 10^{6}$	$2\cdot78$[b]	1.16×10^{6}

[a] $\mu = 0\cdot5$ M (KCl).

[b] In units of s^{-1}.

where B represents primary aliphatic amines and piperidine and morpholine. Under pseudo-first-order conditions, which were used throughout, the first-order rate constant is given by

$$k_{\mathrm{obsd}} = k_1^{\mathrm{H_2O}} + k_1^{\mathrm{OH}} a_{\mathrm{OH}^-} + k_{-1}^{\mathrm{H}} a_{\mathrm{H}^+} + k_{-1}^{\mathrm{H_2O}} + k_1^{\mathrm{B}}[\mathrm{B}] + k_{-1}^{\mathrm{BH}}[\mathrm{BH}] \qquad (3)$$

The individual rate constants were determined by procedures detailed previously.[14] For a given base, k_{obsd} was obtained at six amine concentrations, usually with a [B] : [BH] ratio of 1:1 and in numerous cases also with 4:1 or 1:4 ratios. The raw data are summarized elsewhere.[15] The slopes of the plots of k_{obsd} vs [B] afforded $k_1(1 + a_{\mathrm{H}^+}/K_a^{\mathrm{CH}})$, which from their pH dependence allowed a kinetic determination of $\mathrm{p}K_a^{\mathrm{CH}}$. These kinetic $\mathrm{p}K_a^{\mathrm{CH}}$ values are 9·32 ± 0·05 for **5-H**, 7·47 ± 0·05 for **5-Br** and 5·76 ± 0·05 for **5-NO$_2$**. They agree well with the spectrophotometric values (Table 1).

The intercepts of the plots of k_{obsd} vs [B] were approximated by $k_1^{\mathrm{OH}} a_{\mathrm{OH}^-}$ in the high-pH range and by $k_{-1}^{\mathrm{H}} a_{\mathrm{H}^+}$ in the low pH range, and hence allowed a determination of k_1^{OH} and k_{-1}^{H}, respectively. In conjunction with $\mathrm{p}K_a^{\mathrm{CH}}$, $k_{-1}^{\mathrm{H_2O}}$ and $k_1^{\mathrm{H_2O}}$ were then also obtained.

All rate constants are summarized in Table 1. The estimated error in these rate constants is ±4%.

DISCUSSION

Brønsted correlations

Figure 1 shows plots of $\log k_1^{\mathrm{B}}/q$ and $\log k_{-1}^{\mathrm{BH}}/p$ vs $\Delta\mathrm{p}K + \log(p/q)$, with $\Delta\mathrm{p}K = \mathrm{p}K_a^{\mathrm{BH}} - \mathrm{p}K_a^{\mathrm{CH}}$ (variation of amine), for the reactions of **5-H**, **5-Br** and **5-NO$_2$** with primary amines (p and q are statistical factors[3b]); Figure 2 shows the corresponding plots for the reactions with piperidine and morpholine (strictly these plots are 'Eigen[1] plots' rather than Brønsted plots, but the slopes have the same meaning as in Brønsted plots). The slopes yield β_{B} and α_{BH}, respectively, while the points where the lines cross correspond to $\log k_0$. These parameters are reported in Table 2, which includes standard deviations based on a least-squares analysis for the reactions with primary amines (Figure 1).

Brønsted plots for the variation of k_1^{B} with the $\mathrm{p}K_a^{\mathrm{CH}}$ of the carbon acid are displayed in Figure 3 (primary amines) and Figure 4 (piperidine, morpholine, OH$^-$ and H$_2$O). The α_{CH} values obtained from the slopes, and $\beta_{\mathrm{C}} = 1 - \alpha_{\mathrm{CH}}$, are summarized in Table 3.

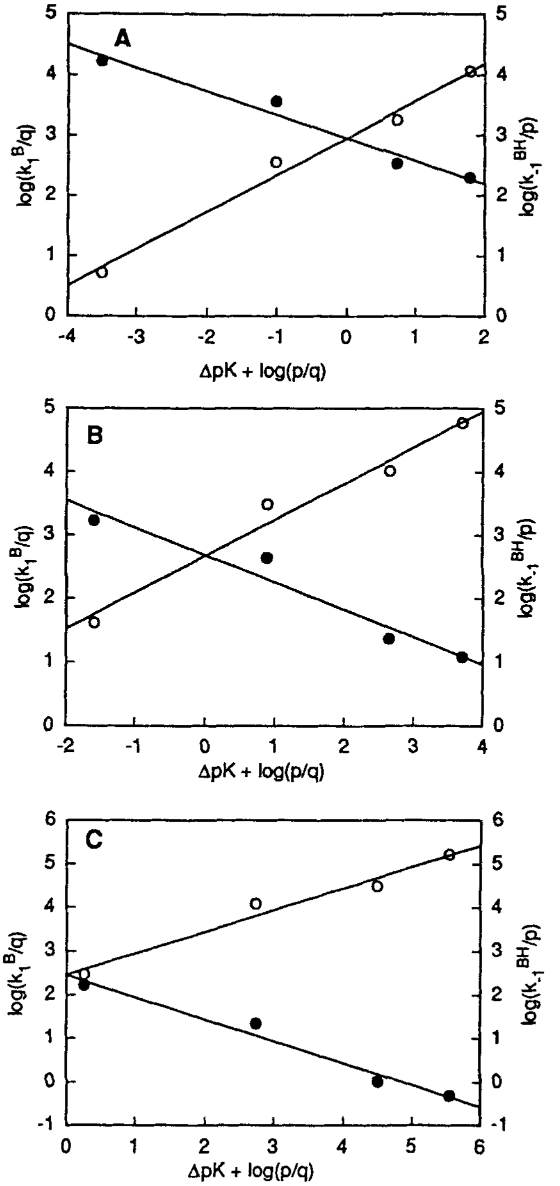


Figure 1. Brønsted (Eigen) plots for the reaction of triphenyl(2-Z-9-fluorenyl)phosphonium ions (**5-Z**) with primary amines (k_1^{B}, open symbols) and its reverse (k_{-1}^{BH}, solid symbols). The slopes yield β_{B} and α_{BH}, respectively, and the point of intersection is $\log k_0$. (A) Z = H; (B) Z = Br; (C) Z = NO$_2$

Changes in β_{B} and α_{CH}

β_{B} decreases with increasing acidity of the carbon acid whereas α_{CH} decreases with increasing basicity of the amine. There is, however, considerable experimental uncertainty in β_{B} for the primary amines which may cast doubt about how significant the dependence of β_{B} on $\mathrm{p}K_a^{\mathrm{CH}}$ really is. In fact, considering the standard deviations, the value of 0·49 ± 0·06 for **5-NO$_2$** is, strictly, barely distinguishable from 0·61 ± 0·05 for

Table 2. Brønsted parameters, β_B and α_{BH}, and intrinsic rate constants obtained from the dependence on pK_a^{BH}

5-Z	Primary amines[a]			Piperidine/morpholine[b]		
	β_B	α_{BH}	Log k_0	β_B	α_{BH}	Log k_0
5-H	0·61 ± 0·05	0·39 ± 0·05	2·96 ± 0·10	0·49	0·51	3·39
5-Br	0·57 ± 0·06	0·43 ± 0·06	2·66 ± 0·16	0·48	0·52	3·11
5-NO₂	0·49 ± 0·06	0·51 ± 0·06	2·45 ± 0·23	0·45	0·55	2·77

[a] Error limits are standard deviations.

[b] No standard deviations can be calculated on the basis of two-point Brønsted plots.

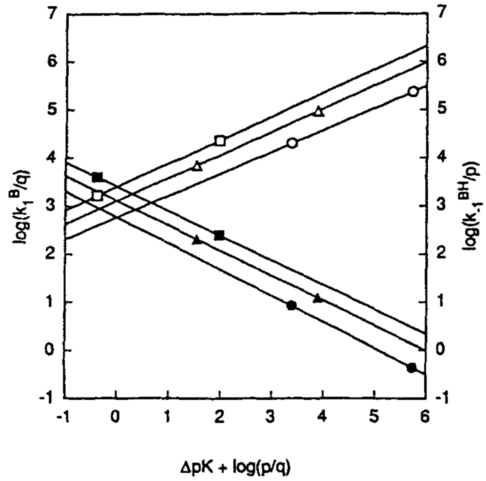


Figure 2. Brønsted (Eigen) plots for the reaction of triphenyl(2-Z-9-fluorenyl)phosphonium ions (**5-Z**) with secondary amines (k_1^B, open symbols) and its reverse (k_{-1}^{BH}, solid symbols) for Z = H (■, □), Br (▲, △) and NO₂ (●, ○). The slopes yield β_B and α_{BH}, respectively, and the point of intersection is log k_0

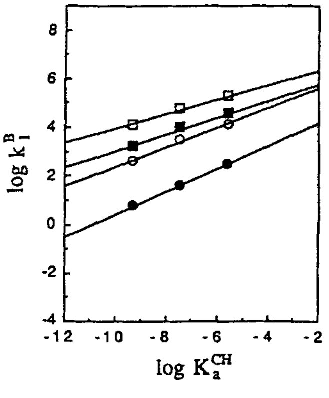


Figure 3. Brønsted plots for triphenyl(2-Z-9-fluorenyl) phosphonium ions (**5-Z**) showing the variation of k_1^B (primary amines) with the pK_a^{CH} of the carbon acid, for the reaction with *n*-butylamine (□), 2-methoxyethylamine (■), glycine ethyl ester (○) and cyanomethylamine (●). The slope of the lines is α_{CH}

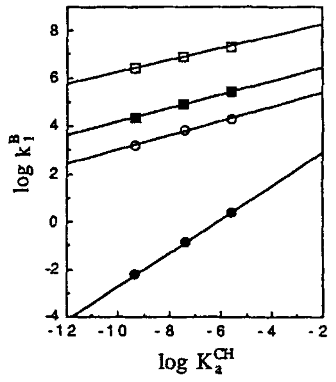


Figure 4. Brønsted plots for triphenyl(2-Z-9-fluorenyl)phosphonium ions (**5-Z**) showing the variation of k_1^B with the pK_a^{CH} of the carbon acid, for the reaction with hydroxide ion (□), piperidine (■), morpholine (○) and water (●). The slope of the lines is α_{CH}

Table 3. Brønsted parameters, α_{CH} and β_C, obtained from the dependence of the proton transfer rate constants on pK_a^{CH}

B	α_{CH}[a]	β_C[a]
OH⁻	0·25 ± 0·02	0·75 ± 0·02
Piperidine	0·27 ± 0·03	0·73 ± 0·03
Morpholine	0·29 ± 0·02	0·71 ± 0·02
n-BuNH₂	0·30 ± 0·03	0·70 ± 0·03
MeOCH₂CH₂NH₂	0·33 ± 0·04	0·67 ± 0·04
EtOOCCH₂NH₂	0·40 ± 0·04	0·60 ± 0·04
NCCH₂NH₂	0·46 ± 0·01	0·54 ± 0·01
H₂O	0·70 ± 0·01	0·30 ± 0·01

[a] Error limits are standard deviations.

There are two features which demonstrate that the trend in β_B is real, as follows.

(i) Plots of log k_1^B(Br) vs log k_1^B(H) and log k_1^B(NO₂) vs log k_1^B(H) (Figure 5) suffer from much less scatter than the Brønsted plots (Figure 1) and have slopes of 0·94 ± 0·03 and 0·81 ± 0·03, respectively. These slopes are significantly different from unity [log k_1^B(H) vs log k_1^B(H)] and from each other; they correspond to β_B(Br)/β_B(H) and β_B(NO₂)/β_B(H), respectively

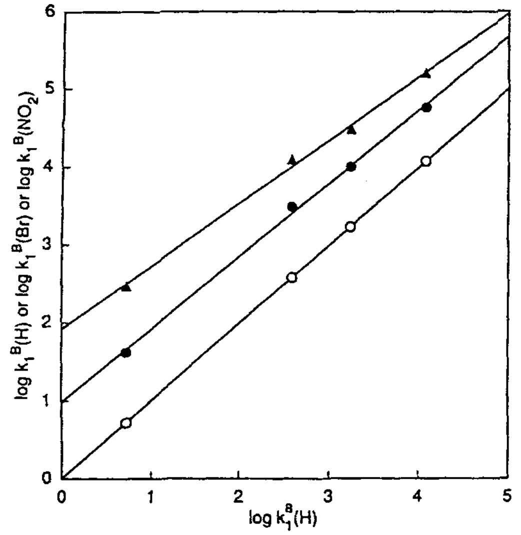


Figure 5. Plot for the reaction of triphenyl(2-Z-9-fluorenyl)phosphonium ion (**5-Z**) with primary amines, showing a comparison of log k_1^B(Z) versus log k_1^B(H), where Z = H (○), Br (●), NO_2 (▲)

[$\beta_B(Br)/\beta_B(H) = 0{\cdot}93$ and $\beta_B(NO_2)/\beta_B(H) = 0{\cdot}80$ from the β_B values in Table 2].

(ii) The experimental error in the α_{CH} values (Table 3) is much smaller relative to the range of the α_{CH} values, leaving little doubt about the authenticity of the trend in α_{CH}. Since, by virtue of the cross-interaction coefficient $p_{xy} = \partial\beta_B/\partial pK_a^{CH} = \partial\alpha_{CH}/-\partial pK_a^{BH}$, [13] a dependence of α_{CH} on pK_a^{BH} requires a corresponding dependence of β_B on pK_a^{CH}, the observed trend in α_{CH} implies that the trend in β_B is real. A plot of α_{CH} vs $-pK_a^{BH}$ is shown in Figure 6. It yields $p_{xy} = 0{\cdot}031 \pm 0{\cdot}002$, while p_{xy} determined from a plot of β_B vs pK_a^{CH} (not shown) yields $p_{xy} = 0{\cdot}031 \pm 0{\cdot}006$. All p_{xy} values, including those for the reaction of **5-Z** with piperidine and morpholine and for the reactions of **4-Z** with primary amines and oxyanions, are summarized in Table 4.

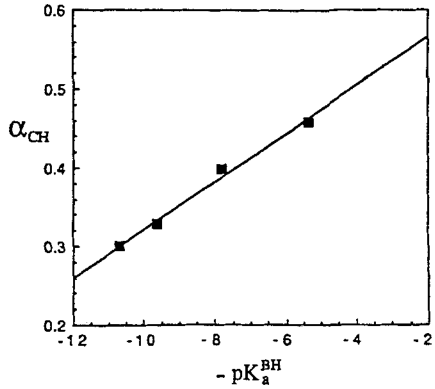


Figure 6. Plot for the reaction of triphenyl(2-Z-9-fluorenyl)phosphonium ions (**5-Z**) with primary amines, showing the variation of α_{CH} with the pK_a^{BH} of the protonated amine. The slope of the line is the interaction coefficient p_{xy}

p_{XY} as a measure of changes in transition-state structure

The p_{xy} values for the deprotonation of the **4-Z** are reported in Table 4. They are all positive and hence reflect qualitatively similar changes in transition-state structure. These changes can be understood on the basis of a reaction coordinate diagram with separate axes for α_{CH} and β_B, as described by Murray and Jencks.[9] Such a diagram is shown in Figure 7, with the transition state for the reaction of **5-H** with *n*-butylamine ($\alpha_{CH} = 0{\cdot}31$, $\beta_B = 0{\cdot}61$) indicated by the symbol ‡. This diagram presumes that β_B can be regarded as some measure of proton transfer to the base and that α_{CH} is related to the progress of proton dissociation from the carbon acid. It is important to realize, though, that this does not imply a linear relationship between proton transfer and the Brønsted parameters, only that an increase in β_B means

Table 4. Cross interaction coefficients, p_{xy}, for the deprotonation of **5-Z** and **4-Z**

Acid	Base	Solvent	T (°C)	p_{xy}	Log k_0 (X = H)
5-Z	Primary amines	50% Me_2SO	20	$0{\cdot}03^{a,b}$	2·97
5-Z	Piperidine/morpholine	50% Me_2SO	20	$0{\cdot}01^{a,c}$	3·39
4-Z	Primary amines	H_2O	28	$0{\cdot}04^{d}$	$\sim 4{\cdot}1^{e}$
4-Z	$RCOO^-$	H_2O	28	$0{\cdot}07^{d}$	~5·0

[a] This work.

[b] $\partial\alpha_{CH}/-\partial pK_a^{BH} = 0{\cdot}031 \pm 0{\cdot}002$, $\partial\beta_B/\partial pK_a^{CH} = 0{\cdot}031 \pm 0{\cdot}006$.

[c] $\partial\alpha_{CH}/-\partial pK_a^{BH} = 0{\cdot}0085$, $\partial\beta_B/\partial pK_a^{CH} = 0{\cdot}0096 \pm 0{\cdot}0022$.

[d] Ref. 9.

[e] Ref. 9 gives 4·0, but our own calculation based on the data in Ref. 9 yields 4.1.

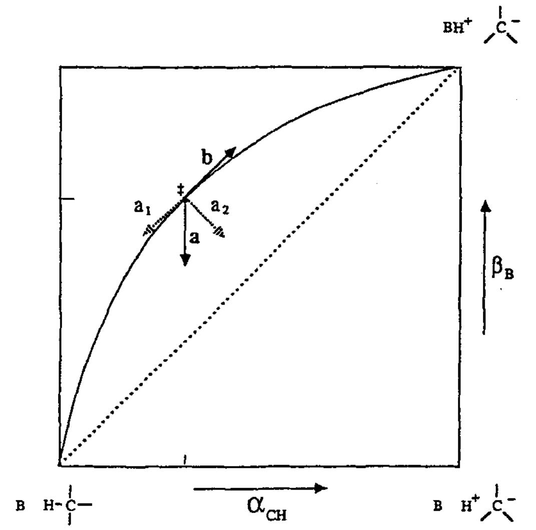


Figure 7. Energy-reaction coordinate diagram for the reaction of **5-H** with *n*-butylamine, with the transition state indicated by the symbol ‡, as described in the text. A change to a more acidic carbon acid (e.g. **5-Br**, **5-NO$_2$**) lowers the right-hand edge, as the carbanion is stabilized; the transition state moves toward the lower left-hand corner (arrow a_1) and the lower right-hand corner (arrow a_2); the result (arrow a) is a lower β_B. A change to a less basic amine raises the upper right-hand corner, as BH^+ is destabilized; the transition state moves toward that corner (arrow b), implying an increase in both α_{CH} and β_B

more protonation of the base and an increase in α_{CH} means a greater loss of the proton from the carbon acid (the meaning of β_B and α_{CH} is considered further under Imbalance).

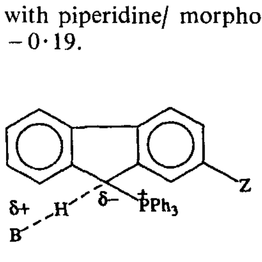
With reference to Figure 7, a change to a more acidic carbon acid lowers the right-hand edge of the diagram, because the carbanion becomes more stable. This induces the transition state to shift along the reaction coordinate towards the lower left corner (arrow a_1) and perpendicular to the reaction coordinate towards the lower right-hand corner (arrow a_2). The resulting vector (arrow a) suggests that the transition state moves in the direction of less protonation of the base, implying a lower β_B as observed (Table 2).

A change to a less basic amine raises the energy of the upper right-hand corner because BH^+ becomes less stable. This induces the transition state to move towards this corner as indicated by arrow b. It implies a more product-like transition state in terms of both a greater degree of protonation of the base and more progress in the dissociation of the proton from the acid, i.e. both α_{CH} and β_B should increase. The increase in α_{CH} is clearly seen in Table 3; the increase in β_B should manifest itself in a downward curvature of the plots of $\log(k_1^B/q)$ vs $\Delta pK_a + \log(p/q)$. However, the relatively small pK_a^{BH} range (5.3 units) and small number of amines, coupled with experimental scatter, make detection of this curvature impossible. Even in more optimum situations, such curvature is often difficult to detect. For example, in the reaction of **4-Br** with eight primary amines spanning a pK_a^{BH} range of 7.3 units, the data at best suggest but definitely do not clearly establish the presence of such curvature.[9]

The large difference in p_{xy} for the deprotonation of **5-Z** by primary amines ($0{\cdot}03$) compared with the reaction with piperidine and morpholine ($0{\cdot}01$) is puzzling. Murray and Jencks[9] also observed a substantial difference in p_{xy} when comparing the deprotonation of **4-Z** by primary amines ($0{\cdot}04$) with that by oxyanion ($0{\cdot}07$). Since there appears to be a tendency for p_{xy} to become larger with increasing intrinsic rate constants (see Introduction), the larger p_{xy} value in the reaction of **4-Z** with the oxyanions may possibly be attributed to the higher $\log k_0$ (*ca* $5{\cdot}0$ for oxyanions, *ca* $4{\cdot}0$ for primary RNH_2). However, this explanation is not applicable to **5-Z** because here the reactions with the higher $\log k_0$ (piperidine/morpholine) are those with the smaller p_{xy} value (Table 2). In the absence of data for other systems which would more firmly establish whether p_{xy} for secondary alicyclic amines is inherently lower than that for primary amines, it seems premature to speculate on possible reasons for our results. It is also unclear at this point whether the difference between $p_{xy} = 0{\cdot}04$ and $0{\cdot}03$ for the reactions of primary amines with **4-Z** and **5-Z**, respectively, can be safely interpreted as a reflection of the higher k_0 for the reactions of **4-Z**, especially in view of the different solvents used in the two studies.

Imbalance

The β_B values are significantly larger than the α_{CH} values, indicating a charge imbalance at the transition state. We have usually taken the difference $\alpha_{CH} - \beta_B$ as a measure of such imbalance.[7] In view of the relatively strong dependence of α_{CH} on pK_a^{BH} and of β_B on pK_a^{CH}, there is some question as to how to define the imbalance in the present situation. For lack of a better method we shall use average α_{CH} and β_B values ($\bar{\alpha}_{CH}, \bar{\beta}_B$), i.e. for the reactions of **5-Z** with primary amines we have $\bar{\alpha}_{CH} - \bar{\beta}_B = 0{\cdot}37 - 0{\cdot}56 = -0{\cdot}19$, with piperidine/ morpholine $\bar{\alpha}_{CH} - \bar{\beta}_B = 0{\cdot}28 - 0{\cdot}47 = -0{\cdot}19$.



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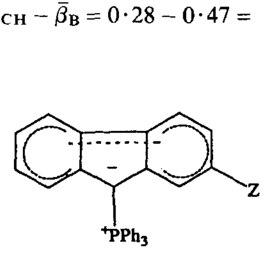
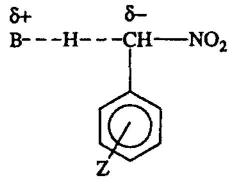


7

The negative imbalances can be understood in terms of a difference in charge distribution between the transition state (**6**) and the product (**7**). In **6** the developing negative charge is mainly localized on the carbon whereas in **7** it is strongly delocalized into the fluorenyl moiety, i.e. charge delocalization in the transition state lags behind charge or proton transfer. As a consequence, the charge seen by the Z substituent is further away in the transition state than in the product, which depresses α_{CH}. This interpretation presumes that β_B can be viewed as at least an approximate measure of proton or charge transfer (this is the traditional view,[13b,16] although this view has been challenged[17]) at the transition state, while α_{CH} is clearly not such a measure.

The kind of lag in the charge delocalization observed here is characteristic of systems that involve resonance stabilization of the product.[7] It is not restricted to proton transfers or even carbanion-forming reactions, but has also been observed in reactions involving resonance-stabilized olefins,[18] carbocations[19] and radicals.[20]

In many reactions for which requisite data are available, the imbalance is positive ($\alpha_{CH} - \beta_B > 0$). This is not because in these cases delocalization is ahead of charge transfer, but because the position of the reporting substituent Z is such as to be closer to the charge in the transition state than in the product. This leads to an enhancement of α_{CH}. A well known example is the deprotonation of arylnitromethanes by secondary alicyclic amines for which $\alpha_{CH} = 1{\cdot}29$ and $\beta_B = 0{\cdot}56$;[21] **8** and **9** show the transition state and product ion, respectively.



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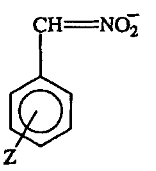
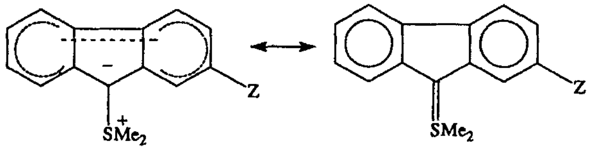


9

If Murray and Jencks[9] data are analyzed in a similar way, the imbalance for the reaction of **4-Z** with oxyanions calculated from their average α_{CH} and β_B values yields $\bar{\alpha}_{CH} - \bar{\beta}_B = 0{\cdot}81 - 0{\cdot}74 = 0{\cdot}07$. They did not report α_{CH} values for the reactions of **4-Z** with amines. However, when such α_{CH} values are calculated from their $k_1^B(\mathbf{4\text{-}Br})/k_1^B(\mathbf{4\text{-}H})$ ratios, one obtains an average $\alpha_{CH} = 0{\cdot}58$ and thus, with the average $\beta_B = 0{\cdot}73$, $\bar{\alpha}_{CH} - \bar{\beta}_B = -0{\cdot}15$. This is close to our $\bar{\alpha}_{CH} - \bar{\beta}_B = -0{\cdot}19$ for the reactions of **5-Z** with amines.

The positive value of $\bar{\alpha}_{CH} - \bar{\beta}_B$ for the reactions of **4-Z** with oxyanions is surprising. There are three possible rationalizations for this result. (i) These reactions constitute the first known exception to the rule that charge delocalization lags behind charge transfer at the transition state. In view of the large body of experimental evidence confirming this rule,[7] including the reactions of **4-Z** with amines, in addition to theoretical reasons why charge delocalization should lag behind charge transfer[22] (inasmuch as charge delocalization involves the breaking and making of bonds, the formation of a delocalized carbanion by proton transfer may be regarded as a multi-bond reaction; hence the factors that make it difficult for multi-bond reactions to be synchronous[23] are relevant here), this rationalization is unattractive.

(ii) π-Backbonding from the carbon to the d-orbitals of the sulfur in the ylide (**10b**) may be important. This would decrease the negative charge in the fluorenyl moiety in the product and could lead to an enhanced α_{CH} value. If this were the correct explanation, it would be difficult to understand why the sign of $\bar{\alpha}_{CH} - \bar{\beta}_B$ changes when amines are used as bases. This explanation also contradicts Murray and Jencks[9] conclusions regarding the unimportance of **10b**, and is inconsistent with our own analysis, presented below, of the relative importance of resonance effects of the Me_2S^+ and Ph_3P^+ groups.



10a **10b**

(iii) The wrong sign of the imbalance may be an artifact resulting from the strong endoergicity of many of carbon acid–base combinations (range of $pK_a^{CH} - pK_a^{BH} = 0{\cdot}6$ to $13{\cdot}0$) and the low curvature of the energy surface near the transition state (high p_{xy}). This endoergicity leads to highly unsymmetrical, product-like transition states located near the upper right-hand corner of the corresponding reaction coordinate diagram (Figure 7), where imbalances tend to become negligible (this is clearly seen from Figure 7, where the distance between the curved reaction coordinate and the diagonal dashed line represents the imbalance $\alpha_{CH} - \beta_B$). It is interesting that when only the reactions of **4-Z** with the two most basic oxyanions [$(CF_3)_2CHO^-$ and AcO^-] are considered, which removes the most endoergic reactions from the correlation (range of $pK_a^{CH} - pK_a^{BH} = 0{\cdot}6$ to $8{\cdot}5$), the average α_{CH} is $0{\cdot}66$, which leads to $\bar{\alpha}_{CH} - \bar{\beta}_B = 0{\cdot}66 - 0{\cdot}74 = -0{\cdot}08$, i.e. the expected negative value. This $pK_a^{CH} - pK_a^{BH}$ range is close to that for the reactions of **4-Z** with the primary amines ($0{\cdot}8$–$9{\cdot}34$).

By way of comparison, for the reactions of **5-Z** with amines, $pK_a^{CH} - pK_a^{BH}$ ranges from $-5{\cdot}43$ to $3{\cdot}99$ and for the reactions of arylnitromethanes with secondary alicyclic amines[21] $pK_a^{CH} - pK_a^{BH}$ ranges from $-1{\cdot}2$ to $-4{\cdot}7$, implying much more symmetrical transition states, consistent with β_B values close to 0·5. These considerations suggest that meaningful imbalances can only be obtained from α_{CH} and β_B when $|pK_a^{CH} - pK_a^{BH}|$ is relatively small, ensuring a transition state that is not too far from the center of the reaction coordinate diagram (Figure 7). A 'permissible' $|pK_a^{CH} - pK_a^{BH}|$ range cannot be given in absolute terms, however, since it depends on how strongly the transition state changes as a function of pK_a^{CH}, i.e. low p_{XY} values allow a larger $|pK_a^{CH} - pK_a^{BH}|$ than high p_{XY} values. In view of the high p_{XY} values for the reactions of **4-Z** with oxyanions, even the reactions with just $(CF_3)_2CHO^-$ and AcO^- probably involve too large $|pK_a^{CH} - pK_a^{BH}|$ values (up to 8·5) to produce a quantitatively meaningful imbalance, although the correct sign is obtained.

Intrinsic rate constants

Effect of the base

The log k_0 values for the deprotonation of **5-Z** by the piperidine/morpholine pair are about 0·4 log units larger than for the reactions with the primary amines (Table 2). The lower intrinsic reactivity of the primary amines is a common phenomenon.[7] It has generally been attributed to the stronger solvation of the primary amines in their protonated form, coupled with the assumption that the solvation of the incipient ammonium ion at the transition state lags behind charge development.[3b,24] In general, the difference in log k_0 between primary and secondary alicyclic amines is 0·7–1·0 log units,[14,25] provided that there are no significant steric effects. For example, in the deprotonation of 9-cyanofluorene in 50% Me_2SO–50% water this difference is 0·82.[8] The relatively small differences of 0·3–0·4 in the reactions of **5-Z** suggest the presence of a significant steric effect, as one might expect on the basis of the large size of the Ph_3P^+ group.

The presence of a substantial steric effect may also be inferred from a comparison of k_1^B values for specific amines with k_1^{OH} for OH^-. For example, $k_1^{n\text{-}BuNH_2}/k_1^{OH} = 4{\cdot}59 \times 10^{-3}$ for **5-H**, $6{\cdot}47 \times 10^{-3}$ for **5-Br** and $7{\cdot}18 \times 10^{-3}$ for **5-NO₂**. In contrast, the same ratios for 9-cyanofluorene and 9-carbomethoxyfluorene in the same solvent are *ca* 6×10^{-2} and $1{\cdot}37 \times 10^{-1}$, respectively,[8] i.e. 10–30 times higher. The smaller $k_1^{n\text{-}BuNH_2}/k_1^{OH}$ ratios for **5-Z** are easily explained if one assumes that it is mainly the reaction with the larger *n*-butylamine that is retarded by the steric effect of the Ph_3P^+ group.

Effect of the 2-substitutent (Z)

The log k_0 values decrease in the order **5-H** > **5-Br** > **5-NO₂**. This decrease is a consequence of the difference in the charge distribution between the transition state (**6**) and the product (**7**) that manifests itself in α_{CH} being smaller than β_B. Since Z is far removed from the developing charge in the transition state but closer to this charge in the product, the stabilization of the transition state by an electron-withdrawing Z is disproportionately small compared with that of the product. Hence the increase in k_1^B is small compared with the increase in the equilibrium constant (small α_{CH}). As described in detail elsewhere,[7] this is equivalent to a decrease in k_0 which can be related to the imbalance by the equation

$$\log k_0(Z) - \log k_0(H) = \delta \log k_0^I(Z) = (\alpha_{CH} - \beta_B)\delta \log K_1^I(Z) \quad (4)$$

In the present case $\delta \log K_1^I(Z)$, with I referring to the inductive/field effect (in contrast to resonance effects), is given by $pK_a^{CH}(H) - pK_a^{CH}(Z)$. {It is assumed that the resonance effect of the nitro substituent is negligible. If resonance were important, the point for **5-NO₂** would show a substantial negative deviation from the Brønsted plots in Figures 3 and 4, as has been observed e.g., in the deprotonation of 4-nitrophenylnitromethane by $PhCOO^-$ in Me_2SO.[26] Note that in the reactions of **4-Z** no negative deviation from the Brønsted plots for **4-NO₂** was observed either.[9] Note also that in a situation such as the deprotonation of arylnitroalkanes, where $\alpha_{CH} > \beta_B$, log k_0 *increases* for electron-withdrawing aryl substituents [$\alpha_{CH} - \beta_B > 0$ in equation (4)], since the closer proximity of the substituent to the charge in the transition state (**8**) leads to a disproportionately large increase in k_1^B compared with the increase in the equilibrium constant.}

Plots of log k_0 vs pK_a^{CH} (not shown) yield $\alpha_{CH} - \beta_B = -0{\cdot}13 \pm 0{\cdot}01$ and $= -0{\cdot}17 \pm 0{\cdot}01$ for the reactions of **5-Z** (Z = H, Br, NO_2) with primary amines and piperidine/morpholine, respectively. These imbalances are, within experimental error, the same as those obtained from the average α_{CH} and β_B values ($-0{\cdot}19$), since the experimental uncertainty in these latter values may be as high as $\pm 0{\cdot}06$ or higher.

Effect of the 9-substituent (X)

Data now exist on log k_0 for the deprotonation of four different 9-X-fluorenes (X = COOMe, CN, Me_2S^+ and Ph_3P^+), which are summarized in Table 5. The data for the dimethylsulfonium derivative (**4-H**) determined in water at 28 °C are not strictly comparable with the bulk of the results that were obtained in 50% Me_2SO–50% water at 20 °C. However, as seen with the CN and COOMe derivatives, log k_0 for these compounds depends very little on solvent. Assuming a similarly weak solvent dependence for **4-H** and taking the slight temperature difference into account, one estimates log k_0 in 50% Me_2SO–50% water at 20 °C to be *ca* 4·10

Table 5. pK_a^{CH} values of 9-X-fluorenes and log k_0 for their deprotonation by primary aliphatic amines at 20 °C

	H_2O		50% Me_2SO		90% Me_2SO	
X	pK_a^{CH}	Log k_0	pK_a^{CH}	Log k_0	pK_a^{CH}	Log k_0
COOMe (**2**)[a]			10·97	2·84	10·03	3·09
Ph_3P^+ (**5-H**)[b]			9·38	2·97		
CN (**3**)[a]	10·71[d]	3·62	9·53	3·76	8·01[f]	3·57
Me_2S^+ (**4-H**)[c]	13·7[e]	~4·1[e]	(~12·5)[g]	(~4·1)[g]		

[a] Ref. 8.
[b] This work.
[c] Ref. 9.
[d] 10% Me_2SO–90% water.
[e] At 28 °C, see footnote e in Table 4.
[f] In Me_2SO, $pK_a^{CH} = 8{\cdot}30$.[27]
[g] Estimated, see text.

(see footnote e in Table 4). Table 5 also reports pK_a^{CH} values. The pK_a^{CH} for **4-H** in 50% Me_2SO–50% water was estimated assuming the same solvent dependence as for the pK_a of **3**, i.e. $pK_a^{CH}(50\%\ Me_2SO) \approx pK_a^{CH}(H_2O) - 1{\cdot}2$.

As indicated in the Introduction, the 9-X substituent may affect k_0 in four major ways: by inductive/field (I), resonance (R), polarizability (P) and steric (S) effects. We wish to estimate the contributions from these factors to the differences in log k_0 among the four 9-X-fluorenes in Table 5. We shall use **2** (X = COOMe) as a reference compound. For any of the other three fluorene derivatives one can then write

$$\log k_0(X) = \log k_0(\text{COOMe}) + \delta \log k_0^{I}(X) + \delta \log k_0^{R}(X) + \delta \log k_0^{P}(X) + \delta \log k_0^{S}(X) \quad (5)$$

With respect to the I effect, an electron-withdrawing substituent should increase and an electron-donating substituent should decrease k_0 because, in contrast to the Z substituent in the 2-position, the X substituent in the 9-position is closer to the negative charge in the transition state than it is in the product (see, e.g. **6** vs **7**). For a substituent with the same R, P and S effects as for COOMe, $\delta \log k_0^{I}(X)$ may be obtained from equation (6) [equation (6) is very similar to equation (4) except that in equation (4) the reference substituent is H and in equation (6) it is COOMe].

$$\delta \log k_0^{I}(X) = \log k_0(X) - \log k_0(\text{COOMe}) \quad (6)$$

In analogy with equation (4) $\delta \log k_0^{I}(X)$ can also be expressed by the equation

$$\delta \log k_0^{I}(X) = (\alpha_{CH}^{X} - \beta_B)\delta \log K_1^{I}(X) \quad (7)$$

where $\delta \log K_0^{I}(X)$ is the change in the equilibrium constant induced by the change in the I effect; since the other effects are assumed to cancel, $\delta \log K_1^{I}(X) = pK_a^{CH}(\text{COOMe}) - pK_a^{CH}(X)$. α_{CH}^{X} is the Brønsted α value obtained by varying the I effect of X.

Among the substituents in Table 5, CN comes closest to meeting the criteria for equation (6). On the basis of various sets of substituent constants, the resonance effects of CN and COOMe appear to be nearly the same, e.g. $\sigma_R = 0{\cdot}16$ for COOMe, 0·18 for CN;[28] $\Delta\sigma_{\bar{R}} = 0{\cdot}28$ for COOMe, 0·29 for CN;[29] $\sigma_{\bar{R}} = 0{\cdot}34$ for COOMe, 0·33 for CN;[29] only the R^- values[28] suggest a slightly stronger R effect for CN (0·49) compared with COOMe (0·41) [In a previous paper[8] it was assumed that it is the COOMe group that has a larger resonance effect, as reflected in the σ_R^0 values[30] (0·08 for CN, 0·16 for COOR), but this now appears unlikely]. A slightly larger R effect for CN would slightly reduce k_0(CN) and with it $\delta \log k_0^{I}(\text{CN})$ calculated from equation (6), but this reduction would be too small to affect our conclusions significantly.

With respect to steric effects, the larger size of COOMe compared with CN does not appear to have a significant rate-retarding effect, as judged by the $k_1^{n\text{-BuNH}_2}/k_1^{OH}$ ratios (see above); in fact, this ratio is slightly larger for the COOMe derivative but this is probably at artifact caused by some uncertainty in k_1^{OH} for the cyano derivative.[8] Since no significant P effects are expected for CN or COOMe, we conclude that, to a good approximation, the difference of 0·92 between the observed log k_0(CN) and log k_0(COOMe) values can be attributed entirely to the stronger I effect of CN, i.e. $\delta \log k_0^{I}(\text{CN}) = 0{\cdot}92$. This allows us to calculate α_{CH}^{X} from equation (7): with $\delta \log K_1^{I}(\text{CN}) = 1{\cdot}44$ and the average β_B value of 0·48 ($\beta_B = 0{\cdot}49$ for **2**, 0·47 for **3**[8]) for reactions of **2** and **3** we obtain $\alpha_{CH}^{X} = 1{\cdot}12$ [this large α_{CH}^{X} value is consistent with findings by Murdoch *et al.*[31] for the reaction of 9-alkylfluorenes with (9-alkylfluorenyl)lithium in diethyl ether; it is reminiscent of $\alpha_{CH} > 1$ found in the deprotonation of nitroalkanes[21,32] and indicates a dramatic difference between the charge distributions in the transition state and the product ion].

δ Log $k_0^{I}(X)$ for X = Me_2S^+ and Ph_3P^+ can now be estimated. From $\delta \log K_1^{I}(\text{CN}) = 1{\cdot}44$ above it follows that $\delta \log K_1^{I}(\text{CN})/\delta\sigma_I(\text{CN}) = 5{\cdot}54$ with $\delta\sigma_I(\text{CN}) =$

$\sigma_I(\mathrm{CN}) - \sigma_I(\mathrm{COOMe}) = 0{\cdot}57 - 0{\cdot}31 = 0{\cdot}26$.[30] We now assume $\delta \log K_1^I(\mathrm{X})/\delta\sigma_I(\mathrm{X}) = \delta \log K_1^I(\mathrm{CN})/\delta\sigma_I(\mathrm{CN})$; from $\sigma_I(\mathrm{Me_2S^+}) = 0{\cdot}89$[30] one obtains $\delta\sigma_I(\mathrm{Me_2S^+}) = \sigma_I(\mathrm{Me_2S^+}) - \sigma_I(\mathrm{COOMe}) = 0{\cdot}58$ and $\delta \log K_1^I(\mathrm{Me_2S^+}) = 3{\cdot}21$, and from $\sigma_I(\mathrm{Ph_3P^+}) = 0{\cdot}76$[30] one obtains $\delta\sigma_I(\mathrm{Ph_3P^+}) = \sigma_I(\mathrm{Ph_3P^+}) - \sigma_I(\mathrm{COOMe}) = 0{\cdot}45$ and $\delta \log K_1^I(\mathrm{Ph_3P^+}) = 2{\cdot}49$. These calculations are based on the premise that $\delta\sigma_I(\mathrm{Me_2S^+})$ and $\delta\sigma_I(\mathrm{Ph_3P^+})$ are an acceptable approximation of the differences in the I effects relative to COOMe even if the R effects of $\mathrm{Ph_3P^+}$ and $\mathrm{Me_2S^+}$ differ from that of COOMe. [As shown below, the R effects of $\mathrm{Ph_3P^+}$ and COOMe are probably not very different so the above approximation should hold fairly well. On the other hand, the R effect of $\mathrm{Me_2S^+}$ appears to be significantly less than that of COOMe. Since the R effect should reduce the I effect, the use of $\sigma_I(\mathrm{Me_2S^+})$ to calculate $\delta \log K_1^I(\mathrm{Me_2S^+})$ may lead to an estimate of $\delta \log K_1^I(\mathrm{Me_2S^+})$ that is too low. However, this will not affect any of the qualitative conclusions.]

With $\beta_B = 0{\cdot}61$ for $\mathrm{Ph_3P^+}$ and $0{\cdot}70$ for $\mathrm{Me_2S^+}$, the average β_B values used in equation (7) become $0{\cdot}55$ for $\mathrm{Ph_3P^+}$ and $0{\cdot}60$ for $\mathrm{Me_2S^+}$. Assuming the same $\alpha_{\mathrm{CH}}^{\mathrm{X}}$ as found for X = CN (1·12) leads to $\delta \log k_0^I(\mathrm{Me_2S^+}) = 1{\cdot}67$ and $\delta \log k_0^I(\mathrm{Ph_3P^+}) = 1{\cdot}42$ (Table 6). These numbers imply that were it not for differences in R, P and S effects, $\log k_0(\mathrm{Me_2S^+})$ and $\log k_0(\mathrm{Ph_3P^+})$ should be larger than $\log k_0(\mathrm{COOMe})$ by *ca* 1·67 and *ca* 1·42, respectively, owing to the stronger polar effect exerted by the charged groups compared with that by COOMe.

We believe that the estimated $\delta \log k_0^I(\mathrm{X})$ values for $\mathrm{Ph_3P^+}$ and $\mathrm{Me_2S^+}$ are reasonably accurate, probably within ±0·4 log units or better. Reliable values for $\delta \log k_0^R(\mathrm{X})$, $\delta \log k_0^P(\mathrm{X})$ and $\delta \log k_0^S(\mathrm{X})$, whose sum is given in the equation

$$\sum_{\mathrm{R,P,S}}(\mathrm{X}) = \delta \log k_0^R(\mathrm{X}) + \delta \log k_0^P(\mathrm{X}) + \delta \log k_0^S(\mathrm{X}) = \log k_0(\mathrm{X}) - \log k_0(\mathrm{COOMe}) - \delta \log k_0^I(\mathrm{X}) \tag{8}$$

and reported in Table 6, are more difficult to obtain, but interesting insights can be gained even from relatively crude estimates. The methods used for these estimates will be illustrated for X = $\mathrm{Ph_3P^+}$.

A first approximation for $\delta \log k_0^S(\mathrm{Ph_3P^+})$ may be obtained from the comparison of the $k_1^{n\text{-}\mathrm{BuNH_2}}/k_1^{\mathrm{OH}}$ ratio for **5-H** ($4{\cdot}59 \times 10^{-3}$) with that for **2** ($1{\cdot}37 \times 10^{-1}$) reported above. If it is assumed that only $k_1^{n\text{-}\mathrm{BuNH_2}}$ and not k_1^{OH} is retarded by the larger steric bulk of $\mathrm{Ph_3P^+}$, the equality $\delta \log k_0^S(\mathrm{Ph_3P^+}) = \log(k_1^{n\text{-}\mathrm{BuNH_2}}/k_1^{\mathrm{OH}})_{\textbf{5-H}} - \log(k_1^{n\text{-}\mathrm{BuNH_2}}/k_1^{\mathrm{OH}})_{\textbf{2}} = -1{\cdot}47$ must hold. If k_1^{OH} were also reduced by the steric effect, the above expression would underestimate the steric effect on $\log k_0(\mathrm{Ph_3P^+})$. Hence we conclude that $\delta \log k_0^S(\mathrm{Ph_3P^+}) \leqslant -1{\cdot}47$.

In estimating the R effect, $\delta \log k_0^R(\mathrm{Ph_3P^+})$, we apply a recent model[4] that derives from a proposal originally advanced by Kresge,[22a] and which is briefly described in the Appendix. According to this model, $\delta \log k_0^R(\mathrm{Ph_3P^+})$ is given by

$$\delta \log k_0^R(\mathrm{Ph_3P^+}) = (\lambda_R^X - \beta_B)\delta \log K_1^R(\mathrm{Ph_3P^+}) \tag{9}$$

where

$$\lambda_R^X = (\beta_B)^n \tag{10}$$

$\delta \log K_1^R(\mathrm{Ph_3P^+})$ is the difference in the resonance effect of $\mathrm{Ph_3P^+}$ and COOMe on $\log K_1$ and n has a value between 2 and 3. We shall use $n = 2{\cdot}5$; with

Table 6. Contributions of I, R, P and S effects to $\log k_0(\mathrm{X})$ relative to $\log k_0(\mathrm{COOMe})$

X	COOMe	CN	$\mathrm{Ph_3P^+}$	$\mathrm{Me_2S^+}$
$\mathrm{p}K_a^{\mathrm{CH}}(\mathrm{X})$	10·97	9·53	9·38	~12·5
$\sigma_I(\mathrm{X})$	0·31	0·57	0·76	0·89
Log $k_0(\mathrm{X})$	2·84	3·76	2·97	~4·1[a]
δ Log $K_1^I(\mathrm{X})$	0	1·44	2·49	3·21[b]
δ Log $k_0^I(\mathrm{X})$	0	0·92	1·42	1·67[b]
$\Sigma_{\mathrm{R,P,S}}$ (X)	0	0	−1·29	~ −0·51[b]
δ Log $k_0^S(\mathrm{X})$	0	0	⩽ −1·47	
δ Log $K_1^R(\mathrm{X}) + \delta$ Log $K_1^P(\mathrm{X})$	0	0	−0·90	~ −4·74[b]
δ log $K_1^R(\mathrm{X})$	0	0	< −0·90	< −4·74[b]
δ Log $K_1^P(\mathrm{X})$	0	0	>0	>0
δ log $k_0^R(\mathrm{X})$	0	0	>0·29	>1·37[b]
δ log $k_0^P(\mathrm{X})$	0	0	>0	>0

[a] See footnote e in Table 4.

[b] If the reduction in the I effect by the R effect for COOMe is taken into account, $\delta \log K_1^I(\mathrm{Me_2S^+})$ would be higher (see text). This would also make $\delta \log k_0^I(\mathrm{Me_2S^+})$ and $\delta \log k_0^R(\mathrm{Me_2S^+})$ higher and $\Sigma_{\mathrm{R,S,P}}$ ($\mathrm{Me_2S^+}$), $\delta \log K_1^R(\mathrm{Me_2S^+}) + \delta \log K_1^P(\mathrm{Me_2S^+})$ and $\delta \log K_1^R(\mathrm{X})$ more negative.

$\beta_B = 0{\cdot}061$ (Table 2) we obtain $\lambda_R^X - \beta_B = -0{\cdot}32$. $\delta \log K_I^R(Ph_3P^+)$ is difficult to estimate but the combined contribution of the R and P effects [P effect: $\delta \log K_I^P(Ph_3P^+)$] to K_1 can be obtained from a comparison of the pK_a^{CH} values after subtracting out the I effect according to the equation

$$\delta \log K_I^R(Ph_3P^+) + \delta \log K_I^P(Ph_3P^+) = pK_a^{CH}(COOMe) - pK_a^{CH}(Ph_3P^+) - \delta \log K_1^I(Ph_3P^+) \tag{11}$$

This yields $\delta \log K_I^R(Ph_3P^+) + \delta \log K_I^P(Ph_3P^+) = -0{\cdot}90$. Since the P effect of Ph_3P^+ is certainly larger than that of COOMe and hence $\delta \log K_I^P(Ph_3P^+)$ has to be >0, this means that $\delta \log K_I^R(Ph_3P^+) < -0{\cdot}90$. With $\lambda_R^X - \beta_B = -0{\cdot}32$, equation (9) yields $\delta \log k_0^R(Ph_3P^+) > 0{\cdot}29$.

Polarizability effects have not been considered in our earlier discussions of factors that affect k_0.[4,7] Using the same model from which equation (9) has been derived, a formalism can be developed that relates $\delta \log k_0^P(Ph_3P^+)$ to $\delta \log K_I^P(Ph_3P^+)$. This formalism is outlined in the Appendix. It provides the equation

$$\delta \log k_0^P(X) = (\lambda_P^X - \beta_B)\delta \log K_I^P(X) \tag{12}$$

where

$$\lambda_P^X = \frac{[\beta_B - (\chi_X + \chi_Y)(\beta_B)^n]^2}{[-1 + \chi_X + \chi_Y]^2} \tag{13}$$

χ_X and χ_Y are the negative charges on X and Y in the product ion [see equation (A6) in the Appendix; with a positively charged X such as Ph_3P^+, χ_X is the amount by which the positive charge has been reduced] and n has the same meaning as in equation (10). Since χ_X and χ_Y are unknown, λ_P^X cannot be calculated. However, it is instructive to consider some limiting cases which give an insights into whether the P effect should be expected to enhance or lower k_0. We shall again use $n = 2{\cdot}5$ and $\beta_B = 0{\cdot}61$.

Case I: $\chi_X + \chi_Y = 0$. This case refers to a situation where neither X nor Y is a π-acceptor. Equation (13) simplifies to $\lambda_P^X = \beta_B^2$ and $\lambda_P^X - \beta_B = -0{\cdot}24$. Since $\delta \log K_I^P(X) > 0$, this means that $\delta \log k_0^P(X) < 0$, i.e. the P effect lowers the intrinsic rate constant.

Case II: $\chi_X + \chi_Y = 1$. This case represents the other extreme from case I where the entire negative charge is delocalized and no charge is left on the carbon in the product. Equations (12) and (13) cannot be applied here since $\delta \log K_I^P(X) = 0$ and $\lambda_P^X = \infty$, but qualitatively it is clear that since only the transition state benefits from the P effect, k_0 is enhanced.

Case III: $\chi_X + \chi_Y = 0{\cdot}5$. This case, or one where $\chi_X + \chi_Y$ is larger than $0{\cdot}5$ but smaller than $1{\cdot}0$, may come close to the actual situation with **5-H**. Here equation (13) gives $\lambda_P^X = 0{\cdot}85$ and hence $\lambda_P^X - \beta_B = 0{\cdot}24$, i.e. k_0 is enhanced. These considerations clearly suggest that if the ylide is stabilized by a P effect this should lead to $\delta \log k_0^P(Ph_3P^+) > 0$.

Further conclusions may be drawn about $\delta \log k_0^P(Ph_3P^+)$ and $\delta \log k_0^R(Ph_3P^+)$ from their sum given by

$$\sum_{R,P} (Ph_3P^+) = \delta \log k_0^R(Ph_3P^+) + \delta \log k_0^P(Ph_3P^+) = \sum_{R,P,S} (Ph_3P^+) - \delta \log k_0^S(Ph_3P^+) \tag{14}$$

With $\Sigma_{R,S,P}\ (Ph_3P^+) = -1{\cdot}29$ and $\delta \log k_0^S(Ph_3P^+) \leqslant -1{\cdot}47$ (Table 6), we obtain $\Sigma_{R,P}\ (Ph_3P^+) \geqslant 0{\cdot}18$. If -1.47 were the actual value for $\delta \log k_0^S(Ph_3P^+)$ rather than an upper limit, the lower limit of $0{\cdot}29$ estimated above for $\delta \log k_0^R(Ph_3P^+)$ would more than fully account for $\Sigma_{R,P}\ (Ph_3P^+)$, *implying that the P effect is* non-existent, or even slightly negative [$\delta \log k_0^P(Ph_3P^+) \leqslant 0$]. This seems unreasonable and suggests that the steric effect is substantially larger, i.e. $\delta \log k_0^S(Ph_3P^+) < -1{\cdot}47$. For example, if $\delta \log k_0^S(Ph_3P^+)$ were $-2{\cdot}47$ this would give $\Sigma_{R,P}\ (Ph_3P^+) = 1{\cdot}18$; using $\lambda_R^X - \beta_B = -0{\cdot}32$ and $\lambda_P^X - \beta_B = 0{\cdot}24$, one obtains $\delta \log K_I^R(Ph_3P^+) = -2{\cdot}50$, $\delta \log K_I^P(Ph_3P^+) = 1{\cdot}60$, $\delta \log k_0^R(Ph_3P^+) = 0{\cdot}38$ and $\delta \log k_0^P(Ph_3P^+) = 0{\cdot}80$. This example is meant to illustrate the effect of a more negative $\delta \log k_0^S(Ph_3P^+)$ value rather than to imply that $\delta \log k_0^S(Ph_3P^+)$ is indeed $-2{\cdot}47$.

Similar conclusions are reached if the reaction of **4-H** ($X = Me_2S^+$) is subjected to the same type of analysis even though the uncertainties in our various estimates are higher than with **5-H** ($X = Ph_3P^+$). [There are two reasons for these additional uncertainties: (a) the $\log k_0(Me_2S^+)$ and $pK_a^{CH}(Me_2S^+)$ values are not known in 50% Me_2SO–50% water and had to be estimated based on values in water; (b) as indicated earlier, $\sigma_I(Me_2S^+)$ may underestimate the difference in the I effects between Me_2S^+ and COOMe, which would lead to an underestimate of $\delta \log K_1^I(Me_2S^+)$ and uncertainties in parameters derived therefrom (see footnote b in Table 6).] With $\beta_B = 0{\cdot}70$ one calculates $\lambda_R^X = 0{\cdot}41$ and $\lambda_R^X - \beta_B = -0{\cdot}29$. By means of an equation analogous to equation (11), $\delta \log K_I^R(Me_2S^+) + \delta \log K_I^P(Me_2S^+) = -4{\cdot}74$ is obtained, from which $\delta \log K_I^R(Me_2S^+) \leqslant -4{\cdot}74$ is derived [assuming $\delta \log K_I^P(Me_2S^+) \geqslant 0$]. With $\lambda_R^X - \beta_B = -0{\cdot}29$, one obtains $\delta \log k_0^R(Me_2S^+) \geqslant 1{\cdot}37$. Assuming $\delta \log k_0^S(Me_2S^+) = -1{\cdot}47$ yields $\Sigma_{R,P}\ (Me_2S^+) = 0{\cdot}96$, i.e. the lower limit of $\delta \log k_0^R(Me_2S^+)$ of $1{\cdot}37$ would more than fully account for $\Sigma_{R,P}(Me_2S^+)$, requiring that $\delta \log k_0^S(Me_2S^+) < -1{\cdot}47$, as was inferred for $\delta \log k_0^S(Ph_3P^+)$.

It should be noted that the much more negative $\delta \log K_I^R(Me_2S^+) \leqslant -4{\cdot}74$ compared with $\delta \log K_I^R(Ph_3P^+) \leqslant -0{\cdot}90$ is consistent *with the notion that* resonance stabilization of the ylide by Me_2S^+ is relatively unimportant and possibly altogether absent,[9,12] but that with Ph_3P^+ there is probably a significant R effect.[12c,d]

The conclusions from our analysis of the I, R, P and S effects on log k_0(X) (X = CN, Ph_3P^+, Me_2S^+) relative to log k_0(COOMe) can now be summarized as follows.

To a good approximation, the entire difference between log k_0(CN) = 3·76 and log k_0(COOMe) = 2·84 may be accounted for by the stronger electron-withdrawing I effect of CN.

For Ph_3P^+ and Me_2S^+ all four factors, i.e. the I, R, P and S effects, contribute to the difference between log k_0(X) and log k_0(COOMe). The first three enhance log k_0(X), whereas the *S* effect lowers log k_0(X). For X = Ph_3P^+ the S effect almost exactly balances the other three factors, resulting in nearly equal log k_0 values for Ph_3P^+ and COOMe. For X = Me_2S^+ there is a net increase of over one log unit in k_0 relative to COOMe or Ph_3P^+. The main factor for this increase appears to be the smaller resonance stabilization by Me_2S^+ [$\delta \log k_0^R(Me_2S^+) > \delta \log k_0^R(Ph_3P^+)$]. There is also a small contribution from the slightly larger I effect [$\delta \log k_0^I(Me_2S^+) > \delta \log k_0^I(Ph_3P^+)$]. Whether the smaller size of Me_2S^+ contributes to the larger k_0 value [i.e. $\delta \log k_0^S(Me_2S^+)$ less negative than $\delta \log k_0^S(Ph_3P^+)$] cannot be ascertained from the data, but it is a reasonable hypothesis.

Ph_3P^+ and Me_2S^+ are likely to exert substantial ylide-stabilizing P effects. Since neither $\delta \log K_1^P(X)$ nor the charge on the carbon of the ylide [$-1 + \chi_X + \chi_Y$ in equation (13)] is known, no numerical estimate of $\delta \log k_0^P(X)$ can be given, but we have shown that the effect should lead to an increase in k_0.

EXPERIMENTAL

Compound 5-H. This was prepared as the bromide salt by reaction of Ph_3P with 9-bromofluorene according to Johnson *et al.*,[33] m.p. 289–291 °C (lit.,[34] 289–291 °C). The ylide of **5-H** was obtained by the method of Pinck and Hilbert,[35] m.p. 264–266 °C (lit.,[33] 258–260 °C). ^1H NMR (60 MHz, $CDCl_3$); δ 6·26–6·42 (m, 2H), 6·73–7·14 (m, 4H), 7·49–8.30 (m, 17H), identical with that of Pouchert.[36] Mass spectrum (MS); *m/z* 426 (M^+).

Compound 5-Br. The precursor, 2,9-dibromofluorene, was synthesized following the general strategy of Dickinson and Eaborn.[37] 2-Bromofluorene (10·2 g 41·5 mmol) and *N*-bromosuccinimide (7·42 g, 41·7 mmol) were dissolved in 120 ml of CCl_4. Benzoyl peroxide (0·12 g 1 mol %) in 30 ml of CCl_4 was added and the solution was stirred at reflux for 8 h. After standing for 13 h, a starch–iodide test was slightly positive. The reaction mixture was chilled and the insoluble succinimide was separated by vacuum filtration. The filtrate was stripped of solvent and the crude product recrystallized from 400 ml of hexane, m.p. 122–124 °C (lit.,[37a] 123–125 °C). Conversion of 2,9-dibromofluorene into **5-Br** (bromide salt) followed the procedure of Johnson *et al.*,[33] m.p. 276–278 °C (lit.,[33] 264–265 °C). The ylide of **5-Br** was obtained by the method of Pinck and Hilbert,[35] m.p. 261–262 °C (decomp.) (lit.,[33] 262–263 °C). ^1H NMR (60 MHz, $CDCl_3$): δ 6·22–6·49 (m, 2H), 6·87–7·12 (m, 3H), 7·35–8·21 (m, 17H). MS; *m/z* 504/506 (M^+).

Compound 5-NO_2. The precursor, 9-bromo-2-nitrofluorene, was prepared from 2-nitrofluorene in a similar manner to 2,9-dibromofluorene. The crude product was dissolved in hot methanol and vacuum filtered; the filtrate was diluted with hot ethanol and allowed to cool, yielding an orange product, m.p. 136–140 °C (lit.,[38] 142–143 °C). Conversion of 9-bromo-2-nitrofluorene into **5-NO₂** (bromide salt) was the same as for **5-H**, m.p. 272–273 °C [lit.,[33] 281–282 °C (decomp.)]. The ylide of **5-NO₂** was prepared in the same way as the others, m.p. 267–268 °C (decomp.) (lit.,[33] 276–277 °C). ^1H NMR (60 MHz, $CDCl_3$): δ 6·40–6·60 (M, 1H), 6·94–7·16 (m, 3H), 7·35–8·38 (m, 16H). MS: *m/z* 471 (M^+).

Reagents. Buffer materials of analytical grade were obtained from Aldrich (unless specified otherwise) and purified as follows. Piperidine, morpholine, *n*-butylamine and 2-methoxyethylamine were refluxed over CaH_2 for 1 h and distilled under nitrogen. Cyanomethylamine hydrochloride and glycine ethyl ester hydrochloride were recrystallized twice from 1:1 isopropanol–ethanol. Cacodylic acid (free acid, Sigma, 98%), glacial acetic acid (Mallinckrodt, AR) and KCl (Mallinckrodt, AR) were used as received. All HCl and KOH solutions originated from 'DILUTE IT' analytical concentrates (J. T. Baker). Dimethyl sulfoxide (Fisher, certified ACS) was distilled from CaH_2 and stored over 4 Å molecular sieves. Ultra-pure water was obtained from a Millipore Milli-Q Plus water system.

Spectra and pK_a^{CH} measurements. The following spectral parameters were obtained in 50% Me_2SO–50% water at 20 °C using a Perkin–Elmer Model 559 UV–visible spectrophotometer. **5-H**: λ_{max} 268 nm (log ε 4·27), ylide λ_{max} 250 nm (log ε 4·62), 285 nm (log ε 4·47), 368 nm (log ε 3·65, broad). **5-Br**: λ_{max} 272 nm (log ε 4·33); ylide λ_{max} 253 nm (log ε 4·65), 289 nm (log ε 4·54), 385 nm (log ε 3·56, broad). **5-NO₂**: λ_{max} < 250 nm (covered with the absorption by Me_2SO) (log ε > 4·5), 330 nm (log ε 4·18); ylide λ_{max} 270 nm (log ε 4·30), 296 nm (log ε 4·40), 340 nm (log ε 4·11), 390 nm (log ε 4·06), 530 nm (log ε 3·26, broad). The ylides have a low solubility in 50% Me_2SO–50% water and tended to precipitate. However, if spectra were taken within a few minutes after mixing, the precipitation of phosphonium bromides could be avoided.

The pK_a^{CH} determinations were carried out at 285 nm for **5-H**, at 253 and 289 nm for **5-Br** and at 396 nm for **5-NO$_2$**. The pH measurements were conducted with an Orion Model 611 pH meter equipped with an Orion Model 910100 glass electrode and a Fisher Model 13-620-51 calomel reference electrode. The meter was calibrated with Hallé[39] buffers.

Kinetic measurements All kinetic determinations were carried out with a Durrum–Gibson stopped-flow spectrophotometer. The general methodology was as described previously.[25,40] The pH of the reaction solutions was determined in mock mixing experiments.

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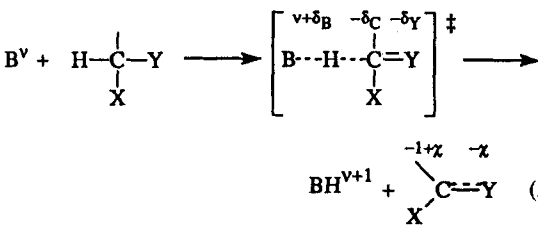
APPENDIX

We first consider the deprotonation of a carbon acid activated by one π-acceptor (Y) and another group (X) that may exert I, P and/or S effects but no R effect. This reaction is schematically represented by


(A1)

It has been shown that $\delta \log k_0^R(\mathrm{Y})$, which is the change in $\log k_0$ caused by the R effect of Y relative to a reference compound, is given by the equation[4,7]

$$\delta \log k_0^R(\mathrm{Y}) = (\lambda_R^Y - \beta_B)\delta \log K_1^R(\mathrm{Y}) \quad (\mathrm{A2})$$

where $\delta \log K_1^R(\mathrm{Y})$ is the contribution of the R effect of Y to the change in K_1 and λ_R^Y measures the progress in resonance development at the transition state, defined as

$$\lambda_R^Y = \delta \log k_1^R(\mathrm{Y})/\delta \log K_1^R(\mathrm{Y}) \quad (\mathrm{A3})$$

with $\delta \log k_1^R(\mathrm{Y})$ representing the contribution of the R effect of Y to the change in k_1.

On the basis of our model,[4] the equations

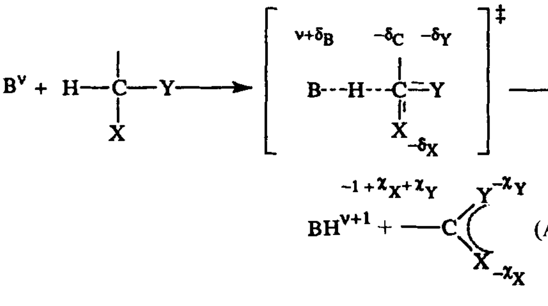
$$\lambda_R^Y = \delta_Y/\chi \quad (\mathrm{A4})$$

$$\delta_Y = \chi(\delta_B)^n \quad (\mathrm{A5})$$

hold with the most likely value of n being between 2 and 3. If we equate δ_B with β_B (this is the traditional view,[13b,16] although this view has been challenged[17]), it follows that λ_R^Y is given by

$$\lambda_R^Y = (\delta_B)^n = (\beta_B)^n \quad (\mathrm{A6})$$

The above formalism may be extended to the situation where X, too, is a π-acceptor, as represented in the equation


(A7)

Besides the $\delta \log k_0^R(\mathrm{Y})$ term given by equation (A2), there is now an additional term, $\delta \log k_0^R(\mathrm{X})$, given by

$$\delta \log k_0^R(\mathrm{X}) = (\lambda_R^X - \beta_B)\delta \log K_1^R(\mathrm{X}) \quad (\mathrm{A8})$$

which contributes to the change in k_0. In this situation the following relationships hold:

$$\delta_Y = \chi_Y(\delta_B)^n \quad (\mathrm{A9})$$

$$\delta_X = \chi_X(\delta_B)^n \quad (\mathrm{A10})$$

$$\lambda_R^Y = \delta_Y/\chi_Y = (\delta_B)^n = (\beta_B)^n \quad (\mathrm{A11})$$

$$\lambda_R^X = \delta_X/\chi_X = (\delta_B)^n = (\beta_B)^n \quad (\mathrm{A12})$$

The result that $\lambda_R^X = \lambda_R^Y$ and that λ_R^Y is the same for reactions (A1) and (A7) may seem surprising because one would expect that the R effect of X would influence (decrease) the R effect of Y. According to our model, the influence of the R effect of X on the R effect of Y exerts itself through a change (decrease) in $\delta \log K_1^R(\mathrm{Y})$ rather than a change in λ_R^Y.

The above model can also be used to estimate the P effect of X on k_0. With reference to reaction (A1), $\delta \log k_0^P(\mathrm{X})$ can be expressed by

$$\delta \log k_0^P(\mathrm{X}) = (\lambda_P^X - \beta_B)\delta \log K_1^P(\mathrm{X}) \quad (\mathrm{A13})$$

where $\delta \log K_1^P(\mathrm{X})$ is the contribution of the P effect to the stabilization of the product ion relative to a reference compound for which there is no P effect and λ_P^X measures the progress of P development at the transition state. λ_P^X, which is defined as

$$\lambda_P^X = \delta \log k_1^P(\mathrm{X})/\delta \log K_1^P(\mathrm{X}) \quad (\mathrm{A14})$$

with $\delta \log k_1^P(\mathrm{X})$ being the increase in $\log k_1$ caused by the P effect on the transition state, may be estimated by assuming that the P effect is limited to the stabilization of the negative charge on the carbon directly adjacent to the substituent. This is a reasonable assumption since P effects fall off with the fourth power of distance.[41] As P effects are proportional to the *square* of the charge,[41] the transition-state stabilization must be proportional to $(\delta_C)^2$ and product stabilization to $(-1+\chi)^2$ and hence λ_P^X is given by

$$\lambda_P^X = \frac{\delta_C^2}{(-1+\chi)^2} \quad (\mathrm{A15})$$

From $\delta_C = \delta_B - \delta_Y$, equation (A5) and again equating δ_B with β_B, one obtains

$$\lambda_P^X = \frac{[\beta_B - \chi(\beta_B)^n]^2}{(-1+\chi)^2} \quad (\mathrm{A16})$$

Extension to reaction (A7) where X also exerts an R effect leads to

$$\delta_C = \delta_B - \delta_X - \delta_Y \quad (\mathrm{A17})$$

In combination with equations (A9) and (A10), equation (A17) yields

$$\delta_C = \delta_B - (\chi_X + \chi_Y)(\delta_B)^n = \beta_B - (\chi_X + \chi_Y)(\beta_B)^n \quad (\mathrm{A18})$$

and hence

$$\lambda_P^X = \frac{[\beta_B - (\chi_X + \chi_Y)(\beta_B)^n]^2}{(-1+\chi_X+\chi_Y)^2} \quad (\mathrm{A19})$$