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**CALCULATIONS OF THE DEPROTONATION ENERGIES OF MONO-SUBSTITUTED BENZENES, AND THEIR SIGNIFICANCE FOR THE MECHANISMS OF BASE-CATALYSED CLEAVAGES OF ARYL—SILICON AND ARYL—TIN BONDS AND HYDROGEN-EXCHANGE IN SUBSTITUTED BENZENES \***

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**Summary**

Ab initio calculations at the STO-3G level have been made on the mono-substituted benzenes,  $\text{XC}_6\text{H}_5$ , and the anions,  $\text{XC}_6\text{H}_4^-$ , derived from them ( $\text{X} = \text{H}$ , and *o*-, *m*-, and *p*- $\text{NO}_2$ ,  $\text{CN}$ ,  $-\text{CF}_3$ ,  $-\text{Cl}$ ,  $-\text{F}$ ,  $-\text{OMe}$ , and  $-\text{NH}_2$ ) and values are given of  $\Delta E_{\text{X}^-}$ , the energy change for the conversion  $\text{XC}_6\text{H}_5 \rightarrow \text{XC}_6\text{H}_4^-$  relative to that for  $\text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5^-$ . Analysis of the effects of substituents X in cleavage of  $\text{XC}_6\text{H}_4\text{SiMe}_3$  compounds by  $\text{NaOH}$  in 1/9 or 1/6 v/v  $\text{H}_2\text{O}-\text{Me}_2\text{SO}$  in the light of the  $\Delta E_{\text{X}^-}$  values indicates that they are consistent with rate-determining separation of the carbanions  $\text{XC}_6\text{H}_4^-$ . The effects of the substituents in this reaction correlate satisfactorily with their  $\sigma^0$  constants. The effects of the X groups in exchange of  $\text{XC}_6\text{H}_4^2\text{H}$  compounds with  $\text{KNH}_2-\text{NH}_3$  are also shown to be consistent with separation of the anions  $\text{XC}_6\text{H}_4^-$ , with a transition state closer to the anion than is the case for the cleavage of the  $\text{XC}_6\text{H}_4\text{SiMe}_3$  compounds. The substituent effects in cleavage of  $\text{XC}_6\text{H}_4\text{SnMe}_3$  compounds by  $\text{MeONa}-\text{MeOH}$  or by  $\text{NaOH}$  in 1/6 v/v  $\text{H}_2\text{O}-\text{Me}_2\text{SO}$  can be quantitatively interpreted in terms of proton transfer from the solvent to the separating carbon atom as the  $\text{XC}_6\text{H}_4-\text{Sn}$  bond breaks as a result of attack by the base on the metal centre.

Approximate  $\text{pK}_a$  values are derived for the several positions of various mono-substituted benzenes.

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\* Reprints available from G.S.

## Introduction

Evidence has accumulated in recent years that base cleavages of R—SiMe<sub>3</sub> bonds (e.g. by NaOMe-MeOH) normally involve separation of the carbanion R<sup>-</sup> in the rate-determining step, whereas in cleavages of R—SnMe<sub>3</sub> bonds a proton is transferred from the solvent to the R group as it separates [1]. This is the case not only for a range of R groups of the type XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> [1,2], but also for aryl groups such as 2-thienyl, -furyl, or -pyrryl [3]\*. One set of results, however, was difficult to reconcile with this pattern, viz. the effects of the substituents X in the cleavage of the arylsilicon compounds XC<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub> by NaOH in 1/9 v/v H<sub>2</sub>O-Me<sub>2</sub>SO [5]. (Cleavage of C<sub>6</sub>H<sub>5</sub>SiMe<sub>3</sub> is too slow for convenient study in MeONa-MeOH.) The difficulty originated in the lack of knowledge about the way in which the X groups could be expected to influence the ease of formation of the anions XC<sub>6</sub>H<sub>4</sub><sup>-</sup>, and was increased (as we now realize) by the observation that an empirical relationship could be discerned between the effects of substituents in the cleavage of the silicon compounds in NaOH-H<sub>2</sub>O-Me<sub>2</sub>SO and those in the cleavage of the tin compounds in NaOMe-H<sub>2</sub>O-MeOH [6] or NaOH-H<sub>2</sub>O-Me<sub>2</sub>SO [7], and also those in hydrogen-exchange for the compounds XC<sub>6</sub>H<sub>4</sub><sup>2</sup>H in KNH<sub>2</sub>-NH<sub>3</sub>, with the implication that all three reactions might have a common mechanism, but with different positions of the transition state along the reaction coordinate [7]. Thus since the concerted, electrophilically-assisted mechanism operates for the tin compounds, it was possible that a similar mechanism applied to the silicon compounds and the hydrogen-exchange, but with a much smaller degree of electrophilic assistance.

As mentioned, the major problem was that of predicting the substituent effects on the stabilities of the anions XC<sub>6</sub>H<sub>4</sub><sup>-</sup>. Thus Hall and his colleagues argued that if the rate-determining step in the hydrogen-exchange were the removal of the proton, the  $\pi$ -electron system of the ring would not be involved in any important way in the proton abstraction and the resonance effects of substituents would be unimportant [8]. Streitwieser and his colleagues, on the other hand, discussed the substituent effects in base-catalysed hydrogen exchange in terms of a combination of  $\pi$ -polarization and inductive field effects, concluding that the  $\pi$ -polarization effects were of significance for the exchange in substituted benzenes but much less important than the field effect in the case of polynuclear hydrocarbons [9]. In contrast, Eaborn, Hornfeld, and Walton suggested that the interaction between a substituent and a non-delocalizable charge at the 1-position might not differ in kind from that between the substituent and a non-delocalizable charge in a side-chain (as for example, in the ionization of the acids XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CO<sub>2</sub>H), so that the effects of the X groups on the ease of formation of the anions XC<sub>6</sub>H<sub>4</sub><sup>-</sup> could be expected to correlate with  $\sigma^o$  or  $\sigma_n$  constants [6]. To help resolve this problem we have carried out ab initio MO calculations on the effects on substituents on the energies of the XC<sub>6</sub>H<sub>5</sub> and XC<sub>6</sub>H<sub>4</sub><sup>-</sup> species. A preliminary account of the results has appeared [10].

\* There are exceptions to the generalization. For example, when the R groups are derived from markedly stronger carbon acids RH (such as fluorene), the tin compounds also appear to give carbanions [1], while for R = CH<sub>2</sub>CH=CHPh, where electrophilic attack is unusually favoured, the silicon compound appears to react by the concerted mechanism [4].

TABLE 1

CALCULATED ENERGIES,  $E_X$ , (in a.u.) FOR CONVERSION OF  $\text{XC}_6\text{H}_5$  INTO  $\text{XC}_6\text{H}_4^-$ 

No. <sup>d</sup>	X	$10^4 \times (E_{\bar{X}} - E_X)$	$-10^3 \Delta E_{\bar{X}}^a$	No. <sup>d</sup>	X	$10^4 \times (E_{\bar{X}} - E_X)$	$-10^3 \Delta E_{\bar{X}}^a$
1	<i>o</i> -NO <sub>2</sub>	7760	48	14	<i>m</i> -F	8139	10
2	<i>m</i> -NO <sub>2</sub>	7895	35	15	<i>p</i> -F	8203	4
3	<i>p</i> -NO <sub>2</sub>	7825	42	16	H	8242	0
4	<i>o</i> -CN	7928	37	17	<i>o</i> -Me	8240	0
5	<i>m</i> -CN	7967	27.5	18	<i>m</i> -Me	8246	-0.5
6	<i>p</i> -CN	7873	31	19	<i>p</i> -Me	8260	-2
7	<i>o</i> -CF <sub>3</sub>	8014	23	20	<i>o</i> -OMe	8182	6
8	<i>m</i> -CF <sub>3</sub>	8084	16	21	<i>m</i> -OMe	8190	5
9	<i>p</i> -CF <sub>3</sub>	8068	17	22	<i>p</i> -OMe	8264	-2
10	<i>o</i> -Cl	7947	29	23	<i>o</i> -NH <sub>2</sub>	8276 <sup>b</sup>	-3
11	<i>m</i> -Cl	8014	23	24	<i>m</i> -NH <sub>2</sub>	8272 <sup>b</sup>	-3
12	<i>p</i> -Cl	8044	20		<i>p</i> -NH <sub>2</sub>	8377 <sup>b</sup>	-13
13	<i>o</i> -F	8109	13	25	<i>p</i> -NH <sub>2</sub>	8311 <sup>c</sup>	-7

<sup>a</sup> Value of  $(E_{\bar{X}} - E_X) - (E_{\bar{H}} - E_H)$ , where  $E_H$  refers to  $\text{C}_6\text{H}_6$ . <sup>b</sup> Assuming planarity at nitrogen. <sup>c</sup> With optimized angle at nitrogen (see text). <sup>d</sup> In the Figures, numbers 24 and 25 are also used for *m*-NMe<sub>2</sub> and *p*-NMe<sub>2</sub>, respectively (see text). Additional substituents are numbered in the Figures as follows: *m*-Ph, 26; *p*-Ph, 27; *p*-t-Bu, 28; *m*-Br, 29; *p*-Br, 30; *p*-Et, 31.

### Method

The standard Gaussian 70 package with minimum basis set (STO-3G) was used [26] usually in association with standard geometries [11]. For the *o*- and *m*-MeOC<sub>6</sub>H<sub>4</sub><sup>-</sup> anions, the configuration having the Me group directed away from C(1) was arbitrarily assumed. Initially the calculation for  $\text{C}_6\text{H}_5\text{NH}_2$  and *o*-, *m*-, and *p*-NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub><sup>-</sup> assumed a planar structure, and results based on these calculations were given in the preliminary communication [10]. However, because of the importance of the *p*-NMe<sub>2</sub> group (which is assumed to have the same effect as a *p*-NH<sub>2</sub> group), we decided to optimize the angle at nitrogen for  $\text{C}_6\text{H}_5\text{NH}_2$  and *p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub><sup>-</sup>; the calculated HNH and HNC angles (constrained to be equal) were 112.1° for the neutral molecule (which agrees satisfactorily with the experimental value of 113.9° for aniline [12]) and 108.5° for the anion, and the calculated deprotonation energy was significantly different from that based on the planar geometry. We did not, however, recalculate the energies based on planar geometries for the less important *o*- and *m*-NH<sub>2</sub> groups.

SCHEME 1

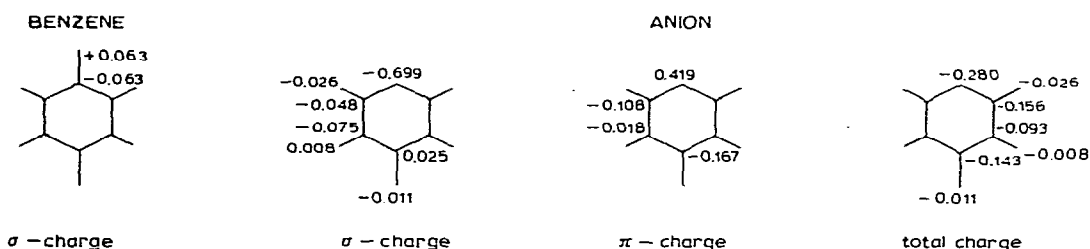
CHARGE DISTRIBUTIONS IN BENZENE AND THE  $\text{C}_6\text{H}_5^-$  ION

TABLE 2  
CHARGES ON THE 1-H ATOM IN XC<sub>6</sub>H<sub>5</sub>

X	10 <sup>3</sup> C(e)	10 <sup>3</sup> ΔC(e) <sup>a</sup>	X	10 <sup>3</sup> C(e)	ΔC(e)
<i>o</i> -NO <sub>2</sub>	99	36	<i>o</i> -F	71	8
<i>m</i> -NO <sub>2</sub>	77	14	<i>m</i> -F	68	5
<i>p</i> -NO <sub>2</sub>	78	15	<i>p</i> -F	64	1
<i>o</i> -CN	80	17	H	63	0
<i>m</i> -CN	73	10	<i>o</i> -Me	60	-3
<i>p</i> -CN	73	10	<i>m</i> -Me	62	-1
<i>o</i> -CF <sub>3</sub>	72	9	<i>p</i> -Me	61	-2
<i>m</i> -CF <sub>3</sub>	69	6	<i>o</i> -OMe	69	+6
<i>p</i> -CF <sub>3</sub>	69	6	<i>m</i> -OMe	64	+1
<i>o</i> -Cl	79	16	<i>p</i> -OMe	60	-3
<i>m</i> -Cl	72	9	<i>o</i> -NH <sub>2</sub>	56 <sup>b</sup>	-7
<i>p</i> -Cl	70	7	<i>m</i> -NH <sub>2</sub>	63 <sup>b</sup>	0
			<i>p</i> -NH <sub>2</sub>	58 <sup>b</sup>	-5

<sup>a</sup> Charge on 1-H relative to that in C<sub>6</sub>H<sub>6</sub>. <sup>b</sup> Values with optimized angle at N. The values for planar N are: *o*-, 53; *m*-, 62; *p*-, 55.

The results of the calculations are shown in Table 1; calculations for species containing fluorine or chlorine can be expected to be subject to larger than average uncertainty. The calculations also gave the charge distributions in the XC<sub>6</sub>H<sub>5</sub> and XC<sub>6</sub>H<sub>4</sub><sup>-</sup> species; these will mainly be discussed elsewhere [16], but

TABLE 3  
CHARGES (×10<sup>3</sup>) TAKEN BY X GROUPS IN XC<sub>6</sub>H<sub>5</sub> AND XC<sub>6</sub>H<sub>4</sub><sup>-</sup>

XC <sub>6</sub> H <sub>5</sub>					<i>o</i> -XC <sub>6</sub> H <sub>4</sub> <sup>-</sup>			
X	σ	π	σ/π	Total	σ	π	σ/π	Total
NO <sub>2</sub>	-292	-31	9.4	-323	-286	-82	3.5	-368
CN	-166	-23	7.2	-189	-169	-60	2.8	-229
CF <sub>3</sub>	-73	-20	3.7	-90	-104	-23	4.5	-127
Cl	-223	+3	-5.3	-180	-255	+30	-8.5	-225
F	-276	+78	-3.5	-198	-247	+64	-3.8	-183
H	0	0		0	0	0		0
Me	-59	+8	-6.6	-51	-57	-5	11.4	-62
OMe	-316	+99	-3.2	-217	-304	+82	-3.7	-222
NH <sub>2</sub> <sup>a</sup>	-223	+120	-1.8	-106	-216	+86	-2.5	-130
NH <sub>2</sub> <sup>b</sup>	-203	+94	-2.2	-109				
<i>m</i> -XC <sub>6</sub> H <sub>4</sub> <sup>-</sup>					<i>p</i> -XC <sub>6</sub> H <sub>4</sub> <sup>-</sup>			
X	σ	π	σ/π	Total	σ	π	σ/π	Total
NO <sub>2</sub>	-291	-65	4.6	-356	-276	-109	2.5	-385
CN	-175	-46	3.8	-221	-161	-73	2.2	-234
CF <sub>3</sub>	-102	-20	5.1	-122	-97	-29	3.3	-126
Cl	-251	+33	-7.6	-218	-244	+25	-9.8	-219
F	-255	+68	-3.8	187	-243	+54	-4.5	-189
H	0	0		0	0	0		0
Me	-72	0		-72	-97	-1	97	-98
OMe	-306	+82	-3.7	-224	-295	+68	-4.3	-227
NH <sub>2</sub> <sup>a</sup>	-217	+90	-2.4	-127	-207	+72	-2.9	-135
NH <sub>2</sub> <sup>b</sup>					-182	+49	-3.7	-133

<sup>a</sup> Planar geometry at N. <sup>b</sup> Optimized angle at N. <sup>c</sup> Relative to those taken by H.

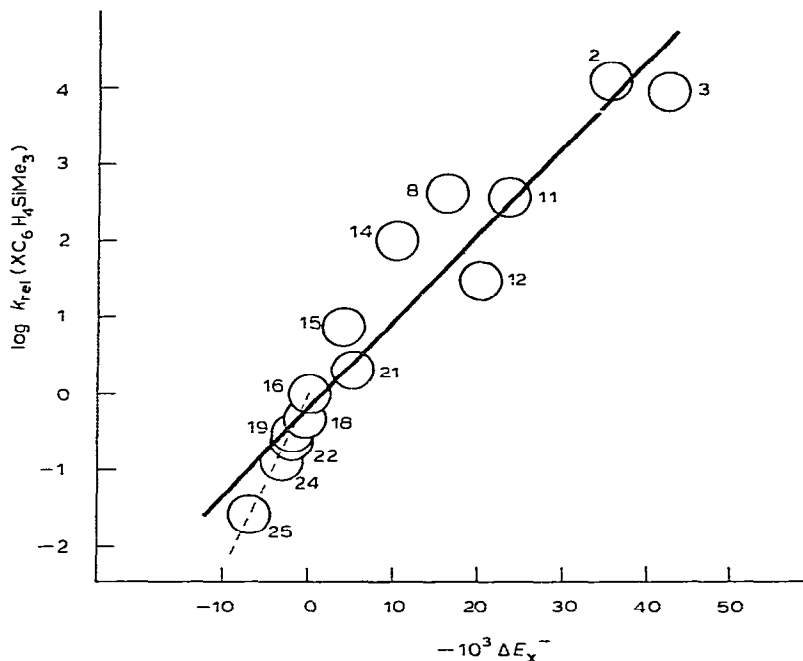


Fig. 1. Plot of  $\log k_{rel}$  for cleavage of  $\text{XC}_6\text{H}_4\text{SiMe}_3$  compounds by  $\text{NaOH}$  in  $1/9$  v/v  $\text{H}_2\text{O}-\text{Me}_2\text{SO}$  [5] against  $\Delta E_{\text{X}^-}$  (a.u.), the relative energies of deprotonation for the 1-position of  $\text{XC}_6\text{H}_5$  species. The solid line is the best least squares line. For numbering of substituents see Table 1.

the results for benzene and the anion  $\text{C}_6\text{H}_5^-$  are shown in Scheme 1, and some further data are included in Tables 2 and 3.

## Results and discussion

### Cleavage of $\text{XC}_6\text{H}_4\text{SiMe}_3$ compounds

The calculated energy differences,  $E_{\text{X}^-} - E_{\text{X}}$ , between  $\text{XC}_6\text{H}_4^-$  and  $\text{XC}_6\text{H}_5$  species are shown in Table 1. The values of  $(E_{\text{X}^-} - E_{\text{X}}) - (E_{\text{H}^-} - E_{\text{H}})$ , where  $E_{\text{H}}$  refers to benzene, denoted by  $\Delta E_{\text{X}^-}$ , are also given;  $(E_{\text{X}^-} - E_{\text{X}})$  is a measure of the acidity of the  $\text{XC}_6\text{H}_5$  at the relevant position, and should also provide a measure of the ease of generating the anion  $\text{XC}_6\text{H}_4^-$  from the corresponding  $\text{XC}_6\text{H}_4\text{SiMe}_3$ . In Figure 1 is shown a plot against the  $\Delta E_{\text{X}^-}$  values of the  $\log k_{rel}$  values for the cleavage of  $\text{XC}_6\text{H}_4\text{SiMe}_3$  compounds by  $\text{NaOH}$  in  $1/9$  v/v  $\text{H}_2\text{O}-\text{Me}_2\text{SO}$  [5], the  $\Delta E_{\text{X}^-}$  values for  $\text{H}_2\text{NC}_6\text{H}_4^-$  anions being used in conjunction with the rate data for *m*- and *p*- $\text{Me}_2\text{N}$  compounds\*. While, as we show later, the plot can probably better be regarded as consisting of two separate lines, a fairly satisfactory single line can be drawn taking all the points into account; the considerable scatter in the plot must be viewed, of course, in the light of the possible errors in the  $\Delta E_{\text{X}^-}$  values; it is noteworthy, in this connec-

\* The similarity of the  $\sigma^0$  constants for  $\text{NH}_2$  and  $\text{NMe}_2$  groups justifies this practice.

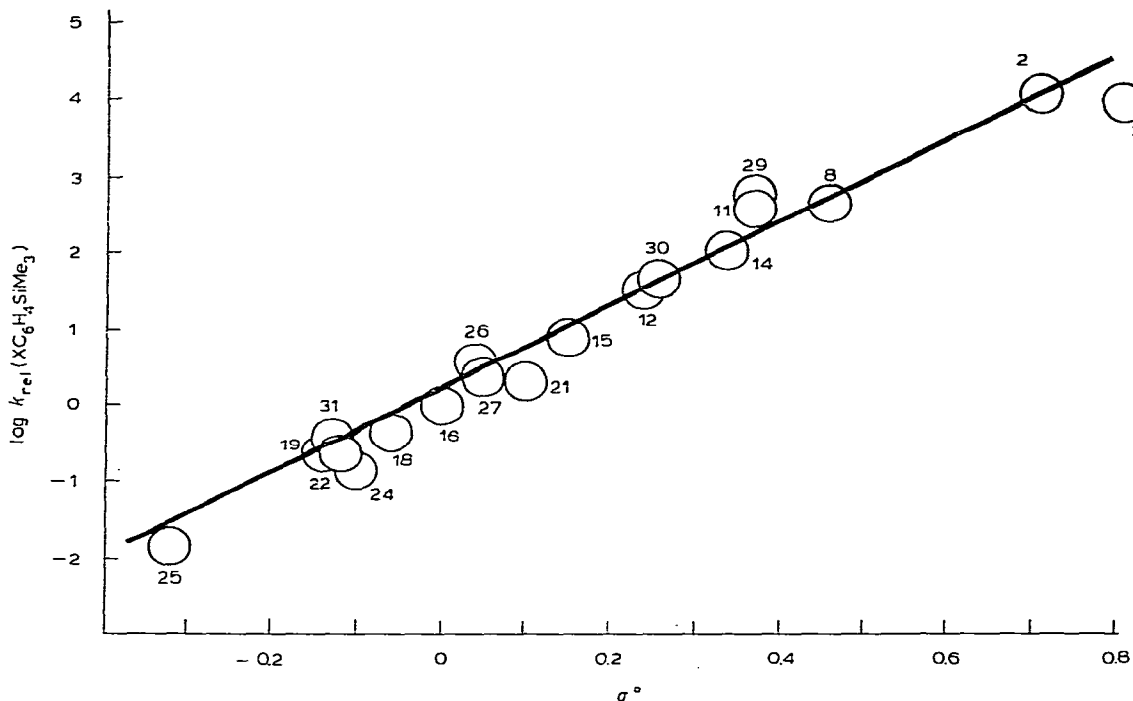


Fig. 2. Plot of  $\log k_{rel}$  for cleavage of  $XC_6H_4SiMe_3$  compounds by NaOH in 1/9 v/v  $H_2O-Me_2SO$  against  $\sigma^0$  constants. The line shown was chosen visually; the best least squares line has a smaller slope and passes further above the point for  $X = p-NMe_2$ . For numbering of substituent see Table 1.

tion, that the most seriously deviant points, those for *m*-F and *m*-CF<sub>3</sub>, refer to substituents for which the uncertainty in the calculations is greater than usual. The correlation coefficient is 0.954 (intercept -0.14) for all 14 points, but this is improved to 0.987 (intercept -0.37) if the points for *m*-F, *p*-F, and *m*-CF<sub>3</sub> are omitted. The existence of this correlation means that the substituent effects in the cleavage of the  $XC_6H_4SiMe_3$  compounds are consistent with rate-determining separation of the anions.

A plot (Figure 2) against  $\sigma^0$  of  $\log k_{rel}$  values for the cleavage of  $XC_6H_4SiMe_3$  compounds by NaOH in 1/9 v/v  $H_2O-Me_2SO$  also gives a fairly good straight line (corrln. coeff. 0.971; intercept, 0.27, 19 points), and this plot involves a markedly larger number of points than that in Figure 1; the only point significantly off the line when account is taken of the estimated uncertainties in the  $\sigma^0$  values [13] is that for the *p*-NO<sub>2</sub> group, and if this is clearly deviant point is omitted, the correlation coefficient becomes 0.988. (A plot (not shown) of  $\log k_{rel}$  versus  $\sigma_n$  [14] is slightly more satisfactory in terms of the overall correlation (corrln. coeff. 0.983; intercept, -0.05; 16 points), but the point for  $X = p-NMe_2$  lies rather badly off the line.) The  $\log k_{rel}$  values for cleavage of a smaller range of  $XC_6H_4SiMe_3$  compounds by NaOH in 1/6 v/v  $H_2O-Me_2SO$  [7] also correlate well with  $\sigma^0$  constants; the correlation coefficient is 0.987 (intercept, -0.06; 9 points), and this is improved to 0.997 if the point for *m*-OMe,

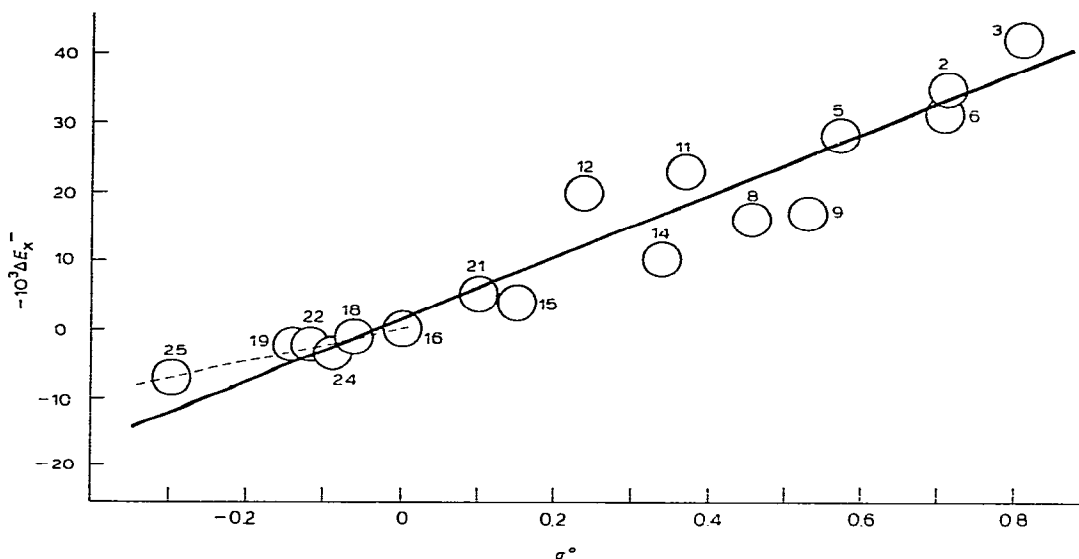


Fig. 3. Plot of relative deprotonation energies,  $\Delta E_{X^-}$  (a.u.), for the 1-position of  $XC_6H_5$  against  $\sigma^o$  constants. The solid line is the best least squares line for all the points. For numbering of substituents see Table 1.

for which the  $\sigma^o$  constant is rather uncertain [13], is omitted. As would be expected, the  $\log k_{rel}$  values for the 1/9 v/v  $H_2O$ - $Me_2SO$  correlate excellently with those for the 1/6 v/v  $H_2O$ - $Me_2SO$  (corrln. coeff. 0.999; intercept 0.04; 6 points).

It follows that a plot of  $\Delta E_{X^-}$  against  $\sigma^o$  [13] for all the *m*- and *p*-substituents for which data are available is a reasonable straight line, as shown in Figure 3 (corrln. coeff. 0.971; intercept, 0.27; 19 points); if the points for F-containing groups and Cl, for which the  $\Delta E_{X^-}$  values are subject to large uncertainty are omitted, the correlation coefficient becomes 0.991 (intercept, 2.56; 11 points). We shall show later, however, than on more detailed analysis the plot in Figure 3 is probably better defined in terms of two separate straight lines.

The  $\log k_{rel}$  values for cleavage in 1/9 v/v  $H_2O$ - $Me_2SO$  give a satisfactory correlation ( $f = 0.12$ ) with  $\sigma_I$  and  $\sigma_R^o$  constants in terms of a Taft-type equation [18]  $\log k_{rel} = \rho_I \sigma_I + \rho_R \sigma_R^o$ , with  $\rho_I = 5.231$  and  $\rho_R = 4.083$ ; the ratio  $\rho_R/\rho_I$  of 0.78 is close to the values observed [18] for saponifications of the esters  $XC_6H_4CH_2COOEt$ , which are often used as model reactions for applications of  $\sigma^o$  constants.

#### Cleavage of $XC_6H_4SnMe_3$ compounds

In contrast, the  $\log k_{rel}$  values for cleavage of the tin compounds  $XC_6H_4SnMe_3$  in  $NaOH$ - $H_2O$ - $MeOH$  [6] do not correlate satisfactorily with the  $\Delta E_{X^-}$  values (or, of course, with the  $\sigma^o$  constants); in particular, the clear rate acceleration by *p*- $NMe_2$  and *p*- $OMe$  groups are quite incompatible with the  $\Delta E_{X^-}$  values (or  $\sigma^o$  constants). They are, as we shall show, fully consistent with the electrophilically-assisted mechanism.

In such a mechanism, the effects of a substituent X on the ease of breaking of the C(1)—Sn bond (notionally to give the anion  $\text{XC}_6\text{H}_4^-$ ) will act in opposition to those on the formation of the C(1)—H bond (notionally to give a Wheland intermediate carbonium ion). If we assume that the two effects operate independently, then the effects on the incipient formation of the carbanion will be related to the  $\log k_{\text{rel}}$  values for the cleavages of the corresponding  $\text{XC}_6\text{H}_4\text{SiMe}_3$  compounds in 1/9 v/v  $\text{H}_2\text{O}-\text{Me}_2\text{SO}$ , while those on the electrophilic attack will be related to the  $\sigma^+$  constants of the X groups, and a relationship of the type shown in equations 1 and 2 will apply, where S is a proportionality constant; we use the form of equation 2 in our plot order to avoid too much bunching of points around the origin.

$$\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SnMe}_3) = S \log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiMe}_3) + z\sigma^+ \quad (1)$$

$$\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SnMe}_3) - z\sigma^+ = S \log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiMe}_3) \quad (2)$$

It will be seen from Figure 4 that an excellent plot (corrln. coeff. 0.997; intercept 0.02; 16 points) is obtained when a value of  $-0.55$  is used for  $z$ .

Again, if we relate the effects of the substituents on the ease of breaking the C(1)—Sn bond to the  $\sigma^0$  constants of the X groups (rather than to the  $\log k_{\text{rel}}$  values for the  $\text{XC}_6\text{H}_4\text{SiMe}_3$  compounds), and the effects on the ease of the electrophilic attack once again to the  $\sigma^+$  constants, then equation 3 (which corresponds to equation 1) will apply, and this can be expressed as a Yukawa-Tsuno

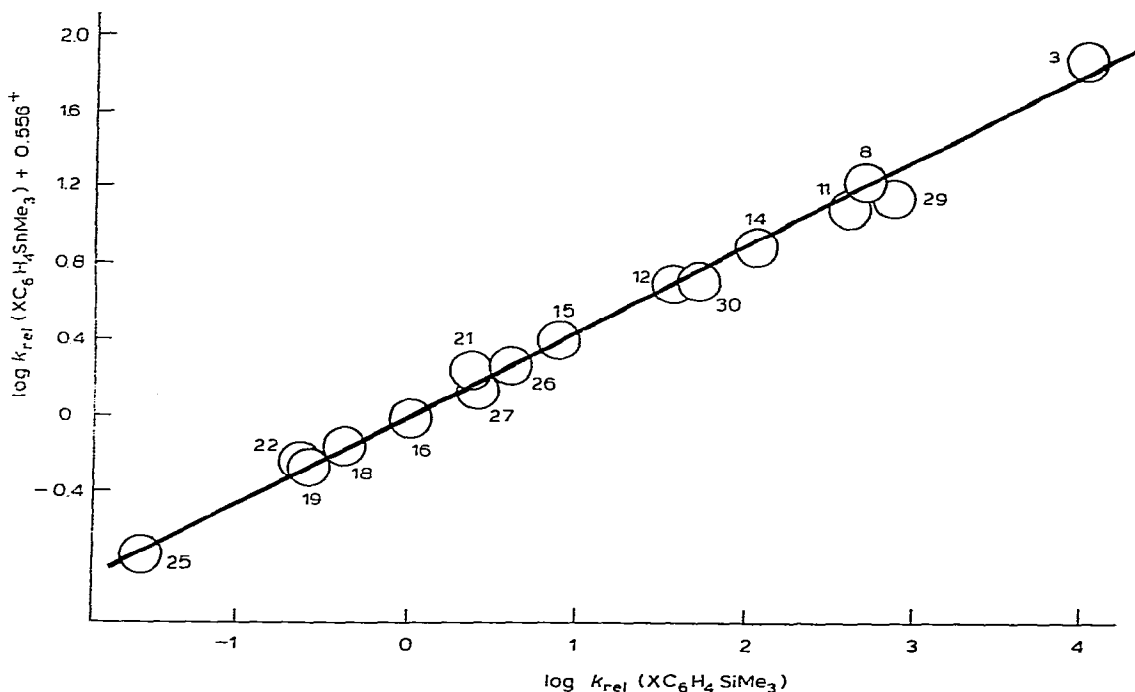


Fig. 4. Plot of  $[\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SnMe}_3) + 0.55\sigma^+]$  against  $\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiMe}_3)$ . The  $k_{\text{rel}}$  values for  $\text{XC}_6\text{H}_4\text{SnMe}_3$  refer to cleavage in  $\text{NaOMe}-\text{MeOH}$  [6], and those for  $\text{XC}_6\text{H}_4\text{SiMe}_3$  to cleavage by  $\text{NaOH}$  in 1/9 v/v  $\text{H}_2\text{O}-\text{Me}_2\text{SO}$  [5]. For numbering of substituents see Table I.



type relationship as in equation 4 (but with a negative value of  $r$  in contrast to the usual positive value), or the equivalent equation 5, (with  $r = r'\rho$ ). A further related relationship is shown in equation 6.

$$\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SnMe}_3) = \rho'\sigma^0 + \rho''\sigma^+ \quad (3)$$

$$\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SnMe}_3) = \rho[\sigma^0 + r'(\sigma^+ - \sigma^0)] \quad (4)$$

$$\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SnMe}_3) - r(\sigma^+ - \sigma^0) = \rho\sigma^0 \quad (5)$$

$$\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SnMe}_3) - r(\sigma^+ - \sigma^0) = \rho[\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiMe}_3)] \quad (6)$$

An excellent correlation is obtained when equation 6 is used with a value of  $r$  of 0.5 (corrln. coeff., 0.997; intercept 0.05; 16 points), and a good correlation (with  $\rho = 1.87$ ) for a larger number of substituents in terms of equation 4 or 5, with  $r = 0.3$  (corrln. coeff., 0.979; intercept 0.09; 21 points), the correlation coefficient in the latter case rises to 0.982 if the points for  $p\text{-CF}_3$  and  $p\text{-SMe}$ , for which  $\sigma^0$  values are subject to large uncertainty, are excluded. The advantage of equations of type 4–6 are that the slopes,  $\rho$ , are fairly close to those which would be obtained by plotting  $\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SnMe}_3)$  values for  $\text{X} = \text{H}$  and *meta*-groups only, since for *meta*-substituents values of  $(\sigma^+ - \sigma)$  are mostly close to zero; a plot of  $\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SnMe}_3)$  against  $\sigma^0$  for  $\text{X} = \text{H}$  or *m*-X (9 points) gives a correlation coefficient of 0.991 with  $\rho = 2.24$ .

We have previously concluded that electrophilic assistance plays a smaller part in cleavage of C–Sn bonds by base in  $\text{H}_2\text{O-Me}_2\text{SO}$  [1]. In keeping with this, when the data for cleavage of  $\text{XC}_6\text{H}_4\text{SnMe}_3$  compounds by NaOH in 1/6 v/v  $\text{H}_2\text{O-Me}_2\text{SO}$  are treated in terms of equation 4, a (numerically) smaller value of  $r$ , viz.  $-0.15$ , has to be used compared with that, viz.  $-0.30$ , which applies for cleavage in  $\text{MeONa-MeOH}$ ; with this  $r$  value, an excellent correlation is obtained (corrln. coeff. 0.996; slope 4.43, intercept 0.00; 7 points). Correlation in terms of equation 2 is also excellent; thus a plot of  $\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SnMe}_3) + 0.6\sigma^+$  against  $\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiMe}_3)$  (the latter for cleavage in 1/9 v/v  $\text{H}_2\text{O-Me}_2\text{SO}$ ) has every point effectively on the line (corrln. coeff. 0.998; slope 0.81; intercept  $-0.03$ ; 6 points).

It is noteworthy that the parent compounds  $\text{C}_6\text{H}_5\text{SiMe}_3$  and  $\text{C}_6\text{H}_5\text{SnMe}_3$  are cleaved by base in the 1/6 v/v  $\text{H}_2\text{O-Me}_2\text{SO}$  at virtually the same rate, and if the same mechanism operated in both cases this would imply fairly similar positions of the transition state along the reaction coordinate and so rather similar  $\rho$  values in plots against  $\sigma^0$ , whereas in fact the  $\rho$  value for the tin compounds, viz. 3.85, is substantially smaller than that for the silicon compounds, viz. 5.7. The lower  $\rho$  value for the cleavage of the tin compounds is consistent with the existence of some electrophilic assistance. It is significant that whereas the cleavage of  $\text{PhSnMe}_3$  is much faster (by a factor of  $>10^3$ ) than that of  $\text{PhSiMe}_3$  in  $\text{NaOH-H}_2\text{O-MeOH}$ , in which there is considerable electrophilic assistance, in  $\text{NaOH-H}_2\text{O-Me}_2\text{SO}$  containing only 3% of water, in which the protons of the water are less available because of hydrogen bonding to the  $\text{Me}_2\text{SO}$ ; the silicon compound is 9 times as reactive as the tin compound [15]. That the two compounds have similar reactivities in 1/6 v/v  $\text{H}_2\text{O-Me}_2\text{SO}$  is thus also in keeping with our conclusion that there is appreciable electrophilic assistance to cleavage of the tin compound in this medium.

TABLE 4

EFFECTS OF SUBSTITUENTS X ON RATE OF HYDROGEN-EXCHANGE OF  $\text{XC}_6\text{H}_4^2\text{H}$  COMPOUNDS IN  $\text{KNH}_2\text{-NH}_3$  <sup>a</sup>

X	$k_{\text{rel}}$	X	$k_{\text{rel}}$
<i>o</i> -F	$>4 \times 10^6$	H	1.0
<i>o</i> -CF <sub>3</sub>	$6 \times 10^5$	<i>p</i> -OMe	0.50
<i>m</i> -CF <sub>3</sub>	$10^4$	<i>p</i> -Me	0.44
<i>p</i> -CF <sub>3</sub>	$10^4$	<i>o</i> -Me	0.41
<i>m</i> -F	$4 \times 10^3$	<i>m</i> -Me	0.36
<i>o</i> -OMe	500	<i>p</i> - <i>t</i> -Bu	0.21
<i>p</i> -F	200	<i>m</i> -NMe <sub>2</sub>	0.2
<i>m</i> -Ph	3.3	<i>p</i> -NMe <sub>2</sub>	0.07
<i>p</i> -Ph	2.9		

<sup>a</sup> Values of  $k_{\text{rel}}$  from refs. 8 and 19; some values refer to  $-33^\circ\text{C}$  and some to  $0^\circ\text{C}$ . An approximate value of 1 for *m*-OMe [19] has been omitted because it seems out of keeping with the value of 50 for *m*-OPh; its use gives points deviating seriously from the plots for the other substituents.

#### Base-catalysed hydrogen-exchange

Relevant  $k_{\text{rel}}$  values for exchange of  $\text{XC}_6\text{H}_4^2\text{H}$  with  $\text{KNH}_2\text{-NH}_3$  are shown in Table 4. It should be appreciated that they are derived from the work of two separate groups [8,19], and refer to two temperatures, though the variation in  $k_{\text{rel}}$  with temperature would probably not be significant over the range involved. While assuming that the reaction involved proton abstraction to give the aryl carbanions, neither of the groups satisfactorily interpreted the substituent effects.

We first note that the pattern of  $k_{\text{rel}}$  value is qualitatively consistent with the calculated  $\Delta E_{\text{X}^-}$  values, and so with formation of the carbanions. Thus the markedly larger activation by the *ortho*-F, -CF<sub>3</sub> and -OMe groups than by the corresponding *para*-groups is reflected in the  $\Delta E_{\text{X}^-}$  values, as is the smallness of the deactivation by the *p*-NMe<sub>2</sub> and *p*-OMe groups. The very large reported activation by the *o*-F group is not, however, reflected in the  $\Delta E_{\text{X}^-}$  value.

In making a quantitative analysis we omit the data for the *ortho*-substituents since there are no experimental results available for the effects of such substituents in other reactions with which comparison might be made; the few points for the *ortho*-groups do, in fact, scatter widely about the line of Figure 5. The significance of the attempted correlation of  $\log k_{\text{rel}}$  with  $\Delta E_{\text{X}^-}$  values for the *m*- and *p*-substituents is limited by the fact that of the 10 relevant points, 4 refer to fluorine-containing substituents; nevertheless, for the 10 points a plot of  $\log k_{\text{rel}}$  against  $\Delta E_{\text{X}^-}$  (Figure 5) is an acceptable straight line (corrln. coeff. 0.968; intercept 0.31) when the rough nature of the experimental data ( $k_{\text{rel}}$  values often being given only as orders of magnitude) and the uncertainties in the calculations are taken into account\*. (The correlation is significantly improved (corrln. coeff., 0.980; intercept 0.23) if the point for the *p*-F compound is omitted; the data for this compound lie off all the plots examined (see below) and the  $k_{\text{rel}}$  value may possibly be in error.)

\* Our earlier statement that the plot was not satisfactory was based on the  $\Delta E_{\text{X}^-}$  value for *p*-NH<sub>2</sub> calculated for planar geometry [10].

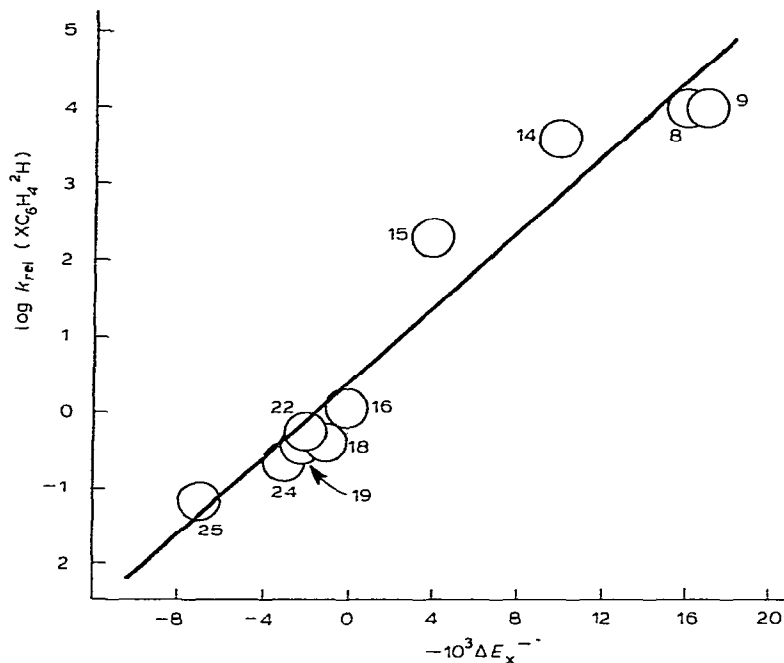


Fig. 5. Plot of  $\log k_{rel}$  for hydrogen-exchange of  $XC_6H_4^2H$  compounds in  $KNH_2-NH_3$  [8,18] against the relative protonation energies  $\Delta E_X^-$  (a.u.) for  $XC_6H_5$  species. For numbering of substituents see Table 1.

A plot (not shown) of  $\log k_{rel}$  for the exchange against  $\log k_{rel}(XC_6H_4SiMe_3)$  is not acceptably linear, a fair overall correlation (corrln. coeff. 0.964; 10 points) obscuring some serious deviations. In order to understand why this is we must first consider the interesting nature of the plot of  $\Delta E_X^-$  against  $\Delta C$  for *meta*- and *para*-substituted compounds, where  $\Delta C$  is the calculated charge on the 1-H atom in  $XC_6H_5$  relative to that on each H atom in  $C_6H_5$ . As Figure 6 shows, a good straight line (corrln. coeff. 0.989; intercept, 0.17; 13 points) can be drawn through the origin ( $X = H$ ) and the points for all the *meta*-substituents and the electron-withdrawing *para*-substituents\*, but the points for the electron-releasing *p*-Me, *p*-OMe and *p*- $NH_2$  groups fall below this line, and can be regarded as lying on a separate straight of greater slope also through the origin\*\*. It must be noted, however, that a fairly good overall correlation (corrln. coeff., 0.985; 17 points) is obtained if all the points in Figure 6 are included in

\* The correlation coefficient remains effectively unchanged if the point for *m*- $NH_2$  is omitted, but the intercept is lowered to  $-0.04$ .

\*\* The existence of such a plot, with division into the two separate lines, has been briefly noted though not discussed by Reynolds and his colleagues, but no data were presented [20]. Somewhat better correlations are obtained if the *meta* and *para* points are treated separately, but the improvements are marginal. The points for the *ortho*-substituents deviate badly from the plot for the *meta*- and *para*-groups, though again the points for the *ortho*-groups Me, OMe, and  $NH_2$  could be regarded as lying on a line passing near the origin which has a much larger slope than a line which can be drawn to pass roughly between the points for most other *ortho*-groups.

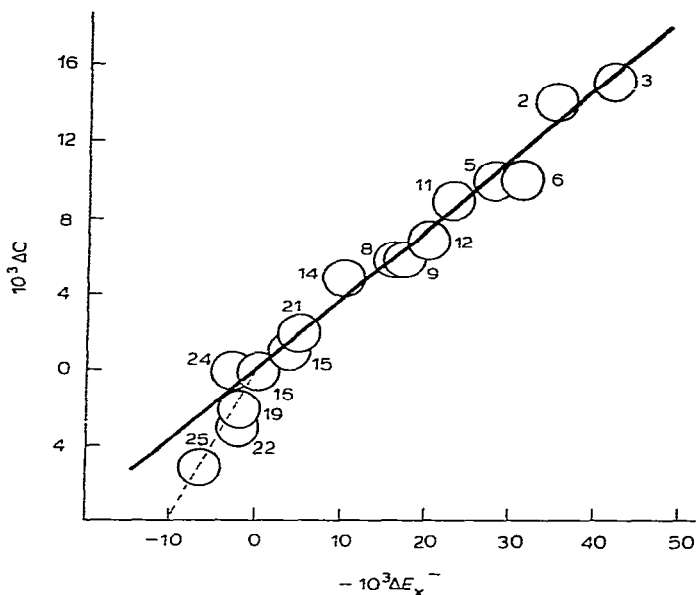


Fig. 6. Plot of  $\Delta C$ , the calculated charge at the 1-H atom in  $\text{XC}_6\text{H}_5$  species minus that for a H atom in  $\text{C}_6\text{H}_5$ , against the relative deprotonation energies  $\Delta E_{\text{X}}^-$ . For numbering of substituents see Table 1.

a single analysis; the resulting line would miss the origin by a larger amount ( $-0.60 \times 10^{-3}$  units in  $\Delta C$ ), but since the calculations are no more accurate for the unsubstituted than for the substituted species it can be argued that the division of the plot into two separate lines is unjustified. The view that the division is real is supported, however, by the fact that closer inspection reveals that the

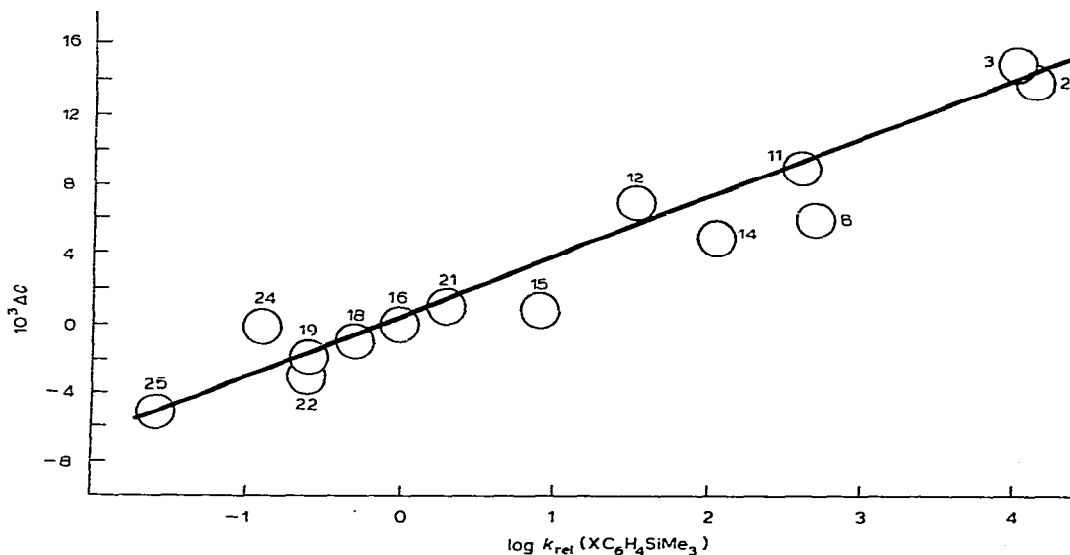


Fig. 7. Plot of  $\Delta C$  for the 1-H atom in  $\text{XC}_6\text{H}_5$  against  $\log k_{\text{rel}}$  for cleavage of  $\text{XC}_6\text{H}_4\text{SiMe}_3$  compounds by  $\text{NaOH-H}_2\text{O-Me}_2\text{SO}$  [5]. For numbering of substituents see Table 1.

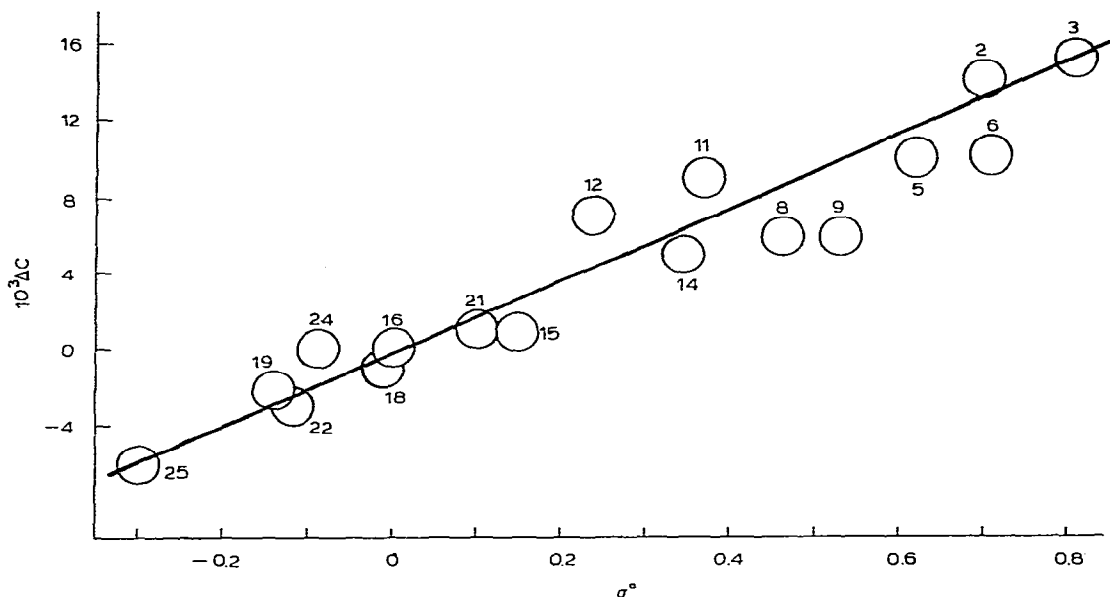


Fig. 8. Plot of  $\Delta C$  (charge on 1-H of  $\text{XC}_6\text{H}_5$  minus that on each H in  $\text{C}_6\text{H}_6$ ) against  $\sigma^0$  constants. For numbering of substituents see Table 1.

plot of  $\Delta E_{\text{X}^-}$  against  $\sigma^0$  (Figure 3) is also better regarded as similarly divided, and the same can be seen to apply to the plot of Figure 1. (The latter plot suggests that the *m*- $\text{NH}_2$  (*m*- $\text{NMe}_2$ ) group should possibly also be included with the *p*-Me, *p*-OMe and *p*- $\text{NH}_2$  (*p*- $\text{NMe}_2$ ) groups.)

In contrast, plots (Figures 7 and 8) of  $\Delta C$  against  $\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiMe}_3)$  or  $\sigma^0$  show no such division; the plot against  $\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiMe}_3)$  gives an overall correlation coefficient of 0.975 (intercept 0.44 in  $10^3 \Delta C$ ; 14 points), and this is improved to 0.981 (intercept 0.09) if the clearly deviant point for *m*- $\text{NH}_2$  is omitted, and to 0.995 (intercept 0.13; 10 points) if the points for fluorine-containing substituents are omitted. For the plot against  $\sigma^0$  the correlation coefficient for all the points is 0.960 (intercept 0.06; 17 points).

The correlations observed indicate that the effects of substituents on the rate of cleavage of the  $\text{XC}_6\text{H}_4\text{SiMe}_3$  compounds are proportional to those on a property of the unperturbed  $\text{XC}_6\text{H}_5$  (and both effects are proportional to  $\sigma^0$  constants). This means either that the transition state in the cleavage is very close to the unperturbed reactant, or, more likely, that the effects of substituents on the transition state are not much different in kind from those on the reactant (both being proportional to  $\sigma^0$  constants). It does not follow, however, that the effects of the substituents on the fully formed  $\text{XC}_6\text{H}_4^-$  anions would also be of the same kind, and the divisions of the plots in Figure 1, 3 and 6 suggest that they are not. The positions of the points for the *p*-Me, *p*-OMe and *p*- $\text{NH}_2$  (*p*- $\text{NMe}_2$ ) groups in these plots of Figures 1, 3 and 6 show that, relative to the other groups, these groups are less electron releasing in the anion  $\text{XC}_6\text{H}_4^-$  than they are in  $\text{XC}_6\text{H}_5$ , or than their  $\sigma^0$  constants would indicate, and this can be tentatively attributed to suppression of the  $\pi$ -electron releasing effects in the

anions (see below). We might thus expect that  $\Delta E_{X^-}$  values would not be proportional to  $\sigma^0$ , but rather to, say,  $[\sigma^0 + r(\sigma^+ - \sigma^0)]$  where  $r$  has a small negative value, the quantity  $(\sigma^+ - \sigma^0)$  being used as a measure of the  $\pi$ -electron-releasing ability of a group. If this were the case, then for a reaction which generates the carbanions  $\text{XC}_6\text{H}_4^-$ , but which has a transition state closer to the fully-formed anion than is the case for the  $\text{XC}_6\text{H}_4\text{SiMe}_3$  cleavage, equation of types 7–9

$$\log k_{\text{rel}} = \rho[\sigma^0 + r(\sigma^+ - \sigma^0)] \quad (7)$$

$$\log k_{\text{rel}} = \rho[\log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiMe}_3) + r(\sigma^+ - \sigma^0)] \quad (8)$$

$$\log k_{\text{rel}} - r'(\sigma^+ - \sigma^0) = \rho \log k_{\text{rel}}(\text{XC}_6\text{H}_4\text{SiMe}_3) \quad (9)$$

would apply. It is thus very revealing that such equations do apply very effectively to the hydrogen-exchange data, as shown in Figures 9 and 10; the correlation coefficients are 0.984 (intercept 0.33; 12 points) and 0.981 (intercept 0.07; 10 points), respectively. (Equation 9 was used rather than equation 8 to avoid bunching of points around the origin.) It thus seems safe to conclude that the hydrogen-exchange does proceed through aryl carbanions, with a transition state closer to the carbanion than is the case in the cleavage of the  $\text{XC}_6\text{H}_4\text{SiMe}_3$  compounds. This latter finding is what would be expected in the light of the much lower reactivity of the  $\text{XC}_6\text{H}_4^2\text{H}$  than of the aryl-silicon compounds.

It also seems safe to conclude that equations of the types 7 to 9 can be used to throw light on the mechanism of reactions which might proceed by generation of aryl carbanions, and to give an indication of the position of the transi-

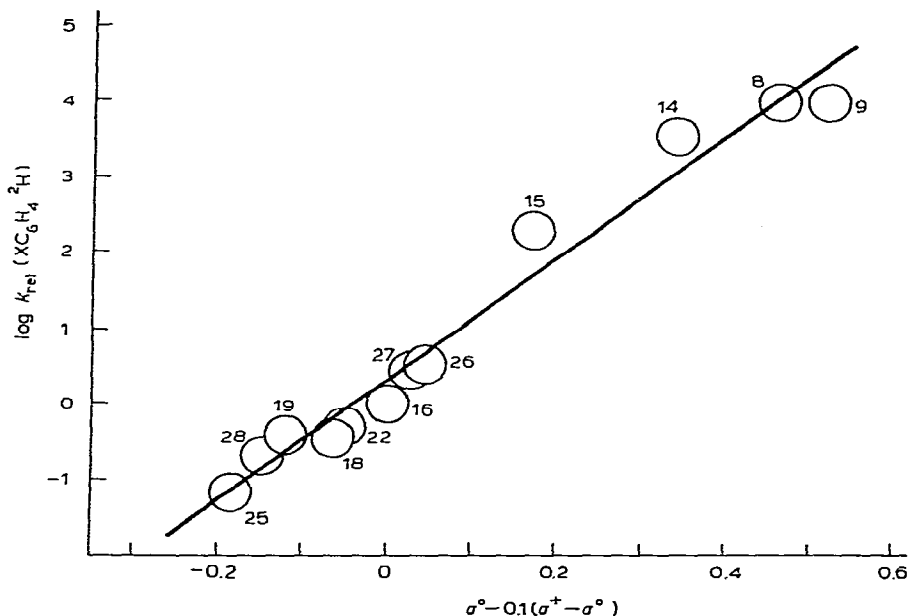


Fig. 9. Plot of  $\log k_{\text{rel}}$  for hydrogen-exchange of  $\text{XC}_6\text{H}_4^2\text{H}$  compounds in  $\text{KNH-NH}_3$  against  $[\sigma^0 - 0.1(\sigma^+ - \sigma^0)]$ . For numbering of substituents see Table 1.

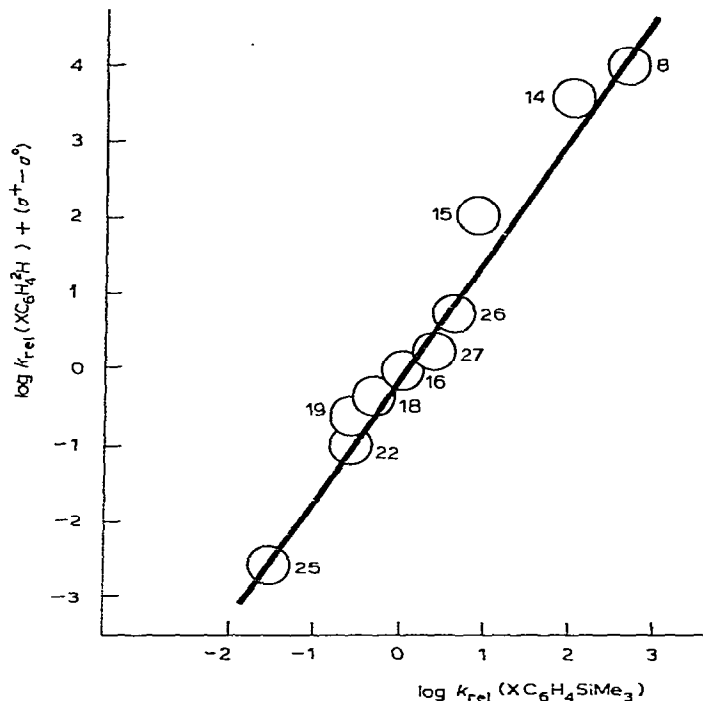


Fig. 10. Plot of  $[\log k_{rel}(XC_6H_4^2H) + (\sigma^+ - \sigma^0)]$  against  $\log k_{rel}(XC_6H_4SiMe_3)$ ; values of  $\log k_{rel}(XC_6H_4^2H)$  refers to exchange of  $XC_5H_4^2H$  species in  $KNH_2-NH_3$ , and those of  $\log k_{rel}(XC_6H_4SiMe_3)$  to cleavage of  $XC_6H_4SiMe_3$  compounds in 1/9 v/v  $H_2O-Me_2SO$ . For numbering of substituents see Table 1.

tion state along the route to the carbanion. It should be noted however, that equations 7 and 9 are identical to equations 4 and 6, respectively. Thus, for example, equations 4 (and 7) with small values of  $r$  will apply both to reactions involving separation of aryl carbanions and to those which involve electrophilic assistance, provided that the contribution of the latter is small. When the contribution is large, so that, for example, the  $p$ - $NMe_2$  group is activating rather than deactivating, as in the cleavage of the  $XC_6H_4SnMe_3$  compounds, this ambiguity disappears. When the values of  $r$  in equation 4 (or 7) are small enough to produce this ambiguity, it may be possible to make a decision between the two mechanisms by studying the solvent isotope effects.

#### Substituent effects in the $XC_6H_4^-$ anions

The discussion in the preceding section implies that for the *meta*-groups and the electron-withdrawing *para*-groups the relative effects on the anion  $XC_6H_4^-$  remain much as indicated by the  $\sigma^0$  constants, while for the releasing groups  $p$ -Me,  $p$ -OMe, and  $p$ - $NH_2$  ( $-NMe_2$ ) the  $\pi$ -electron release is somewhat suppressed below that associated with the  $\sigma^0$  constants. In view of the great change of the electron distribution in the ring on going from the benzene to the phenyl anion it is surprising that there is not a much larger distortion of the substituent effects.

The most striking feature of the charge distribution for the  $C_6H_5^-$  anion, which is shown in Scheme 1, is the large proportion (72%) of the unit negative charge which is dispersed away from the 1-position in spite of the absence of direct conjugative delocalization\*. This dispersal arises more from repulsion of  $\pi$ -electrons from the C(1) atom (giving a  $\pi$ -charge there of +0.419) than from induction through the  $\sigma$ -system (which leaves a  $\sigma$ -charge of -0.699). A fairly large negative  $\pi$ -charge is produced at the 4-position, and a smaller but still substantial such charge at the 2- and 6-positions.

Also noteworthy is the large amount of negative charge taken by the H atoms; the charge on each H changes from +0.063 in  $C_6H_6$  to -0.026, -0.008, and -0.11 at the *o*-, *m*-, and *p*-positions, respectively, of the anion, representing changes of -0.089, -0.071, and -0.074 units. Altogether some 35% of the unit negative charge produced by going to the anion is accommodated by the H atoms, which are by no means the inert substituents which, by convention, they are normally assumed to be in empirical interpretation of substituent effects.

In Table 3 are shown the charges on X in  $XC_6H_4$  and in *o*-, *m*-, and *p*- $XC_6H_4^-$  relative to those on H in  $C_6H_6$  and  $C_6H_5^-$ , respectively. The striking feature is the smallness of the extra charge taken by the strongly electron-withdrawing groups relative to that taken by H. Thus the *p*-NO<sub>2</sub> group bears a total negative charge of 0.260 *e* in  $O_2N \cdot C_6H_5$  and this increases by 0.134, 0.104, and 0.136 units on going to *o*-, *m*-, and *p*- $O_2N \cdot C_6H_4^-$ , respectively, but relative to the change for X = H the changes are only 0.045, 0.033, and 0.062 units. The changes in the amount of  $\pi$ -charge taken by X have the major influence, especially when comparison is made with the changes for X = H; thus while the additional negative  $\sigma$  and  $\pi$  charges taken by the NO<sub>2</sub> group on going from  $O_2N \cdot C_6H_5$  to *p*- $O_2N \cdot C_6H_4^-$  are 0.058 and 0.078 units, respectively, relative to those for X = H the changes are +0.016 and -0.078 respectively; i.e. the *p*-NO<sub>2</sub> group seems to take less of the additional  $\sigma$ -charge than H, but the fairly large increase in the  $\pi$ -charge greatly outweighs this. Even at the *m*-position, for strongly electron-withdrawing groups the change in the  $\pi$ -charge is dominant. Relative to H, the OMe and NH<sub>2</sub> groups also act mainly through the  $\pi$ -charges; e.g., relative to H, on going to the anion the *p*-OMe group takes 0.021 units less of negative  $\sigma$ -charge, but at the same time 0.031 units less of positive  $\pi$ -charge.

Table 3 also shows the value of the ratio between the  $\sigma$ -charge on X, relative to that on H, and the  $\pi$ -charge on X in  $XC_6H_5$  and the  $XC_6H_4^-$  anions, and it will be seen that the positive values of the  $\sigma/\pi$  ratios for the strongly electron-withdrawing NO<sub>2</sub> and CN groups fall greatly on going to the anion for all positions, while the negative value of the ratios for the strongly resonance electron-releasing groups OMe and NH<sub>2</sub> rise as the  $\pi$ -electron release is suppressed relative to the  $\sigma$ -electron withdrawal. In view of these large changes in the balance between  $\sigma$  and  $\pi$  charges on going to the anions, it would appear unlikely that the  $\sigma$  constants would apply to the effects of most of the X groups on the deprotonation, as they do, in fact, rather satisfactorily. The explanation pre-

\* The total charge left at the 1-position, viz. 0.28 *e*, is actually smaller than that, viz. 0.33 *e*, which is shown by calculation to reside on the carbanionic carbon in  $PhCH_2^-$ ; the total negative charge left on the  $CH_2^-$  groups on the latter is -0.49 *e* [17].



sumably lies in the interaction of the  $\sigma$  and  $\pi$  charges [21]. If we assume for simplicity, and in the light of the discussion above, that the effects of the X groups on the *m*- and *p*-positions are related to the  $\sigma^0$  constants of the groups, then the large additional  $\pi$ -charge taken by the *p*-NO<sub>2</sub> group on going to the anion will lower the amount of  $\sigma$ -charge which can be taken, so that overall the increase in the total charge remains reasonably in keeping with the  $\sigma^0$  constant. Since the effects of *o*-substituents relative to those of the corresponding *m*- and *p*-substituents appear to change markedly on going from XC<sub>6</sub>H<sub>5</sub> to XC<sub>6</sub>H<sub>4</sub><sup>-</sup> the compensation appears to be much less effective for them, possibly because direct field effects from the *ortho* positions are large in the anion. The effects of *ortho*-substituents in the hydrogen-exchange correlate satisfactorily with  $\sigma_1$  constants [19].

For the *p*-OMe, and especially the *p*-NH<sub>2</sub> group the partial suppression of the  $\pi$ -electron release on going to the anion seems not to be fully compensated by the reduction in the amount of additional  $\sigma$ -charge which can thereby be taken, and so overall the groups appear to be less electron-releasing than is implied by their  $\sigma^0$  constants; possibly the difference between the *p*-NO<sub>2</sub> and *p*-CN groups, on the one hand, and the *p*-OMe and *p*-NH<sub>2</sub> groups on the other lies in the fact that the resonance effects are normally much larger relative to the inductive effects for the latter groups than for the former.

A final noteworthy feature is that relative to H, even the Me group appears to take more negative charge as the anion is formed. The effect is substantial for the *p*-Me group, and in this case is exerted very predominantly through the  $\sigma$ -charge.

#### *Calculated pK<sub>a</sub>'s of mono-substituted benzenes*

The  $\Delta E_{X^-}$  value calculated for benzene (Table 1) is virtually identical with that previously calculated for toluene (for deprotonation in the side chain) [17], whereas both in solution [22] and in the gas phase [23] benzene actually has a somewhat lower acidity. For ion-pair acidities in CsNHC<sub>6</sub>H<sub>11</sub> [21], the  $pK_a$  for toluene is 41 and that for benzene approximately 43 [22], and the failure of the calculations to reflect such a difference is an indication of their degree of uncertainty. Using the  $pK_a$  value of 43 for benzene, rough  $pK_a$  values can be calculated for the separate positions of each of the XC<sub>6</sub>H<sub>5</sub> compounds by assuming that  $\Delta E^-$  for an acid RH is proportional to its  $pK_a$ . The  $\Delta E^-$  value of 0.75385 a.u. for cyclopentadiene [17], which has a  $pK_a$  of 15 [24], can be used along with the  $\Delta E^-$  and  $pK_a$  values for benzene to give the parameters of the  $\Delta E^-$ - $pK_a$  plot, and the  $pK_a$ 's thus derived for the XC<sub>6</sub>H<sub>5</sub> compounds. The values are shown in Table 5.

However, since there are probably substantial errors in some of the  $\Delta E_{X^-}$  values, as indicated by the scatter in Figure 1, it is probably more satisfactory to use a  $pK_a$  of 43 for benzene along with a  $pK_a$  of 29 for *m*-nitrobenzene, derived as described above, to define the relationship between  $\log k_{rel}(XC_6H_4SiMe_3)$  value and  $pK_a$ , and deduce  $pK_a$ 's for the other XC<sub>6</sub>H<sub>5</sub> species from the corresponding  $\log k_{rel}(XC_6H_4SiMe_3)$  value. The "corrected"  $pK_a$  values,  $pK_a(\text{corr.})$ , thus obtained are also listed in Table 5. Approximate  $pK_a$  values for additional XC<sub>6</sub>H<sub>5</sub> species can be derived by analogous assumption of a linear relationship between  $pK_a$  and  $\sigma^0$ , and values for X = *m*-CN, *p*-CN, and *p*-CF<sub>3</sub> derived in this

TABLE 5

APPROXIMATE CALCULATED  $pK_a$  VALUES FOR THE MONO-SUBSTITUTED BENZENES  $XC_6H_5$ 

X	$pK_a^a$	$pK_a(\text{corr.})$	X	$pK_a$	$pK_a(\text{corr.})$
			<i>m</i> -F	39	36
			<i>p</i> -F	41.5	40
<i>o</i> -NO <sub>2</sub>	24		<i>m</i> -Ph		(41)
<i>m</i> -NO <sub>2</sub>	29	29	<i>p</i> -Ph		(41.5)
<i>p</i> -NO <sub>2</sub>	26	27	H	43	43
<i>o</i> -CN	28		<i>o</i> -Me	43	
<i>m</i> -CN	32	(31)	<i>m</i> -Me	43	44
<i>p</i> -CN	30.5	(29)	<i>p</i> -Me	44	45
<i>o</i> -CF <sub>3</sub>	34		<i>o</i> -OMe	41	
<i>m</i> -CF <sub>3</sub>	37	34	<i>m</i> -OMe	41	42
<i>p</i> -CF <sub>3</sub>	36	(32)	<i>p</i> -OMe	44	45
<i>o</i> -Cl	31		<i>m</i> -NH <sub>2</sub> (-NMe <sub>2</sub> )	44 <sup>d</sup>	46
<i>m</i> -Cl	34	34	<i>p</i> -NH <sub>2</sub> (-NMe <sub>2</sub> )	46 <sup>c</sup>	48
<i>p</i> -Cl	35	38			
<i>m</i> -Br		34			
<i>p</i> -Br		37			
<i>o</i> -F	38				

<sup>a</sup> Values derived assuming proportionality between  $\Delta E_X^-$  and  $pK_a$ , and based on  $pK_a = 43$  for benzene. All the  $pK_a$  values are referred to the scale of ion-pair acidities in  $C_5NH_5C_6H_4-NH_2C_6H_4$  [24]. <sup>b</sup> Values defined assuming proportionality between  $\log k_{rel}$  ( $XC_6H_4SiMe_3$ ) (in 1/9 v/v  $H_2O$ -Me<sub>2</sub>SO) and  $pK_a$ , except for values shown in parentheses, which are observed assuming proportionality between  $\sigma^0$  and  $pK_a$ . <sup>c</sup> The  $\Delta E_X^-$  value based on the optimized angle was used. <sup>d</sup> The  $\Delta E_X^-$  value based on planarity at N was used.

way are included (in parentheses) in Table 5.

It will be seen that the approximate  $pK_a$  values span the range 24–48. If these results are valid, they imply that  $XC_6H_4SiMe_3$  compounds with X groups at least as electron-withdrawing as *m*-F should be cleaved at conveniently measurable rates by MeONa-MeOH or NaOH-H<sub>2</sub>O-MeOH, provided that the relationship between  $\log k_{rel}$  for cleavage of  $RSiMe_3$  compounds and the  $pK_a$  of the corresponding RH species observed for R groups giving conjugatively delocalized carbanions [25] applies also to aryl anions, in which there is no conjugative delocalization.

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