The Effects of *ortho*-Substituents on the Stability of the Phenyl Anion. The Base Cleavage of Aryltrimethylsilanes

By **Giancarlo Seconi,*** Istituto dei composti del carbonio contenenti eteromi e loro applicazione, C.N.R., Via Tolara di Sotto 89, 40064 Ozzano Emilia (Bologna), Italy
Maurizio Taddei, Istituto di Chimica Organica, University of Florence, Via G. Capponi 9, Florence, Italy
Colin Eaborn * and **John G. Stamper**, School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The rates of cleavage of some $XC_6H_4SiMe_3$ compounds by KOH in 9:1 v v $Me_2SO–H_2O$ at 40.0 °C have been measured: the values of $k_{rel.}$, the rate relative to that for X = H, are (X=), *o*-NO_2, 420 000; *p*-NO_2, 10 300; *m*-NO_2, 9 700; *o*-F, 4 000; *o*-Cl, 3 960; *m*-Cl, 375; *p*-Cl, 38; *o*-NMe_2, 14; *o*-OMe, 6.3; *o*-Me, 0.60. The values of log $k_{rel.}$ correlate satisfactorily with the calculated energy for the conversion $XC_6H_5 \longrightarrow XC_6H_4^-$, except for X = *o*-$NMe_2$, for which steric effects may be significant. The previously reported log $k_{rel.}$ values for hydrogen exchange in $XC_6H_4{}^2H$ in $KNH_2–NH_3$ also correlate satisfactorily with the deprotonation energies, confirming that rate-determining formation of the anions $XC_6H_4^-$ is involved in this reaction, as in the desilylation.

WE recently calculated the deprotonation energies for the *o*-, *m*-, and *p*-positions in a range of substituted benzenes XC_6H_5,[1] and showed that in the light of the results the effects of *m*- and *p*-substituents on the rates of (a) cleavage of $XC_6H_4–SiMe_3$ bonds by $KOH–H_2O–Me_2SO$ and (b) hydrogen-exchange in $XC_6H_4{}^2H$ in $KNH_2–NH_3$ could be interpreted in terms of rate-determining formation of the aryl anions, $XC_6H_4^-$, in both cases.† We had to defer discussion of the effects of *ortho*-substituents in the absence of data for the cleavage of *o*-$XC_6H_4SiMe_3$ compounds, and we now present such data for a few selected substituents.

RESULTS AND DISCUSSION

Rates of cleavage of $XC_6H_4SiMe_3$ compounds by KOH in 9 : 1 v/v $Me_2SO–H_2O$ at 40 °C were measured spectrophotometrically, and the values of the observed first-order rate constants, *k*, at the particular base concentration used are shown in the Table.‡ Because of the difficulty of determining the exact base concentration at the lowest concentrations used, and because the observed rate constants could not be assumed to be proportional to the base concentration, we used comparisons of two or more compounds at each base concentration to give relative rates, and the values of $k_{rel.}$, the rate for XC_6H_4-$SiMe_3$ relative to that for $C_6H_5SiMe_3$, are shown in the Table. [In fact the values of *k* appear to be approximately proportional to the (added aqueous) base concentration at least in the range 0.01—0.50M, and values of $k_{rel.}$ derived by assuming this proportionality over the whole concentration would not differ significantly from those listed in the Table.] To provide convenient reference compounds for overlap, and also additional data for comparisons, some $XC_6H_4SiMe_3$ compounds containing *m*- or *p*-X groups were also examined. The values of $k_{rel.}$ obtained for X = *m*-Cl, *p*-Cl, and *p*-NO_2 agree reasonably well with those recorded by Cretney and Wright [3] (listed in a footnote to the Table), but there is a noteworthy difference between the two sets of results in the case of X = *m*-NO_2. The greater activation by *m*- than by *p*-NO_2 reported by Cretney and Wright seemed anomalous in the light of the calculations and correlations we previously described,[1] and use of our $k_{rel.}$ value for X = *m*-NO_2 in place of that given by Cretney and Wright leads to improvements in all the correlations. (It should be noted that while the values of $k_{rel.}$ may be subject to substantial error, direct comparison of the rates at the same base concentration shows clearly that the *m*- is less reactive than the *p*-NO_2 compound.)

Rates of cleavage of $XC_6H_4SiMe_3$ compounds by Me_2SO–aqueous KOH (9 : 1 v/v) at 40.0 °C)

No.	X	λ/nm [a]	[KOH]/M [b]	$10^5k/s^{-1}$	$k_{rel.}$ [c]
1	*o*-NMe_2	270	0.50	48	14
			0.20	20.7	
			0.10	10.5	
2	*o*-OMe	291	0.50	21.3	6.3
3	*o*-Me	276	0.50	2.0	0.60
4	H	270	0.50	3.4	1.0
5	*o*-Cl	277	0.10	2 970	3 960
			0.010	235	
6	*m*-Cl	270	0.10	280	375
7	*p*-Cl	274	0.20	55	38
			0.10	30	
8	*o*-F	271	0.10	2 760	
			0.01	256	4 000
9	*o*-NO_2	270	0.0020	4 170	420 000
10	*m*-NO_2	313	0.010	575	9 700
11	*p*-NO_2	290	0.010	615	10 300
			0.0020	103	

[a] Wavelength used to monitor reaction. [b] Concentration of aqueous KOH, 1 vol. of which was mixed with 9 vol. of Me_2SO. [c] In ref. 3, $k_{rel.}$ values were (X =) *m*-Cl, 400; *p*-Cl, 34.5; *m*-NO_2, 12 960; *p*-NO_2, 10 120.

In considering the correlation between the log $k_{rel.}$ values for the base cleavage of $XC_6H_4SiMe_3$ compounds and the calculated deprotonation energies of XC_6H_5, we omit data for the fluoro-substituent, which is known to give anomalous results in the type of calculation used. We also leave aside for the moment the data for X =

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† A similar approach was successful in accounting for the effects of substituents in the base cleavage of the thiophen derivatives $XC_4H_2S{\cdot}SiMe_3$.[2]

‡ In all cases the aromatic product is the corresponding XC_6H_5, *i.e.* even with X = *o*-Cl there is no formation of benzyne, capture of a proton from the solvent by the anion *o*-$ClC_6H_4^-$ evidently being markedly faster than loss of chloride ion.

o-NMe_2. With these omissions, there is, as Figure 1 shows, a correlation between log $k_{rel.}$ and ΔE_X^- (the calculated energy change for the conversion $XC_6H_5 \longrightarrow XC_6H_4^-$ relative to that for $C_6H_6 \longrightarrow C_6H_5^-$) which is acceptably linear when the approximate nature of the calculations is taken into account, the correlation coefficient, *r*, being 0.988 (14 points); the points for the *ortho*-substituents are, in fact, closer to the line than those for the *para*-substituents, the most seriously deviant points being those for *p*-NO_2 and *p*-Cl, and if these are omitted *r* is improved to 0.996.

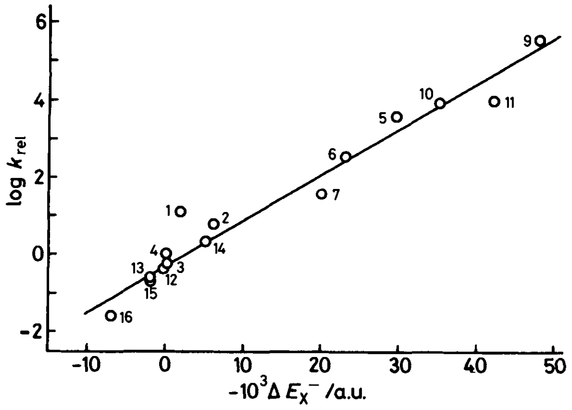

FIGURE 1 Plot of log $k_{rel.}$ for base cleavage of $XC_6H_4SiMe_3$ compounds in 9 : 1 Me_2SO–H_2O against the relative deprotonation energies ΔE_X^- for XC_6H_5. The numbering of the points is as in the Table, and as follows: 12, *m*-Me; 13, *p*-Me; 14, *m*-OMe; 15, *p*-OMe; 16, *p*-NMe_2. For points 1 and 16 the ΔE_X^- values are those for *o*- and *p*-NH_2, respectively

Before considering the log $k_{rel.}$ value for X = *o*-NMe_2 it was first necessary to recalculate the energy for the conversion $H_2NC_6H_5 \longrightarrow$ *o*-$H_2NC_6H_4^-$, since the earlier calculation[1] was based on planar geometry at nitrogen. With optimized geometries the value of the deprotonation energy is 8 220 × 10^{-4} a.u., compared with the value of 8 276 × 10^{-4} a.u. based on planar geometry. (For completeness we also recalculated the deprotonation energy for X = *m*-NH_2 on the basis of optimized geometry, obtaining a value of 8 234 × 10^{-4} compared with the previously reported 8 272 × 10^{-4} a.u.) This gives a value of -2×10^{-3} a.u. for ΔE_X^-, the deprotonation energy relative to that for benzene. While this value correctly implies that the *o*-NMe_2 (in contrast to the *p*-NMe_2) group should activate in the base cleavage of the $XC_6H_4SiMe_3$ compounds, its use in Figure 1 gives a point lying *ca.* 1 log $k_{rel.}$ unit above the line, *i.e.* *o*-$Me_2NC_6H_4SiMe_3$ is *ca.* 10 times as reactive as would be expected from the calculated deprotonation energy for the *o*-position of $H_2NC_6H_5$. It is not surprising that this is the point showing the most serious deviation, since (a) the calculations are for the NH_2 group and the rate data for the NMe_2 group, and this distinction is likely to be more significant for the *o*- than for the *m*- or *p*-position, and (b) steric interaction between the NMe_2 and the $SiMe_3$ group, will tend to reduce the conjugative delocalization of the lone pair of the nitrogen atom, and this can be expected to favour formation of the anion.

If the data for *m*- and *p*-F are again omitted, while the value of ΔE_X^- for *o*-F is assumed, in the light of the similar log $k_{rel.}$ values of X = *o*-F *and* *o*-Cl in the cleavage, to be equal to that for *o*-Cl, a reasonably satisfactory correlation is also revealed between ΔE_X and log $k_{rel.}$ values (some of them rather rough values) for hydrogen exchange of $XC_6H_4{}^2H$ compounds in KNH_2–NH_3.[1,4,5] (For a summary of the data see ref. 1.) As Figure 2 shows, only the point for X = *o*-OMe deviates significantly from the correlation line, and we conclude that the effects of the substituents in both the exchange and the cleavage can be related to the ease of forming the corresponding anions $XC_6H_4^-$. Unfortunately there are insufficient *ortho*-substituent data for a significant plot of log $k_{rel.}$ for the cleavage against that for the exchange, especially since for one of the substituents, *o*-F, the $k_{rel.}$ for the exchange represents only a minimum value.

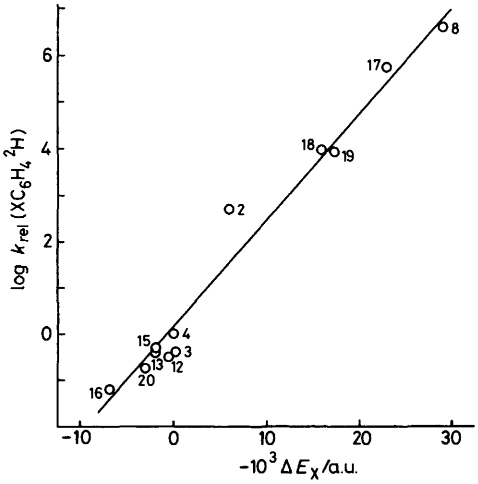

FIGURE 2 Plot of log $k_{rel.}$ for dedeuteriation of $XC_6H_4{}^2H$ in KNH_2–NH_3 against the relative deprotonation energies ΔE_X^- for XC_6H_5. The numbering of the points is as in Figure 1, and as follows: 17, *o*-CF_3; 18, *m*-CF_3; 19, *p*-CF_3; 20, *m*-NMe_2. For points 16 and 20, the ΔE_X^- values are those for *p*- and *m*-NH_2, respectively

It was observed previously that the values of $k_{rel.}$ for exchange of *o*-$XC_6H_4{}^2H$ compounds correlated satisfactorily with σ_I constants,[5] and using more recent values[6] of σ_I we confirm that this is the case (*r* 0.993; slope 12.79; intercept −0.08; 5 points), with only the point for X = OMe deviating significantly from the correlation line. A plot of log $k_{rel.}$ for the cleavage of *o*-$XC_6H_4SiMe_3$ compounds against σ_I (Figure 3) is also a fairly good straight line (*r* 0.987; slope 7.71, intercept 0.191; 6 points) if the point for X = OMe is omitted. It follows that ΔE_X^- (with omission of data for *o*-F) should show a satisfactory correlation with σ_I for *ortho*-substituents, and the appropriate plot (Figure 4) is indeed, reasonably linear, with again only the point for OMe deviating substantially (if this point is omitted, *r* = 0.996 for 6 points).

The approximate correlation of the σ_I constants with the acidities of the *ortho*-positions of XC_6H_5 compounds (and thus with the log $k_{rel.}$ values for *ortho*-substituted derivatives in desilylation and hydrogen exchange) is much more difficult to interpret than might be supposed. In the light of the qualitative empirical electronic theory of substituent effects which has served organic chemists so well, it might seem very likely that in the anions $XC_6H_4^-$ (the stabilities of which could be expected to represent the major factor in the substituent effects), in which the lone pair of electrons cannot be conjugatively delocalized, the effects of substituents would be dominated by the polar interaction between the substituent and the nearby negative charge, and so related to the σ_I constants. (Hall *et al.* considered that in hydrogen exchange the π-electron system of the benzene would not be significantly involved, so that the inductive and field effects of substituents are of major importance and the resonance effects negligible.[4]) But we cannot discern in the calculated charge distributions in XC_6H_6 and $XC_6H_5^-$ any indications of why the effects of *ortho*-substituents should correlate with σ_I. For example, as we have noted before,[1] there is considerable distortion of the π-system in the anion $C_6H_5^-$, so that a π-charge of −0.108e resides on each *ortho*-carbon atom compared with a σ-charge of −0.048e. While the ratio of σ- to π-charge, 0.44 : 1, is higher than that at the *para*-carbon, *viz.* 0.12 : 1, the ratio is much higher at the *meta*-carbon atom, *viz.* 4.2 : 1, and so it might be expected that the inductive effects of substituents would be most dominant at the *meta*-position, whereas the effects of *m*-X groups, in fact, correlate well with σ_o constants. [It should be noted, however, that the calculated total charge at the *ortho*-position (−0.156e) is higher than that at the *para*- (−0.143e) or *meta*-position (−0.093), in keeping with the fact that the activation by the strongly electron-withdrawing groups is largest from the *ortho*-position.] Furthermore, if for simplicity attention is focused on the strongly electron-withdrawing groups, *viz.* NO_2, CN, and CF_3, in which inductive and resonance effects act in the same direction, it can be seen that while the ratio of σ- to π-charge taken by X in $XC_6H_4^-$ is greater for *o*- than for *p*-X, it is substantially larger in all cases for *m*-X,[1] and thus the inductive effect might again be expected to be more dominant at the *m*- than the *o*-position, contrary to observation.

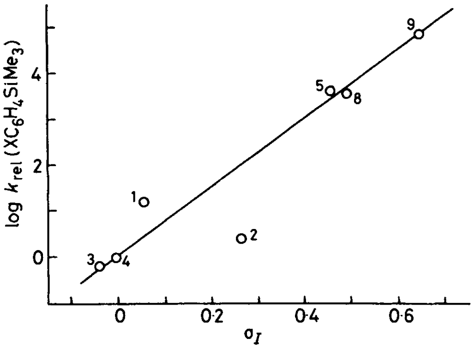

FIGURE 3 Plot of log $k_{rel.}$ for base cleavage of o-$XC_6H_4SiMe_3$ compounds in 9 : 1 Me_2SO–H_2O against σ_I constants for X. The numbering of points is as in the Table

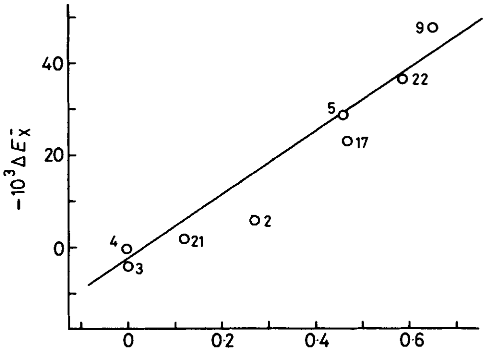

FIGURE 4 Plot of relative deprotonation energies ΔE_X^- for *ortho*-positions of XC_6H_5 against σ_I constants for *o*-X. The numbering of points is as in Figure 2, and as follows: 21, o-NH_2; 22, *o*-CN

In viewing this failure to relate the correlation with σ_I constants for *o*-X groups to calculated charge distributions, it should be remembered that these and related substituent constants were derived empirically from *free energy* relationships, without reference to knowledge of charge distributions, and so it need not be surprising that for the systems under consideration correlations are found with ΔE_X^- or log $k_{rel.}$ values and not with charge distributions, since these free energy quantities cannot themselves be interpreted in any simple way in terms of charge distributions, probably because there is a strong interaction between σ- and π-effects.[1] It may be relevant to note, however, that whereas for *m*- and *p*-X groups the charge ΔC on the 1-H atom in XC_6H_5 relative to that in C_6H_6 correlates with σ_o, for *o*-X there is fair correlation with σ_I for X = CN, Cl, CF_3, OMe, and Me (*r* 0.960; 6 points), though the points for X = NO_2 and OMe lie badly off the correlation line.

EXPERIMENTAL

Calculations.—The calculations of the deprotonation energies for $H_2NC_6H_5 \longrightarrow o$- or m-$H_2NC_6H_4^-$ were carried out as before,[1] but with optimization of the geometries at nitrogen on the anions, which gave HNH and HNC angles (constrained to be equal) of 109.35 and 110.1° for the *o*- and *m*-substituted anion, respectively. The calculated values of the deprotonation energies, ($E_X^- - E_X$) were 0.8220 and 0.8234 a.u. for X = *o*- and m-NH_2, respectively. The charge distributions in the anions are shown in Figure 5.

Preparations of Organosilicon Compounds.—The $XC_6H_4SiMe_3$ compounds were made by standard methods, *viz.* (X =) *o*-Cl, -F, -NO_2, and NMe_2;[7] *o*-Me;[8] p-NO_2;[9] m-NO_2;[10] *o*-OMe.[11] No impurities were revealed by ^1H n.m.r. spectroscopy or g.l.c.

Rate Measurements.—Dimethyl sulphoxide was dried over calcium hydride and distilled from the solid under vacuum. The reaction medium was made up by mixing 1 vol. of aqueous KOH, of the concentration shown in the Table, with 9 vol. of Me_2SO. The mixture was stored at room temperature for two days before use (*cf.* ref. 3). For

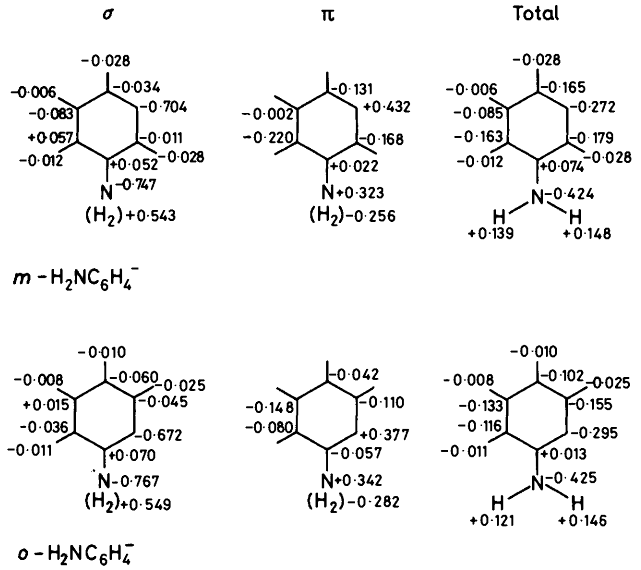

FIGURE 5 Calculated σ, π, and total charge distributions in the anions *o*- and *m*-$H_2NC_6H_4^-$

each run, the medium (3 cm^3) was placed in a quartz cell in the compartment of a Hitachi–Perkin-Elmer model 323 u.v. spectrometer, which was thermostatted at 40.0 °C. After 15 min 1 μl of a solution of the organosilane in Me_2SO was added, and the cell was shaken briefly and returned to the holder. Readings of the absorption at the wavelength specified in the Table were begun. The u.v. spectra of all products were identical with those of the appropriate solutions of the expected XC_6H_5 compounds, and good first-order rate constants, reproducible to ±2%, were obtained.

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