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SUBSTITUENT EFFECTS OF MONO-, BIS-, AND TRIS(TRIMETHYLSILYL)-METHYL GROUPS; DETERMINATION OF σ- AND σ^+-CONSTANTS

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SUMMARY

The apparent dissociation constants of the acids p-[$(Me_3Si)_xCH_{(3-x)}$]C_6H_4-CO_2H in 50% aqueous ethanol at 25° have been measured and used to give the following σ-constants for the p-[$(Me_3Si)_xCH_{(3-x)}$]groups: $x=1$, -0.29; $x=2$, -0.33; $x=3$, -0.27. The rates of solvolysis of the tertiary chlorides p-[$(Me_3Si)_x$-$CH_{(3-x)}$]$C_6H_4CMe_2Cl$ in aqueous acetone have also been measured and used to give the following σ^+-constants: $x=1$, -0.54; $x=2$, -0.62; $x=3$, -0.52. The results are consistent with the existence of substantial hyperconjugative electron release from the Me_3Si–C bonds.

INTRODUCTION

There is considerable current interest in the electronic effects of $(Me_3Si)_x$-$CH_{(3-x)}$ groups, particularly in connection with the concept[1] of hyperconjugation from carbon–metal bonds (σ–π conjugation)*. Quantitative information exists on the effects of the groups on spectroscopic transition energies[5,6] and on some reaction rates[4,7], but values are not available for directly determined Hammett constants, σ, or electrophilic constants, σ^+, which are standard measures of substituent effects**,[8]. To remedy these deficiencies we have measured the apparent dissociation constants of the substituted benzoic acids, $XC_6H_4CO_2H$, and the rates of solvolysis in aqueous acetone of the substituted α,α-dimethylbenzyl chlorides, $XC_6H_4CMe_2Cl$, having X=H or p-$(Me_3Si)_xCH_{(3-x)}$ with $x=0$–3.

RESULTS AND DISCUSSION

The chlorides $XC_6H_4CMe_2Cl$ were not purified but used as obtained from treatment of the corresponding alcohols, $XC_6H_4CMe_2OH$, with hydrogen chloride,

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* The possibilities that hyperconjugation from Me_3Si–C bonds influences spectroscopic properties and reactivity were first suggested in 1954[2,3] and 1956[4], respectively.

** From strengths of substituted benzoic acids measured by Eaborn and Parker[2], a σ-value of -0.21 has been calculated for the Me_3SiCH_2 group[9], but we believe this to be less accurate than that derived in this paper. Using the σ-value of -0.21 in conjunction with reactivity data, Norman and Taylor indirectly derived an approximate σ^+-value of -0.62 for this group[10].

as in the original determinations of σ^+-constants by H. C. Brown and his colleagues[11–14]. The carbinols were made by treatment of acetone with the organolithium reagents obtained from the interaction of n-butyllithium with the aryl bromides XC_6H_4Br.

The chlorides $XC_6H_4CMe_2Cl$ having X = H or Me were solvolysed in 90% aqueous acetone, and those having $X = (Me_3Si)_xCH_{(3-x)}$ with $x = 1$–3, in 94.8% aqueous acetone. For the latter set, the first order rate constants, k, were measured at 0.0, −15.0, and −30.0° (see Table 1) and the good Arrhenius plots obtained were used in the derivation[13] of the corresponding rate constants at 25.0°. Rate constants in 90% aqueous acetone were derived as described by Brown and Okamoto, and hence the value of the rate constants, k_{rel}, relative to that for the parent compound, $C_6H_5CMe_2Cl$[13]. (As a check on our experimental procedure the rate of solvolysis of the compound p-$MeOC_6H_4CMe_2Cl$ in 94.8% aqueous acetone at −30.0° was measured, and found to be in excellent agreement with the value derived by interpolation from Brown and Okamoto's Arrhenius plots[13].) Values of the σ^+-constants were then calculated by use of the relationship[8,15] $\log k_{rel} = -4.54\,\sigma^+$, and are listed in Table 3.

TABLE 1

SOLVOLYSIS OF p-$XC_6H_4CMe_2Cl$ COMPOUNDS IN AQUEOUS ACETONE

X	Temp. (°C)	Medium[a]	$10^5 k$ (sec^{-1})	k_{rel}	E_A (kcal/mole)	log A
OMe	+25.0	A	41700[b]	3360[d]		
	+25.0	B	4220[c]		13.4[d]	8.5[d]
	−30.0	B	27.3			
$CH(SiMe_3)_2$	+25.0	A	8450[b]	682		
	+25.0	B	855[c]		16.1	9.8
	0.0	B	28.8			
	−15.0	B	13.0			
	−30.0	B	2.00			
CH_2SiMe_3	+25.0	A	3470[b]	279		
	+25.0	B	351[c]		17.7	10.6
	0.0	B	79.9			
	−15.0	B	3.9			
	−30.0	B	0.51			
$C(SiMe_3)_3$	+25.0	A	2750[b]	222		
	+25.0	B	279[c]		17.7	10.5
	0.0	B	23.6			
	−15.0	B	3.2			
	−30.0	B	0.42			
CH_3	+25.0	A	315[d]	25.4[e]	17.8[e]	10.6[e]
H	+25.0	A	12.4[d]	1.0	19.5[e]	10.4[e]

[a] A = 90 vol.% aqueous acetone; B = 94.8 wt.% aqueous acetone. [b] Rates extrapolated to 90 vol.% aqueous acetone (*cf.* ref. 13). [c] Rates calculated from Arrhenius equation. [d] Ref. 13. [e] Ref. 12.

TABLE 2

APPARENT DISSOCIATION CONSTANTS OF p-XC_6H_4COOH ACIDS IN 50% AQUEOUS ETHANOL AT 25°

X	pK_a	X	pK_a
$CH(SiMe_3)_2$	6.14	OMe	6.02
CH_2SiMe_3	6.08	CH_3	5.88
$C(SiMe_3)$	6.05	H	5.70

The acids $(Me_3Si)_xCH_{(3-x)}C_6H_4CO_2H$ were obtained by carbonation of the corresponding organolithium compounds, $(Me_3Si)_xCH_{(3-x)}C_6H_4Li$. The apparent dissociation constants pK_a in 50% aqueous ethanol at 25° were measured, along with those for benzoic acid, p-toluic acid, and p-anisic acid by potentiometric titration using a glass electrode, as described by Roberts and Reagan[16]. The results are shown in Table 3. The pK_a values for the acids p-$XC_6H_4CO_2H$ with X=H, Me, and Me_3SiCH_2 are in excellent agreement with those obtained by Eaborn and Parker several years ago with different apparatus in a different laboratory[2]. Even so, the value of pK_a for benzoic acid, *viz.* 5.70, differs significantly from values obtained by other workers using glass electrodes, *viz.* 5.73[17], 5.75[18], and 5.80[16]. Errors in the absolute values of pK_a's are likely to be much greater than those in the differences between pK_a's of similar compounds measured with the same apparatus at the same time, and so we have derived σ-constants from a plot of values of ΔpK_a ($=pK_a-pK_a^0$, where pK_a^0 refers to benzoic acid), using results for large numbers of substituents given by other workers[9,16,18]; a good line is defined by the equation $\Delta pK_a=1.52\,\sigma-0.06$, in which the slope 1.52 is that derived by McDaniel and Brown for a plot of pK_a against σ (their line also missed the origin)[9], but differs substantially from that, *viz.* 1.464, obtained for such a plot by Roberts, McElhill, and Armstrong[18]. Values of σ for p-$[(Me_3Si)_xCH_{(3-x)}]$ groups derived by use of this equation are given in Table 2. The σ-values correspondingly derived from our results for the p-Me and p-OMe groups are −0.16 and −0.25, respectively, in agreement with the accepted[9] values of -0.170 ± 0.02 and -0.268 ± 0.02.

TABLE 3

VALUES OF σ- AND σ^+-CONSTANTS

Substituent	σ	σ^+	$\sigma^+-\sigma$
OMe	−0.268[a]	−0.778[a]	−0.51
$CH(SiMe_3)_2$	−0.33	−0.62	−0.29
CH_2SiMe_3	−0.29	−0.54	−0.25
$C(SiMe_3)_3$	−0.27	−0.52	−0.25
CH_3	−0.170[a]	−0.311[a]	−0.14

[a] Ref. 8.

The values of σ and σ^+ for the $(Me_3Si)_xCH_{(3-x)}$ groups must be used with caution as guides to the electronic effects of the groups, since there can be little doubt that the bulk of these groups will have considerable influence on the solvation of reagents and transition states. [The difference between the values of log A for the $(Me_3Si)_xCH_{(3-x)}$ groups and that for the p-OMe group, revealed in Table 1, may be significant in this connection.] Nevertheless much experience justifies the empirical use of linear *free* energy relationships, which take account only of the gross overall effects, and not of variations either of activation entropies or of the balance of internal and external substituent contributions to the free energy change[19]. The validity of such empirical use can be demonstrated in the present case by use of the derived σ- and σ^+-constants in rationalizing the effects of the $(Me_3Si)_xCH_{(3-x)}$ groups on the cleavage of the aryl–silicon bond of $(Me_3Si)_xCH_{(3-x)}C_6H_4SiMe_3$ compounds by aqueous methanolic perchloric acid[7], a reaction which is an electrophilic aromatic substitution. The relationship $\log k'_{rel} = -5.3\,[\sigma + 0.65\,(\sigma^+ - \sigma)]$ is known to apply to a large range of substituents for this reaction in this medium, where k'_{rel} is the rate of cleavage of the compound $XC_6H_4SiMe_3$ relative to that of the parent compound $C_6H_5SiMe_3$; Fig. 1 shows the appropriate plot incorporating the values of k'_{rel} and the appropriate substituent constants for the $(Me_3Si)_xCH_{(3-x)}$ groups, and it will be seen that the points for these groups effectively lie on the line. Illustrative points for a few other groups[20] are included for comparison.

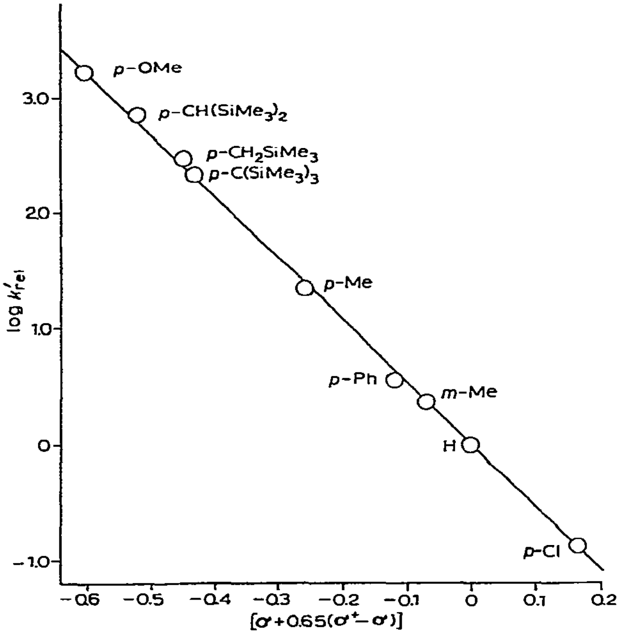

Fig. 1. Plot of log k'_{rel} against $[\sigma + 0.65(\sigma^+ - \sigma)]$ for cleavage of $XC_6H_4SiMe_3$ compounds by aqueous methanolic perchloric acid.

The (numerical) values of σ and σ^+ for the p-$[(Me_3Si)_xCH_{(3-x)}]$ groups both fall in the order ($x=$) $2 > 1 > 3 > 0$, which also applies to the effects of the groups on ^{19}F chemical shifts in p-XC_6H_4F compounds[7]. If this order reflects only the electron releasing ability, it is, as previously indicated[6,7], inconsistent with attribution of the electron release solely to inductive effects.

Values of the quantity $(\sigma^+ - \sigma)$ can be used as a measure of the conjugative (resonance) effects of substituents. For the p-$(Me_3Si)_xCH_{(3-x)}$ groups the values of $(\sigma^+ - \sigma)$ lie between those for the p-Me and p-OMe groups (see Table 2), and indicate that the groups have substantial electron-releasing conjugative effects, consistent with the existence of marked hyperconjugative electron release from the Me_3Si–C bonds[7]. In the absence of steric effects the extent of this hyperconjugation should increase[7] most markedly for the change $x=0$ to $x=1$, then less markedly to $x=2$, and remain unchanged for $x=3$. Except for a small decrease for the change $x=2$ to $x=3$, which may possibly reflect the fact that steric effects are greatest[7] when $x=3$, the variations in the observed values of $(\sigma^+ - \sigma)$ are in agreement with expectation.

EXPERIMENTAL

p-Mono-, -bis- and -tris(trimethylsilyl)methylbenzoic acids

n-Butyllithium (70 ml of a 1.5 *M* solution in hexane) was added during 10 min to a solution of (p-bromobenzyl)trimethylsilane (24 g, 0.1 mole) in ether (100 ml) maintained at 0°. The reaction mixture was subsequently stirred for 10 min at 0° and boiled under reflux for a further 10 min, and was then cooled and added to an excess of ether-washed solid carbon dioxide. Residual carbon dioxide was allowed to evaporate, and the mixture was acidified with 2 *N* hydrochloric acid. Organic products were extracted with ether, and the ether layer was separated and reextracted with 2 *N* aqueous NaOH (3 × 25 ml). The aqueous extract was separated and reacidified, and the precipitated crude acid was filtered off and recrystallised successively from ethanol/water and light petroleum (b.p. 60–80°) to give p-[(trimethylsilyl)methyl]-benzoic acid (18 g, 86%), m.p. 178–179° (lit.[2] m.p. 179°). Similarly, from (p-bromophenyl)bis(trimethylsilyl)methane was prepared p-[bis(trimethylsilyl)methyl]benzoic acid (nc) (60%), m.p. 130° (Found: C, 60.25; H, 8.6. $C_{14}H_{24}O_2Si_2$ calcd.: C, 60.0; H, 8.6%.), and from (p-bromophenyl)tris(trimethylsilyl)methane was prepared p-[tris(trimethylsilyl)methyl]benzoic acid (nc) (62%), m.p. 239°. (Found: C, 58.1; H, 9.2. $C_{17}H_{32}O_2Si_3$ calcd.: C, 58.0; H, 9.15%.)

p-[Mono-, -bis-, and -tris(trimethylsilyl)methyl]-α,α-dimethylbenzyl alcohol

Anhydrous acetone (4.5 g, 0.75 mole) cooled to −50° was added dropwise to p-[(trimethylsilyl)methyl]phenyllithium [prepared from (p-bromobenzyl)trimethylsilane (0.16 mole) and butyllithium (0.20 mole) in ether/hexane (300 ml)] maintained at −50°. The mixture was subsequently allowed to warm to room temperature and saturated aqueous ammonium chloride was added. Organic products were extracted with ether, and the ethereal layer was dried ($MgSO_4$) and distilled to give p-[(trimethylsilyl)methyl]-α,α-dimethylbenzyl alcohol (19.0 g, 54%), b.p. 125°/4.0 mm, (lit.[21] b.p. 125–127°/4 mm), m.p. 35–36°. (Found: C, 70.1; H, 10.1. $C_{13}H_{22}OSi$ calcd.: C, 70.2; H, 9.9%.) The ^1H NMR spectrum had the correct integration pattern, with τ values as follows: $(CH_3)_3Si$, 10.0; CH_2 (benzyl), 7.93; C_6H_4, 2.80 (quartet); $C(CH_3)_2$ 8.47.

The ethereal extract from a similar reaction between acetone and p-[bis(trimethylsilyl)methyl]phenyllithium was worked up differently. Volatile materials were distilled off at reduced pressure (75°/0.1 mm), and the residue was taken up in a small quantity of ether and chromatographed on alumina, with light petroleum as eluent. The residue obtained by evaporation of the petroleum was recrystallized to give p-[bis(trimethylsilyl)methyl]-α,α-dimethylbenzyl alcohol (nc) (75%), m.p. 83–84°.

(Found: C, 65.9; H, 10.7. $C_{16}H_{30}OSi_2$ calcd.: C, 65.3; H, 10.3%.) The ^{1}H NMR spectrum showed τ values as follows: $(CH_3)_3Si$, 10.0; CH (benzal), 8.57; C_6H_4, 2.30 (quartet); $C(CH_3)_2$, 8.50.

In the same way, from acetone and *p*-[tris(trimethylsilyl)methyl]phenyllithium was obtained *p*-[tris(trimethylsilyl)methyl]-α,α-dimethylbenzyl alcohol (nc) (57%), m.p. 118°. (Found: C, 62.8; H, 10.7. $C_{19}H_{38}OSi_3$ calcd.: C, 62.2; H, 10.4%.) The ^{1}H NMR spectrum showed τ values as follows $(CH_3)_3Si$, 10.0; C_6H_4, 2.39 (singlet); $C(CH_3)_2$, 8.68.

Substituted α,α-dimethylbenzyl chlorides

With the exception of *p*-methoxy-α,α-dimethylbenzyl chloride, which was prepared *in situ* from *p*-methoxystyrene[13], the chlorides were prepared by passing hydrogen chloride into a solution of the appropriate α,α-dimethylbenzyl alcohol (ca. 1 g) in dichloromethane at −10° for 1 h. Solvent and residual hydrogen chloride were removed under reduced pressure at low temperature, and the residue was used without further purification (*cf.* refs. 11–13).

Determination of apparent dissociation constants

Apparent dissociation constants of substituted benzoic acids were measured potentiometrically in 50% ethanol/water at 25° by Roberts and Reagan's method[16]. A glass electrode was used in conjunction with a Pye 79 pH meter, and the reported pK_a values are the recorded pH values at half neutralization, the EMF of the glass electrode being assumed to have the same dependence on pH as in aqueous solutions. The pK_a values listed in Table 2 are the means of three separate determinations for each acid; values were reproducible to within ±0.01.

Solvolysis of α,α-dimethylbenzyl chlorides

The procedures described by Brown and his colleagues[11–13] were used.

NMR spectra

Spectra of 10% solutions in chloroform were recorded on a Varian A 60 Spectrometer.

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