SILICON–CARBON HYPERCONJUGATION IN CATION RADICALS
I. LOWERING OF OXIDATION POTENTIALS OF
N-[(TRIMETHYLSILYL)METHYL] AROMATIC AMINES*

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SUMMARY

Large decreases in the oxidation potentials of N-(silylmethyl) aromatic amines (e.g. Me_3SiCH_2NHPh) could not be correlated with Taft σ^* or Hammett σ constants, but a good correlation was obtained with σ^+ constants. This is consistent with silyl-hyperconjugative electron release in the intermediate cation radical.

Large lowering of oxidation potential by (trimethylsilyl)methyl substitution was observed in aromatic systems other than the amines.

INTRODUCTION

In the recent literature, considerable attention has been given to the exceptional reactivity[1] of β-silyl compounds, and to the size and nature of the substituent effect of the (trimethylsilyl)methyl (Me_3SiCH_2-) group[2]. This substituent effect has been described variously from a purely inductive[3] to a predominantly resonance effect[2].

The purely inductive effect can be quantified in terms of a Taft σ^* constant [$\sigma^*(Me_3SiCH_2) - 0.26$], which was originally derived from the pK_a value of (trimethylsilyl)acetic acid[4] (Me_3SiCH_2COOH). We recently obtained the same value[5] for this constant from the stretching frequency (infrared) of the Si–H bond in [(trimethylsilyl)methyl]-dimethylsilane ($Me_3SiCH_2SiMe_2H$), where $p \rightarrow d$ back-donation effects[22] should be inoperative.

The resonance effect of the (trimethylsilyl)methyl group becomes important in reactions where development of positive charge at an atom situated β to silicon can occur, *i.e.*, reactions involving β-silyl cations. Eaborn and his co-workers[2] interpreted a large resonance effect [$\sigma^+(Me_3SiCH_2) - 0.61**$) in the protodesilylation of [p-(trimethylsilyl)benzyl]trimethylsilane in terms of a σ–π conjugation involving delocalisation of the electrons of the benzyl Si–C bond into the benzenoid π system:

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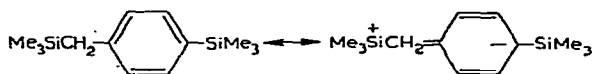
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** These authors have recently re-determined[6] this substituent constant (σ^+ −0.54) using the standard reaction (solvolysis of cumyl chlorides).

A resonance effect in β-silyl radicals was recently postulated by Krusic and Kochi[1d]. These authors decomposed di-tert-butyl peroxide photolytically in tetraethylsilane and detected the unexpected primary (triethylsilyl)ethyl radical (Et_3SiCH_2-$CH_2\cdot$) in the reaction products; they could not generate primary radicals similarly from hydrocarbons, and therefore postulated a stabilisation of the β-silyl radical by silyl-hyperconjugation:

$$R_3SiCH_2CH_2^\cdot \leftrightarrow R_3\overset{\cdot}{Si}CH_2{=}CH_2$$
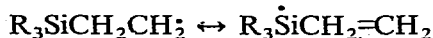
They also suggested that this interpretation is consistent with the large ^{29}Si coupling constant (a 37.4 G) in the electron spin resonance spectrum of the primary radical relative to its secondary analogue ($Et_3Si\overset{\cdot}{C}HCH_3$, a 15.2 G), but the large splitting constant could also be consistent with radical stabilisation by $p{\rightarrow}d$ back-donation, $\overset{\cdot}{\underset{\cdot C}{C}}Si{-}C$, preferred by other authors[1e,f] to explain anomalous behaviour of β-silyl radicals in polymerisation reactions etc.

We have become interested in the generation of more stable β-silyl substituted radicals from their corresponding arylamines and hindered phenols. We believe that studies of such radicals could contribute to the technology of radical inhibitors, and also provide stable radicals for detailed study by electron spin resonance techniques.

One of the methods used in our study of inhibitors has involved determinations of the polarographic oxidation potentials ($E_{P/2}$) of silyl-substituted amines. For a reversible electrode process, oxidation potential is related linearly to the standard free energy (ΔG_0) of the reaction at the electrode surface[7]. For substituted diphenylamines the electrode reaction has been represented as follows[8,9]:

$$\underset{Ph_2}{R{-}N:} \rightarrow \left[\underset{Ph_2}{R{-}N}\right]^{\overset{+}{\cdot}} \rightarrow \text{Products}$$

$$\text{(I)} \qquad \text{(II)}$$
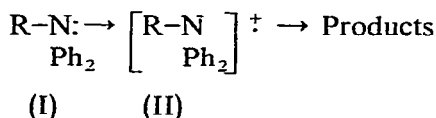
The amine (I) first loses an electron from its highest filled molecular orbital to the anode to form a cation radical (II), which can then dimerise. Most anodic oxidations of amines at solid electrodes are for all practical purposes irreversible, but Adams[8] and Zuman[7] have indicated that satisfactory correlations of observed half wave potentials and substituent constants (e.g., Hammett σ constants) can be obtained within a series of closely related compounds provided the mechanism of the electrode reaction does not change within the series, and provided experimental procedure is strictly standardised. It is also preferable to use a rapid scan rate (0.3−3 V/min) during the determination of $E_{P/2}$ values to ensure that oxidations of decomposition products of the cation radicals do not interfere[8].

RESULTS AND DISCUSSION

Using the method of Adams and his co-workers[9], we have determined that the half wave potentials ($E_{P/2}$) of N-substituted aromatic amines at a platinum anode in acetonitrile with tetraethylammonium perchlorate as support electrolyte, and against a saturated calomel reference cathode.

The most significant observation (Table 1) was a large decrease in the oxidation

potential of N-[(trimethylsilyl)methyl] amines relative to N-alkyl amines; the potential increased again to the fairly constant N-alkyl level on interposing a second methylene group between silicon and nitrogen, indicating that the decrease in potential is not inductive in origin, or a result of solvation or surface effects associated with silicon.

There was also an increase in oxidation potential relative to N-alkyl amines on attaching silicon directly to nitrogen in N-(trimethylsilyl)aniline. This effect could be due to a large p_π–d_π back-donation (or lack of hyperconjugation) lowering the energy of the highest filled molecular orbital and thus increasing the oxidation potential.

Variation of substituents at silicon (Table 2) had very little influence on the oxidation potentials of N-[(trimethylsilyl)methyl] anilines, but a further large decrease was observed on substituting the methoxy group, with its large resonance effect, into the *para* position of N-[(trimethylsilyl)methyl]aniline. It is noteworthy that the decrease in oxidation potential is similar in this system for N-[(trimethylsilyl)methyl] and *p*-methoxy.

TABLE 1

OXIDATION POTENTIALS OF AROMATIC AMINES

$RNPh_2$	$E_{P/2}$	RNHPh	$E_{P/2}$ (V)
$Me_3Si(CH_2)_3NPh_2$	0.75	MeNHPh	0.59
$Me_3Si(CH_2)_2NPh_2$	0.74	EtNHPh	0.59
$Me_3SiCH_2NPh_2$	0.41	BuNHPh	0.60
		Me_3CCH_2NHPh	0.60
		Me_3SiCH_2NHPh	0.44
		$Me_3Si(CH_2)_2NHPh$	0.60
		$Me_3SiNHPh$	0.73

TABLE 2

VARIATION OF OXIDATION POTENTIAL WITH SUBSTITUENTS ON SILICON

Compound	$E_{P/2}$ (V)	Compound	$E_{P/2}$ (V)
Me_3SiCH_2NHPh	0.44	$MeBu_2SiCH_2NHPh$	0.48
$Me_2PhSiCH_2NHPh$	0.45	p-$MeOC_6H_4NHCH_2SiMe_3$	0.26
$Me_2(n\text{-}C_8H_{17})SiCH_2NHPh$	0.48	p-$MeOC_6H_4NH_2$	0.43

We were unable to correlate our oxidation potentials and Taft σ^*, or Hammett σ constants, but the above observation and the striking similarity of the cation radical intermediate (III) to the cation intermediate (IV) in the solvolysis of cumyl chloride (the standard reaction for determining σ^+ constants) prompted us to plot oxidation potentials against σ^+ constants[10]. The linear correlation obtained is shown in Fig. 1.

(III)   (IV)
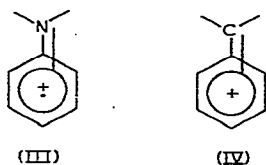
We were surprised to discover that the relationship between $E_{P/2}$ and σ^+ for aromatic amines is not very well known in the literature*, especially when we obtained a good straight line by plotting a large number of oxidation potentials of the amines $(p\text{-}KC_6H_4)_nNR'_{3-n}$, mainly from the work of Adams and his co-workers[9,24], against the sum of σ_R^+ constants (Fig. 2).

With regard to the (trimethylsilyl)methyl group, we believe that the significance of this relationship is best explained in terms of the co-ordinate in Fig. 3 for the reaction at the electrode surface. We suggest a resonance interaction between the developing cation radical centre and the (trimethylsilyl)methyl group, which increases on going from the initial to transition state. This interaction lowers the energy barrier and thus lowers the oxidation potential. In our opinion, $p \rightarrow d$ back-donation cannot be significant in a system where a positive charge is developing on an atom situated β to silicon, although such an interaction may well be present in the neutral amine or a neutral β-silyl radical.
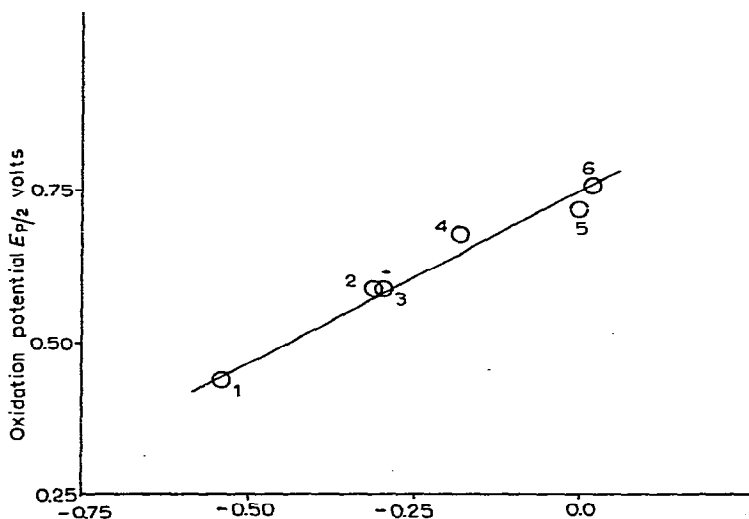

Fig. 1. Variation of $E_{P/2}$ for N-substituted anilines (RNHPh) with σ^+ constants (1, R $=$ Me$_3$SiCH$_2$; 2, R $=$ Me; 3, R $=$ Et; 4, R $=$ Ph; 5, R $=$ H; 6, R $=$ Me$_3$Si).

Furthermore, Traylor and Ware[12] have shown that metal–carbon σ–π conjugation can be correlated with σ^+ constants, whereas $p \rightarrow d$ back-donation would be unlikely to obey normal resonance rules.

Lowering of oxidation potential by σ–π conjugation should not be confined to amines, and results of experiments designed to demonstrate the generality of the effect are given in Table 3. Within each group of compounds, the oxidation potential of the (trimethylsilyl)methyl-substituted compound is substantially lowered.

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* Latta and Taft[11] have correlated σ^+ constants and electron spin resonance coupling constants of *para*-substituted N,N-dimethylaniline cation radicals.
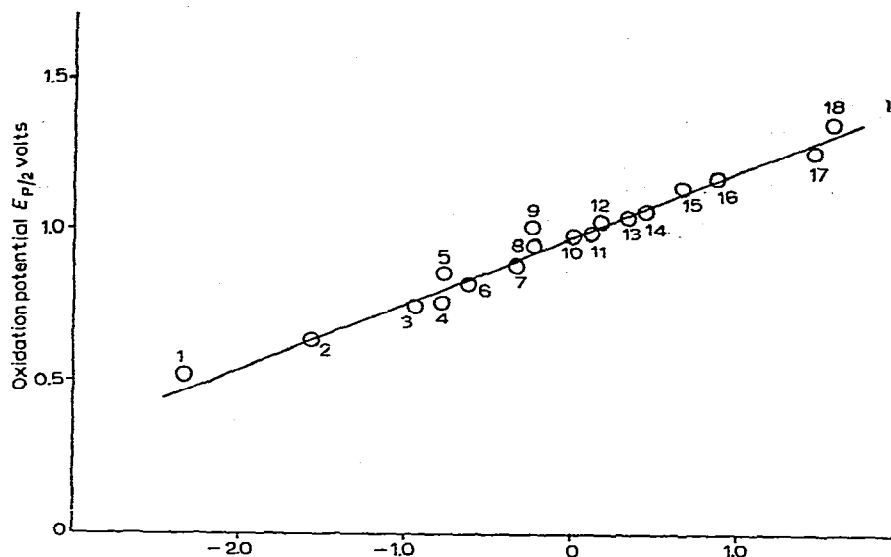
Fig. 2. Variation of $E_{P/2}$ for p-substituted triarylamines with $\Sigma\sigma_p^+$ constants.

1 $(p\text{-MeOC}_6\text{H}_4)_3\text{N}$
2 $(p\text{-MeOC}_6\text{H}_4)_2\text{PhN}$
3 $(p\text{-MeC}_6\text{H}_4)_3\text{N}$
4 $(p\text{-MeOC}_6\text{H}_4)\text{Ph}_2\text{N}$
5 $(p\text{-MeOC}_6\text{H}_4)_2(p\text{-NO}_2\text{C}_6\text{H}_4)\text{N}$
6 $(p\text{-MeC}_6\text{H}_4)\text{Ph}_2\text{N}$

7 $(p\text{-MeC}_6\text{H}_4)\text{Ph}_2\text{N}$
8 $(p\text{-FC}_6\text{H}_4)_3\text{N}$
9 $(p\text{-ClC}_6\text{H}_4)_2\text{PhN}$
10 $(p\text{-MeOC}_6\text{H}_4)(p\text{-NO}_2\text{C}_6\text{H}_4)\text{PhN}$
11 $(p\text{-ClC}_6\text{H}_4)\text{Ph}_2\text{N}$
12 $(p\text{-MeC}_6\text{H}_4)_2(p\text{-NO}_2\text{C}_6\text{H}_4)\text{N}$

13 $(p\text{-ClC}_6\text{H}_4)_3\text{N}$
14 $(p\text{-BrC}_6\text{H}_4)_3\text{N}$
15 $(p\text{-CNC}_6\text{H}_4)\text{Ph}_2\text{N}$
16 $(p\text{-NO}_2\text{C}_6\text{H}_4)\text{Ph}_2\text{N}$
17 $(p\text{-CO}_2\text{MeC}_6\text{H}_4)_3\text{N}$
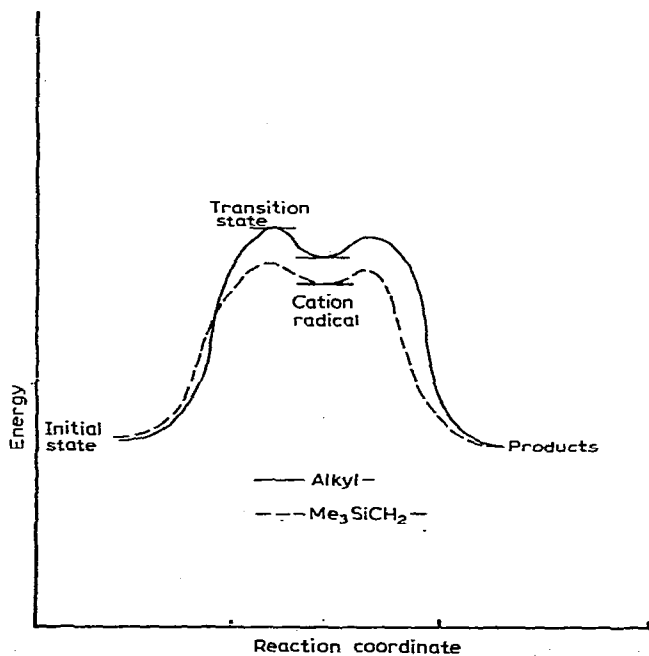18 $(p\text{-NO}_2\text{C}_6\text{H}_4)_3\text{N}$

Fig. 3. Energy profile for reaction at the electrode surface.

EXPERIMENTAL

General comments

    Element analyses were obtained from the Analytical Department, Midland Silicones Ltd.

    Nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Varian T60 instrument. All reactions involving lithium derivatives were carried out under dry argon.

TABLE 3

OXIDATION POTENTIALS OF SILICON SUBSTITUTED COMPOUNDS

Phosphines	$E_{P/2}$ (V)	Sulphides	$E_{P/2}$ (V)	Substituted benzenes	$E_{P/2}$ (V)
MePPh$_2$	0.80	Me$_3$SiSPh	1.26	EtPh	>1.8
Me$_3$Si(CH$_2$)$_2$PPh$_2$	0.88	Me$_3$Si(CH$_2$)$_3$SPh	1.28	Me$_3$SiCH$_2$Ph	1.40
Me$_3$SiCH$_2$PPh$_2$	0.63	Me$_3$Si(CH$_2$)$_2$SPh	1.26	(Me$_3$Si)$_2$CHPh	1.42
		Me$_3$SiCH$_2$SPh	1.15	p-Me$_3$SiCH$_2$C$_6$H$_4$CH$_2$SiMe$_3$	1.16

Determination of oxidation potentials

    Conventional single sweep voltametry (ref. 8, p. 124) was used to obtain $E_{P/2}$ values. The apparatus consisted of a Beckman Electroscan polarograph connected to a single compartment, three electrode cell. The working and auxiliary electrodes were two platinum wires (24 S.W.G., 0.56 mm) and the reference was a saturated calomel electrode (SCE) connected to the bulk solution via a saturated potassium chloride agar/agar tipped side arm.

    The determinations were carried out at 0.05% concentration of electro-active species in a 0.1 M solution of tetramethylammonium perchlorate in acetonitrile (20 ml). A rapid scan rate of 1.2 V/min was used for all the determinations. Nitrogen was bubbled through the test solution, to displace dissolved oxygen, just before adding the electro-active species.

    All the potentials reported (in volts relative to the aqueous SCE) are believed accurate to ± 10 mV.

Synthesis of electro-active compounds

    The following compounds were prepared by methods previously described in the literature: Me$_3$SiCH$_2$NHPh[13], Me$_3$SiMe$_2$SiCH$_2$NHPh[23], Me$_3$SiCH$_2$NPh$_2$[14], Me$_3$Si(CH$_2$)$_2$NPh$_2$[14], Me$_3$Si(CH$_2$)$_3$NPh$_2$[14], Me$_3$SiCH$_2$PPh$_2$[15], Me$_3$SiCH$_2$SPh[16], Me$_3$Si(CH$_2$)$_2$SPh[17], Me$_3$Si(CH$_2$)$_3$SPh[1c], Me$_3$SiCH$_2$Ph[18], (Me$_3$Si)$_2$CHPh[19], p-(Me$_3$SiCH$_2$)$_2$C$_6$H$_4$[20], Me$_3$Si(CH$_2$)$_2$PPh$_2$[22].

(Anilinomethyl)phenyldimethylsilane (nc)

    A mixture of N-lithioaniline (0.25 mole) and (chloromethyl)phenyldimethylsilane (34 g, 0.2 mole) in tetrahydrofuran (150 ml) was stirred and heated under reflux for 20 h, and then treated with ice-cold water (100 ml). The upper layer was separated, dried with sodium sulphate, and fractionated on a 28 plate spinning band column to yield 24 g (50%), b.p. 112 (0.2 mm). (Found: C, 75.0; H, 7.87; N, 5.11. C$_{15}$H$_{19}$NSi calcd.:

C, 74.5; H, 7.89; N, 5.81%.) ^{1}H NMR spectrum: τ(Me$_2$Si) 9.69 (singlet); τ(SiCH$_2$N) 7.15 (singlet); τ(NH) 6.58 (singlet); τ(C$_6$H$_5$) 2.27–3.40 (multiplet).

The following compounds were prepared similarly from the appropriate (chloroalkyl)silane.

n-Octyl(anilinomethyl)dimethylsilane (nc); b.p. 107 (1.0 mm); 30% yield. (Found: C, 73.3; H, 11.5. C$_{17}$H$_{31}$NSi calcd.: C, 73.5; H, 11.3%.)

Di-n-butyl(anilinomethyl)methylsilane (nc); b.p. 110 (0.5 mm). (Found: C, 72.4; H, 11.01. C$_{16}$H$_{29}$NSi calcd.: C, 73.0; H, 11.02%.)

1-Anilino-2-(trimethylsilyl)ethane (nc); b.p. 106 (2.5 mm). (Found: C, 68.6; H, 10.3; N, 8.01. C$_{11}$H$_{19}$NSi calcd.: C, 68.8; H, 9.90; N, 7.30%.) ^{1}H NMR spectrum: τ(Me$_3$Si) 10.23 (singlet); τ(SiCH$_2$CH$_2$N) 7.03–7.44, 9.39–9.81 (A$_2$B$_2$ multiplet); τ(NH) 6.99 (singlet); τ(Ph) 2.84–3.96 (multiplet).

[(p-Methoxyanilino)methyl]trimethylsilane (nc): b.p. 97 (0.5 mm); yield 34%. (Found: C, 63.7; H, 9.1. C$_{11}$H$_{19}$NOSi calcd.: C, 63.3; H, 9.21%.) ^{1}H NMR: τ(Me$_3$Si) 10.00 (singlet); τ(CH$_2$N) 7.74 (singlet); τ(NH) 7.04 (singlet); τ(MeO) 6.52 (singlet); τ(C$_6$H$_4$) 3.56, midpoint (A$_2$B$_2$ quartet).

N-Neopentylaniline

A mixture of *N*-lithioaniline (0.15 mole) and neopentyl iodide (30.8 g, 0.15 mole) in hexane (100 ml) was stirred and heated under reflux for 54 h. The reaction (monitored by gas chromatography) was extremely slow, and the reaction mixture was transferred under argon into a 300 ml stainless steel autoclave and heated for a further 10 h at 100°. After cooling and venting the autoclave, its contents were poured into water (100 ml). The upper layer was separated, dried with anhydrous potassium carbonate and fractionated to yield the amine (4.0 g, 17%), b.p. 59 (0.4 mm). (Found: C, 80.9; H, 10.4; C$_{11}$H$_{17}$N calcd.: C, 81.0; H, 10.4%.) ^{1}H NMR: τ(t-Bu) 9.37 (singlet); τ(CH$_2$N) 7.52 (singlet); τ(NH) 6.91 (singlet); τ(C$_6$H$_5$) 3.0–4.0 (multiplet).

1-(Diphenylphosphino)-2-(trimethylsilyl)ethane (nc)

This compound was prepared using the method described in ref. 21, b.p. 118° (0.5 mm), 42% yield. (Found: C, 70.6; H, 8.15. C$_{17}$H$_{23}$PSi calcd.: C, 71.3; H, 8.05%.)

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