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THE MECHANISM OF THE METHANOLYSIS OF *N*-(TRIALKYLSILYL)-ANILINES

A. R. BASSINDALE, C. EABORN AND D. R. M. WALTON
School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex (Great Britain)

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SUMMARY

The rates of methanolysis of some $ArNHSiR_3$ compounds have been measured spectrophotometrically. The reactions have been shown to be inhibited by base, and the solvolysis of $XC_6H_4N^+HSi\text{-}i\text{-}Pr_3$ compounds in methanol at 50° containing an acetic acid/sodium acetate buffer and lithium perchlorate has been shown to be subject to specific oxonium ion catalysis. The mechanism proposed for neutral and acid-catalysed alcoholysis involves rate-determining nucleophilic attack of solvent on the silicon atom in the protonated species $ArN^+H_2SiR_3$. For the $XC_6H_4NHSi\text{-}i\text{-}Pr_3$ compounds, the effects of the substituents X correlate excellently with their Hammett σ-constants ($\rho = -2.5$).

INTRODUCTION

The transfer of a trialkylsilyl group from nitrogen to oxygen forms the basis of the most commonly used method for silylating hydroxyl groups, a procedure of importance in connection with GLC analysis of hydroxyl compounds[1], but despite this, little is known with certainty about the mechanism of this type of transfer. Alcoholysis of simple organosilylamines seems clearly to be acid-catalysed[1-5], but it is also said on the one hand to be catalysed[6], and on the other to be retarded[5] by base. (Hexaphenyldisilazane, which undergoes solvolysis readily in presence of acid, is known to be attacked only very slowly by aqueous-alcoholic alkali even on boiling[2].) A four-centre mechanism has been proposed for silanolysis of silylamines[7], and a similar mechanism could be written for alcoholysis, but this would require retention of configuration at silicon, whereas inversion predominates in neutral and acid-catalyzed hydrolysis[8,9] and neutral methanolysis[8].

To throw light on the mechanism we have carried out rate studies on the methanolysis of (trialkylsilyl)anilines, represented by the following equation:

$$MeOH + XC_6H_4NHSiR_3 \rightarrow XC_6H_4NH_2 + R_3SiOMe$$

The progress of the reactions can be conveniently followed by the change in the ultraviolet spectrum of the aromatic system on removal of the R_3Si group.

RESULTS AND DISCUSSION

Exploratory experiments showed that the triethylsilyl compound $PhNHSiEt_3$ reacted too quickly for accurate measurement with pure methanol, ethanol, or isopropanol. It was established, however, that the rates decreased as the alcohol was varied in the sequence MeOH, EtOH, and i-PrOH, and that addition of water considerably enhanced the rate of solvolysis in methanol. The compound $PhNEtSiEt_3$ was found to be cleaved more slowly than either $PhNHSiEt_3$ or $PhNEtGeEt_3$ in pure methanol at room temperature. Addition of base completely inhibited the methanolysis of $PhNHSiMe_3$ and $PhNEtSiMe_3$, and of the simple silylamine, Me_3SiNMe_2. In the case of *N*-(trialkylsilyl)anilines we confirmed that the apparent lack of base cleavage was not due to reversibility of the reaction, and an associated unfavourable position of equilibrium, by showing spectrophotometrically that no reaction occurred between aniline and trimethylmethoxysilane under the conditions used for methanolysis.

Subsequently the triisopropylsilyl compound $PhNHSi\text{-}i\text{-}Pr_3$ was found to be unchanged during 100 h in pure methanol, but to undergo methanolysis at a measurable rate in presence of an acidic buffer of acetic acid and sodium acetate at 50°. The rates of cleavage were first measured at a constant $MeCO_2H/NaO_2CMe$ buffer ratio but with varying concentrations of lithium perchlorate, and the results are shown in Table 1 as observed first-order rate constants k (in min^{-1}). The rate constant was found to increase markedly with the lithium perchlorate concentration and to be linearly related to the ionic strength μ of the medium, according to the relationship $k=2.43\ \mu+0.047$. (It is noteworthy that salts have been used in several cases to catalyse the tri-

TABLE 1

SOLVOLYSIS OF $XC_6H_4NHSi\text{-}i\text{-}Pr_3$ COMPOUNDS IN A METHANOLIC SOLUTION OF ACETIC ACID, SODIUM ACETATE, AND LITHIUM PERCHLORATE AT 50.0° [a]

	$[MeCO_2H]$[b] (*M*)	$[MeCO_2Na]$[b] (*M*)	$[LiClO_4]$[b] (*M*)	10^3k (min^{-1})
X=H				
	0.050	0.0050	0.000	60.8
	0.050	0.0050	0.0385	146[c]
	0.050	0.0050	0.0465	179
	0.050	0.0050	0.0650	210
	0.050	0.0050	0.0940	281
	0.050	0.0050	0.1340	384
	0.050	0.0050	0.1840	483
X=*m*-Me				
	0.150	0.0150	0.0285	215
	0.100	0.0100	0.0335	214
	0.075	0.0075	0.0360	218
	0.050	0.0050	0.0430	215
	0.0375	0.0050	0.0430	163
	0.025	0.0050	0.0430	111

[a] Wave lengths of 247 and 250 mμ, respectively, were used for X=H and X=*m*-Me. [b] Concentrations of $MeCO_2H$, $MeCO_2Na$, and $LiClO_4$ in the reaction medium. [c] When MeCOOD and MeOD were used the value of k was 193.5 min^{-1}.

methylsilylation of hydroxyl groups[1], but the salts most commonly used, *viz.* ammonium salts and sodium bisulphate[3], may function more by increasing the hydrogen ion concentration than through simple salt effects.) When the deuterio-compounds $MeCO_2D$ and MeOD were used in place of their protium analogues under one set of acidic conditions, the rate constant was increased by a factor of 1.33.

The effect of varying the acidity was examined with the compound *m*-$MeC_6H_4NHSi\text{-}i\text{-}Pr_3$ (see Table 1). When the amount of added acetic acid was varied over a 3-fold range at a fixed buffer ratio and fixed ionic strength (the latter being maintained by appropriate additions of lithium perchlorate), the rate remained constant within experimental error. When the amount of acetic acid was varied 2-fold at a constant sodium acetate and lithium perchlorate concentration, the rate constant was almost linearly related to the concentration of the acid.

Approximate activation energies of 5.4 and 5.1 kcal/mole, respectively, were derived from runs at two temperatures for the compounds *p*-$MeC_6H_4NHSi\text{-}i\text{-}Pr_3$ and *p*-$MeOC_6H_4NHSi\text{-}i\text{-}Pr_3$.

The results are all consistent with specific oxonium ion catalysis, as in the reaction sequence (1)–(3), in which equilibrium (1) lies well over to the left, with both forward and reverse reactions of the equilibrium (1) very fast, and in which reaction(2) is slow and rate-determining. (This is essentially the mechanism suggested by one of us over ten years ago[2].) The proton transfer represented in (3) as a subsequent fast process may possibly be synchronous with step (2).

$$ArNHSi\text{-}i\text{-}Pr_3 + MeOH_2^+ \overset{\text{fast}}{\rightleftharpoons} \overset{+}{ArNH_2}Si\text{-}i\text{-}Pr_3 + MeOH \qquad (1)$$

$$\overset{+}{ArNH_2}Si\text{-}i\text{-}Pr_3 + MeOH \longrightarrow ArNH_2 + i\text{-}Pr_3\overset{+}{SiOHMe} \qquad (2)$$

$$i\text{-}Pr_3\overset{+}{SiOHMe} + MeOH \longrightarrow i\text{-}Pr_3SiOMe + \overset{+}{MeOH_2} \qquad (3)$$

The very low value of the activation energy and the correspondingly low value of log *A* (*i.e.* the unfavourable entropy change) are consistent with a process in which at least three entities (H^+, $ArNHSiR_3$, and MeOH), originally separate, are involved in a fairly rigid transition state in the rate-determining step. Alternatively, but necessarily equivalently, the smallness of the temperature coefficient can be related to the shift of equilibrium (1) to the left with increasing temperature[10], which tends to offset the rise in the specific rate of step (2).

It was separately established that only a very small amount of the amine, $ArNH_2$, is present as the conjugate acid, $ArNH_3^+$, in the media used; an even smaller proportion of the corresponding silicon-substituted amine, $ArNHSi\text{-}i\text{-}Pr_3$, which is a weaker base, would be present in the protonated form. It was also shown that, as expected, rapid proton exchange occurs between the solvent and the base $PhNHSi\text{-}i\text{-}Pr_3$ even in neutral methanol, which confirms that step (1) must be fast.

In a step of type (2), in which the Si–N cleavage occurs, the neutral amine, RNH_2, separates; since this is a very good leaving group, the observed inversion of configuration at silicon in such reactions would be expected[8,9]. In pure methanol, or similar media, there is apparently sufficient protonation of the silylamine (in an equilibrium such as $R_3SiNHR' + MeOH \rightleftharpoons R_3SiN^+H_2R' + MeO^-$) to enable solvolysis of some silylamines to proceed without added catalysts, but addition of alkali suppresses this protonation and inhibits reaction.

TABLE 2

SOLVOLYSIS OF $XC_6H_4NHSi\text{-}i\text{-}Pr_3$ AND $X_2C_6H_3NHSi\text{-}i\text{-}Pr_3$ COMPOUNDS

In methanol containing acetic acid (0.050 *M*), sodium acetate (0.005 *M*) and lithium perchlorate (0.0385 *M*).

X or X_2	Temp. (°C)	λ^a (mμ)	10^3k_1 (min^{-1})	k_{rel}
H	50	247	146	1.0
o-Me	50	246	92	0.063
m-Me	50	250	209	1.43
p-Me	50	248	350	2.40
	29.6	248	198	
o-Cl	50	246	3.34[b]	~0.006[b]
m-Cl	50	251.5	16.2	0.11
p-Cl	50	256	38.0	0.26
o-OMe	50	250	97	0.66
p-OMe	50	249	700	4.8
	29.6	249	410	
o-F	50	245	3.55	0.038
p-F	50	244	113	0.77
2,3-Me_2	50	247	19.6	0.134
2,6-Me_2	50	245	54	0.37

[a] Wavelength at which cleavage was followed. [b] The $LiClO_4$ was 1.178 *M*; this has been taken into account in deriving the value of k_{rel}

Rates of methanolysis were measured for a series of $XC_6H_4NHSi\text{-}i\text{-}Pr_3$ compounds in a fixed medium, and are shown in Table 2 as observed first order rate constants *k* and as rates k_{rel} relative to that of the parent compound. For *meta*- and *para*-X groups, electron release by the substituent increases and electron release correspondingly decreases the rate, and a plot of log k_{rel} versus the Hammett σ-constants is an excellent straight line, with $\rho = -2.52$ (see Fig. 1). If the reaction scheme (1)–(3) is correct, the observed value of ρ is the sum of the values of ρ_1 for equilibrium (1) and ρ_2 for step (2). The value of ρ for equilibrium protonation of amines $XC_6H_4NH_2$ in methanol at 25° is -4.03[11], and a somewhat higher value, perhaps about -4.5, might be expected for the more weakly basic $XC_6H_4NHSi\text{-}i\text{-}Pr_3$ compounds. This implies that ρ_2 has a value of about $+2$, which is reasonable.

The effects of *ortho*-substituents are revealing. All the *ortho*-substituents used are known to lower the base strength in the parent anilines $XC_6H_4NH_2$[10], probably because of steric hindrance to solvation of the anilinium ion, and consistently all cause a decrease in the rate of solvolysis of the $XC_6H_4NHSi\text{-}i\text{-}Pr_3$ compounds. It is, of course, the base strengths of the silicon-containing anilines, $XC_6H_4NHSi\text{-}i\text{-}Pr_3$, which are of direct significance; for amines containing *meta*- and *para*-X groups, the pK_a's of these silylanilines are likely to be linearly related to those of the parent anilines $XC_6H_4NH_2$, but this will not be generally true for compounds containing *ortho*-substituents. A plot of values of log k_{rel} against the pK_a's of the anilines $XC_6H_4NH_2$[10], shown in Fig. 2, is instructive in this connection. The points for *m*- and *p*-X groups lie near a straight line, as expected from the excellence of the plot of k_{rel} versus σ. The points for the smallest *ortho*-substituents, *o*-F and *o*-OMe, lie reasonably close to this line, but those for the progressively larger *o*-Cl and *o*-Me groups lie

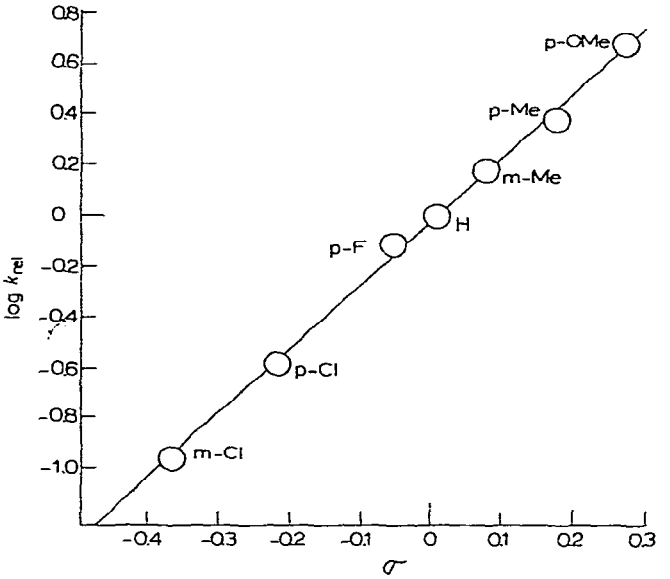


Fig. 1. Plot of log k_{rel} for methanolysis of $XC_6H_4NHSi\text{-}i\text{-}Pr_3$ compounds against Hammett σ-constants.

increasingly further away from it, presumably as steric hindrance to solvation in the ion $XC_6H_4N^+H_2Si\text{-}i\text{-}Pr_3$ becomes markedly more serious than that in the ion $XC_6H_4NH_3^+$. But the point for the even more crowded $2,6\text{-}Me_2C_6H_3NHSi\text{-}i\text{-}Pr_3$ compound lies fairly close to the line, no doubt because of a fortuitous cancellation of opposing effects. On the one hand the steric hindrance to solvation of the ion would be expected to be considerably larger than that for the *o*-Me compound, with the combined effects of the two methyl groups being much more than additive. (The effect of a second *o*-Me group in lowering the pK_a of the parent aniline is markedly greater than that of the first[10]). But, on the other hand, while in $o\text{-}MeC_6H_4NHSi\text{-}i\text{-}Pr_3$

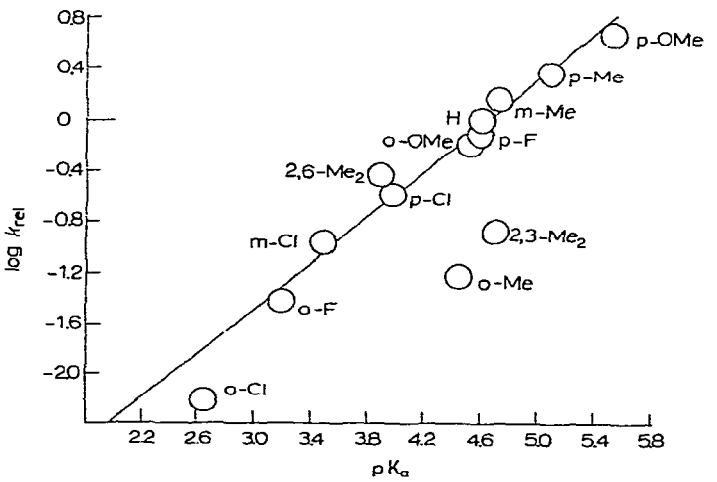
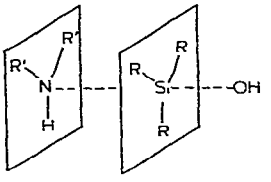


Fig. 2. Plot of log k_{rel} for a methanolysis of $XC_6H_4NHSi\text{-}i\text{-}Pr_3$ and $X_2C_6H_3NHSi\text{-}i\text{-}Pr_3$ compounds against the pK_a's of $XC_6H_4NH_2$ and $X_2C_6H_3NH_2$ compounds.

the Si-i-Pr_3 group and H atoms of the amine group can lie in the plane of the aromatic ring, to give the maximum resonance stabilisation, with the Si-i-Pr_3 group oriented away from the *o*-Me group, introduction of a second *o*-Me group inhibits this coplanarity. The base strength of the aniline 2,6-$Me_2C_6H_3NHSi$-i-Pr_3 should thus be abnormally large in comparison with that of 2,6-$Me_2C_6H_4NH_2$, and along with this will go an "abnormally" high rate of solvolysis of the silylaniline. The combined deactivation by the two *o*-Me groups is, in fact, some 90 times less than would be expected for additivity of the separate effects of the two groups. [For *o*-MeC_6H_4-$NHSi$-i-Pr_3 $k_{rel}=0.063$; for additivity, the value of k_{rel} for the 2,6-Me_2 compound should thus be $(0.063)^2$, *i.e.* 0.0040, whereas the experimental value is 0.37]. The 2,6-Me_2 derivative is, nevertheless, still slightly deactivated compared with the parent compound C_6H_5NHSi-i-Pr_3, so that steric hindrance to solvation of the ion appears to outweigh slightly the base-strengthening effect of the steric inhibition of resonance and electron-release by the methyl groups. The compound 2,3-$Me_2C_6H_3NHSi$-i-Pr_3, by contrast, is only a little less reactive than would be expected for additivity of the separate effects of the *o*- and *m*-Me groups. (Calcd. value of $k_{rel}=0.063\times 1.44$, *i.e.* 0.091; observed value, 0.135.)

More difficult to explain is the fall in reactivity on going from the compound $PhNHSiEt_3$ to $PhNEtSiEt_3$. The *N*-ethyl group would be expected to increase the pK_a through its electron-releasing inductive effect and its steric interference with the resonance between the nitrogen atom and the ring. By analogy with the behaviour of *N*-alkylanilines, the effects would be expected to outweigh steric hindrance to solvation of the anilinium ion; for example, the change from PhNH-t-Bu to PhNEt-t-Bu is known to cause markedly larger increase in pK_a than the change from $PhNH_2$ to PhNHEt[10]. The explanation of the lower rate of solvolysis of the N–Et compound may thus have to be sought in the slow step of the reaction, the cleavage of the Si–N bond, rather than in the prior protonation equilibrium. In the cleavage, as the nucleophile ROH attacks the R_3Si group, three Si–R bonds will move through a state of coplanarity (inversion ultimately occurring), and at the same time, as the NHR'_2 group separates, the N–H and N–R′ bonds will also move towards the state of coplanarity which will exist in the separated amine NHR'_2 when one of the R′ groups is Ph. In a transition state resembling the structure depicted in (I)*, there will be



(I)

considerable face-to-face interaction between the R and R′ groups, and replacement of a hydrogen atom on nitrogen by an ethyl group could cause a considerable increase in steric hindrance.

* In the actual transition state the N–R′ and N–H bonds will not have reached coplanarity, but it is also possible that the Si–R bonds will have moved beyond the coplanar positions and be inclined towards the N–R′ bonds.

The low reactivity of ArNHSi-i-Pr_3 compared with ArNHSiEt_3 compounds can be confidently attributed to steric hindrance; i-Pr_3Si groups are quite generally more resistant than Et_3Si groups towards nucleophilic attack at silicon, and it is not necessary to call upon any specific steric effects such as that postulated in the preceeding paragraph.

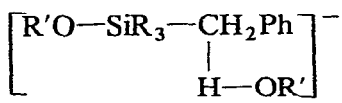
Although there may be exceptions, as exemplified above, probably associated with substantial steric effects, it is likely that for derivatives of simple amines* the dominant effect of structural change in the amine moiety of the silylamines on the ease of solvolysis will normally be exerted mainly through the protonation equilibrium rather than on the ease of the cleavage step. For example, the observation that methanolysis of tris(trimethylsilyl)amine, $(Me_3Si)_3N$, is very slow compared with that of hexamethyldisilazane, $(Me_3Si)_2NH$, (the factor is 20,000/1 in MeOH/CCl_4 at 30°) is probably to be associated with the markedly lower base strength of the tris-compound, rather than, as suggested by authors who made the experimental observation[12], to steric hindrance towards attack of the solvent on an Si–N bond in $(Me_3Si)_3N$.

The effects of change in the nature of the alcohol used in the solvolysis will be more complex, since the solvent is involved in the nucleophilic attack at silicon in step (2) as well as in the protonation equilibrium (1), but in the neutral alcoholysis the acidity of the alcohol must be of considerable significance. Thus the decrease in the ease of alcoholysis on going from primary to secondary and tertiary alcohols must be associated with the fall in the acidity of the alcohols as well as with increased steric hindrance, to which it has been attributed[13]. The increase in the solvolysis rate on addition of water is also to be associated in part with the greater acidity of water.

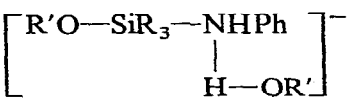
Comment on the absence of base-catalysed cleavage

It is noteworthy that *N*-(triethylsilyl)aniline does not undergo base-catalysed solvolysis under conditions in which benzyltriethylsilane would be rapidly cleaved[14]. In other words, the R_3Si–NHPh bond is broken much less readily under these conditions than the corresponding R_3Si–CH_2Ph bond, although, as far as is known, there is not much difference between the bond energies of Si–C and Si–N bonds[15]. The much greater ease of cleavage of the R_3Si–N^+H_2Ph than of the R_3Si–NHPh bond can clearly be associated with the fact that $PhNH_2$ is a much better leaving group than $PhNH^-$, but $PhNH^-$ might reasonably be expected to be at least as good a leaving group as $PhCH_2^-$. (Aniline is comparable in acidity to acetylene, and markedly more acidic than toluene.) Recent work indicates that the benzyl carbanion is never, in fact, wholly free in the base cleavages of R_3Si–CH_2Ph compounds[16], a proton being acquired from the solvent as the Si–C bond is broken, as in the schematic representation (II) of the transition state, but a similar process (III), which would avoid separation of anilide ion, should be available for the silylaniline cleavages. We plan to study this question further.

* In the absence of relevant experimental evidence we cannot assume that the mechanism proposed above for aniline derivatives operates with other types of nitrogen derivatives, *e.g.* with *N*,*N*-bis(trimethylsilyl)-acetamide, which is much used in silylation of hydroxyl groups[1].



(II)



(III)

EXPERIMENTAL

Preparation of N-(triisopropylsilyl)anilines

Butyllithium (16 ml of a 1.6 *M* solution in hexane) was added during 15 min to a solution of freshly distilled aniline (3.72 g, 0.025 mole) in ether (50 ml) and the mixture was subsequently boiled under reflux for 15 min on an oil bath. Fluorotriisopropylsilane (7.1 g, 0.015 mole) in toluene (60 ml) was then added, the temperature of the bath was gradually raised to 110° as the ether and hexane were fractionated out. The residue was held at 110° for 4 h, then the precipitated lithium salts were filtered off un-

TABLE 3

XC_6H_4NH Si-i-Pr_3 COMPOUNDS PREPARED FROM XC_6H_4NHLi OR $X_2C_6H_3NHLi$ AND i-Pr_3SiHal

X or X_2	B.p. (°C/mm)	n_D^{25}	Yield (%)	Analysis found (calcd.) (%)	
				C	H
o-Me[a]	86–88/0.1	1.5178	65	73.4 (72.9)	11.2 (11.1)
m-Me[a]	100/0.18	1.5190	65	73.1 (72.9)	11.2 (11.1)
p-Me[b]	102/0.2	1.5120	70	72.6 (72.9)	11.3 (11.1)
p-OMe[a]	90/0.14	1.5235	70	68.4 (68.8)	10.6 (10.45)
o-OMe[a]	104/0.25[c]		60	68.7 (68.8)	10.5 (10.45)
o-Cl[a]	116/0.5	1.5195	60	64.3 (63.45)	9.7 (9.2)
m-Cl[b]	105/0.2	1.5233	80	63.7 (63.45)	9.4 (9.2)
p-Cl[b]	106/0.2	1.5233	70	63.0 (63.45)	9.3 (9.2)
o-Et[a]	92/0.2	1.5182	55	73.9 (73.6)	11.3 (11.25)
p-Et[b]	81/0.1	1.5171	70	73.7 (73.6)	11.3 (11.25)
o-F[a]	79/0.3	1.5078	65	67.65 (67.2)	10.35 (10.15)
p-F[a]	92/0.3	1.5041	70	67.9 (67.2)	10.35 (10.15)
2,3-Me_2[b]	106/0.3	1.5141	65	73.0 (73.6)	11.55 (11.25)
2,6-Me_2[a]	98/0.2	1.5167	65	73.6 (73.6)	11.3 (11.25)

[a] Hal=Br. [b] Hal=F. [c] M.p. 34–35°.

TABLE 4

DETAILS OF NMR SPECTRA OF $XC_6H_4NHSi\text{-}i\text{-}Pr_3$ COMPOUNDS[a]

X=	τ Values[b]			
	NH	C_6H_4	Si-i-Pr_3	X
H	6.92	2.0–3.4	9.09 s	
o-Me	6.82	2.85–3.5	8.86 m	7.82
m-Me	6.75	2.9–3.7	8.86 m	7.89
p-Me	6.83	2.8–3.5	8.86 m	7.77
o-Et	6.72	2.8–3.5	8.86 m	7.47[c]; 7.20[d]
p-Et	6.88	2.86–3.6	8.88 m	7.47[c]; 7.20[d]
o-OMe	6.73	3.21 s	8.84 m	6.18; 7.20[d]
p-OMe	6.95	3.32 s	8.88 m	6.31
o-F	6.40	2.9–3.5	8.87 m	
p-F	7.10	3.0–3.6	8.97 s	
o-Cl	5.90	2.7–3.6	8.83 m	
m-Cl	6.63	2.8–3.6	8.87 m	
p-Cl	6.71	2.75–3.5	8.88 m	

[a] Recorded at 60 MHz on 5% solutions in $CDCl_3$ at ca. 20°, with TMS as internal standard. [b] s denotes singlet; m denotes centre of multiplet. [c] Quartet centred here. [d] Triplet centred here.

der nitrogen and the filtrate was distilled to give an orange fluorescent liquid, b.p. 112–114°/1.0 mm, which was chromatographed on acid-washed alumina (Woelm grade H) using light petroleum (b.p. < 40°) as eluent. The progress of the chromatographic separation was monitored by GLC analysis (5′ SE 30 column at 180°) and by ultraviolet spectroscopy, and the fractions rich in aminosilane were combined. Solvent was removed under reduced pressure and the residue distilled to give colourless *N*-(triisopropylsilyl)aniline (nc) (4.7 g, 75%) b.p. 114°/1.0 mm., n^{25} 1.5078. (Found: C, 72.4; H, 11.0. $C_{15}H_{27}NSi$ calcd.: C, 72.2; H, 10.9%.)

Substituted *N*-(triisopropylsilyl)anilines, $XC_6H_4NHSi\text{-}i\text{-}Pr_3$ were prepared analogously, but bromo- was sometimes used in place of fluorotriisopropylsilane, as indicated in Table 3, which also lists some properties of the products.

The ^1H NMR spectra of the prepared compounds, details of which are shown in Table 4, had the correct integration pattern and expected chemical shifts. For the parent compound $PhNHSi\text{-}i\text{-}Pr_3$ and the derivative $p\text{-}FC_6H_4NHSi\text{-}i\text{-}Pr_3$ the isopropyl resonance is a sharp singlet, but for the other $XC_6H_4NHSi\text{-}i\text{-}Pr_3$ compounds this resonance is split into a complex closely-spaced multiplet with a central line of high intensity.

Hydrogen isotope exchange between N-(triisopropylsilyl)aniline and deuteriomethanol

N-(Triisopropylsilyl)aniline (ca. 0.5 g) was added to deuteriomethanol, CH_3OD (4 ml), the solution was shaken for 1 min at room temperature, and methanol was then removed rapidly under reduced pressure. GLC analysis of the residue showed it to be *N*-(triisopropylsilyl)aniline, and the infrared spectrum showed that the characteristic N–H stretching frequency ($\nu = 3400\ cm^{-1}$) had been replaced by the corresponding N–D frequency ($\nu = 2500\ cm^{-1}$).

Kinetic studies

AnalaR glacial acetic acid was purified by distillation from chromium trioxide, and methanol by distillation from magnesium methoxide. They were stored under nitrogen. AnalaR sodium acetate was recrystallized from water and dried in an oven. AnalaR lithium perchlorate was dried in an oven.

In a typical run, a buffer solution was prepared in a 25 ml conical flask by adding 10 ml of a stock solution of acetic acid in methanol to 10 ml of a stock solution of sodium acetate and, where appropriate, lithium perchlorate in the same solvent. An appropriate amount of the (trialkylsilyl)aniline was added as a very small drop. The mixture was shaken briefly, and a sample was transferred to a silica cell in a thermostatted cell holder of an SP500 Unicam spectrophotometer. Optical density readings, at the wave-length λ, shown for each compound in Table 2, were begun 5 minutes later and continued to 10 half-lives: With buffer solutions made up from stock solutions of acetic acid and sodium acetate in methanol, rate constants could be reproduced to within $\pm 2\%$, but in the few cases in which the components of the solution were made up completely afresh, the rates could be reproduced only to within $\pm 10\%$. The results in Table 2 refer to the same batches of the buffer components.

The spectrum of a solution of aniline in the most acidic medium used was identical within experimental error with that in neutral methanol, indicating that an undetectably small amount of the base was converted into the conjugate acid.

Test for reversibility. The positions of the UV absorption maxima of a 10^{-3} *M* solution of aniline or *N*-ethylaniline in methanol containing sodium methoxide (3 *M*) were unchanged when methoxytrimethylsilane (up to 15 vol. %) was added. No change occurred in the positions or intensities of the maxima during 5 h. (If $PhNHSiMe_3$ or $PhNEtSiMe_3$ had been formed the positions of the maxima would have changed by ca. 10–15 mμ.)

Reactions in neutral or basic solution. Rates in separately prepared batches of "neutral" methanol were found to vary by a factor of up to five, presumably because of traces of acid or alkali. Thus only comparisons of two compounds in the same batch of methanol are significant. In such a comparison, the following approximate first-order rate constants were obtained at 30°: $PhNEtSiEt_3$, 60; $PhNEtGeEt_3$, 1900 min^{-1}.

Rate constants were not derived in the comparison of $PhNHSiEt_3$ and $PhNEtSiEt_3$, but in a given batch of solvent the former underwent effectively complete methanolysis in 12–13 min at 20° while the latter required about 2 h.

The absence of any change in the absorption spectrum showed that no appreciable solvolysis occurred in 48 h in 2–8 *M* solutions of sodium methoxide in methanol at 50° in the case of $PhNHSiMe_3$, $PhNEtSiEt_3$ and $PhNHSi\text{-}i\text{-}Pr_3$.

Analysis by GLC showed that no significant amounts of the compounds Me_3SiOMe, Me_3SiOH, or $(Me_3Si)_2O$ were produced in a solution of (trimethylsilyl)-dimethylamine during 24 h at 20° in methanol containing 5 vol. % of water and 7 *M* sodium methoxide, nor was a detectable smell of dimethylamine produced. By contrast, the compound Me_3SiOH and some $(Me_3Si)_2O$, and a small amount of dimethylamine was rapidly formed when neutral methanol containing 5% of water was used. Similarly the compounds Me_3SiOEt (identified by GLC) and NH_3 (identified by smell) were produced immediately on adding hexamethyldisilazane to ethanol,

but neither of these products could be detected after 30 min when ethanol containing 2 *M* sodium ethoxide was used.

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