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ORGANOSILICON COMPOUNDS

LI*. FURTHER STUDIES OF THE BASE-CATALYSED SOLVOLYSIS OF *N*-(TRIORGANOSILYL)ANILINES

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Summary

Relative rates of solvolysis of some *N*-triorganosilylanilines in mixtures of ethanol and aqueous potassium hydroxide have been determined, with results as follows. (i) For $XC_6H_4NHSiEt_3$ compounds in MeOH (5 vol) + aq. alkali (2 vol) at 50°: (X =) H, 1.0; *p*-Me, 0.80; *p*-OMe, 0.83; *m*-Me, 0.90; *o*-Me, 0.87; *p*-SMe, 1.90; *p*-F, 1.7; *p*-Cl, 2.8; *o*-Cl, 14; *m*-Cl, 4.2; *m*-NO_2, 18; *p*-CN, ca. 43; *p*-NO_2, ca. 120. (ii) For $PhNHSi(C_6H_4Y)_3$ compounds in MeOH (10 vol) + aq. alkali (1 vol) at 50°: (Y =) H, 1.0; *p*-OMe, 0.12; *p*-Cl, ca. 32; *m*-Cl, ca. 84. (iii) For $PhNHSiR_3$ compounds in MeOH (5 vol) + aq. alkali (2 vol) : (R_3 =) Et_3, 1.0; Et_2Me, 18 (at 30°); Me_2-i-Pr, 8 (at 30°); Me_2-t-Bu, 0.012 (at 50°); i-Pr_3, 0.006 (at 50°). In series (i) the relative rates correlate with σ, or where appropriate, σ^--constants, with a ρ value of 1.6. It is suggested that in the transition state of the rate-determining step the O—Si bond is fully formed, or almost so, the Si—N bond approximately 20—50% broken, and the bond between the nitrogen atom and a proton from the solvent ca. 10—30% formed.

Introduction

We recently established the main characteristics of the cleavage of the Si—N bonds of $R_3SiNZ(C_6H_4X)$ compounds (Z = H or alkyl) by aqueous methanolic acid and alkali [2,3]. We showed that for the compounds examined, acid catalysis was very much more effective than base catalysis, and that the 'spontaneous' non-catalysed solvolysis was also significant. To gain further insight into the detail of the mechanism of the base-catalysed process we have now examined (a) the influence of the substituents X and Y, respectively, on the ease of cleavage of $XC_6H_4NHSiEt_3$ and $PhNHSi(C_6H_4Y)_3$ compounds, and (b) the influence

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[*] For Part L see ref. 1.

of the nature of the alkyl groups R on the ease of cleavage of $PhNHSiR_3$ compounds. Rates were measured spectrophotometrically as before [3].

Results and discussion

Cleavage of $XC_6H_4NHSiEt_3$ compounds

Observed first order rate constants, k, at various added alkali concentrations are shown in Table 1; it must be appreciated that in the table, and throughout the discussion below, the alkali concentration refers to the strength of the aqueous potassium hydroxide, not that of the reaction mixture. For the compound bearing the electron-releasing *p*-Me or *p*-OMe substituents, the rate profile as the alkali concentration is varied is similar in form to that for the parent compound with X = H, showing minima in the rate at low base concentrations (at ca. 0.25 *M* added alkali for X = H, 0.5 *M* for X = *p*-Me and 0.6—0.7 *M* for X = *p*-OMe), followed by linear portions at higher base concentrations (Fig. 1). For the compounds bearing electron-withdrawing substituents, minima were not observed at the base concentrations used, the plots of rate against alkali concentration being essentially linear over the whole range. Extrapolation of the linear portions of these plots and those in Fig. 1 to zero alkali concentration gives very rough values of the 'spontaneous' rate as follows: *p*-OMe, 80; *p*-Me, 50; H, 35; *p*-SMe, 25; *p*-Cl, 15; *m*-Cl, 10 min^{-1}. The sequence of these rates is the opposite of that for the base-catalysed process, but agrees with that expected for the acid-catalysed process, indicating that the 'spontaneous' process more clearly resembles the acid-catalysed process, the ease of protonation of the nitrogen atom (i.e. the strength of the base) being the dominant influence [3]. The 'spontaneous' rates probably fall even further for the compounds with X = *m*-NO_2, *p*-CN, and *p*-NO_2, but in these cases reliable extrapolation to zero base concentration is not possible. (For X = *m*-NO_2, the rate obtained by extrapolation is apparently higher than for the *m*-Cl compound, but at the very low base concentrations involved the strength of the added aqueous base may not accurately reflect the true base concentration in the reaction medium.)

In order to analyse the influence of the substituents by application of the Hammett equation, we have derived approximate values of the rate constants, k_s, at 1 *M* added base concentration for the true base-catalysed process (i.e. after correction for the spontaneous process) from the linear portions of the rate profiles. [For this, the increase in the rate constant for any compound on going from xM to yM added alkali concentration is divided by $(y—x)$.] The results are shown in Table 1, along with the values of k_{rel}, the rates of the base-catalysed process relative to that for the parent compound $C_6H_5NHSiEt_3$. A plot of log k_{rel} against σ (or σ^-) (values from ref. 4) is shown in Fig. 2, in which the line is drawn somewhat arbitrarily through the origin (X = H) and the points for X = *m*-Cl and *m*-NO_2, and is not the line giving the best overall least squares correlation. There are some marked deviations from linearity, but the two main conclusions drawn are not in doubt, viz. (a) for the *p*-NO_2 and *p*-CN groups σ^--constants give a much better correlation than σ-constants, (b) there is a close similarity between the pattern of the substituent effects in the reaction and that in the base cleavage of $XC_6H_4CH_2SiMe_3$ compounds [5,6] but the ρ value of Fig. 2, viz. 1.6(3), is markedly smaller than that, viz. 4.9, for the latter reaction. There are

TABLE 1

SOLVOLYSIS OF $XC_6H_4NHSiEt_3$ COMPOUNDS IN A MIXTURE OF METHANOL (5 VOL) AND AQUEOUS POTASSIUM HYDROXIDE (2 VOL) AT 50.0[a]

No.	X	λ (nm)	[KOH] (*M*)[b]	$10^3 k$ (min^{-1})[c]	k_B (min^{-1})[d]	k_{rel}
1	H	255	4.0	310	83	1.00
			3.0	250		
			2.0	175		
			1.0	94[e]		
			0.50	65		
			0.25	59		
			0.10	79		
			0.05	122		
2	*p*-Me	255	4.0	265	55	0.66
			3.0	200		
			2.0	151		
			1.0	100		
			0.50	87		
			0.25	112		
			0.10	185		
			0.05	305		
3	*p*-OMe	255	4.0	320	57	0.69
			3.0	265		
			2.0	200		
			1.0	144		
			0.50	136		
			0.25	175		
			0.10	295		
4	*m*-Me	252	1.0	87	(60)[f]	(0.72)
5	*o*-Me	250	1.0	103	(55)[g]	(0.66)
6	*p*-SMe	270	2.0	285	130	1.55
			1.0	153		
			0.50	93		
7	*p*-F	245	1.0	136	(116)[h]	(1.4)
8	*p*-Cl	257	1.0	205	195	2.3
			0.50	113		
			0.25	62		
9	*o*-Cl	249	0.25	290	(1000)[i]	(12)
			0.125	131		
10	*m*-Cl	255	1.0	300	290	3.5
			0.50	165		
			0.25	85		
			0.125	48		
11	*m*-NO_2	250	0.25	340	1210	14.6
			0.125	181		
			0.10	155		
12	*p*-NO_2	370	0.01	155	(12100)[j]	(145)[j]
13	*p*-CN	350	0.01	58	(4600)[j]	(55)[j]

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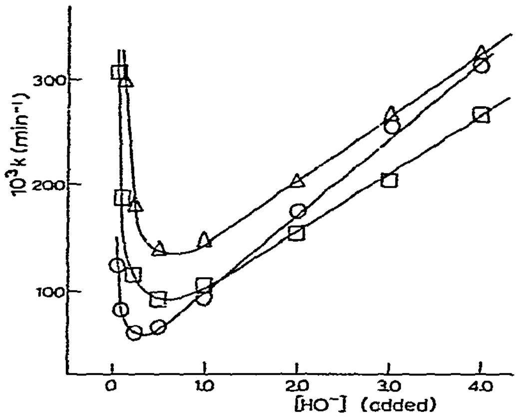
[a] Figures in parentheses are considered less reliable than others.
[b] Concentration of aqueous base, 2 vol of which was mixed with 5 vol of methanol.
[c] Observed first-order rate constant.
[d] Derived rate constant at 1 *M* added base concentration for base-catalysed process alone.
[e] A value of 96 min^{-1} was obtained when the spectroscopic change at 260 nm was used.
[f] An allowance of 27 min^{-1} was made for the spontaneous rate (cf. 25 for X = H).
[g] Assumed to be the same as that for X = *p*-Me on the basis of the similarity in the observed rates at 1 *M* added alkali.
[h] An estimated contribution of 20 min^{-1} from the spontaneous process is assumed.
[i] Based on the rate relative to that for X = *m*-Cl at 1 *M* added alkali.
[j] Very rough value based on the rate relative to that for X = *m*-NO_2 at 0.01 *M* added alkali.



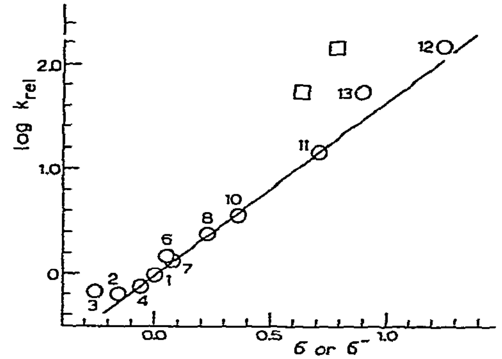


Fig. 1. Plot of observed first-order rate constant against concentration of added alkali for $XC_6H_4NHSiEt_3$ with X = H (○), p-Me (□), and p-OMe (△).

Fig. 2. Plot of log k_{rel} for $XC_6H_4NHSiEt_3$ compounds against σ or σ$^-$. For points 12 and 13, squares denote σ- and circles σ$^-$-constants.

quite marked deviations from the line of Fig. 2 for X = *p*-OMe or *p*-Me, and also for X = *p*-SMe, although it is possible that a σ$^-$constant is needed for this group and would give a better fit to the line. (Our results suggest a value of 0.15 for the σ$^-$-constant.) For most substituents a better correlation is obtained by use of σ^0-constants [4], and the deviations for X = *p*-OMe and *p*-Me are especially reduced, but these constants have the disadvantage that they cannot be used along with σ$^-$-constants.

It is noteworthy that the *p*-F substituent activates the solvolysis in accord with the value of its σ-constant, whereas it deactivates in the base-catalysed cleavage of $XC_6H_4CH_2SiMe_3$ compounds [6] and in base-catalysed detritiation of $XC_6H_4CH_2[^3H]$ compounds [7]. This difference can plausibly be associated with the greater degree of negative charge on the aromatic ring in the transition state of the last two reactions, and thus a greater influence of the π-inductive effect of the fluorine atom.

Cleavage of $PhNHSi(C_6H_4Y)_3$ compounds

These compounds were not sufficiently soluble in the medium used for the $XC_6H_4NHSiEt_3$ compounds, and so a mixture of 10 volumes of methanol to 1 volume of aqueous potassium hydroxide was used. The results are shown in Table 2. For the parent compound $PhNHSi(C_6H_5)_3$ the value of the rate constant showed a linear dependence on the (added) base concentration in the range studied, 0.10 to 1.0 *M*, indicating that at these concentrations there is no significant contribution from the spontaneous or acid-catalysed processes. The rates were measured for the compounds with Y = *m*-Cl and *p*-Cl only at 0.010 *M* added alkali concentration, and it is possible that there is some contribution from the latter processes, but the extent of this is unlikely to be such as to affect significantly the qualitative discussion below.

In a plot (not shown) of log k_{rel} [the rate relative to that of the compound $PhNHSi(C_6H_5)_3$] against σ, the points lie reasonably well about a line of slope 5.2; the ρ value per aryl group is thus ca. 1.7. Perhaps more significantly, a plot of log k_{rel} for the series against the appropriate log k_{rel} values for cleavage of

TABLE 2

SOLVOLYSIS OF $PhNHSiR_3$ COMPOUNDS

R_3	λ (nm)	[KOH] (M)[a]	$10^3 k$ (min^{-1} at 30°)	$10^3 k$ (min^{-1} at 50°)	k_{rel}
(a) Medium: MeOH (5 vol) — aq. KOH (2 vol)					
Et_3	255	8.0	113		1.0[b]
		6.0	101		
		4.0	66	310	
		1.0	23	94	
Et_2Me	248	1.0	230		18[c]
Me_2-i-Pr	248	1.0	104		8[c]
		0.2		150	
Me_2-t-Bu	250	5.0		4.3	0.012[d]
i-Pr_3	246	5.0		2.1	0.006[d]
(b) Medium: MeOH (10 vol) — aq. KOH (1 vol)					
Ph_3	250	1.0	250		1.00
		0.20	52	220	
		0.10	25	105	
$(C_6H_4OMe\text{-}p)_3$	250	1.0	31	155	0.12[c]
$(C_6H_4Cl\text{-}p)_3$	250	0.01	81	255	32[c]
$(C_6H_4Cl\text{-}m)_3$	250	0.01	210		84[c]

[a] Concentration of aqueous alkali before mixing. [b] The true base-catalysed rate constant for $PhNHSiEt_3$ at 1 M added base concentration is taken to be ca. 12 min^{-1}at 30°. [c] At 30°. [d] At 50°.

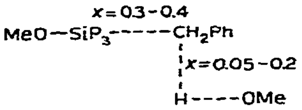
$PhC{\equiv}CSi(C_6H_4Y)_3$ compounds [8] is a better straight line, with a slope of ca. 0.8, suggesting that there may be some similarity between the rate-determining transition states in the two reactions.

Cleavage of $PhNHSiR_3$ compounds

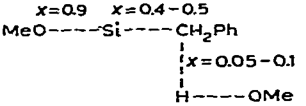
An unusually large decrease in the ease of base cleavage occurs on going from the compound $PhNHSiMe_3$, to $PhNHSiEt_3$, a factor of ca. 2.5×10^4 being involved [3]. We have thus examined the effects of a range of other trialkylsilyl groups, with the results listed in Table 2. The relative reactivities shown there are only approximate, since (a) there may be significant contribution from the spontaneous process at the 1.0 M or lower added alkali concentration used for some compounds, and (b) measurements at two temperatures are involved, but the reactivity sequence is clearly $SiMe_3 > SiMeEt_2 > SiMe_2\text{-i-Pr} > SiEt_3 > SiMe_2\text{-t-Bu} > Si\text{-i-}Pr_3$, and steric effects are evidently dominant.

The nature of the transition state

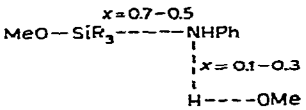
We recently suggested that the transition state for the cleavage of benzyltrimethylsilanes by aqueous methanolic alkali is most satisfactorily represented approximately by structure I, although structure II cannot be ruled out [9]; the difference between them is that I refers to cleavage of the $Si{-}CH_2Ph$ bond within the pentacovalent intermediate $[(MeO)Me_3SiCH_2Ph]^-$, whereas II represents synchronous formation of the $MeO{-}Si$ bond and breaking of the $Si{-}CH_2Ph$ bond, but with the bond-formation much more advanced than the bond-breaking. (In the structures shown, x represents the bond-order.) The rate-determining transition state for the cleavage of the N-triorganosilylanilines in aqueous methanolic alkali can be correspondingly represented by structure III or IV. For simplicity we shall base the discussion on structures I and III only.



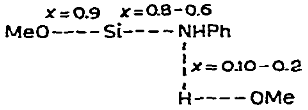
(I)



(II)



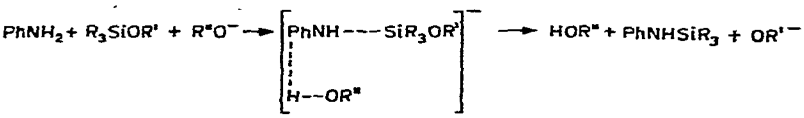
(III)



IV

The main differences between I and III are that (a) the Si—NHPh bond is less broken than the Si—CH$_2$Ph bond, in keeping with the greater ease of cleavage of the former bond, which means that the transition state will be closer to the Si^V intermediate, and (b) there is a greater degree of N—H than of C—H bond formation in the electrophilic attack by the solvent on the leaving group. As a result of these two features, substantially more negative charge resides on the benzylic carbon atom in I than on the nitrogen atom in III, giving rise to a much larger value of ρ for the Me$_3$SiCH$_2$C$_6$H$_4$X than for the Et$_3$SiNHC$_6$H$_4$X compounds. (However, as we have pointed out previously, nitrogen, because of its greater electronegativity, will bear a given excess of negative charge more easily than a carbon atom, and so, other things being equal, for a given degree of such negative charge a somewhat lower ρ value would be expected for the aniline system [3].) The closer the transition state is to the Si^V intermediate, the greater will be the steric effects of bulky alkyl groups attached to the silicon atom, and so the much greater steric effects in the R$_3$Si—NHPh than in the R$_3$Si—CH$_2$Ph cleavage are readily explained. (There is a reactivity difference of only 5 between Me$_3$SiCH$_2$C$_6$H$_4$CO$_2$-*m*$^-$ and Et$_3$SiCH$_2$C$_6$H$_4$CO$_2$-*m*$^-$ [10].) With the much better carbon leaving group C≡CPh, the transition state should again be closer to the Si^V intermediate, and it is thus noteworthy that a large Me$_3$Si/Et$_3$Si reactivity ratio, viz. ca. 280, is found also in base-cleavage of R$_3$SiC≡CPh compounds [8]. A further point of analogy between the cleavage of R$_3$SiNHPh and R$_3$SiC≡CPh compounds is that in both cases the proton being transferred from the solvent can readily interact with the π-electron cloud, whereas with R$_3$Si—CH$_2$Ph the attack has to be into the σ-electron cloud of the Si—CH$_2$Ph bond.

An interesting feature of the proposed mechanism, as indicated by structure III [or, indeed IV], is that by the principle of microscopic reversibility the hypothetical reaction of aniline with a trialkylsilyl alkoxide, to give the anilide R$_3$SiNHPh, should be base-catalysed, the catalysis involving abstraction of the proton from nitrogen as in eqn. 1. Evidence for just this kind of catalysis has



$$\mathrm{PhNH_2 + R_3SiOR' + R''O^- \longrightarrow \left[\begin{array}{l}\mathrm{PhNH---SiR_3OR'}\\ \vdots\\ \mathrm{H--OR''}\end{array}\right]^- \longrightarrow HOR'' + PhNHSiR_3 + OR'^-} \quad (1)$$

recently been obtained in cleavage of Me_3Si—$CHCl_2$ and related bonds by amines in the presence of alkali in aqueous propanol [11].

Experimental

General

All solvents were carefully dried by standard procedures.

Preparation of $XC_6H_4NHSiR_3$ compounds

(a) Except for the compounds with X = *m*-NO_2, *p*-NO_2, or *p*-CN (see below), these were made from a triorganosilyl halide (Et_3SiBr, $Et_2MeSiBr$, t-$BuMe_2SiCl$, i-$PrMe_2SiCl$, or i-Pr_3SiBr) and the appropriate XC_6H_4NHLi reagent. Typically, a cooled solution of n-butyllithium (0.125 mol) in ether (75 ml) was added under nitrogen with stirring during 30 min to a solution of appropriate aniline (0.10 mol) in ether (200 ml), the mixture being kept at 0—10°. The mixture was refluxed for 0.5 h and then cooled to room temperature. The halogenosilane (0.104 mol) in toluene (250 ml) was added dropwise with stirring, and the ether then gradually distilled off through a fractionating column to raise the reflux temperature above 100°. The mixture was refluxed for 4 h, then cooled, and the lithium salts filtered off. Solvent was removed from the filtrate and the residue fractionated under reduced pressure through a column of ca. 12 theoretical plates. (If impurities were detected by GLC, the product was refractionated.) Yields, analyses, and some physical constants of compounds prepared in this way are shown in Table 3, and some spectroscopic data in Table 4.

(b) p-$NO_2C_6H_4NHSiEt_3$. Triethyl(dimethylamino)silane (0.10 mol) in toluene (60 ml) was added under nitrogen with stirring to *p*-nitroaniline (0.10 mol),

TABLE 3

YIELDS, PHYSICAL CONSTANTS AND ANALYSES FOR $XC_6H_4SiR_3$ COMPOUNDS

X	R_3Si	Yield (%)	n_{20}^{D}	B.p. (°C/mm Hg)	Found (calcd.) (%)[a] C	Found (calcd.) (%)[a] H	Lit.
H	Et_3Si	84	1.5212	58/0.1	69.1 (69.5)	10.4 (10.2)	12,13
o-Me		75	1.5158	100/1.5	70.7 (70.5)	10.5 (10.5)	14
m-Me		75	1.5178	112/2.5	70.6 (70.5)	10.6 (10.5)	
p-Me		92	1.5160	110/2.0	70.8 (70.5)	10.4 (10.5)	
p-OMe		85	1.5210	112/0.5	65.7 (65.8)	9.6 (9.8)	
o-Cl		50	1.5270	70/0.1	59.6 (59.6)	8.3 (8.3)	
m-Cl		84	1.5330	103/0.6	60.1 (59.6)	8.8 (8.3)	
p-Cl		95	1.5275	81/0.03	59.6 (59.6)	8.7 (8.3)	
p-F		86	1.5046	66/0.05	63.2 (63.95)	9.0 (8.9)	
p-SMe		88	1.5561	130/0.7	60.1 (60.2)	8.9 (9.1)	
p-CN		90	1.5585	120/2.5	67.7 (67.2)	8.6 (8.7)	
m-NO_2		95		(m.p. 31—32°)	57.1 (57.1)	8.1 (8.0)	
p-NO_2		80		(m.p. 37—39°)	57.2 (57.1)	8.0 (8.0)	
H	Et_2Me	85	1.5204	98/0.6	68.5 (68.3)	10.4 (9.9)	
H	i-$PrMe_2$	60	1.5126	79/1.5	68.5 (68.3)	10.3 (9.9)	
H	t-$BuMe_2$	85	1.5170	76/1.5	69.7 (69.5)	10.4 (10.2)	
H	i-Pr_3	74		105/0.5			2

[a] All the compounds gave the expected molecular ions in the mass spectrum.

TABLE 4

SOME PMR AND IR DATA FOR $XC_6H_4NHSiR_3$ COMPOUNDS[a]

R_3	X	τ (NH)[b] (ppm)	Other ^{1}H peaks[c] (ppm)	γ (NH)[d] (cm^{-1})
Et_3	H	6.92[e]		3380
	o-Me	6.93[e]	7.90s (X)	3415
	m-Me	6.94[e]	7.82s (X)	3386
	p-Me	6.98	7.82s (X)	3397
	o-Cl	5.98		3378
	m-Cl	6.75		3388
	p-Cl	6.79		3382
	p-F	6.92		3396
	p-OMe	6.92	6.42s (X)	3370
	p-SMe	6.70	7.70s (X)	3368
	m-NO_2	6.05		3370
	p-NO_2	5.71		3338[f]
	p-CN	5.79		3325[g]
Et_2Me	H	6.83[e]	9.18m, 8.84s (R_3)	3370
i-$PrMe_2$	H	6.85[e]	9.85s, 9.04s (R_3)	3370
t-$BuMe_2$	H	6.90[e]	9.06s, 9.80s (R_3)	3383
i-Pr_3	H	6.51[e]	8.95s (R_3)	3390

[a] ^{1}H chemical shifts refer to solutions in CCl_4 or $CDCl_3$ with $SiMe_4$ as internal standard. IR bands are for thin films. [b] Singlets. [c] The aryl protons gave rise to the expected multiplets centred between 2.68 (*p*-NO_2) and 3.38 (*p*-OMe). The $SiEt_3$ groups gave multiplets centred between 9.02 (*m*-NO_2) and 9.22 (H and *p*-OMe). [d] Strong or very strong. The expected frequencies arising from the aryl and alkyl groups were also present. [e] Broad. [f] $\gamma(NO_2)$ = 1500s, 1300m cm^{-1}. [g] γ(CN) 2210vs cm^{-1}.

and the mixture was refluxed for 24 h. The solvent was removed and the residue recrystallized from light petroleum by cooling to ca −40° to give triethyl(*p*-nitrophenylamino)silane (20.5 g, 80%), m.p. 37—39°. Analytical and spectroscopic data are shown in Tables 3 and 4.

(c) m-$NO_2C_6H_4NHSiEt_3$. A stirred mixture of *m*-nitroaniline (0.05 mol) and triethyl(dimethylamino)silane (0.05 mol) was heated under nitrogen at ca. 100° for 4 h until a homogeneous system formed, and toluene (50 ml) was then added. The mixture was refluxed for 26 h (the progress of the reaction being monitored by occasional removal of samples for IR examination), and volatile material distilled off through a fractionating column. The residue was fractionated under reduced pressure, to give triethyl(*m*-nitrophenylamino)silane (12.2 g, 95%), b.p. 120°/0.1 mm Hg, m.p. 31—32°. Analytical and spectroscopic data are given in Tables 3 and 4.

(d) p-$NCC_6H_4NHSiEt_3$. Aminotriethylsilane (0.06 mol) in toluene (25 ml) was added dropwise with stirring to *p*-cyanoaniline (0.05 mol) under nitrogen, and the stirred mixture was heated under reflux (bath at 120°) for 5 h. The IR spectrum of a sample revealed that substantial amounts of primary amine were still present, and so the mixture was refluxed for a further 50 h, with occasional sampling. It was then fractionated to give triethyl(*p*-cyanophenylamino)silane (10.6 g, 90%) as a viscous liquid, b.p. 120°/2.25 mm Hg. Analytical and spectroscopic data are listed in Tables 3 and 4.

Preparation of $PhNH(SiC_6H_4Y)_3$ compounds

(a) n-Butyl-lithium (0.062 mol) in ether (75 ml) was added with stirring

under nitrogen to aniline (0.05 mol) at 0°. The mixture was refluxed for 1 h, then cooled, and bromotriphenylsilane (0.05 mol) in benzene (200 ml) was added dropwise with stirring at room temperature. Ether was distilled out, and the mixture refluxed for 6 h. The lithium salts were filtered off, and the filtrate was evaporated. The residue was recrystallized from benzene and then light petroleum (b.p. 60—80°) to give anilino(triphenyl)silane (12.6 g, 72%), m.p. 135—136° (lit. [12], 133—134°); characteristic IR peaks (Nujol) at 3368s (NH), 1600s (aromatic), 1428 cm^{-1} (PhSi); parent ion in mass spectrum at 351 (calcd., 351); NMR ($CDCl_3$) τ 2.82m (C_6H_5); 5.94s ppm (NH).

(b) The compound $PhNHSi(C_6H_4Cl\text{-}p)_3$ (67%) was prepared analogously from bromotris(*p*-chlorophenyl)silane, and had m.p. 148—149°; characteristic IR peaks (Nujol) at 3370s (NH) and 1597s cm^{-1} (aromatic); NMR (CCl_4) τ 2.61m (aryl-H), 7.04s ppm (NH); parent ion in mass spectrum at 454 (calcd., 454). (Found: C, 63.5; H, 4.3; N, 3.0. $C_{24}H_{18}Cl_3NSi$, calcd.: C, 63.4; H, 4.0; N, 3.1%.)

(c) Tris(*m*-chlorophenyl)silane was prepared in 90% yield from trichlorosilane and the Grignard reagent from *m*-bromochlorobenzene, and had b.p. 173°/ca. 0.2 mm Hg, n_D^{20} 1.6270; ν(SiH) 2140 cm^{-1} vs (thin film); NMR (CCl_4) τ 4.60s ppm (SiH); parent ion 363 (calcd., 363). (Found: C, 59.6; H, 3.8. $C_{18}H_{13}Cl_3Si$ calcd.: C, 59.4; H, 3.6%.) Treatment of this with bromine in carbon tetrachloride, followed by distillation, gave bromotris (*m*-chlorophenyl)silane (90%), b.p. 188°/ca. 0.1 mm Hg, n_D^{20} 1.6374; IR peaks (thin film) at 1580s and 1470vs cm^{-1} (aromatic); NMR (CCl_4) τ 2.59m ppm (C_6H_4); parent ion in mass spectrum at 442 (calcd., 442). (Found: C, 49.2; H, 3.0. $C_{18}H_{12}BrCl_3Si$ calcd.: C, 48.8; H, 2.9%.) Treatment with *N*-lithioaniline as in *(a)*, but with low pressure (10^{-4} mm) distillation of the residue before recrystallization (at —40°) from light petroleum (b.p. 40—60°) gave anilinotris(*m*-chlorophenyl)silane (77%), m.p. 73—74°; IR peaks (Nujol) at 3378s (NH), 1600s cm^{-1} (aromatic); NMR (CCl_4) τ 2.88 m (aryl-H); 5.98s ppm (NH); parent ion at 454 (calcd., 454). (Found: C, 63.2; H, 4.3; N, 2.9. $C_{24}H_{18}Cl_3NSi$ calcd.: C, 63.4; H, 4.0; N, 3.1%.)

(d) The procedure described under *(a)*, but from bromotris(*p*-methoxyphenyl)silane, gave anilinotris(*p*-methoxyphenyl)silane as a very viscous liquid (25%), b.p. 170°/ca. 10^{-3} mm Hg which could not be crystallized; IR peaks (thin film) at 3360s (NH), 1595s cm^{-1} (aromatic); NMR (CCl_4) τ 2.88m (aryl-H), 6.05s (NH), 6.28s ppm (CH_3); parent ion at 441 (calcd., 441). (Found: C, 72.9; H, 6.4. $C_{27}H_{27}NO_3Si$ calcd.: C, 73.4; H, 6.2%.)

(e) From bromotris-(*o*-tolyl)silane the procedure described under *(a)*, but with recrystallization at —40° from light petroleum only, gave anilinotris-(*o*-tolyl)silane (73%), m.p. 142—143°; IR peaks (CCl_4) at 3390s (NH) and 1600s cm^{-1} (aromatic); NMR (CCl_4) τ 3.00m (aryl-H), 6.13s (NH), 7.80s ppm (CH_3); parent ion at 393 (calcd., 393). (Found: C, 82.6; H, 7.2; N, 3.7. $C_{27}H_{27}NSi$ calcd.: C, 82.4; H, 6.9; N, 3.6%.)

Rate measurements

The general procedure has been described [3]. With liquid anilinosilanes, an appropriate quantity (0.05—0.08 μl) was injected from a microsyringe into the appropriate mixture of methanol and aqueous alkali contained in a 1 cm stoppered absorption cell and preheated in the thermostatted block of the spectrophotometer. The cell was quickly shaken and returned to the block, and readings of optical density begun after a few minutes.

With solid compounds, an appropriate amount of finely-crushed material was quickly dissolved in the reaction medium at room temperature (or with ice-cooling for the most reactive compounds), and some of the solution was transferred to the absorption cell, which was then placed in the thermostat block. Readings were begun after about 6—10 min.

For all runs good first order plots were obtained for more than 70% completion of the reaction. Rate constants were reproducible within ± 2%, except for the fastest runs and the lowest base concentrations used.

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