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RATES OF BASE-CATALYSED CLEAVAGE OF PYRIDYL-, QUINOLYL-, PICOLYL- AND (QUINOLYLMETHYL)-TRIMETHYLSILANES

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Summary

Rates of cleavage of some picoyl- and (quinolylmethyl)-trimethylsilanes ($RSiMe_3$, where R = $PyCH_2$ or $QnCH_2SiMe_3$) have been measured in "90%" aqueous methanolic sodium methoxide at 50°C. Relative reactivities are: 2-$PyCH_2$, 1.0; 3-$PyCH_2$, 0.030; 4-$PyCH_2$, 8.9; 2-$QnCH_2$, 41; 3-$QnCH_2$, 0.161; 4-$QnCH_2$, 37. The rates correlate well with those for base-catalysed hydrogen-exchange in the parent carbon acids RH. Approximate pK_a's (based on the scale of ion-pair acidities in $CsNHC_6H_{11}$—$H_2NC_6H_{11}$, with pK_a of 9-phenylfluorene = 18.6) for the carbon acids, RH, can be derived as follows: 2-$PyCH_3$, 29.5; 3-$PyCH_3$, 34; 4-$PyCH_3$, 27; 2-$QnCH_3$, 25; 3-$QnCH_3$, 32; 4-$QnCH_3$, 25.

Rates of cleavage of pyridyl- and quinolyl-trimethylsilanes ($PySiMe_3$ and $QnSiMe_3$) by sodium hydroxide in 4 : 1 v/v Me_2SO/H_2O at 50°C have also been measured; and the relative reactivities are: 2-Py, 1.0; 3-Py, 2.9; 4-Py, 8.4; 2-Qn, 15.9; 3-Qn, 12.7; 4-Qn, 184. The sequence of reactivity differes from that for base-catalysed hydrogen-exchange at the relevant positions of pyridine and quinoline, indicating that the reactivities are not determined in both cases (if in either) solely by the stabilities of the corresponding carbanions.

Introduction

Rates of cleavage of $XC_6H_4CH_2$—$SiMe_3$ bonds by sodium hydroxide in 61 : 39 w/w (ca. 2 : 1 v/v) or 5 : 1 v/v $MeOH/H_2O$ are known to correlate well with σ-, or, where appropriate, σ^--constants [1—3]. Furthermore, for base-cleavage in 5 : 1 v/v $MeOH/H_2O$ of a range of $RSiMe_3$ compounds in which R is of the benzyl type (e.g. $PhCH_2$, Ph_3C, 9-fluorenyl) the values of log k_{rel}, where k_{rel} represents the ratio of the specific rate constant for $RSiMe_3$ to that for $PhCH_2$-$SiMe_3$, are linearly related to the pK_a's of the corresponding carbon acids RH

over a pK_a range of 19—41 [4]. Thus rates of cleavage of appropriate R—$SiMe_3$ compounds can be used as a measure of σ- or σ^--constants and of the pK_a's of the corresponding acids RH, and we have used this approach with trimethylsilyl derivatives of the picolines ($PyCH_3$) and methylquinolines ($QnCH_3$). The factors governing the use of cleavage of aryl—$SiMe_3$ bonds are more complex [5], but for a small range of simple $ArSiMe_3$ compounds in which Ar is Ph or a polynuclear aromatic hydrocarbon, the ease of cleavage does seem to reflect the acidity of the ArH compound [6], and we have thus briefly examined the base cleavage of 2-, 3-, and 4-pyridyl- and -quinolyl-trimethylsilanes.

A qualitative study of the cleavages of the 2- and 4-picolyl compounds was made some years ago [7], while the cleavage of the 2-pyridyl compound in neutral media has been studied in detail [8].

Results and discussion

Picoline and quinolylmethane derivatives

We found that the spectroscopic technique normally used for measuring the rates of cleavage of $RSiMe_3$ compounds (see, e.g., refs. 1—6) could not be applied to all the picoline and quinolylmethyl derivatives because in some causes the UV spectra of the $RSiMe_3$ and RH compounds did not differ sufficiently in the appropriate wave-length range. Thus we employed GLC analysis of the reaction mixtures, and this required the use of much larger concentrations of the organosilicon compounds than usual. The mixture used consisted of 4.5 vol. of methanol, 0.5 vol. of aqueous sodium hydroxide, 0.4 vol. of $RSiMe_3$, and approximately 0.1 vol. of toluene as a GLC standard. In view of the 9 : 1 v/v MeOH/H_2O ratio we loosely refer to this medium below as '90% methanol', but it will be appreciated that the rate constants would be somewhat different if the usual very low concentration of the organosilane were taken in 9 : 1 v/v MeOH/H_2O.

The results are shown in Table 1, which lists the concentration of the base (calculated from the concentration of the aqueous sodium hydroxide by assuming a 10-fold dilution), the observed first-order rate constant k, and the specific (second order) rate constant k_s, given by k/[Base]. Features of the results, and some comments, are as follows.

(i) Good linear correlations are revealed (see Fig. 1) when the values of log k_s are plotted against the values of log k_s for hydrogen-exchange at the relevant positions of the corresponding RH compounds for (a) deuteration in ethanolic sodium ethoxide at 25°C [9], and (b) detritiation in methanolic sodium methoxide at 135°C [10].

(ii) By measuring the rates of reaction of the chloropyridines with sodium methoxide in methanol at 50°C, Liveris and Miller derived σ^--constants of 0.996, 0.586 and 1.165, respectively, for the 2-, 3- and 4-positions of pyridine [11], and these values would be expected to apply to reactions in which the corresponding 2-, 3-, and 4-picolyl carbanions, $PyCH_2^-$, are generated *. These

* It will be appreciated that, for convenience, and following many precedents, we are here using σ- or σ^--constants to apply to the whole R group of $RSiMe_3$ or RH. In this usage $PhCH_2$ would have an equivalent σ-value of 0.00, while p-$NO_2C_6H_4CH_2$ would have an equivalent σ^--value of 1.24 (i.e. σ^- for p-NO_2).

TABLE 1

CLEAVAGE OF TRIMETHYLSILYLMETHYL-PYRIDINES AND -QUINOLINES, $RSiMe_3$, BY "90%" AQUEOUS METHANOLIC SODIUM HYDROXIDE AT 50.0°C [a]

R	$10^2[OH^-]$ (M) [b]	k (s^{-1})	k_s ($l\ mol^{-1}\ s^{-1}$)
2-$PyCH_2$	2.00	1.30×10^{-4}	6.5×10^{-3}
	4.00	2.54×10^{-4}	6.35×10^{-3}
3-$PyCH_2$	50.0	9.8×10^{-5}	1.96×10^{-4}
4-$PyCH_2$	2.00	1.16×10^{-3}	5.8×10^{-2}
2-$QnCH_2$	0.200	5.3×10^{-4}	2.65×10^{-1}
3-$QnCH_2$	40.0	5.2×10^{-4}	1.04×10^{-3}
4-$QnCH_2$	0.200	4.8×10^{-4}	2.4×10^{-1}

[a] For exact composition of medium see Experimental section. [b] Derived from the concentration of aqueous alkali used, assuming a 10-fold dilution.

σ^--constants were used by Zatsepina and her colleagues to derive corresponding values of 1.33 and 1.38 for 2- and 4-methylquinoline from the rates of deuteration [12]. As would be expected, in view of the correlations mentioned under *i*, a plot of log k_s for the cleavages of $RSiMe_3$ compounds against the σ^--values is a satisfactory straight line (Fig. 2), which has a slope of 4.1.

(iii) Values of σ^- for the picolyl and quinolylmethyl groups may be calculated from the rate data for the cleavage reaction using $-\log k_s$ for benzyltrimethylsilane and ρ estimated as follows. For cleavage of benzyltrimethylsilane at 50°C, $-\log k_s$ is reported as 6.32 in 66% [1], 6.45 in 84% [3] and 6.53 in 96% methanol * [1].

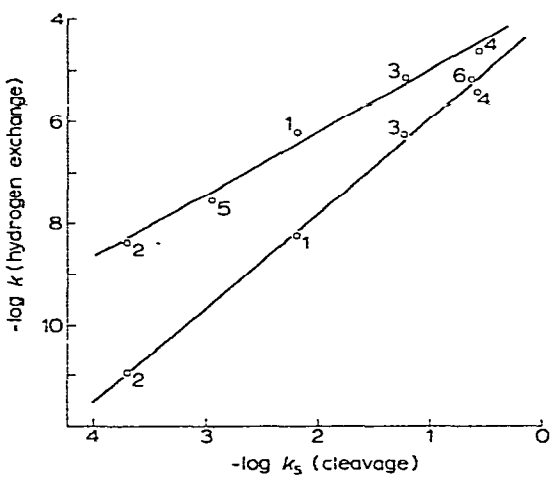

Fig. 1. Plot of log k for hydrogen exhange against log k_s for the cleavage. The numbering is as in Table 1. The upper line refers to detritiation in MeOH/NaOMe at 135°C [10] and the lower line to deuteration in EtOH/EtOK at 25°C [9].

* Where necessary the solvent volume composition has been calculated from the weight ratio and the densities of methanol and water: 61 : 39 w/w MeOH/H_2O is 66 : 34 v/v MeOH/H_2O (66% methanol) and 95 : 5 w/w is 96 : 4 v/v MeOH/H_2O (96% methanol).

TABLE 2

REACTIVITIES, k_{rel}, OF TRIMETHYLSILYLMETHYL-PYRIDINES AND -QUINOLINES, $RSiMe_3$, RELATIVE TO BENZYLTRIMETHYLSILANE, DERIVED σ^--VALUES, AND APPROXIMATE pK_a's OF CORRESPONDING CARBON ACIDS RH

No.	R	log k_{rel} [a]	σ^- [b]	σ^- [c]	σ^- [d]	pK [e]	pK [f]	pK [g]
1	2-$PyCH_2$	4.30	0.88	1.00	0.77	29	27	31
2	3-$PyCH_2$	2.78	0.57	0.59	0.65	34	30 [h]	
3	4-$PyCH_3$	5.25	1.08	1.17	0.96	27	25	29
4	2-$QnCH_2$	5.91	1.21	1.33		25	23	
5	3-$QnCH_2$	3.51	0.72			32		
6	4-$QnCH_2$	5.87	1.20	1.28		25	22.2 [i]	

[a] k_{rel} is the approximate reactivity (see text) in 90% methanol at 50°C relative to $PhCH_2SiMe_3$. [b] This work: calculated from log k_{rel} — 4.88 (see text). [c] From nucleophilic displacement of chloride in chloropyridines [11] and hydrogen exchange in methylquinolines [12]. [d] From hydrolysis of esters of pyridinecarboxylic acids. [e] On scale of ion-pair acidities in $CsNHC_6H_{11}$—$H_2NC_6H_{11}$ relative to pK_a of 9-phenylfluorene = 18.6 (see text). [f] From hydrogen-exchange, on a scale with fluorene 20.5, Ph_3CH 27.2, and Ph_2CH_2 28.6 [17]. [g] From ^1H NMR studies in liquid NH_3 [18]. [h] Derived by use of eq. 1 in ref. 17. The value is given as 28 in ref. 17, probably by error. [i] Direct measurement of ionization equilibrium.

It is evident that —log k_s changes relatively slowly with change in composition of the medium. For 90% methanol we have taken —log k_s to be 6.49, the mean of the values in 84% and 96% methanol. It seems unlikely that this value could be in error by more than 0.03. For cleavage of substituted benzyltrimethylsilanes k_{rel}, the rate relative to that for benzyltrimethylsilane is essentially invariant with change in composition of the medium in the relevant range. The best illustration is provided by the data for the *p*-CONHPh compound for which k_{rel} is 7034 in 66% and 7045 in 96% methanol [1]. It follows that ρ varies very little with change in composition of the medium in the range investigated, and for the cleavage in 90% methanol the value established for the reaction in 66% methanol [1,2], 4.88, may be used. It is unlikely that this value can be in error by as much as 0.1, since a difference of this amount in the ρ values for 66% and 96% methanol would result in a difference of 20% in k_{rel} for the *p*-CONHPh compound in the two media *. Values of log k_{rel} and derived σ^--values for the picolyl and quinolylmethyl groups are shown in Table 2.

(iv) For the 2- and 4-picolyl groups the σ^--constants are greater, by 0.11 and 0.12 units respectively, than the mean values of the σ-constants obtained from (a) the base-catalysed hydrolysis of the ethyl esters of the pyridinecarboxylic acids in aqueous ethanol [14,15] or aqueous acetone [16] and (b) the hydrolysis of the methyl esters in aqueous methanol [15,16] or aqueous dioxan [16] (Table 2). The differences between σ and σ^-, while significant, are markedly smaller than that for the *p*-NO_2 group, viz. 0.56. Our σ^--values for the 2- and 4-picolyl groups are significantly smaller than the σ^--values derived by Liveris and Miller [11]. Likewise, for the 2- and 4-quinolylmethyl groups our values are smaller than those reported by Zatsepina and her colleagues, but their values were derived by correlation of the rates of hydrogen exchange of picolines and their *N*-oxides with the σ^--values given by Liveris and Miller, and thus constrained to be on the same scale as the latter. Fig. 2 represents an analogous correlation

* The value of ρ is in the region of 5.0 in 100% MeOH [13].

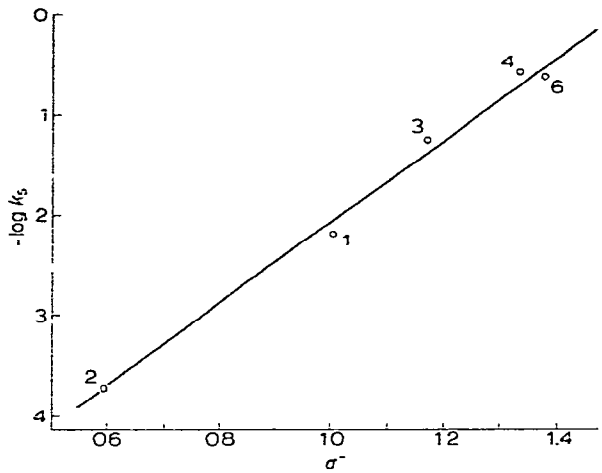

Fig. 2. Plot of log k_s for cleavage of $PyCH_2SiMe_3$ and $QnCH_2SiMe_3$ against σ^-. The numbering is as in Table 2.

for the silane cleavage data. If these previously reported σ^--values [11,12] were appropriate for the cleavage reaction then the slope of the plot in Fig. 2, viz. 4.1, would be ρ. It is evident that this value is much too low *, and that the σ^--values derived from the reaction of chloropyridines with methoxide ion are not appropriate for the silane cleavage. They may also be inappropriate for the hydrogen-exchange, but insufficient information is available to determine this.

It is relevant to note that the Liveris and Miller σ^--value for 4-$PyCH_2$, viz. 1.17, implies that the reactivity of 4-$PyCH_2SiMe_3$ would be very close to that of *p*-$NO_2C_6H_4CH_2SiMe_3$ ($\sigma^- = 1.24$); for $\rho = 4.1$ the predicted *p*-$NO_2C_6H_4CH_2SiMe_3$: 4-$PyCH_2SiMe_3$ reactivity ratio would be 1.9, and for $\rho = 4.88$ it would be 2.2. Use of our σ^--value of 1.08 implies a larger ratio, viz. ca. 6 (for $\rho = 4.88$). The rate constant for *p*-nitrobenzyltrimethylsilane is 0.88 l mol^{-1} s^{-1} at 50° C in 66% MeOH [1], and a value of 0.70 l mol^{-1} s^{-1} can be estimated for 100% MeOH from the k_s value of 0.076 l mol^{-1} s^{-1} at 20°C [17] by use of the activation energy for 66% MeOH [1] **. Thus a value of ca. 0.8 l mol^{-1} s^{-1} seems probable for the medium used for the picoline derivatives, and so *p*-nitrobenzyl- is ca. 13.8 times as reactive as 4-picolyl-trimethylsilane.

(v) From the plot [4] of log k_{rel} for cleavage of $RSiMe_3$ compound against the pK_a's of the corresponding carbon acids RH for ion-pair acidities in $CsNHC_6H_{11}$, approximate pK_a's can be derived for the picolines and methylquinolines and these are listed in Table 2. Some pK_a values derived by other indirect methods [18,19] are also shown for comparison; the agreement is not good, but

* If ρ were as low as 4.1 in 95% methanol, then k_{rel} for cleavage of $PhNHCOC_6H_4CH_2$—$SiMe_3$ would change by a factor of 5 in going from 66% to 95% methanol. The significance of the slope of the line in Fig. 2 is heavily dependent on the accuracy of the σ^--constant for 3-$PyCH_2$, which also greatly influences the accuracy of the Zatsepina values for 2- and 4-$QnCH_2$. The slope of the line defined by points 1 and 3 only in Fig. 2 is 5.6.

** The k_s value of 7600 X 10^{-5} l mol^{-1} s^{-1} was stated in error in ref. [7] to refer to 25°C; it was actually measured at 20°C.

TABLE 3

CLEAVAGE OF PYRIDYL- AND QUINOLYL-TRIMETHYLSILANES' $RSiMe_3$, BY SODIUM HYDROXIDE IN 4 : 1 v/v Me_2SO/H_2O AT 50.0°C

R	λ (nm)	$10^2[HO^-](M)$ [a]	k (s^{-1})	k_S ($l\ mol\ s^{-1}$)
2-Py	270	8.0	4.25×10^{-4}	5.3×10^{-3}
3-Py	268	8.0	1.20×10^{-3}	1.49×10^{-2}
		4.0	6.1×10^{-4}	1.52×10^{-2}
4-Py	273	2.0	8.9×10^{-4}	4.45×10^{-2}
2-Qn	319.5	8.0	6.7×10^{-3}	8.4×10^{-2}
3-Qn	318.5	8.0	5.4×10^{-3}	6.75×10^{-2}
		4.0	2.65×10^{-3}	6.6×10^{-2}
4-Qn	319	1.00	9.7×10^{-3}	9.7×10^{-1}

[a] Derived from the concentration of aqueous alkali assuming a 5-fold dilution.

the apparent discrepancies originate in part from different choices of pK_a values for the acids used as references. Our values relate ultimately to the use of a pK_a of 18.6 for 9-phenylfluorene as the standard, now a fairly well established practice [20].

Pyridine and quinoline derivatives

The pyridyl- and quinolyl-trimethylsilanes are cleaved too slowly for convenient study by aqueous methanolic alkali, and so a mixture of 4 vol. of dimethylsulphoxide with 1 vol. of aqueous sodium hydroxide was used. (Since the usual spectrophotometric method could be used to follow the reactions, only small concentrations of the organosilanes were used.) 2-Trimethylsilylpyridine is known to be cleaved by neutral water or alcohols [8] *, but we found no significant cleavage by neutral 4 : 1 v/v Me_2SO/H_2O at 50°C.

The results are shown in Table 3, and it will be seen that the sequence of reactivity (where Py = pyridine and Qn = quinoline) is 4-Qn > 2-Qn > 3-Qn > 4-Py > 3-Py > 2-Py. The presence of the fused benzo-ring in the quinoline system would be expected to increase the dispersal of the excess of negative charge formed on the heterocyclic ring in the transition state, and so raise the reactivity, as observed. The effect is markedly greater for the 2- and 4-positions (and especially large for the latter) than for the 3-position, so that the 2-position of quinoline is more reactive than the 3-, while the 4-position is exceptionally reactive. For the pyridine positions the same sequence of reactivity, 4 > 3 > 2, was observed in base-catalysed hydrogen-exchange [22,23], but the agreement no longer holds when the quinoline positions are included, the sequence in hydrogen-exchange being 3-Qn > 4-Py > 2-Qn, 3-Py > 2-Py [22]. The disagreement between the sequences for cleavage and exchange means that the relative reactivities cannot be determined in both cases (if in either) solely by the stabilities of the corresponding aryl carbanions, and so discussion of the sequences for the cleavage exclusively in terms of such stabilities, as is usual for hydrogen-exchange

* In view of the analogy between cleavage and hydrogen-exchange, it is noteworthy that hydrogen-exchange occurs at the 2-position of pyridine in neutral water, though at 218°C [21]. Initial protonation at nitrogen is suggested for the exchange [21] whereas a multi-centre process involving the neutral solvent molecule is favoured for the desilylation [8], and we must wonder whether a common mechanism is not more likely.

[22,23], is unlikely to be illuminating. It has been previously suggested that in the cleavage (and possibly also in the exchange a free carbanion may not be formed, there being instead proton transfer from the solvent to the (notionally) forming carbanion centre as the trimethylsilyl group (or the proton) is removed from it by base [5]. On this picture the ease of electrophilic attack at the relevant ring position will also have an influence on the rate, and such a factor could account in part for the relatively high reactivities at the 3-positions of pyridine and quinoline, since these are the most reactive positions towards electrophiles [24]. However, there is little doubt that much carbanion character will be developed in the transition state in both cleavage and exchange, and the low reactivity of the 2-position, for example, can plausibly be accounted for in terms of repulsion between the lone pair on the carbanion centre and that on the adjacent nitrogen atom [22,23].

Experimental

General

^{1}H NMR spectra were recorded on CCl_4 solutions with $SiMe_4$ as internal standard. Mass spectra were recorded at 70 eV.

Trimethylsilylpyridines

(a) A mixture of 2-chloropyridine (50 g, 0.44 mol), trimethylchlorosilane (48 g, 0.44 mol), and tetrahydrofuran (THF) (350 cm^3) was added during 6 h to magnesium turnings (13.5 g, 0.55 mol) in THF (200 cm^3). The mixture was stirred for 8 h at room temperature and then 2 h under reflux. THF (400 cm^3) was distilled off, benzene (250 cm^3) was added, the mixture was boiled under reflux for 1 h, and the liquid was decanted. The addition of benzene, boiling for 1 h, and decantation was repeated twice more, then the extracts were combined and fractionated to give 2-trimethylsilylpyridine (23 g, 34%), b.p. 59—60°C/1.3 kPa (lit. [8], b.p. 69°C/1.9 kPa). ^{1}H NMR: τ 1.32 (H_6) (m, 1H), 2.52 (H_3, H_4) (m, 2H), 2.92 (H_5) (m, 1H), 9.70 (CH_3) (s, 9H). Mass spectrum, *m/e* (relative intensity): 151 (51, *P*). 136 (100, $P - CH_3$), 106 (19).

(b) A solution of 3-bromopyridine (33 g, 0.21 mol) in ether (200 cm^3) was added with stirring during 20 min to n-BuLi (21 g, 0.27 mol) in ether (250 cm^3) cooled in a mixture of dry-ice and acetone. The mixture was stirred for 20 min, then trimethylchlorosilane (30 g, 0.27 mol) in ether (50 cm^3) was added dropwise. The mixture was allowed to warm to room temperature, and then boiled under reflux for 1 h. After treatment with aqueous ammonium chloride, the ethereal layer and ether washings were dried and fractionated, to give 3-trimethylsilylpyridine (12 g, 39%), b.p. 72—73°C/1.3 kPa (lit. [8] b.p. 94°C/4 kPa). ^{1}H NMR: τ 1.41 (H_2) (m, 1H), 1.58 (H_6) (m, 1H), 2.33 (4H) (m, 1H), 2.87 (H_5) (m, 1H), 9.73 (CH_3) (s, 9H). Mass spectrum, *m/e* (relative intensity): 151 (42, *P*), 136 (100, $P - CH_3$), 106 (12).

(c) From 4-bromopyridine, by the method described for the 3-isomer, was made 4-trimethylsilylpyridine (37%), b.p. 72—76°C/1.3 kPa (lit. [8], b.p. 107°C/6.4 kPa). ^{1}H NMR: τ 1.40 (H_2 and H_6) (m, 2H), 2.55 (H_3 and H_5) (m, 2H), 9.63 (CH_3) (s, 9H). Mass spectrum, *m/e* (relative intensity): 151 (44, *P*), 136 (100, $P - CH_3$), 106 (8).

Trimethylsilylquinolines and their hydrochlorides

(a) From 2-quinoline, by the method used for 2-trimethylsilylpyridine, was made 2-trimethylsilylquinoline (14%), b.p. 86—88°C/65 Pa. ^{1}H NMR: τ 1.7—2.8 (ArH) (m, 6H), 9.58 (CH_3) (s, 9H). Mass spectrum, *m/e* (relative intensity): 201 (54, *P*), 186 (100, $P - CH_3$), 156 (8). The hydrochloride had m.p. 160—161°C (Found: C, 60.8; H, 7.0; N, 5.9. $C_{12}H_{16}NSiCl$ calcd.: C, 60.6; H, 6.8; N, 5.9%.)

(b) From 3-bromoquinoline, by the method used for 3-trimethylsilylpyridine, was made 3-trimethylsilylquinoline (49%), b.p. 97—98°C/65 Pa. ^{1}H NMR: τ 0.95 (H_2) (d, 1H), 1.7—2.5 (ArH) (m, 5H), 9.58 (CH_3) (s, 9H). Mass spectrum *m/e* (relative intensity): 201 (54, *P*), 186 (100, $P - CH_3$), 156 (5). The hydrochloride had m.p. 169—170°C. (Found: C, 60.8; H, 6.9; N, 6.0%.)

(c) From 4-bromoquinoline, by the method used for 3-trimethylsilylpyridine, was made 4-trimethylsilylquinoline (36%), b.p. 114—116°C/65 Pa. The product was further purified by elution from silica gel with 5% ether/pentane. ^{1}H NMR: τ 1.20 (H_2) (d, 1H), 1.8—2.9 (ArH) (m, 5H), 9.45 (CH_3) (s, 9H). Mass spectrum, *m/e* (relative intensity): 201 (37, *P*), 186 (100, $P - CH_3$) 156 (5). The hydrochloride had m.p. 136—137°C. (Found: C, 60.9; H, 7.0; N, 5.8%.)

Trimethylsilylpicolines

(a) Phenyllithium was prepared from bromobenzene in ether [25]. Di-isopropylamine (101 g) was added to the ethereal phenyllithium (1 mol) at such a rate as to maintain gentle reflux [26]. 2-Picoline (93 g) in ether (100 cm^3) was added to the refluxing solution, and then trimethylchlorosilane (108 g) in ether (100 cm^3) was added as quickly as possible. The mixture was stirred under reflux overnight, then cooled, and added to water, The etheral layer was separated, dried, and distilled to give 2-(trimethylsilylmethyl)pyridine (75 g, 51%) b.p. 39—40°C/65 Pa (lit. [7] b.p. 191—192°C). ^{1}H NMR: τ 1.63 (H_6) (m, 1H), 2.60 (H_4) (m, 1H), 3.12 (H_3 and H_5) (m, 2H), 7.70 (CH_2) (s, 2H), 9.99 (CH_3) (s, 9H). Mass spectrum, *m/e* (relative intensity): 165 (10, $P - H$), 150 (98, $P - CH_3$), 120 (8), 93 (9), 73 (100, Me_3Si^+).

(b) From 3-picoline, by the method used for the 2-isomer, was obtained 3-(trimethylsilylmethyl)pyridine (20%), b.p. 49—50°C/65 Pa. A sample was further purified by recrystallizing the picrate and then reliberating the amine. ^{1}H NMR: τ 1.77 (H_2 and H_6) (m, 2H), 2.4—3.2 (H_4 and H_5) (m, 2H), 8.00 (CH_2) (m, 2H), 10.03 (CH_3) (s, 9H). Mass spectrum, *m/e* (relative intensity): 165.097 (39, $^{12}C_9{}^1H_{15}{}^{14}H^{28}Si$ = 165.090), 150 (10, $P - CH_3$), 120 (2), 93 (3), 73 (100, Me_3Si^+). The picrate had m.p. 130—131°C. (Found: C, 45.8; H, 4.6; N, 14.2. $C_{15}H_{18}O_7N_4Si$ calcd.: C, 45.7; H, 4.6; N, 14.2%.)

(c) Similarly, from 4-picoline, was obtained 4-(trimethylsilylmethyl)pyridine (31%), b.p. 66—67°C/65 Pa, (lit. [7] b.p. 74°C/600 Pa. ^{1}H NMR: τ 1.67 (H_2 and H_6) (m, 2H), 3.08 (H_3 and H_5) (m, 2H), 7.96 (CH_2) (s, 2H), 10.05 (CH_3) (s, 9H). Mass spectrum, *m/e* (relative intensity): 165 (46, *P*), 150 (13, $P - CH_3$), 120 (4), 93 (9), 73 (100, Me_3Si^+).

(d) Similarly, from 2-methylquinoline, was obtained 2-(trimethylsilylmethyl)-quinoline (32%), b.p. 93—94°C/65 Pa. ^{1}H NMR: τ 1.9—3.1 (ArH) (m, 6H), 7.45 (CH_2) (s, 2H), 9.92 (CH_3) (s, 9H). Mass spectrum, *m/e* (relative intensity): 215.108 (18, $^{12}C_{13}{}^1H_{17}{}^{14}N^{28}Si$ = 215.113), 214 (55, $P - H$), 200 (44, $P - CH_3$), 170 (16), 143 (76), 73 (100, Me_3Si^+).

(e) Similarly from 3-methylquinoline was obtained 3-(trimethylsilylmethyl)-quinoline (8%), b.p. 133—139°C/65 Pa. A sample was further purified by elution from silica gel with 10% ether/pentane. ^{1}H NMR: 1.42 (H_2) (d, 1H), 1.96 (H_8) (m, 1H), 2.2—2.26 (ArH) (m, 4H), 7.74 (CH_2) (s, 2H), 9.90 (CH_3) (s, 9H). Mass spectrum *m/e* (relative intensity): 215.116 (21, *P*), 200 (6), 170 (8), 143 (14), 73 (100).

(f) Similarly, from 4-methylquinoline, was obtained 4-(trimethylsilylmethyl)-quinoline (29%), b,p. 121—122°C/65 Pa. ^{1}H NMR: τ 1.35 (H_2) (d, 1H), 3.03 (H_3), (d, 1H), 1.8—2.7 (ArH) (m, 4H), 7.45 (CH_2) (s, 2H), 9.98 (CH_3) (s, 9H). Mass spectrum, *m/e* (relative intensity): 215.113 (25, *P*), 200 (5), 170 (3), 143 (32), 73 (100).

Rate measurements

The purities of the organosilane samples were checked by GLC on SE 30 and on PEGA (for $ArSiMe_3$) or F.F.A.P. (for $ArCH_2SiMe_3$) columns. The only detectable impurities were the corresponding ArH or $ArCH_3$ compounds, and <5% of these were present.

(i) For cleavage of the (trimethylsilylmethyl)arenes, the organosilane (0.40 cm^3) was added to 5 cm^3 of a mixture at 50°C made up from methanol (4.5 cm^3), aqueous sodium hydroxide (0.5 cm^3, 0.20—0.50 *M*), and 0.10 g (for picoline derivatives) or 0.06 g (for quinoline derivatives) of toluene. The mixture was kept in a thermostat at 50.0°C, and at suitable intervals 0.50 cm^3 samples were withdrawn and added to an ice-cold mixture of distilled water (0.50 cm^3) and pentane (0.50 cm^3). After shaking, the pentane layer was separated and stored at 0°C until analysed. Analyses were carried out with a 3 m × 0.15 cm column of 3% SE30 on Varaport 40 at 45°C, and the combined areas of the $(Me_3Si)_2O$ and Me_3SiOMe peaks were expressed as a fraction of the toluene peak for each sample. The heterocyclic product was shown in each case by its ^{1}H NMR spectrum to be the corresponding picoline or methylquinoline. Good first order kinetics were observed. The values of k listed in Table 1 are the means of several determinations, and are estimated to be accurate to within ±4%. In deriving the specific rate constants, k_s (= $k/[OH^-]$), the base concentration in the reaction medium was assumed to be one-tenth of that of the aqueous alkali taken.

(ii) With the trimethylsilylarenes, the organosilane (0.0160 cm^3) was added with shaking to 25 cm^3 of a solution, at 50.0°C, made up from 1 vol. of aqueous sodium hydroxide (0.10—0.40 *M*) and 4 vol. of dimethylsulphoxide. A portion was transferred to a water-jackered cell maintained at 50.0°C in the spectrophotometer. The progress of the reaction was followed by the change in the absorption at the wave-length shown in Table 3. The product in each case was shown to be pyridine or quinoline by its UV and ^{1}H NMR spectra.

First order rate constants were evaluated by a least squares fit [27] of the exponential form of the first-order rate eq. 1 to the observed absorbance values, *Y*.

$$Y_c = P_1 \times \exp(-P_2/t) + P_3 \quad (1)$$

Trial parameters (P_1, the infinite time absorbance; P_2, the rate constant; P_3, the zero time absorbance) were refined by an iterative process which minimized

the sum of the squares of the deviations of the observed absorbance, Y, from the calculated absorbance, Y_c. The mean rate constants, K, (derived from 3—5 runs) listed in Table 3 are estimated to be accurate to within ±2%. In deriving the specific rate constant, k_s (= $k/[OH^-]$) the base concentration in the reaction medium is assumed to be one-fifth of that in the aqueous sodium hydroxide taken.

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