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The modification of reactivity at silicon centre by a remote phosphorus group

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Abstract

The compounds $X(CH_2)_nSiMe_2(OPh)$ ($X = H$, $n = 2, 3$; $X = PPh_2$, $n = 1, 2, 3$; $X = P(O)Ph_2$, $n = 2, 3$; $X = P(S)Ph_2$, $n = 1, 2, 3$) having silicon and phosphorus bridged by carbon chains, have been synthesized. The kinetics of acid- and base-catalysed solvolytic cleavage of phenoxyl group from these compounds in methanol have been investigated. The kinetic results obtained in the presence of bases can be interpreted in terms of polar and steric effects alone, but there was an unexpected enhancement of the reactivity in the case of the P=O-containing substrates in the acidic media. The solvent kinetic isotope effects are best interpreted in terms of participation by the P=O group as a base rather than as a nucleophile attacking the silicon centre.

Introduction

There has been a considerable interest in the chemistry of compounds containing both silicon and phosphorus since they are often used as reagents or appear as intermediates in synthesis [1,2]. The knowledge of the effect of the linked phosphorus group on the reactivity at the silicon centre is important for understanding of the unusual chemistry of phosphorus and silicon containing compounds. This effect can appear complex, since direct or indirect coordination of a phosphorus group to a silicon centre may modify the reactivity. Phosphorus compounds, particularly those with phosphine or oxyphosphoryl centres, are known to be able to interact intermolecularly with electrophilic silicon centres [3–6]. Analogous intramolecular interaction could be expected to lead to anchimeric assistance to substitution at silicon, analogous anchimeric assistance involving P^{III} has been observed in substitutions at carbon atom [7]. Intramolecular interaction of amine group with silicon has been found to enhance the reactivity at silicon center [8,9]. Intramolecular coordination may influence the ability of phosphorus groups to enter into hydrogen bonding or undergo protonation.

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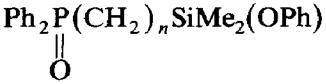
The aim of this study was to examine how various phosphorus substituents $\geqslant$P:, $\geqslant$P=O, $\geqslant$P=S affect the rate of nucleophilic substitution at silicon atom in a solvolytic system when they are linked to the silicon by methylene or polymethylene bridge. For this purpose the kinetics of acid- and base-catalysed solvolytic cleavage of phenoxyl group were studied for the following model compounds:

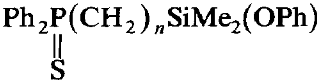
$Me(CH_2)_nSiMe_2(OPh)$ (I) — (**1**) $n = 1$, (**2**) $n = 2$

$Ph_2P(CH_2)_nSiMe_2(OPh)$ (II) — (**3**) $n = 1$, (**4**) $n = 2$, (**5**) $n = 3$



$Ph_2P(=O)(CH_2)_nSiMe_2(OPh)$

(III) — (**6**) $n = 2$, (**7**) $n = 3$



$Ph_2P(=S)(CH_2)_nSiMe_2(OPh)$

(IV) — (**8**) $n = 1$, (**9**) $n = 2$, (**10**) $n = 3$

Phenoxyl was used as the leaving group in these models since earlier studies [10] have shown that this group undergoes a ready first order solvolytic cleavage which can be conveniently monitored by UV spectroscopy.

It is relevant to note that compounds having structures analogous to those of our models, namely functionalized silanes having phosphine groups connected to silicon through polymethylene bridges, are used for immobilizing catalysts on insoluble supports [11].

Results and discussion

Kinetic studies

The rates of acid- and base-catalysed solvolytic cleavage of phenoxy group from compounds **1–10** in methanol were determined by UV spectrometry. The change in the absorption on formation of phenol or phenoxide ion was monitored at the appropriate wavelength. In all cases first order kinetic curves were obtained, and the rate constants determined by the Guggenheim method. According to Akerman [10a] the process is subject to general acid–base catalysis. Since the reactions of our compounds in pure neutral methanol are very slow compared to those catalyzed by the base or the acid used, the spontaneous solvolysis was neglected. The acid-catalyzed solvolysis in methanol was examined in the presence of 10^{-4}–10^{-3} *M* HCl in methanol prepurified by careful distillation from picric acid [12]. The kinetic data were satisfactorily reproducible. The specific rate constants were found to be proportional to the catalyst concentration. Activation parameters were determined from measurements at four temperatures. The data are summarized in Table 1.

Attempts to use sodium methoxide as the base catalyst failed since the reproducibility of the rate constants was poor, and so a trimethylamine-trimethylammonium chloride buffer system was used. In order to get information about the extent to which the relative reactivities of substrates **1–10** are influenced by the medium, the kinetics were also studied in 9/1 v/v propanol/water system in the presence of

Table 1

Kinetic results for the solvolysis of phosphorus substituted trialkylphenoxysilanes $X(CH_2)_nSiMe_2(OPh)$ in methanol in the presence of HCl, 25 °C. (HCl concentration was in the range 0.4 to 10×10^{-4})

Compound			Catalytic constant	Relative rates	k_H/k_D	Activation parameters	
X	n	Number	k_H^{+} (dm^3 mol^{-1} s^{-1})			$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)
CH_3	1	**1**	40.3	1.000	0.94	9.1	−22.7
Ph_2P	1	**3**	5.64	0.14			
Ph_2P	2	**4**	34.2	0.85	0.71	10.6	−18.1
Ph_2P	3	**5**	40.7	1.01		11.2	−15.5
$Ph_2P(O)$	2	**6**	592	14.7	1.08	8.7	−18.7
$Ph_2P(O)$	3	**7**	87.3	2.17		9.9	−18.5
$Ph_2P(S)$	1	**8**	1.07	0.03		9.2	−29.4
$Ph_2P(S)$	2	**9**	23.7	0.59	1.09	10.0	−20.7
$Ph_2P(S)$	3	**10**	32.9	0.82		10.9	−17.1

glycine-sodium glycinate buffer. Since in this medium there is ca. 30% of water on a molar basis, and since the reaction is known to be subject to steric effects [10b], OH^- is assumed to be the reactive nucleophile.

Ionic strengths were kept constant by addition of lithium chloride. Some experiments were repeated and the reproducibility of results was good. The data were in accord with the catalysis by lyate ion; in particular, the rate remained constant upon variation of the base and the salt concentration at a constant buffer ratio.

The specific rate was proportional to the buffer ratio only over a limited catalyst concentration range. The catalytic constants corresponding to the cleavage by lyate ion in methanol were determined from the slope of this dependence over its linear range. In the case of the glycine buffer in propanol-water system, however, values of the first order rate constants observed for the substrates **1**–**10** were directly compared at a selected value of the buffer ratio. The results are presented in Table 2.

Mechanism in acidic media

The most interesting aspect of the results obtained for acidic media lies in the operation of a special effect of a remote phosphorus group on the reactivity. Akerman [10b] showed that the reaction involves an S_N2 displacement at silicon and is retarded by electron-withdrawing substituents in the phenoxyl group. Electron-withdrawing substituents in the alkyl groups on silicon can also thus be expected to lower the rate, and this is observed in the case of the thiophosphoryl and phosphine groups. Steric effects in general change the reactivity in the same direction, i.e. the rate should fall on introduction of the phosphorus-containing group, in line with the observed behaviour. However, there was an enhancement of the reactivity by the oxyphosphoryl substituent, indicating that this group supplies assistance as a result of some direct or indirect interaction with the silicon centre. The comparison of ^{29}Si, ^{31}P and ^{1}H NMR spectra of model compounds (Table 4) leads us to conclude that there is no coordination of the phosphorus group to the silicon atom; in particular all compounds studied have the ^{29}Si NMR signal in the region characteristic of tetracoordinate silicon, with the chemical shift values very

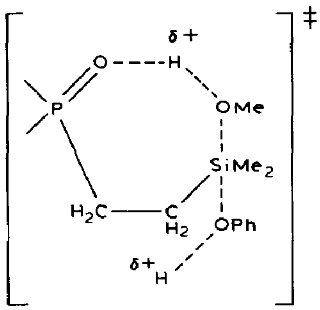
Table 2

Kinetic data for the solvolysis of phosphorus-substituted trialkylphenoxysilanes in methanol at 25 °C in the presence of $Me_3N/Me_3N \cdot HCl$ buffer [a] and in 9/1 v/v propanol-water at 30 °C in the presence of glycine buffer [b], ionic strength $\mu = 0.05$.

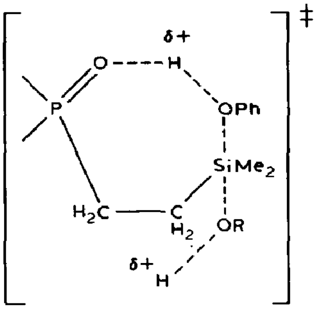
Compound	In methanol				In propanol-water			
	Catalytic rate constants [d] $k_1 \times 10^4$ (dm^3 mol^{-1} s^{-1})	Relative rates	Activation parameters $\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (e.u.)	First order rate constants obsd. [e] $k \times 10^4$ (s^{-1})	Relative rates	Activation parameters [c] $\Delta H^\ddagger$ (kcal mol^{-2})	$\Delta S^\ddagger$ (e.u.)
1	0.91	1.000	4.6	−61	4.05	1.000	8.3	−47
3	1.73	1.91	4.1	−62	20.1	4.96		
4	2.65	2.92	4.4	−60	11.5	2.83	7.9	−46
5	1.41	1.55	5.8	−57	6.01	1.46		
6	10.3	11.36	3.6	−60	132	32.5	5.7	−49
7	2.84	3.13	4.0	−65	19.2	4.84		
8	1.82	2.01	5.6	−57	189	46.6		
9	9.73	10.73	4.1	−59	77.5	19.2	3.9	−55
10	2.93	3.23	5.1	−58	15.8	3.90		

[a] The buffer ratio was in the range 2 to 10, $[Me_3N \cdot HCl] = 5.00 \times 10^{-2}$ mol dm^{-3}. [b] [glycine] $= 10 \times 10^{-3}$ mol dm^{-3} [sodium glycinate] $= 1.0 \times 10^{-2}$ mol dm^{-3}. [c] $\Delta H^\ddagger$ and $\Delta S^\ddagger_{25°}$ were determined to the precision of ±0.5 kcal/mol and ±2. e.u., respectively. [d] Determined as a slope of $k_{obsd} = f$ (buffer ratio). [e] Determined from kinetic curve.

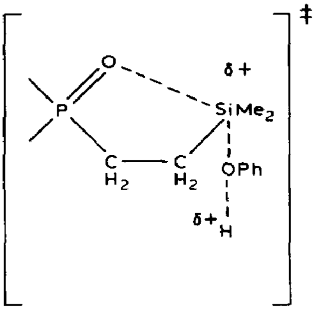
close to that of the unsubstituted compound **1**. The temperature-induced chemical shift is very small, again indicating that there is no coordination to Si [13]. Thus the interaction must take place during the reaction, and be reflected in the transition state.



(A)

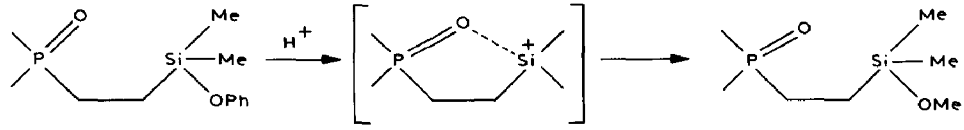


(B)



(C)

Two possiblities seem feasible. First, the P=O group may intervene as a base to stabilize the charge formed on the attacking nucleophile (structure **A**) or on the leaving group (structure **B**). The P=O group is known to be a good proton acceptor in hydrogen bonding, and may stabilize the ancipient proton more effectively than does the solvent. Second, the P=O group may interact directly with silicon atom, (structure **C**), anchimerically assisting the solvolysis. However, in this case the participation by the P=O group would markedly change the mechanism of the process, which would involve an intermediate with tetracoordinate silicocationic charulist (eq. 1).



(1)

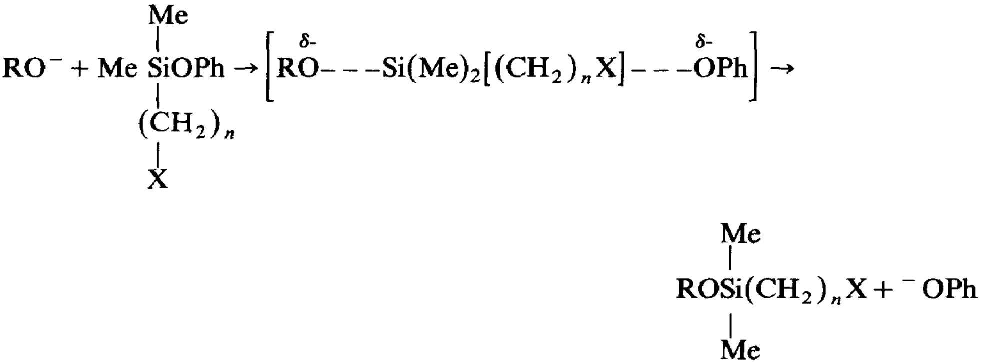
In this mechanism the nucleophile would not be involved in the transition state, and this should lead to a higher value of activation entropy than that associated with the mechanism involving attack of base and presumably also than that for the mechanism not involving phosphorus group assistance. The entropy of activation does, in fact, change in this direction of going from unsubstituted analogue to the P=O substrate, but the variation of the activation parameters in the series is small in relation to the error limits, and cannot be regarded as conclusive.

The solvent kinetic isotope effect gives a better indication of mechanism. The k_H/k_D value is expected to be lower for the pathway 1 since in the transition state the positive charge is concentrated mostly on the silicon atom; in terms of Schowen's simplified analysis [14] k_H/k_D should have a value well below 1.0 (0.44 in the limiting case). On the other hand base assistance by the P=O group should lead to a k_H/k_D value close to one, and close to the value for the unassisted mechanisms (substrate **1**). In both cases the charge is concentrated on hydrogen atoms as in the initial reactant state. The value of k_H/k_D for the P=O substrate **5** is slightly above 1, and is slightly larger than that for the unsubstituted analogue, which strongly supports the base-assisted pathway.

The effect of the rate enhancement by the P=O group decreases with the elongation of the polymethylene bridge between silicon and phosphorus. It is much smaller for substrate **6** ($n = 3$), and presumably would be negligible for longer chains. Phosphines and phosphine sulfides are weak hydrogen bond acceptors compared with phosphine oxides. Consequently, if there is any assistance by the $\geqslant$P: and $\geqslant$P=S groups it is obscured by the polar and steric effects which are the main influences on the reactivity.

Mechanism in basic media

The kinetic data obtained in basic media can be understood on the ground of a classical S_N2 mechanism for substitution at silicon:



$$\mathrm{RO^- + Me\overset{Me}{\underset{\underset{X}{(CH_2)_n}}{Si}}OPh} \rightarrow \left[\overset{\delta-}{\mathrm{RO}}---\mathrm{Si(Me)_2[(CH_2)_nX]}---\overset{\delta-}{\mathrm{OPh}}\right] \rightarrow \mathrm{RO\overset{Me}{\underset{Me}{Si}}(CH_2)_nX + {}^-OPh} \quad (2)$$

(R is Me or H, X is a phosphorus group)

A mechanism involving formation of 5-coordinate silicon intermediate also seems feasible, particularly in view of the high activation entropy *. Some differences in the reactivity pattern for substrates **1–10** observed in the two media used, i.e. methanol and propanol-water, presumably reflect higher steric requirements of MeO^- compared with the OH^- that is the reactive nucleophile in the $PrOH/H_2O$ system. As expected, in all cases the phosphorus substituent increases the reactivity relative to that of the unsubstituted **1**. However, the variation of the rate constant as the phosphorus group or its position is varied is not large. This variation could be rationalized in terms of a combination of the polar effects of the phosphorus groups (which stabilize the partial negative charge on the silicon atom in the transition state and accelerate the reaction) and their steric effects, which operate in the opposite direction. The steric effects are manifested in a lower reactivity of some reactants having phosphorus in the α-position. This is particularly evident when the nucleophile and the phosphorus group have larger steric requirements, i.e. for MeO^- and $Ph_2P(S)$. Phosphorus substituents in the β and γ positions modify the reactivity at the silicon centre mostly by the inductive effect, which is known to be similar for $Ph_2P(O)CH_2$ and $Ph_2P(S)CH_2$ substituents, which have $\sigma^* = 0.67$ and 0.68, respectively [15].

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* It should be remembered that the activation parameters cannot be interpreted straightforwardly since they involve parameters for the equilibrium $\equiv N + ROH \rightarrow \equiv\overset{+}{N}H + RO^-$. ΔH and ΔS for this process are negative, and this leads to a decrease in $\Delta H^{\ddagger}$ and an increase in the negative value of activation entropy for the overall process.

Experimental

Synthesis of model compounds

Model compounds of series II, III and IV for kinetic studies were synthesized by use of reactions 3–6:

$$Ph_2PH + CH_2{=}CH(CH_2)_nSiMe_2(OPh) \xrightarrow{AIBN} Ph_2P(CH_2)_{2+n}SiMe_2(OPh) \quad (3)$$

$(n = 0, 1)$

$$Ph_2PLi + Cl(CH_2)_nSiMe_2(OPh) \rightarrow Ph_2P(CH_2)_nSiMe_2(OPh) \quad (4)$$

$(n = 1, 3)$

$$Ph_2P(OMe) + Cl(CH_2)_nSiMe_2(OPh) \xrightarrow[-MeCl]{} Ph_2P(O)(CH_2)_nSiMe_2(OPh) \quad (5)$$

$$\begin{tikzcd} Ph_2P(CH_2)_nSiMe_2(OPh) \arrow[r, "BSPO"] \arrow[dr, "S_8"'] & Ph_2P(O)(CH_2)_nSiMe_2(OPh) & (6a) \\ & Ph_2P(S)(CH_2)_nSiMe_2(OPh) & (6b) \end{tikzcd}$$

Properties of all new compounds are presented in Tables 3 and 4.

All syntheses were carried out under dry nitrogen or argon. Solvents were purified by standard methods [12] and distilled before use. Chlorosilanes and diphenylphosphine were prepared by published procedures. The new phenoxysilanes **1** and **2** were obtained by the reaction of corresponding chlorosilanes and phenol in n-hexane in the presence of triethylamine. Purities of products were checked by GLC, as well as by MS and NMR spectroscopy. Analytical data are listed in Table 3.

Examples of synthetic procedures

[2-Dimethyl(phenoxy)silylethyl](diphenyl)phosphine (4) was synthesized by the reaction shown in eq. 3, which was used earlier for the preparation of some phosphines bearing silyl substituents in alkyl groups [16–19]. To the mixture of 20.6 g (0.11 mol) of diphenylphosphine and 18.6 g (0.1 mol) of vinyldimethylphenoxysilane was added a small amount (ca. 0.2 g) of azobis(isobutyro)nitrile (AIBN). The mixture was heated under argon at 100 °C for 2 h and then at 150 °C for 8 h. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. Distillation under reduced pressure gave 26 g (yield 72%) of **4**.

The analogous procedure starting from allyldimethylphenoxysilane gave phosphine **5** (yield 30%).

[Dimethyl(phenoxy)silylmethyl](diphenyl)phosphine (3) was synthesized by Capka method [20]. Finely cut lithium (4 g, 0.58 mol) was added to a solution of diphenylchlorophosphine (35 g, 0.16 mol) in tetrahydrofuran (150 ml). An exothermic reaction took place and the solution became deep-red. After 3 h heating, the solution of Ph_2PLi was cooled to room temperature, transferred to a dropping funnel and added slowly to a solution of chloromethyldimethylphenoxysilane (40 g, 0.2 mol) in tetrahydrofuran (160 ml) at 10 °C. The mixture was stirred for 3 h at room temperature and kept overnight, then partly evaporated and filtered. The filtrate was distilled under reduced pressure to give 11.3 g (yield 20%) of **3**. The by-products $(PhO)_2SiMe_2$, $(PhOSiMe_2)_2O$ and $Ph_2MeP(O)$ were isolated and identified.

Table 3

Properties and analyses of new compounds [a]

	b.p. (°C/mmHg) m.p. (°C)	Elemental analysis [b] (Found(calcd.)(%))				Method of preparation	Preparative yield (%)
		C	H	P	S		
$PrSiMe_2(OPh)$ (**2**)	122/15	68.03 (67.98)	9.25 (9.33)			[c]	90
$Ph_2PCH_2SiMe_2(OPh)$ (**3**)	136–138/2×10^{-2}	70.10 (71.39)	6.70 (6.61)	8.62 (8.83)		4	22
$Ph_2P(CH_2)_2SiMe_2(OPh)$ (**4**)	150–160/2×10^{-2}	71.60 (72.49)	6.70 (6.91)	8.52 (8.49)		3	72
$Ph_2P(CH_2)_3SiMe_2(OPh)$ (**5**)	158–162/8×10^{-3}	72.25 (72.98)	7.22 (7.19)	8.20 8.18)		3, 4	30
$Ph_2P(O)(CH_2)_2SiMe_2(OPh)$ (**6**)	172–174/8×10^{-3} (43–45)	68.38 (69.45)	7.01 (6.62)	7.99 (8.14)		6a	92
$Ph_2P(O)(CH_2)_3SiMe_2(OPh)$ (**7**)	186–194/8×10^{-3} (45–50)	68.94 (70.03)	7.08 (6.90)	7.66 (7.85)		6a	94
$Ph_2P(S)CH_2SiMe_2(OPh)$ (**8**)	178–180/10^{-2}	65.42 (65.93)	6.20 (6.06)	8.45 (8.10)	8.33 (8.36)	6b	86
$Ph_2P(S)(CH_2)_2SiMe_2(OPh)$ (**9**)	186–188/5 10^{-2} (55–60)	66.02 (66.63)	6.54 (6.35)	7.65 (7.81)	7.55 (8.08)	6b	91
$Ph_2P(S)(CH_2)_3SiMe_2(OPh)$ (**10**)	190–200/10^{-2}	66.52 (67.28)	6.84 (6.63)	7.80 (7.54)	7.90 (7.81)	6b	75
$AllMe_2SiOPh$	124/18	68.72 (68.69)	8.43 (8.39)			[c]	80
$Cl(CH_2)_3SiMe_2(OPh)$	93–95/4	58.03 (57.75)	7.60 (7.49)			[c]	83

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[a] All new compounds gave the expected mass spectra. [b] Elemental analyses were performed the Microanalytical Service of Centre of Molecular and Macromolecular Studies. [c] By reaction of appropriate chlorosilane with phenol; see Experimental section.

Table 4

NMR spectra, unless otherwise indicated in parentheses, the solvent was methylene chloride and the temperature 20 °C

Compound	^{29}Si NMR-proton decoupled		^{31}P NMR-proton decoupled	^{1}H NMR
	(ppm) [a]	J(Si–P) (Hz)	(ppm) [b]	(ppm) [c]
1	+20.20(s)		–	0.12(s)(MeSi); ~1(m)(EtSi)
	+21.31(s)(−90)			
2	+18.79(s)		–	0.18(s)(MeSi); ~1(m)(PrSi)
3	+17.05(d)	18.4	−24.72(s)(neat)	0.46(s)(MeSi); 1.95(s)(CH_2Si)
4	+18.93(d)	24.2	−10.88(s)(neat)	0.55(s)(MeSi); 1.2(m) and 2.5(m)($(CH_2)_2Si$)
	+19.89(d)(−90)	26.9(−90)		
5	+18.81(s)	–	−17.83(s)	0.58(s)(MeSi); ~1.3(m), ~2(m) and ~2.5(m)
	+19.56(s)(−80)	–		
6	+19.48(d)	25.6	+32.23(s)	0.25(s)(MeSi); ~1.0(m) and ~2.5(m)($(CH_2)_2Si$)
	+20.44(d)(−80)	27.0(−80)		
7	+18.59(s)(C_6H_6)		+29.82(s)	0.30(s)(MeSi); ~1.1(m), ~1.9(m) and ~2.3(m)
8	+15.37(s)	–	+36.06(s)	0.48(s)(MeSi); 2.54(d)(CH_2Si) J(PCH) = 17 Hz
9	+19.55(d)	29.3	+46.83(w)	0.35(s)(MeSi); ~1.2(m) and ~2.5(m)($(CH_2)_2Si$)
10	+18.79(s)	–	+41.95(s)	0.25(s)(MeSi); ~1.3(m), ~2.0(m) and ~2.5(m)

[a] s, singlet; d, doublet; m, multiplet. Recorded at 39.76 MHz in CH_2Cl_2/CD_2Cl_2 (or C_6H_6/C_6D_6) mixture with TMS as internal standard. [b] At 24.2 MHz with 85% H_3PO_4 as external standard. [c] At 80 MHz with TMS as internal standard.

A similar procedure starting from γ-chloropropyldimethylphenoxysilane gave **5** in 58% yield.

[2-Dimethyl(phenoxy)silylethyl]diphenylphosphine oxide (6). Bis(trimethylsilyl) peroxide (BSPO) (2.7 g, 0.015 mol) was added in portions to **4** (5.4 g, 0.015 mol) in 10 ml of benzene. The ^{31}P NMR spectrum of the reaction solution after the addition of BSPO showed that there had been complete conversion of **4** into **6**. The product was isolated by distillation.

Compound **5** was oxidized analogously to give **7** in theoretical yield.

It should be noted that the use of classical oxygenation reagents like molecular oxygen, ozone, N_2O_4 gave considerable amounts of by-products. Attempts to oxidize **3** with BSPO to the corresponding phosphine oxide failed; cleavage of the $Si-CH_2$ bond gave $Ph_2MeP(O)$ as the major product. (The use of BSPO for selective oxygenation of P^{III} centres was described in ref. 21.)

The Arbuzov reaction (eq. 5) was also used, in attempts to synthesis the phosphine oxide ($n = 1$), but did not give the desired product. This reaction was also unsuccessful for synthesis of the phosphine oxide ($n = 3$) **7**, giving only a very small yield. In both above cases diphenylmethylphosphine oxide was obtained as a result of the Arbuzov rearrangement product of the transiently formed $Ph_2P(OMe)$.

[Dimethyl(phenoxy)silyl-methyl](diphenyl)phosphine sulfide (8). A stoichiometric amount of freshly resublimed sulfur (0.64 g) was added to a solution of **3** (7 g, 0.02 mol) in 10 ml of benzene. A slightly exothermic reaction occurred, and after 2 h complete conversion of **3** into the sulfide had taken place (checked by ^{31}P NMR), and **8** was distilled under reduced pressure.

Similar reaction of sulfur with **4** and **5** gave theoretical yields of **9** and **10**.

The purities of all products used for kinetic studies were confirmed by NMR and mass spectroscopy. NMR spectra were recorded with JEOL JMN-Fx-60Ft (^{31}P, 24.2 MHz), Bruker WP 200SY (^{29}Si, 39.76 MHz), and Tesla BS 847C (^{1}H, 80 MHz) spectrometers. Mass spectra were determined with an LKB 2091 spectrometer.

Kinetic studies

All solvents and catalysts used in the kinetic studies were carefully purified by standard methods [12]. Methanol used for the studies in acidic media was also refluxed with picric acid and distilled from it through an efficient column.

Kinetic studies were performed with a Carl Zeiss Specord UV-VIS spectrophotometer fitted with thermostated cell holder. After the addition of a phenoxysilane to thermostated solution containing an appropriate amount of a catalyst the solvolysis was followed by monitoring the absorption at 35500 cm^{-1} (for basic medium) or 36000 cm^{-1} (for acidic medium) up to ca. 90% conversion of the substrate. Initial concentrations of phenoxysilanes were usually 3×10^{-4} mol dm^{-3}.

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