Tetrahedron Vol. 45, No. 9, pp. 2465–2524, 1989
Printed in Great Britain.

0040–4020/89 $5.00+.00
Pergamon Press plc

TETRAHEDRON REPORT NUMBER 251

SILYL ESTERS OF PHOSPHORUS COMMON INTERMEDIATES IN SYNTHESIS

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(*Received* 14 *March* 1988)

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1. INTRODUCTION

Silyl esters of phosphorus are a very broad and well known class of organophosphorus compounds. They are derivatives of phosphorus acids having at least one acidic hydrogen replaced by a triorganosilyl group or sometimes a silyl group of more complex structure. Earlier studies on the synthesis and the reactions of these esters up to 1968 were comprehensively reviewed by Borisov, Voronkov and Lukevits.[1] It was, however, only in the 1970s that the potential of silyl esters of phosphorus as intermediates in synthesis was widely recognized.

A considerable part of the synthetic application of silyl esters of pentavalent P(V) tetracoordinate phosphorus is connected with their use as precursors of phosphorus acids applied as bio-organic models.[2-5] The replacement of the alkyl ester groups by hydrolysable trimethylsilyl groups to convert P(V) esters into acids originates from Rabinovitz,[6] although the silylation of P(V) alkyl esters had been reported earlier.[7] This method found a broader application after 1975 following McKenna's proposal[8,9] to use trialkylsilyl bromides as very reactive silylating agents.

Direct silylation of phosphorus acids was first developed in order to facilitate their analysis by chromatography and mass spectroscopy particularly in nucleotide chemistry.[10-12] They are now often used for synthetic purposes. For example, the silylation of some acids which appear in the tautomeric form of tetracoordinate phosphorus converts them to P(III) compounds thus liberating an electron pair on phosphorus which makes it easier to carry out many reactions at the phosphorus centre.[13,14]

The chemistry of P(III) silyl esters extensively developed by Pudovik and by some other research groups has been partly reviewed.[15] Particularly fruitful has been the application of this chemistry by Hata for solving many synthetic problems in bio-organic chemistry.[16,16a]

These esters easily undergo the Arbuzov reaction,[17-19] the Perkow reaction,[20] addition to carbonyl groups,[21-24] to enones[25] and to other unsaturated systems.[26,27] They are also used for the synthesis of phosphorus esters having various functional and carbofunctional groups. Their reductive properties make them particularly useful in some deoxygenation reactions.[28]

Silyl esters of both P(III) and P(V) acids have been widely used for synthesis of various anhydrides of phosphorus acids which can then be applied in the synthesis of bio-organic models. This aspect of the chemistry of silyl esters of phosphorus has been extensively developed by Michalski and Skowrońska.[29-31]

Other applications should also be mentioned. For example silyl esters of phosphorus appear as intermediates during the synthesis of optically active phosphorus compounds.[31-33] Silyl phosphorus ester groups are introduced in some bio-organic models in order to study the stereochemistry and the mechanisms of reaction of these models.[34] Introduction of silyl ester groups to cyclic phosphorus monomers has made possible the synthesis of polyacids of phosphorus by ring opening polymerization followed by subsequent hydrolysis.[35] Applications in organic synthesis include the preparation of unsymmetrical ketones,[36] substituted carboxylic esters[37,38] and amines.[39] Silyl polyphosphates are used as promoters of many organic reactions[40] including dehydro-condensations and some rearrangements.

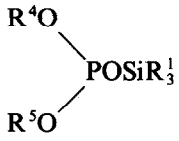
The spectrum of application of silyl esters of phosphorus is thus very broad and the synthetic importance of these compounds is still rapidly developing. The knowledge of their chemistry is scattered over areas of organic, inorganic and bio-organic chemistry. Although some aspects of these esters have been reviewed[1,1a,15,16,16a,41,42,323] there has been so far no attempt to look at silyl esters of phosphorus in a more comprehensive way. The purpose of this Report is to give an account of the most important synthetic applications of this class of compounds and of the most convenient methods for their synthesis in relation to their structural, chemical and physical properties. Although no pretence is made that all the literature on the subject has been included, we believe that the major aspects of the synthetically directed chemistry of silyl esters of phosphorus are mentioned.

2. STRUCTURE AND FUNDAMENTALS OF THE CHEMISTRY OF SILYL ESTERS OF PHOSPHORUS

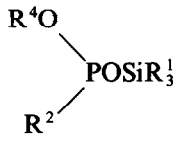
2.1. *Classification*

Any compound having silicon and phosphorus atoms bridged by oxygen, sulphur, or selenium could be classified as a silyl ester of phosphorus. In principle, the scope of this review will be limited to the basic classes of silyl esters of phosphorus represented by the general formulae given below.

Esters of tervalent tricoordinate phosphorus [P(III) esters]



silyl phosphites



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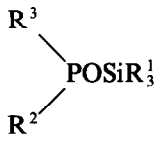
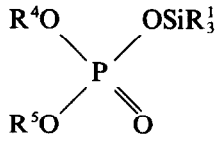
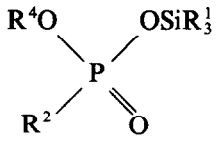


silyl phosphinites

Esters of pentavalent tetracoordinate phosphorus [P(V) esters]



silyl phosphates



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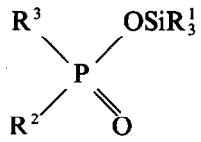


silyl phosphinates

Any oxygen atom may be replaced by a sulphur or selenium atom

R^1 is usually methyl, sometimes ethyl, phenyl or another organic group.
R^2 as well as R^3 is an organic group or hydrogen.
R^4 as well as R^5 is an organic group, hydrogen or a triorganosilyl group, most often R^1_3Si.

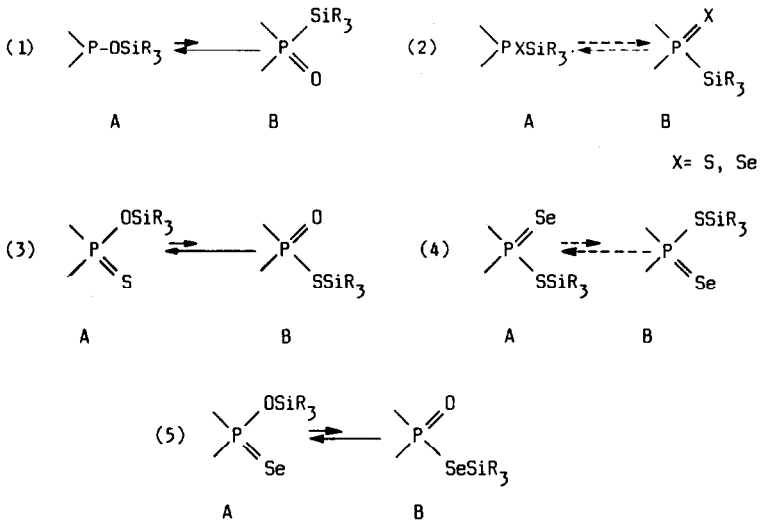
Some attention will also be devoted to silyl polyphosphates including pyrophosphates and to some other phosphorus anhydrides having silyl ester groups. Other structures may occasionally appear as is appropriate.

2.2 *Isomeric forms of silyl esters of phosphorus*

A silyl group may be attached to phosphorus acid residue in different ways, hence some silyl esters of phosphorus may appear as interconvertible isomers. The 1,2-migration of the silyl group in esters of tricoordinate phosphorus transforms these esters into tetracoordinate phosphorus species, eqs (1) and (2). The 1,3-migration in P(V) silyl esters may also lead to other isomeric forms, eqs (3), (4) and (5).

No study of the equilibria (1–5) has been reported. However, a general view on the thermodynamic stability of various isomers is indicated by arrows in the eqs (1–5). For a majority of compounds of classes (**1**), (**3**) and (**5**) then the isomers A are stable. This view is based on the structures of known compounds of these classes and on their chemical behaviour. Efforts directed towards the elucidation of the thermodynamic stability of the above structures were made by Glidewell[43–46] who carried out synthetic experiments involving representative compounds of the classes (**1**), (**2**) X = S, (**3**) and (**5**), and simple calculations (average bond energy summation). Some of their results contradict the views presented here.

Since parent acids of the P(III) esters appear mostly as the tetracoordinate phosphorus species, the stable structure (**1**)**B** containing a strong P=O bond has been taken into consideration. The



silyl phosphonate structure **(1)B** was postulated in some earlier papers for the products of the reactions of silyl halides with sodium dialkyl phosphites[47,48] and with trialkyl phosphites.[49–51] These conclusions could not stand serious criticism[52,53] but recently Ferguson and Glidewell have suggested[43] that the form **(1)B** is thermodynamically more stable. This seems to be in disagreement with results of other authors. For example, it was shown that both reactions **(6)** lead to the same product, which very easily undergoes sulphur addition[53]

$$\left.\begin{array}{l}(EtO)_2PONa + ClSiMe_3 \xrightarrow[-NaCl]{} \\ Me_3SiONa + ClP(OEt)_2 \xrightarrow[-NaCl]{}\end{array}\right\} (EtO)_2P(OSiMe_3) \xrightarrow{S} (EtO)_2(Me_3SiO)P(S). \qquad (6)$$

Compounds $(MeO)_2P(OSiMe_3)$ and $(PhO)_2P(OSiMe_3)$ before and after distillation showed the same ^{31}P NMR signals $\delta = 126.7$ ppm and 123.3 ppm respectively. This indicated their stable phosphite structure.[54] Some other examples of δ ^{31}P value characteristic for P(III) esters are given in Table 1. The high nucleophilic reactivity at the phosphorus centre of many silyl phosphites, phosphonites and phosphinites is strong evidence for their tricoordinate phosphorus structure. However, it cannot be excluded that the structure **(1)B** may occasionally appear to be more stable as a result of a medium effect or a special structural effect within the ester molecule.

Concerning silyl esters of monothioacids of tetracoordinate phosphorus, there is a general agreement that the silicon atom is preferentially bonded to the oxygen atom.[43,44,55,110] According to Duncan and Glidewell, the structure **(3)A** is more stable than **(3)B** by approximately 60 kJ/mol.[44] Besides evidence coming from ^{31}P NMR spectra, a good proof for the thiono structure was the lack of a characteristic P=O stretching vibration band in the IR spectrum at about 1250 cm^{-1}. This situation is contrary to that which is met in alkyl esters of the corresponding thioacids in which the alkyl group is preferentially bonded to the sulphur atom. Transformation of the thiono to the thiolo form of the alkyl esters of thioacids of phosphorus is sometimes known as the Pishchimuka rearrangement.[56]

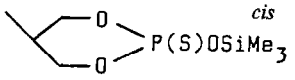
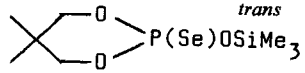
Some ambiguity arose around the structures of the silyl esters of seleno-phosphorus acids **(5)**. The coupling constant $J_{^{31}P-^{77}Se}$ is a good diagnostic tool for the structure of esters of selenoacids of phosphorus. For selenium bridging phosphorus with another atom, it acquires a value in the range 350–500 Hz, while for the P=Se group, the corresponding range is 600–1100 Hz.[45,57–59] Most compounds of the class **(5)**, which have been obtained show J_{P-Se} values indicating clearly their selenono structure **(5)A** (see Table 1). On the other hand the reaction of $(i\text{-PrO})_2POSe^-Na^+$ with

Table 1. Properties of some silyl esters of phosphorus

Compound	^{31}P NMR (in ppm from H_3PO_4)	^{1}H NMR and ^{29}Si NMR (in ppm from Me_4Si)	b.p./pressure, in °C	n_D^{20}	References
		(P(III)–esters)			
$(Me_3SiO)_3P$	113.2	0.20 (CH_3—Si)	129–130/25	1.4145	20, 113, 114
$(Me_3SiO)_2(MeO)P$	117	0.13 (CH_3—Si)	60–62/11	1.4116	289, 53
$(Me_3SiO)_2(EtO)P$	117.8	0.17 (CH_3—Si), 1.17 (*t*, CH_3—C) 3.73 (*m*, CH_2—Si)	79–82/20		20
$Me_3SiO(MeO)_2P$	126.2	0.17 (CH_3—Si), 3.35 (*d*, CH_3—O, J_{PCH} 10.4 Hz)	38/10	1.4105	82
$Me_3SiO(EtO)_2P$	128		66/15	1.4113	82, 20
$(Me_3SiO)_2PI$	190.1				54
$(Me_3SiO)_2PH$	140.8	7.2 (*d*, H—P, J_{PH} 172 Hz)	50/8	1.4120	112, 214
$Me_3SiO(MeO)PH$	160.9	6.23 (H—P, J_{PH} 182 Hz)	46–48/55		128
$Me_3SiO(BuO)PH$	155.2	6.30 (H—P, J_{PH} 189 Hz)	28–30/1		128
$Me_3SiO(n\text{-}Bu_2N)PH$	111.7	6.97 (H—P, J_{PH} 224 Hz)	55–57/1		128
$(Me_3SiO)_2MeP$	122.4		54/10		214
$(Me_3SiO)_2\|MeOC(O)\|P$	125.5	0.56 (CH_3—Si), 3.71 (CH_3—O)	88–96/8		214
$(Me_3SiO)_2\|PhCH_2OC(O)\|P$	155.0	0.24 (CH_3—Si), 2.76 (*d*, CH_2), 6.9 (C_6H_5)	84/0.2		214
$(Me_3SiO)_2CF_3P$	205.0 *q* J_{FCP} 108.5 Hz	0.48 (CH_3—Si)			96
$Me_3SiO(Ph)_2P$	94.1		103–106/0.5		17
$Me_3SiO(Ph)t\text{-}BuP$	113.4	^{29}Si: 19.35 J_{POSi} 10.37 Hz (C_6D_6)	48/0.1	1.4964	55, 74
$NpPhMeSiO(Ph)t\text{-}BuP$	119.17	^{29}Si: 1.02 J_{POSi} 13.92 Hz			55
(diastereoisomers)	119.47	1.29 13.65 Hz			
$(Me_3SiO)_2P(O)H$	−13.8	0.17 (CH_3—Si), 6.75 (*d*, H—P, J_{PH} 700 Hz)	92–93/20	1.4110	20, 69
$Me_3SiO(HO)P(O)H$	−4.2	J_{PH} 678 Hz			274
$Me_3SiO(EtO)P(O)H$	−33	6.73 (H—P, J_{PH} 684 Hz)	32–33/1	1.4102	128
$Me_3SiO(Me)P(O)H$	30.4	J_{PH} 554 Hz			128
$Me_3SiO(n\text{-}Hex)P(O)H$	25.9	J_{PH} 700 Hz	90/3	1.4314	92
$Me_3SiO(CH_2{=}CHCH_2)P(O)H$	21	6.5 (H—P, J_{PH} 549 Hz)	77–79/8	1.4355	182
$(Me_3SiO)_2P(S)H$	44.6	J_{PH} 674 Hz	72/4		214
$(Me_3SiO)_2P(Se)H$	36.2	J_{PH} 632 Hz	56/0.06		214
$Me_3SiO(MeO)P(S)H$	58.0	3.43 (*d*, CH_3O), 7.67 (*d*, H—P, J_{PH} 645 Hz)	63–65/8	1.4590	128
		P(V) esters (—P=O)			
$(Me_3SiO)_3PO$	−25		91–93/5	1.4082	7
$(Me_3SiO)_2(EtO)P{=}O$	−17		102–103/12	1.4062	69, 1
$(Me_3SiO)_2(MeS)PO$	5.2	0.2 (CH_3—Si), 1.7 (CH_3—S, J_{PSCH} 15 Hz)	58/1.5	1.4441	69
$(Me_3SiO)_2(PhS)PO$	0.8	0.2 (CH_3—Si), 7.1–7.6 (*m*, C_6H_5—S)	100/0.05	1.4890	70
$(Me_3SiO)_2(MeSe)PO$	−7.0, J_{PSe} 472 Hz	0.33 (CH_3—Si), 2.15 (*d*, CH_3Se, J_{PSeCH} 15 Hz)	65–67/0.02	1.4608	70
$(Me_3SiO)_2P(OSe)^-H^+NEt_3$	20.0 J_{PSe} 797 Hz				70
$(Me_3SiO)_2P(O)Cl$	−17.1	0.3 (CH_3—Si)	48.01	1.4211	105
$(Me_3SiO)_2P(O)Br$	−33.2				105
$(Me_3SiO)_2P(O)NH_2$	−7.5	0.3 (CH_3—Si), 7.6 (NH_2—P)	m.p. 142		105
$(Me_3SiO)_2P(O)NEt_2$	−7.0	0.4 (CH_3—Si), 1.25 (*t*, CH_3—C), 2.8–3.4 (*m*, CH_2—N, J_{PNCH} 12 Hz)	85/100	1.4200	105

Table 1. (*continued*)

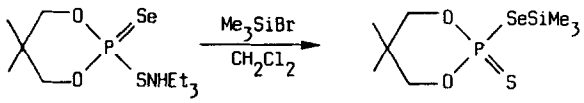
Compound	^{31}P NMR (in ppm from H_3PO_4)	^{1}H NMR and ^{29}Si NMR in ppm from Me_4Si	b.p./pressure, n_D^{20} in °C		References
$Me_3SiO(PhO)_2PO$	−20.8		140–145/0.5		80
$Et_3SiO(MeO)(MeS)PO$	17.6	0.5–1.3 (*m*, $C_2\underline{H}_5$—Si), 2.3 (*d*, $C\underline{H}_3$—S, J_{PSCH} 16 Hz), 3.8 (*d*, $C\underline{H}_3O$, J_{POCH} 15 Hz)	60–65/0.3	1.4638	70
$(Me_3SiO)_2MePO$	11.4	1.14 (*d*, $C\underline{H}_3$—P, J_{PCH} 17 Hz)	105–107.5/27		93, 6
$(Me_3SiO)_2(CCl_3)PO$	12.6	0.8 ($C\underline{H}_3$—Si)			9
$(Me_3SiO)_2(PhCH_2)PO$	−8.0	3.02 (*d*, $C\underline{H}_2$—P), 7.34 ($C_6\underline{H}_5$—C)			9
$(Me_3SiO)_2\|EtOC(O)\|PO$	−23.4	0.21 ($C\underline{H}_3$—Si), 1.0 (*t*, $C\underline{H}_3$—C), 3.98 (*q*, $C\underline{H}_2$—O)	82–87/0.03		93
$(Me_3SiO)(MeS)(Et)PO$	50.3	0.3 ($C\underline{H}_3$—Si), 0.9–2.0 (*m*, $C_2\underline{H}_5$—P)	90–95/100	1.4400	70
$Me_3SiO(Me)_2PO$	41.8	0.31 ($C\underline{H}_3$—Si), 1.41 ($C\underline{H}_3$—P)	58–60/0.5 m.p. 48–49		90
$Me_3SiO(Me)(Ph)PO$	32.2	0.17 ($C\underline{H}_3$—Si), 1.45 (*d*, $C\underline{H}_3$—P, J_{PCH} 15 Hz)	105–110/0.35		93, 80
$Me_3SiO(Ph)_2PO$	−20.7	0.3 ($C\underline{H}_3$—Si), 7.3–8 (*m*, $C_6\underline{H}_5$—P)			69
$Ph_3SiO(Ph)_2PO$	−21.2	7.3–8.0 (*m*, $C_6\underline{H}_5$—Si)	m.p. 100		69
NpPhMeSiO(Ph)(*t*-Bu)PO	43.9, 44.1	^{29}Si: 1.48, 2.13, J_{POSi} 10.39 Hz, 10.37 Hz			55
$Me_3SiO(CF_3)_2PO$	143.4 J_{FCP} 120 Hz				96
$Me_3SiO(F)_2PO$	141.2 J_{FP} 987 Hz	0.13 ($C\underline{H}_3$—Si)			96
$Me_3SiO(Cl)_2PO$	39.2		30/2		109
$Me_3SiO(Br)_2PO$	−61.5		$44/10^{-3}$		109
		P(V) esters (—P=S and —P=Se)			
$(Me_3SiO)_3PS$	31		76–78/1	1.4358	69, 111
$(Me_3SiO)_3PSe$	21.4 J_{PSe} 942 Hz	0.33 ($C\underline{H}_3$—Si)	65–67/0.4	1.4484	70
$Me_3SiO(EtO)_2PS$	55.5		56–57/1.5	1.4433	76, 117
$Me_3SiO(EtO)_2PSe$	55 J_{PSe} 940 Hz	0.33 ($C\underline{H}_3$—Si), 1.25 (*t*, $C\underline{H}_3$—C), 4.05 (oct. $C\underline{H}_2$—O)	52–54/0.2	1.4643	70
$Me_3SiO(Me_2CHO)_2PS$	60.68	0.10 ($C\underline{H}_3$—Si), 1.16 ($C\underline{H}_3$—C), 4.44 ($C\underline{H}$—O)			44
$Ph_3SiO(Me_2CHO)_2PS$	57.94	1.27, 1.32 (*d*, $C\underline{H}_3$—C), 4.60 (*q*, $C\underline{H}$—O), 7.38–7.60 (*m*, $C_6\underline{H}_5$)			44

 *cis*	47.53	0.26 (C<u>H</u>—Si), 0.96 (*dd*, C<u>H</u>$_3$—C)	55°/0.01		29
 *trans*	53.58	0.21 (C<u>H</u>$_3$—Si), 0.85 (*dd*, C<u>H</u>$_3$—C)	55°/0.01		29
	48.9 J_{PSe} 971 Hz		m.p. 88–89		106
$Me_3SiO(Me_3CCH_2O)_2PSe$	55.2 J_{PSe} 940 Hz		60–62/0.05		106
$Me_3SiOP(S)Cl_2$	39.2		30/2		109
$(Me_3SiO)_2$*n*-HexPS	72.6		94–96/2	1.4535	92
$(Me_3SiO)_2$[EtOC(O)]PS	31.70	0.31 (C<u>H</u>$_3$—Si), 1.24 (*t*, C<u>H</u>$_3$—C), 4.02 (*q*, C<u>H</u>$_2$—O)	105–108/4		214
$(Me_3SiO)_2$[EtOC(O)]PSe	−9.9	0.64 (C<u>H</u>$_3$—Si), 1.22 (*t*, C<u>H</u>$_3$—C), 4.22 (*q*, C<u>H</u>$_2$—O)	145/6		214
$Me_3SiO(EtO)EtPSe$	91		52–53/2	1.4740	33
$Me_3SiO(Me)_2PS$	79.9 J_{PSe} 857 Hz	0.33 (C<u>H</u>$_3$—Si), 1.80 (*d*, C<u>H</u>$_3$—P)	m.p. 45		90, 110
$Me_3SiO(Et)_2PS$	94.7	0.32 (C<u>H</u>$_3$—Si), 0.89–2.22 (*m*, C<u>H</u>$_3$C<u>H</u>$_2$—P)	45–46/0.1		90, 110
$Me_3SiO(Ph)_2PS$	70.9		m.p. 81–82		121, 69
$Me_3SiO(Ph)_2PSe$	68.1 J_{PSe} 780 Hz				61
$Me_3SiO(Ph)$(*t*-Bu)PS	94.6	^{29}Si: 23.59 (C_6D_6), J_{POSi} 10.25 Hz (C_6D_6)			172, 55
NpPhMeSiO(Ph)(*t*-Bu)PS	97.15 97.6	^{29}Si: 1.69 J_{POSi} 11.15 Hz 2.05 11.65 Hz	m.p. 112–115		55
NpPhMeSiO(Ph)(*t*-Bu)PSe	98.4 99.2 J_{PSe} 800 Hz				55
$(Me_3SiS)Me_2PS$	51.8	0.50 (C<u>H</u>$_3$—Si), 2.05 (C<u>H</u>$_3$—P)	m.p. 19–20		90, 110
$(Me_3SiS)Et_2PS$	74.5	0.53 (C<u>H</u>$_3$—Si), 1.02–2.46 (*m*, C<u>H</u>$_3$C<u>H</u>$_2$—P)	91–92/0.1		90, 110
$(Me_3SiS)Et_2PS$	54	0.6 (C<u>H</u>$_3$—Si), 7.4 (*m*, C_6C<u>H</u>$_5$—P)	151–153/0.02		90, 110
$(Me_3SiS)P(S)F_2$	24.5 J_{PF} 1200 Hz	0.6 (C<u>H</u>$_3$—Si)			96
Me_3SiS(*t*-Bu)(Ph)PS	83.33	^{29}Si: 22.54 (C_6D_6) J_{PSSi} 4.98 Hz			55
NpPhMeSiS(*t*-Bu)(Ph)PS	84.24 84.64	^{29}Si: 4.96 4.96 Hz 6.36 (C_6D_6) J_{PSSi} 4.94 Hz			55

Me_3SiCl gave a product showing J_{P-Se} = 466.8 Hz and δ ^{31}P = 18.06 ppm[45] characteristic for a selenium atom in the bridging position. The same reaction carried out in another laboratory gave exclusively the product with a selenono structure (J_{P-Se} = 928 Hz, δ ^{31}P = 51.5 ppm)*.[60]

There is very little data on the silyl esters which appear in eqs (2) and (4). According to Ferguson and Glidewell,[43] the reaction of triphenylsilyl thiolate with diisopropyl chlorophosphite eventually led to phosphorothioite **(2)B**. On the other hand Cavel *et al.*[130] proposed the structure **(2)A** for some thioesters belonging to this class. Silylation of diphenyl selenophosphinic acid with Me_3SiBr gave the corresponding silyl esters of the structure **(2)B**, i.e. $Ph_2P(Se)SiMe_3$, judging from δ ^{31}P = 41.5 ppm, J_{P-Se} 744 Hz.[61]

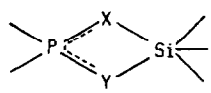
Concerning the structure of the silyl esters of selenothio acids of tetracoordinate phosphorus, the reaction (7) led to one phosphorus containing product showing the value of P—Se coupling constant characteristic for selenium bridging phosphorus and silicon. The values of ^{31}P NMR parameters did not change with temperature.[61]



^{31}P = 77.8 ppm

J_{P-Se} = 440 Hz (7)

A bidentate cyclic structure **(8)** of the compounds of the classes **(3)**, **(4)** and **(5)** could be also considered.



X= O, S, Se Y= O, S, Se (8)

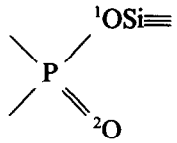
Spectroscopic data, as well as dipole moments,[62–65] are in agreement with the silyl group being bonded exclusively to one atom. In particular, δ ^{29}Si values (Table 1) are characteristic for tetracoordinate silicon. This excludes the pentacoordination structure but the possibility of the transient existence of the structure **(8)** cannot be excluded. It is worth mentioning, that conformational studies of the silyl esters of tetra- and tri-coordinate phosphorus indicate that the silyl group preferentially adopts the *cis* orientation with respect to the phosphoryl group or the free electron pair.[62–65] This conformation is not sterically privileged as compared with the gauche one which is the conformation preferentially adopted by alkyl analogues. This indicates that a weak interaction occurs between the phosphoryl group or free electron pair and the silicon centre.

Another problem which should be discussed is concerned with isomerization. Fast intramolecular migration of silyl groups was observed in the silyl esters of seleno-carboxylic acids.[66,67] It has therefore been suggested that this could also explain some of the features of silyl esters of phosphorus.[68] There is however, no clearcut evidence that such a migration occurs intramolecularly. No kinetic studies, have so far been performed and the exchange may occur intermolecularly as well.

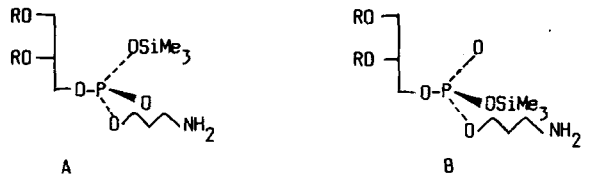
Intermolecular exchange was proved to occur by simple crossover experiment.[68] There are also

* The conditions of the reaction were not strictly specified in ref. 45 (solvent chloroform or nitrometnane room temperature or boiling point, 1–6 h). In ref. 60 the author studied the reaction in methylene chloride at room temperature as well as at −70°C. The same results were obtained at both temperatures.

examples showing that structures

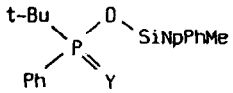


are stable at least on the NMR time scale. Bruzik and Tsai[34] observed separation of ^{31}P NMR signals of an *O*-silylated phospholipid (**9**) due to the existence of diastereoisomers.



A B (9)

Another example has recently been provided. Diastereoisomeric compounds (**10**) having chiral centres at phosphorus and silicon have been synthesized.[55]



Y= O, S, Se, free electron pair (10)

All of them including Y=O showed distinctly separated ^{31}P NMR signals of both diastereoisomers. The spectra were not affected by temperature.

2.3. *Physical and chemical behaviour*

Most known silyl esters of phosphorus are liquids. Only a few have been isolated as crystalline solids. They are generally thermally stable enough to be distilled under reduced pressure. Almost all silyl esters of phosphorus must be handled with care. Those having the P=O group are hygroscopic and undergo hydrolysis extremely easily. P(III) silyl esters demonstrate a tendency to oxidation which is higher than that of their alkyl analogues.

A compilation of physical properties including boiling and melting points, refractive indices and densities may be found in ref. 1. Some spectroscopic data, in particular ^{31}P NMR characteristics of chosen representatives of various classes of silyl esters of phosphorus, are presented in Table 1. The ^{31}P NMR chemical shift is used as a diagnostic tool in structural assignment. Ranges of values of δ (^{31}P) are depicted in Chart 1. Relatively little ^{29}Si NMR data on silyl esters of phosphorus is available (Table 1).

IR and Raman spectroscopies are also used in structural studies.[43–46,62–65,109,110,112] Characteristic of P(V) esters is an intensive P=O stretching vibration band which appears at about 1250 cm^{-1}. Corresponding bands for P=S and P=Se are at 770–840 cm^{-1} and about 550 cm^{-1}.[43–45] They are often obscured by other bands and rarely used for structural diagnosis. Mass spectrometry is another tool.[43]

To our knowledge there has not been any systematic study on the toxicity of silyl esters of phosphorus.

Concerning their chemical behaviour, silyl esters of phosphorus show a high reactivity towards nucleophiles and electrophiles. Most reactions of these compounds which are important in synthesis, are determined a general feature in which silicon is the target for nucleophilic attack. The phosphorus group interacts with electrophiles.

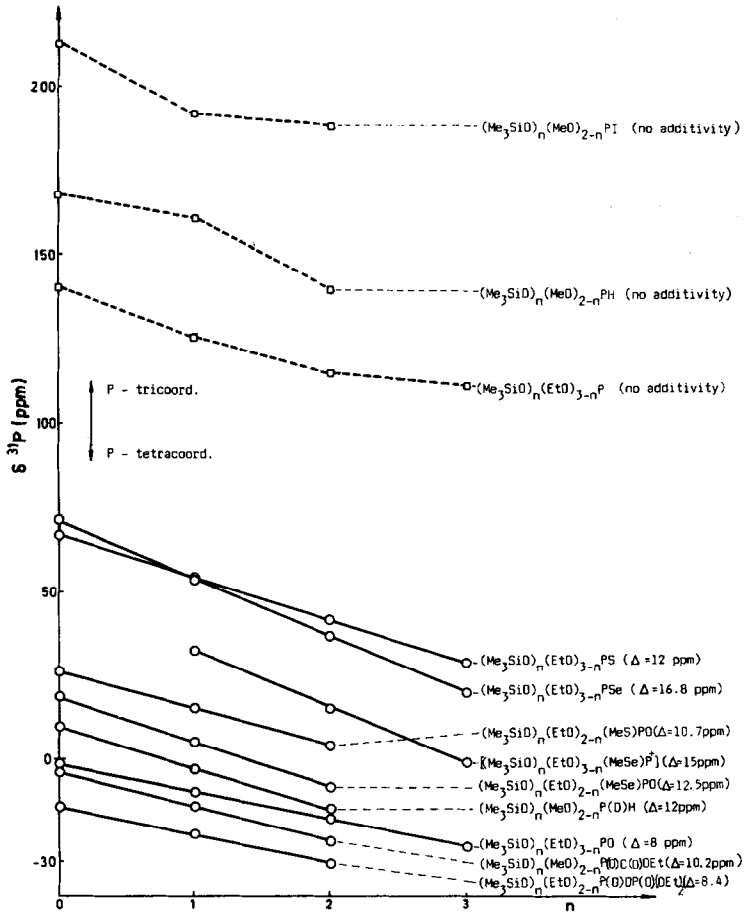
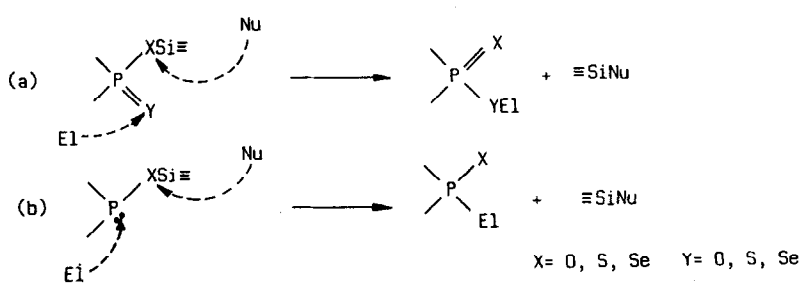


Chart 1. The ^{31}P NMR chemical shift variation in some series of silyl esters of phosphorus. Δ—The change of the chemical shift on replacement of one silyl group by alkyl group.



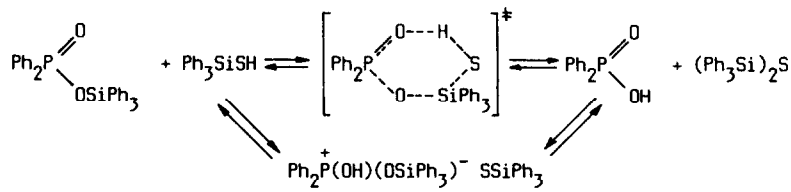
(11)

It should be pointed out that: (1) Nucleophile and electrophile in eq. 11 a and b may also constitute parts of the same molecule as in eqs (12–15) or may interact with each other. (2) Transformations at silicon and phosphorus centres may occur in one concerted step or as two separate steps. (3) Products in the eqs (11a and b) may undergo further transformations.

Nucleophilic attack at the silicon atom is strongly preferred over the attack on phosphorus not only in the case of tetracoordinate phosphorus esters but also in the case of esters of tricoordinate phosphorus. The presence of a silyl group seems to enhance nucleophilicity of the phosphorus group, and the phosphorus group increases the electrophilicity of the silicon centre. Thus many reactions of silyl esters of phosphorus occur much faster than those of corresponding alkyl esters. One reason for their high reactivity is that the interactions of nucleophile and electrophile may be synergetic. Transformations (Scheme 11 a and b) involving one step occur by a classic 'push–pull' mechanism. In a stepwise transformation, where the first step is rate determining, a weak interaction with the centre involved in the following step (for ex. hydrogen bond to P=O) may assist the reaction. If the second step is rate limiting, an intermediate is involved, in which the reactivity of the centre reacting in the rate limiting step is strongly enhanced as a result of the reaction at the other centre (eq. 13).

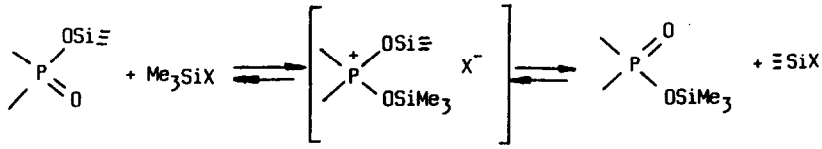
In some cases an alternative explanation of the high reactivity of silyl esters of phosphorus, particularly those having the P=O group, could be a direct interaction of the phosphorus group with silicon in the transition state, lowering the energy barrier to the silyl group cleavage. However, to our knowledge there has not yet been a convincing demonstration of such interaction.

In many cases it is difficult to differentiate between one or two step mechanisms. For example a reversible reaction of triphenylsilyl diphenylphosphinate with triphenylsilanethiol leading to the phosphinic acid and to the bis-silyl thioether is likely to involve either of the routes below.[69]



(12)

It is, however, proved that the reaction of the P=O silyl esters with silyl iodides and bromides in a solvent like methylene chloride occurs with full ionization.[70]

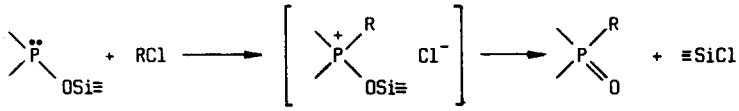


(13)

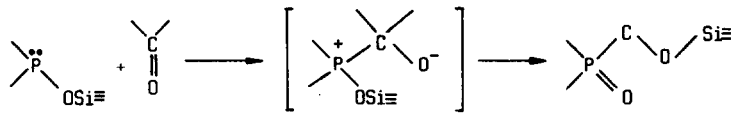
The reactivity pattern of P=O, P=S and P=Se homologues with electrophiles could be rationalized on the basis of the HSAB principle.[71] The P=O esters react readily with hard electrophiles, while P=S and P=Se esters are reactive towards soft electrophiles. For example, silyl group exchange occurs readily as the result of interaction of >P(O)OSi≡ esters with silyl halides as hard electrophiles. The analogous reaction of the ester with softer alkyl halides, in principle, does not occur since reverse reaction is thermodynamically privileged (see Section 4). Instead >P(S)OSi≡ esters react more easily with soft electrophiles. A good example is the chlorination reaction (eq. 54), which most probably involves a nucleophilic attack of sulphur on positive halogen and proceeds fast in temperatures below 0°C.*

* This type of reaction could involve a single electron transfer mechanism.[72]

Most reactions of silyl esters of tricoordinate phosphorus fit schemes similar to the reactions of tetracoordinate phosphorus esters. Interaction of the P(III) centre with an electrophile may lead to the formation of phosphonium salt or zwitterion. This, in a consecutive step, is transformed to a product as a result of nucleophilic attack on silicon. This is illustrated by general schemes for the Arbuzov reaction (14) and addition to a carbonyl group (15).



(14)



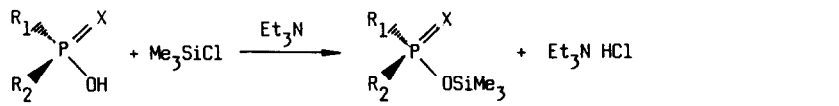
(15)

Concerted one step mechanisms are also feasible.

The above reactions occur faster than the analogous reactions of alkyl esters. This is partly attributed to an increase of nucleophilicity of the P(III) centre by the electropositive silyl group. Recent photoelectron spectroscopic studies have provided evidence for the electron releasing properties of the trimethylsilyl group in silyl phosphites.[73] The P(III) centre in silyl esters readily undergoes classical oxidation reactions, addition of oxygen, sulfur and selenium. These reactions may occur by polar or free radical pathways (Sections 3 and 6).

2.4. *Stereochemistry*

There has been some interest in the synthesis of optically active trimethylsilyl esters of phosphorus with chiral P(III) and P(V) centres. They have usually been prepared by stereospecific silylation of optically active phosphorus acids.



(16)

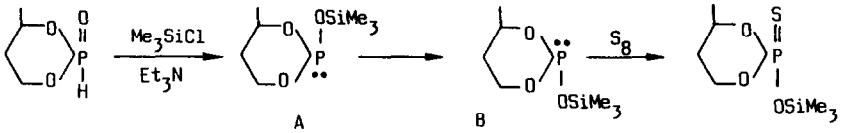
The results of these reactions are summarized in Table 2.

Silylation of phosphorus acids in the presence of amines proceeds with retention of configuration at the phosphorus centre. This was demonstrated by Benshop,[32] and confirmed in later papers.[55,74,75] It was shown that phosphinous acids react with chlorosilanes without change of configuration at phosphorus.[74,55] This was in agreement with a mechanistic pathway involving a phosphonium salt intermediate.

Table 2. Optically active silyl esters of phosphorus with optical activity originating from phosphorus chiral centre

Optically active precursor	Product	Optical activity configuration	Reference
(−)-S-Et(*i*-PrO)P(O)H	(−)Et(*i*-PrO)POSiMe$_3$	(−)*R*	75
(−)-S-*t*-BuPhP(O)H	(−)*t*-BuPhPOSiMe$_3$	(−)*S*$[\alpha]_D^{20} = -31.7°$	74
(+)-R-*t*-Bu(MeO)P(O)H	(+)*t*-Bu(MeO)POSiMe$_3$	(+)*R*$[\alpha]_D^{20} = -11.5°$	74
(−)*t*-BuPhP(S)OH	(+)*t*-BuPhP(S)OSiMe$_3$	(+)*S*$[\alpha]_D^{20} = 13.8°$	55
(−)*t*-BuPhP(O)H	(−)*t*-BuPhPOSiMePhNp	(−)*S*$[\alpha]_D^{20} = -17.4°$	55
(−)*t*-Bu(MeO)P(O)SCl	(+)*t*-Bu(MeO)P(S)OSiMe$_3$	(+)*R*$[\alpha]_D^{20} = 10.8°$	76
(−)Et(EtO)P(Se)OH	(+)Et(EtO)P(Se)OSiMe$_3$	(+)$[\alpha]_D^{20} = 5.06°$	33
(−)Et(EtO)P(O)H	(+)Et(EtO)P(Se)OSiMe$_3$	(+)$[\alpha]_D^{20} = 4.65°$	33

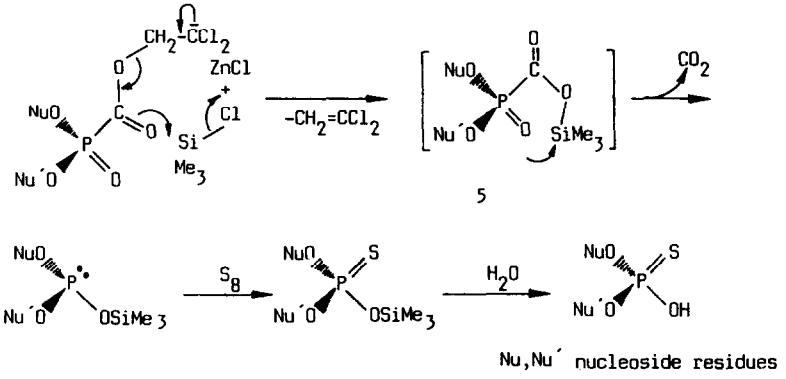
The reaction of the *cis*-isomer of 4-methyl-2-hydro-2-oxo-1,3,2-dioxaphosphoprinan with TMSCl in the presence of triethylamine, yields *cis*-2-trimethylsiloxy-4-methyl-1,3,2-dioxaphosphorinan (**A**), which then undergoes isomerization producing the thermodynamically more stable *trans*-isomer (**B**).



A B (17)

Addition of sulphur to the isomers **A** and **B** proceeds with full retention of configuration.[77] Esters **A** and **B** have been successfully used in the stereoselective synthesis of the diastereoisomers of tetraalkyl dithiopyrophosphates.[29,31]

Hata has described the highly stereoselective conversion of 2,2,2-trichloroethoxycarbonylphosphonates to silyl phosphites and thiophosphates, mediated by TMSCl in the presence of zinc. The proposed mechanism is as follows.[14,78]



(18)

As the result of these transformations, dinucleoside thiophosphate was obtained with known configurations at the phosphorus atom.

Tsai and Bruzik observed the formation of diastereoisomers of silylated phospholipids and used them for stereochemical studies of enzyme-catalysed reactions at the phospholipid phosphorus centre.[34,79]

In contrast with the behaviour of P=O acids, the silylation of alkyl esters with silyl halides was found to occur with complete racemization at the phosphorus centre.[70]

Optically active silyl esters of phosphorus acids with chiral silicon centres have also been prepared. Three general routes lead to these compounds:[55]

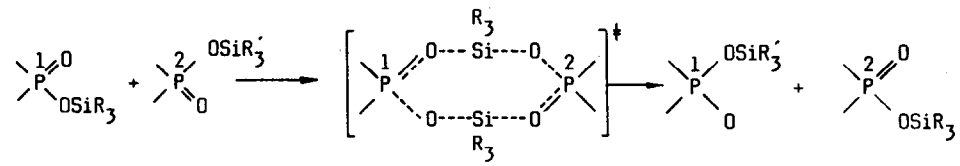
a. Reactions of optically active triorganosilanolates with chloroanhydrides of P(III) acids, followed by addition of oxygen, sulphur or selenium.
b. Reactions of optically active triorganohalosilanes with phosphorus salts or esters.
c. Dehydrocondensation of optically active triorganosilyl hydrides with acids of phosphorus.

The results are collected in Table 3.[55] Spectroscopic data are presented in Table 1. The method of chemical correlation was used to confirm absolute configurations of these esters.[55]

Optical stability of compounds $>P(O)O\overset{*}{S}i\equiv$ is poor. This was attributed to silyl group exchange which had been observed earlier.[80] It is possible that this intermolecular exchange occurs with partial inversion at the silicon centre and this leads to racemization.

Table 3. Optically active silyl esters of phosphorus with optical activity originating from silicon

Phosphorus reagent	Organosilicon reagent	Product (configuration at Si)	Stereochemistry at silicon	Method
t-BuPhPCl	(+)*R*-NpPhMeSiOK	(−)*R*-*t*-BuPhPOSiMePhNp	Retention	1
t-BuPhP(S)OH	(−)-*S*-NpPhMeSiCl	(−)*R*-*t*-BuPhP(S)OSiMePhNp	Inversion	2
t-BuPhP(O)H	(−)-*S*-NpPhMeSiCl	(−)*R*-*t*-BuPhPOSiMePhNp	Inversion	2
t-BuPhP(O)SnMe$_3$	(−)-*S*-NpPhMeSiCl	(+)*S*-*t*-BuPhP(O)OSiMePhNp	Retention	2
t-BuPh(S)OH	(+)-*R*-NpPhMeSiH	(−)*R*-*t*-BuPhP(S)OSiMePhNp	Inversion	3



(19)

The stereochemistry of substitution at silicon in compounds having the structure *t*-BuPhP(Y)O*SiNpPhMe where Y = lone electron pair, O, S, Se with nucleophiles, including H_2O, ROH, $LiAlH_4$, RMgX, has been studied.[81] A distinction in stereochemistry between $\rightarrow$P: and $\rightarrow$PO esters and their thiono- and selenono-analogues, was observed. The former reacted with predominant retention of the configuration at silicon, whereas the latter gave predominant inversion. A cyclic structure for the transition state was invoked to explain retention.

3. SYNTHESIS

The literature on the synthesis of silyl esters of phosphorus is extensive. Many of the papers related to this subject appeared in the late 1950s and 1960s. They were thoroughly reviewed by Borisov, Lukevits and Voronkov.[1] This section gives a short account of the important synthetic routes to silyl esters of phosphorus without discussing in detail earlier results.

The main types of reaction applied to obtain this class of compounds are:

1. Silylation of acids and their salts, i.e. substitution of acidic hydrogen, metal, or ammonium groups by triorganosilyl groups.
2. Silylation of esters—exchange of ester groups into silyl groups.
3. Reactions of silicon reagents with halogen anhydrides of phosphorus and with phosphorus oxides.
4. Transformations of silyl esters of phosphorus and their derivatives.

The most commonly used organosilicon reagents in these reactions are:* halogenosilanes,[6,7,48–53,89–90,93,110,114,117,129–136,140–163] aminosilanes, silazanes and silyl amides,[13–15,35,53,82–84,89–92,95,110,124,127,214] alkoxysilanes and acyloxysilanes,[7,109,211] siloxanes,[40,96,114,130] silanothiolates and silathianes,[43,59,76,96,103,109,130] silanols and silanolates,[43,55,110,117] and hydrosilanes in catalysed reactions.[55] The choice of a proper method of synthesis of silyl esters of phosphorus depends to a considerable extent on the structure of the required silyl phosphorus products.

3.1. *Synthesis of silyl phosphates, phosphonates and phosphinates* (P=O *esters*)

Silylation of esters of tetracoordinate phosphorus is a common route to tetracoordinate oxyesters. It is based on the reaction:

$$>P(O)OR + R'_3SiX \rightarrow >P(O)OSiR'_3 + RX \quad (20)$$

* Earlier papers on this subject are quoted in ref. 1.

X is usually a halogen atom, R is an alkyl group. This reaction does not occur when R is an aryl group. Since the above reaction constitutes part of a selective dealkylation of the esters, it is described in detail in Section 4. The reaction of trialkylstannyl esters of phosphorus with silyl chlorides,[16,55,85-88] as well as the transsilylation processes[1,80,171] proceeding according to the above scheme, R = R''_3Sn or R''_3Si, has also proved to be a convenient route to silyl esters of phosphorus.

Acids of phosphorus are cheap and readily available precursors of the silyl esters. Trimethylsilylchloride (TMSCl) is one of the most convenient silylating agents, because of its low price and relatively high reactivity.

$$>P(O)OH + R_3SiCl \rightleftarrows >P(O)OSiR_3 + HCl \tag{21}$$

Since the reaction (21) leads to equilibrium, the full conversion of the acid to the ester requires removal of HCl, which is usually accomplished by using amines.[1,90,110,111] HCl formation may be prevented by using salts of acids.[1,90,110,118,129] Hexamethyldisilazane (HMDS) and silyl amines[91,92,96,110,130] are also frequently used agents, which may be achieved using mixtures of trimethylsilyl chloride with ammonium chloride.[110] The releasing amine removes HCl. Bis(trimethylsilyl) acetamide (BSA) is a powerful reagent utilized for the introduction of silyl groups to P(V) acids.[35,110,113]

A fairly good yield of silyl esters of P=O acids may be obtained by silylation of acids with alkyl silyl ethers (alkoxysilanes), triorganosilanols, or disiloxanes. In the two latter cases azeotropic distillation of water is required during the synthesis, literature cited in ref. 1.

The reaction of triorganohydrosilanes, R_3SiH, with phosphorus acids, in the presence of transition metal catalysts, lead to the silylation of these acids as the result of a dehydrocondensation process, literature cited in ref. 1.

$$nR_3SiH + (HO)_nP(O)R'_{3-n} \xrightarrow{\text{Ni colloid}} (R_3SiO)_nP(O)R'_{3-n} + nH_2 \tag{22}$$

The yields depend strongly upon the structure of phosphorus acid. The reaction of triorganohydrosilanes with dialkyl phosphates leads only to small amounts of triorganosilyl dialkyl phosphates, although tris(triorganosilyl) phosphates have been obtained with 75–80% yields, literature cited in ref. 1. The dehydrocondensation reactions may be also carried out using palladium(O) supported on carbon, or Wilkinson catalyst.[55]

Examples of the successful silylation of P(V) chloroanhydrides to obtain P=O silyl esters have also been described.[94-96] Silylation agents of high nucleophilicity like Me_3SiONa should be avoided because of the very high sensitivity of silyl esters towards nucleophilic agents. They can undergo subsequent reaction leading to pyro-compounds.[55] This fact limits the scope of the above reaction to chloroanhydrides of phosphorus yielding relatively stable esters.

The reactions of hexaalkyldisiloxanes, triorganosilanols or triorganoalkoxysilanes with phosphoric anhydride are convenient preparative methods for tris(triorganosilyl) phosphates, literature cited in ref. 1.

$$3R_3SiOSiR_3 + P_4O_{10} \rightarrow 2(R_3SiO)_3PO \tag{23}$$

A variety of silyl esters of polyphosphoric acids can be obtained by this method[1,40] or if P_4O_{10} is reacted with some other organosilicon reagents, in particular hexamethyldisilazane.[119]

$$(Me_3Si)_2NH + P_4O_{10} \rightarrow (Me_3SiO)_2\overset{\overset{O}{\|}}{P}\text{—}N\text{—}\overset{\overset{O}{\|}}{\underset{\underset{\text{—NH}}{|}}{P}}\text{—}(NH)_n\text{—}\overset{\overset{O}{\|}}{P}(OSiMe_3)_2$$

$$+ (Me_3SiO)_2\overset{\overset{O}{\|}}{P}\text{—}O\text{—}(\overset{\overset{O}{\|}}{\underset{\underset{OSiMe}{|}}{P}}\text{—}O\text{—})_m\overset{\overset{O}{\|}}{P}(OSiMe_3)_2$$

$n = 1\text{–}4$

$m = 0\text{–}4$

(24)

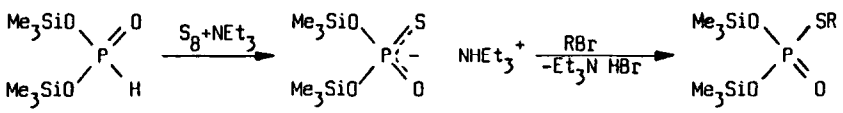
The tetracoordinate silyl esters may also be obtained by oxidation of P(III) silyl esters. Since the silyl ester group easily undergoes solvolytic cleavage, water, alcohols and acids must be avoided in the reaction medium. This limits the use of many common oxygenation reagents.

Direct oxygenation of some reactive P(III) silyl esters with oxygen has been successfully performed.[112,121,128,214] Dimethyl sulfoxide (DMSO) was used to oxidize bis(trimethylsilyl) nucleoside phosphites to bis(trimethylsilyl) nucleoside phosphates.[28] Organic nitro compounds and nitrogen oxides are of value for this purpose.[28,97] Good results have been obtained by the use of bis(trimethylsilyl) peroxide, which oxidizes tricoordinate phosphorus centre chemo- and stereoselectively. This permits the preparation of P(V) silyl esters in high yield and under mild conditions. The oxidation proceeds with retention of configuration at the phosphorus atom.[98,99]

$$R_2POSiR'_3 \xrightarrow{Me_3SiOOSiMe_3} R_2P(O)OSiR'_3 + Me_3SiOSiMe_3 \qquad (25)$$

Bis(trimethylsilyl) peroxide is a very convenient reagent, because it can be used in aprotic solvents: the by-product, hexamethyldisiloxane, is completely inert in the reaction mixture. This reaction was utilized for the synthesis of oligonucleotides in solution, as well as on polymeric support.[100,101] Other attempts to oxidize silyl phosphites have been made, including electrochemical methods.[102]

The addition of sulphur to bis(trimethylsilyl) phosphites, in the presence of amines, leads to the formation of ambident *O,O*-bis(triorganosilyl) phosphorothioate anion, which can be used as a reagent making possible the introduction of the silylated P=O phosphorus group to organic compounds, bridged by the sulphur atom, as the result of reaction with an electrophilic centre.[104]



(26)

Selenium analogues can also be synthesized using this procedure.[70] Another reagent for this purpose may be $(R_3SiO)_2P(O)SCl$, prepared by the chlorination of tris(triorganosilyl) thiophosphate. This reacts with nucleophilic centres or is able to undergo addition to double bonds.[104]

Other transformations of P(III) and P(V) silyl esters to produce new silyl esters of phosphorus is described in Sections 5 and 7.

3.2. *Synthesis of silyl esters of thiono- and selenono-acids of tetracoordinate phosphorus* (P=S *and* P=Se *acids*)

Silylation of alkyl esters having thiophosphoryl or selenophosphoryl groups proceeds slowly[70] and is rarely used. An example is the silylation of some thionopyrophosphates.[5,105] Silylation with the substitution of alkyl groups bound to phosphorus by sulphur or selenium is also very reluctant.[70]

Several methods have been used for the synthesis of $>P(X)OSiR_3$ esters, where X = S, Se. They include direct silylation of proper acids or their salts with: Me_3SiCl (in presence of amines),[1,33,90,106,110] hexamethyldisiloxane,[1] trimethylsilylisocyanate,[107] hexamethyldisilazane,[90,96] or triorganohydrosilanes with palladium as catalyst.[55] The last method is stereospecific and permits the synthesis of optically active compounds with high yields and relatively high chemical and optical stabilities.

Other methods are based on the reactions of some silyl reagents with chloroanhydrides and other anhydrides of phosphorus.[76,94,96,110,119] Some *O*-silyl thionoesters of phosphorus were prepared according to the following scheme:[76]

$$R_2P(O)SX + (Me_3Si)_2S \rightarrow R_2P(S)OSiMe_3 + Me_3SiX + S_8 \qquad (27)$$

R = alkyl or alkoxyl; X = Cl, OR′, SP(O)R′

This reaction proceeds in a stereospecific way at phosphorus. Optically active *O*-methyl-*t*-butyl-*O*-silyl phosphonothioate is produced when optically active *O*-methyl-*t*-butyloxophosphoranesulphenyl chloride reacts with hexamethyldisilathiane.

Silyl esters of thio- and selenophosphoric acids can be obtained as the result of addition of sulphur (selenium) to silyl esters of tricoordinate acids.[17,33,55,108,120,121,214,125]

S-Trimethylsilyl esters of dithiophosphoric acids are formed as the result of the silylation of dithioacids or their sodium salts.[55,90,96,109,110] Another example is the silylation with hexamethyldisilazane:[96]

$$(CF_3)_2P(S)SH \xrightarrow{Me_3SiNHSiMe_3} (CF_3)_2P(S)SSiMe_3 \qquad (28)$$

The reaction of dithioacids of P(V) with trimethylsilyl isothiocyanates also leads to *S*-trimethylsilyl esters of these acids.[107] Silyl bromides are convenient silylating agents, transforming dithioacids into their *S*-triorganosilyl esters.

$$Ph_2P(S)SH + R_3SiBr \xrightarrow{Et_3N} Ph_2P(S)SSiR_3 \qquad (29)$$

$$R = Me, Ph$$

This reaction in the presence of an equimolar amount of triethylamine proceeds smoothly at room temperature in good yield.[55]

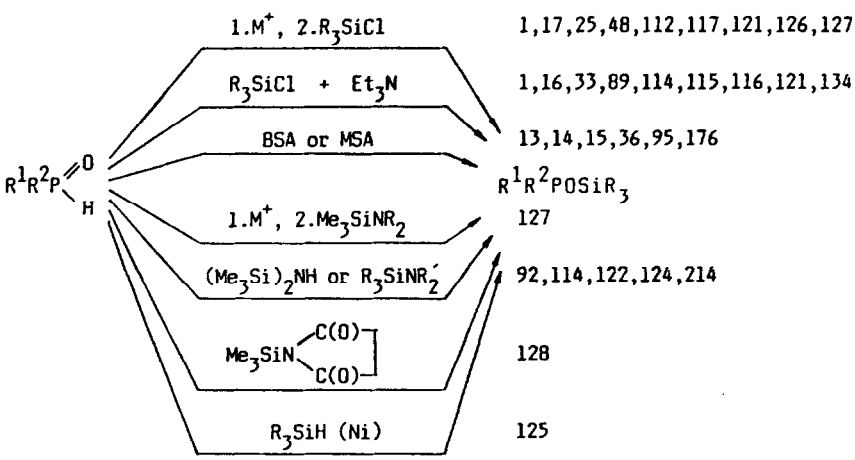
3.3. *Synthesis of silyl phosphites, phosphinites and phosphonites*

Silyl esters of tricoordinate phosphorus can be obtained by silylation of phosphorus acids with different silylating agents.

Tris(trimethylsilyl) phosphite, which is a common reagent in synthesis, is produced in the reaction of phosphorus acid with trimethylsilyl chloride. The first two silyl groups enter easily without any HCl acceptor. However, the introduction of the third group requires the use of amine or another reagent which transforms the diester into P(III) tautomeric form.[1,16,114]

$$(Me_3SiO)_2P(O)H + Et_3N \rightleftarrows (Me_3SiO)_2POHNEt_3 \xrightarrow{Me_3SiCl} (Me_3SiO)_3P + Et_3N \cdot HCl. \qquad (30)$$

It is a rule that the silylation of phosphorus acids of general structure $R^1R^2P(O)H$ (R^1R^2 are alkyls, aryls, alkoxy groups, sililoxy groups etc.) requires either the transformation of the substrate to P(III) form, or using an effective silylating agent:



(31)

1. M^+ denotes a transformation of acid into its metal or NH_4^+ salt, BSA is bis(trimethylsilyl)acetamide, MSA is (trimethylsilyl)acetamide.

Reaction of P(III) alkyl esters can be applied to the synthesis of silyl esters of phosphorus.[1] Reaction of dialkyl phosphites with silyl halides proceeds in an analogous way to that with P(V) esters: the phosphites react in phosphonate tautomeric form.

$$(RO)_2P(O)H + 2Me_3SiCl \xrightarrow[-2RCl]{} (Me_3SiO)_2P(O)H \tag{32}$$

Reaction of trialkyl phosphites with three mole equivalents of silyl halides may lead either to the tris(triorganosilyl) phosphite, or to the bis(triorganosilyl) alkylphosphonate depending upon the reaction conditions.[117] In order to obtain tris(trimethylsilyl) phosphite, it is necessary to remove any alkyl halide by-products from the system, so as to prevent a subsequent Arbuzov reaction with the alkyl halide. Bugerenko used high temperature for this purpose, distilling off alkyl halide.[117]

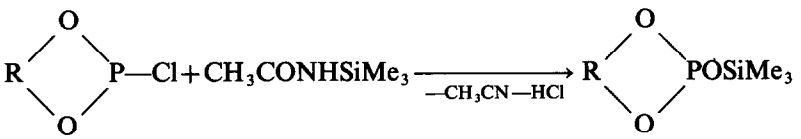
$$3R_3SiX + P(OR')_3 \xrightarrow[-3R'X]{} (R_3SiO)_3P \xrightarrow{R'X} R'P(O)(PSiR_3)_2 \tag{33}$$

$$X = Cl, Br, I$$

It is worth mentioning that the first step of the above scheme is not the Arbuzov type process. At least in the case X = Br, I, the reaction involves the formation of halogenoanhydride:[54,68]

$$Me_3SiI + P(OR')_3 \rightarrow Me_3SiOR' + IP(OR')_2 \rightarrow (Me_3SiO)P(OR')_2 + RI. \tag{34}$$

Other sources of silyl esters of tricoordinate phosphorus are halogenoanhydrides of P(III) acids. An example is presented below.[95]



(35)

$$R = CH_2CH(CH_3), (CH_2)_3, CH_2CH_2CHCH_3, OC_6H_4$$

Some convenient routes to silyl esters of P(III) involving reaction of silicon reagents with P(III) halogenoanhydrides were reviewed in ref. 1. The chloro ligand in chlorophosphines and dialkyl chlorophosphites can be exchanged by the siloxy group from potassium silanolate. This permits the conversion of silanolates to silyl esters without cleavage of any bonds to silicon.[55] Subsequent reactions of the silyl esters with silanolate limit the scope of this reaction to the preparation of relatively stable silyl P(III) esters, that is those having fairly bulky groups at silicon and phosphorus.

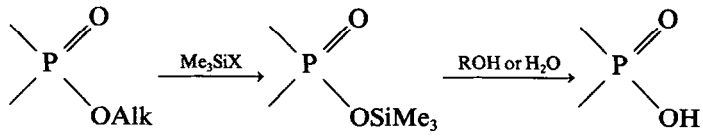
Synthesis of *S*-trimethylsilyl thioesters of P(III) by the silylation of corresponding phosphorus halogen anhydrides with disilathianes, silanethiols and silanethiolates have also been reported.[123,130]

4. SILYL ESTERS OF PHOSPHORUS AS PRECURSORS OF PHOSPHORUS ACIDS

4.1. *Selective dealkylation of esters of tetracoordinate phosphorus*

The selective conversion of alkyl esters of tetracoordinate phosphorus to the corresponding acids is a major problem in the synthesis of analogues of natural phosphates.[137,138] Hydrolysis of alkyl phosphonates or phosphates requires vigorous conditions such as heating with concentrated HCl or HBr[137,139] or refluxing for 24 hr with excess of NaI in acetone.[140] Under these conditions other

bonds in the ester molecule may be cleaved. Rabinovitz first proposed the use of silyl esters of phosphorus as convenient precursors of phosphorus acids.[6] They very easily undergo hydrolysis or alcoholysis and this makes possible the generation of acids of phosphorus under mild conditions. The conversion of alkyl phosphonates or phosphates to the corresponding silyl esters can be done by transesterification with silyl halides.[7,141] The acids are obtained from alkyl esters by a two step process.



(36)

X usually is Cl, Br or I

Rabinovitz used Me_3SiCl as the transesterification substrate. The reaction, however, requires rather vigorous conditions (refluxing for many hours with excess of the silylating agent) and this may lead to undesired transformations of the phosphorus substrate or the product. Nevertheless the process was successfully used in the preparation of phosphonic acids having some labile functional groups[6,131–134,142,143] including phosphonic acid derivatives of nucleosides, carbohydrates and lipids.[131–133] Recently the silylation of phosphorus esters with Me_3SiCl was reported to be effectively accelerated by addition of small amounts of NH_4Cl or hexamethyldisilazanes.[93]

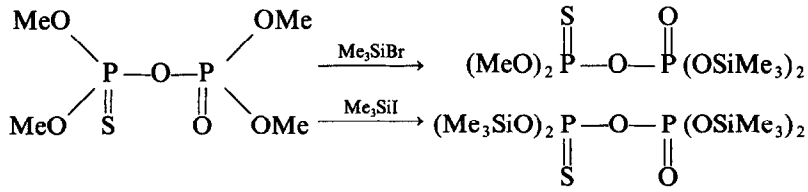
Voronkov and Zgonnik[7] observed that silyl bromides are much more reactive in transesterification than silyl chlorides but it was not until 1975 that McKenna proposed trialkylsilyl bromides as general reagents for removal of alkyl ester groups from phosphorus esters under very mild conditions.[8,9,145] Independently Rudinskas and Hullar used Me_3SiBr as a dealkylation agent in the synthesis of some model phosphonic acids.[136] Indeed, Me_3SiBr removes methyl and ethyl ester groups from phosphonates very effectively at room temperature making possible their conversion to bis(trimethylsilyl) esters in almost theoretical yields. Soon after, trimethylsilyl iodide was reported independently by several research groups to be a powerful reagent for conversion of alkyl esters of phosphorus into the corresponding silyl esters.[146,147,105] The exchange of methyl into a silyl ester group may be accomplished in temperatures as low as $-40°C$, with preservation of other reactive groups bound to phosphorus such as chloro, bromo or amino groups.[105]

A useful modification to this method was introduced by two Japanese groups who found that Me_3SiCl and an equimolar amount or small excess of NaI in acetonitrile,[148–150] or LiI in carbon tetrachloride,[151] was a powerful silylating agent and could be used as Me_3SiI equivalent for the silylation of esters of phosphorus. Since silyl chloride is more readily available than the iodide, this method is particularly attractive and has been used by many chemists. The use of Me_3SiI and its equivalents for the selective dealkylation of esters of phosphorus was reviewed up to 1980 by Olah and Narang.[42]

Both Me_3SiBr[3,144,145,136,105,152–160] as well as Me_3SiI or its equivalent[4,5,105,146–151,156b,161–163,179] have found a wide application in the selective removal of alkyl groups from esters of phosphorus. Some examples are presented in Table 3. In particular those reagents are selective in PO versus CO dealkylation which requires higher temperatures and a longer time.[164] This makes possible the dealkylation of phosphorus ester groups with the preservation of the carboxylic ester groups.[145,146,148,151,164,165,179] This is very important in the chemistry of phospholipids. The high reactivity of Me_3SiBr and Me_3SiI made possible the synthesis of silyl esters of phosphorus which are not stable at room temperature such as $BrP(O)(OSiMe_3)_2$.[105] It was also demonstrated by Bartlett and Long[3] that silylation of esters of phosphorus with Me_3SiBr combined with hydrolysis makes possible the generation of acids of phosphorus in media in which they normally undergo

spontaneous decomposition. This approach permitted these authors to study the kinetics of reactions of unstable diazophosphonic acids.

Differences in the reactivity of silyl bromides and iodides can be used for selective removal of alkyl ester groups[105] from unsymmetric thiopyrophosphates.



(37)

Silyl bromide silylates only the oxyphosphoryl residue whereas silyl iodide substitutes all the alkyl groups. The possibility of dealkylation of polyphosphates without breaking of the POP or PSP bond is of importance for the synthesis of models for enzymatic studies.[4,5] Me_3SiBr has recently been successfully applied for selective dealkylation of the oxyphosphoryl group of derivatives of methanethiodiphosphonate.[160]

The reactivity order in the silylation of esters $(RO)_3P{=}X$ is $X = O > X = Se > X = S$.[70] The transesterification of *O*-alkyl thionophosphates occurs much more slowly than their P=O analogues. This reaction is not brought about by Me_3SiBr. So no conversion of $(EtO)_3PS$ and $(EtO)_3PSe$ was observed by refluxing them in methylene chloride 1:1 v/v for 3 hr with 3 equivalents of Me_3SiBr. It was also shown that the rate of dealkylation decreases rapidly in the series $>P(O)OR > >P(O)SeR > >P(O)SR$.[70] This creates the possibility of synthesising *S*-alkyl monoesters of thiophosphoric and thiophosphonic acids.[105,156a,166] Removal of *S*-alkyl groups from $>P(O)SR$ and $>P(O)SeR$ substrates with Me_3SiX (X = Br, I) leads always to the corresponding $>P(S)OSiMe_3$ and $>P(Se)OSiMe_3$ products.[70]

Alkyl groups are removed stepwise:

$$(RO)_2P(O)R' \xrightarrow[-RX]{Me_3SiX} (RO)(Me_3SiO)P(O)R' \xrightarrow[-RX]{Me_3SiX} (Me_3SiO)_2P(O)R' \qquad (38)$$

X = halogen R = alkyl

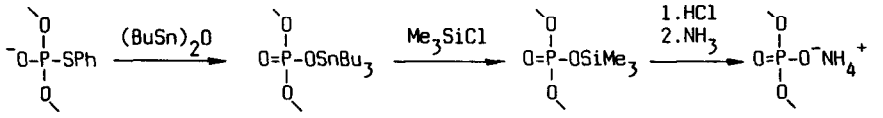
Rates of the substitution of the first silyl group and the others are comparable. For example in the silylation of *O,O*-dimethylphosphorochloridate with an equimolar amount of Et_3SiBr, a 59% conversion to the monosilyl ester and 21% conversion to the bis-silyl ester were recorded.[70] Thus the method is not promising for the synthesis of alkyl monoesters unless the alkyl groups in the substrate are different.

Reactivity in the dealkylation process depends on the size of the alkyl ester group. Competitive experiments on the dealkylation of dimethyl, diethyl and di-isopropyl acylphosphonates with Me_3SiBr indicated the relative reactivities to be 1:0.25:0.04 respectively.[145] This suggests that monodealkylation of mixed methyl isopropyl esters with Me_3SiBr could be a useful route to alkyl mono-esters of phosphonic acids. Increase of the size of substituents at the silicon atom is also expected to lead to differences in the rate of subsequent introduction of silyl groups into phosphorus esters.

Significant differentiation in the rate of removal of the first, second and third alkyl groups from trialkyl phosphates may be achieved by using as the silicon substrate, phenyltrimethylsilyl thioether with catalytic amount of PhS^--crown ether complex.[167] For example in the transformation: $(MeO)_3PO \xrightarrow{I} (MeO)_2(Me_3SiO)PO \xrightarrow{II} (MeO)(Me_3SiO)_2PO \xrightarrow{III} (Me_3SiO)_3PO$ half lives in 30°C were 7.7, 55 and 455 min for steps I, II and III respectively. This method seems to be promising

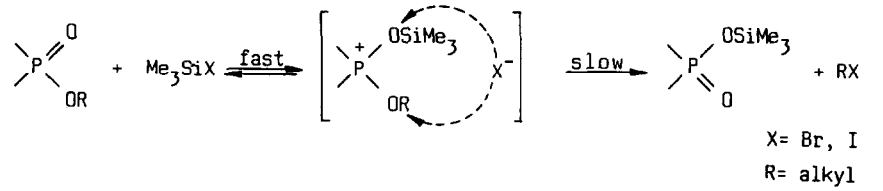
for mono- and di-dealkylation of trialkyl phosphates as well as for monodealkylation of dialkyl phosphonates.

Aromatic ester groups are not cleaved from phosphorus esters by the action of silyl halides.[158] Instead, Sekine and Hata[168] showed that the phenylmercapto group can be effectively removed from internucleotidic thiophosphate using bis(tributyltin) oxide. The tributylstannyl ester which is formed can be easily transformed by transesterification into the silyl ester, which in turn is easily hydrolysed to the corresponding phosphorus acid.[169]



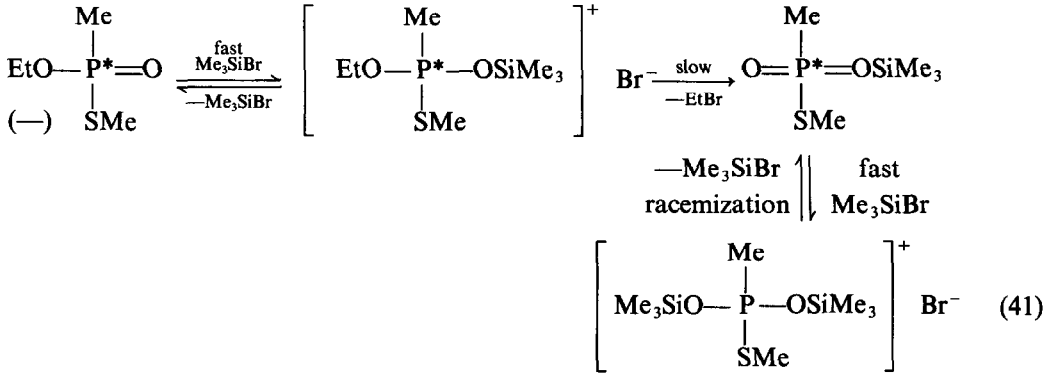
(39)

The mechanism of the transesterification of alkyl esters of phosphorus with Me_3SiBr and Me_3SiI involves the formation of phosphonium ion intermediates. Schmidbaur and Seeber observed that silylation of alkyl phosphates or phosphonates with Me_3SiI leads to the formation of siloxyphosphonium salts.[170] Later, it was demonstrated by low temperature ^{31}P NMR combined with electric conductance study[70] that the silylation is a two step process. The first is a fast reversible formation of phosphonium salt intermediate, which decomposes in the rate limiting step as a result of dealkylation by halide anion.



(40)

When the reaction is carried out in methylene chloride, the fast pre-equilibrium lies well to the right for X = I and to the left for X = Br. The equilibrium is fast as compared with the NMR time-scale even at temperatures as low as −80°C. This indicates that the halide ion attacks the silyl group much more readily than the alkyl groups in the phosphonium salt. Thus the intermediate decomposes much faster to substrates than to products. This mechanism is in agreement with the observation that the trans-silylation is accompanied by complete racemization at the phosphorus centre.

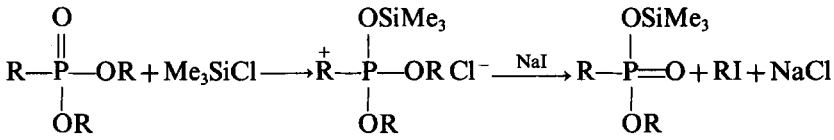


(41)

The kinetic curve of the above reaction carried out in methylene chloride at 23°C obtained from ^{31}P NMR was the same as that from optical rotation change.

As a consequence of the mechanism (40) the trans-silylation process occurs readily when the silyl ester is treated with a silyl halide having substituents at silicon different from those in the ester. Kinetic studies showed that the trans-silylation is fast even in the case of silyl chloride.[68] As a matter of fact this reaction may be conveniently used for the exchange of trimethylsilyl into a heavier silyl group in P=O esters.[80,171] Trimethylsilyl chloride formed is distilled off and the trans-silylation product may be obtained in almost quantitative yield.

In the case of dealkylation with ($Me_3SiCl + NaI$) or ($Me_3SiCl + LiI$) the mechanism proposed does not invoke the intermediacy of Me_3SiI.[148,151]



(42)

However, since the iodide anion attacks silicon much more readily than the alkyl ester group in the phosphonium cation,[70] a stationary concentration of Me_3SiI must be established at the very beginning of the process and presumably the silyl iodide is an important intermediate in the process. Some selected silylations of alkyl esters of phosphorus are collected in Table 4.

4.2. *Generation of phosphorus acids from their silyl esters*

In contrast with the cleavage of the alkyl ester group, which usually occurs via nucleophilic attack at the phosphorus,[47] the silyl ester group is cleaved by water or alcohol as a result of nucleophilic attack on silicon.[81,182] Thus alcoholysis of these esters leads to the formation of acids of phosphorus and is therefore used as a more convenient method than hydrolysis.[16,135,136,153,163,168] In the case of alcoholysis the other product is the corresponding alkyltrimethylsilyl ether (trialkylalkoxysilane). In hydrolysis the major product is hexaalkyldisiloxane formed by condensation of the trialkylsilanol which is formed as a primary hydrolysis product. Although Me_3SiOH easily undergoes condensation in the presence of acids[173] with an equilibrium constant of the order of 10^3,[174] some silanol may also be present in the system. Boiling points for Me_3SiOMe and $Me_3SiOSiMe_3$ are 56 and 100°C, respectively. Me_3SiOMe forms an azetrope with methanol which has a lower boiling point than Me_3SiOMe.[175] Thus it can be easily removed from the system by distillation. This is important because alcoholysis and hydrolysis of the silyl ester are reversible processes.[6] Reasonable excess of alcohol or water is also recommended.[6,145] The acids are often isolated as ammonium salts. For this purpose cyclohexylamine,[145,168] aniline,[151,163,168] *p*-anisidine,[146] triethylamine[176] and some other amines are introduced in hydrolysis or after these processes are accomplished. Sometimes the acids are isolated as sodium[132,154,161,177] barium[2,131] lithium[4] or other metal salts by using alkoxides or carboxylic acid salts as the nucleophilic desilylating reagents.

Conversions of silyl esters of phosphorus to their acids have been performed with the preservation of many reactive groups bound either to phosphorus or to the organic moiety of silyl phosphonates. In particular, it is possible to remove the silyl group without affecting the anhydride phosphorus bond. For example, the PSP bond was preserved in the alcoholysis of symmetric tetrakis(trimethylsilyl) monothiodiphosphate.[4] The silyl group is hydrolysed or alcoholysed without cleaving the aroyl group bound to phosphorus.[13] This group has been used in the synthesis of dinucleoside phosphonates. It serves as a protecting group masking the

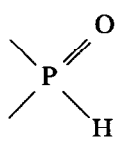


Table 4. Some selected silylation reactions: $(RO)_2P(O)X \xrightarrow{\text{Sil. reagent}} (Me_3SiO)_2P(O)X$

X	R	Silylating reagent	Conditions	Yield %	References
1. Me—	Et	Me_3SiCl	2.1 eq., neat, reflux, 6 hr	91	6
2. CH_2=CH—	Et	Me_3SiCl	ca 3 eq. added gradually, neat reflux, periodically over 30 days	78	6
3. CH_2=CH—	Et	Me_3SiI	2.0 eq., CCl_4 or $HCCl_3$, $-40° \rightarrow$ r.t.	almost theor.[a]	146
4. CH_2=CH—	Et	$Me_3SiCl + LiI$ anh. $+ Et_3N$	2.4+2.4+1 eq. CCl_4 5 ml/g of substr. 50°, 30 min	100[a]	151
5. CH≡C—	Et	Me_3SiI	2.0 eq., CCl_4 or HCC_3, $-40°C \rightarrow$ r.t.	almost theor.[a]	146
6. $PhCH_2$—	Et	Me_3SiI	2.0 eq., CCl_4 or HCC_3, $-40°C \rightarrow$ r.t.	almost theor.[a]	146
7. $HOCH_2CH(CH_3)$—	Me	$Me_3SiCl + NaI$	2+2 eq., CH_3CN, r.t. 30 min	50[b]	163
8. MeC(O)—	Et	Me_3SiI	2 eq., CCl_4, 0°C	76	147
9. MeC(O)—	Et	Me_3SiBr	2–3 eq., neat, 25°C, 1 hr	100[a]	145
10. $MeC(O)CH_2$—	Et	Me_3SiI	2 eq., CCl_4, 0°C	84	147
11. $EtOC(O)CH_2$—	Et	Me_3SiBr	2–3 eq., neat 25°C, 1 hr	100[a]	145
12. $EtOC(O)CH_2$—	Et	$Me_3SiCl + LiI$ anh.	2.4+2.4, CCl_4, 50°C, 30 min	100[a]	151
13. $Et_2NC(O)$—	Et	$Me_3SiCl + NaI$	2+2 eq., CH_3CN, 20−40°C, 30 min	98	148
14. $(MeO)_2CH$—	Me	$Me_3SiCl + NaI$	2+2 eq., CH_3CN, r.t. 15 min	100[a]	148
15. $(EtO)_2CHC$≡C—	Et	Me_3SiCl	10 ml/lg substr., neat in stainless steel Parr bomb., 100°C, 3 days	45[b]	136
16. $(EtO)_2CHC$≡C—	Et	Me_3SiBr	2.4 eq., neat r.t. 15 min + reflux 45 min	79[b]	136
17. $NH_2C(O)CH_2$—	Et	$Me_3SiCl + NaI$	2+2 eq., CH_3CN, 20–40°C, 30 min	98[a]	148
18. $Me(EtO)C$=$NO(CH_2)_2$—	Et	Me_3SiBr	2.1 eq., neat 70°C with distill. of EtBr 4 hr	85	157
19. MeS—		Me_3SiBr	2 eq., CH_2Cl_2, r.t.	100[a]	70
20. $EtSCH_2$—	Et	$Me_3SiCl + LiI$ anh.	2.4+2.4 eq., CCl_4, 50°C, 30 min	100[a]	151
21. Cl—	Me	Me_3SiBr	2 eq., neat r.t. 24 hr	85,[a] 52	105
22. Br—	Me	Me_3SiI	2 eq., CH_2Cl_2, $-70 \rightarrow -30°C$, 15 hr	73[a]	105
23. $BrCH_2$—	Et	Me_3SiBr	2–3 eq., neat, 25°C, 1 hr	100[a]	145
24. $CNCH_2$—	Et	$Me_3SiCl + NaI$	2+2 eq., CH_3CN, r.t. 15 min	100[a]	148
25. NH_2—	Me	Me_3SiI	2 eq., CH_2Cl_2, 0°C, 2 hr	73	105
26. $(EtO)_2P(S)O$—	Et	Me_3SiBr	2 eq., neat, r.t., 24 hr	94,[a] 65	105
27. Cl_3C—	Me	$Me_3SiCl + NaI$	2+2 eq., CH_3CN, r.t. 15 min	100[a]	148

[a] Without isolation (^{31}P NMR).
[b] Yield of isolated acid after hydrolysis (alcoholysis).

function since a variety of nucleophiles attacks selectively on the carbonyl carbon of acylophosphates giving acylated products and dialkyl phosphates.[21]

Examples of the generation of acids or salts from their silyl esters are given below

$$RC(O)OP(O)(OSiMe_3)_2 \xrightarrow{ArNH_2/EtOH} RC(O)OP(O)(OH)O^-NH_3^+Ar^{13} \quad (43)$$

$$RC(N_2)P(O)(OSiMe_3)_2 \xrightarrow[pH\ 8-9]{H_2O} RC(N_2)P(O)O_2^{2-\ 3} \quad (44)$$

$$(Me_3SiO)_2P(O)SPh \xrightarrow{Ba(CH_3COO)_2} PhSP(O)_2^{2-}Ba^{2+\ 2} \quad (45)$$

$$CH_2{=}C[OP(O)(OSiMe_3)_2]{-}C(O)OSiMe_3 \xrightarrow{3NaOEt} CH_2{=}C[OP(O)(\bar{O}\overset{+}{N}a)_2]C(O)\bar{O}\overset{+}{N}a^{177} \quad (46)$$

$$(EtO)_2\overset{O}{\overset{\|}{P}}O\overset{O}{\overset{\|}{P}}(OSiMe_3)_2 \xrightarrow{H_2O} (EtO)_2\overset{O}{\overset{\|}{P}}O\overset{O}{\overset{\|}{P}}(OH)_2{}^{69} \quad (47)$$

$$(Me_3SiO)_2\overset{O}{\overset{\|}{P}}S\overset{O}{\overset{\|}{P}}(OSiMe_3)_2 \xrightarrow[2.\ LiOH]{1.\ Et(iPr)_2N+iPrOH} (\overset{+}{L}i\bar{O})_2\overset{O}{\overset{\|}{P}}S\overset{O}{\overset{\|}{P}}(\bar{O}\ \overset{+}{L}i)_2{}^4 \quad (48)$$

Silyl ester groups of phosphorus acids bridged by sulphur or selenium atoms are cleaved very easily by water, alcohol, or other nucleophiles. On the other hand, an oxygen bridged silyl group in esters of P=S acids undergoes hydrolysis or alcoholysis with some difficulty. These types of silyl esters of phosphorus are also used as precursors of acids of phosphorus.[5,179,180]

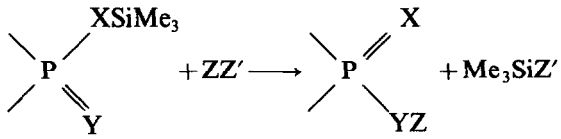
Kinetics of hydrolysis of some sterically hindered models of silyl phosphates and thiophosphates with the general formula $(Me_3SiO)_3SiOP(Y)(OR)_2$ Y = O, S, R = Me, Et, *n*-Pr, have been studied.[181] The reaction is sensitive to acid catalysis and it is probable that spontaneous and base-catalysed hydrolysis occur as well. The reaction when catalysed by a strong acid like H_2SO_4 in acetone–water 95 : 5 v/v shows first order kinetics. In the absence of strong acid, the reaction proceeds much more slowly showing complex kinetics of a product autocatalysed process. The reaction is sensitive to the steric effect of substituents at silicon atom, but seems to be less influenced by the bulkiness of the ester groups at the phosphorus atom. Thiono-esters react more slowly than their P=O analogues by a factor of about 10^3. These and other observations are in agreement with a mechanism involving nucleophilic attack on either the silicon atom of the protonated ester (case of acid catalysed process) or the ester which is hydrogen bonded through the P=Y group (case of spontaneous or base catalysed process).

Hydrolysis of silyl esters of tricoordinate phosphorus is only seldom used in preparation of bio-organic models. The oxygenation step on synthetic routes to these models is usually performed before removal of silyl groups. The cleavage of P(III) silyl esters occurs smoothly and may be performed with water in the presence of pyridine.[113] Reaction with water proceeds by nucleophilic attack at the silicon atom: this was proved by experiment with $H_2{}^{18}O$.[182] Reactions of P(III) silyl esters with alcohols were also found to involve the attack of oxygen at phosphorus leading to appropriate P-acids and alkoxysilanes.[61,81,178]

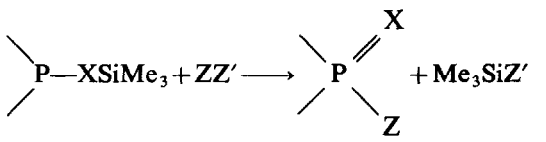
5. SYNTHESIS OF PHOSPHORUS ANHYDRIDES

There has recently been interest in the synthesis of anhydrides of phosphorus acids as well as mixed anhydrides of acids of phosphorus and some inorganic or carboxylic acids. Some of them are important intermediates in phosphorus chemistry and in biological systems. Silyl esters of

phosphorus are often convenient intermediates for these syntheses. The general scheme of the transformation of these esters into anhydrides includes reactions of silyl esters of P(V) and P(III) with symmetric and mixed anhydrides:



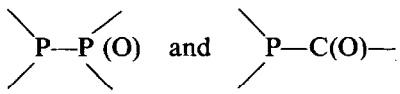
(49)



(50)

X and Y could be O, S, Se, while Z and Z′ are residues of acids.

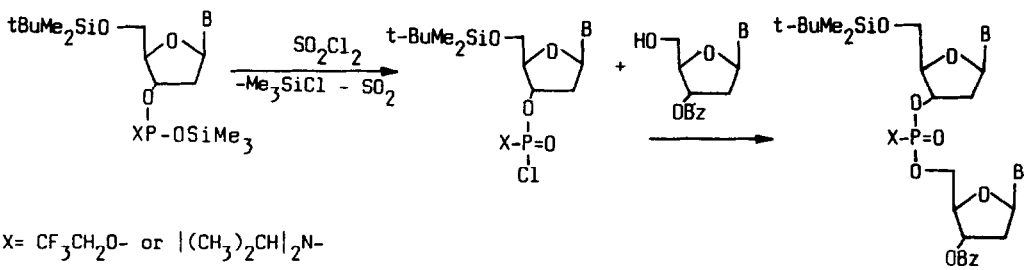
This Section is devoted to the synthesis of halogen–phosphorus anhydrides and anhydrides in which an acid residue is bound to phosphorus by an atom of oxygen, sulphur or selenium. It does not include reactions leading to



structures, which are to be found in the next Section.

5.1. *Phosphorus halogen anhydrides*

Phosphorus halogen anhydrides are important, versatile reagents useful in coupling reactions in the synthesis of nucleotides and peptides.[183,184] Some of them can be obtained from silyl ester precursors. A good example is the transformation of the trimethylsilyl phosphite derivative of a nucleoside into the phosphorochloridate which serves for the formation of an internucleotide bond.[183]



(51)

X= CF_3CH_2O- or $[(CH_3)_2CH]_2N$-

B= thymine or N(6)-benzoyladenine

Silyl phosphites react readily with halogens, giving corresponding phosphorohalidates.[185] The reaction with iodide has been recently used in nucleotide synthesis.[186]

Conversion of the silyl ester group into a chloro-substituent in esters of tetracoordinate phosphorus acids may be accomplished using PCl_5.[149] Bis(trimethylsilyl) phosphonates react smoothly with PCl_5 at 20–30° in carbon tetrachloride giving the corresponding dichloridates in high yield.

$$RP(O)(OSiMe_3)_2 + 2PCl_5 \xrightarrow{CCl_4} RP(O)Cl_2 + 2Me_3SiCl + 2POCl_3 \quad (52)$$

R = Me, Et, cyclohexyl, $PhCH_2$, *p*-EtC_6H_5, $EtOCOCH_2$, $CH_2{=}CH$, $CH_2{=}CHCH_2$

Recently Dąbkowski and Michalski found that silyl esters of P(III) react with sulphuryl chloride fluoride chemospecifically and under mild conditions giving almost theoretical yields of the corresponding phosphorofluoridates.[187]

$$RR'P(OSiMe_3)+SO_2ClF \longrightarrow RR'P(O)F+Me_3SiCl+SO_2 \quad (53)$$

$$R = R' = EtO,\ CF_3CH_2O,\ iPrO,\ PhO \text{ and } R = t\text{-Bu while } R' = Ph$$

The course of the reaction is unexpected in view of the well known high affinity of fluorine for silicon. Since the other products, SO_2 and Me_3SiCl, are volatile and readily separable, this reaction provides an easy access to all types of the fluoridates including those of the highly toxic ones mentioned in ref. 188, needed for enzymatic studies. Fluoridates derived from nucleosides can also be synthesized using this method.[189]

It was shown that the Michalski–Skowrońska reaction of chlorination of thionophosphates with SO_2Cl_2[190] proceeds chemospecifically when applied to tris(trimethylsilyl) thionophosphate giving 100% yield of bis(trimethylsiloxy)phosphorylsulphenyl chloride.[104]

$$(Me_3SiO)_3PS \xrightarrow[-Me_3SiCl]{SO_2Cl_2} (Me_3SiO)_2\overset{\overset{O}{\|}}{P}SCl \xrightarrow{CH_2=CHR} (Me_3SiO)_2\overset{\overset{O}{\|}}{P}SCH_2\text{—}\overset{\overset{Cl}{|}}{C}HR \xrightarrow{H_2O} (HO)_2\overset{\overset{O}{\|}}{P}SCH_2\overset{\overset{Cl}{|}}{C}HR \quad (54)$$

This compound can be used as a reagent for the introduction of the thiophosphoryl group having a hydrolysable ester group, by addition to olefinic bond or by reaction with some nucleophilic centres. It reacts very fast with thionophosphates giving corresponding disulphides[104] as do other phosphorylsulphenyl chlorides.[191]

$$(Me_3SiO)_2\overset{\overset{O}{\|}}{P}SCl+(Me_3SiO)_3P{=}S \longrightarrow (Me_3SiO)_2\overset{\overset{O}{\|}}{P}S\overset{\overset{O}{\|}}{S}P(Me_3SiO)_2 \quad (55)$$

Since the reaction is fast it plays an important role in the chlorination of the thionophosphate. If SO_2Cl_2 is added to the ester then the disulphide is the exclusive product until half the stoichiometric amount of the chlorination agent has been added. A further portion of SO_2Cl_2 converts the disulphide to the sulphenyl chloride.

Stec and Uzański showed that chlorination of trimethylsilyl selenophosphates yields the very unstable phosphorylselenyl chlorides.[192]

$$(NpO)_2(Me_3SiO)P{=}Se+SO_2Cl \xrightarrow{-70°CH_2Cl_2} (NpO)_2P(O)SeCl+Me_3SiCl+SO_2 \quad (56)$$

The selenyl product decomposed when the temperature was raised above $-50°C$.

Bromination of the silyl esters of dithio-acids of phosphorus gives thiophosphorylsulphenyl bromides.[193] The reaction also proceeds via the corresponding disulphide:

$$2RR'P(S)SSiMe_3 \xrightarrow[-2Me_3SiBr]{Br_2} RR'P(S)SSP(S)RR' \xrightarrow{Br_2} 2RRP'(S)SBr \quad (57)$$

$$R = R' = t\text{BuCH}_2O,\ iPrO,\ MeO,\ PhO \text{ or } R = t\text{Bu},\ R' = MeO$$

These sulphenyl bromides may be used as intermediates for synthesis of many useful phosphorus-containing products. Chloro-analogues of the bromides were synthesized as follows:

$$\text{P(S)SBr} \xrightarrow{\text{ROH/base}} \text{P(S)SOR} \xrightarrow{\text{Me}_3\text{SiCl}} \text{P(S)SCl} \qquad (58)$$

Direct chlorination of the corresponding dithioacid, its silyl ester or disulphide leads to easy cleavage of the phosphorus–sulphur bond. Thus the yield of the sulphenyl chloride is minimal or negligible.[194] A moderate yield could be obtained in reaction (59).

$$RR'P(S)SSiMe_3 + SO_2ClF \longrightarrow RR'P(S)SCl + Me_3SiF + SO_2 \qquad (59)$$

Reaction of some trimethylsilyl selenophosphates with chlorocyanide leads to selenocyanophosphates, which show a higher stability than those generated from corresponding selenophosphorus acids.[192]

$$(RO)_2P(Se)OSiMe_3 + Cl{-}C{\equiv}N \longrightarrow \underset{\downarrow}{(RO)_2P(O)SeCN} + Me_3SiCl$$
$$(RO)_2P(O)NCSe \qquad (60)$$

These compounds undergo slow isomerization to corresponding isoselenocyanophosphates on standing at room temperature.

5.2. *Phosphorus carbonyl anhydrides*

The mixed anhydride of acetic and phosphoric acids is important since it belongs to the family of high energy phosphates.[195] The attempted synthesis of this compound by the reaction of tris(trimethylsilyl) phosphate and acetyl chloride followed by removal of silyl group failed because even in the case when one equivalent of acetyl chloride was used, a mixture of the mono-, di-, and tri-acetyl phosphates were formed.[16]

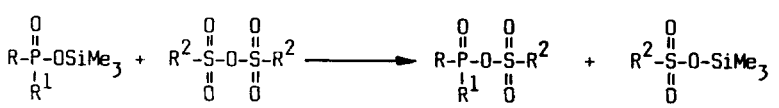
Hata[16,86] found that tris(tri-*n*-butylstannyl) phosphate was selective in its reaction with acetyl chloride or its derivative. Only one stannyl group was exchanged, which was very readily replaced by a silyl group as a result of the interaction with silyl chloride. The silyl group was removed with ethanol–aniline. These authors propose the application of tri-*n*-butylstannyl bis(trimethylsilyl) phosphate, which may be easily prepared by reaction of tris(trimethylsilyl) phosphate with two equivalents of tri-*n*-butyltin methoxide, as a general reagent for the synthesis of acyl phosphates.

$$Bu_3SnO{-}P(O)(OSiMe_3)_2 \xrightarrow[-Bu_3SnCl]{RCOCl} RC(O)OP(O)(OSiMe_3)_2 \xrightarrow{ArNH_2/EtOH}$$
$$RC(O)OP(O)(OH)O^{-}H_3^{+}NAr \qquad (61)$$

5.3. *Anhydrides of phosphorus and oxysulphur acids*

Mixed anhydrides of phosphorus and oxysulphur acids can be also readily synthesized from silyl esters of phosphorus. These types of anhydrides are of interest in some aspects. They serve in the biotransfer of sulphates.[196] Phosphorus-sulphonic anhydrides are postulated to be reactive intermediates in the chemical synthesis of oligonucleotides.[197] They were also suggested to be intermediates in the bio-oxidation of *S*-thiolophosphates.[198]

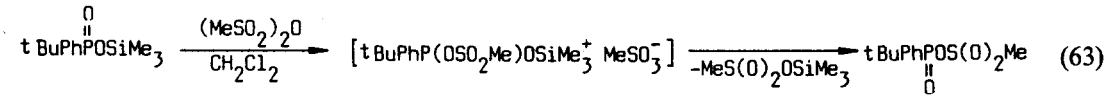
Some silyl esters of phosphorus are surprisingly easily converted into mixed anhydrides as a result of interaction with sulphonic anhydrides.[199]



(62)

R, R^1, R^2 = t-Bu, Ph, Me; t-Bu, OMe, Me; OEt, OEt, Me; t-Bu, Ph, CF_3; t-Bu, OMe, CF_3; $OSiMe_3$, $OSiMe_3$, Me; t-Bu, Ph, pMePh; OEt, OEt, pMePh

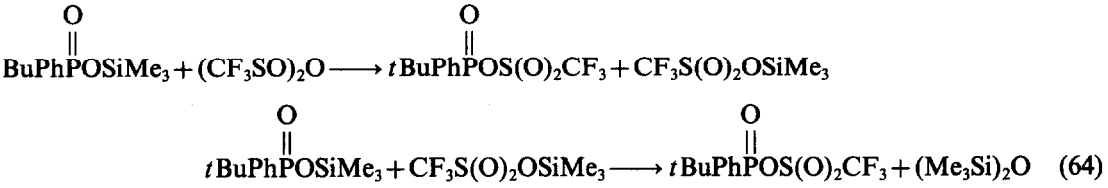
The reaction with methanesulphonic anhydride proceeds in methylene chloride solution at ambient temperature in excellent yield. It was shown by low temperature experiments that the phosphonium salt intermediate is involved.



(63)

Starting from bis(trimethylsilyl) phosphonate, phosphonic sulphonic anhydride containing two residues of methanesulphonic acid bonded to phosphorus was obtained in good yield and high purity.

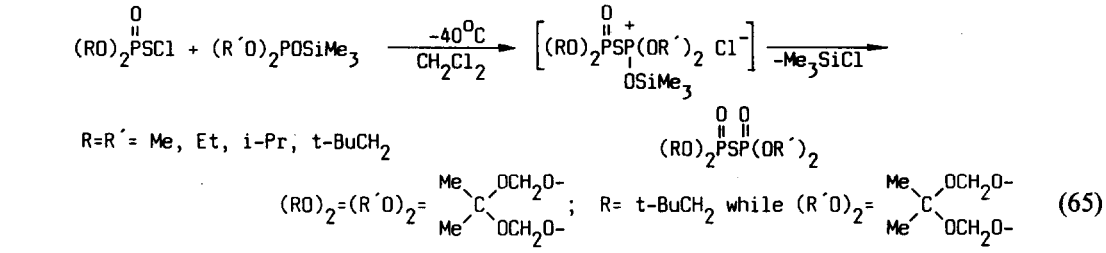
Reaction with $(CF_3SO_2)_2O$ is complicated by the high silylating reactivity of the silyl ester of trifluoromethanesulphonic acid. The reaction can be applied only for the synthesis of anhydrides of phosphinic acids. In the case of phosphonates or phosphates the consecutive silylation with $CF_3SO_2OSiMe_3$ leads to a mixture of products. Since silyl esters of phosphinic acids also react at room temperature with $CF_3SO_2OSiMe_3$ producing the mixed anhydrides, the silyl phosphinates enter into reaction with $(CF_3SO_2)_2O$ in molar ratio 2:1.



(64)

5.4. *Diphosphorus anhydrides*

Recently silyl esters of phosphorus have also been successfully applied for synthesis of diphosphorus anhydrides. Pyrophosphates and their analogues are of interest because they are often used in bio-organic studies. In particular thio-analogues of organic phosphates have been used for enzymatic studies in nucleotide chemistry.[4,5,200,201] The symmetric isomer $(RO)_2P(O)SP(O)(OR)_2$ is more difficult to synthesize because being thermodynamically less stable than the unsymmetrical isomer it readily undergoes thiono-thiolo rearrangement.[202] The original method for the synthesis of symmetric thiopyrophosphates[203] has recently been modified by using dialkyl (trimethylsilyl) phosphites in the place of trialkyl phosphites. This modification permits the generation of symmetric thiopyrophosphates under very mild conditions without the requirement of steric hindrance by the organic ester groups.[204]



(65)

The intermediacy of the phosphonium salt was postulated on the basis of previous results.[205]

Use of the silyl esters of phosphorus also provides access to the seleno-analogues of pyrophosphates.[30] It was discovered that *O,O*-dialkyl *O*-trimethylsilyl selenophosphate undergoes a remarkably selective reaction with equimolar amounts of dialkyl(trimethylsilyl) phosphite and SO_2Cl_2 giving the symmetrical selenopyrophosphate.

$$(RO)_2P(Se)OSiMe_3 + (R'O)_2POSiMe_3 + SO_2Cl_2 \xrightarrow[-78°C]{CH_2Cl_2} (RO)_2P(O)Se-SeP(O)(OR')_2 + SO_2 + 2Me_3SiCl \quad (66)$$

R and R′ as eq. (65).

The reaction proceeds via the selenyl chloride intermediate which is known to be very unstable and decomposes above $-50°C$.[192] Thus the overall process must be carried out at low temperature. If a symmetrically substituted R = R′ seleno-pyrophosphate is to be synthesized, the silyl seleno-phosphate reagent may be prepared *in situ* by the addition of elemental selenium to the phosphite reagent. Unsymmetric selenopyrophosphates $(RO)_2P(Se)OP(O)(OR)_2$ may be obtained from the corresponding symmetric isomers by isomerization on warming above 60°C.

An alternative method for the synthesis of symmetrical selenium pyrophosphates has been recently developed.[206] Diphosphoryl diselenides react with (trimethylsilyl) dialkyl phosphites at low temperature in a very selective way giving *syn*-selenopyrophosphates as the almost exclusive products.

$$(RO)_2P(O)Se-SeP(O)(OR)_2 + (R'O)_2POSiMe_3 \xrightarrow[CH_2Cl_2]{-100^{\circ}\text{ to }-95^{\circ}} \left[(RO)_2P(O)SeP(OR')_2 \; OSiMe_3 \; - \; P(OR)_2 \; Se\right] \longrightarrow (RO)_2P(O)SeP(O)(OR')_2 + (RO)_2P(Se)OSiMe_3 \quad (67)$$

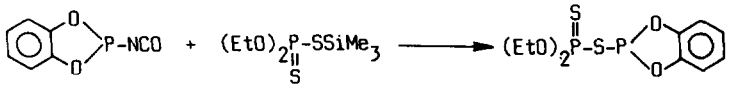
R and R′ like in the eq. 65

Unsymmetrical tetraalkyl dithiopyrophosphates can be synthesized under very mild conditions and in high yield as a result of the reaction of thiophosphorylsulphenyl chlorides with trimethylsilyl phosphites[29] (68):

$$(RO)_2P(S)SCl + Me_3SiOP(OR')_2 \longrightarrow (RO)_2P(S)SP(O)(OR')_2 + Me_3SiCl \quad (68)$$

This reaction has been carried out using chiral cyclic phosphites and was found to occur stereo-selectively with retention of configuration at the phosphorus atom.[207]

Some mixed anhydrides of tri- and tetracoordinate phosphorus can be synthesized in the reaction of cyclic P(III) isocyanates with *S*-silyl dithiophosphates.[208]



(69)

Various thio-, dithio- and trithiophosphinates were synthesized from the corresponding acids and bromo- or chloro-phosphorus anhydrides.[111] NMR spectroscopic investigations of these esters have been made.

Pyrophosphates were shown to be the final products of the reactions of silyl esters of P(V) with some nucleophiles.[209] The Todd–Atherton reaction of silyl phosphites with chloroacetonitrile also leads eventually to pyrophosphates.[210]

6. SYNTHETICALLY DIRECTED REACTIONS OF SILYL ESTERS OF TRICOORDINATE PHOSPHORUS

Silyl esters of tricoordinate phosphorus, in particular the silyl phosphites $(Me_3SiO)_3P$ and $Me_3SiO(RO)_2P$ serve as versatile reagents for synthesis because of their high reactivity towards a

variety of organic and organometallic compounds. Reactions of silyl phosphites leading to phosphorus anhydrides was the subject of the previous section.

6.1. *Reactions with alkyl halides and acyl halides—the Arbuzov reactions*

Silyl phosphites react with different alkyl bromides and iodides,[1,16-19,117,211] also with bromine or iodine[185] by the Arbuzov mechanism. Several reactions of silyl phosphites with α-halocarbonyl compounds lead to Arbuzov type products although they are often accompanied by Perkow products and/or 1 : 1 adducts. They are therefore described separately. (Section 6.3.5.)

The Arbuzov reaction with mixed alkyl silyl phosphites involves desilylation with the formation of silyl halides not dealkylation.[1,54,216] Subsequent introduction of the silyl group in the place of an alkyl group in the phosphite increases the nucleophilicity of the tricoordinate phosphorus centre, so that the reactivity in the Arbuzov reaction increases in the following sequence:[54]

$$P(OR)_3 < P(OR)_2(OSiMe_3) < P(OR)(OSiMe_3)_2 < P(OSiMe_3)_3$$

Primary alkyl halides react with tris(trimethylsilyl) phosphite yielding bis(trimethylsilyl) alkylphosphonates.[18,211]

$$(Me_3SiO)_3P + RBr \longrightarrow RP(O)(OSiMe_3)_2 + Me_3SiBr \qquad (70)$$

$$R = PhCH_2, Bu$$

The Arbuzov reaction of silyl phosphites was used to obtain different phosphorus acids with labile substituents.[19] Tris(trimethylsilyl) phosphite reacted with D,L-3-iodo-1,2-distearoyl propane producing bis(trimethylsilyl) D,L-distearoylpropylphosphonate which can be easily converted to 2,3-distearoylpropylphosphonyl choline derivatives.[134] This approach has proved to be a convenient way to prepare phosphonate containing lipids[212] and other compounds of biological interest.[213,214a]

Bis(trimethylsilyl) trimethylsiloxymethylphosphonite reacted with 3-chloropropionitrile by the Arbuzov mechanism, yielding 2-cyanoethyl(hydroxymethyl)phosphinic acid[19] after hydrolysis.

$$Me_3SiOCH_2P(OSiMe_3)_2 \xrightarrow{ClCH_2CH_2CN} Me_3SiOCH_2\overset{\overset{O}{\|}}{\underset{\underset{OSiMe_3}{|}}{P}}—CH_2CH_2CN \xrightarrow{H_2O} HOCH_2\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}—CH_2CH_2CN \qquad (71)$$

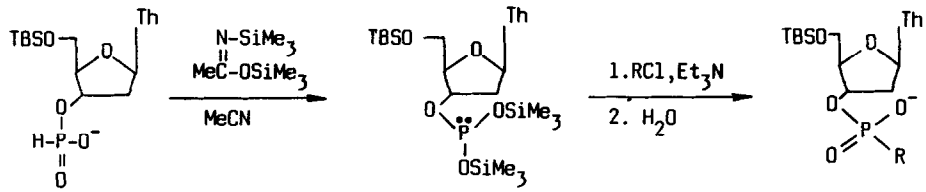
Trimethylsilyl methyl phosphonite reacts with allyl iodide producing *O*-trimethylsilyl allylphosphonite.[128] Less reactive halogenoalkanes (MeI, EtI) under the same conditions give a mixture of the products of the Arbuzov reaction, disproportionation, as well as phosphopolymeric residues (72).

$$(MeO)(Me_3SiO)PH \xrightarrow{RI} R—\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{P}}—OSiMe_3 + (Me_3SiO)_2\overset{\overset{O}{\|}}{P}H + Me_3SiO—\overset{\overset{H}{|}}{\underset{\underset{MeO}{|}}{P}}=O + \text{polymer}$$

$$\downarrow CH_2=CHCH_2I$$

$$CH_2=CH—CH_2\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}OSiMe_3 \qquad (72)$$

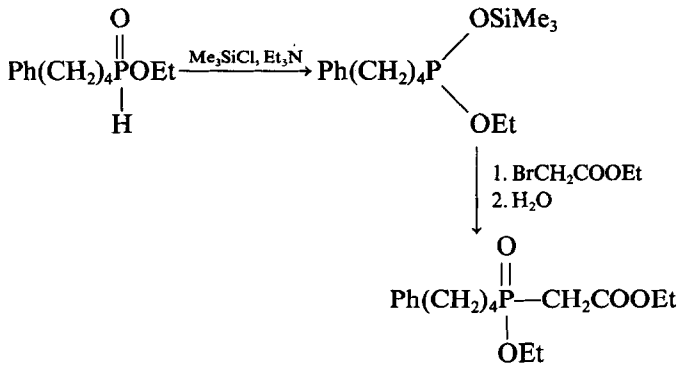
A general procedure to convert nucleoside phosphite mono- and diesters into the valuable phosphonate esters was proposed by De Vroom *et al.*[176] This takes advantage of the Arbuzov reaction of nucleoside bis(trimethylsilyl) phosphites with alkylating agents (73).



(73)

Th - thymine TBS - t-BuMe$_2$Si

Silyl alkylphosphonites and silyl dialkylphosphinites are less reactive, but they do undergo the Arbuzov reaction when a reactive alkylating agent is used.[115] Treatment of these phosphonites with ethyl bromoacetate in chloroform in the presence of trimethylsilyl chloride and triethylamine at room temperature results in their conversion to phosphinic esters.[215]



(74)

This proceeds as a one-pot synthesis according to eq. (74). Under similar conditions silyl phosphites react in a different way giving either carbonyl adducts and/or Perkow-like products.

It was shown by Orlov[216,217] that the reaction of tris(trialkylsilyl) phosphite with acyl halides proceeds in an analogous way to the reaction of trialkyl phosphite with these halides,[218] leading to the Arbuzov products—bis(trialkylsilyl) acylphosphonates. This reaction was explored to obtain acylphosphonic acids.[168]

$$RC(O)Cl \xrightarrow{(Me_3SiO)_3P} RC(O)P(O)(OSiMe_3)_2 \xrightarrow{ROH+PhNH_2} RC(O)P(O)(OH)O^- + {}^+H_3NPh \quad (75)$$

$$R = C_6H_5,\ 4\text{-Cl—}C_6H_4,\ 1\text{-MeO—}C_6H_4,\ CH_3,\ C_2H_5,\ C_2H_5O,\ Cl_3CCH_2O$$

Earlier attempts to generate these acids directly from analogous alkyl esters led to cleavage of the P—C bond.[221] Synthesis of other derivatives of acylphosphonic acid by the Arbuzov reaction was reported: in some cases the process took a complex course leading to different products.[219,220]

The reaction of alkyl esters of P(III) acids with acyl chlorides may proceed in a different way to that of their silyl ester analogues. Recent studies by Lutsenko[222] of the reactions of dialkoxymethanephosphonites with some carbonyl anhydrides led to the corresponding carbonyl phosphonites. The presence of a silyl ester group in the phosphonite substrates directs the reaction towards α-carbonylphosphinates.[222]

$$(RO)_2P[CH(OR)_2] + R^1COCl \longrightarrow (RO)_2PCOR^1 + ROP(O)[CH(OR)_2]$$

$$(Me_3SiO)(RO)P[CH(OR)_2] + t\text{-}BuC(O)Cl \longrightarrow ROP(O)[CH(OR)_2][C(O)t\text{-}Bu] \quad (76)$$

R= Et, R^1= t-Bu, i-Pr, Me

Silyl dialkoxymethanephosphonites undergo the Arbuzov rearrangement when heated under reflux with chloroformates.[223]

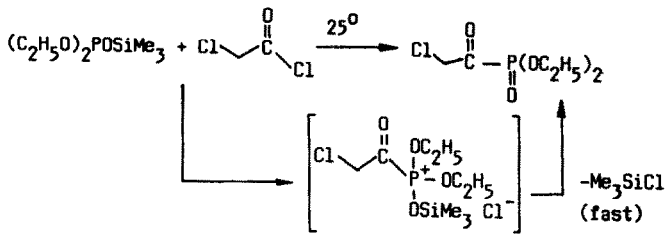
$$\begin{matrix} R^1O \\ Me_3SiO \end{matrix}\!\!>\!PCH(OR^1)_2 \xrightarrow[Et_2O,\text{reflux},2.5\ h]{ClCOOR} R^1O\text{-}P(O)(CH(OR^1)_2)(COOR) + Me_3SiCl \quad (77)$$

77-84%

R^1= Me, Et R= alkyl

Analogous dialkyl phosphonites react under the same conditions, with cleavage of the P—C bond, yielding phosphonites $(RO)_2PCOOR$.

In contrast with alkyl phosphites, in the reaction of chloroacetyl chloride with dialkyl trimethylsilyl phosphite, the only product observed was that of the Arbuzov reaction.[224]



(78)

The Arbuzov-like reactions of silyl phosphites with halogeno-anhydrides of P(III) acids are also promising as synthetic routes to some interesting diphosphorus compounds. Silyl esters of phosphinous acids react with chlorophosphines giving diphosphine oxides.[225]

$$R_2POSiMe_3 + R'_2PCl \xrightarrow[-Me_3SiCl]{} R_2P(O)\text{—}PR'_2 \quad (79)$$

R = R′ = alkyl or Ph

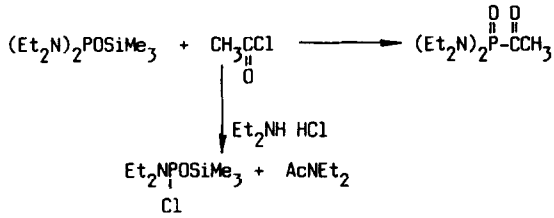
More recently it was shown that trimethylsilyl diethyl phosphite and tris(trimethylsilyl) phosphite react under mild conditions with diethyl dithiochlorophosphite giving the corresponding 1,1-di(ethylthio)-1,2-diphosphine-2-oxides.[226]

$$(RO)_2POSiMe_3 + (EtS)_2PCl \xrightarrow[-Me_3SiCl]{} (RO)_2P(O)P(SEt)_2 \quad (80)$$

R = Et, Me_3Si

The formation of the isomer of the pyrophosphite structure was not observed, even at very low temperatures.

Pudovik[220] showed that amine hydrochlorides present in a reaction mixture can change the direction of reaction of P(III) silyl esters with acyl chlorides.



(81)

Instead of the Arbuzov type reaction, substitution of the diethylamino-group was observed almost exclusively.

6.2. *Reactions of silyl phosphites with azides, azo compounds, imides and imines*

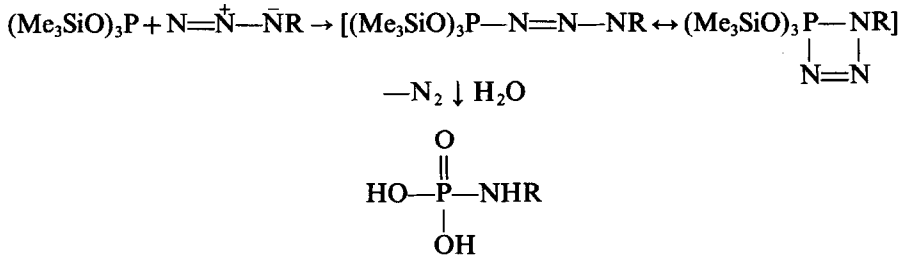
Silyl esters of tricoordinate phosphorus enter easily into the Staudinger reaction with azides which is followed by silyl group migration leading to phosphoroamidates. Presumably the process involves a dipolar intermediate.[16,227]

The reaction of phenyl azide with dimethyl-trimethylsilyl phosphite produces dimethyl-*N*-phenyl-*N*-trimethylsilyl amidophosphate.[228]

$$(MeO)_2POSiMe_3 + PhN_3 \longrightarrow [(MeO)_2P(OSiMe_3)=NPh] \longrightarrow (MeO)_2PN(SiMe_3)Ph \quad (82)$$

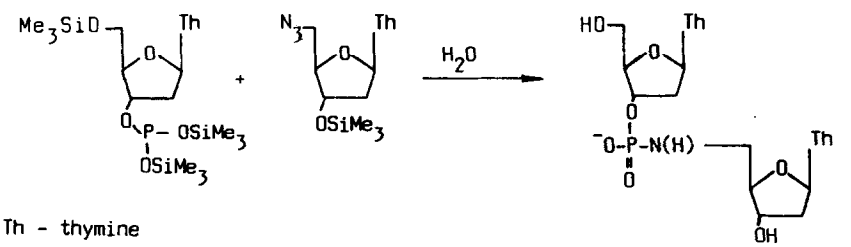
The chemistry of this phosphoroamidate product was explained by the existence of an equilibrium between the reactive *O*-silyl iminophosphate isomer and the more stable *N*-silyl amide isomer.[229]

Tris(trimethylsilyl) phosphite reacts with azides giving the corresponding *O*,*O*-bis(trimethylsilyl) phosphoroamidates,[16,39] which were hydrolysed without isolation to aminophosphonic acid.



(83)

This reaction has been used in nucleotide chemistry, 3′,5′-dinucleoside phosphoroamidates were prepared starting from 5′-azido-5′-deoxyribonucleosides and nucleoside bis(trimethylsilyl) phosphite.[39,230]

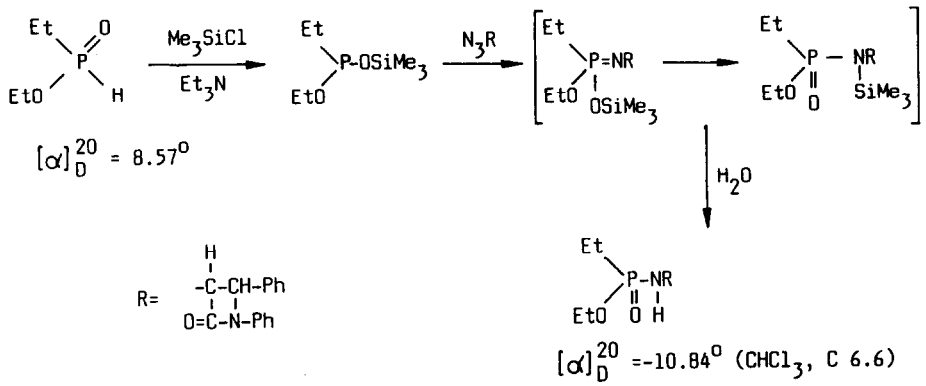


(84)

Th - thymine

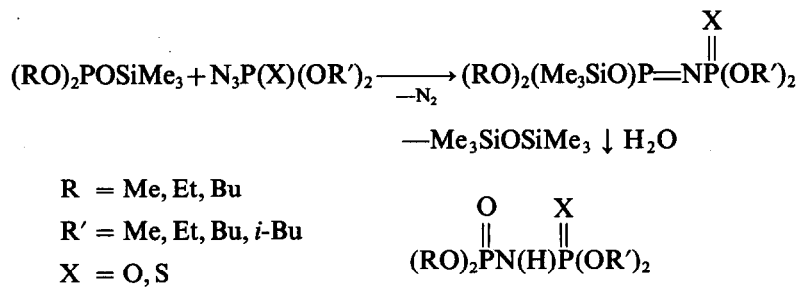
Application of the reaction of silyl phosphites with azides to the synthesis of oligoazanucleotides was also demonstrated by Gibbs.[238]

The Staudinger reaction of silyl phosphites with azides proceeds with retention of configuration at the phosphorus centre according to the following scheme.[231]



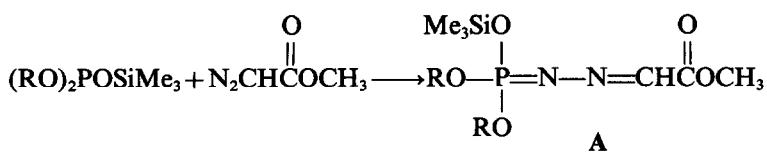
(85)

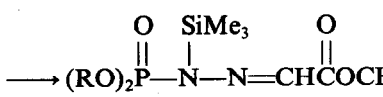
Reaction of silyl phosphites with azides was utilized by Kabachnik to obtain several interesting bis(dialkoxyphosphoryl) imides and unsymmetrical dialkoxyphosphoryl-(dialkoxythiophosphoryl) imides.[232]



(86)

Imidophosphates can also be obtained as the result of the reaction of dialkyl trimethylsilyl phosphites with dialkyl azidophosphates.[233] Earlier Pudovik[234] showed that silyl phosphites reacted with esters of diazoacetic acid, giving phosphazines (87)**A**. These are unstable at room temperature and isomerise to the corresponding hydrazidophosphates (87)**B**.

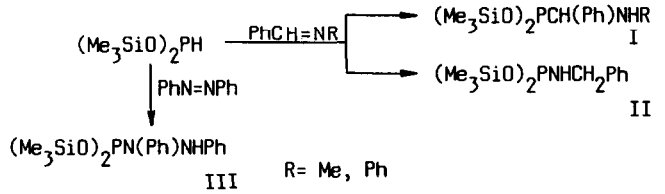




(87)

The reaction with diazoalkanes proceeds in a similar way.[234a]

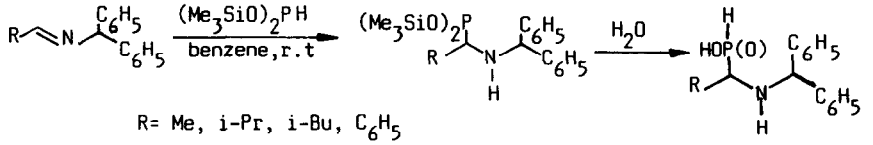
Bis(trimethylsilyl) phosphonite adds to the nitrogen–carbon double bond of imines and nitrogen–nitrogen double bonds of azo compounds with the cleavage of the P—H bond giving 1 : 1 adducts.[235]



(88)

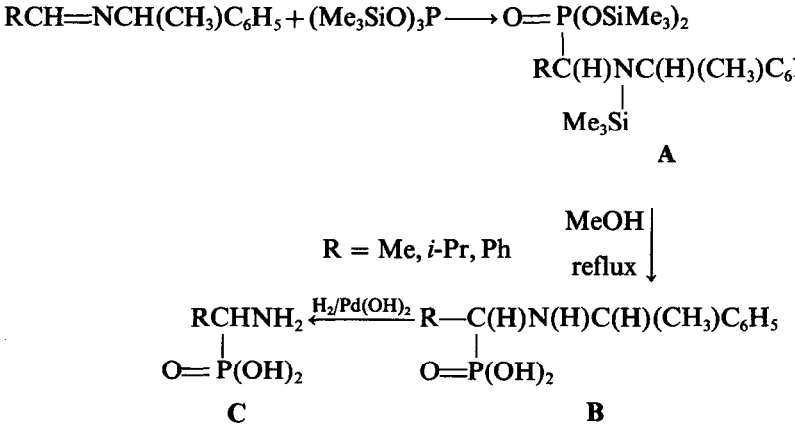
The direction of the addition depends upon reaction conditions.

1-Aminoalkylphosphonous acids are obtained by the addition of bis(trimethylsilyl) phosphonite to *N*-(diphenylmethyl) imines followed by treatment with aqueous alcohol.[236]



(89)

Silyl phosphites also form 1 : 1 adducts with some imines.[237,237a] Antibacterial (+)-*S*-1-aminoethanephosphonic acid was prepared according to a procedure involving asymmetric induction with bis(trimethylsilyl) aminophosphonates.[237] Chiral aldimines reacted with tris(trimethylsilyl) phosphite yielding N-substituted diastereoisomeric phosphonates **A**, which after removal of the chiral 1-phenylethyl group afforded optically active 1-aminoalkanephosphonic acid **C**:



(90)

Relatively high asymmetric induction was observed either without a catalyst or when the addition reaction was catalysed by *p*-toluene-sulphonic acid (R = Me).

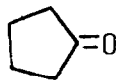
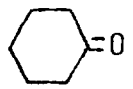
6.3. *Additions of silyl phosphites to carbonyl compounds*

Reactions with carbonyl compounds constitute the largest class of reactions in the synthetic chemistry of silyl phosphites. Reactions with carbonyl anhydrides are included in Section 5.2.

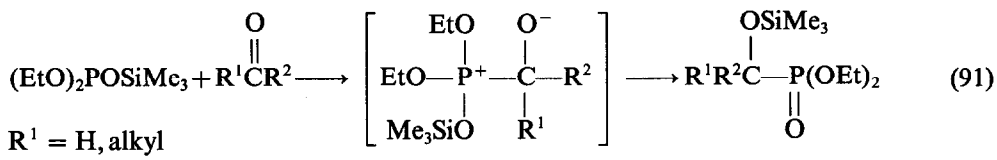
6.3.1. *Addition to saturated aldehydes, ketones and esters.* This section does not include reactions with α-halogenocarbonyl compounds which are treated in Section 6.3.5.

Silyl phosphites add to various carbonyl compounds. Many of these reactions were described in the early 1970s.[23,239–245] Some of these and later results are presented in Table 5.

Table 5. Addition reactions of $(RO)_2POSiR'_3$ to saturated carbonyl compounds

Carbonyl substrate	$(RO)_2POSiR'_3$	% Yield (conditions)	References
C_6H_5CHO	$(EtO)_2POSiMe_3$	80	26
	$(MeO)_2POSiMe_3$	97 (25°, 24 h)	25
	$(Me_2N)_2POSiEt_3$	92 (0°, 0.5 h)	25
	$(Et_2N)_2POSiMe_3$	75	239[a]
$C_6H_5COCH_3$	$(MeO)_2POSiEt_3$	27	244
	$(MeO)_2POSiMe_2t$-Bu	34 (120°, 48 h)	25
CH_3CHO	$(EtO)_2POSiMe_3$	70	26
	$(Me_2N)_2POSiEt_3$	83 (0°, 0.5 h)	25
CCl_3CHO	$(EtO)_2POSiMe_3$	92 (−60°)	242
CH_3COCH_3	$(MeO)_2POSiMe_3$	74 (90°, 24 h)	25
CF_3COCF_3	$(EtO)_2POSiMe_3$	95	243
$CH_3COC_2H_5$	$(EtO)_2POSiMe_3$	55	26
	$(EtO)_2POSiMe_3$	52	96
	$(MeO)_2POSiMe_3$	86 (95°, 13 h)	25

Trimethylsilyl phosphites react under fairly mild conditions with ketones and aldehydes yielding 1 : 1 adducts.[241,246–251,256–258] The reaction is believed to proceed stepwise by nucleophilic attack of phosphorus at the carbonyl centre followed by 1,4-migration of the silyl group[246,247] eq. (91), but a one step concerted mechanism cannot be excluded:[252]



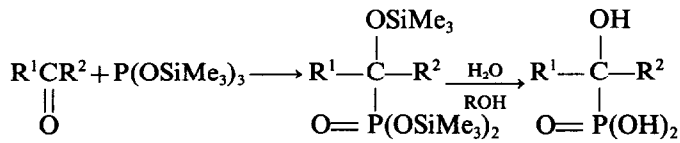
(91)

R^1 = H, alkyl

R^2 = alkyl, C(O)R

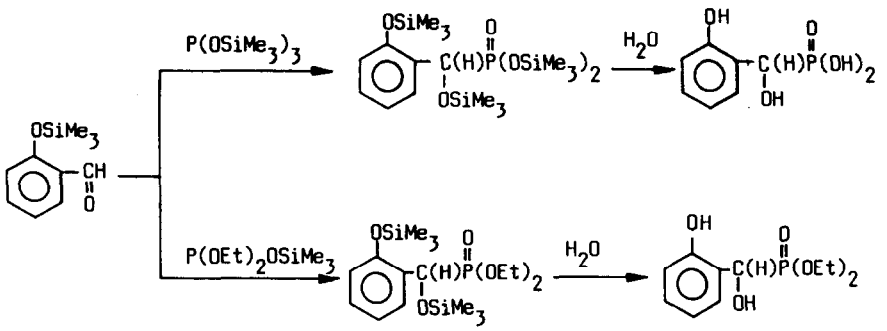
The adducts are stable, although those of silyl phosphites with aromatic aldehydes and ketones decompose to substrates, when heated.[248] Analogous addition of alkyl phosphites has been known as the Abramov reaction.[254] However, this process requires more drastic conditions and often produces by-products.[253]

An important application of the P(III) silyl addition to carbonyl groups is the synthesis of α-hydroxy derivatives of phosphonic and phosphinic acids. Tris(trimethylsilyl) phosphite reacts smoothly with carbonyl compounds giving 1 : 1 addition products, which can be easily converted to α-hydrophosphonic acids:[16,24]



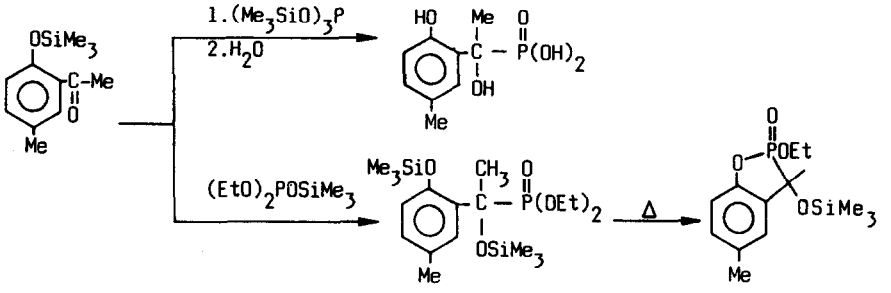
(92)

The reaction of *O*-silylated salicaldehyde with tris(trimethylsilyl) phosphite leads after hydrolysis to dihydroxy derivatives of benzylphosphinic acid.[257] The diethyl ester of this acid is produced when diethyl trimethylsilyl phosphite is used as the reagent.



(93)

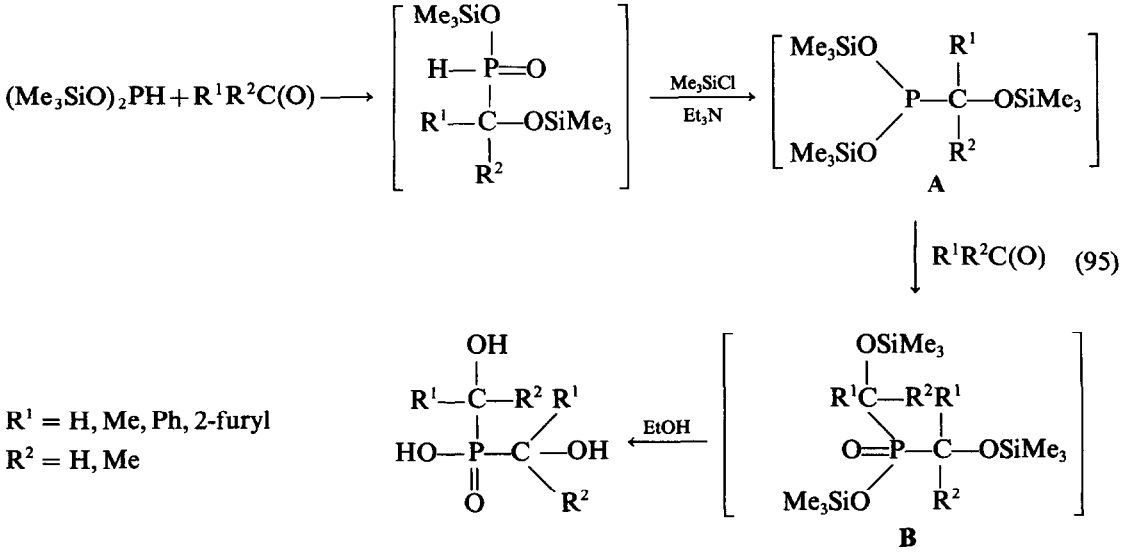
Similarly *O*-silylated hydroxyacetophenones can be readily converted to dihydroxy substituted benzylphosphonates or the corresponding acids by reactions with silyl phosphites.[258] The addition products may be transformed into cyclic phosphonates.



(94)

The addition of silyl phosphites to a carbonyl group which is a part of a substituted ring system may occur stereoselectively. Only one stereoisomer was shown to be formed when dimethyl trimethylsilyl phosphite was added to silyl disubstituted cyclopropanone.[259]

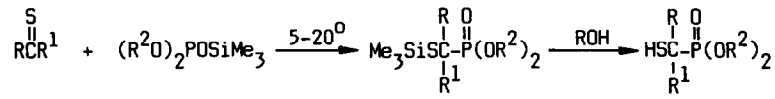
Bis(trimethylsilyl) phosphonites and butanes were used to prepare bis(1-hydroxyalkyl) phosphonic acids.[262] The first step proceeds with preservation of the P—H bond.[260,261] The adduct was silylated giving again a P(III) silyl ester which adds to the second molecule of ketone (95).



(95)

R^1 = H, Me, Ph, 2-furyl
R^2 = H, Me

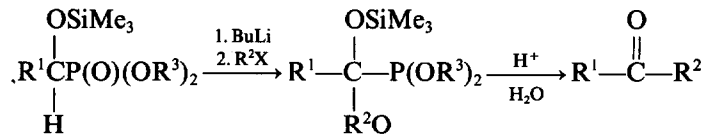
Thioketones react with silyl phosphites in an analogous way producing 1-(trimethylsilylthio)alkane phosphonates.[263] This reaction may be used for the synthesis of phosphonic acids or their esters with an α-thiol group.



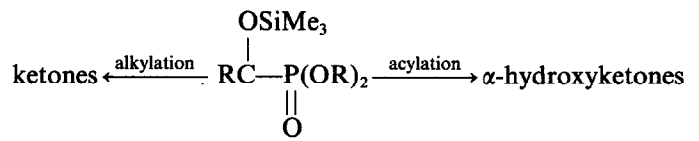
(96)

$R=R^1=$ Me, Et or $R+R^1=(CH_2)_5$ $R^2=$ Me, Et

Adducts of silyl phosphites and aldehydes can be converted to α-lithio-derivatives which can then be used as convenient equivalents of acyl anions[36,38,264-267] according to the 'umpolung' concept.[268] They can be alkylated or acylated by different electrophiles, eq. (97) or used further in the synthesis of ketones and α-hydroxy ketones according to the general scheme (97a). A number of interesting carbonyl compounds was synthesized by this route.[266,267]



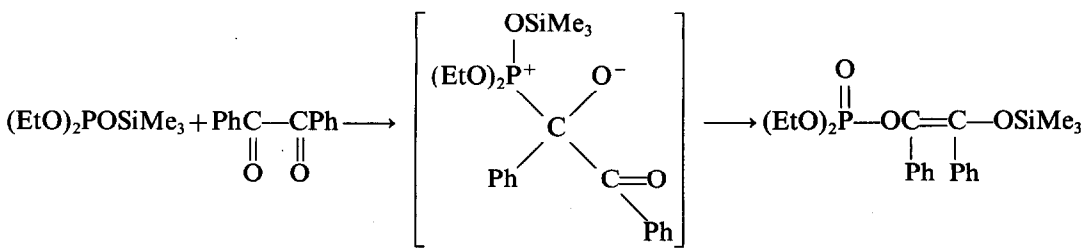
(97)



(97a)

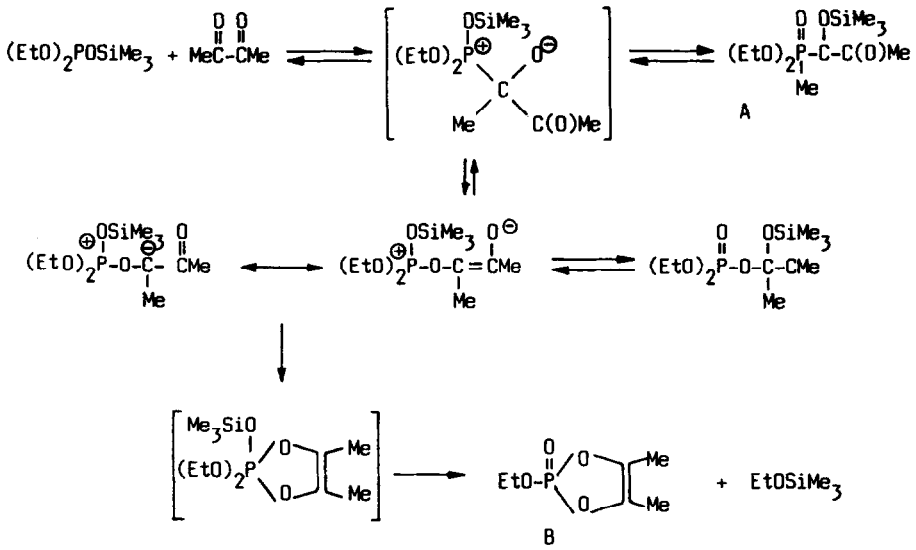
6.3.2. *Addition to dicarbonyl compounds.* Addition of silyl phosphites to dicarbonyl compounds is often followed by rearrangements or other intramolecular reactions.[247,249,256] Some of them can be of synthetic utility.

Reaction of silyl phosphites with dibenzyl,[21,247] eq. (98), leads to phosphates, rather than the expected phosphonates:



(98)

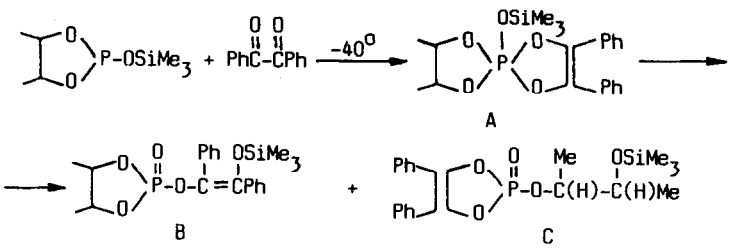
Diethyl trimethylsilyl phosphite reacts with diacetyl according to the following scheme.[251]



(99)

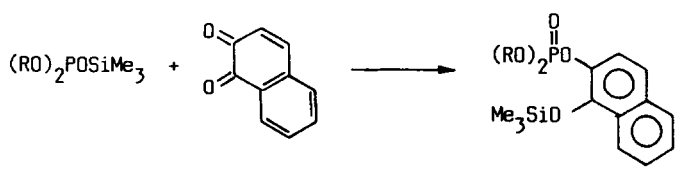
(α-Trimethylsiloxy) phosphonate **A** is the kinetic product of this reaction but heating of the reaction mixture leads to phosphonate → phosphate rearrangement and yields the cyclic phosphate **B**. An analogous rearrangement was observed for the adduct of benzil and diethyl trimethylsilyl phosphite.[21]

2-Trimethylsiloxy-1,3-dioxaphospholan and dibenzyl, when monitored at low temperatures showed that silylated spirophosphoranes (100)**A** were formed as addition products.[269] When heated, the spirophosphorane decomposed, yielding products **B** and **C** of the opening of one of the two cycles (100).



(100)

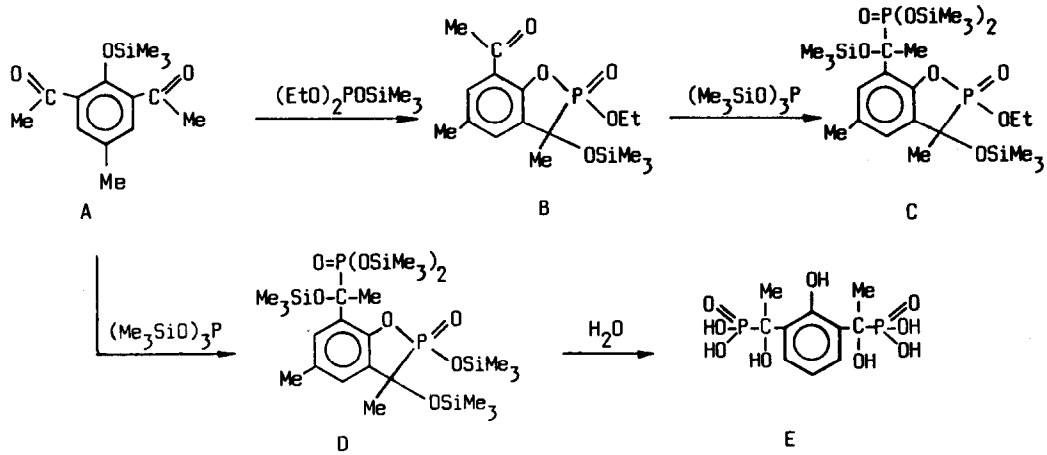
When cyclization was inhibited for structural reasons, then acyclic phosphates were obtained as the main product, as in the reaction of dialkyl trimethylsilyl phosphite with 1,2-naphthoquinone.[270]



(101)

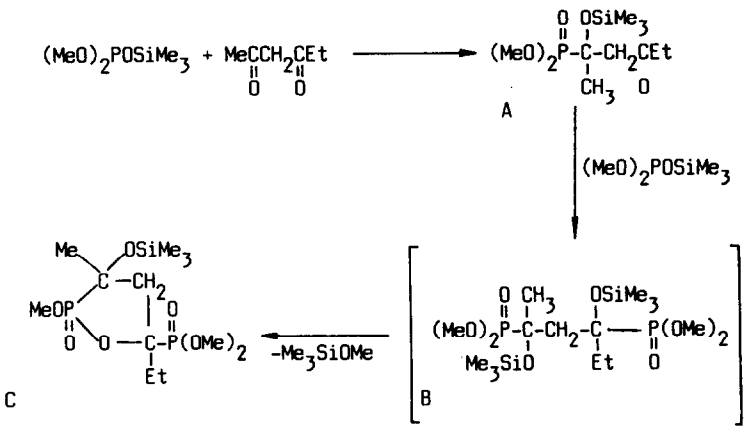
A similar addition occurs with *p*-quinone.[247]

Aromatic 2,5-diketones add silyl phosphites producing phospholans (102)**B**, **C**, **D**. Some of them are hydrolysed to bis(α-hydroxy)phosphonic acids.[271]



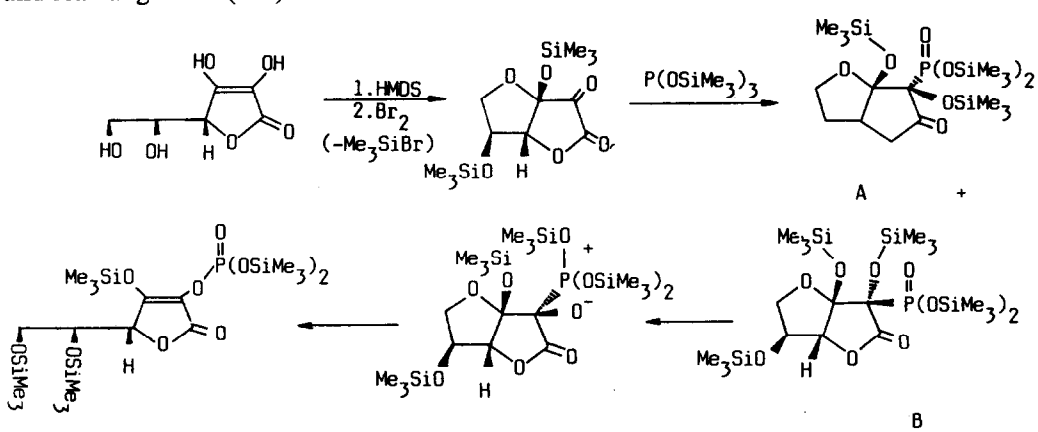
(102)

Dialkyl(trimethylsilyl) phosphites with 1,3-diketones, yield *O,O*-dialkyl *O*-(1-trimethylsiloxy-1-methyl-2-acetyl) ethylphosphonate (103)A, which then combined with a second molecule of silyl phosphite yielding the phosphonate C.[272]



(103)

Hata[273] achieved an interesting synthesis of L-ascorbic acid 2-*O*-phosphate from fully trimethylsilylated L-ascorbic acid, by silylation of L-ascorbic acid, addition to tris(trimethylsilyl) phosphite and rearrangement (104).

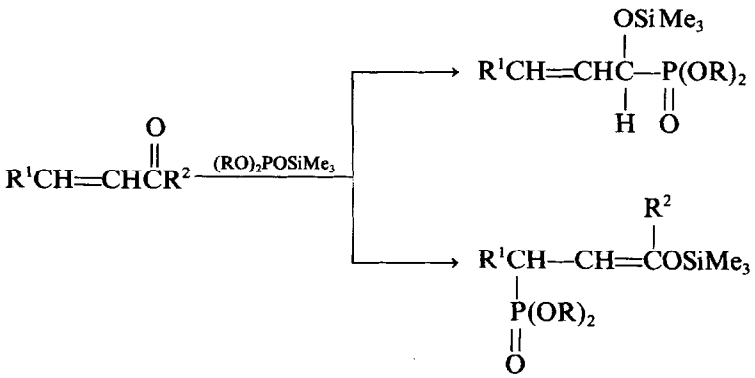


(104)

Diastereoisomers **A** and **B** underwent thermal rearrangement, which was postulated to occur by an intramolecular migration of the phosphoryl group.

Many reactions of P(III) silyl esters with dicarbonyl compounds, when carried out at sufficiently low temperatures lead to simple adducts involving one C=O group.[247,256,276]

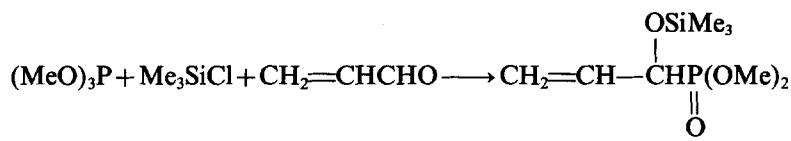
6.3.3. *Additions to conjugated enone systems.* Tris(trimethylsilyl) phosphite and α,β-unsaturated aldehydes affords selectively 1,2-addition products.[24,36] In the case of ketones and esters, the reaction leads predominantly to 1,4-adducts. Both, 1,2- and 1,4-adducts can be easily converted to ammonium salts in nearly quantitative yields. Dialkyl (trialkylsilyl) phosphites react with unsaturated aldehydes and ketones giving 1,2- and/or 1,4-adducts.[25,36,246,275] Most of 1,4-adducts of both aldehydes and vinyl ketones possess the *Z*-olefin geometry exclusively.[25]



(105)

Results are summarized in Table 6.

Aldehyde addition reactions generally proceed with convenient rates at ambient temperatures whereas ketones require heating. Addition of dialkyl (trimethylsilyl) phosphite to acrolein affords a nearly 1 : 1 mixture of 1,2- and 1,4-adducts but only the 1,2-addition product was produced by the reaction of acrolein with an equimolar amount of trimethyl phosphite and trimethylchlorosilane (106).[25]

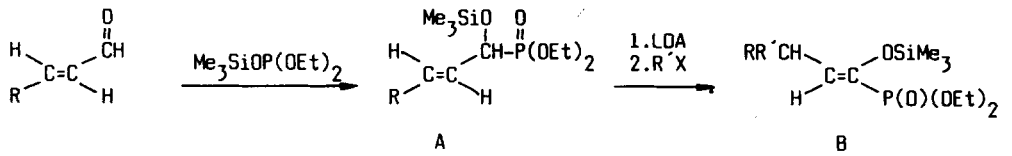


(106)

Hata[38] described a good synthesis of β-alkyl substituted esters from α,β-unsaturated aldehydes.

Table 6. Addition reactions of $(RO)_4POSiR'_3$ to unsaturated carbonyl substrates[25]

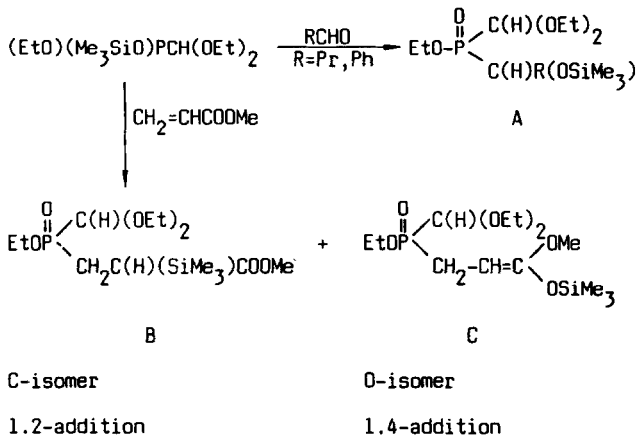
Substrate	$(RO)_2POSiR'_3$	Conditions	Ratio of 1,2/1,4 adducts	Yield
CH_2=CHCHO	$(MeO)_2POSiMe_3$	25°, 12 h	47/53	88
	$(Me_2N)_2POSiEt_3$	0°, 0.25 h	100/0	90
CH_3CH=CHCHO	$(MeO)_2POSiMe_3$	55°, 18 h	75/25	91
	$(Me_2N)_2POSiEt_3$	0°, 0.5 h	100/0	95
PhCH=CHCHO	$(Me_2N)_2POSiEt_3$	0°, 0.5 h	100/0	93
CH_2=$CHCOCH_3$	$(MeO)_2POSiMe_3$	50°, 6 h	0/100	88
	$(MeO)_2POSiEt_3$	100°, 3 h	0/100	36
	$(Me_2N)_2POSiEt_3$	0°, 0.5 h	0/100	82
CH_3CH=$CHOCH_3$	$(MeO)_2POSiMe_3$	80°, 24 h	0/100	64
CH_2=CHCHO	$(Me_3O)_3P$, Me_3SiCl	25°, 4 h	100/0	



(107)

NMR analysis of **B** demonstrated the regioselectivity of the alkylation step at γ-position yielding the *E*-olefin stereoselectively.

The reaction of carbonyl compounds[278] with *O*-silyl (dialkoxymethyl)phosphonites can be used for the synthesis of substituted dialkoxymethylphosphinates.

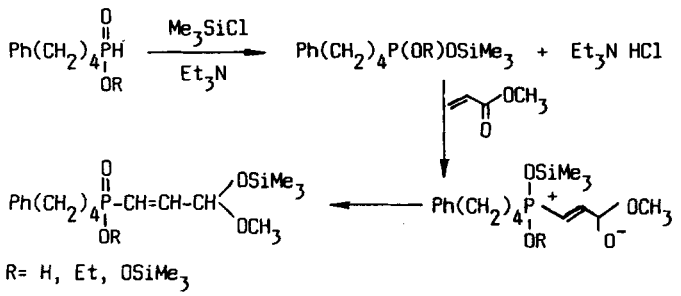


(108)

Reaction with conjugated esters lead to mixtures of the products of 1,2- and 1,4-additions. Compounds (108)**A** and **B** have two chiral centres so they were obtained as mixtures of diastereoisomers.

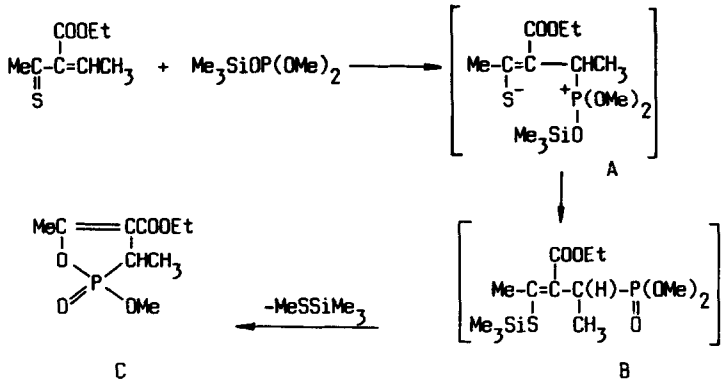
Silyl phosphites add to maleic imides producing phosphonosuccinimides with one or two molecules of imide incorporated. The structure of the adducts depends upon the substituents at the nitrogen atom of the imide.[279,280]

Less reactive silyl alkyl phosphonites can react only with activated enone conjugated systems by the Michael addition giving phosphinic acids or their esters.[281]



(109)

Conjugated thioketones can be interesting substrates because they react with silyl phosphites at room temperature leading to 1,4-adducts. These rearrange when heated with the elimination of silyl thioether and the formation of the cyclic product C.[282]



(110)

Trialkyl phosphites and alkyl acrylates in the presence of trimethylsilyl chloride yield dialkyl 3-alkoxy-3-(trimethylsiloxy)-2-propenephosphonates.[283,284] The reaction pathway can be rationalized in terms of primary formation of dialkyl trimethylsilyl phosphite which then reacts with the acrylate giving a 1,4-adduct, eq. (111). Another mechanism was preferred.[283]

$$(RO)_3P + ClSiMe_3 \longrightarrow [(RO)_2POSiMe_3] \xrightarrow{CH_2=CHCOOR} (RO)_2PCH_2CH{=}C(OSiMe_3){-}OR \qquad (111)$$

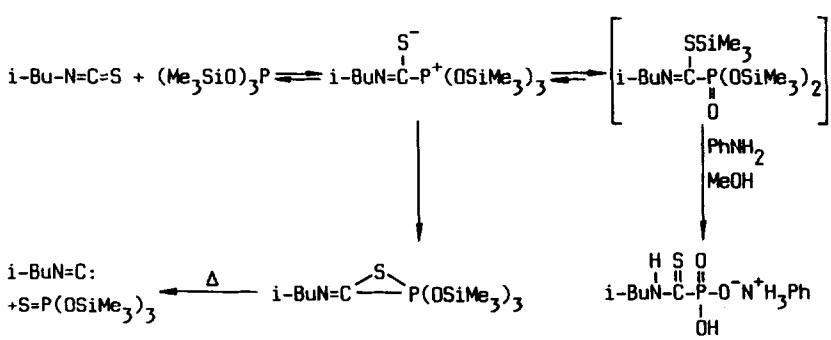
This adduct can be recognized as a ketene silyl acetal derivative which has been utilized in many transformations. They are initiators of group transfer polymerization processes and their modification by substitution of a phosphonate group makes the synthesis of acrylate polymers having reactive end groups possible.[277]

6.3.4. *Reactions with cumulated double bonds* (C=C=O, N=C=O, N=C=S). The reaction between trimethylsilyl diethyl phosphite and ketene leads to diethyl (1-trimethylsilxyvinyl)phosphonate which can be easily converted to acyl phosphonate by reaction with water.[26]

$$(EtO)_2POSiMe_3 + CH_2{=}C{=}O \longrightarrow (EtO)_2P(O){-}C(OSiMe_3){=}CH_2 \xrightarrow{H_2O} (EtO)_2P(O){-}CCH_3 \qquad (112)$$

The reaction with ketene dimers has also been studied.[285]

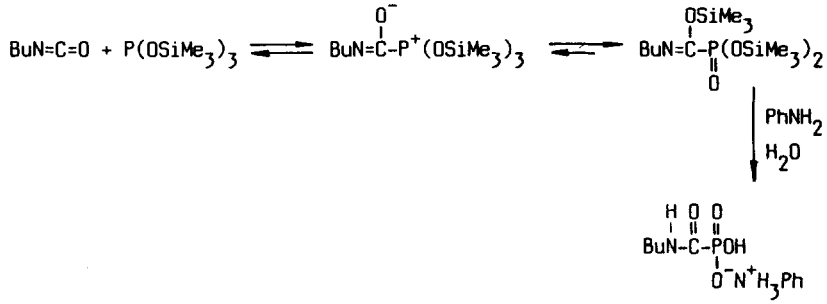
Tris(trimethylsilyl) phosphite reacts with an alkyl isothiocyanate giving a thiocarbonyl adduct.[16,286]



(113)

The anilinium salt of *i*-butylthiocarbamoylphosphonic acid was isolated (60% yield) thus confirming the structure of the adduct.

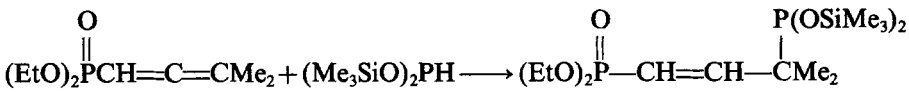
n-Butylcarbamoylphosphonic acid was isolated (96% yield) as the result of the following reaction sequence.



(114)

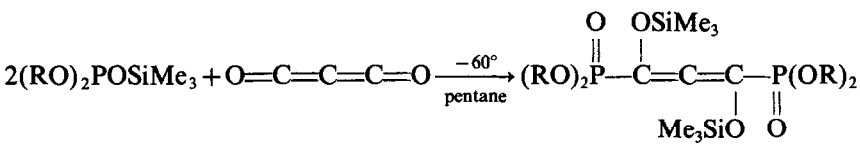
Phenyl isothiocyanates and isocyanates react with $P(OSiMe_3)_3$ leading to high yields of the adducts which are converted easily to monoanilinium salts of phenylthiocarbamoyl- and phenyl-carbamoylphosphonic acids.[286]

Addition of bis(trimethylsilyl) phosphonite to allenyl phosphonate takes place at β,γ-double bond of the cumulene. Phosphapropenylphosphonates were produced as the result of addition of bis(trimethylsilyl) phosphonate to the phosphorylated diene (115).[27]



(115)

1,3-Bis(trimethylsiloxy)-1,3 bis(dialkyl)phosphonoallenes were obtained for the first time from dialkyl trimethylsilyl phosphite and carbon suboxide:



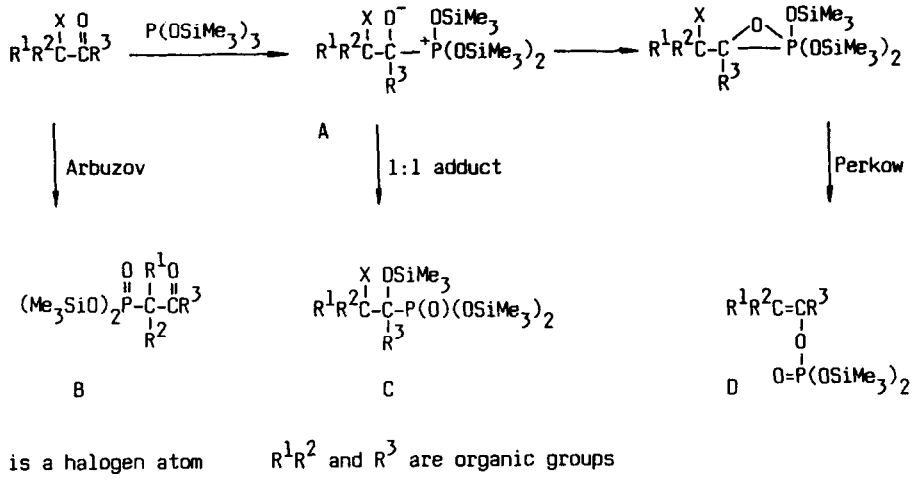
(116)

R = Et, *n*-Pr

These dienes are thermally unstable and decompose when heated giving a mixture of products.[287]

6.3.5. *Reactions of silyl phosphites with α-halocarbonyl compounds.* Trialkylsilyl phosphites react with α-halocarbonyl compounds by three different routes giving either adducts, enol-phosphates (products of the Perkow reaction) or phosphonates (products of the Arbuzov type reaction). The results depend upon the nature of the compounds and the reaction conditions.[16,20,288]

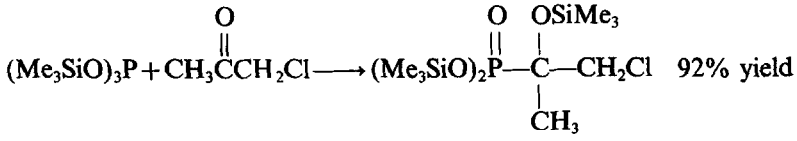
The pathways of carbonyl addition and the Perkow reaction can be explained in terms of the initially formed zwitterionic intermediate **A**. This intermediate may either undergo intermolecular migration of the trimethylsilyl group to anionoid oxygen (adduct formation) or form a three-membered ring intermediate which then undergoes C—P bond cleavage (Perkow). The chemoselectivity of the process is determined by the structure of the reactants.[16,288]



(117)

Alkyl substituted α-halo-aldehydes and α-halo-ketones react with tris(trimethylsilyl) phosphite to yield mainly 1 : 1 carbonyl adducts **C**. This is due to the strong inductive effect of the three trimethylsiloxy groups bound to phosphorus,[20] which decrease the positive charge density on the phosphorus atom in the intermediate **A**.

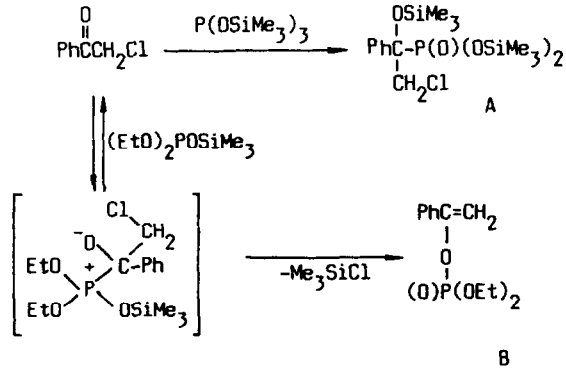
When tris(trimethylsilyl) phosphite reacted with chloroacetone the product was the adduct bis(trimethylsilyl) 2-chloro-1-methyl-1-trimethylsiloxy-ethyl-phosphonate of type **C**:



(118)

This adduct is very useful for the synthesis of phosphonomycin,[16,20,288] by conversion to the unesterified 1,2-epoxyalkylphosphonate. Bromoacetone also yielded the product of the addition to the carbonyl group. This is in contrast to the reactions of trialkyl phosphites, which give predominantly β-oxophosphonates when treated with bromoacetone.

When phenacyl chloride reacted with tris(trimethylsilyl) phosphite, the 1 : 1 adduct **A** was formed. However, with diethyl trimethylsilyl phosphite, the product (about 75%) was that of the Perkow reaction (119)**B**.[21]

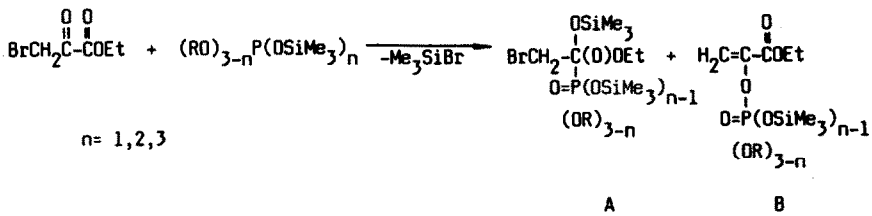


(119)

When phenacyl bromide was reacted with tris(trimethylsilyl) phosphite, under analogous reaction conditions, the predominant product was that of the Perkow reaction (61%) but in addition the product of the Arbuzov reaction (14%) appeared.[18,20]

α-Halogenoesters react with tris(trimethylsilyl) phosphite giving mainly Arbuzov reaction products. Thus chloroacetate gives 64% and bromoacetate 84% of the Arbuzov product.

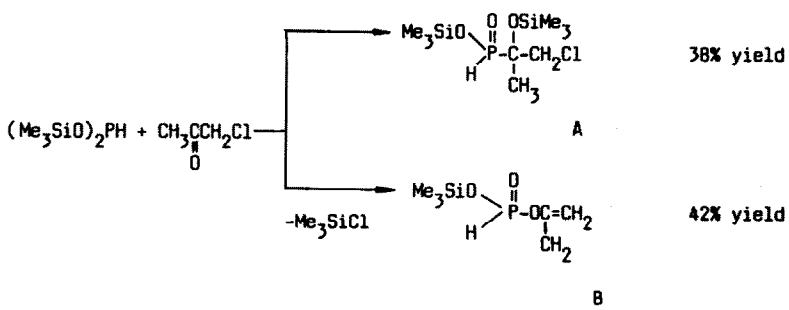
Phosphoenolpyruvate (PEP) and its analogues have been obtained by the Perkow reaction between silyl phosphites and bromopyruvates generated *in situ*.[289,291]



(120)

In all cases but one ($n = 3$), products of the Perkow reactions **B** were formed exclusively. PEP is the high-energy phosphate which plays a vital role in ATP synthesis.

Bis(trimethylsilyl) phosphonite and α-chloroacetone give a mixture of products.[290]

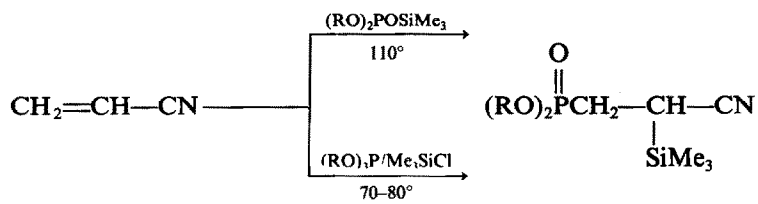


(121)

Adduct **A** was converted into product **B** when heated up to 150°C. Similar thermal rearrangements were observed in some other systems. The reaction of diethyl trimethylsilyl phosphite with chloral at −60°C leads to the simple carbonyl addition product, which after heating (140–150°C), yields diethyl-2,2-dichlorovinyl phosphate, an analogue of dichlorovos, an important insecticide.[242]

6.4. *Addition to carbon–carbon multiple bonds*

Silyl phosphites undergo addition to some electron deficient carbon–carbon multiple bonds.[112] Dialkyl 2-cyano-2-(trimethylsilyl)-ethanephosphonates have been prepared by the reaction of dialkyl trimethylsilyl phosphites with acrylonitrile.[292]

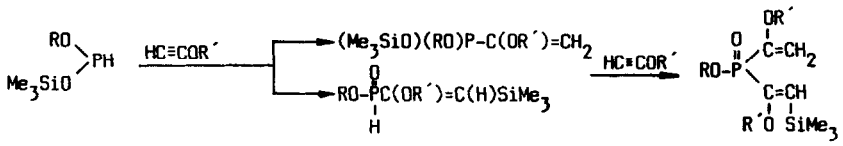


(122)

Products of this reaction are interesting substrates for the synthesis of cyanoolefin derivatives by Peterson or Wittig–Horner olefination.

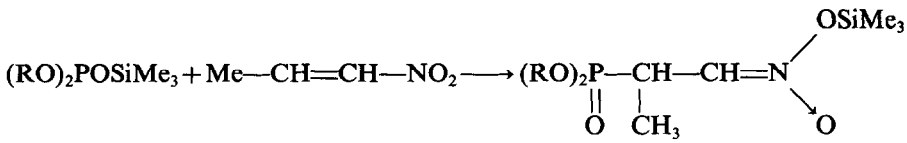
The addition of $HP(OSiMe_3)_2$ to carbon–carbon multiple bonds involving H—P cleavage has been reported.[112,128,214]

Trimethylsilyl alkyl phosphonites react with alkoxyacetylenes by two addition pathways.[293]



(123)

Dialkyl trimethylsilyl phosphites undergo 1,4-addition to 1-nitropropene-1,[294] eq. (124), and to its 1,1,1-trichloro derivative.[295]



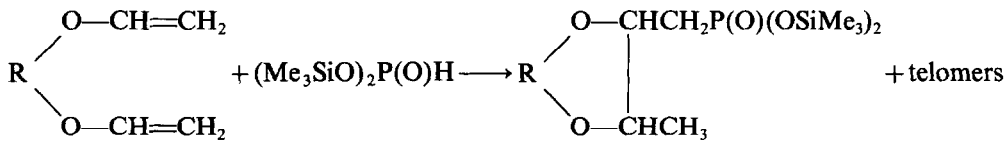
(124)

A

R = Me, Et

The addition products **A** undergo easily hydrolytic desilylation to corresponding β-nitroalkylphosphonates.

Bis(trimethylsilyl) phosphonite reacted with divinyl diethers or divinyl acetals in the same way as dialkyl phosphites.[296]



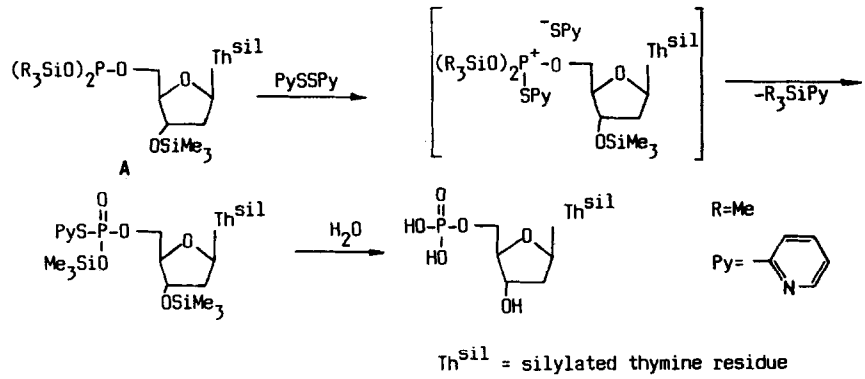
$$R = CH_2, CHCH_3, CH_2CH_2 \qquad (125)$$

Cyclization proceeds stereospecifically yielding the *cis*-isomer.

6.5. *Reactions with disulphides and diselenides*

Dialkyl and monoalkyl phosphites exist in solvents in the phosphonate form, so they are much more resistant either to oxidation or to the addition of sulphur or selenium than trialkyl phosphites. The oxidation of these phosphites to phosphates proceeds, when relatively strong oxidizing agents are used, but these may promote oxidation of more complex molecules such as nucleotides.

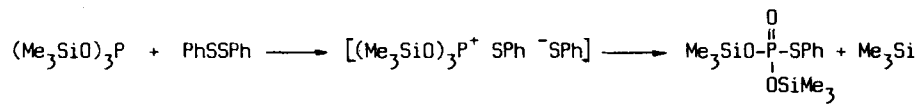
Silyl phosphites exist in the tervalent form so they can be oxidised much more easily. Nucleoside bis(trimethylsilyl) phosphites have been used to fix the tervalent phosphorus form of the phosphites so promoting their oxidation under very mild conditions.[2,108]



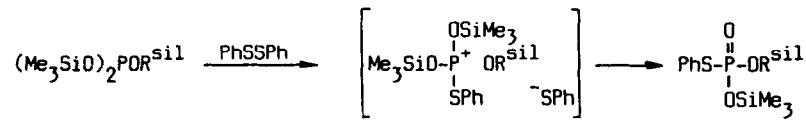
(126)

Silyl ester A obtained by silylation of thymidine 5′-phosphite, was oxidized by 2,2′-dipyridyl disulfide yielding *S*-pyridyl thymidine 5′-phosphorothiate which was easily converted to thymidine 5′-phosphate.[2,13]

Bis(trimethylsilyl) nucleoside phosphite has been used (128) as a reagent in the synthesis of *S*-phenyl nucleoside phosphorothioates by the following reaction with diphenyl disulfide.[2,13,300]

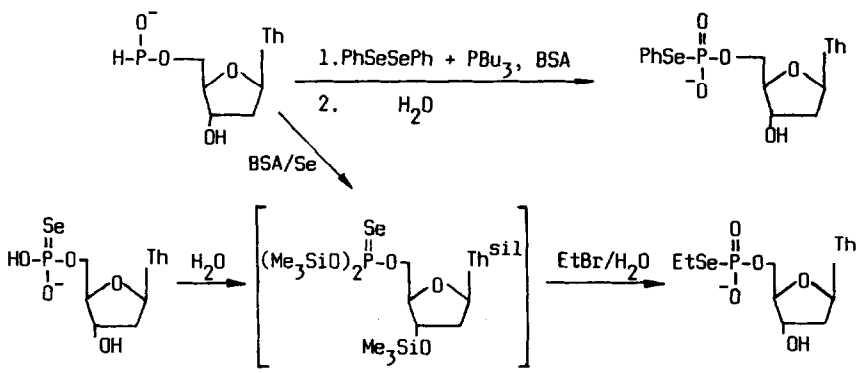


(127)



(128)

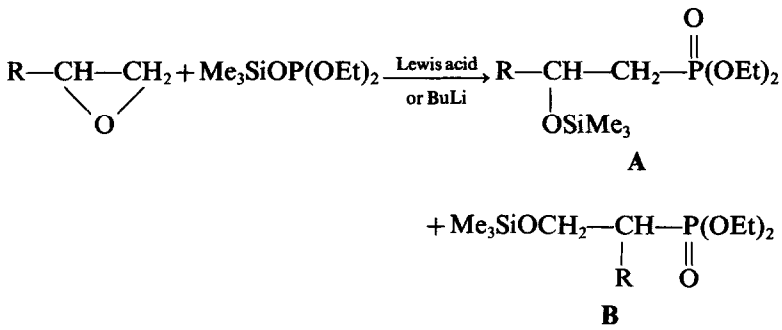
The *S*-phenyl group can be easily removed by use of bis(tributyltin) oxide, followed by silylation and hydrolysis.[87,88] Selenium containing analogues was also obtained.[301]



(129)

6.6. *Reactions with ethers, acetals and esters of orthocarbonyl acids*

Silyl phosphites react with epoxides in the presence of Lewis acids or BuLi, yielding products of ring opening and addition.[302]



(130)

Diethyl trimethylsilyl phosphite reacted with propylene oxide giving diethyl 2-(trimethylsiloxy)-propanephosphonate **A** (R = Me). No selectivity has been observed in the case of phenyloxirane. When ZnI_2 was used as catalyst, an almost equimolar mixture of the regioisomers **A** and **B** was produced.

Oxirane ring opening can also be caused by silyl phosphates.[303] This reaction was found to be effectively catalysed by *N*-methyl imidazole and was utilized to obtain polymeric structures.

Some interesting aspects can be found in reactions of silyl phosphites with esters of orthocarbonyl acids.[304,305] It was shown that dialkyl trimethylsilyl phosphite reacted with triethylorthoformate in the presence of catalysts (HCl, Me_3SiCl, Et_2O, BF_3 or $PhCh_2I$) leading to dialkyl (dialkoxymethyl) phosphonates:

$$(RO)_2POSiMe_3 + CH(OR)_3 \longrightarrow (RO)_2P(O)CH(OR)_2 + Me_3SiOR. \quad (131)$$

The authors postulate 'the Arbuzov-chain' mechanism for this reaction.[305]

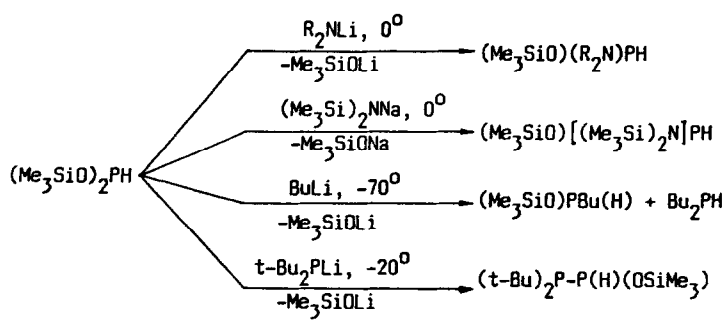
The cleavage of acetal bonds by silyl phosphites catalysed with Lewis acids has been reported.[298]

Silyl phosphites are also able to cleave the ether bond in *N*-bis-silylated 1-alkoxymethyl amines under catalysis with Lewis acids.[297]

$$(RO)_2POSiMe_3 + MeOCH_2N(SiMe_3)_2 \xrightarrow{SnCl_2} (RO)_2P(O)CH_2N(SiMe_3)_2 + Me_3SiOMe. \quad (132)$$

6.7. *Reactions of nucleophilic substitution at phosphorus in silyl esters of* P(III)

Bis(trimethylsilyl) phosphonite[214,306] and trimethylsilyl alkyl phosphonite[128] show high reactivity towards strong nucleophiles yielding the products of substitution at the phosphorus atom.[306]



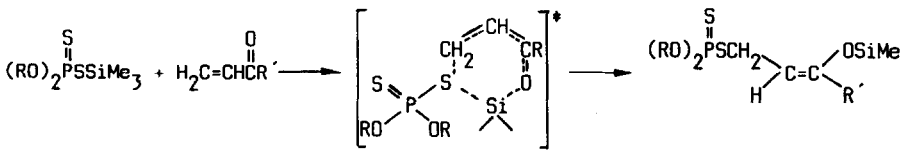
(133)

These reactions proceed under very mild conditions, at low temperatures and lead to reactive products which may undergo additional reactions, when heated.

7. REACTIONS OF *S*-TRIMETHYLSILYL ESTERS OF DITHIOPHOSPHORIC ACIDS

The reactivity of *S*-trimethylsilyl esters of dithiophosphoric acid differ markedly from that of *O*-silyl phosphates. The relatively low energy of Si—S bond and the low affinity of silicon for sulphur as compared to oxygen, make *S*-silyl esters more reactive than their *O*-silyl analogues.[309-311] In contrast with *O*-silyl phosphates and thiophosphates, silyl dithiophosphates undergo addition reactions to many unsaturated systems: carbonyl group, enones, isocyanates, nitro-olefins and others.[15,309-319] The regiochemistry of these reactions strongly depends upon the nature of the unsaturated reagents. In some cases, these esters react similarly to their parent dithioacids which also enter in the addition processes.[307,308] However, a considerable difference in the behaviour of the *S*-silyl esters is often observed.[15]

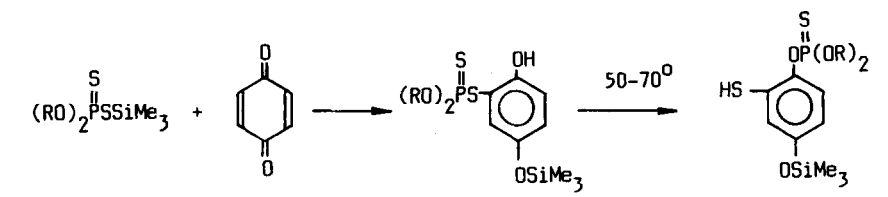
S-Trimethylsilyl dithiophosphates react with unsaturated aldehydes and ketones giving dithiophosphorylated enol-silanes which are the result of 1,4-addition.[309]



(134)

The predominant *Z*-configuration of 1,4-adducts indicates that the reaction proceeds via a cyclic activated complex giving a *cis*-isomer structure for the product.

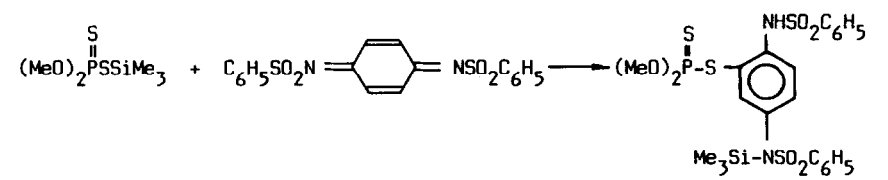
S-Silyl dithiophosphates readily combine with *p*-quinones leading to *S*-aryl dithiophosphates as 1,4-adduct.[312]



(135)

On heating, the latter isomerised to *O,O*-dialkyl *O*-[2-mercapto-4-(trimethylsiloxy)phenyl] thiophosphates.

The tendency for the dithiophosphate → thiophosphate rearrangement depends upon the nature of the substituents at the phosphorus atom and the presence of the basic catalyst. In the case of *p*-quinone-di-imines, the reaction terminates at the formation of the adduct.[313]

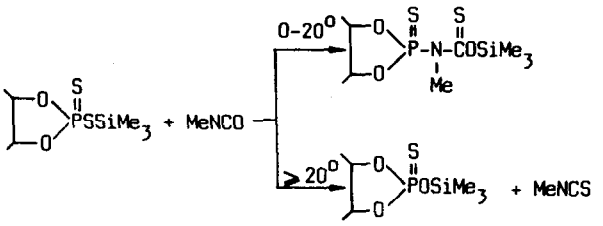


(136)

O,O-Dimethyl *S*-trimethylsilyl dithiophosphate rapidly reacts with *N*-benzene-sulfonyl-*p*-quinone-imine yielding *O,O*-dimethyl *S*-(2-hydroxy-5-*N*-benzenesulphonylamino)phenyl dithiophosphates, which can be transformed easily to the corresponding monothiophosphates.

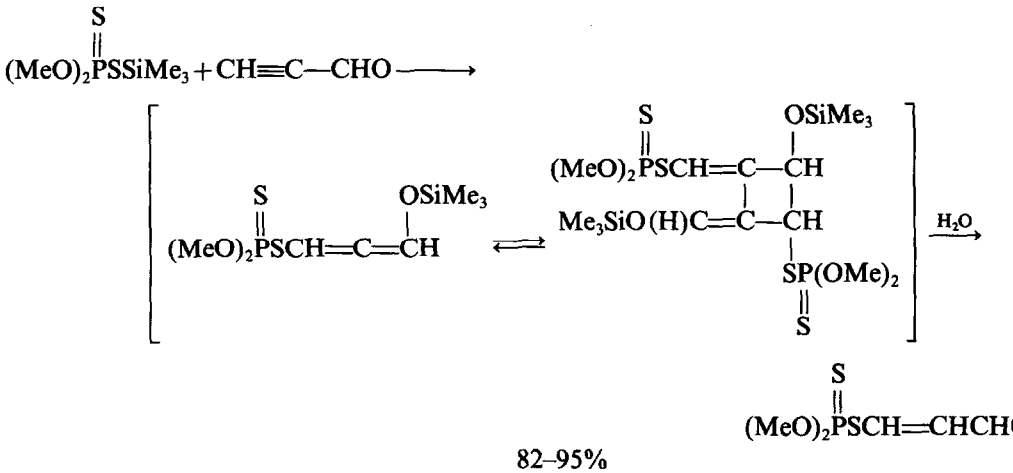
Reactions of *S*-trimethylsilyl dithiophosphates with isocyanates are complex and lead either to

N-thiophosphorylated thiocarbamates or to *O*-trimethylsilyl esters, depending on the nature of substituents at phosphorus and reaction conditions.[314-316] Cyclic esters can give both products, eq. (137). The kinetics and mechanism of these reactions has been studied.[315]



(137)

S-Trimethylsilyl dithiophosphates add to multiple bonds according to the following scheme.[316]

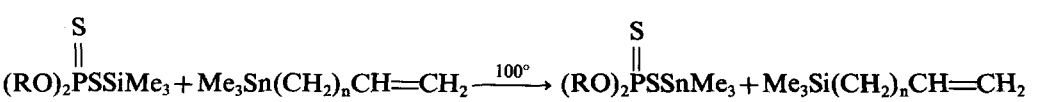


82–95%

(138)

The product of 1,4-addition and its dimer are extremely sensitive to solvolytic agents and in the presence of water give the α,β-unsaturated aldehyde. This reaction seems to be a useful method for preparation with high yields for various *O,O*-dialkyl *S*-substituted dithiophosphates, eq. (138). *O,O*-Dialkyl dithiophosphates and *S*-trimethylsilyl dithiophosphates yield (trimethylsilyl) phosphonates and *S*-dialkyl dithiophosphates.[310]

S-Trimethylsilyl dithiophosphates are capable of cleaving Sn—C bonds in vinyl- and alkyl-stannanes,[318] leading to a transmetallation process:



(139)

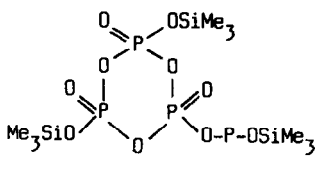
The products of this reaction are *O,O*-dimethyl *S*-trimethylstannyl dithiophosphates, and allyl- or vinyl-silanes.

Bromine, in reaction with *S*-trimethylsilyl dithiophosphates cleaves the S—Si bond producing trimethylsilyl bromide and *O,O*-dialkyl phosphorosulphenyl bromide, a very reactive intermediate useful in synthesis of phosphorus anhydrides.[319]

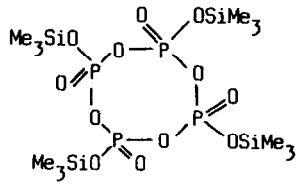
8. SYNTHETIC USE OF TRIMETHYLSILYL POLYPHOSPHATES (PPSE)

Polyphosphoric acid ethyl ester (PPE) synthesized in 1910 by Langheld[320] has been used in organic synthesis for a relatively long time.[321a,b,c] Occasionally some other esters of these acids have also been applied.[321d] However, polyphosphate silyl ester PPSE prepared a few years ago by Imamoto[322] exhibits particularly interesting catalytic* properties promoting many dehydrations, dehydrocondensations, molecular rearrangements and some other processes.[40,323] In the presence of PPSE, reactions often proceed in a very selective way, under mild conditions and with higher yields than those catalysed by PPE.

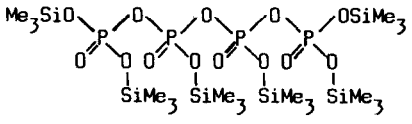
The PPSE polymers are synthesized by condensation of P_4O_{10} with bistrimethylsilyl ether at reflux in an inert solvent like methylene chloride, benzene or chloroform and in the absence of any catalyst.[40] PPSE is a viscous liquid soluble in many organic solvents. According to Watanabe and Yamamoto[324] the major components of the PPSE are: isocyclotetraphosphate **A**, cyclotetraphosphate **B**, and linear tetraphosphate **C**.



A



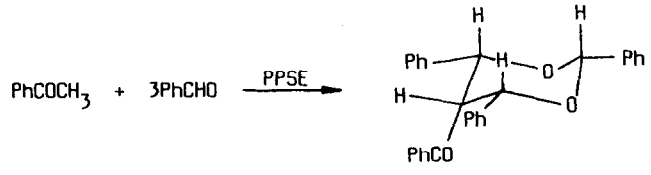
B



C

The exocyclic phosphate group in the tetramer **A** is believed to be the most significant for the activation of the hydroxy group.

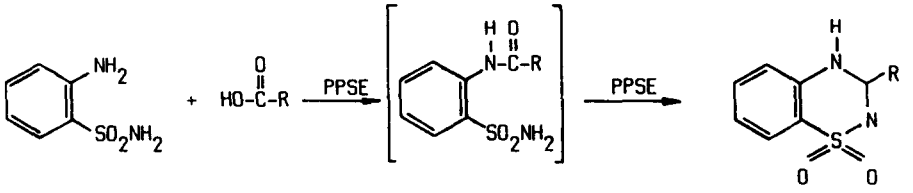
The PPSE proved to be a good catalyst of the Beckmann rearrangement of ketoximes[322,324] and for conversion of alcohols into alkyl iodides with NaI.[325] They may be used for the dehydration of carboxamides and aldoximes to nitriles.[326,333] An important application of PPSE seems to be the promotion of the aldol condensations of ketones with aldehydes,[40,327] because of the usefulness of these reactions in synthesis of natural products. Some of these processes proceed in a non-trivial way. The reaction of benzaldehyde with acetophenone in the presence of PPSE gives cyclic product 5-benzoyl-2,4,6-triphenyl-1,3-dioxane instead of the expected aldol adduct.[40]



(140)

Synthesis of 2H-1,2,4-benzothiadiazine 1,1-dioxide, a potential antihypertensive and antimicrobial agent, also utilizes the catalysis with PPSE.[328]

* PPSE is applied in concentrations comparable to those of substrates and it is used in the course of the reaction, thus it should be considered as reagent rather than as catalyst.



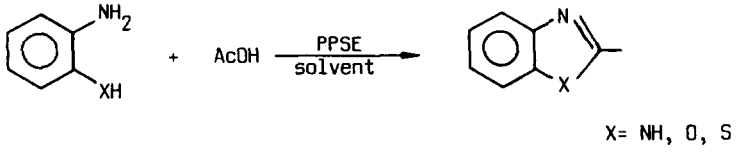
(141)

Another example of PPSE application is synthesis of amidines from carboxylic acids and primary amines.[329]

$$R^1C(O)OH + 2R_2NH_2 \xrightarrow{PPSE} [R^1C(O)NHR^2] \xrightarrow{PPSE} R^1C(NR_2)(NHR_2) \quad (142)$$

This reaction was extended to aromatic diamines which with benzoic acid derivatives produce interesting polymers, aromatic polyamidines.[330] The synthesis of amidines is a two step process. First dehydrocondensation occurs leading to amide, which is then followed by fast consecutive amide dehydration. Under some conditions the reaction of a carboxylic acid with a primary amine may lead to a high yield of amide product. Benzanilide was prepared from benzoic acid and aniline in the presence of PPSE and pyridine.[331] The reaction when carried out at 160°C and without pyridine gives *N,N*-diphenylbenzamidine as the almost exclusive product.

The PPSE is also used in the Philips' synthesis of benzimidazole and its analogues,[324] eq. (143), including various 2-substituted benzoxazoles.[333]



(143)

X= NH, O, S

Promotion of the Pummerer rearrangement of various sulfoxides catalysed with PPSE gave very promising and in some cases unusual results.[332] The PPSE was successfully used to promote the chemoselective and stereospecific oxime rearrangement cyclization producing alkylidene $-\Delta^1$-pyrrolines.[335] It was also applied for synthesis of thioacetals from carbonyl compounds and thiols.[336]

It should be mentioned that the PPSE can be the reagent in such called X, N-double rearrangements (X = N, S, O).[323,338] These processes are cyclization condensations of some substituted acryloamides with benzoic acids involving interchange of nitrogen and sulphur, oxygen or another nitrogen atom.[337] This provides a facile route to many interesting heterocycles.

9. FINAL REMARKS

The application of silyl esters of phosphorus is very broad, thus the area covered by this review had to be limited. Some aspects of the chemistry of these compounds were treated only marginally or even remained beyond the scope of this article. For example, polymers having silyl ester phosphorus groupings in the polymer chain, partly reviewed in ref. 1, were not included here. The use of silyl esters of phosphorus as monomers in polymerization and polycondensation processes was hardly mentioned.[35,303]

It should be added that the interest in these esters in connection with the analytical chemistry and spectroscopy of phosphorus acids, mentioned in the introduction has continued. The direct silylation of phosphorus acids has often been executed to make possible their chromatographic

analysis[10,11,347-352] mass spectroscopy studies[12,350,339-344] and NMR[34,79,345] studies. This analytically directed chemistry of silyl esters of phosphorus seems to be important for understanding of the chemistry of nucleotides,[12,339-342,344,346,350] carbohydrate phosphates[347,349] and lipids[34,79,345] as well as the metabolism of some bioactive substances.[10,343,352]

Some attempts have recently been made to use the silyl ester group bearing a bulky substituent for the protection of the phosphorus function.[213]

Acknowledgements—The authors would like to express their gratitude to scientists who helped them, kindly supplying important information and materials which were of great help in writing their Report. They are particularly indebted to Linda D. Merrill, Associate Project Chemist from the Dow Corning Company, Jan Michalski and Alexandra Skowrońska, Professors of the Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences in Łódź, Tsujiaki Hata, Professor of the Tokyo Institute of Technology, and Tsuneo Imamoto, Professor of the Chiba University. The assistance of Mrs Aurelia Pendyk in the preparation of the typescript of this article is also appreciated.

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