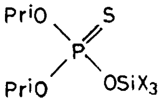
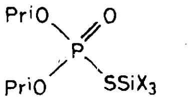
Organosilyl Esters of some Phosphorus Acids: Identification of Kinetic and Thermodynamic Isomers

By **Iain G. T. Ferguson** and **Christopher Glidewell,*** Chemistry Department, University of St. Andrews, Fife KY16 9ST

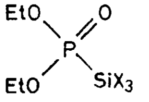
The compounds $Na[OP(OPr^i)_2]$ and $P(OPr^i)_3$ both react with $SiPh_3Cl$ to yield the phosphate $PO(OPr^i)_2(SiPh_3)$ rather than the phosphite $P(OPr^i)_2(OSiPh_3)$: $K[OSiPh_3]$ reacts with $PCl(OPr^i)_2$ to yield this phosphate in a rearrangement reaction, showing that the phosphate is the thermodynamically more stable isomer. Similarly, $Na[OP(OPr^i)_2]$ reacts with $SiMe_3Cl$ to yield only the phosphate $PO(OPr^i)_2(SiMe_3)$, which is formed also in the rearrangement reaction of $Na[OSiMe_3]$ with $PCl(OPr^i)_2$. The compound $[NH_2Et_2][SSiPh_3]$ reacts with $PCl(OPr^i)_2$ to yield the more-stable rearranged phosphorothioate $P(OPr^i)_2S(SiPh_3)$ rather than the phosphorothioite $P(OPr^i)_2(SSiPh_3)$. The salt $K[OSiPh_3]$ reacts with PPh_2Cl and PCl_3 to give the rearranged products $PPh_2O(SiPh_3)$ and $PO(OSiPh_3)_2(SiPh_3)$ respectively, but $Na[OSiMe_3]$ yields respectively $PPh_2O(SiMe_3)$ and unrearranged $P(OSiMe_3)_3$. The salt $K[OSiPh_3]$ reacts with $PCl(OPr^i)_2S$ to yield only $P(OPr^i)_2(OSiPh_3)S$, identical to the product formed by reaction of $Na[OSP(OPr^i)_2]$ with $SiPh_3Cl$: on reaction with $PClO(OPr^i)_2$, $[NH_2Et_2][SSiPh_3]$ gives $PO(OPr^i)_2(SSiPh_3)$ at room temperature, but on reflux in toluene forms the rearranged isomer $P(OPr^i)_2(OSiPh_3)S$ which is therefore the more-stable isomer.

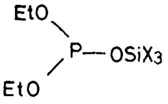
THE (1,3) ambident nucleophile *OO'*-di-isopropyl phosphorothioate(1−), $[PO(OPr^i)_2S]^-$, reacts[1] with the halides of silicon $SiMe_3Cl$ and $SiPh_3Cl$ to form *O*-bonded silyl derivatives (1a), and a simple bond-energy sum calculation suggested[1] that (1a) rather than the *S*-bonded isomer (1b) is thermodynamically the more stable. The (1,2) ambident nucleophile diethyl phosphite(1−), $[PO(OEt)_2]^-$, reacts with halogenosilanes to yield products which have been described variously as phosphites (2b)[2] or 'phosphonates' (2a).[3-5] In this paper the thermodynamically stable isomers from such reactions are experimentally identified as phosphorothioates (1a) and phosphates (2a), respectively: similarly in the phosphorothiate–phosphorothioite system (3a)–(3b) the thermodynamically more stable isomer is identified as (3a).

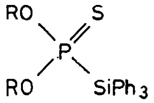

(1a)

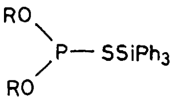

(1b)

X = Me or Ph


(2a)


(2b)


(3a)


(3b)

EXPERIMENTAL

Proton-decoupled ^{31}P n.m.r. spectra were recorded at 32.19 MHz using a Varian CFT-20 spectrometer: the internal reference was D_3PO_4, and the isotopic chemical shift $\delta(D_3PO_4) - \delta(H_3PO_4)$ was +0.29 p.p.m. All the ^{31}P chemical shifts are reported relative to 85% H_3PO_4: downfield shifts are positive. Hydrogen-1 n.m.r. and mass spectra were recorded using HA-100 and MS-902 instruments respectively.

Literature methods were employed for the preparation of $Na[OSiMe_3]$,[6] $Li[SiPh_3]$,[7] $K[OSiPh_3]$,[8] $[NH_2Et_2][SSiPh_3]$,[9] $PHO(OPr^i)_2$[10] [δ(P) +4.2 p.p.m.], $PCl(OPr^i)_2$[11] [δ(P) +166.9 p.p.m.], $PClO(OPr^i)_2$[12] [δ(P) +2.0 p.p.m.], and $PCl(OPr^i)_2S$[13] [δ(P) +65.8 p.p.m.]. Diethyl ether, tetrahydrofuran (thf), and hydrocarbon solvents were dried over sodium wire.

Reactions.—Of $Li[SiPh_3]$, $K[OSiPh_3]$, $[NH_2Et_2][SSiPh_3]$, *and* $Na[OSiMe_3]$. To aliquot portions of the salt (5 mmol) suspended or dissolved in toluene or light petroleum (b.p. 40—60 °C) were added stoicheiometric quantities of the freshly distilled phosphorus halide. The mixtures were stirred at room temperature during 1 h, filtered, and centrifuged: the solvents were evaporated at room temperature, or below, to yield the products. Recrystallisation was from light petroleum or Et_2O. Microanalytical data

---

[1] I. A. Duncan and C. Glidewell, *J. Organometallic Chem.*, 1975, **97**, 51.

[2] E. A. Chernyshev and E. F. Bugerenko, *Izvest. Akad. Nauk S.S.S.R. Otdel. khim. Nauk*, 1963, 769.

[3] W. H. Keeber and H. W. Post, *J. Org. Chem.*, 1956, **21**, 509.

[4] F. Fehér, G. Kuhlbörsch, A. Blümcke, H. Keller, and K. Lippert, *Chem. Ber.*, 1957, **90**, 134.

[5] M. J. Newlands, *Proc. Chem. Soc.*, 1960, 123.

[6] L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 2282.

[7] H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. and Ind.*, 1958, 1479.

[8] L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, 1964, **86**, 3271.

[9] L. H. Sommer and J. McLick, *J. Amer. Chem. Soc.*, 1967, **89**, 5805.

[10] H. McCombie, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 1945, 380.

[11] J. Michalski, T. Modro, and A. Zwierzak, *J. Chem. Soc.*, 1961, 4904.

[12] A. C. Poshkus and J. E. Herweh, *J. Amer. Chem. Soc.*, 1957, **79**, 6127.

[13] J. H. Fletcher, J. C. Hamilton, I. Hechenbleikner, E. I. Hoegberg, B. J. Sertl, and J. T. Cassaday, *J. Amer. Chem. Soc.*, 1948, **70**, 3943.

are in Table 1: the data for $PO(OSiPh_3)_2(SiPh_3)$ were consistently poor. Decomposition temperatures were variable. When aged solutions of $Li[SiPh_3]$ which had been exposed to dry air for some weeks were allowed to react with $PClO(OPr^i)_2$ a second product was formed in addition to $PO(OPr^i)_2(SiPh_3)$, whose composition is $Pr^i{}_2PO_5SiPh_3$, identified by accurate mass measurement (Found: *m/e* 456.1519. $^{12}C_{24}{}^{1}H_{29}{}^{16}O_5{}^{31}P^{28}Si$ requires *m/e* 456.1522 a.m.u.): the mass spectrum suggests that it is a peroxophosphate, $PO_3(OPr^i)_2(SiPh_3)$, but an analytical sample has not yet been isolated.

TABLE 1

Microanalytical data (%)

Compound	Found C	Found H	Calc. C	Calc. H
$PO(OPr^i)_2(SiPh_3)$	67.5	7.4	67.9	6.9
$P(OPr^i)_2S(SiPh_3)$	65.1	6.1	65.4	6.6
$PO(OPr^i)_2(SSiPh_3)$	63.4	6.9	63.1	6.4
$PO(OSiPh_3)_2(SiPh_3)$	76.6	5.5	75.7	5.3
$PPh_2O(SiPh_3)$	77.8	5.9	78.2	5.5
$PO(OPr^i)_2(SiMe_3)$	45.7	9.1	45.4	9.7
$PPh_2O(SiMe_3)$	66.2	6.7	65.7	7.0
$P(COPh)O(OPr^i)_2$	58.1	6.9	57.8	7.1

TABLE 2

N.m.r. parameters *

Compound	$\delta(CH_3Si)$	$\delta(CH_3C)$	$\delta(CHO)$	$\delta(C_6H_5)$	$\delta(P)$
$PO(OPr^i)_2(SiPh_3)$		1.30	4.58	7.1—7.8	+6.5
$P(OPr^i)_2S(SiPh_3)$		1.30, 1.32	4.90	7.2—7.7	+104.7
$P(OPr^i)_2(OSiPh_3)S$		1.27, 1.32	4.60	7.2—7.8	+57.9
$PO(OPr^i)_2(SSiPh_3)$		1.34, 1.38	4.82	7.2—7.8	+15.5
$PO(OSiPh_3)_2(SiPh_3)$				7.1—7.8	−16.5
$PPh_2O(SiPh_3)$				7.1—7.9	+28.6
$PO(OPr^i)_2(SiMe_3)$	0.39	1.29, 1.33	4.78		+4.9
$PPh_2O(SiMe_3)$	0.39			7.2—7.9	+26.1
$P(OSiMe_3)_3$	0.40				+114.0
$P(COPh)O(OPr^i)_2$		1.38, 1.42	4.90	7.3—8.3	−10.1

* $CDCl_3$ solutions: shifts in p.p.m. from $SiMe_4$ (^1H) or H_3PO_4(^{31}P).

Of $Na[OP(OPr^i)_2]$. To aliquot portions of the salt (5 mmol) in diethyl ether were added stoicheiometric quantities of $SiPh_3Cl$, $SiMe_3Cl$, or PhCOCl: the mixture was stirred during 1 h at room temperature, filtered, and the filtrate centrifuged. The solvent was subsequently removed at room temperature. Microanalytical data are in Table 1.

Of $P(OPr^i)_3$ *with* $SiPh_3Cl$. Equimolar quantities (5 mmol) were mixed and heated to 120 °C during 6 h in a distillation apparatus: Pr^iCl was collected at 0 °C. The residue was extracted with benzene (5 × 50 cm^3) and the extract was filtered; removal of the benzene gave $PO(OPr^i)_2(SiPh_3)$ (65%).

Of $NH(SiMe_3)_2$ *with* $PHO(OPr^i)_2$. (*a*) Bis(trimethylsilyl)amine (8.1 g, 0.05 mol) and $PHO(OPr^i)_2$ (16.6 g, 0.10 mol) were refluxed together in light petroleum until evolution of ammonia ceased (*ca.* 12 h). Removal of the volatiles yielded $PO(OPr^i)_2(SiMe_3)$ (18.7 g, 0.079 mol, 79%).

(*b*) To an equimolar mixture of $NH(SiMe_3)_2$ and NEt_3 (25 mmol) in CCl_4 was added, under nitrogen, $PHO(OPr^i)_2$ (4.1 g, 25 mmol). After 1 week at room temperature $[NHEt_3]Cl$ was removed by filtration: subsequent removal of the volatiles yielded 5.7 g of an air-sensitive oil, whose n.m.r. parameters were consistent with the constitution $P\{N(SiMe_3)_2\}O(OPr^i)_2$: $\delta(CH_3Si)$ 0.40 (s, 18 H); $\delta(CH_3C)$ 1.39 (d, 12 H); $\delta(CHO)$ 4.79 (m, 2 H); and $\delta(P)$ +12.43 p.p.m.

Preparation of $P(OPr^i)_2(SPh)$.—Diethylamine (0.73 g, 10 mmol) was added with vigorous stirring to a solution of PhSH (1.10 g, 10 mmol) in light petroleum: a white precipitate formed. Freshly distilled $PCl(OPr^i)_2$ (1.84 g, 10 mmol) was added, and the mixture was stirred during 1 h at room temperature. Filtration and subsequent removal of the solvent yielded the product in almost quantitative yield: $\delta(CH_3)$ 1.24 and 1.26 (12 H); $\delta(CHO)$ 4.55 (2 H); $\delta(C_6H_5)$ 7.1—7.7 (5 H); $\delta(P)$ +183.9 p.p.m. (Found: C, 53.3; H, 7.9. Calc. for $C_{12}H_{19}O_2PS$: C, 55.8; H, 7.4%). On prolonged exposure to air at room temperature partial oxidation occurs to yield $PO(OPr^i)_2(SPh)$ [$\delta(P)$ +20.1 p.p.m.].

N.M.R. Spectra.—The ^1H and ^{31}P n.m.r. parameters of new species are recorded in Table 2. The ^{31}P data provide the best diagnostic for distinguishing between isomers; i.r. spectra have been found not to give definitive indications [2-4] of constitution. In phosphates, containing four-co-ordinate phosphorus, $\delta(P)$ is expected to lie in or near the range +10 to −20 p.p.m.,[14] while in the isomeric phosphites, which contain three-co-ordinate phosphorus, $\delta(P)$ is expected to fall in or near the range 110—155 p.p.m.; on this basis $P(OSiMe_3)_3$ is assigned a phosphite constitution, while $PO(OPr^i)_2(SiPh_3)$, $PO(OPr^i)_2(SiMe_3)$, $PO(OSiPh_3)_2(SiPh_3)$, and $P(COPr^i)O(OPr^i)_2$ are assigned phosphate constitutions. Similarly, $PPh_2O(SiMe_3)$ and $PPh_2O(SiPh_3)$, having $\delta(P)$ of +26.1 and +28.6 p.p.m. respectively, must be tertiary phosphine oxides, since the isomeric phosphinites [15] have $\delta(P)$ of +94.1 and +98.0 p.p.m. respectively [*cf.* also $PEtPh_2O$ and $PPh_2(OEt)$ for which the $\delta(P)$ are [14] +35 and +109 p.p.m. respectively]. The *O*-bonded triphenylsilyl isomer $P(OPr^i)_2(OSiPh_3)S$ has [1] $\delta(P)$ +57.9 p.p.m.; the *S*-bonded constitution $PO(OPr^i)_2(SSiPh_3)$ is therefore assigned to the isomer having $\delta(P)$ +15.5 p.p.m. [*cf.* $PO(OEt)_2(SPh)$ for which [16] $\delta(P)$ is +22 p.p.m. and $PO(OPr^i)_2(SPh)$ for which $\delta(P)$ is +20.1 p.p.m.]. Since the phosphorothioate $PMe(OEt)_2S$ has [17] a $\delta(P)$ of 94.9 p.p.m., and the phosphorothioite $P(OPr^i)_2(SPh)$ is found to have $\delta(P)$ +183.9 p.p.m., a phosphorothioate constitution is assigned to $P(OPr^i)_2S(SiPh_3)$ which has $\delta(P)$ +104.7 p.p.m.

Mass Spectra.—All the compounds exhibited molecular

---

[14] V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 227.

[15] K. Issleib and B. Walther, *Angew. Chem.*, 1967, **79**, 59.

[16] J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Amer. Chem. Soc.*, 1956, **78**, 5715.

[17] H. Finegold, *J. Amer. Chem. Soc.*, 1960, **82**, 2641.

ions in their mass spectra. At high *m/e* values the spectra of certain compounds, *viz.* $P(OPr^i)_2OSSiPh_3$ (both isomers) and $PY(OPr^i)_2(SiPh_3)$ (Y = O or S) (which had all been assigned constitutions containing $\geqslant P{=}Y$ fragments on the basis of their ^{31}P chemical shifts), can be resolved into two corresponding series of ions; in one series the atom Y is present, in the other it is absent. The existence of pairs of ions, with and without Y, corroborates the constitutions deduced from the n.m.r. spectra. Examples of these pairs of ions are presented in Table 3. Thus in the spectrum of $P(OPr^i)_2(OSiPh_3)S$ the pairs $[P(OSiPh_3)S]^+$ and $[P(OSiPh_3)]^+$ and $[P(OSiPh)S]^+$ and $[P(OSiPh)]^+$ (Y = S) occur, while in the spectrum of the isomeric $PO(OPr^i)_2(SSiMe_3)$ the pairs $[PO(SSiPh_3)]^+$ and $[P(SSiPh_3)]^+$ and $[PO(SSiPh)]^+$ and $[P(SSiPh)]^+$ (Y = O) occur. In the spectrum of $P(OSiMe_3)_3$ no such pairs occur. In the spectra of $PY(OPr^i)_2(SiPh_3)$ (Y = O or S), in addition to the ion pairs listed in Table 3, the ions $[P(SiPh_2)]^+$ and $[P(OPr^i)Si]^+$ are observed, again suggesting direct P–Si bonds.

TABLE 3

Pairs of diagnostic ions in mass spectra

Compound	Ion	*m/e*	Relative intensity (%)
$P(OPr^i)_2(OSiPh_3)S$ [a]	$[P(OSiPh_3)S]^+$	338	9.0
	$[P(OSiPh_3)]^+$	306	17
	$[P(OSiPh_2)S]^+$	261	14
	$[P(OSiPh_2)]^+$	229	1.0
	$[P(OSiPh)S]^+$	184	9.1
	$[P(OSiPh)]^+$	152	38
$PO(OPr^i)_2(SSiPh_3)$	$[PO(OPr^i)_2(SSiPh_2)]^+$	379	11
	$[P(OPr^i)_2(SSiPh_2)]^+$	361	23
	$[PO(SSiPh_3)]^+$	338	100
	$[P(SSiPh_3)]^+$	322	20
	$[PO(OPr^i)(SSiPh)]^+$	243	20
	$[P(OPr^i)(SSiPh)]^+$	227	30
	$[PO(OPr^i)_2(SSi)]^+$	225	30
	$[P(OPr^i)_2(SSi)]^+$	209	20
	$[PO(SSiPh)]^+$	184	95
	$[P(SSiPh)]^+$	168	10
$PO(OPr^i)_2(SiPh_3)$	$[PO(OPr^i)(SiPh_3)]^+$	365	22
	$[P(OPr^i)(SiPh_3)]^+$	349	2.0
	$[PO(OPr^i)_2(SiPh)]^+$	270	10
	$[P(OPr^i)_2(SiPh)]^+$	254	100
	$[PO(OPr^i)(SiPh)]^+$	211	20
	$[P(OPr^i)(SiPh)]^+$	195	3.5
$P(OPr^i)_2S(SiPh_3)$ [b]	$[P(OPr^i)S(SiPh_2)]^+$	304	12
	$[P(OPr^i)(SiPh_2)]^+$	272	20
	$[P(OPr^i)_2S(SiPh)]^+$	286	20
	$[P(OPr^i)_2(SiPh)]^+$	254	35
	$[P(OPr^i)_2(SSi)]^+$	209	50
	$[P(OPr^i)_2Si]^+$	177	5.0

[a] Base peak of spectrum: P^+, *m/e* 31. [b] Base peak of spectrum: $PS(SiPh_2)$, *m/e* 245.

In the spectrum of $PO_3(OPr^i)_2(SiPh_3)$ a number of peroxo-ions occur. In this spectrum also, four pairs of ions occur the members of which are separated by 16 mass units, corresponding to species which do or do not contain a terminal oxygen bonded to phosphorus. Other noteworthy ions in this spectrum are $[O_2SiPh]^+$ and $[O_2Si]^+$.

RESULTS AND DISCUSSION

Sodium *OO'*-di-isopropyl phosphorothioate(1−) reacts with chlorotriphenylsilane to yield the *O*-bonded isomer $P(OPr^i)_2(OSiPh_3)S$,[1] with none of the *S*-bonded isomer $PO(OPr^i)_2(SSiPh_3)$. In order to determine whether this *O*-bonded isomer is indeed the more stable thermodynamically, the reactions of the anions $[YSiPh_3]^-$ (Y = O or S) with the substrates $PClZ(OPr^i)_2$ (Z = S or O respectively) were investigated. When Y = O, Z = S, the same phosphorothioate isomer (1a; X = Ph) is formed, both at room temperature and at reflux in toluene [equation (1)]. However, when Y = S, Z = O, the isomer (1b; X = Ph) is formed at room temperature [equation (2)], but at reflux in toluene the rearranged isomer (1a) is produced, demonstrating that this isomer is the more stable.

$$PCl(OPr^i)_2S + K[OSiPh_3] \longrightarrow KCl + P(OPr^i)_2(OSiPh_3)S \quad (1)$$

$$PClO(OPr^i)_2 + [NH_2Et_2][SSiPh_3] \longrightarrow [NH_2Et_2]Cl + PO(OPr^i)_2(SSiPh_3) \quad (2)$$

Sodium di-isopropyl phosphite reacts with $SiPh_3Cl$ to yield the phosphate $PO(OPr^i)_2(SiPh_3)$, with no phosphite $P(OPr^i)_2(OSiPh_3)$: the identical product is formed in an Arbusov-type reaction with tri-isopropyl phosphite [equation (3)], again with no phosphite being formed by exchange. Products of this composition have been observed previously in similar reactions, but no unambiguous evidence for their constitutions has been provided: i.r. spectra have been used to support both phosphonate [3,4] and phosphite [2] constitutions, and a mechanistic analogy with the Arbusov reaction of halogenoalkanes has been used [5] to support the phosphonate constitution. An identical product is formed in the reactions of $PClO(OPr^i)_2$ with $Li[SiPh_3]$ [equation (4)] and of $PCl(OPr^i)_2$ with $K[OSiPh_3]$ [equation (5)].

$$P(OPr^i)_3 + SiPh_3Cl \longrightarrow Pr^iCl + PO(OPr^i)_2(SiPh_3) \quad (3)$$

$$PClO(OPr^i)_2 + Li[SiPh_3] \longrightarrow LiCl + PO(OPr^i)_2(SiPh_3) \quad (4)$$

$$PCl(OPr^i)_2 + K[OSiPh_3] \longrightarrow KCl + PO(OPr^i)_2(SiPh_3) \quad (5)$$

Reaction (5) involves a rearrangement from an Si–O bonded reagent to a P=O bonded product, possible *via* the phosphite $P(OPr^i)_2(OSiPh_3)$ showing that the silylphosphate is thermodynamically more stable than the phosphite. In a similar way $Na[OSiMe_3]$ reacts with $PCl(OPr^i)_2$ to yield a rearranged phosphate $PO(OPr^i)_2(SiMe_3)$, identical to that formed in the reaction of $Na[OP(OPr^i)_2]$ with $SiMe_3Cl$. Reaction of $PHO(OPr^i)_2$ with hexamethyldisilazane in petroleum yielded the same phosphate, but under Atherton–Todd conditions,[18,19] in carbon tetrachloride solution in the presence of base, triethylammonium chloride was produced: no phosphate was formed, but instead a very air-sensitive product was found whose n.m.r. spectra supported its

---

[18] F. R. Atherton, H. T. Openshaw, and A. R. Todd, *J. Chem. Soc.*, 1945, 660.

[19] F. R. Atherton and A. R. Todd, *J. Chem. Soc.*, 1947, 674.

formulation as $P\{N(SiMe_3)_2\}O(OPr^i)_2$, formed according to equation (6): conclusive identification was not however achieved.

$$PHO(OPr^i)_2 + NH(SiMe_3)_2 + NEt_3 + CCl_4 \longrightarrow CHCl_3 + [NHEt_3]Cl + P\{N(SiMe_3)_2\}O(OPr^i)_2 \quad (6)$$

In the phosphorothioate–phosphorothioite system, $Li[SiPh_3]$ reacts with $PCl(OPr^i)_2S$ to yield the phosphorothioate (3a), but the reaction of $[NH_2Et_2][SSiPh_3]$ with $PCl(OPr^i)_2$ yields the same phosphorothioate and trace amounts of the phosphorothioate (1b; X = Ph). It seems probable that the phosphorothioite (3b) is formed initially, and that most rearranges while a small proportion is oxidised [equation (7)]. Such oxidation of a

$$[NH_2Et_2][SSiPh_3] \xrightarrow{PCl(OPr^i)_2} P(OPr^i)_2(SSiPh_3) \longrightarrow P(OPr^i)_2S(SiPh_3) + PO(OPr^i)_2(SSiPh_3) \quad (7)$$

phosphorothioite is observed also in the case of $P(OPr^i)_2(SPh)$ (see Experimental section). The formation of the rearranged phosphorothioate (3a) in reaction (7) shows that this isomer, rather than (3b), is the more stable.

Both $Na[OSiMe_3]$ and $K[OSiPh_3]$ react with chlorodiphenylphosphine at room temperature to yield phosphine oxides rather than phosphinites [equation (8);

$$M[OSiR'_3] + PPh_2Cl \longrightarrow MCl + PPh_2O(SiR'_3) \quad (8)$$

M = Na or K, R′ = Me or Ph]. These reactions again involve migration of SiR'_3 from oxygen to phosphorus and show that the tertiary phosphine oxide is the more stable isomer. Reactions conducted in the reverse sense [equation (9)] in contrast yielded phosphinites:

$$Na[OPPh_2] + SiR'_3Cl \longrightarrow NaCl + PPh_2(OSiR'_3) \quad (9)$$

although these products undergo Arbusov-type reactions with halogenoalkanes, their reactions with halogenosilanes were not investigated.[15] Unlike the reaction of $Li[SiPh_3]$ and $PClO(OPr^i)_2$ observed here, analogous reactions designed[15] to form tertiary oxides by use of $Li[SiPh_3]$ and PR'_2ClO (R′ = Bu or Ph) yielded only Si_2Ph_6 and $P_2R'_4O_2$ which was ascribed to halogen–metal exchange. The salts $Na[OSiMe_3]$ and $K[OSiPh_3]$ differ in their room-temperature reactions with PCl_3. The latter salt yields only the rearranged phosphate $PO(OSiPh_3)_2(SiPh_3)$, whereas $Na[OSiMe_3]$ yields only the phosphite $P(OSiMe_3)_3$, identical to that formed[20] in the reaction of $SiMe_3Cl$ with H_3PO_3 in the presence of base. On prolonged reflux with excess of $SiMe_3Cl$ this phosphite appears to undergo a slow reaction of the Arbusov type to yield a phosphonate, since a new peak, characteristic of a phosphonate, appears in the ^{31}P n.m.r. spectrum with $\delta(P)$ -14.9 p.p.m.

Simple bond-energy summations indicate that approximate $\Delta H^\ominus$ values for the isomerisations (1b) ⟶ (1a), (2b) ⟶ (2a), and (3b) ⟶ (3a) are, respectively, −60, −30, and −90 kJ mol^{-1}, in each case consistent with the experimental deduction that isomers (1a), (2a), and (3a) are the more stable.

Although the anion $[PO(OPr^i)_2S]^-$ reacts with halides sometimes to yield *O*- and sometimes to yield *S*-bonded phosphorothioate species,[1,21] the anion $[PO(OPr^i)_2]^-$ appears always to yield species containing four-coordinate phosphorus: this is so in reactions with halides of H, C, Si, P,[22-24] Cd,[22] and Hg.[22]

[7/737 *Received, 2nd May, 1977*]

---

[20] T. Hata and M. Sekine, *J. Amer. Chem. Soc.*, 1974, **96**, 7363.

[21] C. Glidewell, *Inorg. Chim. Acta*, 1977, **24**, 255.

[22] C. Glidewell, unpublished work.

[23] J. Michalski and A. Zwierzak, *Proc. Chem. Soc.*, 1964, 80.

[24] K. M. Abraham and J. R. Van Wazer, *Inorg. Chem.*, 1976, **15**, 2322.