Journal of Organometallic Chemistry, 277 (1984) 211–225
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

2-TRIETHYLSILYL- AND 2-TRIETHYLGERMYL-1,3-DI-t-BUTYL-1,3,2-DIAZAPHOSPHORINANES: SYNTHESIS, STRUCTURE AND CHEMICAL PROPERTIES

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(Received June 29th, 1984)

Summary

From the reaction of triethylsilyl- and triethylgermyl-lithium (prepared from bis(triethylsilyl-, -germyl-)mercury and lithium in pentane) with 2-chloro-1,3-di-t-butyl-1,3,2-diazaphosphorinane the corresponding derivatives with P^{III}–Si and P^{III}–Ge bonds were obtained. It is shown that oxidation of cyclic diaminosilylphosphines yields the corresponding *o*-silyldiamidophosphates. ^{1}H, ^{13}C, ^{31}P and ^{29}Si NMR spectroscopy has been used to investigate the structures of the novel P^{III}-phosphinanes. It is shown that the chair conformation is strongly preferred. The orientations of the organoelemental substituents are discussed.

In refs. 1 and 2 we reported the first results of investigations of organic derivatives of phosphorous acid in which the phosphorus atom is bonded to both the electronegative X and electron-donating E substituents. The donor–acceptor interactions of the geminal system $X \leftarrow \ddot{P} \leftarrow E$ of such compounds may be active in leading to their degradation. In view of the above, we began our investigation of these compounds with systems containing weak electron-acceptors ($X = \rangle NR$) and electron-donors ($E = -SiPh_3$) as the substituents [1,2]. This paper reports the data concerning the synthesis and investigation of compounds in which the trivalent phosphorus atom is bonded to the same amido group but with novel, more electron-donating substituents, viz. triethylsilyl and triethylgermyl.

Synthesis

The trialkylsilyl and trialkylgermyl derivatives were prepared by nucleophilic substitution of chlorine into 2-chloro-1,3-di-t-butyl-1,3,2-diazaphosphorinane (I) with

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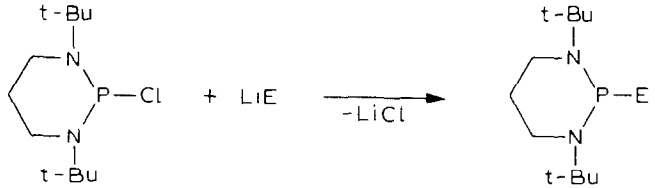
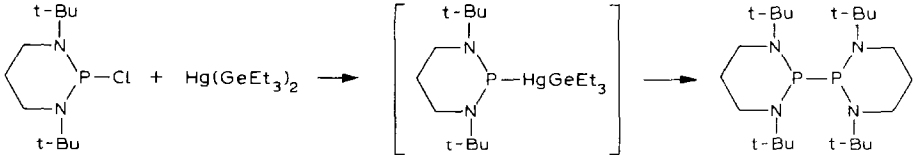
triethylsilyl- and triethylgermyl-lithium.



(I)

(II, E = $SiEt_3$; III, E = $GeEt_3$)

Compounds II and III were obtained in yields close to theoretical. They were sufficiently stable and could easily be recovered in a pure state by distillation in vacuo. The effectiveness of the reaction is largely determined by the method used to generate the organoelemental anions. Triethylsilyl- and triethylgermyl-lithium were obtained by re-metallization of bis(triethylsilyl)- and (-germyl)-mercury with metallic lithium [3]. Since the appropriate anions could be produced in an inert solvent (pentane), it was possible to carry out the synthesis under mild conditions. An attempt to obtain the mercury analogue of II by treating bis(triethylsilyl)mercury with chlorophosphite I led to a reductive dimerization product (IV).

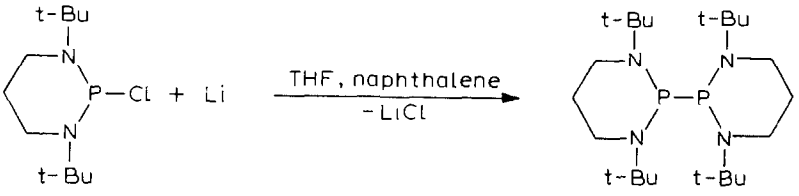


(I)

(IV)

Examples of these conversions in the acyclic series of compounds have already been described in the literature [4].

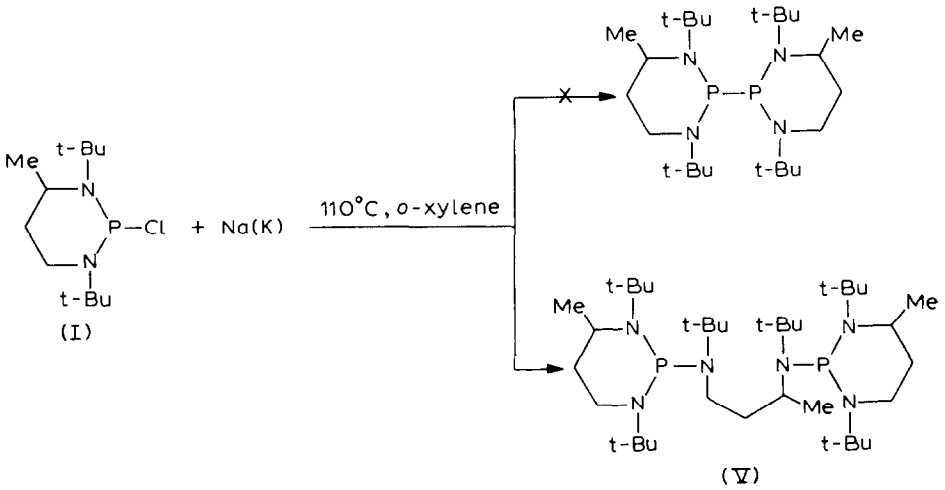
Note that compound IV with a P–P bond has alternatively been obtained by the reaction of the chlorophosphite I directly with metallic lithium in THF in the presence of naphthalene.



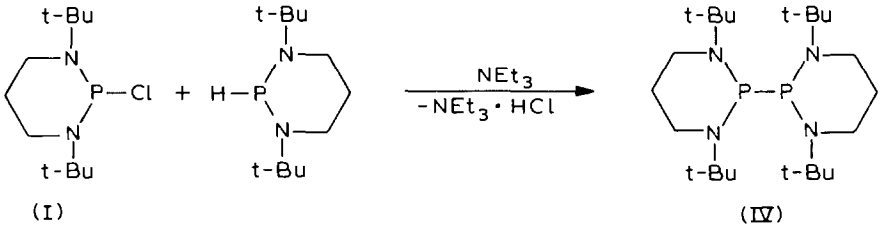
(I)

(IV)

This result merits attention, since we found that the earlier described Würtz reaction between the 1,3-butylenediamido-chlorophosphite and metallic sodium and potassium in *o*-xylene at 110°C [5] does not in fact yield IV as the product, but, as in the case of 1,3,2-dioxaphosphorinanes [1], results in ring-opening and formation of a bis-triamide (V).



Apparently in this case the process is affected by the severe conditions in which the reaction is carried out and by the strong donor–acceptor geminal interactions in the system $N \leftarrow \ddot{P} \leftarrow Na$ in comparison with $N \leftarrow \ddot{P} \leftarrow Li$. To prove this, compound IV was also obtained by counter-synthesis.



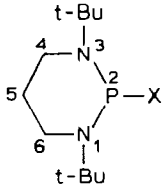
Structures of the novel 1,3,2-diazaphosphorinanes

The structures of compounds II–IV were identified by ^{1}H, ^{13}C, ^{31}P and ^{29}Si NMR spectroscopy. The ^{31}P NMR spectra of compounds II–IV contain signals in the region typical of the corresponding phosphorous acid derivatives (Table 1) [6]. The ^{29}Si NMR spectrum of II contains a doublet which we have attributed to the silicon bonded directly to the phosphorus atom. It should be noted that replacement of the phenyl radical at the silicon in 2-triphenylsilyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane (VI) by an alkyl has little effect on the shielding of the phosphorus nucleus, whereas the ^{29}Si chemical shifts in $SiPh_3$ [2] and $SiEt_3$ are quite different: $\delta(^{31}P)$ ($SiEt_3$) 47.9 ppm, $\delta(^{31}P)$ ($SiPh_3$) 48.8 ppm, $\delta(^{29}Si)$ ($SiEt_3$) −0.24 ppm, $\delta(^{29}Si)$ ($SiPh_3$) −23.7 ppm. The ^{1}H NMR data confirm the structures determined. The results of the complete analysis of the ^{1}H NMR spectra are given in Table 1. The ^{1}H NMR spectra of II and III are substantially identical.

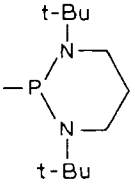
The ring proton signals were attributed on the basis of double homonuclear resonance data and spin–spin coupling constants of H–H. The large coupling between the upfield portion of the C(4,6) protons and the downfield portion of the multiplets of the C(5) protons ($12.2 < J < 12.5$ Hz) indicates that they are *trans*-axially arranged (angle 180°C). Smaller constants have been observed between the

TABLE 1

^{1}H AND ^{31}P NMR DATA FOR 2-*X*-1,3-di-t-BUTYL-1,3,2-DIAZAPHOSPHORINANES



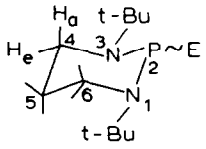
Solvent, C_6D_6; concentration 25%.

X	^{1}H chemical shifts (ppm)							Coupling constants (Hz)								$\delta(^{31}P)$ (ppm)
	$H(4,6)_e$	$H(4,6)_a$	$H(5)_a$	$H(5)_e$	CH_2	CH_3	t-Bu	4a4e	5a5e	4a5a	4a5e	4e5a	4e5e	4aP	4eP	
H	3.51	2.92	1.86	1.52	–	–		−13.0	−12.8	11 6	3.0	4.3	3.3	2.6	3.4	49.6
OCH_2CH_3	2.82	3.23	1.77	1.77				−11.8	12.5	13 2	5.7	4.9	4.9	2.8	5.4	117.0
$Si(CH_2CH_3)_3$	3.36	3.12	1.72	1.33	0.95	1.22	1.33	−14.0	−13.1	12.5	3.0	4.0	4.0	0.9	3.0	47 9
$Ge(CH_2CH_3)_3$	3.37	3.02	1.72	1.30	1.14	1.33	1.30	−14.2	−12.3	12.2	2.3	4.0	5.5	1.3	2.9	62.3
	2.99	3.70	1.63	1.63	–	–	1.31	−13.0	[a]	11.3	4.5	5.2	[a]	0 9	2 0	52.3

[a] Constants not determined.

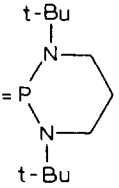
equatorial-equatorial ($J \cong 4$ Hz) protons at C(4,6) and C(5). These constants are consistent with those measured earlier for similar systems [6].

The non-equivalence of the protons at one ring position and the H–H constants are indicative (Table 1) of the fact that compounds II–IV exist predominantly in one "chair"-type conformation, and apparently rule out the possibility of the distorted "bath" forms, in which pseudo-rotation would have caused averaging of the chemical shifts and constants.

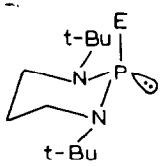


(II – IV)

(II, E = $SiEt_3$; III, E = $GeEt_3$; IV, E = P)



The widely used method of determining the phosphorus substituent orientation in 1,3,2-diheterophosphorines is based on the analysis of the resonance signals of the $H(4,6)_a$ and $H(4,6)_e$ protons, according to which the weak-field location of the 4,6-axial protons in comparison with the 4,6-equatorial protons must be attributed to the axial orientation of the phosphorus substituent [7,8]. Earlier we found that in the transition from P–X- (where X is an electronegative substituent) to P–H-structures the chemical shifts of the geminal $H(4,6)_a$ and $H(4,6)_e$ protons become inverted while the H atom at phosphorus remains in the axial orientation [6]. Similarly to phosphohydrides, the axial protons in II and III resonate in a stronger field than the equatorial ones. The other parameters of the NMR spectra of the P–H and P–E derivatives are also close. This prompts us to conclude that the orientation of the organoelemental substituent in II and III is probably axial, all the more so since we have already pointed out in an earlier paper [2] that the axial orientation is strongly preferred for the triphenylsilyl group in the cyclic system in question.



(VI, E = $SiPh_3$; II, E = $SiEt_3$; III, E = $GeEt_3$)

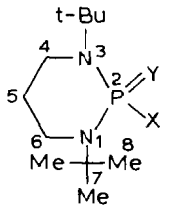
(II, III, VI)

Another approach to determine the orientation of the phosphorus substituent is based on the analysis of vicinal constants: $^3J(P\text{–}N\text{–}CH_e) > {}^3J(P\text{–}N\text{–}CH_a)$, which may also be considered as evidence in favour of the preferred axial position of substituent E in II and III. The only thing we would like to point out are the rather small absolute values of the constants. Earlier, Hutchins et al. [8] showed that in diazaphosphorinane systems the vicinal constant may differ greatly depending on the type of phosphorus substituent. This has been attributed to re-hybridization of nitrogen from sp^2 to sp^3 in transition from the strongly electronegative substituents at phosphorus (Cl, OR) to the Alk or Ph groups. The spin–spin coupling decreases in the same manner as the p–d integration (or the percentage of the 2s-character in the nitrogen orbitals) between N and P which, in turn, decreases when electron-donating groups are added to phosphorus.

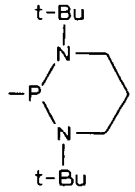
(*Continued on p. 218*)

TABLE 2

^{13}C NMR CHEMICAL SHIFTS (δ, ppm), SPIN–SPIN COUPLING CONSTANTS (J, Hz) AND THE EFFECTS OF PHOSPHORUS SUBSTITUENT X (ppm) IN:



Compound	Y	X	Parameter	C(4,6)	C(5)	C(7)	C(8)	C(9)	C(10)	Substituent effects			
										γ(C(4))	δ(C(5))	γ(C(7))	δ(C(8))
	–	H	δ	49 7	30 7	55.4	29.9						
			J	7.1	0.6	18.7	12 5			0	0	0	0
II	–	$Si(^{9}CH_2{}^{10}CH_3)_3$	δ	47 3	31.6	56.9	31.2	6.5	8.9				
			J	3.7	2.8	20.0	12.5	16.0	3.5 2.33	−2 4	+0.9	+1.5	+1 3

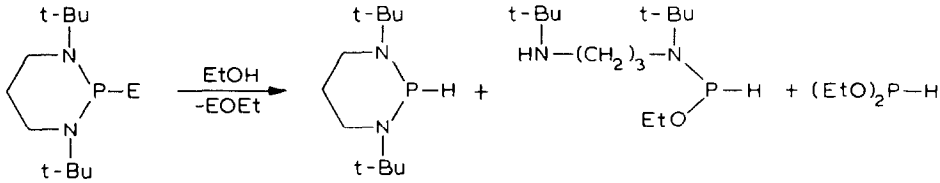
III	–	$Ge(^{9}CH_2{}^{10}CH_3)_3$	σ	47.3	31.2	56.9	31.1	8.05	10.4				
			J	5.5	0.9	19.5	12.5	13.0	3.5 2.38	−2.4	+0.5	+1.5	+1.2
VI	–	$SiPh_3$	δ	45.3	29.4	56.5	31.2						
			J	4.4	0.6	20.0	12.5			−4.4	+1.3	+1.1	+1.3
IV	–		δ	42.9	30.5	56.6	30.9						
			J	0.6	4.9	12.2	7.9			−6.8	−0.2	+1.2	+1.0
VII	–	$OSiPh_3$	δ	39.2	28.1	55.5	30.5						
			J	3.8	0.6	24.0	14.8			−10.5	−2.6	+0.1	0.6
IX	O	$OSi(^{9}CH_2{}^{10}CH_3)_3$	δ	44.6	28.0	56.4	31.3	6.5	7.4				
			J	0.6	3.7	0.6	3.7	0	0 0.9	−5.1	−2.7	+1.0	+1.4
VIII	O	$OSiPh_3$	δ	44.2	27.5	56.5	30.8						
			J	0	4.9	1.4	3.6			−5.6	−3.2	+1.2	+0.9

The structures of the P-organoelemental compounds II–IV were studied by ^{13}C NMR spectroscopy. The spectra contained the signals of all the carbon atoms split into doublets due to spin–spin coupling with the phosphorus nucleus. Table 2 presents the chemical shifts and spin–spin coupling constants for $^{13}C-^{31}P$ and the γ-effects of the phosphorus substituents in transition from the P–H to the P–X derivatives.

It can be seen from Table 2 that the spectral parameters of compounds II and III are very similar, thus II and III must be structurally alike. Note the closeness of the spectral parameters of the R–E and P–H derivatives (the γ-effects are small, viz. 2.4 ppm) which is also observed in their ^{31}P and ^{1}H NMR spectra. We previously noted that in 2-triphenylsilyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane (VI), in which the $SiPh_3$ group is axial, the γ-effect of the phosphorus substituent is also smaller than expected for electron-accepting substituents (Cl, OR, NR_2, $OSiR_3$) [2]. At present, it is too early to discuss the reasons for this effect; we may only assume that it is the nature of the P–E bond (E = Si, Ge, P) which affects the extent of the γ-effect in the ^{13}C NMR spectra and its consequences in the ^{1}H NMR spectra.

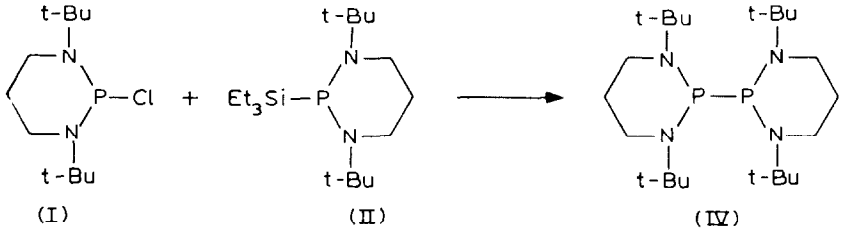
Certain chemical conversions of 2-E-1,3-di-t-butyl-1,3,2-diazaphosphorinanes

Earlier we showed [2] that the alcoholysis of 2-triphenylsilyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane (VI) yields the corresponding P–H derivative [2]. By means of ^{31}P NMR spectroscopy it was shown that the alcoholysis specificity with respect to the P–Si and P–Ge bonds does not manifest itself in the case of compounds II and III. The reaction carried out in the spectrometer cell produces a mixture of three phosphohydrides in which the acyclic products are predominant.



(II, E = SiEt ; III, E = $GeEt_3$)	δ(^{31}P) 49.6 ppm	δ(^{31}P) 108.4 ppm	δ(^{31}P) 162 ppm
	^{1}J(P–H) 214 Hz	^{1}J(P–H) 241 Hz	^{1}J(P–H) 201 Hz

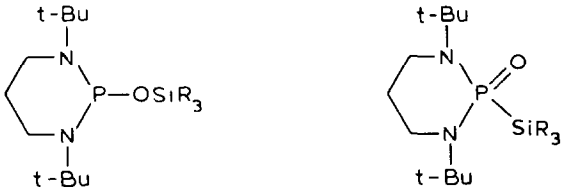
Probably, the P–$SiEt_3$ and P–$GeEt_3$ bonds are more stable towards nucleophilic attack than P–$SiPh_3$. The exchange reactions of II and III are of especial interest. For instance, the reaction of II with the chloroanhydride I at 120°C yields compound IV containing a P–P bond.



(I) (II) (IV)

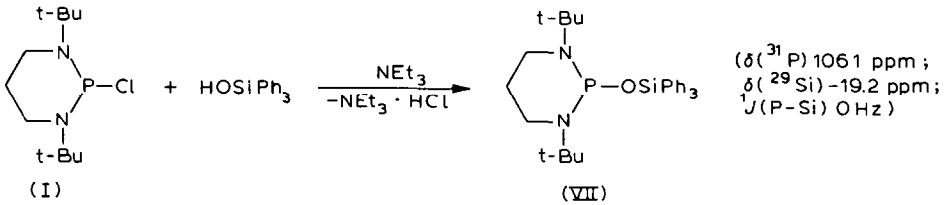
The triphenyl compound VI does not take part in such a reaction since the process is apparently an equilibrium (triphenylchlorosilane is a high-boiling product and is difficult to remove from the reaction mixture).

Of particular interest is the oxidation of the organoelemental derivatives II and VI. From general considerations one would expect the formation of two isomeric compounds as a result of their mono-oxidation, with either a three- or a four-coordinate phosphorus atom (**A** and **B**):



(**A**) (R = Ph, Et) (**B**)

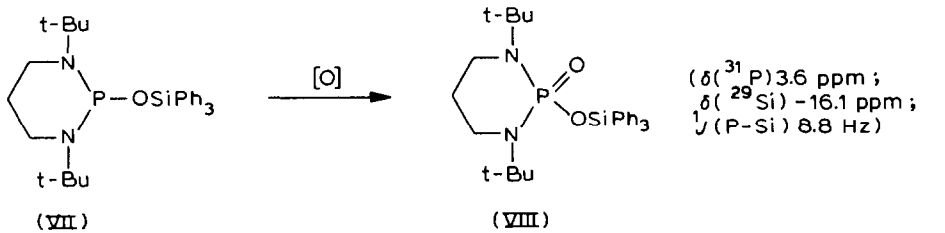
The literature contains controversial data about the thermodynamic stability of silylphosphite isomers. Yet, the assumption that silylphosphites occur in form **A** appears to be more tenable in view of the high oxygen affinity of silicon [9a,9c]. Attempts to obtain the four-coordinate phosphorus form have been reported [9b], where the intention was to create a P–Si bond in the reaction. We deemed it of interest to study another approach to the synthesis using the starting compounds with the P^{III}–SiR_3 fragment already there. The first steps in this direction were taken when we carried out the oxidation of 2-triphenylsilyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane (VI) with nitrogen oxide or iodobenzene. The reaction gave a single product whose ^{31}P NMR spectrum contained a singlet at $\delta(^{31}P)$ 3.1 ppm. This signal apparently excludes the three-coordinate form **A** which was obtained by counter-synthesis.



(I) (VII) ($\delta(^{31}P)$ 106.1 ppm; $\delta(^{29}Si)$ −19.2 ppm; ^1J(P–Si) 0 Hz)

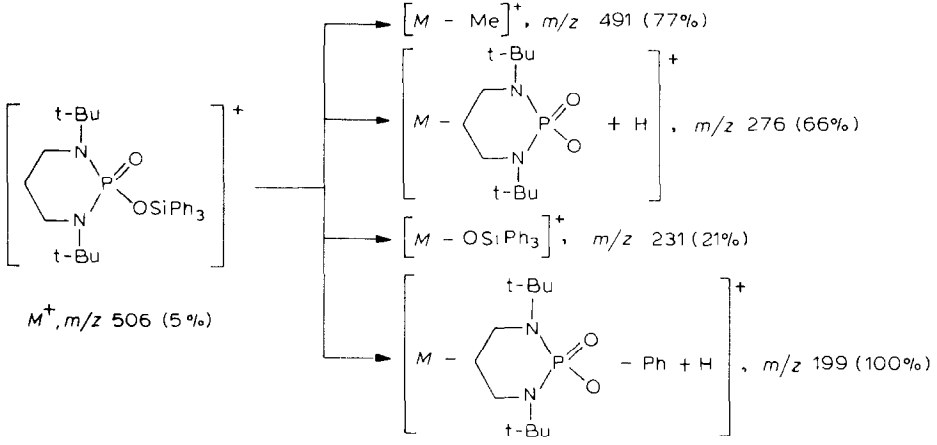
The ^1H, ^{13}C and ^{29}Si NMR spectral data also favoured structure **B** with the four-coordinate phosphorus atom. For example, the ^{29}Si NMR spectrum contained a doublet with $\delta(^{29}Si)$ −16.5 ppm and ^1J(P–Si) 9.3 Hz, whereas for compound VII the constant ^1J(P–Si) equalled zero. On the basis of these results we tentatively concluded that the mono-oxidized product is obtained in form **B** [1].

However, further investigations showed that this is not the case. It was found that an excess of nitrogen oxide oxidizes silylphosphite to the corresponding silylphosphate VIII.



(VII) (VIII) ($\delta(^{31}P)$ 3.6 ppm; $\delta(^{29}Si)$ −16.1 ppm; ^1J(P–Si) 8.8 Hz)

The recovered product VIII had characteristics which were the same as those of the oxidation products of the P–$SiPh_3$ derivative VI. Besides, the mass spectrum of VIII was studied. It showed the following fragments:



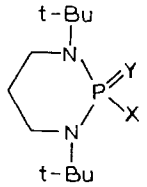
The nature of the fragmentation is proof of the silylphosphate structure of VIII. The mass spectrum of the oxidation product of the P–$SiPh_3$ derivative VI was identical to that of VIII.

To conclude the discussion of the oxidation of the P–Si compound VI, we note the following. It has been shown experimentally that oxidation of this compound with iodobenzene yields silylphosphate VIII, but under the same conditions iodobenzene cannot convert silylphosphite VII to silylphosphate VIII. On these grounds, it may be assumed that silylphosphite might not necessarily be a silylphosphate intermediate.

In this work we have oxidized compound II, too, with nitrogen oxide and iodobenzene. Using NMR spectroscopy to control the reaction for insufficient and

TABLE 3

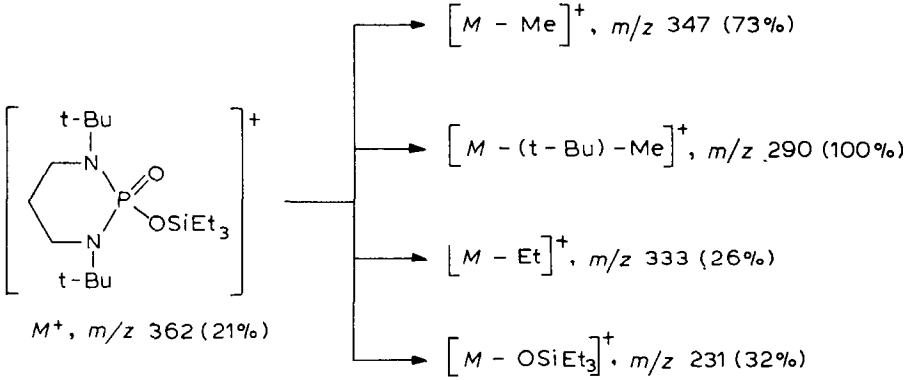
^{29}Si NMR CHEMICAL SHIFTS (δ, ppm) AND SPIN–SPIN COUPLING CONSTANTS FOR $^{29}Si-^{31}P$ (J, Hz) OF THE COMPOUNDS



Compound	X	Y	δ(Si)	^1J(P–Si)
II	$SiEt_3$	–	−0.24	15.9
IX	$OSiEt_3$	O	+18.9	9.8
VI	$SiPh_3$	–	−23.7	28.6
VII	$OSiPh_3$	–	−19.2	0
VIII	$OSiPh_3$	O	−16.1	8.8

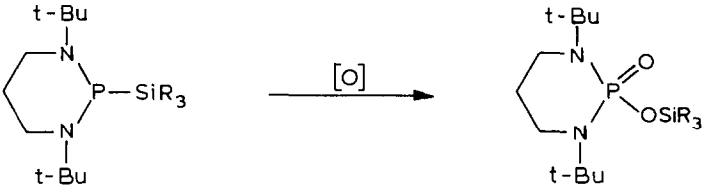
excessive oxidizer contents, we failed, however, to detect the formation, during the reaction, of any compound with a three-coordinate phosphorus atom. The product was invariably a compound which had a ^{31}P NMR chemical shift at 3.4 ppm. The variation of the ^{29}Si nucleus shielding during oxidation of P–$SiEt_3$-II was similar to that of P–$SiPh_3$-VI (Table 3). Transition from P^{III} to P^{V} was accompanied with deshielding of the silicon atom, but the lower field shift was more pronounced in the case of P–$SiEt_3$.

The mass spectrum of the oxidation product of II supports the phosphate structure of IX:



Elemental analysis and the ^1H and ^{13}C NMR spectra also support this structure of IX.

It can therefore be concluded that neither II nor VI can be mono-oxidized. The oxidation is non-specific and yields products of phosphate structure.



(II, R = Et ; VI, R = Ph)

(IX, R = Et ; VIII, R = Ph)

One should note the instability of organoelemental phosphates VIII and IX: they are easily hydrolysed and undergo disproportionation during storage.

Experimental

The P-organoelemental derivatives of phosphorous acid were synthesized in evacuated sealed cells by the procedure described in ref. 10; other compounds containing P^{III} were synthesized in the atmosphere of a dry and deoxygenated inert gas (argon).

The resulting compounds were identified by mass spectrometry (Varian Mat 212 spectrometer) and ^{31}P (Varian FT-80A spectrometer), ^{29}Si (Jeol FX-90Q spectrometer), ^{13}C and ^1H NMR spectroscopy (Bruker WM-250 spectrometer). The ^{31}P

chemical shifts are given in relation to 85% H_3PO_4 as an external standard; the ^{13}C, ^{1}H and ^{29}Si shifts are relative to tetramethylsilane. Sample concentrations were 10 to 15% for ^{1}H NMR spectroscopy and 40 to 50% for the ^{31}P, ^{13}C and ^{29}Si NMR spectra.

The compounds were chromatographed on Silufol UV-254 plates in a benzene/dioxane (3/1) mixture. The chromatograms were developed with iodine vapour.

The procedure of ref. 5 was followed for the synthesis of the starting 2-chloro-1,3-di-t-butyl-1,3,2-diazaphosphorinane (I). 2-H-1,3-Di-t-butyl-1,3,2-diazaphosphorinane has been described in ref. 6; triethylsilyl- and triethylgermyl-lithium were obtained by the method of ref. 3.

2-Triethylsilyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane (II)

To a solution of 5.0 g (0.02 mol) of the chlorophosphite I in 5 ml of pentane frozen at the temperature of liquid nitrogen was added 2.7 g (0.022 mol) of triethylsilyllithium in 30 ml of pentane in small portions. Then over a period of 15 min the reaction mixture was heated to room temperature and agitated with a magnetic mixer for 0.5 h until the reaction was completed. The precipitated LiCl was filtered off and the solvent was removed under vacuum. Fractionation gave 4.9 g (74%) of compound II, b.p. 108–110°C (0.05 torr), n_D^{20} 1.5028, d_4^{20} 1.0054, MR_D 96.99, calcd. 96.71, R_f 0.9. ^{31}P NMR: δ(P) 47.9 ppm; ^{29}Si NMR: δ(Si) −0.24 ppm, d.; ^{1}J(P–Si) 15.9 Hz. Mass spectrum m/z 330 (M^+). Found: C, 61.59; H, 11.69; P, 9.32; N, 8.38. $C_{17}H_{39}N_2PSi$ calcd.: C, 61.63; H, 11.78; P, 9.39; N, 8.40%.

2-Triethylgermyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane (III)

To a solution of 2.9 g (0.017 mol) of triethylgermyllithium in 30 ml of pentane was added 4.0 g (0.016 mol) of chlorophosphite I in small portions under stirring so that the reaction mixture temperature did not exceed 36°C. After the mixture had been cooled to room temperature, it was stirred for another 0.5 h. The LiCl residue was then filtered off, the solvent evaporated, and the residue distilled under vacuum. The yield of compound III was 4.2 g (71%), b.p. 113–114°C (5×10^{-2} mmHg), n_D^{20} 1.5182, d_4^{20} 1.1645, MR_D 97.61, calcd. 97.31, R_f 0.25. ^{31}P NMR: δ(P) 62.3 ppm. Mass spectrum: m/z 375 (M^+). Found: C, 54.58; H, 10.44; P, 8.21; N, 7.52. $C_{17}GeH_{39}N_2P$ calcd.: C, 54.40; H, 10.40; P, 8.27; N, 7.41%.

N,N′,N″,N‴-Tetra-t-butyl-N,N′,N″,N‴-di-1,3-propylenetetramide of hypodiphosphorous acid (IV)

To a mixture of 5.9 g (0.027 mol) of 2-H-1,3-di-t-butyl-1,3,2-diazaphosphorinane and 2.8 g (0.027 mol) of triethylamide in 10 ml of absolute benzene was added in drops under stirring 6.8 g (0.027 mol) of the chlorophosphite I in 9 ml of absolute benzene. To complete the reaction the mixture was left for several days at room temperature, the triethylamine chlorohydrate residue was filtered off, the solvent was run off, and the residue was recrystallized twice from benzene. The yield of compound IV was 3.5 g (30%), m.p. 178–180°C, R_f 0. Mass spectrum: m/z 430 (M^+). ^{31}P NMR: δ(P) 53.3 ppm. Found: C, 61.56; H, 11.04; P, 14.89. $C_{22}H_{48}N_4P_2$ calcd.: C, 61.39; H, 11.16; P, 14.42%.

Reaction of 2-chloro-1,3-di-t-butyl-1,3,2-diazaphosphorinane (I) with bis(triethylgermyl)mercury

To a solution of 1.8 g (0.007 mol) of chlorophosphite I in 8 ml of absolute

benzene at −30°C was added 3.6 g (0.007 mol) of bis(triethylgermyl)mercury in small portions. Then the reaction mixture was heated to room temperature, exposed for 3 h to UV light, and kept for 2 days at room temperature. The precipitated metallic mercury was removed, the solvent was evaporated, and the crystalline residue was washed three times with hexane. The product was 0.8 g (55%) of the hypodiphosphorous acid amide (IV), m.p. 178–180°C. Mass spectrum: m/z 430 (M^+). ^{31}P NMR: δ(P) 53.7 ppm.

Reaction of 2-chloro-1,3-di-t-butyl-1,3,2-diazaphosphorinane (I) with lithium

To 0.4 g (0.06 mol) of finely dispersed metallic lithium was added, at −30°C and under stirring, a solution of 3.8 g (0.015 mol) of the chlorophosphite I in 30 ml of tetrahydrofuran with a catalytically active amount of naphthalene. The mixture was then heated to room temperature and agitated at this temperature for 2 days. The precipitated LiCl was filtered off, the solvent evaporated, and the crystalline residue recrystallized from benzene. The yield of IV was 1.0 g (31%), m.p. 178–180°C. ^{31}P NMR: δ(P) 53.4 ppm.

Reaction of 2-chloro-1,3-di-t-butyl-1,3,2-diazaphosphorinane (I) with 2-triethylsilyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane (II)

To 4.5 g (0.013 mol) of 2-triethylsilyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane (II) was added in small portions 3.3 g (0.013 mol) of chlorophosphite I. The mixture was then heated to 70°C and stirred for 15 min until completely homogenized. It was kept for another hour at 120°C, the solvent was evaporated and the residue recrystallized from benzene. The yield of IV was 0.13 g (25%), m.p. 167–169°C. ^{31}P NMR: δ(P) 52.4 ppm. R_f 0.

2-Triphenylsiloxy-1,3-di-t-butyl-1,3,2-diazaphosphorinane (VII)

To a mixture of 5.0 g (0.018 mol) of triphenylsilanol and 1.8 g (0.018 mol) of triethylamine in 16 ml of absolute benzene was added dropwise at −5 to 0°C and under stirring 4.5 g (0.018 mol) of chlorophosphite (I) in 9 ml of absolute benzene. Then the reaction mixture was agitated for 3 h at room temperature, the triethylamine chlorohydrate residue was filtered off, the solvent run off and the residue distilled under vacuum. The yield of VII was 6.1 g (69%), b.p. (bath) 210–220°C (10^{-4} mmHg), n_D^{20} 1.5571. During storage the compound crystallizes, m.p. 103–106°C, R_f 0.35. ^{31}P NMR: δ(P) 106.1 ppm; ^{29}Si NMR: δ(Si) −19.2 ppm. Found: C, 70.95; H, 7.58; P, 6.30. $C_{29}H_{39}N_2OPSi$ calcd.: C, 71.02; H, 7.95; P, 6.33%.

2-Oxo-2-triphenylsiloxy-1,3-di-t-butyl-1,3,2-diazaphosphorinane (VIII)

Nitrogen oxide was passed through a solution of 6.1 g (0.013 mol) of 2-triphenylsiloxy-1,3-di-t-butyl-1,3,2-diazaphosphorinane (VII) in 10 ml of absolute benzene. After 15 h of this process, the signal at δ(P) 106.1 ppm corresponding to the starting siloxyamide (VII) disappeared and a new signal appeared at δ(P) 3.6 ppm in the ^{31}P NMR spectrum. Then the solvent was removed, the oily residue treated with absolute hexane, the resin powder filtered off and hexane evaporated from the filtrate. The resulting crystalline residue was recrystallized twice from hexane. The yield of VIII was 2.0 g (32%), m.p. 85–87°C, R_f 0. ^{31}P NMR: δ(P) 3.6 ppm; ^{29}Si NMR: δ(Si) −16.1 ppm, d.; ^1J(P–Si) 8.8 Hz. Mass spectrum: m/z 506 (M^+).

Found: C, 68.65; H, 7.67; P, 6.10. $C_{29}H_{39}N_2O_2PSi$ calcd.: C, 68.77; H, 7.71; P, 6.13%.

Oxidation of 2-triphenyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane (VI)

(a) To a solution of 3.0 g (0.006 mol) of 2-triphenylsilyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane in 9 ml of absolute benzene was added, under stirring, 1.4 g (0.006) of iodobenzene; the mixture was kept at room temperature for 1 day. The ^{31}P NMR spectrum of the mixture contained a signal at δ(P) 48.8 ppm, typical of the starting P–Si compound (VI), as well as a new signal at δ(P) 3.0 ppm corresponding to the oxidized product in a 1/1 ratio. Then another 1.4 g (0.006 mol) of iodobenzene was added to the mixture and the mixture was left for another day at room temperature. The iodobenzene residue was filtered off, the solvent evaporated, and the residue washed with absolute hexane and distilled in vacuo. The yield of 2-oxo-2-triphenylsiloxy-1,3-di-t-butyl-1,3,2-diazaphosphorinane (VIII) was 0.6 g (20%), b.p. 220–230°C (10^{-4} mmHg), R_f 0; ^{31}P NMR: δ(P) 3.0 ppm; ^{29}Si NMR: δ(Si) −16.5 ppm, d.; ^1J(P–Si) 9.3 ppm. Mass spectrum: m/z 506 (M^+).

(b) Nitrogen oxide was passed through a solution of 3.0 g (0.006 mol) of 2-triphenylsilyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane in 6 ml of absolute benzene for 10 h. The solvent was then run off and the residue washed with absolute hexane. After evaporation of the hexane extract, the residue was distilled in vacuum. The yield of VIII was 1.0 g (32%), b.p. 220–230°C (10^{-4} mmHg), R_f 0. ^{31}P NMR: δ(P) 3.1 ppm.

Oxidation of 2-triethylsilyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane (II)

(a) Using the procedure described above, from 0.8 g (0.0024 mol) of 2-triethylsilyl-1,3-di-t-butyl-1,3,2-diazaphosphorinane (II) in 3 ml of absolute benzene and 1.0 g (0.0048 mol) of iodobenzene we obtained 0.25 g (29%) of 2-oxo-2-triethylsiloxy-1,3-di-t-butyl-1,3,2-diazaphosphorinane (IX), b.p. 108–110°C (10^{-4} mmHg), n_D^{20} 1.4718, R_f 0.2. ^{31}P NMR: δ(P) 3.4 ppm; ^{29}Si NMR: δ(Si) 18.9 ppm, d.; ^1J(P–Si) 1.8 Hz. Mass spectrum: m/z 362 (M^+). Found: C, 56.42; H, 10.83; P, 8.50. $C_{17}H_{39}N_2O_2PSi$ calcd.: C, 56.36; H, 10.77; P, 8.56%.

(b) As described above, by passing nitrogen oxide for 4 h through a solution of 1.7 g (0.005 mol) of the P–Si compound II in 4 ml of absolute benzene we obtained 0.5 g (28%) of the corresponding triethylsilyl phosphate (IX), b.p. 108–110°C (10^{-4} mmHg), n_D^{20} 1.4710, R_f 0.25. ^{31}P NMR: δ(P) 3.5 ppm.

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