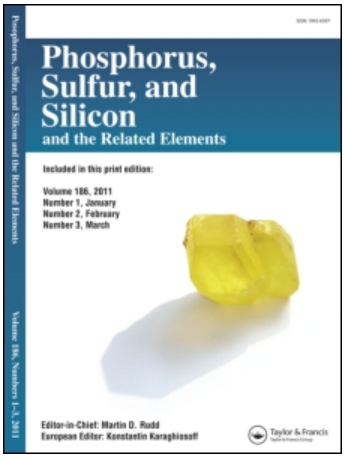

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THE FORMATION OF P(III) PRODUCTS FROM PHOSPHINAMIDES WITH SILICON HYDRIDES

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THE FORMATION OF P(III) PRODUCTS FROM PHOSPHINAMIDES WITH SILICON HYDRIDES

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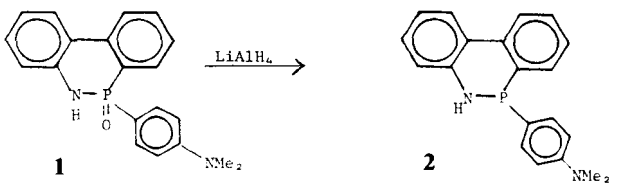
Two *N,N*-diethyl derivatives of phosphinamides in the 3-phospholene series were used as models to develop techniques for reduction to P(III) derivatives. The products from the reduction with $HSiCl_3$ in the presence of pyridine depended on the molar ratio of the participants. A 1 : 1 : 1 amide–$HSiCl_3$–pyridine mixture after 2 h in refluxing benzene provided the phosphinous chlorides in preparatively useful (55–65%) yield. A 1 : 1.5 : 1.5 mixture led to coupling at phosphorus to give the diphosphine, also in good yield (60–65%). The diphosphines also resulted from refluxing a 1 : 1 mixture of the amide with phenylsilane. However, heating a 2 : 1 amide–silane mixture at 100° gave only the product of deoxygenation (65%). A 1-benzylaminophosphetane oxide was also reduced successfully. The conditions with $HSiCl_3$ and $C_6H_5SiH_3$ were applied to a noncyclic phosphinamide $(C_6H_5)_2PO(NEt_2)$; reaction rates were considerably slower than for the cyclic amides, but similar P(III) products were formed. ^{13}C and ^{31}P NMR spectra are reported for all new compounds.

The deoxygenation of phosphine oxides with silanes (especially $HSiCl_3$, $C_6H_5SiH_3$, and Si_2Cl_6) is a well established, reliable method for the synthesis of tertiary phosphines.[1] The deoxygenation of phosphinic acids and phosphinic acid derivatives with these reagents is a more complicated process, since the phosphorus atom contains other substituents that are sensitive to displacement. The only successful straightforward deoxygenation process with such phosphoryl derivatives is that recorded for phosphinic chlorides in their reaction with Si_2Cl_6, which provides phosphinous chlorides.[2] With silicon hydrides, phosphinic chlorides are completely reduced to secondary phosphines, a reaction also occurring with phosphinic acids and their esters.[3] Similarly, phosphonates are completely reduced to primary phosphines.[3] Such total reduction is generally experienced when $LiAlH_4$ is used in reaction with these phosphoryl derivatives,[4] although an exception has been recorded in the case of **1**, which gave the P(III) derivative **2**.[4a]



1 **2**

In another case,[5] the noncyclic phosphinamide $(CH_3)(C_6H_5)PONRC_6H_5$ (R = H or CH_3) underwent only reductive cleavage of the P—N bond to give the secondary phosphine oxide.

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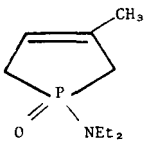
We are examining the possibility of moderating the reducing action of trichlorosilane and phenylsilane towards phosphinic acid derivatives, in hopes of effecting only their deoxygenation to the P(III) derivative. In this paper, we report some results obtained with phosphinamides. Most of our work has made use of amides (**3** and **4**) derived from the readily obtained cyclic phosphinic acids resulting from hydrolysis of the McCormack diene–PX_3 cycloadducts.[6a] Diphenylphosphinic derivative **5** was used as a noncyclic model compound.



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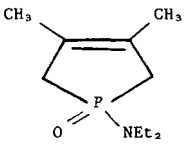

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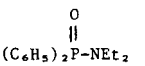

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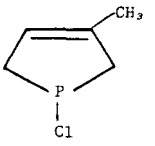
Reduction with trichlorosilane. All reductions were performed in the presence of triethylamine or pyridine. Such mixtures are widely employed in the deoxygenation of phosphine oxides, but have not previously been examined for their effect on reduction of acid derivatives. These bases have definite influences on the mechanism of the action of $HSiCl_3$.[2] However, in no case with the phosphinamides did we find simple deoxygenation as the sole result; the P—N bond was always cleaved, and depending on the molar ratio of the reactants, the phosphorus atom could be found incorporated in three distinct P(III) functional groups.

When an amide–$HSiCl_3$–pyridine mixture in molar amounts of 1 : 1 : 1 or 1 : 1 : 3 was refluxed in benzene for 2 h, the only phosphorus product was found to be the phosphinous chloride. From amide **3**, chloride **6** was obtained in 60% yield after distillation, while amide **4** provided chloride **7** (53%).



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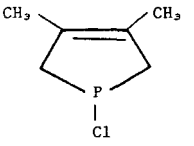

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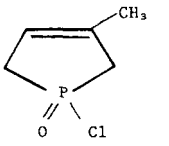

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The identity of these new products was confirmed by their characteristic downfield ^{31}P NMR shifts (δ +125.1 and +111.6) and by their ^{13}C NMR spectra (Table I). It was also found that phosphinic chlorides could be substituted for phosphinamides in the same process and gave comparable results; thus phosphinic chloride **8** was reduced to **6** in 66% yield (distilled). This is a potentially valuable observation, since the only other reagent for effecting this conversion is Si_2Cl_6, which at this time is not available commercially and is difficult to prepare.

The high yield and purity of the products make the reduction process of phosphinamides of preparative value. The exact use of the specified molar ratio is critical to the success of the process, however. It is also important that the phosphinamide be of high purity; **3** and **4** were distilled just before the reduction.

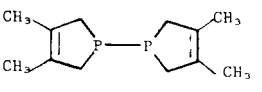
TABLE I

NMR spectroscopic data[a]

Compound	$\delta^{31}P$[b]	$\delta^{31}C$ (J_{PC}, Hz)						
		C-2	C-3	C-4	C-5	$C—CH_3$	$N—CH_2$	$CH_2\underline{C}H_3$
3	+63.2[c]	35.0(83.0)	137.1(15.6)	121.7(9.6)	32.6(80.1)	20.6(11.7)	38.1(3.9)	14.3(2.0)
3 · $HSiCl_3$	+72.7	32.2(91.8)	136.0(17.6)	119.6(11.0)	29.5(89.0)	19.8(13.2)	40.6(2.0)	13.9(4.4)
4	+53.5	37.4(82.0)	128.9(11.0)	128.9(11.0)	37.4(82.0)	16.3(13.9)	38.4(3.0)	14.4(2.9)
6	+125.1	45.4(29.3)	138.5(4.3)	122.6(4.9)	41.6(28.8)	17.5(~ 0)		
7	+111.6	46.6(29.5)	128.3(4.4)	128.3(4.4)	46.6(29.5)	15.6(~ 0)		
9	−42.6	37.2(2.0)	130.7(2.0)	130.7(2.0)	37.2(2.0)	16.5(1.0)		
10	+48.6	41.8(28.5)	128.6(4.4)	128.6(4.4)	41.8(28.5)	16.2(7.7)		
11[d]	−26.18, −26.31	35.3(2.6)	140.1(2.4)	125.0(1.8)	31.2(2.4)	18.5(~ 0)		
12[d]	+57.9	40.0(29.3)	137.7(2.4)	121.4(3.7)	37.1(28.0)	19.3(6.1)		
18	+61.6	39.1(17.6)	139.0(2.0)	124.1(2.9)	35.4(16.6)	18.9(2.0)	43.4(12.7)	15.1(3.9)
19	+88.5	42.8(66.5)	137.0(12.8)	121.1(7.3)	40.0(63.5)	19.8(12.2)	39.4(3.0)	14.0(3.0)
20	+47.0	40.6(14.3)[e]	129.2(2.2)	129.2(2.2)	40.6(14.3)	15.8(~ 0)	42.6(12.1)[e]	14.5(4.4)
21	+79.6	44.3(64.8)	127.5(2.2)	127.5(2.2)	44.3(64.8)	15.5(14.3)	38.8(3.3)	13.5(3.3)
22	+51.0[f]	38.4(14.3)	129.1(3.3)	129.1(3.3)	38.4(14.3)	15.6(~ 0)	39.9(12.0)	
23	+84.1	42.8(67.0)	127.2(4.4)	127.2(4.4)	42.8(67.0)	15.4(14.3)	36.3(~ 0)	

[a] Recorded for $CDCl_3$ solutions.
[b] Positive values are downfield from 85% H_3PO_4 as reference.
[c] + 59.8 in C_6D_6.
[d] Diastereomeric mixture.
[e] Could be reversed.
[f] + 52.6 was reported by P. J. Hammond, G. Scott and C. D. Hall, *J. Chem. Soc. Perkin Trans. II*, 205 (1982).

A totally different process occurred when the amide to $HSiCl_3$ molar ratio was changed to 1 : 1.5, with a molar amount of pyridine ranging from 1.5 to 4.5. Following a period of 2 h in refluxing benzene, the reaction mixture from amide **4** was found to contain a single phosphorus product by ^{31}P NMR spectroscopy (δ −42.6). Distillation of the mixture provided the product as a white solid (mp 67–69°C) in 50% yield. The ^{31}P shift is in the region of a tertiary phosphine or a diphosphine (**9**); the latter structure was suggested from the broadening of the signals for C-2,5. These carbons would give second-order spectra, an AA'X "triplet" whose width is equal to $|^1J_{P_AC} + {}^2J_{P_{A'}C}|$ and denoted N_{PC}. For tetramethyldiphosphine, N_{PC} is 5.5 Hz,[7] but the value is sensitive in other compounds to the conformation about the P—P bond. For **9**, N_{PC} appears to be no greater than about 2 Hz. The diphosphine structure was confirmed by forming the disulfide **10**, also giving the expected NMR spectra as well as elemental analysis.



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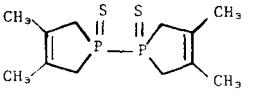

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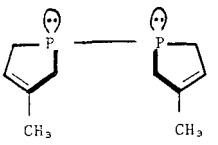
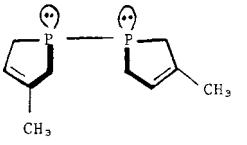
The same result was obtained with phosphinamide **3**, except that the product (63% yield after distillation) consisted of a nearly 1 : 1 mixture of two diastereoisomers (**11a** and **11b**; δ ^{31}P −26.18 and −26.31). The ^{13}C NMR spectrum was not useful for revealing the presence of the isomers, and after conversion to the disulfide (**12**), which gave the correct analysis, the ^{31}P NMR measurement was not able to detect the diastereoisomers.

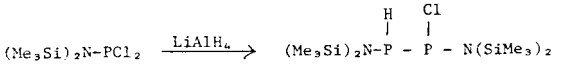


11a (meso)

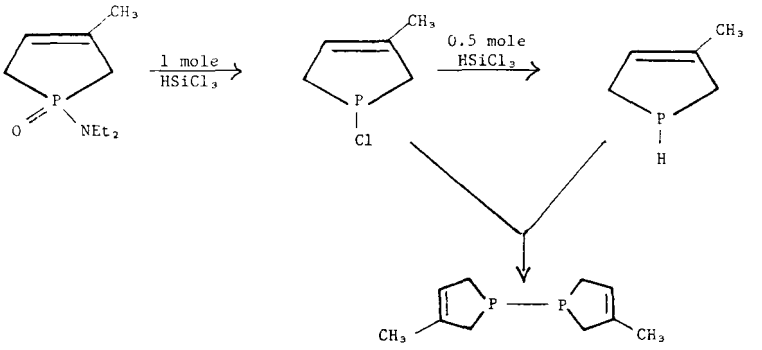


11b (dl)

When the reductions were performed with more than 1.5 to 1 molar ratio of $HSiCl_3$ to the amide (e.g., 1 : 3 : 6), the secondary phosphine could be detected in the reaction mixture by its characteristic high-field ^{31}P NMR signal (e.g., from **3**, δ −68.5, $^1J_{PH}$ = 192.9 Hz). The excess $HSiCl_3$ apparently acts rapidly on the initially formed phosphinous chloride; with a 50% excess, only half of the chloride is reduced to the phosphine, which is available for rapid interaction with the remaining chloride to form the diphosphine (Scheme 1). P—P bond formation has also been observed[8] in a somewhat similar partial reduction of an aminodichlorophosphine.

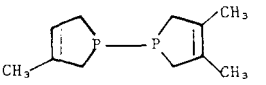


As a further indication of the origin of the diphosphines, we found that $HSiCl_3$–pyridine reduction of a mixture of amides **3** and **4** gave not only the



SCHEME 1

diphosphine from each (**9** and **11**) but also a new diphosphine (**13**) comprised of both phospholene residues.



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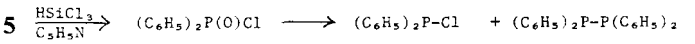
The product was detected by ^{31}P NMR spectroscopy; the two non-equivalent ^{31}P nuclei (δ −25.9 and −43.0) showed the expected[9] coupling ($^1J_{PP}$ = 183 Hz) for a diphosphine. The product was not isolated.

It is necessary to inquire if the reactions discussed above are limited to derivatives in the phospholene series, or if they may have broader occurrence among phosphinamides. We therefore applied the same conditions to the diphenylphosphinamide derivative **5** and followed the course of the reaction with ^{31}P NMR measurements. Results are provided in Table II. It is obvious that the reduction follows the same pathway, but the rate is considerably slower. About one-third of the phosphinamide is unchanged after 20 h. There is an initial buildup, then decay, of the phosphinic chloride as it is reduced to the phosphinous chloride (**14**). The diphosphine (**15**) is the major component at the end of the experiment.



14 **15**

We have not yet further examined this process but the preliminary results suggest that phosphinamides in general may be reduced by our conditions. It remains to be seen if there is any synthetic utility in these reactions beyond their applicability to phospholene derivatives.

The presence of a tertiary amine in the reaction mixture is critical in the $HSiCl_3$ reduction of the phosphinamides. Pyridine was used in most of our work; triethylamine has been employed also in the synthesis of the diphosphines, but gives somewhat lower yields and work-up is more difficult. Refluxing the phosphinamide

TABLE II

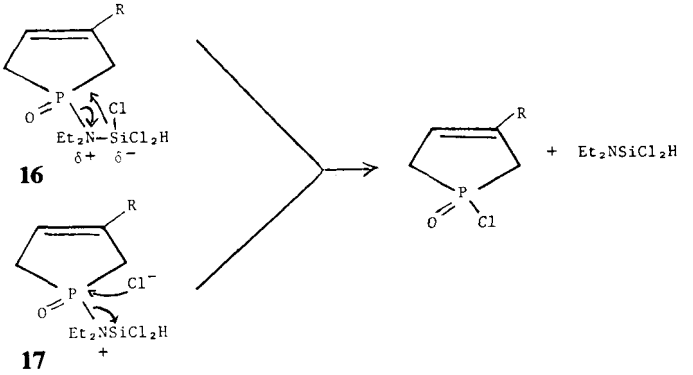
$HSiCl_3$ reduction of **5**

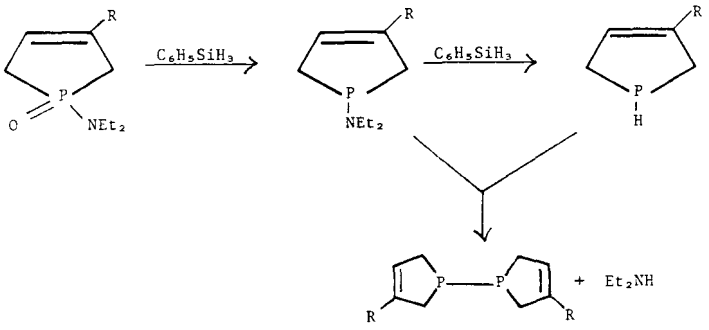
Compound	$\delta^{31}P$	$\delta^{31}P$ (lit.)[a]	Relative Intensity, %[b] 2 h	10 h	20 h
$Ph_2P(O)NEt_2$	+26.9		50	40	30
$Ph_2P(O)Cl$	+40.7	+42.7	17	10	0
Ph_2PCl	+81.4	+80.5	25	20	20
Ph_2P-PPh_2	−15.6	−15.2	8	20	50

[a] Taken from the tables of M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. Van Wazer, *Topics Phosph. Chem.*, **5**, 285 (1967).

[b] The ratio of the integrals of the ^{31}P NMR signals. The values are approximate only, but are useful in showing trends.

with $HSiCl_3$ in benzene in the absence of any amine gives complex mixtures that are of no value. It is probable that the first attack of $HSiCl_3$ on the amide is the cleavage of the P—N bond with formation of the phosphinic chloride. We have noted above that the phosphinic chloride itself can be converted to the phosphinous chloride under conditions identical to those used for the phosphinamide. In the pyridine-assisted process, the P—N bond is probably weakened by an initial interaction with the $HSiCl_3$–pyridine complex. The site of attack may be either the oxygen or the nitrogen atom, but only at the latter will P—N cleavage be facilitated. Some NMR evidence (Table I) suggests that there is indeed a combination of the amide with $HSiCl_3$. When mixed at −20°C in $CDCl_3$, there were definite changes in the ^{31}P shift (downfield by 9.4 ppm) and the $^1J_{CP}$ values (increased by about 9 Hz). That the P—N bond is intact at this point is revealed by the persistence of ^{31}P coupling to the carbons of the N—C_2H_5 group. Since even the structure of the complex formed from $HSiCl_3$ with pyridine is not completely understood,[10] we can only speculate on the bonding in the phosphinamide complex. It is, however, helpful to consider a structure such as **16** or **17** since these make it easy to visualize the P—N cleavage process as resulting from attack of chlorine on P with displacement of a neutral leaving group. The displaced silane would have to function as the hydride donor to accomplish the deoxygenation, since all trichlorosilane would have been converted to this species.



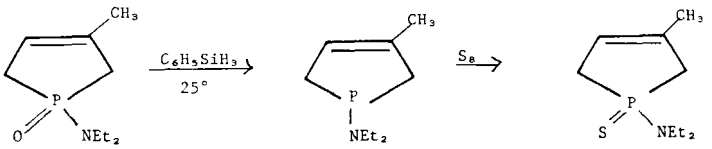


SCHEME 2

The increased positivity on N in either **16** or **17** could account for both the chemical shift and coupling effects observed.

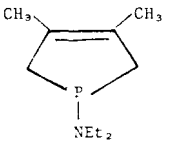
Reduction with Phenylsilane. Tertiary phosphine oxides are reduced to phosphines on refluxing in $C_6H_5SiH_3$ for a few hours.[11] These conditions were applied to phosphinamides **3** and **4**, and in each case (after 3 h) the corresponding *diphosphine* was obtained in good yield on distillation of the mixture (**9**, 67% from **4**; **11**, 69% from **3**). This reaction also is preparatively useful for the diphosphines, which were formed as the sole products. To account for their formation, it may be assumed that the first step is the deoxygenation to the aminophosphine. Some of this material is reduced further to the secondary phosphine, and this combines with the remaining aminophosphine by eliminating diethylamine (Scheme 2).

Horner[12] has recently published a synthesis of tetraphenyldiphosphine by a similar process, involving the reaction of an aminophosphine with diphenylphosphine. If our proposed mechanism is correct, it implies that phenylsilane is indeed capable of reducing phosphinamides to P(III) form, and that if the second reaction of P—N bond cleavage can be avoided then a useful synthesis might be achieved. We have indeed demonstrated this process. We first treated phosphinamide **3** with only one molar equivalent of $C_6H_5SiH_3$ in benzene at room temperature; reduction was very slow but provided a 60% yield (distilled) of the desired aminophosphine **18** after 3 weeks.



3 **18** **19**

A better procedure is to react a 2 : 1 molar mixture of the phosphinamide and $C_6H_5SiH_3$ at 100° for 3 h. Yields of three different 1-dialkylaminophospholenes (**18**, **20**, **22**) prepared by this procedure were around 65%. The products were isolated by Kugelrohr distillation and converted to the thiophosphinamides for analysis. Spectral data for the phosphines and their sulfides are recorded in Table I.



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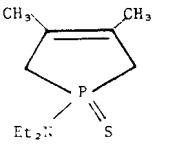

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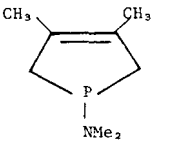

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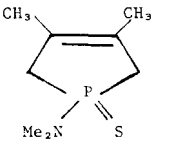
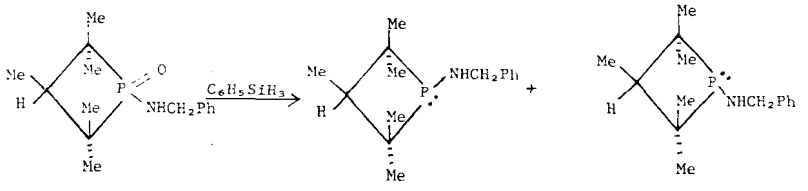


23

Two other types of phosphinamides, the noncyclic diphenylphosphinamide **5** and the phosphetane derivative **24**, were also reacted with $C_6H_5SiH_3$ at 100°. In both cases an excess of silane was used and caused relatively little bond cleavage. The reaction with **5** did give (*N,N*-diethyl)diphenylphosphine (**25**) but was quite slow (about 50% conversion of **5**). However, phosphinamide **24**, of known stereochemistry,[13] reacted completely in the same period, giving a 2 : 1 mixture of the diastereomeric aminophosphetane derivatives **26** (δ ^{31}P +78.0) and **27** (+97.5).

These compounds have been reported previously[13a] and their stereochemistry assigned by ^1H NMR. We have employed ^{13}C NMR also for proving their structures, using concepts described in detail elsewhere.[6b] The 2-CH_3 *cis* to 3-CH_3 can be readily recognized by the upfield shifting of steric compression; this 2-CH_3 can be assigned a *cis* or *trans* relation to the lone pair by the magnitude of $^2J_{PC}$, which is large only when the lone pair is close to the coupled carbon. For **26**, the upfield 2-CH_3 (δ 18.2) had the small $^2J_{PC}$ (4.4 Hz) while the downfield 2-CH_3 (δ 30.4) had $^2J_{PC}$ = 27.5. Also, it is a general property as a result of a conformational effect among phosphines of this series that the 3-CH_3 has a large coupling to ^{31}P when it is *trans*-oriented to the P-substituent, and small when *cis*. For *trans* isomer **26**, 3-CH_3 had $^3J_{PC}$ = 11.0 Hz; **27** had $^3J_{PC}$ = 2.2 Hz. These self-consistent results leave no doubt that the structures are correctly assigned, which establishes that the major product is that of inversion of configuration. A mixture of isomers has also been obtained in the phenylsilane reduction of some 1-arylphosphetane oxides[14] having the same pentamethyl substitution, although retention is a more common result for both reductions and substitutions among phosphetane oxides.[15]



24 **26** **27**

These experiments represent the first successful deoxygenations of phosphinamides with phenylsilane, and show that P—N bond cleavage can be avoided by use of the proper reactant ratio. In this respect, phenylsilane differs greatly from trichlorosilane.

EXPERIMENTAL[16]

1-(N,N-Diethylamino)-3-methyl-3-phospholene-1-oxide. To a solution of 7.3 g (0.055 mol) of 1-hydroxy-3-methyl-3-phospholene-1-oxide in 100 ml of $CHCl_3$ was added 6.55 g (0.055 mol) of $SOCl_2$. The mixture was stirred overnight at room temperature, and then solvent was removed under reduced pressure. The

phosphinic chloride (7.0 g, 85%) was distilled at 84–85°C (0.7 mm), and dissolved in 50 ml of benzene for addition to a solution of diethylamine (10.0 g, 0.15 mol) in 150 ml of benzene. The addition was made dropwise while the temperature was controlled with an ice bath. The mixture was then stirred for 2 h at room temperature, and then filtered to remove precipitated amine salt. Solvent was removed under reduced pressure, and the phosphinamide (**3**, 7.9 g, 76%) was distilled at 118°C (1.2 mm). The compound is hygroscopic and rather readily hydrolyzed. Spectral data are provided in Table I. Anal. Calcd for $C_9H_{18}NOP$: P, 16.38. Found: P, 16.21.

1-(N,N-Diethylamino)-3,4-dimethyl-3-phospholene-1-oxide (**4**). The same procedure as used for **3** provided **4** (hygroscopic) in 72% yield, bp 132–135°C (1.2 mm), mp 56–57°C (from pentane). Spectral data are provided in Table I. Anal. Calcd for $C_{10}H_{20}NOP$: C, 59.70; H, 9.95; P, 15.42. Found: C, 59.53; H, 10.04; P, 15.56.

N,N-Diethyldiphenylphosphinamide (**5**). The reaction of diphenylphosphinic chloride with diethylamine gave **5**, m.p. 141–142° (lit.[17] m.p. 141–142°).

Conversion of Phosphinamide **3** *and Phosphinic Chloride* **8** *to 1-Chloro-3-methyl-3-phospholene* (**6**). A mixture of 7.8 g (0.040 mol) of phosphinamide **3**, 5.96 g (0.044 mol) of $HSiCl_3$ and 9.48 g (0.132 mol) of pyridine in 100 ml of benzene was refluxed for 2 h and then allowed to stand overnight. The precipitated amine salt was filtered off; the filtrate was distilled at atmospheric pressure to remove solvent and then, with a 20-cm Vigreaux column, at reduced pressure to obtain phosphinous chloride **6**. The yield after a re-distillation (78–80°C, 22 mm) was 3.24 g (60%). Spectral data are given in Table I.

The same result was obtained when a sample of phosphinic chloride **8** (2.98 g, 0.022 mol) was substituted for the phosphinamide; the yield of **6** was 1.83 g (66%) after two distillations.

1-Chloro-3,4-dimethyl-3-phospholene (**7**) *from Phosphinamide* **4**. Using the same procedure as described for $HSiCl_3$–pyridine reduction of **3**, phosphinamide **4** (3.6 g, 0.018 mol) gave 1.4 g (53%) of phosphinous chloride **7**, distilled by the Kugelrohr method at 95°C (15 mm). Spectral data are given in Table II.

Reaction of N,N-Diethyldiphenylphosphinamide (**5**) *with $HSiCl_3$–Pyridine*. The course of a reaction of 1.36 g (0.005 mol) of **5**, 1.08 g (0.008 mol) of $HSiCl_3$, and 0.63 g (0.008 mol) of pyridine in 20 ml of benzene was monitored by withdrawing samples for periodic examination by ^{31}P NMR spectroscopy. The identity of all species formed was easily determined by this technique. Peak intensities were taken as a rough measure of relative amounts, but without refinement of spectral conditions do not provide a quantitative analysis. Results are summarized in Table II.

Conversion of Phosphinamide **3** *to Diphosphine* **11**. *With $HSiCl_3$*. A mixture of 2.8 g (0.015 mol) of phosphinamide **3**, 3.25 g (0.024 mol) of $HSiCl_3$, and 1.9 g (0.024 mol) of pyridine in 50 ml of benzene was refluxed for 2 h and allowed to stand overnight. The filtrate from removal of salt was distilled at atmospheric pressure to remove solvent and then at reduced pressure (72–73°C, 1.2 mm) to obtain the diastereomeric mixture (**11**) of the diphosphine (0.93 g, 63%) as a white solid, mp 67–69° (sealed tube). Spectral data are given in Table I. The disulfide was prepared in benzene by adding elemental sulfur (exothermic); the white solid (50% yield) was twice recrystallized from acetone, mp 186–200°C dec. Anal. Calcd for $C_{10}H_{16}P_2S_2$: C, 45.80; H, 6.11; P, 23.66. Found C, 45.87; H, 5.96; P, 23.65.

With $C_6H_5SiH_3$. A mixture of phosphinamide **3** (3.3 g, 0.0176 mol) and 2.1 g (0.0194 mol) of phenylsilane was refluxed for 3 h, and then distilled directly. The diphosphine (1.2 g, 69%) had the same bp and mp as that reported above.

Conversion of Phosphinamide **4** *to Diphosphine* **9**. The $HSiCl_3$ reduction was performed as described for **3** and gave diphosphine **9** (63%) with bp 101–103°C (0.3 mm), mp 83–85°C; spectral data, Table I; disulfide, mp 160–163°C. Anal. Calcd for $C_{12}H_{20}P_2S_2$: C, 49.65; H, 6.90; P, 21.38. Found: C, 49.54; H, 6.77; P, 21.42.

Using $C_6H_5SiH_3$ as for **3** gave the diphosphine in 67% yield.

Conversion of Phosphinamide **3** *to 1-(N,N-diethylamino)-3-methyl-3-phospholene* (**18**). A solution of 4.6 g (0.0246 mol) of **3** and 2.66 g (0.00246 mol) of $C_6H_5SiH_3$ in 5 ml of benzene was allowed to stand at room temperature for 3 weeks. Benzene was then removed under reduced pressure and the residue Kugelrohr-distilled at 110° (23 mm) to give 2.5 g (62%) of aminophosphine **18**, bp 55°C (0.6 mm). Spectral data are provided in Table I. The aminophosphine was converted to the 1-(*N,N*-diethylamino)-3-methyl-3-phospholene-1-sulfide **19** by overnight reaction of 0.50 g (0.0029 mol) in 25 ml of benzene with 0.10 g of sulfur in 10 ml of benzene. Solvent was removed *in vacuo* and the residue chromatographed on silica gel. Elution with benzene provided the sulfide **19** (0.40 g, 64%) as a colorless oil. Spectral data are given in Table I. Anal. Calcd for $C_9H_{18}NPS$: C, 53.20; H, 8.87; P, 15.27. Found: C, 53.14; H, 9.00; P, 15.12.

The aminophosphine was also formed by heating 0.02 mol of **3** and 0.01 mol of $C_6H_5SiH_3$ at 100° for 3 h; yield 65%.

1-(N,N-Diethylamino)-3,4-dimethyl-3-phospholene (**20**). Phosphinamide **4** (0.02 mol) was reacted with 0.01 mol of $C_6H_5SiH_3$ at 100° for 3 h, providing **20** in 69% yield after Kugelrohr distillation at 100° (21 mm). It was converted to the sulfide (**21**), a colorless oil that was purified by chromatography on silica gel. Anal. Calcd for $C_{10}H_{20}NPS$: C, 55.30; H, 9.22, P, 14.28. Found: C, 55.07; H, 9.17; P, 14.48. Spectral data for **20** and **21** are given in Table I.

1-(N,N-Dimethylamino)-3,4-dimethyl-3-phospholene (**22**). The same procedure as used for **20** when applied to 1-(*N,N*-dimethylamino)-3,4-dimethyl-3-phospholene-1-oxide[18] provided **22** in 63% yield, distilling at 115° (21 mm); the sulfide (**23**) was purified by chromatography on silica gel and was a colorless oil. Anal. Calcd for $C_8H_{16}NPS$: C, 50.79; H, 8.46; P, 16.40. Found: C, 51.04; H, 8.61; P, 16.25. Spectral data for **22** and **23** are given in Table I.

Reaction of 1-Benzylamino-2,2,3,4,4-pentamethylphosphetane-1-oxide (**24**) *with Phenylsilane.* A mixture of 2.64 g (0.010 mol) of phosphinamide **24**[19] and 3.24 g (0.03 mol) of phenylsilane was heated at 100° for 3 h. The solution was examined directly by NMR and found to consist of a 2 : 1 mixture of aminophosphine **26** [δ ^{31}P +78.0; δ ^{13}C 7.9 (J = 11.0 Hz, 3-CH_3), 18.2 (J = 4.4, 2-CH_3 *cis* to 3-CH_3), 30.4 (J = 27.5, 2-CH_3 *trans* to 3-CH_3), 33.2 (J = 7.7, C-2), 45.2 (J = 6.6, CH_2), 53.1 (J = 26.4, C-3)] and **27** [(δ ^{31}P +97.5; δ ^{13}C 9.9 (J = 2.2, 3-CH_3), 23.3 (J = 30.7, 2-CH_3 *cis* to 3-CH_3), 25.1 (J ~ 1, 2-CH_3 *trans* to 3-CH_3), 37.4 (J = 5.5, C-2), 45.9 (J = 24.1, CH_2), 50.9 (J = 3.3, C-3)]. The ^{31}P NMR signals amounted to 80% of the mixture; no **24** remained and minor products were not examined.

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