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Reactions of the Phosphinimine, $(Me_3Si)_2NP{=}NSiMe_3$ with Some Unsaturated Bifunctional Alcohols, Ketones, and Amines

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ABSTRACT

Reactions of $(Me_3Si)_2NP{=}NSiMe_3$ with chloroalkanols, N-methylpropargylamine, 3-butyne-2-one, succinimide, and chloroacetic acid were investigated. The first step in the reaction is always an addition of the nucleophilic part of the reagent (OH or NH) to the P-atom. The second step in the reaction, migration of the proton to phosphorus, depends on the substituents on the phosphorus. Highly electronegative substituents increase the stabilization of the P(III) final product.

INTRODUCTION

The chemistry of compounds of two-coordinate (λ^2) trivalent phosphorus has been a subject of intense interest during the past decade. Many examples of addition, cycloaddition, oxidation, and metal coordination reactions of these species have been reported [1], and yet the full potential of these reagents has not been realized. Recently, several novel chemical transformations of λ^2-P species with acetylenes, allenes, diketones, etc. were demonstrated [2,3]. It is known that the P=N double bond in the iminophosphine, $(Me_3Si)_2NP{=}NSiMe_3$, **1**, is highly polar, with a partial positive charge on phosphorus, thus making it an electrophilic center [1,2]. The (sp^2 hybridized) P-atom, however, carries a lone pair of electrons and accordingly might be expected to exhibit nucleophilic properties. We are interested in the investigation of the reactivity of two-coordinate trivalent phosphorus under circumstances in which this center could act as either an electrophile or a nucleophile. From this point of view, bifunctional organic reagents provide an appropriate vehicle for sampling the biphilic nature of the phosphorus.

Herein, we describe the results of a study of the reaction of phosphinimine **1** with chloroalkanols, *N*-methylpropargylamine, 3-butyn-2-one, succinimide, and chloroacetic acid, all of which can be regarded as bifunctional organic compounds.

RESULTS AND DISCUSSION

Chloroalkanols react readily with the phosphinimine **1**. In these cases, one might expect the addition of the OH group across the P=N double bond [1], followed by internal nucleophilic attack of the tricoordinate P(III) center on the C–Cl bond. When the reactions were conducted at room temperature, only the phosphinimines **3a** and **3b** were obtained:

Dedicated to Prof. Adrian Gibbs Brook on the occasion of his seventieth birthday.

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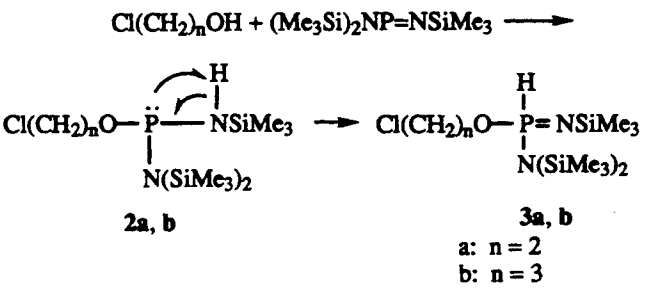
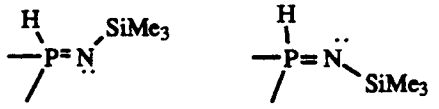


2a, b **3a, b**

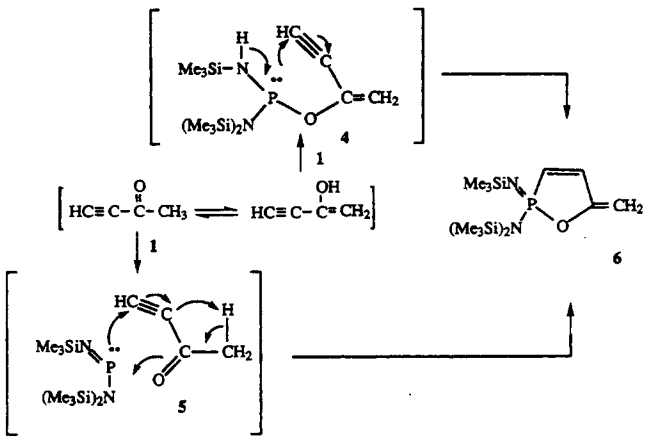
a: n = 2
b: n = 3

We propose that the reactions proceed via the expected intermediates **2** which then suffer proton transfer from N to P to form **3**. Reactions conducted at −50°C indeed revealed the intermediates **2** which were characterized by their low field phosphorus NMR chemical shifts (e.g., **2b**: 140 ppm). Even at −50°C, however, the proton migration from N to P in **2a** or **2b** to form **3a** or **3b** was very fast and only the latter phosphoranimine products could be obtained. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of **3a** and **3b** showed two groups of signals (see the Experimental section) in a 1:1 ratio. We assign these signals tentatively to the syn and anti isomers:



However, we do not yet have proof of this assignment nor can we specify which signal belongs to which isomer. Isomerism of this type has not been previously reported for P(V) imines.

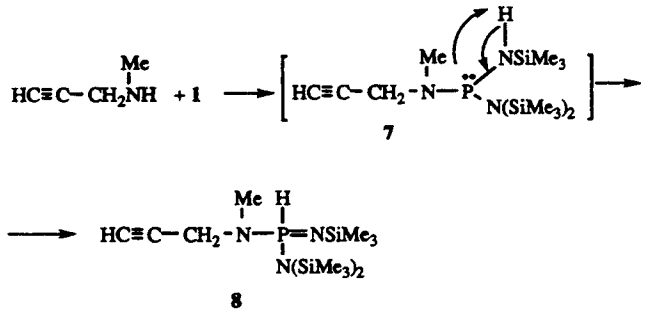
An interesting and unexpected result was obtained when **1** was allowed to react with 3-butyn-2-one at −50°C in methylene chloride. NMR spectral studies showed that the cyclic compound 2,5-dihydro-1,2-oxaphosphole **6** was formed:



The structure of **6** was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectra. In the ^{1}H spectrum, two olefinic protons (δ 6.25 and 6.66) were observed. The protons of the CH_2 group were nonequivalent, giving rise to separate signals. The cyclic structure was shown directly by the presence of four olefinic carbons in the ^{13}C NMR spectrum. The carbon atom bonded to phosphorus has a large direct coupling constant ($^{2}J_{PC}$ 130.1 Hz), strongly indicative of the formation of a P–C bond. The ^{31}P chemical shift (δ 27.0) is typical for oxaphosphole derivatives [4,5].

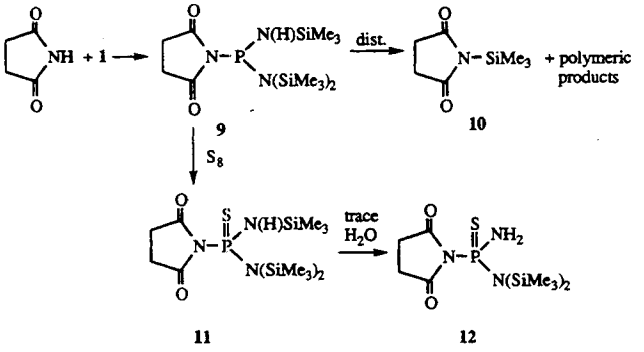
There are two possible mechanisms for this reaction. The first presumes that reaction proceeds through the enol form of the acetylenic ketone, and the OH moiety may add across the P=N double bond to form intermediate **4** which then suffers internal attack of the resultant P(III) center on the acetylenic carbon to form **6**. This path is in accord with similar reactions that have been observed for other λ^2- and λ^3-P compounds [2,3]. All spectral studies, even those conducted at −78°C, showed only **6**. No evidence of the intermediate **4** was obtained. An alternate mechanism can be proposed, which evolves from the keto form of the reactant. In this case, an initial attack of the carbonyl oxygen on phosphorus is presumed to be followed by attack of the P(III) center (e.g., via **5**) on the acetylenic carbon to give the five-membered cyclic transition state in which the P-atom acts simultaneously as an electrophile and a nucleophile. This cyclization of an acetylenic ketone to form a five-membered ring in the reaction with **1** is a new and unexpected result, which warrants further development.

Reactions of **1** with acetylenic amines are illustrated by the behavior of N-methylpropargylamine. Aliphatic amines add H–N across the P=N bond and form either phosphine amines or imino (hydrido)phosphoranes by means of proton transfer from N to P [1]. In some cases, an equilibrium mixture of the two products is obtained [1]. The unsaturated acetylenic amines behave similarly and do not yield the cyclic product produced in the preceding case of the acetylenic ketone [6,7]. Rather, addition of the N–H bond of the amine across the P=N bond of **1**, followed by simple proton migration from nitrogen to phosphorus, as might be expected, gave the phosphoranimine **8**:



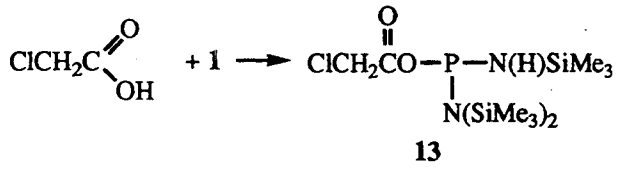
The structure of **8** was confirmed by NMR spectra. These results prompted a study of the reaction of

1 with related classes of organic compounds containing acidic NH or OH groups, such as succinimide and chloroacetic acid. The reaction of **1** with succinimide at 0°C gave the simple addition product **9** expected from addition across the P=N bond:



The structure of the crude product **9** was deduced from the NMR spectra. The chemical shift of ^{31}P (δ 107.6) is typical for trivalent phosphorus in silylated amino phosphines. During distillation, **9** decomposed and only N-trimethylsilylsuccinimide, **10**, was isolated. The treatment of **9** with excess of S_8 gave **11** as light yellow crystals. During the recrystallization of **11**, traces of moisture in the solvent hydrolyzed the $N(H)SiMe_3$ group to give **12** as light brown crystals. Compound **12** is very stable and was subsequently fully characterized by NMR spectra and elemental analysis.

A similar addition reaction was observed when **1** was allowed to react with chloroacetic acid at −50°C:



13

The NMR spectral data of the product **13** are in accord with a structure similar to **9**. Again, the electronegative substituent inhibits proton migration to P. During distillation, however, **13** also decomposed and all our efforts to isolate **13** in pure form were unsuccessful. No changes in the structures of **9** and **13** occurred according to NMR spectra when these compounds were kept in their reaction mixtures at room temperature over several days. Thus, the compounds **9** and **13** seem to be stable at ordinary temperatures despite their sensitivity to hydrolysis. These two reactions, in which highly electronegative substituents are introduced to phosphorus by addition across the P=N bond, show that these electronegative substituents stabilize the trivalent state of phosphorus. Thus, the formation of a σ^5, λ^4-P compound depends on the nucleophilicity of the P(III) center that is developed.

EXPERIMENTAL SECTION

Materials and General Procedures

The bifunctional organic compounds (chloroalkanols, N-methylpropargylamine, 3-butyn-2-one, succinimide, and chloroacetic acid) were obtained from commercial sources and were distilled before use. All experimental manipulations were performed under an atmosphere of dry argon. The silylaminophosphine $(Me_3Si)_2P{=}NSiMe_3$ **1** was prepared according to published procedures.[8] Dichloromethane was distilled from CaH_2 and stored over molecular sieves prior to use. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker WH400 instrument (operating at 400.13, 161.97, and 79.50 MHz, respectively) using 85% H_3PO_4 and $SiMe_4$ as the external standards. In all the NMR spectroscopic studies, $CDCl_3$ was used as the solvent and as an internal lock. Positive shifts lie downfield of the standard in all cases.

Preparation of $Cl(CH_2)_nOP{=}NSiMe_3$ (with H and $N(SiMe_3)_2$)

3a *(n = 2)*, **3b** *(n = 3)*

The iminophosphine **1** (2.8 g, 10 mmol) was added via a syringe to a stirred solution of 2-chloroethanol (0.7 mL, 10 mmol) in CH_2Cl_2 (ca. 10 mL) at −50 °C. The mixture was stirred 2 hours at room temperature. Solvent removal and fractional distillation afforded **3a** as a colorless liquid. The same procedure was used to prepare **3b**.

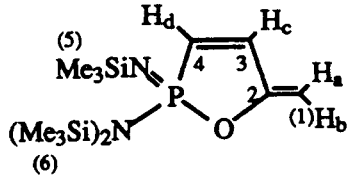
3a: $ClCH_2CH_2OP{=}NSiMe_3$ (with H and $N(SiMe_3)_2$)

2.6 g, 92% yield, bp 60–61°C (0.05 mm). NMR: ^1H δ −0.03 (s, $=NSiMe_3$); 0.24 (s, $N(SiMe_3)_2$, 3.59 (t, $ClCH_2$), $^3J_{HH}$ 5.8), 3.99 (dt, CH_2O, $^3J_{HP}$ −9.2, $^3J_{HH}$ 5.8), 7.18, 7.09 (d, HP, $^1J_{HP}$ 594.3, 596.2). ^{13}C δ 3.2 (d, $^{(3)}C$, J_{PC} 4.1), 3.5 (d, $^{(4)}C$, J_{PC} 2.7), 43.6, 43.1 (d, $^{(1)}C$, J_{PC} 7.8, 7.4), 62.7, 62.1 (d, $^{(2)}C$, J_{PC} 4.9, 4.6). ^{31}P δ −4; −2.05. Anal. calcd. for $C_{11}H_{32}ClN_2OPSi_3$ (359): C, 36.79; H, 8.98; N, 7.80; Cl, 9.87. Found: C, 36.88; H, 8.90; N, 8.21; Cl, 10.2.

3b: $ClCH_2CH_2CH_2OP{=}NSiMe_3$ (with H(a) and $N(SiMe_3)_2$)

2.6 g, 71% yield, bp 65–66°C (0.05 mm). NMR: ^1H δ 0.04 (s, $Me_3SiN=$), 0.25 (s, $(Me_3Si)_2N$), 2.04 (tt, H_c, $^3J_{H_bH_c}$, 6.4, $^3J_{H_cH_d}$, 6.7), 3.63 (tt, H_d, $^3J_{H_cH_d}$, 6.4), $^4J_{H_bH_d}$, 2.0, 3.92 (dtt, H_b, $^3J_{HP}$, 9.8, $^3J_{H_bH_c}$, 6.4, $^4J_{H_bH_d}$, 2, 7.15, 7.06 (d, H_a, $^1J_{HP}$, 589, 588). ^{13}C δ 3.6 (d, $^{(4)}C$ J_{PC} 4), 3.9 (d, $^{(5)}C$, J_{CP} 5.2), 41.3, 41.8 (s, $^{(1)}C$, 34.2, 33.4), (d, $^{(2)}C$, $^3J_{PC}$, 8.8, 8.3), 59.2, 58.9 (d, $^{(3)}C$, J_{PC} 5, 5.2). ^{31}P δ −4.06, −2.59. Anal. calcd. for $C_{12}H_{34}ClN_2OPSi_3$ (373): C, 38.63; H, 9.18; N, 7.51; Cl, 9.50. Found: C, 39.04; H, 9.08; N, 7.52; Cl, 9.75.

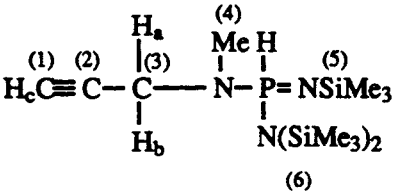
Preparation of



6

The iminophosphine **1** (2.8 g, 10 mmol) was added via a syringe to a stirred solution of 3-butyn-2-one (0.8 mL, 10 mmol) in CH_2Cl_2 (ca. 10 mL) at −50 °C. The mixture was warmed to room temperature (ca. 3 hours). Solvent removal and fractional distillation afforded the oxaphosphole (**6**) as a colorless liquid. 1 g, 30% yield, bp 62–63 °C (0.05 mm). NMR: ^1H δ 0.13 (d, $=NSiMe_3$, $^4J_{HP}$ 1.2), 0.27 (d, $N(SiMe_3)_2$, $^4J_{HP}$, 0.9), 4.42 (ddd, H_a, $^4J_{HP}$, 2.1, $^2J_{H_aH_b}$, 1.8, $^4J_{H_aH_c}$, 0.7), 4.72 (ddd, H_b, $^4J_{HP}$, 1.7, $^2J_{H_aH_b}$, 1.8, $^4J_{H_aH_b}$, 1.9), 6.25 (dddd, H_c, $^3J_{HP}$ 31.3, $^3J_{H_cH_d}$, 8.1, $^4J_{H_cH_a}$, 0.7, $^4J_{H_cH_b}$, 1.9), 6.66 (dd, H_d, $^2J_{HP}$, 43, $^3J_{H_cH_d}$, 8.1). ^{13}C δ 4 (s, $^{(5)}C$), 4.2 (s, $^{(6)}C$), 92.7 (d, $^{(2)}C$, J_{PC}, 7.4), 102.6 (s, $^{(1)}C$), 129.4 (d, $^{(4)}C$, J_{PC}, 103.1), 135.4 (d, *(3)*C, J_{PC}, 10.6). ^{31}P δ 27. Anal. calcd. for $C_{13}H_{31}N_2OPSi_3$ (346.6): C, 45.04; H, 9.02; N, 8.08. Found: C, 45.38; H, 9.21; N, 8.10.

Preparation of

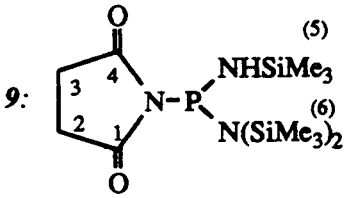


8

The iminophosphine **1** (4.2 g, 15 mmol) was added via a syringe to a stirred solution of N-methylpropargylamine (1.3 mL, 15 mmol) in CH_2Cl_2 (ca. 20 mL) at −20 °C. The mixture was warmed to room temperature (ca. 2 hours). Solvent removal and fractional distillation afforded **8** as a colorless liquid. 2.5 g, 73% yield, bp 62–63°C (0.05 mm). NMR: ^1H δ 0 (s, $=NSiMe_3$), 0.28 (s, $N(SiMe_3)_2$), 2.16 (t, HC≡, $^4J_{H_aH_b}$, 2.3), 2.61 (d, CH_3, $^3J_{HP}$, 11.6), 3.61 (ddd, H_a, $^2J_{H_aH_b}$, 17.4, $^4J_{H_aH_b}$, 2.3, $^3J_{HP}$, 9.8), 3.88 (ddd, H_b, $^2J_{H_aH_b}$, 17.4, $^4J_{H_aH_b}$, 2.3, $^3J_{HP}$, 9.8), 7.22 (d, HP, $^1J_{HP}$, 527). ^{13}C δ 3.52 (d, $^{(5)}C$, J_{PC}, 4.4); 3.55 (d, $^{(6)}C$, J_{PC}, 2.8), 32.5 (d, $^{(4)}C$, J_{PC}, 6.4), 37.4 (d, $^{(3)}C$, J_{PC}, 7.2), 71.5 (s, $^{(1)}C$) 80.5 (d, $^{(2)}C$, J_{PC} 7.1), ^{31}P, δ −8.83. Anal. calcd. for $C_{13}H_{34}N_3PSi_3$ (347.7): C, 44.91; H, 9.86; N, 12.09. Found: C, 44.36; H, 10.06; N, 12.10.

Reaction of Phosphinimine **1** *with Succinimide*

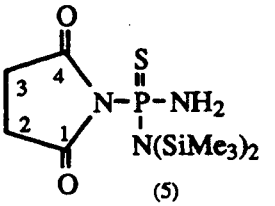
The reaction of phosphinimine **1** with succinimide was carried out at 0°C by the same procedure as that described previously. The NMR spectrum showed that the N-phosphinimine succinimide **9** was obtained. During vacuum distillation, the product **9** decomposed and N-trimethylsilylsuccinimide **10** was isolated.



9:

NMR: ^1H δ −0.01 (s, $SiMe_3$), 0.96 (d, $N(SiMe_3)_2$, $^4J_{HP}$, 1.5), 2.43 (s, $-CH_2CH_2-$), 4.63 (d, NH, $^2J_{HP}$, 4.5), ^{13}C δ 0.8 (d, $^{(5)}C$, J_{PC}, 6.7), 3.8 (d, $^{(6)}C$, J_{PC}, 8.5), 29.3 (d, $^{(2)}C$, $^{(3)}C$, J_{PC}, 2.4), 180.9 (s, $^{(1)}C$, $^{(4)}C$). ^{31}P δ 107.6.

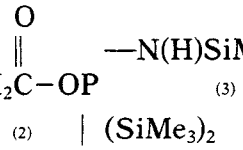
Preparation of



12

The CH_2Cl_2 solution of **9** was treated with an excess of sulfur until no more sulfur was dissolved. Solvent removal afforded light yellow crystals of **11**. Compound **11** was recrystallized from hexane. During recrystallization, traces of moisture hydrolyzed the trimethysilylamino group to an amino group. The light brown crystals of compound **12** were stable in air. 2.5 g/75% yield, mp 98–99 °C. NMR: ^1H δ 0.24 (s, $SiMe_3$), 2.70 (s, $-CH_2CH_2-$), 4.27 (d, NH_2, $^2J_{HP}$, 7.1). ^{13}C δ 1.2 (s, $^{(5)}C$), 29.4 (d, $^{(2)}C$, $^{(3)}C$, J_{PC}, 3.2), 178.0 (s, $^{(1)}C$, $^{(4)}C$). ^{31}P δ 52.7. Anal. calcd. for $C_{10}H_{24}N_3O_2PSi_2S$ (337.5): C, 35.58; H, 7.17; N, 12.45; S, 9.50. Found: C, 35.35; H, 6.91; N, 12.44; S, 9.65.

Preparation of



13

The reaction of **1** with chloroacetic acid was carried out at −50 °C using the procedure described earlier. After removal of the solvent, the crude product **13** remained as a colorless liquid. During distillation, compound **13** decomposed. NMR: ^1H δ 0.09 (d, $SiMe_3$, J_{HP}, 1), 0.19 (d, $N(SiMe_3)_2$, $^4J_{HP}$, 3.1), 2.65 (d, NH, $^2J_{HP}$, 4.6), 3.89 (d, CH_2, $^4J_{HP}$, 0.6). ^{13}C δ 1 (d, $^{(3)}C$, J_{PC}, 6.6), 4.9 (d, $^{(4)}C$, J_{PC}, 8.6), 41.8 (d, $^{(1)}C$, J_{PC}, 5.1), 165.8 (d, $^{(2)}C$, J_{PC}, 5.9). ^{31}P δ 135.9.

CONCLUSIONS

The reactions described herein illustrate the pronounced electrophilic properties of the P-atom in **1**. The first step of the reaction is always an addition of the nucleophilic part of the reagent (OH or NH) to the P atom. The second step of the reaction, migration of the proton to the phosphorus, seems to depend on the substituents on the phosphorus, with highly electronegative substituents increasing the stabilization of the P(III) final product.

ACKNOWLEDGMENT

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REFERENCES

[1] M. Regitz, O. J. Scherer (eds.), *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme Medical Publishers, Inc., New York, NY, 1990.

[2] R. H. Neilson, C. M. Angelov, *ACS Symp. Ser., 486*, 1992, 76–85.

[3] C. M. Angelov, R. H. Neilson, *Tetrahedron, 48*, 1992, 10227–10232.

[4] C. M. Angelov, C. Z. Christov, *Heterocycles, 20*, 1985, 219–225.

[5] C. M. Angelov, *Heterocycles, 20*, 1983, 791–796.

[6] C. M. Angelov, O. Dahl, *Tetrahedron Lett., 24*, 1983, 1643–1646.

[7] C. M. Angelov, D. D. Encher, *Heteroatom Chem., 3*, 1992, 651–653.

[8] E. Niecke, W. Flick, *Angew. Chem. Int. Ed. Engl., 12*, 1973, 585–586.