Journal of Organometallic Chemistry, 65 (1974) 327—334

REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS

XXVII*. SOME REACTIONS OF [(TRIMETHYLSILYL)IMINO]PHOSPHORANE

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(Received June 14th, 1973)

Summary

The reaction of [(trimethylsilyl)imino]methyldiphenylphosphorane: $Ph_2MeP{=}N{-}SiMe_3$ (I) with several acid anhydrides or alkyl isocyanates took place by the simple cleavage of silicon—nitrogen bond. In contrast the interaction of (I) with phenyl isocyanate, isothiocyanate or carbon disulphide led to addition-elimination reactions of the Wittig type. Detailed investigation in the case of phenyl isocyanate indicated the usual elimination of Ph_2MePO is suppressed by the strong affinity of the trimethylsilyl group for anionic oxygen atom.

Introduction

[(Organosilyl)imino]phosphoranes, $R_3P{=}N{-}SiR'_3$, can be represented by the following two canonical forms [2].

$$\underset{\text{(A)}}{R_3P{=}\overline{N}{-}SiR'_3} \longleftrightarrow \underset{\text{(B)}}{R_3P^+{-}\underline{\overline{N}}^-{-}SiR'_3}$$

The acid-base interactions of [(organosilyl)imino]phosphoranes with hydrogen halides [3,4] or Lewis acids [5 - 7] were discussed in terms of the polar form (B).

Except for the acid-base interactions and desilylations by common electrophilic agents [8,9], the chemical behaviour of [(organosilyl)imino]phosphorane remained unexplored.

In this paper, we show that [(trimethylsilyl)imino]methyldiphenylphosphorane; $Ph_2MeP{=}N{-}SiMe_3$ (I) exhibits two types of reactivity, (1) a simple cleavage reaction of the silicon—nitrogen bond by acid anhydrides and alkyl isocyanates, and (*2*), a Wittig-type addition-elimination reaction brought about by phenyl isocyanate, phenyl isothiocyanate, or carbon disulphide.

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* For part XXVI see ref [1], presented (K.I) at the 3rd Intern Symp. on Organosilicon Chemistry, Madison, 1972 (Preprint, p 8)

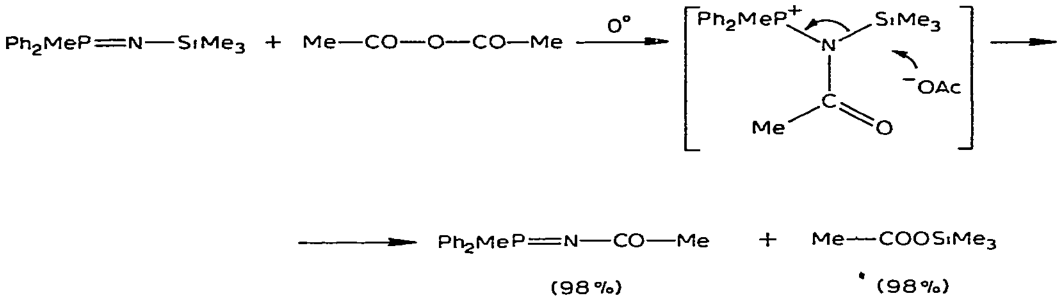
Results and discussion

[(Trimethylsilyl)imino]methyldiphenylphosphorane (I) was prepared by the usual method [5,10 - 14] from methyldiphenylphosphine and trimethylsilylazide in an excellent yield.

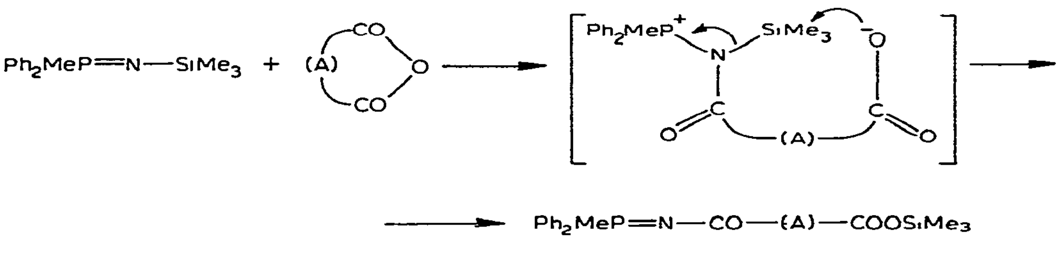
$$Ph_2MeP + Me_3SiN_3 \xrightarrow[93\%]{100^\circ} \underset{(I)}{Ph_2MeP{=}N{-}SiMe_3} + N_2$$

(a) Reaction with acid anhydrides

Recently, Kricheldorf [8] described the selective silicon—nitrogen bond cleavage of [(trimethylsilyl)imino]triphenylphosphorane by various acid chlorides or anhydrides. We found similar results [1b] in the reaction of (I) with acetic and some cyclic acid anhydrides The reaction of acetic anhydride with (I) took place exothermically at 0° to give (acetylimino)methyldiphenylphosphorane and trimethylsilyl acetate in quantitative yields



Cyclic acid anhydrides, such as succinic or phthalic anhydrides, brought about insertions into the silicon—nitrogen bond of (I), and the corresponding 1/1 adducts: (IIa) and (IIb), were isolated

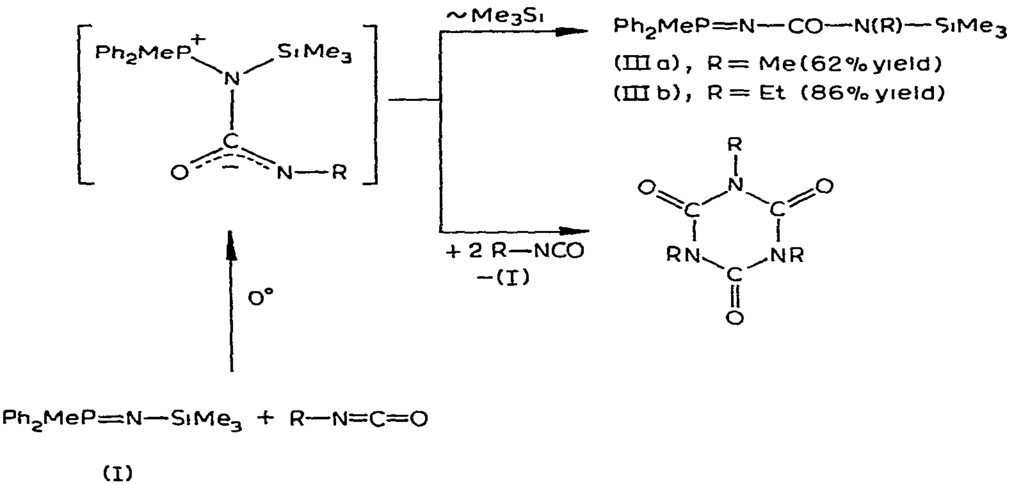


(IIa), (A) = CH_2CH_2 (84% yield)
(IIb), (A) = o-C_6H_4 (77% yield)

The depicted mechanism for this insertion involves a nucleophilic ring-opening by attack of the nitrogen atom on the acyl carbon atom followed by the rapid intramolecular migration of the trimethylsilyl group from the nitrogen atom to the carboxylate anion This kind of intramolecular migration to the carboxylate anion of the trimethylsilyl group is known to be rapid [15,16].

(b) Reaction with alkyl isocyanates

The addition of methyl or ethyl isocyanate to (I) caused the formation of the corresponding 1/1 insertion products (IIIa) and (IIIb), accompanied by small amounts of trialkyl isocyanurate, i e. the cyclic trimer of the isocyanate



Insertion products (IIIa) and (IIIb) were characterized by analysis, and by infrared and NMR spectroscopy, as well as by the formation of the corresponding [(alkylcarbamoyl)imino]phosphoranes on desilylative hydrolyses. However, tert-butyl isocyanate did not react with (I) even under more drastic conditions (80° for 3 days) because of steric hindrance

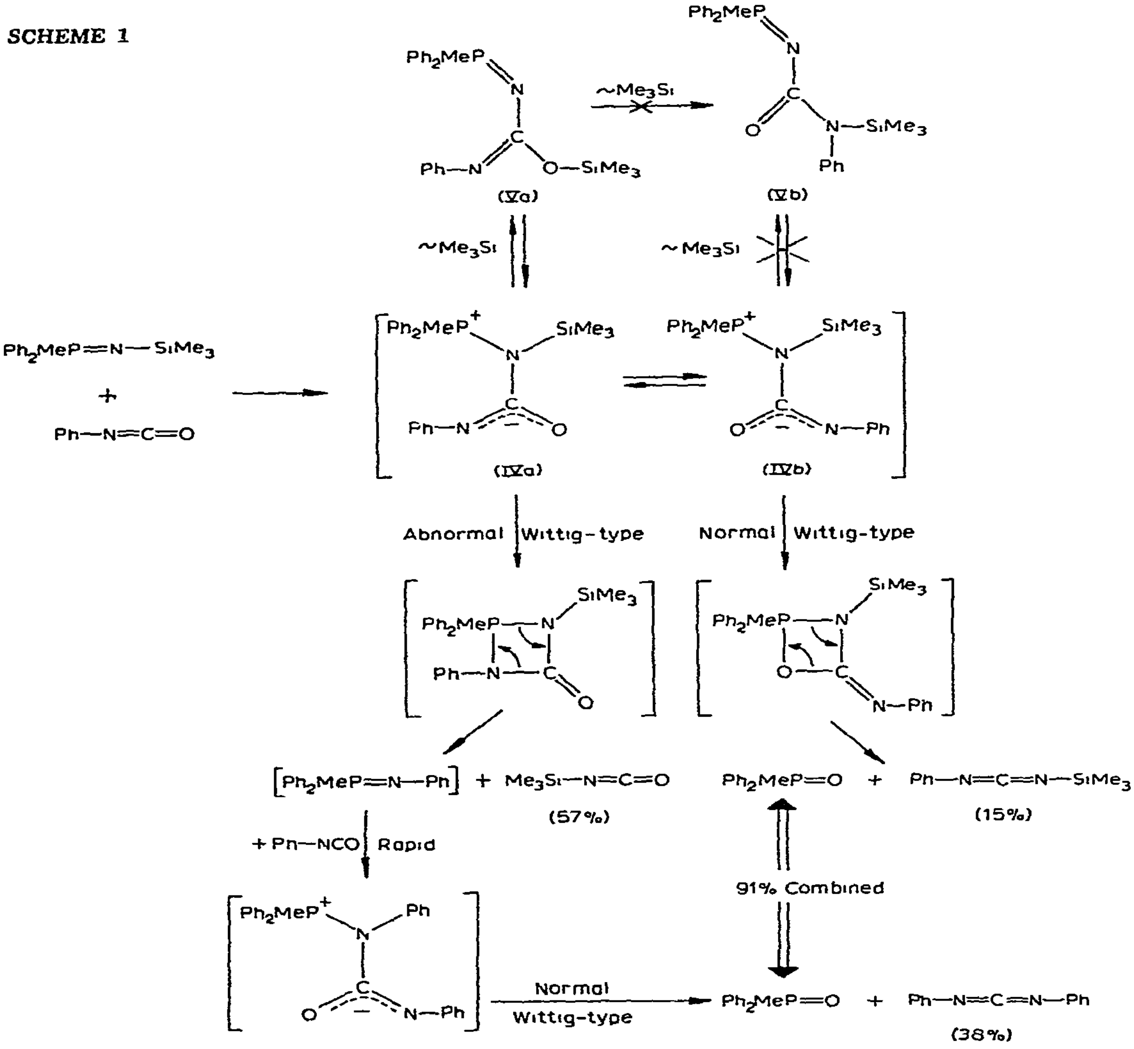
(c). Reaction with phenyl isocyanate or isothiocyanate

Although the equimolar reaction of (I) with phenyl isocyanate took place exothermally, no sign of the formation of 1/1 adduct (V) could be detected by NMR and infrared spectra The separation of the mixture gave the four products, which are discussed later, and the recovery of nearly half of the original (I) In order to achieve complete reaction, 2 moles of phenyl isocyanate were added to (I) at 0°. Although the yield of methyldiphenylphosphine oxide was good, viz 91%, the counter product expected from a Wittig-type reaction [17], viz. phenyl(trimethylsilyl)carbodiimide ($Ph{-}N{=}C{=}N{-}SiMe_3$) [18], was isolated in only 15% yield. A careful separation of the mixture unexpectedly gave trimethylsilyl isocyanate [19] (57%) and diphenylcarbodiimide [20] [19%, based on (I) and 38% based on phenyl isocyanate]. All of these four products, $Ph_2MeP{=}O$, $Ph{-}N{-}C{=}N{-}SiMe_3$, $Me_3Si{-}N{=}C{=}O$ and $Ph{-}N{=}C{=}N{-}Ph$, were identified by comparing their infrared and NMR spectra with those of authentic samples.

The formation of large amounts of trimethylsilyl isocyanate would be consistent with the production of phenyliminophosphorane, $Ph_2MeP{=}N{-}Ph$, if the former were generated by abnormal Wittig-type elimination from the latter. However, all attempts to detect $Ph_2MeP{=}N{-}Ph$ failed, and so we conclude that it was an unstable intermediate and reacts rapidly with the remaining phenyl isocyanate to give diphenylcarbodiimide and methyldiphenylphosphine oxide. This view was strongly supported by the fact that authentic (phenylimino)methyldiphenylphosphorane reacted spontaneously with one molar proportion of phenyl isocyanate to give the same products.

From these observations, a mechanism of the addition-elimination reaction can be proposed (Scheme 1).

SCHEME 1



There are two possible conformations for the intermediate zwitterion, namely, (IVa) leading to the elimination of the P=N bond (*abnormal Wittig-type*) and (IVb) leading to elimination of the P=O bond (*normal Wittig-type*). It is interesting that the former process (57%) is favoured over the latter (15%). This striking result is explained in terms of the strong affinity of the trimethylsilyl group for oxygen atoms. An interaction of the trimethylsilyl group with oxy-anion in (IVa), involving reversible rapid migration of trimethylsilyl group between (IVa) and (Va), would stabilize the conformation (IVa) and overcome the normal interaction of the oxy-anion with organophosphonium group in (IVb). Change in the nature of the Wittig reactions brought about by trimethylsilyl moiety has been reported in the case of (trimethylsilyl)alkylenephosphoranes [21,22], and Schmidbaur and Stuhler [22] recently concluded that the oxy-anion of the intermediate zwitterion generated in the reaction of $Me_3P{=}CH{-}SiMe_3$ with carbonyl compounds is captured selectively by the trimethylsilyl group.

The difference in behavior between alkyl isocyanates and phenyl isocyanate can be explained in terms of the degree of the nucleophilicity of the anionic nitrogen atoms in (IVb). The anionic charge on the nitrogen atom is enhanced by alkyl substitution, and the attack trimethylsilyl group occurs more readily, resulting in insertion products, in the case of alkyl isocyanates. The lower nucleophilic nitrogen atom associated with introduction of the electron-withdrawing phenyl group, which also causes some steric interference, would disfavour the formation of the insertion product (Vb) Consequently, (IVb) induces the Wittig-type elimination reaction or internal rotation around the N—C bond to give (IVa).

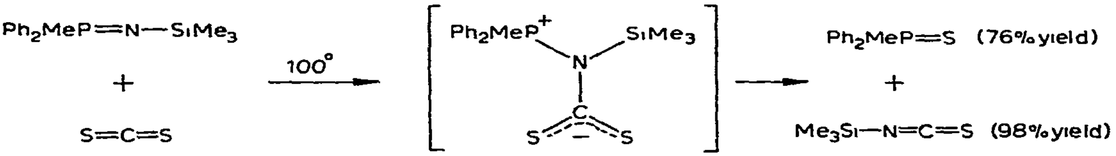
A similar addition-elimination reaction was observed in the interaction of (I) with phenyl isothiocyanate, although much more drastic conditions were required (100° for 4 days).

$$Ph_2MeP{=}N{-}SiMe_3 + Ph{-}N{=}C{=}S \xrightarrow{100^\circ} \underset{(76\%)}{Ph_2MeP{=}S} + \underset{(28\%)}{Me_3Si{-}N{=}C{=}S}$$
$$+ \underset{(12\%)}{Ph{-}N{=}C{=}N{-}SiMe_3} + Ph{-}N{=}C{=}N{-}Ph \text{ and its polymer}$$

All the products may be accounted for in the same manner as for those from phenyl isocyanate. The yield of diphenylcarbodiimide was markedly lowered owing to its thermal polymerization under these conditions.

(d) Reaction with carbon disulphide

The reaction of (I) with carbon disulphide at 100° for 48 h. gave trimethylsilyl isothiocyanate and methyldiphenylphosphine sulphide in excellent yields.



These products can be reasonably explained in terms of the normal Wittig-type addition-elimination mechanism.

Experimental

All experiments were performed under argon. Analyses were carried out by the Alfred Bernhardt Mikroanalytisches Laboratorium, Germany. NMR spectra were recorded on a JEOL C-60HL spectrometer with tetramethylsilane as internal standard. Infrared spectra were recorded on a JASCO-DS-403G spectrometer.

[(Trimethylsilyl)imino] methyldiphenylphosphorane, $Ph_2MeP{=}N{-}SiMe_3$ (I)

A mixture of methyldiphenylphosphine (14 g) and trimethylsilyl azide (12 g) was gradually heated to 100° during 1.5 h with stirring. After the evolution of nitrogen gas had stopped, stirring was continued for an additional 3 h at 100°. The product (I) was isolated by distillation under reduced pressure in 93% yield (18.7 g). (I): B.p 100 - 103°/0.03 mm. IR(C_6H_6), ν(P=N) 1305, 1250 cm^{-1}. NMR($CDCl_3$), δ 0.32d ($C\underline{H}_3$—Si, J 0.4 Hz; 9H) 1 55d ($C\underline{H}_3$—P, J 12 Hz; 3H) and 7 7 - 6.9 ppm m($C_6\underline{H}_5$; 10H). (Found· C, 66.97. H, 7 74 $C_{16}H_{22}NPSi$ calcd.: C, 66.86; H, 7.72%.)

Reaction of (I) with acetic anhydride

Acetic anhydride (0.536 g; 5.25 mmole) was slowly added to (I) (1.38 g, 5 25 mmole) at 0°. Reaction took place exothermically, and the mixture solidified. On vacuum distillation, trimethylsilyl acetate was isolated in dry-ice/acetone trap; 0.67 g (98% yield). The infrared spectra [1728 ν(C=O), 1269 and 1255 in CCl_4] and NMR[δ0 26($C\underline{H}_3$—Si) and 2 01 ppm($C\underline{H}_3$—CO) in $CHCl_3$] were identical with those of authentic material prepared from trimethylchlorosilane and sodium acetate. The residue was recrystallized from ether/benzene (10/1 vol. ratio) to give (acetylimino)methyldiphenylphosphorane (1.26 g; 98%) M p. 90 - 91°. IR(C_6H_6); 1593 ν(C=O) and 1310 cm^{-1} ν(P=N) NMR(C_6D_6), δ1.89 d(J 13.6 Hz, 3H, $C\underline{H}_3$—P), 2.38 d(J 2.4 Hz, 3H, $C\underline{H}_3$—CO) and 6.9 - 7.8 ppm m(10H, $C_6\underline{H}_5$). (Found· C, 70.33, H, 6.32; N, 5.55. $C_{15}H_{10}NOP$ calcd.: C, 70.02, H, 6.27, N, 5.40%.)

Reactions of cyclic acid anhydride with (I)

As an example, the reaction of (I) with phthalic anhydride is described in detail. A suspension of phthalic anhydride (0.704 g, 5 0 mmole) in 4 ml of dry benzene was gradually added to (I) (1 35 g, 4.9 mmole) with vigorous stirring at room temperature. Reaction occurred spontaneously and the mixture became homogeneous After evaporation of benzene under reduced pressure, the residue was recrystallized from ether/benzene (10/1 vol) to give (IIb) as crystalline needles (1.59 g, 77%). {[*o*-(trimethylsiloxycarbonyl)benzolyl] imino} methyldiphenylphosphorane (IIb) M p. 100 - 102°. IR($CHCl_3$); 1707, 1588 ν(C=O), 1333 ν(C—O) and 1255 cm^{-1} δ (Si—CH_3). NMR($CDCl_3$); δ 0.24 s ($C\underline{H}_3$—Si, 9H), 2 36 d($C\underline{H}_3$—P, J 13.5 Hz; 3H) and 7.4 - 8.0 ppm m ($C_6\underline{H}_5$ and $C_6\underline{H}_4$; 14H) (Found. C, 66.36, H, 5.93. $C_{24}H_{26}NO_3PSi$ calcd.: C, 66.99; H, 6.02%.)

With succinic anhydride, a similar procedure gave {[3-(trimethylsiloxycarbonyl)propionyl] imino}methyldiphenylphosphorane (IIa) in 84% yield. (IIa). M.p 101 - 103°. IR($CHCl_3$); 1751, 1581 ν(C=O), 1365 ν(C—O) and 1250 cm^{-1} δ (Si—CH_3). NMR($CDCl_3$), δ 0.23 s ($C\underline{H}_3$—Si; 9H), 2.59 m (two CH_2; 4H), 2.23 d ($C\underline{H}_3$—P, J 13.5 Hz, 3H) and 7.4 - 7.9 ppm m ($C_6\underline{H}_5$, 10H) (Found: C, 62.03; H, 6.60. $C_{20}H_{26}NO_3P$ calcd.: C, 61 99; H, 6.76%.)

Reaction of methyl and ethyl isocyanate with (I)

The reaction of methyl isocyanate is described below as an example. Methyl isocyanate (0.36 g; 5.7 mmol) was added very slowly to 1.64 g (5.7 mmol) of (I) at 0°. Spontaneous reaction occurred and the mixture became solid. Recrystallization from n-hexane gave needles of trimethylisocyanurate (0.054 g), which was identified by mixed melting point (M.p. 169°) and by the comparison of its infrared and NMR spectra with those of authentic material.

The liquid layer was cooled suddenly to — 78°, to give white crystals. After filtration under argon, the crystals were recrystallized from n-hexane to give 1.21 g (62%) of 1/1 adduct; [*N*,*N*-methyl(trimethylsilylcarbamoyl)imino]-methyldiphenylphosphorane (IIIa): M.p. 88 - 89°. IR($\mathrm{CHCl_3}$); 1587 ν(C=O), 1300 ν(P=N) and 1251 cm^{-1} δ (Si—$\mathrm{CH_3}$). NMR($\mathrm{CDCl_3}$), δ 0.29 s ($\mathrm{C\underline{H}_3}$—Si; 9H), 2.21 d ($\mathrm{C\underline{H}_3}$—P, J 13.5 Hz, 3H), 2.74 s ($\mathrm{C\underline{H}_3}$—N; 3H) and 7.2 - 7.8 ppm m ($\mathrm{C_6\underline{H}_5}$, 10H) (Found C,62.68, H, 7.19. $\mathrm{C_{18}H_{22}N_2OPSi}$ calcd.: C, 62.76; H, 7.32%.)

The product (IIIa) was readily hydrolyzed by the moisture in the air to give $\mathrm{Ph_2MeP{=}N{-}CO{-}NH{-}Me}$ in quantitative yield, M.p. 113 - 114°. IR($\mathrm{CHCl_3}$), 3250 ν(N—H), 1567 ν(C=O) and 1298 cm^{-1} ν(C—N) NMR($\mathrm{CDCl_3}$), δ 2.20 d ($\mathrm{C\underline{H}_3}$—P, J 16.6 Hz, 3H), 2.68 d ($\mathrm{C\underline{H}_3}$—N, J 4.7 Hz, 3H), 5.00 br s (N—$\underline{\mathrm{H}}$; 1H) and 7.2 - 7.8 ppm m ($\mathrm{C_6\underline{H}_5}$; 10H).

The reaction of ethyl isocyanate with (I) was performed as above to give the 1/1 adduct [*N*,*N*-ethyl(trimethylsilylcarbamoyl)imino] methyldiphenylphosphorane (IIIb) in 86% yield M.p. 71 - 72°. IR($\mathrm{CHCl_3}$), 1585 ν(C=O), 1290 ν(P=N) and 1255 δ(Si—$\mathrm{CH_3}$). NMR($\mathrm{CDCl_3}$), δ 0.28 s ($\mathrm{C\underline{H}_3}$—Si; 9H), δ 1.08 double triplet ($\mathrm{C\underline{H}_3}$—$\mathrm{CH_2}$; J 7.1 and 7.7 Hz; 3H), δ 2.22 d ($\mathrm{C\underline{H}_3}$—P, J 16.5 Hz, 3H), δ 3.28 q ($\mathrm{CH_2}$, J 7.7 Hz; 2H) and δ 7.3 - 7.9 ppm m ($\mathrm{C_6\underline{H}_5}$, 10H). (Found. C, 63.62, H, 7.39 $\mathrm{C_{19}H_{24}N_2OPSi}$ calcd. C, 63.66, H, 7.59%.)

Reaction of phenyl isocyanate with (I)

Phenyl isocyanate (1.29 g, 10.8 mmol) was slowly added to (I) (1.58 g, 5.5 mmol) at 0°. The reaction took place exothermically, and the mixture was kept for 6 h at room temperature. Distillation under reduced pressure gave phenyl(trimethylsilyl)carbodiimide [18] [0.16 g, 15% based on (I), b.p. 47°/0.04 mm, IR 2170 cm^{-1}, NMR δ 0.28 ppm ($\mathrm{C\underline{H}_3}$—Si)] as the distillate and trimethylsilyl isocyanate [19] [0.40 g, 57% based on (I), IR 2275 and 1258 cm^{-1}, NMR δ 0.26 ppm ($\mathrm{C\underline{H}_3}$—Si)] trapped at — 78°. Both of the products were identified by comparison of their infrared and NMR spectra with those of authentic samples.

Addition to the distillation residue of 3 ml of dry ether gave a white precipitate, which was filtered off under argon. The crystals were washed three times with 2 ml of ether and recrystallized from petroleum ether (b.p. 30 - 40°) to give methyldiphenylphosphine oxide [1.09 g in 91% yield: m.p. 112°, IR 1173 cm^{-1} ν(P=O), NMR δ 8.99 ppm d (J 13.0 Hz)].

The filtrate and ether washings were combined, the ether was removed under vacuum, and the diphenylcarbodiimide [0.4 g (38%), b.p. 111 - 113°/ 0.06 mm, IR 2130 cm^{-1}] was isolated by vacuum distillation. The product was characterized by comparing infrared spectrum with that of an authentic sample prepared in 63% yield by the reaction of *N,N'*-diphenylthiourea with yellow mercuric oxide, as well as by the formation of diphenylurea quantitatively by hydrolysis.

Reaction of phenyl isothiocyanate with (I)

The mixture of (I) (1.64 g, 6.2 mmol) and phenyl isothiocyanate (0.84 g; 6.2 mmol) was kept in a sealed tube at 100° for 48 h. Vacuum distillation of the mixture gave four fractions as follows. (*1*) trimethylsilyl isothiocyanate [0.22 g (28%) in a trap at −78°], (*2*) phenyl(trimethylsilyl)carbodiimide [0 14 g (12%), b.p. 47°/0.02 mm], (*3*) a mixture of diphenylcarbodiimide and a small amount of starting (I) [0.20 g, b.p. 105 - 125°/0.02 mm] and (*4*) methyldiphenylphosphine sulphide [1.09 g (76%); b.p. 140 - 145°/0.02 mm, IR 1109 cm^{-1} ν(P=S), NMR δ 2 08 ppm d ($C\underline{H}_3$—P, J 13.5 Hz)]. All the products were characterized by comparing their infrared and NMR spectra with those of authentic samples

Reaction of carbon disulphide with (I)

A mixture of (I) (1.26 g, 4.8 mmol) and carbon disulphide (0.36 g; 4.8 mmol) was heated in a sealed tube at 100° for 48 h. Vacuum distillation gave trimethylsilyl isothiocyanate [0.53 g (92%), collected in a dry ice/acetone trap at −78°] and methyldiphenylphosphine sulphide 0.78 g (76%), b.p. 143 - 147°/0.04 mm]. Both products had infrared and NMR spectra identical with those of authentic materials.

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