SYNTHESIS OF C-(N,N-DIALKYLAMINO)PHOSPHAALKENES

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UDC 542.91:547.1'118+547.233.2

New C-(N,N-dialkylamino)phosphaalkenes were synthesized by the reaction of phenylphosphine with amidacetals. Such compounds may also be synthesized by the reaction of bis(trimethylsilyl)phenylphosphine with amidacetals.

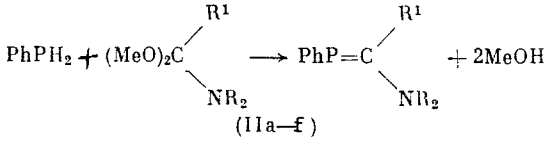
Dicoordinated phosphorus compounds with the P=C–N structural element form a new class of compounds with C_{2p}–P_{3p} π bonding. Several methods have been reported for the preparation of this type of phosphaalkenes [1]. One such method is the reaction of primary aromatic phosphines with amidacetals. Aliphatic phosphines do not undergo this reaction [2]. However, the range of phosphaalkenes, which may be prepared by this reaction, is limited by the range of reported amidacetals. Thus, we have synthesized new amidacetals by the exchange reaction of secondary amines with the dimethylacetal of dimethylformamide [3].

$$(MeO)_2CHNMe_2 + R_2NH \rightarrow \underset{(Ia-d)}{(MeO)_2CHNR_2} + Me_2NH$$

$R_2 = -(CH_2)_4-$ (Ia); $-(CH_2)_5$ (Ib); $-(CH_2)_6-$ (Ic); $-CH_2CH_2OCH_2CH_2-$ (Id).

Bis(trimethylsilyl)amine does not enter this reaction, i.e., the basicity of the amine apparently also has importance in addition to the condition that the amine used must have a higher boiling point than dimethylamine. Amidacetals (Ib) and (Id) were also synthesized by the reaction of sodium methylate with the corresponding adducts of dimethyl sulfate with formamides [4].

C-(N,N-Dialkylamino)phosphaalkenes were synthesized by the reaction of equimolar amounts of phenylphosphine and amidacetals at 80-100°C [2]



(IIa–f)

$R^1 = H$, $R_2 = -(CH_2)_4-$ (IIa); $-(CH_2)_5-$ (IIb); $-(CH_2)_6-$ (IIc); $-CH_2CH_2OCH_2CH_2-$ (IId); $R = Me$ (IIe); $R^1 = R = Me$ (IIf).

The ^{31}P NMR spectra of the reaction mixtures of phenylphosphine with (Ia) and (Ic) as well as with the acetal of dimethylacetamide display only signals of monomers at 64, 66, and 84 ppm, while the spectra for the reaction mixtures with (Ib) and (Id) show signals both from the monomers and dimers in 1:1 ratio (72 and –13 ppm for (IIb), 78 and –18 ppm for (IId). Analogous results were obtained for (IIe) [2].

Distillation of the reaction mixtures in high vacuum leads to pure phosphaalkenes. Dissociation of the dimer to give the monomer occurs upon the distillation of (IIb). Such dissociation does not occur in the distillation of (IId) and the reaction mixture decomposes.

Phosphaalkenes (IIa)-(IIc) are bright yellow liquids which crystallize upon cooling to 10°C. Phosphaalkenes (IIa) and (IIc) do not tend to dimerize, while (IIb) undergoes 50% dimerization in 24 h at ~20°C. This discrepancy in the tendency of the phosphaalkenes to undergo dimerization is attributed to steric hindrance created by the tetramethyleneimino and hexamethyleneimino groups at the double bond in comparison with the piperidino group with approximately the same basicity, which determines the thermodynamic stabilization of such phosphaalkenes.

The E configuration may be assigned on the basis of the $^2J_{PH}$ value for phosphaalkenes (IIa)-(IIc) (14.0 Hz) [2].

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1639-1641, July, 1990. Original article submitted June 8, 1989.

0568-5230/90/3907-1489$12.50

We developed a method for the preparation of C-(N,N-dialkylamino)phosphaalkenes using the reaction of amidacetals and bis(trimethylsilyl)phosphines.

$$PhP(SiMe_3)_2 + (MeO)_2CHNMe_2 \rightarrow PhP{=}CHNMe_2 + 2Me_3SiOMe$$

This reaction does not require heating, proceeds exothermally at room temperature, and leads in quantitative yield to C-(N,N-dimethylamino)methylene-P-phenylphosphine as indicated by ^{31}P NMR spectroscopy.

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a KGU-4 NMR spectrometer at 10.2 MHz with noise suppression of protons at 24.3 MHz relative to 85% H_3PO_4. The PMR spectra were taken on a Varian T-60 spectrometer at 34.5°C. All the operations were carried out in argon.

General procedure for the preparation of amidacetals (Ia)-(Id). A mixture of equimolar amounts of a secondary amine and the dimethylacetal of dimethylformamide was heated for 2 h on an oil bath at 190°C. The reaction mixture was then distilled on a Vigreaux column.

Tetramethyleneimino(dimethoxy)methane (Ia) was obtained in 56%, bp 54°C (10 mm), n_D^{20} 1.4385. Found: C, 58.28; H, 10.44; N, 9.91%. Calculated for $C_7H_{15}NO_2$: C, 57.93; H, 10.35; N, 9.66%.

Piperidino(dimethoxy)methane (Ib) [4] was obtained in 64% yield, bp 62°C (10 mm), n_D^{20} 1.4465. Found: C, 60.37; H, 10.75%. Calculated for $C_8H_{17}NO_2$: C, 60.38; H, 10.69%.

Hexamethyleneimino(dimethoxy)methane (Ic) was obtained in 61% yield, mp 85°C (10 mm), n_D^{20} 1.4580. Found: C, 62.89; H, 10.91%. Calculated for $C_9H_{19}NO_2$: C, 62.43; H, 10.98%.

Morpholino(dimethoxy)methane (Id) was obtained in 52% yield, bp 76°C (10 mm), n_D^{20} 1.4460. Found: C, 52.38; H, 9.38; N, 8.86%. Calculated for $C_7H_{15}NO_3$: C, 52.17; H, 9.32; N, 8.70% [4].

C-(Tetramethyleneimino)methylidene-P-phenylphosphine (IIa). A mixture of 4.86 g (0.44 mole) phenylphosphine and 6.41 g (0.44 mole) (Ia) was heated at reflux for 30 min. The reaction mixture was distilled to give 7.76 g (92%) (Ia), bp 125-126°C (10^{-3} mm), $\delta^{31}P$ 64 ppm. PMR spectrum in CD_2Cl_2 (TMS, δ, ppm): 2.03-2.33 m (4H), 3.40-3.67 m (4H), 7.30-7.87 m (5H), 9.27 d (1H, $^2J_{PH}$ = 14.0 ppm), Found: C, 69.03; H, 7.73; N, 6.51; P, 15.91%. Calculated for $C_{11}H_{14}NP$: C, 69.11; H, 7.73; N, 7.33; P, 16.23%.

C-(Piperidino)methylidene-P-phenylphosphine (IIb). A mixture of 5.33 g (0.049 mole) phenylphosphine and 7.70 g (0.049 mole) (Ib) was heated at reflux for 30 min. The reaction mixture was distilled in vacuum to give 8.25 g (83%) (IIb), bp 126-127°C (10^{-3} mm), $\delta^{31}P$ 72 ppm. PMR spectrum in CD_2Cl_2 (δ, ppm): 1.67-1.93 m (6H), 3.27-3.57 m (4H), 7.23-7.87 m (5H), 9.33 d (2H, $^2J_{PH}$ = 14.0 Hz). Found: N, 6.85; P, 14.89%. Calculated for $C_{12}H_{16}NP$: N, 6.83; P, 15.12%.

2,4-Bis(piperidino)-1,3-diphenyl-1,3-diphosphetane. A mixture of 4.7 g (0.043 mole) phenylphosphine and 6.79 g (0.043 mole) (Ib) was heated at reflux for 30 min. Methanol formed was distilled off using a water pump. The precipitate formed was filtered off and washed on the filter with ether to give 3.25 g (37%) product, mp 112°C, $\delta^{31}P$ = −13 ppm. PMR spectrum in CD_2Cl_2 (TMS, δ, ppm): 1.67-1.80 m (12H), 2.7-2.9 m (8H), 3.77 t (2H, $^2J_{PH}$ = 3.2 Hz), 7.37-7.9 m (10H). Found: C, 70.58; H, 7.78; N, 7.73; P, 14.74%. Calculated for $C_{24}H_{32}N_2P_2$: C, 70.24; H, 7.81; N, 6.83; P, 15.12%.

C-(Hexamethyleneimino)methylidene-P-phenylphosphine (IIc). A mixture of 5.6 g (0.051 mole) phenylphosphine and 8.86 g (0.051 mole) (Ic) was heated at reflux for 30 min. The reaction mixture was distilled in vacuum to give 8.36 g (75%) (IIc), bp 135-136°C (10^{-3} mm), $\delta^{31}P$ 66 ppm. PMR spectrum in CD_2Cl_2 (TMS, δ, ppm): 1.87 s (8H), 3.47-3.73 m (4H), 7.27-7.83 m (5H), 9.07 d (1H, $^2J_{PH}$ = 14.0 Hz). Found: P, 13.54%. Calculated for $C_{13}H_{18}NP$: P, 14.16%.

2,4-Bis(morpholino)-1,3-diphenyl-1,3-diphosphetane. A mixture of 5.0 g (0.046 mole) phenylphosphine and 7.33 g (0.046 mole) (Ic) was heated at reflux for 30 min. Methanol formed was distilled off using a water pump. The precipitate formed was filtered off and washed on the filter with ether to give 5.46 g (58%) product, mp 167-168°C, $\delta^{31}P$ = −18 ppm. PMR spectrum in CD_2Cl_2 (TMS, δ, ppm): 2.50-2.70 m (8H), 3.40-3.63 m (8H), 3.67 t (2H, $^2J_{PH}$ = 3.4 Hz), 7.27-7.83 m (10H). Found: C, 63.67; H, 6.92; N, 6.59; 15.09%. Calculated for $C_{22}H_{28}N_2O_2P_2$: C, 63.77; H, 6.76; N, 6.76; P, 14.98%.

C-(N,N-Dimethylamino)methylidene-P-phenylphosphine. A sample of 3.89 g (0.033 mole) dimethylacetal of dimethylformamide was added dropwise with cooling to 8.3 g (0.033 mole) bis(trimethylsilyl)phenylphosphine. Me_3SiOMe was distilled off at normal pressure. Distillation gave 4.69 g (87%) product, bp 76°C (10^{-3} mm), $\delta^{31}P$ 68 ppm (68 ppm [2]).

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REACTION OF C,N-DIPHENYLNITRONE WITH N,N-DIMETHYLAMINOMETHYLENE-P-PHENYLPHOSPHINE

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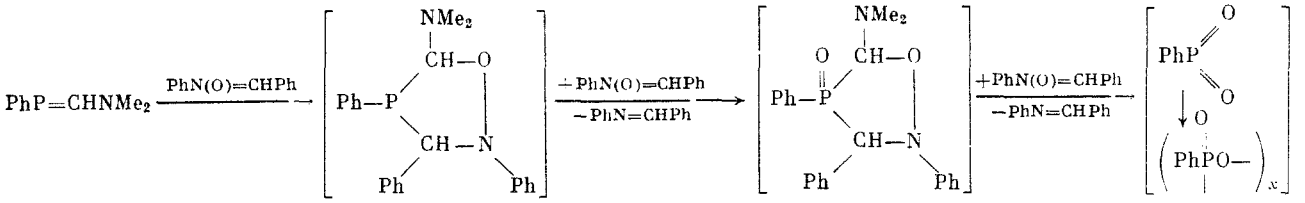
UDC 542.91:547.558.1

C,N-Diphenylnitrone oxidizes N,N-dimethylaminomethylene-P-phenylphosphine to give dioxophenylphosphorane and dimethylformamide and is reduced to benzalaniline.

Examples have been reported for the reactions of nitrones as 1,3-dipolar reagents in [3 + 2] cycloaddition with monocoordinated phosphorus compounds [1] and dicoordinated arsenic compounds [2]. The reaction of nitrones with dicoordinated phosphorus compounds have not yet been reported.

A study of the reaction of nitrones with phosphaalkenes containing the P=C–N structural elements was indicated since such phosphaalkenes have high specific reactivity [3].

We studied the reaction of N,N-dimethylaminomethylene-P-phenylphosphine with C,N-diphenylnitrone. The completion of this reaction requires a 1:3 mole ratio of the starting reagents.



$$+\ O{=}CHNMe_2 + PhN{=}CHPh$$

The only phosphorus-containing product of this reaction is a dioxophenylphosphorane, which proved unstable to polymerization [4]. The IR spectrum of the product of the polymerization of dioxophenylphosphorane lacks bands for OH and P(O)OH groups, while the ^{31}P NMR spectrum shows signals at from 30 to 6 ppm, which is in accord with the literature data [5]. Attempts to detect reaction intermediates using low-temperature ^{31}P NMR spectroscopy were unsuccessful. Methylenephosphine oxides, in contrast to methylenephosphine sulfides, are not trapped by 2,3-dimethylbutadiene in a Diels–Alder reaction [6]. Trapping with methanol [7] is unsuitable in this case since the starting phosphaalkene reacts with alcohols [8].

Benzalaniline and dimethylformamide were isolated and characterized from the products of this reaction. These compounds are formed upon the decomposition of the cycloaddition adducts. A similar type of decomposition leading to azomethine was observed for the adduct of a phosphaalkyne and nitrone [1]. The oxygen atom of the nitrone likely adds to the carbon

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1641-1643, July, 1990. Original article submitted June 8, 1989.

0568-5230/90/3907-1491$12.50