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LETTERS TO THE EDITOR

Diad Phosphorus–Nitrogen Prototropism of Tris(alkylamino)phosphines

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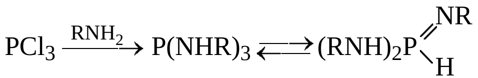
We found that tris(alkylamino)phosphines **I** exist in a tautomeric prototropic equilibrium with PH-iminophosphoranes **II**. The diad phosphorus–nitrogen prototropism of tris(alkylamino)phosphines has not been previously reported, though the attempted synthesis of compounds **I** has been reported by Michaelis. However, a conclusion has been made that these compounds are unstable, which is probably explains the fact that they remained unexplored until now. PH-Iminophosphoranes with strong electron-acceptor substituents of nitrogen (sulfonyl, acyl, silyl) have only been described. From this point of view, tris(trialkylamino)phosphines **I** containing the electron-donor alkyl groups on nitrogen present undoubtful theoretical interest, and their prototropism can be regarded as an independent type of diad phosphorus–nitrogen tautomerism.



$$PCl_3 \xrightarrow{RNH_2} P(NHR)_3 \rightleftarrows (RNH)_2P\overset{\diagup NR}{\underset{\diagdown H}{}}$$

Ia–Ic **IIa–IIc**

R = *i*-Pr (**a**), *t*-Bu (**b**), Ph(Me)CH (**c**).

The tris(alkylamino)phosphines were prepared by the reaction of phosphorus trichloride with 6 mol of alkylamines or 3 mol of alkylamines and 3 mol of triethylamine. Compounds **I** were isolated in high yields as spectroscopically pure liquids or crystalline compounds. The ^{31}P NMR spectra of compounds **I** showed two signals. An upfield signal is a doubled triplet with $^1J_{PH}$ 500–600 Hz (PH bond) and $^2J_{PH}$ 10 Hz (two NH groups). In the ^{31}P–{^1H} NMR spectrum it becomes a singlet assigned to the PH form of compound **I**. The second signal belonging to the NH form is in the range of 90–100 ppm. It is a quartet with $^2J_{PH}$ 10 Hz due to coupling with the protons of the three NH groups. A doublet with the same coupling constant is found in the ^1H NMR spectra. In the IR spectra, the absorption band of the P–H bond is at 2380 cm^{-1}. The tautomeric ratio depends on the nature of the solvent. As the polarity of the solvent inclreases, the aminophosphine content increases and the content of the PH form decreases in the series: $CHCl_3 < CH_2Cl_2 < C_6H_6 < Et_2O < C_6H_{12}$. Inspite of the fact that compounds **Ia**–**Ic** exist mainly in the PH form, they exhibit properties of trivalent phosphorus compounds. They are alkylated with methyl iodide to form ether-insoluble phosphonium salts. In benzene solutions, they react with sulfur with heat evolution to give the corresponding tris(alkylamino)phosphine sulfides **III** in quantitative yield. The same compounds **III** were prepared by the reaction of thiophosphoryl chloride with alkylamines.

$$PSCl_3 \xrightarrow{RNH_2} \underset{\mathbf{III}}{S{=}P(NHR)_3} \xleftarrow{S_8} \mathbf{I} \rightleftarrows \mathbf{II}$$

$$\xrightarrow{MeI} \underset{\mathbf{IV}}{[MeP^+(NHR)_3]I^-}$$

Tris(isopropylamino)phosphine (Ia). Yield 95%, colorless viscous oil decomposing during vacuum distillation. ^{31}P NMR spectrum, δ_P, ppm: 5.52 d.t, $^1J_{PH}$ 555.67 Hz, $^3J_{PH}$ 10 Hz (PH form); 94.24 q, $^3J_{PH}$ 18 Hz (PNH form). Tautomeric ratio 20 : 1 (ether) or 10 : 1 ($CDCl_3$).

Tris(isopropylamino)phosphine sulfide (III). Yield 80%, mp 91–92°C (petroleum ether): 1.13 d (12H, CH_3, $^3J_{PH}$ 6.5), 2.15 m (2H, CH), 3.466 m (3H, NH). ^{31}P NMR spectrum ($CDCl_3$): δ_P 58.76 ppm. Found, %: S 13.80. $C_9H_{24}N_3PS$. Calculated, %: S 13.51.

Tris(isopropylamino)methylphosphonium iodide (IVa). Yield 60%, mp 142°C. ^{31}P NMR spectrum: δ_P 41.87 ppm. Found, %: 9.11. $C_{10}H_{27}IN_3P$. Calculated, %: P 8.93.

Tris(*tert*-butylamino)phosphine (Ib). Yield 75%,

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mp 121°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.26 s [27H, $(CH_3)_3C$], 2.465 m [3H, m (NH)]. ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: –7.24 d ($^1J_{PH}$ 582 Hz, PH form), 88.72 (PNH form). Tautomeric ratio 8 : 92. Found, %: N 16.50. $C_{12}H_{30}N_3P$. Calculated, %: N 16.98.

Tris(2-methylbenzylamino)phosphine (Ic). Yield 30%, mp 190°C. ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 6.93 d ($^1J_{PH}$ 568.34 Hz, PH form), 94.4 (PNH form). Tautomeric ratio 92 : 8.

Tris(2-methylbenzylamino)phosphine sulfide (IIIc). Yield 60%, mp 105–106°C (ethyl acetate–hexane). ^{1}H NMR spectrum ($CDCl_3$) δ, ppm: 1.62 d [9H (CH_3); $^3J_{PH}$ 6.5 Hz], 2.52 m [3H, (CH)], 4.33 m [3H (NH)], 7.17 m [15H (C_6H_5)]. ^{31}P NMR spectrum ($CDCl_3$): δ_P 58.76 ppm. Found, %: P 7.39, S 7.90. $C_{24}H_{30}N_3PS$. Calculated, %: P 7.31, P 7.56.

The NMR spectra were recorded on Varian (300 MHz) and Jeol (90 MHz) spectrometers in deuterated solvents against 85% phosphoric acid. All operations were carried out in thoroughly purified and dried solvents with protection from air moisture.

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