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Some Reactions of Hydrazino- and Aminophosphonium Bromides

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Hydrazonophosphorane has two reaction sites, P=N bond and amino group, and reacts with carbonyl compounds to give hydrazones[1] and phosphazines,[2] respectively.

A reaction at both sites being expected, excess amount of phenyl isocyanate was allowed to react with hydrazonotriphenylphosphorane (I) produced *in situ* from the corresponding phosphonium bromide and potassium *t*-butoxide. The product was *N*-(phenylcarbamoylazomethylene)aniline (II) (12%).

$$\underset{\text{I}}{Ph_3P{=}NNH_2} + 2PhNCO \xrightarrow{-Ph_3PO}$$

$$[PhN{=}C{=}NNHCONHPh] \longrightarrow \underset{\text{II}}{PhN{=}CH{-}N{=}NCONHPh}$$

Oxidation of I was carried out with mercuric oxide at -60°C, the formation of triphenyldiazophosphorane (III) being anticipated, but the reaction products isolated were triphenylphosphine (10%) and oxide (65%).

$$\underset{\text{I}}{Ph_3P{=}NNH_2} \xrightarrow{HgO} \underset{\text{III}}{[Ph_3PN_2]} \xrightarrow{-N_2} Ph_3P \xrightarrow{HgO} Ph_3P{=}O$$

Formation of triphenylphosphine strongly suggests the presence of III as an intermediate. However, III could not be trapped with styrene or diphenylacetylene. III seems to be too unstable to be isolated. Oxidation of I with bromine or lead tetraacetate gave analogous results.

No report has appeared on the reactivity of the amino group in aminotriphenylphosphonium bromide (IV). IV did not react with phenyl isocyanate, but in the presence of triethylamine gave *N*-phenylcarbamoyliminotriphenylphosphorane (V) in a good yield.

$$\underset{\text{IV}}{Ph_3\overset{+}{P}NH_2\ Br^-} + R{-}N{=}C{=}X \xrightarrow{Et_3N} Ph_3P{=}NCXNHR$$

V: $R{=}Ph$, $X{=}O$; VI: $R{=}Ph$, $X{=}S$
VII: $R{=}c\text{-}C_6H_{11}$, $X{=}c\text{-}C_6H_{11}N$

Phenyl isothiocyanate and dicyclohexyl carbodiimide reacted similarly, but *N*-sulfinylaniline gave only tarry material. Acyl and tosyl chlorides gave VIII—X

TABLE 1. *N*-SUBSTITUTED IMINOTRIPHENYLPHOSPHORANES FROM IV

Reactant	Reac. temp. (°C)	R′	$Ph_3P{=}N{-}R'$ Yield (%)	Mp (°C) (lit. mp)
PhNCO	-40	PhNHCO (V)	95	181—182 (178—179)[3]
PhNCS	-40	PhNHCS (VI)	90	172—174 (174—176)[4]
$(c\text{-}C_6H_{11}N{=})_2C$	82	$c\text{-}C_6H_{11}N{=}\underset{\displaystyle c\text{-}C_6H_{11}NH}{\underset{\vert}{C}}{-}$ (VII)	70	138—142
PhCOCl	-40	PhCO (VIII)	93	193—194 (194—195.5)[5]
MeCOCl	-40	MeCO (IX)	40	161—163 (163—165)[6]
$p\text{-}MeC_6H_4SO_2Cl$	20	$p\text{-}MeC_6H_4SO_2$ (X)	30	175—177 (177)[7]

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similarly.

$$\underset{\text{IV}}{Ph_3\overset{+}{P}NH_2\,Br^-} + R\text{-}Cl \xrightarrow{2Et_3N} Ph_3P{=}N\text{-}R$$

$$\text{VIII: } R{=}PhCO;\ \text{IX: } R{=}MeCO$$
$$\text{X: } R{=}p\text{-}MeC_6H_4SO_2$$

The results are summarized in Table 1. The low yield of *N*-acetyl compound (IX) is attributable to easy hydrolysis.

These *N*-substituted iminophosphoranes are usually prepared from iminophosphorane[3,4,8] prepared from IV and sodium in liquid ammonia. In the present method, however, *N*-substituted iminophosphoranes are directly obtained from IV in high yields.

In the course of preparation of IV,[9] it was found that addition of triethylamine gave triphenyl(triphenylphosphoranylideneamino)phosphonium tribromide (XI), which differs from the corresponding bromide,[10,11] in the place of IV in 40% yield. Addition of triethylamine does more harm than good in the preparation of IV.

$$Ph_3PBr_2 \xrightarrow{NH_3} \underset{\text{IV}}{Ph_3\overset{+}{P}NH_2\,Br^-} \xrightarrow[Et_3N]{Ph_3PBr_2} \underset{\text{XI}}{(Ph_3P{=}N\text{-}PPh_3)^+\,Br_3^-}$$

Experimental

Materials. Hydrazinotriphenylphosphonium bromide was prepared according to literature,[12] mp 218—220°C (lit, 210—212°C). Aminotriphenylphosphonium bromide (IV) was prepared from triphenylphosphine dibromide and ammonia gas,[9] mp 242.5—244°C (lit, 243°C).

Reaction of Hydrazonotriphenylphosphorane (I) with Mercuric Oxide. To 0.05 mol of potassium *t*-butoxide in 200 m*l* of anhydrous ether was added 14.9 g (0.04 mol) of hydrazinotriphenylphosphonium bromide with stirring under nitrogen. After filtration of inorganic precipitate under nitrogen, 8.6 g (0.04 mol) of yellow mercuric oxide was added to the deep red filtrate (I) at −50—−60°C. The mixture was stirred for 30 min and the temperature was gradually raised, during which time small bubbles evolved constantly. Precipitates were filtered off at room temperature and the filtrate was evaporated *in vacuo*. The residue was washed with ether to give 7.2 g (64.7%) of triphenylphosphine oxide, mp 153—155°C (from ether). The ethereal washings were evaporated to give 1 g (9.6%) of triphenylphosphine, mp 75—77°C (from petroleum ether).

Reaction of I with Phenyl Isocyanate. Phenyl isocyanate (3 g, 25.2 mmol) was added at room temperature to an ether solution (10 m*l*) of I, prepared from 3.73 g (10 mmol) of the phosphonium bromide, and the reaction mixture was chromatographed on alumina after concentration. After elution of triphenylphosphine oxide with benzene, elution with benzene - dichloromethane (1:1) gave 0.3 g (12%) of brown crystals (II), mp 185—186°C (dec) (from ethyl acetate-petroleum ether (1:3)). IR: 3320 (N-H), 3080 (C-H), 1670 (C=O), 1610 (C=N), and 1560 cm^{-1} (N-H, N=N). MS: *m/e* 252 (M$^+$).

Found: C, 66.94; H, 4.42; N, 22.41%. Calcd for $C_{14}H_{12}N_4O$: C, 66.66; H, 4.79; N, 22.21%.

Preparation of N*-Substituted Iminophosphoranes.* Typical procedures are described.

a) With Phenyl Isocyanate: Phenyl isocyanate (3.6 g, 0.03 mol) in acetonitrile (30 m*l*) was added dropwise to a suspension of 10.7 g (0.03 mol) of IV in 70 m*l* of acetonitrile containing 3.5 g (0.035 mol) of triethylamine with stirring at −30—−40°C for 2 hr. The mixture was stirred at room temperature for one hour, then cooled to −40°C and 150 m*l* of ether was added. The precipitate thus obtained was washed three times with 200 m*l* of water, and dissolved in 200 m*l* of benzene to remove unchanged IV. The benzene solution was dried over anhydrous sodium sulfate. Removal of solvent gave 11.3 g (95%) of white crystals (V), mp 181—182°C (from ethanol).

b) With Dicyclohexyl Carbodiimide: A mixture of 5.3 g (0.015 mol) of IV, 3.1 g (0.015 mol) of the carbodiimide and 2 g (0.02 mol) of triethylamine was refluxed in 50 m*l* of acetonitrile for 6 hr, and 150 m*l* of ether was added at room temperature. After washing with 100 m*l* of water, removal of the solvent gave 5.1 g (70.4%) of iminophosphorane (VII), mp 138—142°C (from acetonitrile). IR: 3300 (N-H), 1610 (C=N), 1560 (N-H), 1305 (P=N), and 1110 cm^{-1} (P-Ph). VII was slowly hydrolyzed with moisture in air to triphenylphosphine oxide (mp 155°C) and dicyclohexylurea (mp 229—230°C). It was, therefore, difficult to obtain an analytically pure sample.

Triphenyl(triphenylphosphoranylideneamino)phosphonium Tribromide. Triethylamine (13.1 g, 0.13 mol) was added to a suspension of triphenyldibromophosphorane (42.2 g, 0.1 mol) in chlorobenzene (120 m*l*) at 95°C, ammonia gas being passed. After stirring for one hour, the mixture was treated in the usual manner. Orange-yellow crystals thus obtained (31 g, 39.8%), mp 170—175°C, were recrystallized twice from acetonitrile, mp 191.5—193.5°C.

Found: C, 56.01; H, 3.82; N, 1.87; Br, 30.14%. Calcd for $C_{36}H_{30}NP_2Br_3$: C, 55.56; H, 3.89; N, 1.80; Br, 30.80%.

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