

were calculated, taking concentrations as equal to activities. A mean value,  $K = 0.14$ , with an average deviation of 0.016, was obtained. Values calculated on the assumption that a pentachloro- or hexachloro-complex acid was formed showed large changes with hydrogen chloride concentration. In Fig. 7 is shown the agreement between optical

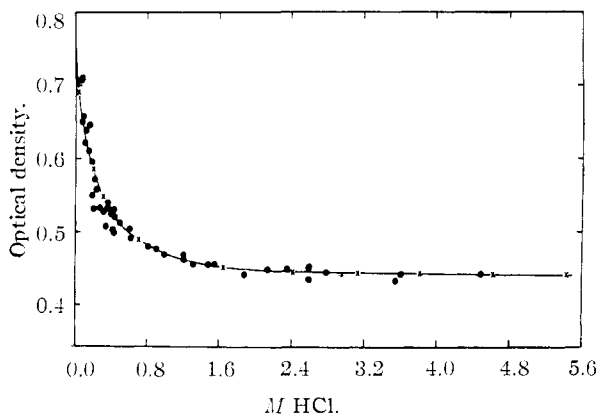


Fig. 7.—Optical density of  $1 \times 10^{-3} M$   $\text{FeCl}_3$  in  $\text{HCl}$ -dioxane solutions at  $340 \text{ m}\mu$ ; ●, experimental; ×, calculated from  $K = 0.14$ .

densities, calculated from the equilibrium expression, using  $K$  equal to 0.14, and a large number of experimental optical densities. The agreement between the observed and calculated optical densities gives an independent basis for concluding that the complex is tetrachloroferric(III) acid.

Preliminary qualitative observations had indicated that, in alkyl ethers, iron(III) chloride was completely converted to tetrachloroferric(III) acid at much lower hydrogen chloride concentrations than in dioxane. To obtain more quantitative in-

formation on this point, a limited number of spectral measurements were made on hydrogen chloride solutions of iron(III) chloride in *n*-butyl ether, tetrahydrofuran and isopropyl ether. From these data the dissociation constants of tetrachloroferric(III) acid were calculated in the same manner as for the dioxane solution. The values obtained are not considered to be precise but to represent correctly the order of magnitude. The dissociation constants in these ethers are listed in Table III. The value for dioxane, and a value calculated from the stability constant reported by Gamelin and Jordan<sup>7</sup> for aqueous solutions, are also listed in Table III.

TABLE III

DISSOCIATION CONSTANTS OF TETRACHLOROFERRIC(III) ACIDS IN VARIOUS SOLVENTS	
Solvent	$K$
Water	95
Dioxane	0.14
Tetrahydrofuran	.0025
<i>n</i> -Butyl ether	.002
Isopropyl ether	.0001

It is evident from the values of the dissociation constants that the chloro-complex is much less stable in water than in the ethers and that the stability in the ethers is least for dioxane. The high value of the dissociation constant in water is understandable, as discussed above, because of the competing reaction of water with iron(III) chloride resulting in the formation of cationic species. Differences in the stability of tetrachloroferric(III) acid in the various ethers must similarly be due to differences in the solvation interaction of the various ethers with iron(III) chloride and with hydrogen chloride.

NOTRE DAME, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

## The Reaction of Chloramine with Some Trisubstituted Phosphines<sup>1</sup>

BY HARRY H. SISLER, ADIB SARKIS, H. S. AHUJA, R. J. DRAGO AND NATHAN L. SMITH

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The reaction of chloramine with trisubstituted phosphines has been explored. The ionic quaternary aminophosphonium chlorides,  $[\text{R}_3\text{PNH}_2]\text{Cl}$ , formed by this reaction are analogs of the 1,1,1-trisubstituted hydrazinium chlorides prepared by the reaction of chloramine with tertiary amines. Stable, crystalline salts are formed by the interaction of the aminophosphonium chlorides with the sodium, potassium or ammonium salts of the following anions: hexafluorophosphate, perchlorate, anthraquinone-2-sulfonate, nitroprusside, periodate, hexachloroplatinate, picrate. Tertiary phosphine oxide and ammonium chloride are products of the aqueous and alkaline hydrolysis of the aminophosphonium chlorides. A mechanism for the reaction of chloramine with tertiary phosphine is suggested.

In earlier communications<sup>2,3</sup> we reported new methods for the synthesis of substituted hydrazines

(1) From a portion of the dissertation by Adib Sarkis in partial fulfillment for the degree of Doctor of Philosophy. This research was reported in part at a Meeting of the American Chemical Society in Chicago, Ill., in September, 1958.

(2) G. M. Omietanski and H. Sisler, *THIS JOURNAL*, **78**, 1211 (1956).

(3) G. M. Omietanski, A. D. Kelmers, R. W. Shellman and H. H. Sisler, *ibid.*, **78**, 3874 (1956).

and hydrazinium salts by the chloramination of primary, secondary and tertiary amines. This paper describes analogous chloramination reactions with a series of tertiary phosphines which produced P-trisubstituted aminophosphonium chlorides in excellent yields. Further chloramination studies of phosphorus compounds as well as of arsenic, anti-

mony and bismuth compounds will be reported in future publications.

The new trisubstituted aminophosphonium chlorides,  $[R_3P-NH_2]Cl$ , were prepared by the direct reaction of chloramine, produced by the gas-phase reaction of chlorine and ammonia, with tertiary phosphines. The P-phenyl-P, P-(cyclo-tetramethylene)-; the P-phenyl-P, P-(cyclopentamethylene)-; the P-triphenyl-; and the P-(tri-*n*-butyl)-aminophosphonium chlorides were all prepared in this way. Ether solutions of chloramine, prepared by the reaction of ammonia with sodium hypochlorite (Raschig process), were also used for the preparation of some aminophosphonium chlorides but this method is, in general, not preferred, because of the inconvenience in obtaining an anhydrous reaction system. The chloramination of the tertiary phosphines occurs in accordance with the equation



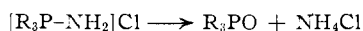
The reaction of N-methylchloramine with triphenylphosphine yielded impure P-(triphenyl)-N-methylaminophosphonium chloride. The formation of this compound was confirmed by the preparation of four derivatives.

The identity of the aminophosphonium ion was established by elemental analysis of the aminophosphonium chlorides and their derivatives, the observation of their infrared spectra and, in one case, by the quantitative isolation of the analogous phosphine oxide as the hydrolysis product of the reaction.

The infrared absorption spectra of the aminophosphonium salts are useful for characterization.<sup>4</sup> The stretching frequencies in PNH- and PNH<sub>2</sub> groups lie in the region 3330–3150 cm.<sup>-1</sup> and the NH<sub>2</sub> deformation occurs near 1550 cm.<sup>-1</sup>,<sup>5,6</sup> The aminophosphonium salts exhibit absorptions at or very near the observed ranges for these groups. The phosphorus-fluorine stretching frequencies of the hexafluorophosphate derivatives were observed in the expected region (980–840 cm.<sup>-1</sup>). The phenylphosphorus group in P-(triphenyl)-aminophosphonium salts exhibits bands in the regions of 1000 and 1440 cm.<sup>-1</sup> as reported in the literature.

A variety of stable, crystalline derivatives was prepared by treating aqueous or ethanolic solutions of the aminophosphonium chlorides with aqueous or ethanolic solutions of the sodium, potassium or ammonium salts of the following anions: hexafluorophosphate, perchlorate, anthraquinone-2-sulfonate, nitroprusside, periodate, hexachloroplatinate, picrate.

The aminophosphonium chlorides react slowly with boiling water to form the corresponding phosphine oxide and ammonium chloride in quantitative yields. Treatment with sodium hydroxide solution hastens the hydrolysis.



The chloramine-tertiary phosphine reactions appear to be almost quantitative based upon the re-

acted tertiary phosphine or chloramine. However, the very hygroscopic, easily hydrolyzed aminophosphonium chlorides are in some instances difficult to isolate in the pure state.

### Experimental<sup>7</sup>

All operations were conducted in a moisture-free, nitrogen atmosphere.

**Materials.**—Tri-*n*-butylphosphine<sup>8</sup> and triphenylphosphine are commercially available. P-Phenyl-P, P-(cyclo-tetramethylene)- and P-phenyl-P, P-(cyclopentamethylene) phosphine were prepared by the method of Gruttner,<sup>9</sup> involving the reaction of phenyldichlorophosphine with the appropriate di-Grignard reagent. The chloramine used in this study was produced by the gas-phase<sup>10</sup> or ammonia-hypochlorite method.<sup>11</sup> The Cl<sub>2</sub>:N<sub>2</sub>:NH<sub>3</sub> ratio used in the chloramine generator was 1:3:30 and the yield of chloramine produced varied from 75 to 95% based on the chlorine used.

**P-(Triphenyl)-aminophosphonium Chloride.**—A typical reaction of triphenylphosphine with chloramine produced by both methods is described.

**Method 1.**—The gaseous effluent of the chloramine generator (*ca.* 0.04 mole of chloramine per hr.) was passed directly into a solution of triphenylphosphine (10.0 g.) in sodium-dried ether (70 ml.) for 45 minutes at 15–20°. The reaction mixture was allowed to warm to room temperature (accompanied by evaporation of excess ammonia) and then washed thoroughly with ether to remove adhering triphenylphosphine. The washed residue consisted of the aminophosphonium chloride contaminated with ammonium chloride produced by the decomposition of chloramine. To remove the contaminant, the residue was treated with a minimum of water to form a paste and then filtered quickly. This product was washed with benzene to remove any triphenylphosphine oxide formed by hydrolysis. The yield of the crude P-(triphenyl)-aminophosphonium chloride, as based on the chloramine retained in the reaction mixture, was nearly quantitative.

**Method 2.**—One hundredth mole of chloramine<sup>11</sup> in 25 ml. of ether was added slowly to 0.01 mole of triphenylphosphine in 25 ml. of ether. A vigorous reaction ensued, resulting in the deposition of a white, crystalline product. The isolation procedure was conducted as described above. The yield of the crude aminophosphonium salt, as based on the chloramine reacted, was practically quantitative. Table I provides physical and analytical data for the P-(triphenyl)-aminophosphonium salts.

**Reaction of Triphenylphosphine with N-Methylchloramine.**—N-Methylchloramine was prepared by the reaction of methylamine with sodium hypochlorite in alkaline solution in a manner analogous to the Raschig method for production of chloramine.<sup>12</sup> One hundredth mole of N-methylchloramine in 25 ml. of ether was added to 0.01 mole of triphenylphosphine in 25 ml. of ether. A vigorous reaction ensued resulting in the formation of a colorless, crystalline product. Because of the ease of hydrolysis, the P-(triphenyl)-N-methylaminophosphonium chloride was very difficult to purify. However, the synthesis of the compound was confirmed by the formation of the following salts: hexafluorophosphate, perchlorate, hexachloroplatinate, picrate. The physical and analytical data for these derivatives are summarized in Table II.

***p*-(Tri-*n*-butyl)-aminophosphonium Chloride.**—A typical reaction of tri-*n*-butylphosphine with chloramine is described. The gaseous stream of chloramine and ammonia from the generator (*ca.* 0.04 mole of chloramine per hr.) was passed into 30.0 g. of tri-*n*-butylphosphine chilled to 5–10°. After 30 minutes, the reaction vessel became clogged with P-(tri-*n*-butyl)-aminophosphonium chloride. The product was warmed to room temperature and the ammonia allowed to

(7) All melting points are uncorrected. The microanalyses are by Galbraith Laboratories, Knoxville, Tenn.

(8) Kindly supplied by the Food Machinery and Chemical Corporation, New York, N. Y.

(9) G. Gruttner and M. Wiernik, *Ber.*, **48**, 1473 (1915); G. Gruttner and E. Krause, *ibid.*, **49**, 437 (1916).

(10) H. H. Sisler and G. M. Omietanski, *Inorg. Syntheses*, **V**, 91 (1957).

(11) G. H. Coleman and H. L. Johnson, *ibid.*, **1**, 59 (1939).

(12) F. Raschig, *Ber.*, **40**, 4580 (1907).

(4) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

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(6) D. E. Corbridge, *J. Appl. Chem.*, **6**, 456 (1956).

TABLE I  
 P-(TRI-PHENYL)-AMINOPHOSPHONIUM SALTS [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PNH<sub>2</sub>]<sup>+</sup>X<sup>-</sup>

Anion	M.p., °C.	Emp. formula	C, % Calcd. Found	H, % Calcd. Found	N, % Calcd. Found	P, % Calcd. Found	X, % Calcd. Found
Chloride	230-232	C <sub>18</sub> H <sub>17</sub> ClNP	68.90	5.42	4.46	9.89	11.32 <sup>a</sup>
			68.50	5.75	4.40	9.78	11.18
Hexafluorophosphate	185-187	C <sub>18</sub> H <sub>17</sub> F <sub>6</sub> NP <sub>2</sub>	51.06	4.02	3.32	14.66	26.95 <sup>b</sup>
			50.90	4.11	3.32	14.64	26.70
Perchlorate	172-175	C <sub>18</sub> H <sub>17</sub> ClNO <sub>4</sub> P	57.22	4.50	3.71	8.21	9.40 <sup>c</sup>
			57.43	4.67	3.65	8.17	9.44
Anthraquinone-2-sulfonate	214-216	C <sub>22</sub> H <sub>24</sub> NO <sub>5</sub> SP	67.96	4.25	2.48	5.49	5.66 <sup>d</sup>
			68.05	4.23	2.59	5.23	5.61
Nitroprusside	193-195	C <sub>23</sub> H <sub>17</sub> N <sub>6</sub> OPFc	63.75	4.40	14.51	8.03	
			63.59	4.47	14.89	8.83	
Periodate	163-165	C <sub>18</sub> H <sub>17</sub> INO <sub>4</sub> P	46.05	3.62	2.98	6.61	27.07 <sup>e</sup>
			45.80	3.57	3.11	6.56	27.19
Hexachloroplatinate	190-193	C <sub>18</sub> H <sub>17</sub> ClNPt	44.80	3.53	2.90	6.43	
			43.79	3.37	2.82	6.29	

<sup>a</sup> X = Cl. <sup>b</sup> F. <sup>c</sup> Cl. <sup>d</sup> S. <sup>e</sup> J.

 TABLE II  
 P-(TRI-PHENYL)-N-METHYL-AMINOPHOSPHONIUM SALTS [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PNH(CH<sub>3</sub>)]<sup>+</sup>X<sup>-</sup>

Anion	M.p., °C.	Emp. formula	C, % Calcd. Found	H, % Calcd. Found	N, % Calcd. Found	P, % Calcd. Found
Hexafluorophosphate	185-188	C <sub>19</sub> H <sub>19</sub> F <sub>6</sub> NP <sub>2</sub>	52.17	4.35	3.20	14.18
			52.79	4.38	3.23	13.96
Perchlorate	175-177	C <sub>19</sub> H <sub>19</sub> ClNO <sub>4</sub> P	58.23	4.34	3.57	7.92
			58.63	4.87	3.51	8.14
Hexachloroplatinate	185-187	C <sub>19</sub> H <sub>19</sub> Cl <sub>6</sub> NPt	45.96	3.83	2.82	6.25
			45.88	3.86	2.52	5.98
Picrate	118-120	C <sub>25</sub> H <sub>21</sub> N <sub>4</sub> O <sub>7</sub> P	57.69	4.04	10.77	5.96
			57.78	4.31	10.86	5.99

 TABLE III  
 P-(TRI-*n*-BUTYL)-AMINOPHOSPHONIUM SALTS [(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>PNH<sub>2</sub>]<sup>+</sup>X<sup>-</sup>

Anion	M.p., °C.	Emp. formula	C, % Calcd. Found	H, % Calcd. Found	N, % Calcd. Found	P, % Calcd. Found	Cl, % Calcd. Found
Chloride	62-65 (scaled tube)	C <sub>12</sub> H <sub>29</sub> ClNP	56.78	11.52	5.52	12.21	13.97
			56.76	11.65	5.48	12.28	14.02
Hexafluorophosphate	72-73	C <sub>12</sub> H <sub>29</sub> F <sub>6</sub> NP	39.67	8.04	3.86	17.05	
			39.67	7.92	3.92	16.91	
Anthraquinone-2-sulfonate	89-90	C <sub>26</sub> H <sub>36</sub> NO <sub>5</sub> SP	61.76	7.18	2.77	6.13	
			61.32	7.07	2.77	6.11	

evaporate. The solid was filtered, washed with ether and dried *in vacuo* at room temperature. It weighed 5.8 g. (92% of theory based on tributylphosphine used). The data on the P-(tri-*n*-butyl)-aminophosphonium salts are summarized in Table III.

**P-Phenyl-P,P-(cyclohexamethylene)-aminophosphonium Chloride.**—A gaseous mixture of chloramine and ammonia was passed through an ethereal solution (40 ml.) of P-phenyl-P,P-(cyclohexamethylene)-phosphine (2.0 g.) at 5 to 10° for 10 minutes. The product was washed with ether and dried *in vacuo* at room temperature. Satisfactory analytical results were not achieved because of the hygroscopic nature of the product, in addition to the difficulty of freezing the raw product from ammonium chloride. However, a number of stable crystalline derivatives were obtained from the crude aminophosphonium chloride. Calculated on the amount of chloramine used, the yield of crude product was essentially quantitative. For physical and analytical data on the P-phenyl-P,P-(cyclohexamethylene)-aminophosphonium salts (see Table IV).

**P-Phenyl-P,P-(cyclopentamethylene)-aminophosphonium Chloride.**—This compound was prepared by the reaction of chloramine with P-phenyl-P,P-(cyclopentamethylene)-phosphine in the manner described above. The product was isolated as colorless crystals, soluble in water and hygroscopic. The yield of crude product based on the chloride ion present in the reaction mixture (which is a measure of the total chloramine introduced) was nearly quantitative. The salt was sufficiently pure to be used for other syntheses but could not be further purified by the usual solvents or solvent mixtures. The physical and analytical data for the derivatives are shown in Table V.

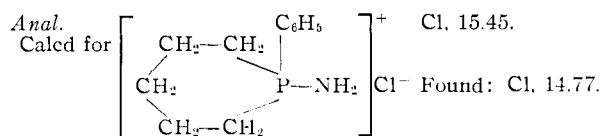


TABLE IV

P-PHENYL-P,P-(CYCLOTETRAMETHYLENE)-AMINOPHOSPHONIUM CHLORINE

$$\left[ \begin{array}{c} \text{CH}_2-\text{CH}_2 \quad \text{C}_6\text{H}_5 \\ | \quad \quad \quad | \\ \text{P} \\ | \quad \quad \quad | \\ \text{CH}_2-\text{CH}_2 \quad \text{NH}_2 \end{array} \right] \text{X}$$

Anion	M.p., °C.	Emp. formula	C, % Calcd. Found	H, % Calcd. Found	N, % Calcd. Found	P, % Calcd. Found
Hexafluorophosphate	76-76	C <sub>10</sub> H <sub>15</sub> F <sub>6</sub> NP <sub>2</sub>	36.93	4.65	4.31	
			36.14	4.82	4.39	
Anthraquinone-2-sulfonate	207-208	C <sub>24</sub> H <sub>22</sub> NO <sub>7</sub> SP	61.66	4.74	3.00	6.63
			60.88	4.78	3.11	6.66
Picrate	171-172	C <sub>16</sub> H <sub>17</sub> N <sub>4</sub> O <sub>7</sub> P	47.06	4.02	13.72	7.59
			46.82	3.99	13.91	7.50

TABLE V

P-PHENYL-P,P-(CYCLOPENTAMETHYLENE)-AMINOPHOSPHONIUM SALTS

$$\left[ \begin{array}{c} \text{CH}_2-\text{CH}_2 \quad \text{C}_6\text{H}_5 \\ | \quad \quad \quad | \\ \text{P} \\ | \quad \quad \quad | \\ \text{CH}_2-\text{CH}_2 \quad \text{NH}_2 \end{array} \right] \text{X}$$

Anion	M.p., °C.	Emp. formula	C, % Calcd. Found	H, % Calcd. Found	N, % Calcd. Found	P, % Calcd. Found
Hexafluorophosphate	120-121	C <sub>16</sub> H <sub>17</sub> F <sub>6</sub> NP	38.95	5.05	4.13	18.26
			38.86	5.08	4.39	17.98
Anthraquinone-2-sulfonate	243 (decomp.)	C <sub>25</sub> H <sub>24</sub> NO <sub>7</sub> SP	62.36	5.02	2.91	6.43
			61.42	5.17	3.32	6.43
Picrate	150-151	C <sub>22</sub> H <sub>21</sub> N <sub>4</sub> O <sub>7</sub> P			13.33	7.37
					13.11	7.25

**Trisubstituted Aminophosphonium Hexafluorophosphates.**—These salts were prepared by treating an aqueous or dilute ethanolic solution of the corresponding aminophosphonium chloride with a saturated aqueous solution of potassium hexafluorophosphate. The precipitates were filtered, washed with cold water and recrystallized from dilute ethanol. Many of the aminophosphonium hexafluorophosphates were prepared directly from the untreated reaction products since the ammonium chloride contamination did not interfere with the reaction. The data on the aminophosphonium hexafluorophosphates are included under the corresponding aminophosphonium chloride.

**Trisubstituted-aminophosphonium Anthraquinone-2-sulfonates.**—The anthraquinone-2-sulfonates were made by the simple metathesis of aqueous ethanolic solutions of the aminophosphonium chlorides with ethanolic solutions of sodium anthraquinone-2-sulfonate. The data on the trisubstituted aminophosphonium anthraquinone-2-sulfonates are provided under the respective aminophosphonium chlorides.

**Miscellaneous Aminophosphonium Salts.**—The perchlorate, chloroplatinate, picrate, nitroprusside, periodate derivatives were prepared by treating the corresponding aminophosphonium chloride in water or ethanol with an aqueous or ethanolic solution of the appropriate sodium or potassium salt. The data on the miscellaneous salts are summarized under the respective aminophosphonium chlorides.

**Hydrolysis of Trisubstituted-aminophosphonium Chlorides.**—Several experiments on the hydrolysis of [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PNH<sub>2</sub>]<sup>+</sup>Cl<sup>-</sup> and [(C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>PNH<sub>2</sub>]<sup>+</sup>Cl<sup>-</sup> were conducted. The corresponding phosphine oxides are obtained quantitatively in these hydrolyses. A typical experiment for the aqueous and alkaline hydrolysis of the latter is described.

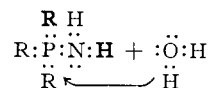
(a) **With Water.**—P-(Tri-*n*-butyl)-aminophosphonium chloride (1.159 g.) was heated with water on a water-bath for 50 hr. at 60-70°. The reaction mixture was extracted with ether. The ether was removed and the oily residue distilled, b.p. 165-170° (30 mm.). This product gave an infrared absorption spectrum compatible with that of an authentic sample of tributyl phosphine oxide. Evaporation of the water phase afforded 0.241 g. of NH<sub>4</sub>Cl (yield quantitative). The identity of the ammonium chloride was

checked by Volhard analysis of chloride. *Anal.* Calcd. for NH<sub>4</sub>Cl: Cl, 66.29. Found: 65.91.

(b) **With Alkali.**—P-(Tri-*n*-butyl)-aminophosphonium chloride (1.0574 g.) in 25 ml. of 1 *N* sodium hydroxide was kept for 48 hr. at room temperature. The tributylphosphine oxide was isolated and identified as described in (a). The yield of ammonia produced was determined by Kjeldahl analysis. Calcd.: 0.7095 g. NH<sub>3</sub>. Found: 0.6994 g. NH<sub>3</sub>.

### Discussion

The reaction of chloramine and methylchloramine with trisubstituted phosphines to form compounds analogous to the 1,1,1-trisubstituted hydrazinium compounds has been established. Kinetic studies of the reactions of trisubstituted phosphines with chloramine have not yet been made. However, by analogy with the reaction of chloramine with ammonia and amines,<sup>2</sup> it may be suggested that the chloramine-tertiary phosphine reactions occur by an S<sub>N</sub>2 type mechanism (bimolecular displacement). With the chloramine molecule acting as electron acceptor. The apparently greater susceptibility of ions of the type R<sub>3</sub>PNH<sub>2</sub><sup>+</sup> than of trisubstituted hydrazinium ions, R<sub>3</sub>NNH<sub>2</sub><sup>+</sup>, to hydrolysis may be related to the availability of d-orbitals on the phosphorus atom. This would facilitate the attack by a water molecule as



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