

starting material was recovered as a colorless precipitate, m.p. and mixed m.p. 130–131°.

*Reaction of  $\alpha$ -aminoisobutyric acid with sodium hypochlorite.* The ultraviolet spectrum of a mixture made by adding a sodium hypochlorite solution to a suspension of  $\alpha$ -aminoisobutyric acid in water at 15° had a strong absorption maximum at 266 m $\mu$ , suggesting that acetone had been formed. The mixture was distilled in the manner described in the section on *N*-chloroisopropylamine, and the infrared spectrum of a dried carbon tetrachloride extract of the distillate was examined in a 0.1 mm. cell. The spectrum was exactly that expected of a mixture of *N*-chloroisopropylamine and acetone in this solvent. Bands characteristic of IV only were found at 2900 m, 2830 w, 1635 m, 1618 m, 1236, 1075 m, 1054 m, and 699 vs cm.<sup>-1</sup>, acetone bands were at 1720 vs, 1218 vs, 1089 w, and 897 w cm.<sup>-1</sup>, and bands due to both compounds appeared at 2980 m, 2940 m, 1436, and 1360 vs cm.<sup>-1</sup>

To a stirred solution of  $\alpha$ -aminoisobutyric acid (1.08 g.,  $1.05 \times 10^{-2}$  mole) in 500 ml. of 0.25*M* borate buffer (*pH* 9) was added dropwise (15 min.) a solution of sodium hypochlorite (0.745 g.,  $10^{-2}$  mole) in 500 ml. of 0.25*M* borate buffer at 23°. The clear solution, which had an odor of *N*-chloroisopropylamine, was allowed to stand at room temperature and aliquot portions were titrated iodometrically. After 5, 31, and 55 min., 2.5, 15, and 39 hr. there remained 36, 16, 12.8, 11.5, 11.0, and 8.9% respectively of the original active chlorine. The ultraviolet spectrum of the reaction

mixture after 23 hr. exhibited strong absorption below 240 m $\mu$ , presumably due to IV and the slight excess of  $\alpha$ -aminoisobutyric acid used, and a well-defined shoulder ( $\lambda_{\max}$  260,  $\lambda_{\min}$  247 m $\mu$ ) ending at 305 m $\mu$ , above which the solution was transparent. The shoulder must be caused by acetone (lit.<sup>20</sup>  $\lambda_{\max}^{0.04M}$  264 m $\mu$ ,  $\epsilon = 18.8$ ); its concentration may be estimated very roughly from the absorbance at 260 m $\mu$  (0.14) to be in the neighborhood of  $7.5 \times 10^{-2}M$  (75% yield). The conversion to IV in the first hour cannot have been more than about 12%, while that to acetone may have been 88% and was probably at least 70%. No indication of hypochlorite was found in the spectrum. During the first hour portions of the reaction mixture oxidized potassium iodide to iodine at *pH* 9, which hypochlorite will do, but after 1 hr., did not give iodine until acidified, which is typical of very weak oxidizing agents, including IV.

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SOUTH GATE, CALIF.

(20) F. O. Rice, *J. Am. Chem. Soc.*, **42**, 731 (1920).

[CONTRIBUTION FROM SOUTHERN REGIONAL RESEARCH LABORATORY,<sup>1</sup> UNITED STATES DEPARTMENT OF AGRICULTURE]

## N-Methyl Amides of Phosphorus(V) Acids<sup>2</sup>

RICHARD L. ARCENEUX, J. G. FRICK, JR., ETHEL K. LEONARD, AND J. DAVID REID

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A number of *N*-methyl amides of phosphorus (V) acids, have been prepared and characterized. Reactions involving thermal deamination and salt formation were studied on some of the compounds.

In the research conducted at the Southern Regional Research Laboratory leading to the development of flame-retardant finishes for cotton textiles, one phase of the work was directed toward the practical use of amides of phosphorus(V) acids. This report deals with the preparation and properties of some *N*-methyl amides of the acids which were studied during the course of this investigation. Most of the compounds have not been reported previously.

In general the amides were prepared by the addition of the acid chloride of a phosphoric or phosphonic acid to an excess of methylamine in inert solvent at reduced temperature under anhydrous conditions. The amine served also as an acid ac-

ceptor. The properties of the *N*-methyl amides which were prepared are shown in Table I. With the exception of *N,N'*-dimethyl-*P*-trichloromethylphosphonic diamide and *N,N',N''*-trimethylphosphorothionic triamide all of the amides are very soluble in water. Michaelis<sup>4</sup> has reported that the imido derivatives of phosphorothionic triamides have better organic solubility than the corresponding oxygen analogs. The same solubility relationship was found to hold for the sulfur-oxygen analogs examined in this investigation.

Michaelis<sup>4</sup> described the synthesis of *N,N'*-disubstituted phosphoramidic imides, with the structure RHN<sub>2</sub>P(O):NR, by the thermal decomposition of trisubstituted phosphoramides. These compounds were reported as being monomeric when the substituents are alkyl groups and dimeric when the substituents are aryl groups. The thionic analogs were reported to be monomeric also.

(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) This is a report on one phase of a program of research on the flame-resistant treatment of cotton textiles, being supported at the Southern Utilization Research and Development Division by funds supplied by the Air Research and Development Command, United States Air Force and conducted under the general supervision of the Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

(3) J. R. Geigy A.-G., Brit. Patent 790,663, Feb. 12, 1958.

(4) A. Michaelis, *Ann.*, **407**, 290 (1915).

TABLE I  
 N-METHYL AMIDES OF PHOSPHORUS(V) ACIDS

Formula	Yield, %	B.P.		$n_D^{25}$	Analysis %						
		at 3 mm.	M.P.		N		P		Other		
					Calcd.	Found	Calcd.	Found	Element	Calcd.	Found
$C_2H_5OP(O)(NHCH_3)_2$	40	132-6 <sup>a</sup>	...	1.4489	18.4	18.4	20.4	20.2	....	..	..
$P(O)(NHCH_3)_3^b$	66	..	102-3	..	30.6	30.0	22.6	23.0	....	..	..
$P(S)(NHCH_3)_3$	87	..	105-7	..	27.4	27.1	20.2	20.2	Sulfur	20.9	20.7
$P(O)[N(CH_3)_2]_2NHCH_3$	47	137-43	...	1.4551	25.4	24.9	..	..	....	..	..
$CCl_3P(O)(NHCH_3)_2$	38	..	133-5	..	12.4	12.3	13.8	13.6	Chlorine	47.2	47.2
$[(CH_3)_2NP(O)NCH_3]_2^c$	..	..	168-170	..	23.3	22.8	25.8	23.8	....	..	..
$[CH_3HN(P(S)NCH_3)]_2$	95	..	220-5	..	22.9	22.6	25.4	25.5	Sulfur	26.2	26.5
$(C_2H_5O)_2P(O)NCH_3-$ $\begin{array}{c} O \\ \diagup \quad \diagdown \\ (CH_2CHCH_2) \end{array}$	40	118-9	...	1.4365	6.3	6.0	13.9	13.3			

<sup>a</sup> Lit. <sup>b</sup> B. p. 110-111 at 0.005 mm. <sup>b</sup> Previously reported as a liquid. <sup>c</sup> Product formed during distillation of  $P(O)[N(CH_3)_2]_2NHCH_3$ .

In this investigation, it was found that thermal deamination occurred when no less than two amido groups, at least one of which is not completely substituted, are attached to the phosphorus. In no case, however, was a monomeric product isolated. *N,N',N''*-Trimethylphosphoric triamide yielded a resinous product with higher than dimeric molecular weight, presumably a polymer. Ethyl *N,N'*-dimethylphosphorodiamidate also yielded a resinous product. Diethyl *N*-methylphosphoramidate did not deaminate below 250°.

Pentamethylphosphoric triamide was partially deaminated on distillation. The crystalline "imide" formed was dimeric.

*N,N',N''*-Trimethylphosphorothionic triamide also gave, on thermal deamination, a crystalline "imide" which had a dimeric molecular weight.

It has been reported by Arbuzov, Alimov, and Zvereva<sup>5</sup> that sodium salts can be formed from the *N*-methyl amides of phosphorus (V) acids by reaction of the amide with metallic sodium. Diethyl *N*-methyl-*N*-(2,3-epoxypropyl) phosphoramidate was prepared by treating the sodium salt of diethyl *N*-methylphosphoramidate with epichlorohydrin. An attempt was made to prepare the *N,N'*-bis(2,3-epoxypropyl) derivative of ethyl *N,N'*-dimethylphosphorodiamidate by a similar procedure. Sodium, however, would react with the diamidate only in equimolar quantities. Epichlorohydrin reacted with the monosodium salt to yield a product containing epoxy groups. The product could not be purified but is believed to be crude ethyl *N,N'*-dimethyl-*N*-(2,3-epoxypropyl) phosphorodiamidate.

The reaction of epichlorohydrin with the sodium salt of the *N*-methyl amides probably proceeds by reaction of the epoxy group, followed by dehalogenation of the sodium alkoxide formed to regenerate an epoxy group. Treatment of the

sodium salt of diethyl *N*-methylphosphoramidate with benzyl chloride gave only a small yield of a product that appeared to be diethyl *N*-benzyl-*N*-methylphosphoramidate.

#### EXPERIMENTAL

*Ethyl N,N'*-dimethylphosphorodiamidate. Ethyl phosphorodichloridate<sup>6</sup> 210 g. (1.29 moles) was added dropwise with stirring to 180 g. (5.80 moles) of methylamine dissolved in 1 l. of dry benzene at 5 to 10°. After addition was completed, the mixture was allowed to warm to room temperature and stand overnight. The methylamine hydrochloride was removed by filtration, and the benzene was distilled under vacuum. The residue, 123 g., was crude ethyl *N,N'*-dimethylphosphorodiamidate. A 25 g. portion was vacuum distilled and yielded 10 g. of purified material.

*N,N',N''*-Trimethylphosphoric triamide. Phosphoryl chloride, 153.5 g. (1.0 mole) was added dropwise with stirring to methylamine, 186 g. (6.0 moles) in 1.4 l. of dry chloroform at -40 to -20°. The mixture was allowed to stand overnight at room temperature and the methylamine hydrochloride, 162.1 g. (79.5%), removed by filtration. The filtrate was evaporated under reduced pressure and the residue dissolved in methanol. The remainder of the methylamine hydrochloride was neutralized with an amount of potassium hydroxide in methanol equivalent to the unprecipitated hydrochloride. The potassium chloride formed was filtered and the filtrate evaporated under reduced pressure. The residual oil was taken up in boiling benzene and boiled until the remaining methanol was removed. The solution was filtered hot and *N,N',N''*-trimethylphosphoric triamide crystallized on cooling.

*N,N',N''*-Trimethylphosphorothionic triamide. Phosphorothionyl chloride, 34 g. (0.2 mole), was added dropwise with stirring to 37 g. (1.2 moles) of methylamine in 250 ml. of dry toluene at -30° to -20°. The methylamine hydrochloride and product separated as a gummy precipitate. After addition was completed, the mixture was allowed to warm to room temperature with stirring and stand overnight. The mixture was heated to boiling and filtered hot to remove the methylamine hydrochloride. *N,N',N''*-Trimethylphosphorothionic triamide crystallized from the filtrate.

*Pentamethylphosphoric triamide and trimethylphosphoramidic imide*. Tetramethylphosphorodiamidic chloride,<sup>7</sup> 85.25 g. (0.5 mole), was added dropwise with stirring to 36 g.

(5) B. A. Arbuzov, P. I. Alimov, and M. A. Zvereva, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1042 (1954); *Chem. Abstr.*, 50, 2151 (1956).

(6) B. C. Saunders, G. J. Stacey, F. Wild, and I. G. E. Wilding, *J. Chem. Soc.*, 699 (1948).

(7) J. E. Gardiner and B. A. Kilby, *J. Chem. Soc.*, 1769 (1950).

(1.16 mole) of methylamine in 400 ml. of dry benzene between 5° and 10°. After addition was completed, the mixture was allowed to warm to room temperature and stand overnight. The methylamine hydrochloride was removed by filtration and the benzene distilled from the filtrate under reduced pressure. The residue was distilled under reduced pressure. Some deamination occurred during distillation with the release of dimethylamine. Crystals formed in the distillate and were separated by filtration. The filtrate, 39 g. was pentamethylphosphoric triamide.

The crystalline material was washed with ether and could not be further purified. This product is believed to be trimethylphosphoramidate.

Mol. wt. 242 determined ebullioscopically<sup>8</sup> in benzene.

*N,N'*-Dimethyl-*P*-trichloromethylphosphonic diamide. Methylamine, 40 g. (1.28 moles), in 500 ml. of chloroform was cooled to 2° and trichloromethylphosphonic dichloride<sup>9</sup> 75 g. (0.32 mole), in 100 ml. chloroform was added dropwise with stirring below 8°. The mixture was stirred for 1 hr. after addition was complete and then allowed to warm to room temperature. The methylamine hydrochloride was removed by filtration and the chloroform distilled from the filtrate under reduced pressure. The residue was recrystallized from benzene yielding 27 g. of *N,N'*-dimethyl-*P*-trichloromethylphosphonic diamide, m.p. 122–124°. Recrystallization from water raised the m.p. to 133–135°.

*Thermal deaminations.* A sample, 20 g., of the amides listed below was heated at 200–250° under vacuum until a weight loss equal to one equivalent of methylamine was observed. This required 4 to 8 hr. of heating. *N,N',N''*-Trimethylphosphoric triamide yielded a resinous solid.

*Anal:* Calcd. for C<sub>3</sub>H<sub>7</sub>N<sub>3</sub>OP: N, 26.4.

Found: N, 26.2. Mol. wt. 301, determined ebullioscopically<sup>8</sup> in methanol.

*N,N',N''*-Trimethylphosphorothionic triamide yielded a crystalline solid which was recrystallized from toluene.

Mol. wt. 244, determined ebullioscopically in benzene. (See Table I.)

(8) A. W. C. Menzies and S. L. Wright, Jr., *J. Am. Chem. Soc.*, **43**, 2314 (1921).

(9) K. C. Kennard and C. S. Hamilton, *J. Am. Chem. Soc.*, **77**, 1156 (1955).

Ethyl *N,N'*-dimethylphosphorodiamidate yielded a resinous-like material.

*Anal:* Calcd. for C<sub>2</sub>H<sub>8</sub>NO<sub>2</sub>P: N, 11.6. Found: N, 15.5.

Diethyl *N*-methylphosphoramidate did not diaminate at 250°.

*Reactions of sodium salts.* Diethyl *N*-methylphosphoramidate,<sup>6,10</sup> 27 g. (0.15 mole), was dissolved in 100 ml. of dry benzene and 3.5 g. (0.15 mole) of sodium sand was added. There was a slight temperature rise and the evolution of hydrogen. Warming the mixture to 50° was necessary to completely dissolve the sodium. The solution was added to epichlorohydrin, 14 g. (0.15 mole), and the mixture stirred for 1 hr. at 50°, then allowed to stand overnight at room temperature. The solution was decanted off leaving a gummy residue. The solvent was removed under vacuum from the decanted solution, and the residue distilled under reduced pressure, yielding 13.0 g. (40%) diethyl *N*-methyl-*N*-(2,3-epoxypropyl)phosphoramidate.

A similar preparation using 30.4 g. (0.2 mole) ethyl *N,N'*-dimethylphosphorodiamidate, 9.2 g. (0.4 mole) sodium sand, and 20 g. (0.2+ mole) epichlorohydrin yielded 4.6 g. unreacted sodium and 34 g. of undistillable oil.

*Anal:* Calcd. for C<sub>7</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>P: Oxirane oxygen 7.8. Found: Oxirane oxygen<sup>11</sup> 6.6.

An attempted preparation of diethyl *N*-benzyl-*N*-methylphosphoramidate by the reaction of equimolar quantities of diethyl-*N*-methyl phosphoramidate, sodium sand, and benzyl chloride by this procedure yielded only 1 g. of product. B.p. 110–119° (1 mm.).

*Anal:* Calcd. for C<sub>12</sub>H<sub>20</sub>NO<sub>2</sub>P: N, 5.45. Found: N, 5.35.

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NEW ORLEANS, LA.

(10) H. McCombie, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 921 (1945).

(11) A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF TULANE UNIVERSITY]

## Pyrolysis of Thiophene<sup>1</sup>

HANS WYNBERG AND A. BANTJES

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Pyrolysis of thiophene at 850° gives a mixture of the three isomeric bithiophenes in 7–8% conversion. Mass spectral analysis of the pyrolyzate furnishes evidence for the occurrence of a variety of additional condensation products.

In 1894 Auwers and Bredt<sup>2</sup> published a brief study on the isolation of two crystalline fractions, m.p. 44–48° and 127–128°, respectively, from the pyrolyzate when thiophene was passed through a tube at "cherry-red" heat. In view of the proximity of these melting points as well as those of the derived bromides to those reported for authentic 2,2'- and 3,3'-bithiophene, the authors concluded that these compounds were present in their crystal-

line pyrolyzate. Inspection of the data in Table I appears to confirm these conclusions.

We have now reinvestigated the pyrolysis of thiophene, and have found that passage through a Vycor glass tube at 800–850° converts 40% of the thiophene into other products. Table II contains the results of the initial fractionation of this crude pyrolyzate.

Fraction I could be separated into an oily fraction A (38%) and a crystalline fraction B (55%) by repeated sublimation. Mass spectral analysis, as well as the infrared and ultraviolet spectra of frac-

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(2) K. Auwers and T. V. Bredt, *Ber.*, **27**, 1741 (1894).