

TABLE 6: Formation Constants of the One-to-One Complexes of Various Metal Ions with Organic Acids in Solution at Room Temperature

Acid	Solvent	$K_f, 10^3 \text{ l/mole}$				
		Ni ²⁺	Mn ²⁺	Cd ²⁺	Co ²⁺	Zn ²⁺
Succinic	H ₂ O	0.061	0.11	0.28	0.50	0.88
	20 % Etanol-H ₂ O	0.11	0.18	0.80	0.87	1.5
	20 % Acetone-H ₂ O	0.059	0.20	0.98	1.3	1.7
Malonic	H ₂ O	0.74	0.29	0.55	0.59	1.8
	20 % Etanol-H ₂ O	0.91	0.64	1.4	1.1	2.3
	20 % Acetone-H ₂ O	1.5	0.76	0.70	1.7	2.3
o-Phthalic	H ₂ O	0.24	0.49	0.65	1.1	2.0
	20 % Etanol-H ₂ O	0.45	0.79	2.2	1.3	2.3
	20 % Acetone-H ₂ O	0.43	0.80	1.2	1.8	2.0
Tartaric	H ₂ O	0.35	1.0	1.1	1.5	2.2
	20 % Etanol-H ₂ O	0.34	1.3	1.9	1.8	2.4
	20 % Acetone-H ₂ O	0.90	1.5	1.4	2.0	2.6
Reference		*	1	*	1	1

*The present study.

“naked” metal ions may play a major role on the determination of relative stabilities of the complexes of the metal ions with various organic acids in solution. If this is the case, the smallest ion among the above-mentioned metals, Ni²⁺, is expected to form the most stable complexes with the dibasic acids in solution. The experimental facts shown in Table 6 indicate, however, that this is not true. Hence, factors other than the crystal radii of the “naked” metal ions may also play important role on the relative stabilities of the metal-acid complexes in solution. One possible factor could be the degree of solvation of the metal ions in solution. Unfortunately, the factors to play major role on the formation of various metal-acid complexes in solution are not completely known. It is hoped that future study should be undertaken to examine the controlling factors for the formation of complexes between various metal ions and dibasic organic acids in solution.

It is also seen from Table 6 that all the complexes examined

are more stable in ethanol-water and acetone-water solutions than in aqueous solution.

Aqueous < mixed solvent systems.

This may be attributed to the difference in dielectric constant between water and organic solvents. Smaller values of dielectric constants of ethanol and acetone may cause stronger electrostatic attraction between the metal ions and the organic acid anions in solution.

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Study of Oganophosphorus Compound (I). Synthesis of Heterocyclic Compounds Containing Phosphorus Atom

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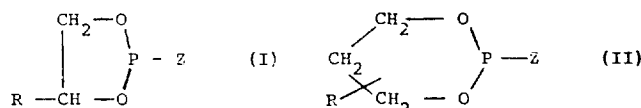
Trichloromethylphosphonyl dichloride was prepared by the aluminium chloride method. We synthesized several heterocyclic compounds containing phosphorus atom by the stepwise esterification of trichloromethylphosphonyl dichloride with ethylene glycol, 2-mercaptoethanol, ethylene diamine, and 2-aminoethanol and the resulting heterocyclic compounds are 2-trichloromethyl-1,3,2-dioxo-, 2-trichloromethyl-1,3,2-thioxa-, 2-trichloromethyl-1,3,2-diaza-, and 2-trichloromethyl-1,3,2-oxazaphospholane-2-oxide. The best results were obtained in the solution of triethylamine as hydrochloric acid trapping agent. The structure of five-membered heterocyclic phosphonates were characterized by their IR, NMR, and elementary analysis and the mass spectra of the compounds were analyzed.

Introduction

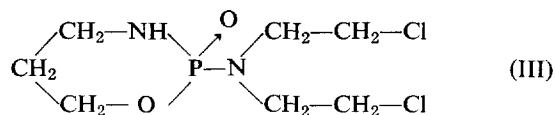
New synthetic methods and reactions using trichloromethylphosphonyldichloride derivatives have been extensively studied by Marcel Corallo's group¹⁻³ and others.^{4,5}

Not only these reactions but their further useful intermediates in the preparation of a variety of organophosphorus compounds were also reported.

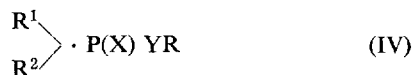
Over the past several years, there has been an increasing amount of interest in saturated heterocyclic compounds containing phosphorus and oxygen in five- and six-membered rings. The trivalent 1,3,2-dioxaphospholanes (I) and 1,3,2-dioxaphospholinanes (II) were well studied,⁶⁻⁹ but the tetravalent phospholanes and phospholinanes less studied.



Especially, synthesis and stereochemistry of cyclophosphamide (III) has been interesting field and developed up to the present time, because such compound can be useful as anticancer drugs.^{10,11}



The vast majority of insecticidal organophosphorus compounds so far prepared has the general structure (IV); R¹, R² alkoxy; X, Y=O or S; R³=electron withdrawing group).



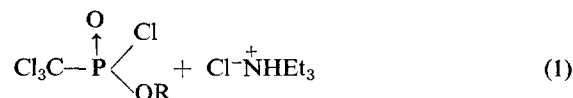
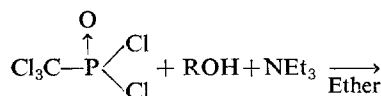
Cyclic organophosphorus compounds as possible pesticides were studied by R. S Edmundson, *etc.*¹²

On the other hand, it has been studied that a stereoselective method for the conversion of vicinal diols to alkenes *via* reduction-elimination of cyclic phosphonate derivatives with dissolving metals.¹⁵

Now we have synthesized several phosphonates using trichloromethylphosphonyldichloride Cl₃CP(O)Cl₂, and intend to report about the new synthesis of five-membered heterocyclic phosphonates, have never been reported yet.

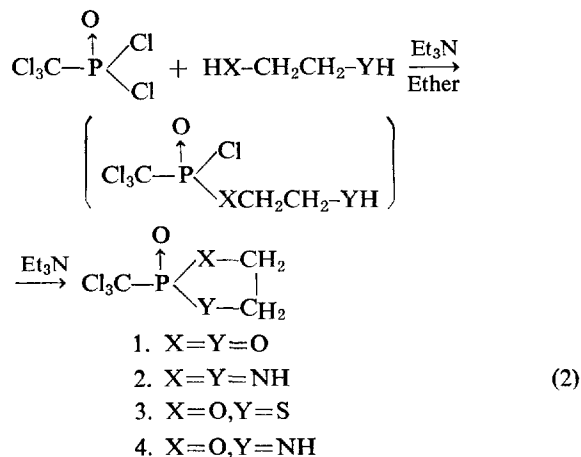
Results and Discussion

Condensation reaction between alcohols and trichloromethylphosphonyldichloride took place smoothly at proper temperature. It was reported that the reactivity of mono-esterification was proportional to acidity of alcohols³, and we obtained agreeable result by experiment as following, esterification of trichloromethylphosphonyldichloride with ethanol, 2-chloroethanol, and 2,2,2-trichloroethanol. (eq. 1)



- 1) R = -CH₂CH₃: -20° (Reaction temperature)
- 2) R = -CH₂CH₂Cl: -30°
- 3) R = -CH₂CCl₃: below -35°

Five-membered heterocyclic phosphonates were obtained from the reaction of trichloromethylphosphonyldichloride with ethylene glycol, ethylene diamine, 2-mercaptoethanol, and 2-aminoethanol and the products were isolated and identified by ir, nmr, and mass spectra. The reaction of cyclization took place at low temperature in ethylether solvent we assume that the mechanism of cyclization is following (eq. 2)



Ethylene diamine afforded low yield in comparison with other reactions because ethylene diamine itself acted as base. In this reaction, as the one of side reactions was confirmed the formation of triethylammonium phosphonate.

It is important that the reaction mixture should be kept in anhydrous condition, because 2-aminoethanol absorbs moisture and CO₂. The reaction of trichloromethylphosphonyldichloride with 2-aminoethanol was carried out in nitrogen atmosphere.

Since the mass spectra of phosphonyldichlorides^{13,14} have been little studied, we examined to take mass spectra of trichloromethylphosphonyldichloride and five-membered heterocyclic phosphonates were given in the Table 1.

The molecular ion peaks of heterocyclic trichloromethylphosphonates are low abundance, but the spectra of trichloromethylphosphonyldichloride and 2-trichloromethyl-1,3,2-oxazaphospholane-2-oxide are absent the molecular ion peaks. Cleavage of the P-C bond is known to be facile process and the base peaks are probably from the cleavage of P-C bond, but the mass spectra of dioxaphospholane is not from cleavage of the P-C bond.

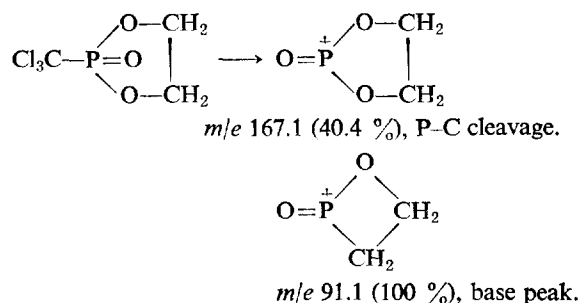


TABLE 1: The Mass Spectra of the Type $\text{Cl}_3\text{C}-\text{P}(\text{O})(\text{X}-\text{CH}_2)(\text{Y}-\text{CH}_2)$

Compounds	M ⁺		R ⁺		(P ⁺ =O) %
	m/e	%	m/e	%	
1. X=Y=O	225.1	0.1	91.1	100	$\text{O}=\overset{\oplus}{\text{P}}\left(\begin{array}{l} \text{O} \\ \text{CH}_2 \end{array}\right)\text{CH}_2$ 39.7
2. X=Y=NH	224.1	0.1	105.1	100	$\text{O}=\overset{\oplus}{\text{P}}\left(\begin{array}{l} \text{NH}-\text{CH}_2 \\ \text{NH}-\text{CH}_2 \end{array}\right)$ 3.3
3. X=O, Y=S	242.3	3.2	123.2	100	$\text{O}=\overset{\oplus}{\text{P}}\left(\begin{array}{l} \text{O}-\text{CH}_2 \\ \text{S}-\text{CH}_2 \end{array}\right)$ 19.9
4. X=O, Y=NH	224.2	0	106	100	$\text{O}=\overset{\oplus}{\text{P}}\left(\begin{array}{l} \text{O}-\text{CH}_2 \\ \text{NH}-\text{CH}_2 \end{array}\right)$ 24.9
5. $\text{C}_3\text{CP}(\text{O})\text{Cl}_2$	234	0	117.1	100	$\text{Cl}_3\overset{\oplus}{\text{C}}$
			119.2	90.7	$\text{O}=\overset{\oplus}{\text{P}}\text{Cl}_2$

TABLE 2:

Compounds	P=O(cm ⁻¹)	P-O(cm ⁻¹)	N-H(cm ⁻¹)
1. X=Y=O	1305	1030	
2. X=Y=NH	1220		3225
3. X=O, Y=S	1260	1010	
4. X=O, Y=NH	1255	1005	3250
5. $\text{Cl}_3\text{CP}(\text{O})\text{Cl}_2$	1290		

The phosphamides studied had a strong absorption band in the infrared at 3225cm⁻¹ and 3250cm⁻¹ due to the N-H stretching vibration. This is in agreement with the proposal structure. The ir spectra of synthesized compounds showed a phosphoryl (P=O) absorption peak at 1300-1210 cm⁻¹, respectively. Infrared spectra analyses of these reaction products are shown in Table 2.

In the nmr spectrum of phospholane the 60 MHz resonance is shown to the unexpected multiple peaks since this resonance was affected by phosphorus atom.

Experimental

1. General

All the chemicals used were of reagent grade and purified prior to use, if necessary, by the known methods.

The ¹H-NMR spectra were recorded on a Varian T-60A spectrometer. Unless otherwise stated, deuteriochloroform was used as a solvent and internal TMS as a standard. All NMR spectra are described in ppm.

Melting points were obtained with a Thomas Hoover capillary melting point apparatus and are uncorrected.

Mass spectra were obtained on a Hewlett-Packard HP5985A mass spectrometer. Infrared spectra were measured on a Perkin-Elmer Model 267 spectrophotometer on KBr pellet. The following descriptive abbreviations are used: vs=very strong, s=strong, m=medium, w=weak. Elemental analyses were obtained on a Hewlett-Packard HP185B C.H.N. analyzer. Phosphorus atoms were measured on Cary 14

spectrophotometer, and chlorine was measured by titration after ignited in Oxygen Bomb Calorimeter (Parr).

2. Preparation of Trichloromethyl Phosphonyl Dichloride

Trichloromethylphosphonyl dichloride was prepared by the aluminium chloride method.³

In an equipment protected from moisture were placed 1 mole of anhydrous, powdered aluminum chloride, 1 mole of phosphorus trichloride and 1.2 moles of carbon tetrachloride. The reaction mixture was stirred slowly until they were thoroughly mixed and then heated until the exothermic reaction began. When the mixture became solid, it was suspended in 1 l of methylene chloride and the suspension was cooled in a dry ice-acetone bath to -10° to -20°. Distilled water (10 moles) was added dropwise over a period of 30 minutes with vigorous stirring. The solid aluminum chloride hydrate was filtered and the filtrate was concentrated by distillation to about 250 ml and the remaining solvent was removed under reduced pressure. The yield was 203.5 g (86%) of white, crystalline solid which melt at 155-156° C. IR (KBr): 1290 cm (P=O, stret.) (S), 785 cm (C-Cl, strong) Mass: 199.1 (1%), 117.1 (100%), 119.2 (96.7%), 47.1 (39.7%).

3. Synthesis of Five-Membered Heterocyclic Phosphonates

In a 250 ml three-neck flask fitted with a sealed mechanical stirrer, a low-temperature thermometer, and a 100 ml dropping funnel was dissolved 12.2 g (0.05 mole) of trichloromethylphosphonyldichloride in 40 ml of dry ethyl ether, and the solution was cooled to -25°.

To the cooled solution, 0.05 moles of ethylene glycol, ethylene diamine, and 2-mercaptoethanol was added dropwise with stirring over a period of 30 minutes. After the reactant was added completely, and a solution of 0.1 mole of triethylamine in 20 ml of dry ethyl-ether was added dropwise over a period of approximately 1 hr, the reaction temperature was allowed to rise 0°. After the addition of triethylamine was completed, the mixture was stirred for 2 hours.

Triethylammonium chloride was removed by filtration and the filtrate was concentrated on rotatory evaporator. The remaining solid was recrystallized in a proper solvents.

3.1 2-Trichloromethyl-1,3,2-dioxaphospholane-2-oxide.

The resulting solid was recrystallized from chloroform and ether. The yield was 6.5 g (55%), m.p 131-133°.

Elementary analysis: Obs., (calc. %) C, 16.5(16), H, 1.8(1.7). IR (KBr): 2995 m, 1360 m, 1300 s, 1030 vs, 940 s, 865 s, 760 s. NMR (CDCl₃): δ 4.6 (m, 4H). Mass spectra: m/e (rel. intens. %) 225.1(0.1, M⁺), 126.1(49.1), 107(40.4), 91.1 (100), 81.0(29.0), 47.1(15.2).

3.2 2-Trichloromethyl-1,3,2-diazaphospholane-2-oxide.

The residual white solid was recrystallized from ethylether and chloroform. The yield was 3.2 g(30.3%) of a white crystal which decomposed at 207-208°.

Elem. anal. Obs. (calc. %), Cl, 46.6 (47.6), N, 12.6 (12.5). IR: 3250 vs, 2950, 2900 m, 1430 s, 1300, 1255 s, 1090 s, 930 s, 890, 820 w, 770, 740 s. NMR: (DMSO): δ 5.5, 5.7 (NH, 2H, broad), δ 3.2 (4H, N-CH₂). Mass spec: m/e (rel. intens. %): 224.1 (M⁺, 0.1), 105.1(100) 76(8) 47(3.3).

3.3 2-Trichloromethyl-1,3,2-thioxaphospholane-2-oxid.

The white crystal was recrystallized from acetone and chloroform to give fine crystal of 2-trichloromethyl-1,3,2-thioxaphospholane-2-oxide, the yield was 5.9 g (47%). m.p 117–119°.

Elem. anal. Obs. (calc. %): Cl, 44.2(44.1), H, 1.6(1.6). IR: 2920 m., 1360 m, 1255 vs, 1220, 1180 m, 1010 vs, 950 s, 770 s, 680 w. NMR: δ 4.5 (mul. O-CH₂, 2H), δ 3.67 (tri. S-CH₂, 2H). Mass spect.: *m/e* (rel. intens. %): 242.3 (M⁺, 3.2), 123.2 (100), 97.2(10.0), 59.2(15.4), 47.1(19.9).

3.4 2-Trichloromethyl-1,3,2-oxazaphospholane-2-oxide.

To 14.1 ml (0.1 mole) of triethylamine dissolved in 50 ml of drying ethylether was added 3.1 ml (0.05 moles) of 2-aminoethanol. The flask is flushed with nitrogen and placed on a magnetic stirrer, and the reaction flask was placed in a dry ice-ice bath, and added dropwise 12.2 g (0.05 moles) of trichloromethylphosphonyl dichloride and 40 ml of ethylether.

The resulting solution was stirred for 18 hours at 15°, and the mixture was filtered through a glass filter.

The filtrate was concentrated on rotatory evaporator, and the remaining solid was dissolved in water, and insoluble solid was collected on a glass filter, washed with 10 ml of water, and dried in a desiccator. The yield was 4.2 g(41%). m.p 131–133°.

Elementary Analysis: Obs. (calc. %) C, 16.3(16.04), H, 2.3(2.22), N, 6.2 (6.23). IR (KBr) : 3250 cm⁻¹ (N-H), (s) 2990, 1910 (m), 1470, 1405 (m), 1290, 1255 (s) 1080, 1005 (vs), 940 (m), 880, 780 (m). NMR (CDCl₃) δ 4.5 (O-CH₂, mult.), δ 4.1 (N-H, broad), δ 3.6 (mult., N-CH₂). (DMSO): 6.4, 6.8 (broad, N-H), δ 4.5 (O-CH₂, mult.), δ 3.5 (N-CH₂, mult.). Mass spectra: *m/e* (rel. intens.%) 187.9 (0.5), 106.1(100) 47.0(24.9), 79.1 (15.1).

4. Monoesterification of trichloromethylphosphonyldichloride

4.1 O-Ethyl trichloromethylchlorophosphonate

C₃H₅Cl₄O₂P: b.p 92 (6 mmHg)

IR (NaCl plate):

2980 cm⁻¹ (m), 1290 cm⁻¹ (s), 1020 cm⁻¹ (vs), 870 cm⁻¹ (s), 760 cm⁻¹ (s)

NMR (CCl₄):

4.5 (2H, mul.), 1.5 (3H, trip.)

4.2 O-2-Chloroethyltrichloromethylchlorophosphonate.

C₃H₄Cl₅O₂P : b.p 131 (4mmHg)

IR (NaCl plate): 2980 cm⁻¹ (m), 1290 cm⁻¹ (s), 1075 cm⁻¹ (s), 1020 cm⁻¹ (vs), 970 cm⁻¹ (m), 870, 780, 760 cm⁻¹ (m)

NMR (CDCl₃):

δ 3.7 (2H, trip.), 4.6 (2H, mutl.)

4.3 O-2,2,2-trichloroethyltrichloromethylchlorophosphonate

C₃H₂Cl₆O₂P: m.p 102–103°

IR(KBr):

3000, 1445, 1290 cm⁻¹ (s), 1090, 1020 cm⁻¹ (vs), 850, 770 cm⁻¹

NMR(CDCl₃): δ 4.8 (mul.)

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MO Studies of Configurations and Conformations (IX). Molecular Structure of Sulfamoyl Chlorides

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Semi-empirical MO calculations were performed to investigate stereochemical properties of sulfamoyl chlorides; R₂NSO₂Cl Where R=H or CH₃ It was found that for all the molecules considered the most preferred conformation was the form in which n_N-σ*_{SCl} conjugative interaction is a maximum and the least favored conformation was the form in which steric repulsion is large due to eclipsing of Cl and R. In case of the molecule with no symmetry *i.e.*, CH₂NHSO₂Cl, the stability was also dependent upon nonbonded interactions between the eclipsing groups.