Studies on Organophosphorus Compounds. III. On Phosphite Copper Cyanide Complex Compounds[*1]

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In a previous paper1), it has been reported on a few new properties of phosphite[*2] cuprous halide complex compounds. During the course of an investigation of organophsphorus complex compounds, the present author has also found that phosphites react with copper cyanide to give new complex compounds2) having strong fungicidal action3).

There has been no report on copper cyanide complex compounds having the phosphorus atom, but recently Birum4) prepared independently the same compounds as those of the present author and reported that they have insecticidal activity towards a few insects.

Preparation of Phosphite Copper Cyanide Complex Compounds.—Phosphite copper cyanides were prepared from phosphites and copper cyanides in a benzene solution. After copper cyanide was dissolved in benzene solution, and the benzene was evaporated under reduced pressure, the complex compounds were obtained as white crystals or colorless oil.

According to the mole ratio of phosphites to copper cyanide two complex compounds were obtained; namely, phosphite copper cyanide (I) and bis-phosphite copper cyanide (II), but tri-phosphite copper cyanide could not be prepared from three moles of phosphite and one mole of copper cyanide; instead, a product was one mole of bis-phosphite copper cyanide (II) and one mole of phosphite was unreacted.

$$(RO)_3P + CuCN \rightarrow \underset{(I)}{(RO)_3PCuCN}$$

$$2(RO)_3P + CuCN \rightarrow \underset{(II)}{((RO)_3P)_2CuCN}$$

[*1] Presented at the Annual Meeting of Chemistry of Complex Compounds of Japan, Fukuoka, October, 1959.

[*2] The phosphorus compounds in this paper were named according to the Drake Committee's Report (*Chem. Eng. News*, **30**, 4515 (1952)).

1) Y. Nishizawa, This Bulletin, **34**, 1170 (1961).

2) Y. Nishizawa, and M. Nakagawa, Japanese Pat. Applied No. 12895 (1959).

3) J. Hattori and Y. Nishizawa, Japanese Pat. Applied No. 12896 (1959).

4) G. H. Birum, U. S. Pat., 2909544 (1959).

$$3(RO)_3P + CuCN \rightarrow \underset{(II)}{((RO)_3P)_2CuCN} + (RO)_3P$$

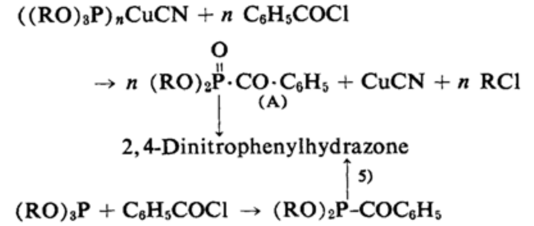
Phosphite copper cyanides (I) gave bis-phosphite copper cyanides (II) by adding one mole ratio of phospite and II gave also I by adding one mole ratio of copper cyanide, and II were converted to phosphite copper cyanide (I) by heating under a reduced pressure.

$$\underset{(I)}{(RO)_3PCuCN} + (RO)_3P \rightarrow \underset{(II)}{((RO)_3P)_2CuCN}$$

$$\underset{(II)}{((RO)_3P)_2CuCN} + CuCN \rightarrow \underset{(I)}{2(RO)_3PCuCN}$$

$$\underset{(II)}{((RO)_3P)_2CuCN} \xrightarrow{\text{heat}} \underset{(I)}{(RO)_3PCuCN} + (RO)P\uparrow$$

It is clear from the following experimental facts that these complex compounds have the phosphite group in their molecules. The compounds I and II reacted with benzoyl chloride in benzene solution to give *O, O*-dialkylbenzoyl phosphonates (A) and copper cyanide. The melting point of 2, 4-dinitrophenylhydrozone of the phosphonate A coincided with that of 2, 4-dinitrophenylhydrazone of the product prepared from trialkyl phosphite and benzoyl chloride by Kosolapoff's method[5]



$$((RO)_3P)_nCuCN + n\ C_6H_5COCl \rightarrow n\ \underset{(A)}{(RO)_2\overset{O}{\overset{\|}{P}}\cdot CO\cdot C_6H_5} + CuCN + n\ RCl$$

$$(RO)_2P(O)\cdot CO\cdot C_6H_5 \downarrow \text{2, 4-Dinitrophenylhydrazone} \xleftarrow{5)} (RO)_2P\text{-}COC_6H_5$$

$$(RO)_3P + C_6H_5COCl \rightarrow (RO)_2P\text{-}COC_6H_5$$

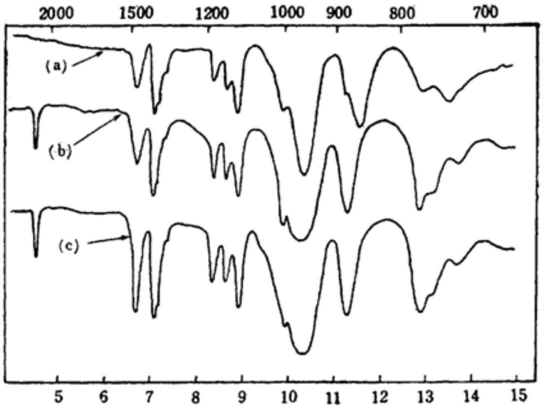


Fig. 1. (a) Infrared absorption spectrum of triisopropyl phosphite (in Nujol). (b) Infrared absorption spectrum of triisopropyl phosphite copper cyanide (Id) (in Nujol). (c) Infrared absorption spectrum of bis-(triisopropyl phosphite) copper cyanide (IId) (in Nujol).

The infrared absorption spectra[*3] of these compounds, I and II, showed the absorption band of P–O-isopropyl group at 1010 cm^{-1} (see Fig. 1). But the absorption bands of P–O stretching vibration[6] of phosphite at 857 and 769 cm^{-1} shift to 879 and 779 cm^{-1}, respectively. From this shift, it is considered that P–O bonds are shortened by formation of the complex; namely, P–O bonds in these complex compounds become stronger than that of phosphite (see Fig. 1).

In the ultraviolet absorption spectra[*4] of these compounds, the absorption maximum did not appear.

Molecular Weights of Bis-phosphite Copper Cyanide Complex Compounds.—In many cases, it has been reported that organometallic cyanide complex compounds form the polymer[7,8], so the present author measured the molecular weights of the crystalline bis-phosphite copper

TABLE I. YIELDS, PHYSICAL CONSTANTS AND MICROANALYTICAL DATA OF PHOSPHITE AND BIS-PHOSPHITE COPPER CYANIDES, I AND II, $((RO)_3P)_nCuCN$

No.	R	n	Yield %	M. p., °C or $n_D^{(t°C)}$	Nitrogen, %		Phosphorus, %		Copper, %	
					Found	Calcd.	Found	Calcd.	Found	Calcd.
Ia	CH_3	1	98.6	1.5299$^{(27)}$	6.41	6.56	13.5	13.4	29.3	29.7
Ib	C_2H_5	1	97.9	1.5031$^{(25)}$	5.63	5.47	12.2	12.1	25.1	24.9
Ic	n-C_3H_7	1	98.4	1.5000$^{(27)}$	4.76	4.71	10.2	10.4	21.4	21.3
Id	iso-C_3H_7	1	98.6	1.4830$^{(25)}$	4.75	4.71	10.6	10.4	21.0	21.3
Ie	n-C_4H_9	1	99.1	1.4850$^{(27)}$	4.01	4.12	9.3	9.1	18.3	18.7
IIa	CH_3	2	99.3	60～61	4.15	4.15	18.3	18.4	18.6	18.8
IIb	C_2H_5	2	99.6	121～122	3.61	3.32	14.9	14.7	15.0	15.1
IIc	n-C_3H_7	2	98.9	1.4708$^{(25)}$	2.61	2.77	12.3	12.3	12.8	12.6
IId	iso-C_3H_7	2	98.7	85～86	2.69	2.77	12.4	12.3	12.9	12.6
IIe	n-C_4H_9	2	98.4	1.4742$^{(25)}$	2.99	2.75	12.0	12.1	12.3	12.5

[*3] A Perkin Elmer 21 spectrophotometer was used.

[*4] A Shimadzu QB-50 spectrophotometer was used.

5) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **69**, 2112 (1947).

6) J. Bellamy, "The Infrared Spectra of Complex Molecules", John Wiley, New York (1958).

7) R. F. Phillips, *Chem. Abstr.*, **34**, 1532 (1940).

8) A. Burawoy, *J. Chem. Soc.*, **1935**, 1024.

TABLE II. THE MOLECULAR WEIGHTS OF BIS-PHOSPHITE COPPER CYANIDE (II) $[(RO)_3P]_2CuCN$

No.	R	Cryoscopic solvent (k)	Ebullioscopic solvent (k)	Concn. (g./G %)	ΔT, °C	Molecular weight		Degree of association
						Experimental	Calcd. (Monomeric)	
IIa	CH_3	Benzene (5120)		**0**	—	**1346**	337.7	3.99
				0.445	0.017	1340		
				1.651	0.041	1312		
				2.326	0.092	1294		
			Benzene (2570)	**0**	—	**630**		1.87
				0.417	0.017	631		
				1.452	0.060	621		
				2.725	0.112	625		
		Bromoform (14050)		**0**	—	**556**		1.65
				0.387	0.097	561		
				1.263	0.350	507		
				2.509	0.703	501		
		Cyclohexane (20100)		**0**	—	**651**		1.93
				0.335	0.104	647		
				0.681	0.211	649		
				1.511	0.473	642		
				2.255	0.721	629		
				2.901	0.918	635		
				3.751	1.201	628		
				4.338	1.397	624		
				4.903	1.600	616		
IIb	C_2H_5	Benzene		**0**	—	**1676**	421.5	3.98
				0.384	0.012	1681		
				1.623	0.050	1661		
				2.553	0.078	1671		
			Benzene	**0**	—	**840**		1.99
				1.035	0.032	831		
				2.315	0.073	815		
				2.659	0.084	814		
		Bromoform		**0**	—	**678**		1.61
				0.381	0.079	678		
				1.025	0.219	658		
				2.472	0.527	659		
		Cyclohexane		**0**	—	**856**		2.03
				0.438	0.104	846		
				1.250	0.302	832		
				2.081	0.516	811		
IId	iso-C_3H_7	Benzene		**0**	—	**999**	505.5	1.98
				0.369	0.019	994		
				1.156	0.059	1003		
				2.462	0.127	993		
			Benzene	**0**	—	**1020**		2.02
				0.436	0.011	1019		
				1.396	0.037	970		
				2.599	0.069	968		
		Bromoform		**0**	—	**975**		1.93
				0.375	0.054	976		
				1.443	0.213	952		
				2.769	0.412	944		
		Cyclohexane		**0**	—	**1040**		2.06
				0.201	0.039	1036		
				1.518	0.296	1031		
				2.485	0.492	1015		

cyanide as represented in these compounds. Molecular weights of these complex compounds were measured by the cryoscopic method[9] in benzene, bromoform, and cyclohexane and by the ebullioscopic method[10] in benzene. All of these solvents were prepared by purification of guaranteed reagents in the usual manner[11].

The results of these experiments are shown in Table II.

It is made clear from Table II that the complex compounds having methyl or ethyl groups as alkyl form tetramer in benzene solution at the freezing point and that they form dimer in other solvents, such as bromoform and cyclohexane, and moreover by the ebullioscopic method in benzene they also form dimer.

With isopropyl group as alkyl, the compound forms dimer in all cases.

It seems to be possible that the apparent values of molecular weights may be smaller, if the associated molecules dissociate in organic solvents. These possibilities are supported by the fact that the degree of association in nonpolar solvents are greater than that in a polar solvent. So the present author measured the molecular weight of bis-(trimethyl phosphite) copper cyanide (IIa) by cryoscopy in cyclohexane in various concentrations ranging from 0.3 to 5 per cent.

If the associated molecules dissociate in organic solvents, the apparent values of molecular weight will become greater with the increase of concentration.

As shown in Table II, an increase of apparent values of molecular weight could not be found in the above range of concentration. So it seems to be right that the compound IIa forms dimer in cyclohexane, and does not form dimer from the dissociation of tetramer.

These problems of their structures or degree of association must be determined by X-ray analysis.

Experimental

Preparation of Phosphites.—Trialkyl phosphites were prepared by Ford-Moore's method[12] and their yields, physical constants and microanalytical data are shown in Table III.

Preparation of Phosphite or Bis-phosphite Copper Cyanides.—The following examples illustrate the preparations of phosphite and bis-phosphite copper cyanides, I and II. Other examples are shown in Table I and their molecular weights are shown in Table II.

Preparation of Triethyl Phosphite Copper Cyanide (Ib).—To a solution of 33.2 g. (0.2 mol.) of triethyl phosphite in 50 ml. of benzene was gradually added 17.8 g. (0.2 mol.) of copper cyanide. The temperature rose gradually and copper cyanide dissolved in benzene. After stirring one hour, the reaction mixture was filterd and concentrated under reduced pressure. Colorless oil (49.6 g.) was obtained, n_D^{25} 1.5031.

Found: N, 5.63; P, 12.2; Cu, 25.1. Calcd. for $C_6H_{15}O_3PCuCN$: N, 5.47; P, 12.1; Cu, 24.9%.

To a solution of 8.5 g. of Ib in 20 ml. of benzene, was added 5.6 g. of triethyl phosphite. The temperature did not rise. After concentrating the benzene solution, 13.9 g. of a white crystalline substance were obtained and the melting point of this substance was 121°C upon recrystallization from ligroin. This melting point coincided with that of authentic bis-(triethyl phosphite) copper cyanide (IIb) and a mixed melting point showed no depression.

Preparation of Bis-(trimethyl phosphite) Copper Cyanide (IIa). — This compound was prepared from 24.8 g. (0.2 mol.) of trimethyl phosphite and 8.9 g. (0.1 mol.) of copper cyanide in benzene solution as above mentioned. White crystals (33.5 g. 99.3%) were obtained and melted at 60~61°C.

Found: N, 4.15; P, 18.3; Cu, 18.6. Calcd. for $C_6H_{18}O_2P_2CuCN$; N, 4.15; P, 18.4; Cu, 18.8%.

To a solution of 11.2 g. of the compound IIa in 20 ml. of benzene was added 4.3 g. of trimethyl phosphite. After the benzene was evaporated, 15.1 g. of colorless oil were obtained and gave n_D^{26} 1.5296. The refractive index, the infrared spectrum and the microanalytical data of this compound coincided with authentic trimethyl phosphite copper cyanide (Ia).

Pyrolysis of Bis-(triethyl phosphite) Copper Cyanide (IIb). — The compound IIb (21.1 g. 0.05 mol.) was set in a distillation flask (50 mol.) which was combined with the trap cooled at −50°C, and heated at 130°C under 0.1 mmHg pressure for 8 hr.

The colorless oil which was captured in the trap,

TABLE III. YIELDS, PHYSICAL CONSTANTS AND MICROANALYTICAL DATA OF PHOSPHITES $(RO)_3P$

R	Yield %	B. p.		$n_D^{(t°C)}$	Phosphorus, %		Carbon, %		Hydrogen, %	
		°C	mmHg		Found	Calcd.	Found	Calcd.	Found	Calcd.
CH_2	71	111~112	760	1.4096(21)	24.9	25.0	29.17	29.03	7.31	7.26
C_2H_5	82	55~57	19	1.4135(20)	19.8	19.9	46.31	46.15	9.25	9.04
n-C_3H_7	85	82~83	10	1.4263(20)	15.1	14.9	52.06	51.92	10.09	10.10
iso-C_3H_7	80	60~61	9	1.4079(29)	15.0	14.9	51.88	51.92	10.41	10.10
n-C_4H_9	87	119~120	10	1.4329(21)	12.1	12.4	57.51	57.60	10.83	10.80

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[9] J. Sameshima, "Buturi-kagaku Jikken Hō", Shōkabō, Tokyo. p. 227.

[10] J. Sameshima, ibid., p. 220.

[11] T. Kuwata, "Yōzai, (Solvents)", Maruzen, Tokyo.

[12] A. H. Ford-Moore, "Organic Syntheses", Vol. 31 (1951), p. 111.

was 7.1 g. and was distilled at 55～56°C/19 mmHg, n_D^{20} 1.4133.

Found: P, 19.7; C, 46.05; H, 9.18. Calcd. for $C_6H_{15}O_3P$: P, 19.9; C, 46.15; H, 9.04%.

To a solution of 4.1 g. of this oil in 5 ml. of benzene was added 1.1 g. of copper cyanide. After filtering and concentrating, 5.0 g. of white crystals were obtained and melted at 121°C (recryst. from petroleum ether). This melting point coincided with that of authentic bis-(triethyl phosphite) copper cyanide (IIb) and the mixed melting point did not go down. So it was made clear that this oil was triethyl phosphite.

On the other hand, residual oil in a distillating flask gave 11.6 g. and had n_D^{25} 1.4999, and the microanalytical data and the infrared absorption spectrum of this oil coincided with that of authentic triethyl phosphite copper cyanide.

Found: P, 12.5; N, 5.21; Cu, 24.6. Calcd. for $C_6H_{15}O_3PCuCN$: P, 12.1; N, 5.48; Cu, 24.9%.

To a solution of 5.1 g. of this oil in 10 ml. of benzene was added 3.3 g. of triethyl phosphite. After the benzene was evaporated off, 8.0 g. of white crystals were obtained and melted at 121°C. This melting point coincided with that of authentic bis-(triethyl phosphite) copper cyanide (IIb) and the mixed melting point did not go down. So, it was determined that the residual oil was triethyl phosphite copper cyanide (Ib).

Reaction of Triethyl Phosphite Copper Cyanide (Ib) with Benzoyl Chloride. — To a solution of 5.1 g. of triethyl phosphite copper cyanide (Ib) in 10 ml. of ether was added gradually 2.8 g. of benzoyl chloride. The temperature rose and copper cyanide was precipitated. The reaction mixture was filtered and concentrated. The residual oil was distilled under reduced pressure, b. p. 140°C/2.5 mmHg, n_D^{23} 1.5068, yield 3.6 g.

Found: P, 12.6; C, 54.39; H, 6.18. Calcd. for $C_{11}H_{15}O_4P$: P, 12.8; C, 54.55; H, 6.20%.

2,4-Dinitrophenylhydrazone of this product was prepared in the usual manner and melted at 171～172°C (recryst. from ethanol). This melting point coincided with that of 2,4-dinitrophenylhydrazone of authentic *O,O*-diethylbenzoyl phosphonate[4] and mixed melting point did not go down.

Summary

Trialky phosphite reacts with copper cyanide to give phosphite or bis-phosphite copper cyanides according to the mole ratio of phosphite to copper cyanide.

It is made clear from their molecular weights that these products form polymer in various organic solvents. Moreover, these products have strong fungicidal action but this will be reported in another paper.

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