

*Studies on Organophosphorus Compounds. II. On Phosphite  
Cuprous Halide Complex Compounds\*<sup>1)</sup>*

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Although many workers have studied complex compounds having phosphorus atom, many of them reported on phosphine\*<sup>2</sup> complex compounds such as phosphine platinum halides<sup>1)</sup>, phosphine cuprous iodides<sup>2)</sup> and phosphine chromium halides<sup>3)</sup>, while phosphite complex compounds were reported on only by Arbuzov<sup>4)</sup> and others.

Arbuzov has reported that phosphites give phosphite cuprous halide complex compounds which have two experimental formulae,  $(\text{RO})_3\text{PCuX(I)}$  and  $[(\text{RO})_3\text{P}]_2\text{CuX (II)}$ , and that *O, O*-dialkyl phosphonates give no complex compounds. Therefore, this reaction has been utilized as an identification of phosphite from phosphonate.

The present author separated two compounds having formulas I and II and measured their molecular weights in various organic solvents. It was made clear as a result, that these complex compounds showed an interesting behavior in organic solvents and reacted with pyridine, aniline and their analogues and produced new complex compounds having phosphites and amines.

**Preparation of Phosphite Cuprous Halide Complex Compounds.**—Phosphite cuprous halides were prepared by the reaction of phosphite with cuprous halide in a benzene solution. After cuprous halides were dissolved in benzene, the benzene was evaporated under reduced pressure, the complex compounds were obtained as white crystals or colorless oil.

Changing the mole ratio of phosphites to cuprous halides obtained two complex compounds, namely, phosphite cuprous halides I and bis-phosphite cuprous halides II. Tri-phosphite cuprous halide could not be prepared from three moles of phosphite and one mole

\*<sup>1</sup> Presented at the annual meeting of Chemistry of Coordination Compounds of Japan, Fukuoka, Oct., 1959.

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

1) J. Chatt, *J. Chem. Soc.*, 1951, 625.

2) F. G. Man, *ibid.*, 1936, 1503.

3) K. Issleib, *Z. anorg. u. allgem. Chem.*, 298, 84 (1959).

4) A. Arbuzov, *Ber.*, 38, 1171 (1905).

TABLE I. YIELDS, MELTING POINTS AND MICROANALYTICAL DATA OF PHOSPHITE CUPROUS HALIDES (RO)<sub>3</sub>PCuX (I)

No.	R	X	Yield %	M.p. °C	M.p. (°C) by A. Arbuzov <sup>4)</sup>	Halogen, %		Phosphorus, %		Copper, %	
						Found	Calcd.	Found	Calcd.	Found	Calcd.
Ia	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	Cl	95.1	117	112 ~114	11.63	11.60	10.3	10.1	20.5	20.8
Ib	C <sub>6</sub> H <sub>5</sub>	Cl	98.1	88~89	95 ~96	8.55	8.68	7.7	7.6	15.2	15.5
Ic	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	Br	96.2	146~147	149 ~150	22.61	22.82	9.0	8.8	18.3	18.1
Id	C <sub>6</sub> H <sub>5</sub>	Br	97.7	91~92	90.5~91.5	17.51	17.64	6.8	6.8	14.3	14.0
Ie	C <sub>2</sub> H <sub>5</sub>	I	88.6	110~111	109 ~110	—	—	8.9	8.7	17.8	17.8
If	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	I	90.2	61~63	—	—	—	7.7	7.8	16.4	16.0
Ig	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	I	93.5	199~200	184 ~185	—	—	7.7	7.8	16.2	16.0

TABLE II. YIELDS, MELTING POINTS AND MICROANALYTICAL DATA OF BIS-PHOSPHITE CUPROUS HALIDES (RO)<sub>3</sub>PCuXP(OR')<sub>3</sub> (II)

No.	R	R'	X	Yield %	M.p. °C	M.p., °C by A. Arbuzov <sup>4)</sup>	Halogen, %		Phosphorus, %		Copper, %	
							Found	Calcd.	Found	Calcd.	Found	Calcd.
II a	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	Cl	93.1	69~70	—	6.75	6.89	11.9	12.0	12.8	12.3
II b	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Cl	95.9	98~99	—	4.71	4.94	8.4	8.6	9.1	8.8
II c	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	Br	91.9	58~59	—	14.22	14.30	10.9	11.1	10.6	11.3
II d	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Br	93.2	67~68	73~77	10.34	10.48	8.0	8.1	8.6	8.3
II e	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	I	95.6	94~95	—	—	—	10.3	10.2	10.6	10.5
II f	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	I	94.8	70~72	73~75	—	—	7.8	7.6	8.1	7.8
II g	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	Cl	97.8	75~76	—	6.15	6.17	11.2	10.9	10.8	11.0

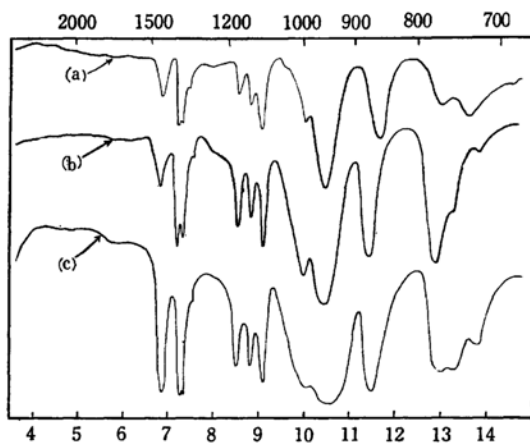


Fig. 1. Infrared absorption spectra (in Nujol) of (a) triisopropyl phosphite, (b) triisopropyl phosphite cuprous chloride (Ia) and (c) bis-(triisopropyl phosphite) cuprous chloride (IIa).

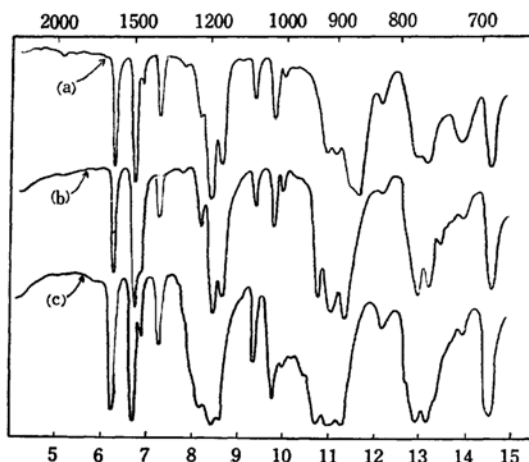
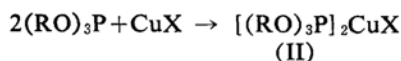
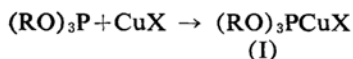


Fig. 2. Infrared absorption spectra (in Nujol) of (a) triphenyl phosphite, (b) triphenyl phosphite cuprous chloride (Ib) and (c) bis-(triphenyl phosphite) cuprous chloride (IIb).

of cuprous halides, but a product corresponding to one mole of bis-phosphite cuprous halides II and one mole of phosphite was obtained.



Phosphite cuprous halides I gave bis-phosphite cuprous halides II by adding one mole

ratio of phosphite and II gave also I by adding one mole ratio of cuprous halides.

Bis-phosphite cuprous halides II were converted to phosphite cuprous halides I by heating under reduced pressure.

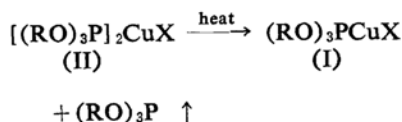
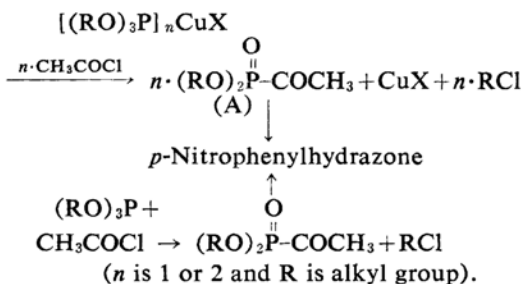


TABLE III. MOLECULAR WEIGHTS OF PHOSPHITE CUPROUS HALIDES  
(RO)<sub>3</sub>PCuX (I) IN VARIOUS SOLVENTS

No.	R	X	Cryoscopic solvent (K)	Concn. g./G%	$\Delta T$ °C	Molecular Weight		Degree of association
						Experimental	Calcd. (monomeric)	
I a	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	Cl	Benzene (5120)	0	—	1230	306	4.02
				0.635	0.027	1204		
				1.172	0.050	1200		
				2.005	0.088	1167		
			Cyclohexane (20100)	0	—	1265		4.13
				0.636	0.103	1241		
				1.201	0.200	1207		
				1.605	0.268	1204		
I b	C <sub>6</sub> H <sub>5</sub>	Cl	Benzene	0	—	1555	409	3.80
				0.639	0.021	1558		
				1.333	0.044	1551		
				1.901	0.062	1569		
			Bromoform (14050)	0	—	1230		3.01
				0.532	0.061	1225		
				1.426	0.168	1193		
				2.106	0.249	1188		
I c	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	Br	Benzene	0	—	1565	350.5	3.83
				0.775	0.099	1573		
				1.426	0.183	1566		
				2.221	0.283	1577		
			Benzene	0	—	1410		4.02
				0.436	0.016	1395		
				1.326	0.049	1386		
				2.108	0.079	1366		
I d	C <sub>6</sub> H <sub>5</sub>	Br	Benzene	0	—	1730	453.5	3.81
				0.476	0.014	1741		
				1.181	0.036	1680		
				2.700	0.081	1707		
			Bromoform	0	—	780		1.72
				0.663	0.123	757		
				1.641	0.309	746		
				2.326	0.460	710		
I e	C <sub>2</sub> H <sub>5</sub>	I	Benzene	0	—	1200	356.5	3.37
				0.536	0.023	1193		
				1.487	0.070	1088		
				2.235	0.150	1090		
I f	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	I	Benzene	0	—	1135	397.5	2.86
				0.500	0.023	1113		
				0.841	0.040	1076		
				2.011	0.100	1030		
I g	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	I	Benzene	0	—	1160	397.5	2.92
				0.638	0.028	1167		
				1.273	0.057	1143		
				2.081	0.092	1158		

It is clear from the following experimental facts that these complex compounds I and II have the phosphite group in their molecules. These compounds reacted with acetyl chloride in benzene solution to give *O,O*-dialkyl-acetyl phosphonates (A) and cuprous halides. The melting point of *p*-nitrophenylhydrazone of the phosphonate A coincided with that of *p*-nitrophenylhydrazone of the product prepared from trialkyl phosphite and acetyl chloride by Arbuzov's reaction<sup>5)</sup>.



The infrared absorption spectra\*<sup>3</sup> of these

5) M. I. Kabachnik, *Izvest. Akad. Nauk. SSSR.*, 1945, 364.

\*<sup>3</sup> Perkin Elmer 21 Spectrophotometer was used.

TABLE IV. MOLECULAR WEIGHTS OF BIS-PHOSPHITE CUPROUS HALIDES  
[(RO)<sub>3</sub>P]<sub>2</sub>CuX (II) IN VARIOUS SOLVENTS

No.	R	X	Cryoscopic solvent (K)	Concn. (g./G%)	$\Delta T$ °C	Molecular Weight		Degree of association
						Experimental	Calcd. (monomeric)	
IIa	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	Cl	Benzene (5120)	0	—	498	515	0.97
				0.431	0.045	490		
				1.231	0.130	485		
				2.260	0.250	463		
			Bromoform (14050)	0	—	513	515	1.00
				0.251	0.070	504		
				1.449	0.400	509		
				2.396	0.685	491		
			Cyclohexane (20100)	0	—	503	515	0.98
				0.509	0.205	499		
				1.581	0.640	497		
				2.561	1.050	490		
IIb	C <sub>6</sub> H <sub>5</sub>	Cl	Benzene	0	—	713	719	0.99
				0.412	0.030	703		
				1.636	0.120	698		
				2.511	0.190	677		
				0	—	553	559.5	0.99
				0.565	0.053	546		
IIc	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	Br	Benzene	1.401	0.130	552		
				2.611	0.250	535		
				0	—	530		
		Bromoform		0.395	0.105	529		0.95
				1.405	0.390	506		
				2.793	0.770	510		
IId	C <sub>6</sub> H <sub>5</sub>	Br	Benzene	0	—	782	763.5	1.02
				0.599	0.040	767		
				1.315	0.090	748		
				2.461	0.175	720		
				0	—	580	606.5	0.96
				0.431	0.038	581		
IIe	<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	I	Benzene	1.691	0.151	573		
				2.813	0.253	569		
				0	—	598		
		Bromoform		0.813	0.192	594		0.99
				1.906	0.461	581		
				2.741	0.661	583		
IIf	C <sub>6</sub> H <sub>5</sub>	I	Benzene	0	—	802	810.5	0.99
				0.685	0.044	797		
				1.801	0.117	788		
				2.589	0.170	780		

compounds I and II showed the absorption band of *P-O*-isopropyl group at 1010 cm<sup>-1</sup> or *P-O*-phenyl group at 1200 cm<sup>-1</sup> according to the kinds of phosphites in complex compounds I and II. (see Figs. 1 and 2).

However, the absorption bands of P-O stretching vibration<sup>6)</sup> of phosphite at 857 and 769 cm<sup>-1</sup> shift to 879 and 779 cm<sup>-1</sup> respectively. Form this shift, it is considered that P-O bonds are shortened by the formation of the complex, namely, the bonding strength of P-O in these complex compounds becomes stronger than that of phosphite (see Figs. 1 and 2).

In the ultraviolet absorption spectra<sup>\*4)</sup> of

these complex compounds, absorption maximum  $\lambda_{\max}$  of phosphite at 263.5 shifts to 265 and absorption bands became more broad by the formation of complex (see Fig. 3). This shift seems to show the usual correlation between the coordination compound and its donor<sup>7)</sup>.

**Molecular Weights of Phosphite Cuprous Halide Complex Compounds.**—The molecular weights of these complex compounds were measured by the cryoscopic method<sup>8)</sup> in benzene, bromoform and cyclohexane, which are all prepared by purification of guaranteed reagents in the usual manner<sup>9)</sup>.

7) K. Sone, *J. Am. Chem. Soc.*, **75**, 5207 (1953).

8) J. Sameshima, "Buturikagaku-Zikken-Hô", Syokabo, Tokyo, (1959).

9) T. Kuwata, "Yôzai", Maruzen Pub. Co., Tokyo, (1951).

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

\*4 Shimadzu QB-50 Spectrophotometer was used.

TABLE V. YIELDS, MELTING POINTS AND MICROANALYTICAL DATA OF DIISOPROPYL PHENYL PHOSPHONITE CUPROUS HALIDES  $[(iso-PrO)_2PC_6H_5]_m CuX$  (III), (IV).

No.	X	m	Yield %	M.p., °C	Halogen, %		Phosphorus, %		Copper, %	
					Found	Calcd.	Found	Calcd.	Found	Calcd.
IIIa	Cl	1	98.5	141~142	10.88	10.92	9.4	9.5	19.8	19.5
IIIb	Br	1	97.9	143~144	21.91	21.64	8.1	8.4	17.3	17.2
IIIc	I	1	95.6	183~184	—	—	7.5	7.4	15.6	15.2
IVa	Cl	2	98.4	144~145	6.39	6.44	11.0	11.2	11.9	11.5
IVb	Br	2	99.0	148~149	13.18	13.43	10.3	10.4	10.5	10.7
IVc	I	2	98.0	187~189	—	—	9.8	9.6	9.6	9.9

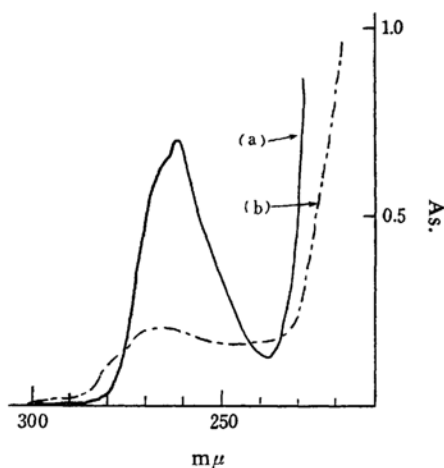


Fig. 3. Ultraviolet absorption spectra (in ethanol) of (a) triphenyl phosphite and (b) bis-(triphenyl phosphite) cuprous Chloride (IIb).

The results of these experiments are shown in Tables III and IV.

It is clear from Tables III and IV that the complex compounds I form associated molecules in organic solvents and that the degree of association are changed according to the kinds of halogens or solvents; on the contrary, the complex compounds II form simple molecules in organic solvents unconcerned with the kinds of halogens or solvents.

It seems to be possible that the apparent values of molecular weights will become smaller, if the associated molecules are dissociated in organic solvents. These possibilities are supported by the fact the degrees of association in nonpolar solvents are greater than that in polar solvent.

So, the present author prepared phenyl phosphonite, which is an analogue of phosphite but has the property of phosphine to a slight degree, and leads<sup>10)</sup> to the complex compounds III and IV.

**Preparation and Molecular Weight of *O, O*-Diisopropylphenyl Phosphoniten Cuprous Halides (III) and (IV).**—Complex compounds III and IV were prepared from *O, O*-diisopropylphenyl phosphonite<sup>11)</sup> and cuprous halide by the same method as phosphite I and II. The yield, the melting points and the microanalytical data of the complex compounds III and IV are shown in Table V.

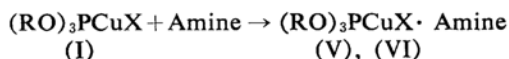
As is clearly shown in Table VI, phenyl phosphonite cuprous halides (III) form tetramer and bis-(phenyl phosphonite) cuprous halides (IV) form dimer in organic solvents irrespectively of the kinds of halogens or solvents.

From the above results of Table VI and phosphine cuprous iodide which is reported as tetramer<sup>2)</sup>, it may be considered that complex compounds I will also be tetramer and complex compounds II dimer but these compounds I and II will be dissociated in organic solvents.

But the real structures of these compounds must be determined by x-ray analysis.

**Phosphite Cuprous Halide Amine Complex Compounds.**—It was mentioned already that phosphite cuprous halides I reacted with more one mole ratio of phosphite and gave bis-phosphite cuprous halides II. In this reaction when aniline, pyridine and their derivatives are used instead of the phosphite, new complex compounds were prepared<sup>12)</sup> on the contrary bis-phosphite cuprous halides II did not react with the above amines.

That is to say, to the acetone solution containing one mole of phosphite cuprous halides I, one mole of aniline, pyridine or their derivatives was added and thus, white crystals were obtained. These crystals had sharp melting points and showed the experimental formula of  $(RO)_3PCuX \cdot \text{Amine}$ .



Changing the mole ratio of amines to phosphite cuprous halides I neither phosphite cuprous halide bis-amines  $(RO)_3PCuX(\text{Amine})_2$

10) Y. Nishizawa and Y. Suzuki, Japan. Pat. Applied No. 21678 (1959).

11) A. Arbuzov, *Chem. Abstr.*, **40**, 3411 (1946).

12) Y. Nishizawa and M. Nakagawa, Japan. Pat. Applied No. 21679 (1959).

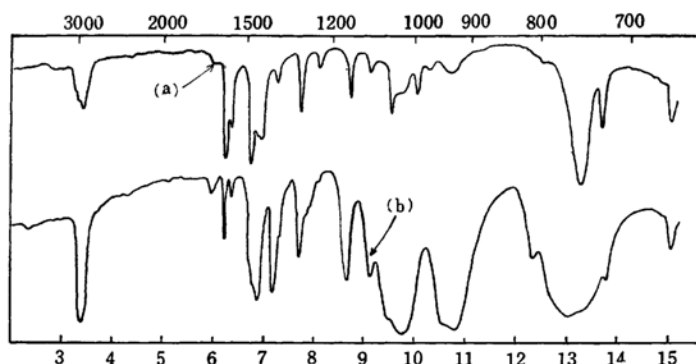


Fig. 4. Infrared absorption spectra of (a)  $\alpha$ -picoline (liquid) and (b) triethyl phosphite cuprous iodide  $\alpha$ -picoline complex compound (Ve) (in Nujol).

TABLE VI. MOLECULAR WEIGHTS OF PHENYL PHOSPHONITE CUPROUS HALIDES [ $(iso-C_3H_7O)_2PC_6H_5$ ] $_mCuX$  (III) AND (IV) IN VARIOUS SOLVENTS

No.	X	$m$	Cryoscopic solvent ( $K$ )	Concn. (g./G%)	$\Delta T$ °C	Molecular weight		Degree of association
						Experimental	Calcd. (monomeric)	
IIIa	Cl	1	Benzene (5120)	0	—	1280	325	3.93
				0.593	0.024	1265		
				1.911	0.086	1138		
			Bromoform (14050)	2.730	0.127	1101		
				0	—	1220		3.75
				0.465	0.055	1188		
				1.382	0.166	1170		
			Cyclohexane (20100)	2.655	0.322	1158		
				0	—	1340		4.12
				0.298	0.046	1302		
				0.951	0.147	1300		
				2.411	0.389	1261		
IIIb	Br	1	Benzene	0	—	1450	369.5	3.92
				0.675	0.025	1382		
				1.715	0.069	1273		
			Bromoform	2.816	0.125	1153		3.86
				0	—	1425		
				0.593	0.059	1412		
				1.491	0.151	1387		
				2.615	0.270	1361		
IIIc	I	1	Benzene	0	—	1685	416.5	4.05
				0.427	0.013	1682		
				1.793	0.054	1700		
				2.381	0.072	1693		
IVa	Cl	2	Benzene	0	—	1100	551	2.00
				0.298	0.014	1090		
				1.613	0.076	1087		
			Bromoform	2.803	0.135	1063		1.96
				0	—	1080		
				0.445	0.058	1077		
				1.412	0.187	1061		
				2.561	0.342	1052		
IVb	Br	2	Benzene	0	—	1265	595.5	2.12
				0.343	0.014	1254		
				1.612	0.065	1270		
				2.635	0.108	1249		
IVc	I	2	Benzene	0	—	1190	642.5	1.85
				0.441	0.019	1188		
				1.391	0.061	1181		
				2.546	0.111	1172		

TABLE VII. YIELDS, MELTING POINTS AND MICROANALYTICAL DATA OF PHOSPHITE CUPROUS HALIDE AMINE COMPLEX COMPOUNDS  $(RO)_3PCuX \cdot \text{Amine}$  (V), (VI)

No.	R	X	Amine	Yield %	M.p. °C	Nitrogen, %		Halogen, %		Phosphorus, %		Copper, %	
						Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
Va	C <sub>2</sub> H <sub>5</sub>	Cl	Pyridine	98.8	56~57	4.22	4.07	10.00	10.32	8.9	9.0	19.1	18.5
Vb	C <sub>2</sub> H <sub>5</sub>	Br	Pyridine	97.2	105~106	3.81	3.60	20.38	20.59	7.9	8.0	15.8	16.3
Vc	C <sub>2</sub> H <sub>5</sub>	I	Pyridine	97.9	72~73	3.50	3.21	—	—	6.8	7.1	14.6	14.6
Vd	C <sub>6</sub> H <sub>5</sub>	Cl	Pyridine	93.5	126~127	2.76	2.87	7.55	7.27	6.6	6.4	13.3	13.0
Ve	C <sub>2</sub> H <sub>5</sub>	I	$\alpha$ -Picoline	90.4	59~60	3.35	3.11	—	—	7.2	7.1	14.6	14.1
Vf	C <sub>2</sub> H <sub>5</sub>	I	$\beta$ -Picoline	96.2	84~85	3.08	3.11	—	—	6.9	7.1	14.0	14.1
Vg	C <sub>2</sub> H <sub>5</sub>	I	$\gamma$ -Picoline	88.2	76~77	3.31	3.11	—	—	7.3	7.1	13.8	14.1
Vh	C <sub>2</sub> H <sub>5</sub>	I	2,4-Lutidine	77.5	97~99	3.15	3.02	—	—	6.7	6.9	14.1	13.7
Vi	C <sub>2</sub> H <sub>5</sub>	I	2,6-Lutidine	82.8	70~71	3.31	3.02	—	—	6.8	6.9	13.6	13.7
Vj	C <sub>2</sub> H <sub>5</sub>	Cl	$\alpha, \alpha'$ -Dipyridyl	98.1	105~106	3.66	3.42	—	—	7.1	7.4	15.2	15.1
VIa	C <sub>2</sub> H <sub>5</sub>	I	Aniline	71.5	80~81	3.50	3.11	—	—	6.8	6.9	14.3	14.1
VIb	C <sub>2</sub> H <sub>5</sub>	I	<i>p</i> -Toluidine	97.2	60~61	3.15	3.01	—	—	6.5	6.7	13.9	13.7
VIc	C <sub>2</sub> H <sub>5</sub>	I	<i>p</i> -Anisidine	96.5	66~67	2.65	2.91	—	—	6.3	6.4	12.9	13.2
VI d	C <sub>2</sub> H <sub>5</sub>	I	<i>p</i> -Chloroaniline	95.5	72~73	2.65	2.83	—	—	6.5	6.3	12.6	12.8
VI e	C <sub>2</sub> H <sub>5</sub>	I	<i>m</i> -Chloroaniline	98.3	60~62	2.91	2.83	—	—	6.3	6.3	13.1	12.8

TABLE VIII. 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.
C <sub>2</sub> H <sub>5</sub>	82	55~57	19	1.4135 <sup>(20)</sup>	19.8	19.9	46.31	46.15	9.25	9.04
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	85	82~83	10	1.4263 <sup>(20)</sup>	15.1	14.9	52.06	51.92	10.09	10.10
<i>iso</i> -C <sub>3</sub> H <sub>7</sub>	80	60~61	9	1.4079 <sup>(20)</sup>	15.0	14.9	51.88	51.92	10.41	10.10
C <sub>6</sub> H <sub>5</sub>	63	170	0.3	m.p. 25°C	9.8	10.0	69.53	69.68	4.97	4.84

nor bis-amine cuprous halides  $(\text{Amine})_2\text{CuX}$  were obtained.

The yields, the melting points and the microanalytical data of these new complex compounds V and VI are shown in Table VII. The infrared absorption spectra of these complex compounds V and VI showed that these compounds V and VI have both the amine molecule and the phosphite molecule. Infrared absorption spectrum of triethyl phosphite cuprous iodide  $\alpha$ -picoline (Ve) is shown in Fig. 4 as a representation.

It was interesting to see that ortho-substituted anilines, *O*-chloroaniline, *O*-toluidine, *O*-anisidine etc., did not give these complex compounds VI. The cause may be considered from models of complex molecules to be a steric hindrance owing to the ortho-substituent in aniline.

In the pyridine series, all derivatives gave new complex compound, irrespective of the position of substituents.

It was also made clear by the present author that all of the above mentioned compounds I, II, III, IV, V and VI had strong fungicidal activities<sup>13)</sup>, and the data of their biological activities will be reported in other paper.

## Experimental

**Preparations of Phosphites.**—Trialkyl or triphenyl phosphites were prepared by Ford-Moore's methods<sup>14)</sup> and their yields, physical constants and microanalytical data are shown in Table VIII.

**Preparation of Diisopropyl Phenyl Phosphonite.**—This phosphonite was prepared from phenyl dichlorophosphine and isopropyl alcohol by Arbuzov's method<sup>11)</sup>. The boiling point is 110°C/0.5 mmHg, the refractive index is  $n_D^{25}$  1.5000 and the yield is 84%.

Found, P, 13.7; C, 63.59; H, 8.59. Calcd. for  $C_{12}H_{19}O_2P$ , P, 13.7; C, 63.72; H, 8.41%.

**Preparation of Phosphite or Phosphonite Cuprous Halides I or III.**—The following example illustrates the preparation of phosphite or phosphonite cuprous halides I or III. Other examples are shown in Tables I and V and their molecular weights are shown in Tables III and VI.

**Preparation of Diisopropyl Phenyl Phosphonite Cuprous Chloride (IIIa).**—To a solution of 14.3 g. (0.05 mol.) of diisopropyl phenyl phosphonite in 50 ml. of benzene was gradually added 4.95 g. (0.05 mol.) of cuprous chloride. The temperature rose gradually and cuprous chloride was dissolved in benzene. After one hour's stirring, the trace of insoluble matter was filtered off and concentrated under reduced pressure. White crystals (18.9 g.,

13) J. Hattori and Y. Nishizawa, Japan. Pat. Applied No. 36382 (1958), 3506, 22572, 22573 (1959).

14) A. H. Ford-Moore, "Organic Syntheses", Vol. 31, John Wiley & Sons, New York, (1951), p. 111.

98.5%) were obtained and recrystallized from petroleum ether, m. p. 141~142°C.

Found: Cl, 10.88; P, 9.4; Cu, 19.8. Calcd. for  $C_{12}H_{10}O_2PCuCl$ : Cl, 10.92; P, 9.5; Cu, 19.5%.

**Preparation of Bis-phosphite or Bis-phosphonite Cuprous Halides II or IV.**—The following example illustrates the preparation of bis-phosphite or bis-phosphonite cuprous halides II or IV. Other examples are shown in Tables II and V and their molecular weights are shown in Tables IV and VI.

**Preparation of Bis-(diisopropyl Phenyl Phosphonite) Cuprous Chloride (IVa).**—The compound was prepared from 28.5 g. (0.1 mol.) of diisopropyl phenyl phosphonite and 4.95 g. (0.05 mol.) of cuprous chloride in benzene solution as above mentioned. White crystals (32.9 g., 98.4%) were obtained and melted at 144~145°C (from ligroin).

Found: Cl, 6.39; P, 11.0; Cu, 11.9. Calcd. for  $C_{24}H_{38}O_4P_2CuCl$ : Cl, 6.44; P, 11.2; Cu, 11.5%.

**Reaction of Triisopropyl Phosphite Cuprous Chloride (Ia) with Triisopropyl Phosphite.**—To a solution of 15.3 g. (0.05 mol.) of triisopropyl phosphite cuprous chloride (Ia) in 50 ml. of benzene was added 10.4 g. (0.05 mol.) of triisopropyl phosphite. The temperature did not rise during this addition. The benzene was evaporated under reduced pressure, white crystals (23.8 g.) were obtained and melted at 69~70°C. A mixture of the crystals and the authentic bis-(triisopropyl phosphite) cuprous chloride which was prepared from two moles of triisopropyl phosphite and one mole of cuprous chloride, melted at 69~70°C.

**Reaction of Triethyl Phosphite Cuprous Chloride<sup>4</sup> with Triphenyl Phosphite.**—Triphenyl phosphite (15.5 g., 0.05 mol.) was added to a solution of 13.3 g. (0.05 mol.) of triethyl phosphite cuprous chloride in 50 ml. of benzene. After the benzene was evaporated off, white crystals of triethyl phosphite triphenyl phosphite cuprous chloride (IIg) (28.1 g, 97.8%) were obtained and melted at 75~76°C.

Found: Cl, 6.15; P, 11.2; Cu, 10.8. Calcd. for  $C_{24}H_{30}O_6P_2CuCl$ : Cl, 6.17; P, 10.9; Cu, 11.0%.

**Reaction of Bis-(triisopropyl phosphite) Cuprous Chloride (IIa) with Cuprous Chloride.**—There was added 4.95 g. (0.05 mol.) of cuprous chloride to a solution of 25.7 g. (0.05 mol.) of bis-(triisopropyl phosphite) cuprous chloride (IIa) in 50 ml. of benzene. After cuprous chloride was dissolved in benzene, the reaction mixture was filtered off and concentrated. White crystals (29.6 g) were obtained and melted at 117°C.

This melting point coincides with that of the authentic triisopropyl phosphite cuprous chloride (Ia) prepared from one mole ratio of triisopropyl phosphite and one mole ratio of cuprous chloride, and the mixed melting point was not depressed.

**Reaction of Triethyl Phosphite Cuprous Iodide (Ie) with Acetyl Chloride.**—To a solution of 17.8 g. (0.05 mol.) of triethyl phosphite cuprous iodide (Ie) in 50 ml. of benzene, there was gradually added 3.9 g. of acetyl chloride. The temperature of the reaction mixture rose and white inorganic compounds were precipitated. After one hour's refluxing, the precipitates were filtered off and the filtrate was concentrated. The residual oil was

fractionated under reduced pressure. The main product was distilled at 78~79°C/3 mmHg, and yielded 7.7 g.

$n_D^{20}$  1.4209. Found: P, 17.1; C, 39.81; H, 7.34. Calcd. for  $C_6H_{13}O_4P$ : P, 17.2; C, 40.00; H, 7.22%. *p*-Nitrophenylhydrazone of the aforesaid main product was prepared from *p*-nitrophenylhydrazine in the usual manner.

This hydrazone melted at 131~132°C (recryst. from ethanol) and the mixed melting point with authentic *p*-nitrophenylhydrazone of *O,O*-diethylacetyl phosphonate prepared from triethyl phosphite and acetyl chloride was not depressed.

Found: P, 9.6; C, 45.59; H, 5.89; N, 13.31. Calcd. for  $C_{12}H_{18}N_3O_5P$ : P, 9.8; C, 45.71; H, 5.71; N, 13.33%.

**Pyrolysis of Bis-(triisopropyl Phosphite) Cuprous Chloride (IIa).**—The compound IIa (25.8 g., 0.05 mol.) was set in a distillation flask (50 ml.) which was combined with a trap cooled at -50°C and heated at 100°C under 0.3 mmHg for 6 hr.

The crystals IIa melted and then crystallized again. The product was recrystallized from petroleum ether and melted at 116~117°C. This melting point coincides with that of the authentic triisopropyl phosphite cuprous halide (Ia) prepared from one mole ratio of triisopropyl phosphite and one mole ratio of cuprous chloride and the mixed melting point was not depressed.

On the other hand, colorless oil which was captured in a trap, was distilled at 60~62°/9mmHg and yielded 7.7 g,  $n_D^{25}$  1.4081.

Found: P, 14.6; C, 15.80; H, 10.35. Calcd. for  $C_9H_{21}O_3P$ : P, 14.9; C, 15.92; H, 10.10%.

This oil was added to a benzene solution containing 5.3 g. of cuprous chloride and gave white crystals which melted at 116~117°C. The melting point of these crystals coincided with the authentic triisopropyl phosphite cuprous chloride (Ia) and the mixed melting point was not depressed.

**Reaction of Phosphite Cuprous Halides I with Amines.**—The following example illustrates the preparation of phosphite cuprous halide amine complex V or VI. Other examples are shown in Table VII.

**Reaction of Triethyl Phosphite Cuprous Chloride with Pyridine.**—To a solution of 26.5 g. (0.1 mol.) of triethyl phosphite cuprous chloride in 100 ml. of acetone was added 7.9 g. (0.1 mol.) of pyridine.

The acetone was evaporated off under reduced pressure and light green crystals (33.9 g.) were obtained. White needles were recrystallized from ligroin and melted at 56~57°C.

Found: N, 4.22; Cl, 10.00; P, 8.9; Cu, 19.1. Calcd. for  $C_{11}H_{20}ClNO_3PCu$ : N, 4.07; Cl, 10.32; P, 9.0; Cu, 18.5%

### Summary

Phosphites or phosphonites react with cuprous halides in one to one or two to one mole ratio to give phosphite, phosphonite, bisphosphite or bis-phosphonite cuprous halides complex compounds. Their molecular weights



in various organic solvents showed that these compounds formed polymer.

Phosphite cuprous halides react with pyridine, aniline or their derivatives and gave new complex compounds having phosphite, cuprous chloride and amine.

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