cooled to room temperature, and 5 g. of naphthalene was added. To this stirred mixture was slowly added a solution of 1.0 g. of cobaltous chloride and 5.45 g. (0.05 mole) of ethyl bromide in 40 ml. of tetrahydrofuran. Gas was evolved continuously throughout the addition (535 ml. at S.T.P., 48% of the theoretical yield). Analysis of this gas indicated that it was 28% ethane and 72% ethylene.

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Crystalline Complexes of the Phosphoryl Group with Polyphenols[1]

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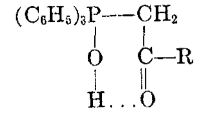
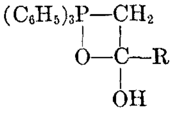
The "quasi-phosphonium" compounds,[3] for instance $[R_3P(OR')X]$, constitute an interesting variation of the phosphonium structure, $[R_4PX]$, in which one or more R groups are replaced by OR groups. This structural change might conceivably alter significantly the bonding characteristics of the phosphorus atom. A substance of composition $[R_3PO, HX]$ could be formulated as a hydrogen-bonded complex, $[R_3PO...HX]$, a phosphonium hydroxide, $[R_3P(OH)]^+X^-$, or as a structure with pentacovalent phosphorus, $[R_3P(OH)X]$. Halmann and Pinchas[4] have discussed recently the structure of triphenylphosphine oxide hydrate, which they formulate as $[(Ph_3PO)_2, H_2O]$. It was concluded that the hydrate is a molecular complex between the phosphine oxide and the water molecule, and that it does not have the dihydroxy structure, $[Ph_3P(OH)_2]$.

We have recently shown[5] that the "acylphosphinemethylene hydrates" which had been previously formulated[6] with pentacovalent phosphorus, such as in I[6a] or II,[6b] are actually *ylides* of type III. These ylides have a strong tendency to retain water.



I



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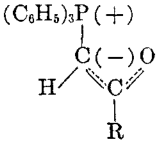

III

In another investigation,[7] it was shown that the crystalline, sharp-melting adducts formed from triphenylphosphine oxide and tetrachlorohydroquinone do not have the quasi-phosphonium structure $[(C_6H_5)_3P(OAr)(OH)]$. These adducts are formed: (a) when the oxide and the polyphenol are fused together in a 2:1 molar ratio or (b) when an alcoholic solution containing the oxide and the polyphenol is evaporated to dryness or is diluted with water. The adducts were formulated as hydrogen-bonded complexes, such as IV. Related compounds[8] are probably of the same type.

We have now extended these observations to include other polyphenols, as shown in Table I. Furthermore, it was found that certain *phosphate esters* also form crystalline, sharp-melting complexes with tetrachlorohydroquinone. The infrared spectra of these complexes, the ease with which they are formed and the ease with which they are split into their components by cold, dilute alkali, are consistent with the hydrogen-bonded formulations VIII, IX, X, and XI. The substances listed in Table 1 were obtained by addition of water to an alcoholic solution containing the phosphoryl derivative and the polyphenol in the proper molar ratio. The melting point of the original precipitate does not change significantly by recrystallization. It should be noted that the solubility of the polyphenol itself in a nonpolar solvent like benzene is quite small; the adducts, however, are appreciably soluble in benzene. The adducts derived from phosphate esters are quite soluble even in cyclohexane.

TABLE I

CRYSTALLINE COMPLEXES OF THE PHOSPHORYL GROUP ($\geqslant$PO) WITH POLYPHENOLS[a]

			Analyses[d]			
			Calcd.		Found	
Formula	Molar Ratio[b]	M.P.,[c] °C.	C	H	C	H
IV	2:1	180–182	62.7	4.0	62.3	4.3[e,]
V	2:1	164–165	68.6	4.7	68.5	4.9[f,]
VI	2:1	144–146	75.7	5.5	75.9	5.9[f]
VII	1:1	120–121	54.8	3.3	54.9	3.4[f]
VIII	2:1	106–108	29.2	2.0	29.3	2.2[h]
IX	2:1	74–75	33.9	3.0	33.6	3.3[i]
X	1:1	193–194	27.0	2.0	27.4	2.2[j]
XI	1:1	140–141	31.3	2.9	31.8	3.1[h]

[a] A methanol solution containing the components in the molar ratio indicated, was diluted with water. The crystalline precipitate was dried and its m.p. determined; the m.p. did not change significantly upon repeated recrystallizations. For the preparation of the phosphoryl components see ref. 12. [b] Phosphoryl derivative: polyphenol. [c] Corrected capillary – m.p. [d] Micro-Tech Laboratories, Skokie, Ill. [e] Calcd.: P, 7.7; Cl, 17.6. Found: P, 7.6; Cl, 17.5. [f] Recrystallized from benzene–petroleum ether. [g] Calcd.: P, 8.4; Cl, 9.4. Found: P, 8.5; Cl, 9.5. [h] Recrystallized from cyclohexane. [i] Recrystallized from hexane. [j] Recrystallized from benzene.

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[3] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1950, Chapter II.

[4] M. Halmann and S. Pinchas, *J. Chem. Soc.*, 3264 (1958).

[5] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

[6] (a) G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 (1954); (b) A. Michaelis and E. Kohler, *Ber.*, **32**, 1566 (1899).

[7] F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **78**, 5614 (1956).

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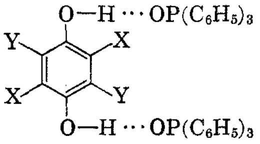
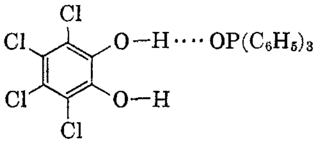
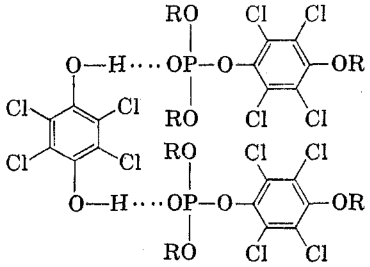
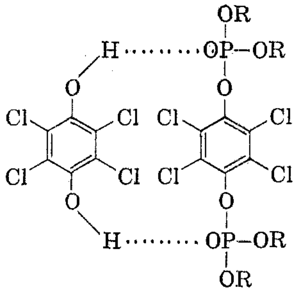
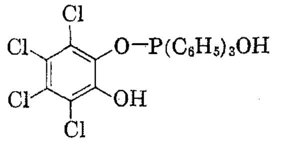
The composition of the complexes depend, as shown by X and XI, on the number of phosphoryl groups in the molecule or, as in the case of VII, on steric requirements in the polyphenol. The latter complex, m.p. 122°, has already been encountered by Horner[9] as a product of the hydrolysis of the tetrachloro-*o*-benzoquinone-triphenylphosphine adduct. It was formulated by him as a hydrate VIIA.


IV. X = Y = Cl
V. X = Cl; Y = H
VI. X = Y = H


VII


VIII. R = CH_3
IX. R = C_2H_5


X. R = CH_3
XI. R = C_2H_5


VIIA

The structural problems involved in the formulation of some of the compounds of the general type $(RO)_xPZ_{5-x}$ have been clarified by recent investigations of Lipkin[10] and of Rydon.[11] For the particular instance in which one R group = H, a satisfactory representation seems to be that of loosely bonded complex, probably of the hydrogen-bonded type.

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Some Heterocyclic Compounds Containing Phosphorus

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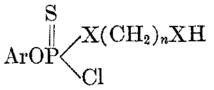
In the course of investigations involving *O*-halophenyl phosphorodichloridothioates, $ArOPSCl_2$,[1] it became desirable to study reactions of these acid dichlorides with difunctional nucleophiles of the structure $HX(CH_2)_yXH$ (X being oxygen or —NH—, *y* being zero or integer). At a constant mole ratio of 1:1, the formation of four types of compound appeared possible: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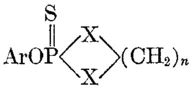
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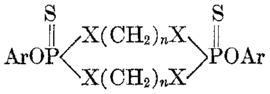
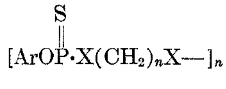

III


$[ArO\overset{S}{\overset{\|}{P}}\cdot X(CH_2)_nX\text{—}]_n$
IV

In order to investigate the tendencies of formation[2] of the heterocyclic structures II and III, experiments were carried out with hydrazine, ethylenediamine, and ethylene glycol as representative dinucleophiles and with various substituted phenyl groups in place of Ar.

Reactions involving *hydrazine*[3–5] were reported to produce compounds of structure III, *viz.*, $C_6H_5OP(O)(NHNH)_2P(O)OC_6H_5$[5] and $C_6H_5OP(S)(NHNH)_2P(S)OC_6H_5$[4]. Repetition of the work involving $C_6H_5OPSCl_2$ gave a crystalline compound which melted at 184–185° and showed analytical data as required for structure III. The yield of this compound was found to be 16% of theory, when prepared in the presence of a water-glycerol mixture, as mentioned in the literature.[4] The other reaction products formed were not found to represent structures I, II, or IV, but to consist of hydrazine salts of *O*-phenyl phosphoro-

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