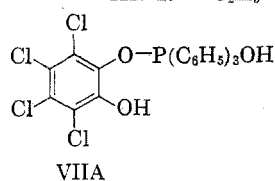
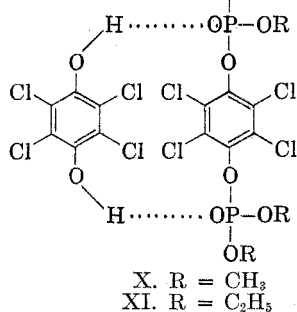
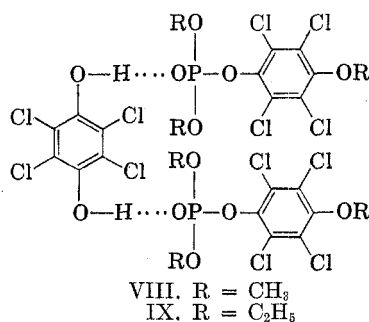
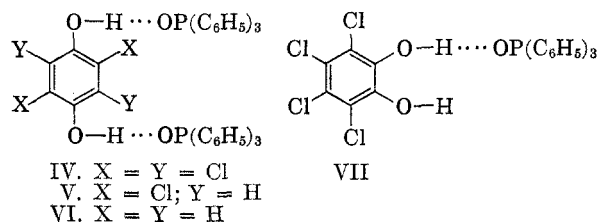


The composition of the complexes depend, as shown by X and XI, on the number of phosphoryl groups in the molecule or, as in the case of VII, on steric requirements in the polyphenol. The latter complex, m.p. 122°, has already been encountered by Horner<sup>9</sup> as a product of the hydrolysis of the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



The structural problems involved in the formulation of some of the compounds of the general type (RO)<sub>x</sub>PZ<sub>5-x</sub> have been clarified by recent investigations of Lipkin<sup>10</sup> and of Rydon.<sup>11</sup> 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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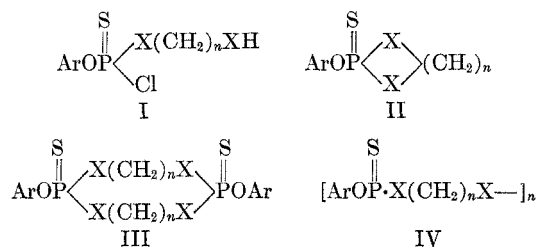
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### Some Heterocyclic Compounds Containing Phosphorus

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Received November 3, 1958

In the course of investigations involving *O*-halophenyl phosphorodichloridothioates, Ar-OPSCl<sub>2</sub>,<sup>1</sup> it became desirable to study reactions of these acid dichlorides with difunctional nucleophiles of the structure HX(CH<sub>2</sub>)<sub>y</sub>XH (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:



In order to investigate the tendencies of formation<sup>2</sup> 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*<sup>3-5</sup> were reported to produce compounds of structure III, *viz.*, C<sub>6</sub>H<sub>5</sub>OP(O)(NHNH)<sub>2</sub>P(O)OC<sub>6</sub>H<sub>5</sub><sup>5</sup> and C<sub>6</sub>H<sub>5</sub>OP(S)-(NHNH)<sub>2</sub>P(S)OC<sub>6</sub>H<sub>5</sub>.<sup>4</sup> Repetition of the work involving C<sub>6</sub>H<sub>5</sub>OPSCl<sub>2</sub> 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.<sup>4</sup> 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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(10) J. P. Forsman and D. Lipkin, *J. Am. Chem. Soc.*, **75**, 3145 (1953).

(11) (a) D. G. Coe, H. N. Rydon, and B. L. Tonge, *J. Chem. Soc.*, 323 (1957); (b) H. N. Rydon in *Phosphoric Esters and Related Compounds*, The Chemical Society, London (1957), Special Publication No. 8, p. 61.

(1) H. Tolkmith, *J. Org. Chem.*, **23**, 1685 (1958).

(2) Cf. F. G. Mann, "The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, Bismuth and Silicon," Interscience Publishers Inc., New York (1950).

(3) W. Strecker and H. Heuser, *Ber.*, **57**, 1372 (1924).

(4) W. Autenrieth and W. Meyer, *Ber.*, **58**, 848 (1925).

(5) W. Autenrieth and E. Bolli, *Ber.*, **58**, 2144 (1925).

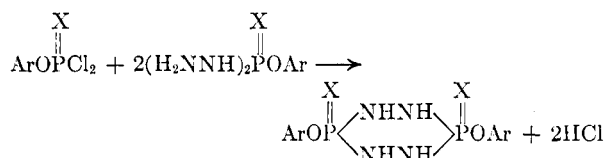
TABLE I  
 HETEROCYCLIC COMPOUNDS FROM HYDRAZINE

Compound	Yield, % Th.	M.P.	Mol. Wt.		% N		% P		% S	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{C}_6\text{H}_5\text{OP} \begin{array}{c} \text{S} \\ \parallel \\ \text{NHNH} \\ \parallel \\ \text{S} \end{array} \text{POC}_6\text{H}_5$	53.5	184-185	372.35	404 <sup>a</sup>	15.05	14.89	16.64	16.20	17.22	16.71
$\text{C}_6\text{H}_5\text{OP} \begin{array}{c} \text{O} \\ \parallel \\ \text{NHNH} \\ \parallel \\ \text{O} \end{array} \text{POC}_6\text{H}_5$	8.0	210-211	340.21	330 <sup>b</sup>	16.47	16.75	18.21	18.45		
$\text{C}_6\text{H}_5\text{P} \begin{array}{c} \text{S} \\ \parallel \\ \text{NHNH} \\ \parallel \\ \text{S} \end{array} \text{PC}_6\text{H}_5$	12.5	168-169	340.33	383 <sup>c</sup>	16.46	16.48	18.2	17.86	18.8	18.27

<sup>a</sup> In tetrahydrofuran. <sup>b</sup> In dimethylformamide. <sup>c</sup> In methyl ethyl ketone.

thioic acid. Anhydrous reactants in benzene were found to produce compounds possessing structure III in varying yields depending upon the structure of the dichloride employed (*cf.* Table I). The melting point found for  $\text{C}_6\text{H}_5\text{OP}(\text{O})(\text{NHNH})_2\text{P}(\text{O})\text{OC}_6\text{H}_5$ , when prepared under anhydrous conditions, varied considerably from the value given in the literature (m. p. 132°).<sup>5</sup>

The following reaction was investigated also (X being oxygen or sulfur):



This reaction required the presence of stoichiometric quantities of triethylamine and gave the compound,  $\text{C}_6\text{H}_5\text{OP}(\text{S})(\text{NHNH})_2\text{P}(\text{S})\text{OC}_6\text{H}_5$ , in a yield of 89% of theory. Reactions involving negatively substituted phenyl groups in place of Ar were found to produce mixtures of reaction products from which no heterocyclic components could be isolated.

Autenrieth and Meyer<sup>4</sup> reported formation of an insoluble reaction product from *O*-phenyl phosphorodichloridothioate and ethylenediamine and assigned structure II to it, although analytical evidence was insufficient. It was found that *O*-aryl phosphorodichloridothioates and ethylenediamine, when reacting under anhydrous conditions, at a mole ratio of 1:2, produced heterocyclic derivatives for which structure II could be proved. The yields of these compounds increased with increasing negative substitution of their aryl group. The melting points also were found to increase in first approximation with increasing negative substitution of the phenyl group (*cf.* Table II) with the notable exception of the derivative of  $\text{C}_6\text{H}_5\text{OPSCl}_2$  whose melting point was found to be almost as high as already reported (m.p. 189°).<sup>4</sup> Contrary to statements in the literature,<sup>4</sup> these compounds were found to be appreciably soluble in acetone, dimethylformamide, methanol, and tetrahydrofuran.

Reactions of *O*-aryl phosphorodichloridothioates with glycols were not described in the past. Conceivably, all four structures (I, II, III, and IV) could be formed from these reactants. The existence of a five-membered, heterocyclic ring as present in structure II (X being oxygen, *n* being two) with aliphatic groups in place of Ar, was proved by A. E. Arbuzov and V. M. Zoroastrova.<sup>6</sup>

The investigation reported in the following involved reactions in the absence of HCl-acceptors and catalysts at temperatures of 50-60° under a pressure of less than 200 mm. Under these conditions reaction occurred readily with evolution of HCl, although *O*-aryl phosphorodichloridothioates have been reported to possess remarkable resistance to attack by hydroxyl compounds.<sup>7,8</sup> Independent of the mole ratio of the reactants employed, the mixture of reaction products was always found to contain compounds representing structure II. The yield of this type of component increased with increasing negative substitution of the phenyl group in  $\text{ArOPSCl}_2$ . The yields were particularly good with two negative substituents in *ortho*-position (*cf.* Table III). The structure of side products formed could not be established with certainty but might have corresponded to structure III whose nonsulfurated, ten-membered ring probably exists.<sup>9</sup> Compounds of structure I were not isolated, even at a 1:1 mole ratio of reactants. The heterocyclic *O*-halophenyl *O,O*-ethylene glycol phosphorothioates obtained were found to be well crystallizing compounds, being soluble in acetone, aromatic hydrocarbons, and methanol.

It has been shown in this laboratory that reactions of *O*-halophenyl phosphorodichloridothioates with primary monohydric alcohols and primary monoamines, under reaction conditions almost

(6) A. E. Arbuzov and V. M. Zoroastrova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 357 (1950).

(7) W. Autenrieth and O. Hildebrand, *Ber.*, **31**, 1094 (1898).

(8) W. Strecker and Ch. Grossmann, *Ber.*, **49**, 63 (1916).

(9) H. G. Cook, J. D. Ilett, B. C. Saunders, G. J. Stacey, H. G. Watson, I. G. E. Wilding, and S. J. Woodcock, *J. Chem. Soc.*, 2921 (1949).

TABLE II  
 HETEROCYCLIC COMPOUNDS FROM ETHYLENEDIAMINE

Compound	Yield, (% Th)	M.P.	Mol. Wt.		% N		% P		% S	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{C}_6\text{H}_5\text{OP}(\text{S})(\text{NHCH}_2)_2$	25.5	185.5-186.5	214.23	203	13.08	13.01	14.46	14.35	14.97	14.57
$4\text{F}\cdot\text{C}_6\text{H}_4\text{OP}(\text{S})(\text{NHCH}_2)_2$	57.5	63-64	232.22	220	12.08	11.91	13.33	13.04	13.8	13.6
$3\text{Cl}\cdot 4\text{NO}_2\cdot\text{C}_6\text{H}_3\text{OP}(\text{S})(\text{NHCH}_2)_2$	55.0	108-109	293.67	271	14.3	13.8	10.58	10.6	10.9	10.8
$2,4,5\text{-Cl}_3\cdot\text{C}_6\text{H}_2\text{OP}(\text{S})(\text{NHCH}_2)_2$	83.0	156.5-158	317.57	298	8.84	8.81	9.76	9.82	10.10	10.01
$2,4,6\text{-Cl}_3\cdot\text{C}_6\text{H}_2\text{OP}(\text{S})(\text{NHCH}_2)_2$	83.0	207-208	317.57	285	8.84	8.37	9.76	9.61	10.10	9.91
$2,4,6\text{-Br}_3\cdot\text{C}_6\text{H}_2\text{OP}(\text{S})(\text{NHCH}_2)_2$	51.5	222-223	450.95	463	6.22	5.95	6.89	6.95	7.10	7.34

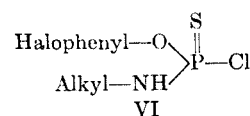
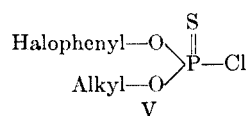
 TABLE III  
 HETEROCYCLIC COMPOUNDS FROM ETHYLENE GLYCOL

Compound	Ratio <sup>a</sup>	Yield, (% Th)	M.P.	Mol. Wt.		% Halogen		% P		% S	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$2,4,5\text{-Cl}_3\text{C}_6\text{H}_2\text{OP}(\text{S})(\text{OCH}_2)_2$	1:0.5	32	123-124	319.54	268	33.4	33.1	9.7	9.9	10.0	10.3
	1:2	30	122-123								
$2,4,6\text{-Cl}_3\text{C}_6\text{H}_2\text{OP}(\text{S})(\text{OCH}_2)_2$	1:2	69	80-81	319.54	315	33.4	33.5	9.7	9.87	10.0	10.2
$2,4,6\text{-Br}_3\text{C}_6\text{H}_2\text{OP}(\text{S})(\text{OCH}_2)_2$	1:2	44	64-65	452.92	395	53.0	53.24	6.84	6.73	7.06	6.93
$2\text{Cl}\cdot 4\text{NO}_2\cdot\text{C}_6\text{H}_3\text{OP}(\text{S})(\text{OCH}_2)_2$	1:1	35.5	93.5-94.5	295.64	273	12.02	12.3	10.48	9.8	10.83	10.7
$4\text{NO}_2\cdot\text{C}_6\text{H}_4\text{OP}(\text{S})(\text{OCH}_2)_2$	1:2	16	48-49	261.19	238			11.57	11.3	11.92	12.01

<sup>a</sup> Mole ratio,  $\text{ArOPSCl}_2:\text{HOCH}_2\text{H}_2\text{OH}$ .

identical to those employed with the analogous dinucleophiles of the present investigation, produce near-quantitative yields of the following types of compound.<sup>10,11</sup> Hersman and Audrieth<sup>12</sup> have found that the reaction of aryl phosphonodichloridates

and dichloridothioates with alcohols gives compounds of a structure analogous to V.



(10) H. Tolkmith, E. H. Blair, and K. C. Kauer, Can. Patent 555,938 (April 15, 1958).

(11) E. H. Blair and H. Tolkmith, paper presented before the Division of Organic Chemistry at the 134th meeting of the American Chemical Society, September 7-12, 1958, Chicago, Ill.

(12) M. F. Hersman and L. F. Audrieth, *J. Org. Chem.*, **23**, 1889 (1958).

In view of these findings the following conclusions may be drawn:

Phosphorodichloridothioates,  $\text{ArOPSCl}_2$ , and dinucleophiles (as defined) may well react with initial formation of compounds representing structure I,

but at temperatures of at least 20°, these intermediates undergo dehydrochlorination of reaction rates evidently faster than the rates of formation of the intermediates themselves. Such dehydrochlorination reactions produce heterocyclic phosphorus compounds predominantly, with formation of five- and six-membered heterorings and, possibly, ten-membered rings (structures II and III). The formation organic, five-membered rings (structure II) evidently is favored by increased electron-attracting power of the halophenyl group as well as by increasing nucleophilicity of the dinucleophile participating. The formation of inorganic, six-membered P—N rings appears to be hindered by increasing electrophilicity of the Ar group. Electron withdrawal by this group from the hydrazine nitrogens may decrease the extent of hydrogen-hydrogen repulsion, which is considered to be the cause for fixation of the hydrazine molecule in *trans* position.<sup>13</sup> With acquisition of free rotation about the N—N axis, hydrazine becomes more likely to form nonheterocyclic polycondensation products instead of heterocyclics of structure III.

#### EXPERIMENTAL

The *O*-aryl phosphorodichloridothioates employed were of a quality as described previously,<sup>1</sup> while the dinucleophiles were anhydrous, commercial grade products.

**Hydrazine derivatives.** Anhydrous hydrazine (1.5 gram moles) was added dropwise over a period of 3 hr. at room temperature to an agitated solution prepared from 500 cc. of benzene and 0.5 gram mole of C<sub>6</sub>H<sub>5</sub>OPSCl<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>OPOCl<sub>2</sub>, or C<sub>6</sub>H<sub>5</sub>PSCl<sub>2</sub>, respectively. After completed reaction the reaction mixture was filtered and the solid thus isolated was dissolved in ethanol. Addition of water to this solution gave the crude main product which was recrystallized from methanol. The products obtained showed yields, melting points and analyses as given in Table I. The molecular weights were determined ebullioscopically as indicated in this table.

The compound, C<sub>6</sub>H<sub>5</sub>OPS(NHNH)<sub>2</sub>PS.OC<sub>6</sub>H<sub>5</sub>, was also prepared by dropwise addition of triethylamine (0.225 gram mole) to an agitated solution of C<sub>6</sub>H<sub>5</sub>OPSCl<sub>2</sub> (0.1 gram mole) and C<sub>6</sub>H<sub>5</sub>OPS(NHNH)<sub>2</sub> (0.1 gram mole) in 400 cc. of toluene. After completed addition the mixture was slowly heated to reflux over a period of 5 hr., cooled to room temperature, and treated with 400 cc. of water. Separation of the solid phase from this mixture gave 36 grams of a white solid which was recrystallized from aqueous ethanol. Obtained was 33 grams of desired compound, melting at 184–185°. Its infrared analysis showed identity with the compound obtained from C<sub>6</sub>H<sub>5</sub>OPSCl<sub>2</sub> and anhydrous hydrazine.

**Reactions involving ethylenediamine.** One fourth of a gram mole of ethylenediamine was added dropwise to an agitated solution of one tenth of a gram mole of ArOPSCl<sub>2</sub> in 500 cc. of ethylene dichloride at such a rate that the reaction mixture maintained a temperature of +15 to +25° when cooled with ice water. After completed reaction the mixture was washed twice with 200 cc. of water in order to remove ethylenediamine hydrochloride formed. The ethylene dichloride layer was separated and evaporated. The evaporation residues were recrystallized from methanol and gave main products with yields, analyses, and melting points as

given in Table II. The molecular weights of these products were determined ebullioscopically in methanol.

**Reactions involving ethylene glycol.** Mixtures of one-half gram mole of *O*-aryl phosphorodichloridothioate with one-fourth to one gram mole of ethylene glycol, as indicated in Table III, were heated with agitation for eight hours at 55° under a pressure of about 100 mm. The reaction mixtures were taken up with benzene and washed with water in order to remove unreacted glycol. The benzene layers were separated and evaporated. The evaporation residues were recrystallized from methanol to give main products with yields, analyses, and melting points as shown in Table IV. The molecular weights of these products were determined cryoscopically in benzene.

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### Selective Hydrogenation of Olefins with Ruthenium

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Received November 5, 1958

In common with the other platinum metals, ruthenium can be a very active hydrogenation catalyst, but its use has been limited, so far, mainly to carbonyl reduction,<sup>1</sup> to ring hydrogenation, especially where hydrogenolysis is to be avoided,<sup>2</sup> and to reduction of acids to alcohols.<sup>3</sup>

We examined ruthenium catalysts for the hydrogenation of olefins and discovered the catalyst was very selective. Monosubstituted olefins were reduced preferentially in the presence of di- and trisubstituted olefins, as shown in the following

#### COMPETITIVE HYDROGENATION OF OLEFINS BY RUTHENIUM ON CARBON

4-Methyl-1-pentene and 2-methyl-2-pentene	Selective
4-Methyl-1-pentene and 2-methyl-1-pentene	Selective
4-Methyl-1-pentene and 2-octene	Selective
4-Methyl-1-pentene and cyclohexene	Selective
2-Methyl-2-pentene and 2-methyl-1-pentene	Not selective
2-Methyl-2-pentene and 2-octene	Not selective
2-Methyl-2-pentene and 1-octene	Selective
2-Methyl-2-pentene and cyclohexene	Not selective <sup>c</sup>
2-Methyl-1-pentene and 2-octene	Not selective <sup>c</sup>
2-Methyl-1-pentene and 1-octene	Selective
2-Methyl-1-pentene and cyclohexene	Not selective
2-Octene and 1-octene	Selective
2-Octene and cyclohexene	Not selective
1-Octene and cyclohexene	Selective

(1) G. Gilman and G. Cohn, *Advances in Catalysis*, Academic Press Inc., New York, 1957, Vol. IX, pp. 733–742.

(2) (a) L. C. Behr, J. E. Kirby, R. N. MacDonald, and C. W. Todd, *J. Am. Chem. Soc.*, **68**, 1296 (1946). (b) A. E. Barkdoll, D. C. England, H. W. Gray, W. Kirk, Jr., and G. M. Whitman, *J. Am. Chem. Soc.*, **75**, 1156 (1953). (c) M. Freifelder and G. R. Stone, *J. Am. Chem. Soc.*, **80**, 5270 (1958).

(3) T. A. Ford, U. S. Patent 2,607,807 (August 19, 1952).

(13) W. J. Penney and G. B. B. M. Sutherland, *J. Chem. Phys.*, **2**, 498 (1934).