RESEARCHES ON ORGANO-PHOSPHORUS COMPOUNDS

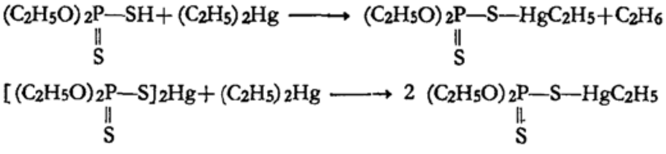
III. THE SYNTHESIS OF ETHYL MERCURIC O, O-DIALKYL-DITHIOPHOSPHATES *

HU PING-FANG (胡秉方) and CHENG WAN-YI (陳萬義)

(*Peking Agricultural University*)

ABSTRACT

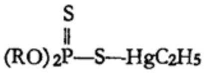
The reaction between o,o-diethyl-dithiophosphoric acid and diethylmercury, and that between mercuric o,o-diethyl-dithiophosphate and diethylmercury have been investigated, and it is found that they both proceed smoothly according to the following equations:



$$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}{-}SH + (C_2H_5)_2Hg \longrightarrow (C_2H_5O)_2\underset{\underset{S}{\|}}{P}{-}S{-}HgC_2H_5 + C_2H_6$$

$$[(C_2H_5O)_2\underset{\underset{S}{\|}}{P}{-}S]_2Hg + (C_2H_5)_2Hg \longrightarrow 2\ (C_2H_5O)_2\underset{\underset{S}{\|}}{P}{-}S{-}HgC_2H_5$$

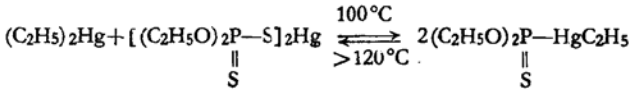
These reactions can be satisfactorily utilized for the synthesis of a series of ethyl mercuric o,o-dialkyl-dithiophosphates:



$$(RO)_2\overset{\overset{S}{\|}}{P}{-}S{-}HgC_2H_5$$

$R = CH_3, C_2H_5, i\text{-}C_3H_7, n\text{-}C_4H_9, i\text{-}C_4H_9, n\text{-}C_5H_{11}, i\text{-}C_5H_{11}, C_6H_5, \beta\text{-}C_{10}H_7$.

The following equilibrium has also been established:



$$(C_2H_5)_2Hg + [(C_2H_5O)_2\underset{\underset{S}{\|}}{P}{-}S]_2Hg \underset{>120°C}{\overset{100°C}{\rightleftarrows}} 2(C_2H_5O)_2\underset{\underset{S}{\|}}{P}{-}HgC_2H_5$$

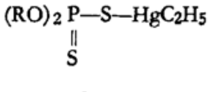
The preliminary biological evaluation of these organo-phosphorus compounds reported in part II and part III gives some interesting results. o,o-Di-β-naphthyl-dithiophosphoric acid exhibits mild but significant auxin properties, the translocation and persistence of the compound in the plant being observed. A series of bis-(o,o-dialkyl-dithiophosphate) disulfides show inferior insecticidal properties, although the diethyl derivative is stronger in comparison with the others.

The ethyl mercuric o,o-dialkyl-dithiophosphates listed in the present report demonstrate both insecticidal and fungicidal properties. The inhibitory power of six lower aliphatic derivatives, namely, from methyl to iso-pentyl (see Table 3), against *Alternaria tenius* is 13-36% stronger than that of ethyl mercuric chloride on the basis of mercury content.

---

* First published in Chinese in *Acta Chimica Sinica*, Vol. XXII, No. 6, pp. 478–484, 1956.

We were led to the investigation of ethyl mercuric o,o-dialkyl-dithiophosphates in consideration of the structural resemblances of this series of compounds to ethyl mercuric phosphate, a well-known fungicide, and also to many organo-phosphorus insecticides. Nine derivatives of the series with the following general formula were synthesized.

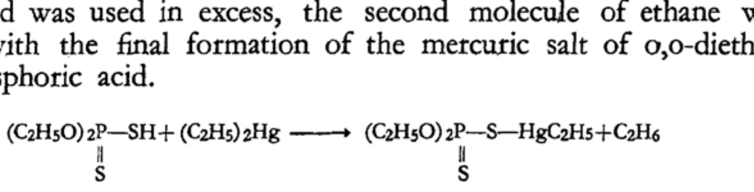


$$(RO)_2\underset{\underset{S}{\|}}{P}\text{—S—}HgC_2H_5$$

$R = CH_3, C_2H_5, i\text{-}C_3H_7, n\text{-}C_4H_9, i\text{-}C_4H_9, n\text{-}C_5H_{11}, i\text{-}C_5H_{11}, C_6H_5, \beta\text{-}C_{10}H_7$

In seeking for a preparatory method for the series of the compounds mentioned above, the reaction between o,o-diethyl-dithiophosphoric acid and ethyl mercuric chloride or diethyl mercury was investigated. It was found that the reaction between o,o-diethyl-dithiophosphoric acid and ethyl mercuric chloride proceeded rather violently with the evolution of hydrogen chloride and heat, but the product was found to be mainly the mercuric salt of o,o-diethyl-dithiophosphoric acid instead of the expected ethyl mercuric diethyl-dithiophosphate. It was assumed that the presence of hydrogen chloride was responsible for the splitting of ethyl-mercuric linkage. Although the addition of pyridine or anhydrous sodium carbonate to the reaction mixture improved the result accordingly, the product was invariably contaminated with a considerable amount of mercuric sulfide which indicated the partial decomposition of the expected product in the alkaline reaction medium.

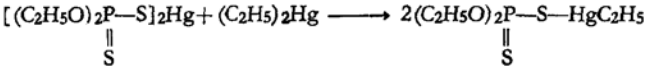
When o,o-diethyl-dithiophosphoric acid was added in portions to an excess of diethyl mercury, the reaction proceeded immediately with the evolution of heat and ethane. After an appropriate wash to remove the unreacted acid, and the removal of the excess diethyl mercury under reduced pressure, it afforded 70-80% yield of pure product without the necessity of further purification. In case the o,o-diethyl-dithiophosphoric acid was used in excess, the second molecule of ethane was evolved with the final formation of the mercuric salt of o,o-diethyl-dithiophosphoric acid.



$$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}\text{—SH} + (C_2H_5)_2Hg \longrightarrow (C_2H_5O)_2\underset{\underset{S}{\|}}{P}\text{—S—}HgC_2H_5 + C_2H_6$$

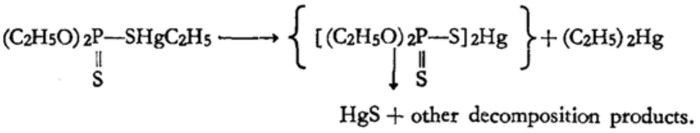
$$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}\text{—S—}HgC_2H_5 + (C_2H_5O)_2\underset{\underset{S}{\|}}{P}\text{—SH} \longrightarrow [(C_2H_5O)_2\underset{\underset{S}{\|}}{P}\text{—S}]_2Hg + C_2H_6$$

In the hope of developing a simpler preparatory method to synthesize the ethyl mercuric o,o-diethyl-dithiophosphate, we exploited the reaction between mercuric o,o-diethyl-dithiophosphate and diethyl mercury. It was found that at 100°C, they reacted satisfactorily in the following manner.



$$[(C_2H_5O)_2\underset{\underset{S}{\|}}{P}-S]_2Hg + (C_2H_5)_2Hg \longrightarrow 2(C_2H_5O)_2\underset{\underset{S}{\|}}{P}-S-HgC_2H_5 \qquad (1)$$

The ethyl mercuric o,o-dialkyl-dithiophosphates are heavy oily liquid. They are stable at room temperature, but above 120°C, they gradually decomposed with the formation of diethyl mercury, mercuric sulfide, and some unidentified substances. It was reasonably assumed that the thermal decomposition of o,o-diethyl-dithiophosphate was in fact a reversible reaction of reaction I, since it was evidenced that mercuric sulfide had been found to be a decomposition product of the mercuric salt of o,o-dialkyl-dithiophosphate.

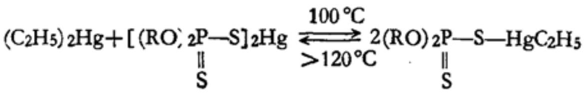


$$(C_2H_5O)_2\underset{\underset{S}{\|}}{P}-SHgC_2H_5 \longrightarrow \left\{ [(C_2H_5O)_2\underset{\underset{S}{\|}}{P}-S]_2Hg \right\} + (C_2H_5)_2Hg \qquad (2)$$
$$\downarrow$$
$$HgS + \text{other decomposition products.}$$

It was already known that a general equilibrium between mixed and simple organo-mercurials exists in the following manner.

$$R_2Hg + HgX_2 \rightleftharpoons 2\,RHgX \qquad (3)$$

Any reagent, for example, metallic sodium, which removes mercuric salt from the zone of reaction, will shift the equilibrium to the left[2]. It was not surprising, therefore, to see that the removal of mercuric salt of o,o-diethyl-dithiophosphate from the equilibrium system by thermal decomposition shifts reaction 2 to the right. In the light of these facts, we could safely conclude that the following equilibrium occurred between diethyl mercury, mercuric o,o-dialkyl-dithiophosphate, and ethyl mercuric o,o-dialkyl-dithiophosphate.



$$(C_2H_5)_2Hg + [(RO)_2\underset{\underset{S}{\|}}{P}-S]_2Hg \underset{>120°C}{\overset{100°C}{\rightleftharpoons}} 2(RO)_2\underset{\underset{S}{\|}}{P}-S-HgC_2H_5$$

EXPERIMENTAL

1. *The Preparation of Ethyl Mercuric o,o-Diethyl-dithiophosphate*

(1) To diethyl mercury (6 g) in dry ether (10 cc), stirred constantly, was added in portions o,o-diethyl-dithiophosphoric acid (3 g) in dry ether (10 cc, mol. ratio 1 : 1.7). The solution became warm with gas evolution. After 20 minutes' shaking to complete the reaction, the solution was left overnight, then washed with 1% aqueous sodium hydroxide repeatedly until free from acid, and then washed with cold water and dried over calcium chloride. The solvent was removed by heating the solution on a water bath, and under reduced pressure (10-30 mm, Hg),

the excess diethyl mercury was removed. A colourless heavy oily liquid was obtained, weighing 5.2 g (yield 66.7%).

The preparations of dimethyl, di-i-propyl, di-n-butyl, di-i-butyl, di-n-amyl, and di-i-amyl derivative of the series of ethyl mercuric dithiophosphate were similarly carried out.

(2) Mercuric salt of o,o-diethyl-dithiophosphate (5.7g, m.p. 124°C) and diethyl mercury (3.6g) were refluxed in benzene (30cc) for 6 hours. Both the solvent and the excess diethyl mercury were removed under reduced pressure. The residual liquid was slightly yellowish and was proved to be the identical compound obtained from procedure (1).

2. *The Preparation of Ethyl Mercuric o, o-Diphenyl-dithiophosphate*

To diethyl mercury (12g) was added in portions o,o-diphenyldithiophosphoric acid (m.p. 58°C, 13g) in benzene (10cc) with constant stirring. The solution was cooled by cold water, with the temperature kept below 50°C. After the reaction subsided, the solution was heated gently for half an hour in a hot water bath. From the solution, the crystalline solid was separated after standing for several days at room temperature. Alternatively, the crystals were quickly obtained by adding twice the volume of absolute alcohol, m.p. 57°C, and recrystal-

Table 1

Ethyl Mercuric o,o-Dialkyl-dithiophosphates

$(RO)_2\underset{\underset{S}{\|}}{P}-SHgC_2H_5$	Yield %	m. p. °C	Refractive Index n_D^{25}	Analysis							
				% C		% H		% P		% Hg	
				A	B	A	B	A	B	A	B
R = CH_3	73	—	1.6009	—	—	—	—	8.02	8.14	—	—
C_2H_5	67	—	1.5880	17.39	17.54	3.62	3.94	7.48	7.24	48.36	48.59
C_2H_5 *	87	—	1.5900	—	—	—	—	7.48	7.29	48.36	48.76
i–C_3H_7	90	—	1.5668	—	—	—	—	7.17	6.95	45.29	45.52
n–C_4H_9	75	—	1.5600	25.50	25.33	4.90	5.14	6.57	6.22	42.60	42.64
i–C_4H_9	72	—	1.5595	—	—	—	—	6.57	6.45	42.60	43.15
n–C_5H_{11}	64	—	1.5447	—	—	—	—	6.22	6.16	40.21	39.98
i–C_5H_{11}	76	—	1.5452	—	—	—	—	6.22	5.91	40.21	40.22
C_6H_5	76	58	—	—	—	—	—	6.19	6.19	39.25	39.21
β–$C_{10}H_7$	70	103–5	—	43.21	43.24	3.14	3.20	5.08	5.08	32.83	32.69

A. Required B. Found

* Product from procedure I (2).

lized from 1 : 1 benzene and ethyl alcohol solution, m.p. 58°C. The preparation of o,o-di-β-naphthyl-dithiophosphate was similarly carried out.

3. *The Decomposition of Ethyl Mercuric o, o-Diethyl-dithiophosphate*

Pure ethyl mercuric o, o-diethyl-dithiophosphate (5 g) was heated in a test tube which was placed in a 120-140°C oil bath. The pressure in the tube was reduced by water suction. Another test tube containing alcoholic mercuric chloride was served to absorb any volatile substance which appeared during decomposition. Leaflet crystals which separated gradually from alcoholic mercuric chloride solution were collected and recrystallized from ethanol, m.p. 192°C (identical with ethyl mercuric chloride). The dark residue of the decomposition product consisted of mercuric sulfide, but no original mercuric salt of phosphate ester could be found. The thermal decomposition of ethyl mercuric di-n-amyldithiophosphate gave diethyl mercury likewisely, and was identified in the same manner.

APPENDIX

The preliminary biological evaluation of the organo-phosphorus compounds reported in part II[1] and part III is now summarized as follows:

1. Treatment of tomato plant with 100 p.p.m. of aqueous solution of o,o-di-β-naphthyldithiophosphate indicated that the compound exhibited the mild but significant auxin properties. The translocation and persistence (for 2 to 3 months) of the compound in plant was observed.

2. The bis-(o,o-dialkyldithiophosphate) disulfides show inferior insecticidal activity. 10% dust of the methyl and ethyl derivatives caused only 10-39% mortality of the armyworm (*Cirphis unipuncta*), and house fly (*Musca vicina*), and their homologues were completely inactive. Bartlett[3] reported the insecticidal value of bis-(o,o-diethyldithiophosphate) disulfide which seemed of little practical significance. The fungicidal activity of the series of compound against *Alternaria tenius* was found much inferior to that of TMTD.

3. Ethyl mercuric o,o-dialkyldithiophosphates exhibited both insecticidal and fungicidal properties. The inhibitory power of the most active member in this series of compounds against *Alternaria tenius* was 136% that of ethyl mercuric chloride. The methyl, ethyl, and i-butyl derivatives demonstrated similar activities as γ-666. These results were shown in Tables 2 and 3.

Table 2

The Mortality of Armyworm (*Cirphis unipuncta*) (3rd instar) by 1% dust

Compounds	After 2 Hours	After 6 Hours	After 24 Hours
$(CH_3O)_2\overset{\overset{S}{\|}}{P}—SHgC_2H_5$	0 %	44.5 %	98 %
$(C_2H_5O)_2\overset{\overset{S}{\|}}{P}—SHgC_2H_5$	33	88	99
$(i\text{-}C_3H_7O)_2\overset{\overset{S}{\|}}{P}—SHgC_2H_5$	0	28	84
$(i\text{-}C_4H_9O)_2\overset{\overset{S}{\|}}{P}—SHgC_2H_5$	0	70	98
$(n\text{-}C_4H_9O)_2\overset{\overset{S}{\|}}{P}—SHgC_2H_5$	0	25	81
$(i\text{-}C_5H_{11}O)_2\overset{\overset{S}{\|}}{P}—SHgC_2H_5$	0	0	39
$(n\text{-}C_5H_{11}O)_2\overset{\overset{S}{\|}}{P}—SHgC_2H_5$	0	0	57
$(C_6H_5O)_2\overset{\overset{S}{\|}}{P}—SHgC_2H_5$	0	0	0
$(\beta\text{-}C_{10}H_7O)_2\overset{\overset{S}{\|}}{P}—SHgC_2H_5$	0	0	2
γ-666	0	36.5	97.5

Table 3

Activity against *Alternaria tenius* in Comparison with C_2H_5HgCl by Paper disc Method. (concentration : 10 p.p.m.)

Compounds	Hg % (A)	Radius of the Inhibition of Spore Germination (R) (cm)	R/A	Activity in Terms of C_2H_5HgCl Based upon Hg Content R/1.299A (%)
$(CH_3O)_2P(S)SHgC_2H_5$	51.86	0.89	1.716	132
$(C_2H_5O)_2P(S)SHgC_2H_5$	48.36	0.74	1.530	118
$(i\text{-}C_3H_7O)_2P(S)SHgC_2H_5$	45.29	0.78	1.723	133
$(i\text{-}C_4H_9O)_2P(S)SHgC_2H_5$	42.60	0.75	1.762	136
$(n\text{-}C_4H_9O)_2P(S)SHgC_2H_5$	42.60	0.63	1.479	114
$(i\text{-}C_5H_{11}O)_2P(S)SHgC_2H_5$	40.21	0.59	1.467	113
$(n\text{-}C_5H_{11}O)_2P(S)SHgC_2H_5$	40.21	0.47	1.169	90
$(C_6H_5O)_2P(S)SHgC_2H_5$	39.25	0.42	1.070	82
$(\beta\text{-}C_{10}H_7O)_2P(S)SHgC_2H_5$	32.83	0.17	0.518	40
C_2H_5HgCl	75.44	0.98	1.299	100

REFERENCES

[1] Hu, P. F. and Cheng, W. Y., 1956. *Acta Chimica Sinica*, **22**, 215.

[2] Gilman, *Organic Chemistry*, 2nd ed., **1**, p. 551.

[3] Bartlett, J. H., Rudel, H. W., and Cypher, E. B., 1955. *U.S. Pat.*, **2**, 694 & 705; 1955. *C.A.*, **49**, 12766.