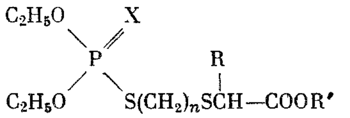
DITHIO- AND MONOTHIOPHOSPHATES THAT CONTAIN MERCAPTOACETIC AND MERCAPTOSUCCINIC ACID MOIETIES

T. A. Mastryukova, A. E. Shipov,
Z. K. Emkuzheva, L. G. Grineva,
M. Ky. Berkhamov, and M. I. Kabachnik

UDC 542.91:547.1'118

In connection with a search for effective insecticides which have a low toxicity toward warm-blooded animals and do not leave harmful residues in the atmosphere, we obtained a number of compounds of general formula:

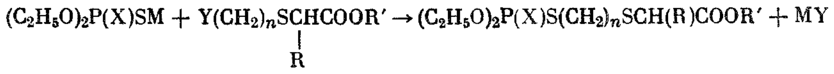

(I)—(XVI)

$R = H$ or CH_2COOR'; $R' = CH_3$, C_2H_5, $i\text{-}C_3H_7$; $X = S$ or O;
$n = 1$ or 2

These compounds contain the fragments of the widely known and highly effective insect acaricides, like Mercaptophos, M-74, and Thimet, in the molecule, and differ from them by the presence of either one or two carbalkoxyl groups in the sulfide portion of the molecule. As is known, these groupings are capable of being hydrolyzed by carboxyesterase enzymes, which should lead to a faster detoxification of the compounds in the organism of warm-blooded animals, and consequently to a decrease in the animal toxicity.

Two members of this type of compounds were described previously: 0,0-diethyl S-(carbomethoxymethylmercapto)methyl dithiophosphate (I), which was obtained by condensing 0,0-diethyldithiophosphoric acid with methylmercapto acetate and formaldehyde [1], and 0,0-diethyl S-β-(1,2-dicarbethoxyethylmercapto)ethyl dithiophosphate (XIII), which was synthesized by adding diethyl maleate to 0,0-diethyl S-β-mercaptoethyl dithiophosphate [2, 3].

We obtained compounds (I)-(XVI) by reacting the salts of either 0,0-diethyldi- or 0,0-diethylmonothiophosphoric acid with the appropriate haloalkyl sulfide derivatives. The yields,



$$(C_2H_5O)_2P(X)SM + Y(CH_2)_nS\underset{\displaystyle R}{\underset{|}{C}}HCOOR' \rightarrow (C_2H_5O)_2P(X)S(CH_2)_nSCH(R)COOR' + MY$$

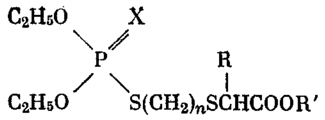
$M = Na, K$; $Y = Cl$ or Br

constants, and elemental analysis data are given in Table 1; the purity of the compounds was also checked by TLC.

The IR spectra of dithiophosphates (I)-(VI) and (IX)-(XIV) have the P = S absorption at 650-670 cm^{-1}, while the spectra of monothiophosphates (VII), (VIII) and (XV), (XVI) have the P = 0 vibration in the 1250-1260 cm^{-1} region. The spectra of all of the compounds have bands at 1015-1020 cm^{-1} (P—O(C)) and 1730-1750 cm^{-1} (C = 0), which is in agreement with the data given in [4].

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 699-705, March, 1977. Original article submitted September 6, 1976.

TABLE 1. Constants and Elemental Analysis Data for Dithio- and Thiophosphates



$(C_2H_5O)_2P(=X)S(CH_2)_nSCH(R)COOR'$

Compound	R	R′	X	n	Yield, %	bp, °C (p·10^{-2}, mm of Hg)	n_D^{20}	d_4^{20}	MR $\frac{\text{Found}}{\text{Calculated}}$	$\frac{\text{Found}}{\text{Calculated}}$, % C	H	P	Empirical formula
(I)*	H	CH_3	S	1	55	129–130(2,5)	1,5339	1,2462	$\frac{75,95}{75,66}$	$\frac{31,90}{31,57}$	$\frac{5,71}{5,63}$	$\frac{10,13}{10,18}$	$C_8H_{17}O_4PS_3$
(II)	H	C_2H_5	S	1	55	122–123(1,2)	1,5270	1,2152	$\frac{80,60}{80,28}$	–	–	$\frac{10,14}{9,72}$	$C_9H_{19}O_4PS_3$
(III)	H	$i\text{-}C_3H_7$	S	1	60	131–132(1,2)	1,5198	1,1832	$\frac{85,39}{84,90}$	–	–	$\frac{9,33}{9,31}$	$C_{10}H_{21}O_4PS_3$
(IV)	H	CH_3	S	2	52	131–132(1,5)	1,5325	1,2292	$\frac{80,35}{80,28}$	–	–	$\frac{10,15}{9,72}$	$C_9H_{19}O_4PS_3$
(V)	H	C_2H_5	S	2	67	140–141(1,4)	1,5256	1,1942	$\frac{85,39}{84,90}$	$\frac{35,91}{36,12}$	$\frac{5,98}{6,36}$	$\frac{9,31}{9,34}$	$C_{10}H_{21}O_4PS_3$
(VI)	H	$i\text{-}C_3H_7$	S	2	68	139–140(1,6)	1,5180	1,1702	$\frac{89,74}{89,52}$	–	–	$\frac{9,18}{8,94}$	$C_{11}H_{23}O_4PS_3$

TABLE 1 CONTINUED

Compound	R	R′	X	n	Yield, %	bp, °C(p · 10^{-2}, mm of Hg)	n_D^{20}	d_4^{20}	MR Found / Calculated	Found / Calculated, % C	H	P	Empirical formula
(VII)	H	CH_3	O	1	37	119–120(1,2)	1,4919	1,2242	$\frac{68{,}32}{67{,}99}$	$\frac{33{,}03}{33{,}33}$	$\frac{5{,}94}{5{,}94}$	$\frac{10{,}58}{10{,}74}$	$C_8H_{17}O_5PS_2$
(VIII)	H	CH_3	O	2	50	129–130(1,1)	1,4982	1,2242	$\frac{72{,}41}{72{,}61}$	–	–	$\frac{10{,}10}{10{,}23}$	$C_9H_{19}O_5PS_2$
(IX)	CH_2COOCH_3	CH_3	S	1	72	–	1,5219	1,2642	$\frac{90{,}82}{91{,}17}$	$\frac{35{,}20}{35{,}09}$	$\frac{5{,}56}{5{,}62}$	–	$C_{11}H_{21}O_6PS_3$
(X)	$CH_2COOC_2H_5$	C_2H_5	S	1	93	–	1,5120	1,2042	$\frac{100{,}80}{100{,}41}$	–	–	$\frac{7{,}36}{7{,}66}$	$C_{13}H_{25}O_6PS_3$
(XI)	$CH_2COOC_3H_7$-*i*	*i*-C_3H_7	S	1	66	–	1,5015	1,1618	$\frac{109{,}70}{109{,}64}$	$\frac{42{,}10}{41{,}65}$	$\frac{6{,}68}{6{,}76}$	$\frac{6{,}80}{7{,}16}$	$C_{15}H_{29}O_6PS_3$
(XII)	CH_2COOCH_3	CH_3	S	2	64	–	1,5203	1,2412	$\frac{95{,}72}{95{,}79}$	$\frac{36{,}93}{36{,}91}$	$\frac{5{,}96}{5{,}94}$	–	$C_{12}H_{23}O_6PS_3$
(XIII)†	$CH_2COOC_2H_5$	C_2H_5	S	2	98	–	1,5092	1,1852	$\frac{105{,}40}{105{,}03}$	–	–	$\frac{6{,}88}{7{,}40}$	$C_{14}H_{27}O_6PS_3$
(XIV)	$CH_2COOC_3H_7$-*i*	*i*-C_3H_7	S	2	58	–	1,5019	1,1478	$\frac{114{,}80}{114{,}26}$	–	–	$\frac{6{,}71}{6{,}94}$	$C_{16}H_{31}O_6PS_3$
(XV)	CH_2COOCH_3	CH_3	O	1	52	–	1,4899	1,2482	$\frac{83{,}49}{83{,}50}$	$\frac{36{,}93}{36{,}66}$	$\frac{5{,}76}{5{,}87}$	$\frac{8{,}43}{8{,}59}$	$C_{11}H_{21}O_7PS_2$
(XVI)	CH_2COOCH_3	CH_3	O	2	44	–	1,4912	1,2382	$\frac{87{,}64}{88{,}12}$	$\frac{38{,}78}{38{,}49}$	$\frac{5{,}96}{6{,}19}$	$\frac{7{,}76}{8{,}27}$	$C_{12}H_{23}O_7PS_2$

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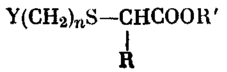
*From [1]: bp 140–142° (0.4 mm); n_D^{31} 1.5159.

†From [3]: n_D^{20} 1.5181; d_4^{20} 1.1963; the compound was obtained by adding O,O-diethyl S-β-mercaptoethyl dithiophosphate to diethyl maleate in the presence of catalysts.

TABLE 2. Constants and Elemental Analysis Data for Carbalkoxyalkyl Haloalkyl Sulfides



$$Y(CH_2)_nS\underset{R}{-CHCOOR'}$$

Y	n	R	R′	Yield, %	bp, °C (p ·10⁻², mm of Hg)	n_D^{20}	d_4^{20}	MR Found/Calculated	C, Found/Calculated, %	H, Found/Calculated, %	Br, Found/Calculated, %	Empirical formula
Cl	1	H	CH_3	35,5	59–61(2) *	1,4962	1,2862	35,14/35,19	30,94/31,14	4,54/4,56		$C_4H_7ClO_2S$
Cl	1	H	C_2H_5	35,9	64–66(2) †	1,4856	1,2252	39,50/39,81	–	–	–	$C_5H_9ClO_2S$
Cl	1	H	i-C_3H_7	46,1	72–74(2)	1,4768	1,1622	44,39/44,43	39,19/39,45	5,94/6,06	–	$C_6H_{11}ClO_2S$
Br	2	H	CH_3	21,8	80–81(1,5)	1,5095	1,4731	43,23/42,71	–	–	–	$C_5H_9BrO_2S$ ‡
Br	2	H	C_2H_5	52,0	94–96(2)	1,5072	1,4132	47,84/47,33	31,41/31,73	4,90/4,88	34,80/35,18	$C_6H_{11}BrO_2S$
Br	2	H	i-C_3H_7	58,6	104–105(2)	1,4982	1,3512	52,36/51,94	34,73/34,86	5,50/5,43	–	$C_7H_{13}BrO_2S$
Cl	1	CH_2COOCH_3	CH_3	40,0	112–113(2·10⁻²)	1,4916	1,2992	50,58/50,70	37,16/37,09	4,87/4,89	–	$C_7H_{11}ClO_4S$
Cl	1	$CH_2COOC_2H_5$	C_2H_5	46,0	95–97(3·10⁻²)	1,4779	1,2052	59,82/59,94	42,85/42,43	6,02/5,93	–	$C_9H_{15}ClO_4S$
Cl	1	$CH_2COOC_3H_7$-i	i-C_3H_7	41,9	108–109(2·10⁻²)	1,4699	1,1417	69,05/69,17	46,74/46,72	6,78/6,77	–	$C_{11}H_{19}ClO_4S$
Br	2	CH_2COOCH_3	CH_3	49,1	135–136(1)	1,5051	1,4452	58,55/58,22	34,44/33,69	4,57/4,59	27,76/28,02	$C_8H_{13}BrO_4S$
Br	2	$CH_2COOC_2H_5$	C_2H_5	48,5	132–133(4·10⁻²)	1,4901	1,3322	68,00/67,45	38,57/38,34	5,46/5,47	25,85/25,51	$C_{10}H_{17}BrO_4S$
Br	2	$CH_2COOC_3H_7$-i	i-C_3H_7	51,1	117–120(2·10⁻²)	1,4824	1,2612	77,23/76,69	42,77/42,23	6,30/6,20	23,44/23,42	$C_{12}H_{21}BrO_4S$

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*From [5]: bp 98° (14 mm). Found: S 20.33%; Calculated: 20.73%.

†From [7]: bp 68-69° (2 mm); n_D^{20} 1.4880; d_4^{20} 1.2322.

‡Found: S 14.90%; Calculated: 15.46%.

The starting carbalkoxyalkyl haloalkyl sulfides were obtained either by the chloromethylation of the mercaptoacetic and mercaptosuccinic esters [5, 6] or by the reaction of the mercaptides of these esters with ethylene bromide [7]. The properties of the obtained haloalkyl sulfides are given in Table 2.

EXPERIMENTAL

Potassium 0,0-diethyl dithiophosphate [8] and sodium 0,0-diethyl monothiophosphate [9] were obtained by known procedures. The carbalkoxyalkyl haloalkyl sulfides were synthesized like the esters described in [6, 7].

Carbalkoxyalkylmercapto Alkyl Esters of Phosphorus Thioacids (I)-(XVI). To 0.035 mole of the salt of the phosphorus thioacid (sodium 0,0-diethyl thiophosphate or potassium 0,0-diethyl dithiophosphate) in 70 ml of abs. alcohol was added in drops 0.034 mole of the appropriate carbalkoxyalkyl haloalkyl sulfide, and the mixture was heated for 3 h at 65°C. The alcohol was removed in vacuo, ether was added to the residue, the ether solution was washed in succession with 5% $NaHCO_3$ solution and water, dried over $MgSO_4$, the ether was removed in vacuo, and the residue was either vacuum-distilled or purified by TLC (using 100/160 μ silica gel L and either a 3:2 or 4:1 hexane—acetone mixture as the eluant) until one spot was obtained. The IR spectra were taken on a UR-20 spectrometer as a film, and also in $CHCl_3$ solution (C ~ 0.2 mole/liter).

CONCLUSIONS

Some 0,0-diethyl dithio- and monothiophosphates, containing either mercaptoacetic or mercaptosuccinic acid moieties in the alkthiol radical, were synthesized by the alkylation of the salts of either 0,0-diethyldithiophosphoric or 0,0-diethylmonothiophosphoric acid with halo derivatives.

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