[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORIES, THE LUBRIZOL CORP.]

The Preparation of Mercaptans by the Saponification of *O,O,S*-Trialkyl Phosphorodithioates[1]

W. E. BACON, N. A. MEINHARDT, AND W. M. LESUER

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Saponification of *O,O,S*-trialkyl phosphorodithioates gave alkyl mercaptans and sulfides. Good yields of mercaptans were obtained when the *O*-alkyl group of the phosphorus triester was isopropyl or 2-ethylhexyl.

The facile preparation of *O,O,S*-trialkyl phosphorodithioates in high yields[1,2,3] makes these esters attractive starting materials for the preparation of alkyl mercaptans and sulfides. Earlier work in this laboratory has shown that alkoxide cleavage of the *O,O,S*-trialkyl phosphorodithioates yields alkyl sulfides exclusively.[3] The aqueous saponification of *O,O*-di-*n*-propyl-*S*-2-octyl phosphorodithioate and *O,O*-di-*n*-propyl-*S*-α-phenethyl phosphorodithioate was reported to give 29% yields of 2-octyl mercaptan and α-phenethyl mercaptan respectively.[2]

This investigation was a continuation of the study on the saponification of the *O,O,S*-trialkyl phosphorodithioates as a method for the preparation of mercaptans. This would be of particular utility in connection with the hydrolysis of the *O,O,S*-trialkyl phosphorodithioates prepared by the addition of *O,O*-dialkyl hydrogen phosphorodithioates to olefins. The addition exhibits the peroxide effect so that either *O,O*-dialkyl-*S*-*n*-alkyl phosphorodithioates or *O,O*-dialkyl-*S*-2-alkyl phosphorodithioates are available.[3]

This paper describes the aqueous, alcoholic, and glycolic saponification of *O,O,S*-trialkyl phosphorodithioates.

Aqueous saponification of O,O,S-trialkyl phosphorodithioates. There was a considerable variation in the ease of hydrolysis of the *O,O,S*-trialkyl phosphorodithioates in aqueous media. These results are indicated in Table I, in which the percent of ester recovered after ten-hour reflux in 30% aqueous sodium hydroxide is shown. It appears probable that solubility of the ester in the reaction mixture is not a primary factor in this hydrolysis study, as *O,O,S*-triethyl phosphorodithioate was largely unsaponified in the 30% aqueous system, while *O,O*-di-*n*-hexyl phosphorodithioate esters and *O,O*-di-2-ethylhexyl phosphorodithioate esters were readily saponified in the same system (Table II). It would be expected that the *n*-hexyl and 2-ethylhexyl derivatives would be considerably less soluble than the triethyl ester in the aqueous system.

TABLE I

SAPONIFICATION OF *O,O,S*-TRIALKYL PHOSPHORODITHIOATES IN 30% AQUEOUS SODIUM HYDROXIDE (10-HR. REFLUX) $(RO)_2PSSR'$

R	R′	Unchanged Ester, %	R	R′	Unchanged Ester, %
C_2H_5	C_2H_5	70	i-C_3H_7	i-C_3H_7	87
C_2H_5	t-C_4H_9	70	i-C_3H_7	2-C_8H_{17}	84
C_2H_5	2-C_8H_{17}	55	i-C_3H_7	$C_6H_5CH_2CH_2$	82
C_2H_5	$C_6H_5CH_2CH_2$	30	i-C_3H_7	$C_6H_5(CH_3)CH$	89
C_2H_5	$C_6H_5(CH_3)CH$	20	n-C_4H_9	$C_6H_5CH_2CH_2$	10

The products obtained by the aqueous hydrolysis of a series of *O,O,S*-trialkyl phosphorodithioates are shown in Table II. It can be seen that the *O,O*-di-*n*-alkyl phosphorodithioate esters tended to yield mixtures of mercaptan and sulfide. The *O,O*-diethyl phosphorodithioate derivatives hydrolyzed in the aqueous system to give the corresponding ethyl sulfides in up to 60% yield. However, increasing the chain length of the *n*-alkyl group appeared to result in the formation of a higher ratio of mercaptan to sulfide in the hydrolysis product. With these esters, the tendency to form mercaptan was also increased by the presence of branching in the alkyl groups attached to the sulfur.

O,O-Di-2-ethylhexyl-*S*-2-octyl phosphorodithioate and *O,O*-di-2-ethylhexyl-*S*-α-phenethyl phosphorodithioate hydrolyzed to yield 60% 2-octanethiol and 65% α-phenethyl mercaptan, respectively.

Ethanolic and glycolic saponification of O,O,S-trialkyl phosphorodithioates. The *O,O,S*-trialkyl phosphorodithioates which resisted saponification in the aqueous system were readily saponified by the use of 21% potassium hydroxide in 70 weight % ethanol or in a 34% solution of potassium hydroxide in ethylene glycol. The results of the ethanolic saponifications are shown in Table III. In these hydrolyses, the same trend was noted as in the aqueous saponifications. The *O,O*-diisopropyl phosphorodithioates yielded from 57% to 65% of mercaptans, with an attendant yield of 0 to 9% of the corresponding isopropyl sulfides.

(1) Paper V. "Chemistry of the Aliphatic Esters of the Phosphorodithioic Acids." For previous paper in this series see N. A. Meinhardt and P. W. Vogel, *J. Org. Chem.*, **24**, 1604 (1959).

(2) G. R. Norman, W. M. LeSuer, and T. W. Mastin, *J. Am. Chem. Soc.*, **74**, 161 (1952).

(3) W. E. Bacon and W. M. LeSuer, *J. Am. Chem. Soc.*, **76**, 670 (1954).

TABLE II

AQUEOUS SAPONIFICATION OF *O,O,S*-TRIALKYL PHOSPHORODITHIOATES

$$(RO)_2PSSR' + NaOH\ (30\%) \longrightarrow \begin{cases} R'SH + (RO)_2PSONa \\ R'SR + ROP(S)(ONa)_2 \end{cases}$$

R	R'	Yield, %		% Sulfur			
				R'SH[a]		R'SR[b]	
		R'SH	R'SR	Found	Calcd.	Found	Calcd.
C_2H_5	n-C_8H_{17}	0	48	—	—	18.10	18.20
n-C_4H_9	n-C_8H_{17}	37	35	21.70	21.90	15.92	15.80
C_2H_5	2-C_8H_{17}	14	49	21.74	21.90	18.25	18.40
n-C_4H_9	2-C_8H_{17}	46	21	21.73	21.90	15.57	15.85
n-C_6H_{13}	2-C_8H_{17}	30	18	21.65	21.90	13.80	13.90
2-Ethylhexyl	2-C_8H_{17}	60	5	21.73	21.90	12.60	12.40
C_2H_5	$C_6H_5CH_2CH_2$	48	19	[a]		19.10	19.26
n-C_4H_9	$C_6H_5CH_2CH_2$	43	28	22.90	23.20	16.48	16.50
n-C_6H_{13}	$C_6H_5CH_2CH_2$	40	17	23.15	23.20	14.52	14.40
C_2H_5	$C_6H_5(CH_3)CH$	0	60	—	—	19.10	19.20
n-C_4H_9	$C_6H_5(CH_3)CH$	51	20	23.00	23.20	16.35	16.50
n-C_6H_{13}	$C_6H_5(CH_3)CH$	51	8	23.02	23.20	14.34	14.40
2-Ethylhexyl	$C_6H_5(CH_3)CH$	65	0	23.13	23.20	—	—

[a] Mercaptans were also identified by conversion to the corresponding 2,4-dinitrophenyl alkyl sulfides.[4,5] [b] Sulfides were also converted to their sulfones for identification purposes.[3]

TABLE III

ETHANOLIC SAPONIFICATION OF *O,O,S*-TRIALKYL PHOSPHORODITHIOATES

$$(RO)_2PSSR' + KOH(21\%) \longrightarrow \begin{cases} R'SH + (RO)_2POSK \\ R'SR + ROP(S)(OK)_2 \end{cases}$$

R	R'	Yield, %		Sulfur, %			
				R'SH[a]		R'SR[b]	
		R'SH	R'SR	Found	Calcd.	Found	Calcd.
i-C_3H_7	n-C_8H_{17}	57	6	21.70	21.90	17.20	17.00
i-C_3H_7	2-C_8H_{17}	53	9	21.98	21.90	16.86	17.00
i-C_3H_7	$C_6H_5CH_2CH_2$	65	0	23.11	23.20	—	
i-C_3H_7	$C_6H_5(CH_3)CH$	65	6	23.00	23.20	17.85	17.75
C_2H_5	$C_6H_5CH_2CH_2$	57	24	23.00	23.20	19.00	19.20
C_2H_5	$C_6H_5(CH_3)CH$	44	20	[a]		[b]	
C_2H_5	Cyclohexyl	41	31	27.60	27.60	22.10	22.10
n-C_6H_{13}	n-C_8H_{17}	53	3	21.70	21.90	14.00	13.90

[a] Mercaptans were identified also by their 2,4-dinitrobenzene derivatives.[4,5] [b] Sulfides were also converted to their sulfones for identification purposes.[3]

The *O,O*-diethyl phosphorodithioate esters gave mixtures of mercaptan and the corresponding ethyl sulfide, although with a higher ratio of mercaptan to sulfide than was obtained from the same ester in the aqueous system. Thus, ethanolic hydrolysis of *O,O*-diethyl-*S*-α-phenethyl phosphorodithioate gave 44% α-phenethyl mercaptan and 20% ethyl α-phenethyl sulfide. In the aqueous saponification of the same ester only the sulfide was obtained, in 60% yield.

Diethyl sulfide, ethyl isopropyl sulfide, and ethyl *t*-butyl sulfide azeotrope with ethanol, which made their isolation difficult in the ethanolic saponifications. Therefore, *O,O,S*-triethyl phosphorodithioate (I), *O,O*-diethyl-*S*-isopropyl phosphorodithioate (II), and *O,O*-diethyl-*S*-*t*-butyl phosphorodithioate (III) were saponified by use of a 34% solution of potassium hydroxide in ethylene glycol. The results of these hydrolyses are shown in Table IV. The saponification of I yielded only diethyl sulfide, while the saponification of both II and III gave both mercaptan and sulfide.

It may be concluded from these studies that satisfactory yields of mercaptan may be obtained by the saponification of *O,O,S*-trialkyl phosphorodithioates in which the *O*-substituents are sterically hindered.

Peroxide effect in the addition of O,O-dialkyl hydrogen phosphorodithioates to olefins. As was reported previously, the addition of *O,O*-diethyl hydrogen phosphorodithioate to octene-1 and styrene is subject to the peroxide effect,[3] Equations (1) and (2). Utilization of the peroxide effect offers

(4) R. W. Bost, J. O. Turner, and R. D. Norton, *J. Am. Chem. Soc.*, 54, 1985 (1932).

(5) M. S. Kharasch, E. S. May, and F. R. Mayo, *J. Org. Chem.*, 3, 175 (1934).

TABLE IV

ETHYLENE GLYCOL SAPONIFICATION OF *O,O,S*-TRIALKYL PHOSPHORODITHIOATES

$$(RO)_2PSSR' + KOH(34\%) \longrightarrow \begin{cases} R'SH + (RO)_2PSOK \\ R'SR + ROP(S)(OK)_2 \end{cases}$$

R	R'	Yield, % R'SH[a]	Yield, % R'SR	Sulfur, % R'SR[b] Found	Sulfur, % R'SR[b] Calcd.
C_2H_5	C_2H_5	0	42	35.40	35.60
C_2H_5	*i*-C_3H_7	28	29	30.50	30.80
C_2H_5	*t*-C_4H_9	13	24	27.00	27.10

[a] Mercaptans were identified by their 2,4-dinitrobenzene derivatives.[4,5] [b] Sulfides were also converted to their sulfones for identification.[3]

$$(C_2H_5O)_2PSSH + C_6H_5CH{:}CH_2 \longrightarrow \underset{\text{(crude)}}{} (C_2H_5O)_2PSSCH(CH_3)C_6H_5 \quad (1)$$

$$(C_2H_5O)_2PSSH + C_6H_5CH{:}CH_2 \xrightarrow{\text{peroxide}} \underset{\text{(pure)}}{} (C_2H_5O)_2PSSCH_2CH_2C_6H_5 \quad (2)$$

a convenient route to certain *O,O*-dialkyl-*S*-*n*-alkyl phosphorodithioates. This method was used in the preparation of a series of the *O,O,S*-trialkyl phosphorodithioates used in this saponification study. The esters prepared and their analyses are shown in Table V.

When purified *O,O*-dialkyl hydrogen phosphorodithioates were added to either octene-1 or styrene, the peroxide normally present in the olefin was sufficient to cause formation of the *O,O*-dialkyl-*S*-*n*-octyl (or β-phenethyl) phosphorodithioate. The crude acid contains a reducing agent which destroys the peroxide present in ordinary samples of olefin and results in the formation of *O,O*-dialkyl-*S*-2-octyl (or α-phenethyl) phosphorodithioates in this reaction.[2]

The structures of the adducts were established by the saponification of the triesters as reported here.

EXPERIMENTAL

O,O-Dialkyl hydrogen phosphorodithioates were prepared by previously reported methods.[6]

Purification of O,O-dialkyl hydrogen phosphorodithioate. The crude acid was dissolved in an equivalent quantity of 4*M* sodium hydroxide solution. The aqueous solution was extracted three times with naphtha (b.p. 90–120°), then acidified with an equivalent amount of hydrochloric acid. The *O,O*-dialkyl hydrogen phosphorodithioate was extracted with ethyl ether and the ethereal solution was dried over magnesium sulfate. The magnesium sulfate was removed by filtration and the ether was distilled.

O,O-Diethyl hydrogen phosphorodithioate, *O,O*-diisopropyl hydrogen phosphorodithioate and *O,O*-di-*n*-butyl hydrogen phosphorodithioate were then distilled under reduced pressure.

O,O-Diethyl hydrogen phosphorodithioate boiled at 66.1° (0.6 mm.).

Anal. Calcd. for $C_4H_{11}O_2PS_2$: P, 16.69; S, 34.4; neut. equiv., 186. Found: P, 16.6; S, 34.2; neut. equiv., 190.

O,O-Diisopropyl hydrogen phosphorodithioate boiled at 75–80° (2.0 mm.).

Anal. Calcd. for $C_6H_{15}O_2PS_2$: P, 14.5; S, 29.9; neut. equiv., 214. Found: P, 14.4; S, 29.4; neut. equiv., 211.

O,O-Di-n-butyl hydrogen phosphorodithioate boiled at 110–115° (1.5 mm.).

Anal. Calcd. for $C_8H_{19}O_2PS_2$: P, 12.8; S, 26.4; neut. equiv., 242. Found: P, 12.7; S, 26.1; neut. equiv., 243.

TABLE V

PEROXIDE EFFECT IN THE PREPARATION OF *O,O,S*-TRIALKYL PHOSPHORODITHIOATES

$$(RO)_2PSSH + \text{Olefin} \longrightarrow (RO)_2PSSR'$$

R	R'[a]	Method[b]	Yield, %	n_D^{20}	Phosphorus, % Found	Phosphorus, % Calcd.	Sulfur, % Found	Sulfur, % Calcd.
i-C_3H_7	$C_6H_5(CH_3)CH$	A	89	1.5374	9.45	9.75	20.1	20.2
i-C_3H_7	$C_6H_5CH_2CH_2$	B	89	1.5400	9.80	9.75	19.9	20.2
i-C_3H_7	2-C_8H_{17}	A	78	1.4834	9.82	9.52	20.0	19.6
i-C_3H_7	*n*-C_8H_{17}	B	68	1.4823	9.55	9.52	19.9	19.6
n-C_4H_9	$C_6H_5(CH_3)CH$	A	90	1.5341	8.82	8.95	18.7	18.5
n-C_4H_9	$C_6H_5CH_2CH_2$	B	94	1.5348	8.95	8.95	18.8	18.5
n-C_4H_9	*n*-C_8H_{17}	B	91	1.4915	8.71	8.73	18.0	18.0
n-C_6H_{13}	2-C_8H_{17}	A	70	1.4841	7.65	7.55	15.8	15.6
n-C_6H_{13}	*n*-C_8H_{17}	B	87	1.4859	7.38	7.55	15.5	15.6
n-C_6H_{13}	$C_6H_5(CH_3)CH$	A	82	1.5208	7.68	7.78	15.9	15.9
n-C_6H_{13}	$C_6H_5CH_2CH_2$	B	79	1.5222	7.58	7.78	16.1	15.9

[a] Structure assignments were made on the basis of the hydrolysis studies. Infrared spectra of the α-phenethyl esters exhibited absorptions at 9.5 (s) and 13.0 (m) μ, which were not present in the spectra of the β-phenethyl esters. The infrared spectra of the β-phenethyl esters exhibited absorptions at 13.3 (m) and 14.0 (w) μ, which were not present in the spectra of the α-phenethyl esters; (s = strong, m = medium, and w = weak.) Structural assignments for these absorptions will be the subject of another publication. No differences in the infrared spectra of the *n*-octyl and the 2-octyl esters were observed. [b] Method: A, crude $(RO)_2PSSH$ + olefin. B, purified $(RO)_2PSSH$ + olefin.

O,O-Di-n-hexyl hydrogen phosphorodithioate was heated to 100° at 0.5 mm. after the extraction procedure.

Anal. Calcd. for $C_{12}H_{27}O_2PS_2$: P, 10.4; S, 21.5; neut. equiv., 298. Found: P, 10.6; S, 21.1; neut. equiv., 308.

Octene-1 and *styrene* were commercial reagents, used as received.

(6) T. W. Mastin, G. R. Norman, and E. A. Weilmuenster, *J. Am. Chem. Soc.*, **67**, 1662 (1945).

O,O,S-Trialkyl Phosphorodithioates were prepared as previously described.[2,3]

General procedure for the aqueous saponification of O,O,S-trialkyl phosphorodithioates. The *O,O,S*-trialkyl phosphorodithioate, 0.5 mole, was added rapidly to a 30% aqueous solution of sodium hydroxide, 2 moles, and heated under reflux for 10 hr. The reaction mixture was cooled to 30°, blown with carbon dioxide for 1 hr. and then steam distilled. The distillate was saturated with sodium chloride and extracted with benzene. The benzene layer was dried over magnesium sulfate. The magnesium sulfate was removed by filtration and the benzene distilled. The products were fractionated under reduced pressure.

Mercaptans were identified by elemental analysis, and the corresponding 2,4-dinitrophenyl alkyl sulfides[4,5] were prepared in order to confirm the structure of the products.

Sulfides were identified by elemental analysis and converted to the sulfones in order to confirm structures.

The esters saponified by this procedure and the products obtained are summarized in Table II.

General procedure for the ethanolic saponification of O,O,S-trialkyl phosphorodithioates. The *O,O,S*-trialkyl phosphorodithioate, 0.4 mole, was added rapidly to a solution of potassium hydroxide, 147 g. (2.6 moles) in 534 g. of 70% ethanol, and heated under reflux for 5 hr. The reaction solution was cooled to 30°, blown with carbon dioxide for 1 hr., and then steam distilled. The isolation and identification procedure used for the products was the same as in the aqueous saponification. The results are summarized in Table III.

General procedure for the glycolic saponification of O,O,S-trialkyl phosphorodithioates. The *O,O,S*-trialkyl phosphorodithioate, 0.5 mole, was added dropwise, to a 34% solution of potassium hydroxide, 0.9 mole, in ethylene glycol, at 140°. The reaction was exothermic and the temperature rose to 160° during the 1-hr. addition period. The products were collected as they distilled from the reaction mixture. The mixture of mercaptan and sulfide was dried over calcium chloride; the calcium chloride was removed by filtration and the products were separated by fractionation at atmospheric pressure. The products were identified by the methods outlined previously. The results of these experiments are shown in Table IV.

Infrared spectra of the esters were measured on the Perkin-Elmer Infracord, Model 137, as neat films on sodium chloride plates.

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CLEVELAND 17, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Phosphorus Compounds. II. Synthesis of Unsymmetrical Tertiary Phosphines[1,2]

WILLIAM J. BAILEY, SHELDON A. BUCKLER,[3] AND FRITZ MARKTSCHEFFEL[4]

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The reduction of benzyl-containing phosphonium compounds with lithium aluminum hydride has been used for the synthesis of two unsymmetrical tertiary phosphines. Thus ethylmethylphenylphosphine was prepared from dichlorophenylphosphine in an over-all yield of 59%. Similarly, ethylmethylpentylphosphine was prepared from dichloromethylphosphine in an over-all yield of 50%.

The methods available for the synthesis of unsymmetrical tertiary phosphines are long and tedious and in general result in poor yields. Kosolapoff[5] lists very few unsymmetrical tertiary phosphines and only one of these contains three aliphatic radicals. The most widely used method for their synthesis, introduced by Hofmann[6] and Michaelis,[7] was one in which the halogens of a phosphorus halide are replaced stepwise by treatment with Grignard reagents, organozinc compounds or organolithium compounds.[8] Although there are new procedures available for the preparation of the monosubstituted dichlorophosphines in good yields,[9-13] the synthesis of disubstituted monochlorophosphines is still somewhat unsatisfactory.[14,15]

The treatment of a phosphine with an alkyl halide appears to be a general synthetic procedure but gives satisfactory yields of an unsymmetrical tertiary phosphine only with unsymmetrical secondary phosphines.[6] Although there are new procedures available for the preparation of primary

(1) Previous paper in this series, *J. Am. Chem. Soc.*, **79**, 3567 (1957).

(2) This work was done in fulfillment of a contract with the Army Chemical Corps.

(3) Member of the Armed Forces assigned to the Army Chemical Corps, 1954–1956.

(4) Chemical Corps Postdoctoral Fellow, 1957–1959.

(5) G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, New York, N. Y., 1950, p. 37.

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(14) E. Wedekind, *Ber.*, **45**, 2933 (1912).

(15) A. Michaelis, *Ann.*, **315**, 43 (1901).