of 2-(1,1,3,3-tetramethylbutyl)aminoethanol[9c] (173 g., 1 mole), ethyl acrylate (200 g., 2 moles), di-β-naphthol (14 g.) and aluminum isopropoxide (2 g.) was distilled as before. There was collected 53 g., b.p. 74–80°, over a period of 21 hr. and then the temperature was allowed to rise and 74 g. of excess ethyl acrylate was collected, b.p. 80–95° over the next 6 hr. The product was then distilled and 135 g. (59%), b.p. 140–147° (25 mm.) was collected. A residue of 69 g. remained in the flask.

2-(1,1,3,3-Tetramethylbutyl)aminoethyl methacrylate. The procedure given above for the corresponding *t*-butylaminoethyl methacrylate was followed. On distillation of the product there was obtained a small forerun boiling 115–125° (9 mm.) which was apparently a mixture of the aminoethanol and the methacrylate. The product (63%) was collected at 125–132° (9 mm.).

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT OF THE UNION OIL COMPANY OF CALIFORNIA]

Synthesis of Unsymmetrical Trialkyl Phosphorotetrathioates

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Mercaptans react with phosphorus pentasulfide to give, among other products, alkyl phosphenotrithioates, dialkyl hydrogen phosphorotetrathioates, and trialkyl phosphorotetrathioates. This paper is concerned with the use of these reactions, as well as the addition of olefins to dialkyl hydrogen phosphorotetrathioates, to produce unsymmetrical trialkyl phosphorotetrathioates.

Infrared spectra of these compounds were helpful in their identification.

Trialkyl phosphorotetrathioates are organophosphorus compounds of the general structure $(RS)_3PS$. They are classified as symmetrical if all the R groups are identical; unsymmetrical if at least one R group is dissimilar.

A few compounds of this type are described in the literature. Schulze, Short, and Crouch prepared several tri-*t*-alkyl phosphorotetrathioates from phosphorus pentasulfide and *t*-alkyl mercaptans.[1] Triethyl phosphorotetrathioate, tri-*t*-amyl phosphorotetrathioate, tribenzyl phosphorotetrathioate, tri-*p*-tolyl phosphorotetrathioate, and triphenyl phosphorotetrathioate are described by Kosolapoff,[2] and tridodecyl phosphorotetrathioate is discussed by Salzberg and Werntz in a patent.[3] Methods of preparing these compounds include the reactions of mercaptans or sodium mercaptides with thiophosphoryl chloride, of mercaptans with alkyl phosphenotrithioates ($RSPS_2$), as well as of mercaptans with phosphorus pentasulfide.[4] Reference 2 is a general reference for all these reactions.

From the known reactivity of the alkyl phosphenates,[5] it appeared that if the corresponding alkyl phosphenotrithioates could be prepared easily they could become key intermediates in the synthesis of a wide variety of organophosphorus compounds. This paper, part of such a program, is concerned with unsymmetrical trialkyl phosphorotetrathioates prepared from methyl phosphenotrithioate as the intermediate.

The pertinent reactions in the preparation of unsymmetrical trialkyl phosphorotetrathioates are

$$2CH_3SH + P_2S_5 \longrightarrow 2CH_3SPS_2 + H_2S \qquad (1)$$

$$CH_3SPS_2 + RSH \longrightarrow \begin{matrix} CH_3S \\ | \\ P(S)SH \\ | \\ RS \end{matrix} \qquad (2)$$

$$\begin{matrix} CH_3S \\ RS \end{matrix}\!\!>\!P(S)SH + \text{olefin} \longrightarrow \begin{matrix} CH_3S \\ RS \end{matrix}\!\!>\!P(S)SR' \qquad (3)$$

Methyl mercaptan can react with phosphorus pentasulfide to yield a number of products. The simplest route to methyl phosphenotrithioate is shown in reaction (1), in which two moles of the mercaptan react with one mole of phosphorus pentasulfide. As the ratio of mercaptan to phosphorus pentasulfide increases, reactions (4) and (5) assume importance and eventually predominate.

$$4CH_3SH + P_2S_5 \longrightarrow 2(CH_3S)_2P(S)SH + H_2S \qquad (4)$$

$$6CH_3SH + P_2S_5 \longrightarrow 2(CH_3S)_3PS + 3H_2S \qquad (5)$$

The use of excess phosphorus pentasulfide results in a higher yield of methyl phosphenotrithioate

$$(CH_3S)_3PS + P_2S_5 \longrightarrow 3CH_3SPS_2 \qquad (6)$$

By using the proper amounts of reactants, and by carefully controlling the release of hydrogen sulfide, reaction (1) can provide at least 60 mole percent yields of methyl phosphenotrithioate. Control of hydrogen sulfide enhances the yield because of the possibility of reaction (7).

$$CH_3SPS_2 + H_2S \longrightarrow CH_3SP(S)(SH)_2 \qquad (7)$$

A simple way to achieve this control is to run reac-

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(2) G. M. Kosolapoff, *Organophosphorus Compounds*, pp. 259, 260, 262, 346, John Wiley & Sons, Inc., New York, N. Y., 1950.

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(4) L. Rosnati, *Gazz. chim. ital.*, **76**, 272 (1946). *Chem. Abstr.*, **42**, 876 (1948).

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TABLE I

SYMMETRICAL TRIALKYL PHOSPHOROTETRATHIOATES

Phosphorotetrathioate	Mercaptan, Moles	P_2S_5, Moles	Reaction Temp., °C.	Reaction Pressure, P.S.I.G.	Reaction Time, Hours	Boiling Point of Product, °C./Mm.	Conversion Based on P_2S_5, Mole %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found	Sulfur, % Calcd.	Sulfur, % Found
$(CH_3S)_3PS$	42	3.5	100	195	6	126–130/0.2	86	17.7	17.1	4.4	4.3	15.2	15.1	62.7	62.8
$(C_2H_5S)_3PS$	15	3	100	0	14	110/0.15	46	29.3	28.8	6.1	6.3	12.6	12.6	52.0	51.8
$(CH_3CH_2CH_2S)_3PS$	8.2	2	100	0	5	136–137/0.15	38	37.5	37.1	7.3	7.4	10.8	10.9	44.4	44.6
$\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH\!-\!S\right)_3\!PS$	3	0.5	70	0	40	123–125/0.3	79	37.5	36.6	7.3	7.4	10.8	10.7	44.4	44.7

[a] Based on distilled product.

TABLE II

UNSYMMETRICAL TRIALKYL PHOSPHOROTETRATHIOATES

Phosphorotetrathioates	CH_3SPS_2, Moles	Mercaptan, Moles	Olefin, Moles	Reaction Temp., °C.[a,b]	Reaction Time, Hours[c]	Boiling Point of Product, °C./Mm.[d]	Conversion, Mole %[e]	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Phosphorus, % Calcd.	Phosphorus, % Found	Sulfur, % Calcd.	Sulfur, % Found
$(CH_3S)_2P(S)\!-\!SC_2H_5$	0.62	CH_3SH 0.62	$CH_2{=}CH_2$ excess[f]	40 95	3 2	135–139/1.0	34	—	—	—	—	—	—	—	—
$CH_3S\!-\!P(S)(S\!-\!CH(CH_3)_2)\!-\!SC_2H_5$	0.37	C_2H_5SH 0.37	$CH_2{=}CHCH_3$ 1.0	25–28 100	66 16	105–115/0.2	15	29.2	26.9	6.1	5.9	12.6	12.8	52.1	53.2
$(CH_3S)_2P(S)\!-\!SCH(CH_3)_2$	0.5	CH_3SH 0.15	$CH_2{=}CHCH_3$ 1.0	40 80–110	21.5 2.5	125–130/0.8	22	25.8	26.0	5.6	5.7	13.4	13.7	55.2	55.2
$(CH_3S)_2P(S)\!-\!S\!-\!CH(CH_3)\!-\!C_4H_9$	0.5	CH_3SH 0.5	$CH_2{=}CHC_4H_9$ 1.0	40 100	16 16	Did not distill	100	35.0	33.4	6.9	6.1	11.3	12.2	46.8	47.8
$CH_3S\!-\!P(S)(SC_2H_5)_2$	0.37	C_2H_5SH 0.37	$CH_2{=}CH_2$ excess[f]	25–28 100–150	66 18	109–129/0.5	34	25.8	24.4	5.6	5.7	13.4	14.2	55.2	56.3
$CH_3SP(S)\left(S\!-\!CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}\right)_2$	0.75	i-C_3H_7SH 0.75	$CH_2{=}CHCH_3$ 1.0	34 100	2 1.5	130–135/0.6	45	32.3	31.6	6.5	6.8	11.9	11.7	49.3	49.0

[a] First number is temperature of reaction of CH_3SPS_2 with RSH. Second number is temperature of addition of olefin. [b] Pressures were autogeneous. [c] First number is time of reaction of CH_3SPS_2 and RSH. Second number is time of addition of olefin. [d] All distillations were in a small Claisen flask equipped with Vigreux-type indentations. [e] Based on $CH_3S\!-\!P(S)(RS)\!-\!SH$ and amount of distilled product. Some decomposition during distillation. [f] 300-ml. bomb at 500 p.s.i.g./25°, 3000 p.s.i.g./95°.

tion (1) in an inert solvent under conditions of pressure and temperature such that refluxing is continuous, yet hydrogen sulfide cannot liquefy in the condenser.

Reaction (2) is analogous to reaction (7) in that methyl phosphenotrithioate combines very readily with mercaptans to form methyl alkyl hydrogen phosphorotetrathioates. These compounds are moderately unstable and very reactive. They can be handled and stored in inert solvents for several weeks, but isolation for more than a few hours results in a slow decomposition, apparently back to the mercaptan and phosphenotrithioate. Exposure to air or moisture causes the rapid formation of an unidentified syrup, hydrogen sulfide, and possibly some methyl mercaptan.

In reaction (3) the olefins add according to Markownikoff's rule, *i.e.*, 1-olefins add in the 2-position. The additions of dialkyl hydrogen phosphorotetrathioates to olefins were so nearly quantitative that distillations usually were unnecessary. In most cases vacuum stripping to remove solvent gave a material indistinguishable from distilled product. This was fortunate because many of these compounds have poor thermal stability.

Trimethyl, triethyl, tri-*n*-propyl, and tri-*i*-propyl phosphorotetrathioates were prepared by the classical reaction of mercaptans and phosphorus pentasulfide. The infrared spectra of these known compounds, as well as the spectra of several mercaptans, dialkyl sulfides and dialkyl disulfides greatly assisted in the characterization of the unsymmetrical phosphorotetrathioates.[6]

EXPERIMENTAL

Preparation of methyl phosphenotrithioate. The apparatus consisted of a 1-gal. stainless steel autoclave fitted with stirrer, reflux condenser, and back-pressure controller. Dry phosphorus pentasulfide, 1110 g. (5 moles), was placed in the autoclave, followed by a solution of 432 g. (9 moles) of methyl mercaptan in 2000 ml. of toluene. The system was held at 100–110 p.s.i.g. and 125–150° for 20 hr. Hydrogen sulfide evolution was rapid during the first hour, but ceased almost entirely after 2 hr. Rapid draining of the autoclave, followed by filtration while the products were still hot, gave 140 g. (0.63 mole) of unreacted phosphorus pentasulfide. Crude methyl phosphenotrithioate crystallized from the toluene upon cooling to room temperature. Recrystallization from benzene gave 953 g. (67%) of large, yellow plates, m.p. 112° (uncorr.) with partial softening at 68° and 102°.

This reaction time was dictated by convenience only. The true reaction time appears to be less than 4 hr., but no serious attempts were made to define optimum conditions.

Anal. Calcd. for CH_3PS_3: C, 8.4; H, 2.1; P, 21.8; S, 6.7. Found: C, 8.4; H, 2.6; P, 21.6; S, 64.1. Considerable difficulties were encountered in analyzing all the samples in this work. The formation of glassy, fireproof masses tended to cause errors in the burning procedures.

Preparation of dimethyl hydrogen phosphorotetrathioate. The reaction vessel was a 500 ml. Parr hydrogenation bottle closed with a rubber stopper. Stirring was achieved by rotating the bottle end-over-end. Heat was supplied by a heat lamp. A mixture of 48 g. (1 mole) methyl mercaptan, 142 g. (1 mole) methyl phosphenotrithioate, and 200 ml. of inert solvent was tumbled in the bottle for 3 hr. or more at a temperature of 30–50°. The product was isolated by removing the solvent under vacuum.

When the solvent was carbon disulfide, ether, or an aromatic, a homogeneous solution was formed. When a paraffinic solvent was used, two liquid phases were formed. The lower phase was acid contaminated with solvent, and the upper phase was solvent contaminated with acid. Because of the instability of the acid, it was difficult to obtain in a pure form, thereby complicating elemental analyses.

Anal. Calcd. for $C_2H_7PS_4$: C, 12.6; H, 3.7; S, 67.4. Found: C, 14.2; H, 4.2; S, 61.3.

Preparation of methyl ethyl hydrogen phosphorotetrathioate. A mixture of 62 g. (1 mole) ethyl mercaptan, 142 g. (1 mole) methyl phosphenotrithioate, and 300 ml. of Skellysolve B was stirred at room temperature for 68 hr. Removal of the Skellysolve left a light yellow oil still containing traces of solvent.

Preparation of methyl i-propyl and methyl n-propyl hydrogen phosphorotetrathioates. Equimolar mixtures of methyl phosphenotrithioate and the appropriate mercaptan were refluxed for 2 hr. in an equal volume of ether. Removal of the ether *in vacuo* gave the crude acids.

Preparation of trimethyl phosphorotetrathioate. The apparatus was the same as for methyl phosphenotrithio te. Excess methyl mercaptan was used to suppress side reactions. Phosphorus pentasulfide, 778 g. (3.5 moles), was placed in the autoclave, nitrogen added to 100 p.s.i.g., and 2020 g. (42 moles) methyl mercaptan pumped in. With the back-pressure controller set at 195 p.s.i.g., refluxing began when the temperature in the autoclave reached 74° accompanied by a heavy evolution of hydrogen sulfide. The temperature in the autoclave was raised to 93° over a period of 2.5 hr. Gas evolution decreased steadily, but the excess mercaptan was kept at reflux throughout the entire run. After 3.5 hr. at 93° the excess mercaptan was removed by reducing the pressure to 1 atm. Distillation of the product through a 12 inch helix-packed column gave 1226 g. (86%), b.p. 126–130/0.2 mm. This product forms very large, waxy crystals at 20–25°.

Preparation of other symmetrical trialkyl phosphorotetrathioates. Data for triethyl, tri-*n*-propyl, and tri-*i*-propyl phosphorotetrathioates are summarized in Table I. They were prepared in essentially the same manner as trimethyl phosphorotetrathioate.

Addition of olefins to dialkyl hydrogen phosphorotetrathioates. The olefins were either refluxed with the acids at 1 atm. or rocked in a bomb under pressure. The data are summarized in Table II.

Trimethyl phosphorotrithioite. This material was prepared by the procedure of McLeod.[7]

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