[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORIES, THE LUBRIZOL CORPORATION]

# Chemistry of the Aliphatic Esters of Thiophosphoric Acids. II. O,O,S-Trialkyl Thionophosphates by the Addition of O,O-Dialkyl Thiolthionophosphoric Acids to Olefins[1]

BY GEORGE R. NORMAN, W. M. LESUER AND T. W. MASTIN

Several methods for the synthesis of O,O,S-trialkyl thionophosphates are described. The synthesis based on the addition of O,O-dialkyl thiolthionophosphoric acids to olefins affords various triesters in good yield from readily available reactants. Products appearing in the table, with the exception of XXI, have not been reported previously.

O,O,S-Trialkyl thionophosphates have previously received little attention in the chemical literature. Only two esters, O,O,S-trimethyl and triethyl thionophosphates have been reported.[2] Kovalevskii[3] obtained the trimethyl ester in low yield by the action of $P_4S_{10}$ on MeOH (method A), while Pishchimuka[4] obtained the triethyl ester on treating $((C_2H_5O)_2PSS)_2Pb$ with ethyl iodide (method D).

In the present work we have re-examined the two methods described above and also have studied four additional reactions which could lead to the formation of the desired triesters. The six general methods are represented as

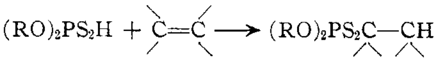
(A) $ROH + P_4S_{10} \longrightarrow (RO)_2PS_2R + Z^a$

(B) $ROH + P_4S_7 \longrightarrow (RO)_2PS_2R + Z^a$

(C) $(RO)_2PS_2H + R'OH \longrightarrow (RO)_2PS_2R'$

(D) $(RO)_2PS_2Na + R'Br \longrightarrow (RO)_2PS_2R' + NaBr$

(E) $(RO)_2PSCl + R'SK \longrightarrow (RO)_2PS_2R' + KCl$

(F) 

$(RO)_2PS_2H + C{=}C \longrightarrow (RO)_2PS_2C{-}CH$

[a] Acidic products were not identified.

The following comments may be made about the results obtained with each of the preparational methods. (A) Of the various alcohols studied, methanol alone gave the desired ester. Yields were 20% or less. (B) Methanol and ethanol were the only alcohols giving the desired type ester. Yields of 40–60% were obtained. (C) The direct esterification method was unsuccessful in all attempts. Decomposition of the reactants resulted in a complex mixture of products from which no pure product could be isolated. No neutral ester was obtained. (D) Good yields (60–80%) of the desired triesters were obtained. (E) Good yields (60–80%) of the desired triesters were obtained. (F) By this method mixed triesters were obtained in good yield (60–85%) from a wide variety of olefinic materials.

The three O,O-dialkyl thiolthionophosphoric acids used in reaction F were prepared by the reaction of alcohols with $P_4S_{10}$.[1] The acids were all of 80–90% purity as determined by titration with standard alkali. Acids containing the ethyl, *n*-propyl and *n*-butyl alkyl groups added readily in liquid phase to 1-octene, 2-octene, styrene, cyclohexene and methyl acrylate. Higher molecular weight acids added in a similar manner, but the resulting esters could not be distilled without decomposition. More complex olefins, such as diisobutylene and α-pinene, also gave triesters which did not yield to purification by distillation. Analyses and the non-acidity of the washed crude products indicated the desired triesters were obtained in these reactions. Low molecular weight olefins such as ethylene and propylene reacted with the dithio acids with difficulty under atmospheric conditions. At pressures of 100 to 1000 pounds per square inch these gaseous alkenes added with considerable ease.

In Table I are listed a number of triesters which have been prepared. The method of preparation and some of their physical properties are indicated.

The addition of the O,O-dialkyl thiolthionophosphoric acids to olefins appears to take place according to Markownikoff's rule. Reaction of the various acids with 1-octene yielded the S-(2-octyl) triesters.

In an effort to determine the structure of compound I (see Table I), compounds II and III, the two possible isomers from the addition reaction, were prepared by method D. The physical constants of the three products were so similar that no conclusions could be drawn. The structure of the addition product from 1-octene was proven through hydrolysis studies, using both aqueous NaOH and alcoholic $NaOC_2H_5$ as shown in the reactions

$$(RO)_2PSSR' + NaOH \xrightarrow{H_2O} R'SH + (RO)_2PSONa$$

$$(RO)_2PSSR' + NaOC_2H_5 \xrightarrow{C_2H_5OH} R'SC_2H_5 + (RO)_2PSONa$$

$$(R' = \text{2-octyl})$$

Hydrolysis of (V) with aqueous NaOH solution yielded only a 29% yield of 2-octyl mercaptan. Due to the low yield of mercaptan no effort was made to isolate the sodium dipropyl thionophosphate. This hydrolysis reaction will be the subject of a subsequent communication.

When a cleavage reaction was carried out on I with alcoholic sodium ethoxide the expected 2-octyl ethyl sulfide (62%) and sodium diethyl thionophosphate (49%) were obtained. Pishchimuka[4] has previously reported the sodium ethoxide cleavage of O,O,S-triethyl thionophosphate as yielding diethyl sulfide and a sodium salt, m.p. 181°. We have on four occasions isolated sodium diethyl thionophosphate and the purified product melts at 204°. The analyses which we have obtained indicate that this product is the expected salt. An authentic sample of 2-octyl ethyl sulfide, prepared by the action of 2-octyl bromide on $C_2H_5SNa$, had physical properties identical with those of the sulfide obtained in alkoxide cleavage. No crystalline sulfone could be obtained on peroxide oxidation.

---

(1) For previous paper in this series see T. W. Mastin, G. R. Norman and E. A. Weilmuenster, THIS JOURNAL, **67**, 1662 (1945).

(2) U. S. Patents 2,266,514 and 2,198,915 apply to O,O,S-trialkyl thionophosphates; however, no pure products are described.

(3) Kovalevskii, *Ann.*, **119**, 303 (1861).

(4) P. S. Pishchimuka, *J. Russ. Phys. Chem. Soc.*, **44**, 1406 (1912).

TABLE I

| No. | R | Triester $(RO)_2PS_2R'$ R' | Method | Yield, % | B.p. °C. | B.p. Mm.[i] | $n^{20}D$ | Sp. gr.$^{20}{}_{20}$ | Phosphorus, % |  | Sulfur, % |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |  | Calcd. | Found | Calcd. | Found |
| I | $C_2H_5$ | 2-Octyl[a] | F | 76 | 74–76 | 0.02 | 1.4917 | 1.0179 | 10.38 | 10.21 | 21.48 | 21.20 |
| II | $C_2H_5$ | 2-Octyl | D | 53.5 | 68–70 | .04 | 1.4918 | 1.0187 | 10.38 | 10.11 | 21.48 | 21.60 |
| III | $C_2H_5$ | $n$-Octyl | D | 87.5 | 75–76 | .02 | 1.4925 | 1.0184 | 10.38 | 10.05 | 21.48 | 21.80 |
| IV | $C_2H_5$ | $n$-Octyl | E | 63 | 80 | .03 | 1.4930 | 1.0155 | 10.38 | 9.94 | 21.48 | 21.72 |
| V | $n$ $C_3H_7$ | 2-Octyl[a] | F | 74 | 80 | .03 | 1.4893 | 0.9970 | 9.49 | 9.20 | 19.64 | 19.92 |
| VI | $n$-$C_4H_9$ | 2-Octyl[a] | F | 75 | 98–99 | .03 | 1.4870 | 0.9830 | 8.74 | 8.56 | 18.08 | 18.00 |
| VII | $C_2H_5$ | ?-Octyl[b] | F | 64 | 84–86 | .12 | 1.4920 | 1.0181 | 10.38 | 10.38 | 21.48 | 21.55 |
| VIII | $n$-$C_3H_7$ | ?-Octyl[b] | F | 64 | 88–90 | .06 | 1.4897 | 1.0003 | 9.49 | 9.35 | 19.64 | 20.00 |
| IX | $C_2H_5$ | $-CH_2CH_2CO_2CH_3$[c] | F | 83 | 65–66 | .01 | 1.5026 | 1.1860 | 11.38 | 11.32 | 23.55 | 23.35 |
| X | $C_2H_5$ | $-CH_2CH_2CO_2CH_3$ | D | 65 | 77–78 | .025 | 1.5052 | 1.1859 | 11.38 | 11.10 | 23.55 | 23.86 |
| XI | $n$-$C_3H_7$ | $-CH_2CH_2CO_2CH_3$[c] | F | 76 | 85–86 | .04 | 1.4984 | 1.1421 | 10.31 | 10.27 | 21.35 | 21.18 |
| XII | $n$-$C_4H_9$ | $-CH_2CH_2CO_2CH_3$[c] | F | 67 | 96–97 | .03 | 1.4942 | 1.1375 | 9.43 | 9.35 | 19.52 | 19.75 |
| XIII | $C_2H_5$ | $-CH(CH_3)C_6H_5$[d] | F | 75.5 | 85 | .02 | 1.5540 | 1.1401 | 10.67 | 10.61 | 22.08 | 22.01 |
| XIV | $C_2H_5$ | $-CH(CH_3)C_6H_5$ | D | 64 | 89–90 | .05 | 1.5552 | 1.1363 | 10.67 | 10.47 | 22.08 | 22.40 |
| XV | $C_2H_5$ | $-CH_2CH_2C_6H_5$ | D | 67 | 85–86 | .02 | 1.5543 | 1.1395 | 10.67 | 10.52 | 22.08 | 22.31 |
| XVI | $n$-$C_3H_7$ | $-CH(CH_3)C_6H_5$[d] | F | 75.5 | 99.5–101 | .03 | 1.5428 | 1.1022 | 9.73 | 9.37 | 20.14 | 20.10 |
| XVII | $n$-$C_4H_9$ | $-CH(CH_3)C_6H_5$[d] | F | 11.1[h] | 119–121 | .16 | 1.5315 | 1.0712 | 8.94 | 8.70 | 18.51 | 19.45 |
| XVIII | $C_2H_5$ | Cyclohexyl[e] | F | 73.5 | 62 | .02 | 1.5203 | 1.1098 | 11.54 | 11.31 | 23.89 | 24.10 |
| XIX | $n$-$C_3H_7$ | Cyclohexyl[e] | F | 74 | 82–83 | .06 | 1.5135 | 1.0751 | 10.45 | 10.08 | 21.63 | 21.75 |
| XX | $n$-$C_4H_9$ | Cyclohexyl[e] | F | 35 | 101–103 | .13 | 1.5073 | 1.0475 | 9.55 | 9.55 | 19.76 | 20.00 |
| XXI | $C_2H_5$ | $C_2H_5$[f] | F | 38 | 74–77 | 1.0 | 1.5033 | 1.1138 | 14.46 | 14.25 | 29.92 | 30.26 |
| XXII | $C_2H_5$ | Isopropyl[g] | F | 69 | 73–77 | 1.0 | 1.4993 | 1.0834 | 13.57 | 13.33 | 28.09 | 28.43 |

Acid added to: [a] 1-octene; [b] 2-octene; [c] methyl acrylate; [d] styrene; [e] cyclohexene; [f] ethylene; [g] propylene. [h] Decomposition of this product occurred during distillation. [i] The boiling points recorded were obtained in a pot still employing a short distillation path.

In a similar manner (XVI) was hydrolyzed with aqueous NaOH giving α-phenethyl mercaptan in 29% yield. Again no isolation of the sodium dipropyl thionophosphate was attempted.

The mercaptans obtained, 2-octyl mercaptan and α-phenethyl mercaptan, were identified through their 2,4-dinitrophenyl thioethers. The authentic samples of the two mercaptans were prepared by the method of Frank and Smith.[5] Mixed melting points of the 2,4-dinitrophenyl thioethers of the authentic mercaptans with the derivatives obtained from the hydrolysis product showed no depression.

## Experimental[6]

**Method A. O,O,S-Trimethyl Thionophosphate.**—Phosphorus pentasulfide (222 g., 1.0 mole) was added slowly in small portions over a period of two hours to refluxing methanol (192 g., 6.0 moles). The temperature of the reaction mixture was maintained at 55–65° during the addition and was held there for an additional two hours. (Caution—if the temperature reaches 100° the reaction mixture may decompose with violence.) Excess methanol and hydrogen sulfide were removed under reduced pressure. A small amount of yellow solid residue was then removed by filtration and the filtrate was washed with excess 10% aqueous sodium hydroxide. The neutral ester was extracted with benzene and the extract washed with water. The organic layer was dried over anhydrous $MgSO_4$ and the benzene was removed at reduced pressure. Fractionation of the residue yielded 62 g. (18%) of the desired triester, b. p. 86° (8 mm.), $n^{20}D$ 1.5285, sp. gr.$^{20}{}_{20}$ 1.2443.

*Anal.* Calcd. for $C_3H_9O_2PS_2$: P, 17.99; S, 37.24. Found: P, 17.8; S, 37.7.

**Method B. O,O,S-Triethyl Thionophosphate.**—The triester was prepared from absolute ethanol (12.0 moles) and phosphorus sulfide ($P_4S_7$, 1.0 mole) by the procedure described in method A. The product obtained in 35% yield, b. p. 128–129° (20 mm.), has been described previously by Pishchimuka.[4] Methanol and $P_4S_7$ gave the trimethyl ester in 44% yield.

**Method D. O,O-Diethyl-S-(2-octyl) Thionophosphate (II).**—O,O-Diethyl thiolthionophosphoric acid (1.05 moles) was added dropwise to a stirred mixture of 54 g. (1.0 mole) of sodium methoxide and 250 ml. of ethanol. When the addition was completed the resulting solution was heated to reflux and 154 g. (0.8 mole) of 2-bromoöctane was added dropwise over a period of one-half hour. The mixture was then heated to reflux for seven hours. After cooling the sodium bromide was removed by filtration. The filtrate was washed with water, dried over $MgSO_4$, and distilled *in vacuo*.

**Method E. O,O-Diethyl-S-($n$-octyl) Thionophosphate (IV).**—$n$-Octyl mercaptan (73 g., 0.5 mole) was slowly added to a stirred mixture of 20 g. (0.51 mole) of potassium and 500 ml. of anhydrous diisopropyl ether. Separation of the potassium mercaptide occurred immediately. The mixture was stirred at room temperature for two hours after the addition was completed. Diethyl chlorothionophosphate[1] (95 g., 0.5 mole) was added dropwise to the resulting heavy white sludge. The mixture was heated to reflux for six hours, cooled, and poured into water. The organic layer was further washed with water and dried over anhydrous $MgSO_4$. The diisopropyl ether was removed under reduced pressure and the residue distilled *in vacuo*.

**Method F. General Procedure for the Preparation of Trialkyl Thionophosphates by the Addition of O,O-Dialkyl Thiolthionophosphoric Acids to: (a) Liquid Olefins.**—The olefin (1.1 moles) was added dropwise to the stirred O,O-dialkyl thiolthionophosphoric acid (1.0 mole) at such a rate that the temperature did not rise above 100°.[7] After the addition was complete the stirred solution was heated to 100–110° and maintained at this temperature until the acidity of the reaction mixture had decreased to a substantially constant value. The reaction mixture was cooled and washed with a 10% excess of 1 $N$ potassium hydroxide solution. The organic layer was washed with water (sodium chloride was used to break troublesome emulsions). The product was then dried over anhydrous $MgSO_4$ and the excess olefin was removed by heating to a pot temperature of 100° (3 mm.). The residue was then distilled *in vacuo*. Yields and physical constants are recorded in the table.

**(b) Gaseous Olefins.**—The O,O-dialkyl thiolthionophosphoric acid (2.0 moles) was placed in a three-liter autoclave. The gaseous olefin was charged into the autoclave, with intermittent shaking, until an initial pressure of 100

---

(5) R. L. Frank and P. V. Smith, THIS JOURNAL, **68**, 2103 (1946).

(6) Only one preparation is described to illustrate each method, as the procedures recorded are general.

(7) The addition reaction is in general exothermic.

to 1000 p.s.i. was maintained. Shaking of the autoclave was commenced and the reaction mixture was heated to 100–115° for 5 hours. The crude reaction product was washed with excess 5% NaOH solution, extracted with isopropyl ether, water-washed and dried over anhydrous magnesium sulfate. The solvent was removed and the product fractionated *in vacuo.* Yields and physical constants are recorded in the table.

**Hydrolysis of O,O-Di-(*n*-propyl)-S-(2-octyl) Thionophosphate** (V).—A mixture of 126 g. (0.38 mole) of triester, 240 ml. of water and 86.5 g. (2.16 moles) of sodium hydroxide was heated to reflux with stirring for 20 hours. The mixture was then added to 500 ml. of water and the organic layer was extracted with ether. The extract was washed with water and dried over anhydrous $MgSO_4$. The ether was removed and the residue fractionated *in vacuo* yielding 16.2 g. (29%) of 2-octyl mercaptan, b. p. 82° (24 mm.); $n^{20}\text{D}$ 1.4497. This material was identified through its 2,4-dinitrophenylthio ether, m. p. 47.5°, prepared by the method of Bost, Turner and Norton.[8]

*Anal.* Calcd. for $C_{14}H_{20}N_2O_4S$: S, 10.26. Found: S, 10.16.

**Hydrolysis of O,O-Di-(*n*-propyl)-S-(α-phenethyl) Thionophosphate (XVI).**—A 29% yield of α-phenethyl mercaptan, b. p. 80–81.5° (16 mm.), $n^{20}\text{D}$ 1.5580, was obtained on hydrolysis of this triester by the procedure described above. The 2,4-dinitrophenylthio ether was prepared for characterization purposes, m. p. 110.5–111.5°.[9]

*Anal.* Calcd. for $C_{14}H_{12}N_2O_4S$: S, 10.53. Found: S, 10.65.

**Alkoxide Cleavage of O,O-Diethyl-S-(2-octyl) Thionophosphate** (I).—Sodium ethoxide was prepared by dissolving 23 g. (1 mole) of sodium in 300 ml. of absolute ethanol. The resulting solution was heated to reflux and 149 g. (0.5 mole) of triester was added dropwise over a period of one-half hour. After the addition was complete the solution was refluxed for six hours. The cooled solution was then blown with carbon dioxide to precipitate unreacted caustic as sodium carbonate. The latter was removed by filtration and the filtrate was diluted with 500 ml. of water. The organic layer was extracted with ether and the extract dried over anhydrous $MgSO_4$. The ether was removed and the residue fractionated *in vacuo*, yielding 54 g. (62%) of 2-octyl ethyl sulfide, b. p. 92.7–94° (10 mm.), $n^{20}\text{D}$ 1.4563.

*Anal.* Calcd. for $C_{10}H_{22}S$: S, 18.4. Found: S, 18.47.

The extracted aqueous solution obtained above was evaporated to dryness on a steam-bath. The salt obtained was dried by refluxing in benzene until no further water was trapped. The benzene was then removed under vacuum. The crystalline product was then dissolved in 150 ml. of cold ethyl acetate and the solution filtered to remove a small amount of $Na_2CO_3$. This solution was then diluted with 1500 ml. of petroleum ether (80–110°). On standing the hygroscopic product, sodium diethyl thionophosphate, crystallized as fine white needles, m.p. 204–204.5°; yield 47 g. (49%). Recrystallization did not raise the melting point.

*Anal.* Calcd. for $C_4H_{10}O_3PSNa$: Na, 12.0; P, 16.14; S, 16.66. Found: Na, 11.9; P, 15.95; S, 16.7.

**2-Octyl Ethyl Sulfide.**—Sodium ethyl mercaptide was prepared by adding ethyl mercaptan (37.2 g., 0.6 mole) to a mixture of 12.7 g. (0.55 mole) of sodium ribbon in 300 ml. of anhydrous dioxane. The mixture was heated to reflux under a Dry Ice–acetone condenser for four hours, until no trace of unreacted sodium remained. 2-Octyl bromide (96.5 g., 0.5 mole) was then added dropwise to the mixture over a one-half hour period. After refluxing for an additional eight hours the mixture was poured into one liter of water. The aqueous layer was saturated with NaCl and the organic layer was extracted with ether. The extract was washed with water and dried over anhydrous $MgSO_4$. The ether was removed and the residue fractionated *in vacuo* yielding 48 g. (55%) of 2-octyl ethyl sulfide, b.p. 87–88° (8 mm.), $n^{20}\text{D}$ 1.4564.

**Acknowledgment.**—The authors wish to thank Mr. Harry Ferber, who carried out the phosphorus and sulfur determinations.

CLEVELAND, OHIO RECEIVED MARCH 7, 1951

---

[8] R. W. Bost, J. O. Turner and R. D. Norton, THIS JOURNAL, **54**, 1985 (1932).

[9] Previously reported as melting at 109° by M. S. Kharasch, E. M. May and F. R. Mayo, *J. Org. Chem.*, **3**, 175 (1938).

---

[CONTRIBUTION FROM SOCONY-VACUUM LABORATORIES (A DIVISION OF SOCONY-VACUUM OIL CO., INC.) RESEARCH AND DEVELOPMENT DEPARTMENT]

# The Chlorination of Thiophene. III. Influence of Catalysts in the Exhaustive Chlorination of Thiophene

BY HARRY L. COONRADT, HOWARD D. HARTOUGH AND HENRY D. NORRIS

Exhaustive chlorination of thiophene in the presence of catalytic amounts of iodine yields a compound to which the structure 2,2,3,4,5,5-hexachloro-3-thiolene has been assigned. In contrast, non-catalytic chlorination and chlorination in the presence of other chlorination catalysts yields tetrachlorothiophene, 2,2,3,4,5,5-hexachlorothiolane or resinous products. Physical constants, proof of structure, and some of the reactions of 2,2,3,4,5,5-hexachloro-3-thiolene are reported.

Prior communications[1,2] in this series have discussed the chlorine addition products and the substitution products of thiophene. In the absence of catalysts exhaustive chlorination of thiophene could be directed to produce either 2,2,3,4,5,5-hexachlorothiolane (I)[1] or tetrachlorothiophene (II).[2]

An investigation of the exhaustive chlorination of thiophene in the presence of catalysts has now been made. A catalytic amount of iodine brings about formation of a compound, $C_4Cl_6S$, to which the structure 2,2,3,4,5,5-hexachloro-3-thiolene (III)[3] has been assigned.

Bromine has no such catalytic influence and instead 2,2,3,4,5,5-hexachlorothiolane (I) is formed. Phosphorus trichloride also yields compound I. Iron gives low yields of compound I and decomposition products, and antimony trichloride gives only resinous decomposition products. Thus, the formation of III is peculiar to the catalytic influence of iodine.

The course of the reaction leading from thiophene to III is not clear. However, there is evidence that it differs substantially from the course of the non-catalytic reaction and is not merely catalytic chlorination of one of the exhaustive chlorination products I or II formed by a non-catalytic mechanism.[2] Firstly, I, hexachlorothiolane, is recovered unchanged when treated further with chlorine in the presence of iodine. Secondly, as already described,[2] II is formed from thiophene

---

[1] H. L. Coonradt and H. D. Hartough, THIS JOURNAL, **70**, 1158 (1948).

[2] H. L. Coonradt, H. D. Hartough and G. C. Johnson, *ibid.*, **70**, 2564 (1948).

[3] This nomenclature was first described in ref. 1. Alternate nomenclature is 2,2,3,4,5,5-hexachlorothiacyclopent-3-ene and 2,2,3,4,5,5-hexachloro-2,5-dihydrothiophene.