TABLE IV

INFRARED ABSORPTION MAXIMA, WAVE LENGTH IN MICRONS

I, n = 2, X = F	II, n = 2, X = F	Thermal rearrangement product
14.86 m	14.88 v.w.	14.88 w
13.65 m	13.60 w	13.61 w
13.15 s	13.25 m	13.26 m
12.97 m	12.60 w	12.64 w
12.17 s		
11.33 s	11.32 w	11.33 w
10.83 vs	10.74 m	10.74 m
10.32 vs	10.33 m	10.34 m
9.83 vs	9.83 s	9.84 s
9.18 vs	9.17 vs	9.18 vs
8.87 vs	8.84 vs	8.86 vs
8.45 vs	8.45 vs	8.46 vs
8.13 vs	8.13 vs	8.14 vs
7.70 m	7.67 m	7.68 m
7.37 vs	7.45 vs	7.44 vs
7.09 m	7.08 m	7.08 m
6.84 m		
5.05 vw		
4.04 vw		
3.44 vw		
3.35 w	3.35 vw	3.34 vw

Calcd. for $C_{32}H_{16}F_{56}N_4P_4O_8$: mol. wt. determination (Rast) 1772; found: 1638, 1612.

α,α-Dichloro-polyfluoroalkyl- and α,α,ω-Trichloro-polyfluoroalkyl Phosphonitrilates. *Trimeric Bis-1,1-dichloro-pentafluoropropyl Phosphonitrilate* (*V*, n = 1, *X* = *F*).—Eight g. of I (n = 1, X = F) was dissolved in 50 ml. of carbon tetrachloride and the solution exposed to ultraviolet light, while a stream of dry chlorine gas was passed in for 48 hr. After removal of the solvent by distillation in a moderate vacuum, a waxy residue was obtained which was redissolved in ether for subsequent extractions with sodium bicarbonate solution and water. After drying the ethereal solution with sodium sulfate and removing the solvent by distillation, the obtained residue was subjected to vacuum distillation to give compound V (n = 1, X = F, Table III).

Trimeric Bis-1,1-dichloro-heptafluorobutyl Phosphonitrilate (**V**, n = **2**, **X** = **F**) was obtained by similar chlorination of 120 g. of I (n = 2, X = F) in 1200 ml. of carbon tetrachloride with the exception that the flow of the chlorine gas was extended to 96 hr.

Tetrameric Bis-1,1-dichloro-heptafluorobutyl Phosphonitrilate (**VI**, n = **2**, **X** = **F**) was obtained by passing a slow stream of chlorine into 23.2 g. of molten II (n = 2, X = F) at 90° for 3 days. After this time, chlorination was continued for 3 additional days at room temperature. Resinous impurities were removed by adding petroleum ether (b.p. 90–97°) to the reaction product. The remaining crystalline VI (n = 2, X = F) amounted to 12 g.

Tetrameric Bis-1,1,11-trichloro-eicosa-fluoroundecanyl Phosphonitrilate (**VI**, n = **9**, **X** = **Cl**).—Ten g. of compound II (n = 9, X = H) was melted and chlorine passed into the melt at 170° oil-bath temperature. After 4 days, complete exchange of all hydrogen by chlorine atoms had been achieved.

Stability Tests on Bis-1,1-di-*H*-polyfluoroalkyl Phosphonitrilates.—A 5 g.-sample of I (n = 1, X = F) was heated at 210° and a rapid stream of dry air passed in for 1 hr. The refractive index of I (n = 1, X = F) did not change at all after this treatment. (b) A sample of II (n = 2, X = F; 0.403 g.) was refluxed in 10 ml. of 68% nitric acid for 1 hr. After subsequent cooling, an amount of 0.38 g. of unchanged colorless II (n = 2, X = F) was recovered. After two recrystallizations from petroleum ether (b.p. 90–97°) the melting point was found to be 107° (compared with 107° before the refluxing). Treatment of the nitric acid mother liquor with ammonium-molybdate reagent gave no indication for the presence of monophosphate ions. (c) A sample of II (n = 2, X = F; 0.2849 g.) was refluxed with 15 ml. of 30% aqueous sodium hydroxide for 1 hr. An amount of 0.260 g. of a slightly brown crystalline material was recovered which became colorless after washing with 5 ml. of water. After two recrystallizations from petroleum ether, the unchanged product melted at 107°.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH AND DEVELOPMENT CENTER, ARMSTRONG CORK COMPANY
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The Reaction of Neutral Esters of Trivalent Phosphorus Acids with Inorganic Acid Chlorides. III. The Reaction of Trialkyl Phosphites with Thionyl Chloride[1]

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The reaction between thionyl chloride and a trialkyl phosphite gives a mixture of a dialkyl phosphorochloridate, a trialkyl phosphorothionate, a trialkyl phosphate, an alkyl chloride and sulfur dioxide in relative amounts dependent upon reaction conditions. The reaction is vigorous even at −60° and intermediate adducts are not observed. Sulfur monoxide is speculated as a primary reaction intermediate to account for the results obtained. Sulfur dichloride reacts with triethyl phosphite to give diethyl phosphorochloridate and triethyl phosphorothionate as major non-volatile products. Sulfur dioxide converts trialkyl phosphites into trialkyl phosphorothionate and trialkyl phosphate at about 100°.

Introduction

The application of phosphorus compounds as pneumatogens to provide a gas for expanding resinous compositions into foamed plastics prompted some studies on the reaction of neutral esters of trivalent phosphorus acids with a variety of inorganic acid chlorides. Thionyl and sulfuryl chlorides were reported, but without adequate evidence, to give moderately stable 1:2 adducts with trialkyl phosphites.[2] Such adducts with phosphites of lower alkyl homologs, which were claimed to decompose into alkyl halides only at temperatures above 100°, would have applications for expanding plastics into cellular or spongeous products. Unfortunately for the anticipated application as pneumatogens, our attempts to prepare

[1] Presented before the Division of Inorganic Chemistry at the September 1959 Meeting of the American Chemical Society, Atlantic City, N. J.

[2] A. Bell. U. S. Patent 2,508,364 (1950).

the alleged compounds led to the conclusion that neither trialkyl phosphites[3] nor triaryl phosphites[4] give adducts with sulfuryl chloride stable even at −20°. The failure to obtain addition products from triphenyl phosphite and thionyl chloride[4] diminished further any expectations of obtaining moderately stable adducts from thionyl chloride and trialkyl phosphites.

The unusually vigorous reactions between thionyl chloride and triaryl[4] or trialkyl phosphites contrast markedly to that between phosphorus trichloride and thionyl chloride.[5,6] The latter react slowly below 160° in a sealed tube—complete reaction being achieved in about 16 hr. Similarly, the related reactions of sulfinyl and sulfonyl chlorides

$$2PCl_3 + SOCl_2 \longrightarrow PCl_5 + PSCl_3 + POCl_3$$

with triaryl phosphites[7] require higher temperatures. Reactions analogous to those we found with sulfuryl and thionyl chlorides have been reported for nitrosyl and nitryl chlorides[8] and for phosgene.[9] In none of these investigations were addition products found.

Aside from our interest in phosphorogenic pneumatogens, the reaction between thionyl chloride and trialkyl phosphites assumed considerable significance as a possible source of sulfur monoxide and as additional examples on the deoxygenation of oxygen-bearing sulfur compounds.

By analogy to the reaction of trialkyl phosphites with sulfuryl chloride to give sulfur dioxide[3] or with phosgene to give carbon monoxide,[9] we anticipated that with thionyl chloride sulfur monoxide would form as a primary product.

$$(RO)_3P + SOCl_2 \longrightarrow RCl + SO + (RO)_2P(O)Cl$$

Recent studies[10] demonstrate rather convincingly that if sulfur monoxide is an intermediate species in the dechlorination of thionyl chloride with metals,[11,12] it is highly reactive and must have but a transitory existence. Consequently, much of the earlier work on the chemistry of sulfur monoxide has doubtful validity since the transit time from the source of the alleged sulfur monoxide to the site of reaction was such that any sulfur monoxide formed would have converted into other sulfur oxides. The possibility of producing sulfur monoxide *in situ* at low temperatures would obviate earlier experimental difficulties and provide an opportunity to examine the reactions of sulfur monoxide in solution.

In addition to a contribution on the chemistry of thionyl chloride and possibly sulfur monoxide, our study furnishes additional examples on the deoxygenating action of esters of trivalent phosphorus acids on oxygen-bearing sulfur compounds. Despite the growing number of examples being reported, investigators seem unaware that these deoxygenations are general reactions. Oxygen abstraction occurs not only with sulfur compounds[3–7] but also with nitrogen compounds,[8,13,14a] peroxides[14] and organic compounds.[15] The ease with which trivalent phosphorus compounds abstract oxygen depends markedly on the phosphorus ester and the oxygen-bearing compound used.

Experiments

Materials.—All reagents were distilled before use. Solvents were dried over sodium; anhydrous conditions were maintained in a nitrogen atmosphere during the reactions. The phosphites and triethyl phosphorothionate were obtained from Virginia-Carolina Corporation; sulfur dichloride, from Hooker Chemical Company.

Reaction of Thionyl Chloride with Triethyl Phosphite. A. Mole Ratio 2:3.—(1) Thionyl chloride (23.8 g., 0.20 mole) in 75 ml. of petroleum ether was added over a period of 1.5 hr. to a well-stirred solution of triethyl phosphite (49.8 g., 0.30 mole) in 75 ml. petroleum ether at 0°. A vigorous reaction ensued at each drop of reactant. The reaction mixture was refluxed about 2 hr. and worked up after the mixture had been kept at room temperatures for about 16 hr. Gases evolved during this time were scrubbed through two towers containing 5% aqueous sodium hydroxide, dried over Drierite and passed through a trap cooled in Dry Ice-2-propanol.

The material in the Dry Ice trap consisted of ethyl chloride and petroleum ether. Ethyl chloride was identified by its sweet odor, positive Beilstein test and volatility. The sodium hydroxide solutions were found to contain 0.008 gram atoms of chlorine and 0.036 mole sulfur[16] present as chloride and sulfite, respectively.

The reaction mixture was distilled at 35–40 mm. while maintaining the pot temperature below 35°. During this operation the volatile materials were collected in Dry Ice traps and the effluent gases were scrubbed through aqueous sodium hydroxide. The distillate (containing some ethyl chloride) was washed with aqueous sodium hydroxide solution; the combined washings and scrubbing solution were analyzed as before to give 0.076 gram atoms chlorine

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(16) This value is based on an analysis for sulfate after oxidation with bromine. A value of 0.035 moles sulfur was found by iodimetric analysis for sulfite.

and 0.046 mole sulfur[17] present as chloride and sulfite respectively.

The clear yellow residual oil[18] was mixed with 100 ml. of diethyl ether, a solution of aniline (74.4 g., 0.8 mole) in 150 ml. of diethyl ether added, and the white precipitate which formed immediately was filtered after the mixture had been kept 16 hr. at ambient room temperatures. The precipitate was identified as aniline hydrochloride by its melting point and mixture melting point; yield 20.1 g. (0.16 mole). Dry hyrogen chloride was passed into the clear yellow filtrate and washings to remove excess aniline and the aniline hydrochloride (63.1 g., 0.49 mole) filtered. The filtrate and washings were concentrated and cooled; crude (18.3 g., 0.08 mole) diethyl N-phenylphosphoramidate, m.p. 88–93° was filtered and washed with petroleum ether. One recrystallization from heptane gave material which failed to depress the m.p. of authentic amidate; reported m.p. 96.5°.[19] The filtrate was washed with cold aqueous 5% sodium hydroxide and water before removing the volatile solvents. Since triethyl phosphate is miscible with water, the aqueous washings were extracted four times with ether by a countercurrent procedure and these extracts combined with the main organic solution. After removing the volatile solvents from the dried organic solution, distillation at 1–2 mm. gave 0.8 g. clear colorless forerun, b.p. 33–36°, 22.4 g. of a clear colorless fraction, b.p. 66–67° (n^{20}_D 1.4375) and 15.5 g. of residual oily pot residue which solidified on cooling. The main liquid fraction was analyzed: Found S, 11.3%; P, 15.4%.[20]

The infrared absorption spectra of this fraction differed from that of an authentic sample of triethyl phosphate in two respects: (a) the characteristic P—O absorption at 7.70–8.00 μ[21] was greatly attenuated, (b) absorption in the 12.10–12.30μ region which may quite possibly be due to P—S[22] was accentuated.

The pot residue was identified as diethyl N-phenylphosphoramidate (0.068 mole). The small amount of yellow impurity was not identified.

(2) In an earlier run using the same quantities under the same conditions as above but with 37.2 g. (0.40 mole) of aniline to form the amidate and without precautions to avoid loss of triethyl phosphate in aqueous washings, essentially similar results were obtained; the mole fraction of phosphorothionate was found to be 86%. The total yield of phosphoramidate was 34.9 g. (0.15 mole); aniline hydrochloride, 25.0 g. (0.19 mole); and 27.0 g. of the fraction b.p. 53–57° (1 mm.), n^{20}_D 1.4434. The latter, on the basis of its refractive index, consisted of 86 mole % triethylphosphorothionate.

(3) A repetition of experiments in which the order of adding the reactants was reversed and triethyl phosphite was added to thionyl chloride over a period of 2.5 hr. gave 24.0 g. (0.19 mole) of aniline hydrochloride, 34.8 g. (0.15 mole) of diethyl N-phenylphosphoramidate and 24.9 g. of a fraction b.p. 54–60° (1 mm.), n^{20}_D 1.4448, which consisted of 88 mole % triethyl phosphorothionate.

B. Mole Ratio 1:4.—A solution of thionyl chloride (11.9 g., 0.10 mole) in 35 ml. of petroleum ether was added dropwise as before to triethyl phosphite (66.4 g., 0.40 mole in 75 ml. of petroleum ether. During the reaction (1.5 hr.) any gases formed were swept out with nitrogen and scrubbed through an iodine solution. Sulfur dioxide (0.024 mole) was evolved; previous qualitative tests had shown that hydrolyzable chloride was negligible. The reaction product was worked up as before except that the excess triethyl phosphite was distilled from the reaction mixture at low pressures before the aqueous washes. The following compounds were isolated and identified in the usual way: 10.7 g. (0.083 mole) of aniline hydrochloride m.p. 195–197°; 27.1 g. (0.16 mole) of triethyl phosphite, b.p. 36–39° (6 mm.), n^{20}_D 1.4193; 22.1 g. (0.097 mole) of diethyl N-phenyl phosphoramidate, m.p. 87–93°; and 10.7 g. of a colorless fraction b.p. 65–66° (2 mm.), n^{20}_D 1.4444 calculated as before to consist of 9.6 g. (0.049 mole) of triethyl phosphorothionate and 1.1 g. (0.006 mole) of triethyl phosphate.

C. Large Excess of Triethyl Phosphite.—(1) Thionyl chloride (2.38 g., 0.020 mole) in 25 ml. of petroleum ether was added over a period of 30 min. to triethyl phosphite (66.5 g., 0.40 mole) vigorously stirred in a baffled reaction flask. The clear homogeneous contents, maintained at 0 ± 2° while adding the reactants, were allowed to come to ambient room temperatures overnight and then heated to 40–45°. Throughout these operations any gases evolved were swept out of the reaction flask with nitrogen and scrubbed through a 5% aqueous sodium hydroxide. Total sulfur 0.070 g. (0.0022 mole) and chlorine, 0.003 g. (8×10^{-5} g. atoms) was accounted for in the acidic gases. The sulfur came over as sulfur dioxide (odor and decolorization of iodine solution).

The reaction mixture was flash-distilled at 8–10 mm. pressure and pot temperatures 75–80°. The distillate, containing no sulfur and only 0.006 g. atoms hydrolyzable chlorine, was essentially triethyl phosphite. The pale yellow liquid still residue (9.2 g.) had no perceptible odor of triethyl phosphate and was analyzed: sulfur, 4.6%; chlorine, 1.7%; phosphorus, 17.6%.

(2) Another reaction was carried out by distilling thionyl chloride (5.22 g., 0.044 mole) slowly over a period of 1 hr. from a side tube into a flask containing 132.9 g. (0.8 mole) of triethyl phosphite maintained with stirring at − 70 to − 60°. This assembly was completely closed to the atmosphere. The reaction was vigorous, but pressure did not develop to cause any difficulties. Throughout the course of reaction the mixture remained water-white and clear; dense white fumes formed initially later disappeared. The flask was connected to a train consisting of Ascarite, Drierite and 2-propanol-Dry Ice traps. The mixture was then heated slowly to 60–70° (about 3 hr.) maintained at this temperature for 2 hr. and after 15 hr. the flask contents analyzed. During the entire operations nitrogen was bubbled through the reaction mixture and passed through the train to pick up volatile acidic vapors or gases. Analysis of the flask contents (135.3 g.) showed 0.98%, 0.92% (av. 0.95%, 0.040 g. atoms) sulfur and 1.13%, 1.17% (av. 1.15%, 0.044 g. atoms) chlorine. There was no detectable odor of sulfur dioxide.

The Ascarite absorbed 0.19 g. (0.003 mole) of sulfur dioxide, and 0.05 g. (0.001 mole) of ethyl chloride was collected in the cold-trap.

D. Large Excess Thionyl Chloride.—Triethyl phosphite (8.3 g., 0.050 mole) in 75 ml. of petroleum ether was added dropwise over a period of 45 minutes into 59.5 g. (0.50 mole) of thionyl chloride stirred vigorously in a baffled flask and maintained at 0 ± 2°. The stirring was continued for 2 hr. after the clear faintly yellow reaction mixture came to room temperatures. Gases liberated during these operations were flushed out with nitrogen, passed through a 5% aqueous sodium hydroxide and the basic solution analyzed for sulfur and chlorine. The total sulfur and chlorine swept out as gases and absorbed in sodium hydroxide solution was found to be 0.0072 and 0.00021 g. atoms respectively.

Petroleum ether, unreacted thionyl chloride and any other volatile products which may have formed were removed at 20 mm. and pot temperatures less than 30°. The clear colorless distillate was discarded. Petroleum ether was added to the clear lightly amber-colored residual oil and distilled at low pressure as before; this operation was repeated two more times in order to remove completely residual thionyl chloride. The resulting oil (8.7 g.) was analyzed for sulfur (found 6.6%) and chlorine (found 12.5%).

In one experiment 0.05 mole of triethyl phosphite in 75 ml. of petroleum ether was added to 0.5 mole thionyl chloride at 0° and the reaction mixture analyzed for sulfate. About 1% of the thionyl chloride had been converted into products giving sulfate ions. Controls indicate that this sulfate arises either by air oxidation or is present as sulfuryl chloride in the original reactant.

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[17] After oxidation with bromine and determination as sulfate. Iodimetric determination for sulfite gave 0.044 mole sulfur.

[18] Some volatile material which decolorized an iodine solution is believed to be sulfur dioxide.

[19] H. McCombie, B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).

[20] From the refractive index of authentic mixtures of triethyl phosphate and triethyl phosphorothionate and assuming only these two components present, this fraction was computed to contain 73 mole % triethylphosphorothionate. This agrees reasonably well with 68 mole % based on the analytical data for sulfur.

[21] L. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 258.

[22] D. Corbridge, *J. Appl. Chem.*, **6**, 456 (1956). Also see *Chem. & Ind. (London)*, 197 (1957).

E. **Reaction of Triethyl Phosphite with Thionyl Chloride at −65°.**—When 1.5 g. of thionyl chloride at −60° was added carefully to a stirred solution of triethyl phosphite (4.2 g.) at −70 to −60°, the reaction was as vigorous as that observed at higher temperatures. After about one-fourth of the thionyl chloride had been added, a turbidity developed and the solution separated into two clear colorless phases. The remaining thionyl chloride was added and the two-phase mixture warmed slowly. Complete miscibility occurred at about −45°. As the solution became warmer the odor of sulfur dioxide and ethyl chloride could be detected. The mixture consisted of those phosphorus compounds described in earlier experiments. No evidence was found for an intermediate addition product nor was there any apparent reaction, subsequent to the one initially observed, when the mixture was warmed to room temperatures.

The Reaction of Thionyl Chloride with Tris-*n*-butyl Phosphite (Mole Ratio 1:4).—The reaction was carried out as described previously for triethyl phosphite by adding 8.2 g. (0.075 mole) of thionyl chloride in 35 ml. of diethyl ether to 75.2 g. (0.30 mole) of tris-*n*-butyl phosphite in 75 ml. diethyl ether at 0° over a period of 30 minutes. The reaction was relatively mild and fuming did not occur. The gases evolved during this operation and the subsequent 2-hr. refluxing were scrubbed through 5% aqueous sodium hydroxide solution. Analysis for sulfite showed 0.030 mole sulfur present as sulfite; after oxidation with bromine and analysis for sulfate, 0.032 mole. Chloride was absent.

The clear colorless reaction mixture was distilled at 35–40 mm. and pot temperature <40° to remove solvent and low-boiling reaction products. The distillate was fractionated at 751 mm. to give 0.5 g. forerun b.p. 35–73° and 3.7 g. (0.04 mole) *n*-butyl chloride, b.p. 73–74°, $n^{20}\mathrm{D}$ 1.4062.[23]

A solution of 27.9 g. (0.3 mole) of aniline in 200 ml. of diethyl ether was added to the residual oil dissolved in 200 ml. of diethyl ether at 25° in about 30 minutes. A white solid precipitated when about half of the aniline had been added. The slurry was refluxed 3 hr. and filtered the following day. The yield of aniline hydrochloride, m.p. 197–198°, was 8.5 g. (0.07 mole). Evaporation of ether at reduced pressures from the filtrate and washings left a pale yellow liquid (94.2 g.) which was fractionated. The condensate (0.9 g.) in the dry ice trap had the odor of butyl chloride and gave a positive Beilstein test. The fraction (14.2 g., 0.15 mole) b.p. 44.5–45° (2 mm.) was identified as aniline. Tributyl phosphite (34.4 g., 0.14 mole, $n^{20}\mathrm{D}$ 1.4305) distilled at 53–56° (0.04 mm.).[24] The next fraction (22.9 g.) was taken off at 85–87° (0.07 mm.), $n^{20}\mathrm{D}$ 1.4418, and is probably a mixture of tributyl phosphite[25] and tributylphosphorothionate.[26] The mixture was found to contain 6.8% S and 10.9% P. The final fraction (17.7 g., 0.06 mole) is di-*n*-butyl N-phenylphosphoramidate, b.p. 150–154° (0.03 mm.), $n^{20}\mathrm{D}$ 1.4973, and reported b.p. 191° (1 mm.), $n^{20}\mathrm{D}$ 1.4907.[27] The residue (0.5 g.) was a deep yellow acidic oil containing no chlorine or sulfur.

Attempted Reaction of Triethyl Phosphate with Thionyl Chloride.—An equimolar (0.20 mole) mixture of triethyl phosphate and thionyl chloride in 100 ml. of petroleum ether was refluxed for 18 hr. No exchange or reaction occurred and 92% of the triethyl phosphate [b.p. 93–96° (11 mm.), $n^{20}\mathrm{D}$ 1.4070] was recovered.

Reaction of Sulfur Dioxide with Triethyl Phosphite.—Triethyl phosphite (9.9 g., 0.070 mole) was shaken at 30° in a sulfur dioxide atmosphere for 7 hr. at which time 115 ml. (S.T.P.) of sulfur dioxide had been absorbed. The liquid reaction product was fractionated into the starting material, triethyl phosphite 7.3 g., b.p. 59–65° (21 mm.), $n^{20}\mathrm{D}$ 1.4133; 2.7 g. of product, b.p. 101–107° (21 mm.), $n^{20}\mathrm{D}$ 1.4185; and 0.8 g. still residue which was discarded. The fraction boiling at 101–107° (21 mm.) contained sulfur and, as in the previous cases, was calculated from its refractive index to consist of 28 mole % triethyl phosphorotionate and 72 mole % triethyl phosphate.

When sulfur dioxide (7 g., 0.11 mole) was passed into 54.8 g. (0.33 mole) of triethyl phosphite heated to 98°, the temperature rose to 160° in about 30 minutes but dropped to the initial temperature during continued passage of sulfur dioxide; total time for this operation was about 1 hr. After heating the reaction mixture for an additional 1.5 hr. at 100° the clear solution (61 g.) was cooled to room temperature and distilled the following morning. The fraction 3.6 g., b.p. 30–32° (24–26 mm.) and Dry Ice trap contents (1.7 g.) had an odor resembling triethyl phosphite but apparently was not this compound which boils at 60–62° (23–24 mm.); they were not characterized further. The clear residual oil (54 g.) gave no further distillate even on heating to 135° (12 mm.). Its refractive index $n^{20}\mathrm{D}$ 1.4212 is consistent for a binary mixture of 66 mole % triethyl phosphate and 34% triethyl phosphorothionate. This composition agrees very well with that calculated from its sulfur content (S found 5.68%).

In another experiment sulfur dioxide was passed through diethyl hydrogen phosphite at 80° for several hours; 87% of the acid phosphite was recovered. The orange-colored still-residue which was not identified contained sulfur.

Reaction of Sulfur Dichloride with Triethyl Phosphite.—A solution of triethyl phosphite (35.1 g., 0.21 mole) in petroleum ether (100 ml.) was added over a period of 75 minutes to a vigorously stirred solution of sulfur dichloride (13.3 g., 0.13 mole) in petroleum ether (50 ml.) at 5°. A vigorous and immediate reaction ensued upon adding the reagents; the initial garnet color of the reaction mixture faded progressly to a final clear yellow. No effort was made to collect the ethyl chloride presumably evolved; however, the exit gases did not carry any hydrogen sulfide.

Solvent, sulfur dichloride and other volatile materials were removed on the following day at reduced pressures. Any residual sulfur dichloride in the pot residue was purged twice by adding petroleum ether and distilling out the volatile diluent at low pressures. The pale yellow residual oil was taken up in diethyl ether (100 ml.), aniline (19.6 g., 0.21 mole) diluted with 75 ml. of diethyl ether added, the mixture refluxed 4 hr., filtered and the white solid (13.1 g., m.p. 96–98°) identified as aniline hydrochloride. The amber colored filtrate and washings were distilled leaving behind an oily solid which after washing with portions of cold petroleum ether gave a solid (14.3 g., m.p. 92–94°) identified as diethyl-N-phenylphosphoramidate (yield 60%). The ethereal filtrate and washings from the amidate were washed consecutively three times each with 5% aqueous hydrochloric acid, 5% aqueous sodium carbonate and water followed by a saturated sodium chloride solution rinse. The ethereal solution dried over anhydrous sodium sulfate was fractionated; ether and low boiling components were discarded and 14.5 g. of a fraction b.p. 65–70° (1.7 mm.) was collected. The semi-solid lavender residue (10.0 g.) failed to give additional diethyl-N-phenylphoramidate as expected and was not characterized further. The only distillate collected [b.p. 65–70° (1.7 mm.)] was redistilled [b.p. 71.2° (2.5 mm.), $n^{20}\mathrm{D}$ 1.4479] and identified as triethyl phosphorothionate; reported b.p. 94–95° (12 mm.), $n^{20}\mathrm{D}$ 1.4488.[26] Calcd. for: $C_6H_{15}O_3PS$; P, 15.6%; S, 16.2. Found: P, 15.8; S, 16.1.

Reaction of Diethyl Phosphorochloridate and Aniline.—A solution of aniline (6.29 g., 0.067 mole) in 25 ml. ether was poured into 4.83 g. (0.028 mole) of the chloridate in 50 ml. diethyl ether at 10°. The stirred mixture was brought to room temperatures and filtered after 6 hr. Yield of aniline hydrochloride (m.p. 197–198°) after washing with ether was 3.20 g. (0.025 mole). Hydrogen chloride was passed into the clear filtrate and washings after having been kept for two days to remove unreacted aniline; 1.90 g. (0.015 mole) of aniline hydrochloride was recovered. The final filtrate and washings after washing consecutively with dilute hydrochloric acid (5%) and water were evaporated to leave 5.0 g. (0.022 mole) of a light tan solid m.p. 89–93° and identified as diethyl N-phenylphosphoramidate; yield 79%. Similar results were obtained in presence of triethyl phosphite.

Rearrangement of Triethyl Phosphorothionate.—The phosphorothionate, b.p. 84.5–85.0 (7.2 mm.), alone and as an equimolar solution with triethyl phosphate, b.p. 88–89° (7.8–8.6 mm.), were heated at 150 ± 1° in a nitrogen atmosphere in the absence and in the presence of 1 mole %

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(23) Reported b.p. 78.5° (760 mm.), $n^{20}\mathrm{D}$ 1.4015; N. A. Lange, "Handbook of Chemistry," 8th Ed., Handbook Publishing Co., 1952.

(24) Reported b.p. 122° (12 mm.), $n^{19}\mathrm{D}$ 1.4321. W. Gerrard, *J. Chem. Soc.*, 1464 (1940).

(25) A. Vogel and D. Cowan, *ibid.*, 16 (1943). Reported b.p. 138.5° (6 mm.) and $n^{20}\mathrm{D}$ 1.42496.

(26) Reported b.p. 158–159° (11 mm.), $n^{20}\mathrm{D}$ 1.4515. B. A. Arbuzov and T. G. Shavsha, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 785 (1951); *C. A.*, **46**, 3817d (1952).

(27) D. Ramaswami and E. R. Kirch, *J. Am. Chem. Soc.*, **75**, 1763 (1953).

TABLE I

ISOMERIZATION OF TRIETHYL PHOSPHOROTHIONATE

Compounds	Catalyst	Refractive index $n^{20}\text{D}$ 0 hr.	4 hr.	15 hr.
$(EtO)_3PS$	None	1.4490	1.4490	1.4492
	Et_2OBF_3	1.4490	1.4553	1.4560
	$N(CH_2CH_2)_3N$	1.4490	1.4530	1.4553
$(EtO)_3PS$ +	None	1.4280	1.4280	1.4290
$(EtO)_3PO$	Et_2OBF_3	1.4280	1.4304	1.4315
	$N(CH_2CH_2)_3N$	1.4281	1.4310	1.4305

of a base or acid. The results are summarized herewith in Table I.

A refractive index of 1.4552 @ 25° has been reported for diethyl S-ethyl phosphorothiolate.[28]

O,O,S-Triethyl Phosphorothiolate.—Triethyl phosphorothionate[29] (49.5 g., 0.25 mole) containing 0.35 g. of boron trifluoride-etherate was heated for 4.5 hr. at 155° under nitrogen. During the reaction the refractive index of the mixture increased to $n^{20}\text{D}$ 1.4573 and a foul odor developed although qualitative tests for hydrogen sulfide, ethyl mercaptan and ethyl sulfide were negative. Distillation gave 10.8 g. of a forerun b.p. 69–95° (4 mm.) and 25.7 g. of O,O,S-triethyl phosphorothiolate, b.p. 95–96° (4 mm.), $n^{20}\text{D}$ 1.4588. The acidic still residue (6.6 g.) was discarded.

O,O,S-Triethyl phosphorothiolate was also prepared in 67% by heating diethyl disulfide and triethyl phosphite for 3 hr. instead of 20 hr. according to the procedure reported by Jacobson, Harvey and Jensen.[37] The properties, b.p. 96–98° (4.2 mm.), $n^{20}\text{D}$ 1.4581, agree with the values reported by the earlier investigators[37] and identifies the compound made by isomerization. Neutral aqueous 1% potassium permanganate was not decolorized even on heating. Neither bromine water nor a 2% solution of bromine in carbon tetrachloride were decolorized at room temperatures even on exposure to sunlight; warming the solutions effected decolorization. With sulfuryl chloride a vigorous reaction ensued giving rise to sulfur dioxide and a strong mercaptan-like odor.

Reaction of Thionyl Chloride with Triethyl Phosphorothionate.—A mixture of thionyl chloride (14.8 g., 0.13 mole) and triethyl phosphorothionate (9.84 g., 0.05 mole) was refluxed (about 80°) for 3 hr. Only a small amount of ethyl chloride (<0.1 g.) was found in the Dry Ice trap. Thionyl chloride was distilled and the high boiling product (9.4 g.) fractionated. The main fraction (4.5 g.; b.p. 67–70° at 3 mm.; $n^{20}\text{D}$ 1.4476) is triethyl phosphorothionate. The faintly orange colored mildly acidic residual liquid (4.6 g.) contained no chlorine, it was not miscible in dilute aqueous sodium hydroxide, and its infrared spectrum identifies it as being primarily O,O,S-triethyl phosphorothiolate. Small amounts of anhydrides may be present.

Reaction of Thionyl Chloride with O,O,S-Triethyl Phosphorothiolate.—Thionyl chloride (14.8 g., 0.13 mole) and 9.77 g. (0.05 mole) of triethyl phosphorothiolate[30] gave two phases which became consolute at about 56°. The mixture was refluxed 3 hr. during which time 0.4 g. of ethyl chloride was collected. Low boiling products[31] were removed at 20 mm. (pot temperature < 70°). The high boiling contents were distilled at 2.9 mm. The forerun (0.6 g.; b.p. < 35°) was a yellow liquid bearing hydrolyzable chlorine and having a mercaptan-like stench. After hydrolysis the presence of a mercaptan was demonstrated by the nitroprusside test.[32] The fraction (1.7 g.) coming over at 53–58° also was a yellow liquid containing hydrolyzable chlorine. Reaction with aniline gave aniline hydrochloride and a neutral sulfur containing product (1.7 g.) probably ethyl sulfenamide. The still residue (6.9 g.) was an amber colored, strongly acidic liquid containing only a small amount of hydrolyzable chlorine. No definable product was isolated.

Results

The reactions of triethyl phosphite with thionyl chloride were studied in detail by varying the proportions of reactants and the order of their addition. The reaction products were identified and in the case of non-volatile components, determined quantitatively (Table II).

The chlorine content of the non-volatile components was determined as aniline hydrochloride by treatment with an excess aniline in ether solution at room or reflux temperatures. It was demonstrated previously that aniline hydrochloride is formed quantitatively in the reaction between aniline and diethyl phosphorochloridate. No chlorine-bearing substances were detected in the filtrate as judged by the Beilstein flame test with a copper wire. The correct melting point of the unpurified hydrochloride precludes possible contamination by other anilinium salts, *e.g.*, those which would be expected if anhydrides or sulfonium phosphates were present. In some cases the chlorine content of the reaction mixture was verified independently by direct analysis for chlorine.

With the exception of Experiment C-1, 50% of the chlorine was present in the non-volatile fraction. The low chlorine value found for the non-volatiles in Experiment C-1 is attributed in part to loss of chlorine as ethyl chloride in a reaction between diethyl phosphorochloridate and triethyl phosphite during distillation of triethyl phosphite from the reaction mixture[33] and partly to co-distillation of diethyl phosphorochloridate with triethyl phosphite. An examination of the analytical data shows 52 meq. of phosphorus present. This value compares favorably with a calculated value of 49 meq. based on the reasonable assumption that unaccounted sulfur was lost as sulfur dioxide, the residual oxygen is present as triethyl phosphate and two equivalents of phosphorus are gained for each equivalent of diethyl phosphorochloridate lost other than by co-distillation. This interpretation becomes more creditable in the light of results from Experiment C-2 (Table II). In this experiment the reaction mixture was analyzed before distillation.

$$(EtO)_3P + (EtO)_2POCl \longrightarrow (EtO)_2P(O){-}O{-}P(OEt)_2 + EtCl \text{ or } [(EtO)_2{-}P(O)]_2$$

The failure to obtain an equivalent recovery of diethyl N-phenyl phosphoramidate (75–95% yield) is attributed to losses in working up the reaction product. Fifty per cent of the chlorine in thionyl chloride reacted is found as diethyl phosphorochloridate (Table II). We conclude, therefore, that one molecule of phosphorochloridate is produced from each molecule of thionyl chloride reacting. It also follows from these results and supplementary experiments with tributyl phosphite, that trialkyl phosphites do not react with

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[28] H. Jacobson, R. Harvey and E. Jensen, *J. Am. Chem. Soc.*, **77**, 6064 (1955).

[29] B.p. 78–79° (5.0 mm.); $n^{20}\text{D}$ 1.4499.

[30] Prepared by acid catalyzed rearrangement of triethyl phosphorothionate. B.p. 95–96° (4.0 mm.); $n^{20}\text{D}$ 1.4588.

[31] This distillate was a pale yellow color unlike the clear colorless distillate from the phosphorothionate reaction mixture. Hydrolysis and oxidation with iodine gave rise to a mercaptan-like odor probably due to diethyl dilsulfide. This indicates ethyl sulfenyl chloride in the distillate.

[32] N. Cheronis and J. Entrikin, "Semimicro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1958, p. 275.

[33] M. Baudler and W. Giese, *Z. anorg. u. allgem. Chem.*, **290**, 258 (1957).

TABLE II

SUMMARY OF RESULTS FROM THE REACTION OF THIONYL CHLORIDE WITH TRIETHYL PHOSPHITE

Experiment	Reactants, mole ratio $(EtO)_3P$: $SOCl_2$	Products formed, mole ratio			Element accounted for in non-volatile fraction (%)		
		$PhNH_3^+Cl^-$: $(EtO)_2PONHPh$	$(EtO)_3PS$: $(EtO)_3PO$	$(EtO)_2POCl$: $(EtO)_3PS$	S	P	Cl
A-1	1.9[b]	1.1	2	1.9	50[b,c]	90	50[b]
A-2	1.5	1.4	6	1.2	63	100	50
A-3[a]	1.5	1.4	7	1.3	57	93	50
B	4	0.9	8	2.0	49[c]	80	42
C-1	20	..	..	..	65[d]	..	11[f]
C-2	20	..	..	1.1	90[e]	..	50
D[a]	0.1	..	..	2.0	..	94	..

[a] Triethyl phosphite added to thionyl chloride. [b] Based on reacted thionyl chloride. Some thionyl chloride (0.04 mole) escaped from the reaction mixture thus changing the initial ratio of 1.5. [c] Additional 25% accounted as sulfur dioxide. [d] Additional 11% accounted as sulfur dioxide. [e] Additional 8% accounted as sulfur dioxide. [f] Direct analysis of reaction mixture after removing volatile fractions.

aniline hydrochloride under the conditions of our experiments otherwise up to 10% of the chlorine would have been lost by acidolysis.

$$(EtO)_3P + PhNH_3^+Cl^- \longrightarrow (EtO)_2PHO + PhNH_2 + EtCl$$

Such acidolysis can be expected on the basis of the well-known reaction of phosphite esters with hydrogen chloride.[34] We demonstrated that aniline

$$(EtO)_3P + HCl \longrightarrow (EtO)_2PHO + EtOH$$

hydrochloride does not react with triethyl phosphite even after refluxing the ethereal solutions for several hours; nor is there any reaction involving triethyl phosphite when diethyl phosphorochloridate reacts with aniline. At temperatures above 120° triethyl phosphite reacts rapidly with aniline hydrochloride to give ethyl chloride and N-ethylaniline.

The other chlorine on thionyl chloride escapes as ethyl chloride, although we made no effort to recover the compound quantitatively.

In general, 90–100% of triethyl phosphite reacting was converted into a mixture of triethyl phosphate, triethyl phosphorothionate and diethyl phosphorochloridate. Any unreacted phosphite normally would be lost during our experimental operations and most likely is a major factor in our failure to get a better material balance for phosphorus.

The amount of sulfur associated with the non-volatile fraction is quite variable, but 50–90% of the thionyl chloride reacting had been converted into triethyl phosphorothionate (Table II). Since it is difficult to separate triethyl phosphate from triethyl phosphorothionate by distillation and separation was not effected, the evidence for the exclusive presence of triethyl phosphorothionate may appear somewhat circumstantial. Furthermore, since diethyl ethylphosphonate and O,O,S-triethyl phosphorothiolate may reasonably be expected in the reaction mixture, our confidence that the fraction b.p. 66–67° (2 mm.) is a binary mixture of the phosphate and phosphorothionate bears closer scrutiny. The evidence for our belief rests on several observations:

(a) The composition calculated from sulfur analysis and refractometrically by comparison with an authentic binary mixture of triethyl phosphate and triethyl phosphorothionate are in good agreement. Such agreement cannot be expected if other esters also were present.

(b) The mixture had an ozone-like odor characteristic of triethyl phosphorothionate, rapidly decolorized bromine water, reduced aqueous permanganate and reacted with sulfuryl chloride[35] without giving rise to mercaptan-like odors. These reactions are in marked contrast to those given by O,O,S-triethyl phosphorothiolate which did not decolorize either bromine water[36] or aqueous permanganate and with sulfuryl chloride gave a vigorous reaction emitting an easily detected odor of ethyl mercaptan.[37] This reaction is useful for distinguishing phosphorothiolates from phosphorothionates.

Our inability to account for all of the sulfur, somewhat puzzling at first, was attributed to loss of volatile sulfur compounds while working up our reaction mixture. During the reaction and preliminary stripping of volatile compounds, any acidic vapors produced were absorbed in a sodium hydroxide trap. The sodium hydroxide solution remained clear; analysis showed small amounts of chloride from thionyl chloride unavoidably swept through the system without reacting and sulfate (about 1% of the total sulfur content). Iodimetric analysis of one portion of the absorbant and a sulfate analysis after oxidation of another portion of the same solution gave the same sulfur equivalence. Thus, sulfur was carried over exclusively as sulfur dioxide and small amounts of thionyl chloride; other oxides of sulfur which would be expected to produce sulfur or thio acids were absent. Sulfur dioxide present in the absorbant and alkaline washings of the volatile fractions accounted for 8–25% of the total sulfur used. It was obvious

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(34) (T) T. Milobendzki and K. Szulgin, *Chem. Polski*, **15**, 66 (1917); *C. A.*, **13**, 2867 (1919). (b) W. Gerrard and E. G. G. Whitbread, *J. Chem. Soc.*, 914 (1952).

(35) J. Michalski and A. Skowronska, *Chem. & Ind.* (*London*), 1199 (1958).

(36) Our qualitative observations seem to disagree with the result of the detailed studies by C. J. M. Stirling, *J. Chem. Soc.*, 3597 (1957), and a note by B. Saville, *Chem. & Ind.* (*London*), 660 (1956). Also see N. G. Lordi and J. Epstein, *J. Am. Chem. Soc.*, **80**, 509 (1958). The disagreement is not real because decoloration of bromine is not a criterion for reaction; yellow to orange colored reaction products obscure the test.

(37) Sulfuryl chloride reacts rapidly and exothermally with both phosphorthionates and phosphorothiolates. The phosphorothiolates give a strong garlic-like odor; sulfur dioxide also is detected. Trialkyl phosphorothionates, on the other hand, produce considerable amounts of sulfur dioxide without any other odor than that of sulfur dioxide.

that 15–25% of the sulfur was lost in subsequent operations.[38]

An examination of the non-volatile fraction immediately after removal of the volatile materials gave a mild odor of sulfur dioxide. The vapors decolorized iodine paper and gave no precipitate with a silver chloride solution. After subjecting a sample of the non-volatile mixture to prolonged pumping at 25° and about 1 mm. pressure, the odor disappeared and iodine paper was no longer decolorized. The volatile compound, therefore, was sulfur dioxide, diethyl sulfite or a mixture of the two. If diethyl sulfite had formed to an appreciable extent, the amount of diethyl phosphorochloridate would have been noticeably greater than the quantity found. Apparently, sulfur dioxide is retained strongly in the solution of phosphorus compounds but can be purged by prolonged treatment under vacuum or scrubbing with an inert gas. A somewhat similar situation was experienced during our work with triphenyl phosphite.[4]

We conclude that the sulfur from thionyl chloride reacted is found exclusively as sulfur dioxide and triethyl phosphorothionate. The variable ratios of these two compounds and of triethyl phosphate and triethyl phosphorothionate reflects the influence of reaction conditions on the course of reactions leading to these three products. An interpretation consistent with these observations will be given later in this paper.

In order to ascertain whether volatile sulfur compounds can form and be lost during the distillation, an equimolar mixture of triethyl phosphate and triethyl phosphorothionate was heated at 150° for 18 hr.; only 0.1 ml. of a nauseous liquid, most likely diethyl sulfide,[39] was obtained. In working up the products from the thionyl chloride reaction, high temperatures and prolonged heating were avoided, malodorous substances were not produced, and consequently no loss of sulfur by this route occurred during distillation. Diethyl sulfide can arise by ethylation reactions of the phosphorothionate or phosphorothiolate. The alkylating action of trialkyl phosphates,[40] phosphorothiolates and phosphorothionates[41] is well-known.

Trialkyl phosphorothionates are known to rearrange into the isomeric phosphorothiolates.[42,41d] Such a rearrangement was examined briefly with triethyl phosphorothionate in order to assess its importance in our studies. In absence of catalysts at 150° (alone or in triethyl phosphate) rearrangement from the thiono to the thiolo ester occurs, if at all, to only a slight extent in 15 hr. A base or Lewis acid, *e.g.*, 1,4-ethenopiperazine or borontrifluoride-etherate, accelerates the reaction and the refractive index changes appreciably (Table I). These experiments, in substantial agreement with the work of other investigators,[42] confirm the validity of determining the composition of the phosphate-phosphorothionate mixture refractometrically since rearrangements did not occur in working up the products from the thionyl chloride reaction.

Some experiments were carried out to ascertain whether sulfur dioxide reacts with triethyl phosphite. At 30° triethyl phosphite reacts slowly—only 30% of the phosphite was converted in 7 hr. into a mixture of the phosphate and phosphorothionate (mole ratio about 3:1). At about 100° the reaction was rapid, the temperature rose spontaneously to about 160° and the reaction was over in 0.5 hr. Over 90% of triethyl phosphite was converted into a mixture of the phosphate and phosphorothionate (mole ratio 2:1). This reaction, however, is probably negligible under conditions at which the reaction with thionyl chloride was carried out. We had shown previously[3] that sulfur dioxide had no effect on triphenyl phosphite[43] at 35°.

During the course of these studies, it was suggested that sulfur dioxide may have arisen from an exchange between triethyl phosphate and thionyl chloride followed by decomposition of the labile ethoxysulfinyl chloride.

$$(\mathrm{EtO})_3\mathrm{PO} + \mathrm{SOCl_2} \longrightarrow$$

$$[(\mathrm{EtO})_2\mathrm{POCl} + \mathrm{EtOSOCl}] \xrightarrow{(\mathrm{EtO})_3\mathrm{PO}} [(\mathrm{EtO})_2\mathrm{P(O)}]_2\mathrm{O} + \mathrm{SO_2}$$

$$\mathrm{EtOSOCl} \longrightarrow \mathrm{EtCl} + \mathrm{SO_2}$$

This possibility seemed creditable because thionyl chloride[44] and ethoxysulfinyl chloride[45] are reported to react with triethyl phosphates to give tetraethyl pyrophosphates which we presumed to form from the intermediate diethyl phosphorochloridate and triethyl phosphate.[46] Decompositions of alkoxysulfinyl chlorides are well-known.[47] The reactions, however, occur at temperatures greater than those imposed on the reactions we studied. When an equimolar mixture of triethyl phosphate and thionyl chloride in petroleum ether was refluxed for 18 hr., there was no exchange and 92% of triethyl phosphate was recovered. No evidence for diethyl phosphorochloridate could be found.

Thionyl chloride appears to react with neither phosphorothionates nor phosphorothiolates even when heated for a short time. When O,O,S-

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[38] Except in Experiment C-2 (Table II) where 98% of the sulfur was tallied. The good recovery of sulfur dioxide (8% of the thionyl chloride used) is a consequence of sweeping out the gas by bubbling a fine stream of nitrogen *through* the reaction mixture for several hours.

[39] No derivative could be obtained with 1-chlor-2,4-dinitrobenzene, thus excluding ethyl mercaptan as the alternate possibility.

[40] (a) J. H. Billman, A. Radike and B. W. Mundy, *J. Am. Chem. Soc.*, **64**, 2977 (1942). (b) A. D. F. Toy, *ibid.*, **66**, 499 (1944). (c) W. Rueggeberg and J. Chernack, *ibid.*, **70**, 1802 (1948). (d) J. H. Werntz, U. S. Patent 2,563,506 (1951). (e) A. Bell and M. B. Knowles, U. S. Patent 2,659,750 (1953).

[41] (a) G. Hilgetag, G. Schramm and H. Teichmann, *Angew. Chem.*, **69**, 205 (1957). (b) G. Hilgetag, G. Lehmann, A. Martini, G. Schramm and H. Teichmann, *J. prakt. chem.*, **8**, 207 (1959). (c) N. N. Melnikov, K. D. Shvetsova-Shilovskaya and I. M. Milshtein, *Zhur. Obshchei. Khim.*, **30**, 197 (1960); *C. A.*, **54**, 22322a. (d) G. Hilgetag, G. Shramm and H. Teichmann, *J. prakt. chem.*, **8**, 73 (1959).

[42] (a) L. E. Tammelin, *Acta Chem. Scand.*, **11**, 1738 (1957). (b) N. Muller and G. Goldenson, *J. Am. Chem. Soc.*, **78**, 5182 (1956). (c) T. R. Fukuto and E. M. Stafford, *ibid.*, **79**, 6083 (1957). (d) F. W. Hoffmann and T. R. Moore, *ibid.*, **80**, 1150 (1958).

[43] Neither triphenyl phosphine nor triphenyl phosphite react to any appreciable extent with sulfur dioxide even at 100° in 30 minutes. Diethyl phosphonate reacts very slowly at 80°.

[44] A. Bell, Brit. Patent 652,632 (1951); U. S. Patent 2,495,220 (1950).

[45] K. Brannock, U. S. Patent 2,639,292 (1953).

[46] A. D. F. Toy, *J. Am. Chem. Soc.*, **71**, 2268 (1949).

[47] (a) W. Gerrard, *J. Chem. Soc.*, 218 (1940). (b) P. Carré, *Bull. Soc. Chim. (France)*, [5] **3**, 1064, 1073 (1936).

triethyl phosphorothiolate is refluxed with thionyl chloride for several hours, however, ethyl chloride, low boiling products tentatively identified as ethyl sulfenyl chloride, and uncharacterized acidic sulfur-bearing high-boiling liquids are produced. Triethyl phosphorothionate, on the other hand, does not react appreciably under similar conditions; about 50% of the starting material was recovered, and the remainder is converted to the isomeric phosphorothiolate during distillation of the phosphorothionate. These results must be contrasted with analogous reactions reported by Pelchowicz,[48] who found that a dialkyl methylphosphonothionate reacts readily with thionyl chloride resulting in desulfuration and formation of an alkyl methyl phosphonochloridate. This difference in reactivity between an alkylphosphonothionate and a phosphorothionate is somewhat surprising.

At one time we entertained the speculation that sulfur dichloride may be an intermediate in reactions between thionyl chloride and trialkyl phosphites because we had found some evidence for sulfur chlorides in reactions involving triaryl phosphites.[4] We anticipated the reaction

$$(EtO)_3P + SCl_2 \longrightarrow EtCl + (EtO)_3PS + (EtO)_2POCl$$

Somewhat earlier Morrison[49] suggested, without giving experimental details, a similar reaction with sulfur monochloride; our work on the reactions of triphenyl phosphite with sulfur dichloride and monochloride supported this view. Arbuzov and his co-workers,[50] however, were unable to isolate any definite product from the reaction with triethyl phosphite. We found[51] the reaction to proceed vigorously in petroleum ether at low temperatures to give triethyl phosphorothionate and diethyl phosphorochloridate (converted to diethyl N-phenyl phosphoramidate in good yields). No effort was made to collect ethyl chloride or identify the still residue (probably a mixture the phosphorothionate, phosphoroamidate and reaction products of sulfur dichloride and phosphorothionate).

Despite the ease with which sulfur dichloride reacts with phosphite esters the absence of yellow colored products, particularly when the phosphite is added to an excess of thionyl chloride, makes this reaction an unlikely step.

Interpretation

Thionyl Chloride.—Our experimental results are reasonably interpreted by postulating sulfur monoxide as a primary reactive intermediate with participation in subsequent reactions. Sulfur monoxide has been suggested as an intermediate and sometimes supported rather convincingly in the oxidation of sulfur and its compounds by oxygen. Recent papers[52] on chlorinations with thionyl chloride suggest sulfur monoxide as a reaction product but its role, if it is formed at all in the chlorination, is obscure. Except for Truce and his co-workers[52c] who stated that sulfur, sulfur dioxide and sulfur monochloride were found in various reaction mixtures, none of the investigators express evidence for or the logic of their beliefs. All failed to validate their statements with experimental data.

Truce, Birum and McBee[52c] suggested that sulfur resulting from disproportionation of sulfur monoxide is chlorinated by excess thionyl chloride. We found, on the contrary, that sulfur, appreciably soluble in hot thionyl chloride to give a pale yellow solution, can be recovered quantitatively after refluxing such a solution for over 2 hr. with no evidence of sulfur monochloride or sulfur dioxide. These results are in agreement with those reported by Harrington and Boyd,[53] who found that in absence of ferric chloride no reaction occurred, and by other investigators[6,54] who reported that sulfur is chlorinated by thionyl chloride at an appreciable rate only at temperatures above 150°.

Later Bordwell and Pitt[55] found that thionyl chloride acts as a deoxygenative chlorinating agent on sulfoxides by a reaction sequence involving no sulfur monoxide. The deoxygenative effect of monoxide has been speculated in thermolytic decompositions of some sulfoxides of 1,4-dithiadienes; here again experimental data was lacking.[56]

In an earlier paper[4] we suggested that the small amounts of triphenyl phosphorothionate formed when triphenyl phosphite reacts with a large excess of thionyl chloride is due to concurrent reactions involving sulfur monoxide. More recently Pelchowicz[48] reported that dialkyl methylphosphonothionates were converted to the corresponding phosphonochloridates by thionyl chloride and proposed a facile isomerization to the phosphonothiolate followed by a chlorinative cleavage at the phosphorus–sulfur bond. The hypothetical alkyl thiosulfinyl chloride was assumed to decompose into an alkyl chloride, sulfur and sulfur monoxide. These results bear comparison with our observations concerning the reaction of O,O,S-triethyl phosphorothiolate and of triethyl phosphorothionate with an excess of thionyl chloride refluxed for 3 hr. With triethyl phosphorothionate, over 50% of the phosphorothionate was recovered, the remainder isomerized to O,O,S-triethyl phosphorothiolate during distillation of triethyl phosphorothionate. Sulfur dioxide was absent indicating that no sulfur monoxide had formed and no chlorine-ethoxyl exchange occurred; no evidence for elemental sulfur was found, and ethyl chloride was produced in small amounts only. With O,O,S-triethyl phosphorothiolate, a slow reaction occurred with formation of some ethyl chloride, ethyl sulfenyl chloride and an uncharacterized acidic still residue (probably anhydrides). No evidence for sulfur or sulfur dioxide was found.

No one has yet developed a sound rationale for

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(48) Z. Pelchowicz, *J. Chem. Soc.*, 238 (1961).

(49) D. C. Morrison, *J. Am. Chem. Soc.*, **77**, 181 (1955).

(50) A. E. Arbuzov, B. A. Arbuzov, P. I. Alimov, N. K. Nikonorov, N. I. Rizpolozhenskii and O. N. Fedorova, *Trudy Kazan Filiala Akad. Nauk S.S.S.R. Ser. Khim. Nauk*, 1956, No. 2, 7.

(51) A. C. Poshkus and J. E. Herweh, *Chem. & Ind.* (*London*), 1316 (1961).

(52) (a) S. Patai and F. Bergmann, *J. Am. Chem. Soc.*, **72**, 1034 (1950). (b) W. Wilson, *J. Chem. Soc.*, 2173 (1950). (c) W. E. Truce, G. H. Birum and E. T. McBee, *J. Am. Chem. Soc.*, **74**, 3594 (1952).

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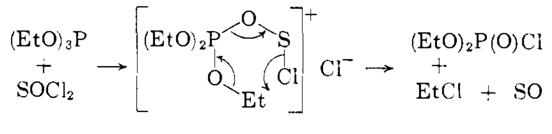
sulfur monoxide as an intermediate in these reactions or provided adequate experimental data to support the speculation proffered. As a consequence of growing evidence[10] casting doubt on the identity of sulfur monoxide claimed by earlier workers, uncritical citation of earlier work no longer affords a convincing basis for speculation. Despite the current state of sulfur monoxide chemistry our experimental results are consistent with the hypothesis that sulfur monoxide may be a short-lived[10a] intermediate in reactions between thionyl chloride and trialkyl phosphites.



Sulfur monoxide may form either through a transitory cyclic complex analogous to that proposed for reactions between sulfuryl chloride and trialkyl phosphites[3] or through a radical chain sequence.[4,57] An attractive radical chain hypothesis was abandoned reluctantly since we found no evidence for diethyl ethylphosphonate or, when the reaction was carried out in olefins,[58] for diethyl chloroalkylphosphonates. The failure to polymerize styrene when the reaction was carried out in styrene as a solvent[59] indicated further that radicals active in promoting polymerization were absent. The possibility, however, of a radical chain reaction involving radical species inactive as polymerization initiators is not excluded. Until further information is available, the cyclic complex hypothesis provides an adequate interpretation for the reaction. The hypothesis is consistent with our observation that 50% of the chlorine on thionyl chloride is found as the phosphorochloridate (Table II); the other 50% will be found as ethyl chloride.

Because of its reactivity sulfur monoxide will not build up to appreciable concentrations but react either with itself or with the phosphite. When the reactions are carried out by adding thionyl chloride slowly to a large excess of triethyl phosphite, sulfur monoxide will react with the available phosphite to form a sulfoxide. Sulfur monoxide disproportionations will be unimportant. This complex will disappear primarily by oxygen transfer to a molecule of triethyl phosphite thus

$$(EtO)_3P + SO \rightleftarrows (EtO)_3PSO$$

accounting for the phosphorothionate to phosphate ratio approaching unity—the value expected if this were the only reaction. Variable amounts

$$(EtO)_3PSO + (EtO)_3P \longrightarrow (EtO)_3PS + (EtO)_3PO$$

of sulfur dioxide are produced, however, and triethyl phosphorothionate in amounts greater than that of the phosphate invariably are obtained. The relative amounts of these products appear to depend upon reaction conditions: stirring, rate of adding reactants, temperature, etc. These results are interpreted readily by considering disproportionation of the sulfur monoxide adduct and to a lesser extent reaction of the adduct with sulfur monoxide. Such reactions would become progressively more important as the mole ratio of triethyl phosphite to thionyl chloride approached unity.

$$2(EtO)_3PSO \longrightarrow (EtO)_3PS + (EtO)_3P + SO_2$$

$$(EtO)_3PSO + SO \longrightarrow (EtO)_3PS + SO_2$$

It can be seen (Table II) that the trend is in the right direction; the yield of phosphorothionate is greater when the ratio is large and thionyl chloride is added slowly in high dilution to triethyl phosphite. When the reactant ratio is 3:2, 50–65% of the thionyl chloride is converted into the phosphorothionate and the rest to sulfur dioxide.

When triethyl phosphite is added to a large excess of thionyl chloride, on the other hand, triethyl phosphate would not be expected, which is indeed the case, and the amount of phosphorochloridate relative to the phosphorothionate should be great—again the trend is in the right direction. In this case sulfur monoxide will have little possibility to react with triethyl phosphite but will disappear by disproportionation.[10] Sulfur dioxide

$$2SO \longrightarrow S + SO_2$$

$$3SO \longrightarrow S_2O + SO_2$$

was found as expected. We have no evidence for sulfur, but it may be dissolved in the residual oil.

It is important to note that absence of sulfur dichloride (no yellow or orange color) and of sulfuryl chloride (no sulfate in the hydrolysis products) indicates that oxygen exchange between thionyl chloride and sulfur monoxide or other reactive species did not occur. Furthermore, if sulfur is present it will not react with thionyl chloride as we demonstrated experimentally contrary to the opinion expressed by Truce and his colleagues.[52c] Sulfur is known, however, to react with phosphite esters,[60] but such reactions, apparently, are considerably slower than those involving phosphites and thionyl chloride; hence, if present it would play only a minor role except in those reactions where the phosphite is present in excess.

Sulfur Dichloride.—The reaction of triethyl phosphite with sulfur dichloride proceeds vigorously probably by a radical chain sequence suggested earlier for the reaction of triaryl phosphites with sulfur chlorides.[4] Walling and Rabinowitz[57a,d] proposed a radical chain reaction to explain the desulfuration of mercaptans by trialkyl phosphites.[61] Such a reaction sequence explains the formation of triethyl phosphorothionate and diethyl phosphorochloridate. An alternate sequence

$$(EtO)_3P + ClS\cdot \longrightarrow (EtO)_3\dot{P}SCl$$

$$(EtO)\ \dot{P}\ Cl + (EtO)_3P \longrightarrow (EtO)_3PS + (EtO)_3\dot{P}Cl$$

$$(EtO)_3\dot{P}Cl + SCl_2 \longrightarrow (EtO)_3P(O)Cl + EtCl + ClS\cdot$$

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(57) (a) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79**, 5326 (1957). (b) F. Ramirez and N. McKelvie, *ibid.*, **79**, 5829 (1957). (c) C. E. Griffin, *Chem. & Ind.* (*London*), 415 (1958). (d) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1243 (1959). (e) C. Walling, O. H. Basedow and E. S. Savas, *ibid.*, **82**, 2181 (1960).

(58) Studies on the reaction between phosphites and acid chlorides of sulfur acids in presence of unsaturated organic compounds are being continued.

(59) Unpublished results.

(60) (a) W. Broeker, *J. prakt. chem.*, 2, **118**, 287 (1928). (b) L. Anschutz and H. Walbrecht, *ibid.*, **133**, 65 (1932).

(61) F. W. Hoffmann, R. J. Ess, T. C. Simmons and R. S. Hanzel, *J. Am. Chem. Soc.*, **78**, 6414 (1956).

through diethyl phosphoryl radicals is less attractive because diethyl ethyl phosphonate was not found. The low yield of diethyl N-phenylphosphoramidate relative to aniline hydrochloride and the considerable amount of residue indicates that another compound besides the phosphorochloridate and also bearing a reactive chlorine had formed. This compound is probably diethyl phosphorylsulfenyl chloride which Michalski and Skowronska[35] prepared from triethyl phosphorothionate and chlorine or sulfuryl chloride. The formation of the phosphorylsulfenyl chloride would be favored if the phosphorothionate is added to a

$$(EtO)_3\dot{P}SCl + SCl_2 \longrightarrow (EtO)_2P(O)SCl + ClS\cdot + EtCl$$

large excess of sulfur dichloride—the condition existing during the early phase of our reaction. When aniline is added to the reaction mixture, the sulfenyl chloride will give a sulfenamide.[62] The uncharacterized still residue probably contains the phosphorylsulfenamide.

Sulfur Dioxide.—The reaction between sulfur dioxide and various phosphite esters was not examined in detail. We have noted previously[4] that sulfur dioxide is difficult to remove from a reaction mixture containing phosphorus compounds. This would indicate some kind of complex, and oxygen transfer can be expected with trivalent phosphorus compounds. We found that trialkyl phosphites are highly reactive at about 100°, the dialkylphosphonates considerably less reactive and triaryl phosphites or aryl phosphines essentially unreactive. In view of the ease with which triaryl phosphites abstract an oxygen from sulfuryl, thionyl, sulfonyl and sulfinyl chlorides the failure of sulfur dioxide to oxidize triaryl phosphites was unexpected.

The manner in which sulfur dioxide reacts is somewhat obscure. Two possibilities seem reasonable. One involves a direct attack at the oxygen with the formation of sulfur monoxide and the other, a sulfur dioxide adduct without liberation of sulfur monoxide. The latter possibility may

$$(EtO)_3P + SO_2 \longrightarrow [(EtO)_3P\text{-}OSO] \longrightarrow (EtO)_3PO + SO$$

explain the failure of aryl phosphites or phosphines

$$(EtO)_3P + SO_2 \longrightarrow (EtO)_3PSO_2$$

$$(EtO)_3PSO_2 + (EtO)_3P \longrightarrow (EtO)_3PSO + (EtO)_3PO$$

to react because of steric effects. Further studies obviously are necessary to clarify the reaction.

Conclusions.—1. Thionyl chloride reacts with trialkyl phosphites without any evidence of stable intermediates even at −60° to give dialkyl phosphorochloridate and ethyl chloride with variable amounts of trialkyl phosphates, trialkyl phosphorothionates and sulfur dioxide.

2. The formation of trialkyl phosphates, trialkyl phosphorothionates and sulfur dioxide is attributed to sulfur monoxide as a primary reactive intermediate.

3. The reaction of sulfur dichloride with trialkyl phosphite, yields mainly trialkylphosphorothionate, a dialkyl phosphorochloridate, and an alkyl chloride.

4. Sulfur dioxide reacts with trialkyl phosphites at about 100° to give a mixture of trialkyl phosphates and phosphorothionates in a 2:1 mole ratio.

5. Sulfuryl chloride reacts rapidly with phosphorothionates to produce sulfur dioxide and with phosphorothiolates to produce substances having odors characteristic of mercaptans or disulfides. The reaction is a simple diagnostic test to distinguish between the two types of compounds.

6. Thionyl chloride does not react with phosphorothionates but reacts slowly with phosphorothiolates.

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(62) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946).