analyzed for residual 1-hydroxynaphthalene by the method of Pearse.[24]

Induction Periods. The induction periods were measured in the oxygen absorption apparatus previously described.[25] The end of the induction period was chosen as that point at which the rate of oxygen absorption was the same as the uninhibited rate, correcting for the consumption of initiator. The total number of radicals stopped by the phenol was calculated from the first-order rate constant for the decomposition of 2,2,3,3-tetraphenylbutane.

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Thermal Rearrangement of Phosphorodihalidothioites. A New Synthesis of Phosphonothioic Dihalides

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Abstract: The preparation of phosphonothioic dihalides, $RP(S)X_2$, by the thermal rearrangement of phosphorodihalidothioites, $RSPX_2$, in a sealed vessel is described. A second product of the reaction is the corresponding phosphinothioic halide, $R_2P(S)X$. The reaction has a wide scope and is promoted by catalysts, preferably iodine, methyl iodide, and iodide salts, and it can be carried out in the vapor phase at atmospheric pressure. It also has been found that a phosphonothioic dihalide can be prepared by the reaction of an alkyl sulfide or alkyl disulfide with phosphorus trichloride at elevated temperatures.

Phosphonothioic dihalides ($RP(S)X_2$) are important intermediates in the preparation of petroleum additives, agricultural chemicals, organophosphorus polymers, and other products of commercial interest. A number of procedures have been reported[1-8] for the preparation of these intermediates. With respect to yield, scope, and ease of reaction, the addition of sulfur to a dihalophosphine[1,2] is the only satisfactory method. Unfortunately, this method is practically limited to the preparation of phenylphosphonothioic dichloride from the readily available dichlorophenylphosphine, since other dihalophosphines are relatively difficult to prepare.

As a result of our search for a new route to alkylphosphonothioic dihalides, we wish to report their preparation by the thermal rearrangement of alkyl phosphorodihalidothioites ($RSPX_2$) in a sealed vessel (reaction 1). The reaction was applied also to the synthesis

$$RSPX_2 \xrightarrow{\Delta} RP(S)X_2 \text{ (and } R_2P(S)X) \qquad (1)$$

of the cycloalkyl, allyl, benzyl, and aromatic analogs. The scope of the reaction was demonstrated by the preparation of 21 phosphonothioic dihalides. Whereas a pure alkyl phosphorodichloridothioite was employed initially in the rearrangement, it was found that the use of undistilled material, obtained by the reaction of equimolar quantities of a mercaptan and phosphorus trichloride, was equally satisfactory for the rearrangement reaction. The reaction is general, with yields varying from 40 to 70%. Thirteen known compounds have been prepared in this manner, as shown in Table I.

In addition, eight other higher homologs were treated at temperatures ranging from 265 to 300°. These were *t*-butyl, pentyl, hexyl, heptyl, octyl, dodecyl, *p*-(*t*-butyl)phenyl, and *p*-nonylphenyl. Nuclear magnetic resonance (nmr) spectra made from the reaction products showed P^{31} resonance peaks which were very similar in chemical shift and in intensity to the ones obtained with the lower homologs. Vapor phase chromatography (vpc) also indicated the formation of the corresponding phosphonothioic dihalides.

In general, the temperature required for the reaction varied from 135–165° for $R = CH_2CH{=}CH_2$ to 275–400° for $R = CH_3$. The duration of heating usually depended upon the temperature and could be reduced to less than 1 hr at the higher temperatures. The pressures which developed during the rearrangement varied according to the nature of the substituents and the reaction temperature. In a typical autoclave preparation of the low-boiling methylphosphonothioic dichloride at 300°, the maximum pressure measured was *ca.* 40 atm. In most of the experiments involving the alkyl analogs, small quantities of the corresponding hydrocarbons were formed. Samples of the gases were collected and analyzed by infrared spectroscopy. Methane was the main component in the gas collected after rearrangement of the methyl compound, propane from the propyl and isopropyl, butane from the butyl, isobutane from the isobutyl and *t*-butyl, pentane from

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Table I. Preparation of Phosphonothioic Dichlorides from the Reaction Product of RSH and PCl_3

R in RSH used	Temp, °C	Time, hr	Yield, %[a]	Nmr chemical shift, ppm
CH_3	305	24	74	−79.4[b−d]
CH_3[e]	300	48	80	−79.4[b,c]
C_2H_5	260	8	44	−95.4[d−g]
C_3H_7	300	21	60	−90.1[d,h]
i-C_3H_7	300	65	50	−107.0[d,h]
C_4H_9	290	8	45	−90.6[d,g]
i-C_4H_9	290	8	42	−89.0[d,i,j]
C_6H_{11}	290	8	66	−101.8[g]
$CH_2{=}CHCH_2$	140	60	50	−84.6[d,j,k]
$C_6H_5CH_2$	230	60	90	−85.0[l]
C_6H_5	265	70	77	−74.4[d,m]
C_6H_5[e]	265	70	90	−74.4[m]
p-ClC_6H_4	290	12	86	−71.4[i,n]
p-$CH_3C_6H_4$	290	8	52	−75.3[i,o]
2-$C_{10}H_7$	290	12	61	−74.4[i,p]

[a] The yield is expressed as mole % of the phosphorus present, as determined by nmr. [b] N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956); chemical shift = −79.8 ppm. [c] H. Finegold, *Ann. N. Y. Acad. Sci.*, **70**, 875 (1958); chemical shift = −79.8 ppm. [d] Nmr identification verified by vpc. [e] In this instance, the fractionated phosphorodichloridothioite was rearranged. [f] See references cited in footnotes *b* and *c*; chemical shift = −94.3 ppm. [g] This value agrees with the chemical shift of an authentic sample prepared from the corresponding phosphonic dichloride by D. K. Lynch, Monsanto Co., using a published procedure.[7] [h] This value agrees with the chemical shift of an authentic sample prepared from the corresponding phosphonic dichloride by J. P. Chupp, Monsanto Co., using a published procedure.[7] [i] See ref 2. [j] In the case of compounds for which no chemical shift has been established, assignments were based on the size and position of the peaks in the quadruply connected region of the spectrum; see L. C. D. Groenweghe, L. Maier, and K. Moedritzer, *J. Phys. Chem.*, **66**, 901 (1962). [k] A. I. Razumov, B. G. Liorber, M. B. Gazizov, and Z. M. Khammatova, *Zh. Obshch. Khim.*, **34** (6), 1851 (1964); *Chem. Abstr.*, **61**, 8334 (1964). [l] See ref 9; chemcal shift = −85.3 ppm. [m] See references cited in footnotes *b* and *c*; chemical shift = −74.8 ppm. [n] H. Maier-Bode and G. Kotz, German (East) Patent 11,241 (1956); *Chem. Abstr.*, **53**, 6156 (1959). [o] See ref 3. [p] See ref 6.

pentyl, cyclohexane from cyclohexyl, propene from allyl, and toluene from the benzyl analog. Benzene was not isolated from the phenyl analog. Identification was made by comparison of the infrared spectra with published spectra of the hydrocarbons. The weight loss due to the formation and escape of volatile materials varied from 1 to 10%.

In addition to the compounds listed in Table I, methylphosphonothioic dibromide (chemical shift = −20.5 ppm[9]) was obtained in 60% yield by heating the corresponding phosphorodibromidothioite[9,10] at 300° for 6 hr.

The corresponding phosphinothioic halides ($R_2P(S)X$) were formed with the phosphonothioic dihalides in varying quantities, depending on the reaction conditions. These compounds are not readily obtained economically, either due to the unavailability of the corresponding halophosphine, to which sulfur may be added,[11−13] or due to the lack of other satisfactory synthetic routes.[8,14−17] The yield of these second products was more thoroughly studied in sealed-tube experiments in the case of the methyl derivative. The results are reported in Table II. The major factor controlling the ratio of the yields of the phosphonothioic and phosphinothioic chlorides was the ratio of mercaptan to phosphorus trichloride employed in the preparation of the unrearranged material. As shown in Table II, it was possible to increase the yield of dimethylphosphinothioic chloride to 65%, with a concomitant decrease in the yield of methylphosphonothioic dichloride.

Table II. Influence of Mercaptan/Phosphorus Trichloride Ratio on Yields of $CH_3P(S)Cl_2$ and $(CH_3)_2P(S)Cl$

CH_3SH/PCl_3 ratio for preparation of unrearranged material	Rearr temp, °C	Time, hr	Product compn[a] $CH_3P(S)Cl_2$	Product compn[a] $(CH_3)_2PSCl$
0.50:1.00	305	8	27	4
0.85:1.00	305	8	55	11
	305	24	66	8
1.00:1.00	305	8	59	12
	305	24	69	10
	305	4	68	11
	395	1	60	10
1.15:1.00	305	8	64	17
	305	24	70	16
1.30:1.00	305	8	52	24
1.75:1.00	305	8	26	35
	305	24	29	46
2.00:1.00	305	24	15	65

[a] The results are expressed in weight per cent, as determined by gas chromatography.

Using the same experimental technique, the rearrangement of methyl phosphorodichloridothioite was studied in the presence of a number of catalysts (Table III). The most effective substances were iodine, methyl iodide, and inorganic iodide salts, followed by inorganic bromide and chloride salts.

As an alternate to the sealed-tube procedure, vapor phase experiments for the preparation of methylphosphonothioic dichloride were conducted. The desired product was obtained, but the yield was lower. These vapor phase reactions were carried out in two ways. In one case, the reaction product obtained from phosphorus trichloride and methyl mercaptan (1:1 ratio) was passed through a Vycor tube at 500–550°. Alternately, unreacted methyl mercaptan and phosphorus trichloride were simultaneously introduced into the heated tube. The yields obtained were up to 42% for methylphosphonothioic dichloride and up to 17% for dimethylphosphinothioic chloride.

Additional investigation showed that an alkyl sulfide or an alkyl disulfide could be substituted for the alkyl mercaptan. In these cases, equimolar amounts of the sulfide (or disulfide) and phosphorus trichloride were

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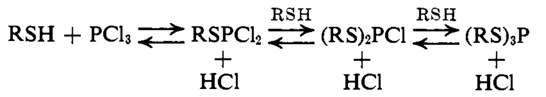
Table III. Preparation of $CH_3P(S)Cl_2$ and $(CH_3)_2P(S)Cl$ from the CH_3SH/PCl_3 (1:1) Reaction Product Using a Catalyst Concentration of 0.05 Mole/Mole of Phosphorus

Catalyst	Temp, °C	Time, hr	Product compn[a] CH_3P-(S)Cl_2	Product compn[a] $(CH_3)_2$-P(S)Cl
None	275	8	43	9
I_2	275	8	67	8
CH_3I	275	8	61	9
ZnI_2	275	8	65	9
KI	275	8	60	7
NaI	275	8	61	5
CuI	275	8	58	8
$ZnBr_2$	275	8	53	11
$AlCl_3$	275	8	52	13
$ZnCl_2$	275	8	50	9
$FeCl_3$	275	8	50	5
$TiCl_4$	275	8	48	10
$HgCl_2$	275	8	48	8
None	275	24	54	10
I_2[b]	275	24	66	10
None	305	8	58	12
I_2[b]	305	8	68	9
None	130	8	0[c]	0[c]
$(t\text{-}C_4H_9O)_2$[b]	130	8	0[c]	0[c]
None	275	24	54	10
$(t\text{-}C_4H_9O)_2$[b]	275	24	54	12

[a] The results are expressed in weight per cent, as determined by gas chromatography. [b] Catalyst concentration was 0.025 mole/mole of phosphorus. [c] The nmr spectrum verified the absence of quadruply connected phosphorus.

heated at *ca.* 275° in sealed tubes. As observed in the experiments with the phosphorodichloridothioites, catalysts such as methyl iodide and iodine promoted the reaction. Yields as high as 54 and 44% of methylphosphonothioic dichloride were obtained from the sulfide and disulfide, respectively.

Several mechanisms may be proposed for the rearrangement (represented in its simplest form by reaction 1) using a complex system arising from interaction of a mercaptan and phosphorus trichloride as a starting point.



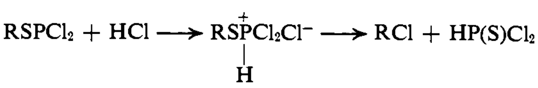
$$RSH + PCl_3 \rightleftarrows \underset{+\ HCl}{RSPCl_2} \overset{RSH}{\rightleftarrows} \underset{+\ HCl}{(RS)_2PCl} \overset{RSH}{\rightleftarrows} \underset{+\ HCl}{(RS)_3P} \qquad (2)$$

$$2RSPCl_2 \rightleftarrows (RS)_2PCl + PCl_3 \qquad (3)$$

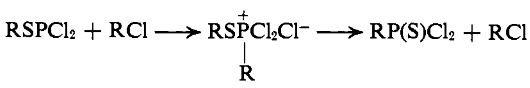
$$2(RS)_2PCl \rightleftarrows (RS)_3P + RSPCl_2 \qquad (4)$$

Reactions 3 and 4 are examples of reorganization or disproportionation and have been observed in many triply connected phosphorus compounds.[18] They occur at a rapid rate at the rearrangement temperature and are the controlling factor toward the establishment of an equilibrium between the four components involved. These reactions even take place slowly at room temperature.[18] In cases where the mercaptan and phosphorus trichloride were allowed to react in a 1:1 ratio the starting material, according to nmr analysis, consists primarily of the phosphorodichloridothioite ($RSPCl_2$), although the over-all composition corresponds exactly to this compound.

The first proposed mechanism, similar to the mechanism of the Michaelis–Arbuzov rearrangement,[19] is the ionic type illustrated by reactions 5 and 6 and applies



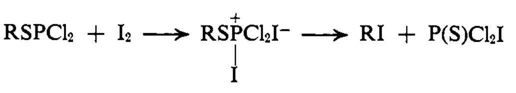
$$RSPCl_2 + HCl \longrightarrow RS\underset{H}{\overset{+}{P}}Cl_2Cl^- \longrightarrow RCl + HP(S)Cl_2 \qquad (5)$$



$$RSPCl_2 + RCl \longrightarrow RS\underset{R}{\overset{+}{P}}Cl_2Cl^- \longrightarrow RP(S)Cl_2 + RCl \qquad (6)$$

to the cases where R = alkyl. Initial reaction 5, arising from traces of residual hydrogen chloride, produces a small quantity of an alkyl chloride which reacts according to reaction 6. By analogy to the reported mechanism of the Michaelis–Arbuzov rearrangement,[19] nucleophilic attack by the phosphorus atom on the α carbon of the alkyl chloride forms a phosphonium chloride, which loses alkyl chloride by an S_N2 reaction.

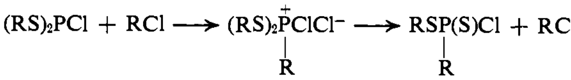
Catalysis, after addition of methyl iodide, iodine, and metal halides, is readily correlated with this mechanism. Methyl iodide could react directly in a manner analogous to reaction 6. Iodine and the metal halides could react with the phosphorodichloridothioite to form an alkyl iodide (reaction 7) or an alkyl halide (reaction 8), which likewise catalyze the rearrangement.



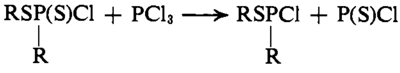
$$RSPCl_2 + I_2 \longrightarrow RS\underset{I}{\overset{+}{P}}Cl_2I^- \longrightarrow RI + P(S)Cl_2I \qquad (7)$$

$$RSPCl_2 + MX \longrightarrow RX + MSPCl_2 \qquad (8)$$

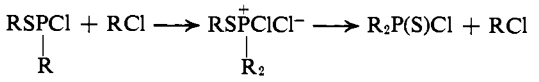
Dialkylphosphinothioic halides may be formed stepwise as follows.



$$(RS)_2PCl + RCl \longrightarrow (RS)_2\underset{R}{\overset{+}{P}}ClCl^- \longrightarrow RS\underset{R}{P}(S)Cl + RCl \qquad (9)$$



$$RS\underset{R}{P}(S)Cl + PCl_3 \longrightarrow RS\underset{R}{P}Cl + P(S)Cl_3 \qquad (10)$$

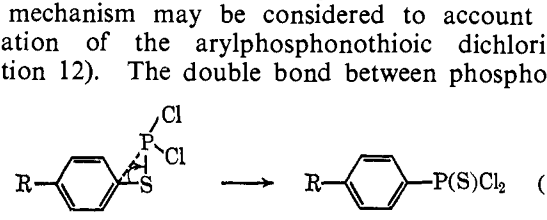


$$RS\underset{R}{P}Cl + RCl \longrightarrow RS\underset{R_2}{\overset{+}{P}}ClCl^- \longrightarrow R_2P(S)Cl + RCl \qquad (11)$$

The formation of thiophosphoryl chloride (reaction 10) has been verified by nmr spectroscopy.

Reactions 2, 3, and 4, in which there have been exchanges between alkylthio and chloro groups, are reversible.[18] In contrast, the reactions involving the rearrangement, in which a carbon–phosphorus bond and an isolated sulfur (*i.e.*, S bonded only to the P) result, are irreversible. The P–C bond cannot undergo any further reorganization at the rearrangement temperature.[20] The isolated sulfur itself, however, may be subject to removal upon interaction with suitable reagents (as in reaction 10).

Since aromatic phosphites generally do not undergo the Michaelis–Arubzov rearrangement, an intramolecular mechanism may be considered to account for formation of the arylphosphonothioic dichlorides (reaction 12). The double bond between phosphorus



(12)

R = H, Cl, alkyl

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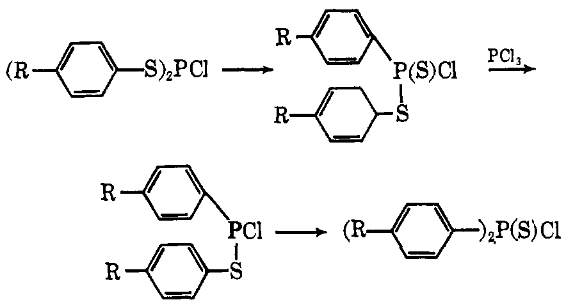
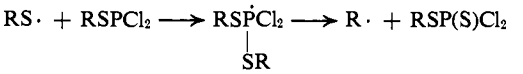
and sulfur is formed in a concerted-type reaction in which simultaneous shift of the aromatic ring to the phosphorus atom occurs. Formation of the double bond can be compared to the reported[21] formation of phosphorus–oxygen double bonds from trialkyl phosphites and carbonyl compounds. In support of this mechanism, retention of substitution in the *para* position (R = Cl, alkyl) was demonstrated by infrared spectroscopy. The spectra in these cases showed the typical pattern for *para* substitution in the 5.0- to 6.0-μ region.[22]

If similar rearrangement of diaryl phosphorochloridodithioites ($(ArS)_2PCl$) occurs to form an intermediate ($Ar(ArS)P(S)Cl$) from which sulfur is extracted (analogous to reaction 10),[23] a second intramolecular rearrangement yields the diarylphosphinothioic chlorides (reaction 13).



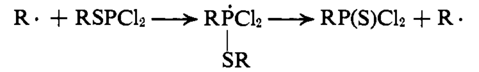
(13)

The observation that hydrocarbons were being formed during some of the rearrangements, even at a low temperature (140°, R = $CH_2CH{=}CH_2$), suggested that a radical mechanism in addition to an ionic one is involved, even though di(*t*-butyl) peroxide did not catalyze the reaction (see Table III). The ionic mechanism does not account for hydrocarbon formation. Conditions for formation of the radical RS· are favorable, *i.e.*, mercaptan, high temperature, and the presence of oxygen in the air space above the reaction mixture. This radical can initiate the following sequence which is similar to the free-radical mechanism assigned to the reaction between mercaptans and triethyl phosphite yielding hydrocarbons.[24,25]



$$RS\cdot + RSPCl_2 \longrightarrow RS\underset{\textstyle SR}{\underset{|}{\dot{P}}}Cl_2 \longrightarrow R\cdot + RSP(S)Cl_2 \quad (14a)$$

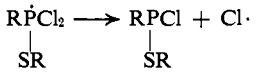
$$RS\cdot + PCl_3 \longrightarrow RS\dot{P}Cl_3 \longrightarrow R\cdot + P(S)Cl_3 \quad (14b)$$



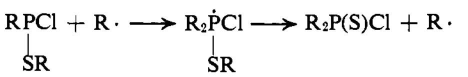
$$R\cdot + RSPCl_2 \longrightarrow R\underset{\textstyle SR}{\underset{|}{\dot{P}}}Cl_2 \longrightarrow RP(S)Cl_2 + R\cdot \quad (15)$$

$$R\cdot + RSH \longrightarrow RH + RS\cdot \quad (16)$$

Phosphinothioic halides can also be formed *via* a radical mechanism.



$$R\underset{\textstyle SR}{\underset{|}{\dot{P}}}Cl_2 \longrightarrow R\underset{\textstyle SR}{\underset{|}{P}}Cl + Cl\cdot \quad (17)$$



$$R\underset{\textstyle SR}{\underset{|}{P}}Cl + R\cdot \longrightarrow R_2\underset{\textstyle SR}{\underset{|}{\dot{P}}}Cl \longrightarrow R_2P(S)Cl + R\cdot \quad (18)$$

Our observation that no benzene was formed when phenyl phosphorodichloridothioite was rearranged is analogous to an exception noted in the mercaptan–phosphite reaction,[24,25] referred to above. In that instance, the formation (analogous to reactions 14 and 16) of benzene from the intermediate $C_6H_5S\dot{P}(O)(OC_2H_5)_2$ was greatly suppressed. This was attributed to the small resonance energy of the phenyl radical and the strong phenyl–sulfur bond.

In conclusion, the rearrangement may proceed exclusively *via* an intramolecular concerted mechanism for the aromatic analogs, while in the aliphatic cases, it may involve primarily a Michaelis–Arbuzov-type ionic mechanism accompanied to a minor extent by a free-radical-type mechanism.

In the preparation of methylphosphonothioic dichloride from either methyl sulfide or methyl disulfide and phosphorus trichloride, reactions similar to those described above presumably occur after initial formation of methyl phosphorodichloridothioite. There have been both ionic[26] and free-radical[24,25] mechanisms postulated for related reactions involving disulfides.

Experimental Section

Analytical Methods. Gas chromatography and nuclear magnetic resonance spectroscopy were utilized during this work for most of the qualitative and quantitative analyses.

Nmr measurements were made with a Varian Model V-4300B high-resolution nuclear magnetic resonance spectrometer at a frequency of 16.2 Mc and a magnetic field of approximately 9395 gauss. The chemical shifts of the P^{31} resonances are reported in ppm relative to 85% H_3PO_4 as a standard. Quantitative nmr data are expressed in mole per cent.

Gas chromatographic analyses of methylphosphonothioic dichloride and dimethylphosphinothioic chloride were carried out using a Perkin-Elmer 154D vapor fractometer with a 70-cm column packed with 30% Dow Corning Silicone Oil 550 on Chromosorb W. The injection block temperature was 155° and a helium flow of 60 ml/min was used. Results are expressed in weight per cent.

Reaction of Mercaptans with Phosphorus Trihalides. A. Methyl Phosphorodichloridothioite. Phosphorus trichloride (274.7 g, 2.0 moles) was stirred at 60–65° during the subsurface introduction of 48.1 g (1.0 mole) of methyl mercaptan over a period of 1.5 hr. The rate of addition was adjusted to a slow rate at first and then gradually increased as the mercaptan became more soluble in the reaction mixture. A Dry Ice condenser was used to prevent loss of mercaptan. The reaction mixture was stirred for 1 additional hr at 65° and the temperature was raised to 105–110° to complete the removal of hydrogen chloride. Upon fractionation, the product[27] was collected at 30° (9 mm), yield 72.2 g (48%), nmr chemical shift −206.0 ppm.[9]

The initial rate of mercaptan addition was increased substantially by the addition of reaction product from a previous experiment. For example, about 1 g of reaction product per 3 g of PCl_3 was added to the PCl_3 before mercaptan addition.

In other experiments in which the reaction mixture was not fractionated, methyl mercaptan and phosphorus trichloride were allowed to react in ratios varying from 0.5:1.0 to 2.0:1.0. Also, in one instance, methyl phosphorodibromidothioite (chemical shift −203.5 ppm[9]) was prepared by substituting phosphorus tribromide for phosphorus trichloride (1:1 ratio).

B. Other Phosphorodichloridothioites. Other mercaptans were treated with phosphorus trichloride[27–32] according to the following

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general procedure. Phosphorus trichloride (1 to 4 moles) was stirred vigorously at 70° during the dropwise (liquid mercaptans) or portionwise (solid mercaptans) addition of an equimolar quantity of the mercaptan (in the case of the lower boiling mercaptans, a 1 to 2% excess was added and, for ethyl mercaptan, a Dry Ice condenser and cooled funnel were utilized). After the addition, the temperature was raised to 90° and held for 1 to 2 hr. Dry nitrogen was then passed through the stirred mixture for 0.5 to 1 hr to facilitate the removal of an equimolar quantity of hydrogen chloride.

All of these reaction mixtures were thermally rearranged to the phosphonothioic dichlorides. In addition, two of the unrearranged reaction mixtures were distilled under reduced pressure and the isolated phosphorodichloridothioites were rearranged. These were phenyl phosphorodichloridothioite (46% yield), bp 93-98° (2 mm) (lit.[30] bp 125° (10 mm)), chemical shift −204.2 ppm,[9] and heptyl phosphorodichloridothioite (31% yield), bp 111-116° (2 mm), chemical shift −211.0 ppm.[9]

Phosphonothioic Dihalides. A. Sealed-Tube Procedure (Table I). The phosphorodichloridothioites (about 7 ml of the 1:1 $RSH-PCl_3$ reaction products or the distilled material) were heated in sealed tubes constructed from Pyrex glass (15 mm o.d., $^3/_{32}$-in. wall thickness) and enclosed in metal shields bearing vent holes at each end. After cooling, the products were analyzed by nmr directly or, if required, the tubes were opened and the contents analyzed by gas chromatography or nmr.

In all cases, peaks were present in the quadruply connected region of the nmr spectra which could be assigned to the corresponding phosphinothioic chlorides, *e.g.*, diethylphosphinothioic chloride, chemical shift −108.0 ppm,[9] and diphenylphosphinothioic chloride, chemical shift −79.4 ppm.[9]

In some cases, due to formation of hydrocarbons and other gases, it was necessary to cool the tubes in Dry Ice prior to opening so that spraying and foaming were minimized.

B. Autoclave Procedure. Methylphosphonothioic Dichloride. The reaction product (583 g) of equimolar quantities of methyl mercaptan and phosphorus trichloride was placed in a 1-l. Parr pressure reaction apparatus (Series 4500, stirrer type) constructed of Hastelloy B and fitted with a Teflon gasket and stirrer bushing, Rulon Red shaft packing material, and Viton A "O" rings. The temperature was maintained at 300° for 6 hr. The maximum pressure observed was *ca.* 40 atm. Gas chromatographic analysis of the reaction product, using authentic samples as standards, indicated the presence of 58% methylphosphonothioic dichloride and 16% dimethylphosphinothioic chloride. Distillation through a 2 ft × 24 mm column packed with Berl saddles yielded 54% of the phosphonothioic dichloride, bp 67-70° (50 mm) (lit.[8] bp 69.5-70.5° (50 mm)), and 14% of the phosphinothioic chloride, bp 58-61° (10 mm) (lit.[15] bp 82-83° (16 mm)).

In another experiment carried out at 300° for 72 hr, without stirring, the phosphonothioic dichloride was isolated in 63% yield.

C. Vapor Phase Procedures. 1. Rearrangement of the Reaction Product of CH_3SH and PCl_3 (1:1). A Vycor U tube (13 mm i.d.) was submerged to a depth of 10 in. in a lead-tin bath maintained at 550°. The $CH_3SH-PCl_3$ reaction product was pumped into the tube with a Micro-Bellows pump at a rate of 1 ml/min using a stream of nitrogen as a carrier gas (100 ml/min). The U tube was connected to an ice-cold receiver. The product collected contained 42% methylphosphonothioic dichloride and 17% dimethylphosphinothioic chloride as determined by gas chromatography.

2. Simultaneous Addition of CH_3SH and PCl_3 (1:1). This procedure was similar to the one described above except that the phosphorus trichloride was added dropwise into a vaporization chamber and mixed with methyl mercaptan prior to their introduction into the U tube. The product contained 36% methylphosphonothioic dichloride and 5% dimethylphosphinothioic chloride.

Preparation of Methylphosphonothioic Dichloride from Phosphorus Trichloride and Either Methyl Sulfide or Methyl Disulfide. A. Methyl Sulfide. Equimolar quantities of methyl sulfide and phosphorus trichloride were heated in a sealed tube at 290° for 12 hr. Methylphosphonothioic dichloride and dimethylphosphinothioic chloride were formed in 39 and 7% yields, respectively. Using methyl iodide as a catalyst (0.1 ml/5 ml of reaction mixture), two products were formed in 54 and 8% yields, respectively, when heated at 260° for 8 hr. Under the same conditions except using iodine as a catalyst (0.3 g/5 ml), the yields were 49 and 18%, respectively. Analyses were obtained by use of gas chromatography.

B. Methyl Disulfide. Substitution of methyl disulfide for methyl sulfide in the above experiments gave similar results. At 275° for 12 hr, the yields were 36 and 3% for the phosphonothioic and phosphinothioic compounds, respectively. Using methyl iodide as a catalyst at 260° for 8 hr, the products were obtained in 44 and 4% yields, respectively. These yields were determined by means of gas chromatography.

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