REACTION OF PHOSPHOROUS ACID CHLORIDES

WITH OXETANES

B. A. Arbuzov, O. N. Nuretdinova, L. Z. Nikonova, and É. I. Gol'dfarb

The reaction of PCl_3 and the dichlorides of alkylphosphorous acids with 2-methyloxetane and 3,3-dimethyloxetane, using a 1:1 ratio of the reactants, was studied previously [1]. In the present paper these reactions were studied using other ratios of the starting components. The acid chloride of O,O-di-(1methyl-3-chloropropyl)phosphorous acid (II) is obtained when PCl_3 is reacted with 2 M 2-methyloxetane

$$PCl_{3} + 2H_{3}CCH CH_{2} \rightarrow ClP(OCHCH_{2}CH_{2}Cl)_{2}$$

$$(I) O CH_{3} - (II)$$

Phosphite (III) is obtained as the result of the reaction of (II) with (I), or of 3 moles of (I) with PCl₃

 $\begin{array}{c} \operatorname{PCl}_{3}+3 \ (\mathrm{I}) \longrightarrow & \operatorname{P(OCHCH_{2}CH_{2}Cl)_{3}} \\ (\mathrm{II})+(\mathrm{I}) \longrightarrow & \operatorname{CH}_{3} & (\mathrm{III}) \end{array}$

Since (III) decomposes when distilled with the liberation of 1,3-dichlorobutane, it was analyzed in the undistilled form. Thiophosphate (IV) is obtained when (III) is reacted with sulfur

$$(III) + S \rightarrow \begin{matrix} S = P(OCHCH_2CH_2Cl)s \\ | \\ CH_3 & (IV) \end{matrix}$$

The following compounds are obtained when (III) is heated (150°C) in a nitrogen atmosphere

$$(ClCH_{2}CH_{2}CHO)_{3}P \xrightarrow{150^{\circ}} (ClCH_{2}CH_{2}CHOP)_{3}P \xrightarrow{1} (ClCH_{2}CH_{2}CHOP)_{2}CH_$$

1,3-Dichlorobutane and compound (V) are the principal products of this reaction. Compound (V) after distillation is usually contaminated with the dialkyl phosphite:

the amount of which depends on the moisture content of the starting 2-methyloxetane (I). Based on the ³⁴P NMR spectrum, the amount of (VII) in admixture with (V) is ~15-20% when (I) is distilled simply over Na metal. If prior to reaction with PCl_3 , (I) is refluxed over CaH_2 and then distilled, then the amount of (VII) in the mixture decreases to 10-12%. Pure (V) was obtained when (V), contaminated with (VII), was refluxed with Na metal, the amount of which was calculated on the basis of the amount of (VII) in the mixture. When phosphite (VIII), obtained by the reaction:

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$$PCl_{3} + 3CH_{2} \longrightarrow P(OCH_{2}CH_{2}CH_{2}Cl)_{3} \quad (VIII)$$

$$CH_{2} \longrightarrow P(OCH_{2}CH_{2}CH_{2}Cl)_{3} \quad (VIII)$$

is heated the principal reaction product is the acyclic compound (IX)



Phosphite (X) is obtained by the reaction of ethyl dichlorophosphite with 2 moles of 2-methyloxetane CH_3

$$C_2H_5OPCl_2 + 2(I) \rightarrow C_2H_5OP(OCHCH_2CH_2Cl_2)$$
(X)

Phosphite (X) is an unstable compound that undergoes disproportionation when stored, heated, or distilled. The amount of disproportionation products, contained in the reaction mixture, depends on the temperature conditions of the reaction. If during the addition of (I) the temperature of the reaction mixture is kept be-low 25-30°, and then the calculated amount of sulfur is added immediately, then ethyl di-(1-methyl-3-chloro-propyl)thiophosphate (XI) can be obtained in 60-70% yield

(X)
$$+ S \rightarrow S CH_3$$

 $\parallel \parallel L C_2H_5OP(OCHCH_2CH_2CI)_2$
(XI)

When (X) is heated at 150° the principal product is (V), contaminated with a small amount of (VII). The dichloride of tert-(2,2,2-trichloro)butylphosphorous acid reacts with 1 mole of 2-methyloxetane to give the acid chloride (XII)

$$\begin{array}{c} \text{Cl}_{3}\text{C} & \text{Cl}_{3}\text{C} \\ & \text{COPCl}_{2} + (\text{I}) \rightarrow & \text{COPOCHCH}_{2}\text{CH}_{2}\text{Cl} \\ (\text{H}_{3}\text{C})_{2} & (\text{H}_{3}\text{C})_{2} & \text{Cl} & \text{CH}_{3} & (\text{XII}) \end{array}$$

Phosphite (XIII) is obtained in the reaction of (XII) with 1 mole of (I), or of 2 mole of (I) with the starting dichloride, which, the same as (III), decomposes when distilled with the liberation of 1,3-dichlorobutane Cl₃C

$$(XII) + (I) \rightarrow COP(OCHCH_2CH_2CI)_2 \\ (H_3C)_2 CH_3 (XIII)$$

In contrast to (X), phosphite (XIII) does not undergo disproportionation when heated at $40-60^{\circ}$, and was analyzed without distillation.

Thiophosphate (XIV) is obtained by the reaction of (XIII) with sulfur

When heated at 140-150° (30-60 min), (XIII) gives products (XV), (XVI), and 1,3-dichlorobutane in nearly quantitative yield



 P_2S_5 reacts with (XV) to give the thionoxaphospholane (XVII)

$$(XV) + P_2S_5 \rightarrow \begin{array}{c} Cl_3C & S & O - - CH - CH_3 \\ \parallel & & \parallel \\ (H_3C)_2 & CH_2 - CH_2 \end{array} (XVII)$$

Opening of the oxaphospholane ring occurs as the result of the reaction of (XV) with PCl_{5}

$$(XV) + PCl_5 \rightarrow \begin{array}{c} Cl_3C & O \\ & \parallel \\ & COPCH_2CH_2CHClCH_3 \\ & (H_3C)_2 & Cl & (XVIII) \end{array}$$

In contrast to (XIII), phosphite (XIX) at 150-160° gives the acyclic compound (XX) as the principal product



Diethyl (1-methyl-3-chloropropyl)phosphite (XXI) is obtained by the reaction of the acid chloride of diethylphosphorous acid with 2-methyloxetane, which, the same as the analogous 2-chloroalkyl phosphites, rapidly undergoes disproportionation when stored or during distillation [2-4]. Triethyl phosphite is formed when (XXI) is distilled

$$(C_{2}H_{5}O)_{2}PCI + H_{3}CCH CH_{2} \rightarrow (C_{2}H_{5}O)_{2}POCHCH_{2}CH_{2}CI O CH_{3} CH_{3$$

If the calculated amount of sulfur, when based on (XXI), is added to the reaction mixture immediately after adding the 2-methyloxetane, then, besides diethyl (1-methyl-3-chloropropyl)thiophosphate (principal product), other thiophosphates are formed as the result of the addition of sulfur to the phosphites – the disproportionation products of (XXI). Diphenyl chlorophosphite reacts with 2-methyloxetane more slowly than diethyl chlorophosphite. In order to obtain diphenyl (1-methyl-3-chloropropyl)phosphite in 50-60% yield the reaction mixture should not be cooled. Phosphite (XXIII) can be distilled in vacuo without disproportionation, and remains trivalent ($\delta^{31}P = -133$ ppm)

 $\begin{array}{c} (C_6H_5O)_2PCl + (I) \rightarrow \begin{array}{c} (C_6H_5O)_2POCHCH_2CH_2Cl \\ i \\ CH_3 \end{array} (X X III) \end{array}$

EXPERIMENTAL METHOD

The ³¹P NMR spectra were taken on a KGU-4 NMR instrument (10.2 MHz); 85% H₃PO₄ was taken as the standard.

 $\begin{array}{c} \label{eq:relation} \frac{\text{Reaction of PCl}_3 \text{ with 2-Methyloxetane (I). 1) Ratio of Reactants = 1:2. With stirring, to 8.3 g of PCl_3 at 20-25°, in a nitrogen stream, was slowly added 8.6 g of (I). We isolated 6.8 g (40%) of the chloride of di-(1-methyl-3-chloropropyl)phosphorous acid with bp 101-102° (0.25 mm): d_4^{20} 1.2112; n_D^{20} 1.4791. Found: C 34.42; H 5.77; P 10.76\%. C_8H_{16}Cl_3O_2P. Calculated: C 34.10; H 5.64; P 11.01\%. \end{array}$

2) Ratio of Reactants = 1:3. With stirring and cooling in ice water, from a mixture of 3 g of PCl₃ and 5 g of (I) was obtained tri-(1-methyl-3-chloropropyl)phosphite (III), which was analyzed without distillation: d_4^{20} 1.1808; n_D^{20} 1.4702. Found: P 8.93%. C₁₂H₂₄Cl₃O₃P. Calculated: P 8.77%. The reaction of phosphite (III) with sulfur gave tri-(1-methyl-3-chloropropyl)thiophosphate in 48% yield, bp 146-148° (0.25 mm); d_4^{20} 1.2254; n_D^{20} 1.4928. Found: C 37.37; H 6.35; P 7.94; S 8.32%. C₁₂H₂₄Cl₃O₃PS. Calculated: C 37.35; H 6.22; P 8.04; S 8.30%.

When phosphite (III), obtained from 4.5 g of PCl₃ and 7.1 g of (I) (dried over CaH₂), was heated in a nitrogen stream at 140-150° for 30-40 min, followed by distillation, we obtained: a) 4.8 g (64%) of 2-oxo-2-(1-methyl-3-chloropropoxy)-5-methyl-1,2-oxaphospholane (V) contaminated with phosphite (VII), bp 112-114° (0.1 mm); d_4^{20} 1.1950; n_D^{20} 1.4640. Found: C 41.27; H 7.02; P 13.18%. C₈H₁₆ClO₃P. Calculated: C 42.38;

H 7.06; P 13.68%. When 3 g of (V), contaminated with (VII), was refluxed with 0.05 g of Na in toluene we isolated the pure (V) with bp 108-109° (0.1 mm); d_4^{20} 1.1967; n_D^{20} 1.4649. Found: C 42.16; H 7.24; P 13.76%. $\delta^{31}P = -48$ ppm; b) 0.9 g of the O,O-di-(1-methyl-3-chloropropyl) ester of 3-chlorobutylphosphonic acid (VI) with bp 162° (0.25 mm); d_4^{20} 1.1928; n_D^{20} 1.4683. Found: C 40.66; H 7.13; P 8.70%. $C_{12}H_{24}Cl_3OP$. Calculated: C 40.73; H 6.80; P 8.77%. $\delta^{31}P = -30$ ppm. The 1,3-dichloroalkane that was obtained in this reaction, as well as in all of the other similar reactions, was not isolated, and instead was removed from the reaction mixture in vacuo at 10 mm. In contrast to (III), the tri-(3-chloropropyl)phosphite (VIII), obtained from 2.5 g of PCl₃ and 3.2 g of the unsubstituted oxetane, after heating (150-160°, 1 h) and distillation in the range 120-145° (0.2 mm), gave 3.5 g of a mixture that, according to the ³⁴P NMR spectrum, contains 20-30% of 2-oxo-2-(3-chloropropyl)-1,2-oxaphospholane ($\delta^{34}P = -30$ ppm). The latter product (IV) was isolated: bp 144-145° (0.18 ram); d_4^{20} 1.2941; n_D^{20} 1.4792. Found: C 34.89; H 5.80; P 9.91%. C₁₂H₁₈Cl₃O₃P. Calculated: C 34.67; H 5.77; P 9.95%.

Preparation of Di-(1-methyl-3-chloropropyl)phosphite (VII). With stirring, to 8.4 g of the acid chloride of di-(1-methyl-3-chloropropyl)phosphorous acid in 50 ml of CHCl₃ was added 0.54 g of water, after which the mixture was refluxed for 30 min and then distilled. We obtained 7.5 g (95%) of (VII) with bp 113-114° (0.2 mm); d_4^{20} 1.2098; n_D^{20} 1.4620. Found: C 36.54; H 6.51; P 11.60%. C₈H₁₇Cl₂O₃P. Calculated: C 36.50; H 6.46; P 11.″8%. $\delta^{31}P = -8$ ppm.

Reaction of Ethyl Dichlorophosphite with 2-Methyloxetane (I). With stirring, to 7 g of ethyl dichlorophosphite was added in a nitrogen stream 7 g of (I) at $\leq 30^{\circ}$. When the temperature of the reaction mixture had dropped to room temperature, 1.54 g of sulfur was added and the mixture was heated at 100-110° for 30 min. Distillation gave 10.4 g (67%) of ethyl di-(1-methyl-3-chloropropyl)thiophosphate (XI) with bp 108-110° (0.1 mm); d¹⁰₄ 1.1943; n²⁰_D 1.4778. Found: C 37.28; H 6.43; P 9.51; S 9.81%. C₁₀H₂₁Cl₂O₃PS. Calculated: C 37.15; H 6.50; P 9.60; S 9.90%. $\delta^{31}P = -68$ ppm.

Reaction of Dichloride of tert-(2,2,2, -Trichloro)butylphosphorous Acid with 2-Methyloxetane. To 11.4 g of the dichloride ($\delta^{31}P = -193$ ppm) was added 3 g of (I). The temperature of the mixture rose to 60°. Distillation gave 5.1 g of the chloride of tert-(2,2,2-trichloro)butyl-(1-methyl-3-chloropropyl)phosphorous acid (XII) with bp 112-113° (0.28 mm); d_4^{20} 1.3736; n_D^{20} 1.5013. Found: P 8.85%. $C_3H_{14}Cl_5O_2P$. Calculated: P 8.84%. tert-(2,2,2-Trichloro)butyl-di-(1-methyl-3-chloropropyl)phosphite (XIII) was obtained from 2.8 g of (XII) and 0.6 g of (I); d_4^{20} 1.3162; n_D^{20} 1.4893. Found: C 33.70; H 5.15; P 7.84%. $C_{12}H_{22}Cl_5O_3P$. Calculated: C 34.08; H 5.20; P.7.33%. $\delta^{31}P = -140$ ppm. A mixture of 3 g of (XIII) and 0.22 g of sulfur when heated at 100° for 30 min gave 1.2 g (37%) of thiophosphate (XIV), bp 134° (0.2 mm); d_4^{20} 1.3387; n_D^{20} 1.5048. Found: C 31.57; H 4.78; P 7.12; S 7.16%. $C_{12}H_{22}Cl_5O_3PS$. Calculated: C 31.68; H 4.84; P 6.82; S 7.04%. Phosphite (XIII) (from 13.8 g of the dichloride of tert-(2,2,2-trichloro)butylphosphorous acid and 7.5 g of (I)) when heated in a nitrogen stream at 140-150° for 30-50 min gave: 1) 8 g (60%) of 2-0x0-2-[tert-(2,2,2-trichloro)-butoxy]-5-methyl-1,2-oxaphospholane (XV) with bp 114-115° (0.2 mm); d_4^{20} 1.3556; n_2^{20} 1.4857. Found: C 32.66; H 4.76; P 10.23%. $C_8H_4Cl_3O_3P$. Calculated: C 32.49; H 4.73; P 10.49%. $\delta^{31}P = -42$ ppm; and 2) 4 g (20%) of phosphorite (XVI) with bp 167-168° (0.25 mm); d_4^{20} 1.3133; n_D^{20} 1.4897. Found: C 34.07; H 5.39; P 7.27%. $C_{12}H_{22}Cl_5O_3P$. Calculated: C 34.08; H 5.20; P 7.33%. $\delta^{31}P = -26$ ppm.

In contrast to (XIII), phosphite (XIX), obtained from 4.8 g of the dichloride of tert-(2,2,2-trichloro)butylphosphorous acid and 2 g of the unsubstituted oxetane, gave, after heating and distillation, 4 g of a mixture of substances, which, according to the ³¹P NMR spectrum, contains more than 70% of the acyclic phosphonate (XX), bp 138-140° (0.15 mm); d_4^{20} 1.3751; n_D^{20} 1.4891. Found: P 7.89%. $C_{10}H_{18}Cl_5O_3P$. Calculated: P 7.85%. $\delta^{31}P = -24$ ppm.

Reaction of Oxaphospholane (XV) with P_2S_5 . A mixture of 3.3 g of (XV) and 0.5 g of P_2S_5 in 50 ml of toluene was refluxed for 2 h. Distillation gave 1.2 g (34%) of 2-thio-2-[tert-(2,2,2-trichloro)butoxy]-5-methyl-1,2-oxaphospholane (XVII) with bp 140-142° (0.25 mm); d_4^{20} 1.3608; n_D^{20} 1.5280. Found: C 30.70; H 4.44; P 9.84%. $C_8H_{14}Cl_3O_2PS$. Calculated: C 30.81; H 4.49; P 9.95%.

<u>Reaction of (XV) with PCl₅</u>. A mixture of 3 g of (XV) and 2.1 g of PCl₅ in 30 ml of CHCl₃ when refluxed for 30 min gave 1.7 g of chlorophosphonate (XVIII) with bp 114° (0.2 mm); d_4^{20} 1.4180; n_D^{20} 1.4081. Found: C 27.40; H 4.24; P 8.84%. C₃H₁₄Cl₅O₂P. Calculated: C 27.39; H 3.99; P 8.84%.

Reaction of Diethyl Chlorophosphite with 2-Methyloxetane. To 6 g of diethyl chlorophosphite in a nitrogen atmosphere was slowly added 3 g of (I) at $25-30^\circ$. Then 1.2 g of sulfur was added and the mixture

was heated at 100° for 20 min. Distillation of the products gave: 1) 3.8 g (38%) of diethyl (1-methyl-3-chloropropyl)thiophosphate (XXII) with bp 75-76° (0.2 mm); d_4^{20} 1.1402; n_D^{20} 1.4660. Found: C 36.89; H 6.74; P 12.10; S 12.43%. C₈H₁₈ClO₃PS. Calculated: C 36.85; H 6.91; P 11.90; S 12.28%; and 2) 1.1 g (10%) of thiophosphate (XI) with bp 112° (0.25 mm); d_4^{20} 1.1879; n_D^{20} 1.4770. Found: C 37.39; H 6.43; P 10.04%. C₁₀H₂₁Cl₂ ·O₃PS. Calculated: C 37.15; H 6.50; P 9.60%.

Reaction of Diphenyl Chlorophosphite with (I). From 6.8 g of diphenyl chlorophosphite and 2 g of (I) was obtained 5.3 g (60% yield) of diphenyl (1-methyl-3-chloropropyl)phosphite, bp 142-144° (0.25 mm) d_4^{20} 1.1808; n_D^{20} 1.5508. Found: C 59.05; H 5.59; P 9.24%. C₁₆H₁₈ClO₃P. Calculated: C 59.16; H 5.55; P 9.55%. $\delta^{31}P = -133$ ppm.

CONCLUSIONS

The reactions of some oxetanes with phosphorous acid chlorides were studied.

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