REACTION OF OXETANES WITH PHOSPHORUS TRICHLORIDE AND ALKYLDICHLOROPHOSPHINES

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Reactions of phosphorus acid chlorides with α -oxides were investigated more thoroughly than those with β -oxides. Certain halides of pentaphosphorus acids react with oxetanes in the presence of catalytic amounts of TiCl₄ with disruption of the oxetane cycle [1]. Phosphorus trichloride readily reacts with 3,3-di (chloromethyl)oxetane [2] and 2-methyloxetane [3]. However, Shuikin and co-workers [3] did not specify how the disruption of the 2-methyloxetane cycle is directed.

We have investigated the reactions of PCl_3 and certain alkyldichlorophosphines with 3,3-dimethyloxetane and 2-methyloxetane. The reaction with 3,3-dimethyloxetane yields chlorides of γ -chloroalkyl esters of phosphorous acid (whose constants are given in Table 1) according to the scheme



It is known that PCl_3 disrupts propylene oxide at the C - O bond adjacent the methyl group [4]:

$$\underbrace{ \begin{array}{c} CH_2-CH--CH_3\\ \swarrow \end{array} }_O + \operatorname{PCl}_3 \rightarrow \operatorname{Cl}_2\operatorname{POCH}_2\operatorname{CHCH}_3\\ \downarrow\\ Cl \end{array}$$

It was of interest to find out how the disruption of the 2methyloxetane cycle is directed. The reaction between 2-methyloxetane and PCl_3 or alkyldichlorophosphines may yield two isomers (A) and (B):



$$R = Cl, CH_3O, C_2H_5O, C_3H_7O$$

When the addition product of PCl_3 and 2-methyloxetane was hydrolyzed we obtained a mixture of chlorobutanols containing (according to gas - liquid chromatography, Fig. 1) more than 90% of one of the isomers of chlorobutanol.

When this isomeric mixture was oxidized, β -chloroethyl methyl ketone was obtained in a yield exceeding 60%; dehydrochlorination of this product yielded methyl vinyl ketone (bp 80°; d₄²⁰ 0.8647; n_D²⁰ 1.4079; according to [5] bp 79° (743 mm); d₄²⁰ 0.8666; n_D²⁰ 1.4115). The same ratio of isomeric chlorobutanols was obtained during the hydrolysis of the addition products of

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Fig. 1. Chromatogram of the mixture of chlorobutanols obtained by hydrolysis of the addition product of PCl_3 and 2-methyloxetane. Cl CH₃ CH₃

TABLE 1. Constants of RPOCH2CCH2Cl

Com- pound No.	R	Bp, °C (p, mm Hg)	d_4^{20}	n_D^{20}	Found, P,%	Empirical formula	Calcula- ted, P. %	Yield, %
I II	C1 CH₃O	86,5 (10) 41-41,5	1,2867 1,1949	1,4926 1,4710	14,00 14,22	$\begin{array}{c} C_5H_{10} OPCl_3\\ C_6H_{13}O_2PCl_2 \end{array}$	13,87 14,15	82 32
III IV	$\mathrm{C_{2}H_{5}O}_{\mathrm{C_{3}H_{7}O}}$	$\begin{array}{c} (0,12) \\ 102-104 (10) \\ 113 (12) \end{array}$	1,1536 1,1253	1,4620 1,4620	$13,24 \\ 12,71$	$\mathrm{C_7H_{15}O_2PCl_2} \\ \mathrm{C_8H_{17}O_2PCl_2}$	$13,30 \\ 12,55$	31 30

C1 CH₃

TABLE 2. Constants of RPOCHCH₂CH₂Cl

Com- pound No.	R	Вр, °С (р, mm Hg)	d_4^{20}	n_{D}^{20}	Found, P,%	Empirical formula	Calcula- ted, P, %	Yield, %
V	Cl	79,5—80 (10)	1,3347	1,4951	14,76	C ₄ H ₈ OPCl ₃	14,80	79
VI	CH ₃ O	89—91 (10)	1,2316	1,4712	15,03	C ₅ H ₁₁ O ₂ PCl ₂	15,12	33
VII	C ₂ H₅O	96—98 (10)	1,1688	1,4620	14,18	C ₆ H ₁₃ O ₂ PCl ₂	14,15	36
VIII	C ₃ H ₇ O	110,5 (11)	1,1421	1,4600	13,62	C ₇ H ₁₅ O ₂ PCl ₂	13,30	31

methyldichlorophosphine and 2-methyloxetane. It follows that the reaction of PCl_3 or alkyldichlorophosphines with 2-methyloxetane yields mainly compounds of the (A) type, whose constants are given in Table 2.

Compound (VI) (cf. Table 2) was also produced by reacting (V) with methanol:

 $\begin{array}{c} \mathrm{Cl}_{2}\mathrm{POCHCH}_{2}\mathrm{CH}_{2}\mathrm{Cl} + \mathrm{CH}_{3}\mathrm{OH} \xrightarrow[(C, \, \mathrm{H}_{3})_{3}\mathrm{N}]{} \\ \mathrm{CH}_{3} \\ \mathrm{CH}_{3} \\ \end{array} \xrightarrow[(C, \, \mathrm{H}_{3})_{3}\mathrm{N}]{} \\ \begin{array}{c} \mathrm{CH}_{3}\mathrm{OPOCHCH}_{2}\mathrm{CH}$

When (VI) was heated with an equimolar quantity of sulfur, the corresponding derivative of thiophosphoric acid was obtained:

$$\begin{array}{c|c} S \\ & \parallel \\ CH_3OPOCHCH_2CH_2CI + S \rightarrow CH_3OPOCHCH_2CH_2CI \\ & \downarrow \\ Cl CH_3 \\ & Cl CH_3 \\ & Cl CH_3 \end{array}$$

EXPERIMENTAL

<u>Reactions of 3,3-Dimethyloxetane or 2-Methyloxetane with Phosphorus Trichloride or Alkyldichloro-phosphines</u>. An alkyldichlorophosphine (or PCl_3) was placed in a four-necked flask provided with a stirrer, a dropping funnel, a thermometer, and a reflux condenser. Oxetane was slowly added (with stirring and water-cooling) in an equivalent amount, or slightly less. The temperature of the reaction mixture during the addition of the oxetane was maintained at 25-40°. When the temperature dropped to 25-20°, the reaction mixture was distilled. The constants of the products (I-VIII) are given in Tables 1 and 2.

<u>Hydrolysis of the Addition Product of Phosphorus Trichloride and 2-Methyloxetane</u>. To 26 g of water and 150 ml of benzene were added 51 g of the addition product of PCl₃ and 2-methyloxetane. The mixture was heated at the boiling temperature of benzene for 8 h. Then benzene was driven off under normal pressure, and the residue was distilled at 10 mm. After the first distillation, 22.4 g of crude chlorobutanol were obtained; bp 50-53° (10 mm); n_D^{20} 1.4430. After drying over MgSO₄ and fourfold distillation, the 1chlorobutanol-3 obtained had bp 60° (10 mm); d_4^{20} 1.0825; n_D^{20} 1.4420.

<u>Oxidation of 1-Chlorobutanol-3</u>. A mixture of 17 g $K_2Cr_2O_7$, 14.1 g H_2SO_4 and 8.5 g water was added to 6.2 g of chlorobutanol dissolved in 100 ml of ether. The mixture was stirred for 10 h; then the ethereal layer was thrice extracted with ether. The ethereal extracts were dried over $CaCl_2$ and distilled. After the first distillation 4 g of β -chloroethyl methyl ketone were obtained; bp 50-51° (15 mm). The second distillation yielded 3.6 g of β -chloroethyl methyl ketone with bp 43° (13 mm); $d_4^{20} 1.0830$; $n_D^{20} 1.4326$. Found: C 45.21; H 6.76%. C₄H₇OCl. Calculated: C 45.07; H 6.57%. According to [6], bp 53° (15 mm).

Reaction of α -Methyl- γ -dichloropropyl Phosphorous Acid Dichloride with Methanol. To 13 g of α -methyl- γ -chloropropyl phosphorous acid dichloride, dissolved in 150 ml of petroleum ether and cooled to -10°, was slowly added a mixture of 2 g methanol and 6.3 g (C₂H₅)₃N dissolved in 50 ml ether. After 2 h (C₂H₅)₃N·HCl was filtered off, and the ethereal solution was distilled; 4 g of (VI) were obtained; bp 89-91° (11 mm); d₄²⁰ 1.2310; nD²⁰ 1.4710. Found: P 15.28%. C₅H₁₁O₂PCl₂. Calculated: P 15.10%.

Reaction of Methyl α -Methyl- γ -chloropropyl Phosphorous Acid Chloride (VI) with Sulfur. A mixture of 3.8 g of (VI) and 0.5 g of S was heated for 30 min at 140-160°, and 1 g of thiophosphate (IX) was obtained; bp 80-82° (0.25 mm); d₄²⁰ 1.2953; n_D²⁰ 1.5018. Found: P 12.84%. C₅H₁₁O₂PSCl₂. Calculated: P 13.08%.

Analysis of chlorobutanol was carried out on chromatograph Pye-104 with a differential flame-ionization detector, using a glass column (length 3 m, inner diam. 0.5 cm). The stationary phase consisted of fluorinated silicone oil QF-1 applied onto "gaschrom Q" (80/120 mesh). The temperature of the column was 75°. The rate flow of the gas carrier (argon) was 25 ml/min. The weight of the sample was 0.5 g.

CONCLUSIONS

Reactions of phosphorus trichloride or alkyldichlorophosphines with 3,3-dimethyloxetane or 2-methyloxetane yields (alkyl) β , β -dimethyl- γ -chloropropyl phosphorous acid (di)chlorides or (alkyl) α -methyl- γ chloropropyl phosphorous acid (di)chlorides respectively.

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