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## ON THE REACTIONS BETWEEN PHOSPHORUS PENTACHLORIDE AND LACTONES

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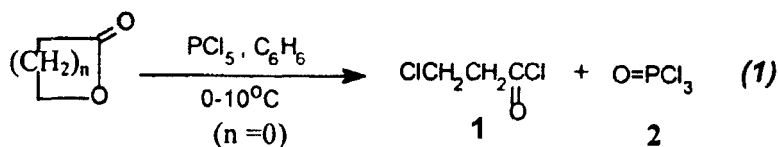
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Reactions between  $\text{PCl}_5$  and substituted or unsubstituted  $\beta$ -,  $\gamma$ - and  $\epsilon$ - lactones have been investigated. Although  $\gamma$ - butyrolactone substituted at  $\alpha$ - position with an alkyl radical has given phosphorylated products of both cyclic ethers and chlorinated carboxylic acid chlorides along with  $\gamma$ - chlorobutanoic acid chloride, halogen substituted  $\gamma$ -butyrolactone such as  $\alpha$ -bromo- $\gamma$ -butyrolactone yielded  $\alpha$ -bromo- $\gamma$ -chlorobutanoic acid chloride in similar manner with  $\beta$ -propiolactone which gives  $\beta$ -chloropropionic acid chloride. The nature of radicals present at  $\gamma$ -position also affects the reaction products. Methyl or heptyl radicals yielded different products; in the latter case phosphorylated products were not isolated. The reaction pathway of  $\epsilon$ -caprolactone with  $\text{PCl}_5$  is changed by the temperature of the reaction mixture. It reacts at 20–30°C to give  $\alpha,\alpha$ -dichlorooxepane and  $\epsilon$ -chlorohexanoic acid chloride, while a phosphorylated product was observed at 60–70°C. Possible mechanisms of these reactions are discussed.

**Keywords:** Lactones; phosphorus pentachloride; phosphonic acids; phosphonic dichlorides; chlorocarboxylic acid chlorides

It has long been known that esters react with phosphorus pentachloride to yield phosphoncarbonic acid trichloride and  $\beta$ -chloro- $\beta$ -alkoxyvinylphosphonic acid dichloride<sup>[1]</sup>. On the other hand, several papers appeared in the literature dealing with exploration of the reaction between lactones and  $\text{PCl}_5$ . Particularly, phosphorus pentachloride has been reported to react with lactones in a variety of ways depending on the size of the lactonic cycle. Thus,  $\beta$ -lactones decompose in reactions with  $\text{PCl}_5$  at even 0–10°C to give  $\beta$ -chloropropionic acid chloride 1.

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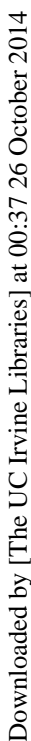
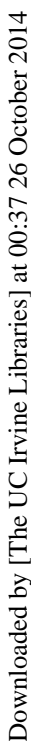
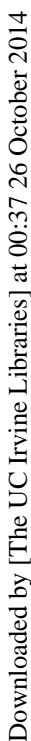
However, under these conditions,  $\gamma$ -butyrolactone ( $n=1$ ) easily reacts with  $\text{PCl}_5$  affording a reaction mixture from which several compounds, namely  $\gamma$ -chlorobutanoic acid chloride,  $\alpha,\gamma$ -dichloro- $\alpha$ -phosphonbutanoic acid trichloride and 2,3-dihydrofuryl-5-chloro-4-phosphonic acid dichloride were isolated by decomposition of the reaction complex with  $\text{SO}_2$ <sup>[2,3]</sup>. In one of the papers, where  $\alpha,\gamma$ -dichloro- $\alpha$ -phosphonbutanoic acid trichloride was not isolated individually, was stated that lactones bearing substituents at any position were not phosphorylated with  $\text{PCl}_5$  at all<sup>[3]</sup>. Our further investigation revealed this conclusion to be erroneous.

These reactions are always very rapid towards decomposition of the lactonic cycle with all  $\alpha$ -substituted  $\gamma$ -lactones, but there are some differences in terms of reaction courses. Thus, reactions of  $\text{PCl}_5$  with  $\alpha$ -alkylated  $\gamma$ -lactones appeared to proceed as with  $\gamma$ -butyrolactone, while  $\alpha$ -halogenated( $\text{Cl}, \text{Br}$ ) lactones react with  $\text{PCl}_5$  according to Eq. 1. For example, treatment of  $\alpha$ -bromo- $\gamma$ -butyrolactone with  $\text{PCl}_5$  under conditions mentioned above affords  $\alpha$ -bromo- $\gamma$ -chlorobutanoic acid chloride in 60% yield.

To the best of our knowledge, reactions of  $\gamma$ -substituted  $\gamma$ -lactones with  $\text{PCl}_5$  are not described. Therefore, considering previous experiences of others and ourselves we decided to investigate these reactions. The present paper reports the preliminary results of our study on this topic.

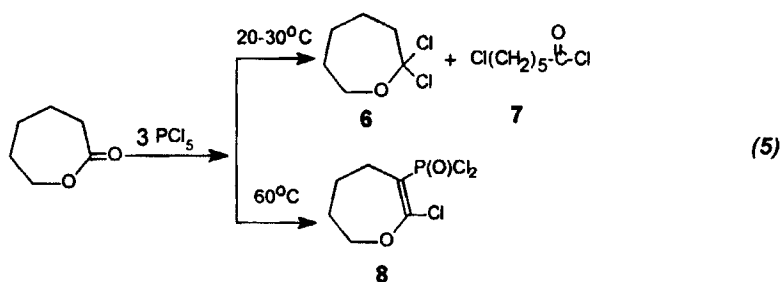
From the obtained data can be concluded that the nature of groups present at the  $\gamma$ -position plays a crucial role for the reaction products. The most interesting feature of these reactions has to be seen in the obtained products. It should be noted that the presence of a  $n$ -heptyl group completely retards the formation of phosphorylated products, while a methyl group relieves the retardation (Eqs. 2, 3).

Once the complex containing the  $\text{PCl}_4^+$  moiety had been formed, the composition of the reaction products has been found to be dependent on the nature of the radical present at the  $\gamma$ -position. The formation of both acid chlorides and phosphorylated products from the complex may be illustrated as follows (Eq. 4).



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$\alpha,\alpha$ -dichlorocyclic ethers, should have determined the reaction products. Contrary to the intermediate formed from  $\gamma$ -butyrolactone,  $\alpha,\alpha$ -dichlorooxepane is stable around 20–30°C, but is decomposed at 50–60°C by hydrogen chloride elimination to give an  $\alpha, \beta$ -unsaturated- $\alpha$ -chlorocyclic ether intermediate which reacts further with  $\text{PCl}_5$  to yield the phosphorylated product **8**.

It has to be admitted that the problem is undoubtedly very involved and conclusions drawn solely from the reaction products must be treated with reserve. Hence further work is necessary to better understand the mechanisms of these reactions. We will be involved, therefore, in this task in order to achieve the ultimate goal. Further developments concerning some details of suggested mechanism will be reported in due course.

## EXPERIMENTAL

### General Procedure for the Phosphorylation Reactions of Lactones with $\text{PCl}_5$

To the suspension of 0.3 mol  $\text{PCl}_5$  in 150 mL benzene, 0.1 mol lactone was added at 0–5°C and stirred at around 20°C for 10 hrs, and finally at 30–35°C for 10 hrs. At the end of this period, sulfur dioxide was passed through the suspension. Following the predistillation at atmospheric pressure to remove the solvent and low boiling compounds, the residue was distilled under high vacuum.

According to the general procedure, 112 g (87%) of  $\beta$ -chloropropionic acid chloride **1** was obtained from 72 g (1mol)  $\beta$ -propiolactone and 625.5 g (3 moles)  $\text{PCl}_5$ . B.p.: 130–132°C,  $d_4^{20}$ : 1.4615.

20 g  $\alpha$ -Bromo- $\gamma$ -butyrolactone and 75 g PCl<sub>5</sub> reacted in similar manner to give  $\alpha$ -bromo- $\gamma$ -chlorobutanoic acid chloride in 60% yield. B.p.: 63–66 °C (0.8 Torr);  $d_4^{20}$ : 1.6426;  $n_D^{20}$ : 1.4870. -IR(NaCl):  $\nu$  = 1810 cm<sup>-1</sup> (C=O); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, TMS int.):  $\delta$  = 2.2 ppm(m, 2H, CH<sub>2</sub>), 3.1(t, 1H, CHBr), 3.85(t, 2H, CH<sub>2</sub>Cl).

C <sub>4</sub> H <sub>5</sub> BrCl <sub>2</sub> O (219.9):	Calcd. C 21.82 Hal 68.64 %
	Found. C 21.80 Hal 68.01 %

From the reaction between 30 g  $\gamma$ -valerolactone and 187 g PCl<sub>5</sub> two products were obtained by fractional distillation. The first fraction was 21 g (50%)  $\gamma$ -chloropentanoic acid chloride **3**, b.p.: 40–43°C (1 Torr);  $d_4^{20}$ : 1.2793. The second fraction was 9 g (~15%) 2,3-dihydrofuryl-2-methyl-5-chloro-4-phosphonic acid dichloride **4**. B.p.: 102–104°C (1 Torr);  $d_4^{20}$ : 1.4778. -IR(NaCl):  $\nu$  = 1605 cm<sup>-1</sup> (C=C); 1190 (C-O), 1280 (P=O); <sup>1</sup>H-NMR(CDCl<sub>3</sub>, TMS int.):  $\delta$ =2.25 ppm (m, 2H, CH<sub>2</sub>-C=), 4.0 (m, 1H, CH), 1.25 (d, 3H, CH<sub>3</sub>).

C <sub>5</sub> H <sub>6</sub> Cl <sub>3</sub> O <sub>2</sub> P(235.5)	Calcd. C 25.48 H 2.55 P 13.16 %
	Found C 25.11 H 2.48 P 12.87 %

Under similar conditions, 50 g  $\gamma$ -*n*-heptyl- $\gamma$ -butyrolactone reacted with 115 g PCl<sub>5</sub> to give 64 g (~100%) of  $\gamma$ -chloroundecanoic acid chloride **5**. B.p.: 114–115°C (0.5 Torr),  $d_4^{20}$ : 1.0630;  $n_D^{20}$ : 1.4690.

## Reactions Between PCl<sub>5</sub> and $\epsilon$ -Caprolactone

### a. At 20–30°C

0.1 mol  $\epsilon$ -caprolactone reacted with 0.3 mol PCl<sub>5</sub> at 20–30°C to give a mixture of 6-chlorohexanoic acid chloride **7** (15–20 %) and  $\alpha$ ,  $\alpha$ -dichlorooxepane **6** (55–60%) in 76% yield, identified by IR and NMR data. B.p.: 82–84°C (1 Torr),  $d_4^{20}$ : 1.0634;  $n_D^{20}$ : 1.4161.

### b. At 40–60°C

From the reaction between 0.1 mol  $\epsilon$ -caprolactone and 0.3 mol PCl<sub>5</sub> at 40–60°C (6 hrs) were isolated the mixture (32.4%) of  $\alpha$ , $\alpha$ -dichlorooxepane **6** and 6-chlorohexanoic acid chloride **7** as the first fraction, and 2,3,4,5-tetrahydrooxepanyl-7-chloro-6-phosphonic acid dichloride **8** (51%) as the second fraction. B.p.: 122–125°C (1 Torr),  $d_4^{20}$ : 1.3276;  $n_D^{20}$ : 1.4995;

-IR(NaCl):  $\nu = 1596 \text{ cm}^{-1}$  (C=C); 1230 (P=O), 1190 (C-O);  
- $^1\text{H-NMR}(\text{CDCl}_3, \text{TMS int.}): \delta = 2.25 \text{ ppm}$  (m, 2H,  $\text{CH}_2$ ), 1.2–1.8 (m, 4H,  $(\text{CH}_2)_2$ ), 4.1 (m, 2H,  $\text{OCH}_2$ ).

$\text{C}_6\text{H}_8\text{Cl}_3\text{O}_2\text{P}$  (249.5):      Calcd C 28.85 H 3.21 P 12.42 %  
   Found C 28.53 H 3.01 P 12.12 %

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