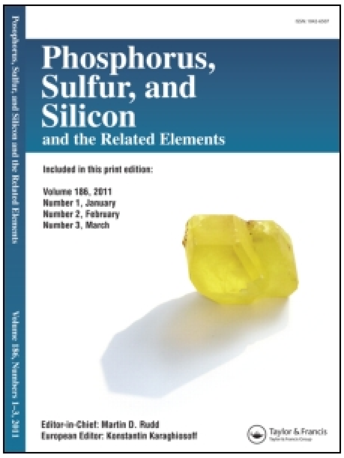

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Valeh Mehralioğlu Ismaili[a]; Adnan Aydin[b]; M. M. Kantaeva[a]
[a] Baku State University, Baku, Azerbaijan [b] Faculty of Science and Letters, Department of Chemisty, Marmara University, Istanbul, Turkey

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ON THE REACTIONS BETWEEN PHOSPHORUS PENTACHLORIDE AND LACTONES

VALEH MEHRALIOĞLU ISMAILI[a], ADNAN AYDIN[b]* and M.M. KANTAEVA[a]

[a]*Baku State University, Baku 370146 Azerbaijan and* [b]*Marmara University, Faculty of Science and Letters, Department of Chemistry, Göztepe – Istanbul, Turkey*

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Reactions between PCl_5 and substituted or unsubstituted β-, γ- and ε- lactones have been investigated. Although γ- butyrolactone substituted at α- position with an alkyl radical has given phosphorylated products of both cyclic ethers and chlorinated carboxylic acid chlorides along with γ- chlorobutanoic acid chloride, halogen substituted γ-butyrolactone such as α-bromo-γ-butyrolactone yielded α-bromo-γ-chlorobutanoic acid chloride in similar manner with β-propiolactone which gives β-chloropropionic acid chloride. The nature of radicals present at γ-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 ε-caprolactone with PCl_5 is changed by the temperature of the reaction mixture. It reacts at 20–30°C to give α,α-dichlorooxepane and ε-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 β-chloro-β-alkoxyvinylphosphonic acid dichloride[1]. On the other hand, several papers appeared in the literature dealing with exploration of the reaction between lactones and 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, β-lactones decompose in reactions with PCl_5 at even 0–10°C to give β-chloropropionic acid chloride **1**.

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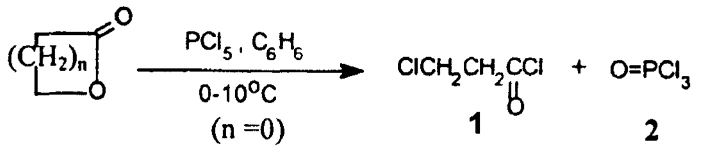
* Correspondence Author.



(1)

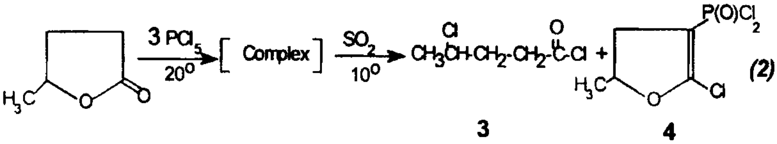
However, under these conditions, γ-butyrolactone (n=1) easily reacts with PCl_5 affording a reaction mixture from which several compounds, namely γ-chlorobutanoic acid chloride, α,γ-dichloro-α-phosphonbutanoic acid trichloride and 2,3-dihydrofuryl-5-chloro-4-phosphonic acid dichloride were isolated by decomposition of the reaction complex with SO_2[2,3]. In one of the papers, where α,γ-dichloro-α-phosphonbutanoic acid trichloride was not isolated individually, was stated that lactones bearing substituents at any position were not phosphorylated with PCl_5 at all[3]. Our further investigation revealed this conclusion to be erroneous.

These reactions are always very rapid towards decomposition of the lactonic cycle with all α-substituted γ-lactones, but there are some differences in terms of reaction courses. Thus, reactions of PCl_5 with α-alkylated γ-lactones appeared to proceed as with γ-butyrolactone, while α-halogenated(Cl,Br) lactones react with PCl_5 according to Eq. 1. For example, treatment of α-bromo-γ-butyrolactone with PCl_5 under conditions mentioned above affords α-bromo-γ-chlorobutanoic acid chloride in 60% yield.

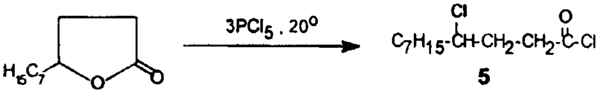
To the best of our knowledge, reactions of γ-substituted γ-lactones with PCl_5 are not described. Therefore, considering previous experiences of others and ourselves we decided to investigate these reactions. The present paper reports the preliminary results of our study on this topic.

From the obtained data can be concluded that the nature of groups present at the γ-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 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 γ-position. The formation of both acid chlorides and phosphorylated products from the complex may be illustrated as follows (Eq. 4).



(2)



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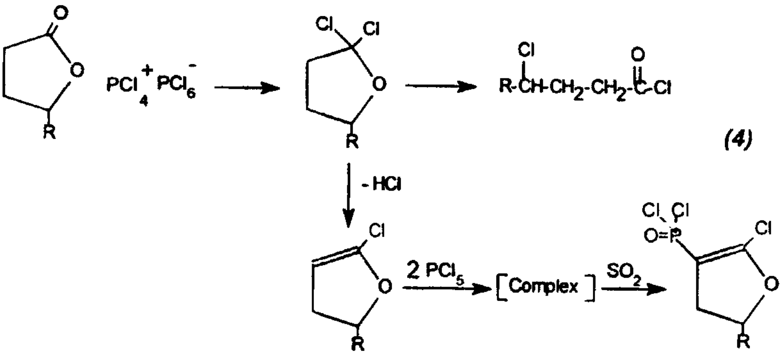
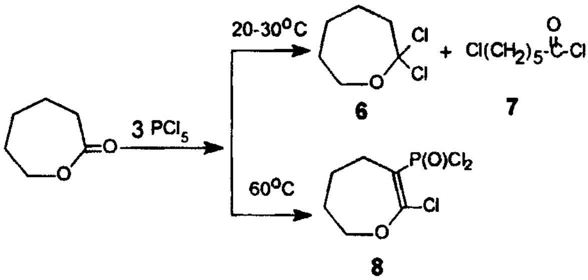


(4)

With the aim of extending this reaction to other lactones we have investigated the reactivity of PCl_5 in relation to ε-caprolactone under the reaction conditions employed. The reaction course has yielded various products depending on the temperature. The behaviour of ε-caprolactone differed from γ-butyrolactone or γ-valerolactone. When the reaction has been performed at 20–30°C ε-caprolactone has yielded α,α-dichlorooxepane **6** and ε-chlorohexanoic acid chloride **7** without the formation of the phosphorylated products. Phosphorylated product, namely 2,3,4,5-tetrahydrooxepanyl-7-chloro-6-phosphonic acid dichloride **8**, has been obtained only when the reaction has been run at 60°C.

We shall find it interesting to consider the reason for the difference in products. But it turned out not to be so simple a problem as it seems. It is reasonable to assume that thermal stabilities of the intermediates, namely



(5)

α,α-dichlorocyclic ethers, should have determined the reaction products. Contrary to the intermediate formed from γ-butyrolactone, α,α-dichlorooxepane is stable around 20–30°C, but is decomposed at 50–60°C by hydrogen chloride elimination to give an α, β-unsaturated-α-chlorocyclic ether intermediate which reacts further with 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 PCl_5

To the suspension of 0.3 mol 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 β-chloropropionic acid chloride **1** was obtained from 72 g (1mol) β-propiolactone and 625.5 g (3 moles) PCl_5.B.p.: 130–132°C, d^{20}_4: 1.4615.

20 g α-Bromo-γ -butyrolactone and 75 g PCl_5 reacted in similar manner to give α-bromo-γ-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): $\nu = 1810\ cm^{-1}$ (C=O); -^1H-NMR ($CDCl_3$, TMS int.): $\delta = 2.2$ ppm(m, 2H, CH_2), 3.1(t, 1H, CHBr), 3.85(t, 2H, CH_2Cl).

$C_4H_5BrCl_2O$ (219.9):	Calcd. C 21.82 Hal 68.64 %
	Found. C 21.80 Hal 68.01 %

From the reaction between 30 g γ-valerolactone and 187 g PCl_5 two products were obtained by fractional distillation. The first fraction was 21 g (50%) γ-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): $\nu = 1605\ cm^{-1}$ (C=C); 1190 (C-O), 1280 (P=O); -^1H-NMR($CDCl_3$, TMS int.): δ=2.25 ppm (m, 2H, CH_2-C=), 4.0 (m, 1H, CH), 1.25 (d, 3H, CH_3).

$C_5H_6Cl_3O_2P$(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 γ-*n*-heptyl-γ-butyrolactone reacted with 115 g PCl_5 to give 64 g (~100%) of γ-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_5 and ε-Caprolactone

a. At 20–30°C

0.1 mol ε-caprolactone reacted with 0.3 mol PCl_5 at 20–30°C to give a mixture of 6-chlorohexanoic acid chloride **7** (15–20 %) and α, α-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 ε-caprolactone and 0.3 mol PCl_5 at 40–60°C (6 hrs) were isolated the mixture (32.4%) of α,α-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): $\nu = 1596$ cm^{-1} (C=C); 1230 (P=O), 1190 (C-O); -^{1}H-NMR($CDCl_3$, TMS int.): $\delta = 2.25$ ppm (m, 2H, CH_2), 1.2–1.8 (m, 4H, $(CH_2)_2$), 4.1 (m, 2H, OCH_2).

$C_6H_8Cl_3O_2P$ (249.5):	Calcd C 28.85 H 3.21 P 12.42 %
	Found C 28.53 H 3.01 P 12.12 %

Acknowledgements

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