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The Reaction of β-Lactones with Acid Chlorides Catalyzed by Aluminum Chloride[1]

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Aluminum chloride-catalyzed reactions of β-lactones with acid chlorides were studied. 3-Propanolide and 3-methyl- and 2-methyl-3-propanolide all undergo predominantly the O-alkyl bond fission to give mixed anhydrides of β-chloropropionic acid. The reaction was postulated to proceed *via* dichloraluminum β-chloropropionate.

3-Propanocide(I) is well known to be cleaved through either the alkyl-oxygen bond or the acyl-oxygen bond in reactions with various reagents.

The reactions of I with acid chlorides in the presence of sulfuric acid[2] or hydrogen chloride[3] have been shown to involve exclusively the fission of the O-acyl bond of I to give β-acyloxypropionyl chlorides (Path A).

On the other hand, it has been reported that I is

TABLE 1. THE REACTIONS OF β-LACTONES WITH ACID CHLORIDES

β-Lactone (mol)	Acid chloride (mol)		Mol of $AlCl_3$	Product (Yield, mol)		
I(1.0)	AcCl	(1.0)	0.022	Acetic anhydride	(0.08)	
				$AcOCOCH_2CH_2Cl$	(0.20)	a)
				$AcOCH_2CH_2COOCOCH_2CH_2Cl$	(0.08)	
				$(ClCH_2CH_2CO)_2O$	(0.11)	
I(1.0)	$AcOCH_2CH_2COCl$	(1.0)	0.022	$AcOCH_2CH_2COOCOCH_2CH_2Cl$	(0.87)	
I(0.25)	$ClCH_2CH_2COCl$	(0.25)	0.0056	$(ClCH_2CH_2CO)_2O$	(0.19)	
I(0.5)	$(CH_2COCl)_2$	(0.5)	0.022	Succinic anhydride	(0.45)	
				$(ClCH_2CH_2CO)_2O$	(0.06)	
				$ClCH_2CH_2COCl$	(0.31)	
I(1.0)	$(CH_2COCl)_2$	(0.5)	0.022	Succinic anhydride	(0.44)	
				$(ClCH_2CH_2CO)_2O$	(0.29)	
				$ClCH_2CH_2COCl$	(0.12)	
I(0.5)	$C_6H_4(COCl)_2$	(0.5)	0.022	Phthalic anhydride	(0.43)	
				$(ClCH_2CH_2CO)_2O$	(0.07)	
				$ClCH_2CH_2COCl$	(0.31)	
I(1.0)	$C_6H_4(COCl)_2$	(0.5)	0.022	Phthalic anhydride	(0.39)	
				$(ClCH_2CH_2CO)_2O$	(0.41)	
				$ClCH_2CH_2COCl$	(0.05)	
II(0.25)	AcCl	(0.25)	0.0056	Acetic anhydride	(0.051)	
				$AcOCOCH(CH_3)CH_2Cl$	(0.010)	a)
				$AcOCH_2CH(CH_3)COOCOCH(CH_3)CH_2Cl$	(0.039)	
				$(ClCH_2CH(CH_3)CO)_2O$	(0.034)	
III(0.15)	AcCl	(0.15)	0.0034	Acetic anhydride	(0.002)	
				$AcOCOCH_2CH(CH_3)Cl$	(0.008)	a)
				$AcOCH(CH)_3CH_2COOCOCH_2CH(CH_3)Cl$	(0.016)	
				$(ClCH(CH_3)CH_2CO)_2O$	(0.020)	

a) These products were obtained as a mixture, and their yields are shown in calculated values from the amounts of the component acids.

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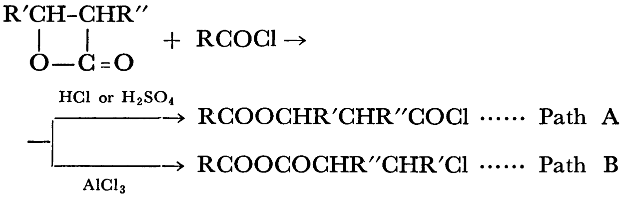
[1] Partly presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

[2] T. L. Gresham, J. E. Jansen and F. W. Shaver, *J. Amer. Chem. Soc.*, **72**, 72 (1950).

[3] T. Nakabayashi, T. Matsumoto, and Y. Tanaka, *Kogyo Kagaku Zasshi*, **69**, 1245 (1966).

subjected to the O-alkyl bond fission, along with the O-acyl bond fission, in the aluminum chloride-catalyzed reaction with benzene to give β-phenylpropionic acid, 1-hydroindone, β-hydroxypropiophenone, and phenyl vinyl ketone respectively.[4]

The present paper will report that β-lactones undergo predominantly the O-alkyl bond fission in the aluminum chloride-catalyzed reaction with acid chlorides to afford mixed anhydrides of β-chloropropionic acids (Path B).



Results and Discussion

The reactions were carried out without any solvent.[5] To an acid chloride containing aluminum chloride as a catalyzer, β-lactone was added at near 0 °C. After the removal of the insoluble and the low-boiling products from the reaction mixture, the high-boiling acid anhydrides were obtained by means of molecular distillation. During distillation, disproportionation should take place; therefore, the resulting anhydrides were contaminated with the disproportionation products.

Acetic anhydride did not react with I under these reaction conditions. The results are summarized in Table 1.

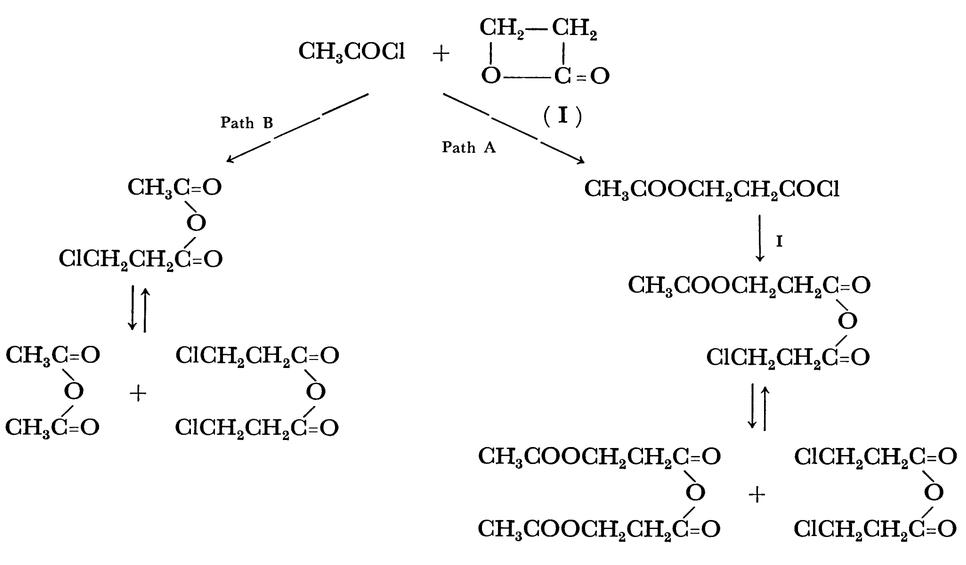
The molecular distillate of the product obtained by the reaction of acetyl chloride with I exhibited strong characteristic absorptions of acid anhydride, along with weak ones of ester, in its IR spectrum. The component acids of this fraction were determined by means of glc as methyl esters, which were derived by hydrolysis or methanolysis of the product, followed by treatment with diazomethane. The NMR analysis was also applied; its values were in fair agreement with the glc data (Table 2).

TABLE 2. THE MOLAR RATIO OF THE ACID COMPONENTS OF THE ACID ANHYDRIDES OBTAINED BY THE REACTION OF ACETYL CHLORIDE WITH I

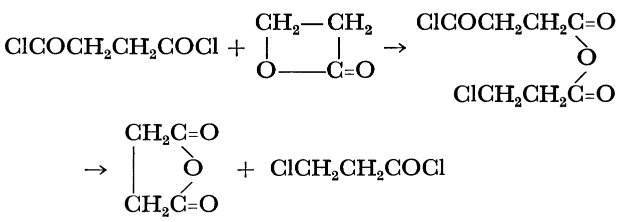
Method of analysis	$ClCH_2CH_2COOH$	$AcOCH_2CH_2COOH$	AcOH
1 a)	1.0	0.18	0.44
2 b)	1.0	0.18	0.47
3 c)	1.0	0.18	0.56

a) NMR. b) Methanolysis followed by treatment with CH_2N_2, glc. c) Hydrolysis followed by treatment with CH_2N_2, glc.

It follows from this that the acid anhydrides produced by the reaction are acetic β-chloropropionic anhydride, β-acetoxypropionic β-chloropropionic anhydride, and their disproportionation products. The reaction route can be illustrated as follows:



The reaction of I with succinyl chloride gave β-chloropropionyl chloride, β-chloropropionic anhydride, and succinic anhydride, which was precipitated from the reaction mixture in the course of the reaction. β-Chloropropionic β-chlorocarbonylpropionic anhydride should be the intermediate of the reaction, which gave succinic anhydride and β-chloropropionyl chloride through a chloride-anhydride exchange reaction:



The reaction of phthaloyl chloride with I proceeded in a similar manner. β-Chloropropionyl chloride afforded β-chloropropionic anhydride in a good yield.

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4) K. Nagakubo, Y. Iwakura, M. Takei, and T. Okada, *Nippon Kagaku Zasshi*, **78**, 1209 (1957).

5) Use of a solvent such as carbon disulfide or nitrobenzene did not change or improve the reaction, and gave the same result as in the absence of a solvent.

The component acids of the molecular distillate obtained by the reaction of β-acetoxypropionyl chloride with I were β-acetoxypropionic and β-chloropropionic acid in a rough ratio of 1 : 1.

Although the crude products obtained by the reactions of succinyl, phthaloyl, and β-chloropropionyl chloride also showed weak absorptions which may be assigned to an ester group in the IR spectra, almost no detectable amounts of products of the O-acyl bond fission of I were observed in any molecular distillate; this may be because such a constituent containing a β-acyloxypropionyl group is hardly distillable under these operating conditions.

The reactions of propionyl, butyryl, and isobutyryl chloride with I proceeded in a manner similar to that of acetyl chloride; no significant difference between them was noticed except for the fact that isobutyryl chloride was somewhat less reactive, probably on account of its steric factor.

2-Methyl-3-propanolide(II) reacted with acetyl chloride in analogy with I. The molar ratio of the acid components of the distilled anhydrides is given in Table 3.

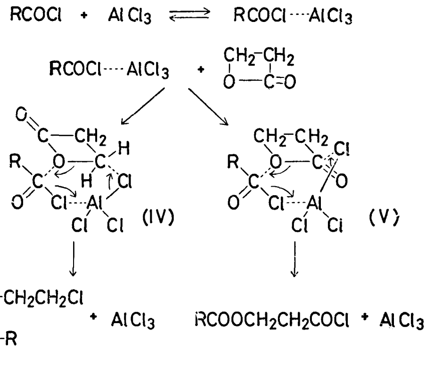
TABLE 3. THE MOLAR RATIOS OF THE ACID COPONENTS OF THE ACID ANHYDRIDES OBTAINED BY THE REACTION OF ACETYL CHLORIDE WITH II AND WITH III

β-Lactone	Component acid	Molar ratio[a]
II	$ClCH_2CH(CH_3)COOH$	1.0
	$AcOCH_2CH(CH_3)COOH$	0.25
	AcOH	0.091
III	$ClCH(CH_3)CH_2COOH$	1.0
	$AcOCH(CH_3)CH_2COOH$	0.22
	AcOH	0.15

a) Determined by means of NMR.

3-Methyl-3-propanolide(III) was fairly less reactive and hardly reacted at all near 0 °C. III was ultimately allowed to react with acetyl chloride at 11—15 °C to give a mixture of mixed anhydrides (Table 3).

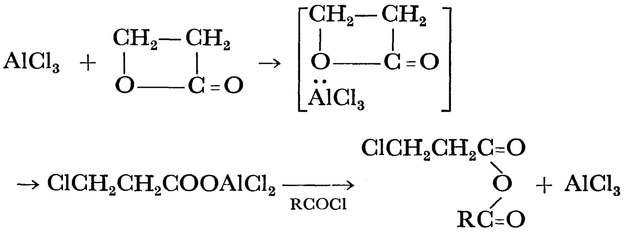
A mechanism of the reaction of I with acid chloride catalyzed by aluminum chloride may be postulated to be as follows (Scheme 1):



Scheme 1.

The preference of Reaction Path B to Path A can be attributed to the greater stability of the (IV) cyclic transition state, chiefly because of the lack of dipole-dipole interaction between the carbonyl oxygen of the lactone and the chlorine moieties of aluminum chloride, than that of the (V) cyclic transition state. The lower reactivity of 3-methyl-3-propanolide can be explained by the steric effect of the methyl group at the 3-position.

An alternate mechanism for the formation of anhydride can be given by assuming the formation of aluminum salt of β-chloropropionic acid as an intermediate (Scheme 2):



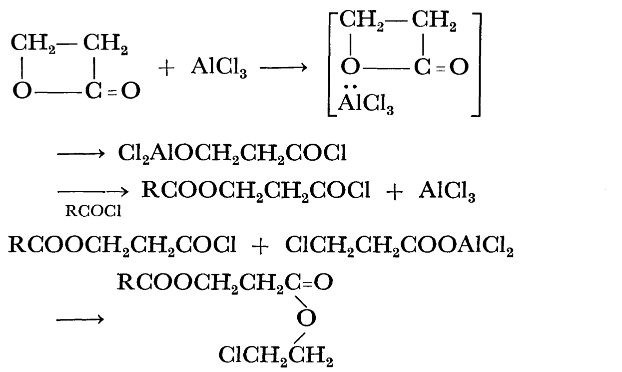
Scheme 2

When I was allowed to react with aluminum chloride (molar ratio, 1.3 : 1.0) in nitrobenzene, there was obtained a yellow homogeneous solution, in the IR spectrum of which the characteristic absorptions of β-lactone had almost disappeared. From this nitrobenzene solution, β-chloropropionic acid, along with a small amount of β-hydroxypropionic acid, could be obtained in an almost quantitative yield.[6] Using the above nitrobenzene solution as a catalyzer instead of aluminum chloride, the same results were obtained in the reaction of I with acid chloride.

In addition, a slight rise in the temperature observed at the beginning of the addition of I to acid chloride containing aluminum chloride (see Experimental section) may be attributable to the exothermic reaction of I with aluminum chloride to form dichloraluminum β-chloropropionate.[7]

The lower reactivity of 3-methyl-3-propanolide may be due to the steric influence of the 3-methyl group on the substitution at the 3-position of the lactone by a chlorine of aluminum chloride.

Although the first mechanism can not be rejected completely, in view of these experimental results the second mechanism is more reasonable, and the formation of the β-acyloxypropionyl group can be explained as follows:



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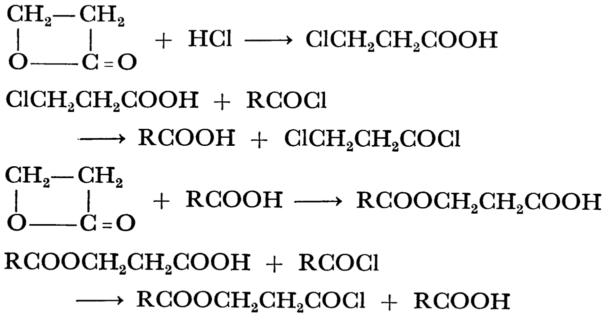
[6] Nagakubo and co-workers[4] obtained β-chloropropionic acid as a by-product in the aluminum chloride-catalyzed reaction of β-propiolactone with benzene.

[7] Dichloraluminum β-chloropropionate may be formed by a concerted reaction between β-lactone and aluminum chloride. The possibility of a four-membered cyclic transition state involving β-lactone has been suggested in literature; see J. Koketsu, S. Kojima, and Y. Ishii, This Bulletin, **43**, 3232 (1970).

An additional route for the O-acyl bond fission of β-lactones is possible, in which the fission is catalyzed by hydrogen chloride[2] present in aluminum chloride or acid chloride as an impurity:



$$\begin{array}{l}CH_2-CH_2\\ |\qquad\ |\\ O\text{——}C{=}O\end{array} + HCl \longrightarrow ClCH_2CH_2COOH$$

$$ClCH_2CH_2COOH + RCOCl \longrightarrow RCOOH + ClCH_2CH_2COCl$$

$$\begin{array}{l}CH_2-CH_2\\ |\qquad\ |\\ O\text{——}C{=}O\end{array} + RCOOH \longrightarrow RCOOCH_2CH_2COOH$$

$$RCOOCH_2CH_2COOH + RCOCl \longrightarrow RCOOCH_2CH_2COCl + RCOOH$$

In the reaction of 3,3-dimethyl-3-propanolide with acetyl chloride, the evolution of isobutene and carbon dioxide was observed, even near 0 °C.[8] From the resulting reaction mixture, most of the acetyl chloride was recovered; there was also obtained an undistillable viscous oil which exhibited the characteristic absorptions of ester in its IR spectrum. Because of the great stability of a tertiary carbonium ion, in this case the alkyl-oxygen bond of the lactone should be cleaved with ease by the action of aluminum chloride to give a carbonium ionic intermediate, which may decompose to isobutene and carbon dioxide, and which may competitively attack another molecule of the lactone to result in the formation of a polyester.

Experimental

General. The reactions of β-lactones with acid chlorides were conducted at 0—2 °C for 20 hr, unless otherwise noted. For the glc determination, a Shimadzu Gas Chromatograph Model GC-2C was employed. The IR spectra were measured with a JASCO DS-301 spectrometer. The NMR spectra were recorded at 100 MHz with a JEOL JNH-4H-100 spectrometer in carbon tetrachloride, with tetramethylsilane as an internal standard.

Materials. 3-Propanolide(I) provided by the Daicel Co., Ltd., was dried with calcium hydride and distilled; bp 54 °C/11 mmHg. 2-Methyl-3-propanolide (II, bp 41 °C/3 mmHg),[9] 3,3-dimethyl-3-propanolide (bp 40 °C/5 mmHg),[10] β-acetoxypropionyl chloride (bp 62—64 °C/5 mmHg),[2] and β-chloropropionyl chloride (bp 57—58 °C/30 mmHg)[2] were prepared according to the literature. 3-Methyl-3-propanolide-(III) from acetaldehyde and ketene; bp 41—43 °C/8 mmHg. The aluminium chloride used was purified by sublimation.

Reaction of I with Acetyl Chloride. To a solution of 78.5 g (1.0 mol) of acetyl chloride and 3 g (0.022 mol) of aluminum chloride cooled in an ice bath was added 72.0 g (1.0 mol) of I under stirring over a period of 1.5 hr. A slight temperature rise(∼5 °C) was observed at the beginning of the addition, but after that the temperature remained constant at 1—2 °C. The reaction mixture was kept at this temperature for 18.5 hr; then it was submitted to vacuum distillation (∼0.1 mmHg, ∼60 °C) to give 24 g of a mixture of acetic anhydride and unaltered acetyl chloride. The residual liquid was distilled two times at 60—100 °C/1—3×10^{-3} mmHg, using a molecular still, to yield 72 g of a colorless liquid; this liquid showed the characteristic absorptions of acid anhydride at 1821, 1750, and 1065 cm^{-1} and those of acetate at 1367 and 1235 cm^{-1}. No absorption at 1790 cm^{-1} to be assigned to acid chloride was observed.

NMR(δ, ppm): 4.28(t, $AcOC\underline{H}_2CH_2C{=}O$), 3.75 (t, $ClC\underline{H}_2CH_2C{=}O$), 2.95(t, $ClCH_2C\underline{H}_2C{=}O$), 2.79(t, $AcOCH_2$-$C\underline{H}_2C{=}O$), 2.21 (s, $C\underline{H}_3COOC{=}O$), 2.00(s, $C\underline{H}_3COOCH_2$-$CH_2C{=}O$). A mixture of acetyl chloride, acetic anhydride, and a small amount of acetic acid was also collected in a cold trap; the total amounts of acetic anhydride and the recovered acetyl chloride were determined by means of glc (2.25-meter silicone grease DC 550 column, 110 °C; anisole as an internal standard) to be 8.6 and 19.5 g respectively.

An aliquot of the high-boiling product was hydrolyzed and titrated with a sodium hydroxide solution and then a silver nitrate solution. Acid: 11.5×10^{-3} mol/g sample, reactive chlorine(–COCl): 1.66×10^{-4} mol/g sample.

A portion of the product was allowed to react with methanol in a sealed tube at 100 °C for 30 min, and then treated with diazomethane. The resulting methyl esters in methanol were detected by means of glc using a 2.25-meter polyethylene glycol-6000 column at 50 °C, with *n*-propanol as an internal standard, and using a 2.25-meter DEGS column at 110 °C, with acetophenone as an internal standard. Methyl acetate, 3.90×10^{-3}; methyl β-chloropropionate, 5.99×10^{-3}; methyl β-hydropropionate, 1.08×10^{-3} mol/g sample. Assuming that the molecular distillate contains only acetic β-chloropropionic, β-chloropropionic β-acetoxypropionic, and β-chloropropionic anhydride, the yields of these anhydrides were calculated to be 0.20, 0.078, and 0.11 mol respectively.

A 20-g portion of the moelcular distillate was hydrolyzed with 20 ml of water at room temperature. The resulting aqueous solution was saturated with sodium chloride and extracted continuously with ether for 24 hr; the ether extract was then concentrated by fractionally distilling-off the solvent, and then treated with an etherial solution of diazomethane. Methyl acetate (5.14 g, 0.0715 mol), methyl β-chloropropionate (15.6 g, 0.127 mol), and methyl β-acetoxypropionate (3.25 g, 0.0223 mol) were determined by means of glc using a 2.25-meter polyethylene glycol-6000 column at 50 °C, with *n*-propanol as an internal standard, and a 2.25-meter DEGS column at 120 °C, with acetophenone as an internal standard, respectively.

Reaction of β-Acetoxypropionyl Chloride with I. I (72.0 g, 1.0 mol) was allowed to react with β-acetoxypropionyl chloride (150.5 g, 1.0 mol) in a similar manner. The yield of the molecular distillate was 192 g. IR: 1820, 1750(sh), 1050, 1740, 1368, 1240 cm^{-1}. NMR: 4.28(t), 3.73(t), 2.95(t), 2.79(t), 2.00(s). Molar ratio of $ClCH_2CH_2C{=}O$: $AcOCH_2CH_2C{=}O$ by the NMR analysis was 1.0 : 0.98.

A portion of the distillate was treated with methanol (10 hr, room temp.) and then with diazomethane to give methyl chloropropionate and methyl β-acetoxypropionate in 90.5% and 74.1% yields (based on β-chloropropionic β-acetoxypropionic anhydride) respectively.

The methanolysis of the distillate at 100 °C in a sealed tube, followed by treatment with diazomethane, afforded methyl acetate (3.89×10^{-3} mol/g sample), methyl β-chloropropionate (3.81×10^{-3} mol/g sample), and methyl β-hydroxypropionate (3.82×10^{-3} mol/g sample).

Reaction of β-chloropropionyl Chloride with I. I (18.0 g) 0.25 mol) was allowed to react with β-chloropropionyl chloride (38.8 g, 0.25 mol) in a similar manner. Unaltered acid

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8) In water at room temperature, 3,3-dimethyl-3-propanolide decomposes rapidly to carbon dioxide and isotubene to the near exclusion of hydrolysis.[10]

9) Y. Yamashita, Y. Ishikawa, T. Tsuda, and T. Miura, *Kogyo Kagaku Zasshi*, **66**, 104 (1963).

10) T. L. Gresham, J. E. Jansen, F. W. Shaver, and W. L. Beears, *J. Amer. Chem. Soc.*, **76**, 486 (1954).

chloride (4.6 g) was thus recovered. The yield of the molecular distillate was 38.5 g, n_D^{20}: 1.4662. IR: 1820, 1750, 1050 cm^{-1}. NMR: 3.73(t, 2H), 2.95(t, 2H).

A mixture of 1.99 g (0.01 mol as pure β-chloropropionic anhydride) of the distillate and 40-ml portions of ethanol and benzene was refluxed for 1 hr, and then the bulk of solvent was removed by means of fractional distillation. From the residual liquid, 2.70 g(0.0198 mol) of ethyl β-chloropropionate was detected by means of glc using a 2.25-meter DEGS column at 120 °C, with acetophenone as an internal standard.

Reaction of Succinyl Chloride with I. The reaction was started at 10 °C to avoid the crystallization of succinyl chloride and then gradually brought to 0—2 °C. Succinic anhydride was precipitated from the reaction mixture. After the removal of the succinic anhydride (mp 115—117 °C) by filtration, followed by washing with ether, the residual liquid distilled to give β-chloropropionyl chloride (n_D^{20}: 1.4566, bp 58—59 °C/32 mmHg; anilide, mp 118—119 °C) and β-chloropropionic anhydride (n_D^{20}: 1.4666, bp 78 °C/0.02 mmHg).

Reaction of Phthaloyl Chloride with I. The reaction proceeded in the same way as above. The phthalic anhydride obtained was contaminated with a small amount of phthalyl chloride.

Reactions of Propionyl, Butyryl, and Isobutyryl Chloride with I. These reactions were conducted in a manner similar to that of acetyl chloride. The molar ratios of the acid components of the molecular distillates, determined by means of NMR, are as follows:

RCOCl	$\mathrm{ClCH_2CH_2}$-COOH	$\mathrm{RCOOCH_2}$-$\mathrm{CH_2COOH}$	RCOOH
$\mathrm{CH_3CH_2COCl}$	1.0	0.20	0.70
$\mathrm{CH_3CH_2CH_2COCl}$	1.0	0.19	0.73
$\mathrm{(CH_3)_2CHCOCl}$	1.0	0.20	0.51

Reaction of II with Acetyl Chloride. The reaction was conducted in a manner similar to that used for I. From 21.8 g (0.25 mol) of II and 19.6 g (0.25 mol) of acetyl chloride, 22.4 g of a molecular distillate was obtained. IR: 1825, 1750, 1240, 1040 cm^{-1}. NMR: 4.18(approx. d, $\mathrm{AcOC\underline{H}_2\text{-}CH(CH_3)C{=}O}$), 3.68(octet, $\mathrm{ClC\underline{H}_2CH(CH_3)C{=}O}$), 2.6—3.2 (m, $\mathrm{ClCH_2C\underline{H}(CH_3)C{=}O}$, $\mathrm{AcOCH_2C\underline{H}(CH_3)C{=}O}$), 2.23(s, $\mathrm{C\underline{H}_3COOC{=}O}$), 2.01 (s, $\mathrm{C\underline{H}_3COOCH_2CH(CH_3)C{=}O}$), 1.35 (d, $\mathrm{ClCH_2CH(C\underline{H}_3)C{=}O}$), 1.27(d, $\mathrm{AcOCH_2CH(C\underline{H}_3)C{=}O}$). Glc analysis (as methyl ester; columns: 2.25-meter polyethylene glycol-6000 column at 50 °C and 2.25-meter DEGS column at 110 °C; internal standards: *n*-propanol and acetophenone): Methyl acetate, 0.44×10^{-3}; methyl β-chloroisobutyrate, 5.22×10^{-3}; methyl β-acetoxyisobutyrate, 1.73×10^{-3} mol/g sample.

Reaction of III with Acetyl Chloride. III was almost unreactive near 0 °C. At 11—15 °C for 10 days, 12.9 g (0.15 mol) of III was allowed to react with 11.8 g (0.15 mol) of acetyl chloride to give 0.2 g of acetic anhydride, 4.7 g of unaltered acetyl chloride, 1.0 g of unaltered III, and 15.0 g of a high-boiling oil. The yield of the moelcular distillate was 10.6 g. IR: 1825, 1745, 1365, 1240, 1050 cm^{-1}. NMR: 5.18(m, $\mathrm{AcOC\underline{H}(CH_3)CH_2C{=}O}$), 4.36(m, $\mathrm{ClC\underline{H}\text{-}(CH_3)CH_2C{=}O}$), 2.90(approx. d, $\mathrm{ClCH(CH_3)C\underline{H}_2C{=}O}$), 2.70 (m, $\mathrm{AcOCH(CH_3)C\underline{H}_2C{=}O}$), 2.24(s, $\mathrm{C\underline{H}_3COOC{=}O}$), 2.02 (s, $\mathrm{C\underline{H}_3COOCH(CH_3)CH_2C{=}O}$), 1.64(d, $\mathrm{ClCH(C\underline{H}_3)CH_2C{=}O}$), 1.36(d, $\mathrm{AcOCH(C\underline{H}_3)CH_2C{=}O}$). Glc analysis (as methyl ester; columns: 2.25-meter polyethylene glycol-6000 column at 50 °C and 2.25-meter DEGS column at 110 °C; internal standards: *n*-propanol and acetophenone): Methyl acetate, 0.82×10^{-3}; methyl β-chlorobutyrate, 6.2×10^{-3}; methyl β-acetoxybutyrate, 1.5×10^{-3} mol/g sample.

Reaction of 3,3-Dimethyl-3-propanolide with Acetyl Chloride. The lactone (50.1 g, 0.5 mol) was allowed to react with acetyl chloride (39.3 g, 0.5 mol) containing aluminum chloride (1.5 g, 0.011 mol). In the course of the reaction, 4.8 g of isobutene was condensed in a cold trap. Most of the acetyl chloride used was recovered, and 45.0 g of a viscous, undistillable product was obtained; this product showed the characteristic absorptions of ester in the IR spectrum.

Reaction of I with Aluminum Chloride. To a solution of 1.5 g (0.011 mol) of aluminium chloride and 20 ml of nitrobenzene, was added 1.0 g (0.014 mol) of I in 5 ml of nitrobenzene at 0—2 °C with external cooling. After stirring for 1 hr (including the addition period) at this temperature, the IR spectrum of the reaction mixture was taken; it showed that most of the I had already been consumed. The reaction mixture was then hydrolyzed and extracted with ether, and the ether extract was reextracted with an aqueous sodium hydroxide solution. The aqueous solution was acidified and then extracted with ether continuously for 30 hr to give 1.1 g (92%) of β-chloropropionic acid and 0.07 g (7%) of β-hydroxypropionic acid (determined as methyl ester by means of glc using a 2.25-meter DEGS column at 110 °C, with acetophenone as an internal standard).