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The Synthesis of Novel α, ω-Oxaalkanedioic Acids with Long Methylene Chain Units

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α, ω-Oxaalkanedioic acids with the general formula $HOOC(CH_2)_mO(CH_2)_nCOOH$ ($m, n=$ 3—10, but in unsymmetric structures $m=3$ or 4) were synthesized. The symmetric acids were prepared by the catalytic dehydration of ω-hydroxyalkanoic acids or by the condensation of ω-chloroalkanoic acids in the presence of alkali hydroxide. The unsymmetric acids ($m=3$ or 4) were prepared by the reaction of γ-butyrolactone or δ-valerolactone with alkali alcoholates of ω-hydroxyalkanoic acids. The reaction mechanisms were also discussed. In the plots of the melting points of the two unsymmetric series ($m=3$, 4 in m/n) against the carbon atoms in a molecule, the minimum melting points are found at 3/5 and 4/5 respectively.

The synthesis of some α, ω-oxaalkanedioic acids with a formula $O[(CH_2)_nCOOH]_2$ ($n=$ 2—5) has been reported hitherto.

Alexander and Schniepp[1] prepared 6-oxaundecanedioic acid from bis(4-chlorobutyl)ether through its biscyano derivative. 7-Oxatridecanedioic acid was also derived from bis(4-bromobutyl)-ether by malonic ester synthesis.[2] Reppe et al.[3] prepared 5-oxaazelaic acid by treating γ-butyrolactone with alkali hydroxide at temperatures above 200°C.[4-6] The conversion of β-propiolactone to 4-oxapimelic acid proceeds easily in the presence of water at about 100°C.[7,8]

In the present work, the authors will report on the synthesis of α, ω-oxaalkanedioic acids with the general formula of $HOOC(CH_2)_mO(CH_2)_n COOH$, in which m and n are integers from 3 to 10 respectively, although m is 3 or 4 in unsymmetric structures. In the synthesis of the above α, ω-oxaalkanedioic acids, the ω-carboxyalkyl groups of C_4 and C_5 are derived from γ-butyrolactone and δ-valerolactone as raw materials in each case. The reaction between γ-butyrolactone and alkali alcoholates to form γ-carboxypropyl derivatives was precisely investigated by Reppe et al.[3] The reaction is considered to proceed through alkyl-fission in the γ-butyrolactone ring. On the other hand, the reactivities of δ-valerolactone have been little studied.

The synthesis and the polymerization of δ-valerolactone were reported on in previous papers.[9,10] During the course of the investigation of the reactivities of δ-valerolactone in comparison with those of γ-butyrolactone, it was found that δ-valerolactone reacts with alkali alcoholates in the same manner as γ-butyrolactone to afford δ-carboxybutyl derivatives.

For example, a mixture of sodium phenolate and δ-valerolactone gives δ-phenoxyvaleric acid in a good yield.[11] The preparation of 6-oxaundecanedioic acid from δ-valerolactone was carried out by three different methods, in which the formation of the ether linkage was effected through the following processes: 1) the dehydration of alkali δ-hydroxyvalerate in the presence of alumina as the catalyst, 2) the reaction between δ-valerolactone and the alkali alcoholate of sodium δ-hydroxyvalerate, and 3) the reaction of δ-valerolactone with sodium carbonate. By the second type of reaction, unsymmetric 5-oxasebacic acid was also found to be produced by the reaction between γ-butyrolactone and the sodium alcoholate of sodium δ-hydroxyvalerate, which had been prepared by heating a mixture of δ-valerolactone and two times as many moles of sodium hydroxide under reduced pressure. The reactions of the first two types were investigated using various lactones, ω-hydroxyalkanoic and ω-chloroalkanoic acids; novel α, ω-oxaalkanedioic acids with both symmetric and unsymmetric structures were thus obtained. It was found that δ-valerolactone reacted with alkali alcoholates of ω-hydroxyalkanoic salts in the same manner as γ-butyrolactone to give both symmetric and unsymmetric α, ω-oxaalkanedioic acids. ε-Caprolactone, however, did not react with the

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[2] V. Prelog, M. Fausy EL-Neweihy and O. Häfliger, *Helv. Chim. Acta*, **33**, 1937 (1950).

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[4] I. Nishigori, B. Tatsuya and S. Murahashi, *Chem. High Polymer (Japan)*, **8**, 249 (1951).

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[7] H. J. Hagemeyer, Jr., U. S. Pat. 2466419 (1949); *Chem. Abstr.*, **43**, 5037 (1949).

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[10] K. Saotome and Y. Kodaira, *Makromol. Chem.*, **82**, 41 (1965).

[11] A. N. Nesmeyanov and L. L. Zakharkin, *Izv. Akad. Nauk S. S. S. R., Otd. Khim. Nauk*, **1955**, 224.

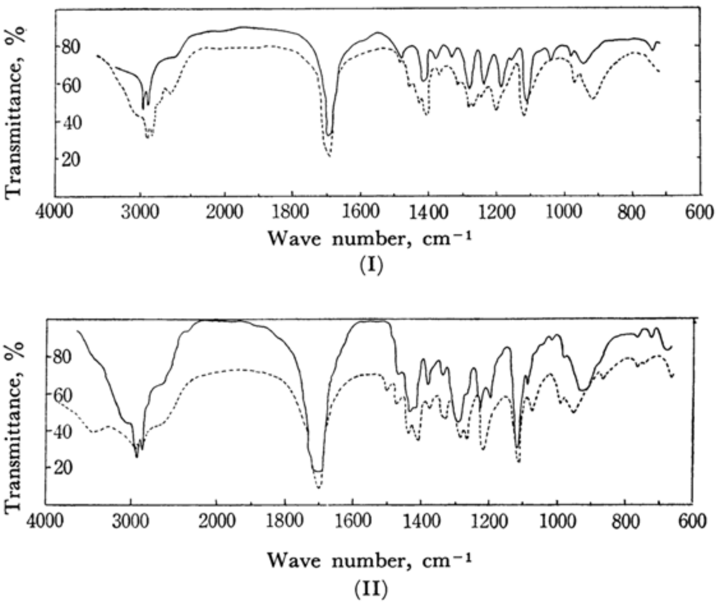

Fig. 1. Infrared spectra of α, ω-oxaalkanedioic acids.

(I) —— $HOOC(CH_2)_6O(CH_2)_6COOH$, …… $HOOC(CH_2)_4O(CH_2)_6COOH$
(II) —— $HOOC(CH_2)_3O(CH_2)_8COOH$, …… $HOOC(CH_2)_3O(CH_2)_4COOH$

alcoholates as above; rather, a resinous product was obtained under severe conditions. The symmetric α, ω-oxaalkanedioic acids with longer methylene chain units than C_4 were prepared either by the condensation of ω-hydroxyalkanoic salts in the presence of the dehydration catalyst or by the treatment of ω-chloroalkanoic acids with potassium hydroxide. We tried to obtain unsymmetric α, ω-oxaalkanedioic acids of which had methylene chain units longer than C_4, by the reaction between ω-chloroalkanoic acids and the alkali alcoholates of ω-hydroxyalkanoic salts with carbon numbers different from those of the chloroacids. However, the reaction products seemed to be mixtures of symmetric and unsymmetric α, ω-oxaalaknedioic acids, each with the ω-carboxyalkyl group of the starting compounds. It was difficult to separate the individual α, ω-oxaalkanedioic acids from the reaction mixtures.

The mechanisms of these condensation reactions will be discussed.

Experimental

Materials.—δ-Valerolactone was prepared according to the method described in a previous paper.[9] ω-Chloroalkanoic and ω-hydroxyalkanoic acids were also prepared from the telomers of ethylene with carbon tetrachloride. The characteristics of these intermediates agreed with those in the literature.[12]

6-Oxaundecanedioic Acid.—1) A mixture of 50 g. of δ-valerolactone and 20 g. of sodium hydroxide was heated at about 200°C in order to make a homogeneous solution. Then, 10 g. of activated alumina (grains) was added to the solution, and the temperature was gradually raised to 260—265°C over a 3 hr. period. During this period, a vigorous foaming due to the dehydration reaction was observed. After the reaction mixture had been kept at that temperature for a further 6 hr., the product was cooled and dissolved in 500 ml. of water. The aqueous solution was acidified by adding sulfuric acid a little over the neutral point of methyl orange. The precipitate and the solution were extracted with ether. After the evaporation of the ether, the residue was distilled under reduced pressure. The recrystallization of a fraction (b. p. 200—230°C/1 mmHg) from ethyl acetate afforded white crystals; m. p. 89.5—90°C (lit.[1] 88.5—89°C). Yield, 29 g. (53%).

A mixture of 25 g. of δ-valerolactone and 14 g. of potassium hydroxide was treated as above, but the reaction was carried out at temperatures of 255—260°C for 4 hr. White crystals of the same melting point were obtained. Yield, 19 g. (70%).

Found: C, 55.13; H, 8.29; mol. wt. (titration), 219. Calcd. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31%; mol. wt., 218.3.

2) A solution of 42 g. of sodium hydroxide dissolved in 50 ml. of water was gradually added to 50 g. of δ-valerolactone under cooling. After the evaporation of water with an aspirator, the mixture was heated to 220°C under the reduced pressure of 1 mmHg for 3 hr. until the water in the system was completely removed. Then, 60 g. of δ-valerolactone was added, and the mixture was refluxed under the atmosphere of nitrogen. When the mixture became homogeneous after several minutes, the temperature was raised to 255—260°C and kept there for a further 8 hr. When the product was treated as above, 88 g. (74%)

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[12] A. N. Nesmeyanov, R. Kh. Freidlina and L. I. Zakharkin, *Quart. Rev.*, **10**, 330 (1956).

of 6-oxaundecanedioic acid was obtained.

3) A mixture of 25 g. of δ-valerolactone and 14 g. of sodium carbonate was refluxed. The temperature was gradually raised to 260°C over a 1.5 hr. period and then maintained at that point for 3 hr. During this period, the generation of 2.5 l. of carbon dioxide (nearly theoretical) was observed. When the reaction product was treated as above, 14 g. (51%) of 6-oxaundecanedioic acid was obtained.

5-Oxaazelaic Acid.—The preparation of this acid from γ-butyrolactone has already been reported in the cited articles. In these experiments, however, the reaction was carried out under somewhat different conditions; γ-butyrolactone was treated with potassium hydroxide and sodium carbonate under conditions similar to those in the cases of δ-valerolactone described above. No large difference in the yields between the two lactones was observed in either case, and the melting point of the obtained crystals agreed with that of the literature (81°C).

5-Oxasebacic Acid.—From a mixture of 50 g. of δ-valerolactone and 42 g. of sodium hydroxide in 60 ml. of water, the water was completely removed by heating it to 250°C for 3 hr. under the reduced pressure of 1 mmHg. Then 60 g. of γ-butyrolactone was added, and the mixture was heated at 250—260°C for 8 hr. under nitrogen. Just before the end of the reaction, the unreacted lactone was recovered by distillation under reduced pressure. The treatment of the product was carried out much as in the case of 6-oxaundecanedioic acid. From the ether extract, a fraction with a b. p. of 180—210°C/2 mmHg was separated by distillation. Recrystallization from ether-petroleum ether afforded white crystals; m. p. 67°C. Yield based on δ-valerolactone, 72 g. (71%).

Found: C, 53.00; H, 8.06; mol. wt. (titration), 206. Calcd. for $C_9H_{16}O_5$: C, 52.93; H, 7.90%; mol. wt., 204.2.

A mixture of 43 g. of γ-butyrolactone and 42 g. of sodium hydroxide was treated as above. Then 60 g. of δ-valerolactone was added, and the mixture was heated similarly. Crystals identical with the above product were separated. Yield based on γ-butyrolactone, 62 g. (61%). The infrared spectrum is shown in Fig. 1.

5-Oxaundecanedioic Acid.—A mixture of 28 g. of ε-caprolactone and 32 g. of potassium hydroxide in 50 ml. of water was treated as in the case of 6-oxaundecanedioic acid (2). Then 25 g. of γ-butyrolactone was added, and the mixture was treated similarly. A fraction with a b. p. of 200—215°C/1 mmHg was distilled from the ether extract. Recrystallization from ether - petroleum ether gave white crystals; m. p. 34—35°C. Yield based on ε-caprolactone, 38 g. (71%).

Found: C, 54.96; H, 8.07; mol. wt. (titration), 220. Calcd. for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31%; mol. wt., 218.3.

5-Oxadodecanedioic Acid.—A mixture of 55 g. of ω-chloroenanthic acid and 64 g. of potassium hydroxide in 150 ml. of water was refluxed for 4 hr. After the complete evaporation of the water from the mixture according to the above procedure, 35 g. of γ-butyrolactone was added; and the mixture was then treated similarly. The recrystallization of a fraction with a b. p. of 200—220°C/1 mmHg with ether - petroleum ether afforded white crystals; m. p. 57.5—58°C. Yield based on ω-chloroenanthic acid, 45 g. (58%).

Found: C, 56.72; H, 8.52; mol. wt. (titration), 229. Calcd. for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68%; mol. wt., 232.3.

5-Oxatetradecanedioic Acid.—Into a solution of 9.2 g. of metallic sodium dissolved in 100 ml. of dry methanol, 35 g. of crystalline ω-hydroxypelargonic acid was added. The methanol was completely removed from the mixture by heating it to 220°C over a 3 hr. period under the reduced pressure of 1 mmHg. To the residue 20 g. of γ-butyrolactone was then added, and the mixture was refluxed for 2 hr. Then the excess γ-butyrolactone was recovered by distillation under reduced pressure. The reaction was continued for a further 6 hr. at temperatures of 250—260°C. The product was treated as above. The recrystallization of a fraction with a b. p. of 220—250°C/0.4—0.8 mmHg with ether - petroleum ether afforded white crystals; m. p. 64.5—65°C. Yield based on ω-hydroxypelargonic acid, 31 g. (59%).

Found: C, 59.82; H, 9.35; mol. wt. (titration), 264. Calcd. for $C_{13}H_{24}O_5$: C, 59.98; H, 9.29%; mol. wt., 260.3.

The infrared spectrum is shown in Fig. 1.

5-Oxahexadecanedioic Acid.—The reaction was carried out under conditions similar to those above. Thus 35 g. of ω-hydroxyundecanoic acid was treated with 8.0 g. of metallic sodium and 20 g. of γ-butyrolactone. A crystalline product was obtained after the evaporation of ether from the extract. Recrystallization from an ether - petroleum ether solution afforded white crystals; m. p. 74—74.5°C. Yield based on ω-hydroxyundecanoic acid, 26 g. (52%).

Found: C, 62.39; H, 9.67; mol. wt. (titration), 286. Calcd. for $C_{15}H_{28}O_5$: C, 62.47; H, 9.79%; mol. wt., 288.4.

6-Oxadodecanedioic Acid.—The reaction was carried out under conditions similar to those in the case of 5-oxaundecanedioic acid. The intermediate product from 28 g. of ε-caprolactone and 32 g. of potassium hydroxide was treated with 29 g. of δ-valerolactone. The recrystallization of a fraction with a b.p. of 200—220°C/1mmHg from an ether - petroleum ether solution afforded white crystals; m. p. 52.5—53°C. Yield based on ε-caprolactone, 37 g. (65%).

Found: C, 56.91; H, 8.58; mol wt. (titration), 234. Calcd. for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68%; mol. wt., 232.3.

6-Oxatridecanedioic Acid.—The reaction was carried out under conditions similar to those in the case of 5-oxadodecanedioic acid. The intermediate product from 55 g. of ω-chloroenanthic acid and 64 g. of potassium hydroxide was treated with 41 g. of δ-valerolactone. The recrystallization of a fraction with a b. p. of 200—225°C/1 mmHg with ether-petroleum ether afforded white crystals; m. p. 57.5—58°C. Yield based on ω-chloroenanthic acid, 56 g. (68%).

Found: C, 58.17; H, 8.94; mol. wt., (titration), 249. Calcd. for $C_{12}H_{22}O_5$: C, 58.51; H, 9.00%; mol. wt., 246.3.

The infrared spectrum is shown in Fig. 1.

6-Oxapentadecanedioic Acid.—The reaction was carried out under conditions similar to those in the case of 5-oxatetradecanedioic acid. The intermediate product from 35 g. of ω-hydroxypelargonic acid and

9.2 g. of metallic sodium was treated with 24 g. of δ-valerolactone. The recrystallization of a fraction with a b. p. of 210—240°C/0.5—1 mmHg from ether-petroleum ether afforded white crystals; m. p. 64.5—65°C. Yield based on ω-hydroxypelargonic acid, 34 g. (62%).

Found: C, 62.89; H, 9.10; mol. wt. (titration), 277. Calcd. for $C_{14}H_{26}O_5$: C, 62.91; H, 9.15%; mol. wt., 274.3.

6-Oxaheptadecanedioic Acid.—The reaction was carried out under conditions similar to those in the case of 5-oxahexadecanedioic acid. The intermediate product from 35 g. of ω-hydroxyundecanoic acid and 8.0 g. of metallic sodium was treated with 24 g. of δ-valerolactone. A crystalline product was obtained after the evaporation of ether from the extract. Recrystallization from ether-petroleum ether afforded white crystals; m. p. 84.5—85°C. Yield based on ω-hydroxyundecanoic acid, 33 g. (63%).

Found: C, 63.36; H, 9.70; mol. wt. (titration), 304. Calcd. for $C_{16}H_{30}O_5$: C, 63.54; H, 10.00%; mol. wt., 302.4.

7-Oxatridecanedioic Acid.—A mixture of 28 g. of ε-caprolactone and 15 g. of potassium hydroxide in 20 ml. of water was treated much as in the case of 6-oxaundecanedioic acid (1). The recrystallization of a fraction with a b. p. of 210—250°C/1 mmHg from water-ethanol afforded white crystals; m. p. 90—91°C, (lit. 91°C). Yield, 16 g. (53%).

Found: C, 58.49; H, 8.90; mol. wt. (titration), 245. Calcd. for $C_{12}H_{22}O_5$: C, 58.51; H, 9.00%; mol. wt., 246.3.

8-Oxapentadecanedioic Acid.—From a mixture of 55 g. of ω-chloroenanthic acid and 39 g. of potassium hydroxide in 40 ml. of water, the water was rapidly removed (within 20 min.) by heating the mixture to 240°C under reduced pressure. After the evaporation of the water, the mixture was kept at temperatures of 250—260°C for 8 hr. under the reduced pressure of 1 mmHg. The product was then treated as above. The recrystallization of a fraction with a b. p. of 210—250°C/0.5—1 mmHg from water-ethanol afforded white crystals; m. p. 95.5—96°C. Yield, 28 g. (61%).

Found: C, 61.19; H, 9.50; mol. wt. (titration), 271. Calcd. for $C_{14}H_{26}O_5$: C, 61.29; H, 9.55%; mol. wt., 274.3.

10-Oxanonadecanedioic Acid.—A mixture of 48 g. of ω-chloropelargonic acid and 29 g. of potassium hydroxide was treated much as above. A crystalline product was obtained after the evaporation of ether from the extract. Recrystallization from toluene afforded white crystals; m. p. 99—99.5°C. Yield, 21 g. (51%).

Found: C, 65.56; H, 10.08; mol. wt. (titration), 327. Calcd. for $C_{18}H_{34}O_5$: C, 65.45; H, 10.30%; mol. wt., 330.4.

The infrared spectra of some of these novel α, ω-oxaalkanedioic acids are shown in Fig. 1. The characteristic band at 1110—1125 cm⁻¹ due to the ether linkages of these α, ω-oxaalkanedioic acids is observed in every chart.

The melting points of these dicarboxylic acids are plotted against the carbon numbers of the oxaalkylene groups in Fig. 2.

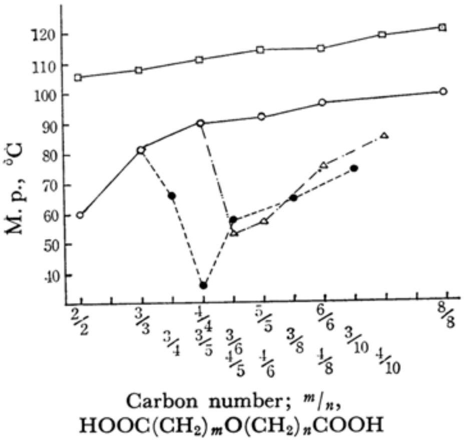


Fig. 2. M. p. of α, ω-oxaalkanedioic acids.
—□— $HOOC(CH_2)_pCOOH$, p, odd
—○— $HOOC(CH_2)_nO(CH_2)_nCOOH$
···●··· $HOOC(CH_2)_3O(CH_2)_nCOOH$
—··△··— $HOOC(CH_2)_4O(CH_2)_nCOOH$

Discussion

The synthetic processes for the preparation of these α, ω-oxaalkanedioic acids may be classified into the following four types. During every course of the reaction, the carboxyl groups are protected as alkali salts.

1) The catalytic dehydration of ω-hydroxyalkanoic acids:

$$2HO(CH_2)_nCOOM \underset{-H_2O}{\rightarrow} MOOC(CH_2)_nO(CH_2)_nCOOM$$

where M denotes sodium or potassium.

2) The addition of γ-butyrolactone or δ-valerolactone to the alkali alcoholates of ω-hydroxyalkanoic acids:

$$\underline{O(CH_2)_mCO}(m=3 \text{ or } 4)+MO(CH_2)_nCOOM \rightarrow MOOC(CH_2)_mO(CH_2)_nCOOM$$

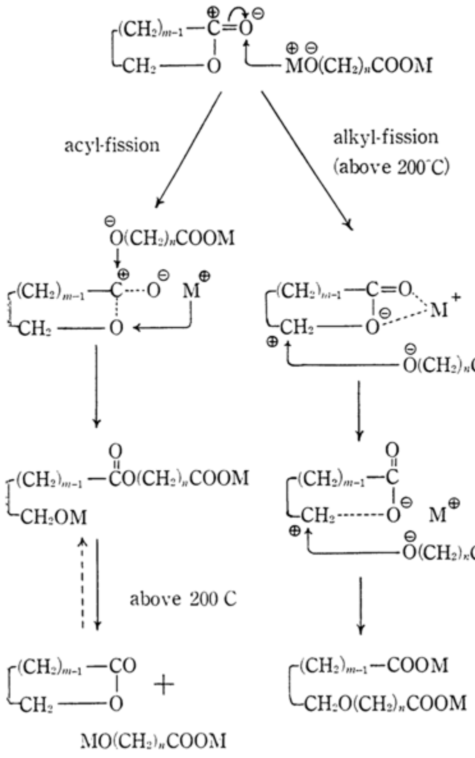
3) The reaction of γ-butyrolactone or δ-valerolactone with sodium carbonate:

$$2\ \underline{O(CH_2)_mCO}+Na_2CO_3 \rightarrow NaOOC(CH_2)_mO(CH_2)_mCOONa+CO_2$$

4) The condensation of ω-chloroalkanoic acids with alkali hydroxide:

$$2\ Cl(CH_2)_nCOOH+4MOH \underset{-3\ H_2O}{\rightarrow} MOOC(CH_2)_nO(CH_2)_nCOOM+2MCl$$

The unsymmetric α, ω-oxaalkanedioic acids, in which one of the methylene chain units interrupted by an ether linkage consists of 3 or 4 methylene units, can be prepared through the Type 2 process. In the synthesis of 5-oxasebacic acid, it is interesting that no symmetric dicarboxylic acid (neither 5-oxaazelaic nor 6-oxaundecanedioic acid) was found in the product. Moreover, the same product was obtained in similar yields whichever of the two lactones had been treated with sodium hydroxide first. These facts indicate that no interchange reaction between these lactones and the alcoholates occurs. The mechanisms of the addition of γ-butyrolactone and δ-valerolactone to the alkali alcoholates of ω-hydroxyalkanoic salts may thus be presented as follows:



The acyl-fission is considered to occur more smoothly than the alkyl-fission in the ring opening of these lactones under these experimental conditions. In the polymerization of δ-valerolactone initiated with sodium alcoholate, the acyl-fission mechanism is supported by the presence of the end hydroxyl groups in a polyvalerolactone molecule.[10] The ester intermediate of δ-valerolactone formed by the acyl-fission is unstable at elevated temperatures, and δ-valerolactone is recovered almost quantitatively by distillation under reduced pressure. In the case of γ-butyrolactone, which can not usually be polymerized, the ester intermediate is supposed to be far more unstable and to be dissociated into the monomeric lactone immediately. Therefore, the acyl-fission can be disregarded for these reaction mechanisms. In the case of ε-caprolactone, however, the ester intermediate is stable enough, and the lactone can not be recovered, even at elevated temperatures. No large difference is observed in the tendencies toward the acyl-fission between γ-butyrolactone and δ-valerolactone, because the yields of the corresponding α, ω-oxaalkanedioic acids are much alike under similar conditions.

In the Type 4 process, the chlorine atom may be considered to be eliminated, thus forming ω-hydroxyalkanoic salts at the initial stage of the reaction. However, large differences between the Type 1 and Type 4 reactions are observed. When ω-hydroxyenanthic and ω-hydroxypelargonic acids were treated according to the directions for the Type 1 process, only poor yields of the corresponding dicarboxylic acids were obtained, even in the presence of relatively large amounts of alumina. Therefore, the reaction mechanism in the Type 4 process is considered to be differed from that of Type 1. The eminent depression of yields was actually observed when the water was evaporated slowly (for one hour or more) in the preparation of 8-oxapentadecanedioic and 10-oxanonadecanedioic acids. Moreover, when ω-chloroalkanoic acids of which carbon atoms in a molecule are less than 6 were subjected to this process, only poor yields of the dicarboxylic acids were obtained. Perhaps the rapid hydrolysis of the chloride due to the formation of lactonic rings prevented the progress of the reaction of this type. In an experiment in which an equimolar mixture of ω-chloroenanthic and ω-hydroxypelargonic acids was treated with potassium hydroxide according to the procedure for the preparation of 8-oxapentadecanedioic acid, a crystalline product was separated from a water-ethanol solution. From the molecular weight and the elementary analysis, this product was estimated to be a mixture consisting of three α, ω-oxaalkanedioic acids: 8-oxaheptadecanedioic, 8-oxapentadecanedioic, and a small amount of 10-oxanonadecanedioic acids.

From these experimental results, the reaction of the following mechanism is considered to take place dominantly for the formation of the ether linkage:

$$\mathrm{Cl(CH_2)_{\mathit{n}}COOM + MO(CH_2)_{\mathit{n}}COOM} \\ \rightarrow \mathrm{MOOC(CH_2)_{\mathit{n}}O(CH_2)_{\mathit{n}}COOM + MCl}$$

In the relations between the melting points of the dicarboxylic acids of two types—$\mathrm{HOOC(CH_2)_3O(CH_2)_{\mathit{n}}COOH}$ and $\mathrm{HOOC(CH_2)_4O(CH_2)_{\mathit{n}}COOH}$—and their carbon atoms in a molecule, shown in Fig. 2, the minimum melting points are observed at 3/5 and 4/5 respectively. The remarkable depression of melting point around these minimum points may be attributed to the decrease in the symmetry in the configuration, in other words, the increase in the entropy of fusion ($\varDelta S_m$).

Polyamides from these α, ω-oxaalkanedioic acids have also been prepared. They will be reported in detail in the near future.