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Studies of Polymerization and Ring Formation. XXIII.[1] ε-Caprolactone and its Polymers

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Bifunctional esterifications[2] generally yield either cyclic monomers or linear polyesters. Choice between these possibilities is controlled by (a) the unit length of the reactant, (b) the nature of the unit, and (c) the experimental conditions (especially dilution). Factor (a) is generally by far the most important and its effect has been illustrated in previous papers. Unit lengths of 7 and 8 however constitute transition cases and factor (b) may here become the controlling one. It is well known that substitution (*e. g.*, by methyl) favors ring closure but otherwise the effect of variations in the nature of the unit are not easy to foresee. The simplest possible structural situation for self-esterification is found in the ω-hydroxy acids, $HO(CH_2)_{n-2}COOH$, and information concerning them is available for all values of n from 3 to 22[3] excepting 7 and 8. These acids have never been isolated or their self-esterification studied.[4]

A

The experiments presently reported were prompted by the considerations outlined above and by the fact that several grams of ε-hydroxycaproic acid had become available as a by-product in the preparation of hexamethylene glycol by the reduction of diethyl adipate. The acid could neither be distilled nor crystallized, and it was therefore impossible to isolate it as such in a state of purity. It was however found possible, as described in **B** (below), to isolate an oil composed essentially of the acid (80%) and its lactone (20%). This mixture was dehydrated by heating it in a distilling flask at 150 to 210°. The residue was completely volatile, and, when purified by redistillation, it was found to consist of the lactone of ε-hydroxycaproic acid, a colorless liquid having a pleasant, spicy odor. It crystallized when strongly cooled and melted at about −5°. The yield of purified lactone was about 63% of the theoretical. The only other product of the reaction consisted of a very small amount (·1%) of a volatile crystalline solid melting at 111 to 113°. This was identified as the dimeric, cyclic self-ester of ε-hydroxycaproic acid, a 14-membered ring.

The monomeric lactone showed no appreciable tendency to polymerize spontaneously when allowed to stand at the ordinary laboratory conditions; but when heated at 150° in a sealed tube it gradually became more viscous and, after twelve hours, when cooled to room temperature, it solidified to an opaque mass. When a trace of potassium carbonate was added to the lactone the same result was obtained in five hours at 150°. The product crystallized from alcohol as a white powder melting at 53 to 55°. It was very soluble in ethyl acetate, acetone, and benzene but only slightly soluble in alcohol or ether. The analytical composition and chemical behavior of this material demonstrated that it was a linear polyester, and molecular weight determinations in freezing benzene gave values about 4000.

Anal. Calcd. for $HO—[—(CH_2)_5—CO—O—]_{35}—H$: C, 62.83; H, 8.84; mol. wt. 4008. Found: C, 62.15; H, 8.86; mol. wt. 3660, 4300.

All three of the above esters (lactone, dimer, and polyester) were actually derivatives of ε-hydroxycaproic acid, and no shift of the hydroxyl oxygen was involved in their formation,[5] since they all yielded the same hydrazide when treated with hydrazine hydrate. This hydrazide was also obtained from the ethyl ester described in **C**.

To test its susceptibility to depolymerization the polyester was placed in a molecular still and heated by a bath at 250° and at a pressure of 1 to 2 mm. for ninety hours.[6] During this time only a very small amount of distillate was collected—a viscous, dark-colored oil containing a few minute crystals of the cyclic dimer. The polymeric residue was darker in color but otherwise appeared to be unchanged.

Conclusions.—Under the conditions described, the principal primary product of the self-esterification of ε-hydroxycaproic acid is the monomeric lactone; a trace of the dimeric ester is formed at the same time but little if any of the higher polyester. Like 6-membered cyclic esters, the lactone of ε-hydroxycaproic acid is polymerized by the action of heat. (Apparently it polymerizes only slightly less readily than δ-valerolactone.) The polyester thus obtained can be depolymerized only with great difficulty under the action of heat. In this respect it differs from the

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[1] Previous papers of this series are: (a) THIS JOURNAL, **51**, 2548 (1929); (b) *ibid.*, 2560; (c) *ibid.*, **52**, 314 (1930); (d) *ibid.*, 711; (e) *ibid.*, 3292; (f) *ibid.*, 4110; (g) *ibid.*, 5279; (h) *ibid.*, 5289; (i) *Chem. Reviews*, **8**, 353 (1931); (j) THIS JOURNAL, **54**, 761 (1932); (k) *ibid.*, 1557; (l) *ibid.*, 1559; (m) *ibid.*, 1566; (n) *ibid.*, 1569; (o) *ibid.*, 1579; (p) *ibid.*, 1588; (q) *ibid.*, 4105; (r) *ibid.*, **55**, 4714 (1933); (s) *ibid.*, 5023; (t) *ibid.*, 5031; (u) *ibid.*, 5039; (v) *ibid.*, 5043.

[2] For terminology see Refs. 1a and 1s.

[3] Chuit and Hausser, *Helv. Chim. Acta*, **12**, 463 (1929); Bougault and Bourdier, *Compt. rend.*, **147**, 1311 (1908); Lycan and Adams, THIS JOURNAL, **51**, 625, 3450 (1929); also Ref. 1j.

[4] Some of their derivatives are meagerly described in the following references: Baeyer and Villiger, *Ber.*, **33**, 863 (1900); Helferich and Malkomes, *ibid.*, **55**, 704 (1922); Marvel and Birkhimer, THIS JOURNAL, **51**, 260 (1929).

[5] *Cf.* Blaise and Koehler, *Compt. rend.*, **148**, 1772 (1909).

[6] Under these conditions polyesters having 6-atom units depolymerize very rapidly and smoothly.[1g] Those having longer units depolymerize very slowly and incompletely if at all, although in many such cases a smooth depolymerization can be effected in the presence of an ester-interchange catalyst.[1t]

polyesters that result from 6-membered cyclic esters, and resembles polyesters derived from the higher ω-hydroxy acids.

The following comparisons with other compounds having 7-atom units are also of interest. Tetramethylene carbonate[1c] and trimethylene oxalate[1e] are obtained only in the form of linear polyesters. These are depolymerized with great difficulty and the only products identified are the cyclic dimers.[1f] The lactone of 3,7-dimethyl-6-hydroxyoctanoic acid is reported[7] to exist in two forms, a liquid and a solid. The authors suggest that these are stereoisomers, but no molecular weight determinations are recorded, and it seems more likely that they represent a monomeric and a dimeric form. Another ε-lactone results from tetrahydrocarvone by oxidation with Caro's acid.[8] It is hydrolyzed to the acid, HO—CH(CH_3)—(CH_2)$_2$—CH(C_3H_7)—CH_2—COOH, from which the lactone is regenerated by the action of heat. A simple lactone is also obtained from ε-hydroxyoctanoic acid by direct distillation.[5] When ε-aminocaproic acid is heated it is partly converted to the monomeric lactam (about 30%) and partly to polyamide (about 70%). These are not directly interconvertible.[1h]

B

Preparation of ε-Hydroxycaproic Acid.—The acid was isolated from the product obtained by reducing a large amount of ethyl adipate. After the hexamethylene glycol had been removed by ether extraction of the completely saponified reaction mixture, the latter was acidified with sulfuric acid and continuously extracted with ether. From the concentrated ethereal extract, a part of the adipic acid was removed by filtration. Attempts to remove the ε-hydroxycaproic acid from the filtrate by distillation were unsuccessful. The mixture was therefore acetylated,[9] and the acetate of the hydroxy acid was isolated by distillation (b. p. 134 to 145° at 2 mm.). This was saponified, acidified with dilute sulfuric acid, extracted with ether and concentrated *in vacuo*. The acetic acid was removed by evaporation *in vacuo* at room temperature in an all glass apparatus, the condenser bulb being cooled with carbon dioxide snow and acetone. After four days the bulbs were opened. The distillate consisted of dilute acetic acid. The residue was a pale yellow, viscous liquid having a slightly rancid odor. It solidified to a glass when cooled with solid carbon dioxide. Titration indicated that it consisted of a mixture of ε-hydroxycaproic acid and its self-ester containing about 80% of the free acid.

Anal. Calcd. for hydroxycaproic acid: neutral equivalent or saponification equivalent, 132. Found: neutral equivalent, 164.1, 164.3; saponification equivalent, 130.5.

ε-Caprolactone.—The lactone prepared as described in A was very soluble in alcohol, benzene, ether, ethyl acetate and water, but insoluble in petroleum ether; b. p. 98 to 99° at 2 mm.; d_4^{24} 1.0698; n_D^{24} 1.4608; M_R calcd., 29.44; M_R found, 29.15.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.11; H, 8.84; mol. wt., 114; saponification equivalent, 114. Found: C, 62.81, 63.39; H, 8.68, 9.07; mol. wt. (in freezing benzene) 120, 122; saponification equivalent, 113.4, 113.3.

Dimeric ε-Caprolactone.—Obtained as described in **A**: granular crystals; soluble in most organic solvents, but insoluble in petroleum ether or water; m. p. 112 to 113°.

Anal. Calcd. for $C_{12}H_{20}O_4$: C, 63.11; H, 8.84; mol. wt., 228. Found: C, 62.98, 63.39; H, 8.84, 9.09; mol. wt. (in freezing benzene), 243, 226.

Hydrazide of ε-Hydroxycaproic Acid.—The monomeric and dimeric lactones as well as the polyester described in A, and the ethyl ester described in C (below) were separately warmed with hydrazine hydrate for several hours on a steam-bath. In each case the mixture solidified on being cooled; and after crystallization from ethyl acetate or alcohol, the hydrazide was obtained in the form of white crystals melting at 114 to 115°. It was very soluble in water.

Anal. Calcd. for $C_6H_{14}O_2N_2$: N, 19.18. Found: N, 18.68, 18.74.

C

Attempts to Prepare ε-Caprolactone from ε-Bromocaproic Acid.—Prior to the experiments described above, attempts had been made to prepare ε-caprolactone by the action of sodium ethylate on ε-bromocaproic acid. By this method Marvel and Birkhimer[10] obtained a small amount of material "which seemed to be slightly impure ε-caprolactone," but its identity was not established.

ε-Bromocaproic acid with an equivalent amount of sodium ethylate in absolute alcohol was refluxed for eight hours. The mixture was made very slightly acid with a few drops of hydrochloric acid, then filtered, concentrated, and distilled *in vacuo*. After a small preliminary fraction, a halogen-free product distilling at 104 to 106° at 4 mm. was obtained in 37% yield.

This, presumably, is similar to the product described by Marvel and Birkhimer, but it proved to be the ethyl ester of ε-hydroxycaproic acid. Unlike ε-caprolactone it was insoluble in water; and it did not crystallize on being strongly cooled but merely became very viscous. It was soluble in most organic solvents; d_4^{25} 0.9944; n_D^{25} 1.4381; M_R calcd., 42.32; M_R found, 42.24.

Anal. Calcd. for $C_8H_{16}O_3$: C, 60.0; H, 10.0; mol. wt., 160; saponification equivalent, 160. Found: C, 59.98; H, 10.08; mol. wt. (in boiling acetonitrile) 151, 154; saponification equivalent, 158.7, 158.8.

When treated with hydrazine hydrate it yielded the hydrazide already described in **B** (above).

The residue from the distillation of the ethyl ester was distilled further and yielded a small fraction boiling at 110–200° at 4 mm. From this halogen-free distillate

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[7] Baeyer, *Ber.*, **32**, 3619 (1899); Baeyer and Villiger, *ibid.*, 3628.

[8] Baeyer, *ibid.*, **29**, 27, 30 (1896); Baeyer and Villiger, *ibid.*, **32**, 3629 (1899).

[9] *Cf.* Chuit and Hausser, *Helv. Chim. Acta*, **12**, 463 (1929).

[10] Marvel and Birkhimer, THIS JOURNAL, **51**, 260 (1929).

granular crystals of the caprolactone dimer described in B separated (identified by mixed melting point).

The residue still remaining (41%) solidified to a paste on standing, and was obtained as a light colored powder melting at 51 to 53° after several crystallizations from alcohol. It was similar to the polyester described in A, but it had a somewhat lower apparent molecular weight.

Anal. Calcd. for $HO—[—(CH_2)_5—CO—O—]_{16}—H$: C, 62.7; H, 8.8; mol. wt., 1842. Found: C, 63.56; H, 9.08; mol. wt. (in freezing benzene) 1980, 1660.

When treated with hydrazine hydrate it yielded the hydrazide already described.

From the above described reaction of sodium ethylate on bromocaproic acid no monomeric lactone was isolated. It is, however, not permissible to infer that no caprolactone was formed, since hydrochloric acid was present, and this, doubtless, would strongly catalyze the polymerization of any caprolactone that might have been formed.[11]

Summary

ε-Caprolactone has been prepared for the first time. It is the principal product of the self-esterification of the corresponding acid. A small amount of the cyclic dimeric ester (14-membered ring) is formed at the same time. Under the action of heat ε-caprolactone is converted to a polyester of high molecular weight. The process is not easily reversible. This behavior is compared with that already observed for other cyclic and polyesters.

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Essential Oil in Desert Plants. III.
Examination of the Oil of Artemisia Tridentata Typica

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The scattered stunted shrubs which grow on the arid plains and mountains of the western United States are collectively called sagebrush. The name is more correctly applied to the family of plants classed as *Artemisia* of which more than 30 varieties are listed (Coulter and Nelson). Of this group of plants the oils from *Artemisia Cana*,[1] *Artemisia Frigida*, *Artemisia Leudoviciana*[2] and *Artemisia Caudata*, have been extracted and some of their physical and chemical properties observed.

Artemisia Tridentata Typica, often designated as black sage, is widely distributed, its habitat extending very generally over the United States west of the Missouri River. It grows as a densely branched shrub from a half meter in height on the upland barren soils, to three or four meters on alluvial fans. The aromatic nature of the shrub is very conspicuous. After a summer shower of rain the desert atmosphere is usually highly charged with the odor of the plant. The leaves when crushed have a very pungent characteristic odor and when steam distilled yield an oil, the physical constants of which have been determined.[3] The oil is best secured from the leaves of the brush which has been cut in the late autumn and allowed to dry thoroughly. The leaves and small twigs are collected after being threshed from the larger branches. The dry leaves yield almost 1% of a colorless oil which on standing turns light yellow. It has a very strong odor and a camphor-like taste. A 180-g. portion of this oil, after redistilling with steam and drying over anhydrous sodium sulfate, was placed in a 500-cc. round-bottomed distilling flask fitted with a Glinsky ball and bulb fractionating column. The distilling flask was set in an oil-bath and fractionated several times at ordinary pressure (650 mm.). The table shows the result of the sixth fractionation.

TABLE I

Number	Temp., °C.	Oil, g.	Density at 25°
I	130–165	37.9	0.8752
II	165–175	12.4	.9081
III	175–185	10.6	.9266
IV	185–198	28.7	.9474
V	198–201	21.3	.9712
Residues		72.0	

The combined residues from the above distillations, which were not volatile at 200°, were then distilled under diminished pressure using the above type of apparatus with a Bruhl receiver. The table gives the results.

TABLE II

Number	Temp., °C.	Pressure, mm.	Oil, g.	Density at 25°
I	95–105	14	25.0	0.9413
II	105–115	14	9.9	.9223
III	115–125	14	8.1	.9225
IV	125–135	13	3.0	.9093
V	135–150	13	5.3	.9221
Residues			20.7	

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(1) Theo. Whittelsey, "Otto Wallach's Festschrift," Göttingen, 1909, p. 668.

(2) Rabak, *Pharm. Rev.*, **24**, 324 (1906).

(3) Adams, THIS JOURNAL, **49**, 2895 (1927).