condenser, the distillate, like that from brassylic anhydride, collected as a liquid which changed in the course of a day to a pasty mass and in the course of two to a hard wax, m. p. 88–91°. The distillate, before it changed completely to the hard wax, possessed a strong odor like that of musk. This odor was completely lost on saponification (saponification equivalent found, 120.4, 119.1; calcd., 120.1) and on heating to 100° which brought about the change to the γ-anhydride instantly.

1,18-Octadecanedioic Anhydride.—The behavior of this α-anhydride was identical in every respect with that of tetradecanedioic anhydride. The fresh liquid distillate likewise possessed the odor of musk but was rather fainter. It polymerized instantly on being heated to 100°, to a wax of m. p. 98–100° (γ-anhydride), losing its odor in the change. About 1 cc. of β-anhydride was collected using a still adapted for the collection of liquids. It crystallized on chilling or seeding and melted at 36–37° (saponification equivalent found, 146.5; calcd. for $C_{18}H_{32}O_3$, 148.1). After two weeks it had changed to the wax of m. p. 98-100°.

Summary

Data are presented on the anhydrides of dibasic acids $COOH(CH_2)_n$-COOH where n is 4, 5, 6, 7, 8, 9, 10, 11, 12 and 16. The anhydrides are all linear polymers and when heated in a molecular still they are depolymerized yielding volatile products (β-anhydrides). The latter are either cyclic monomers or dimers depending upon the unit length, $n + 3$. The compounds thus obtained are rings of 7, 8, 18 (dimeric), 10, 22 (dimeric), 12, 26 (dimeric), 14, 15 and 19 atoms. The dimers are crystalline solids which polymerize instantly when heated above their melting points. The monomers are liquids or low melting solids which polymerize at lower temperatures than the dimers. The monomers of 8, 10 and 12 atoms are exceedingly unstable and polymerize rapidly even below room temperature.

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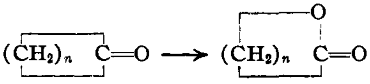
Studies of Polymerization and Ring Formation. XX. Many-Membered Cyclic Esters

BY JULIAN W. HILL AND WALLACE H. CAROTHERS

The only generally applicable method known for the synthesis of macrocyclic esters consists in oxidation of cyclic ketones with Caro's acid. This



I II (n = 12, 13, 14, 15, 16)

method, discovered by Baeyer and Villiger,[1] has been applied by Ruzicka and Stoll[2] to the synthesis of the lactones, II.

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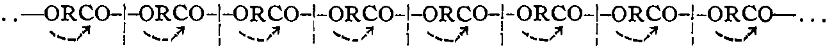
(1) Baeyer and Villiger, *Ber.*, **32**, 3625 (1899).

(2) Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

The reaction is far from clean-cut, while the requisite ketones (I) are obtained in yields not exceeding 5%.[3] The necessity for adopting this devious and extravagant method for synthesizing macrocyclic lactones is due to the fact, repeatedly illustrated in previous papers[4] of this series, that bifunctional esterifications involving unit lengths greater than seven yield almost exclusively linear polyesters instead of the desired cyclic esters. When linear polyesters of unit length greater than seven are heated, *e. g.*, to 275°, there is generally no evidence of depolymerization or distillation,[5] but at temperatures somewhat above 300° destructive general decomposition occurs, and from the complicated mixture of distillable products in four cases[6] true depolymerization products have been isolated. These cyclic esters however are not monomers but dimers, and the yields are very poor (5% or less).

When linear polyesters of unit length greater than seven are heated (*e. g.*, to 200–250°) under the conditions of molecular distillation,[7] the long chains couple to form still longer chains.[8] The products (superpolyesters) have molecular weights above 10,000 and are capable of being drawn out into tough, pliable, highly oriented fibers.[9]

It was recognized in advance that the conditions of the molecular still at high temperature would be likely to favor either this type of coupling or a depolymerization by ester interchange:[10]



$\ldots\text{—ORCO-}\vdots\text{-ORCO-}\vdots\text{-ORCO-}\vdots\text{-ORCO-}\vdots\text{-ORCO-}\vdots\text{-ORCO-}\vdots\text{-ORCO-}\vdots\text{-ORCO—}\ldots$

Evidences of such depolymerization, at least in traces, were in fact frequently observed in the formation of superpolyesters, and after methods had been developed for the smooth depolymerization of polyanhydrides, attention was again turned to the polyesters. The result was the development of the method presently described by means of which it became possible to prepare with good yields and without unreasonable difficulty a whole series of macrocyclic esters, both monomeric and dimeric. Briefly,

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(3) Since this paper was prepared for publication Ziegler, Eberle and Ohlinger [*Ann.*, **504**, 94 (1933)] have described an ingenious method based on Ruggli's dilution principle for the preparation of large cyclic ketones in good yields. This principle has been referred to in previous papers of the present series [*e. g.*, THIS JOURNAL, **51**, 2551 (1929)] and we hope to describe its application to the synthesis of cyclic esters in future papers.

(4) Carothers, THIS JOURNAL, **51**, 2548 (1929); Carothers and Arvin, *ibid.*, **52**, 711; Carothers, Arvin and Dorough, *ibid.*, 3292; Carothers, *Chem. Reviews*, **8**, 353 (1931). *Cf.* Chuit and Hausser, *Helv. Chim. Acta*, **12**, 463 (1929); Lycan and Adams, THIS JOURNAL, **51**, 625, 3450 (1929).

(5) Compounds of molecular weight higher than 1000 cannot be distilled even under the highest vacua, Carothers, Hill, Kirby and Jacobson, THIS JOURNAL, **52**, 5279 (1931).

(6) The cases referred to are ethylene succinate, Tilitschejew, *J. Russ. Phys.-Chem. Soc.*, **57**, 143 (1925); Carothers and Dorough, THIS JOURNAL, **52**, 711 (1930); tetramethylene carbonate, Carothers and Van Natta, *ibid.*, **52**, 314 (1930); trimethylene oxalate, Tilitschejew, *J. Russ. Phys.-Chem. Soc.*, **58**, 447 (1926); Carothers, Arvin and Dorough, THIS JOURNAL, **52**, 3292 (1930); self-ester of hydroxydecanoic acid, Lycan and Adams, *ibid.*, **51**, 625, 3450 (1929).

(7) Carothers and Hill, *ibid.*, **54**, 1557 (1932).

(8) *Ibid.*, p. 1559.

(9) *Ibid.*, p. 1579.

(10) *Cf.* the discussion of 6-membered cyclic esters and their polymers in Carothers, Dorough and Van Natta, *ibid.*, **54**, 761 (1932).

the method consists in heating linear polyesters *in vacuo* at a temperature just below the point of thermal destruction under conditions that permit any volatile product to be removed by distillation as fast as it is formed.

The success of the new method, practically, depends upon numerous factors not all of which have yet been completely isolated and defined; the two most important however are the identity of the polyester and the use of catalysts. On the first point it may be said that esters of carbonic acid and of oxalic acid depolymerize more readily and smoothly than any others yet examined. On the second point, ester interchange catalysts (*e. g.*, sodium added as metal in the preparation of the initial polyester) are almost indispensable.

After some experimentation it was discovered that esters of carbonic acid and of oxalic acid can be depolymerized merely by heating them (with catalyst) under diminished pressure in an ordinary distilling flask. Most of the experiments now reported were however made in a simplified molecular still (described below) operated at pressures ranging from 0.1 to 2 or 3 mm.

The depolymerization of the polyester in favorable cases progresses smoothly and fairly rapidly, the cyclic ester distilling to the condenser and being collected as it is formed. The residual ester at the same time progressively increases in viscosity (formation of superpolymer); if this increase in viscosity does not proceed too far, depolymerization still continues and is ultimately almost complete and quantitative. In many cases however the residue, before complete depolymerization, becomes converted to a gel; even at 250° it is completely immobile and resembles a piece of porous, vulcanized, gum rubber. Depolymerization then practically ceases. This residue incidentally is extraordinarily resistant to attack by solvents and chemical agents generally. It evidently results from a polymerization which has progressed beyond the linear superpolymer stage. It seems likely that some quantitatively minor side-reaction (dehydrogenation at a venture) occurs permitting accessory polymerization to form a three-dimensional macromolecule.

The product of the depolymerization is generally a mixture of cyclic monomer and cyclic dimer although in many cases one of these forms predominates to the practical exclusion of the other. The ratio of the two forms is in some cases quite sensitive to the experimental conditions (temperature, pressure, shape of apparatus) but the data on this point recorded in Table I were all obtained under closely similar conditions.

Preparation of Polyesters.—Polymeric carbonates derived from the glycols $HO(CH_2)_nOH$ where n is 3, 4, 6 and 10 and from diethylene glycol have already been described.[11] The new polymeric carbonates prepared as intermediates in the present work include those derived from the glycols $HO(CH_2)_nOH$ where n is 5, 7, 8, 9, 11, 12, 13, 14 and 18, and from

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[11] Carothers and Van Natta, THIS JOURNAL, 52, 314 (1930).

TABLE I

NATURE AND PHYSICAL PROPERTIES OF CYCLIC ESTERS

	Unit length	Proportions of monomer and dimer in distillate	M. p. of monomer, °C.	B. p. of monomer, °C.	n_D of monomer	d_4 of monomer	M. p. of dimer, °C.
Ethylene carbonate	5	Exclusively monomer	39	238	1.4158 (50°)	1.3079 (50°)	
Trimethylene carbonate	6	Exclusively monomer	47–48	135 at 4 mm.	1.4409 (50°)	1.2282 (50°)	
Tetramethylene carbonate	7	Mixture of dimer and tetrahydrofuran					175–176
Pentamethylene carbonate	8	Exclusively dimer					117–118
Hexamethylene carbonate	9	Almost exclusively dimer; odor of monomer					128–129
Heptamethylene carbonate	10	Almost exclusively dimer; odor of monomer					97–98
Octamethylene carbonate	11	Almost exclusively dimer; odor of monomer	21.5–23	74– 76 at 0.5 mm.	1.4665 (20°)	1.0727 (20°)	116–117
Nonamethylene carbonate	12	Almost exclusively dimer; odor of monomer	34–35	63– 64 at 0.1 mm.	1.4528 (50°)	1.0240 (50°)	95–95.5
Decamethylene carbonate	13	Mixture of monomer and dimer	10–11	92– 93 at 1 mm.	1.4659 (20°)	1.0354 (20°)	105–106
Undecamethylene carbonate	14	Mixture of monomer and dimer	40–41	104.5 at 7 mm.	1.4544 (50°)	0.9968 (50°)	97–97.5
Dodecamethylene carbonate	15	Almost exclusively monomer; small amount of dimer identified	11–12	118–119 at 3 mm.	1.4639 (20°)	1.0036 (20°)	93–95
Tridecamethylene carbonate	16	Almost exclusively monomer; no dimer isolated	23–24.5	149–150 at 4.5 mm.	1.4622 (25°)	0.9888 (25°)	
Tetradecamethylene carbonate	17		21–22	144–146 at 2 mm.	1.4622 (20°)	0.9814 (20°)	
Octadecamethylene carbonate	21		36–37	165–169 at 1 mm.	1.4537 (50°)	0.9273 (50°)	
Triethylene glycol carbonate	11	Mixture of monomer and dimer	Liq.				
Tetraethylene glycol carbonate	14	Exclusively monomer	42–44	128–130 at 1 mm.	1.4569 (50°)	1.1961 (50°)	
Decamethylene oxalate	14	Exclusively monomer	Liq.	125–126 at 0.2 mm.	1.4730 (20°)	1.0812 (20°)	
Undecamethylene oxalate	15	Exclusively monomer	23–24.5	120–123 at 0.5 mm.	1.4700 (25°)	1.0623 (25°)	
Decamethylene malonate	15	Exclusively monomer	Liq.	117–118 at 0.5 mm.	1.4695 (20°)	1.0599 (20°)	
Decamethylene succinate	16	Almost exclusively dimer; no monomer isolated					108–109
Ethylene sebacate	14	Almost exclusively dimer; trace of monomer isolated	40–41				80–81
Ethylene undecanedioate	15		35				143
Ethylene dodecanedioate	16	Almost exclusively dimer; no monomer isolated					95–96
Ethylene brassylate	17						145–146
Ethylene tetradecanedioate	18						102–103
Trimethylene sebacate	15						108–110
Self ester of ω-hydroxypentadecanoic acid	16	Almost exclusively dimer; odor of monomer	31–32[a]				83–84

[a] Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

diethylene and triethylene glycols. The fact that these compounds are lacking in crucial physical properties (*e. g.*, sharply characteristic melting points) makes it unnecessary to describe them individually. They are all insoluble in water and soluble in certain organic solvents such as chloroform. They separate from solvents in the form of soft powders (microcrystalline). The molten polyesters are very viscous liquids which crystallize on cooling in the form of small radiating clusters of microscopic needles or spherulites and finally solidify to more or less hard, tough waxes. The polymeric carbonate derived from triethylene glycol, however, failed to solidify and was obtained only as a thick sirup.

The general method of preparation used for the new polycarbonates was the same as that already described,[11] but, on account of the boiling points involved, dibutyl carbonate was found to be a more convenient source of the acid radical than diethyl carbonate. To the mixture of glycol and alkyl carbonate a small amount of sodium was added; the mixture was heated at 170–220° until the distillation of alcohol ceased, and removal of the alcohol was completed by continuing the heating for two hours or more in vacuum. The residue was usually depolymerized without any purification. The alkylene oxalates and malonates were prepared from the glycols and the diethyl esters of the acids in the same manner as the carbonates. The other esters were prepared directly from the acids and the glycols.

Depolymerization.—The apparatus used in the depolymerizations for which data are listed in Table I consisted simply of a 250-cc. Pyrex suction filter flask. Through a rubber stopper in the neck of the flask was inserted a test-tube about 1.5 cm. in diameter. Its bottom was about 3 cm. distant from the bottom of the flask. The outside of this test-tube served as the condenser and receiver; the inside was cooled with a stream of tap water (in some cases a mixture of solid carbon dioxide and acetone); the distillate collected on the outside. At intervals the test-tube was removed and the solid or pasty distillate was scraped from it. When the distillate was sufficiently fluid to flow, a small glass thimble was hung on the end of the test-tube to catch the drip.

The side-tube of the flask was connected to a vacuum line. This line was connected to an oil pump and the pressure in the line was about 0.1 to 2 mm. No attempt was made to secure an exceedingly high vacuum. The flask was immersed to a depth of about 2 cm. in a metal bath which was kept at 210–240° by means of an electric heater.

Nature of the Depolymerization Products.—For the sake of completeness Table I includes the physical constants of ethylene and trimethylene carbonates. The former, a 5-atom ring, is known only as the monomer; the latter, which has a unit length of 6 atoms, can be obtained either as monomer or polymer, but the polymer depolymerizes so rapidly and smoothly on distillation that the use of a molecular still is quite unnecessary.[11]

The rest of the compounds listed in Table I are obtained by the ordinary methods of preparation only as linear polyesters; and the polyesters were all depolymerized in the apparatus and under the conditions described above.

The behavior of tetramethylene carbonate (7-atom unit) was exceptional: the distillate was found to contain a considerable amount of tetrahydrofuran, which obviously might arise by the loss of carbon dioxide from the structural unit. The chief product, however, was the dimer, a 14-membered ring which has already been described.[11] No detectable amount of monomeric ester was formed. The products from the next five members of the series (unit lengths 8 to 12 atoms) also were chiefly dimeric. Pentamethylene carbonate (8-atom unit) gave no detectable amount of monomer. The presence of some monomer in the distillate from hexamethylene carbonate was inferred from the odor, but the attempt to obtain isolable amounts of monomer by carrying out the depolymerization in ordinary distillation equipment gave only indefinite unsaturated products. The odors of the distillates from heptamethylene, octamethylene and nonamethylene carbonates also indicated the presence of monomer, and in the last two of these cases monomer was actually isolated and identified when the depolymerization was carried out in ordinary distillation equipment.

The next member of the series, decamethylene carbonate, showed a sharp change in the nature of the depolymerization products: considerable amounts of the monomer were formed even in the molecular still. Undecamethylene carbonate (14-atom unit) behaved similarly. Beyond this point the ratio was reversed: dodecamethylene carbonate (15-atom unit) gave only a small amount of dimer, and with higher members of the carbonate series the isolated products were exclusively monomeric.

The oxalates (decamethylene and undecamethylene) showed a greater tendency to yield monomers than did the carbonates of the same unit length. Decamethylene malonate also gave almost exclusively the monomer.

The rest of the compounds listed in Table I, compared with the carbonates, exhibited a peculiar reluctance toward the formation of monomers. Even ethylene tetradecanedioate yielded a 36-membered dimer and no appreciable amount of the 18-membered monomer. Similarly ω-hydroxypentadecanoic acid yielded the 32-membered dimer instead of the 18-membered monomer which has already been obtained by oxidation of the corresponding cyclic ketone.[12] It should be added that the depolymerization of all the esters referred to in this paragraph is especially slow and difficult. Depolymerization of carbonates, oxalates, and even malonates, proceeds much more rapidly and completely.

Effect of Conditions on the Ratio of Monomer to Dimer.—The data on the carbonates listed in Table I indicate that polyesters of this series on depolymerization yield dimers almost exclusively when the unit length is 7 to 12 inclusive, both monomer and dimer when the unit length is 13 and 14, and monomers almost exclusively when the unit length is more than 14. It will be shown later that this characteristic change in the

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(12) Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

nature of the products under a given set of conditions is probably due to stereochemical factors inherently associated with the structure of the cyclic esters. It is also true, however, that the ratio of monomer to dimer can be controlled within certain limits by the experimental conditions. Thus octamethylene and nonamethylene carbonates in the modified molecular still yield almost exclusively the cyclic dimers, but when the depolymerization is conducted in an ordinary distilling flask the product is almost entirely the monomer. The distilling flask (unlike the molecular still) permits refluxing, so that while most of the monomer escapes most of the dimer is returned to the residue, where it is either cracked to monomer or converted to higher polymer. Limitations of this method of experimental control are indicated by the fact that when it was applied to hexamethylene carbonate no smooth depolymerization occurred and only indefinite unsaturated products were obtained. Esters of dibasic acids above malonic also depolymerize very slowly if at all in an ordinary distilling flask.

The depolymerization of polymeric decamethylene carbonate in an ordinary distilling flask gave a much higher yield of monomer than dimer and the examination of a large sample of crude product showed the presence of a by-product, decen-9-ol-1, $CH_2{=}CH(CH_2)_7CH_2OH$. The following data are typical.

The depolymerization was conducted in ordinary distilling flasks in batches of various sizes up to 100 g. and at (bath) temperatures up to 290°. The product was a mixture of colorless liquid and crystalline material. The crystals (a mixture of dimeric carbonate and decamethylene glycol) were removed by filtration, and the filtrate (2425 g.) was distilled, yielding 1276 g. of pure monomer, 400 g. of crystalline residue (chiefly dimer) and 742 g. of low-boiling material. The latter by redistillation was separated into four fractions of which the two largest were: A, b. p. 76–81° (2 mm.), 81%, and B, b. p. 87–89° (2 mm.), 9%. The latter was practically pure monomer. Analytical data for B indicated that it was a mixture of decamethylene carbonate (monomer) and decenol (apparently a constant-boiling mixture). The ester was destroyed by saponification with alcoholic sodium hydroxide, and the recovered alcohol was purified by distillation.

Decen-9-ol-1.—B. p. 85–86° (2 mm.); n_D^{20} 1.4480; d_4^{20} 0.8446; M_D calcd., 49.53; M_D found, 49.45.

Anal. Calcd. for $C_9H_{18}O$: C, 76.9; H, 12.8. Found: C, 76.51; H, 13.09.

Its structure was established by the fact that it was oxidized to azelaic acid by neutral aqueous permanganate (in one experiment a small amount of suberic acid was found) and hydrogenated to decanol-1 which was identified by comparison of the phenylurethan with a known specimen (crys. from 80% alcohol, m. p. 61–62°).

Decen-9-ol-1 yields a phenylurethan of m. p. 49–50° (crys. from 80% alcohol).

Polymerization of Macrocyclic Esters.—Macrocyclic esters, unlike 6-membered cyclic esters,[11] show no tendency to polymerize spontaneously. They do, however, polymerize at elevated temperatures especially in the presence of catalysts for ester-interchange, and the following observations are typical.

TABLE II

ANALYSIS OF CYCLIC ESTERS

Compound	Calculated, %			Found, %		
	C	H	Mol. Wt.	C	H	Mol. wt. in freezing benzene
Pentamethylene carbonate *dimer* $[-(CH_2)_5OCOO-]_2$	55.4	7.7	260	55.4	8.3	258 (b. p.)
Hexamethylene carbonate *dimer* $[-(CH_2)_6OCOO-]_2$	58.3	8.3	288	58.2	8.4	284 286
Heptamethylene carbonate *dimer* $[-(CH_2)_7OCOO-]_2$	60.8	8.9	316	61.2	8.9	313 312 (b. p.)
Octamethylene carbonate *monomer* $[-(CH_2)_8OCOO-]$	62.8	9.3	172	62.2	9.4	174
Octamethylene carbonate *dimer* $[-(CH_2)_8OCOO-]_2$	62.8	9.3	344	63.2	9.6	325 329 (b. p.)
Nonamethylene carbonate *monomer* $[-(CH_2)_9OCOO-]$	64.5	9.7	186	64.8	9.9	171
Nonamethylene carbonate *dimer* $[-(CH_2)_9OCOO-]_2$	64.5	9.7	372	64.6	9.7	330 329 (b. p.)
Decamethylene carbonate *monomer* $[-(CH_2)_{10}OCOO-]$	66.0	10.0	200	66.3	10.1	216 204
Decamethylene carbonate *dimer* $[-(CH_2)_{10}OCOO-]_2$	66.0	10.0	400	66.4	10.1	395 391
Undecamethylene carbonate *monomer* $[-(CH_2)_{11}OCOO-]$	67.3	10.3	214	67.5	10.3	213 211
Undecamethylene carbonate *dimer* $[-(CH_2)_{11}OCOO-]_2$	67.3	10.3	428	67.2	10.4	400 409
Dodecamethylene carbonate *monomer* $[-(CH_2)_{12}OCOO-]$	68.4	10.5	228	68.2	10.6	249 223
Dodecamethylene carbonate *dimer* $[-(CH_2)_{12}OCOO-]_2$	68.4	10.5	456	68.2	10.4	
Tridecamethylene carbonate *monomer* $[-(CH_2)_{13}OCOO-]$	69.4	10.7	242	69.2	10.5	265 238
Tetradecamethylene carbonate *monomer* $[-(CH_2)_{14}OCOO-]$	70.3	10.9	256	69.6	10.9	242 242
Octadecamethylene carbonate *monomer* $[-(CH_2)_{18}OCOO-]$	73.1	11.5	312	73.3	11.8	268 273 (b. p.)
Triethylene glycol carbonate $[-(CH_2CH_2O)_3COO-]_n$ probably mixture of monomer and dimer	47.7	6.8	$(176)n$	47.6	6.8	266 284 (b. p.)
Tetraethylene glycol carbonate *monomer* $[-(CH_2CH_2O)_4COO-]$	49.1	7.3	220	48.9	7.3	216 211
Decamethylene oxalate *monomer* $[-(CH_2)_{10}OCOCOO-]$	63.2	8.8	228	63.4	8.7	220 222
Undecamethylene oxalate *monomer* $[-(CH_2)_{11}OCOCOO-]$	64.5	9.1	242	64.4	9.1	253
Decamethylene malonate *monomer* $[-(CH_2)_{10}OCOCH_2COO-]$	64.5	9.1	242	64.5	9.1	238
Decamethylene succinate *dimer* $[-(CH_2)_{10}OCOCH_2CH_2COO-]_2$	65.6	9.4	512	65.4	9.3	478
Ethylene sebacate *monomer* $[-(CH_2)_2OCO(CH_2)_8COO-]$	63.1	8.9	228	63.1	8.9	
Ethylene sebacate *dimer* $[-(CH_2)_2OCO(CH_2)_8COO-]_2$	63.1	8.9	456	63.3	9.0	431 433 (b. p.)
Ethylene 1,11-undecanedioate *monomer* $[-(CH_2)_2OCO(CH_2)_9COO-]$	64.5	9.1	242	64.2	9.4	
Ethylene 1,11-undecanedioate *dimer* $[-(CH_2)_2OCO(CH_2)_9COO-]_2$	64.5	9.1	484	64.3	9.3	451 (b. p.)
Ethylene 1,12-dodecanedioate *dimer* $[-(CH_2)_2OCO(CH_2)_{10}COO-]_2$	65.6	9.4	512	65.6	9.4	481 (b. p.)
Ethylene brassylate *dimer* $[-(CH_2)_2OCO(CH_2)_{11}COO-]_2$	66.7	9.6	540	66.7	9.6	494 (b. p.)
Ethylene 1,14-tetradecanedioate *dimer* $[-(CH_2)_2OCO(CH_2)_{12}COO-]_2$	67.6	9.6	568	67.6	9.5	
Trimethylene sebacate *dimer* $[-(CH_2)_3OCO(CH_2)_8COO-]_2$	64.5	9.1	484	63.8	9.2	
Self-ester of ω-hydroxypentadecanoic acid *dimer* $[-(CH_2)_{14}COO-]_2$	75.0	11.7	480	75.0	11.8	

Small samples of monomeric decamethylene, dodecamethylene, tridecamethylene, and tetradecamethylene carbonates were heated for twenty hours at 200° together with parallel samples each containing a trace of potassium carbonate. The uncatalyzed samples of tridecamethylene and tetradecamethylene carbonates showed a considerable increase in viscosity; the decamethylene and dodecamethylene carbonates a much larger increase. The catalyzed samples of decamethylene and dodecamethylene carbonates were completely changed to solid, waxy polymers; while the catalyzed samples of the other two esters were still semi-solid.

Samples of dimeric hexamethylene and decamethylene carbonates, both with and without traces of potassium carbonate, were heated for eight hours at 200°. The catalyzed samples changed to very viscous liquids which solidified to hard waxes; the uncatalyzed samples were unchanged.

Summary

By heating linear polyesters with catalysts under certain conditions it is possible in many cases to bring about a smooth depolymerization to the corresponding monomeric and/or dimeric esters. This method makes it possible for the first time to prepare macrocyclic esters in good yields. Thirty new macrocyclic esters are described, mostly esters of dibasic acids. The cyclic carbonates and oxalates are obtained most easily. The ratio in which the two forms, monomer and dimer, are obtained is determined in part by the experimental conditions and in part by the nature of the ester—especially by its unit length. Monomers of 7 to 12 atoms are especially difficult to obtain.

WILMINGTON, DELAWARE

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Studies of Polymerization and Ring Formation. XXI. Physical Properties of Macrocyclic Esters and Anhydrides. New Types of Synthetic Musks

BY JULIAN W. HILL AND WALLACE H. CAROTHERS

Odors.—The monomeric cyclic anhydrides and cyclic esters described in the two preceding papers have highly characteristic odors. In particular some of the higher members have odors closely resembling musk. This observation is especially interesting because of the bearing of odor on the general problem of macrocyclic compounds.

The essential principles of musk and civet are the macrocyclic ketones I and II. Ruzicka's demonstration[1] of this fact was followed by the discovery[2] that the lactones III and IV are odorous principles of angelica oil and musk-seed oil. These materials are highly valued as perfume ingredients. In spite of the great difficulties involved in their synthesis, a

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[1] Ruzicka, *Helv. Chim. Acta*, **9**, 230, 716, 1008 (1926).

[2] Kerschbaum, *Ber.*, **60**, 902 (1927); Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).