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## Macrocyclic Esters<sup>1</sup>

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The depolymerization of linear polyesters derived from carbonic oxalic, or malonic acid to the corresponding cyclic monomers and dimers proceeds smoothly and rapidly in the presence of alkaline catalysts,<sup>2</sup> but the same conditions give very poor results when applied to polyesters derived from succinic acid or from higher acids of the series. We have, however, now found a number of catalysts that act effectively in these cases. The result is a considerable extension of the useful range of the interchange method in the preparation of macrocyclic esters. Since  $n$  different glycols and an equal number of dibasic acids may give  $2n^2$  different cyclic monomers and dimers, the number of possible compounds is very large. In this paper, we describe thirty-six new macrocyclic esters. Their properties are listed in Table I and are discussed in a later paragraph. Details of procedure are presented in the Experimental Part, but points of essential importance are as follows.

The depolymerizations are carried out in the glass apparatus depicted in Fig. 1.<sup>3</sup> The outer flask contains a liquid whose refluxing vapors heat the inner chamber where the depolymerization occurs. This makes it possible to control the temperature very exactly and ensures an adequate heat input. The optimum temperature appears to lie in the neighborhood of 270°; the pressure should be about 1 mm. or lower. Materials that act as effective catalysts with esters from higher acids are  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnCO}_3$ ,  $\text{MgO}$ ,  $\text{MgCO}_3$  and  $\text{Mg}$  powder.

By way of specific example, it may be mentioned that 20 g. of polymeric hexamethylene sebacate with 0.2 g. of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , in two hours gave 15 g. of distillate from which 11.4 g. of pure crystalline monomer was isolated. In the preparation of other esters listed in Table I, the crude yields generally ranged from 40 to 85%, while in favorable cases the yields of pure monomers approached 70%. Presumably both monomers and dimers are always present in the crude depoly-

merizate. In fact, for unit lengths of 8, 9, 10 and 11, the dimers tend to predominate whereas for unit lengths above 13 very little dimer, if any, is ordinarily isolated. The ratio of dimer to monomer can be controlled within certain limits since if refluxing in the depolymerization vessel is permitted relatively little dimer can escape.

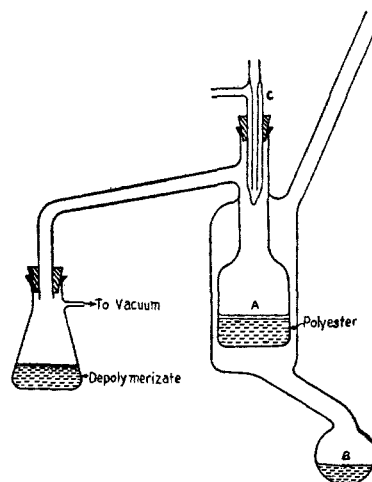


Fig. 1.—Apparatus for depolymerizing.

**Physical Properties.**—The molecular refractions of large rings are generally considerably less than the calculated values,<sup>4</sup> the depressions commonly ranging from about 0.4 to 0.7. This peculiarity is, however, for the most part restricted to rings of 8 to 15 atoms, and some of the largest rings (*e. g.*, 30–34 members) even show considerable exaltations.<sup>4</sup> In Table I molecular refractions for 26 new macrocyclic esters are listed. The average depression is 0.32. The values fluctuate rather widely, and this may be due in part to experimental error since the measurements had to be made at a relatively high temperature. It must, however, be regarded as a significant fact that, in general, the largest depressions are found for the smaller rings (9 to 14 atoms) where the strains or interferences of the peripheral atoms are greatest, while depressions very close

(1) Paper XXV on Polymerization and Ring Formation; Paper XXIV, THIS JOURNAL, **57**, 925 (1935).

(2) Hill and Carothers, *ibid.*, **55**, 5031 (1933).

(3) This design was suggested to us by Mr. C. H. Greenwalt.

(4) Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928); Ruzicka, Stoll, Huyser and Boekenoogen, *ibid.*, **13**, 1152 (1930); Ruzicka and Boekenoogen, *ibid.*, **14**, 1319 (1931); Ruzicka, Hürbin, and Furter, *ibid.*, **17**, 78 (1934); Hill and Carothers THIS JOURNAL, **55**, 5042 (1933).

to zero are found only in three cases. These are listed below together with one of the cyclic carbonates<sup>5</sup> which shows a similar peculiarity.

Ring size	Formula	$\Delta M_D$
21	$\text{---O(CH}_2\text{)}_{18}\text{OCO---}$	+0.01
20	$\text{---O(CH}_2\text{)}_{14}\text{OCO(CH}_2\text{)}_2\text{CO---}$	.00
16	$\text{---(OCH}_2\text{CH}_2\text{)}_3\text{OCO(CH}_2\text{)}_4\text{CO---}$	-.09
17	$\text{---(OCH}_2\text{CH}_2\text{)}_2\text{OCO(CH}_2\text{)}_8\text{CO---}$	+ .03

The first two of these are larger rings than any other esters for which values are available. The other two have in the ring extra oxygens which are capable of relieving steric interferences.<sup>6</sup>

Densities of the new esters for which values are available are plotted in Fig. 2. The curve shows no maximum, and the densities of isomers lie quite close together.

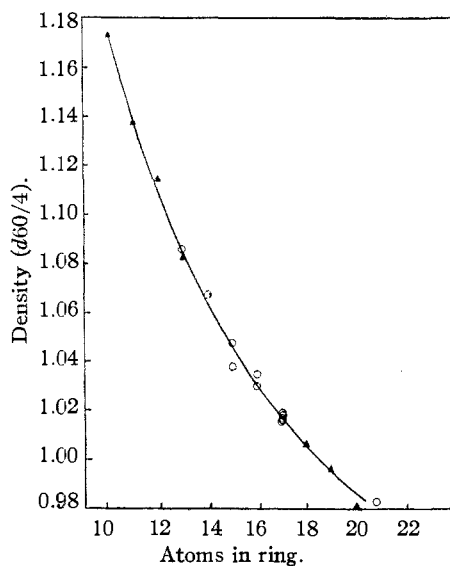


Fig. 2.—Densities ( $d_{60}^4$ ) of cyclic esters:  $\blacktriangle$ , succinates;  $\circ$ , other cyclic esters.

The odors of the macrocyclic esters are especially interesting, but characterizations are not sufficiently exact to justify a detailed discussion. It may be pointed out, however, that Table I includes 3 new rings of 14 atoms, 3 of 15, 4 of 16, 7 of 17, 2 of 18, and one each of 19 and 20 atoms. Those of 18, 19 and 20 atoms are practically odorless; the odors most prominent in the others are woody or cedary, earthy, camphoraceous and musk-like. The musk-like odor is very pronounced in all of the 17-atom rings.

(5) THIS JOURNAL, **55**, 5042 (1933).

(6) Hill and Carothers, *ibid.*, **57**, 925 (1935); **55**, 5049 (1933).

Data on melting points are rather incomplete, but here, as in the series previously examined, there is little to indicate any regular relation between ring size and melting point. Values for succinates are shown in Fig. 3. As the ring

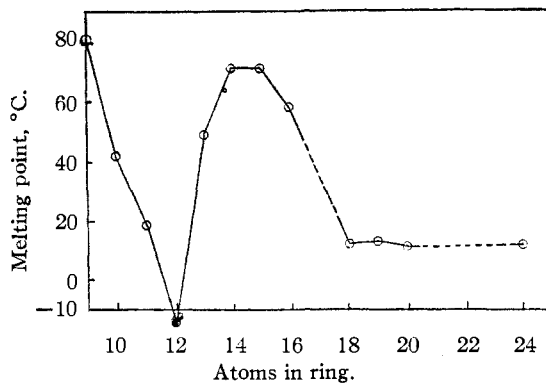


Fig. 3.—Melting points of monomeric alkylene succinates.

size increases, the melting point first falls to a minimum, then it rises to a maximum, falls again, and becomes almost constant. The isomeric 17-membered rings have the general formula  $\text{---OCO(CH}_2\text{)}_n\text{COO(CH}_2\text{)}_m\text{---}$  where  $n = 17 - (m + 4)$ . The melting points for various values of  $n$  are

$n$ .....	3	4	6	7	8	11
M. p., °C.	14	26	47	59	37	-8

**Ease of Ring Formation.**—As measured by yields, it has been found for every series thus far examined that rings of 9 to 12 atoms are more difficult to form than rings of 15 to 20 atoms. Stoll and Stoll-Comte<sup>7</sup> have suggested that this is due to a type of steric hindrance caused by mutual repulsions of peripheral hydrogens which are crowded against one another in rings of intermediate sizes. The position of the minimum in the yield *vs.* ring-size curve is not the same in different series. For cyclic ketones it lies at 10 to 11 atoms; for esters derived from dibasic acids, it apparently lies at 7 to 8 atoms. At any rate, monomers of this size have not yet been obtained among the dibasic esters, while, for example, the 7-atom lactone is obtained as a major primary product from  $\epsilon$ -hydroxycaproic acid.<sup>8</sup>

Another point of interest is that in the intermediate range odd-membered rings are relatively more difficult to produce than the adjacent even

(7) Stoll and Stoll-Comte, *Helv. Chim. Acta*, **13**, 1185 (1930).

(8) Van Natta, Hill and Carothers, THIS JOURNAL, **56**, 455 (1934).

TABLE I  
 PROPERTIES OF CYCLIC ESTERS

Cyclic ester	Number of atoms in monomeric ring	M. p. of monomer	B. p. of monomer °C. Mm.	Density of monomer $d_4^{20}$	Refractive index of monomer $n_D^{20}$	Mol. ref. $M_D$		Diff. $EM_D$	M. p. of dimer
						Obsd.	Calcd.		
Ethylene succinate	8								131
Trimethylene succinate	9	81	94-100 2						138
Tetramethylene succinate	10	42	95- 96 2	1.1732	1.4567	39.91	40.56	-0.65	121
Pentamethylene succinate	11	19	88- 89 1	1.1373	1.4583	44.66	45.16	- .50	87
Hexamethylene succinate	12	-15	108-110 2	1.1140	1.4606	49.21	49.77	- .56	110
Heptamethylene succinate	13	49	116-118 1-2	1.0821	1.4576	53.92	54.37	- .45	86
Octamethylene succinate	14	71		1.0540 (80°)	1.4528 (80°)	58.46	58.97	- .51	109
Nonamethylene succinate	15	71		1.0357 (80°)	1.4529 (80°)	63.15	63.58	- .43	
Decamethylene succinate	16	58	135-140 2	1.0308	1.4592	67.91	68.18	- .27	109 <sup>d</sup>
Dodecamethylene succinate	18	12	156-159 2	1.0060	1.4588	77.14	77.38	- .24	
Tridecamethylene succinate	19	13	154 1-2	0.9958	1.4579	81.62	81.99	- .37	
Tetradecamethylene succinate	20	11	167 2	0.9807	1.4568	86.59	86.59	.00	
Octadecamethylene succinate	24	13	199-201 2		1.4553				
Decamethylene glutarate	17	14	136-139 1	1.0168	1.4585	72.51	72.78	- .27	
Hexamethylene adipate	14	70	117 2	1.0535 (80°)	1.4542 (80°)	58.64	58.97	- .33	
Triethylene glycol adipate	16	59	162 2	1.1289 (80°)	1.4545 (80°)	64.35	64.44	- .09	
Nonamethylene adipate	17	26	144-146 2	1.0186	1.4594	72.53	72.78	- .25	
Heptamethylene suberate	17	47	158-160 1-2	1.0188	1.4592	72.46	72.78	- .32	
Ethylene azelate	13	52		1.0851	1.4593	53.96	54.37	- .41	145
Tetramethylene azelate	15	9	123-124 2	1.0471	1.4595	63.23	63.58	- .35	
Hexamethylene azelate	17	59		1.0032 (80°)	1.4520 (80°)	73.59	72.78	- .19	
Ethylene sebacate	14	42 <sup>a</sup>	119-123 2	1.0669	1.4599	58.51	58.97	- .46	81 <sup>a</sup>
Trimethylene sebacate	15	7	130-133 2	1.0372	1.4560	63.43	63.58	- .15	110 <sup>a</sup>
Tetramethylene sebacate	16	6	136-138 2	1.0344	1.4605	67.84	68.18	- .34	
Pentamethylene sebacate	17	37	159-160 2	1.0176	1.4594	72.60	72.78	- .18	
Diethylene glycol sebacate	17	15	156-157 2	1.0635	1.4586	69.89	69.86	+ .03	
Hexamethylene sebacate	18	47		1.0053	1.4589	77.20	77.38	- .18	
Ethylene decamethylene dicarboxylate	16	18	139-141 2	1.0303	1.4588	67.89	68.18	- .29	96 <sup>a</sup>
Ethylene brassylate	17	- 8	139-142 1	1.0180	1.4582	72.38	72.78	- .40	146 <sup>a</sup>
Decamethylene octadecanedioate	30	60			1.4576			Av. -0.32	

<sup>a</sup> Previously reported in THIS JOURNAL, 55, 5034 (1933).

ones. An alternating effect of this kind was first observed in the dibasic acid anhydride series.<sup>9</sup> Although rings of 8, 10 and 12 atoms were formed, those of 9, 11 and 13 atoms were not (the corresponding dimers were formed instead). More recently, an alternation in yield of cyclic ketones in passing from one member to the next has also been observed by Ziegler and Aurnhammer<sup>10</sup> in syntheses by the dilution method. The type of alternation observed in the present study is illustrated by Fig. 4 where the yield of dimer is plotted against unit length for glycol esters of succinic acid. The material not dimer is mostly monomer, and so by inverting the ordinate scale, a rough plot of monomer yield is obtained. The alternating effect is more clearly brought out by the inset of Fig. 4 which shows the rate of change of dimer yield with increasing unit length. One is tempted to compare this behavior with the well-known alternation in physical properties of certain series of open chain compounds, but the responsible factors are probably quite different in the two cases. Examination of models (with large hydro-

gens) shows that the interferences to ring closure in chains of 9 to about 13 atoms appear to be

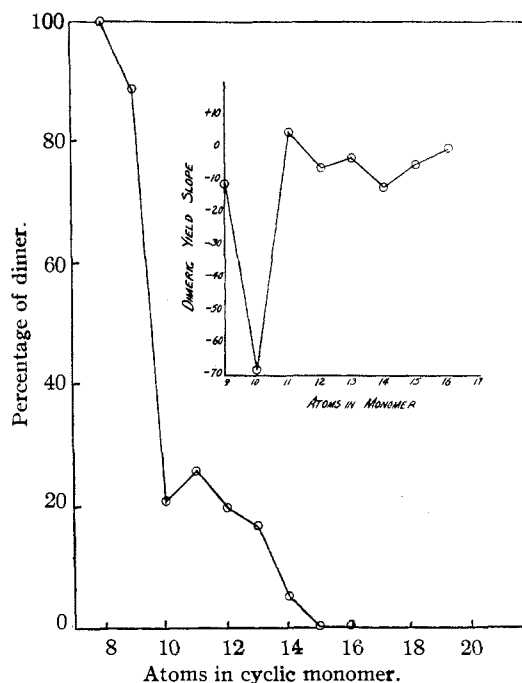


Fig. 4.—Yield vs. ring size in the preparation of alkylene succinates.

(9) Hill and Carothers, THIS JOURNAL, 55, 5025 (1933).

(10) Ziegler and Aurnhammer, Ann., 513, 43 (1934).

greater for the odd members,<sup>11</sup> and it is probable that these interferences are still operative after the chains are closed so that the odd-membered rings are less stable than the even ones.

Since the rates at which different rings are formed are sure to be differently affected by changes in conditions, the inherent relative ease of ring formation is a concept to which no quantitative significance can be attached. Nevertheless, the effect of structure and particularly of chain length is so pronounced that even crude data permit a qualitative comparison of the inherent relative ease of forming rings of different sizes. A comparison of this kind for glycol esters of dibasic acids is shown in Fig. 5, and it includes a similar plot for the stability of cyclic anhydrides. Ease of ring formation and stability will, in general, run parallel, but 6-membered cyclic esters furnish a notable exception to this rule. They are both more easily formed and less stable than larger ester rings.

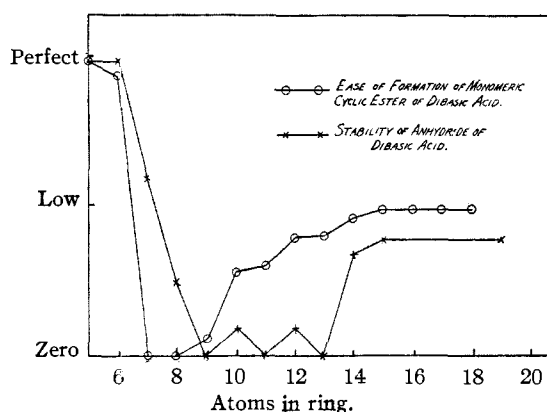


Fig. 5.—Ease of formation and stability vs. ring size.

**Methods of Ring Formation.**—For the synthesis of large rings, there are now available two methods based upon rational principles: the dilution method first explicitly formulated and applied by Ruggli in 1912<sup>12</sup> and the interchange method described above.

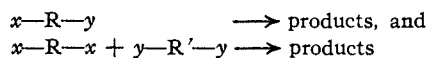
Ruggli's dilution method was cited in early papers of this series<sup>13</sup> where the general theory of bifunctional reactions was developed, but it received no further published attention until very recently. Ziegler and his co-workers<sup>14</sup> have now applied it in a very ingenious fashion to the synthesis of cyclic ketones in good yields, and further

successful applications have been made by various investigators to the preparation of macrocyclic amides,<sup>15</sup> imines<sup>16</sup> and lactones.<sup>17</sup>

In a recent discussion of ring formation,<sup>18</sup> Ziegler suggests that the interchange method will be severely restricted in the range of its applicability. On the contrary, as we have shown in this and the preceding paper, it presents extensive possibilities, and it may be appropriate to point out some of the peculiar advantages of this method.

It is true, of course, that the interchange method is inherently restricted to reversible bifunctional condensations, but almost all condensations are reversible to a certain extent. We have already presented some evidence<sup>19</sup> indicating that even polyketones can be depolymerized and that this is what is involved in Ruzicka's thorium salt method for the synthesis of large carbon rings. Practically, the interchange method will be restricted to those bifunctional condensations that are *easily* reversible, but, as the present paper shows, much can be accomplished in that direction by the choice of suitable catalysts, and the formation of esters and anhydrides by no means represents the limit of the possibilities.

One other point that deserves mention is this: there are two general types of bifunctional reactions symbolized in the two formulas



In the first type (simple bifunctional), both the mutually reactive groups are present on the same molecule; in the second (bibifunctional)<sup>18</sup> the mutually reactive groups are initially present on separate molecules. An example of the first type is an hydroxy acid, of the second type, a dibasic acid plus a glycol. The second type is much the more numerous, and it is one to which the theoretical advantages of the dilution method are not applicable with full efficiency since the initial step toward ring formation necessarily involves an intermolecular reaction. Practical advantages of the interchange method in connection with such problems as the preparation of lactones and *p*-rings will be illustrated in future papers.

(15) Reid and Lippert, St. Petersburg Meeting of the A. C. S., March, 1934.

(16) Salomon, *Helv. Chim. Acta.*, **17**, 851 (1934); Ruzicka, Salomon and Meyer, *ibid.*, **17**, 882 (1934).

(17) Stoll, Rouvé and Stoll-Comte, *ibid.*, **17**, 1289 (1934).

(18) Ziegler, *Ber.*, **67**, 139 (1934).

(19) *THIS JOURNAL*, **55**, 5045 (1933).

(11) Hill and Carothers, *THIS JOURNAL*, **55**, 5050 (1933).

(12) Ruggli, *Ann.*, **392**, 92 (1912).

(13) *E. g.*, *THIS JOURNAL*, **51**, 2551 (1929).

(14) Ziegler, Eberle and Ohlinger, *Ann.*, **504**, 94 (1933); Ziegler and Aurnhammer, *ibid.*, **513**, 43 (1934).

TABLE II  
 ANALYTICAL DATA FOR NEW CYCLIC ESTERS

Compound	Calculated		Mol. wt.	Found		Mol. wt. in freezing benzene	
	C, %	H, %		C, %	H, %		
Trimethylene succinate, Monomer	53.16	6.32	158	53.10	6.42	162	159
Trimethylene succinate, Dimer	53.16	6.32	316	53.52	6.45	270	
Tetramethylene succinate, Monomer	55.81	6.97	172	55.56	6.76	170	166
Tetramethylene succinate, Dimer	55.81	6.97	344	56.33	6.87	332	
Pentamethylene succinate, Monomer	58.06	7.52	186	57.59	7.88	177	182
Pentamethylene succinate, Dimer	58.06	7.52	372	57.86	7.42	395	376
Hexamethylene succinate, Monomer	60.00	8.00	200	59.76	8.04	199	197
Hexamethylene succinate, Dimer	60.00	8.00	400	60.41	8.14	418	393
Heptamethylene succinate, Monomer	61.68	8.41	214	60.61	8.67	206	
Heptamethylene succinate, Dimer	61.68	8.41	428	61.91	8.82	428	
Octadecamethylene succinate, Monomer	63.15	8.77	228	63.32	8.76	228	228
Octadecamethylene succinate, Dimer	63.15	8.77	456	63.40	8.83	498	
Nonamethylene succinate, Monomer	64.46	9.09	242	64.04	9.08	236	229
Decamethylene succinate, Monomer	65.62	9.37	256	65.36	9.35	250	246
Dodecamethylene succinate, Monomer	67.60	9.85	284	67.77	10.03	283	271
Tridecamethylene succinate, Monomer	68.45	10.06	298	68.98	10.27	290	277
Tetradecamethylene succinate, Monomer	69.23	10.25	312	69.24	10.20	314	300
Octadecamethylene succinate, Monomer	71.74	10.88	368	71.58	10.73	365	348
Decamethylene glutarate, Monomer	66.67	9.63	270	67.14	9.64	271	265
Hexamethylene adipate, Monomer	63.16	8.77	228	63.21	8.81	214	217
Triethylene glycol adipate, Monomer	54.96	8.39	262	55.26	7.74	283	275
Nonamethylene adipate, Monomer	66.67	9.63	270	66.54	9.10	266	256
Heptamethylene suberate, Monomer	66.67	9.63	270	66.92	9.79	272	269
Ethylene azelate, Monomer	62.15	8.41	214	61.93	8.25	216	212
Ethylene azelate, Dimer	62.15	8.41	428	62.13	8.81	466	431
Tetramethylene azelate, Monomer	64.46	9.09	242	64.55	9.21	244	234
Hexamethylene azelate, Monomer	66.67	9.63	270	66.98	9.44	260	269
Ethylene sebacate, Monomer			228			232	224
Trimethylene sebacate, Monomer	64.46	9.09	242	64.05	8.89	248	236
Tetramethylene sebacate, Monomer	65.62	9.37	256	65.55	9.58	268	254
Pentamethylene sebacate, Monomer	66.67	9.63	270	66.08	9.37	264	258
Diethylene glycol sebacate, Monomer	61.76	8.82	272	62.37	9.37	257	258
Hexamethylene sebacate, Monomer	67.60	9.85	284	67.41	9.75	260	256
Ethylene decamethylene dicarboxylate, Monomer	65.62	9.37	256	65.41	9.45	256	249
Ethylene brassylate, Monomer	66.67	9.63	220	66.88	9.93	242	252
Decamethylene octadecanedioate, Monomer	74.33	11.50	452	74.72	11.83	465	443

### Experimental Part

The apparatus used in the present work is shown in Fig. 1. The flask B contains a liquid whose refluxing vapors heat the chamber A. This method makes it possible to control the temperature very exactly and ensures an adequate heat input. The dephlegmator C may be cooled with steam if reflux is desired to restrict the distillation of dimer, or it may be omitted entirely. For amounts of polymer in the neighborhood of 50 g., the chamber A should be of about 800 cc. capacity since considerable foaming occurs at the start of the depolymerization.

Preliminary experiments were made with decamethylene carbonate using a sodium catalyst. The importance of low pressure was soon demonstrated, and in further work a pump with high capacity was used and the pressure kept at 1 mm. or below. The rate increased, but the purity of the distillate dropped off somewhat as the temperature was raised above 250°. A temperature of 270° appeared to be about the optimum, and it was conveniently supplied by boiling *o*-chlorodiphenyl. These observations were applied to the preparation of monomeric tetradeca-

methylene carbonate on a one hundred gram scale using an alkaline catalyst; a 93% yield of monomer having a purity of 97% was obtained in less than two hours.

These conditions, however, gave no satisfactory results with polyesters derived from higher dibasic acids, and attention was therefore turned to a further exploration of catalysts. The polyesters used were prepared from the appropriate dibasic acid and a slight excess of glycol by heating at 200° (bath) finally at a pressure of 2-3 mm. Products obtained in this manner were gray waxy masses of varying degrees of hardness. One of the first catalysts tried was stannous chloride, and the following results are typical.

Fifty grams of polymeric hexamethylene succinate with 0.5 g. of SnCl<sub>2</sub>·2H<sub>2</sub>O was heated at 270° at 1 mm. or less. The polymer became soft and bubbled, and after about ten minutes distillation started. The rates observed were: after fifteen minutes, 12 drops/min.; after thirty minutes, 14 drops/min. At this point the residue became a stiff porous gel occupying about half the volume of the flask, but distillation continued: after forty-five minutes,

10 drops/min.; after sixty minutes, 8 drops/min.; after seventy-five minutes, 3 drops/min. The ultimate residue was a light porous mass of tough, insoluble, yellow resin. The distillate (40 g.), consisting of a light yellow liquid and a white solid, was filtered. The solid on recrystallization from alcohol yielded 8 g. of dimer, white plates melting at 110°. Any catalyst present in the monomer was removed by dissolving the filtrate in ether and washing with water. The dried ether solution was concentrated and distilled. The yield of cyclic monomeric hexamethylene succinate boiling at 108–110° (2 mm.) was 21 g. This general procedure was used in isolating other cyclic esters except that when the monomer was a solid it was usually purified by crystallization from alcohol at low temperature. Yields of crude distillate varied from 40 to 85%.

For further study of catalysts, experiments were made with hexamethylene sebacate since its monomer is a readily purified crystalline solid. The polyester (20 g.) was heated with 0.2 g. of the possible catalyst in a glass still at 270° (1 mm.) for two hours. The crude distillate was dissolved in 50 cc. of alcohol, cooled, and the pure monomer isolated by filtration. Results are shown in Table III.

TABLE III  
CATALYSTS FOR DEPOLYMERIZATION

Catalyst	Distillate, %	Pure monomer, %
SnCl <sub>2</sub> ·2H <sub>2</sub> O	65	45
MnCl <sub>2</sub> ·4H <sub>2</sub> O	75	55
FeCl <sub>2</sub> ·4H <sub>2</sub> O	75	57
MgCl <sub>2</sub> ·6H <sub>2</sub> O	75	57
CoCl <sub>2</sub> ·6H <sub>2</sub> O	80	65
Co(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	70	55
Mg (powd.)	75	60
MnCO <sub>3</sub>	60	40
MgO	70	45
MgCO <sub>3</sub>	70	55
PbCl <sub>2</sub>	15	8
FeCl <sub>3</sub>	25	18
Ti <sub>2</sub> CO <sub>3</sub>	15	8
SbCl <sub>3</sub>	15	8
Th(NO <sub>3</sub> ) <sub>4</sub> ·12H <sub>2</sub> O	10	5
None (control)	5	...

The following substances were also tried but gave very small distillates, from which no monomer could be isolated: NiCl<sub>2</sub>·6H<sub>2</sub>O, FeSO<sub>4</sub>, TiCl<sub>4</sub>, tin dust, Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, CrCl<sub>3</sub>, CaCO<sub>3</sub>, CrCl<sub>2</sub>, ZnCl<sub>2</sub>.

Typical yields of cyclic esters obtained at 270°/1 mm. using 1 to 3% SnCl<sub>2</sub>·2H<sub>2</sub>O as catalyst are shown below.

TABLE IV  
YIELDS OF CYCLIC ESTERS

Ester	Unit length	Time, hrs.	Crude distillate, %	Distillate isolated as mono-mer, %	dimer, %
Ethylene succinate	8	4	80	0	95
Trimethylene succinate	9	4	46	9	89
Tetramethylene succinate	10	4	48	70	21
Pentamethylene succinate	11	4	77	46	26
Heptamethylene succinate	13	4	68	30	17
Octamethylene succinate	14	4	81	55	5
Nonamethylene succinate	15	4	84	83	0
Octadecamethylene succinate	24	6	60	76	0
Decamethylene glutarate	17	5	81	30	0
Nonamethylene adipate	17	3	75	48	0
Heptamethylene suberate	17	7	70	58	0
Ethylene azelate	13	4	68	79	4
Trimethylene sebacate	15	7	52	84	0
Tetramethylene sebacate	16	6	40	70	0
Pentamethylene sebacate	17	7	51	60	0
Hexamethylene sebacate	18	4	73	73	0
Diethylene glycol sebacate	17	5	67	81	0
Ethylene brassylate	17	4	72	58	0

Losses in purification are due in part to polymerization during redistillation, and these can be largely avoided by first washing out the catalyst. Considerable improvements can also be effected by suitable precautions in preparing the polymer.

#### Summary

The optimum conditions for the depolymerization of linear polyesters have been more clearly defined and new catalysts have been found which make it possible to apply this method generally to the rapid preparation of macrocyclic esters in good yields. Thirty-six new cyclic esters, monomeric and dimeric, derived from succinic acid and from other higher dibasic acids are described. Conclusions developed in the study of other macrocyclic compounds have been confirmed and extended.

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