Studies of Polymerization and Ring Formation. XIX.[1] Many-Membered Cyclic Anhydrides

By Julian W. Hill and Wallace H. Carothers

Terminology.—To clarify the text of subsequent papers the following definitions are presented. Some of the terms here defined were first introduced in previous papers of this series,[2] but they have not yet gained very wide currency, while in some cases they have been used in a sense different from that suggested.

Linear Polymers, e. g.

$$\dots-CH_2CH_2O-CH_2CH_2O-CH_2CH_2O-CH_2CH_2O-CH_2CH_2O-CH_2CH_2O-\dots$$
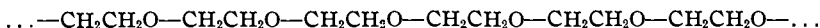
are those whose molecules are built up from a recurring bivalent radical or *structural unit*, e. g., —CH_2CH_2O—. Linear polymers are not necessarily open chains; they may be rings. *Superpolymers* are linear polymers having molecular weights above 10,000. The *unit length* is the number of atoms in the chain of the structural unit; in polyethylene glycol (or oxide) the unit length is three. *Macrocyclic compounds* are rings of more than seven atoms. *Monomers* are compounds containing only one structural unit; ethylene oxide and ethylene glycol are both monomers, since each has one —CH_2CH_2O— group. *Dimers* contain two units: dioxane and diethylene glycol are both dimers. *Bifunctional compounds* are chains bearing two groups capable of mutual reaction with the formation of a new bond. Bifunctional compounds always formally present two possibilities of self-reaction: *intramolecular* leading to ring closure, and *intermolecular* leading to chain formation.

Cyclic Anhydrides.—In previous papers, studies of adipic[3] and sebacic[4] anhydrides have been reported. The present paper describes the extension of these studies to the anhydrides of pimelic, suberic, azelaic, undecanedioic, dodecanedioic, brassylic, tetradecanedioic and octadecanedioic acids. The results closely resemble those already reported.

The anhydrides obtained by the action of acetic anhydride or acetyl chloride on the acids are linear polymers of the type formula —O—CO—R—CO—O—CO—R—CO—O—CO—R—CO—... These products are called α-anhydrides to distinguish them from other forms (β, γ, ω) that originate in other ways. They are very reactive, microcrystalline powders which are only slightly soluble in organic solvents and have molecular weights in the neighborhood of 3000 to 5000. They react with ani-

(1) An abstract of papers XIX, XX, XXI and XXII was presented at the Washington meeting of the American Chemical Society, March 28, 1933.

(2) Carothers, THIS JOURNAL, **51**, 2548 (1929); Carothers, *Chem. Rev.*, **8**, 353 (1931); Carothers and Hill, THIS JOURNAL, **54**, 1559 (1932).

(3) Hill, *ibid.*, **52**, 4110 (1930).

(4) Hill and Carothers, *ibid.*, **54**, 1569 (1932).

line to yield a mixture of the dianilide, the monoanilide, and the dibasic acid in the ratio 1:2:1.[3,4]   This reaction serves to distinguish any sort of polymeric dibasic acid anhydride from the cyclic monomer, which yields exclusively with monoanilide.

When the α-anhydrides are heated in a high vacuum with a condenser placed close to the evaporating surface (molecular still),[5] they undergo the transformations summarized in the following scheme:
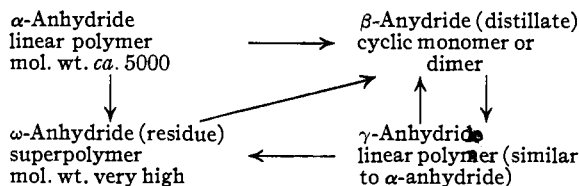
The α-anhydride yields β-anhydride and ω-anhydride simultaneously. As the β-anhydride collects on the condenser, the residue increases progressively in viscosity and molecular weight.   The resulting ω-anhydride when cold is a very tough, opaque, solid; it becomes transparent (melts) at a definite temperature without flowing; and at still higher temperatures it can be drawn into pliable, highly oriented fibers.[6]   The ω-anhydride depolymerizes just as the α-anhydride does, and if heating in the molecular still is continued long enough complete conversion to β-anhydride finally occurs.   The β-anhydrides on being heated or allowed to stand readily revert to a polymeric form, the γ-anhydride.   In their physical properties the γ-anhydrides are generally practically indistinguishable from the α-anhydrides.   However, the latter structurally are probably open chains terminated by acetyl groups while the former at least when freshly formed under anhydrous conditions are perhaps giant rings.[4]

Adipic anhydride differs from the higher homologs in that the α-anhydride depolymerizes relatively easily even in an ordinary distillation apparatus.   The other anhydrides differ from each other only in the nature of the volatile β-anhydride which they yield on depolymerization. The facts in this connection are shown in Table II.   It will be observed that those anhydrides whose unit lengths are 7, 8, 10, 12, 14, 15 and 19 yield monomeric β-anhydrides and that those whose unit lengths are 9, 11 and 13 yield only dimeric β-anhydrides.   These relations are represented graphically in Table I.

The three dimeric anhydrides (suberic, sebacic and dodecanedioic) are sharply crystalline solids sufficiently stable that their molecular weights can be determined cryoscopically in benzene.   When allowed to react with aniline they furnish the dibasic acid, its monoanilide, and its dianilide in

(5) Cf. Carothers and Hill, THIS JOURNAL, 54, 1557 (1932).   The Washburn type of still was used in this work.

(6) Carothers and Hill, ibid., 54, 1579 (1932).

TABLE I
NATURE AND STABILITY OF β-ANHYDRIDES

Dimers stable up to melting point	Unit length	Monomers Unstable	Extremely unstable
	7 ——(adipic)——→ 7		
	8 ——(pimelic)——————————————→ 8		
18 ←——(suberic)——— 9			
	10 ——(azelaic)——————————————→ 10		
22 ←——(sebacic)——— 11			
	12 ——(undecanedioic)——————————→ 12		
26 ←——(dodecanedioic)——— 13			
	14 ——(brassylic)——————→ 14		
	15 ——(tetradecanedioic)——→ 15		
	⋮		
	19 ——(octadecanedioic)——→ 19		

the ratio 1:2:1. When heated above their melting points the dimeric anhydrides polymerize almost instantly to γ-anhydrides.

The monomeric anhydrides are not sufficiently stable to permit cryoscopic molecular weight determinations, but their identity as monomers is established by the fact that they react with aniline to yield pure monoanilide. The first and last members of the series are low-melting crystalline solids; the others are all liquids.

The monomers show characteristic differences in stability. Adipic β-anhydride, the seven-membered ring, polymerized completely in about seven hours at 100° under rigorously anhydrous conditions and fairly rapidly at room temperature in the presence of traces of moisture. The 8-, 10- and 12-membered monomers polymerize so rapidly even at very low temperature that a special technique was required to demonstrate their temporary existence. When distilled in the molecular still onto a condenser cooled by tap water, they condensed as transparent fluid drops, which in the course of an hour or less became opaque, and in several hours set to hard waxes. Distillate collected under these conditions invariably contained polymer, since its reaction with aniline always yielded dianilide. In the method devised, the condenser was cooled by means of liquid air. At this temperature the monomers condensed as solids. When, after several hours, a sufficient quantity of distillate had collected, a small reservoir of aniline (Fig. 1) was connected with the vacuum system by opening a stopcock, and a layer of crystalline aniline was deposited by evaporation on top of the anhydride distillate. The condenser was then allowed to warm up gradually, and as soon as the aniline started to melt,

was quickly removed from the still and the lower part, bearing the distillate, was submerged in aniline. When the reaction was completed, the mixture was examined for dianilide and monoanilide.

When this method was applied to pimelic anhydride (8-atom unit) it yielded pure monoanilide. The next two members, azelaic and undecanedioic anhydrides (10- and 12-atom units) gave mixtures of acid, monoanilide and dianilide. However, the presence of some monomer in the distillate was established by the fact that the ratio of monoanilide was considerably higher than that required by the theory for dimer or other polymer. Moreover, when the condenser was operated at a higher temperature, these anhydrides first collected as transparent fluid drops with no evidence of the presence of crystalline mater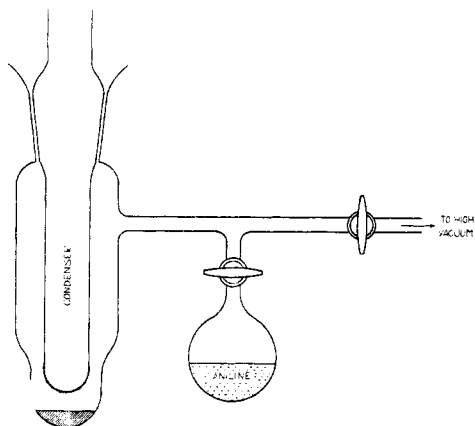ial (dimer). It seems very probable therefore that the distillates were initially pure monomers and that the presence of dianilide in the aniline reaction product was due to subsequent polymerization.

Fig. 1.

The next three members of the monomer series were much more stable than those of 10- and 12-atoms. Brassylic anhydride (14-atom unit) yielded pure monoanilide when the condenser was cooled with solid carbon dioxide and acetone. The liquid distillates from the 15- and 19-membered anhydrides (tetradecanedioic and octadecanedioic) when condensed at the temperature of tap water yielded pure monoanilide if allowed to react with aniline within a few hours of distillation. These two monomeric anhydrides, like that of adipic acid, could also be preserved for several days at room temperature without complete polymerization.

TABLE II

CYCLIC ANHYDRIDES

Acid	Structural unit of anhydride	Product of depolymerization and size of ring		Stability	M. p., °C.
Adipic	—OC(CH$_2$)$_4$CO—O—	Monomer	7	Unstable	20
Pimelic	—OC(CH$_2$)$_5$CO—O—	Monomer	8	Extremely unstable	Liq.
Suberic	—OC(CH$_2$)$_6$CO—O	Dimer	18	Stable up to m. p.	56–57
Azelaic	—OC(CH$_2$)$_7$CO—O	Monomer	10	Extremely unstable	Liq.
Sebacic	—OC(CH$_2$)$_8$CO—O	Dimer	22	Stable up to m. p.	68
Undecanedioic	—OC(CH$_2$)$_9$CO—O—	Monomer	12	Extremely unstable	Liq.
Dodecanedioic	—OC(CH$_2$)$_{10}$CO—O	Dimer	26	Stable up to m. p.	76–78
Brassylic	—OC(CH$_2$)$_{11}$CO—O—	Monomer	14	Unstable	Liq.
Tetradecanedioic	—OC(CH$_2$)$_{12}$CO—O—	Monomer	15	Unstable	Liq.
Octadecanedioic	—OC(CH$_2$)$_{16}$CO—O—	Monomer	19	Unstable	36–37

Experimental Part

Preparation of α-Anhydrides.—The α-anhydrides were prepared by the following method. A small quantity of the acid (5 to 20 g.) was refluxed with three parts by weight of acetic anhydride for four to six hours. In the case of the less soluble octadecanedioic acid six parts of acetic anhydride was used. The volatile material was distilled off under the vacuum of a water aspirator. The crude anhydrides were dissolved in hot dry benzene and precipitated, after filtration of the solutions, with petroleum ether. They were then preserved in a vacuum over potassium hydroxide, phosphorus pentoxide and paraffin. The α-anhydrides separate from solution as white microcrystalline powders. In the molten state they are very viscous liquids which crystallize on cooling in the form of small radiating clusters of microscopic needles and finally solidify to hard waxes.

TABLE III

ANALYTICAL DATA FOR α-POLYANHYDRIDES

α-Anhydride	Empirical formula	M. p., °C.	Calcd. C	Calcd. H	Found C		Found H	
Pimelic	$C_7H_{10}O_3$	53–55	59.11	7.11	...	...	...	...
Suberic	$C_8H_{12}O_3$	65–66	61.50	7.75	61.67	61.04	7.68	7.42
Azelaic	$C_9H_{14}O_3$	53–53.5	63.49	8.29	63.04	63.09	7.86	7.91
Undecanedioic	$C_{11}H_{18}O_3$	69–70	66.60	9.18	65.90	65.71	9.31	9.29
Dodecanedioic	$C_{12}H_{20}O_3$	86–87	67.86	9.52	66.88	67.01	9.63	9.84
Brassylic	$C_{13}H_{22}O_3$	76–78	68.97	9.81	68.80	68.98	9.96	10.05
Tetradecanedioic	$C_{14}H_{24}O_3$	89–91	69.94	10.08	69.17	69.32	9.94	9.79
Octadecanedioic	$C_{18}H_{32}O_3$	94–95	72.90	10.90	72.69	72.02	10.69	10.49

Reaction of the Anhydrides with Aniline.—A small sample of the anhydride (*ca.* 2 g.) was added to 5 to 10 cc. of aniline and triturated with a stirring rod until a smooth cream was formed. The mixture was then treated with 10% hydrochloric acid to dissolve the excess aniline, cooled and filtered. The mixtures derived from the anhydrides below undecanedioic were separated by treatment with boiling water, in which the dianilides are completely insoluble. The monoanilides separated from the filtrate on cooling. Sufficient water was used to keep the dibasic acids in solution. The separation of the mixtures from the anhydrides above sebacic was accomplished by means of dilute aqueous sodium hydroxide, which dissolved the monoanilide and the dibasic acids as sodium salts and left the dianilide. The monoanilide and the dibasic acid were precipitated from the filtered solution by acidification, and separated by means of boiling water. In the cases of tetradecanedioic and octadecanedioic anhydrides, the alkaline separation was carried out hot, as the sodium salts of these monoanilides are difficultly soluble in the cold. Up to and including undecanedioic α-anhydride, the dianilide was estimated quantitatively and in each case was obtained in 25% yield, as required by theory. A clean separation was difficult with the higher homologs as the alkaline solutions were increasingly soapy. The properties of the anilides are given in Table IV.

Depolymerization.—The molecular still (Fig. 1) used in these experiments was a cylindrical vessel, 18 cm. high and 5 cm. in diameter, with a rather flat curved bottom and an outlet to a high vacuum system. Into this vessel was fitted, by means of a large ground joint at the top, another cylinder 3 cm. in diameter, the rounded bottom of which was 3 cm. from the bottom of the larger vessel. This inner vessel constituted the condenser. A sample of α-anhydride was introduced into the outer vessel, the condenser was placed in position and the apparatus was evacuated by means of a mercury diffusion pump backed by a Hyvac oil pump. A trap cooled by solid carbon dioxide in acetone was placed in the system. The still was heated by means of a metal bath.

TABLE IV

MONOANILIDES

	M. p., °C.	Cryst. from	Empirical formula	Calcd. C	Calcd. H	Found C		Found H	
Pimelic	108–109	H₂O	$C_{18}H_{17}O_3N$	66.35	7.27	66.23		7.55	
Suberic	128–129	Benzene	$C_{14}H_{19}O_2N$	67.42	7.70	67.51		7.86	
Azelaic	107–108	Dil. EtOH	$C_{15}H_{21}O_3N$	68.39	8.05	68.05	68.32	7.89	8.02
Undecanedioic	112.5–113	50% EtOH	$C_{17}H_{25}O_3N$	70.06	8.65	70.28	70.10	8.94	9.03
Dodecanedioic	123	50% EtOH	$C_{18}H_{27}O_3N$	70.77	8.91	70.85	71.13	8.96	8.72
Brassylic	118.5–119.5	50% EtOH	$C_{19}H_{29}O_3N$	71.41	9.18	71.71	71.46	9.60	9.37
Tetradecanedioic	124–125	60% EtOH	$C_{20}H_{31}O_3N$	72.01	9.39	71.97	72.27	9.42	9.10
Octadecanedioic	128–129	60% EtOH	$C_{24}H_{39}O_3N$	73.98	10.10	74.15	74.09	10.02	9.92

DIANILIDES

	M. p., °C.	Cryst. from	Empirical formula	Calcd. C	Calcd. H	Found C		Found H	
Pimelic	155–156	MeOH–H₂O	$C_{19}H_{22}O_2N_2$	73.50	7.16	73.16		7.11	
Suberic	186–187	MeOH	$C_{20}H_{24}O_2N_2$	74.03	7.46	73.87	73.95	7.52	7.29
Azelaic	186–187	Xylene	$C_{21}H_{26}O_2N_2$	74.51	7.75	74.03		7.94	
Undecanedioic	160–161	EtOH	$C_{23}H_{30}O_2N_2$	75.35	8.27	75.44	75.32	8.28	8.44
Dodecanedioic	170–171	EtOH	$C_{24}H_{32}O_2N_2$	75.73	8.49	76.28	76.09	8.47	8.46
Brassylic	160–161	EtOH	$C_{25}H_{34}O_2N_2$	76.08	8.70	75.86	76.16	8.84	8.74
Tetradecanedioic	169.5–170	EtOH	$C_{26}H_{36}O_2N_2$	76.41	8.89	76.41		8.91	
Octadecanedioic	162–163	EtOH	$C_{30}H_{44}O_2N_2$	77.52	9.56	77.38	77.64	9.76	9.78

Pimelic Anhydride.—The α-anhydride was heated at 150°. The β-anhydride collected on the water-cooled condenser as a dew which solidified to a pasty gel in about one hour and to a hard wax overnight (γ-anhydride). The saponification equivalent of the wax was 70.7 [(C₇H₁₀O₃)ₙ requires 71.0]. The experiment was repeated with liquid air in the condenser and the heating bath at 125°. The heating was continued for six hours, after which the still was isolated from the vacuum system by closing a stopcock and put in communication with a small evacuated bulb containing aniline by opening a stopcock (see Fig. 1). Aniline was distilled into the still until a layer of crystalline aniline completely covered the distillate on the condenser. To accomplish this, it was necessary to let the liquid air evaporate almost completely from the condenser. The liquid air was finally allowed to evaporate completely. As soon as the condenser had warmed up to a point where the aniline started to melt, the vacuum was relieved and the condenser removed and immersed in aniline to a level slightly above the coating of distillate. When the mixture had come to room temperature, it was treated with dilute hydrochloric acid. Complete solution indicated the absence of any dianilide in the :ᴵᵘᴸ .on product. The solution was made alkaline and extracted three times with ether. It was then concentrated and acidified to Congo Red. The precipitate was filtered off and treated carefully with cold water to remove sodium chloride. The residue of monoanilide was recrystallized from water; m. p. 107–108. It did not depress the melting point of an authentic sample of melting point 108–109°. The absence of any dianilide in the aniline reaction product demonstrates that the β-anhydride was monomeric.

Suberic Anhydride.—A sample of α-anhydride was heated at 160° in the molecular still. The β-anhydride collected as a crystalline solid on the water-cooled condenser at the rate of about 0.1 g. a day. It melted at 55–57°. This compound proved to be the cyclic dimer of suberic anhydride.

Anal. Calcd. for C₁₆H₂₄O₆: C, 61.50; H, 7.75; mol. wt., 312.2; saponification equiv., 78.0. Found: C, 61.57, 61.67; H, 7.72, 7.89; mol. wt. (cryoscopic in benzene), 343, 355, 346; saponification equiv., 77.5.

It reacted with aniline to form the monoanilide (m. p. 125–127°) and the dianilide (m. p. 186–187°) of suberic acid, which were identified by mixed melting points. When heated above its melting point it rapidly polymerized to the γ-anhydride, a waxy solid melting at 65–68°; mol. wt. observed in boiling benzene, 703, 718.

Azelaic Anhydride.—The α-anhydride was heated in the molecular still at 150°. The β-anhydride collected on the water-cooled condenser as a liquid and soon solidified to a gel and then in about twelve hours to a wax (γ-anhydride). The observed saponification equivalent of the wax was 84.8, and 84.5 [(C₉H₁₄O₃)ₓ requires 85]. Two runs were made in which the condenser was cooled with liquid air and the cold distillate was treated with aniline as described under pimelic anhydride, but products free of dianilide were not obtained. The amounts of the two anilides were determined quantitatively, taking advantage of the insolubility of the dianilide in hot water and the insolubility of the monoanilide in cold.

(1) Four hours: Dianilide, 0.18 g.; monoanilide, 0.35 g.—A polymeric anhydride yields 2 moles of monoanilide for one of dianilide; a monomeric anhydride yields only monoanilide. The dianilide found indicates an amount of polyanhydride that could produce only 0.28 g. of monoanilide. The excess, 0.07 g., must arise from monomeric anhydride, and this amount corresponds with 11% of monomer in the total anhydride sample.

(2) Six hours: Dianilide, 0.22 g., equivalent to 0.34 g. of monoanilide (from polyanhydride). Monoanilide found, 0.49 g.; excess due to monomeric anhydride, 0.15 g., equivalent to 18% of monomer in the total anhydride sample.

Since there was no evidence of any dimer (which should be a crystalline solid) in the distillate, the failure to demonstrate that the distillate was initially pure monomer was

probably due to the fact that the latter polymerized to a considerable extent before the examination could be completed.

The distillate if removed when still liquid or pasty, had a spicy, aromatic odor. This disappeared when the distillate solidified completely.

1,11-Undecanedioic Anhydride.—The α-anhydride was heated in the molecular still with a water-cooled condenser. The β-anhydride condensed first as a dew which soon became pasty and finally after a few hours set to a hard wax, m. p. 85–88°. Before complete solidification it had a spicy odor. The saponification equivalent of the wax was 98.8 [$(C_{11}H_{18}O_3)_n$ requires 99.1]. The experiment was repeated using liquid air in the condenser and the aniline technique described under pimelic anhydride. As the reaction product was found to contain dianilide, the amounts of dianilide and mono-anilide formed were estimated quantitatively. The product from the aniline reaction was treated with a slight excess of warm dilute aqueous sodium hydroxide and the in-soluble dianilide was filtered off and weighed (0.079 g.). The filtrate was acidified, cooled and filtered (weight of crystalline precipitate 0.281 g.). This material was shown by a determination of the neutralization equivalent to be pure monoanilide (calcd. 291; found, 289). The dianilide found (0.079 g.) indicates an amount of polymeric anhydride capable of yielding only 0.125 g. of monoanilide. The excess of the latter (0.156 g.) must have come from monomeric anhydride, and calculation indicates 38% of mono-meric anhydride in the mixture.

1,12-Dodecanedioic Anhydride.—The α-anhydride was heated in the molecular still at 110°. A beautifully crystalline distillate of melting point 76–78° collected on the condenser at the rate of about 0.1 g. in two days. This β-anhydride was identified as the cyclic dimeric anhydride of dodecanedioic acid.

Anal. Calcd. for $C_{24}H_{40}O_6$: C, 67.86; H, 9.52; mol. wt., 424.4; saponification equiv., 106.1. Found: C, 67.15, 67.54; H, 9.46, 9.60; mol. wt. (cryoscopic in ben-zene), 496, 450; saponification equiv., 105.5.

It polymerized at the melting point and then melted again at 85–87°. It reacted with aniline in the usual way to yield monoanilide of m. p. 123° and dianilide of m. p. 169–170°.

Brassylic Anhydride.—The α-anhydride was heated in the molecular still for four hours at 150° with the condenser cooled with solid carbon dioxide and acetone. The dis-tillate of β-anhydride was shown to be pure monomer by its reaction with aniline. The product was completely soluble in dilute aqueous sodium hydroxide. The monoanilide separated on acidification of the alkaline solution and was recrystallized from 50% alcohol. It melted at 118.5–119.5° and showed no depression when mixed with an authentic sample.

When the depolymerization of the anhydride was carried out using a water-cooled condenser, the β-anhydride collected as a liquid which changed in the course of a day to a pasty mass and in the course of two days to a hard wax (saponification equivalent found 112.7, calculated 113.1). The liquid was fragrant and aromatic and when al-lowed to react with aniline shortly after distillation yielded only a small amount of dianilide. The odor disappeared during the change to the wax.

1,14-Tetradecanedioic Anhydride.—The α-anhydride was heated four and one-half hours at 145–150° in the molecular still using solid carbon dioxide in acetone as the refrigerant in the condenser. The distillate of β-anhydride was shown to be pure mono-mer by its reaction with aniline. The product was completely soluble in a large volume of warm, dilute sodium hydroxide and consequently consisted of monoanilide free of dianilide. The monoanilide separated on acidification of the alkaline solution and was recrystallized from 60% alcohol. It melted at 124–125° and did not depress the melt-ing point of an authentic sample.

When the depolymerization of the anhydride was carried out using a water-cooled

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.
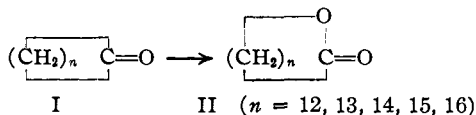

Studies of Polymerization and Ring Formation. XX. Many-Membered Cyclic Esters

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

$$(\overset{\boxed{}}{CH_2})_n \ \ \overset{\boxed{}}{C}{=}O \ \longrightarrow \ (CH_2)_n \ \ C{=}O$$

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.

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

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