

investigation was to take 1.5 g. of tetramethoxystilbylamino-acetal and 2.0 g. of arsenic pentoxide, together with 20 cc. of sulfuric acid, and to heat the mixture on the water-bath for thirty minutes. The reaction mixture was poured into water and neutralized. Nothing but black amorphous material which could not be purified and from which no derivatives were obtainable was ever found. The starting material was evidently completely destroyed. Acid of 30, 50, 65 and 75% strength was tried in the hot as well as 65 and 75% acid in the cold. Dimethylenedioxyystilbylamino-acetal was completely destroyed by 75% sulfuric acid and arsenic pentoxide in the cold.

It is, therefore, evident that the stilbylamino-acetals are unstable under the rather drastic treatment required to produce a Rügheimer cyclization and that further work along these lines would be profitless.

Summary

Tetramethoxystilbylamino-acetal and dimethylenedioxyystilbylamino-acetal were prepared from veratric aldehyde and piperonal, respectively, in an attempt to synthesize papaverine and the corresponding dimethylenedioxybenzylisoquinoline. The stilbylamino-acetals were found to be unstable to the usual cyclizing agents, thus precluding the synthesis of papaverine and its homologs by this method.

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[CONTRIBUTION NO. 19 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

STUDIES ON POLYMERIZATION AND RING FORMATION. III. GLYCOL ESTERS OF CARBONIC ACID

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The glycol esters of dibasic acids described in a previous paper¹ are all highly polymeric. This was expected from the generalization² that bi-functional reactions which, if intramolecular, could lead only to larger-than-6 rings proceed intermolecularly. It seemed desirable to examine an homologous series of similar compounds in which the length of the structural unit might be as short as 5 or 6 atoms, since in these cases reaction should be intramolecular and the products monomeric, and in the longer chains of the same series reaction should be intermolecular and the products polymeric.

Such a series is found in the glycol esters of carbonic acid. The first member of this series, ethylene carbonate, $\text{O}=\text{C} \begin{array}{l} \diagup \text{O}-\text{CH}_2 \\ \diagdown \text{O}-\text{CH}_2 \end{array}$, has long been known.³ It is a crystalline solid which boils at 238° and it is definitely

¹ Carothers and Arvin, *THIS JOURNAL*, **51**, 2560 (1929).

² Carothers, *ibid.*, **51**, 2548 (1929).

³ Nemirowski, *J. prakt. Chem.*, [2] **28**, 439 (1883); *Chem. Zentr.*, 23 (1884).

established to be the monomeric 5-ring by both cryoscopic and vapor density data.⁴

We have now prepared the trimethylene, tetramethylene, hexamethylene, decamethylene, diethylene and *p*-xylylene esters of carbonic acid. The properties of these esters, together with the apparent mean molecular weights determined by cryoscopic and ebullioscopic methods, are indicated in Table I. The analytical compositions of all these esters correspond with the formulas of their structural units $\text{—O—(CH}_2\text{)}_n\text{—CO—}$, but where the length of the chain of this unit is 5 or 6, only one such unit is present in a molecule of the ester. On the other hand, where the length of the chain of the structural unit is 7, 8, 9 or 13, eight to twenty-two structural units are present in each molecule. The method of preparation and the analytical compositions of the polymeric esters indicate a structure which may be represented by the general formula $\text{—O—(CH}_2\text{)}_n\text{—O—CO—O—(CH}_2\text{)}_n\text{—O—CO—O—(CH}_2\text{)}_n\text{—O—CO—O—(CH}_2\text{)}_n\text{—O—CO—O—(CH}_2\text{)}_n\text{—O—CO—}$, etc. To complete this formula, it is necessary to discover whether the valences at the ends of the chains are saturated mutually with the formation of a ring, or are saturated by univalent groups to give open chains. The 7-, 8-, 9- and 13-membered rings which might be formed in this reaction are not found, and there is no reason to suppose that much larger rings would be formed more readily. For some poly-esters similar to those described here we have direct experimental proof of the open-chain structure. It seems quite certain, therefore, that these polycarbonates are also open chains. From the method of preparation it follows that the ends of the chains must bear hydroxyl groups (from an extra molecule of glycol) or carbethoxy groups (from an extra molecule of ethyl carbonate). In this connection it is interesting to observe that when an excess of ethyl carbonate was used in the preparation of hexamethylene carbonate, pure dicarbethoxyhexane, $\text{C}_2\text{H}_5\text{O—CO—O(CH}_2\text{)}_6\text{O—CO—OC}_2\text{H}_5$, was isolated, and an oil which, judging by its composition, was composed chiefly of $\text{C}_2\text{H}_5\text{O—CO—O(CH}_2\text{)}_6\text{O—CO—O(CH}_2\text{)}_6\text{O—CO—O(CH}_2\text{)}_6\text{O—CO—OC}_2\text{H}_5$.

Properties of the Polycarbonates.—The physical properties of these polycarbonates again illustrate the fact that neither melting points nor solubilities offer any general criteria of molecular size.

In this connection trimethylene carbonate is of especial interest since it has been obtained in both the monomeric form and a form in which the degree of polymerization is 38–45. The monomeric form is hygroscopic and is soluble in water, benzene and alcohol, but only slightly soluble in ether and ligroin. The polymeric form is not soluble in water and alcohol, but is still soluble in benzene. Solubility here diminishes with considerable increase in molecular size, but it does not disappear. Practically all the polymeric esters described in this and the previous paper

⁴ Vorländer, *Ann.*, **280**, 186 (1894).

TABLE I
GLYCOL ESTERS OF CARBONIC ACID

Names of carbonates	Formula of structural unit	No. of atoms in chain of structural unit	Anal. calcd. for structural unit	Analysis found, ^a	Mol. wt. obs.	Method	Av. no. of structural units per molecule	Physical properties
Ethylene	$-\text{O}(\text{CH}_2)_2-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$	5	C 40.91 H 4.54	41.07% 4.88	90 93 ^b 76	F. p. C_6H_6 Vapor density	1	M. p. 39° B. p. 238°
Trimethylene (monomeric)	$-\text{O}(\text{CH}_2)_3-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$	6	C 47.06 H 5.92	46.97 47.14 5.96 5.98	105 114 112 114	F. p. C_6H_6 B. p. C_6H_6	1	Colorless needles M. p. 47-8° B. p. 135° at 4 mm.
Trimethylene (polymeric)	$-\text{O}(\text{CH}_2)_3-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$	6	C 47.06 H 5.92	47.06 47.08 6.01 6.19	4670 3880	B. p. C_6H_6	38-45	Glass gradually changes to powder
Tetramethylene	$-\text{O}(\text{CH}_2)_4-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$	7	C 51.71 H 6.94	52.18 52.32 7.05 7.06	1450 1400 1350 1310	B. p. C_6H_6	11-12	Powder M. p. 59°
Pentamethylene	$-\text{O}(\text{CH}_2)_5-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$	8	C 55.96 H 7.75	55.29 55.47 7.90 7.83	2840 2830 2550	F. p. C_6H_6 B. p. C_6H_6	20-22	Powder M. p. 44-6°
Hexamethylene	$-\text{O}(\text{CH}_2)_6-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$	9	C 58.33 H 8.33	58.58 58.54 8.46 8.21	2740 2970 2610	B. p. C_6H_6	18-21	Horny and elastic M. p. 55-60°
Decamethylene	$-\text{O}(\text{CH}_2)_{10}-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$	13	C 65.96 H 10.07	65.80 66.04 10.18 10.10	1880 1800 1810 1840	B. p. C_6H_6 F. p. C_6H_6	8-10	Powder M. p. 55°
Diethylene	$-\text{O}(\text{CH}_2)_2-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$	8	C 45.44 H 6.11	45.53 45.33 6.30 6.38	1540 1550	B. p. C_6H_6	12	Sirup
<i>p</i> -Xylylene (soluble)	$-\text{O}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$	9	C 65.84 H 4.91	65.81 66.00 5.60 5.63	840 780 810	B. p. $\text{C}_2\text{H}_5\text{Cl}_2$	5	Powder M. p. 137-8°
<i>p</i> -Xylylene (insoluble)	$-\text{O}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-$	9	C 65.84 H 4.91	65.02 65.03 5.29 5.19	1010 1030	M. p. camphor	6	Powder M. p. 177-83°

^a The analyses were carried out by the Pregl micro method
^b Vorländer, *Ann.*, 280, 187 (1894).

are insoluble in water and alcohol, but soluble in chloroform and somewhat soluble in acetone. Those poly-esters in which the structural units contain polymethylene chains, $(\text{CH}_2)_x$, in which x is greater than 3-5, show great solubility in benzene.

Poly-esters of high molecular weight may be either liquid (diethylene carbonate, ethylene malonate,¹ decamethylene phthalate¹) or solids. Most of the solid poly-esters are *crystalline*. These crystalline poly-esters differ from analogously constituted crystalline esters of low molecular weight in that the crystals are always microscopic. In some cases it is not possible to decide even by microscopic examination whether these solid polymers are crystalline, but x-ray examination always shows definite crystallinity. Thus hexamethylene carbonate was an opaque, tough, horny material with considerable elasticity. Nevertheless, it had a fairly definite melting point and it gave a quite sharp x-ray diffraction pattern (Fig. 3).

The following generalizations concerning the influence of the structure of the structural units of poly-esters on their physical properties can now be offered. As the lengths of the poly-methylene chains, $(\text{CH}_2)_x$, which separate the ester groups increase, solubility in organic solvents increases and viscosity of the molten ester diminishes. This would be expected from the fact that carbonyl groups contribute much more heavily to intermolecular association forces than do methylene groups. With one exception (ethylene malonate¹) all of the linear poly-esters in which the ester groups are separated only by polymethylene chains, $(\text{CH}_2)_x$, are solids. Less symmetrical linear polyesters such as the alkylene phthalates are resins (transparent glasses or sirups). The solid poly-esters when melted and then cooled yield opaque masses. These may be brittle and porcelain-like or soft and waxy. The waxy quality increases with the lengths of the polymethylene chains just as it does in the glycols and the acids from which the poly esters are derived.

The problem of the more precise expression of the relationship between the structure and the properties of high polymers is complicated by the fact that some of the properties of this class of substances which are of the greatest practical importance and which distinguish them most sharply from simple compounds cannot be accurately measured and indeed are not precisely defined. Examples of such properties are toughness and elasticity. We have found these two properties in only one of the poly-esters which we have prepared. This poly-ester is hexamethylene carbonate. Like pentamethylene and decamethylene carbonates, this material is crystalline; it has a fairly definite melting point ($55-60^\circ$) and it gives a sharp x-ray diffraction pattern (see Fig. 3). But the higher and lower members of this series separate from solution as powders, while hexamethylene carbonate separates in the form of rubbery flakes. It is not yet certain that this peculiar combination of properties is inherently

associated with the molecular structure of this particular ester (*i. e.*, with the linear union of a large number of the structural units $\text{—CO—O—(CH}_2\text{)}_6\text{—O—}$) rather than with some accidental features of its formation which may have been absent in the preparation of other members of the series, but the important problem of the relationship between chemical or physical structure and rubber-like properties is so poorly provided with material suitable for inductive argument that the discovery of a new synthetic and analytically homogeneous material exhibiting these properties is of some significance. So far as we are aware there is nothing in current theories which would lead one to expect that polymeric hexamethylene carbonate would be elastic.

As indicated above, high polymers, like materials of low molecular weight, may show great variety in certain physical properties—they may be either liquids or high-melting solids; they may show slight or very great solubility. The following properties, however, are inherently associated with the highly polymeric state.

(1) **Lack of Volatility.**—None of the poly-esters which we have prepared can be volatilized as such even at very low pressures and high temperatures. Volatility diminishes continuously with increase in molecular size due to the increase in intermolecular forces. It is probably true in general that compounds whose molecular cohesions lie above 75,000 cal. (the heat of separation of a carbon-carbon bond) cannot be distilled. The calculated molecular cohesion (about 250,000 cal.),⁵ of our poly-esters lie far above this value.

(2) **Viscosity in Liquid State.**—This would be expected to increase with the intermolecular forces and so with molecular size. All of the poly-esters which we have studied are extremely viscous in the molten state.

(3) **Micro-crystallinity in the Solid State.**—This has been referred to above. In this connection it is interesting to observe that considerable difficulty was experienced in preparing and keeping crystals of monomeric trimethylene carbonate sufficiently small to yield a powder diagram in an x-ray diffraction experiment. On the other hand, it has not been possible to prepare macroscopic crystals of any polymeric ester.

Trimethylene Carbonate.—Among all the esters formed from bi-functional reactions which we have studied, trimethylene carbonate and ethylene oxalate⁶ present the peculiar property of exhibiting reversible transformation between a monomeric and a polymeric form. These monomeric esters contain 6-membered rings. The polymerization of trimethylene carbonate is brought about by heating and is catalyzed by a trace of potassium carbonate. The polymer is a perfectly colorless, transparent

⁵ Meyer and Mark, *Z. angew. Chem.*, **41**, 943 (1928).

⁶ See Bischoff, *Ber.*, **40**, 2803 (1907). Our own studies of alkylene oxalates will be described later.

glass, which on long standing becomes opaque (crystallization). X-ray diffraction patterns of the monomeric and polymeric forms are shown in Figs. 1 and 2. The polymer has the same apparent analytical composition as the monomer. Its degree of polymerization as measured by molecular weight determinations in boiling benzene is 38-45. On heating *in vacuo*, it distills and the distillate is found to be the monomeric form. Examination of the literature shows that the property of undergoing reversible polymerization is common to many 6-rings containing ester linkages. Thus, the lactones of δ -hydroxyvaleric acid and of the hydroxyethyl ether of glycolic acid polymerize on heating⁷ and so does glycolide.⁸ The action of heat on lactic acid leads to polylactyl lactic acids, and these on further heating are converted to the 6-ring lactide.⁹

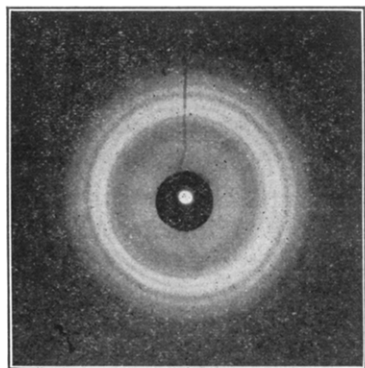


Fig. 2.—Polymeric trimethylene carbonate (Cu radiation).

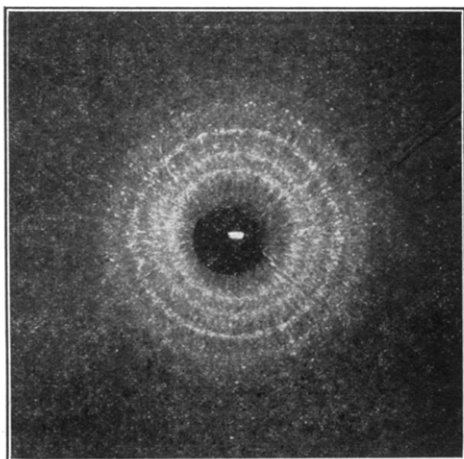


Fig. 1.—Monomeric trimethylene carbonate (Mo radiation). The intensity of the numerous outer rings is weak and these do not appear in the reproductions.

The unique position occupied in this respect by 6-rings containing an ester linkage is indicated by the following facts. No record of the polymerization of a γ -lactone (5-ring) is found. Our own attempts to polymerize ethylene carbonate (5-ring) were unsuccessful. The polyesters which we have prepared and in which the length of the chain of the structural unit is greater than 7 are not depolymerized on heating. The monomeric form of none of these esters is known.

In an attempt to force the depolymerization of tetramethylene carbonate, it was heated above 300° at 0.9 mm. This caused it to decompose with the evolution of considerable gas. From the dis-

⁷ Hollo, *Ber.*, **61**, 895 (1928).

⁸ Bischoff and Walden, *Ann.*, **279**, 45 (1894).

⁹ Dietzel and Krug, *Ber.*, **58**, 1307 (1925).

tillate was isolated a very small amount (about 1% of the calculated) of a crystalline solid having the analytical composition of tetramethylene carbonate. Molecular weight determinations indicated that it is a dimer:

$\text{[COO(CH}_2\text{)}_4\text{OCOO(CH}_2\text{)}_4\text{O]}$. The absence of a monomer was not definitely established, but it could only have been present in very small amount. Thus, the behavior of polymeric tetramethylene carbonate is very different from that of its next lower homolog.

In the self-esters of some of the higher ω -hydroxy fatty acids, $\text{HO(CH}_2\text{)}_x\text{-COOH}$, both the monomeric lactones and the poly-esters are known.¹⁰ The

poly-esters, however, are not depolymerized on heating, and the poly-esters, not the lactones, are formed on heating the acids.

These facts, together with others which will be discussed later, indicate clearly that poly-esters formed by bifunctional reactions in which the length of the structural unit is greater than 6 atoms are the direct result of intermolecular condensation (C polymerization).² The formation of polymeric trimethylene carbonate from its monomer is obviously A polymerization, and the same is true of the polym-

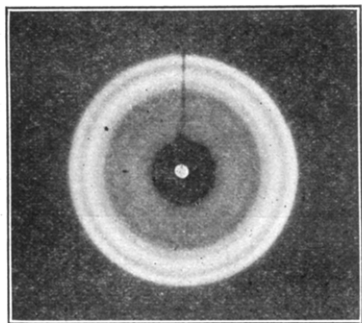


Fig. 3.—Hexamethylene carbonate (Cu radiation).

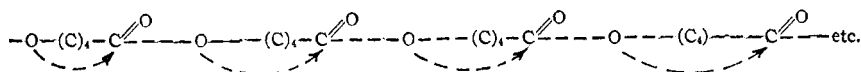
erization of lactides and of δ -lactones.

A fairly satisfactory explanation of these peculiarities may be found in the Mohr theory,¹¹ which has proved adequate to explain all of the previously observed influences of structural features on the course of bifunctional reactions.² In accordance with the terms of this theory, 5-rings will be readily formed and very stable since they are free from strain. The formation of seven-membered and larger rings by bifunctional reactions is very improbable, but such rings once they are formed will be quite stable, since they too are practically free from strain. Six-rings will be readily formed, but they present the possibility of strains which are absent or present only to a diminished degree in larger rings. Thus, the Mohr theory predicts the possible existence of two cyclohexanes (*cis* and *trans*) but only one is known. However, where structural features would preclude the possibility of the interconversion of these two forms, as in decalin, both forms are known. It is concluded, therefore, that in simple 6-rings, such as cyclohexane, equilibrium with reversible interconversion

¹⁰ Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928); Lycan and Adams, *This Journal*, **51**, 625 (1929); Chuit and Hausser, *Helv. Chim. Acta*, **12**, 463 (1929); Lycan and Adams, *This Journal*, **51**, 3450 (1929).

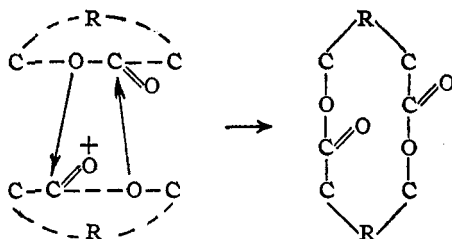
¹¹ Mohr, *J. prakt. Chem.*, **98**, 348 (1918).

of the two forms exists. At every such interconversion the molecule must pass through a position of considerable strain. This picture presents the features necessary to rationalize the peculiar position of 6-membered ester rings. A poly-ester in which the recurring structural unit is a chain of six atoms would be readily converted into the corresponding monomeric 6-ring by a process of ester interchange, as indicated below:



If the chain of the structural unit were longer than 6 atoms, this reaction would be less probable for the same reason that the higher ω -hydroxy fatty acids do not yield lactones, *i. e.*, the number of points of rotation in the chain between carbonyl and alcoholic oxygen are so numerous that the probability of close intramolecular approach of these groups is very low.

The polymerization of the 6-ring esters seems also to involve ester interchange. This process may involve the coalescence of two such rings, as indicated below



The resulting 12-ring might then coalesce with another six-ring, and so on, with the formation of very large rings. It is possible also that traces of water may intervene at some stage in the process and that the large molecules produced are open rather than closed chains. In any event the peculiar mobility of the 6-ring esters may be ascribed to the fact that these rings are subject to strains, and that the strains may be relieved by an ester interchange resulting in an enlargement of the molecule.

The precise mechanism of the polymerization of the 6-membered ester rings shares to a certain extent the obscurity which is common to most cases of A polymerization, but further attention is being devoted to this problem and the study is being extended to the corresponding amides. In this connection the analogy which exists between lactides and diketopiperazines on the one hand, and poly-esters and polypeptides on the other hand, is of especial interest because of its possible relationship to the structure of proteins.

Dimeric Tetramethylene Carbonate.—The dimeric tetramethylene carbonate referred to above deserves special mention. There can be little doubt that it is a 14-membered cyclic ester, and as such it represents a

class of compounds of which few members are known. Other dimeric cyclic esters have been obtained and will be described in later papers.

Previous Work on the Carbonates of Dihydric Alcohols.—Reference to ethylene carbonate has already been made. Carbonates of the three dihydroxybenzenes were prepared by Bischoff and v. Hedenström.¹² The carbonate of catechol is apparently monomeric since it can be distilled. The *m*-phenylene carbonate is a non-volatile, brown, glassy material of uncertain melting point (197–202°) and low solubility, and the corresponding para compound shows similar properties. These two compounds are evidently polymeric.

Experimental Part

Preparation of Carbonates.—The carbonates here described were all prepared by ester interchange (alcoholysis) between the glycol and ethyl carbonate. This reaction proceeds very smoothly in the presence of an alkaline catalyst and may be forced to completion; the process need not be modified to take into account the solubility of the resulting ester, as is necessary when phosgene and the glycol are used as starting materials.

Trimethylene Carbonate.—A mixture of 60.8 g. (0.8 mole) of trimethylene glycol, 114 g. (16% excess) of ethyl carbonate and a small cube of sodium was warmed in a Claisen flask until the sodium had completely dissolved. The flask was then immersed in an oil-bath at 130°. During three hours the temperature was allowed to rise to 170°. The evolved alcohol condensed and collected weighed 69.1 g. or 94% of the calculated.

The oily residue was dissolved in benzene, washed twice with 20-cc. portions of water and dried over calcium chloride. After removal of the solvent, the residue was subjected to vacuum distillation. A small initial fraction, b. p. 120–135° at 20 mm., was unchanged glycol. The pure trimethylene carbonate then distilled fairly constantly; b. p. 160–165° at 6 mm.; 135° at 4 mm., 105° at 0.2 mm.; weight 53 g., or 65% of the calculated. It completely crystallized in the receiver; recrystallization from absolute ether produced colorless needles, m. p. 47–48°. This hygroscopic ester is very soluble in benzene, alcohol and water and slightly soluble in ether and ligroin. It decomposes on distillation at ordinary pressure. This ester gave a sharp x-ray powder diagram (Fig. 1) slightly scattered due to the difficulty of obtaining sufficiently small crystals. For analysis, see Table I.

Polymerization of Trimethylene Carbonate.—In the distillation of trimethylene carbonate it was frequently observed that the distilling residue was very thick and viscous while the warm distillate was comparatively thin and mobile. The distillation of 53 g. of trimethylene carbonate was interrupted while still incomplete. The distillate was monomeric trimethylene carbonate, m. p. 48°. The undistilled residue (15.6 g.) was very viscous even when hot and it cooled to a colorless sticky resin. Molecular weight determinations showed it to be polymeric; molecular weight in boiling benzene, found: 2390, 2320.

This residue was distilled at 10 mm. It yielded 13.6 g. of monomeric trimethylene carbonate (observed b. p. 150–190°) which completely crystallized on cooling; mol. wt., calcd. for monomeric trimethylene carbonate: 102. Found: (in boiling benzene) 115, 118.

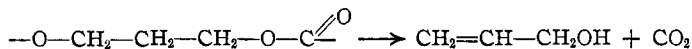
¹² Bischoff and v. Hedenström, *Ber.*, **35**, 3431 (1902).

The tarry residue (1.7 g.) remaining in the flask was insoluble in the common organic solvents.

A trace (0.1%) of finely powdered anhydrous potassium carbonate was added to a sample of the pure crystalline monomeric ester and the mixture was heated at 130°. After shaking and heating for ten minutes the mixture suddenly became very viscous and a slight amount of gas was evolved. After five hours of heating the colorless product formed a clear glassy mass on cooling; mol. wt., found: (in boiling benzene) 4670, 3880. For analysis see Table I. After standing for a week, this glassy polymer became opaque and x-ray examination showed it to be crystalline (Fig. 2).

Under similar conditions (temp. 130°; time of reaction, four hours) ethylene carbonate did not polymerize.

When polymeric trimethylene carbonate was heated to 210° at ordinary pressure, it was decomposed. Allyl alcohol was identified as one of the products of this reaction by its boiling point and by the melting point of its phenylurethan. This fact indicated decomposition according to the scheme



The allyl alcohol isolated accounted for only about 25% of the ester decomposed. Higher boiling unsaturated materials present in the products of this reaction were not identified.

Tetramethylene Carbonate.—This was prepared from 9.0 g. of tetramethylene glycol, to which a small piece (2 mm.³) of sodium had been added and 11.8 g. of ethyl carbonate. The mixture was heated to 120° and then the temperature was allowed gradually to rise to 160° during seven hours. The distillate was poured back several times to insure complete reaction of the ethyl carbonate. From the distillate was isolated 5.7 g. or 62% of the calculated amount of ethyl alcohol.

The non-volatile reaction product was dissolved in benzene and the solution washed with water, dilute hydrochloric acid and water. It was dried with calcium chloride and the solvent was removed by distillation. On heating the residue *in vacuo* there was obtained a very small amount of distillate boiling at 100–110° at 1 mm. This was chiefly unchanged tetramethylene glycol since it gave a di-*p*-nitrobenzoate, m. p. 175°. No further distillation could be effected when the bath was heated to 250° and the pressure reduced to 0.2 mm.

The residue was purified by dissolving it in chloroform and precipitating it with absolute alcohol while cold. The oily precipitate soon crystallized to a cream-colored powder; weight 6.3 g. or 54% of the calculated; m. p. 55–59°; very soluble in cold benzene, chloroform, acetone, and acetic acid; insoluble in ether, alcohol and petroleum ether. It gave a sharp x-ray diffraction pattern. Before analysis it was dried for four days at 80° in high vacuum. For analytical data see Table I.

Di-*p*-nitrobenzoate of Tetramethylene Glycol.—Prepared from the glycol and the acid chloride in pyridine; crystallized from boiling acetic acid; m. p. 175°.

Anal. Calcd. for C₁₈H₁₆O₈N₂: C, 55.67; H, 4.12. Found: C, 56.19, 56.00; H, 4.31, 4.14.

Thermal Decomposition of Tetramethylene Carbonate.—An attempt was made to bring about the depolymerization of tetramethylene carbonate by heating it to high temperature *in vacuo*. The tetramethylene carbonate was prepared from 9.0 g. of glycol and 11.8 g. of ethyl carbonate in the same manner as described above. It was heated at 0.9 mm. in a small Claisen flask by means of a metal-bath. Very slight distillation occurred as the temperature of the bath was raised from 270 to 300°. Between 300 and 325° evolution of gas occurred and the pressure increased. From the distillate were isolated 0.1 g. of crystalline solid and 2.8 g. of oil. The residue remaining in the distilling

flask weighed 3 g. and was apparently identical with the polymeric tetramethylene carbonate described above; it melted at 55° and had the same physical appearance and solubility behavior.

The crystalline distillate separated from alcohol in minute prisms melting at 175–176°. Analysis and molecular weight determinations showed it to be dimeric tetra-

methylene carbonate, $\overline{\text{CO—O(CH}_2\text{)}_4\text{O—CO—O(CH}_2\text{)}_4\text{O}}$.

Anal. Calcd. for $(\text{C}_5\text{H}_8\text{O}_3)_2$: C, 51.71; H, 6.94; mol. wt., 232. Found: C, 51.77; 51.80; H, 6.95; 7.02; mol. wt., in boiling ethylene chloride, 194, 231; mol. wt., in freezing benzene, 204.

The liquid distillate had a pungent mint-like odor and readily absorbed bromine in acetic acid solution. It is a mixture and no chemical individuals have as yet been isolated from it.

Pentamethylene Carbonate.—This was prepared from 5.9 g. of ethyl carbonate and 5.2 g. of pentamethylene glycol to which a small amount of sodium had been added. The mixture was heated for twelve hours at 120–160°; 76% of the calculated amount of alcohol was found in the distillate. The residue after it had been freed from sodium was heated at 250° under 0.15 mm. The distillate (1.1 g.) boiled at 110–130° and consisted chiefly of unchanged glycol; di-*p*-nitrobenzoate, m. p., 104–105°. The non-volatile sirupy residue crystallized on standing to a hard waxy material; weight, 4.1 g. or 63% of the theoretical. It was purified by precipitation with absolute alcohol from a cold chloroform solution as a granular and slightly colored powder; m. p., 44–46°; very soluble in benzene, chloroform, acetone and acetic acid; insoluble in ether, alcohol and petroleum ether. Before analysis it was dried to constant weight in high *vacuo*. For analysis see Table I.

Di-*p*-nitrobenzoate of Pentamethylene Glycol.—From the glycol and the acid chloride in pyridine; crystallized from a mixture of benzene and alcohol; m. p., 104–105°.

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_8\text{N}_2$: C, 56.71; H, 4.51. Found: C, 56.95, 57.02; H, 4.59, 4.69.

Hexamethylene Carbonate.—This was prepared from 12 g. of ethyl carbonate and 12 g. of hexamethylene glycol to which a small piece of sodium had been added. The mixture was heated from 130 to 170° during two hours; 86% of the calculated amount of alcohol was found in the distillate. The residue after the removal of the sodium was subjected to distillation in high vacuum. A very small amount of distillate was found to consist of unchanged glycol. The residue, which amounted to 10 g. or 67% of the calculated, solidified on cooling to a light colored, horny, tough mass. It was soluble in benzene, acetone and chloroform; insoluble in ether and alcohol; m. p. 55–60°. A sharply defined x-ray diffraction pattern (Fig. 3) showed it to be crystalline. For analysis see Table I.

Dicarbethoxyhexane.—In an experiment similar to the above, ethyl carbonate and glycol were used in the ratio of 2 moles to 1 (24 g. of ester and 12 g. of glycol). The calculated amount (9.2 g.) of alcohol was collected. The residue after removal of sodium was subjected to vacuum distillation. It yielded 5.5 g. of distillate, b. p. 130–140° at 0.8 mm. The residue could not be distilled, and neither the distillate nor the residue could be induced to crystallize. No ethyl carbonate was found in the distillate. The distillate was dicarbethoxyhexane; n_D^{20} 1.4310; d_4^{20} 1.065; d_4^{25} 1.056.

Anal. Calcd. for $\text{C}_{12}\text{H}_{22}\text{O}_6$: C, 54.94; H, 8.41; mol. wt., 262. Found: C, 55.00; H, 8.41; mol. wt. in boiling benzene, 236, 240, 245.

The oily residue was very soluble in alcohol and ether. Its analytical composition corresponded with the formula $\text{C}_2\text{H}_5\text{O—CO—O(CH}_2\text{)}_6\text{O—CO—O(CH}_2\text{)}_6\text{O—CO—O(CH}_2\text{)}_6\text{O—CO—OC}_2\text{H}_5$.

Anal. Calcd. for $C_{28}H_{46}O_{12}$: C, 56.73; H, 8.36; CO_2 on hydrolysis, 33.1%; mol. wt., 532. Found: C, 56.77, 57.00; H, 8.41, 8.53; CO_2 , 34.15; mol. wt. in boiling benzene, 573, 549, 528. The CO_2 was determined by saponifying with alcoholic sodium hydroxide and weighing the sodium carbonate formed.

Carbonate of Diethylene Glycol.—This was prepared in 43% yield by the method used in the preparation of the other carbonates. It was a light colored sirup which could not be induced to crystallize; insoluble in alcohol and ether, quite soluble in acetone and benzene, very soluble in chloroform and hot ethyl acetate. On standing it appeared to decompose to some extent into acetaldehyde and carbon dioxide and for this reason it could not be dried to constant weight. For analysis see Table I.

Decamethylene Carbonate.—This was prepared in 75% yield by the method used for the preparation of the other carbonates. It was soluble in benzene and chloroform but insoluble in alcohol. It was purified by precipitation from chloroform with alcohol in the cold. The oily product gradually solidified to a cream-colored powder; m. p. 55°; very soluble in chloroform, slightly soluble in ether, benzene, acetone and acetic acid; insoluble in alcohol and petroleum ether. This powder gave a sharply defined x-ray diffraction pattern. Before analysis it was dried to constant weight in high vacuum at 90°. For analysis see Table I.

***p*-Xylylene Carbonate.**—This was prepared from *p*-xylylene glycol and ethyl carbonate as in the preparation of the other carbonates. The residue after completion of the ester interchange was insoluble in hot benzene, absolute alcohol, chloroform and carbon tetrachloride; slightly soluble in acetic acid. It dissolved more or less completely in ethylene chloride, anisole and dioxane. It was thoroughly triturated with water and with cold alcohol to remove sodium and excess glycol and ethyl carbonate. The amount of the white solid remaining corresponded to 82% of the calculated. It was separated into two fractions by extraction with ethylene chloride.

(a) **Soluble Fraction.**—This was precipitated with ether from ethylene chloride in the form of white flocks; m. p. 137–138°. For analysis see Table I.

(b) **Fraction Insoluble in Ethylene Chloride.**—This was insoluble in the common organic solvents; m. p. 177–185° (rather indefinite). For analysis see Table I.

Attempted Preparation of Methylene Carbonate.—Silver carbonate (81 g.) was heated with methylene bromide (51 g.) in dry toluene solution. Formaldehyde and carbon dioxide were formed and free silver was produced. From the reaction mixture there was isolated only a small amount of oil with a sweet odor—probably methylene carbonate. This liberated formaldehyde on heating: $CH_2CO_3 \longrightarrow H_2CO + CO_2$.

We are indebted to Dr. A. W. Kenney and Mr. Henry Aughey for the x-ray diffraction pictures, to Mr. W. H. Taylor for many molecular-weight determinations and to Mr. G. A. Jones for determinations of carbon and hydrogen.

Summary

The following compounds have been prepared by the action of the appropriate glycols on ethyl carbonate: trimethylene carbonate, tetramethylene carbonate, pentamethylene carbonate, hexamethylene carbonate, decamethylene carbonate, diethylene carbonate and *p*-xylylene carbonate. Their properties are described. In accordance with a generalization already set forth, ethylene carbonate and trimethylene carbonate are monomeric and the other carbonates are polymeric. Trimethylene carbonate undergoes reversible A polymerization. A stable dimeric form of tetra-

methylene carbonate has been prepared by thermal decomposition of its usual polymeric form. Hexamethylene carbonate is tough and elastic.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

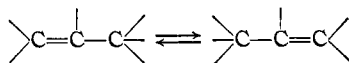
STUDIES OF CONJUGATED SYSTEMS II. THE BROMINATION OF VINYLACRYLIC ACID

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The abnormal addition reactions of conjugated systems have been the subject of a great deal of experimental work ever since Fittig¹ and Baeyer² found that compounds containing two double bonds in conjugation were reduced in the 1,4- rather than in the 1,2- or 3,4-positions, and did not exhibit the properties common to ordinary ethylenic double bonds. In 1899 Thiele³ proposed his "partial valence" theory to interpret these 1,4-addition reactions to conjugated systems and brought a great deal of experimental evidence in its favor. According to this theory the type of addition taking place in a conjugated system depends solely on the valence relations of that system. Later work⁴ proved this general theory to be incorrect, and it was modified by Hinrichsen⁴ to take into consideration the electrochemical nature of the entering atoms or groups, as well as the nature of the original unsaturated compound in which the addition is taking place. More recent work,⁵ carried out with greater precision and more refined technique, has shown that in many addition reactions where 1,4-addition is found, it is not due primarily to 1,4-addition but rather to an isomerization of the 1,2- or 3,4-addition compounds. Such isomerizations are common in three-carbon systems containing a double bond



Because of the theoretical importance of the addition reactions of conjugated systems, it was considered desirable to make a thorough investigation of such addition processes, particularly in simple conjugated systems. It was hoped that such studies would also throw some light on the mecha-

¹ Fittig, *Ann.*, **227**, 46 (1888).

² Baeyer, *ibid.*, **251**, 271 (1889); **256**, 1 (1890).

³ Thiele, *ibid.*, **306**, 87 (1899).

⁴ Michael, *J. prakt. Chem.*, **60**, 467 (1899); Erlenmeyer, Jr., *Ann.*, **316**, 43 (1901); Vorländer, *Ber.*, **36**, 2339 (1903); Kohler, *Am. Chem. J.*, **31**, 642 (1904); **33**, 153, 333 (1905); Hinrichsen, *Ann.*, **336**, 174 (1904); Strauss, *Ber.*, **42**, 2866 (1909); Ingold, *J. Chem. Soc.*, **121**, 329, 1306 (1921); and many others.

⁵ Ingold and Shoppee, *J. Chem. Soc.*, **129**, 1477 (1926); Farmer, *ibid.*, 172 (1929); Prevost, *Ann. chim.*, [10] **10**, 113 (1928); Claisen, *J. prakt. Chem.*, **105**, 65 (1922).