(1 mol.) was dissolved in 500 ml. benzene in which 56 g. soda ash was kept suspended by agitation. The acid chloride, 232 g. (1 mol.) was added dropwise while holding the reaction mass at reflux temperature. After washing with water and stripping the solvent, the product was distilled. There was a forecut, 12 g., b.p. 103–178° (0.25 mm.) and the product, 266 g., 71% yield, b.p. 180–182° (0.1 mm.), with 32 g. still residue. An 86% yield was obtained with *n*-butyl alcohol, b.p. 116° (0.3 mm.).

Characterization of half esters by half saponification of mixed esters. Deviations from theoretical values for neutral and saponification equivalents of the various half esters and diesters were used in calculating purity and characterization of the esters. These results, however, gave no indication of the composition with respect to structural differences. This type of difference was established by half saponification of some of the mixed esters.

Half saponification of the butyl and hydronopyl ethyl pinates (ethyl acetate forms) from the above acid chloride reactions gave good yields of the corresponding alkoxycarbonyl half esters. Although some monoethyl pinate may have been present, the foreruns in the distillation (less than 10%) failed to crystallize when seeded with solid *cis-dl*-2,2-dimethyl-3-(ethoxycarbonyl)cyclobutaneacetic acid.

Similarly, saponification of alkyl ethoxycarbonylcyclobutaneacetates resulted in no detectable amounts of the alkylcarbonyl type monoester. The half ester obtained was good quality *cis*-2,2-dimethyl-3-(ethoxycarbonyl)cyclobutaneacetic acid.

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OLUSTEE, FLA

[CONTRIBUTION FROM DEPARTMENT OF PHARMACEUTICAL CHEMISTRY, SCHOOL OF PHARMACY, HEBREW UNIVERSITY]

Organic Carbonates. IV.[1a,b,c] Factors Affecting Formation of Homologous Cyclic Carbonates

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The preparation and properties of a number of branched 1,2-, 1,3-, and 1,4-cyclic carbonates are described. The formation of homologous cyclic carbonates by reaction of diols with diethyl carbonate is described as a two-step mechanism, involving first the formation of a mono-ester and then cyclization with an accompanying elimination of ethanol. The effect of both substitution and chain length in homologous alkylene glycols upon their tendencies to yield monomeric cyclic carbonates is discussed.

In a previous communication[1c] we have described the effect of substitution in 1,3-propanediol carbonates upon their tendencies to undergo reversible polymerization. This paper is concerned with a similar study regarding the effect of both substitution and chain-length in 1,2-, 1,3-, and 1,4-diol upon their tendencies to form cyclic and/or polymeric carbonates.

In this study we employed two methods: (1) ester interchange between an appropriate diol and diethyl carbonate in the presence of catalytic amounts (2.5–5% mole) of dry sodium methoxide[1c]; (2) the reaction of phosgene with diols in the presence of antipyrine, according to the method of Ludwig and Piech.[3] In each method it was found that the nature and yields of the reaction products obtained are largely dependent upon reaction conditions and molecular structure of reactants. For example, in the transesterification of neopentylene glycol by means of diethyl carbonate, three distinct organic carbonates (II, III, and V) could be obtained, upon varying the molar ratio catalyst/reactants. Thus, in the presence of large amounts of dry sodium methoxide catalyst (5–10 mol. %), high yields of the cyclic carbonates (IIId) are obtained. Upon 10-fold decrease of the amount of catalyst (0.5–1.0 mol. %), the polymeric form (Vd) is obtained almost exclusively. Upon further decrease in the amount of catalyst (0.45 mol. %) a monoester (IId) is obtained along with Vd, but none of IIId. A more detailed study of this phenomenon will be given in a subsequent paper.

In the series of 1,3-propanediols, we observed that branching at carbon atoms 1, 2, and 3, favors the formation of the requisite cyclic esters, and at the same time it exerts a hindrance upon their tendencies to undergo a polymerization reaction. Thus, upon ester interchange between 1,3-butanediol (Ib) and 2,4-pentanediol (Ic) and diethyl carbonate, the corresponding 1,3-cyclic carbonates (IIb and IIc) were produced in 70–72% yields, whereas IIIa was obtained in 50% yield. Similarly, disubstitution at carbon atom 2, while it suppresses or even abolishes the tendency to polymerization, has, however, an enhancing effect toward the formation

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[1] (a) Part I, *Compt. rend.*, **245**, 2321 (1957); (b) Part II, *Bull. Research Council Israel*, **7A**, 42; (c) Part III, S. Sarel and L. A. Pohoryles, *J. Am. Chem. Soc.*, **80**, 4596 (1958).

[2] Formerly Shalom Israelashvili; to whom inquiries should be sent.

[3] B. J. Ludwig and E. C. Piech, *J. Am. Chem. Soc.*, **73**, 5779 (1951).

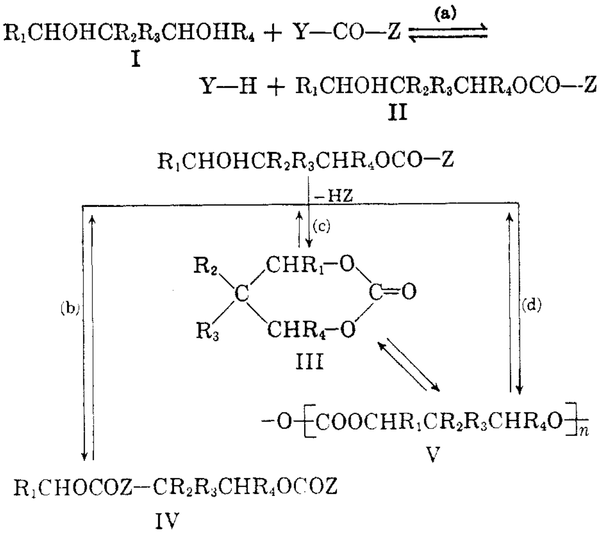
of cyclic esters (IIId–IIIh). On the other hand, the yields of the inner carbonates seemingly tend to drop markedly upon increasing the bulkiness of the alkyl substituents. For example, only a 25% yield of IIIi was obtained on condensation of Ii with diethyl carbonate, whereas similar reaction with Ie afforded IIIe in 75% yield.

Depending upon molar ratio, the condensation of 1,3-diols with ethyl urethane in the presence of ester-interchange catalysts may lead to the formation of either the mono- or dicarbamate derivatives along with small amounts of the corresponding cyclic carbonate. The latter is seemingly produced as a result of an intramolecular amide alcoholysis. Thus, in the case of monocarbamate of IIg ($Z = NH_2$) we found that its conversion into IIIg could be achieved only at high temperatures, and even then it was produced at an exceedingly slow rate as indicated by measuring the flow of ammonia liberated. This result is consistent with the theory concerning the reversible formation of amides from esters.[4] Chart I describes in outline all the reactions involved in the interactions between 1,3-glycols and appropriate derivatives of carbonic acid.

1,4-Cyclic carbonate. In contrast to the 1,2- and 1,3-cyclic carbonates, which can be prepared rather conveniently by either method described here, the synthesis of the seven-membered homolog has so far been unsuccessful. Thus, when VI was brought into reaction with diethyl carbonate in the presence of an ester-interchange catalyst both under nondilute[5] and dilute[6] conditions, no monomeric 1.4-cyclic carbonate could be isolated. Instead, the linear polymer, polytetramethylene carbonate XI, and a dimeric cyclic carbonate (XII) containing a fourteen-membered ring was obtained. Carothers and Van Natta[5] showed that, unlike polytrimethylene carbonate Va, XI was not reversibly converted to the monomeric form (IX), and that upon heating it produced only the fourteen-membered dimer.

In our hands, however, the requisite monomeric 1,4-cyclic carbonate IX was obtained under dilute conditions, by both the phosgene-antipyrine method and by ester-interchange reaction between VI and diethyl carbonate, in 26% and 12% yields, respectively. The structure of IX was indicated by its analysis, molecular weight determination and infrared spectra. Again, the main reaction product found consisted of fractions of an average molecular weight of 200–600, corresponding to an average chain length of 2–5 units. Under nondilute conditions, 11–12 structural units of $—O—CO—(CH_2)_3—O—$ have been reported for the polymeric form.[5] In addition, the cyclic dimer(XII) has also been isolated, only in the ester-interchange reaction. Charts I and II, describe all the reactions between diols and carbonic acid derivatives as involving a multistage mechanism. This involves first the formation of a monoester (II or VII) and then its cyclization and/or polymerization with accompanying elimination of either ethanol or hydrogen chloride. In the series of 1,3-propanediols, factors such as would accelerate rates of reaction and/or the presence of alkyl substituents in the carbon chain of the diol, positively favor the formation of cyclic carbonates at the expense of the concurrent polymerization reaction.[7] However, the increase of the unit length in the series of polymethylene glycols does not favor the formation of the monomeric cyclic carbonates, but at the same time it does favor the formation of the polymeric forms. The same mechanism should hold similarly for the reactions of 1,2-diols, despite the fact that the presumed monoester has never been isolated in these reactions.[8] It appears, therefore, that in these systems the ring-closure stage of the reaction must be much more rapid than the first, and the monoester does not build up during the reaction.[9]

Chart 1



$Z = Y = Cl, OEt; Z = OEt, Y = Cl; Y = OEt, Z = NH_2$

Ia and IIIa. $R_1 = R_2 = R_3 = R_4 = H$.
Ib, IIb, and IIIb. $R_1 = R_2R_3 = H; R_4 = Me$
Ic and IIIc. $R_1 = R_4 = Me; R_2 = R_3 = H$.
Id, IId, and IIId. $R_1 = R_4 = H; R_2 = R_3 = Me$
Ie and IIIe. $R_1 = R_4 = H; R_2 = R_3 = Et$.
If and IIIf. $R_1 = R_4 = H; R_2 = Me; R_3 = Ph$
Ig and IIIg. $R_1 = R_4 = H; R_2 = Et; R_3 = Ph$.
Ih and IIIh. $R_1 = R_4 = H; R_2 = Me; R_3 = n$-Pr
Ii and IIIi. $R_1 = R_4 = H; R_2 = Et; R_3 = i$-Am

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(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 782.

(5) W. M. Carothers and F. J. Van Natta, *J. Am. Chem. Soc.*, **52,** 314 (1930).

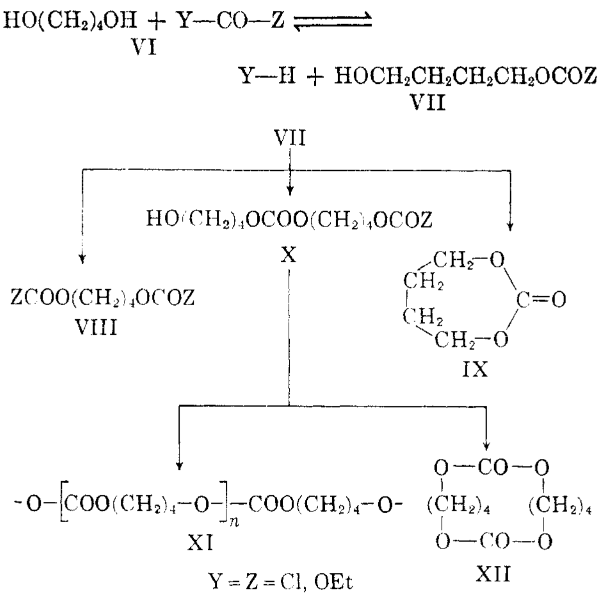
(6) W. J. Bailey and W. R. Sorenson, *J. Am. Chem. Soc.*, **78,** 2287 (1956).

(7) H. K. Hall, *J. Am. Chem. Soc.*, **80,** 6404 (1958).

(8) W. N. Haworth and C. R. Porter, *J. Chem. Soc.*, 151 (1930); 2796 (1929); 2254 (1932). A. Contardi and A. Ercoli, *Gazz. chim. ital.*, **64,** 522 (1934).

(9) S. Sarel, I. Levin, and L. A. Pohoryles, paper sent for publication.

Chart 2



It is interesting to note that upon ester-interchange conditions, pinacol tends to undergo, to some extent, a C—C bond fission, thus yielding a mixture of acetone and isopropanol. The former has actually been isolated and identified as its 2.4-dinitrophenyl-hydrazone.[10]

EXPERIMENTAL[11]

Materials. The sources and purification procedures for the diols were as follows: Commercial 2,3-butanediol (B.D.H.) was fractionated and the cut boiling at 83–85 (14 mm.), n_D^{25} 1.4368 was used.[12] Commercial trimethylene glycol was fractionated and the fraction of b.p. 106–110° at 15 mm., n_D^{15} 1.4418, d_4^{15} 1.0590 (reported[12] b.p. 217.4° at 760 mm., n_D^{21} 1.4394) was used. 2,2-Dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol ("Eastman"), and 2-methyl-2-*n*-propyl-1,3-propanediol (Abic) were used without further purification.

α-Phenylpropionaldehyde, b.p. 91–94° at 12 mm., was prepared in 65% yield by hydrolysis of phenylmethylglycidic ester as described.[13]

2-Methyl-2-phenyl-1,3-propanediol, b.p. 150–155° (2 mm.), was obtained by the reductive aldol condensation of formaldehyde with α-phenylpropionaldehyde, according to Franke and Frank[14] in 45–50% yield. Recrystallization from carbon tetrachloride gave a crystalline product melting at 75° (reported[14] m.p. 75°).

Pinacol was prepared according to the literature.[15] A cut of b.p. 86–90° (26 mm.) was used.

The following paper[16] describes the preparation of other diols employed herein.

Preparation of 1,2- and 1,3-cyclic carbonates. Method A. The general method adopted for the preparation of cyclic carbonate esters is essentially that previously described by Ludwig and Piech,[3] and the following procedure is typical for the preparation of compounds listed in Table I. To a solution containing 0.1 mol. of phosgene in dry toluene, was added dropwise, with stirring, at a rate to maintain the temperature between 30–40°. After addition being completed the mixture was stirred for an additional 30 min. and allowed to stand at room temperature overnight. It was then worked up in a manner as described.

Method B. The procedure previously described for the preparation of monomeric neopentylene carbonate[1(c)] illustrates the method that was adopted for the production of cyclic carbonates listed in Table I. As has previously been shown, the ratio catalyst/substrate may affect markedly both the course and the yields in the formation of cyclic carbonate esters. Bests yields are obtained upon employing 2.5–5.0% mol. of sodium methoxide catalyst and small excess (10%) of diethyl carbonate.

1,4-Cyclic carbonate. Method C. This illustrates an adaptation of Method A for dilute conditions which was used in the preparation of the seven-membered ring carbonate. A solution of 1,4-butanediol (30 g., 0.33 mol.) in 1400 ml. anhydrous chloroform was mixed with a solution of antipyrine (120 g., 0.67 mol.) in 100 ml. dry toluene, and to the resulting system was added dropwise, under stirring, a 43% solution (w/w) (70 g.) of phosgene in toluene at such a rate as to maintain a temperature of 45–50°. After being left overnight at room temperature, it was worked up in the usual way. Fractionation of reaction mixture afforded two cuts: (1) the desired monomeric cyclic carbonate (compound No. 14 listed in Table I), and (2) a dimeric cyclic carbonate (XII), 3.9 g. (10%), b.p. 110° (3 mm.), m.p. 174–175° (from chloroform) reported,[5,6] m.p. 175–176°. In the distillation flask a residue of a viscous low polymeric product remained (XI), n_D^{17} 1.4575, which amounted to 32% yield.

Anal. Calcd. for $(C_5H_8O_3)_x$: C, 51.7; H, 6.9. Found: C, 51.4; H, 7.4; av. mol. wt., 200–300 (Rast).

In nondilute conditions (Method A) the viscous polymeric product obtained constituted the main reaction product, having an av. mol. wt. 400–600 (Rast).

Method D. It represents Method B modified by diluting the reaction mixture with toluene. A mixture of tetramethylene glycol (45 g., 0.5 mol.) diethyl carbonate (65 g., 0.55 mol.) and about 2 mol. % of sodium methoxide was dissolved in 500 ml. dry toluene and refluxed for 10 hr. The ethanol-toluene azeotrope which formed (boiling at 72–76°) was removed continuously by distillation through a short Vigreux column. At the end, solvent and unreacted materials were removed by fractionation at reduced pressure using a Widmer column. The residue was then subjected to distillation in high vacuum, thereby yielding two cuts: (1) 1,4-butanediol cyclic carbonate (IX) (see Table I), and (2) colorless liquid (5 g.) b.p. 95–103° (0.6 mm.), n_D^{25} 1.4260, which, according to analysis and molecular weight determination, can be formulated as 1,4-bisethoxycarbonyloxybutane (VIII, Z = OEt).

Anal. Calcd. for $C_{10}H_{18}O_6$: C, 51.3; H, 7.7; mol. wt., 234. Found: C, 51.2; H, 8.4; mol. wt., 200.

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(10) This observation is at variance with that described by C. B. Wooster and D. S. Latham, *J. Am. Chem. Soc.*, **58**, 76 (1936), who found that the reaction between ordinary pinacol and metallic sodium in liquid ammonia is confined to the replacement of one of the hydroxyl hydrogen atom.

(11) All melting points were determined by the use of Dr. Tottoli melting point apparatus, and are uncorrected. Infrared spectra were taken with a Baird double beam recording spectrophotometer, model B. Analyses were performed by Mrs. Marika Goldstein at the microanalytical laboratory of the department of organic chemistry, The Hebrew University.

(12) This fraction is mainly the meso- form. O. J. Schierholtz and M. L. Staples, *J. Am. Chem. Soc.*, **57**, 2710 (1935), give n_D^{25} 1.4364 for *meso*-2,3-butanediol. See also S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, 61, 1579 (1939).

(13) C. F. H. Allen and J. Van Allen, *Org. Syntheses*, **Coll. Vol. III**, 733 (1955).

(14) A. Franke and F. Frank, *Monatsh.*, **34**, 1907 (1913).

(15) R. Adams and E. W. Adams, *Org. Syntheses*, **Coll. Vol. I**, 459 (1941).

(16) L. A. Pohoryles, S. Sarel, and R. Ben-Shoshan, *J. Org. Chem.*, 24, 1878 (1959).

TABLE I

CYCLIC CARBONATES OF 1,2-, 1,3-, AND 1,4-DIOLS

No.	Compound Cyclic Carbonate of	M.P. or B.P.	Press., Mm. Hg	n_D^{15}	d_0^{15}	$(M_R)_D$ Calcd.	$(M_R)_D$ Found	Yield, %	Method	Formula	Analysis Calcd. C	Analysis Calcd. H	Analysis Found C	Analysis Found H
1	2,3-Butanediol[a]	93	3.5	1.4241	1.1408	26.39	25.98	55	B	$C_5H_8O_3$	51.72	6.94	51.37	7.03
2	2-Methyl-2,3-butanediol[b]	59–60						39	A	$C_6H_{10}O_3$	55.37	7.75	55.60	7.30
3	2,3-Dimethyl-2,3-butanediol[c]	180–181						42 18	A B	$C_7H_{12}O_3$	58.31	8.39	58.80	8.19
4	Hydrobenzoin[d]	127						67	B	$C_{15}H_{12}O_3$	75.00	5.03	74.70	4.94
5	1,3-Propanediol[e]	45						50	B	$C_4H_6O_3$	47.06	5.92	46.86	6.10
6	1,3-Butanediol	113–115	0.2	1.4465	1.965	26.39	25.91	70	B	$C_5H_8O_3$	51.70	6.90	51.6	6.6
7	2,4-Pentanediol	116–117	2.5	1.4443	1.1179	31.01	30.85	66	B	$C_6H_{10}O_3$	55.4	7.8	55.0	8.0
8	2,2-Dimethyl-1,3-propanediol[f]	109–110						85	B					
9	2-Methyl-2-*n*-propyl-1,3-propanediol[g]	117–119	0.5	1.4545[h]	1.0733[h]	40.25	40.96	65	B					
10	2,2-Diethyl-1,3-propanediol[i]	44–45						75	B					
11	2-Ethyl-2-isoamyl-1,3-propanediol[j]	130–135	1.0	1.4705				25	B	$C_{10}H_{20}O_3$	63.79	10.71	64.50	10.56
12	2-Ethyl-2-phenyl-1,3-propanediol[k]	99–100						67	B	$C_{12}H_{14}O_3$	69.87	6.80	70.0	6.66
13	2-Methyl-2-phenyl-1,3-propanediol[l]	100						50	B	$C_{11}H_{12}O_3$	68.75	6.25	68.73	6.34
14	1,4-Butanediol[m]	88–93	0.8	1.4260[h]	1.0867[h]	26.39	27.38	16 12	C D	$C_5H_8O_3$	51.7	6.9	51.3	7.5

[a] J. J. Kolfenbach, E. I. Fulmer, and L. A. Underkofler, *J. Am. Chem. Soc.*, **67**, 502 (1945) give b.p. 96° (8 mm.), n_D^{26} 1.4225, d_4^{26} 1.129. [b] Recrystallized once from ligroin and then from methanol. [c] Recrystallization solvent methanol. [d] Recrystallized from aqueous ethanol. [e] Purified by first distillation at reduced pressure, b.p. 123° (1 mm.), 119° (0.9 mm.), and then recrystallized from ether; Ref. 5 records b.p. 135° (4 mm.), 105° (0.2 mm.), m.p. 47–48° (ether). [f] It was purified by resublimation *in vacuo*; see also ref. 1(c). [g] Ref. 3 reports b.p. 95–104° (0.25 mm.), n_D^{25} 1.4550. [h] Determinations being carried out at 16°. [i] Recrystallized from aqueous ethanol; Ref. 3 records a m.p. 45–46° and 66% yield by means of Method A. Attempts to polymerize this product by using sodium methoxide as catalyst, according to W. H. Carothers and Van Natta, Ref. 5, failed. [j] Inspection of the infrared spectrogram revealed the presence of some starting diol but it could not be purified any further. [k] Recrystallized from carbon tetrachloride; Ref. 3 reports m.p. 99.5–100.5°. [l] Recrystallized from carbon tetrachloride. [m] Mol. wt., calcd.: 116; found: 122 (benzene).

The solid polymeric residue left in the distilling pot amounted to 55–60% yield, and gave, upon recrystallization from carbon tetrachloride, a white amorphous solid product, m.p. 63–65°.

Anal. Calcd. for $(C_5H_8O_3)_x$: C, 51.7; H, 6.9. Found: C, 51.5; H, 7.4; av. mol. wt., 600 (Rast).

The infrared spectrum of compound No. 14 (IX) listed in Table I shows bands (cm.$^{-1}$) at 2976, 2950 (C—H stretching), 1730, 1718 (carbonyl), 1476, 1404, 1390, 1374 (C—H deformation), 1282, 1266, 1251, 1093, 1043, 1036, 1020, 1012 (C—O ethers), 952, 876, 796.

2,2-Dimethyl-3-hydroxypropyl carbamate (IId, Z = NH_2). A mixture of neopentylene glycol (13 g., 0.125 mol.) and ordinary urethane (11 g., 0.123 mol.) was placed in a flask equipped with a 12-inch Vigreux column, and to it was added a solution of 0.3 g. of aluminum isopropoxide in 50 ml. dry xylene. The resulting solution was heated and the ethanol was removed, as soon as formed, by distillation. At the end, 1 ml. of water was added and then the solvent was removed by distillation at reduced pressure. Fractionation of the residue *in vacuo* gave: (1) 3 g. (23%) of starting glycol, b.p. 76–80° at 1 mm., m.p. 122–124° (from benzene); (2) 10 g. (55%) of 2,2-dimethyl-3-hydroxypropyl carbamate of b.p. 110–120° at 1 mm. (reported[3] m.p. 60–61°).

Anal. Calcd. for $C_6H_{13}NO_3$: C, 49.0; H, 8.8. Found: C, 49.4; H, 9.2.

The infrared spectrum of this monocarbamate shows bands (cm.$^{-1}$) at 3330, 2970, 1700, 1695, 1620.

In the distillation flask 1–2 g. of a solid residue remained, which gave after two recrystallizations from hot water a crystalline dicarbamate of neopentylene glycol melting at 147–149° (reported[3] m.p. 151.5–152.5°).

When the heating of the reaction mixture was continued, after collecting the estimated amount of ethanol formed, measurable amounts of ammonia could be detected at the receiving flask. Upon fractionation of the reaction residue, small amounts of neopentylene carbonate could be isolated.

Isolation of 3-ethoxycarbonyloxy-2,2-dimethyl-1-propanol[17] (IId, Z = OEt). When 2.0 mol. of Id brought to reaction with 0.3 mol. of diethyl carbonate in the presence of 0.45% mol. of sodium methoxide in a fashion described above, a reaction mixture was obtained, consisting of 13.5 g. (52%) of a polymeric product (Vd) and 15.8 g. (45%) of a crude monoester IId. Refractionation of the latter at reduced pressure afforded 10 g. (28.5%) of a colorless liquid of b.p. 85–90° (0.5 mm.), n_D^{28} 1.4320.

Anal. Calcd. for $C_8H_{16}O_4$: C, 54.5; H, 9.1. Found: C, 54.6; H, 9.1.

The infrared spectrum shows band (cm.$^{-1}$) at 3430 (hydroxyl), 2963 (C—H stretching), 1739, 1731 (carbonyl), 1476, 1404, 1379 (C—H deformation), 1266–1262, 1190, 1122, 1053 (C—O ethers).

Conversion of IId into IIId.[17] To 8.8 g. (0.05 mol.) of IId (Z = OEt) was added 5 mol. % of catalyst and the resulting solution was heated at 130° in conditions described above. The ethanol was distilled as soon as formed, yielding the calculated amount (2.2 g.) after 3 hr. of heating. The residue was distilled *in vacuo* to give 6.0 g. (90%) of colorless product, boiling at 90° (0.5 mm.), m.p. 108–109°. It was identical, as to melting point, mixed melting point, and infrared spectrum, with an authentic sample of neopentylene carbonate. The infrared spectrum of pure neopentylene carbonate shows bands (cm.$^{-1}$) at 2920, 2878, 1739, 1730, 1476, 1408, 1377, 1323, 1294, 1242, 1227, 1198, 1187, 1124, 1117, 805, 774.

Isolation of 1-ethoxycarbonyloxy-3-butanol (IIb, Z = OEt). Transesterification of 1,3-butanediol by means of diethyl carbonate in the presence of a catalyst, gave, in one run, a considerable amount of a forerun, from which it was obtained upon refractionation, a colorless liquid, b.p. 81–84° (0.6 mm.), n_D^{29} 1.4235, in 10% yield.

Anal. Calcd. for $C_7H_{14}O_4$: C, 51.85; H, 8.64. Found: C, 51.60; H, 8.0.

Infrared: 3509 cm.$^{-1}$ (OH), 2985 cm.$^{-1}$ (C—H), 1780 cm.$^{-1}$, 1754 cm.$^{-1}$, 1739 cm.$^{-1}$ (C=O), 1471 cm.$^{-1}$, 1460 cm.$^{-1}$, 1370 cm.$^{-1}$ (C—H deformation), 1205 cm.$^{-1}$, 1149 cm.$^{-1}$, 1075–1058 cm.$^{-1}$, 1034 cm.$^{-1}$ (C—O ethers).

Cyclic carbonate of 1,3-butanediol (IIIb). The cyclization of 1-ethoxycarbonyloxy-3-butanol into the corresponding cyclic carbonate ester (IIIb) with accompanying elimination of the theoretical amount of ethanol was effected in a like manner as described above for IIId, with the same yield. The infrared spectrum of pure compound No. 6 (in Table I) shows bands (cm.$^{-1}$) at 3008, 2985 (methyl), 1733–1724 (carbonyl), 1498, 1488, 1408, 1365 (C—H stretching), 1250 (ester), 1200–1205, 1117 (C—O ethers), and at 772.

3-Carbamoxy-2-ethyl-2-phenyl-1-propanol (IIg, Z = NH_2). Ammonolysis of compound No. 12 in Table I (IIIg) to yield the monocarbamate IIg (Z = NH_2), was effected by means of concentrated aqueous ammonia solution (36–40%) at 0°. Five g. of IIIg were suspended in 50 ml. concentrated ammonia solution at 0–4°, and stirred for 2 hr., at which time the solution became completely clear, and then left to stand in an icebox overnight. From the acidified solution a crystalline monocarbamate m.p. 89–90° (lit.,[3] m.p. 89–90°) was recovered by removing the solvent *in vacuo*, followed by ether extraction and crystallization from carbon tetrachloride. The yield: 90%.

Anal. Calcd. for $C_{12}H_{17}NO_3$: C, 64.57; H, 7.62; N, 6.28. Found: C, 64.62; H, 7.67; N, 6.16.

Conversion of monocarbamate (IIg, Z = NH_2) *into cyclic carbonate ester* (IIIg). A solution of 3-carbamoxy-2-ethyl-2-phenyl-1-propanol (1 g.) in dry xylene (10 ml.) containing 15 mg. of sodium methoxide was refluxed for 100 hr. The ammonia was removed, as soon as formed, by a nitrogen stream bubbled through the solution, and was intermittently estimated. At the end no ammonia could be detected in the nitrogen stream, and heating was stopped. After removal of solvent and catalyst the residue was subjected to several recrystallizations from carbon tetrachloride, until it reached a m.p. of 95–98°. The infrared spectrum revealed that it was contaminated with some starting monocarbamate.

The infrared spectrum of 2-ethyl-2-phenyl-1,3-propanediol carbonate shows bands (cm.$^{-1}$) at 2985, 2933, 1739, 1731, 1605, 1586, 1488, 1413, 1399, 1389, 1359, 1258, 1205, 1190, 1183, 1147, 1110, 1099, 1064, 1058, 1034, 972, 946, 915, 794, 772, 757, 702.

Transesterification of pinacol. In the conditions described above, the reaction between ordinary pinacol and 20% excess of diethyl carbonate, in the presence of 3 mol. % of sodium methoxide (or more), was markedly slow, as shown by measuring the amount of ethanol formed at 1-hr. intervals. At the end of 12 hr., about 30% of the calculated amount of ethanol was collected. That this distillate contained other components than ethanol, is indicated by its positive response to carbonyl reagents, such as 2,4-dinitrophenylhydrazine. The carbonyl-containing component was proved to be acetone, yielding a 2,4-dinitrophenylhydrazone of m.p. 126–127° (lit.,[18] 128°), giving no depression of mixed melting point with an authentic specimen of dinitrophenylhydrazone of acetone. In addition to the desired cyclic carbonate (No. 3 in Table I), we were able to recover, from the reaction mixture, about 50% of starting materials.

The infrared spectrum of pinacole carbonate shows bands (cm.$^{-1}$) at 2975, 2912, 1782, 1754, 1563, 1460, 1379, 1294–1286, 1227, 1221, 1151, 1090, 1031, 1010, 883, 787, 716.

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(17) Work done by Mrs. S. Joseph.

(18) C. F. H. Allen, *J. Am. Chem. Soc.*, 52, 2955 (1930)

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Anomalous Reactions of Lithium Aluminum Hydride

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The preparation and properties of a number of branched 1,2- and 1,3-diols are described. The lithium aluminum hydride reduction of β-hydroxybutyraldehyde gives ethanol, among other products. The reduction of acetylacetone leads to a mixture consisting of 19% diketone (starting material), 70.5% pent-3-en-2-ol, and 2.5% of corresponding diol.

In connection with the study of the formation of homologous cyclic carbonates in the accompanying paper[2] it was necessary to prepare the required diols. The present paper describes the methods of preparation and properties of some of the needed compounds.

The methods used for the synthesis of the necessary diols were: (1) lithium aluminum hydride reduction of ketols and esters of dicarboxylic acids; (2) addition of Grignard reagents to β-hydroxyketones; (3) solvolysis of olefin dibromides.

The lithium aluminum hydride reduction of esters of ethylphenyl- and ethylisoamylmalonic acids proceeds smoothly, giving the corresponding 1,3-diols in 75% and 72% yield, respectively. However, the reduction of diethyl succinate resulted in a low yield of the desired 1,4-diol. This result is probably due to incomplete extraction of the diol from the reaction mixture.[3]

In the reduction of benzoin, we observed temperature-dependence in the stereochemical specificity of the hydride attack. Thus, whereas the reduction at 0° produced mesohydrobenzoin in 90% yield, the reduction similarly in boiling tetrahydrofuran gave a mixture of the isomers, meso- and isohydrobenzoins, in a ratio 3:1. This ratio is changed into 1.5:1, upon performing the reduction in boiling dioxane. The data here produced amplify the observations already recorded regarding the effect of temperature on the stereospecificity of the hydride attack.[4]

Unlike compounds described above, the lithium aluminum reduction of aldol took an anomalous course. This reaction yielded a complex mixture consisting of the required diol, ethanol, crotyl alcohol, and some other unidentified polymeric materials. The yield of 1,3-butanediol was 39%, whereas that of ethanol, actually isolated, amounted to 15%.

The observation described here clearly suggest that the reduction of aldol might have taken, at least partially, an anomalous course, involving C—C bond cleavage. Of course, the latter reaction might possibly have occurred either prior to or after the carbonyl group was reduced. In an experiment designed toward this establishment, 1,3-butanediol was similarly treated with a molar equivalent of lithium aluminum hydride. It was found that in comparable working conditions the unchanged diol could be recovered in high yield, but no ethanol could be detected.

From this, one can conclude that in the reduction process of aldol a carbon-carbon bond cleavage occurs prior to the hydride attack at the carbonyl group. This indicates that the final product in this reduction is determined by the order in which the groups are attacked. Initial reduction of the carbonyl group leads to the desired diol while prior reaction of the hydroxyl group can subsequently result in diol, or, by reversal of the aldol formation and further reduction, ethanol. In contrast to the reduction reaction, the addition of methyl magnesium iodide to acetaldol in ordinary conditions resulted in 70% yield of the corresponding diol. This reflects the different capacities of the above organometallic complexes of initiating a retrograde reaction of the aldol formation.

An inspection of the literature revealed that, although certain β-hydroxyketones are not affected by the mixed metal hydride complexes,[5] yet C—C bond cleavages have actually been observed in the lithium aluminum hydride reductions of certain 1,3-bifunctional systems, of which at least one was of unsaturated character. Thus, similar C—C bond

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[2] S. Sarel, L. A. Pohoryles, and R. Ben-Shoshan, *J. Org. Chem.*, **24**, 1873 (1959).

[3] Compare K. M. Mann and R. F. Nystrom, *J. Am. Chem. Soc.*, **73**, 5894 (1951).

[4] See L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 1675 (1949).

[5] (a) A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953); (b) R. L. Wear, *J. Am. Chem. Soc.*, **73**, 2390 (1951); S. P. Findlay and L. F. Small, *J. Am. Chem. Soc.*, **73**, 4001 (1951).