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DIETHYLENE GLYCOL *BIS*-CARBONATES OF LACTIC ESTERS[2]

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The acylation of several alkyl lactates with diethylene glycol *bis*-chloroformate (I) and the properties of the resulting diethylene glycol *bis*-carbonates (II)

$$\underset{\text{I}}{O[CH_2CH_2OCOCl]_2} \qquad \underset{\text{II}}{O[CH_2CH_2OCOOCH(CH_3)COOR]_2}$$

were reported in a previous paper from this Laboratory (1). Because of the commercial availability of the *bis*-chloroformate (I) and the potential value of the *bis*-carbonates (II) as plasticizers and resin intermediates (2–4), several additional *bis*-carbonates were made. They (Table I) were prepared as before (1) by acylating appropriate lactic esters with diethylene glycol *bis*-chloroformate.

The distilled *bis*-carbonates (II) were colorless and relatively viscous liquids having densities greater than one (Table II). The less viscous *bis*-carbonates were characterized by relatively long straight chains, such as those made from 2-ethoxyethyl, 2-butoxyethyl, and 2-(2-butoxyethoxy)ethyl lactates. The previously described (1) *bis*-carbonates made from *n*-alkyl lactates also were relatively fluid. The *bis*-carbonates having branched alkyl groups and rings were relatively viscous (Table II). The *bis*-carbonates (II) were thermally stable below about 225 to 250°.

It has been shown (1) that a straight line relationship[3] exists between the normal boiling points of ROH and the boiling points at 4 mm. of the corresponding *bis*-carbonates (II). The *sec*-alkyl and branched alkyl compounds of the present paper also fit moderately well into this relationship. The boiling points (Figures 1 and 2) at 4 mm. of the 2-alkoxyethyl, cyclohexyl, and methylcyclohexyl compounds, however, were about 10° higher than those predicted from the relationship.[3]

In agreement with earlier work on esters having two or more allyl groups (5, 6) the *bis*-carbonate made from allyl lactate (II, R = allyl) polymerized when heated in the presence of benzoyl peroxide. The polymer, presumably cross-linked, was transparent, colorless, hard, insoluble and infusible. The *bis*-carbonate made from allyl lactyllactate (II, R = $-CH(CH_3)COOCH(CH_3)COOCH_2CH{:}CH_2$) polymerized sluggishly when heated with benzoyl peroxide, the product being a soft, sticky, semisolid. Since the monomeric ester was not distilled (molecular weight too high), possibly impurities inhibited polymerization.

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Some of the material in this paper was presented before the Division of Paint, Varnish and Plastics Chemistry at the New York Meeting of the American Chemical Society, September 1947.

[3] B.p. (°C.) of ester at 4 mm. = 0.534 (b.p. of ROH at 760 mm.) + 187.

TABLE I

PREPARATION AND ANALYSES OF DIETHYLENE GLYCOL *bis*-CARBONATES OF LACTIC ESTERS

LACTATE USED	CONVERSION, %	C		H		CARBONATE AS CO_2, %		SAPN. EQUIV.	
		Calc'd	Found	Calc'd	Found	Calc'd	Found	Calc'd	Found
4-Methyl-2-pentyl[a]	—	56.9	57.2	8.4	8.5				
2,6-Dimethyl-4-heptyl	47					14.9	16.8	98.5	94.6
Cyclohexyl[a]	—	57.4	57.7	7.6	7.5				
Methylcyclohexyl[a]	—	58.9	59.1	8.0	8.1				
2-Methoxyethyl	71					19.4	19.7	75.7	76.1
2-Ethoxyethyl	67					18.2	18.2	80.4	80.4
2-Butoxyethyl	97					16.3	16.6	89.8	89.8
2-(2-Chloroethoxy)ethyl[b]	80					16.0	15.9	68.9	73.3
2-(2-Butoxyethoxy)ethyl[b]	95	53.7	53.4	8.0	8.3				
Tetrahydrofurfuryl	80	52.2	51.9	6.8	6.8	17.4	17.2	84.4	85.4
Allyl[a]	—					20.0	21.0	69.7	69.4
1-Carballyloxyethyl[b,c]	72	51.2	51.0	6.1	6.6	15.7	14.6	70.3	76.0
Isobutyl[d]	53					20.8	20.6	70.4	70.4

[a] Technical grades of these esters, kindly supplied by Franklin Strain and associates of the Columbia Chemicals Division of the Pittsburgh Plate Glass Company, were distilled and examined by the authors. [b] Undistilled. [c] Allyl lactyllactate. [d] Glycolate instead of lactate.

TABLE II

PROPERTIES OF DIETHYLENE GLYCOL *bis*-CARBONATES OF LACTIC ESTERS

LACTATE USED	n_D^{20}	n_D^{40}	d_4^{20}	d_4^{40}	MOL. REFRACTION			VISCOSITY, CPS.	
					Calc'd	Found at 20°	Found at 40°	20°	40°
4-Methyl-2-pentyl	1.4408	1.4340	1.0719	1.0560	124.6	124.8	124.9	593	96
2,6-Dimethyl-4-heptyl	1.4450	1.4380	1.0461	1.0294	152.3	150.3	150.6	1313	169
Cyclohexyl	1.4658	1.4590	1.1566	1.1392	120.2	120.3	120.6	22565	1092
Methylcyclohexyl	1.4630	1.4564	1.1254	1.1085	129.4	129.8	130.2	16240	832
2-Methoxyethyl	1.4480	1.4402	1.2167	1.1968	100.2	100.0	100.1	742	127
2-Ethoxyethyl	1.4462	1.4395	1.1776	1.1575	109.4	109.3	109.8	432	88
2-Butoxyethyl	1.4468	1.4400	1.1268	1.1104	128.9	127.6	127.9	330	78
2-(2-Chloroethoxy)ethyl	1.4622	1.4553	1.2645	1.2460	119.1	119.9	120.1	822	155
2-(2-Butoxyethoxy)ethyl	1.4485	1.4419	1.1146	1.0978	149.6	150.6	151.0	136	143
Tetrahydrofurfuryl	1.4660	1.4590	1.2297	1.2148	114.2	114.1	114.0	4440	516
Allyl	1.4550	1.4480	1.1873	1.1696	95.9	95.6	95.8	263	63
1-Carballyloxyethyl	1.4542	1.4437	1.1924	1.1721	127.0	127.8	127.4	1630	115
Isobutyl[a]	1.4440	1.4372	1.1620	1.1433	96.9	96.6	96.8	472	94

[a] Glycolate instead of lactate.

The diethylene glycol *bis*-carbonate of isobutyl glycolate was prepared for purposes of comparison. This glycolate boiled about 6° higher at 1 mm. than the corresponding isobutyl lactate derivative (1). This is in agreement with the boiling points of previously prepared derivatives of glycolic and lactic acid.

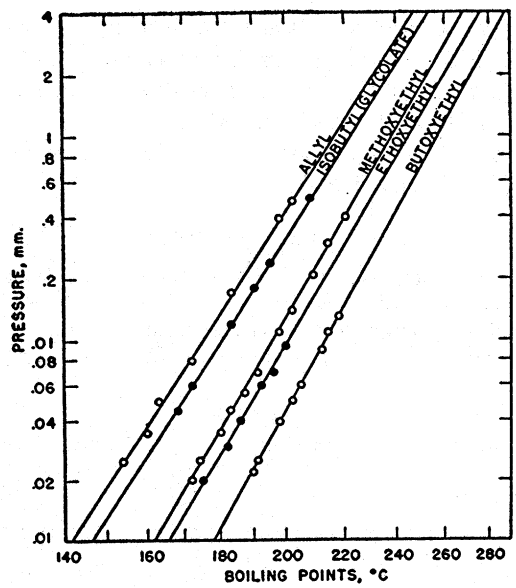

FIG. 1 BOILING POINTS OF DIETHYLENE GLYCOL BIS-CARBONATES OF LACTIC ESTERS

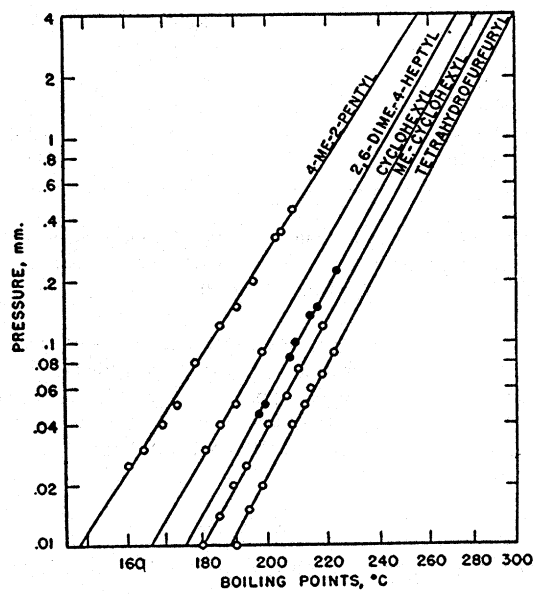

FIG. 2 BOILING POINTS OF DIETHYLENE GLYCOL BIS-CARBONATES OF LACTIC ESTERS

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EXPERIMENTAL

The lactic esters were prepared by previously described methods (2, 7). Table III gives data on the new lactates. Allyl lactylactate ($HOCH(CH_3)COOCH\cdot(CH_3)COOCH_2CH{:}CH_2$), was obtained as a by-product in the preparation of allyl lactate (7). Commercial diglycol *bis*-chloroformate was used as received. The lactic esters were acylated (1, 2)

TABLE III

PREPARATION AND PROPERTIES OF LACTIC ESTERS

PROPERTY		4-METHYL-2-PENTYL	2,6-DIMETHYL-4-HEPTYL	1-CARBALLYLOXY-ETHYL
Conversion, %		69	86	22
Boiling point °C., (mm.)		55 (1)	54 (0.1)	105 (1)
n_D^{20}		1.4220	1.4298	1.4448
d_4^{20}		0.9359	0.9166	1.1172
Mol. Refraction,	Calc'd	46.94	60.80	48.13
	Found	47.30	60.93	48.15
Sapn. Equiv.,	Calc'd	174.2	216.3	101.1
	Found	179.0	220.9	100.9
Carbon, %	Calc'd	62.0	66.6	53.5
	Found	61.9	67.6	53.5
Hydrogen, %	Calc'd	10.4	11.2	7.0
	Found	10.6	11.4	7.0

with the *bis*-chloroformate in the presence of pyridine and ether at about 0°. The products were washed successively with dilute acid and with water; most of the carbonates were then distilled at reduced pressure. The washed products, however, were light amber or almost colorless.

The distillations and boiling-point determinations were conducted in an improved tensimeter still (8), which was continuously agitated by a mechanical shaker. Refractive indices, densities, and viscosities were determined with an Abbé type refractometer, Sprengel type pycnometer, and modified Ostwald tube (9), respectively. For these measurements, a constant-temperature bath (10) set with a precision of 0.1° was used to maintain the temperature within ±0.02°.

SUMMARY

Several diethylene glycol *bis*-carbonates of lactic esters [R = 4-methyl-2-

$$O[CH_2CH_2OCOOCH(CH_3)COOR]_2$$

II

pentyl; 2,6-dimethyl-4-heptyl; cyclohexyl; methylcyclohexyl; 2-methoxyethyl; 2-ethoxyethyl; 2-butoxyethyl; 2-(2-chloroethoxy)ethyl; 2-(2-butoxyethoxy)

ethyl; tetrahydrofurfuryl; allyl; and 1-carballyloxyethyl] were made by acylation of the appropriate lactic ester with diethylene glycol *bis*-chloroformate ($O[CH_2CH_2OCOCl]_2$). The boiling points at different pressures, densities, refractive indices, and viscosities of the *bis*-carbonates (II) were determined. Some of these high-boiling esters are potentially useful as plasticizers and resin intermediates.

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