[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

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

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Received November 3, 1949

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

$O[CH_2CH_2OCOCl]_2$ (I) $\qquad O[CH_2CH_2OCOOCH(CH_3)COOR]_2$ (II)

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°	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.

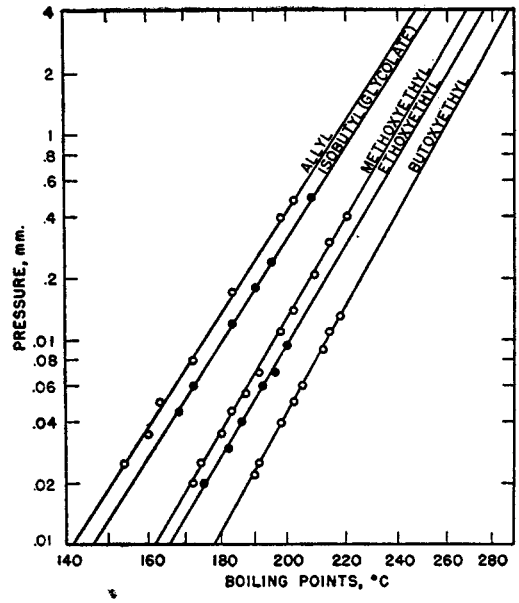

FIG. 1 BOILING POINTS OF DIETHYLENE GLYCOL BIS-CARBONATES OF LACTIC ESTERS

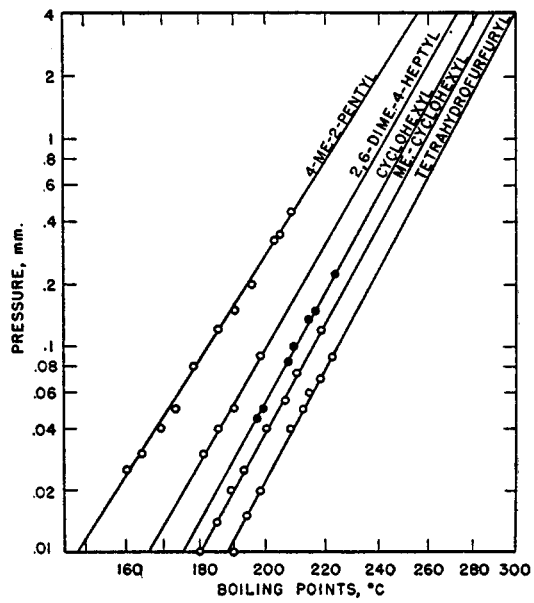

FIG. 2 BOILING POINTS OF DIETHYLENE GLYCOL BIS-CARBONATES OF LACTIC ESTERS

Acknowledgment. The authors are indebted to C. O. Willits and C. L. Ogg of this laboratory for analytical data; to Franklin Strain of Columbia Chemicals

Division of the Pittsburgh Plate Glass Company for diethylene glycol *bis*-chloroformate and technical, undistilled samples of some of the *bis*-carbonates (II); to R. L. Bateman, Carbide and Carbon Chemicals Corporation for the glycol monoethers; to K. R. Edlund, Shell Chemical Corporation for diisobutyl carbinol; and to the Barrett Division, Allied Chemical and Dye Corporation for cyclohexyl and methylcyclohexyl lactate.

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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