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

PREPARATION AND PROPERTIES OF DIETHYLENE GLYCOL BIS-CARBONATES OF ALKYL LACTATES[2] $O[CH_2CH_2OCOOCH(CH_3)COOR]_2$

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Received February 18, 1949

Recent papers (1,2) described various carbonates of lactic esters, most of which have high boiling points and the structure $ROCOOCH(CH_3)COOR'$. In extending this study of lactic acid derivatives having high boiling points[3], a series of diethylene glycol bis-(1-carbalkoxyethylcarbonates)

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

I

was prepared by treating alkyl lactates with diethylene glycol *bis*-chloroformate, $O[CH_2CH_2OCOCl]_2$. These compounds are of considerable interest because of their potential value as plasticizers (4) and the ease with which they can be made from commercially available intermediates. The preparation and certain properties (Table I) of the lactate diethylene glycol *bis*-carbonates (I) are reported in this paper.

Physical properties. Straight lines (Figs. 1 and 2) resulted when the boiling points were plotted against pressure on a Cox chart (10). Straight lines were obtained also by plotting log (pressure + 0.01) against temperature.

Working with homologous series of relatively simple compounds, such as *n*-paraffins (6,11), *n*-alkanols (6,12), aliphatic monoesters (13,14), diesters (6) and ether esters (15), the authors and other workers have previously determined linear relationships between M/d (M, molecular weight; d, density), M/n (n, refractive index), T^2 (T = b.p., °K.), log p (p, vapor pressure), and log η (η, viscosity) on the one hand and molecular weight or carbon atoms (x) on the other. These relationships were applied to the homologous diethylene glycol *bis*-carbonates of *n*-alkyl lactates (Tables II and III and Figures 3 and 4) (a) to determine whether such relationships are applicable to complex compounds having several functional groups, (b) to develop equations for calculating the physical properties of the missing members of the homologous series, (c) to provide quantitative relations[4], between any one property, such as boiling point, and the other

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[2] Much of the material described in this paper was included in two papers presented by one of the authors (C. E. Rehberg) before the Division of Organic Chemistry and the Division of Paint, Varnish, and Plastics Chemistry at the New York meeting of the American Chemical Society, September 1947.

[3] Many of the high-boiling lactic acid derivatives thus far prepared are useful as plasticizers (1–7).

[4] Achieved, for example, by selecting the two equations giving the relationship between boiling point and carbon atoms (x) and that between density and x, and then relating boiling point to density by eliminating x from the two equations.

TABLE I

YIELDS, ANALYSES, AND VISCOSITIES OF DIETHYLENE GLYCOL *bis*-CARBONATES OF ALKYL LACTATES

$O[CH_2CH_2OCOOCH(CH_3)COOR]_2$

ALKYL LACTATE	YIELD, %	CARBON %		HYDROGEN, %		SAPON. EQUIV.		CARBONATE AS CO_2		VISCOSITY, CENTIPOISES AT	
		Calc'd	Found	Calc'd	Found	Calc'd	Found	Calc'd	Found	20°	40°
Methyl	[a]	45.9	46.0	6.1	6.1					1818	187.0
Ethyl	85	48.7	48.5	6.7	6.9	65.7	65.8	22.3	22.3	375.4	70.76
n-Propyl	[a]					70.6	70.6	20.8	20.6	309.8	68.61
Isopropyl	[a]					70.6	70.6	20.8	20.6	555.4	88.93
n-Butyl	75	53.3	53.1	7.6	7.6					206.3	52.80
Isobutyl	74					75.1	75.3	19.5	20.4	482.2	87.77
sec-Butyl	77					75.1	74.9	19.5	19.6	476.2	88.22
n-Hexyl	93					84.4	85.5	17.4	17.2	232.1	59.83
2-Ethylbutyl	95					84.4	84.3	17.4	17.3	327.5	75.01
n-Octyl	97					93.8	96.4	15.6	15.9	204.5	58.60
2-Ethylhexyl	70					93.8	93.4	15.6	15.6	307.5	73.18

[a] Technical grades of these esters, kindly supplied by Franklin Strain and associates of the Columbia Chemical Division of the Pittsburgh Plate Glass Company, were redistilled and examined by the authors.

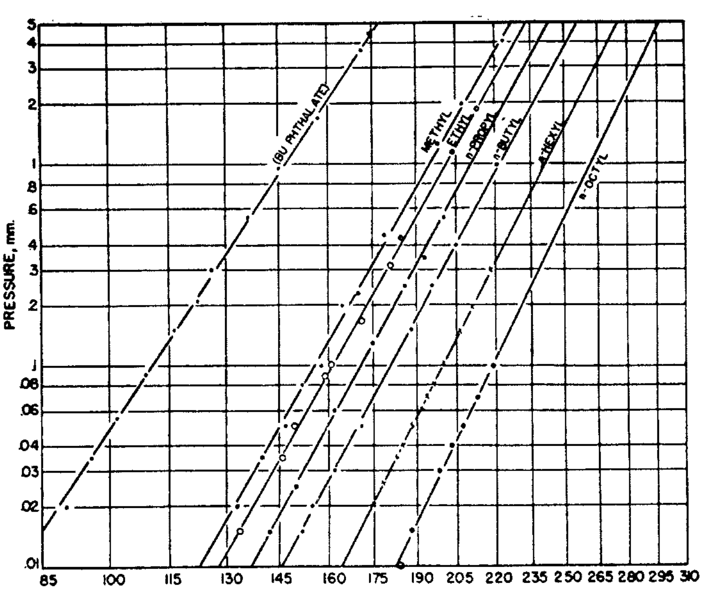

FIGURE 1. Boiling Points of Diethylene Glycol *bis*-Carbonates of Lactic Esters ($O(CH_2CH_2OCOOCH(CH_3)COOR)_2$)

properties, (that is, density, refractive index, etc.,) and (d) to provide an additional criterion of purity.

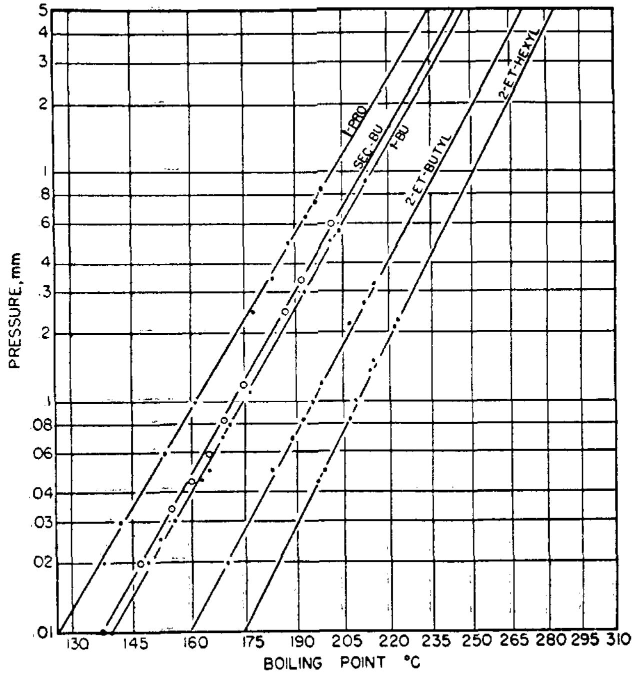

FIGURE 2. Boiling Points of Diethylene Glycol *bis*-Carbonates of Lactic Esters ($O(CH_2CH_2OCOOCH(CH_3)COOR)_2$)

TABLE II

PROPERTIES OF DIETHYLENE GLYCOL *bis*-CARBONATES OF ALKYL LACTATES
$O[CH_2CH_2OCOOCH(CH_3)COOR]_2$

LACTATE	n_D^{20}	n_D^{40}	d_D^{20}	d_D^{40}	MOLECULAR REFRACTION		
					Calc'd	Found at	
						20°	40°
Methyl	1.4432	1.4366	1.2411	1.2228	78.40	78.27	78.43
Ethyl	1.4407	1.4336	1.1882	1.1690	87.63	87.59	87.78
Propyl	1.4420	1.4348	1.1539	1.1356	96.87	96.85	97.01
Isopropyl	1.4370	1.4300	1.1430	1.1232	96.87	96.81	97.14
Butyl	1.4432	1.4360	1.1270	1.1087	106.11	106.00	106.25
Isobutyl	1.4413	1.4347	1.1224	1.1045	106.11	106.04	106.37
sec-Butyl	1.4400	1.4328	1.1213	1.1046	106.11	105.90	105.95
Hexyl	1.4455	1.4387	1.0842	1.0672	124.58	124.48	124.79
2-Ethylbutyl	1.4472	1.4406	1.0919	1.0761	124.58	124.01	124.41
Octyl	1.4477	1.4409	1.0565	1.0413	143.05	142.48	142.66
2-Ethylhexyl	1.4488	1.4420	1.0580	1.0420	143.05	142.58	142.89

Although the relationships used earlier with simpler homologous compounds were applicable for the boiling points, vapor pressures, densities, and refractive indices of the diethylene glycol *bis*-carbonates of *n*-alkyl lactates (Table III),

TABLE III

EQUATIONS RELATING PHYSICAL CONSTANTS OF $O[CH_2CH_2OCOOCH(CH_3)COOR]_2$ TO THE CARBONS IN R[a]

EQUATION NO.	CONDITIONS	EQUATION	DEVIATIONS[b]		
	Pressure, mm.		Members excluded[c]	Maximum	Average
1	4	$T^2\ 10^{-4} = 1.09x + 23.1$	1	2	0.7
2	1	$T^2\ 10^{-4} = 0.99x + 20.5$	1	1	0.6
3	0.4	$T^2\ 10^{-4} = 0.97x + 18.93$	1	1	0.2
	Temp., °C.				
4	200	$\text{Log p} = -0.2465x + 0.477$	1	0.01	0.00
			2	0.00	0.00
5	20	$M/d = 33.75x + 264.4$	1	0.00	0.00
			2[d]	0.00	0.00
6	20	$M/n = 19.15x + 235.5.$	1	0.0003	0.0001

[a] R = *n*-alkyl group; T = b.p., °K; x = carbon atoms in alkyl group; p = pressure, mm. Hg; $d = d_4^{20}$; and $n = n_D^{20}$.

[b] Given in terms of the physical constant concerned.

[c] First members of the homologous series unless otherwise stated.

[d] Methyl and octyl esters excluded.

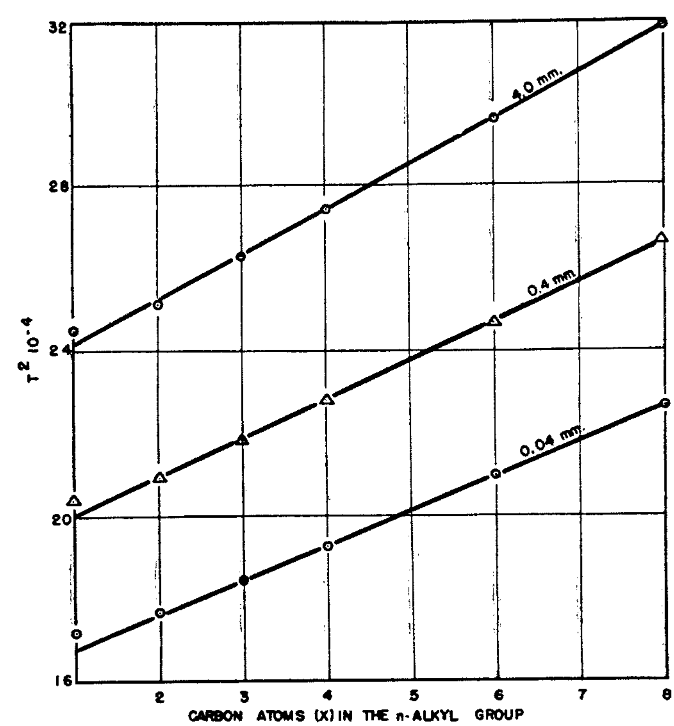

FIGURE 3. Relation between $T^2\ 10^{-4}$ and Carbon Atoms (x) of Diethylene Glycol *bis*-Carbonates of *n*-Alkyl Lactates $(O(CH_2CH_2OCOOCH(CH_3)COO(CH_2)_xH)_2)$ (T = b.p., °K.).

the previously recommended method of relating log viscosity to molecular weight was not satisfactory, that is, the relationship was not linear. As usual, the first one or two members of the series did not fit into any of these linear relationships.

The boiling points of the *n*-alkyl lactate carbonates are a straight line function of the normal boiling points of the corresponding *n*-alkanols. The relationship is defined by the equation:

B.p. of ester at 4 mm. = 0.534 (b.p. of ROH at 760 mm.) + 187

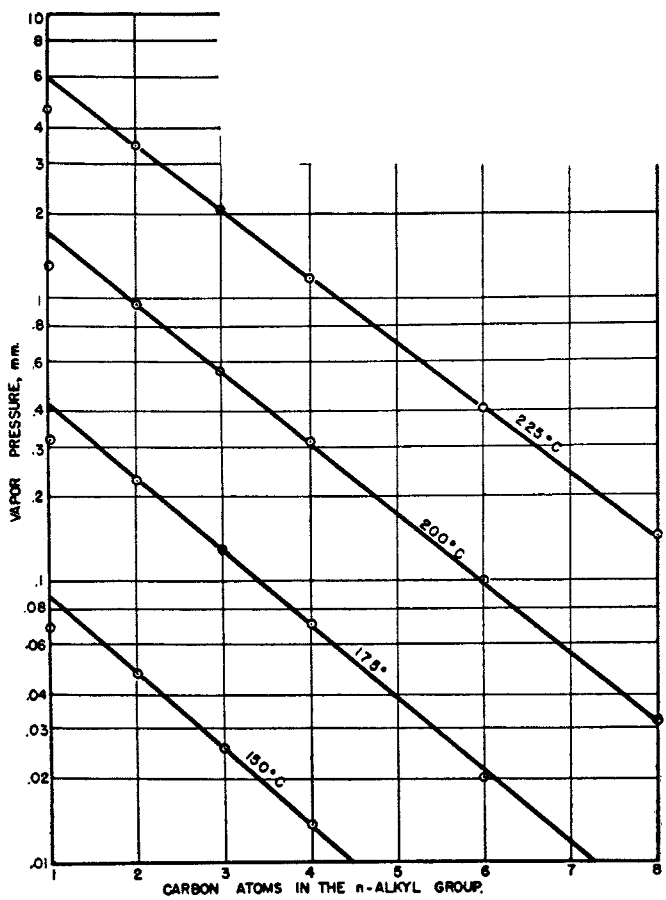

FIGURE 4. Relation Between Vapor Pressures of Diethylene Glycol *bis*-Carbonates of *n*-Alkyl Lactates and the Number of Carbon Atoms in the *n*-Alkyl Group.

The boiling points at 4 mm. calculated by this equation for the lactate carbonates prepared from secondary and branched-chain alcohols also are in good agreement with the determined boiling points except for the 2-ethylhexyl ester. The calculated boiling point for this compound is 5.0° high.

The boiling points at 1 mm. of the diethylene glycol bis-carbonates of *n*-alkyl lactates are compared with those of *n*-paraffins, *n*-alkanoic acids, and *n*-alkyl phthalates in Figure 5. This graphic representation clearly illustrates the unusually high boiling points of the lactate carbonates (I) and the relatively low slope of the lines representing the boiling point versus $M^{1/2}$ of polar compounds.

The boiling points of ethers, simple carbonates, and lactate carbonates were compared with each other to ascertain the relative effectiveness of the different functional groups in raising the boiling points (Table IV). The elevating effects are: Carbonate, 60 to 73°; lactate, 33–40°; carbonate plus lactate, 93–106°; and ether, 20°. The effectiveness of the functional groups appears to be inversely proportional to the molecular weight of the lactate carbonate.

Since the boiling points at 3 mm. of *n*-butyl phthalate (8) and diethylene glycol *bis*-(*n*-butyl carbonate) (9) are 169° and 175°, respectively, the diethylene

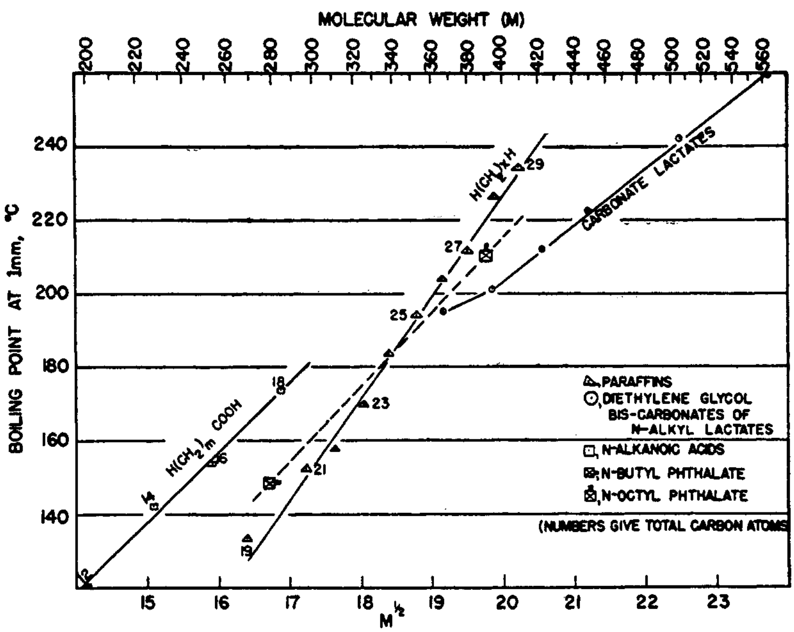

FIGURE 5. Boiling Points at 1 mm. of Diethylene Glycol *bis*-Carbonates of *n*-Alkyl Lactates, *n*-Paraffins, *n*-Alkanoic acids, *n*-Butyl Phthalate, and *n*-Octyl Phthalate.

glycol *bis*-carbonates in general might be expected to have boiling points somewhat higher than those of the corresponding phthalates. The boiling points of the lactate phthalates (2) and the alkyl lactate diethylene glycol *bis*-carbonates (I) are in agreement with this generalization. For example, the boiling points at 1 mm. of *n*-butyl lactate phthalate and *n*-butyl lactate diethylene glycol *bis*-carbonate (I) are 208° and 221°, respectively.

The diethylene glycol *bis*-carbonates of alkyl lactates (I) prepared from secondary or branched-chain alcohols had higher viscosities than the isomeric *n*-alkyl compounds. The *n*-propyl and *n*-butyl esters had higher densities and refractive indices than the corresponding isomeric esters, whereas the *n*-hexyl and *n*-octyl esters had lower densities and refractive indices than the corresponding 2-ethylbutyl and 2-ethylhexyl compounds.

TABLE IV

EFFECTS OF FUNCTIONAL GROUPS ON BOILING POINT[a] OF $O(CH_2CH_2-R)_2$

R	B.P., °C. (MM.)	B.P., DIFFERENCES °C[b]	EFFECT OF FUCTIONAL GROUP, °C.	REFERENCE
$-OMe$	13 (1);			19
	37.6 (5)	183		
$-OCOOCH(CH_3)COOMe$	196 (1);	189	93[c] ($-COOCH(CH_3)COO-$)	This paper
	227 (5)			
$-Et$	20 (4.8)			20
		40	20 ($-O-$)	20
$-OEt$	20 (0.4)			
	60 (4.8)			
		163	84[c] ($-COOCH(CH_3)COO-$)	This paper
		173		
$-OCOOCH(CH_3)COOEt$	183 (0.4)			
	233 (4.8)	213	106.5 ($-OCOOCH(CH_3)COO-$)	
$-$isopropyl	18.6 (1);			
	44.3 (5)	183	93[c] ($-OCOOCH(CH_3)COO-$)	19
$-OCOOCH(CH_3)COO-i-Pr$	202 (1);	190		This paper
	234 (5)			
$-n-Bu$	46 (3)			
		129	64.5 ($-OCOO-$)	20
$-OCOOBu$	175 (3)			
		71	35.5 ($-OCH(CH_3)COO-$)	9
$-OCOOCH(CH_3)COOBu$	246 (3)		100 ($-OCOOCH(CH_3)COO-$)	This paper

[a] Range of values: Ether, 20°; carbonate + lactate, 93–106°; lactate, 33–40°; and carbonate, 60–73°.

[b] Differences between boiling points observed under idential pressures.

[c] Average of two values.

As reported elsewhere (4), some of the diethylene glycol *bis*-carbonates of alkyl lactates, particularly the *n*-butyl, *n*-hexyl, *n*-octyl, and 2-ethylhexyl esters, are good plasticizers for vinyl chloride resins.

Acknowledgment. Analytical data were kindly supplied by C. O. Willits, C. L. Ogg, and their coworkers. The authors are indebted to Franklin Strain of Columbia Chemical Division, Pittsburgh Plate Glass Company, for supplying diethylene glycol *bis*-chloroformate and technical grades of some of the diethylene glycol *bis*-carbonates of alkyl lactates, and to R. L. Bateman of Carbide and Carbon Chemicals Corporation for 2-ethylbutanol and 2-ethylhexanol.

EXPERIMENTAL

Synthesis. Methyl, ethyl, and *n*-butyl lactates are commercially available. The others were prepared by alcoholysis of methyl lactate or by direct esterification of lactic acid (1). They have all been reported in the literature, though *sec-butyl lactate* has not been adequately characterized. The following properties were observed with our material: b.p., 35° (1 mm.); n_D^{20}, 1.4170; d_4^{20}, 0.9734; MR, calc'd, 37.71, obs., 37.76.

The reaction between the lactate and the chloroformate was conducted in ether solution. Pyridine was used to neutralize the hydrogen chloride evolved (1). After the chloroformate had been added to the reaction mixture at about 0°, the mixture was allowed to warm to room temperature. It was then washed to remove pyridine and salts, dried, and distilled.

Physical constants. The distillations and the boiling-point determinations were conducted in an improved tensimeter-still (8), which was continuously agitated by a mechanical shaker. With this equipment, reliable boiling points could be measured at pressures as low as a few hundredths of a millimeter. Pressures in the range 0.01 to 5.0 mm. were measured with a McLeod gauge.

Refractive indices, densities and viscosities were determined with an Abbe type refractometer, Sprengel type pycnometer, and modified Ostwald tube (16, 17), respectively. For these measurements, a constant temperature bath (18) was used to maintain the temperature within ± 0.02°.

Boiling points used in Table IV and in the construction of Fig. 5 were taken from the literature (8, 19, 20).

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