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

MIXED ESTERS OF LACTIC AND CARBONIC ACIDS. REACTION OF CHLOROFORMATES WITH ESTERS OF LACTIC ACID

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Although many esters of lactic acid have been described (1–3), and some of them have been acylated with various acid chlorides and anhydrides (1–9), few of the carbonates (I) have been reported. Since several alkyl chloroformates are now readily available, and esters of lactic acid are becoming increasingly important commercially (10–12), the preparation and study of additional mixed carbonic esters (I) of alkyl lactates appeared to be of interest.

$$\mathrm{ROCOCl} + \mathrm{HOCH(CH_3)COOR'} \rightarrow \underset{\mathrm{I}}{\mathrm{ROCOOCH(CH_3)COOR'}} + \mathrm{HCl}$$

Ritchie (4) and Kolfenback (13) treated methyl lactate with phosgene[2] and with methyl chloroformate and pyrolyzed the products [bis-(carbomethoxyethyl) carbonate (II, R = Me) and methyl carbomethoxyethyl carbonate, respectively] to make methyl acrylate. Both bis-(carbethoxyethyl) carbonate [II, R = Et (90% yield)] and carbethoxyethyl chloroformate have been prepared from ethyl lactate and phosgene (7, 14). Muskat and Strain (15) used the reaction between allyl or methallyl chloroformate and allyl, methallyl, or vinyl lactate to prepare several polymerizable carbonates (I, R and R′ = alkenyl). Bis-(carbalkenoxyethyl) carbonates (II, R = alkenyl) also were prepared (16), starting with alkenyl lactates and phosgene.

$$\underset{\mathrm{II}}{\mathrm{CO[OCH(CH_3)COOR]_2}}$$

Fischer (17) and Freudenberg (18) and their co-workers prepared several methyl and ethyl carbonate derivatives, respectively, of lactic acid. Carbonates of α-hydroxy acids other than lactic acid also have been made (19, 20).

In the present work, the carbonates (Table I) were made by treating an hydroxy ester, usually a lactate, with a chloroformate. In some experiments an alkyl glycolate or α-hydroxyisobutyrate was used instead of a lactate. The lactates and glycolates were observed to undergo acylation more readily than the alkyl α-hydroxyisobutyrates. All the resulting carbonates were clear, colorless, mobile liquids having relatively low vapor pressures and, in general, good chemical and thermal stability.

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[2] The unidentified product (boiling point 197–200°) obtained by Ritchie (4) by treating methyl lactate with phosgene appears from its physical constants and analytical data to be methyl carbomethoxyethyl carbonate (I, R, and R′ = Me). This product might have been formed from methyl lactate and methyl chloroformate; methanol, a possible precursor of methyl chloroformate, might have resulted from the hydrolysis or auto-alcoholysis of methyl lactate.

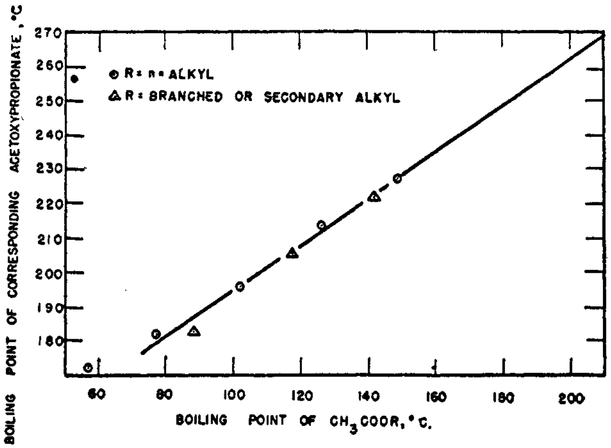

FIG. 1. RELATION BETWEEN NORMAL BOILING POINTS OF CH_3COOR AND THOSE OF THE CORRESPONDING ACETOXYPROPIONATES

($CH_3COOCH(CH_3)COOR$)

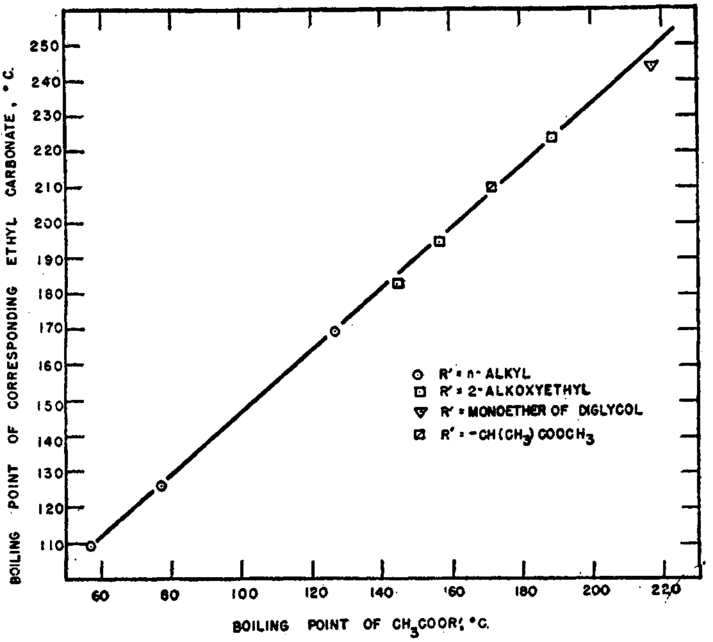

FIG. 2. RELATION BETWEEN NORMAL BOILING POINTS OF CH_3COOR' AND THOSE OF THE CORRESPONDING ETHYL CARBONATES

(CH_3CH_2OCOOR')

In agreement with observations made previously (16, 21, 22) with esters having two or more allyl groups, the carbonates formed in the reaction of allyl chloroformate with allyl and 3-buten-2-yl lactates were readily polymerizable.

Their polymers, presumably cross-linked, were clear, colorless, hard, insoluble, and infusible.

Drake and Carter (23) observed that certain alkyl and alkoxyethyl carbonates are compatible with cellulose acetate, and pointed out that the carbonates examined by them might be useful as plasticizers. In making a brief study of the suitability of our carbonates as plasticizers, we determined compatibility with some of the commercial resins (Table II). Several of the carbonates were compatible with polymethyl acrylate, Vinylite VYHH, low-acetyl cellulose acetate, and ethylcellulose, but in general they were incompatible with high-

TABLE I

α-CARBALKOXYALKYL CARBONATES [DERIVATIVES OF LACTIC ACID, ($ROCOOCH(CH_3)COOR'$), UNLESS OTHERWISE INDICATED]

NO.	R	R′	YIELD, %	n_D^{20}	d_4^{20}	ANALYSIS[a] Mol. refr. Calc'd	Mol. refr. Found	Carbon, % Calc'd	Carbon, % Found	Hydrogen, % Calc'd	Hydrogen, % Found
1	Ethyl	Octyl	49	1.4281	.9846	71.80	71.70	61.26	61.28	9.55	9.61
2	Chloroethyl	Methyl	44	1.4392	1.2568	44.34	44.09	39.92	39.88	5.27	5.20
3	Ethyl	Allyl	40	1.4280	1.0776	48.25	48.28	53.46	53.53	6.98	7.07
4	Allyl	Allyl	64	1.4410	1.0790	52.40	52.43	56.07	56.14	6.59	6.58
5	Allyl	3-Buten-2-yl	75	1.4380	1.0608	57.02	56.47	57.89	57.48	7.06	7.12
6	Ethyl	β-Ethoxyethyl	42	1.4229	1.0791	54.97	55.30	51.28	51.32	7.75	7.87
7	Ethyl	β-Chloroethoxyethyl	68	1.4439	1.1923	59.84	59.86	44.70	44.67	6.38	6.43
8	Ethyl	β-Butoxyethyl	69	1.4268	1.0481	64.21	64.24	54.94	54.64	8.46	8.45
9	Ethyl	Cyclohexyl	36	1.4436	1.0743	60.47	60.36	58.98	58.75	8.25	8.19
10	Ethyl	Methylcyclohexyl	48	1.4422	1.0492	65.09	65.16	60.43	60.40	8.59	8.61
11	Ethyl	Tetrahydrofurfuryl	85	1.4434	1.1390	57.39	57.37	53.64	53.24	7.37	7.28
12[b]	*n*-Butyl	*sec.*-Butyl	82	1.4221	1.0206	57.95	57.96	56.87	56.71	8.68	8.02
13[b]	*n*-Amyl	Ethyl	78	1.4239	1.0442	53.33	53.31	55.04	54.99	8.31	8.18
14[c]	*n*-Butyl	Ethyl	40	1.4202	1.0162	57.95	57.88	56.88	57.18	8.68	8.76
15[c]	*n*-Amyl	Ethyl	29	1.4237	1.0038	62.57	62.57	58.51	58.25	8.28	9.01
16	*i*-Propyl	Methyl	35	1.4118	1.0734	44.10	44.07	50.52	50.16	7.42	7.42
17	*i*-Butyl	Methyl	84	1.4180	1.0549	48.71	48.73	52.93	52.76	7.90	8.06
18[d]	Diethylene glycol	Ethyl	86	1.4407	1.1882	87.63	87.59	48.73	48.52	6.65	6.86
19[e]	Diethylene glycol	*n*-Butyl	75	1.4428	1.1270	106.11	105.92	53.32	53.07	7.61	7.61

[a] We are indebted to C. O. Willits and C. L. Ogg of the Analytical and Physical Chemistry Division for analytical data.

[b] Derivative of glycolic acid, *i.e.*, $ROCOOCH_2COOR'$.

[c] Derivative of α-hydroxyisobutyric acid, *i.e.*, $ROCOOC(CH_3)_2COOR'$.

[d] Diethylene glycol bis-(α-carbethoxyethyl carbonate).

[e] Diethylene glycol bis-(α-carbobutoxyethyl carbonate).

acetyl cellulose acetate and polyvinyl chloride. The tetrahydrofurfuryl ester was compatible with all the resins studied except polyvinyl chloride.

The stability to boiling water of some of the carbonates was determined by the method of Fordyce and Meyer (24). The two chlorine-containing esters (Table II) were least stable, presumably owing to the formation and catalytic action of hydrochloric acid. Some of the esters of ether-alcohols were relatively unstable to boiling water. The carbonates containing relatively little oxygen were most stable.

TABLE II

Compatibility and Boiling Water Stability Data

ESTER NO.[b]	COMPATIBILITY WITH RESINS[a]						FREE ACIDITY[h]	BOILING WATER STABILITY[i]
	Cellulose acetate[c]		Ethyl-cellulose[d]	Vinylite VYHH[c, e]	Vinylite QYNA[d, f]	Polymethyl acrylate[c, g]		
	Low-acetyl	High-acetyl						
1		CI	CI	C	I	C	0.48	0
2	C	C	C	C	I	C	0.35	573.6
5		I	CI	CI	—	—	—	—
6	C	CI	—	—	—	—	—	—
7	C	CI	CI	C	I	C	2.59	203.1[j]
8	C	CI	C	C	I	C	5.96	21.4[j]
9	C	I	C	C	CI	C	7.90	2.85
10	I	CI	C	CI	CI	C	0.27	0.08
11	C	C	C	C	I	C	2.47	107.6[j]
12	CI	I	CI	C	CI	C	0.18	0.33
13	I	I	C	C	CI	C	0.25	1.50
15	I	I	C	C	—	—	—	—
18	C	C	I	C	I	C	0.60	53.4
19	C	C	I	C	I	C	0.96	61.5

[a] C = compatible; I = incompatible; CI = borderline compatibility.

[b] Numbers are those used in Tables I and III.

[c] Twenty per cent plasticizer.

[d] Forty per cent plasticizer.

[e] Copolymer (88–90% vinyl chloride and 12–10% vinyl acetate); the use of specific brands of commercial products should not be construed as an endorsement or recommendation of these products over similar materials not mentioned.

[f] Polyvinyl chloride.

[g] Emulsion polymerized.

[h] Reported as the ml. *N* NaOH required to neutralize 100-g. sample.

[i] Difference between free acidity (footnote h) and the *N* NaOH required to neutralize 100-g. sample after boiling with water for 24 hours.

[j] End point of titration uncertain because of fading.

Boiling points at 760 mm. of the carbonates were estimated from the determined boiling point at 10 mm. and by other methods (Table III). Comparison of these boiling points with those of widely used plasticizers[3] shows that some

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[3] For example, methyl and butyl phthalate boil at 150° and 200°, respectively, under 10 mm. pressure (25, 38).

of the carbonates are sufficiently nonvolatile for use as plasticizers. Compounds 18 and 19 (Tables I to III), prepared by acylating ethyl and butyl lactate with diglycol chloroformate [$O(CH_2CH_2OCOCl)_2$], are of particular interest from the standpoint of low vapor pressure.

TABLE III

Boiling Points and Viscosities of $ROCOOCH(CH_3)COOR'$

ESTER NO.[a]	R	R′	BOILING POINT, °C.				VISCOSITY AT 20°C.	
			10 mm. (determined)	760 mm. (est.)			Centistokes	Centipoises
				A[b]	B[c]	C[d]		
1	Et	Octyl	168	312	295	317	8.96	9.10
2	$ClCH_2CH_2$	Me	136	272	—	—	28.82	22.93
3	Et	Allyl	111	240	231	229	—	—
4	Allyl	Allyl	125	258	—	244	—	—
5	Allyl	3-Buten-2-yl	126	259	—	257	—	—
6	Et	$EtOCH_2CH_2$	139	276	261	264	—	—
7	Et	$ClCH_2CH_2OCH_2CH_2$	176	323	296	—	26.21	21.98
8	Et	$BuOCH_2CH_2$	159	301	281	297	9.70	9.26
9	Et	Cyclohexyl	151	291	274	291	21.24	19.77
10	Et	Me cyclohexyl	157	298	278	307	20.39	19.43
11	Et	Tetrahydrofurfuryl	162	305	285	284	22.86	20.07
12[e]	Bu	sec.-Bu	135	270	—	272	6.75	6.67
13[e]	Am	Et	139	275	—	265	6.36	6.09
14[f]	Bu	Et	120	251	—	252	—	—
15[f]	Am	Et	131	265	—	273	—	—
16	Isopropyl	Me	100	226	—	211	—	—
17	Isobutyl	Me	110	238	—	233	—	—
18	Diethylene glycol	Et	258	427	—	410	221.7	263.4
19	Diethylene glycol	Bu	278	453	—	459	133.6	150.6

[a] Numbers are those used in Tables I and II.

[b] Estimated from the boiling point at 10 mm., using the equation, b.p. at 760 mm. = 1.276 (b.p. at 10 mm.) + 98, and the group 3 classification of C. Bordenca (26). Boiling points about 4° lower than those of Column A would be obtained by using Bordenca's group 4 classification.

[c] The boiling point of $CH_3COOCH(CH_3)COOR$ (taken from Fig. 1) was used with Fig. 2 to estimate the boiling point of $CH_3CH_2OCOOCH(CH_3)COOR'$ (See experimental section for further details).

[d] Estimated by C. R. Kinney's method (27, 28).

[e] Derivative of glycolic acid.

[f] Derivative of hydroxyisobutyric acid.

Although the agreement among the estimated boiling points in Table III is unsatisfactory in some instances, estimated boiling points should be frequently useful for predicting whether proposed plasticizers would be too volatile.

A straight line was obtained by plotting the boiling points at 10 mm. of the carbonates

$$CH_3CH_2OCOOCH(CH_3)COOR$$
$$\text{III}$$

against the normal boiling points of the corresponding alcohols, that is, ROH (Fig. 3). A somewhat similar relationship, which appears to be applicable to all the carbonates (I), is shown in Figure 4. The relationships of Figures 3 and 4 should be useful for predicting the boiling points of other alkyl carbalkoxyethyl carbonates. Figure 4 indicates also that the effect of the lactic acid segment [—$OCH(CH_3)CO$—] in alkyl carbalkoxyethyl carbonates is to raise the boiling point approximately 60°.

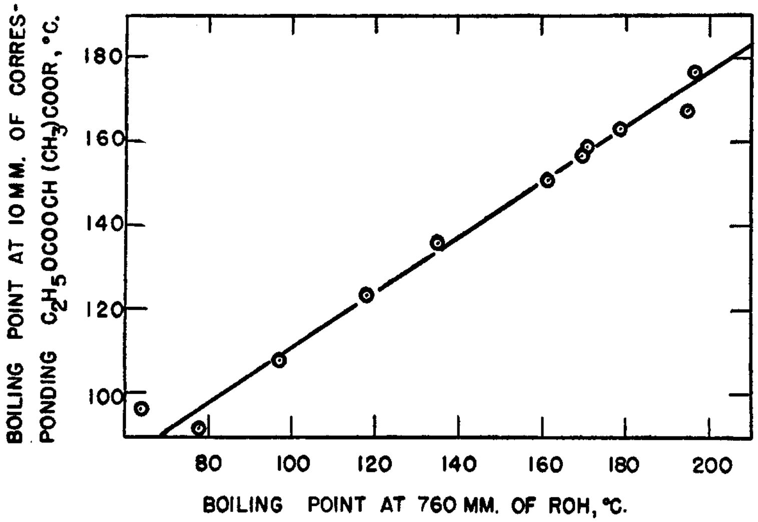

FIG. 3. RELATION BETWEEN BOILING POINTS OF ROH AND CORRESPONDING $C_2H_5OCOOCH(CH_3)COOR$

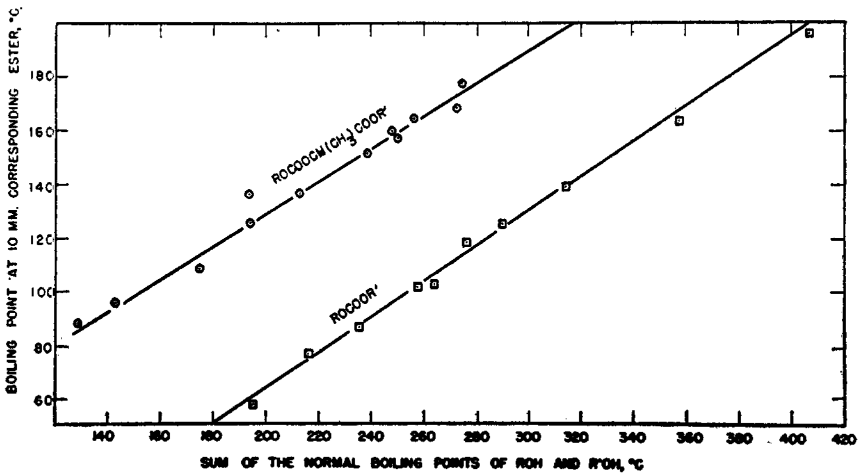

FIG. 4. RELATION BETWEEN THE SUM OF THE NORMAL BOILING POINTS OF ROH AND R'OH AND THE BOILING POINT AT 10 MM. OF THE CORRESPONDING $ROCOOCH(CH_3)COOR'$ OR $ROCOOR'$

The viscosity of the carbonates (Table III) varied over a wide range, the compounds containing chlorine, rings, or two carbonate groups being relatively viscous.

ACKNOWLEDGMENT

We are indebted to U. S. Industrial Chemical Company for furnishing ethyl chloroformate, to Pittsburgh Plate Glass Company, Columbia Chemical Division, for allyl chloroformate, diethylene glycol bis-chloroformate, and technical, undistilled diglycol carbonate of butyl lactate, to Carbide & Carbon Chemicals Corporation for Cellosolve, Butyl Cellosolve, and diglycol chlorohydrin, to Rohm and Haas Company for ethyl α-hydroxyisobutyrate, and to the Barrett Division of Allied Chemical and Dye Company for cyclohexyl and methylcyclohexyl lactates.

TABLE IV

LACTIC ESTERS

ESTER	YIELD, %	BOILING POINT		n_D^{20}	d_4^{20}	MOLECULAR REFRACTION		SAP. EQUIV.	
		°C.	mm.			Calc'd	Found	Calc'd	Found
n-Octyl[a]	52	78	0.1	1.4350	0.9362	56.18	56.38	202.3	202.1
3-Buten-2-yl	77	70	13	1.4326	1.0091	37.24	37.10	144.2	144.5
Chloroethoxyethyl	90	101	0.6	1.4565	1.2088[b]	44.22	44.26	98.3	98.9[b]
Tetrahydrofurfuryl	94	80	1.1	1.4570	1.1361	41.77	41.75	—	—
β-Butoxyethyl	88	70	0.4	1.4332	1.0177	48.58	48.59	—	—

[a] Wood, Such, and Scarf (2) obtained a 50% yield of n-octyl lactate and reported: b.p. 137° (11 mm.); d_4^{20}, 0.9304

[b] These data were taken from Reference 29.

EXPERIMENTAL

Lactates. β-Ethoxyethyl, β-butoxyethyl, β-chloroethoxyethyl, and tetrahydrofurfuryl lactates were prepared by a previously described method (3, 29). The last compound was also prepared in 94% yield by the alcoholysis of methyl lactate. A mixture of methyl lactate and tetrahydrofurfuryl alcohol (four moles of alcohol to one of methyl lactate; no catalyst was added) was refluxed under a column, through which methanol was removed as rapidly as it was formed. When the reaction ceased, the product (Table IV) was fractionated in vacuum. Similarly, butoxyethyl lactate (Table IV) was prepared by alcoholysis of methyl lactate, aluminum isopropoxide being used as catalyst.

3-Buten-2-yl and n-octyl lactates (Table IV) were prepared by the direct esterification of edible-grade lactic acid (82% concentration), sulfuric or toluene sulfonic acid being used as catalyst and benzene as an entraining agent. Five times the theoretical amount of alcohol was used for the 3-buten-2-yl ester, resulting in a yield of 77%. Twice the theoretical amount of octanol produced a yield of 52% of lactate. Purification of octyl lactate was difficult because of the presence of lactide. The latter appeared to be formed when the lactate was distilled, and since its boiling point is near that of octyl lactate, the two distilled together. The difficulty was minimized but not eliminated by distilling under low pressure and at a rapid rate. The addition of an alkaline buffer salt such as sodium acetate also helped to stabilize the lactate.

Chloroethoxyethyl lactate (Table IV) was prepared in 90% yield by the alcoholysis of methyl lactate, no catalyst being used. This ester has also been prepared by direct esterification, without catalyst, with a yield of 96% (29).

Reaction of chloroformates with hydroxy esters. The hydroxy ester (1.0 equivalent) and pyridine (1.1 eq.) were placed in a flask fitted with stirrer and dropping-funnel. The chloroformate (1.1 eq.) was added slowly, the temperature of the mixture being kept below 15°. After mixing of the reagents was complete, the flask was left overnight at room temperature and was then heated at about 80° for 2 hours. The product was cooled, washed several times with water, once with dilute acid to remove traces of pyridine, again with water, and then dried and distilled under reduced pressure. Relatively low yields were obtained in the acylation of the alkyl α-hydroxyisobutyrates (Table I).

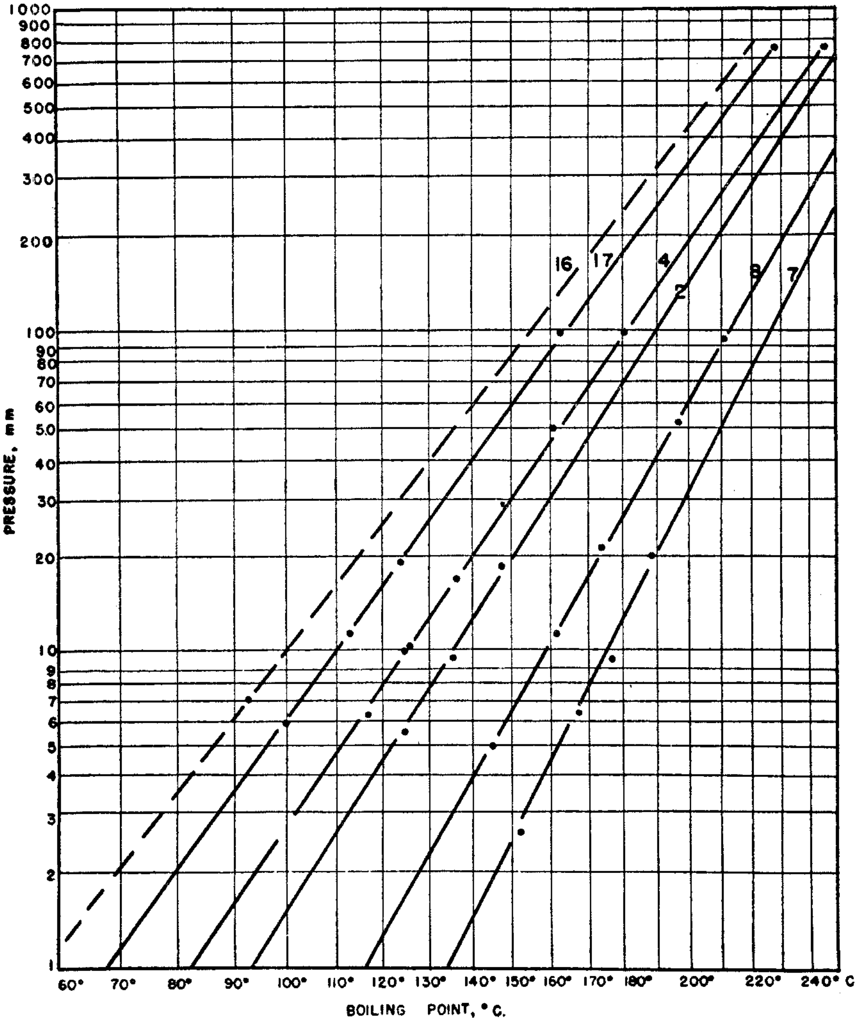

FIG. 5. BOILING POINTS OF CARBONATES (COMPOUNDS ARE NUMBERED AS IN TABLE I)

Although the carbonates were prepared as described in the preceding paragraph, more recent experiments indicate that a temperature of about −10° to +10° during addition of the chloroformate and omission of the subsequent heating lead to higher yields. It also seems preferable to filter out the pyridine hydrochloride before washing and to treat the residue and the filtrate separately. The use of dry ether as a reaction solvent also seems advantageous.

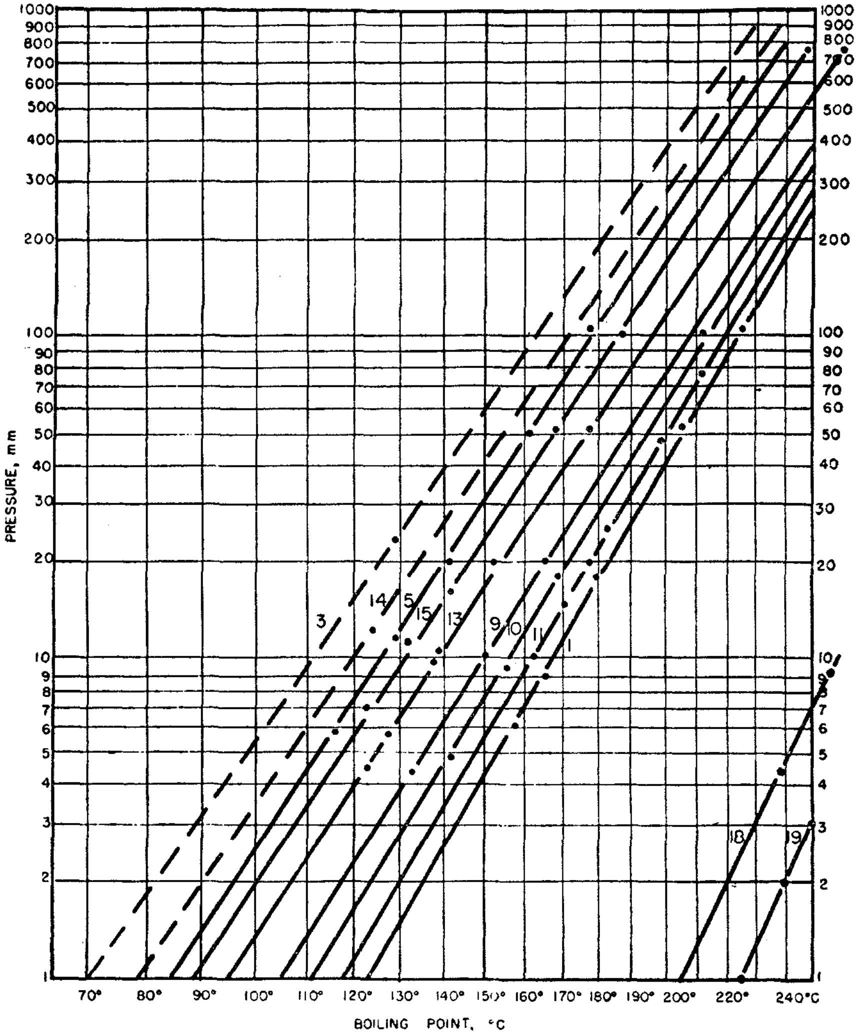

FIG. 6. BOILING POINTS OF CARBONATES (COMPOUNDS ARE NUMBERED AS IN TABLE I)

Polymerization of unsaturated esters. The esters produced by the reaction of allyl chloroformate with allyl and 3-buten-2-yl lactates readily polymerized when 1% of benzoyl peroxide was added and the monomers, in sealed tubes, were left overnight in an oven at 80°. The polymers were hardened by baking for another 24 hours at 100° and were then clear, colorless, bubble-free, insoluble, and infusible.

Boiling points. The esters were distilled under various pressures, and the boiling points thus observed were used in constructing Figures 5 and 6. The boiling points at 10 mm. pressure recorded in Table III were taken from Figures 5 and 6. The supply of esters No.

3, 14, and 16 was exhausted before other boiling points were determined, so that only one point for each is shown on Figures 5 and 6. In order to estimate their boiling points at other pressures, tentative lines were drawn through these single points; the slopes of these tentative lines were estimated from those of the adjacent lines. Esters No. 2, 6, and 12 are represented by a single line in Figure 5. The points shown are for No. 2, but those for No. 6 and 12, in the same pressure range, fell approximately on the same line.

Most of the esters began to decompose slowly when heated to 220° to 260°, and only a few boiling points at atmospheric pressure could be determined. In addition to those shown in Figures 5 and 6, ester No. 3 boiled at 220°, with considerable decomposition and polymerization. Hydroquinone was added to No. 4, after which it could be distilled (b.p. 247°) with little decomposition and no polymerization.

Cox charts (30, 31) and semi-log paper (32) have been used previously for plotting boiling points as a function of pressure. Recently described methods (26, 35) were used to estimate normal boiling points from those observed at 10 mm. (Table III).

Figure 1, prepared with data taken from references 1, 8, and 9, and Figure 2 are based on the existence of linear or approximately linear relationships between the boiling points of CH_3COOR and those of the corresponding acetoxypropionates [$CH_3COOCH(CH_3)COOR$] and ethyl carbonates (CH_3CH_2OCOOR). The authors, who have observed that similar relationships exist between acetates and various other esters (such as butyrates, octanoates, and benzoates), believe that figures such as 1 and 2 should be generally useful for predicting boiling points of unknown esters and checking the accuracy of determined boiling points. Figure 2 may be used to estimate the boiling point of an ethyl carbonate (CH_3CH_2OCOOR') if the boiling point of the acetate (CH_3COOR') is known. For the carbonates considered herein, R′ is $-CH(CH_3)COOR$, and the acetate is $CH_3COOCH(CH_3)COOR$. The boiling point of this acetate (acetoxypropionate) may be estimated from Figure 1 if the boiling point of the simple acetic ester CH_3COOR is known. The latter can usually be found in the literature.

The boiling points of the carbonates used in the construction of Figures 2, 3, and 4 were taken from references 23, 33, 34, 36, and 37 or from the present work.

SUMMARY

Various carbalkoxyalkyl carbonates were prepared by acylating esters of lactic acid, glycolic acid, and α-hydroxyisobutyric acid with several chloroformates. Lactic esters (methyl, octyl, allyl, 3-buten-2-yl, β-ethoxyethyl, β-chloroethoxyethyl, β-butoxyethyl, cyclohexyl, methylcyclohexyl, and tetrahydrofurfuryl) were used in most of the preparations. The acylating agents included ethyl, butyl, amyl, β-chloroethyl, allyl, and diethylene glycol chloroformates.

Carbonates having two olefinic linkages were made by treating allyl and 3-buten-2-yl lactates with allyl chloroformate. These two unsaturated carbonates polymerized readily when heated in the presence of benzoyl peroxide. The polymers were hard, colorless, insoluble and infusible.

Several of the carbonates, which were compatible with cellulose derivatives and vinyl resins and had relatively low vapor pressures, are potentially useful as plasticizers.

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REFERENCES

(1) Smith and Claborn, *Ind. Eng. Chem.*, **32**, 692 (1940).
(2) Wood, Such, and Scarf, *J. Chem. Soc.*, **123**, 600 (1923).

(3) Fein, Ratchford, and Fisher, *J. Am. Chem. Soc.*, **66**, 1201 (1944).
(4) Ritchie, *J. Chem. Soc.*, 1054 (1935).
(5) Claborn, U. S. Patent 2,350,388, June 6, 1944.
(6) Rehberg, Dixon, and Fisher, *J. Am. Chem. Soc.*, **67**, 208 (1945).
(7) Gerrard, *J. Chem. Soc.*, 218 (1940).
(8) Claborn and Smith, *J. Am. Chem. Soc.*, **61**, 2727 (1939).
(9) Fein and Fisher, *Ind. Eng. Chem.*, **36**, 235 (1944).
(10) Peckham, Jr., *Chem. Eng. News*, **22**, 440 (1944).
(11) Filachione and Fisher, *Ind. Eng. Chem.*, **38**, 228 (1946).
(12) Haworth, Gregory, and Wiggins, *J. Soc. Chem. Ind.*, **65**, (3) 95 (1946).
(13) Kolfenback, *Iowa State College J. Sci.*, **19**, 35 (1944).
(14) Thiele and Dent, *Ann.*, **302**, 245 (1898).
(15) Muskat and Strain, U. S. Patent 2,384,126, Sept. 4, 1945; U. S. Patent 2,385,934, Oct. 2, 1945; and U. S. Patent 2,387,931, Oct. 30, 1945.
(16) Muskat and Strain, U. S. Patents 2,384,116-7-8, Sept. 4, 1945; U. S. Patents 2,384,124-6, Sept. 4, 1945.
(17) Fischer and Fischer, *Ber.*, **47**, 768 (1914).
(18) Freudenberg and Meister, *Ann.*, **515**, 86 (1935).
(19) Heintz, *Ann.*, **154**, 257 (1870).
(20) McKenzie and Lesslie, *Ber.*, **61**, 153 (1928).
(21) Simpson, *J. Soc. Chem. Ind.*, **65**, (4) 107 (1946).
(22) Rehberg, Dixon, and Fisher, *J. Am. Chem. Soc.*, **68**, 544 (1946).
(23) Drake and Carter, *J. Am. Chem. Soc.*, **52**, 3720 (1930).
(24) Fordyce and Meyer, *Ind. Eng. Chem.*, **32**, 1053 (1940).
(25) Mellan, "Industrial Solvents," **1939**, 480 pp., Reinhold Publishing Corp., New York N. Y.
(26) Bordenca, *Ind. Eng. Chem., Anal. Ed.*, **18**, 99 (1946).
(27) Kinney, *J. Am. Chem. Soc.*, **60**, 3032 (1938).
(28) Lange, Editor, "Handbook of Chemistry," 5th Ed., **1944**, p. 853, Handbook Publishers, Inc., Sandusky, Ohio.
(29) Fein and Fisher, *J. Am. Chem. Soc.*, **68**, 2631 (1946).
(30) Cox, *Ind. Eng. Chem.*, **15**, 592 (1923).
(31) Calingaert and Davis, *Ind. Eng. Chem.*, **17**, 1287 (1925).
(32) Thomson, *Chem. Rev.*, **38**, 1 (1946).
(33) Bowden and Butler, *J. Chem. Soc.*, 75 (1939).
(34) Hunter, *J. Chem. Soc.*, **125**, 1389 (1924).
(35) Lippincott and Lyman, *Ind. Eng. Chem.*, **38**, 320 (1946).
(36) Woodward, Kohman, and Harris, *J. Am. Chem. Soc.*, **63**, 120 (1941).
(37) Bowden, *J. Chem. Soc.*, 310 (1939).
(38) Hickman, *J. Franklin Inst.*, **221**, 383 (1936).