

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY¹]Preparation and Physical Properties of *n*-Alkyl β -*n*-Alkoxypropionates

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A previous paper² described the addition of various alcohols to acrylic esters, and demonstrated that this reaction, discovered by Purdie and Marshall,³ can be used conveniently to prepare many alkyl β -alkoxypropionates. The primary purpose

pounds of the type $\text{ROCH}_2\text{CH}_2\text{COOCH}_3$ and $\text{CH}_3\text{OCH}_2\text{CH}_2\text{COOR}$ (where R is *n*-alkyl) have virtually identical boiling points, densities and refractive indices. The data obtained with additional alkoxypropionates (Table I and Fig. 1) con-

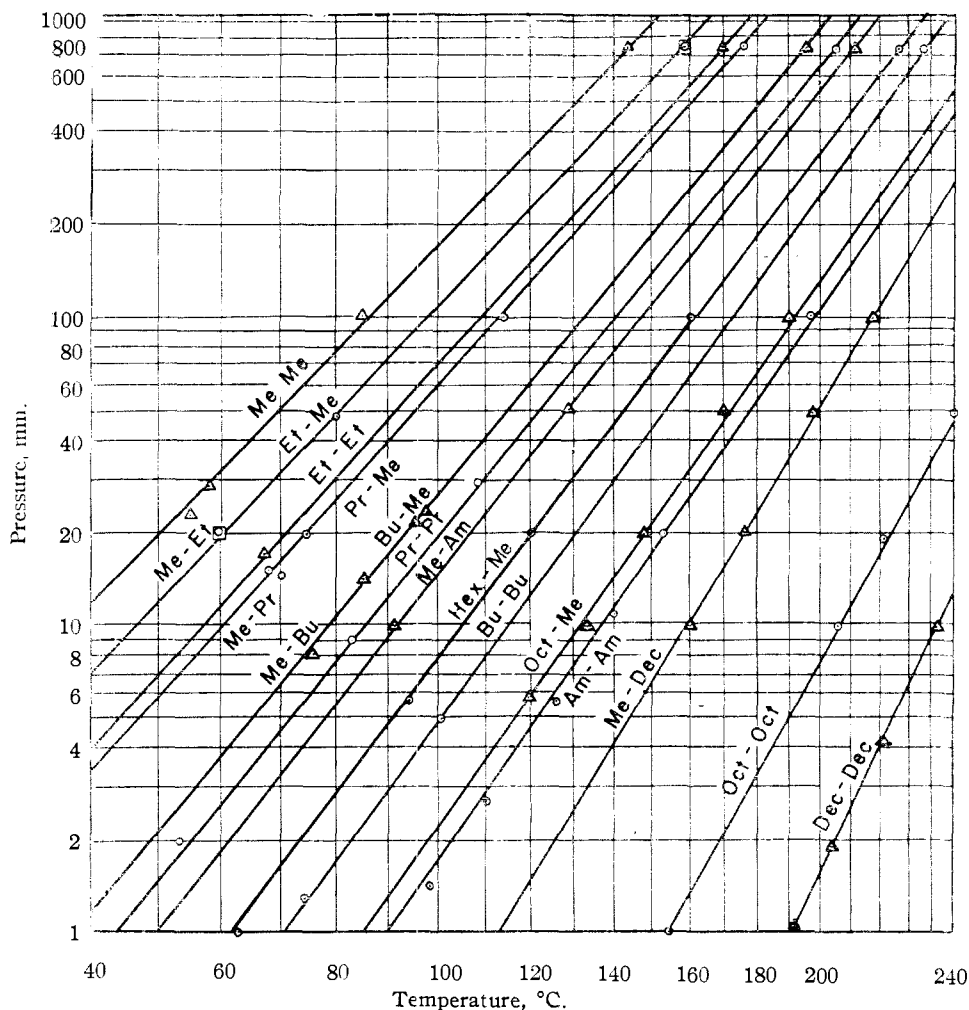


Fig. 1.—Vapor pressure of *n*-alkyl alkoxypropionates, $\text{ROCH}_2\text{CH}_2\text{COOR}'$, given in order R—R'.

of the present work was to prepare additional *n*-alkyl β -*n*-alkoxypropionates and to determine certain of their properties, particularly those having usefulness in predicting the suitability of these ether-esters as solvents and plasticizers.

It was indicated previously² that isomeric com-

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) C. E. Rehberg, Marion B. Dixon and C. H. Fisher, *THIS JOURNAL*, **65**, 544 (1946).

(3) T. Purdie and W. Marshall, *J. Chem. Soc.*, **59**, 468 (1891).

firm this observation, and in the present paper the methyl alkoxypropionates and the alkyl methoxypropionates are treated as one homologous series. The boiling points, densities and refractive indices of $\text{ROCH}_2\text{CH}_2\text{COOR}$ (R = identical *n*-alkyl groups) are lower than those of the isomeric methyl alkoxypropionates and *n*-alkyl methoxypropionates.⁴ Not all members of the homologous

(4) Presumably these differences are due to the higher association of the methyl esters and the isomeric methyl ethers [E. C. Bingham and L. W. Spooner, *Physics*, **4**, (11), 387 (1933)].

TABLE I
 β -ALKOXYPROPIONATES

ROCH ₂ CH ₂ COOR' R	Yield, % ^a	<i>d</i> ₄ ²⁰	<i>n</i> _D ²⁰	<i>M</i> _w ²⁰		Sapon. equiv.		Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>n</i> -Hexyl Methyl	36 ^b	0.9249	1.4220	51.68	51.70	188.3	192.0				
<i>n</i> -Octyl Methyl	13 ^c	.9130	1.4295	60.91	61.15	216.3	215.5	66.63	66.55	11.18	10.57
<i>n</i> -Amyl <i>n</i> -Amyl	38 ^d	.9027	1.4286	65.53	65.72	230.3	230.8	67.78	67.89	11.38	11.12
<i>n</i> -Hexyl <i>n</i> -Hexyl	42 ^b	.8940	1.4318	74.77	74.94	258.4	264.9	69.72	69.16	11.70	11.89
<i>n</i> -Octyl <i>n</i> -Octyl	15 ^c	.8868	1.4407	93.24	93.59	314.5	310.9	72.56	72.70	12.18	12.18
<i>n</i> -Decyl <i>n</i> -Decyl	58 ^d	.8797	1.4450	111.71	112.11	370.6	369.7	74.53	74.31	12.51	12.18

^a Per cent. of theoretical based on methyl acrylate or acrylonitrile. ^b The reaction of *n*-hexanol with methyl acrylate yielded 36% methyl hexyloxypropionate and 42% hexyl hexyloxypropionate. The latter boiled at 110° (0.2 mm.). ^c Both methyl octyloxypropionate and octyl octyloxypropionate were produced by allowing octanol to react with methyl acrylate. ^d Prepared from acrylonitrile as described in the experimental section.

series mentioned above were prepared, but relationships between molecular weight and observed physical constants were noted from which the boiling points, densities, refractive indices and viscosities of the missing members can be estimated.

The relationship between boiling point at vari-

ous pressures and number of carbon atoms (Figs. 1 and 2) for the homologous series CH₃OCH₂CH₂COOR and ROCH₂CH₂COOCH₃ is given by equations 1, 2 and 3 (R = *n*-alkyl, *T* = °K. and *X* = carbon atoms). Equations 4, 5 and 6 express the same relationship⁵ for the series ROCH₂CH₂COOR (Figs. 1 and 3).

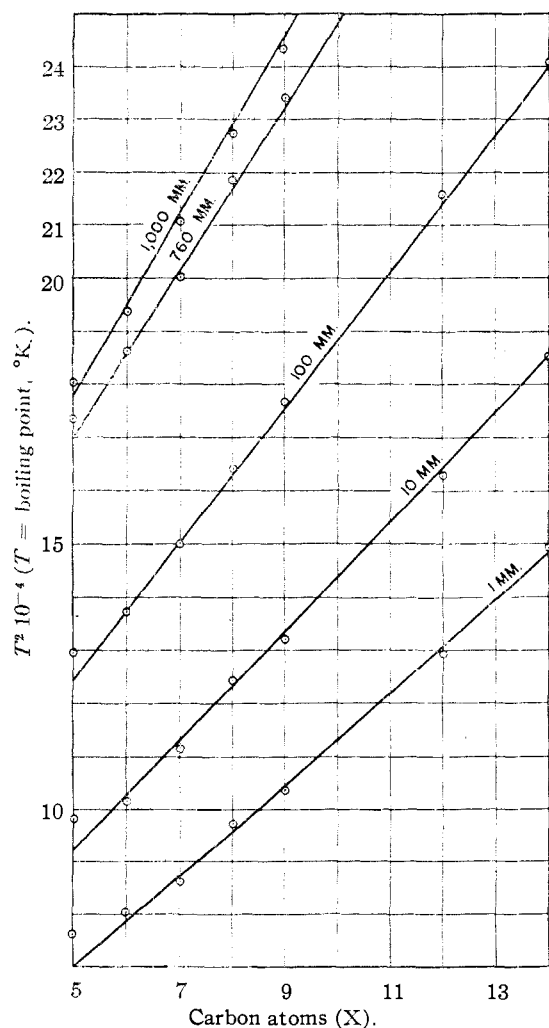


Fig. 2.—Boiling points of CH₃OCH₂CH₂COOR and ROCH₂CH₂COOCH₃.

$$\begin{aligned}
 10 \text{ mm.} : T^2 10^{-4} &= 1.040X + 3.90 & (1) \\
 100 \text{ mm.} : T^2 10^{-4} &= 1.310X + 5.86 & (2) \\
 760 \text{ mm.} : T^2 10^{-4} &= 1.675X + 8.50 & (3) \\
 10 \text{ mm.} : T^2 10^{-4} &= 1.010X + 3.75 & (4) \\
 100 \text{ mm.} : T^2 10^{-4} &= 1.272X + 5.60 & (5) \\
 760 \text{ mm.} : T^2 10^{-4} &= 1.624X + 8.10 & (6)
 \end{aligned}$$

The slopes, *m*, and intercepts, *b*, of Figs. 2 and 3

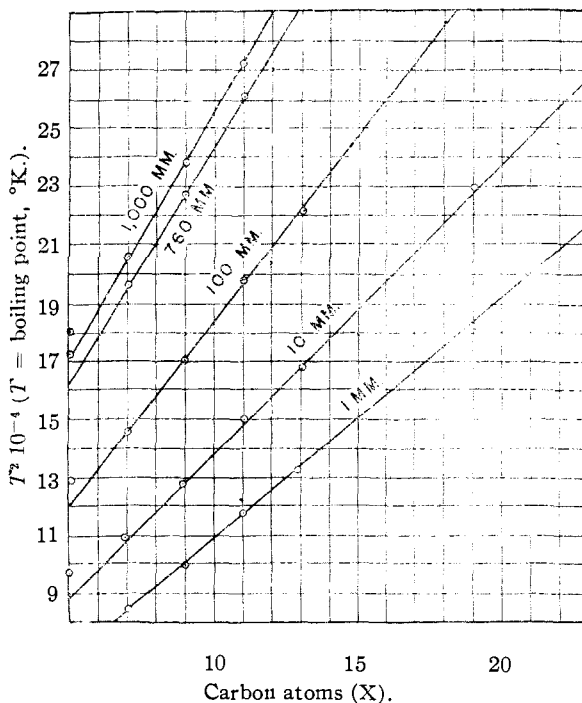


Fig. 3.—Boiling points of ROCH₂CH₂COOR.

(5) This method of relating boiling point at 760 mm. and number of carbon atoms has been used by E. Boggia-Lera, *Gazz. chim. ital.*, **29**, I, 441 (1899); A. H. W. Aten, *J. Chem. Phys.*, **5**, 260 (1937); and F. Klages, *Ber.*, **76**, 788 (1943).

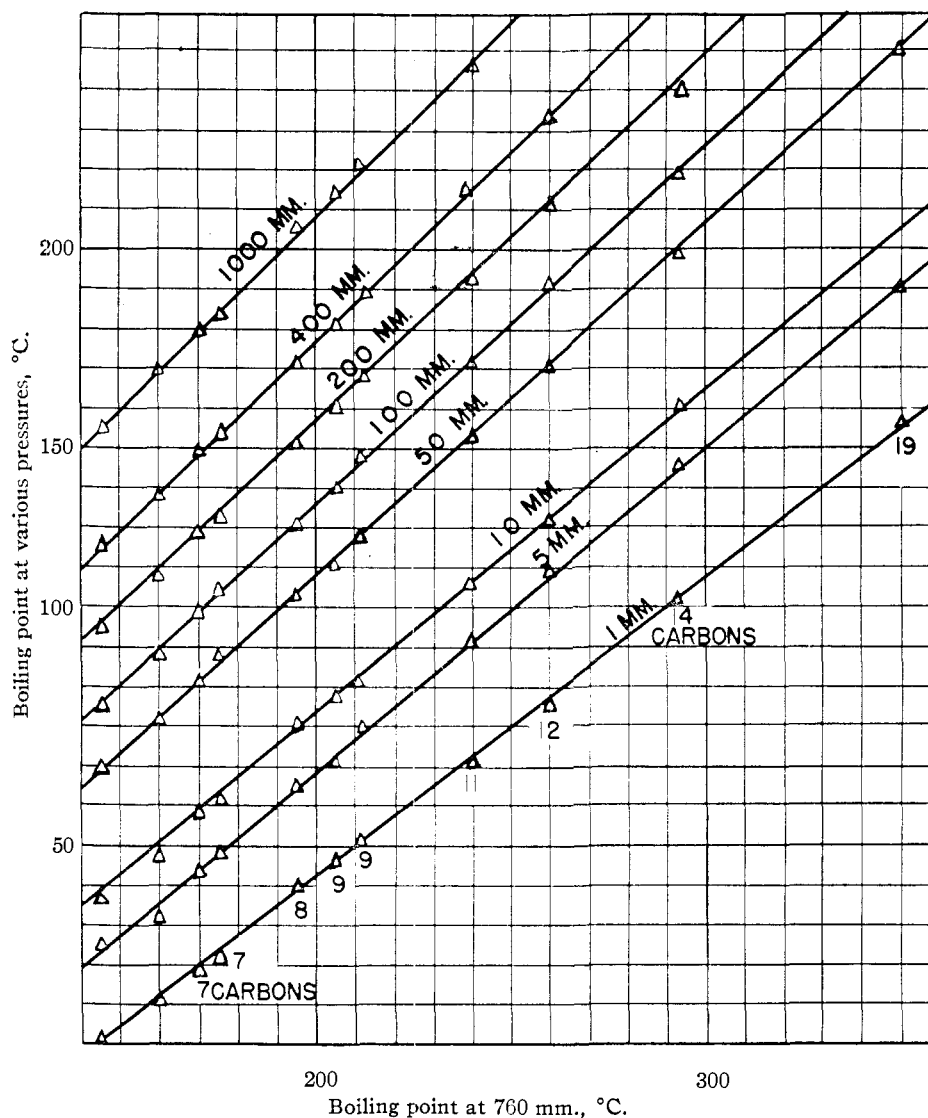


Fig. 4.—Boiling points of *n*-alkyl alkoxypropionates at different pressures.

have the relationships shown by equations 7, 8, 9 and 10 (p = pressure, mm.)

$$\text{Figure 2: } 10/(m + 0.1) = -1.666 \log p + 10.44 \quad (7)$$

$$b = 7.213 m - 3.58 \quad (8)$$

$$\text{Figure 3: } 10/(m + 0.1) = -1.711 \log p + 10.73 \quad (9)$$

$$b = 7.071 m - 3.38 \quad (10)$$

For other pressures, equations 1–6 can be modified by using equations 7–10 to determine the proper slopes and intercepts.

The boiling points (B) of the alkoxypropionates are related to the pressure (p) as shown in Fig. 4 and equations 11 to 15.

$$Bp = mB_{760} + b \quad (11)$$

$$B_{10} = 0.800 B_{760} - 76 \quad (12)$$

$$B_{100} = 0.891 B_{760} - 41.4 \quad (13)$$

$$10/(m - 0.2) = -2.228 \log p + 18.92 \quad (14)$$

$$b = 380(m - 1) \quad (15)$$

The boiling points at 760 mm. of the higher alkoxypropionates may be calculated⁶ (Table II)

TABLE II
ESTIMATED BOILING POINTS AT 760 MM. OF *n*-ALKYL *n*-ALKOXYPROPIONATES

Estimated by equation	Carbon atoms				
	12 ^a	13 ^b	14 ^c	19 ^b	23 ^b
3	262	...	292
6	...	267	...	351	401
12	260	266	295	353	399
16	261	...	294
17	...	266	...	349	404
(Obs.)	261

^a C₂H₁₇OCH₂CH₂COOCH₃.

^b ROCH₂CH₂COOR.

^c CH₂OCH₂CH₂COOC₁₀H₂₁.

(6) Boiling points somewhat higher than those of Table II would be estimated by the method of C. Bordenca (*Ind. Eng. Chem., Anal. Ed.*, **18**, 99 (1946)).

TABLE III
 VISCOSITY AND SOLUBILITY IN WATER OF *n*-ALKYL *n*-ALKOXYPROPIONATES (ROCH₂CH₂COOR')

R	R'	Viscosity at 20°		Centi-stokes at 25°	I at 20° ^a		I/M ^b	Soluble in 100 ml. H ₂ O at room temp., g. ^c
		Centi-stokes	Centi-poises		Found	Calcd.		
Me	Me	0.966	75 ^d
Et	Me	1.210	1.180	1.076	397.1	403.1	11.95	11.2
Et	Et	1.220	5.5
Me	Pr	...	1.374 ^e	1.286	3.2
Pr	Me	1.452	1.388	1.297	452.3	458.7	11.97	3.4
Me	Bu	1.702	1.602	1.515	507.4	514.3	11.91	0.98
Bu	Me	...	1.613 ^e	1.56582
Pr	Pr	1.66336
Me	Am	1.976	1.845	1.796	560.4	569.9	11.88	.29
Hex	Me	2.443	2.260	...	617.1	625.5	11.94	...
Bu	Bu	2.24908
Oct	Me	...	3.065 ^e	3.169
Am	Am	3.237
Me	Dec	4.690	4.241	4.237	840.8	847.9	11.95	...
Oct	Oct	7.873
Dec	Dec	11.5

^a Souders' viscosity constant, *I* (Mott Souders, Jr., THIS JOURNAL, 60, 154 (1938); R. T. Lagemann, *ibid.*, 67, 498 (1945)). ^b According to Lagemann, *I/M* (relation between viscosity constant and molecular refraction) should be approximately 12. ^c Room temperature, approximately 25°. ^d Approximately. ^e Calculated from equation 22.

from the number of carbon atoms (equations 3 and 6) or from the observed boiling points at reduced pressures (equations 11 to 15). The boiling points of the corresponding alcohols, ROH, may also be used to calculate the normal boiling points of the alkoxypropionates (equations 16 and 17, $B_E = b. p., ^\circ C.$, of alkoxypropionate and $B_A = b. p., ^\circ C.$, of ROH at 760 mm.).

$$\left. \begin{array}{l} \text{CH}_3\text{OCH}_2\text{CH}_2\text{COOR} \\ \text{and} \\ \text{ROCH}_2\text{CH}_2\text{COOCH}_3 \end{array} \right\} B_E = 0.877 B_A + 91 \quad (16)$$

$$\text{ROCH}_2\text{CH}_2\text{COOR} \quad B_E = 1.48 B_A + 62 \quad (17)$$

Huggins and Davis⁷ used the equation $V = 16.50X + A + B/X$ to describe the relation between molal volume and number of carbon atoms (*X*) for several homologous series. This general equation is applicable to the members of the three homologous series: ROCH₂CH₂COOCH₃, CH₃OCH₂CH₂COOR, and ROCH₂CH₂COOR (*M* = molecular weight, *d* = *d*²⁰, and *X* = carbon atoms)

$$\left. \begin{array}{l} \text{ROCH}_2\text{CH}_2\text{COOCH}_3 \\ \text{and} \\ \text{CH}_3\text{OCH}_2\text{CH}_2\text{COOR} \end{array} \right\} M/d = 16.50X + 41.40 - 28.5/X \quad (18)$$

$$\text{ROCH}_2\text{CH}_2\text{COOR} \quad M/d = 16.50X + 43.62 - 35/X \quad (19)$$

A previously described method⁸ for relating *n*²⁰_D and number of carbon atoms was found applicable to the β -alkoxypropionates of the present study (equations 20 and 21)

(7) M. L. Huggins and D. L. Davis, "Densities of Some Simple Aliphatic Compounds in the Liquid State," presented before the Division of Physical and Inorganic Chemistry at the 107th Meeting of the American Chemical Society, Cleveland, Ohio, April 3, 1944.

(8) C. E. Rehberg, W. A. Faucette and C. H. Fisher, THIS JOURNAL, 66, 1723 (1944).

$$\left. \begin{array}{l} \text{ROCH}_2\text{CH}_2\text{COOCH}_3 \\ \text{CH}_3\text{OCH}_2\text{CH}_2\text{COOR} \end{array} \right\} M/n = 9.551X + 36.78 \quad (20)$$

$$\text{ROCH}_2\text{CH}_2\text{COOR} \quad M/n = 9.520X + 37.48 \quad (21)$$

The viscosity ($\eta = \text{poises at } 20^\circ$) and solubility ($S = \text{g. per } 100 \text{ ml. water at room temperature}$) of CH₃OCH₂CH₂COOR and *n*-ROCH₂CH₂COOCH₃ are related⁹ to the total number of carbon atoms (*X*) by equations 22 and 23. The viscosity and solubility of the symmetrical *n*-alkyl *n*-alkoxypropionates¹⁰ are lower and higher, respectively, than those of the isomeric *n*-alkyl methoxypropionates (Table III).

$$\log(\eta 10^6) = 0.0697X + 2.650 \quad (22)$$

$$\log(S 10^3) = -0.534X + 7.26 \quad (23)$$

The lower and higher alkoxypropionates described in the present paper should have value as solvents and plasticizers, respectively. Because of their relatively low viscosities and vapor pressures, the higher alkoxypropionates should be suitable for plasticizing elastomers intended for use at low temperature. It is desirable for plasticizers to have vapor pressure as low as or lower than that of butyl phthalate, a widely used plasticizer. By substituting $T^2 \cdot 10^{-4}$ (21.9) of *n*-butyl phthalate¹¹ in equations 1 and 4 and solving for *X*, it was estimated that *n*-alkyl *n*-alkoxypropionates of 18 or more carbon atoms have vapor pressures sufficiently low for use as plasticizers.

The alkyl alkoxypropionates prepared in the

(9) These methods of relating viscosity and solubility to molecular weight have been used by A. E. Dunstan and F. B. Thole, J. Chem. Soc., 103, 127 (1913), and H. Sobotka and J. Kahn, THIS JOURNAL, 53, 2935 (1931), respectively.

(10) A viscosity higher than that shown in Table III for decyl decyloxypropionate would be predicted from the viscosities of its homologs; the cause of the low viscosity of this ester is not known.

(11) Using the vapor pressure data (10 mm. at 468°K.) of K. C. D. Hickman, J. Franklin Inst., 221, 383 (1936).

TABLE IV

Alkoxy	Alkyl	B. p., °C. (mm.)		d_{20}^{20}		n_D^{20}	
		α	β	α	β	α	β
Me ^b	Me	45 (22)	54 (22)	0.9967	1.0088
Me ^c	Me	129.9-131 (760)	144	.995 ^d	1.0088	1.3975	1.4022
Me ^c	Et	133-135.5 (760)	159
Me ^b	Et	46 (12)	50 (12)	.9551	0.9754
Et ^b	Me	40-41 (10)	46 (10)	.9610	.9751
Et ^a	Et	153-155 (755)	170	.9446	.9490	1.4013	1.4070
Et ^b	Et	58.5-60 (16-19)	66-70 (16-19)	.9355	.9490
<i>n</i> -Bu ^f	Me	168-169 (750)	195	.9346	.9423	1.4090	1.4152
<i>n</i> -Bu ^f	<i>n</i> -Bu	219-221 (750)	237	.9058	.9103	1.4208	1.4221
<i>n</i> -Pr ^g	<i>n</i> -Pr	187-188	204

^a Physical constants of β -alkoxypropionates taken from Fig. 1, Table I, and ref. 2. ^b T. Purdie and J. C. Irvine, *J. Chem. Soc.*, 75, 483 (1899). ^c O. Burkard and L. Kahovec, *Monatsh.*, 71, 333 (1938). ^d T. S. Patterson and W. C. Forsyth, *J. Chem. Soc.*, 103, 2263 (1913). ^e A. Karvonen, *Ann. Acad. Sci. Fenn.*, [A] 10, No. 6, 14 pp. (1914); *C. A.*, 14, 2177 (1920). ^f H. R. Henze and J. T. Murchison, *THIS JOURNAL*, 55, 4255 (1933). ^g T. Purdie and G. D. Lander, *J. Chem. Soc.*, 73, 862 (1898).

present work have higher boiling points, densities, and refractive indices than the corresponding α -alkoxypropionates (Table IV). This indicates that the compounds obtained by adding alcohols to alkyl acrylates are β - instead of α -alkoxypropionates. Further evidence that alcohols and alkyl acrylates react to yield β -alkoxypropionates was obtained by preparing *n*-amyl amyloxypropionate and *n*-decyl decyloxypropionate from acrylonitrile by the reactions: $\text{CH}_2=\text{CHCN} \rightarrow \text{ROCH}_2\text{CH}_2\text{CN} \rightarrow \text{ROCH}_2\text{CH}_2\text{COOR}$. The compounds obtained in this manner from acrylonitrile, which are assumed from earlier work¹² to be β -alkoxypropionates, had the physical constants of compounds prepared directly from alkyl acrylates.

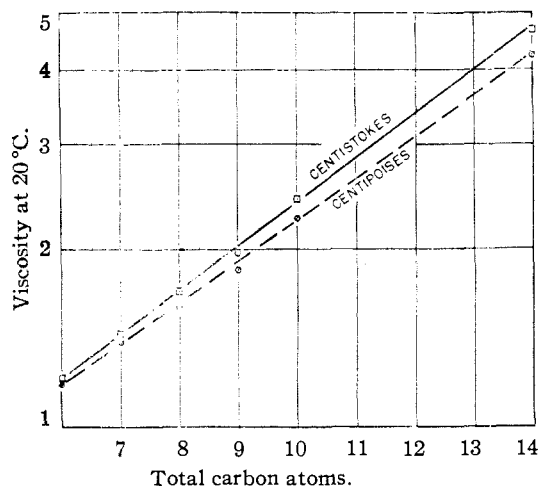


Fig. 5.—Viscosity of *n*-alkyl β -methoxypropionates and methyl β -*n*-alkoxypropionates.

The authors gratefully acknowledge their indebtedness to C. O. Willits, Polly E. McDowell and Frances J. Cooper, of this Laboratory, who supplied the saponification equivalents and carbon and hydrogen analyses.

(12) W. P. Utermohlen, Jr., *THIS JOURNAL*, 67, 1505 (1945).

Experimental

Previously described methods were used to prepare the alkoxypropionates² from alkyl acrylates.³ The boiling points in Fig. 1 were determined experimentally, whereas those represented in Figs. 2, 3, and 4 were taken from Fig. 1.

Reaction of Alcohols with Acrylonitrile.—Amyl amyloxypropionate and decyl decyloxypropionate were prepared from acrylonitrile and the appropriate alcohols by a two-step reaction: (1) addition of alcohol to acrylonitrile to produce β -alkoxypropionitrile,¹³ and (2) alcoholysis of this nitrile to produce the β -alkoxy ester. In the first step, 2 g. of sodium was dissolved in 3 moles of alcohol, and one mole of acrylonitrile was slowly added, with stirring, to this solution at 25 to 35°. After standing overnight, the solution was heated to 90° for two hours. In the second step the mixture was cooled to 30° and saturated with dry hydrochloric acid, then washed several times with warm water, dried and distilled. Yields of the amyl and decyl derivatives were 38 and 58%, respectively.

A product having the physical constants and saponification equivalent of *n*-decyl decyloxypropionate (7% yield) was formed along with decyl methoxypropionate in the acid-catalyzed interaction² of *n*-decanol and methyl methoxypropionate.

Boiling points at various pressures were generally determined by distilling the pure materials through a short Vigreux column and observing the still-head temperatures. The pressures were simultaneously read on a mercury manometer, a Dubrovin¹³ gage or a McLeod gage, depending on the pressure range being measured. A few of the higher-boiling compounds were also distilled through a modified alembic still, no difference in vapor pressure lines being thus detected.

Summary

Additional members of the homologous series, $\text{ROCH}_2\text{CH}_2\text{COOCH}_3$, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{COOR}$, and $\text{ROCH}_2\text{CH}_2\text{COOR}$ (R = *n*-alkyl), were prepared (1) by adding an *n*-alkanol to *n*-alkyl acrylate or (2) by adding the alcohol to acrylonitrile followed by alcoholysis of the resulting β -alkoxypropionitrile.

Densities, refractive indices, boiling points at various pressures, viscosities and water solubilities of the β -alkoxypropionates were determined. Relationships between these properties and molecular weight are given.

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(13) J. Dubrovin, *Instruments*, 6, 194 (1933); F. E. E. Germann and K. A. Gagos, *Ind. Eng. Chem., Anal. Ed.*, 15, 285 (1943).