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

Preparation and Physical Properties of *n*-Alkyl β-Ethoxypropionates

BY MARION B. DIXON, C. E. REHBERG AND C. H. FISHER

A recent paper[2] described the preparation and certain physical properties of several members of the two homologous series of β-alkoxypropionates.

$$\underset{\text{I}}{CH_3OCH_2CH_2COO(CH_2)_mH}$$

$$\underset{\text{II}}{H(CH_2)_rOCH_2CH_2COO(CH_2)_rH}$$

In addition, it was shown[2] that the physical constants of the missing members of the homologous series (I and II) can be calculated by equations that relate physical properties to either the total number of carbon atoms or molecular weight. The fact that the β-methoxypropionates (I) had higher boiling points, viscosities, refractive indices and densities than the isomeric *n*-alkoxypropionates (II) was attributed to the greater association[3] of the methoxypropionates.

TABLE I

n-ALKYL β-ETHOXYPROPIONATES PREPARED BY ALCOHOLYSIS OF ETHYL ETHOXYPROPIONATE

n-Alkyl	Mol. ratio alc./ester[a]	Conversion, %	Yield, %, based on Alcohol	Ester	Sapn. eq. Calcd.	Found	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
Methyl	...	..	..	..	132.2	132.2	54.5	54.6	9.2	9.0
Ethyl	...	..	..	..	146.2	144.7	57.5	57.9	9.7	9.9
Propyl	3.0	97	97	97	160.2	161.2	60.0	59.7	10.1	10.1
Butyl	3.0	88	93	88	174.2	173.4	62.0	61.8	10.4	10.5
Amyl	2.9	98	96	98	188.3	187.3	63.8	64.0	10.7	10.5
Hexyl	3.0	95	87	95	202.3	204.0	65.3	65.4	11.0	..
Octyl	1.0	72	92	89	230.3	230.2	67.8	67.9	11.4	..
Decyl	1.4	82	84	92	258.4	259.8	69.7	69.7	11.7	..

[a] Ratio of *n*-alkanol to ethyl β-ethoxypropionate.

TABLE II

PROPERTIES OF *n*-ALKYL β-ETHOXYPROPIONATES[a]

n-Alkyl	n^{20}_D	n^{40}_D	$\Delta n/\Delta t \times 10^4$	d^{20}_4	d^{40}_4	$\Delta d/\Delta t \times 10^4$	Mol. refraction Calcd.	Found 20°	40°	Viscosity Centipoises 20°	40°	Centistokes 20°	40°	Solubility in H_2O at 25°, g./100 cc.
Methyl	1.4050	1.3964	4.3	0.9751	0.9533	10.9	33.21	33.23	33.34	1.180	0.847	1.210	0.888	11.2
Ethyl	1.4070	1.3983	4.4	.9490	.9282	10.4	37.82	37.92	38.05	1.260	0.901	1.328	0.971	5.55
Propyl	1.4120	1.4030	4.5	.9354	.9156	9.9	42.44	42.62	42.71	1.475	1.066	1.577	1.164	1.54
Butyl	1.4161	1.4073	4.4	.9256	.9068	9.9	47.06	47.26	47.34	1.681	1.189	1.816	1.311	0.40
Amyl	1.4204	1.4118	4.3	.9191	.9007	9.2	51.68	51.89	51.98	2.079	1.410	2.262	1.565	.12
Hexyl	1.4238	1.4152	4.3	.9120	.8942	8.9	56.30	56.58	56.67	2.368	1.573	2.597	1.759	.03
Octyl	1.4294	1.4213	4.1	.9028	.8859	8.5	65.53	65.83	65.97	3.437	2.184	3.807	2.465	< .01
Decyl	1.4343	1.4262	4.1	.8960	.8789	8.5	74.77	75.16	75.36	4.630	2.794	5.167	3.179	...

[a] Boiling points are given in Figs. 1 to 5.

In the investigation reported here, various *n*-alkyl β-ethoxypropionates were prepared, and equations were developed which were generally similar to those of the earlier study defining the relationships between physical constants and the total number of carbon atoms. It was found that the physical constants of the β-ethoxypropionates generally lie between those of the isomeric methoxypropionates (I) and *n*-alkoxypropionates (II). This finding is in harmony with the view that the degree of association of ethoxy compounds is usually less than that of similar methoxy compounds but greater than that of the isomeric higher *n*-alkoxy compounds.[3]

The equations relating physical constants to total carbons (x) are based on the straight-line relationship[4-12] for homologous compounds between x and certain functions of the physical

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[2] C. E. Rehberg, M. B. Dixon and C. H. Fisher, THIS JOURNAL, **69**, 2966 (1947).

[3] E. C. Bingham and L. W. Spooner, *Physics*, [11] **4**, 387 (1933).

(4) In agreement with earlier work, the first one or two members of the homologous series usually failed to agree with the linear relationships.

(5) F. Klages, *Ber.*, **76**, 788 (1943); A. H. W. Aten, *J. Chem. Physics*, **5**, 260 (1937).

(6) G. Egloff, J. Sherman and R. B. Dull, *J. Phys. Chem.*, **44**, 730 (1940).

(7) D. F. Wilcox, THIS JOURNAL, **68**, 691 (1946).

(8) S. S. Kurtz, Jr., and M. R. Lipkin, *Ind. Eng. Chem.*, **33**, 779 (1941).

(9) C. E. Rehberg and C. H. Fisher, THIS JOURNAL, **66**, 1203 (1944); C. E. Rehberg, W. A. Faucette and C. H. Fisher, *ibid.*, 1723.

(10) A. E. Dunstan and F. B. Thole, *J. Chem. Soc.*, **103**, 127 (1913).

(11) H. Sobotka and J. Kahn, THIS JOURNAL, **53**, 2935 (1931).

(12) M. L. Fein and C. H. Fisher, *ibid.*, **70**, 52 (1948).

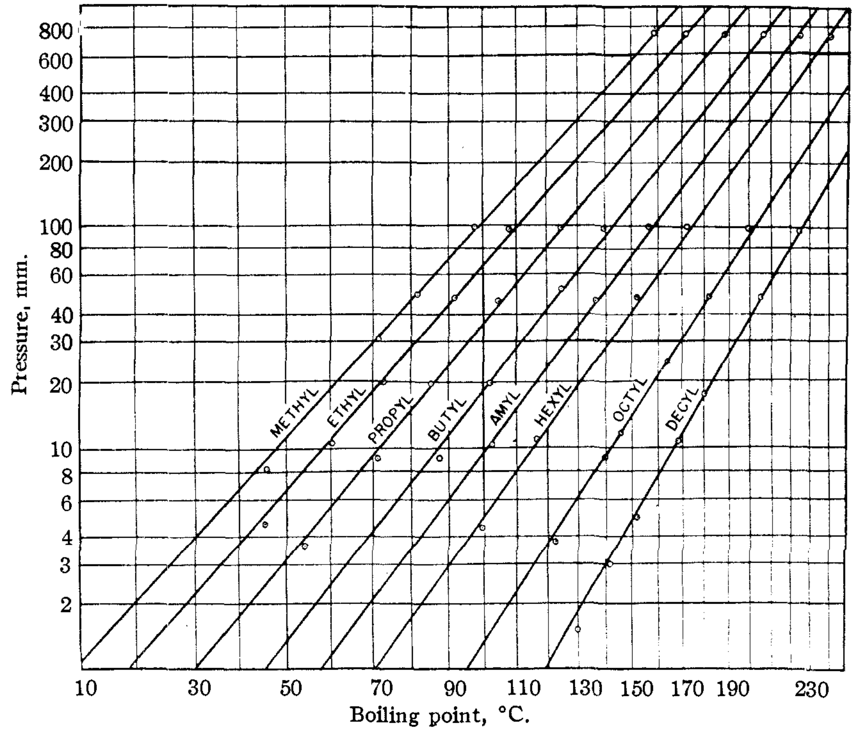

Fig. 1.—Boiling points of *n*-alkyl *β*-ethoxypropionates at various pressures.

properties, such as T^2, M/d, M/n and $\log \eta$, where T, M, d, n, and η are absolute boiling point, molecular weight, density, refractive index and viscosity, respectively. These equations are of value in checking the accuracy of the physical measurements, calculating properties of missing homologs by interpolation or extrapolation, comparing the physical properties of the *β*-ethoxypropionates with those of other homologous series, and correlating, within the homologous series I and II, any one physical constant with the others.[13]

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Experimental

Materials.—The methyl *β*-ethoxypropionate was prepared by the addition of ethanol to methyl acrylate, the procedure previously described being used.[3,14] The propyl and higher esters were prepared by the alcoholysis[14] of the commercially available ethyl ester. All the esters were carefully purified by rectification in efficient stills. Only middle fractions having constant boiling points, refractive indices, and densities were used for determination of physical and analytical data. Yields, analyses, and experimentally determined constants are given in Tables I and II and Fig. 1.

Physical Measurements.—Boiling points were determined by distilling the pure esters through a short Vigreux column and noting the vapor temperature at the still head. A high reflux ratio was maintained to eliminate superheating the vapor. The pressure near the still head was simultaneously observed, a closed tube mercury manometer being employed for pressures above 20 mm. and a Dubrovin gage[15] for pressures below 20 mm. The octyl and

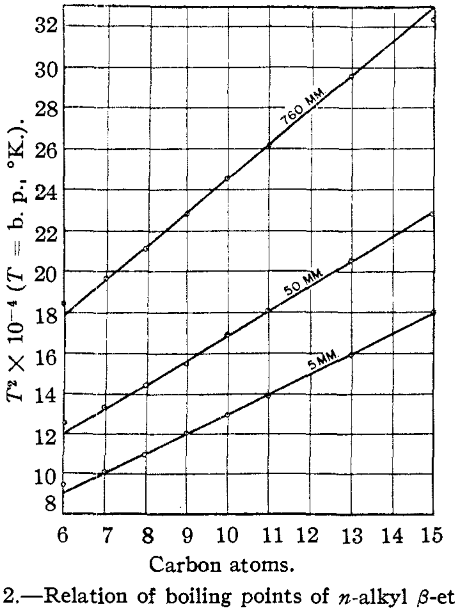

Fig. 2.—Relation of boiling points of *n*-alkyl *β*-ethoxypropionates at various pressures to number of carbon atoms.

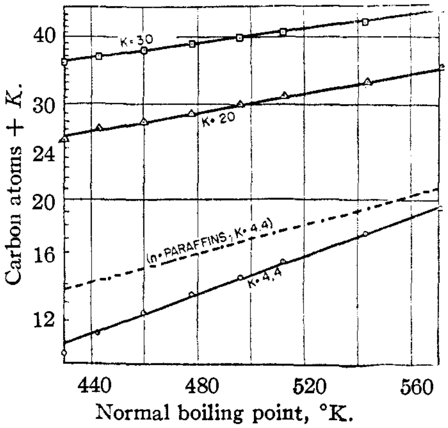

Fig. 3.—Relation of normal boiling points of *n*-alkyl *β*-ethoxypropionates to total number of carbon atoms + *K*.

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[13] Achieved by using the various equations relating physical properties to x, selecting the two equations concerned with the two properties of interest, and eliminating x from the equations.

[14] C. E. Rehberg, M. B. Dixon and C. H. Fisher, THIS JOURNAL, **68**, 544 (1946).

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

TABLE III

CORRELATION OF PHYSICAL CONSTANTS OF n-ALKYL β-ETHOXYPROPIONATES BY EQUATIONS OF THE FORM[a] $A = Bx + C$

Equation	Property	A	B	C	Const. temp., °C.	Esters excluded[b]	Deviation Max.[c]	Deviation Average Numerical[c]	Deviation Average %	Ref.[d]
1	Boiling point	$10^{-4}[T_{b.p.}]_2$	1.66	7.90	760[e]	1	5[f]	1	0.2	2, 5
2	Boiling point	$10^{-4}[T_{b.p.}]_2$	1.22	4.65	50[e]	1	2	0.5	.1	2, 12
3	Boiling point	$10^{-4}[T_{b.p.}]_2$	0.987	3.10	5[e]	1	2	1	.2	2, 12
4	Vapor pressure	Log P	−0.285	3.83	100	1	1	0.2	.4	7
5	Vapor pressure	Log P	− .240	4.29	150	1	1	0.4	.2	7
6	Vapor pressure	Log P	− .200	4.608	200	1	6	2.5	.8	7
7	Density	M/d	16.75	37.35	20	2	0.0008	0.0005	.05	8
8	Density	x/d	1.170	−0.81	20	1	.0009	.0003	.03	2, 12
9	Density	M/d	17.00	39.0	40	2	.0009	.0003	.03	8
10	Density	x/d	1.190	−0.79	40	1	.0007	.0004	.04	2, 12
11	Refr. index	M/n	9.52	37.35	20	2	.0006	.0002	.01	2, 9
12	Refr. index	x/n	0.685	0.188	20	2	.0007	.0005	.03	2, 12
13	Refr. index	M/n	9.57	37.65	40	2	.0002	.0001	.01	2, 9
14	Refr. index	x/n	0.689	0.190	40	2	.0009	.0005	.03	2, 12
15	Viscosity	Log η	.0720	− .408	20	1	.069	.036	2	10
16	Viscosity	Log η	.0616	− .471	40	1	.047	.027	2	10
17	Solubility	Log S	− .567	4.713	25	1	.04	.01	1	11

[a] M = Molecular weight; x = number of carbon atoms; T = boiling point, °K.; P = vapor pressure, mm.; d = density, d^t_4; n = refractive index; η = viscosity, centipoises; S = solubility, g. per 100 g. H_2O. [b] First members of the homologous series. [c] Deviations are expressed not in per cent. but in units used in the equations. [d] Investigations in which the straight-line relationships were used with other homologous series. [e] Constant pressure, mm. [f] The maximum deviation of 5° was with the decyl ester; its determined boiling point (partial decomposition) apparently was approximately 5° too low.

decyl esters boiled at 270 and 295°, respectively, at atmospheric pressure, the latter ester showing some decomposition at its boiling point. This probably accounts for the fact that all the correlations of boiling points indicate that 295° is slightly low, the expected boiling point being about 300°. Other observed boiling points are shown on Figs. 1 (Cox Chart) and 3. Corner's[16] boiling points of the n-paraffins were used in the construction of Fig. 3.

Refractive indices were measured with an Abbe-type refractometer, the temperature of which was kept within ±0.1° of the specified point.

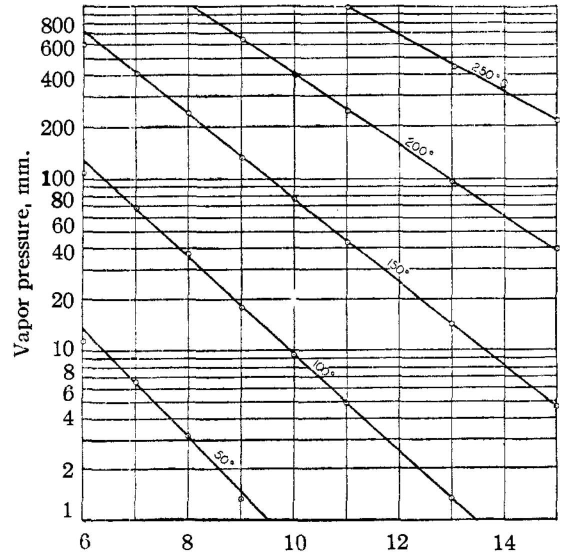

Fig. 4.—Relation of vapor pressures of n-alkyl β-ethoxypropionates to number of carbon atoms.

Densities were measured with a Sprengel-type pycnometer of approximately 8-ml. capacity and kept within ±0.1° of the specified temperature.

Viscosities were measured with modified Ostwald pipets that had been calibrated with samples of standard oils furnished by the National Bureau of Standards. The pipets were immersed in a bath whose temperature was controlled within ±0.05°, and the time of flow of the samples was checked within ±0.3 sec. Water solubility was determined by the method of Fordyce and Meyer.[17]

Correlation of Physical Properties with Number of Carbon Atoms

Boiling Points and Vapor Pressure.—Figure 1, prepared from experimentally determined boiling

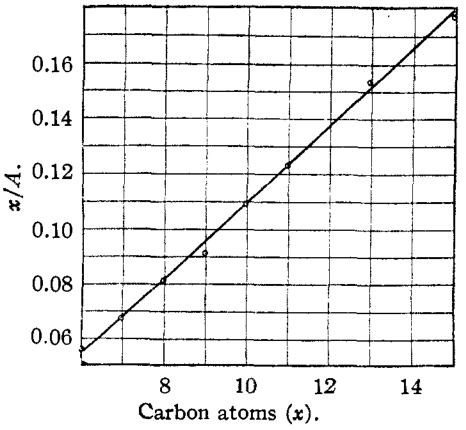

Fig. 5.—Relation of temperature coefficients of density of n-alkyl β-ethoxypropionates to number of carbon atoms (A = 10^5 temp. coefficient and x = carbon atoms).

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(16) J. Corner, *Trans. Faraday Soc.*, **41**, 617 (1945).

(17) C. R. Fordyce and L. W. A. Meyer, *Ind. Eng. Chem.*, **32**, 1053 (1940).

points, was used, by interpolation, to provide the data for the construction of Figs. 2, 4, 8 and 9. Except for the first member of the homologous series, the square of the absolute boiling point was a straight line function[18] of the number of carbon atoms, x (Fig. 2 and Equations 1, 2 and 3, Table III).

It has been observed[6] that the normal boiling points of several homologous series of hydrocarbons are a straight line function of log $(x + 4.4)$. This general method of plotting the boiling points of homologous compounds against log $(x + R)$ ($R = 4.4$ or some other constant) is applicable to the *n*-alkyl β-alkoxypropionates, but the correlation is better when R is 20 or 30 instead of 4.4 (Fig. 3). For purposes of comparison, the boiling points of *n*-paraffins[16] also are shown in Fig. 3.

It has been shown[7] that the logarithm of the vapor pressure (P) at a given temperature for methylpolysiloxanes is a straight-line function of the number of silicon atoms. This general relationship is valid also for the *n*-alkyl β-ethoxypropionates (Fig. 4 and Equations 4 to 6, Table III).

Densities.—Both the molecular volume (M/d) and x/d were found to be straight-line functions of x, as shown by Equations 7 to 10, Table III. It was observed also that the temperature coefficient of density can be related to x by plotting x/A ($A = 10^5$ temperature coefficient) against x (Fig. 5).[19]

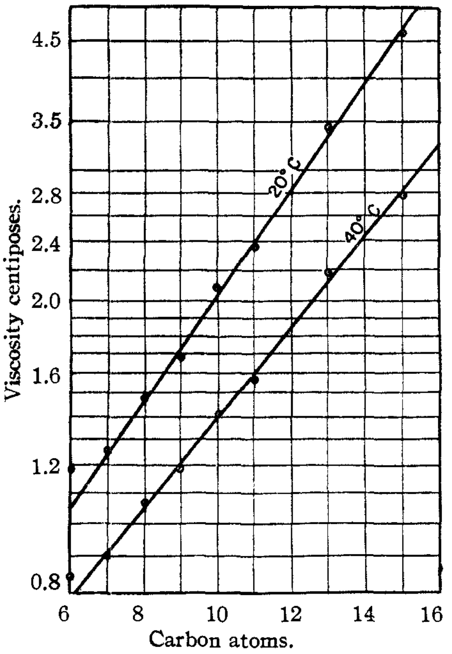

Fig. 6.—Relation of viscosity of *n*-alkyl β-ethoxypropionates to number of carbon atoms.

Refractive Indices.—As shown by Equations 11 to 14, Table III, both M/n and x/n were straight-line functions of the total number of carbon atoms (x).

The M/n *versus* x relationship, now known to be valid for several homologous series,[9,12] apparently should be generally useful for correlating refractive indices with molecular weight for homologous compounds.

The refractive indices determined at 20 and 40° were used to calculate $10^5 \Delta n/\Delta t$, which was about 43 for all the β-ethoxypropionates.

Without exception, the experimental values for the molecular refractions at both 20 and 40° were higher than the calculated values. The molecular refractions at 40° were about 0.11 higher than those determined at 20° (Table II).

Viscosity.—The β-ethoxypropionates resembled certain other homologous series,[10,12] in that straight lines were obtained by plotting the logarithm of viscosity against carbon atoms (Fig. 6 and Equations 15 and 16, Table III).

Solubility in Water.—The first three members of the β-ethoxypropionates were appreciably soluble in water at room temperature; the logarithm of the solubility was a straight-line function of x (Fig. 7 and Equation 17, Table III).

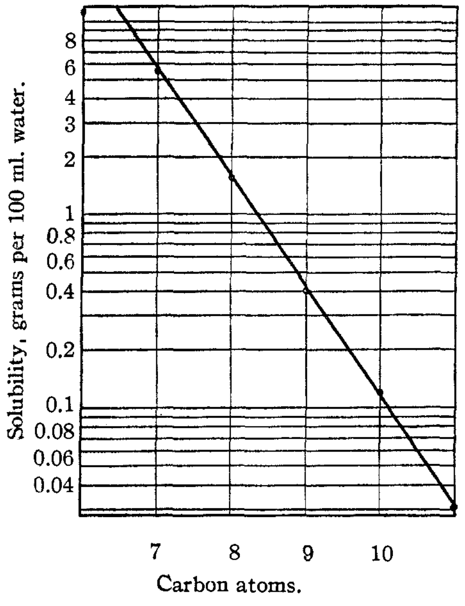

Fig. 7.—Relation of solubility of *n*-alkyl β-ethoxypropionates in water at room temperature (approx. 25°) to number of carbon atoms.

Additional Correlations

The equations of Table IV may be used to calculate the boiling points of the *n*-alkyl β-ethoxypropionates from the normal boiling points of the corresponding *n*-alkanols. Probably the boiling points of various alkenyl, *s*-alkyl and branched

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[18] Approximately straight lines were obtained also by plotting log T against log x.

[19] It has been shown (M. R. Lipkin and C. C. Martin, *Ind. Eng. Chem., Anal. Ed.*, **18**, 380 (1946)) that A for certain homologous hydrocarbons is a straight-line function of both density and refractive index. With the exception of the first two members of the series, the A values of the present work are similarly related to d^{20}_4 and n^{20}_D.

TABLE IV

RELATION OF THE NORMAL BOILING POINTS (t_A) OF ROH TO THE BOILING POINTS (t_E) OF $C_2H_5OCH_2CH_2COOR$

Equation	Press., mm.	Equation	Esters excluded[a]	Deviation, °C. Max.	Deviation, °C. Average
18	760	$t_E = 0.85\,t_A + 105$	0	5	1.4
			2[b]	1	0.5
19	50	$t_E = .75\,t_A + 34$	0	2	.7
			1	1	.5
20	5	$t_E = .70\,t_A - 10$	0	1	.2

[a] First members unless otherwise stated. [b] First and last members (boiled with decomposition) excluded.

alkyl β-ethoxypropionates could also be estimated[20] roughly from Equations 18 to 20.

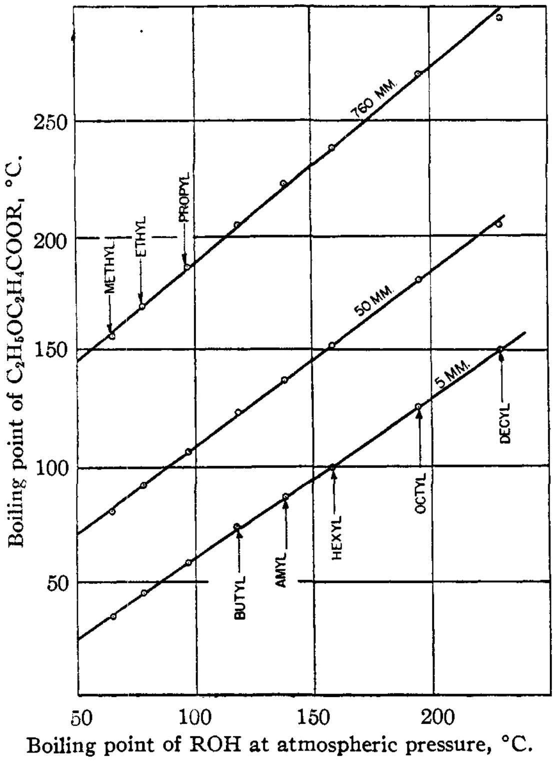

Fig. 8.—Relation of boiling points of *n*-alkyl β-ethoxypropionates to boiling points of *n*-alkanols.

In investigations[2,21] concerned with other homologous series, straight lines were obtained by plotting boiling points of the members at 760 mm. against boiling points at some other pressure. As is shown by Equation 21 and Fig. 9, the normal boiling points of the *n*-alkyl β-ethoxypropionates have a similar relationship to boiling points at other pressures (B = boiling point, °C., at pressure, p; m and c = constants).

$$B_p = mB_{760} + c \qquad (21)$$

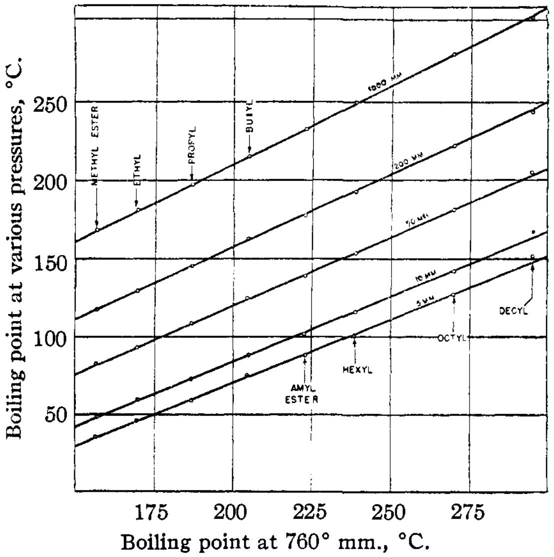

Fig. 9.—Relation of boiling points of *n*-alkyl β-ethoxypropionates at 760 mm. to those at other pressures.

The constants m and c, respectively, have the following values at different pressures; 5 mm., 0.814 and −94; 10 mm., 0.834 and −84; 50 mm., 0.89 and −58; 200 mm., 0.938 and −31.5; 1000 mm., 1.01 and 8. The constant m is related to pressure over a considerable pressure range as shown in Equation 22.

$$m = 0.083 \log p + 0.75 \qquad (22)$$

The functions of the physical constants (such as T^2, M/d, $M/n \log p$, and $\log \eta$) having a straight-line relationship to x have a straight-line relationship to each other, thus offering the opportunity of relating any one of the physical constants to each of the others. Not all the possible combinations afforded by the equations of Tables III and IV were examined in the present work, but viscosity was related to both boiling point and vapor pressure (Fig. 10 and Equations 23 to 28, Table V).

Relationships between viscosity and boiling

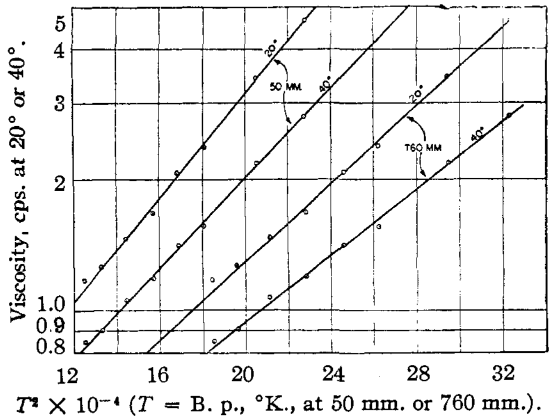

Fig. 10.—Relation of viscosity of *n*-alkyl β-ethoxypropionates to boiling points.

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[20] Similar relationships between the boiling points of alcohols and those of the corresponding esters have been observed for other compounds (C. E. Rehberg, M. B. Dixon and C. H. Fisher, *J. Org. Chem.*, **13**, 254 (1948)).

[21] C. Bordenca, *Ind. Eng. Chem., Anal. Ed.*, **18**, 99 (1946).

TABLE V

RELATION OF VISCOSITY TO BOILING POINT AND VAPOR PRESSURE OF *n*-ALKYL β-ETHOXYPROPIONATES[a]

Equation	Pressure or temperature	Equations	Esters excluded	Deviation, cps. Max.	Deviation, cps. Average
23	760 mm.	$\log \eta_{20} = 4.5\ (10^{-6})T^2 - 0.794$	1	0.07	0.04
24	50 mm.	$\log \eta_{20} = 6.0\ (10^{-6})T^2 - 0.700$	1	.06	.035
25	760 mm.	$\log \eta_{40} = 3.87(10^{-6})T^2 - 0.804$	0	.053	.02
26	50 mm.	$\log \eta_{40} = 5.10(10^{-6})T^2 - 0.72$	0	.036	.023
27	150°	$\log \eta_{20} = 0.877 - 0.3 \log p$	0	.08	.05
28	150°	$\log \eta_{40} = 0.628 - 0.257 \log p$	0	.046	.029

[a] η = Viscosity, cps.; T = boiling point, °K., and p = vapor pressure, mm.

point (or vapor pressure) should be of interest in the evaluation of plasticizers, particularly when it is desired to combine minimum viscosity with minimum vapor pressure.

Summary

Carefully purified samples of the methyl, ethyl, *n*-propyl, *n*-butyl, *n*-amyl, *n*-hexyl, *n*-octyl and *n*-decyl esters of β-ethoxypropionic acid were used in the determination of boiling points at various pressures, density (d^{20}_4 and d^{40}_4), refractive index (n^{20}_D and n^{40}_D), viscosity at 20 and 40°, and solubility in water at room temperature. Straight-line relationships between certain functions of these physical properties and the number of carbon atoms are given. From the data given here and in previous papers, it should be possible to estimate the boiling points at various pressures, densities, refractive indices, viscosities and water solubilities of all the *n*-alkyl β-alkoxypropionates.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

Reduction of Organic Compounds by Lithium Aluminum Hydride. III. Halides, Quinones, Miscellaneous Nitrogen Compounds[1]

BY ROBERT F. NYSTROM[2] AND WELDON G. BROWN

In two previous publications[3] we have described the reduction of various carboxylic acid derivatives and of the free carboxylic acids to primary alcohols, and of aldehydes and ketones to the corresponding alcohols, by means of lithium aluminum hydride. Our survey of the potentialities of this reagent in organic synthesis revealed several additional types of organic compounds which are readily reduced. The experimental observations with respect to any one class of compounds have not been as extensive as might be desired but the present results will at least serve to indicate a greatly broadened range of applications.

Collectively, the data now available on the reactions of lithium aluminum hydride with organic compounds point to a far-reaching analogy with the Grignard reagent with respect to the types of compounds which are attacked. This analogy provides a useful basis for prediction; thus the alkyl halides which we find to be smoothly reduced are those which can be made to react with Grignard reagents. There are of course important differences with respect to the nature and extent of the reactions. These differences arise in part from the higher reactivity of the hydride. Thus the smooth reduction of acetomesitylene by the hydride[3] is to be contrasted with the hindrance shown in its behavior toward Grignard reagents. The reduction of carboxylic acids, previously reported, has its analogy in the formation of tertiary alcohols by the action of Grignard reagents on acids but the latter reaction takes place less readily and less completely.

The similarity between lithium aluminum hydride and the Grignard reagent is shown also by the response of the former to the Gilman–Schulze[4] color test. This test, which is based on a reaction with Michler ketone, is considered to be characteristic for compounds having carbon-metal bonds. The observation that the hydride produces similar color phenomena strongly suggests that the first step is a reduction forming Michler hydrol. An example showing the usefulness of this test in determining the stoichiometry of a reaction with lithium aluminum hydride is given in the experimental part of this paper.

The reduction of nitriles and of cyanohydrins is likely to become an important method for the synthesis of pharmacologically active amines and aminoalcohols. For this reason it seems desirable to point out that cyanohydrins and di-nitriles tend to form highly insoluble precipitates which remove hydride from the solution and hence are reduced in relatively poor yield. A substantial improvement would doubtless result from the use of a greater excess of hydride in such cases, or from the use of solvents which would permit elevated reaction temperatures. The absence of secondary and tertiary amines in the product is a highly advantageous feature of this method of reduction.

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(1) The major portion of the results recorded herein were contained in a paper presented before the Symposium on Hydrides and Related Compounds at the Chicago meeting of the American Chemical Society, September 10, 1946.

(2) Present address: University of Illinois, Urbana, Illinois.

(3) Nystrom and Brown, THIS JOURNAL, 69, 1197, 2548 (1947).

(4) Gilman and Schulze, *ibid.*, 47, 2002 (1925).