

130. *Physical Properties and Chemical Constitution. Part XIII.*
Aliphatic Carboxylic Esters.

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New measurements have been made of the parachors and refractivities of alkyl esters of formic, acetic, propionic, *n*-butyric, *isobutyric*, *n*-valeric, *isovaleric*, *n*-hexoic, *n*-heptoic, *n*-octoic, and *n*-dodecoic acids and the dialkyl esters of oxalic, succinic, adipic, suberic, and sebacic acids. The experimental data have been employed to compute, with the aid of the experimental figures for the aliphatic hydrocarbons (Part IX, *J.*, 1946, 133) and the values for alkyl groups deduced from them (Part XI, this vol., p. 610), the contributions of the CO·O group. The mean values for this, excluding the formates, oxalates, and malonates, are :

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}.</i>
CO·O	63·4	6·173	6·200	6·261	6·315	64·14
O ₂ (in esters)	54·8	3·601	3·609	3·660	3·660	38·43

If the values for C (Part IX, *loc. cit.*) are subtracted, the figures for O₂ (in carboxylic esters) are obtained. The value for O₂ of the parachor differs from that of Sugden (60.0) and the refractivities differ from the figures deduced by Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 585). Furthermore, if one combines the figures for the carbonyl group (Part XI) and for O in ethers (*not acetals*) (Part XII, preceding paper), the following results are obtained :

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}.</i>
CO	45.9	4.684	4.713	4.768	4.830	42.38
O (in ethers)	19.8	1.753	1.764	1.786	1.805	22.74
CO + O (in ethers) -	65.7	6.437	6.477	6.554	6.635	65.12

The values for CO + O (ethers) are not identical with those deduced for CO·O from esters; Eisenlohr's assumption that

$$O_2 \text{ (esters)} = O'' \text{ (ketones)} + O < \text{ (ethers)}$$

therefore has no experimental foundation.

New experimental data are also provided for the parachors and refractivities of the dialkyl esters of methyl-, ethyl-, *n*-propyl-, and *n*-amyl-malonic acids. These figures differ (in most cases by quantities in excess of the experimental error) from those of the isomeric esters of the polymethylene carboxylic acids.

THE main objects of this investigation were : (1) To provide trustworthy data for the parachors and refractivities of a wide variety of pure liquid esters, (*a*) for the calculation of the contributions of the CO·O group, (*b*) as reference compounds in the computation of other atomic and structural constants, and (*c*) for their characterisation in qualitative organic analysis. (2) To test the validity of the assumption made by Eisenlohr and others that for esters the refractivities may be calculated from $[CH_2]_n O''O <$, *i.e.*, that the O₂ in carboxylic esters is the sum of the constants for the ketonic (O'') and ethereal oxygen (O <) atoms.

The values for the CO·O group in all the aliphatic esters investigated by the author are simply calculated by subtracting the figures for the corresponding hydrocarbons (Part IX, *J.*, 1946, 113) or, if this is not possible, the values for hydrogen and/or alkyl groups (Part XI, *loc. cit.*). It should be noted that the CH₂ figures, although accurately known (Part IX, *loc. cit.*), have not been widely employed in the calculations. The results are shown in Table I. The

TABLE I.

CO·O Values from aliphatic esters.

R =	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}.</i>	R =	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}.</i>
Alkyl formates, H·CO ₂ R.													
Et	65.7	6.34	6.38	6.44	6.52	64.57	Am [†] ‡ ...	65.2	6.40	6.44	6.50	6.57	64.66
Pr ⁿ	65.8	6.39	6.42	6.49	6.56	64.62	C ₆ H ₁₃ ⁿ ...	66.5	6.51	6.54	6.61	6.68	64.69
Bu ⁿ	65.5	6.44	6.48	6.54	6.61	64.61	Pr ⁱ	68.9	6.56	6.58	6.65	6.72	64.12
Am [†] † ...	65.4	6.35	6.38	6.46	6.53	64.63	Bu ⁱ	67.0	6.55	6.58	6.65	6.72	64.52
Alkyl acetates, CH ₃ ·CO ₂ R.													
Me	66.6	6.15	6.18	6.24	6.32	64.62	Bu ⁱ	64.2	6.31	6.35	6.40	6.46	63.82
Et	64.4	6.25	6.29	6.35	6.42	64.05	Bu ⁿ * ...	66.8	6.43	6.46	6.54	6.59	63.05
Pr ⁿ	63.9	6.31	6.33	6.40	6.47	64.01	Am ⁿ ...	64.0	6.31	6.34	6.41	6.47	64.06
Pr ⁱ	64.8	6.30	6.33	6.40	6.46	63.58	Am [†] † ...	63.9	6.28	6.31	6.36	6.44	63.98
Bu ⁿ	63.7	6.23	6.25	6.32	6.38	63.96	C ₆ H ₁₃ ⁿ ...	63.6	6.29	6.31	6.38	6.42	64.18
Alkyl propionates, CH ₃ ·CH ₂ ·CO ₂ R.													
Me	63.6	6.14	6.19	6.24	6.30	64.45	Pr ⁿ	62.1	6.14	6.16	6.21	6.28	63.85
Et	64.0	6.13	6.17	6.23	6.30	63.90	Bu ⁿ	63.0	6.20	6.22	6.28	6.34	63.89
Alkyl <i>n</i> -butyrates, CH ₃ ·CH ₂ ·CH ₂ ·CO ₂ R.													
Me	63.0	6.14	6.17	6.23	6.30	64.31	Bu ⁿ	61.8	6.17	6.19	6.25	6.30	63.77
Et	62.0	6.19	6.20	6.27	6.33	63.74	Am ⁿ ...	63.3	6.30	6.33	6.38	6.43	63.86
Pr ⁿ	63.3	6.19	6.21	6.28	6.33	63.70	Am [†] † ...	63.1	6.20	6.21	6.29	6.34	63.80
Alkyl isobutyrate, (CH ₃) ₂ CH·CO ₂ R.													
Me	64.0	6.13	6.19	6.24	6.31	64.17	Pr ⁿ	63.1	6.19	6.21	6.26	6.33	63.47
Et	63.3	6.18	6.20	6.26	6.32	63.43	Bu ⁿ	63.0	6.21	6.23	6.28	6.34	63.49
Alkyl <i>n</i> -valerates, CH ₃ ·[CH ₂] ₃ ·CO ₂ R.													
Me	62.6	6.14	6.16	6.23	6.29	64.29	Bu ⁿ	62.2	6.15	6.19	6.24	6.28	63.81
Et	62.7	6.21	6.23	6.30	6.35	63.81	Am ⁿ ...	61.4	6.19	6.22	6.27	6.30	63.73
Pr ⁿ	61.6	6.15	6.17	6.24	6.28	63.82							

TABLE I—(continued).

R =	P.	R _C .	R _D .	R _F .	R _G .	Mn _D ^{20°} .	R =	P.	R _C .	R _D .	R _F .	R _G .	Mn _D ^{20°} .
Alkyl isovalerates, (CH ₃) ₂ CH·CH ₂ ·CO ₂ R.													
Me	62.8	6.14	6.19	6.24	6.30	64.11	Pr ⁿ	62.7	6.24	6.26	6.32	6.39	63.55
Et	62.3	6.22	6.25	6.32	6.37	63.50	Bu ⁿ	62.3	6.19	6.22	6.28	6.33	63.56
Alkyl n-hexoates, CH ₃ ·[CH ₂] ₄ ·CO ₂ R.													
Me	62.4	6.10	6.12	6.19	6.25	64.40	Et	61.4	6.14	6.16	6.23	6.26	63.89
Alkyl n-heptoates, CH ₃ ·[CH ₂] ₅ ·CO ₂ R.													
Me	61.1	6.05	6.06	6.13	6.17	64.51	Et	62.6	6.13	6.16	6.21	6.26	63.94
Alkyl n-octoates, CH ₃ ·[CH ₂] ₆ ·CO ₂ R.													
Me	63.7	6.10	6.13	6.18	6.23	64.60	Et	63.0	6.08	6.10	6.17	6.19	64.04
Alkyl n-decoates, CH ₃ ·[CH ₂] ₈ ·CO ₂ R.													
Me	64.1	6.09	6.10	6.16	6.22	64.66	Pr ⁿ	63.9	6.22	6.24	6.31	6.36	63.89
Et	63.3	6.11	6.15	6.21	6.26	64.05	Bu ⁿ	63.2	6.10	6.14	6.20	6.25	63.90
Alkyl n-dodecoates, CH ₃ ·[CH ₂] ₁₀ ·CO ₂ R.													
Me	65.4	6.15	6.16	6.23	6.29	64.72	Pr ⁿ	61.7	6.07	6.10	6.15	6.19	63.97
Et	61.6	6.17	6.20	6.26	6.32	64.03	Bu ⁿ	61.7	6.27	6.30	6.36	6.39	64.10
Dialkyl oxalates, (CO ₂ R) ₂ .													
Et	66.2	6.45	6.48	6.55	6.63	64.33	Bu ⁿ	64.4	6.48	6.52	6.59	6.65	64.13
Pr ⁿ	65.5	6.49	6.52	6.60	6.66	64.13	Am ⁿ ...	64.0	6.44	6.47	6.54	6.60	64.09
Pr ⁱ	69.0	6.82	6.85	6.93	7.00	64.11	Am ⁱ † ...	64.0	6.47	6.50	6.58	6.63	64.13
Dialkyl malonates, CH ₂ (CO ₂ R) ₂ .													
Me	66.2	6.30	6.33	6.40	6.48	64.95	Et	64.9	6.28	6.31	6.38	6.45	64.20
Dialkyl succinates, [CH ₂] ₂ (CO ₂ R) ₂ .													
Me	65.5	6.16	6.20	6.26	6.32	65.00	Bu ⁿ	62.7	6.18	6.20	6.26	6.31	64.20
Et	63.8	6.17	6.19	6.25	6.31	64.42	Bu ⁱ	61.7	6.25	6.28	6.33	6.38	64.16
Pr ⁿ	62.9	6.21	6.24	6.30	6.36	64.32	Am ⁿ ...	61.8	6.19	6.22	6.28	6.33	64.18
Pr ⁱ	63.5	6.22	6.24	6.30	6.35	63.83	Am ⁱ ‡ ...	63.1	6.21	6.25	6.31	6.35	64.30
Dialkyl glutarates, [CH ₂] ₃ (CO ₂ R) ₂ .													
Me	64.8	6.06	6.08	6.14	6.22	65.02	Et	63.9	6.15	6.17	6.23	6.30	64.43
Dialkyl adipates, [CH ₂] ₄ (CO ₂ R) ₂ .													
Me	65.6	6.12	6.14	6.20	6.25	65.16	Bu ⁿ	63.3	6.16	6.19	6.26	6.29	64.31
Et	64.3	6.16	6.19	6.25	6.29	64.57	Am ⁿ ...	62.3	6.12	6.15	6.21	6.25	64.27
Pr ⁿ	64.2	6.14	6.16	6.22	6.27	64.39	Am ⁱ † ...	62.8	6.11	6.13	6.20	6.24	64.43
Pr ⁱ	64.2	6.17	6.20	6.25	6.29	64.00							
Dialkyl pimelates, [CH ₂] ₅ (CO ₂ R) ₂ .													
Me	65.7	6.11	6.14	6.20	6.24	65.06	Et	64.9	6.16	6.19	6.24	6.31	64.42
Dialkyl suberates, [CH ₂] ₆ (CO ₂ R) ₂ .													
Me	66.4	6.10	6.13	6.19	6.24	64.98	Pr ⁿ	64.8	6.19	6.21	6.28	6.33	64.33
Et	65.8	6.18	6.21	6.27	6.37	64.46	Bu ⁿ	62.8	6.12	6.13	6.21	6.24	64.25
Dialkyl sebacates, [CH ₂] ₈ (CO ₂ R) ₂ .													
Et	66.1	6.20	6.23	6.29	6.34	64.48	Pr ⁿ	64.6	6.11	6.13	6.19	6.23	64.30
Mean CO·O 63.4 6.173 6.200 6.261 6.315 64.14													

† With Bisol fermentation *isoamyl* alcohol.‡ With Sharples synthetic *isoamyl* alcohol.

experimental figures for dialkyl malonates, glutarates, and pimelates are those of Part I (*J.*, 1934, 333). In the calculation of the mean values, the experimental data for alkyl formates, *sec.*-butyl acetate, dialkyl oxalates, and dialkyl malonates have been omitted; the individual variations are comparatively large and therefore there seems no valid reason for excluding the methyl esters from the computations. The high values for the dialkyl oxalates are doubtless due to some interaction between the two carboxyl groups (an effect which is apparent, but less marked, with the malonates): the subject will be discussed again in connexion with computations of bond refractivities. The mean values are:—

	P.	R _C .	R _D .	R _F .	R _G .	Mn _D ^{20°} .
CO·O	63.4	6.173	6.200	6.261	6.315	64.14

These figures may be compared with those deduced from CO (Part XI, *loc. cit.*) + O in alkyl ethers (Part XII, preceding paper) :

CO	45.9	4.684	4.713	4.768	4.830	42.38
O (ethers)	19.8	1.753	1.764	1.786	1.805	22.74
CO + O (ethers)	65.7	6.437	6.477	6.554	6.635	65.12

It is evident that the constants for CO·O are not equal to the sum of those for CO (ketones) and O (alkyl ethers), and hence the assumption of Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 585) and others that

$$O_2 \text{ (esters)} = O'' \text{ (ketones)} + O < \text{ (ethers)}$$

has no experimental foundation. In view of the constancy of the values for CO·O and CO, it follows that the values for (CO·O - CO) will also be constant, but they are *not* the constants for ethereal oxygen O < as understood by Eisenlohr. To avoid ambiguity the author suggests that for calculations of the molecular refractivities of carboxylic esters, the figures for CO·O should be employed.

If the author's values for the constants of carbon (Part IX, *loc. cit.*) are subtracted from those for CO·O, the following figures are obtained for O₂ in carboxylic esters :

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}.</i>
O ₂ (esters)	54.8	3.601	3.609	3.660	3.660	38.43

Sugden (*J.*, 1924, **125**, 1177; "The Parachor and Valency", 1930, 42) gives *P* 60.0, whilst Eisenlohr's values (*loc. cit.*) for O'' + O < are *R_C* 3.828, *R_D* 3.854, *R_F* 3.896, and *R_G* 3.929, respectively.

TABLE II.

Comparison of CH₃·[CH₂]_{*n*}·CH(CO₂R)₂ and [CH₂]_{*n*+2}(CO₂R)₂.

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}.</i>
CH ₃ ·CH(CO ₂ Me) ₂	320.6	33.04	33.18	33.53	33.79	206.47
(CH ₂ ·CO ₂ Me) ₂	321.7	32.84	32.99	33.34	33.59	207.45
CH ₃ ·CH(CO ₂ Et) ₂	398.7	42.25	42.44	42.90	43.23	246.06
(CH ₂ ·CO ₂ Et) ₂	398.5	42.12	42.30	42.75	43.08	247.32
CH ₃ ·CH(CO ₂ Pr ⁿ) ₂	476.3	51.57	51.79	52.34	52.74	287.02
(CH ₂ ·CO ₂ Pr ⁿ) ₂	476.2	51.42	51.65	52.20	52.62	288.24
CH ₃ ·CH(CO ₂ Bu ⁿ) ₂	553.8	60.89	61.02	61.68	62.15	328.20
(CH ₂ ·CO ₂ Bu ⁿ) ₂	555.3	60.63	60.89	61.55	62.01	329.30
C ₂ H ₅ ·CH(CO ₂ Me) ₂	358.4	37.63	37.82	38.21	38.49	227.09
[CH ₂] ₃ (CO ₂ Me) ₂	361.4	37.27	37.43	37.83	38.16	228.01
C ₂ H ₅ ·CH(CO ₂ Et) ₂	437.0	46.85	47.07	47.56	47.94	266.63
[CH ₂] ₃ (CO ₂ Et) ₂	439.6	46.73	46.93	47.43	47.83	267.89
C ₂ H ₅ ·CH(CO ₂ Pr ⁿ) ₂	515.1	56.17	56.44	57.02	57.47	307.64
C ₂ H ₅ ·CH(CO ₂ Bu ⁿ) ₂	592.0	65.31	65.62	66.30	66.82	348.72
C ₃ H ₇ ⁿ ·CH(CO ₂ Me) ₂	396.2	42.23	42.42	42.87	43.20	247.56
[CH ₂] ₄ (CO ₂ Me) ₂	402.0	42.02	42.20	42.65	42.97	248.80
C ₃ H ₇ ⁿ ·CH(CO ₂ Et) ₂	475.5	51.57	51.81	52.36	52.76	287.12
[CH ₂] ₄ (CO ₂ Et) ₂	479.1	51.31	51.54	52.09	52.47	288.74
C ₃ H ₇ ⁿ ·CH(CO ₂ Pr ⁿ) ₂	555.3	60.81	61.08	61.73	62.21	328.22
[CH ₂] ₄ (CO ₂ Pr ⁿ) ₂	558.2	60.55	60.82	61.48	61.93	329.68
C ₃ H ₇ ⁿ ·CH(CO ₂ Bu ⁿ) ₂	630.7	69.99	70.30	71.06	71.60	369.24
[CH ₂] ₄ (CO ₂ Bu ⁿ) ₂	636.6	69.77	70.09	70.84	71.35	370.81
C ₅ H ₁₁ ⁿ ·CH(CO ₂ Me) ₂	473.9	51.55	51.79	52.34	52.74	288.76
[CH ₂] ₆ (CO ₂ Me) ₂	483.3	51.19	51.42	51.97	52.37	289.57
C ₅ H ₁₁ ⁿ ·CH(CO ₂ Et) ₂	553.4	60.80	61.08	61.73	62.19	328.32
[CH ₂] ₆ (CO ₂ Et) ₂	561.4	60.64	60.91	61.56	62.13	329.83
C ₅ H ₁₁ ⁿ ·CH(CO ₂ Pr ⁿ) ₂	631.8	70.06	70.37	71.12	71.68	369.40
[CH ₂] ₆ (CO ₂ Pr ⁿ) ₂	639.6	69.82	70.13	70.87	71.43	370.84
C ₅ H ₁₁ ⁿ ·CH(CO ₂ Bu ⁿ) ₂	709.0	79.32	79.67	80.52	81.15	410.33
[CH ₂] ₆ (CO ₂ Bu ⁿ) ₂	717.0	79.02	79.36	80.21	80.82	411.99

Although it cannot be claimed that the purity of all the methyl and ethyl esters of the monobasic acids (particularly *n*-hexoic to *n*-dodecoic acid) is as high as that obtained for the normal aliphatic hydrocarbons (Part IX, *loc. cit.*), they do provide two homologous series (acetic acid

to *n*-dodecoic acid—*n*-nonoic and *n*-undecoic acids are absent) from which the CH₂ contributions may be calculated by the method of least squares. The results are :

CH₂ from esters of monobasic acids, CH₃·[CH₂]_{*n*}·CO₂R.

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D²⁰.</i>
Methyl esters	39·87	4·623	4·638	4·698	4·721	20·62
Ethyl esters	39·75	4·619	4·640	4·688	4·725	20·61

These are in satisfactory agreement with the values found from other homologous series (compare Part IX).

Measurements have also been made upon esters of methyl-, ethyl-, *n*-propyl-, and *n*-amyl-malonic acids. Apart from their own intrinsic merit and as reference compounds in the calculation of certain structural constants in subsequent papers of this series, the results are of importance in connexion with the deduction of bond refractivities of C-H in compounds of the

type $\text{H}-\text{C} \begin{array}{l} \diagup \text{C} \\ \diagdown \text{C} \\ \diagdown \text{C} \end{array}$. The final results are collected in Table II.

EXPERIMENTAL.

Preparation of Esters.

Alkyl Formates.—A.R. (98/100%) Formic acid was used throughout, and the alcohols were of the highest purity (see Part VII, *J.*, 1943, 638) : *n*-propyl and the higher alcohols were purified, after drying (CaSO₄ or K₂CO₃), by fractional distillation. A mixture of the alcohol (1 mol.) and excess of formic acid (2 mols.) was refluxed for 24—30 hours and the ester was isolated by a procedure in which due regard was paid to its solubility in water.

Ethyl formate. A mixture of 61 g. of pure formic acid and 31 g. of absolute ethyl alcohol was refluxed on a steam-bath for 30 hours. It was then distilled from a flask with fractionating side arm until the temperature rose to 62°; the distillate was washed successively with saturated sodium chloride solution, saturated sodium hydrogen carbonate solution in the presence of solid sodium chloride, and dried (MgSO₄). Distillation gave 36 g. of ethyl formate, b. p. 53·5°/767 mm.

n-Propyl formate. A mixture of 46 g. of formic acid and 30 g. of *n*-propyl alcohol was refluxed for 22 hours and then fractionally distilled. The distillate, b. p. below 85°, was worked up as for ethyl formate and yielded 30 g. of ester, b. p. 81—82°/768 mm.

isoPropyl formate. A mixture of 46 g. of formic acid and 30 g. of *isopropyl* alcohol was refluxed for 22 hours. The excess of acid was removed by adding 10 ml. of saturated sodium hydrogen carbonate solution, followed by 15 g. of the solid salt in small portions; the lower layer was discarded, 10 ml. of saturated salt solution were added, and then solid sodium hydrogen carbonate until effervescence ceased. The ester was washed with saturated salt solution, dried, and distilled. The yield of *isopropyl* formate, b. p. 67·5—68°/767 mm., was 32 g.

n-Butyl formate. A mixture of 46 g. of formic acid and 37 g. of *n*-butyl alcohol was refluxed for 26 hours, then washed successively with saturated salt solution, saturated sodium hydrogen carbonate solution in the presence of saturated salt solution until effervescence ceased, saturated salt solution, and finally dried and distilled. The yield of ester, b. p. 105—107°/765 mm. (mainly 106·5°), was 40 g.

isoButyl formate. A mixture of 46 g. of formic acid and 37 g. of *isobutyl* alcohol was refluxed for 26 hours and yielded, when worked up as for *n*-butyl formate, 45 g. of the ester, b. p. 96—98°/767 mm. (mainly 97·5°).

n-Amyl formate. A mixture of 46 g. of formic acid and 44 g. of *n*-amyl alcohol, after refluxing for 24 hours, yielded, after the usual procedure, 47 g. of ester, b. p. 130—131°/753 mm.

isoAmyl formate. The yield of ester from 46 g. of formic acid and 44 g. of *isoamyl* alcohol (Sharples synthetic), after refluxing for 18 hours, was 44 g. of b. p. 123—125°/763 mm. (mainly 124°). A similar preparation but with Bisol fermentation *isoamyl* alcohol gave 45 g. of b. p. 123—124°/761 mm.

n-Hexyl formate. A mixture of 46 g. of formic acid and 51 g. of *n*-hexyl alcohol was refluxed for 24 hours and yielded, when worked up as for *n*-butyl formate, 56 g. of ester, b. p. 153—154°/753 mm. (mainly 154°).

Alkyl Acetates.—A.R. Glacial acetic acid was used throughout and in large excess.

Methyl acetate. A mixture of 48 g. of absolute methyl alcohol, 270 g. of pure acetic acid, and 3 g. of concentrated sulphuric acid was refluxed for 5 hours. Upon fractionation of the reaction mixture, 112 g. of the crude ester passed over at 55—56° and the residual acid weighed 209 g.; the latter may be employed for the conversion of more methyl alcohol into the ester. The ester was washed successively with saturated salt solution, saturated sodium hydrogen carbonate solution until effervescence ceased, saturated salt solution, dried (MgSO₄), and distilled. The yield of pure methyl acetate, b. p. 56°/754 mm., was 92 g.

Ethyl acetate. A mixture of 58 g. of absolute ethyl alcohol, 225 g. of acetic acid, and 3 g. of concentrated sulphuric acid was refluxed for 12 hours. Water was added, the mixture saturated with sodium chloride to separate the ester layer, the latter was washed with saturated sodium hydrogen carbonate solution until neutral, then with saturated salt solution, and finally dried (MgSO₄). The yield of ethyl acetate, b. p. 76—77°/770 mm. (mainly 77°), was 32 g. An improved yield may be obtained by fractionating the crude reaction mixture as detailed for methyl acetate.

n-Propyl acetate. A mixture of 40 g. of *n*-propyl alcohol, 160 g. of glacial acetic acid, and 2 g. of concentrated sulphuric acid was refluxed for 12 hours. An equal weight of water was then added, and

the ester worked up as in the preceding preparation. The yield of *n*-propyl acetate, b. p. 101—102°/767 mm., was 36 g.

*iso*Propyl acetate. A mixture of 40 g. of *isopropyl* alcohol, 160 g. of acetic acid, and 2 g. of concentrated sulphuric acid was refluxed for 18 hours. After being worked up as above, the yield was 32 g.; b. p. 87—88°/759 mm.

n-Butyl acetate. Dry hydrogen chloride was passed into 37 g. of *n*-butyl alcohol until 1 g. was absorbed, 120 g. of acetic acid were added, and the mixture was refluxed for 8 hours. The reaction mixture was diluted with excess of water, and worked up as for ethyl acetate, but without the washing with saturated brine. The yield of *n*-butyl acetate, b. p. 125°/755 mm., was 40 g.

*iso*Butyl acetate. A mixture of 37 g. of *isobutyl* alcohol (containing 1 g. of dissolved hydrogen chloride) and 120 g. of acetic acid was refluxed for 11 hours. It was worked up as for *n*-butyl acetate and yielded 36 g. of ester, b. p. 115.5—116.5°/764 mm.

sec.-Butyl acetate. A mixture of 50 g. of *sec.*-butyl alcohol (containing 2.5 g. of dissolved hydrogen chloride) and 90 g. acetic acid was refluxed for 10 hours. It was worked up as for *n*-butyl acetate and afforded 35 g. of ester, b. p. 111—112°/765 mm.

tert.-Butyl acetate. This was prepared from 12 g. of magnesium, 37 g. of *tert.*-butyl alcohol, 100 ml. of anhydrous ether and a solution of 55 g. of pure acetyl chloride in 50 g. of anhydrous ether (see *Org. Synth.*, 1940, 20, 21). The fractionation was conducted through a four-section, Pyrex, modified Young and Thomas column. The yield of ester, b. p. 96.5—98°/763 mm. (mainly 97.5°), was 49 g.

n-Amyl acetate. A mixture of 44 g. of *n*-amyl alcohol, 160 g. of acetic acid, and 2.5 g. of concentrated sulphuric acid was refluxed for 20 hours and yielded, when worked up as usual, 47 g. of ester, b. p. 147—148°/762 mm. (mainly 148°).

*iso*Amyl acetate. This was prepared exactly like the *n*-amyl ester except that 44 g. of Bisol fermentation *iso*amyl alcohol were used. The yield of ester, b. p. 141—142°/761 mm., was 46 g.

n-Hexyl acetate. A mixture of 34 g. of *n*-hexyl alcohol, 60 g. of acetic acid, and 1.7 g. of concentrated sulphuric acid was refluxed for 30 hours. It yielded, when worked up in the usual manner, 40 g. of ester, b. p. 167—170°/768 mm. (mainly 168—169°).

Alkyl Propionates.—The propionic acid (Boake Roberts) was carefully fractionated and the fraction of b. p. 141.5°/772 mm. was used. The "excess acid" method was employed throughout.

Methyl propionate. A mixture of 16 g. of absolute methyl alcohol, 111 g. of propionic acid, and 0.8 g. of concentrated sulphuric acid was refluxed for 24 hours and then distilled through an efficient column. The distillate (39 g.), b. p. 70—80°, was washed successively with saturated sodium hydrogen carbonate solution until neutral, then saturated salt solution, and dried, and distilled. The yield of ester, b. p. 79—80°/762 mm., was 31 g.

Ethyl propionate. A mixture of 23 g. of absolute ethyl alcohol, 111 g. of propionic acid, and 1.2 g. of concentrated sulphuric acid was refluxed for 24 hours. It was then fractionated and the portion distilling below 110° was collected as crude ester. This was purified as for methyl propionate and yielded 40 g. of ethyl propionate, b. p. 98—99°/763 mm.

n-Propyl propionate. A mixture of 30 g. of *n*-propyl alcohol, 111 g. of propionic acid, and 1.5 g. of concentrated sulphuric acid was refluxed for 24 hours, then poured into excess of water and worked up as usual. The yield of ester, b. p. 122—123°/767 mm., was 45 g.

n-Butyl propionate. A mixture of 37 g. of *n*-butyl alcohol, 111 g. of propionic acid, and 1.9 g. of concentrated sulphuric acid, refluxed for 24 hours, yielded, when worked up as usual, 55 g. of ester, b. p. 145.5°/767 mm.

Alkyl n-Butyrates.—The pure commercial acid (Boake Roberts) was carefully fractionated and the fraction of b. p. 163°/756 mm. used.

Methyl n-butyrate. A mixture of 44 g. of absolute methyl alcohol, 30 g. of *n*-butyric acid, and 6 ml. of concentrated sulphuric acid was refluxed for 14 hours. It was then poured into 300 ml. of water, the excess of acid neutralised with sodium hydrogen carbonate, and the ester extracted with ether and dried (MgSO₄). After removal of the ether, 18 g. of ester, b. p. 103°/774 mm., were obtained.

Ethyl n-butyrate. A mixture of 16 g. of absolute ethyl alcohol, 60 g. of *n*-butyric acid, and 4 ml. of concentrated sulphuric acid was refluxed for 14 hours. It was then poured into excess of water, washed with saturated sodium hydrogen carbonate solution until neutral and then with water, and dried and distilled. The yield of ethyl *n*-butyrate, b. p. 121°/771 mm., was 26 g.

n-Propyl *n*-butyrate. A mixture of 40 g. of *n*-propyl alcohol, 85 g. of *n*-butyric acid, and 6 ml. of concentrated sulphuric acid was refluxed for 24 hours, and the ester separated as for the ethyl compound. The yield of ester, b. p. 142—143°/767 mm., was 38 g.

n-Butyl *n*-butyrate. A mixture of 30 g. of *n*-butyl alcohol, 80 g. of *n*-butyric acid, and 6 ml. of concentrated sulphuric acid was refluxed for 25 hours. After being worked up as usual, 32 g. of ester, b. p. 164.5—165.5°/755 mm., were obtained.

n-Amyl *n*-butyrate. The yield of ester, b. p. 185—186°/757 mm., from a mixture of 27 g. of *n*-amyl alcohol, 60 g. of *n*-butyric acid, and 6 ml. of concentrated sulphuric acid refluxed for 28 hours, was 29 g.

*iso*Amyl *n*-butyrate. A mixture of 30 g. of *n*-butyric acid, 27 g. of *iso*amyl alcohol (Bisol fermentation), 70 ml. of sodium-dried A.R. benzene, and 6 ml. of concentrated sulphuric acid was refluxed for 27 hours. It was then poured into excess of water, the benzene layer separated and washed successively with water, saturated sodium hydrogen carbonate solution and water, and dried, and distilled. After the benzene had been removed, 42 g. of ester, b. p. 179.5°/780 mm., were collected.

Alkyl isoButyrates.—Commercial *isobutyric* acid was distilled and the fraction, b. p. 154—154.5°/775 mm., collected.

Methyl isobutyrate. A mixture of 44 g. of *isobutyric* acid, 12 g. of absolute methyl alcohol, and 0.6 g. of concentrated sulphuric acid was refluxed for 26 hours and fractionally distilled. The distillate boiling below 110° (50 g.) was washed with saturated sodium hydrogen carbonate solution until neutral, then with saturated salt solution, and dried and distilled. The yield of ester, b. p. 91—92°/761 mm., was 30 g.

Ethyl isobutyrate. A mixture of 37 g. of *isobutyric* acid, 196 g. of absolute ethyl alcohol, and 10 g. of concentrated sulphuric acid was refluxed for 20 hours, the excess of alcohol distilled off on a water-bath

and the residue poured into excess of water. The upper layer of ester was separated and purified as usual. The yield of ester, b. p. 110°/762 mm., was 20 g.

n-Propyl isobutyrate. A mixture of 37 g. of isobutyric acid, 51.5 g. of *n*-propyl alcohol, 90 ml. of sodium-dried A.R. benzene, and 7 g. of concentrated sulphuric acid was refluxed for 31 hours, poured into excess of water, the benzene layer washed with saturated sodium hydrogen carbonate solution and water, and dried (MgSO₄). After removal of the benzene, 27 g. of ester, b. p. 133—134°/752 mm., were obtained upon fractionation.

n-Butyl isobutyrate. A mixture of 37 g. of isobutyric acid, 64 g. of *n*-butyl alcohol, 90 ml. of pure benzene, and 7 g. of concentrated sulphuric acid was refluxed for 31 hours. This was worked up as for the *n*-propyl ester and yielded 40 g. of ester, b. p. 155—156°/762 mm.

Alkyl n-Valerates.—The *n*-valeric acid, prepared by the hydrolysis of *n*-butyl cyanide, had b. p. 184°/767 mm.

Methyl n-valerate. A mixture of 46 g. of *n*-valeric acid, 8.6 g. of absolute methyl alcohol, and 0.5 g. of concentrated sulphuric acid was refluxed for 40 hours and then fractionally distilled until the b. p. reached 140°. The distillate consisted of two layers: the lower, aqueous layer was discarded, and the upper layer was washed with saturated sodium hydrogen carbonate solution until neutral and then with water, and dried and distilled. The yield of ester, b. p. 126°/750 mm., was 16 g.

Ethyl n-valerate. A mixture of 40 g. of *n*-valeric acid, 9 g. of absolute ethyl alcohol, and 0.5 g. of concentrated sulphuric acid was refluxed for 38 hours and then fractionally distilled until the temperature rose to 160°. The subsequent procedure was as given for the methyl ester and afforded 16 g. of ethyl *n*-valerate, b. p. 144°/762 mm.

n-Propyl n-valerate. A mixture of 25.5 g. of *n*-valeric acid, 30 g. of *n*-propyl alcohol, 50 ml. of sodium-dried A.R. benzene, and 10 g. of concentrated sulphuric acid was refluxed for 39 hours. This was poured into water, etc., and yielded 23 g. of ester, b. p. 162—164°/750 mm.

n-Butyl n-valerate. A mixture of 25.5 g. of *n*-valeric acid, 37 g. of *n*-butyl alcohol, 50 ml. of pure benzene, and 5 g. of concentrated sulphuric acid was refluxed for 53 hours. It was then poured into water, etc., and yielded 27 g. of ester, b. p. 183—185°/753 mm.

n-Amyl n-valerate. A mixture of 20.4 g. of *n*-valeric acid, 44 g. of *n*-amyl alcohol, 6 g. of concentrated sulphuric acid, and 60 ml. of pure benzene was refluxed for 21 hours and then poured into excess of water. The benzene layer was washed with saturated sodium hydrogen carbonate solution and water, dried (MgSO₄) and distilled. After the benzene had passed over, 19 g. of ester, b. p. 202—204°/749 mm. (mainly 202—202.5°), were obtained. This was redistilled and had b. p. 103°/23 mm.

Alkyl isoValerates.—Kahlbaum's pure isovaleric acid was redistilled and the fraction, b. p. 176°/762 mm., collected.

Methyl isovalerate. A mixture of 51 g. of isovaleric acid, 12 g. of absolute methyl alcohol, and 0.6 g. of concentrated sulphuric acid was refluxed for 20 hours and then fractionally distilled until the temperature rose to 135°. The distillate was washed successively with saturated sodium hydrogen carbonate solution and saturated salt solution, dried, and distilled. The yield of ester, b. p. 115—116°/760 mm., was 26 g.

Ethyl isovalerate. A mixture of 51 g. of isovaleric acid, 11 g. of absolute ethyl alcohol, and 1 g. of concentrated sulphuric acid was refluxed for 20 hours, and then fractionally distilled until the temperature rose to 155°. After the usual procedure, the yield of ester, b. p. 132.5—134°/777 mm., was 24 g.

n-Propyl isovalerate. A mixture of 34 g. of isovaleric acid, 40 g. of *n*-propyl alcohol, 67 ml. of pure benzene, and 13.5 g. of concentrated sulphuric acid was refluxed for 30 hours, and then poured into water. The ester was isolated as usual. The yield was 38 g., b. p. 156—156.5°/755 mm.

n-Butyl isovalerate. A mixture of 34 g. of isovaleric acid, 49 g. of *n*-butyl alcohol, 67 ml. of pure benzene, and 13.5 g. of concentrated sulphuric acid was refluxed for 30 hours, and worked up as usual. The yield of ester, b. p. 175—176°/755 mm., was 42 g.

Alkyl n-Hexoates (n-Caproates).—Commercial *n*-hexoic acid (Carbon and Carbide Corporation) was fractionated, and the portion of b. p. 202—203°/768 mm. collected.

Methyl n-hexoate. A mixture of 58 g. of *n*-hexoic acid, 10.7 g. of absolute methyl alcohol, and 0.5 g. of concentrated sulphuric acid was refluxed for 30 hours and then fractionally distilled until the temperature rose to 155° (most passed over at 145—155°). The lower layer of the distillate was discarded, the ester washed with saturated sodium hydrogen carbonate solution and water, then dried and distilled. The yield of ester, b. p. 148—150°/760 mm., was 35 g.

Ethyl n-hexoate. A mixture of 58 g. of *n*-hexoic acid, 11.5 g. of absolute ethyl alcohol, and 0.6 g. of concentrated sulphuric acid was refluxed for 40 hours and then fractionally distilled until the temperature rose to 175°. The aqueous layer of the distillate was discarded and, after purification, 28 g. of the ester, b. p. 163.5—165.5°/752 mm., were isolated.

Alkyl n-Heptoates.—Pure commercial *o*-naphthanthic acid (B.D.H.) was fractionated, and the fraction of b. p. 220—222°/768 mm. collected.

Methyl n-heptoate. A mixture of 35 g. of *n*-heptonic acid, 86 g. of absolute methyl alcohol, and 4.3 g. of concentrated sulphuric acid was refluxed for 12 hours, then poured into a large excess of water, and the ester layer separated and purified. The yield of ester, b. p. 170—173°/761 mm., was 35 g.

Ethyl n-heptoate. A mixture of 35 g. of *n*-heptonic acid, 134 g. of absolute ethyl alcohol, and 6.2 g. of concentrated sulphuric acid was refluxed for 12 hours and yielded, as for the methyl ester, 38 g. of ethyl *n*-heptoate, b. p. 184—186.5°/764 mm.

Alkyl n-Octoates.—Commercial pure *n*-octoic acid (Deutsche Hydrierwerke) was distilled, and the portion of b. p. 235—239°/762 mm. collected.

Methyl n-octoate. The yield of ester from 36 g. of *n*-octoic acid, 80 g. of absolute methyl alcohol, and 4 g. of concentrated sulphuric acid after refluxing for 12 hours was 33 g. of b. p. 191—192°/759 mm.

Ethyl n-octoate. The yield from 36 g. of *n*-octoic acid, 115 g. of absolute ethyl alcohol, and 6 g. of concentrated sulphuric acid after refluxing for 30 hours was 33 g. of b. p. 205—208°/742 mm.

Alkyl n-Decoates.—Commercially pure capric acid (Deutsche Hydrierwerke), m. p. 31—32°, was used.

Methyl n-decoate. The yield of ester from 43 g. of *n*-decoic acid, 80 g. of absolute methyl alcohol, and 4 g. of concentrated sulphuric acid, after refluxing for 25 hours, was 39 g. of b. p. 227—229°/758 mm.

Ethyl n-decoate. The yield of ester from 43 g. of decoic acid, 115 g. of absolute ethyl alcohol, and 6 g. of concentrated sulphuric acid, after refluxing for 22 hours, was 41 g. of b. p. 241—242.5°/760 mm.

n-Propyl n-decoate. The yield of ester from 34.5 g. of capric acid, 24 g. of *n*-propyl alcohol, 40 ml. of pure benzene, and 8 g. of concentrated sulphuric acid, after refluxing for 12 hours, was 39 g. of b. p. 114—115°/4.5 mm. (Found: C, 73.0; H, 11.9. $C_{13}H_{26}O_2$ requires C, 72.8; H, 12.2%).

n-Butyl n-decoate. The yield of ester from 34.5 g. of *n*-decoic acid, 30 g. of *n*-butyl alcohol, 40 ml. of pure benzene, and 8 g. of concentrated sulphuric acid, after refluxing for 12 hours, was 40 g. of b. p. 122—124°/4 mm. (Found: C, 73.6; H, 12.3. $C_{14}H_{28}O_2$ requires C, 73.6; H, 12.4%).

Alkyl n-Dodecoates.—Commercially pure lauric acid (Deutsche Hydrierwerke), m. p. 45—46, was used.

Methyl n-dodecoate. The yield of ester from 40 g. of lauric acid, 64 g. of absolute methyl alcohol, and 3.5 g. of concentrated sulphuric acid, after refluxing for 18 hours, was 35 g. of b. p. 261—263°/766 mm.

Ethyl n-dodecoate. The yield of ester from 40 g. of lauric acid, 92 g. of absolute ethyl alcohol, and 4.6 g. of concentrated sulphuric acid, after refluxing for 20 hours, was 39 g. of b. p. 272—274°/764 mm.

n-Propyl n-dodecoate. The yield of ester from 33 g. of lauric acid, 20 g. of *n*-propyl alcohol, 35 ml. of pure benzene, and 6.5 g. of concentrated sulphuric acid, after refluxing for 38 hours, was 35 g. of b. p. 139—140°/4 mm. (Found: C, 74.3; H, 12.3. $C_{15}H_{30}O_2$ requires C, 74.3; H, 12.5%).

n-Butyl n-dodecoate. The yield of ester from 33 g. of the acid, 25 g. of *n*-butyl alcohol, 35 ml. of pure benzene, and 6.5 g. of concentrated sulphuric acid, after refluxing for 38 hours, was 40 g. of b. p. 152—153.5°/4.5 mm. (Found: C, 75.0; H, 12.3. $C_{16}H_{32}O_2$ requires C, 74.9; H, 12.6%).

Dialkyl Oxalates.—A.R. Oxalic acid dihydrate was dehydrated by heating the finely-powdered acid, spread upon large clock-glasses, in an electrically-heated oven at 105° for 6 hours, and then allowing it to cool in a desiccator. The loss in weight was theoretical.

The general method of preparation consisted in refluxing a mixture of 1 mol. of acid, 2.5—3.5 mols. of the alcohol, sodium-dried A.R. benzene (twice the volume of alcohol), and concentrated sulphuric acid for 6—12 hours, pouring the reaction mixture into a large excess of water, and separating the benzene layer; the aqueous extract phase was extracted with ether, and the extract combined with the benzene layer. The combined extracts were washed with saturated sodium hydrogen carbonate solution until free from acid, then with water, dried ($MgSO_4$), and distilled: the benzene passed over first, followed by the oxalate. The quantities used and the yields and b. p.s obtained are tabulated below.

Oxalate.	Acid, g.	Alcohol, g.	C_6H_6 , ml.	H_2SO_4 (conc.), g.	Refluxing period (hrs.).	B. p.	Yield, g.
Ethyl	37	67	125	24	24	182—183°/764 mm.	47
<i>n</i> -Propyl	37	87	125	27	34	211—212°/749 mm.	59
<i>iso</i> Propyl	37	87	125	27	23	188—191°/757 mm.	57
<i>n</i> -Butyl	37	108	125	27	20	242—245°/773 mm.	59
<i>n</i> -Amyl	18.5	64	63	13.5	32	138—139°/9 mm.	34
<i>iso</i> Amyl †	18.5	64	63	13.5	22	127—128°/7 mm.	40

Dialkyl Succinates.—A.R. Succinic acid, m. p. 185°, was used throughout.

Succinate.	Acid, g.	Alcohol, g.	C_6H_6 , ml.	H_2SO_4 (conc.), g.	Refluxing period (hrs.).	B. p.	Yield, g.
Methyl	20	32	80	14	5	195°/756 mm.	17.5
Ethyl	40	46	120	14	8	81°/3 mm.	47
<i>n</i> -Propyl	30	45	110	11	12	101.5°/3 mm.	37.5
<i>iso</i> Propyl	30	45	120	14	12	82°/3 mm.	34
<i>n</i> -Butyl	30	54	140	14	20	121°/3 mm.	45
<i>iso</i> Butyl	30	75	100	2	28	116°/4 mm.	39
<i>n</i> -Amyl	30	90	220	18	22	129°/2 mm.	58
<i>iso</i> Amyl †	30	90	220	21	14	130°/4 mm.	57
<i>iso</i> Amyl †	20	45	60	8	32	150°/9 mm.	38

Dialkyl Adipates.—Commercially pure adipic acid was crystallised from acetone and dried in a vacuum desiccator; m. p. 152.5°.

Adipate.	Acid, g.	Alcohol, g.	C_6H_6 , ml.	H_2SO_4 (conc.), g.	Refluxing period (hrs.).	B. p.	Yield, g.
Methyl	40	40	100	14	6	120—121°/17 mm.	42
Ethyl	30	38	80	12	15	134.5°/17 mm.	40
<i>n</i> -Propyl	30	39	75	12	14	145—146°/9 mm.	40
<i>iso</i> Propyl	30	39	75	12	12	120—121°/6—7 mm.	32
<i>n</i> -Butyl	40	66	100	16	26	158—159°/7 mm.	56
<i>n</i> -Amyl	30	57	75	12	27	185—186°/10 mm.	46
<i>iso</i> Amyl	30	57	75	12	23	184—185°/13 mm.	42

Dialkyl Suberates.—The suberic acid had m. p. 140° and was prepared from castor oil (compare Vogel, *J.*, 1928, 2033).

Suberate.	Acid, g.	Alcohol, g.	C_6H_6 , ml.	H_2SO_4 (conc.), g.	Refluxing period (hrs.).	B. p.	Yield, g.
Methyl	29	20	65	10	33	120°/6 mm.	30
Ethyl	29	23	65	10	33	131°/5 mm.	23
<i>n</i> -Propyl ¹	29	30	65	10	38	164—165°/8 mm.	36
<i>n</i> -Butyl ²	29	37	65	10	31	175—176°/4.5 mm.	40

¹ Found: C, 64.9; H, 9.9. $C_{14}H_{26}O_4$ requires C, 65.1; H, 10.1%.

² Found: C, 66.9; H, 10.4. $C_{16}H_{30}O_4$ requires C, 67.1; H, 10.6%.

Dialkyl Sebacates.—Schuchardt's pure acid was recrystallised from acetone and had m. p. 133—134°.

Sebacate.	Acid, g.	Alcohol, g.	C ₆ H ₆ , ml.	H ₂ SO ₄ (conc.), g.	Refluxing period (hrs.).	B. p.	Yield, g.
Ethyl	34	23	65	10	36	156°/6 mm.	38
<i>n</i> -Propyl ³	34	23	65	10	28	178—179/5 mm.	40

³ Found: C, 66.8; H, 10.3. C₁₈H₃₀O₄ requires C, 67.1; H, 10.6%.

Dialkyl Methylmalonates.—Although methylmalonamide, m. p. 207°, can be readily prepared, the isolation of pure methylmalonic acid is a long and tedious process (Meyer and Bock, *Annalen*, 1896, **347**, 93). To prepare the pure esters, the method adopted was the hydrolysis of the pure amide, followed by conversion of the resulting solution of the sodium salt into the insoluble silver salt: the latter was then treated with the appropriate alkyl halide.

Crude diethyl methylmalonate, b. p. 193—195°/768 mm. (Meyer and Bock, *loc. cit.*), was shaken mechanically with 3 times its weight of concentrated ammonia solution for 12 hours and the resulting crude amide was recrystallised from 70% ethyl alcohol to constant m. p. (207°). 67 G. of the pure amide were heated under reflux with a solution of 54 g. of A.R. sodium hydroxide in 250 ml. of water until the evolution of ammonia ceased, the solution was then cautiously acidified with dilute nitric acid and then neutralised with concentrated ammonia solution to nitrazine-yellow indicator, and the precipitated silica filtered off. The filtrate was diluted somewhat, and a solution of 170 g. of silver nitrate in 200 ml. of water was added with stirring. The precipitate was collected after 12 hours, washed, and dried at 50—70°. The yield of silver methylmalonate was 185 g.

Dimethyl methylmalonate. A mixture of 47 g. of dry silver methylmalonate, 41 g. of pure colourless methyl iodide, and 100 ml. of sodium-dried ether was refluxed for 11 hours, the ether decanted, and the solid extracted with four 25-ml. portions of ether. After removal of the ether from the combined extracts, 15.5 g. of ester, b. p. 176—177°/761 mm., were obtained.

Diethyl methylmalonate. A mixture of 41.5 g. of silver methylmalonate, 40 g. of pure colourless ethyl iodide, and 75 ml. of sodium-dried A.R. benzene was refluxed for 8 hours. The mixture was filtered, and the solid was washed with three 40-ml. portions of pure benzene. The combined benzene extracts were washed successively with saturated sodium hydrogen carbonate solution (to remove traces of acid) and water, and dried, and distilled. The yield of ester, b. p. 195—196°/775 mm., was 13 g.

Di-n-propyl methylmalonate. A mixture of 41.5 g. of silver methylmalonate, 45 g. of pure colourless *n*-propyl iodide, and 75 ml. of pure, dry benzene was refluxed for 10 hours and yielded (details as for the ethyl ester) 15 g. of the ester, b. p. 225—226°/771 mm. (Found: C, 59.3; H, 8.9. C₁₆H₁₈O₄ requires C, 59.4; H, 9.0%).

Di-n-butyl methylmalonate. A mixture of 41.5 g. of silver methylmalonate, 46 g. of pure colourless *n*-butyl iodide, and 75 ml. of pure, dry benzene, refluxed for 14 hours, afforded (details as for the ethyl ester) 18 g. of the ester, b. p. 254—256°/761 mm. (Found: C, 62.5; H, 9.8. C₁₈H₂₂O₄ requires C, 62.6; H, 9.6%).

Dialkyl Ethylmalonates.—Ethylmalonic acid was prepared in the usual manner from ethyl sodiomalonate and ethyl iodide, followed by hydrolysis of the resulting diethyl ethylmalonate with aqueous-alcoholic potassium hydroxide; upon recrystallisation from benzene-ether-light petroleum (b. p. 40—60°), it had m. p. 110—111°.

The esters were prepared by the alcohol-benzene-sulphuric acid method. The experimental details are summarised below.

Ethyl-malonate.	Acid, g.	Alcohol, g.	C ₆ H ₆ , ml.	H ₂ SO ₄ (conc.), g.	Refluxing period (hrs.).	B. p.	Yield, g.
Methyl	39.6	40	120	18	22	190°/761 mm.; 85°/15 mm.	24
Ethyl	19.8	28	60	9	19	109/24 mm.	21
<i>n</i> -Propyl ⁴	19.8	42	60	9	20	123/15 mm.	23
<i>n</i> -Butyl ⁵	19.8	55	60	9	20	145/14 mm.	25

⁴ Found: C, 60.8; H, 9.2. C₁₁H₂₀O₄ requires C, 61.1; H, 9.3%.

⁵ Found: C, 64.0; H, 9.9. C₁₃H₂₄O₄ requires C, 63.9; H, 9.9%.

Dialkyl n-Propylmalonates.—*n*-Propylmalonic acid was prepared as follows. To a solution of 34.5 g. of sodium in 345 g. of absolute ethyl alcohol were added 240 g. of dry diethyl malonate; after 2 hours 185 g. of *n*-propyl bromide were introduced during 90 minutes. The mixture was refluxed until neutral (2—3 hours), most of the alcohol was distilled off on a water-bath, the residue diluted with water, the ester layer separated, and the aqueous layer extracted with ether. The ester and extracts were dried (MgSO₄) and distilled; the yield of diethyl *n*-propylmalonate, b. p. 219—226°/775 mm. (mainly 220—222°), was 220 g. 156 G. of pure potassium hydroxide were dissolved in 156 g. of water, rectified spirit (500 ml.) was added until a homogeneous solution resulted, and the 220 g. of ester were introduced. The mixture was refluxed until a test portion dissolved completely in water (3 hours), and the alcohol was distilled off from a water-bath. The residue was dissolved in water, cooled to 0°, and dilute sulphuric acid was added slowly with vigorous stirring until the solution was acid to Congo-red. The acid was separated by three extractions with ether, the extracts dried, and the solvent removed on a water-bath. The syrupy residue was spread in thin layers upon large clock-glasses and largely crystallised when left overnight; the acid was collected on a sintered-glass funnel and washed with a little light petroleum (b. p. 40—60°); the *n*-propylmalonic acid (39 g.) had m. p. 95—96° after drying on a porous tile. The filtrate was spread on large clock-glasses, and the process repeated. The total yield of pure acid, m. p. 95—96° (*ex benzene*), was 115 g.

The experimental data relating to the preparation of the esters are summarised below.

<i>n</i> -Propylmalonate.	Acid, g.	Alcohol, g.	C ₆ H ₆ , ml.	H ₂ SO ₄ (conc.), g.	Refluxing period (hrs.).	B. p.	Yield, g.
<i>Methyl</i> ⁶	20.5	18.5	55	9	38	203—204°/760 mm.	18.5
<i>Ethyl</i>	18.5	23.5	50	8	38	221—222/767 mm.	18
<i>n-Propyl</i> ⁷	20.5	36	55	8.5	30	120—121/6 mm.	25
<i>n-Butyl</i> ⁸	20.5	42	55	8.5	35	150/9 mm.	32

⁶ Found: C, 55.0; H, 8.1. C₈H₁₄O₄ requires C, 55.2; H, 8.1%.

⁷ Found: C, 62.3; H, 9.5. C₁₂H₂₂O₄ requires C, 62.6; H, 9.6%.

⁸ Found: C, 65.3; H, 10.4. C₁₄H₂₆O₄ requires C, 65.1; H, 10.2%.

Dialkyl n-Amylmalonates.—*n*-Amylmalonic acid was prepared similarly to *n*-propylmalonic acid except that crystallisation of the crude acid was achieved by leaving it in a vacuum desiccator over anhydrous calcium chloride and silica gel. Recrystallisation from benzene gave the pure acid, m. p. 82°. The experimental data for the preparation of the esters are summarised in the following table.

<i>n</i> -Amylmalonate.	Acid, g.	Alcohol, g.	C ₆ H ₆ , ml.	H ₂ SO ₄ (conc.), g.	Refluxing period (hrs.).	B. p.	Yield, g.
<i>Methyl</i> ⁹	25	18.5	55	8.5	18	104°/4.5 mm.	25
<i>Ethyl</i> ¹⁰	25	26.5	55	8.5	26	113/3.5 mm.	28.5
<i>n-Propyl</i> ¹¹	20	28	45	7.5	28	136/4 mm.	25.5
<i>n-Butyl</i> ¹²	20	34	45	7.5	34	152—152.5/3.5 mm.	29

⁹ Found: C, 59.4; H, 8.8. C₁₀H₁₈O₄ requires C, 59.4; H, 9.0%.

¹⁰ Found: C, 62.8; H, 9.6. C₁₂H₂₂O₄ requires C, 62.6; H, 9.6%.

¹¹ Found: C, 65.2; H, 10.0. C₁₄H₂₆O₄ requires C, 65.1; H, 10.1%.

¹² Found: C, 67.2; H, 10.5. C₁₆H₃₀O₄ requires C, 67.1; H, 10.6%.

Physical Measurements.—The above esters were redistilled immediately before use and a middle fraction was employed in the measurements.

180. *Ethyl formate.* B. p. 53.5°/767 mm.; *M* 74.08; *n*_C 1.35799, *n*_D 1.35983, *n*_F 1.36425, *n*_G 1.36735; *R*_C 17.63, *R*_D 17.71, *R*_F 17.90; *R*_G 18.04; *Mn*_{40°}^{20°} 100.73. Densities determined: *d*_{4°}^{20°} 0.9229, *d*_{4°}^{40°} 0.8985. Apparatus *A*.

(These headings apply to corresponding columns in all the following tables.)

<i>t</i> .	<i>H</i> .	<i>d</i> _{4°} ^{20°} .	<i>γ</i> .	<i>P</i> .	<i>t</i> .	<i>H</i> .	<i>d</i> _{4°} ^{20°} .	<i>γ</i> .	<i>P</i> .
22.9°	13.68	0.9218	23.56	177.3	41.4°	12.52	0.8971	21.03	177.3
22.7	13.58	0.9197	23.39	177.2					Mean 177.3

181. *n-Propyl formate.* B. p. 81.5°/768 mm.; *M* 88.10; *n*_C 1.37492, *n*_D 1.37693; *n*_F 1.38159, *n*_G 1.38494; *R*_C 22.31, *R*_D 22.41, *R*_F 22.66, *R*_G 22.84; *Mn*_{40°}^{20°} 121.31. Densities determined: *d*_{4°}^{20°} 0.9039, *d*_{4°}^{41.5°} 0.8812, *d*_{4°}^{50°} 0.8602. Apparatus *A*.

26.1°	14.18	0.8973	23.83	216.9	41.5°	13.36	0.8812	22.04	216.8
33.2	13.87	0.8907	23.13	217.0	61.2	12.40	0.8589	19.94	217.2
									Mean 217.0

182. *n-Butyl formate.* B. p. 106.5°/765 mm.; *M* 102.13; *n*_C 1.38706, *n*_D 1.38903, *n*_F 1.39383, *n*_G 1.39727; *R*_C 26.97, *R*_D 27.09, *R*_F 27.38, *R*_G 27.60; *Mn*_{40°}^{20°} 141.86. Densities determined: *d*_{4°}^{20°} 0.8917, *d*_{4°}^{41.7°} 0.8701, *d*_{4°}^{51.8°} 0.8492, *d*_{4°}^{55.5°} 0.8231. Apparatus *D*.

21.3°	11.32	0.8904	24.89	256.2	61.9°	9.88	0.8491	20.72	256.6
41.3	10.64	0.8705	22.87	256.6	86.7	8.95	0.8219	18.17	256.6
									Mean 256.5

183. *n-Amyl formate.* B. p. 130.5°/753 mm.; *M* 116.16; *n*_C 1.39768, *n*_D 1.39974, *n*_F 1.40469, *n*_G 1.40829; *R*_C 31.67, *R*_D 31.81, *R*_F 32.16, *R*_G 32.41; *Mn*_{40°}^{20°} 162.59. Densities determined: *d*_{4°}^{20°} 0.8846, *d*_{4°}^{42.0°} 0.8644, *d*_{4°}^{50.9°} 0.8463, *d*_{4°}^{56.6°} 0.8208. Apparatus *D*.

24.8°	11.78	0.8801	25.60	296.9	60.7°	10.45	0.8465	21.85	296.7
30.3	11.56	0.8749	24.98	296.8	86.7	9.50	0.8207	19.25	296.5
42.1	11.13	0.8643	23.76	296.7					Mean 296.7

184. *n-Hexyl formate.* B. p. 154°/753 mm.; *M* 130.18; *n*_C 1.40499, *n*_D 1.40706, *n*_F 1.41214, *n*_G 1.41576; *R*_C 36.30, *R*_D 36.47, *R*_F 36.86, *R*_G 37.15; *Mn*_{40°}^{20°} 183.18. Densities determined: *d*_{4°}^{20°} 0.8789, *d*_{4°}^{41.5°} 0.8609, *d*_{4°}^{50.4°} 0.8440, *d*_{4°}^{56.5°} 0.8218. Apparatus *D*.

22.8°	12.31	0.8765	26.65	337.4	61.1°	10.97	0.8434	22.85	337.5
27.7	12.13	0.8723	26.13	337.4	86.4	10.11	0.8209	20.50	337.4
40.9	11.62	0.8614	24.72	337.1					Mean 337.4

185. isoPropyl formate. B. p. 67.5—68°/767 mm.; M 88.10; n_D 1.36588, n_D 1.36783, n_F 1.37232, n_G 1.37561; R_C 22.49, R_D 22.59, R_F 22.84, R_G 23.02; Mn_D^{20} 120.51. Densities determined: d_4^{20} 0.8774, d_4^{30} 0.8541. Apparatus *D*.

<i>t.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>
18.7°	10.34	0.8789	22.44	218.3	40.3°	9.46	0.8540	19.95	218.6
25.3	10.05	0.8713	21.63	218.2					Mean 218.4

186. isoButyl formate. B. p. 97.5°/767 mm.; M 102.13; n_C 1.38352, n_D 1.38546, n_F 1.39025, n_G 1.39700, n_F 1.40191, n_G 1.40546; R_C 31.55, R_D 27.23, R_F 27.53, R_G 27.75; Mn_D^{20} 141.50. Densities determined: d_4^{20} 0.8798, d_4^{30} 0.8588, d_4^{50} 0.8386. Apparatus *D*.

15.4°	11.20	0.8846	24.47	256.8	40.2°	10.17	0.8591	21.58	256.3
18.7	11.02	0.8811	23.98	256.5	59.6	9.41	0.8383	19.48	256.3
22.3	10.92	0.8775	23.66	256.7					Mean 256.5

187A. isoAmyl formate (from Bisol fermentation alcohol). B. p. 123.5°/761 mm.; n_C 1.39497, n_D 1.39700, n_F 1.40191, n_G 1.40546; R_C 31.55, R_D 31.69, R_F 32.04, R_G 32.29; Mn_D^{20} 162.28. Densities determined: d_4^{20} 0.8827, d_4^{40} 0.8629, $d_4^{61.8}$ 0.8417, $d_4^{85.7}$ 0.8175. Apparatus *D*.

16.9°	11.54	0.8858	25.24	293.9	61.1°	9.92	0.8424	20.64	294.1
41.3	10.67	0.8620	22.71	294.2	87.8	8.95	0.8154	18.02	294.4
									Mean 294.2

187B. isoAmyl formate (from Sharples synthetic alcohol). B. p. 124°/763 mm.; M 116.16; n_C 1.39606, n_D 1.39807, n_F 1.40298, n_G 1.40659; R_C 31.52, R_D 31.66, R_F 32.00, R_G 32.26; Mn_D^{20} 162.40. Densities determined: d_4^{20} 0.8857, $d_4^{39.4}$ 0.8662, $d_4^{59.7}$ 0.8465, $d_4^{85.4}$ 0.8207. Apparatus *A*.

17.2°	15.20	0.8885	25.29	293.2	61.5°	13.12	0.8447	20.75	293.7
23.3	14.91	0.8824	24.64	293.3	87.2	11.86	0.8189	18.19	293.4
40.8	14.15	0.8648	22.91	293.9					Mean 293.5

188. Methyl acetate. B. p. 56°/754 mm.; M 74.08, n_C 1.36015, n_D 1.36193, n_F 1.36629, n_G 1.36930; R_C 17.42, R_D 17.49, R_F 17.68, R_G 17.81; Mn_D^{20} 100.89. Densities determined: d_4^{20} 0.9390, $d_4^{40.9}$ 0.9125. Apparatus *D*.

21.0°	10.87	0.9377	25.17	177.1	41.0°	10.04	0.9124	22.62	177.4
25.7	10.76	0.9318	24.76	177.4					Mean 177.3

A Bisol sample of methyl acetate was purified by washing with saturated potassium carbonate solution, and water, and the ester was salted out with A.R. sodium chloride, dried with A.R. anhydrous potassium carbonate, and distilled through a three-section, Pyrex Young and Thomas column; it had b. p. 56.5°/758 mm., d_4^{20} 0.9315, n_D^{20} 1.36189; the low density would appear to indicate the presence of impurities not removable by fractionation.

189. Ethyl acetate. B. p. 77°/770 mm.; M 88.10; n_C 1.37050, n_D 1.37233, n_F 1.37683, n_G 1.37993; R_C 22.15, R_D 22.24, R_F 22.48, R_G 22.65; Mn_D^{20} 120.90. Densities determined: d_4^{20} 0.9009, $d_4^{42.0}$ 0.8747, $d_4^{69.0}$ 0.8533. Apparatus *D*.

20.3°	10.68	0.9005	23.75	216.0	42.6°	9.76	0.8740	21.07	216.2
29.1	10.41	0.8899	22.87	216.5	61.4	8.95	0.8504	18.80	216.2
									Mean 216.2

190. n-Propyl acetate. B. p. 101.5°/767 mm.; M 102.13; n_C 1.38249, n_D 1.38442, n_F 1.38899, n_G 1.39230; R_C 26.84, R_D 26.95, R_F 27.24, R_G 27.45; Mn_D^{20} 141.39. Densities determined: d_4^{20} 0.8867, $d_4^{41.5}$ 0.8658, $d_4^{61.6}$ 0.8432, $d_4^{77.0}$ 0.8150. Apparatus *A*.

22.1°	14.55	0.8845	24.13	255.8	62.0°	12.40	0.8428	19.57	255.2
41.1	13.58	0.8662	22.03	255.4	87.3	11.06	0.8147	16.87	254.7
									Mean 255.3

191. isoPropyl acetate. B. p. 88°/759 mm.; M 102.13; n_C 1.37542, n_D 1.37730, n_F 1.38187, n_G 1.38507; R_C 26.84, R_D 26.96, R_F 27.26, R_G 27.46; Mn_D^{20} 140.66. Densities determined: d_4^{20} 0.8718, $d_4^{41.7}$ 0.8502, $d_4^{62.1}$ 0.8251. Apparatus *D*.

21.0°	10.32	0.8708	22.14	254.4	41.4°	9.56	0.8505	20.08	254.4
22.0	10.29	0.8697	22.10	254.6	61.1	8.75	0.8262	17.85	254.5
									Mean 254.5

192. n-Butyl acetate. B. p. 125°/755 mm.; M 116.16; n_C 1.39208, n_D 1.39406, n_F 1.39881, n_G 1.40228; R_C 31.39, R_D 31.53, R_F 31.87, R_G 32.11; Mn_D^{20} 161.94. Densities determined: d_4^{20} 0.8813, $d_4^{41.0}$ 0.8630, $d_4^{61.3}$ 0.8431, $d_4^{74.0}$ 0.8177. Apparatus *A*.

20.9°	15.29	0.8804	25.21	295.6	60.8°	13.30	0.8426	20.99	295.1
29.3	15.01	0.8726	24.53	296.2	86.4	12.00	0.8159	18.33	295.0
41.0	14.38	0.8630	23.24	295.5					Mean 295.5

211. *n*-Propyl isobutyrate. B. p. 134°/752 mm.; *M* 130·18; n_D 1·39356, n_D 1·39552, n_F 1·40033, n_G 1·40383; R_C 35·99, R_D 36·15, R_F 36·53, R_G 36·82; Mn_D^{20} 181·67. Densities determined: d_4^{20} 0·8643, d_4^{15} 0·8432, d_4^{11} 0·8236, d_4^{8} 0·7967. Apparatus *D*.

<i>t.</i>	<i>H.</i>	d_4^*	$\gamma.$	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4^*	$\gamma.$	<i>P.</i>
15·3°	11·35	0·8690	24·36	332·8	61·5°	9·58	0·8235	19·48	332·0
19·1	11·19	0·8652	23·91	332·7	86·9	8·69	0·7972	17·11	332·1
41·5	10·34	0·8430	21·53	332·6					Mean 332·4

212. *n*-Butyl isobutyrate. B. p. 156°/762 mm.; *M* 144·21; n_C 1·40056, n_D 1·40248, n_F 1·40739, n_G 1·41098; R_C 40·62, R_D 40·79, R_F 41·23, R_G 41·55; Mn_D^{20} 202·25. Densities determined: d_4^{20} 0·8618, d_4^{15} 0·8416, d_4^{11} 0·8239, d_4^{8} 0·7984. Apparatus *A*.

16·4°	15·34	0·8652	24·86	372·2	61·5°	13·21	0·8233	20·34	372·4
18·9	15·24	0·8628	24·62	372·3	86·9	11·98	0·7991	17·93	371·3
42·3	14·12	0·8409	22·23	372·4					Mean 372·1

213. Methyl *n*-valerate. B. p. 126·5°/756 mm.; *M* 116·16; n_C 1·39493, n_D 1·39690, n_F 1·40167, n_G 1·40505; R_C 31·30, R_D 31·44, R_F 31·78, R_G 32·02; Mn_D^{20} 162·27. Densities determined: d_4^{20} 0·8895, d_4^{15} 0·8694, d_4^{11} 0·8492, d_4^{8} 0·8236. Apparatus *D*.

19·3°	11·76	0·8902	25·85	294·2	60·0°	10·27	0·8504	21·57	294·4
26·2	11·51	0·8834	25·11	294·4	86·6	9·27	0·8220	18·82	294·7
40·8	10·98	0·8695	23·58	294·4					Mean 294·4

214. Ethyl *n*-valerate. B. p. 144°/762 mm.; *M* 130·18; n_C 1·39843, n_D 1·40042, n_F 1·40525, n_G 1·40869; R_C 36·00; R_D 36·16, R_F 36·55, R_G 36·82; Mn_D^{20} 182·30. Densities determined: d_4^{20} 0·8736, d_4^{15} 0·8539, d_4^{11} 0·8331, d_4^{8} 0·8097.

16·3°	15·53	0·8770	25·50	333·6	60·6°	13·46	0·8361	21·07	333·6
20·4	15·38	0·8732	25·15	333·9	87·0	12·19	0·8093	18·47	333·5
41·5	14·38	0·8542	23·00	333·7					Mean 333·6

215. *n*-Propyl *n*-valerate. B. p. 163·5°/750 mm.; *M* 144·21; n_C 1·40470, n_D 1·40672, n_F 1·41168, n_G 1·41520; R_C 40·59, R_D 40·77, R_F 41·21, R_G 41·52; Mn_D^{20} 202·86. Densities determined: d_4^{20} 0·8702, d_4^{15} 0·8514, d_4^{11} 0·8330, d_4^{8} 0·8092. Apparatus *D*.

18·3°	12·07	0·8707	25·95	373·8	61·3°	10·54	0·8324	21·67	373·8
29·1	11·72	0·8619	24·95	373·9	86·7	9·63	0·8087	19·23	373·4
40·9	11·24	0·8516	23·64	373·4					Mean 373·6

216. *n*-Butyl *n*-valerate. B. p. 184°/753 mm.; *M* 158·23; n_C 1·40992; n_D 1·41197, n_F 1·41703, n_G 1·42055; R_C 45·15, R_D 45·36, R_F 45·84, R_G 46·18; Mn_D^{20} 223·42. Densities determined: d_4^{20} 0·8680, d_4^{15} 0·8500, d_4^{11} 0·8313, d_4^{8} 0·8104. Apparatus *A*.

18·2°	16·19	0·8696	26·36	412·3	61·8°	14·21	0·8312	22·12	412·8
26·3	15·89	0·8624	25·66	413·0	86·0	13·17	0·8098	19·57	413·1
40·9	15·11	0·8495	24·04	412·4					Mean 412·7

217. *n*-Amyl *n*-valerate. B. p. 202°/749 mm. and 103°/23 mm.; *M* 172·26; n_C 1·41412, n_D 1·41635, n_F 1·42128, n_G 1·42499; R_C 49·85, R_D 50·07, R_F 50·60, R_G 50·99; Mn_D^{20} 243·97. Densities determined: d_4^{20} 0·8638, d_4^{15} 0·8460, d_4^{11} 0·8298, d_4^{8} 0·8070. Apparatus *E*.

17·1°	13·15	0·8663	26·53	451·3	60·5°	11·66	0·8295	22·53	452·4
40·9	12·31	0·8457	24·24	452·0	88·1	10·73	0·8056	20·13	452·7
									Mean 452·1

218. Methyl isovalerate. B. p. 115·5°/760 mm.; *M* 116·16; n_C 1·39074, n_D 1·39270, n_F 1·39750, n_G 1·40086; R_C 31·31, R_D 31·46, R_F 31·80, R_G 32·04; Mn_D^{20} 161·78. Densities determined: d_4^{20} 0·8807, d_4^{15} 0·8592, d_4^{11} 0·8401, d_4^{8} 0·8132. Apparatus *D*.

16·1°	11·29	0·8846	24·66	292·6	42·0°	10·34	0·8587	21·93	292·7
19·9	11·14	0·8808	24·23	292·6	60·7	9·62	0·8395	19·94	292·4
25·3	10·98	0·8753	23·73	292·6	85·9	8·68	0·8134	17·44	292·2
									Mean 292·5

219. Ethyl isovalerate. B. p. 134°/771 mm.; *M* 130·18; n_C 1·39424, n_D 1·39621, n_F 1·40105, n_G 1·40446; R_C 36·01, R_D 36·17, R_F 36·57, R_G 36·84; Mn_D^{20} 181·76. Densities determined: d_4^{20} 0·8652, d_4^{15} 0·8456, d_4^{11} 0·8252, d_4^{8} 0·8008. Apparatus *A*.

21·1°	14·72	0·8641	23·82	332·8	61·3°	12·66	0·8252	19·56	331·8
23·0	14·53	0·8623	23·46	332·3	85·0	11·55	0·8013	17·33	331·5
41·4	13·56	0·8451	21·46	331·5					Mean 332·0

238. Diisopropyl oxalate. B. p. 191°/765 mm.; M 174.19; n_D 1.41061, n_D 1.41281, n_F 1.41820, n_G 1.42212; R_C 43.44, R_D 43.65, R_F 44.15, R_G 44.51; Mn_D^{20} 246.11. Densities determined: d_4^{20} 0.9947, $d_4^{1.3}$ 0.9732, $d_4^{2.9}$ 0.9496, $d_4^{8.4}$ 0.9244. Apparatus *D*.

<i>t.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4^*	γ .	<i>P.</i>
21.0°	11.55	0.9937	28.34	404.5	62.1°	10.24	0.9504	24.03	405.8
25.1	11.40	0.9894	28.11	405.4	88.3	9.50	0.9224	21.64	407.3
41.2	10.86	0.9733	26.10	404.5					Mean 405.5

239. Di-n-butyl oxalate. B. p. 242°/773 mm.; M 202.24; n_C 1.42119, n_D 1.42341, n_F 1.42876, n_G 1.43260; R_C 51.96, R_D 52.20, R_F 52.78, R_G 53.19; Mn_D^{20} 287.87. Densities determined: d_4^{20} 0.9874, $d_4^{1.5}$ 0.9684, $d_4^{6.6}$ 0.9503, $d_4^{8.2}$ 0.9262. Apparatus *A*.

22.2°	15.94	0.9854	29.41	476.9	63.3°	14.46	0.9479	25.67	480.2
28.2	15.76	0.9800	28.92	478.6	87.3	13.57	0.9252	23.51	481.3
41.3	15.26	0.9686	27.68	478.9					Mean 479.2

240. Di-n-amyl oxalate. B. p. 139°/9 mm.; M 230.30; n_C 1.42665, n_D 1.42887, n_F 1.43426, n_G 1.43823; R_C 61.16, R_D 61.44, R_F 62.11, R_G 62.59; Mn_D^{20} 329.08. Densities determined: d_4^{20} 0.9662, $d_4^{1.4}$ 0.9483, $d_4^{2.5}$ 0.9304, $d_4^{6.5}$ 0.9093. Apparatus *D*.

24.6°	12.30	0.9623	29.23	556.5	62.0°	11.26	0.9308	25.88	558.1
42.0	11.88	0.9478	27.81	558.0	88.1	10.56	0.9079	23.68	559.6
									Mean 558.0

241. Diisoamyl oxalate (from Bisol fermentation alcohol). B. p. 127.5°/7 mm.; M 230.30; n_C 1.42488, n_D 1.42712, n_F 1.43253, n_G 1.43643; R_C 61.27, R_D 61.55, R_F 62.23, R_G 62.71; Mn_D^{20} 328.66. Densities determined: d_4^{20} 0.9609, $d_4^{1.3}$ 0.9437, $d_4^{1.2}$ 0.9266, $d_4^{8.3}$ 0.9043. Apparatus *D*.

24.8°	11.72	0.9568	27.69	552.4	61.9°	10.79	0.9260	24.68	554.3
41.5	11.32	0.9435	26.38	553.2	87.0	10.17	0.9037	22.70	556.2
									Mean 554.0

242. Dimethyl succinate. B. p. 195°/759 mm.; M 146.14; n_C 1.41742, n_D 1.41951, n_F 1.42456, n_G 1.42830; R_C 32.84, R_D 32.99, R_F 33.34, R_G 33.59; Mn_D^{20} 207.45. Densities determined: d_4^{20} 1.1198, $d_4^{8.7}$ 1.0791, $d_4^{5.5}$ 1.0508, $d_4^{20.1}$ 1.0132. Apparatus *A*.

17.0°	17.65	1.1229	37.11	321.3	84.9°	14.65	1.0510	28.83	322.2
24.1	17.32	1.1155	36.18	321.3	120.6	13.08	1.0127	24.80	322.0
61.7	15.57	1.0759	31.37	321.5					Mean 321.7

243. Diethyl succinate. B. p. 81°/3 mm.; M 174.19; n_C 1.41772, n_D 1.41981, n_F 1.42488, n_G 1.42860; R_C 42.12, R_D 42.30, R_F 42.75, R_G 43.08; Mn_D^{20} 247.32. Densities determined: d_4^{20} 1.0416, $d_4^{1.4}$ 1.0198, $d_4^{8.8}$ 1.0013, $d_4^{8.2}$ 0.9759. Apparatus *A*.

20.5°	16.38	1.0411	31.93	397.7	61.2°	14.65	1.0009	27.46	398.4
28.3	16.02	1.0333	31.00	397.8	86.0	13.75	0.9751	25.11	399.9
42.1	15.49	1.0191	29.56	398.5					Mean 398.5

244. Di-n-propyl succinate. B. p. 101.5°/3 mm.; M 202.24; n_C 1.42296, n_D 1.42521, n_F 1.43038, n_G 1.43425; R_C 51.42, R_D 51.65, R_F 52.20, R_G 52.62; Mn_D^{20} 288.24. Densities determined: d_4^{20} 1.0015, $d_4^{1.8}$ 0.9831, $d_4^{6.1}$ 0.9647, $d_4^{8.7}$ 0.9435. Apparatus *D*.

19.6°	12.55	1.0019	31.05	476.5	61.3°	11.24	0.9648	26.78	476.9
26.4	12.13	0.9959	29.76	474.6	87.7	10.51	0.9426	24.47	477.2
41.4	11.81	0.9835	28.68	475.9					Mean 476.2

245. Diisopropyl succinate. B. p. 82°/3 mm.; M 202.24; n_C 1.41562, n_D 1.41771, n_F 1.42284, n_G 1.42650; R_C 51.49, R_D 51.72, R_F 52.28, R_G 52.68; Mn_D^{20} 286.72. Densities determined: d_4^{20} 0.9847, $d_4^{1.1}$ 0.9653, $d_4^{6.5}$ 0.9467, $d_4^{8.0}$ 0.9221. Apparatus *D*.

18.5°	11.62	0.9861	28.30	473.0	61.3°	10.42	0.9460	24.34	474.9
25.8	11.50	0.9792	27.81	474.3	85.1	9.75	0.9230	22.22	475.7
41.3	11.02	0.9651	26.27	474.4					Mean 474.3

246. Di-n-butyl succinate. B. p. 121°/3 mm.; M 230.30; n_C 1.42777, n_D 1.42992, n_F 1.43519, n_G 1.43904; R_C 60.63, R_D 60.89, R_F 61.55, R_G 62.01; Mn_D^{20} 329.30. Densities determined: d_4^{20} 0.9768, $d_4^{1.0}$ 0.9602, $d_4^{2.0}$ 0.9427, $d_4^{8.5}$ 0.9213. Apparatus *D*.

16.7°	12.80	0.9795	30.96	554.6	60.7°	11.53	0.9438	26.87	555.6
24.2	12.57	0.9734	30.22	554.7	87.2	10.74	0.9207	24.42	556.0
41.5	12.11	0.9598	28.70	555.4					Mean 555.3

247. Diisobutyl succinate. B. p. 116°/4 mm.; M 230.30; n_D 1.42450, n_D 1.42666, n_F 1.43190, n_G 1.43571; R_C 60.81, R_D 61.08, R_F 61.73, R_G 62.20; Mn_D^{20} 328.57. Densities determined: d_4^{20} 0.9675, d_4^{15} 0.9498, d_4^{10} 0.9337, d_4^{5} 0.9110. Apparatus *D*.

t .	H .	d_4^* .	γ .	P .	t .	H .	d_4^* .	γ .	P .
20.3°	11.90	0.9672	28.42	549.8	60.7°	10.79	0.9334	24.87	551.0
28.1	11.71	0.9607	27.85	550.4	86.9	10.15	0.9107	22.83	552.8
41.6	11.82	0.9497	26.55	550.5					Mean 550.9

248. Di-n-amyl succinate. B. p. 129°/2 mm.; M 258.35; n_D 1.43208, n_D 1.43425, n_F 1.43959, n_G 1.44349; R_C 69.83, R_D 70.14, R_F 70.88, R_G 71.43; Mn_D^{20} 370.55. Densities determined: d_4^{20} 0.9598, d_4^{15} 0.9435, d_4^{10} 0.9272, d_4^{5} 0.9078. Apparatus *D*.

23.6°	12.64	0.9570	29.87	631.1	60.9°	11.81	0.9283	27.07	634.8
42.0	12.28	0.9434	28.61	633.3	87.5	11.06	0.9073	24.78	635.3
									Mean 633.6

249A. Diisoamyl succinate (from Sharples synthetic alcohol). B. p. 130°/4 mm.; M 258.35; n_D 1.43132, n_G 1.43355, n_D 1.43886, n_G 1.44275; R_C 69.85, R_D 70.18, R_F 70.92, R_G 71.47; Mn_D^{20} 370.37. Densities determined: d_4^{20} 0.9579, d_4^{15} 0.9429, d_4^{10} 0.9278, d_4^{5} 0.9067. Apparatus *D*.

21.5°	12.63	0.9568	29.84	631.1	61.7°	11.54	0.9268	26.41	631.9
24.6	12.49	0.9545	29.44	630.5	87.9	10.77	0.9054	24.08	632.1
41.2	12.08	0.9431	28.14	630.9					Mean 631.3

249B. Diisoamyl succinate (from Bisol fermentation alcohol). B. p. 150°/9 mm.; M 258.35; n_D 1.43053, n_D 1.43274, n_F 1.43803, n_G 1.44206; R_C 69.89, R_D 70.21, R_F 70.95, R_G 71.53; Mn_D^{20} 370.14. Densities determined: d_4^{20} 0.9579, d_4^{15} 0.9403, d_4^{10} 0.9228, d_4^{5} 0.9032. Apparatus *C*.

18.6°	12.95	0.9569	29.42	628.8	61.1°	11.60	0.9228	25.41	628.6
41.0	12.46	0.9395	27.79	631.4	86.8	11.05	0.9030	23.69	631.2
									Mean 630.0

The measurements of the capillary rise were not altogether satisfactory because of the slow response to rise of temperature which was doubtless connected with the high viscosity of the liquid.

250. Dimethyl adipate. B. p. 120.5°/17 mm.; M 174.19; n_D 1.42618, n_D 1.42832, n_F 1.43349, n_G 1.43720; R_C 42.02, R_D 42.20, R_F 42.65, R_G 42.97; Mn_D^{20} 248.80. Densities determined: d_4^{20} 1.0625, d_4^{15} 1.0434, d_4^{10} 1.0244, d_4^{5} 1.0002. Apparatus *D*.

18.2°	13.76	1.0642	36.16	401.4	61.2°	12.37	1.0236	31.27	402.4
22.4	13.69	1.0602	35.84	402.0	86.7	11.53	0.9989	28.44	402.7
41.2	12.98	1.0432	33.44	401.5					Mean 402.0

251. Diethyl adipate. B. p. 134.5°/17 mm.; M 202.24; n_D 1.42551, n_D 1.42767, n_F 1.43287, n_G 1.43650; R_C 51.31, R_D 51.54, R_F 52.09, R_G 52.47; Mn_D^{20} 288.74. Densities determined: d_4^{20} 1.0088, d_4^{15} 0.9881, d_4^{10} 0.9698, d_4^{5} 0.9473. Apparatus *A*.

24.1°	17.04	1.0050	32.07	478.9	62.0°	15.38	0.9692	27.91	479.6
41.1	16.23	0.9887	30.05	478.9	86.7	14.36	0.9463	25.45	480.0
									Mean 479.4

252. Di-n-propyl adipate. B. p. 146°/9 mm.; M 230.32; n_D 1.42924, n_D 1.43143, n_F 1.43669, n_G 1.44044; R_C 60.55, R_D 60.82, R_F 61.48, R_G 61.93; Mn_D^{20} 329.68. Densities determined: d_4^{20} 0.9810, d_4^{15} 0.9629, d_4^{10} 0.9453, d_4^{5} 0.9243. Apparatus *A*.

9.7°	17.68	0.9899	32.77	556.7	42.3°	16.44	0.9619	29.61	558.6
16.2	17.45	0.9843	32.16	557.2	62.4	15.63	0.9442	27.63	559.3
22.4	17.32	0.9789	31.75	558.5	86.0	14.72	0.9242	25.36	559.2
									Mean 558.2

253. Diisopropyl adipate. B. p. 120°/6.5 mm.; M 230.32; n_D 1.42252, n_D 1.42466, n_F 1.42933, n_G 1.43343; R_C 60.65, R_D 60.93, R_F 61.57, R_G 62.02; Mn_D^{20} 328.14. Densities determined: d_4^{20} 0.9659, d_4^{15} 0.9455, d_4^{10} 0.9277, d_4^{5} 0.9054. Apparatus *D*.

17.7°	12.41	0.9679	29.66	555.4	61.6°	10.92	0.9271	25.00	555.6
22.0	12.23	0.9640	29.12	555.0	87.1	10.24	0.9044	22.87	556.9
41.2	11.66	0.9456	27.23	556.4					Mean 555.9

254. Di-n-butyl adipate. B. p. 158.5°/7 mm.; M 258.35; n_D 1.43304, n_D 1.43525, n_F 1.44055, n_G 1.44434; R_C 69.77, R_D 70.09, R_F 70.84, R_G 71.35; Mn_D^{20} 370.81. Densities determined: d_4^{20} 0.9624, d_4^{15} 0.9448, d_4^{10} 0.9282, d_4^{5} 0.9093. Apparatus *D*.

15.9°	13.29	0.9657	31.69	634.8	61.0°	12.04	0.9286	27.61	637.7
22.4	13.16	0.9605	31.22	635.8	87.7	11.29	0.9093	25.35	637.7
41.0	12.65	0.9453	29.53	637.1					Mean 636.6

255. Di-n-amyl adipate. B. p. 185.5°/10 mm.; M 286.40; n_D 1.43644, n_D 1.43867, n_F 1.44406, n_G 1.44792; R_C 79.03, R_D 79.39, R_F 80.23, R_G 80.83; Mn_D^{20} 412.04. Densities determined: d_4^{20} 0.9478, $d_4^{1.8}$ 0.9316, $d_4^{1.1}$ 0.9159, $d_4^{0.4}$ 0.8974. Apparatus *D*.

t .	H .	d_4^t .	γ .	P .	t .	H .	d_4^t .	γ .	P .
15.3°	13.46	0.9514	31.63	713.9	61.4°	12.20	0.9161	27.60	716.6
41.4	12.80	0.9319	29.46	716.0	85.1	11.54	0.8985	25.61	717.0
Mean 715.9									

256. Diisomyl adipate (from Bisol fermentation alcohol). B. p. 184.5°/13 mm.; M 286.40; n_D 1.43498, n_D 1.43721, n_F 1.44258, n_G 1.44646; R_C 79.05, R_D 79.40, R_F 80.25, R_G 80.87; Mn_D^{20} 411.62. Densities determined: d_4^{20} 0.9454, $d_4^{1.5}$ 0.9286, $d_4^{0.7}$ 0.9130, $d_4^{0.2}$ 0.8931. Apparatus *D*.

22.1°	12.87	0.9437	29.99	710.2	61.4°	11.83	0.9123	26.65	713.3
42.0	12.27	0.9282	28.13	710.6	87.3	11.08	0.8924	24.43	713.2
Mean 711.8									

257. Dimethyl suberate. B. p. 120°/6 mm.; M 202.24; n_D 1.43163, n_D 1.43380, n_F 1.43908, n_G 1.44303; R_C 51.19, R_D 51.42, R_F 51.97, R_G 52.37; Mn_D^{20} 289.97. Densities determined: d_4^{20} 1.0238, $d_4^{0.9}$ 1.0048, $d_4^{0.1}$ 0.9869, $d_4^{0.5}$ 0.9645. Apparatus *D*.

14.5°	14.23	1.0288	36.15	482.0	61.4°	12.69	0.9865	30.92	483.4
22.0	14.13	1.0220	35.66	483.6	86.1	11.93	0.9649	28.43	484.0
42.1	13.36	1.0037	33.12	483.4	Mean 483.3				

258. Diethyl suberate. B. p. 131°/5 mm.; M 230.30; n_D 1.43003, n_D 1.43219, n_F 1.43748, n_G 1.44465; R_C 60.64, R_D 60.91, R_F 61.56, R_G 62.13; Mn_D^{20} 329.83. Densities determined: d_4^{20} 0.9811, $d_4^{1.5}$ 0.9634, $d_4^{0.1}$ 0.9490, $d_4^{0.6}$ 0.9261. Apparatus *D*.

13.5°	13.63	0.9865	33.21	560.4	41.1°	12.82	0.9637	30.51	561.7
17.8	13.51	0.9829	32.79	560.7	88.7	11.37	0.9235	25.93	562.7
23.3	13.34	0.9784	32.33	560.9	Mean 561.4				

259. Di-n-propyl suberate. B. p. 165°/8 mm.; M 258.35; n_D 1.43317, n_D 1.43535, n_F 1.44070, n_G 1.44465; R_C 69.82, R_D 70.13, R_F 70.87, R_G 71.43; Mn_D^{20} 370.84. Densities determined: d_4^{20} 0.9621, $d_4^{2.0}$ 0.9438, $d_4^{1.5}$ 0.9285, $d_4^{0.0}$ 0.9086. Apparatus *D*.

16.8°	13.48	0.9647	32.12	637.5	61.9°	12.24	0.9282	28.06	640.6
23.2	13.36	0.9595	31.66	638.7	85.4	11.55	0.9090	25.93	641.3
41.0	12.83	0.9446	29.93	639.7	Mean 639.6				

260. Di-n-butyl suberate. B. p. 175.5°/4.5 mm.; M 286.40; n_D 1.43631, n_D 1.43852, n_F 1.44387, n_G 1.44777; R_C 79.02, R_D 79.36, R_F 80.21, R_G 80.82; Mn_D^{20} 411.99. Densities determined: d_4^{20} 0.9483, $d_4^{1.5}$ 0.9319, $d_4^{0.8}$ 0.9169, $d_4^{0.9}$ 0.8978. Apparatus *A*.

17.2°	17.96	0.9504	31.96	716.5	40.7°	17.02	0.9328	29.73	716.9
20.5	17.77	0.9479	31.54	716.0	62.1	16.24	0.9179	27.91	717.2
27.9	17.64	0.9423	31.13	717.9	86.3	15.29	0.8975	25.70	718.3
Mean 717.1									

261. Diethyl sebacate. B. p. 156°/6 mm.; M 258.35; n_D 1.43440, n_D 1.43660, n_F 1.44193, n_G 1.44578; R_C 69.85, R_D 70.16, R_F 70.90, R_G 71.44; Mn_D^{20} 371.15. Densities determined: d_4^{20} 0.9640, $d_4^{1.2}$ 0.9456, $d_4^{1.9}$ 0.9310, $d_4^{0.8}$ 0.9114. Apparatus *A*.

20.1°	18.14	0.9639	32.74	641.1	61.9°	16.48	0.9310	28.73	642.5
27.3	17.94	0.9582	32.19	642.3	87.1	15.48	0.9104	26.37	643.1
43.5	17.15	0.9454	30.36	641.5	Mean 642.1				

262. Di-n-propyl sebacate. B. p. 178—179°/5 mm.; M 286.40; n_D 1.43695, n_D 1.43913, n_F 1.44453, n_G 1.44841; R_C 79.01, R_D 79.34, R_F 80.19, R_G 80.80; Mn_D^{20} 412.10. Densities determined: d_4^{20} 0.9495, $d_4^{0.7}$ 0.9336, $d_4^{0.6}$ 0.9179, $d_4^{0.9}$ 0.8983. Apparatus *A*.

20.4°	18.15	0.9492	32.26	719.0	61.9°	16.54	0.9169	28.40	721.0
27.9	17.99	0.9433	31.78	720.8	86.7	15.58	0.8977	26.19	721.6
41.2	17.39	0.9332	30.39	720.5	Mean 720.6				

263. Dimethyl methylmalonate. B. p. 176—176.5°/761 mm; M 146.14; n_D 1.41070, n_D 1.41276, n_F 1.41770, n_G 1.42141; R_C 33.04, R_D 33.18, R_F 33.53, R_G 33.79; Mn_D^{20} 206.47. Densities determined: d_4^{20} 1.0977, $d_4^{0.6}$ 1.0751, $d_4^{1.2}$ 1.0528, $d_4^{0.2}$ 1.0247. Apparatus *A*.

14.9°	16.49	1.1033	34.07	320.0	41.0°	15.36	1.0747	30.90	320.6
20.3	16.35	1.0974	33.60	320.6	61.0	14.44	1.0530	28.47	320.6
24.2	16.15	1.0931	33.06	320.6	85.9	13.37	1.0250	25.66	320.9
Mean 320.6									

264. Diethyl methylmalonate. B. p. 195.5—196°/773 mm.; M 174.19; n_D 1.41052, n_D 1.41261, n_F 1.41770, n_G 1.42125; R_C 42.25, R_D 42.44, R_F 42.90, R_G 43.23; Mn_D^{20} 246.06. Densities determined: d_4^{20} 1.0225, d_4^{30} 1.0020, d_4^{50} 0.9816, d_4^{80} 0.9552. Apparatus D.

t .	H .	d_4^* .	γ .	P .	t .	H .	d_4^* .	γ .	P .
16.5°	11.97	1.0260	30.33	398.4	41.4°	11.22	1.0014	27.75	399.2
21.2	11.82	1.0213	29.81	398.5	60.3	10.53	0.9819	25.53	398.2
24.2	11.74	1.0183	29.52	398.7	80.4	9.94	0.9616	23.61	399.3
Mean 398.7									

265. Di-n-propyl methylmalonate. B. p. 222.5—226°/771 mm.; M 202.24; n_C 1.41705, n_D 1.41906, n_F 1.42431, n_G 1.42799; R_C 51.57, R_D 51.79, R_F 52.34, R_G 52.74; Mn_D^{20} 287.02. Densities determined: d_4^{20} 0.9865, d_4^{30} 0.9675, d_4^{50} 0.9506, d_4^{80} 0.9271. Apparatus A.

15.9°	15.93	0.9902	29.54	476.1	41.4°	14.90	0.9677	27.00	476.4
18.5	15.81	0.9880	29.25	476.0	62.0	14.04	0.9487	24.88	476.4
22.9	15.65	0.9839	28.83	476.3	87.4	13.02	0.9249	22.55	476.5
Mean 476.3									

266. Di-n-butyl methylmalonate. B. p. 254.5—255.5°/761 mm.; M 230.30; n_C 1.42291, n_D 1.42506, n_F 1.43030, n_G 1.43413; R_C 60.89, R_D 61.02, R_F 61.68, R_G 62.15; Mn_D^{20} 328.20. Densities determined: d_4^{20} 0.9652, d_4^{30} 0.9472, d_4^{50} 0.9294, d_4^{80} 0.9085. Apparatus D.

19.4°	12.08	0.9657	28.81	552.5	60.5°	10.94	0.9297	25.12	554.6
41.2	11.53	0.9476	26.98	553.8	87.2	10.13	0.9067	22.68	554.3
Mean 553.8									

267. Dimethyl ethylmalonate. B. p. 85°/15 mm.; M 160.17; n_C 1.41555, n_D 1.41781, n_F 1.42273, n_G 1.42633; R_C 37.63, R_D 37.82, R_F 38.21, R_G 38.49; Mn_D^{20} 227.09. Densities determined: d_4^{20} 1.0669, d_4^{30} 1.0442, d_4^{50} 1.0200, d_4^{80} 0.9997. Apparatus E.

18.3°	13.12	1.0686	32.65	358.3	59.2°	11.71	1.0262	27.99	359.0
25.1	12.84	1.0616	31.75	358.1	86.7	10.66	0.9982	24.78	358.0
40.8	12.31	1.0444	29.94	358.7	Mean 358.4				

268. Diethyl ethylmalonate. B. p. 109°/24 mm.; M 188.23; n_C 1.41437, n_D 1.41656, n_F 1.42151, n_G 1.42525; R_C 46.85, R_D 47.07, R_F 47.56, R_G 47.94; Mn_D^{20} 266.63. Densities determined: d_4^{20} 1.0047, d_4^{30} 0.9845, d_4^{50} 0.9651, d_4^{80} 0.9412. Apparatus E.

16.3°	12.76	1.0083	29.96	436.7	63.0°	11.14	0.9633	24.99	436.9
20.8	12.60	1.0039	29.46	436.8	86.7	10.43	0.9402	22.84	437.5
40.3	11.93	0.9848	27.36	437.1	Mean 437.0				

269. Di-n-propyl ethylmalonate. B. p. 123°/15 mm.; M 216.27; n_C 1.42022, n_D 1.42246, n_F 1.42748, n_G 1.43127; R_C 56.17, R_D 56.44, R_F 57.02, R_G 57.47; Mn_D^{20} 307.64. Densities determined: d_4^{20} 0.9748, d_4^{30} 0.9552, d_4^{50} 0.9379, d_4^{80} 0.9159. Apparatus E.

15.1°	12.98	0.9792	29.60	514.7	61.6°	11.40	0.9376	24.89	515.0
19.6	12.77	0.9752	29.00	514.5	84.8	10.78	0.9167	23.02	516.5
41.4	12.06	0.9558	26.85	514.9	Mean 515.1				

270. Di-n-butyl ethylmalonate. B. p. 145°/14 mm.; M 244.32; n_C 1.42504, n_D 1.42732, n_F 1.43239, n_G 1.43628; R_C 65.31, R_D 65.62, R_F 66.30, R_G 66.82; Mn_D^{20} 348.72. Densities determined: d_4^{20} 0.9566, d_4^{30} 0.9394, d_4^{50} 0.9221, d_4^{80} 0.9003. Apparatus E.

16.4°	13.06	0.9596	29.19	591.8	61.5°	11.58	0.9216	24.86	591.9
18.9	12.94	0.9575	28.86	591.4	87.1	10.86	0.9000	22.76	593.0
40.9	12.30	0.9395	26.91	592.0	Mean 592.0				

271. Dimethyl n-propylmalonate. B. p. 203.5—204°/760 mm.; M 174.19; n_C 1.41905, n_D 1.42121, n_F 1.42632, n_G 1.43012; R_C 42.23, R_D 42.42, R_F 42.87, R_G 43.20; Mn_D^{20} 247.56. Densities determined: d_4^{20} 1.0418, d_4^{30} 1.0204, d_4^{50} 0.9996, d_4^{80} 0.9767. Apparatus D.

16.9°	12.27	1.0449	31.66	395.4	61.9°	10.88	1.0007	26.89	396.4
25.2	12.06	1.0366	30.87	396.1	87.1	10.12	0.9755	24.38	396.8
41.9	11.49	1.0198	28.94	396.2	Mean 396.2				

272. Diethyl n-propylmalonate. B. p. 221—221.5°/767 mm.; M 202.24; n_C 1.41748, n_D 1.41966, n_F 1.42475, n_G 1.42851; R_C 51.57, R_D 51.81, R_F 52.36, R_G 52.76; Mn_D^{20} 287.12. Densities determined: d_4^{20} 0.9873, d_4^{30} 0.9682, d_4^{50} 0.9470, d_4^{80} 0.9259. Apparatus A.

19.9°	15.68	0.9874	28.99	475.3	62.2°	13.93	0.9482	24.73	475.6
24.0	15.52	0.9836	28.58	475.4	87.4	12.94	0.9244	22.40	475.9
42.4	14.72	0.9665	26.64	475.4	Mean 475.5				

273. *Di-n-propyl n-propylmalonate.* B. p. 121°/6 mm.; M 230.30, n_D 1.42300, n_D 1.42516, n_F 1.43039, n_G 1.43418; R_C 60.81, R_D 61.08, R_F 61.73, R_G 62.21; $Mn_D^{20^\circ}$ 328.22. Densities determined: $d_4^{20^\circ}$ 0.9644, $d_4^{21.2^\circ}$ 0.9461, $d_4^{20.9^\circ}$ 0.9287, $d_4^{28.4^\circ}$ 0.9068. Apparatus *D*.

t .	H .	d_4^t .	γ .	P .	t .	H .	d_4^t .	γ .	P .
22.1°	12.02	0.9626	28.57	553.1	61.5°	10.80	0.9282	24.76	553.4
41.7	11.36	0.9457	26.53	552.7	85.9	10.10	0.9064	22.61	554.0
Mean 553.3									

274. *Di-n-butyl n-propylmalonate.* B. p. 150°/9 mm.; M 258.35; n_C 1.42700, n_D 1.42917, n_F 1.43477, n_G 1.43831; R_C 69.99, R_D 70.30, R_F 71.06, R_G 71.60; $Mn_D^{20^\circ}$ 369.24. Densities determined: $d_4^{20^\circ}$ 0.9477, $d_4^{40.7^\circ}$ 0.9305, $d_4^{59.5^\circ}$ 0.9151, $d_4^{85.1^\circ}$ 0.8939. Apparatus *D*.

19.4°	12.17	0.9482	28.50	629.5	61.3°	11.0 0	0.9136	24.82	631.2
41.1	11.56	0.9302	26.56	630.5	87.1	10.28	0.8922	22.65	631.7
Mean 630.7									

275. *Dimethyl n-amylmalonate.* B. p. 104°/4.5 mm.; M 202.26; n_C 1.42548, n_D 1.42767, n_F 1.43292, n_G 1.43669; R_C 51.55, R_D 51.79, R_F 52.34, R_G 52.74; $Mn_D^{20^\circ}$ 288.76. Densities determined: $d_4^{20^\circ}$ 1.0042, $d_4^{1.7^\circ}$ 0.9849, $d_4^{62.6^\circ}$ 0.9665, $d_4^{87.2^\circ}$ 0.9452. Apparatus *D*.

16.3°	12.44	1.0075	30.95	473.5	40.4°	11.72	0.9816	28.54	474.1
21.4	12.26	1.0030	30.37	473.4	61.4	11.09	0.9676	26.50	474.3
22.7	12.21	1.0016	30.20	473.4	86.0	10.39	0.9463	24.28	474.5
Mean 473.9									

276. *Diethyl n-amylmalonate.* B. p. 113°/3.5 mm.; M 230.32; n_C 1.42328, n_D 1.42546, n_F 1.43065, n_G 1.43442; R_C 60.80, R_D 61.08, R_F 61.73, R_G 62.19; $Mn_D^{20^\circ}$ 328.32. Densities determined: $d_4^{20^\circ}$ 0.9652, $d_4^{11.0^\circ}$ 0.9473, $d_4^{30.8^\circ}$ 0.9306, $d_4^{86.8^\circ}$ 0.9068. Apparatus *D*.

16.1°	12.29	0.9686	92.40	553.7	61.9°	10.86	0.9297	24.93	553.6
19.6	12.12	0.9655	28.90	553.1	86.8	10.10	0.9068	22.62	553.9
42.1	11.38	0.9464	26.60	552.7	Mean 553.4				

277. *Di-n-propyl n-amylmalonate.* B. p. 136.5°/4 mm.; M 258.35; n_C 1.42729, n_D 1.42947, n_F 1.43475, n_G 1.43865; R_C 70.06, R_D 70.37, R_F 71.12, R_G 71.68; $Mn_D^{20^\circ}$ 369.40. Densities determined: $d_4^{20^\circ}$ 0.9474, $d_4^{11.0^\circ}$ 0.9307, $d_4^{60.4^\circ}$ 0.9151, $d_4^{86.1^\circ}$ 0.8929. Apparatus *D*.

17.0°	12.35	0.9498	28.97	631.0	60.8°	11.10	0.9148	25.08	632.0
40.6	11.67	0.9310	26.83	631.6	86.1	10.35	0.8929	22.77	632.5
Mean 631.8									

278. *Di-n-butyl n-amylmalonate.* B. p. 152.5°/3.5 mm.; M 286.36; n_C 1.43070, n_D 1.43289, n_F 1.43822, n_G 1.44213; R_C 79.32, R_D 79.67, R_F 80.52, R_G 81.15; $Mn_D^{20^\circ}$ 410.33. Densities determined: $d_4^{20^\circ}$ 0.9339, $d_4^{0.0^\circ}$ 0.9192, $d_4^{50.1^\circ}$ 0.9032, $d_4^{85.7^\circ}$ 0.8828. Apparatus *A*.

21.3°	16.19	0.9329	28.35	707.9	60.8°	14.79	0.9027	25.00	709.3
41.3	15.51	0.9182	26.67	708.7	86.5	13.86	0.8822	22.90	710.0
Mean 709.0									

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