

133. *Physical Properties and Chemical Constitution. Part XVI.* *Ethylenic Compounds.*

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New measurements are presented of the parachors and the refractivities (20°) for esters of vinylacetic, undecylenic, and allylmalonic acid, for unsaturated aliphatic hydrocarbons, and for allyl esters of aliphatic monobasic acids and of succinic acid. The contributions of the carbon-carbon double bond have been computed from the general relationship $\bar{v} = CR_1R_2:CR_3R_4 + 2H - CHR_1R_2:CHR_3R_4$, employing the values for $2H$ from Part IX (*J.*, 1946, 133) and the appropriate saturated compounds to be found in previous papers of this series. These lead to the following mean values:

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G'.</i>	<i>M_D^{20°}.</i>
\bar{v}	19.9	1.545	1.575	1.672	1.720	-6.07

These constants differ considerably from those previously accepted.

Similar measurements have also been made upon alkyl maleates and fumarates, citraconates and mesaconates, methylsuccinates, *trans*-crotonates, and cinnamates. The ethylenic double-bond contributions were similarly calculated and possessed the following values:

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G'.</i>	<i>M_D^{20°}.</i>
Maleates	19.6	2.24	2.31	2.47	2.60	-4.54
Fumarates	22.3	2.86	2.96	3.24	3.44	-4.19
Citraconates	21.8	2.42	2.50	2.72	2.88	-3.41
Mesaconates	18.6	2.71	2.81	3.09	3.33	-2.50
<i>trans</i> -Crotonates	21.3	2.23	2.30	2.49	2.62	-4.32
Cinnamates	21.0	4.96	5.26	6.14	7.06	-3.29

THE parachor increment for the carbon-carbon double bond, given as 23.2 by Sugden (see Sugden, *J.*, 1924, 125, 1177; Sugden, Reed, and Wilkins, *J.*, 1925, 127, 1525), was apparently based upon data for ethylene, propylene, amylenes, and diallyl. Eisenlohr (*Z. physikal. Chem.*, 1910, 75, 604) has utilised the figures for "amylenes, hexylene, octylene, decylene, allyl alcohol, allyl acetate, allyl ethyl ether, allyl acetone, butenyl dimethyl carbinol, allyl methyl propyl carbinol, tetrahydrobenzene, valerylene, diallyl, *d*-limonene, sylvestrene, diallyl acetone and diallyl acetic acid" for the evaluation of the refractivities of the double bond and gives the following mean values:

	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G'.</i>
\bar{v}	1.686	1.733	1.824	1.893

It is clear that the resulting constants are not altogether satisfactory since, apart from the not too happy choice of compounds for the deduction of such fundamental constants, the CH_2

values themselves employed in the computations are subject to error (compare Part IX, *J.*, 1946, 133). The authors have employed five independent series of compounds in their own determinations of the constants of the C=C double bond, *viz.* : (1) Esters of vinylacetic acid; (2) esters of undecylenic acid; (3) unsaturated aliphatic hydrocarbons; (4) esters of allylmalonic acid; (5) allyl esters of monobasic acids and also of succinic acid. The general method of calculation of the constants may be expressed by :

$$\bar{\nu} = CR_1R_2:CR_3R_4 + 2H - CHR_1R_2:CHR_3R_4$$

It will be noted that the procedure does not involve a knowledge of the values of the CH₂ increment. The values for H are those of Part IX (*loc. cit.*), the saturated hydrocarbons are from Part IX (*loc. cit.*), and the saturated esters are given in Part XIII (this vol., p. 624). No experimental data are available for esters of *n*-undecylenic acid CH₃·[CH₂]₉·CO₂R required in the calculations under (2), but the necessary figures have been evaluated with sufficient accuracy by taking the mean values deduced from (a) the experimental data for *n*-decoates and *n*-dodecoates, *i.e.*, 0.5{CH₃·[CH₂]₈·CO₂R + CH₃·[CH₂]₁₀·CO₂R} (Part XIII, *loc. cit.*) and (b) the experimental data for *n*-decoates (Part XIII, *loc. cit.*) and CH₂ (Part IX, *loc. cit.*), *i.e.*, from CH₃·[CH₂]₈·CO₂R + CH₂. The figures obtained by methods (a) and (b) were in excellent agreement.

All the compounds, with the exception of octene to hexadecene, were prepared by the authors from the purest available starting materials. The unsaturated hydrocarbons (octene to hexadecene) were commercial products and were carefully purified: nevertheless, the final purity cannot confidently be stated to be as high as those of the other unsaturated compounds because data for the purity of the normal alcohols from which they were prepared are not available. The physical properties are, however, in good agreement with those recently

TABLE I.

Values for carbon-carbon double bond from ethylenic compounds (20°).

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D²⁰.</i>
Esters of vinylacetic acid, CH ₂ :CH·CH ₂ ·CO ₂ R.						
R = H	19.6	1.54	1.57	1.66	1.71	-5.68
R = Me	20.4	1.54	1.57	1.66	1.69	-5.84
R = Et	19.7	1.49	1.53	1.62	1.66	-5.78
R = Pr ⁿ	19.7	1.53	1.57	1.65	1.70	-5.95
R = Bu ⁿ	19.5	1.54	1.59	1.69	1.72	-5.98
R = Am ⁿ	19.0	1.52	1.56	1.65	1.68	-5.95
Esters of undecylenic acid, CH ₂ :CH·[CH ₂] ₈ ·CO ₂ R.						
R = Me	21.0	1.62	1.64	1.75	1.78	-6.02
R = Et	20.5	1.55	1.56	1.65	1.70	-5.95
R = Pr ⁿ	20.6	1.56	1.60	1.70	1.74	-5.92
R = Bu ⁿ	19.7	1.57	1.59	1.68	1.74	-5.72
Unsaturated aliphatic hydrocarbons.						
C ₅ H ₁₀	18.3	1.59	1.61	1.72	1.79	-6.48
C ₆ H ₁₂	21.1	1.54	1.57	1.68	1.73	-6.48
C ₈ H ₁₆	19.7	1.60	1.65	1.74	1.80	-6.63
C ₁₀ H ₂₀	20.2	1.51	1.52	1.63	1.71	-6.72
C ₁₂ H ₂₄	20.2	1.55	1.57	1.69	1.74	-6.59
C ₁₄ H ₂₈	19.4	1.49	1.51	1.62	1.68	-6.51
C ₁₆ H ₃₀	20.4	1.56	1.58	1.71	1.74	-6.52
Diallyl	20.3	1.58	1.61	1.71	1.76	-6.76
Esters of allylmalonic acid, C ₃ H ₅ ·CH(CO ₂ R) ₂ .						
R = Me	19.7	1.55	1.59	1.68	1.72	-5.64
R = Et	19.1	1.50	1.52	1.61	1.66	-5.81
R = Pr ⁿ	19.9	1.50	1.53	1.63	1.67	-5.92
R = Bu ⁿ	19.5	1.56	1.59	1.67	1.74	-5.96
Allyl esters of aliphatic acids.						
CH ₃ ·CO ₂ C ₃ H ₅	20.6	1.46	1.50	1.59	1.62	-5.96
CH ₃ ·CH ₂ ·CO ₂ C ₃ H ₅	20.4	1.56	1.59	1.69	1.73	-5.95
CH ₃ ·CH ₂ ·CH ₂ ·CO ₂ C ₃ H ₅	19.0	1.53	1.57	1.66	1.72	-5.85
(CH ₂ ·CO ₂ C ₃ H ₅) ₂	20.7	1.62	1.65	1.74	1.78	-5.36
Mean	19.9	1.545	1.575	1.672	1.720	-6.07

published for alkenes with terminal double bond by Wibaut and Geldof (*Rec. Trav. chim.*, 1946, 65, 125), but here also no evidence of purity has, so far, been given. There seems, however, to be no adequate reason for excluding the results for the alkenes from the calculation of the mean values for the ethylenic linkage.

The results are collected in Table I. It will be observed that the mean values differ considerably from the previously accepted figures.

The values for the ethylenic bond deduced from allyl halides, 2H, and the propyl halides (Part VIII, *J.*, 1943, 636) are shown below. The unsatisfactory result for allyl bromide may be connected with its relative instability.

	<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 ₂ :CH·CH ₂ Cl	19·3	1·59	1·63	1·73	1·79	-5·81
CH ₂ :CH·CH ₂ Br	20·2	1·89	1·94	2·08	2·15	-3·81

We have also measured the parachors and refractivities of a series of dialkyl maleates and fumarates and also of dialkyl citraconates and mesaconates. The double-bond contributions for the former pair were calculated with the aid of the experimental figures for dialkyl succinates (Part XIII, *loc. cit.*), and for the latter new experimental data for dialkyl methylsuccinates have been provided. The results are collected in Table II. It will be observed that whilst the parachor contributions appear to be fairly constant, the *cis*-isomers seem to give lower values for the refractivities than the corresponding *trans*-isomers. The absolute values are different in the two pairs of *cis-trans*-isomerides, and all the values are higher than those for the simple ethylenic compounds because of conjugation.

TABLE II.

Values for carbon-carbon double bond for cis-trans-esters (20°).

	<i>P.</i>	<i>R_C.</i>	<i>R_D.</i>	<i>R_F.</i>	<i>R_G.</i>	<i>Mn_D^{20°}.</i>
Dialkyl maleates, CO ₂ R·CH:CH·CO ₂ R.						
R = Me	21·6	2·20	2·25	2·41	2·54	-4·69
R = Et	19·6	2·26	2·34	2·51	2·62	-4·47
R = Pr ⁿ	20·7	2·19	2·27	2·43	2·53	-4·35
R = Bu ⁿ	18·7	2·28	2·35	2·52	2·65	-4·46
R = Bu ^t	19·8	2·40	2·46	2·68	2·82	-4·56
R = Am ⁿ	19·0	2·22	2·30	2·48	2·57	-4·61
R = Am ^t	—	2·14	2·20	2·38	2·47	-4·63
Mean	19·6	2·24	2·31	2·47	2·60	-4·54
Dialkyl fumarates, CO ₂ R·CH:CH·CO ₂ R.						
R = Et	22·2	2·85	2·96	3·22	3·40	-4·36
R = Pr ⁿ	22·7	2·82	2·92	3·19	3·37	-4·23
R = Bu ⁿ	21·9	2·86	2·96	3·22	3·46	-4·12
R = Bu ^t	24·2	2·91	3·00	3·28	3·51	-4·24
R = Am ⁿ	21·9	2·92	3·02	3·31	3·52	-4·09
R = Am ^t	21·1	2·82	2·91	3·20	3·39	-4·12
Mean	22·3	2·86	2·96	3·24	3·44	-4·19
Dialkyl citraconates, CO ₂ R·CH:CMe·CO ₂ R.						
R = Me	22·9	2·39	2·46	2·70	2·82	-3·53
R = Et	21·4	2·43	2·51	2·72	2·91	-3·28
R = Pr ⁿ	20·4	2·44	2·52	2·74	2·91	-3·41
Mean	21·8	2·42	2·50	2·72	2·88	-3·41
Dialkyl mesaconates, CO ₂ R·CH:CMe·CO ₂ R.						
R = Me	17·9	2·62	2·71	2·99	3·21	-2·44
R = Et	18·9	2·68	2·79	3·07	3·33	-2·53
R = Pr ⁿ	19·1	2·82	2·92	3·21	3·45	-2·53
Mean	18·6	2·71	2·81	3·09	3·33	-2·50

The results of similar measurements and computations for alkyl crotonates and alkyl cinnamates are summarised in Tables III and IV, respectively. The experimental data for alkyl *n*-butyrates required as reference compounds for the former are in Part XIII (*loc. cit.*) and those for alkyl β-phenylpropionates are in Part XV (preceding paper).

TABLE III.

Values for carbon-carbon double bond from alkyl trans-crotonates, $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{R}$.

	P.	R_C .	R_D .	R_F .	R_G .	$Mn_D^{20^\circ}$.
R = Me	21.6	2.25	2.32	2.51	2.63	-4.08
R = Et	21.4	2.27	2.34	2.53	2.66	-4.22
R = Pr ⁿ	21.3	2.19	2.26	2.45	2.59	-4.23
R = Bu ⁿ	21.4	2.25	2.32	2.51	2.64	-4.24
R = Am ⁿ	21.1	2.21	2.27	2.47	2.60	-4.26
R = Am ^t	21.1	2.20	2.29	2.46	2.61	-4.33
Mean	21.3	2.23	2.30	2.49	2.62	-4.32

TABLE IV.

Values for carbon-carbon double bond from alkyl cinnamates, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{R}$.

	P.	R_C .	R_D .	R_F .	R_G .	$Mn_D^{20^\circ}$.
R = Et	21.3	4.90	5.20	6.07	—	-3.36
R = Pr ⁿ	21.3	5.00	5.30	6.20	7.06	-3.27
R = Bu ⁿ	20.4	4.97	5.27	6.17	7.06	-3.25
Mean	21.0	4.96	5.26	6.14	7.06	-3.29

EXPERIMENTAL.

Esters of Vinylacetic Acid.—Allyl cyanide. The following modification of the procedure of *Org. Synth.*, Coll. Vol. I, 1941, 46, gave an improved yield. In a 1.5-l. three-necked flask, equipped with two efficient double-surface condensers, was placed a mixture of 226 g. of dry cuprous cyanide (Barber, *J.*, 1943, 79) and 293 g. of freshly distilled allyl bromide, b. p. 70—71°/751 mm. The mixture was gently refluxed on a water-bath; after 15 minutes a very vigorous reaction set in, and the water-bath was immediately replaced by an ice-water-bath. When the reaction had subsided, a mercury-sealed mechanical stirrer was introduced into the central aperture of the flask and the mixture was heated, with stirring, on a water-bath for 1 hour. The allyl cyanide, isolated as detailed in *Org. Synth.*, boiled at 116—121°/754 mm. and weighed 145 g.

Vinylacetic acid. This was prepared from allyl cyanide as in *Org. Synth.*, 1944, 24, 96: distillation of the dried (Na_2SO_4) ethereal extract of the acid always gave a small low-b. p. fraction from which water separated on standing; the pure acid was readily obtained from this by separating the water, drying (CaSO_4) and distilling. The yield of vinylacetic acid, b. p. 73—74°/14 mm. (mainly 72.5°/14 mm.), from 140 g. of the nitrile was 120 g. Upon redistillation, the acid boiled constantly at 77.5°/19 mm. and a middle fraction was removed for the physical measurements.

The pure acid can readily be obtained by distillation under diminished pressure and, contrary to *Org. Synth.* (*loc. cit.*), no by-products which cannot be removed by distillation were found. The purification procedure described in *Org. Synth.* leads to considerable loss and it is doubtful whether the purity of the acid is improved. Linstead, Noble, and Boorman (*J.*, 1933, 560) give for the pure acid, b. p. 69°/10 mm., 78°/21 mm., $d_4^{20^\circ}$ 1.0090—1.0098, $n_D^{20^\circ}$ 1.4220—1.4222.

Vinylacetyl chloride. 150 G. of pure thionyl chloride (redistilled over quinoline; b. p. 77°/768 mm.) were placed in a 500-ml. round-bottomed flask fitted (ground glass joint) with a double-surface condenser, and 95 g. of pure vinylacetic acid were slowly added during 1 hour. The mixture was refluxed for 30 minutes, the reflux condenser replaced by an all-glass Dufton column, etc., and the mixture fractionated: 87 g. of vinylacetyl chloride, b. p. 98—99°/774 mm., were obtained.

Methyl vinylacetate. 8.1 G. of pure anhydrous methyl alcohol contained in an all-glass apparatus (250 ml. flask, reflux condenser and dropping-funnel, both protected by calcium chloride drying tubes) were cooled to 0° and 24 g. of vinylacetyl chloride were added during 30 minutes. The mixture was kept at room temperature for 1 hour, poured into excess of water, the ester separated, washed successively with saturated sodium hydrogen carbonate solution and water, and then dried (CaSO_4). Distillation from a Claisen flask with fractionating side arm gave 15 g. of the pure *methyl* ester, b. p. 108—108.5°/774 mm. (Found: C, 59.8; H, 8.2. $\text{C}_6\text{H}_8\text{O}_2$ requires C, 60.0; H, 8.1%).

Ethyl vinylacetate. Method 1. The interaction of 11.2 g. of absolute ethyl alcohol and 26 g. of vinylacetyl chloride exactly as for the methyl ester gave, after standing for 1 hour at the laboratory temperature and working up as usual, 17.5 g. of ester, b. p. 124.5—126.5°/760 mm., and 2 g. of b. p. 126.5—140°: there was no appreciable residue in the flask. Redistillation of the main fraction afforded the pure ester, b. p. 124°/745 mm.

In another experiment with 8.4 g. of absolute ethyl alcohol and 18 g. of vinylacetyl chloride, the reaction mixture was kept overnight and then worked up as usual. Fractionation then yielded (a) b. p. 125—127°/774 mm., 7 g. [ethyl vinylacetate, $d_4^{20^\circ}$ 0.9177, $n_D^{20^\circ}$ 1.4110, R_D 30.88, P (mean) 281.9]; (b) b. p. 127—140°/774 mm., 2 g. (probably largely ethyl crotonate); and (c) b. p. 140—170°/774 mm., mainly 168—170°, 2 g. (ethyl β -chlorobutyrate). It is evident that prolonged contact of the reaction product with the hydrogen chloride produced in the reaction should be avoided when the pure alkyl vinylacetate is required.

Method 2. Silver vinylacetate was prepared by cooling a mixture of 95 g. of vinylacetic acid and 200 ml. of water in ice and adding dropwise and with mechanical stirring the theoretical quantity of ammonia solution (342 ml. of 3.2N); a solution of 206 g. of silver nitrate in 500 ml. of water was then added with stirring. About 1500 ml. of water were run into the thick suspension, and the solid was filtered off, washed with water and then rectified spirit, and dried at 40°. The yield of silver salt was 112 g.; it was finely ground and kept in a vacuum desiccator covered with brown paper.

A mixture of 38 g. of dry silver vinylacetate, 31 g. of ethyl iodide, and 50 ml. of sodium-dried A.R. benzene was refluxed for 30 hours, and the precipitate filtered off and washed with dry benzene. The combined filtrate and extracts was washed successively with sodium hydrogen carbonate solution and water, dried (CaSO₄), and distilled. The resulting ester (7 g.) boiled at 122—128° and was unsatisfactory for the physical measurements. Boorman, Linstead, and Rydon (*J.*, 1933, 573) give for the ester prepared from the silver salt and ethyl iodide d_{40}^{20} 0.9192, n_D^{20} 1.4102 but do not record a b. p.

n-Propyl vinylacetate. Method 1. The interaction between 13.2 g. of pure, dry *n*-propyl alcohol and 21 g. of vinylacetyl chloride in an all-glass apparatus yielded, exactly as detailed for the methyl ester, 19 g. of ester, b. p. 143—148°/774 mm. (mainly 144—145°). Redistillation gave the pure *n*-propyl vinylacetate, b. p. 144.5°/774 mm. (Found: C, 65.7; H, 9.6. C₇H₁₂O₂ requires C, 65.6; H, 9.4%).

Method 2. A mixture of 38 g. of silver vinylacetate, 25 g. of pure *n*-propyl bromide, and 75 ml. of absolute ethyl alcohol was refluxed for 23 hours, poured into 400 ml. of water, saturated with pure sodium chloride, and the upper layer separated. This was washed with sodium hydrogen carbonate solution and water, dried (CaSO₄), and distilled: the liquid ester passed over at 138—149°. Upon redistillation from a Claisen flask with fractionating side arm, it boiled at 141—144°/754 mm. (mainly at 141.5—143.5°) and had d_{40}^{20} 0.9068, n_D^{20} 1.4151. The acid chloride method was superior since the resulting ester had a sharper b. p. and a lower density (d_{40}^{20} 0.9003, n_D^{20} 1.4150).

n-Butyl vinylacetate. Method 1. The reaction between 15.6 g. of pure, dry *n*-butyl alcohol and 20 g. of vinylacetyl chloride gave, as detailed for the methyl ester, 23 g. of pure *n*-butyl vinylacetate (Found: C, 67.5; H, 10.0. C₈H₁₄O₂ requires C, 67.6; H, 9.9%).

Method 2. A mixture of 38 g. of silver vinylacetate, 27 g. of pure *n*-butyl bromide, and 50 ml. of sodium-dried A.R. benzene was refluxed for 25 hours and the product isolated as described for the ethyl ester: 16 g. of *n*-butyl ester, b. p. 54—56°/9 mm., were obtained. Upon redistillation, this boiled at 58—60°/10 mm., and a middle fraction, b. p. 59°/10 mm., gave d_{40}^{20} 0.8965, n_D^{20} 1.42167, R_D 40.28, P (mean) 361.8. These results are in moderate agreement with those for the ester prepared from the acid chloride, but the latter procedure is to be preferred for the preparation of the pure ester.

n-Amyl vinylacetate. The reaction between 18.6 g. of dry *n*-amyl alcohol (Sharples, carefully fractionated) and 20 g. of vinylacetyl chloride, as detailed for the methyl ester, gave 23 g. of *n*-amyl vinylacetate, b. p. 74.5°/12 mm. (Found: C, 69.1; H, 10.3. C₉H₁₆O₂ requires C, 69.2; H, 10.3%).

Esters of Undecylenic Acid.—Purification of undecylenic acid. The pure commercial acid was redistilled and the fraction, b. p. 152—154°/6 mm., was collected; this had a setting point of 22.6—22.8°. A mixture of 240 g. of the redistilled acid, 430 g. of A.R. absolute methyl alcohol, and 22 g. of concentrated sulphuric acid was refluxed for 20 hours, most of the excess of methyl alcohol was distilled off from a water-bath, and the residue poured into 2 l. of water. The ester (260 g.) was separated, washed successively with saturated sodium hydrogen carbonate solution and water, dried (yield 252 g.), and distilled in two lots; the methyl undecylenate was collected at 247—250°/771 mm. (mainly at 247—249°). In a 1.5- or 2-l. round-bottomed flask were placed 300 ml. of 20% sodium hydroxide solution and 0.2 g. of "pentrone" (largely sodium oleylsulphonate), the latter to reduce the foaming during the subsequent hydrolysis. The methyl undecylenate (150 g.) was added dropwise to the warm alkali solution (if the ester is added in one lot, a very vigorous reaction sets in after a few minutes and the mixture is shot out of the flask) and reacted rapidly. When the ester layer was no longer visible, the product was carefully acidified with concentrated hydrochloric acid, allowed to cool, the acid extracted with ether, the ethereal extract dried (Na₂SO₄), and the solvent removed. The undecylenic acid was isolated by distillation: b. p. 148°/4.5 mm., 157°/6 mm.; s. p. 23.5°. Distillation of the acid at atmospheric pressure (b. p. 276—280°/756 mm.) leads to considerable loss.

Methyl undecylenate. This was prepared from the pure acid, m. p. 23.5° (1 mol.), A.R. absolute methyl alcohol (10 mols.), and concentrated sulphuric acid; b. p. 247—248°/776 mm.

Ethyl undecylenate. A mixture of 26 g. of undecylenic acid, m. p. 23.5°, 66 g. of absolute ethyl alcohol, and 3.5 g. of concentrated sulphuric acid was refluxed for 20 hours. The mixture was poured into a large excess of water, saturated with salt, the ester separated and washed successively with saturated sodium hydrogen carbonate solution and saturated salt solution, and then twice distilled. The yield of pure ester, b. p. 258—259°/761 mm., was 24 g.

n-Propyl undecylenate. A mixture of 23 g. of pure undecylenic acid, 15 g. of pure *n*-propyl alcohol, 25 ml. of sodium-dried A.R. benzene, and 5 g. of concentrated sulphuric acid was refluxed for 30 hours, poured into water, the benzene layer separated, washed successively with saturated sodium hydrogen carbonate solution and water, and dried. The benzene was removed at atmospheric pressure and the residue twice distilled under reduced pressure. The yield of pure *n*-propyl undecylenate, b. p. 139.5°/7 mm., was 17.5 g. (Found: C, 74.2; H, 11.9. C₁₄H₂₆O₂ requires C, 74.2; H, 11.6%).

n-Butyl undecylenate. A mixture of 23 g. of pure undecylenic acid, 19 g. of pure *n*-butyl alcohol, 25 ml. of sodium-dried A.R. benzene, and 5 g. of concentrated sulphuric acid was refluxed for 20 hours and yielded, as for the *n*-propyl ester, 17 g. of pure *n*-butyl undecylenate, b. p. 150°/6 mm. (Found: C, 75.1; H, 11.6. C₁₅H₂₈O₂ requires C, 75.0; H, 11.7%).

Unsaturated Aliphatic Hydrocarbons.—Pent-2-ene. This was prepared from the low-b. p. by-product obtained in the preparation of 3-bromopentane from diethylcarbinol (Sharples) by the hydrogen bromide-sulphuric acid procedure (8, 77). It was fractionated from excess of sodium and the portion boiling at 36—38° again fractionated from sodium; it boiled constantly at 36.3—36.4°/755 mm.

Hexene. 100 G. of *n*-hexyl alcohol, b. p. 156—157°/752 mm., were mixed with 4 g. of concentrated sulphuric acid and slowly fractionated from a three-section Pyrex Young and Thomas column; the temperature of the distillate was not allowed to rise above 90° (compare Wibaut *et al.*, *Rec. Trav. chim.*, 1939, 58, 338). The aqueous layer in the distillate was discarded, the organic phase was washed successively with dilute sodium hydroxide solution and water, dried, and twice fractionated from sodium. The product boiled at 65.5—66°/752 mm. and consisted of a mixture of hexenes.

1-Octene to 1-hexadecene. 100 G. samples of the highly purified alkenes were kindly supplied by the Connecticut Hard Rubber Co., of 407 East Street, New Haven, Conn., U.S.A. These were dried over anhydrous calcium sulphate for several days and then fractionated; over 95% boiled at the temperatures

given below and a middle fraction was removed for the physical measurements: oct-1-ene, b. p. 120.5°/765 mm.; dec-1-ene, b. p. 169°/761 mm.; dodec-1-ene, b. p. 80°/5 mm.; tetradec-1-ene, b. p. 125°/14 mm.; hexdec-1-ene, b. p. 153°/14 mm.

Esters of Allylmalonic Acid.—Allylmalonic acid was prepared by the method of Linstead and Rydon (*J.*, 1933, 582) and was recrystallised from benzene; it had m. p. 103°. The yield of pure acid from 43.5 g. of sodium, 435 g. of absolute ethyl alcohol, 300 g. of ethyl malonate, and 234 g. of allyl bromide did not exceed 75 g.

Dimethyl allylmalonate. A mixture of 20.5 g. of allylmalonic acid, 18.5 g. of anhydrous methyl alcohol, 55 ml. of sodium-dried A.R. benzene, and 9 g. of concentrated sulphuric acid was refluxed for 21 hours, then poured into water, the benzene layer separated, washed successively with saturated sodium hydrogen carbonate solution and water, dried, and the solvent removed. Distillation yielded 16.5 g. of pure *dimethyl allylmalonate*, b. p. 206.5—207.5°/771 mm. (Found: C, 56.0; H, 6.8. $C_8H_{12}O_4$ requires C, 55.8; H, 7.1%).

Diethyl allylmalonate. A mixture of 20.5 g. of allylmalonic acid, 26 g. of absolute ethyl alcohol, 55 ml. of sodium-dried A.R. benzene, and 6 g. of concentrated sulphuric acid was refluxed for 24 hours and yielded, as for the methyl ester, 20 g. of ethyl allylmalonate, b. p. 222.5—223°/766 mm.

Di-n-propyl allylmalonate. A mixture of 15 g. of allylmalonic acid, 25 g. of pure, absolute *n*-propyl alcohol, 37.5 ml. of sodium-dried A.R. benzene, and 6 g. of concentrated sulphuric acid was refluxed for 24 hours, and afforded, as for the methyl ester, 17 g. of *di-n-propyl allylmalonate*, b. p. 121.5°/7 mm. (Found: C, 63.4; H, 8.8. $C_{12}H_{20}O_4$ requires C, 63.5; H, 9.0%).

Di-n-butyl allylmalonate. A mixture of 15 g. of allylmalonic acid, 31 g. of pure, anhydrous *n*-butyl alcohol, 37.5 ml. of sodium-dried A.R. benzene, and 6 g. of concentrated sulphuric acid was refluxed for 31 hours and yielded, after the usual procedure, 21 g. of *di-n-butyl allylmalonate*, b. p. 149.5°/8.5 mm. (Found: C, 65.6; H, 9.4. $C_{14}H_{24}O_4$ requires C, 65.6; H, 9.4%).

Allyl Esters of Aliphatic Carboxylic Acids.—*Allyl acetate.* A mixture of 40 g. of dry, redistilled allyl alcohol, b. p. 96.5—97°/767 mm., 97°/773 mm., 120 g. of A.R. glacial acetic acid, and 2 g. of concentrated sulphuric acid was refluxed for 20 hours, poured into excess of brine, the ester layer separated and washed successively with saturated sodium hydrogen carbonate solution and brine, dried, and distilled. The yield of allyl acetate, b. p. 104°/773 mm., was 44 g.

Allyl propionate. A mixture of 40 g. of pure anhydrous allyl alcohol, 148 g. of propionic acid (b. p. 141—142°/773 mm.), and 2 g. of concentrated sulphuric acid was refluxed for 18 hours and yielded, as for allyl acetate, 43 g. of allyl propionate, b. p. 123°/767 mm.

Allyl n-butyrate. A mixture of 40 g. of pure anhydrous allyl alcohol, 176 g. of *n*-butyric acid (b. p. 161.5—162.5°/765 mm.), and 2 g. of concentrated sulphuric acid was refluxed for 31 hours and yielded, after pouring into water, etc., 60 g. of allyl *n*-butyrate, b. p. 141—142°/747 mm.

Diallyl succinate. A mixture of 44 g. of pure, anhydrous allyl alcohol, 30 g. of A.R. succinic acid, 95 ml. of sodium-dried A.R. benzene, and 15 g. of concentrated sulphuric acid was refluxed for 22 hours and yielded, after being worked up in the usual manner and distilled twice, 26 g. of allyl succinate, b. p. 100°/0.8 mm.

Allyl Halides and Diallyl.—*Allyl chloride.* 87 G. of pure anhydrous allyl alcohol were added to a cold mixture of 285 g. of concentrated hydrochloric acid and 408 g. of zinc chloride sticks, and the whole refluxed for 5 hours. The crude chloride (56 g.) was isolated by distillation as for *n*-propyl chloride (VIII, 50), and was washed successively with water, saturated sodium hydrogen carbonate solution, and water, dried ($CaSO_4$), and distilled. It boiled constantly at 45°/764 mm.

Allyl bromide. Method 1. A mixture of 58 g. of pure anhydrous allyl alcohol and 520 g. of A.R. constant-b. p. hydrobromic acid was slowly distilled from a 500-ml. distilling flask during 7 hours. The bromide layer (112 g.) in the distillate was separated, washed twice with an equal volume of concentrated hydrochloric acid (loss 4 g.), water, saturated sodium hydrogen carbonate solution, and water, dried, and distilled. The allyl bromide boiled constantly at 70°/759 mm.

Method 2. Pure allyl alcohol was converted into allyl bromide by the hydrogen bromide-sulphuric acid procedure (*Org. Synth.*, Coll. Vol. I, 1941, 27) and boiled at 69.5—72°/745 mm., mainly at 69.5—71°. This was redistilled, and a middle fraction, b. p. 70°/750 mm., collected; it had d_4^{20} 1.4314, n_D^{20} 1.4689, R_D 23.54, P (mean) 193.3.

Allyl iodide. A mixture of 29 g. of pure anhydrous allyl alcohol and 337 g. of constant-b. p. hydriodic acid was distilled slowly from a 500-ml. distilling flask during 7 hours. The lower layer of crude allyl iodide (83 g.) in the distillate was removed, a further 29 g. of allyl alcohol was added to the acid layer, and the distillation was repeated, a further 71 g. of crude allyl iodide being obtained. The crude iodide was washed with dilute sodium hydroxide solution, dried, and distilled from a little pure silver in the dark. The allyl iodide was collected at 100°/765 mm. and had d_4^{20} 1.7765, n_D^{20} 1.5437, whence R_D 29.84. The compound darkened considerably upon exposure to light and was too unstable for satisfactory physical measurements.

Diallyl (hexa-1:5-diene). 56 G. of clean sodium (small pieces) were placed in a 500-ml. round-bottomed flask fitted with two 10'' or 12'' double-surface condensers in series. 136 G. of freshly distilled allyl iodide were employed. About one-quarter of the allyl iodide was added to the sodium, and the flask gently warmed until the sodium just commenced to melt; the flame was then immediately removed. A vigorous reaction set in and a liquid refluxed. The remainder of the iodide was added during 2 hours. The reaction mixture was allowed to cool, and the hydrocarbon distilled off from a butyl phthalate bath at 90—100°. The yield of colourless liquid was 24 g. Upon redistillation from a little sodium, the diallyl boiled constantly at 59.5°/775 mm. and the sodium remained unattacked.

Dialkyl Maleates and Fumarates.—*Maleic acid.* Pure commercial maleic acid was converted into the anhydride by distillation with tetrachloroethane (Mason, *J.*, 1930, 700); the anhydride distilled at 195—197° and, after recrystallisation from chloroform, melted at 54°. This was evaporated with a little water on a water-bath and dried in a vacuum desiccator over concentrated sulphuric acid. The m. p. of the pure maleic acid depends to a marked degree upon the rate of heating and values between 133° and 143° may be observed. Slow heating (about 20 minutes) gives a value of 133—134° and more

rapid heating (*ca.* 10 minutes) 139—140°. If the acid is immersed in a bath at 140°, it melts sharply at 143°. The low m. p. s observed upon slow heating are evidently due to the formation of maleic anhydride and/or fumaric acid, which depress the m. p.

Fumaric acid. The commercial acid was recrystallised from *n*-hydrochloric acid, and, after drying in a vacuum desiccator over anhydrous calcium chloride and sodium hydroxide pellets, melted at 283.5° (sealed capillary tube). A further recrystallisation raised the m. p. to 286—287°.

Silver maleate. 130 G. of pure maleic acid were dissolved in 650 ml. of 3.5*N*-ammonia solution, and a solution containing 400 g. of silver nitrate added; the precipitated silver maleate was washed with water and dried at 40—50°. The yield was 295 g. The silver salt may also be prepared from the solution obtained by dissolving a known weight of pure maleic anhydride in water.

Silver fumarate. 100 G. of pure fumaric acid, 580 ml. of 3*N*-ammonia solution, and a solution of 290 g. of silver nitrate in 500 ml. of water similarly yielded 272 g. of silver fumarate.

Two methods of preparation of dialkyl maleates and fumarates were employed, *viz.*, from the silver salt and the alkyl bromide or iodide (usually in the presence of pure dry ether or benzene) and from the acid, alcohol, pure dry benzene, and concentrated sulphuric acid. Both procedures yielded identical esters as the following typical results prove.

Ester.	Method.	d_4^{20} .	n_D^{20} .	R_D .	P .
Me maleate	Ag salt, MeI (ether)	1.1502	1.4424	33.18	311.9
Me maleate	Acid, CH ₃ ·OH, C ₆ H ₆ , H ₂ SO ₄	1.1512	1.4418	33.11	311.9
Et maleate	Ag salt, EtI (benzene)	1.0662	1.4402	42.58	386.7
Et maleate	Acid, C ₂ H ₅ ·OH, C ₆ H ₆ , H ₂ SO ₄	1.0674	1.4402	42.58	—
Am ⁴ maleate	Ag salt, Am ⁴ Br (benzene)	0.9714	1.4459	70.35	613.0
Am ⁴ maleate	Acid, Am ⁴ OH, C ₆ H ₆ , H ₂ SO ₄	0.9712	1.4460	70.38	613.5
Et fumarate	Ag salt, EtI (benzene)	1.0521	1.4408	43.20	389.3
Et fumarate	Acid, EtOH, C ₆ H ₆ , H ₂ SO ₄	1.0512	1.4407	43.19	—
Am ⁴ fumarate	Ag salt, Am ⁴ Br (benzene)	0.9655	1.4479	71.06	619.5
Am ⁴ fumarate	Acid, Am ⁴ OH, C ₆ H ₆ , H ₂ SO ₄	0.9653	1.4481	71.10	619.7

General procedure for the preparation of esters by the silver salt method. The silver salt, suspended in pure anhydrous ether (for methyl maleate only) or in sodium-dried A.R. benzene, was mixed with a slight excess of the pure alkyl bromide or iodide, and the mixture was refluxed on a water-bath for the stated number of hours. If an alkyl iodide was employed, it was first shaken mechanically with pure silver powder until colourless, since traces of iodine appear to act catalytically in the interconversion of the *cis-trans*-isomers. The mixture was filtered through a sintered-glass funnel, and the residual silver salt extracted with the solvent medium, usually benzene. Small quantities of acid by-products are formed in most preparations of esters by the silver salt method. The solution of the ester was then washed successively with saturated sodium hydrogen carbonate solution, and water, dried (MgSO₄ or CaSO₄), the solvent removed, and the ester distilled.

General procedure for the preparation of esters by the acid, alcohol, benzene, sulphuric acid method. A mixture of the pure acid, anhydrous alcohol, sodium-dried A.R. benzene, and concentrated sulphuric acid was refluxed for 10—30 hours, poured into a large volume of water, the benzene layer separated (on occasion it was advisable to extract the aqueous layer with ether and combine the ethereal extract with the benzene layer), washed with water, saturated sodium hydrogen carbonate solution and water, dried (MgSO₄ or CaSO₄), and the solvent distilled off at atmospheric pressure. Further distillation yielded the pure ester.

Methyl maleate. Method 1. A mixture of 140 g. of silver maleate, 117 g. of colourless methyl iodide, and 75 ml. of anhydrous ether was refluxed for 1 hour, and yielded 16 g. of ester, b. p. 201°/770 mm.

Method 2. A mixture of 29 g. of maleic acid, 26 g. of absolute methyl alcohol, 95 ml. of benzene, and 4 g. of concentrated sulphuric acid was refluxed for 12 hours and yielded 21 g. of ester, b. p. 202°/762 mm.

Ethyl maleate. Method 1. A mixture of 90 g. of silver maleate, 84 g. of colourless ethyl iodide, and 50 ml. of benzene was refluxed for 10 hours and afforded 26.5 g. of ester, b. p. 219.5°/758 mm.

Method 2. A mixture of 29 g. of maleic acid, 37 g. of absolute ethyl alcohol, 95 ml. of benzene, and 4 ml. of concentrated sulphuric acid was refluxed for 12 hours and yielded 26 g. of ester, b. p. 219.5°/762 mm.

n-Propyl maleate. A mixture of 70 g. of silver maleate, 52 g. of *n*-propyl bromide, 50 ml. of benzene, and 4 ml. of concentrated sulphuric acid was refluxed for 28 hours and afforded 25 g. of ester, b. p. 126°/12 mm.

n-Butyl maleate. A mixture of 70 g. of silver maleate, 61 g. of *n*-butyl bromide, and 50 ml. of benzene was refluxed for 19 hours and afforded 26.5 g. of ester, b. p. 147.5°/12 mm.

isoButyl maleate. A mixture of 30 g. of maleic acid, 66 g. of *isobutyl* alcohol, 100 ml. of benzene, and 16 g. of concentrated sulphuric acid was refluxed for 35 hours and afforded 50 g. of ester, b. p. 125.5°/5 mm. (Found : C, 63.4; H, 8.6. C₁₂H₂₀O₄ requires C, 63.1; H, 8.8%).

n-Amyl maleate. A mixture of 70 g. of silver maleate, 66 g. of *n*-amyl bromide, and 50 ml. of benzene was refluxed for 26 hours and gave 32 g. of ester, b. p. 161°/10 mm.

isoAmyl maleate. Method 1. A mixture of 70 g. of silver maleate, 66 g. of *isoamyl* bromide (from Bisol fermentation alcohol), and 50 ml. of benzene was refluxed for 20 hours and yielded, after two distillations, 17 g. of ester, b. p. 157°/13 mm. There was a large high-b. p. residue in the first distillation.

Method 2. A mixture of 29 g. of maleic acid, 72 g. of Bisol fermentation *isoamyl* alcohol, 100 ml. of benzene, and 9 ml. of concentrated sulphuric acid was refluxed for 35 hours and yielded 60.5 g. of ester, b. p. 155°/10 mm. There was no high-b. p. residue.

Ethyl fumarate. Method 1. A mixture of 70 g. of silver fumarate, 70 g. of colourless ethyl iodide, and 50 ml. of benzene was refluxed for 15 hours and yielded 17 g. of ester, b. p. 214°/760 mm. If the benzene was replaced by absolute ethyl alcohol, the yield of pure ester was about 3 g.

Method 2. A mixture of 29 g. of fumaric acid, 37 g. of ethyl alcohol, 95 ml. of benzene, and 4 g. of concentrated sulphuric acid was refluxed for 12 hours and gave 30 g. of ester, b. p. 213.5°/749 mm.

n-Propyl fumarate. A mixture of 70 g. of silver fumarate, 52 g. of *n*-propyl bromide, and 60 ml. of benzene was refluxed for 13 hours and afforded 28 g. of ester, b. p. 110°/5 mm.

n-Butyl fumarate. A mixture of 70 g. of silver fumarate, 61 g. of *n*-butyl bromide, and 50 ml. of benzene was refluxed for 18 hours and yielded 26.5 g. of ester, b. p. 138.5°/8 mm. (Found: C, 63.4; H, 8.2. $C_{12}H_{20}O_4$ requires C, 63.1; H, 8.8%).

isoButyl fumarate. A mixture of 25 g. of fumaric acid, 55 g. of *isobutyl* alcohol, 85 ml. of benzene, and 13.5 g. of concentrated sulphuric acid was refluxed for 28 hours and yielded 40 g. of ester, b. p. 122°/5 mm.

n-Amyl fumarate. A mixture of 70 g. of silver fumarate, 66 g. of *n*-amyl bromide, and 50 ml. of benzene was refluxed for 19 hours and afforded 31 g. of ester, b. p. 162°/7 mm. (Found: C, 65.6; H, 9.1. $C_{14}H_{24}O_4$ requires C, 65.6; H, 9.4%).

isoAmyl fumarate. Method 1. A mixture of 62 g. of silver fumarate, 57 g. of *isoamyl* bromide (from Bisol fermentation alcohol), and 50 ml. of benzene was refluxed for 22 hours and yielded, after two distillations, 16.5 g. of ester, b. p. 166°/11 mm. There was a large high-b. p. residue in the first distillation.

Method 2. A mixture of 29 g. of fumaric acid, 72 g. of Bisol fermentation *isoamyl* alcohol, 100 ml. of benzene, and 9 g. of concentrated sulphuric acid was refluxed for 29 hours and yielded 55.5 g. of ester, b. p. 156°/7 mm. There was no high-b. p. residue.

Dialkyl Citraconates and Mesoconates.—Citric acid was converted into itaconic anhydride (*Org. Synth.*, 1931, 11, 71) and then successively into citraconic anhydride (*loc. cit.*, p. 29) and citraconic acid, m. p. 92—93°.

The authors were unable to confirm all the observations given in *Org. Synth.* (*loc. cit.*, p. 75) for the conversion of citraconic anhydride into mesaconic acid; in particular, red fumes were observed initially, but not at the end of the reaction, although this is regarded as an essential criterion that the rearrangement had occurred. Our observations are accordingly recorded. A mixture of 110 g. of citraconic anhydride, b. p. 91°/11 mm., 110 ml. of water, and 165 ml. of dilute nitric acid (33 ml. concentrated acid, 132 ml. water) were slowly evaporated in a 500-ml. Pyrex flask until solid commenced to separate (6 hours). After standing overnight, the almost solid mass was filtered off on a sintered-glass funnel and washed with a little water. The yield of crude product was 52—55 g., and upon recrystallisation from 100 ml. of water 45 g. of pure citraconic acid, m. p. 204°, were obtained. The original filtrate upon concentration yielded a further 5 g. of acid.

Methyl citraconate. A mixture of 30 g. of citraconic acid, 30 g. of methyl alcohol, 100 ml. of benzene, and 5 g. of concentrated sulphuric acid was refluxed for 36 hours and yielded 29 g. of the ester, b. p. 209.5°/764 mm.

Ethyl citraconate. A mixture of 25 g. of citraconic acid, 29 g. of ethyl alcohol, 100 ml. of benzene, and 4 g. of concentrated sulphuric acid was refluxed for 22 hours and afforded 28 g. of the ethyl ester, b. p. 228°/766 mm.

n-Propyl citraconate. A mixture of 25 g. of citraconic acid, 38 g. of *n*-propyl alcohol, 100 ml. of benzene, and 4 g. of concentrated sulphuric acid was refluxed for 25 hours and yielded 28 g. of the *n*-propyl ester, b. p. 112°/6 mm. (Found: C, 61.9; H, 8.2. $C_{11}H_{18}O_4$ requires C, 61.7; H, 8.5%).

Methyl mesaconate. A mixture of 30 g. of mesaconic acid, 30 g. of methyl alcohol, 100 ml. of benzene, and 5 g. of concentrated sulphuric acid was refluxed for 21 hours and yielded 22 g. of ester, b. p. 86°/6 mm. Distillation under 764 mm. gave a b. p. of 205°, but a little charred residue remained in the flask.

Ethyl mesaconate. A mixture of 25 g. of mesaconic acid, 29 g. of ethyl alcohol, 100 ml. of benzene, and 4 g. of concentrated sulphuric acid was refluxed for 24 hours and yielded 27.5 g. of ester, b. p. 95°/6 mm. The b. p. under 754 mm. is 224°, but slight decomposition occurs.

n-Propyl mesaconate. A mixture of 25 g. of mesaconic acid, 38 g. of *n*-propyl alcohol, 100 ml. of benzene, and 4 g. of concentrated sulphuric acid was refluxed for 24 hours and afforded 30 g. of the *n*-propyl ester, b. p. 128°/10 mm. (Found: C, 61.7; H, 8.2. $C_{11}H_{18}O_4$ requires C, 61.7; H, 8.5%).

Dialkyl Methylsuccinates.—*Methylsuccinic acid.* 440 G. of redistilled thionyl chloride were placed in a 1.5-l. flask fitted with a dropping-funnel and a double-surface condenser attached to a gas-absorption device. 250 G. of redistilled propionic acid were added to the warm thionyl chloride at such a rate that the mixture refluxed gently (*ca.* 1 hour); it was then refluxed for 30 minutes to remove dissolved sulphur dioxide. One g. of purified red phosphorus was added, followed by 620 g. of dry bromine during 7 hours whilst the mixture was refluxed gently. The resulting dark product was refluxed for 7 hours, *i.e.*, until evolution of hydrogen bromide almost ceased; the liquid then had a much lighter colour. The resulting crude α -bromopropionyl chloride was added during 2.5 hours to 500 ml. of absolute ethyl alcohol contained in a three-necked flask, fitted with a dropping-funnel, mechanical stirrer and reflux condenser, and cooled externally in running water. When the addition was complete, the mixture was heated on a water-bath for 4 hours (some hydrogen chloride was evolved). The reaction product was filtered into 1 l. of water, the heavy oil separated and washed successively with water, saturated sodium hydrogen carbonate solution and water, dried, and distilled. Some ethyl bromide passed over first, followed by ethyl α -bromopropionate (450 g.) at 65—67°/20 mm. (or 69—70°/25 mm.).

To a suspension of ethyl sodiocyanoacetate, prepared from a solution of 25.9 g. of sodium in 315 ml. of absolute ethyl alcohol and 128.3 g. of ethyl cyanoacetate, were added slowly 189 g. of ethyl α -bromopropionate: heat was evolved and the mixture became more fluid. The mixture was heated on a water-bath for 1 hour, poured into 1.5 l. of water, and the ester extracted several times with ether. The ethereal extract was washed with dilute sodium carbonate solution and water, dried, and distilled: the crude ethyl 1-cyano-2-methylsuccinate (145 g.) was collected at 161—176°/28 mm., chiefly at 167°/28 mm. (compare Bone and Sprankling, *J.*, 1899, 75, 845, who give b. p. 140—165°/24 mm.). Redistillation afforded 110 g. of the pure ester, b. p. 161—166°/25 mm. (largely 163°/25 mm.). The following method of hydrolysis is superior to that described by Bone and Sprankling (*loc. cit.*). 100 G. of the pure ester were mixed with 400 ml. of concentrated hydrochloric acid and refluxed for 16 hours

whilst a stream of hydrogen chloride was passed into the liquid. The reaction product was extracted several times with ether, the extract dried, and the solvent removed: the residue was recrystallised from benzene and yielded 52 g. of pure methylsuccinic acid, m. p. 112°.

Methyl methylsuccinate. A mixture of 25 g. of methylsuccinic acid, 20 g. of methyl alcohol, 100 ml. of benzene, and 3 g. of concentrated sulphuric acid was refluxed for 20 hours and yielded 18 g. of ester, b. p. 196°/760 mm.

Ethyl methylsuccinate. A mixture of 20 g. of methylsuccinic acid, 24 g. of ethyl alcohol, 100 ml. of benzene, and 3 g. of concentrated sulphuric acid was refluxed for 24 hours and yielded 21.5 g. of ester, b. p. 217°/764 mm.

n-Propyl methylsuccinate. A mixture of 20 g. of methylsuccinic acid, 30 g. of *n*-propyl alcohol, 100 ml. of benzene, and 3 g. of concentrated sulphuric acid was refluxed for 24 hours and yielded 27.5 g. of the *n*-propyl ester, b. p. 246.5°/763 mm. (Found: C, 61.3; H, 9.0. C₁₁H₂₀O₄ requires C, 61.1; H, 9.3%).

Alkyl trans-Crotonates.—*trans-Crotonic acid.* Crystallisation of the commercially pure crotonic acid from organic solvents does not always give satisfactory results. The simplest procedure is to distil (say) 100 g. of the acid contained in a 100-ml. Claisen flask, using an air-bath; the pure *trans*-crotonic acid passes over at 180—182°/759 mm. and crystallises on cooling; m. p. 72—73°. The recovery is about 90%.

The esters were prepared by the silver salt method, following the general procedure described under alkyl maleates and fumarates. Methyl and ethyl crotonate were also prepared by the excess acid method, but the results for *n*-propyl crotonate by this procedure were unsatisfactory. It is noteworthy that acid by-products are formed in the silver salt method and the proportion appears to increase with the molecular weight of the alkyl radical; the washing with sodium hydrogen carbonate solution is therefore essential.

Silver crotonate. 120 G. of pure crotonic acid were dissolved in 410 ml. of 3.5*N*-ammonia solution, and a solution containing 240 g. of silver nitrate was added slowly and with stirring. The precipitate was filtered off, washed, and dried in a vacuum desiccator or at 40—50°. The yield was almost quantitative.

Methyl crotonate. Method 1 (excess acid procedure). 16 G. of absolute methyl alcohol were mixed with 4 g. of concentrated sulphuric acid and 80 g. of crotonic acid were added. The mixture was refluxed on a water-bath for 21 hours (a homogeneous liquid was produced within 2—3 hours) and then allowed to stand overnight, some solid separating out. The liquid portion was decanted, and the solid well washed with water; the combined liquid and washings was washed successively with water, saturated sodium hydrogen carbonate solution, and water, dried, and twice distilled. The yield of ester, b. p. 119°/768 mm., was 23 g.; some high-b. p. residue was obtained in the first distillation.

Method 2. A mixture of 100 g. of silver crotonate, 71 g. of colourless methyl iodide, and 100 ml. of anhydrous ether was refluxed for 22 hours and yielded 22.5 g. of ester, b. p. 119°/772 mm.

Ethyl crotonate. Method 1. A mixture of 16 g. of absolute ethyl alcohol and 6 g. of concentrated sulphuric acid with 60 g. of crotonic acid was refluxed for 24 hours and yielded, as for the methyl ester, 19 g. of ethyl crotonate, b. p. 136.5°/761 mm., after two distillations.

Method 2. A mixture of 65 g. of silver crotonate, 52 g. of colourless ethyl iodide, and 75 ml. of anhydrous ether was refluxed for 11 hours and afforded 18 g. of ester, b. p. 136.5°/765 mm.

n-Propyl crotonate. A mixture of 120 g. of silver crotonate, 74 g. of *n*-propyl bromide, and 150 ml. of pure anhydrous benzene was refluxed for 30 hours, and the solid filtered off and washed with benzene. Attempts to wash the benzene solution of the ester with saturated sodium hydrogen carbonate solution led to considerable emulsification; it was therefore washed with water, dried, and distilled, 38 g. of ester, b. p. 154—158°/764 mm., being collected. This (or its solution in ether) was washed with saturated sodium hydrogen carbonate solution and water, dried, and distilled. The yield of pure *n*-propyl crotonate, b. p. 157.5°/768 mm., was 30 g.

n-Butyl crotonate. A mixture of 75 g. of silver crotonate, 55 g. of *n*-butyl bromide, and 75 ml. of anhydrous benzene was refluxed for 36 hours and yielded (experimental details as for the *n*-propyl ester) 20 g. of ester, b. p. 55°/4 mm., after two distillations.

n-Amyl crotonate. A mixture of 75 g. of silver crotonate, 60 g. of *n*-amyl bromide, and 75 g. of anhydrous benzene was refluxed for 26 hours and yielded (as for the *n*-propyl ester—more acidic by-products were formed) 30 g. of the *n*-amyl ester, b. p. 71.5°/5 mm. (Found: C, 69.2; H, 10.3. C₉H₁₆O₂ requires C, 69.2; H, 10.3%).

isoAmyl crotonate. A mixture of 75 g. of silver crotonate, 60 g. of *iso*amyl bromide, and 75 ml. of absolute ethyl alcohol was refluxed for 40 hours. The solid was filtered off and washed with rectified spirit. The combined alcoholic solutions were poured into three times the volume of water, sodium hydrogen carbonate was added, the mixture shaken, and the ester separated, washed, dried, and twice distilled. The yield of ester, b. p. 60°/3.5 mm., was 30 g.

Alkyl Cinnamates.—*Cinnamic acid.* Commercial ethyl cinnamate was washed successively with 10% sodium carbonate solution and water, dried (MgSO₄), and distilled: the fraction, b. p. 150—151°/20 mm., was collected. 118 G. of the purified ester were treated with a solution of 100 g. of potassium hydroxide in 100 ml. of water, 250 ml. of rectified spirit were added, the mixture refluxed for 7 hours, and the alcohol distilled off. The residue was extracted with ether (to remove any unreacted ester), acidified to Congo-red with dilute sulphuric acid, and the precipitated acid filtered off, washed with water, and dried at 90°. Its m. p. was 133.5°.

Ethyl cinnamate. A mixture of 25 g. of cinnamic acid, 23 g. of absolute ethyl alcohol, 4 g. of concentrated sulphuric acid, and 100 ml. of anhydrous benzene was refluxed for 15 hours and afforded, by the usual procedure, 23.5 g. of ester, b. p. 127°/6 mm.

n-Propyl cinnamate. A mixture of 25 g. of cinnamic acid, 30 g. of absolute *n*-propyl alcohol, 4 g. of concentrated sulphuric acid, and 100 ml. of anhydrous benzene was refluxed for 19 hours and yielded 26.5 g. of ester, b. p. 148°/10 mm.

n-Butyl cinnamate. A mixture of 25 g. of cinnamic acid, 37 g. of *n*-butyl alcohol, 4 g. of concentrated

sulphuric acid, and 100 ml. of anhydrous benzene was refluxed for 20 hours and afforded 28 g. of ester, b. p. 162°/12 mm.

Physical Measurements.—**331. Vinylacetic acid.** B. p. 77.5°/19 mm.; M 86.09; n_D 1.42386, n_F 1.43064, n_G 1.43575; R_D 21.60, R_D 21.73, R_F 22.03, R_G 22.26; Mn_D^{20} 122.58. Densities determined: d_4^{20} 1.0108, d_4^{14} 0.9895, d_4^{11} 0.9693, $d_4^{8.7}$ 0.9470. Apparatus *A*.

(These headings apply to corresponding columns of all subsequent tables.)

<i>t</i> .	<i>H</i> .	d_4^t .	γ .	<i>P</i> .	<i>t</i> .	<i>H</i> .	d_4^t .	γ .	<i>P</i> .
14.3°	15.48	1.0164	29.46	197.3	61.9°	13.52	0.9692	24.59	197.7
18.5	15.29	1.0123	28.98	197.3	87.3	12.57	0.9444	22.23	197.9
40.9	14.38	0.9900	26.66	197.6					Mean 197.5

332. Methyl vinylacetate. B. p. 108°/774 mm.; M 100.11; n_D 1.40658, n_D 1.40909, n_F 1.41523, n_G 1.41949; R_C 26.16, R_D 26.30, R_F 26.64, R_G 26.89; Mn_D^{20} 141.07. Densities determined: d_4^{20} 0.9413, d_4^{10} 0.9177, $d_4^{6.5}$ 0.8947. Apparatus *A*.

16.0°	15.76	0.9458	27.91	243.3	42.3°	14.36	0.9162	24.64	243.4
19.7	15.56	0.9416	27.43	243.3	61.3	13.41	0.8949	22.47	243.6
									Mean 243.4

333. Ethyl vinylacetate. B. p. 124°/745 mm.; M 114.14; n_D 1.40860, n_D 1.41107, n_F 1.41705, n_G 1.42159; R_C 30.79, R_D 30.95, R_F 31.35, R_G 31.64; Mn_D^{20} 161.06. Densities determined: d_4^{20} 0.9158, d_4^{10} 0.8944, $d_4^{6.7}$ 0.8731, $d_4^{4.7}$ 0.8445. Apparatus *E*.

17.1°	12.40	0.9189	26.54	281.9	61.1°	10.62	0.8727	21.59	282.1
40.5	11.44	0.8941	23.82	282.0	87.2	9.55	0.8429	18.75	282.3
									Mean 282.1

334. n-Propyl vinylacetate. B. p. 144.5°/774 mm.; M 128.17; n_D 1.41250, n_D 1.41496, n_F 1.42090, n_G 1.42523; R_C 35.46, R_D 35.65, R_F 36.09, R_G 36.42; Mn_D^{20} 181.36. Densities determined: d_4^{20} 0.9003, $d_4^{12.6}$ 0.8788, $d_4^{6.9}$ 0.8607, $d_4^{5.1}$ 0.8340. Apparatus *A*.

13.1°	15.90	0.9069	27.00	322.4	61.4°	13.67	0.8602	22.02	322.8
20.3	15.60	0.9000	26.29	322.5	86.9	12.41	0.8332	19.36	322.7
41.9	14.56	0.8789	23.96	322.6					Mean 322.6

335. n-Butyl vinylacetate. B. p. 53°/7 mm.; M 142.19; n_D 1.41784, n_D 1.42026, n_F 1.42615, n_G 1.43049; R_C 40.11, R_D 40.32, R_F 40.82, R_G 41.18; Mn_D^{20} 201.95. Densities determined: d_4^{20} 0.8930, $d_4^{12.6}$ 0.8721, $d_4^{9.0}$ 0.8556, $d_4^{6.5}$ 0.8302. Apparatus *E*.

13.0°	13.03	0.8993	27.29	361.4	61.4°	11.33	0.8544	22.55	362.6
19.3	12.80	0.8936	26.64	361.5	87.2	10.32	0.8295	19.94	362.1
42.7	11.96	0.8720	24.29	362.0					Mean 361.9

336. n-Amyl vinylacetate. B. p. 74.5°/12 mm.; M 156.22; n_D 1.42204, n_D 1.42446, n_F 1.43036, n_G 1.43460; R_C 44.77, R_D 45.00, R_F 45.54, R_G 45.93; Mn_D^{20} 222.54. Densities determined: d_4^{20} 0.8868, $d_4^{12.6}$ 0.8677, $d_4^{9.7}$ 0.8509, $d_4^{7.7}$ 0.8264. Apparatus *A*.

18.3°	16.20	0.8883	26.95	400.7	61.0°	14.34	0.8506	22.84	401.5
41.8	15.23	0.8676	24.74	401.6	87.1	13.21	0.8269	20.45	401.8
									Mean 401.4

337. Methyl undecylenate. B. p. 247—248°/776 mm.; M 198.30; n_D 1.43639, n_D 1.43882, n_F 1.44481, n_G 1.44921; R_C 58.56, R_D 58.84, R_F 59.54, R_G 60.05; Mn_D^{20} 285.31. Densities determined: d_4^{20} 0.8861, $d_4^{12.6}$ 0.8690, $d_4^{11.8}$ 0.8541, $d_4^{7.6}$ 0.8331. Apparatus *D*.

16.1°	13.84	0.8891	30.39	523.7	43.0°	12.94	0.8686	27.76	524.0
18.4	13.72	0.8873	30.06	523.3	61.4	12.33	0.8544	26.02	524.2
28.1	13.43	0.8799	29.18	523.8	88.1	11.47	0.8327	23.59	524.8
									Mean 524.0

338. Ethyl undecylenate. B. p. 258—259°/761 mm.; M 212.32; n_D 1.43580, n_D 1.43822, n_F 1.44418, n_G 1.44859; R_C 63.15, R_D 63.45, R_F 64.20, R_G 64.75; Mn_D^{20} 305.36. Densities determined: d_4^{20} 0.8788, d_4^{10} 0.8625, d_4^{13} 0.8472, $d_4^{6.6}$ 0.8270. Apparatus *A*.

13.3°	18.02	0.8840	29.83	561.3	40.7°	16.94	0.8627	27.36	562.9
16.0	17.93	0.8819	29.61	561.6	60.3	16.19	0.8480	25.71	563.8
24.5	17.58	0.8753	28.81	562.0	87.1	14.99	0.8266	23.20	563.7
									Mean 562.6

339. n-Propyl undecylenate. B. p. 139.5°/7 mm.; M 226.35; n_D 1.43751, n_D 1.43993, n_F 1.44587, n_G 1.45029; R_C 67.79, R_D 68.12, R_F 68.92, R_G 69.51; Mn_D^{20} 325.92. Densities determined: d_4^{20} 0.8756, $d_4^{12.1}$ 0.8590, $d_4^{11.7}$ 0.8442, $d_4^{8.2}$ 0.8259. Apparatus *A*.

16.0°	18.14	0.8786	29.84	602.1	61.8°	16.21	0.8441	25.62	603.3
24.4	17.83	0.8723	29.13	602.8	87.3	15.09	0.8243	23.29	603.2
42.2	17.04	0.8589	27.41	603.0					Mean 602.9

349. *Ethyl allylmalonate*. B. p. 222.5—223°/766 mm.; M 200.23; n_D 1.42806, n_D 1.43048, n_F 1.43642, n_G 1.44080; R_D 51.02, R_D 51.27, R_F 51.88, R_G 52.34; Mn_D^{20} 286.43. Densities determined: d_4^{20} 1.0098, d_4^{19} 0.9889, d_4^{18} 0.9710, d_4^{16} 0.9465. Apparatus *A*.

t .	H .	d_4^t .	γ .	P .	t .	H .	d_4^t .	γ .	P .
18.8°	15.77	1.0109	29.85	463.0	60.4°	13.99	0.9716	25.45	462.9
22.8	15.60	1.0071	29.42	463.0	86.2	13.05	0.9468	23.14	463.8
41.5	14.79	0.9893	27.40	463.1					Mean 463.2

350. *n-Propyl allylmalonate*. B. p. 121.5°/7 mm.; M 228.23; n_D 1.43189, n_D 1.43430, n_F 1.44020, n_G 1.44464; R_D 60.26, R_D 60.55, R_F 61.27, R_G 61.80; Mn_D^{20} 327.42. Densities determined: d_4^{20} 0.9824, d_4^{19} 0.9640, d_4^{18} 0.9454, d_4^{16} 0.9225. Apparatus *D*.

20.3°	12.13	0.9821	29.42	541.3	61.9°	10.82	0.9447	25.24	541.6
40.6	11.50	0.9640	27.38	541.7	86.7	10.15	0.9227	23.13	542.6
									Mean 541.8

351. *n-Butyl allylmalonate*. B. p. 149.5°/8.5 mm.; M 256.33; n_D 1.43477, n_D 1.43716, n_F 1.44304, n_G 1.44745; R_D 69.50, R_D 69.83, R_F 70.64, R_G 71.26; Mn_D^{20} 368.40. Densities determined: d_4^{20} 0.9621, d_4^{19} 0.9456, d_4^{18} 0.9286, d_4^{16} 0.9083. Apparatus *A*.

14.4°	16.30	0.9666	29.50	618.1	41.2°	15.32	0.9456	27.13	618.6
18.1	16.09	0.9636	29.03	618.9	61.5	14.54	0.9285	25.28	619.0
27.0	15.89	0.9565	28.46	619.0	86.5	13.61	0.9075	23.13	619.4
									Mean 618.8

352. *Allyl acetate*. B. p. 104°/773 mm.; M 100.11; n_D 1.40150, n_D 1.40396, n_F 1.41001, n_G 1.41445; R_D 26.25, R_D 26.39, R_F 26.74, R_G 26.99; Mn_D^{20} 140.55. Densities determined: d_4^{20} 0.9277, d_4^{19} 0.9042, d_4^{18} 0.8818. Apparatus *D*.

20.9°	11.47	0.9267	26.25	244.5	41.4°	10.72	0.9054	23.97	244.8
21.6	11.42	0.9260	26.12	244.4	60.5	9.85	0.8828	21.47	244.4
28.0	11.19	0.9190	25.40	244.5					Mean 244.5

353. *Allyl propionate*. B. p. 123°/767 mm.; M 114.14; n_D 1.40805, n_D 1.41048, n_F 1.41643, n_G 1.42084; R_D 30.81, R_D 30.97, R_F 31.36, R_G 31.66; Mn_D^{20} 161.00. Densities determined: d_4^{20} 0.9140, d_4^{19} 0.8923, d_4^{18} 0.8718, d_4^{16} 0.8442. Apparatus *A*.

15.3°	11.85	0.9189	26.89	282.9	40.8°	10.90	0.8932	24.04	283.0
18.7	11.68	0.9157	26.41	282.6	61.9	10.10	0.8702	21.71	283.1
25.6	11.49	0.9082	25.77	283.2	85.3	9.13	0.8440	19.03	282.8
									Mean 282.9

354. *Allyl n-butyrate*. B. p. 141.5—142°/747 mm.; M 128.17; n_D 1.41332, n_D 1.41576, n_F 1.42176, n_G 1.42631; R_D 35.46, R_D 35.65, R_F 36.10, R_G 36.44; Mn_D^{20} 181.46. Densities determined: d_4^{20} 0.9017, d_4^{19} 0.8797, d_4^{18} 0.8607, d_4^{16} 0.8356. Apparatus *D*.

14.4°	11.92	0.9075	26.71	321.1	61.1°	10.29	0.8598	21.88	322.3
19.2	11.77	0.9025	26.23	321.4	86.1	9.35	0.8342	19.26	321.9
41.1	11.00	0.8796	23.90	322.2					Mean 321.8

355. *Allyl succinate*. B. p. 100°/0.8 mm.; M 198.21; n_D 1.44890, n_D 1.45167, n_F 1.45856, n_G 1.46384; R_D 50.56, R_D 50.85, R_F 51.52, R_G 52.02; Mn_D^{20} 287.74. Densities determined: d_4^{20} 1.0510, d_4^{19} 1.0321, d_4^{18} 1.0128, d_4^{16} 0.9890. Apparatus *A*.

20.1°	17.12	1.0509	33.69	454.4	61.0°	15.44	1.0131	29.29	455.1
28.4	16.83	1.0433	32.88	454.9	87.3	14.43	0.9880	26.70	456.0
40.9	16.30	1.0322	31.51	454.9					Mean 454.9

356. *Allyl chloride*. B. p. 45°/764 mm.; M 76.53; n_D 1.41282, n_D 1.41566, n_F 1.42272, n_G 1.42807; R_D 20.30, R_D 20.42, R_F 20.73, R_G 20.96; Mn_D^{20} 108.34. Densities determined: d_4^{20} 0.9397, d_4^{19} 0.9469. Apparatus *A*.

10.2°	13.82	0.9493	24.57	179.6	23.8°	13.22	0.9361	23.17	179.6
20.5	13.43	0.9392	23.62	179.7					Mean 179.6

357. *Allyl bromide*. B. p. 70°/759 mm.; M 120.99; n_D 1.46582, n_D 1.46968, n_F 1.47933, n_G 1.48692; R_D 23.40, R_D 23.57, R_F 23.98, R_G 24.30; Mn_D^{20} 177.82. Densities determined: d_4^{20} 1.4316, d_4^{19} 1.3920, d_4^{18} 1.3655. Apparatus *A*.

11.9°	10.34	1.4466	28.01	192.4	41.2°	9.26	1.3918	24.13	192.9
15.4	10.21	1.4402	27.53	192.4	54.5	8.86	1.3683	22.70	193.4
21.9	9.97	1.4281	26.66	192.5					Mean 192.7

(ii) From acid. B. p. 155°/10 mm.; n_D 1.44334, n_D 1.44601, n_F 1.45254, n_G 1.45747; R_G 70.01, R_D 70.38, R_F 71.27, R_G 71.95; Mn_D^{20} 370.65. Densities determined: d_4^{20} 0.9712, $d_4^{40.5}$ 0.9549, $d_4^{60.7}$ 0.9394, $d_4^{85.0}$ 0.9181. Apparatus *D*.

<i>t.</i>	<i>H.</i>	d_4^t	γ .	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4^t	γ .	<i>P.</i>
24.5°	11.90	0.9676	28.44	611.8	60.9°	11.16	0.9392	25.65	614.2
41.4	11.44	0.9542	26.96	612.1	88.2	10.36	0.9155	23.42	616.0
Mean 613.5									

366. Ethyl fumarate. (i) From silver salt. B. p. 214°/760 mm.; M 172.18; n_C 1.43764, n_D 1.44083, n_F 1.44881, n_G 1.45497; R_C 42.92, R_D 43.20, R_F 43.88, R_G 44.40; Mn_D^{20} 248.08. Densities determined: d_4^{20} 1.0521, $d_4^{41.5}$ 1.0304, $d_4^{60.7}$ 1.0110, $d_4^{86.9}$ 0.9844. Apparatus *A*.

15.9°	16.26	1.0562	32.16	388.2	61.2°	14.45	1.0105	27.34	389.6
24.9	16.04	1.0472	31.45	389.4	86.9	13.45	0.9844	24.79	390.2
41.6	15.25	1.0303	29.42	389.2	Mean 389.3				

(ii) From acid. This had b. p. 213.5°/749 mm.; d_4^{20} 1.0512, n_D^{20} 1.44068.

367. n-Propyl fumarate. B. p. 110°/5 mm.; M 200.23; n_C 1.44089, n_D 1.44395, n_F 1.45165, n_G 1.45768; R_C 52.19, R_D 52.51, R_F 53.30, R_G 53.91; Mn_D^{20} 289.13. Densities determined: d_4^{20} 1.0129, $d_4^{41.4}$ 0.9924, $d_4^{61.4}$ 0.9744, $d_4^{86.5}$ 0.9506. Apparatus *A*.

14.1°	16.57	1.0184	31.60	466.2	41.1°	15.50	0.9927	28.81	467.3
18.6	16.44	1.0142	31.22	466.7	62.2	14.75	0.9736	26.89	468.3
24.1	16.22	1.0090	30.65	466.9	86.1	13.90	0.9510	24.75	469.6
Mean 467.5									

368. n-Butyl fumarate. B. p. 138.5°/5 mm.; M 228.28; n_C 1.44395, n_D 1.44691, n_F 1.45433, n_G 1.46026; R_C 61.44, R_D 61.79, R_F 62.68; R_G 63.39; Mn_D^{20} 330.30. Densities determined: d_4^{20} 0.9869, $d_4^{42.6}$ 0.9675, $d_4^{61.3}$ 0.9513, $d_4^{86.3}$ 0.9513. Apparatus *A*.

16.5°	16.73	0.9899	31.01	544.2	42.1°	15.79	0.9678	28.61	545.5
17.9	16.64	0.9887	30.81	544.0	60.2	15.17	0.9522	27.05	546.7
22.6	16.65	0.9847	30.70	545.7	87.4	14.23	0.9296	24.77	547.8
Mean 545.8									

369. isoButyl fumarate. B. p. 122°/5 mm.; M 228.28; n_C 1.44019, n_D 1.44315, n_F 1.45053, n_G 1.45635; R_C 61.67, R_D 62.03, R_F 62.92, R_G 63.63; Mn_D^{20} 329.45. Densities determined: d_4^{20} 0.9760, $d_4^{42.0}$ 0.9581, $d_4^{61.1}$ 0.9410, $d_4^{87.0}$ 0.9182. Apparatus *D*.

20.3°	11.99	0.9758	28.89	542.4	61.7°	10.94	0.9405	25.41	544.9
23.1	11.91	0.9734	28.63	542.5	87.9	10.19	0.9176	23.09	545.3
41.6	11.46	0.9584	27.12	543.6	Mean 543.7				

370. n-Amyl fumarate. B. p. 162°/7 mm.; M 256.33; n_C 1.44669, n_D 1.44962, n_F 1.45685, n_G 1.46256; R_C 70.70, R_D 71.10, R_F 72.10, R_G 72.87; Mn_D^{20} 371.58. Densities determined: d_4^{20} 0.9681, $d_4^{41.6}$ 0.9510, $d_4^{60.0}$ 0.9361, $d_4^{85.6}$ 0.9147. Apparatus *D*.

15.3°	12.92	0.9719	31.01	622.4	42.3°	12.19	0.9504	28.61	623.8
19.5	12.82	0.9685	30.66	622.8	62.1	11.73	0.9344	27.08	625.8
22.8	12.72	0.9659	30.34	622.9	86.6	11.04	0.9139	24.92	626.6
Mean 624.1									

371. isoAmyl fumarate. (i) From silver salt. B. p. 166°/11 mm.; M 256.33; n_C 1.44501, n_D 1.44791, n_F 1.45518, n_G 1.46092; R_C 70.66, R_D 71.06, R_F 72.06, R_G 72.84; Mn_D^{20} 371.14. Densities determined: d_4^{20} 0.9655, $d_4^{41.8}$ 0.9483, $d_4^{60.5}$ 0.9326, $d_4^{86.6}$ 0.9127. Apparatus *A*.

24.4°	16.06	0.9620	28.93	618.0	63.2°	14.73	0.9304	25.66	620.1
41.4	15.41	0.9486	27.37	618.1	86.3	13.87	0.9125	23.70	619.8
Mean 619.5									

(ii) From acid. B. p. 156°/7 mm.; n_C 1.44515, n_D 1.44806, n_F 1.45530, n_G 1.46098; R_C 70.70, R_D 71.10, R_F 72.09, R_G 72.87; Mn_D^{20} 371.19. Densities determined: d_4^{20} 0.9653, $d_4^{41.0}$ 0.9487, $d_4^{61.3}$ 0.9320, $d_4^{85.3}$ 0.9125. Apparatus *A*.

21.8°	16.17	0.9639	29.19	618.1	61.0°	14.85	0.9322	25.92	620.4
28.2	16.01	0.9587	28.74	619.1	87.3	13.99	0.9109	23.86	621.9
41.3	15.48	0.9485	27.49	618.8	Mean 619.7				

372. Methyl citraconate. B. p. 209.5°/764 mm.; M 158.15; n_C 1.44474, n_D 1.44781, n_F 1.45559, n_G 1.46170; R_C 37.83, R_D 38.06, R_F 38.66, R_G 39.08; Mn_D^{20} 228.97. Densities determined: d_4^{20} 1.1119, $d_4^{42.2}$ 1.0894, $d_4^{62.3}$ 1.0694, $d_4^{87.1}$ 1.0442. Apparatus *D*.

19.3°	13.28	1.1126	36.49	349.4	62.0°	11.80	1.0697	31.17	349.3
28.3	13.00	1.1036	35.43	349.6	87.7	10.96	1.0436	28.25	349.4
41.3	12.49	1.0903	33.63	349.3	Mean 349.4				

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373. Ethyl citraconate. B. p. 228°/766 mm.; M 186.20; n_D 1.44115, n_D 1.44405, n_F 1.45134, n_G 1.45696; R_C 47.25, R_D 47.52, R_F 48.19, R_G 48.71; Mn_D^{20} 268.89. Densities determined: d_4^{20} 1.0410, d_4^{40-65} 1.0232, d_4^{51-55} 1.0041, d_4^{87-65} 0.9801. Apparatus A.

t .	H .	$d_4^{t_0}$.	γ .	P .	t .	H .	$d_4^{t_0}$.	γ .	P .
21.1°	16.48	1.0400	32.09	426.1	60.5°	14.89	1.0050	28.02	426.3
41.2	15.65	1.0227	29.97	426.0	87.0	13.85	0.9805	25.43	426.4
Mean 426.2									

374. n-Propyl citraconate. B. p. 112°/6 mm.; M 214.25; n_C 1.44341, n_D 1.44626, n_F 1.45337, n_G 1.45899; R_C 56.39, R_D 56.71, R_F 57.49, R_G 58.11; Mn_D^{20} 309.87. Densities determined: d_4^{20} 1.0080, d_4^{41-65} 0.9883, d_4^{51-65} 0.9711, d_4^{85-65} 0.9492. Apparatus D.

20.1°	12.51	1.0079	31.14	502.1	62.2°	11.25	0.9700	26.95	503.2
27.8	12.33	1.0010	30.48	502.9	85.7	10.64	0.9491	24.94	504.5
41.3	11.82	0.9886	28.86	502.3	Mean 503.0				

375. Methyl mesaconate. B. p. 86°/6 mm.; M 158.15; n_C 1.45128, n_D 1.45472, n_F 1.46356, n_G 1.47068; R_C 38.06, R_D 38.31, R_F 38.95, R_G 39.47; Mn_D^{20} 230.06. Densities determined: d_4^{20} 1.1195, d_4^{40-65} 1.0999, d_4^{50-65} 1.0793, d_4^{83-65} 1.0533. Apparatus D.

18.9°	12.77	1.1206	35.34	344.1	60.4°	11.40	1.0784	30.36	344.2
25.3	12.66	1.1142	34.84	344.8	85.8	10.63	1.0510	27.59	344.9
40.5	12.06	1.0994	32.74	344.1	Mean 344.4				

376. Ethyl mesaconate. B. p. 95°/6 mm.; M 186.20; n_C 1.44485, n_D 1.44806, n_F 1.45620, n_G 1.46261; R_C 47.50, R_D 47.80, R_F 48.54, R_G 49.13; Mn_D^{20} 269.64. Densities determined: d_4^{20} 1.0429, d_4^{41-65} 1.0233, d_4^{61-65} 1.0039, d_4^{86-65} 0.9784. Apparatus D.

20.1°	12.27	1.0428	31.60	423.3	61.2°	11.01	1.0042	27.30	423.9
24.1	12.16	1.0390	31.20	423.6	87.2	10.26	0.9781	24.78	424.8
41.2	11.55	1.0232	29.19	423.0	Mean 423.7				

377. n-Propyl mesaconate. B. p. 128°/10 mm.; M 214.25; n_C 1.44725, n_D 1.45037, n_F 1.45823, n_G 1.46453; R_C 56.77, R_D 57.11, R_F 57.96, R_G 58.65; Mn_D^{20} 310.75. Densities determined: d_4^{20} 1.0090, d_4^{40-65} 0.9899, d_4^{50-65} 0.9739, d_4^{86-65} 0.9483. Apparatus A.

16.3°	16.51	1.0123	31.30	500.6	59.8°	14.87	0.9732	27.10	502.3
18.4	16.44	1.0104	31.10	500.8	86.0	13.90	0.9489	24.70	503.3
40.9	15.57	0.9899	28.86	501.6	Mean 501.7				

378. Methyl methylsuccinate. B. p. 196°/760 mm.; M 160.17; n_C 1.41747, n_D 1.41956, n_F 1.42460, n_G 1.42825; R_C 37.49, R_D 37.66, R_F 38.05, R_G 38.34; Mn_D^{20} 227.38. Densities determined: d_4^{20} 1.0755, d_4^{39-65} 1.0558, d_4^{55-65} 1.0360, d_4^{85-65} 1.0096. Apparatus A.

22.1°	16.40	1.0734	32.96	357.5	60.6°	14.76	1.0352	28.61	357.9
25.1	16.34	1.0704	32.75	358.0	93.7	13.41	1.0015	25.15	358.1
40.2	15.67	1.0552	30.96	358.1	Mean 357.9				

379. Ethyl methylsuccinate. B. p. 217°/764 mm.; M 188.22; n_C 1.41667, n_D 1.41876, n_F 1.42380, n_G 1.42701; R_C 46.87, R_D 47.07, R_F 47.56, R_G 47.88; Mn_D^{20} 267.05. Densities determined: d_4^{20} 1.0094, d_4^{42-65} 0.9896, d_4^{52-65} 0.9702, d_4^{86-65} 0.9464. Apparatus D.

22.4°	11.92	1.0072	29.65	436.1	61.0°	10.72	0.9712	25.71	436.4
24.4	11.82	1.0057	29.36	435.7	87.3	9.98	0.9454	23.30	437.4
41.1	11.31	0.9906	27.67	436.1	Mean 436.2				

380. n-Propyl methylsuccinate. B. p. 246.5°/763 mm.; M 216.27; n_C 1.42272, n_D 1.42486, n_F 1.43001, n_G 1.43381; R_C 56.00, R_D 56.25, R_F 56.84, R_G 57.28; Mn_D^{20} 308.16. Densities determined: d_4^{20} 0.9829, d_4^{40-65} 0.9654, d_4^{50-65} 0.9473, d_4^{85-65} 0.9252. Apparatus D.

23.0°	12.08	0.9802	29.24	513.1	41.9°	11.61	0.9641	27.65	514.4
26.3	12.01	0.9764	28.97	513.9	60.5	11.02	0.9476	25.79	514.3
31.3	11.85	0.9730	28.47	513.5	86.0	10.27	0.9243	23.44	514.9
Mean 514.0									

381. Methyl crotonate. B. p. 119°/768 mm.; M 100.11; n_C 1.42151, n_D 1.42466, n_F 1.43262, n_G 1.43890; R_C 26.87, R_D 27.05, R_F 27.49, R_G 27.83; Mn_D^{20} 142.63. Densities determined: d_4^{20} 0.9458, d_4^{41-75} 0.9251, d_4^{59-75} 0.9058, d_4^{85-85} 0.8771. Apparatus D.

19.0°	12.26	0.9468	28.67	244.7	60.5°	10.67	0.9050	23.83	244.4
22.9	12.20	0.9429	28.41	245.1	87.4	9.56	0.8755	20.67	244.4
41.4	11.37	0.9254	25.98	244.2	Mean 244.6				

A sample of ester prepared from the silver salt and methyl iodide had b. p. 120°/772 mm., d_4^{20} 0.9457, n_D 1.42161, n_D 1.42476, n_F 1.43262, n_G 1.43904.

382. Ethyl crotonate. B. p. 136.5°/761 mm.; M 114.14; n_D 1.42167, n_D 1.42471, n_F 1.43228, n_G 1.43822; R_C 31.57, R_D 31.76, R_F 32.26, R_G 32.64; Mn_D^{20} 162.62. Densities determined: d_4^{20} 0.9183, d_4^{30} 0.8986, d_4^{40} 0.8772, d_4^{50} 0.8530. Apparatus D.

t .	H .	d_4^t .	γ .	P .	t .	H .	d_4^t .	γ .	P .
20.3°	12.01	0.9180	27.23	284.0	61.6°	10.47	0.8776	22.69	283.9
25.1	11.78	0.9138	26.58	283.6	87.5	9.51	0.8526	20.02	283.5
40.9	11.23	0.8985	24.92	283.8					Mean 283.8

A sample of ester prepared from silver crotonate and ethyl iodide had b. p. 136.5°/765 mm.; d_4^{20} 0.9181, n_D 1.42179, n_D 1.42481, n_F 1.43238, n_G 1.43837.

383. n-Propyl crotonate. B. p. 157.5°/768 mm.; M 128.17; n_D 1.42549, n_D 1.42842, n_F 1.43576, n_G 1.44147; R_C 36.12, R_D 36.34, R_F 36.89, R_G 37.31; Mn_D^{20} 183.08. Densities determined: d_4^{20} 0.9082, d_4^{30} 0.8892, d_4^{40} 0.8700, d_4^{50} 0.8451. Apparatus A.

14.1°	16.62	0.9136	28.43	324.0	61.5°	14.34	0.8701	23.36	323.9
27.8	16.05	0.9010	27.08	324.5	87.5	13.13	0.8446	20.77	323.8
41.9	15.34	0.8889	25.53	324.1					Mean 324.1

384. n-Butyl crotonate. B. p. 55°/4 mm.; M 142.19; n_D 1.42960, n_D 1.43249, n_F 1.43971, n_G 1.44532; R_C 40.81, R_D 41.05, R_F 41.64, R_G 42.10; Mn_D^{20} 203.69. Densities determined: d_4^{20} 0.8994, d_4^{30} 0.8811, d_4^{40} 0.8630, d_4^{50} 0.8403. Apparatus D.

18.5°	12.57	0.9007	27.96	363.0	61.8°	11.16	0.8626	23.72	364.0
25.3	12.38	0.8947	27.35	363.5	87.1	10.35	0.8393	21.45	364.6
41.2	11.90	0.8814	25.90	363.9					Mean 363.8

385. n-Amyl crotonate. B. p. 71.5°/5 mm.; M 156.22; n_D 1.43315, n_D 1.43600, n_F 1.44308, n_G 1.44848; R_C 45.46, R_D 45.71, R_F 46.36, R_G 46.85; Mn_D^{20} 224.33. Densities determined: d_4^{20} 0.8935, d_4^{30} 0.8761, d_4^{40} 0.8587, d_4^{50} 0.8370. Apparatus A.

18.3°	17.00	0.8949	28.49	403.3	62.0°	15.06	0.8584	24.21	403.7
27.3	16.62	0.8874	27.62	403.6	87.3	14.01	0.8363	21.94	404.3
41.1	15.94	0.8763	26.16	403.2					Mean 403.8

386. isoAmyl crotonate. B. p. 60°/3.5 mm.; M 156.22; n_D 1.43130, n_D 1.43415, n_F 1.44123, n_G 1.44672; R_C 45.42, R_D 45.69, R_F 46.33, R_G 46.83; Mn_D^{20} 224.05. Densities determined: d_4^{20} 0.8908, d_4^{30} 0.8712, d_4^{40} 0.8540, d_4^{50} 0.8326. Apparatus D.

19.7°	12.42	0.8911	27.34	400.8	62.4°	11.00	0.8535	23.19	401.6
25.0	12.26	0.8864	26.84	401.1	86.9	10.26	0.8322	21.09	402.2
41.5	11.67	0.8716	25.12	401.3					Mean 401.4

387. Ethyl cinnamate. B. p. 127°/6 mm.; M 176.21; n_D 1.55219, n_D 1.55983, n_F 1.58085; R_C 53.67, R_D 54.28, R_F 55.95; Mn_D^{20} 274.85. Densities determined: d_4^{20} 1.0494, d_4^{30} 1.0310, d_4^{40} 1.0158, d_4^{50} 0.9939. Apparatus A.

22.3°	19.18	1.0475	37.62	416.6	40.2°	18.49	1.0325	35.75	417.3
26.0	19.04	1.0444	37.24	416.8	60.6	17.68	1.0154	33.62	417.9
32.9	18.86	1.0386	36.68	417.5	87.1	16.62	0.9930	30.90	418.4
									Mean 417.4

388. n-Propyl cinnamate. B. p. 148°/10 mm.; M 190.23; n_D 1.54403, n_D 1.55123, n_F 1.57094, n_G 1.58908; R_C 58.41, R_D 59.05, R_F 60.79, R_G 62.36; Mn_D^{20} 295.12. Densities determined: d_4^{20} 1.0282, d_4^{30} 1.0107, d_4^{40} 0.9963, d_4^{50} 0.9756. Apparatus A.

21.4°	18.92	1.0270	36.38	455.0	42.1°	18.17	1.0106	34.38	455.9
24.6	18.85	1.0245	36.16	455.4	62.1	17.48	0.9951	32.57	456.7
31.0	18.66	1.0195	35.62	455.9	85.5	16.52	0.9758	30.19	457.0
									Mean 456.0

389. n-Butyl cinnamate. B. p. 162°/12 mm.; M 204.26; n_D 1.53736, n_D 1.54417, n_F 1.56283, n_G 1.5799 (line faint; value may be in error); R_C 63.03, R_D 63.69, R_F 65.49, R_G 67.12; Mn_D^{20} 315.42. Densities determined: d_4^{20} 1.0127, d_4^{30} 0.9961, d_4^{40} 0.9810, d_4^{50} 0.9608. Apparatus A.

22.5°	18.75	1.0108	35.49	493.2	61.5°	17.28	0.9798	31.70	494.7
30.9	18.50	1.0042	34.87	494.0	87.3	16.42	0.9598	29.51	496.0
41.1	18.06	0.9964	33.70	493.9					Mean 494.4