134. *Physical Properties and Chemical Constitution. Part XVII. Acetylenic Compounds and Cyanides.*

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New measurements are described of the parachors and refractivities (20°) of esters of but-3-yne-1-carboxylic acid and of dec-9-yne-1-carboxylic (10 : 11-undecynolic) acid. The contributions of the terminal triple bond have been computed from the general relationship

$$|\!\equiv\; = \mathrm{CH{\equiv}CR} + 4\mathrm{H} - \mathrm{CH_3{\cdot}CH_2R}$$

employing the values for H of Part IX (*J.*, 1946, 133) and the appropriate saturated compounds to be found in previous papers of this series. The constants, which differ considerably from those previously accepted, are :

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$|\!\equiv$ (terminal)	40·6	1·959	1·977	2·061	2·084	−12·56

The constants similarly deduced from new experimental data for dialkyl acetylenedicarboxylates (I) and alkyl phenylpropiolates (II), in which the triple bond is non-terminal and conjugated with other groups in the molecule, are :

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$|\!\equiv$ in (I) (non-terminal)	46·8	3·890	3·960	4·190	4·330	−11·83
$|\!\equiv$ in (II) (non-terminal)	45·9	5·503	5·677	6·277	6·780	−6·23

New measurements upon a series of alkyl and other cyanides are also presented and these lead, when combined with the values for alkyl groups (Part XI, this vol., p. 610), to the following constants for the C≡N group in saturated aliphatic cyanides :

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
CN	64·6	5·431	5·459	5·513	5·561	36·46

THE parachor contribution of 46·6 for the carbon–carbon triple bond appears to have been deduced initially (Sugden, *J.*, 1924, **125**, 1180) from the values for acetylene and octyne, to which were later added ethyl and "*i*-butyl" phenylpropiolates (Sugden, "The Parachor and Valency", 1930, p. 42; no details of the preparation, densities, and surface tensions seem to have been published), and it is stated (*J.*, *loc. cit.*) that this value "agress well with that found for nitriles". Sugden does not disclose how the parachor for nitrogen was calculated, nor have figures been published supporting the constancy (or otherwise) of the parachor in different types of nitrogen-containing compounds (*e.g.*, in primary, secondary, and tertiary amines). The agreement claimed for the triple bond in acetylenic compounds and in cyanides is therefore not entirely convincing. We prefer, in the first instance to separate the two problems and to deduce independent values for the carbon–carbon triple bond in acetylenic compounds and for the C≡N grouping.

Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 604; compare von Auwers, *Ber.*, 1935, **68**, 1635) utilised the data for "propargyl alcohol, propargyl acetate, propargyl ethyl ether, oenanthilidene, caprylidene, amyl propiolacetal, hexyl propiolacetal and diacetal", but states that the figures for the acetylene bond varied considerably and consequently the final mean value could only be regarded as approximate. Notwithstanding this admission, the constants are given to four significant figures as follows :

	R_C.	R_D.	R_F.	$R_{G'}$.
$|\!\equiv$	2·328	2·398	2·506	2·538

In recent years a number of pure acetylenic hydrocarbons and their derivatives have been prepared (compare Campbell and O'Connor, *J. Amer. Chem. Soc.*, 1939, **61**, 2898; Campbell and Eby, *ibid.*, 1940, **62**, 180; 1941, **63**, 2384; Henne and Greenlee, *ibid.*, 1945, **67**, 484; Hennion and Banigan, *ibid.*, 1946, **68**, 1202, 1380) and their densities ($d_4^{20°}$) and refractivities ($n_D^{20°}$) determined. The refractivities R_D, calculated with Eisenlohr's constants, are not in good agreement with the observed values : attempts to obtain improved agreement have been made by Campbell and Eveslage (*ibid.*, 1945, **67**, 1851) by assigning a new set of increments for 1-, 2-, 3-, 4- and 5-acetylenes respectively and by Hennion and Banigan (*ibid.*, 1946, **68**, 1380) by employing the following atomic refractions : $C^{\equiv}$ 3·240, C^{α} 2·779, C^{β} 2·605, C^{γ} 2·436, $C^{\delta\ldots\omega}$ 2·418, and H 1·100. Apart from the fact that the values for C and H were in error (Vogel, Part IX, *J.*, 1946, 133), the procedures of the American authors are clearly empirical : a simple method is described below which gives reasonable results.

We have determined the parachors and refractivities of a number of esters of but-3-yne-1-

carboxylic acid, $CH\vdots C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, and of dec-9-yne-1-carboxylic (10 : 11-undecynolic) acid and computed the contributions of the terminal triple bond by means of the relationship

$$\vert\!\!\equiv\ = CH\vdots CR + 4H - CH_3{\cdot}CH_2R$$

utilising the values for H deduced in Part IX (*loc. cit.*) and the data for alkyl *n*-valerates (Part XIII, this vol., p. 624) and for alkyl *n*-undecylates as computed in Part XVI (preceding paper).

Our dec-9-yne-1-carboxylic acid was prepared by the action of excess of concentrated aqueous potassium hydroxide solution upon 9 : 10-dibromodecane-1-carboxylic acid (10 : 11-dibromoundecoic acid) at 150—160° in the presence of small quantities of crude sodium oleylsulphonate to reduce the attendant frothing (compare Krafft, *Ber.*, 1896, **29**, 2232; Myddelton and Barrett, *J. Amer. Chem. Soc.*, 1927, **49**, 2260). It melted at 42° and its constitution was established (*a*) by oxidation with potassium permanganate solution, whereby an almost quantitative yield of sebacic acid was obtained :

$$CH\vdots C{\cdot}[CH_2]_8{\cdot}CO_2H \longrightarrow [CH_2]_8(CO_2H)_2,$$

and (*b*) by reduction of the ethyl ester with hydrogen in the presence of Adams's platinum oxide catalyst, whereupon ethyl *n*-undecylate was isolated in quantitative yield and its physical properties were in excellent agreement with those deduced in Part XVI (*loc. cit.*).

It should be noted that dec-8-yne-1-carboxylic acid (9 : 10-undecolic acid), $CH_3{\cdot}C\vdots C{\cdot}[CH_2]_7{\cdot}CO_2H$, *m. p. 61°*, is formed from 9 : 10-dibromodecane-1-carboxylic acid and excess of concentrated aqueous potassium hydroxide solution *at 170°* (Harris and Smith, *J.*, 1935, 1108 : compare Krafft, *Ber.*, 1878, **11**, 1414; Welander, *ibid.*, 1895, **28**, 1445; Myddelton and Barrett, *loc. cit.*; Ashton and Smith, *J.*, 1934, 435) ; the reaction is under investigation.

The results for the triple-bond contributions are collected in Table I.

TABLE I.

Parachor and refractivities of the triple bond from esters, $CH\vdots C{\cdot}[CH_2]_n{\cdot}CO_2R$.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Esters of but-3-yne-1-carboxylic acid, $CH\vdots C{\cdot}[CH_2]_2{\cdot}CO_2R$.						
R = Me	40·7	1·97	1·99	2·08	2·09	−12·27
R = Et	40·2	1·98	2·00	2·08	2·12	−12·40
R = Pr^n	40·1	2·01	2·03	2·11	2·13	−12·71
R = Bu^n	39·6	2·05	2·06	2·15	2·17	−12·81
Esters of dec-9-yne-1-carboxylic acid, $CH\vdots C{\cdot}[CH_2]_8{\cdot}CO_2R$.						
R = Me	41·8	1·92	1·94	2·04	2·05	−12·53
R = Et	41·1	1·87	1·88	1·94	1·98	−12·59
R = Pr^n	40·7	1·91	1·94	2·03	2·05	−12·60
Mean $\vert\!\!\equiv$	40·6	1·959	1·977	2·061	2·084	−12·56

It will be observed that the mean values for the parachors and refractivities differ appreciably from those previously accepted. The new constants apply only to terminal acetylenic compounds $CH\vdots CR$; it is hoped in the near future to investigate compounds containing non-terminal carbon–carbon triple bonds $CR_1\vdots CR_2$. Von Auwers (*Ber.*, 1935, **68**, 1635) gives for the D line values of 2·325 for terminal acetylenes and 2·573 for non-terminal acetylenes.

The results of similar measurements upon dialkyl acetylenedicarboxylates and alkyl phenylpropiolates—all of which are conjugated compounds—are presented in Tables II and III respectively : the experimental data for dialkyl succinates were taken from Part XIII (*loc. cit.*) and those for alkyl β-phenylpropionates from Part XVI (preceding paper). The high values for the refractivities were, of course, anticipated, but the higher values for the parachor (which normally does not reflect the influence of conjugation—see Part XVI on ethylenic compounds) are noteworthy.

TABLE II.

Parachor and refractivities for the triple bond in dialkyl acetylenedicarboxylates, $CO_2R{\cdot}C\vdots C{\cdot}CO_2R$.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
R = Me	46·2	3·79	3·84	4·05	4·18	−12·09
R = Et	48·4	3·94	4·03	4·25	4·39	−12·10
R = Pr^n	48·2	3·94	4·02	4·25	4·38	−11·83
R = Pr^i *	51·6	3·99	4·07	4·30	4·45	−11·72
R = Bu^n	46·3	3·86	3·91	4·14	4·30	−11·75
R = Am^n	46·9	3·97	4·05	4·29	4·42	−11·67
R = Am^i	45·0	3·84	3·91	4·16	4·31	−11·52
Mean (excluding *)	46·8	3·890	3·960	4·190	4·330	−11·83

TABLE III.

Parachor and refractivities for the triple bond in alkyl phenylpropiolates, $\text{CPh⁝C·CO}_2\text{R}$.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	Mn_D^{20}.
R = Et	47·0	5·48	5·68	6·27	6·77	−6·21
R = Pr^n	46·3	5·63	5·75	6·35	6·85	−6·25
R = Bu^n	44·4	5·40	5·60	6·21	6·72	−6·24
Mean	45·9	5·503	5·677	6·277	6·780	−6·23

Determination of the parachors and refractivities of seven aliphatic cyanides, allyl cyanide, trimethylene dicyanide, phenyl cyanide, and benzyl cyanide have also been made. The CN contributions for the aliphatic nitriles have been computed with the aid of the constants for the alkyl groups given in Part XI (this vol., p. 610), for trimethylene dicyanide using the CH_2 values from Part IX (*J.*, 1946, 133), phenyl cyanide from phenyl (Part XV, this vol., p. 654), and benzyl cyanide from $C_6H_5{\cdot}CH_3$ − H (Part X, this vol., p. 607, and Part IX, *loc. cit.*). The preferred values for CN are derived from the saturated aliphatic nitriles. The results are given in Table IV. Measurements of the densities and refractivities at 0°, 15°, and 30° of a long series of carefully purified aliphatic nitriles have been made by Merckx, Verhulst, and Bruylants (*Bull. Soc. chim. Belg.*, 1933, **42**, 177): although the methods of preparation, in many cases, differed from our own, the interpolated values for $d_{4°}^{20°}$ and $n_D^{20°}$ are in good agreement.

TABLE IV.

Parachor and refractivities for the CN *group in cyanides.*

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
MeCN	66·2	5·40	5·44	5·49	5·54	37·05
EtCN	65·5	5·42	5·45	5·51	5·56	36·51
Pr^{n}CN	64·9	5·45	5·46	5·52	5·57	36·41
Bu^{n}CN	64·9	5·40	5·42	5·47	5·51	36·58
Am^{n}CN	63·0	5·44	5·47	5·51	5·56	36·23
Am^{i}CN	63·9	5·49	5·52	5·58	5·63	36·30
$C_6H_{13}^n{\cdot}CN$	—	5·42	5·45	5·51	5·56	36·12
Mean C≡N	64·6	5·431	5·459	5·513	5·561	36·46
$[CH_2]_3(CN)_2$	65·8	5·31	5·33	5·36	5·42	36·39
$C_3H_5{\cdot}CN$	63·5	5·13	5·15	5·18	5·21	36·72
$C_6H_5{\cdot}CN$	69·0	6·07	6·12	6·23	6·32	35·70
$C_6H_5{\cdot}CH_2{\cdot}CN$	64·4	5·14	5·17	5·19	5·19	37·93

We have employed the experimental data given by Henne and Greenlee (*J. Amer. Chem. Soc.*, 1945, **67**, 484) and by Hennion and Banigan (*ibid.*, 1946, **68**, 1380) for $d_{4°}^{20°}$, $n_D^{20°}$, and R_D for the calculation of the refractivity for the triple bond, utilising our own values for H and for saturated aliphatic hydrocarbons (Part IX, *loc. cit.*). The results for terminal acetylenes (which alone are strictly comparable with our own data for terminal acetylenic compounds) are collected in Table V.

TABLE V.

Values for the triple bond in hydrocarbons and alcohols with terminal acetylenic groups.

Compound.	|≡.	R_D, obs.	R_D, calc. (Authors.)	R_D, calc. (H. and B.)
Pent-1-yne	1·95	23·12	23·16	23·10
Hex-1-yne	1·95	27·77	27·79	27·74
Hept-1-yne	1·95	32·44	32·43	32·34
5-Methylhex-1-yne	1·98	32·47	32·43	32·34
Oct-1-yne	2·00	37·06	37·08	36·95
Hepta-1 : 6-diyne	1·96	30·30	30·28	29·92 *
Nona-1 : 8-diyne	1·94	39·52	39·58	39·36 *
Prop-1-yne-3-ol	1·91	15·34	15·36	15·18 *
But-1-yne-4-ol	1·96	19·90	20·01	19·99 *
3 : 3-Dimethylprop-1-yne-3-ol	2·01	24·77	24·65	24·79 *

In deducing the figures for the triple bond we have employed our own (unpublished) data for the corresponding saturated alcohols. The values for the triple bond agree well with those deduced from our own measurements. The calculated values for R_D employing our own figures for C, H, OH (2·543), and |≡ (in CH⁝CR) are given in col. 4. Hennion and Banigan's figures are in col. 5; those marked with an asterisk have been computed by us with their constants and Eisenlohr's values for OH.

The results for acetylenic hydrocarbons with non-terminal acetylene groups are given in Table VI. The mean value of the refractivity of the triple bond for the D line at 20° is 2·35 with a variation from the mean of ± 0·10. It would therefore appear that the refractivity of the triple bond in these compounds is greater than that in compounds with the terminal ⋮CH group. The calculated refractivities derived with the aid of the authors' C and H constants and the above non-terminal triple bond value are reasonably satisfactory and render the highly empirical procedures of Campbell and Eveslage (*J. Amer. Chem. Soc.*, 1945, **67**, 1851) and of Hennion and Banigan (*loc. cit.*) superfluous.

TABLE VI.

Values for the triple bond in hydrocarbons with non-terminal acetylenic groups.

Hydrocarbon.	$\equiv$.	R_D, obs.	R_D, calc. (Authors.)	R_D, calc. (H. and B.)
Pent-2-yne	2·28	23·44	23·53	23·44
Hex-3-yne	2·39	28·20	28·18	28·25
Oct-2-yne	2·25	37·31	37·47	37·32
Oct-3-yne	2·40	37·46	37·47	37·50
Oct-4-yne	2·45	37·51	37·47	37·52
Non-3-yne	2·35	42·09	42·12	42·12
Dec-5-yne	2·36	46·75	46·76	46·75
Undec-5-yne	2·27	51·31	51·41	51·37
Nona-2 : 7-diyne	2·42	40·57	40·36	39·88
Mean	2·35			

EXPERIMENTAL.

Esters of But-3-yne-1-carboxylic Acid.—*But-3-yne-1-carboxylic acid.* Allyl bromide, b. p. 71—72° (XVI, **357**), was converted into 1 : 2 : 3-tribromopropane, b. p. 92—93°/10 mm. (*Org. Synth.*, Coll. Vol. I, 1941, 521), and then condensed with ethyl sodioacetoacetate (Gardner and Perkin, *J.*, 1907, **91**, 848). The pure ester, $CH_2{:}CBr{\cdot}CH_2{\cdot}CH(COMe){\cdot}CO_2Et$, b. p. 114—115°/10 mm. (Gardner and Perkin, *loc. cit.*, give b. p. 120—121°/8 mm.), was isolated by fractionation from a Scorah flask and was treated with methyl-alcoholic potassium hydroxide (Perkin and Simonsen, *J.*, 1907, **91**, 822) to give but-3-yne-1-carboxylic acid, m. p. 54°; recrystallisation from light petroleum (b. p. 40—60°) raised the m. p. to 56—57°. The yield of acid from 46 g. of sodium, 600 ml. of absolute ethyl alcohol, 260 g. of ethyl acetoacetate, and 290 g. of tribromopropane was 21 g. A mixture of 10 g. of the acid, 80 g. of absolute methyl alcohol, and 6 g. of concentrated sulphuric acid was kept at room temperature for 1 week, poured into water, and the separated oil extracted with ether, dried, and distilled. This gave 9 g. of the *methyl* ester, b. p. 146·5°/754 mm. (Found : C, 64·0; H, 7·3. $C_6H_8O_2$ requires C, 64·3; H, 7·2%).

Ethyl ester. (1) By the above method, but with 90 g. of absolute ethyl alcohol, 9 g. of this ester were obtained; b. p. 159°/763 mm. (Perkin and Simonsen, *loc. cit.*, give b. p. 160—161°).

(2) A mixture of 10 g. of the acid, 9 ml. of absolute ethyl alcohol, 1 ml. of concentrated sulphuric acid, and 18 ml. of sodium-dried A.R. benzene was refluxed for 12 hours. The resulting dark liquid, after being poured into water and worked up in the usual manner, afforded 7 g. of a liquid ester, b. p. 195°/763 mm., $d_{4^\circ}^{20^\circ}$ 1·0049, $n_D^{20^\circ}$ 1·4241. It was evidently not the desired ester and was not further investigated.

n-*Propyl ester.* A mixture of 10 g. of the acid, 120 g. of pure *n*-propyl alcohol, and 8 g. of concentrated sulphuric acid, kept at room temperature for 21 days and worked up in the usual manner, gave 6 g. of the n-*propyl* ester, b. p. 174·5—175·5°/763 mm. (Found : C, 68·4; H, 8·7. $C_8H_{12}O_2$ requires C, 68·5; H, 8·6%).

n-*Butyl ester.* To a cold solution of 10 g. of concentrated sulphuric acid in 180 ml. of pure *n*-butyl alcohol were added 12·5 g. of the acetylenic acid, the mixture was kept at room temperature for 24 days, and then poured into excess of water. The upper, organic layer was removed, washed successively with water, saturated sodium hydrogen carbonate solution until effervescence ceased, and water, dried ($CaCl_2$), and fractionated. *n*-Butyl alcohol passed over first and when the volume was about 25 ml. much solid separated (presumably the addition compound $CaCl_2,xBu^nOH$). When this was cold, anhydrous ether was added, the solid filtered off, the ether removed, and the residue distilled; 8 g. of the n-*butyl* ester (a very pale yellow liquid) were collected at 193·5—194·5°/759 mm. Redistillation gave a perfectly colourless liquid, b. p. 71°/6 mm. (Found : C, 69·8; H, 9·1. $C_9H_{14}O_2$ requires C, 70·1; H, 9·2%).

Esters of Dec-9-yne-1-carboxylic Acid.—*Dec-9-yne-1-carboxylic acid.* Undecylenic acid was purified through the methyl ester (preceding paper) and had a setting point of 23·5°; practically identical results were obtained with the redistilled acid, b. p. 152—154°/6 mm., s. p. 22·6—22·8°. In a 1500-ml. three-necked flask, equipped with a double-surface condenser, a mercury-sealed mechanical stirrer, and a dropping-funnel, was placed a solution of 108 g. of purified undecylenic acid in 285 ml. of dry A.R. carbon tetrachloride. The solution was cooled in a bath of ice and salt and 96 g. of dry A.R. bromine were added during 1 hour. The product was allowed to attain room temperature, the solvent distilled off from a water-bath, and the residue transferred to a basin; after standing in the air for several days (or keeping in a vacuum desiccator over silica gel), it solidified completely. The yield of 9 : 10-dibromodecane-1-carboxylic acid was quantitative.

The solid dibromo-acid was mixed with a solution of 263 g. of potassium hydroxide in 158 ml. of water in a 2-l. round-bottomed flask equipped with a double-surface condenser, and the whole heated in a bath at 150—160° for 8 hours; foaming was reduced by addition of small quantities of crude sodium oleylsulphonate ("pentrone-T") from time to time. After the product had stood overnight, 1·5 l. of water were added, and the mixture was shaken until the solid had dissolved, acidified with dilute sulphuric acid to Congo-red, and set aside for 12 hours, whereupon a cake of acid separated on the surface. This was extracted with four 250-ml. portions of ether, the ether removed, and the residue distilled with a free flame. Two fractions were collected: (*a*) b. p. 177—182°/15 mm., 52 g., solidifying completely on cooling to a solid, m. p. 38—41°, and (*b*) b. p. 182—200°/15 mm., 15 g., solidifying on cooling to a somewhat sticky solid. Recrystallisation of (*a*) from A.R. light petroleum (b. p. 60—80°) yielded a first crop of 31 g. of acid, m. p. 42°; the filtrate was allowed to evaporate spontaneously, and the resulting sticky solid, after being spread on porous porcelain and recrystallised, gave a further 2 g. of acid, m. p. 42°. Fraction (*b*), after similar treatment afforded 3 g. of acid, m. p. 42°. Further recrystallisation did not alter the m. p.

In another experiment a mixture of 120 g. of the dibromo-acid and a solution of 140 g. of potassium hydroxide in 90 ml. of water, contained in a 2-l. flask fitted with a reflux condenser, was heated in an oil-bath at 160° for 30 minutes; much foaming occurred. Upon working up as above, there were obtained: (*a*) 25 g., b. p. 177—180°/17 mm.; this solidified immediately on cooling (m. p. 40—42°) and after recrystallisation from light petroleum (b. p. 40—60°) had m. p. 42° (16 g.); (*b*) 19 g., b. p 180—210°/17 mm., which set to a soft sticky mass on cooling and yielded only 1 g. of the acid, m. p. 42° (Found: equiv., 184. Calc. for $C_{11}H_{18}O_2$: equiv., 182).

Oxidation of the acetylenic acid of m. p. 42°. 2·00 G. of the acid were dissolved in 50 ml. of water containing 0·585 g. of A.R. anhydrous sodium carbonate, the solution was kept saturated with carbon dioxide, and 0·1N-potassium permanganate solution was added slowly and with constant stirring until a slight excess was present after standing for 30 minutes (compare Perkin and Simonsen, *J.*, 1907, **91**, 828): 1500 ml. were required and the addition occupied 3 hours. The solution was decolorised with sulphur dioxide and kept for 24 hours at room temperature. The acid was filtered off through a weighed Gooch crucible and dried to constant weight; its m. p. was 133°, unaffected by recrystallisation from acetone, and unaltered by admixture with pure sebacic acid, m. p. 133—134°. The yield of sebacic acid was 1·45 g.; to this must be added the dissolved acid contained in 1550 ml. of solution. There can therefore be little doubt that the acid, m. p. 42°, is dec-9-yne-1-carboxylic acid.

Methyl ester. A mixture of 13 g. of the acetylenic acid, 80 g. of absolute methyl alcohol, and 10 g. of concentrated sulphuric acid was kept at room temperature for 14 days, poured into excess of water, and extracted with ether. The ethereal extract was washed with saturated sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and the solvent removed. Distillation gave 12 g. of the pure *methyl* ester, b. p. 121°/5 mm. (Found: C, 72·9; H, 10·1. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·0%).

Ethyl ester. (1) A mixture of 15 g. of the acid, 9 g. of absolute ethyl alcohol, 1 ml. of concentrated sulphuric acid, and 25 ml. of sodium-dried A.R. benzene was refluxed for 38 hours and yielded, after being worked up in the usual manner, 12·5 g. of ester, b. p. 134·5°/6·5 mm.

(2) A mixture of 10 g. of the acid, 50 g. of absolute ethyl alcohol, and 6 g. of concentrated sulphuric acid was kept at room temperature for 8 days and afforded, as for the methyl ester, 10 g. of ethyl ester of b. p. 142°/13 mm.

n-*Propyl ester.* (1) A mixture of 10 g. of the acid, 80 g. of pure anhydrous *n*-propyl alcohol, and 6 g. of concentrated sulphuric acid was kept at room temperature for 20 days, poured into excess of water, and extracted with ether. The extract was purified as above, and the ether and the excess of alcohol were removed at atmospheric pressure. Further distillation gave 9 g. of the n-*propyl* ester, b. p. 142°/6 mm. (Found: C, 75·0; H, 10·7. $C_{14}H_{24}O_2$ requires C, 75·0; H, 10·8%).

(2) A mixture of 12 g. of the acid, 10 g. of pure *n*-propyl alcohol, 3 g. of concentrated sulphuric acid, and 25 ml. of sodium-dried A.R. benzene was refluxed for 20 hours. After working up as usual, 12 g. of ester, b. p. 161—162°/13 mm., 138°/5 mm., were obtained; this had $d_{4°}^{20°}$ 0·9051, $n_D^{20°}$ 1·4457, R_D 66·06 (*M*, 224·33), and was evidently not the desired product.

Reduction of ethyl ester: ethyl n-*undecylate.* 19·5 G. of the acetylenic ester were mixed with 25 ml. of absolute ethyl alcohol and reduced with hydrogen at atmospheric pressure in the presence of 0·3 g. of Adams's platinum oxide catalyst. 4470 Ml. of hydrogen were absorbed during 4·5 hours and no further absorption occurred during 5 hours; the theoretical absorption (765 mm. and 20°) is 4505 ml. plus 60 ml. for the reduction of the platinum oxide catalyst. The platinum was filtered off, the alcohol removed at atmospheric pressure and the ester distilled, whereby 18 g., b. p. 115·5°/5 mm., were obtained. The ester was slightly turbid; the turbidity was removed by dissolving in ether, washing with sodium hydrogen carbonate solution (there was no apparent reaction) and water, drying, and distilling: b. p. 118°/7 mm. The physical properties agreed with those calculated from 0·5(ethyl *n*-decoate + ethyl *n*-dodecoate) and from ethyl *n*-decoate + CH_2 (Part XIII, this vol., p. 624; compare preceding paper).

Esters of Acetylenedicarboxylic Acid.—Acetylenedicarboxylic acid, prepared from pure fumaric acid as described in *Org. Synth.*, 1938, **18**, 17, 3, had m. p. 177—178° (*Org. Synth.*, *loc. cit.*, gives m. p. 175—176°; Moureu and Bongrand, *Ann. Chim.*, 1920, **14**, 9, give m. p. 178·5—179°).

Dimethyl ester. (1) The following modification of Moureu and Bongrand's method (*loc. cit.*) was employed. In a 1-l. three-necked flask, provided with a thermometer, mechanical stirrer, and reflux condenser protected by a calcium chloride tube, was placed a cold mixture of 80 g. of pure anhydrous methyl alcohol and 40 g. of concentrated sulphuric acid: 20 g. of acetylenedicarboxylic acid were added, the mixture kept at room temperature for 66 hours and then, with stirring, at 50° for 58 hours. The mixture was poured into 120 ml. of saturated salt solution and extracted with five 80-ml. portions of ether: the combined extracts were washed with water, saturated sodium hydrogen carbonate solution (until colourless), and water, dried (Na_2SO_4), and the solvent removed on a water-bath. The residue upon distillation gave 13·7 g. of ester, b. p. 76·5°/3 mm.

(2) A mixture of 20 g. of acid, 16 g. of absolute methyl alcohol, 40 ml. of sodium-dried A.R. benzene, and 7 g. of concentrated sulphuric acid was refluxed for 5 hours, poured into 120 ml. of saturated salt solution, the benzene layer separated, and the aqueous phase extracted with three 150-ml. portions of ether. The combined extracts were worked up as in (1), the ether was removed on a water-bath and the

benzene under reduced pressure (water-pump), and the residue distilled (oil-pump); 15·5 g. of ester, b. p. 78·5°/4 mm., were obtained.

Diethyl ester. A mixture of 20 g. of the acid, 23 g. of absolute ethyl alcohol, 60 ml. of dry benzene, and 4 ml. of concentrated sulphuric acid was refluxed for 12 hours and yielded, as for the methyl ester, 20·5 g. of the ester, b. p. 85·5°/2·5 mm.

Di-n-*propyl ester.* A mixture of 20 g. of the acid, 30 g. of anhydrous *n*-propyl alcohol, 5 ml. of concentrated sulphuric acid, and 80 ml. of dry benzene was refluxed for 12·5 hours and yielded 24·9 g. of the *di*-n-*propyl* ester, b. p. 116°/5 mm. (Found: C, 60·5; H, 7·1. $C_{10}H_{14}O_4$ requires C, 60·6; H, 7·1%).

*Di*iso*propyl ester.* The same procedure (same quantities, 10 hours' refluxing) afforded 21·6 g. of ester, b. p. 96°/3 mm.

Di-n-*butyl ester.* A mixture of 15 g. of acid, 27 g. of absolute *n*-butyl alcohol, 70 ml. of dry benzene, and 5 ml. of concentrated sulphuric acid was refluxed for 19 hours and yielded, after two distillations, 15·5 g. of the n-*butyl* ester, b. p. 139°/5 mm. (Found: C, 63·6; H, 8·2. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%).

Di-n-*amyl ester.* A mixture of 20 g. of acid, 60 g. of *n*-amyl alcohol (Sharples, b. p. 136·5—137·5°/765 mm.), 150 ml. of dry benzene, and 8 ml. of concentrated sulphuric acid was refluxed for 18 hours and yielded, after two distillations, 26·0 g. of the n-*amyl* ester, b. p. 143°/1·5 mm. (Found: C, 66·0; H, 8·9. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·7%).

*Di*iso*amyl ester.* *iso*Butylcarbinol (Sharples, b. p. 129—130°/763 mm.), under exactly the same conditions (but 24 hours' refluxing), gave 28·5 g. of the iso*amyl* ester, b. p. 133°/2·5 mm. (Found: C, 66·1; H, 8·7. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·7%).

Esters of Phenylpropiolic Acid.—Phenylpropiolic acid, prepared according to *Org. Synth.*, 1932, **12**, 60, and recrystallised from A.R. carbon tetrachloride, had m. p. 134—135°.

Ethyl ester. A mixture of 120 g. of absolute ethyl alcohol and 9 g. of concentrated sulphuric acid was treated with 20 g. of phenylpropiolic acid, kept at room temperature for 7 days, poured into water, and the separated oil extracted with ether. The extract was washed successively with water, saturated sodium hydrogen carbonate solution, and water, dried, and the solvent removed. Distillation gave 18 g. of the ester, b. p. 124°/6 mm. Attempts to prepare the ester from silver phenylpropiolate and ethyl iodide in benzene solution were unsuccessful.

n-*Propyl ester.* A solution of 10 g. of concentrated sulphuric acid in 156 g. of absolute *n*-propyl alcohol was treated with 20 g. of phenylpropiolic acid and kept for 14 days at room temperature. After the same procedure as for the ethyl ester, the ether and excess of *n*-propyl alcohol were removed by heating in a bath to 130—140°. The residue, after two distillations, gave 17 g. of the n-*propyl* ester, b. p. 143°/7 mm. (Found: C, 76·4; H, 6·4. $C_{12}H_{12}O_4$ requires C, 76·6; H, 6·4%).

n-*Butyl ester.* To a cold solution of 13 g. of concentrated sulphuric acid in 195 g. of absolute *n*-butyl alcohol were added 20 g. of phenylpropiolic acid, and the mixture kept for 28 days at room temperature. This yielded, when worked up as for the *n*-propyl ester, 10 g. of the n-*butyl* ester, b. p. 149°/5 mm. (Found: C, 76·9; H, 7·1. $C_{13}H_{14}O_2$ requires C, 77·2; H, 7·0%).

Cyanides.—*Methyl cyanide.* 80 G. of pure acetamide (b. p. 219°/762 mm., m. p. 80—81°) were heated with 140 g. of phosphoric oxide and yielded, in the usual manner, 38 g. of methyl cyanide, b. p. 81°/757 mm.

Ethyl cyanide. The following procedure is based upon that given by Adams and Marvel ("Organic Chemical Reagents", 1921, III, 47; University of Illinois, 1921) (compare Walden, *Ber.*, 1907, **40**, 3215). In a 500-ml. three-necked flask, mounted on a wire gauze and equipped with a dropping funnel, mechanical stirrer, and wide-bored "knee-tube" attached to a double-surface condenser set for downward distillation, was placed a solution of 118 g. of sodium cyanide in 150 ml. of water. 192 G. of commercial ethyl sulphate were added to the boiling mixture at about the same rate as the liquid distilled; the addition was complete in 1 hour, 50 ml. of water were added, and the residual ethyl cyanide boiled out. The upper layer in the distillate was separated; the aqueous phase was saturated with calcium chloride, cooled in ice, and the small quantity of cyanide removed. To destroy the *iso*cyanide present, the product was shaken twice for 5 minutes with 5-ml. portions of concentrated hydrochloric acid; it was then washed with saturated potassium carbonate solution, shaken with calcium chloride solution, and dried (Na_2SO_4). The crude ethyl cyanide (62 g.) was fractionated and yielded 21 g., b. p. 96·5—98·5°/760 mm.; the low b. p. fraction (*ca.* 20 g.) was again dried ($NaSO_4$) and redistilled to give 10 g., b. p. 55—96° (a liquid with a pungent odour, which was not further investigated), and 10 g., b. p. 96—98°. Upon redistillation, the ethyl cyanide boiled constantly at 97·5°/765 mm. Attempts to prepare ethyl cyanide from aqueous methyl-alcoholic sodium cyanide and ethyl bromide gave unsatisfactory results.

n-*Propyl cyanide.* To a solution of 60 g. of sodium cyanide in 80 ml. of water contained in a 1-l. round-bottomed flask was added a solution of 124 g. of *n*-propyl bromide in 260 ml. of methyl alcohol. The mixture was refluxed for 39 hours, the liquid decanted into another flask, and the residual solid washed with 50 ml. of methyl alcohol. The methyl alcohol was removed by careful fractionation through a 3-section, Pyrex Young and Thomas column from a water-bath; further fractionation from an air-bath gave two fractions, b. p. 70—90° and 90—102°. Each was saturated with calcium chloride, the upper layers removed, combined, and shaken successively with a few ml. of concentrated hydrochloric acid (to remove *iso*cyanide), sodium hydrogen carbonate solution, calcium chloride solution, and dried (Na_2SO_4). Fractionation of the dry crude product (25 g.) afforded 19 g. of *n*-propyl cyanide, b. p. 117·8—118·8°/758 mm. Redistillation gave the pure compound, b. p. 118°/757 mm.

n-*Butyl cyanide.* The following modification of Adams and Marvel's method (*J. Amer. Chem. Soc.*, 1920, **42**, 311) was employed. To a warm solution (steam-bath) of 195 g. of sodium cyanide in 250 ml. of water contained in a 3-l. round-bottomed flask was added a solution of 450 g. of *n*-butyl bromide in 575 ml. of methyl alcohol. The mixture was refluxed for 30 hours and, when cold, filtered through a sintered-glass funnel, and the solid washed with 200 ml. of methyl alcohol. The combined filtrate and washings were distilled from a 2-l. flask and three-section, Young and Thomas column mounted on a water-bath; the temperature of the vapours did not rise above 68—69°. One litre of water was added to the residue in the flask, the latter fitted with a " knee-tube " attached to a downward condenser, and the liquid distilled until oil ceased to pass over. The water in the distillate was discarded, and the crude cyanide (200 g.) washed twice with half its volume of concentrated hydrochloric acid (to remove *iso*cyanides), then with saturated sodium hydrogen carbonate solution, and dried with ($MgSO_4$). Distillation gave the pure cyanide, b. p. 141°/764 mm.

n-*Amyl cyanide.* A solution of 30 g. of sodium cyanide in 40 ml. of water was mixed with a solution of 100 g. of *n*-amyl iodide in 125 ml. of methyl alcohol, and the whole refluxed for 30 hours : no solid separated. The crude cyanide, isolated as for *n*-butyl cyanide, weighed 39 g. It boiled constantly at 162°/777 mm.

iso*Amyl cyanide.* This was prepared by refluxing a mixture of 30 g. of sodium cyanide in 40 ml. of water and 77 g. of *iso*amyl bromide (*ex* Sharples's synthetic alcohol) in 150 ml. of methyl alcohol for 27 hours. The yield, b. p. 153·5°/756 mm., was 25 g.

n-*Hexyl cyanide.* This was prepared by refluxing a mixture of 30 g. of sodium cyanide in 40 ml. of water and a solution of 82 g. of *n*-hexyl bromide in 150 ml. of methyl alcohol for 21 hours. The cyanide was isolated as detailed for *n*-butyl cyanide except that it was preferable to separate the crude cyanide layer from the diluted reaction product after the methyl alcohol had been removed by careful fractionation : steam distillation was rather slow. The yield of *n*-hexyl cyanide, b. p. 182—182·5°/757 mm., was 40 g.

Allyl cyanide. A large-scale preparation, b. p. 116—121°/754 mm. (preceding paper), was carefully fractionated, and a large middle fraction, b. p. 118·5°/753 mm., was employed in the physical measurements.

Trimethylene dicyanide. This was prepared from the dibromide, b. p. 164—165·5°/759 mm., as detailed in *Org. Synth.*, Coll. Vol. I, 1941, 536, and boiled at 140°/8 mm.

Phenyl cyanide. 45 G. of benzamide, m. p. 128°, were mixed with 75 g. of phosphoric oxide in a 250-ml. Claisen flask, arranged for distillation under diminished pressure (*ca.* 100 mm.). The flask was heated with a free flame and the cyanide (32 g.) passed over at 126—130°/100 mm. The product was washed with potassium carbonate solution, dried, and distilled : the phenyl cyanide boiled constantly at 189°/758 mm.

Benzyl cyanide. This was prepared by refluxing a mixture of a solution of 30 g. of sodium cyanide in 40 ml. of water and a solution of 63 g. of redistilled benzyl chloride in 125 ml. of methyl alcohol for 30 hours. The cyanide was isolated as detailed for *n*-butyl cyanide except that it was necessary to separate the benzyl cyanide from the steam distillate by ether extraction. The yield was 40 g., b. p. 108·5°/15 mm.

Physical Measurements.—**390**. *Methyl but-3-yne-1-carboxylate.* B. p. 146·5°/754 mm.; *M* 112·12; n_{C} 1·42670, n_{D} 1·42917, n_{F} 1·43526, $n_{\mathrm{G'}}$ 1·43979; R_{C} 29·17, R_{D} 29·32, R_{F} 29·69, $R_{\mathrm{G'}}$ 29·95; $Mn_{\mathrm{D}}^{20^\circ}$ 160·24. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9861, $d_{4^\circ}^{41\cdot8^\circ}$ 0·9641, $d_{4^\circ}^{61\cdot0^\circ}$ 0·9450, $d_{4^\circ}^{86\cdot1^\circ}$ 0·9186. Apparatus *D*.

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

t.	*H.*	$d_{4^\circ}^{t^\circ}$.	*γ.*	*P.*	*t.*	*H.*	$d_{4^\circ}^{t^\circ}$.	*γ.*	*P.*
15·3°	13·68	0·9908	33·47	272·2	63·3°	11·82	0·9427	27·52	272·4
19·4	13·59	0·9867	33·12	272·6	86·2	10·85	0·9185	24·61	271·9
42·6	12·61	0·9633	30·00	272·4				Mean	272·3

391. *Ethyl but-3-yne-1-carboxylate.* B. p. 159°/763 mm.; *M* 126·15; n_{C} 1·42563, n_{D} 1·42803, n_{F} 1·43403, $n_{\mathrm{G'}}$ 1·43849; R_{C} 33·88, R_{D} 34·05, R_{F} 34·46, $R_{\mathrm{G'}}$ 34·78; $Mn_{\mathrm{D}}^{20^\circ}$ 180·14. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9532, $d_{4^\circ}^{41\cdot0^\circ}$ 0·9328, $d_{4^\circ}^{61\cdot0^\circ}$ 0·9126, $d_{4^\circ}^{85\cdot0^\circ}$ 0·8879. Apparatus *A*.

17·4°	17·15	0·9558	30·69	310·7	61·4°	14·99	0·9122	25·60	311·1
21·4	17·04	0·9518	30·37	311·1	87·8	13·69	0·8851	22·69	311·1
41·4	15·97	0·9324	27·88	310·9				Mean	311·0

[Perkin and Simonsen, *loc. cit.*, give b. p. 160—161°/765 mm., $d_{4^\circ}^{16\cdot7^\circ}$ 0·95585, $n_{\mathrm{C}}^{16\cdot7^\circ}$ 1·42673, $n_{\mathrm{F}}^{16\cdot-^\circ}$ 1·43516, $n_{\mathrm{G'}}^{16\cdot7^\circ}$ 1·44001.]

392. n-*Propyl but-3-yne-1-carboxylate.* B. p. 174·5—175·5°/763 mm.; *M* 140·18; n_{C} 1·42714, n_{D} 1·42952, n_{G} 1·43542, $n_{\mathrm{G'}}$ 1·43975; R_{C} 38·50, R_{D} 38·69, R_{F} 39·15, $R_{\mathrm{G'}}$ 39·49; $Mn_{\mathrm{D}}^{20^\circ}$ 200·39. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9351, $d_{4^\circ}^{41\cdot2^\circ}$ 0·9141, $d_{4^\circ}^{60\cdot1^\circ}$ 0·8958, $d_{4^\circ}^{86\cdot2^\circ}$ 0·8704. Apparatus *D*.

14·1°	13·13	0·9409	30·51	350·1	40·4°	12·19	0·9149	27·54	351·0
18·4	13·01	0·9367	30·10	350·5	61·3	11·44	0·8946	25·27	351·3
22·3	12·89	0·9328	29·69	350·8	85·9	10·57	0·8707	22·73	351·5
								Mean	350·9

393. n-*Butyl but-3-yne-1-carboxylate.* B. p. 193·5—194·5°/759 mm. and 71°/6 mm.; *M* 154·20; n_{C} 1·42980, n_{D} 1·43219, n_{F} 1·43807, $n_{\mathrm{G'}}$ 1·44244; R_{C} 43·10, R_{D} 43·31, R_{F} 43·82, $R_{\mathrm{G'}}$ 44·19; $Mn_{\mathrm{D}}^{20^\circ}$ 220·85. Densities determined : $d_{\mathrm{D}}^{20^\circ}$ 0·9239, $d_{4^\circ}^{44\cdot5^\circ}$ 0·9015, $d_{4^\circ}^{61\cdot7^\circ}$ 0·8858, $d_{4^\circ}^{85\cdot1^\circ}$ 0·8643. Apparatus *D*.

22·1°	12·86	0·9220	29·28	389·1	63·0°	11·48	0·8846	25·08	390·1
27·3	12·67	0·9172	28·70	389·1	85·6	10·72	0·8638	22·87	390·4
41·3	12·15	0·9054	27·17	388·8				Mean	389·5

394. *Methyl dec-9-yne-1-carboxylate.* B. p. 121°/5 mm.; *M* 196·28; n_{C} 1·44403, n_{D} 1·44646, n_{F} 1·45242, $n_{\mathrm{G'}}$ 1·45688; R_{C} 56·81, R_{D} 57·09, R_{F} 57·75, $R_{\mathrm{G'}}$ 58·24; $Mn_{\mathrm{D}}^{20^\circ}$ 283·92. Densities determined : $d_{4^\circ}^{20^\circ}$ 0·9177, $d_{4^\circ}^{40\cdot0^\circ}$ 0·9020, $d_{4^\circ}^{62\cdot0^\circ}$ 0·8845, $d_{4^\circ}^{84\cdot3^\circ}$ 0·8665. Apparatus *D*.

t.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.	t.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.
17·0°	14·72	0·9201	33·45	513·0	61·5°	13·16	0·8849	28·76	513·7
20·0	14·60	0·9177	33·09	513·0	86·7	12·27	0·8646	26·20	513·6
41·9	13·85	0·9003	30·79	513·6				Mean	513·4

395. *Ethyl dec-9-yne-1-carboxylate.* B. p. 134·5°/6·5 mm.; M 210·31; n_{C} 1·44232, n_{D} 1·44475, n_{F} 1·45061, $n_{\text{G}'}$ 1·45505; R_{C} 61·42, R_{D} 61·72, R_{F} 62·41, $R_{\text{G}'}$ 62·95; $Mn_{\text{D}}^{20^\circ}$ 303·86. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9066, $d_{4^\circ}^{41\cdot6^\circ}$ 0·8897, $d_{4^\circ}^{61\cdot9^\circ}$ 0·8734, $d_{4^\circ}^{87\cdot1^\circ}$ 0·8534. Apparatus *D*.

12·3°	14·56	0·9123	32·80	551·7	61·9°	12·77	0·8734	27·54	551·6
20·5	14·28	0·9062	31·96	551·8	88·6	11·89	0·8522	25·02	552·0
42·2	13·49	0·8892	29·62	551·8				Mean	551·8

The ester prepared by the cold esterification process had b. p. 142°/13 mm., $d_{4^\circ}^{20^\circ}$ 0·9069, $n_{4^\circ}^{20^\circ}$ 1·44480.

396. n-*Propyl dec-9-yne-1-carboxylate.* B. p. 142°/6 mm.; M 224·33; n_{C} 1·44343, n_{D} 1·44586, n_{F} 1·45175, $n_{\text{G}'}$ 1·45618; R_{C} 66·09, R_{D} 66·41, R_{F} 67·17, $R_{\text{G}'}$ 67·74; $Mn_{\text{D}}^{20^\circ}$ 324·36. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9006, $d_{4^\circ}^{40\cdot8^\circ}$ 0·8849, $d_{4^\circ}^{61\cdot9^\circ}$ 0·8690, $d_{4^\circ}^{85\cdot5^\circ}$ 0.8509. Apparatus *D*.

19·2°	14·30	0·9012	31·83	591·2	41·7°	13·60	0·8840	29·69	591·0
20·3	14·25	0·9004	31·69	591·1	61·0	12·93	0·8697	27·77	592·1
29·5	13·98	0·8934	30·84	591·7	87·2	12·08	0·8496	25·35	592·4
								Mean	591·6

397. *Ethyl* n-*undecylate.* B. p. 118°/7 mm.; M 214·34; n_{C} 1·42630, n_{D} 1·42847, n_{F} 1·43376, $n_{\text{G}'}$ 1·43760; R_{C} 63·65, R_{D} 63·94, R_{F} 64·63, $R_{\text{G}'}$ 65·12; $Mn_{\text{D}}^{20^\circ}$ 306·18. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8633, $d_{4^\circ}^{41\cdot2^\circ}$ 0·8476, $d_{4^\circ}^{61\cdot7^\circ}$ 0·8319, $d_{4^\circ}^{86\cdot3^\circ}$ 0·8123. Apparatus *A*.

16·8°	17·65	0·8658	28·61	572·6	61·3°	15·75	0·8322	24·54	573·3
20·7	17·48	0·8628	28·24	572·7	86·4	14·72	0·8122	22·39	574·0
42·4	16·68	0·8467	26·45	573·9				Mean	573·3

398. *Dimethyl acetylenedicarboxylate.* B. p. 76·5°/3 mm.; M 142·11; n_{C} 1·44389, n_{D} 1·44681, n_{F} 1·45483, $n_{\text{G}'}$ 1·46094; R_{C} 32·53, R_{D} 32·72, R_{F} 33·22, $R_{\text{G}'}$ 33·61; $Mn_{\text{D}}^{20^\circ}$ 205·60. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·1601, $d_{4^\circ}^{41\cdot2^\circ}$ 1·1353, $d_{4^\circ}^{64\cdot3^\circ}$ 1·1106, $d_{4^\circ}^{85\cdot6^\circ}$ 1·0850. Apparatus *A*.

15·1°	17·63	1·1657	38·48	303·6	61·3°	15·72	1·1141	32·80	305·2
26·9	17·25	1·1522	37·22	304·6	87·1	14·71	1·0832	29·84	306·8
41·7	16·56	1·1347	35·19	305·0				Mean	305·1

Dimethyl acetylenedicarboxylate, prepared by the acid, MeOH, C_6H_6, concentrated H_2SO_4 method, had b. p. 78·5°/4 mm., $d_{4^\circ}^{20^\circ}$ 1·1606, n_{C} 1·44380, n_{D} 1·44701, n_{F} 1·45498, $n_{\text{G}'}$ 1·46119; R_{C} 32·51, R_{D} 32·71, R_{F} 33·22, $R_{\text{G}'}$ 33·61; $Mn_{\text{D}}^{20^\circ}$ 205·63.

399. *Diethyl acetylenedicarboxylate.* B. p. 85·5°/2·5 mm.; M 170·16; n_{C} 1·43944, n_{D} 1·44245, n_{F} 1·44989, $n_{\text{G}'}$ 1·45573; R_{C} 41·96, R_{D} 42·22, R_{F} 42·83, $R_{\text{G}'}$ 43·31; $Mn_{\text{D}}^{20^\circ}$ 245·46. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0675, $d_{4^\circ}^{41\cdot4^\circ}$ 1·0459, $d_{4^\circ}^{60\cdot4^\circ}$ 1·0265, $d_{4^\circ}^{85\cdot9^\circ}$ 1·0009. Apparatus *D*.

14·3°	12·79	1·0732	33·90	382·6	61·5°	11·44	1·0254	28·97	385·0
21·7	12·62	1·0658	33·22	383·3	86·9	10·72	0·9999	26·47	386·0
41·9	11·98	1·0454	30·93	383·9				Mean	384·1

400. *Di*-n-*propyl acetylenedicarboxylate.* B. p. 116°/5 mm.; M 198·21; n_{C} 1·44329, n_{D} 1·44621, n_{F} 1·45344, $n_{\text{G}'}$ 1·45909; R_{C} 51·26, R_{D} 51·56, R_{F} 52·28, $R_{\text{G}'}$ 52·84; $Mn_{\text{D}}^{20^\circ}$ 286·65. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0256, $d_{4^\circ}^{40\cdot8^\circ}$ 1·0068, $d_{4^\circ}^{62\cdot1^\circ}$ 0·9875, $d_{4^\circ}^{85\cdot8^\circ}$ 0·9646. Apparatus *D*.

18·1°	12·78	1·0273	32·42	460·4	61·7°	11·56	0·9879	28·20	462·4
25·3	12·60	1·0208	31·76	461·0	87·4	10·84	0·9631	25·78	463·8
41·3	12·16	1·0063	29·94	460·8				Mean	461·6

401. *Di*iso*propyl acetylenedicarboxylate.* B. p. 96°/3 mm.; M 198·21; n_{C} 1·43621, n_{D} 1·43908, n_{F} 1·44623, $n_{\text{G}'}$ 1·45179; R_{C} 51·38, R_{D} 51·68, R_{F} 52·41, $R_{\text{G}'}$ 52·97; $Mn_{\text{D}}^{20^\circ}$ 285·24. Densities determined: $d_{\text{D}}^{20^\circ}$ 1·0090, $d_{4^\circ}^{42\cdot5^\circ}$ 0·9895, $d_{4^\circ}^{61\cdot5^\circ}$ 0·9725, $d_{4^\circ}^{86\cdot7^\circ}$ 0·9486. Apparatus *D*.

20·3°	12·26	1·0087	30·54	461·9	61·5°	11·18	0·9725	26·85	464·0
27·4	12·13	1·0015	30·00	463·2	87·5	10·39	0·9488	24·35	464·0
42·3	11·74	0·9897	28·72	463·6				Mean	463·3

402. *Di*-n-*butyl acetylenedicarboxylate.* B. p. 139°/5 mm.; M 226·28; n_{C} 1·44579, n_{D} 1·44861, n_{C} 1·45565, $n_{\text{G}'}$ 1·46106; R_{C} 60·36, R_{D} 60·69, R_{F} 61·52, $R_{\text{G}'}$ 62·15; $Mn_{\text{D}}^{20^\circ}$ 327·79. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9993, $d_{4^\circ}^{41\cdot4^\circ}$ 0·9820, $d_{4^\circ}^{63\cdot1^\circ}$ 0·9625, $d_{4^\circ}^{85\cdot7^\circ}$ 0·9431. Apparatus *D*.

16·0°	12·95	1·0027	32·07	537·0	61·4°	11·76	0·9639	27·99	540·0
30·3	12·58	0·9906	30·78	538·0	85·6	11·08	0·9432	25·81	540·7
41·0	12·31	0·9823	29·86	538·5				Mean	538·8

403. *Di*-n-*amyl acetylenedicarboxylate.* B. p. 143°/1·5 mm.; *M* 254·32; n_{C} 1·44858, n_{D} 1·45137, n_{F} 1·45826, $n_{\mathrm{G'}}$ 1·46353; R_{C} 69·70, R_{D} 70·08, R_{F} 71·00, $R_{\mathrm{G'}}$ 71·69; $Mn_{\mathrm{D}}^{20^\circ}$ 369·12. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9779, $d_{4^\circ}^{40\cdot8^\circ}$ 0·9619, $d_{4^\circ}^{62\cdot5^\circ}$ 0·9453, $d_{4^\circ}^{85\cdot7^\circ}$ 0·9256. Apparatus *A*.

t.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.	*t*.	*H*.	$d_{4^\circ}^{t^\circ}$.	γ.	*P*.
18·3°	17·16	0·9788	31·45	615·3	61·1°	15·79	0·9464	27·98	618·1
27·2	17·01	0·9723	30·97	617·1	86·1	14·92	0·9252	25·85	619·8
42·0	16·36	0·9610	29·44	616·4				Mean	617·7

404. *Diisoamyl acetylenedicarboxylate.* B. p. 133°/2·5 mm.; *M* 254·32; n_{C} 1·44842, n_{D} 1·45132, n_{F} 1·45825, $n_{\mathrm{G'}}$ 1·46359; R_{C} 69·59, R_{D} 69·98, R_{F} 70·91, $R_{\mathrm{G'}}$ 71·62; $Mn_{\mathrm{D}}^{20^\circ}$ 369·09. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9791, $d_{4^\circ}^{41\cdot4^\circ}$ 0·9623, $d_{4^\circ}^{61\cdot6^\circ}$ 0·9454, $d_{4^\circ}^{86\cdot5^\circ}$ 0·9247. Apparatus *D*.

25·3°	12·57	0·9749	30·26	611·9	62·2°	11·61	0·9449	27·09	614·0
41·8	12·14	0·9620	28·84	612·6	86·4	10·98	0·9248	25·08	615·4
								Mean	613·5

405. *Ethyl phenylpropiolate.* B. p. 124°/6 mm.; n_{C} 1·54582, n_{D} 1·55231, n_{F} 1·56962, $n_{\mathrm{G'}}$ 1·58458; R_{C} 52·20, R_{D} 52·71, R_{F} 54·07, $R_{\mathrm{G'}}$ 55·24; $Mn_{\mathrm{D}}^{20^\circ}$ 270·40. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0563, $d_{4^\circ}^{41\cdot1^\circ}$ 1·0381, $d_{4^\circ}^{61\cdot5^\circ}$ 1·0209, $d_{4^\circ}^{85\cdot9^\circ}$ 0·9999. Apparatus *A*.

14·2°	19·71	1·0613	39·17	410·6	40·9°	18·76	1·0383	36·47	412·3
21·1	19·38	1·0554	38·30	410·6	61·5	17·89	1·0209	34·20	412·6
21·7	19·32	1·0548	38·16	410·4	85·3	16·96	1·0004	31·77	413·4
								Mean	411·7

406. n-*Propyl phenylpropiolate.* B. p. 143°/7 mm.; *M* 188·22; n_{C} 1·53928, n_{D} 1·54464, n_{F} 1·56083, $n_{\mathrm{G'}}$ 1·57480; R_{C} 56·99, R_{D} 57·45, R_{F} 58·86, $R_{\mathrm{G'}}$ 60·07; $Mn_{\mathrm{D}}^{20^\circ}$ 290·72. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0352, $d_{4^\circ}^{42\cdot1^\circ}$ 1·0168, $d_{4^\circ}^{61\cdot6^\circ}$ 1·0003, $d_{4^\circ}^{86\cdot7^\circ}$ 0·9793. Apparatus *A*.

13·9°	19·35	1·0403	37·69	448·3	41·8°	18·26	1·0171	34·78	450·0
18·6	19·18	1·0364	37·22	448·6	61·6	17·47	1·0003	32·72	450·0
28·5	18·86	1·0281	36·31	449·4	87·0	16·56	0·9791	30·36	451·2
								Mean	449·6

407. n-*Butyl phenylpropiolate.* B. p. 149°/5 mm.; *M* 202·24; n_{C} 1·53217, n_{D} 1·53802, n_{F} 1·55350, $n_{\mathrm{G'}}$ 1·56676; R_{C} 61·41, R_{D} 61·97, R_{F} 63·45, $R_{\mathrm{G'}}$ 64·70; $Mn_{\mathrm{D}}^{20^\circ}$ 311·05. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0208, $d_{4^\circ}^{40\cdot0^\circ}$ 1·0056, $d_{4^\circ}^{61\cdot0^\circ}$ 0·9892, $d_{4^\circ}^{86\cdot1^\circ}$ 0·9684. Apparatus *A*.

19·3°	14·38	1·0213	36·27	485·7	41·9°	13·80	1·0041	34·22	487·1
22·0	14·32	1·0193	36·05	486·2	60·5	13·25	0·9896	32·38	487·5
27·2	14·18	1·0153	35·55	486·4	86·2	12·59	0·9683	30·11	489·2
								Mean	487·0

408. *Methyl cyanide.* B. p. 81°/757 mm.; *M* 41·05; n_{C} 1·34233, n_{D} 1·34408, n_{F} 1·34806, $n_{\mathrm{G'}}$ 1·35087; R_{C} 11·04, R_{D} 11·09, R_{F} 11·21, $R_{\mathrm{G'}}$ 11·29; $Mn_{\mathrm{D}}^{20^\circ}$ 55·18. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7843, $d_{4^\circ}^{40\cdot4^\circ}$ 0·7639, $d_{4^\circ}^{60\cdot4^\circ}$ 0·7429. Apparatus *A*.

19·1°	20·03	0·7852	29·45	121·8	40·6°	18·66	0·7637	26·68	122·2
26·7	19·50	0·7776	28·40	121·9	60·4	17·40	0·7429	24·20	122·7
								Mean	122·1

[Merckx, Verhulst, and Bruylants (*Bull Soc. chim. Belg.*, 1933, **42**, 777) found $d_{4^\circ}^{20^\circ}$ 0·7820, $n_{\mathrm{D}}^{20^\circ}$ 1·34381 when extrapolated from data at 15° and 30°.]

409. *Ethyl cyanide.* B. p. 97°/758 mm.; *M* 55·08; n_{C} 1·36398, n_{D} 1·36578, n_{F} 1·37016, $n_{\mathrm{G'}}$ 1·37327; R_{C} 15·68, R_{D} 15·75, R_{F} 15·92, $R_{\mathrm{G'}}$ 16·04; $Mn_{\mathrm{D}}^{20^\circ}$ 75·23. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7828, $d_{4^\circ}^{41\cdot4^\circ}$ 0·7618, $d_{4^\circ}^{61\cdot9^\circ}$ 0·7418. Apparatus *D*.

19·9°	14·08	0·7829	27·22	160·7	41·3°	13·24	0·7619	24·91	161·6
28·3	13·85	0·7745	26·49	161·3	60·7	12·31	0·7430	22·59	161·7
								Mean	161·4

[Bruylants *et al.* found $d_{4^\circ}^{20^\circ}$ 0·7817, $n_{\mathrm{D}}^{20^\circ}$ 1·36585].

410. n-*Propyl cyanide.* B. p. 118°/757 mm.; *M* 69·11; n_{C} 1·38232, n_{D} 1·38423, n_{F} 1·38885, $n_{\mathrm{G'}}$ 1·39221; R_{C} 20·35, R_{D} 20·43, R_{F} 20·65, $R_{\mathrm{G'}}$ 20·81; $Mn_{\mathrm{D}}^{20^\circ}$ 95·66. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7913, $d_{4^\circ}^{40\cdot8^\circ}$ 0·7742, $d_{4^\circ}^{60\cdot6^\circ}$ 0·7559, $d_{4^\circ}^{85\cdot3^\circ}$ 0·7328. Apparatus *D*.

20·1°	14·03	0·7912	27·41	199·9	60·1°	12·39	0·7563	23·14	200·4
28·4	13·75	0·7841	26·62	200·2	85·7	11·44	0·7325	20·69	201·5
41·0	13·23	0·7740	25·29	200·2				Mean	200·4

[Bruylants *et al.* found $d_{4^\circ}^{20^\circ}$ 0·7909, $n_{\mathrm{D}}^{20^\circ}$ 1·38385.]

411. n-*Butyl cyanide.* B. p. 141°/764 mm.; *M* 83·13; n_{C} 1·39492, n_{D} 1·39690, n_{F} 1·40168, $n_{\mathrm{G'}}$ 1·40505; R_{C} 24·93, R_{D} 25·04, R_{F} 25·31, $R_{\mathrm{G'}}$ 25·50; $Mn_{\mathrm{D}}^{20^\circ}$ 116·12. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·7992, $d_{4^\circ}^{41\cdot0^\circ}$ 0·7834, $d_{4^\circ}^{60\cdot3^\circ}$ 0·7667, $d_{4^\circ}^{86\cdot6^\circ}$ 0·7437. Apparatus *D*.

t.	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	*P.*	*t.*	*H.*	$d_{4^\circ}^{t^\circ}$.	γ.	*P.*
20·0°	13·90	0·7992	27·43	238·1	61·6°	12·42	0·7657	23·49	239·0
24·6	13·79	0·7955	27·09	238·4	86·5	11·56	0·7438	21·23	239·9
40·6	13·07	0·7837	25·30	237·9				Mean	238·7

[Bruylants *et al.* found $d_{4^\circ}^{20^\circ}$ 0·7992, $n_D^{20^\circ}$ 1·39711.]

412. n-*Amyl cyanide.* B. p. 162°/777 mm.; *M* 97·16; n_C 1·40481, n_D 1·40687, n_F 1·41183, $n_{G'}$ 1·41543; R_C 29·58, R_D 29·72, R_F 30·03, $R_{G'}$ 30·26; $Mn_D^{20^\circ}$ 136·69. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8047, $d_{4^\circ}^{40\cdot7^\circ}$ 0·7901, $d_{4^\circ}^{61\cdot7^\circ}$ 0·7733, $d_{4^\circ}^{86\cdot2^\circ}$ 0·7526. Apparatus *A*.

23·2°	18·32	0·8023	27·52	277·4	61·2°	16·62	0·7737	24·08	278·2
28·4	18·14	0·7984	27·12	277·6	86·8	15·47	0·7521	21·79	279·1
41·0	17·50	0·7898	25·88	277·5				Mean	278·0

[Bruylants *et al.* found $d_{4^\circ}^{20^\circ}$ 0·8053, $n_D^{20^\circ}$ 1·40694.]

413. iso*Amyl cyanide.* B. p. 153·5°/756 mm.; *M* 97·16; n_C 1·40391, n_D 1·40592, n_F 1·41092, $n_{G'}$ 1·41462; R_C 29·59, R_D 29·72, R_F 30·04, $R_{G'}$ 30·28; $Mn_D^{20^\circ}$ 136·60. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8030, $d_{4^\circ}^{41\cdot6^\circ}$ 0·7869, $d_{4^\circ}^{61\cdot3^\circ}$ 0·7707, $d_{4^\circ}^{86\cdot8^\circ}$ 0·7495. Apparatus *A*.

20·5°	17·89	0·8026	26·89	275·7	61·0	16·04	0·7703	23·15	276·5
27·1	17·83	0·7975	26·63	276·8	87·0	14·96	0·7493	20·99	277·5
41·6	17·00	0·7869	25·05	276·2				Mean	276·5

414. n-*Hexyl cyanide.* B. p. 182—182·5°/757 mm.; *M* 111·18; n_C 1·41200, n_D 1·41406, n_F 1·41914, $n_{G'}$ 1·42285; R_C 34·15, R_D 34·31, R_F 34·67, $R_{G'}$ 34·95; $Mn_D^{20^\circ}$ 157·22. Densities determined; $d_{4^\circ}^{20^\circ}$ 0·8100, $d_{4^\circ}^{40\cdot5^\circ}$ 0·7945, $d_{4^\circ}^{60\cdot0^\circ}$ 0·7796, $d_{4^\circ}^{85\cdot0^\circ}$ 0·7597. Apparatus *A*.

21·3°	18·10	0·8089	27·42	314·5	62·5°	16·34	0·7777	23·80	315·7
41·8	17·16	0·7934	25·49	314·9	85·0	15·46	0·7597	21·99	316·9
								Mean	315·3

The surface-tension measurements were somewhat erratic and not always accurately reproducible; some selected results are given above. The results cannot be regarded as more than approximate, consequently the parachor values are untrustworthy.

[Bruylants *et al.* found $d_{4^\circ}^{20^\circ}$ 0·8096, $n_D^{20^\circ}$ 1·41419.]

415. *Allyl cyanide.* B. p. 118·5°/753 mm.; *M* 67·09; n_C 1·40342, n_D 1·40593, n_F 1·41214, $n_{G'}$ 1·41678; R_C 19·56, R_D 19·67, R_F 19·93, $R_{G'}$ 20·13; $Mn_D^{20^\circ}$ 94·32. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·8377, $d_{4^\circ}^{41\cdot6^\circ}$ 0·8163, $d_{4^\circ}^{60\cdot6^\circ}$ 0·7988, $d_{4^\circ}^{8\;\cdot9^\circ}$ 0·7739. Apparatus *D*.

13·4°	14·37	0·8441	29·96	186·0	42·0°	13·28	0·8159	26·76	187·0
17·1	14·25	0·8406	29·58	186·1	62·1	12·51	0·7973	24·63	187·5
21·2	14·10	0·8365	29·13	186·3	87·5	11·51	0·7723	21·95	188·0
								Mean	187·8

416. *Trimethylene dicyanide.* B. p. 140°/8 mm.; *M* 94·12; n_C 1·42728, n_D 1·42947, n_F 1·43492, $n_{G'}$ 1·43880; R_C 24·48, R_D 24·59, R_F 24·80, $R_{G'}$ 25·05; $Mn_D^{20^\circ}$ 134·55. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9879, $d_{4^\circ}^{41\cdot1^\circ}$ 0·9721, $d_{4^\circ}^{61\cdot2^\circ}$ 0·9575, $d_{4^\circ}^{85\cdot0^\circ}$ 0·9398. Apparatus *D*.

16·0°	19·66	0·9909	48·11	250·2	60·6°	18·33	0·9579	43·36	252·1
41·0	19·04	0·9720	45·70	251·8	86·1	17·52	0·9390	40·62	253·1
								Mean	251·8

The surface-tension measurements presented some difficulty, possibly because the liquid did not wet the glass too well. The results for γ and hence for *P* must be regarded as approximate only; it is hoped to repeat the measurements by the maximum bubble-pressure method.

417. *Phenyl cyanide.* B. p. 189°/758 mm.; *M* 103·12; n_C 1·52283, n_D 1·52823, n_F 1·54208, $n_{G'}$ 1·55346; R_C 31·31, R_D 31·58, R_F 32·27, $R_{G'}$ 32·83; $Mn_D^{20^\circ}$ 157·59. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0058, $d_{4^\circ}^{40\cdot3^\circ}$ 0·9885, $d_{4^\circ}^{60\cdot5^\circ}$ 0·9713, $d_{4^\circ}^{86\cdot6^\circ}$ 0·9486. Apparatus *A*.

19·3°	20·97	1·0064	39·52	256·9	61·2°	19·03	0·9707	34·59	257·6
27·0	20·53	0·9998	38·43	256·8	87·0	17·80	0·9483	31·61	257·8
40·9	20·01	0·9880	37·02	257·4				Mean	257·3

418. *Benzyl cyanide.* B. p. 108·5°/15 mm.; *M* 117·15; n_C 1·51830, n_D 1·52271, n_F 1·53161, $n_{G'}$ 1·54260; R_C 34·97, R_D 35·22, R_F 35·72, $R_{G'}$ 36·34; $Mn_D^{20^\circ}$ 178·38. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0155, $d_{4^\circ}^{40\cdot5^\circ}$ 1·0013, $d_{4^\circ}^{60\cdot1^\circ}$ 0·9860, $d_{4^\circ}^{86\cdot0^\circ}$ 0·9659. Apparatus *D*.

19·5°	16·80	1·0159	42·15	293·8	60·3°	15·48	0·9861	37·71	294·3
27·3	16·60	1·0102	41·42	294·1	86·3	14·47	0·9657	34·51	294·0
40·5	16·19	1·0013	40·04	294·3				Mean	294·1

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