

38. Physical Properties and Chemical Constitution. Part IX. Aliphatic Hydrocarbons.

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New experimental data for the parachors and refractivities of the normal hydrocarbons (*n*-pentane to *n*-hexadecane) and certain branched-chain hydrocarbons are presented. The data for the normal paraffins give for CH₂, *P* 39.98, *R*_C 4.618, *R*_D 4.643, *R*_F 4.687, *R*_G, 4.731, and *Mn*_D^{20°} 20.63. By combining these figures with those deduced in Part VIII (J., 1943, 638), the following figures for CH₂, H, and C (in CH₂) have been obtained:

	<i>P</i> .	<i>R</i> _C .	<i>R</i> _D .	<i>R</i> _F .	<i>R</i> _G .	<i>Mn</i> _D ^{20°}
CH ₂	40.02	4.624	4.647	4.695	4.735	20.59
H	15.7	1.026	1.028	1.043	1.040	-2.56
C (in CH ₂)	8.6	2.572	2.591	2.601	2.655	25.71

IN Part VIII (*loc. cit.*) it was pointed out that the new data for *n*-alkyl halides led to the following values for CH₂ differences when evaluated by the method of least squares:

	<i>P</i>	<i>R</i> _C .	<i>R</i> _D .	<i>R</i> _F .	<i>R</i> _G .	<i>Mn</i> _D ^{20°} .
Chlorides	40.10	4.621	4.641	4.691	4.734	20.71
Bromides	40.02	4.625	4.646	4.696	4.733	20.79
Iodides	39.98	4.631	4.656	4.707	4.743	20.24

These values differed so seriously from the hitherto accepted figures (*P* 39.0, Sugden, J., 1924, 125, 1180; *R*_C 4.598, *R*_D 4.618, *R*_F 4.668, *R*_G, 4.710, Eisenlohr, *Z. physikal. Chem.*, 1911, 75, 605; *Mn*_D^{20°} 20.56, *Fortschr. Chem. Physik, u physikal. Chem.*, 1925, Band 18, Heft 9, p. 5) that a thorough reinvestigation was deemed desirable. Moreover, since the atomic and structural parachors and refractivities, as computed by Sugden and by Eisenlohr respectively, are based upon the values of the CH₂ grouping, any change in the magnitudes of the latter constants will, of necessity, require recalculation of all the atomic and structural constants.

The normal hydrocarbons, *n*-pentane to *n*-hexadecane, have been prepared in a high degree of purity and their parachors and refractivities determined.* The results are summarised in Table I; molecular refractivities refer to a temperature of 20°. The mean values of the CH₂ increments were calculated, using the data for *n*-pentane as standard, by the method of least squares. These results provide independent confirmation of those obtained in Part VIII from the experimental figures upon *n*-alkyl chlorides, bromides, and iodides, and suggest that both Sugden's and Eisenlohr's atomic and structural constants require revision.

TABLE I.
Parachors and refractivities of normal hydrocarbons.

	<i>P</i> .	<i>R</i> _C .	<i>R</i> _D .	<i>R</i> _F .	<i>R</i> _G .	<i>Mn</i> _D ^{20°}
C ₅ H ₁₂	231.8	25.16	25.28	25.55	25.73	97.98
C ₆ H ₁₄	270.9	29.79	29.93	30.25	30.47	118.49
C ₇ H ₁₆	312.0	34.44	34.60	34.97	35.24	139.04
C ₈ H ₁₈	350.5	39.00	39.17	39.60	39.90	159.61
C ₉ H ₂₀	390.7	43.66	43.85	44.33	44.69	180.24
C ₁₀ H ₂₂	429.9	48.28	48.50	49.03	49.40	200.91
C ₁₁ H ₂₄	470.6	52.92	53.15	53.72	54.13	221.51
C ₁₂ H ₂₆	510.0	57.45	57.71	58.32	58.77	242.19
C ₁₃ H ₂₈	550.5	62.14	62.41	63.09	63.56	262.77
C ₁₄ H ₃₀	591.4	66.79	67.10	67.81	68.34	283.50
C ₁₅ H ₃₂	631.3	71.35	71.67	72.44	73.02	304.17
C ₁₆ H ₃₄	671.3	75.92	76.27	77.07	77.66	324.86
<i>Mean values for CH₂ calculated by the method of least squares.</i>						
CH ₂	39.98	4.618	4.643	4.687	4.731	20.63

* The author's work was completed in September 1939, but publication was not considered desirable during the period of hostilities. Quayle, Day, and Brown (*J. Amer. Chem. Soc.*, 1944, 66, 938) have determined the densities and surface tensions (maximum bubble pressure method), chiefly at 20°, 30°, and 40°, of the normal hydrocarbons, *n*-pentane to *n*-duodecane, but the method of preparation of the hydrocarbons is not given. The parachors are in good agreement with those obtained in the present work (capillary rise method) and lead to an average CH₂ increment of 40.0. Mumford and Phillips (J., 1929, 2112) had put forward a value of 40, based upon the data upon fatty acids by Hunten and Maass (*J. Amer. Chem. Soc.*, 1929, 51, 153) and the normal hydrocarbons C₂₆H₅₄, C₃₂H₆₆, and C₆₀H₁₂₂.

The average values for CH_2 deduced by the method of least squares from the data on n -hydrocarbons, n -alkyl chlorides, bromides and iodides are P 40.02, R_C 4.624, R_D 4.647, R_F 4.695, R_G 4.735, $Mn_D^{20^\circ}$ 20.59. These figures will be employed in all calculations.

It is of interest to compare the individual variations in the four homologous series used by the author in the computation of the mean CH_2 contributions with those utilised by Eisenlohr (*loc. cit.*) for a similar purpose.

Eisenlohr's data for CH_2 .

	R_C .	R_D .	R_F .	R_G .		R_C .	R_D .	R_F .	R_G .
Hydrocarbons	4.6054	4.6247	4.6783	4.7233	Alcohols	4.6141	4.6343	4.6849	4.7265
Aldehydes and ketones	4.6064	4.6265	4.6757	4.7136	Esters	4.5863	4.6056	4.6561	4.6961
Acids	4.5911	4.6137	4.6617	4.7139	Mean	4.5977	4.6178	4.6861	4.7102

The large variations in the different series are noteworthy, and it is questionable whether Eisenlohr's mean values possess any serious significance when expressed to four (or five) significant figures.

The atomic constants for hydrogen have been determined by two procedures: (a) From $\text{C}_n\text{H}_{2n+2} - n\text{CH}_2$ as applied to each normal hydrocarbon, and the mean value taken. (b) By comparing $n\text{-C}_5\text{H}_{12}$ and $n\text{-C}_5\text{H}_{11}$ ($= 0.5 \times n\text{-C}_{10}\text{H}_{22}$), $n\text{-C}_6\text{H}_{14}$ and $n\text{-C}_6\text{H}_{13}$, $n\text{-C}_7\text{H}_{16}$ and $n\text{-C}_7\text{H}_{15}$, and $n\text{-C}_8\text{H}_{18}$ and $n\text{-C}_8\text{H}_{17}$, and averaging the results. The latter method requires no knowledge of the CH_2 contribution. The average figures obtained by both methods are given in Table II.

TABLE II.

*Atomic constants for hydrogen.**

	P .	R_C .	R_D .	R_F .	R_G .	$Mn_D^{20^\circ}$.
$\text{C}_n\text{H}_{2n+2} - n\text{CH}_2$	15.4	1.012	1.011	1.026	1.014	-2.46
$\text{C}_n\text{H}_{2n+2} - \text{C}_n\text{H}_{2n+1}$	16.0	1.040	1.045	1.060	1.065	-2.66
Mean	15.7	1.026	1.028	1.043	1.040	-2.56

* The accurate measurements of the refractive indices for the normal hydrocarbons (n -pentane to n -duodecane) by Shepard *et al.* (*loc. cit.*; see Experimental), with the author's mean values for CH_2 , give for hydrogen R_C 1.009, R_D 1.008, and R_F 1.034, whilst the determinations of Wibaut *et al.* (*loc. cit.*) for n -pentane to n -nonane lead to R_C 1.002, R_D 1.001, R_F 1.020, and R_G 1.034.

The atomic constants for carbon in CH_2 are therefore ($\text{CH}_2 - 2\text{H}$) P 8.6, R_C 2.572, R_D 2.591, R_F 2.601, R_G 2.655, and $Mn_D^{20^\circ}$ 25.71.

Sugden (*loc. cit.*) found C, 4.8 and H, 17.1, whilst Eisenlohr (*loc. cit.*) deduced for hydrogen R_C 1.092, R_D 1.110, R_F 1.115, R_G 1.122, and for carbon R_C 2.413, R_D 2.418, R_F 2.438, and R_G 2.466. Eisenlohr's values for hydrogen were evaluated from the existing data upon the hydrocarbons (hexane, octane, decane, and diisomylyl) and a number of alcohols. These are given as:

	R_C .	R_D .	R_F .	R_G .		R_C .	R_D .	R_F .	R_G .
2H from hydrocarbons	2.2601	2.2704	2.3016	2.3170	Mean 2H	2.1848	2.1998	2.2306	2.2447
2H from alcohols	2.1093	2.1292	2.1597	2.1723	Mean H	1.0924	1.0999	1.1153	1.1224

By subtracting the above mean values for 2H from CH_2 , the figures for carbon were obtained. No further comments are necessary on the possible inaccuracies in Eisenlohr's constants.

The results for a number of branched-chain hydrocarbons are summarised in Table III. These will be utilised in subsequent papers of this series.

TABLE III.

Branched-chain aliphatic hydrocarbons.

	P .	R_C .	R_D .	R_F .	R_G .	$Mn_D^{20^\circ}$.
3: 4-Dimethylhexane (di- <i>sec</i> -butyl)	342.3	38.66	38.84	39.25	39.55	160.42
2: 5-Dimethylhexane (diisobutyl)	347.5	39.06	39.24	39.68	39.98	159.07
2: 6-Dimethylheptane (diisobutylmethane)	386.5	43.68	43.88	44.35	44.71	179.65
2: 7-Dimethyloctane (diisomylyl, "synthetic") *	425.1	48.19	48.39	48.92	49.30	200.60
2: 7-Dimethyloctane (diisomylyl, "fermentation") † ...	426.1	48.34	48.56	49.08	49.46	200.41
4: 5-Dimethyloctane	419.4	47.79	48.00	48.51	48.88	201.65
3: 4-Diethylhexane	417.0	47.63	47.85	48.34	48.71	201.90

* From synthetic isomylyl alcohol.

† From fermentation isomylyl alcohol.

Succeeding papers of this series will be devoted to the provision of new data for different classes of organic compounds, and the evaluation of atomic and structural constants with the aid of the experimental figures for the hydrocarbons.

EXPERIMENTAL.

Physical Measurements.—Full details are given in Part VII (J., 1943, 18). Surface tensions were measured by the method of capillary rise, and only the values for H ($= h - 0.24$ mm.) are given. Unless otherwise stated, all b. p.'s are corrected.

Previous Work.—Reference will be made to what appear to be the most trustworthy recorded values of the parachor and refractive indices. Unless otherwise indicated, refractive indices and densities ($d_4^{20^\circ}$) refer to a temperature of 20° . Where the method of preparation differs from that used in the present work, it will be briefly stated. The n -paraffin hydrocarbons obtained by Shepard, Henne, and Midgley (*J. Amer. Chem. Soc.*, 1931, 53, 1948) were isolated by careful

fractionation of a special gasoline; the preparation of the hydrocarbons employed by Quayle, Day, and Brown (*loc. cit.*) in their parachor determinations is not described.

99.* *n*-Pentane. The method detailed in *Organic Syntheses*, 1931, **11**, 85 was modified as follows. Into a 2-litre, three-necked flask, equipped with a 25-cm. double-surface condenser, a mercury-sealed mechanical stirrer and a thermometer, were placed 60.7 g. of magnesium turnings and a crystal of iodine. Part of a solution of 2-bromopentane (VIII, **76**) in 250 ml. of *n*-butyl ether (dried over anhydrous magnesium sulphate) was placed in a separatory funnel (protected by a calcium chloride guard tube) supported in the top of the double-surface condenser by means of a grooved cork. About 35 ml. of the bromide solution were run on to the magnesium in the flask immersed in a water-bath at about 80°: an extremely vigorous reaction set in after 5 minutes and the liquid refluxed in the condenser. The remainder of the solution of 2-bromopentane in *n*-butyl ether was then added at such a rate that the temperature inside the flask was maintained at 50–60°; careful watching is required during the addition as the reaction becomes vigorous from time to time and external cooling is necessary. After the addition was complete, the mixture was heated on a steam-bath for 1 hour. A 2-litre, three-necked flask was fitted with a separatory funnel having a wide-bored tap, a mercury-sealed mechanical stirrer, a still-head connected to two double-surface condensers in series and set for downward distillation; the receiver was cooled in ice. The flask was charged with a solution of 75 ml. of concentrated sulphuric acid and 500 ml. of water, the stirrer started and half of the solution of the Grignard reagent (this contained much sludge) added during 2 hours; the reaction mixture was then heated on a water-bath until no more pentane distilled. The decomposition was repeated with the other half of the Grignard reagent. The combined distillates were dried (anhydrous magnesium sulphate) and distilled through a four-section Pyrex Young and Thomas column, and the crude *n*-pentane (95 g.) was collected at 33–36°: *n*-butyl ether remained in the flask. The crude pentane was washed repeatedly with 10 ml. portions of concentrated sulphuric acid until the acid remained colourless (7 washings), then successively with water, 10% sodium carbonate solution, and water, and dried with anhydrous magnesium sulphate. It was then distilled from sodium in a Claisen flask with a fractionating side arm; practically all passed over at 36.1°/763 mm., and a middle portion was used for the physical measurements. B. p. 36.1°/763 mm.; *M* 72.15; n_D 1.35616, n_D 1.35796, n_F 1.36225, n_G 1.36518. Densities determined: d_4^{20} 0.6269, d_4^{18} 0.6348. Apparatus *D*.

<i>t.</i>	<i>H.</i>	d_4^{20}	γ .	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4^{20}	γ .	<i>P.</i>
11.2°	10.89	0.6345	17.06	231.8	21.8°	10.48	0.6254	16.18	232.0
13.2	10.76	0.6328	16.82	231.6					Mean 231.8

Shepard *et al.* (*J. Amer. Chem. Soc.*, 1931, **53**, 1948) give b. p. 36.00°, *d* 0.62632, n_D 1.35581, n_D 1.35769, n_F 1.36208. Mair (*Bur. Stand. J. Res.*, 1932, **9**, 457), for *n*-pentane obtained by hydrogenation of pentene over nickel at 140°, gives b. p. 36.06°, n_D^{25} 1.35470. Wibaut *et al.* (*Rec. Trav. chim.*, 1939, **58**, 337), for *n*-pentane prepared by hydrogenation of pentene, give b. p. 35.95°, *d* 0.62624, n_D 1.35587, n_D 1.35769, n_F 1.36200, n_G 1.36561, *P* 230.7.† Quayle *et al.* (*J. Amer. Chem. Soc.*, 1944, **66**, 940) give *d* 0.6260, *P* 231.0.

100. *n*-Hexane. Method 1. 46 G. of clean sodium pieces were placed in a 1.5-litre Pyrex round-bottomed flask fitted with two 25-cm. double-surface condensers in series, and 123 g. of dry *n*-propyl bromide (VIII, **69**) were weighed out separately. About 25 g. of the *n*-propyl bromide were added to the sodium: there was no immediate reaction. The mixture was refluxed gently and within a few minutes the sodium became blue; the reaction commenced and proceeded steadily whilst the blue colour slowly deepened. The flame was removed and the remainder of the *n*-propyl bromide was added in *ca.* 10 ml. portions during 90 minutes with frequent vigorous shaking of the flask. The reaction proceeded steadily for 2–3 hours. After the mixture had been left overnight, 150 ml. of rectified spirit were added during 3 hours, followed by a mixture of 75 ml. of rectified spirit and 75 ml. of water during 1 hour, and 150 ml. of water during 15 minutes. The mixture (three layers) was refluxed for 3 hours (to decompose any unchanged bromide), diluted with a large excess of water, and the hydrocarbon layer (20 g.; 32 ml.) separated. This was washed with a little water, dried with anhydrous magnesium sulphate, and distilled from sodium in a Claisen flask with a fractionating side arm, the fraction of b. p. 68.5–70° (18 g.) being collected separately. The crude *n*-hexane was washed with 3-ml. portions of concentrated sulphuric acid until the acid remained colourless (16 washings), then successively with water, 10% sodium carbonate solution and water, and finally dried with anhydrous magnesium sulphate. It was then distilled from sodium and passed over constantly at 68.7°/769 mm.: a middle fraction was used for the physical measurements. B. p. 68.7°/769 mm.; *M* 86.17; n_D 1.37313, n_D 1.37505, n_F 1.37958, n_G 1.38268; *R*₀ 29.79, *R*_D 29.93, *R*_F 30.25, *R*_G 30.47. The refractive indices at 25° were n_D 1.37048, n_D 1.37234, n_F 1.37687, n_G 1.37997; *R*₀ 29.80, *R*_D 29.93, *R*_F 30.26, *R*_G 30.48. Densities determined: d_4^{20} 0.6592, d_4^{25} 0.6548, $d_4^{42.4}$ 0.6394. Apparatus *A*.

<i>t.</i>	<i>H.</i>	d_4^{20}	γ .	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4^{20}	γ .	<i>P.</i>
18.5°	15.01	0.6606	18.57	271.1	41.4°	13.56	0.6403	16.26	270.7
22.5	14.74	0.6570	18.13	271.0					Mean 270.9

Method 2. A Grignard reagent was prepared from 12.0 g. of magnesium, 100 ml. of sodium-dried ether and a crystal of iodine contained in a 1-litre three-necked flask equipped with a separatory funnel (with guard tube), a mercury-sealed mechanical stirrer, and a long double-surface condenser (with guard tube). The separatory funnel was charged with a solution of 72.5 g. of dry *n*-hexyl bromide (VIII, **78**) in 200 ml. of anhydrous ether, and 10 g. of dry *n*-hexyl bromide were added through the condenser. The reaction started upon warming gently, and the solution of the bromide in ether was added at such a rate (*ca.* 2 hours) that the reaction was under control. The mixture was then gently refluxed, with stirring, for 2 hours, by which time most of the magnesium had reacted. The resulting solution of the Grignard reagent was then slowly added from a tap funnel into vigorously stirred ice water. The ethereal solution was separated, washed with water, saturated sodium bicarbonate solution, and water, dried (anhydrous magnesium sulphate), and distilled through a four-section Pyrex Young and Thomas column; 15 g. of crude *n*-hexane, b. p. 67–69°, were obtained. This was washed with concentrated sulphuric acid, etc., as in Method 1. B. p. 68.5°/755 mm.; n_D 1.37333, n_D 1.37518, n_F 1.37974, n_G 1.38286; *R*₀ 29.79, *R*_D 29.92, *R*_F 30.24, *R*_G 30.47; *M*_D 86.17. Densities determined: d_4^{20} 0.6595, $d_4^{41.8}$ 0.6399. Apparatus *A*.

<i>t.</i>	<i>H.</i>	d_4^{20}	γ .	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4^{20}	γ .	<i>F.</i>
15.4°	15.35	0.6637	19.08	271.6	41.6°	13.67	0.6396	16.37	271.5
21.1	14.97	0.6585	18.46	271.5					Mean 271.6
23.5	14.88	0.6563	18.29	271.8					

* The numbering of compounds in Clarendon type follows from Part VIII (J., 1943, 639). References to compounds, the preparation of which is described in Part VIII, will be abbreviated to, *e.g.*, VIII, **50**.

† Surface-tension measurements by method of maximum bubble pressure.

Timmermans and Martin (*J. Chim. physique*, 1928, **25**, 413), for hydrocarbon from *n*-propyl bromide and sodium, give b. p. 68-80°, *d* 0.65940, *n*_C 1.37321, *n*_D 1.37512, *n*_F 1.37976, *n*_G 1.38354. Lek (Thesis, Bruxelles, 1930, p. 43) gives *d* 0.65942, *P* 270.4. Shepard *et al.* (*loc. cit.*) give b. p. 68-71°, *d* 0.65945, *n*_C 1.37310, *n*_D 1.37506, *n*_F 1.37979. Mair (*loc. cit.*), for material from *n*-propyl bromide and sodium, gives b. p. 68-70°, *n*_D^{25°} 1.37224. Wibaut *et al.* (*loc. cit.*), for hydrocarbon obtained by hydrogenation of *n*-hexene over nickel, give b. p. 68-75°, *d* 0.65943, *n*_C 1.37300, *n*_D 1.37499, *n*_F 1.37950, *n*_G 1.38325, *P* 270.7. Quayle *et al.* (*loc. cit.*) give *d* 0.6593, *P* 270.8.

101. *n*-Heptane. 200 G. of amalgamated zinc were prepared from 200 g. of purified zinc wool in a 2-litre three-necked flask, and the latter was equipped with an efficient double-surface condenser, a mercury-sealed mechanical stirrer, and a lead-in tube which dipped almost to the bottom of the flask and was connected through an intermediate empty wash bottle to a Kipp's apparatus generating hydrogen chloride. The amalgamated zinc was covered with a mixture of 500 ml. of concentrated hydrochloric acid and 100 ml. of water, and 80 g. of di-*n*-propyl ketone, b. p. 142.3—143.3°/758 mm. (Part V, J., 1940, 171) added. The flask was heated with a minute flame, and the mixture stirred whilst a slow stream of hydrogen chloride was passed in: the passage of gas was temporarily stopped when the reaction became too vigorous. Most of the zinc had reacted after 8 hours, and the reaction mixture was set aside overnight. It was then steam-distilled from the same flask, the organic layer (54 g.) separated, washed with water, 10% sodium carbonate solution, water, dried (anhydrous magnesium sulphate), and fractionated over sodium: the crude *n*-heptane was collected at 97—99°. This was washed repeatedly with 10% of its volume of concentrated sulphuric acid until the washings were colourless, and the pure *n*-heptane isolated as described under *n*-hexane, Method 1. B. p. 98°/763 mm.; *M* 100.20; *n*_C 1.38564, *n*_D 1.38758, *n*_F 1.39231, *n*_G 1.39572. Densities determined: *d*_{4°}^{20°} 0.6827, *d*_{4°}^{31°} 0.6661, *d*_{4°}^{60.1°} 0.6502. Apparatus *A*.

<i>t.</i>	<i>H.</i>	<i>d</i> _{4°} ^{20°}	<i>γ.</i>	<i>P.</i>	<i>t.</i>	<i>H.</i>	<i>d</i> _{4°} ^{20°}	<i>γ.</i>	<i>P.</i>
19.5°	16.03	0.6831	20.50	312.1	60.1°	13.67	0.6502	16.64	311.7
24.2	15.84	0.6794	20.15	312.5					
41.4	14.69	0.6662	18.33	311.5					Mean 312.0

Shepard *et al.* (*loc. cit.*) give b. p. 98-38°, *d* 0.68378, *n*_C 1.38580, *n*_D 1.38775, *n*_F 1.39261. Mair (*loc. cit.*), for *n*-heptane from Jeffrey pine, gives b. p. 98-38°, *n*_D^{25°} 1.38510. Wibaut *et al.* (*loc. cit.*), sample from Bureau of Standards, Washington, give b. p. 98-40°, *d* 0.68378, *n*_C 1.38573, *n*_D 1.38775, *n*_F 1.39247, *n*_G 1.39637, *P* 310.8. Quayle *et al.* (*loc. cit.*) give *d* 0.6837, *P* 311.4.

102. *n*-Octane. Method 1. The crude *n*-octane, b. p. 122—125° (30 g.), was prepared from 46 g. of sodium and 137 g. of *n*-butyl bromide (VIII, 71)—see method under *n*-hexane. Upon purification by treatment with 10% of its volume of concentrated sulphuric acid until the acid remained colourless, etc., the *n*-octane boiled at 124.5°/760 mm. B. p. 124.5°/760 mm.; *M* 114.22; *n*_C 1.39544, *n*_D 1.39743, *n*_F 1.40227, *n*_G 1.40576. Densities determined: *d*_{4°}^{20°} 0.7028, *d*_{4°}^{99°} 0.6861, *d*_{4°}^{61.1°} 0.6700, *d*_{4°}^{84.9°} 0.6497. Apparatus *A*.

<i>t.</i>	<i>H.</i>	<i>d</i> _{4°} ^{20°}	<i>γ.</i>	<i>P.</i>	<i>t.</i>	<i>H.</i>	<i>d</i> _{4°} ^{20°}	<i>γ.</i>	<i>P.</i>
22.9°	16.26	0.7004	21.32	350.4	60.3°	14.27	0.6706	17.92	350.7
23.5	16.22	0.6999	21.26	350.4	86.0	12.83	0.6488	15.59	350.3
40.7	15.30	0.6863	19.66	350.5					Mean 350.5

Method 2. By the Clemmensen reduction of commercial methyl *n*-hexyl ketone, b. p. 171—172° (for details, see under **101**). The *n*-octane had b. p. 125.5°/771 mm., *d* 0.7022, *n*_D 1.39778, *P* 351.7. Timmermans and Martin, *loc. cit.*, for octane from *n*-butyl bromide and sodium, give b. p. 125-80°, *d* 0.70197, *n*_C 1.39512, *n*_D 1.39727, *n*_F 1.40240. Lek (*loc. cit.*) gives *d* 0.70232, *P* 350.3. Shepard *et al.* (*loc. cit.*) give b. p. 125-59°, *d* 0.70279, *n*_C 1.39557, *n*_D 1.39760, *n*_F 1.40255. Mair (*loc. cit.*), for octane from *n*-butyl bromide and sodium, gives b. p. 125-59°, *n*_D^{25°} 1.39509. Wibaut *et al.* (*loc. cit.*), for octane obtained by hydrogenation of octene over nickel, give b. p. 125-75°, *d* 0.70280, *n*_C 1.39562, *n*_D 1.39770, *n*_F 1.40252, *n*_G 1.40648, *P* 350.6. Quayle *et al.* (*loc. cit.*) give *d* 0.7027, *P* 351.1.

103. *n*-Nonane. This was obtained by the Clemmensen reduction (for details, see under *n*-heptane) of methyl *n*-heptyl ketone, b. p. 192—193°/749 mm.; the latter was prepared by passage of a mixture of 3 mols. of glacial acetic acid and 1 mol. of *n*-octoic acid (b. p. 235—239°/760 mm.; Deutsche Hydrierwerke) over thoria at 400—450°. 96 G. of the ketone yielded 63 g. of crude *n*-nonane, b. p. 147—152° (largely 148—150°). After being shaken 18 times with 5-ml. portions of concentrated sulphuric acid, the pure *n*-nonane was isolated in the usual manner. B. p. 150.5°/759 mm.; *M* 128.25; *n*_C 1.40339, *n*_D 1.40543, *n*_F 1.41041, *n*_G 1.41420. Densities determined: *d*_{4°}^{20°} 0.7174, *d*_{4°}^{41.5°} 0.7015, *d*_{4°}^{61.5°} 0.6858, *d*_{4°}^{84.6°} 0.6672. Apparatus *D*.

<i>t.</i>	<i>H.</i>	<i>d</i> _{4°} ^{20°}	<i>γ.</i>	<i>P.</i>	<i>t.</i>	<i>H.</i>	<i>d</i> _{4°} ^{20°}	<i>γ.</i>	<i>P.</i>
17.4°	12.99	0.7194	23.02	391.6	61.2°	11.19	0.6863	18.97	390.9
20.6	12.88	0.7169	22.80	390.9	87.7	10.14	0.6656	16.67	389.3
26.3	12.66	0.7126	22.28	391.0					
41.4	12.00	0.7016	20.79	390.3					Mean 390.7

Shepard *et al.* (*loc. cit.*) give b. p. 150-71°, *d* 0.71780, *n*_C 1.40356, *n*_D 1.40563, *n*_F 1.41077. Mair (*loc. cit.*), for nonane from *n*-nonylmagnesium bromide *ex n*-heptyl bromide and ethylene oxide, gives b. p. 150-72°, *n*_D^{25°} 1.40340. Wibaut *et al.* (*loc. cit.*), for nonane obtained by hydrogenation of nonene over nickel, give b. p. 150-70°, *d* 0.71808, *n*_C 1.40353, *n*_D 1.40561, *n*_F 1.41058, *n*_G 1.41462, *P* 390.5. Quayle *et al.* (*loc. cit.*) give *d* 0.7175, *P* 391.1.

104. *n*-Decane. The crude *n*-decane, b. p. 171—179° (mainly 173—175°) (45 g.), was prepared from 46 g. of sodium and 151 g. of *n*-amyl bromide (VIII, 74)—for method see under *n*-hexane. After 19 washings with 5-ml. portions of concentrated sulphuric acid, the latter remained colourless, and the pure *n*-decane was isolated in the usual manner. B. p. 172.5°/762 mm.; *M* 142.28; *n*_C 1.40999, *n*_D 1.41206, *n*_F 1.41715, *n*_G 1.42080. Densities determined: *d*_{4°}^{20°} 0.7301, *d*_{4°}^{40.5°} 0.7159, *d*_{4°}^{61.0°} 0.7007, *d*_{4°}^{86.3°} 0.6812. Apparatus *A*.

<i>t.</i>	<i>H.</i>	<i>d</i> _{4°} ^{20°}	<i>γ.</i>	<i>P.</i>	<i>t.</i>	<i>H.</i>	<i>d</i> _{4°} ^{20°}	<i>γ.</i>	<i>P.</i>
17.1°	17.56	0.7322	24.08	430.4	60.8°	15.28	0.7006	20.05	429.7
19.0	17.42	0.7308	23.84	430.2	87.8	13.90	0.6801	17.70	429.1
22.3	17.21	0.7284	23.47	429.9					
41.4	16.35	0.7153	21.90	430.3					Mean 429.9

Lek (*loc. cit.*) gives *d* 0.73064, *P* 429.7. Shepard *et al.* (*loc. cit.*) give b. p. 174.06°, *d* 0.73014, *n*_C 1.40994, *n*_D 1.41203, *n*_F 1.41728. Mair (*loc. cit.*), for decane obtained by addition of sodium to *n*-amyl bromide, gives b. p. 174.02°, *n*_D^{25°} 1.40961. Quayle *et al.* (*loc. cit.*) give *d* 0.7295, *P* 431.3.

105. *n*-Undecane. This hydrocarbon was obtained by Clemmensen reduction of di-*n*-amyl ketone, b. p. 222—224° (prepared by passing *n*-hexoic acid over thoria at 400—450°). 100 G. of the ketone yielded 82 g. of distillate (for details, see under *n*-heptane). This contained an appreciable quantity of di-*n*-amylcarbinol; distillation gave a fraction of b. p. 195—220° (75 g.). The secondary alcohol was removed as the non-volatile sodium compound by refluxing it for several hours over, and then distilling it from, a large excess of sodium; this treatment gave 41 g. of crude *n*-undecane, b. p. 185—195°, or 190—194° upon redistillation. The crude hydrocarbon was treated with concentrated sulphuric acid until the acid layer was colourless (17 washings with 4-ml. portions of concentrated sulphuric acid were required), water, 10% sodium carbonate solution, water, and dried over anhydrous magnesium sulphate. The last traces of moisture were removed by standing over sodium for several hours, and the hydrocarbon was twice distilled under reduced pressure; there is slight decomposition at atmospheric pressure. B. p. 87°/20 mm.; *M* 156.30; *n*_D 1.41507, *n*_D 1.41716, *n*_F 1.42229, *n*_G 1.42603. Densities determined: $d_{4^{\circ}}^{20^{\circ}}$ 0.7398, $d_{4^{\circ}}^{41^{\circ}}$ 0.7252, $d_{4^{\circ}}^{60^{\circ}}$ 0.7108, $d_{4^{\circ}}^{87^{\circ}}$ 0.6913. Apparatus A.

<i>t.</i>	<i>H.</i>	$d_{4^{\circ}}^{\circ}$	γ .	<i>P.</i>	<i>t.</i>	<i>H.</i>	$d_{4^{\circ}}^{\circ}$	γ .	<i>P.</i>
26.3°	17.47	0.7353	24.05	470.7	62.1°	15.73	0.7099	20.19	470.8
28.1	17.38	0.7340	23.89	470.8	87.2	14.46	0.6912	18.72	470.3
40.8	16.74	0.7254	22.73	470.5					Mean 470.6

Shepard *et al.* (*loc. cit.*) give b. p. 195.84°, *d* 0.74025, *n*_D 1.41514, *n*_D 1.41727, *n*_F 1.42252. Mair (*loc. cit.*), for undecane from undecylene and hydrogen over copper chromite catalyst, gives *n*_D 1.41495. Quayle *et al.* (*loc. cit.*) gives *d* 0.7406, *P* 470.8.

106. *n*-Dodecane. The crude product (75 g.) produced by the action of 165 g. of *n*-hexyl bromide (VIII, 78) upon 46 g. of sodium (for method, see under *n*-hexane) was washed with 5-ml. portions of concentrated sulphuric acid until the acid layer was colourless (16 washings), water, 10% sodium carbonate solution, water, and dried over anhydrous magnesium sulphate, followed by sodium. The hydrocarbon was then distilled twice under diminished pressure. B. p. 94°/13.5 mm.; *M* 170.33; *n*_D 1.41967, *n*_D 1.42186, *n*_F 1.42697, *n*_G 1.43068. Densities determined: $d_{4^{\circ}}^{90^{\circ}}$ 0.7498, $d_{4^{\circ}}^{41^{\circ}}$ 0.7348, $d_{4^{\circ}}^{61^{\circ}}$ 0.7204, $d_{4^{\circ}}^{88^{\circ}}$ 0.7026. Apparatus D.

<i>t.</i>	<i>H.</i>	$d_{4^{\circ}}^{\circ}$	γ .	<i>P.</i>	<i>t.</i>	<i>H.</i>	$d_{4^{\circ}}^{\circ}$	γ .	<i>P.</i>
14.5°	13.86	0.7537	25.80	509.3	63.0°	12.13	0.7193	21.55	510.2
18.5	13.78	0.7509	25.55	510.2	86.5	11.26	0.7020	19.52	510.0
22.5	13.72	0.7480	25.34	510.9					Mean 510.0
41.5	12.86	0.7344	23.32	509.7					

Shepard *et al.* (*loc. cit.*) give b. p. 216.23°, $d_{4^{\circ}}^{25^{\circ}}$ 0.74542, *n*_D 1.41965, *n*_D 1.42188, *n*_F 1.42720. Mair (*loc. cit.*), for dodecane from sodium and *n*-hexyl bromide, gives *n*_D 1.41967.

107. *n*-Tridecane. Clemmensen reduction of 78 g. of di-*n*-hexyl ketone, m. p. 32°, b. p. 117.5°/7 mm. (prepared by passing redistilled *n*-heptoic acid over thoria at 400—450°) yielded 74 g. of steam-volatile products (for details, see under *n*-heptane) consisting largely of *n*-tridecane and di-*n*-hexylcarbinol. The latter was converted into the sodium derivative by heating with a large excess of sodium at 150—160°, and, after cooling, this was filtered off and washed with a little sodium-dried ether. The filtrate was distilled under reduced pressure and 45 g. of crude *n*-tridecane, b. p. 99—100°/7 mm., were obtained. After treatment with 4-ml. portions of concentrated sulphuric acid until the acid layer was colourless (18 washings), the pure *n*-tridecane was isolated as described under *n*-undecane. B. p. 92.5°/4.5 mm.; *M* 184.35; *n*_D 1.42326, *n*_D 1.42541, *n*_F 1.43068, *n*_G 1.43438. Densities determined: $d_{4^{\circ}}^{20^{\circ}}$ 0.7559, $d_{4^{\circ}}^{41^{\circ}}$ 0.7414, $d_{4^{\circ}}^{60^{\circ}}$ 0.7289, $d_{4^{\circ}}^{86^{\circ}}$ 0.7110. Apparatus A.

<i>t.</i>	<i>H.</i>	$d_{4^{\circ}}^{\circ}$	γ .	<i>P.</i>	<i>t.</i>	<i>H.</i>	$d_{4^{\circ}}^{\circ}$	γ .	<i>P.</i>
21.3°	18.30	0.7550	25.87	550.7	87.7°	15.15	0.7097	20.13	550.2
41.1	17.35	0.7419	24.10	550.6					Mean 550.5
61.9	16.36	0.7279	22.30	550.4					

108. *n*-Tetradecane. 27.5 G. of clean sodium were allowed to react with 107 g. of *n*-heptyl bromide (VIII, 79), the procedure described under *n*-hexane being followed. The mixture was then treated with 120 ml. of rectified spirit (90 minutes), 60 ml. of 50% alcohol (30 minutes), and 60 ml. of water (10 minutes), the whole (three layers) refluxed for 3 hours, allowed to cool, and then poured into a large excess of water. The hydrocarbon layer (52.5 g.) was then shaken with 5-ml. portions of concentrated sulphuric acid until the acid remained colourless (16 washings), washed with water 10% sodium carbonate solution, and water, and dried with anhydrous magnesium sulphate and then with sodium. The *n*-tetradecane (44 g.) was twice distilled under diminished pressure—the first distillation removes high-boiling impurities.* B. p. 123°/12 mm.; *M* 198.38; *n*_D 1.42688, *n*_D 1.42907, *n*_F 1.43433, *n*_G 1.43818. Densities determined: $d_{4^{\circ}}^{20^{\circ}}$ 0.7624, $d_{4^{\circ}}^{40^{\circ}}$ 0.7494, $d_{4^{\circ}}^{61^{\circ}}$ 0.7348, $d_{4^{\circ}}^{86^{\circ}}$ 0.7175. Apparatus D.

<i>t.</i>	<i>H.</i>	$d_{4^{\circ}}^{\circ}$	γ .	<i>P.</i>	<i>t.</i>	<i>H.</i>	$d_{4^{\circ}}^{\circ}$	γ .	<i>P.</i>
21.5°	14.11	0.7614	26.53	591.3	60.2°	12.74	0.7357	23.15	591.5
25.2	13.96	0.7589	26.16	591.2	87.8	11.78	0.7165	20.84	591.6
40.9	13.46	0.7492	24.90	591.5					Mean 591.4

109. *n*-Pentadecane. 58.5 G. of di-*n*-heptyl ketone, m. p. 43°, b. p. 139.5°/5 mm. [prepared by passing *n*-octoic acid, b. p. 235—239° (Deutsche Hydrierwerke) over thoria at 400—450°], was reduced with 200 g. of amalgamated zinc (for details, see under *n*-heptane). After 24 hours, the organic layer (52 g.) was separated from the reaction mixture, and washed successively with water, 10% sodium carbonate solution, and water, and then dried over anhydrous magnesium sulphate. It was then heated with a large excess of sodium at 120—130° for 6 hours, the resulting sodium derivative of di-*n*-heptylcarbinol filtered off on a sintered-glass funnel, and washed with a little sodium-dried ether. The filtrate was distilled under reduced pressure and 30 g. of crude *n*-pentadecane, b. p. 112—116°/3.3—3.7 mm., were obtained. This was shaken with 4-ml. portions of concentrated sulphuric acid until the acid layer was colourless (25 washings), and the pure hydrocarbon isolated as under *n*-undecane. B. p. 120°/4.5 mm.; *M* 212.41; *n*_D 1.42980, *n*_D

* It is noteworthy that Bachmann and Clarke (*J. Amer. Chem. Soc.*, 1927, 49, 4097), by treating 1074 g. of *n*-heptyl bromide, heated to 150° and vigorously stirred, with 100 g. of sodium, followed by adding water, isolating the oil and again treating the latter with sodium until no further action took place, obtained yields of 9% of *n*-heptane, b. p. 96—99°, 3% of heptylene, 67% of *n*-tetradecane, b. p. 115—117°/10 mm., m. p. 4—4.5°, 3% of heneicosane, b. p. 340—345°, and hydrocarbons of higher molecular weight.

1.43199, n_D 1.43734, n_G 1.44126. Densities determined: d_4^{20} 0.7687, $d_4^{15.0}$ 0.7549, $d_4^{11.4}$ 0.7412, $d_4^{8.6}$ 0.7236. Apparatus A.

<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>
22.6°	18.78	0.7670	26.97	631.1	86.0°	15.97	0.7241	21.65	631.1
40.9	17.97	0.7550	25.43	631.1					Mean 631.3
62.0	16.99	0.7408	23.57	631.8					

110. *n*-Hexadecane. Interaction of 31 g. of sodium and 129 g. of *n*-octyl bromide, b. p. 199—200°/764 mm. (VIII, 80), as described under *n*-hexane gave 73 g. of the crude hydrocarbon. After 20 washings with 6-ml. portions of concentrated sulphuric acid,* the acid layer still had a deep yellow colour; the residual hydrocarbon was accordingly washed with water, 10% sodium carbonate solution, water, dried over anhydrous magnesium sulphate (weight dry, 54 g.), and distilled. The crude *n*-hexadecane (32 g.) was collected at 146—150°/11 mm. and a considerable dark residue remained. After three washings with 3-ml. portions of concentrated sulphuric acid, the acid remained colourless: the *n*-hexadecane, which was isolated in the usual manner, distilled at a constant temperature. B. p. 143.5°/9 mm., m. p. 18°; *M* 226.43; n_D 1.43241, n_D 1.43465, n_F 1.44004, n_G 1.44391. Densities determined: d_4^{20} 0.7743, $d_4^{15.0}$ 0.7598, $d_4^{11.4}$ 0.7464, $d_4^{8.6}$ 0.7291. Apparatus A.

<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>
21.1°	19.00	0.7735	27.52	670.6	62.1°	17.16	0.7457	23.96	671.8
27.4	18.77	0.7693	27.04	671.2	87.5	16.04	0.7287	21.89	672.1
41.4	18.08	0.7595	25.71	671.0					Mean 671.3

Wibaut *et al.* (*loc. cit.*), for hexadecane obtained by hydrogenation of cetene over nickel, give m. p. 17.9°, *d* 0.77387, n_D 1.43242, n_D 1.43470, n_F 1.44022, n_G 1.44451.

111. 2 : 6-Dimethylheptane (diisobutylmethane). 60 G. of redistilled diisobutyl ketone, b. p. 164—166°/753 mm. (General and Metallurgical; Carbon and Carbide Corporation) was reduced by 200 g. of amalgamated zinc (for details, see under *n*-heptane). The steam distillate was washed with water, saturated sodium bicarbonate solution, water, dried, and distilled; the fraction, b. p. 138—155°, was collected. This contained some diisobutylcarbinol, which was removed by refluxing it for 3 hours with a large excess of sodium, allowing it to stand overnight, and distilling it; 12 g. of crude diisobutylmethane, b. p. 131—134° (mainly 133—134°), were obtained. The crude hydrocarbon was purified by shaking with 1-ml. portions of concentrated sulphuric acid until the acid remained colourless (14 washings), etc. B. p. 134.5°/761 mm.; *M* 128.25; n_D 1.39872, n_D 1.40077, n_F 1.40574, n_G 1.40936. Densities determined: d_4^{20} 0.7098, $d_4^{15.0}$ 0.6921, $d_4^{11.4}$ 0.6773, $d_4^{8.6}$ 0.6576. Apparatus A.

<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>
12.9°	16.18	0.7155	21.68	386.8	63.0°	13.47	0.6757	17.04	385.7
18.8	15.86	0.7108	21.11	386.7	86.8	12.37	0.6558	15.19	386.1
22.7	15.68	0.7076	20.78	387.0					Mean 386.5
42.9	14.58	0.6915	18.88	386.6					

112. 2 : 5-Dimethylhexane (diisobutyl). This was prepared in the usual manner (see under *n*-hexane) from 46 g. of sodium and 137 g. of isobutyl bromide (VIII, 72A). When all the bromide had been introduced, the flask was well shaken, whereupon a vigorous reaction set in and the liquid refluxed in the condenser. After 15—20 minutes, the flask was shaken again, etc.; the shaking and standing were repeated until no visible reaction occurred upon shaking. After 2 hours, the excess of sodium was decomposed as before, the liquid mixture refluxed for 4 hours, and allowed to stand overnight. Dilution with excess of water gave 48 g. of the crude hydrocarbon. This was purified by shaking with concentrated sulphuric acid until the acid remained colourless (10 3-ml. portions). The yield of pure diisobutyl was 43 g. B. p. 109°/760 mm.; *M* 114.22; n_D 1.39069, n_D 1.39270, n_F 1.39756, n_G 1.40099. Densities determined: d_4^{20} 0.6942, $d_4^{15.0}$ 0.6759, $d_4^{11.4}$ 0.6586, $d_4^{8.6}$ 0.6379. Apparatus A.

<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>
15.1°	15.48	0.6984	20.24	346.9	61.1°	13.03	0.6583	16.06	347.8
23.8	15.13	0.6909	19.57	347.7	83.0	11.79	0.6399	14.13	347.0
40.9	14.21	0.6761	17.99	347.9					Mean 347.5

Wibaut *et al.* (*loc. cit.*), for hydrocarbon obtained by electrolysis of potassium isovalerate with a platinum anode, give b. p. 109.25°, *d* 0.69426, n_D 1.39081, n_D 1.39285, n_F 1.39772, n_G 1.40169, *P* 346.8.

113. 3 : 4-Dimethylhexane (di-sec-butyl). To 46 g. of sodium, contained in a 1-litre round-bottomed flask equipped with two 25-cm. double-surface condensers in series, was added about one-quarter of the total quantity (137 g.) of dry *sec*-butyl bromide (VIII, 73). The mixture was gently heated under reflux for 1 hour, but little action occurred apart from the formation of a few blue spots upon the sodium. Reaction was initiated by addition of 3 ml. of rectified spirit; the whole surface of the sodium then acquired a blue colour. The remainder of the *sec*-butyl bromide was added in two equal quantities during 1 hour with frequent shaking. A further 4 ml. of rectified spirit was added, the mixture refluxed for 1 hour, and the process repeated. Upon allowing the mixture to cool somewhat and shaking it vigorously, a lively reaction set in, resulting in the formation of molten sodium and some unsaturated hydrocarbon (probably butene). Further shaking had little effect, but the dropwise addition of 10 ml. of rectified spirit produced a renewed vigorous reaction. After standing overnight, the excess of sodium was decomposed in the usual manner by addition of 100 ml. of rectified spirit (90 minutes), 100 ml. of 50% alcohol (45 minutes), and 150 ml. of water (15 minutes). The mixture was refluxed for 6 hours to hydrolyse any unchanged bromide, poured into a large excess of water, and, after filtering from a little tarry matter, the crude hydrocarbon (9 g.) was separated. Repetition of the above experiment but with ethyl acetate (in 1-ml. portions) as catalyst gave 7 g. of the crude hydrocarbon. The combined products were shaken with 1-ml. portions of concentrated sulphuric acid until the acid layer was colourless (17 washings) and the hydrocarbon was isolated in the usual manner and fractionated twice from sodium. B. p. 117°/758 mm.; *M* 114.22; n_D 1.40242, n_D 1.40445, n_F 1.40933, n_G 1.41289. Densities determined: d_4^{20} 0.7200, $d_4^{15.0}$ 0.7033, $d_4^{11.4}$ 0.6871, $d_4^{8.6}$ 0.6662. Apparatus A.

<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>
21.2°	16.13	0.7190	21.72	342.9	61.9°	13.84	0.6869	17.80	341.9
41.8	14.98	0.7032	19.72	342.3	86.6	12.57	0.6660	15.68	342.0
									Mean 342.3

* The number of washings with concentrated sulphuric acid would probably be considerably reduced if the crude hydrocarbon were first subjected to a preliminary distillation to remove low- and high-boiling impurities.

Wibaut *et al.* (*loc. cit.*), for hydrocarbon from "molecular" sodium and *sec.*-butyl bromide in ethereal solution, give b. p. 117.85°, d_4^{20} 0.71951, n_D^{20} 1.40224, n_D^{25} 1.40436, n_F^{20} 1.40924, n_G^{20} 1.41323, P 342.4.

114. 2: 7-Dimethyloctane (*diisoamyl*, "synthetic"). The reaction between 46 g. of sodium and 151 g. of *isoamyl* bromide (VIII, **75A**, from Sharples's synthetic *isoamyl* alcohol) (for details, see under *n*-hexane) yielded, after refluxing the solution for 6 hours, 48 g. of dry crude hydrocarbon. The crude *diisoamyl*, b. p. 155–163° (mainly 159–161°) (36 g.) was separated by fractionation, and then shaken with 3-ml. portions of concentrated sulphuric acid until the acid layer remained colourless (10 washings), etc. The yield of pure 2: 7-dimethyloctane was 34 g. B. p. 160–161°/773 mm.; M 142.28; n_D 1.40786, n_D^{20} 1.40994, n_F^{20} 1.41501, n_G^{20} 1.41867. Densities determined: d_4^{20} 0.7283, d_4^{21-3} 0.7119, d_4^{21-7} 0.6963, d_4^{28-9} 0.6766. Apparatus A.

<i>t.</i>	<i>H.</i>	d_4^{20}	γ	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4^{20}	γ	<i>P.</i>
14.0°	16.79	0.7329	23.04	425.3	62.1°	14.31	0.6960	18.65	424.4
16.3	16.69	0.7311	22.85	425.5	87.3	13.05	0.6763	16.53	424.2
41.4	15.41	0.7118	20.54	425.5					Mean 425.1

Von Auwers and Eisenlohr (*Z. physikal. Chem.*, 1913, **83**, 430) give b. p. 158.0–159.5°/760 mm., d_4^{18-1} 0.7278, n_D^{18-1} 1.40715, n_D^{18-1} 1.41435, n_D^{18-1} 1.41854.

114A. 2: 7-Dimethyloctane (*diisoamyl*, "fermentation"). The reaction between 46 g. of sodium and 151 g. of *isoamyl* bromide (VIII, **75**, from Bisol "fermentation" *isoamyl* alcohol) gave 52 g. of the crude hydrocarbon, which was treated as under **114**. B. p. 160.5°/773 mm.; n_D 1.40647, n_D^{20} 1.40855, n_F^{20} 1.41363, n_G^{20} 1.41717. Densities determined: d_4^{20} 0.7237, d_4^{21-1} 0.7084, d_4^{28-2} 0.6947, d_4^{28-0} 0.6740. Apparatus A.

<i>t.</i>	<i>H.</i>	d_4^{20}	γ	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4^{20}	γ	<i>P.</i>
13.0°	16.76	0.7289	22.87	426.9	62.1°	14.30	0.6926	18.55	426.3
24.2	16.35	0.7206	21.56	425.5	86.1	13.03	0.6739	16.44	425.1
41.6	15.29	0.7080	20.27	426.4					Mean 426.1

Lek (*loc. cit.*) gives d 0.72257, P 426.9.

115. 4: 5-Dimethyloctane. The reaction between 46 g. of sodium and 151 g. of 2-bromopentane (VIII, **76**) proceeded similarly to that already described under *di-sec.*-butyl, and 3 ml. of anhydrous ethyl acetate (catalyst) were added in several portions. Some pentene was formed and the yield of purified 4: 5-dimethyloctane (Found: C, 84.5; H, 15.6. $C_{10}H_{22}$ requires C, 84.4; H, 15.6%) was 10 g. B. p. 159–160°/769 mm.; M 142.28; n_D 1.41517, n_D^{20} 1.41726, n_F^{20} 1.42233, n_G^{20} 1.42595. Densities determined: d_4^{20} 0.7458, d_4^{21-9} 0.7304, d_4^{28-2} 0.7148, d_4^{28-0} 0.6964. Apparatus D.

<i>t.</i>	<i>H.</i>	d_4^{20}	γ	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4^{20}	γ	<i>P.</i>
21.5°	12.66	0.7447	23.28	419.7	60.0°	11.22	0.7164	19.85	419.2
41.5	11.97	0.7307	21.60	419.8	86.8	10.24	0.6958	17.60	418.8
									Mean 419.4

116. 3: 4-Diethylhexane. This was prepared from 59 g. of sodium and 258 g. of 3-bromopentane (VIII, **77**), the procedure described under *di-sec.*-butyl being followed; 5 ml. of pure ethyl acetate, added in 1-ml. portions, were employed as catalyst. Much low-boiling material (containing pentene) was produced and the yield of purified 3: 4-diethylhexane (Found: C, 84.6; H, 15.6. $C_{10}H_{22}$ requires C, 84.4; H, 15.6%) was 12 g. B. p. 158.5–159.5°/764 mm.; M 142.28; n_D 1.41687, n_D^{20} 1.41896, n_F^{20} 1.42401, n_G^{20} 1.42769. Densities determined: d_4^{20} 0.7510, d_4^{21-4} 0.7347, d_4^{28-6} 0.7194, d_4^{28-8} 0.7005. Apparatus D.

<i>t.</i>	<i>H.</i>	d_4^{20}	γ	<i>P.</i>	<i>t.</i>	<i>H.</i>	d_4^{20}	γ	<i>P.</i>
22.0°	12.61	0.7495	23.34	417.3	60.5°	11.16	0.7211	19.87	416.6
42.3	11.89	0.7340	21.55	417.6	88.5	10.13	0.6992	17.49	416.2
									Mean 417.0

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