CCCCXXII.—*Studies in the Olefin Series. Part I. The Synthesis of Δ^1-Olefins.*

By REGINALD WILKINSON.

IN a series of researches upon the detonation characteristics of hydrocarbons it was found necessary to prepare a number of highly purified olefins. The present paper describes the preparation and physical properties of the Δ^1-olefins from pentene to nonene : the data in the literature are either incomplete or, in many cases, contradictory, and the discrepancies have given rise in the past to discussions as to the structure of the compounds in question (compare Brooks and Humphrey, *J. Amer. Chem. Soc.*, 1918, **40**, 838). The author, therefore, deemed it advisable first to investigate these hydrocarbons with the object of accurately determining their physical constants.

The majority of the methods employed for the preparation of these compounds, notably those involving the use of drastic reagents and high temperatures as in the dehydration of alcohols, and the removal of halogen acid from alkyl halides, lead to mixtures of isomerides (Zelinsky and Przewalsky, *Chem. Zentr.*, 1908, ii, 1854; Nef, *Annalen*, 1899, **309**, 126; 1901, **318**, 1; Klages, *Ber.*, 1902, **35**, 2633; Mason, *Compt. rend.*, 1901, **132**, 483; Sabatier and Mailhe, *ibid.*, 1913, **156**, 658), but there are three general methods capable of yielding pure compounds. Of these, that of Dykstra, Lewis, and Boord (*J. Amer. Chem. Soc.*, 1930, **52**, 3396), involving the bromination of chloroethyl ethers, suffers from the fact that the initial materials are not readily available.

The second method is that discovered by von Braun (*Annalen*, 1911, **382**, 22) in which quaternary ammonium hydroxides are decomposed by gentle distillation. He thus obtained from trimethyl-*n*-hexylammonium hydroxide a very small amount of a hydrocarbon, b. p. 62—63°, which he regarded as Δ^1-hexene.

Brooks and Humphrey (*loc. cit.*), in the third general method, confirmed von Braun's olefin as Δ^1-hexene by synthesising it by means of a reaction which had been applied by Tiffeneau (*Compt. rend.*, 1904, **139**, 481) to the synthesis of allyl derivatives of benzene. They treated *n*-propylmagnesium bromide with allyl bromide, the reaction taking place smoothly at room temperature.

In the present investigation the same general procedure was adopted, in which allyl bromide was treated with the appropriate Grignard reagent :

$$CH_2R{\cdot}MgBr + CH_2Br{\cdot}CH{:}CH_2 \longrightarrow CH_2R{\cdot}CH_2{\cdot}CH{:}CH_2 + MgBr_2$$

The details of the method of carrying out this reaction were considerably modified, particularly the process of purification, which in any case is long and tedious. It is claimed that the method described involves least possibility of change in constitution. Several hundred grams (200—650) of hydrocarbon were prepared in each case and therefore refined methods of purification could be used. The attendant losses were fairly large, but of comparative unimportance, as the sole aim was to obtain a final pure product.

The olefin (yield, 77—94%) was isolated from the crude hydrocarbon mixture by conversion into the dibromide by the theoretical amount of bromine, determined by a modification of McIlhiney's method (*J. Amer. Chem. Soc.*, 1899, **21**, 1084), at a temperature below − 5°. Under these conditions, no substitution of bromine for hydrogen is likely to occur, since Johansen (*J. Ind. Eng. Chem.*, 1922, **14**, 291) has shown that with hydrocarbons of high molecular weight substitution is negligible at temperatures as high as 25°, and that it decreases rapidly with fall of temperature. The results given by the McIlhiney method were checked by using erucic acid and oleic acid (Kahlbaum). The figures obtained were lower than the theoretical values by less than 2%.

The 1 : 2-dibromides were isolated by fractional distillation, finally in a vacuum, as heavy, colourless, highly refracting liquids having pleasant fruity odours. 1 : 2-Dibromohexane, when highly diluted, has an odour of oranges. The dibromides were decomposed by the method of Gladstone and Tribe (J., 1878, **21**, 306). The dried and fractionated olefins had the physical properties tabulated below.

Δ^1-Olefins.

Olefin.	B. p. /760 mm.	$d_{4°}^{20°}$.	$n_{4°}^{20°}$.	$[R_L]_D$ calc.	$[R_L]_D$ found.
Pentene	30·1— 30·3°	0·6414	1·3736	24·72	24·83
Hexene	61·5— 62·5	0·6766	1·3868	29·32	29·24
Heptene	93·5— 94·5	0·6977	1·3976	33·93	33·82
Octene	121·5—122·5	0·7158	1·4082	38·53	37·19
Nonene	145·0—145·6	0·7315	1·4163	43·13	43·19

Dibromides.

Dibromide.	B. p./mm.	$d_{4°}^{20°}$.	$n_{4°}^{20°}$.	$[R_L]_D$ calc.	$[R_L]_D$ found.
1 : 2-Dibromopentane	85°/30	1·6740	1·5090	40·87	41·00
1 : 2-Dibromohexane	82/12	1·6110	1·5061	45·47	45·00
1 : 2-Dibromoheptane	116/25	1·5180	1·5022	50·07	50·03
1 : 2-Dibromo-octane	118·5/15	1·4580	1·4970	54·68	54·46
1 : 2-Dibromononane	141·5/20	1·3980	1·4942	59·28	59·57

EXPERIMENTAL.

The same experimental technique was adopted with each olefin prepared, and a description of one is typical. The primary alkyl halides were dried over anhydrous calcium chloride and fractionated before use. The Grignard reagent was prepared (the recommendations of Gilman, *J. Amer. Chem. Soc.*, 1929, **51**, 1576, for obtaining the maximum yield being adopted) from magnesium (50 g.) and alkyl bromide (2 mols.) in dry ether (1400 c.c.), and the reaction completed by refluxing for 1 hour on the water-bath. The olefin was prepared from the Grignard reagent in a flask having three necks, carrying a reflux condenser, a mercury-sealed stirrer, and a dropping-funnel and an inlet tube. The Grignard reagent was introduced through the inlet tube, being driven over from the flask in which it was prepared by means of a stream of nitrogen which had been washed with caustic potash and pyrogallol and dried by passing through pumice saturated with concentrated sulphuric acid. (It is highly important to avoid traces of moisture or carbon dioxide, both of which tend to lower the yield. In the case of the higher aliphatic Grignard reagents, moisture gives rise to the high-boiling paraffin hydrocarbon corresponding to the alkyl group present in the reagent.) This procedure not only ensured the absence of moisture but also made certain that no undissolved magnesium was present in the reaction mixture during the later addition of the allyl bromide.

The fact that diallyl was found in the Δ^1-pentene prepared by Norris and Joubert (*J. Amer. Chem. Soc.*, 1927, **49**, 885) suggests either (*a*) that some magnesium remained undissolved and reacted with the allyl bromide to give allylmagnesium bromide, which reacted, on the further addition of allyl bromide, to give diallyl; or (*b*) that excess of allyl bromide was added to the Grignard reagent, and when the distillate from the reaction mixture was boiled with metallic magnesium, diallyl was formed in the normal way.

Before the final experimental details were worked out, a repetition of Norris and Joubert's experiment showed that diallyl was present in the pentene fraction. It was isolated from the brominated product as the crystalline tetrabromide.

The flask containing the Grignard reagent was wholly immersed in cold water, the stirrer started, and allyl bromide corresponding in amount to the magnesium present in solution slowly dropped in. The mixture, which soon assumed a greenish-brown colour, instantly became colourless when the addition was complete. The amount of allyl bromide added agreed within 3% with the amount theoretically necessary according to the yields of the alkyl Grignard reagents given by Gilman (*loc. cit.*). Stirring was continued for 30 minutes, the cold water was replaced by warm so that the ether gently refluxed, and the precipitate of magnesium bromide was allowed to settle. Often the mixture was kept over-night, and the clear upper layer then decanted into a large distillation flask. Kirrmann (*Bull. Soc. chim.*, 1926, **39**, 988) states that by introducing the allyl bromide into the Grignard reagent the yield of olefin is lowered owing to the thickening of the reaction mixture. This was overcome in the present case by the vigorous stirring and no difference in yield was observed on reversal of the order of addition, always provided that no decomposition of the Grignard reagent had taken place during the transference. During the distillation of the ethereal olefin solution a further small amount of solid magnesium bromide separated. The distillate was washed repeatedly with cold water until no further diminution in volume was apparent. The hydrocarbon was dried over calcium chloride and fractionated through a special column (containing a central glass rod round which was wound a spiral of thin glass rod). The tube of the column itself was surrounded with a jacket which could be evacuated. The whole apparatus gave excellent results. The fractions obtained are given in the following table with the corresponding bromine addition values (third column), obtained by a slight modification of McIlhiney's method (*loc. cit.*).

Crude product.	Fraction, b. p.	Br, calc.	Br, found.	Olefin, %.	$d_{4^\circ}^{20^\circ}$.
Pentene	29— 31°	228·6	215	94	0·6550
Hexene	61— 63	190·5	147	77	0·7045
Heptene	93— 95	163·3	147	90	0·7100
Octene	121—123	142·8	127	89	0·7281
Nonene	144—146	127·0	108	85	0·7368

These bromine values show that the fractionated product from the reaction contains 6—23% of saturated hydrocarbon as impurity. The Beilstein test for halogen gave a negative result in each case.

Determination of Bromine Addition Values.—A small test-tube about 4 cm. long was drawn out to a capillary, bent to the shape of a Dumas bulb, and weighed, about 0·2 g. of olefin introduced, the capillary sealed off, and the whole reweighed, the difference giving the weight of olefin taken. This procedure was adopted owing to the loss in weight of the more volatile members during weighing and transference. Carbon tetrachloride (10 c.c.) was placed in the bottle, and the tube dropped in and broken. The rest of the method was identical with that described by McIlhiney.

Formation of Dibromides.—Each of the olefin fractions above was cooled to $-12°$, and the amount of bromine required for saturation of the olefin present was added at such a rate that the temperature did not rise above $-5°$. The product was distilled at atmospheric pressure to remove saturated lower-boiling compounds, and the residual dibromides were fractionated in a vacuum.

Decomposition of Dibromides.—Freshly prepared zinc–copper couple was covered with 90% ethyl alcohol, which was gently boiled during the addition of the dibromide. The heat of the reaction sufficed to distil the olefin as it was formed, except in the case of nonene, where it was necessary to heat the mixture after the addition of the dibromide. The alcohol–hydrocarbon distillate was diluted with much water, and the olefin was separated, dried over calcium chloride, and fractionated until the density showed no further change.

Determination of Physical Data.—The molecular refractivities of the olefins and their dibromides recorded on p. 3058 have been calculated by means of the atomic refractivities given by Swientoslawski (*J. Amer. Chem. Soc.*, 1920, **42**, 1945).

The boiling points were obtained during the final distillation, the vacuum-jacketed column and a distillation rate of 2 drops per second being used. The thermometers were checked against Anschütz N.P.L. standards and the boiling points were corrected for exposed mercury thread and reduced to the standard pressure of 760 mm. of mercury.

The refractive indices were determined by an Abbe refractometer.

The critical solution temperatures with aniline were determined in a semimicro-apparatus, immersed in a large water-bath, the temperature of which could be very slowly varied. To 1 c.c. of the olefin were added successive amounts of 0·1 c.c. of freshly distilled aniline, and the temperatures at which the mixture became homogeneous and again cloudy (on cooling) determined. It is important that the temperature should not be raised too far above that at which the mixture becomes clear. The temperatures (falling cloud point) were then plotted against amount of aniline added. The maxima obtained from these graphs are as follows :

Number of carbon atoms	5	6	7	8	9
Critical soln. temp.	19·3°	22·9°	26·6°	32·8°	38·6°

Relationship between Properties and Chemical Structure.—The physical data for the five Δ^1-olefins are compared below with the most trustworthy data for the corresponding Δ^2- and *iso*-olefins and *n*-paraffins.

Number of C atoms.	5	6	7	8	9
			Boiling points.		
*iso*Olefin	21·2°[9]	53·5°[7]	85·0°[7]	111·5°[6]	—
Δ^1-Olefin	30·2	62·0	94·0	122·0	145·3°
Δ^2-Olefin	35·8[5]	68·1[1]	—	125·5[8]	148·5[8]
Paraffin	36·3[10]	68·9[2]	98·4[3]	125·0[4]	151·0[4]
			Densities ($d^{20°}_{4°}$).		
Paraffin	0·6278[10]	0·6610[2]	0·6836[3]	0·7012[4]	0·7161[4]
*iso*Olefin	0·6320[9]	0·6707[7]	0·6944[7]	0·7125[6]	—
Δ^1-Olefin	0·6414	0·6766	0·6977	0·7158	0·7315
Δ^2-Olefin	0·6481[5]	0·7000*[1]	—	0·7250[8]	0·7380[8]

* Density $^{0°}_{4°}$.

[1] Risseghem, *Bull. Soc. Chim. belg.*, 1926, **35**, 328. [2] Brown and Carr, *J. Ind. Eng. Chem.*, 1926, **18**, 721. [3] Edgar and Calingaert, *J. Amer. Chem. Soc.*, 1929, **51**, 1483. [4] Morgan, Carter, and Duck, J., 1925, **127**, 1255. [5] Sherrill, Baldwin, and Haas, *J. Amer. Chem. Soc.*, 1929, **51**, 3034. [6] Brooks and Humphrey, *ibid.*, 1918, **40**, 822. [7] Dykstra, Lewis, and Boord, *ibid.*, 1930, **52**, 3396. [8] Bourguel, *Bull. Soc. chim.*, 1927, **41**, 1475. [9] Norris and Reuter, *J. Amer. Chem. Soc.*, 1927, **49**, 2624. [10] Karvonen, *Suomen Kem.*, 1930, **3**, 101. [11] Clarke, *J. Amer. Chem. Soc.*, 1911, **33**, 523.

In the olefin series the *iso*-group at the end of the chain has the effect of lowering the boiling point of the corresponding Δ^1-*n*-olefin by approximately 9°. This is in all probability due to the mutually repellent action of the contiguous methyl groups, thereby producing a compound of relatively low boiling point and density.

Movement of the double bond towards the centre of the molecule is accompanied by an increase in both density and boiling point.

The author desires to thank the Institution of Automobile Engineers for a grant which partly defrayed the cost of materials for this investigation, Professor A. W. Nash and Dr. A. R. Bowen for their interest and advice, and Dr. F. H. Garner of the Anglo-American Oil Company for his helpful criticism.

DEPARTMENT OF OIL ENGINEERING AND REFINING,
THE UNIVERSITY OF BIRMINGHAM. [*Received, September 19th*, 1931.]