96. *The Polymerisation of Dideuteroacetylene.*

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Modifications of the method of preparation of hexadeuterobenzene by the pyrogenic polymerisation of dideuteroacetylene are described. Five of the more complex " heavy " hydrocarbons simultaneously formed have been isolated and characterised, *viz.*, octadeuterotoluene, octadeuteroindene, octadeuteronaphthalene, decadeuterofluorene, and decadeuteropyrene.

The apparatus and method for the conversion of dideuteroacetylene into " heavy " hydrocarbons were essentially the same as those originally used [Clemo and (the late) McQuillen, J., 1935, 851], but the method of purifying the hexadeuterobenzene fraction has been elaborated.

The yield of liquid hydrocarbons from a given volume of dideuteroacetylene has been more than doubled by the following modifications : (1) The carrier or diluent gas was dispensed with, as there was little danger of explosive decomposition occurring at pressures below 2 atmospheres (Berthelot, *Compt. rend.*, 1896, **123**, 525—30) ; (2) the dideuteroacetylene was circulated through the reaction tube heated to 650° in 500 c.c. batches under a pressure of 115—120 cm. of mercury, each particle of gas remaining for approximately two minutes in the heated zone. Previously, the gas was allowed to flow continuously over the catalyst under reduced pressure.

The phenomenon of " flashing " occurs when the gas is initially admitted into the hot vacuous tube containing the catalyst (Bone and Coward, J., 1908, **93**, 1222) and the hydrocarbon mist is rapidly condensed at −70°. From 80—85% of the dideuteroacetylene polymerises after being circulated 4—5 times over the catalyst. By heating the carbide mixture after the addition of 10 g. of deuterium oxide, a further volume of gas (1½ l.) can be generated ; this, however, polymerises to the extent of only 40% when circulated through the furnace, as the dideuteroacetylene evolved is considerably affected by the temperature required to generate the gas.

The average yield of solid and liquid condensation products obtained from 10 g. of 99·6% deuterium oxide was 5 g. (or 70% of the theoretical) and consisted of a reddish-brown oil showing a strong yellow-green fluorescence.

Although the total yield of hydrocarbons has thus been increased by more than 100%, the amount of hexadeuterobenzene obtained is the same. Therefore the effect of the carrier gas, while inhibiting the polymerisation of dideuteroacetylene, favours the formation of hexadeuterobenzene at the expense of other hydrocarbons.

R. Meyer (1912—1920) made an exhaustive study of the aromatic products formed in the pyrogenic polymerisation of acetylene and definitely characterised nine hydrocarbons (benzene, toluene, indene, naphthalene, diphenyl, fluorene, anthracene, pyrene and chrysene) in 600 g. of the tar (*Ber.*, 1912, **45**, 1609). Although the present work was carried out primarily for preparing hexadeuterobenzene, the collected complex mixture of polymerisation products resulting after the removal of hexadeuterobenzene has been examined with a view to the isolation of the higher " heavy " aromatic hydrocarbons, of which only octadeuteronaphthalene has been previously described (J., 1935, 1325).

The yellow condensation products formed by acting on both ordinary and " heavy " indene with benzaldehyde and methyl-alcoholic potassium hydroxide, according to the conditions used for preparing 1-benzylideneindene (Thiele, *Ber.*, 1900, **33**, 3398), consist mainly of 1-(α-hydroxybenzyl)-3-benzylideneindene (Thiele, *loc. cit.*, p. 3396) and its *hexadeutero*-derivative respectively, with only traces of the mono-condensation products.

A trace of the decadeuterofluorene has been oxidised to " heavy " fluorenone.

Experimental.

Separation of Hexadeuterobenzene.—The " heavy " hydrocarbon mixture obtained from deuterium oxide (10 g.) was distilled at atmospheric pressure and the fraction collecting below 180° (2·2—2·5 g.) was treated as the main hexadeuterobenzene fraction.

After successive distillations over picric acid (0·5 g.), phosphoric oxide (0·5 g.), and sodium (0·1 g.) the colourless liquid was only very slightly aromatic in odour. Further purification was carried out by shaking with small amounts (0·5—1 c.c.) of " heavy " sulphuric acid (95%), until the latter was no longer coloured. In order to repair any slight loss of deuterium content which might have occurred by exchange during the purification process, the " heavy " benzene was shaken with 50% " heavy " sulphuric acid for 2 days (compare Ingold, Raisin, and Wilson, J., 1936, 916). After distilling over barium oxide and a trace of phosphoric oxide, the fraction (1·3 g. or approximately 25% of the original distillate), b. p. 78—82°, melted above 5·5°. By redistillation, the m. p. was raised to 6·2—6·5°, a value agreeing favourably with that of pure hexadeuterobenzene, 6·8° (Ingold, Raisin, and Wilson, *loc. cit.*).

Octadeuterotoluene and Octadeuteroindene.—The fraction (2·4 g.), b. p above 180°, of the original mixture was fractionally redistilled at 1 mm. pressure and collected as follows : fraction (1) consisted of a colourless liquid (0·64 g., b. p. 10—25°/1 mm.), which was condensed by means of solid carbon dioxide and alcohol and redistilled at 750 mm. The following two fractions were examined : (a) B. p. 105—120° (0·14 g.), mainly octadeuterotoluene. 0·1 G. of this in fuming nitric acid (1 c.c.) was warmed on the water-bath for 20 minutes, " heavy " sulphuric acid (1 c.c., 95%) added, and the mixture refluxed for ½ hour, poured into ice-water (10 c.c.), and rapidly extracted with carbon disulphide. The solution was dried with anhydrous potassium carbonate, and the solvent evaporated; the resulting solid, after being pressed on porous tile, had m. p. 65—66°, and mixed m. p. with 2 : 4-dinitrotoluene (m. p. 69°) 65—69°. (b) B. p. 175—190° (0·18 g.). This was mainly octadeuteroindene, since without further purification it gave *hexadeutero*-1-(α-*hydroxybenzyl*)-3-*benzylideneindene,* on treatment with benzaldehyde and alcoholic potassium hydroxide, as yellow crystals, m. p. 136°. A mixture with the derivative (m. p. 134°) similarly obtained from ordinary indene had m. p. 134—136° [Found : C, 87·0; water ($H_2O + D_2O$), 51·6. $C_{23}H_{12}D_6O$ requires C, 87·3; water, 53·1%].

Octadeuteronaphthalene.—Fraction (2), amounting to about 7% of the original mixture, has been proved to be octadeuteronaphthalene. It formed large colourless plates, m. p. 80—81°, from aqueous methyl alcohol (Found : C, 88·6; D, 11·5. Calc. for $C_{10}D_8$: C, 88·2; D, 11·8%), and its picrate formed yellow prisms from alcohol, m. p. 147°, not depressed by naphthalene picrate, m. p. 149° (Found : C, 52·3; water, 33·2. Calc. for $C_{10}D_8,C_6H_3O_7N_3$: C, 52·6; water, 29·3%).

Decadeuterofluorene.—Fraction (3) (0·3 g., b. p. 95—120°/1 mm.) was a yellow semi-solid mass which gave a reddish-brown *picrate,* m. p. (indef.) 80°, raised by recrystallisation from ether to 81—83°, not depressed by fluorene picrate of m. p. 80° (Found : C, 56·5; water, 35·5. $C_{13}D_{10},C_6H_3O_7N_3$ requires C, 56·3; water 31·35%. Calc. for $C_{13}H_{10},C_6H_3O_7N_3$: C, 57·7; water, 29·6%).

The crude solid was separated from oily material on a tile (indefinite m. p. 100°) and sublimed in a vacuum at 100°, giving crystalline *decadeuterofluorene,* m. p. 105—107°, raised to 115—117° by two recrystallisations from alcohol, mixed m. p. with fluorene (m. p. 116°), 115—117° (Found : C, 88·7; D, 13·5. $C_{13}D_{10}$ requires C, 88·6; D, 11·3%. Calc. for $C_{13}H_{10}$: C, 94·0; H, 6·0%).

A small amount of this hydrocarbon, oxidised with sodium dichromate in acetic acid, gave octadeuterofluorenone in yellow prisms, m. p. 84°, not depressed by authentic fluorenone.

Decadeuteropyrene.—Fraction (4) (0·3 g., b. p. 120—155°/1 mm.) set to a yellow semi-solid mass, which gave a red *picrate,* m. p. 140—150°. After several recrystallisations from alcohol, this separated in long, bright red needles, m. p. 217—219°, not depressed by pyrene picrate (Found : C, 60·3; water, 41·4. $C_{16}D_{10},C_6H_3O_7N_3$ requires C, 60·0; water, 28·8%. Calc. for $C_{16}H_{10},C_6H_3O_7N_3$: C, 61·2; water, 27·1%).

The picrate was decomposed with aqueous ammonia, the hydrocarbon extracted with ether and dried over anhydrous potassium carbonate, the solvent removed, and the residue pressed on tile and then sublimed in a vacuum at 200°, giving *decadeuteropyrene* in pale yellow, rectangular prisms, m. p. 135°, raised to 148—149° by two crystallisations from alcohol; mixed m. p. with pyrene (m. p. 150°) 148—150° (Found : C, 90·2; D, 9·4. $C_{16}D_{10}$ requires C, 90·6; D, 9·4%. Calc. for $C_{16}H_{10}$: C, 95·0; H, 5·0%).

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