

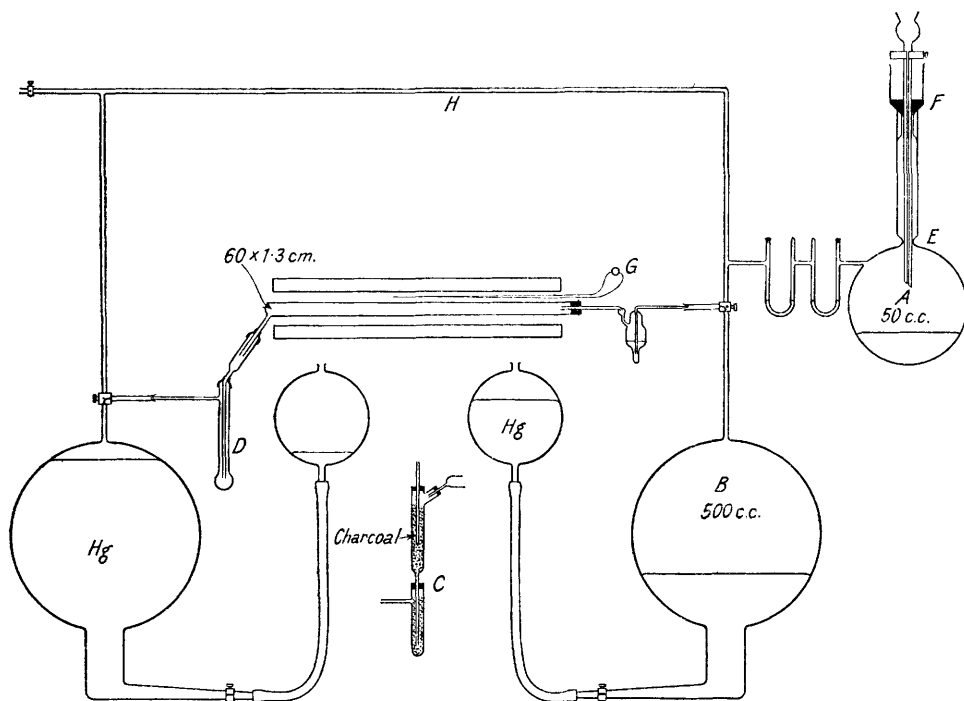
193. *Experiments on Hexadeuterobenzene. Part I.*

By G. R. CLEMO and A. MCQUILLEN.

THE quantitative preparation of acetylene by the action of water on calcium carbide has been investigated, and a generator of the type A found to be the most effective. An amount of almost pure acetylene corresponding to 60% of the total hydrogen of the water was obtained in this way, and, by heating finally to 500—600° with excess of carbide, 90% of

the theoretical yield, contaminated with some air and methane, could be obtained. The further volume of gas evolved on heating was used separately in the earlier work in order to avoid complications arising from the presence of these impurities.

The literature does not contain any really helpful account of the small-scale polymerisation of acetylene to benzene and much time has been spent in examining this question. The apparatus shown in the diagram is suitable for laboratory experiments. In this part of the work we were greatly helped by Mr. H. G. Dickenson. The acetylene was passed over the catalyst in a heated silica tube, and the distillate collected. Gas-mask charcoal in C was used to absorb the benzene in the earlier experiments, but was abandoned in favour of the receiver (D) cooled in solid carbon dioxide. Several catalysts were tried, including charcoal and tellurium oxide on porous pot (D.P. 547,080; *Zentr.*, 1932, 3113). Carbon had the disadvantage that it required priming by the passage of large amounts of acetylene before it became active, thus confirming the view that finely divided carbon deposited by



the decomposition of acetylene was the real catalyst (compare, however, Fischer, Bangert, and Pickler, *Brennstoff-Chem.*, 1929, **10**, 279; Zelinski, *Ber.*, 1924, **57**, 264). The optimum temperature for the production of benzene was 650° (Pease, *J. Amer. Chem. Soc.*, 1929, **51**, 3470).

With a tellurium catalyst and carbon dioxide as the carrier gas, complete contraction could be obtained if an "askarite" tube was used in the return circuit at H to remove progressively the carbon dioxide. In all cases 40% of inert gases inhibited further polymerisation. The resultant benzene was contaminated with water, and another oxygen-containing substance which reacted with sodium only at 60°. As the benzene could not be easily purified, it was converted into the *m*-dinitro-compound, of which 80 mg. were obtained from 1.5 g. of water.

When hydrogen was used as the carrier gas, benzene free from oxygen-containing impurities was obtained (yield, 85 mg. from 2 g. of water).

When nitrogen was used, the initial batch of acetylene gave a 50% contraction, but after the discharge of the residual gases (containing the majority of the nitrogen) subsequent

batches gave a 70% contraction. A yield of 0.40 g. of benzene was thus obtained from 2 g. of water.

This work was then repeated with 99% "heavy" water, and a similar yield of dideutero-acetylene (60%) obtained and polymerised. In this case also nitrogen was found to be preferable to carbon dioxide as a carrier gas. A yield of 2.3 g. of liquid distillate was obtained from 10 g. of "heavy" water. This was purified as described in the experimental section and gave 1.3 g. of analytically pure *hexadeuterobenzene*.

The micro-analyses of hexadeuterobenzene were carried out with a furnace and absorption train which had not been used for compounds containing ordinary hydrogen, after extended practice on a similar furnace had given consistent values for ordinary benzene. The results, with C values 6.6 units lower than that for "light" benzene and, with one exception, good values for D, seem to prove the product to be pure hexadeuterobenzene. The value marked *₂ was obtained in an ordinary furnace immediately after the C₆H₆ value *₁, and it will be seen that the D value is 0.6 low. The H value found for alizarin, analysed next in this furnace, was 0.6 high, the C being quite good.

Nitration of hexadeuterobenzene with "light" sulphuric and nitric acids gave a good yield of a dinitro-compound, m. p. 89°, not depressed by admixture with authentic *m*-dinitrobenzene. The analyses (Table II) do not settle whether exchange has occurred. When the nitration was effected with "heavy" acids,* the dinitro-compound obtained had m. p. 78° and thus it appears that exchange had taken place in the nitration above.

Hexadeuterobenzene has b. p. 82.5° (C₆H₆, b. p. 80.5°), m. p. — 1.0° approx., and *d*¹⁷ 0.954 ± 0.0005.

EXPERIMENTAL.

Generation of Acetylene.—A generator A† was found to be suitable. The three-way tap was adjusted until it was in communication with the reservoir B, which was partially evacuated. A weighed amount of water was introduced into the funnel of A and was added to the carbide drop by drop under a pressure of nitrogen, the carbide being shaken so as to present a fresh surface to each drop. The carbide was passed through a 20-mesh sieve and preheated to 200° to remove any atmospheric moisture. The moist acetylene passed through two U tubes containing carbide and phosphoric oxide respectively. In this way 750 c.c. of either dideutero- or ordinary acetylene could be obtained from 1 g. of the corresponding water.

An additional 380 c.c. of gas containing some 10% of air and methane could be obtained by heating the mixture to 500–600°. In the experiments with "heavy" water the second volume of gas was not generated, the carbide-calcium deuterioxide mixture being stored.

Receivers.—The gaseous benzene could not be collected from the gas stream by mere cooling, for it formed a mist which passed through the receiver. A receiver of the type (C), cooled in ice and packed with absorption charcoal, absorbed this mist, but only some 30% of the benzene could be recovered even by heating the charcoal to a dull red heat in an inert atmosphere. Finally a receiver of the type (D), in which the mist was filtered out by passage through a column of glass-wool, was used successfully. This was cooled in solid carbon dioxide.

Polymerisation of "Light" Acetylene.—(a) *Charcoal catalyst.* The apparatus shown, fitted with the receiver (C), was swept out with carbon dioxide at 700° for 24 hours. Acetylene (1.5 l.) was passed repeatedly (40 times) through the tube containing charcoal (Sutcliffe, Speakmann and Co., H/Q Grade 6–10 Absorption Charcoal) at 650° before any contraction occurred. Acetylene (2 l.) was then passed through the furnace in 500 c.c. batches, each being passed five times. The resultant gases were trapped in (C), packed with absorption charcoal and cooled in ice. Distillation of the charcoal gave a colourless liquid (0.53 g.). This was refluxed with nitric acid (2 c.c.) and sulphuric acid (2 c.c.) for ½ hour, then poured into water, and the crystalline precipitate filtered off. After recrystallisation from 50% aqueous alcohol, *m*-dinitrobenzene (30 mg., m. p. 89°, mixed m. p. 89°) was obtained (Found: C, 43.1; H, 2.7. Calc.: C, 42.8; H, 2.4%).

(b) *Tellurium catalyst.* Tellurium (2 g.) was dissolved in excess of dilute nitric acid (1 : 4),

* We are deeply indebted to Mr. M. P. Applebey of Billingham for these reagents.

† The long stem of the generator removed the ground joint from the heated zone, the mercury cup seal (F) rendered the use of a lubricant at the joint unnecessary, and the constriction at (E) prevented loss of water in the annular space.

porous pot sufficient to fill the combustion tube was added, and the whole evaporated to dryness. The tube was filled with the catalyst and ignited at 700° for 48 hours in a stream of carbon dioxide. Acetylene ($\frac{1}{2}$ l.) was collected in B, over mercury, and passed through the furnace six times. An "askarite" tube for the absorption of carbon dioxide was inserted at (H). A colourless liquid (0.25 g.), distilled from the charcoal of the trap, gave *m*-dinitrobenzene m. p. 89°, on nitration. The residual gas (58 c.c.) contained acetylene (65.5%) and carbon dioxide (34.5%).

Polymerisation of Dideuteroacetylene.—The furnace was swept out with oxygen for 24 hours at 700°, no water being collected, and then with oxygen-free nitrogen for a similar period, both gases having been dried by passage through towers of quick lime, calcium chloride, and then phosphoric oxide. Cylinder nitrogen, which contained about 5% of oxygen, was purified by passing up one inclined tube (1 m.) filled with alkaline pyrogallol and a second filled with chromous chloride and amalgamated zinc (Carter and Hartshorne, J., 1926, 363; *J. Soc. Chem. Ind.*, 1926, 474).

0.57 G. of "heavy" water (99%, d^{20} 1.1051) gave 300 c.c. of dideuteroacetylene, which, after passage five times at the rate of 2 l./hour through the furnace, showed no further contraction. The residual gas (150 c.c.) was discharged from the apparatus.

2.04 G. of "heavy" water gave 1150 c.c. of gas, which was passed in three batches through the furnace. A total contraction of 70% of the original volume was obtained after five passings. The benzene vapour was trapped in a receiver (type D), cooled in solid carbon dioxide. The crude product (0.24 g.) was fractionated, the tail being neglected, and distilled thrice from excess of picric acid (to retain the naphthalene fraction), twice from phosphoric oxide, and finally from sodium. This product was then fractionated, and the middle fraction, b. p. 82.5°, analysed.

A similar experiment with 10 g. of "heavy" water in $\frac{1}{2}$ g. batches gave 2.3 g. of crude distillate, which, after purification, gave 1.3 g. of pure *hexadeuterobenzene*. The analytical results given in Table I were obtained in chronological order.

TABLE I.

	Ordinary benzene.		Hexadeuterobenzene.		
	C.	H.	C.	D.	N.
Calc.	92.3	7.7	85.7	14.3	0
Found	92.1	7.7	—	—	—
	92.9	7.9	—	—	—
—	—	—	85.8	14.8	—
—	—	—	86.0	14.7	0
—	—	—	86.0	15.45	—
—	92.1	8.0	—	—	—
—	—	—	86.4	15.2	—
—	92.5	8.0 * ₁	—	—	—
—	—	—	85.8	13.7 * ₁	—
—	—	—	86.4	14.8	—
—	—	—	86.6	14.7	—

Nitration.—The crude product (0.2 g.) after a two-fold distillation from picric acid was refluxed for $\frac{1}{2}$ hour with concentrated nitric acid (2 c.c.) and concentrated sulphuric acid (2 c.c.), giving 0.31 g. of a crystalline solid, m. p. 89° after three recrystallisations from 50% aqueous alcohol, and not depressed by admixture with *m*-dinitrobenzene. Pure hexadeuterobenzene (0.14 g.) was also nitrated in a similar fashion with sulphuric and nitric deuteracids. After three-fold recrystallisation from petroleum (b. p. 60–80°) a white crystalline solid (0.2 g.), melting at 78° and giving m. p. 87° when mixed with *m*-dinitrobenzene, was obtained. The analytical data obtained are in Table II.

TABLE II.

<i>m</i> -Dinitrobenzene.	C ₆ D ₆ nitrated with "light" reagents.	C ₆ D ₆ nitrated with "heavy" reagents.
Calc.: C, 42.8; H, 2.4; N, 16.7.	C ₆ D ₄ O ₄ N ₂ requires C, 41.9; D, 4.4; N, 16.3.	
Found: C, 42.5; H, 3.0; N, 16.6%.	Found: C, 42.4; D, 5.1; N, 16.1. 42.4; 5.2; 15.7. 42.5; 5.3; 15.7%.	Found: C, 41.4; D, 4.9; N, 16.5, 16.4%.

Thanks are due to the Armstrong College Council for a post-graduate grant to one of us (A. McQ.), to the Research Committee for a grant, and to Messrs. O. Telfer and G. Pendleton for the micro-analyses.

ARMSTRONG COLLEGE (UNIVERSITY OF DURHAM),
NEWCASTLE-UPON-TYNE.

[*Received, May 24th, 1935.*]
