57. *Structure of Benzene. Part XIII. Hydrogen Exchange Reactions with Benzene Derivatives. Preparation of* 1 : 3 : 5-*Tri-,* 1 : 2 : 4 : 5-*Tetra-, and Penta-deuterobenzene.*

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The attainment of equilibrium in the hydrogen exchange reaction between aniline hydrochloride and water containing deuterium has been followed. After a very rapid exchange of the N-hydrogen atoms, a slow but quantitative exchange of the ortho- and para-hydrogen atoms takes place; but no exchange of meta-hydrogen atoms could be detected. The reaction has been used to prepare isotopically pure 2 : 4 : 6-trideuteroaniline; and from this 1 : 3 : 5-trideuterobenzene was obtained by deamination.

The hydrogen exchange reaction between p-dibromobenzene and sulphuric acid–water mixtures containing

deuterium has been studied. The exchange occurs with all four nuclear hydrogen atoms, and there is accompanying sulphonation. The reaction has been employed to prepare isotopically pure 1 : 4-dibromo-2 : 3 : 5 : 6-tetradeuterobenzene; and this substance has been converted through its Grignard derivatives into 1-bromo-2 : 3 : 5 : 6-tetradeuterobenzene, and 1 : 2 : 4 : 5-tetradeuterobenzene.

The hydrogen exchange reaction between bromobenzene and sulphuric acid–water mixtures containing deuterium has likewise been studied. Three nuclear hydrogen atoms are exchanged fairly rapidly, and the other two more slowly. Under the conditions investigated, the rate of sulphonation was comparable with the rate at which the last two hydrogen atoms are exchanged, and so the exchange reaction could not conveniently be used for the preparation of pentadeuterobenzene. This substance was therefore prepared from hexadeuterobenzene by bromination, and replacement of the bromine atom in the bromopentadeuterobenzene by light hydrogen by the use of the Grignard reaction.

THE partly deuterated benzenes whose preparation we here describe were prepared by Langseth and Klit by their modified Grignard method, but, as explained in the preceding paper (this vol., p. 235), not in an isotopically pure form. The preceding paper also shows that our step-wise method of using the Grignard reaction for the preparation of deuterated benzenes, although it gives a pure product where applicable, fails when more than two deuterium atoms require to be introduced. Hence, for the preparation of more highly deuterated benzenes we turned to the group of exchange reactions, the study of which is here reported.

Hydrogen Exchange between Aniline Hydrochloride and Heavy Water : Preparation of 1 : 3 : 5-*Trideutero-benzene.*—It has been shown by Ingold, Raisin, and Wilson (J., 1936, 1037) that hydrogen exchange between acids (in the generalised sense of proton- or deuteron-donors) and the aromatic nucleus of benzene derivatives shows all the characteristics of an electrophilic substitution process : it is facilitated or retarded, and therefore oriented, in just the same way as are other typical electrophilic aromatic substitutions, such as nitration. Later, we demonstrated (J., 1938, 28) that, in the reaction between aniline hydrochloride and heavy water (in which the interacting species can plausibly be assumed to be the aniline molecule and the deuteroxonium ion), the ortho- and para-positions of the aromatic molecule are the only nuclear positions which participate in the hydrogen exchange.

It remained to define the exact conditions for the attainment of equilibrium, and for this purpose dilute heavy water (3 atoms % of deuterium) was used in some exchange experiments, the results of which are summarised in Table I. The amount of exchange is expressed in terms of a partition coefficient, calculated on the assumption that only three nuclear positions are affected : it represents the atomic proportion of deuterium in the hydrogen of the affected positions, divided by the atomic proportion of deuterium in the hydrogen of the residual heavy water. The results show that equilibrium is attained in 24 hours at 100°. The partition coefficient at equilibrium, 0·844, has about the usual value for equilibria in exchange between aromatic hydrogen and water hydrogen. The constancy of this value up to 72 hours shows that no appreciable exchange at the meta-positions begins within this period at the temperature of the experiments.

TABLE I.

Hydrogen Exchange between Aniline Hydrochloride and Water containing a Small Proportion of Deuterium.

PhNH$_3$Cl (g.).	Heavy water (g.).	Temp.	Time (hrs.)	Deuterium partition coeff.	PhNH$_3$Cl (g.).	Heavy water (g.).	Temp.	Time (hrs.).	Deuterium partition coeff.
13·05	16·19	100°	0·5	0·047	13·06	16·45	100°	24·0	0·846
13·00	15·15	100	3·0	0·481	13·10	18·01	100	48·0	0·843
12·99	17·71	74	3·0	0·00015	13·08	16·61	100	72·0	0·842
13·42	17·60	100	12·0	0·801					

For the preparation of pure 1 : 3 : 5-trideuterobenzene, aniline hydrochloride was brought to equilibrium repeatedly with fresh samples of pure heavy water, and the amino-group in the formed 2 : 4 : 6-trideutero-aniline was then replaced by protium by diazotisation and treatment of the diazo-solution with sodium stannite. It was shown that the nuclear hydrogen atoms are not affected by the deamination process.

Three independent preparations of 1 : 3 : 5-*trideuterobenzene* by this method gave material having $d_{25°}^{25°}$ 0·91100, 0·91113, and 0·91116, respectively. Assuming the linear relationship discussed in the preceding paper and the figures there given for the densities of benzene and hexadeuterobenzene, the density of pure 1 : 3 : 5-trideuterobenzene is calculated to be 0·91103. The above three experimental samples therefore respectively contain 49·96, 50·15, and 50·18 atoms % of deuterium in their hydrogen. The first of the three samples was submitted to the combustion method of isotopic analysis, and this gave the figure 49·82 atoms % of deuterium. According to the spectroscopic evidence, all three samples consist of very pure 1 : 3 : 5-trideuterobenzene : no hydrogen-isotopic isomeride could be detected.

Hydrogen Exchange between p-*Dibromobenzene and Sulphuric Acid. Preparation of* 1 : 2 : 4 : 5-*Tetradeutero-benzene.*—The method was first to replace all four hydrogen atoms of *p*-dibromobenzene by deuterium by exchange with heavy sulphuric acid, and then to replace the two bromine atoms by light hydrogen by means of the Grignard reaction.

Preliminary experiments showed that conditions such as would have sufficed for hydrogen exchange between benzene and sulphuric acid, *e.g.*, shaking benzene at the ordinary temperature with aqueous sulphuric acid of more than 50 mols. % sulphuric acid concentration, were useless for *p*-dibromobenzene, doubtless because of the deactivating effect of the bromine atoms towards an electrophilic substituting agent. We employed in these tests carbon tetrachloride as a solvent for the *p*-dibromobenzene, and used sulphuric acid of 80 mols. %

sulphuric acid concentration, but no exchange took place. Exchange occurred fairly readily, however, when we omitted the organic solvent, and shook the fused *p*-dibromobenzene with the aqueous sulphuric acid at 107°.

It was next necessary to establish conditions in which the hydrogen exchange could be completed without the incursion of too much loss by sulphonation, and for this purpose a series of experiments was instituted with aqueous sulphuric acid of various acid concentrations, but with only 3 atoms % of its total hydrogen in the form of deuterium. The acid and *p*-dibromobenzene were shaken together at 107°, and the recovered dibromobenzene was isotopically analysed by combustion. The results are in Table II. The amount of hydrogen exchange is expressed in the last column by means of a " hydrogen exchange number." This is simply the deuterium partition coefficient, as previously defined, multiplied by 4, the number of aromatic hydrogen atoms available for exchange. Since the partition coefficient for an equilibrium distribution of deuterium between benzenoid compounds and sulphuric acid is 1·1, the figure 4·3 represents substantial equilibrium with respect to exchange in all four aromatic positions. The data show that by use of mixtures of 88·5 mols. % of sulphuric acid and 11·5 mols. % of water, it is possible to secure complete exchange without excessive sulphonation.

TABLE II.

Hydrogen Exchange between p-*Dibromobenzene and Sulphuric Acid–Water Mixtures containing a Small Proportion of Deuterium in their Hydrogen.*

Compn. of mixtures.		Time at 107° (hrs.).	Sulphon-ation (mols. %).	Hydrogen exchange number.	Compn. of mixtures.		Time at 107° (hrs.).	Sulphon-ation (mols. %).	Hydrogen exchange number.
Sulphuric acid (mols. %).	Water (mols. %).				Sulphuric acid (mols. %).	Water (mols. %).			
50·1	49·9	6	1·3	0	88·5	11·5	6	2·3	3·6
62·3	37·7	6	0·5	2·8	88·5	11·5	24·5	5·7	4·3
79·6	20·4	6	1·2	3·0	99·6	0·4	6	22·3	4·3
79·6	20·4	18	3·0	3·8					

For the preparation of pure 1 : 2 : 4 : 5-tetradeuterobenzene, a sulphuric acid mixture was made from sulphur trioxide and pure deuterium oxide to the stoicheiometric composition : D_2SO_4 88·5 mols. %, D_2O 11·5 mols. %. *p*-Dibromobenzene was shaken at 107° with successive portions of this mixture until substantially the whole of the light hydrogen in the former should, according to our previous work, have been replaced. An analysis of the 1 : 4-*dibromotetradeuterobenzene* by combustion gave, as the hydrogen isotopic composition, 99·5 atoms % of deuterium. The material was converted into its Grignard derivative, which was decomposed by light water to give 1 : 2 : 4 : 5-*tetradeuterobenzene*. The density $d_{25°}^{25°}$ was 0·92274, which corresponds exactly to the theoretical hydrogen isotopic composition, 66·67 atoms % of deuterium. Analysis by combustion gave the slightly lower figure 66·04 atoms %. 1-*Bromo*-2 : 3 : 5 : 6-*tetradeuterobenzene* was obtained as a by-product in the Grignard reaction.

Hydrogen Exchange between Bromobenzene and Sulphuric Acid.—This group of experiments, which might have led to the preparation of pentadeuterobenzene if we could, without sulphonation, have replaced all the light hydrogen in bromobenzene by deuterium, and then the bromine atom by protium, is recorded for the sake of the additional light it throws on the course of aromatic deuterium exchange. Bromobenzene was shaken at 107° for various periods with sulphuric acid–water mixtures, containing about 2 atoms % of their total hydrogen in the form of deuterium. With an equimolecular mixture of sulphuric acid and water, three aromatic hydrogen atoms, presumably those of the ortho- and para-positions, were exchanged to equilibrium within 6 hours. After this, however, the remaining nuclear positions began to enter appreciably into the exchange reaction, which proceeded a substantial distance towards equilibrium in the course of several days. Sulphonation proceeded at a comparable rate, and this was still true when a less aqueous sulphuric acid was employed. The detailed results are set out in Table III. The hydrogen exchange number in this case is the deuterium partition coefficient multiplied by 5. Since the partition coefficient for an equilibrium distribution of deuterium is 1·1, the exchange number 3·3 corresponds to complete exchange in three aromatic positions, whilst an exchange number of 5·5 would have been found if we could have effected complete exchange in all five positions.

TABLE III.

Hydrogen Exchange between Bromobenzene and Sulphuric Acid–Water Mixtures containing a Small Proportion of Deuterium in their Hydrogen.

Compn. of mixtures.				Sulphonation (mols. %).	Hydrogen exchange number.
Sulphuric acid (mols. %).	Water (mols. %).	Temp.	Time (hrs.).		
50·1	49·9	20°	51	0	0
50·1	49·9	107	6	6	3·3
50·1	49·9	,,	57	36	4·9
79·6	20·4	,,	44	20	3·0
79·6	20·4	,,	141	50	3·7
79·6	20·4	,,	354	64	4·1

The fact that the rate of sulphonation is comparable to the rate at which two of the aromatic positions, presumably the meta-positions, exchange their hydrogen prevented the use of this exchange reaction for the preparation of pentadeuterobenzene.

Preparation of Pentadeuterobenzene.—This was eventually prepared from hexadeuterobenzene, by bromination with hypobromous acid to give bromopentadeuterobenzene, and replacement of the bromine atom in this compound by light hydrogen by means of the Grignard reaction. The crucial stage of the process is the separation by distillation, after the bromination, of perfectly pure *bromopentadeuterobenzene*, free from any trace of formed dibromotetradeuterobenzene or surviving hexadeuterobenzene. Hexadeuterobenzene containing 99·7 atoms % of deuterium in its hydrogen thus gave *pentadeuterobenzene* containing 83·1 atoms % of deuterium (theoretical, 83·3 atoms %), the analyses being by the method of combustion.

<center>EXPERIMENTAL.</center>

Particulars concerning the isotopic analysis of aromatic deuterium compounds are given in Part XII (this vol. p. 236).

Preparation of Heavy Sulphuric Acid.—Although it is possible to prepare acid containing a small proportion of deuterium by dilution of a stronger acid with heavy water, the method is obviously limited. The process of combining known weights of sulphur trioxide and water was briefly described in Part II (J., 1936, 916), but subsequent private correspondence has suggested that an amplified description would prove useful.

The apparatus consisted of a Hyvac pump and a gas line carrying a liquid-air trap, a manometer, a tap lubricated with grease, and two B 14 cone standard joints about 20 cm. apart. Several 100 c.c. flasks with necks 20 cm. long were made to fit conveniently into Dewar vessels, and each was furnished with a B 14 socket, a stopper, and some suspension wire for weighing. Concentrated oleum was made by adding oleum, or concentrated sulphuric acid, to a bottle containing sulphur trioxide, and heating it in an oven to 50—60°. The resulting solution (about 70 c.c.), together with a few pieces of porous pot, was added to one of the flasks, which was cooled to −80°, and attached to the apparatus, together with an empty flask. Joints were lubricated by partially hydrated phosphoric oxide, prepared by adding a few drops of the same water as that which was to be used for making the sulphuric acid : the hot viscous mixture was applied to the heated joints, which were held together by springs. The pressure was then reduced to 0·1 mm., the tap closed, and the oleum warmed in water to 30—60°, whilst the empty flask was surrounded by melting ice. Rapid distillation of sulphur trioxide ensued, which condensed in a metastable liquid form. When about the desired quantity was judged to have been collected, air was admitted through a drying tube, and the flask was weighed. From the weight of distilled trioxide the weight of heavy water necessary to give a required strength of acid was calculated. This amount, less 0·2 g., was put into one of the flasks, which was weighed, and, together with the flask of sulphur trioxide, attached to the apparatus. Both flasks were cooled to −80° and the pressure was reduced as before. Special care was needed when freezing water to prevent breakage : it was found best to swirl the water round the inside of the flask whilst cooling. After closing the vacuum tap, and thawing the frozen water, its flask was immersed in melting ice, and the flask of sulphur trioxide in a water-bath at 50—70°, the temperature being regulated according to the rate of distillation. When all the sulphur trioxide had disappeared, the flask now containing the sulphuric acid was again weighed, to give the exact amounts (to 0·01 g.) of sulphur trioxide and water which had been combined. Any further water required, usually between 0·1 and 0·2 g., was added from a microburette.

Exchange between Aniline Hydrochloride and Heavy Water.—Recrystallised and thoroughly dried aniline hydrochloride, and water, the hydrogen of which contained 3 atoms % of deuterium, in the molecular ratio of approximately 1 : 9 (the exact quantities are given in Table I), were heated together in sealed bulbs in a bath of boiling water for various lengths of time. After cooling, the water was removed by distillation in a vacuum, and then replaced by distilled tap water (16 c.c.) which, after solution was complete, was also removed in a vacuum. This procedure was repeated twice further in order to normalise the easily replaceable hydrogen atoms attached to nitrogen. The hydrochloride was then dissolved in water (60 c.c.), concentrated hydrochloric acid (20 c.c.) added, and the mixture cooled to 0°. Sodium nitrite (about 8 g.) was added slowly until a positive starch–iodide reaction was obtained, the temperature being kept below 5°. After having been kept in the dark for 30 minutes, the solution was added to a solution of sodium hydroxide (15 g.) in water (60 c.c.), and the whole was cooled to −8°. This solution was added slowly to a solution of sodium stannite in a flask (500 c.c.) fitted with a reflux condenser and cooled in ice. [The stannite solution was prepared by adding 30% sodium hydroxide slowly to a solution of stannous chloride (30 g.) in water (75 c.c.) until the precipitate just redissolved.] As the mixture warmed to room temperature an oily layer separated. The benzene was removed by steam distillation, and collected in a receiver cooled in ice. From this it was distilled in a vacuum into a bulb containing phosphoric oxide, and thence into a storage bulb. Its deuterium content was determined in the usual way. The yield of benzene was between 60 and 70% of the theoretical.

Since it was necessary to be certain that the deamination process did not affect the nuclear hydrogen atoms, an additional experiment was performed in which double the usual amount of reactants was heated for 24 hours. After isotopic normalisation of the amino-hydrogen, the hydrochloride was divided into halves. One half was treated as described above to give benzene, whilst the other was basified, and the aniline purified by distillation. The deuterium content of both the benzene and the aniline was determined. The result showed that, after due allowance had been made for the different number of light hydrogen atoms present in each molecule, the three nuclear positions concerned were exchanged to the same extent.

1 : 3 : 5-Trideuterobenzene.—Before carrying out successive exchanges with pure heavy water it was necessary to know whether the reaction proceeded with the same speed in heavy water as in light. Therefore, two equivalent mixtures of aniline hydrochloride and pure heavy water were heated at 100°, one for 24 hours, and the other for 96 hours. The deuterium content of the residual water was the same in both cases to within experimental error. This showed that with pure heavy water, just as with dilute heavy water, 24 hours is sufficient time for the attainment of equilibrium in exchange with aniline hydrochloride at 100°.

Three samples (each 13 g.) of aniline hydrochloride were each heated with deuterium oxide (20 g.) in sealed Pyrex bulbs immersed in boiling water for 24 hours. The amounts of the reactants correspond to a molecular ratio of 1 : 9. The water was distilled in a vacuum, and replaced by a fresh sample of heavy water, and the bulbs were then heated further. Six such treatments of each sample were carried out, the first five with water containing 99·2 atoms %, and the last 99·95 atoms % of deuterium. Isotopic normalisation of the amino-hydrogen was carried out by treatment with five successive portions (each 30 c.c.) of distilled tap water. Deamination, and the purification of the formed 1 : 3 : 5-*trideuterobenzene*, were carried out according to the procedure described above. The yields were about 65% of theoretical. The densities and analytical data have been given earlier.

Hydrogen Exchange between p-Dibromobenzene and Heavy Sulphuric Acid.—Purified *p*-dibromobenzene (10 g.) was shaken in a sealed Pyrex tube with sulphuric acid–water mixtures (10 c.c.), the hydrogen of which contained 3 atoms % of deuterium. The first experiments were carried out at ordinary temperature with the addition of carbon tetrachloride (35 c.c.). In later experiments the temperature was raised to 107°, and the use of a solvent abandoned. After reaction was complete the tube was allowed to stand undisturbed, and, in the experiments without solvent, the upper layer of

acid was poured away from the solid dibromo-compound. The latter was then dissolved in carbon tetrachloride. In both series of experiments the carbon tetrachloride solution was washed with sodium carbonate solution and water, and dried over phosphoric oxide. The carbon tetrachloride was removed by distillation and the deuterium content of the residue determined by combustion. The results of the experiments at 107° are in Table II.

1 : 4-*Dibromotetradeuterobenzene.*—*p*-Dibromobenzene (British Drug Houses) was twice recrystallised from ethyl alcohol, and then distilled at ordinary pressure; it had m. p. 88·1—88·4°. The purified material (122·6 g.) in three approximately equal portions was shaken in sealed Pyrex bulbs with heavy aqueous sulphuric acid at 107° for 30 hours. The acid mixture contained 88·5 mols. % of D_2SO_4 and 11·5 mols. % of D_2O. The quantity of the mixture used was sufficient to provide three times as many hydrogen atoms as the number present in the *p*-dibromobenzene. After the shaking, the tubes were cooled in a vertical position, and the acid layer was removed and replaced by fresh acid. Each sample of dibromobenzene was thus treated five times. The first three treatments employed acid containing 99·2 atoms % of deuterium in its hydrogen; they raised the deuterium content of the hydrogen of the dibromo-compound to 97·0 atoms %. The last two treatments, which employed acid containing 99·95 atoms % of deuterium, increased the deuterium content of the hydrogen of the dibromo-compound to 99·45 atoms %. The 1 : 4-*dibromotetradeuterobenzene* was dissolved in carbon tetrachloride, washed with sodium carbonate solution and water, and then distilled at ordinary pressure. The weight of material obtained was 78·6 g., the loss (44 g.) largely representing sulphonation. The dibromotetradeuterobenzene had m. p. 87·7—88·4°.

1 : 2 : 4 : 5-*Tetradeuterobenzene.*—*p*-Dibromotetradeuterobenzene (50 g.) was converted into its Grignard compound by reaction with magnesium (9 g.) in ether (140 c.c.). The solution was cooled in ice, and decomposed by the addition of concentrated hydrochloric acid. The ethereal layer was washed with sodium carbonate solution and water, dried over anhydrous potassium carbonate, and fractionated. This gave a benzene fraction containing a little ether, and a residue (3·4 g.) of 1-bromo-2 : 3 : 5 : 6-*tetradeuterobenzene*. Residual ether was removed from the benzene by treatment with perchloric acid (60% by weight) as described below. Subsidiary experiments showed that this acid was superior to concentrated hydrochloric acid, or to 70% (by weight) sulphuric acid, for this purpose, although none of the three reagents caused any isotopic exchange in benzene under the conditions employed.

The extraction with perchloric acid was performed in an all-glass apparatus consisting of three 50 c.c. bulbs connected by standard joints to a gas line, and capable of isolation from one another, and from an attached liquid air trap and Hyvac pump, by taps. The benzene sample, together with perchloric acid (15 c.c.), was placed in one flask and cooled to −80°. The apparatus was then evacuated, and the flask isolated from the pump. The cooling bath was removed, and the benzene and acid thoroughly shaken together at room temperature. By cooling one of the empty flasks in ice, the benzene was transferred into it, and this flask was then isolated from the pump. Hard pumping of the perchloric acid caused the evolution of ether vapour, and warming facilitated this process. The benzene was then distilled back into the acid, and the whole process was repeated. The removal of ether was judged to be complete when the perchloric acid no longer evolved vapours on pumping, but to be on the safe side the benzene was given a further four treatments after this stage was reached. The final sample of 1 : 2 : 4 : 5-*tetradeuterobenzene* (9·49 g.) was distilled through a column, in order to ensure the separation of any bromo-compounds. Thereafter it was dried over phosphoric oxide, and distilled into the stock bulb. Its physical constants have been given earlier.

Hydrogen Exchange between Bromobenzene and Heavy Sulphuric Acid.—Bromobenzene (British Drug Houses) was purified by shaking with 96% (by weight) sulphuric acid for 20 hours, washing with aqueous sodium carbonate, drying with phosphoric oxide, and fractionating. A little *p*-dibromobenzene was separated during the distillation. The bromobenzene was twice cooled until about two-thirds had solidified, the liquid portion being rejected.

Purified bromobenzene (5 c.c.) (b. p. 155·0—155·2°/764 mm.) and aqueous sulphuric acid (10 c.c.) were shaken together in sealed tubes. The hydrogen of the aqueous sulphuric acid contained 2—3 atoms % of deuterium. The stoicheiometric concentrations of the aqueous acid with respect to sulphuric acid and water are recorded in Table III, which also gives the periods of shaking, and the temperatures. The bromobenzene was recovered, any loss being attributed to sulphonation, and, after being washed with aqueous sodium carbonate, was dried by means of phosphoric oxide, and distilled. It was isotopically analysed by combustion, with the results given in Table III.

Hexadeuterobenzene.—Pure thiophen-free benzene (22 g.) was deuterated with successive portions of heavy sulphuric acid (containing 51 mols. % of D_2SO_4 and 49 mols. % of D_2O) as described in Part II. These later experiments were carried out during the winter months, when the average temperature was below that encountered in the earlier work, and this is doubtless why the attainment of equilibrium required about 10 days, as against 3—4 days which previously sufficed. The hydrogen of the final sample (16 g.) of hexadeuterobenzene contained 99·69 atoms % of deuterium.

Bromopentadeuterobenzene.—Bromine (53 g.) and mercuric oxide (160 g.) were added alternately, each in ten separate portions, to water (530 c.c.) with shaking, which was continued for 10 mins. after the addition was complete. The solution was then filtered (cf. Houben, " Die Methoden der Organischen Chemie," 1930, Vol. 3, p. 1160). The filtrate, together with hexadeuterobenzene (8 g.), was shaken in a stoppered bottle for 16 hours. The lower layer was separated, and dissolved in ether, and the ethereal solution was shaken with sodium carbonate solution (in order to remove mercuric oxybromide), dried, and distilled through a column. The chief impurities present at this stage in the bromopentadeutero-benzene were hexadeutero- and dibromotetradeutero-benzene, and their removal by fractionation was followed by determination of refractive index and density. These properties were shown, by preliminary experiments with light materials, to be sensitive indicators of benzene and dibromobenzene respectively. In this way the crude bromopenta-deuterobenzene (14 g.) was separated into hexadeuterobenzene (1·3 g.), *bromopentadeuterobenzene* (8 g.), $n_D^{20°}$ 1·5600, b. p. 154—155°/761 mm., and a small amount of crystalline *p*-dibromotetradeuterobenzene.

Pentadeuterobenzene.—Magnesium (1·5 g.) and a few crystals of iodine were heated in a 500 c.c. flask fitted with a condenser, a dropping funnel, and a gas-inlet tube. When activation was complete, the air was displaced by dry, oxygen-free nitrogen, and 5 c.c. of a solution of bromopentadeuterobenzene (7·5 g.) in ether (30 c.c.) were added, together with some additional ether (45 c.c.). Reaction began readily, and the rest of the solution of bromo-compound was added slowly; gentle refluxing completed the reaction. The Grignard compound was subsequently decomposed by the cautious addition of concentrated hydrochloric acid, and the ethereal layer was separated, washed, dried, and distilled through a column. The traces of ether remaining in the pentadeuterobenzene were removed by means of perchloric acid, as described above. The hydrogen of the final sample of *pentadeuterobenzene* (1·7 g.), m. p. 6·2°, contained 83·14 atoms % of deuterium.

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