# 56. *Structure of Benzene. Part XII. Preparation of Deuterated Benzenes by the Grignard Reaction. Mono- and* 1 : 4-*Di-deuterobenzene.*

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Details are given for the preparation of monodeuterobenzene and of 1 : 4-dideuterobenzene from bromobenzene and *p*-dibromobenzene, respectively, by conversion into a Grignard reagent and decomposition of this by means of deuterium oxide. The monodeuterobenzene obtained in this way was isotopically pure. However, the 1 : 4-dideuterobenzene, prepared directly through the dimagnesium compound of *p*-dibromobenzene, was found to have acquired much unwanted *light* hydrogen : all samples contained a considerable proportion of monodeuterobenzene. On the other hand, the monomagnesium derivative of *p*-dibromobenzene, on decomposition by means of deuterium oxide, gave isotopically pure *p*-bromomonodeuterobenzene, which could be converted into 1 : 4-dideuterobenzene exactly as bromobenzene had been converted into monodeuterobenzene. It seems essential to proceed in two stages, thus avoiding the employment of the dimagnesium compound. It is suggested that this highly reactive substance may undergo one-electron transfer reactions (Boyd and Hatt) forming free-radical intermediates which acquire light hydrogen from the ether solvent (Hey and Waters). Langseth and Klit's method of preparing polydeuterated benzenes from corresponding halogenated benzenes by reactions with magnesium and deuterium chloride in ether has been reinvestigated in the example of 1 : 4-dideuterobenzene. Here also a certain amount of unwanted light hydrogen appears in the product, possibly because the intermediate formation of some of the dimagnesium compound cannot be avoided.

A revised figure for the density of hexadeuterobenzene is recorded. Isotopic analysis of samples of partly deuterated benzenes is much facilitated by the now well-supported conclusion that the atomic fraction of deuterium is a closely linear function of the density of benzene.

The preparation of monodeuterobenzene, and of 1 : 2-, 1 : 3-, and 1 : 4-di-deuterobenzene, by the use of the Grignard compounds derived from bromo- and *o*-, *m*-, and *p*-dibromo-benzene has been described by Redlich and Stricks (*Monatsh.*, 1936, **67**, 213; 1937, **68**, 374). They mention no special precautions to secure the absence of light hydrogen from the positions in which it was desired to introduce deuterium; and they record no analytical data which would show the isotopic composition of their products. They prepared these materials for the purpose of studying their Raman spectra, and in each case recorded a number of Raman frequencies, together with qualitative indications of the relative intensities of the Raman lines. These data alone show that the samples must have been seriously impure. The monodeuterobenzene certainly contained a considerable proportion of benzene, and the dideuterobenzenes a large amount of monodeuterobenzene, and even some benzene. Our own experience of the preparation of deuterated benzenes by the Grignard method makes it evident that better results could not have been expected in the absence of precautions such as we have been led by experience to adopt. In one case Redlich and Stricks shook their deuterated product with concentrated sulphuric acid as a measure of purification, though even at that date this reagent was known rapidly to exchange its hydrogen with aromatic nuclear hydrogen.

Our first attempts at deuteration by the Grignard method were not encouraging. Taking such precautions to exclude adventitious moisture as are customary with Grignard reagents in preparative organic chemistry, we obtained from phenylmagnesium bromide a sample of " monodeuterobenzene " the hydrogen of which was shown by isotopic analysis (combustion and measurement of the density of the water formed) to contain only 11·5 atoms % (instead of 16·7 atoms %) of deuterium. Thereafter each stage of the process was studied in detail with a view to preventing the inadvertent introduction of light hydrogen; and an apparatus was employed (Fig. 1, p. 237) in which the preparation could be carried out without transferences in a moist atmosphere. With due attention to various points of detail (cf. Experimental Section) we eventually obtained a sample of *monodeuterobenzene* of the correct composition (16·5 atoms % by combustion and measurement of the density of the water; 17·0 atoms % directly from the density of the monodeuterobenzene). A careful study of its Raman and infra-red spectra (Part XX, this vol., p. 299) has failed to reveal any isotopic impurity, except such as arises from the inevitable presence of a small proportion of heavy carbon ($^{13}C$).

A point of general chemical interest arose in connexion with the preparation of 1 : 4-*dideuterobenzene*. When excess of magnesium is allowed to react in ether with *p*-dibromobenzene, a mixture of mono- and di-magnesium derivatives is formed, which contains a preponderance of the latter compound; for treatment with water yields a mixture of bromobenzene and benzene. When we carried out the decomposition of this Grignard mixture with heavy water, carefully excluding adventitious moisture, the hydrogen in the resulting deuterated benzene never contained more than about 30 atoms % of deuterium (theoretical figure, 33·3 atoms %). By contrast, the simultaneously formed p-*bromomonodeuterobenzene* had the correct isotopic composition with respect to its hydrogen (20·2 atoms % of deuterium by combustion and measurement of the density of the water. Calc.: 20·0 atoms %). Evidently in the formation of this compound the removed bromine atom has become quantitatively replaced by deuterium. This fact opened a route for the preparation of *p*-dideuterobenzene, because we had only to put the isolated *p*-bromomonodeuterobenzene through the same process by which bromobenzene had already been converted into monodeuterobenzene: our better samples of 1 : 4-dideuterobenzene were prepared from *p*-dibromobenzene by this two-stage method.

The notable difference of isotopic composition between the deuterated benzene and *p*-bromodeuterobenzene, which are produced together by the addition of deuterium oxide to the Grignard mixture obtained from *p*-dibromobenzene, shows at once that, towards some source of light hydrogen, the *p*-phenylene dimagnesium bromide is much more reactive than *p*-bromophenylmagnesium bromide. This is intelligible on general electrostatic grounds: each magnesium-containing (electron repelling) aromatic substituent in the dimagnesium compound must increase the electron density in the para-position, and therefore the affinity of that position for a proton, or its activity as a reducing centre. The question of where the unwanted light hydrogen in the benzene comes from is difficult to answer. Obviously we remain open to the criticism that we have failed to exclude ordinary moisture. On the other hand, we took great care in trying to do so, and an alternative explanation of the facts can be suggested. This is that, with the dimagnesium compound in particular, secondary reactions take place by a radical (odd-electron) mechanism. There is a good deal of evidence that some of the reactions of Grignard compounds in general proceed by a radical mechanism. Reducing behaviour is especially likely to consist in the transfer of single electrons; and it is known that, in the reduction of carbonyl compounds by Grignard reagents, pinacols are amongst the products (Boyd and Hatt, *J.*, 1927, 898). If this can be assumed there is no difficulty; for Hey and Waters have comprehensively shown (*Chem. Reviews*, 1937, **21**, 169; cf. Hey, *Ann. Reports*, 1940, **37**, 268) that it is characteristic of free-radical centres (including aryl radical centres), when formed in hydrocarbon, or other hydrogen-containing, organic solvents, to abstract a hydrogen atom from the solvent; and it can plausibly be supposed that towards some highly reactive Grignard compounds, such as our dimagnesium compound, under suitable conditions, the solvent ether may yield hydrogen in this way.

A special variant of the Grignard method for the preparation of deuterated benzenes has been developed by Langseth and Klit (*Kgl. Danske Vidensk. Selsk.*, 1937, **15**, 13). They allowed an appropriate mono- or polyhalogenobenzene to react in ether with magnesium and deuterium chloride, thereby replacing halogen by deuterium. The Raman spectra of the compounds obtained in this way are stated to have revealed the presence of appreciable amounts of less highly deuterated benzenes. But no analyses appear to have been performed on the samples, nor are their densities, or other physical constants, recorded. It is thus impossible on the basis of the particulars given to assess the value of the method. We therefore repeated Langseth and Klit's preparation of *p*-dideuterobenzene, using the apparatus shown in Fig. 2, and taking all those precautions against the incursion of unwanted light hydrogen which had been suggested by our previous experience. The hydrogen in the deuterated benzene so produced contained 30·8 atoms % of deuterium (theoretical figure 33·3%). A slightly better value, 31·4 atoms %, was obtained by the use of deuterium bromide in place of deuterium chloride for the reaction. It seems probable that the appearance of unwanted light hydrogen in benzenes obtained by Langseth and Klit's method from polyhalogenated benzenes is an inherent defect of the method, and arises from the impossibility of avoiding entirely the formation of intermediate Grignard compounds containing more than one magnesium atom.

## EXPERIMENTAL.

*Deuterium Content by Combustion* (cf. Part II, J., 1936, 916; also J., 1934, 493, 1593; 1935, 492; 1936, 1328, 1550, 1552).—About 0·1 g., weighed accurately to $10^{-5}$ g., of the deuterated benzene was enclosed in a thin glass bulb with a long drawn-out capillary tube, which was sealed before weighing. The bulb was broken under a weighed, larger quantity (up to 100 times as large) of pure light benzene. The mixture was burned over red-hot copper oxide, and the density of the combustion water determined (to 1 in $10^6$) after purification.

The atomic fraction ($x$) of deuterium in the hydrogen of the sample was calculated from the formula

$$x = [F_0(1 + h/l) - 0{\cdot}00017]/[h/l - \Delta M/M_1(F_0 - 0{\cdot}00017)]$$

where $F_0$ is the absolute atomic fraction of deuterium in the hydrogen of the combustion water, $h$ and $l$ the weights (corrected to vacuum) of heavy and light material mixed before combustion, $M_1$ the molecular weight of the light compound (78·01 in the case of benzene) and $\Delta M$ the molecular weight difference between the completely light and the completely deuterated molecules (1·013 $n$, where $n$ is the number of hydrogen atoms in the molecule). In deriving this formula allowance has been made for the deuterium content (0·00017) of the light material. This is taken to be the same as for tap water; but the deuterium contributed by any unexchanged positions of deuterated benzene has been neglected, calculation having showed that it was negligible in all the cases considered. The figure 0·00017 for the atomic fraction of deuterium in tap water was taken from recent publications (cf. Swartout and Dole, *J. Amer. Chem. Soc.*, 1939, **61**, 2025). The atomic fraction ($F_0$) of deuterium in the combustion water is given by

$$F_0 = \{(d^{25^\circ}_{25^\circ} - 0{\cdot}000006)/0{\cdot}10764\} + 0{\cdot}00017$$

where $d^{25^\circ}_{25^\circ}$ is the excess density relatively to tap water at 25°, and the term $6 \times 10^{-6}$ is a correction due to differences in the oxygen isotopic ratio of air and water. The divisor, 0·10764, represents the excess density of pure deuterium oxide. The over-all accuracy of analysis was 0·1—0·2%.

In our earlier work (Part II) the need for correction due to variations in the oxygen isotope ratio was not appreciated; in fact, the natural variation of this ratio had not been discovered. Our combustions united oxygen from the air with hydrogen from the sample under analysis, whereas the density of the water formed was compared with that of purified tap water. It is now known (Swartout and Dole, *loc. cit.*) that, using the same standard hydrogen, the density of water produced from air-oxygen is greater than that produced from water-oxygen by 6 p.p.m. Before 1939 the best value for density of pure heavy water relative to purified tap water was $d_{25^\circ}^{25^\circ}$ 1·1074. This figure is now known to be too low. Data made available in the last few years (Swift, *J. Amer. Chem. Soc.*, 1939, **61**, 198; Johnston, *ibid.*, p. 878; Johnston and Davis, *ibid.*, 1942, **64**, 2613; Wirtz, *Physikal. Z.*, 1942, **43**, 465; *Chem. Abs.*, 1943, **37**, 6539) indicate that the value is very close to 1·10764. This figure relates to heavy water having the oxygen isotope ratio of tap water. The assumption of a linear relation between deuterium content and excess density would appear to be strictly correct, since water containing small proportions of deuterium oxide has been shown (Swift, *loc. cit.*; Longsworth, *ibid.*, 1937, **59**, 1483) to be ideal at 25° from the standpoint of density.

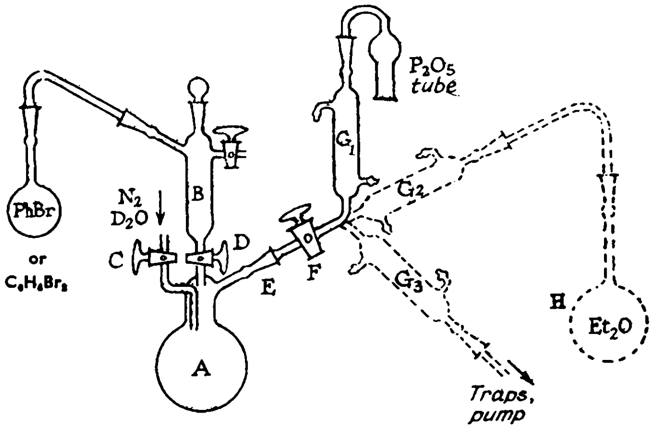
*Recalculation of Density of Pure Hexadeuterobenzene.*—Using the new formulæ we find that the deuterium content of the hydrogen in the best sample of hexadeuterobenzene used for the earlier measurement of physical properties was 99·1 and not 99·8 atoms % as recorded in Part II (*loc. cit.*).* Extrapolation gives for the density of pure hexadeuterobenzene, $d_{25^\circ}^{25^\circ}$ 0·94611; the corresponding figure for light benzene of normal hydrogen isotope ratio is 0·87596, and for completely deuterium-free benzene, 0·87595. The refractive index, dispersion and vapour-pressure data previously recorded (*loc. cit.*) are not appreciably affected.

*Deuterium Content of Benzene by Density Measurement.*—Using these new figures, the deuterium content of any sample of a partly deuterated benzene can be calculated from the density by assuming a linear relation between the atomic fraction of deuterium in the total hydrogen and density of the benzene. The general consistency of analytical results, obtained in this way and by combustion, shows that the linear relation is accurately fulfilled.

*Apparatus for Reaction of Grignard Compounds.*—All operations were carried out with purified and dried reagents and with the exclusion of atmospheric moisture and oxygen. The apparatus (Fig. 1) consisted of a one-litre Pyrex flask (*A*) fitted with a dropping funnel (*B*) and two side arms (*C* and *E*) sealed into the neck. The funnel (*B*) was used for the addition of either bromobenzene or *p*-dibromobenzene. In the latter case the funnel, its tap and the neck of the flask were lapped round with metal tubing carrying steam to keep the bromo-compound liquid. The side-arm (*E*) carried a standard joint, a tap (*F*), and a condenser (*G*), which by rotation about the standard joint could be held in three positions suitable for reflux or direct distillation.

FIG. 1.

*Apparatus for reaction of Grignard compounds and deuterium oxide.*



*Preparation of Grignard Compounds.*—The flask and auxiliary apparatus were thoroughly cleaned and dried before assembly. Magnesium (British Drug Houses, Ltd., "Special for Grignards") was rolled, cut into small pieces and introduced through *E*. The flask was then closed at *D* and *C*, and evacuated through *F*, and the metal, and as much of the apparatus as possible, were heated with a Bunsen flame for half-an-hour. Dry nitrogen was then introduced through *C* and a few dry crystals of resublimed iodine added. When connecting or disconnecting pieces of apparatus momentary contact with the atmosphere was unavoidable, and the precaution was always taken to have a counter current of dry nitrogen.

Various methods of desiccating ether were investigated and the following procedure finally adopted. Pure ether was treated with successive portions of sodium wire and then distilled into a one-litre flask attached to condenser (*G*) in position 3. Magnesium and ethyl bromide were added and allowed to react to form some ethylmagnesium bromide, whilst a stream of dry nitrogen was admitted. After 12 hours the condenser was then rotated into position 2, and ether was distilled into *A*. When distillation was complete, the ether container was removed and replaced by a phosphorus pentoxide drying tube, nitrogen being introduced at *C*. In some experiments phosphorus pentoxide was used for the final drying of the ether instead of ethylmagnesium bromide.

Bromobenzene was purified by fractional distillation followed by three successive partial freezings. *p*-Dibromobenzene was recrystallised three times from ethyl alcohol (cf. following paper). The purified bromo-compound was distilled directly into *B* after neglecting a first portion of about 5%. About 5 c.c. were run into the flask (*A*) containing ether and magnesium. Reaction was initiated by warming, and thereafter controlled by the addition of further bromo-compound and by ice-cooling if necessary. Formation of the Grignard compound usually took about 4 hrs., and was completed by gentle refluxing for a further hour. Some undissolved magnesium usually remained.

When the solid Grignard reagent instead of its ethereal solution was required, the ether was removed by distillation through the condenser in position 3, first at atmospheric pressure, and then in an oil-pump vacuum. The temperature of *A* was not allowed to rise above 100°.

*Reaction of Deuterium Oxide with the Grignard Compounds.*—The dry Grignard compound from bromobenzene was used in order to diminish the amount of ether subsequently to be separated from the formed benzene. This procedure could not be followed with the Grignard product from *p*-dibromobenzene because of the intense local heating: this

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* Purer material has since been obtained (Part XIII).

material was therefore hydrolysed in the presence of the ether. In such a case the method was to deliver the calculated amount of deuterium oxide during 45 mins. from a container attached to *C*. The rate of addition was controlled to keep the ether gently boiling, and the apparatus was frequently shaken during the process. It was found advantageous to interrupt the process when only part of the deuterium oxide had been added, then to distil off most of the ether and benzene, and then to add the remainder of the deuterium oxide: the hydrolysis of the Grignard compound could thus be rendered more complete. The reaction of heavy water with solid Grignard products was effected much more slowly. Flask *A* was left evacuated in this case, and the apparatus was removed from its supporting clamps so that the water could be distributed more evenly all over the layer of solid. The mixture was allowed to remain for 12 hrs. before distillation of the formed benzene.

*Isolation and Purification of the Benzenes.*—Volatile materials were removed from the reaction product by distillation, first at atmospheric pressure and then in a vacuum, flask *A* being heated to 100°. Most of the ether, and the whole of any bromobenzene present, were first removed by fractional distillation. The procedure recommended by Redlich and Stricks (*loc. cit.*) for purifying the resulting ether–benzene mixture was investigated. Such a mixture (5 c.c., containing 50 mols. % of each constituent) was shaken repeatedly with successive portions (each 5 c.c.) of cold water, the funnel and contents being kept just above the freezing point of benzene. After 8, 16, and 20 such washes the density of the benzene indicated the presence of 21, 2, and 0·5 mol. % of ether respectively. The remaining benzene had a volume of only 1·1 c.c. The method, therefore, leaves much to be desired. On the other hand, concentrated hydrochloric acid was found to be much more effective than water for the removal of ether: four washes reduced the ether concentration from 2·0 to below 0·05%, the smallest quantity detectable by density measurement. Similar treatment with cold water only reduced the concentration of ether to 0·5%. Hydrochloric acid did not cause hydrogen exchange between benzene and water. This was established by shaking concentrated hydrochloric acid (100 g.), deuterium oxide (3 g.) and benzene (10 g.) together for one week. The benzene was separated, washed and dried, and burnt over copper oxide. The combustion water had an excess density over tap water of 9 p.p.m., and, subtracting 6 p.p.m. for oxygen isotope variation, this leaves 3 p.p.m. for hydrogen isotope exchange, which is thus too small to be of significance. Equilibrium in exchange would have meant an excess density of about 3800 p.p.m.

As the present series of experiments was being completed, perchloric acid was found to be a much better reagent than hydrochloric acid for removing ether from benzene. The perchloric acid method is described in the following paper, since it was used in only two experiments of the present series.

*Monodeuterobenzene from Bromobenzene.*—(a) *Grignard reagent, ether and deuterium oxide.* Ether (300 c.c., dried over sodium wire) was transferred with minimum contact with atmospheric moisture to a 3-neck flask containing magnesium (5 g., 0·21 g.-mol.), and carrying a mercury-sealed stirrer, a dropping funnel and a reflux condenser fitted with a tube containing phosphorus pentoxide. Bromobenzene (31·5 g., 0·2 g.-mol.) was added slowly, and, after reaction was complete, deuterium oxide (3·67 c.c., 4·06 g., 0·20 g.-mol.) was added. After ½ hour excess iodine was added to decompose unreacted Grignard compound. Benzene and ether were removed by distillation and then separated by fractionation, the last traces of ether being removed by shaking the benzene with aqueous sulphuric acid (70% $H_2SO_4$ by weight). Acid of this concentration is known not to cause isotopic exchange with benzene. The benzene was dried over potassium carbonate and phosphoric oxide, and distilled in a vacuum. Density measurement showed the deuterium content to be only 11·5% (theory 16·67%).

(b) *Grignard reagent, dioxan, and water.* In this and subsequent experiments the apparatus shown in Fig. 1 was employed. The Grignard reagent was prepared from bromobenzene (41·6 c.c., 0·4 g.-mol.) in ether (205·6 c.c., dried over sodium). The bulk of the ether was removed at 100° at ordinary pressure, and then the temperature was raised gradually to 220°, and the pressure reduced to below 1 mm. Under these conditions some benzene accumulated in the traps, and, when no more appeared to distil, dioxan (400 c.c., dried over sodium) was added, followed by light water (7·2 g., 0·4 g.-mol.). After shaking for one hour the benzene (12 c.c.) and some dioxan were removed by distillation at atmospheric pressure. Owing to the difficulty of drying and transferring dioxan, it was thought preferable to omit it if possible.

(c) *Solvent-free Grignard reagent and water.* The ether was removed from the reagent at a final temperature of 250° in a vacuum. Some benzene was collected. Water (5·4 g., 0·3 g.-mol.) was added slowly to the solid reagent (from 0·3 g.-mol. of bromobenzene). The reaction was very violent, and external cooling was applied. Distillation in a vacuum at 100° gave benzene (14·5 c.c.) together with some ether.

(d) *Attempts to prepare the Grignard compound in other solvents.* Bromobenzene (15·6 g., 0·1 g.-mol.), magnesium (0·2 g.-atom) and dioxan (45 c.c., dried by sodium), or methylal (61·5 c.c., redistilled), or anisole (53 c.c., redistilled) were treated with iodine and heated, but without any sign of reaction. The experiment with dioxan was repeated, using Gilman's active magnesium, but without effect.

(e) *Thermal decomposition of phenylmagnesium bromide.* An experiment showed that benzene was formed on heating the solid Grignard reagent, prepared in ether, to a temperature exceeding 200°.

(f) *Dry Grignard reagent and deuterium oxide.* The above experiments led to the choice of the following optimum conditions. Bromobenzene (British Drug Houses, 31·2 c.c., 0·3 g.-mol.) was caused to react in ether (154 c.c., dried over sodium in flask *H*) with magnesium (7·2 g., 0·3 g.-atom). The Grignard compound was heated to 100° in a vacuum for 48 hrs. before adding the heavy water (5·4 c.c., 0·3 g.-mol., containing 99·95 atoms % of deuterium) to it in the cooled but still evacuated flask (*A*). Benzene and ether were then removed by distillation in a vacuum (sample 1). A further quantity (5·4 c.c. of the same quality) of deuterium oxide was added, and the benzene removed as before (sample 2). The benzene samples were each treated with hydrochloric acid to remove ether, and washed and dried over phosphoric oxide. The deuterium content as deduced from the density was high (18·0 atoms % of the total hydrogen), but this was shown to be partly due to the presence of bromobenzene. The samples were carefully fractionated, but the deuterium content (by combustion) did not fall below 17·0 atoms % (theoretical 16·7 atoms %). The high figure was ascribed to the presence of a little dideuterobenzene formed from *p*-dibromobenzene, which was subsequently shown to be present in the original bromobenzene used for this experiment. The experiment was therefore repeated, using bromobenzene purified as noted above. The yield of *monodeuterobenzene* (Found: D, 16·5 atoms % by combustion, 17·0 atoms % by density) was 40% of theory.

p-*Dideuterobenzene from* p-*Dibromobenzene.*—(a) *Solvent-free dimagnesium compound and deuterium oxide.* The solvent ether was removed from a solution prepared from *p*-dibromobenzene (189 g., 0·8 g.-mol.) and magnesium (38·4 g., 1·6 g.-atom) in ether (500 c.c.). On addition of deuterium oxide (32 g.), however, a violent reaction ensued with incandescence after an initial induction period.

(b) *Dimagnesium compound in ether and deuterium oxide.* The ether was first dried in flask (*H*) by using ethylmagnesium bromide. After the addition of deuterium oxide to the Grignard product from *p*-dibromobenzene, fractions containing dideuterobenzene, b. p. 45—88° (50 c.c.), and p-*bromomonodeuterobenzene* (yield, 17 c.c. = 25 g. = 20%) (Found: D, 20·2 atoms % by combustion. $C_6H_4DBr$ requires D, 20·0 atoms %) were obtained by distillation. The former fraction after ten washes with concentrated hydrochloric acid had a volume of 37 c.c. (yield 52%) (Found: D, 29·8, 29·9 atoms % by combustion, 31·4 atoms % by density. Calc. for $C_6H_4D_2$: D, 33·3 atoms %). In another experiment the product consisted of deuterated benzene (yield 54%) (Found: D, 29·6 atoms % by combustion) and *p*-bromomonodeuterobenzene (yield 20%) (Found: D, 20·2 atoms % by combustion).

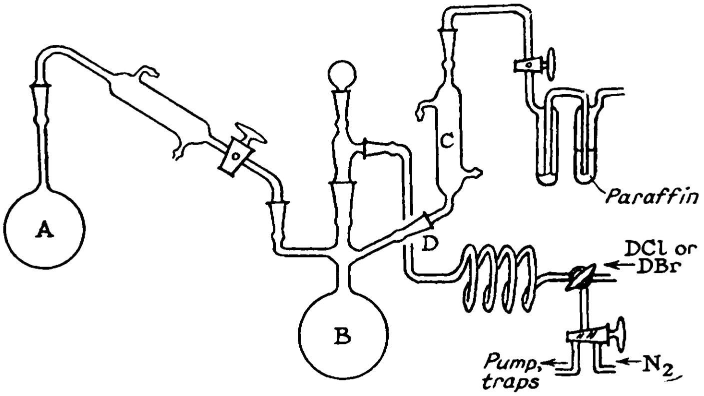
(c) *Reaction of 4-deuterophenylmagnesium bromide with deuterium oxide in ether.* *p*-Bromodeuterobenzene (34·5 g., 0·22 g.-mol., containing 20·2 atoms % of deuterium in its hydrogen) was treated with magnesium (6 g., 0·25 g.-atom) in ether (112 c.c.). Deuterium oxide (12·45 c.c., 13·8 g., 0·69 g.-mol.) was added and 1 : 4-*dideuterobenzene*, m. p. 5·9° (Found: D, 32·2 atoms % by combustion, 32·5 atoms % by density), was isolated (yield 9 c.c. = 46%) as described above.

*Attempts to Prepare* 1 : 3 : 5-*Trideuterobenzene by Grignard Reaction.*—3 : 5-Dibromoiodobenzene, m. p. 122° after recrystallisation from benzene, was prepared from *o*-nitroaniline by bromination in acetic acid solution followed by deamination, reduction with iron, and a Sandmeyer reaction to replace the amino-group by iodine (Jackson and Russe, *Amer. Chem. J.*, 1906, **35**, 149; Holleman, *Rec. Trav. chim.*, 1906, **25**, 183). No reaction could be induced between magnesium and either 1 : 3 : 5-tribromobenzene or 3 : 5-dibromoiodobenzene in diethyl or di-*n*-propyl ether. Added iodine, bromine and magnesium activated by iodine vapour (Gilman), methyl iodide and methyl bromide failed to initiate reaction.

1 : 4-*Dideuterobenzene by Langseth and Klit's Method.*—(a) *Using deuterium chloride.* Ether (400 c.c.), previously dried with sodium wire, was left overnight in flask *A* (Fig. 2) with phosphoric oxide, and then distilled into flask *B*, which already contained magnesium (24 g.) and *p*-dibromobenzene (118 g.). The entire apparatus had been cleaned and baked out, as described above. Nitrogen, freed from oxygen by passing over red-hot copper, was dried by cooling in a trap surrounded by liquid air, and passed slowly through the apparatus, so that it finally escaped through a trap containing heavy paraffin. When the formation of Grignard compound began, deuterium chloride generated by reaction of deuterium oxide (10 g., containing 99·95 atoms % of deuterium) with thionyl chloride (Nevell, de Salas, and Wilson, J., 1939, 1195) was introduced. The reaction was completed by gentle heating. Benzene and ether were removed by distillation, first under atmospheric pressure and then under reduced pressure, the condenser *C* being rotated about joint *D* through 180° for this purpose. After purification by fractional distillation, the last traces of ether were removed by means of perchloric acid (see following paper). 1 : 4-Dideuterobenzene (15 g.) (Found: D, 30·8 atoms % by combustion; 31·4 atoms % by density) was obtained. The reaction became very sluggish in its later stages, owing to the separation of magnesium chloride: magnesium (8 g.) and *p*-dibromobenzene (36 g.) were recovered.

FIG. 2.

*Apparatus for repetition of Langseth and Klit's preparation of deuterated benzenes.*



(b) *Using deuterium bromide.* *p*-Dibromobenzene (92·5 g.), iodine (0·5 g.), magnesium (20 g.), and ether (450 c.c., dried as before) were introduced into flask *B*, and, when reaction began, deuterium bromide (74 g., 0·9 g.-mol., containing 99·9 atoms % of deuterium in its hydrogen) was slowly introduced. The deuterium bromide was prepared from electrolytic deuterium (Wilson and Wylie, J., 1941, 600). The experiment lasted 2·5 hrs., and, although no solid separated, an upper liquid layer of about 20 c.c. was formed. The distillate, which contained hydrogen bromide, was washed with sodium hydroxide and dried with anhydrous potassium carbonate. After removal of ether by means of perchloric acid, the density of the deuterated benzene was found to be high. This was traced to the presence of ethyl iodide, which was finally removed, with some loss of benzene, by shaking with aqueous silver perchlorate (made by neutralising concentrated aqueous perchloric acid with silver oxide). The resulting 1 : 4-dideuterobenzene (Found: D, 31·4 atoms % by combustion, 32·0 atoms % by density) weighed 23 g.

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[*Received, May 7th,* 1945.]