58. *Structure of Benzene. Part XIV. Limitations of the Decarboxylation Method for preparing Partly Deuterated Benzenes.*

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Calcium trimesate was decarboxylated by heating with calcium deuteroxide, but the deuterium content of the benzene produced depended on the proportions of the reactants. Further investigation showed that two hydrogen exchange reactions were going on, one between calcium deuteroxide and calcium trimesate before the decarboxylation, and the other between calcium deuteroxide and the benzenes formed by decarboxylation. The second exchange reaction could be minimised by working at a low pressure, but even when, with the aid of this device, a product of the correct analytical composition was obtained, it was nevertheless a complicated mixture of isotopic isomerides, as was shown by its infra-red spectrum.

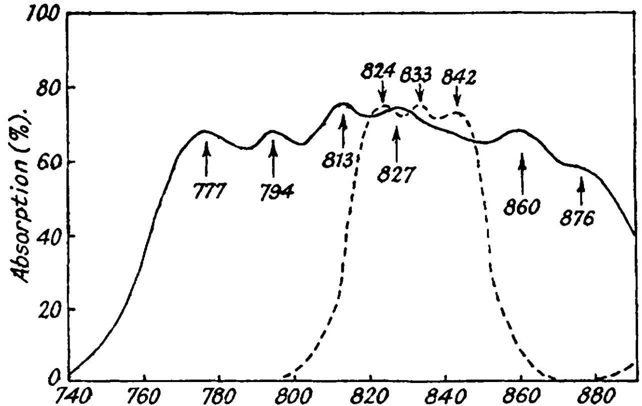
Experiments on the decarboxylation of calcium benzoate by means of calcium deuteroxide, or of sodium benzoate by means of sodium deuteroxide, gave similar results. In the latter case, indeed, there appeared, under some conditions, to be an almost complete randomisation of deuterium between the reactants.

The preparation of deuterated benzenes by decarboxylation with calcium deuteroxide has been reported by Morita and Titani (*Bull. Soc. Chim. Japan*, **1935**, **10**, 557) and Redlich and Stricks (*Monatsh.*, 1936, **68**, 47, 374). The former authors used benzoic acid, but did not completely examine the product, which they assumed to be monodeuterobenzene. Redlich and Stricks used phthalic, *iso*phthalic, and pyromellitic acids, and studied the Raman spectra of their products. They found that the deuterobenzenes from phthalic and *iso*phthalic acids gave the same spectrum, and that the deuterobenzene from pyromellitic acid appeared to be a mixture of isomerides. None of these authors determined the deuterium in their products.

Fig. 1.

Infra-red spectra of trideuterobenzene in the region 740—890 *cm.*$^{-1}$ *showing complex mixture of isomers produced by decarboxylation of calcium trimesate.*

(*Pressure,* 5 *cm.* ; *length,* 45 *cm.*)



Full line : Deuterobenzene from trimesic acid.
Broken line : Pure 1 : 3 : 5*-trideuterobenzene from aniline.*

We first decarboxylated calcium trimesate by using three equivalents of calcium deuteroxide, but the hydrogen of the product contained 62·8 instead of 50·0 atoms % of deuterium. Further experiment showed that two unforeseen exchange reactions were causing the excessive deuteration. One, between calcium trimesate and calcium deuteroxide, occurred before the decarboxylation. This was demonstrated by the presence of 1·9 atoms % of deuterium in the nuclear hydrogen [*] of trimesic acid recovered from an uncompleted experiment. The second exchange reaction was between benzene and calcium deuteroxide, and must have taken place after decarboxylation. It was established by the deuteration of light benzene to an extent of 9·6 atoms % by passage over calcium deuteroxide at the reaction temperature. It is not clear whether calcium deuteroxide or deuterium oxide was the deuterating agent. Decarboxylation did not appear to take place until the temperature, 430°, was reached, at which the dissociation pressure of the deuteroxide approaches one atmosphere. By the use of a low pressure, the amount of deuteration of benzene vapour was reduced from 9·6 to 2·9 atoms %. Under these conditions, the decarboxylation of trimesic acid led to benzene of more nearly the theoretical deuterium content, though the effect of the exchange reactions was still evident. By using different ratois of calcium deuteroxide to calcium trimesate, samples of benzene containing 49·7, 52·3, and 54·6 atoms % of deuterium were prepared. The first sample has almost the theoretical deuterium content for trideuterobenzene, but its infra-red spectrum showed it to be a mixture of isomerides, and the possibility that both more and less highly deuterated benzenes were also present is not excluded. Fig. 1, for which we are indebted to Messrs. R. R. Gordon and J. B. Hale, represents a portion of the spectrum, and shows a complicated group of overlapping bands. The same region of the spectrum of pure 1 : 3 : 5-trideuterobenzene contains only a single band (with P, Q, and R branches) due to the vibration frequency 833 cm.$^{-1}$. Obviously the decarboxylation product, in spite of its nearly correct deuterium content, is a mixture of several different molecular species.

Our next experiments concerned the decarboxylation of benzoic acid. Repetition of Morita and Titani's experiment, using 1·05 equivalents of calcium deuteroxide, gave material the hydrogen of which contained 17·5 atoms % of deuterium. Using 2·6 equivalents of calcium deuteroxide the deuterium content of the product rose to 28·8 atoms %, though this value fell to 17·2 atoms % on operating at a low pressure. All the samples contained more deuterium than pure monodeuterobenzene (16·7 atoms %)

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[*] The carboxylic hydrogen of the acid was isotopically normalised by exchange with ordinary water before the isotopic analysis.

Finally, sodium salts were used instead of calcium salts, but the results were even less simple. The use of three molecular equivalents of sodium deuteroxide gave a benzene with hydrogen containing as much as 32·1 atoms % of deuterium. Under reduced pressure this figure rose to 36·9 atoms %, corresponding to an almost completely random distribution of the hydrogen of the reactants. The failure to reduce the hydrogen exchange by operating under low pressure would indicate rapid deuteration of sodium benzoate by sodium deuteroxide. The increase may be attributed to the increased time the fused salts were together (the reaction took 30 instead of 8 minutes). This exchange between benzoic acid and fused alkali may explain the observation by Erlenmeyer and Loback (*Helv. Chim. Acta*, **1936**, **19**, 546) that nuclear deuterium is lost when the deuterated benzanilide, $C_6D_5 \cdot CO \cdot ND \cdot C_6H_5$, is hydrolysed to benzoic acid by fused alkali.

EXPERIMENTAL.

Materials.—*Trimesic acid* (cf. Ullmann and Uzbachian, *Ber.*, 1903, **36**, 1799). Mesitylene (45 g., b. p. 163—164°) and water (5 l.) were vigorously stirred at 95°, and potassium permanganate (360 g.) was added in portions of 20 g. over a period of 26 hours. The resultant mass was filtered, and the filtrate added to a hot water extract (200 c.c.) of the manganese dioxide and acidified with concentrated hydrochloric acid. The acid, crystallised from glacial acetic acid, had m. p. 370° (corr.). *Calcium trimesate.* An aqueous solution of the sodium salt was treated with 50% excess of calcium chloride, and the precipitate thoroughly washed with water. The salt contains 12 molecules of water of crystallisation, and retained one of these even at 185°, but it was removed by heating at 150° at less than 1 mm. pressure over phosphoric oxide. *Calcium benzoate.* The dihydrate (Kahlbaum) was dried in the above manner. *Sodium benzoate.* The monohydrate (British Drug Houses) was dried by heating at 170° for 18 hours. *Calcium phthalate.* Phthalic acid was converted into the anhydrous calcium salt by the procedure used for trimesic acid. *Calcium deuteroxide.* The requisite amount of heavy water was distilled in a vacuum on to pure powdered calcium oxide previously heated at 600° in a stream of dry air for 2 hours. *Sodium deuteroxide.* A weighed amount of freshly cut sodium was placed in a copper tube in which the decarboxylation was to be carried out. The tube was about the same size as that used for sodium hydroxide reactions (see later), but was closed at one end, and had only one semi-circular baffle plate to prevent the molten salts from flowing out of the heated zone when the tube was horizontal. A stream of dry nitrogen was introduced by a tube passing almost to the bottom of the copper chamber. The sodium was gently heated until the last traces of naphtha in which it had been stored had disappeared. The tube was then clamped vertically in a bath of ice, and a slight excess of heavy water was introduced from a dropping funnel during ½ hour. The reaction went very smoothly and was completed by heating. (The evolved deuterium was burnt over red-hot copper oxide.) The copper tube was then placed in the furnace in a horizontal position, and heated to remove the slight excess of heavy water, and to fuse the sodium deuteroxide so that it formed a layer along the tube as far as the baffle plate. When cold, the appropriate sodium salt was added. Precautions were taken throughout to prevent the access of moisture.

Apparatus.—Decarboxylation with calcium salts was carried out in Pyrex tubes (100 cm. long and 4 cm. diam.) heated in an electric furnace, temperatures being measured by thermocouples placed alongside the tube. The products were swept from the reaction chamber by a current of dry nitrogen (freed from oxygen by alkaline pyrogallol) into suitable cooled traps. The same apparatus was used for experiments under reduced pressure, a manometer being included in the gas line. The copper tube used for decarboxylation with sodium deuteroxide has already been described.

Method.—Calcium salts were intimately mixed by shaking in a large flask, and the mixture was then introduced into the Pyrex reaction chamber by attaching the neck of the flask to it with rubber. Reaction commenced at 430°, and was usually complete after 1 hour's heating at 430—550°. About half the combined water in the calcium deuteroxide was recovered as water. The benzene and water, together with a little benzophenone, were separated, and the benzene was dried over phosphoric oxide and distilled.

The reactions under rdeuced pressure at 430—480° gave back about ¾ of the combined water of the calcium deuteroxide as water, and the amount of benzophenone formed was rather greater than before. With sodium hydroxide, benzene appeared at 370°, and the whole of it was evolved below 380°. Using sodium deuteroxide, the reaction occurred between 460° and 470° at ordinary pressure, and between 350° and 380° under reduced pressure (0·2—0·4 mm.).

Exchange Experiments.—Deuterium exchange between benzene and calcium hydroxide was carried out in the same apparatus as that used for decarboxylation. The benzene was introduced as vapour.

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