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# Preparation of Cyclohexane-$d_{12}$ by Deuteration of Benzene-$d_6$

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Dedicated to Professor *Ole Lamm* on his 60th birthday

A method for the preparation of cyclohexane-$d_{12}$ is described, which utilizes the deuteration of benzene-$d_6$ in a heterogeneous catalytic process. A mixture of benzene-$d_6$ damp and excess electrolytically generated deuterium gas is supplied to a furnace containing cobalt on pumice as a catalyst, and the cyclohexane-$d_{12}$ formed is collected in a cold trap. The excess of deuterium is recycled continuously which gives a nearly stoichiometric yield.

Several methods concerning the introduction of deuterium into cyclohexane have been published in the literature. Most of the exchange reactions, as a rule in the liquid state, have given rather low yields. Thus, several attempts to let $D_2SO_4$ exchange hydrogens with ordinary cyclohexane, were discouraging [1,2]. Experiments performed in a $ND_3$-milieu and with $KND_2$ present as a catalyst gave negative results [3,4], as did an investigation using a platinum catalyst in an acetic acid medium [5].

Methods utilizing gaseous reactants and some kind of metal catalyst have in some cases given good results of exchange [6], but evidently the choice of the catalyst and its treatment have been rather critical.

Hydrogenation reactions readily converting benzene to cyclohexane are reported in literature and should be more suitable to produce a highly deuterated cyclohexane. Hall and Emmet [7] obtained a nearly complete conversion of benzene to cyclohexane at 162°C over certain copper-nickel alloys. However, the preparation of the catalyst required very highly purified materials and extreme care with the treatment. These disadvantages did not pertain to a method worked out by Lihl *et al.*[8,9] They prepared a cobalt catalyst which was not easily poisoned, but instead apparently improved with time. Furthermore, the temperature ranges for the catalyst formation and the hydrogenation itself were generously wide.

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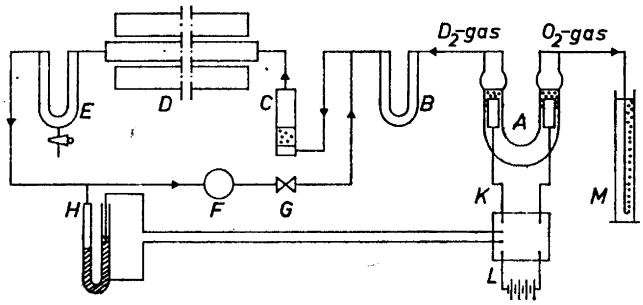


*Fig. 1.* Apparatus for the deuteration of benzene-$d_6$ to cyclohexane-$d_{12}$. A, electrolyzer; B, cold trap; C, bubble flask containing benzene-$d_6$; D, tube-type furnace; E, cold trap; F, pump; G, valve; H , mercury manometer with a contact point; K, d.c. relay; L, voltage source; M, level regulator.

Accordingly, by letting deuterium gas react with benzene-$d_6$ on such a catalyst, a deuterated cyclohexane should result. Such experiments are described in this report.

## APPARATUS

A schematic diagram of the apparatus is shown in Fig. 1. Deuterium gas prepared in the heavy water electrolyzer (A) is brought through a cold trap (B), for trapping heavy water damp, into a small bubble flask (C) containing benzene-$d_6$. The gas mixture formed is then supplied to a tube-type furnace (D) containing the catalyst. The reaction product is collected in another cold trap (E), while the excess deuterium is forced back into the system with a pump (F). When the increasing excess of deuterium gas creates a certain over-pressure, contact will be established between the mercury column (H) and the contact point, and the d.c. relay (K) switches off the electrolyzing current supplied by the voltage source (L). The levels of the electrolyte in the two half-cells of the electrolyzer can easily be adjusted by the level regulator (M).

The *electrolyte*, a 4 M solution of KOD, is prepared in a nitrogen box by letting potassium metal react with heavy water which contains 99.80 % $D_2O$, by weight.

The *electrodes* are made of rolled platinum foils, giving a very large surface area.

The *production capacity* of the electrolyzer, working continuously, is a deuterium gas flux corresponding to 20 ml cyclohexane-$d_6$ per 24 h.

The *benzene-$d_6$* used is a product of a method described by Rupprecht [10], and has a deuterium content of 99.50 atom %. In order to obtain a wanted molar ratio of $D_2$:$C_6D_6$ of 5:1 in the gas mixture formed, the temperature of the benzene bubble flask is controlled at 32.5°C.

The temperature of the electrically heated *tube-type furnace* is measured by a copper-constantan thermocouple.

The preparation of the *catalyst* follows quite nearly the description given by Lihl [8,9]. 170 g pumice is supplied to a slurry of 60 g $CoCO_3$ in water, 75 ml

formic acid (70 %) is added, and cobaltous formiate is formed with the development of carbon dioxide. After the reaction is finished, the water and excess acid are evaporated by a heat lamp. The cobalt formiate and its carrier are supplied to the furnace (D) and a hydrogen gas flux of 40 l/h is introduced. Reduction at 400°C is continued for a 6-h period and then the temperature is lowered to 180°C, which is the temperature chosen for hydrogenation/deuteration. When the apparatus is not in use, nitrogen gas is blown through in order to impede entrance of air oxygen into the system.

The working point of the *mercury manometer-d.c.-relay circuit* is chosen at about 5 mm Hg above the air pressure. Thus no eventual leakages of the system allow air to enter and spoil the catalyst.

The *pump* used is of a membrane type and in combination with the valve it nicely maintains the deuterium flux adjusted.

## EXPERIMENTS

In order to test the effectiveness of the catalyst, ordinary benzene and water were used as starting materials. In a 48-h run, 11.75 g $H_2O$ and 16.97 g benzene were consumed; this corresponds to a molar ratio of $H_2O:C_6H_6 = 3.002$, while the theoretical value is 3. The refractive index of the product was $n_D^{20} = 1.4258$ while a reference specimen of cyclohexane showed a value $n_D^{20} = 1.4256$. However, the weight of the product was only 16.59 g, a yield of 90.8 %. Since the cold trap could be expected to trap 100 % of the product, the loss was ascribed to material still adsorbed on the catalyst.

After this successful test, two runs were made with heavy water and benzene-$d_6$ (about 5 g in each run) as starting materials. In the first of these runs, newly reduced catalyst was used, while in the other run the catalyst after reduction was swept through with nitrogen for 48 h to remove the light hydrogen adsorbed. The light hydrogen content of the starting materials and of the product was measured with a proton magnetic resonance method [11] and with a refractive index measurement. The latter, when compared with literature data [12], showed the same degree of conversion as in the light hydrogen run. The results from the PMR analysis are shown in Table 1.

*Table 1.* Analytical data from proton magnetic resonance measurements.

| | Atom percentage of deuterium | | |
|---|---|---|---|
| Run | $C_6D_6$ | $D_2O$ | $C_6D_{12}$ |
| 1 | 99.50 | 99.78 | 95.37 |
| 2 | 99.50 | 99.78 | 97.51 |

## DISCUSSION

The expected atom percentage of deuterium in cyclohexane-$d_{12}$ should be the arithmetical average of the values of benzene-$d_6$ and heavy water, *i.e.* 99.64 %. This value was not reached in either of the two runs; the second run was the better of the two. The only explanation for this is that rather large amounts of light hydrogen remain strongly adsorbed at the surface of the reduced catalyst and the intended elimination of this light hydrogen by blowing through nitrogen gas was not completely effective. Successive runs with the same catalyst (without further reduction with light hydrogen), however, should render the maximum deuterium content. If only a high deuterium

content product is desired, recirculation of deuterium through the catalyst at 400°C before its use is a more economical way to get rid of the light hydrogen adsorbed.

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