SYNTHESIS OF 3,4,5,6-TETRADEUTERIOBENZENE-1,2-$^{13}C_2$.

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In connection with the measurement of proton and ^{13}C resonances of benzene [1] and its behaviour under electron impact [2], it became desirable to synthesize the doubly labelled benzene mentioned in the title. The most convenient synthesis appeared to be that shown of figure 1.

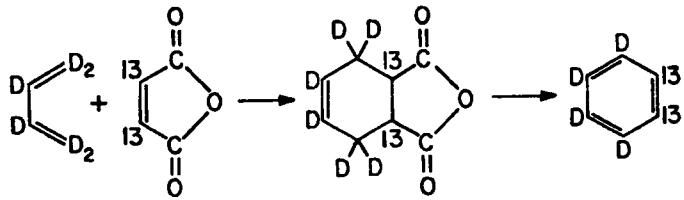

Figure 1

The deuterated diene was prepared as reported by us [3]. The ^{13}C-labelled maleic anhydride was prepared from 1,2-dibromoethane-1,2-$^{13}C_2$ via the cyanide, succinic acid, bromosuccinic acid, fumaric acid and maleic anhydride [4,5].

The Diels-Alder synthesis from the deuterated diene and maleic anhydride-2,3-$^{13}C_2$ in benzene gave an 87 % yield of adduct.

Attempted dehydrogenation and decarboxylation with P_2O_5 at 200° as described for other compounds by Skvarchenko, Levina and Belyavskaya [6] gave only a 39 % yield of benzene and, furthermore, the mass analysis showed considerable scrambling of deuterium.

Two general methods are mentioned in the literature for the formation of an olefinic bond from vicinal dicarboxylic acids namely electrolytic oxidation [7,8] and lead tetraacetate oxidation [9,10].

Normally, the electrolytic decarboxylation of bicyclic dicarboxylic acids gives better results than lead tetraacetate decarboxylation. However, only very low yields of impure dihydrobenzene were obtained by electro-oxidation of tetrahydrophthalic acid.

The yield was not greatly improved by lead tetraacetate oxidation in pyridine as reported in the literature [10] but in DMSO, an 85% yield of a mixture of dihydrobenzene and benzene was obtained. With an excess of lead tetraacetate, the dihydrobenzene was rapidly oxidized to benzene but the deuterio analogue oxidized only very slowly. It was found that tetrachloro-o-quinone at 75° gave a quantitative yield of deuterated benzene from the deuterated hydrobenzene without any deuterium scrambling.

EXPERIMENTAL

A mixture of Δ^4-3,3,4,5,6,6-hexadeuterio-1,2-dihydrophthalic acid-1,2-$^{13}C_2$ (610 mg) (obtained in 90% yield from the hydrolysis of the anhydride in water on a steam bath for 5 h), dimethylsufoxide (5 ml) and finally lead tetraacetate (3.4 g) was placed in a 25 ml two necked round bottom flask equipped with a gas inlet tube and a magnetic stirring bar. The other neck held a reflux condenser which was connected in series with a spiral side arm trap cooled

to -78°C and a gas bubbler. The apparatus was flushed with nitrogen for 1 h and the mixture was then heated slowly with an oil bath to 65°C, at which temperature evolution of CO_2 was very rapid. The dark solution gradually turned colorless. The flow of water in the condenser was stopped and nitrogen gas was passed through the apparatus for 24 h while keeping the reaction mixture at 70-75°C. Then, the trap was connected to a vacuum line and the condensed material was distilled through KOH pellets into a tube containing tetrachloro-o-quinone (0.5 g). The tube was sealed at a constriction and placed in an oven at 75°C for 20 h. The tube was cooled to -20° and opened. The volatile material, collected in a vacuum manifold, afforded 203 mg (70%) of the labelled benzene melting at 3°C. Another 45 mg of less pure benzene could be obtained from the reaction mixture by flushing the apparatus at higher temperature.

Mass-spectrum

m/e	Isotopic species present	relative abundance %
84	$^{13}C_2$, D_4	29.8
83	$^{13}C_2$, D_3	2.5
	$^{13}C_1$, D_4	45.8
82	$^{13}C_1$, D_3	3.5
	$^{13}C_0$, D_4	17.6
81	$^{13}C_0$, D_3	0.9

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