

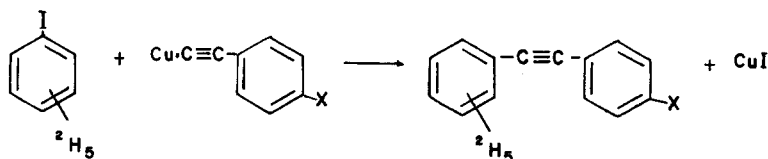
NOTESPreparation of Iodobenzene-d<sub>5</sub> and Diphenylacetylene-d<sub>5</sub> \*

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Easy access to deuterated or tritiated iodobenzene is important for the synthesis of a wide variety of aromatic compounds containing these isotopes. Previous work has shown the tritiated iodobenzene can be obtained *via* diazotization of aniline<sup>(1)</sup> and iodobenzene-d<sub>5</sub> from decomposition of the Grignard reagent prepared from bromobenzene-d<sub>5</sub><sup>(2, 3)</sup>. The former example uses relatively expensive aniline-d<sub>5</sub> (or tritiated aniline) as a starting material and the latter reaction yields only 94.5% isotopically pure C<sub>6</sub>D<sub>5</sub>I.

In the present study iodobenzene-d<sub>5</sub> was prepared from readily available benzene-d<sub>6</sub>. Benzene-d<sub>6</sub> was monoiodinated by the method of Wirth and co-workers<sup>(4)</sup> in which treatment with iodic acid, iodine, acetic acid-d<sub>4</sub>, deuterium oxide and sulfuric acid-d<sub>2</sub> gives iodobenzene-d<sub>5</sub> in 60-80% yield. Mass spectrometry indicates a purity of >98.5% C<sub>6</sub>D<sub>5</sub>I. The above procedure could also be used to prepare tritiated iodobenzene by using suitably enriched tritiated benzene.

The iodobenzene-d<sub>5</sub> was readily converted into a series of diphenyl acetylenes as shown in equation 1<sup>(5)</sup>.



The reaction was carried out at 100° C in pyridine and the products isolated by preparative thin-layer chromatography. In all cases the isotopic purity of the products was >98.5% C<sub>6</sub>D<sub>5</sub>C≡C·C<sub>6</sub>H<sub>4</sub>X as shown by mass spectrometry.

## EXPERIMENTAL.

Mass spectra were measured with a Consolidated Electroynamics Corporation 21-110B high resolution instrument using electrical detection. Samples were introduced by a direct introduction technique using a low temperature probe at -30° to +10° C<sup>(6)</sup>.

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*Preparation of Iodobenzene-d<sub>5</sub>.*

Benzene-d<sub>6</sub> (1.25 g), iodine (1.1 g), iodic acid (0.45 g), acetic acid-d<sub>4</sub> (3.0 ml), sulfuric acid-d<sub>2</sub> (.18 ml) and deuterium oxide (0.6 ml) were stirred at 80° C for 4 hours. The mixture was cooled, diluted with water (10 ml) and extracted with pentane (20 ml). The pentane extract was washed with dilute aqueous bisulfite solution (2 × 20 ml), water (2 × 20 ml), dried, evaporated and the iodobenzene-d<sub>5</sub> recovered in 60-80 % yield by chromatography on silica gel or by microdistillation. When non-deuterated acetic acid, sulfuric acid and water was used C<sub>6</sub>D<sub>5</sub>I of 97-98 % isotopic purity was obtained.

*Preparation of Diphenyl Acetylenes.*

Iodobenzene-d<sub>5</sub> (200 mg) and the cuprous derivative of 4-chlorophenylacetylene (100 mg) in pyridine (10 ml) were stirred for 18 hours at 100° C under a stream of dry nitrogen. The reaction mixture was then poured into water and the product isolated with ether and purified by thin-layer chromatography (50 % yield). The series of diphenylacetylenes (X = H, F, Br, Me) were all prepared as described above in 40-70 % yield. In most cases higher yields were obtained with extended reaction times of 24-48 hours.

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