

comparing favorably with nicotine for use against aphids.

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THE PREPARATION AND PROPERTIES OF BENZENE-d₆

Sir:

We have developed a technique for the exchange reaction between deuterium oxide and benzene, discovered by Horiuti and Polanyi [*Nature*, **134**, 377 (1934); *Trans. Faraday Soc.*, **30**, 1164 (1934)] which permits the ready production of benzene-d₆. Two cylindrical Pyrex vessels of about 50-cc. capacity are connected by a Pyrex U-tube containing an active nickel catalyst supported on kieselguhr. The catalyst tube is heated externally by a closely fitting electric furnace, and the catalyst reduced (in our case with deuterium) at 420°. After the system is thoroughly evacuated and sealed a sample of 5 cc. of benzene and 10–20 cc. of heavy water is introduced *in vacuo* through a special breakable seal. By means of an electric furnace, which closely fits either cylinder, the water is brought to ebullition and, carrying with it a proportion of benzene vapor, is driven over the catalyst, heated to 200°, where some exchange occurs, the product condensing in the second cylinder appropriately cooled. By reversing the procedure the benzene-water mixture can then be passed once more through the catalyst. Frequent repetition of the process ultimately establishes an equilibrium partition of deuterium between water and benzene. By replacing the hydrogen-diluted deuterium oxide with fresh pure deuterium oxide and continuing the passage over the catalyst, further conversion toward benzene-d₆ can be obtained.

We traced the progress of the exchange by attaching to the reaction system via a quartz-Pyrex seal a cylindrical quartz absorption cell 30 mm. thick. Benzene vapor at room temperatures gives a series of sharply defined ultraviolet absorption bands. Each of the substituted benzenes, C₆H₅D, C₆H₄D₂, etc., shows similar bands, displaced toward the ultraviolet by frequency differences varying for each band but roughly constant for each additional D atom. As exchange occurs forming an equilibrium among the 13 benzenes this results in a considerable over-

lapping and complication of the spectrum. With continued progress toward the final state, the overlapping disappears, the sharply defined bands of C₆D₆ only remaining.

In four successive equilibrations with 5 cc. of benzene using an initial 10 cc. of 95% D₂O and then successively 10, 20 and 20 cc. of 100% D₂O a product containing 55, 85, 97 and >99% of the hydrogen as deuterium has been prepared. The deuterium contents have been *estimated* from the absorption spectra. For example, in the 97% product, the bands corresponding to C₆D₅H and C₆D₆ were the only ones visible, the former with about one-fifth the intensity of the latter. Densities of the carefully purified and redistilled samples at the first two stages were, 55%, *d*₂₅⁴ 0.9146; 85%, *d*₂₅⁴ 0.9349; and the final product had a density of 0.9417. After four separate processes of purification we received approximately 3.5 cc. of final product. Measurements are being made of the Raman spectra, infra-red and ultraviolet absorptions and other physical properties. We are continuing our study of the variables in the preparation and also extending the procedure to other compounds.

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THE HYDROLYSIS OF ERGOTININE AND ERGOCLAVINE

Sir:

Following our preliminary communications [*J. Biol. Chem.*, **104**, 547 (1934); *THIS JOURNAL*, **57**, 383 (1935); *Science*, **81**, 256 (1935)] regarding the cleavage of ergotinine by alkali to lysergic acid, isobutyrylformic acid, ammonia and a polypeptide which on further hydrolysis with acid yielded proline and phenylalanine, we have made a logical extension of the investigations to the study of the cleavage of ergotinine by acid. Heating with hydrochloric acid resulted in the destruction of the lysergic acid portion of the molecule with the formation of obscure amorphous material. On the other hand, *l*-phenylalanine, [α]₂₀^D -28° (*c* = 0.39 in H₂O), was obtained as such while proline was isolated as the methyl ester (*Anal.* C, 55.70; H, 8.81), [α]₂₅^D +33° (*c* = 0.65 in CH₃OH), which was further characterized by the gold salt (*Anal.* C, 15.70; H, 2.62; Au, 41.83).