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C, 59.79; H, 5.96; N, 4.36; S, 9.98%. Found in material dried at 100° *in vacuo*: C, 59.87; H, 6.15; N, 4.38; S, 9.94%.

2,4-Dimethyl-5-carbethoxypyrrole (*Ib*)

The pyrrole sulphone (1.22 gm.) was refluxed for four hours with freshly prepared W-6 catalyst (1) (20 cc.) in absolute ethanol (60 cc.). The catalyst was separated and washed by centrifuging, and the ethanol evaporated. The residue was extracted with petrol ether (b.p. 60–75°, 50 cc.) (thimble), giving the pyrrole as colorless prisms (0.342 gm.) m.p. 123–124° on cooling of the extract; concentration gave a second crop (0.143 gm.; total 76%) m.p. 122.5–123.5°. Both crops gave a positive Ehrlich's reaction cold, and did not depress the melting point of authentic material of m.p. 123–124°. Calc. for $C_9H_{13}O_2N$: C, 64.65; H, 7.83; N, 8.38%. Found in material recrystallized from hexane and dried *in vacuo*: C, 64.44; H, 7.54; N, 8.37%; Lassaigne test for sulphur, negative.

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ORGANIC DEUTERIUM COMPOUNDS
XII. BENZENE-d_6*

By L. C. Leitch

Several methods of preparing benzene-d_6 were reviewed and evaluated by Ingold and Wilson (3). These authors reported that the exchange reaction between benzene and 50 mole % deuterium sulphate – deuterium oxide solution gave benzene-d_6 of higher deuterium content than any other method. They pointed out that the nickel catalyzed vapor phase exchange between benzene and deuterium oxide discovered by Horiuti and Polanyi (2) and developed by Bowman, Benedict, and Taylor (1) gave benzene-d_6 which contained 14 mole % C_6D_5H.† Notwithstanding this criticism by Ingold and Wilson, it seemed desirable to reinvestigate the heterogeneous exchange reaction between benzene and deuterium oxide on account of its simplicity. After exchanging benzene four times with deuterium oxide at 110°C. in the presence of platinum black, a product was obtained which contained less than 4 mole % C_6D_5H and was 99.2% deuterated. Such material is satisfactory for most purposes. The advantages of the present method are that the reaction

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†Shortly after this paper had been submitted for publication Dixon and Schiessler (J. Am. Chem. Soc. 76: 2197. 1954) reported the method of preparation of benzene-d_6 of Ingold and Wilson (3) to be superior to that of Bowman, Benedict, and Taylor (1).

time is shortened and the rather tedious preparation of deuterium sulphate is avoided.

EXPERIMENTAL

Benzene-d_6

A mixture of benzene (5.0 ml., previously dried and distilled over sodium), deuterium oxide (10.0 ml., 99.5%), and platinum black (0.3 gm., prepared by reducing Adams' catalyst with deuterium) was heated in a sealed tube with a re-entrant joint in a rocking furnace for 12 hr. at 110°C. After the tube had been opened with a magnetic hammer while attached to a vacuum line the deuterated benzene was fractioned and then distilled through a U-tube containing Drierite into a trap. The benzene was recovered nearly quantitatively. A small sample was removed for mass spectrometric analysis and the balance was distilled into another reaction tube containing platinum black and fresh deuterium oxide. This operation was repeated twice more. The deuterium content after each exchange is shown in Table I.

TABLE I
DEUTERIUM CONTENT IN MOLE PER CENT AFTER EACH EXCHANGE

	1st	2nd	3rd	4th
C_6D_6	19.8	65.6	86.7	95.24
C_6D_5H	42.7	31.8	12.0	3.96
$C_6D_4H_2$	37.6	3.18	2.4	—

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