The Preparation and Purification of Methane-*d*, Ethane-*d*, Propane-1-*d*, Propane-2-*d*, *n*-Butane-1-*d*, *n*-Butane-2-*d*, Isobutane-1-*d*[1] and Isobutane-2-*d*[1]

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Recent notes[2,3] describe the use of several of the above compounds in studying hydrogen exchange reactions of the lower molecular weight alkanes in contact with acid catalysts. Since they were used in those studies and have been used in others yet to be reported, it seems worthwhile to record the methods of their preparation. While the results of their mass spectrometric analyses are reported below, the methods used have been reported separately.[4]

Several monodeutero-alkanes, including some of the above, have been prepared previously by treating the appropriate Grignard reagent with deuterium oxide or a deutero-acid. Methane-*d* has been prepared in this way by a number of investigators[5–10] and in another way by MacWood and Urey.[11] In addition, ethane-*d*,[5,12] propane-1-*d*,[5,6,13] propane-2-*d*,[5,6,13] 2-methylbutane-1-*d*[14] and 2,2-dimethylpropane-1-*d*[15] have been prepared. However, an accurate determination was not made of the isotopic purity of any of the deutero-paraffins except methane-*d*.

In the present work, Grignard reagents were prepared from alkyl halides of known purity, taken in most cases from a group of samples maintained as standards for analysis. After the preparation of the Grignard reagent and before the introduction of the deuterium-containing reagent, a large portion of the ether solvent and any hydrocarbon produced prematurely were removed by distillation. The deutero-hydrocarbon products were removed from ether by low temperature fractional distillation, examined by use of the mass spectrometer, and treated to remove the olefin usually present. Mass spectrometric (and in one case, infrared spectrophotometric) examination then was used to determine the chemical, isomeric and isotopic purity.[16]

Determination of Purity

Chemical and "Isomeric" Purity.—The samples after distillation were found to contain no ether (<0.03%), alkyl halides (<0.03%), or homologous hydrocarbons (<0.05%—within the limits of mass spectrometric analysis).

The "crude" propane and butane preparations invariably contained small amounts of olefins. A special method of mass spectrometric analysis[4] involving use of low energy (<10 volt) electrons showed that the purified preparations contained less than 0.03% olefin (<0.1% in the case of ethane-*d*).

Isotopic Purity.—The only impurities in the purified deuteroalkanes that are impossible to remove are the ordinary hydrocarbons, produced partly from the small amount of HDO in the D_2O reagent, but mostly through disproportionation of the Grignard radical during addition of deuterium oxide

$$2C_4H_9\cdot \longrightarrow C_4H_8 + C_4H_{10}$$

Where the crude products were analyzed for olefin and alkane, the amounts found were approximately equal, in agreement with the above hypothesis.

Since the alkane impurities are impossible to remove, it is important to determine the amounts present if the deuteroalkanes are to be used in quantitative applications such as kinetic studies. Special methods of mass spectrometric analysis involving low voltage electrons were used in determining ordinary alkanes as well as olefins. Details of these methods are discussed in the accompanying paper.[4] Results of the analyses are shown in Table I.

TABLE I

PREPARATIONS OF MONODEUTEROALKANES

	Product, millimoles	Yield based on halide, %	Temp. of distillation cut, °C.	Olefin content, %[a]	Alkane-d_0 content, %
Methane-*d*	15	94			4.2
Ethane-*d*	13.2	67		<0.1	2.3
Propane-1-*d*	37.5	75	−43 to −18	< .03	2.1
Propane-2-*d*	33.5	67	−43.5 to −43	< .03	1.0
n-Butane-1-*d*	40.8	82	−1 to 0	< .01	0.5
n-Butane-2-*d*	34.6	69	−1$^1/_2$ to $^1/_2$	< .01	2.0
Isobutane-1-*d*	36.7	73	−12.5 to −11.5	< .01	2.0
Isobutane-2-*d*	39.3	43	−12.5 to −11.5	< .02	0.5

[a] None detected—values given are limits of detectability of mass spectrometric methods used.

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[1] For clarity, the names isobutane-1-*d* and isobutane-2-*d* have been used in place of the more correct 2-methylpropane-1-*d* and 2-methylpropane-2-*d*, respectively.

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[12] L. K. Posey, Jr., and E. F. Barker, *ibid.*, **17**, 182 (1949).

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[14] H. C. Brown and C. Groot, THIS JOURNAL, **64**, 2563 (1942).

[15] F. C. Whitmore, G. H. Fleming, D. H. Rank, E. R. Bordner and K. D. Larson, *ibid.*, **56**, 749 (1934).

[16] For complete experimental details of these syntheses order Document 3029 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $0.50 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.40 for photocopies (6 × 8 inches) readable without optical aid.