The Synthesis and Properties of *n*-Octane-d_{18} and 2,2,4-Trimethylpentane-d_{18}[1]

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A relatively simple apparatus and procedure for preparing a variety of perdeuterated aliphatic compounds are applied to the synthesis of *n*-octane-d_{18} and 2,2,4-trimethylpentane-d_{18}. The properties of these compounds are reported.

As part of a continuing study of the relationship of physical properties to hydrocarbon structure, the changes in the properties when deuterium is substituted for hydrogen in hydrocarbons have been under study in this laboratory. Earlier, benzene-d_6 and cyclohexane-d_{12} were prepared[4] and the properties determined.[5–7] The changes in the properties upon deuteration observed with these two hydrocarbons and the recent corresponding states treatments of classically, isotopically substituted liquids[8] suggested that the preparation and study of additional perdeuterated hydrocarbons having significantly different spatial and symmetry characteristics might be worthwhile.

Although the literature[9–12] records the preparation of a number of perdeuterated hydrocarbons, none of the procedures appeared to be satisfactory for the synthesis of molar quantities in the C_6 to C_{12} molecular weight range. The reported syntheses may be divided into two broad classes.

(1) Syntheses starting from available chemical intermediates and utilizing classical chemical reactions to construct the desired perdeuterated molecule. An example of this procedure is the synthesis of spiropentane-d_8 starting from calcium carbide by House, Lord, and Rao.[11]

(2) Syntheses starting from a hydrocarbon possessing the same carbon skeleton as that desired in the final product and involving exchange of the hydrogens of the hydrocarbon with the deuterium atoms in a deuterium-containing molecule, *e.g.*, D_2O, D_2SO_4. The synthesis of benzene-d_6 by Ingold and co-workers[12] is a classic example of this approach.

Group 1 syntheses suffer from the fundamental disadvantage that each hydrocarbon structural-type requires a different synthetic route. Further, as the carbon skeleton of the molecule becomes more complex, the number of synthetic steps frequently increases rapidly. Since group 2 routes do not have these disadvantages, the present effort was confined to developing a procedure of this type but avoiding the problems noted below.

The exchange of deuterium between deuteriosulfuric acid and aromatic hydrocarbons proceeds readily at temperatures where no skeletal changes or other side reactions occur to any significant extent. Unfortunately, with aliphatic hydrocarbons Setkina and co-workers[13] have found that under mild conditions only the tertiary hydrogens are exchanged. Under forcing conditions the expected carbonium ion rearrangements accompany the exchange.[14] Similarly, Dixon and Schiessler[15] found that the vapor phase exchange between deuterium oxide and hydrocarbons is attended by significant cracking and/or isomerization.

In contrast, Burwell and co-workers[16–19] in their study of the mechanism of hydrogen exchange observed that the exchange of deuterium gas with aliphatic hydrocarbons proceeded rapidly in the vapor phase over metal catalysts and was accompanied by little or no carbon skeletal rearrangement. This procedure suffers only from the disadvantage that for the synthesis of molar quantities of a C_6 to C_{12} paraffin hydrocarbon extremely large volumes (of the order of thousands of liters at STP) of deuterium must be used. To avoid this a scheme involving the direct deuterium–hydrocarbon exchange but avoiding the handling of large amounts of deuterium was developed.

The Apparatus and Procedure.—Figure 1 is a flow diagram of the apparatus. A complete description of the apparatus and full experimental details may be found in ref. 20. The principal operations occurring in the system are the following.

(1) Hydrogen–deuterium gas is continuously circulated through the entire apparatus.

(2) In the "deuterator" section this gas mixed with hydrocarbon vapor passes over a pelleted nickel on kieselguhr[21] catalyst. A statistical distribution of deuterium and hydrogen atoms between the gas and the hydrocarbon results, *e.g.*

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[3] Abstracted from a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree, 1959.

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[21] Manufactured by Universal Oil Products Co., Detroit, Mich.

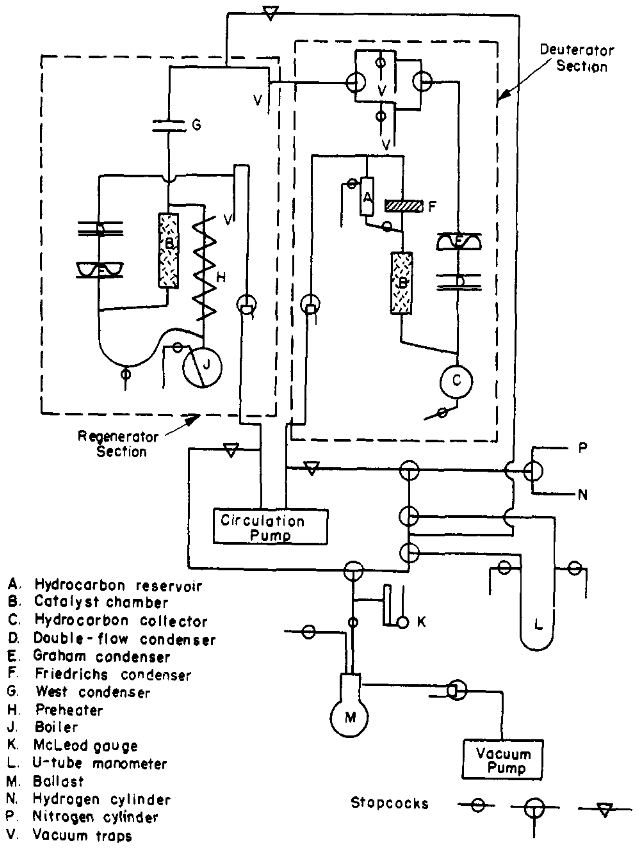

Fig. 1.—Deuteration apparatus.

$$D_2 + C_8H_{18} \rightleftarrows C_8H_{17}D + HD$$

The partially deuterated hydrocarbon is then separated by condensation and the hydrogen–deuterium gas passes to the "regenerator" section.

(3) Here, the hydrogen–deuterium gas, mixed with superheated deuterium oxide vapor, is passed over the nickel on kieselguhr catalyst at 300°. The gas is reenriched in deuterium from the heavy water and as

$$HD + D_2O \rightleftarrows HDO + D_2$$

the gases leave the "regenerator" the water is separated by condensation while the hydrogen–deuterium gas returns to the "deuterator" section.

By this technique, the advantages of both the deuterium–hydrocarbon and deuterium oxide–hydrocarbon exchange processes are realized without the disadvantages of either. Although the hydrocarbon was in contact with approximately 1000 liters of deuterium gas during each twenty-four-hour period of operation, there were only twelve liters of gas in the apparatus at any given time.

The apparatus was all glass except for the circulation pump which consisted of two counteracting brass Sylphon[22] bellows. Neither the deuterium oxide nor the hydrocarbon came in contact with the pump.

The maximum transfer of deuterium from heavy water to hydrocarbon is obtained by passing the hydrocarbon through the deuterator only once per charge of heavy water to the boiler. A method of operation for accomplishing this and an equation for calculating the number of equilibrations (or cycles) to obtain a given amount of a hydrocarbon of a given deuterium content are discussed in detail in ref. 20.

Catalysts.—An extensive investigation of catalysts was not made. However, it was observed that nickel supported on kieselguhr produced rapid deuterium exchange with less cracking and isomerization than platinum on carbon or platinum on glass beads.

Preparation of *n*-Octane-d_{18} and 2,2,4-Trimethylpentane-d_{18}.—*n*-Octane-d_{18} and 2,2,4-trimethylpentane-d_{18} were chosen for synthesis because: complete physical property and thermodynamic data are available on the hydrocarbons; they have appreciably different (for isomers) viscosities, viscosity–temperature characteristics and boiling points; in many approaches to the correlation of molecular structure and physical properties the normal paraffins are used as base-line or reference compounds[23]; they are liquid over a relatively extensive temperature range; and the corresponding deuteriocarbons should be separable by efficient fractional distillation from any impurities resulting from isomerization or cracking. *n*-Octane is the highest-boiling octane and 2,2,4-trimethylpentane is the lowest-boiling octane.

n-Octane-d_{18} was prepared from Phillips Research grade *n*-octane by the exchange procedure described previously. At 115–130° the mixture of hydrocarbon vapor and deuterium gas reached isotopic equilibrium very rapidly, and there was almost no cracking or isomerization as shown by efficient fractional distillation and gas–liquid chromatography.[24] The product of the exchange reaction contained approximately 0.2% of lower-boiling impurities. These were removed by fractional distillation to yield an *n*-octane-d_{18} containing less than 0.1% of hydrocarbons having a different carbon skeleton and of isotopic composition 99.1% D, 0.9% H. Isotope per cents were estimated from density and quantitative infrared measurements.

Unfortunately, the rate of attainment of isotopic equilibrium between 2,2,4-trimethylpentane vapor and deuterium was extremely slow at the temperature used for the deuteration of *n*-octane. It is believed that this was due to the phenomenon described by Burwell[16–19]; *i.e.*, a single adsorption–desorption of the hydrocarbon on the catalyst surface will not result in complete isotopic equilibration if the hydrocarbon possesses a quaternary carbon atom. The quaternary carbon atom in 2,2,4-trimethylpentane has attached to it a 2-methylpropyl group and three methyl groups. Should the 2-methylpropyl group be chemisorbed on the catalyst surface one-half of the hydrogen atoms in the hydrocarbon molecule will equilibrate with deuterium and the deuterium content will be half that produced by an equivalent chemisorption of *n*-octane and deuterium. However, chemisorption of the hydrocarbon molecule *via* a methyl group (the probability of this event is 0.5, on the basis of the hydrogen atoms accessible to the catalyst) will yield a deuterium con-

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(22) Manufactured by the Fulton Sylphon Co., Knoxville, Tenn.

(23) (a) H. Wiener, *J. Am. Chem. Soc.*, **69**, 17, 2636 (1947); *J. Chem. Phys.*, **15**, 766 (1947); *J. Phys. Chem.*, **52**, 425, 1082 (1948); (b) J. R. Platt, *ibid.*, **56**, 328 (1952); (c) J. B. Greenshields and F. D. Rossini, *ibid.*, **62**, 271 (1958).

(24) A 10-ft column of Apiezon L on firebrick was used at 85°. The retention times of seventeen of the eighteen possible octanes were individually determined with this column and it was established that as little as 0.1% of any of the isomers could be detected in either *n*-octane or 2,2,4-trimethylpentane. The missing isomer was 2,2,3,3-tetramethylbutane. See ref. 20 for details including the retention times of the various isomers.

TABLE I

DENSITIES AND VISCOSITIES OF n-OCTANE-d_{18} AND 2,2,4-TRIMETHYLPENTANE-d_{18}

Hydrocarbon	% D	Density (g./cc.) 0°	20°	37.8°	60°	Viscosity (cp.) 0°	20°	37.8°	60°
n-Octane	0.0	0.7185	0.7027	0.6884	0.6703	0.7091	0.5428	0.4437	0.3524
	99.1	0.8337	0.8152	0.7984	0.7765	0.7668	0.5895	0.4852	0.3794
	100.0[a]	0.8347	0.8162	0.7794	0.7774	0.7673	0.5899	0.4856	0.3796
2,2,4-Trimethylpentane	0.0	0.7081	0.6919	0.6774	0.6587	0.6495	0.5042	0.4146	0.3323
	97.4	0.8197	0.8007	0.7835	0.7612	0.6989	0.5406	0.4424	0.3536
	100.0[a]	0.8226	0.8036	0.7863	0.7639	0.7001	0.5415	0.4430	0.3541

[a] Obtained by linear extrapolation of the property of the most highly deuterium-substituted product.

TABLE II

REFRACTIVE INDICES, MOLAR REFRACTIONS, AND MOLAR VOLUMES OF n-OCTANE-d_{18} AND 2,2,4-TRIMETHYLPENTANE-d_{18}

Hydrocarbon	% D	n^tD 20°	30°	40°	Molar refraction 20°	Molar volume 20°
n-Octane	0.0	1.3975_6	1.3927_0	1.3878_9	39.193	162.55
	99.1	1.3931_1	1.3883_1	1.3834_8		
	100.0[a]	1.3930_7	1.3882_7	1.3834_4	38.706	162.15
2,2,4-Trimethylpentane	0.0	1.3913_7	1.3865_7	1.3815_2	39.256	165.09
	97.4	1.3871_5	1.3823_5	1.2773_6		
	100.0[a]	1.3870_4	1.3822_4	1.3772_5	38.776	164.69

[a] Obtained by linear extrapolation of the property of the most highly deuterium-substituted product.

TABLE III

TEMPERATURE COEFFICIENTS

Compound	$-d\eta/dT \times 10^3$ (cp. deg.$^{-1}$, 20°)[a]	$-1/\eta\ d\eta/dT \times 10^2$ (deg.$^{-1}$, 20°)[a]	(g./cc.$^{-1}$ deg.$^{-1}$, 20°)	$d\eta/dT \times 10^4$ 30°
n-Octane	5.328	0.982	7.96	4.84
n-Octane-d_{18}	7.629	1.293	9.34	4.82
2,2,4-Trimethylpentane	6.076	1.205	8.12	4.93
2,2,4-Trimethylpentane-d_{18}	6.511	1.202	9.60	4.90

[a] Calculated from the differential form of the equation $\log \eta = A - B/(C + T)$.

tent one-eighteenth that produced by the equivalent chemisorption of n-octane and deuterium.

An attempt was made to produce equilibration by raising the temperature of the catalyst chamber. Not only should complete equilibration be favored by more frequent adsorption–desorption of the hydrocarbon on the catalyst surface, but the temperature increase should also increase the probability of a methylene-type adsorption suggested by both Burwell[9] and Kemball.[25] Such adsorption would by its nature increase the deuterium content of the molecule.

Equilibrium between deuterium and the hydrocarbon was approached rapidly in the 181–195° range but was accompanied by extensive cracking and isomerization. A temperature of 154–164° was used as a compromise between a rapid reaction with extensive production of impurities and a very slow reaction without production of detectable impurities.

The 2,2,4-trimethylpentane-d_{18} obtained under these conditions had approximately 1.8% of impurities due to cracking and isomerization. Upon efficient fractional distillation a material was obtained with the isotopic composition 97.4% D, 2.6% H, and containing less than 0.1% of any material with a different carbon skeleton.

It was shown by g.l.c. and fractional distillation that of the 1.8% impurities in the crude product approximately 1.6% were lower molecular weight compounds. These were not further identified, but the 0.2% of isomeric octanes were concentrated by fractional distillation and analyzed by g.l.c. Three peaks were observed. However, under the conditions used, 2,5-dimethylhexane had the same retention time as 2,4-dimethylhexane and 2,2,3-trimethylpentane had the same retention time as 3,3-dimethylhexane. Thus there may have been as many as five isomeric octanes present. The major isomeric impurity (~0.1%) was 2,4-dimethylhexane and/or 2,5-dimethylhexane; the other impurities were 2,2-dimethylhexane and 3,3-dimethylhexane and/or 2,2,3-trimethylpentane.

Properties.—The physical properties of the hydrocarbons and corresponding deuteriocarbons are shown in Tables I, II, and III. The procedures for obtaining the properties have been described previously.[4,5]

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