Isoprene-d_8 and Other Intermediates for the Synthesis of Deuterio-SN Rubber

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Perdeuterio isoprene was synthesized from acetone-d_6 and acetylene-d_2. 2-Methyl-3-butyn-2-ol-d_8 and 2,5-dimethyl-3-hexyn-2,5-diol-d_{14} were isolated and the latter decomposed to acetone and the ynol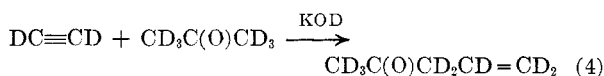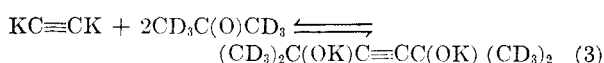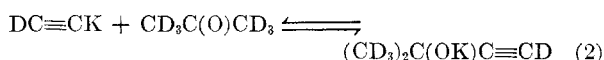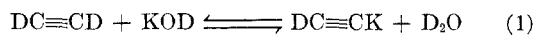. The ynol was deuteriumated to 2-methyl-3-buten-2-ol-d_{10} over the Lindlar catalyst and the enol then dehydrated to isoprene. The maleic anhydride adduct as well as the α- and β-sulfones of isoprene-d_8 were prepared. The D compounds were more dense, less refractive, and had lower boiling points than the corresponding H compounds.

The synthesis[1] of perdeuterio SN rubber (all cis, all head-to-tail, all 1,5-diene polyisoprene), a preliminary report of which appeared recently, was possible as the result of the availability of D_2, D_2O, and geometrically specific polymerization techniques.[2] The present paper describes the preparation and properties of the required isoprene-d_8 and other intermediates.

The Favorskiĭ-Bergmann isoprene synthesis. Of the many possible routes to isoprene-d_8 from various simple compounds, the one chosen for adapting to the D series involves the Favorskiĭ[3] synthesis from acetone and acetylene as modified by Bergmann.[4] The following reactions are involved:

$$DC \equiv CD + KOD \rightleftharpoons DC \equiv CK + D_2O \quad (1)$$

$$DC \equiv CK + CD_3C(O)CD_3 \rightleftharpoons (CD_3)_2C(OK)C \equiv CD \quad (2)$$

$$KC \equiv CK + 2CD_3C(O)CD_3 \rightleftharpoons (CD_3)_2C(OK)C \equiv CC(OK)(CD_3)_2 \quad (3)$$

$$DC \equiv CD + CD_3C(O)CD_3 \xrightarrow{KOD} CD_3C(O)CD_2CD = CD_2 \quad (4)$$

$$(CD_3)_2C(OD)C \equiv CD + D_2 \xrightarrow[40°]{Pd} (CD_3)_2C(OD)CD = CD_2 \quad (5)$$

$$(CD_3)_2C(OD)CD = CD_2 \xrightarrow[300°]{Al_2O_3} D_2O + D_2C = C(CD_3)CD = CD_2 \quad (6)$$
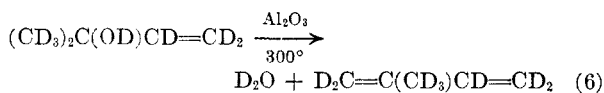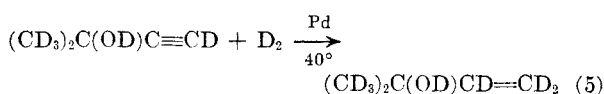
Each intermediate was confirmed in the protium series before being tried as a deuterio intermediate. In addition to D_2 and D_2O, the starting materials include potassium, calcium carbide, and acetone-h_6. In two of the steps diethylene glycol dimethyl ether (diglyme) and ethyl ether were used as the solvents. Catalysts needed were potassium carbonate, Lindlar palladium, and alumina. Of these materials, only acetone and the ethers contain protium, the protium of the latter not being exchangeable. Acetone-h_6 was converted to acetone-d_6

by a standard technique[5] with potassium carbonate as catalyst. Other intermediates were acetylene-d_2, 85% KOD, DC≡CK, 2-methyl-3-butyn-2-ol-d_8, and 2-methyl-3-butene-2-ol-d_{10}. A rather special intermediate of the synthesis was 2,5-dimethyl-3-hexyl-2,5-diol-d_{14} which was found to cleave smoothly at 150–160° in the presence of potassium carbonate to form acetone, acetylene, and 2-methyl-3-butyn-2-ol. A similar cleavage in the presence of sodium methylate was reported by Mauge.[6]

The work of Bergmann and associates[4] showed that, in 100% excess, 85% potassium hydroxide reacts with acetylene to form a mono potassium salt and that a diether of appropriate boiling point is almost essential. The excess potassium hydroxide acts as a water acceptor in aiding the neutralization. In the presence of the diether a reactive voluminous precipitate is secured. They reported that yields of over 90% of the ynol were feasible when an excess of potassium acetylide and also excess acetylene were contacted with acetone at about −12°. We believe their work to be authentic although our yields of deuterio as well as of protio acetylenic alcohols were only 65–73% ynol and 17.5% yndiol. Acetylene-h_2 and -d_2 were generated by adding H_2O or D_2O to calcium carbide covered with diglyme. Actually Bergmann and others reported a yield of 67% ynol and 27% yndiol when ethylene glycol ethyl butyl ether was used in place of their preferred diether which was an aldehyde acetal. We avoided the use of an acetal because of its instability and presumed tendency to undergo H to D interchange.

The most troublesome feature of the isoprene-d_8 synthesis was the preparation of 85 to 87% KOD. This was successful when D_2O and potassium were added alternately to diglyme and when the amount of D_2O was great enough so that the potassium droplets (m.p. 62°) did not coat over with solid KOD. Infrared spectra of recovered diglyme were superposable over the spectrum of the starting

(1) W. L. Semon and others, *Science*, 128, 359 (1958).

(2) S. E. Horne and others, *Ind. Eng. Chem.*, 48, 784 (1956); *Rubber Chem. and Technol.*, 29, 687 (1956).

(3) A. E. Favorskiĭ, *Bull. acad. sci. U.R.S.S. Classe. sci. chim.*, 1940, 181; *Chem. Abstr.*, 37, 3046 (1943).

(4) E. D. Bergmann, M. Sulzbacher, and D. F. Herman, *J. Appl. Chem.*, 3, 39 (1953) and previous articles.

(5) J. R. McNesby, T. W. Davis, and A. S. Gordon, *J. Am. Chem. Soc.*, 76, 823 (1954); F. E. Condon, *J. Am. Chem. Soc.*, 73, 4675 (1951).

(6) R. Mauge, C. Malen, and J. R. Boissier, *Bull. soc. chim. France*, 1956, 425.

diether. This showed that H did not interchange with D during this or any subsequent stage of the synthesis.

The Lindlar[7] palladium catalyst was important though not essential for Reaction 5 of the synthesis. Quinoline was found not to be needed as a poison in addition to the usual lead acetate added during the catalyst preparation. Deuterium absorption in the absence of a solvent does not slow down appreciably during deuteriumation, but if the reaction is stopped when the ynol has disappeared it will be found that almost no reduction of the enol will have occurred. In contrast, in the presence of a solvent, reduction did slow down when the ynol was nearly used up. The complete removal of ynol by deuteriumation is obviously most essential. Its presence in the enol led during dehydration to acetone (reversal of the Favorskiĭ reaction) and to 2-methyl-1-butene-3-yn in the isoprene. These are specific poisons in the polymerization of isoprene.

The dehydration (Reaction 6) of 2-methyl-3-buten-2-ol (isoprene alcohol) at 300° over alumina was straightforward. Purification of isoprene-d_8 so produced was gaged by various techniques, including infrared and mass spectroscopy, diene analysis, vapor phase chromatography, and polymerization. Impurities detected include acetone, n-pentane and n-pentenes, 2-methylbutane, 2-methyl-1-butene, 2-methyl-2-butene, and 2-methyl-1-butene-3-yn. More or less obvious reactions account for the impurities including the straight chain hydrocarbons which no doubt result from the vinylation of acetone (Reaction 4). Fractionation through an efficient column was effective but for the removal of traces of acetone, acetylenes, peroxides, water, and alcohols, as well as of unknown impurities, it was necessary to treat with sodium in order to secure polymerization-grade isoprene. The h_8 and isoprene-d_8 hydrocarbons, as finally isolated, gave single-peak vapor-phase chromatograms. The positions of these peaks were not changed by "purification" through the sulfones.[8]

Physical properties of protio and deuterio compounds. Data are given in Tabels I and II for eleven isotopic pairs of compounds. The data for benzene and cyclohexane were taken from the literature. The other data, except for water, are for "best" samples (mostly heart cuts). The deuterio derivatives are more dense and less refractive than the corresponding protio compounds. All the data, especially the boiling points, are of interest in the study of molecular interaction in rubbers, liquids, and solids. Thus, for all six of the pairs of easily volatile organic compounds (Table I) the deuterio derivative has the lower boiling point. Even for water above 221°, the crossover temperature,[9] it is noted

(7) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).
(8) D. Craig, *J. Am. Chem. Soc.*, **65**, 1010 (1943).
(9) G. O. Oliver and J. W. Grisard, *J. Am. Chem. Soc.*, **78**, 561 (1956).

TABLE I
PERPROTIO AND PERDEUTERIO COMPOUNDS AND AZEOTROPIC MIXTURES

Compound or Azeotrope	Perprotio Derivatives of Compounds and Mixtures					Perdeuterio Derivatives of Compounds and Mixtures					
	B.P., °C., 740 mm.	M.P., °C.	Wt. % Water	n_D^{20}	d_4^{20}	B.P., °C., 740 mm.	M.P., °C.	Wt. % Water	n_D^{20}	d_4^{20} Found	d_4^{20} Calcd.
2-Methyl-3-butyn-2-ol	104	3.2	...	1.4215	0.8609	102	1.9	...	1.4188	0.9423	0.9435
	103–104[a]	2.6[a]	...	1.4211[a]	0.8623[a]						
2-Methyl-3-butyn-2-ol water azeotrope	80.0	−10.5	27	1.4050	...	89.5	...	27	1.4034	...	...
	90.7[a]		28.4[a]								
2-Methyl-3-buten-2-ol	96.5	−28.0	...	1.4172	0.8231	96.0	−28.8	...	1.4134	0.9185	0.9194
	96–97.5[a]	−30.5[a]		1.4163[a]	0.8249[a,b]						
2-Methyl-3-buten-2-ol water azeotrope	85.3	−9.0	23.2	1.4078	0.7895	86.0	...	20.0	1.4053	0.8719	0.8700
Acetone	55.3	...	...	1.3592	0.7787[d]	54.3	...	...	1.3565	0.8927[d]	0.8901
Cyclohexane	80.6[c], 80.738[e]	...	...	...	...	78.0,[c] 78.43[e]	...	...	...	...	...
Benzene[e]	80.099	5.5	...	1.4998	0.8760	79.31	6.8	...	1.4978	0.9456	0.9435
Isoprene	33.3	...	...	1.4219	0.6802	31.8	...	...	1.4189	0.7604	0.7605
Water	99.2	0.0	100	1.333	0.99823	100.6	3.8	100	1.3286	1.1075	1.1100

[a] Value from data sheet of Air Reduction Chemical Co., New York 17, N. Y. [b] d_{20}^{20}. [c] Value from A. Langseth and B. Bak. *J. Chem. Phys.*, **8**, 406 (1956). [d] Value from Ref. 10; b.p. at 760 mm. [e] Values from Ref. 15; b.p. is for 760 mm., density is d_{25}^{25}, and n is n_D^{22}.

TABLE II

PERPROTIO AND PERDEUTERIO DERIVATIVES

| Compound	Perprotio Derivative			Perdeuterio Derivative		
	M.P., °C.	n_D^{25}	d, g./ml. at 25°C.	M.P., °C.	n_D^{25}	d, g./ml. at 25°C.
SN rubber[a]	...	1.5190	0.901	...	1.5147	1.005
Isoprene sulfone	63.5	...	...	65.5	...	...
2,5-Dimethyl-3-hexyn-2,5-diol	96.5	...	...	95	...	...
Isoprene–maleic anhydride adduct	63.2	...	...	62.2[b]	...	...

[a] The SN rubbers will be described in a later paper. [b] Two of the ten hydrogen atoms in this derivative are protium.

that D_2O has the higher vapor pressure. Hydrogen-bridge bonding probably makes a greater contribution below 221° than above. Deuterium seems to contribute more to hydrogen-bridge bonding and less to van der Waals forces than protium. The weaker interaction revealed for deuterio molecules suggests that deuterio rubber segments should be faster acting (show greater escaping tendency) than corresponding protio segments. This is to say that D-SN rubber should be faster acting than H-SN rubber. The dynamics and other properties of the two rubbers are under study and will be reported separately.

It is noted that isoprene-d_8 of formula weight 76.17 boils 1.5° lower than isoprene-h_8 of formula weight 68.12. The ratio of the formula weights is 1.118 and this multiplied by the density of isoprene-h_8 gives 0.7605 g./ml. as the calculated density of isoprene-d_8. This value, within experimental error of the found value, is given in Table I along with similarly calculated densities for D_2O, acetone-d_6, benzene-d_6, cyclohexane-d_{12}, methyl butynol-d_8, and methyl butenol-d_{10}. The method is seen to give slightly low values for the densities of acetone, cyclohexane, and benzene, and slightly high values for water and the two alcohols. For D-SN rubber a value, 1.007, in good agreement with the actual value of 1.005, Table II, was also found using this method. The molecular volumes of five of the deuterio compounds thus are shown to be nearly equal, and in the case of isoprene exactly equal, to those of the corresponding protio compounds. Recently, Dixon and Schiessler[10] reported the molar volumes of perdeuterio benzene and cyclohexane to be nearly equal to those of the corresponding perprotio derivatives.

The melting points of the two deuterio alcohols (Table I and II), the yndiol-d_{14} and the deuterio isoprene-MA adduct, are lower than those of the protio derivatives. This also appears to indicate weaker intermolecular action for the D compounds. Understandably, for water in which hydrogen bonds are strong, D_2O melts 3.8° above H_2O. This rather consistent behavior is disturbed by the melting point of C_6D_6 being 1.3° higher than the melting point of C_6H_6 and by the melting points of

perdeuterio isoprene sulfone (65.6°) and perprotio isoprene sulfone (63.5°). The reason for the higher melting points for the D members of the two pairs of compounds is obscure. However, the hydrogen atoms in the 2- and 5-positions of the sulfone ring no doubt contribute significantly to the rather unique physical and chemical properties[11] of the diene sulfones. The rise in melting point here resulting from replacement of H with D suggests that the bonds connecting hydrogen atoms to the 2- and 5-positions are in reality hydrogen-bridge bonds between carbon and oxygen in different molecules. Jeffrey[12] recalculated the previously reported x-ray diffraction data[11] and found them to show all of the bonds in the five-membered ring to be of abnormal length. The O—S and C—CH₃ bonds, however, appeared to be of normal length. Koch[13] summarized the properties of the sulfone and concluded that extensive conjugation accounted for both the abnormal bond lengths and the α-methylenic nature of the molecule. We have found that isoprene-d_8 sulfone does not react with H_2O at 50 to 60° but that it rearranges at this temperature in the presence of 1% potassium carbonate to the α-sulfone, m.p. 79–80°, with simultaneous replacement of four of the D atoms with H, the replacement being established by the mass spectrum of the recovered α-sulfone.[14] Thus the "loosening" of the 2- and 5-position hydrogen atoms appears to be confirmed. The rearrangement probably occurs as follows:
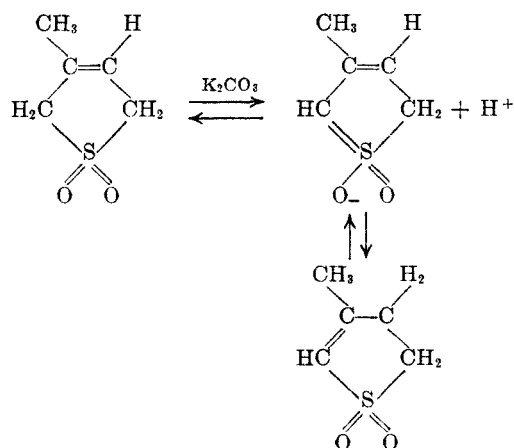
(10) J. A. Dixon and R. W. Schiessler, J. Am. Chem. Soc., 76, 2197 (1954); R. T. Davis, Jr., and R. W. Schiessler, J. Phys. Chem., 57, 966 (1953).

(11) E. G. Cox and G. A. Jeffrey, Trans. Faraday Soc., 38, 241 (1943); Rubber Chem. and Technol., 16, 486 (1943).

Finally, with respect to the effect on melting and boiling points of replacing H with D, it is noted that Ingold, Raisin, and Wilson[15] who found benzene-d_6 to melt higher (m.p. 6.8°) but to boil lower (b.p. 79.3°) than benzene-h_6 (m.p. 5.5° and b.p. 80.1°) also found H to D interchange in benzene to be catalyzed by acids.

EXPERIMENTAL

Source and purity of reagents. Deuterium oxide, 99.5% D_2O, and 99.5% deuterium gas were purchased from the Stuart Oxygen Co., San Francisco, Calif. Acetone was a commercial grade with properties given in Table I. Diethylene glycol dimethyl ether, or diglyme, was purchased from the Ansul Chemical Co. under the label Ansul Ether 141. Potassium metal, Code 2080, came from the General Chemical Co., and calcium carbide from Fisher Scientific Co. Alumina was catalyst grade, Harshaw Scientific Co., Al-0104T 1/8 inch.

Potassium deuteroxide, 87%. A 300 g. quantity of diglyme was added to a 2-liter, 3-necked Pyrex flask. One neck was fitted with a glass paddle stirrer driven by a compressed air motor. The other necks accommodated a thermometer, nitrogen inlet, dropping funnel, and water-cooled reflux condenser. A gas vent led from the top of the condenser through a Dry Ice trap to the hood. Evolved D_2 was not recovered. Diglyme is miscible with D_2O or H_2O, is readily salted out by potassium hydroxide or carbonate, but not by sodium chloride. A solution of 300 g. (15 moles) of D_2O in 150 g. of diglyme was dropped in and pieces of potassium (m.p. 62°) added from time to time so that the temperature remained at 60-70°. As the reaction proceeded it became necessary to heat the flask with a mantle. At first the potassium reacted vigorously to form a turbid mixture, but soon a white solid precipitate appeared and the liquid became blue. The blue color, not fully understood, disappeared when the rate of water-diglyme addition was increased in relation to the rate of potassium addition. A total of 248 g. (6.36 g.-atoms) of potassium was added during approximately 9 hr. after which a 120-g. quantity (6 moles) of D_2O was added during 2 hr. In this way a solid-free, two-liquid phase mixture at 60° was secured. It weighed 1100 g. and was transferred to a five-liter stainless steel flask, capped with a three-necked Pyrex head. The three necks accommodated a stainless steel thermometer well, stainless steel loop stirrer, nitrogen inlet, and connection to a condenser. The flask was heated with a glass mantle and the diglyme-water mixture distilled until the pot temperature reached 280-290°. The remaining product weighed 410 g. and by titration with standard acid was found to be 87.4% KOD. Assuming complete recovery from 6.36 g.-atoms of potassium, the 410 g. of product should contain 88.5% KOD.

Potassium deuterio acetylide, 2-methyl-3-butyn-2-ol-d_8, and 2,5-dihydroxy-2,5-dimethyl-3-hexyne-d_{14}. A 900-g. portion of diglyme was added to the 87.4% KOD which had crystallized on cooling. As soon as possible the temperature was raised to 150° after which it was allowed to fall while stirring vigorously. Crystallization occurred at 100-105° to form a slurry. The temperature was allowed to fall to 65-70° and finally brought to −5° by use of an ice salt bath. Acetylene-d_2, prepared by adding 176 g. of D_2O to a mixture of 675 g. diglyme and 433 g. (6.8 moles) of 20-30 mesh calcium carbide at 42-47° was then passed in for 4 hr. During this time the nitrogen stream was stopped. The rate of

acetylene was easily controlled by rate of D_2O addition. The potassium acetylide was a fluffy solid.

Acetone-d_6, 204 g. (3.19 moles), was next added during 2.7 hr. while continuing the stream of acetylene. The acetylene absorbed amounted to a minimum of 90 g. (3.2 moles) as determined by increase in weight. Actually the weights of acetone and diglyme swept from the mixture are unknown but they are believed to be small. The reaction mixture was stored at −14° for 14 hr. during which time it thickened. The mixture was returned to a salt ice bath and the nitrogen stream turned on. A 733 g. (36.7 moles) quantity of D_2O was dropped in during 2.7 hr. while maintaining the temperature at −4 to −6°. After stirring 1.3 hr., the oil layer was separated and treated with carbon dioxide to neutralize any KOD present. The lower KOD layer was extracted with three 150-ml. portions of ethyl ether to recover dissolved product. The extracts were also treated with carbon dioxide. The dilute KOD was concentrated and the D_2O and KOD used in subsequent runs.

The D_2O-diglyme-ynol-yndiol mixture was fractionated through a one-inch glass helices filled column 24 inches high. This column was fitted with a small-holdup, water-cooled, total-reflux, variable-takeoff stillhead. The butynol-d_8-D_2O azeotrope (see Table I) fraction came over at 86-99°, and anhydrous diglyme at about 161°. A residue of yndiol remained. The ynol-D_2O azeotrope was dehydrated by alternate distillation through a 0.25-inch coil column 24 inches high and salting out of the ynol with NaCl previously dried in an oven at 120°. Fractions of 181 g., collected at 101.8-102.2° at 730 mm., m.p. + 1.9°, and 34 g. at 101.2-102.4°, m.p. 1.7°, were secured, the latter from foreruns and the ether extract of the KOD layer. The total yield, 215 g., was 73%. The residue was distilled to give 43.5 g. (17.5%) of nearly pure yndiol, m.p. 89° or at 94.5-95.0° after recrystallization from benzene. The perprotio yndiol melted at 95.5-96.6° (Lit.[4] 94.5°) or at 95-96° mixed with the perdeuterio derivative.

Cleavage of 2,5-dimethyl-3-hexyn-2,5-diol-d_{14} and 2-methyl-3-butyn-3-ol-d_8. A 125-ml. flask fitted with a mantle heater and a short, punched-in side-arm was charged with 40.0 g. yndiol-d_{14} 6.0 g. acetone-d_6, and 0.003 g. potassium carbonate. It was connected to a Dry Ice-cooled receiver. The liquid mixture was heated to 150°-160° for 1 hr. during which time distillate (44.2 g.) came over at 55°-93° leaving a distilland (1.3 g.) of nearly pure yndiol. A total of 245 g. (1.57 moles, 3.14 acetone equivalents) of yndiol was decomposed in this way in six runs. The distillates were united and fractionated through the 0.25 × 24 inch coil column to give 121 g. (1.89 moles) of acetone-d_6 and 101.4 g. (1.10 moles, 70%) of pure 2-methyl-3-butyn-3-ol-d_8, m.p. 1.9°, $n_D^{20°}$ 1.4188. Material lost during the decompositions and fractionation amounted to 23 g. (9.5%) consisted mostly of acetylene and acetone.

A mixture of 2.5 g. acetone-h_6, 25.0 g. 2-methyl-3-butyn-2-ol-h_8, and 0.10 g. potassium carbonate was distilled during 7 hr. through the 0.25 × 24 inch coil column. A gas, presumably acetylene and acetone, was lost through the water-cooled (10°) reflux condenser, the loss amounting to 8.7 g. Nearly pure acetone (15.9 g.), $n_D^{20°}$ 1.3598 (lit. 1.3592) was collected at 55-57°, while the liquid temperature remained at 103°. The final distilland, mostly ynol, weighed 3.0 g.

2-Methyl-3-buten-2-ol-d_{10} (isoprene alcohol-d_{10}). The Lindlar catalyst was prepared exactly as described by him. All reductions with H_2 and later with D_2 were conducted with catalyst from a single preparation. In the first few experiments quinoline was added to the ethinyl carbinol in accordance with Lindlar's procedure. This was discontinued when it was found that the presence of quinoline did not cause the hydrogenation either to slow down or to stop at the desired stage and that the amount of overhydrogenation was about the same with or without quinoline present provided the reaction was stopped at the theoretical hydrogen uptake.

A Parr Instrument Company hydrogenation apparatus model CA, consisting of gas reservoir, pressure gage, shaker,

(12) G. A. Jeffrey, *Acta Cryst.*, **4**, 58 (1951).

(13) H. P. Koch, *J. Chem. Soc.*, **1949**, 412.

(14) A study of this rearrangement will be reported separately.

(15) C. K. Ingold, C. G. Raisin and C. L. Wilson, *J. Chem. Soc.*, 915 (1936).

TABLE III

PERDEUTERIOISOPRENE FRACTIONATION AND CHROMATOGRAPHIC ANALYSIS

Fraction	B.P., °C.	Pressure, Mm. Hg	Amount, G.	$n_D^{20°}$	Gas Chromatographic Analysis		
					Isoprene	2-Me-2-butene	2-Me-1-butene
1	31.5–31.8	731	23.2	1.4151	...	...	...
2[a]	31.8–31.9	731	51.0	1.4165	97.1	0.5	2.4
3	32.2–32.3	740	64.5	1.4184	98.9	0.6	0.5
4[a]	32.0–32.1	731	55.0	1.4186	98.5	1.3	0.2

[a] The mass spectra for fractions 2 and 4 revealed the presence of about 20 mole % C_5D_7H and 80 mole % C_5D_8, corresponding to one H per 39 D or to 97.5% deuteration.

and 0.5 l. stainless steel pressure flask was used for the hydrogenations. A second gas reservoir for the deuteriumations was constructed from a small breathing oxygen cylinder. The gas volumes of the systems were measured with a wet gas flow meter and were also determined by reduction of pure cinnamic acid. The hydrogen (and deuterium) consumption was calculated from the pressure drop and the gas volume. To avoid deuterium-hydrogen exchange in the deuteriumation runs the reactions were run solvent-free. The heat of reaction was controlled by blowing an air jet onto the reaction flask. The reductions were carried out with gas pressures between 40 and 2 p.s.i. For all runs this necessitated repressurizing with H_2 or D_2 while the run was in progress. Some runs were repressurized as many as twelve times. Thus a considerable error in gas measurement occurred. Most runs were, therefore, stopped short of the theoretical H_2 or D_2 uptake and were run to completion after determination of the α-acetylene content. A typical deuteriumation run will be described.

184.2 g. (2.0 moles) of 3-methyl-1-butyne-3-ol-d_8 and 2.0 g. Lindlar catalyst were charged to the reaction flask. The flask was closed with a calcium chloride tube and chilled in Dry Ice. It was then fastened to the shaker, rapidly evacuated to about 0.2 mm., and the vacuum broken with deuterium. The flask was allowed to warm to room temperature before pressurizing with deuterium to about 40 lb. After starting the shaker, the temperature rose rapidly but was kept below 50°C. by a strong air jet directed at the flask. The pressure was allowed to drop to 2 lb., the shaker stopped, and the system repressurized to 40 lb. This was repeated until the sum of pressure drops was 314.5 lb. (theory 316 lb.). The elapsed reaction time was 242 min. The rates of deuterium uptake for two similar pressures at the beginning and toward the end of the reaction were identical: After about 10% deuteriumation the rate was 0.85 lb. per minute for a pressure drop from 5.5 lb. to 2.0 lb. and after about 90% deuteriumation the rate was 0.83 lb. per minute for a pressure drop from 6.0 to 1.0 lb.

The flask was allowed to cool to room temperature and the reaction mixture filtered through a bed of activated charcoal on a sintered glass filter. Product recovered: 189.1 g. or 98.5% of theory. The reaction flask, the filter, and the receiver were rinsed with pentane and the rinses combined with those from other runs to be worked up separately. The filtrate contained 5.46% α-acetylene calculated as C_5D_8O. It was combined with a previous run of similar α-acetylene content for deuteriumation to completion. As a rule the isoprene alcohol was not purified prior to dehydration. A sample was distilled through the 0.25 × 24 in. coil column (see Table I).

Isoprene-d_8. A stainless steel tube 36 in. long with an ID of 5/8 in., fitted with a thermocouple well extending through the length of the tube, was filled with 133 g. alumina, 1/8 in. tablets. Two furnaces of 750 watts each were used to heat the tube over its entire length. Additional heaters were provided at the upper end and at the joining point of the two

furnaces, by wrapping with Nichrome resistance wire. The tube was inclined about 25° to the horizontal. The inlet end was fitted with a glass adapter accommodating a dropping funnel, gas inlet, and the thermocouple well. The lower exit end was connected to a glass elbow ending in a 24/40 ℥ joint. Sauereisen cement, glazed with water glass, was used to join the glass parts to the tube. The alumina was heated *in situ* to 300° for 12 hr. in a nitrogen stream saturated hot with steam from 10 ml. D_2O and then dried at 300° for 36 hr. in a nitrogen stream. The temperature was maintained at 300° ± 10°. With the exit end connected to a 0.5 l. two-necked flask carrying a Dry Ice–acetone cold finger type condenser which in turn was connected to a Dry Ice–acetone trap. The stream of dry nitrogen was adjusted to a rate of about five bubbles per second. When the catalyst packing had reached equilibrium the addition of 321.0 g. (3.34 moles) isoprene alcohol-d_{10} was started from a dropping funnel and adjusted to a rate of about 2.0 g. per min. The material collected in the receiver flask separated into a D_2O layer (54.5 g., 2.72 moles) and an organic layer of 245.3 g. (The material loss of 21.2 g. was due to a leak at a glass-to-steel connection which was corrected later.) The organic layer was dried with sodium sulfate and fractionated through a vacuum-jacketed column 5/16 × 36 in. filled with stainless steel No. 2917 HeliPak packing (Podbielniak, Inc., Chicago, Ill.). Methanol at −30 to −20° was circulated through the condenser. The reflux ratios varied from 80 to 100:1. A forerun was collected at 26–31.3° at 740 mm. The main fraction (164.7 g.) distilled at 31.3–32.0° at about 740 mm. The residue (50 g.) was recycled through the dehydration tube. The combined main fractions (226 g.) from two runs of this type were rectified through a 1 × 24 in., 20-plate, improved Oldershaw bubble plate column[16] at a reflux ratio of about 70:1. A series of four fractions totaling 194 g. was obtained and analyzed with results given in Table III. Polymerization-grade isoprene was secured by addition of sodium dispersed in petrolatum, refluxing for 30 min., and flash distilling.

Yields. A total of 1367 g. of dimethylethinylcarbinol-d_8 was catalytically deuteriumated in nine runs, yielding 1398 g. of crude isoprene alcohol-d_{10} or 98.0% of the theoretical yield.

From 1237 g. of isoprene alcohol-d_{10}, dehydrated in five runs (of which two runs were recycles), 924 g. of crude dehydration product was recovered. Purification of this gave 509 g. isoprene-d_8 of a chemical purity of at least 96% and 281 g. of product containing a minimum of 87% isoprene-d_8. Based on the minimum concentrations the yield of pure isoprene-d_8 was at least 75% of theory for the dehydration step and the over-all yield for deuteriumation and dehydration thus was at least 74%.

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