[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

# The Synthesis of Spiropentane-$d_8$[1]

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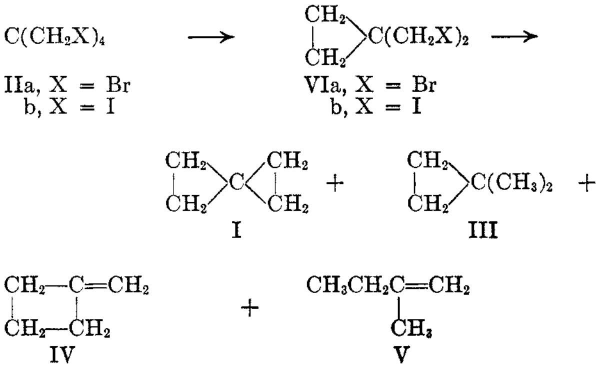
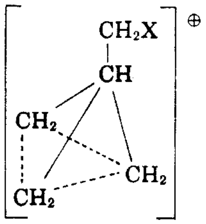
Spiropentane has been synthesized by the reaction sequence: ethylene dibromide → 1,1-dicarbethoxycyclopropane → 1,1-bis-(hydroxymethyl)cyclopropane → the dibenzenesulfonate of 1,1-bis-(hydroxymethyl)cyclopropane → 1,1-bis-(iodomethyl)cyclopropane → spiropentane. The same reaction sequence, when initiated with 1,2-dibromotetradeuteroethane, served to produce spiropentane-$d_8$.

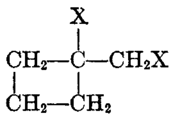
To complete a study[2] of the vibrational spectra of spiropentane (I) a sample of completely deuterated spiropentane was required. The present investigation was undertaken in order to develop a synthesis for spiropentane (I) which would be applicable to the preparation of the corresponding perdeuterated compound.

The only successful synthetic route to spiropentane (I) which has been reported, the reaction of a pentaerythrityl tetrahalide (II) with zinc,[3-6] was the first method to be considered. The mixture of hydrocarbons I, III, IV, and V isolated from this reaction[5] presumably arises from the common intermediate 1,1-bis-(halomethyl)cyclopropane (VI). The carbon-skeleton rearrangement which results in the formation of the hydrocarbons IV and V may be supposed to involve a cation such as VII, an analog of the cation previously proposed as an intermediate in the rearrangement of cyclopropylcarbinyl derivatives.[7]

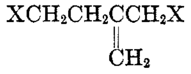




VII



VIIIa, X = Br
b, X = I



$XCH_2CH_2CCH_2X$

IXa, X = Br
b, X = I

The same ion VII has been proposed as in intermediate in the ready interconversion of the halides VIa, VIIIa and IXa.[8] The lack of isomerization which attends the cyclization of acyclic analogs of VI[9] is in agreement with the idea that some intermediate, such as the ion VII, which involves the participation of the cyclopropane ring, is responsible for the extensive isomerization which is observed. Further evidence for the formation of an intermediate cation such as VII is found in the fact that the methylenecyclobutane (IV) content of the hydrocarbon mixture is increased if the weak Lewis acid zinc bromide is added to the reaction mixture[10]; such an additive would be expected to favor the formation of an intermediate cation.

These considerations led us to study the conversion of the pentaerythrityl tetrahalides (II) to spiropentane under conditions which would favor either free radical or anionic rather than cationic intermediates in an effort to favor the formation of spiropentane (I).[11] Accordingly, pentaerthrityl tetrabromide (IIa) and pentaerythrityl

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[2] R. C. Lord and H. S. Rao, to be published.

[3] S. F. Marrian, *Chem. Revs.*, **43**, 195 (1948).

[4] M. J. Murray and E. H. Stevenson, *J. Am. Chem. Soc.*, **66**, 314, 812 (1944).

[5] V. A. Slabey, *J. Am. Chem. Soc.*, **68**, 1335 (1946).

[6] Y. M. Slobodin and I. N. Shokhor, *Zhur. Obshcheĭ Khim.*, **23**, 42 (1953); *Chem. Abstr.*, **48**, 543 (1954).

[7] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951).

[8] D. E. Applequist and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 874 (1956).

[9] (a) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **70**, 946 (1948); (b) Y. M. Slobodin, V. I. Grigor'eva, and Y. E. Shmulyakovskiĭ, *Zhur. Obshcheĭ Khim.*, **23**, 1480 (1953); *Chem. Abstr.*, **48**, 11358 (1954).

[10] J. D. Roberts and C. W. Sauer, *J. Am. Chem. Soc.*, **71**, 3925 (1949).

[11] A radical or anionic intermediate analogous to structure VII would be expected to be less stable than the cationic intermediate VII (see ref. 7).

tetraiodide (IIb) were treated with metallic sodium[12] in dioxane. The results of these reactions are summarized in Table I.

TABLE I

Treatment of Pentaerythrityl Halides with Sodium in Dioxane

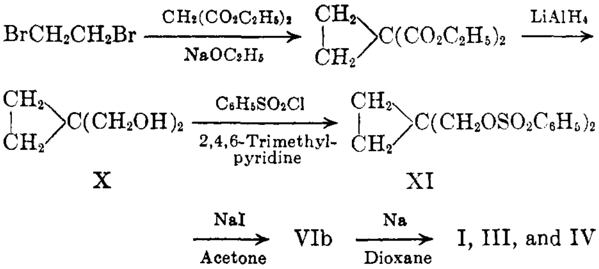
| Halide | Yield of hydrocarbon, % | Composition of hydrocarbon[a] I, % | IV, % | V, % |
|---|---|---|---|---|
| IIa | 51 | 49 | 30 | 21 |
| IIb | 61 | 44 | 43 | 13 |
| VIb | 54 | 50 (50.3)[b] | 35 (35.4)[b] | 15 (14.3)[b] |

[a] Except where noted the compositions of the hydrocarbon mixtures were determined with an accuracy of ±5% from the infrared spectra of the hydrocarbon mixtures.

[b] The figures in parentheses indicate composition of the hydrocarbon mixture as determined by mass spectroscopic analysis.

In each case the proportion of spiropentane (I) in the hydrocarbon mixture exceeded the proportion of I found in the hydrocarbon mixtures obtained from the reaction of the pentaerythrityl tetrahalides (II) with zinc in ethanol.[4,5] Although the yields of spiropentane (I) listed in Table I were not as good as those obtained by the reaction of pentaerythrityl tetraiodide (IIb) with zinc in acetamide,[6] the ring closures effected with sodium in dioxane were not complicated by the experimental difficulties which accompany the use of acetamide as a reaction solvent.[4]

Since all of our attempts to prepare completely deuterated pentaerythritol, a necessary intermediate for the synthesis of spiropentane-$d_8$ by the procedure discussed previously, were unsuccessful, we turned our attention to the synthetic scheme first proposed by Zelinsky and Krawetz.[13] These authors attempted to prepare spiropentane (I) by the stepwise ring closure of appropriate pentaerythritol derivatives, the intermediate prior to the final ring closure being the dihalide VIa. Reinvestigation of this synthesis has established that the hydrocarbon formed by this reaction sequence is essentially pure methylenecyclobutane (IV); no spiropentane (I) could be detected in the product.[14] The intermediate dihalide, formulated by Zelinsky and Krawetz as VIa, was found to be a mixture.[14] The vigorous reaction conditions employed for the synthesis of the dihalide would be expected to produce a mixture of the dihalides VIa, VIIIa, and IXa, the predominant component of the mixture being the cyclobutane derivative VIIIa.[8] It was apparent, therefore, that any synthetic scheme based on the cyclopropane VI must utilize reactions which would minimize the intervention of carbonium ion intermediates. For this purpose we selected the series of reactions shown in the accompanying equations. The physical constants for the diol X, prepared by this reaction sequence, differed from the values previously reported for this compound.[13,14] The previous preparation involved the cyclization of 2,2-*bis*-(bromomethyl)1,3-diacetoxypropane with zinc followed by saponification of the diacetate; no evidence was presented as to the homogeneity of the product. We were unable to find evidence that our diol X was not homogeneous; the diol X formed a single, crystalline bis-(phenylurethan) and a single, crystalline bis-(benzenesulfonate) (XI). The conversion of the diol X to the diester XI was expected to proceed without rearrangement since the carbon-oxygen bonds of the diol are not broken in this process. An analogous reaction is found in the conversion of cyclopropylcarbinol to cyclopropylcarbinyl *p*-toluenesulfonate without rearrangement under similar conditions.[15] Treatment of the diester XI with sodium iodide in acetone, conditions favorable to an $S_N2$ type reaction, resulted in the rapid conversion of the diester XI to a diiodide. Since the diester XI is sterically similar to neopentyl derivatives which undergo bimolecular nucleophic displacement reactions only very slowly, it might be supposed that the conversion of XI to VIb does not represent a simple $S_N2$ reaction. The product, the diiodide VIb, was isolated from the reaction mixture as a low-melting crystalline solid. Samples of the dihalide purified by recrystallization and by distillation under reduced pressure had identical infrared spectra and very similar physical constants. Evidence for the presence of a cyclopropane ring in the diol X and the diiodide VIb was gained from the infrared spectra of these products; the spectrum of each compound ex-



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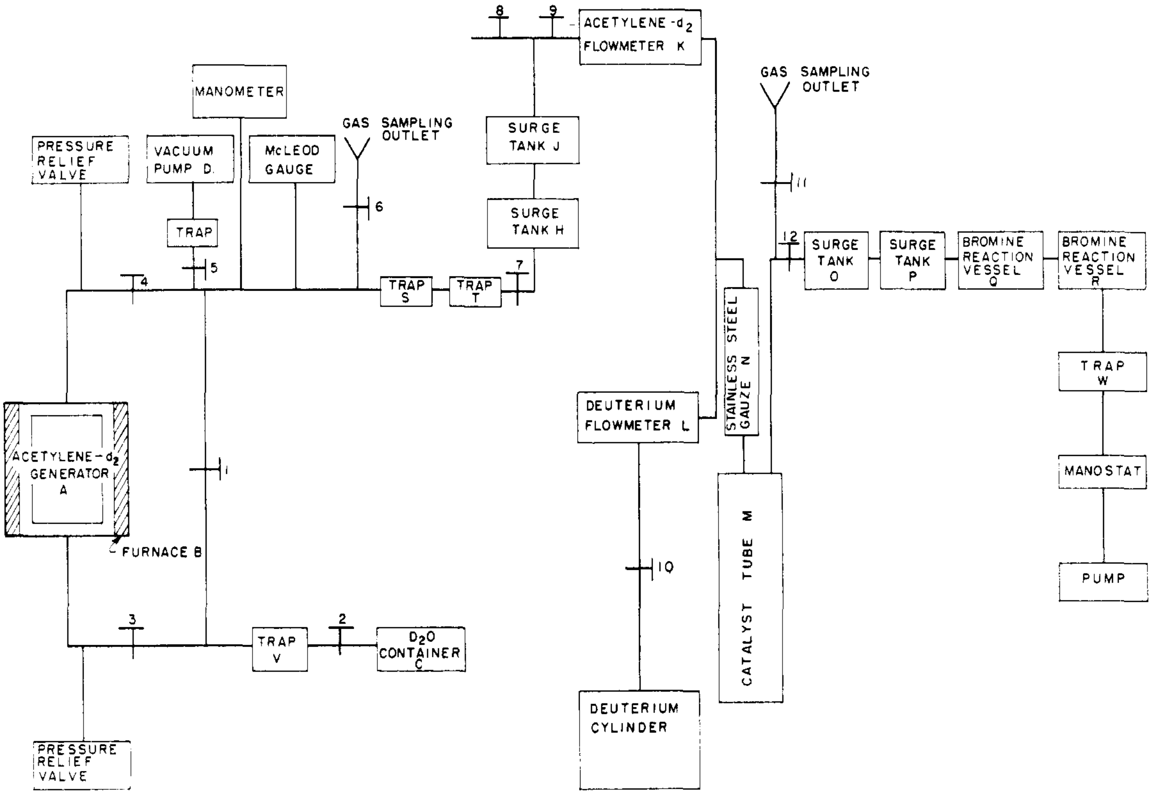
[12] The products obtained from the reaction of the neopentyl halides with sodium were formed without rearrangement of the carbon skeleton in contrast to the extensive rearrangement which was observed when neopentyl halides underwent reactions involving carbonium ion intermediates [F. C. Whitmore, A. H. Popkin, H. I. Bernstein, and J. P. Wilkins, *J. Am. Chem. Soc.*, **63**, 124 (1941)]. This observation was most easily explained by the assumption that the reaction of the halides with sodium did not proceed *via* carbonium-ion intermediates.

[13] N. Zelinsky and W. Krawetz, *Ber.*, **46**, 163 (1913).

[14] Y. M. Slobodin and I. N. Shokhor, *J. Gen. Chem. (U.S.S.R.)*, **21**, 2231 (1951).

[15] C. G. Bergstrom and S. Siegel, *J. Am. Chem. Soc.*, **74**, 145 (1952).

FIGURE I



hibits absorption in the range 2995–3007 cm.$^{-1}$ and 3068–3087 cm.$^{-1}$ believed to be diagnostic for the carbon-hydrogen stretching vibration of methylene groups in a cyclopropane ring.[16] These bands could not be detected in the spectrum of the diester XI since the region was obscured by absorption arising from the carbon-hydrogen stretching vibrations of the phenyl rings.

Although our evidence is compatible with structures VIb, X, and XI for the intermediates which we have prepared, we have not excluded the possibility that the diiodide VIb is in fact an equilibrium mixture of VIb and VIIIb at room temperature.[8] However, the absence in the infrared spectrum of our sample of the diiodide VIb of absorption in the region 890–910 cm.$^{-1}$, a region characteristic of a terminal methylene group, does permit us to exclude the possibility that appreciable quantities of the diiodide IXb are present.

Treatment of the diiodide VIb with sodium in dioxane produced a hydrocarbon mixture very similar in composition to the mixtures obtained from the pentaerythritol tetrahalides II under comparable conditions (Table I). This result is in agreement with the idea that the dihalide VI is an intermediate in the conversion of the tetrahalide II to the hydrocarbon mixture composed of I, IV, and V. We are unable to distinguish among the possible mechanisms for the conversion of the diiodide VIb to the rearranged hydrocarbons IV and V; a free-radical intermediate derived from the dihalide VIb may undergo rearrangement,[17] the diiodide may be partially isomerized to VIIIb and IXb before each dihalide reacts with sodium without rearrangement, or the reaction of VIb with sodium in dioxane may be ionic in nature.

In order to use this stepwise synthetic scheme for the preparation of spiropentane-$d_8$, a convenient synthesis of 1,2-dibromo-1,1,2,2-tetradeuteroethane (XII)[18] was required. Accordingly, dideuteroacetylene (XIII) prepared from calcium carbide and deuterium oxide, was reduced catalytically in the presence of deuterium over a palladium catalyst. The resulting tetradeuteroethylene (XIV) was converted to the dibromide XII by reaction with bromine. Subsequent reaction of the dibromide XII with malonic ester followed by reduction with

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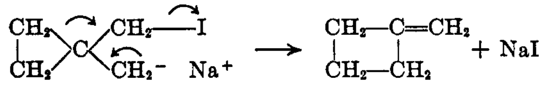
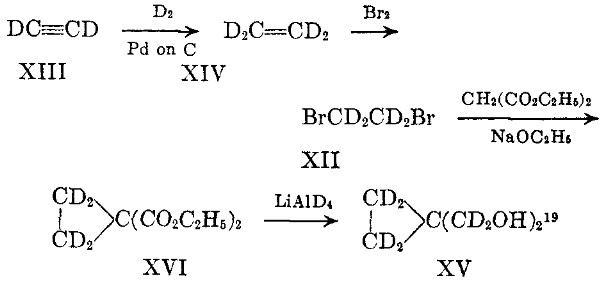
[16] (a) S. E. Wiberley and S. E. Bunce, *Anal. Chem.*, **24**, 623 (1952); (b) J. M. Derfer, E. E. Pickett, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 2482 (1949).

[17] This possibility seems improbable since the 2,2-dimethylbutyl free radical was found not to rearrange [F. H. Seubold, Jr., *J. Am. Chem. Soc.*, **76**, 3732 (1954)]. The referee has suggested that the concerted process shown in the accompanying equation may account for the formation of methylenecyclobutane.



[18] The preparation of this dibromide XII by the light-catalyzed addition of deuterium bromide to dideuteroacetylene has been described by L. C. Leitch and A. T. Morse [*Can. J. Chem.*, **30**, 924 (1952)].

lithium aluminum deuteride afforded the diol XV. The synthetic procedure employed in the nondeuterated series served to convert the diol XV to a mixture of hydrocarbons which was treated with bromine[4] to remove the olefinic components from the mixture. The volatile, unchanged spiropentane-$d_8$ was separated from the mixture by entrainment in a stream of nitrogen.*



## EXPERIMENTAL[20]

*The reaction of pentaerythrityl tetrabromide* (IIa) *with sodium.* To a boiling, vigorously stirred suspension of 113.4 g. (4.9 g.-atoms) of sodium in 500 ml. of dioxane was added, dropwise over a period of 140 minutes, a solution of 266 g. (0.687 mole) of pentaerythrityl tetrabromide[21] in 1.2 l. of dioxane. After the addition was complete the mixture was refluxed with stirring for an additional 16 hours during which time nitrogen was passed over the surface of the reaction mixture. The mixture of hydrocarbons and dioxane entrained by the nitrogen stream was collected in a receiver cooled in a Dry Ice-acetone bath. The volatile hydrocarbon components of this mixture, separated by entrainment in a stream of nitrogen and collected in a second cold trap, amounted to 23.7 g. (51%), $n_D^{20}$ 1.4039. The composition of this mixture (Table I) was estimated by means of its infrared spectrum.[22,23]

The spiropentane was separated from a 32.7-g. sample of this mixture by the procedure of Murray and Stevenson,[4] the hydrocarbon being first repeatedly extracted with aqueous silver nitrate and then treated with a sufficient quantity of bromine to remove the residual olefinic components. The pure spiropentane, $n_D^{20.5}$ 1.4112 (lit. $n_D^{20}$ 1.4117,[4] 1.4122[5]), isolated from the mixture amounted to 10.5 g. (31% based on the hydrocarbon mixture). The infrared spectrum[22,23] of the product is identical with the spectrum[24] of an authentic sample of spiropentane.

*The reaction of pentaerythrityl tetraiodide* (IIb) *with sodium.* Pentaerythrityl tetraiodide[25] (35.7 g., 0.062 mole) was added to a boiling, vigorously stirred suspension of 12 g. (0.52 g.-atom) of sodium in 200 ml. of dioxane and the resulting mixture was refluxed with stirring for 3 hours. The yield of mixed hydrocarbons, isolated and analyzed as previously described, was 2.56 g. (61%). The pure spiropentane isolated from a 1.2-g. sample of this mixture amounted to 0.4 g. (21% based on the tetraiodide).

*1,1-Bis-(hydroxymethyl)cyclopropane* (X). To a solution of 13.9 g. (0.366 mole) of lithium aluminum hydride in 1 l. of ether was added, dropwise and with stirring, over a period of 1 hour a solution of 54.2 g. (0.29 mole) of diethyl cyclopropane-1,1-dicarboxylate,[26] b.p. 143° (66.5 mm.), $n_D^{25}$ 1.4306–1.4309 [lit.[27] b.p. 114° (22 mm.), $n_D^{20}$ 1.4331], in 250 ml. of ether. After the resulting mixture had been boiled under reflux for an additional 12 hours, the reaction mixture was cooled, treated with 8.7 ml. of water, and filtered with suction. The residual lithium aluminate was extracted with three portions of boiling tetrahydrofuran, each extraction being run for 12 hours.[28] The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. Distillation of the residual oil afforded 22.2 g. (75%) of the diol, a colorless liquid, b.p. 125–128° (10 mm.), $n_D^{25}$ 1.4713. A sample of the diol was redistilled for analysis, $n_D^{26}$ 1.4716. The properties previously reported for the diol[14] were b.p. 123–127° (12 mm.), $n_D^{20}$ 1.46455.

*Anal.* Calc'd for $C_5H_{10}O_2$: C, 58.82; H, 9.88. Found: C, 58.84; H, 9.88.

The infrared spectrum[22,29] of the diol has a broad band at 3300 cm.$^{-1}$, attributable to a hydroxyl function as well as bands at 3087 and 3007 cm.$^{-1}$ believed to be characteristic of a cyclopropane ring.[16] The diol yielded a bis-phenylurethan derivative which separated from a methylene chloride–carbon tetrachloride mixture as colorless crystals, m.p. 159.3–159.5°, yield 54%.

*Anal.* Calc'd for $C_{19}H_{20}N_2O_4$: C, 67.04; H, 5.92; N, 8.23. Found: C, 66.82; H, 6.05; N, 8.15.

*1,1 - Bis - (hydroxymethyl)cyclopropane dibenzenesulfonate* (XI). To a mixture of 15.98 g. (0.157 mole) of 1,1-bis-(hydroxymethyl)cyclopropane and 69.5 g. (0.575 mole) of 2,4,6-trimethylpyridine, cooled to −5°, was added, drop-

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* *Note Added in Proof.* A sample of the spiropentane-$d_8$ was examined with a vapor-phase chromatographic column composed of a 6 ft. × 6 mm. column of Dow No. 550 Silicone Oil suspended on 50–80 mesh firebrick. The sample, eluted with helium at 30°, was detected with a thermal conductivity cell. The chromatogram exhibited only one major peak whose area corresponded to 99.1% of the total material eluted. Under the same conditions the chromatogram of the hydrocarbon mixture obtained from 1,1-bis-(iodomethyl)cyclopropane exhibited three major peaks corresponding to spiropentane, methylenecyclobutane, and 2-methyl-1-butene. The mass spectrum of the spiropentane-$d_8$ sample, determined by the Mass Spectrometry Section, National Bureau of Standards, through the courtesy of Dr. F. L. Mohler, showed 94.6 mole-percent $C_5D_8$ and 5.4 mole-percent $C_5D_7H$, corresponding to 99.3 atom-percent deteurium in the sample. No mass peaks above 76 were reported, but the relative abundance of $C_5D_8^{\oplus}$ and $C_5D_7^{\oplus}$ were different from those expected on the mass pattern of ordinary spiropentane. This might indicate the presence of an isometric impurity, but the results of the spectroscopic (ref. 2) and vapor-phase chromatographic studies show that no unsaturated isomers are present. Bicyclo[1.1.1.]pentane cannot be excluded rigorously, but seems an unlikely contaminant.

(19) The hydroxylic hydrogen atoms of the diol XV were partially protium and partially deuterium. Since both of these atoms are lost in subsequent transformations, no attempt was made to prepare the pure dideuteroxy compound.

(20) All melting points are corrected and all boiling points are uncorrected. The microanalyses were performed by Dr. S. M. Nagy and his associates.

(21) H. L. Herzog, *Org. Syntheses*, **31**, 82 (1951).

(22) Determined as a pure liquid.

(23) Determined with a Baird double beam infrared recording spectrophotometer, model AB-2, fitted with a sodium chloride prism.

(24) We are indebted to Dr. A. V. Slabey who kindly furnished us with the spectrum of spiropentane.

(25) H. B. Schurink, *Org. Syntheses*, Coll. Vol. 2, 476 (1943).

(26) Prepared according to the directions of A. W. Dox and L. Yoder [*J. Am. Chem. Soc.*, **43**, 2097 (1921)]. The product was purified by distillation through a heli-grid packed 60 cm. Podbielniak column.

(27) G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1804 (1948).

(28) This extraction process was found to be essential since most of the product was absorbed on the lithium aluminate residue.

(29) Determined with a Perkin-Elmer single beam infrared recording spectrometer, modified model 12B, equipped with a lithium fluoride prism.

wise and with stirring, 85 g. (0.48 mole) of benzenesulfonyl chloride. Throughout the addition the temperature of the reaction mixture was maintained at −5 to 0°. After the addition was complete, the mixture was stirred for 2 hours, diluted with 48 ml. of methylene chloride, and stirred for an additional 1 hour. The excess benzenesulfonyl chloride was destroyed by the dropwise addition of 30 ml. of water and then the trimethylpyridine was neutralized by the dropwise addition of 80 ml. of 10% aqueous sulfuric acid. Throughout these processes the temperature of the reaction mixture was kept at 0°. The organic phase of the resulting mixture was separated and the aqueous phase was extracted with three 50-ml. portions of methylene chloride. The combined extracts were washed with cold, dilute, aqueous sulfuric acid, dried over potassium carbonate, and concentrated under reduced pressure. The dibenzenesulfonate separated from a methylene chloride-ether mixture as colorless crystals, m.p. 50–51°, yield 41 g. (68.2%). An additional crystallization raised the melting point of the product to 52.5–53°.

*Anal.* Calc'd for $C_{17}H_{18}S_2O_6$: C, 53.38; H, 4.72; S, 16.77. Found: C, 53.42; H, 4.68; S, 16.53.

*1,1-Bis-(iodomethyl)cyclopropane* (VIb). To a solution of 40.6 g. (0.106 mole) of 1,1-bis-(hydroxymethyl)cyclopropane dibenzenesulfonate in 250 ml. of acetone was added, dropwise and with stirring, a solution of 50 g. (0.33 mole) of sodium iodide in 200 ml. of acetone. After the mixture had been stirred overnight, it was filtered and the filtrate was poured into 1.5 l. of water which contained a small amount of sodium thiosulfate. After the organic layer had been separated, the aqueous phase was repeatedly extracted with ether. The combined organic layers were washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. When solution of the residue in petroleum ether was chilled to −30°, the diiodide separated as colorless crystals, m.p. 16–16.4°, $n_D^{25}$ 1.6300, yield 27.2 g. (79.5%).

Although the diiodide was not stable, tending to decompose spontaneously with the evolution of iodine, a sample was successfully distilled through a Holtzmann column in one instance. The product, collected over the range b.p. 76–94° (1.2 mm.), $n_D^{25}$ 1.6304–1.6310, had an infrared spectrum[22,23,29] which was identical with the spectrum of the product purified by recrystallization. The spectra exhibit bands at 3068, 2995, 1015, and 875 cm.$^{-1}$ which are characteristic of a cyclopropane ring.[16]

*Anal.* Calc'd for $C_5H_8I_2$: C, 18.65; H, 2.51; I, 78.86. Found: C, 18.71; H, 2.65; I, 78.92.

*Reaction of 1,1-bis(iodomethyl)cyclopropane* (VIb) *with sodium.* A solution of 26.8 g. (0.083 mole) of 1,1-bis-(iodomethyl)cyclopropane in 150 ml. of dioxane was added, dropwise and with vigorous stirring, over a period of 1.25 hours to a boiling suspension of 9 g. (0.39 g.-atom) of sodium in 400 ml. of dioxane. After the addition was complete, the mixture was refluxed with stirring for an additional 12 hours. The hydrocarbon mixture produced, collected and purified as in the previous cases, amounted to 3.07 g. (54%), $n_D^{20}$ 1.4090. The mixture was analyzed (Table I) both by infrared spectroscopy[22,23] and by mass spectroscopy. A 0.53-g. sample of the hydrocarbon mixture was treated with bromine. The pure spiropentane separated by this procedure amounted to 0.2 g. (20%, based on the diiodide) $n_D^{20}$ 1.4115 (lit. $n_D^{20}$ 1.4117,[4] 1.4122[5]). The infrared spectrum[22,23] of the product is identical with the spectrum[24] of an authentic sample of spiropentane.

*1,2-Dibromo-1,1,2,2-tetradeuteroethane* (XII). A schematic diagram of the apparatus employed is given in Figure 1. The dideuteroacetylene, prepared as previously described,[30] was mixed with deuterium and reduced in the gas phase over a 0.75% palladium-on-carbon catalyst (M in Fig. 1) at a pressure 10–20 cm. less than atmospheric pressure. Since the reduction was exothermic, external heating of the catalyst was not necessary. The isotopic purity of the acetylene and both the isotopic purity and composition of the gaseous mixture from the reduction were followed by the periodic examination of the infrared spectra of gas samples removed from the system. Prior to reaction the entire apparatus was heated under reduced pressure (0.01 mm. or less) and repeatedly flushed with both deuterium and dideuteroacetylene. The mixture of gases, dideuteroacetylene, tetradeuteroethylene, hexadeuteroethane and deuterium, obtained from the reduction was passed through two traps (Q and R, Fig. 1) containing approximately 5% (by volume) solutions of bromine in carbon tetrachloride.

Deuterium oxide[31] (300 g.) was converted in part to 1,2-dibromo-1,1,2,2-tetradeuteroethane as outlined. The combined carbon tetrachloride solutions were washed with aqueous sodium bisulfite, dried over magnesium sulfate, and distilled through a 60-cm. Fenske column. The crude product, amounting to 204 g. collected over the range 120–137°, $n_D^{25.3}$ 1.5286–1.5294, was redistilled through a 150-cm. Podbielniak column packed with Castaloy-B heligrids. The dibromide obtained amounted to 142 g. (9.9% based on the deuterium oxide), b.p. 129.5–130.3°, $n_D^{26}$ 1.5312–1.5324 [lit.[18] b.p. 129.5°, $n_D^{20}$ 1.5360]. The infrared spectrum[22,23] of the dibromide indicated that the isotopic purity of the sample was 99 atom-percent.

*1,1-Dicarbethoxy-2,2,3,3-tetradeuterocyclopropane* (XVI). 1,2-Dibromo-1,1,2,2-tetradeuteroethane (140 g., 0.73 mole) was converted to the diester as previously described.[26] The yield of the diester, b.p. 133–133.6° (47.5–49 mm.), $n_D^{25.5}$ 1.4308–1.4310, was 54.8 g. (39.6%). The infrared spectrum[22,23] of the ester exhibits bands at 2370 and 2225 cm.$^{-1}$ (C—D) and at 1718 cm.$^{-1}$ (ester C═O).

*1,1-Bis-(hydroxydideuteromethyl)-2,2,3,3-tetradeuterocyclopropane* (XV). A 54.8-g. (0.288 mole) sample of the deuterated diester XVI was reduced with 16 g. (0.38 mole) of lithium aluminum deuteride[32] as described previously except that the excess lithium aluminum deuteride was decomposed by the addition of deuterium oxide rather than water. The yield of the deuterated diol XV, b.p. 103° (2.5–3 mm.), $n_D^{25.1}$ 1.4678, was 23.3 g. (74%). The infrared spectrum[22,23] of the product has bands at 3340 cm.$^{-1}$ (O—H) and 2480 cm.$^{-1}$ (O—D) as well as bands attributable to carbon-deuterium stretching vibrations at 2370, 2210, and 2080 cm.$^{-1}$.

*1,1-Bis(hydroxydideuteromethyl)-2,2,3,3-tetradeuterocyclopropane dibenzenesulfonate.* The reaction of 23 g. (0.21 mole) of the deuterated diol XV with 114 g. (0.64 mole) of benzenesulfonyl chloride and 93 g. (0.77 mole) of 2,4,6-trimethylpyridine in the manner described earlier produced 65.2 g. (80%) of the dibenzenesulfonate, m.p. 54–55°.

*1,1-Bis-(iododideuteromethyl)-2,2,3,3-tetradeuterocyclopropane.* Application of the procedure described previously converted the deuterated dibenzenesulfonate (65 g., 0.165 mole) to the diiodide, m.p. 15–15.6°, $n_D^{25}$ 1.6285, yield 44.4 g. (81.5%). The infrared spectrum[22,23] of the diiodide exhibits bands at 2320, 2270, and 2000 cm.$^{-1}$ with a shoulder at 2140 cm.$^{-1}$ all attributable to carbon-deuterium stretching vibrations.

*Spiropentane-$d_8$.* A suspension of 15 g. (0.65 g.-atom) of sodium in 400 ml. of dioxane was treated with a solution of 44 g. (0.134 mole) of 1,1-bis-(iododideuteromethyl)-2,2,3,3-tetradeuterocyclopropane in 260 ml. of dioxane as previously described. After a total reaction time of 9.6 hours the mixture of hydrocarbons (7 g., 69%) was isolated as in the previous cases and treated with bromine. The pure spiropentane-$d_8$ isolated amounted to 2.13 g. (21%), $n_D^{14}$ 1.4145. The Raman spectrum[2] of the sample indicates that the isotopic purity of the product is better than 98 atom-percent.

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(30) D. G. Rea, Ph.D. Thesis, Massachusetts Institute of Technology, 1954.

(31) Purchased from the Stuart Oxygen Company, purity 99.5 mole-percent.

(32) Purchased from Metal Hydrides, Inc., Beverly, Mass.