

isomer (Compound 4A) of 2-ethyl-4-methyl-2-phenyl-1,3-dithiolane in about 50 ml. of glacial acetic acid and 10 ml. of acetic anhydride was added 53 ml. of 30% hydrogen peroxide. After the heat of the initial reaction had been dissipated, the reaction mixture was heated on a steam cone for 12 hr. The solvents were removed by distillation leaving a crude crystalline product which melted at 127–129°. Three recrystallizations from 95% ethanol brought the melting point to 134.0–135.5°. Two more recrystallizations, from ethanol and then from benzene-petroleum ether, did not raise the melting point. The yield of recrystallized product was 4.5 g. (50%).

Oxidation of 8.1 g. of the higher-boiling isomer (Compound 4B) was carried out similarly. The crude product melted at 112–115°, but one recrystallization from 95% ethanol gave crystals, m.p. 129–130.5°, which differed in appearance from those from the lower-boiling isomer. A further recrystallization from benzene-petroleum ether did not raise the melting point; 4.0 g. (42%) of recrystallized product was obtained. The melting point of a mixture of the two disulfones was 110–127°. Analyses are given in Table III.

(c) *Oxidation of the unseparated isomers of a 2-monosubstituted-1,3-dithiolane with subsequent isolation of a single disulfone.* 2-Hexyl-4-methyl-1,3-dithiolane (Compound 12), 21.8 g., was dissolved in 60 ml. of glacial acetic acid and 182 g. of 30% hydrogen peroxide was added with swirling, while the flask was cooled in an ice bath. After several hours at room temperature, the reaction mixture was heated on a steam bath for 40 hr. The disulfone separated as a layer at the bottom and, after it had been separated from the upper layer, it began to crystallize. Recrystallized from aqueous alcohol, it melted at 61–62° and amounted to 19 g. (66%). Analysis is given in Table IV.

(d) *Oxidation of the separated isomers of a 2-monosubstituted-1,3-dithiolane with subsequent isolation of a single disulfone.* To a mixture of 3 g. of the high-melting isomer (Compound 14A) of 4-(3',5'-dinitrobenzoxymethyl)-2-phenyl-1,3-dithiolane, 50 ml. of glacial acetic acid, and 10 ml. of acetic

anhydride was added slowly 50 g. of 30% hydrogen peroxide. After the initial reaction had ceased, the mixture was heated on the steam bath for 12 hr. The solvents were distilled and the residue was recrystallized from ethanol to give 2.5 g. (72%) of white crystals, m.p. 178–180°.

Three grams of the lower-melting isomer (Compound 14B) was oxidized in the same manner; 2.1 g. (61%) of the same disulfone, m.p. 178–180°, was obtained. The melting point of a mixture of these two products was not depressed. Analyses are given in Table IV.

Hydrolysis of 4-(3',5'-dinitrobenzoxymethyl)-2-phenyl-1,3-dithiolanes. Five grams of the higher-melting isomer (Compound 14A) was suspended in 200 ml. of water containing 5 g. of potassium hydroxide. The mixture was refluxed for three hours and then cooled. Crystals separated and were collected and washed with water. Recrystallization from aqueous ethanol gave 1.8 g. (70%) of white crystals, m.p. 88.5–89° (Compound 13A).

Similar treatment of 3 g. of the lower-melting isomer (Compound 14B) gave 0.85 g. (54%) of white crystals, m.p. 87.5–88° (Compound 13B). A mixture of these two products melted at 69–75°.

Oxidation of a mixture of Compounds 13A and 13B with hydrogen peroxide in acetic acid-acetic anhydride gave the disulfone, m.p. 159–161°, after recrystallization. Two grams of this disulfone was treated with 2 g. of 3,5-dinitrobenzoyl chloride in 30 ml. of dry benzene and 30 g. of dry pyridine. The mixture was stirred for 0.5 hr. and then allowed to stand at room temperature for two days. The reaction mixture was decomposed by addition of 150 ml. of water containing two grams of sodium bicarbonate. The mixture was evaporated slowly to dryness and the residue was extracted with a mixture of benzene and heptane. The crystals obtained by cooling this solution weighed 2.3 g., and melted at 178–180°. This product did not depress the melting point of the product obtained by oxidizing Compounds 14A and 14B.

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[CONTRIBUTION FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL]

Organic Deuterium Compounds. XX. Synthesis of the Deuterated Propadienes¹

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Propadiene-*d*₁, -1,1-*d*₂, -1,3-*d*₂, -*d*₃, -*d*₄ and butadiene-*d*₆ were synthesized by dehalogenation of the appropriate halides. A few new halides and their deuterated analogs are reported. A tentative mechanism for their dehalogenation is proposed.

Several recent spectroscopic investigations have dealt with the geometry of the allene molecule.² Since the deuterated forms of allene were expected to provide information not obtainable by other means, syntheses were developed in this laboratory which eventually led to the preparation of all four possible deuterated allenes in moderate yields. This paper reports a number of routes to these compounds which have been rather fully explored.

Only two deuterated allenes have been reported

up to now. The tetradeutero compound was isolated in small quantities from a mixture of allene-*d*₄ and propyne-*d*₄ prepared by the action of deuterium oxide on magnesium sesquicarbide, Mg₂C₃,³ by removing the alkyne as the silver derivative.⁴ An indication of the tedious nature of this process can be gained by observing that from sixty-five ml. of liquid hydrocarbons only four ml. of pure allene-*d*₄ was isolated. This method of preparing allene-*d*₄ was quite unsatisfactory for our requirements.

(1) Presented at the 132nd meeting of the American Chemical Society, New York, N. Y., September 1957. Issued as NRC No. 4808.

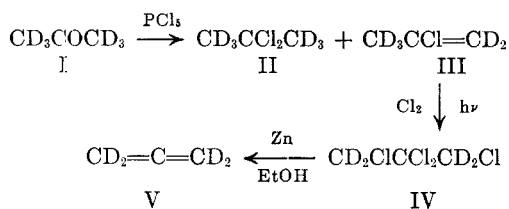
(2) B. P. Stoicheff, *Can. J. Phys.*, **33**, 811 (1955).

(3) L. C. Leitch and R. Renaud, *Can. J. Chem.*, **30**, 79 (1952).

(4) R. C. Lord and P. Venkateswarlu, *J. Chem. Phys.*, **20**, 1237 (1952).

Allene-1,1- d_2 was prepared in six steps very recently⁵ from propyne- d_4 .

Our first experiments were directed to the synthesis of allene- d_4 by the following route:

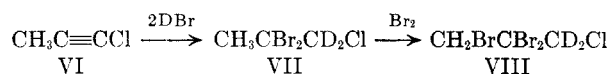


Deuteroacetone, prepared from acetylene- d_2 and heavy water vapor, was further enriched in deuterium by repeated exchange with alkaline deuterium oxide. Reaction of acetone- d_6 (I) with phosphorus pentachloride gave a 30% yield of 2-chloropropene- d_5 (III) along with 42.7% of 2,2-dichloropropane- d_6 (II). It is interesting to note that in pilot runs with ordinary acetone the yields of 2-chloropropene and 2,2-dichloropropane were 47% and 25% respectively. The lower yield of 2-chloropropene- d_5 is believed to be due to an isotopic effect, the rate of proton transfer being appreciably more rapid than the rate of deuterium transfer and thereby favoring the formation of the dichloroalkane. A similar isotopic effect has been noted in the conversion of nitroethane-1,1- d_2 to acetaldehyde- d_1 .⁶

Simultaneous additive and substitutive chlorination of III gave a mixture of 1,2,2,3-tetrachloropropane- d_4 (IV) and 1,1,2,2-tetrachloropropane- d_5 . On dechlorination, the former led to allene- d_4 (V).

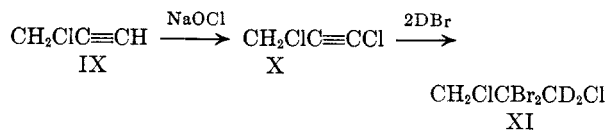
Other deuterated allenes cannot be synthesized by the route outlined above because a partly deuterated acetone such as CH_3COCD_3 rapidly equilibrates to $\text{CH}_2\text{DCOCHD}_2$ and consequently mixtures of deuterated chloropropenes would be obtained with phosphorus pentachloride. Besides, the deuterated acetone thus labelled would be rather difficult to prepare.

Several routes to the synthesis of tetrahalopropanes that would have led to other deuterated allenes on dehalogenation were explored without success. For instance, we hoped to prepare 1,2,2-tribromo-3-chloropropane-3,3- d_2 (VIII) from 1-chloro-propyne (VI)⁷ by the route shown below:

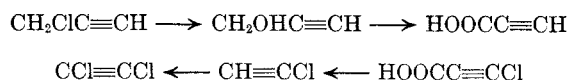


However (VII) could not be brominated further under ultraviolet illumination or in the presence of ferric chloride.

Another possible route to allene-1,1- d_2 was the series of reactions:



A word of caution seems in order here regarding the preparation of 1,3-dichloropropyne (X). The first time this preparation was carried out a violent explosion took place in the stillhead shortly after distillation of the product had begun. Just prior to the detonation, liquid was refluxing in the stillhead at 34° C. This observation provided a clue as to the probable cause of the explosion. Small amounts of mono- or dichloroacetylene, which form dangerously explosive mixtures with air, may have been formed during the chlorination by a series of side reactions:



Be that as it may, in later experiments explosions were avoided by adding a little ether to the propargyl chloride. Any dichloroacetylene formed then distilled over with ether as a stable constant boiling complex.⁸

Addition of deuterium bromide to (X) evidently did not proceed as expected since the product on dehalogenation gave not allene- d_2 but allene- d_1 . While this synthesis unwittingly afforded a route to the monodeuterated allene it left us without a route to the dideutero compound.

At this point further attempts to synthesize allene-1,1- d_2 and the other deuterated allenes by halogen elimination were abandoned in favor of halogen displacement using a variety of simpler and more readily available halides. This decision proved to be a fruitful one since all the deuterated allenes were subsequently prepared by this method.

From propargyl bromide, Jacobs, Teach, and Weiss⁹ had obtained allene and propyne in a 2:1 ratio. In the present work allene- d_1 and propyne-3- d were obtained on dechlorinating propargyl chloride with zinc dust in deuterium oxide. 1,3-Dichloropropyne was dechlorinated to allene-1,1- d_2 and propyne-1,3- d_2 . Similarly, 1,2,3,3-tetrachloropropene-1 gave allene-1,3- d_2 and propyne-1,3- d_2 . Allene- d_3 and propyne-3- d_3 were obtained from 1,1,1,2,2,3,3-heptachloropropane. Finally, hexachloropropene reacted in the same way to give allene- d_4 and propyne- d_4 .

Since hexachlorobutadiene-1,3 is readily available and easily dechlorinated to butadiene-1,3¹⁰ it seemed of interest to prepare butadiene- d_6 in the same manner. The latter was obtained in 80% yield,

(5) W. E. Shuler and W. H. Fletcher, *J. Mol. Spect.*, **1**, 95 (1957).

(6) L. C. Leitch, *Can. J. Chem.*, **33**, 400, 1953.

(7) A. T. Morse and L. C. Leitch, *Can. J. Chem.*, **32**, 500 (1954).

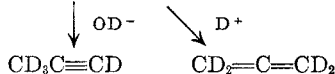
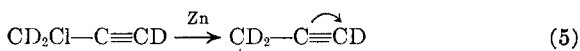
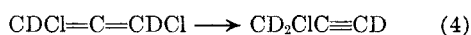
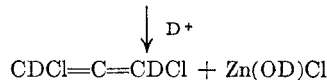
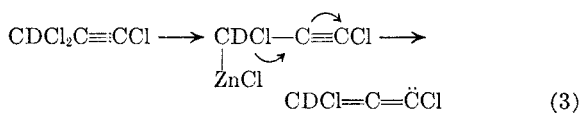
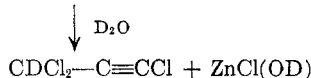
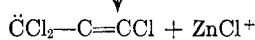
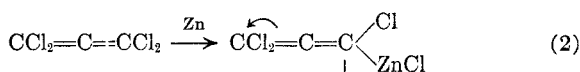
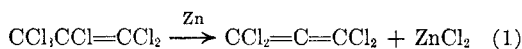
(8) E. Ott, W. Ottenmeyer, and K. Packendorf, *Ber.*, **63**, 1941 (1930).

(9) T. L. Jacobs, E. G. Teach, and D. Weiss, *J. Am. Chem. Soc.*, **77**, 6254 (1955).

(10) O. Frühwirth, *Ber.*, **74**, 1700 (1941).

thus providing in one step a highly reactive intermediate for further synthetic work.

The formation of propadiene- d_4 and propyne- d_4 can be accounted for by the mechanism outlined below:



The same mechanism would apply to the dehalogenation of propargyl chloride, 1,3-dichloropropyne, etc., but cannot, however, be invoked to explain the dechlorination of hexachlorobutadiene.

EXPERIMENTAL

Acetone- d_6 . Acetylene- d_2 was prepared as described previously.¹¹ A mixture of deuterium oxide vapor and acetylene- d_2 in the ratio 5 to 1 was preheated to 410° and passed over a composite ZnO-FeO¹² oxide catalyst also at 410° in a bath of molten nitrates. The reaction product was condensed in a series of traps cooled with running water, acetone, and carbon dioxide at -30° and Dry Ice and acetone at -78°. The deuterium formed was oxidized over cupric oxide heated to 500° and thereby recovered as deuterium oxide. The crude product was purified by fractional distillation. The yield of deuterioacetone, b.p. 55°, was 348 grams (65%). Mass analysis indicated it was 87.4 mole % acetone- d_6 , 9.4 mole % acetone- d_8 , and contained in addition small amounts of less deuterated acetone.

The deuterium content was increased to 94 mole % - d_8 by repeated exchange with deuterium oxide containing a little dissolved sodium or potassium carbonate. There was little loss of acetone during the exchanges.

2,2-Dichloropropane- d_6 and 2-chloropropene- d_5 . Deuterioacetone (31.0 ml.; 28.4 g.; 0.475 mole) was added dropwise to 105 g. (0.475 mole) of phosphorus pentachloride in a flask fitted with a cold finger condenser packed with Dry Ice. When reaction was complete the reaction products were distilled into a Stock trap cooled to -78° on a vacuum

line.¹³ On distillation through a Vigreux column, 11.7 (30.2%) of 2-chloropropene- d_5 , b.p. 22-23° and 24.0 g. (42.7%) of 2,2-dichloropropane- d_6 , b.p. 68-70°, were obtained. The latter contained dissolved deuterium chloride and phosphorus oxychloride which were removed by washing with two 100-ml. portions of ice cold water followed by distillation through soda-lime and then P₂O₅ on the vacuum line. The purified dichloropropane was now refracted through a Vigreux column. A middle fraction b.p. 68.5-69.0°, n_D^{20} 1.4128, amounted to 10.8 g. For ordinary 2,2-dichloropropane, n_D^{20} is 1.4151.

Chlorination of 2-chloropropene- d_5 . Chlorine was passed into a solution of 11.7 g. (0.15 mole) of 2-chloropropene- d_5 in 15 ml. of carbon tetrachloride in a flask fitted with a cold finger condenser filled with Dry Ice. The trichloropropane- d_5 was not isolated but 15 ml. of antimony pentachloride were then added to the reaction mixture and chlorination continued at 50-70° until DCl was no longer evolved. The reaction mixture was worked up in the usual manner. The product, which was a mixture of tetrachloro- and possibly penta-chloropropanes, was fractionated in a Vigreux column under reduced pressure. The fraction b.p. 77-81°/55 mm., n_D^{20} 1.4861, was probably a mixture of 1,2,2,3- and 1,1,2,2-tetrachloropropane. The yield was 9.3 ml., 14.0 g. The pentachloropentane fraction b.p. 83-97°/55 mm., n_D^{20} 1.4920 amounted to 2.2 ml.

Propadiene- d_4 . The mixed tetrachloropropanes (13.5 g.; 0.075 mole) were added dropwise from a separatory funnel to a stirred suspension of 15 g. of zinc dust in 50 ml. of ethanol in a flask fitted with a reflux condenser and a trap cooled to -78° in Dry Ice and acetone. After reaction was completed, nitrogen was swept slowly through the apparatus. The contents of the trap were distilled on the vacuum line through a U-tube containing phosphorus pentoxide. The distillate (2.5 ml.) was fractionated also on the vacuum line, collecting separately product with a vapor pressure of 46-47 mm. at -78°. Yield: 2.0 ml. of allene- d_4 measured at -78°. Mass analysis: 88.2 mole % C₃D₄, 8.85 mole % C₃D₃H.

On distillation of the zinc-ethanol residues and pouring the distillate into excess ice water, 3.0 ml. of a mixture of *cis*- and *trans*-1,2-dichloropropene- d_4 was precipitated. This volume of dichloropropene corresponds to 4.0 ml. of 1,1,2,2-tetrachloropropene- d_4 in the original mixture dechlorinated. The yield of allene- d_4 was therefore approximately 60%.

Addition of DBr to CH₃C=CCl. 1-Chloropropyne (17.0 g., 0.24 mole) prepared as described in ref. (7) was stirred at 0° under an atmosphere of deuterium bromide. Absorption of gas ceased after 9.0 ml. of liquid deuterium bromide had been added in portions, even when the reaction mixture was warmed to room temperature. The product was freed of deuterium bromide by distilling it on the vacuum line through a U-tube filled with soda-lime. The yield of crude product was 34.0 g. (95%). It was fractionated at atmospheric pressure in a column filled with glass helices. The first fraction b.p. 103-107°, n_D^{20} 1.4894, which amounted to 4.9 ml. was probably *trans*-1-chloro-2-bromo-1-propene-1- d . The *cis*-fraction, b.p. 114°, n_D^{20} 1.4931 amounted to 10.2 ml.

Addition of DBr to CH₃CBr=CCl. Fractions (1) and (2) from the preceding experiment were allowed to stand for two days in a sealed tube with 5.0 ml. of deuterium bromide. No decrease in the volume of liquid took place. On irradiating the tube with a Hanovia lamp, however, the level of liquid fell about 20 mm. in 4 hr. The reaction mixture was taken up in methylene chloride, the solution washed with water and then dried. Fractionation of the residue after distilling off the solvent gave 10.0 ml. (20.8 g.) of product b.p. 93-95°/50 mm., n_D^{20} 1.5388, which was evidently 1-chloro-2,2-dibromopropene-1- d_2 , CD₂ClCBr₂CH₃. The pro-

(11) L. C. Leitch and A. T. Morse, *Can. J. Chem.*, **30**, 924 (1952).

(12) The composition of this catalyst is protected by several patents.

(13) A. Weissberger and N. Cheronis, *Technique of Organic Chemistry*, Vol. V, Chap. XIII, Interscience Publishers, New York, 1954, p. 375.

ton magnetic resonance spectrum of the compound showed signals only for the methyl group.

1,3-Dichloropropyne, $\text{CH}_2\text{ClC}\equiv\text{CCl}$. Aqueous sodium hypochlorite was prepared by passing chlorine into a solution of 102 g. of sodium hydroxide in 140 ml. of water mixed with 600 g. of crushed ice until the increase in weight was 75 g. Forty grams (0.53 mole) of propargyl chloride prepared by the method of Hatch and Chiola¹⁴ and 10 ml. of ether were added to the solution of hypochlorite and the mixture was stirred for 3 hr. at 20°. After this time the organic layer had settled on the bottom. It was taken up in 100 ml. of ether and the aqueous layer was drawn off and extracted with the same volume of fresh ether. The combined ether extracts were washed with a little water and dried over calcium chloride. After removal of ether, the residue was fractionated under reduced pressure. The yield of 1,3-dichloropropyne, b.p. 51–52°/130 mm.; 100°/760, n_D^{20} 1.4798, was 48.5 g. (84%).

Addition of HBr to 1,3-dichloropropyne. 1,3-Dichloropropyne (16.5 ml.) was stirred under reflux for 4 hr. with 100 ml. of constant boiling hydrobromic acid. The reaction mixture was quite dark by this time and the organic layer settled on the bottom when stirring was stopped. The lower layer was taken up in methylene chloride, and worked up in the usual manner. Fractional distillation in a Vigreux column gave 8.5 ml. (27.0 g.) of product, b.p. 81–82°/14 mm., n_D^{20} 1.5730.

When this product was dehalogenated with zinc dust in ethanol 2.5 ml. of allene measured at –78° were obtained (65% yield).

Propadiene-d. Propadiene-d was prepared by the addition of dry propargyl chloride (22.3 g.) to a stirred, refluxing mixture of deuterium oxide (6.0 ml.), zinc dust (20 g.), and dioxane (40 ml.). The product which was collected in a spiral trap cooled to –78° amounted to 13.0 ml. Analysis for double and triple bonds indicated 20% propyne-d and 80% allene-d. Infrared analysis showed that the propyne-d was chiefly $\text{CH}_2\text{DC}=\text{CH}$ with a small amount of $\text{CH}_2\text{C}=\text{CD}$ also present.

Propadiene-1,1-d₂. 1,3-Dichloropropyne (25 g.) in dry dioxane (25 ml.) was added to a stirred, refluxing mixture of deuterium oxide (5.0 ml.), zinc dust (40 g.), and dioxane (125 ml.). A small portion of the halide solution was added and after 10 min. refluxing a gas began to be evolved. The remaining halide was added over 45 min. and 13 ml. of product collected in a spiral trap at –78°. Fractionation through a whirling band column separated this into three fractions.

Fraction I (1.1 ml.) distilled at –38° to –35°. Infrared analysis showed strong bands at 2940 cm^{-1} and in the 1600– cm^{-1} region again believed to be due to propylene-d₄ formed during the reaction. Mass spectral analysis gave peaks of 172.0 and 33.0 at 42 and 46 mass numbers, respectively. The latter corresponds to propylene-d₄.

Fraction II distilled at –35° to –34°. This was pure allene-d₂. The yield was 4.2 ml. (32.5% of the total). Mass spectroscopic analysis indicated the isotopic purity to be 96.2 atom % D.

Fraction III distilled at –32° to –24°, practically all being collected at the latter temperature. This was prop-1-yne-1,3-d₂ contaminated with a trace of allene-1,1-d₂. The yield was 5.5 ml. (43% of the total). Mass spectral analysis showed a deuterium content of 96.0 atom % D.

Allene-1,1-d₂ was also prepared by the addition of 1,3-dichloropropyne (40 g.) to a refluxing mixture of methanol-d (25 g.), dioxane (125 ml.), and zinc dust (65 g.). The product collected (16 ml.) was treated with aqueous potassium mercuric oxide to remove the propyne-d₂ present. Analysis by mass spectrometer upon the remaining sample (9.5 ml.; 60% of the total) gave an isotopic purity of 90.0 atom % D and showed a trace of propylene-d₄ present as an impurity

indicated by a peak at 46 mass numbers. The methanol-d used in this preparation had a lower deuterium content than the heavy water used above, hence the reason for the allene-1,1-d₂ showing a poorer analysis.

Propadiene-1,3-d₂. 1,2,3,3-Tetrachloropropene-1 (63 g., 0.35 mole), prepared according to Heilbron¹⁵ in dioxane (25 ml.) was added to a mixture of methanol-d (23 g.), zinc dust (75 g.), and dioxane (250 ml.) in the same manner as described previously. The product which was collected (18 ml.) was separated into three fractions.

Fraction I (1.5 ml.) distilled at –37° to –34.5° and contained the usual amount of propylene-d₄ as an impurity.

Fraction II was allene-1,3-d₂ and distilled at –34.5° to –34°. The yield was 11.0 ml. (60% of the total). Mass spectrometric analysis showed 87.0 atom % D.

Fraction III (2.5 ml.) was a mixture of prop-1-yne-3,3-d₂ and prop-1-yne-1,3-d₂ with the latter predominating as indicated by the infrared spectrum.

Propadiene-d₃. Addition of *unsym*-heptachloropropane (75 g.; 0.27 mole) in dioxane (20 ml.) to a mixture of deuterium oxide (5.0 ml.), zinc dust (110 g.), and dioxane (300 ml.) gave 11.0 ml. of product measured at –78°. Three fractions were obtained on distillation.

Fraction I (10 ml.) was allene-d₃ contaminated with propylene-d₅.

Fraction II was allene-d₃. This distilled at –35° to –34° and amounted to 4.0 ml. (36.5% of the total). Mass spectrometric analysis gave a deuterium content of 97.6 atom % D.

Fraction III was a mixture of prop-1-yne-3,3,3-d₃ and prop-1-yne-1,3,3-d₃ with the latter predominating. The yield was 3.6 ml. (33% of the total). Mass spectrometric analysis indicated 97.3 atom % D.

Propadiene-d₄ and propyne-d₄. Hexachloropropene was obtained from Columbia Chemicals Limited, Columbia, S. C.

In a 1-l. three-necked, round-bottomed flask with a dropping funnel, a magnetic stirrer, and a reflux condenser to which was connected a spiral trap cooled to –78° with Dry Ice and acetone were added 600 ml. of anhydrous dioxane (purified by distillation over sodium), 42.0 ml. of 99.8% deuterium oxide, and 200 g. of zinc dust. When the stirred mixture had refluxed gently for 20 min. to 0.5 hr., addition of 83.0 g. (50.0 ml.) of hexachloropropene was begun and completed in 1.5 hr. Stirring was continued for another half hour and the apparatus was flushed with a slow stream of dry nitrogen. The yield of propadiene-d₄ and propyne-d₄ mixture varied between 15.0 and 18.0 ml. of liquid measured at –78° (68 to 80% of the theoretical amount) after distillation on the vacuum line.

The mixture was separated in a column with a whirling band. The propadiene-d₄ and propyne-d₄ mixture was distilled on vacuum line into a 25-ml. thermally insulated stillpot which was then attached to the distilling column. The head of the column was cooled by circulating through it pentane cooled in liquid nitrogen. Fractions were collected in a spiral trap cooled to –78°. From 18.0 ml. of liquid hydrocarbons there was obtained 11.3 ml. of propadiene-d₄, b.p. –34 to –32° and 4.8 ml. of propyne-d₄ contaminated with a little propadiene-d₄.

The yield of propadiene-d₄ is thus approximately 40%. The infrared spectrum showed only a faint band due to acetylenic hydrogen (or deuterium).

Butadiene-d₆. Hexachlorobutadiene was obtained from Columbia Chemicals, Columbia, S. C. Dechlorination of hexachlorobutadiene was carried out essentially as described for the lower halide. From 230 g. of anhydrous dioxane, 85 g. of zinc dust, 30 ml. of 99.8% deuterium oxide, and 65 g. (0.25 mole) of hexachlorobutadiene there was obtained 12.0 ml. of butadiene-d₆ measured at –60°. Its vapor pressure at –30° was nearly constant. The yield was 80%

(14) L. F. Hatch and V. Chiola, *J. Am. Chem. Soc.*, **73**, 360 (1951).

(15) I. M. Heilbron, R. N. Hislop, and F. Irving, *J. Chem. Soc.*, 782 (1936).

of the theoretical amount. A mass analysis of an aliquot gave the following figures:

Mass	Mass Peak
60	375.97
59	32.53
58	174.41
57	13.36
56	44.4
55	2.85

The isotopic purity is thus 92.3 mole % C_4D_6 .

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

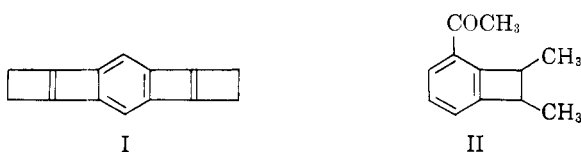
Identification of Lagidze's Hydrocarbon

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The hydrocarbon obtained by the reaction of 2-butyne-1,4-diol diacetate and benzene in the presence of aluminum chloride has been identified as 2-phenylnaphthalene. Acetophenone and 2-acetyl-5,6,7,8-tetrahydronaphthalene were also isolated.

The reaction of 2-butyne-1,4-diol diacetate with benzene in the presence of aluminum chloride has been described by Lagidze and Petrov.¹ Two of the products isolated were assigned molecular formulas $C_{14}H_{10}$ and $C_{12}H_{14}O$, on the basis of elemental analysis and molecular weights. These authors suggested that these compounds had structures (I) and (II), respectively.



Although little degradative evidence was advanced in support of these formulations, the physical and analytical data were difficult to dismiss, particularly for the hydrocarbon. This substance was isomeric with phenanthrene and melted within 2° of that compound. However, a mixture melting point with phenanthrene showed a considerable depression. An x-ray crystallographic examination placed this substance in space group $P2_1/a$ with two molecules in the unit cell. In the absence of orientational disorder in the crystal, this information is very strong evidence that the molecule has a center of symmetry. While the data did not establish (I) as the structure for the hydrocarbon, other structural possibilities meeting these specifications appear equally improbable. A re-investigation of the products of this reaction seemed indicated.

(1) R. M. Lagidze and A. D. Petrov, *Doklady Akad. Nauk. S.S.S.R.*, **83**, 235 (1952).

A mixture of freshly sublimed aluminum chloride and 2-butyne-1,4-diol diacetate in a molar ratio of approximately 2.5 : 1 was heated at the reflux temperature with excess benzene for six hours. After the lower boiling products had been removed by distillation, a colorless crystalline solid was separated from the viscous residue by sublimation. This solid was established to be Lagidze's hydrocarbon by comparisons of its physical properties with those described.¹ These results are shown in Table I.

TABLE I
COMPARISON OF CRYSTALLOGRAPHIC DATA

	This Study	Lagidze & Petrov
M.p.	103–104°	103°
<i>a</i>	8.08 ± 0.03 Å	8.10 Å
<i>b</i>	5.85 ± 0.03 Å	5.98
<i>c</i>	35.63 ± 0.12	11.8
β	94° ± 1°	94°
Space group	$P2_1$ or $P2_1/m$	$P2_1/a$
d_{obs}	1.218 g./cm. ³	1.06–1.16 g./cm. ³

That this hydrocarbon was actually 2-phenylnaphthalene was established on the basis of the following evidence. Values of the molecular weight determined by freezing point depression and the x-ray data were 196 and 211, respectively, which are in substantial agreement with the value 188 ± 10 reported by Lagidze and Petrov. Elemental analysis corresponded to an empirical formula, C_4H_3 , and hence to a molecular formula, $C_{16}H_{12}$. Ozonolysis gave a mixture of benzoic and phthalic acids. Finally, direct comparison of the infrared and ul-