ORGANIC DEUTERIUM COMPOUNDS

XVII. A SYNTHESIS OF DEUTERATED METHYL CHLOROFORM[1]

J. E. FRANCIS AND L. C. LEITCH

ABSTRACT

1,1,1-Trichloroethane-d_3 has been synthesized from trichloroethylene in four steps via trichloroethylene-d, 1,1,1,2-tetrachloroethane-d_2, and 1,1-dichloroethylene-d_2.

The recent interest of spectroscopists in methyl chloroform (1) seemed to justify the preparation of its deuterated analogue. Deuteromethyl chloroform was therefore prepared by the series of reactions outlined below:

$$\mathrm{CHCl{=}CCl_2 \overset{^{-}OD}{\leftrightarrows} CDCl{=}CCl_2}$$

$$\mathrm{CDCl{=}CCl_2 \xrightarrow{DCl} CD_2Cl{-}CCl_3}$$

$$\mathrm{CD_2Cl{-}CCl_3 \xrightarrow{Zn/EtOH} CD_2{=}CCl_2}$$

$$\mathrm{CD_2{=}CCl_2 \xrightarrow{DCl} CD_3CCl_3}$$

Apart from trichloroethylene-d, which was reported earlier by one of us (6), the compounds or their mode of preparation are new. After three equilibrations with alkaline deuterium oxide trichloroethylene-d showed no C—H absorption in either the Raman or the infrared. 1,1,1,2-Tetrachloroethane-d_2 was formed when trichloroethylene-d was stirred under an atmosphere of deuterium chloride, in the presence of aluminum chloride. Dehalogenation of the tetrachloroethane with zinc dust in ethanol gave 1,1-dichloroethylene-d_2, which had been reported previously (8) but without any mention of the manner in which it was prepared.

Since the addition of hydrogen chloride to 1,1-dichloroethylene had been reported only in patents (3, 7), it appeared desirable to reinvestigate this reaction before exposing easily polymerized deuterated dichloroethylene to the combined action of deuterium chloride and anhydrous aluminum chloride. Contrary to reports in the patent literature (2, 4), 1,1-dichloroethylene could not be prepared by dehydrochlorination of 1,1,1-trichloroethane. However, the isomeric 1,1,2-trichloroethane reacted smoothly with aqueous calcium hydroxide to give a satisfactory yield of 1,1-dichloroethylene.

Hydrogen chloride added without too much difficulty to 1,1-dichloroethylene in the presence of anhydrous aluminum chloride. The addition of deuterium chloride to 1,1-dichloroethylene-d_2 carried out in the same manner gave a moderate yield of 1,1,1-trichloroethane-d_3 or deuterated methyl chloroform.

In the belief that it would also be of interest to obtain the semideuterated compounds $\mathrm{CHDClCCl_3}$ and $\mathrm{CHD{=}CCl_2}$, the addition of deuterium chloride to trichloroethylene was carried out under the same conditions. The Raman spectrum of the product indicated it was a mixture of all three tetrachloroethanes—$\mathrm{CH_2ClCCl_3}$, $\mathrm{CHDClCCl_3}$, and $\mathrm{CD_2Cl\text{-}CCl_3}$. Apparently, the presence of anhydrous aluminum chloride had catalyzed hydrogen—

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deuterium exchange as well as addition to the double bond. In the aromatic series this reaction is known, having been employed by Klit and Langseth (5) to prepare benzene-d_6 from benzene and deuterium chloride. However its occurrence with olefins is not believed to have been noted before.

EXPERIMENTAL

Trichloroethylene-d

A mixture of trichloroethylene (25 ml.), deuterium oxide (25 ml.), and calcium deuteroxide (4.0 g.) (or an equivalent amount of freshly calcined calcium oxide) was heated with stirring under gentle reflux for 12 hours in a 100 ml. round-bottomed flask surmounted by a Vigreux column and still head. In some experiments the desiccant in the tube attached to the still head was blown out and a deposit of carbon was formed in the column. This was probably produced by the spontaneous combustion of traces of chloroacetylene formed by dehydrochlorination of the trichloroethylene. The exchanged trichloroethylene was then distilled off as an azeotrope, collected in a separatory funnel. After it was dried over anhydrous potassium carbonate the exchange was repeated with fresh portions of deuterium oxide and calcium deuteroxide (or calcium oxide). After three exchanges the trichloroethylene-*d*, n_D^{20} 1.4771, contained only traces of the normal compound, n_D^{20} 1.4776 according to its nuclear magnetic resonance spectrum. The yield was nearly quantitative.

The deuterium oxide recovered from each exchange was re-used to enrich a second run of trichloroethylene.

Deuterium Chloride

The gas was generated by adding deuterium oxide dropwise to phosphorus pentachloride in an evacuated round-bottomed flask. It was freed of phosphorus halides by being cooled to −78° C. in a spiral trap immersed in dry ice and acetone and collected in a 2 l. evacuated gas bulb. The entire apparatus was flushed out once with deuterium chloride to remove hydrogen adsorbed as water on the walls.

1,1,1,2-Tetrachloroethane-d_2

Trichloroethylene-*d* (25 ml.) and anhydrous aluminum chloride (2.0 g.) were placed in a 100 ml. round-bottomed flask, a small magnetized bar sealed in glass was introduced for stirring, and the flask was attached to the deuterium chloride generator by an adapter. After cooling and evacuating, stirring was started and deuterium chloride introduced from the gas bulb until the pressure was nearly one atmosphere. Addition of deuterium chloride took place slowly over 2 days, a total of about 4 l. being consumed.

The reaction mixture was connected to a stock trap cooled to −78° on a vacuum line and distilled. The distillate (24.5 ml.) was fractionated in a column packed with glass helices. The pure product, b.p. 128–129° C., n_D^{20} 1.4815, amounted to 23.0 g. (58% of the theoretical amount). Its Raman spectrum showed only very faint absorption in the C—H region.

1,1-Dichloroethylene

Dehydrochlorination of 1,1,1-trichloroethane by means of calcium hydroxide was unsuccessful. A suspension of 20 g. of the trichloroethane in 50 ml. of water to which 5.0 g. of calcium oxide had been added was heated under reflux for 5 hours without obtaining a trace of 1,1-dichloroethylene. With 1,1,2-trichloroethane, however, yields of

75–80% 1,1-dichloroethylene were readily obtained. The product was dried by distillation through a U-tube containing phosphorus pentoxide on the vacuum line. To prevent polymerization the monomer was treated with a few crystals of hydroquinone.

1,1,1-Trichloroethane

1,1-Dichloroethylene (5.0 ml.) and 0.05 g. of anhydrous aluminum chloride were stirred in a 100 ml. round-bottomed flask under an atmosphere of hydrogen chloride at 20° C. After 1½ hours no more hydrogen chloride was absorbed. The product was distilled out into a trap on the vacuum line. Yield: 7.5 g. Fractional distillation in a column packed with glass beads gave 5.0 g. of 1,1,1-trichloroethane, b.p. 72–74° C., n_D^{20} 1.4384.

1,1-Dichloroethylene-d_2

To a boiling stirred suspension of 28 g. of zinc dust in 50 ml. of 95% ethanol in a 250 ml. round-bottomed flask with a reflux condenser to which was attached a spiral trap cooled in dry ice and acetone to −78° C. was added dropwise over a period of 2 hours 24.8 g. of 1,1,1,2-tetrachloroethane-d_2. After addition of the halide the dichloroethylene was swept out of the apparatus by a slow current of nitrogen. The product in the spiral trap was distilled through a tube containing phosphorus pentoxide on the vacuum line. The yield of pure product was 12.8 g. (89%).

1,1,1-Trichloroethane-d_3

In a 500 ml. round-bottomed flask were placed a magnetized bar and 107 mg. of pulverized anhydrous aluminum chloride. The flask was pumped out thoroughly and then 6.2 ml. at 0° C. of 1,1-dichloroethylene-d_2 was distilled into the flask from a trap. One atmosphere of deuterium chloride was then introduced and stirring started. After a short induction period absorption began. The flask was immersed in water at 18° C. to prevent polymerization. After about 1 hour absorption of deuterium chloride ceased; the reaction mixture was purple. The product was distilled *in vacuo* as described for the light compound. Yield: 8.5 g. (78%). It was purified by fractional distillation in a column packed with glass helices, b.p. 73–74° C., n_D^{20} 1.4370. Yield: 4.7 g.

1,1,1,2-Tetrachloroethane-d

Deuterium chloride was reacted with trichloroethylene as described for the synthesis of the dideuterated compound. The Raman spectrum of the product showed absorption due to CH_2 and CD_2 groups as well as the CHD group.

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