ORGANIC DEUTERIUM COMPOUNDS

V. THE CHLORINATION OF PROPYNE AND PROPYNE-d_4[1]

By L. C. Leitch[2]

ABSTRACT

Chlorination of propyne at 70° C. gave 60 to 65% yields of 1,1,2,2-tetrachloropropane and 15 to 20% yields of *trans*-1,2-dichloro-1-propene. 1,1,2,2-Tetrachloropropane-d_4 was similarly prepared from propyne-d_4. Nearly theoretical yields of *cis*- and *trans*-1,2-dichloro-1-propene were obtained by partial dechlorination of tetrachloropropane. Deuterated *cis*- and *trans*-1,2-dichloro-1-propene were obtained in the same manner from 1,1,2,2-tetrachloropropane-d_4.

INTRODUCTION

Some time ago normal and deuterated *cis*- and *trans*-1,2-dichloro-1-propene were required to establish the configuration of this pair of geometrical isomers. The spectroscopic results of this investigation have already been reported by Bernstein and Powling (1). Since these compounds were prepared from propyne and propyne-d_4 by a novel method, it was felt that the synthetic part of the work should be reported in a separate paper.

cis- and *trans*-1,2-Dichloro-1-propene have been previously prepared from sodium 2,3,3-trichlorobutyrate (7) and 1,2,2-trichloropropane (4) respectively. Neither of these methods is suitable for the preparation of the deuterated dichloropropenes. These compounds might be obtainable, however, from propyne-d_4 (5) by chlorination to 1,1,2,2-tetrachloropropane-d_4 followed by partial dechlorination with zinc dust in ethanol.

Although the literature on the chlorination of acetylene is voluminous (3) the reaction of other acetylenic hydrocarbons with chlorine has not been extensively investigated. Hexyne-1 was reported by Hennion and Welsh (2) to give a 30.6% yield of 1,1,2,2-tetrachlorohexane and a 19.6% yield of *trans*-1,2-dichloro-1-hexene when chlorinated at 40° C. in carbon tetrachloride in the presence of antimony pentachloride. Rengert and Schumacher (6) obtained a mixture of compounds which were not all characterized from the vapor phase chlorination of vinylacetylene at 150° C.

In the present work, the chlorination of propyne was first investigated in carbon tetrachloride at −20, −40, and −60° C. in the presence of antimony pentachloride. The reaction products boiled over a wide range and only low yields of 1,1,2,2-tetrachloropropane were obtained. Chlorination by substitution as well as by addition appeared to have taken place. In the vapor phase, however, propyne reacted smoothly at 65 to 70° C. to give, in 60 to 65% yields, 1,1,2,2-tetrachloropropane. In addition, *trans*-1,2-dichloro-1-propene was obtained in 15 to 20% yields. The *cis*- isomer was prepared by fractional distillation of the mixture resulting from the dechlorination of 1,1,2,2-tetrachloropropane. The corresponding deuterated compounds were prepared from propyne-d_4.

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Contribution from the Division of Applied Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 2948.
[2] *Present address—Division of Pure Chemistry, National Research Council, Ottawa, Canada.*

EXPERIMENTAL

1,1,2,2-Tetrachloropropane

The apparatus used in these experiments was similar to that described by Taylor and Morey (8). The reactor (2 liters) was heated by means of an infrared lamp at a distance of six inches from the flask. Dry chlorine and propyne were introduced into the reactor through flowmeters in the ratio 2:1. After a short induction period, during which the temperature of the gases in the reactor rose to 60 to 70° C., the reaction started and liquid product began to form. When 17.0 liters of propyne had been introduced at the rate of 2.0 liters per hour, the liquid product was withdrawn, washed with aqueous potassium carbonate, and dried over anhydrous potassium carbonate. The yield was 107 gm.

On distillation at atmospheric pressure in a Stedman column (12 in. × $\frac{3}{4}$ in.) a fraction, b.p. 62 to 98° C., largely at 75° C., was collected. This product was redistilled in a smaller Stedman column (12 in. × $\frac{3}{8}$ in.); it was mainly *trans*-1,2-dichloro-1-propene, b.p. 75° C., n_D^{20} 1.4498. Yield: 15.0 gm. (20%).

The 1,1,2,2-tetrachloropropane was fractionated under reduced pressure. After collecting a forerun (5.5 ml.) up to 79° C. at 64 mm., the main product distilled at 81° C. at 64 mm. The yield of 1,1,2,2-tetrachloropropane, n_D^{20} 1.4866, was 82.5 gm. (63% of the theoretical amount).

Propyne-d_4 prepared as described in a previous paper (5) gave similar yields of 1,1,2,2-tetrachloropropane-d_4, n_D^{20} 1.4848.

cis- and trans-1,2-Dichloro-1-propene

1,1,2,2-Tetrachloropropane (37.5 gm.) was added gradually to a boiling suspension of zinc dust (20.0 gm.) in 200 ml. of ethanol in a 1 liter three-necked round-bottomed flask equipped with a stirrer and reflux condenser. Any allene which was formed owing to the presence of isomeric 1,2,2,3-tetrachloropropane was condensed in a trap cooled to −78° C. by dry ice and acetone. The reaction mixture was heated under reflux for one hour after the chlorocompound had been added. The mixed dichloropropenes formed were then distilled off through a Stedman column as azeotropes with ethanol and water. The yield was nearly quantitative. The product was separated into the *cis*- and *trans*-isomers boiling at 92° and 75° C. respectively by means of a Stedman column. For *trans*-1,2-dichloro-1-propene, n_D^{20} 1.4498; for the *cis* form, n_D^{20} 1.4549.

The corresponding deuterated compounds were prepared in exactly the same way. For *trans*-1,2-dichloro-1-propene, n_D^{20} 1.4479 and for the *cis* form, n_D^{20} 1.4528.

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