XI. SYNTHESIS OF 1-CHLORO-1-ALKYNES AND 1-CHLORO-1-PROPYNE-d₃¹

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ABSTRACT

Dehydrohalogenation of *cis*-1,2-dichloro-1-alkenes, RCCI=CHCI, with potassium hydroxide in butanol has been used to prepare a number of new 1-chloro-1-alkynes, viz. 1-chloro-1-propyne- d_3 , 1-chloro-1-propyne, 1-chloro-1-butyne, and 1-chloro-1-pentyne in good yields. The last three compounds were also prepared by chlorination of 1-propyne, 1-butyne, and 1-pentyne with sodium hypochlorite.

INTRODUCTION

The synthesis of several deuterated organic compounds of potential use in molecular spectroscopy has been reported in previous papers of this series (9, 10, 11). We have now synthesized normal and deuterated 1-chloro-1-propyne for further investigations in this field, which will be reported in this journal in a separate paper by Bernstein and Davidson (1).

As a class, the 1-chloro-1-alkynes have not been studied as extensively as other chlorinated hydrocarbons. In 1931, Truchet (18) obtained 1-chloro-1-hexyne (I) from benzenesulphonyl chloride and the sodium derivative of hexyne-1 instead of the expected sulphone (II).

$$C_4H_9C \equiv CCl + C_6H_5SO_2Na \qquad (I)$$

 $(n)C_{4}H_{9}C \equiv CNa + C_{6}H_{5}SO_{2}CI \qquad O$ $\uparrow C_{4}H_{9}C \equiv CS.C_{6}H_{5} + NaCI \qquad (II)$ $\downarrow O$

This result is not surprising in view of the charge distribution between the sulphur and chlorine atoms in sulphonyl chlorides (III).



1-Hexyne, 1-octyne, and 1-nonyne reacted similarly. These chloroalkynes were later prepared by the same method by Pflaum and Wenzke (15) for dipole moment measurements. Cleveland, Taufen, and Murray (3) failed to obtain

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1

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1-chloro-1-propyne from sodium methyl acetylide but an impure product, b.p. 37 to 41°C. was isolated in low yield using the magnesium derivative. In the present work, 1-chloro-1-propyne was actually obtained by Truchet's method but only in 10% yield; no improvement was observed using *p*-toluenesulphonyl chloride.

Another synthesis of 1-chloro-1-alkynes was reported by McCusker and Vogt (13). These authors prepared the potassium derivative of 1-heptyne in the usual manner and chlorinated a suspension of the solid in ether at -70° C. The yield of 1-chloro-1-heptyne was good, but the rate of adding the chlorine was an important factor affecting the yield. This method appeared unpromising to us and was not tried. Chlorination of the lithium derivative, however, might be advantageous.

According to Strauss, Kollek, and Hauptmann (17), the methine or acetylenic hydrogen is replaced by bromine when heptyne-1 is shaken with alkali hypobromite; the reaction with hypochlorite was reported to be too slow to make this method a useful preparative route to 1-chloro-1-alkynes. However, vinylacetylene is reported to give 60 to 65% yields of 1-chloro-3-butene-1-yne when shaken at 0°C. with aqueous sodium hypochlorite for 16 hr. (8). There is also a reference to the chlorination of the methine hydrogen in propargyl alcohol by aqueous sodium hypochlorite by Copenhaver and Bigelow (4). In the present work, it was found that propyne, butyne-1, and pentyne-1 were converted into the corresponding 1-chloroalkynes at approximately the same rate when stirred for 80 hr. with 10% sodium hypochlorite. While slow, the reaction is satisfactory, particularly for the preparation of 1-chloro-1pentyne.

Theoretically, this reaction may proceed by a carbanion, a carbonium ion, or even a free radical mechanism. Of these alternatives, we believe the carbonium ion mechanism shown below is the most probable.

$$RC \equiv CH \leftrightarrow RC = CH \rightarrow RC = CHCl \rightarrow RC \equiv CCl + H^{+}$$
(IV) (V)

Electrophilic attack of the positive chlorine ion on the resonance hybrid (IV) gives the carbonium ion (V) which is converted into the 1-chloroalkyne by loss of a proton. A free radical mechanism appears to us ruled out by the failure to isolate any product other than the chloroalkyne. A carbanion mechanism, though improbable, cannot be excluded on the basis of the present experiments. In this connection, it is proposed to investigate the behavior of other 1-alkynes with sodium hypochlorite at some future date, as syntheses of suitable alkynes will first have to be devised.

Although dehydrohalogenation has been widely used in the preparation of acetylenic hydrocarbons (6), there are few references to its application to the synthesis of chloroalkynes (2, 5). 1-Bromo-1-propyne was prepared in 25% yield (12) by dehydrohalogenation of 1,1,2-tribromopropane. No doubt, one of the reasons this method has not been exploited in the past has been the inaccessibility of the required 1,2-dichloro-1-alkenes, RCCl=CHCl. In a previous paper of this series (9), the preparation of *cis*- and *trans*-1,2-dichloro-1-propene and their deuterated analogues was described. It was felt that these compounds might serve as starting materials for the synthesis of 1-chloro-1-propyne, depending upon the manner in which hydrogen chloride is split off by alcoholic alkali.

When *cis*-1,2-dichloro-1-propene was added to a boiling solution of potassium hydroxide in butanol, a liquid (b.p. approx. 32°C.) distilled over which was





identified by its mass spectrum as 1-chloro-1-propyne. The alternative product, 1-chloropropadiene (CH = C = CHCl), was recently reported by Jacobs and Brill (7) and boils at 44°C. The product, b.p. 32°C., was identical with that obtained by chlorination of propyne with sodium hypochlorite. By treating *cis*-1,2-dichloro-1-propene- d_4 in the same manner, the corresponding deuterated chloropropyne was obtained.

The vapor pressures of 1-chloro-1-propyne and its deuterated analogue were measured by the method described in earlier papers of this series (9, 10, 11). The values obtained at various temperatures were then plotted logarithmically to give the curves shown on Fig. 1. For temperatures below 16°C., the results were expressed by the equations

$$\log_{10} p \text{ (mm.)} = -(1.480 \times 10^3)/T + 7.740$$

and

$$\log_{10} p \text{ (mm.)} = -(1.487 \times 10^3)/T + 7.782$$

for $CH_3C \equiv CCl$ and $CD_3C \equiv CCl$ respectively.

The structure of 1-chloro-1-propyne was proved by chlorination at 0°C. to 1,1,1,2,2-pentachloropropane identical with the product recently reported by Nesmayanow, Friedlina, and Firstov (14). Furthermore, dehalogenation of the pentachloropropane with zinc dust gave 1,1,2-trichloro-1-propene.

trans-1,2-Dichloro-1-propene reacted much more sluggishly than the *cis*isomer and was largely recovered after refluxing for a long period. This observation is in agreement with those of other workers who have investigated the dehydrohalogenation of 1,2-dichloroethylene (2) and of 1-ethoxy-1chloro-1-propene (5). In each case, the *cis* form showed a considerably greater rate of reaction due also to *trans* elimination.

Dehydrohalogenation of *cis*-1,2-dichloro-1-butene and of *cis*-1,2-dichloro-1pentene likewise gave 1-chloro-1-butyne and 1-chloro-1-pentyne respectively. These products were also identical with those obtained from the chlorination of 1-butyne and 1-pentyne by sodium hypochlorite.

The synthesis of these new chloro alkynes now completes the series to C₃.

EXPERIMENTAL

1-Chloro-1-propyne

cis-1,2-Dichloro-1-propene (36.0 gm.) prepared as in (9) was dissolved in 20 ml. of *n*-butanol and added dropwise to a refluxing solution of 25 gm. of potassium hydroxide in 300 ml. of *n*-butanol during stirring with a magnetic bar. Water entering the reflux condenser was precooled to 5°C. by circulation through a copper spiral immersed in ice water in a Dewar flask. By this means loss of the volatile 1-chloro-1-propyne was avoided. After addition of the halide, the reaction mixture was cooled to 0°C. and the reflux condenser was replaced by a 12 in. Stedman column and a still-head. The 1-chloro-1-propyne distilled as an azeotrope, b.p. 31 to 32°C. It was dried by distillation through a U-tube containing phosphorus pentoxide on a vacuum line. Redistillation through the Stedman column gave a product, b.p. 32.8 to 33°C., n_D^{20} 1.4131 in 68% yield. The mass spectrum showed two strong peaks at 74 and 76.

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1-Chloro-1-propyne-d₃

This compound was prepared from 36.4 gm. of *cis*-1,2-dichloro-1-propene- d_4 in exactly the same manner. The yield was 19.4 gm. (78.5%) of product b.p. 31.7°C. at 750 mm., $n_{\rm D}^{20}$ 1.4105. Mass spectrometric analysis: 98.17 atom % D.

1-Chloro-1-butyne

(a) Dehydrochlorination method.—cis-1,2-Dichloro-1-butene (20 gm.) (preparation to be described in a forthcoming paper) gave 13.2 gm. (93.5%) of 1-chloro-1-butyne, b.p. 63–64.5°C., n_D^{20} 1.4221. The mass spectrum showed two strong peaks at 88 and 90 corresponding to the two chlorine isotopes.

(b) Hypochlorite method.—A solution of sodium hypochlorite prepared on one tenth the scale reported by Smith and McLeod (16) was attached to a vacuum line which was then evacuated. 1-Butyne was introduced from a gasholder into the apparatus. After four days' stirring, all the butyne had been absorbed and there was a layer of oily liquid above the hypochlorite solution. This upper layer was separated, dried over phosphorus pentoxide on the vacuum line, and fractionated. Four liters of unreacted 1-butyne were recovered. The 1-chloro-1-butyne had b.p. $63.5-64.5^{\circ}$ C., $n_{\rm D}^{20}$ 1.4210. Yield: 76%.

1-Chloro-1-pentyne

(a) Dehydrochlorination method.—cis-1,2-Dichloro-1-pentene (8.5 gm.) which was prepared by a method to be reported in a forthcoming paper was treated as described for the lower homologues. It gave 6.0 gm. (96%) of 1-chloro-1-pentyne, b.p. 91.5–92.0°C., $n_{\rm D}^{20}$ 1.4302. Calc. for C₅H₇Cl: Cl, 34.56%. Found: Cl, 33.58%.

(b) Hypochlorite method.—A mixture of 34.0 gm. of pentyne-1 and 800 ml. of sodium hypochlorite was stirred with a magnetic bar for 180 hr. The upper layer was then separated, dried, and fractionated. It gave 29.2 gm. (76.5%) of 1-chloro-1-pentyne, b.p. 91.5–92.0°C., $n_{\rm D}^{20}$ 1.4302.

1,1,1,2,2-Pentachloropropane

A solution of 14.0 gm. of 1-chloro-1-propyne in 50 ml. of methylene chloride was placed in a 100 ml. flask equipped with a cold finger condenser cooled with dry ice. Chlorine was introduced through a side-arm while the reaction mixture was kept at 0° in the dark. Five liters of chlorine were introduced in three hours. The mixture was allowed to stand at room temperature overnight, the volatile material was then removed under vacuum, and a white residue remained. Sublimation on a vacuum line gave 34.8 gm. (85% yield) of white solid, which after recrystallization from 15 ml. of petroleum ether gave 25.0 gm. of product m.p. 179–180°C., identical with the value reported in (14) for 1,1,2,2-pentachloropropane. Dehalogenation with zinc dust in ethanol gave a liquid b.p. 114–5°C., $n_{\rm D}^{20}$ 1.4827, identical with the values reported for 1,1,2-trichloro-2-propene obtained by the dehydrohalogenation of 1,1,2,2tetrachloropropane (9).

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