cis-crotyl chloride, 2.00 hours, 74.0%, k = 1.61; 2.50 hours, 78.2%, k = 1.67; 3.50 hours, 79.0%, k = 1.08.

The last two values for the specific reaction rate constant are definitely in variance with those obtained for shorter periods of time. The deviation for the *trans* isomer was not appreciable.

For the purpose of comparison with the crotyl chlorides, the specific reaction rate constant of 3-chloro-1-butene was determined. The rate of this reaction was very slow at 20° so the measurements were made at 60° in order that better values could be obtained. The average value for the specific velocity constant for 3-chloro-1-butene was 0.044 at 60°.

Reaction with Sodium Ethoxide in Ethanol.—These rates were also determined using a previously described procedure.[12] The usual equation for a bimolecular reaction was used and a straight line was obtained when log $b(a - x)/a \cdot (b - x)$ was plotted against time. The molar concentration of the *cis*-crotyl chloride was 0.05075 and the sodium ethoxide in ethanol was 0.05605. The molar concentration of the *trans* isomer was 0.05065 and the sodium ethoxide in ethanol was 0.04594. Table II contains the rate constants and other data.

Cuprous Chloride Catalyzed Acid Hydrolysis.—The same procedure and apparatus was used as that described in a

(12) Hatch and Alexander, This Journal, **71**, 1037 (1949).

previous paper of this series.[13] Thirty-nine-thousandth (0.039) of a mole of the chloride and 0.0035 mole of cuprous chloride (added as cuprous oxide) were used in 100 ml. of 1.5% hydrochloric acid. Because of the high rate of hydrolysis of the *cis*-crotyl chloride, the data for this isomer are not considered too accurate. It is clearly shown, however, that the *cis* isomer is appreciably more reactive than the *trans* isomer. The data are given in Table II.

Summary

The relative reactivities of *cis*- and *trans*-crotyl chloride have been determined for their reaction with potassium iodide in acetone, sodium ethoxide in ethanol and cuprous chloride catalyzed acid hydrolysis.

The replacement of a hydrogen atom on the number one carbon atom of allyl chloride by a methyl group increases the reactivity of the allylic chloride toward all three of these reagents.

With each reagent the *cis* isomer of crotyl chloride was more reactive than the *trans* isomer.

(13) Hatch and Ballin, *ibid.*, **71**, 1041 (1949).

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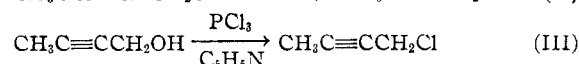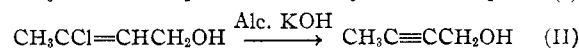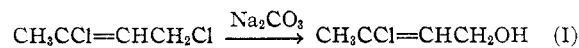# The Preparation and Properties of 3-Chloro-1-propyne and 1-Chloro-2-butyne

By Lewis F. Hatch and Vincent Chiola

Occasional reference has been made in the literature to 3-chloro-2-propyne (propargyl chloride) and 1-chloro-2-butyne (methylpropargyl chloride) but no investigation has been reported on the influence of the carbon–carbon triple bond on the reactivity of these chlorides, especially in comparison with their olefinic and saturated counterparts. The present study was made both to clarify some apparent discrepancies in the literature of these compounds and to investigate their relative reactivities.

3-Chloro-1-propyne was first prepared by Henry[1] in 1875 by the reaction between phosphorus trichloride and 2-propyn-1-ol (propargyl alcohol). The same method was used in this investigation with the exception that pyridine was used as a solvent. We were not, however, able to obtain a material which boiled at the reported boiling point (65°) of 3-chloro-1-propyne. Three different preparations gave a chloride boiling consistently between 56 and 57°. Considering the source of the starting material, the method of synthesis and the results of the chlorine analysis, it is concluded that the boiling point reported by Henry for 3-chloro-1-propyne is incorrect.

In 1939 Hurd and Cohen[2] reported the synthesis of 1-chloro-2-butyne from 2-butyn-1-ol using phosphorus trichloride. The 2-butyn-1-ol was prepared from methylethynylmagnesium bromide and formaldehyde (from trioxymethylene). A boiling range (81–84°) and chlorine analysis were given to characterize their compound. The following series of reactions represent the method of preparation used in the present investigation to give a product which

(1) Henry, *Ber.*, **8**, 398 (1875).
(2) Hurd and Cohen, This Journal, **53**, 1074 (1931).

boiled approximately 20° higher (102°) than the boiling range reported by Hurd and Cohen.

$$CH_3CCl{=}CHCH_2Cl \xrightarrow{Na_2CO_3} CH_3CCl{=}CHCH_2OH \quad (I)$$

$$CH_3CCl{=}CHCH_2OH \xrightarrow{Alc.\ KOH} CH_3C{\equiv}CCH_2OH \quad (II)$$

$$CH_3C{\equiv}CCH_2OH \xrightarrow[C_5H_5N]{PCl_3} CH_3C{\equiv}CCH_2Cl \quad (III)$$

The identity of our compound was checked by chlorine analysis and by the preparation of the 3,5-dinitrobenzoate of both the chloride and the alcohol from which it was made. Mixture melting points of these two derivatives showed no depression. It is of interest to note that the water azeotrope of 1-chloro-2-butyne boils at 81.5° and it is suggested that the boiling point of this azeotrope was reported by Hurd and Cohen instead of the boiling point of the pure compound. The various physical data obtained for both 3-chloro-1-propyne and 1-chloro-2-butyne are given in Table I.

TABLE I

B. p., °C.	3-Chloro-1-propyne 56–57	1-Chloro-2-butyne 102	
$n^{20}D$	1.4329	1.4581	
$n^{25}D$	1.4298	1.4552	
$n^{30}D$		1.4529	
d^{20}_4	1.0297	1.0152	
d^{25}_4	1.0239	1.0100	
d^{30}_4		1.0063	
Molecular (calcd.)	18.92	23.54	
refract. (obs.)	18.78	23.74	
Chlorine, % (calcd.)	47.58	40.05	
(found)	47.78 47.83	39.86 39.96	

The availability of 3-chloro-1-propyne and 1-chloro-2-butyne permitted an investigation of their relative reactivities with potassium iodide in acetone, sodium ethoxide in ethanol and cuprous chloride catalyzed acid hydrolysis. The study of these compounds also permitted a comparison of the influence of a double bond and a triple bond on the reactivity of a chlorine atom on an adjacent, terminal carbon atom toward these reagents. The data are given in Table II. The relative reactivity of 1-chlorobutane[3] is taken as 1.00 for the reaction with potassium iodide and the reactivity of allyl chloride is taken as 1.00 for the reaction with sodium ethoxide.
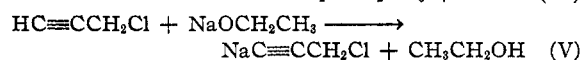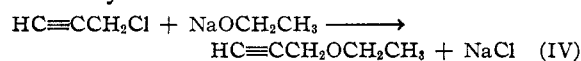
TABLE II

RELATIVE REACTIVITIES OF SEVERAL ALIPHATIC CHLORIDES

	Potassium iodide in acetone	Sodium ethoxide in ethanol
$CH_3CH_2CH_2Cl$	1.03	
CH_2=$CHCH_2Cl$	79.0	1.00
CH≡CCH_2Cl	99.5	a
$CH_3CH_2CH_2CH_2Cl$	1.00	
cis CH_3CH=$CHCH_2Cl$	630	5.10
trans CH_3CH=$CHCH_2Cl$	125	4.38
CH_3C≡CCH_2Cl	152	1.89

a Not an uncomplicated second order reaction.

In the reaction with *potassium iodide* there is a slight increase in activity in going from a double bond to a triple bond.[3a] This is noted for both the 3 and 4 carbon compounds if it is assumed that the *trans* isomer of crotyl chloride[4] is reacting essentially without appreciable activation or deactivation caused by geometrical configuration. Replacement of the acid hydrogen atom of 3-chloro-1-propyne by a methyl group has a slight activating action of about the same magnitude as a similar replacement of a hydrogen atom of allyl chloride to give *trans*-crotyl chloride. This further substantiates the assumption that the much greater reactivity of *cis*-crotyl chloride in comparison with *trans*-crotyl chloride is caused by an activation by the *cis* configuration rather than by deactivation caused by the *trans* configuration.

The reaction between 3-chloro-1-propyne and *sodium ethoxide* took place with an appreciable amount of side reaction and the resulting plot of log $b(a - x)/a(b - x)$ against time gave a smooth curve instead of a straight line. The reaction also appeared to approach about 60% completion as a limiting figure. These data can be explained by the simultaneous reaction of 3-chloro-1-propyne and sodium ethoxide to form both the corresponding ether and sodium chloride and the sodium acetylide and ethyl alcohol. Similar reactions could take

HC≡CCH₂Cl + NaOCH₂CH₃ ⟶
          HC≡CCH₂OCH₂CH₃ + NaCl   (IV)

HC≡CCH₂Cl + NaOCH₂CH₃ ⟶
          NaC≡CCH₂Cl + CH₃CH₂OH   (V)

place with the products of both these reactions.

(3) Conant, Kirner and Hussey, THIS JOURNAL, **46**, 232 (1924); **47**, 476, 488 (1925).

(3a) Murray [*ibid.*, **60**, 2662 (1938)] states "The most active acetylenic chloride measured (3-chloro-1-phenylpropyne-1) has a somewhat lower activity than the corresponding ethylenic compound."

(4) Hatch and Nesbitt, *ibid.*, **73**, 358 (1950).

The determination of the extent of reaction was made by titration of the unreacted sodium ethoxide using hydrochloric acid and under these conditions the sodium acetylide would also titrate and be recorded as unreacted sodium ethoxide.

The reaction of 1-chloro-2-butyne with sodium ethoxide appears to be an uncomplicated second order reaction. The presence of a triple bond reduces the reactivity of the chlorine atom by a factor of about 2.5 in comparison with a double bond.[4]

It was not possible to hydrolyze 3-chloro-1-propyne in an acid solution using *cuprous chloride* as the catalyst. In both the presence and absence of cuprous chloride there was actually a small decrease in the chloride ion concentration in the solution after a period of 3.5 hours. This decrease indicated an addition of hydrogen chloride to the carbon–carbon triple bond. This same action was noted with 1-chloro-2-butyne in the absence of cuprous chloride. In the presence of cuprous chloride there was a slow but definite hydrolysis of the 1-chloro-2-butyne. The hydrolysis of an acetylenic compound of this type has not been reported previously. The failure of 3-chloro-1-propyne to react probably was caused by the presence of an acid hydrogen atom in the molecule which reacted preferentially with the catalyst.

Experimental

All temperatures are corrected.

3-Chloro-1-propyne.—3-Chloro-1-propyne was prepared from propargyl alcohol using phosphorus trichloride in pyridine. The propargyl alcohol was obtained from the Farchan Research Laboratories (b.p. 114.5°; n^{20}D 1.4310; lit.[5] b.p. 114–115°; n^{20}D 1.4310) and was used without further purification. The procedure used was the same as that in the preparation of *trans*-crotyl chloride from the corresponding alcohol.[6] Three moles of propargyl alcohol, 1.2 moles of phosphorus trichloride and 0.67 mole of pyridine were used and a 61% yield of 3-chloro-1-propyne (b.p. 56–57°) was obtained. The physical constants for this material are given in Table I.

1-Chloro-2-butyne.—Crude 1,3-dichloro-2-butene[7] was distilled through a 4-ft. glass-helix packed column to obtain a relatively pure material (b.p. 127–129°; n^{25}D 1.4696; lit.[8] b.p. 127–128°; n^{25}D 1.4695 for the low boiling isomer of 1,3-dichloro-2-butene). The 1,3-dichloro-2-butene, 6.0 moles, was hydrolyzed to 3-chloro-2-buten-1-ol using 4.2% sodium carbonate at 80° for 3 hours. A 63% yield of 3-chloro-2-buten-1-ol (b.p. 160–161°; n^{25}D 1.4635; lit.[9] b.p. 160.5°; n^{25}D 1.4635 for the low boiling isomer) was obtained. It (3.88 moles) was dehydrochlorinated using a 10% alcoholic potassium hydroxide solution between 80 and 85° for 1.5 hours. A fraction, 184 g. (2.73 moles, 70% yield), boiling between 140 and 143° was obtained and redistilled to give a center cut with the following constants: b.p. 140–141°; n^{25}D 1.4517, 3,5-dinitrobenzoate m.p. 102–103.5°.[10]

The 2-butyn-1-ol, 1.62 moles, was converted to 1-chloro-2-butyne (0.97 mole, 60% yield) in a manner similar to that used in the preparation of 3-chloro-1-propyne from

(5) Hennion and Murray, *ibid.*, **64**, 1220 (1942).

(6) Hatch and Nesbitt, *ibid.*, **72**, 727 (1950).

(7) Furnished by E. I. du Pont de Nemours and Company, Wilmington, Delaware.

(8) Hatch and Ballin, THIS JOURNAL, **71**, 1039 (1949).

(9) Hatch and Hudson, *ibid.*, **72**, 2505 (1950).

(10) The figure of 71.0° given by Hatch and Nesbitt (*ibid.*, **72**, 727 (1950)) apparently was in error.

2-propyn-1-ol. The 3,5-dinitrobenzoate was prepared from silver 3,5-dinitrobenzoate and it had a melting range of 102–104°. A mixture melting point with the 3,5-dinitrobenzoate (m.p. 102–103.5°) prepared from 2-butyn-1-ol had a melting range of 103–105°.

One part of the chloride and two parts of water were distilled to determine the boiling point of the water azeotrope of the chloride. The azeotrope boiled at 81.5°.

Reaction with Potassium Iodide in Acetone.—The same procedure was used as previously described.[11] The usual modified second order equation, $k = 1/4bt \log (5 - z)/5(1 - z)$, was used and a plot of log $(5 - z)/5(1 - z)$ vs. time gave a straight line between 25 and 77% reaction for 3-chloro-1-propyne and between 18 and 70% reaction for 1-chloro-2-butyne. The pertinent data are given in Table III.

Reaction with Sodium Ethoxide in Ethanol.—These rates were also determined using a previously described procedure.[12] The usual equation for a bimolecular reaction was used with the molar concentration of 3-chloro-1-propyne being 0.05300 and sodium ethoxide 0.05245, and the molar concentration of 1-chloro-2-butyne being 0.05633 and the sodium ethoxide 0.05605.

A straight line was obtained for 1-chloro-2-butyne between 34 and 67% reaction when log $b(a - x)/a(b - x)$ was

TABLE III

RELATIVE REACTIVITIES OF 3-CHLORO-1-PROPYNE AND 1-CHLORO-2-BUTYNE. POTASSIUM IODIDE IN ACETONE AT 20° AND SODIUM ETHOXIDE IN ETHANOL AT 50°

	Potassium iodide k, hr. mole l.	Sodium ethoxide k, hr. mole l.
3-Chloro-1-propyne	0.279 ± 0.007	a
1-Chloro-2-butyne	.419 ± 0.030	2.24 ± 0.04

Cuprous Chloride Catalyzed Acid Hydrolysis at 40°

1-Chloro-2-butyne,

time, hr.	0.25	0.50	1.00	2.00	3.50	6.00
% reacted	5.8	7.9	10.5	14.7	21.7	36.6

Acid Hydrolysis at 40°

1-Chloro-2-butyne,

time, hr.	1.00	2.00	3.50	6.00
% reacted	4.1	5.4	2.6	0.0

a k values gave a smooth curve from 1.03 for 24% reacted to 0.413 for 60% reacted.

(11) Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1093 (1948).
(12) Hatch and Alexander, ibid., **71**, 1037 (1949).

plotted against time. The data obtained for 3-chloro-1-propyne, however, were not amenable to treatment as either a first or second order reaction. The reaction, as measured by hydrochloric acid titration, appeared to approach 60% as a limiting figure. Data for these reactions are given in Table III.

Cuprous Chloride Catalyzed Acid Hydrolysis.—The method of Hatch, Brown and Bailey[13] was used and involved the treatment of 0.0195 mole quantities of the chloride by 50 ml. of 1.5% hydrochloric acid to which had been added 0.00087 mole of cuprous oxide (98%) in one run and no cuprous oxide in another run. Both runs were heated for 3.5 hours at 40° and both showed a small decrease in chloride ion concentration.

The results of catalytic hydrolysis of 1-chloro-2-butyne are given in Table III. This chloride was also treated with a 1.5% hydrochloric acid solution under conditions identical with those used in the catalyzed hydrolysis study but without the added cuprous oxide. The data obtained are also in Table III.

Summary

3-Chloro-1-propyne and 1-chloro-2-butyne have been prepared and characterized. Boiling point data in the literature have been shown to be incorrect.

Reaction of these chlorides with potassium iodide in acetone indicates that a carbon–carbon triple bond increases slightly the reactivity of the chlorine atom in comparison with a carbon–carbon double bond.

1-Chloro-2-butyne reacted more slowly than the crotyl chlorides with sodium ethoxide in ethanol by a factor of about 2.5. This indicates a deactivating influence of the carbon–carbon triple bond for this reaction.

In the reaction between sodium ethoxide in ethanol and 3-chloro-1-propyne there were at least two simultaneous reactions.

1-Chloro-2-butyne was slowly hydrolyzed by a hydrochloric acid solution of cuprous chloride but 3-chloro-1-propyne gave no indication of hydrolysis under the same conditions.

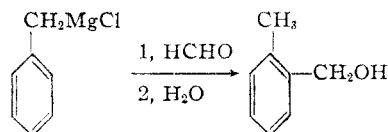(13) Hatch, Brown and Bailey, ibid., **72**, 3198 (1950).

The Reaction of Benzylmagnesium Halides with Alkyl α-Haloalkyl Ethers[1]

BY LLOYD MALM[2] AND LAWRENCE SUMMERS[3]

Many of the reactions of benzylmagnesium halides yield products in which the entering group becomes attached to the ortho or para carbon atom of the aromatic ring.

With most reactants the rearrangement does not proceed to the exclusion of the "normal" reaction; instead, there is usually obtained a mixture of the

ortho-rearranged, para-rearranged and "normal" products. This rearrangement has been the subject of considerable research.[4] However, the publications on this subject have not included any investigation of the effect of regular structural variations in a series of related compounds on the extent of rearrangement. A brief study of this sort is therefore reported here. The reactants chosen were the alkyl α-haloalkyl ethers of the type

(1) From the M.S. thesis of Lawrence Summers, 1941.
(2) Department of Chemistry, University of Utah, Salt Lake City.
(3) Department of Chemistry, University of North Dakota, Grand Forks, N. D.

(4) Leading references: Gilman and Kirby, THIS JOURNAL, **54**, 345 (1932); Austin and Johnson, ibid., **54**, 647 (1932); Johnson, ibid., **55**, 3029 (1933). For studies of analogous rearrangements of related types of organometallic compounds see Gilman and Harris, ibid., **49**, 1825 (1927); Gilman and Breuer, ibid., **56**, 1127 (1934); Gilman and Nelson, ibid., **61**, 741 (1939); and the publications of Young and colleagues on the butenyl Grignard reagent, e.g., Young and Roberts ibid., **68**, 1472 (1946).