[CONTRIBUTION FROM SHELL DEVELOPMENT COMPANY AND THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Dehydrochlorination of 3-Chloro-2-propen-1-ol: Preparation of Propargyl Alcohol[1]

BY LEWIS F. HATCH AND ALLEN C. MOORE[2]

Propargyl alcohol has recently been prepared by interaction of paraformaldehyde and sodium acetylide in liquid ammonia[3] and by dehydrochlorination of 2-chloro-2-propen-1-ol[4] following the method described by Henry.[5] By the first procedure a yield of but 10% was reported while for the other preparation no percentage yield was stated; however, in analogy to the results of Henry, the yield must have been low. Several other methods for the preparation of propargyl alcohol[6] or of its homologs[7] also have been described, but in every case the yields were low. This evident interest in propargyl alcohol coupled with the lack of an adequate method for its preparation instigated the present investigation of the dehydrochlorination of *cis* and *trans* 3-chloro-2-propen-1-ol.

Of the possible starting materials, the isomeric *cis* and *trans* 3-chloro-2-propen-1-ols seemed the most promising for they should react in an analogous manner to the 2-bromo-2-propen-1-ol used by Henry to give propargyl alcohol. The isomeric chloroalcohols are easily prepared from the readily available corresponding dichlorides [*cis*- and *trans*-1,3-dichloropropene], by-products of the semi-commercial production of allyl chloride.[8] The 3-chloroalcohols have been reported,[9] but no note was taken of the presence of two isomeric forms, and the physical constants are unreliable.[10] As the geometric configuration of the isomers of both the 3-chloroalchohol and the dichloride has not as yet been definitely established, α- will be used to designate the lower boiling isomer and β- the higher boiling isomer in each case.

The β-isomer is less reactive than the α-, and, under the reaction conditions necessary for removal of hydrogen chloride, yields no propargyl alcohol. This is not surprising, since, under the conditions used (strong alkali at elevated temperatures), acetylenic alcohols are known to be decomposed.[11] The known decomposition products,[12] acetylene and sodium formate, were obtained from the reaction mixture.

When the sodium hydroxide concentration is greater than 10% there is also a certain amount of polymerization, yielding a polymer similar in properties to that obtained from acrolein under similar circumstances.[13] In view of the possible side reactions it would be anticipated that unreactive olefinic chloroalchols would give poor yields of acetylene derivatives. Since the α-3-chloroalcohol used in this work is more reactive than those hitherto employed, the reaction in this case proceeds satisfactorily and good yields are obtained.

TABLE I

DEHYDROCHLORINATION OF 3-CHLORO-2-PROPEN-1-OL

Run no.	Isomer	Moles of 3-chloro-alcohol	Time, hr.	NaOH, %	% Conversion from Cl^-	% Yield of propargyl alcohol
1	β	0.20	2	3.8	7.2	*a*
2	β	.25	2	12.0	12.8	*a*
3	β	.25	2	22.0	15.2	*a*
4	β	.25	2	29.3	20.2	*a*
5	β	.16	2	38.0	27.5	*a*
6	α	.20	0.5	9.0	36.0	*b*
7	α	.20	1	9.0	58.0	*b*
8	α	.20	3	9.0	72.5	*b*
9	α	.20	5	9.0	86.0	*b*
10	α	.20	2	3.2	52.5	*b*
11	α	.50	2	7.6	61.6	42.2
12	α	.50	2	12.6	70.6	65.1
13	α	.50	2	22.2	75.4	40.0
14	α	.50	2	29.2	79.2	37.8
15	α	.50	2	38.3	80.4	35.0
16	α	.50	3	12.4	76.0	65.8
17	α	1.00	3	12.5	81.0	69.3
18	Mixture	2.00	3	10.0	64.0	50.2[c]

[a] Propargyl alcohol was not obtained in these reactions. [b] Because of the small amount of α-3-chloroalcohol used, no attempt was made to isolate propargyl alcohol. [c] Yield calculated from 3-chloroalcohol applied instead of alcohol reacted.

Physical and chemical data were assembled in the hope of assigning configurations to the stereoisomers, but comparison of the data with the available known compound, 1-bromopropene-1, failed to give clear-cut results. The isomeric

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[1] The process described in this paper for the production of propargyl alcohol is the subject of a patent application assigned to Shell Development Co., Emeryville, California.

[2] From the M.A. thesis of A. C. Moore, June, 1943. Present address: The Citadel, Charleston, S. C.

[3] Hennion and Murray, THIS JOURNAL, **64**, 1220 (1942).

[4] Pauling, Gordy and Saylor, *ibid.*, **64**, 1753 (1942).

[5] Henry, *Ber.*, **5**, 453, 569 (1872); **6**, 729 (1873).

[6] Paal and Heupel, *ibid.*, **24**, 3039 (1891).

[7] See Salkind and Teterin, *ibid.*, **66B**, 321 (1933); Guest, THIS JOURNAL, **47**, 860 (1925); Tchao yin Lai, *Bull. soc. chim.*, **53**, 682 (1933).

[8] Williams, *Trans. Am. Inst. Chem. Engrs.*, **37**, 157 (1941); *Chem. & Met. Eng.*, **47**, 834 (1940).

[9] van Romburgh, *Bull. soc. chim.*, [2] **36**, 555 (1881).

[10] van Romburgh[9] prepared the 3-chloro-2-propen-1-ol by hydrolyzing 1,3-dichloropropene. Apparently he used essentially pure high boiling (β) dichloride and carried out the hydrolysis under conditions (aqueous potassium hydroxide, refluxed for thirty hours) which would have dehydrochlorinated any low boiling (α) chloroalcohol present. He noted the formation of propargylic derivatives and obtained a chloroalcohol of b. p. 153°, d^{15} 1.162.

[11] Thompson and Margnetti, THIS JOURNAL, **64**, 573 (1942).

[12] Henry, *Ber.*, **8**, 398 (1875).

[13] Gilbert and Donleavy, THIS JOURNAL, **60**, 1911 (1938).

pairs which have higher indices of refraction have lower densities (Table II). When the press of war commitments permits, further work will be done on the characterization of these compounds.

TABLE II

PHYSICAL PROPERTIES OF 3-CHLORO-2-PROPEN-1-OL, 1-BROMOPROPEN-1 AND PROPARGYL ALCOHOL

Constant	3-Chloro-2-propen-1-ol Alpha	Beta	1-Bromopropen-1[a] *cis*	*trans*	Propargyl alcohol
B. p. °C.	146.3	153.6	57.8	63.25	112.9
B. p. Mm.	746	756			740
$d^{15.75}_4$			1.4338	1.4169	
d^{20}_4	1.1769	1.1729			0.9488
d^{25}_4	1.1720	1.1681			
d^{35}_4	1.1623	1.1582			
$n^{15.75}_D$				1.4549	
$n^{16.2}_D$			1.4564		
n^{20}_D	1.4638	1.4664			1.4305
n^{25}_D	1.4617	1.4641			
n^{35}_D	1.4573	1.4600			
MR(calcd.)	21.98	21.98	23.35	23.35	15.58
MR(obsd.)	21.69	21.86	22.96	23.16	15.26

[a] From Freudenberg, "Stereochimie," Franz Deuticke, Wien, 1933, p. 751.

Acknowledgment

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Experimental

1,3-Dichloropropene.—In the semi-commercial distillation of crude allyl chloride, prepared by the chlorination of propylene, there remains an appreciable amount of higher boiling material which contains approximately 60% 1,3-dichloropropene and 30% 1,2-dichloropropane.[8] This crude material[13a] served as the source of 1,3-dichloropropene for this investigation. The unsaturated dichlorides were obtained by distillation through a 26 theoretical plate spiral column.[14] Fractions with a boiling range of 102.5–105.5° and 109.5–112.5° were taken and then refractionated to obtain constant boiling fractions at 104.3° and 112.0°. This careful separation was necessary because the isomeric dichlorides are more easily separated by fractionation than are the chloroalcohols.

α-1,3-Dichloropropene: 104.3°; d^{20}_4 1.224; n^{20}_D 1.4682; *MR* (calcd.) 25.32, (obsd.) 25.25.

β-1,3-Dichloropropene: 112.0°; d^{20}_4 1.217; n^{20}_D 1.4730; *MR* (calcd.) 25.32, (obsd.) 25.58.

3-Chloro-2-propen-1-ol.—Both α- and β-1,3-dichloropropene were hydrolyzed to the corresponding chloroalcohols by using a 10% excess of 10% sodium carbonate. The reaction mixture was refluxed two hours (reflux temperature: α-1,3-dichloropropene, 82.5–89°; β-1,3-dichloropropene, 86.0–93.5°), then extracted with diethyl ether, dried, and fractionated; yield, α = 81%; β = 76%. The physical data for the two chloroalcohols are given in Table II. Both isomers have a delayed vesicant action and care should be taken in handling them.

Anal. Calcd. for C_3H_5OCl: Cl, 38.32. Found: α-3-chloro-2-propen-1-ol, 38.22; β-3-chloro-2-propen-1-ol, 38.20.

Dehydrochlorination of β-3-Chloro-2-propen-1-ol.—The chloroalcohol was dehydrochlorinated by refluxing for two hours with a 10% excess of the desired concentration of sodium hydroxide. The reflux temperature varied from 102° for 3.8% sodium hydroxide to 117° for 38% sodium hydroxide. During this reflux period a gas was given off which did not condense at *ca.* −75°. The gas formed explosive salts of both copper and silver and was assumed to be acetylene. The extent of dehydrochlorination was determined by Cl^- titration (Volhard) and OH^- titration. In every case the moles of OH^- utilized by the reaction were greater than the moles of Cl^- produced, indicating a side reaction involving OH^-.

The remaining reaction mixture was made slightly acid with hydrochloric acid, filtered and extracted with diethyl ether. Only unreacted chloroalcohol was obtained. When the reaction mixture was acidified, a small amount of a light brown flocculent precipitate separated. This non-crystallizable solid was readily soluble in alkali and in concentrated sulfuric acid, ethyl alcohol and acetic acid but insoluble in benzene and only slightly soluble in water and diethyl ether. After the flocculent precipitate had been removed by filtration, the remaining solution was distilled to recover any unextracted propargyl alcohol as its water azeotrope (b. p. 97°). None was obtained. The presence of a small amount of formic acid, however, was indicated by the precipitation of manganese dioxide from dilute aqueous potassium permanganate and confirmed by crystals of sodium formate (melting at 253° (cor.)) which were obtained by evaporation of the basic solution.

The effect of sodium hydroxide concentration on the extent of dehydrochlorination is shown by runs 1–5 in Table I. Due to the unreactive nature of this isomer, no study was made of the effect of time on the extent of dehydrochlorination.

Dehydrochlorination of α-3-Chloro-2-propen-1-ol.—The method of dehydrochlorinating α-3-chloro-2-propen-1-ol was the same as that used for the β-isomer. Because the reactivity of α-3-chloro-2-propen-1-ol was considerably greater, not only was the effect of sodium hydroxide concentration studied (runs 10–15) but also the effect of time on the extent of dehydrochlorination was determined (runs 6–9). Data for these experiments are given in Table I.

The propargyl alcohol was recovered by distillation from the reaction mixture after acidification with hydrochloric acid. The water–alcohol azeotrope thus obtained contained in addition to propargyl alcohol any unreacted α-3-chloroalcohol. This azeotrope was saturated with potassium carbonate and extracted with diethyl ether; the ether extract was subsequently distilled through an efficient fractionating column to recover both propargyl alcohol and the unreacted α-3-chloro-2-propen-1-ol. The recovery of the propargyl alcohol from a dilute solution presents a difficult problem for there is only a 3° temperature differential between the boiling point of its water azeotrope and that of water. Continuous ether extraction is suggested as a useful alternative to the method used.

The yields of propargyl alcohol reported are calculated from the amount of 3-chloroalcohol converted (reacted) as indicated by chloride ion formation. The unconverted 3-chloroalcohol was in every case recovered nearly quantitatively and used in subsequent experiments for the production of propargyl alcohol.

Dehydrochlorination of a Mixture of α- and β-3-Chloro-2-propen-1-ol.[15]—An equimolar mixture of the two isomers of 3-chloro-2-propen-1-ol was dehydrochlorinated in a manner similar to that previously described. The only modification in technique was in the use of sodium chloride and isopropyl ether in recovering the alcohols from the water–alcohol azeotrope. The data for this experiment (run 18) are given in Table I. Because the unreacted 3-chloroalcohol consisted mainly of the unreactive β-isomer which could not be used in subsequent preparations of propargyl alcohol, the yield is calculated from the total chloroalcohol applied.

Summary

1. The two isomers of 3-chloro-2-propen-1-ol

[13a] Obtainable from Shell Development Co., Emeryville, California.

[14] Lecky and Ewell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 544 (1940).

[15] This work was done by the senior author (L. F. H.) while in the employ of Shell Development Co., Emeryville, California.

have been prepared and several physical constants have been determined.

2. The dehydrochlorination of the two isomers has been studied and the lower boiling isomer (α) is appreciably more reactive than the higher boiling isomer (β).

3. Propargyl alcohol has been prepared in good yields from the lower boiling isomer (α) and from a mixture of the two isomers.

4. It is impossible to assign definite geometrical structures to the two isomers from the data available.

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

The Preparation of Some Unsaturated Fatty Acid Chlorides[1]

BY THOMAS R. WOOD, F. L. JACKSON, A. R. BALDWIN AND H. E. LONGENECKER

A valuable approach to an understanding of the physical nature and physiological properties of natural fats is afforded by the synthesis of mixed triglycerides of known constitution.[2,3] As our attention turned to the important group of unsaturated triglycerides,[4,5,6] it became desirable to develop a satisfactory method for making unsaturated acyl chlorides of oleic, elaidic, linoleic and linolenic acids.

Attempts to prepare the unsaturated chlorides with thionyl chloride were unsatisfactory.[7] The use of oxalyl chloride had been suggested[8] for some saturated fatty acids and was found in this work to be distinctly preferable for the unsaturated acids.

The possibility of double bond rearrangement during the reaction and subsequent purification merits attention. We have considered the possible formation of conjugated systems, known to arise in polyene acids during alkali treatment or following oxidative changes.[9] No consideration has been given here to possible changes in geometric configuration during reaction. Evidence has been presented[10] for the existence of isomers of the *cis-trans* type in debromination linoleic and linolenic acids, such as were employed in the present study.

Conjugated diene, triene and tetraene linkages in preparations of linoleic and linolenic acids and their acid chlorides were estimated by comparison of the ultraviolet absorption of these compounds in appropriate spectral regions with that of pure 18-carbon conjugated polyene acids. We have employed standard absorption values compiled by Bradley and Richardson[11] for 9,11-(or 10,12)-linoleic, eleostearic and parinaric acids, whose molecular extinction coefficients (ϵ) are 33,600 (232 mμ), 46,700 (270 mμ), and 57,700 (320 mμ), respectively.

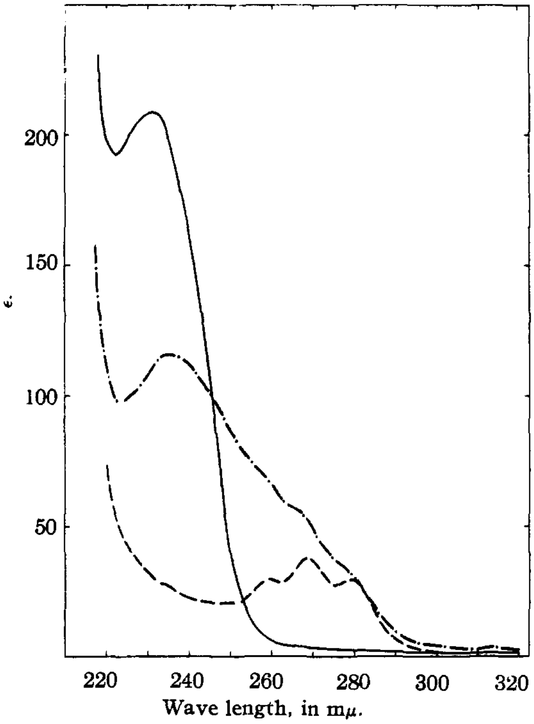

Fig. 1.—Molecular extinction curves in heptane: ———, undistilled linoleic acid; - - - - - -, distilled linoleic acid; -·-·-·-, linoleyl chloride.

The ultraviolet absorption spectra of our linoleic acid and linoleyl chloride are plotted in Fig. 1, while Fig. 2 presents similar data for linolenic acid and linolenyl chloride. It is evident that conversion of the acids to the acid chlorides was in each instance accompanied by an increase in conjugation. In no case, however, was more than 1% of the total acid or acid chloride conjugated (Table II). Moreover, it has been our experience that any manipulation of these highly unsaturated compounds tends to introduce conjugation. Con-

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(1) The authors are indebted to the Buhl Foundation for support of this investigation.

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(2) Daubert and King, *Chem. Rev.*, **29**, 269 (1941).

(3) Daubert and Longenecker, *Oil and Soap*, in press.

(4) Jackson, Longenecker, Daubert and King, THIS JOURNAL, **66**, 289 (1944).

(5) Daubert, Fricke and Longenecker, *ibid.*, **65**, 2142 (1943).

(6) Daubert, Spiegl and Longenecker, *ibid.*, **65**, 2144 (1943).

(7) Jackson, F. L., Ph.D. Thesis, University of Pittsburgh, 1943.

(8) Adams and Ulich, THIS JOURNAL, **42**, 599 (1920).

(9) Mitchell and Kraybill, *ibid.*, **64**, 988 (1942).

(10) Mathews, Brode and Brown, *ibid.*, **63**, 1064 (1941).

(11) Bradley and Richardson, *Ind. Eng. Chem.*, **34**, 237 (1942).