The replacement of the hydrogen on the number 2 carbon by chlorine or bromine decreases the reactivity of the allylic chlorine. The effect of a methyl group in this position is very slight.

The replacement of the hydrogen on the number 1 carbon by chlorine causes a marked increase in reactivity.

It has been confirmed that geometrical configuration has only a slight effect on this reaction. It is suggested that the reaction mechanism for the reaction with sodium ethoxide is different from that in the reaction between allylic chlorides and potassium iodide.

AUSTIN, TEXAS RECEIVED JANUARY 20, 1948

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

Allylic Chlorides. VI. Preparation of the 1,3-Dichloro-2-butenes

BY LEWIS F. HATCH AND STUART G. BALLIN

Several investigators have reported the preparation of 1,3-dichloro-2-butene from either vinylacetylene[1,2] or methyl vinyl ketone,[3] but no attempt was reported of the isolation and characterization of its two geometrical isomers. This is understandable, because the two isomers boil within 2 degrees of one another, and the higher boiling isomer rearranges to the lower boiling isomer rather readily.

Recently, 1,3-dichloro-2-butene has become available commercially and is called DCB.[4] It was possible, however, to obtain only the lower boiling isomer from this material probably because previous heating had rearranged the higher boiling isomer to the lower.

The two isomers of 1,3-dichloro-2-butene have now been prepared by the addition of hydrogen chloride to chloroprene. The isomers have been separated and various physical constants obtained. The same constants were also obtained for the corresponding isomeric chloro-alcohols (3-chloro-2-buten-1-ol). These data, together with available data from the literature, are given in Table I.

The 3,5-dinitrobenzoates were prepared from the dichlorides by use of silver 3,5-dinitrobenzoate and from the chloro-alcohols using 3,5-dinitrobenzoyl chloride. The high boiling chloro-alcohol gave a derivative of each isomer, probably because the hydrogen chloride (produced in the reaction) brought about interconversion.[5] This interconversion was also observed in the regeneration of the dichlorides from the corresponding chloro-alcohols. These interconversions of the high boiling isomer to the low boiling isomer would indicate that the high boiling isomer had the *cis* configuration. The geometrical configuration of the two isomers as indicated by their relative reactivities with potassium iodide,[6] cuprous chloride catalyzed hydrolysis[7] and sodium ethoxide[8] is discussed in the following paper.[9]

Experimental

Attempt to Obtain the Geometrical Isomers of 1,3-Dichloro-2-butene from Commercial Sources.—Only the low boiling isomer of 1,3-dichloro-2-butenes ($n^{25}\mathrm{D}$ 1.4695) was isolated from DCB[4] by distillation at various pressures down to 20 mm.

Hydrochlorination of Chloroprene.—Two moles of chloroprene distilled from a chloroprene solution[10] containing 50% xylene and 0.1% catechol by weight was shaken for twelve hours in a pressure bottle at room temperature with 37% hydrochloric acid (4 moles), 50 g. of cuprous chloride, and 20 g. of ammonium chloride. The reaction mixture was then cooled and the organic layer was separated and distilled at 20 mm. pressure through a 40-cm. vacuum-jacketed column without packing. A 58% yield of relatively pure high boiling 1,3-dichloro-2-butene ($n^{25}\mathrm{D}$ 1.4708 to 1.4712) was obtained together with some unreacted chloroprene and polymers. Repeated distillations of the center cut at 20 mm. pressure caused no change in the refractive index of $n^{25}\mathrm{D}$ 1.4711 if the kettle temperatures were no higher than 35–40°.

Attempts to cause hydrogen chloride to add to chloroprene at room temperature without the use of cuprous chloride or under anhydrous conditions were unsuccessful.

Separation of the Isomeric 1,3-Dichloro-2-butenes.—When the products from the hydrochlorination of chloroprene were distilled through a 4-ft. glass-helices packed column at atmospheric pressure with kettle temperatures in the range of 130–135° a 30–40% yield of relatively pure low boiling 1,3-dichloro-2-butene ($n^{25}\mathrm{D}$ 1.4692–1.4699) was obtained. Further distillations at pressures of 1 atmosphere or less caused no further change in the refractive index of $n^{25}\mathrm{D}$ 1.4695. Moreover, when the higher boiling isomer was distilled at atmospheric pressure, or even at pressures of 150 and 100 mm., only the lower boiling isomer could be obtained in appreciable quantities.

Apparently the high boiling isomer is the labile form and can readily be converted to the stable isomer by heat. Attempts to demonstrate this by maintaining the two isomers at 100° were unsuccessful primarily because polymerization occurred with both isomers, and the resulting products could not be identified. The rate of polymerization of the high boiling isomer exceeded that of the low boiling isomer, as indicated by changes in index of refraction.

Small quantities of each isomer were stored in dark bottles at 0° and at 27° for five months; no change of the index of refraction was observed, but a discoloration developed in each case.

---

(1) Carothers, Collins and Berchet, THIS JOURNAL, **54**, 4066 (1932).

(2) Carothers and Collins, U. S. Patent 2,102,611.

(3) Churbakov, *J. Gen. Chem.* (*U. S. S. R.*), **10**, 977 (1940).

(4) From E. I. du Pont de Nemours & Co., Wilmington, Delaware.

(5) Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 454.

(6) Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1093 (1948).

(7) Hatch and Roberts, *ibid.*, **68**, 1196 (1946).

(8) Hatch and Alexander, *ibid.*, **71**, 1037 (1949).

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

(10) Commercial grade of chloroprene solution was furnished us for this work by the du Pont de Nemours Co., Wilmington, Delaware.

TABLE I

1,3-DICHLORO-2-BUTENE AND 3-CHLORO-2-BUTEN-1-OL

	1,3-Dichloro-2-butene (Low boiling) (alpha)	1,3-Dichloro-2-butene (High boiling) (beta)	3-Chloro-2-buten-1-ol (Low boiling) (alpha)	3-Chloro-2-buten-1-ol (High boiling) (beta)
Boiling point, °C. (mm.)	127.9 (745)	129.9[f] (745)	164.0[f] (738)	166.0[f] (745)
	127–128.5[a]		161–162[c]	
	127–129[b]		115.5 (150)	
	79 (150)		91.5 (50)	
	53 (50)		92[d] (50)	
	53–54[b] (50)			
	33.3 (20)	34.0 (20)	72 (20)	75.0 (20)
Freezing point, °C.	Below −75	Below −75	−40	−47
Index of refract. n^{20}_D	1.4719	1.4735	1.4651	1.4673
	1.4695[a]		1.4678[c]	
	1.4724[b]		1.4652[d]	
n^{25}_D	1.4695	1.4711	1.4630	1.4653
n^{30}_D	1.4670	1.4687	1.4610	1.4633
Density d^{20}_4	1.1585	1.1605	1.1099	1.1128
	1.1582[a]		1.1139[c]	
	1.1591[b]		1.106[d]	
	1.1952[e]			
d^{25}_4	1.1528	1.1542	1.1058	1.1085
d^{30}_4	1.1465	1.1473	1.1014	1.1049
Molecular refract. Calcd.	29.94	29.94	26.60	26.60
Molecular refract. Found	30.21	30.24	26.53	26.52
Anal., % Cl Calcd.	56.8	56.8	33.3	33.3
Anal., % Cl Found	56.5, 57.0	56.6, 56.6	33.1	33.2
3,5-Dinitrobenzoate melting point °C. (cor.)	75–76	58–59	75–76	[g]

[a] Churbakov, *J. Gen. Chem.* (*U. S. S. R.*), 10, 977 (1940). [b] Carothers, Collins and Berchet, THIS JOURNAL, **54**, 4066 (1932). [c] Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **10**, 1418–1424 (1940). [d] Klebanskii and Chevuichalova, *Sintet. Kauchuk* (1935) No. 6 (16–21) (1935), (*Chem. Abst.*, **30**, 1024 (1936)). [e] Tishchenko, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 658 (1937). Maybe this should have been 1.1592. [f] Determined by using a semimicro ebulliometer. [g] Apparently interconversion—both derivatives were isolated.

Various physical data for these dichlorides are given in Table I.

3,5-Dinitrobenzoxy Derivative of the 1,3-Dichloro-2-butenes.—The silver salt of 3,5-dinitrobenzoic acid was prepared by dissolving 4 g. of the acid in 80 ml. of 5% sodium hydrogen carbonate at room temperature. After filtration the solution was acidified with 10% nitric acid until the first permanent cloudiness of the free acid appeared. A 10% silver nitrate solution was added dropwise until no further silver salt precipitated. The product was filtered with suction, washed successively with hot water, ethanol, and ethyl ether, and dried in a vacuum desiccator. A 2-g. yield of a very light, flaky, white solid melting at 315° was obtained. Silver 3,5-dinitrobenzoate is very insoluble in water and all common organic solvents, but it dissolves readily in pyridine. It burns with a flame leaving a silver residue.

One gram of silver 3,5-dinitrobenzoate (0.0031 mole) was refluxed in 3 ml. of 95% ethanol with 0.3 ml. (0.0028 mole) of 1,3-dichloro-2-butene for one hour. The solid product was extracted with three 3-ml. portions of boiling ether, filtered and evaporated to dryness. The resulting yellowish solid was triturated with 5 ml. of 5% sodium carbonate solution and filtered with suction. More sodium carbonate solution followed by distilled water was used to wash the derivative.

Recrystallization of the benzoates from an ethanol-water solution produced nearly white crystals, melting at 75–76° for the low boiling dichloride, and 58–59° for the high boiling isomer. Further purification by this procedure produced no change in the melting points.

Basic Hydrolysis of the 1,3-Dichloro-2-butenes.—One hundred and twenty-five grams of the dichloride (1.0 mole) was treated with 106 g. of sodium carbonate (1.0 mole) in 2500 g. of water (4% sodium carbonate) in a 3-l. three-necked flask equipped with a stirrer. After three hours at 80° the two phases became homogeneous. The chloro-alcohol was distilled off as an azeotrope (98.1° for the low boiling isomer and 98.8° for the high boiling isomer). The aqueous layer in the distillate was further concentrated by distilling through a 3-ft column packed with glass helices; an additional quantity of the chloro-alcohol separated when the solution was saturated with sodium chloride. Yield of the crude 3-chloro-2-buten-1-ol was 75%.

Catalytic Hydrolysis of the 1,3-Dichloro-2-butenes.—The hydrolysis procedure used was similar to that for the basic hydrolysis except that the hydrolyzing solution contained 1.5% hydrochloric acid and enough copper (I) oxide to have 0.1 mole of cuprous chloride for each mole of allylic chloride and hydrogen chloride. The reaction was completed in less than a third of the time required for the basic hydrolysis, but the yield of the 3-chloro-2-buten-1-ol was not as high, because of a side reaction producing methylvinyl ketone.[9]

The isomeric chloro-alcohols were obtained by distillation through a 40-cm. column at 20 mm. pressure. As in the case of the corresponding dichloride, the high boiling isomer was readily converted to the low boiling, stable isomer by heat. Atmospheric boiling points were obtained on a semi-micro scale. The physical data obtained for these compounds are given in Table I.

3,5-Dinitrobenzoate of the 3-Chloro-2-buten-1-ols.—One ml. of each isomer of the chloro-alcohol was heated for ten minutes near its boiling point in a small test-tube with 0.5 g. of 3,5-dinitrobenzoyl chloride. The products were recrystallized from hot ethanol-water solution and identified by their melting points. The 3,5-dinitrobenzoxy derivative of the low-boiling 3-chloro-2-buten-1-ol melted at the same point as the 3,5-dinitrobenzoxy derivative of the low boiling 1,3-dichloro-2-butene (75–6°). A mixture of the two dinitrobenzoxy derivatives also melted at 75–6°. The high boiling 3-chloro-2-buten-1-ol apparently gave a mixture of both isomers of 1-(3,5-dinitrobenzoxy)-3-chloro-2-butene.

Regeneration of the 1,3-Dichloro-2-butenes from the 3-Chloro-2-buten-1-ols.—Hydrogen chloride was passed for fifteen hours at room temperature into a 20-ml. sample of the chloro-alcohol contained in a small flask fitted with a reflux condenser. Heat developed at first, and there was an aqueous layer toward the end of the reaction. The product was washed twice with 25-ml. portions of water and dried over calcium chloride. Analysis by distillation at 20 mm. showed that while the corresponding dichloride was obtained from the low boiling chloro-alcohol, the high boiling isomer gave both isomeric 1,3-dichloro-2-butenes.

Summary

The two geometrical isomers of 1,3-dichloro-2-butene have been prepared and the index of refraction, density, boiling point and the melting point of the 3,5-dinitrobenzoxy derivative of each isomer have been obtained.

The higher boiling isomer was converted into the lower boiling isomer at its boiling point, but it was stable at room temperature.

The index of refraction, density, freezing point, and boiling point of each isomer of 3-chloro-2-buten-1-ol have also been determined.

The low boiling 3-chloro-2-buten-1-ol gave the same 3,5-dinitrobenzoxy derivative as the low boiling dichloride but the high boiling chloro-alcohol gave a mixture of the two isomeric benzoates.

The high boiling 3-chloro-2-buten-1-ol is converted to the low boiling isomer by heat, and when treated with hydrogen chloride, a mixture of the isomeric 1,3-dichloro-2-butenes is formed.

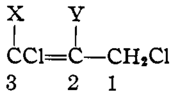
AUSTIN, TEXAS RECEIVED APRIL 20, 1948

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

Allylic Chlorides. VII. Relative Reactivities of the 1,3-Dichloro-2-butenes

BY LEWIS F. HATCH AND STUART G. BALLIN

Current work on allylic chlorides has shown that geometrical isomerism plays an important part in determining the reactivity of the allylic chlorine with potassium iodide in acetone,[1] sodium ethoxide in ethanol,[2] and in the cuprous chloride catalyzed hydrolysis reaction.[3] These studies have been made using dichlorides with the basic structure



$$\underset{3}{\overset{\text{X}}{\text{C}}}\text{Cl}=\underset{2}{\overset{\text{Y}}{\text{C}}}-\underset{1}{\text{CH}_2\text{Cl}}$$

where X and Y are either both hydrogens, or where X is hydrogen and Y is a methyl group.

The recent availability of the two isomers of 1,3-dichloro-2-butene[4] has made possible an extension of this investigation to include a compound where X is a methyl group and Y is hydrogen. A compound of this type should be especially useful in evaluating the influence of steric hindrance of groups on the number 3 carbon for an S_N2 type reaction involving the number 1 carbon. A study of the influence of the relative position of the vinyl chlorine has been made by Tishchenko[5] for hydrolysis using calcium carbonate and water. He made no effort to separate the two isomers of 1,3-dichloro-2-butene.

Experimental

1,3-Dichloro-2-butenes.—The isomeric 1,3-dichloro-2-butenes were prepared by the addition of hydrogen chloride to chloroprene.[4] They had the following physical properties: low boiling (alpha) isomer: b. p. (20 mm.) 33.3°; n^{25}_D 1.4695; d^{25}_4 1.1528; high boiling (beta) isomer: b. p. (20 mm.) 34.0°; n^{25}_D 1.4711; d^{25}_4 1.1542.

Catalytic Hydrolysis with Cuprous Chloride in Hydrochloric Acid.—The procedure previously reported[3] was modified to permit the use of the more stable cuprous oxide (Baker C. P. Analyzed, 98.8%) instead of cuprous chloride. One-fourth gram (0.0017 mole) of cuprous oxide was placed in a 200-ml. 3-necked flask fitted with a stirrer, condenser, and combination thermometer-well and carbon dioxide delivery tube. One hundred milliliters of 1.5% hydrochloric acid (0.041 mole) was added to the reaction flask and the cuprous oxide dissolved in about fifteen minutes at 75–85°. Carbon dioxide was slowly passed over the surface of the solution from the time the hydrochloric acid was added to the flask until the run was completed.

A five gram sample of the 1,3-dichloro-2-butene was weighed to the nearest milligram into 4 gelatin capsules (size 000). These capsules were added to the flask by removing the condenser, and dissolved within ten seconds under vigorous stirring. The reaction was carried out at a temperature of 40 ± 0.5°. At the end of the desired time the reaction mixture was cooled to 20° in about three minutes and a 1-ml. sample of the aqueous layer was pipetted into 50 ml. of distilled water containing 2 ml. of 10% sodium hydrogen carbonate solution. The extent of reaction was determined from the increase in chloride ion in a manner similar to that previously reported.[3]

Data for the hydrolysis of both isomers are given in Table I and Fig. 1. Both isomers gave chloride ion concentrations indicating that both chlorine atoms were hydrolyzable under the conditions of the reaction. The lower boiling isomer (alpha) gave the following data in addition to those in Table I: 6.25 hours, 122.0%; 9.00 hours, 131.5%.

The reaction mixtures apparently contained in addition to 3-chloro-2-buten-1-ol, a relatively large amount of methyl vinyl ketone. Tishchenko has reported[5] the formation of about 2% methyl vinyl ketone when 1,3-dichloro-2-butene was hydrolyzed with calcium carbonate.

Attempted Catalytic Hydrolysis of 3-Chloro-2-buten-1-ol.—Attempts were made to hydrolyze the vinyl chlorine of the lower boiling isomer of 3-chloro-2-buten-1-ol using the same conditions as used for the dichloride. There was no appreciable hydrolysis in half an hour at 40°, 60°, 80° or in 4.5 hours at 60°.

---

(1) Hatch, Gordon and Russ, THIS JOURNAL, **70**, 1093 (1948).

(2) Hatch and Alexander, *ibid.*, **71**, 1037 (1949).

(3) Hatch and Roberts, *ibid.*, **68**, 1196 (1946).

(4) Hatch and Ballin, *ibid.*, **71**, 1039 (1949).

(5) Tishchenko, *J. Gen. Chem.* (*USSR*), **7**, 658 (1937).