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.

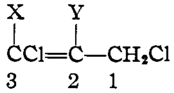
AUSTIN, TEXAS RECEIVED APRIL 20, 1948

[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



$$\underset{3}{\overset{X}{\overset{|}{C}}}Cl=\underset{2}{\overset{Y}{\overset{|}{C}}}-\underset{1}{CH_2Cl}$$

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°.

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[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).

TABLE I

RELATIVE REACTIVITIES OF THE 1,3-DICHLORO-2-BUTENES

Hydrolysis with Cuprous Chloride at 40°						
Low boiling	Time, hr.	0.50	1.00	2.00	3.50	4.50
	% reacted	17.3	32.8	57.3	89.5	101.5
High boiling	Time, hr.	0.50	1.00	2.00	4.00	8.00
	% reacted	25.9	42.7	69.3	106.5	141.2
Reaction with Potassium Iodide in Acetone at 20°						
Low boiling	Time, min.	15	30	45	54	80
	% reacted	44.6	62.7	77.9	83.6	94.7
	k	5.40	4.63	4.85	4.90	5.57
	Av. k			5.07		
	Relative reactivity[a]			23.3		
High boiling	Time, min.	12	24	36	54	72
	% reacted	40.4	64.5	79.2	88.4	94.6
	k	5.88	6.09	6.32	5.91	6.13
	Av. k			6.07		
	Relative reactivity[a]			27.8		
Reaction with Sodium Ethoxide in Ethanol in 50°						
Low boiling	Time, hr.	3.00	4.00	5.00	6.00	7.00
	% reacted	42.5	48.9	54.5	58.7	61.1
	k	5.62	5.89	5.64	5.74	5.49
	Av. k			5.68		
	Relative reactivity[b]			4.77		
High boiling	Time, hr.	3.00	4.00	5.00	6.00	7.00
	% reacted	46.5	56.3	61.1	64.3	66.5
	k	6.80	7.75	7.68	7.31	7.12
	Av. k			7.33		
	Relative reactivity[b]			6.16		

[a] Allyl chloride as 1.00 with $k = 0.218$. [b] Allyl chloride as 1.00 with $k = 1.19$ (Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 119 (1941)).

Reaction with Potassium Iodide in Acetone.—The same procedure was used as previously described.[1] Reaction rates and other data are given in Table I.

Reaction with Sodium Ethoxide in Ethanol.—These rates were also determined using a previously described procedure.[2] The concentration of the 1,3-dichloro-2-butenes was 0.1000 molar and the sodium ethoxide solution in ethanol was 0.0905 molar. The rate constants and other data are also given in Table I.

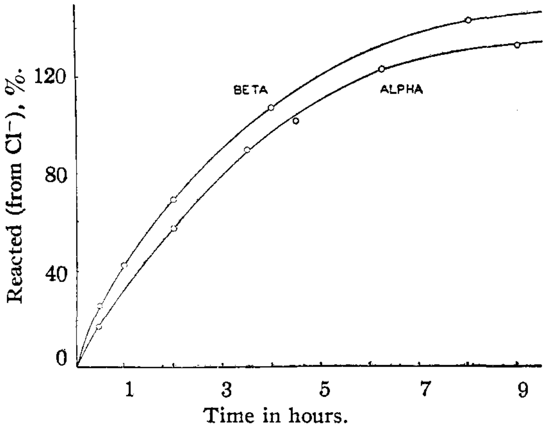

Fig. 1.—Catalytic hydrolysis of 1,3-dichloro-2-butene with cuprous chloride in hydrochloric acid.

Discussion

Previous work on the influence of geometrical isomerism on the reactivity of allylic chlorides has been with isomers of the types Cab–Cad and Cab–Cdc. The *cis* configuration for the latter type has been assigned to the isomer with the vinyl chlorine and the chloromethyl group on the same side of the molecule. The same convention is used with 1,3-dichloro-2-butene.

Neither of the isomers of either 1,3-dichloropropene or 1,3-dichloro-2-methyl-1-propene undergoes interconversion to the more stable form at its boiling point. With 1,3-dichloro-2-butene, however, the higher boiling isomer is readily converted at its boiling point to the lower boiling isomer.[4] Usually the *cis* form of geometrical isomers is the labile form and the *trans* form the stable one. The higher boiling (beta) isomer of 1,3-dichloro-2-butene is therefore tentatively assigned the *cis* configuration and the lower boiling (alpha) isomer the *trans* configuration.

It has previously been proposed from chemical evidence that the higher boiling isomers of both 1,3-dichloropropene and 1,3-dichloro-2-methyl-1-propene have the *cis* configuration. Chemical evidence of the type obtained in these studies, however, may be amenable to several interpretations. Andrews and Kepner[6] have interpreted some of these results in such a way as to indicate that the higher boiling isomers have the *trans* configuration.

Catalytic Hydrolysis.—From the nature of the reaction and the errors inherent in following its course it has not been considered desirable to calculate a rate constant for the cuprous chloride catalyzed hydrolysis of 1,3-dichloro-2-butene. Figure 1 gives a graphic indication of the differences in rate of reaction between the two isomers.

As with 1,3-dichloropropene[3,7] the high boiling isomer of 1,3-dichloro-2-butene is the more reactive, but the difference in reactivity between the two isomers is not as great as it is between the isomers of 1,3-dichloropropene. This would indicate that a methyl group on the number 3 carbon of the *cis* isomer offers some interference to this reaction, although the over-all effect of a methyl group on this carbon is one of activation.

The fact that both chlorines of 1,3-dichloro-2-butene are hydrolyzable by cuprous chloride in hydrochloric acid while the vinyl chlorine in 3-chloro-2-buten-1-ol is not hydrolyzed under the same conditions is being studied further. Because both chlorines are removed from the dichloride, it was not possible to compare the rate of reaction of this compound with 1,3-dichloropropene to evaluate the effect of replacing a hydrogen on the number 3 carbon with a methyl group.

Potassium Iodide.—An interpretation of the results of the S_N2 reaction of potassium iodide with 1,3-dichloro-2-butene is based on the assumption that the reaction involves a nucleophilic attack on the carbon atom holding the allylic chlorine. A reaction of this type would be inhibited by the group in the *cis* position on the number 3 carbon with the size of the group governing the degree of inhibition. With 1,3-dichloropropene and 1,3-dichloro-2-methyl-1-propene the two substit-

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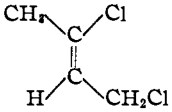
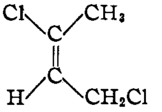
[6] Andrews and Kepner, THIS JOURNAL, **69**, 2230 (1947).

[7] Data for the 1,3-dichloro-2-methyl-1-propenes will be given in a forthcoming paper.

uents are chlorine and hydrogen with a consequent wide difference in the relative reactivity of the geometrical isomers. When the two substituents are chlorine and a methyl group as with 1,3-dichloro-2-butene the difference in reactivity is only slight with the *cis* form being the most reactive.



cis, more reactive



trans, less reactive

The larger methyl group would be expected to cause the *trans* isomer to be less reactive.

A methyl group increases the reactivity of the allylic chlorine for this reaction when it is not in the *cis* position, where its activating effect is counteracted by its steric hindrance. This activation of the allylic chlorine by a methyl group on the number 3 carbon has been noted by Tamele, *et al.*,[8] and in these laboratories with 1-chloro-3-methyl-2-butene.[9]

Sodium Ethoxide.—The two isomers of 1,3-dichloro-2-butene show a relatively small difference in reactivity with the higher boiling isomer being the more reactive. This is similar to the results obtained with 1,3-dichloropropene and 1,3-dichloro-2-methyl-1-propene[2] and provides further evidence that this reaction is of a type different from that with potassium iodide and is only slightly affected by geometrical isomerism. As with the reaction with potassium iodide, substituting a methyl group for a hydrogen on the number 3 carbon increases the reactivity of the allylic chlorine. This observation has also been made by Tamele, *et al.*[8]

Summary

The relative reactivity of the geometrical isomers of 1,3-dichloro-2-butene has been determined for their reaction with potassium iodide, sodium ethoxide, and the cuprous chloride catalyzed hydrolysis reaction.

The high boiling (beta) isomer was the most reactive with each reagent.

The high boiling (beta) isomer is converted at its boiling point into the low boiling (alpha) isomer.

For these reasons the low boiling (stable) isomer of 1,3-dichloro-2-butene has tentatively been assigned the *trans* structure.

A methyl group on the number 3 carbon increases the reactivity of the allylic chlorine of 1,3-dichloro-2-butene.

AUSTIN, TEXAS RECEIVED APRIL 20, 1948

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[8] Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

[9] Unpublished work of Louis S. Gerhardt.

[CONTRIBUTION FROM PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

Preparation and Properties of Certain Alkyl Azamalonates[1]

BY CHESTER E. SLIMOWICZ AND ED., F. DEGERING

Although urethan, or ethyl carbamate, and many of its derivatives have been investigated as physiologically active agents,[2,3] no record has been found of a similar study of the unsubstituted alkyl azamalonates. The preparation of a few of these compounds has been reported, namely, ethyl methyl,[6] dimethyl,[7] diethyl,[4] and the ethyl phenyl[5] azamalonates.

Recently, Tompkins and Degering[10] have described a series of N-substituted diethyl azamalonates. In connection with this work, it was deemed desirable to prepare a series of N-unsubstituted azamalonates of the general formula ROOCNHCOOEt. These compounds were prepared by a modification of the procedure employed by Kraft.[8] The reaction may be represented by the equations

$$\mathrm{H_2NCOOEt + Na \longrightarrow H(Na)NCOOEt + {}^1/_2H_2,\ then}$$
$$\mathrm{H(Na)NCOOEt + ClCOOR \longrightarrow ROOCNHCOOEt + NaCl}$$

It was found, however, that besides the expected mixed alkyl ethyl ester there were obtained the symmetrical diethyl and dialkyl di-esters. It is significant to note that the yield of the dialkyl di-ester, in general, was higher than that for the expected mixed ester. This result may be interpreted by assuming that a redistribution reaction occurred.

The compounds were either white crystalline solids having fairly low melting points, or colorless liquids having high boiling points. In all cases the di-esters were solids and the mixed esters were liquids. All of the compounds were generally soluble in the common organic solvents and insoluble in water. Their identification was based

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[1] Abstracted from a thesis presented by Chester E. Slimowicz to the Faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Master of Science, Feb., 1947.

[2] Dixon, "Manual of Pharmacology," Arnold, London, 1908, p. 68.

[3] Hirshfelder and Bieter, *Physiol. Rev.*, **12**, 190 (1932).

[4] Diels, *Ber.*, **36**, 736 (1903); see also refs. 6, 8, 9a, 9b, 9c.

[5] Diels and Jacoby, *ibid.*, **41**, 2397 (1908).

[6] Diels and Nawiasky, *ibid.*, **37**, 3672 (1904).

[7] Franchimont and Klobbie, *Rec. trav. chim.*, **8**, 294 (1889).

[8] Kraft, *Ber.*, **23**, 2786 (1890).

[9] (a) Wurtz and Henninger, *Chem. Zentr.*, **56**, 564 (1885); (b) *Bull. soc. chim.*, **44**, 30 (1885); (c) *Compt. rend.*, **100**, 1419 (1885).

[10] Tompkins with Degering, THIS JOURNAL, **69**, 2616 (1947).