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DEHYDROHALOGENATION OF SEVERAL VINYL HALIDES[1]

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The dehydrohalogenation of unsaturated alcohols containing vinyl halogen atoms has been used since 1872 (1) for the production of acetylenic alcohols, but no attempt has been made to relate either the nature of the halogen atom or its position on the carbon chain with the extent of reaction. The influence of geometrical isomerism has, however, been determined for both 3-chloro-2-propen-1-ol (2) and 3-chloro-2-buten-1-ol (3), and the information obtained has been used to elucidate the structures of these compounds (3, 4, 5) under the assumption that *trans*-elimination takes place more readily than *cis*-elimination.

The present study was made to obtain quantitative data pertaining to the ease of removal by aqueous alkali of a bromine atom and a chlorine atom on the number 2 carbon atom of 2-halo-2-propen-1-ol and to compare these reactivities with those previously reported for the 3-chloro-2-propen-1-ols and the 3-chloro-2-buten-1-ols. The data plotted in Figure 1 show the effect of sodium hydroxide concentration on the extent of reaction, while Figure 2 gives data related to the effect of time on the extent of reaction using a 10% solution of sodium hydroxide at 100°.

The dehydrobromination reaction was expected to take place more readily than the dehydrochlorination reaction but the great ease of dehydrobromination found was surprising. The low yields of propargyl alcohol from 2-bromo-2-propen-1-ol reported in the literature (1) probably resulted from using conditions much more severe than actually were required, with subsequent decomposition of the propargyl alcohol originally formed. It is also possible that the dehydrohalogenation reaction may, in part, involve a hydrogen atom on the number 3 carbon atom, to give hydroxyallene which would rearrange to acrolein. The formation of 2,3-epoxypropene is also a possibility. It is felt, however, that these side reactions are not the main cause for the low yields of propargyl alcohol. It is also obvious that any method of preparation of 2-bromo-2-propen-1-ol involving a basic medium will have dehydrobromination as an important side reaction.

The relationship between the ease of dehydrochlorination and the position of the chlorine atom on the carbon chain can not be ascertained from the available data because 2-chloro-2-propen-1-ol has a reactivity greater than the *trans*-isomer of 3-chloro-2-propen-1-ol and less than the *cis*-isomer and also because

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of the possibility of side reactions with 2-chloro-2-propen-1-ol. In comparison with 3-chloro-2-buten-1-ol (3) it appears that there is only a small difference

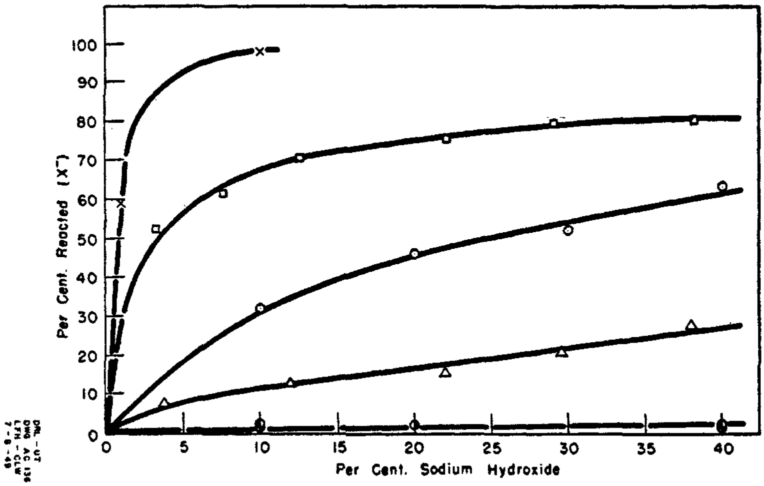

FIGURE 1. EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON THE EXTENT OF REACTION FOR 2 HOURS AT REFLUX TEMPERATURE

2-Bromo-2-propen-1-ol—X; 2-chloro-2-propen-1-ol—○; *cis*-3-chloro-2-propen-1-ol—□; *trans*-3-chloro-2-propen-1-ol—△; *cis*-3-ethoxy-1-chloro-1-propene—◐; *trans*-3-ethoxy-1-chloro-1-propene—◑.

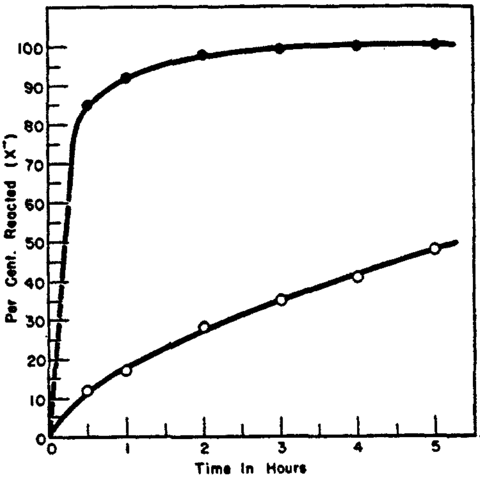

FIGURE 2. EFFECT OF TIME ON THE EXTENT OF REACTION USING 10% SODIUM HYDROXIDE AT 100°

2-Bromo-2-propen-1-ol—●; 2-chloro-2-propen-1-ol—○

in reactivity between the number two position and the number three position when the chlorine atom involved is attached to a carbon atom which in turn is attached to two other carbon atoms. Under comparable conditions of time

(2 hrs.), temperature (101.5°), and sodium hydroxide concentration (10%), 2-chloro-2-propen-1-ol reacted to the extent of 31%, α-3-chloro-2-buten-1-ol 32%, and β-3-chloro-2-buten-1-ol 27%. *trans*-3-Chloro-2-propen-1-ol has been dehydrochlorinated in the course of other work in this laboratory to give a 79% yield of 2-butyn-1-ol, which indicates the substantial absence of side reactions.

The two isomers of 3-ethoxy-1-chloro-1-propene were prepared from the corresponding isomers of 1,3-dichloropropene by reaction with sodium ethoxide. Both *cis*- and *trans*-3-ethoxy-1-chloro-1-propene were very resistant to the action of sodium hydroxide in aqueous solution, but they both developed hydrochloric acid rapidly on standing at room temperature in the presence of moisture. The lack of reaction with aqueous sodium hydroxide is attributable to the very low solubility of the ethers in a solution of this nature. When a 20% solution of potassium hydroxide in a 15% ethyl alcohol-85% water solvent was used as the dehydrochlorination medium, the lower-boiling isomer dehydrochlorinated more extensively than the higher-boiling isomer.

Assuming a greater ease for *trans*-elimination, then the lower-boiling isomer of 3-ethoxy-1-chloro-1-propene would be assigned the *cis*-structure (in respect to the two hydrogen atoms attached to the carbon atoms associated with the carbon-carbon double bond). This assignment of configuration is consistent with the origin of the ether from the lower-boiling isomer of 1,3-dichloropropene to which the *cis*-configuration has been assigned (5). The higher-boiling isomer would then have the *trans*-configuration.

Incidental to this study of dehydrohalogenation there have been obtained more accurate physical data for 2,3-dibromo-1-propene and 2-bromo-2-propen-1-ol and *cis*- and *trans*-3-ethoxy-1-chloro-1-propene have been prepared and characterized for the first time. The two previous references in the literature to these ethers apparently pertained in one incidence (6) to a mixture of the two isomers and in the other (7) to the *trans*-isomer[4].

EXPERIMENTAL

2,3-Dibromo-1-propene. This compound was prepared from 1,2,3-tribromopropane by the action of a concentrated solution of sodium hydroxide in a manner similar to that described in *Organic Syntheses* (8). Yield 72%; b.p. 40.5° (18 mm.), n_D^{25} 1.5416, d_4^{25} 2.0346 [Lit. (9) n_D^{20} 1.5157, d_4^{20} 1.9336]; MR (obs'd), 31.12; MR (calc'd), 30.91.

2-Bromo-2-propen-1-ol. This bromo alcohol was prepared from 2,3-dibromo-1-propene by hydrolysis, using a 10% excess of 10% sodium carbonate solution at 95° for seven hours. The yield was only 47% because of the severity of the conditions; subsequent dehydrobromination studies suggest that there was some loss through removal of both bromine atoms.

The 2-bromo-2-propen-1-ol was separated from the reaction mixture, dried with magnesium sulfate, and distilled through a three-foot glass helix-packed fractionating-column. B.p. 60–61° (18 mm.), n_D^{25} 1.4973, d_4^{25} 1.6360; MR (obs'd), 24.88; MR (calc'd), 24.52.

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[4] While this paper was in press Smith and King, *J. Am. Chem. Soc.*, **72**, 95 (1950) published the following data on these ethers: "product from the 112° 1,3-dichloropropene-1, b.p. 128.0° (740 mm.), n_D^{25} 1.4306; product from the 104° 1,3-dichloropropene-1, b.p. 120–121° (740 mm.), n_D^{25} 1.4282".

2-Chloro-2-propen-1-ol. The 2-chloro-2-propen-1-ol used in this investigation was furnished by Shell Development Co., Emeryville, California and had the following constants: b.p. 134°, n_D^{20} 1.460, d_4^{20} 1.162. It was used without further purification other than simple distillation.

cis- and trans-3-Ethoxy-1-chloro-1-propene. Both isomers of 3-ethoxy-1-chloro-1-propene were prepared in a similar manner by treating the appropriate isomer of 1,3-dichloropropene with sodium ethoxide in ethanol. *cis-* and *trans-*1,3-Dichloropropene were isolated from D-D (furnished by Shell Chemical Co., Houston, Texas) by fractionation. *cis-*1,3-Dichloropropene: b.p. 103.5–104.5° (746 mm.), n_D^{25} 1.4650 [Lit. (5) n_D^{25}1.4652]. *trans-*1,3-Dichloropropene: b.p. 112.0–112.3° (745 mm.), n_D^{25} 1.4696 [Lit. (5) n_D^{25} 1.4712].

One mole (111 g.) of 1,3-dichloropropene and one mole of sodium ethoxide in 500 ml. of ethanol were mixed at room temperature in a one-liter three-necked flask fitted with a thermometer, stirrer, and reflux condenser. The heat of the reaction caused the temperature of the mixture to rise to 75° within 30 minutes. Stirring was continued for another 1½ hours, during which time the temperature dropped to 40°. The sodium chloride was removed; then distilled water was added until two layers were formed. The organic layer was separated and dried with calcium chloride which removed both the water and the ethanol. After a 24-hour treatment with calcium chloride, the ether was distilled through an 18-inch glass helix-packed column.

cis-3-Ethoxy-1-chloro-1-propene[4]*:* Yield 71%; b.p. 120.5° (749 mm.), n_D^{25} 1.4290, n_D^{30} 1.4270; d_4^{25} 0.9941; MR (obs'd), 31.36; MR (calc'd), 31.33.

Anal. (10) Calc'd: Cl, 29.40. Found: Cl, 29.31, 29.26.

trans-3-Ethoxy-1-chloro-1-propene[4]*:* Yield 76%; b.p. 126° (747 mm.), n_D^{25} 1.4310, n_D^{30} 1.4291; d_4^{25} 0.9935; MR (obs'd), 31.34; MR (calc'd), 31.33.

Anal. (10) Calc'd: Cl, 29.40. Found: Cl, 29.49, 29.56.

Dehydrohalogenation of 2-chloro-2-propen-1-ol and 2-bromo-2-propen-1-ol. Two series of dehydrohalogenation runs were made with the chloro and bromo alcohols to evaluate the influence of both sodium hydroxide concentration and time on this reaction. The procedure used was essentially the same as that previously described by Hatch and Moore (2).

The first series of runs used 2-chloro-2-propen-1-ol and sodium hydroxide concentrations of 10%, 20%, 30%, and 40% for two hours at the reflux temperature of the solution. These conditions permitted a direct comparison of the reactivity of a chlorine atom on the number 2 carbon atom with data previously reported (2) pertaining to the reactivity of a chlorine atom on the number 3 carbon atom under these conditions. This comparison is made in Figure 1. Two runs under similar conditions using 2-bromo-2-propen-1-ol are also plotted in Figure 1.

A second series of runs was made at 100° using 2-chloro-2-propen-1-ol and a 10% sodium hydroxide solution with time as a variable. These data are given in Figure 2 along with comparable data for 2-bromo-2-propen-1-ol.

The reaction mixtures from the various runs were combined and a low yield (30%) of propargyl alcohol was obtained which had the following constants: b.p. 113.0° (747 mm.), n_D^{25} 1.4292, d_4^{25} 0.9446; MR (obs'd), 15.31; MR (calc'd), 15.58 [Lit. (11) b.p. 113.6° (760 mm.), n_D^{20} 1.4320, d_4^{20} 0.9478; MR (obs'd), 15.33; MR (calc'd), 15.58).

Dehydrochlorination of cis- and trans-3-ethoxy-1-chloro-1-propene. Several attempts were made to dehydrochlorinate both *cis-* and *trans-*3-ethoxy-1-chloro-1-propene using aqueous sodium hydroxide solutions. The amount of chloride ion produced in every case was negligible as indicated in Figure 1.

Under the assumption that the lack of reactivity was primarily caused by the low solubility of the ethers in the reaction medium, an alcohol (15%)-water (85%) solution of 20% potassium hydroxide was used. The following results were obtained: *cis-*3-ethoxy-1-chloro-1-propene—2 hrs. 8.5% (Cl^-), 4 hrs. 10.9% (Cl^-); *trans-*3-ethoxy-1-chloro-1-propene —4 hrs. 2.2% (Cl^-). Although the extent of reaction is not great in any case, a distinct difference in reactivity is shown between the two isomers with the lower-boiling isomer being the more reactive.

SUMMARY

Both 2-chloro-2-propen-1-ol and 2-bromo-2-propen-1-ol have been dehydrohalogenated under various conditions of time and sodium hydroxide concentration.

The 2-bromo-2-propen-1-ol was shown to be appreciably more reactive than either the 2-chloro-2-propen-1-ol or the two isomers of 3-chloro-2-propen-1-ol previously reported while 2-chloro-2-propen-1-ol has a reactivity between those of the two isomers of 3-chloro-2-propen-1-ol and about the same reactivity as the two isomers of 3-chloro-2-buten-1-ol.

More accurate physical constants have been obtained for 2,3-dibromo-1-propene and 2-bromo-2-propen-1-ol.

cis- and *trans*-3-Ethoxy-1-chloro-1-propene have been prepared and characterized.

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