CHEMISTRY

Academician of the Academy of Sciences of the Armenian SSR V. I. ISAGULYANTS and I. S. MAKSIMOVA

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Abstract

Full Text

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TRANSFORMATIONS OF β-CHLORO ETHERS IN THE PRESENCE OF METALS

In an earlier communication (^{1}) a new reaction of β-chloro ethers was described —their ability, under certain conditions, to split off hydrogen chloride with the almost quantitative formation of α-substituted vinyl ethers. The new method for obtaining α-substituted vinyl ethers at the same time makes it possible to obtain from them any ketones.

Developing our investigations in the field of transformations of β-chloro ethers, we studied their transformations in the presence of various metals. The experiments were carried out mainly with the methyl ether of α-amylene chlorohydrin and with the metals sodium, copper, aluminum, and magnesium.

Under the action of metallic sodium on the methyl ether of α-amylene chlorohydrin, the following transformations could have been expected:

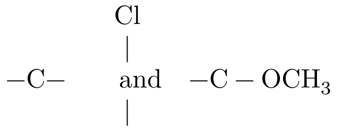
$$CH_3CH_2CH_2CH(OCH_3)-CH_2Cl+2Na+ClCH_2-CH(OCH_3)-CH_2CH_2CH_3 \longrightarrow$$

$$\longrightarrow CH_3CH_2CH_2CH(OCH_3)-CH_2-CH_2CH(OCH_3)-CH_2CH_2CH_3+2NaCl$$

with the formation, as the final product of the reaction, of the dimethyl ether of decanediol. However, as a result of the reaction, amylene, an alcoholate, and sodium chloride were isolated according to the scheme:

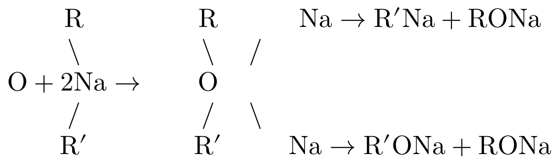
$$CH_3CH_2CH_2CH(OCH_3)-CH_2Cl+2Na \rightarrow CH_3CH_2CH_2CH{=}CH_2+CH_3ONa+NaCl,$$

i.e., cleavage of the bonds



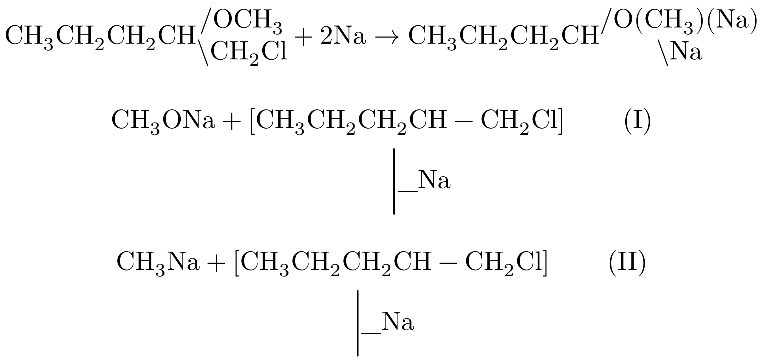
$$\begin{array}{ccc} & \text{Cl} & \\ & | & \\ -\text{C}- & \text{and} & -\text{C}-OCH_3 \\ & | & \end{array}$$

takes place. According to P. P. Shorygin (2), under the action of metallic sodium on simple ethers, cleavage of the ROR bond occurs according to the scheme:



$$\begin{array}{c} R \\ \backslash \\ O \\ / \\ R' \end{array} + 2Na \rightarrow \begin{array}{c} R \\ \backslash \\ O \\ / \\ R' \end{array} \begin{array}{l} \quad Na \rightarrow R'Na + RONa \\ / \\ \\ \backslash \\ Na \rightarrow R'ONa + RONa \end{array}$$

If this scheme is applied to a β-chloro ether (without taking the chlorine atom into account) under the action of metallic sodium, the cleavage of the bond may be expressed by the scheme:



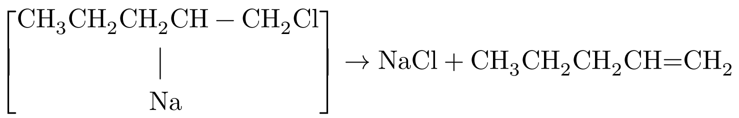
$$CH_3CH_2CH_2CH\begin{array}{l}/OCH_3\\ \backslash CH_2Cl\end{array} + 2Na \rightarrow CH_3CH_2CH_2CH\begin{array}{l}/O(CH_3)(Na)\\ \quad\quad \backslash Na\end{array}$$

$$CH_3ONa + [CH_3CH_2CH_2\underset{|\_Na}{CH} - CH_2Cl] \qquad (I)$$

$$CH_3Na + [CH_3CH_2CH_2\underset{|\_Na}{CH} - CH_2Cl] \qquad (II)$$

From the reaction products the alcoholate of methanol was isolated, i.e., an alcoholate with a radical containing no chlorine; consequently, the direction of reaction (I) is confirmed.

The presence of a chlorine atom adjacent to the sodium atom in the intermediate organosodium compound accounts for the easy elimination of sodium chloride and the formation of a double bond:



$$\left[\begin{array}{c} CH_3CH_2CH_2CH - CH_2Cl \\ | \\ Na \end{array}\right] \rightarrow NaCl + CH_3CH_2CH_2CH{=}CH_2$$

In the interaction of metallic sodium with the methyl and butyl ethers of amylene chlorohydrin, it was found that metallic sodium does not react in the cold with the β-chloro ether, and only when the reaction mixture is heated to 60–70° does decomposition of the starting ether begin according to the above scheme, with a conversion of 55–60%.

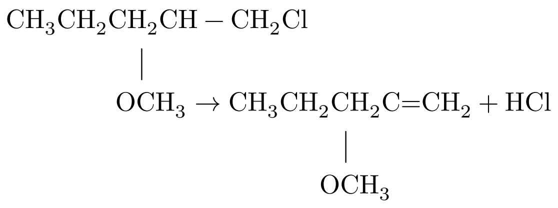
Under the described conditions, on treating 43.6 g of the methyl ether of α-amylene chlorohydrin with 9 g of metallic sodium, 12 g of α-amylene and 19.5 g of unreacted ether were obtained. The conversion of the ether is about 60%.

The catalytic action of copper on organic compounds containing a relatively inert halide has long been known (the Gattermann reaction in the case of an aromatically bound halide). It was therefore of interest to test its action on β-chloro ethers. Copper does not cause transformations of the β-chloro ether. When heated with copper dust to boiling for 3 hours, the β-chloro ether was recovered unchanged.

However, when the temperature is raised to 170-300° and the reaction is carried out under a pressure of 10 to 40 ata, a reaction involving elimination of HCl takes place and a substituted vinyl ether and the products of its hydrolysis and polymerization are formed. The conversion of the initial β-chloro ether, depending on the experimental conditions, reaches 86–96%.

As a result of the experiment a gas was isolated containing from 16 to 20% unsaturated compounds, and a fraction with b.p. 80-120°, consisting of a mixture of vinyl ether and methyl propyl ketone, as well as high-boiling fractions, which are condensation products of the substituted vinyl ether.

It may be assumed that initially, in the presence of copper, HCl is eliminated from the starting β-chloro ether:



$$CH_3CH_2CH_2\underset{\displaystyle OCH_3}{\underset{|}{CH}} - CH_2Cl \rightarrow CH_3CH_2CH_2\underset{\displaystyle OCH_3}{\underset{|}{C}}{=}CH_2 + HCl$$

The hydrogen chloride liberated reacts with copper to form its chloride. Copper chloride promotes further elimination of hydrogen chloride.

Many examples are known of the use of copper and its chlorides as catalysts accelerating the course of reactions in the described direction (3–7).

The presence of copper chloride also causes polymerization of the vinyl ether, but the degree of polymerization is not high. The molecular weight of the isolated polymers, determined by the cryoscopic method, is 400–470. The low degree of polymerization may be explained by the presence in the reaction mixtures of ketone: the presence of even traces of aldehydes, ketones, or other oxygen-containing compounds breaks the polymer chains as a result of peroxide formation.

Finely dispersed aluminum, like copper, is used as a catalyst for the elimination of hydrogen halide from organic halogen-containing compounds (8,9).

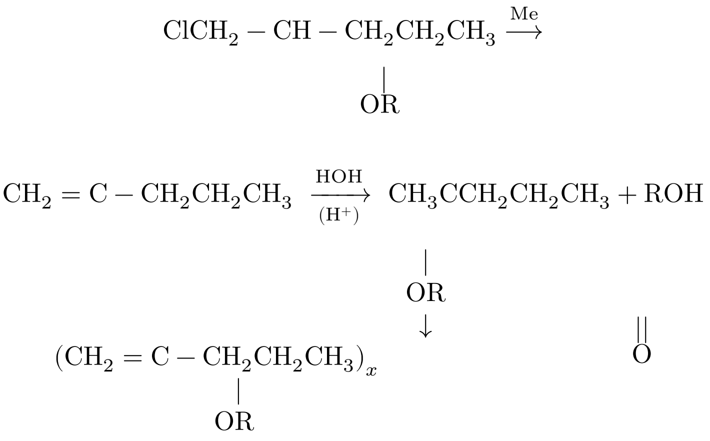
Experiments with aluminum powder were carried out in an autoclave. The temperature was varied within the range 180-280°, and the pressure from 10 to 25 ata. The conversion of the initial chloro ether reached 75-91%. The reaction proceeded in the same direction as in the case of copper, only with an increased yield of polymerization products in comparison with copper.

The most probable direction of the reaction in the case of the action of magnesium on β-chloro ethers is the formation of an organomagnesium compound; however, in reality the reaction, as in the case of copper and aluminum, proceeds toward the elimination of hydrogen chloride from the initial β-chloro ether. A special feature of magnesium in this reaction is its ability to catalyze the hydrolysis reaction of the vinyl ether. The volatile portion of the catalyzate consists of almost pure methyl propyl ketone with a small admixture of vinyl ether.

Experiments with magnesium were carried out in the temperature range 180–280° and at pressures within 10–30 atm. The conversion of the initial ether, depending on the experimental conditions, reached 76–80%.

Comparing the action of copper, aluminum, and magnesium on β-chloro ethers, one may conclude that the mechanism of action of these metals is the same: all of them initially promote the catalytic elimination of HCl from the initial ether (as described above), and then the hydrogen chloride evolved reacts with the free metals, giving chlorides.

The chlorides formed deepen the hydrogen chloride elimination reaction and catalyze the secondary reactions of hydrolysis and polymerization of the α-substituted vinyl ether formed:



$$ClCH_2-\underset{\displaystyle OR}{\underset{|}{CH}}-CH_2CH_2CH_3 \xrightarrow{Me}$$

$$CH_2=\underset{\displaystyle OR}{\underset{|}{C}}-CH_2CH_2CH_3 \xrightarrow[(H^+)]{HOH} CH_3\underset{\displaystyle O}{\underset{||}{C}}CH_2CH_2CH_3+ROH$$

$$\downarrow$$

$$(CH_2=\underset{\displaystyle OR}{\underset{|}{C}}-CH_2CH_2CH_3)_x$$

Table 1

Action of metallic magnesium on the methyl ether of amylene chlorohydrin

Ether taken, g	Magnesium taken, g	Temperature, °C	Pressure, atm	Gas, L	Amylene glycol, g	Liquid catalyzate, g	Vinyl ether, %	Methyl propyl ketone, %	Unchanged ether, %	Conversion, %
25	6	280	25–30	2	1.8	20.8	17.1	80.05	20	80
25	6	180–200	18	1	0.8	18.6	27	72	24	76

Note. Identification of the α-substituted vinyl ether and methyl propyl ketone was carried out by the methods described previously (1).

Table 2

Physicochemical properties and analysis of α-propyl vinyl ether

Formula	B.p., °C	d_4^{20}	n_D^{20}	MB found	MB calc.	MR found	MR calc.	Bromine number found	Bromine number calc.
$C_6H_{12}O$	85–86	0.8043	1.4020	100.08	100	30.25	31.08	156.8	160

Table 3

Physicochemical properties and analysis of 2-methoxy-1-chloropentane

Formula	B.p., °C	d_4^{20}	n_D^{20}	MB found	MB calc.	MR found	MR calc.	C, % found	C, % calc.	H, % found	H, % calc.	Cl, % found	Cl, % calc.
$C_6H_{13}OCl$	140–43	0.9720	1.4290	136.15	136.5	36.54	36.28	52.42	52.79	9.44	9.52	25.9	26.40

Table 4

Action of metallic copper on the methyl ether of amylene chlorohydrin

Ether taken, g	Copper powder taken, g	Experimental conditions: temperature, °C	Experimental conditions: pressure, atm	Obtained gas, l	Obtained liquid amylene, g	Obtained: liquid catalyst, g	Obtained: vinyl ether, %	Obtained: methyl-propyl ketone, %	Obtained: unchanged ether, %	Obtained: conversion, %
25	1	250–300	30–40	2	0.8	18.0	13.2	67.2	4	96
20	1	200–220	20–25	1.2	0.5	15.4	30.0	70	8	92
25	1	160–170	11–12	0.8	–	20.1	76	58	14	86

Table 5

Action of metallic aluminum on β-chloro ethers (methyl ether of amylene chlorohydrin)

Ether taken, g	Aluminum powder taken, g	Experimental conditions: temperature, °C	Experimental conditions: pressure, atm	Obtained gas, l	Obtained liquid amylene, g	Obtained: liquid catalyst, g	Obtained: unchanged ether, %	Obtained vinyl ether, %	Obtained ketone, %	Obtained: conversion of ether, %
20	1	280	20–25	1.8	1	17	1.5	41.65	58.3	92
25	1	200–220	10–15	0.8	–	22.4	1.6	60	39	83.6

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Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.