UNSATURATED ALDEHYDES

COMMUNICATION 1. PROPERTIES OF THE PRODUCTS OF THE ADDITION OF 2-CHLOROETHANOL TO ACROLEIN

(UDC 547.381 + 542.91)

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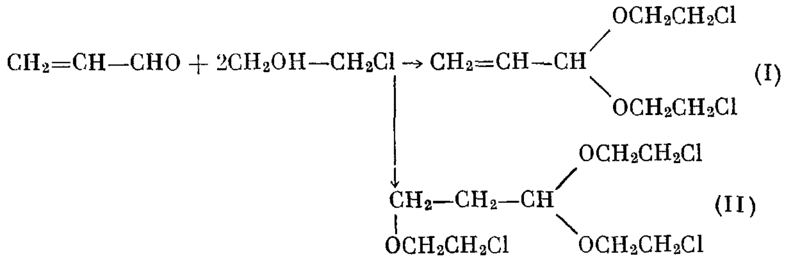
In order to prepare acrolein acetals containing various functional groups able to take part in further chemical transformations we studied the addition of 2-chloroethanol to acrolein. Several ways of preparing acrolein acetals have been described in the literature: From 3-chloro- and 3-bromo-propionaldehyde acetals by the action of potassium hydroxide powder and subsequent distillation [1, 2]. By the reaction of acrolein with orthoformic ester and ammonium nitrate in alcohol (at room temperature) [3, 4] (a formimidic ester hydrochloride can be used instead of the ortho ester [5]); also, by the direct reaction of alcohols with acrolein in presence of acid catalysts (sulfuric, sulfamic, benzene-, toluene-, or naphthalene-sulfonic acid etc.) with simultaneous removal of water as an azeotropic mixture [6]. Here, reaction does not stop at the first stage, and to some extent a third molecule of alcohol adds with formation of a 1,1,3-trialkoxypropane. The reaction of acrolein with primary alcohols goes more readily than with secondary and tertiary alcohols. It goes fairly well with polyhydric alcohols. The specificity of the reaction is greatly affected by the amount of acid taken as catalyst. Thus, when p-toluenesulfonic acid is used in an amount exceeding 0.01 mole per 100 moles of acrolein, the main product is the 1,1,3-trialkoxypropane. As azeotrope-former we used benzene, toluene, xylene, carbon tetrachloride, cellosolve F, and methylene chloride. It is recommended that the reaction temperature be kept in the range 25-50°, because below 25° reaction is slow, and above 50° the 1,1,3-trialkoxypropane is formed to a greater extent. Hall and Stern [7] prepared acrolein acetals in presence of neutral salts and a small amount of acid.

For the synthesis of acrolein bis-2-chloroethyl acetal (I) we carried out the reaction of acrolein with 2-chloroethanol in presence of p-toluenesulfonic acid. As the solvent forming an azeotrope with water we used methylene chloride. The acetal is referred to in a paper by Schultz, Fauth, and Kern [8], but its constants and method of preparation are not given. The yield of (I) was 16%, and 1,1,3-tris-2-chloroethoxypropane (II) was formed simultaneously in 18% yield.



$$CH_2{=}CH{-}CHO + 2CH_2OH{-}CH_2Cl \rightarrow CH_2{=}CH{-}CH(OCH_2CH_2Cl)_2 \quad (I)$$

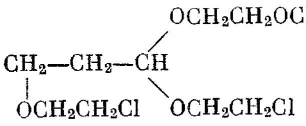
$$\downarrow$$

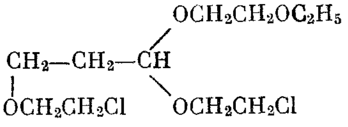
$$CH_2(OCH_2CH_2Cl){-}CH_2{-}CH(OCH_2CH_2Cl)_2 \quad (II)$$

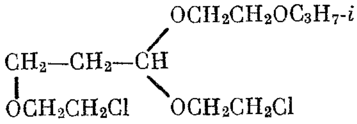
Reduction in the reaction time and the amount of alcohol lowered the total yield of products without changing their proportions appreciably (see table). It is known that the 1,1,3-trialkoxypropane is obtained in good yield when mineral acids are used as catalyst [9, 10]. We prepared (II) in 72% yield in presence of hydrochloric acid with removal of water as an azeotrope.

We made an attempt to polymerize (I). According to the literature, acrolein acetals cannot be caused to undergo either ionic or radical polymerization, despite the presence of a double bond [8]. The acetal studied in this work did not give a polymer when heated in presence of azodiisobutyronitrile.

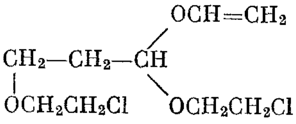
To determine the possibility of the systhesis of unsaturated acetals from (II) we studied its reaction with sodium alkoxides. It is known [11] that the treatment of chloroacetaldehyde bis-2-chloroethyl acetal with a solution of potassium t-butoxide results in the elimination of HCl from the 2-chloroethyl group. It was found that further treatment with solid potassium alkoxide leads to the elimination of a molecule of hydrogen chloride from the aldehyde part. The compound (II) contains three chlorine atoms capable of being replaced by an alkoxy group or of being eliminated as HCl when treated with alkoxides. We carried out the reaction of (II) with various alkoxides at a reactant ratio of 1 : 1. Depending on the alkoxide taken reaction may occur either with replacement of a chlorine atom by an alkoxy group or with the elimination of one molecule of hydrogen chloride. Thus, under the action of one molecular proportion of sodium methoxide, ethoxide (20 h, 70°), or isopropoxide (20 h, 80°) a chlorine atom was replaced by a methoxy, ethoxy, or isopropoxy group with formation of 1,3-bis-2-chloroethoxy-1-(2-methoxyethoxy)propane (III), 1,3-bis-2-chloroethoxy-1-(2-ethoxyethoxy)propane (IV), or 1,3-bis-2-chloroethoxy-1-(2-isopropoxyethoxy)propane (V).


(III)





Infrared spectroscopy showed the absence of a double bond in these compounds. Unlike the reactions with sodium methoxide, ethoxide, and isopropoxide, the reactions of (II) with sodium butoxide and t-butoxide resulted not in the replacement of a chlorine atom, but in the elimination of a molecule of hydrogen chloride with formation of 1,3-bis-2-chlorethoxy-1-(vinyloxy)propane (VI) bis-2-chloroethoxy-1-(vinyloxy)propane (VI)



In the reaction of (II) and (III) with 5% hydrochloric acid,hydrolytic breakdown occurs, and at room temperature mainly 3-(2-chloroethoxy)propionaldehyde (IX) is formed,together with small amounts of acrolein (VII), while with heating acrolein is isolated. It is evident that under more severe conditions a molecule of alcohol is eliminated from the aldehyde part. The aldehydes isolated were characterized as their 2,4-dinitrophenylhydrazones (DNPH). DNPH were also obtained by the direct action of 2,4-dinitrophenylhydrazine (DNP) on the acetals. The hydrolysis of (IV), (V), and (VI) was carried out only at room temperature. The DNPH were separated by thin-layer chromatography.

Reaction of 2-Chloroethanol with Acrolein in Presence of p-Toluenesulfonic Acid (reaction temperature 47-50°)

Acrolein	Chlorethanol	Solvent	Reaction time, h	Yield of (I), %	Yield of (II), %	Ratio of (I) : (II)
1	2	Methylene chloride	24	15.7	18.5	1 : 1.17
1	2	The same	15	7.3	16.4	1 : 2.2
1	2	Petroleum ether	24	6.8	19.7	1 : 2.8
1	1	Methylene chloride	24	8.1	9.7	1 : 1.2

EXPERIMENTAL

Reaction of Acrolein with 2-Chloroethanol in Presence of p-Toluenesulfonic Acid. A mixture of 56 g of acrolein, 161 g of 2-chloroethanol, 500 ml of methylene chloride, and 0.003 g of p-toluenesulfonic acid was heated for 25-30 hours at 47-50° until no more water separated. The reaction mixture was neutralized with barium carbonate, methylene chloride and 2-chloroethanol were distilled off, and the mixture was washed with water. It was dried with potassium carbonate, and vacuum distillation gave 33.5 g of a substance of b.p. 65-79° (2 mm) and 51.7 g of a dark-colored residue. By repeated fractionation from the product of b.p. 65-79° (2 mm) we isolated acrolein bis-2-chloroethyl acetal (I) in 15-16% yield; b.p. 74-75° (1.5 mm); n_D^{20} 1.4608; d_4^{20} 1.1669. Found: C 41.96; 42.06; H 6.39; 6.41; Cl 35.26; 35.57%; MR 46.79; mol. wt. 188.6; 182.8. $C_7H_{12}O_2Cl_2$. Calculated: C 42.23; H 6.07; Cl 35.62; MR 47.07; mol. wt. 199.078.

The residue referred to above was distilled in a high vacuum to avoid decomposition. We obtained 1,1,3-tris-2-chloroethylpropane (II), b.p. 108-115° ($2.3 \cdot 10^{-2}$ mm); n_D^{20} 1.4761; d_4^{20} 1.2459. The results of experiments on the addition of 2-chloroethanol to acrolein in presence of p-toluenesulfonic acid are summarized in the table.

Reaction of Acrolein with 2-Chloroethanol in Presence of Hydrochloric Acid. A mixture of 15 g of acrolein, 160 g of 2-chloroethanol, 250 ml of methylene chloride, and 2 ml of hydrochloric acid was heated for 32 hours at 50-52° with simultaneous removal of water as an azeotrope. The product was treated as in the preceding experiment and distilled in a high vacuum. We obtained 54 g (72%) of (II), b.p. 104.5-111° ($1.8\text{-}1.7 \cdot 10^{-2}$ mm); n_D^{20} 1.4763; d_4^{20} 1.2453. Found: C 38.93; 38.91; H 5.96; 6.12; Cl 38.10; 38.34%; mol. wt. 245.6; 247.1; MR 63.35; $C_9H_{17}O_3Cl_3$. Calculated: C 38.8; H 6.12; Cl 38.04%; mol. wt. 279.6; MR 63.29.

Polymerization of (I). A mixture of 5.6 g of (I) and 0.03 g of azodiisobutyronitrile was heated in a sealed tube for 100 hours at 60°. Slight resinification was observed. No polymer was formed. By distillation in a high vacuum ($2 \cdot 10^{-2}$ mm) unchanged monomer was isolated.

Reaction of (II) with One Molecular Proportion of Sodium Methoxide. 4.8 g of sodium was dissolved in 45 ml of methanol, 60 g of (II) was added, and the mixture was heated for 20 hours at 70°. The precipitate was filtered off and washed with benzene several times, and the filtrate was washed with water to remove alcohol. The benzene extract was dried over potassium carbonate, benzene was driven off, and the residue was distilled in a high vacuum. We obtained 1,3-bis-2-chloroethoxy-1-(2-methoxyethoxy)propane (III), b.p. 102.5-104° ($2 \cdot 10^{-2}$ mm); n_D^{20} 1.4636; d_4^{20} 1.1720. The yield of (III) was 27.1 g (45.9%). Found: C 43.98; 44.08; H 7.27; 7.25; Cl 26.22; 26.32%; MR 64.57. $C_{10}H_{20}O_4Cl_2$. Calculated: C 43.64; H 7.32; Cl 26.13%; MR 64.68.

Reaction of (II) with Sodium Ethoxide. 2.4 g of sodium was dissolved in 50 ml of absolute ethanol, 30 g of (II) was added, and the mixture was heated for 30 hours at 70°. The product was treated in the usual way. By distillation in a high vacuum we isolated 10.1 g (32.2%) of 1,3-bis-2-chloroethoxy-1-(2-ethoxyethoxy)propane (IV), b.p. 86-88° ($2 \cdot 10^{-2}$ mm); n_D^{20} 1.4602; d_4^{20} 1.1379. Found: C 46.55; 46.36; H 7.79; 7.58; Cl 24.27; 24.13%; MR 69.64. $C_{11}H_{22}O_4Cl_2$ Calculated: C 45.68; H 7.67; Cl 24.52%; MR 69.30.

Reaction of (II) with Sodium Isopropoxide. 2.4of sodium was dissolved in 130 ml of isopropyl alcohol, 30 g of (II) was added, and the mixture was heated at 80° for 20 hours. The precipitate was filtered off and washed with heptane, and the extract was washed with water to remove alcohol and dried over potassium carbonate; heptane was then driven off. The residue was distilled in a high vacuum, and we isolated 1,3-bis-2-chloroethoxy-1-(2-isopropoxyethoxy)propane (V) in 47% yield; b.p. 87.5° ($3.6 \cdot 10^{-2}$ mm); n_D^{20} 1.4618; d_4^{20} 1.1274. Found: C 47.22; 47.44; H 7.60; 7.64; Cl 22.94; 22.80%; MR 73.90. $C_{12}H_{24}O_4Cl_2$. Calculated: C 47.56; H 7.97; Cl 23.38%; MR 73.90.

Reaction of (II) with Sodium Butoxide. 4.8 g of sodium was dissolved in 90 ml of butyl alcohol, 60 g of (II) was added, and the mixture was heated at 70° for 30 hours. The precipitate was filtered off and washed with benzene, and the filtrate was washed with water and dried over potassium carbonate; benzene was driven off, and the residue was distilled in a high vacuum. We obtained 39.5 g (64.6%) of 1,3-bis-2-chloroethoxy-1-(vinyloxy)propane (VI); b.p. 102-103° ($2.8 \cdot 10^{-2}$ mm); n_D^{20} 1.4668; d_4^{20} 1.1676; MR 57.75; mol. wt. 250.9; 255.3. Found: C 44.46; 44.52; H 7.19; 7.01; Cl29.12; 29.18%. $C_9H_{16}O_3Cl_2$. Calculated: C 44.46; H 6.63; Cl 29.17%; mol. wt. 243.1; MR 57.96. Infrared spectroscopy showed the presence of absorption bands characteristic for a double bond in the region 1635-1650 cm^{-1}.

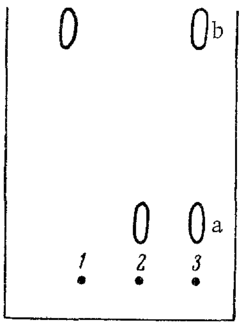


Fig. 1. Chromatogram of various DNPH: 1) DNPH of (VIII), R_f 0.71; 2) DNPH of (IX), R_f 0.46; 3) DNPH of substance investigated: a) DNPH of (IX), R_f 0.46; b) DNPH of (VIII), R_f 0.71.

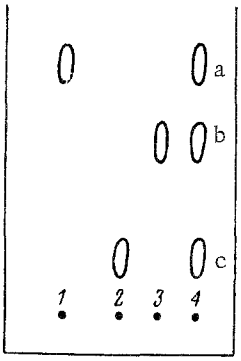


Fig. 2. Chromatogram of various DNPH: 1) DNPH of (VIII), R_f 0.71; 2) DNPH of (IX), R_f 0.47; 3) DNPH of acetaldehyde, R_f 0.63; 4) DNPH of substance investigated: a) DNPH of (VIII), R_f 0.71; b) DNPH of acetaldehyde, R_f 0.63; c) DNPH of (IX), R_f 0.46.

Reaction of (II) with Sodium t-Butoxide. 1.6 g of sodium was dissolved in 50 ml of t-butyl alcohol, 20 g of (II) was added, and the mixture was heated at 80° for 20 hours. The product was treated as described above and was then distilled in a high vacuum. We isolated 31.8% of (VI), b.p. 92.5-97° ($2.3 \cdot 10^{-2}$ mm); n_D^{20} 1.4668; d_4^{20} 1.1688. Found: C 44.13; 44.57; H 7.02; 6.95%; MR 57.69. $C_9H_{16}O_3Cl_2$. Calculated: C 44.46; H 6.63%; MR 57.96.

Hydrolysis. A hydrochloric acid of DNP was added to 2 ml of (IV), (V), or (VI). After 24-30 hours the precipitate was filtered off, washed with water, dried, and investigated by thin-layer chromatography on alumina in a 2 : 1 mixture of diethyl ether and petroleum ether (Fig. 1). By the action of DNP on (IV) and (V) we obtained the DNPH of acrolein (VIII) and the DNPH of 2-(2-chloroethoxy)propionaldehyde (IX).

By heating (II) and (III) to the boil with 5% hydrochloric acid we obtained acrolein, characterized as its DNPH, R_f 0.71. At room temperature with DNP we obtained the DNPH of (IX) and a very small amount of the DNPH of (VIII). The DNPH of (IX) was isolated by crystallization from alcohol and had m.p. 84-86°. Found: Cl 11.22; 11.34; N 18.13; 17.90%. $C_{11}H_{13}O_5Cl$. Calculated: Cl 11.19; N 17.69%. By the action of DNP on (VI) we obtained the DNPH of (VIII), the DNPH of (IX), and the DNPH of acetaldehyde (Fig. 2).

SUMMARY

1. The reaction of 2-chloroethanol with acrolein was studied. Acrolein bis-2-chloroethyl acetal (I) and 1,1,3-tris-2-chloroethoxypropane (II) were synthesized.

2. The reaction of (II) with sodium methoxide, ethoxide, and isopropoxide was investigated. One chlorine atom was replaced with formation of 1,3-bis-2-chloroethoxy-1-(2-methoxyethoxy)propane (III), 1,3-bis-2-chloroethoxy-1-(2-ethoxyethoxy)propane (IV), and 1,3-bis-2-chloroethoxy-1-(2-isopropoxyethoxy)propane (V).

3. In the reaction of (II) with sodium butoxide and t-butoxide the elimination of hydrogen chloride occurred with formation of 1,3-bis-2-chloroethoxy-1-(vinyloxy)propane (VI).

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