SYNTHESIS OF ETHOXYACETALDEHYDE, AND ITS CHEMICAL REACTIONS

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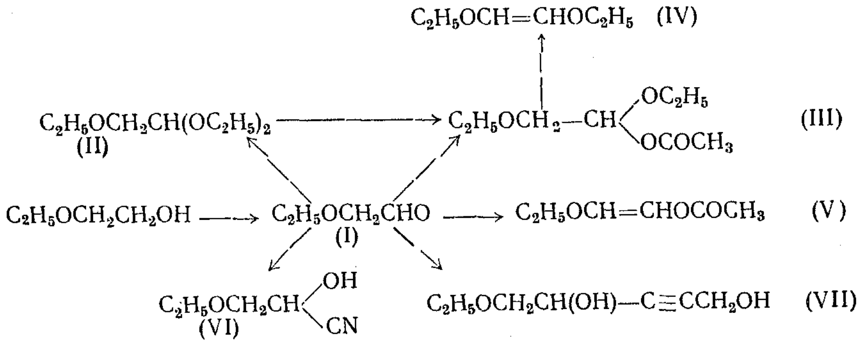
In an investigation of the dehydrogenation of alcohols over various catalysts we decided to study the dehydrogenation of 2-ethoxyethanol. The catalytic dehydrogenation of 2-ethoxyethanol over a catalyst prepared by the reduction of cupric oxide [1-4], and also over a copper-silicon alloy [5], has been described several times in the literature. However, in these experiments neither the conversion nor the yield of ethoxyacetaldehyde exceeded 20-30%. Later investigations [6] showed that even these results were not reproducible, and the yield of ethoxyacetaldehyde did not exceed 10-15%.

After a study of the catalytic dehydrogenation of 2-ethoxyethanol and also of its aqueous solutions over various catalysts (reduced cupric oxide, brass, copper rings, copper-silicon alloy, etc.) we came to the conclusion that it is impossible to obtain satisfactory results in this way, as it is always mainly cleavage of the 2-thoxyethanol that occurs, and the final products are gases, acetaldehyde, and only traces of ethoxyacetaldehyde. We therefore went over to a study of the dehydrogenation of 2-thoxyethanol over metal catalysts in a stream of air. No information about such investigations was found in the literature, and we carried out much work in order to select the conditions required in this reaction. The results obtained are given in part in the table.

We succeeded in increasing the yield of ethoxyacetaldehyde to 60-65%. The best conditions for the dehydrogenation were found to be: pressure 300-400 mm, temperature 600°, and catalyst in the form of silver triangles.

Ethoxyacetaldehyde, which had now become accessible, is an extremely reactive compound which rapidly polymerizes on standing; however, like formaldehyde solutions, its solutions in water and alcohols do not change. In the study of the chemical properties of ethoxyacetaldehyde, we therefore decided to use its azeotrope with water, which is stable to keeping. Our experiments showed that many reactions take place with the azeotrope with the same yields as those obtained with pure ethoxyacetaldehyde. In studying the chemical behavior of this little-studied aldehyde, we examined it in various reactions, which may be represented as follows:



Ethoxyacetaldehyde (I), and also its azeotrope, is readily converted into its diethyl acetal (II), which, on being heated with acetic anhydride in presence of p-toluenesulfonic acid, is converted into the acylal (III), which at 160° loses a molecule of acetic acid and is converted into 1,2-diethoxyethylene (IV). When ethoxyacetaldehyde is boiled for a long time with acetic anhydride and a little potassium acetate, 2-ethoxyvinyl acetate (V) is formed in a yield of about 20%.

Air Oxidation of 2-Ethoxyethanol Diluted with Water in the Proportions of 1 Mole of 2-Ethoxyethanol to 1.5 Moles of Water

Catalyst	Temp. (°C)	Amt. of ethoxythanol taken (moles)	Time (min)	Oxygen (% of theor. amt)	Yield of aldehyde (moles)	Conversion of alcohol
Copper triangles, silvered; same size as silver ones	545	2,300	159	218	0,840	
ditto	500	1,140	43	115	0,373	67,5
» »	500	1,080	40	180	0,490	89
» »	470	0,366	15,5	217	0,142	
» »	490	0,390	19,5	127	0,156	
Fine copper turnings, silvered	535	2,660	178	158	1,060	
ditto	550	0,940	40	80	0,250	
Pumice, silvered	600	0,486	21,5	98	0,104	
Silver triangles						
ditto	565	0,662	32,5	143	0,270	
» »	530	0,365	17	90	0,165	
» »	520	0,945	69	83 Air diluted with nitrogen 4,5-fold	0,384	74
» »	600	0,637	29	130 Vacuum 345mm	0,388	
» »*	600	0,62	27	135 Vacuum 210mm	0,386	
» »*	600	1.07	19	131 Vacuum 530mm	0,61	90

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* Without water.

On reaction of ethoxyacetaldehyde, or its azeotrope, with acetone cyanohydrin in presence of potassium carbonate, 3-ethoxy-2-hydroxypropionitrile is formed in 60% yield. Ethoxyacetaldehyde also condenses smoothly with 2-propyn-1-ol in presence of cuprous oxide. The acetylenic glycol (VII) is then formed in a yield of about 60%.

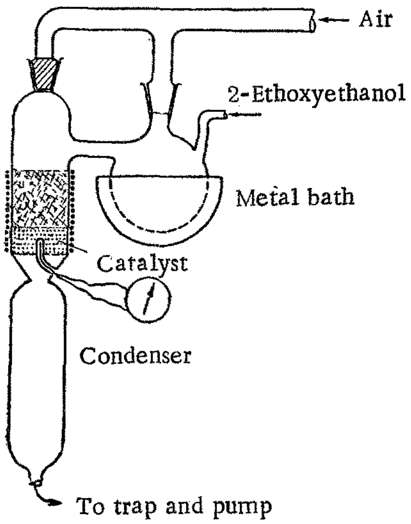
We studied also the reaction between the chloro ether (VIII) (which was prepared from ethoxyacetaldehyde, ethanol, and hydrogen chloride) and potassium acetate. We isolated the acylal (III) in low yield, and we obtained also some of the diethyl acetal (II), formed probably by the disproportionation of the unsymmetrical acylal (III).

Hydrolysis of the acetal (II), and also of 2-thoxyvinyl acetate (V) and the unsymmetrical acylal (III), in presence of hydroxylamine gave rather high values for the carbonyl content of the molecule, so that this method is not suitable for analytical purposes in this case. It is interesting to note that in the hydrolysis of acetals [7] in presence of 2,4-dinitrophenylhydrazine the glyoxal hydrazone is formed as well as the hydrazone of ethoxyacetaldehyde, i.e., the hydrazine is consumed not only in the formation of the hydrazone, but also in the oxidation of ethoxyacetaldehyde to glyoxal.

EXPERIMENTAL

Preparation of ethoxyacetaldehyde. Ethoxyacetaldehyde was prepared by the dehydrogenation of 2-ethoxyethanol (b.p. 134-135°; n_D^{20} 1.4075) over various catalysts in a quartz reactor, which is shown diagrammatically in figure. After a series of experiments had been carried out (see table) it was found that the best method for the preparation of ethoxyacetaldehyde was the dehydrogenation of 2-ethoxyethanol in a vacuum over a catalyst consisting of silver triangles having sides of length 1.5 mm, which were prepared from wire of diameter 0.3 mm (silver content 99.99%). After long use the catalyst fell appreciably in activity, but it could be regenerated by the passage of air at about 400°.

A mixture of 57.3 g of 2-ethoxyethanol (0.637 mole) and 17.2 g of water (0.955 mole) was passed into an evaporator, in which the vapor was mixed with air. The liquid was fed at such a rate that there was no accumulation of condensate in the evaporator. The amount of air fed in was 45 liters (130% of the theoretical amount). The mixture of vapor and air was passed through the reactor, which contained 15 ml of silver triangles as catalyst. The process was carried out at 600° and 345 mm for 30 minutes. The resulting condensate was fractionated through a column of 20 plate efficiency. We obtained 44.5 ml of a mixture of ethoxyacetaldehyde and water in the form of an azeotrope of b.p. 90-91° and n^{18} 1.4236 (the literature [2, 4] gives b.p. 90-91°), and according to analysis this contained 0.388 mole of ethoxyacetaldehyde. The yield of ethoxyacetaldehyde was thus 61%.



Apparatus for the preparation of ethoxyacetaldehyde (one-half true size).

Azeotrope (b.p. 90-91°) from a series of experiments (158 ml in all) and 150 ml of benzene were boiled together in an apparatus with a water separator until the separation of water ceased. Xylene (60 ml) was then added to the reaction mixture as a carrier liquid, and the mixture was fractionated through the 20-plate column. We then obtained 77 g of ethoxyacetaldehyde, b.p. 103-105° and $n_D^{22.5}$ 1.3935, i.e., 67% of the amount present in the azeotrope. The literature [2, 4] gives 104-106°. The residue consisted of ethoxyacetaldehyde polymers, which were depolymerized to the monomer on being heated with 0.1% of p-toluenesulfonic acid. The yield of ethoxyacetaldehyde obtained by the depolymerization of its polymers was 50%. Pure ethoxyacetaldehyde polymerizes fairly rapidly on standing, but its solutions in water or alcohol are stable.

Preparation of ethoxyacetaldehyde diethyl acetal (II). a) With stirring, 62.4 g (1.36 moles) of absolute alcohol containing 1% of hydrogen chloride was added gradually to 29.5 g (0.33 mole) of ethoxyacetaldehyde (I) cooled with a mixture of ice and salt. The mixture was left at room temperature for 44 hours and then neutralized by adding dry sodium carbonate with stirring; it was poured into an equal volume of concentrated sodium carbonate solution. The reaction product was extracted with three 35 ml portions of ether, and the ether extract was dried over potassium carbonate. Ether was distilled off, and distillation of the residue through a column gave 34 g (72%) of ethoxyacetaldehyde diethyl acetal (II); b.p. 52.5-54° (8 mm); n_D^{21} 1.4040. The literature [7, 8] gives: b.p. 164-165°; n_D^{25} 1.3889.

b) A mixture of 234 g of ethanol, 0.13 g of p-toluenesulfonic acid, and 290 ml of benzene was added to 91 g of the aqueous azeotrope of ethoxyacetaldehyde (b.p. 90-91°) containing 72 g of the aldehyde. The mixture was boiled with a water separator until water ceased to separate (four days). The reaction product was fractionated through a column of 20 plate efficiency (20 ml of decalin was added as carrier liquid). This gave 67 g of ethoxyacetaldehyde diethyl acetal (II), b.p. 165-167°; $n_D^{24.5}$ 1.3990.

Synthesis of 2-ethoxyvinyl acetate (V). A mixture was 49 g of anhydrous ethoxyacetaldehyde, 148 g of acetic anhydride, and 8.75 g of potassium acetate was refluxed for one hour. The reaction mixture was washed six times with ice water, and then three times with 5% sodium carbonate solution. The reaction product was extracted with ether and fractionated through the 20 plate column. We then obtained 13 g of 2-ethoxyvinyl acetate (V); b.p. 86.5-88° (38 mm); $n_D^{23.5}$ 1.4358. Found: C 54.60, 54.71; H 7.7, 7.54%. $C_6H_{10}O_3$. Calculated: C 55.38; H 7.66%. The molecular weight, determined cryoscopically in benzene, was 130.9 (calculated 130). The substance decolorized bromine water.

3-Ethoxy-2-hydroxypropionitrile (VI). A mixture of 20 g of the azeotrope of ethoxyacetaldehyde (0.266 mole), 47.6 g (0.54 mole) of acetone cyanohydrin, and 18 ml of catalyst (concentrated methanolic potassium carbonate) was left overnight at room temperature. The reaction mixture was acidified with concentrated sulfuric acid, methanol and acetone was distilled off, a further 60 ml of methanolic potassium carbonate was added, and the reaction mixture was left further for 12 hours at room temperature. After analogous treatment of the reaction products and vacuum fractionation of the residue (after removal of solvents), we obtained 17.5 g (57%) of ethoxyacetaldehyde cyanohydrin (3-ethoxy-2-hydroxypropionitrile) (VI); b.p. 112-113° (14 mm); $n_D^{25.5}$ 1.4250. Found: C 52.00, 51.81; H 7.77, 7.89%. $C_5H_9O_2N$. Calculated: C 52.16; H 7.83%.

Condensation of ethoxyacetaldehyde with 2-propyn-1-ol. A mixture of 61.3 g of 2-propyn-1-ol, 174.8 g of the aqueous azeotrope of ethoxyacetaldehyde, 74 ml of water, 0.8 g of calcium carbonate, and catalyst (prepared by the precipitation of cuprous oxide from a solution of 12 g of cuprous chloride in 180 ml of 18% hydrochloric acid with 180 ml of 40% potassium hydroxide) was stirred in a nitrogen atmosphere at 100° for 42 hours. After removal of catalyst, the filtrate combined with 400 ml of ethanol (washings) was evaporated, and the residue was vacuum-distilled. This gave 67 g (62%) of 5-ethoxy-2-pentyne-1,4-diol (VII); b.p. 121-122° (1 mm); $n_D^{22.5}$ 1.4791. Found: C 58.48, 58.67; H 8.32, 8.35%. $C_7H_{12}O_3$. Calculated: C 58.33; H 8.33%.

Reaction of ethoxyacetaldehyde diethyl acetal with acetic anhydride. A mixture of 32.6 g of the acetal (II), 20.5 g of acetic anhydride, and 0.2 g of p-toluenesulfonic acid was refluxed for six hours. After the removal of ethyl acetate the residue was vacuum-distilled through a column, which gave 7.4 g of ethoxyacetaldehyde diethyl acetal and 12.4 g (50%) of the acylal 1,2-diethoxyethyl acetate (III); b.p. 78-81° (14 mm); $n_D^{21.5}$ 1.4077. After redistillation (III) had: b.p. 80-80.5° (13.5 mm); $n_D^{19.5}$ 1.4082. Found: C 54.54, 54.61; H 8.97, 9.1%. $C_8H_{16}O_4$. Calculated: C 54.54; H 9.09%.

Preparation of 1,2-diethoxyethylene (IV). The acylal (III) (59.3 g) was refluxed for two hours, after which the mixture was distilled very slowly from a flask fitted with a long column. The reaction product was washed twice with 20% sodium carbonate solution, dried over potassium carbonate, and finally fractionated over potassium hydroxide. The fraction of b.p. 132-159° then obtained was fractionated through a column. This gave 21.15 g (32%) of 1,2-diethoxyethylene; b.p. 131-133°; $n_D^{19.5}$ 1.4218. The literature [7, 8] gives: b.p. 131-134°; n_D^{25} 1.4205.

Reaction of 1-chloro-2-ethoxyethyl ethyl ether (VIII) with potassium acetate. The chloro ether (VIII) (0.56 mole) was prepared in accordance with [4] and added to 55 g (0.56 mole) of potassium acetate contained in a flask fitted with a stirrer and a calcium chloride tube; the reaction mixture was then left overnight at room temperature. On the next day the reaction product was stirred further for two hours at 100°, cooled, and diluted with 50 ml of ether. After removal of ether, the residue was vacuum-distilled through a column. We then isolated 8 g of ethoxyacetaldehyde diethyl acetal (II), b.p. 64.5-68.5° (15 mm) and n_D^{24} 1.4004, and 4 g of the acylal (III), b.p. 80.7-85° (15 mm) and n_D^{23} 1.4150.

SUMMARY

1. A convenient method for the synthesis of ethoxyacetaldehyde was developed.

2. Ethoxyacetaldehyde readily undergoes the usual reactions of aldehydes. Some of its acetals, its cyanohydrin, and the product of its condensation with 2-propyn-1-ol were prepared for the first time.

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