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Corresponding Member of the USSR Academy of Sciences M. F. Shostakovskii, N. A. Keiko

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Abstract

Full Text

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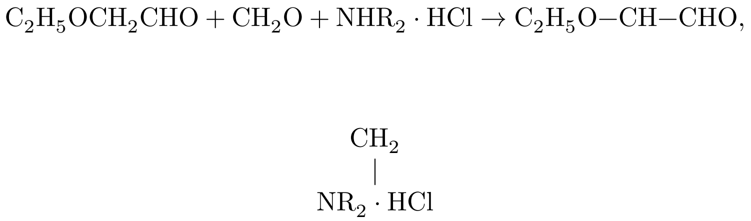
Chemistry

Corresponding Member of the USSR Academy of Sciences M. F. Shostakovskii, N. A. Keiko

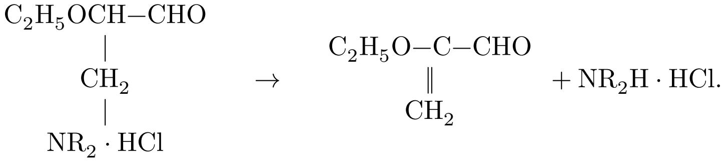
Synthesis of α-Ethoxyacrolein

In the present communication a method is described for obtaining α-ethoxyacrolein on the basis of the Mannich reaction. This is a very little-studied compound. Owing to the $+C$-effect of the oxygen atom that is part of the ethoxy group located in the α-position, conjugation of the double bond with the carbonyl group is undoubtedly disturbed. In this connection, α-ethoxyacrolein possesses distinctive chemical properties, different from those of α,β-unsaturated aldehydes and simple vinyl ethers, whose structures are combined in the structure of this compound. From a practical point of view, α-ethoxyacrolein is a valuable carbonyl monomer, on the basis of which polymers and copolymers with an active functional group can be obtained; these may be used as adhesives with high adhesion properties, and also as waxes and plasticizers (^{1,2}).

The synthesis of α-ethoxyacrolein consists in the interaction of ethoxyacetaldehyde with formaldehyde in the presence of hydrochlorides of secondary amines and the subsequent decomposition of the intermediate product—the hydrochloride of the Mannich base:



$$C_2H_5OCH_2CHO + CH_2O + NHR_2 \cdot HCl \rightarrow \begin{array}{c} C_2H_5O{-}CH{-}CHO, \\ | \\ CH_2 \\ | \\ NR_2 \cdot HCl \end{array} \qquad (1)$$



$$\begin{array}{c} C_2H_5OCH{-}CHO \\ | \\ CH_2 \\ | \\ NR_2 \cdot HCl \end{array} \rightarrow \begin{array}{c} C_2H_5O{-}C{-}CHO \\ \| \\ CH_2 \end{array} + NR_2H \cdot HCl. \qquad (2)$$

Attempts to obtain α-ethoxyacrolein under the conditions described for α-alkylacroleins (^{3}) were not successful. Therefore we had to investigate the conditions for obtaining α-ethoxyacrolein, for which purpose we carried out a considerable series of experiments; the conditions of some of them are given in Table 1.

Table 1

Conditions for obtaining α-ethoxyacrolein

Amine-to-ethoxyacetaldehyde ratio	Reaction temperature, °C	Reaction duration, h	Medium pH	Yield, %
$NH(CH_3)_2HCl$				
1 : 1	60	0.5	6.9	23.4
1 : 2	60	1	7–7.2	56.6
$NH(C_2H_5)_2HCl$				
1 : 1	40	1.5	7.2	26.2
1 : 1	60	2	7.2	26.2
1 : 1	120*	1	–	11.5
1 : 1	60	3	7.1–7.2	38.7
1 : 1	60	1	7.2	51
1 : 1	80	1	7.2	51
1 : 1	60	1	7	53.6
1 : 2	60	2	6.8–7.8	33.2
1 : 1	60	2	7–7.8	66.4
1 : 1	60	2	7.1	70.8

* The reaction was carried out in an autoclave. The approximate yield was determined by bromide-bromate titration.

The rate of reaction (1) was determined by us from the decrease in the concentration of formaldehyde by the gas-liquid chromatography method. In this case it proved to be considerably higher than the rate of reaction (2), which was determined from the increase in the concentration of α-ethoxyacrolein. For example, reaction (1) with diethylamine hydrochloride at 60° and pH 7 is practically complete in 0.5 h. The same dependence was observed for alkylacroleins (^{3,4}).

Decomposition of the hydrochloride of the Mannich base usually occurs at

on heating or on distillation with steam (5-11). As regards the preparation of α-ethoxyacrolein, the best conditions are: temperature 60°, reaction time 2 h. More prolonged and stronger heating leads to considerable resin formation and thereby lowers the yield of the desired product.

In carrying out the synthesis it is very important to control the pH of the medium. At pH < 7 reaction (1) slows down (3, 4) and rapid hydrolysis of

α-ethoxyacrolein occurs because it is at the same time an α-substituted simple vinyl ether and in this case exhibits the properties of the latter. In an alkaline medium the yield decreases owing to polymerization of α-ethoxyacrolein as an aldehyde.

We isolate the final product by extracting the oily layer with ether and subsequent fractionation. The amine solution remaining after extraction can be used for repeated syntheses without reducing the yield of the main product. The use of diethyl- and dimethylamine gives identical yields, but the latter somewhat increases the reaction rate. Paraform can be used instead of formalin with equal success.

Experimental Part

Preparation of α-ethoxyacrolein. Into a four-necked flask equipped with a reflux condenser, a tube for introducing nitrogen, a burette for adding a 10% sodium carbonate solution, and electrodes to an LPP-5 potentiometer are placed 42.8 g (0.5 mole) of 34% formalin solution and 54.9 g (0.5 mole) of diethylamine hydrochloride. The contents of the flask are heated in a nitrogen atmosphere with stirring to 60°, neutralized to pH 7, 59.1 g (0.5 mole) of 74.4% ethoxyacetaldehyde solution and a little hydroquinone are added, and the mixture is stirred for another two hours at this temperature. The reaction mixture is then cooled and extracted with ether (9 × 50 ml). The extract is dried with magnesium sulfate. After removal of the ether the residue is distilled in vacuo. This gives 33.3 g (66.6%) of a substance with b.p. 23° (4 mm), n_D^{20} 1.4440. After azeotropic removal of water with benzene, a substance was obtained with b.p. 27° (6 mm), n_D^{20} 1.4450, d_4^{20} 0.9766. MR_D found 27.27; MR_D calc. 26.48.

Found, %:	C 59.60; 69.49; H 8.15; 8.07
$C_5H_8O_2$. Calculated, %:	C 59.98; H 8.05

The molecular weight, determined cryoscopically from benzene, was 106; calculated 100. α-Ethoxyacrolein is a colorless mobile liquid with weak lachrymatory properties, readily soluble in organic solvents and poorly soluble in water.

The IR spectrum of α-ethoxyacrolein has intense absorption bands corresponding to the bonds $> C{=}C <$ and $> C{=}O$ (1614 and 1712 cm^{-1}). Both values are somewhat lowered, which may be explained by conjugation of the double bonds with one another and with the p-electrons of the ether oxygen.

Irkutsk Institute of Organic Chemistry
Siberian Branch of the Academy of Sciences of the USSR

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