N. V. VOLKOVA, A. A. YASNIKOV

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Abstract

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N. V. VOLKOVA, A. A. YASNIKOV

ON THE MECHANISM OF THE CONDENSATION OF ENAMINES WITH ALDEHYDES

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Enamines condense with aldehydes, forming products of crotonic condensation (^{1})

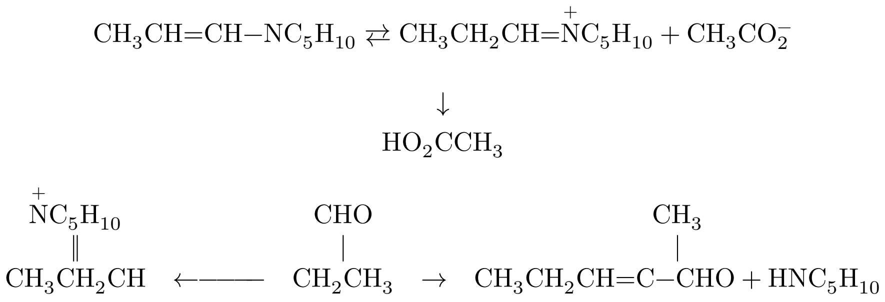
$$RCH_2CHO + RCH{=}CH{-}N \rightarrow RCH_2{-}CH{=}CH{-}CHO.$$

This condensation proceeds smoothly in the presence of organic acids and small amounts of water. We found that, for the condensation of the simplest enamine —N-propenylpiperidine—with propionic aldehyde, the maximum yield of the condensation product, α-methyl-β-ethylacrolein, is attained if N-propenylpiperidine in absolute ether solution is added at 0° to a mixture of equimolecular amounts of propionic aldehyde and acetic acid (98%) in ether.

The enamine, in the presence of weak acids, in particular benzoic acid, in absolute ether or benzene, does not undergo self-condensation to α-methyl-β-ethylacrolein, even if this mixture is heated on a water bath. If 96% H_2SO_4 is added to a mixture of N-propenylpiperidine and propionic aldehyde, the enamine is rapidly converted into aldehyde and piperidine, and the yield of α-methyl-β-ethylacrolein is only 4%. The aprotic acid $ZnCl_2$ converts N-propenylpiperidine into a red resin, but not into the product of crotonic condensation. Thus, the product of crotonic condensation is formed in the reaction of an enamine with an aldehyde in the presence of proton donors.

Two following mechanisms of condensation may be proposed:

Scheme I



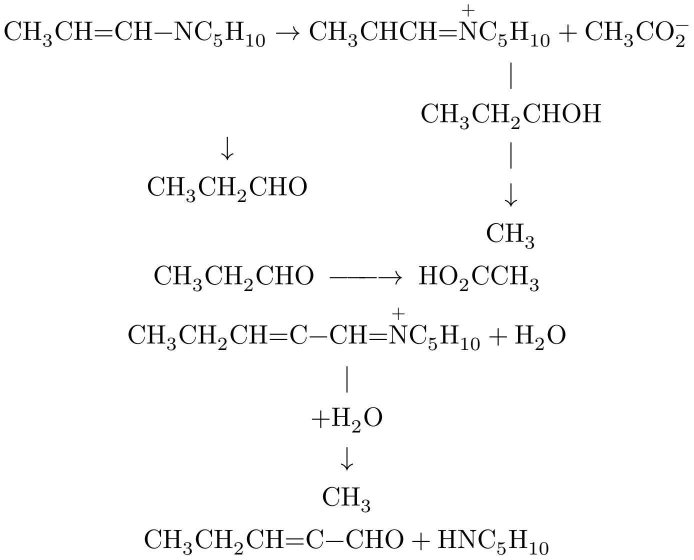
$$CH_3CH{=}CH{-}NC_5H_{10} \rightleftarrows CH_3CH_2CH{=}\overset{+}{N}C_5H_{10} + CH_3CO_2^-$$

$$\downarrow$$

$$HO_2CCH_3$$

$$\overset{\overset{+}{N}C_5H_{10}}{\overset{\|}{CH_3CH_2CH}} \longleftarrow \overset{CHO}{\overset{|}{CH_2CH_3}} \rightarrow CH_3CH_2CH{=}\overset{CH_3}{\overset{|}{C}}{-}CHO + HNC_5H_{10}$$

Scheme II



$$CH_3CH{=}CH{-}NC_5H_{10} \rightarrow CH_3CHCH{=}\overset{+}{N}C_5H_{10} + CH_3CO_2^-$$

$$|$$

$$CH_3CH_2CHOH$$

$$\downarrow \qquad |$$

$$CH_3CH_2CHO \qquad \downarrow$$

$$CH_3$$

$$CH_3CH_2CHO \longrightarrow HO_2CCH_3$$

$$CH_3CH_2CH{=}C{-}CH{=}\overset{+}{N}C_5H_{10} + H_2O$$

$$|$$

$$+H_2O$$

$$\downarrow$$

$$CH_3$$

$$CH_3CH_2CH{=}C{-}CHO + HNC_5H_{10}$$

As is known (^{2}), enamines add a proton with formation of imonium salts, which are very active in various condensations of carbonyl compounds. Scheme I takes these properties of enamines into account and establishes that the catalytic action of acids is reduced to the reaction converting the imine into the corresponding imonium ion. In mechanism II the proton-donor molecule catalyzes the addition of the aldehyde group to the double bond of the enamine, in the manner of an aldol condensation.

To determine the course of the reaction we used the tracer-atom method, employing aldehyde-1-C^{14} for condensation with an enamine that did not contain C^{14}. After ozonization of the condensation product we isolated propionaldehyde in the form of the 2,4-dinitrophenylhydrazone and determined its C^{14} content. If the reaction proceeds by mechanism I, then the propionaldehyde obtained after ozonolysis of the condensation product, α-methyl-β-ethylacrolein, will not contain C^{14}; conversely, reaction according to Scheme II will lead to propionaldehyde with the same molar radioactivity as that contained in α-methyl-β-ethylacrolein. The ratio of the molar radioactivities of propionaldehyde after ozonolysis of α-methyl-β-ethylacrolein and of α-methyl-β-ethylacrolein itself will determine the fraction of the reaction proceeding by mechanism II. Labeled propionaldehyde was prepared from propyl alcohol by oxidation with $K_2Cr_2O_7$.

N-Propenylpiperidine was obtained according to the procedure of Mannich and Davidsen (^{3}). In experiment 1, to a solution of 2.02 g of propionaldehyde-1-C^{14} and 3.2 g of 98% CH_3CO_2H in 15 ml of absolute ether, with ice cooling and stirring, a solution of 4 g of N-propenylpiperidine in absolute ether was added over 15 min. After this, 10 ml of water and 5 ml of 10% H_2SO_4 were added to the mixture. From the ether layer, α-methyl-β-ethylacrolein was isolated by distillation, b.p. 40°/14 mm, yield 2 g. Experiments 2 and 3 were carried out analogously; the amounts of propionaldehyde taken were, respectively, 1.5 and 2.24 g.

Ozonization of α-methyl-β-ethylacrolein was carried out in acetic acid solution. The ozonide was decomposed with Zn dust, and the propionaldehyde formed was distilled off with steam. From the aqueous solution, propionaldehyde was precipitated as the 2,4-dinitrophenylhydrazone. The 2,4-dinitrophenylhydrazone was freed from traces of 2,4-dinitrophenylhydrazine by filtering its solution in chloroform through a column with $MgSO_4$, and then this solution was passed through a column with Al_2O_3. The 2,4-dinitrophenylhydrazone of propionaldehyde was eluted from the column with chloroform.

For determination of radioactivity, in all cases the 2,4-dinitrophenylhydrazones of aldehydes were used. The results of the radioactivity determinations are presented in Table 1.

Table 1

Experiment no.	Radioactivity, imp/min per 1 mmol · 10^{-2}: initial C_3H_7CHO	Radioactivity, imp/min per 1 mmol · 10^{-2}: α-methyl-β-ethylacrolein	Radioactivity, imp/min per 1 mmol · 10^{-2}: C_3H_7CHO after ozonolysis of α-methyl-β-ethylacrolein	α*, %
1	500	470	435	92.5
2	712	682	650	95.5
3	530	496	460	93

* Ratio of the radioactivity of C_3H_7CHO after ozonolysis to the radioactivity of α-methyl-β-ethylacrolein.

The data of Table 1 show that in the presence of weak acids the aldehyde condenses with the enamine according to Scheme II, and only a certain fraction of the reaction proceeds by mechanism I. However, if a compound with an active methylene group that does not contain a carbonyl function, for example malonic ester, is taken into condensation with the enamine, then mechanism II cannot be realized and the reaction proceeds in accordance with Scheme I.

We found that N-propenylpiperidine in ether at 0°, in the presence of acetic acid, condenses into propylidenemalonic ester. To 11 g of N-propenylpiperidine in 10 ml of ether, 16.8 g of malonic ester was added. Then, while cooling with ice water, 5 ml of glacial acetic acid was gradually poured in. After standing at room temperature for 30 min, the reaction mixture was mixed with 5 ml of water and acidified with $2M$ H_2SO_4 to pH 1. The condensation products were extracted with ether. From the ether solution, propylidenemalonic ester was isolated by distillation, b.p. 75—80°/1.5 mm, yield 3.5 g, $n_D^{25.5}$ 1.4404; according to the literature data (^{4}), n_D^{25} 1.4402. After ozonization of the product in acetic acid, propionaldehyde was isolated as the 2,4-dinitrophenylhydrazone.

Thus, enamines in the presence of proton-donor substances enter into condensation reactions with aldehydes and with compounds containing an active methylene group in two ways: on the one hand, aldehydes add directly to the double bond of the enamine; on the other hand, upon adding a proton, they are converted into imonium-ion compounds, which participate as intermediates in condensation reactions.

Institute of Organic Chemistry
Academy of Sciences of the USSR

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

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