SYNTHESIS OF 2-SUBSTITUTED ISOXAZOLINE AND IMIDAZOLINE, CONTAINING A VINYLACETYL FRAGMENT

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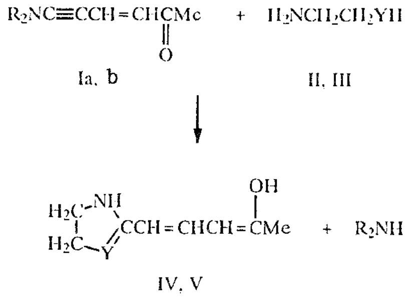
The reaction of 4-dialkylamino-1-acetyl-1-buten-3-ynes with 1-hydroxy-2-aminoethane and 1,2-diaminoethane was used to synthesize 2-substituted oxazoline and imidazoline, containing a fully enolized vinylacetyl fragment.

A method for the synthesis of 2-substituted imidazolines and oxazolines by the reaction of ynamines and alkenylynamines with α,β-difunctional reagents has been proposed in [1, 2]. Acetylene ynaminocarbonyl compounds contain an alkynamine fragment, conjugated with an acceptor carbonyl group; they must therefore possess a stronger electrophilic character. Data on the reactivity of ynaminocarbonyl compounds [3] show that they react differently from the ynamines [1], alkenylynamines [2], and acetylene ketones [4].

In the reactions with 1-hydroxy-2-aminoethane and 1,2-diaminoethane the nature of the hetero atom as well as of the carbonyl function has a considerable effect on the direction of the addition. Thus, the 4-dialkylamino-3-butyn-2-ones formed derivatives of imidazoline and oxazoline [3, 5]. The replacement of the acetyl group by an ester group reflected itself on the direction of cyclization: The dialkylaminomethyl propiolate reacted in the reaction with 1,2-diaminoethane with the participation of both electrophilic centers of the substrate and with the formation of diazepine derivatives [6, 7].

In continuing earlier research we have studied the reaction of ynamino ketones of the vinylacetylene series I with 1,2-diaminoethane (II) and 1-hydroxy-2-aminoethane (III), which led to the formation of imidazoline and oxazoline rings IV and V.



Ia R=Me, b R=Et; II, IV Y=NH; III, V Y=O

The IR spectrum of compound IV contains the absorption bands of the conjugated bond system in the region 1630-1600 cm^{-1} and the broad band of the associated hydroxyl group in the region 3400-3600 cm^{-1}. In the PMR spectrum of compound IV the protons of the methyl group resonate in the form of a singlet at 2.10 ppm, the protons of the methylene groups of the imidazoline ring as a singlet at 3.3 ppm, and the proton at the nitrogen atom in the region of 3.45 ppm. The vinyl protons are represented by two doublets in the region of 5.35 and 6.13 ppm, and by a doublet of doublets at 6.70 ppm. Compound V gives an analogous PMR spectrum.

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The formation of the imidazoline and oxazoline rings obeys the rules, established in the reactions with ynamines [2] and ynamino ketones [3]. The reaction of the ynamino ketones of the vinylacetylene series with 1-hydroxy-2-aminoethane proceeds in stages. Thus, according to PMR data, an O,N-ketene acetal with a diene structure was detected in the products of the addition of monoethanolamine to 4-dialkylamino-1-acetyl-1-buten-3-ynes besides the cyclic product; in the course of the synthesis the acetal was converted to isoxazoline. The enol structure of the final products of the synthesis IV and V is stabilized by conjugation with the formation of an intramolecular hydrogen bond.

Analogous imidazolines, containing in the position 2 of the cycle the fully enolized β-ketoalkyl fragment, have been described in the literature [8].

EXPERIMENTAL

The IR spectra were taken on an IKS-29 spectrophotometer, the thickness of the absorbing layer was 40 μm. The PMR spectra were recorded on Tesla BS-487 C (80 MHz) and Tesla BS-497 C (100 MHz) spectrometers with HMDS as an internal standard. The data obtained in the elemental analysis for C, H, and N correspond to the calculated values.

1-(2-Imidazolinyl)-1,3-pentadien-4-ol (IV, $C_8H_{12}N_2O$). In a reaction flask filled with argon 1.65 g (0.01 mole) 4-dialkylamino-1-acetyl-1-buten-3-yne is mixed with 0.60 g (0.01 mole) 1,2-diaminoethane in 20 ml THF. The mixture is heated to 65-70°C for 2 h, until the disappearance of the absorption band at 2200 cm^{-1} ($C \equiv C$) in the IR spectrum of a sample. After stripping off of the solvent the residue is distilled in vacuum; bp 89-90°C (1 mm). The crystallized product is washed with ether; mp 67°C, yield 0.55 g (36%).

1-(Oxazolinyl)-1,3-pentadien-4-ol (V, $C_8H_{11}NO_2$). Prepared in the same way with the use of ethanolamine and by catalyzing the reaction with two drops of a 5% solution of H_2SO_4 in dioxane. Reaction time 7 h; mp 170°C (from ethanol): yield 0.44 g (32%).

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