Previously it was shown that dienic $\delta$-dialkylamino ketoesters are formed when acetylenic $\beta$-alkoxy ketoesters of the (I) type and vinylacetylenic ketoesters of the (II) type are reacted with secondary amines [1]. In the present paper we continued to study the nucleophilic addition of amines to compounds (I) and (II), and also to acetylenic $\beta$-alkoxy ketones (III) and vinylacetylenic esters (IV), in order to ascertain if it is possible to use primary amines in the addition reactions and also to study the properties and stereo-isomerism of dienic $\delta$-aminocarbonyl compounds. The literature data on the addition of amines to carbonyl-containing conjugated vinylacetylene derivatives are very scanty. They deal with the addition of amines to certain aldehydes and ketones; it is only indicated that labile products, which could not be identified, are formed when reaction is with primary amines [2, 3].

We studied the reaction of primary amines with acetylenic $\beta$-alkoxy ketoesters in greatest detail on the example of the addition of butylamine to (I)

\[
\begin{align*}
\text{CH}_3\text{CO} \rightarrow \text{C} \equiv \text{CH} \rightarrow \text{CH} \equiv \text{CH} \rightarrow \text{NH} \\
\text{EtO} \downarrow \\
\text{CH}_2\text{C} \equiv \text{CH} \rightarrow \text{CO} \rightarrow \text{CH} \equiv \text{CH} \\
\text{EtO} \\
\text{(I)} \\
\text{OEt}
\end{align*}
\]

It proved that this reaction, in contrast to the addition of secondary amines, is very sensitive to temperature. At $-10^\circ$C the ethyl ester of 5-butylamino-2-acetyl-2,4-pentadienoic acid (Va) was isolated as the sole reaction product in 58% yield. At $10^\circ$C, together with a substantial amount of tarry products, we obtained a mixture of three compounds: (Va) (identified without isolation by the UV spectrum and TLC), N-butylaminocrotonic ester (VI) (16%), and N-butyl-3-acetylpyridone (VII) (30%), which were separated by fractional distillation in vacuo and purified by chromatography. The structure of (VI) was proved by comparing it with an authentic specimen, while the structure of (VII) was proved by the elemental analysis data and by the NMR, IR, UV, and mass spectra. The formation of (VII) is the result of the intramolecular cyclization of (Va), which will be described later.

Previously we had reported on the cleavage of acetylenic $\beta$-alkoxy ketones by secondary amines, which leads to the dialkylaminocrotonic acid and acetonone enamne; in view of its lability, the latter could not be isolated [4]. In the present case the opposite picture is observed: the acetoacetic ester enamne (VI) was isolated, while the formation of the butylaminocrotonic ketone could not be ascertained.

In [4] it was shown that the cleavage takes place only in the case of an alkoxycrotonic ketone, but not of a vinylacetylenic ketone. In the present paper it was shown that (VI) is formed in 16% yield when vinylacetylenic ketoester (II) is reacted with butylamine. Apparently, profound dehydration occurs when (I) and (II) are reacted with primary amines at $0^\circ$, as a result of which one of the formed products is (VI). The reactions of (I) with other primary amines also proceed in a similar manner. The yields and constants of amino ketoesters (Va, b, c, d) and (IX), which were obtained at low temperature, are given in Table 1.
The same amino ketoesters are formed when (II) is reacted with primary amines at low temperature.

\[ \begin{align*}
\text{CH}_2\text{CO} & \xrightarrow{\text{ENH}_2} \text{CH}_2\text{CO} \\
\text{EtOCO} & \xrightarrow{(\text{II})} \text{EtOCO} \\
\text{R} & = \text{C}_6\text{H}_5, \text{C}_3\text{H}_7, \text{CH}_2\text{C}_6\text{H}_5.
\end{align*} \]

We were unable to add primary amines to \( \beta \)-alkoxy ketoesters containing a substituted acetylenic bond, or to 3-ethoxy-5-hexyn-2-one (III). Only N-butyraminocrotonal found in the latter case; 6-butyramino-3,5-hexadien-2-one, in view of its lability, could not be isolated, although its formation was confirmed by the UV spectrum. For a subsequent comparison of the properties, stereoisomerism and reactivity we prepared the dienic \( \delta \)-amino esters (VIIa, b, c) by the addition of primary and secondary amines to the "trans" ester of 2-penten-4-yne-2-carboxylic acid (IV), and a number of dienic dialkylamino ketoesters (X, Xib, c, d) and (XII) from acetylenic \( \beta \)-alkoxy ketoesters using the method described in [1]*

\[ \begin{align*}
\text{CH}=\text{C}-(\text{CH} & =\text{CH})\text{COOR} \xrightarrow{\text{ENH}_2} \text{R}^+\text{RC} \tag{IV} \\
\text{R} & = \text{CH}_3, \text{R}^+ = \text{Et} (a); \text{R} = \text{C}_6\text{H}_5, \text{R}^+ = \text{C}_6\text{H}_5 (b); \text{R} = \text{C}_6\text{H}_5, \text{R}^+ = \text{H}, \text{R}^2 = \text{C}_6\text{H}_5 (c).
\end{align*} \]

It should be mentioned that although amines add less vigorously to (IV) than to (II), still the dienic \( \delta \)-amino esters (VIIa, b, c) are formed in quite good yields here and are completely stable compounds both in the crystalline state and in solutions. The yields, constants, and analyses of all of the synthesized compounds are given in Table 1.

The monoalkylamino ketoesters (Va, b, c) and (IX) are completely unstable in solutions: they are converted completely to a tar within 10-20 min after they have been dissolved at 20° in ether, acetone, benzene, or CC14. A comparison of the spectral data for the dienic amino ketoesters containing a secondary amino group with the esters containing a tertiary amino group discloses that the former are also found in the form of dienic amines, and not of iminoenols. Thus, the UV spectrum of (Va) in ethanol has \( \lambda_{\text{max}} \) 395 nm (\( \varepsilon \) 52,750), it is practically the same as in the case of compound (XIa); \( \lambda_{\text{max}} \) 396 nm (\( \varepsilon \) 57,100); the indicated relationship can also be followed on other examples (see Table 1). By analogy with enaminoketones [5], a hypsochromic shift of \( \lambda_{\text{max}} \) could be expected in the case of the iminoenols when compared with the authentic dienic amino ketoesters. The IR spectra also corroborate the dieneamine, and not the iminoenol structure: (Va) as a solid gives a broad band of medium intensity in the vicinity of 3160 cm\(^{-1} \) (it is absent in compounds of the (XI) type), which relates to the stretching vibrations of the associated NH group; this band disappears in dilute CC14 solution (~0.01 M), and a narrow band of the vibrations of the free NH group appears at 3450 cm\(^{-1} \).

The protonation of the dienic amino ketoesters (Va), (XIa), and (XII) proceeds in identical manner. It was established that the O-protonation of \( \alpha, \beta \)-unsaturated \( \beta \)-aminocarbonyl compounds, having three reactive centers for attack by electrophilic reagents, occurs predominantly [6, 7].

The UV spectra of (Va), (XIa), and (XII) in methanol, saturated with HCl, respectively have \( \lambda_{\text{max}} \) 347, 354, and 352 nm, while in CCl4, saturated with Cl2CCOOH, the respective values are 362, 356, and 357 nm. These data show that O-protonation also occurs predominantly in the case of the dienic amino ketoesters, since in the case of N-protonation the free electron pair on nitrogen would be excluded from the conjugation, while the formed salt would have the chromophore of the dienic ketoester with \( \lambda_{\text{max}} \) 276-295 nm [8].

The disappearance of geometric isomerism at the \( \alpha, \beta \)-double bond [1] and the strong shift of the \( \delta \)-proton downfield by approximately 1 ppm in the spectrum of compounds (Va) and (XIa) in CH3OH + HCl can also be explained by O-protonation. Not excluded is the fact that N-protonation does exist, but the concentration of the N-protonated form is very small. The conjugation would be upset if there was noticeable protonation of the \( \gamma \)-C atom in (Va) and (XIa), which would lead to a substantial shift of \( \lambda_{\text{max}} \) toward shorter wavelengths. Here in the NMR spectrum could be expected either the appearance of the signal of the protons of the methylene group at \( \gamma \)-C, or, if rapid exchange between the O- and \( \gamma \)-C-protonated forms is present, a substantial shift of the methine proton at \( \gamma \)-C upfield, which actually was not observed. However, the replacement of the proton at \( \gamma \)-C by deuterium to the extent of 42% is observed in the NMR.

*We were unable to obtain the ester of 6-(ethylenimino)-2-acetyl-4-pentadienoic acid by the addition of ethylenimine to (I) and (II).