It is demonstrated that 3,5-dibromo-3,4-dihydropyridones are formed in the bromination of derivatives of δ-keto amides. The course of the bromination was investigated in the case of N-substituted and N-unsubstituted δ-keto amides. Dibromo-3,4-dihydropyridones were converted to the corresponding monobromopyridones. The stabilities of the compounds obtained were studied by subjecting them to thermal analysis. The structures of the compounds obtained were confirmed by their PMR, IR, and UV spectra.

We have previously shown that δ-keto amides I undergo intramolecular cyclization to dihydro-2-pyridone derivatives under the influence of acids or bases [1]. N-Alkyl-substituted δ-keto amides II do not form a dihydropyridone ring (III) under similar conditions because of steric hindrance. This paper is devoted to a study of the bromination of N-alkyl- and N-unsubstituted δ-keto amides in order to synthesize bromo derivatives of dihydro-2-pyridones.

The bromination of N-alkyl-δ-keto amides II with a twofold excess of bromine in chloroform or in acetic acid at room temperature leads to 1-alkyl-3,5-dibromo-3-(N-alkylcarbamoyl)-4,6-diphenyl-3,4-dihydro-2-pyridones (VIII). The UV and IR spectra of pyridones VIII (Table 1) are similar to those obtained for nitrogen-unsubstituted 3,4-dihydro-2-pyridones [1, 2], and this indicates that they have a dihydro structure. The PMR spectra of VIII (Table 2) contain, in addition to signals of protons of two phenyl and alkyl groups and an exocyclic amide group, singlets at 4.63-4.66 ppm, which correspond to the 4-H proton, and this confirms the presence of bromine in the 3 and 5 positions of the pyridone ring.

γ-Bromo-δ-keto amides IV are formed initially in the reaction of δ-keto amides II with 2 moles of bromine. This is confirmed by the bromination of amides II with an equivalent amount of bromine, as a result of which we obtained γ-butyrolactones V [3], which are capable of being formed only from γ-bromo-substituted δ-keto amide IV. The subsequent bromination of IV takes place in the α position to give α,γ-dibromo-substituted δ-keto amides VII, which, in contrast to IV, undergo cyclization to pyridones VIII. The bromine atom in the α position in amide VII promotes both spatial drawing together of the N-alkylamido and δ-carbonyl groups and hydrolysis of the N-alkylamido group. The spatial drawing together, which is responsible for the production of bromo derivatives of dihydropyridones VIII rather than lactones VI, which can be obtained only by bromination of lactone V, is the decisive factor in this case.
Dihydropyridones VIII in a slightly alkaline medium readily split out a molecule of HBr to give 5-bromo-2-pyridone derivatives IX. As compared with dihydro derivatives VIII, the signal of a 4-H proton is absent in the PMR spectra of pyridones IX (Table 2), a 70-nm bathochromic shift of the long-wave maximum is observed in the UV spectra, in connection with the formation of a pyridone ring, and a 30-38 cm\(^{-1}\) decrease in the frequencies of absorption of the endocyclic amide carbonyl groups is observed in the IR spectra (Table 1).

The bromination of N-unsubstituted \(\delta\)-keto amides proceeds via a different pathway. Regardless of the amount of bromine (1:1 and 1:2) introduced into the reaction mixture, \(\delta\)-keto amide I forms 3,5-dibromo-3,4-dihydro-2-pyridone, which is isolated in the form of hydrobromide salt XII. It is difficult to establish the sequence of the bromination and cyclization reactions in this case. It may be assumed that the initial product is \(\gamma\)-bromo-substituted X, which, under the influence of the liberated hydrogen bromide undergoes cyclization to 5-bromo-3,4-dihydro-2-pyridone (XI) and upon further reaction with bromine gives 3,5-dibromo-3,4-dihydro-2-pyridone (XII). \(\alpha\)-Cyano-\(\delta\)-keto amides are brominated similarly [4]. Compound XII is also formed by bromination of dihydropyridone XIII, which may be formed simultaneously with X under the influence of the liberated hydrogen bromide, since it is known that \(\delta\)-keto amide I in an acidic medium readily forms a 3,4-dihydropyridone. In