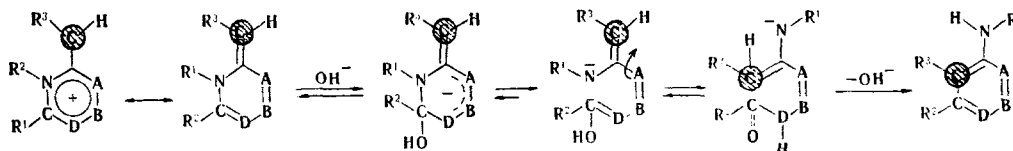


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We have observed that recyclization with cleavage of a carbon-nitrogen bond and the formation of a carbon-carbon bond can occur under the influence of bases on the electron-deficient ring (for example, the pyridine ring) of a compound with an electron-surplus fragment within the ring. Thus opening of the pyridine ring with subsequent attack on the pyrrole portion of the molecule and the development of a benzene ring, which leads to the formation of indoles, occurs in the reaction of an alkali with indolizines [1, 2]. Similarly, 1-alkyl-2-methylpyridinium salts are converted to substituted anilines [3]. The reaction proceeds through the open form, which can simultaneously undergo hydrolytic cleavage or, when amines are used as the bases, can undergo cyclization with complete or partial exchange of the amino group. The conversion of the pyrimidine ring to a pyridine ring under the influence of bases on pyrazolo[1,2-a]pyrimidines [4] or pyrimido[1,2-a]indoles [5] proceeds similarly. Correspondingly, the 1,2-dialkylpyrimidinium salts are converted to 2-alkylaminopyridines. Except for those cases in which the amino group undergoes exchange, these reactions proceed without inclusion of the reagent in the composition of the product molecule, i.e., they have the character of isomerization reactions. The observed group of rearrangements has something in common with the Dimroth rearrangement but differs with respect to the fact that a new carbon-carbon bond is formed during ring closure. The overall scheme of these isomerization processes can be formally depicted as follows:



The atom at which ring closure occurs is usually the β -carbon atom of the enamine fragment that is present in the starting molecule or develops during the reaction. The initial steps are reversible, but the formation of a new carbon-carbon bond is irreversible under normal conditions. If there is a strong electron-acceptor group in the ring, quaternization of the nitrogen atom is not necessary. On the basis of these concepts we were able to predict and subsequently realize a number of new reactions. The description of some of them is being prepared for publication.

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