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REACTION OF BICYCLIC BROMIDE DERIVATIVES WITH PIPERIDINE AND MORPHOLINE

G.B. Raxmatova

Karshi State Technical University, Department of Natural Sciences

rakhmatova 85guzal@mail.ru

Abstract. This article studies the nucleophilic substitution reactions of α-bromoacyl derivatives of thiainden and thiachroman, which have a bicyclic structure containing sulfur, with secondary amines, namely piperidine and morpholine, which have a cyclic structure.

Keywords. Thiainden, thiachroman, bromacyl, aminoketone, bicyclic, nucleophile, piperidine, morpholine, hydrochloride.

All halogen-containing organic compounds react quite well with amino compounds and their derivatives. In particular, as a result of the reaction of β-bromoacyl derivatives of thiamin and thiachroman with amino compounds, the corresponding β-aminoketones of these substances were synthesized and their pharmacological properties were studied. From a pharmacological point of view, it was known that β-aminoketones of these substances have very good anesthetic properties [1,2].

In the same place, in order to study how the pharmacological properties of these substances can change when the amino group in the side chain of the molecule of these substances passes from the β-state to the α-state, we studied the reaction of α-bromoacylthiain and α-bromoacylthiachroman with cyclic amines. At the same time, the reaction conditions, reaction mechanism, reaction rate, factors affecting the reaction, the substrate entering the reaction, and the reactivity of the reagent were studied.

In this article, the nucleophilic substitution reactions of α-bromoacyl derivatives of thiain and thiachroman, which have a bicyclic structure containing sulfur, with secondary amines, namely piperidine and morpholine, which have a cyclic structure, were studied.

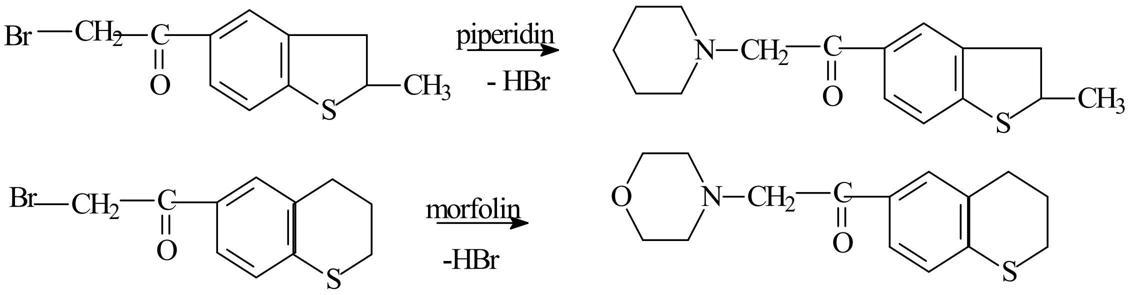
The ease of substitution of the bromine atom in the α-bromoacylthiain and α-bromoacylthiachroman molecules depends on the presence of a partial positive charge on the attacked carbon atom and the strength of the nucleophilic reagent. The greater the positive charge on the attacked carbon atom, the easier the nucleophilic substitution will be in reactions under the same conditions. The value of this charge depends on the electronegativity of the atom directly bonded to the attacked carbon atom. Although halide ions are considered weak nucleophiles among anions, they significantly create a partial positive charge on the attacked carbon atom in the substrate, i.e., they reduce the electron density. Also, if the carbon atom adjacent to the halogen atom has electron-withdrawing substituents, the rate of the nucleophilic substitution reaction proceeding according to the SN2 mechanism increases.

The nucleophilicity of a reagent (nucleophilicity) refers to anions or neutral molecules that form a covalent bond with one of the electron-deficient carbon atoms in an organic molecule (substrate) due to the lone pair of electrons of any atom in the compound. The higher the nucleophilicity of a reagent in an SN2 nucleophilic substitution reaction, the higher the reaction rate under the same reaction conditions.

The number and size of the substituents also affect the nucleophilic reactivity. For example, the nucleophilicity of piperidine and morpholine is higher than that of diethylamine, because the ring formed by the methylene groups in piperidine and morpholine is tightly packed in space, while the mobile ethyl group of diethylamine makes it difficult for the lone electron pair on the nitrogen atom to interact with the electron-deficient carbon atom in the α-bromoacylthiain and α-bromoacylthiachromane molecules.

The dielectric permittivity and dipole moments of the solvents also affect the reaction rate to some extent. It is known that nucleophilic substitution reactions that proceed in the SN_2 mechanism are slower when carried out in nonpolar solvents (for example, hexane or benzene) than in aprotic solvents. The main reason for using the nonpolar solvent benzene in this reaction was to selectively carry out the reaction in the SN_2 mechanism. Of course, SN_2-type reactions are easy to carry out in aprotic solvents, including ethers, dioxane, acetone, acetonitrile, nitromethane, and similar solvents. However, these solvents also exhibit nucleophilic properties. These solvents retain lone pairs of electrons and, in turn, solvate cations. Replacing weakly solvating solvents with strongly solvating solvents allows you to shift the SN_2-type reaction zone to the SN_1 zone and affects the selectivity of the reaction.

The reaction of α-bromoacylthiain and α-bromoacylthiachromans with secondary amines, namely piperidine and morpholine, for 30 minutes in a benzene solution yielded the corresponding α-aminoketones of these substances. By passing dry hydrogen chloride gas through the resulting α-aminoketones in benzene, the corresponding hydrochloride compounds of these substances were obtained. Each nucleophilic reagent exhibits basic properties to a greater or lesser extent. This indicates that it can not only react with the electron-deficient carbon atom due to its lone pair of electrons, but also can abstract mobile hydrogen and protons from the substrate. Due to this, it can also form compounds that are less dissociable than the original substrate. Therefore, to a greater or lesser extent, the nucleophilic substitution reaction of the halogen atom is accompanied by a dehydrohalogenation reaction (elimination of hydrogen halide) in parallel. As a product of such reactions, alkenes are formed and it has a quantitative effect on the yield of the main product of the reaction.



As a result of the reaction, it was found that aminoketones with a thiachroman fragment have a higher mass fraction in the reaction than aminoketones with a thiainden fragment. Also, it was found that the nucleophilicity of piperidine and morpholine obtained as an active reagent in this reaction is higher in the morpholine molecule. According to the yield of the products formed as a result of the reaction, it was found that the nucleophilicity of the morpholine molecule in both substrates is higher than that of piperidine.

The reaction progress and purity were monitored by thin-layer chromatography on Silufol plates in a benzene-hexane system (1:9). The structure and composition of the obtained substances were confirmed by IR and PMR spectroscopic methods and elemental analysis methods.

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