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Experimental and theoretical study of the fragmentation of dichloro-3-aryl-2,1-benzisoxazoles

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Abstract

2,1-Benzisoxazoles or anthranyls have different types of biological activity, are used to obtain monomers for polymeric materials, dyes and other heterocyclic compounds. In addition, 2,1-benzisoxazoles attract the attention of researchers due to the presence of a weak N-O bond, which is a potential place for the opening of the cycle in the reactions of reduction, oxidation, and various transformations. Therefore, it is very important to study their structure, methods of identification and reactivity in the processes taking place with their participation. One of the most effective modern research methods in chemistry is chromatography-mass spectrometry and quantum-chemical modeling. And since the fragmentation of molecules during their electron impact ionization depends on the nature of the compounds and characterizes their reactivity in various types of chemical reactions, the aim of this work was to experimentally and theoretically study the fragmentation of dichloro-3-phenyl-2,1-benzisoxazoles. For this, the corresponding dichloro-3-aryl-2,1-benzisoxazoles were synthesized by condensation of nitroarenes with arylacetonitriles in the presence of an excess of sodium hydroxide. The chromatography-mass spectrometry method was used to study the directions of fragmentation of their molecular ions. It was found that for all the compounds studied, similar fragment fragments are observed in the mass spectra, which indicates similar patterns of their fragmentation. Based on the data of quantum chemical modeling using the PC GAMESS/FireFly 8.2 software package using the density functional theory method, it was suggested that even before the decay of the molecular ions of dichloro-3-aryl-2,1-benzisoxazoles, they rapidly transform into the corresponding cation radicals of dichloroacridinones with the same atomic composition. Further decomposition of dichloroacridinone ions is accompanied by the release of a chlorine atom, carbon monoxide and skeletal rearrangement with the formation of the corresponding chlorocarbazole ions. Chlorocarbazole ions then eject a hydrogen chloride molecule to form a cation with m/z 164 and atomic composition $C_{12}H_6N$.

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