QUANTUM CHEMICAL STUDY OF THE EFFECT OF N,N-ACYL GROUP NATURE ON THE STRUCTURE AND GIBBS FREE ENERGY OF THE SULFUR KETOYLIDES AND PRODUCTS OF THEIR TRANSFORMATIONS

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With the purpose to study the effect of the nature of the imido-group of N,N-acyl-protected β-methyl-substituted keto-stabilized sulfonium ylides on the formation of methylthiopyrrolisinediones by cyclization, the structure features of these ylides are investigated by *ab initio* methods. The imido-group nature is shown to insignificantly affect in most cases the structure and the relative free energy of conformers of the ketoylides in question and the products of a cyclization reaction with their participation. The energy difference between the *anti-peri*-planar and *syn*-clinal orientation of nitrogen atoms in the imido-group and ylide carbon atom is negligible. The latter orientation is necessary for the reaction of intramolecular cyclization to proceed because in this case carbon atoms between which the bond forms are drawn together. The structure of cyclic pentanomial N,N-acyl group slightly affects the calculated values of Gibbs free energy of sulfur ketoylide reactions, and a temperature increase promotes the intramolecualr cyclization reactions. Wittig and Corey–Chaykovsky reactions typical of ylides are the least thermodynamically favorable for the sulfonium ketoylides under study.

Keywords: conformation analysis, sulfonium ylides, Gibbs free energy, intramolecular cyclization, effect, imido-group, non-empirical study.