

Molecular Rearrangements of Terpenoids: Prognosis and Reality

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The lecture analyzes the key factors permitting one to control multistep and multiroute cationoid molecular rearrangements. This study was accomplished for natural compounds - terpenoids and their analogs, which are characterized by conformational mobility and polyfunctionality and are apt to undergo various acid-catalyzed rearrangements. It is shown that the chief «levers» for control over such processes in superacid media at superlow temperatures are 1) the nature of an acid medium, 2) the type of cation center generation reaction, 3) the temperature of cation center generation, 4) the temperature of ``defreezing'' of an acid solution. Several techniques for predicting the most probable routes of multiroute cationoid rearrangements, simultaneously taking into account the orbital and thermodynamic factors, are suggested. It is shown that in liquid superacids all possible cationoid transformations of substrates are feasible. To prepare a substrate, it is necessary to select a solid acid catalyst -- aluminosilicate (clay, zeolite) or superacid. The role of these heterogeneous catalysts in (intra- or intermolecular) reactions of terpenoids is not only acid catalysis, but also determining the mutual spatial arrangement of substrate and reagent and the site of cation center generation. Due to this, using solid acid catalysts is promising from the viewpoint of discovering new unusual transformations to drastically expand the synthetic utility of recyclable raw materials under ecologically safe conditions.