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New bimolecular mechanistic pathway for 1,3-hydrogen shift in allenamide and allene system: A theoretical prediction

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ABSTRACT

Thermal isomerization of allenes or allenamides are commonly viewed as a [1,3] hydrogen shift process from a substituent alkyl group to the central sp-hybridized carbon atom in the molecule. Though it is a common believe that the reaction is feasible in antarafacial migration of hydrogen, the mechanistic pathway has to cross a huge activation barrier to carry out the process. Here we have proposed several bimolecular pathways that are found to be energetically more favorable than the commonly believed mechanism of antarafacial migration of hydrogen. The carboxylic acid catalyzed reaction requires minimum activation energy and may be considered as the most favorable process. The mechanism involves the proton transfer through a relay process. Solvent acetonitrile, can catalyze the isomerization through a tandem ene/retro-ene pathway and demands higher activation energy. Other mechanisms through a similar tandem process may be capable to isomerize allenamide and allene system through self catalysis and have to cross similar activation barrier as shown by acetonitrile catalyzed mechanism. All the mechanistic pathways are validated by DFT calculation using B3LYP/6-31G* method.

1. Introduction

Synthesis of conjugated dienes through various approaches has drawn a great deal of attention of organic chemists for many years [1–8]. These molecules serve as the key starting material for the synthesis of enormous array of structurally complex skeletons occurring in several biologically active natural products [9–17]. A very simple and logical scheme for the synthesis of such diene is the allene [18,19] isomerization [20–23] in which a [1,3]-H shift is believed to occur from a substituent alkyl group to the sp-hybridized carbon atom present at the center of the allene system (Scheme 1) [24–26].

Meier and Schmitt [27] showed that such process in a cyclic allene system (ethynylidene cyclopentane) can occur at high temperature (540 °C) under flash vacuum pyrolytic condition. The requirement of such high temperature obviously put the difficulties to control the selectivity of the reaction thus prohibits the process to adopt as a first choice for synthesizing conjugated dienes. The Woodward–Hoffmann symmetry rules for [1,3] sigmatropic migration of hydrogen in an antarafacial manner has generally been put forward as a probable explanation for the need of high temperature [28]. However, the estimation of activation energy by Jensen showed [24] a large difference between the experimentally observed value and theoretical proposal of [1,3]-H migration in concerted process for the reaction. It was argued by the author that the process may likely take place through a mechanism other than simple [1,3]-H shift in a concerted manner.

Of late, Hsung and his group have published an interesting protocol for easy isomerization of allene derivative to 2-amido diene [29,30]. They observed that allenamide [31], a subclass of allene, when heated in acetonitrile solution isomerizes to 2-amido conjugated diene. Both stereoselectivity (in favor of E-isomer) and regioselectivity (in favor of α-isomerization) was noted when proper substrate was selected (Scheme 2). The reaction becomes facile at room temperature when carboxylic acid or sulfonic acid is present in the reaction mixture.

Such facile transformation of allenamide to conjugated amido diene and the related stereo and regioselective features of the reaction put serious questions before the assumption of the energetically unfavorable concerted [1,3]-H migration as a plausible mechanism of the process. Still now it remains an unsolved problem how the reaction occurs with a lower activation barrier.

In this report we have primarily paid attention in designing several pathways for allenamide isomerization process that can answer successfully all the questions regarding energetic, stereoselective and regioselective features related to the reaction. While designing the pathways we have considered the active participation of solvents or other reagents in the mechanism for lowering the activation barrier of isomerization. Relative energies of the possible transition structures (TSs), calculated using standard

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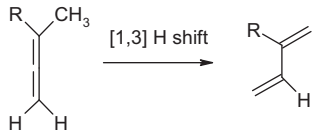


Scheme 1. Isomerization of allene to conjugated diene.

DFT method, allow us to compare the probability of each pathway. Several stereoselective and regioselective features, reported so far, have been explained on the basis of the proposed reaction mechanisms. Knowledge gained from these studies is then utilized for designing another bimolecular pathway for allenamide or allene isomerization proceeding via self catalysis without the assistance of any solvent molecule. Our ultimate result supports that isomerization of allene should follow a pathway different from concerted [1,3]-H migration that puts low activation barrier before the necessary hydrogen shift and allow it to occur at low or room temperature.

2. Computational methods

All reactants, transition structures and products were optimized at DFT level using B3LYP hybrid functional [32] and 6-31G* basis set [33–35]. Our previous experiences show that this quantum mechanical method is quite suitable to predict the geometries and energies of the stationary points on the Potential Energy Surface (PES) of Alder ene reaction [36–38]. As our proposed mechanistic pathways consist of this fundamental step we have selected this method for the present study. Since solvent molecules have been used explicitly to catalyze the isomerization in the proposed mechanism, the solvent effect to stabilize the TSs has not been investigated separately. Moreover the allene isomerization was previously studied under flash vacuum pyrolytic condition [27] for which the gas phase calculation may be a better approximation. All the structures were characterized by frequency analysis. Thermodynamic functions were calculated at the reported experimental temperatures. Kinetic isotope effects (KIEs) have been calculated using the difference of standard free energies of activation [39,40].

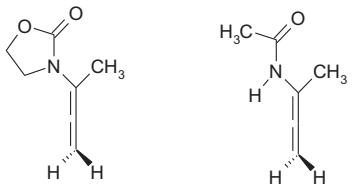
$$k_H/k_D = \exp[(\Delta G_D - \Delta G_H)/RT] \quad \Delta G = G^{\neq} - G.$$

For constructing trial structures and analyzing the optimized geometries MOLDEN [41] software was used and all the calculations were performed using GAMESS [42] software.

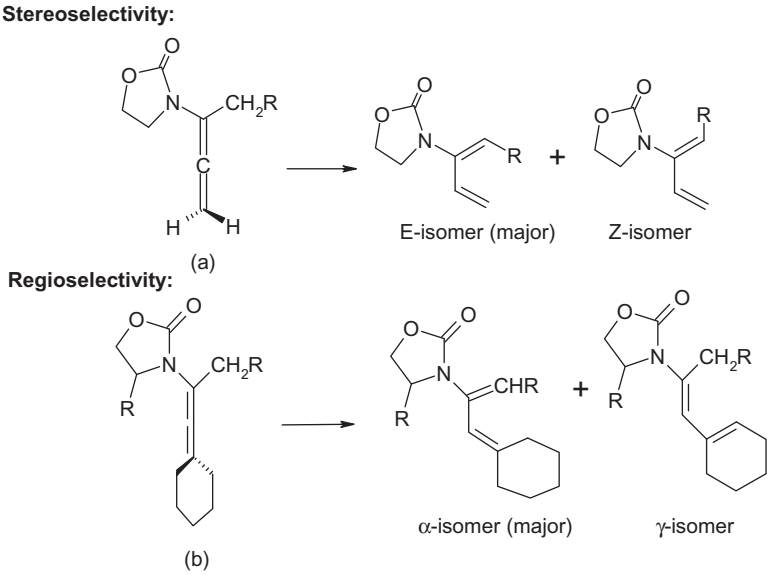
3. Results and discussions

3.1. Model reactant and its conformational analysis

Different types of allenamide derivatives were used for the study of isomerization reaction by several authors. Though recent studies rely on cyclic allenamide (e.g. **1**) [29–31] previous observations were based on some acyclic systems [43]. In order to avoid structural complexity a simple acyclic model system (**2**) has been selected for the present investigation.



Conformational analysis of structure **1** and the model structure **2** shows that the molecules are energetically biased towards a nearly planar conformation around the C—N bond in which the allenic carbons and the atoms of amides connected to nitrogen lie approximately on a single plane (Fig. 1). The two possible planar geometries, *syn* and *anti*, are stabilized by delocalizing the lone pair of nitrogen in the allenic double bond and carbonyl oxygen. However, such conformations suffer from the eclipsing interactions between the groups connected to C—N bond. The antiperiplanar arrangement of the associated groups (structure **1a** and **2a** in Fig. 1) is found to be more favorable over the synperiplanar one (**1b** and **2b**). The electrostatic repulsion between the carbonyl oxygen and allenic double bond in the synperiplanar conformation (**1b**, **2b**) is the probable reason behind it. Such destabilizing factor distorts the ideal shape of the molecule in synperiplanar arrangement and thus the conformation **1b** deviates from its planar structure by forming 49.57° dihedral angle around the C—N bond whereas the linear shape of the allenic carbon chain in **2b** is



Scheme 2. Allenamide isomerization.