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Thermal rearrangement of 2-acetoxy-2,6,6-trimethylbicyclo[3.1.0]hexane: Theoretical elucidation of the mechanism

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Abstract

Bicyclohexenes are believed to be the immediate precursors of aromatic compounds. As a part of the exploratory study of thermal aromatization reactions, 2,6,6-trimethylbicyclo[3.1.0]hexan-2-ol and its ester derivative 2-acetoxy-2,6,6-trimethylbicyclo[3.1.0]hexane were synthesized. Pyrolysis of 2-acetoxy-2,6,6-trimethylbicyclo[3.1.0]hexane at 350 °C gave 1,3,3-trimethyl-1,4-cyclohexadiene instead of the expected product, 2,6,6-trimethylbicyclo[3.1.0]hex-2-ene. Computational methods such as PM3, HF/6-31G*, B3LYP/6-31G*, UHF/6-31G*, UB3LYP/6-31G*, and UMP2/6-31G* were employed in order to elucidate the mechanism of this reaction. The Gibbs free energy of activation and the reaction energy were calculated for the proposed polar and biradical mechanisms. The results showed that a two-step mechanism is plausible at 350 °C in which the expected product 2,6,6-trimethylbicyclo[3.1.0]hex-2-ene is the intermediate. The first step is the 1,2-elimination of the ester, leading to 2,6,6-trimethylbicyclo[3.1.0]hex-2-ene. The second step is the sigmatropic rearrangement of 2,6,6-trimethylbicyclo[3.1.0]hex-2-ene via concerted homodienyl 1,5-hydrogen shift, which is also the rate-determining step. UB3LYP/6-31G* calculations reveal that the cyclopropyl moiety of bicyclo[3.1.0]hex-2-ene can undergo homolytic bond cleavage to give an allylically stabilized biradical intermediate. However, the formation of 1,4-cyclohexadiene from such an intermediate through a biradical transition state involving 1,2-hydrogen migration does not seem to be plausible.

Keywords: Diradical intermediates; Singlet diradicals; Reaction profile; Bicyclic alkenes; Spin density

1. Introduction

The bicyclo[3.1.0]hexane system and its analogues have been the subject of numerous computational and experimental studies because of their strain energy and interesting ring-opening and skeletal-ring-rearrangement reactions [1–3]. Research on alkene analogs of these systems is also important especially for the petroleum industry, because such bicyclic alkenes can produce aromatic compounds at high temperatures. Theoretical studies on the thermal isomerization of bicyclo[3.1.0]hex-2-ene have also attracted much attention recently, because this system is an ideal model for studying degenerate rearrangement involving the continuous biradical transition state [4–6].

The pyrolysis of bicyclo[3.1.0]hex-2-ene in the range 314–347 °C in a flow system affords cyclohexadienes, benzene, and hydrogen [7]. Skeletal rearrangement occurs at the bicyclo ring system and may occur by one or both of two "ring walk" sequences. In order to gain insight into the thermal aromatization of this bicyclic system, a series of bicyclo[3.1.0]hexene derivatives were synthesized, and their pyrolysis reactions were studied in previous investigations [8,9]. Along this line, 2-acetoxy-2,6,6-trimethylbicyclo[3.1.0]hexane **1** was synthesized as a precursor of 2,6,6-trimethylbicyclo[3.1.0]hex-2-ene and then pyrolyzed. To our surprise, pyrolysis of **1** in a flow system at 350 °C gave

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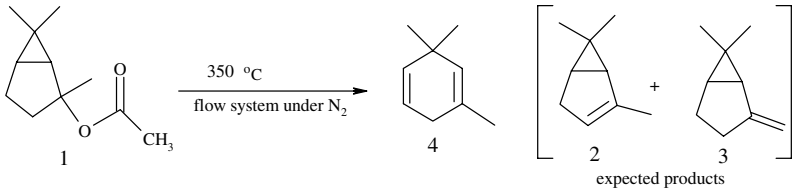
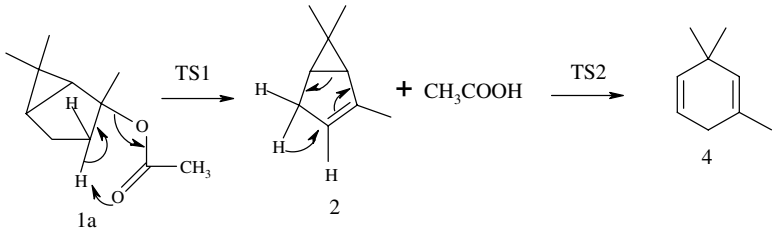


Scheme 1. Pyrolysis of **1**.

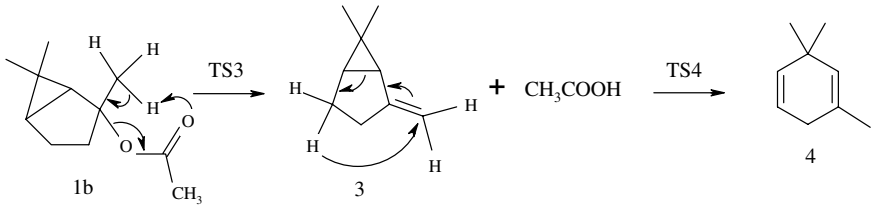
1,3,3-trimethyl-1,4-cyclohexadiene **4** instead of the expected bicyclic alkene products **2** and **3**, as shown in Scheme 1.

Along with these experimental findings, computational investigation of the conversion mechanism of compound **1**–**4** will be discussed in this paper.

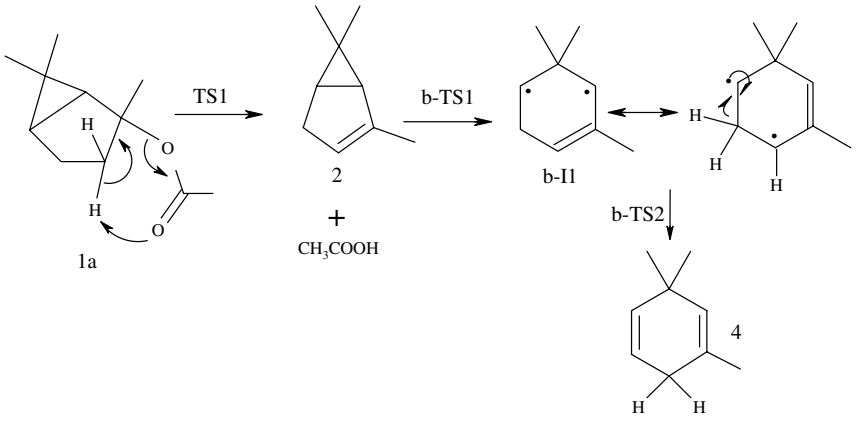
We proposed several mechanisms for the reaction shown in Scheme 1. Mechanism I (Scheme 2) and Mechanism II (Scheme 3) were formulated to take into account the possibility that the expected bicyclohexene products **2** and **3** could be the intermediates of the thermal rearrangement leading to **4**. Both of these mechanisms involve two steps. The first step is the ester pyrolysis of the initial compound **1** to give the expected products **2** or **3**, and the second step is the 1,5-homodienyl hydrogen shift to produce the observed product **4**. Mechanisms III and IV (Schemes 4 and 5) were formulated to take into account the possibility of formation of biradical intermediates during the reaction, because various biradicals are believed to appear in the course of thermal aromatization reactions [7,9,10]. In addition, biradical intermediates and transition structures are also proposed to explain the thermal rearrangement mech-



Scheme 2. Mechanism I.



Scheme 3. Mechanism II.



Scheme 4. Mechanism III.