



Study on the mechanism of isomerization of oxaspirohexane catalyzed by Zeise's Dimer

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ABSTRACT

Mechanism of the rearrangement of oxaspirohexane to 3-methylenetetrahydrofuran under the catalysis of Zeise's dimer has been studied using DFT methods. Our results reveal that the catalyst, at the initial stage, undergoes a considerable change in structure under the influence of the substrate and the two metal atoms bind the substrate at different positions. Rearrangement of the substrate molecule then takes place to generate the tetrahydrofuran derivative through the formation of platinacyclobutane intermediate, as revealed in the experimental report. Depending on the variation of substrate structure and environmental condition the diversion of the mechanistic pathway to generate different products can also be explained by the DFT methods. Application of several functionals in calculating the global activation barrier also reveals that M06 functional is the most suitable choice to deal with this type of problem and to predict the global activation barrier.

1. Introduction

Zeise's salt, the first organometallic compound [1] isolated in the year of 1827, is a platinum metal complex obtained in monomeric and dimeric forms. During the past two or three decades the catalytic activity of many platinum [2] and gold [3] complexes on a variety of substrates has been reported which include the action of Zeise's salt on several organic substrates [4]. Many of these reports revealed the rearrangement of cyclopropane derivatives. One such recent report has caught our attention for the absolute necessity of the Zeise's salt as catalyst in its dimeric form [5] (Scheme 1). The substrate in this transformation is an oxaspirohexane derivative where two rings connected to a common carbon atom are nearly perpendicular to each other. Upon treatment with Zeise's salt at 45 °C in DCM, the substrate changes to a nearly planar tetrahydrofuran derivative.

In the proposed mechanistic pathway [5] the authors suggested an initial activation of the cyclopropane ring by forming a coordinate bond to the metal centre (Scheme 2). After binding to the substrate structure the metal atom, on oxidative addition, gets inserted into the cyclopropane ring forming a platinum-cyclobutane derivative. Using ¹³C NMR spectroscopy the authors also confirmed the formation of this four-membered derivative as an effective intermediate in the reaction pathway. This intermediate, on subsequent rearrangement, transforms to the final product of tetrahydrofuran derivative. Though the proposed pathway gives us a qualitative picture of the mechanism of the reaction,

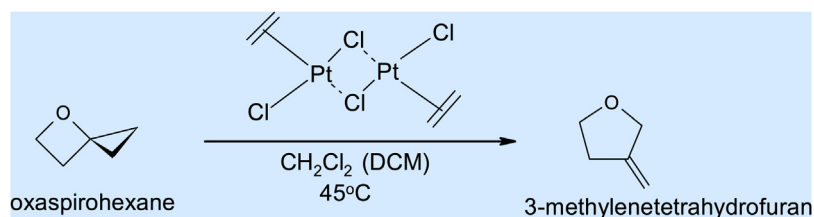
it cannot explain several facts observed in the experimental reports. Various mono nuclear platinum complexes were found to be ineffective to bring out the transformation. However, the mechanism, proposed by the authors, shows the involvement of only one platinum atom in the reaction pathway.

The authors also observed that the presence of other reagents in reaction medium and the variation of substrate structure divert the pathway to form products other than the tetrahydrofuran derivative (Scheme 3). Specifically the presence of sufficient amount of methanol in the reaction medium leads to an open chain compound, which reveals the involvement of the nucleophilic activity of the methanol in the reaction (Scheme 3(b)).

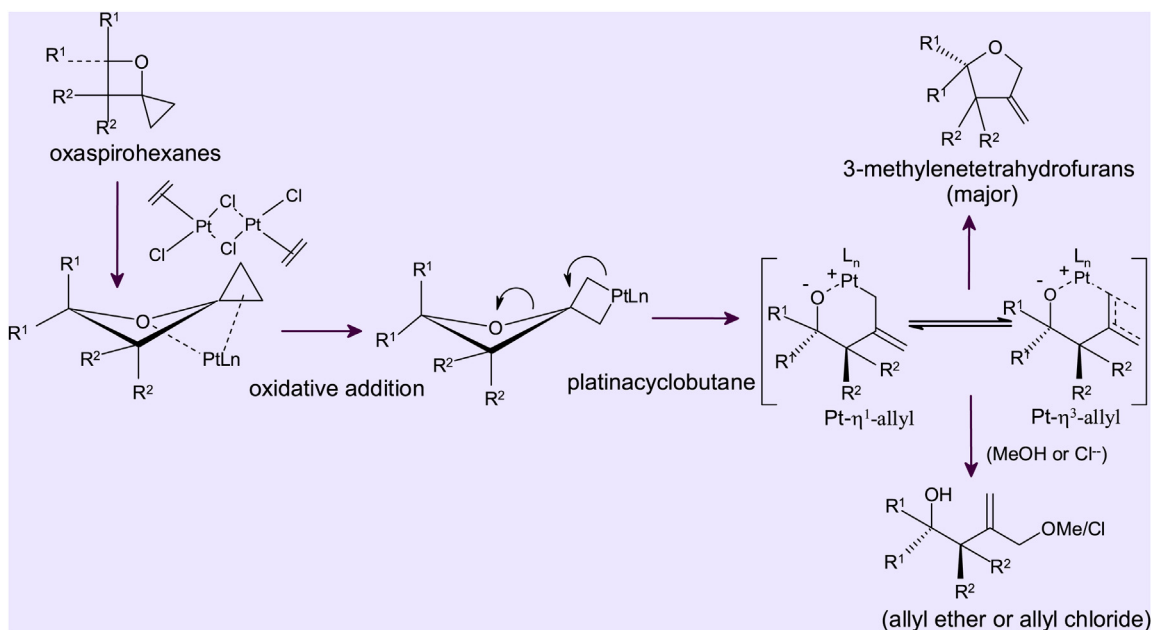
Moreover the dimethyl diphenyl derivative of oxaspirohexane, on similar treatment by Zeise's dimer, does not result any product of tetrahydrofuran derivative; instead, a fragmentation reaction was observed, yielding dimethyl diphenyl ethane as the sole product (Scheme 3(c)). Another derivative of oxaspirohexane, containing a cyclohexyl ring as the substituent, furnishes an elimination reaction to generate β , γ unsaturated cyclohexene ketone (Scheme 3(d)). Inactivity of the substrates was noted when nitrogen containing substituent is present in the substrate structure (Scheme 3(e)). Formation of such a variety of products on the variation of the substrate structure and the inactivity of some specific oxaspirohexane derivatives clearly reveal that the activation of the substrate molecule by a single metal atom may be an oversimplified mechanism and thus demand a re-investigation to find

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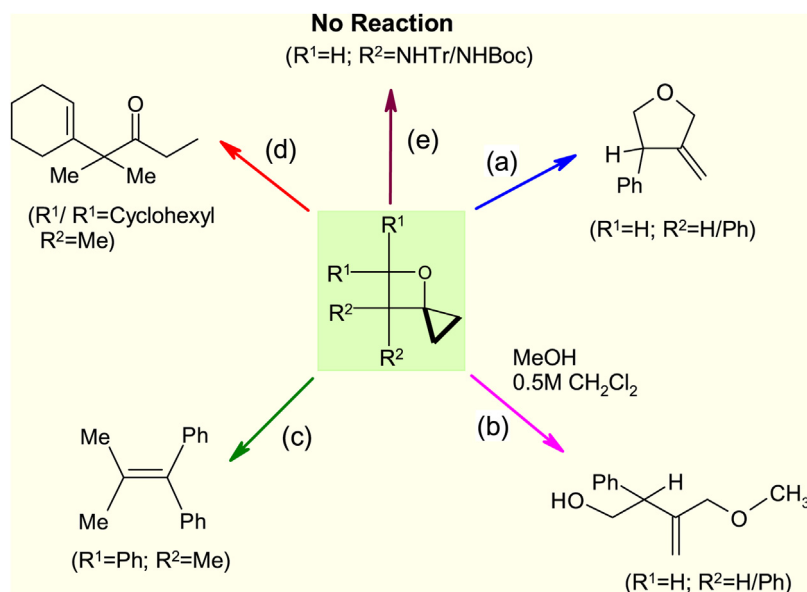
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Scheme 1. Rearrangement of the oxaspirohexane to 3-methylenetetrahydrofuran.



Scheme 2. Mechanism of the rearrangement of oxaspirohexane proposed by Howell et al.



Scheme 3. Variation of products depending on the variation of the substituents on oxaspirohexane. All reactions are catalyzed by Zeise's salt.

out a more appropriate mechanism for proper explanation of the formation of different products.

In order to understand the mechanism of isomerisation using various catalytic platforms, including Zeise's catalyst a number of investigations have now been performed using various quantum chemical calculations [6]. Catalysis of platinum complexes in reaction of cyclopropane derivative had previously been studied theoretically by

Bäckvall et al. [6]; they identified the two pathways for activation before insertion of metal atom into the cyclopropane ring. The corner activation, which occurs through the transition state by positioning the metal atom at the corner of the cyclopropane ring was reported to be more favourable than the edge activation process [6]. The later process of edge activation involves the coordination of a specific bond of cyclopropane ring by the metal centre. However these studies were

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