Pergamon

Tetrahedron Letters, Vol. 37, No. 42, pp. 7573-7576, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01832-1

The Tandem Diels-Alder Reaction of Dimethyl Acetylenedicarboxylate to Bicyclopentadiene. A Theoretical Study of the Molecular Mechanisms

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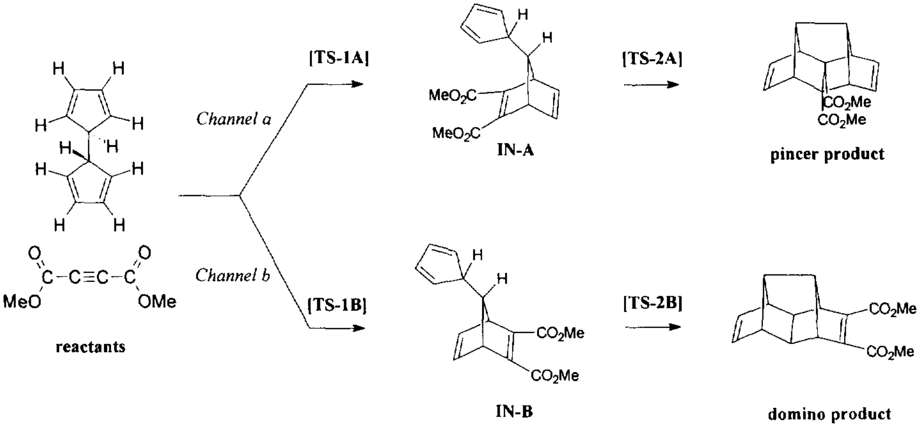
Abstract: The molecular mechanisms for the tandem Diels-Alder reaction of dimethyl acetylenedicarboxylate to bicyclopentadiene have been studied by means of *ab initio* RHF/3-21G calculations. The first step of the pincer and domino reaction pathways present similar energy barriers and corresponds to the rate limiting step of both processes. Copyright © 1996 Elsevier Science Ltd

The tandem Diels-Alder reaction is a powerful method for the construction of bridged polycyclic systems.[1] From a theoretical point of view, this intramolecular form has not received the amount of attention of its counterpart, the intermolecular Diels-Alder reaction.[2] We are engaged in a program for the study of the intramolecular [4+2] cycloaddition reactions.[3] This report details our theoretical studies of the cycloaddition reactions of dimethyl acetylenedicarboxylate to bicyclopentadiene system. For this reaction experimental data are available;[4] however this is the first theoretical study to understanding the molecular mechanisms for this type of cycloadditions.

The molecular mechanisms associated with the pincer and domino reaction pathways have been characterized by means of the localization of four transition structures and two intermediates on the potential energy surface using *ab initio* calculations at RHF/3-21G basis set level.[5] The corresponding stationary points are presented in Scheme 1. The energy profiles for the two channels are sketched in Figure 1. The first [4+2] intermolecular cycloaddition of dimethyl acetylenedicarboxylate to bicyclopentadiene takes place



Scheme 1

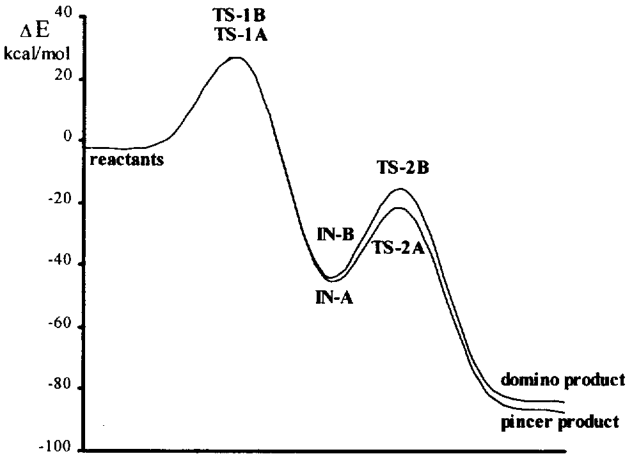


Figure 1. Schematic representation of the energy profile for the tandem cycloaddition of dimethyl acetylenedicarboxylate to bicyclopentadiene

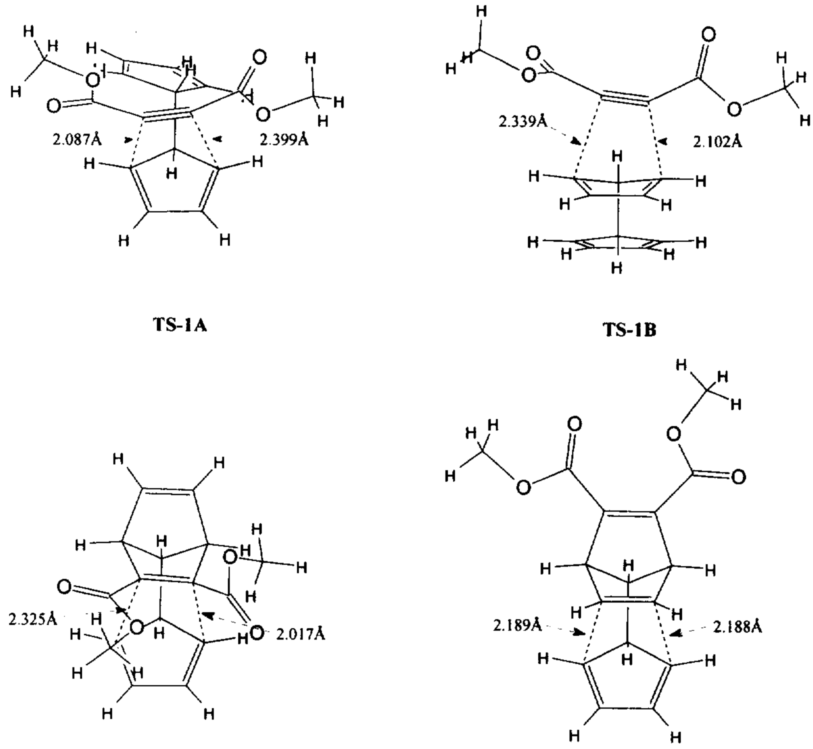
along the channels a and b, via the corresponding transition structures, **TS-1A** and **TS-1B**, respectively. The second step is the [4+2] intramolecular cycloaddition of **IN-A** or **IN-B** to yield the pincer and domino products, via the corresponding transition structures, **TS-2A** and **TS-2B**, respectively. In Table 1, the relative energies for these stationary points are presented. The global processes are very exothermic for both channels, being the first intermolecular cycloaddition the rate limiting step. The intermediates formed in the initial stage are unstable, carrying out the intramolecular cycloaddition by surmounting the second barrier height. The pincer/domino product ratio determined by the relative energy between **TS-1A** and **TS-1B** is close to 1. These theoretical results are in agreement with experimental data.[4]

Table 1. Relative energies* (kcal/mol) of transition structures, intermediates and products with respect to reactants.

TS-1A	26.04	**TS-1B**	25.98
IN-A	-43.36	**IN-B**	-43.17
TS-2A	-21.82	**TS-2B**	-16.23
pincer product	-79.73	domino product	-76.57

*Total energy of dimethyl acetylenedicarboxylate plus bicyclopentadiene is -909.411471 hartree.

The **TS-1A** and **TS1-B** are stereoisomer structures with similar energy (26.04 and 25.98 kcal/mol, respectively). The electron-withdrawing ability of the two carboxylate substituents on dienophile fragment of **IN-A** facilitate the intramolecular cycloaddition, gives account for a lower barrier height for **TS-2A** (21.5 kcal/mol) than for the **TS-2B** (26.9 kcal/mol). The exothermicity of the first step are larger (in the range 7-10 kcal/mol) than in the second step for both channels, because of the increase of annular strain with the formation of bridged tetracyclic products.



TS-1A **TS-1B**

TS-2A **TS-2B**

Figure 2

The geometries for the four transition structures are depicted in Figure 2. Along the cycloaddition the two carboxylate groups of dimethyl acetylenedicarboxylate system are located on perpendicular planes. This arrangement has the following influences on the transition structures: i) allows a π-electron delocalization effect; ii) increases the electron-withdrawing ability of both carboxylate groups; iii) decreases the synchronicity as well as the activation energy for **TS-1A**, **TS-1B** and **TS-2A**; iv) the absence of these effects on **TS-2B**, promotes a synchronous process for the formation of the domino product. A similar behaviour has been found for the related cycloaddition of the dimethyl acetylenedicarboxylate to 1-methyl-2-vinylpyrrole.[6]

The vibrational frequency analysis gives for **TS-1A**, **TS-1B**, **TS-2A** the following values: 505i, 546i and 571i cm^{-1}, respectively. These relatively low values indicate that these stationary points are associated with the heavy atom motions. However, this value increases for the **TS-2B** (723i cm^{-1}) because in this case the carboxylate moiety does not appears in the components of the transition vector.

As reported by Paquette et al.,[4] the cycloaddition of dimethyl acetylenedicarboxylate to bicyclopentadiene yields similar amounts of pincer and domino products, being unstables the corresponding intermediates. The theoretical characterization of stationary point on potential energy surface support the available experimental data. Whether substitution effects or the use of unsymmetrical dienes/dienophiles can modify the corresponding reaction pathways will require further investigation.[7]

Acknowledgements

This work was supported by research funds of the Ministerio de Educación, DGICYT (Projects PB93-0661 and PB92-0825). All calculations were performed on an IBM Power PC 25T workstation of the Departament de Química Orgànica of the Universitat de València, and on a Silicon Graphics Power Challenge L workstation of the Centre de Procés de Dades of the Universitat Jaume I. We are indebted to these centres for providing us with computer capabilities.

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(7) A complete theoretical study of the tandem cycloaddition of ditrifluoromethylacetylene to N-N`-dipyrrolylmethane is in progress.

(*Received in UK* 7 *June* 1996; *accepted* 6 *August* 1996)