Toward an Understanding of the Selectivity in Domino Reactions. A DFT Study of the Reaction between Acetylenedicarboxylic Acid and 1,3-Bis(2-furyl)propane

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The mechanism of the domino reaction between acetylenedicarboxylic acid and 1,3-bis(2-furyl)-propane has been theoretically studied in the framework of density functional theory. This domino process comprises two consecutive cycloaddition reactions: the first one is initialized by the nucleophilic attack of the C5 position of the furan ring to a conjugate position of acetylenedicarboxylic acid to give a zwitterionic intermediate, which by a subsequent ring-closure process affords an oxanorbornadiene intermediate. The second reaction is an intramolecular concerted cycloaddition of this intermediate to give the final dioxapentacyclic adduct. For the second cycloaddition, which corresponds to the step controlling the selectivity, eight alternative reaction pathways are found. Chemoselectivity, facial selectivity, and stereoselectivity of this domino reaction are related with the different approach modes of the tethered furan to the oxanorbornadiene system of the intermediate. The most favorable pathway takes place along an endo/syn approach of the furan ring relative to the bridged oxygen atom of the oxanorbornadiene system, with participation of the substituted double bond. An analysis of energetic contributions to the potential energy barriers for the intramolecular cycloadditions identifies the different factors controlling the reactive channels. Selectivity outcome is reproduced by these calculations.

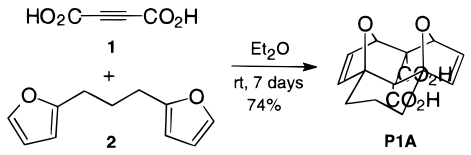
Introduction

Diels−Alder-type rearrangements are by themselves extremely useful transformations in organic chemistry. However, by combining two or more cycloadditions of this type, the effects can be multiplied. This type of domino reaction is synthetically valuable and leads to mechanistically intriguing rearrangements involving two or more bond-forming processes which take place under the same reaction conditions, without adding additional reagents and catalysts, and in which the subsequent reactions result as a consequence of the functionality formed in the previous step.[1−3]

Obtention of polycyclic skeletons plays a central role in the development of regio- and stereochemically controlled synthetic methodology. The elaboration of ring-fused carbocycles based upon domino cycloadditions offers efficient methods for the rapid and stereocontrolled synthesis of polycyclic skeletons.[4,5] Despite the active interest, the mechanistic details of this type of synthetic procedure still remain unclear.

Our research program has long maintained an interest in this kind of chemical reactions and the understanding of the characteristic feature of these consecutive cycloadditions prompted us to explore further the mechanistic aspects. In previous theoretical works, the domino cycloaddition reactions between acetylene derivatives, as dienophiles, and bicyclopentadiene,[6] *N*,*N*′-dipyrrolylmethane,[7,8] and two cyclophanes containing furan ring,[9] as diene systems have been studied. Therefore, it seemed of interest to extend these studies to domino reactions containing furan rings that have not been treated by computational methods and no generally accepted mechanism has emerged.

Scheme 1



In the present work, the domino reaction between acetylenedicarboxylic acid, **1**, and 1,3-bis(2-furyl)propane, **2**, reported by Lautens and Fillion[10] has been studied as a computational model. Experimental data show that the reaction takes place with a total chemoselectivity, facial selectivity, and stereoselectivity, and only one dioxapentacyclic cycloadduct, **P1A**, has been isolated[10] (see Scheme 1). This experimental study opens the possibility to carry out a complementary theoretical analysis in order to interplay between theory and experiment.

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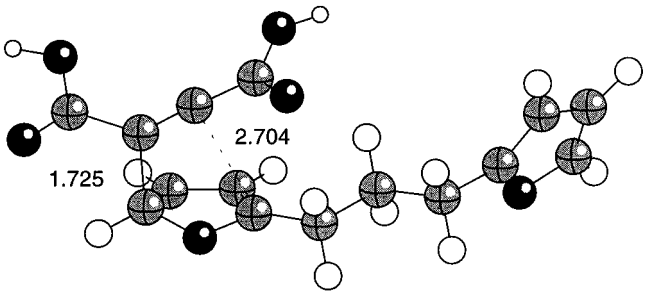
Investigation of the potential energy surface (PES), by means of the location of transition structures (TSs) and related minima, shows the competitive reactive channels, provides knowledge regarding the nature of the mechanism, improves knowledge of the factors that determine the energetic parameters, and allows us to rationalize and to explain the experimental observations.

Computational Methods

The PES has been calculated in detail to ensure that all relevant stationary points have been located and properly characterized. All geometry optimizations of reactants, intermediate, cycloadducts, and TSs were performed with the Gaussian 98 suite of programs.[11] Stationary points have been located without any geometry restriction and have been characterized through the calculation of the force constants matrix by ensuring that they correspond to minima or TS on PES; i.e., they have zero or one and only one imaginary frequency, respectively. The transition vectors (TV),[12] i.e., the eigenvector associated to the unique negative eigenvalue of the force constants matrix, have been characterized. Several conformations related to the rotation around the C−C bond involving the carboxylic acid groups have been considered and those presented correspond to the most stable ones. Optimized geometries of all stationary points on PES are available from the authors.

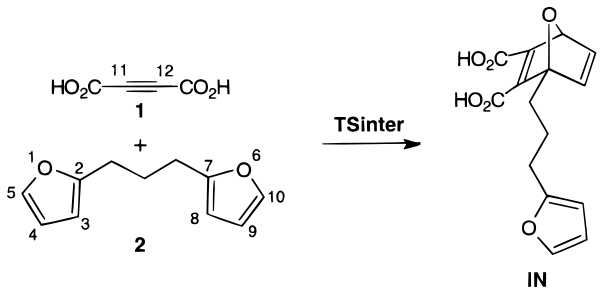
Previous theoretical studies of Diels−Alder reactions have indicated that the activation energies calculated at the RHF level are too large, whereas MP2 method tends to underestimate them. However, energy calculations for stationary points using MP3/6-31G* are in accord with experimental values.[13−15] Recently, DFT[16−19] studies using the B3LYP hybrid functional have been shown to be in good agreement with experimental activation energy values and to give similar PEBs to those obtained using time-consuming MP3 calculations.[7,20,21] Consequently, we have used the gradient corrected functionals of Becke, and Lee, Yang and Parr (B3LYP)[22,23] for exchange and correlation, respectively, and the 6-31G* basis set.[24] The PES was first explored at the RHF/3-21G level, and then, the stationary points corresponding to the four more favorable reactive channels were completely optimized at the B3LYP/6-31G* level.



TSinter

Figure 1. B3LYP/6-31G* transition stucture corresponding to the second step of the intermolecular cycloaddition reaction between **1** and **2**. The values of the bond lengths directly involved in the reaction are given in angstroms.

Scheme 2



Results and Discussion

The domino reaction between **1** and **2** takes place along two consecutive cycloaddition reactions. The first one is an intermolecular cycloaddition between **1** and **2** to give an oxanorbornadiene intermediate, **IN**, while the second reaction is an intramolecular cycloaddition of this intermediate to give the final dioxapentacyclic cycloadduct **P1A**.

We will start with a theoretical investigation on the intermolecular cycloaddition between **1** and **2**. This reaction takes place along both faces of one furan ring of **2** to give two enantiomeric oxanorbornadiene intermediates, via two enantiomeric routes; in the present study we report only one of the two enantiomeric possibilities (see Scheme 2). A detailed exploration of the PES for this cycloaddition at the B3LYP/6-31G* level only renders a **TSinter** (see Figure 1). The lengths of the two forming bonds at this TS, 2.704 Å (C2−C11) and 1.725 Å (C5−C12), indicate that it corresponds to a very asynchronous process. Moreover, the analysis of the TV of **TSinter** shows that the main component is associated to the larger C2−C11 forming bond. These data, together with the analysis of the atomic motion of the unique imaginary frequency indicate that **TSinter** corresponds to the second step of a stepwise cycloaddition. However, all attempts to locate the TS of the first step and the corresponding intermediate were unsuccessful.

Therefore, it is necessary carry out an study of the possible stepwise nature of this intermolecular cycloaddition. So, we have selected to study the reaction between **1** and a reduced system of **2**, 2-methylfuran.[25] Although B3LYP/6-31G* calculations give an unique TS similar to **TSinter**, the inclusion of diffuse functions at the B3LYP/

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Table 1. HF/3-21G and B3LYP/6-31G* Total Energies (au) and Relative Energies[a] (kcal/mol, in Parentheses) for the Stationary Points of the Domino Reaction between Acetylenedicarboxylic Acid 1 and 1,3-Bis(2-furyl)propane 2

	HF/3-21G		B3LYP/6-31G*	
1	−570.018 146		−576.796 226	
2	−449.502 280		−454.459 608	
TSinter	−1019.481 953	(24.1)	−1031.235 471	(12.8)
IN	−1019.561 204	(−25.6)	−1031.282 418	(−16.7)
TS1A	−1019.530 584	(−6.4)	−1031.254 261	(1.0)
TS2A	−1019.509 433	(6.9)	−1031.230 612	(15.8)
TS3A	−1019.497 003	(14.7)		
TS4A	−1019.484 395	(22.6)		
TS1B	−1019.516 307	(2.6)	−1031.250 190	(3.5)
TS2B	−1019.499 847	(12.9)	−1031.232 761	(14.5)
TS3B	−1019.479 721	(25.5)		
TS4B	−1019.472 036	(30.4)		
P1A	−1019.606 706	(−54.1)	−1031.287 275	(−19.7)
P2A	−1019.575 885	(−34.8)	−1031.257 107	(−0.8)
P3A	−1019.568 782	(−30.3)		
P4A	−1019.546 344	(−16.3)		
P1B	−1019.616 381	(−60.2)	−1031.310 328	(−34.2)
P2B	−1019.586 963	(−41.8)	−1031.281 371	(−16.0)
P3B	−1019.585 325	(−40.7)		
P4B	−1019.553 509	(−20.8)		

[a] Relative to **1** + **2**.

6-31+G* level allows to find the stationary points corresponding to the stepwise mechanism; two TSs and one intermediate. These stationary points are located on a very flat zone on PES, they are within an energetic range lower than 0.2 kcal/mol. This result accounts for the difficulty to find these stationary points at B3LYP/6-31G* level. A comparison of the bond orders and charge transfer between **TSinter** and the TS corresponding to the second step of the reaction between **1** and 2-methylfuran, points out that the former corresponds to the second step of the stepwise cycloaddition between **1** and **2**. Therefore, the relative energy of **TSinter** can be taken as a measure of the PEB associated with the first intermolecular cycloaddition reaction. B3LYP/6-31G* calculations given a relative energy for **TSinter** of 12.8 kcal/mol, and the relative energy of **IN**, −16.7 kcal/mol, indicates that their formation is an exothermic process. The energetic results are presented in Table 1.

The intermolecular cycloaddition between **1** and **2** can be described as a nucleophilic attack of the C5 position of one furan ring of **2** on the C11 conjugated position of **1** to give a zwitterionic intermediate, which by a subsequent ring closure, via **TSinter**, affords the oxanorbornadiene intermediate **IN**. The presence of the donor oxygen atom in the furan ring, which allows a stabilization of a positive charge, and the presence of the two electron-withdrawing carboxylic acids on the acetylenic system, which allow an effective delocation of a negative charge, favor the charge transfer along a non concerted process. These factors make that **1** and **2** act as electrophile and nucleophile rather than dienophile and diene, respectively. Moreover, the presence of the electron-releasing methylene group in the C2 position of furan ring does the C5 center more nucleophilic than the C2 one. Inclusion of solvent effects can increase the stability of the zwitterionic intermediate emphasizing the stepwise nature of this intermolecular cycloaddition.[26]

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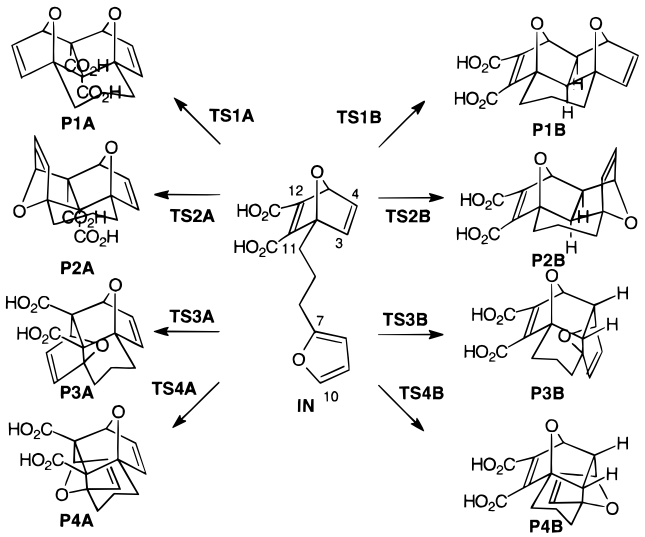
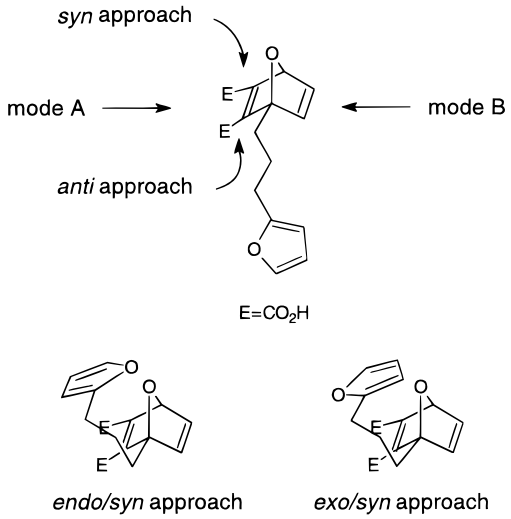
Scheme 3



Scheme 4



The intermediate **IN** formed in the first stage, after the corresponding conformational interconversion, can carry out the next intramolecular cycloaddition by surmounting the second barrier height. This interconversion takes place easily along a free-bond rotation of the propane chain; the relative energies of the different rotamers are in the narrow range of 4.0 kcal/mol. These conformers are the starting points for the competitive approaches of the tethered furan ring (diene fragment) to the different reactives sites of the oxanorbornadiene system (dienophile moiety), allowing in the second process eight modes of intramolecular cycloaddition. Therefore, the selectivities of this domino reaction are determined in this intramolecular cycloaddition, and a schematic representation of the competitive reactive pathways is presented in Scheme 3. The eight reactive channels starting from **IN** can be classify, depending on the attack mode of the furan ring to the oxanorbornadiene system, as follows (see Scheme 4): (i) mode A and mode B correspond to the attack of the furan ring to the substituted or nonsubstituted double bonds of the oxanorbornadiene system, respectively; (ii) the approach of the furan ring can takes place along the same or opposite face of the O1 bridge oxygen atom of the oxanorbornadiene system, defining the syn or anti facial approaches,

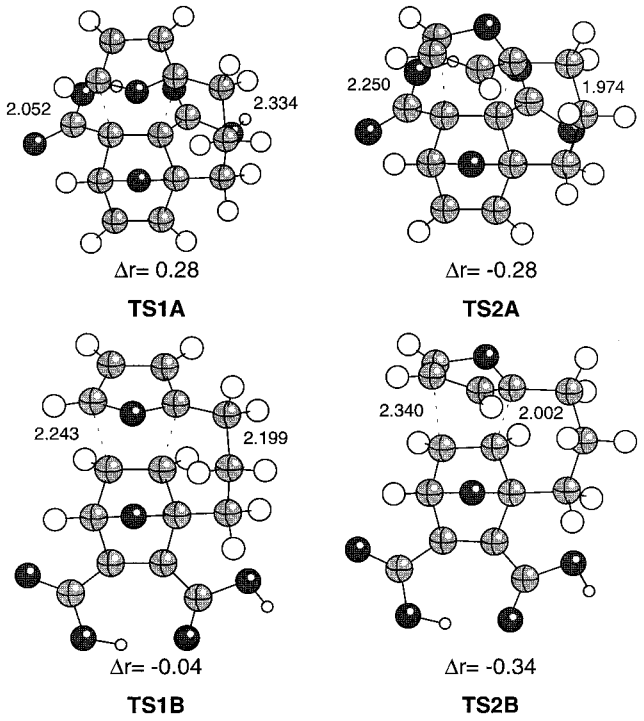


Figure 2. Transition stuctures corresponding to the syn intramolecular cycloadditions of the intermediate **IN**, **TS1A**, **TS2A**, **TS1B**, and **TS2B**. The values of the bond lengths directly involved in the reaction are given in angstroms. The geometrical asynchronicity is $\Delta r = (l_1 - l_2)$, where l_1 and l_2 are the lengths of the two C−C forming bonds.

respectively;[27] (iii) finally, along the syn attacks, the endo or exo approaches can be defined depending on the relative approach of the oxygen atom of the furan ring to the bridge oxygen atom.

Eight final products (**P1A**, **P2A**, **P3A**, **P4A**, **P1B**, **P2B**, **P3B,** and **P4B**) can be formed via the corresponding TSs **TS1A**, **TS2A**, **TS3A**, **TS4A**, **TS1B**, **TS2B**, **TS3B**, and **TS4B**, respectively. A preliminary HF/3-21G exploration of the PES along the eight reactive channels points out that the anti pathways present the larger values of the PEBs relative to the syn ones (see Table 1). Therefore, only the syn channels are taken into account at the B3LYP/6-31G* level: **TS1A** (endo/syn mode A), **TS2A** (exo/syn mode A), **TS1B** (endo/syn mode B), and **TS2B** (exo/syn mode B). Thus, the larger energies corresponding to the anti pathways relative to the syn ones justify the facial selectivity found at this domino reaction. The geometries of these TSs are depicted in Figure 2. An analysis of the relative energies for the second stage reported in Table 1 shows that the most favorable reactive channel corresponds to the formation of the final cycloadduct **P1A**, via **TS1A**. The PEB associated to this intramolecular cycloaddition is 17.7 kcal/mol, the domino reaction being very exothermic, −19.7 kcal/mol. Therefore, the formation of **P1A** corresponds to the reactive channel of the kinetic control, while **P1B** corresponds to the cycloadduct of thermodynamic control, −34.2 kcal/mol.

The endo/syn approach along the mode A, **TS1A**, is 2.5 kcal/mol more favorable that the endo/syn approach along the mode B, **TS1B**. The electron-withdrawing ability of the −COOH groups activate the substituted double bond, attack mode A, relative to the nonsubstituted double bond, attack mode B. This favorable factor, that also appears along the pathways of related domino reactions,[6−9] is responsible of the chemoselectivity found in this domino reaction. It is interesting to note that for this domino reaction, the endo approaches are more favorables than the exo ones. Thus, **TS2A** and **TS2B**, corresponding to the exo channels, are 14.8 and 11.0 kcal/mol more energetic than **TS1A** and **TS1B**, corresponding to the endo ones, respectively. Therefore, this domino reaction takes place with a total chemo, facial, and endo stereoselectivity in agreeement with the experimental data.

For **TS1A** the lengths of the C7−C11 and C10−C12 forming bonds are 2.334 and 2.052 Å, respectively. This TS corresponds to a concerted cycloaddition process where the two σ-bonds are asynchronously formed. The extent of the asynchronicity can be measured by means of the difference between the lengths of the two σ-bonds that are being formed in the cycloaddition process, i.e., Δr = l(C7−C11) − l(C10−C12). Figure 2 shows the geometrical asynchronicity for the transition structures corresponding to the syn cycloaddition mode. For **TS1A** this value is $\Delta r = 0.28$. However, a different behavior is found for the other TSs, where the formation of the C7−C11 and C3−C7 bonds are more advanced than C10−C12 and C4−C12 ones, and negative values for Δr are found. For these TSs there is a correlation between the asynchronicity of the bond formation process and the corresponding relative energies; an increase of the negative asynchronicity is accompanied by an increase of PEB.

The asynchronicity of the most favorable **TS1A** can be undertook as a consequence of the endo/syn mode A attack. This cycloaddition process can be considered as a normal-electron-demand Diels−Alder reaction. Such as the first intermolecular cycloaddition, the presence of the two electron-withdrawing −COOH groups in the dienophile fragment and the oxygen atom in the furan ring (diene fragment) favor the charge transfer along an asynchronous process. Moreover, the presence of the electron-releasing methylene group at the C7 carbon atom of the furan ring causes the C10−C12 forming bond to be shorter than the C7−C11 one. Absence of the two electron-withdrawing −COOH groups in the dienophile fragment along the endo/syn mode B, **TS1B**, avoid the charge transfer and a more synchronous TS is found.

A different behavior is found for the more defavorable **TS2A** and **TS2B** where a reverse asynchronicity is found, $\Delta r = -0.3$; the C7−CX (X = 3 or 11) forming bond is shorter than the C10−CY (Y = 4 or 12). These TSs display a geometrical distortion (see the arrangement of the furan ring in **TS2A** and **TS2B** in Figure 2), which is present also in the final dioxapentacyclic adducts **P1B** and **P2B**. When we optimize the endo/syn and exo/syn dioxatetracyclic adducts **P5** and **P6**, which have no propane chain, two symmetrical structures are found (see Figure 3); **P5** is now only 2.7 kcal/mol more energetic that **P6**. Moreover, the optimization of **P1A** and **P1B** using molecular mechanics calculations[28] affords **P1B** 14.4 kcal/mol more strained than **P1A**. These geometrical and

(27) Some authors refer to this stereochemistry as endo/exo. We choose the syn/anti facial steroselectivity along the discussion to avoid confusions with the endo/exo approach of the dienophile to the diene.

(28) Molecular mechanics calculations have been carried out using the MMX force field implemented in PCMODEL V4.0 program; Serena Software; Bloomington, 1990.

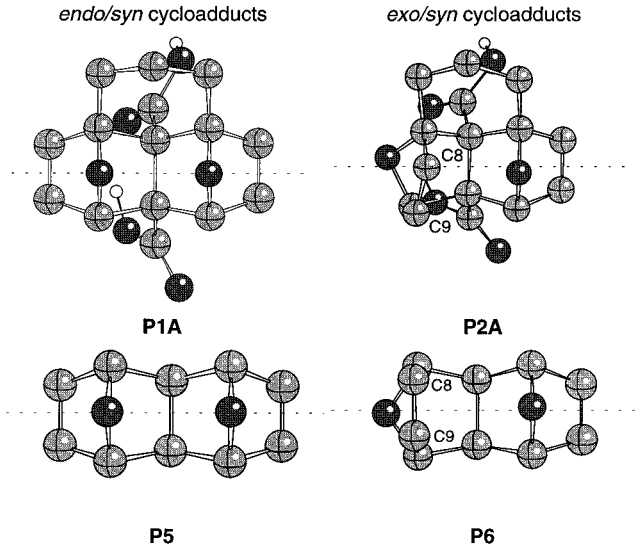


Figure 3. Top view of the cycloadducts **P1A**, **P1B**, **P5**, and **P6**. The dotted line shows the dissymmetry at the endo/syn cycloadduct **P2A** relative to the endo/syn cycloadduct **P6**, which is imposed by the tether present in **P2A**.

energetic results suggest that the strain imposed by the tether along the exo approach is responsible for the larger negative asynchronicity and the larger energy of **TS2A** relative to **TS1A**. This finding allows us to justify the endo selectivity found in this domino reaction.

A closer analysis of the experimental work carried out by Lautens and Fillion shows that the present theoretical results are capable to explain the experimental data.[10] The electron-withdrawing effect of the two carboxylic acids together with the more defavorable exo/syn approach of the furan ring to the oxabyciclic system justify the total chemo and stereoselectivities observed experimentally, and the formation of the final cycloadduct **P1A**. The large value of the PEB associated with the retro-Diels−Alder for the cycloadduct **P1A** prevents the formation of the cycloadduct **P1B**, which is the product of thermodynamic control of the global process.

Conclusions

In the present work we have carried out a theoretical study on the mechanism for the domino reaction between acetylenedicarboxylic acid and 1,3-bis(2-furyl)propane using density functional theory methods with the B3LYP functional and the 6-31G* basis set.

The different reactive channels have been mapped out and TSs, intermediate and final cycloadducts have been located and properly characterized. The results give a quantitative picture of this complex domino reaction. The theoretical results are in agreement with the experimental outcome and they are capable to explain the origin of the chemo and stereoselectivity. We can conclude that the correct behavior of the systems under investigation is reproduced.

This domino reaction comprise two consecutive cycloadditions. The first one takes place along the nucleophilic attack of the C5 position of the furan ring on a conjugate position of the acetylenic system of acetylenedicarboxylic acid to give a zwitterionic intermediate, which by a subsequent ring closure affords an oxanorbornadiene intermediate. The second step is an intramolecular concerted cycloaddition of this intermediate to give the final dioxapentacyclic adduct. For the second cycloaddition, which corresponds to the step controlling the selectivity, eight alternative reaction pathways are found.

The present theoretical study points out that the different reactivity pattern is due to the different attack modes between the tethered furan and the oxanorbornadiene system of the intermediate formed in the first intermolecular cycloaddition. An analysis of the energetic contributions to the PEBs corresponding to the second intramolecular cycloaddition identifies the different factors controlling the reactive channels. The most favorable reactive channel takes place along an endo/syn arrangement of the tethered furan ring relative to the oxygen atom of the oxanorbornadiene system together with the participation of substituted double bond of the dienophile fragment. The large strain imposed by the tether along the exo approach is responsible for the endo selectivity found in this domino reaction.

These theoretical results are consistent with experimental investigations and shed light of the mechanisms for other domino transformations and underline the role played by the different energetic contributions along the competitive reactive channels.

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