

A Theoretical Study of the Molecular Mechanism of the Reaction between *N,N*-Dimethylmethylen ammonium Cation and Cyclopentadiene

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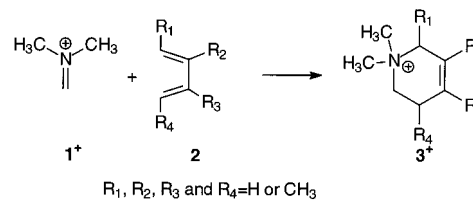
The development of synthetic methodologies based on aza-Diels–Alder reactions of imine derivatives and substituted 1,3-butadienes to obtain six-membered heterocycles has attracted much interest.¹ Early examples of aza-Diels–Alder reactions of *N,N*-dialkylmethylen ammonium cations with 2,3-dimethyl-1,3-butadiene and isoprene in aprotic solvents were reported by Böhme et al.² and Babayan et al.³ respectively. Katritzky and Gordeev have recently reinvestigated and supplemented this work.⁴

Two new σ -bonds, a C–C and a C–N, are formed in the course of the cycloaddition reaction, and the question of whether bond-formation is concerted or not still remains unclear. The structural information obtained by theoretical methods based on quantum mechanical calculations of possible intermediates and transition structures (TSs) provides powerful assistance for the study of organic reaction mechanisms.⁵ These methods are accepted as available tools for the interpretation of experimental results, since such data are rarely obtainable through experiments.^{5d}

The mechanism of the Diels–Alder reaction has been controversial for a long time.⁶ The archetypal Diels–Alder reaction of butadiene and ethylene⁷ may occur via either a synchronous concerted mechanism associated with a pericyclic transition state or through a stepwise mechanism involving diradical intermediates.⁶ The butadiene + ethylene reaction, however, is not the typical case. In general, the Diels–Alder reaction requires opposite electronic features in the substituents at the diene and the dienophile in order to be reasonably fast. Furthermore, it is well-known that this type of substitution favors an asynchronous mechanism.⁸

These reactions appear to occur under frontier control, and the frontier molecular orbital (FMO) model is capable

Scheme 1



of explaining satisfactorily the substituent effects at these cycloadditions.⁹ For the usual Diels–Alder reaction, the main HOMO–LUMO interaction occurs between the HOMO of the diene and the LUMO of the dienophile. The increase of the electron-poor character of the dienophile decreases the LUMO_{dienophile} energy; this effect decreases the HOMO_{diene}–LUMO_{dienophile} gap and, consequently, the activation enthalpy decreases.⁹ Moreover, this occurs along with an increase in the asynchronicity and the charge transfer along the bond-formation.^{8g}

Houk et al. have published several theoretical studies on the TSs of hetero-Diels–Alder reactions.¹⁰ For the cycloaddition between the protonated formalimine and butadiene, a very asynchronous TS is obtained where the lengths of C–C and C–N forming bonds are 1.919 and 3.058 Å, respectively (HF/3-21G level).^{10b} In this TS, the C–N bond is essentially not formed, and the reaction has a negative activation energy, which is not modified with the inclusion of solvent effects. These authors also found several possible acyclic intermediates associated with a stepwise mechanism.^{10b} Sauer and co-workers have studied recently the cycloaddition between several salts of *N,N*-dimethylmethylen ammonium cation, **1**⁺, and substituted butadienes **2** both experimentally and theoretically using AM1 semiempirical calculations (see Scheme 1).¹¹ These authors suggest that the aza-Diels–Alder reactions of cation **1**⁺ with the acyclic 1,3-butadienes **2** proceed via transition structures that closely resemble to those yielding intermediate allyl cations. Only in the case of reaction with cyclopentadiene, **CP**, did these authors conclude that the reaction takes place along a pericyclic transition state.¹¹

According to a preliminary FMO analysis, we found that the AM1 calculations render for the ylidene ammonium cation **1**⁺ very low HOMO and LUMO energies, –17.1257 and –5.8387 eV, respectively; these data suggest a large HOMO_{CP}–LUMO₁₊ interaction which should progress with a large acceleration along a polar reaction. This is in agreement with the fact that ylidene ammonium salts as *N,N*-dimethylmethylen ammonium

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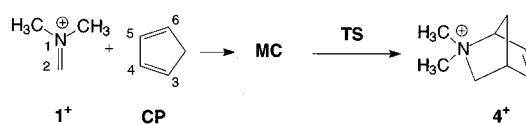
iodide, frequently referred to as the Eschenmoser salt,¹² are powerful electrophiles, conveniently used in Mannich reactions¹³ and aminoalkylation of activated aromatic rings.¹⁴

In view of these precedents, and as part of our research program devoted to the study of molecular mechanisms of the cycloaddition reactions that take place via asynchronous mechanisms,¹⁵ a theoretical study for the reaction between *N,N*-dimethylmethyleammonium, **1**⁺, and cyclopentadiene, **CP**, is now presented. The purpose of this study is to contribute to a better understanding of the mechanistic features of these processes, especially by location and characterization of all stationary points involved at the formation of these formally [4 + 2] cycloadducts.

Computational Methods

Density functional theory¹⁶ (DFT) calculations have been carried out using the B3LYP¹⁷ exchange-correlation functionals, together with the standard 6-31G* basis set.¹⁸ The optimizations were carried out using the Bery analytical gradient optimization method.¹⁹ The stationary points were characterized by frequency calculations in order to verify that minima and transition structures have zero and one imaginary frequency, respectively. The transition vectors,²⁰ i.e., the eigenvector associated with the unique negative eigenvalue of the force constants matrix, have been characterized. Zero-point vibrational energies (ZPVEs) have been computed, and the ZPVEs have been scaled by 0.98.²¹ Finally, single-point calculations were performed at the MP2/6-31G*/B3LYP/6-31G* level in order to check the energetic results. The intrinsic reaction coordinate (IRC)²² paths were traced in order to check the energy profiles connecting each transition structure to the two associated minima of the proposed mechanism by using the second-order González–Schlegel integration method.²³ The electronic structures of stationary points were analyzed by the natural bond orbital (NBO) method.²⁴ Since the reaction presents highly asynchronous TSs, diradical structures could in principle be involved. This has been ruled out by obtaining the wave functions of the TSs and possible intermediate with unrestricted DFT theory. UB3LYP/6-31G* calculations, using the keyword STABLE in Gaussian 98, predict the same structures as the ones

Scheme 2



obtained from the restricted B3LYP/6-31G*, indicating that the restricted DFT solutions are stable, ruling out the presence of diradical species.^{15e,25} All gas-phase calculations were carried out with the Gaussian 98 suite of programs.²⁶ Optimized geometries of all structures are available from the author. Finally, solvent effects in this cycloaddition have been estimated using a relatively simple self-consistent reaction field (SCRF) method²⁷ based on the polarizable continuum model of the Tomasi's group.²⁸

Results and Discussion

Analysis of the DFT results for the reaction between the ylide ammonium cation **1**⁺ and cyclopentadiene, **CP**, renders that the cycloaddition takes place along a highly asynchronous concerted mechanism. Thus, one TS, **TS**, and one cycloadduct, **4**⁺, have been found and characterized.^{29,30} An exhaustive exploration of the potential energy surface also identifies a molecular complex, **MC**, associated with a very early stage of the reaction that controls access to the reactive channel.^{15e} The distance between the two fragments at the **MC** is around 4–5 Å, and it is more stable than the isolated reactants **1**⁺ + **CP**. The stationary points corresponding to the reaction between **1**⁺ and **CP** are presented in Scheme 2 together with the atom numbering, while the total and relative energies are summarized in Table 1. The geometries of the **MC** and **TS** are presented in Figure 1.

The B3LYP/6-31G* relative energy for **TS** has negative values (–3.5 kcal/mol). However, when the formation of the **MC** is considered, the **TS** energy lies slightly above that of its corresponding molecular complex. This feature

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(29) Although the anti approach of **1**⁺ to **CP** is also possible, the corresponding stepwise reactive channel has been discarded to have the corresponding intermediate a larger barrier for the C2–C3 bond rotation than that for the breaking of C2–C3 bond.

(30) An acyclic intermediate, **IN**, and a second TS, **TS2**, which lie slightly above the concerted **TS**, associated with the stepwise mechanism along the syn-clinal approach mode is also found (see Supporting Information). However, all attempts to locate the corresponding stationary point connecting the **MC** with **IN** were unsuccessful. Despite this, restricted optimizations frozen the C2–C3 (1.86 Å) and the N1–C6 (3.65 Å) forming bonds allow one to find a constrained structure, **TS1**, with very low gradient values that lies 0.96 kcal/mol above the **TS**. Even though full optimization of **TS1** affords **TS**, the IRC from **TS1** establishes its connection with **MC** and **IN**.

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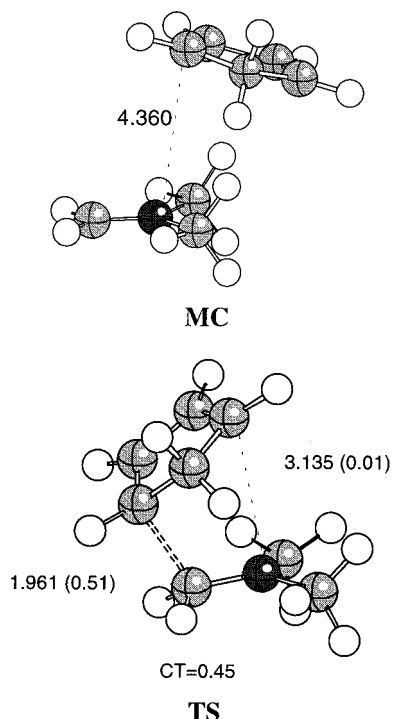


Figure 1. Molecular complex, **MC**, and transition structure, **TS**, corresponding to the reaction between the ylidene ammonium cation **1**⁺ and cyclopentadiene, **CP**. The lengths of the forming bonds involved in the reaction are given in angstroms. Values in parentheses correspond to the Wiberg bond orders. The charge transfer, CT in au, is also given.

Table 1. Total Energies^a (au) and Relative Energies^b (kcal/mol, in Parentheses) for the Stationary Points Corresponding to the Reaction between the Ylidene Ammonium Cation **1⁺ and Cyclopentadiene **CP****

	B3LYP/6-31G*	MP2/6-31G** B3LYP/6-31G*	B3LYP/6-31G* (in dichloromethane)
1 ⁺	-173.516199	-172.900758	-173.585088
CP	-194.011879	-193.336074	-194.013329
MC	-367.536900 (-5.5)	-366.249164 (-7.7)	-367.599639 (-0.8)
TS	-367.533706 (-3.5)	-366.243269 (-4.0)	-367.596522 (1.2)
4 ⁺	-367.555602 (-17.3)	-366.289873 (-33.3)	-367.618244 (-12.4)

^a Including ZPEs. ^b Relative to **1**⁺ + **CP**.

implies an inverted energy profile, and the corresponding value of the barrier height is then 2.0 kcal/mol.³¹ To test the usefulness of the B3LYP/6-31G* energetic results, single point calculations were carried out at the MP2/6-31G* level. These calculations give for **TS** relative energies similar to those obtained at DFT level, while the formation of cycloadduct **4**⁺ becomes more exothermic (see Table 1).

FMO analysis of the reaction between **1**⁺ and **CP** explains these energetic results. The HOMO and LUMO energies are -14.9573 and -7.3921 eV, for **1**⁺, and -5.7549 and -0.2688 eV, for **CP**, respectively. These data show a large HOMO and LUMO stabilization for the ylidene ammonium cation **1**⁺. Moreover, for the reaction between **1**⁺ and **CP**, the LUMO₁₊ energy lies

below the HOMO_{CP} energy; consequently, there is a negative HOMO_{CP}-LUMO₁₊ gap energy in agreement with the inverted energy profile found for this polar process.

Analysis of the geometry of the TS corresponding to attack of **CP** to **1**⁺ indicates that it is associated with a highly asynchronous bond formation (see Figure 1). The lengths of the C2-C3 forming bond at **TS** is 1.961 Å, while the distance between the N1 nitrogen and C6 carbon atoms, 3.135 Å, indicates that these atoms are not bonding in the TS. Moreover, the arrangement of the hydrogen and carbon atoms around the C3 and C6 carbons belonging to the cyclopentadiene residue indicate that while the C3 carbon atom is changing the hybridization from sp² to sp³ along the C2-C3 bond formation, the C6 carbon remains sp² in agreement with a C4-C5-C6 allyl cation structure. The N1-C2-C3-C4 dihedral angle at this TS, ca. 71°, shows a syn-clinal arrangement of the N1-C2 and the C3-C4 bonds, which favors the concomitant N1-C6 bond-formation.

The value of the imaginary frequency associated with **TS** is 249i cm⁻¹. Analysis of the atomic motion along this vibrational frequency indicates that this TS is mainly associated with the motion of the C2 and C3 carbon atoms along the C-C bond-formation process; the motion of the N1 and C6 atoms is negligible. Moreover, analysis of the eigenvector associated with the unique negative eigenvalue of the Hessian matrix corresponding to this TS shows that the transition vector is associated mainly with the C2-C3 bond length.

The extent of bond-formation along a reaction pathway is provided by the concept of bond order (BO).³² This theoretical tool has been used to study the molecular mechanism of chemical reactions.^{15e} The BO value for the C2-C3 forming bond at **TS** is 0.5, while the BO value between the N1 and C6 atoms is 0.0 (see Figure 1). This value shows that the N1 and C6 atoms are not being bonded at this TS.

The NBO analysis allows us to evaluate the charge transferred along the cycloaddition process. The atomic charges have been shared between the donor cyclopentadiene, **CP**, and the acceptor ylidene ammonium cation **1**⁺. The large value of the negative charge transferred from the **CP** to the cation **1**⁺ at **TS**, 0.45 au, indicates that the nature of this TS can be seen to occur from some ionic character, where the cyclopentadiene residue supports a large positive charge. Thus, bond order and charge transfer analysis indicate that this cycloaddition reaction, which takes place along a highly asynchronous TS, is associated with a polar process characterized by the nucleophilic attack of the cyclopentadiene to the C2 carbon atom of electron-poor ylidene ammonium cation, instead of a pericyclic process.

The high asynchronicity of the process is also supported by an analysis of the evolution of bond-formation along the IRC path. Thus, the geometries of the points "halfway" between the saddle point **TS** and the cycloadduct **4**⁺ show that while the C2-C3 bond is readily formed up to 80%, the C2-C3 bond lengths at these points are ca. 1.7 Å, the N1-C6 bond-formation is very delayed, and the N1-C6 distances remain at 3.0 Å (see Figure 2). Moreover, these points are located in a smooth drop in energy after the barrier height, explaining the

(31) The calculated activation free energy for **TS** is ΔG[‡] = 8.5 kcal/mol.^{8g} This value is lower than that obtained from the experimental rate constant, ca. 18 kcal/mol, because of the low solubility of **1**-SbCl₆ salt.¹¹

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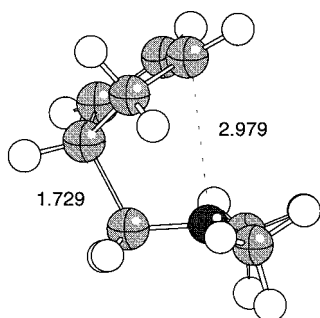


Figure 2. Structure of an IRC point “halfway” between the saddle point **TS** and the cycloadduct **4⁺**. The lengths of the bonds involved in the reaction show that while the C2–C3 bond formation is very advanced, the N1–C6 one remains very delayed.

unfeasibility of finding the corresponding acyclic allyl cation intermediate as a stationary point.

Finally, solvent effects in this cycloaddition have been estimated. The solvent used in the experimental work¹¹ is dichloromethane; its dielectric constant, 8.93, was used. SCRF B3LYP/6-31G* optimization of the stationary points along the reactive channel gives also a highly asynchronous concerted process with a barrier similar to that obtained in gas phase calculations (see Figure 1). Inclusion of solvent effects stabilizes ca. 5 kcal/mol more effectively the ylidene ammonium cation **1⁺** than the other stationary points because of a large localization of the positive charge in the former; therefore, inclusion of solvent effects increases the relative energies. In dichloromethane, the **TS** energy lies slightly above that of the reactants **1⁺** + **CP**. Finally, inclusion of solvent effects on the geometry optimization does not modify substan-

tially the geometries obtained in a vacuum. The C2–C3 and N1–C7 lengths at **TS** in dichloromethane are 1.975 and 3.033 Å, respectively.

In summary, this DFT study suggests that the reaction between *N,N*-dimethylmethylenammonium cation and cyclopentadiene takes place as a highly asynchronous concerted process with a large polar character. A complete analysis of the features of the **TS** indicates that the process can be characterized by the nucleophilic attack of cyclopentadiene to the electron-poor ylidene ammonium cation instead of a pericyclic process. The concomitant cyclization process affords the final cycloadduct without the participation of any allyl cation intermediate. In consequence, the ylidene ammonium cation and cyclopentadiene behave as electrophile and nucleophile, respectively, instead of as dienophile and diene. This behavior is in agreement with the electrophilic reactivity shown by the Eschenmoser salt.^{13,14}

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Supporting Information Available: Figure giving the geometries of the constrained **TS1** and the stationary points **IN** and **TS2** corresponding to the stepwise syn-clinal reactive channel.³⁰ Transition vectors and selected geometrical parameter for the transition structure **TS**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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