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On the Synchronous 1,4-Addition of Methylene to *cis*-Butadiene

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Abstract: The concerted 1,4-addition of methylene to *cis*-butadiene has been investigated by the semiempirical MINDO/3 method. The orbital symmetry allowed reaction is impeded by repulsion between the orbital σ (of the methylene) and the subfrontier MO π_1 (of the diene). An energy barrier of 28 kcal/mol is obtained. Trajectories requiring less energy (by about 5 kcal/mol) can be traced from a two-dimensional plot of the computed energy for the concerted reaction path.

Although the addition of singlet carbenes to olefins has been under active investigation for about 20 years,¹ very few 1,4-additions have been reported.²⁻¹³ Most of them turned out to be two-step processes. Either the singlet carbene underwent relaxation to the triplet state, or a cyclopropane adduct was initially formed, and subsequently underwent a vinylcyclopropane rearrangement. Only in one case, the homo 1,4-addition of difluorocarbenes to norbornadiene, has a one-step process been established.¹⁴

On the basis of an orbital correlation diagram the reaction is symmetry allowed (Figure 1). Transfer of electron density can occur from (a) the HOMO π_2 to the empty p orbital of the methylene (type I interaction) and (b) the σ orbital (of the methylene) into the LUMO π_3^* (type II interaction). In this respect the carbene can act as an *electrophilic* ($\pi_2 \rightarrow p$) and *nucleophilic* ($\sigma \rightarrow \pi_3^*$) species toward the diene.¹⁵

Results and Discussion

In order to deepen the understanding of the mechanism of the concerted 1,4-addition we have performed a theoretical study on this reaction employing the semiempirical MINDO/3 method.¹⁸ All calculated geometries were optimized for a single Slater determinant wave function with the gradient procedure.¹⁹

As a model reaction the approach of methylene in its energy lowest σ^2 state^{16a,20} to *cis*-butadiene was investigated.

The selection of the reaction coordinate is shown in Figure 2. For the computation of the pathway directing the 1,4 adduct, C_s symmetry had to be imposed ($\beta = 90^\circ$). All other parameters were optimized.

The calculated energy path as a function of the reaction coordinates R is plotted in Figure 3. A sizable energy barrier of 28 kcal/mol is predicted for the reaction path. This is in contrast to the findings on the 1,2-addition of methylene to

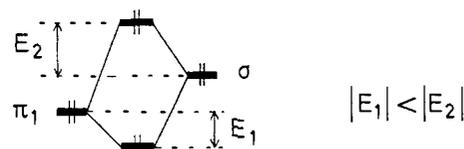
ethylene, where no activation energy is required for the process.¹⁶

In view of the fact that the 1,4-addition of singlet methylene to *cis*-butadiene has been classified as a concerted process (Figure 1)²¹ the magnitude of the energy barrier seems to be unexpectedly high²² (compared with the corresponding symmetry-forbidden 1,2-addition).

A first analysis which helps to explain this anomaly is provided by an inspection of the energy hypersurface. In Figure 4 the reaction path obtained from the complete energy optimization is summarized in a series of snapshots, the methylene approaching the butadiene unit.

With decreasing values of R the methylene tends to avoid the σ approach ($R < 2.7 \text{ \AA}$). When R is further reduced a sudden change in the geometry of the butadiene unit takes place. The methylene groups at C_1 and C_4 in butadiene start to rotate (disrotatory). At this point of the reaction path the overlap of the π MOs of the diene with the orbitals of the methylene is maximized. Hence the concerted 1,4-addition occurs in two crucial different stages.

The effect which counterparts the σ approach with maximum overlap involves *repulsion* between the electrons in the σ orbital of the methylene and the subfrontier²³ π_1 MO of the butadiene (Figure 1).



Since these orbitals possess like symmetry they will interact. The σ orbital will be raised in energy more as the π_1 MO is

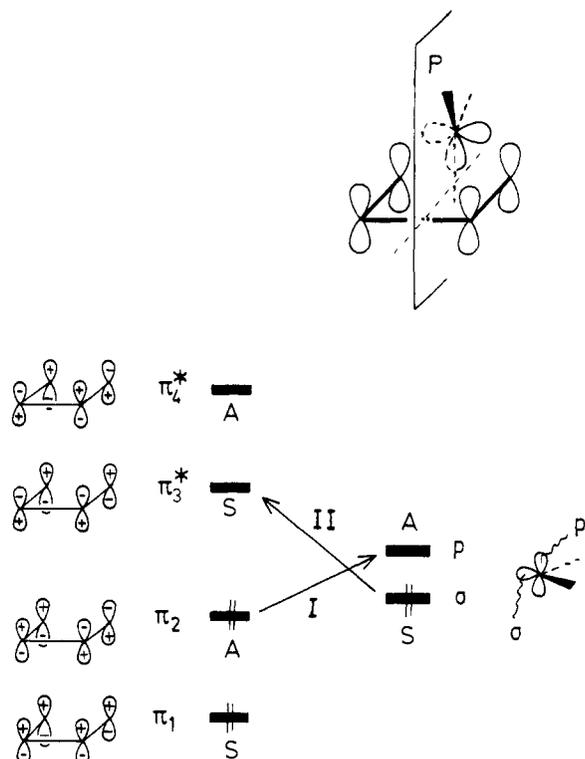


Figure 1. Orbital correlation diagram for the σ approach^{16a,c} of methylene to *cis*-butadiene. The symmetry designations are with respect to a symmetry plane P.

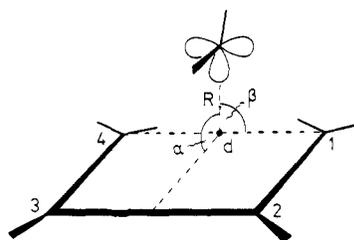


Figure 2. Selection of parameters for the description of the reaction coordinate. C_s symmetry is imposed and butadiene held in a *cis* conformation. The dummy atom d bisects the line between the atoms C_1 and C_4 .

lowered. As a net effect electronic destabilization results. In the case studied here this overlap repulsion²⁴ controls the reaction path.

Our view of the mechanism of the concerted 1,4-addition is still not complete. From theoretical studies²⁵ on the addition reaction $:\text{CH}_2 + \text{H}_2$ it is known that the trajectories of the methylene do not necessarily follow the reaction path of lowest electronic energy. Although a study of the dynamics of the 1,4-addition seems rather laborious, since it would require the knowledge of the potential surface in $3N$ dimensions²⁶ (N = number of degrees of freedom), a good deal of information is provided in a section through the electronic hypersurface presented in Figure 5.

The electronic energy of the system methylene plus *cis*-butadiene is plotted as a function of the two variables α and R . A value of $\alpha = 90^\circ$ corresponds to the "perfect" σ approach, i.e., a path perpendicular to the plane of the diene system (see Figure 2).

The contour map (Figure 5) corroborates the assertion of Figure 4. In the σ approach the repulsion between the electrons in the σ orbital and π_1 of the diene is strongly dominant at distances of $R \sim 1.5 \text{ \AA}$.

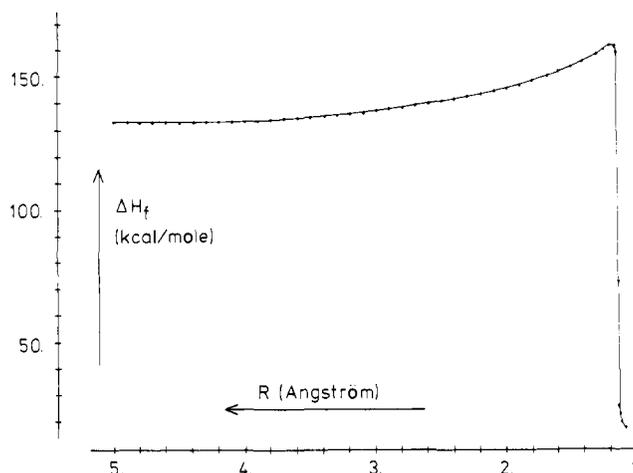


Figure 3. Plot of the calculated heats of formation (ΔH_f , kcal/mol) vs. the reaction coordinate R (in Ångström units) for the energy optimized approach of methylene to *cis*-butadiene. For the choice of the reaction coordinate see Figure 2.

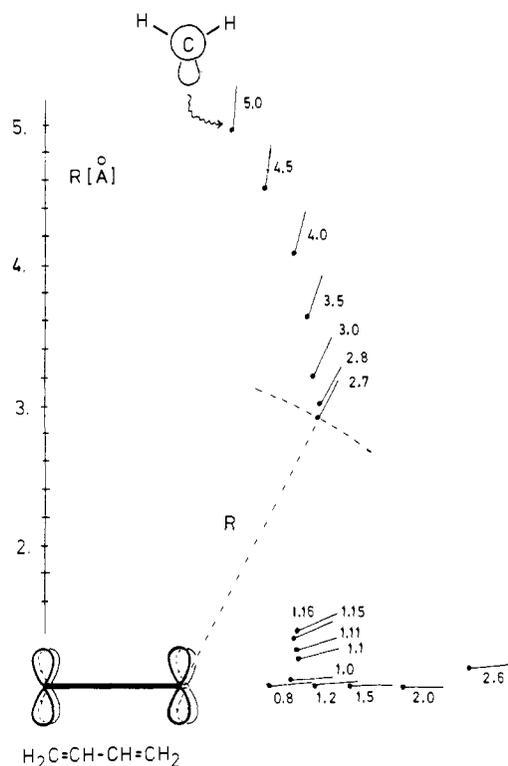


Figure 4. Snapshots for the energy-optimized approach of methylene to *cis*-butadiene and leading to the 1,4 adduct (cyclopentene). The full drawn lines correspond to a bisector of the HCH angle of the methylene. The corresponding numbers belong to the different values of R (in Ångström units).

The saddle point of the contour map presented in Figure 5 lies at $R = 1.75 \text{ \AA}$ and $\alpha = 125^\circ$. Hence, the energy path plotted in Figure 4 does not pass through this point. In other words, trajectories can be constructed which are lower in energy than the one presented in Figure 3. On this basis the minimal energy²⁷ required for the concerted 1,4-addition of methylene to *cis*-butadiene amounts to 23 kcal/mol.

Conclusion and Consequences

We have presented a section through the electronic hypersurface for the reaction of methylene with *cis*-butadiene leading to the 1,4 adduct (cyclopentene). All experimental investigations to prove the concerted nature of this reaction

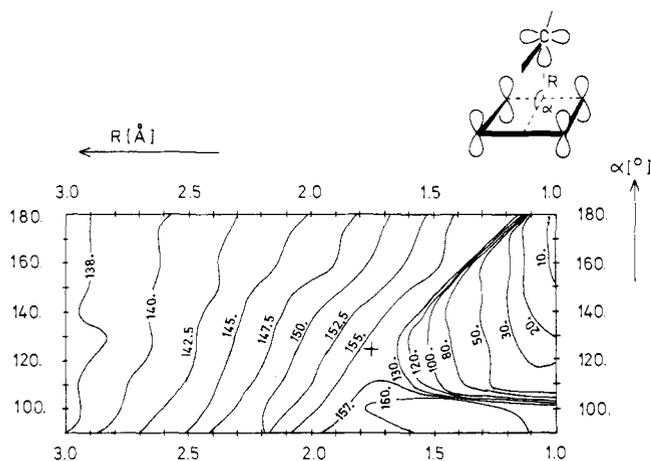


Figure 5. Contour map of the potential energy hypersurface for the 1,4-addition of methylene to *cis*-butadiene as a function of the two parameters R (in ångström units) and α (in degrees). All points on the hypersurface are totally optimized with respect to C_s symmetry. The numbers correspond to the heats of formation in kcal/mol. The saddle point (marked with a cross) corresponds to $R = 1.75$ Å, $\alpha = 125^\circ$.

have been unsuccessful so far. We have given an explanation for this fact: The favorable orbital interaction $\sigma \rightarrow \pi_3^*$ is superseded by repulsion between the orbitals σ and π_1 .

Is it possible to devise a strategy in such a way that the reaction path directing the 1,4 adduct is favored over the competing 1,2 adduct? According to the interaction diagram presented in Figure 1 this goal may be achieved by (a) reducing the energy gap between the σ and π_3^* orbitals and (b) increasing the energy difference between the σ and π_1 orbitals. This would require the introduction of electron-withdrawing substituents. Further investigations on this problem are in progress.

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