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Recebido em 5/11/99; aceito em 17/1/00

Four commonplace concerted reactions are examined using (i) correlation diagrams, (ii) frontier molecular orbital analyses for transition states, (iii) Zimmerman-Dewar analyses for transition states and (iv) modified Zimmerman-Dewar analyses for transition states. Only the latter approach is consistently satisfactory.

Keywords: Hückel-Möbius transition states; correlation diagrams; Frontier-orbital analyses; modified Zimmerman-Dewar arguments.

INTRODUCTION

Three major approaches have been developed to predict outcomes for concerted reactions controlled by orbital symmetry - analysis using (i) correlation diagrams¹, (ii) frontier orbital interactions in transition states² and (iii) incipient aromatic/antiaromatic character in transition states³⁻⁵. The latter approach (Zimmerman-Dewar or Hückel-Möbius) is particularly simple to teach to undergraduate students. However, as it was originally advanced, the Zimmerman-Dewar approach relied on so-called Möbius transition states. The notion of "aromatic" Möbius annulenes is problematic both from the pedagogical standpoint and from the standpoint of modern semiempirical molecular orbital results. For those reasons, I have previously proposed a modification of the Zimmerman-Dewar method which removes its dependence on Möbius structures⁶.

The earlier paper⁶, demonstrated that such a modification of the Zimmerman-Dewar approach (ending its dependence on Möbius structures) does not impair its predictive capacity. Indeed, my proposed shift to assessing transition state aromaticity using kinetic-stability-based aromaticity arguments removed the ambiguity which marred pre-existing Zimmerman-Dewar analyses for some electrocyclic and some cycloaddition reactions.

This report presents four examples of familiar concerted chemical reactions and compares the performance of the established approaches with that of the modified Zimmerman-Dewar method.

DISCUSSION

For the first example, consider the well-known Diels-Alder reaction. Application of the Woodward-Hoffmann approach¹ involves the construction of a correlation diagram which in turn requires an assessment of transition-state symmetry. In their discussion of Diels-Alder reactions (reference 1, pp 22-27), Woodward and Hoffmann propose a *quasi-endo* transition state (see Figure 1) which, for the simplest Diels-Alder reaction, would produce cyclohexene in a pseudo-boat conformation. A $\pi 4_s + \pi 2_s$ process, proceeding as in Figure 1, is physically realistic, conserves a plane of symmetry and can be shown to be thermally allowed (reference 1, pp 22-27).

For a $\pi 4_a + \pi 2_s$ process, the *quasi-endo* approach (Figure 1) is physically unrealistic because it precludes effective orbital overlap between one pair of terminal carbon atoms. Moreover, the transition state has no symmetry. Thus no correlation diagram can be drawn and no orbital-symmetry-based conclusion reached about the viability of this reaction pathway.

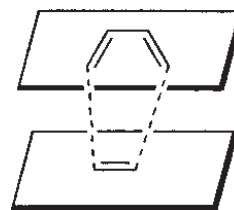


Figure 1. Formation of a quasi-endo transition state for the Diels-Alder reaction of butadiene and ethylene.

Given that cyclohexene prefers the half-chair conformation⁷, a least motion argument⁸, might lead to the conclusion that butadiene and ethylene should approach each other so that all carbon atoms lie in a common plane (vide Figure 2). Disrotatory motion of the diene termini would lead to a $\pi 4_s + \pi 2_s$ transition state and would proceed in a manner conserving a mirror plane (assuming initial formation of cyclohexene in a pseudo-boat conformation).

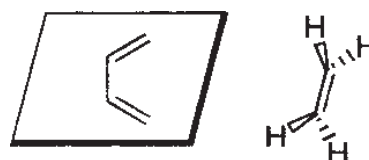


Figure 2. Coplanar approach of carbon skeleta for the Diels-Alder reaction of butadiene and ethylene.

Conrotatory motion of the diene termini would lead to a $\pi 4_a + \pi 2_s$ transition state and would proceed in a manner conserving a C_2 axis (assuming formation of cyclohexene in a half-chair conformation).

The construction of a correlation diagram to examine both pathways (see Figure 3) is now a straightforward exercise. It is evident, from Figure 3, that both coplanar pathways are thermally allowed. Thus, the Woodward-Hoffmann approach offers no clear basis for rejecting the $\pi 4_a + \pi 2_s$ process. For the Diels-Alder reaction between *trans,trans* 1,4-dimethyl butadiene and ethylene, no prediction emerges regarding the relative stereochemistry in the dimethylcyclohexene product.

In accord with experiment, the $\pi 4_a + \pi 2_s$ pathway is found, unambiguously, to be forbidden using (i) either the original Zimmerman-Dewar approach or my modification of it⁶ or (ii) Fukui's frontier orbital approach^{3,9}.

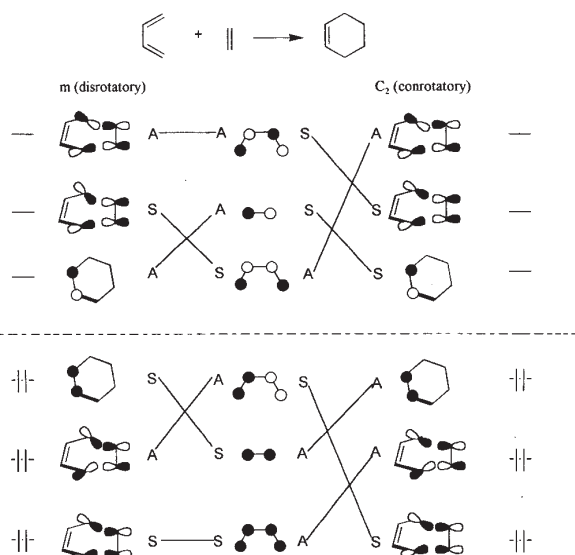
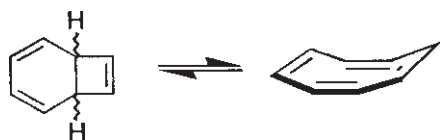


Figure 3. A correlation diagram for $\pi A_s + \pi 2_s$ and $\pi A_a + \pi 2_s$ pathways for the reaction between butadiene and ethylene, assuming a coplanar skeletal approach (Figure 2).

Now consider the electrocyclic opening/closing of the bicyclooctatriene/cyclooctatetraene pair (*vide* Scheme 1).



Scheme 1

Disrotatory closure conserves a mirror plane but conrotatory closure conserves no symmetry and cannot be assessed with a correlation diagram. Application of the original Zimmerman-Dewar approach is also unsatisfactory. Both disrotatory closure (see Figure 4) and conrotatory closure (see Figure 4) go through "aromatic" transition states and are allowed.



Disrotatory transition state
0 nodes, \therefore Hückel array
6 e^- , \therefore aromatic
 \therefore Δ allowed

Conrotatory transition state
1 node, \therefore Möbius array
4 e^- , \therefore aromatic
 \therefore Δ allowed

Figure 4. Zimmerman-Dewar transition state analyses for electrocyclic opening of bicyclooctatetraene.

The frontier orbital approach provides a direct answer to this problem. In terms of the bicyclooctatriene opening, a σ bond must interact with two adjacent π -systems: a diene and an isolated CC π -bond. The dominant interaction involves the HOMO-LUMO pair closest in energy. Thus the diene is the appropriate π -system and opening/closing is expected to occur in a disrotatory fashion (see Figure 5).

Similarly, the modified Zimmerman-Dewar treatment of this reaction leads to the straightforward conclusion that cyclooctatetraene should close in a disrotatory fashion⁶. The reaction is known to proceed in a disrotatory fashion¹⁰.

For the third case, consider the cycloaddition reaction¹¹

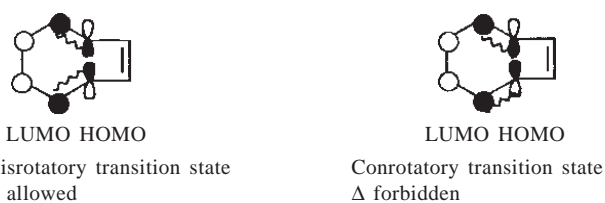
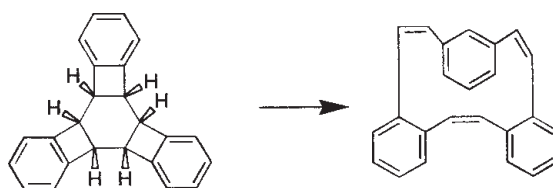


Figure 5. Frontier orbital transition state analyses for electrocyclic opening of bicyclooctatetraene.

shown in Scheme 2. While the construction of a correlation diagram for this $\sigma 2_s + \sigma 2_s + \sigma 2_s$ reaction is simple, potentially competitive processes like $\sigma 2_s + \sigma 2_s + \sigma 2_a$ do not conserve symmetry and can not be examined using a correlation diagram. No HOMO/LUMO pair can be defined for such three-component reactions so that the frontier-orbital approach breaks down.



Scheme 2

The original Zimmerman-Dewar approach encounters no difficulty in this case (see Figure 6) finding that $\sigma 2_s + \sigma 2_s + \sigma 2_s$ is allowed and $\sigma 2_s + \sigma 2_s + \sigma 2_a$ is forbidden. The modified Zimmerman-Dewar approach⁶ leads to the same straightforward conclusions based on δE_{FMO} values (see Figure 7).

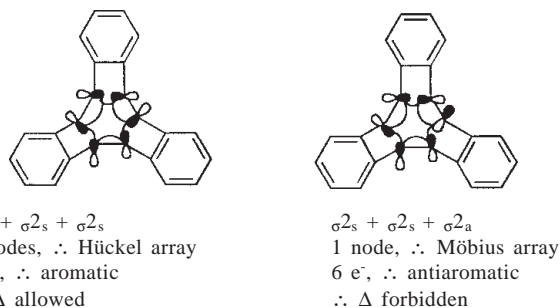


Figure 6. Zimmerman-Dewar transition state analyses for the cycloaddition in Scheme 2.

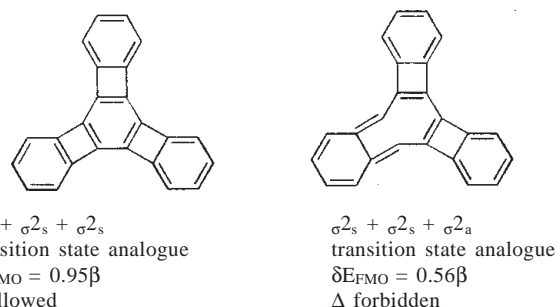


Figure 7. Modified Zimmerman-Dewar transition state analyses for the cycloaddition in Scheme 2.

Finally, let's examine the cheletropic expulsion depicted in Scheme 3 and reported earlier¹². So-called linear departure

conserves a plane of symmetry (see Figure 8) and can be shown to be thermally allowed by constructing a correlation diagram.



Scheme 3

From the pedagogical standpoint, it is very poor practice to encourage students to see "orbital symmetry" for structures which do not have the molecular symmetry to impose it. For the non-linear transition state (see Figure 8), there is no plane or axis passing through the mid-point of the central CC bond and through the S atom. Thus no correlation diagram can be drawn for the non-linear process and the Woodward-Hoffmann approach offers no clear view of that and other alternative pathways.

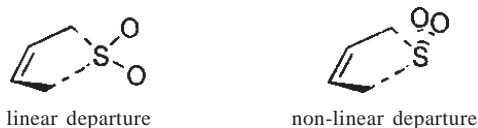


Figure 8. Transition state structures for cheletropic expulsion of SO_2 from sulfolenes.

The frontier-molecular orbital approach successfully differentiates between linear expulsion with disrotatory motion (thermally allowed - see Figure 9) and linear expulsion of SO_2 with conrotatory motion of the newly-terminal carbon atoms (thermally forbidden). Unhappily, the frontier-orbital approach also finds that non-linear departure with conrotatory motion is thermally allowed (see Figure 9). Thus linear departure with disrotatory motion would produce *trans,trans* or *cis,cis* 1,4-dimethylbutadiene



Figure 9. Frontier molecular orbital transition state analyses for cheletropic expulsion of SO_2 from sulfolenes.

and non-linear departure with conrotatory motion would produce *trans,cis* 1,4-dimethylbutadiene - leading to a list of all possible product stereochemistries and no clear prediction of which product should be favored.

Precisely the same breakdown occurs for the established Zimmerman-Dewar approach (see Figure 10).

In this case, the modified Zimmerman-Dewar approach is uniquely able to anticipate which product stereochemistry will be observed (see Figure 11).

Only linear departure with disrotatory motion goes through an "aromatic" transition state and *cis,cis* or *trans,trans* stereochemistry is unambiguously predicted for the product diene (Scheme 3).

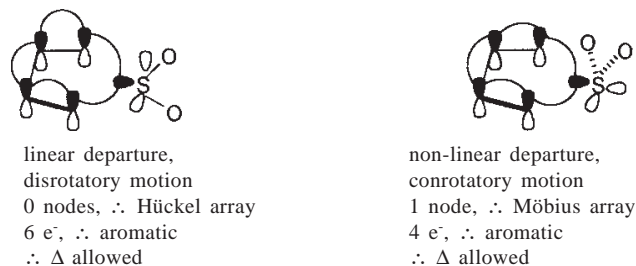


Figure 10. Zimmerman-Dewar transition state analyses for cheletropic expulsion of SO_2 from sulfolenes.

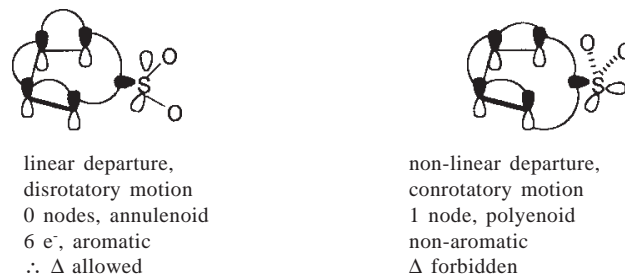


Figure 11. Modified Zimmerman-Dewar transition state analyses for cheletropic expulsion of SO_2 from sulfolenes.

An examination of four commonplace concerted reactions has shown that the Woodward-Hoffmann approach frequently breaks down or can't be properly applied to each of the commonly considered reaction pathways for a given starting material - product pair. Frontier-molecular orbital arguments are consistently hamstrung when there are more than two reacting components and occasionally break down for other reactions (e.g. cheletropic expulsion of SO_2 from sulfolenes). Zimmerman-Dewar analyses can break down when transition states have polycyclic p-orbital arrays and occasionally fail to give clear predictions for monocyclic arrays. The modified Zimmerman-Dewar approach⁶, which avoids so-called Möbius transition states, is (i) easier to learn and apply and (ii) gives more reliable predictions.

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