

Organic Cume, September 2004
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The cume topic *Organizing Principles of Complex Reactions and Theory of Coarctate Transition State* was announced with reference to the article by Rainer Herges (*Angew. Chem. Int. Ed. Engl.* **1994**, 33, 255-276) and students are allowed to bring the article to the test.

(1) Types of transition states. Provide very brief but complete definitions for linear, pericyclic, and complex transition states. In each case, provide a transition state structure of a specific example of your choice as best as you can (try to get the relative bond lengths right). (20 points)

(a) Linear (6 points)

(b) Pericyclic (6 points)

(c) Complex (8 points)

(2) Explain why the Diels-Alder Reaction between butadiene and ethene is thermally allowed using (a) the Conservation of Orbital Symmetry Method, (b) the Frontier Orbital Method, and (c) the Aromaticity of Transition States Method. (20 points)

(a) Orbital Symmetry (10 points)

(b) Frontier Orbital Method (5 points)

(c) Aromaticity of Transition State Method (5 points)

(3) Fill in the matrix with YES or NO or a name. (15 points)

| | Conservation of Orbital Symmetry | Frontier Orbital Method | Aromaticity of Transition State Method |
|--|--|-------------------------------|--|
| Use AOs only? | | | |
| Use all MOs? | | | |
| Use some MOs? | | | |
| Main Inventor? | | | |
| Method can be used for complex reactions? | | | |

(4) The “pin-up reaction” of the “complex reactions” is the cyclopropylcarbene fragmentation. (a) Draw Lewis structures for the cyclopropylcarbene and for the products. (b) Which carbon is the “atom with 2 p-AOs that are involved in forming/breaking of two bonds.” (c) Draw a Lewis structure of the transition state. Use perspective drawing. (d) Draw a Hueckel ribbon for this reaction. Use perspective drawing. (15 points)

| | |
|-------------------|---------------|
| (a & b, 5 points) | |
| (c, 5 points) | (d, 5 points) |

(5) The cyclopropylcarbene is used as a singlet in the cyclopropylcarbene fragmentation. This singlet can have two structures; draw both and indicate clearly the type(s) of MO(s) that is/are occupied by the carbene electrons. There also exists a triplet of this carbene; draw its structure and indicate clearly the type(s) of MO(s) that is/are occupied by the carbene electrons. Perspective drawings please! (15 points)

| Singlet #1 | Singlet #2 | Triplet |
|------------|------------|---------|
| | | |

(6) Consider the synthesis of the imidazole shown, the “HCN tetramer”, in space. This molecule can be synthesized by a path that begins with a “complex reaction” of HCN with $\text{HN}=\text{C}(\text{CN})_2$ and subsequent hydrogenation (*really* easy in space). Provide a mechanism for this reaction. Note: The article does not contain this exact reaction, but there is a discussion of a very closely related reaction. (15 points)

The “HCN Tetramer”: Key to life as we know it.

