QUESTION 1

Which describes the ALLOWED product of this reaction?

A  Hückel transition state, suprafacial/suprafacial reaction
B  Hückel transition state, suprafacial/antarafacial reaction
C  Möbius transition state, suprafacial/suprafacial reaction
D  Möbius transition state, suprafacial/antarafacial reaction

**Explaining this using AROMATIC TRANSITION STATE THEORY....**

There are 8 electrons in this reaction, therefore the transition state can not be Hückel, since this would be aromatic, the transition state must be Möbius.

In comparison to the Diels-Alder reaction, which we know has a Hückel transition state and is a suprafacial/suprafacial addition reaction, the allowed reaction must be suprafacial/antarafacial.

With seven atoms in the cyclic system there is just enough flexibility to allow a suprafacial/antarafacial reaction, which means both bonds are formed on the same side of one reactant and on the OPPOSITE sides of the other.

The reaction can be suprafacial on A and antarafacial on B to give one allowed product.

The reaction can ALSO be suprafacial on B and antarafacial on A to give a second (different) allowed product.

**note the OPPOSITE stereochemistry for the 2 Me groups compared to what the expected for a suprafacial reaction**

**note: in this case you COULDN’T TELL the reaction was (a)+(s) because there is no stereochemistry associated with reactant A**
QUESTION 2

Which correctly and completely describes the product of the following Diels-Alder reaction?

A

B

C

D

The REGIOCHEMISTRY of the Diels-Alder reaction is such that the 1,2- and 1,4 addition products are always formed (are the Major products), thus A and B can’t be correct, only a 1,4-product can be formed in this case. The hybridization at THIS carbon in the product is sp2, thus the MeO- donating group can NOT be wedged or dashed, it has to be "plain" in the plane of the paper. Thus, D is silly and can’t be correct. C is correct. Note that there is a chiral/asymmetric center HERE. No wedged/or dashed bond is shown since there is only one such center, and the (†) symbol means that it must be both wedged and dashed. It wouldn’t really be correct to draw like this, since even though the withdrawing group is shown going "down" as we learned in class, there isn’t any "inside" or "outside" group on the diene to compare the W group to (there are only hydrogens on the "ends" of the diene) so it isn’t "down" with respect to a substituent on the diene end, and the dashed bond is redundant, particularly because it is also wedged!
QUESTION 3

MC30g

Give the product of the following reaction under THERMODYNAMIC control conditions (high temperature).

allylic bromide, good for SN1 and SN2

CH₂Br \text{EtOH} \rightarrow \text{polar protic solvent and heat}

MUST BE SN1!!

the thermodynamic product is the more stable and substituted alkene isomer (3 bold bonds to substituents, 1 hydrogen), but it is formed slower.

this would have been the kinetic product, the alkene is the isomer with the less substituted C=C bond (two substituents, bold bonds and two hydrogens not shown), but it is formed faster.
QUESTION 4

MC30h

Give the product of the following reaction under THERMODYNAMICALLY controlled conditions (high temperature):

\[
\text{A} \quad \text{OH} \quad \text{H}^- \cdot \text{Cl}^- \quad \text{CCl}_4
\]

inert solvent does not get involved in the reaction directly

\[
\begin{align*}
\text{B} & \quad \text{Cl}^- \\
\text{C} & \quad \text{Cl}^- \\
\text{D} & \quad \text{Cl}^- 
\end{align*}
\]


\[
\begin{align*}
\text{H}^- \cdot \text{Cl}^- & \quad \text{H}_2 \quad \text{OH} \quad \text{H}_2 \quad \text{OH} \quad \text{Cl}^- \\
\text{MINOR} & \quad \text{MAJOR} \\
\text{slower reaction} & \quad \text{faster reaction} \\
\end{align*}
\]

thermodynamic product, more stable than the disubstituted isomer kinetic product (3 substituents on the C=C bond shown in bold and only 1 H)

kinetic product, formed faster (attacks carbon with more positive charge), but less stable than thermodynamic product, it has a disubstituted C=C bond (2 bold bonds and 2 hydrogens)
QUESTION 5
MC40d

Which best describes the following reaction?

A  Conrotatory  
B  Disrotatory  
C  Neither Conrotatory or Disrotatory  
D  Not Enough Information To Tell

rotating clockwise

rotating opposite directions thus DISROTATORY
QUESTION 6

How many VERTICAL nodes do the Highest Occupied and Lowest Unoccupied π-Molecular Orbitals of the anion formed upon deprotonation of the structure shown?

A) HOMO = 0 and LUMO = 1
B) HOMO = 1 and LUMO = 2
C) HOMO = 2 and LUMO = 3
D) HOMO = 3 and LUMO = 4

the EXACT positions of the nodes, especially in π5 and π6, are somewhat arbitrary, it is more important to get the NUMBER correct and to distribute them approximately symmetrically. The problem is that we are using "binary" pictures of the p A.O.s (up or down) to represent the shapes of the waveforms, that have real non-binary wave behavior. The nodes at the CENTERS of the π-systems, however, should be exactly in the center.

SEVEN p A.O.s thus SEVEN M.O.s
EIGHT π electrons
**QUESTION 7**

MC400

Which best describes the following reaction?

A suprafacial on the anion and suprafacial on the alkene
B suprafacial on the anion and antarafacial on the alkene
C antarafacial on the anion and suprafacial on the alkene
D antarafacial on the anion and antarafacial on the alkene

suprafacial: both bonds are made on the same side
antarafacial: the bonds are made on opposite sides

for cycloaddition reactions it is easiest to think of them in relation to the Diels-Alder reaction, the stereochemistry of the Diels-Alder reaction is the way it is because the reaction is suprafacial on the diene and also suprafacial on the dienophile

both methyl groups are on the "outside"
there are two H on the "inside"

the two Me- groups are on the same side in the product
(wedged or dashed is irrelevent, what matters is that they are both the same, this is "Diels-Alder" type stereochemistry, the reaction is suprafacial on the anaion
the two Ph- groups are trans- in the reactant and also trans- in the product, this is Diels-Alder type stereochemistry, the reaction is suprafacial on the alkene
QUESTION 8
MC30aa

Which answer describes the number of VERTICAL nodes for the HOMO and the LUMO of ozone?

A) HOMO = 0 and LUMO = 1  
B) HOMO = 1 and LUMO = 2  
C) HOMO = 2 and LUMO = 3  
D) HOMO = 3 and LUMO = 4

Ozone [ ] there are 3 p AOs involved, one on each oxygen

the electrons in BLUE are NOT INVOLVED in the conjugated π-system, they do not get involved in resonance and each is in an sp2 hybridized AO on oxygen

so, there are only 4 electrons in the π-system

<table>
<thead>
<tr>
<th>Energy</th>
<th>Vertical Nodes</th>
<th>Ozone</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>π₁</td>
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</tr>
<tr>
<td></td>
<td>π₂</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>π₃</td>
<td>2</td>
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</tbody>
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non-bonding energy level