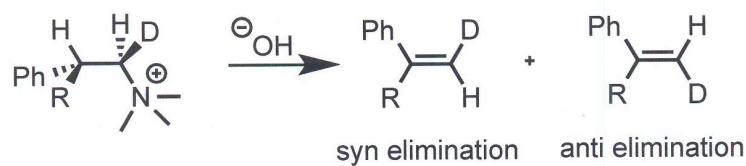


386J Exam 3
December 6th, 2014

Name: Key

1	/8
2	/8
3	/8
4	/4
5	/8
6	/6
7	/8
8	/6
9	/12
10	/6
11	/12
12	/6
13	/8
14	/8
15	/4
Total	/112

1. (8 pts) In the following E2 reaction, the syn vs. anti elimination switches upon changing R = Me to R = *i*Pr.



a) What product, syn or anti, is favored when R = CH₃?

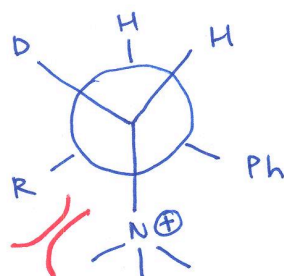
anti +2

b) What product, syn or anti, is favored when R = *i*Pr?

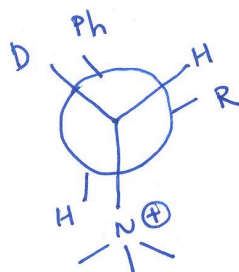
syn +2

c) By drawing a Newman projection, explain your answers to parts a) and b).

+4

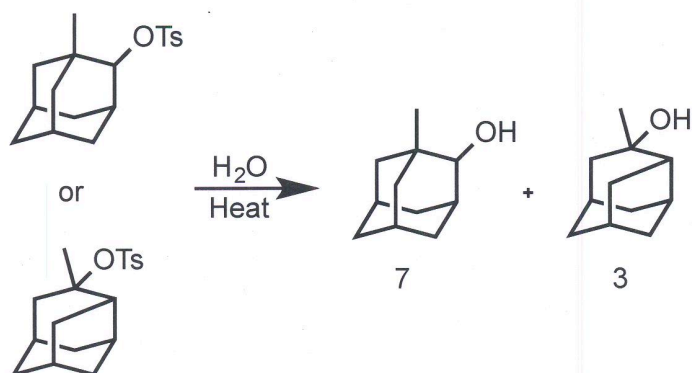


Anti-elimination disfavored by large R group

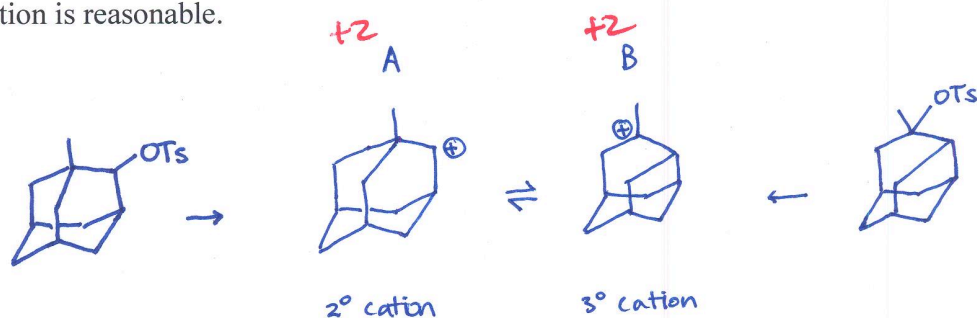


Large R group favors syn-elimination

2. (8 pts) Solvolysis of the reactants shown in aqueous solvent give essentially identical ratios of the same two alcohols (7:3).

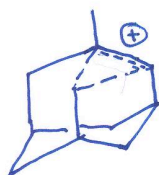


a) One explanation is that two carbocations are formed that rapidly interconvert and have essentially the same energy. Draw these two carbocations and comment on whether this explanation is reasonable.



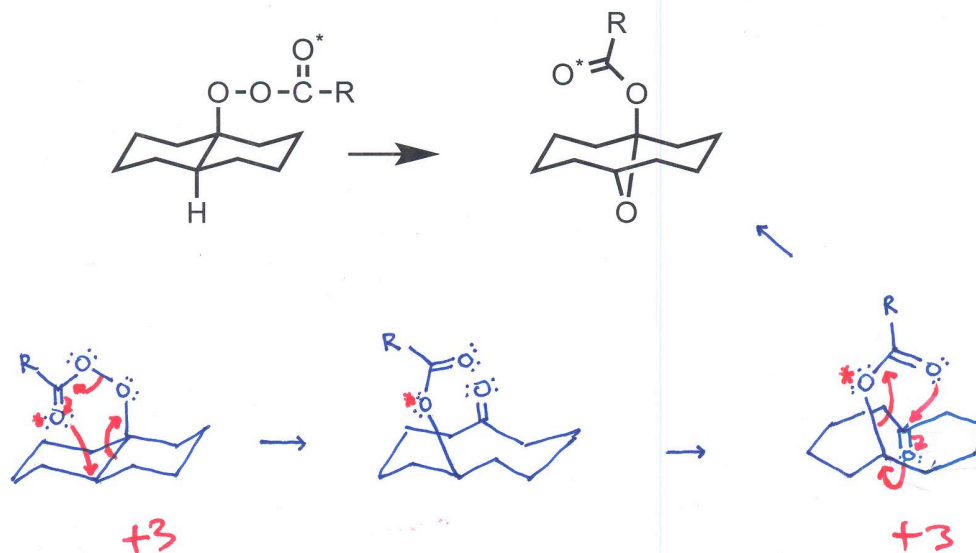
Yes, it is reasonable. Although 2° ions are usually less stable than 3° ions, it appears to be more ring strain in the 3° cation. Instead of all six-membered rings B has one five- and one seven-membered ring.

b) An alternative explanation is that the same non-classical carbocation is formed from both reactants. Draw this carbonium ion.



8

3. (pts) The thermal Criegee rearrangement is shown below. Write a mechanism for this reaction with all electron pushing. Explain the fact that when the carbonyl oxygen of the perester is labeled with ^{18}O , it is almost entirely retained in the product carbonyl oxygen position. Propose another experiment that might help support the mechanism you wrote.

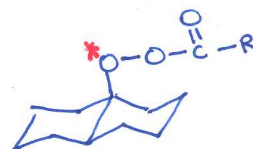


Other experiment that might support this mechanism would be the measurement of the rate at different temperature and the determination of activation parameters. Both steps shown have highly organized T.S. and the reaction would be expected to have a negative $\Delta S^\ddagger$.

+2

Or,

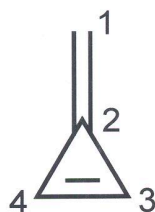
label other oxygen with ^{18}O .



4. (4 pts) In class, we have learned Huckel's theory. This theory was originally introduced to permit qualitative study of the π -electron systems in planar, conjugated hydrocarbon molecules.

Provide the Huckel secular determinant for the following molecule.

Hint: i) The energy of any carbon p orbital anywhere in the molecule is the same value, α .
 ii) The energy of interaction between any two adjacent C $2p$ orbitals is called the resonance integral, β .



$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & \beta \\ 0 & \beta & \alpha - E & \beta \\ 0 & \beta & \beta & \alpha - E \end{vmatrix} = 0$$

or

$$\begin{vmatrix} -x & 1 & 0 & 0 \\ 1 & -x & 1 & 1 \\ 0 & 1 & -x & 1 \\ 0 & 1 & 1 & -x \end{vmatrix} = 0$$

$$E = \alpha + x\beta$$

$$\alpha - E = -x\beta$$

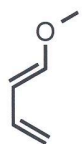
$$\alpha = E - \beta$$

$$\frac{\alpha - E}{\beta} = -x$$

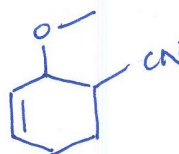
5. (8 pts) Draw the HOMO of the 4π -system and the LUMO of the 2π -system for the following Diels-Alder reactions. Make sure to show the character of the p -orbitals accentuated in an appropriate manner that reflects resonance structures. Next, predict the major product of the reaction. Be sure to show the correct regiochemistry of the product.

+4

a)



+

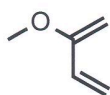


major

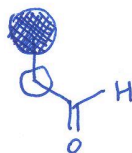
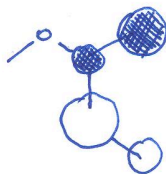
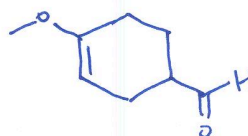
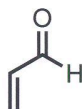


+4

b)

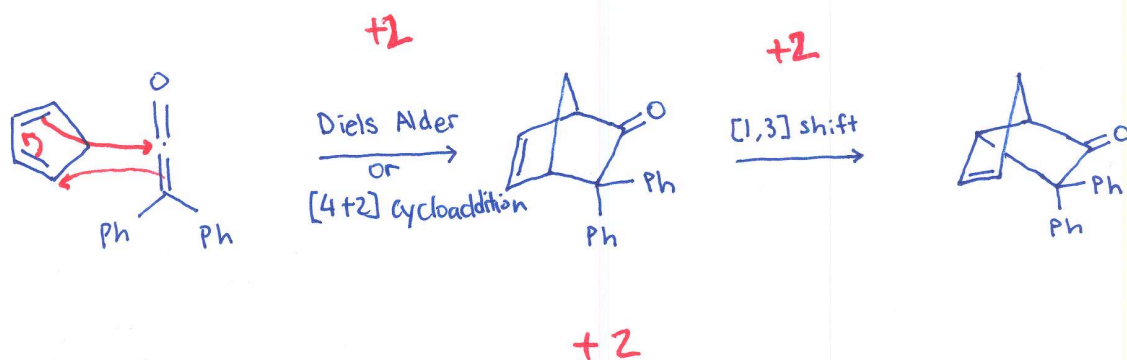
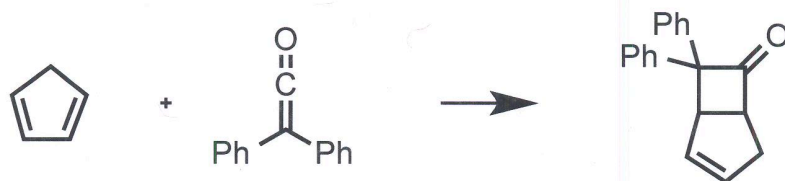


+

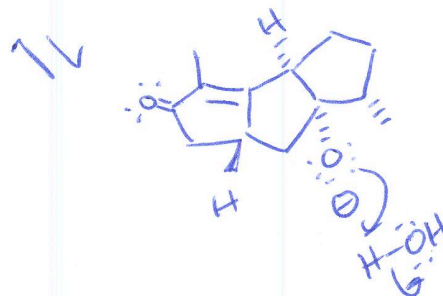
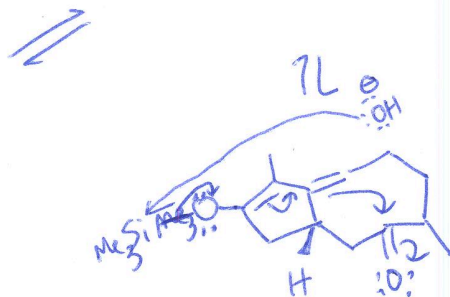
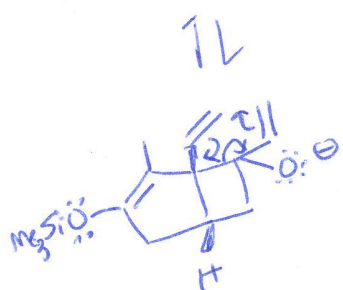
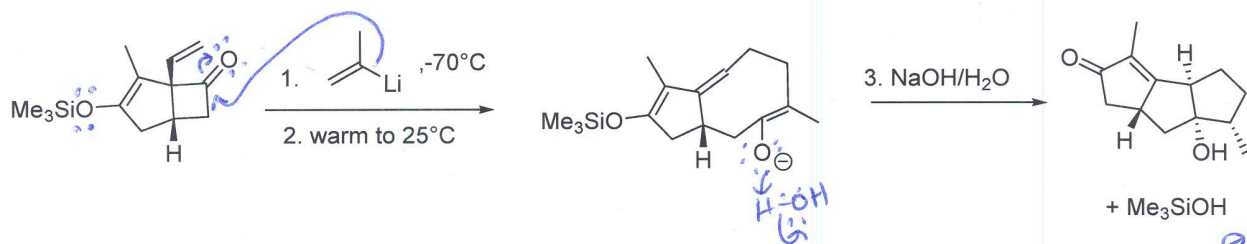


6

6. pts) At first glance, the following reaction appears to be a [2+2] cycloaddition of a single double bond from cyclopentadiene with the C=C double bond of diphenylketene. However, it has been experimentally shown that the product actually results from two conventional pericyclic reactions that we all know are allowed. Show by writing an alternative mechanism what these two reactions must be.



7. (8 pts) Show the full arrow pushing for the reaction below. Draw all products made in each step as well as all formal charges and lone pairs. The intermediate obtained before the basic workup is given below to help you.

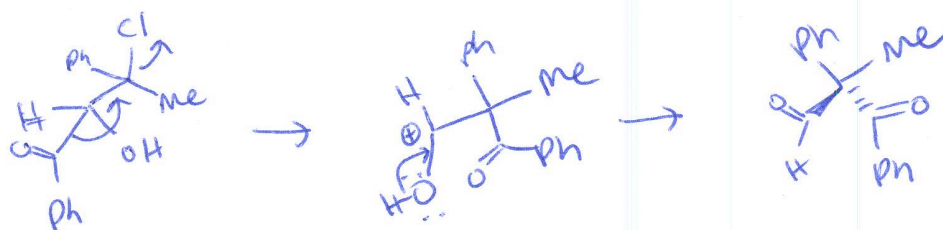
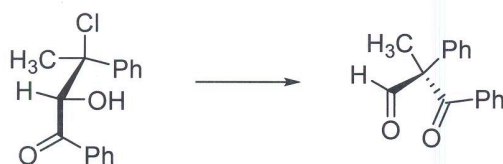
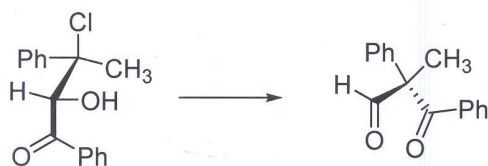


5 arrows

3 intermediates

4 minor intermediates

- 6
8. (5 pts) Explain the products and stereochemistry of the following reactions.



migration of the acyl group occurs at the same time as the C-Cl cleavage since stereochemistry is retained → anchimeric assistance

1P
9. (10 pts) Short answers on quantum mechanics.

a) Use ∇^2 to explain the following common notions:

i) The more nodes an orbital has, the higher in energy that orbital is.

↳ higher frequency wave $\rightarrow$ greater rate of change of slope (∇^2)

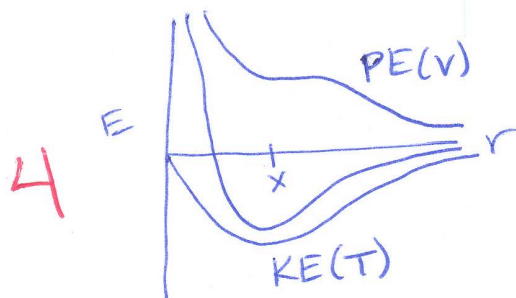
2

ii) The more resonance structures a molecule has, the lower its energy.

KE of an e^- is lower the more diffuse its ψ

2

b) Draw a Morse potential and explain how its shape arises.



$V+T = \text{Morse potential}$

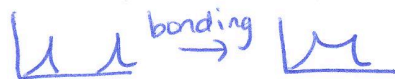
Short $r \rightarrow V$ dominates

at some $r=x \rightarrow T$ dominates

c) Why do bonds form?

KE of bonding is lower than KE of isolated e^- in atomic orbitals

2



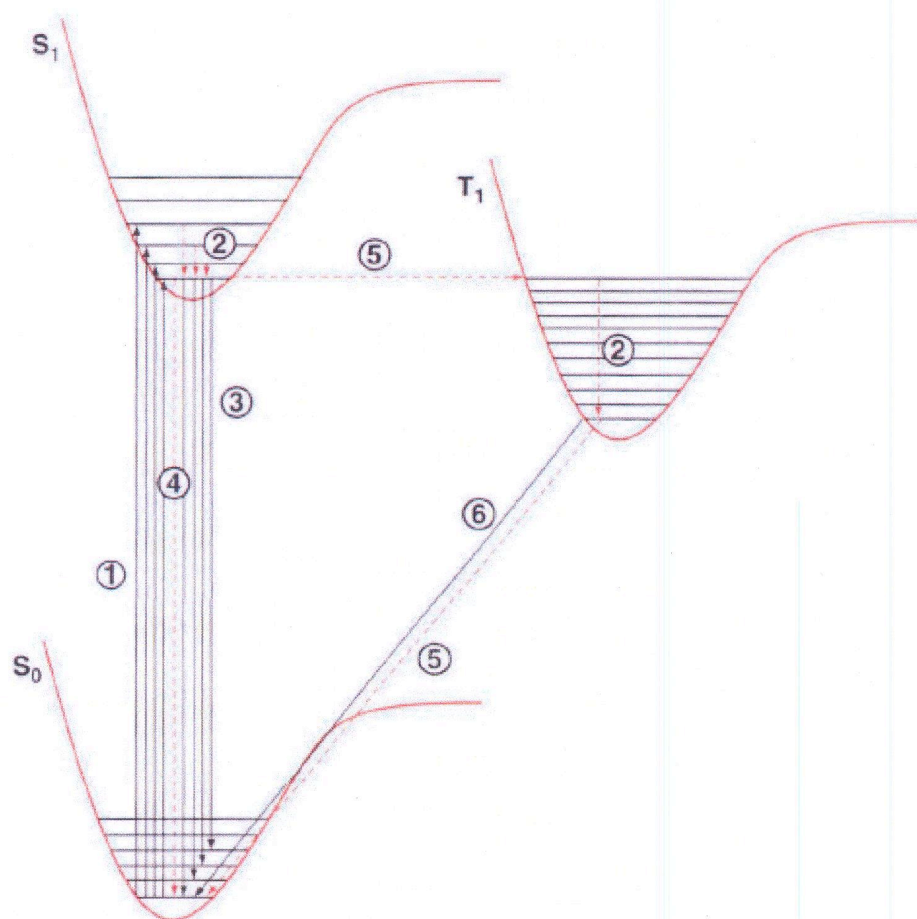
d) Why are antibonding orbitals more destabilized than bonding orbitals are stabilized?

$E_{\psi} = \frac{\sim}{s+1}$ $E_{\psi^*} = \frac{\sim}{s-1}$ $s = \text{overlap integral}$

2

$|s+1| > |s-1|$, hence $E_{\psi} < E_{\psi^*}$

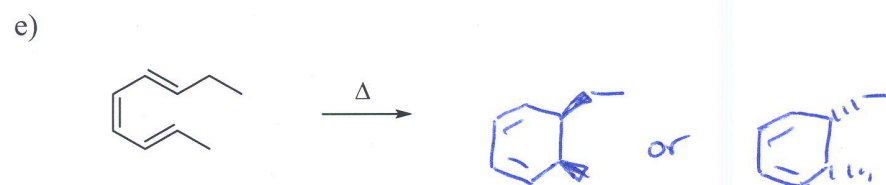
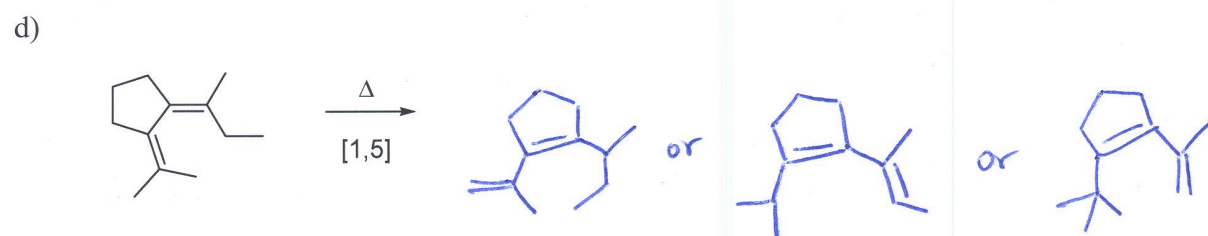
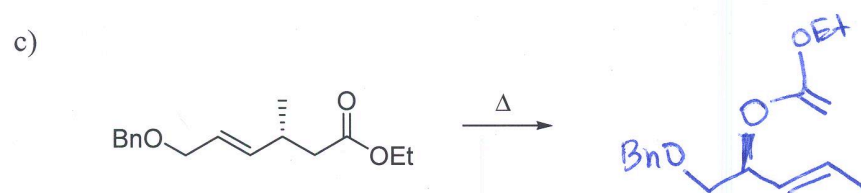
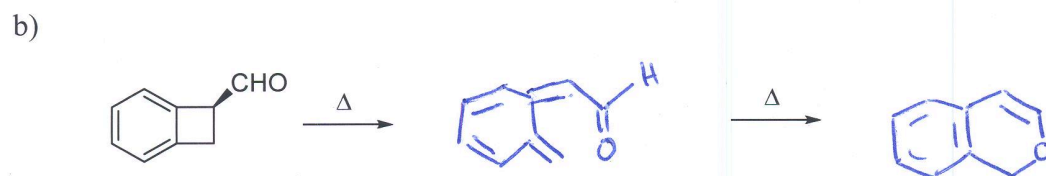
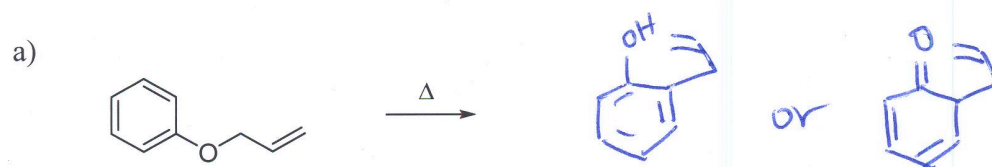
10. (6pts) For the following Jablonski diagram, give the name that corresponds to each process.



1. absorption
2. relaxation
3. fluorescence
4. internal conversion
5. intersystem crossing
6. phosphorescence

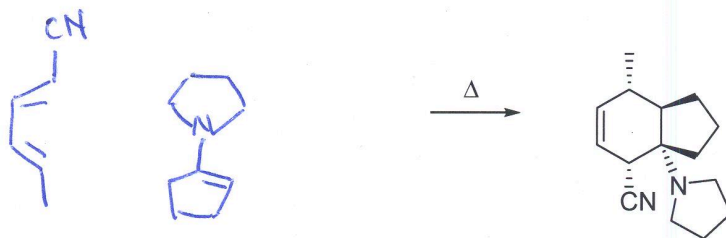
leach

11. (12 pts) For the following pericyclic reactions, give the predominant product. Show stereochemistry as appropriate.



12. (6 pts) For the following pericyclic reactions, draw the appropriate starting materials.

a)



b)

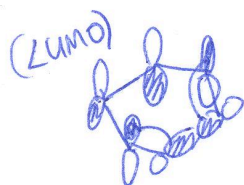
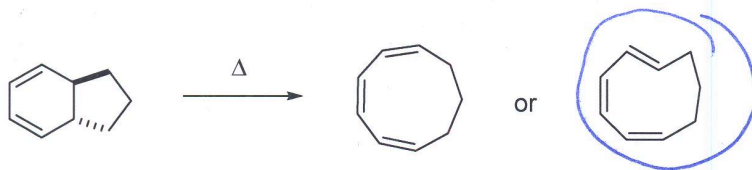


c)



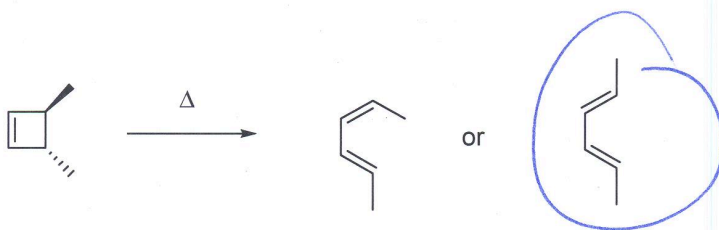
13. (8 pts) Draw the orbitals involved in FMOT to determine whether the following ring opening reactions will be allowed as disrotatory or conrotatory. Circle the product with the correct stereochemistry for each reaction.

a)



disrotatory

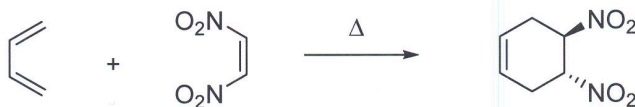
b)



conrotatory

14. (8 pts) For the stereochemistry shown in each reaction 1) classify the $[x\#y+x\#y]$ process which occurs, where $x = \pi$ or σ , $\#$ = number of electrons, and $y = s$ or a (for example, $[\pi 2s + \pi 2a]$), and 2) use the generalized orbital symmetry rule (Woodward-Hoffman rule) to determine if the reaction is allowed or forbidden as drawn.

a)



$$[\pi 4s + \pi 2a]$$

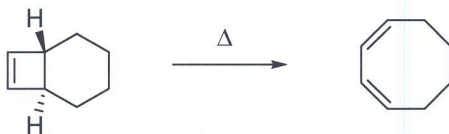
$$0 + 0 = 0 \quad \text{forbidden}$$

or

$$[\pi 4a + \pi 2a]$$

$$1 + 0 = 1 \quad \text{allowed}$$

b)

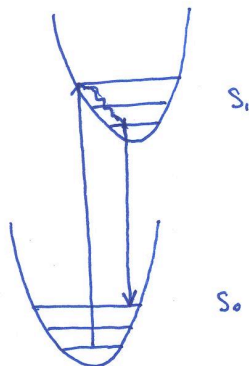


$$[\pi 2a + \sigma 2s] \quad \text{or} \quad [\pi 2s + \sigma 2a]$$

$$0 + 1 = 1$$

$$\text{allowed}$$

15. (4 pts) Why does the change of geometry upon excitation leads to a Stokes shift?
Explain



A change in molecule geometry leads to a vibrational excitation, which in turn leads to a large amount of ~~vibration~~ of vibrational relaxation both in S_1 and S_0 and ultimately to a Stokes shift.