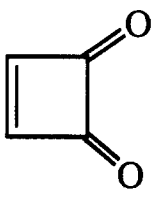
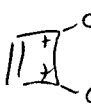
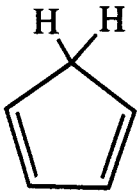
1. (10 pts) Label the following compounds as having aromatic, antiaromatic, or simple olefinic (double bonding) character. 1pt each

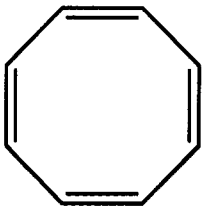


Aromatic



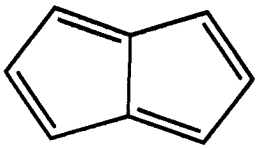


Simple olefin

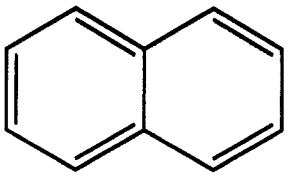


Simple olefin

Not conj.

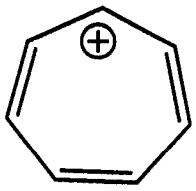


antiaromatic
4n electrons

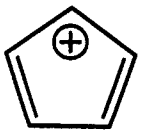


Aromatic
4n + 2 electrons

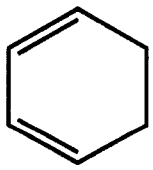
antiaromatic



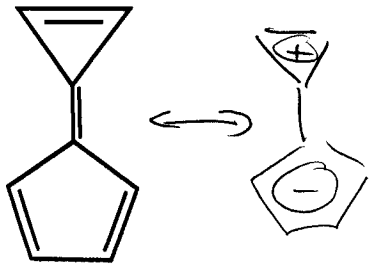
aromatic



antiaromatic

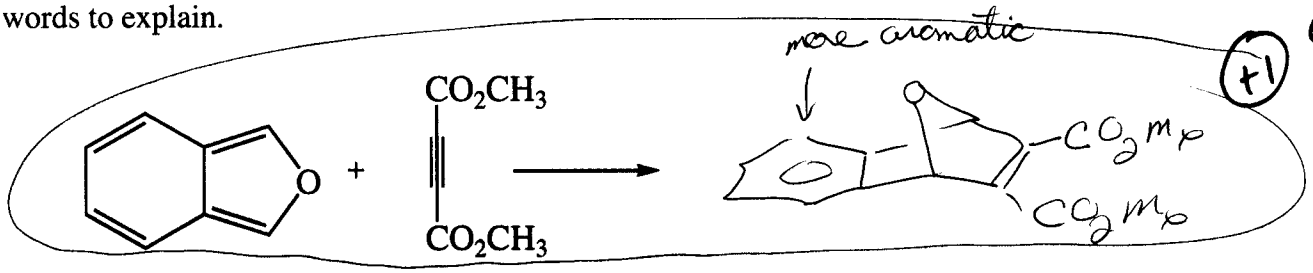


simple olefin

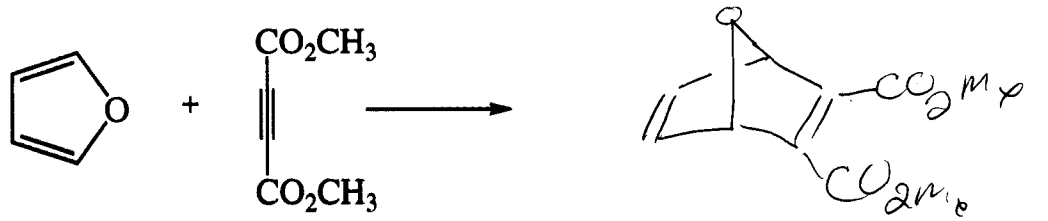


aromatic

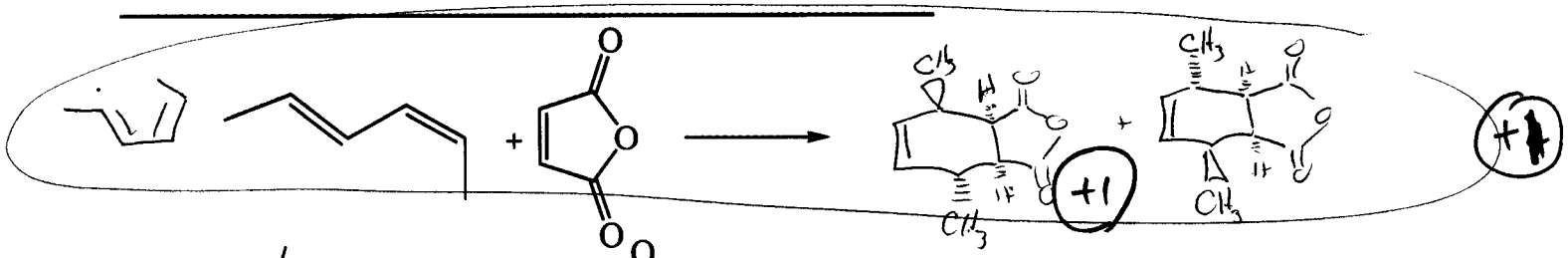
2. (15 pts) Consider the following pairs of reactions. Write down the products and circle the reaction that is faster in each pair. If you think that no reaction will occur, write NR and provide a couple of words to explain.



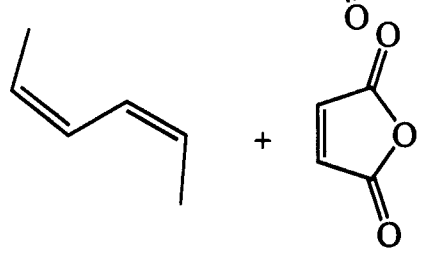
correct circle +1 +1



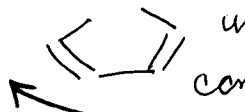
+1



+1 +1

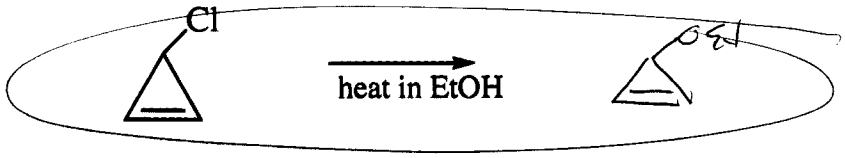


NR

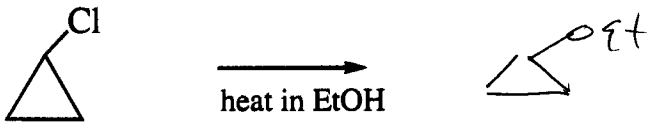


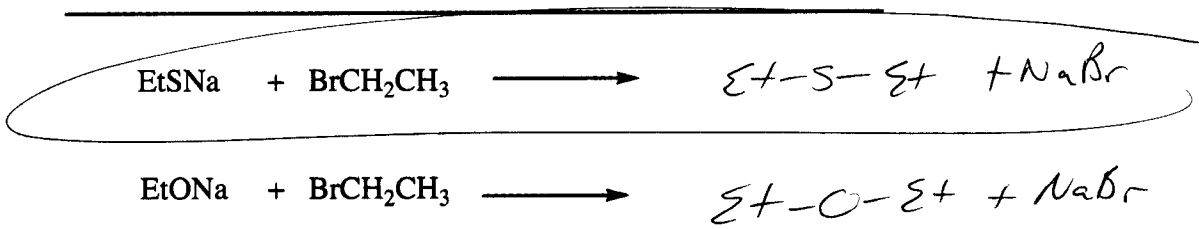
unstable conformation +1

explanation +2



aromatic intermediate +1





more nuc. +1

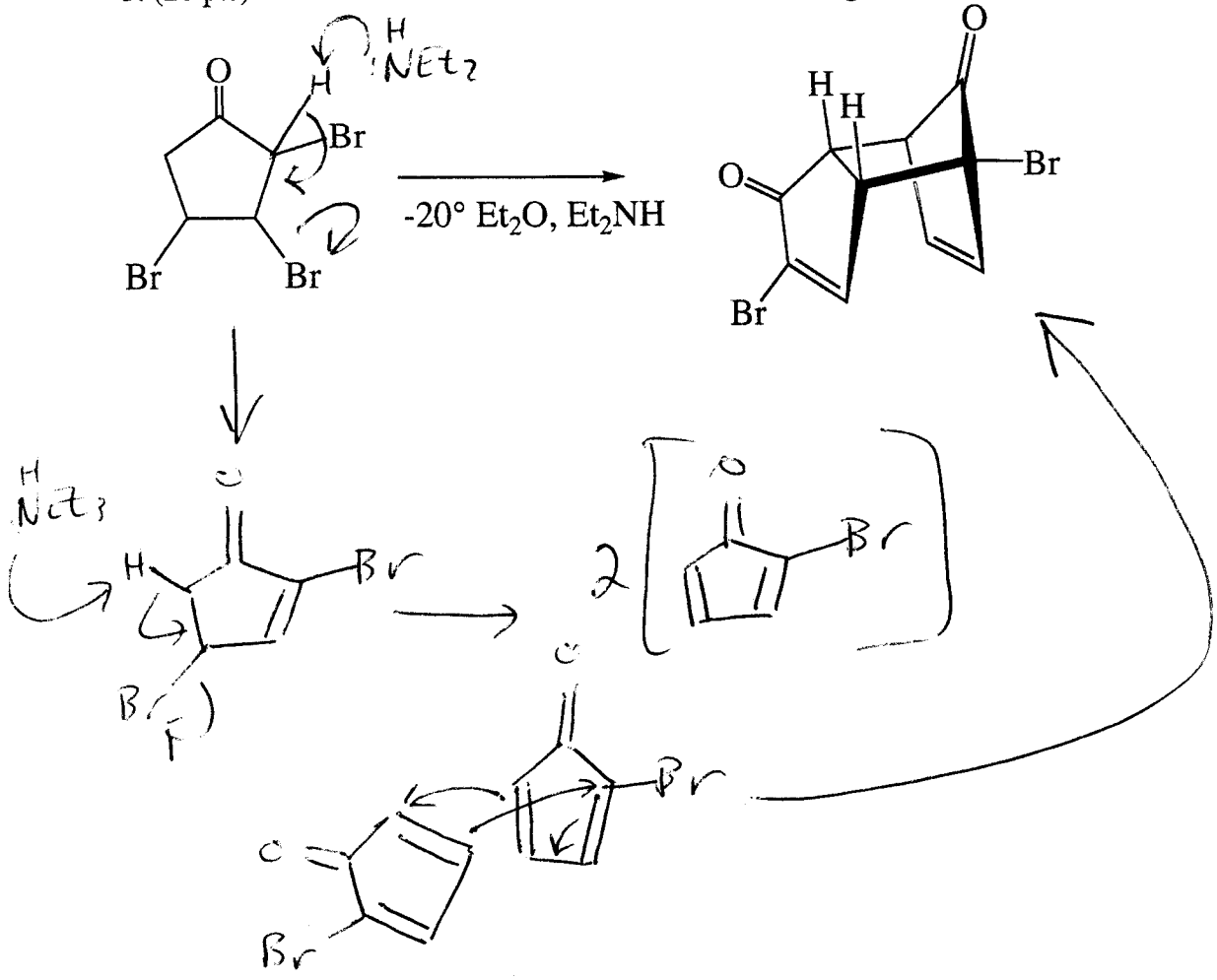
+1 for correct product for each (+2)

+1 for correct faster RXn (+4)

+2 for correct NR explanation (+2)

+15

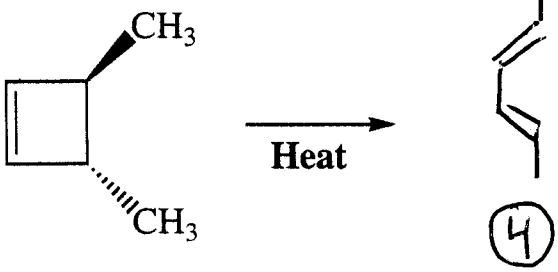
3. (20 pts) Provide a detailed mechanism for the following transformation.



12 pts. for 2 eliminations
(-4) for using Et_2O as base
(-2) when 2 E2 were in 1 step

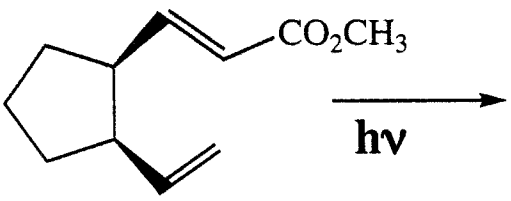
8 pts. for Diels-Alder

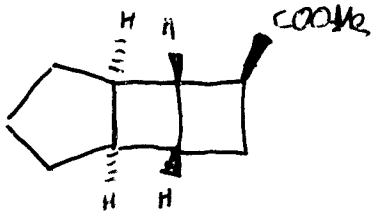
4. (40 pts) Provide the products for the following reactions. Show all major products and stereoisomers.



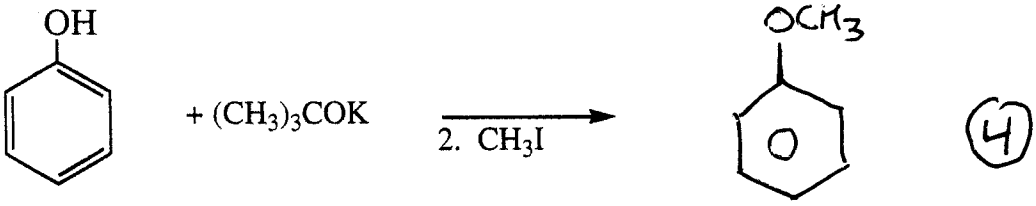
(4)

- ALSO OKAY TO SHOW ONLY IF MINOR
- WRONG CIS/TRANS: (-2)
- WRONG MAJOR/MINOR (-2)

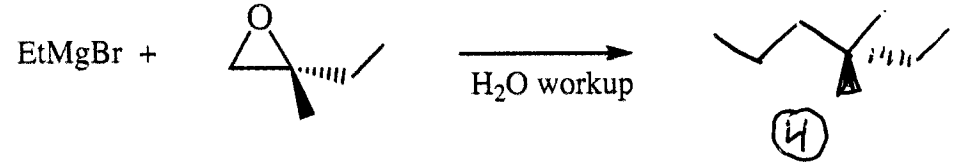




FULL (4)
WRONG STEREO CHEM: (-2) PER RELATION

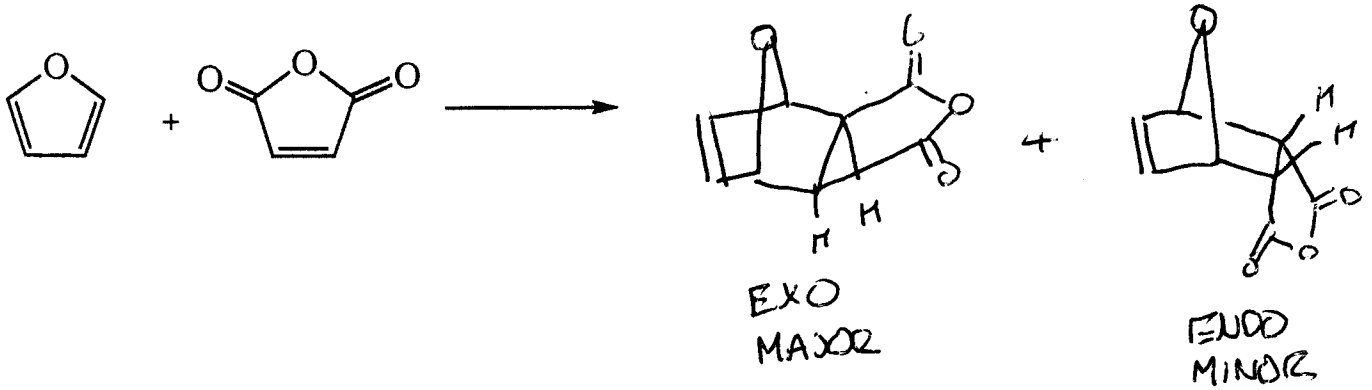


(4)



(4)

- BOTH ENANTIOMERS (0)
- STEREOCHEM WRONG (-2)
- BOTH ATTACKS IFF MENTIONNED MAJOR/MINOR (3)



EXO MAJOR

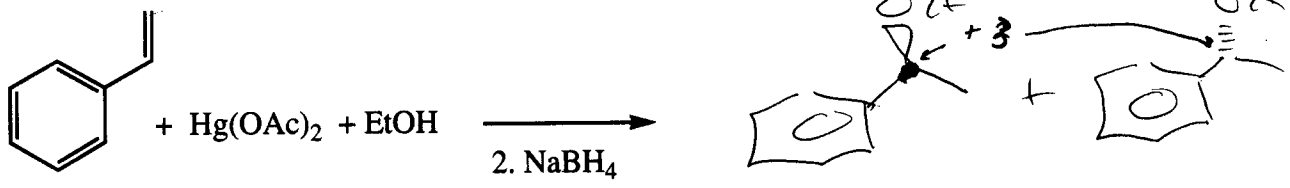
ENDO MINOR

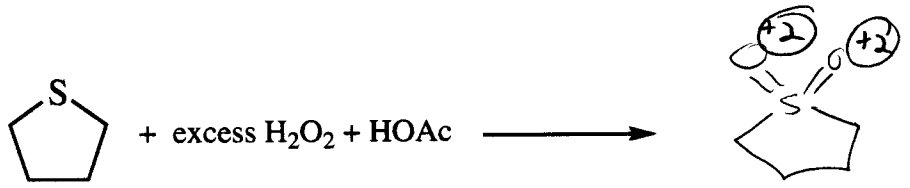
2 ISOMERS (4)

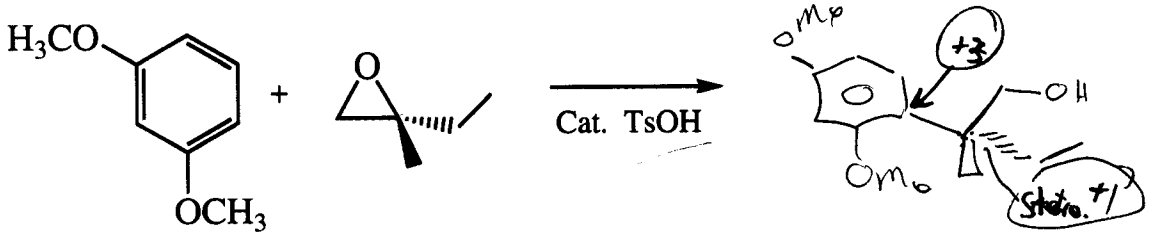
MISSING 1 (2)

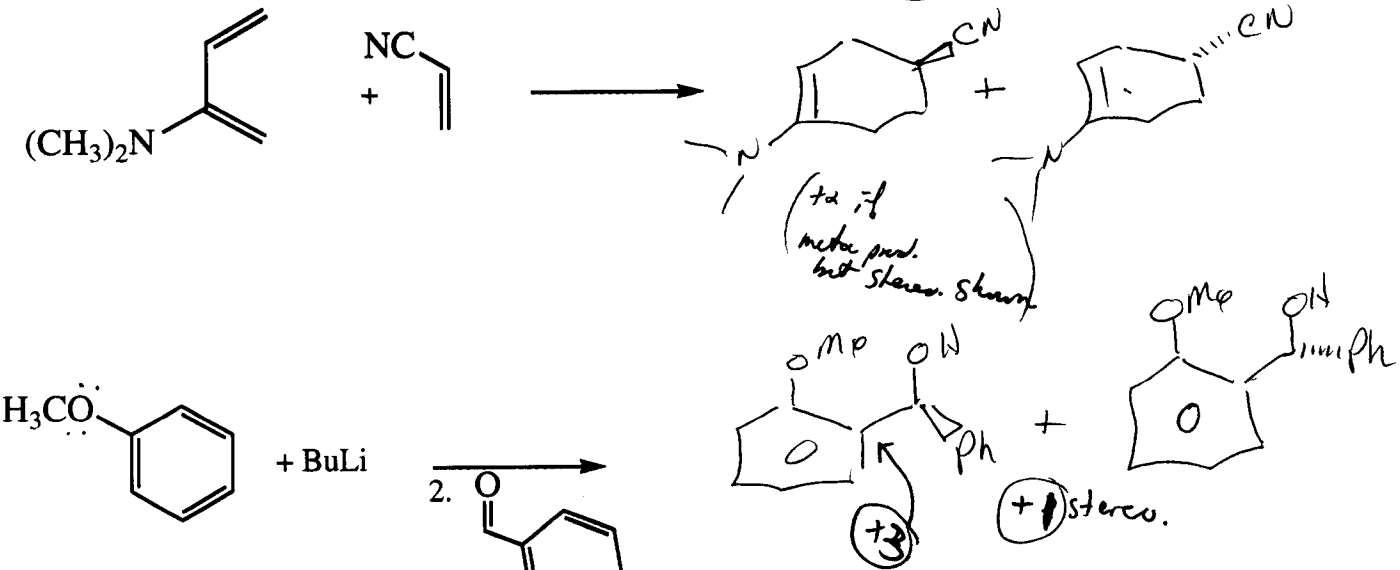
MISSING MAJOR/MINOR: NO PENALTY

Problem 4 continued.

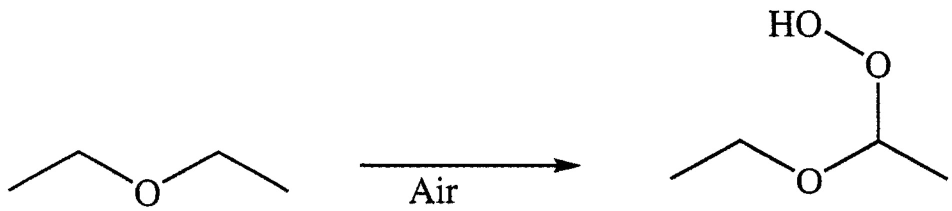




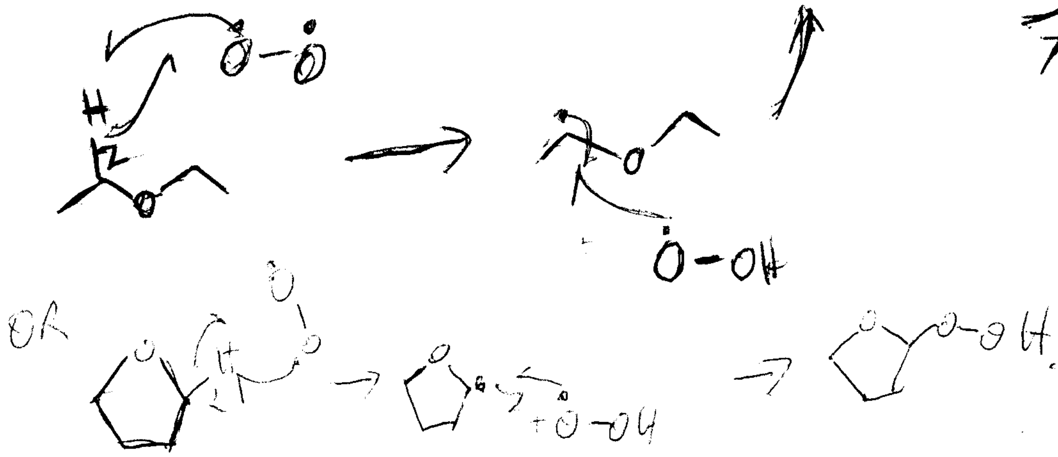


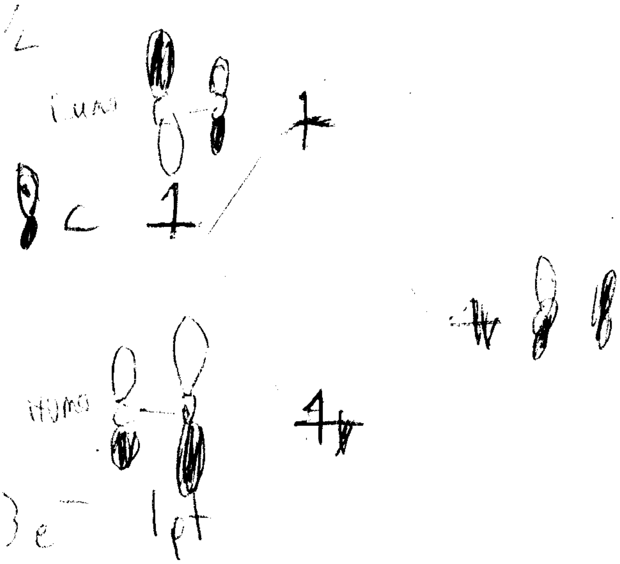


5. (15 pts) Diethyl-ether forms peroxides slowly in the presence oxygen. Give a mechanism and explain using a molecular orbital interaction diagram why the organic radical reactive intermediate in this process is more stable than typical isolated carbon centered radicals.



7 pts





2 stabilized e⁻
1 destabilized e⁻
net stabilization

/8 pts

3e⁻ 1pt

Oxygen lone pair can overlap w/ partially filled p-orbital of carbon to give net stabilization.

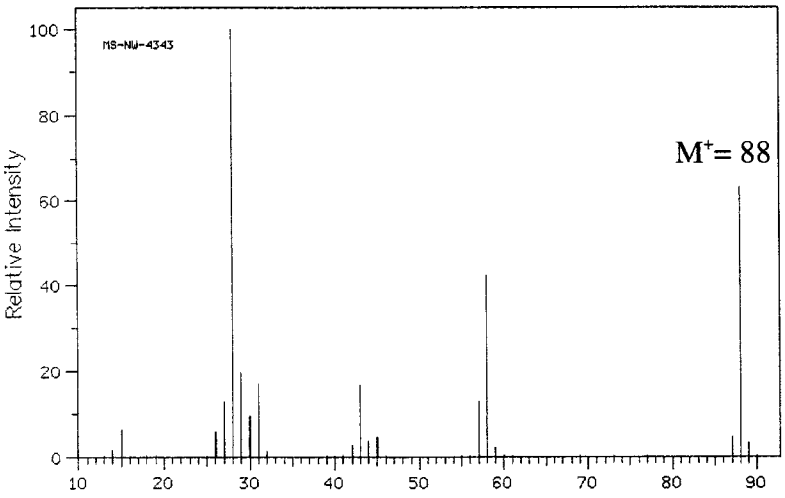
(2 center 3 e⁻ bond)

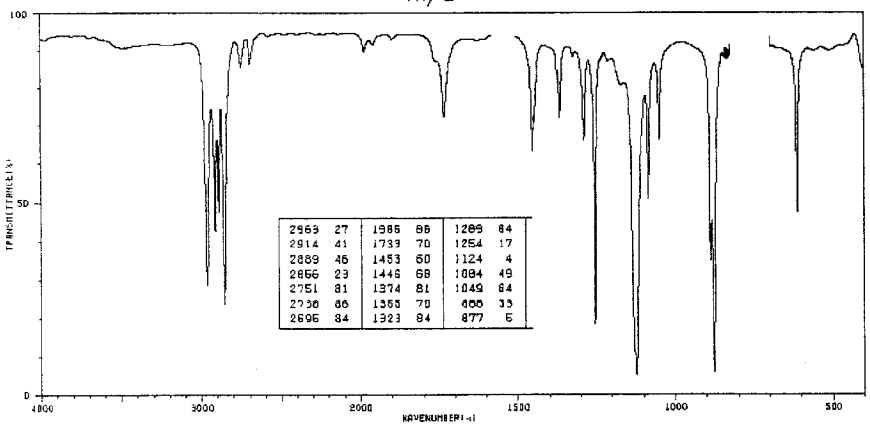
properly drawn HOMO & LUMO 2 pts

explanation up to 3 pts

Extra Credit. (10 pts) A graduate student was attempting to polymerize a solution of ethylene-oxide with catalytic anhydrous acid. However he ran the reaction too dilute and found that his reaction gave molecule **A** rather than polymer. Using the spectroscopic data given identify molecule **A** and provide a detailed mechanistic explanation for its formation.

^{1}H NMR 3.92 ppm (s), ^{13}C NMR 67.15 ppm





2963	27	1986	86	1289	84
2914	41	1733	70	1254	17
2889	46	1453	60	1124	4
2866	23	1446	68	1084	49
2751	81	1374	81	1049	84
2736	66	1365	70	666	33
2696	84	1323	84	877	6

1

+ [redacted] for proper Molecular formula

+2 for recognizing it as a dimer

-1 for wrong arrow

-4 for not acid catalysed

-5 for no mech