Dr. Steven Pedersen March 4, 2013

Chemistry 3B

Midterm 1

Student name: ANSWER KEY

Student signature: ____

Problem 1	_________	(21 pts)
Problem 2(a-d)	_________	(22 pts)
Problem 2(e-h)	_________	(12 pts)
Problem 3	_________	(15 pts)
Problem 4 (a-b)	_________	(16 pts)
Problem 4 (c-d)	_________	(16 pts)
Problem 5	_________	(16 pts)
Problem 6 (a-b)	_________	(16 pts)
Problem 6 (c-e)	_________	(16 pts)
Total Points	__________	(150 pts)

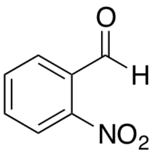
No Calculators Allowed
No Molecular Models Allowed
Be Sure Your Exam has 10 Pages

1 H							2 He
3 Li	4 Be	5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca					35 Br	36 Kr
						53 I	54 Xe

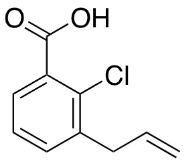
1. (21 pts)

A. Draw a structure for each of the following names. For cycloalkanes use flat rings. For all others use bond-line notation.

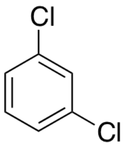
- *ortho*-nitrobenzaldehyde



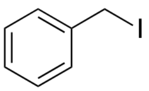
- 2-chloro-3-allylbenzoic acid



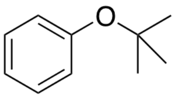
- *meta*-dichlorobenzene



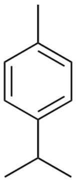
- benzyliodide



- phenyl *tert*-butyl ether

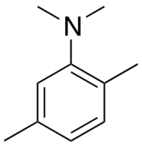


- *para*-isopropyltoluene

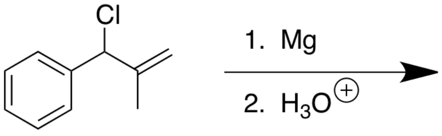


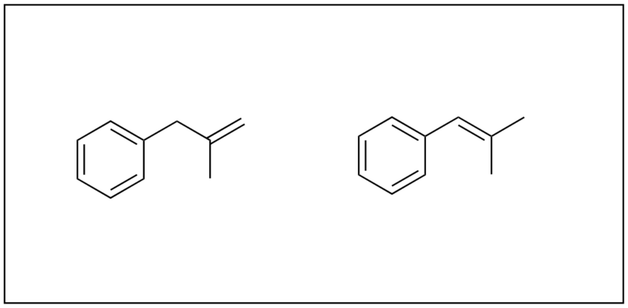
B. Even though we do not yet know the nomenclature associated with amines, we do know what the structure of aniline is. Based on this and your keen intuition, provide the structure of the following compound:

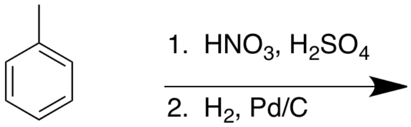
N,*N*,2,5-tetramethylaniline

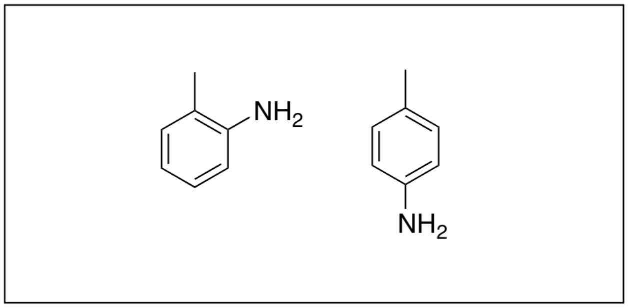


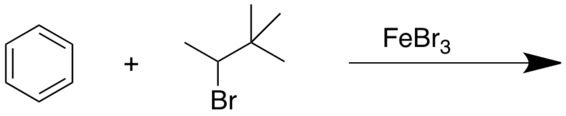
2. Predict the product(s) of the following reactions. Where relevant, show all stereoisomers. Each redundant or wrong answer cancels one correct answer within any given box. (34 pts)

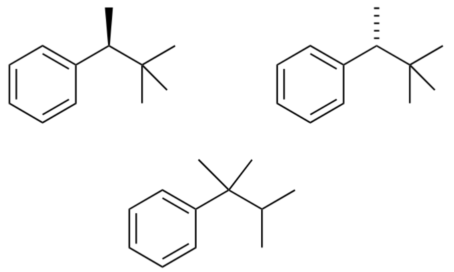




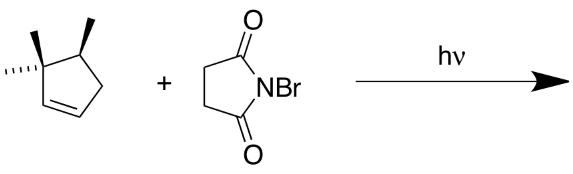




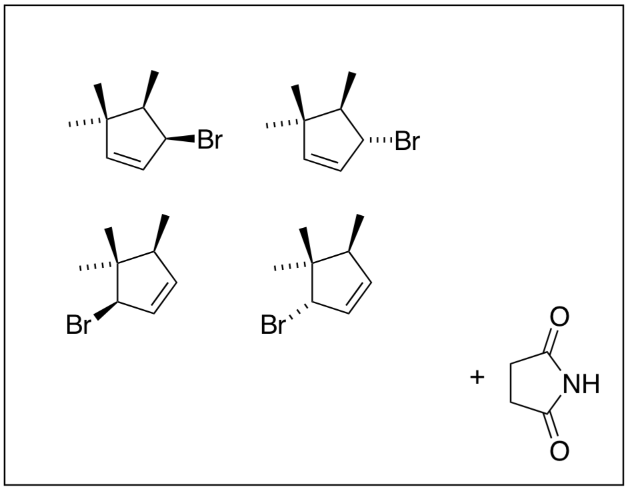


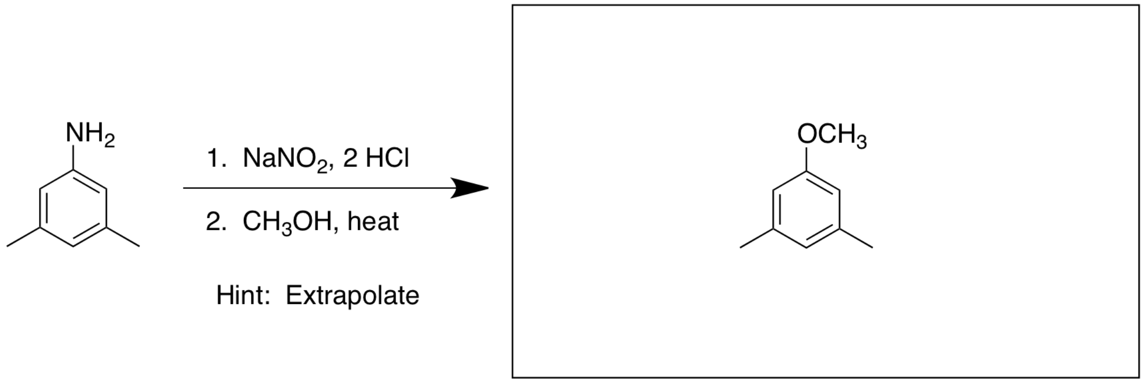


three organic products (one or more of the products is the result of a carbocation rearrangement)

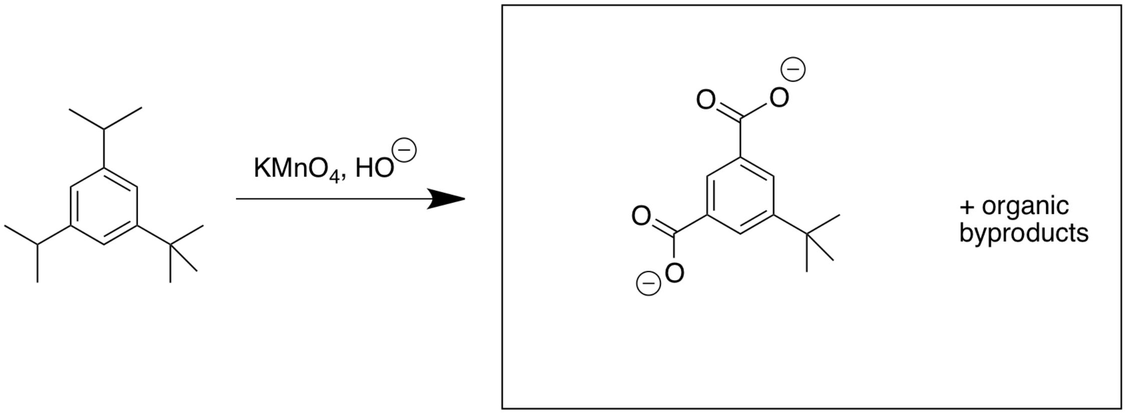


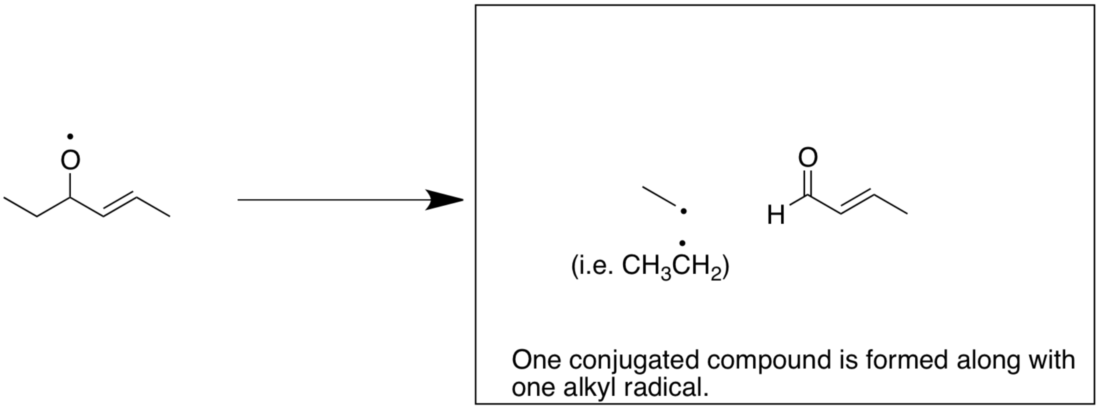
(more problems on the next page)



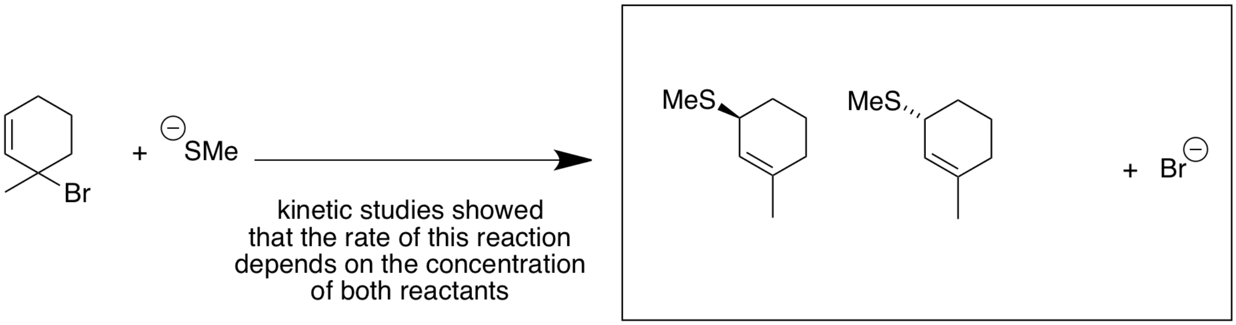


Hint: Extrapolate





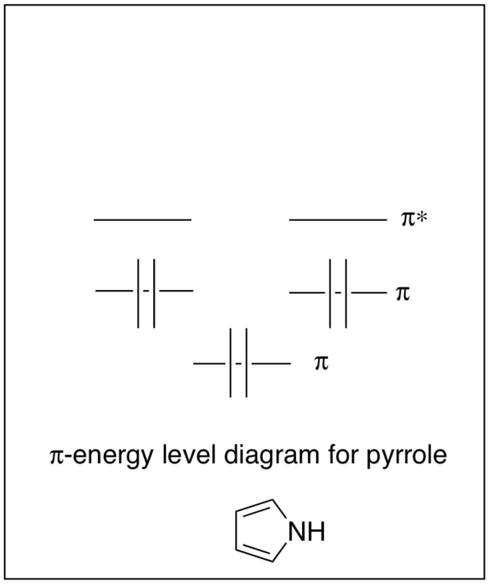
One conjugated compound is formed along with one alkyl radical.



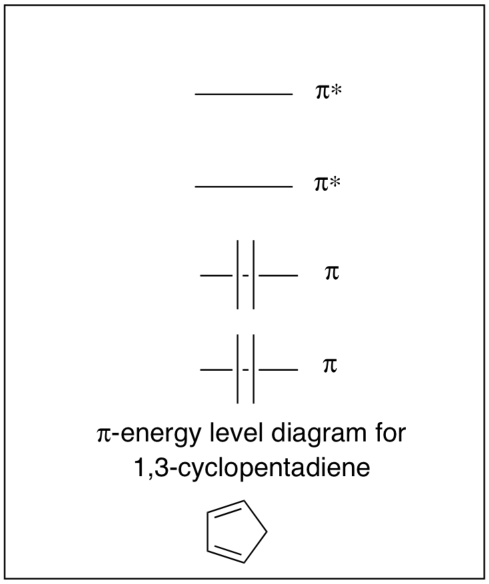
kinetic studies showed that the rate of this reaction depends on the concentration of both reactants

3. (15 pts)

A. Draw the π-energy level diagrams for pyrrole and 1,3-cyclopentadiene. Label each energy level as π -bonding (π), π -antibonding (π *) or non-bonding (NB). Fill in the π -electrons on both diagrams.

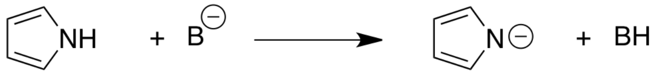


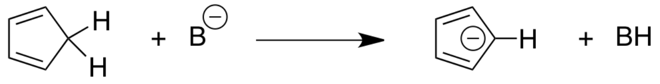
π-energy level diagram for pyrrole



π-energy level diagram for 1,3-cyclopentadiene

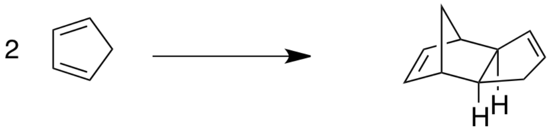
B. The pKa of pyrrole is 23 whereas the pKa of 1,3-cyclopentadiene is 15. Draw the acid-base reaction for each of these compounds (use a generic base B^-). Explain why the pKa of 1,3-cyclopentadiene is lower than pyrrole even though nitrogen is more electronegative than carbon. Use terminology we have discussed in class.

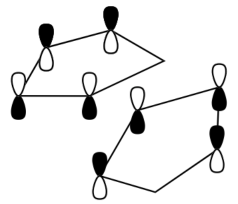




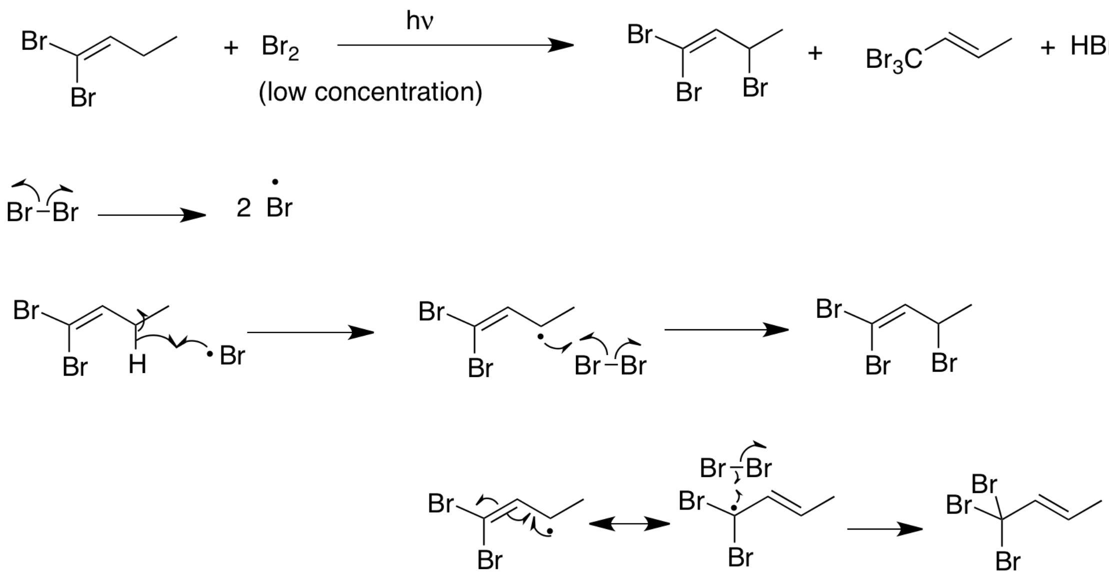
Pyrrole is an aromatic compound. Removing the proton from the nitrogen of pyrrole in an acid-base reaction does not change the aromaticity of pyrrole. 1,3-cyclpentadiene is not aromatic. However, removing one of the protons from 1,3-cyclopentadiene does lead to an aromatic compound. Aromaticity is a favorable state for any molecule and will often lead to unexpected chemistry as seen in the dramatic pKa differences between pyrrole and 1,3-cyclopentadiene, even considering that nitrogen is more electronegative than carbon.

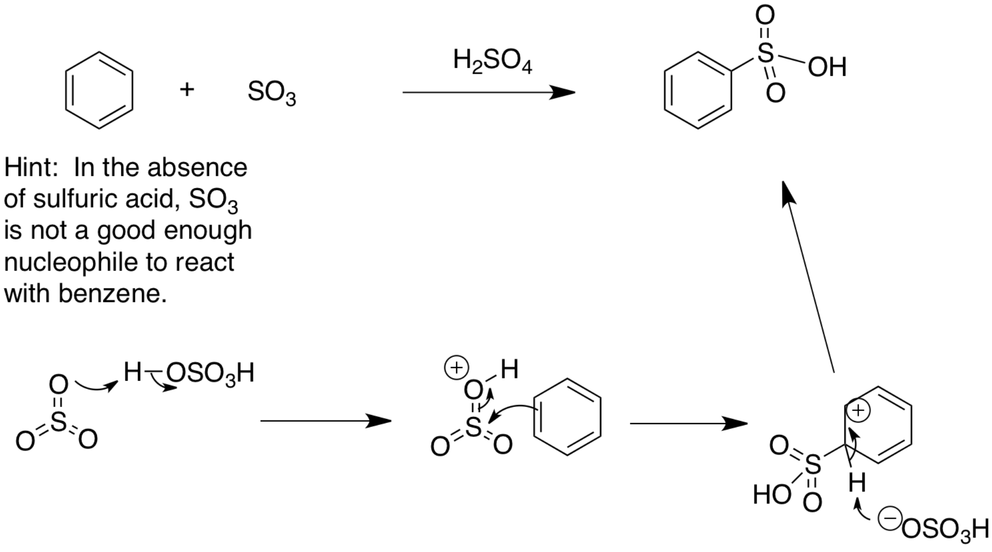
C. Provide a molecular orbital picture that accurately represents the transition state leading to the exact compound shown. Your picture must include orbitals with correct phases.





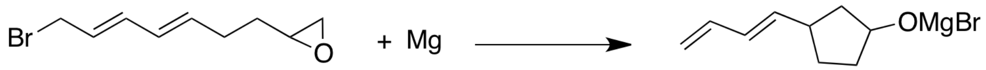
4. Write logical arrow-pushing mechanisms for the following reactions. Be sure that your mechanism accounts for all products shown. (32 pts)



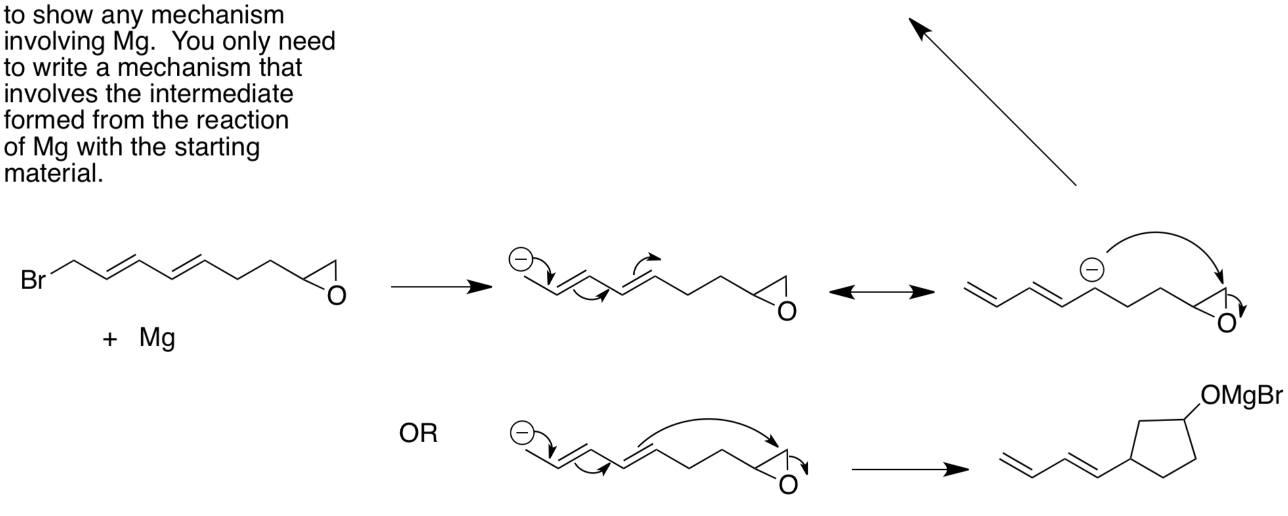


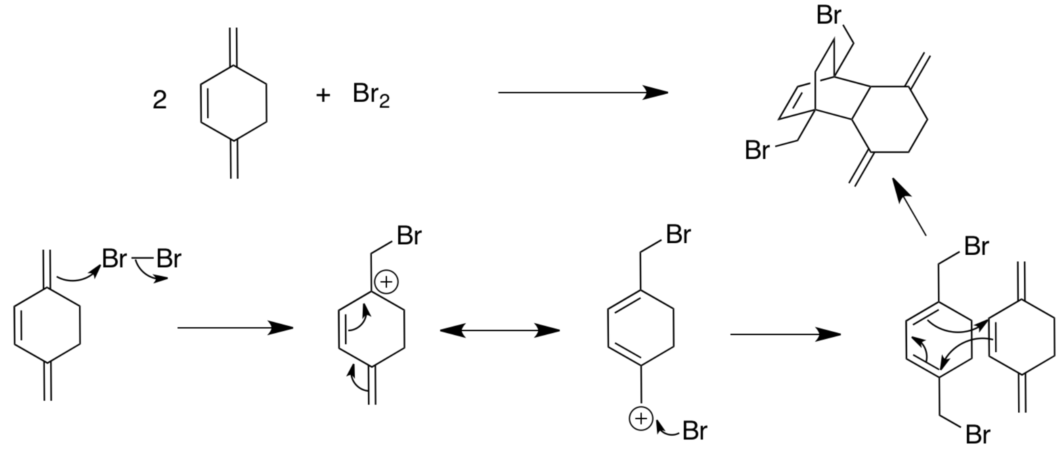
Hint: In the absence of sulfuric acid, SO_3 is not a good enough nucleophile to react with benzene.

More problems on the next page.

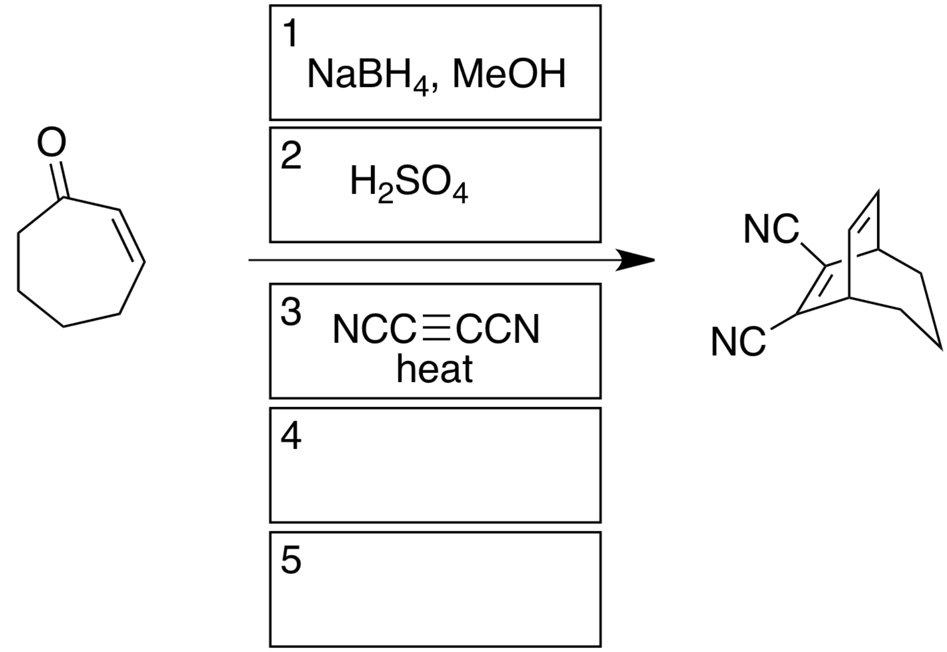


Hint: You do not need to show any mechanism involving Mg. You only need to write a mechanism that involves the intermediate formed from the reaction of Mg with the starting material.





5. Provide the reagents and any other organic compounds necessary to synthesize the indicated product from the starting material shown. For each problem, five boxes are provided in which to place each step of your synthesis. **No synthesis will require more than five steps. However, some or all, may require fewer than five steps.** (16 pts)



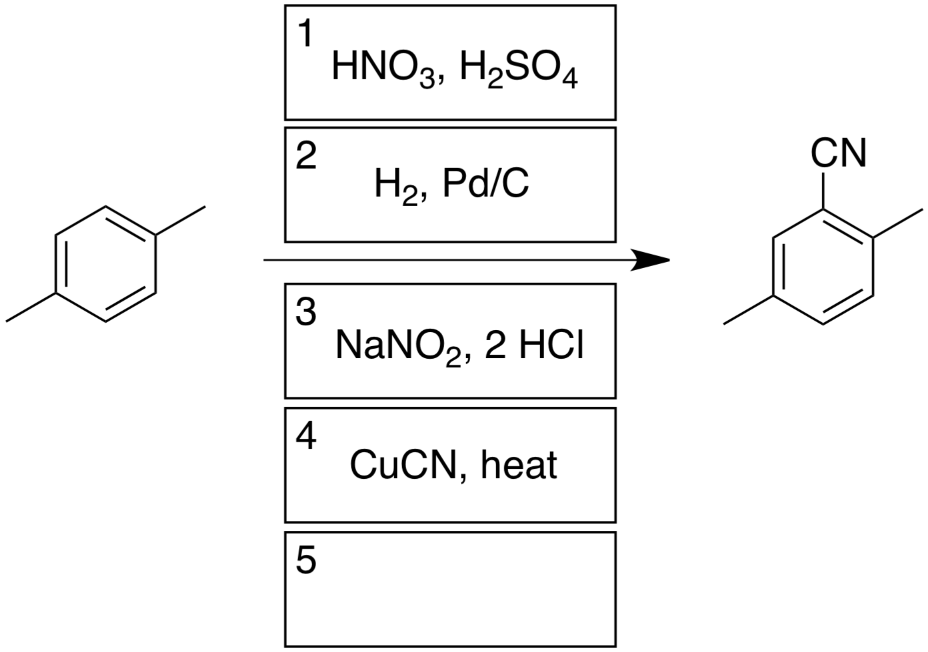
1 $NaBH_4$, MeOH

2 H_2SO_4

3 NCC≡CCN
heat

4

5



1 HNO_3, H_2SO_4

2 H_2, Pd/C

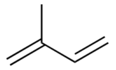
3 $NaNO_2$, 2 HCl

4 CuCN, heat

5

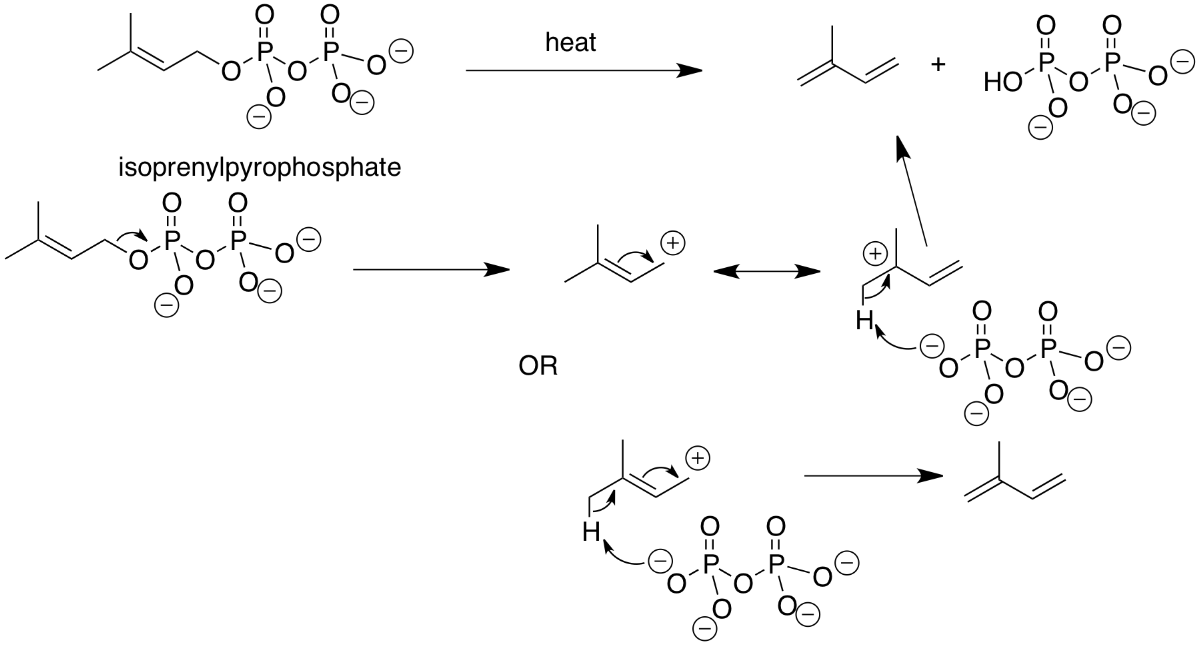
Isoprene, etc.

6. Isoprene is the common name for the naturally occurring diene shown. (32 pts)



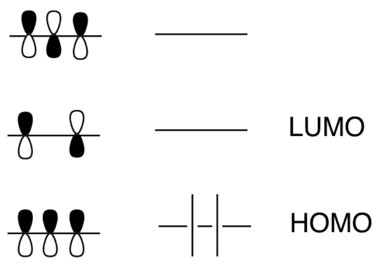
isoprene

A. One biological pathway leading to isoprene starts with isoprenylpyrophosphate. Write a logical arrow-pushing mechanism for the following reaction. Please note that the pyrophosphate ion, $P_2O_7^{4-}$, is a reasonable leaving group. Also, the reaction is NOT concerted.



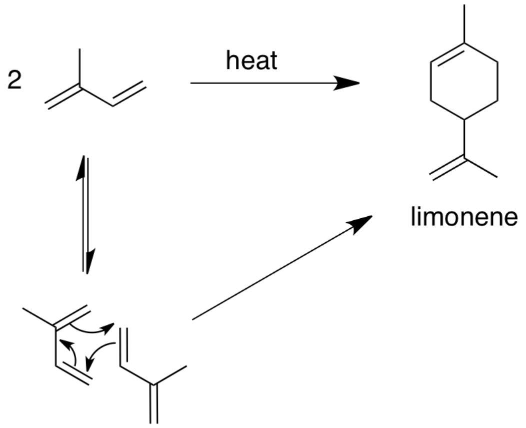
isoprenylpyrophosphate

B. Draw the π-molecular orbital diagram (be sure to show the orbitals) for the allylic cation derived from isoprenylpyrophosphate by loss of the pyrophosphate ion (see Part A for structures). On the diagram include all π-electrons and label the HOMO and LUMO.

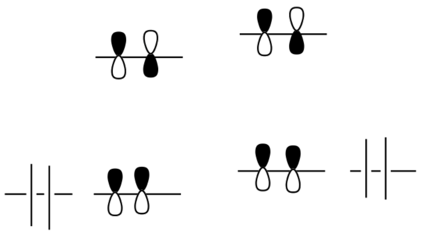


π-molecular orbital diagram of the allylic cation derived from loss of pyrophosphate from isoprenylpyrophosphate.

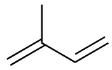
C. Write a logical arrow-pushing mechanism for the formation of limonene from two equivalents of isoprene.



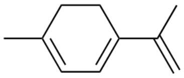
D. Draw the π-molecular orbital diagram for limonene. Be sure to show the orbitals and add the electrons.



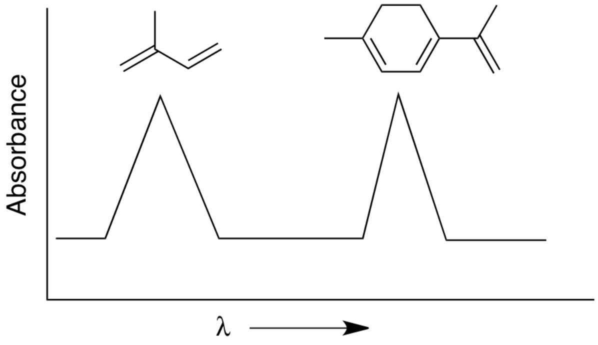
E. The structure of isoprene and a derivative of limonene are shown below. On the blank UV-Spectrum draw where you expect the π to π* of each compound to be relative to one another. Label each peak. Briefly explain why you chose the order you did (no points for a correct spectrum without a correct explanation).



isoprene



limonene derivative



The limonene derivative has six p-orbitals on adjacent carbons whereas isoprene has 4 p-orbitals. The energy gaps between the π and π orbitals of the limonene derivative will be smaller than those in isoprene because the π molecular orbitals of each compound must "fit" into approximately the same energy regime. There will be 4 π–MO's for isoprene and 6 π–MO's for the limonene derivative. Since E is inversely proportional to λ, the smaller the energy gap, the longer the wavelength of light necessary to cause absorption leading to a π to π* transition.*