CHEM 234, Spring 2011		Sec	ond Midterm		Ian R. Gould
PRINTED FIRST NAME	ANSWER	PRINTED LAST NAME	KEY	ASU ID or Posting ID	

Person on your LEFT (or Aisle)		Perso	n on your <b>RIGHT</b> (d	or <b>Aisle</b> )					
	1 nome	en /10		pori2	,				
• PRINT YOUR NAME ON EACH PAGE!	2 peri 1	/20							
• READ THE DIRECTIONS CAREFULLY!	3 rxns								
$\cdot$ USE BLANK PAGES AS SCRATCH PAPER	4 D/A								
work on blank pages will not be graded	·								
•WRITE CLEARLY!	J								
• MOLECULAR MODELS ARE ALLOWED	6 peri								
• DO NOT USE RED INK	7_orbita	<mark>al/18</mark>							
	8 spec	t /24							
• DON'T CHEAT, USE COMMON SENSE!	Extra C	Credit	_/5	Total (incl Extra	)/175+5				
н	-		He	Interaction H	Inergies, kcal/mol				
Li Be	в	сло	F Ne	Eclipsing	Gauche				
Na Mg	Al	Si P S	Cl Ar	H/H ~1.0	Me/Me ~0.9				
K Ca Sc Ti V Cr Mn Fe Co Ni Cu				H/Me ~1.4	Et/Me ~0.95				
				Me/Me ~2.6	i-Pr/Me ~1.1				
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag	-	Sn Sb Te		Me/Et ~2.9	t-Bu/Me ~2.7				
Cs Ba Lu Hf Ta W Re Os Ir Pt Au		Pb Bi Po							
Small range −O−H −C≡N usua	ally	frared Corre	lation Charl		Approximate Coupling Constants, J (Hz), for				
H range of values → broad peak	ng		≻c∕	∖շ∕	<sup>1</sup> H NMR Spectra				
			н <sup>-С</sup> ~ 1	600–1660 N	нн				
				o Ì	-C-C- ~7				
→ =C, → 3300 → H 2720-2820	—c≡	= NI		_ <sup>ë</sup> _					
3000– 2 peaks	$\overline{\Omega}$		0	<u>Ф</u> І    н					
N−н <sup>3100</sup>	220	00		1680	C=C ~10 ~8				
broad with spikes ~3300	0-	≡сн	1735	₽U	н ~				
О-н	 ひ		0	1600	С=С́_~2 н,				
broad ~3300	220		<b>1</b>						
 broad ~3000			1710	$\left  \frac{\nabla}{1650} - \frac{C}{NR_2} \right  $	C=C ~15 H				
L. 4.	500	2000		1500	/ `н				
amine R-NH <sub>2</sub> variable and condition NMR Correlation Charts -OCH <sub>2</sub> - 0									
alcohol R-OH dependent, ca. 2 - 6 δ			H		3				
O . Aromatic	∶Ar—H				·				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $									
				UH₂ −C≣CH	$3^{Y} > 2^{Y} > 1^{Y}$				
$(\delta, ppm)  \frac{11}{220}  \frac{10}{0}  \frac{9}{200}  \frac{8}{180}  \frac{160}{160}$	7	6	5	4 3	<u>2 1 0</u>				
B-C≣N −OCH₂−									
$\begin{array}{c c c c c c c c c c c c c c c c c c c $									
		0-012			<u>-x</u>				
Aromatic C-NR <sub>2</sub>									
		•		'	•				

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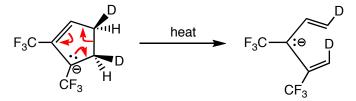
NAME

Question 1 (10 pts.) Give the IUPAC name for the following compound. Be sure to use cis/trans, E/Z or R/S where appropriate.

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Question 2 (20 pts) In this question you will be determining whether the provided reaction is allowed or forbidden



a) give the curved arrow-pushing that describes the bond-making and bond breaking

b) does the REACTION SHOWN, proceed via a conrotatory or disrotatory ring-opening? answer <u>conrotatory</u>

c) how many electrons are involved in the transition state for the provided reaction? answer  $\frac{6}{2}$ 

d) Give a justification for whether the REACTION SHOWN is allowed or forbidden. Your answer must include the following terms: Huckel and/or Mobius, conrotatory and/or disrotatory, aromatic, low energy and high energy transition state

the reaction shown has 6 electrons and proceeds via conrotatory ring-opening, which has a high energy Mobius transition state compared to the corresponding disrotatory transition state, which would be Huckel and aromatic, the reaction is thus forbidden

Extra Credit Question (5 pts.) Which important type of biological molecule has this cis-enediyne been shown to damage?





proteins

lipids

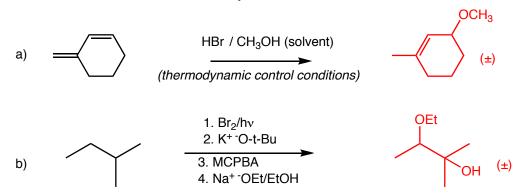
carbohydrates

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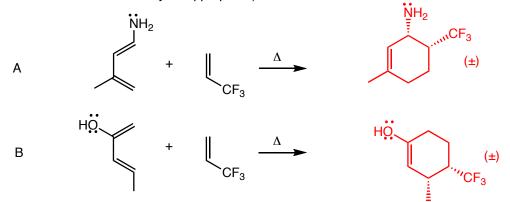
Question 3 (16 pts) Give the major organic products of the following reactions, indicate both the **relative** and the **absolute** stereochemistry.

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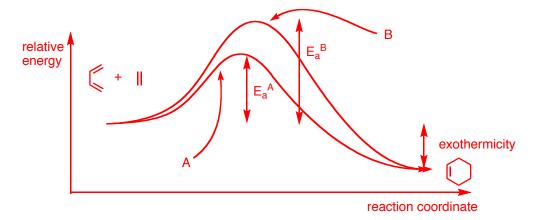


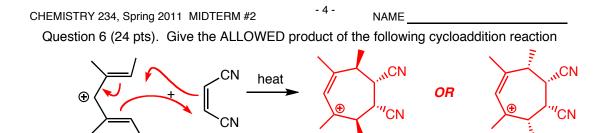
Question 4 (23 pts)

a) Give the products of the following two Diels-Alder reactions (be sure to specify both absolute and relative stereochemistry as appropriate).



 b) Draw a reation energy diagram for these two reactions, clearly indicating which diagram refers to reaction A and which to reaction B. Clealy indicate the activation energy for the reactions A and B. Assume both reactions have similar exothermicities, indicate the exothermicity.



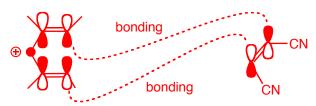


a) Give the curved arrow-pushing that describes the bond-making and breaking.

В

b) Redraw the cation **A** and give a pictorial representation of the wavefunction of the HOMO ON TOP OF THE STRUCTURE

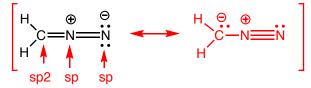
c) Redraw the dicyanoethylene **B** and give a pictorial representation of the wavefunction of the LUMO ON TOP OF THE STRUCTURE



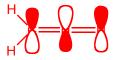
d) Give a brief justification for the structures of your allowed product, you must include the following terms in your justification: suprafacial and/or antarafacial, HOMO, LUMO, bonding and/or anti-bonding

the ALLOWED product of the reaction must have two bonding interactions in the transition state, consideration of the wavefunctions of the HOMO and the LUMO indicates that suprafacial/suprafacial reaction is allowed, thus the 2 -CN groups start cisand are on the same side in the product, and the two Me-groups on the outside of the cation end on the same side in the product

Question 7 (18 pts). For the provided structure: a) Give all reasonable resonance contributors and indicate the hybridization of the carbon and BOTH nitrogen atoms



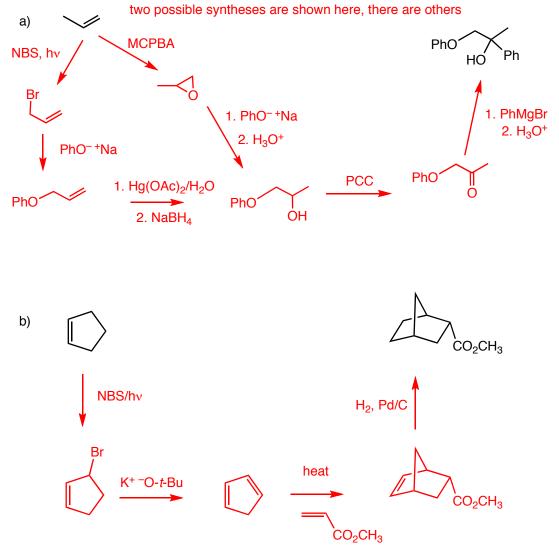
b) Redraw the structure and draw a schematic representation of the wavefunction of the LUMO on TOP of your re-drawing of the structure



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Question 5 (40 pts.) Show how you would make the target componds on the right from the starting compounds on the left. Show reagents and conditions where appropriate, and the structures of important intermediate compounds. Do not show any (arrow pushing) mechanisms.



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Question 8 (24 pts.) Provided are spectra for a compound with molecular formula C10H14

