CHEM 14D Midterm 2
November 19, 2018

Full Name on Every Page* *Write Dark* *Only front pages will be scanned

Name (Last) (First) **Student ID**

Lecture _____

Question	1	2	3	4	5	**FULL Name on every page**	Total
Points	12	20	25	20	21	2	100

1. **Write your full name on every page.**
2. **Answers written on the back of the exam will not be graded.**
3. **This is a closed book exam. The use of notes, cell phones, calculators, or other devices will not be allowed during exam.**
4. **Where applicable, answers without a clear indication of stereochemistry will not be given any credit.**
5. **You may use model sets brought in a clear ziplock bag.**
6. **For full credit show your work, partial credit will be awarded.**
7. **A periodic table will be provided to you.**
8. **Show your student ID when turning in your exam.**

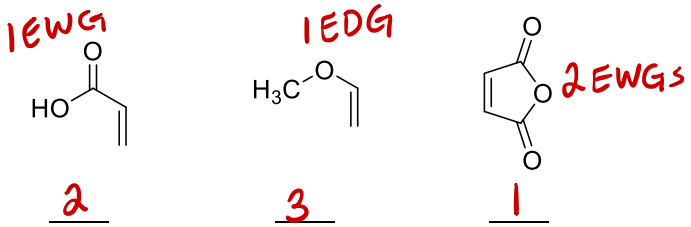
1.1. (3 points) Circle the option that best completes the sentence.

Reacting an alkyne with 2 equivalents of HCl gives a (**vicinal** / **geminal**) dichloride. 1pt.

Alkenes typically undergo (**addition** / **elimination**) reactions with electrophiles. 1pt.

Markovnikov's rule can be used to describe (**stereo-** / **regio-**) selectivity. 1 pt.

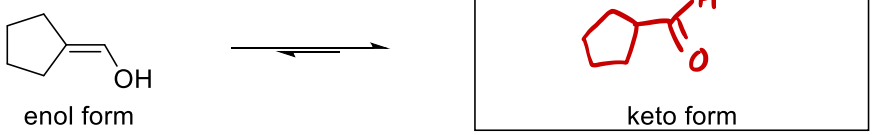
1.2. (3 points) Rank the following dienophiles in order of reactivity in a Diels-Alder reaction. (1 = most reactive)



2 3 1

+3 pts all or nothing

1.3. (3 points) Show the product of tautomerization of the following enol to its keto form.



+3 pts all or nothing

1.4. (3 points) Circle true or false for the following statements:

Reacting OsO_4 with an alkene adds two –OH groups with anti addition.

True or **False** (syn

The pKa of an alkyne is 25.

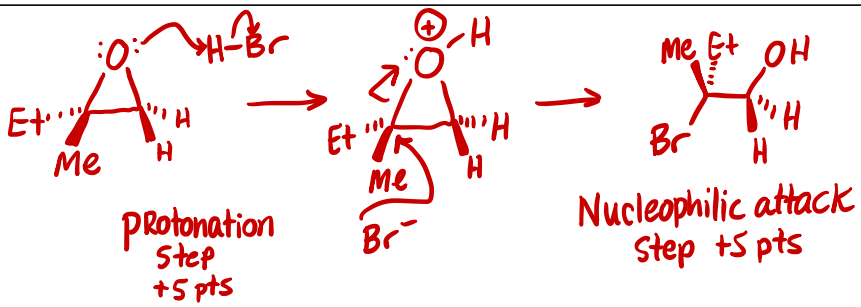
True or **False**

Epoxides are attacked by Me-Li at the most-substituted carbon.

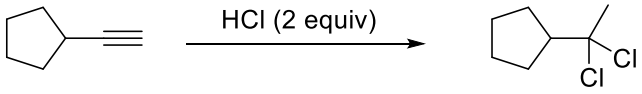
less↑

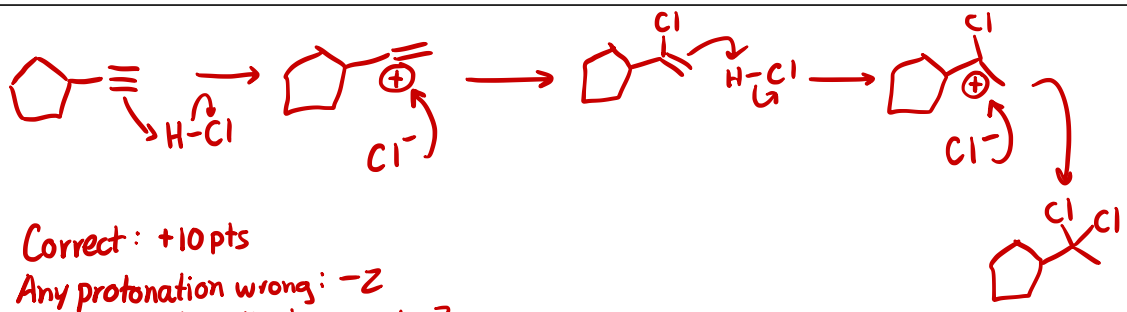
True or **False**

2.1. (20 points) For each part, provide a detailed arrow-pushing reaction mechanism for the reaction shown.



Any formal charge error: -2
Any missing/extra carbon: -2
Stereochem error: -2

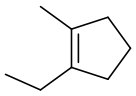




Correct: +10 pts
Any protonation wrong: -2
Any nucleophilic attack wrong: -2
Any missing carbocation: -3
Any other formal charge error: -2
Any extra/missing carbon: -2

3.1. (25 points) Predict the major organic product(s) derived from the substrates shown to the left of the arrow in the following reactions. **If multiple stereoisomers would form, just draw one.**

(a)

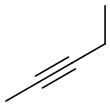


1. O_3, CH_2Cl_2
2. DMS

5 pts.

If C=C bond broken but C=O bonds are in the wrong position or any missing/extra atoms: -3 pts

(b)



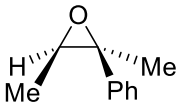
H_2, Pd/C

EtOH

5pts.

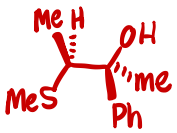
If alkane shown but wrong # of C's -3 pts

(c)



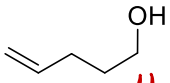
1. NaSMe, DMF
2. H_2O

5pts



If stereochem wrong or ambiguous -3 pts
If wrong regiochemistry -2 pts
Formal charge error -1pt
Any extra/missing C -1pt

(d)



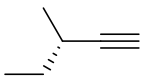
Br_2, CCl_4

Haloether formation
See Practice MT 2.16

5 pts

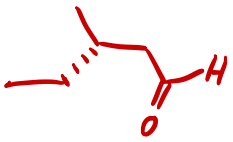
If dibromide shown and no haloether -4 pts
Haloether shown but wrong ring connectivity -3 pts
Haloether shown but non-markovnikov (6 membered ring) -2 pts
Any extra/missing C -1 pt

(e)



1. Cy_2BH, THF
2. H_2O_2, NaOH, H_2O

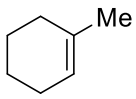
5 pts



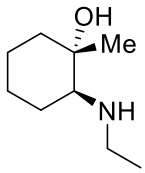
Any extra/missing C -2 pts
Stereochem error -1 pt
No credit if ketone shown!

4.1. (20 points) Predict the missing reagent(s) to accomplish the following transformations.

(a)



4pts
1. mCPBA 2pts
2. NaNHEt (EtNH$_2$ also ok) 2pts
3. H_2O ← No workup after NaNHEt? -1pt.



+ enantiomer

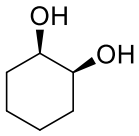
From Syllabus

Did not use separate steps but otherwise correct? -2 pts

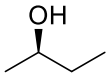
(b)

4 pts
1. OsO_4, THF
2. H_2S

If no H_2S -2 pts
Combined step 1+2 -1 pt

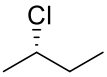


(c)

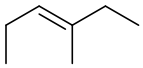


4 pts
$SOCl_2$, Et_3N

Missing Et_3N -1pt
Used H-Cl -2 pts
(wrong stereochem)

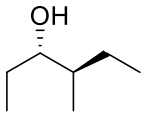


(d)



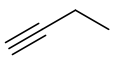
4 pts
1. BH_3, THF +2 pts
2. H_2O_2, NaOH, H_2O +2 pts

No separate steps -1



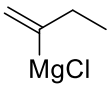
+ enantiomer

(e)

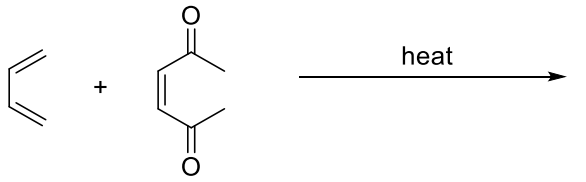


optional
1. H-Cl (1 equiv) 2 pts
2. Mg, Et_2O 2 pts

If said "2 equiv" -1 pt
No separate steps -1pt
Protic solvent w/ Mg -1pt

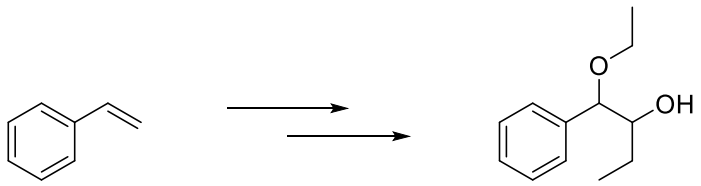


5.1. (6 points) Draw the product of the following Diels-Alder reaction (showing relative stereochemistry).

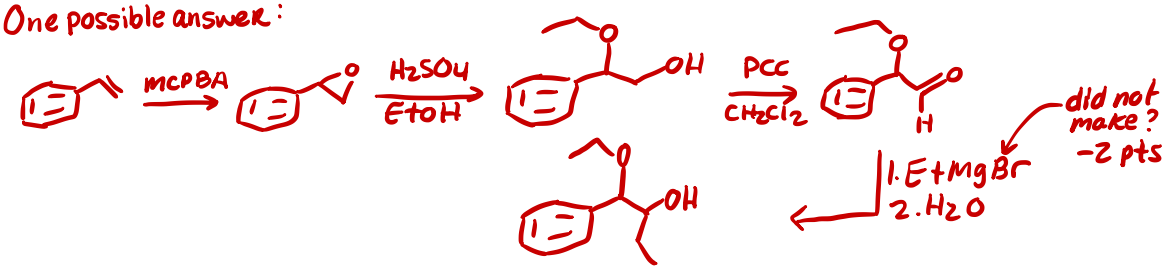


Incorrect stereochem or no stereochem -2 pts

5.2. (15 points) Propose syntheses for the molecule shown from the indicated starting material. You may also use fragments of 2-carbons or less. These fragments may only contain combinations of the following atoms: C, H, O, Br, I, Cl (with single or double bonds). Please be sure to include key reagents and solvents in your solutions, consistent with what you have learned in this course. If you must use an organometallic, show how it's made. It is not necessary to show mechanisms or retrosynthetic analyses in your solutions. Hint: There is often more than one correct answer! **Don't worry about stereochemistry.**



One possible answer:



Mostly correct, but minor issue (e.g. 1 missing/wrong reagent but intention is clear and otherwise correct.) -3 pts

Partial Plan to product (e.g. formation of epoxide, Williamson Ether Synth., or haloether synthesis) but overall did not work. -10 pts.

Any use of OsO_4 and then an attempt to react only 1 -OH group -10 pts

At some point, if an aldehyde was made and attacked w/ Et-MgBr or Et-Li +3 pts

Used illegal reagent (more than 3 C's) but overall correct -13 pts.

Any missing workup -2 pts Any formal charge error -1 pt.

Any 1 missing/extra carbon that does not have major impact on plan -1 pt.