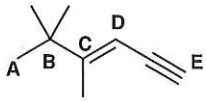
CHEM 108A, Summer 2015 Last Name, First Initial _____

1. Fundamentals

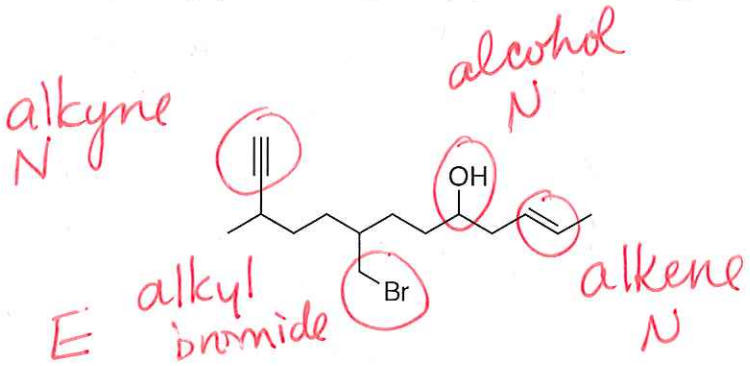
(a) (*15 points*) Consider the structure below and fill in the table to indicate **hybridization, geometry, and substitution pattern for carbons A-E.**



Carbon	Hybridization (sp^3, sp^2, sp)	Geometry (tetrahedral, trigonal planar, or linear)	Substitution (1°, 2°, 3°, or 4°)
A	sp^3	tetrahedral	1°
B	sp^3	tetrahedral	4°
C	sp^2	trigonal planar	3°
D	sp^2	trigonal planar	2°
E	sp	linear	1°

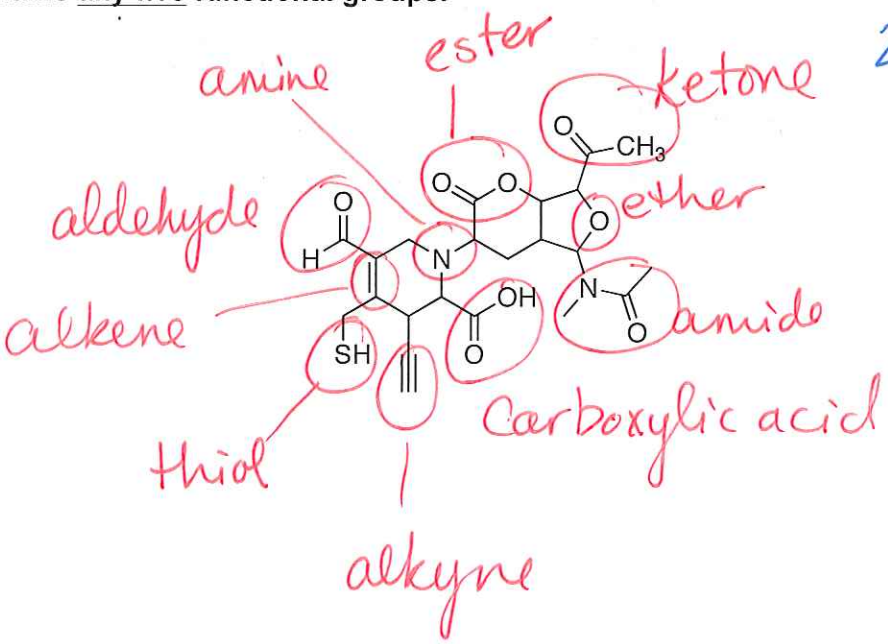
1 pt/box

(b) (*16 points*) **Circle and name each functional group** and indicate whether that functional group is likely to act as a **nucleophile (N) or electrophile (E)** based on the synthesis reactions learned in 108A.



2pts/FG
2pts → N/E

(c) (*10 points*) Consider the large and hopefully familiar molecule below. **Circle and name <u>any five</u> functional groups.**



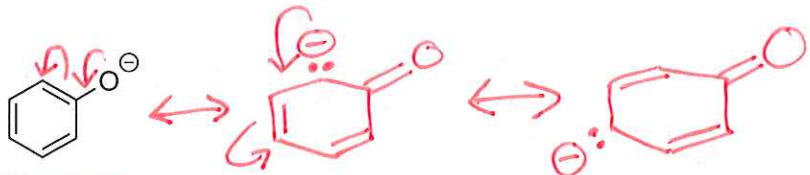
2pts/FG

 41

2. Resonance and Aromaticity More possibilities than below!

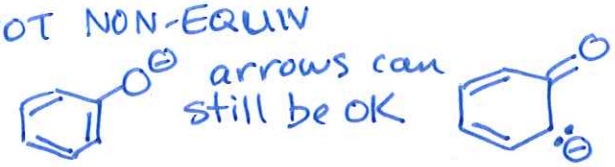
(a) (*36 points*) **Draw two additional non-equivalent resonance structures** for the following compounds. Use **arrow-pushing** to show electron movement from one structure to the next. Be sure to indicate formal charges where appropriate.

(i)



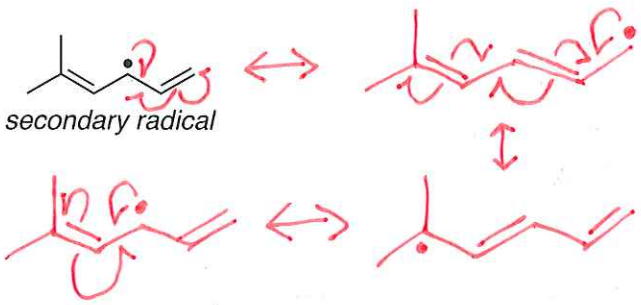
2pts/arrow set
2pts/structure
↓
1pt-charge
1pt-bonds

NOT NON-EQUIV



arrows can still be OK

(ii)

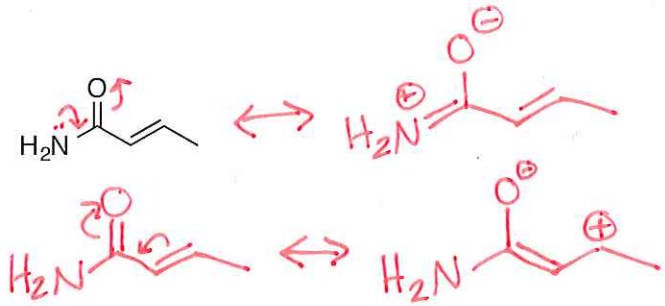


secondary radical

or start over

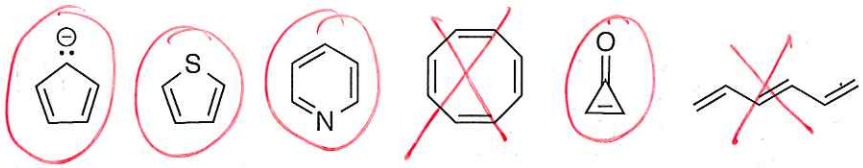
2pts/fishhook arrow set
2pts/structure
↓
1pt-radical
1pt-bonds

(iii)



2pts/fishhook arrow set
2pts/structure
↓
1pt-charges
1pt-bonds

(b) (*12 points*) **Circle all the compounds that are aromatic.**



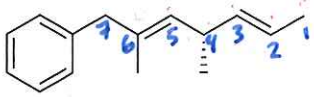
2pts each
-Don't need X, just circle

correct
1pt/#ing

3. Nomenclature

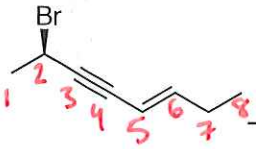
(a) (*15 points*) **Name** the following compounds. **Include stereochemistry** in the name, where appropriate.

7pts **(i)**



(4S, 2E, 5E) — 4,6-Dimethyl-7-phenyl-2,5-heptadiene

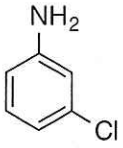
5pts **(ii)**



(2R, 5E) — 2-Bromoocta-3-yn-5-ene

(iii)

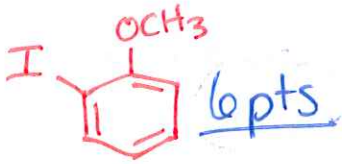
3pts



meta-chloroaniline

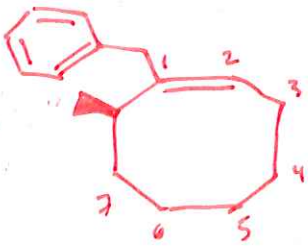
(b) (*28 points*) **Draw structures** corresponding to the following names.

orthoIodo ~~meta~~-Chloroanisole



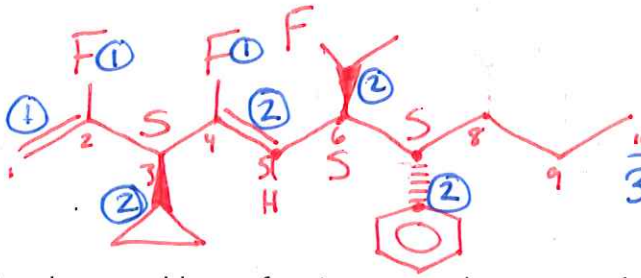
6pts

(8R)- 8-Methyl-1-benzylcyclooctene



8pts

(3*S*,6*S*,7*S*,~~8*R*~~,4*Z*)-
3-Cyclopropyl-2,4-difluoro-6-(1-fluoroethyl)-~~8-(2-fluoro-2-propyl)~~-7-phenyl-1,4-decadiene
Have fun with this one!



3pts (10 c's)

14pts

(c) (*6 points*) The above problem refers to an organic compound with the stereochemistry (3*S*,6*S*,7*S*,~~8*R*~~,4*Z*). **What is the relationship of that compound to the following stereoisomers?**

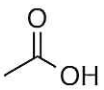
(3*R*,6*S*,7*S*,~~8*R*~~,4*Z*) — diastereomer — 2

(3*R*,6*R*,7*R*,~~8*S*~~,4*E*) (4Z) — enantiomer — 2

(3*S*,6*R*,7*R*,~~8*S*~~,4*Z*) — diastereomer — 2

4. Acid-Base Chemistry

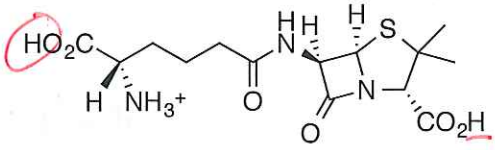
(a) (*8 points*) **List the pKa values** that belong to each compound in the boxes below. 1pt/each

HCl	H_3O^+		NH_4^+	H_2O		NH_3	CH_4
-7	∅	5	10	16	19	35	50

±2 pKa units OK

(b) (*8 points*) **Circle the most acidic proton** on each molecule and **approximate its pKa** (think pKa family).

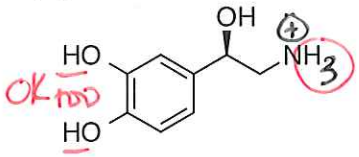
(i)



Isopenicillin N OK too

Approx. pKa 5 actually 2!

(ii)



Norepinephrine

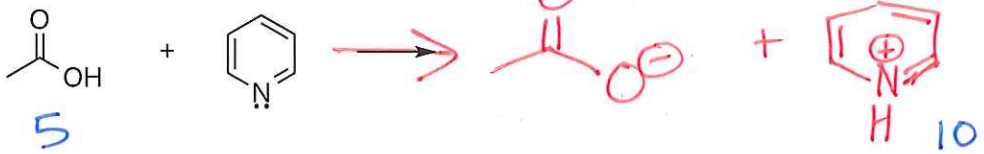
Approx. pKa 10

2pts - (H)
2pts - pKa (±2)

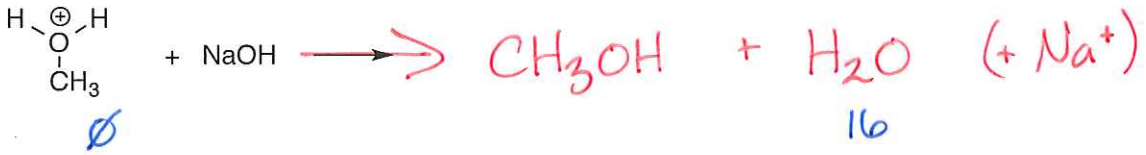
(c) (*18 points*) **Choose any two.** Draw the **products** in the following reactions and indicate the **direction of the equilibrium**. No arrow-pushing necessary.

3 pts/product
↓
1-charge
2-bonds

(i)

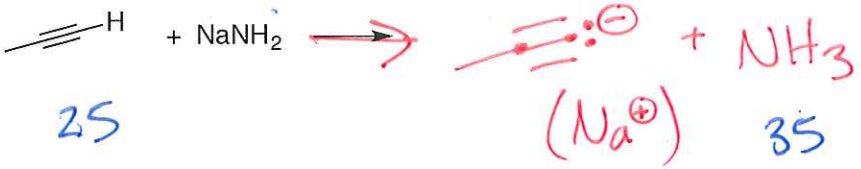


(ii)



3pt → eq=m

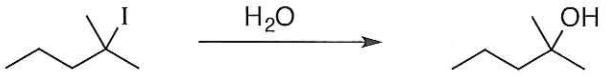
(iii)



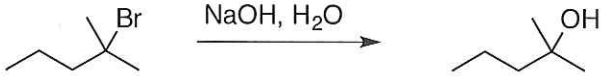
5. Substitution and Elimination Reactions

(a) (*6 points*) Consider the following reactions. **Which reaction is faster?**

Reaction 1



Reaction 2



Reaction 1 or **Reaction 2** or **Neither** (Circle one)

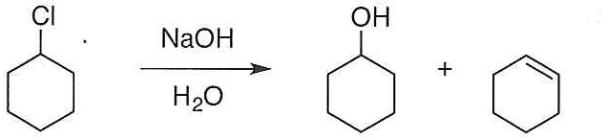
(b) (*14 points*) **Fill in the box** to indicate whether the reaction as written proceeded by **SN1, SN2, E1, or E2.**

2pts/box

(i)

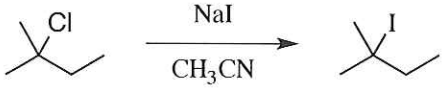
SN2 E2

(ii)



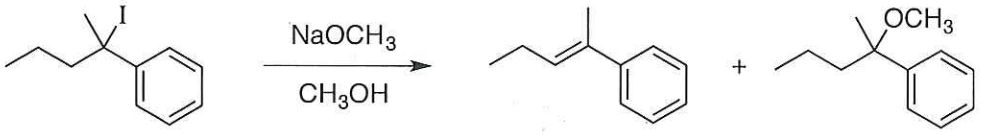
SN1 E2

(iii)



SN1

(iv)

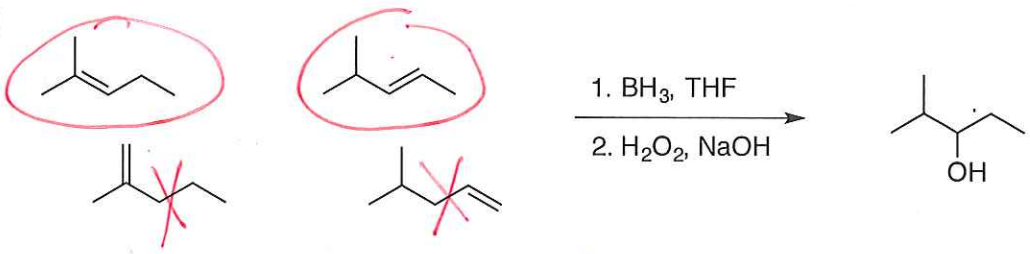


E2 SN1

6. Reaction Puzzles

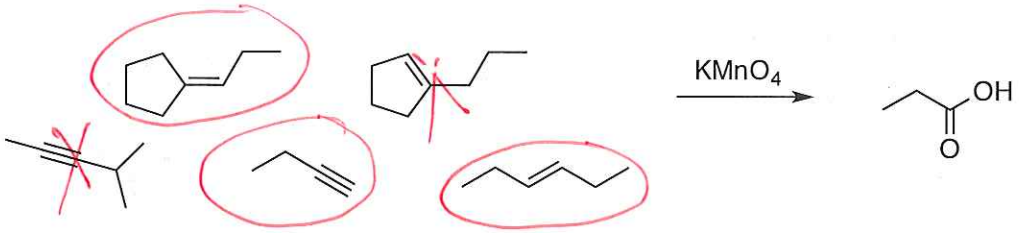
(*18 points*) **Circle each of the starting materials** that could potentially give the indicated compound as one of the products.

(i)

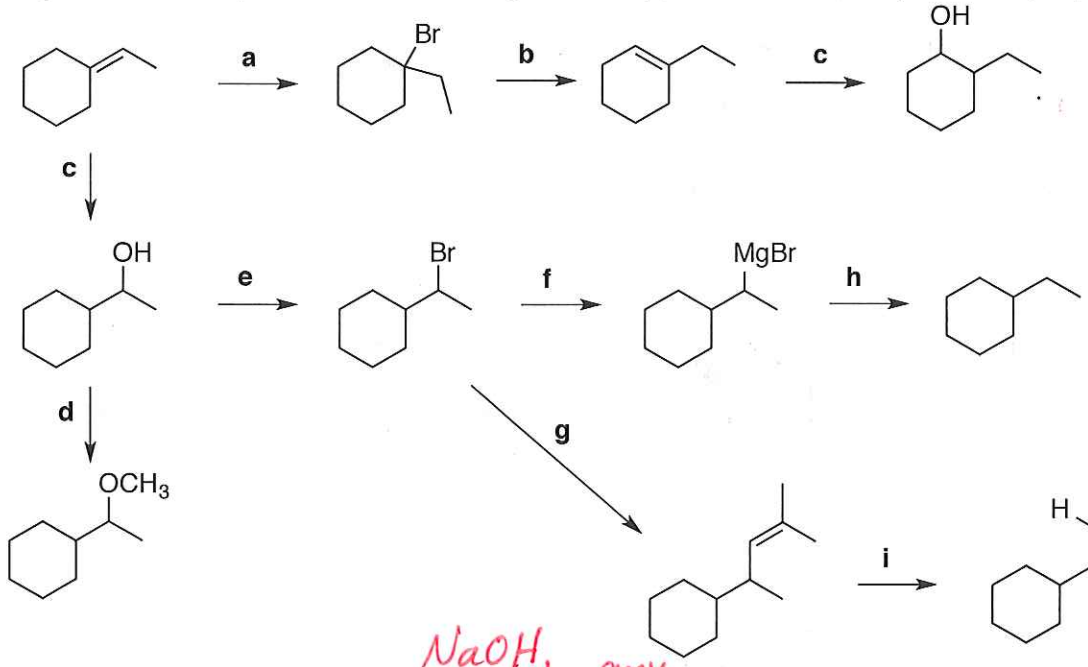


2pts/each - correctly circled or not

(ii)



(*27 points*) Consider the following reaction puzzle and **indicate the reagents** required for each step in the blanks provided below. Reagents "**c**" appears twice in the puzzle on purpose!



3pts/line

a HBr

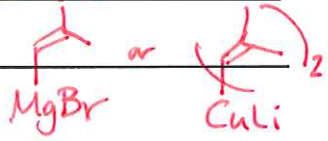
b NaOH, amy tBuOK, any base

c 1. BH_3, THF 2. NaOH, H_2O_2

d CH_3I

e PBr_3 or HBr

f Mg^0, Et_2O or THF

g  $)_2$ (MgBr or CuLi)

h H_2O

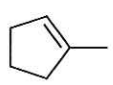
i 1. O_3 2. Zn, H^+

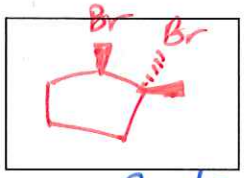
7. Single Step Reactions

(*20 points*) **WHAT'S IN THE BOX??**
Choose any four of the five reactions below and fill in the missing **product**. If no reaction occurs as written, fill in the box with "NR." Put a **large "X"** over the problem you are skipping. Otherwise the first four will be graded. **Indicate stereochemistry** where appropriate.

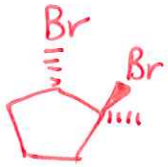
5pts ea.

(a)



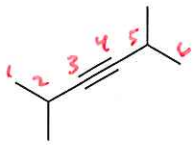


or



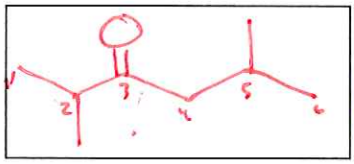
2pts-stereochem (anti)

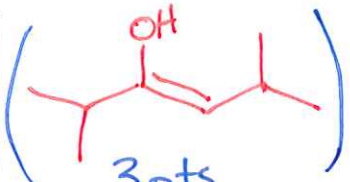
(b)



$HgSO_4$, H_2SO_4

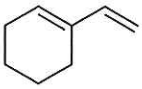
H_2O





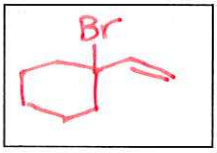
3pts

(c)

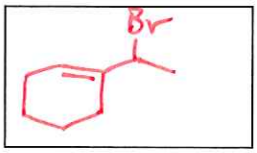


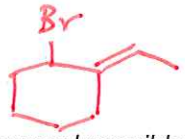
HBr (1 equiv.)

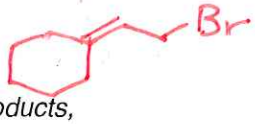
Et_2O



+



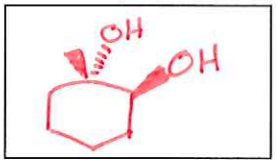




several possible products, draw any two

(d)

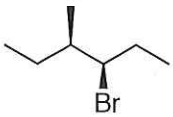
H_3O^+



or

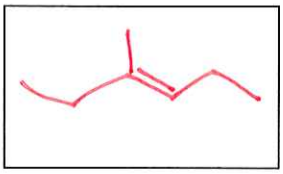
2pts-stereochem (anti)

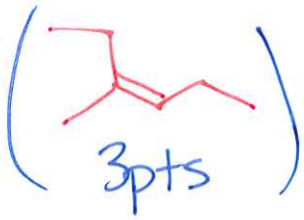
(e)



KO*t*-Bu

t-BuOH





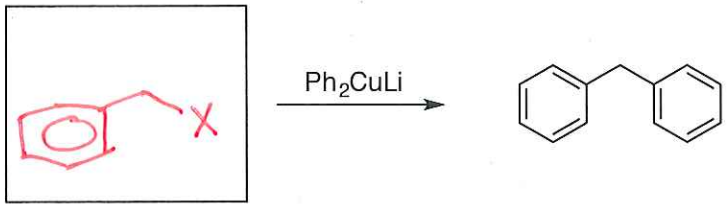
3pts

8. Single-Step Reactions

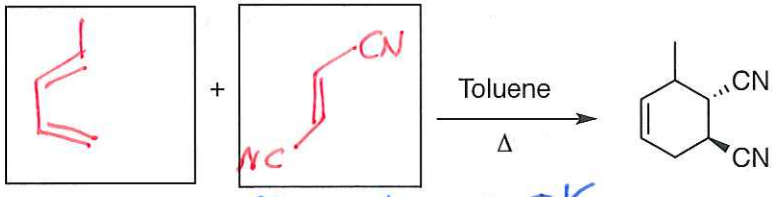
(*20 points*) **WHAT'S IN THE BOX??**
Choose any four of the five reactions below and fill in the missing **reactant**. Put a **large "X"** over the problem you are skipping. Otherwise the first four will be graded. **Indicate stereochemistry** where appropriate.

5pts each

(a)

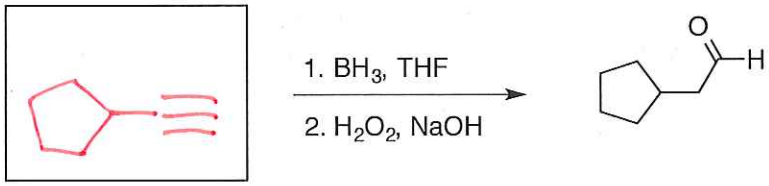


(b)

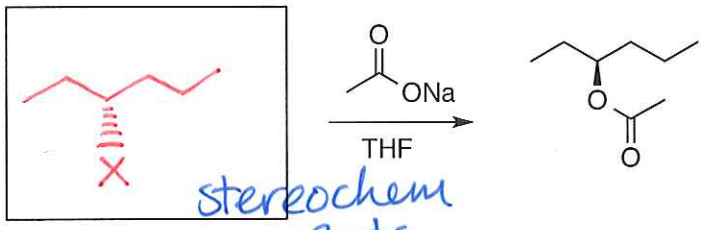


cis or trans OK
↳ should be trans, not discussed
5545

(c)

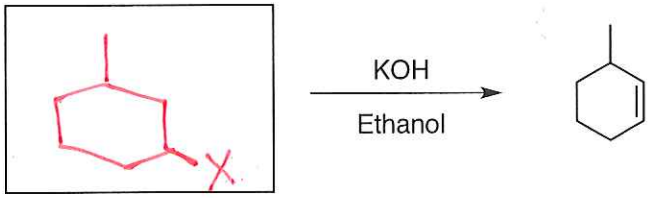


(d)



stereochem
2pts

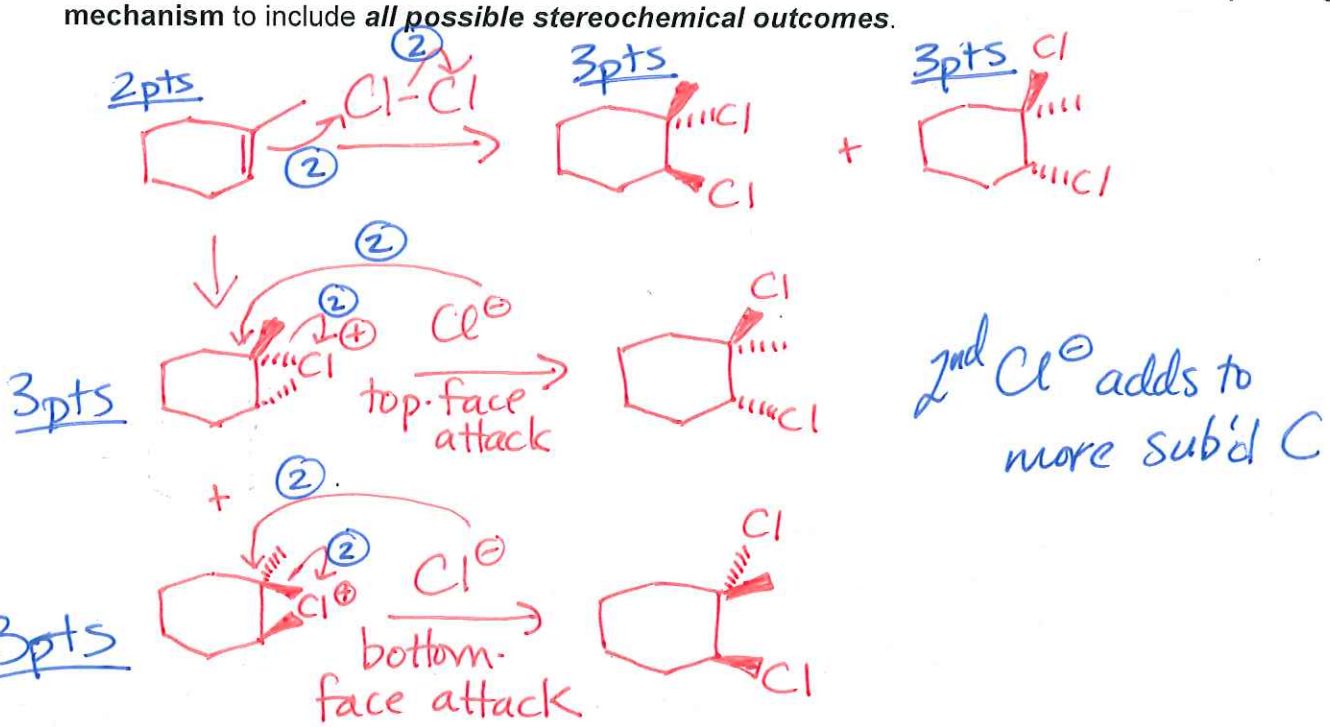
(e)



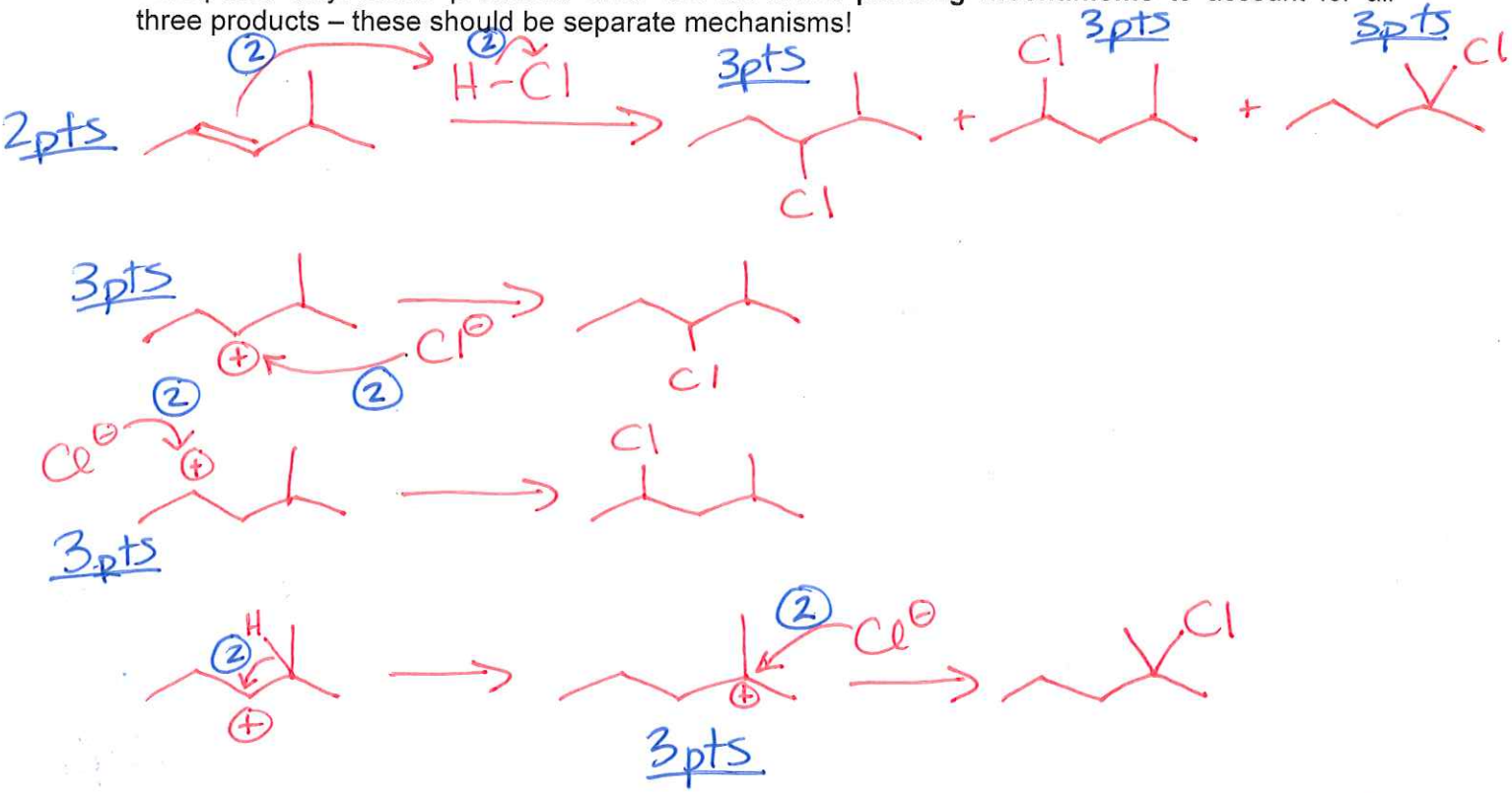
(Br →) 3pts

9. Mechanisms

(*26 points*) Draw the **reaction scheme** (reactants, reagents, and products) for the halogenation of **methylcyclohexene** with molecular chlorine in dichloromethane. Draw the full **arrow-pushing mechanism** to include ***all possible stereochemical outcomes***.

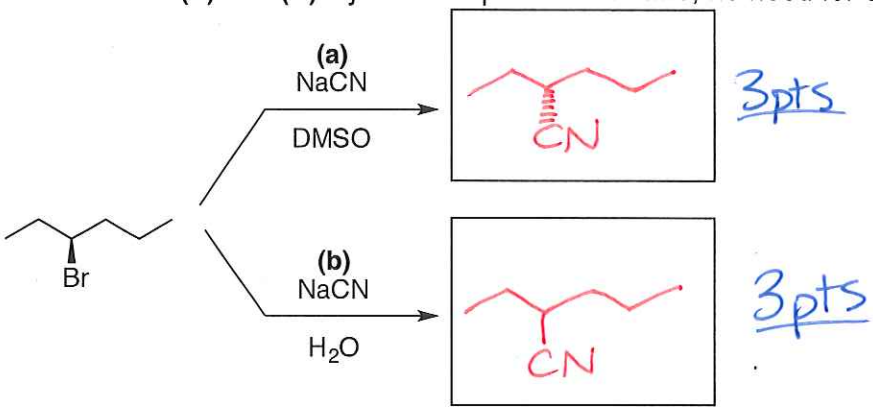


(*32 points*) Draw the **reaction scheme** for the hydrohalogenation of **4-methyl-2-pentene** with hydrochloric acid. This reaction gives an unexpected rearrangement product as a mixture with the anticipated alkyl halide products. Draw the full **arrow-pushing mechanisms** to account for all three products – these should be separate mechanisms!



10. Mechanisms

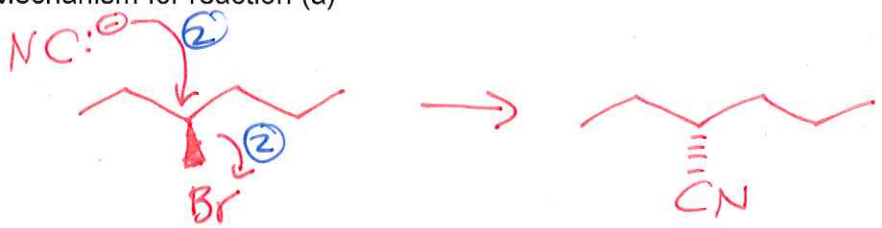
(*23 points*) The stereochemical outcome of substitution reactions can be controlled with the choice of solvent. **Draw the products** in reactions **(a)** and **(b)** below then **draw the full arrow-pushing mechanism** for each reaction in the space provided. Briefly comment on the difference in stereochemistry between reactions **(a)** and **(b)** – just a few phrases are fine, no need for essays!



3pts

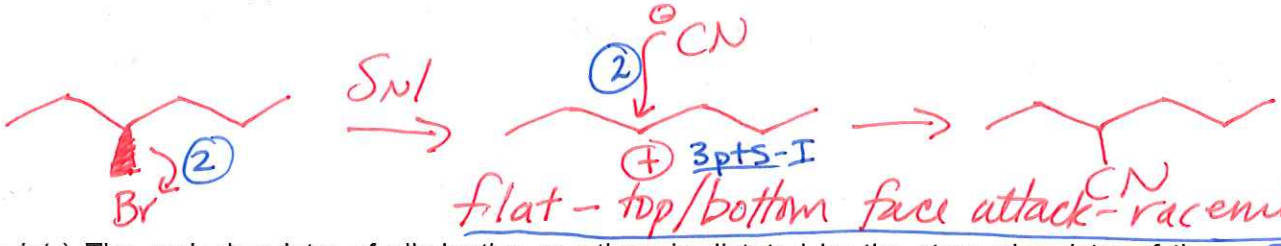
3pts

Mechanism for reaction (a)



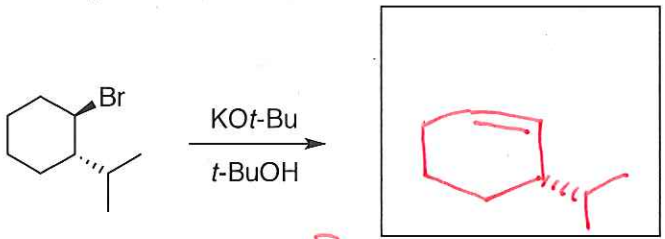
S_N2 - backside attack, single chiral product
3 pts

Mechanism for reaction (b)

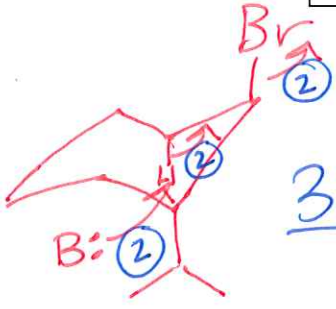


flat - top/bottom face attack - racemic
3pts

(*12 points*) The regiochemistry of elimination reactions is dictated by the stereochemistry of the starting material. Consider the alkyl halide below and its reaction with potassium *tert*-butoxide. There is only one product in this reaction and it is slightly unexpected, unless you understand the 3D-nature of the mechanism. Draw the alkyl halide in the proper **chair conformation** to facilitate the elimination mechanism (not necessarily the most stable conformation), **add arrows** to show the mechanism, and **draw the product**.



3pts

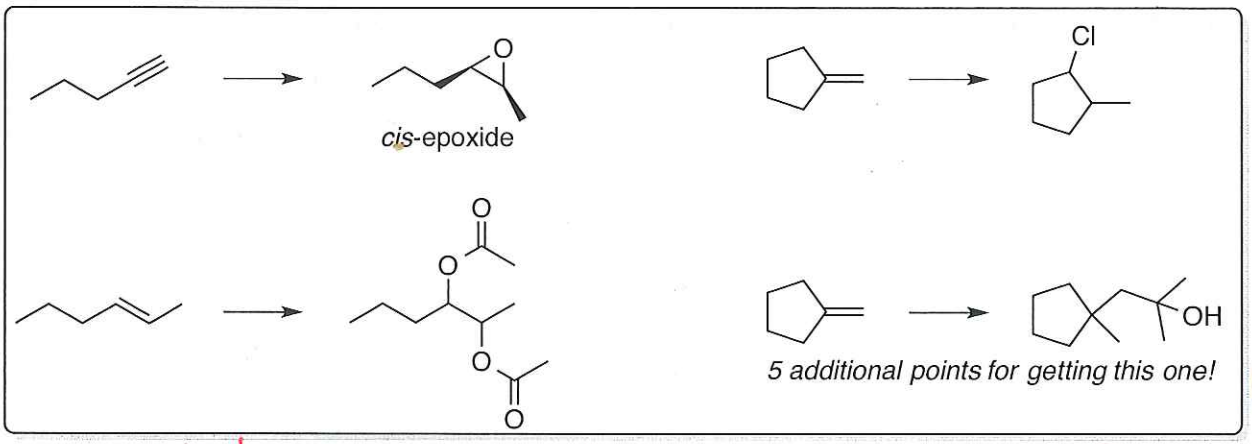


3pts - chair

CHEM 108A, Summer 2015 Last Name, First Initial _____

11. (*30 points*) **Multi-Step Synthesis** 15 pts ea.

Choose any two of the following synthetic problems. You may use any alkyl halide to introduce new carbons and any other reagents necessary. Show the product after each step.



(2-HCl instead)

add C!

3 1. $NaNH_2$, NH_3 2. CH_3Br

mCPBA 3

H_2 Lindlar 3

2 HX

$SOCl_2$ 3

2 1. BH_3, THF 2. H_2O_2, $^{\ominus}OH$

Base 2

5 X_2

5

5 Cl

3 HX

3 H_2O, H_2SO_4

3

MgX 3 Mg°

3