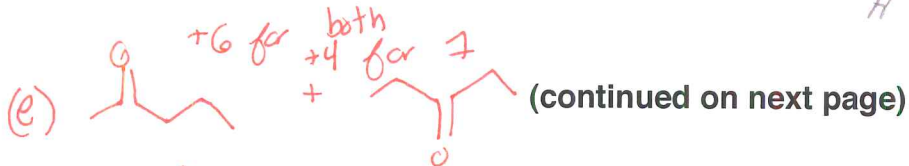
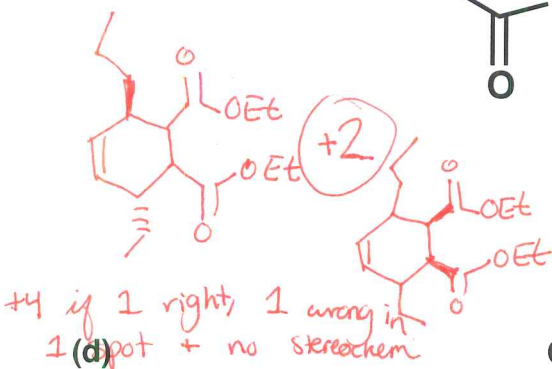
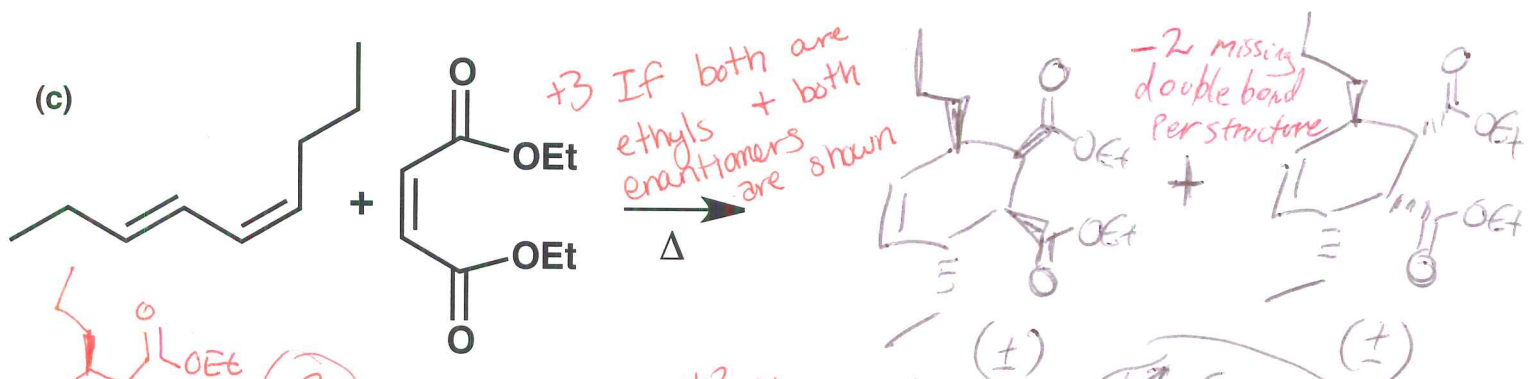
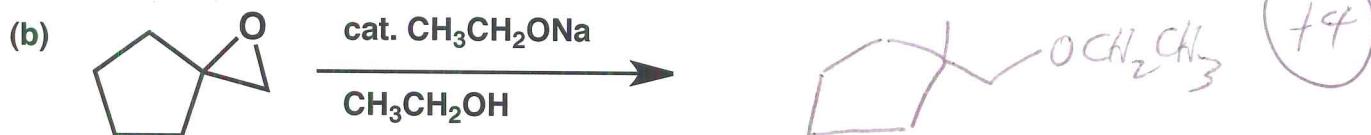
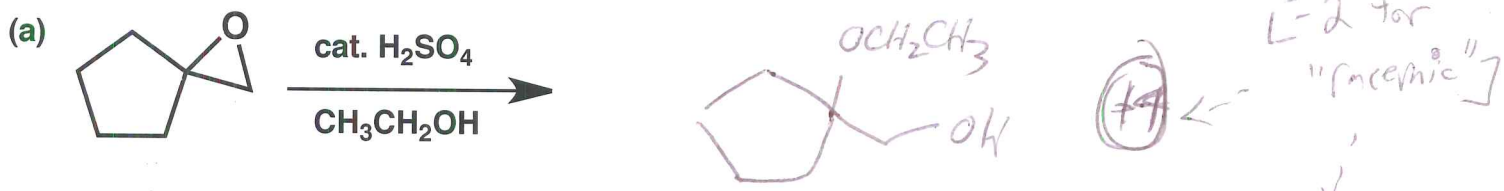


General Instructions:

- (i) Use scratch paper at back of exam to work out answers; final answers must be recorded at the proper place on the exam itself for credit. Models are allowed.
- (ii) Print your name on each page.
- (iii) Please keep your paper covered and your eyes on your own work. Misconduct will lead to failure in the course.

1. (29 points) Show the major product or products expected from each reaction.

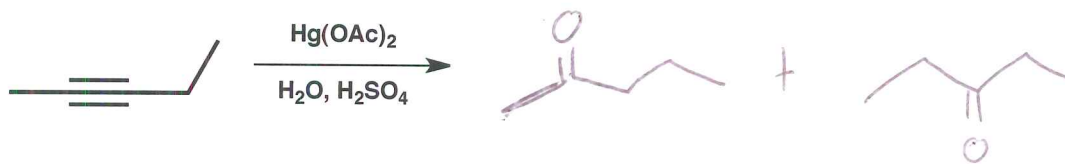


[+2 if stereochem unclear]

1. (cont.)

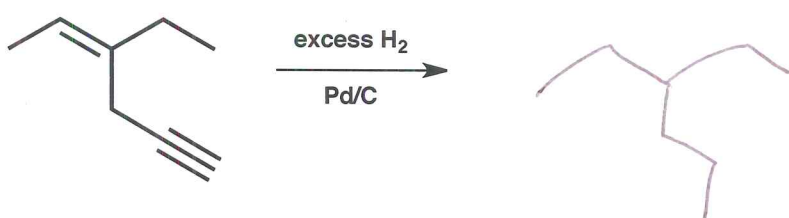
Name _____

(e)



+4 for one;
+6 for both

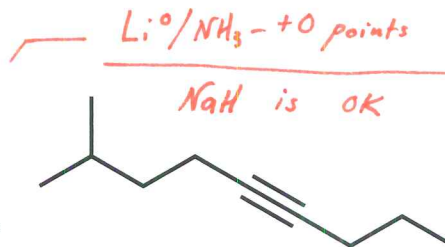
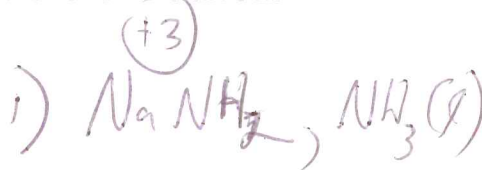
(f)



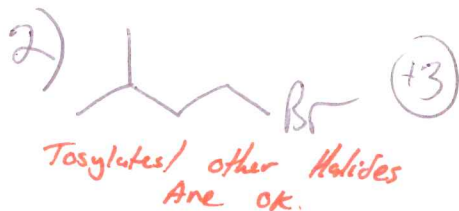
+4

2. (32 points) Show the reagents required to convert the starting molecule to the indicated product. If necessary, be sure to differentiate clearly between distinct steps, by using "1)," "2)," etc. over the arrow.

(a)



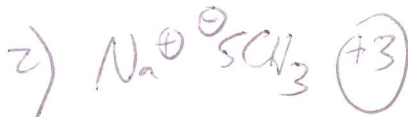
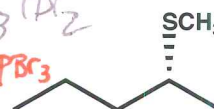
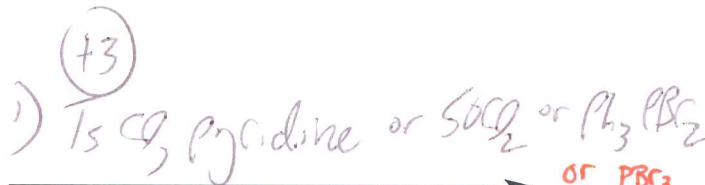
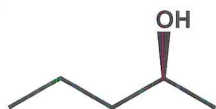
+2 for only showing



[Tosylate or other halide OK]

-2 for No
1) ...
2) ...
or wrong order.

(b)



+2 for only showing $\text{Na}^\oplus \text{SCH}_3$

[solvent does not matter]

-- cont. on next page --

1) $\text{H}_2\text{O}, \text{H}_2\text{SO}_4$ → 3/6

2) $\text{NaSCH}_3, \text{HSCH}_3$

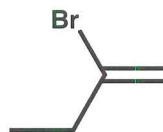
Name _____

2. (cont.)

(c)

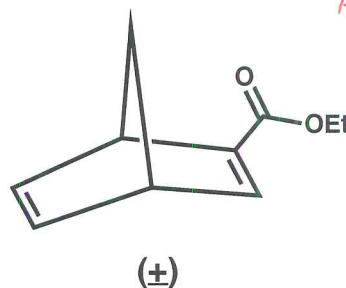
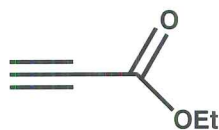


(+1) (+3)
1 equiv. HBr



if with Peroxides, \rightarrow 0/4

(d)

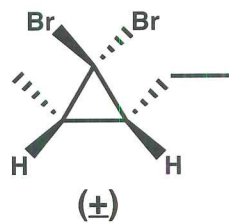


All or nothing

(e)



KOtBu (+3)
HCB₃ (+3)



1) KOtBu

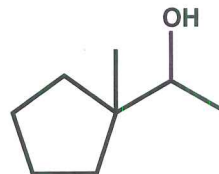
2) HCB₃

Also accepted
full credit

(f)



(+2) (+2)
1) Hg(OAc)₂, H₂O, THF
2) NaBH₄



(±)

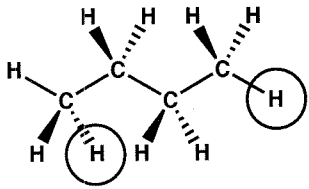
(+2)

Peroxides in 2nd step
= No points for
2nd step.

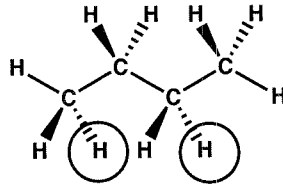
-2 if lacking
"1" + "2"

Name _____

3. (12 points) For each drawing below, write on the line (below the structure), the relationship between the two circled H atoms (homotopic, enantiotopic, diastereotopic or constitutionally non-equivalent).

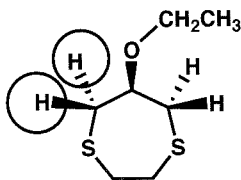


Homotopic

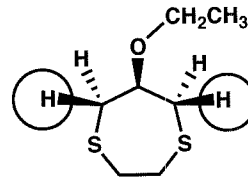


Non-equivalent

+3 each

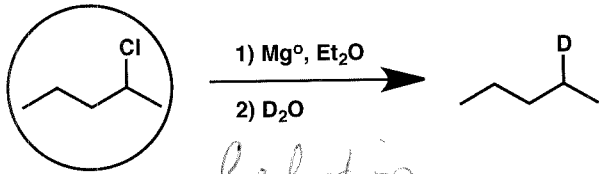


Diastereotopic

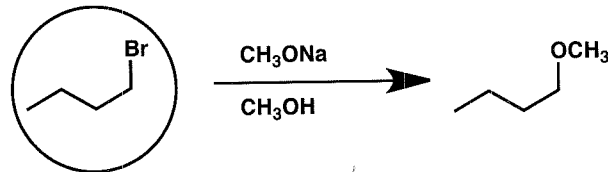


Enantiotopic

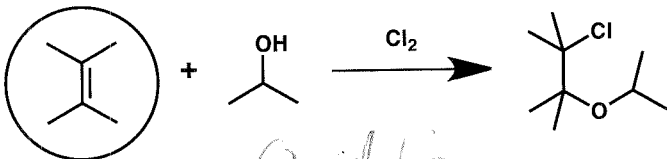
4. (12 points) For each reaction shown below, based on the CIRCLED starting material, write on the line (below reaction) whether the reaction involves oxidation, reduction or no redox change.



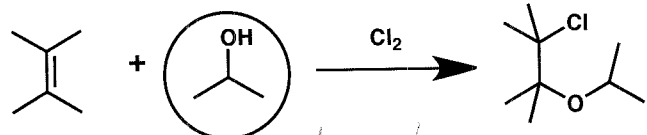
Reduction



No change



Oxidation



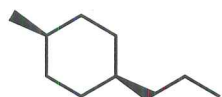
No change

+3 each

5. (22 points)

Name _____

(a) For each cyclohexane derivative shown below, draw both chair conformations in the appropriate place. These three molecules are isomers. For each molecule, circle the chair conformation that you expect to be more stable. If you think both chairs should be similar in stability, circle them both.



I

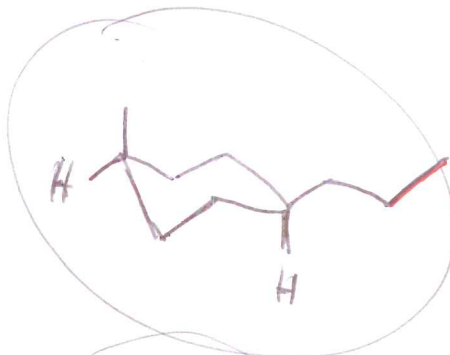
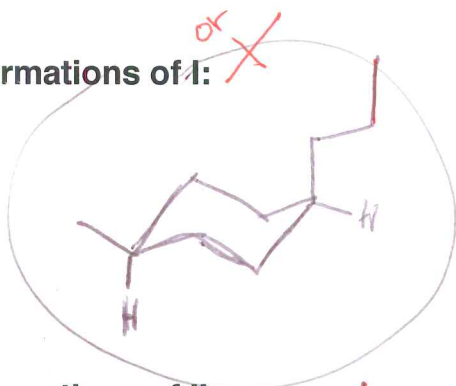


II



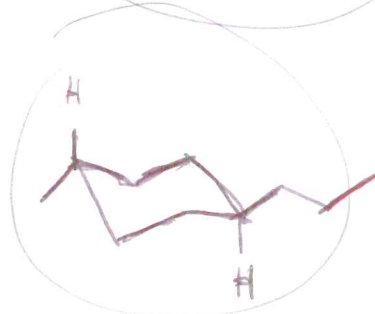
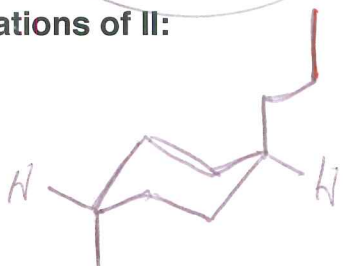
III

Chair conformations of I:

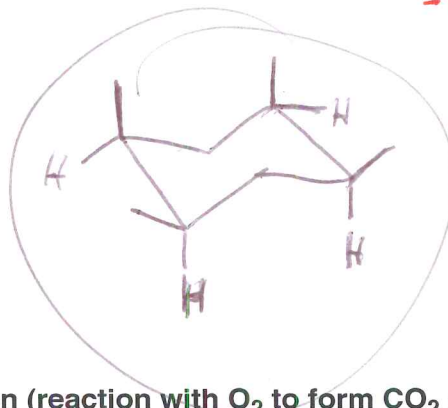
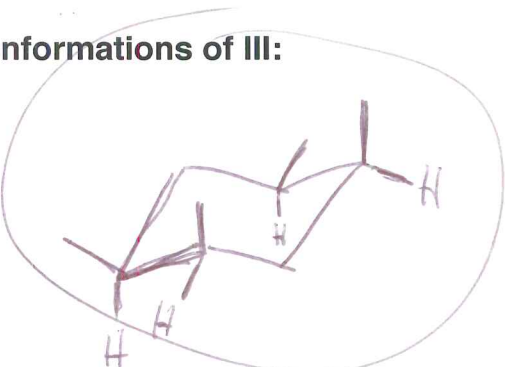


circle both +2 OR right one ONLY

Chair conformations of II:



Chair conformations of III:



Must circle BOTH +2

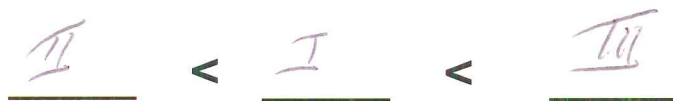
+2 for each correct chair
/12 chair

+2 for each correct circle(s)
[for I + III, must have both circles for +2]
/6 stability

-1 for missing Hydrogens if line is drawn

-2 for ethyl substituent

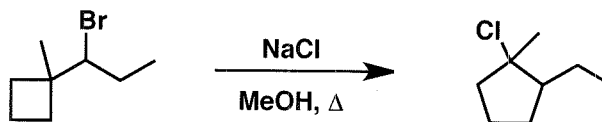
(b) Hydrocarbons give off heat upon combustion (reaction with O_2 to form CO_2 and H_2O). Rank the three isomers above in order of least heat given off (on the LEFT) to most heat given off (on the RIGHT) below. (Technically, you should be comparing the absolute values of the heats of combustion.)



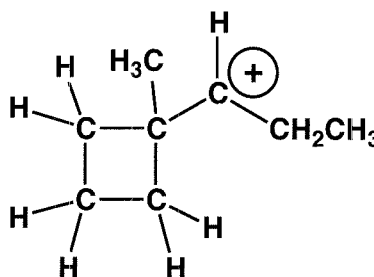
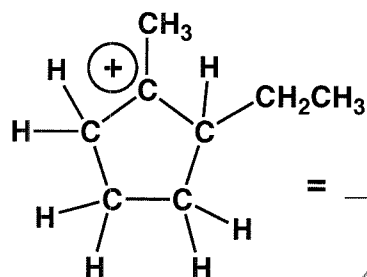
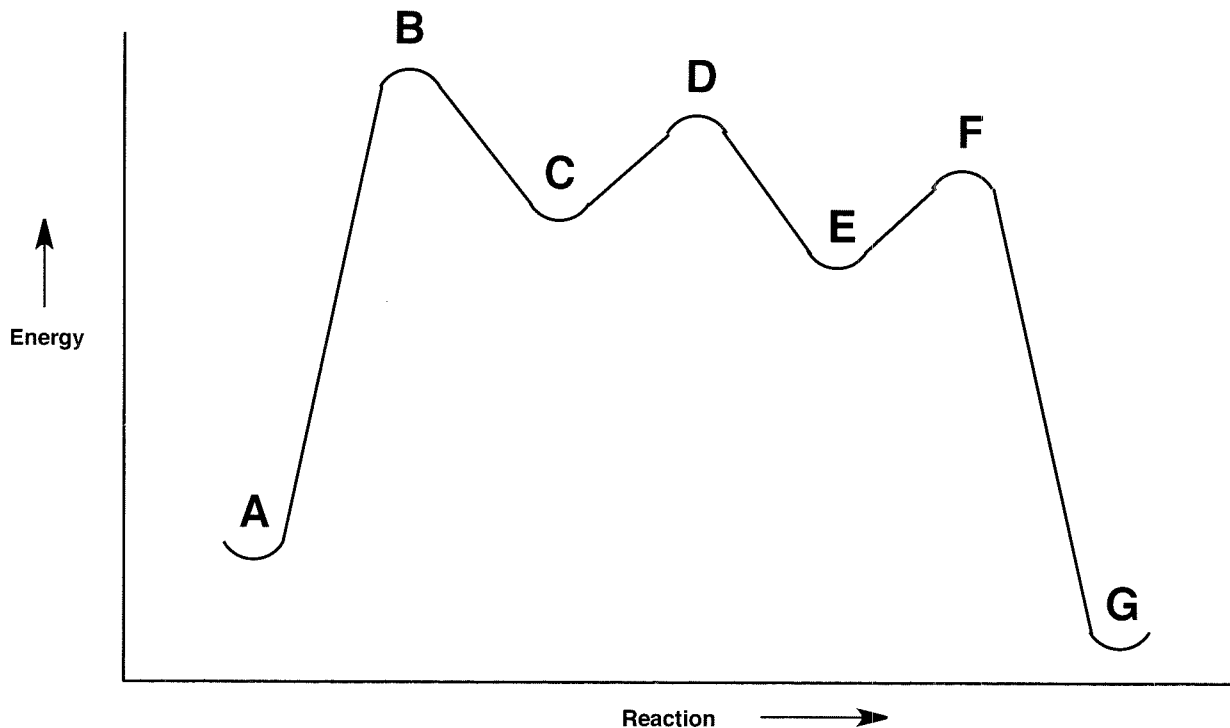
+4

Name _____

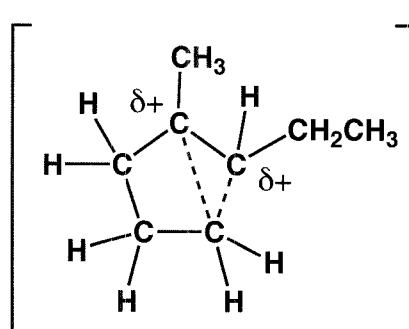
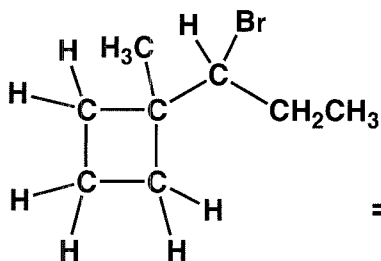
6. (16 points) Shown below are a reaction and an energy diagram that corresponds to the mechanism for that reaction. The local maximum and minimum energy points on the diagram are labeled (A, B, etc.). For each of the structures drawn below the energy diagram, indicate the correct point on the energy diagram (i.e., write A or B or C or etc. on the line).



(NOTE: Do not be concerned about stereochemistry.)



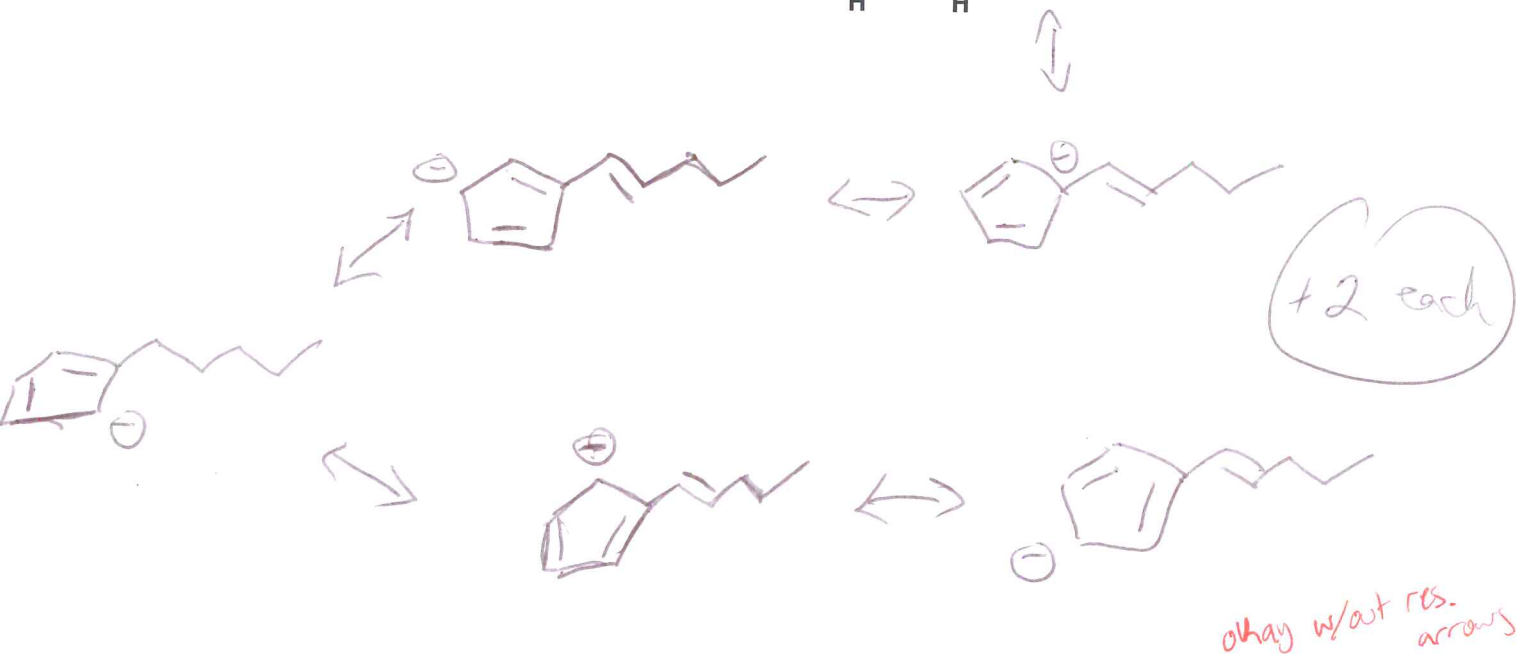
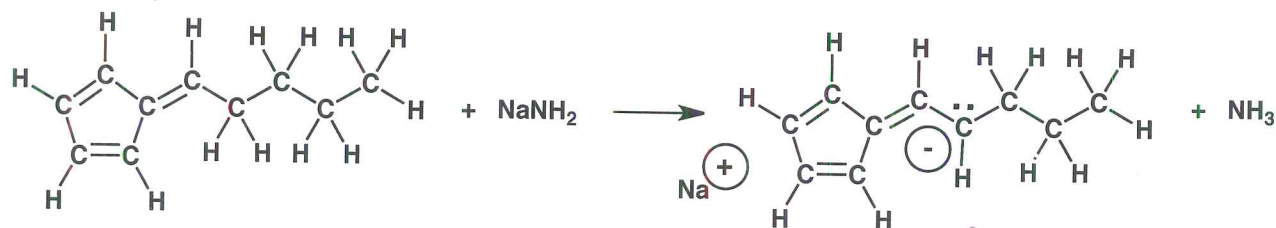
+4 each



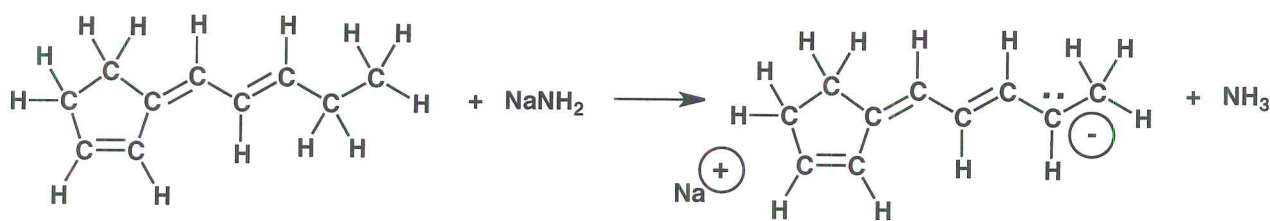
7. (14 points)

Name _____

(a) For the acid-base reaction shown below, draw out all other resonance structures of the anion on the right side of the equation.



(b) Compare the reaction above with the one below, and focus on the hydrocarbons on the LEFT sides of each equation. Do you expect these molecules to have similar pK_a values, or should one have a lower pK_a than the other?



Answer by writing the appropriate numeral in the box:

- 0 if the pK_a values should be SIMILAR
- 1 if the UPPER hydrocarbon should have a lower pK_a
- 2 if the LOWER hydrocarbon should have the lower pK_a .

1

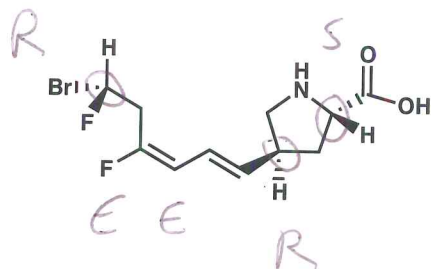
14

8. (22 points)

No pts of for not circling

Name _____

(a) Circle every sp^3 stereogenic center in the molecule, and assign configuration (R vs. S). In addition, assign configuration (E vs. Z) to the C=C double bonds.



+2 each

(10)

+1 each for

*adding/subtracting carbon
but correct res. structure*

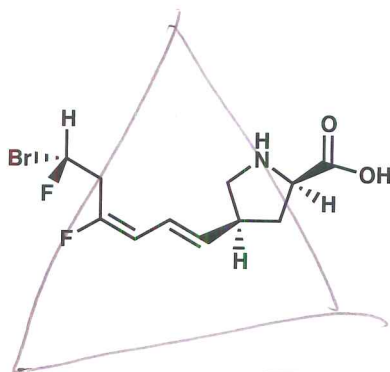
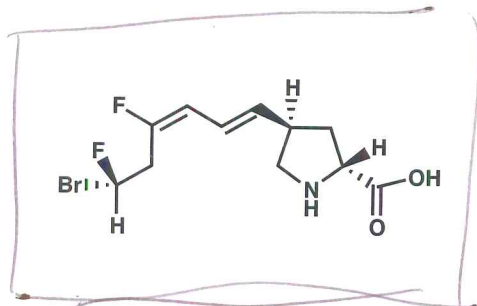
(b) For each structure drawn below, indicate the isomeric relationship to the molecule above. Follow the directions below. (Conformational differences are not relevant to this question.)

Put a CIRCLE around any structure that is identical to the molecule above (i.e., a different drawing of the same molecule).

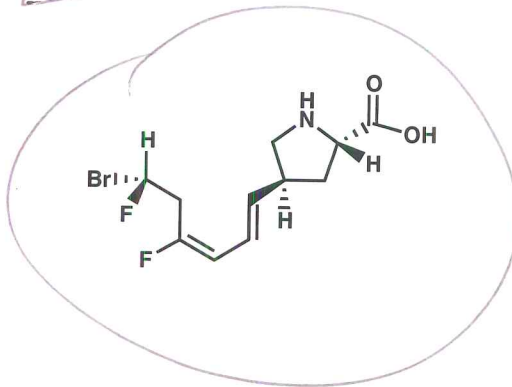
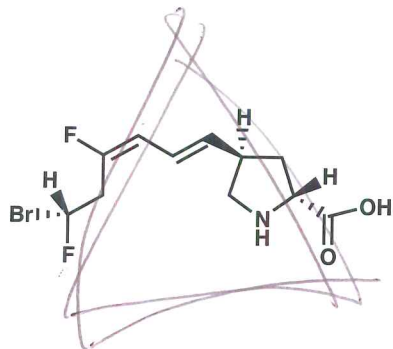
Put a SQUARE around any structure that corresponds to the ENANTIOMER of the molecule above.

Put a TRIANGLE around any structure that corresponds to a DIASTEREOMER of the molecule above.

Put an X across any structure that corresponds to a CONSTITUTIONAL ISOMER of the molecule above.

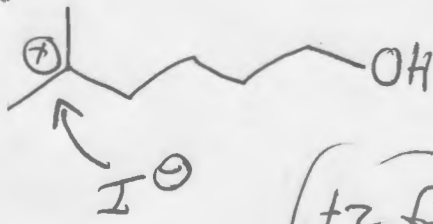
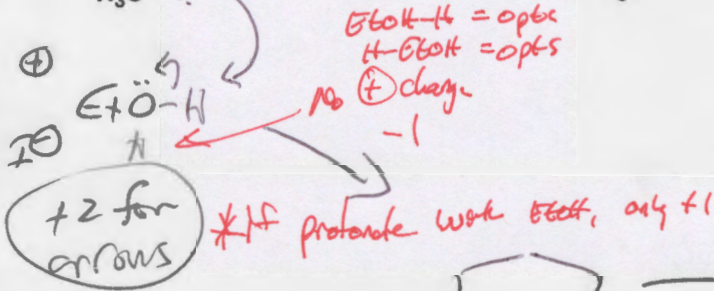
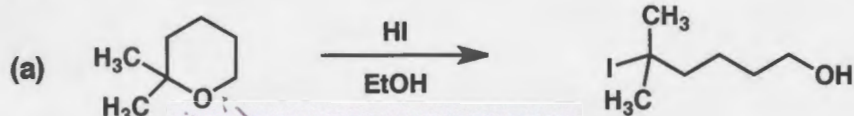


(12)

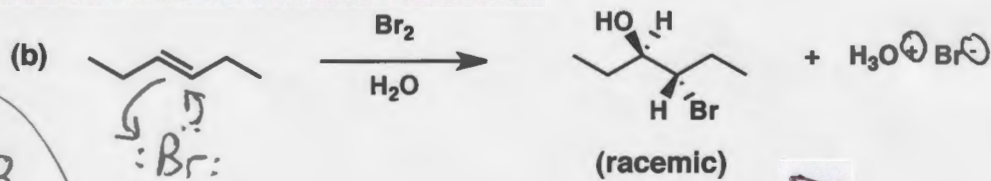


+3 each

9. (21 points) Provide a mechanism (curved arrows) for each reaction shown below. Be sure to show any intermediates.

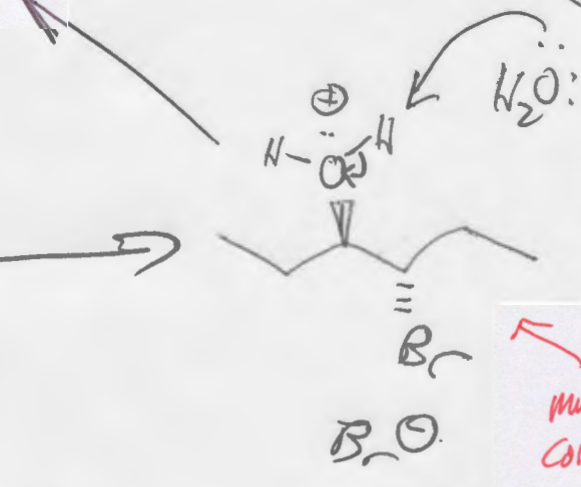
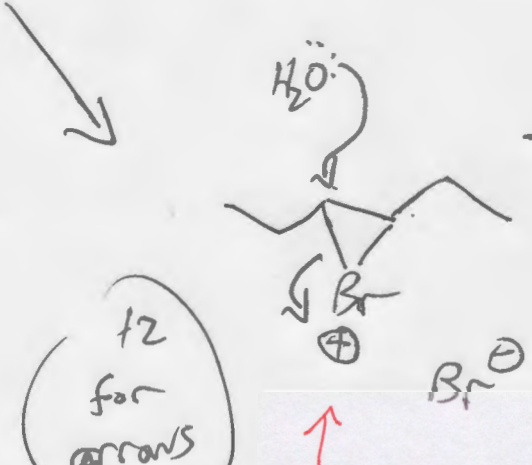


1 pt if protonate ether with HF



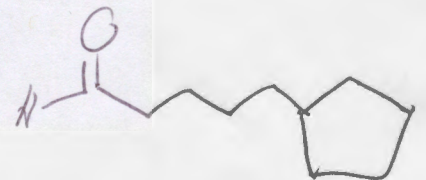
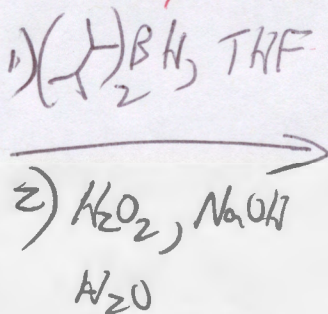
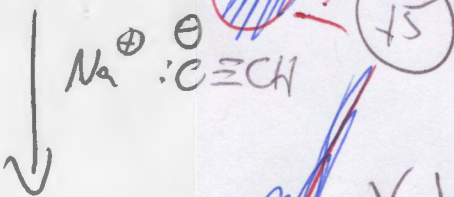
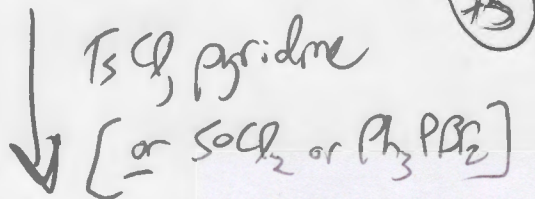
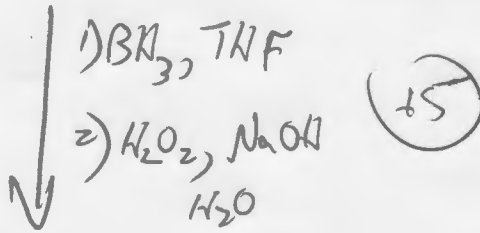
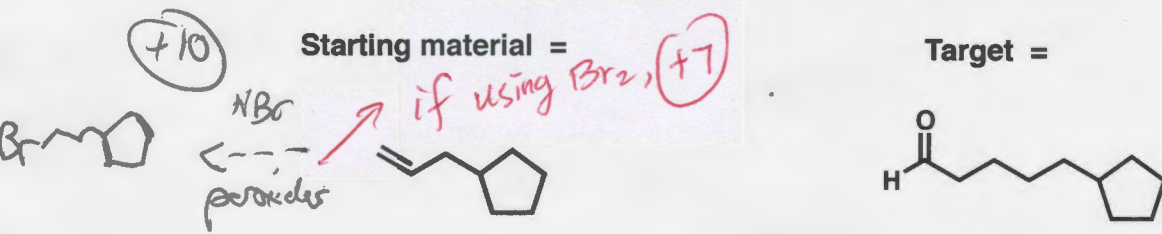
+3 for arrows

+2 for arrows



[+11 total]

10. (20 points) Devise a synthetic route from the indicated starting material to the indicated target. The route should be as short and as selective as possible. You may use any other organic molecules or inorganic reagents in your synthetic plan. Show the expected product after each step in each synthetic route. (Do not provide mechanistic information.)



All the points are assigned based on the reagents !!

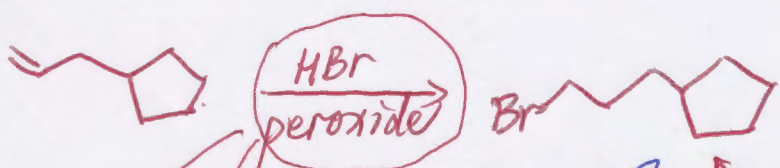
if the reagents are $\text{CH}\equiv\text{C}^-$ and some other unnecessary reagents. BH_3 : (+2)

+2

+5

Alternative routes for Q 10.

1)



if using H_2O_2 , just (+2)

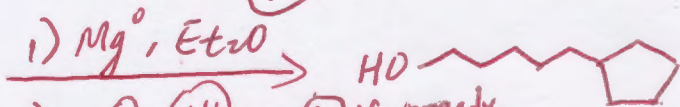
if using Br_2 , just (+2)

(+5)

~~reagent~~
~~+3 intermediate~~

step 1): no solv or wrong solv. (+3)

- 1) $\text{Mg}^0, \text{Et}_2\text{O}$ (+5)
 2) \triangle (+4) \rightarrow (+2) if wrong solv.
 3) H_3O^+ (+1)

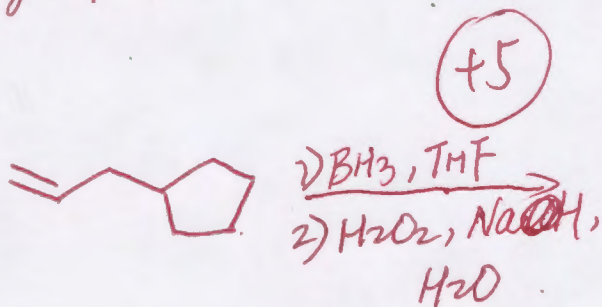


\downarrow
 $\text{PCl}_5, \text{CH}_2\text{Cl}_2$ (+5)
 pdt. (no solv, wrong +2)

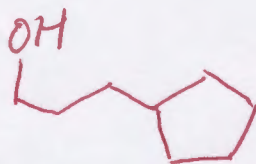
2 pts off for extra unnecessary steps.

~~right inter~~

2)

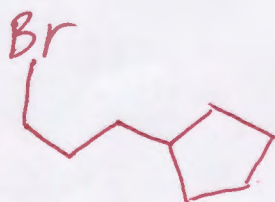


(+5)



(+5)

w/ PBr_3 or Ph_3PBr_2



$\text{CH}\equiv\text{CNa}$

(+5)



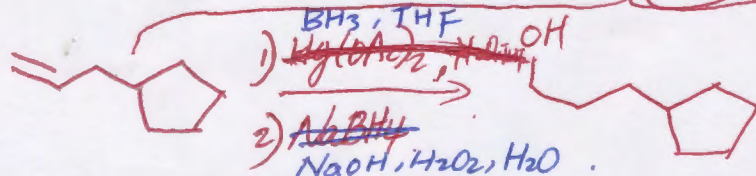
1) $(\text{CH}_2)_2\text{BH}, \text{THF}$
 2) $\text{H}_2\text{O}_2, \text{NaOH}, \text{H}_2\text{O}$

(+5)

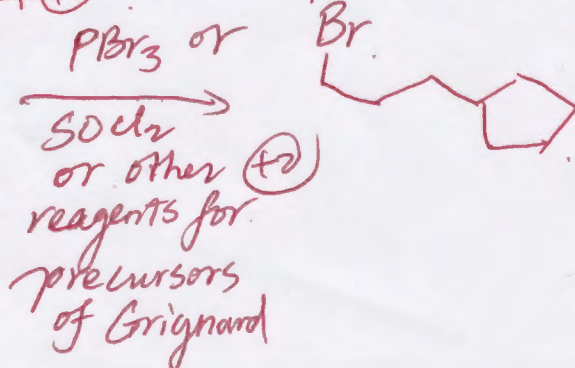
2 pts off for incorrect steps

Half pts. for wrong sm, correct reagents, correct product

3)



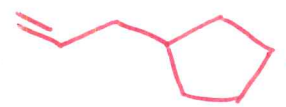
1) BH_3, THF
 2) $\text{AlEt}_3, \text{NaOH}, \text{H}_2\text{O}_2, \text{H}_2\text{O}$ (+3)



Grignard route

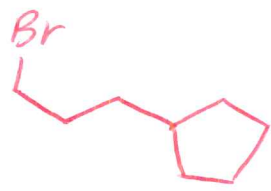
as in 1)


4

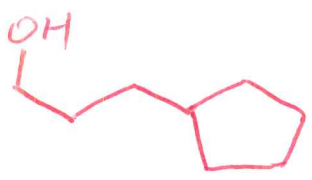


HBr
ROOR

+5



- 1) Li⁺ +3
- 2) CuX (X=Br, Cl, I) +3
- 3)  +3
- 4) H₂O +1



PCC
DCM

+5

Pdt.