Chemistry 112A, Final

Wednesday, December 17, 2008

Student name: Answer Key

Student signature: _____

Write TA's full name (section number) or Lecture Only: _____

1. Please make sure that the exam has 14 pages including this one.
2. Please write your answers in the spaces provided.
3. Write clearly; illegible or ambiguous answers will be considered incorrect.
4. Only writing implements are allowed **(No Calculators)**.

GOOD LUCK!

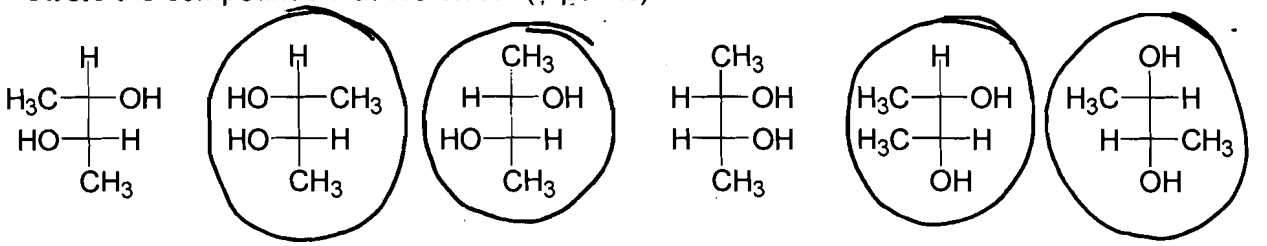
1.	70 points	_____
2.	60 points	_____
3.	80 points	_____
4.	18 points	_____
5.	24 points	_____
6.	16 points	_____
7.	20 points	_____
8.	16 points	_____
9.	20 points	_____
10.	26 points	_____
Total	**350 points**	_____

MINI-PERIODIC TABLE

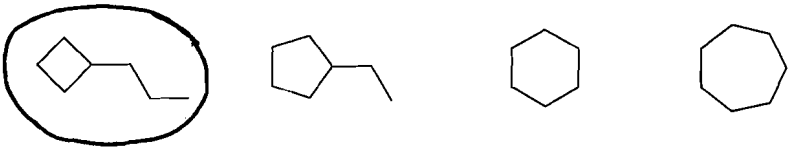
I	II	III	IV	V	VI	VII	VIII
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr

1. Answer the following questions. Every wrong answer cancels a correct answer (70 points).

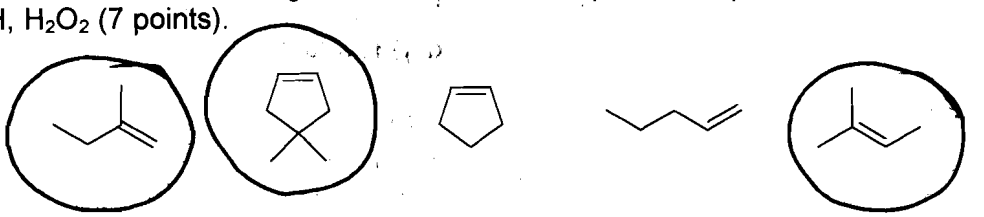
(a). **Circle** the compounds that are **chiral** (7 points).



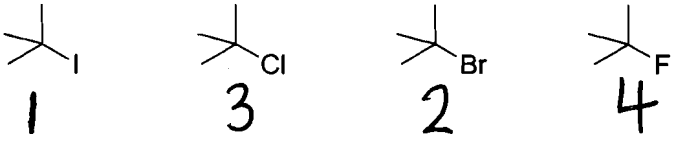
(b). **Circle** the structural isomer that has the **largest** heat of combustion (7 points):



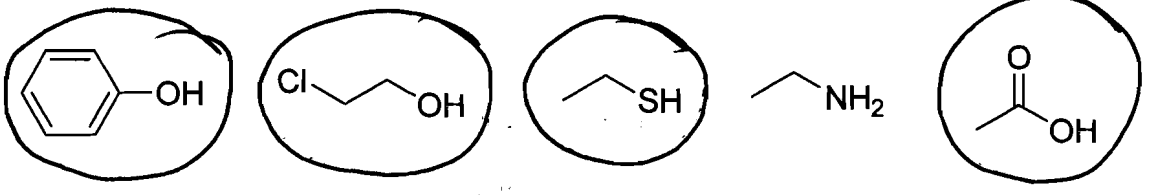
(c). **Circle** the alkenes that would give chiral but racemic products upon reaction with: 1. BH_3, then 2. NaOH, H_2O_2 (7 points).



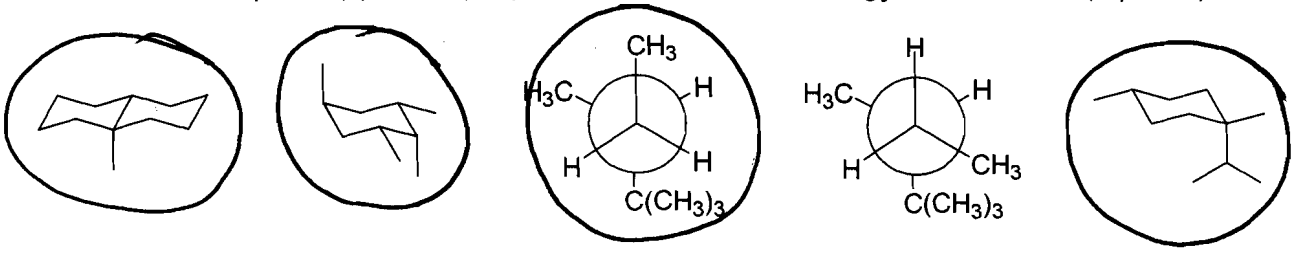
(d). **Rank** the alkyl chlorides from 1 to 4 from fastest to slowest S_N1 substrates [1 = **fastest**] (7 points).



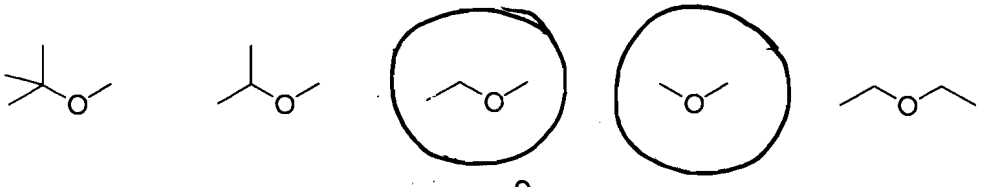
(e). **Circle** the compounds that are more acidic than ethanol (7 points).



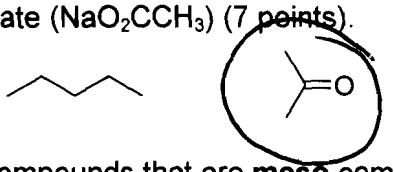
(f). **Circle** the compound(s) that is(are) drawn in the **lowest** energy conformation (7 points).



(g). **Circle** the ether(s) listed below that could be prepared by reaction of methoxide (CH_3O-) with an alkyl halide (7 points).

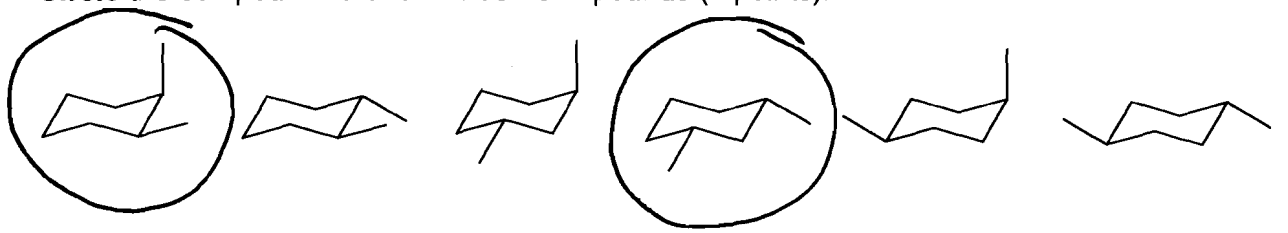


(h). **Circle** the solvent that would provide the **fastest** S_N2 reaction between propyl bromide and sodium acetate (NaO_2CCH_3) (7 points).

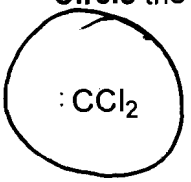


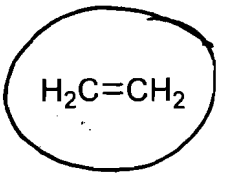
H_2O CH_3OH

(i). **Circle** the compounds that are **meso** compounds (7 points):



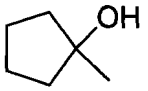
(j). **Circle** the compound(s) for which the carbon atom(s) is(are) sp^2 hybridized (7 points):



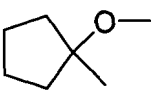
H_3C-CH_3 

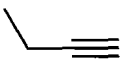
$HC\equiv CH$ CO_2

2. For each of the following reactions supply the missing starting materials, reagents, or major organic products in the space provided. Show the stereochemistry of the product. If the product is chiral indicate whether or not it is racemic (60 points total).

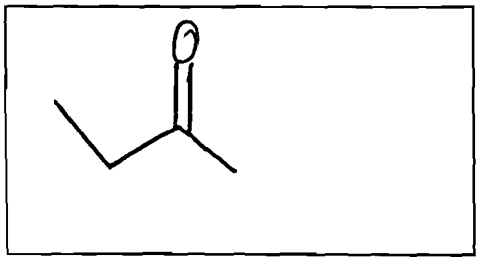
(a) 

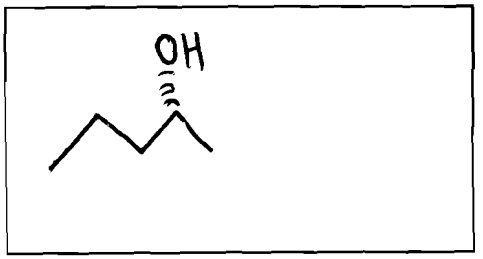
KOH, H_2SO_4 (or H_3PO_4)
or
1. NaH, 2. MeX



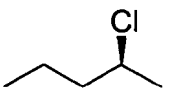
(b) 

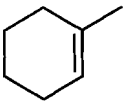
H_2O, $HgSO_4$, H_2SO_4



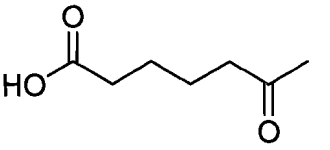
(c) 

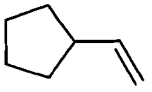
$SOCl_2$, pyridine



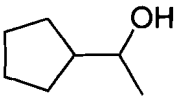
(d) 

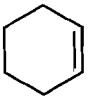
1. O_3
2. H_2O_2, H_2O



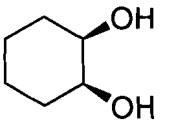
(e) 

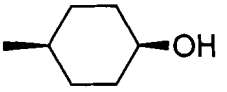
1. $Hg(OAc)_2$, H_2O
2. $NaBH_4$, $NaOH$

(±) 

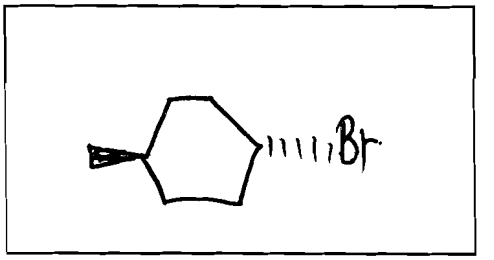
(f) 

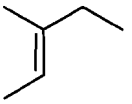
OsO_4, H_2O_2, Me_3NO



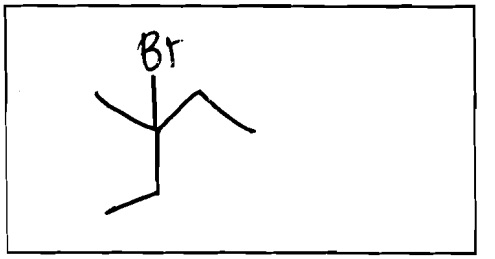
(g) 

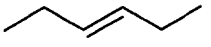
PBr_3



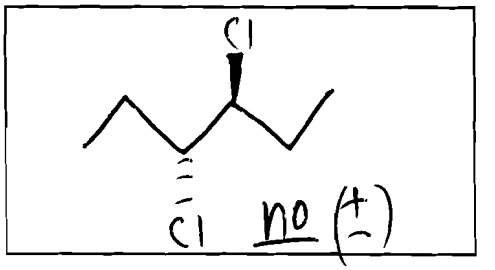
(h) 

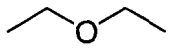
HBr

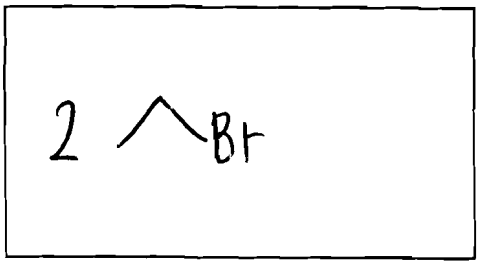


(i) 

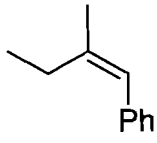
Cl_2



(j)  HBr (excess), Δ

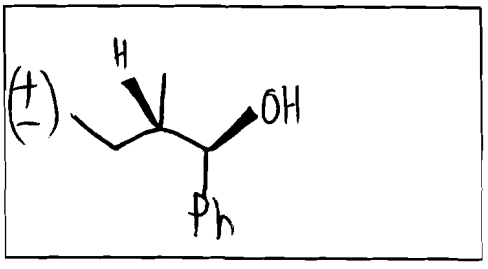


3. For each of the following reactions supply the missing starting materials, reagents, or major organic products in the space provided. Show the stereochemistry of the product. If the product is chiral indicate whether or not it is racemic (80 points total).

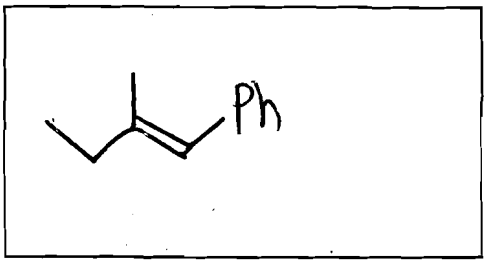
(a) 

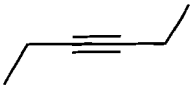
(Ph = benzene)

1. BH_3
2. H_2O_2, NaOH

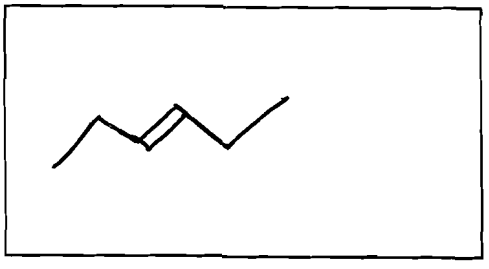


1. RSO_2Cl, pyridine
2. $K^{\oplus}\,^{\ominus}OC(CH_3)_3$

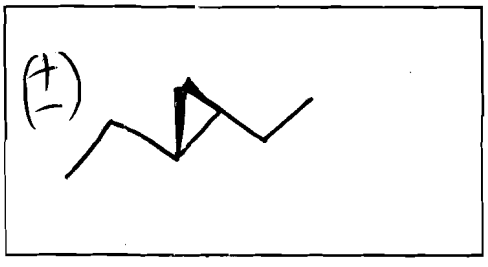


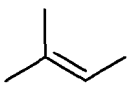
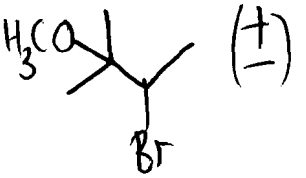
(b) 

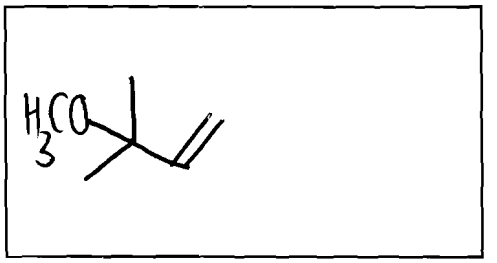
Na, NH_3

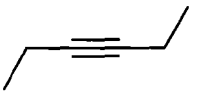
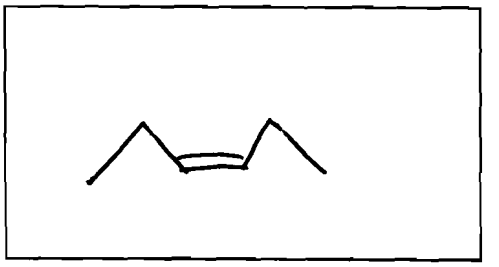


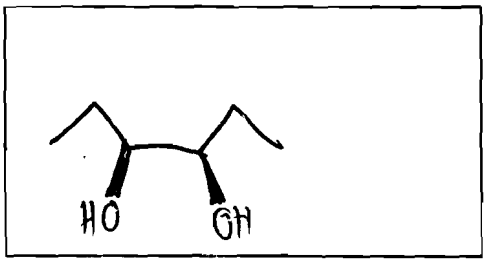
CH_2I_2,
Cu-Zn couple

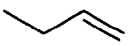
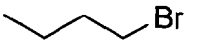


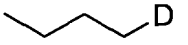
(c)  Br_2, CH_3OH → 

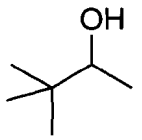
$\overset{\oplus}{K}\ \overset{\ominus}{O}C(CH_3)_3$ → 

(d)  Lindlar catalyst, H_2 → 

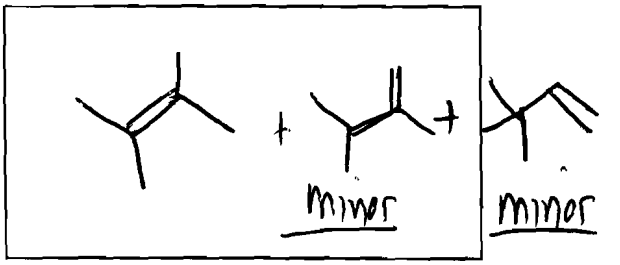
OsO_4, H_2O
Me_3NO → 

(e)  HBr, ROOR
lengthier routes also possible → 

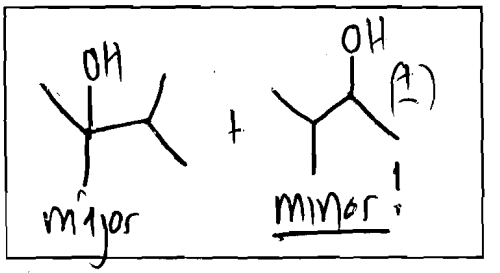
1. Mg or Li
2. D_2O → 

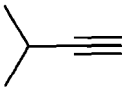
(f) 

H_2SO_4

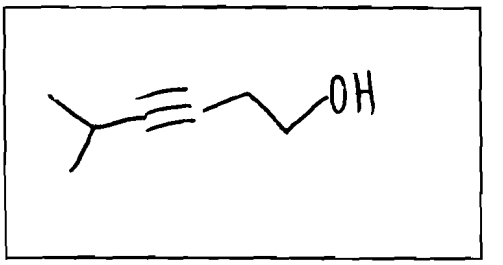


H_2O, H_2SO_4



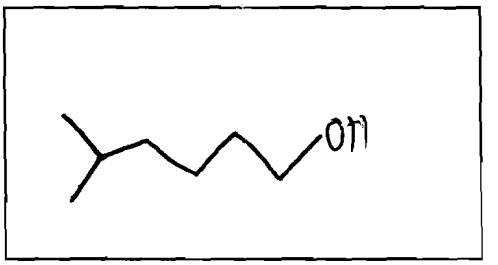
(g) 

1. $NaNH_2$
2. 
3. H_2O, H^+



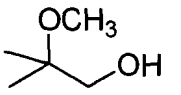
H_2 (excess),

Pd/C

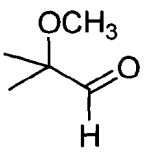


(h) 

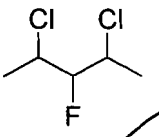
1. RCO_3H
2. MeOH, $H^\oplus$

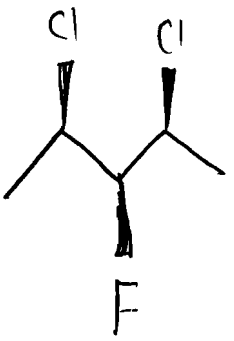


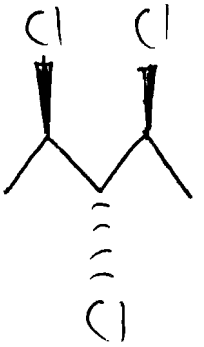
PCC, CH_2Cl_2

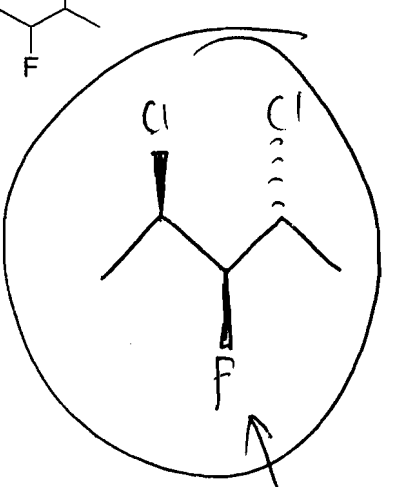


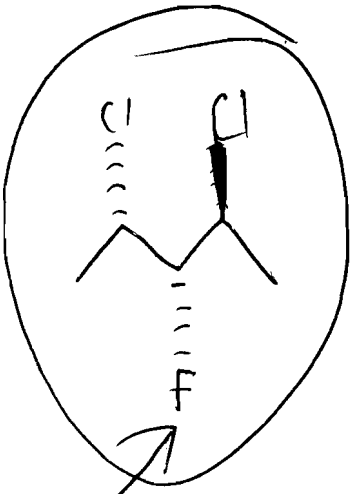
4. (18 total points).
(a) Draw **all** of the possible stereoisomers of structure shown below. Show enantiomers, but points will be marked off for writing the same structure twice.
(b) **Circle** all of the chiral compounds.











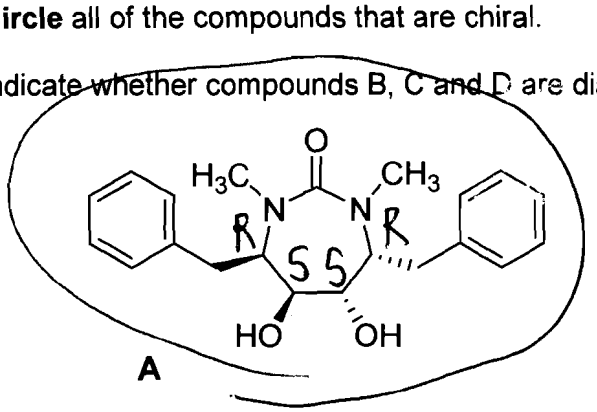
either or no config could be drawn for the F substituent

5. Compound A shown below has very potent anti-HIV activity and was evaluated in clinical trials for the treatment of AIDS. Stereoisomers B, C, and D are completely inactive (24 total points).

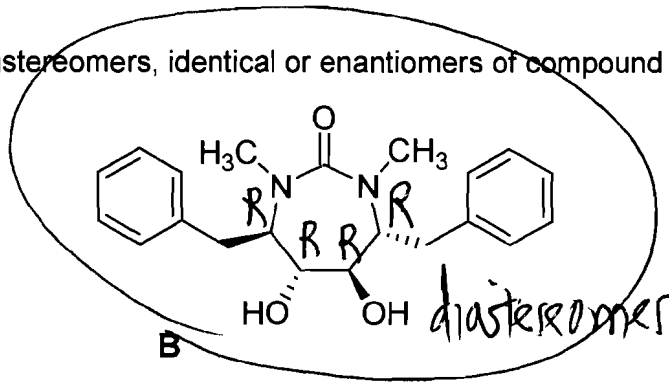
(a) Assign the absolute configurations of **all** stereocenters in **each** compounds.

(b) **Circle** all of the compounds that are chiral.

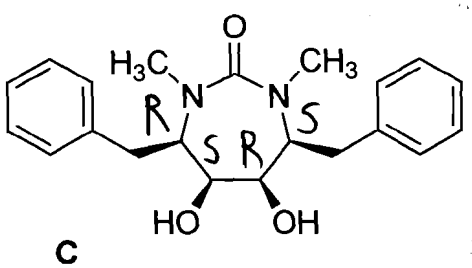
(c) Indicate whether compounds B, C and D are diastereomers, identical or enantiomers of compound A.



A

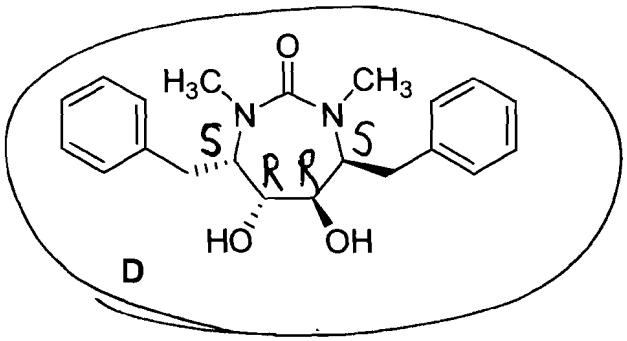


B diastereomer



C

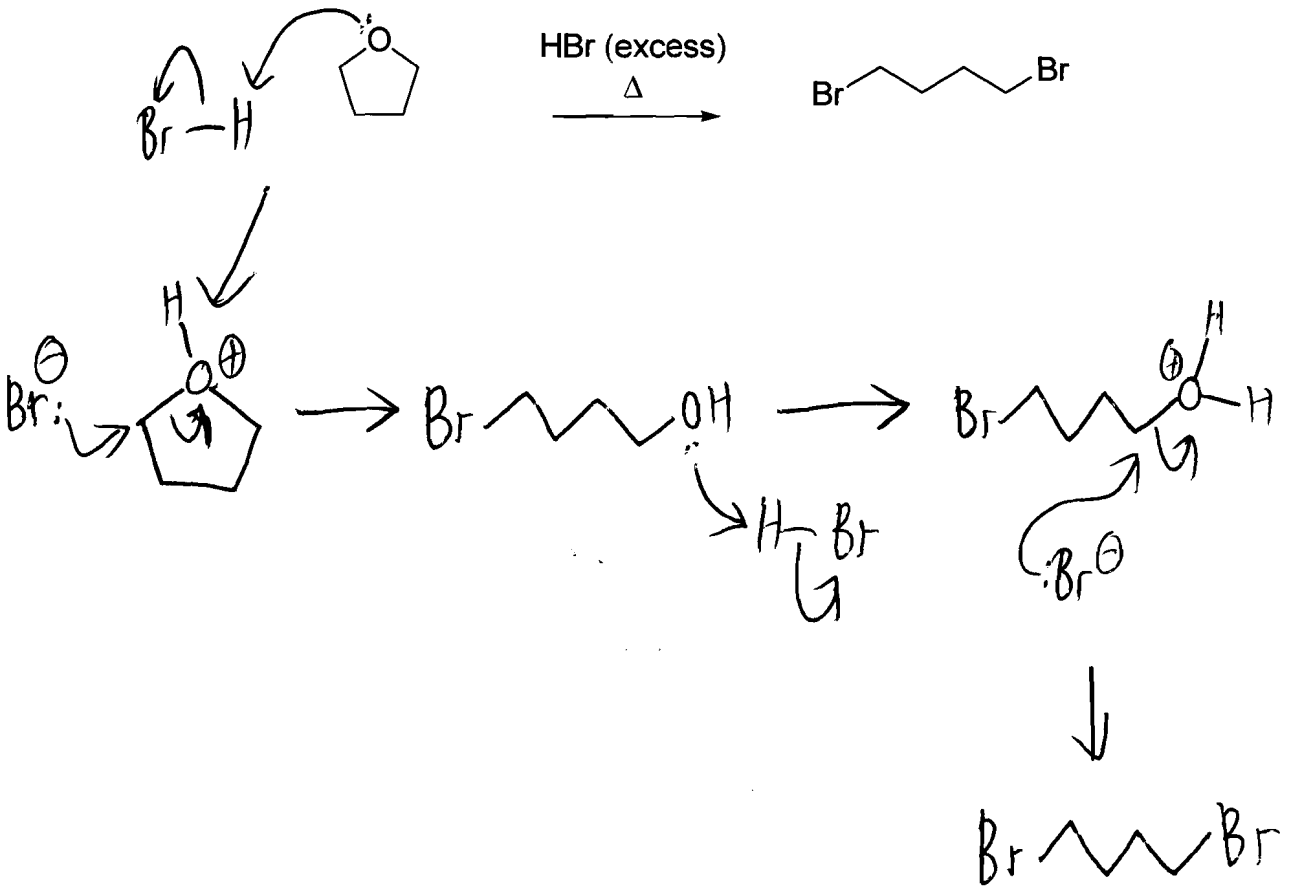
Diastereomer



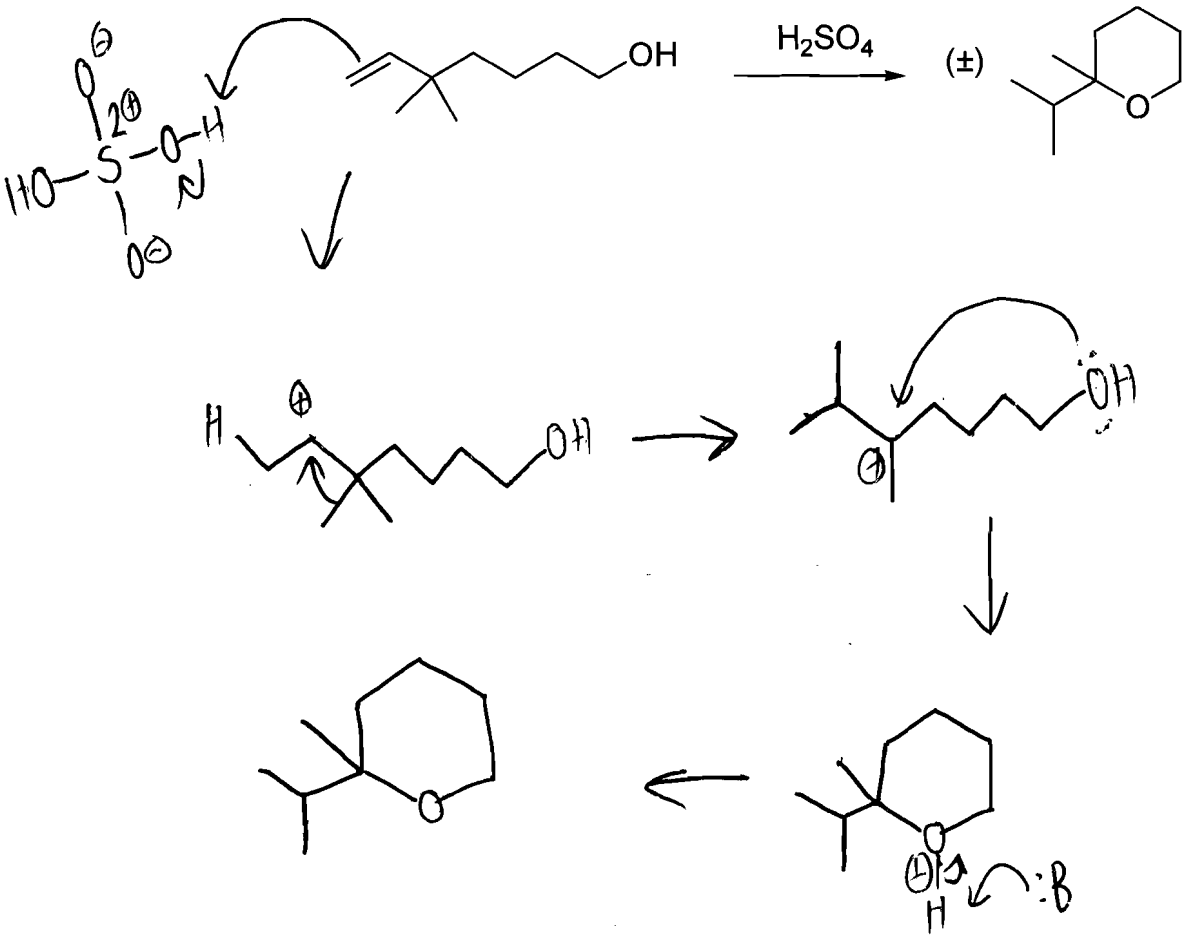
D

enantiomer

6. Tetrahydrofuran shown below is a very popular reaction solvent, but it is not stable to all reaction conditions. Provide a mechanism for the reaction shown below (16 points).

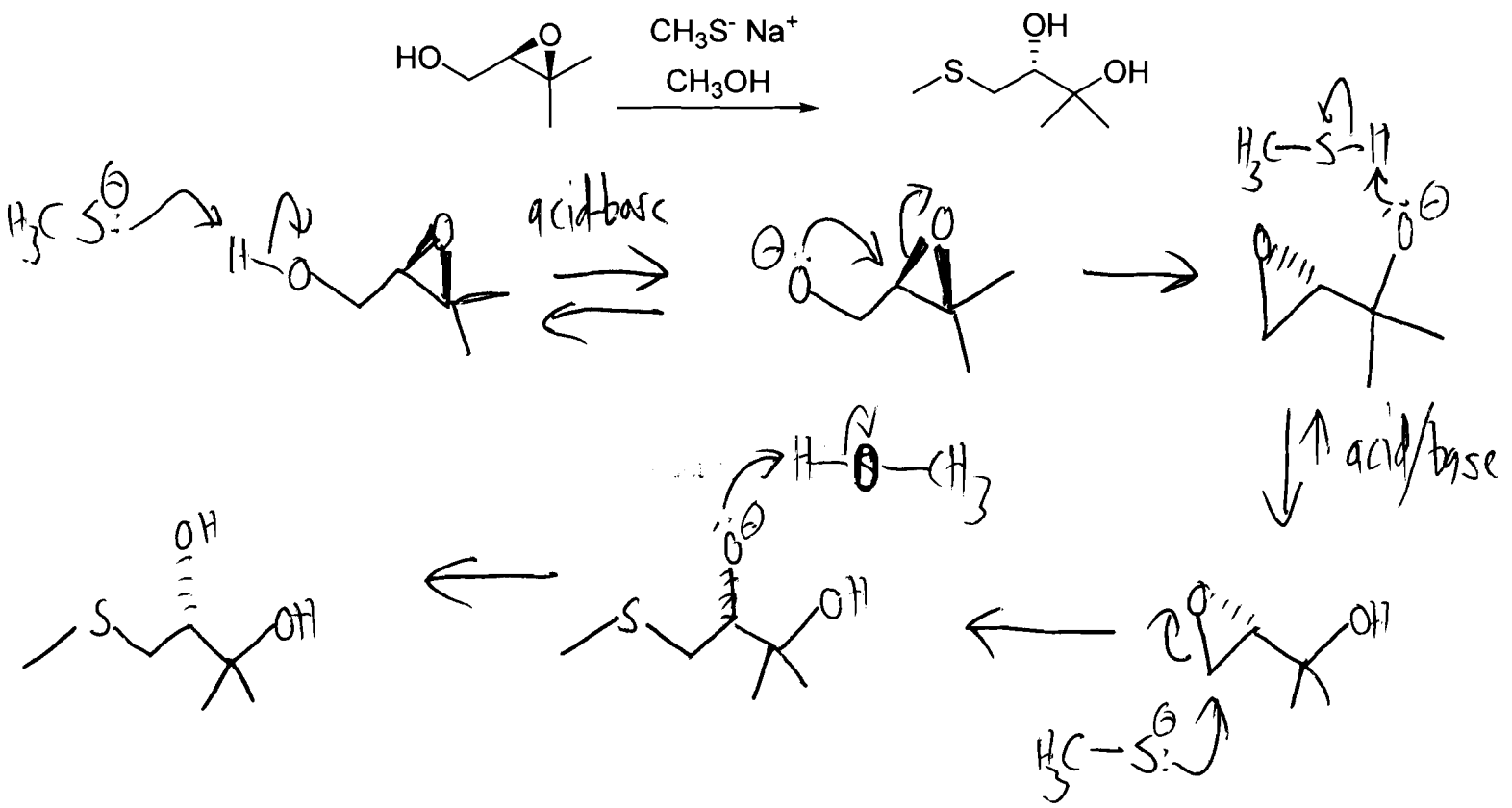


7. Provide a mechanism for the reaction shown below (20 points).

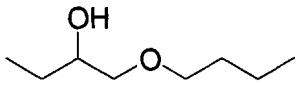
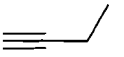


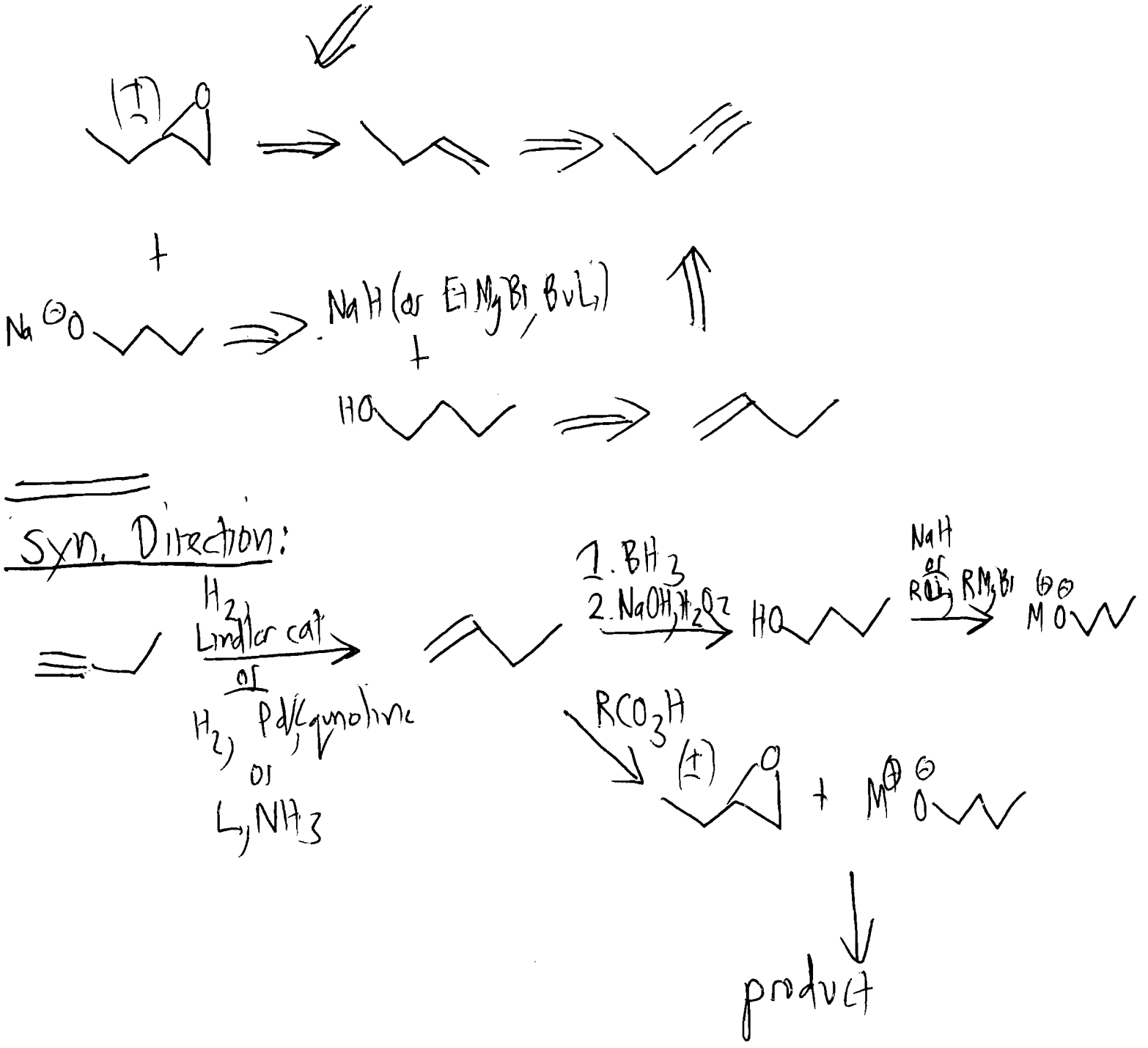
8. (Provide a mechanism for the following reaction (16 points).

Hint: pay close attention to stereochemistry.



9. Design a synthesis of the compound indicated below from two molecules of 1-butyne and any other reagents [20 points].

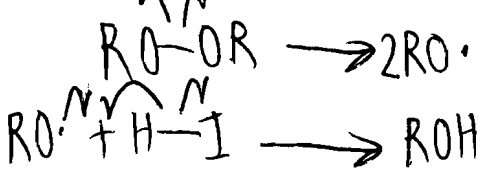
Prepare (±)  from two molecules of 



10.

(a) Provide a mechanism for the **propagation** steps of the radical transformation shown below (10 points).

initiation:



propagation:

step 1:

step 2:

(b) Calculate the ΔH° for **each propagation** step using the approximate DH° given below (8 points).

Bond	~DH° (kcal/mole)
= (π-bond)	65
— (σ-bond)	90
I—I	36
H—I	71
C—I	53
C–H	100

$\Delta H^\circ = DH^\circ(\text{broken}) - DH^\circ(\text{formed})$

step 1: $65 - 53 = \oplus 12$

step 2: $71 - 100 = \ominus 29$

(c) Indicate whether each propagation step is exothermic or endothermic (4 points).

step 1 - endothermic, step 2, - exothermic

(d) Do you think that this transformation should occur under radical conditions? Provide a **brief** explanation (4 points)?

NO: The overall process is exothermic, but step 1 is endothermic shutting down the rxn