Final Exam
Chemistry 343 (PM)
Professor Gellman
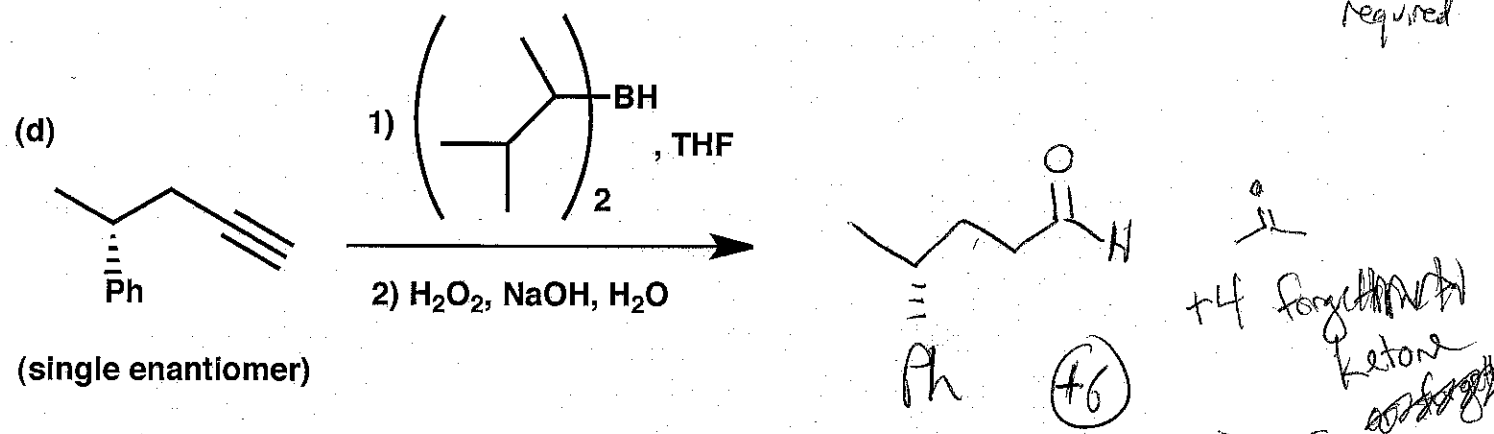**21 December 2012**

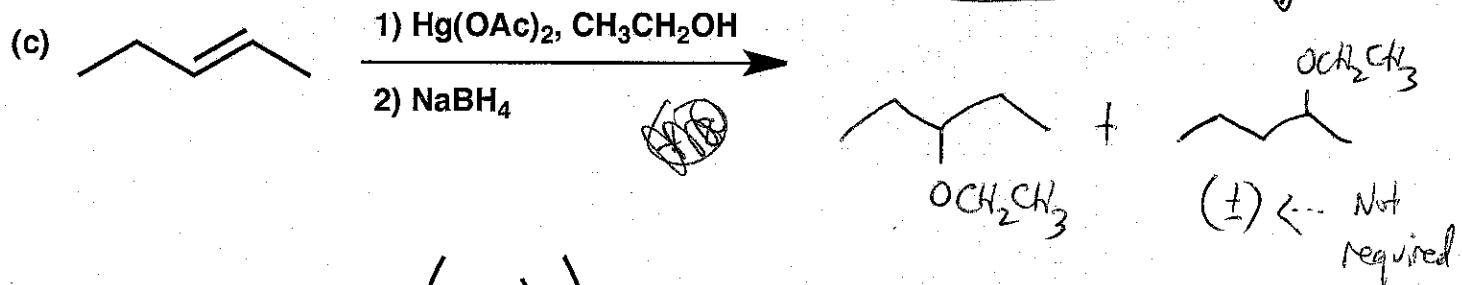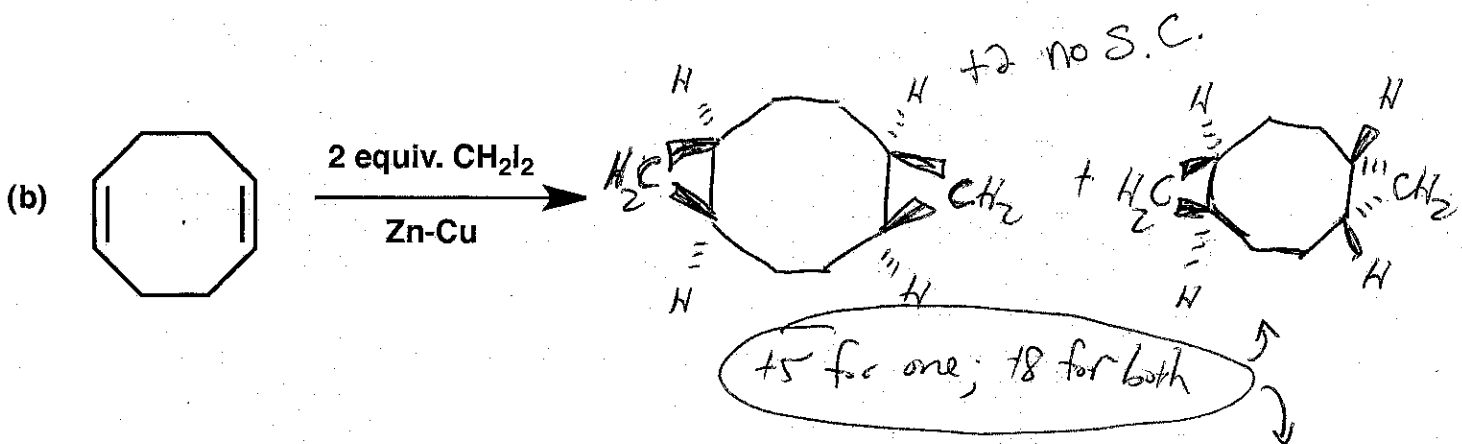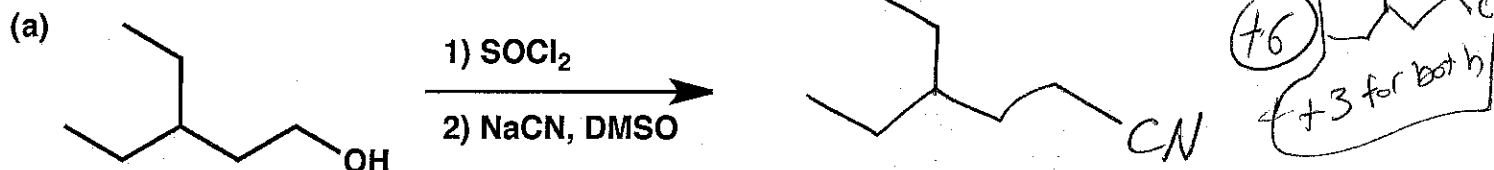Last Name ___Answer___

First Name ___Key___

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.
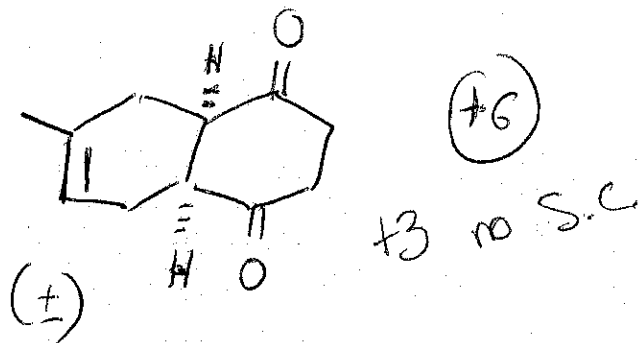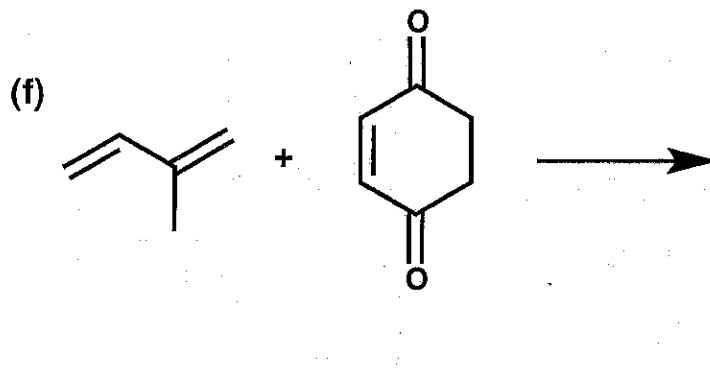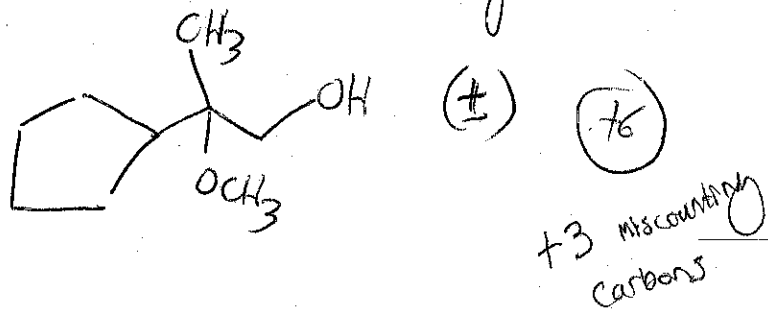
1. (40 points) Show the major product or products expected from each reaction.

(a)

1) $SOCl_2$

2) NaCN, DMSO

No partial
(+6)
+3 for both

(b)

2 equiv. CH_2I_2

Zn-Cu

+2 no S.C.

+5 for one; +8 for both

(c)

1) $Hg(OAc)_2$, CH_3CH_2OH

2) $NaBH_4$

OCH_2CH_3 OCH_2CH_3 $(\pm)$ ← Not required

(d)

Ph

(single enantiomer)

1) ⟨borane reagent⟩ BH , THF 2

2) H_2O_2, NaOH, H_2O

Ph (+6)

+4 for ⟨ketone⟩ ketone
+3 for (±) pair

(continued on next page)

1. (cont.)

(e)

H_3C — (epoxide on cyclopentane) $\xrightarrow[\text{cat. } H_2SO_4]{CH_3OH}$ (product: cyclopentane with CH_3, OH, OCH_3 substituents)

(±)

(±)   +6

+3 miscounting carbons

(f)

(diene) + (cyclohexadienedione) $\longrightarrow$ (bicyclic product) with O, O

+6

+3 no S.C

(±)
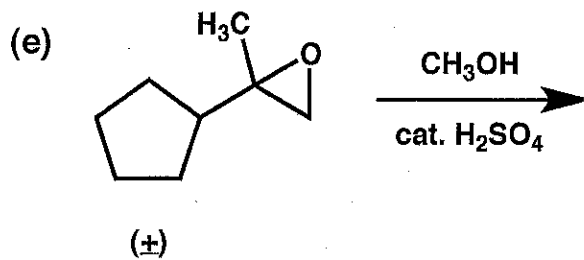
2. (8 points) Draw all of the other resonance structures for the carbocation shown below. Skeletal drawings (no H's) are acceptable, if they are correct.
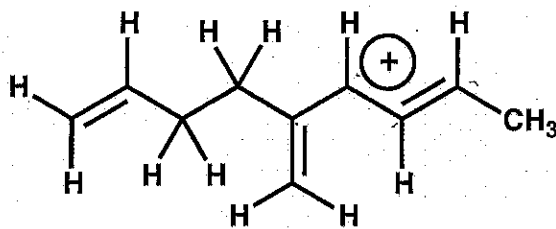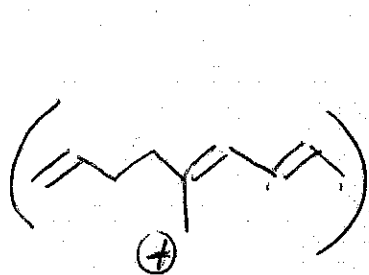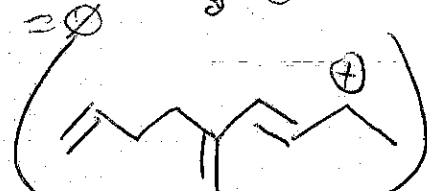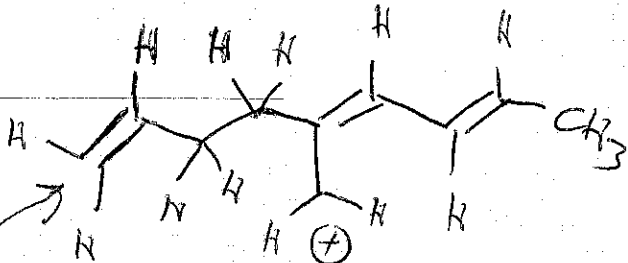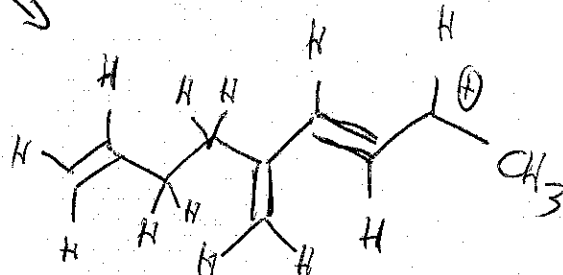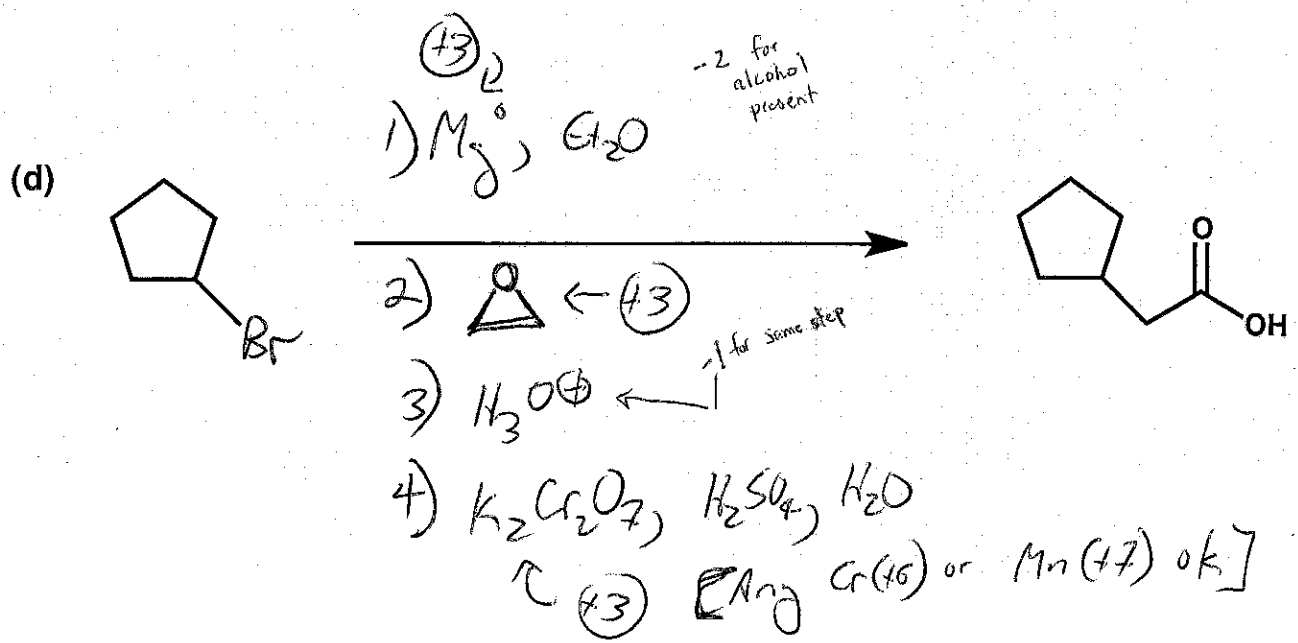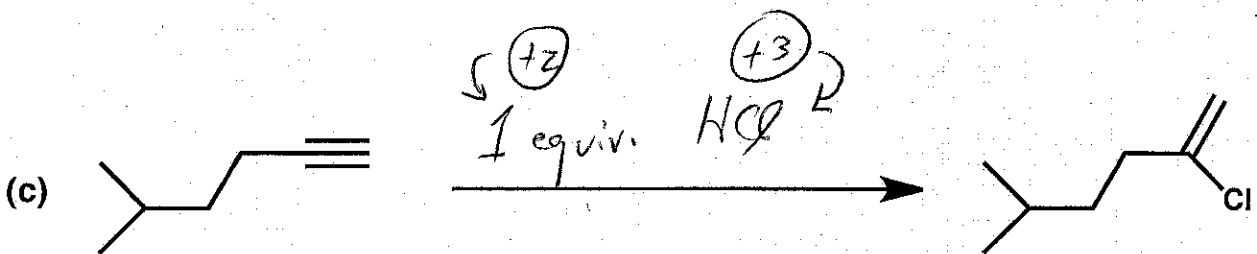
*NO positive charge specified = Ø

unnecessary pushing of these e⁻
+2 each

+4 for each correct structure
(-1 for additional/incorrect structure) each
forgetting a double bond (-1)

3. (25 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 H

+5

+2 H

OCH_3

CH_3O

O

O

O

OCH_3

OCH_3

O

(b)

$CHCl_3$ +3

$tBuO^{\ominus} K^{\oplus}$ +3

Cl   Cl

(c)

+2

1 equiv.

+3

HCl

Cl

(d)

+3

1) Mg^0, Et_2O

−2 for alcohol present

2) △ ← +3

−1 for same step

3) $H_3O^{\oplus}$ ←

4) $K_2Cr_2O_7$, H_2SO_4, H_2O

+3   [ArO $Cr(+6)$ or $Mn(+7)$ ok]

Br

O

OH
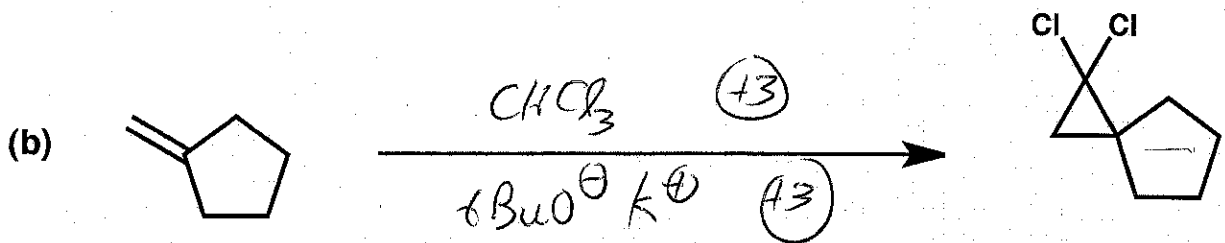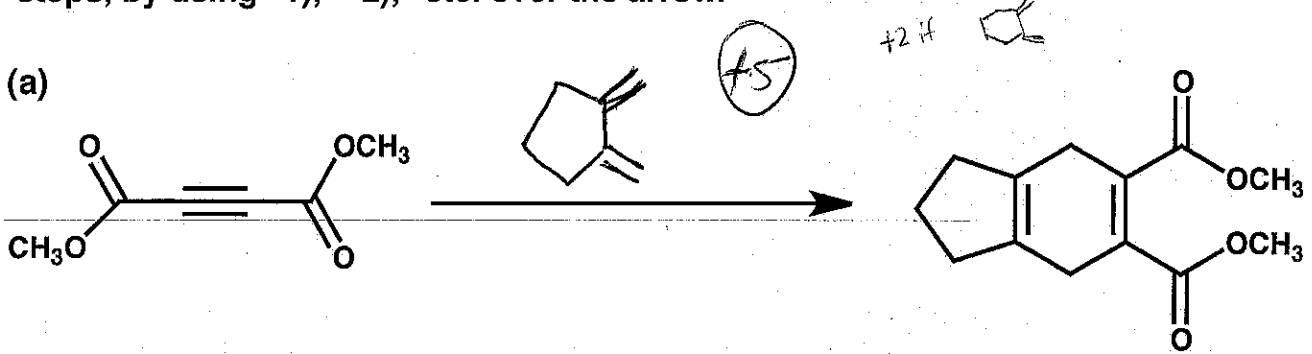
4. (16 points) Propose one structure each for molecules A and B (there may be more than one correct answer).

Molecule A has the formula $C_{10}H_{14}$ and is not chiral.
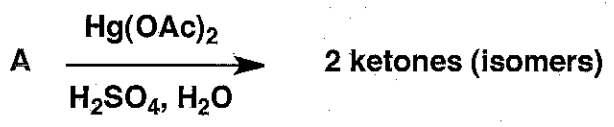
Molecule A reacts with 1 equivalent of H_2 in the presence of a poisoned catalyst, but with 2 equivalents of H_2 in the presence of Pd/C.

A =

$$A \xrightarrow[\text{H}_2\text{SO}_4,\ \text{H}_2\text{O}]{\text{Hg(OAc)}_2} \text{2 ketones (isomers)}$$

(+8)

Many possibilities ✓

General: R–C≡C–R'

etc.

Molecule B has the formula C_7H_7F and is not chiral.

$$B \xrightarrow{\text{Br}_2} \text{No reaction}$$

$$B \xrightarrow[\substack{\text{poisoned} \\ \text{catalyst}}]{\text{H}_2} \text{no reaction}$$

B =

(+8)

(or multi-rings...)

5. (30 points)

Ph   Cl

CH₃CH₂CH₂ ⟍ ⟍ OH   **G**
        CH₃
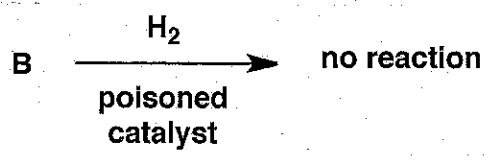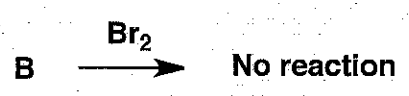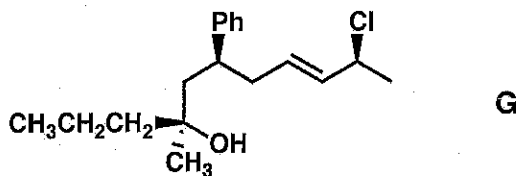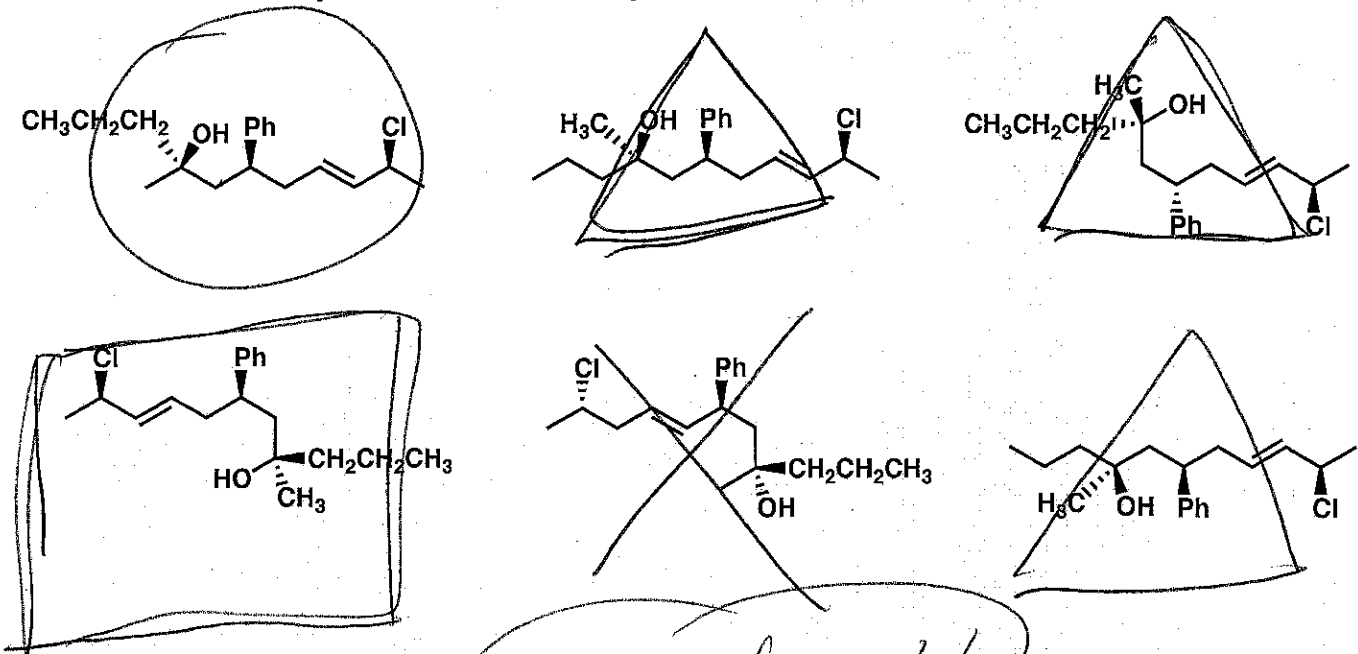
Among the structures drawn below the line, indicate isomeric relationships to the structure of molecule G, drawn above, by following the directions below. Molecule G is a single enantiomer.

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

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

Put a TRIANGLE around any structure that corresponds to a DIASTEREOMER of G.

Put an X across any structure that corresponds to a CONSTITUTIONAL ISOMER of G.

CH₃CH₂CH₂ OH Ph   Cl

H₃C, OH Ph   Cl

H₃C OH
CH₃CH₂CH₂ Ph Cl

Cl Ph
HO CH₂CH₂CH₃
CH₃

Cl Ph
CH₂CH₂CH₃
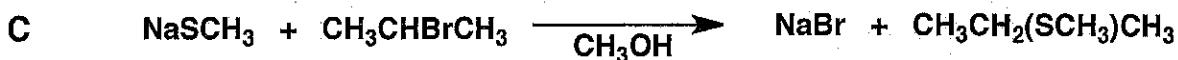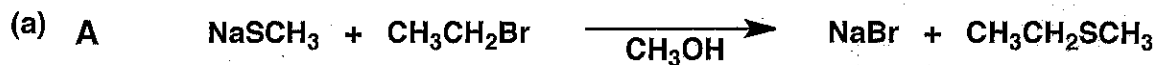OH

H₃C OH Ph   Cl

+5 each symbol

6. (12 points) Provide drawings for the most stable conformation of the molecule shown below (which is a single enantiomer), and for the most stable conformation of the diastereomer that has the opposite configuration at the carbon bearing the bromine atom.

Diastereomer:

C(CH₃)₃

⋯Cl
CH₃
Br

Br

H₃C

Cl

Br

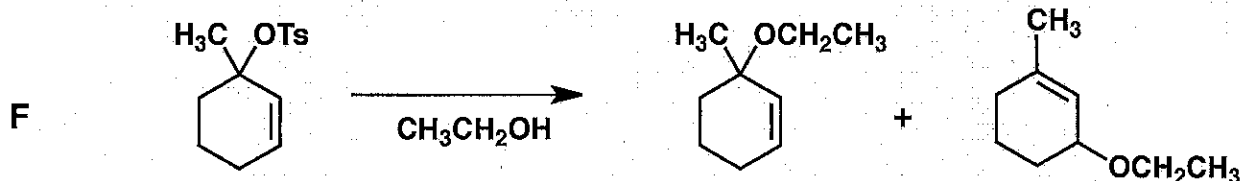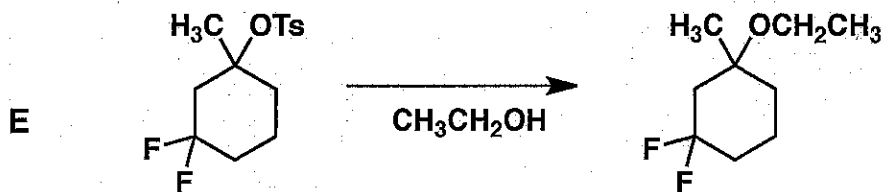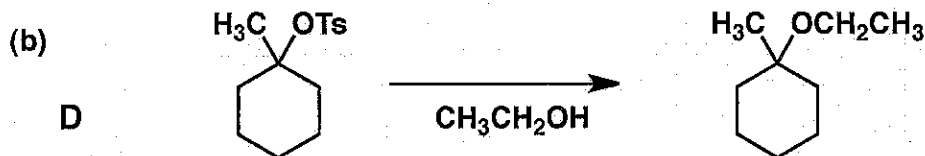H₃C

Cl

+3 enantiomer   +6

+6
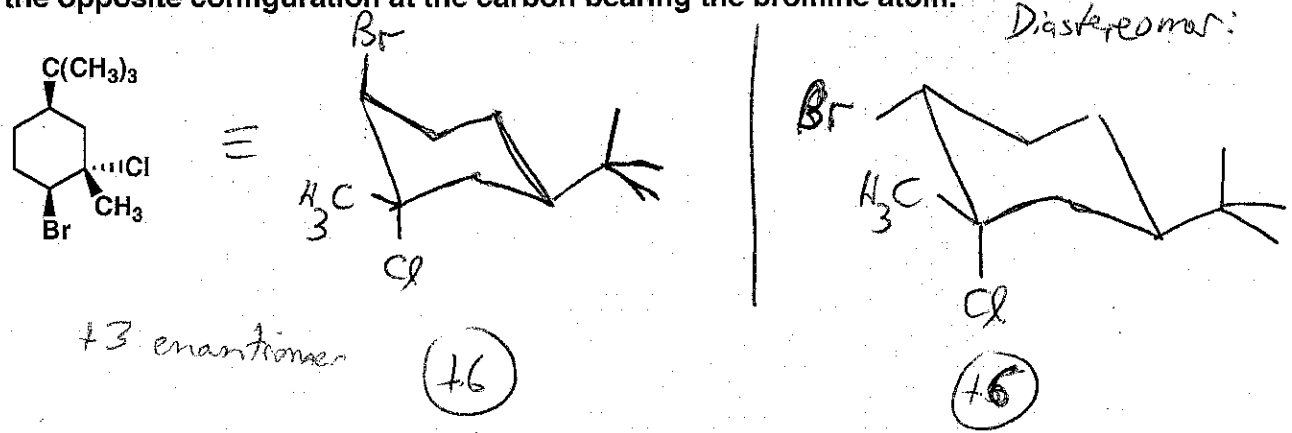
7. (10 points) For each set of reactions shown below, indicate the expected order of reaction rates (fastest vs. intermediate vs. slowest) using the designations A-C or D-F. Note: Do not be concerned about other products that might form during these reactions.

(a) A $NaSCH_3$ + CH_3CH_2Br $\xrightarrow{CH_3OH}$ $NaBr$ + $CH_3CH_2SCH_3$

B $NaSCH_3$ + CH_3CH_2Br $\xrightarrow{DMF}$ $NaBr$ + $CH_3CH_2SCH_3$

C $NaSCH_3$ + $CH_3CHBrCH_3$ $\xrightarrow{CH_3OH}$ $NaBr$ + $CH_3CH_2(SCH_3)CH_3$

Fastest = __B__   Intermediate = __A__   Slowest = __C__

(+5)

(all or none)

(b)

D

$\xrightarrow{CH_3CH_2OH}$

E

$\xrightarrow{CH_3CH_2OH}$

F

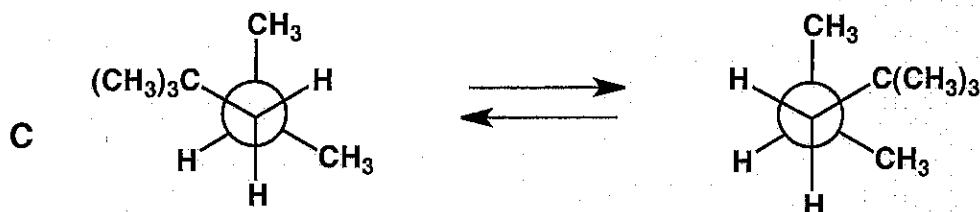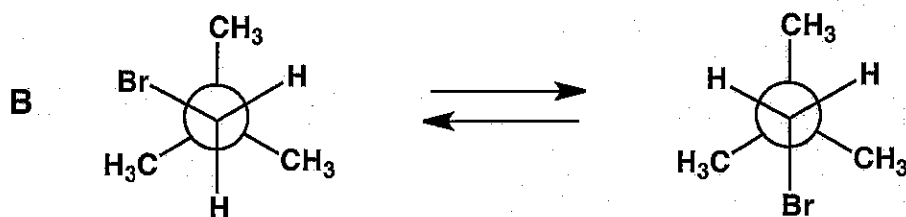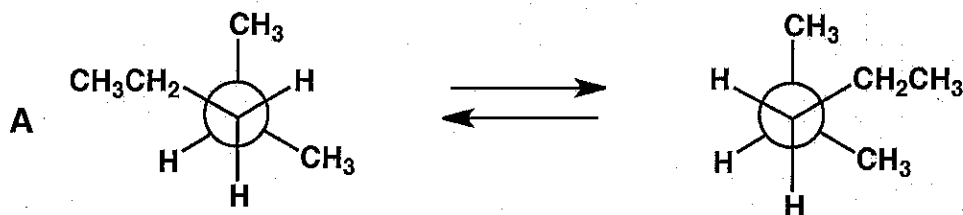$\xrightarrow{CH_3CH_2OH}$

Fastest = __F__   Intermediate = __D__   Slowest = __E__

(+5)

(all or none)

Name *PM key*

8. (5 points) For the set of equilibria shown below, indicate the order in propensity to lie to the right (most vs. intermediate vs. least), using the designations A-C.

A

B

C

Most = **B**   Intermediate = **A**   Least = **C**

(+5)

(all or none)

9. (6 points) Using the 'simplified' rules we discussed in class for assigning oxidation states to carbon atoms within molecules, categorize each of the reactions below as "oxidation", "reduction" or "no redox change". These categorizations should be based on the organic molecules to the left and right of the arrow; do not be concerned with any reagents. Also, do not concern yourself with the mechanism of any reaction below, which will be covered in Chemistry 345.

CIRCLE ONE
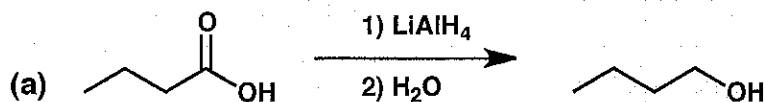
(a)

1) $LiAlH_4$

2) H_2O

Oxidation
Reduction
No redox change

+3

(b)

CH_3ONa

CH_3OH

Oxidation
Reduction
No redox change

+3
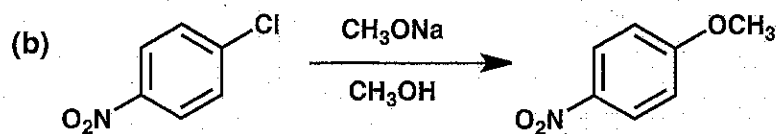
10. (18 points) Provide a mechanism (curved arrows) for each reaction shown below. Be sure to show intermediates.

(a)

cat. CH₃CH₂ONa

CH₃CH₂OH

OCH₂CH₃
OH

(+ CH₃CH₂O:⁻ Na⁺)

CH₃CH₂O:⁻
Na⁺

+2 for arrows

[16 total]

+2 for arrows

H–OCH₂CH₃

10° carbocation → ∅

+2 for intermediate

+2 for intermediate

∅ points total

(b)

OH

cat. HCl

CH₃OH

O

(+ CH₃OH₂⁺ Cl⁻)

(ok if Cl⁻ acts as base)

CH₃O:H

CH₃–O⁺–H
H

Cl⁻

ok if HCl is proton source)

Cl⁻

H–O⁺

Cl⁻

⁺

OH

⁺
OH

Cl⁻
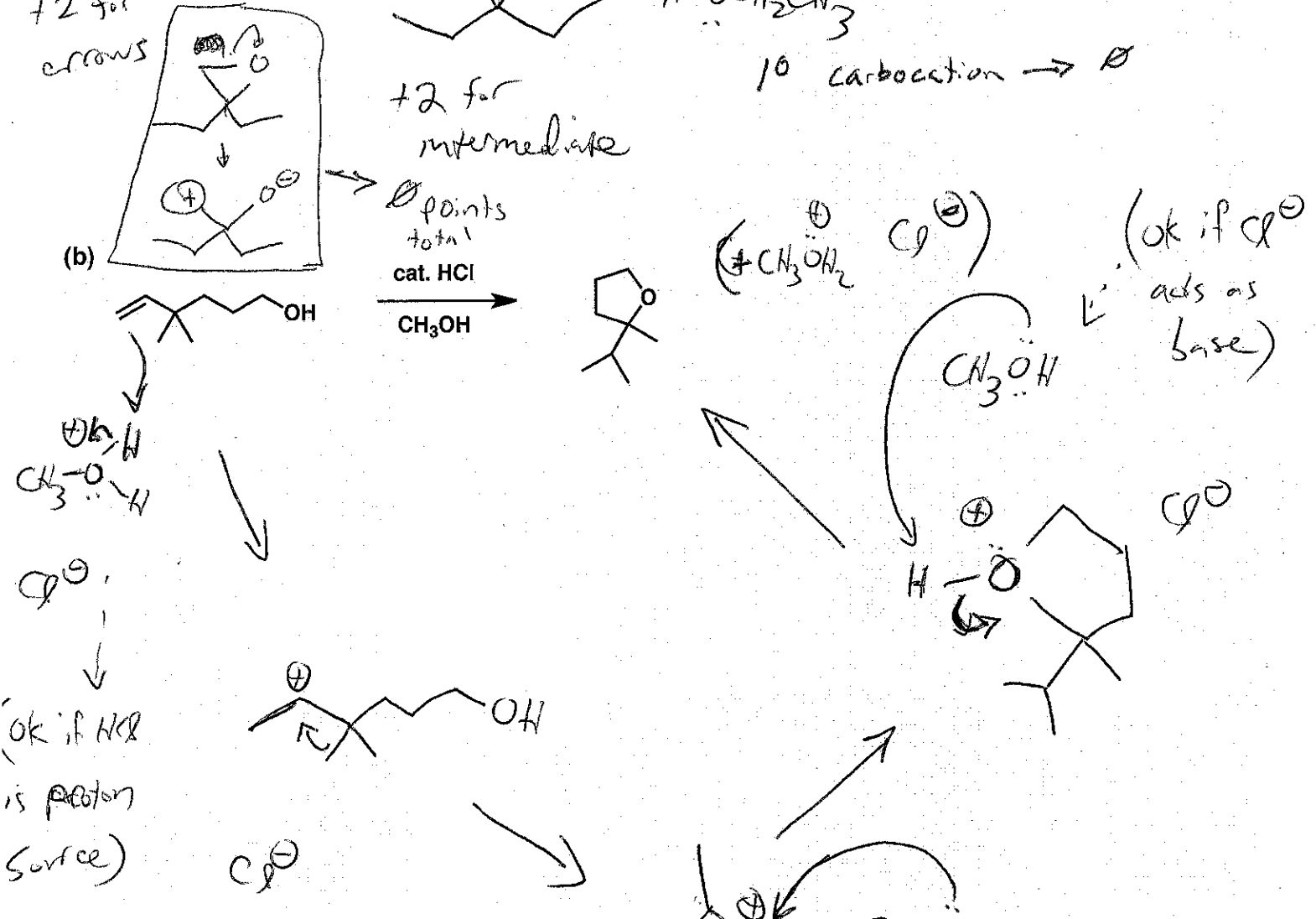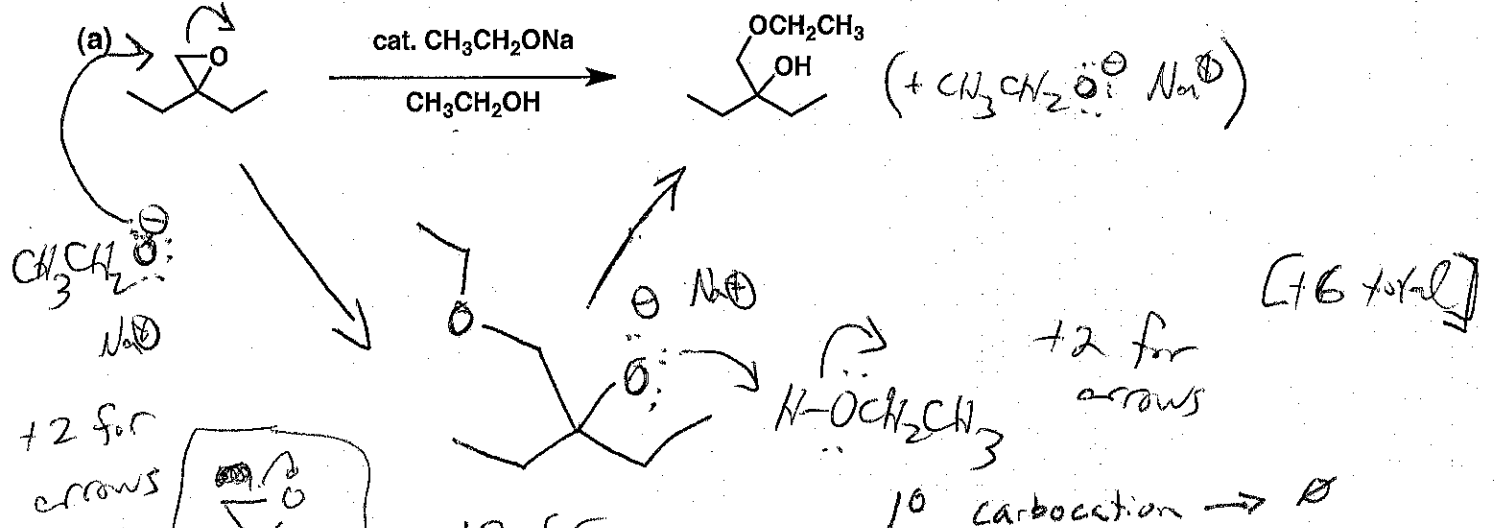
+1 for each curved arrow
(16 total)

+2 for each intermediate
(16 total)

11. (30 points) Devise a synthetic route from the indicated starting material to the indicated target in each of the two cases below. Each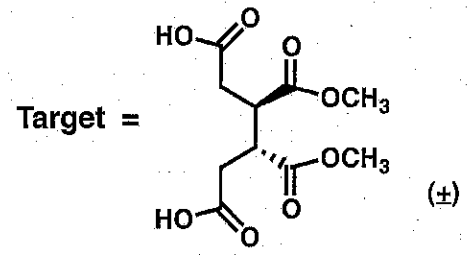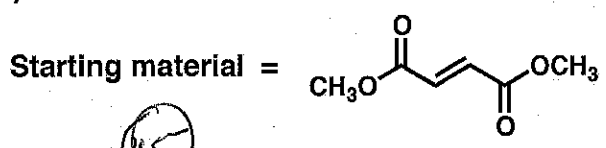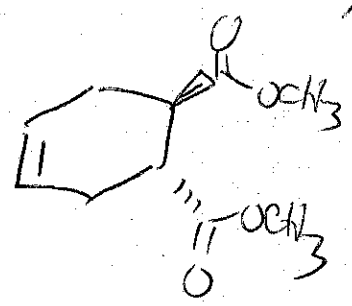 route should be as short and as selective as possible. You may use _any_ other organic molecules and any inorganic reagents in your synthetic plans. Show the expected product after each step in each synthetic route. (Do not provide mechanistic information.)

(a) 10 points

Starting material = CH₃O—C(=O)—CH=CH—C(=O)—OCH₃

Target = HO—C(=O)—CH₂—CH(—C(=O)—OCH₃)—CH(—C(=O)—OCH₃)—CH₂—C(=O)—OH   (±)

(Diels-
Alder)
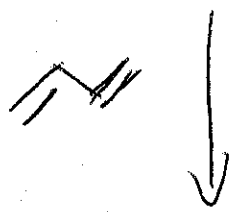
Can not go through
a route where form 2°
alkyl halide and use
acetylenic ~~acid~~ anion
b/c acetylenic anion
only works on 1° RX

1) O₃   (+3)
2) H₂O₂ (+2)

-- cont. on next page --

11. (cont.)

20 points

Starting material =
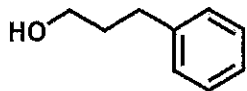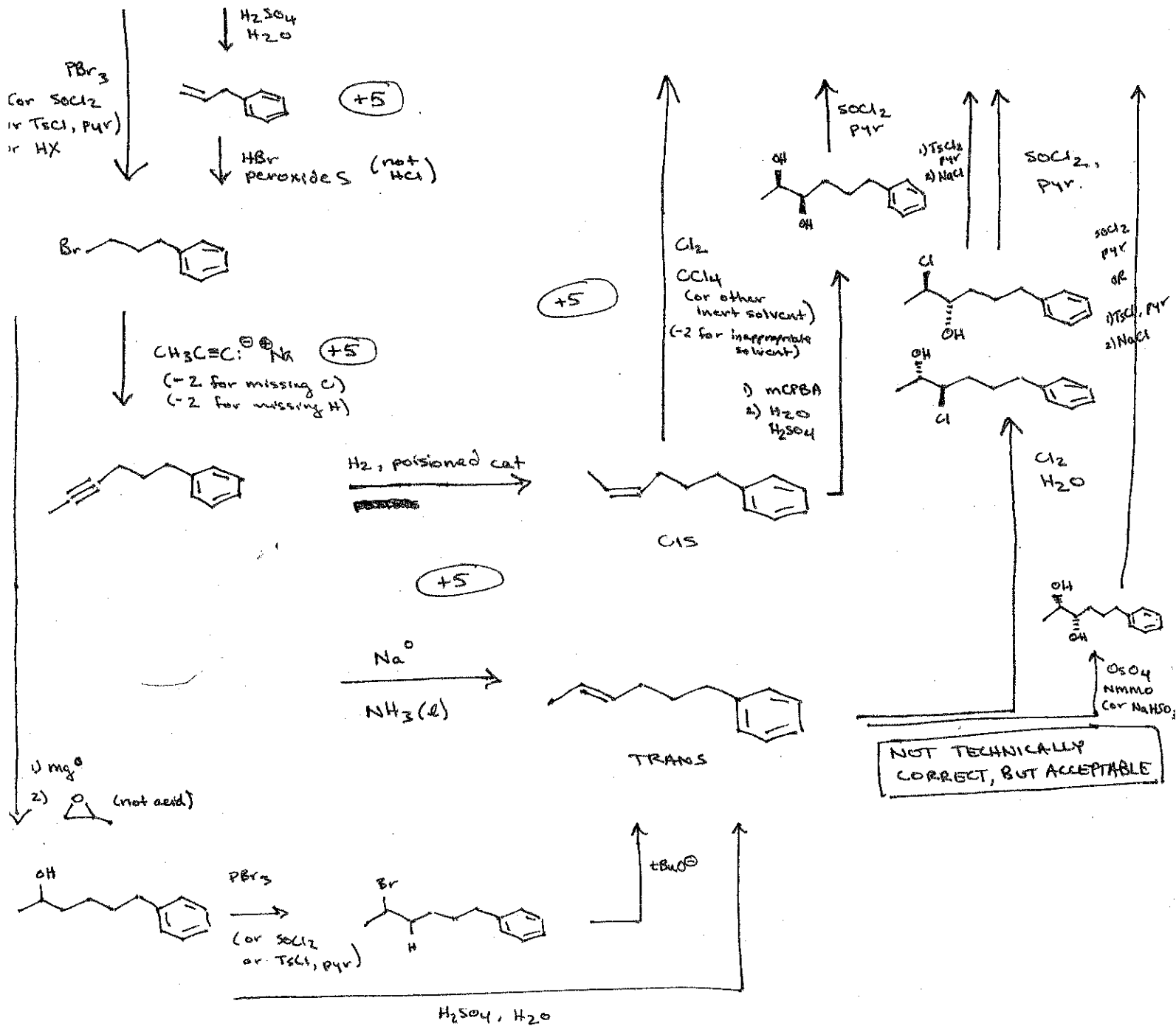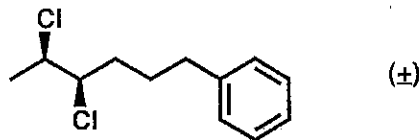

HO CH₂CH₂CH₂-phenyl

Target =

Cl, Cl dichloro with phenyl chain

(±)

PBr₃
(or SOCl₂
or TsCl, Pyr)
or HX

↓ H₂SO₄ / H₂O

allylbenzene   (+5)

↓ HBr peroxides (not HCl)

Br-CH₂CH₂CH₂-phenyl

↓ CH₃C≡C:⁻ ⊕Na   (+5)
(−2 for missing C)
(−2 for missing H)

alkyne chain

→ H₂, poisioned cat
~~Pd/CaCO₃~~

cis alkene

CIS

Cl₂
CCl₄
(or other inert solvent)
(−2 for inappropriate solvent)

1) mCPBA
2) H₂O / H₂SO₄

→ SOCl₂ / Pyr

OH diol intermediate OH   (+5)

1) TsCl₂ Pyr
2) NaCl

→ SOCl₂ Pyr

Cl ... OH intermediate

SOCl₂, Pyr.

SOCl₂ Pyr OR
1) TsCl, Pyr
2) NaCl

OH ... Cl intermediate

Cl₂ H₂O

OH ... OH intermediate

OsO₄ NMMO (or NaHSO₃)

[NOT TECHNICALLY CORRECT, BUT ACCEPTABLE]

→ Na° / NH₃(l)

TRANS

↓ 1) Mg°
2) epoxide (not acid)

OH secondary alcohol with phenyl chain

→ PBr₃
(or SOCl₂
or TsCl, Pyr)

Br / H intermediate

→ tBuO⁻

→ H₂SO₄, H₂O

can not use excess HCl w/ alkyne b/c both Cl groups will add to the same carbon (p. 653)