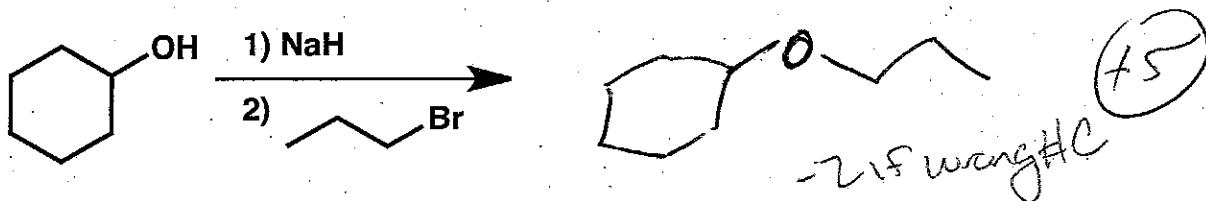Last Name *Answer*
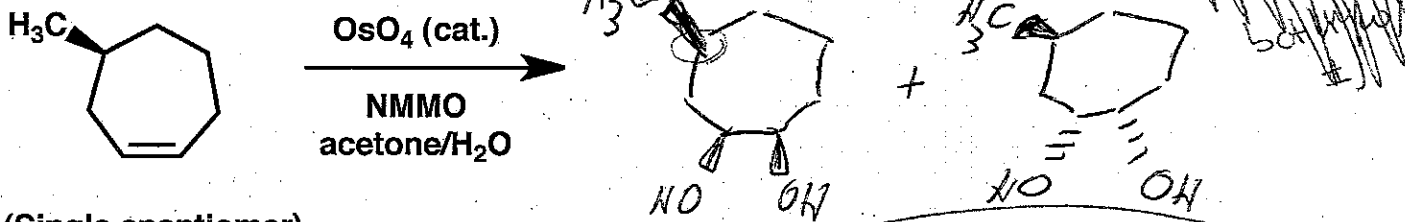
First Name *Key*

General Instructions:

(i) Use scratch paper at the back of the 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.

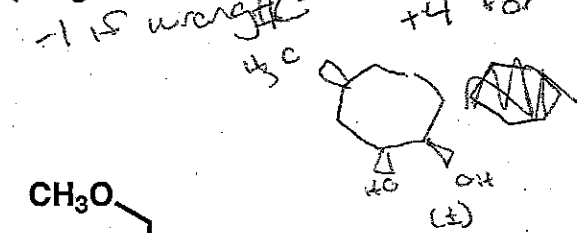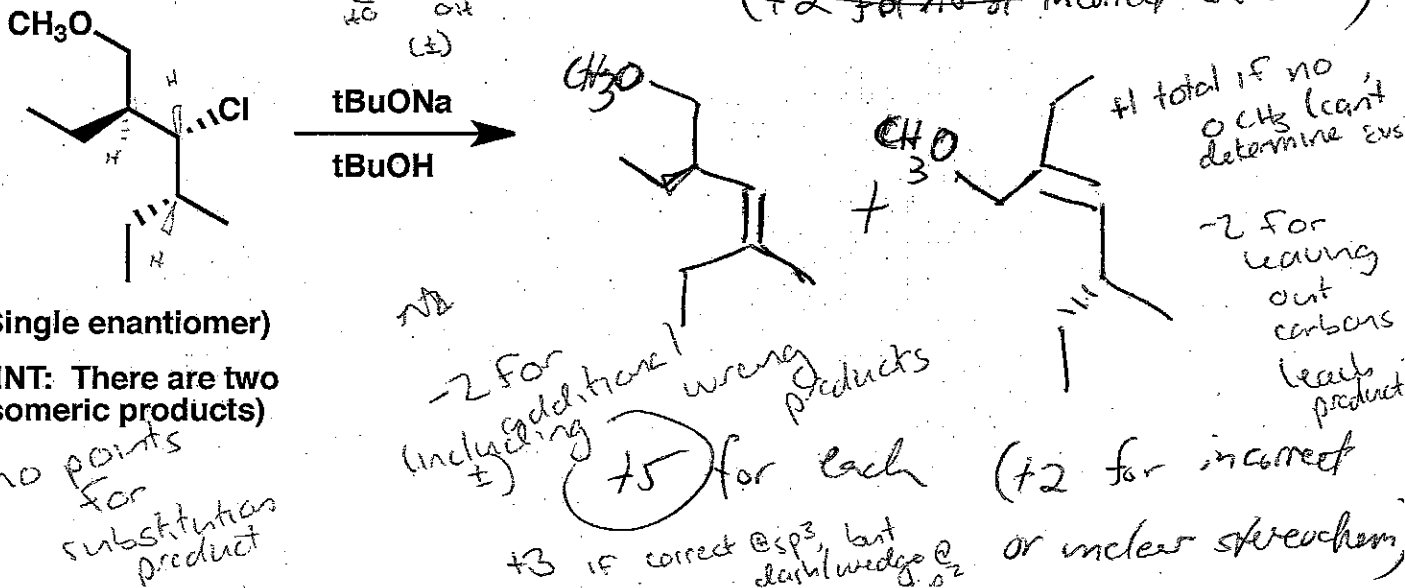1. (21 points) Show the major product(s) expected from the reactions below.

(a)

1) NaH

2) ~~~Br

+5

−2 if wrong HC

(b)

OsO₄ (cat.)

NMMO
acetone/H₂O

(Single enantiomer)

no points if anti diol

+4 for one; +6 for both

(+2 for AD or incorrect stereochem)

−1 if wrong HC

+4 for

(±)

(c)

tBuONa

tBuOH

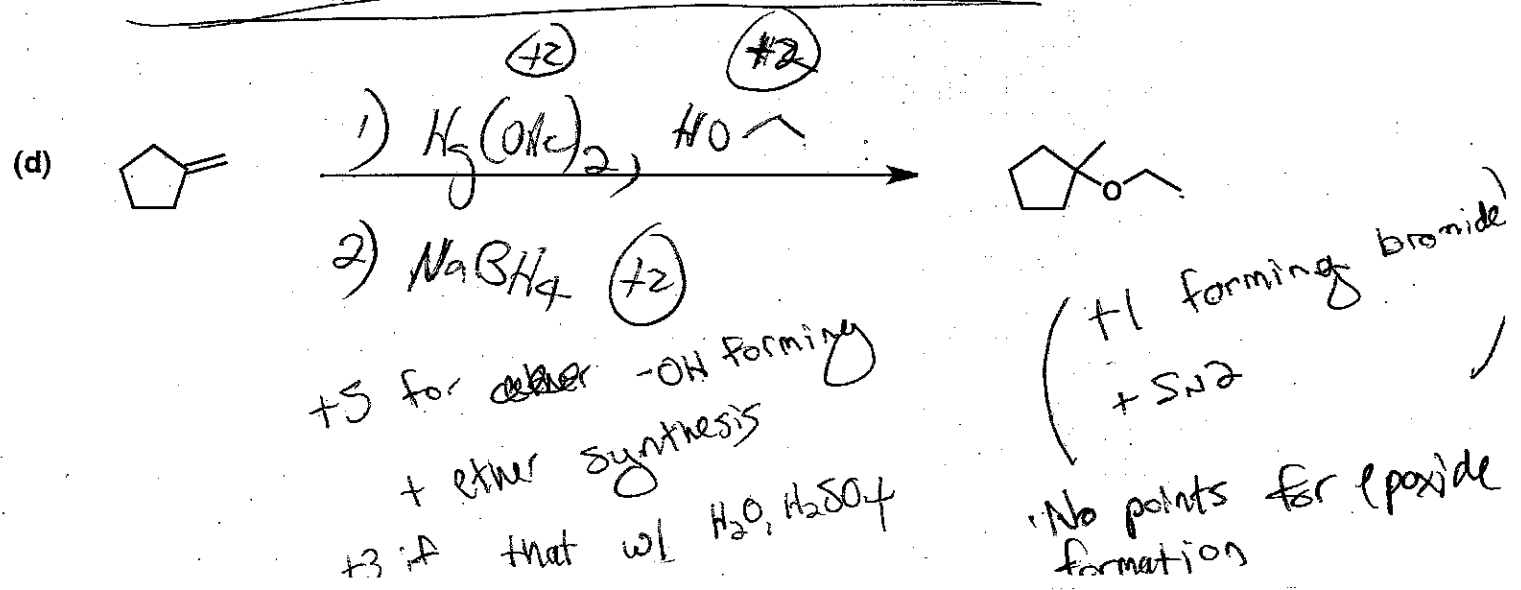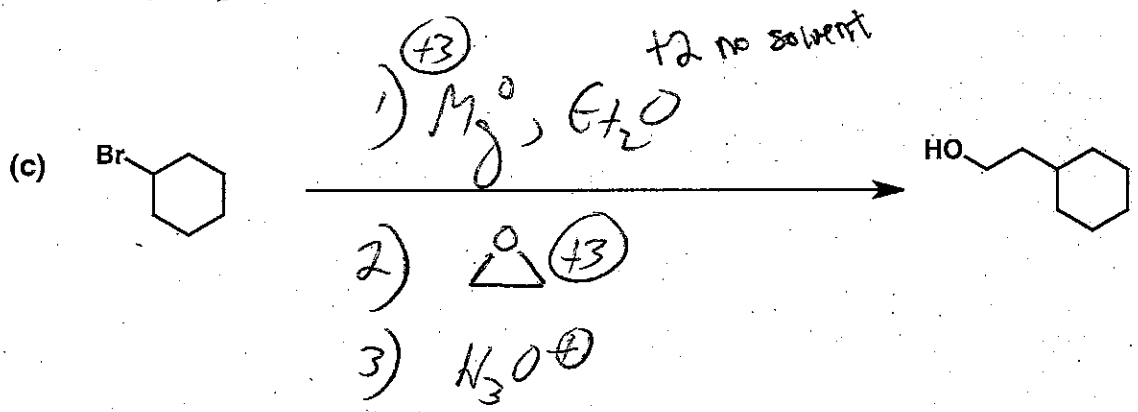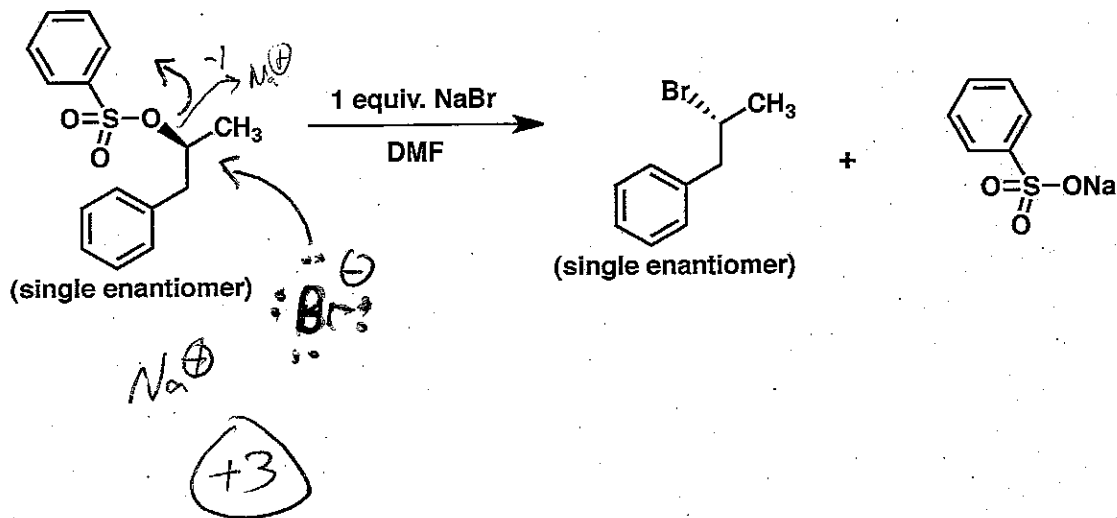(Single enantiomer)

(HINT: There are two isomeric products)

no points for substitution product

−2 for additional wrong products (including ±)

+5 for each

+1 total if no OCH₃ (can't determine E vs)

−2 for leaving out carbons in each product

(+2 for incorrect or unclear stereochem)

+3 if correct @ sp³ but dash/wedge @ sp²

2. (22 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.
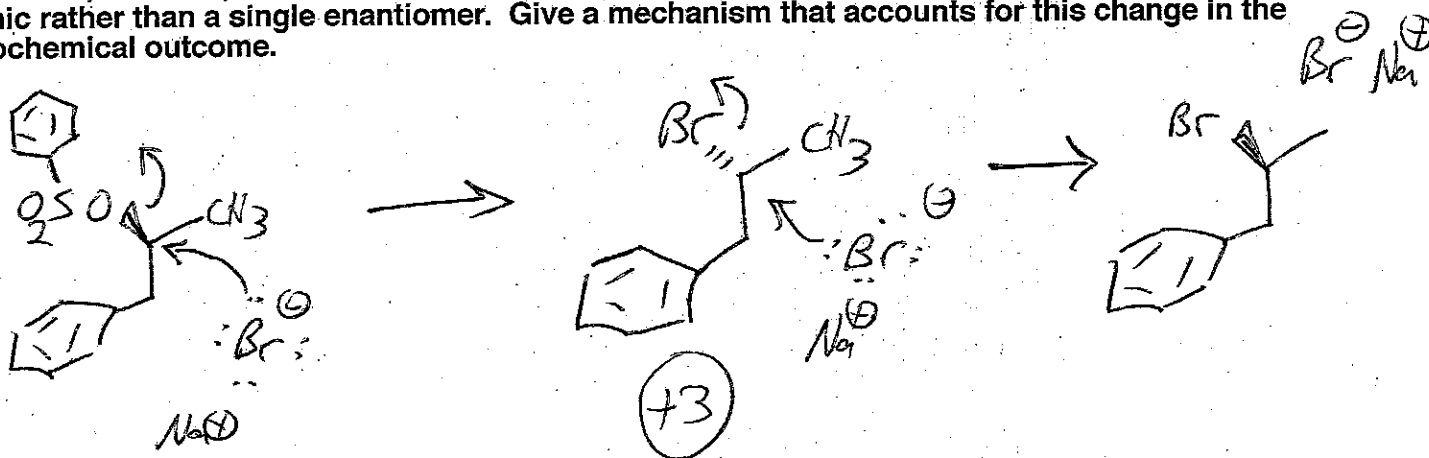
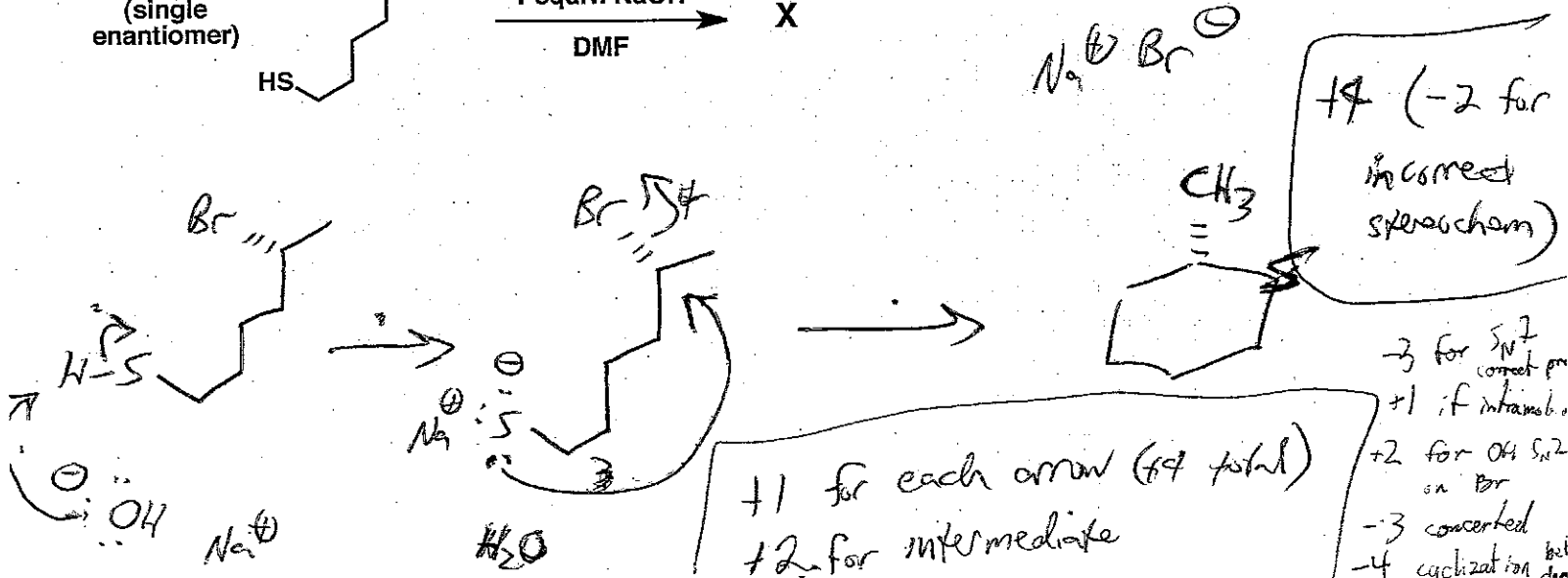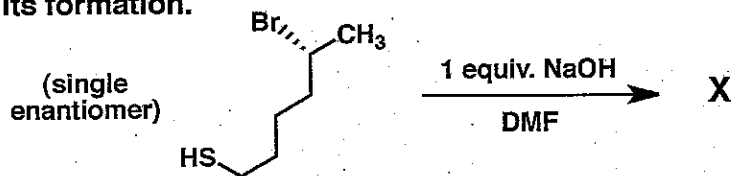(a) [structure: decalin with OH] $\xrightarrow[\text{$H_2O$, H_2SO_4 (+1)}]{\text{$K_2Cr_2O_7$ (+4) (PCC)}}$ [structure: decalin with ketone]

(minus points w/ excess stuff)

(b) [structure: alkene with OH] $\xrightarrow[\text{pyridine (+1)}]{\text{$SOCl_2$ (+4)}}$ [structure: alkene with Cl]

(c) Br–[cyclohexane] $\xrightarrow{}$ HO–[chain]–[cyclohexane]

1) Mg^0, Et_2O (+3)   +2 no solvent

2) [epoxide] (+3)

3) $H_3O^{\oplus}$

(d) [methylenecyclopentane] $\xrightarrow{}$ [cyclopentane with O-ethyl]

1) $Hg(OAc)_2$, $HO\frown$ (+2) (+2)

2) $NaBH_4$ (+2)

+5 for ether -OH forming
+ ether synthesis
+3 if   that w/ H_2O, H_2SO_4

(+1 forming bromide
  + S_N2)

No points for epoxide formation

3. (16 points)

3 pts (a) Provide a mechanism (curved arrows) for the reaction shown below.

(single enantiomer)   1 equiv. NaBr / DMF →   (single enantiomer)   +

+3

3 pts (b) In the reaction above, the organic starting material and NaBr are added in equimolar amounts. If, however, a 10-fold molar excess of NaBr is used, the resulting alkyl bromide is racemic rather than a single enantiomer. Give a mechanism that accounts for this change in the stereochemical outcome.
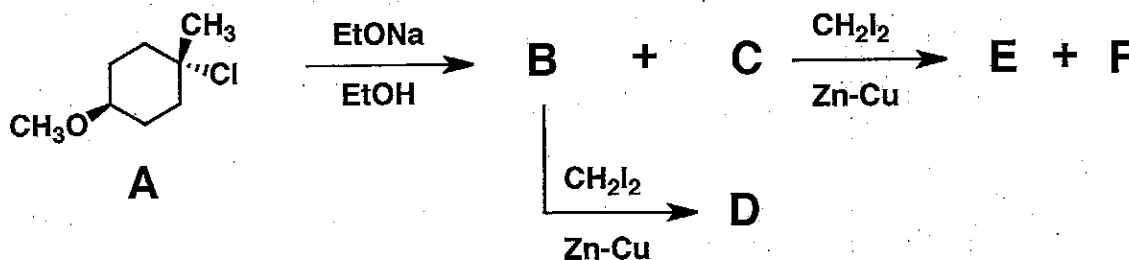

+3

10 pts. (c) The reaction below leads to formation of one organic product, X, which does not react further when exposed to H_2 and Pd/C. Show the structure of X and a mechanism to account for its formation.

(single enantiomer)   1 equiv. NaOH / DMF →   X

+1 for each arrow (+4 total)
+2 for intermediate

+4 (-2 for incorrect stereochem)

-3 for S_N1 correct pr
+1 if intramol.
+2 for OH S_N2 on Br
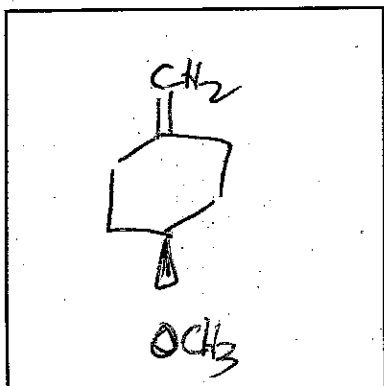-3 concerted
-4 cyclization but ...

4. (25 points) Treatment of molecule A with sodium ethoxide in ethanol produces two isomeric products, B and C. B is achiral, while C is a racemic mixture. After B and C are separated from one another, each is allowed to react with the reagents shown. B produces a single achiral product, D, while C produces two isomeric products, E and F, each of which is a racemic mixture.

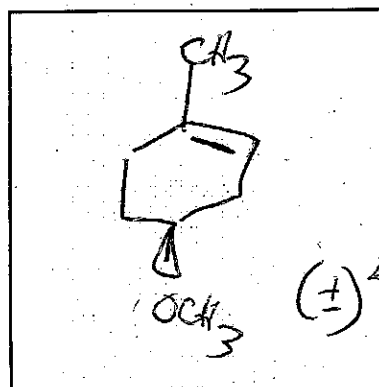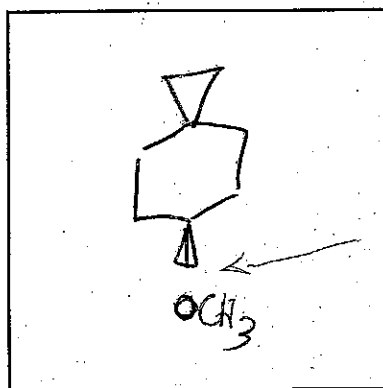Draw structures for B-F in the boxes. For racemic mixtures, only one enantiomer need be drawn.

A → EtONa / EtOH → B + C → CH$_2$I$_2$ / Zn-Cu → E + F

B → CH$_2$I$_2$ / Zn-Cu → D

−1 for =CH$_3$

B =

C =

reverse B and C 3 for each

(±) ← Not required

+5 each
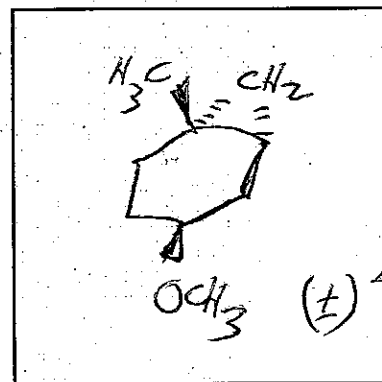
D =

E =

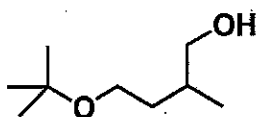(±) ← Not required

F =

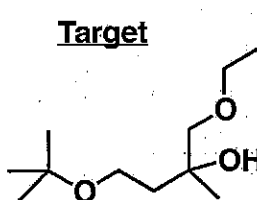(±) ← Not required

missing stereochem −1 each
missing line −2

combining racemers of E + F −1 each

5. (16 points) Suggest a synthetic route (i.e., a specific sequence of reactions) that would be expected to produce the "target" molecule from the indicated starting material. You may use any reagents in your proposed route. Try to reach the target with the fewest possible reactions, and try to choose reactions that are as selective as possible for one target (rather than a mixture of targets).
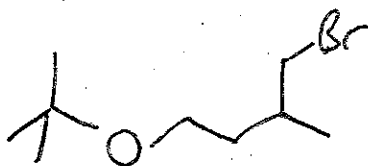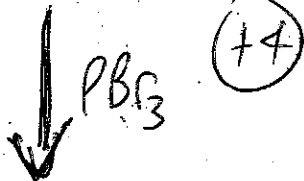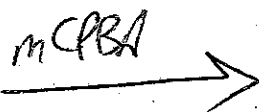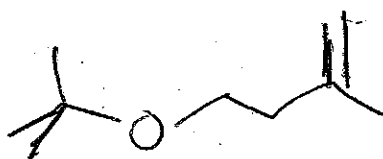
Starting Material   **Target**
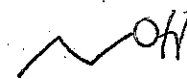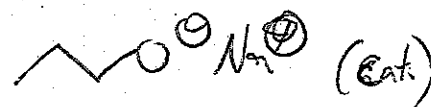

(SOCl₂, pyridine
        or
TsCl, pyridine
ok)

PBr₃   (+4)

(+4)

(±)

↑BuOK, ↑BuOH   (+4)

−2 ❓ in general
for reagent
mistakes

−2 for no ↑BuOK
(just ↑BuOH)

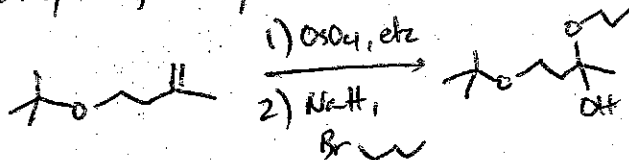mCPBA

(any peracid
ok)

(+4)

∼∼∼O⁻ Na⁺ (Cat.)

∼∼∼OH

O points for acidic
ring opening
‑‑‑‑‑‑‑‑‑‑‑
2 pts for
H₂O-ring opening
then alkylation

+4 (out of 8) points for
dihydroxylation/monoalkylation

1) OsO₄, etc.
2) NaH,
   Br∼∼

2 pts for alkylating starting
alcohol and getting nowhere

R∼∼OH →(NaH, Br∼∼)→ R∼∼O∼∼

+2 points (out of 8) for trying:

R∼∼OH →(H₂SO₄, H₂O)→ R∼∼