Name (First, MI, Last): ANSWER KEY

Student ID Number: PROF CANTRILL

Chem 30B Fall 2003

FINAL EXAM
(180 Min)

Monday December 8th

Q1	30 / 30	**Q6**	18 / 18	**Q11**	18 / 18
Q2	18 / 18	**Q7**	18 / 18	**Q12**	15 / 15
Q3	16 / 16	**Q8**	15 / 15	**Q13**	15 / 15
Q4	20 / 20	**Q9**	12 / 12	**Total**	230 / 200
Q5	15 / 15	**Q10**	20 / 20	**Final Course Grade**	A+

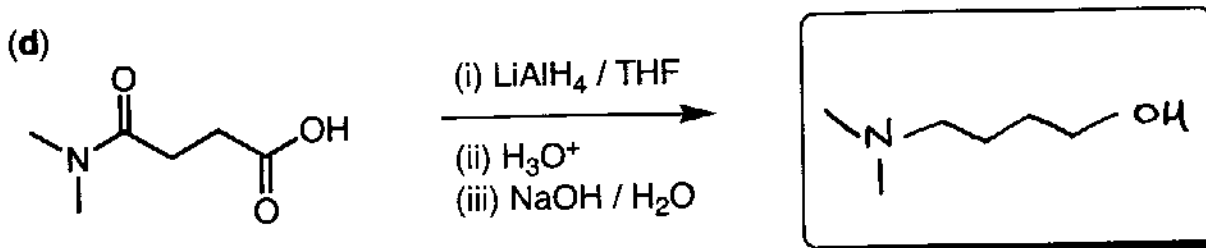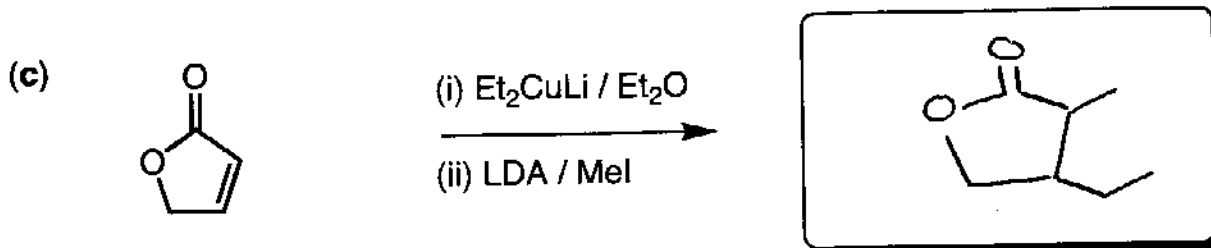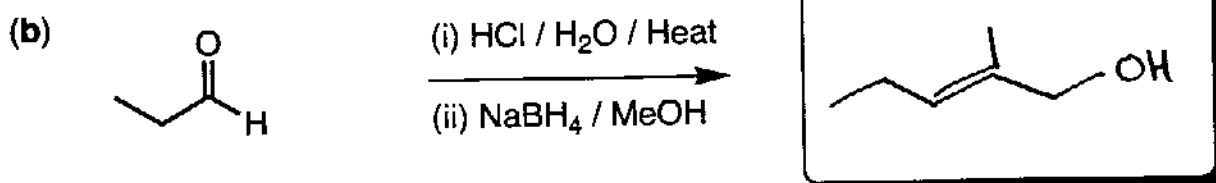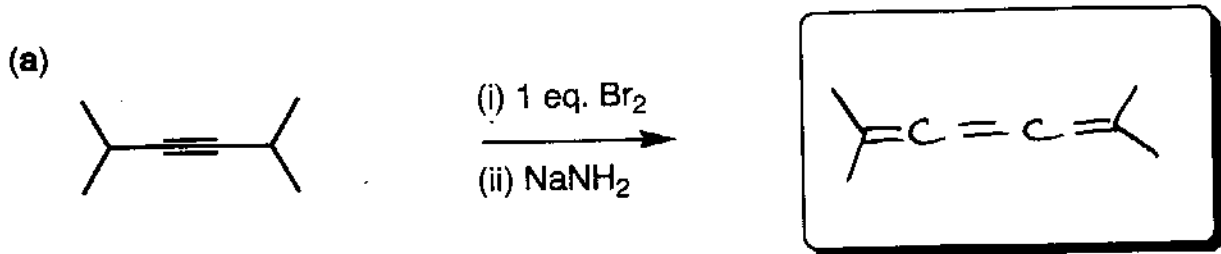***DO NOT OPEN THIS EXAM UNTIL INSTRUCTED TO DO SO***

ONLY ANSWERS WRITTEN IN THE BOXES PROVIDED WILL BE GRADED

*INTERPRETATION OF THE QUESTIONS IS PART OF THE EXAM –
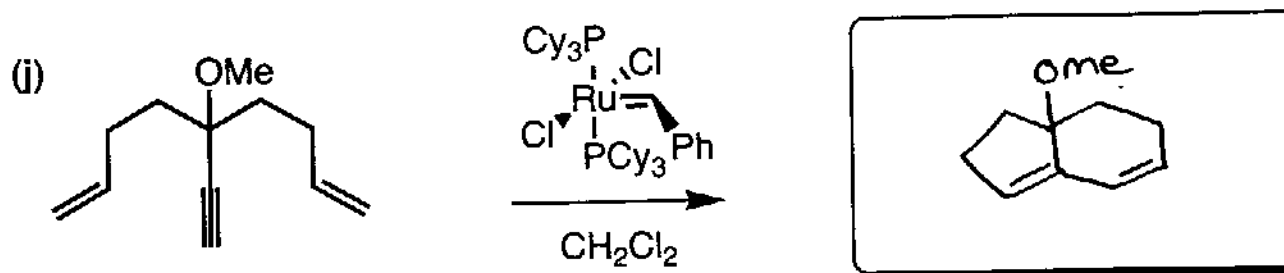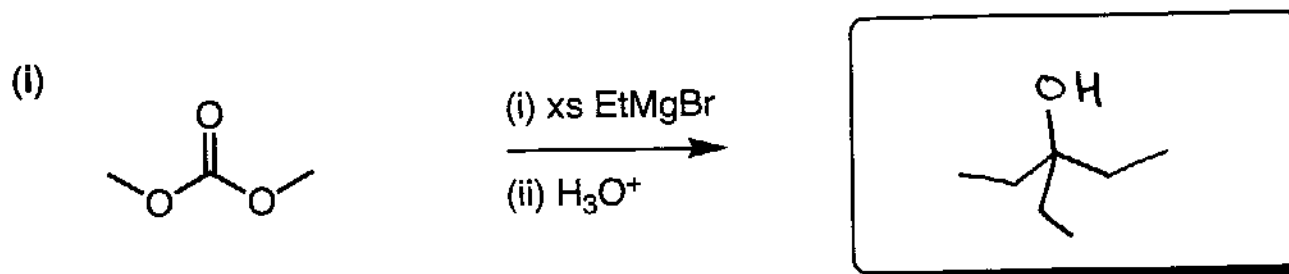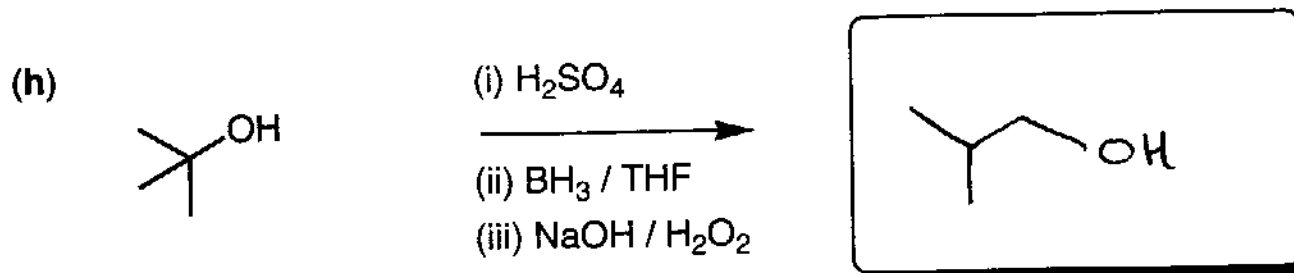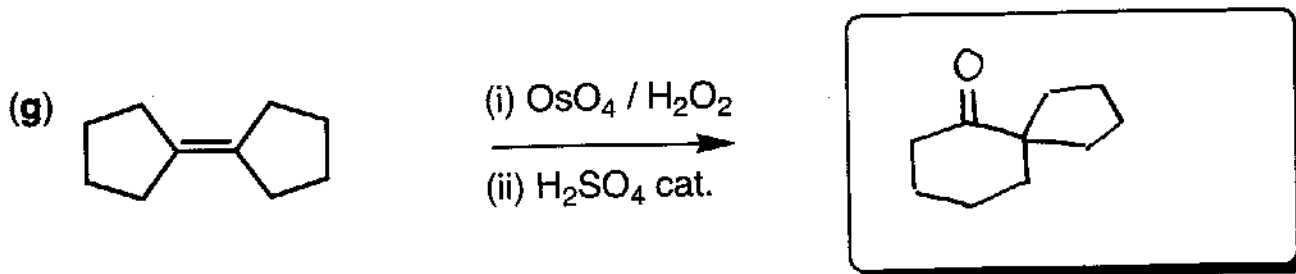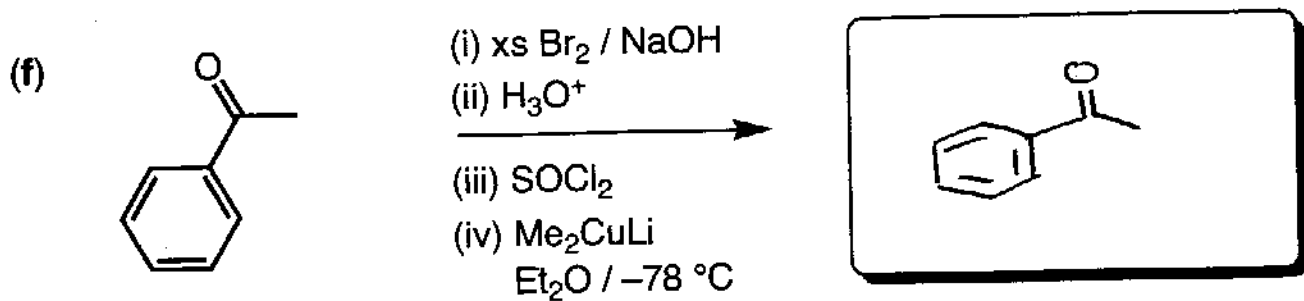DO NOT ASK FOR THE QUESTIONS TO BE EXPLAINED TO YOU*

"Every day you may make progress. Every step may be fruitful. Yet there will stretch out before you an ever-lengthening, ever-ascending, ever-improving path. You know you will never get to the end of the journey. But this, so far from discouraging, only adds to the joy and glory of the climb"

- Sir Winston Churchill

Question 1 Each of these reactions produces ONE MAJOR PRODUCT. In each case, draw this product in the box provided. For multi-step reactions just give the FINAL product, *i.e.*, no intermediates. (2 points each)

(a)

(i) 1 eq. Br_2
(ii) $NaNH_2$

(b)

(i) HCl / H_2O / Heat
(ii) $NaBH_4$ / MeOH

(c)

(i) Et_2CuLi / Et_2O
(ii) LDA / MeI

(d)

(i) $LiAlH_4$ / THF
(ii) H_3O^+
(iii) NaOH / H_2O

(e)

(i) O_3 / Me_2S
(ii) $NaBH_4$ / MeOH
(iii) TsCl / Et_3N
(iv) Na_2S
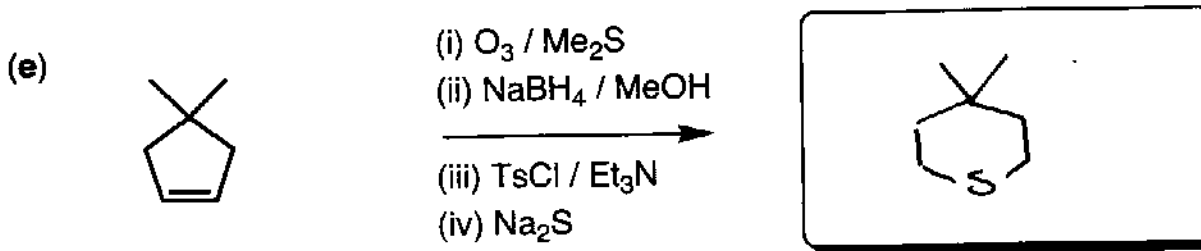
Question 1 continued on next page...

1

(f)

(i) xs Br₂ / NaOH
(ii) H₃O⁺

(iii) SOCl₂
(iv) Me₂CuLi
   Et₂O / −78 °C

(g)

(i) OsO₄ / H₂O₂

(ii) H₂SO₄ cat.

(h)

(i) H₂SO₄

(ii) BH₃ / THF
(iii) NaOH / H₂O₂

(i)

(i) xs EtMgBr

(ii) H₃O⁺

(j)

OMe

Cy₃P Cl
   Ru
Cl   PCy₃ Ph

CH₂Cl₂

OMe

(k)

Br_2 / KOH

$\xrightarrow{}$

H_2O

(l)

(i) $SOCl_2$

$\xrightarrow{}$

(ii) NaN_3

(iii) Heat

(m)

(i) $LiAlH_4$ / Et_2O

(ii) H_2O

$\xrightarrow{}$

(iii) H^+ /

(n)

MeOH / H^+

$\xrightarrow{}$

(o)

(i) PhLi / pentane

$\xrightarrow{}$

(ii) H_3O^+

3
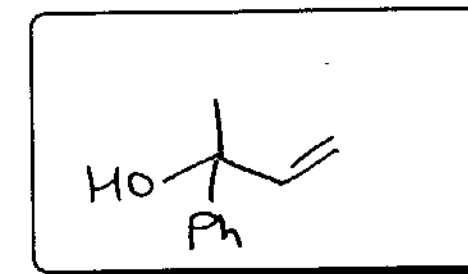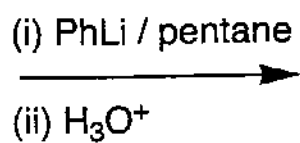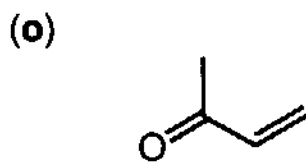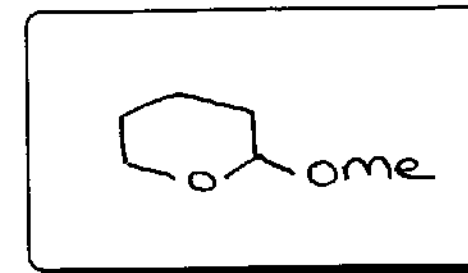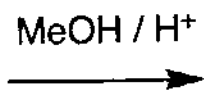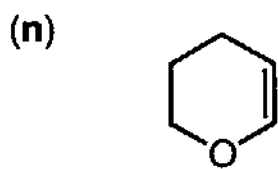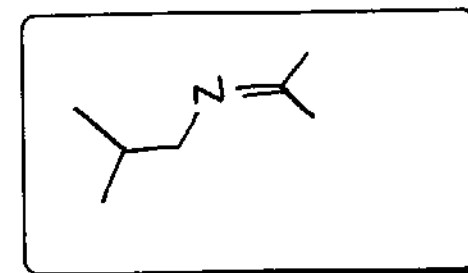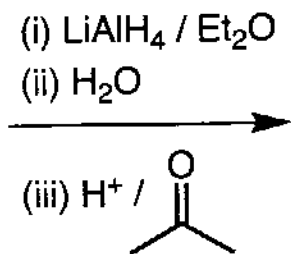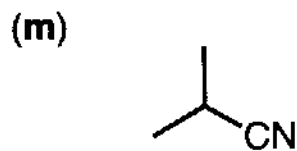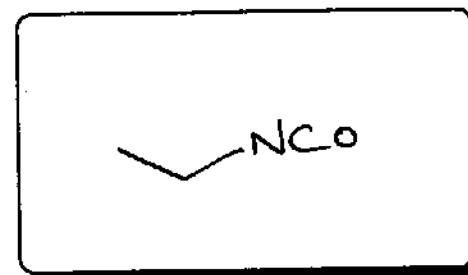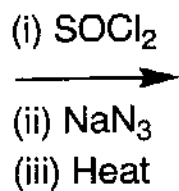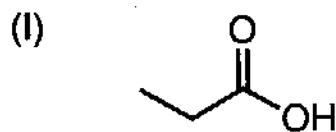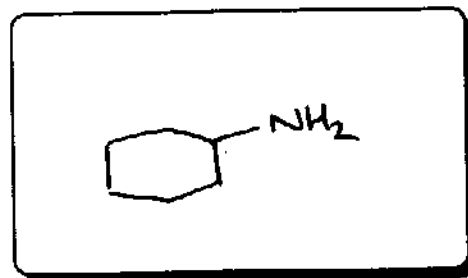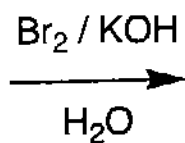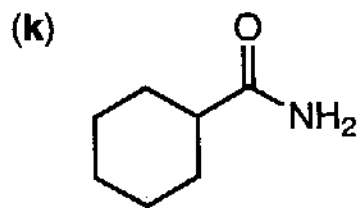
Question 2 Deuterium (D) is a heavier isotope of hydrogen (H). Chemical reagents in which certain H atoms have been replaced by D are used to perform reactions in which the products are isotopically labeled. For each of the reactions below, draw the structure of the final product, CAREFULLY INDICATING the position of the D atoms in the products. (3 points each)

(a)

xs D_2O / DCl (cat.)

(b)

Lindlar / D_2

(c)

(i) sia_2BD / THF

(ii) CH_3COOH

(d)

(i) $NaBD_4$

(ii) H_2O

(e)

(i) $LiAlD_4$ / Et_2O

(ii) D_2O

(f)

(i) Br_2
(ii) t–BuOK

(iii) Na / ND_3 (l)

4
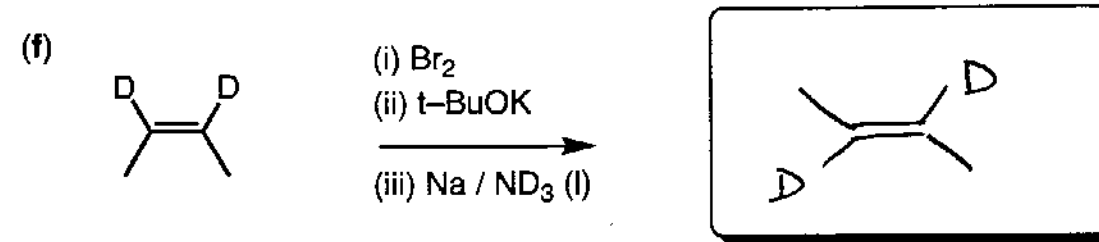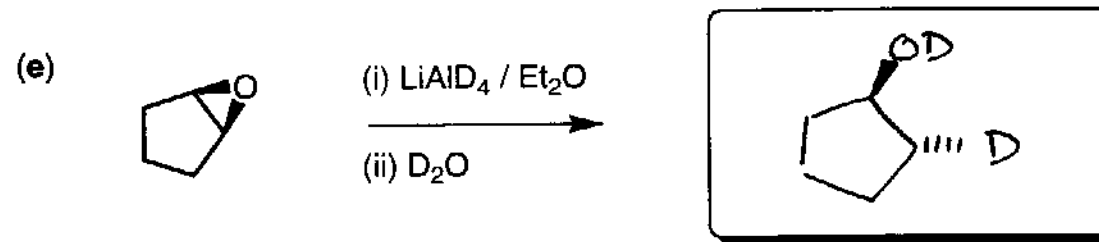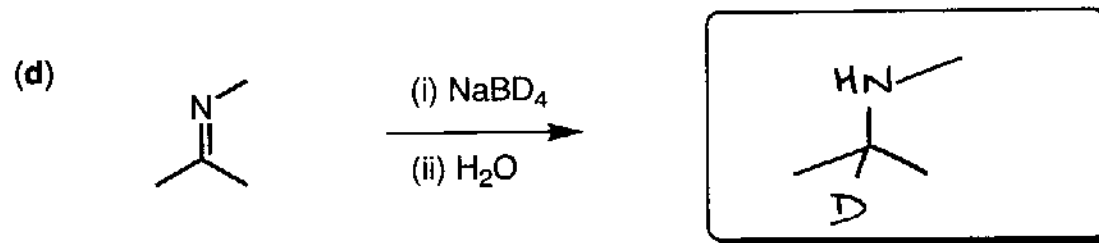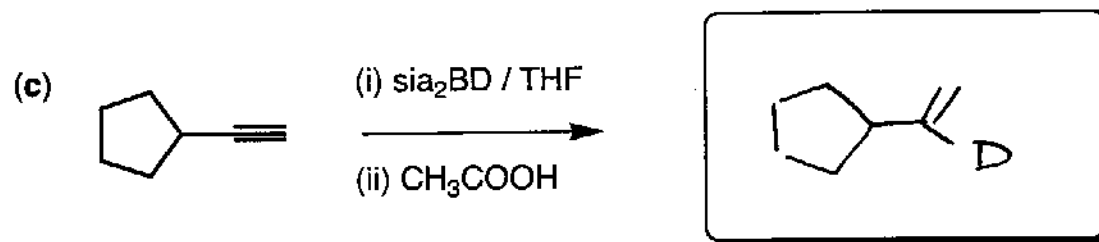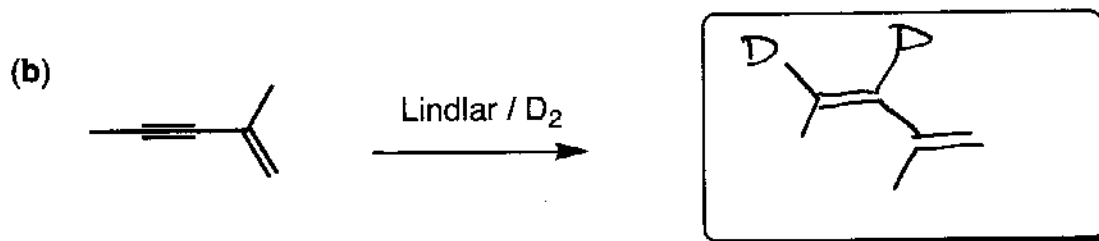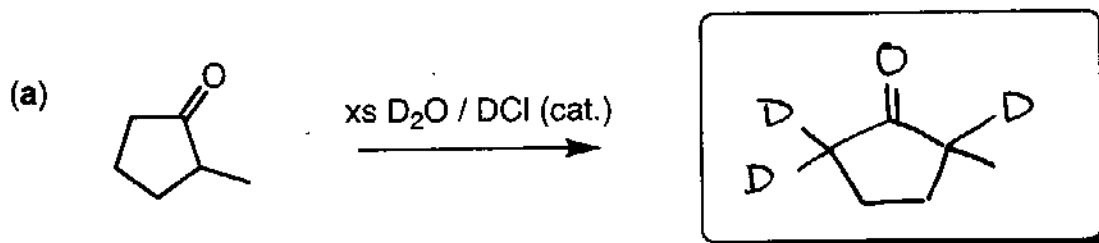
Question 3 Propose a synthesis for each of the transformations shown below, include all intermediates, in addition to conditions and reagents for each synthetic step – do not worry about solvents. (8 points each)

(a)

As many steps as you need

H_2O_2

HEAT

(COPE ELIMINATION)

(b)

As many steps as you need

(HOFMANN ELIMINATION)

MeI

HEAT

Ag_2O

I^-

OH^-
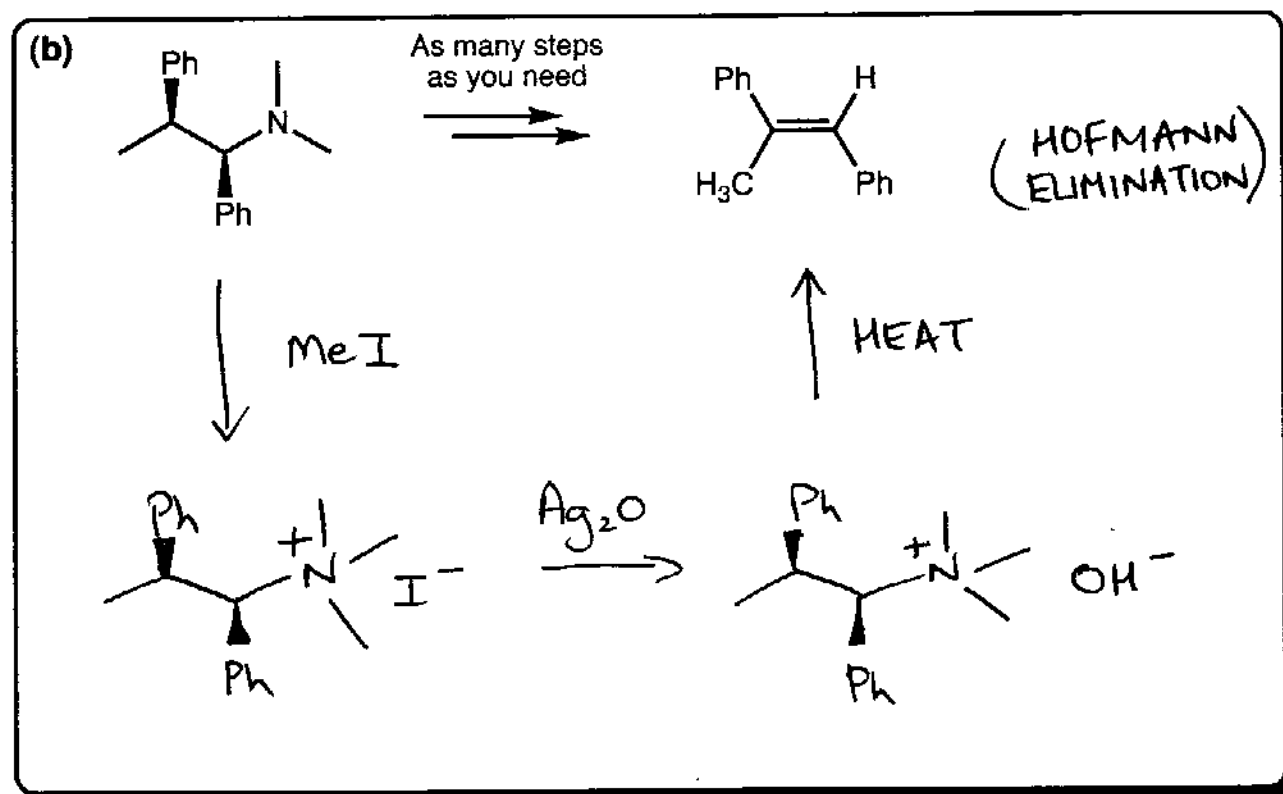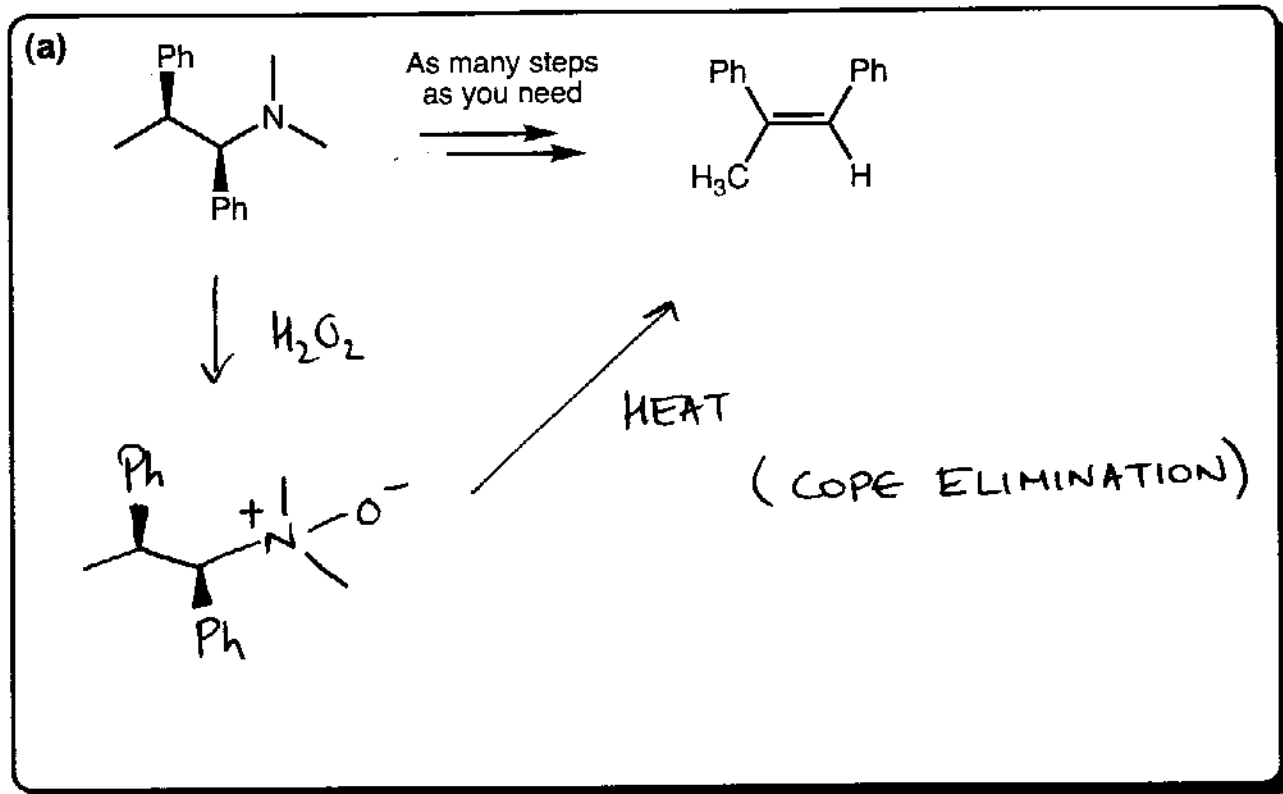
Question 4 Propose a synthesis for each of the transformations shown below, include all intermediates, in addition to conditions and reagents for each synthetic step – do not worry about solvents. (10 points each)

(a)

As many steps as you need

$\longrightarrow$

(TIFFENEAU DEMJANOV)

HCN

$\downarrow$

$\uparrow$ NaNO$_2$ HCl H$_2$O

OH CN

LiAlH$_4$ $\longrightarrow$

OH NH$_2$

(b)

As many steps as you need

$\longrightarrow$ NH

NH$_2$OH H$_2$SO$_4$ (BECKMANN)

$\downarrow$

$\uparrow$

O NH

LiAlH$_4$

6
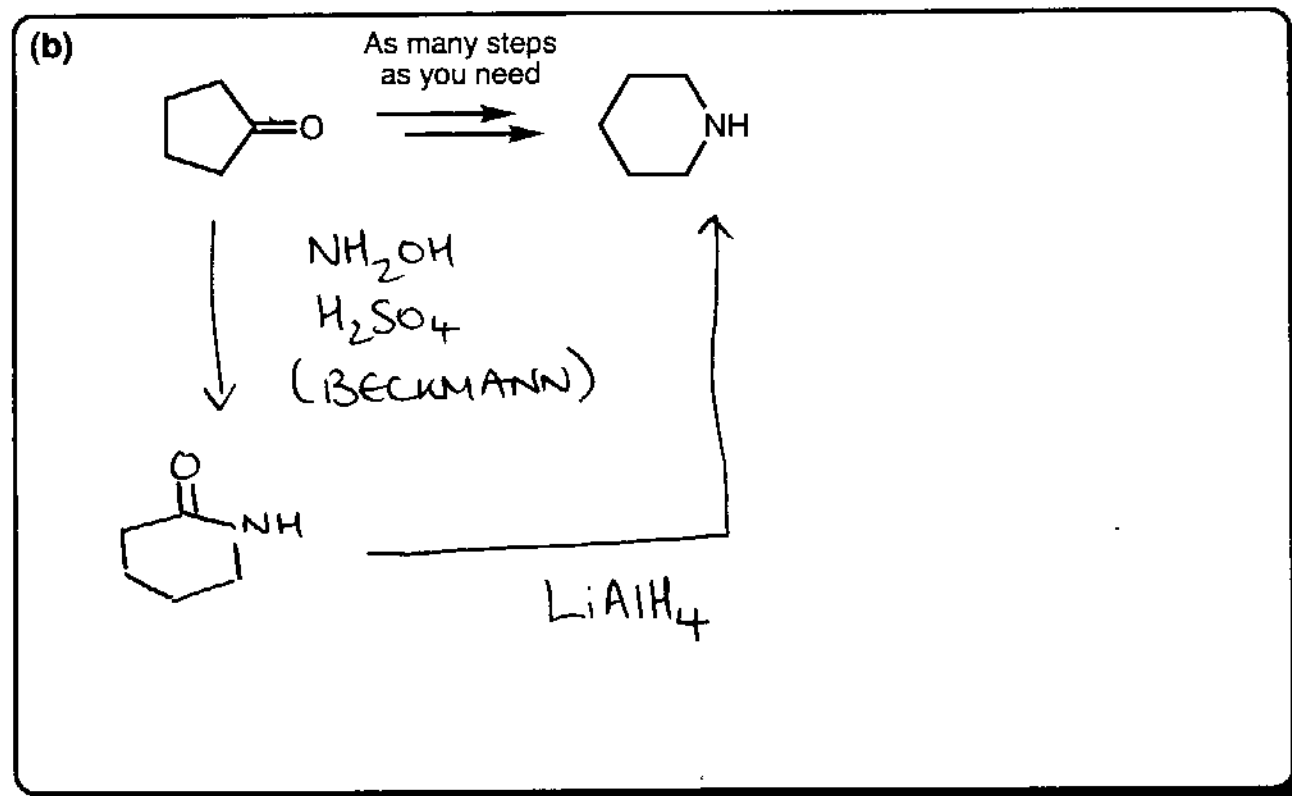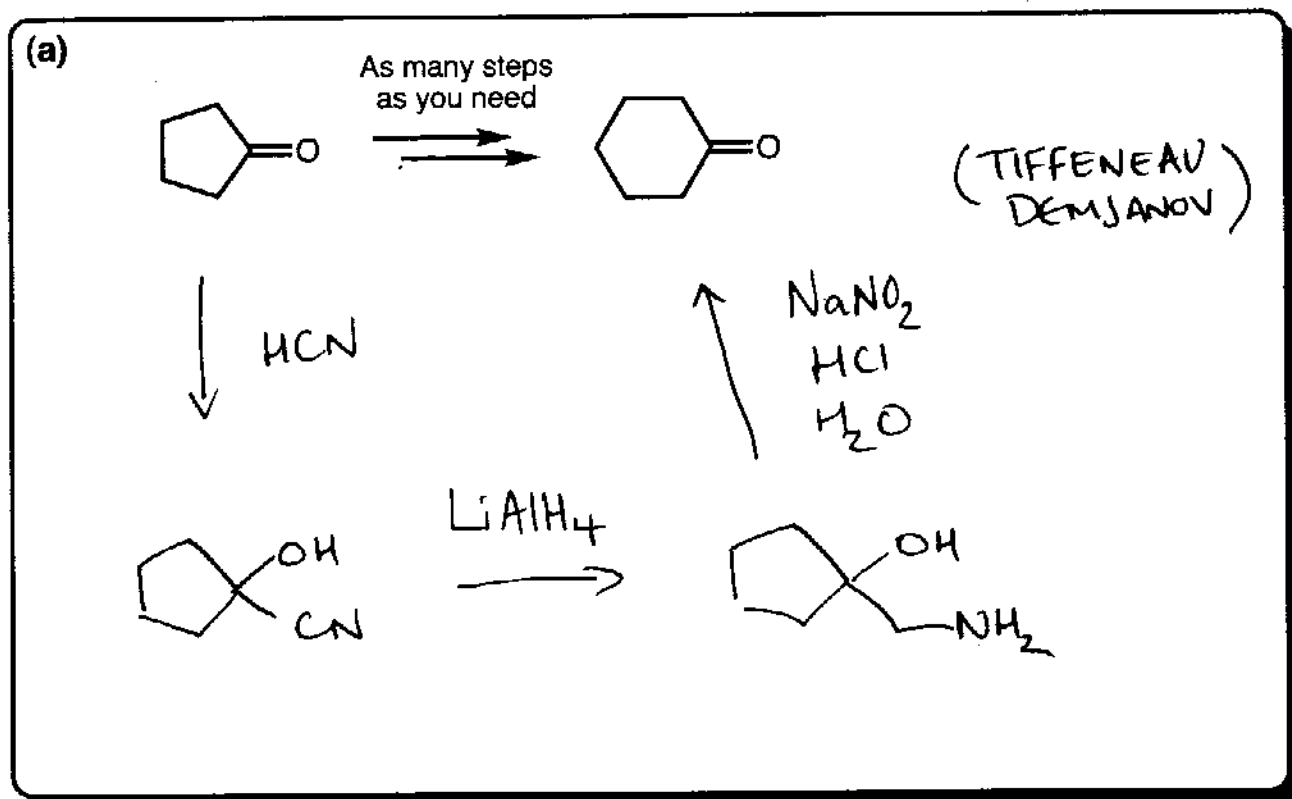
Question 5 Propose a reasonable mechanism that accounts for the transformation shown in the box below – SHOW ALL STEPS. (15 points)

What is the name of this reaction? WOLFF - KISHNER
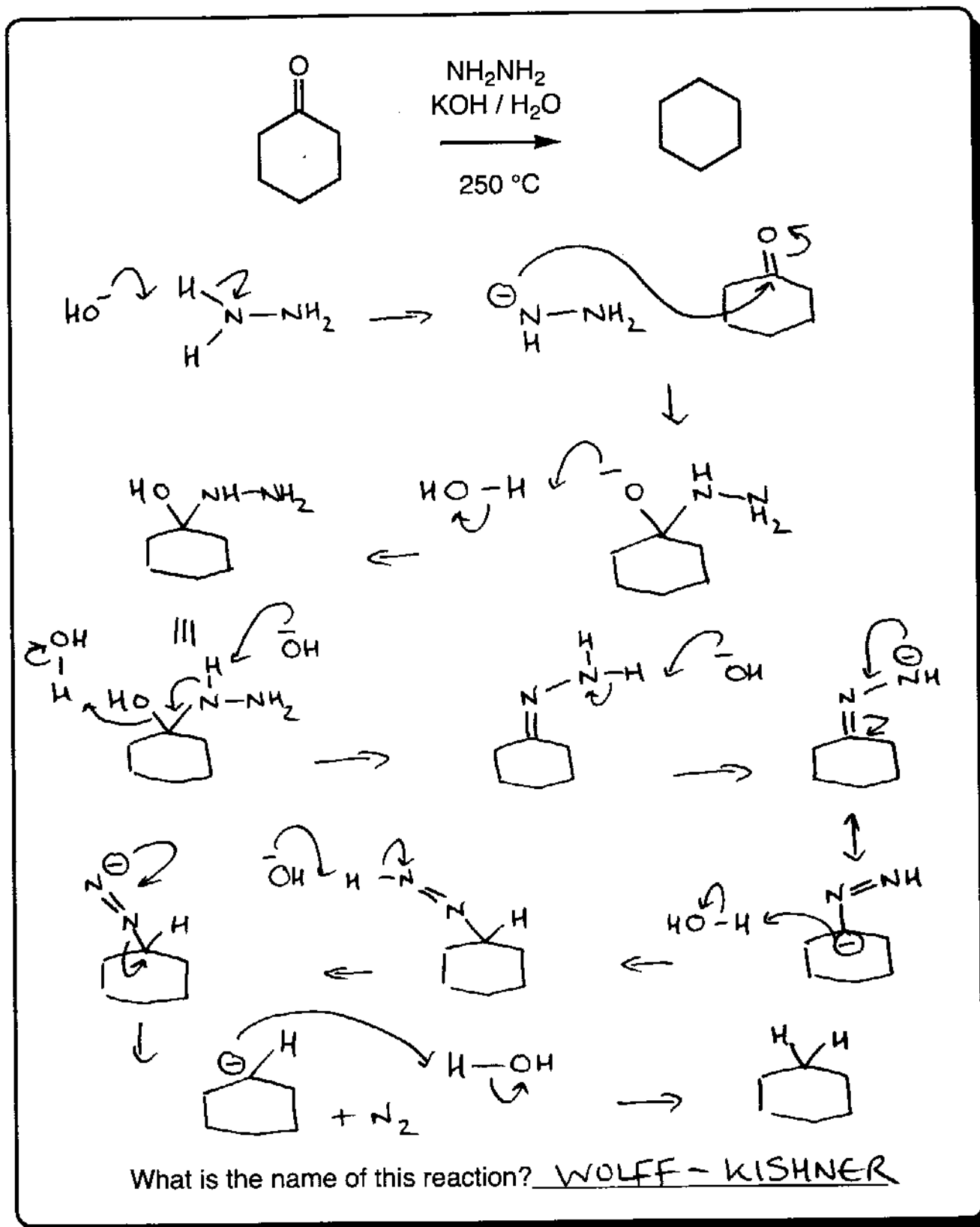
Question 6 Propose a synthesis to convert cyclopentene into the acyclic hydroxy-amide compound shown below. Show all intermediates, and the reagents necessary for each step (do not concern yourself with solvents). Points will be deducted for syntheses that result in a mixture of compounds. (18 points)

As many steps as you need

H_2SO_4 / H_2O

—OH

PCC / H_2CrO_4
or

O

mCPBA
(BAEYER VILLIGER)

NH_3

H_2N —OH
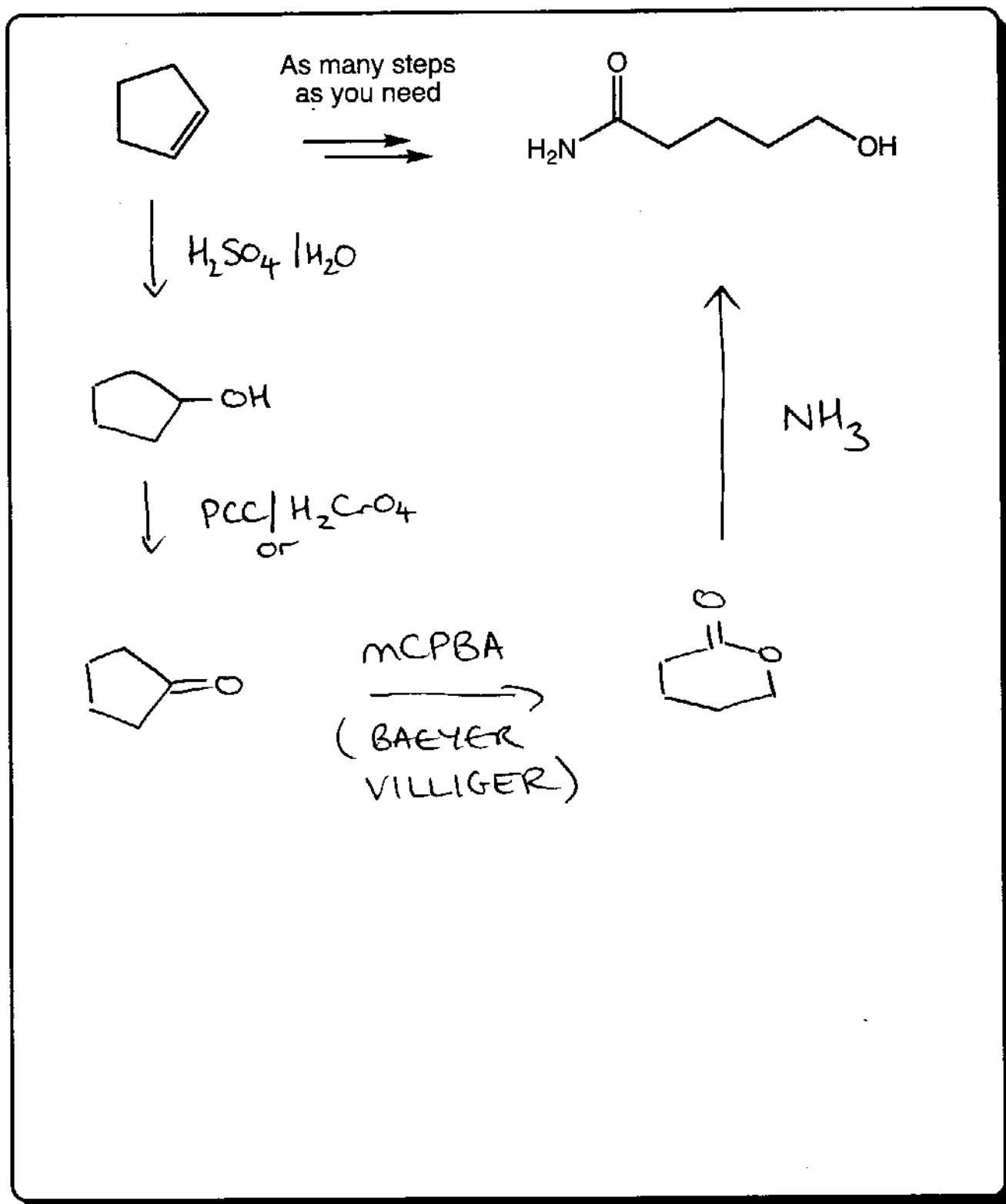
Question 7 Using ONLY acetylene (C_2H_2) as your carbon source, and other NON-CARBON containing reagents, propose a synthesis for *syn*-3,4-hexandiol in the box below. Show all intermediates and reagents for each transformation (do not concern yourself with solvents). Points will be deducted if your synthesis results in *anti*-3,4-hexandiol!! (18 points)

As many steps as you need

H_2 / LINDLAR

HBr

NaH / H—≡—H

Na / NH_3 (ℓ)

H_2 / LINDLAR

mCPBA

trans

cis

OsO_4

H_3O^+

Question 8   Propose a reasonable mechanism that accounts for the transformation shown in the box below – SHOW ALL STEPS. (15 points)

Question 9 Answer the following questions about a novel class of highly branched compounds called dendrimers. (12 points)

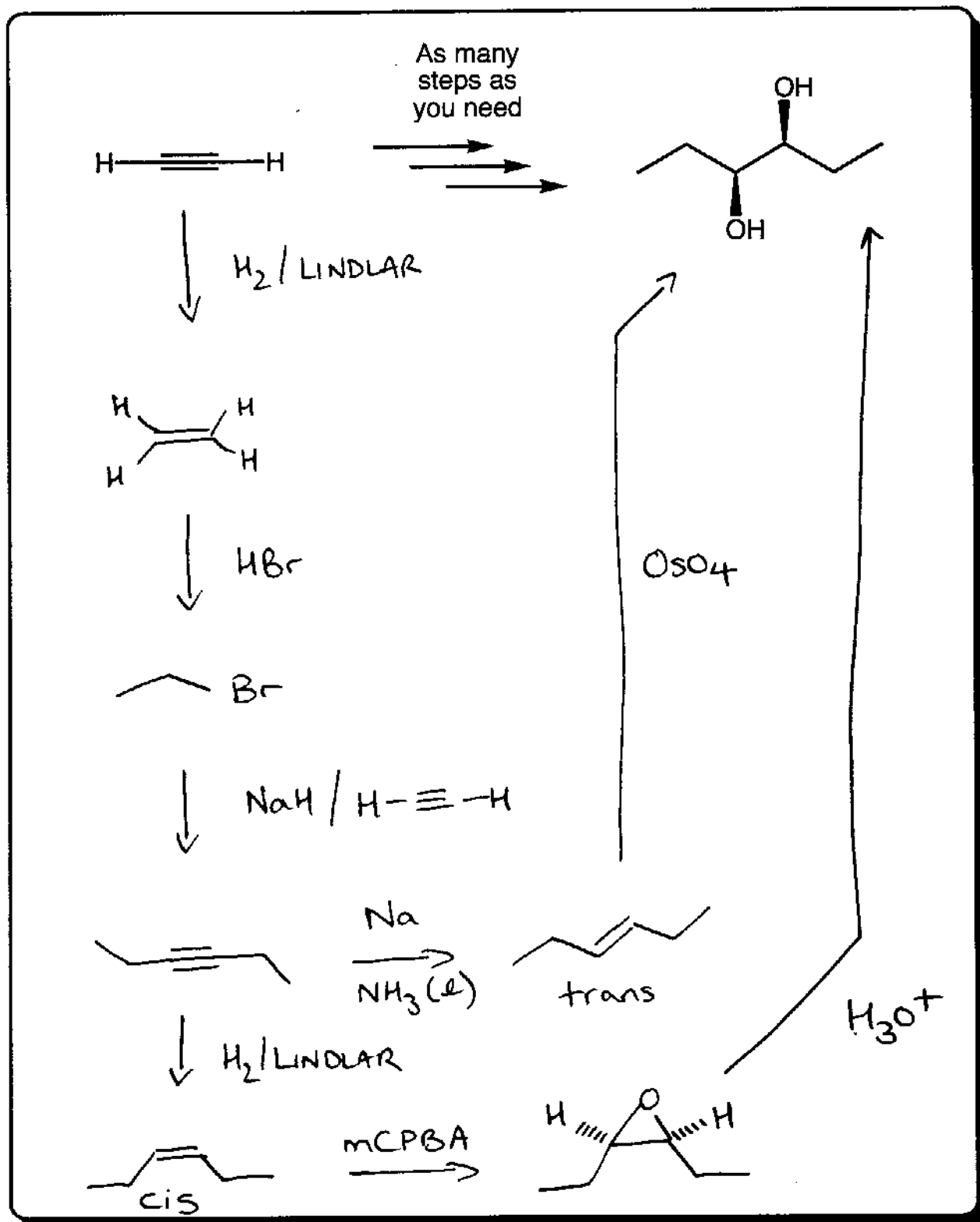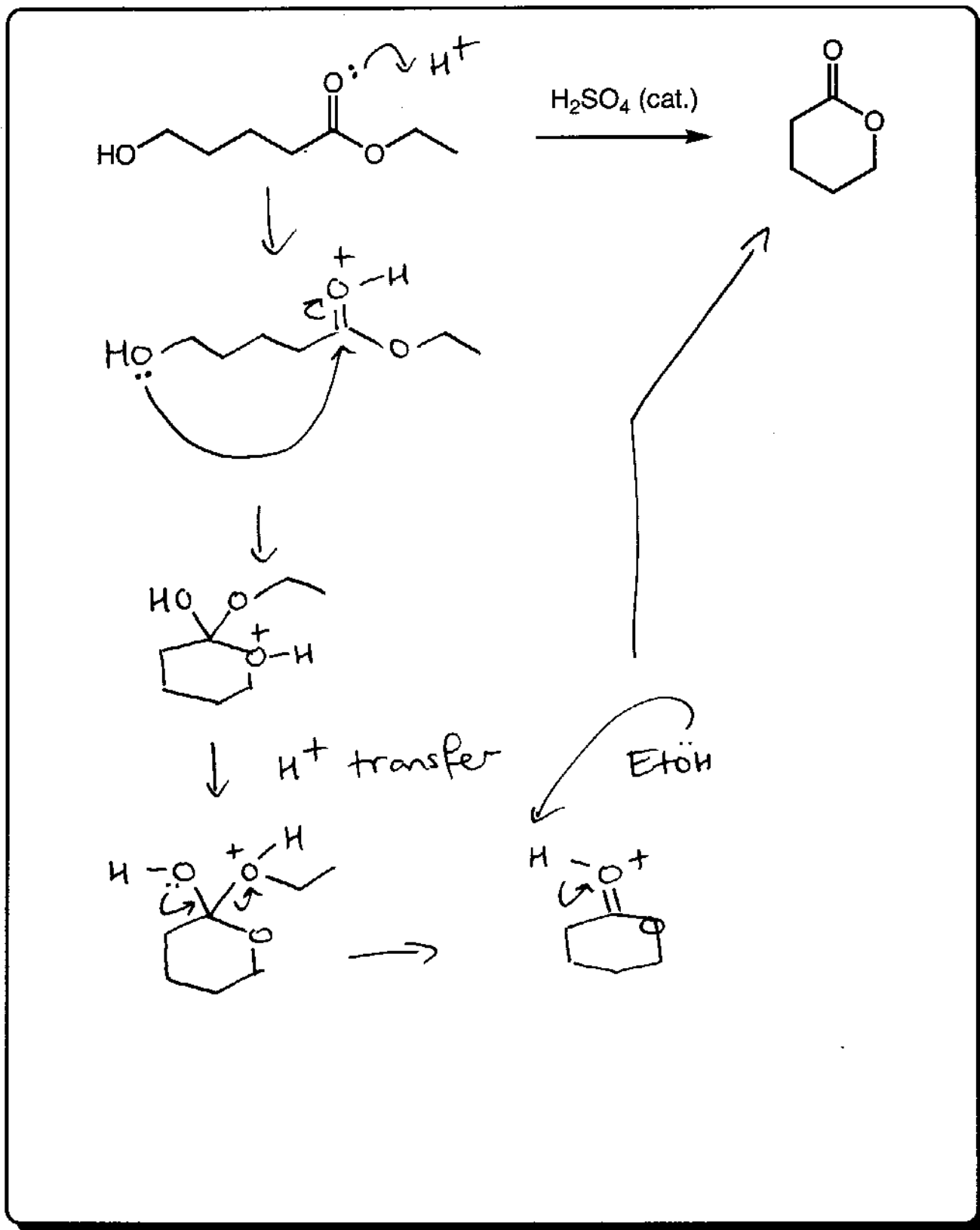NH₃ — Large excess ⟋CN → A → (i) B, (ii) C, (iii) B → D
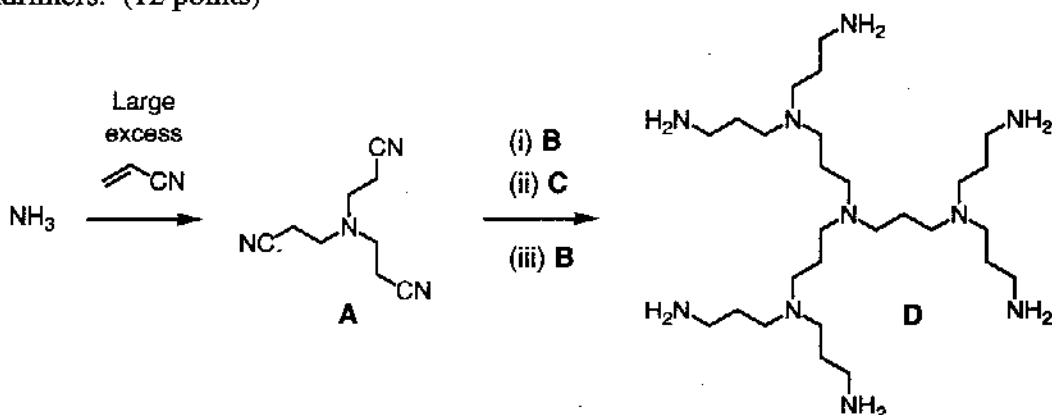
(a) Explain why the product of the reaction of an excess of acrylonitrile with ammonia gives the tris-nitrile compound **A** (Show Intermediates)

NH₃ ⟶ H₂N~~CN (still nucleophilic) ⟶ HN(~~CN)₂ (still nucleophilic) ⟶ A

4 points
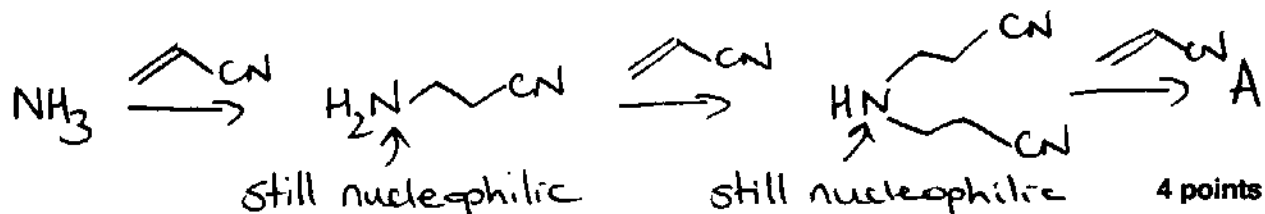
(b) A three step reaction sequence [(i) **B**, (ii) **C**, (iii) **B**, *i.e.*, steps (i) and (iii) are the same] gives the branched polyamine compound **D** (a 1st generation dendrimer). What are the reagents **B** and **C**?

B = LiAlH₄   C = ⟋~~CN

4 points

(c) Subjecting compound **D** to a two step reaction [(i) **C**, then (ii) **B**] gives a 2nd generation dendrimer – what is its structure?

4 points
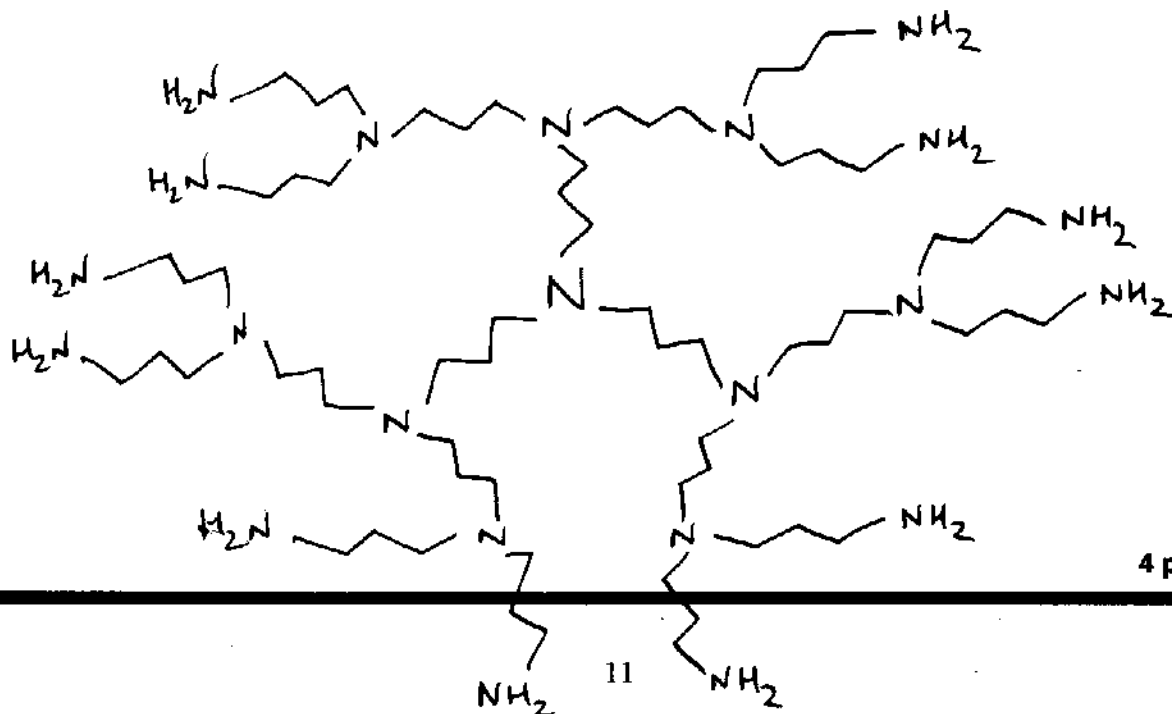
Question 10 Shown below are two short synthetic schemes, the one on the left results in the formation of compound **E** (molecular formula C_4H_6O), and the one on the right results in the formation of compound **J** (molecular formula $C_7H_{13}N$). When **E** and **J** are reacted together (box at bottom of page), 2,6-heptadione is formed. In the large boxes (**B**, **E**, **G**, **J**), fill in the structures of plausible intermediate compounds, and in the small boxes (**A**, **C**, **D**, **F**, **H**, **I**) fill in the reagents necessary to achieve each transformation. (20 points)

Left scheme:

Starting material: acetaldehyde (CH_3CHO)

A H_2CrO_4

B acetic acid (CH_3COOH)

C $SOCl_2$

Intermediate: acetyl chloride (CH_3COCl)

D ($CH_2=CH$)$_2$CuLi

E (structure: but-3-en-2-one / methyl vinyl ketone) C_4H_6O

Right scheme:

Starting material: acetaldehyde (CH_3CHO)

F i MeMgBr, ii H_3O^+

G isopropanol (structure with OH)

H H_2CrO_4

Intermediate: acetone

I pyrrolidine (N–H ring) / H^+

J (enamine structure) $C_7H_{13}N$

Bottom box:

$$J \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } E} \text{(2,6-heptadione structure)}$$

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Question 11 Propose a synthesis of the cyclic five-membered target molecule shown below using propanal as your only starting material. You may use any reagents of your choosing, but all of the carbon atoms in the final product MUST come from propanal. Show all intermediates and reagents for each transformation (do not concern yourself with solvents). (18 points)
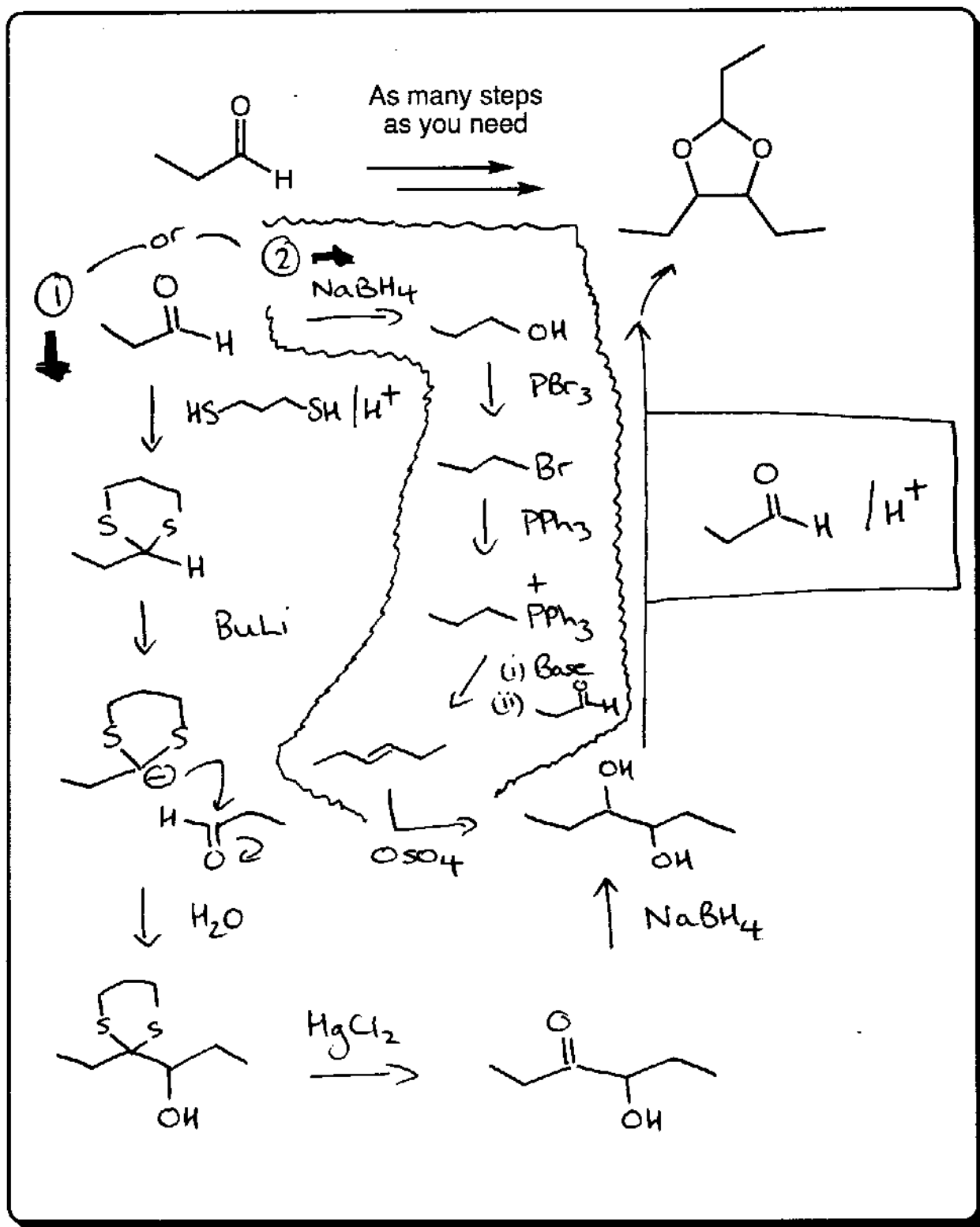
Question 12 (EXTRA CREDIT SYNTHESIS QUESTION)   Propose a synthesis of hexamethyl-cyclopropane using propyne as your starting material. You may use any reagents of your choosing, but all of the carbon atoms in the final product MUST come from propyne. Show all intermediates and reagents for each transformation (do not concern yourself with solvents). (15 points)

(i) 1 eq EtONa / EtOH

(ii) H₂O / HCl (acidic workup)

(DATE ... SEE IF YOU CAN FIGURE IT OUT!)

Maybe... OPEN, BUT THIS REQUIRES THE FORMATION OF A VERY STRAINED INTER...

ENOLATE EXCHANGE

This is an example of what kind of reaction? **DIECKMANN**

What is the driving force? **FORMATION OF MOST STABLE ENOLATE**

(NOTE: THERE MAY BE ANOTHER ROUTE VIA WHICH THE RING DOES NOT

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