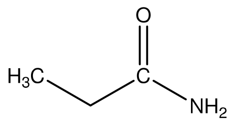
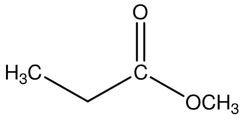
Note: This document is a compilation of questions and is NOT representative of the length of the final exam.

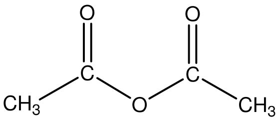
Question 1

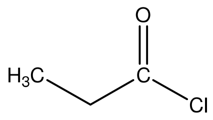
a) Correctly list these compounds in order of **increasing** rate of base hydrolysis. Circle the correct answer.

↳ nucleophilic acyl substitution with OH^-


A


B


C

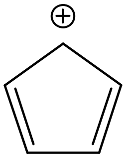

D

reactivity order → ch.16.

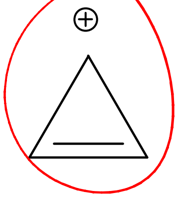
a. B < A < C < D   b. A < B < D < C   [✓ c. A < B < C < D]   d. D < C < B < A

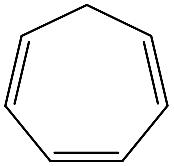
b) Circle the compound(s) that exhibit Hückel aromatic stability.

4n+2 = # πe^-

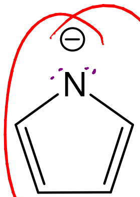


2π e^-





6 π e^-



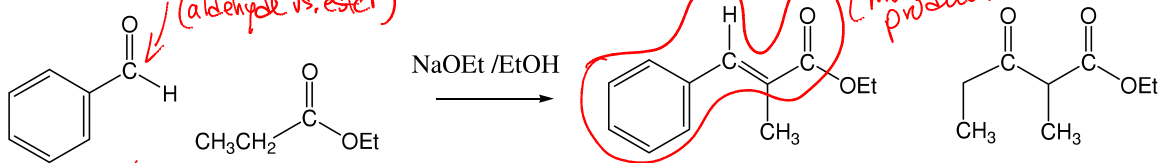
c) An L-Aldose sugar rotates plane–polarized light :

to the rights (clockwise)   to the left (counterclockwise)

[✓ must be determined experimentally]   does not rotate plane–polarized light

Question 2.

a) Briefly explain why the major product from the reaction below is the mix aldol rather than the self condensation product.



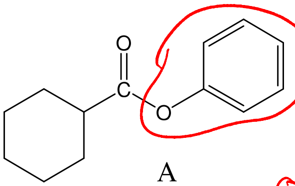
Better electrophile (aldehyde vs. ester)

conjugated system (more stable product)

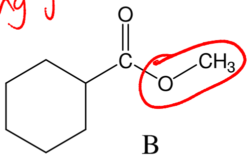
no acidic protons (no α protons)

(major)   (minor)

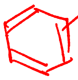
b) Base hydrolysis of ester A occurs much faster than hydrolysis of ester B. Briefly explain why.


A

Better leaving group


B

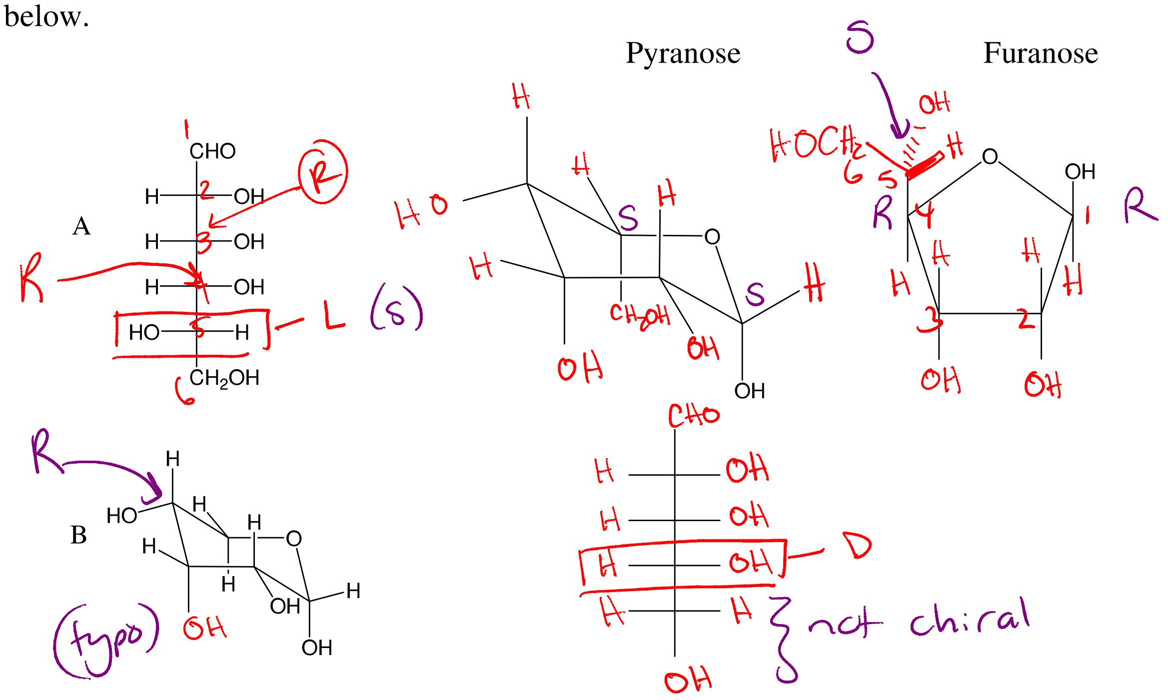
worse leaving group


O⊖. is the more stable conjugate base (delocalized neg. charge)

thus, the better leaving group is more likely to leave.

Question 3.

a) Draw the pyanose and furanose forms for sugar A and the Fischer projection of sugar B on the structures given below.



b) Circle the correct answer to complete the sentences below:

i) Sugar A shown above is a { D / [✓ L] } sugar.

ii) Sugar B shown above is a { [✓ D] / L } sugar.

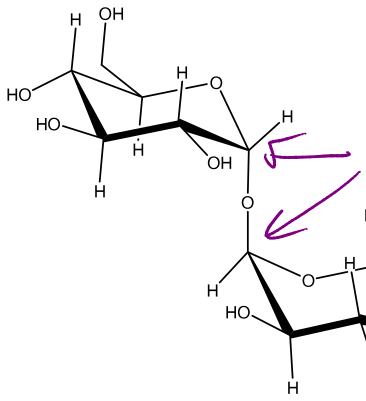
iii) The Pyranose form of Sugar A above is the { alpha / [✓ beta] } anomer. S/S

iv) The Pyranose form of Sugar B above is the { [✓ alpha] / beta } anomer. R/S

v) Carbon 3 of Sugar A is an { [✓ R] / S } stereocenter.

c) i) The disaccharide below has a { [✓ 1-1] \ 1-2 \ 1-3 \ 1-4 \ 3-1 } { [✓ alpha] \ beta } linkage.

ii) The disaccharide is a { reducing \ [✓ non-reducing] } sugar



anomeric carbons joined together

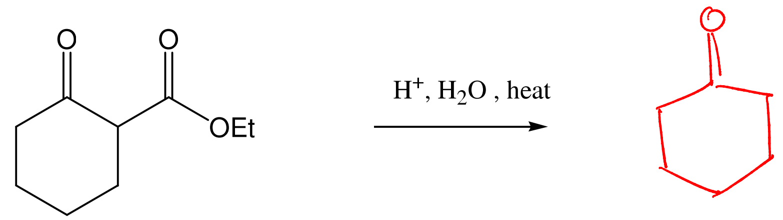
- no hemiacetals, hemiketals, aldehydes, ketones.

Question 4.

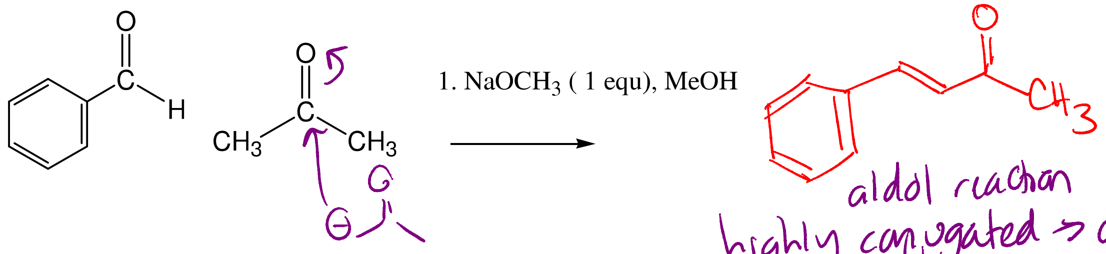
Provide the structures of the **MAJOR** organic product(s) obtained from each of the following reactions.

hyardlysis of the ester followed by decarboxylation

a)



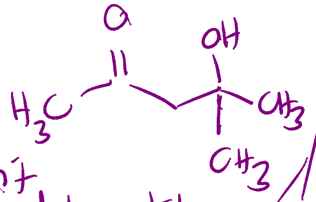
b)



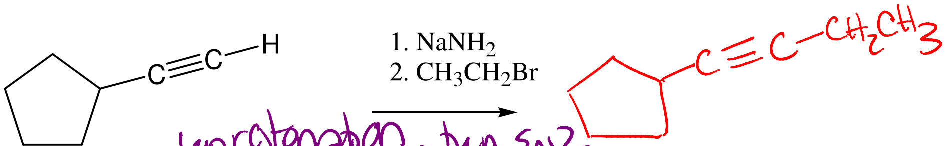
aldol reaction

highly conjugated → don't need heat to dehydrate.

may get same self aldol:



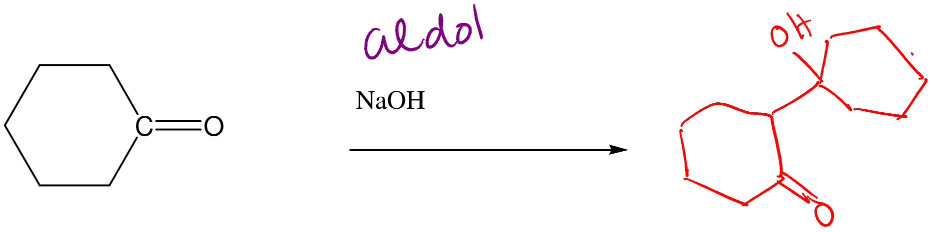
c)



deprotonation, then S_N2

aldol

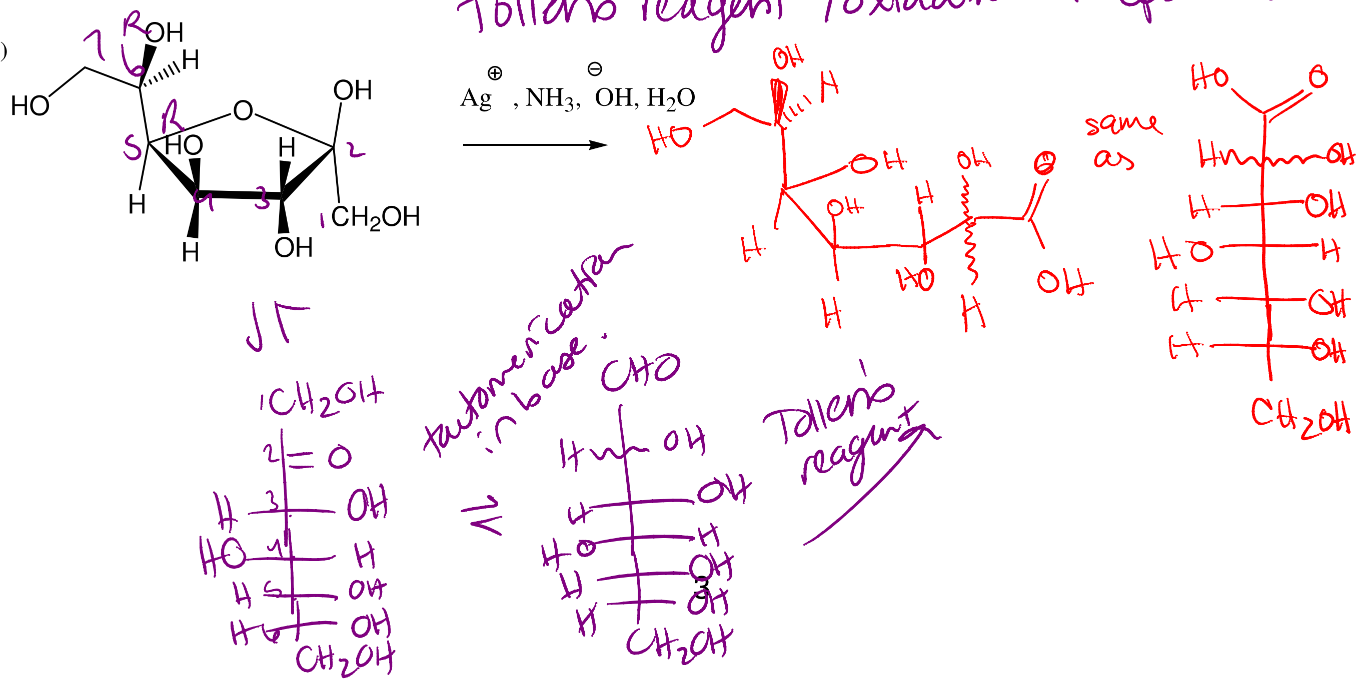
d)



no heat → do not dehydrate.

Tollen's reagent / oxidation of open chain version.

E)



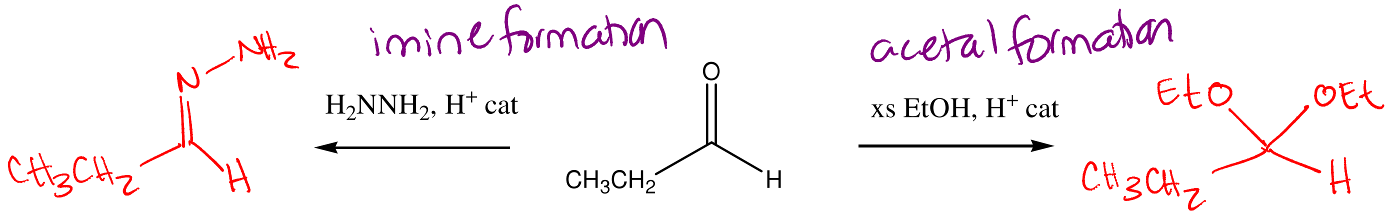
tautomerization in base.

Tollen's reagent

Question 5.

Different reagents may react with the same starting material to produce very different products. Provide the structures of the major organic product(s) obtained from each of the following reactions.

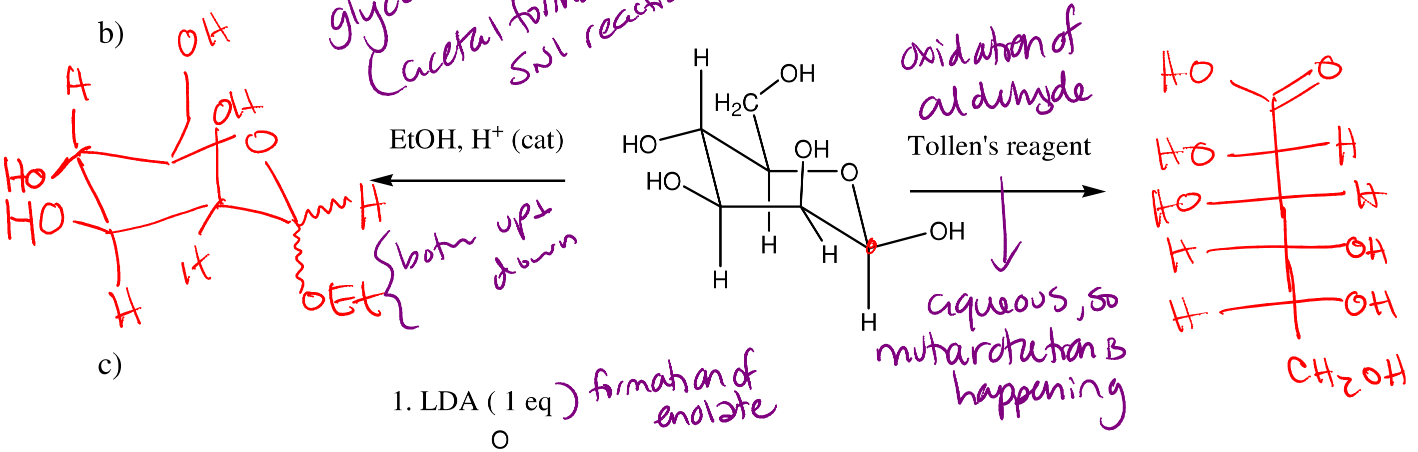
a)



imine formation

acetal formation

b)



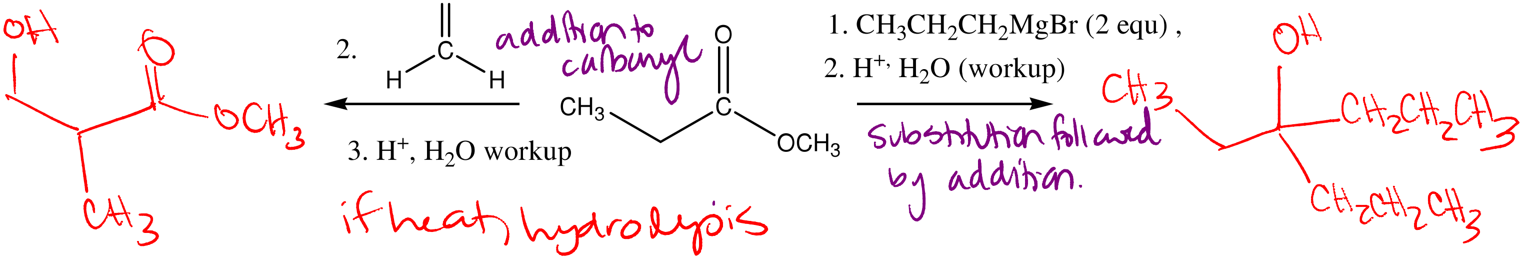
glycoside formation (acetal formation) SN1 reaction

{both up & down}

oxidation of aldehyde

aqueous, so mutarotation is happening

c)



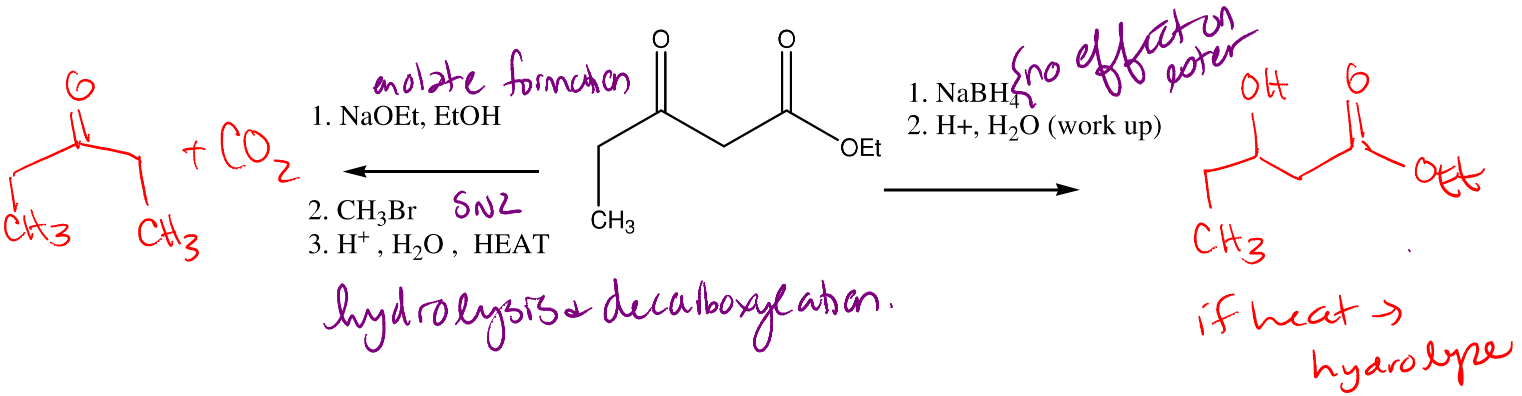
formation of enolate

addition to carbonyl

if heat, hydrolysis

substitution followed by addition.

d)



enolate formation

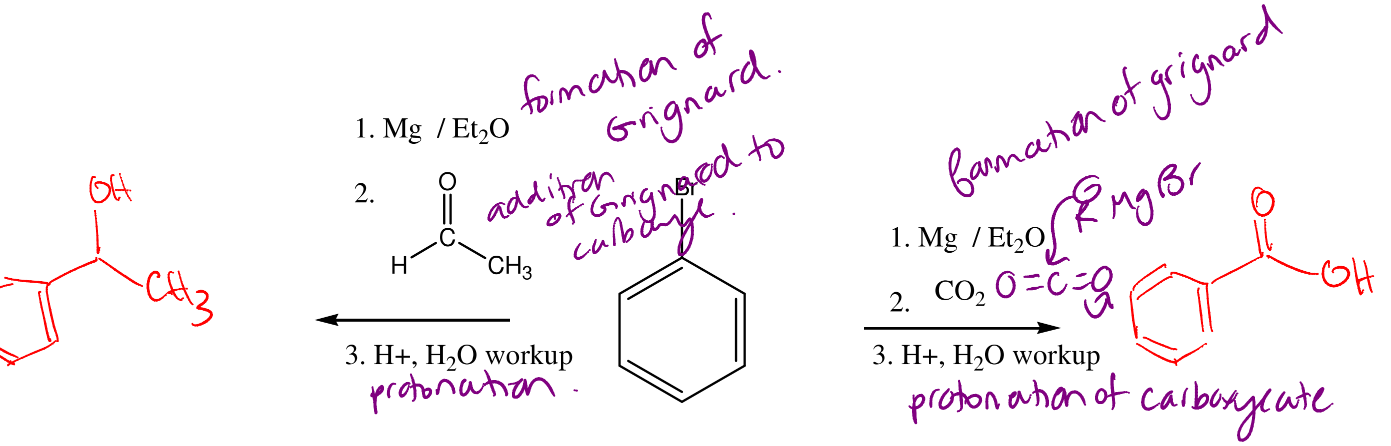
SN2

hydrolysis & decarboxylation.

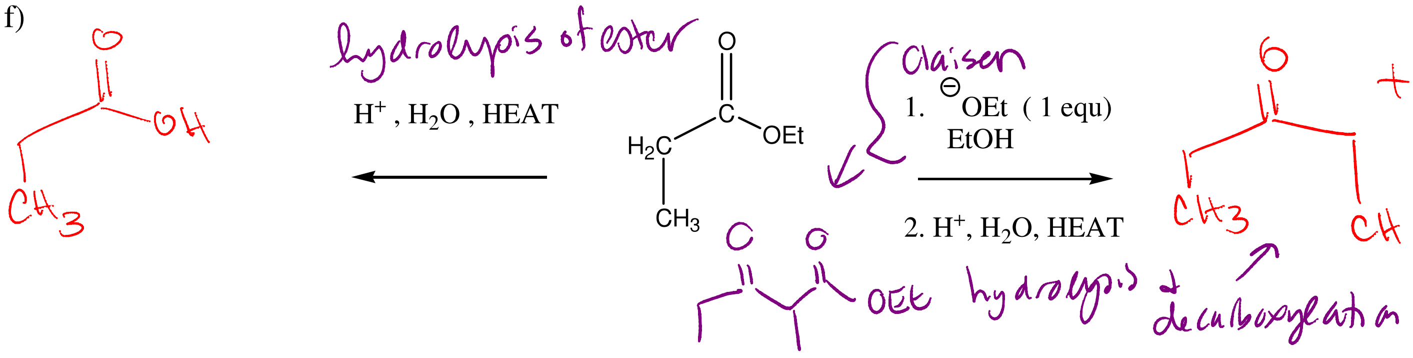
{no effect on ester

if heat → hydrolyze ester

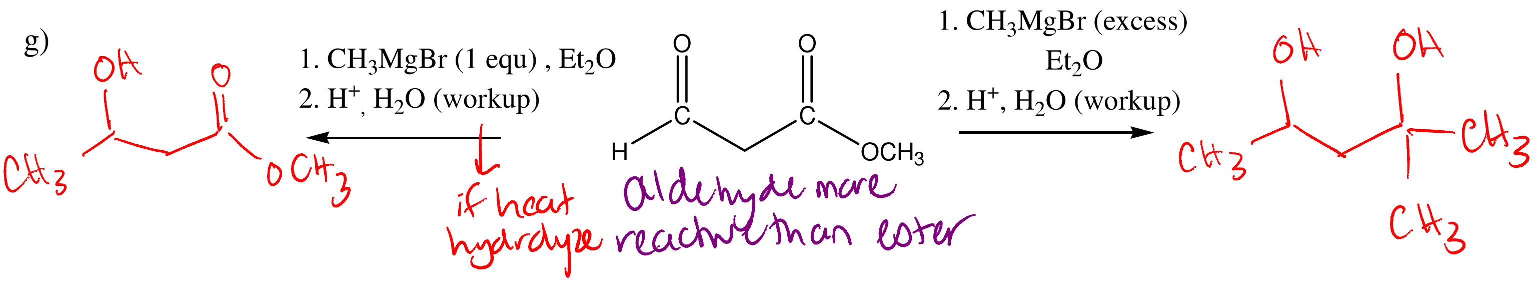
e)



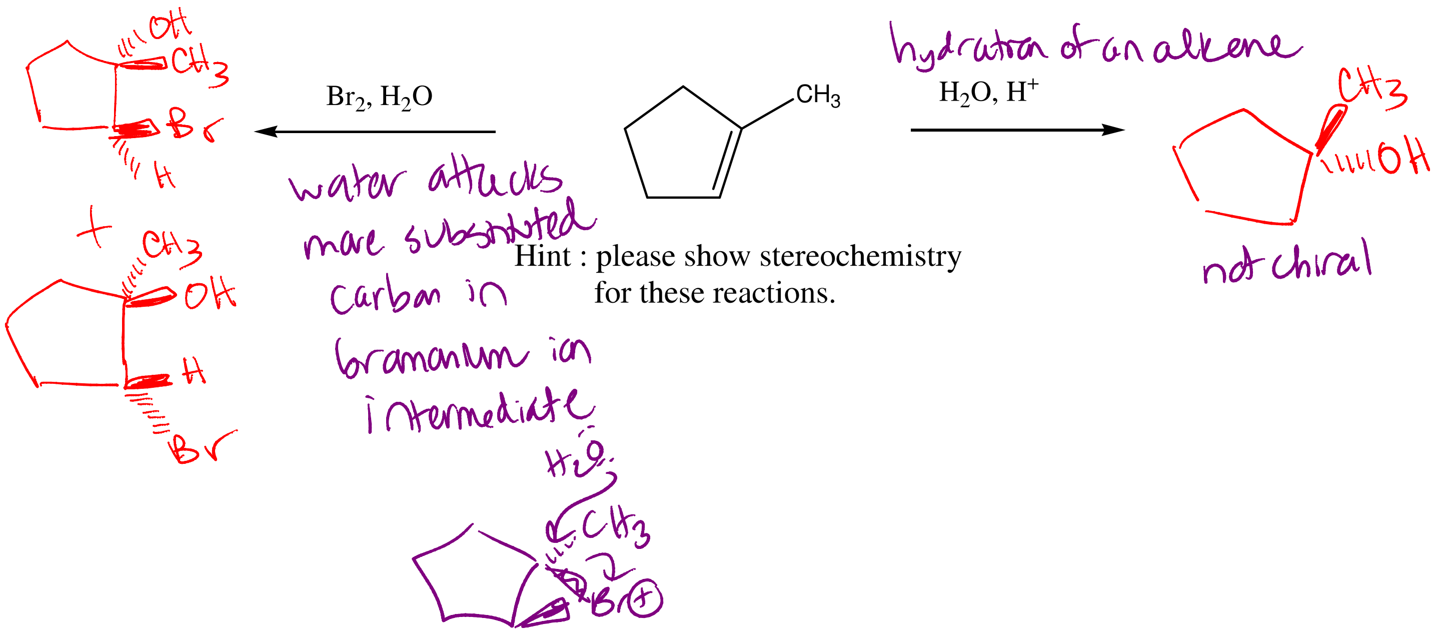
f)



g)



h)

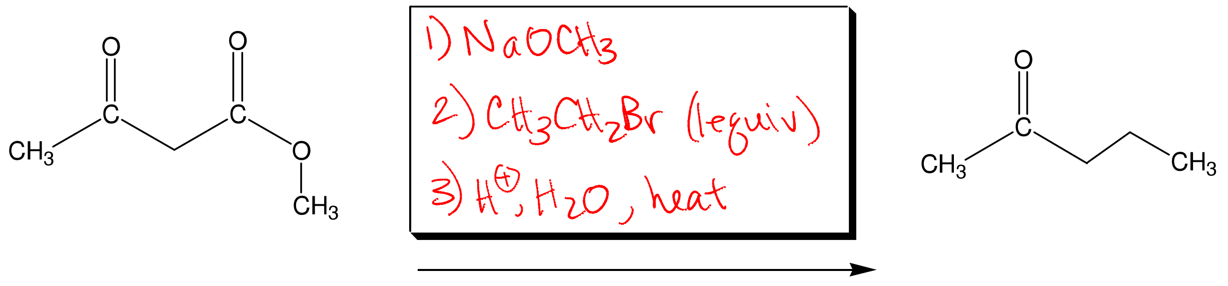


Hint : please show stereochemistry
for these reactions.

Question 6

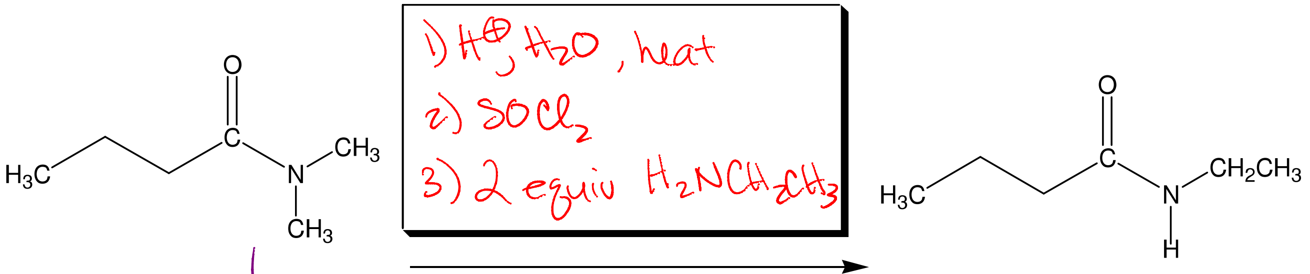
Add the missing reagents necessary to carry out the steps below.

a)



1) $NaOCH_3$
2) CH_3CH_2Br (1 equiv)
3) $H^{\oplus}$, H_2O, heat

b)

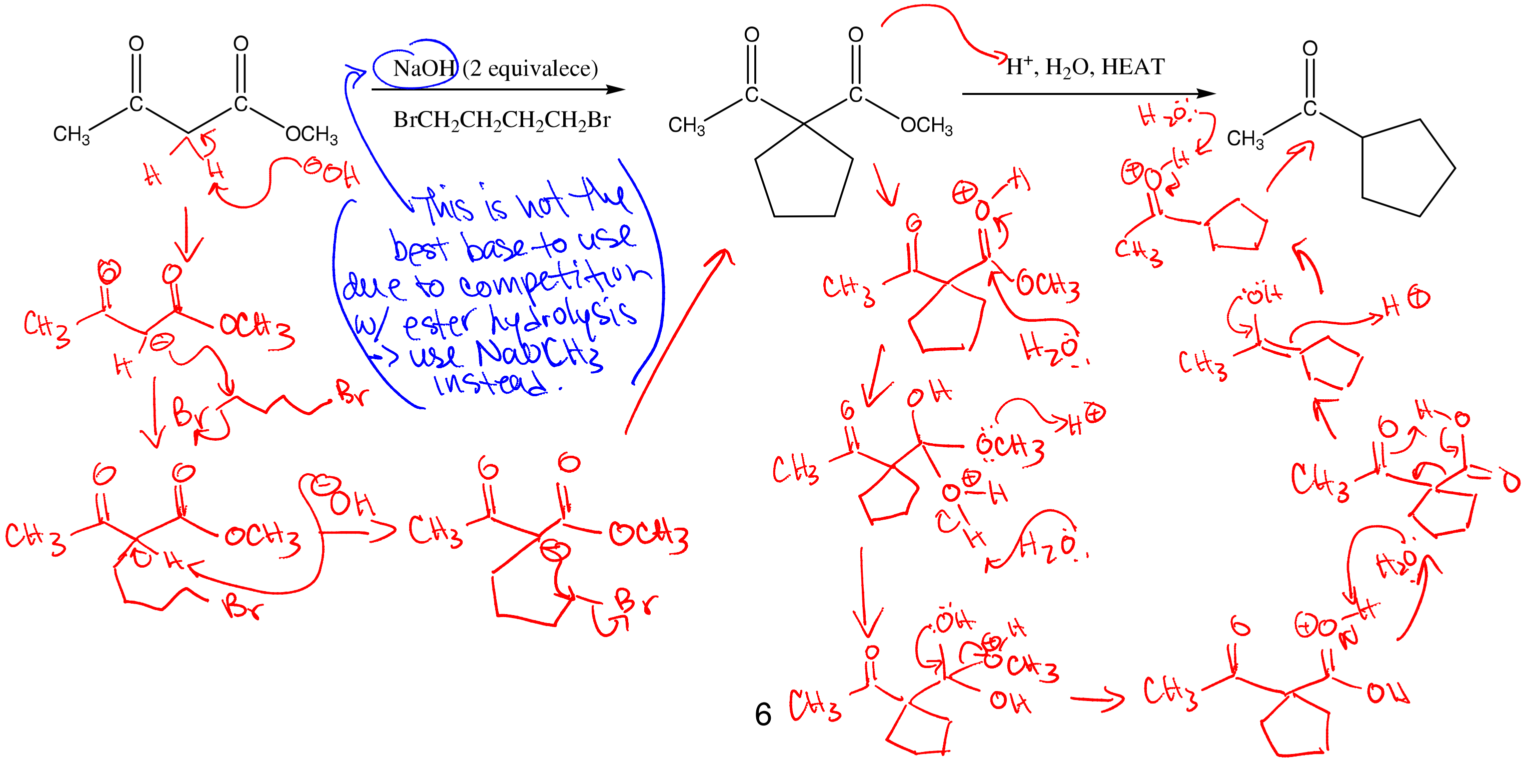


1) $H^{\oplus}$, H_2O, heat
2) $SOCl_2$
3) 2 equiv $H_2NCH_2CH_3$

could also use excess $H_2NCH_2CH_3$, H^+

Question 7.

a) Including the correct use of electron-movement arrows, lone pairs of electrons, and the position of any formal charges, show the detailed step-by-step mechanism involved in the two step reaction below.



NaOH (2 equivalece)

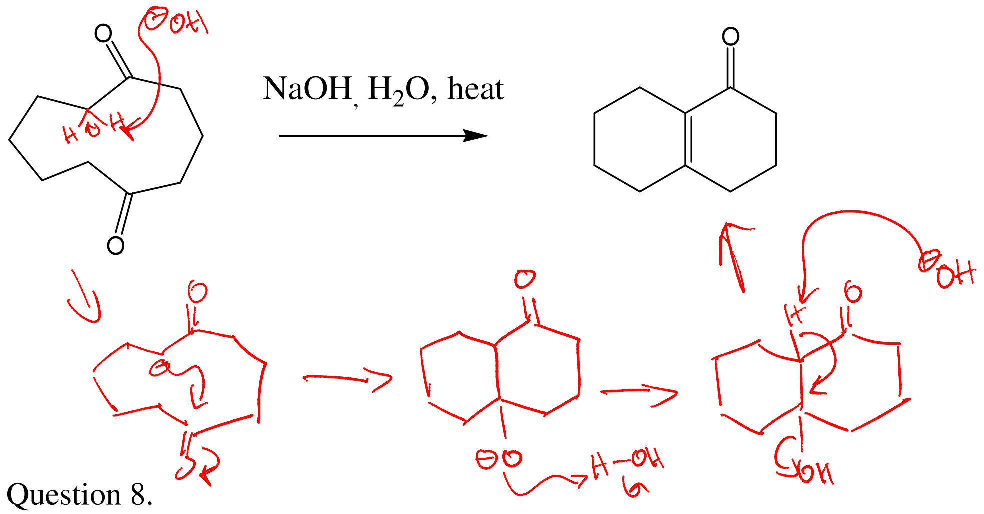
$BrCH_2CH_2CH_2CH_2Br$

H^+, H_2O, HEAT

This is not the best base to use due to competition w/ ester hydrolysis → use $NaOCH_3$ instead.

Question 7 cont'd.

b) Including the correct use of electron-movement arrows, lone pairs of electrons, and the position of any formal charges, show the detailed step-by-step mechanism involved in the reaction below.



Question 8.

Compound **A** is one of 76 constitutional isomers with the formula C_6H_{10}. Inclusion of stereoisomers brings the total to well over 100 possibilities for **A** and thus it is clear that you should not try to guess a structure solely from a molecular formula.

$U = C + 1 - \frac{1}{2}(H + X - N)$

terminal alkyne hint

Use the following chemical information to solve the unique structures of **A** – **E**.

i) Compound **A** is chiral and is known to have the R-configuration.

ii) Reaction of **A** with H_2/Pt yields a **single** compound **B** (C_6H_{14}) which is **not** chiral.

iii) Reaction of **A** with $NaNH_2$ followed by addition of **C** (C_4H_9Br) and an appropriate workup yields a **single** compound **D** ($C_{10}H_{18}$) which is **not** chiral.

iv) Reaction of **D** with H_3O^+/Hg^{2+} produces a racemic mixture of **E** ($C_{10}H_{20}O$).

(A) $U = 6 + 1 - \frac{1}{2}(10)$

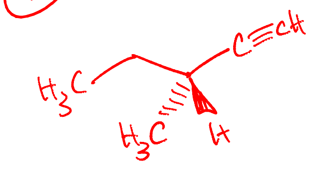
$= 7 - 5 = 2$

π bond or rings.

Draw stereochemical structures of **A** – **E** consistent with all of the information above.

Use the wedge/dash notation to ensure that the stereochemistry of all stereogenic centres is clear.

Ⓐ



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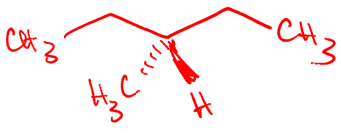

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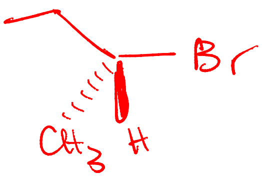
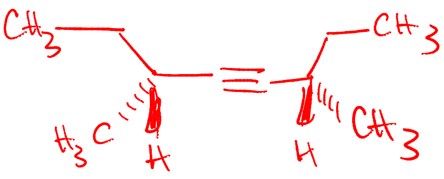


Ⓓ

internal plane of symmetry.



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