UNIVERSITY OF VICTORIA
FINAL EXAMINATION, APRIL 2016

CHEMISTRY 232

(CRN 20504; A01)

Organic Chemistry with Biological Applications

Name: MARKING GUIDE **ID:** V00
(USE CAPITALS)

ANSWER ALL QUESTIONS ON THE EXAM PAPER

Time: 3 hours
Instructor: Dr. P. Wan
Pages: 14 (including this cover page)

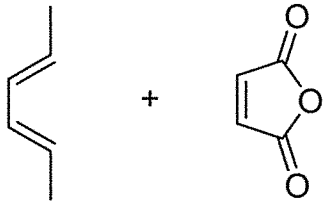
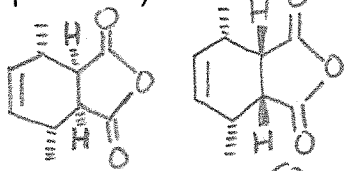
Molecular models are permitted. No other aids allowed.
Students **must count the number of pages** in this examination paper before starting to write the exam. Report any discrepancy immediately to the invigilator.

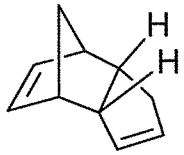
There are **10** questions worth a grand total of **144** marks.

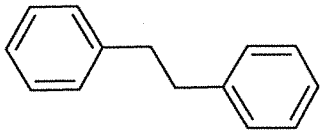
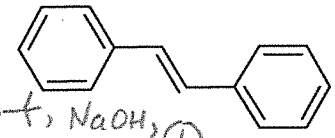
Question	MARK	Question	MARK
1 (40 *marks*)		**9** (6)	
2 (30)		**10** (8)	
3 (8)			
4 (6)			
5 (18)			
6 (10)			
7 (8)		**RAW SCORE (/144)**	
8 (10)		**% EXAM**	

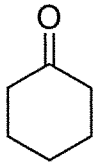
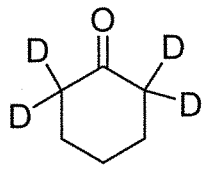
1. **Reactions.** Give the expected major product(s) or required reagent(s) for each of the following reactions. ***No need*** *to indicate formation of enantiomers in all questions.* [40 marks]

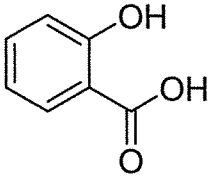
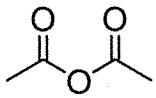
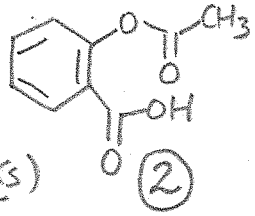
(a)  HCl → ? (distinct products only)  (2) (0.5) (stereochem not required)

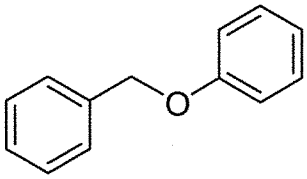
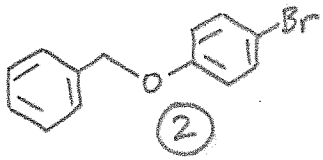
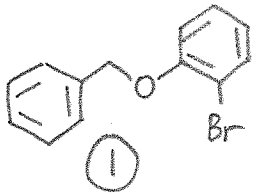
(b)  → ? (exo and endo products)  (1) (1)

(c)  + ?  (2) (No part marks)  (1) (Could be drawn upside down!)

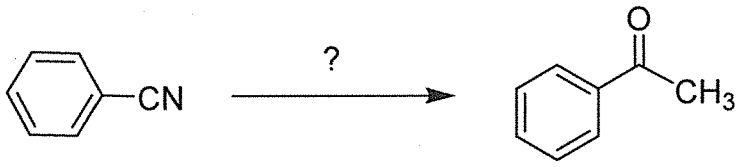
(d)  1. NBS, hν or Br_2, hν (1) ? 2. base such as KO-t, NaOH, NaOEt, etc (1) 

(e)  ?  or NaOEt/D_2O NaOD, D_2O or NaOH, D_2O or D_3O^+ (2) or D_2SO_4 or DCl/D_2O

(f)   ? (acetylsalicylic acid)  (No part marks) (2)

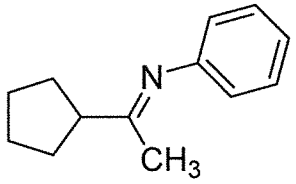
(g)  Br_2, $FeBr_3$ → ? (monobrominated)  (2)  (1)

1. (continued)

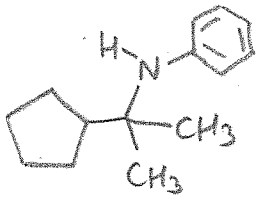
(h) 

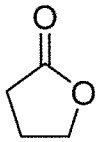
1. CH_3MgBr (or CH_3Li) (1.5)
2. H_3O^+ (0.5)

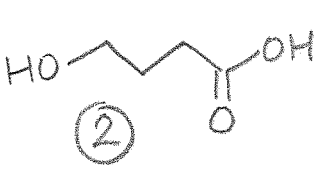
(No Marks For OTHER METHOD)

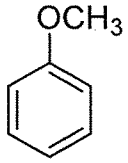
(i) 

1. CH_3MgBr, ether
2. dil H_3O^+

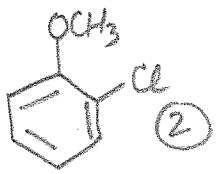
?  (2) (No part marks)

(j) 

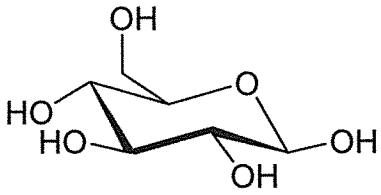
H_3O^+, Δ → ? (GHB)  (2) (No part marks)

(k) 

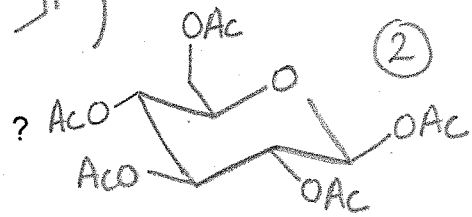
1. SO_3/H_2SO_4
2. $Cl_2/FeCl_3$

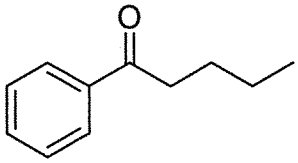
H_3O^+ → ? ~~(C_7H_7Cl)~~ (C_7H_7OCl)  (2)

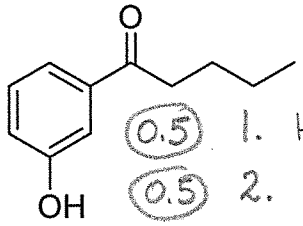
(No part marks)

(l) 

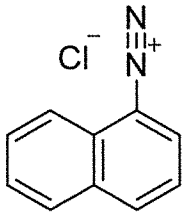
(excess) (Ac ≡ )

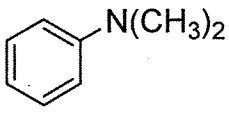
?  (2)

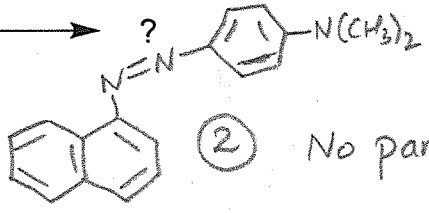
(m) 

? → 

(0.5) 1. HNO_3, H_2SO_4
(0.5) 2. $NaNO_2$, HCl
(1.0) 3. H_2O (with or without Cu^{+2}, Cu_2O)

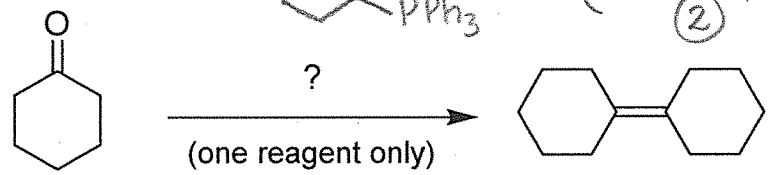
(n) 

 →

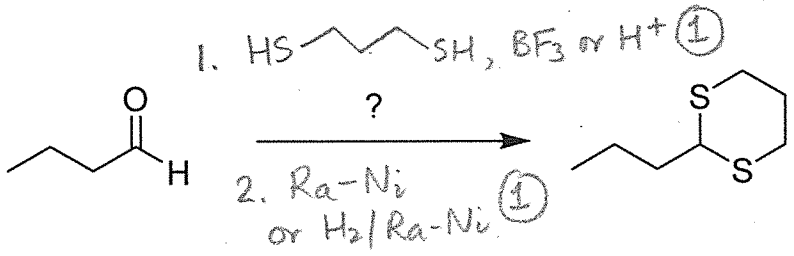
?  (2) No part marks

1. (continued)

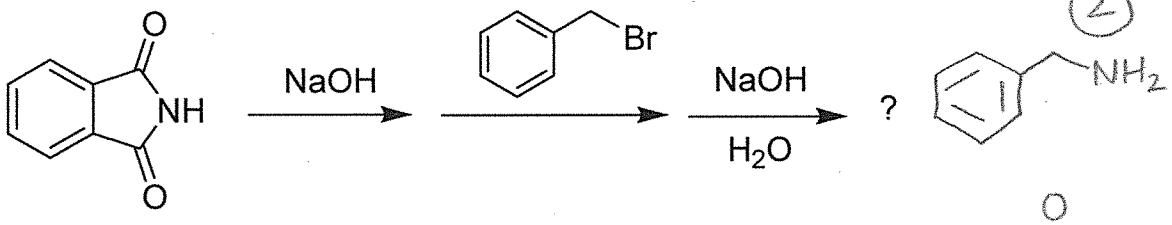
(o)



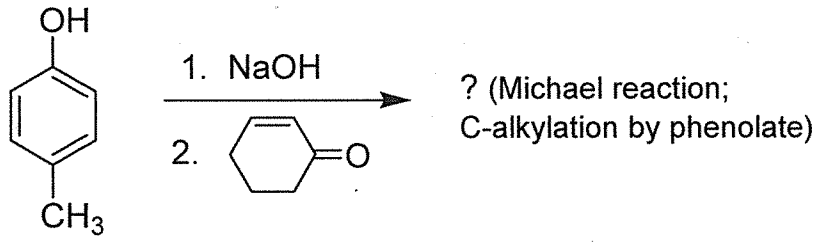
(p)

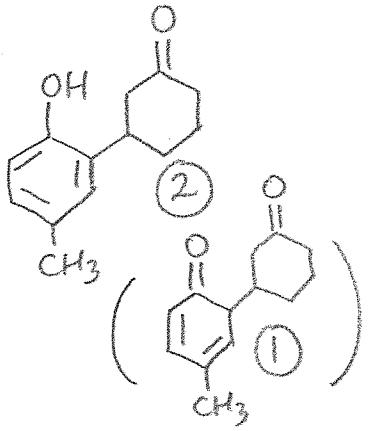


(q)

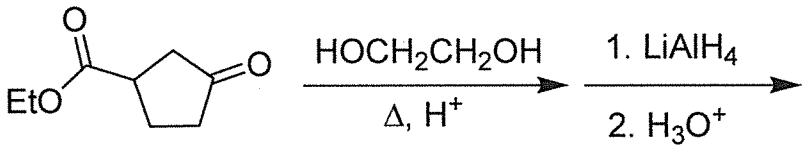


(r)



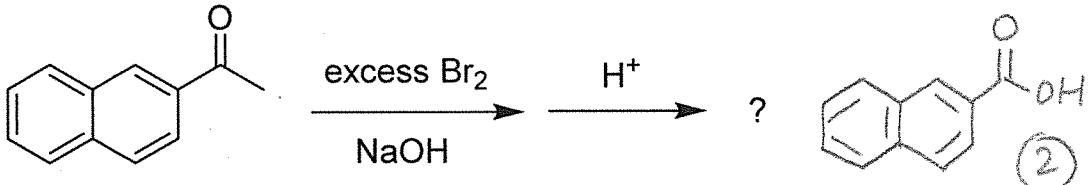


(s)



(No part marks)

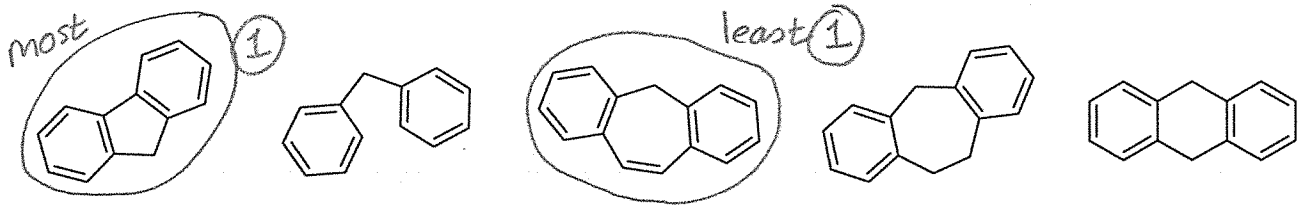
(t)



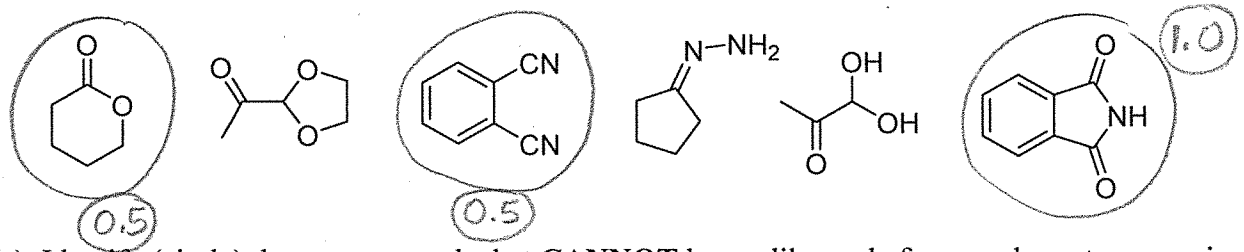
(No part marks)

2. **Multiple Choice** [30 marks].

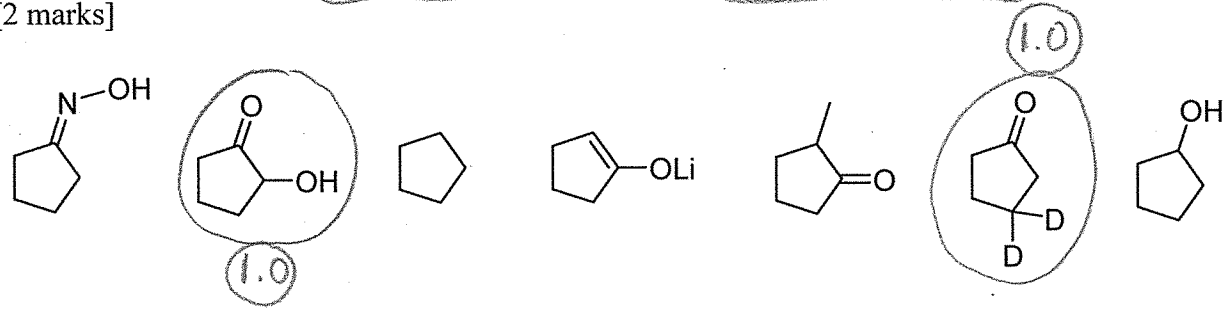
(a) Identify and label the **most acidic** and **least acidic** compound, as C-H acids. [2 Marks]



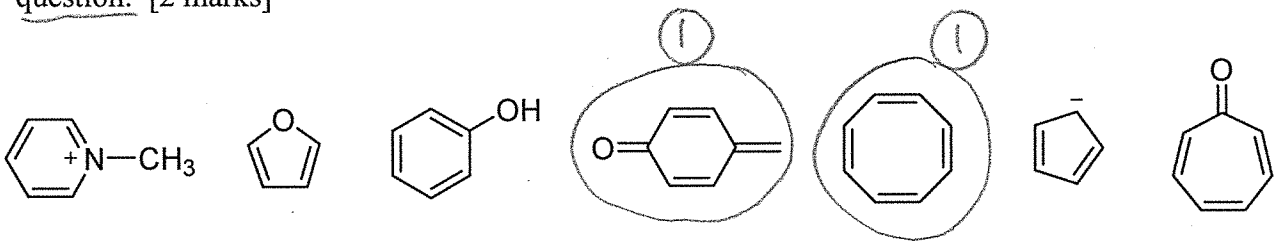
(b) Identify those compounds (circle them) that can be hydrolyzed in H_3O^+ to a carboxylic acid. For each incorrect choice, 0.5 mark will be deducted in this question. [2 Marks]



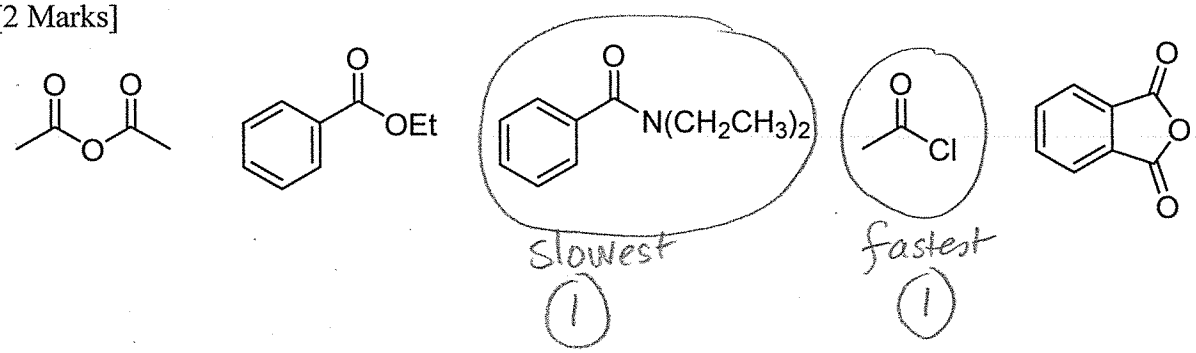
(c) Identify (circle) those compounds that **CANNOT** be readily made from cyclopentanone using a reaction learned to date. For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



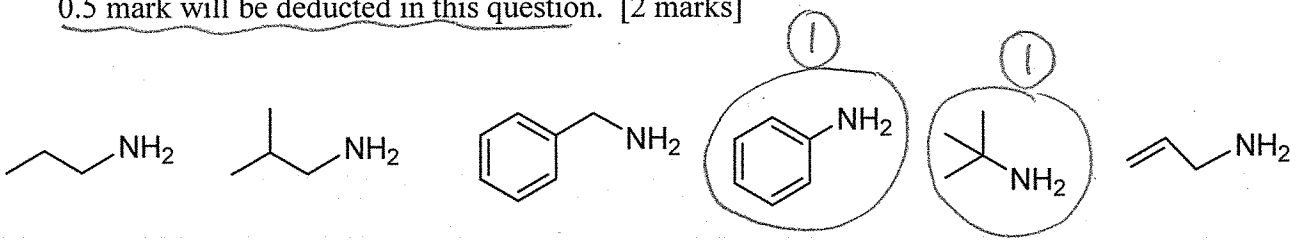
(d) Circle the **non-aromatic** molecules. For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



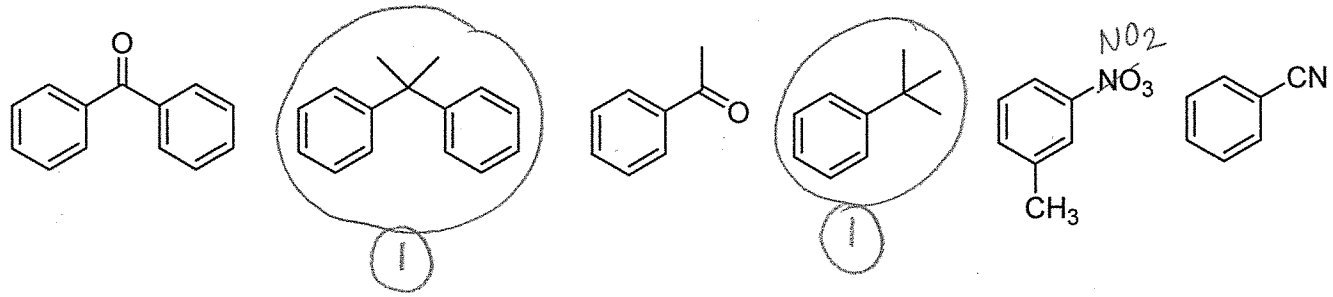
(e) Identify the **fastest** and **slowest** reacting compound for hydrolysis in water. [2 Marks]



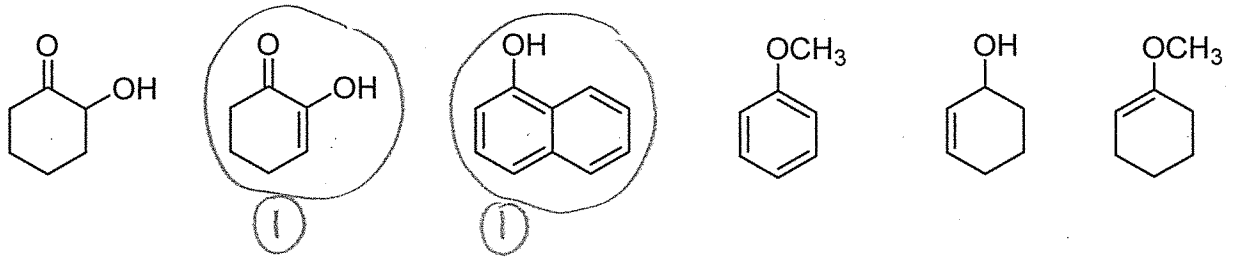
(f) Circle the compounds that **CANNOT** be made using the Gabriel synthesis. For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



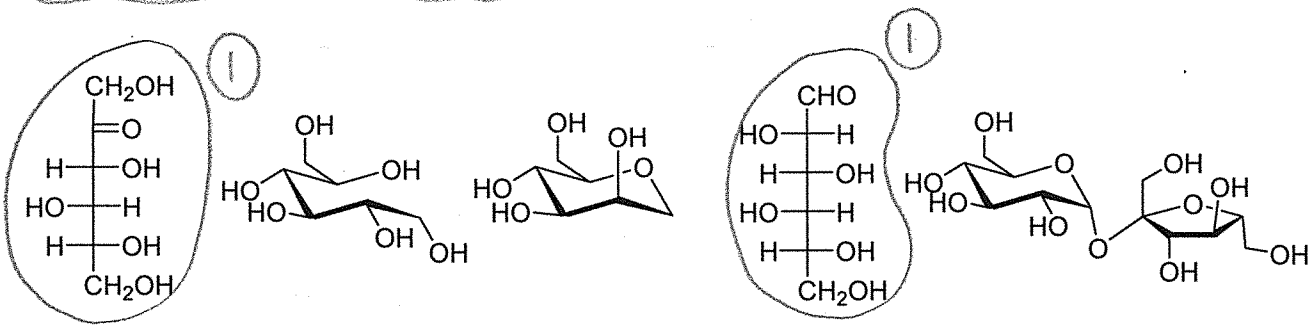
(g) Circle those compounds that can be made by direct Friedel-Crafts alkylation. For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



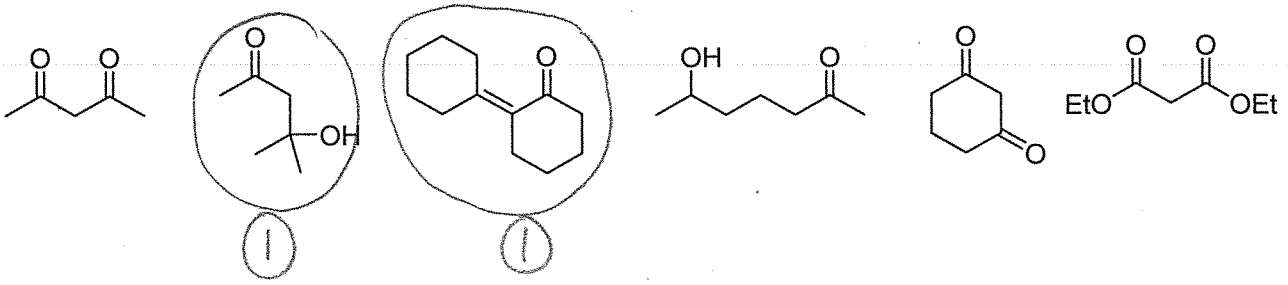
(h) Circle the enols. For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



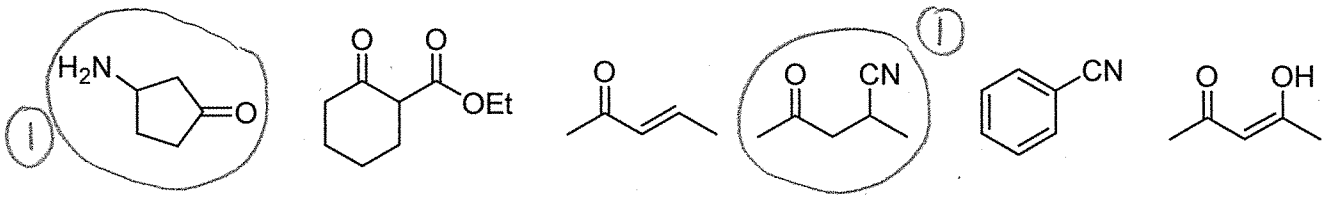
(i) Identify (circle) the **reducing** sugar(s) (or sugar derivatives) from the list below. For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



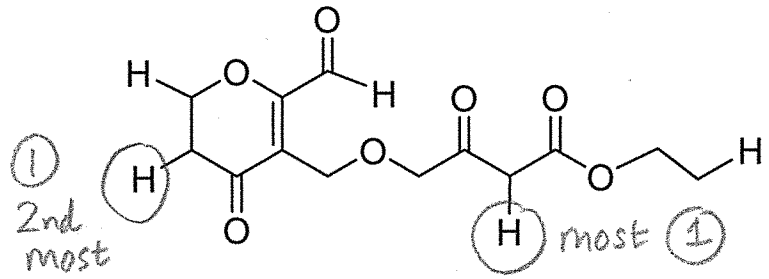
(j) Circle those compounds that **can** be made using simple application of the Aldol condensation. For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



(k) Circle those compounds that can be made from a simple Michael reaction. [2 marks]



(l) Circle and identify the **most** acidic and the **second most** acidic proton of those shown for the molecule below. [2 marks]



(m) With one of the following general methods **CANNOT** be used to make amines? [2 marks]

(i) Reduction of azides.
(ii) Gabriel synthesis.
(iii) Reduction of aromatic nitro compounds.
(iv) Reduction of oximes.
(v) Reduction of lactones.

(n) Which statement concerning lipids and sugars is **incorrect**? [2 marks]

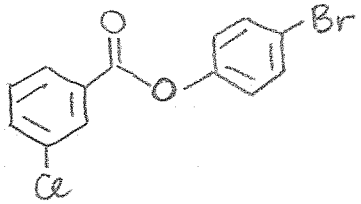
(i) Hydrolysis of fats and oils in $NaOH/H_2O$ gives soap.
(ii) They can be transesterified in methanol to give biodiesel.
(iii) Sugars can be oxidized with bromine in water.
(iv) Polyesters and polyamides are useful polymers used extensively in clothing.
(v) The hydrolysis of fats in NaOH/water proceeds via hemiacetal intermediates..

(o) Which statement concerning lipids is **incorrect**? [2 marks]

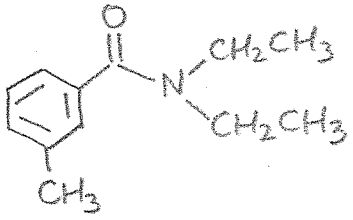
(i) Steroids have three cyclohexane rings.
(ii) Testosterone has a ketone and an alkene.
(iii) Estrone and testosterone are readily interconvertible.
(iv) Estrone has a phenol ring.
(v) Vitamin D is derived from a steroid by UV irradiation.

3. Drawing and Identifying Structural Fragments. [8 marks total]

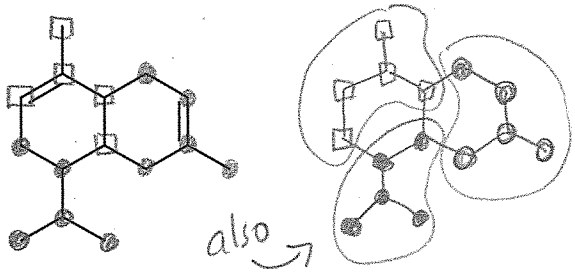
(a) Draw 4-bromophenyl 3-chlorobenzoate. [2 marks]



(b) Draw *N,N*-diethyl-3-methylbenzamide. [3 marks]



(d) Identify the isoprene units (use circles or squares as required) of the sequiterpene shown below. [3 marks]

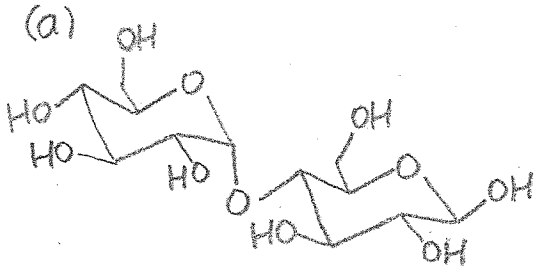


Sugar chairs must be drawn as shown Howarth

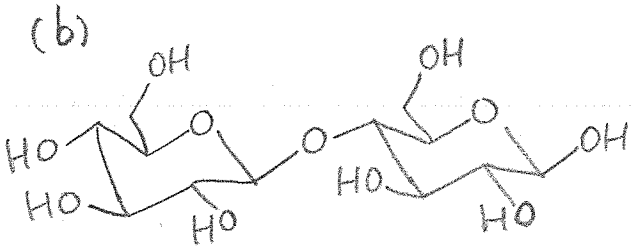
4. Draw **any two** (2) of the following molecules in their **most stable CHAIR conformation**. Show stereochemistry clearly. [6 marks total] 3 each NOT ALLOWED.

(a) maltose (b) cellobiose (c) β-(D)-glucose (d) estradiol

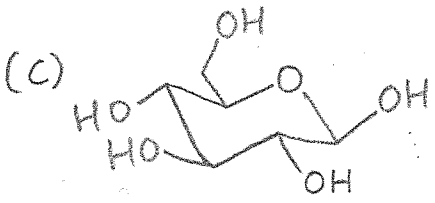
(a)



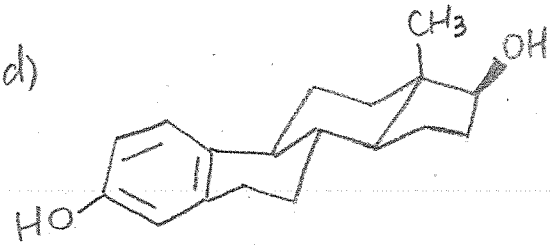
(b)



(c)

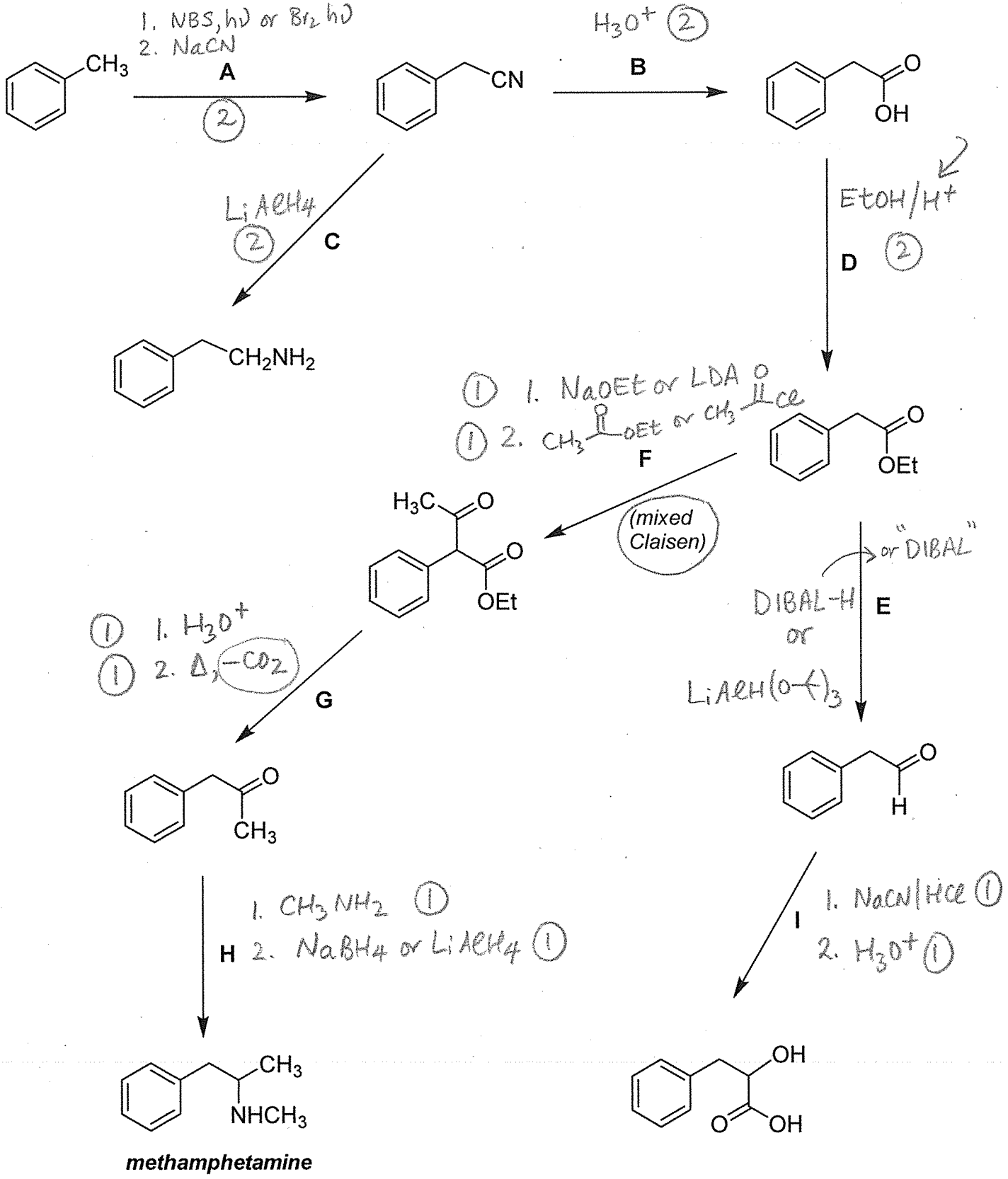


(d)



→ except as shown
(heat or work-up not required)

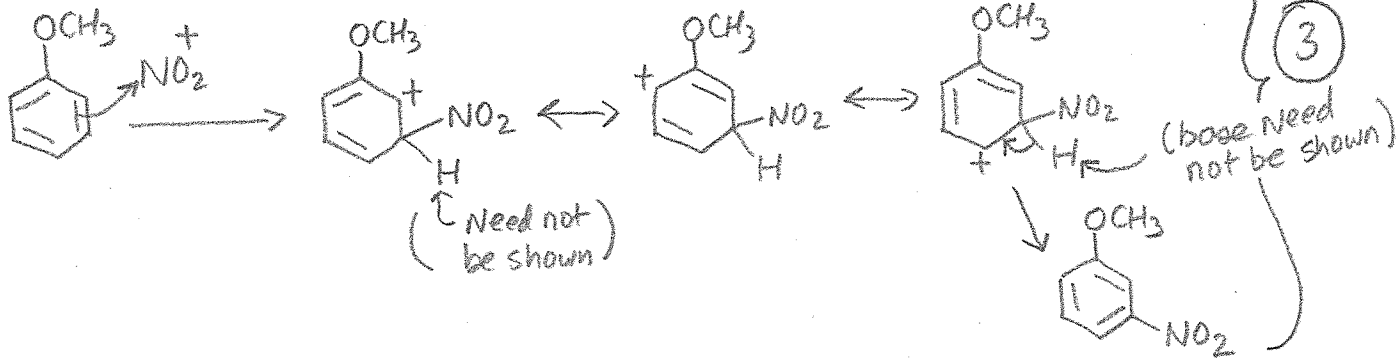
5. Propose the correct reagents for each step marked **A-I** to successfully accomplish the reactions shown below. [18 marks]



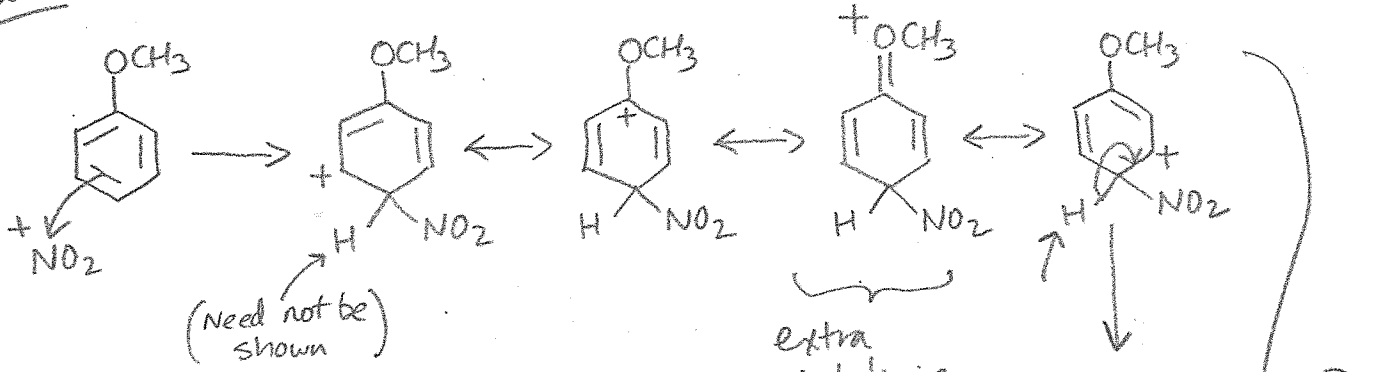
6. Nitration of **anisole** ($PhOCH_3$; Ph = benzene ring) gives only **ortho** and **para**-substituted products. Explain this preference by writing out the step-wise mechanisms of reaction (using curved arrow notation) for attack of the electrophile at the **meta** and **para** positions only, showing the formation of the cyclohexadienyl cations that are formed (and all their resonance structures) and deducing their relative stability, and then show how each is transformed to the final substitution product. (Use NO_2^+ to represent the critical nitrating agent). [10 marks]

(if student shows attack at meta and ortho positions, deduct 2 marks, so maximum is (8) marks)

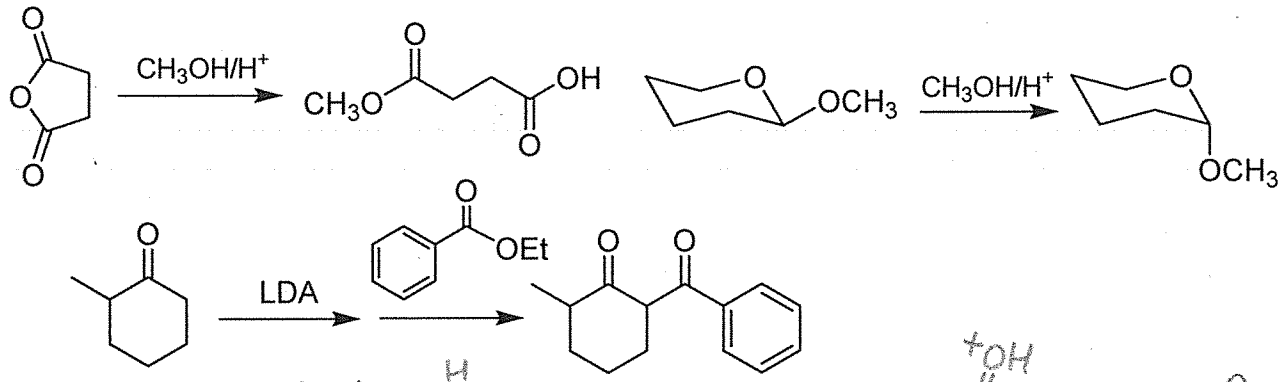
meta

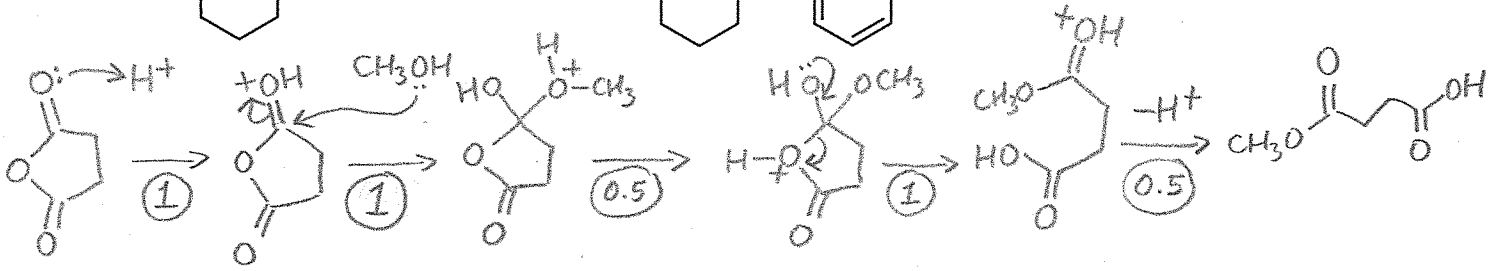


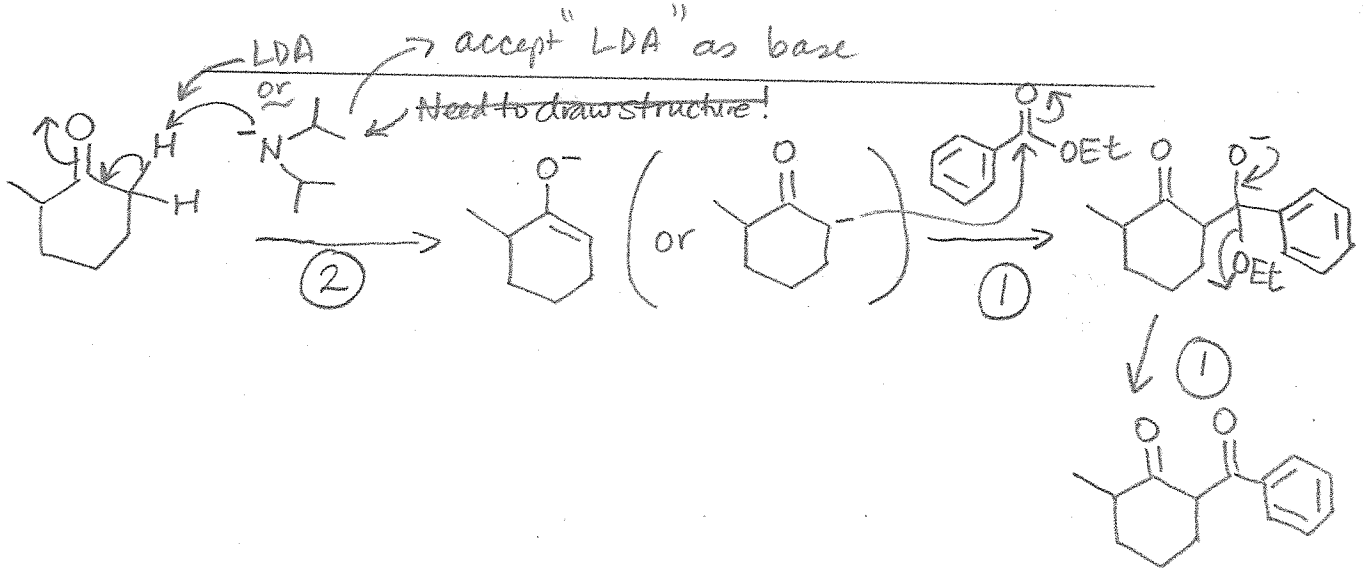
para

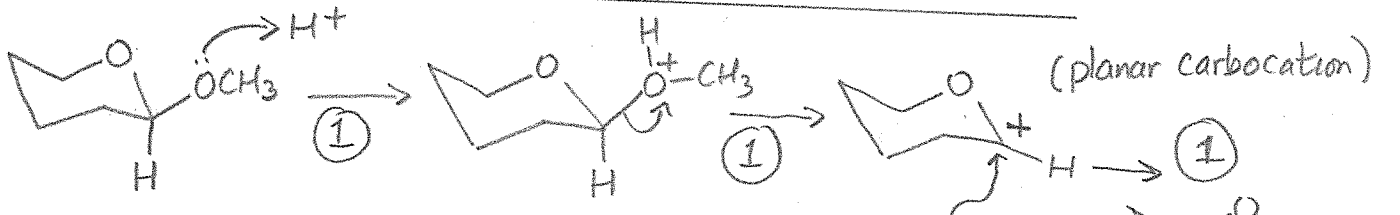


7. Propose **step-wise** mechanisms (using curved arrow notation) for **any two (2)** of the following reactions. You must show all importance steps. [8 marks]

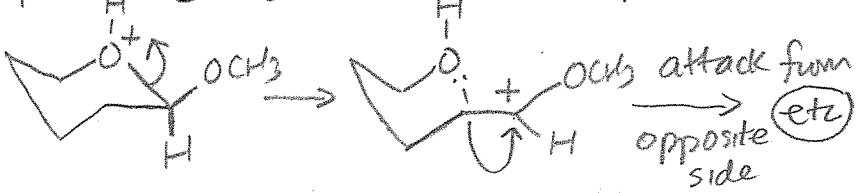




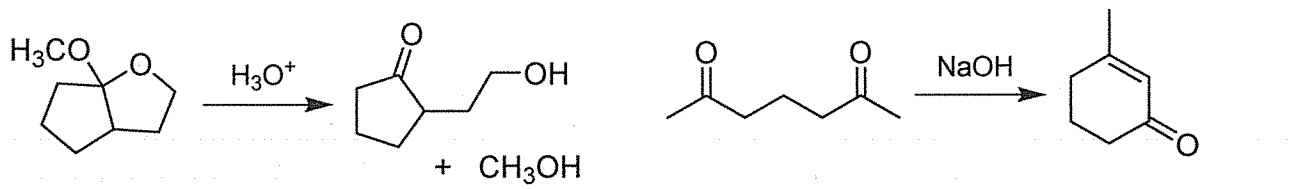


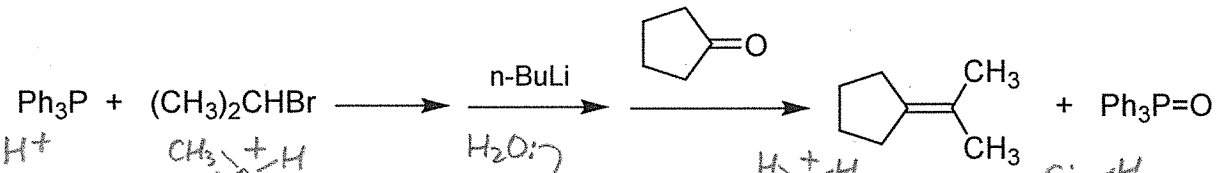


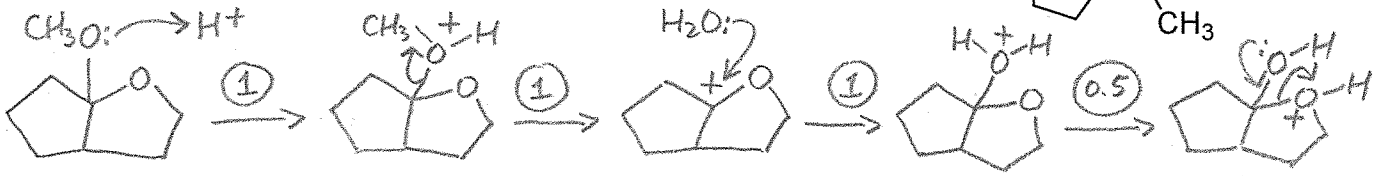
Students can also start mechanism by protonating oxygen in ring, but it will require ring opening:



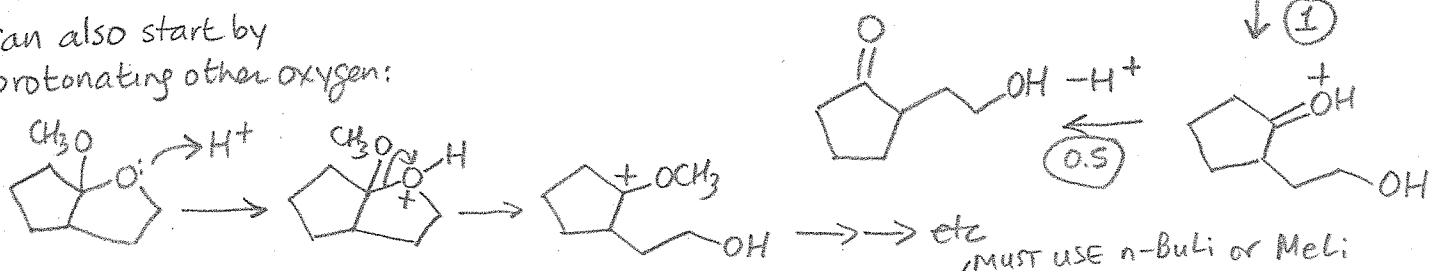
8. Propose **step-wise** mechanisms (using curved arrow notation) for **any two (2)** of the following reactions. [10 marks]



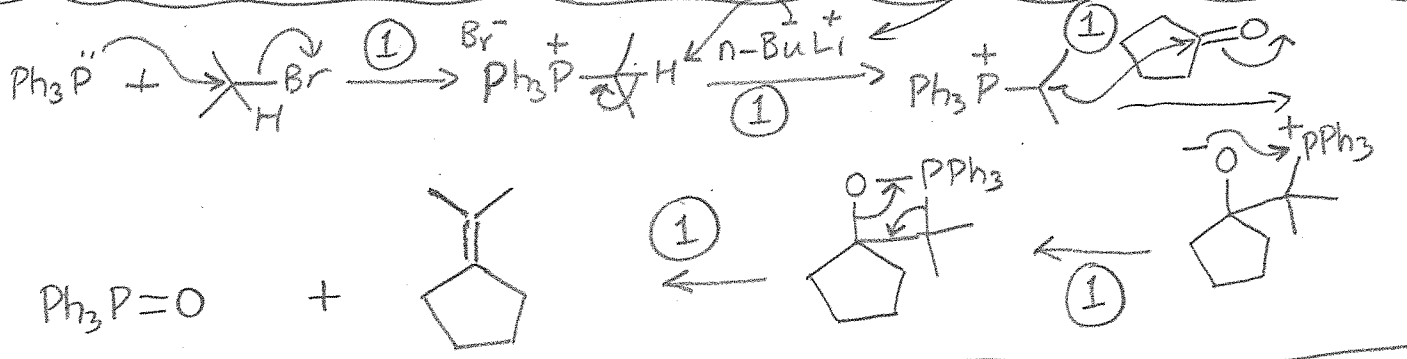


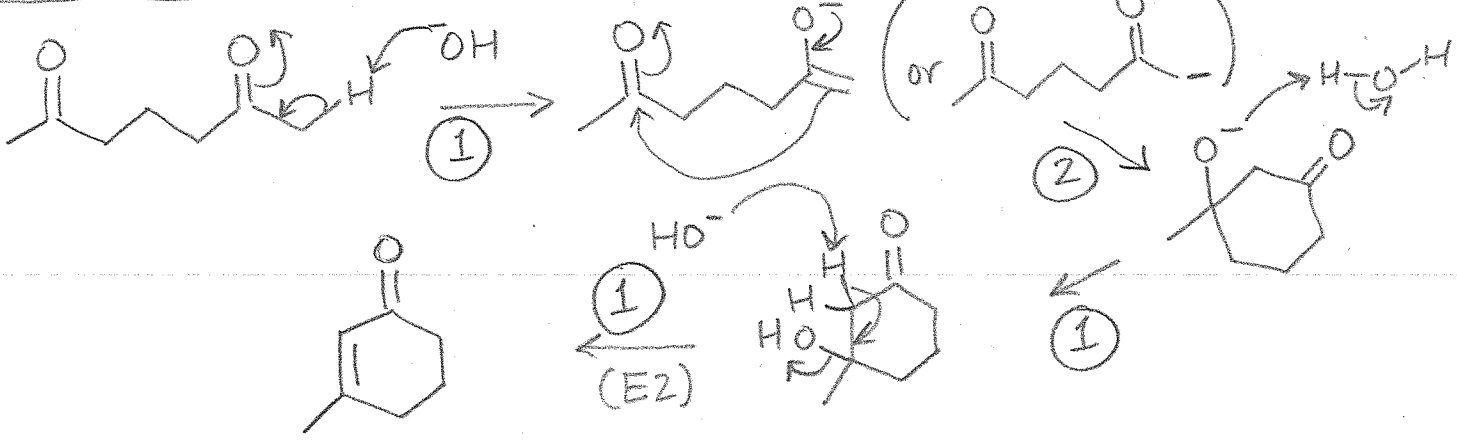


Can also start by protonating other oxygen:

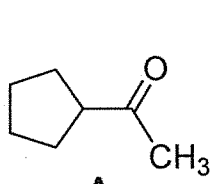


MUST USE n-BuLi or MeLi

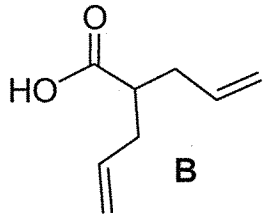




9. Synthesize **A** or **B** using malonic ester synthesis or acetoacetic ester synthesis (**only one will work for each target!**). Show all important steps. Simple reagents and compounds with 4 carbons or less are available. [6 marks]



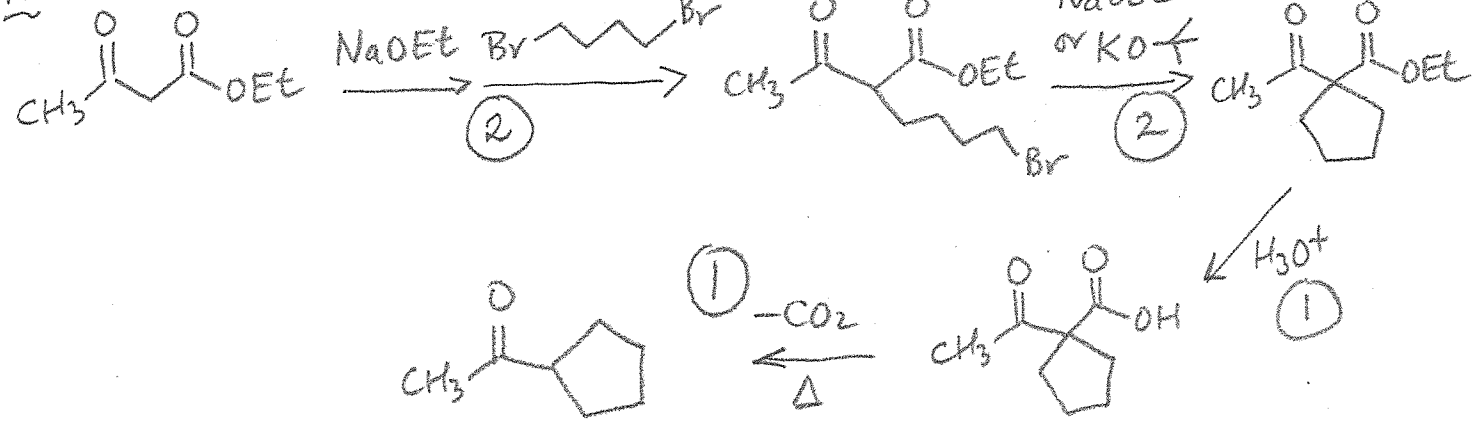
A



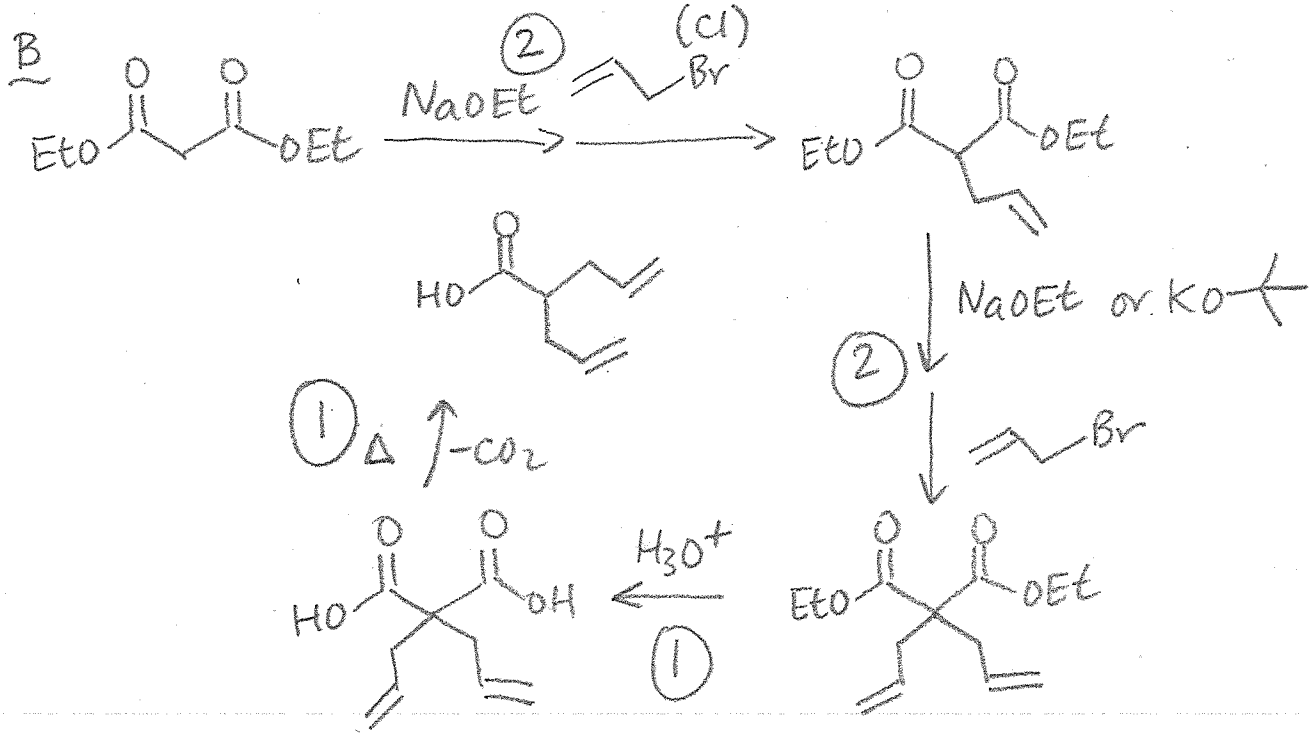
B

(If student uses wrong method, max (3) marks)

A



B



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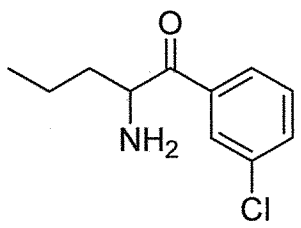
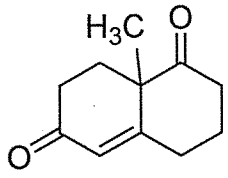
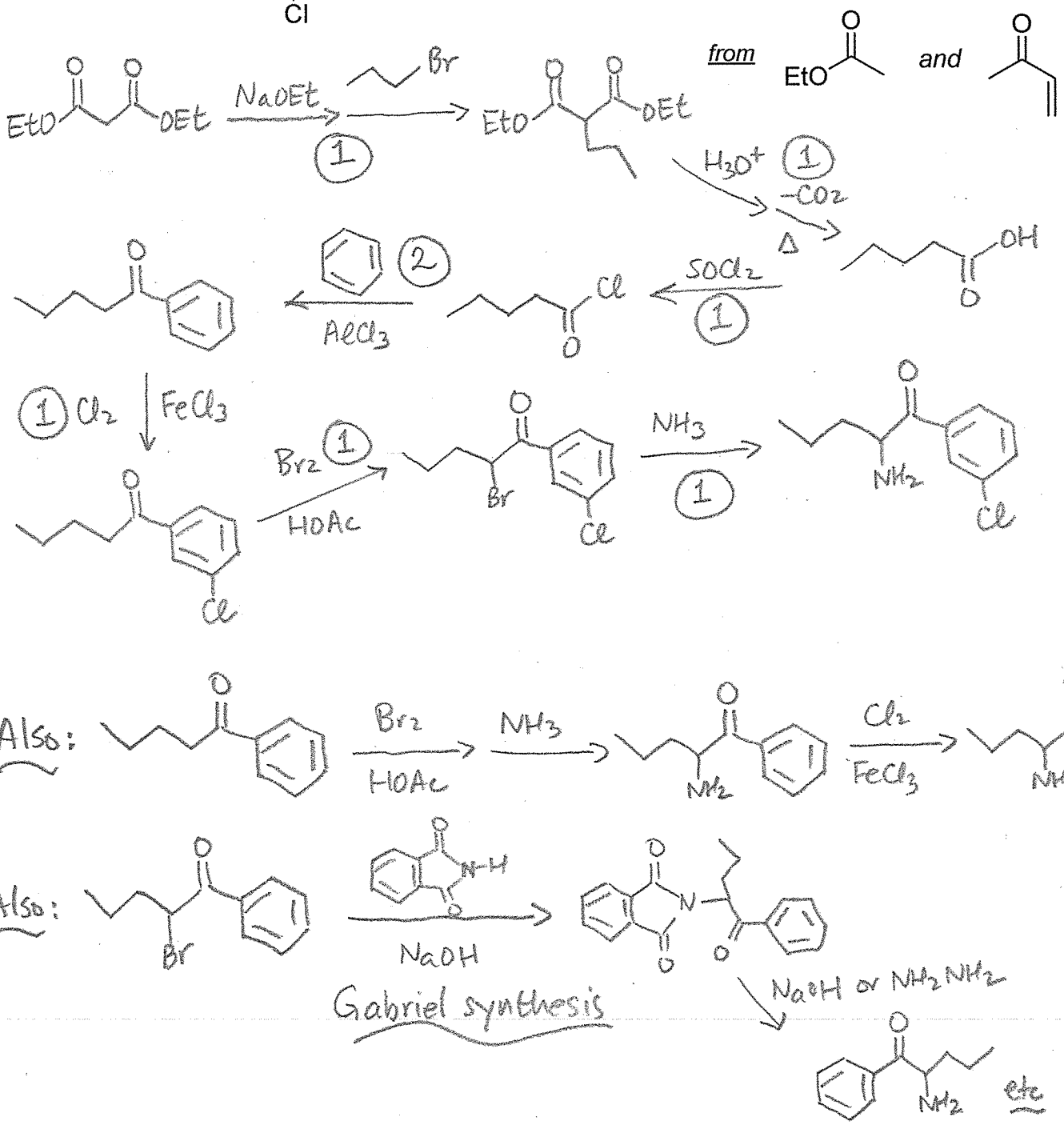
10. Propose a viable synthesis for **ONE** of the targets shown below. Commonly available reagents (in addition to the starting materials shown) are available. Show all important steps in your proposed synthetic route. [8 marks]



from $CH_2(CO_2Et)_2$ *and* benzene

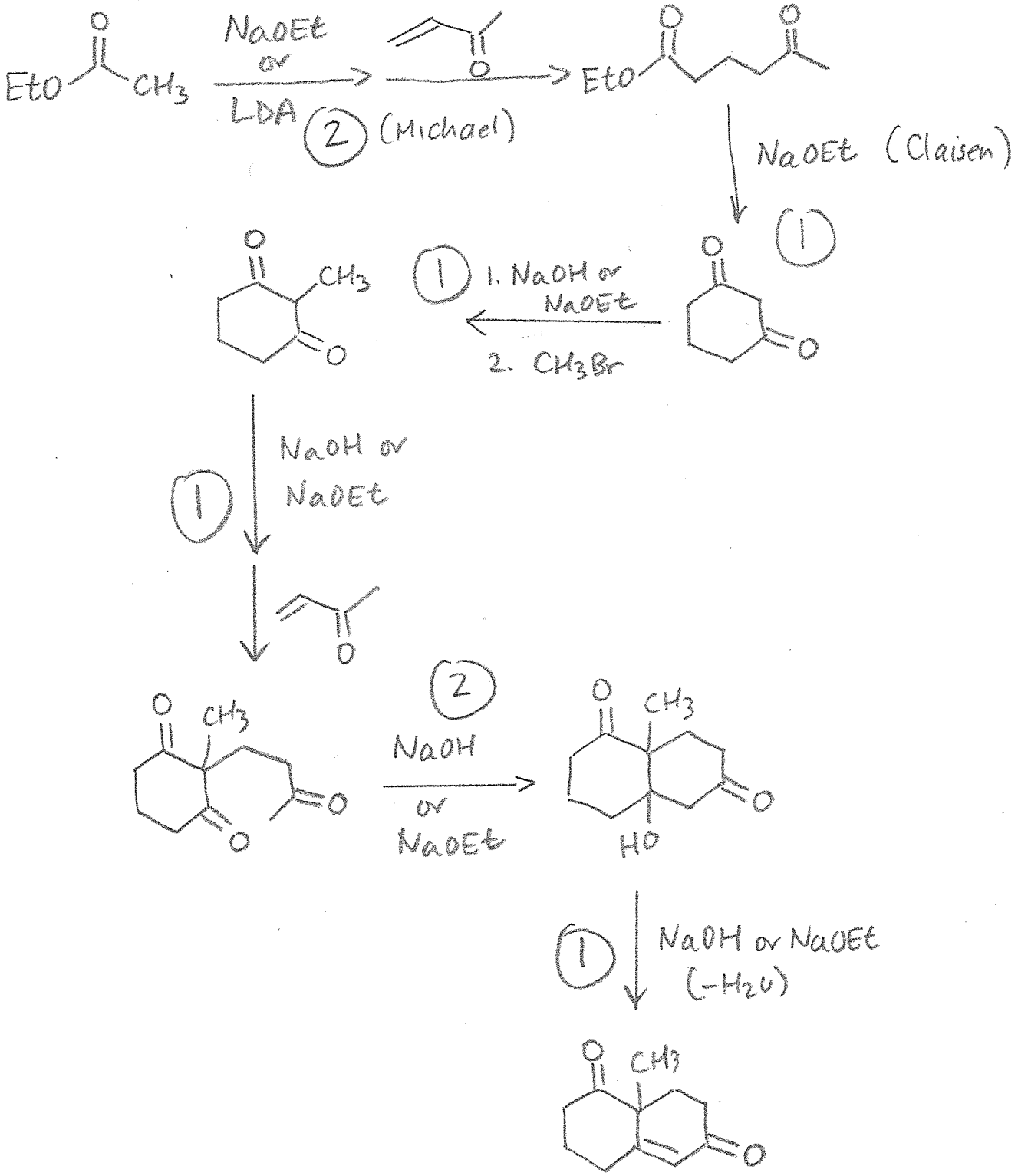
OR





END

(Continued →)


EtO
CH3
NaOEt
or
LDA
2
(Michael)
EtO
NaOEt (Claisen)
1
1
1. NaOH or NaOEt
2. CH3Br
CH3
1
NaOH or
NaOEt
2
NaOH
or
NaOEt
CH3
HO
1
NaOH or NaOEt
(-H2O)
CH3

UNIVERSITY OF VICTORIA
FINAL EXAMINATION, APRIL 2015

CHEMISTRY 232 (CRN 20491; A01)

Organic Chemistry for Health and Biological Sciences

Name: ANSWER GUIDE **ID:** V00
(use capitals)

ANSWER ALL QUESTIONS ON THE EXAM PAPER

Time: 3 hours
Instructor: Dr. P. Wan
Pages: 14 (including this cover page)

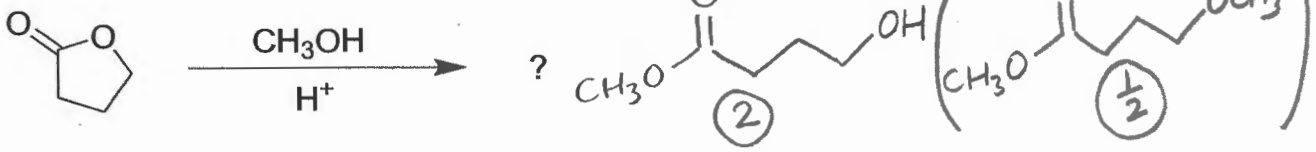
Molecular models are permitted. No other aides are allowed.
Students **must count the number of pages** in this examination paper before starting to write the exam. Report any discrepancy immediately to the invigilator.

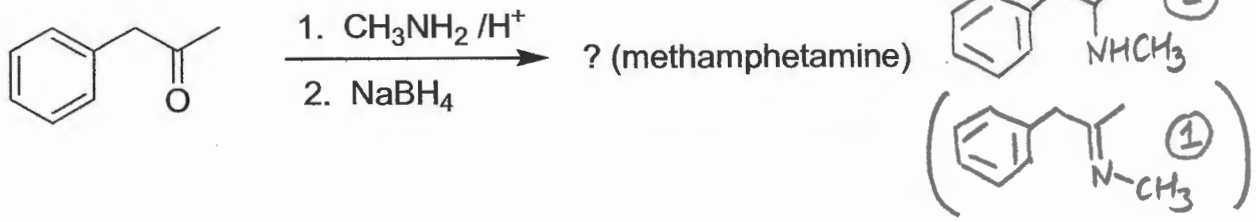
There are **10** questions worth a grand total of **140** marks.

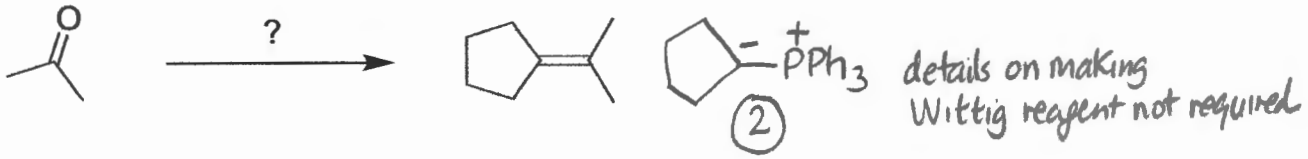
Question	MARK	Question	MARK
1 (40 *marks*)		9 (6)	
2 (28)		10 (8)	
3 (6)			
4 (6)			
5 (18)			
6 (10)			
7 (8)		RAW SCORE (/140)	
8 (10)		% EXAM	

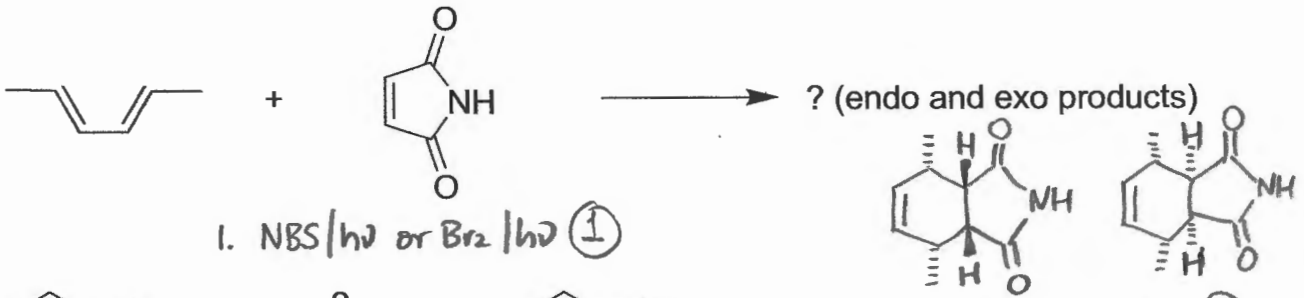
1. **Reactions.** Give the expected major product(s) or required reagent(s) for each of the following reactions. **DO ALL REACTIONS** (2 marks each; total of 40 marks)

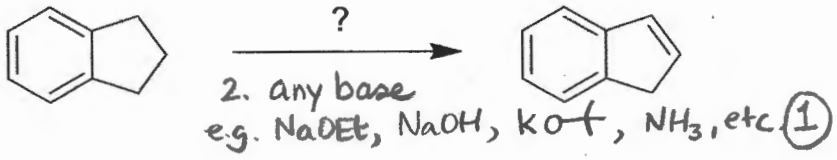
(a) 

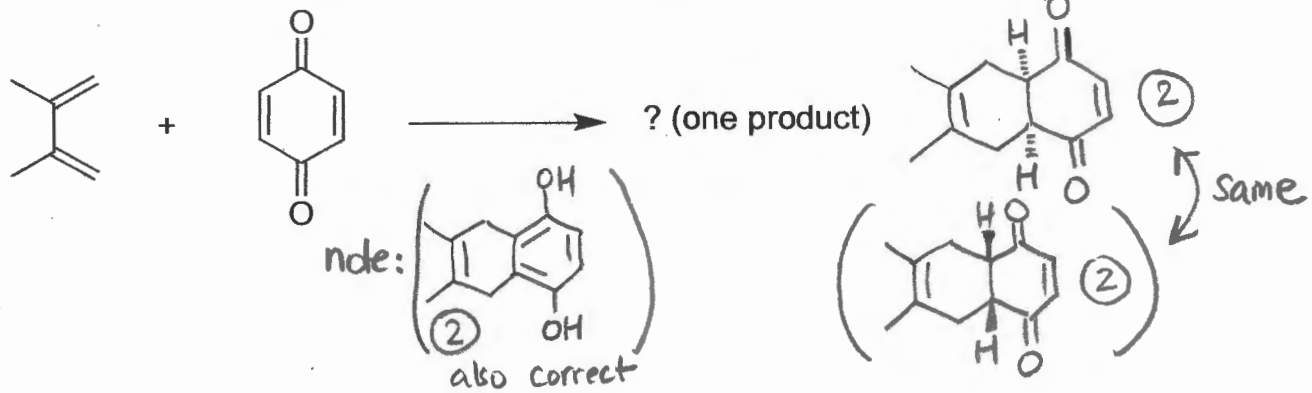
(b) 

(c) 

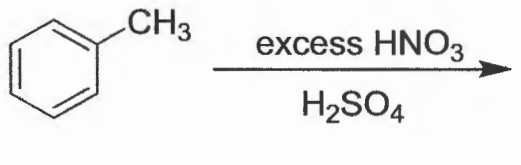
(d) 

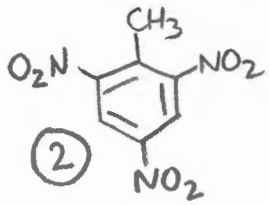
(e) 

(f) 

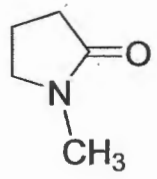
(g) 

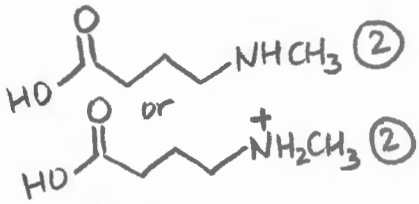
1. (continued)

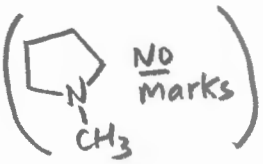
(h) 

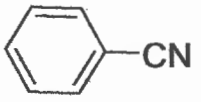


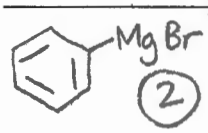
(1) mark for answers with 1 or 2 nitro groups at ortho & para; no marks at meta

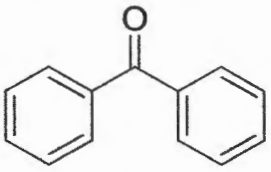
(i) 

H_3O^+, Δ → ?


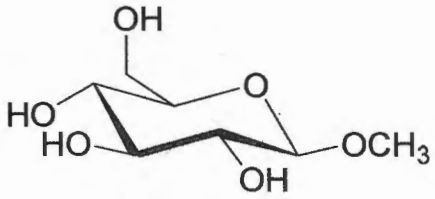


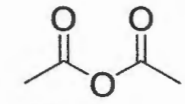
(j) 

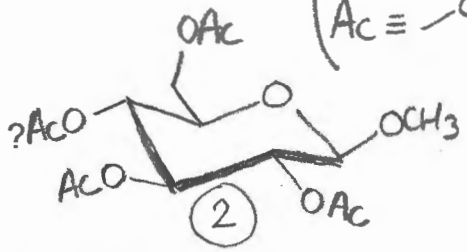
? 



(No need to show work-up in H_3O^+)

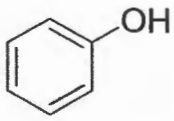
(k) 

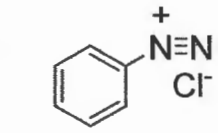


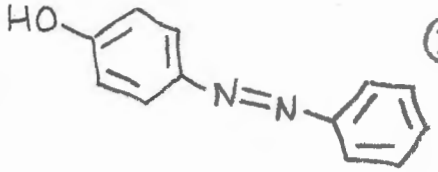


(Ac ≡ 

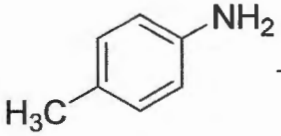
)

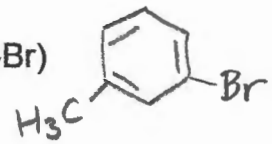
(l) 

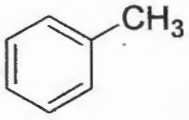


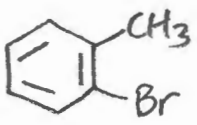
→ ?


(1 mark for ortho isomer)

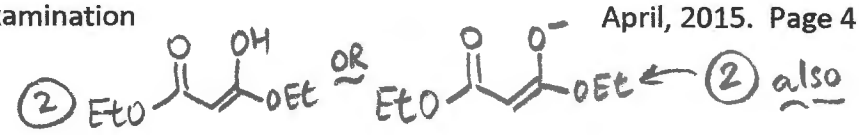
(m) 

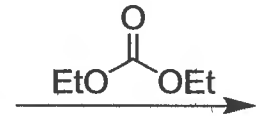
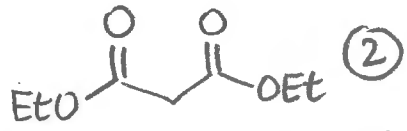
$Br_2/FeBr_3$ (1 mole) → 1. $NaNO_2/HCl$ 2. H_3PO_2 → ? (C_7H_7Br)


(n) 

1. SO_3/H_2SO_4 2. $Br_2/FeBr_3$ → H_3O^+ → ? (C_7H_7Br)


1. (continued)

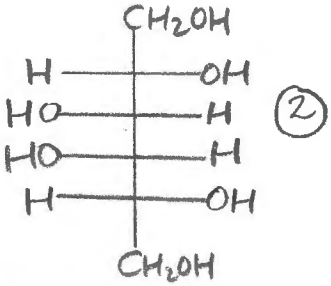


(o) CH_3CO_2Et —LDA→  → ?  (2)

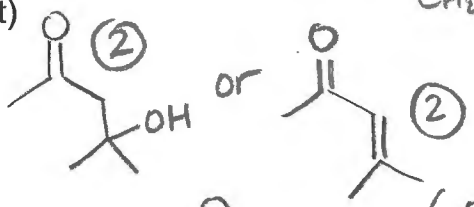
(can be written as $CH_3COCH_2CO_2Et$ (2))

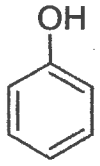
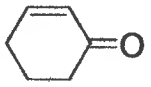
(p) D-galactose —excess $NaBH_4$→ ? (Draw in Fischer projection with carbon 1 at top)

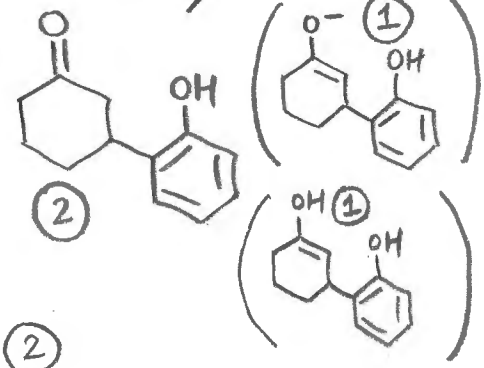
(no part marks)

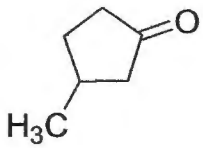
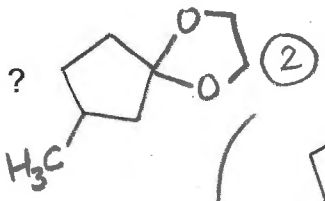


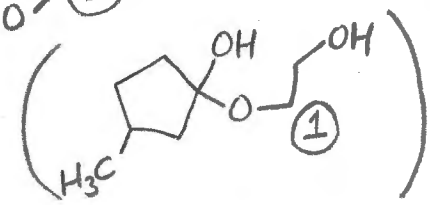
(q) CH_3COCH_3 —NaOH, H_2O→ ? (aldol product)

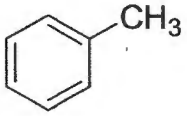
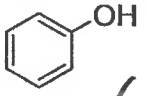
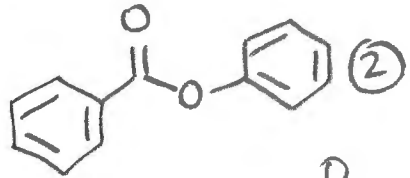


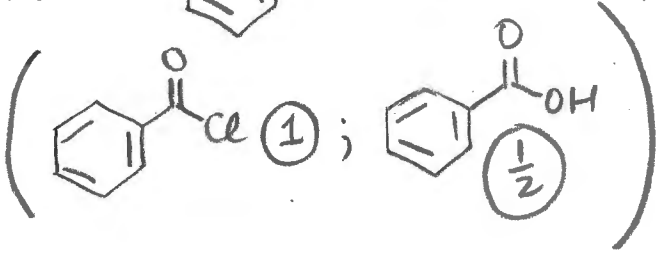
(r)  —1. NaOH, 2.  → ? (Michael reaction; C-alkylation by phenolate)



(s)  —$HOCH_2CH_2OH$, Δ, H^+→ ?  (2)

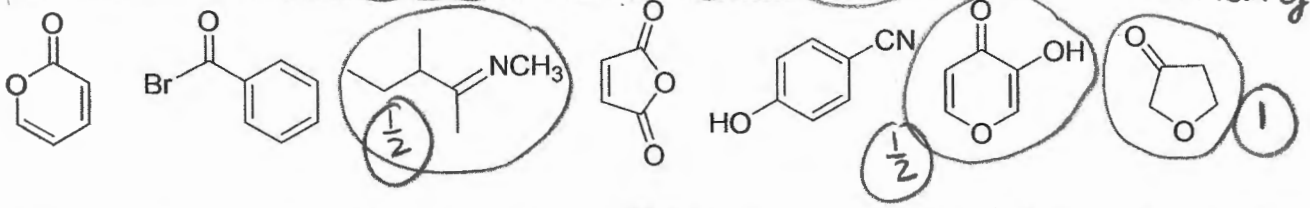


(t)  —$KMnO_4/^-OH$→ —1. $SOCl_2$, 2.  → ?  (2)

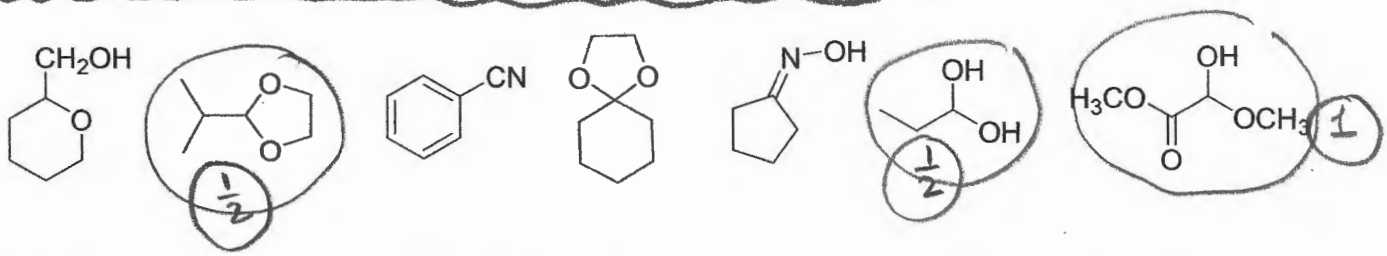


2. **Multiple Choice** (28 marks total).

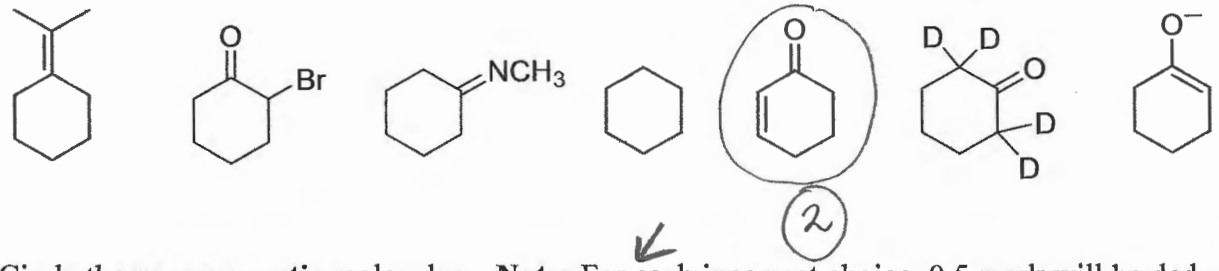
(a) Identify those compounds (circle them) that are **NOT** carboxylic acid derivatives. **Note:** For each incorrect choice, 0.5 mark will be deducted in this question. [2 Marks] → to a minimum of "zero"



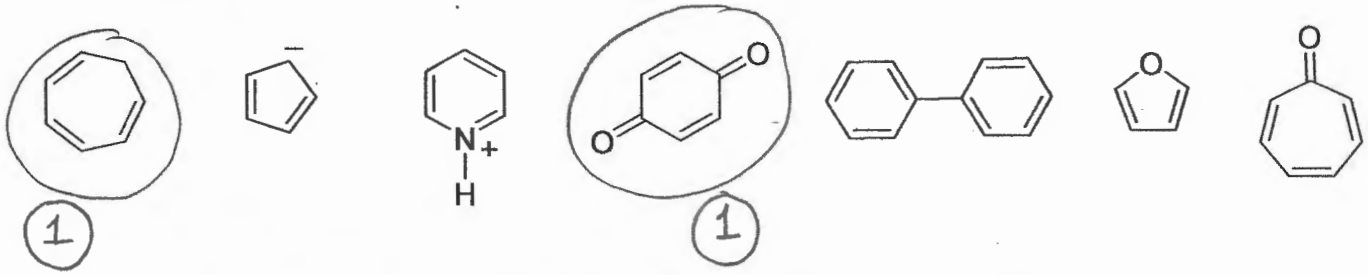
(b) Identify those compounds (circle them) that **WILL** be hydrolyzed (in H_3O^+) to an **aldehyde**. **Note:** For each incorrect choice, 0.5 mark will be deducted in this question. [2 Marks]



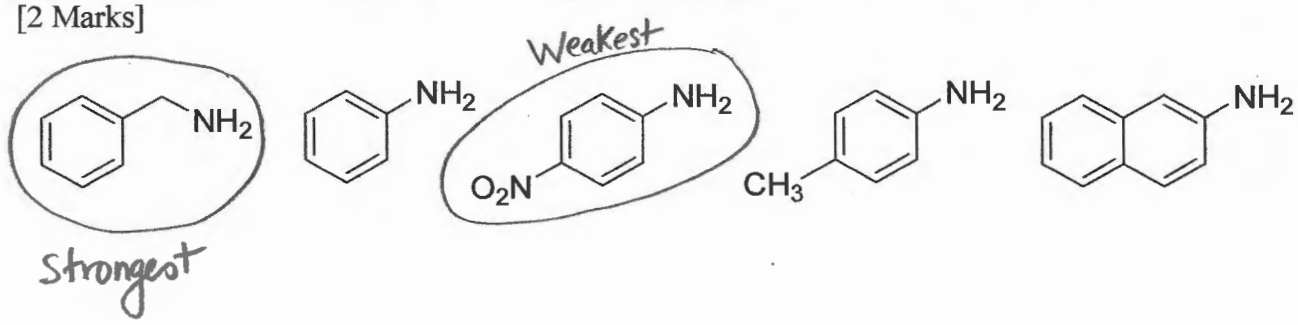
(c) Identify (circle) those compounds that **CANNOT** be readily made from cyclohexanone using a reaction learned to date. **Note:** For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



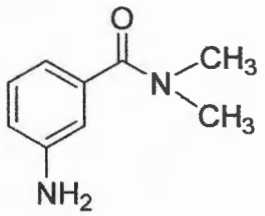
(d) Circle the **non-aromatic** molecules. **Note:** For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



(e) Circle and identify the **strongest** and the **weakest** **amine** base from the list below. [2 Marks]

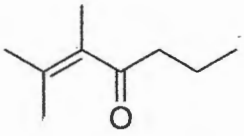


(f) The IUPAC name for the following compound is: [2 marks]



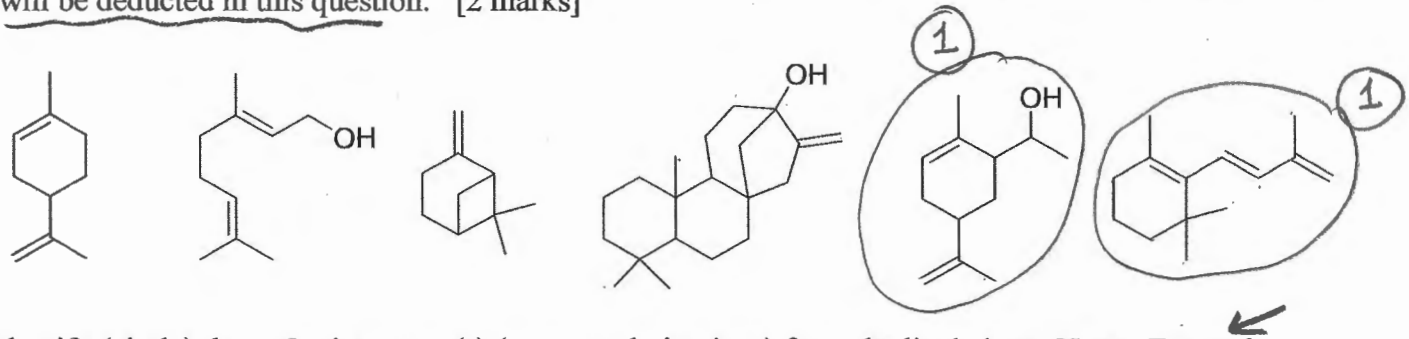
(i) Dimethylaminobenzamide
(ii) N,N-dimethyl-3-aminoacetamide
(iii) N,N-dimethylbenzamide
(iv) N,N-dimethyl-3-aminobenzamine
(v) N,N-dimethyl-3-aminobenzamide

(g) The IUPAC name for the following compound is: [2 marks]

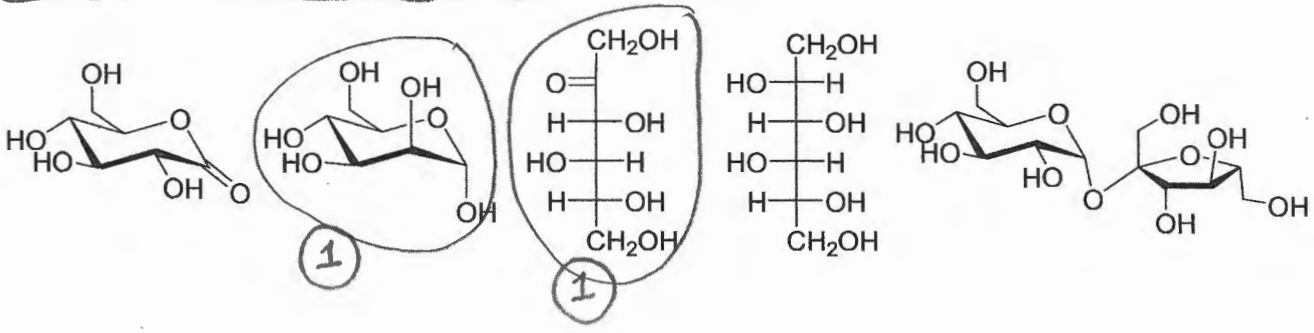


(i) 2,3-dimethyl-2-hepten-4-one
(ii) (Z)-2,3-dimethyl-2-hepten-4-one
(iii) (E)-2,3-dimethyl-2-hepten-4-one
(iv) 4,5-dimethyl-5-hepten-4-one
(v) 2,3-dimethyl-2-hexen-4-one

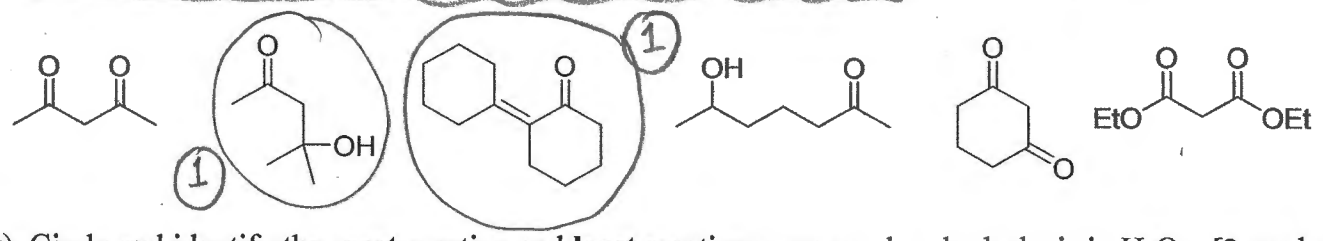
(h) Identify (circle) the structure(s) that is **not** a terpenoid. **Note:** For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



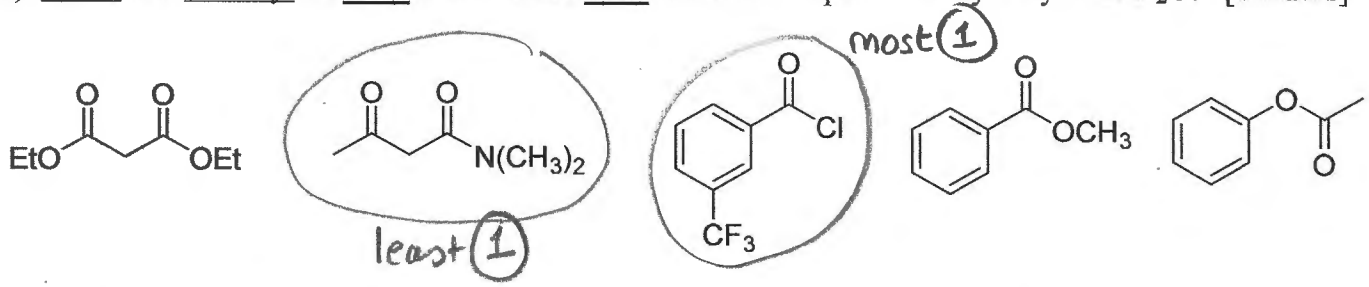
(i) Identify (circle) the **reducing** sugar(s) (or sugar derivatives) from the list below. **Note:** For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



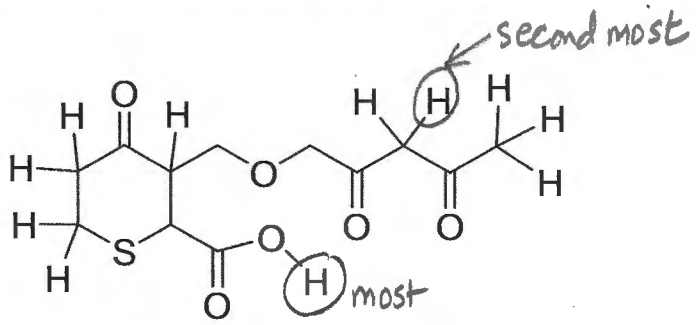
(j) Circle those compounds that **can** be made using simple application of the Aldol condensation. **Note:** For each incorrect choice, 0.5 mark will be deducted in this question. [2 marks]



(k) Circle and identify the **most** reactive and **least** reactive compound on hydrolysis in H_2O. [2 marks]



(l) Circle and identify the **most** acidic and the **second most** acidic proton of those shown for the molecule below. [2 marks]



(m) With respect to the chemistry of sugars and lipids, which of the following statements is **incorrect**? [2 marks]

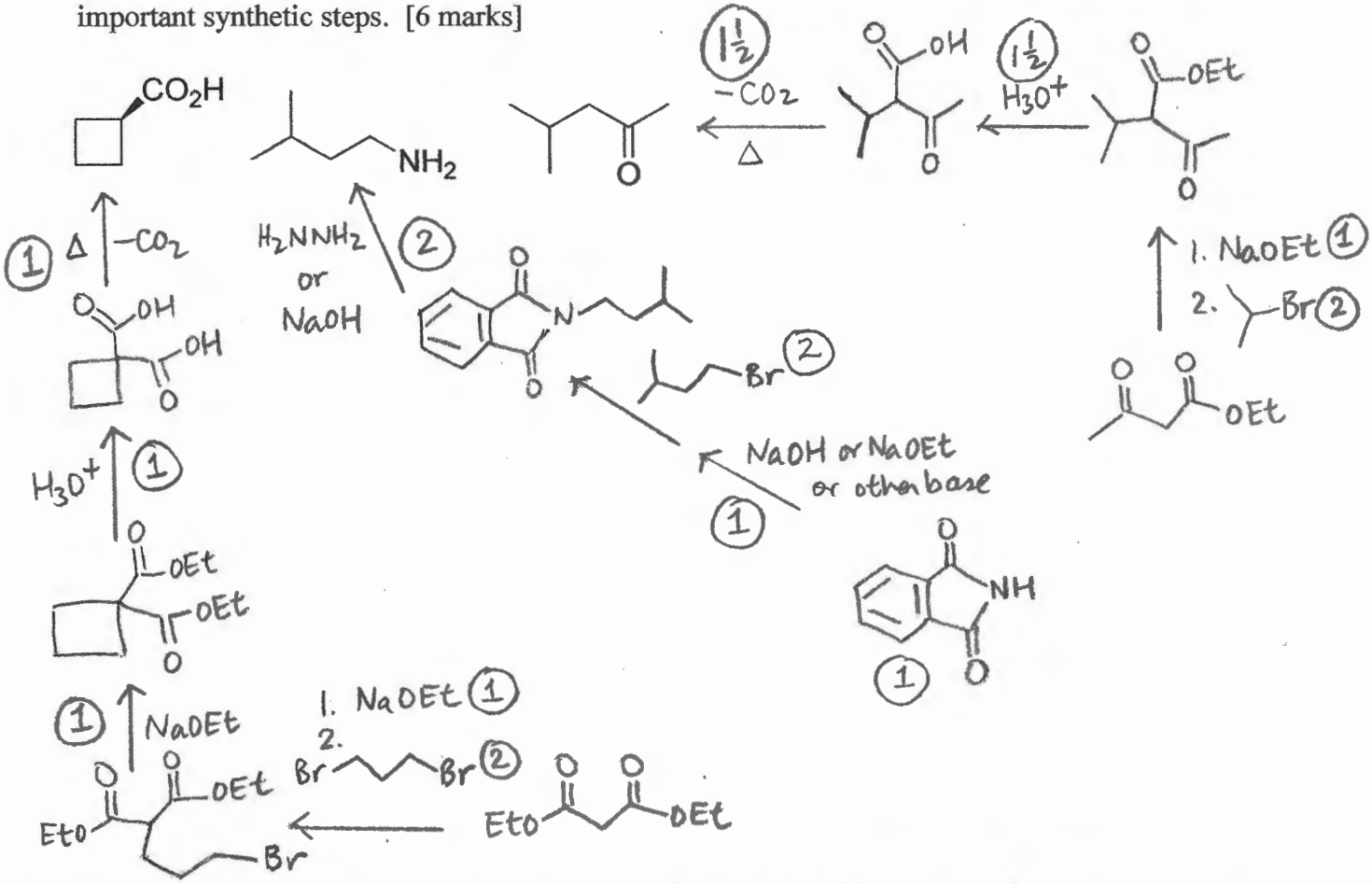
(i) Maltose is a disaccharide.
(ii) Vitamin D can only be made on exposure of the precursor to UV light.
(iii) Estradiol has an aromatic ring.
(iv) Testosterone can be converted to estradiol by enolization followed by air oxidation.
(v) Mannose and glucose are epimers.

(n) Which statement concerning fats and oils and esters in general is **incorrect**? [2 marks]

(i) Hydrolysis in $NaOH/H_2O$ gives soap.
(ii) They can be transesterified to give new esters such as biodiesel.
(iii) The hydrolysis of esters in acid proceeds via formation of intermediate acetals.
(iv) Polyesters are carboxylic acid derivatives and made into clothing fabric.
(v) A δ-lactone is a cyclic ester with 5 carbons in the ring.

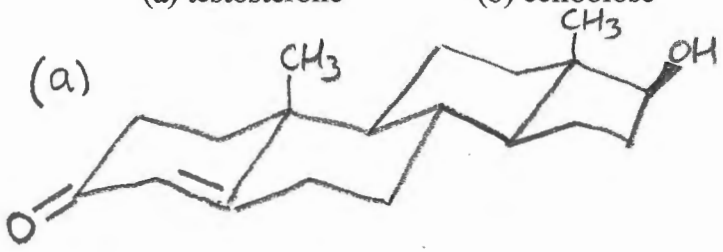
↪ If synthesis is essentially correct, give full (6) marks. ←

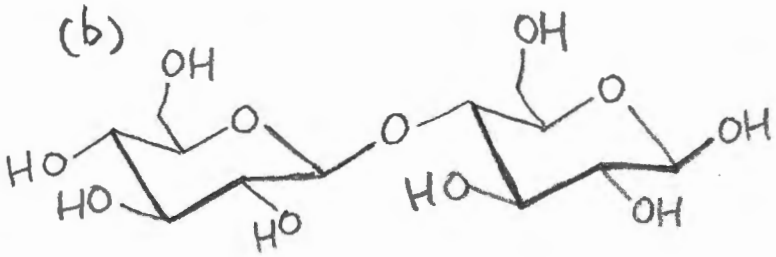
3. The three molecules shown below can each be made using one of acetoacetic ester synthesis, malonic ester synthesis, or the Gabriel synthesis. Synthesize **ONE** of them using one of these synthetic methods starting from carbon compounds with 8 carbons or less, and standard reagents. Show all important synthetic steps. [6 marks]

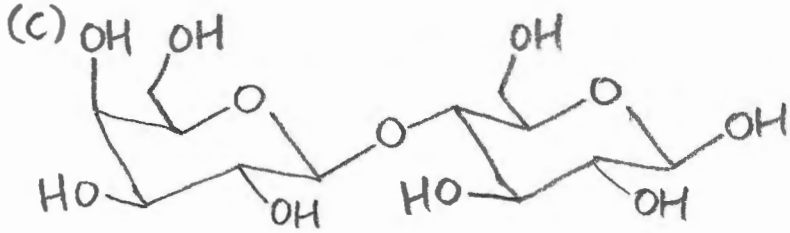


4. Draw **any two** (2) of the following molecules in their **most stable chair conformations**. Show all stereochemistry clearly. [6 marks] (3) marks each; (½) mark deduction for minor errors

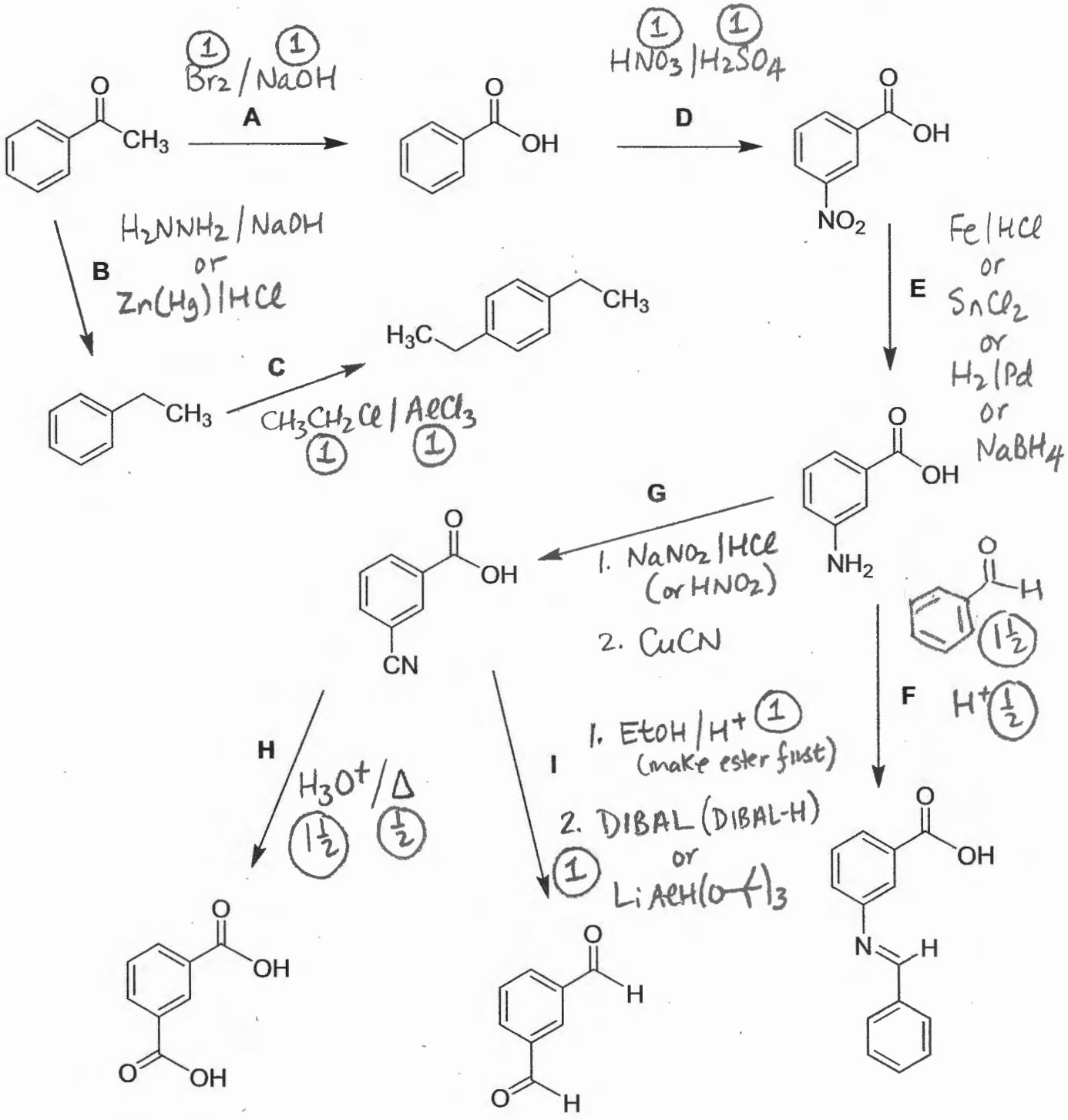
(a) testosterone (b) cellobiose (c) lactose (d) estradiol





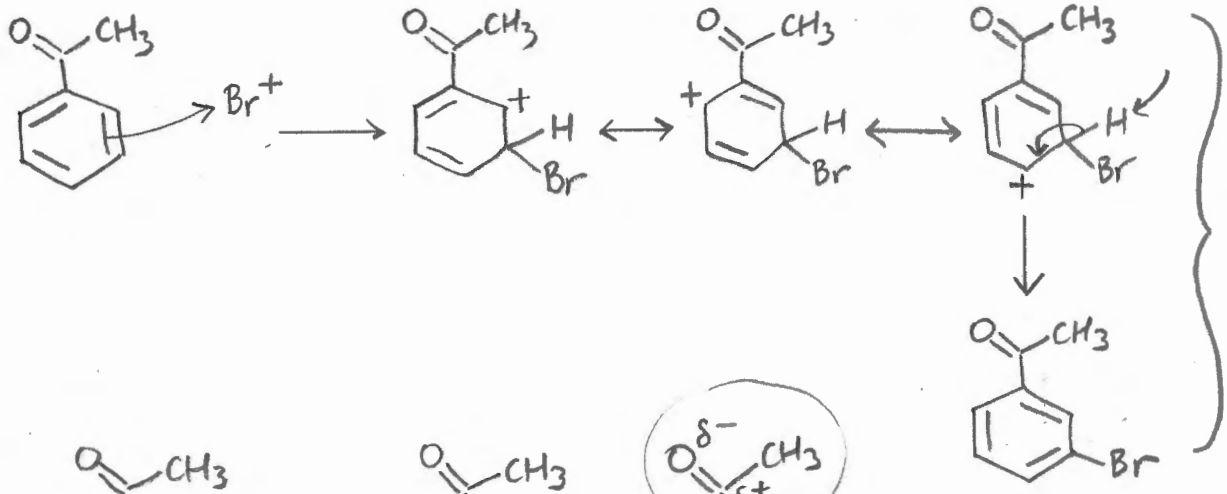


5. Propose the correct reagents for each step marked **A-I** to successfully accomplish the reactions shown below. [18 marks] (2) marks each



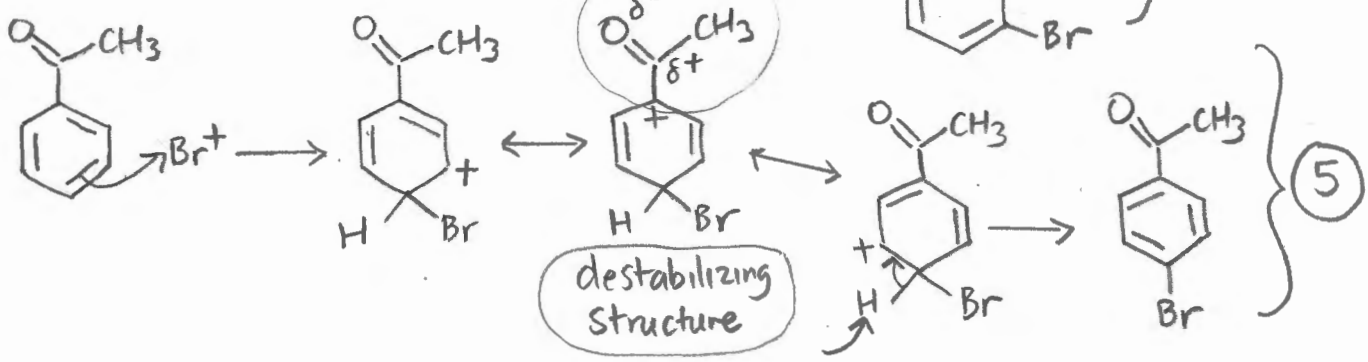
6. Bromination of **acetophenone** ($PhCOCH_3$; Ph = benzene ring) gives only the **meta-substituted product**. Explain this preference by first writing out the step-wise mechanism of reaction (using curved arrow notation) for attack of the electrophile at the **meta** and **para** positions, showing the formation of the cyclohexadienyl cations that are formed (and all their resonance structures) and deducing their relative stability, and then show how each is transformed to the final substitution product. (Use Br^+ to represent the critical brominating agent). [10 marks]

meta attack



(4)

para attack

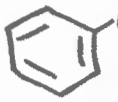


(5)

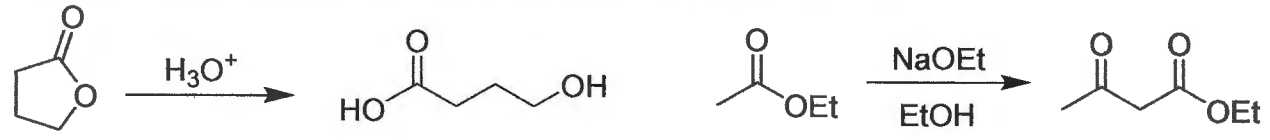
attack at para generates one destabilizing resonance structure → (½)

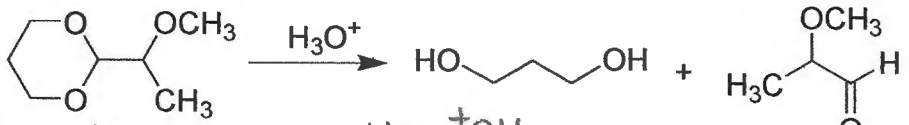
raises activation barrier; hence slower rx (½)

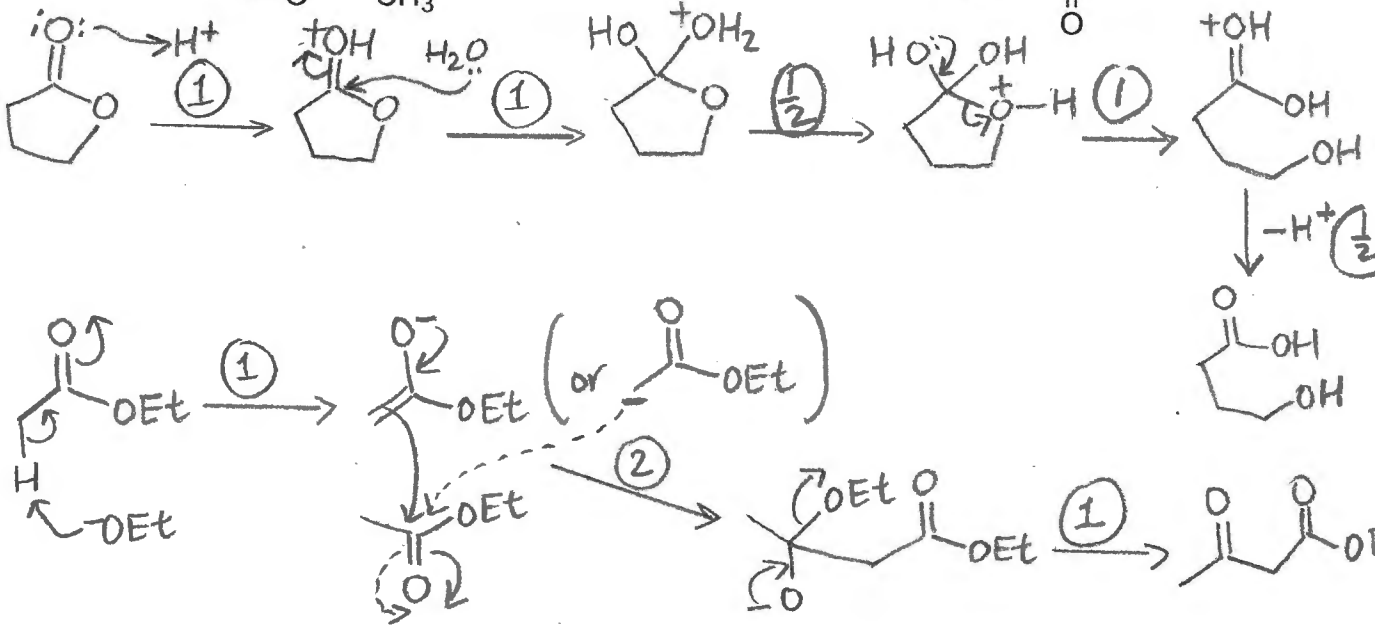
If ortho attack is shown instead of para attack, accept it, and mark it as above, but maximum is (4) marks ((1) mark deduction).

Some students will not draw acetophenone correctly, and may assume it is  (!). They will get completely different answers. Mark it, and give a maximum of (5) marks if everything seems OK. That is, do not give zero if students starts with incorrect compound.

7. Propose **step-wise** mechanisms (using curved arrow notation) for **any two (2)** of the following reactions. You must show all importance steps. [8 marks]

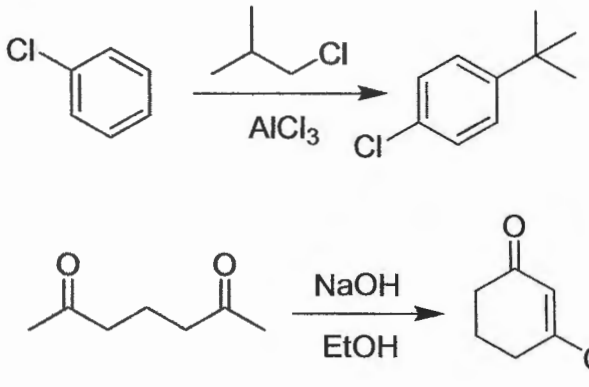


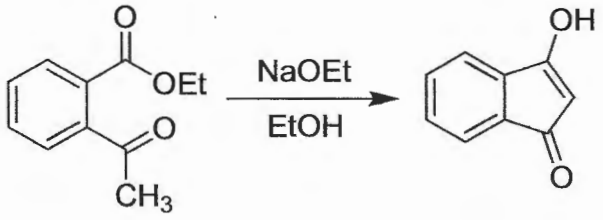


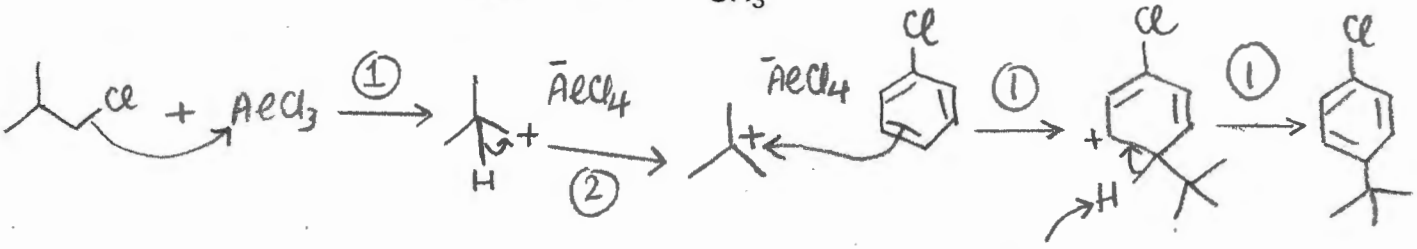


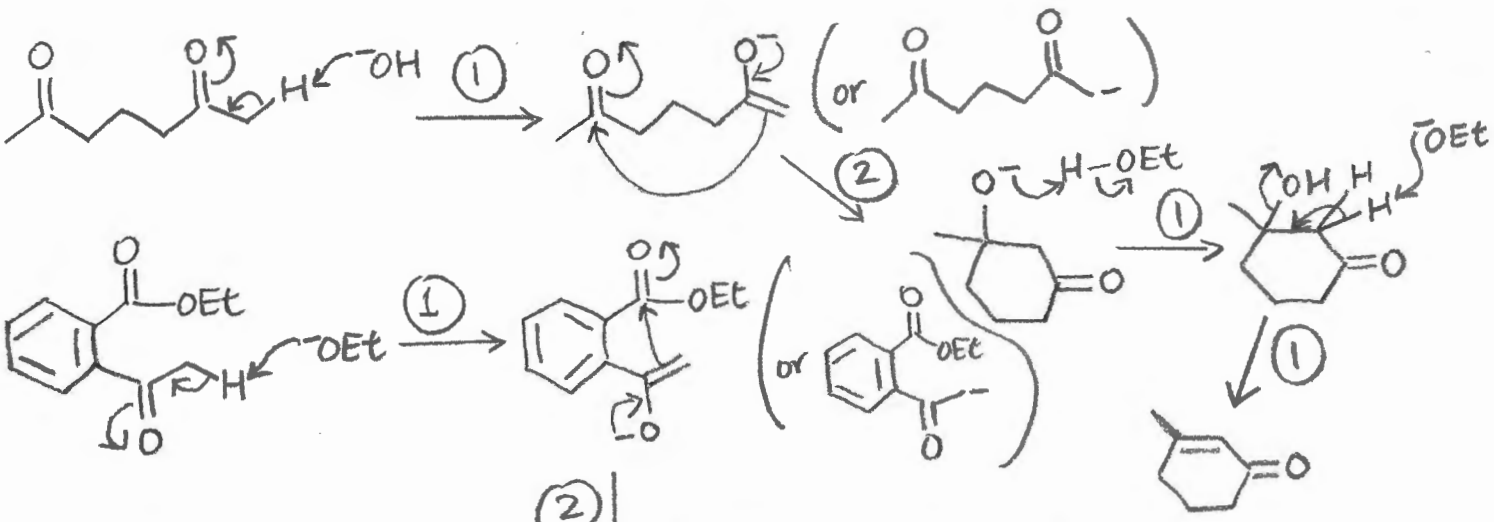
IF overall mechanism seems correct, give full marks

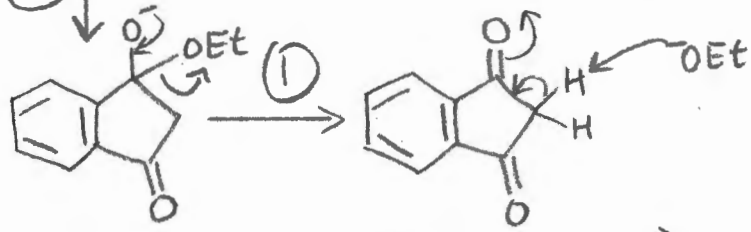
8. Propose **step-wise** mechanisms (using curved arrow notation) for **any two (2)** of the following reactions. [10 marks]

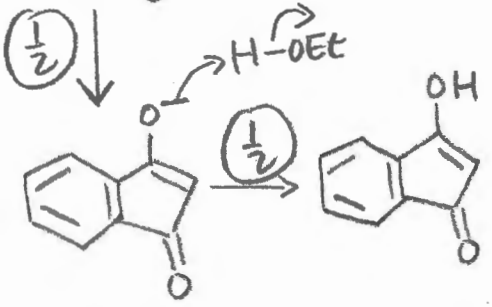






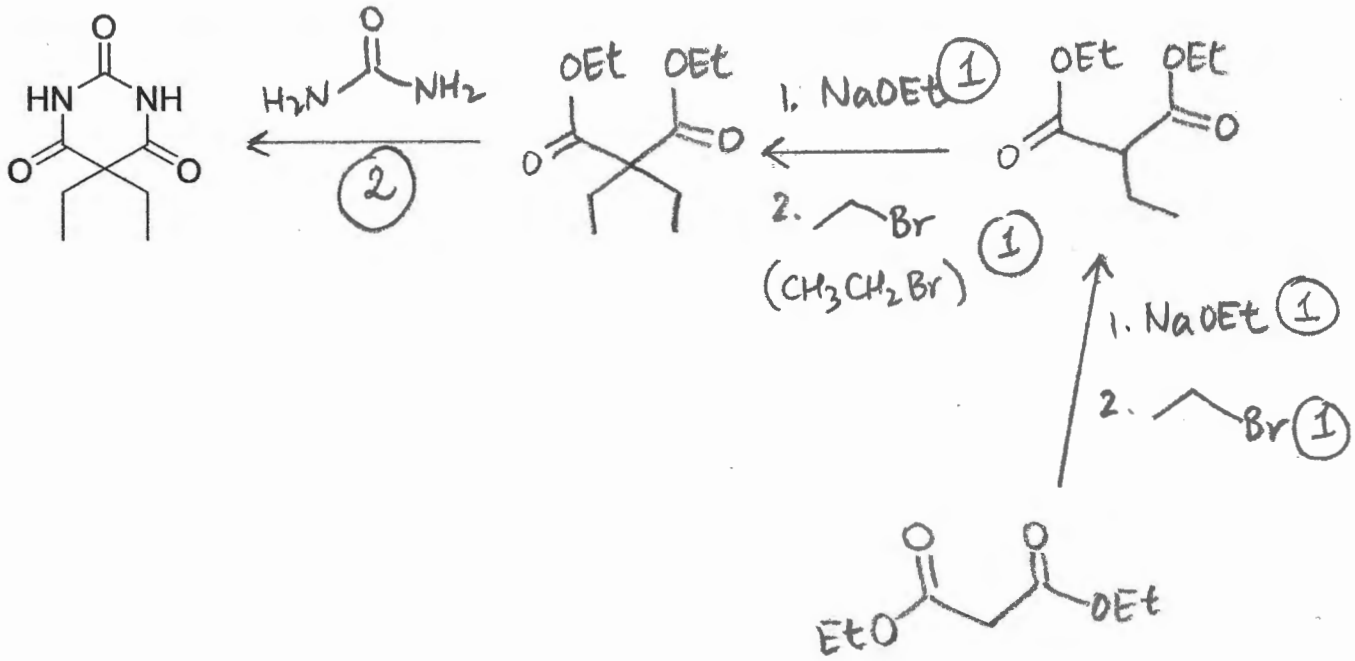






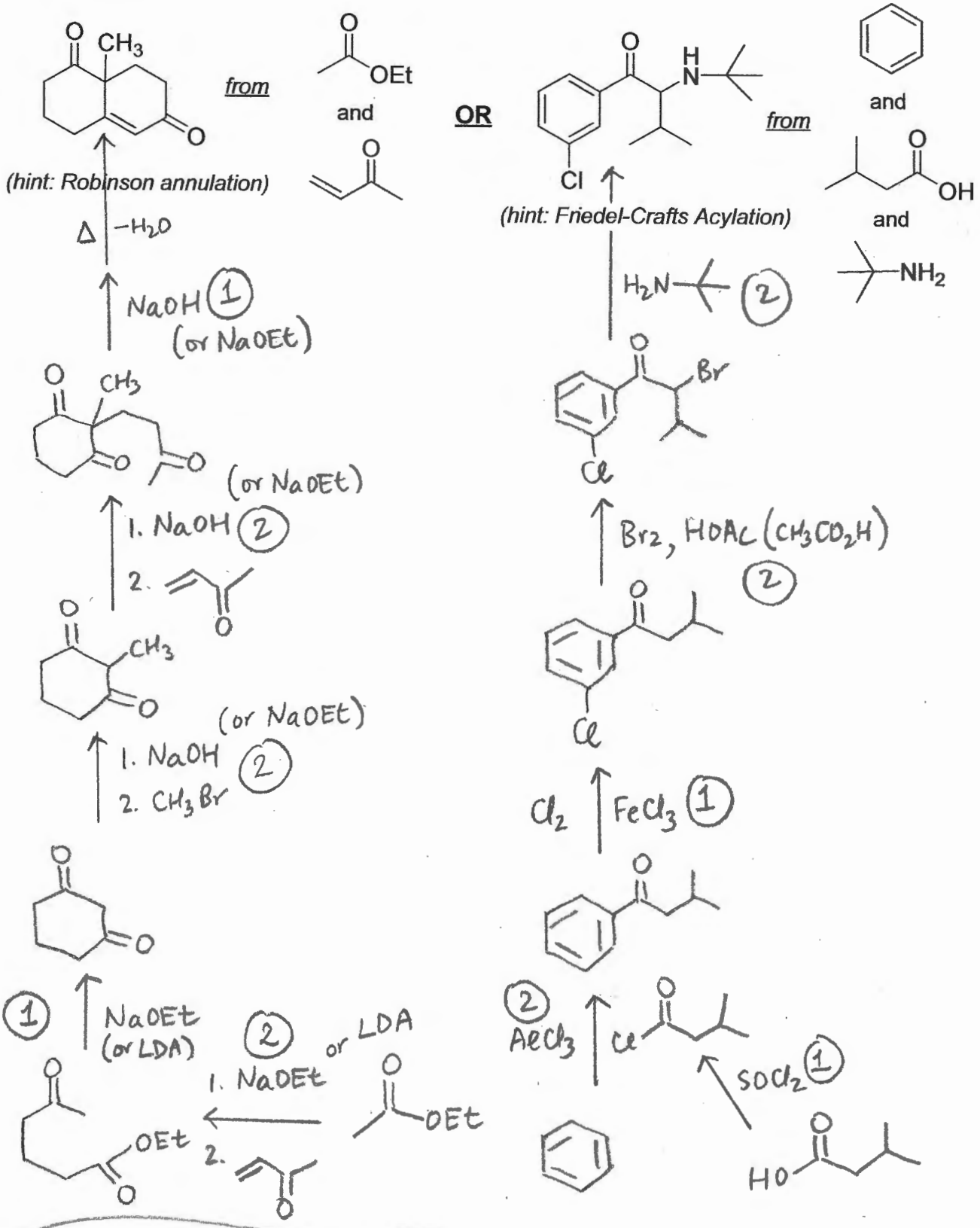
IF overall mechanism seems correct, Give full marks

9. **Barbital** (shown below), the first "sleeping pill", can be made starting from diethyl malonate (using the first few steps of the ***malonic ester synthesis***) followed by reaction of the diester with urea (H_2NCONH_2). Show all important steps in your proposed synthetic route starting from diethyl malonate. Assume all simple reagents are available including urea. [6 marks]



If overall synthesis seems correct, give full marks

10. Carry out **ONE** of the syntheses shown below. Commonly available reagents are available. Show all important steps in your proposed synthetic route. [8 marks]



END

If overall synthesis seems correct, give full marks