Chemistry 3B, Final Examination

Monday, December 16, 2002

Student name: _____

Student signature: _____

Write TA's name or Lecture Only: _____

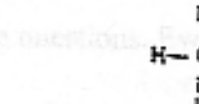
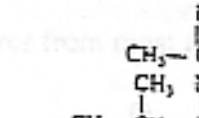
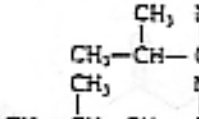
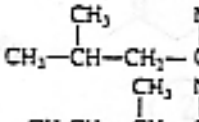
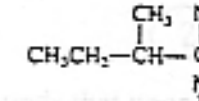
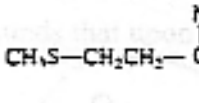
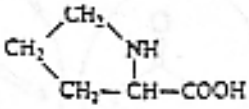
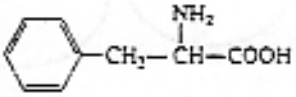
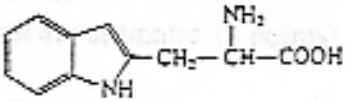
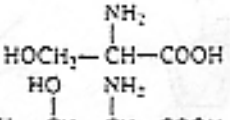
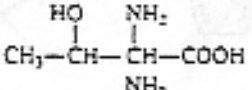
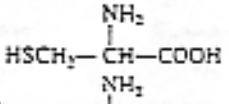
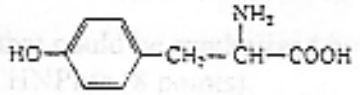
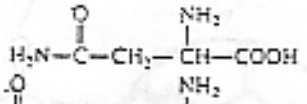
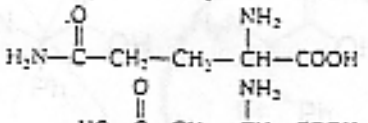
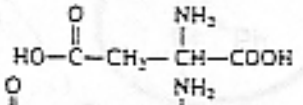
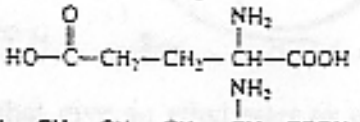
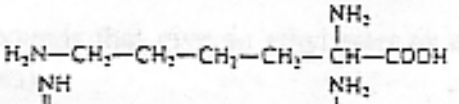
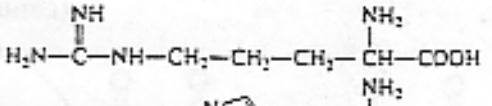
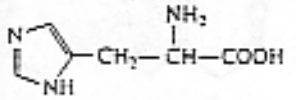
1. Please make sure that the exam has 15 pages including this one.
2. Please write your answers in the spaces provided.
3. Write clearly; illegible or ambiguous answers will be considered incorrect.
4. Only writing implements are allowed **(No Calculators)**.

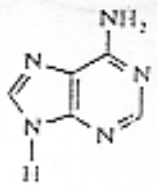
GOOD LUCK!

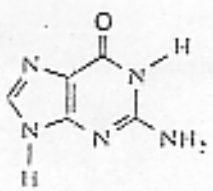
1.	40 points	34
2.	60 points	56
3.	60 points	54
4.	25 points	25
5.	25 points	18
6.	30 points	18
7.	30 points	30
8.	30 points	30
9.	30 points	30
10.	15 points	15
11.	15 points	15
Total	**360 points**	325

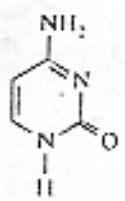
MINI-PERIODIC TABLE

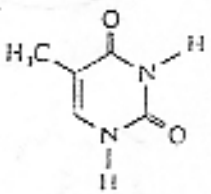
I	II	III	IV	V	VI	VII	VIII
H							He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
K	Ca	Ga	Ge	As	Se	Br	Kr

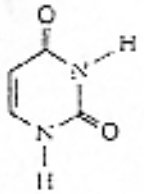
	glycine	Gly	G
	alanine	Ala	A
	valine	Val	V
	leucine	Leu	L
	isoleucine	Ile	I
	methionine	Met	M
	proline	Pro	P
	phenylalanine	Phe	F
	tryptophan	Trp	W
	serine	Ser	S
	threonine	Thr	T
	cysteine	Cys	C
	tyrosine	Tyr	Y
	asparagine	Asn	N
	glutamine	Gln	Q
	aspartic acid	Asp	D
	glutamic acid	Glu	E
	lysine	Lys	K
	arginine	Arg	R
	histidine	His	H


Adenine (A)


Guanine (G)

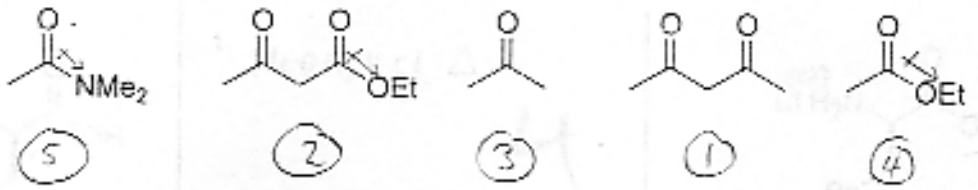

Cytosine (C)


Thymine (T)


Uracil

1. Answer the following questions. Every wrong answer cancels a correct answer (40 points total).

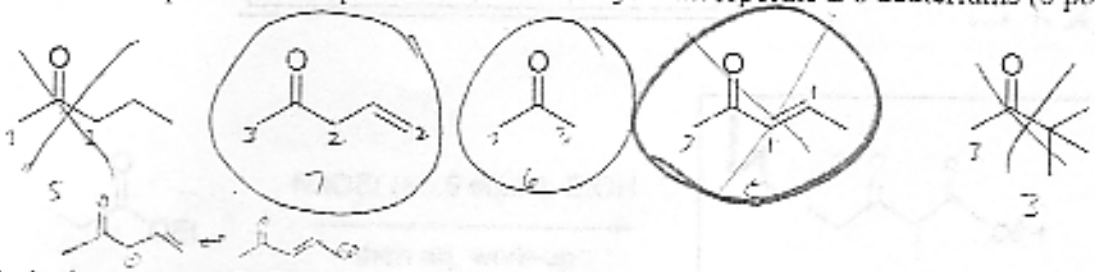
(a). Rank the structures from most acidic to least acidic [1 = **most** acidic, 5 = **least** acidic] (8 points).



5 2 3 1 4

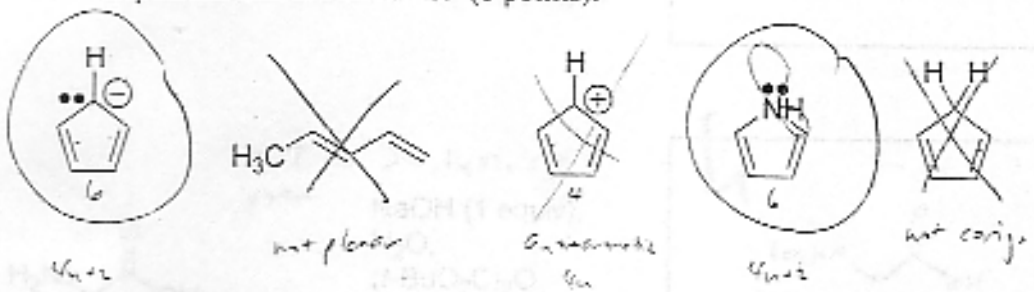
8

(b). Circle the compounds that upon treatment with D_3O^+ incorporate ≥ 6 deuteriums (8 points).



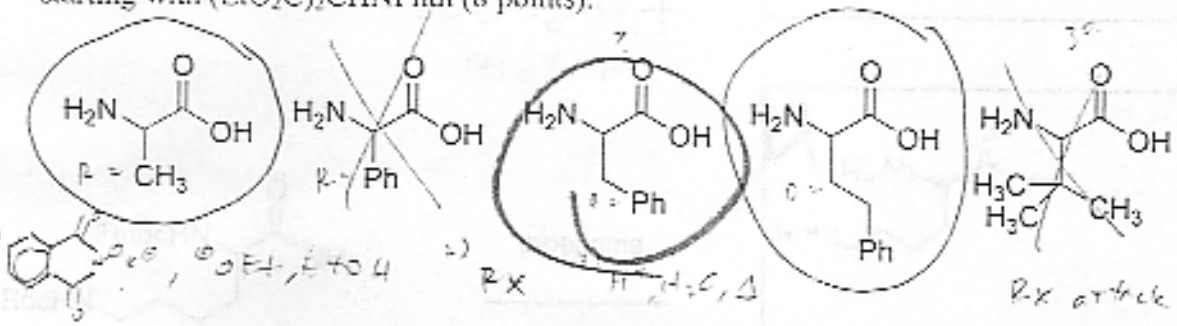
5

(c). Circle the compounds that are aromatic (8 points).



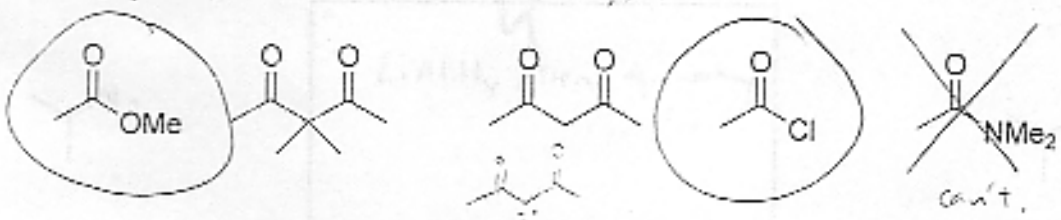
8

(d). Circle the amino acids that could be synthesized by the Gabriel amino acid synthesis method, i.e., starting with $(EtO_2C)_2CHNPhth$ (8 points).



5

(e). Circle the compounds that give an ethyl ester as one of the products upon reaction with EtO-, EtOH, Δ (8 points).



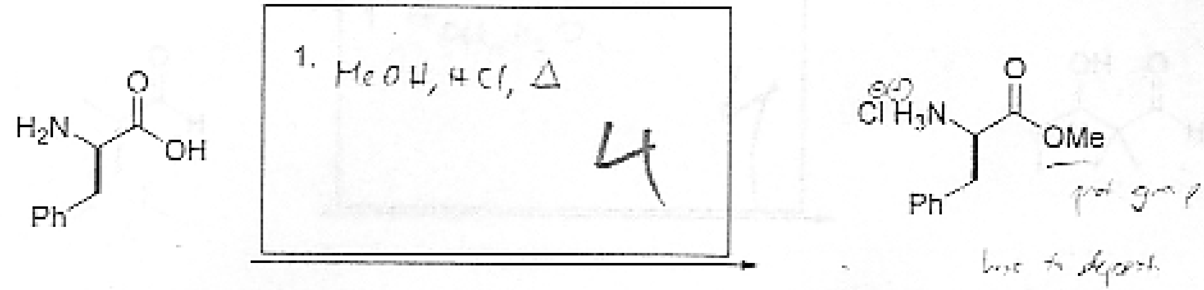
8

34

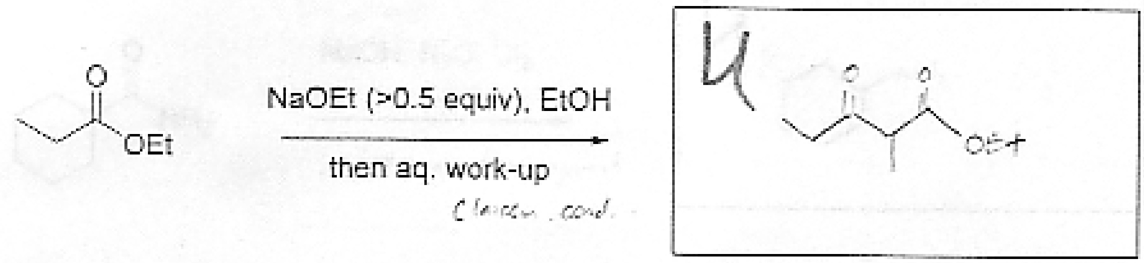
56

2. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (60 points total, 4 points each question).

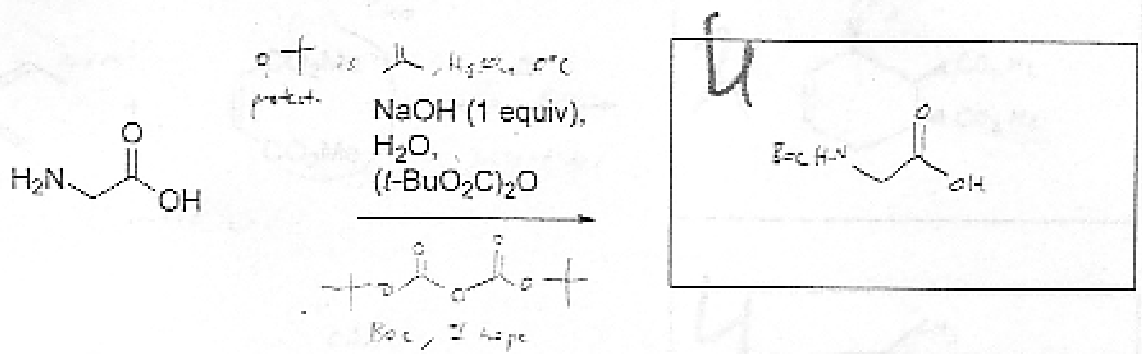
(a)



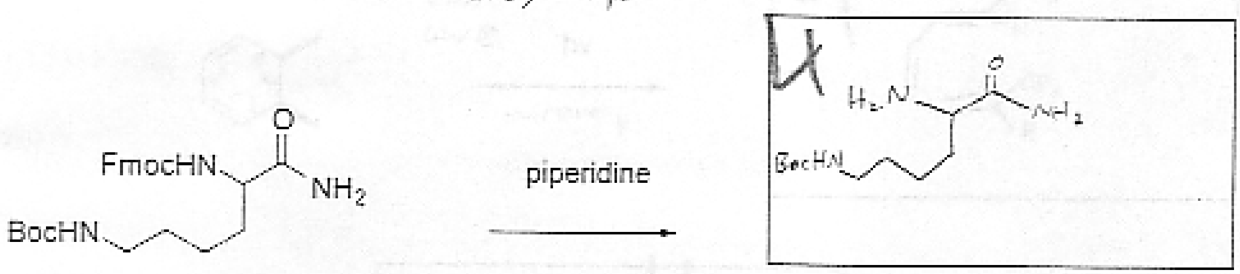
(b)



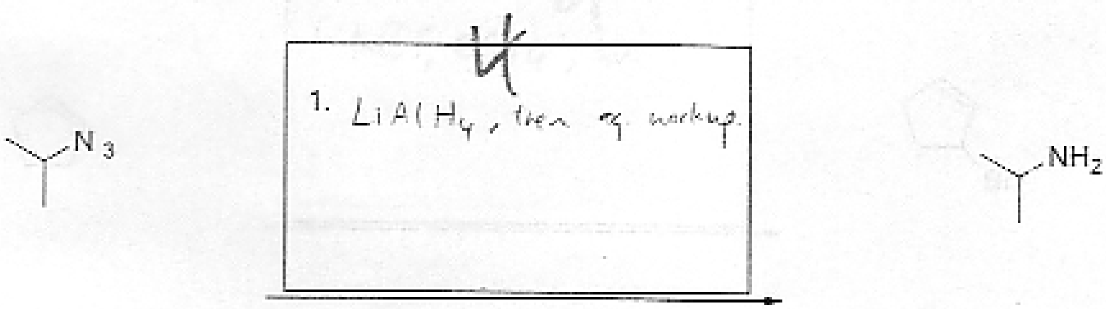
(c)



(d)

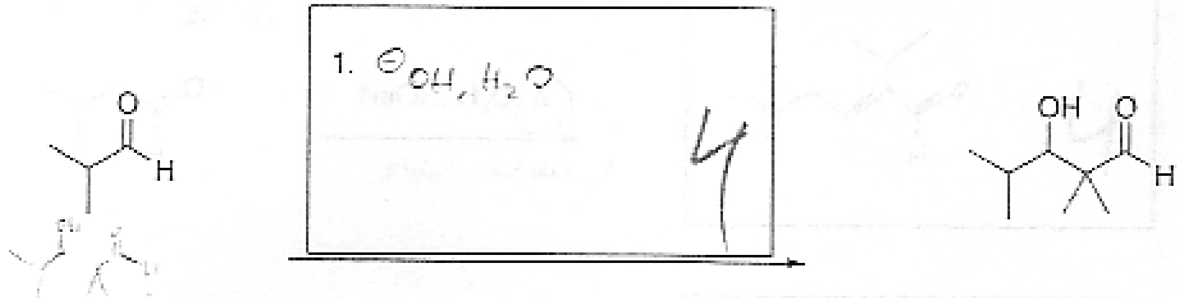


(e)

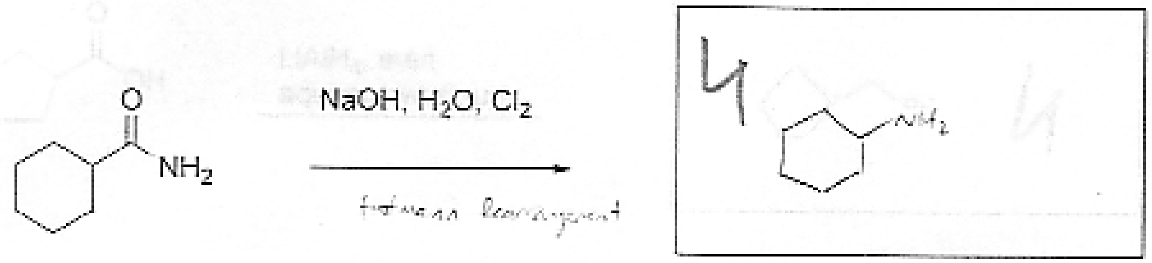


20

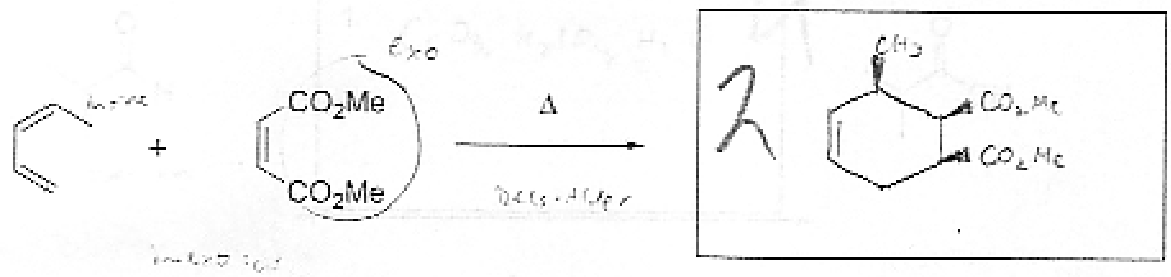
(f)


1. ⊖OH, H_2O
H
OH
O
H

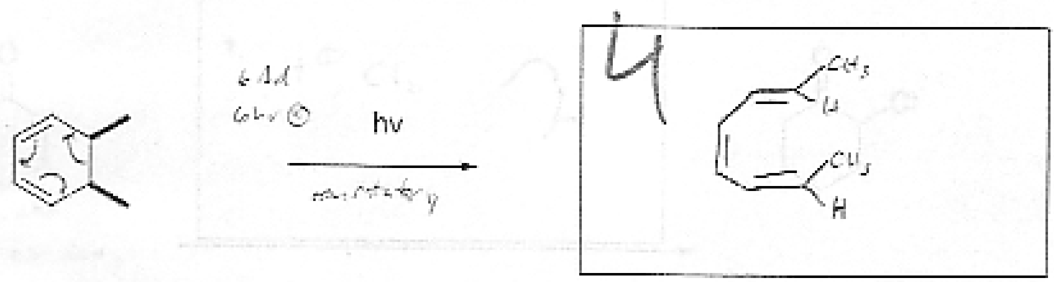
(g)


O
NH_2
NaOH, H_2O, Cl_2
NH_2

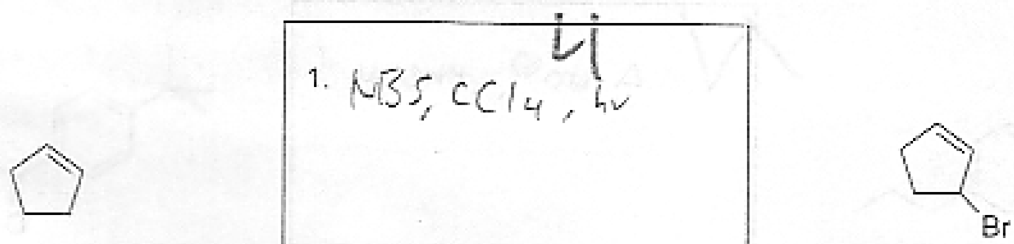
(h)

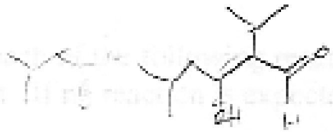

+
CO_2Me
CO_2Me
Δ
CH_3
CO_2Me
CO_2Me

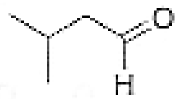
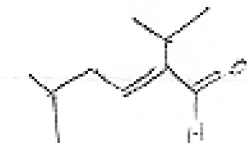
(i)


hv
CH_3
H
CH_3
H

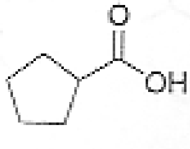
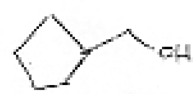
(j)

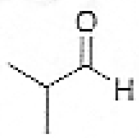
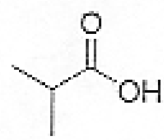

1. NBS, CCl_4, hv
Br

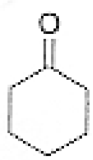
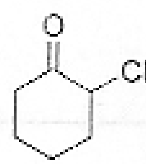


(k)  NaOH, H_2O, Δ →  4

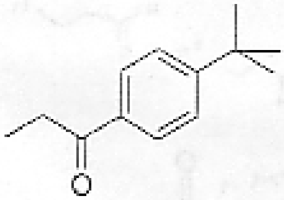
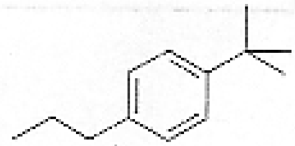
aldol w/ dehyd

(l)  LiAlH$_4$, then aqueous work-up →  4

(m)  → 1. CrO_3, H_2SO_4, H_2O 4 → 

(n)  → 1. $H^{\oplus}$, Cl_2. 2 → 

halogenation
acid /cat.
not base-cat.

(o)  → 1. H_2NNH_2, $^{\ominus}OH$, Δ 4 → 

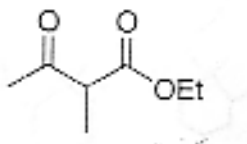
(or Zn(Hg), HCl, Δ)

Wolff Kishner
or
Clemmensen

18

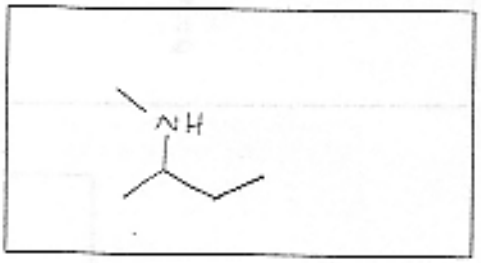
3. For each of the following reactions supply the missing reagents or major organic product in the space provided. If no reaction is expected indicate by N.R. (60 points total, 6 points each question).

(a)



1. H_3O+, H_2O, Δ

2. $MeNH_2$, EtOH, $NaBH_3CN$



6

(b)

1. NaN_3, DMF

2. $LiAlH_4$, then aq. workup

6

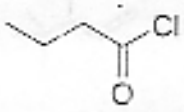
(c)

1. $NaCN$, DMF

2. $LiAlH_4$, then aq. workup

6

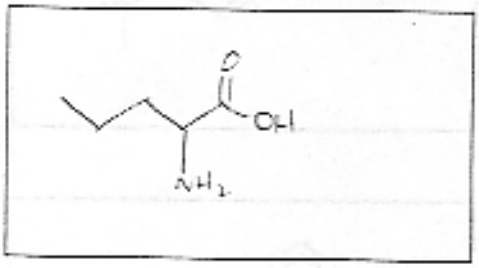
(d)



1. $LiAl[OCH(CH_3)_3]_3H$ then aqueous work-up

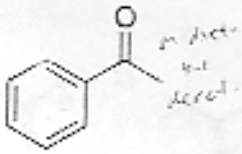
2. HCN, NH_3

3. H_3O+, H_2O, Δ

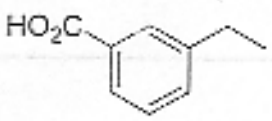


6

(e)



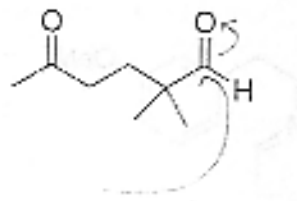
1) Br_2, $FeBr_3$
2) Mg, ether
3) $Zn(Hg)$, HCl, Δ
4) CO_2, H^+/H_2O



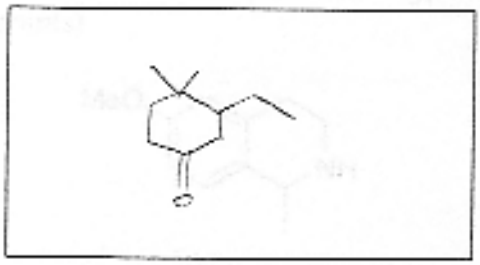
3

27

(f)

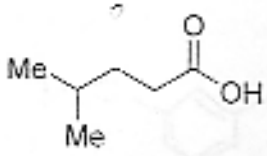


1. $NaOH$, H_2O, Δ
2. Et_2CuLi, then aqueous work-up

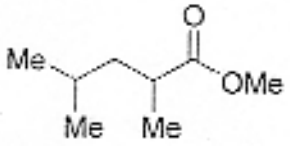


6

(g)

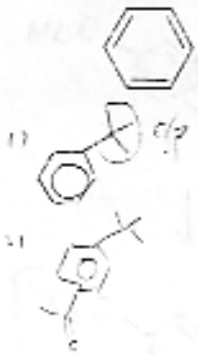


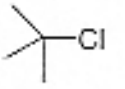
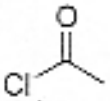
1) $SOCl_2$, Δ
2) $H^{\oplus}$, MeOH, Δ
3) $^{\ominus}OMe$, MeOH, MeBr (1 equiv.) (2.0 equiv.)

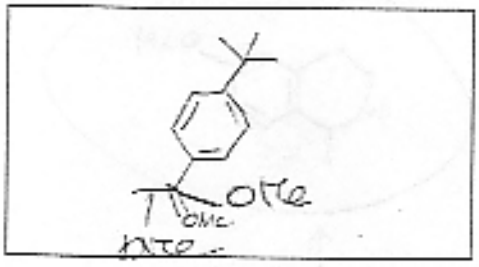


6

(h)

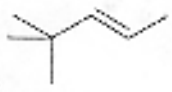


1. $AlCl_3$, 
2. $AlCl_3$  aqueous work-up
3. MeOH, HCl, sieves

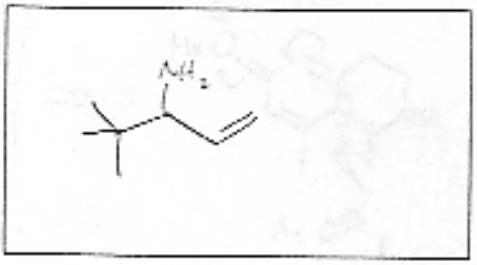


3

(i)

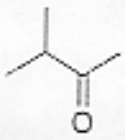


1. NBS, hv, CCl_4
2. NaN_3
3. $LiAlH_4$, aq. work-up

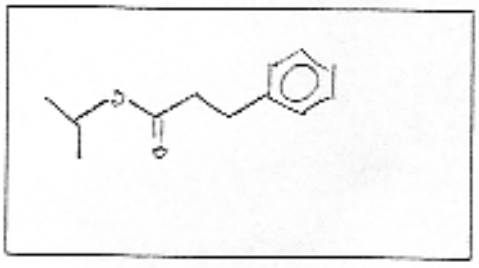


6

(j)



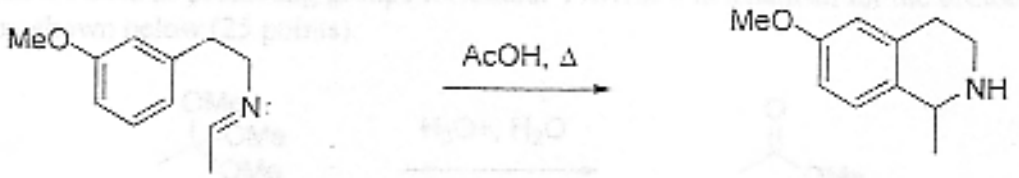
1. LDA
2. $PhCH_2Br$
3. F_3CCO_3H



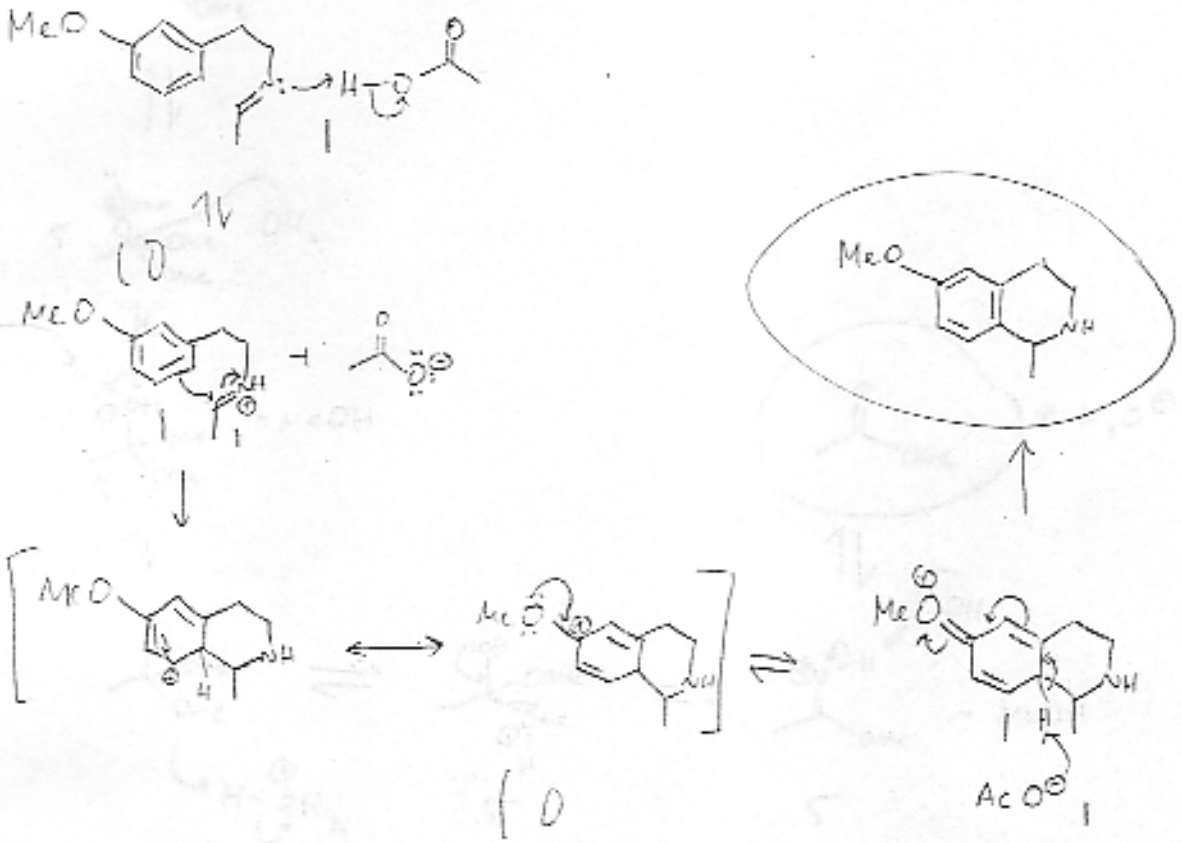
6

25

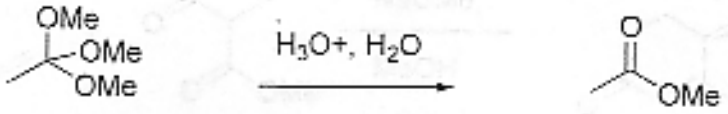
4. Provide a mechanism for the below transformation (25 points).

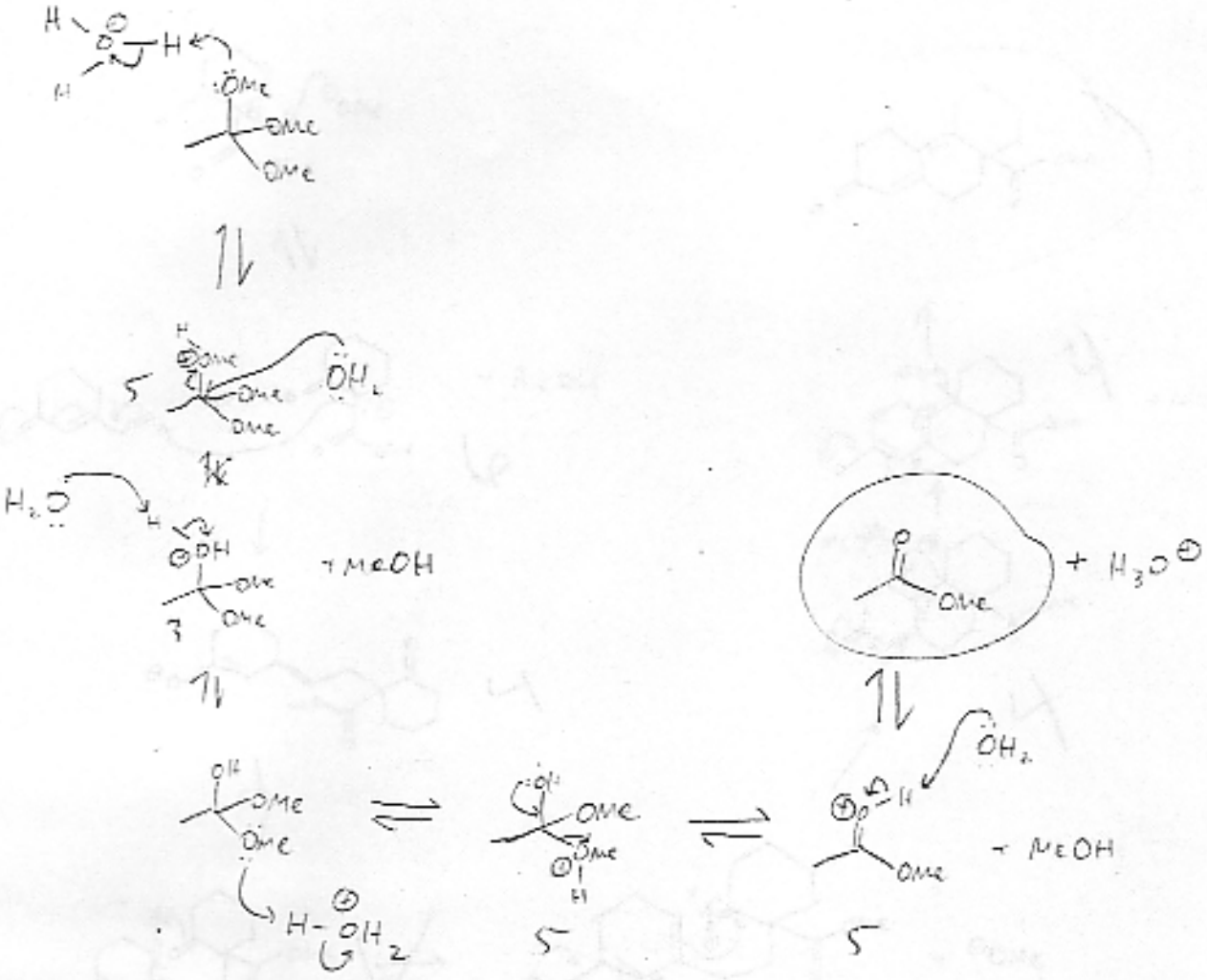


This type of reaction is called the Pictet Spengler reaction and can be used to synthesize morphine, vicodin and related compounds

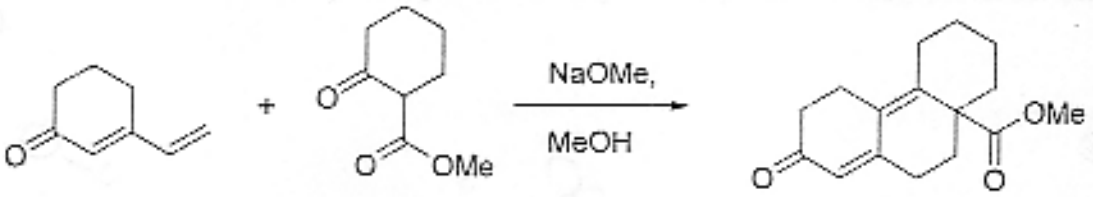


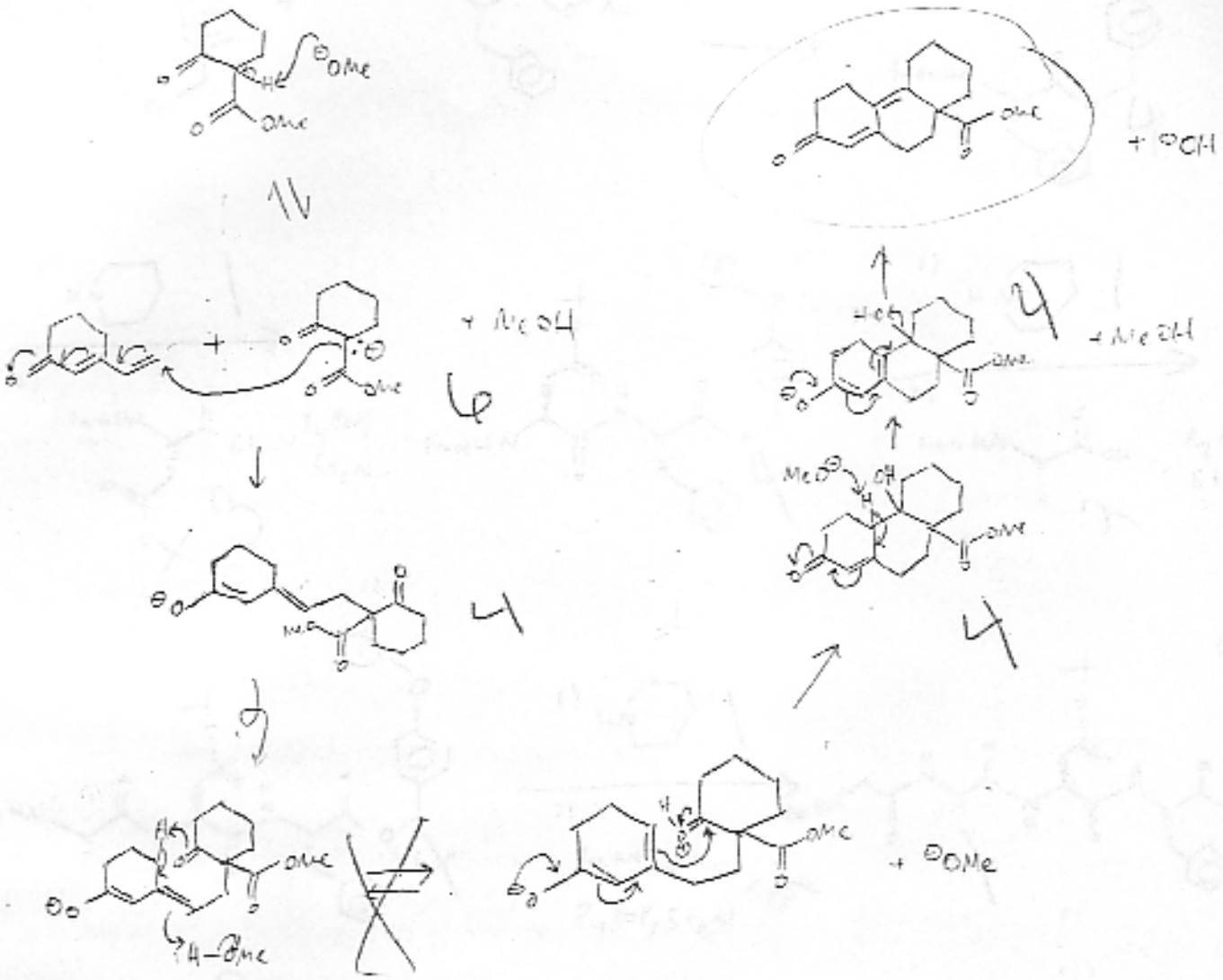
5. Orthoesters are used as protecting groups for esters. Provide a mechanism for the orthoester to ester transformation shown below (25 points).





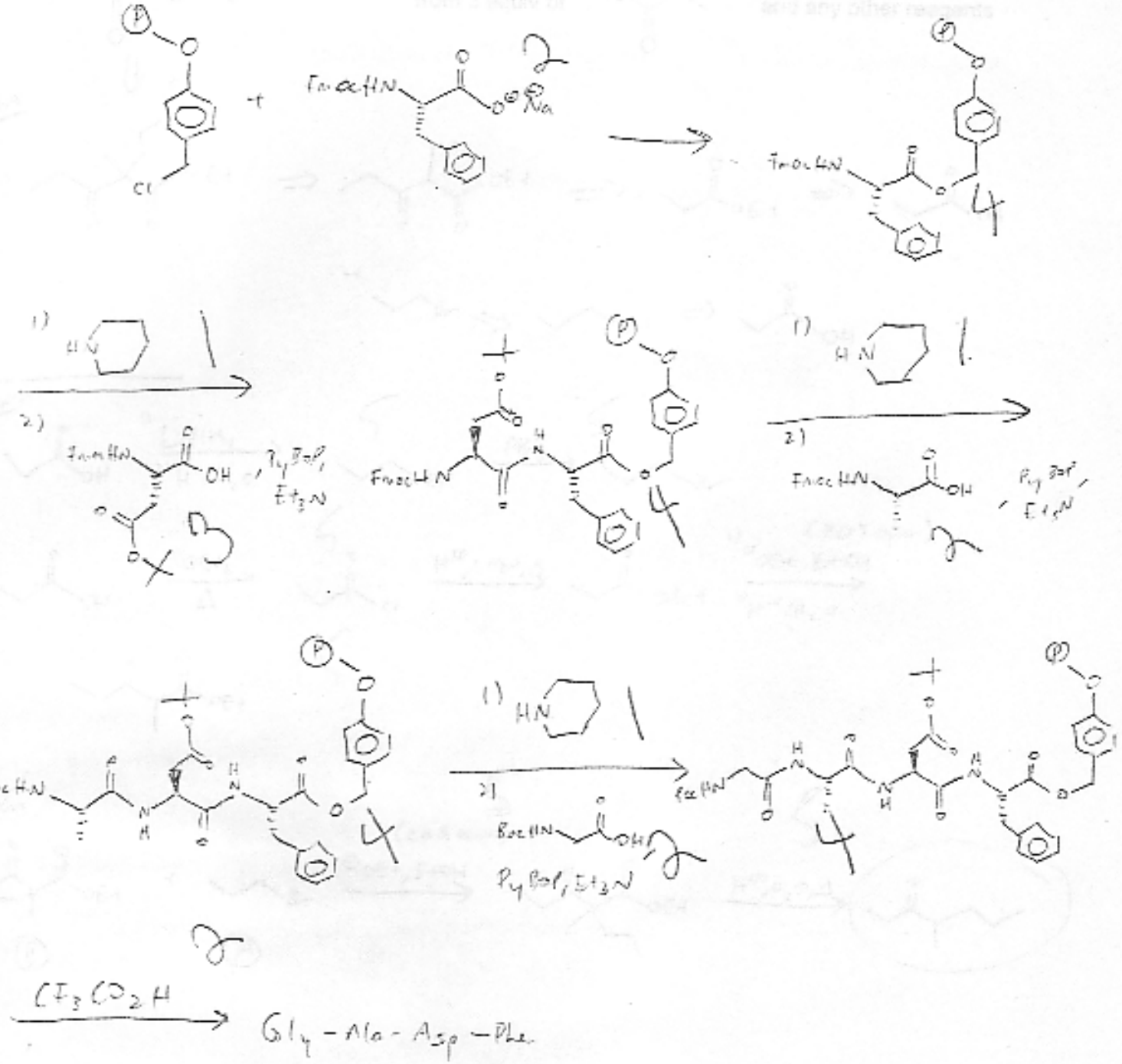
6. Provide a mechanism for the below transformation. **Hint:** think about the relationship of the below transformation to the Robinson annulation (30 points).





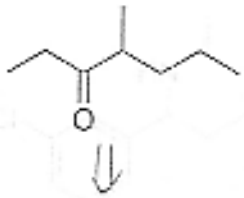
30

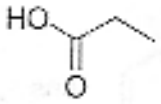
7. Provide the most efficient solid-phase synthesis of Gly-Ala-Asp-Phe from any protected amino acids (30 points).



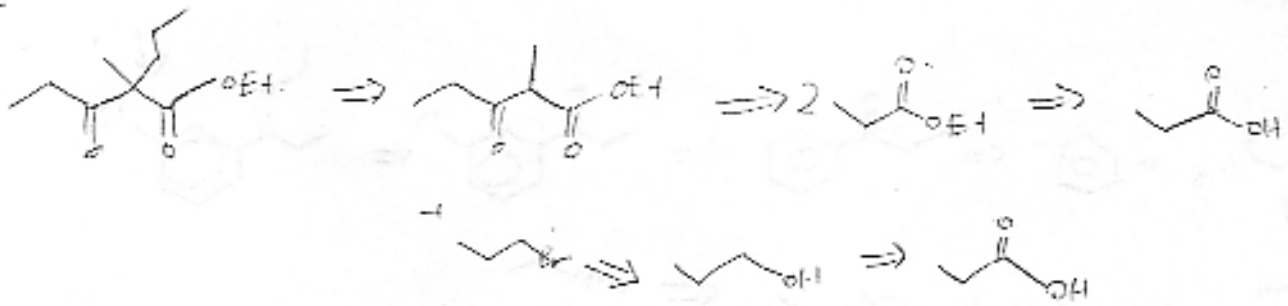
30

8. Provide the most efficient synthesis (30 points). 30

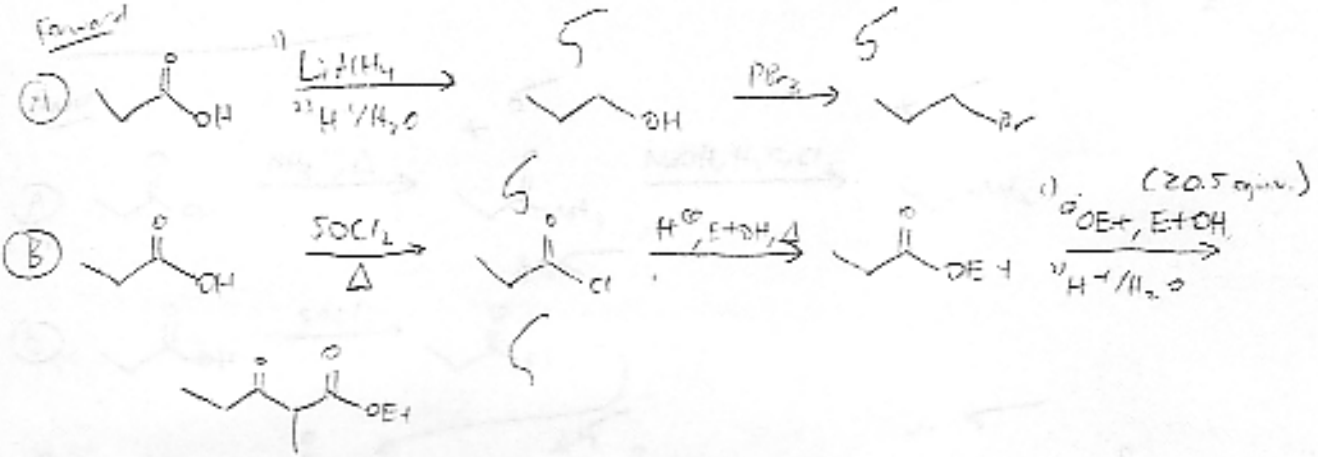


from 3 equiv of  and any other reagents

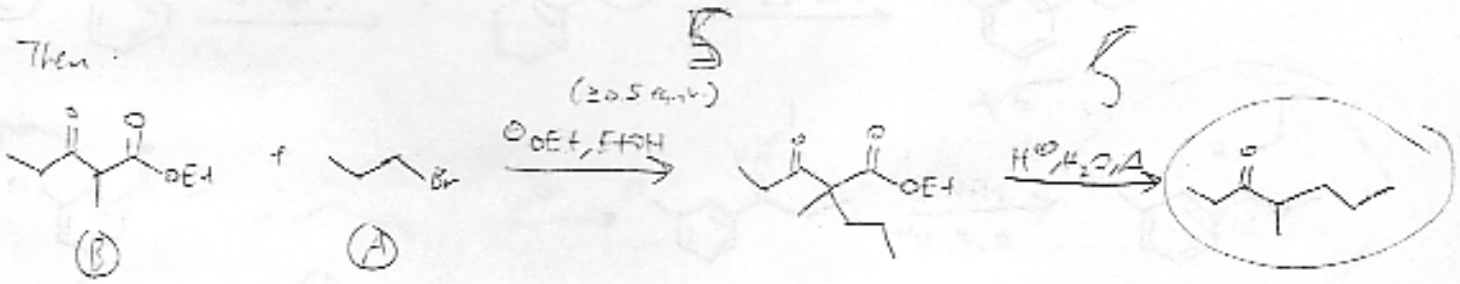
Retro:



Forward

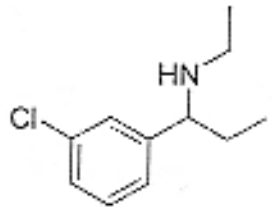


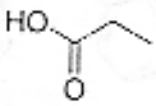
Then:

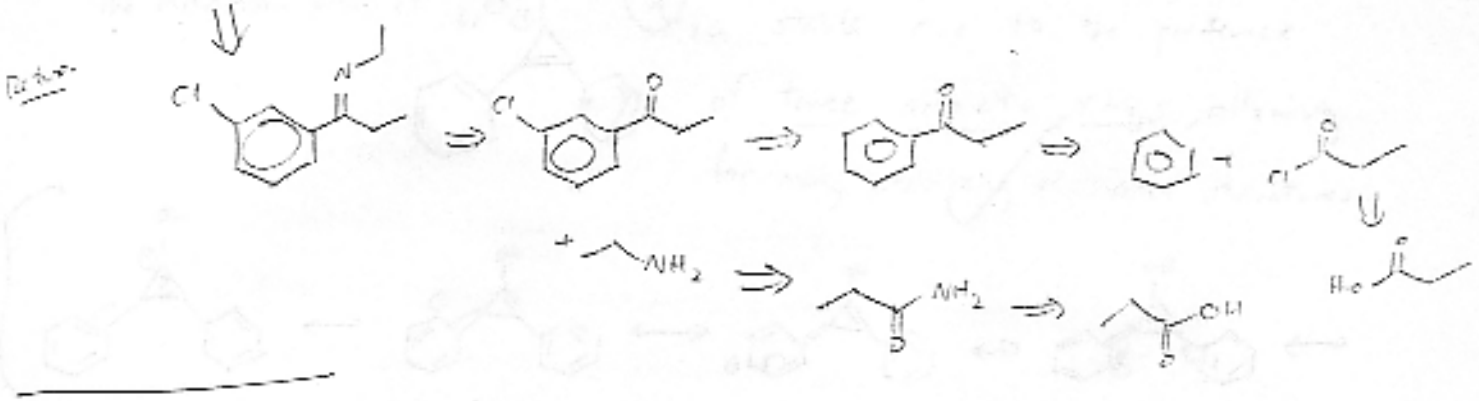


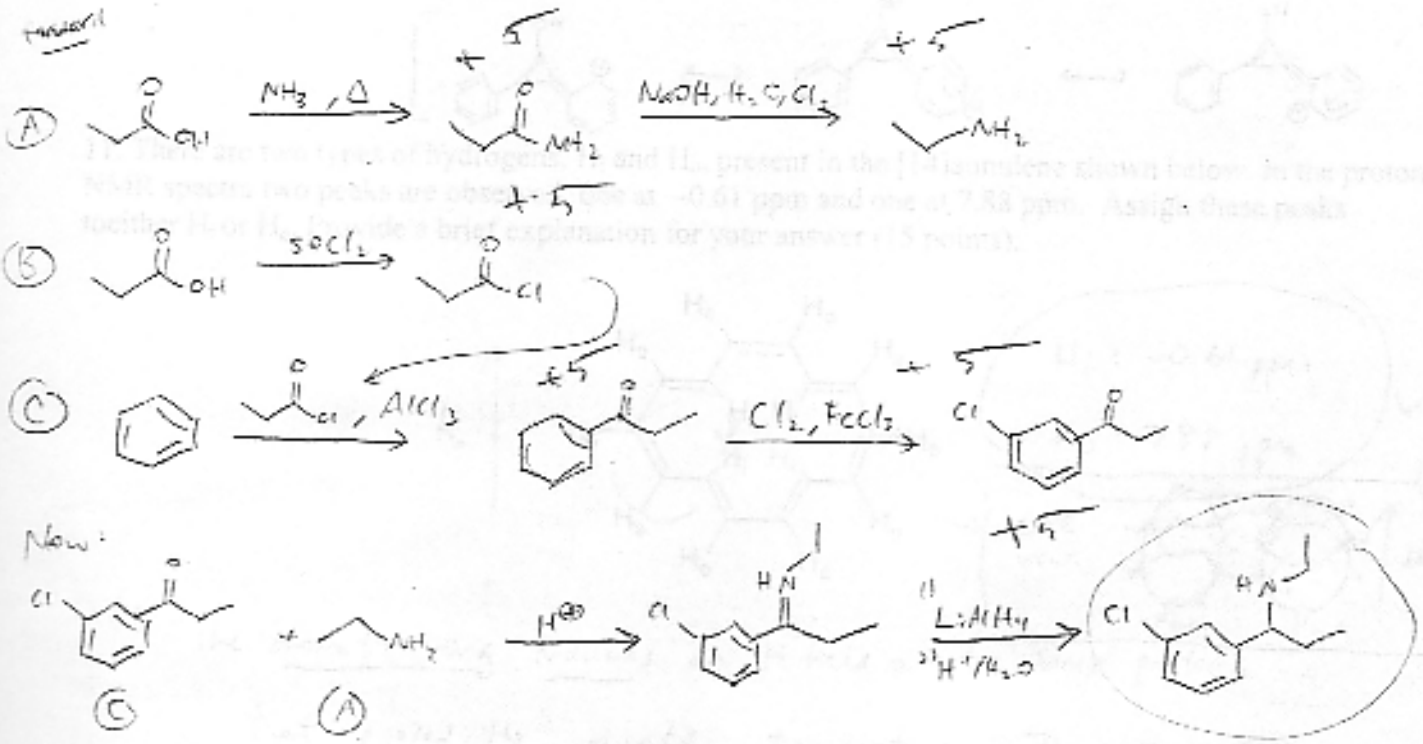
-13-

9. Provide the most efficient synthesis (30 points).



from 2 equiv of  and  and any other reagents





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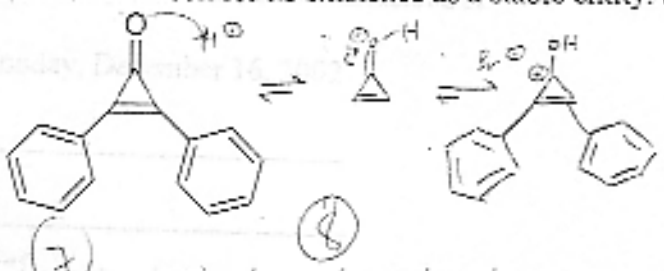
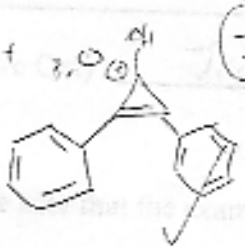
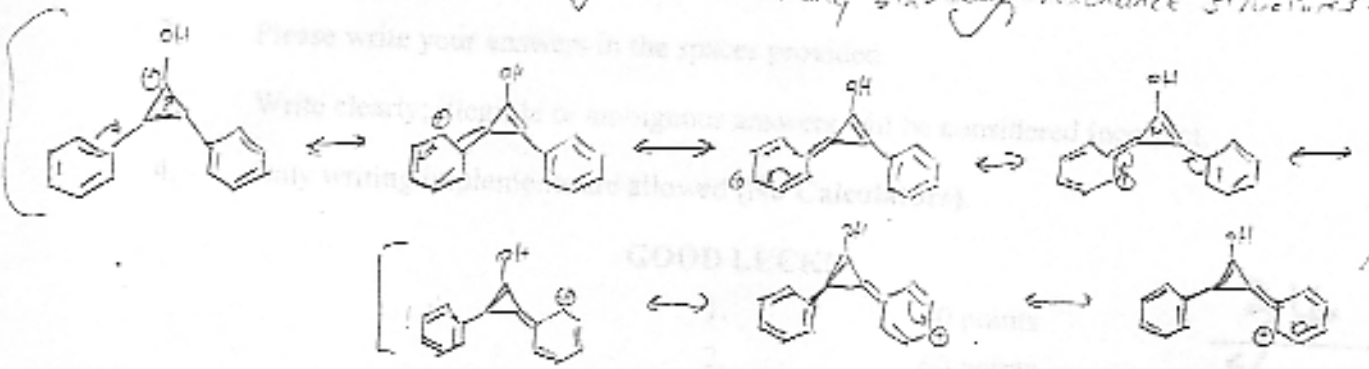
10. The cyclopropenone shown below forms an addition product with HBr that exhibits the properties of an ionic salt. Suggest a structure for this product and a reason for its existence as a stable entity. (15 points).

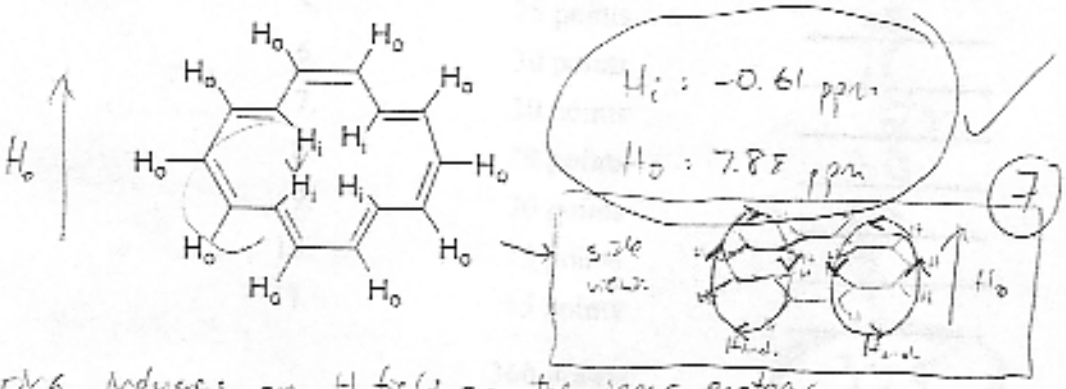


(7) (8)

The addition product  is stable due to the presence of three aromatic rings, allowing for many stabilizing resonance structures:



11. There are two types of hydrogens, H_i and H_o, present in the [14]annulene shown below. In the proton NMR spectra two peaks are observed, one at −0.61 ppm and one at 7.88 ppm. Assign these peaks toeither H_i or H_o. Provide a brief explanation for your answer (15 points).



(7)

The aromatic ring induces an H field on the inner protons that opposes H_o, shielding the protons. The outer protons, on the other hand, are deshielded by the induced H field, as $H_{ind.}$ is in the same direction as H_o.

(8)

30