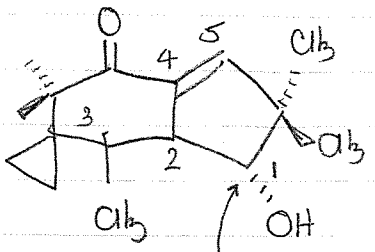
EXAM 1A
SOLUTIONS
S 2017

1.



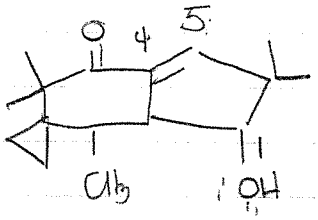
1 EQUIV. HCl →

2° Alcohol
(NOT ALLYLIC)

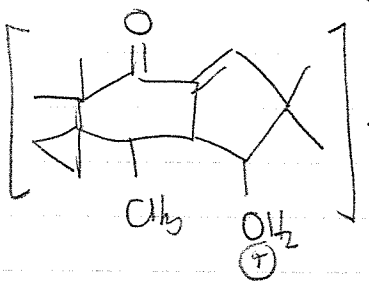
(A)

Rxn w/ 1 equiv can occur via
EITHER SN1 @ C1 2° alcohol
OR ELECTROPHILIC ADDITION @
C4-C5 ALKENE

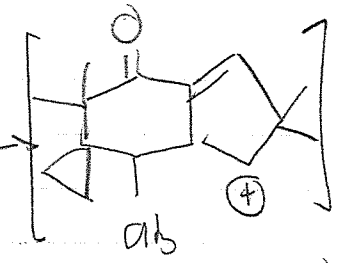
SN1:



→ H-Cl



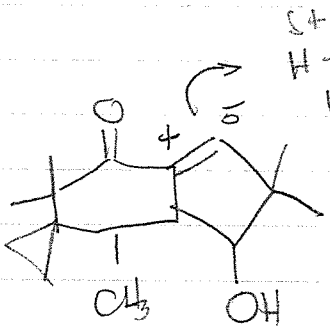
RATE-DETERMINING STEP

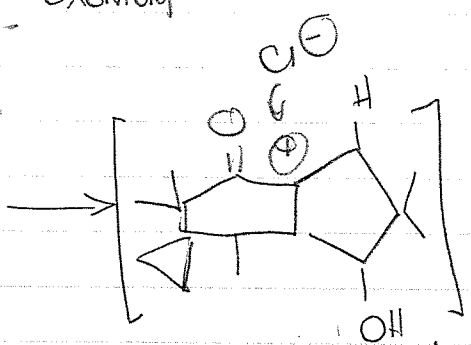


2° CARBOCATION

OXONIUM

ELECTROPHILIC ADDITION

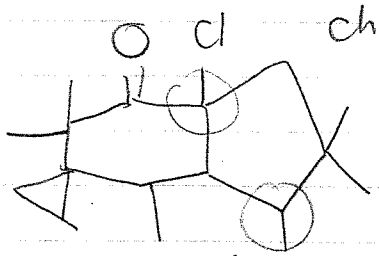




3° CARBOCATION

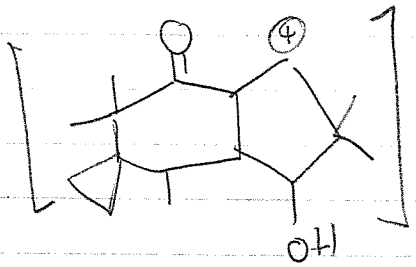
MOST STABLE
- gives major product

3° Alkyl chloride



2° Alcohol

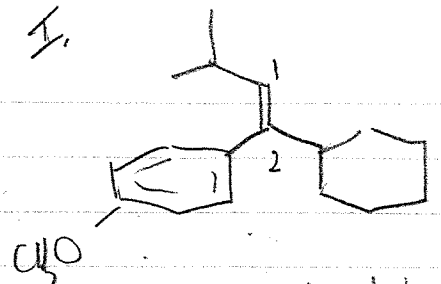
MAJOR PRODUCT



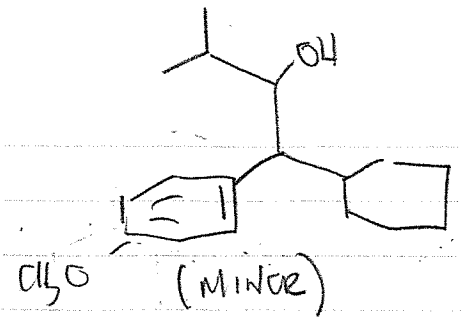
2° CARBOCATION

I.

2,



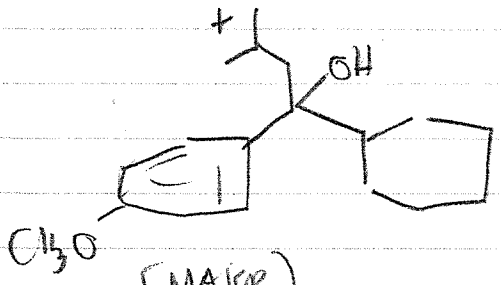
1. $HgCl_2, H_2O$
2. $NaBH_4$



(MINOR)

1. HgX_2, H_2O
2. $NaBH_4$

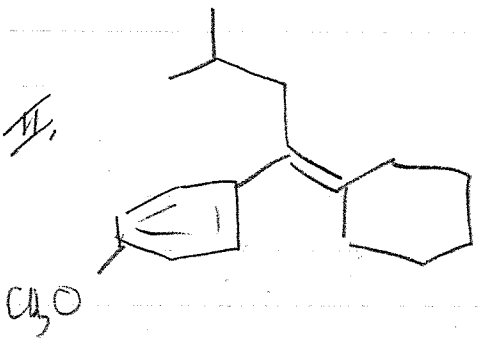
} Electrophilic addition MARKOVNIKOV



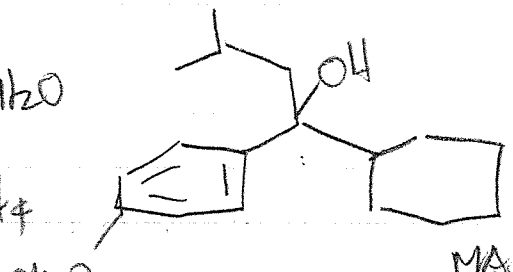
(MAJOR)

Not Venlafaxine

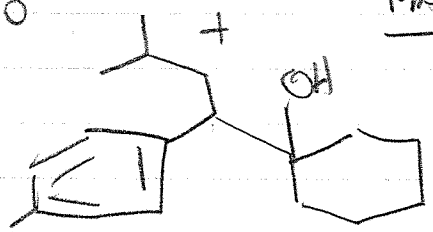
II.



1. $HgCl_2, H_2O$
2. $NaBH_4$



MAJOR

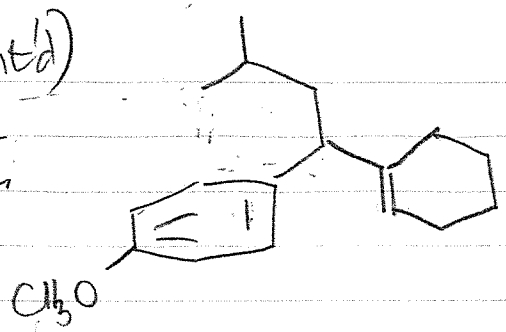


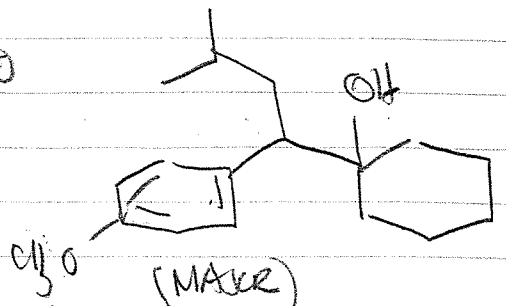
MAJOR

This is venlafaxine, but there are TWO major products since both and in fact $C^{\oplus}$ from other product is more stable since it is Benzylic

2. (cont'd)

III

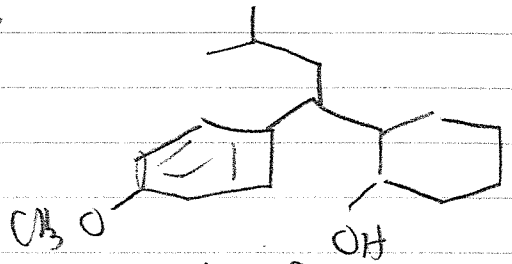




(MAJOR)
Venlafaxine

Only one major product and it is venlafaxine

(D)



(MINOR)

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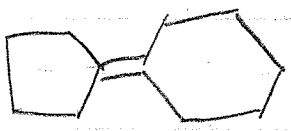
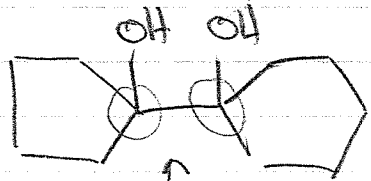
3. I

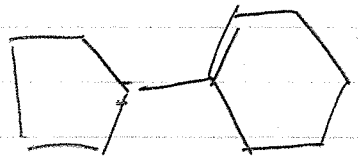


cold, dilute $KMnO_4$

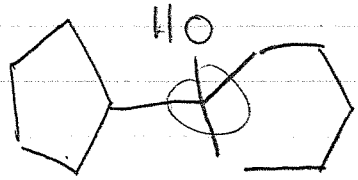


NO CHIRAL CENTERS
NO ENANTIOMERS

II.

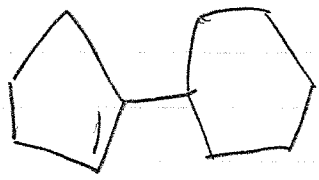


H_2SO_4
H_2O

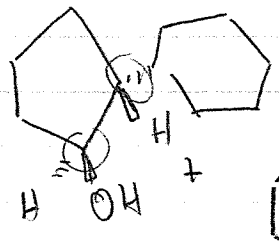


NOT CHIRAL
NO ENANTIOMERS

III.



1. BH_3
2. H_2O_2, NaOH



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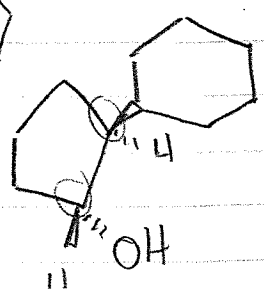
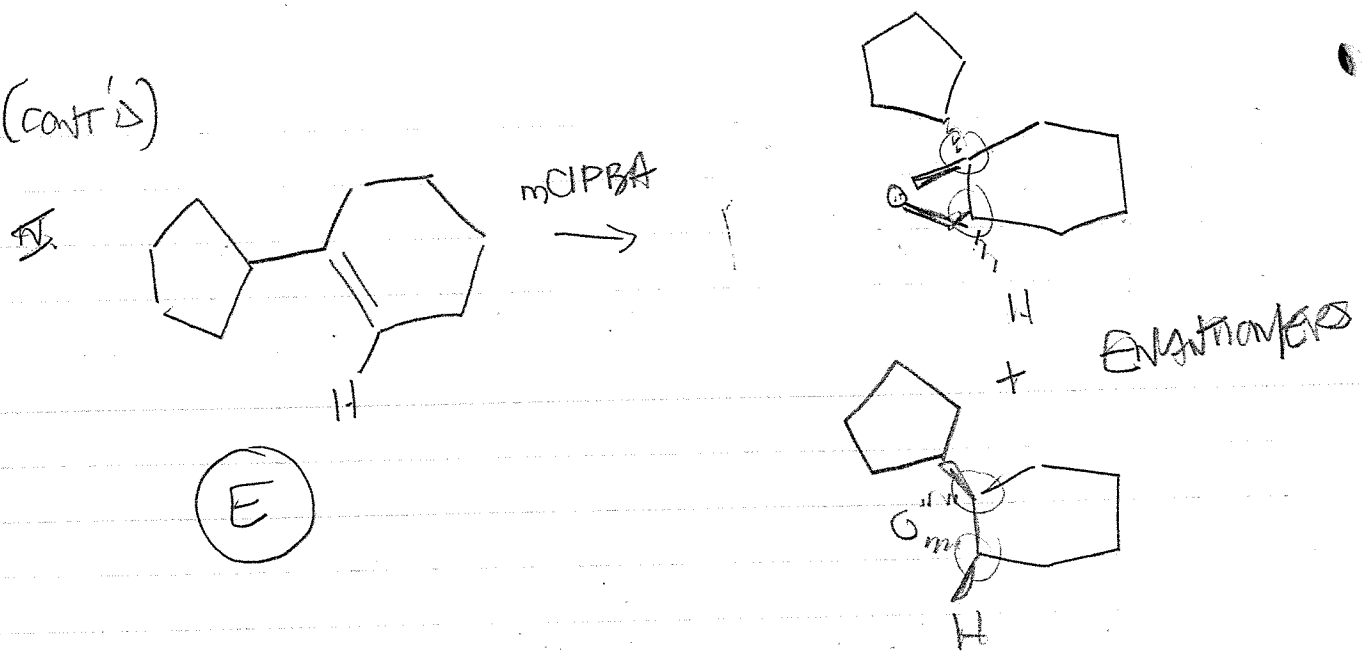


ENANTIOMERS

3. (CONT'D)



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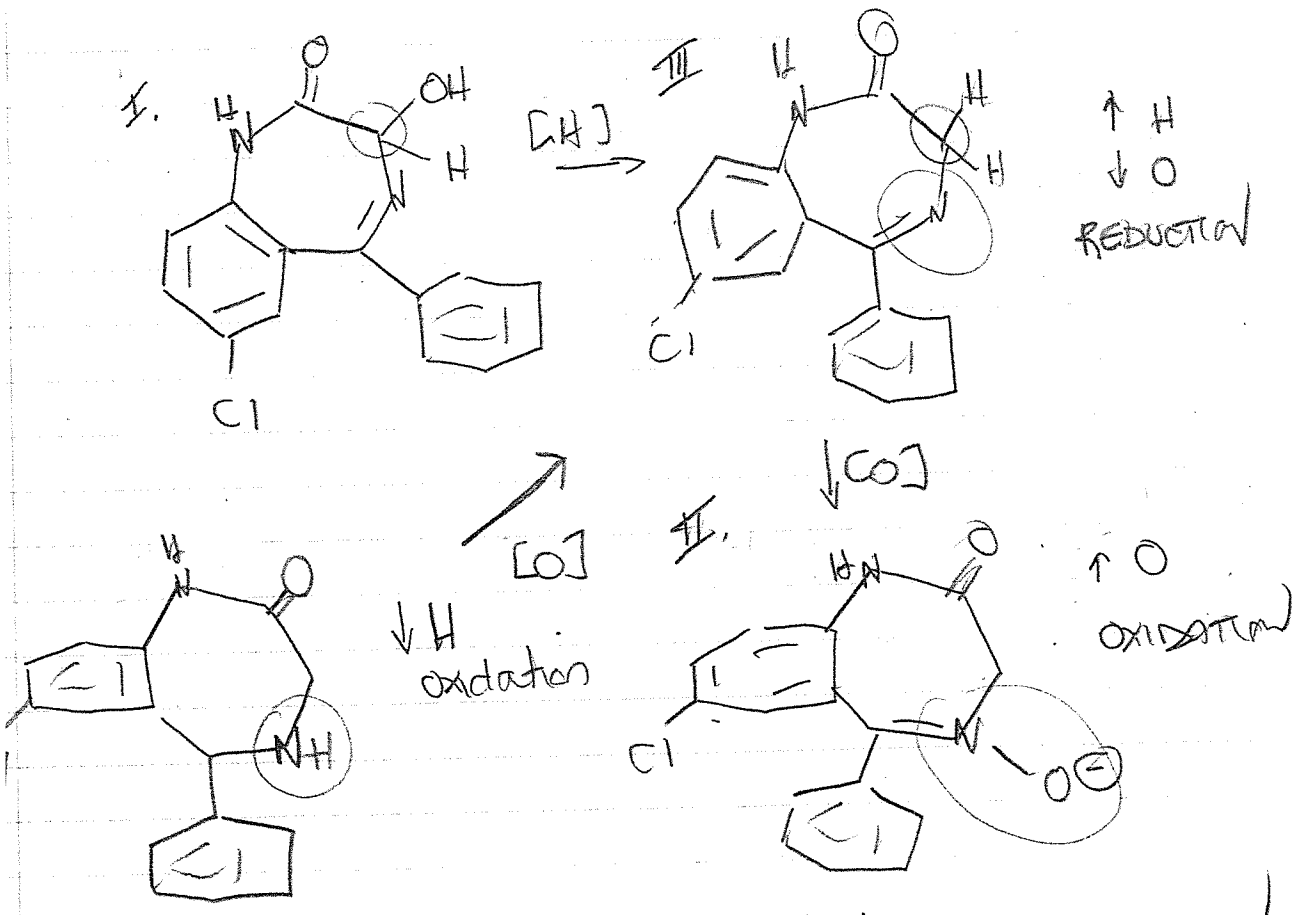
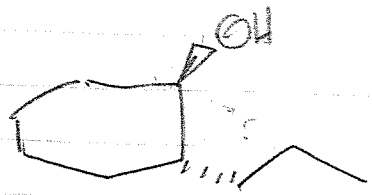


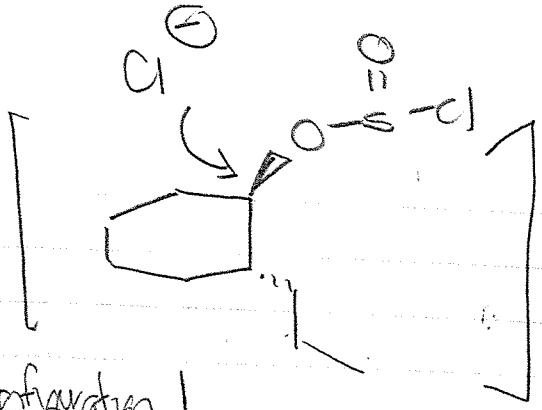
A = REDUCTION B = OXIDATION C = OXIDATION

E

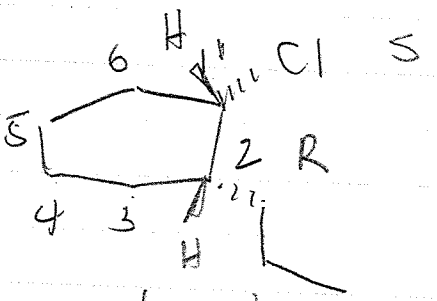
5.



$SOCl_2$ (SN2)



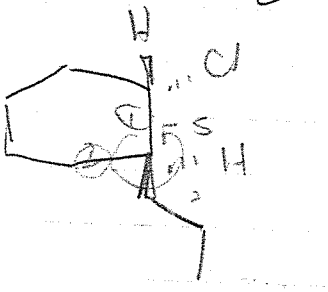
SN2 invert configuration at C_1



C_1 — H (4), Cl (1), C_6 (3), C_2 (2)

1S

switch H and propyl

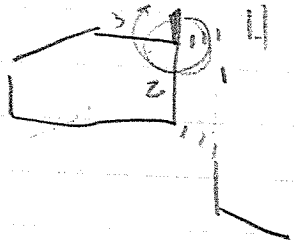


C_2 — H (4), C_1 (1), C_3 (2), propyl (3)

2R

E

switch H and Cl @ C_1 (INVERT)



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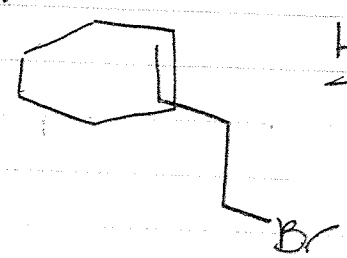
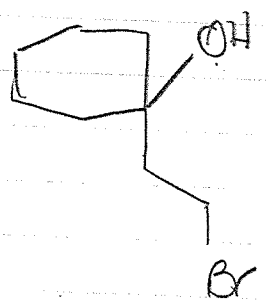
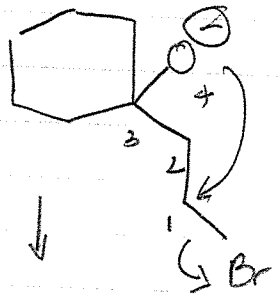


H_3PO_4, H_2O



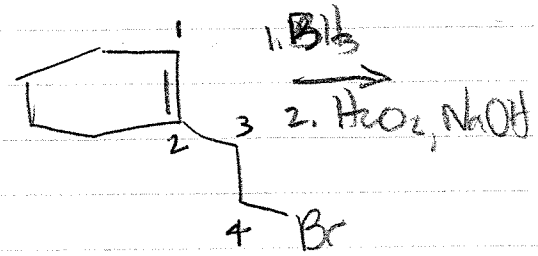
NaH

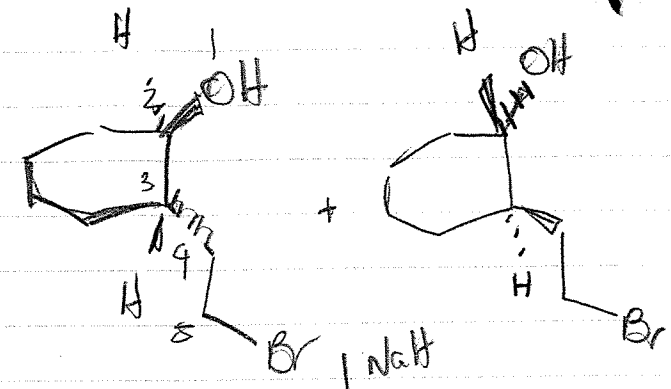


ONLY MAJOR PRODUCT

6. (cont'd)

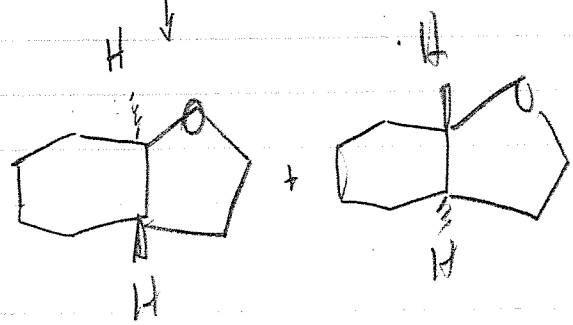
II.





NaH

ONLY MAJOR PRODUCTS



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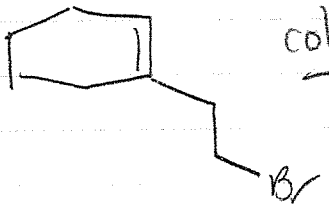
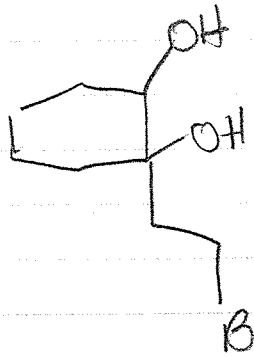
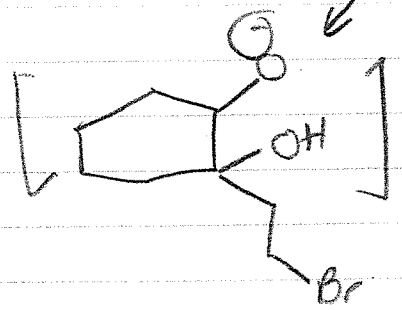
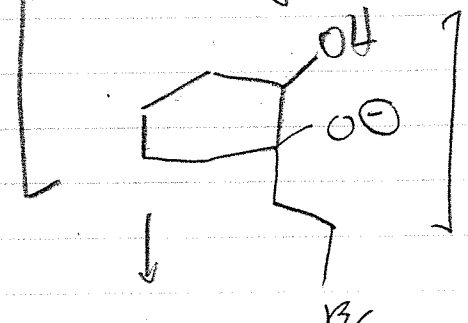


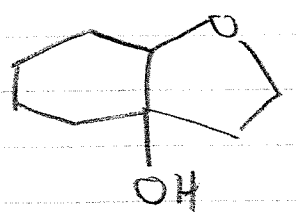
cold, dilute
KMnO4







MAJOR PRODUCTS



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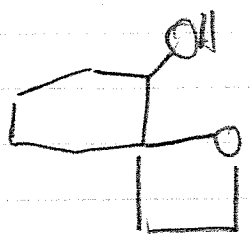
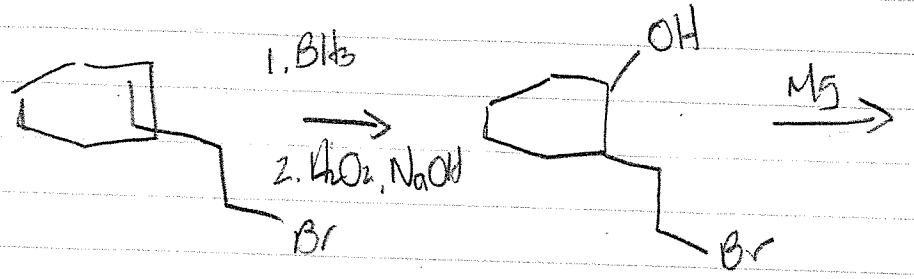
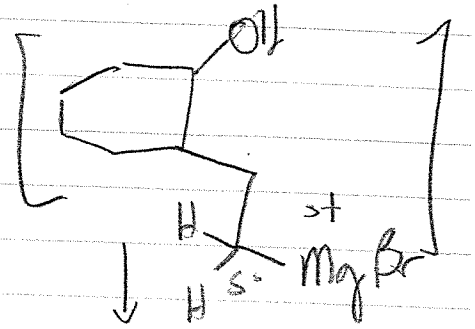


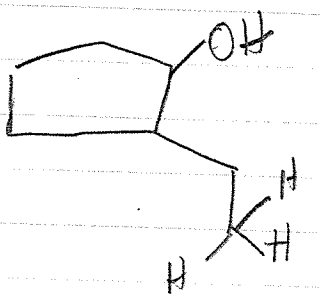
6. (cont'd)

IV





MAJOR PRODUCT



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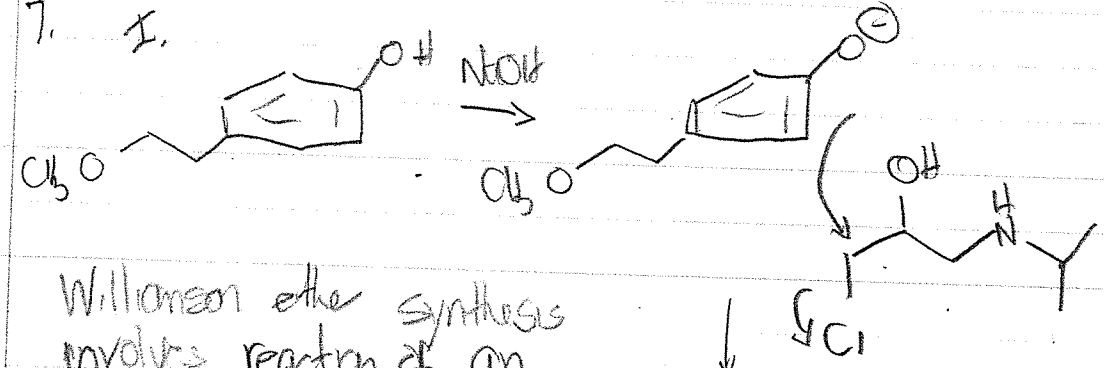
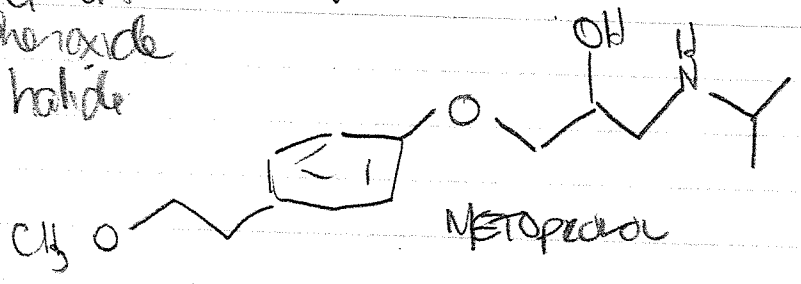


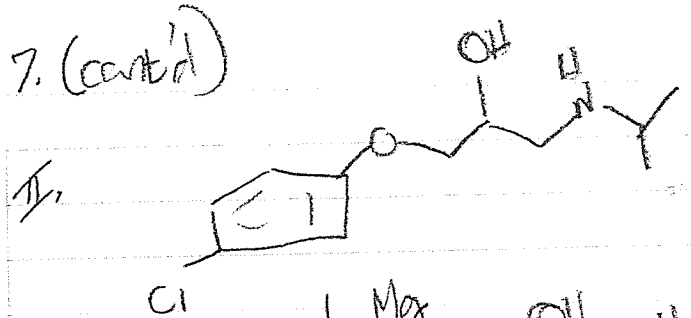
Williamson ether synthesis involves reaction of an alkoxide or phenoxide w/ an alkyl halide

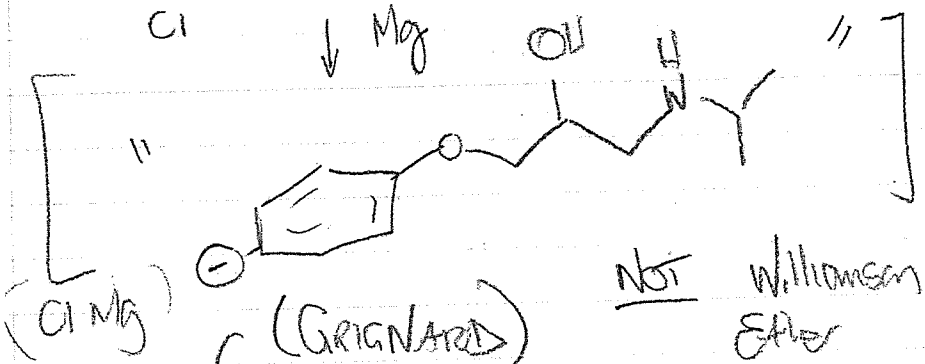


METOPROLOL

7. (cont'd)

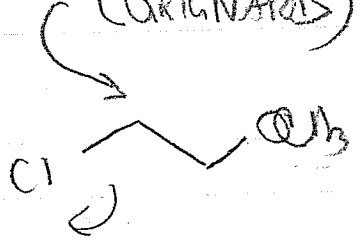
II.

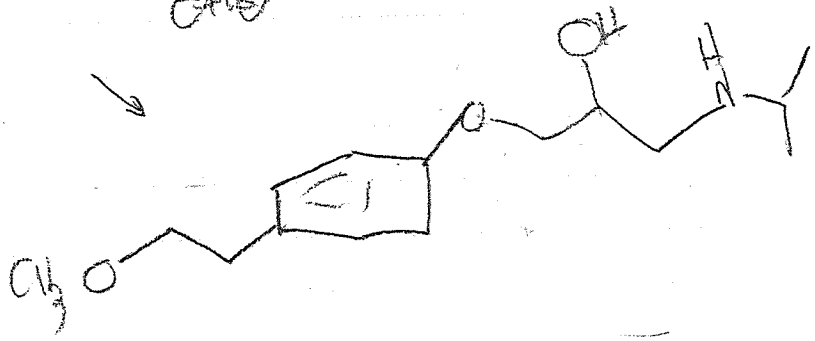




(GRIGNARD)

NOT Williamson Ether





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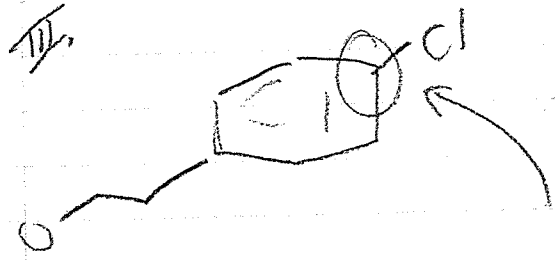
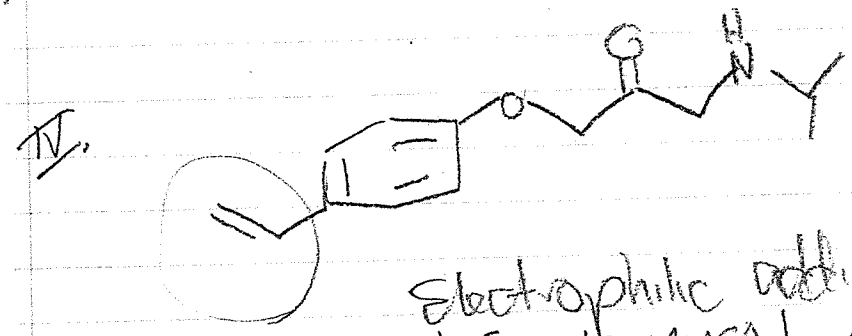


cannot do SN2 on sp^2 carbon

IV.



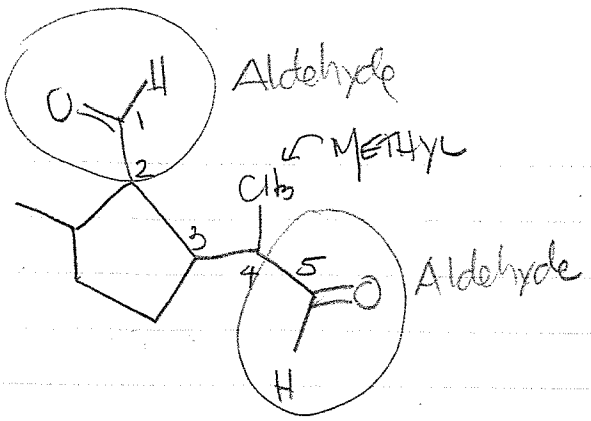
H_3PO_4

CH_3OH

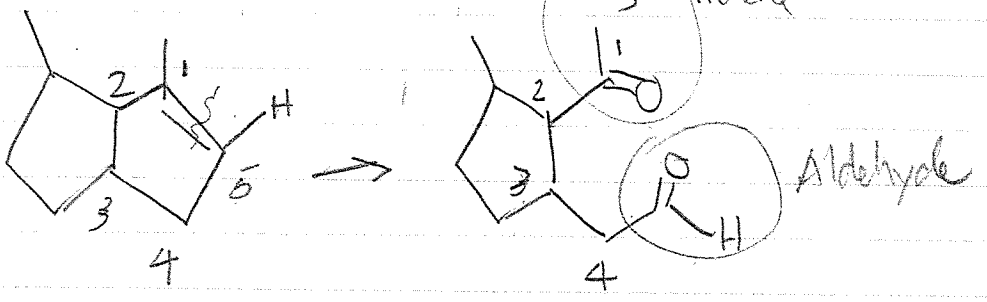
Electrophilic addition

NOT WILLIAMSON ETHER SYNTHESIS.

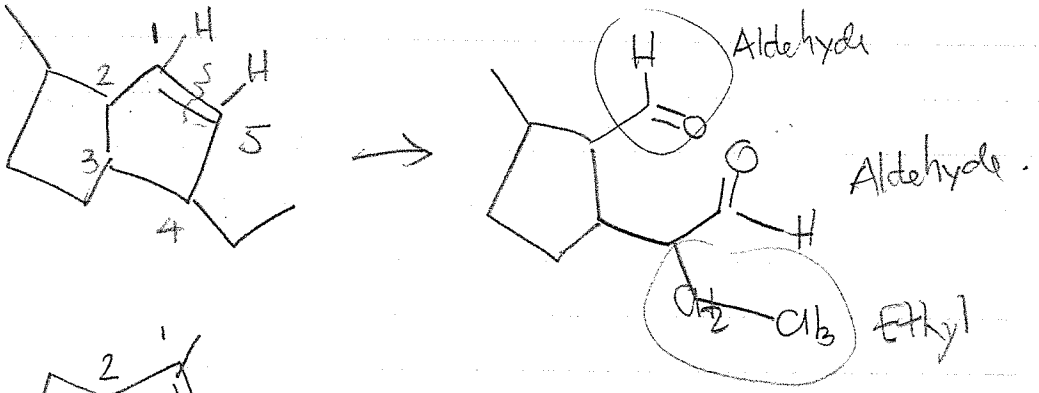
8.


Aldehyde
METHYL
Aldehyde

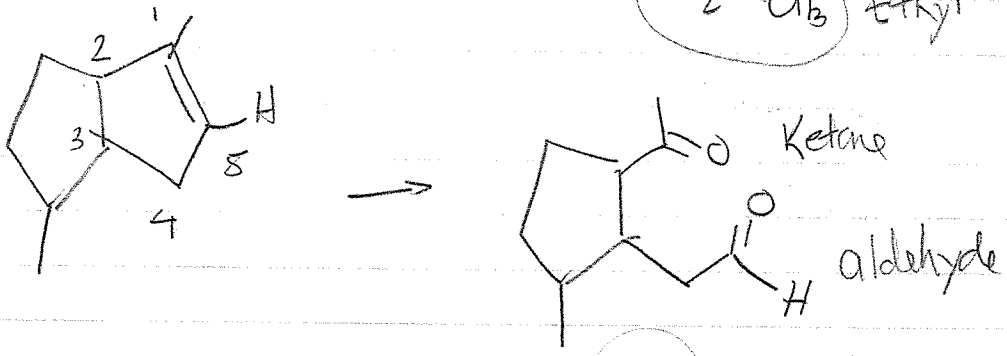
I.


Ketone
Aldehyde

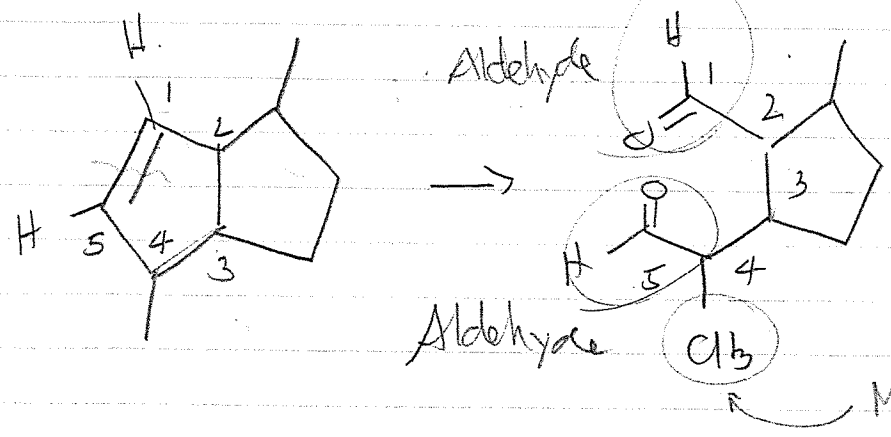
II.


Aldehyde
Aldehyde.
Ethyl

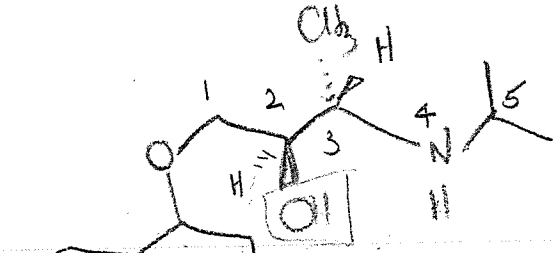
III.

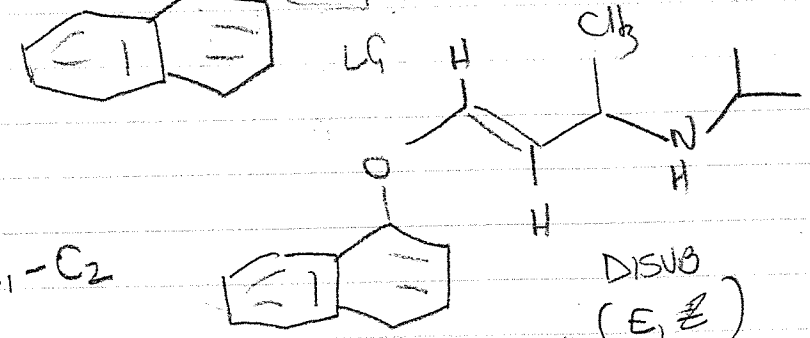

Ketone
aldehyde.

IV.


Aldehyde
Aldehyde
Methyl

A

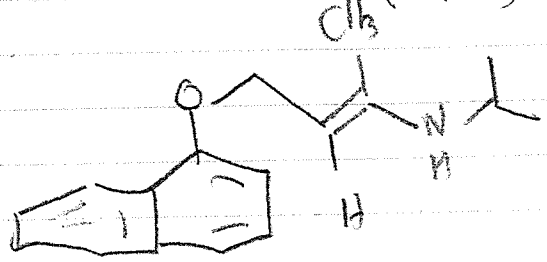




E_2 occurs across C_2-C_3 to give more sub. alkene.

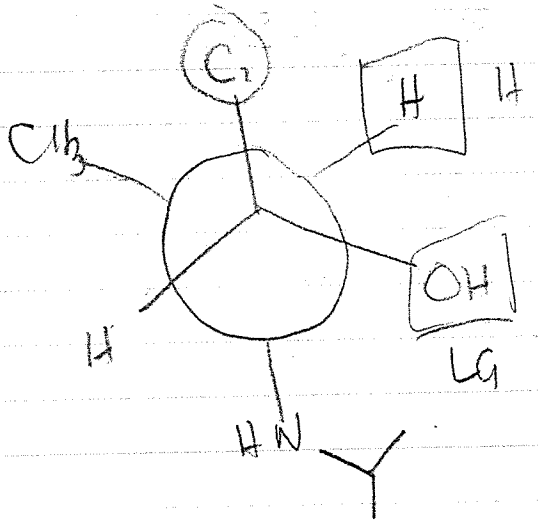
C_1-C_2

DISUB (E, Z)

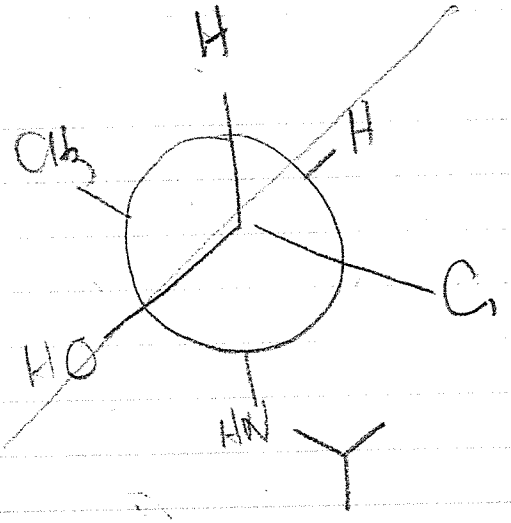


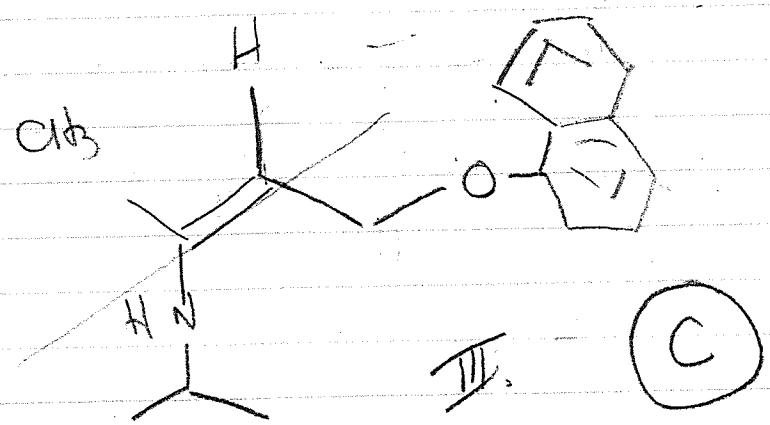
TRISUB

C_2-C_3

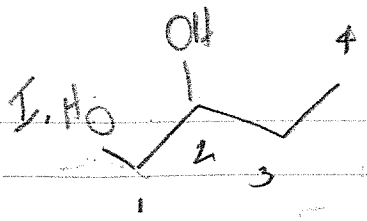


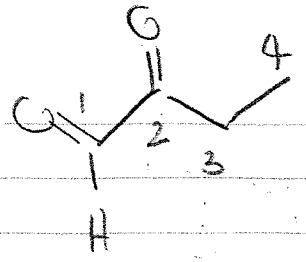
ROTATE →

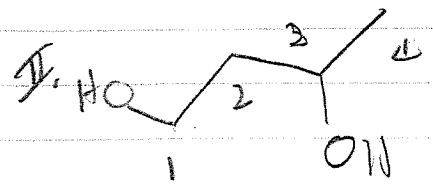


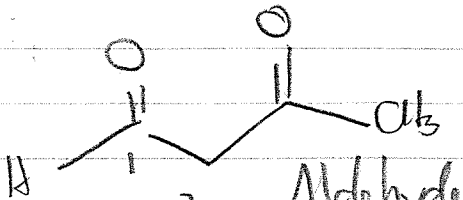


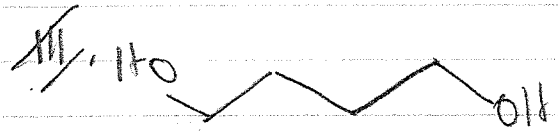
III. (C)

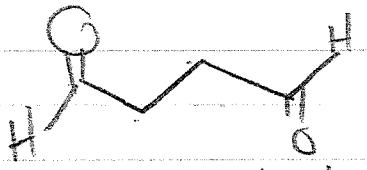
10. 

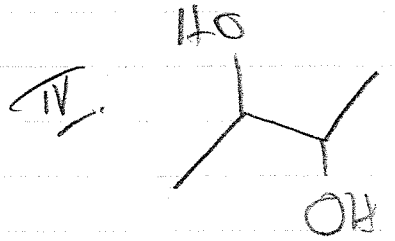

Aldehyde
Ketone

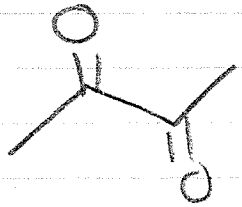



Aldehyde
Ketone

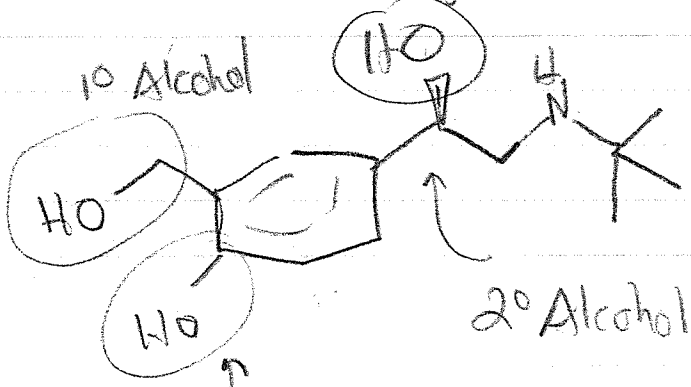


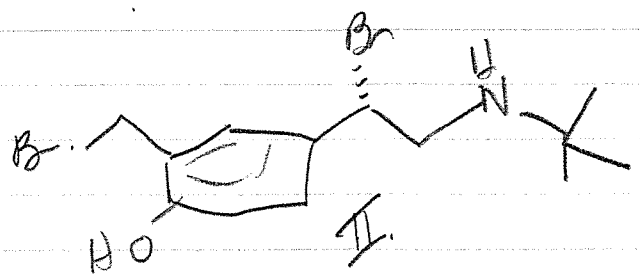
(D)

2 Aldehydes.




2 Ketones

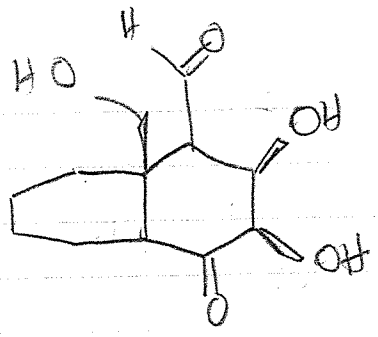
11. Reaction w/ PBr_3 occurs with alcohols (sp^3 C bonded to OH, NOT sp^2) S_N2 ⇒ inversion



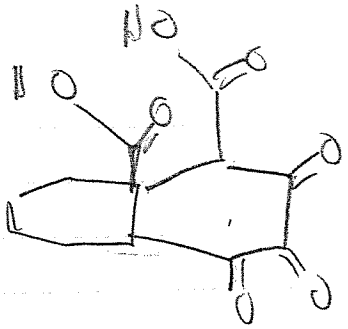


(C)

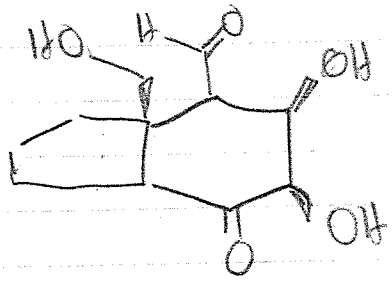
12.

I. 

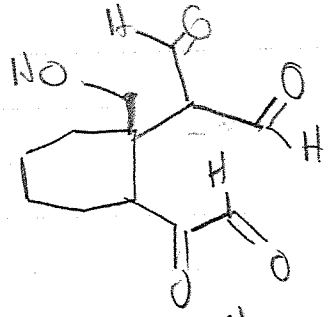
$Na_2Cr_2O_7$ →



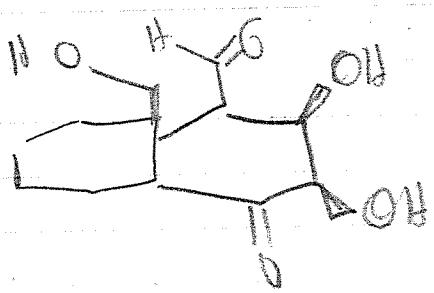
D

II. 

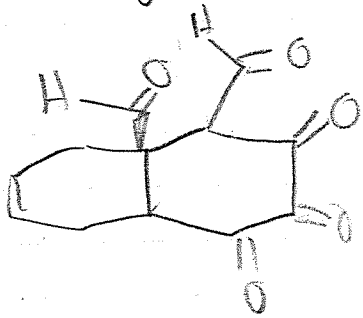
HIO_4 →
H_2O, THF



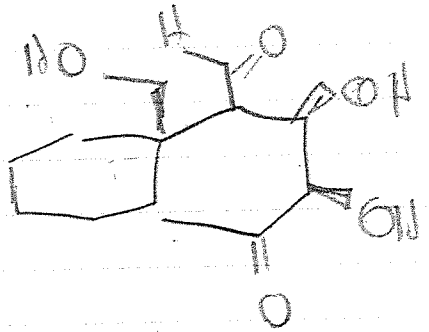
A

III. 

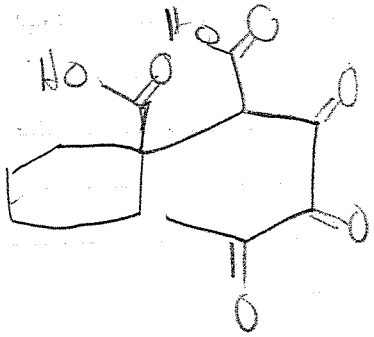
PDC →



C

IV. 

CrO_3 →
H_2SO_4
(Jones)

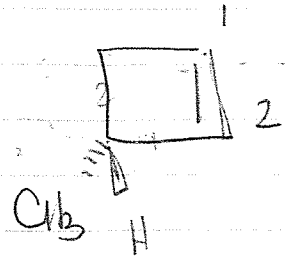


D

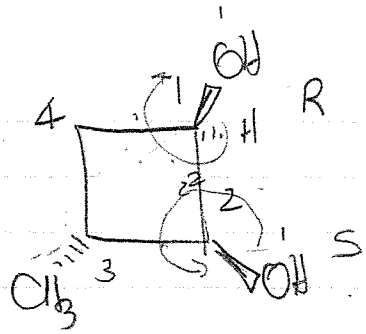
I = D II = A III = C IV = D

(A)

13



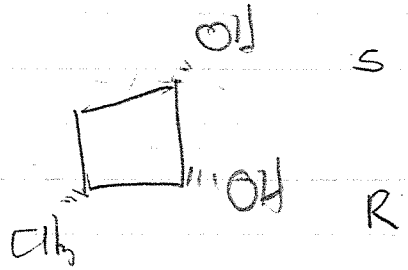
cold, dilute
$KMnO_4$



I & II (B)

1R, 2S, 3R-

1S, 2R, 3R-



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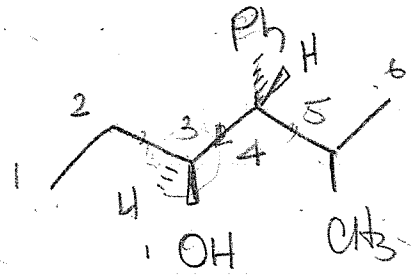
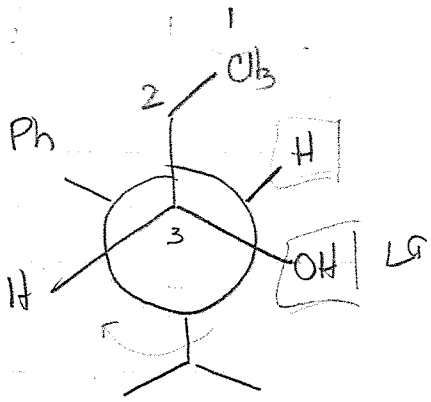
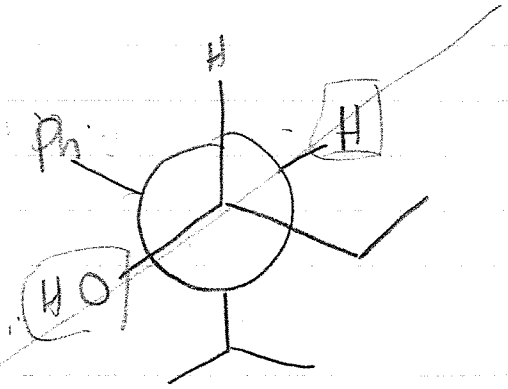
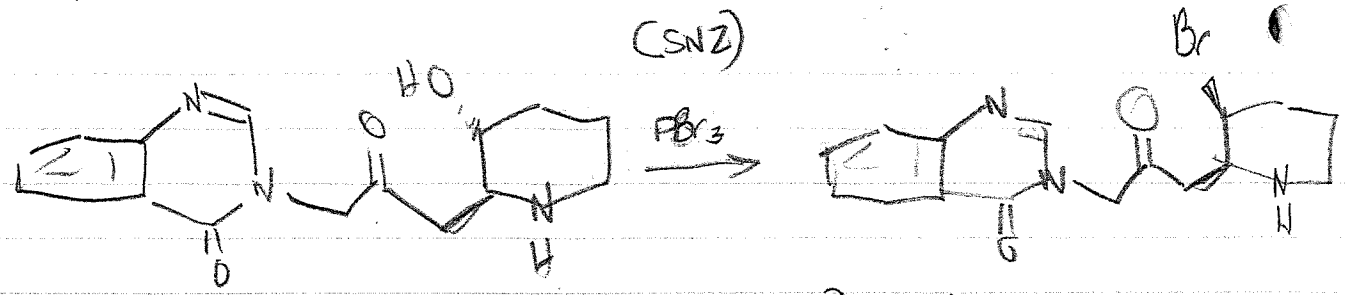
14. 3S,4S-5-methyl-4-phenyl-3-hexanol

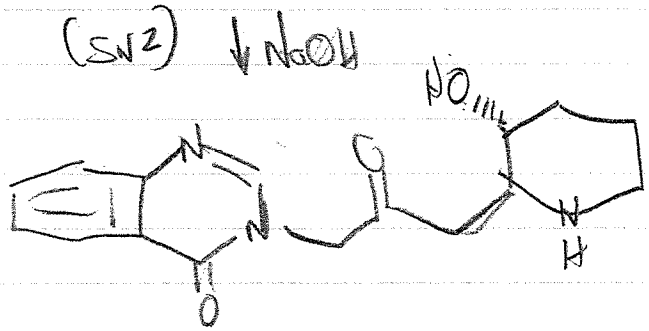


(B)



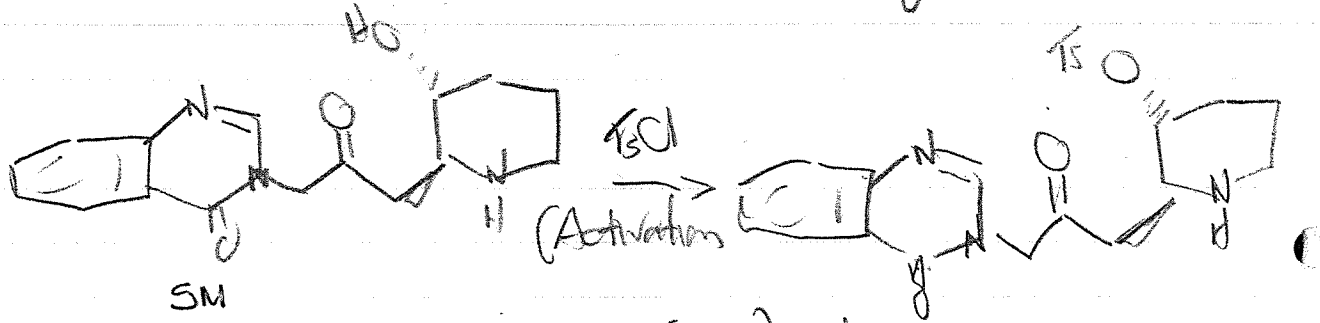


I. 

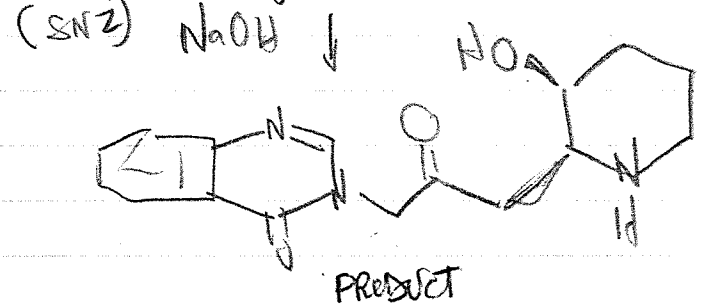


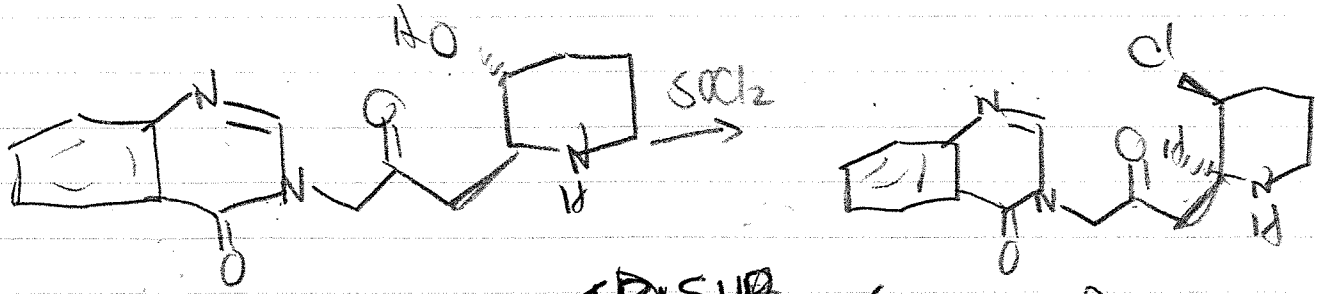
False I.
~~True~~ II
True III
False IV

B

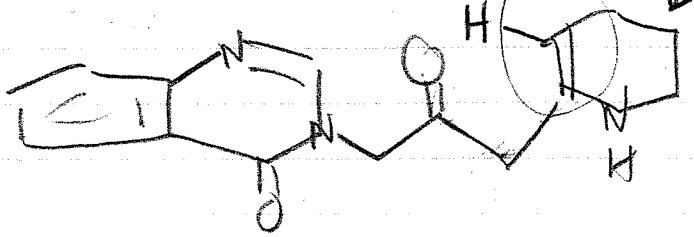
II. 

SM is a diastereomer of product



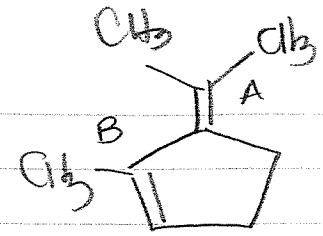
III. 

TRISUB



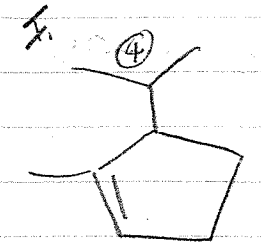
Electrophilic Addition
- only one alkene will react

16.

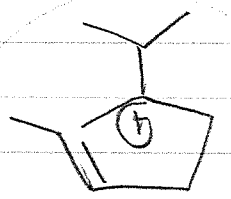


1 equiv
H_3PO_4
H_2O

A:



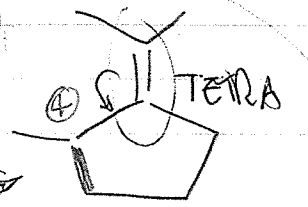
3° ALKYL



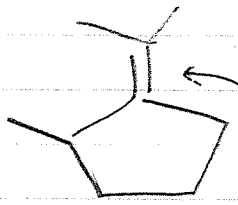
3° ALLYLIC

(D)

B

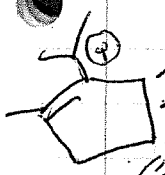


3° ALLYLIC

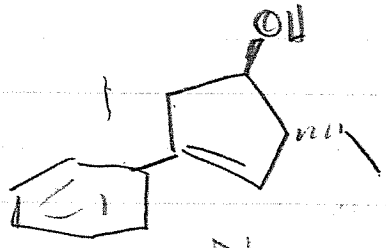


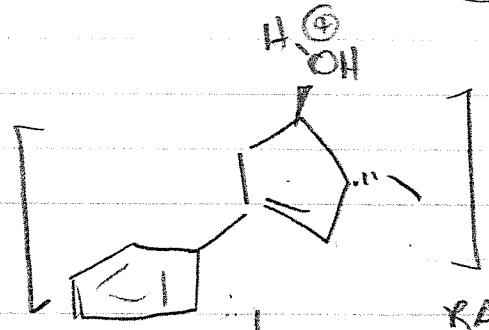
NOT SHOWN

2° ALKYL

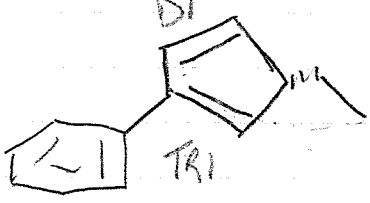


17. E1 Reaction (no nucleophile)

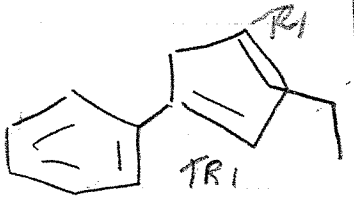




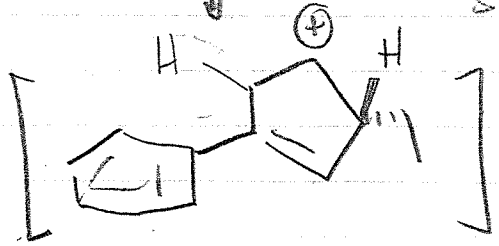
RATE-DET STEP



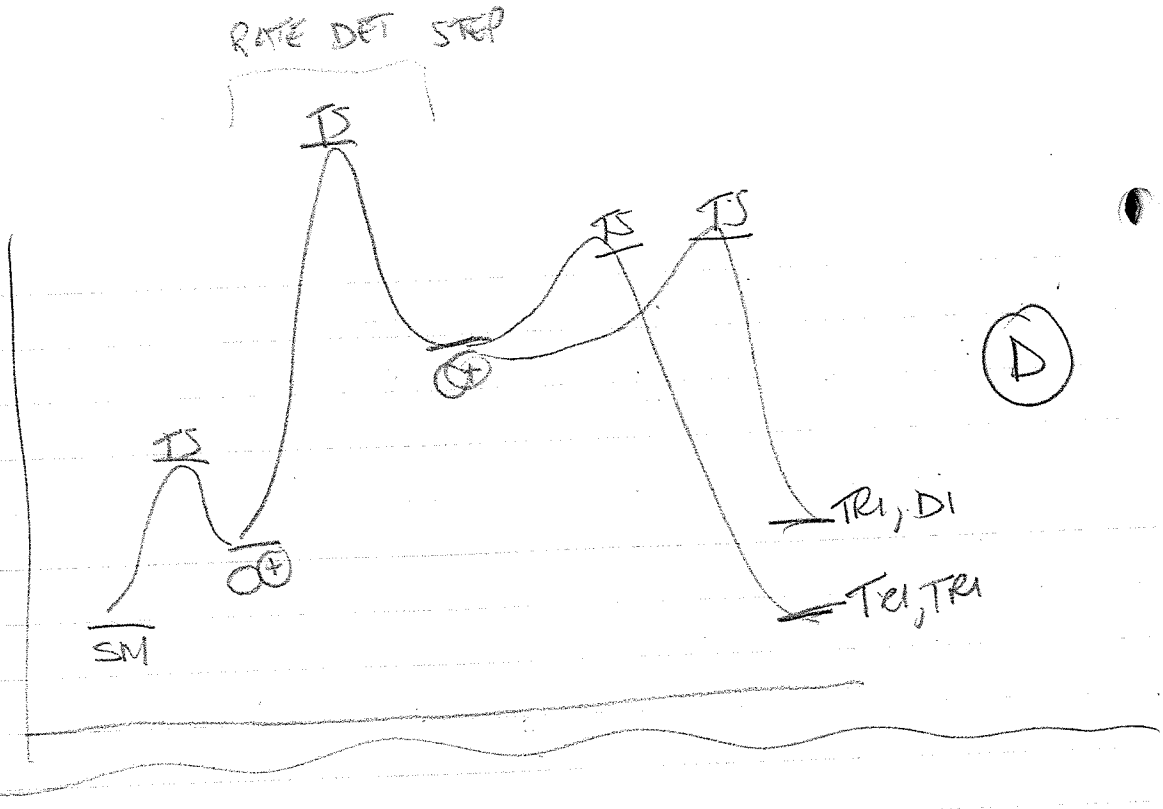
+



(MORE STABLE

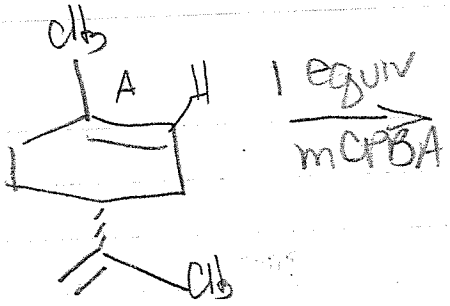


12. (cont'd)



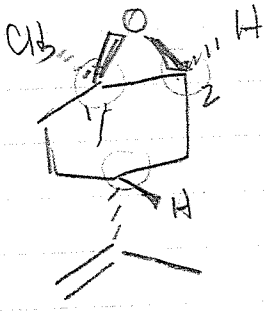
D

18.



1 equiv
mCPBA

A:



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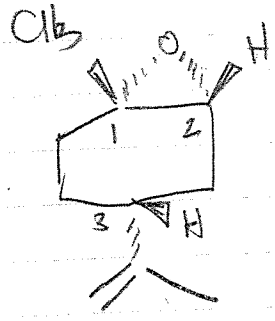
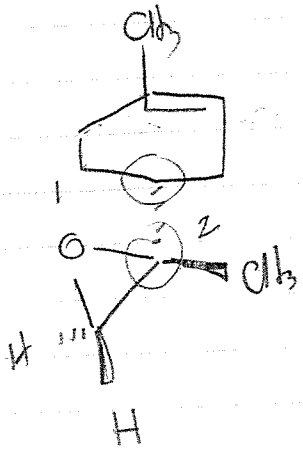


1, 2 inverted
3 same
DIASTEREOMERS

A

B.



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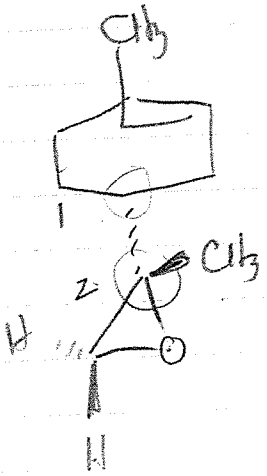


1 is same
2 is inverted
Diastereomers

19. (C)

MTX = methotrexate
RLX = raloxifene
TRF = terfenedine
INDO = indomethacin

pH = 2
Amines ionize
Carboxylic acids
Phenols NOT ionized.
Alcohol not ionized.

pH = 2
I ionized
II not ionized (no amine, only AMIDE)
III ionized
IV ionized

I must be indomethacin

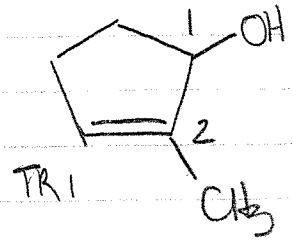
pH = 8 (carboxylic acid)
I, ionize, H-bonding — MTX
II, ionize, no H-bonding — INDO
III, not ionize, H-bonding
IV not ionize, H-bonding

pH = 7
Carboxylic acid ionize
Phenol not ionized
Alcohol not ionized
Amine not ionized

pH = 12
I, ionize, H-bonding — MTX
II, ionize, no H-bonding — INDO
III not ionize, H-bonding — TRF
IV ionize, H-bonding — RLX
(PHENOL)

pH = 12
acids, phenols ionize,
amines not ionized
alcohols not ionized.

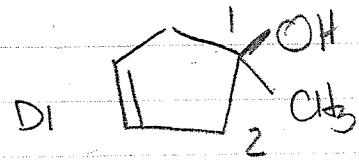
20. I.



2° Allylic alcohol

2-methyl-cyclopent-2-en-1-ol

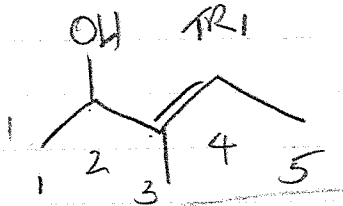
II.



3° Alcohol

1-methylcyclopent-3-en-1-ol

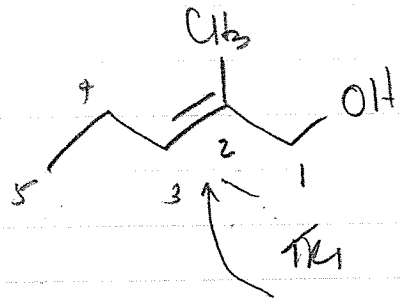
III.



2° Allylic

CH3

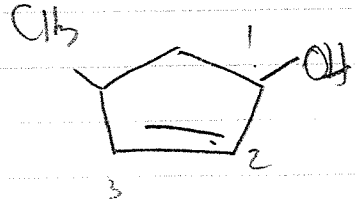
IV.



1° Alcohol

A

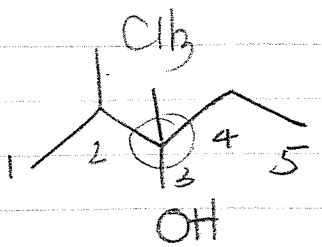
V.

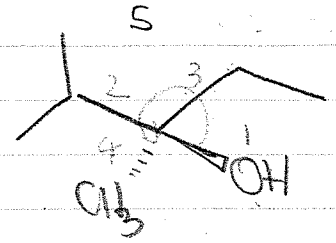


2° Allylic

DI

21. R; 2,3-dimethyl-3-pentanol



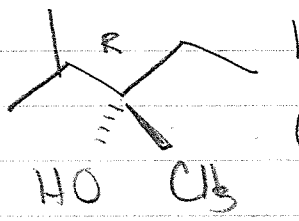


I. false NO π bonds broken

II. True C⊕ is sp^2

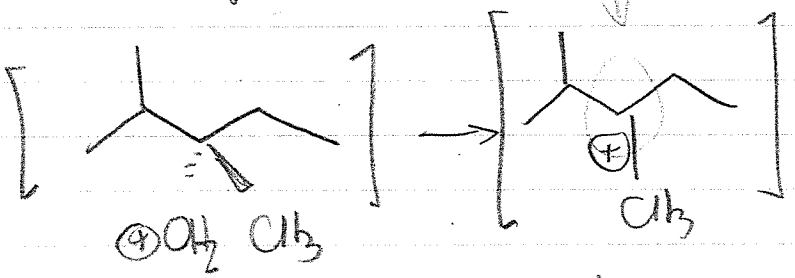
III. True

IV. True

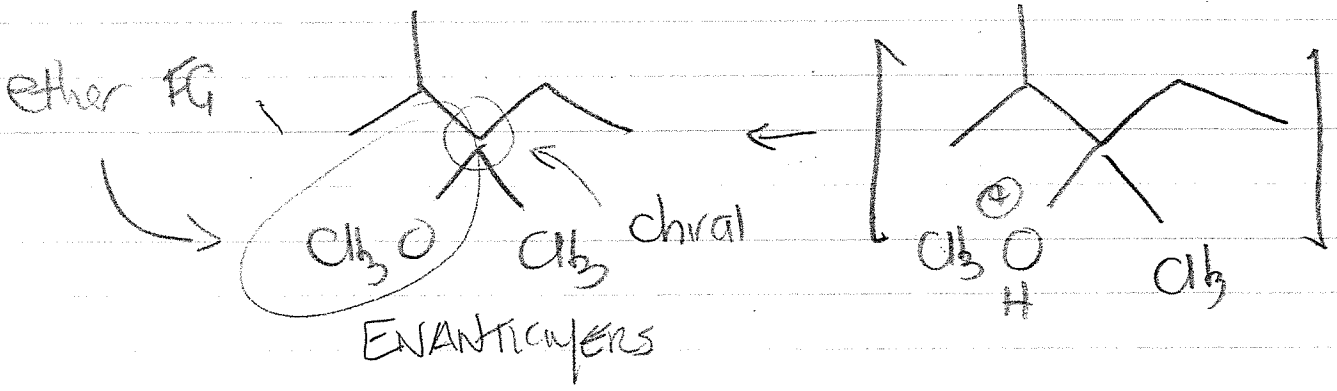


H_2SO_4

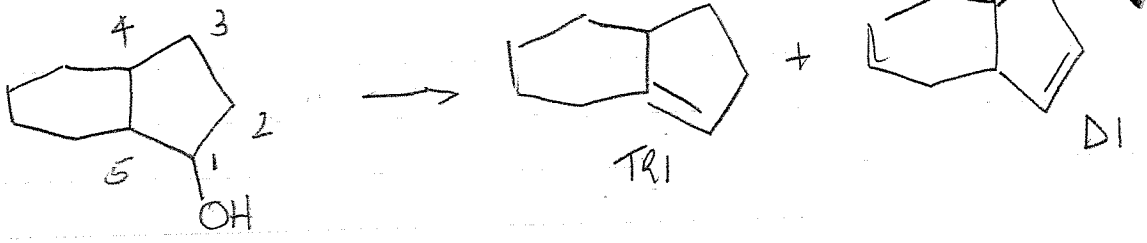
CH_3OH (S_N1)



(B)

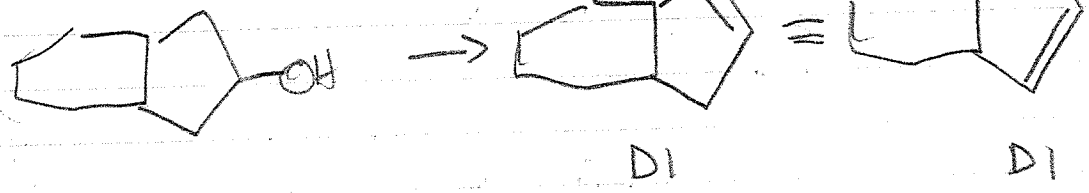


22. I.

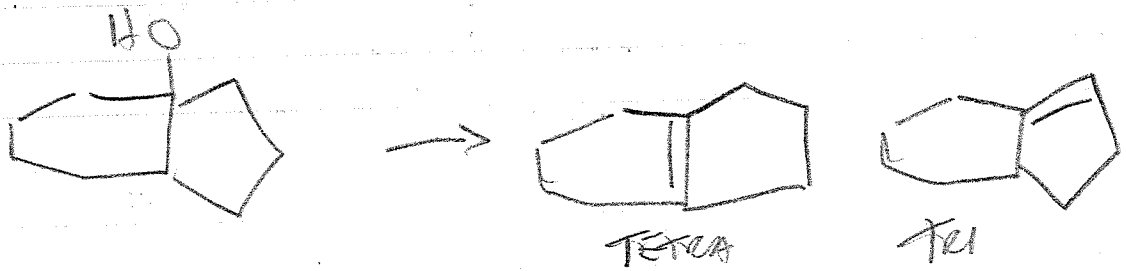


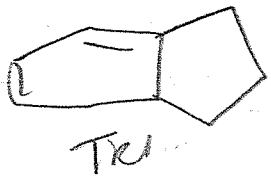
(A)

II.



III.





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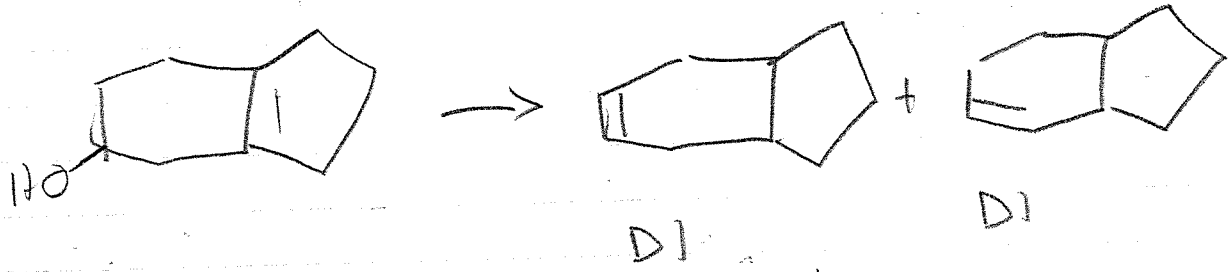

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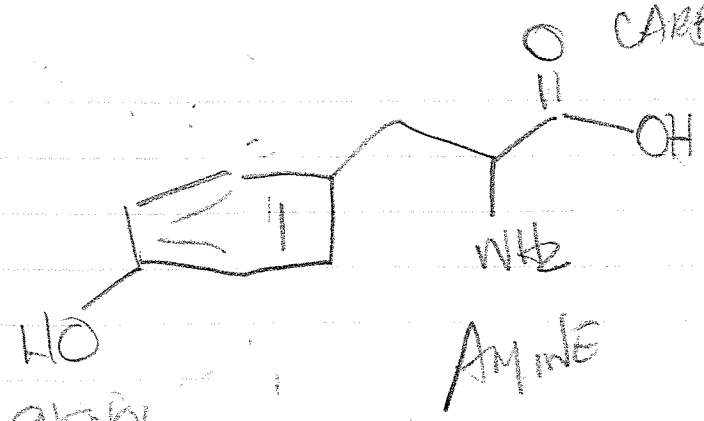


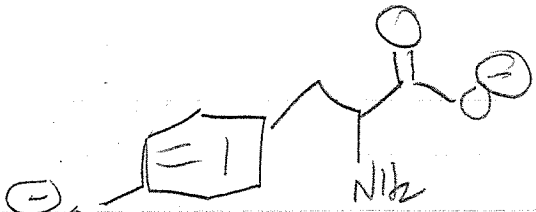
CARBOXYLIC ACID

AMINE

PHENOL

(a) pH 8.4

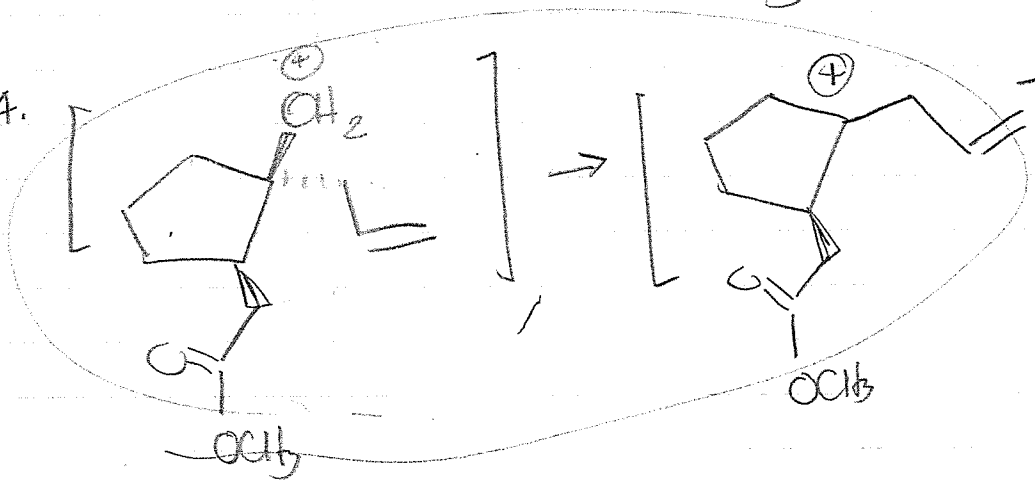
CA ionized
Phenol ionized
Amine NOT ionized



(B)

3° CARBOCATION

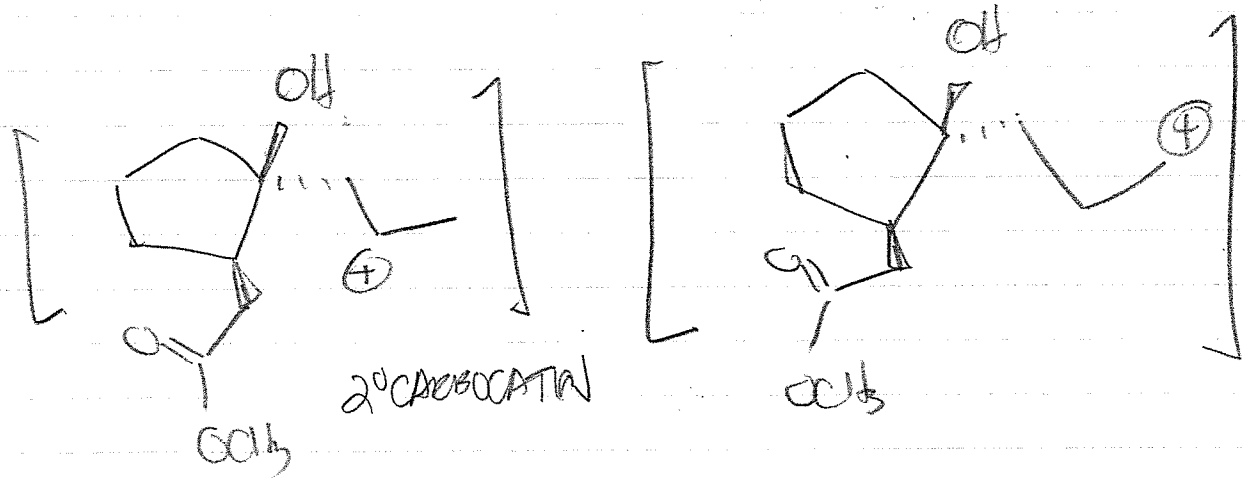
24.



1 & III

(D)

10 CARBOCATION



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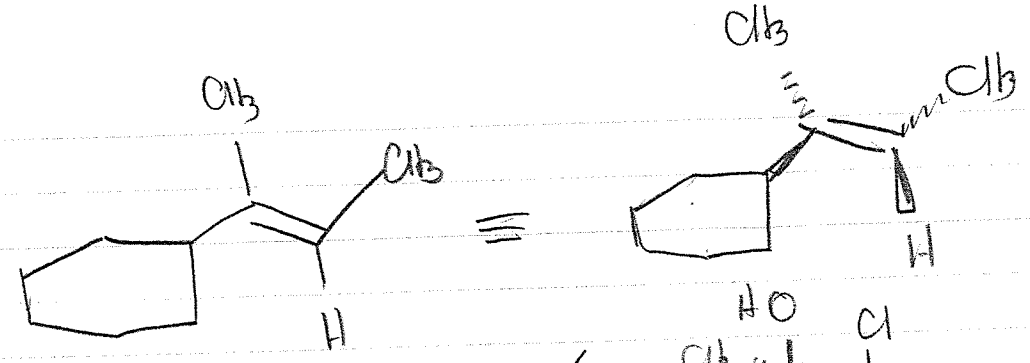
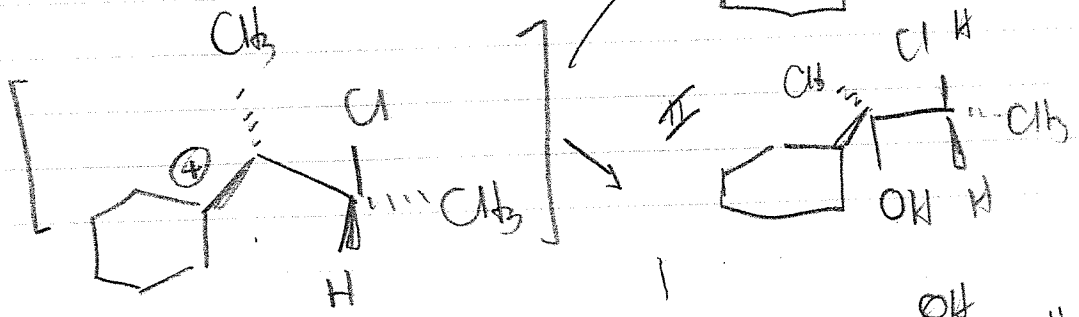
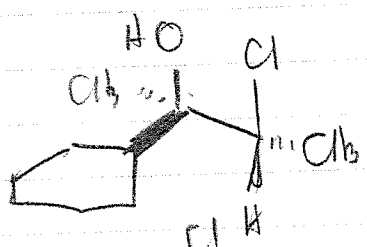
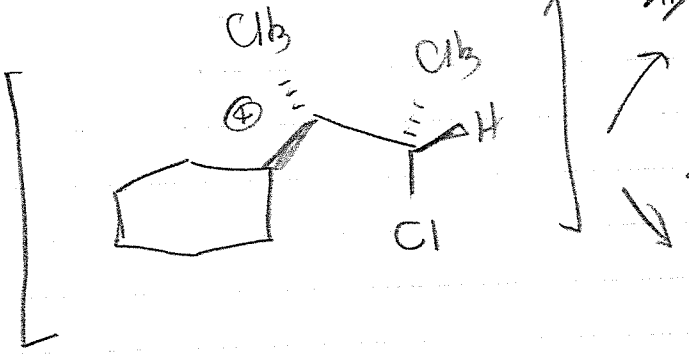




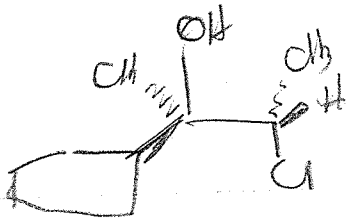
I



II



III



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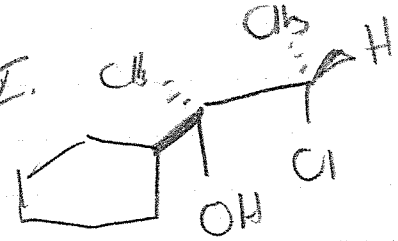
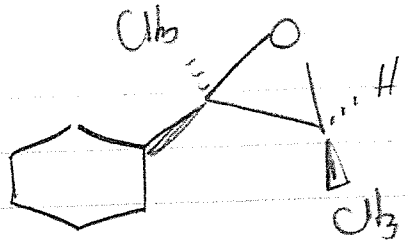
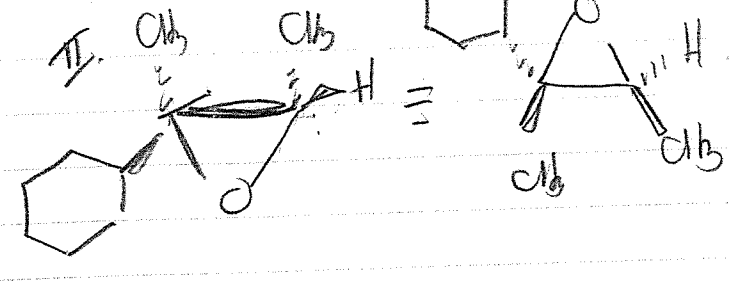


E

I.



II.



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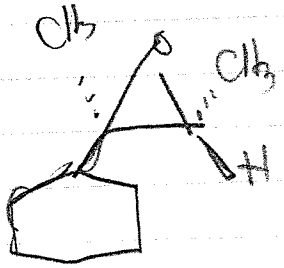

IV