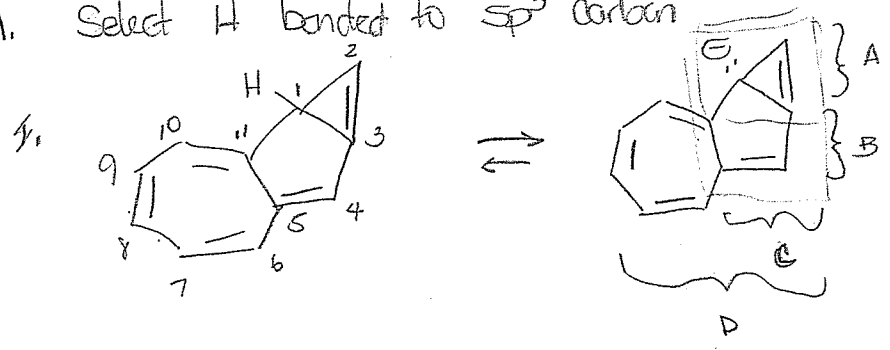
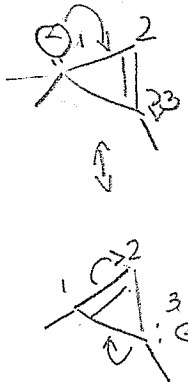


I. Select H bonded to sp^3 carbon



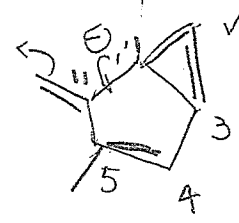
Once conjugate base is formed, check for aromatic of individual/combined rings that involve the lone pair of the conjugate base

RING A



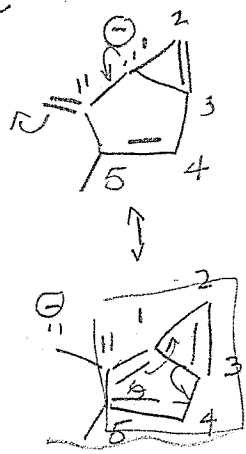
- ✓ CYCLIC
- ✓ PLANAR
- ✓ CONT π
- X $4n+2=4$
- $n = \frac{1}{2}$
- NOT AROMATIC

RING B



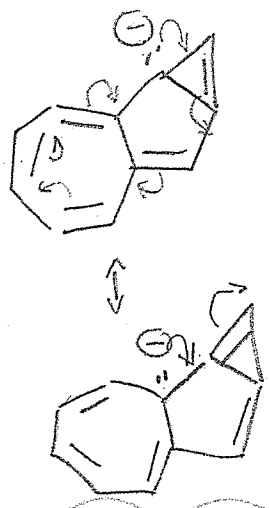
- ✓ CYCLIC
- ✓ PLANAR
- X NOT CONTINUOUS
- NOT AROMATIC

RING C



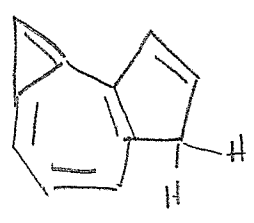
- ✓ CYCLIC
- ✓ PLANAR
- ✓ CONT π
- ✓ $4n+2=6$
- $n=1$

RING D



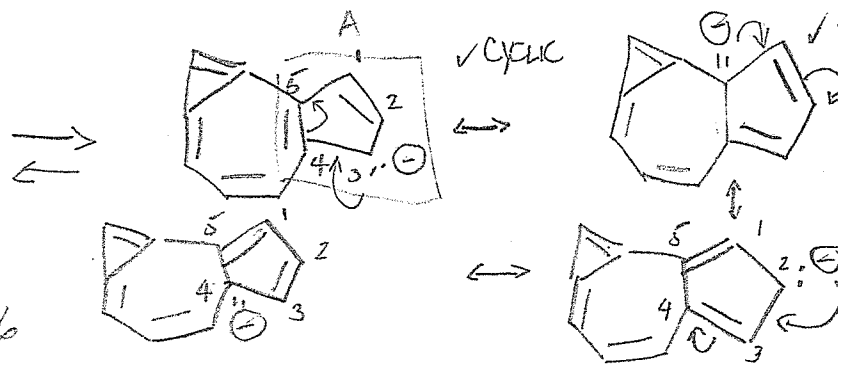
- ✓ CYCLIC
- ✓ PLANAR
- ✓ CONT π
- $4n+2=12$
- $4n=10$
- $n \neq \text{integer}$
- NOT AROM

II



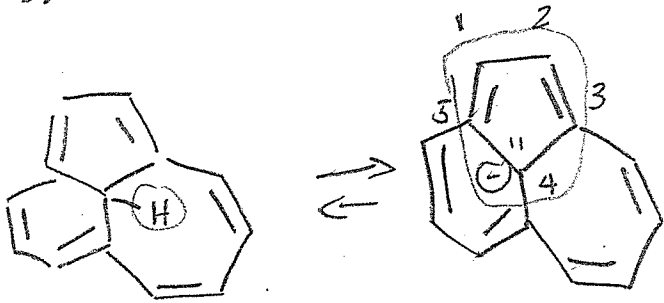
AROMATIC
CB

- ✓ CONT π
- ✓ $4n+2=6$



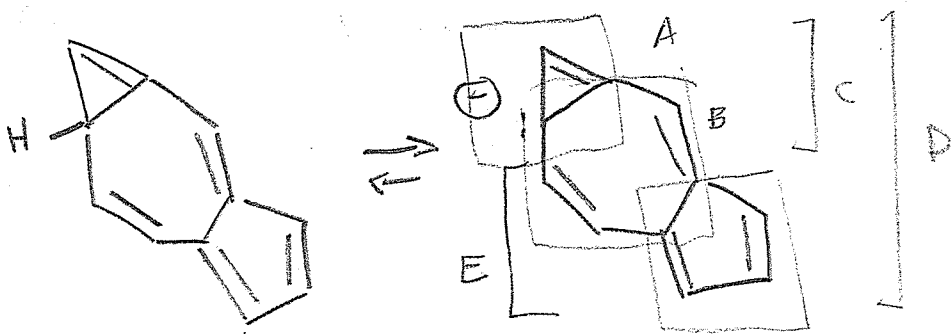
(CONT'D)

III

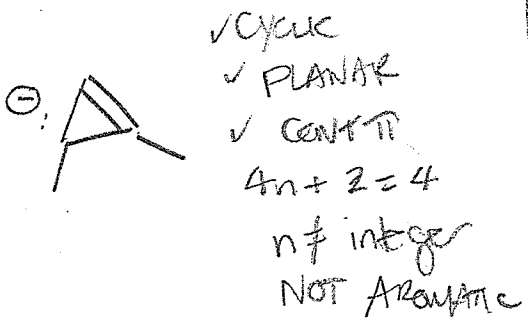


- ✓ CYCLIC
- ✓ PLANAR
- ✓ CONT Π
- ✓ $4n+2=6$
- AROMATIC

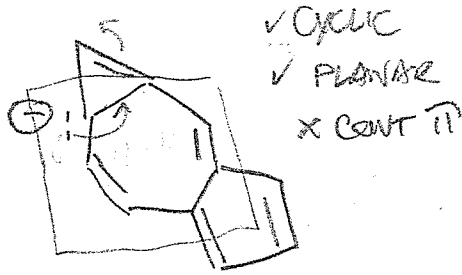
IV



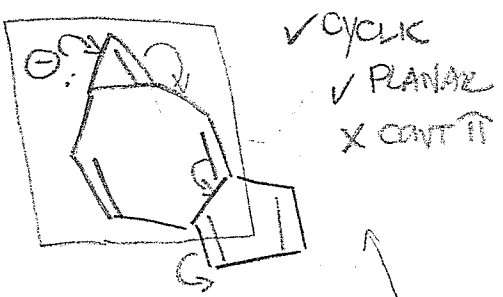
RING A



RING B

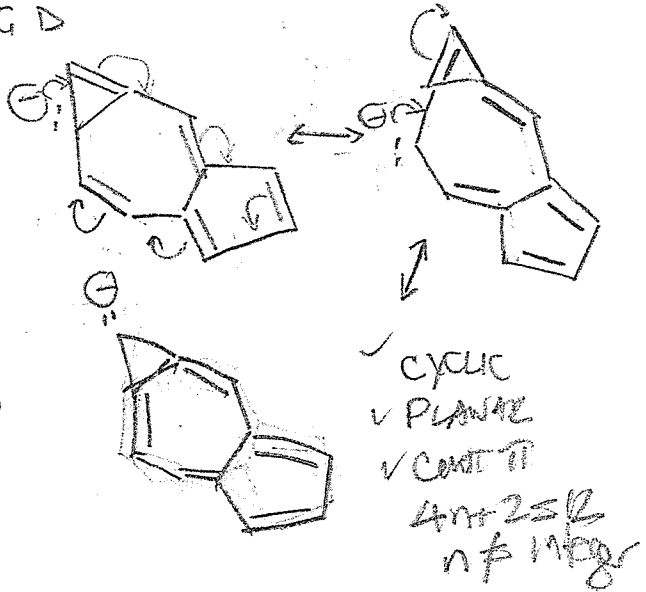


RING C



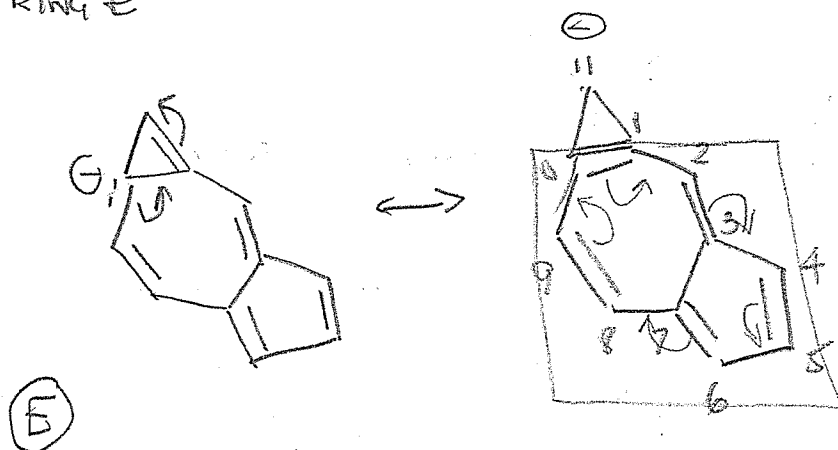
NOT AROMATIC
CB

RING D



1. (cont'd)

IV RING E



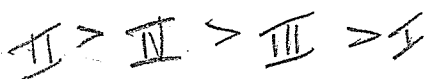
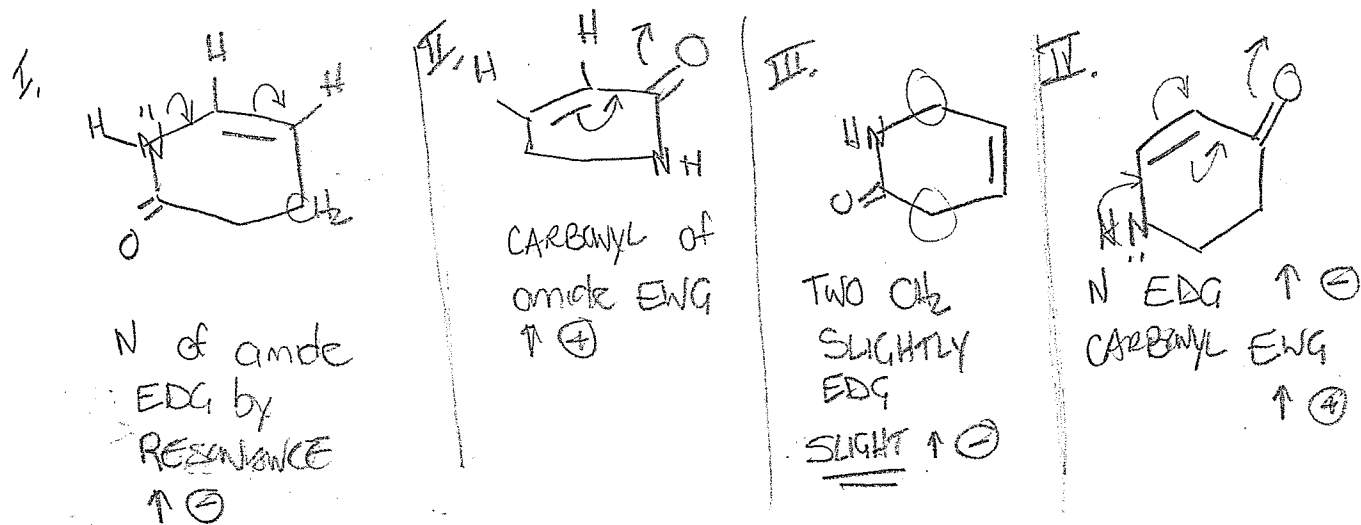
- ✓ CYCLIC
- ✓ PLANAR
- ✓ CONT π

$$4n + 2 = 10$$

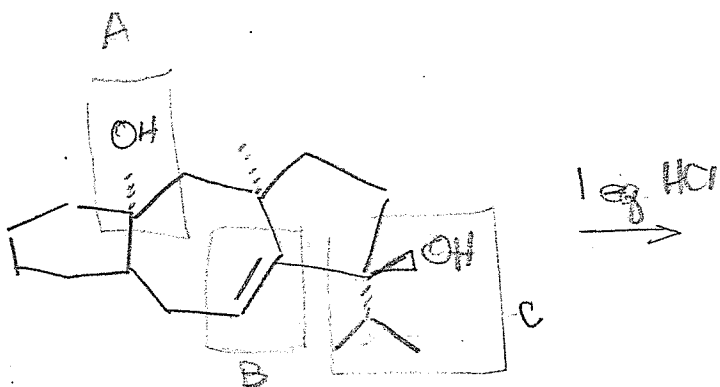
$$n = 2$$

AROMATIC

2. Most reactive dienophile is most ⊕ as determined by EDG / EWG by resonance

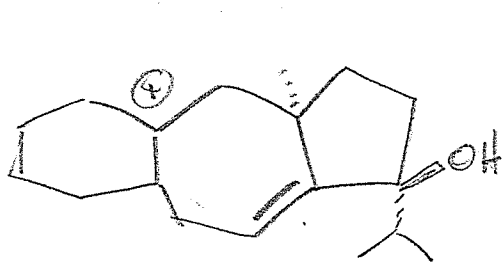


(B)

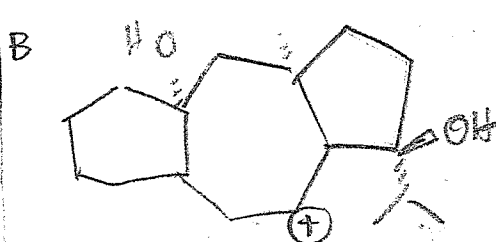


HCl can react w/ 3° Alcohol (A) via S_N1
 HCl can react w/ Alkene (B) via electrophilic addition
 HCl can react w/ 3° Allylic (C) Alcohol via S_N1

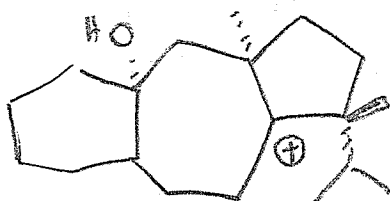
The major kinetic product is derived from the most stable carbocation formed from each of these 3 possible reactions.



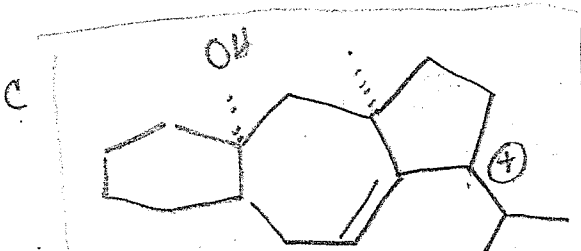
3° Alkyl



2° Alkyl

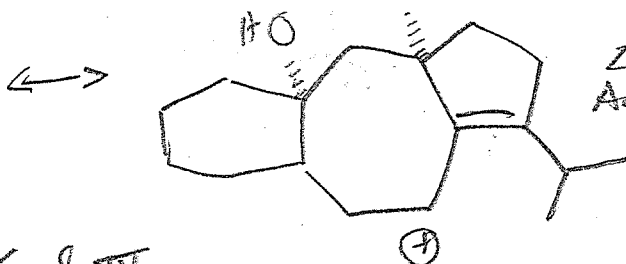


3° Allylic



3° Allylic
 MOST STABLE

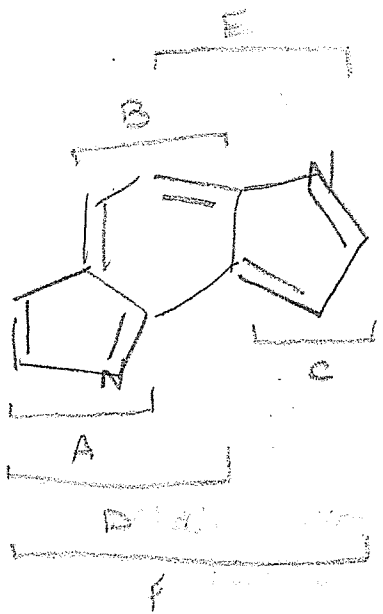
I & IV
 (A)



2° Alkyl

Cl⁻ attacks C⁺ from top and bottom side

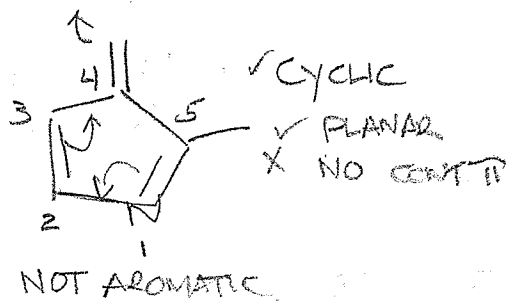
4.



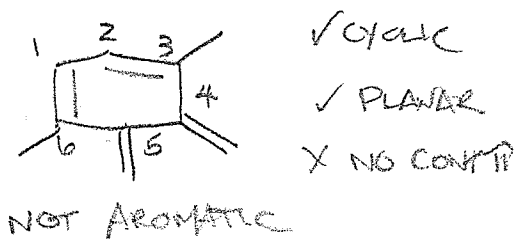
There are 6 possible ring systems to consider for aromaticity.
(A, B, C, D, E, F)

(E)

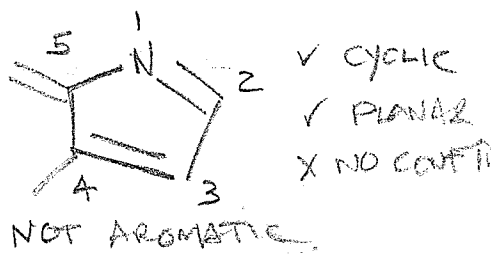
RING A



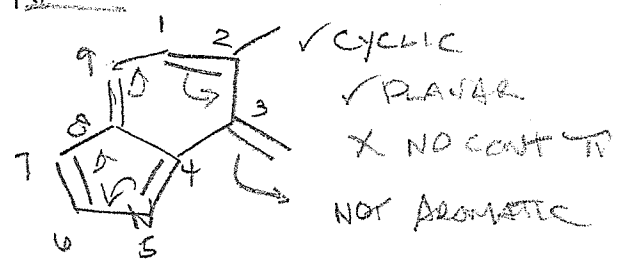
RING B



RING C

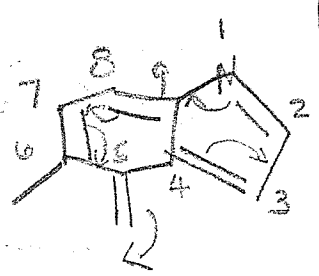


RING D

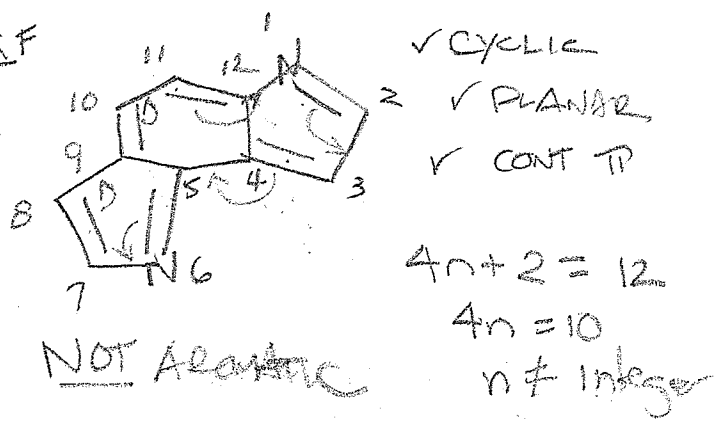


RING E

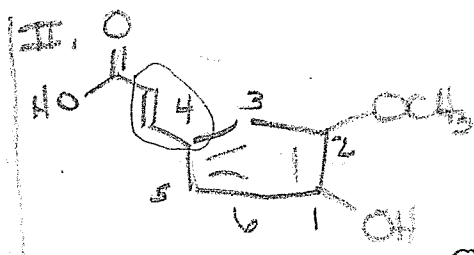
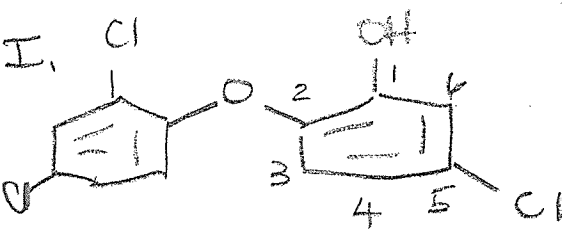
✓ CYCLIC
✓ PLANAR
X NO CONT π
NOT AROMATIC



RING F

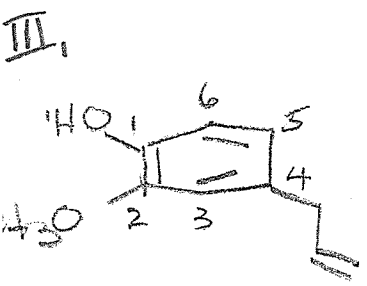


NO RINGS ARE AROMATIC

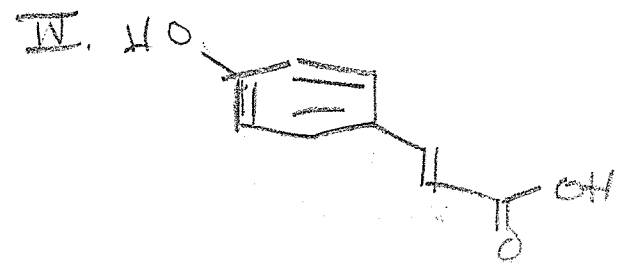


21 ORTHO PHENOXY (relative to OH)
 Use σ_p PHENOXY -0.21
 Use META CHLORO $+0.37$
 $\sigma_{sum} = +0.16$

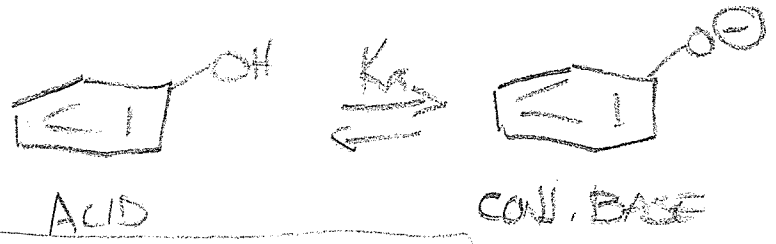
C_2 OH -0.27
 C_4 O METHOXY -0.02
 $\sigma_{sum} = -0.29$



σ METHOXY -0.27
 σ ETHYL -0.15
 $\sigma_{sum} = .42$



σ_p ALKENYL -0.02
 $\sigma_{sum} = -0.02$



$K_a = \frac{[CB]}{[A]}$

$\uparrow \oplus$ of Ring
 \uparrow STABILITY OF CB
 $\uparrow [CB] \uparrow K_a$
 $\downarrow pK_a$
 MOST ACIDIC

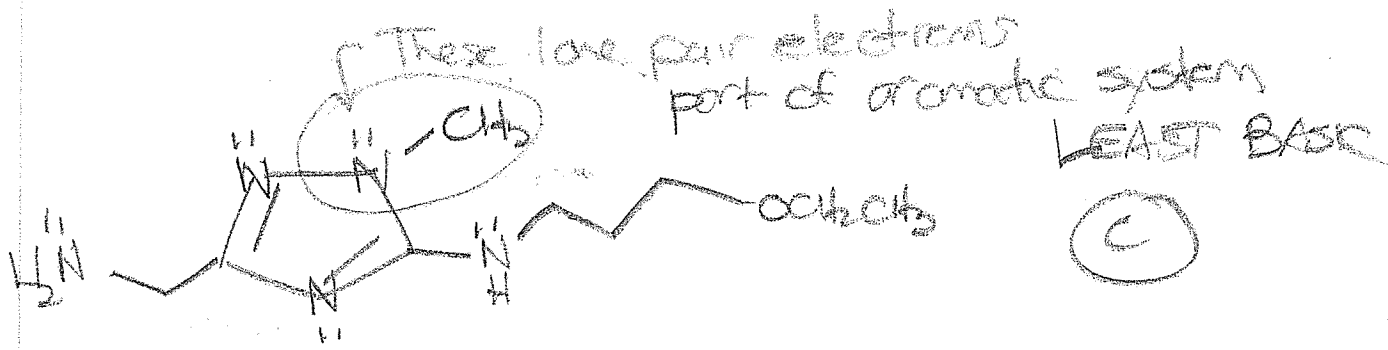
$I > IV > II > III$ (C)

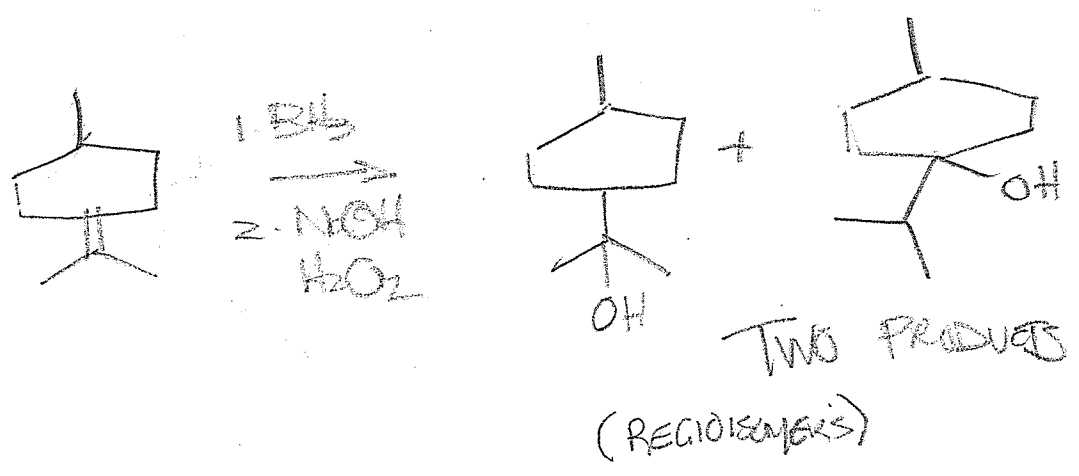
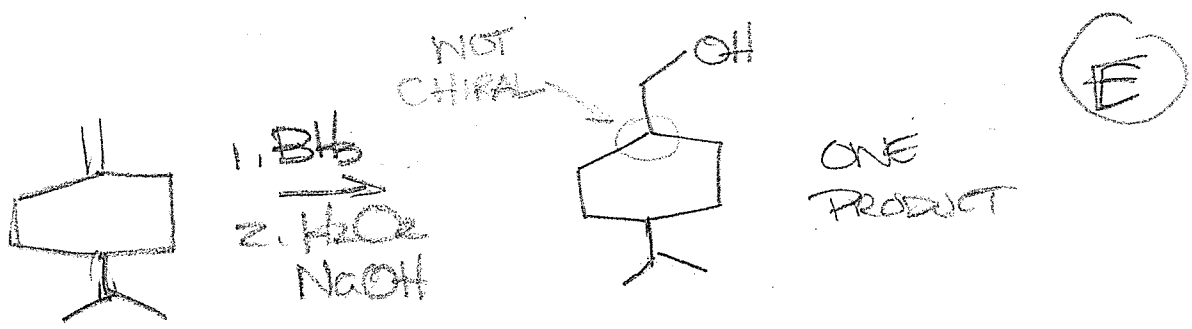
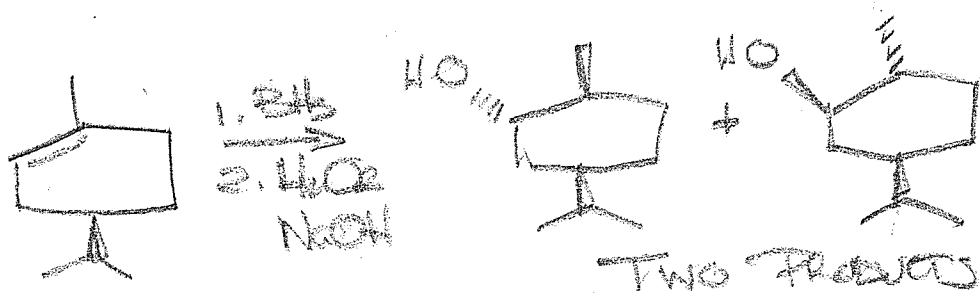
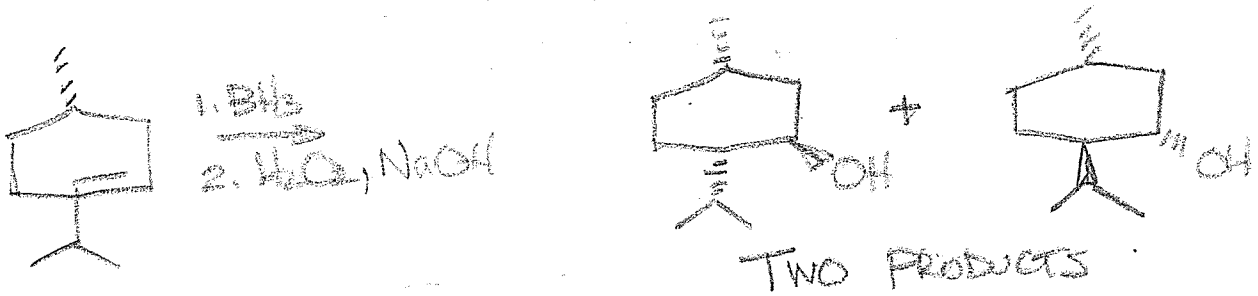
6. Lone pair electrons on N atom that is part of an aromatic system are least basic.

Highest pK_b , least basic

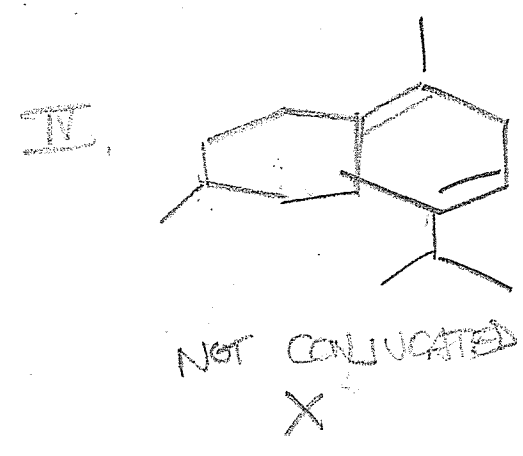
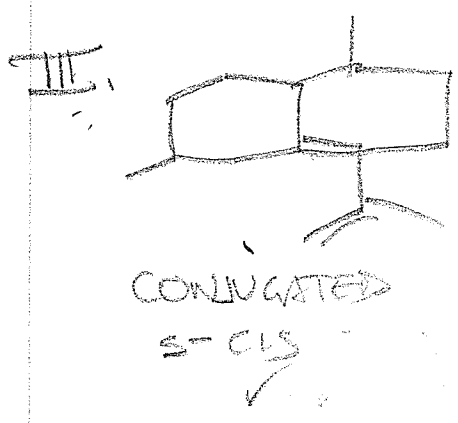
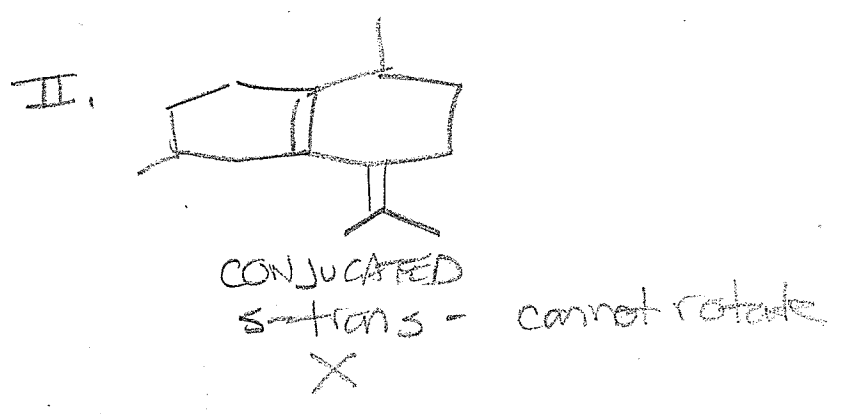
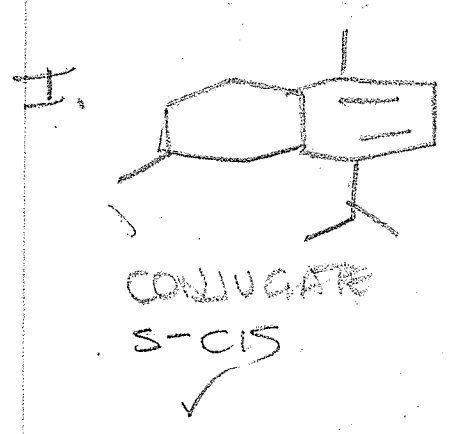
Lone pair electrons on N atom that can be delocalized via resonance are less basic since they are tied up in resonance.

Most basic N is one w/ lone pair electrons completely available to accept a proton.

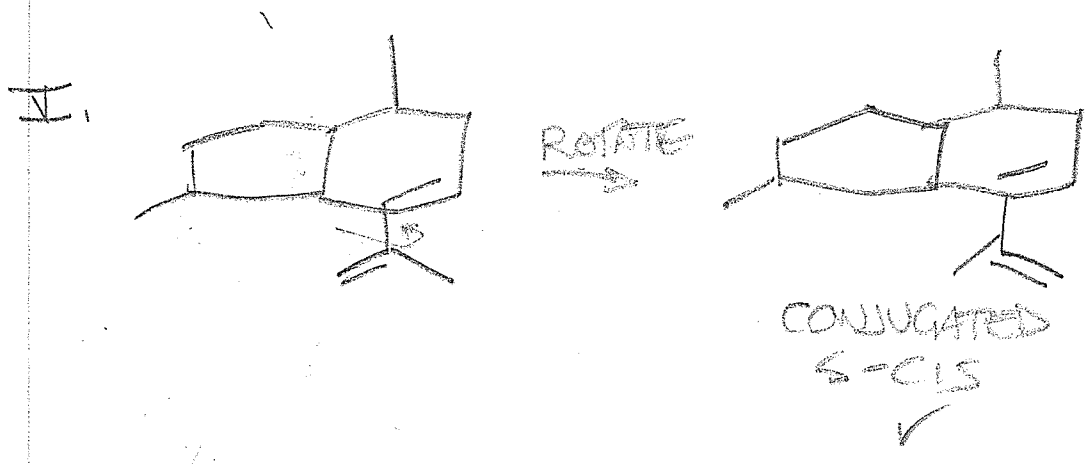


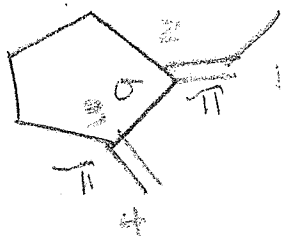


8. Diene in Diels-Alder must be conjugated and it must be able to adopt s-cis conformation.



(C)





I. TRUE - CONJUGATED DIENE

II. TRUE - Either alkene can serve as dienophile in Diels-Alder

III. FALSE

IV. TRUE

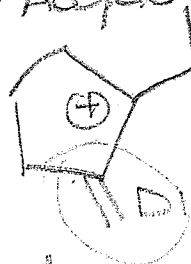
D

A

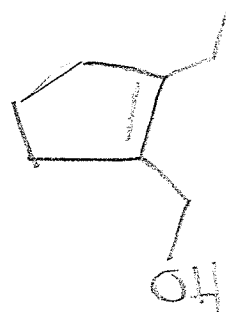
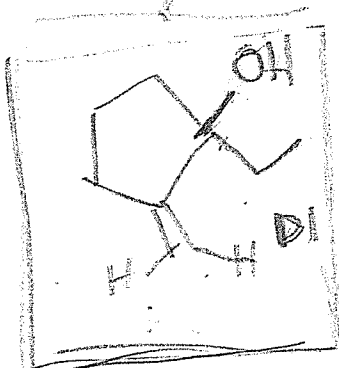
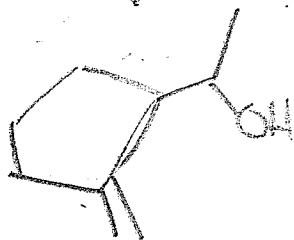
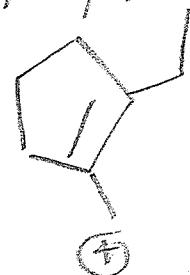
2° ALKYL



3° ALLYLIC



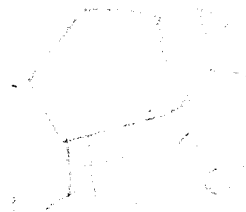
1° ALLYLIC



DI

TETRA
THERMO

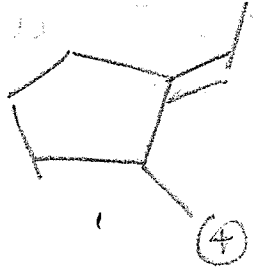
1° ALCOHOL



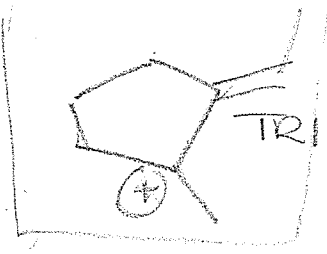
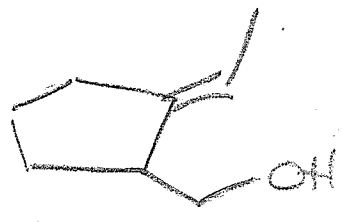
9. (CONT'D)

This 3° Allylic
MORE STABLE
b/c TRI SUB ALLENE

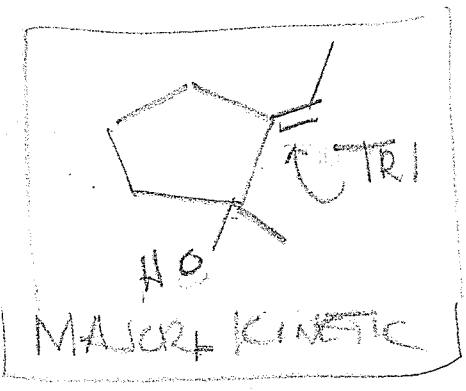
B.



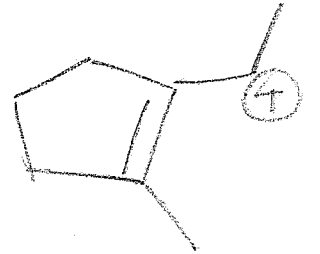
1° ALKYL



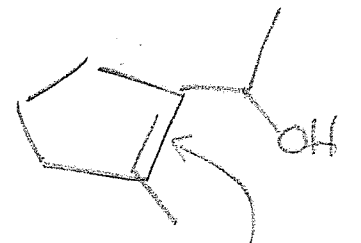
3° ALLYLIC



MAJOR KINETIC

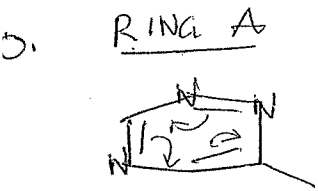


2° ALLYLIC



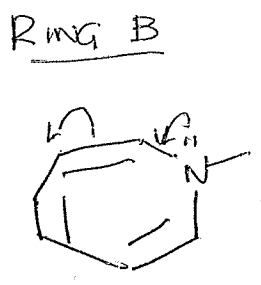
TETRASUB
THERMODYNAMIC
2° ALCOHOL

Of all possible \oplus , 3° allylic w/ trisub allene
IS MOST STABLE. ONLY product from this rxn
intermediate is MAJOR kinetic product. \therefore Statement
III is FALSE This product contains a TRISUB allene.

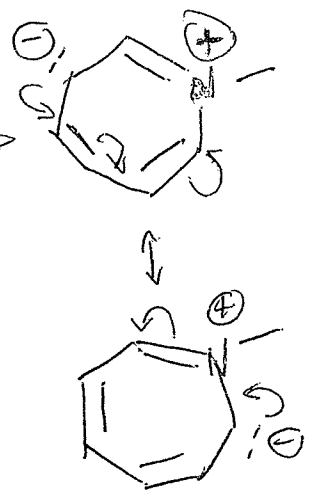


- ✓ CYCLIC
- ✓ PLANAR
- ✓ CONST. TP
- ✓ $4n+2=6$
- $n=1$

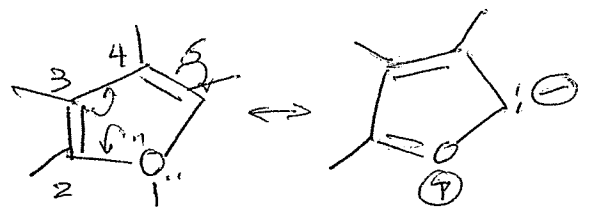
$t = 1, II, III, IV$



- ✓ CYCLIC
- ✓ PLANAR
- ✓ CONST. TP
- ✗ $4n+2=8$
- $n \neq \text{integer}$
- $B = 1, II, III$



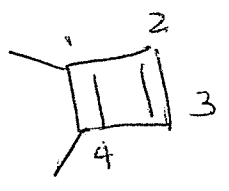
RING C



- ✓ CYCLIC
- ✓ PLANAR
- ✓ CONST TP
- ✓ $4n+2=6$
- $n=1$

$C = 1, II, III, IV$

RING D

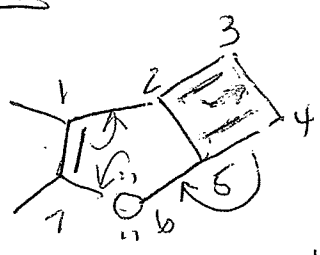


- ✓ CYCLIC
- ✓ PLANAR
- ✓ CONST TP
- ✗ $4n+2=4$
- $n \neq \text{integer}$

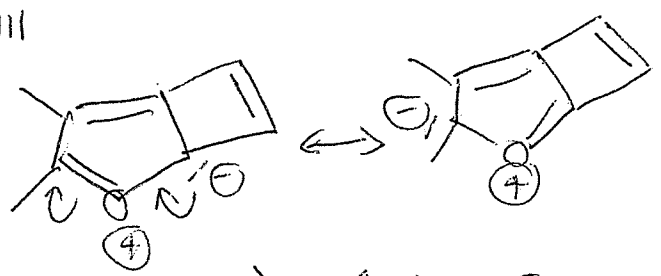
(B)

$D = 1, II, III$

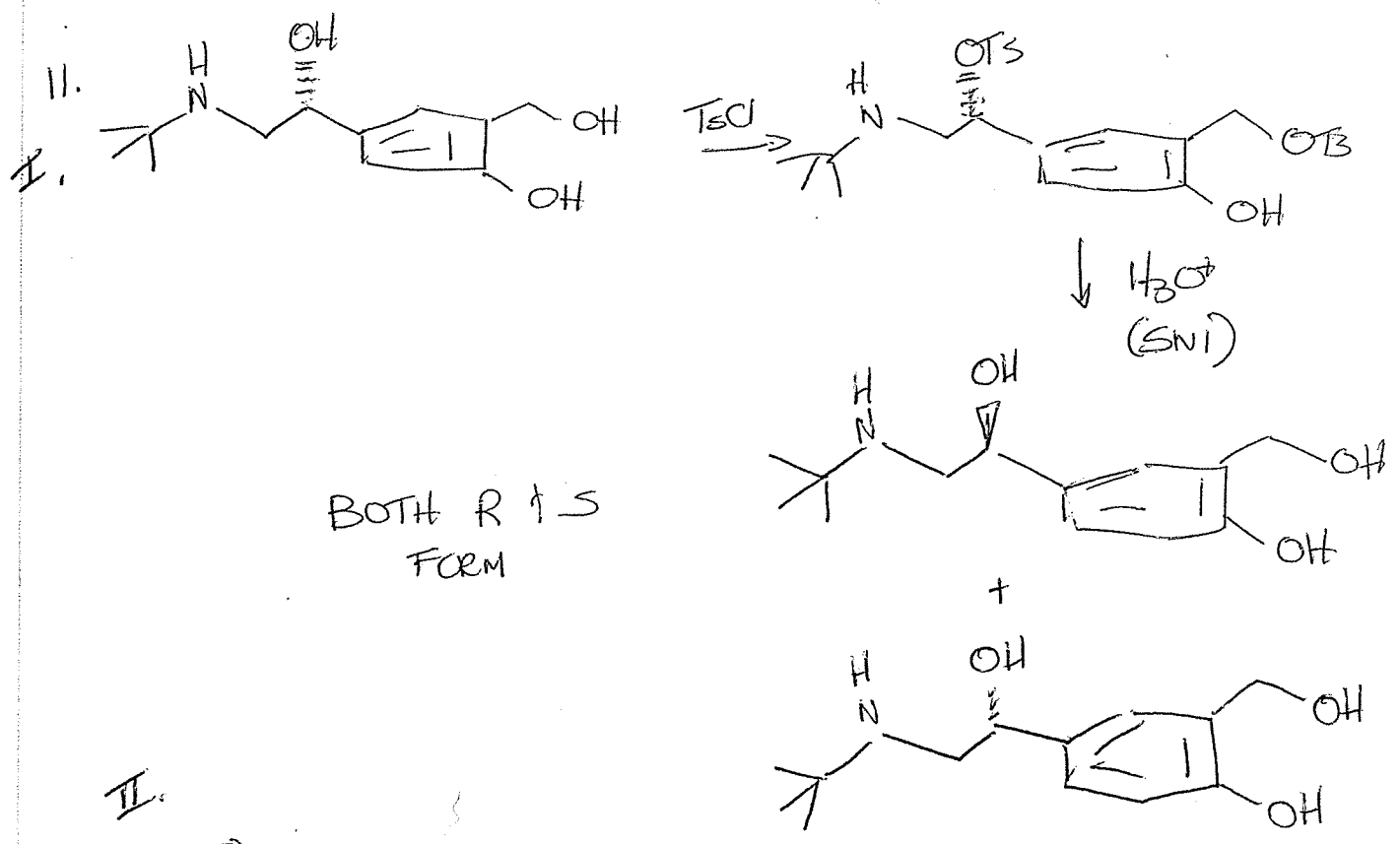
RING E



- $E = 1, II, III$
- ✓ CYCLIC
 - ✓ PLANAR
 - ✓ CONST TP



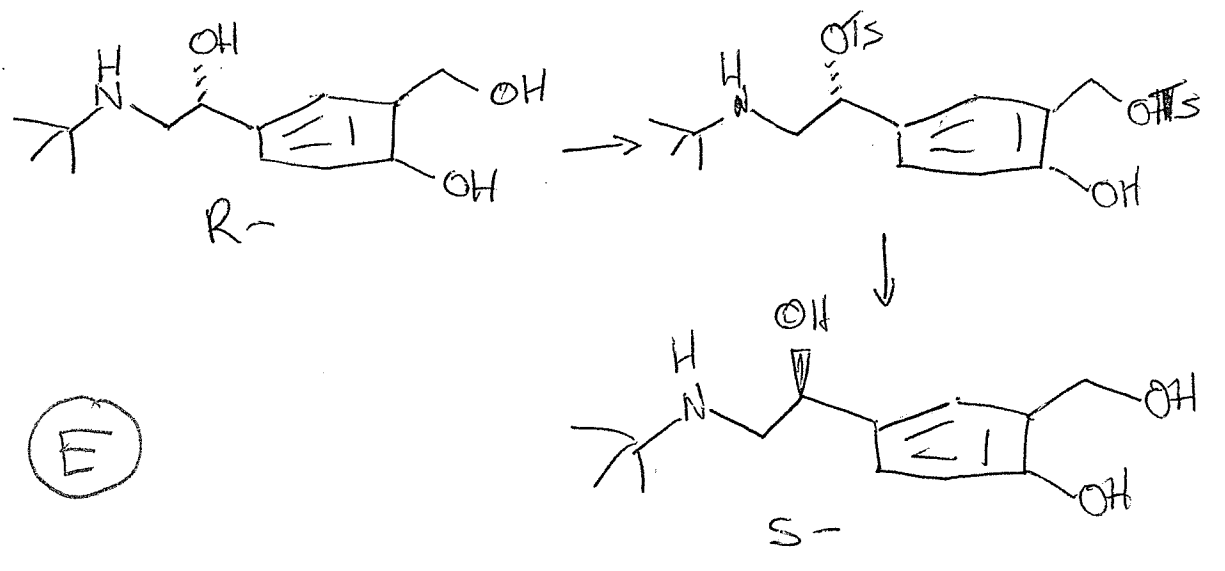
- ✗ $4n+2=8$
- $n \neq \text{integer}$



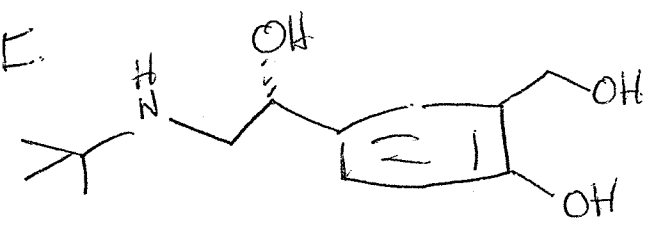
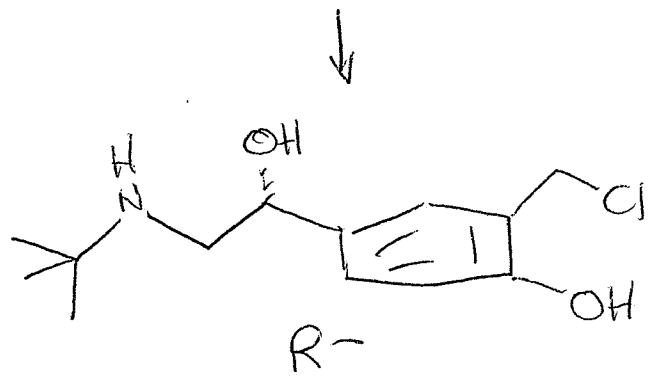
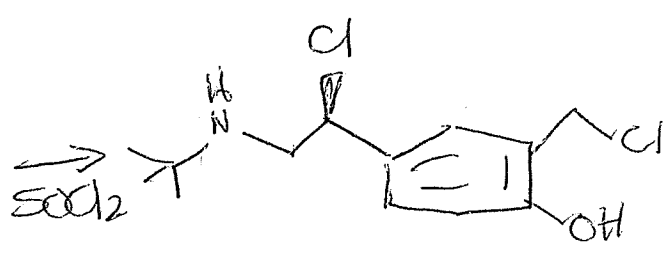
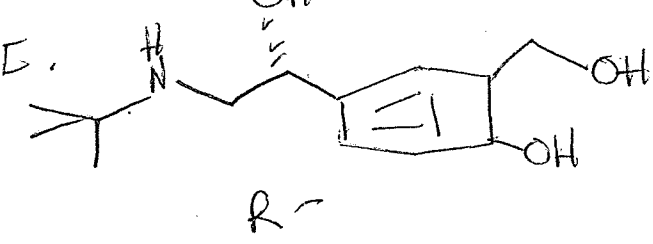
II.

$\ominus \text{OH}$ from NaOH will NOT react directly w/ 1° and 2° alcohol of albuterol since these hydroxyl groups are NOT activated.

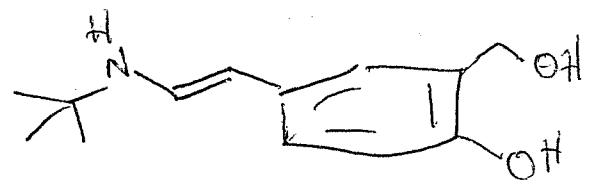
III.



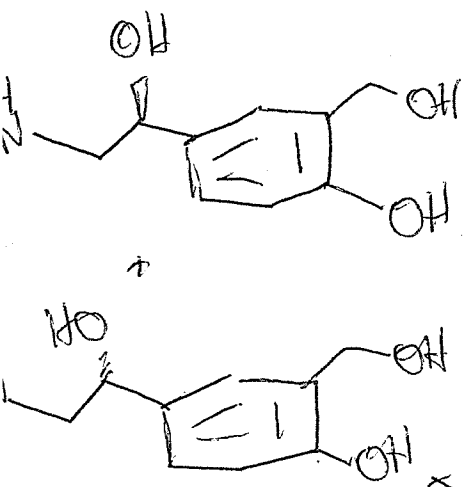
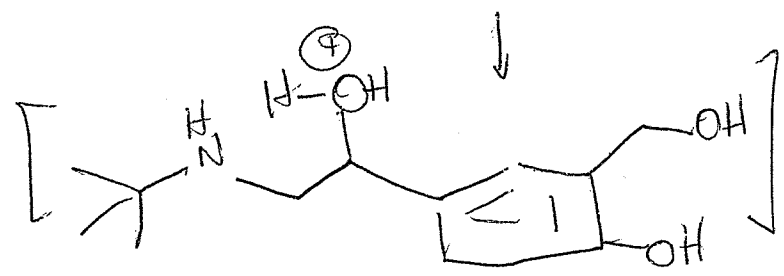
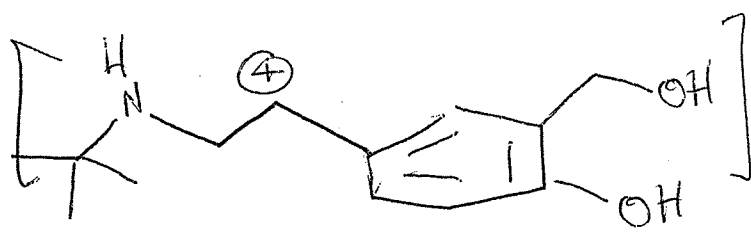
(CONT'D)



$\xrightarrow[\text{PYR}]{POCl_3}$



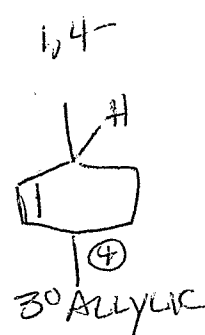
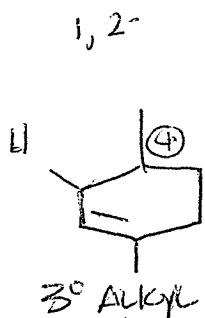
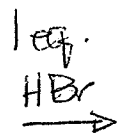
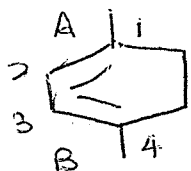
$\downarrow H_3O^+$



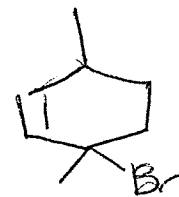
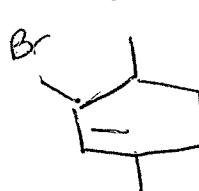
BOTH R+S FORM

12.

I,



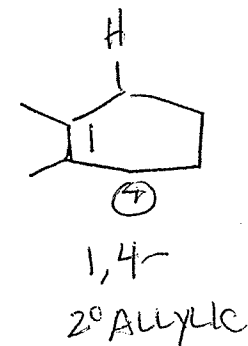
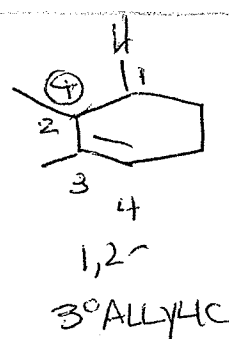
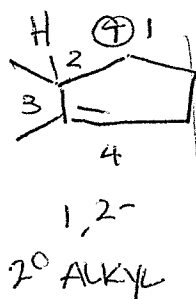
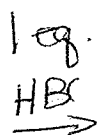
A & B give same products



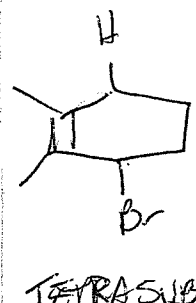
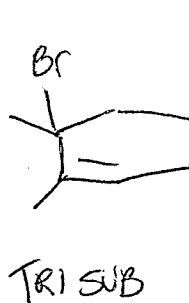
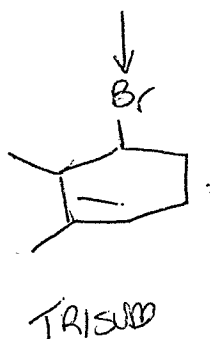
TRI SUBSTITUTED ALKENES
(MAJOR THERMO)
FROM 1,2-

DISUB
(MAJOR KINETIC)
FROM 1,4

II,



(C)

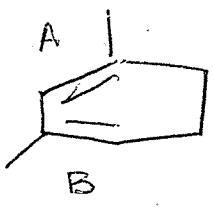


(MAJOR KINETIC)
FROM 1,2-

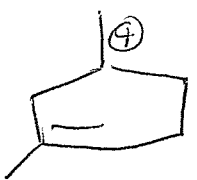
(MAJOR THERMO)
FROM 1,4

12. (CONT'D)

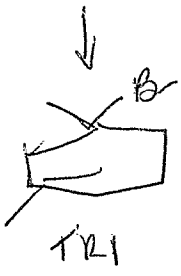
III.



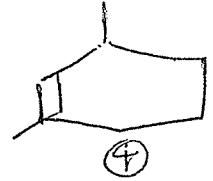
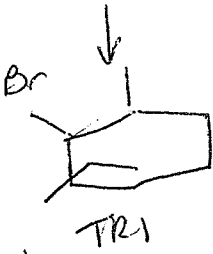
A



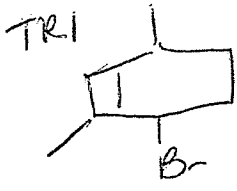
1,2-
3° ALKYL



1,2-
2° ALLYLIC

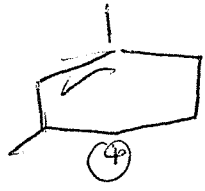


1,4-
2° ALLYLIC

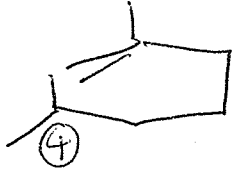
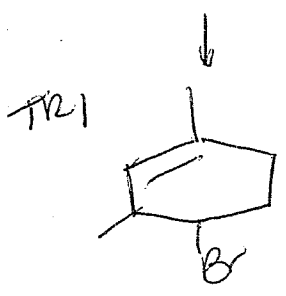


ALL FIVE
PRODUCTS
ARE THERMO
SAME STABILITY
FROM BOTH 1,2-
and 1,4-

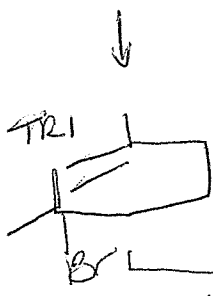
B.



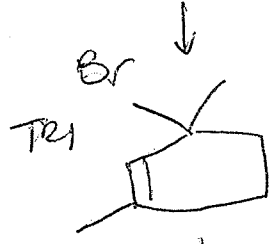
2° ALKYL
1,2-



3° ALLYLIC
1,2-



3° ALLYLIC
1,4-



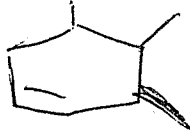
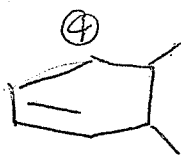
SAME
COMPOUNDS
← from BOTH 1,2-
and 1,4-
MAJOR KINETIC

12. (cont'd)



2° ALKYL

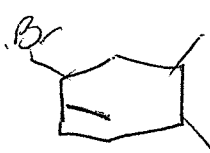
1,2-



D1

2° ALLYLIC

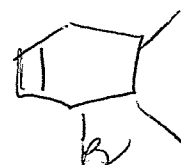
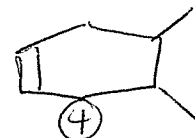
1,2-



D1

2° ALLYLIC

1,4-



D1

BOTH 1,2- and 1,4-

KINETIC PRODUCTS

ALL THREE ARE THERMO-
FROM BOTH 1,2- and 1,4-

13.



CONJ ACID



BASE

$$K_a = \frac{[B]}{[CA]}$$

$\uparrow \ominus \uparrow pK_a$

- ↑ \ominus ON RING
- ↑ STABILITY CA
- ↑ [CA], ↓ K_a , ↑ pK_a

$pK_a + pK_b = 14$

↑ pK_a , ↓ pK_b STRONGER BASE

- I. NO SUBSTITUENT 0.00
- II. σ_p ETHOXY: -0.24
- III. σ_m ETHOXY: +0.10

II. σ_m ACETYL +0.38

I. σ_p ACETYL +0.50

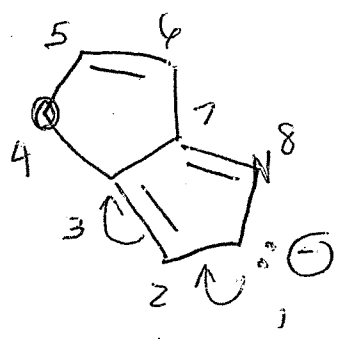
Met \ominus has HIGHEST pK_a
II > I > III > IV > V

~~XXXXXXXXXX~~

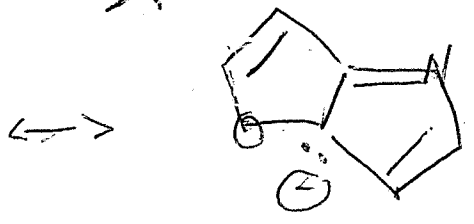
E = II D = I C = III B = IV A = V

(A)

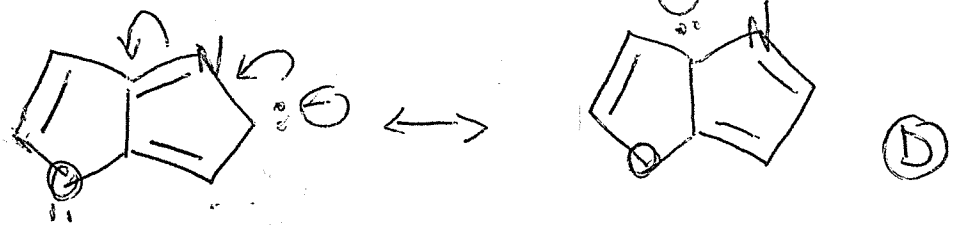
4.



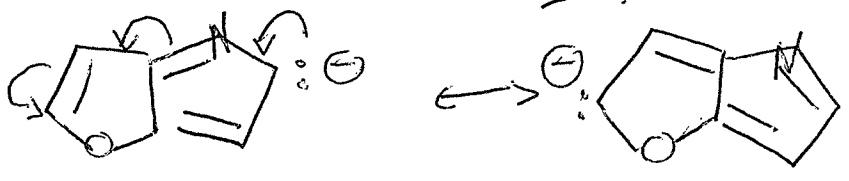
I.



IV



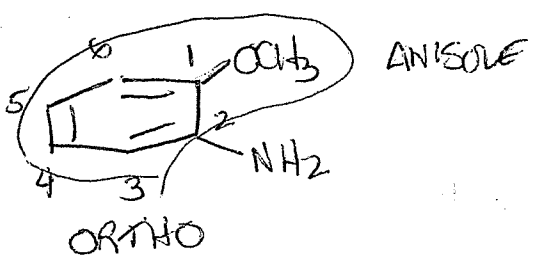
III



π NOT POSSIBLE

15.

a)



2-AMINO ANISOLE
σ-AMINO ANISOLE

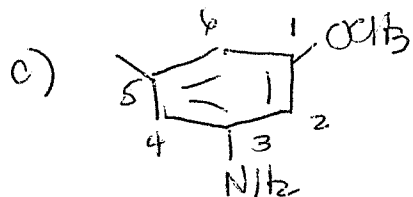
b)



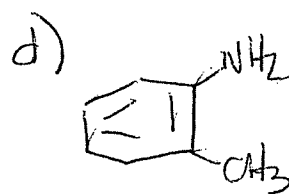
m-AMINOTOLUENE
or
m-METHYLANILINE

15. (cont'd)

(E)



3-AMINO-5-METHYL ANISOLE



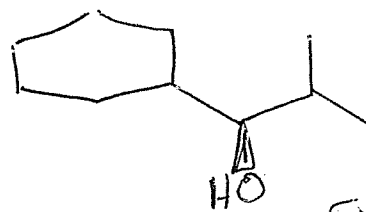
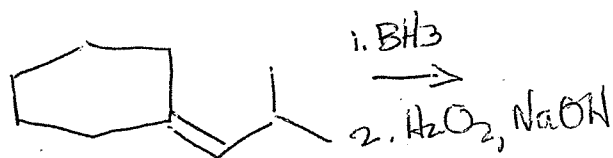
o-amino toluene



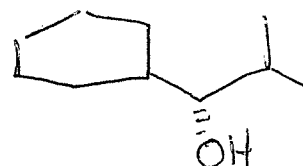
m-AMINO ANISOLE

16.

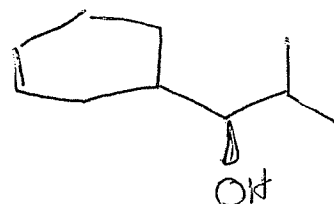
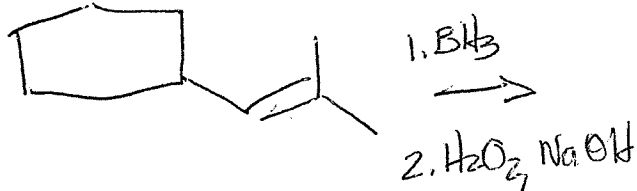
I.



ENANTIOMERS

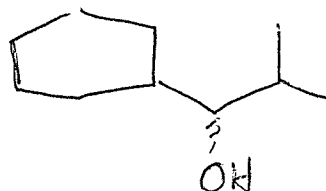


II.



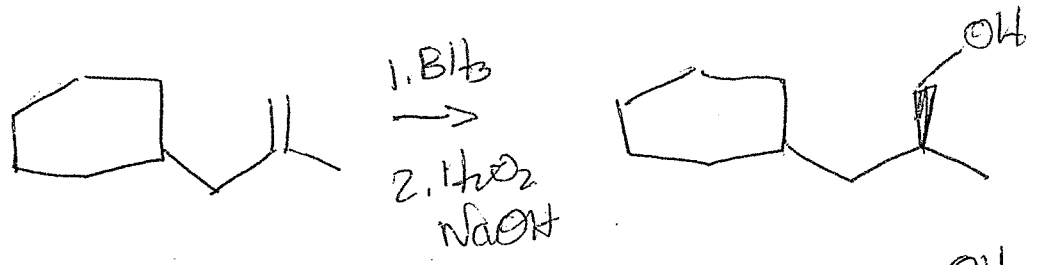
+

ENANTIOMERS

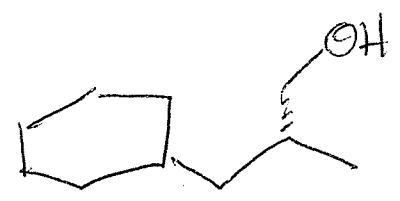


(CONT'D)

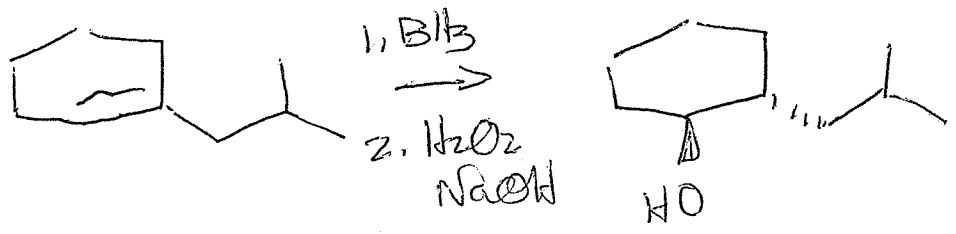
III.



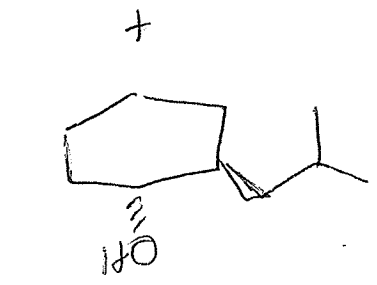
EWANTOMERS



IV.



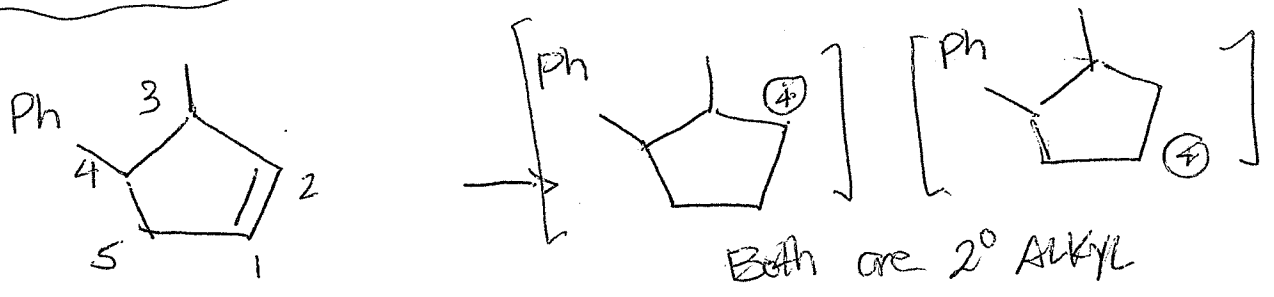
EWANTOMERS



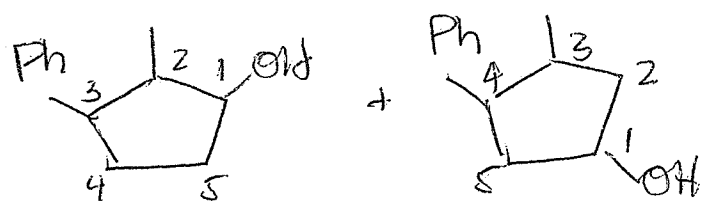
(A)

17.

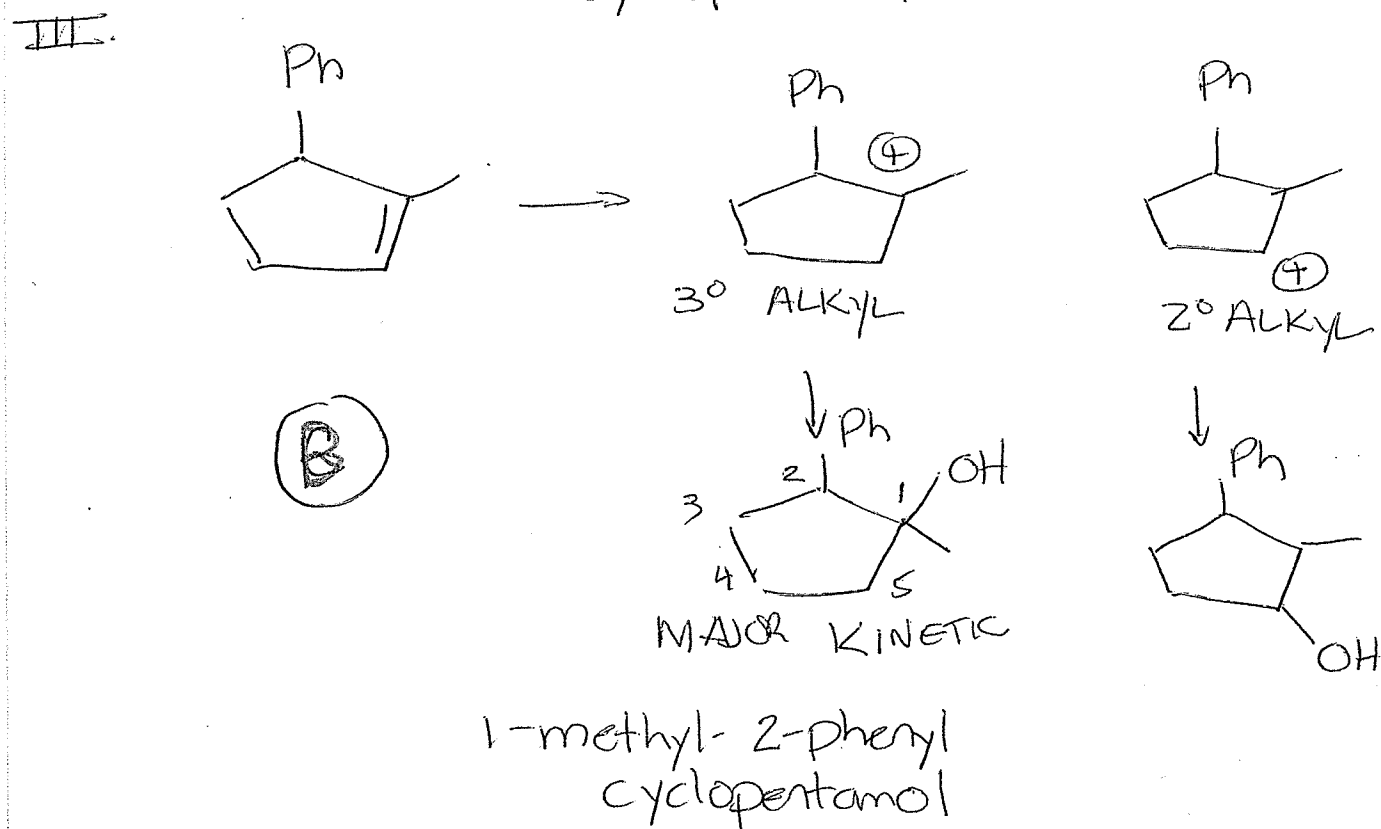
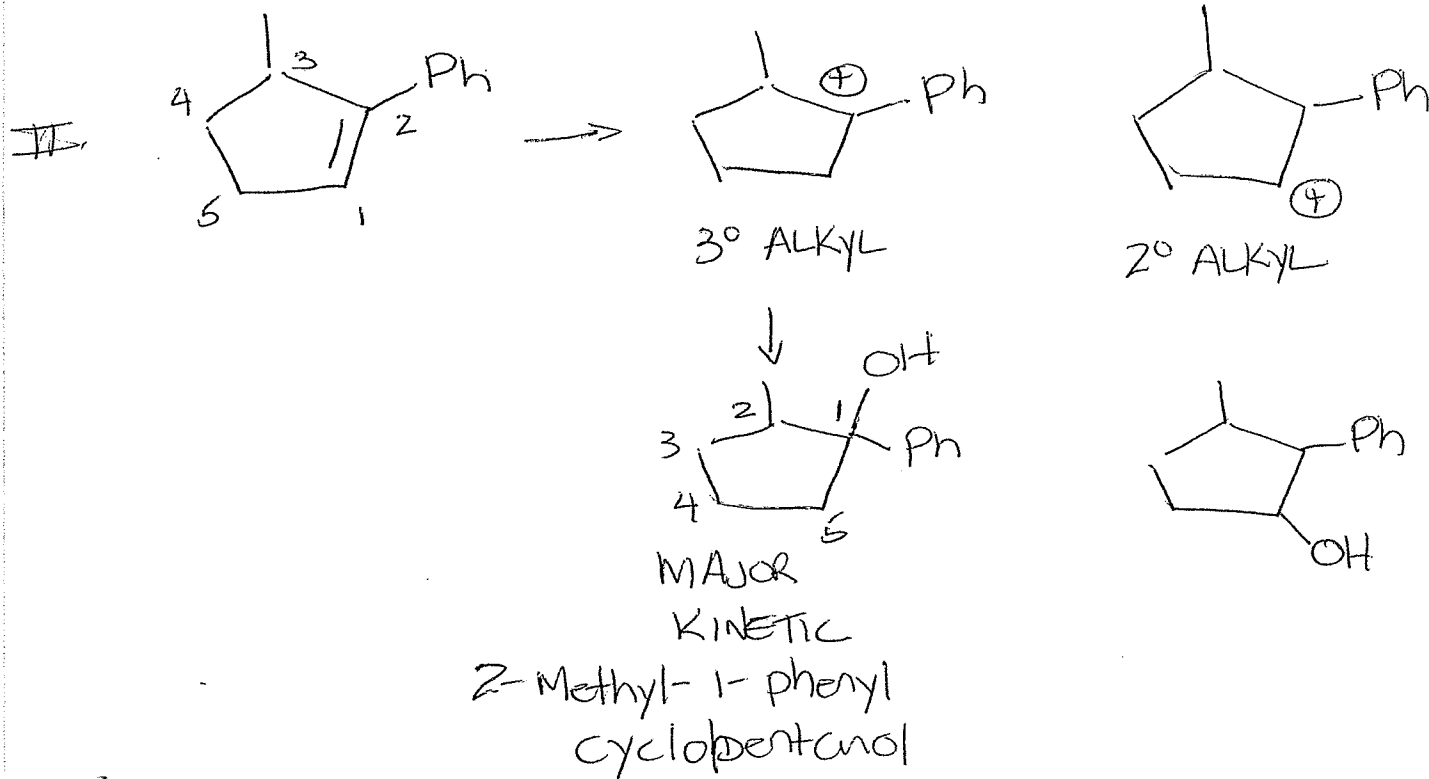
I.



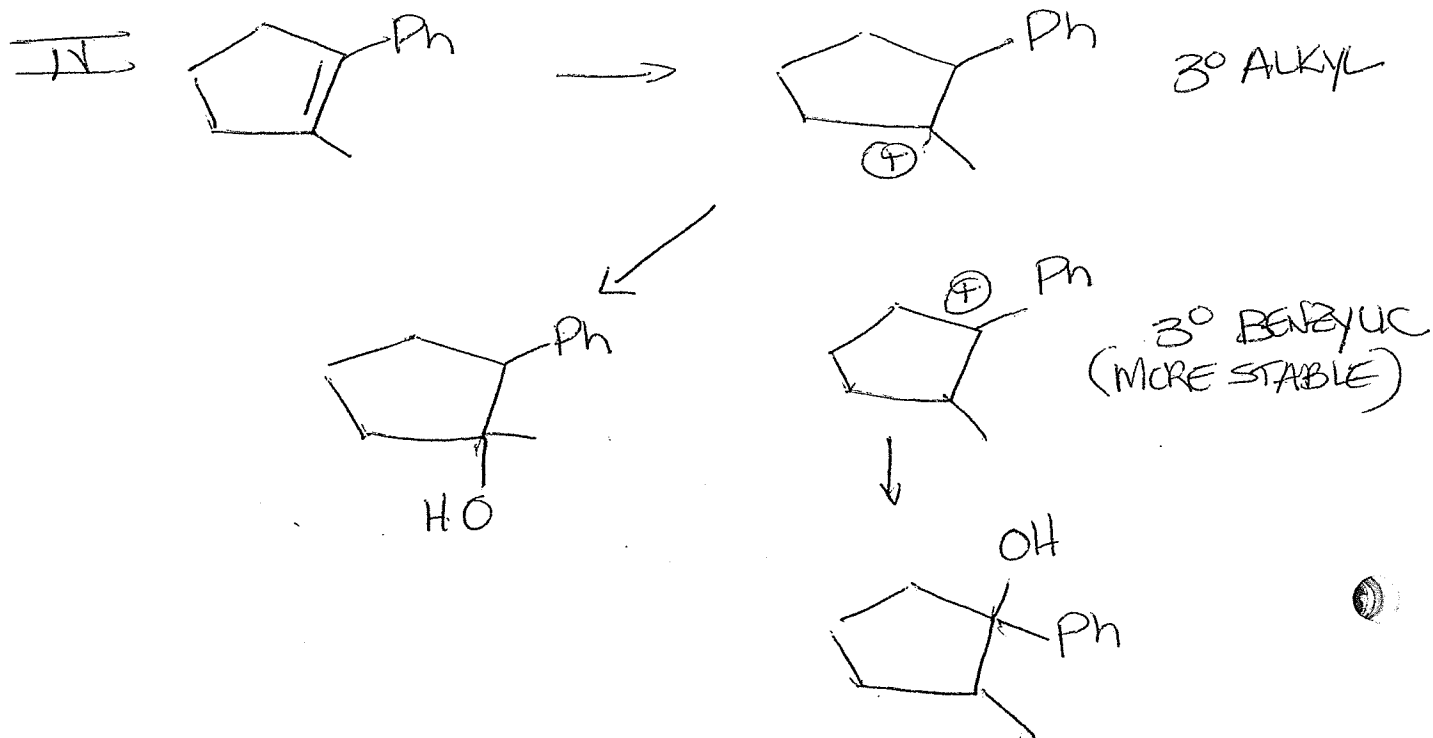
Both are 2° ALKYL



17. (CONT'D)

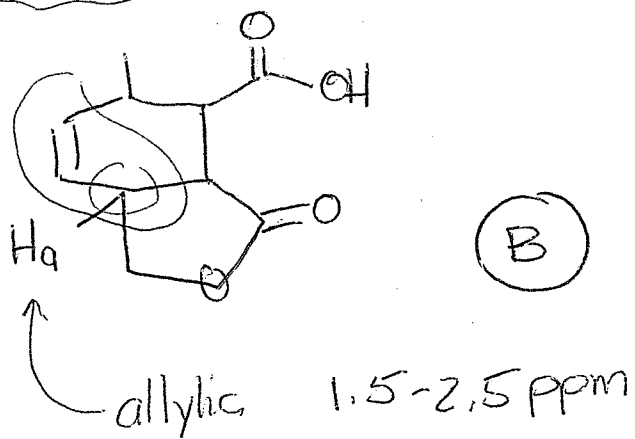


17. (CONT'D)



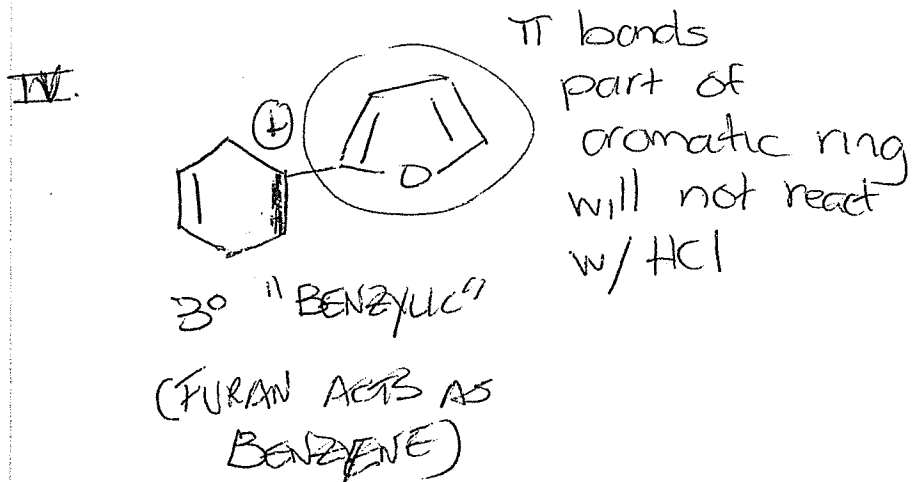
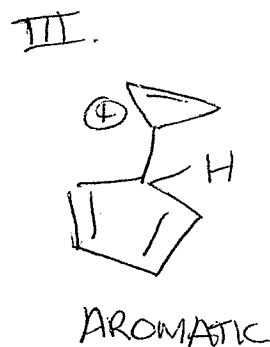
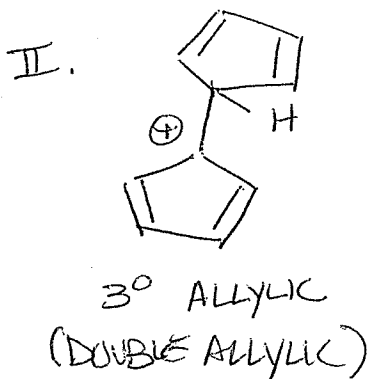
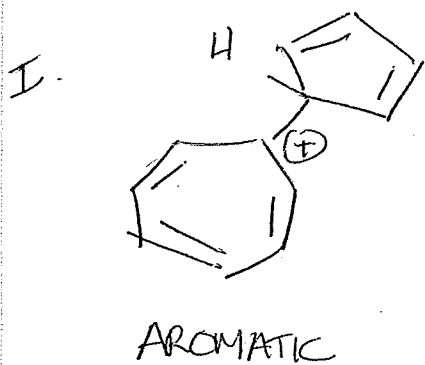
2-methyl-1-phenyl
cyclopentanol
MAJOR KINETIC

19.



18. Starting material that generates the most stable c^{\oplus} reacts FASTEST.

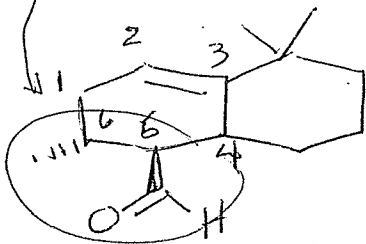
MOST STABLE AROMATIC > 3° > 2° > 1°
ALLYLIC > ALKYL



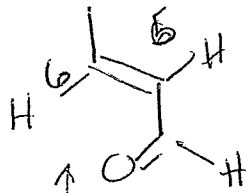
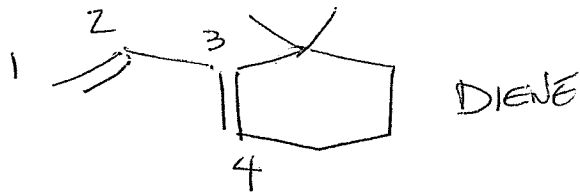
This stereochemistry is derived from the chiralophile.

Trans stereochemistry

20.



2,3 π bond
in product
is 2,3 bond
in DIENE
starting material



DIENOPHILE

TRANS (E)
stereochemistry

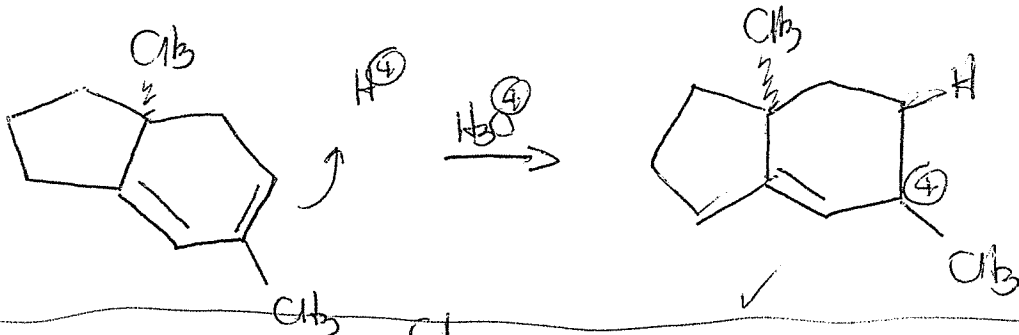
III

NO CORRECT
ANSWER PROVIDED

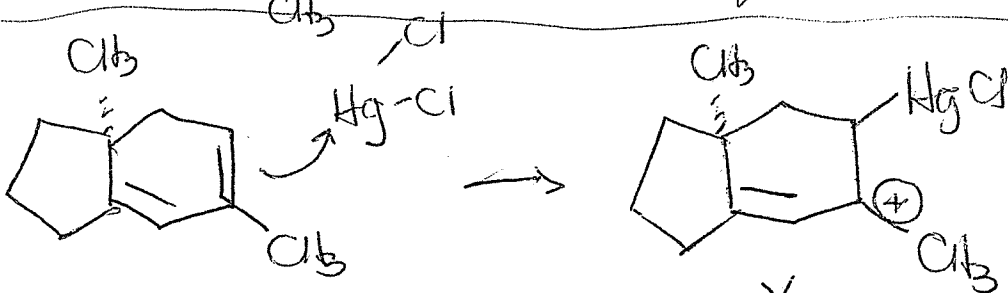
CREDIT FOR ALL

21.

I.



II

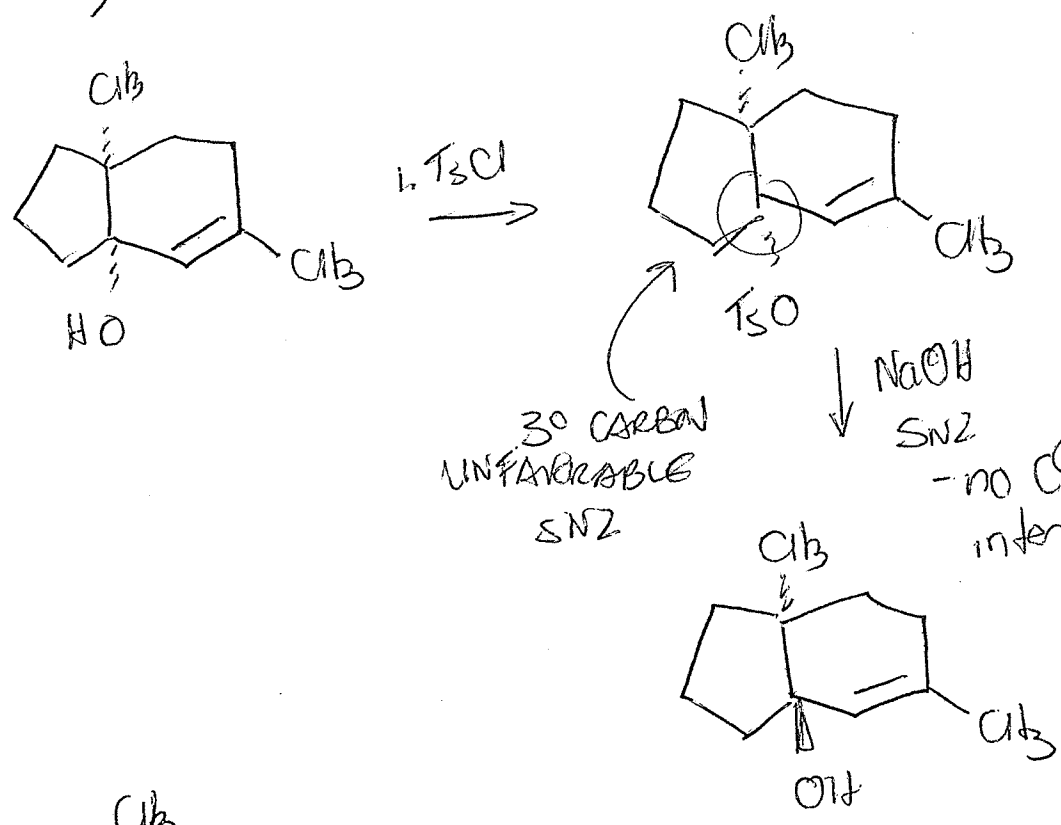


NOT same as

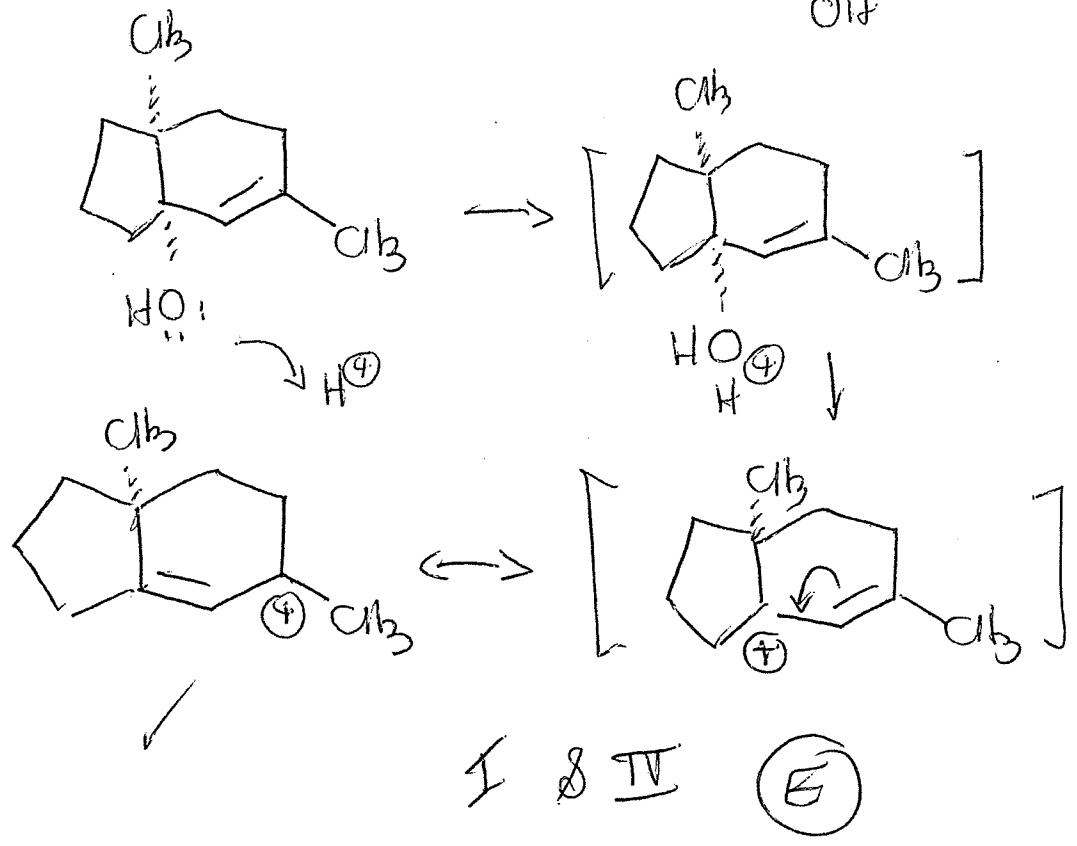
shown

21. (CONT'D)

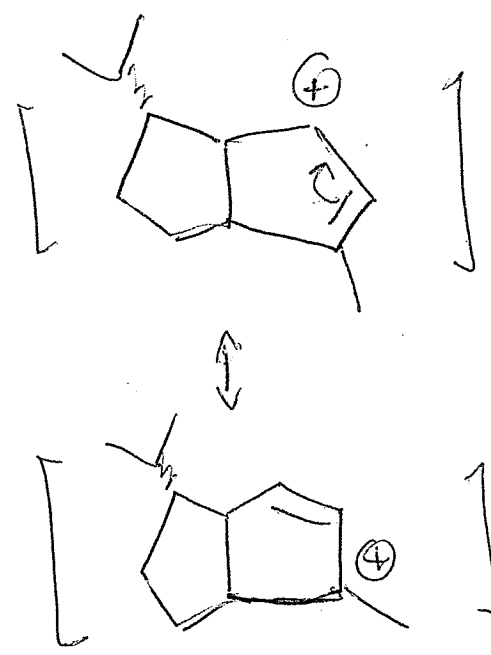
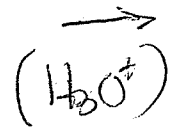
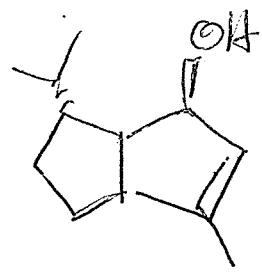
III



IV



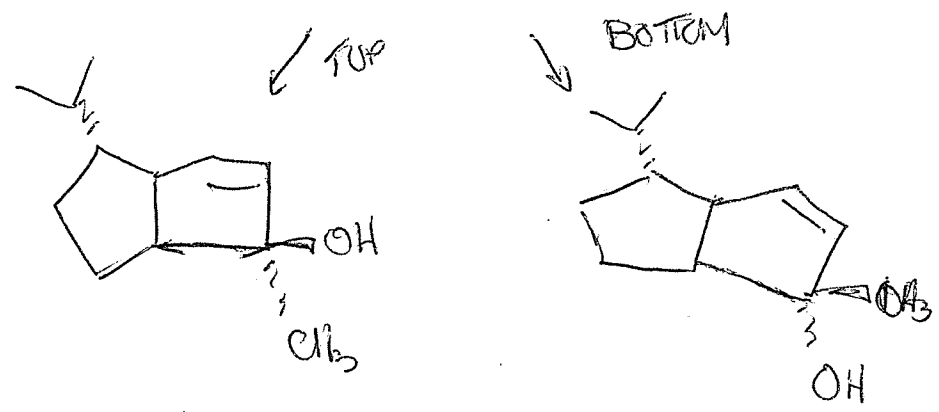
2.



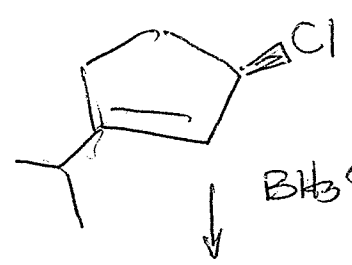
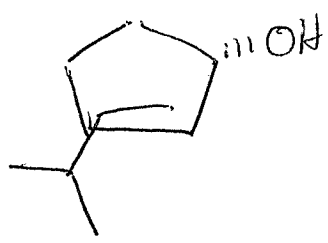
Must form \oplus to get to product shown

MUST BE SN1

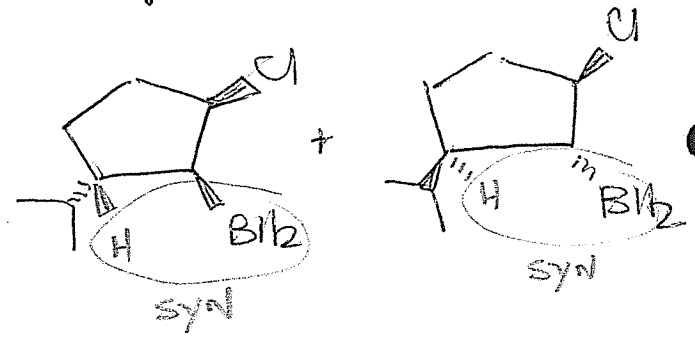
(A)



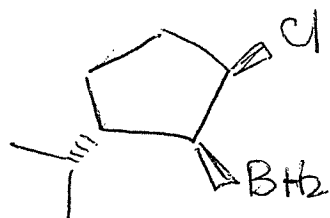
23.



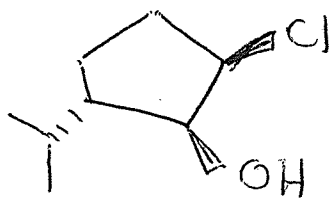
Adds to least sub carbon of alkene from top + bottom



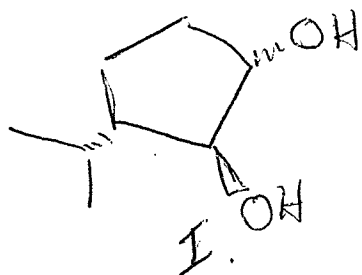
23. (CONT'D)



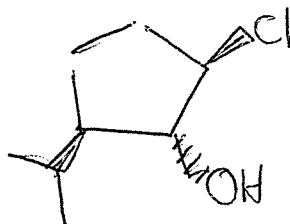
↓ H₂O₂, NaOH



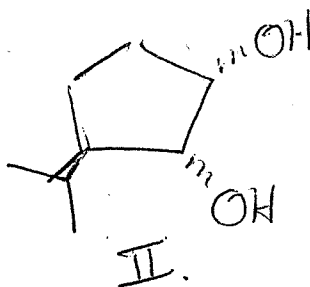
↓ NaOH (S_N2)



↓ H₂O₂, NaOH



↓ NaOH (S_N2)



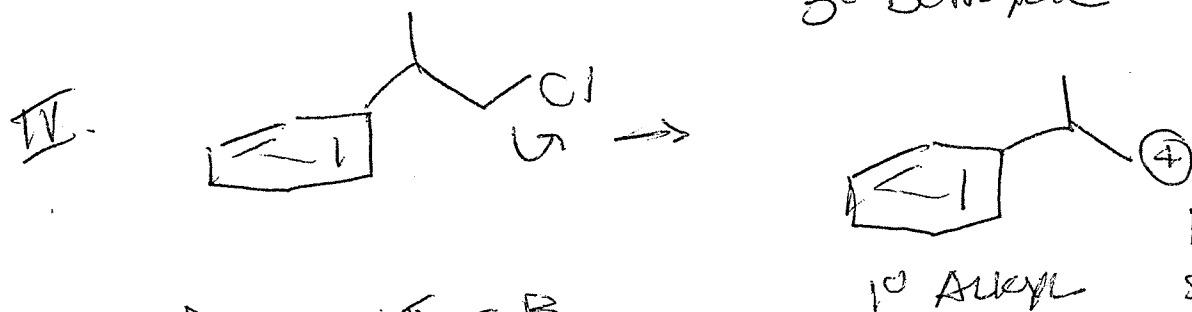
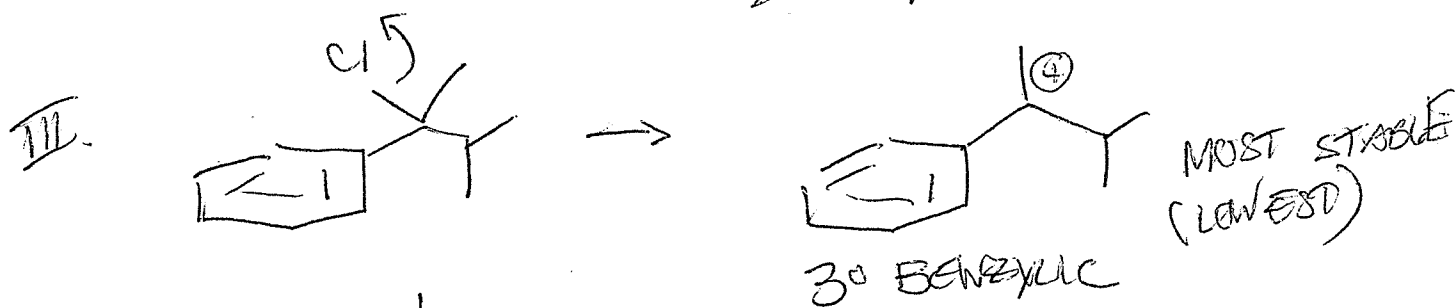
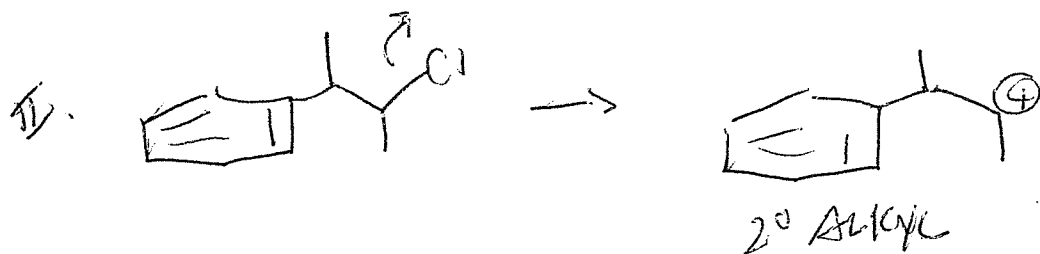
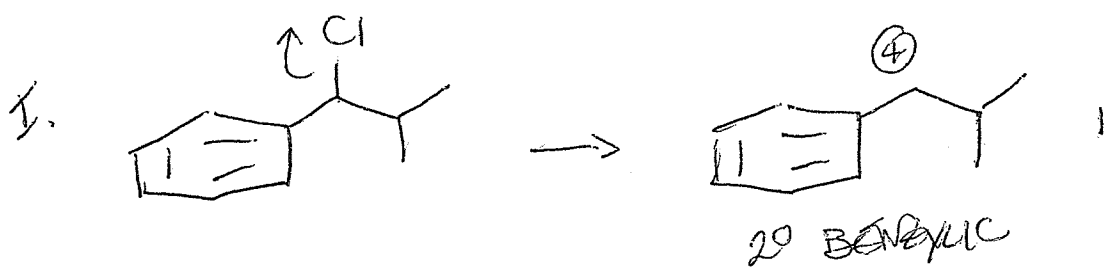
OH substitutes
Br with
retention of
stereochemistry.

NaOH only
substitutes
Cl not
OH

(A)

All of the starting materials are alkyl halides and react with H_3O^+ via an S_N1 reaction

The lowest energy pathway in the reaction energy diagram corresponds to the starting material that gives rise to the most stable carbocation



III = D

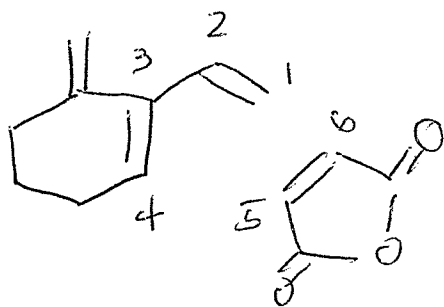
II = B

I = C

IV = A

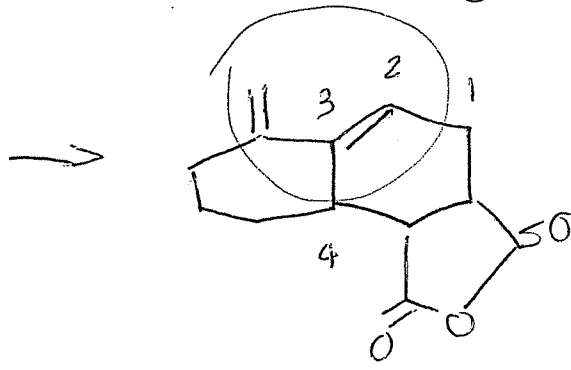
(B)

25.



The CONJUGATED diene labeled reacts w/ the 1st equivalent of maleic anhydride

CONJUGATED DIENE 29-



This initial Diels-Alder product can react again with the maleic anhydride Dieneophile

