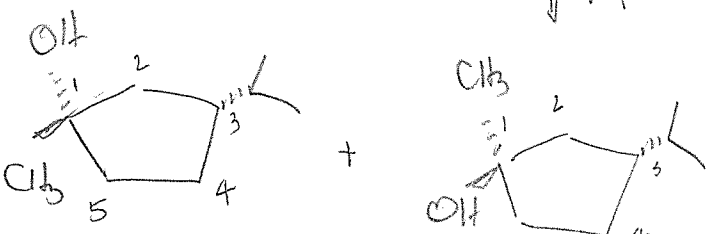
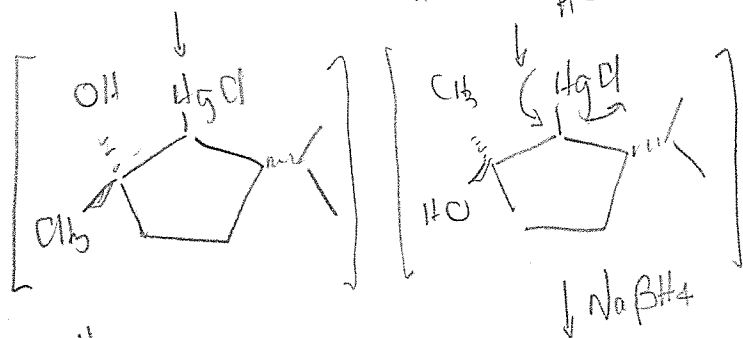
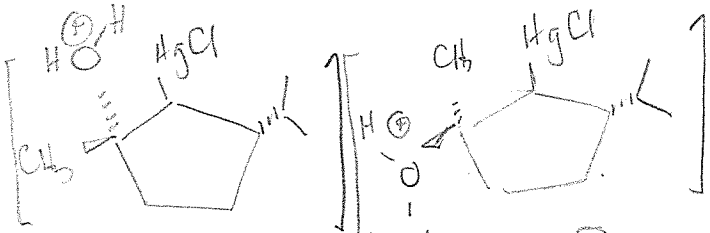


BOTTOM

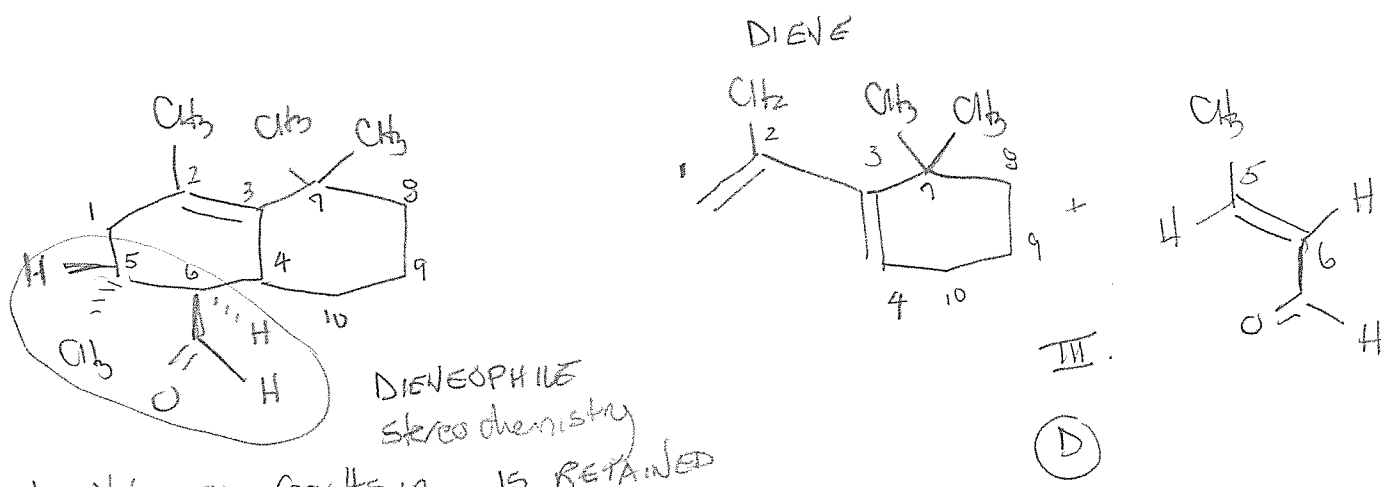
TOP



II TWO MAJOR
 PRODUCTS

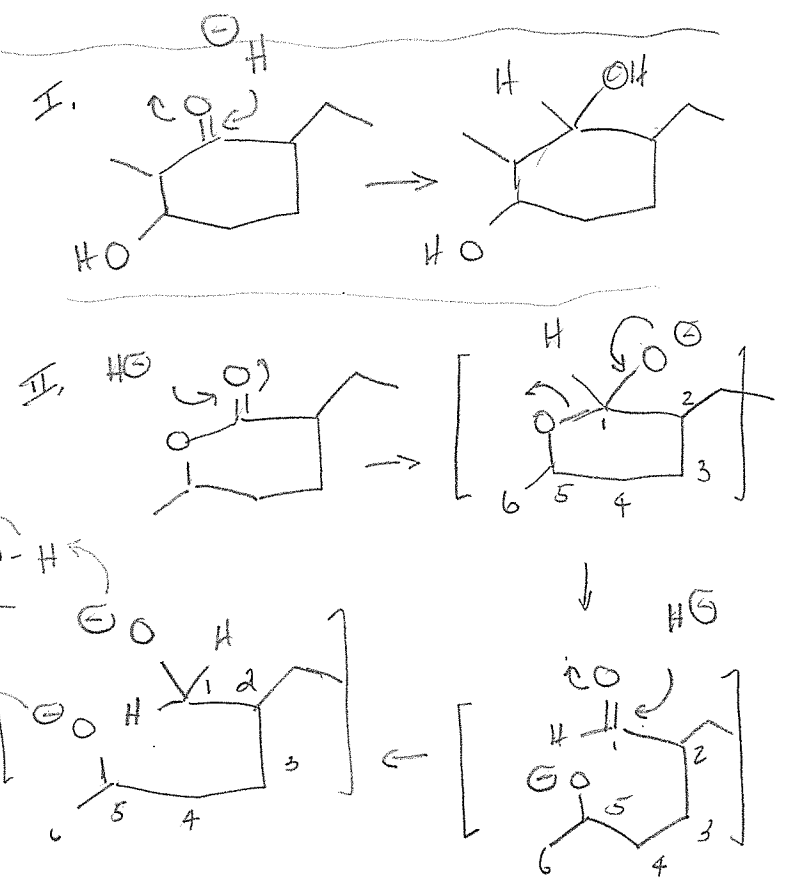
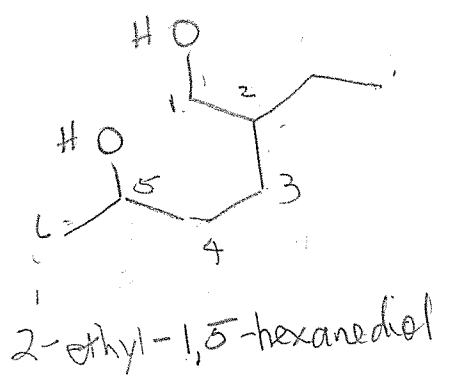
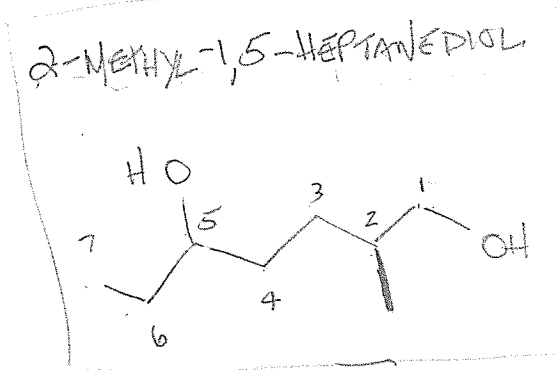
(C)

2.



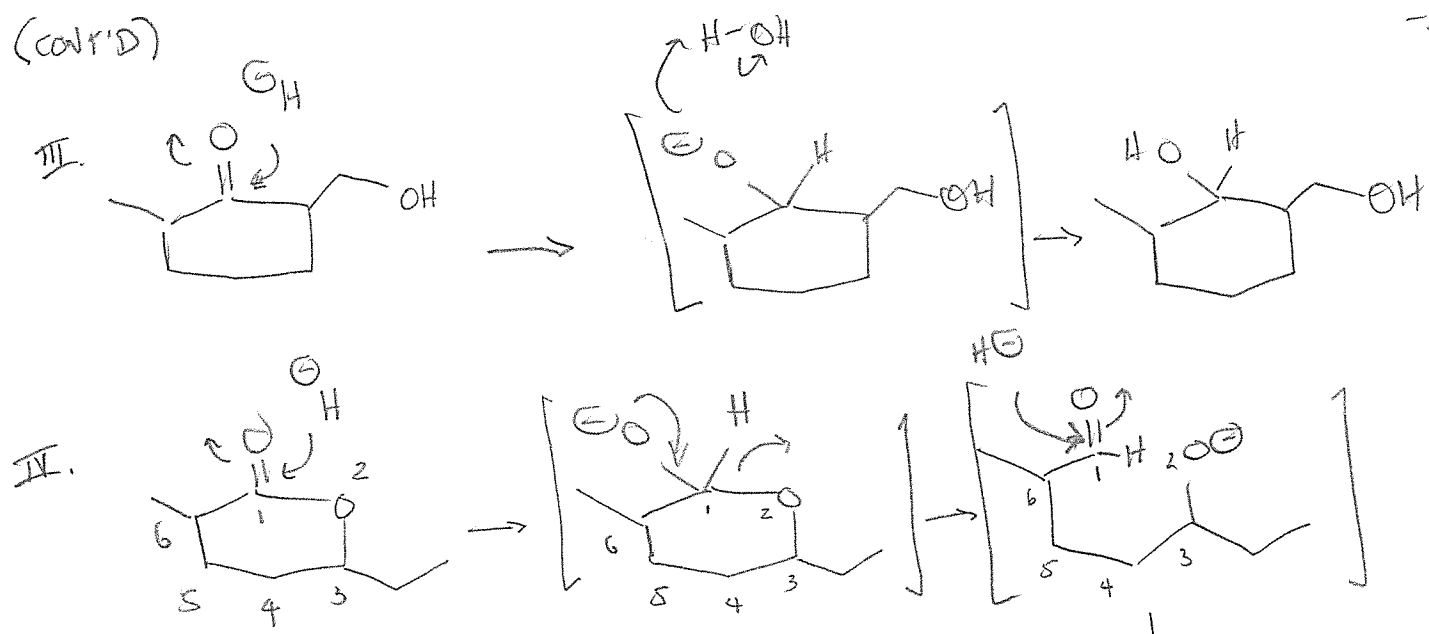
Diels-Alder rxn results in cyclohexene product w/ alkene derived from "C₂-C₃" carbons (σ bond) of starting diene. IS RETAINED in the reaction. CH₃ of C₅ and C-H of C₆ must be TRANS (E) in starting alkene of DIENOPHILE.

3.

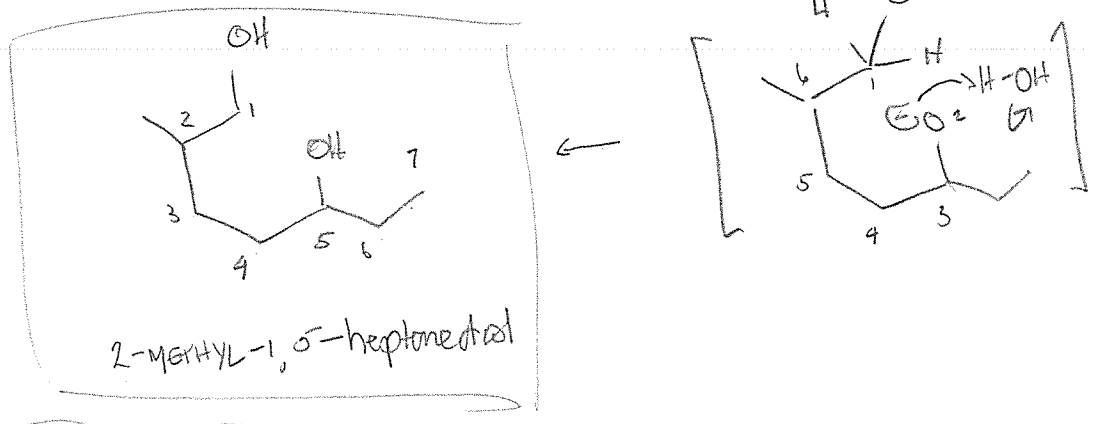


(cont'd)

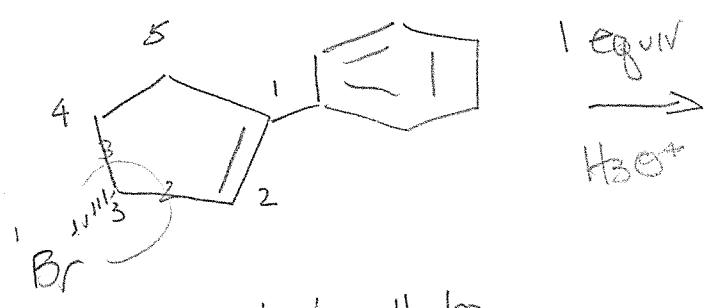
3. (cont'd)



(D)



4. 3R-3-Bromo-1-phenylcyclopentene

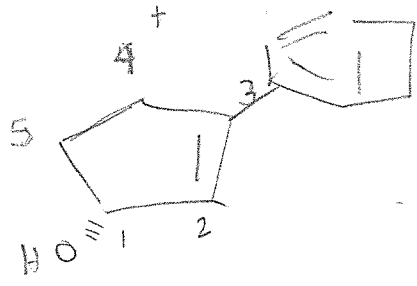
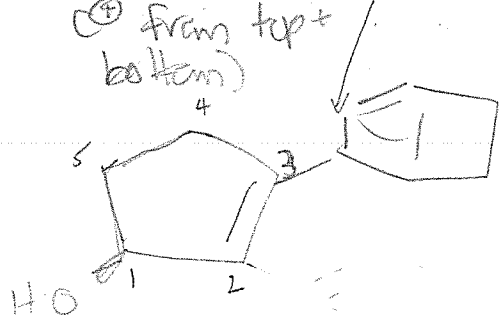
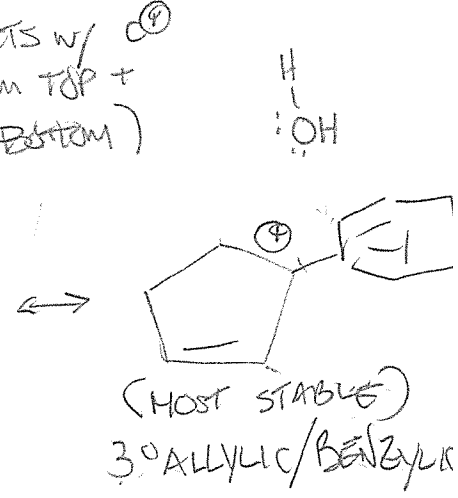
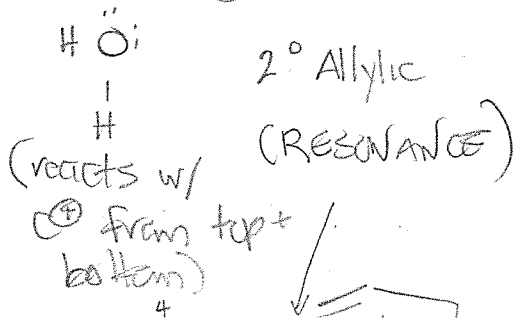
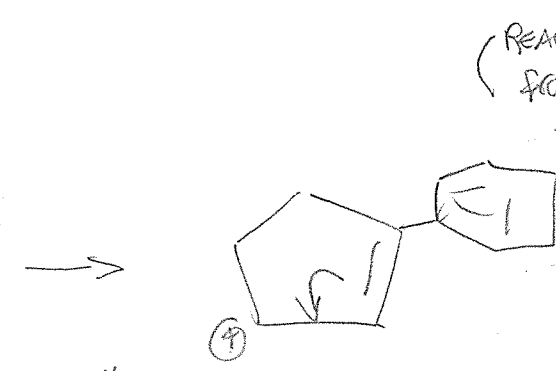
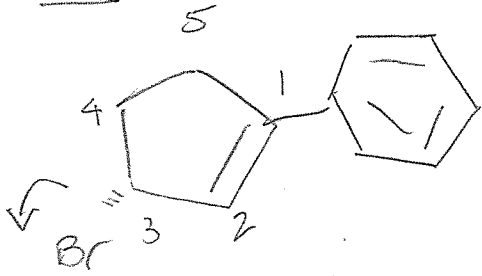


H_3O^+ can react w/
at C_3 via S_N1
or via an electrophilic
addition with the
alkene at C_1-C_2

Kinetic product will be
derived from MOST STABLE
(fastest forming) carbocation

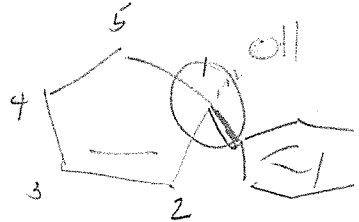
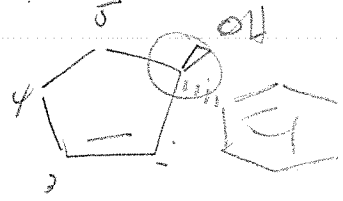
4. (CONT'D)

SN1



3-PHENYLCYCLOPENT-2-EN-1-OL

ENANTIOMERS



MAJOR KINETIC PRODUCTS

1-PHENYLCYCLOPENT-2-EN-1-OL

50:50 MIXTURE OF ENANTIOMERS

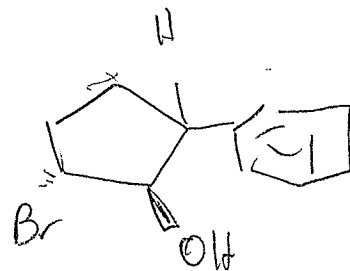
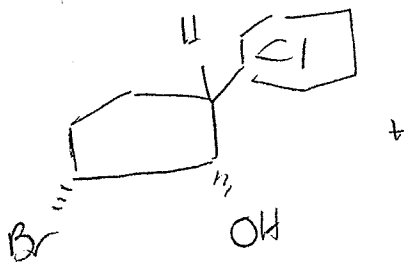
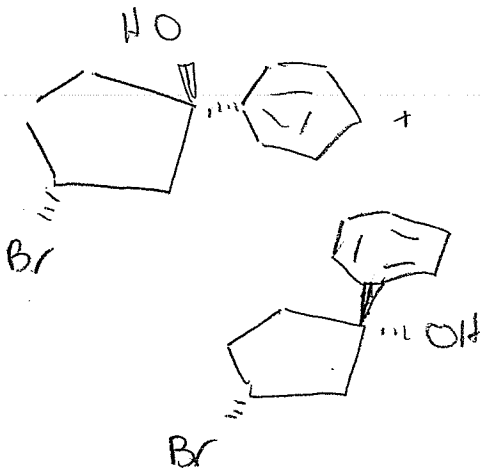
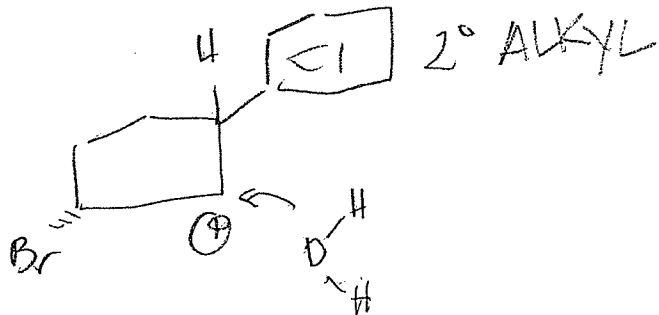
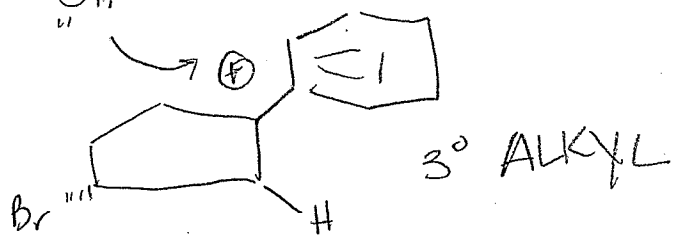
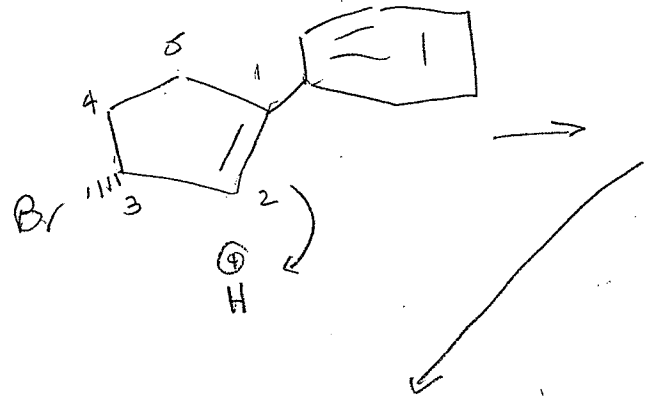
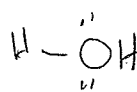
RACEMIC MIXTURE

A

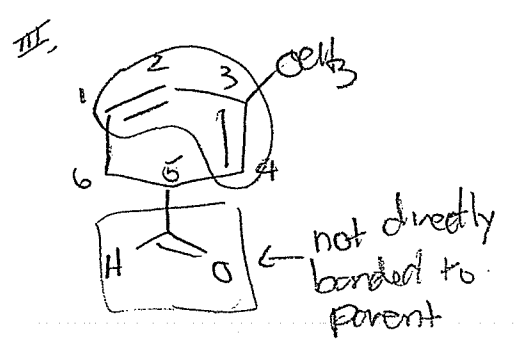
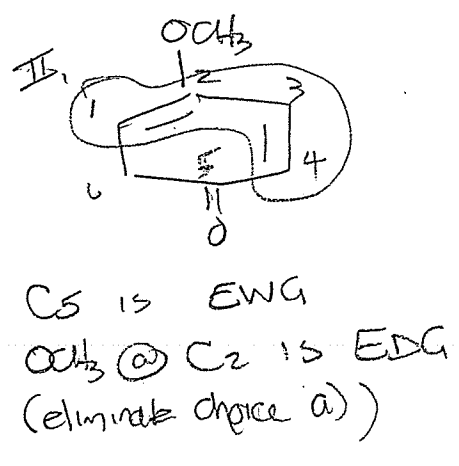
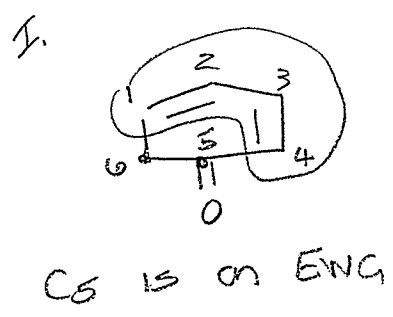
7. (CONT'D)

ELECTROPHILIC ADDITION

(Reacts from TOP + BOTTOM)



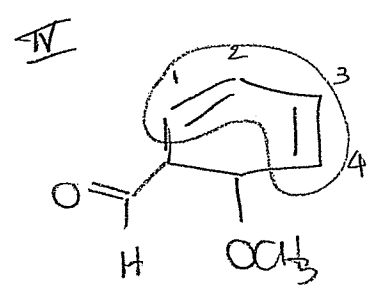
5. The most reactive DIENE in a DIELS-ALDER reaction is the most negative by virtue of one or more electron donating group by resonance. (EDG)
 An EDG is defined as group whose atom directly bonded to the parent (i.e. one of the sp² carbons of the diene) has at least one lone pair.



OCH₃ @ C₃ EDG
 Aldehyde @ C₅ not influencing diene since not directly bonded to parent

II > I

III > II
 (eliminate choice d)

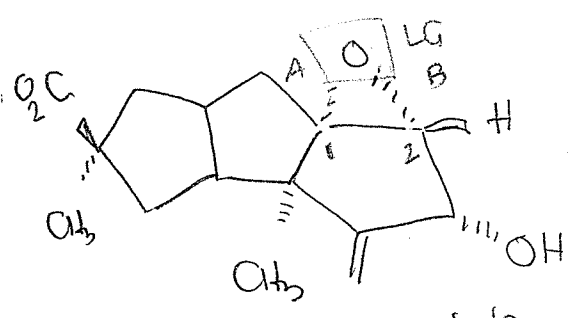


IV > I
 III > IV
 (eliminate choice c) and e)

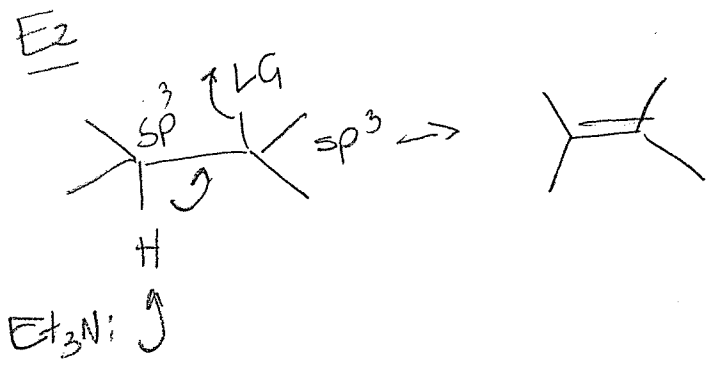
III > IV > II > I
 (B)

Neither OCH₃ or aldehyde affects diene
 More reactive than I, but less reactive than III

b. Et_3N is a base and will react w/ the EPOXIDE of bicyclic acid via an E_2 ring opening reaction -9-

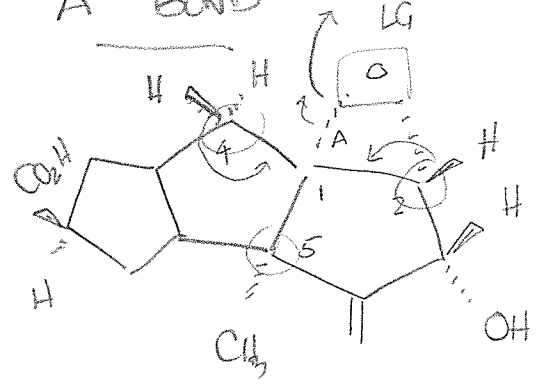


CONSIDER RING OPENING
w/ O as LG and first
A bond breaking (C_1-O)
then separately B bond
breaking (C_2-O)

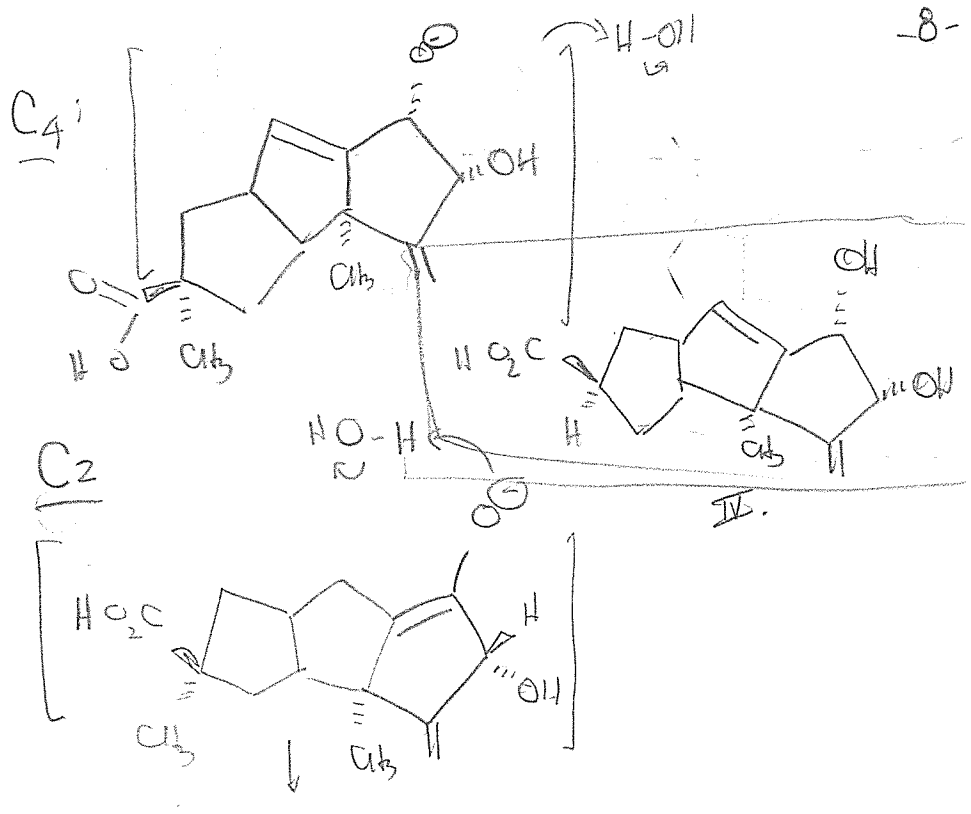


6. (CONT'D)

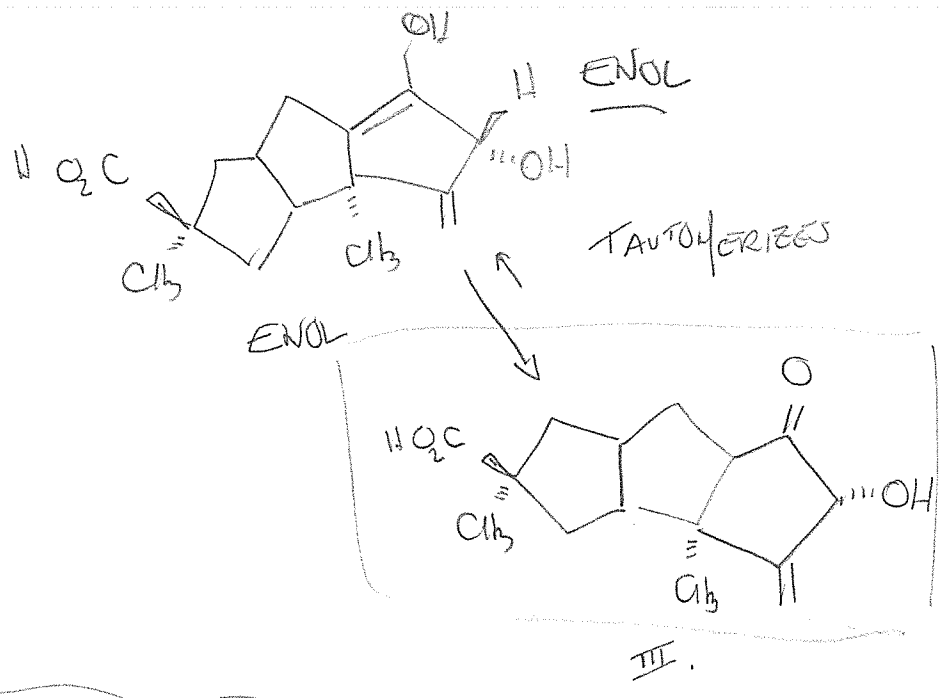
A BOND



When A bond breaks, can lose H from C2 or C4 but NOT C5

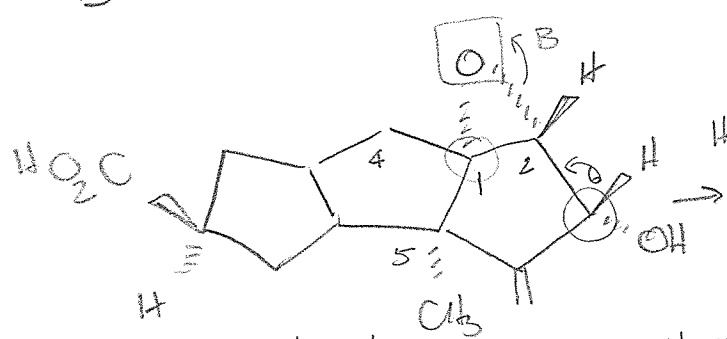


I, II + III all are formed.

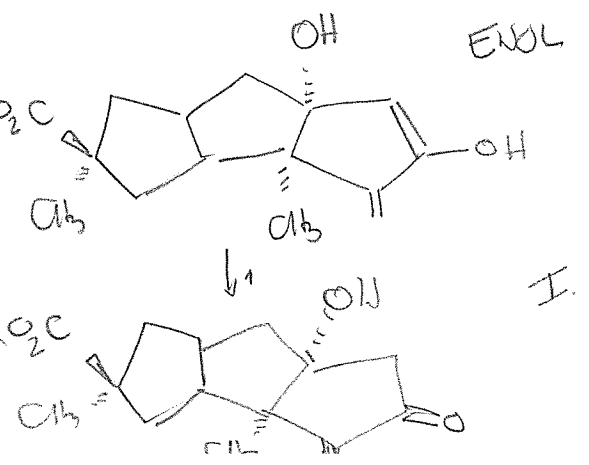


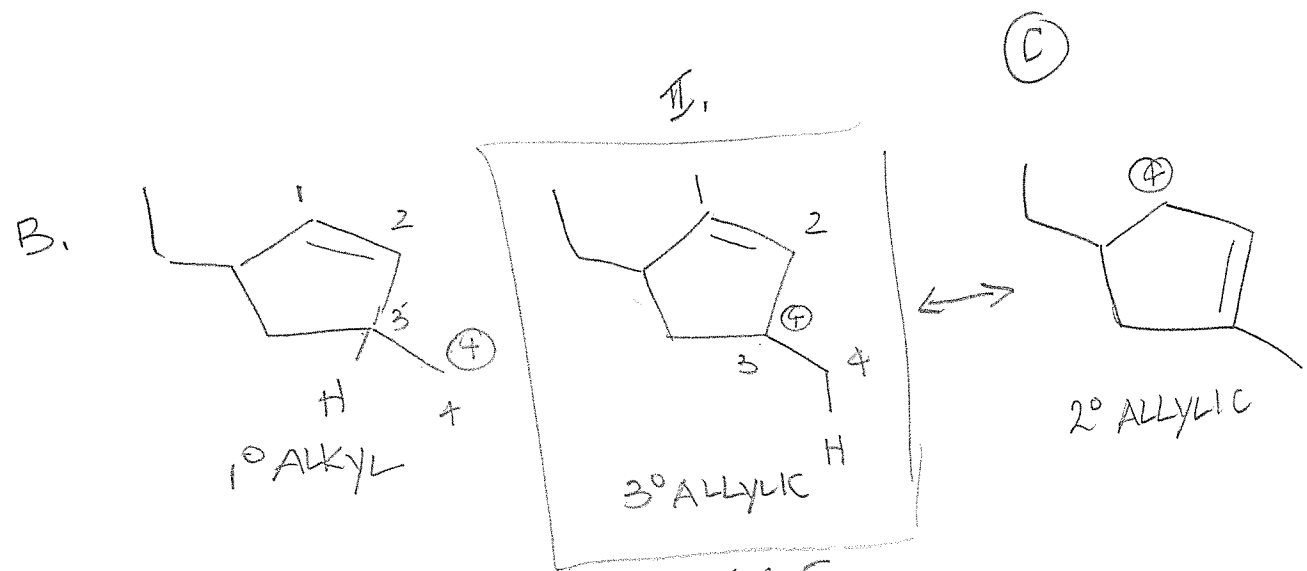
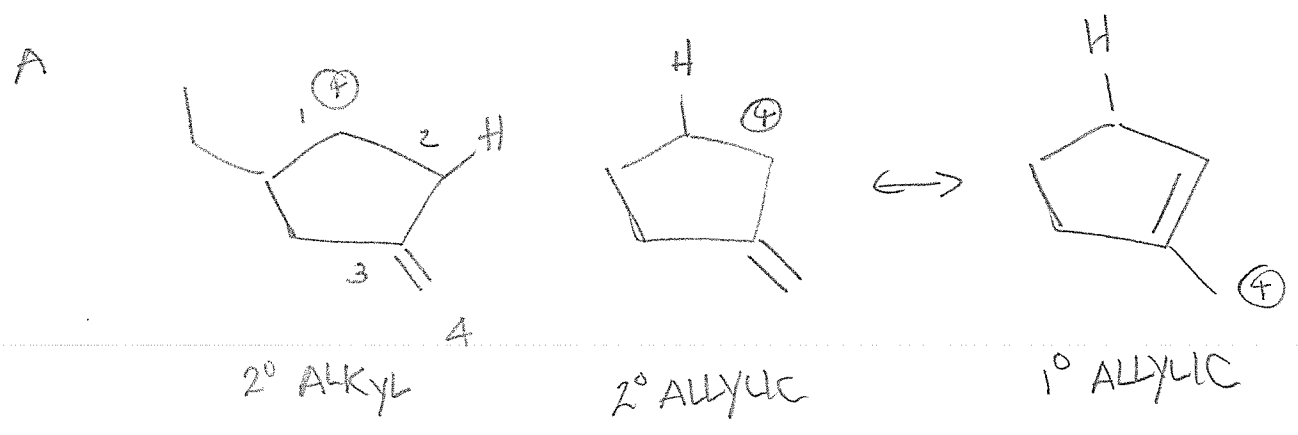
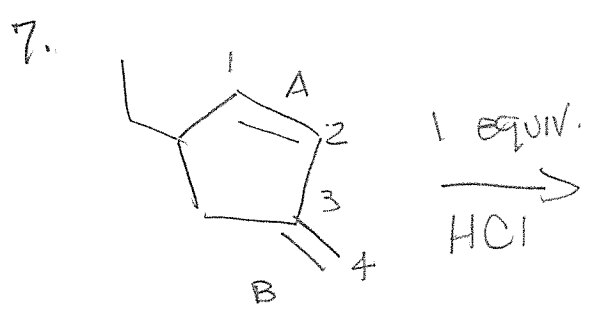
(C)

B BOND



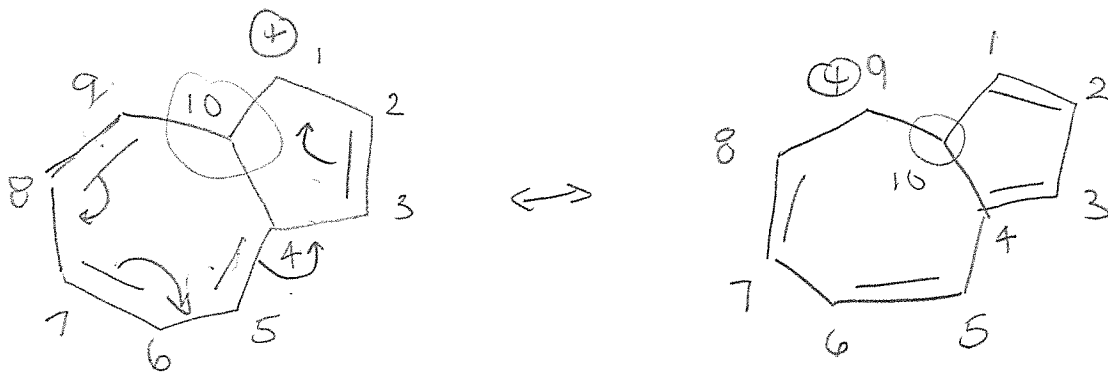
When B bond breaks, only H available is on C6





MOST STABLE
 FORMS FASTEST
 GIVES RISE TO MAJOR
 KINETIC PRODUCT

8.



C_{10} is sp^3 hybridized and is not planar. A resonance form cannot be drawn that allows C_{10} to adopt sp^2 (PLANAR) geometry

πe^- can delocalize through C_{10} so continuous π system through 5-membered ring, 7-membered ring or 10-membered ring cannot be achieved.

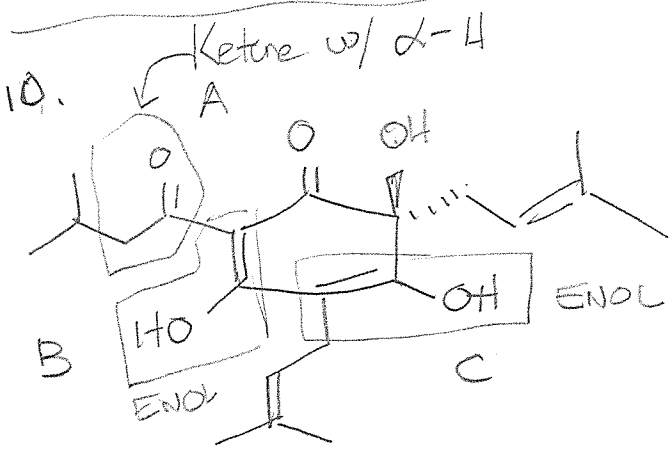
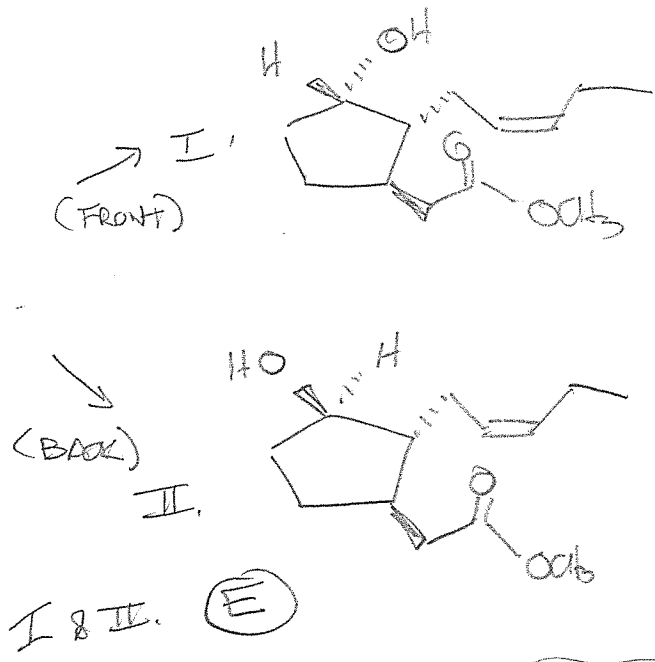
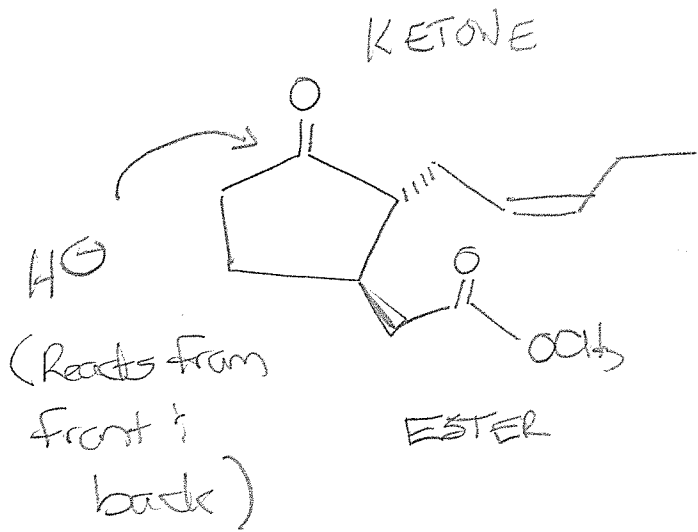
Total # πe^- is 8
 $4n+2=8 \quad n = 1\frac{1}{2}$ NOT AROMATIC

II, III + IV
 (D)

9. $NaBH_4, CH_3OH$ reacts with ketones and aldehydes but NOT esters. Only the ketone of methyl jasmonate reacts w/ $NaBH_4$ to give a 2° alcohol.

The H^- of $NaBH_4$ reacts from front & back of planar sp^2 carbon of the ketone carbonyl to give a mixture of R- and S- configurations at this carbon.

9. (CONT'D)



There are multiple sites/functional groups where humulone can tautomerize.

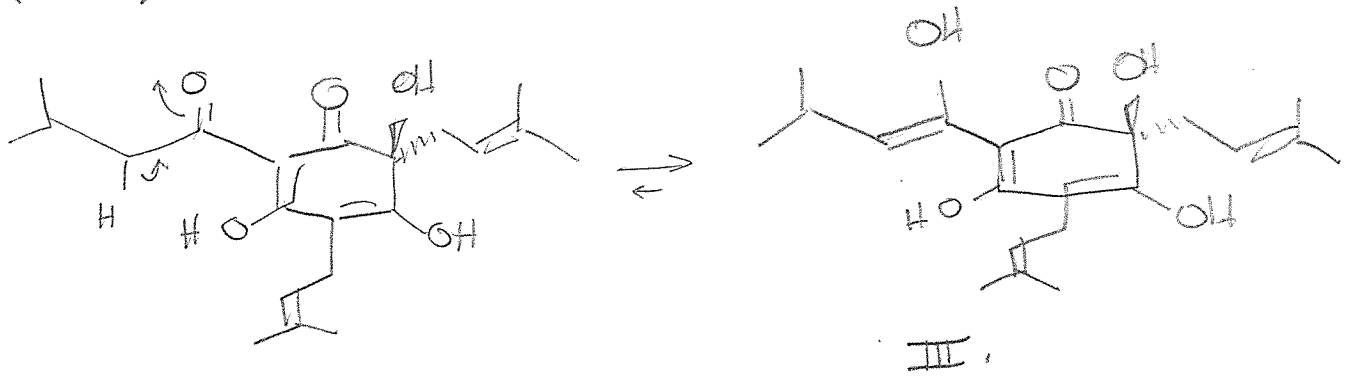
In order for tautomerization to occur, there must be an ENOL (tautomerizes to keto) or a carbonyl with at least one α -H (CARBONYL \rightarrow ENOL)

TAUTOMERIZE is an equilibrium process that describes the rearrangement of an enol to a carbonyl or carbonyl to enol.

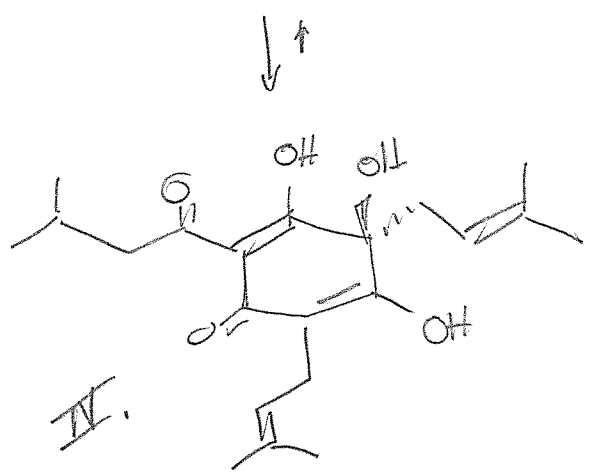
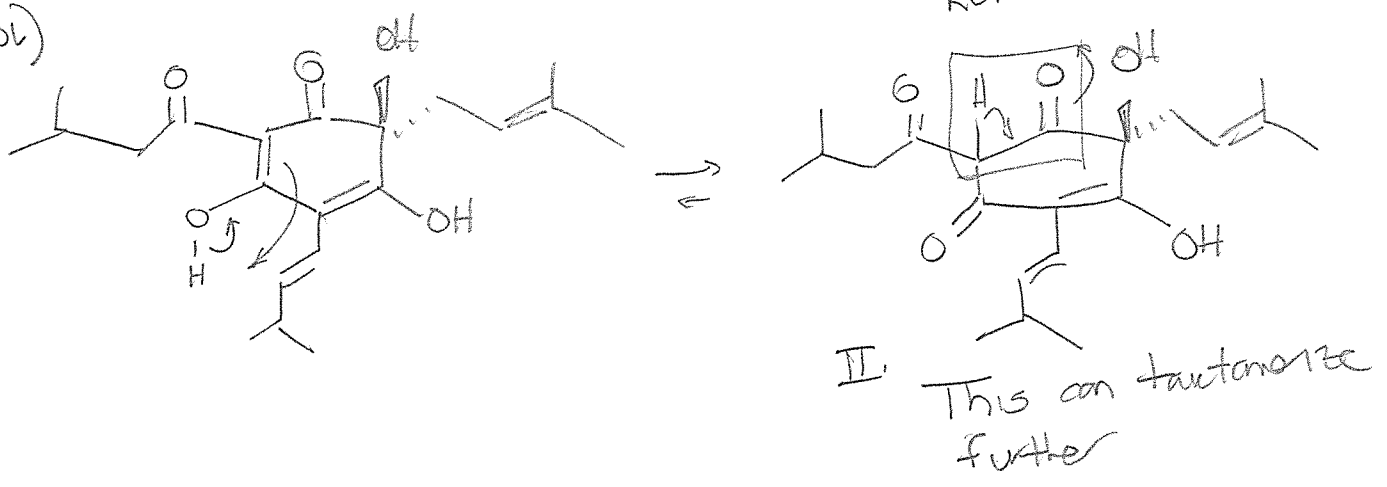
The 3 sites where humulone can tautomerize are labeled as, A, B and C.

10. (CONT'D)

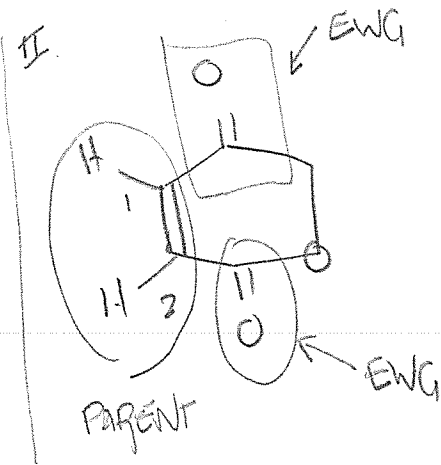
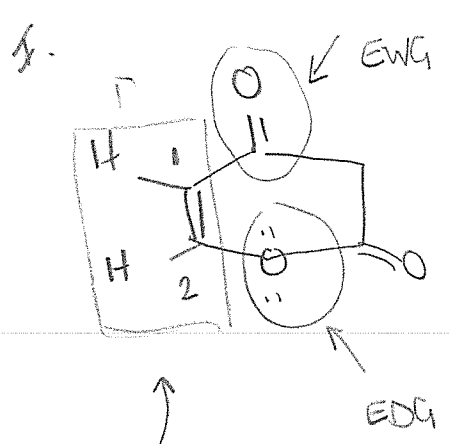
A (KETONE)



B (ENOL)

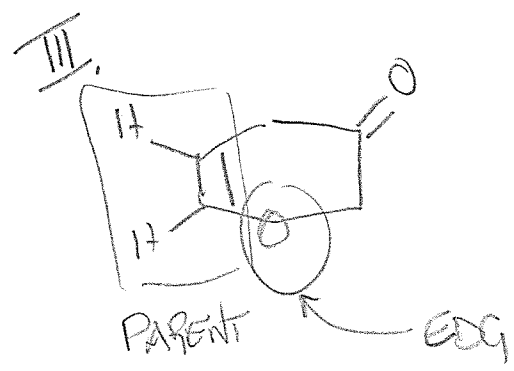


11. DIENOPHILE ; Most reactive has most \oplus character i.e. Electron withdrawing group (EWG)
 EWG defined as substituent with atom directly bonded to parent (i.e. sp^2 carbons of dienophile alkene) has EXTERNAL π bond



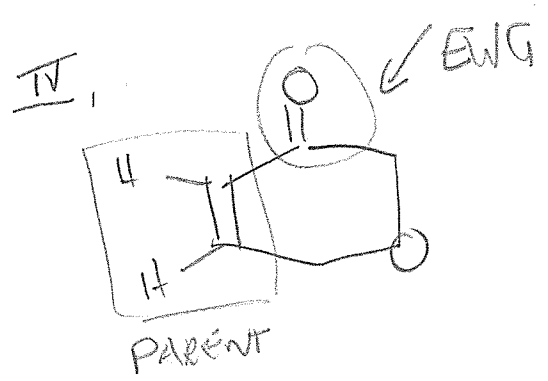
DIENOPHILE
PARENT

II > I (eliminate choices a, b, e)

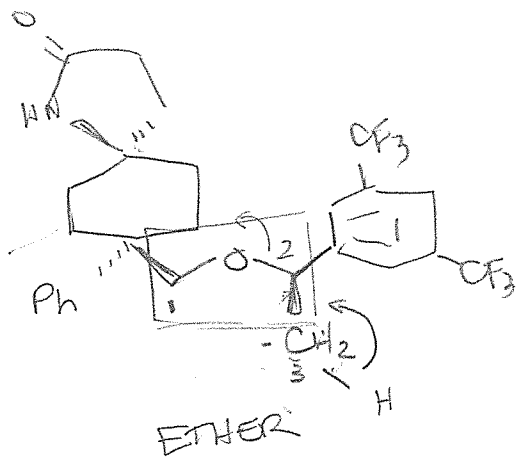


Less reactive than
BOTH I, II
(eliminate d)

II > III > IV > I

C


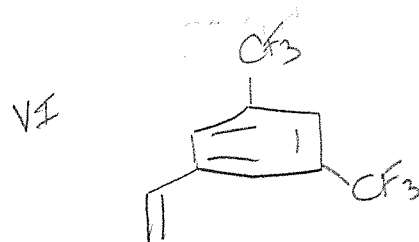
IV > I
II > IV



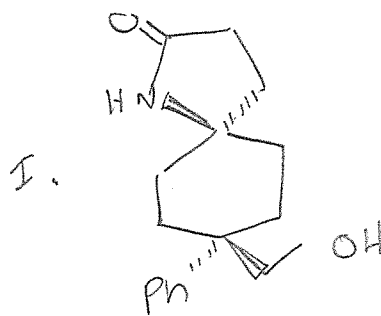
A. 1. Et_3N 2. H_2O This is an E_2 elimination

LG is O of the ether.
Must have adjacent sp^3C
with at least 1 H for
 E_2 to occur

E_2 cannot occur on C_1 carbon
b/c there is no adjacent sp^3
C w/ a hydrogen. E_2 CAN occur
① C_2 by losing H from C_3



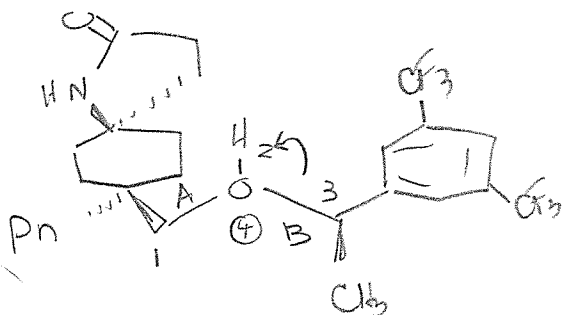
+



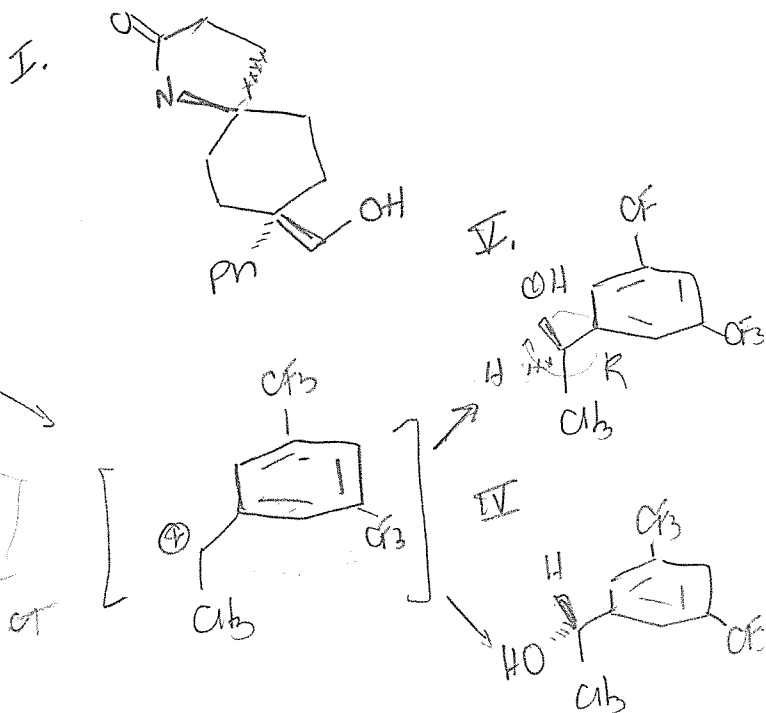
A = I + IV

B. H_3O^+ is $\text{S}_\text{N}1$

B = I, IV, V

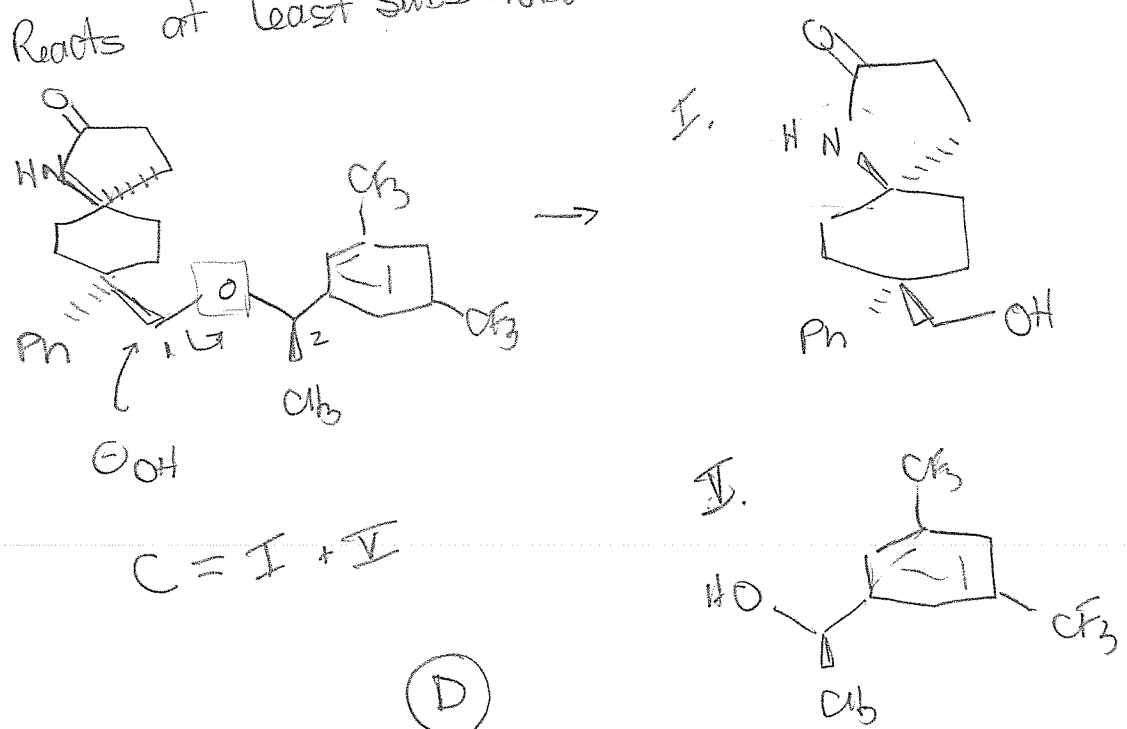


If break A bond, get 1° \oplus
If break B bond, get 2° benzylic \oplus
MORE STABLE \Rightarrow MAJOR PRODUCT

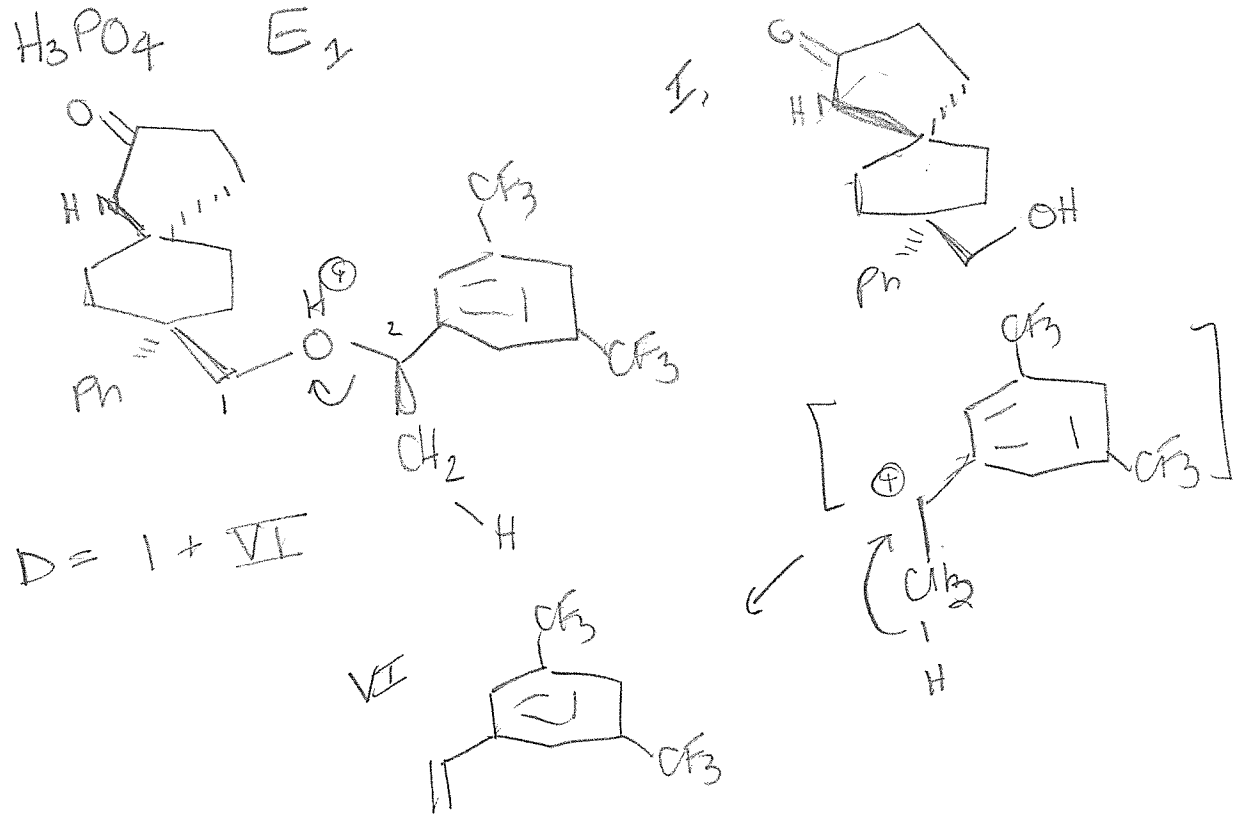


12. (cont'd)

C. NaOH SN2
Reacts at least substituted carbon

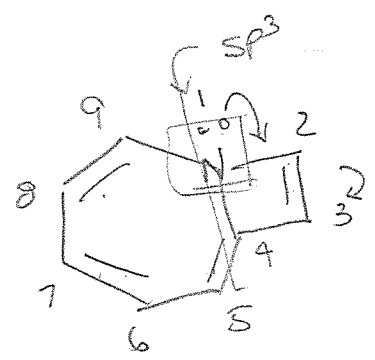


D. H₃PO₄ E₁



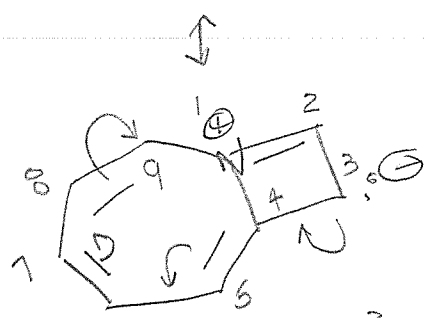
13. With polycyclic aromatics, consider all 4 criteria for aromaticity on each ring. Break down into A ring, B ring, C ring etc... If any ring is aromatic, the compound is considered to be aromatic.

I.

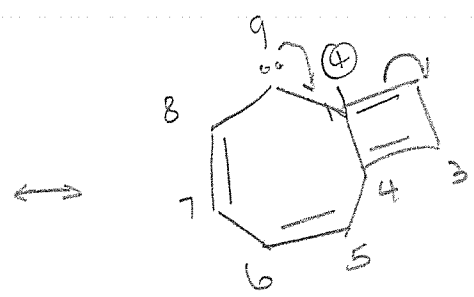


Consider 9 membered ring

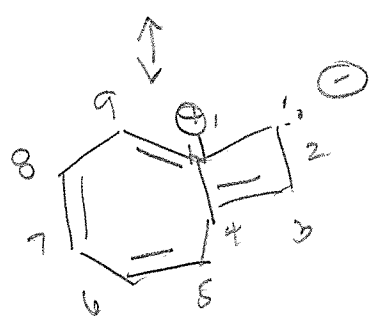
- Cyclic ✓
- Planar $C_{2v}-C_9$ sp^2 planar ✓
- N can adopt sp^2 via resonance ✓
- Continuous π ✓



N can adopt sp^2 hybridization (PLANAR)



πe^- , starting w/ lone pair on N can delocalize completely around ring back to N



AROMATIC

Huckel: $4n + 2 = 10$ ✓
 $n = 2$

13. (CONT'D)

Consider 11-membered ring

CYCLIC ✓

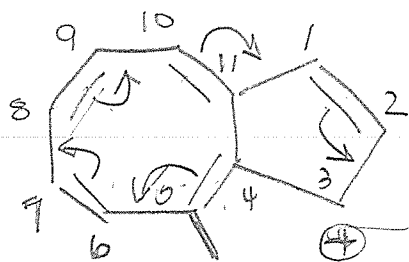
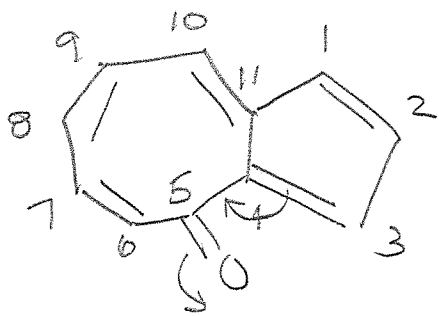
PLANAR ✓

All 11 atoms are sp^2 hybridized

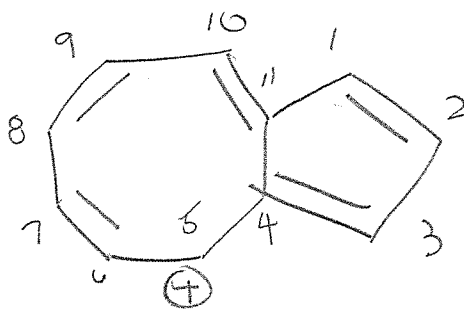
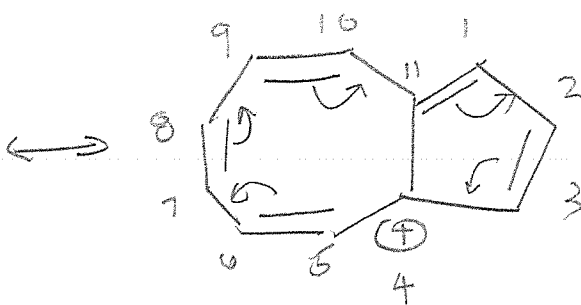
CONT- π ✓

Huckel

$4n+2 = 10$ $n=2$ ✓



DON'T COUNT THESE e^- b/c OUTSIDE OF RING

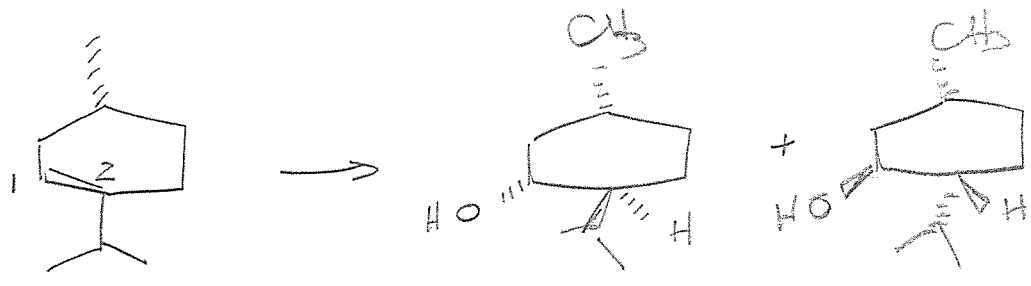


πe^- start @ C_1-C_2 and can delocalize around to get back to C_1-C_2

(E)

14.

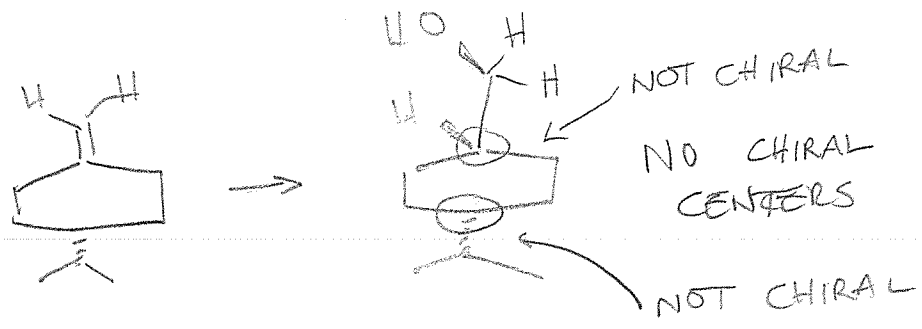
I.



DIASTEREOMERS

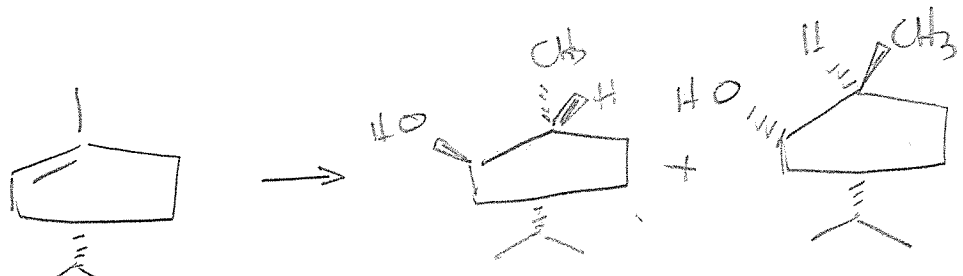
1. BH_3 2. $H_2O_2, NaOH$
 ANTI-MARKOVNIKOV
 SYN ADDITION

II



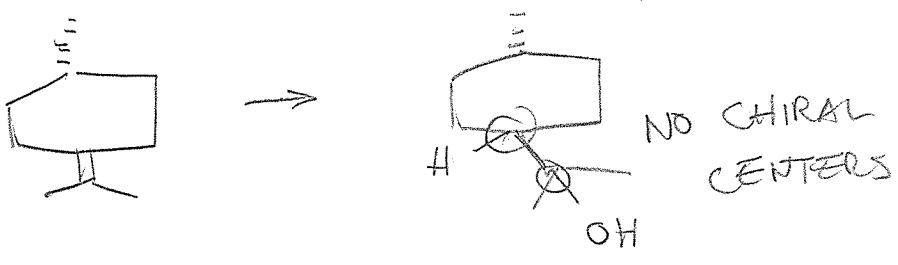
I + III
 (A)

III.

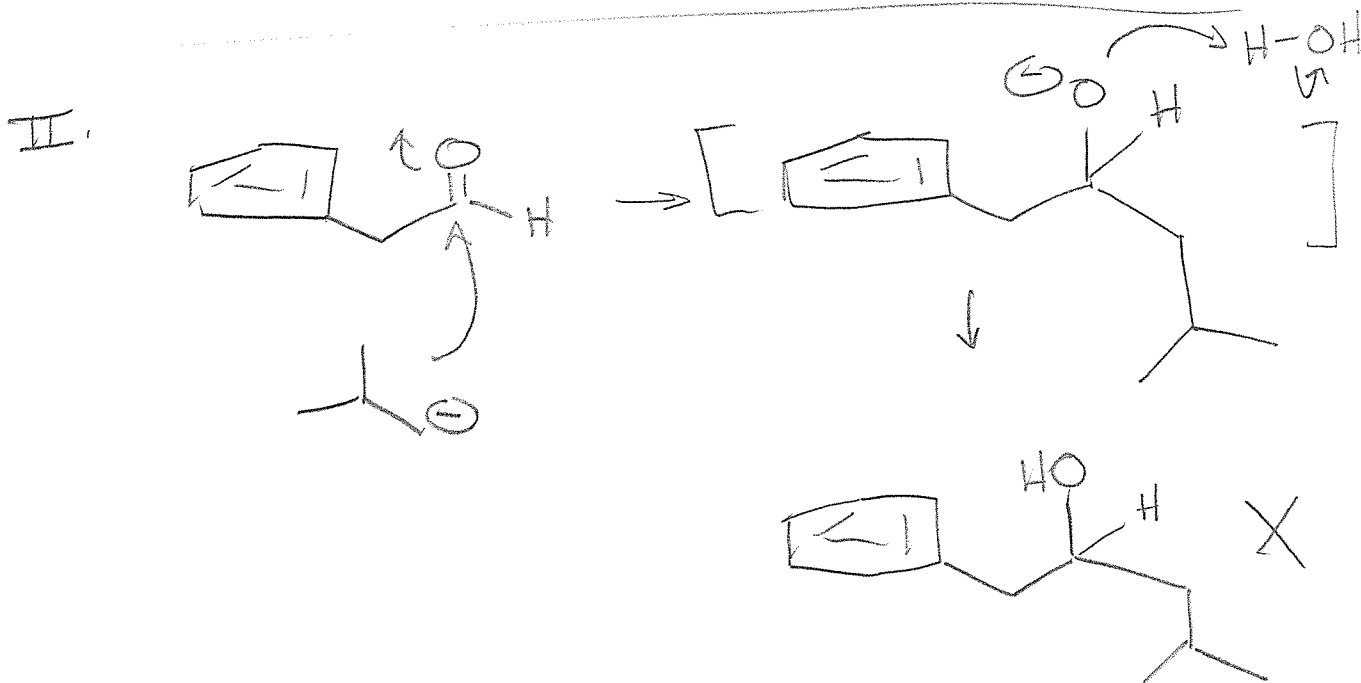
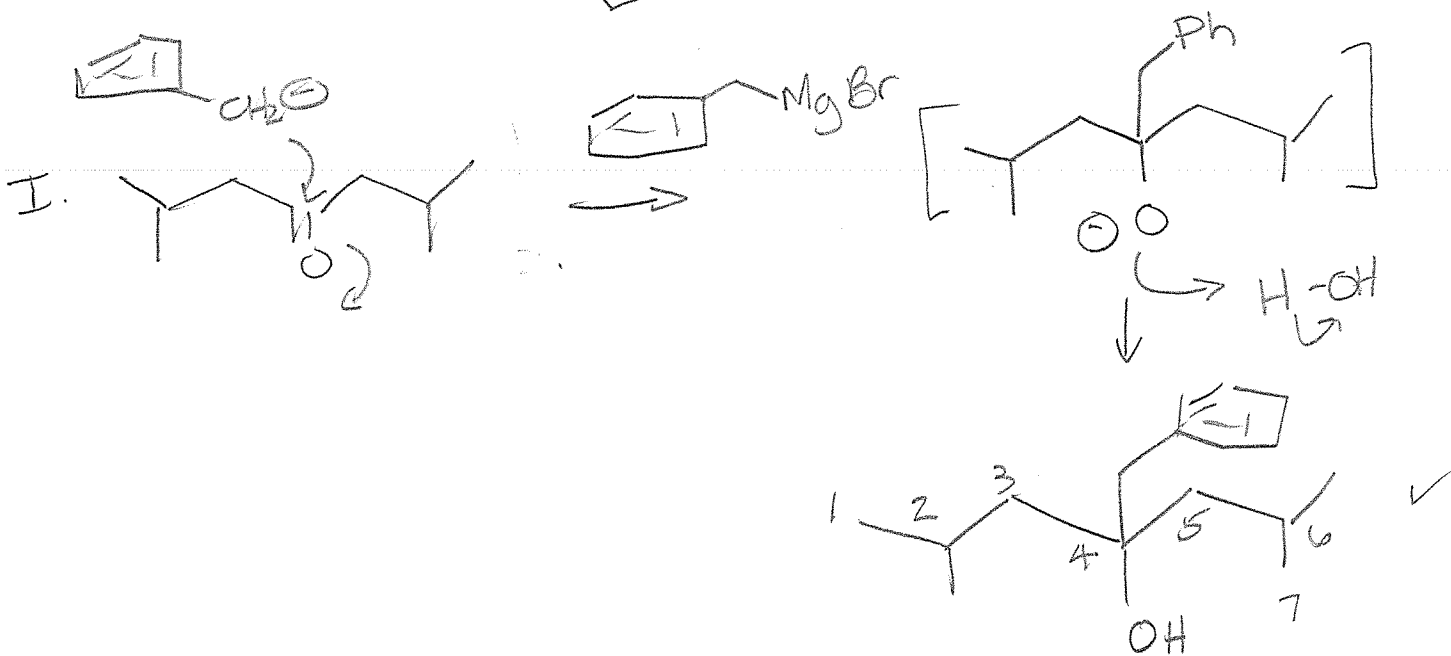
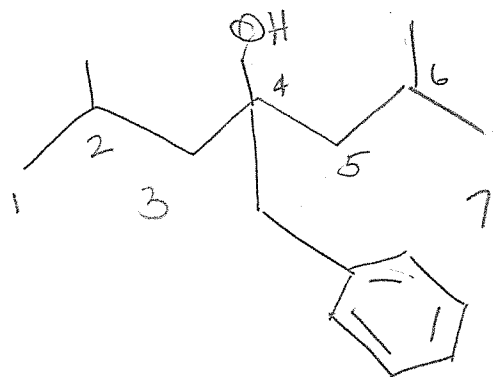


DIASTEREOMERS

IV.

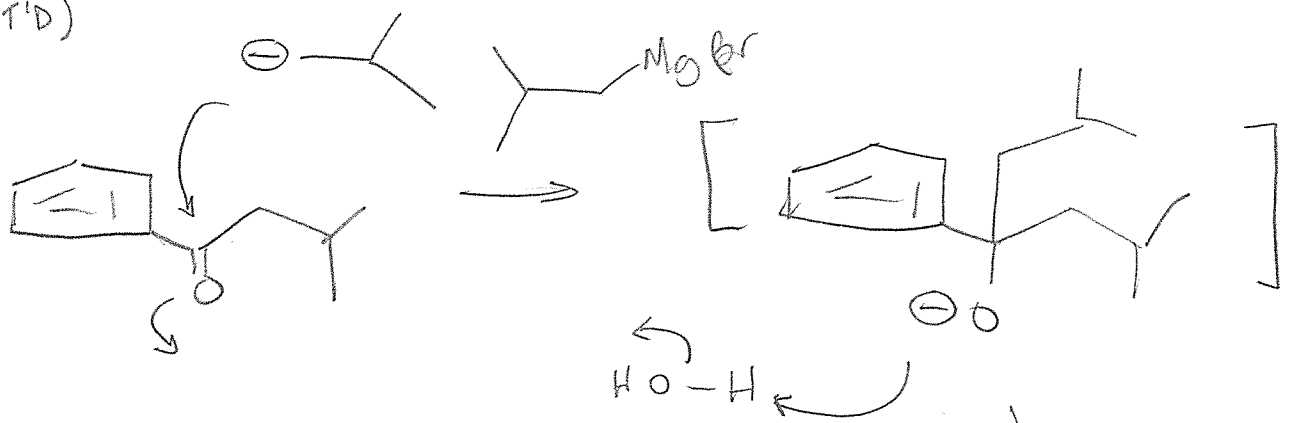


4-BENZYL-2,6-DIMETHYL-4-HEPTANOL



15. (CONT'D)

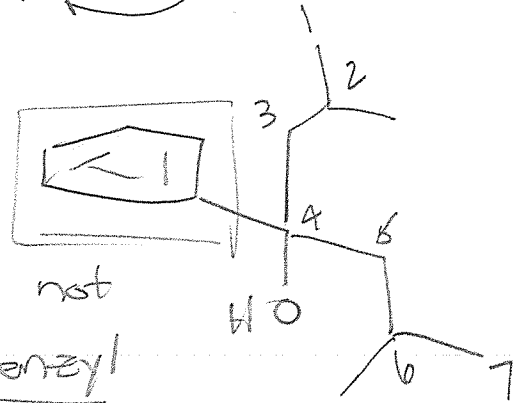
III.



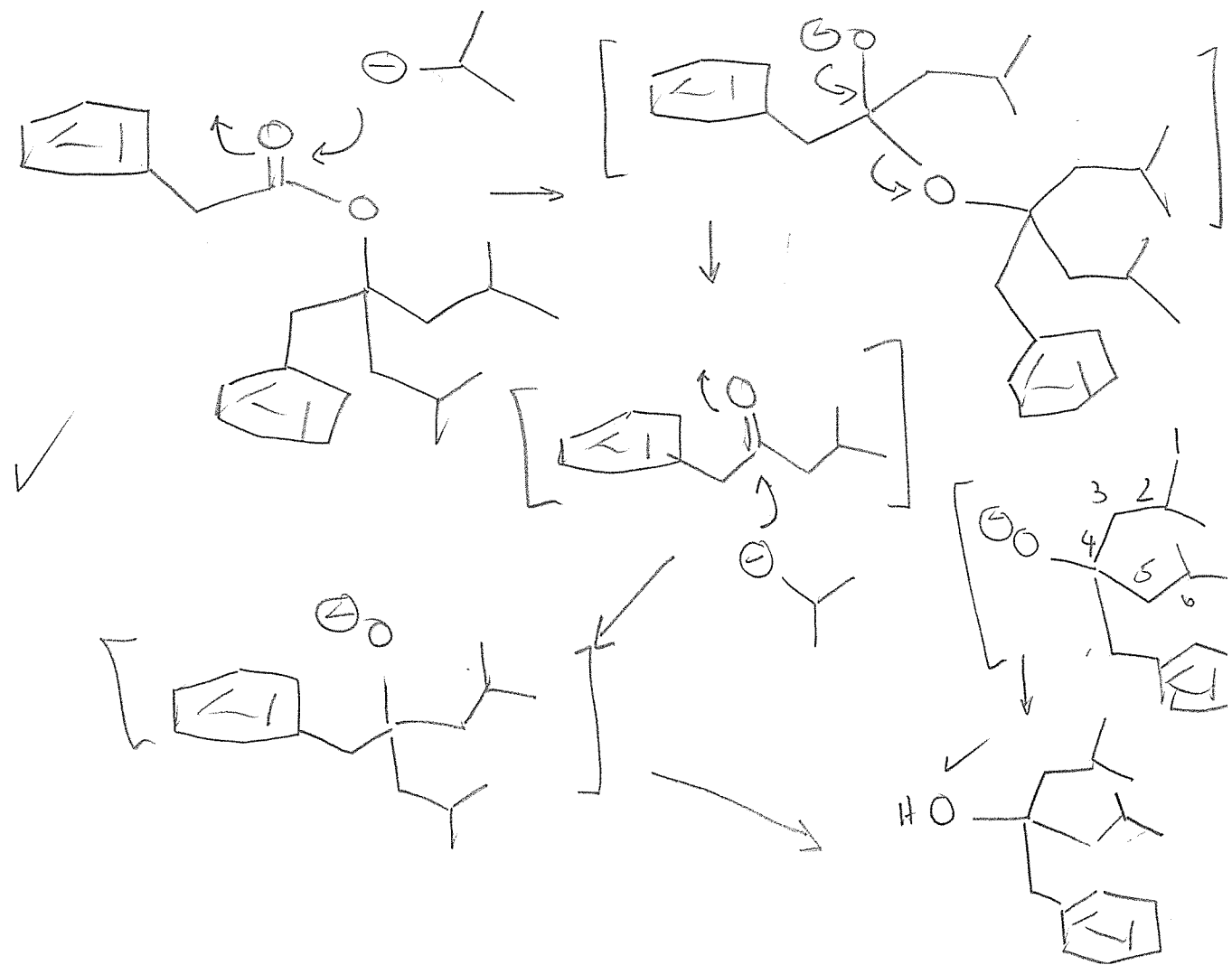
X

(D)

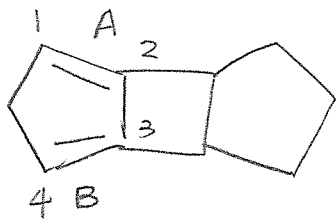
Phenyl not benzyl



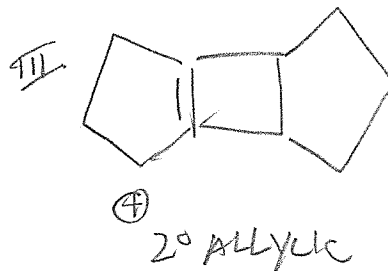
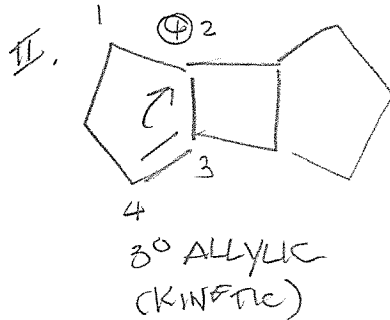
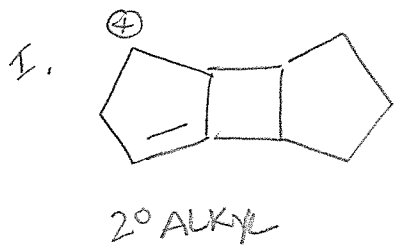
IV.



16.



A

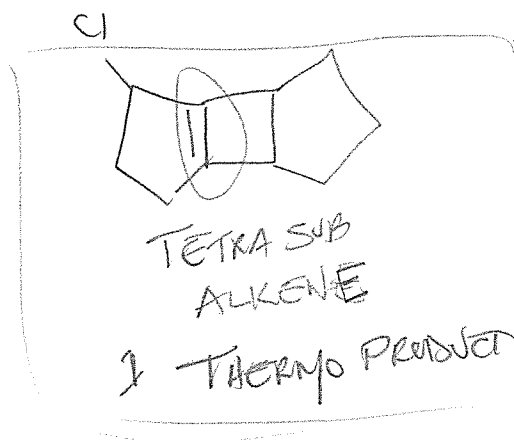
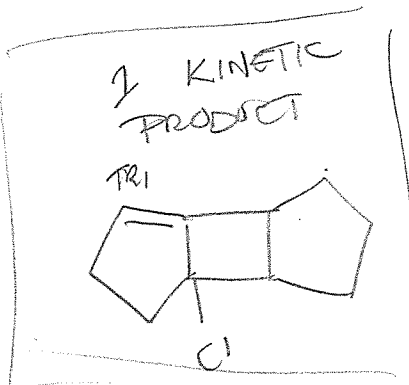
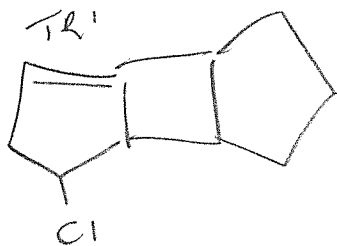
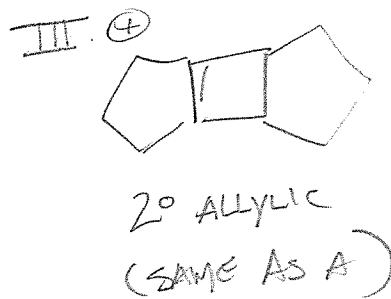
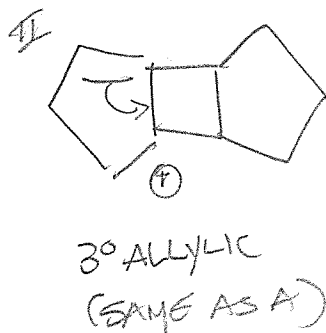
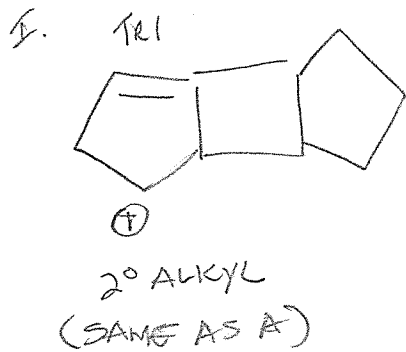


|||

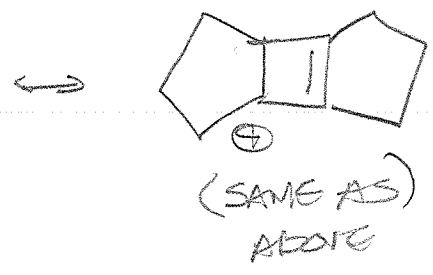
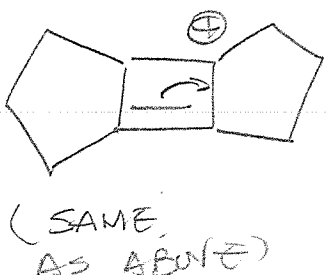
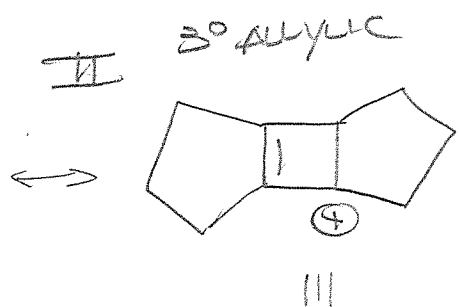
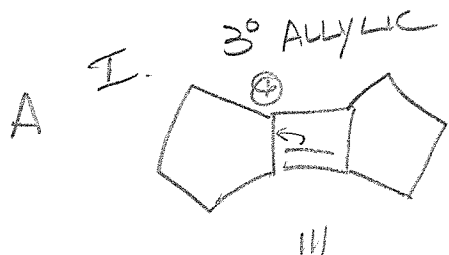
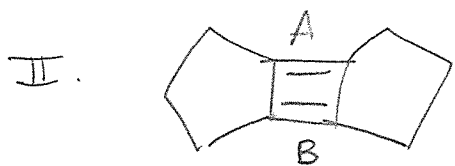
|||

|||

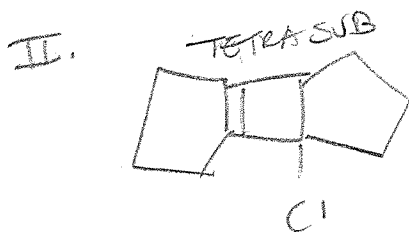
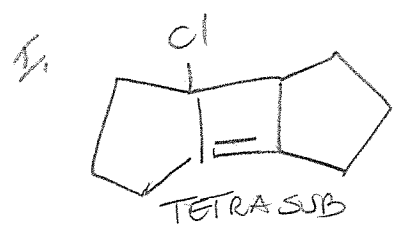
B



16. (CONT'D)



B Will give same as A

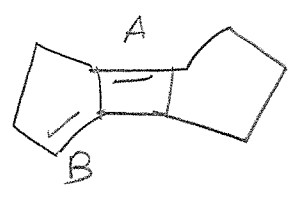


Both are kinetic AND thermo

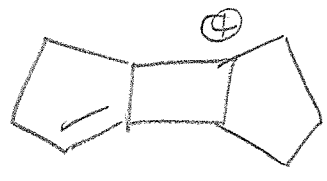
2 KINETIC
2 THERMO

16. (CONT'D)

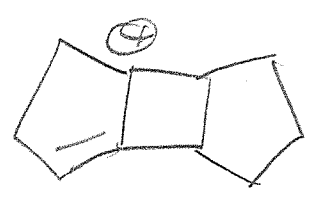
III.



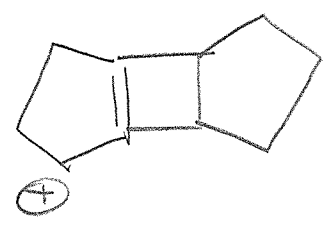
A



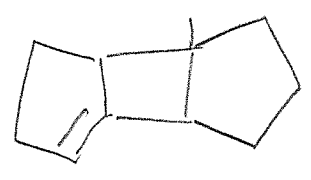
3° ALKYL



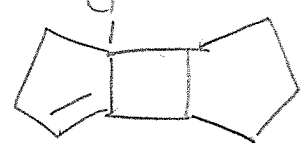
TRISUB
3° ALLYLIC



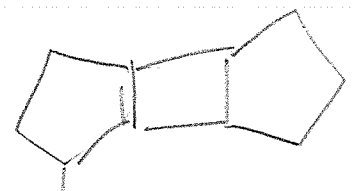
2° ALLYLIC



TRISUB

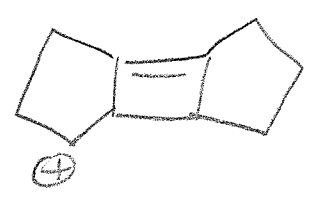


TRISUB

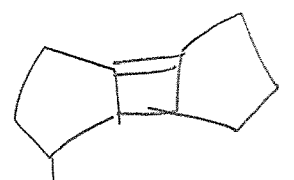


Cl TETRASUB

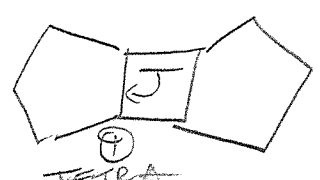
B



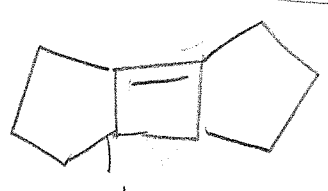
2° ALKYL



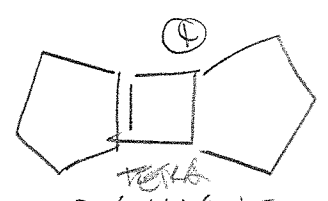
TETRASUB



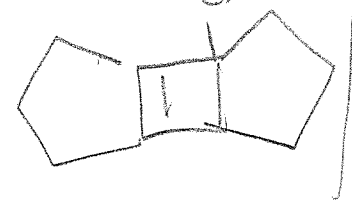
TETRA
3° ALLYLIC



TETRASUB



TETRA
3° ALLYLIC

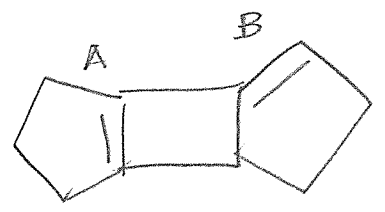


TETRASUB

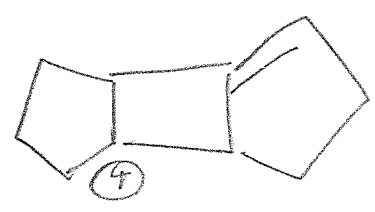
4 THERMO PRODUCTS
2 KINETIC PRODUCTS

16. (CONT'D)

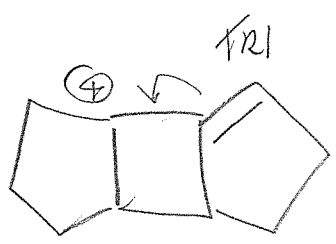
IV



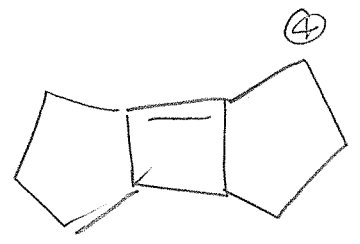
A



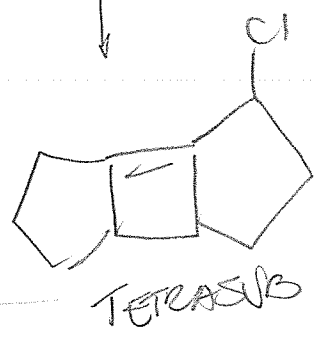
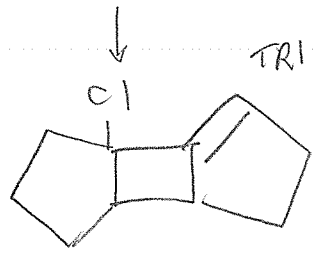
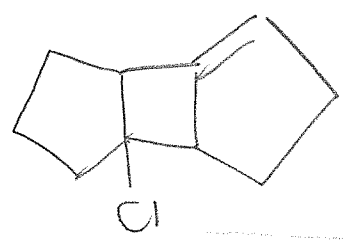
3° ALKYL



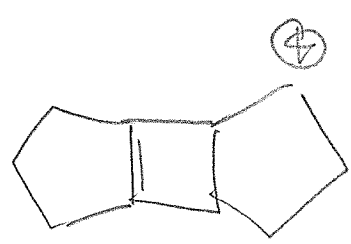
3° ALLYLIC



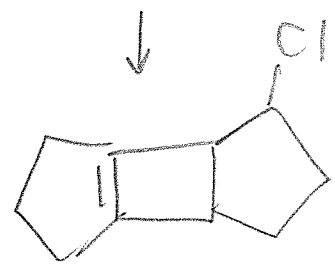
2° ALLYLIC



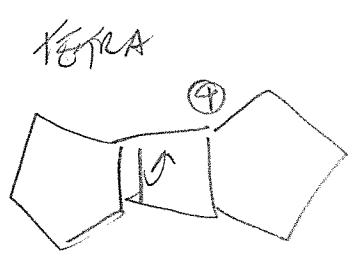
B



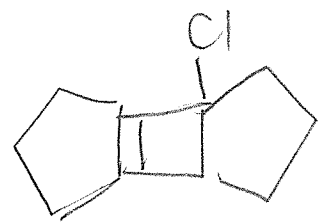
2° ALKYL



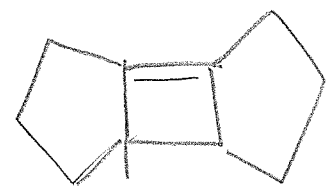
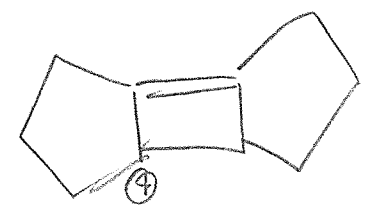
TETRASUB



3° ALLYLIC



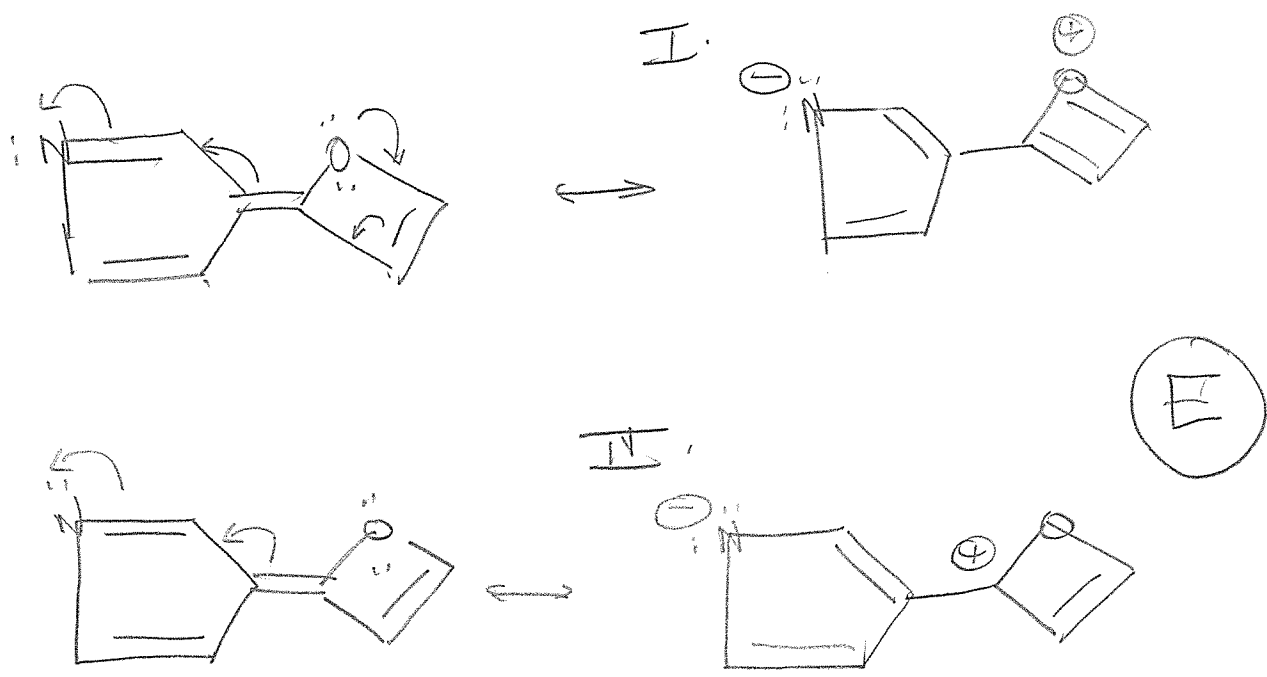
TETRASUB



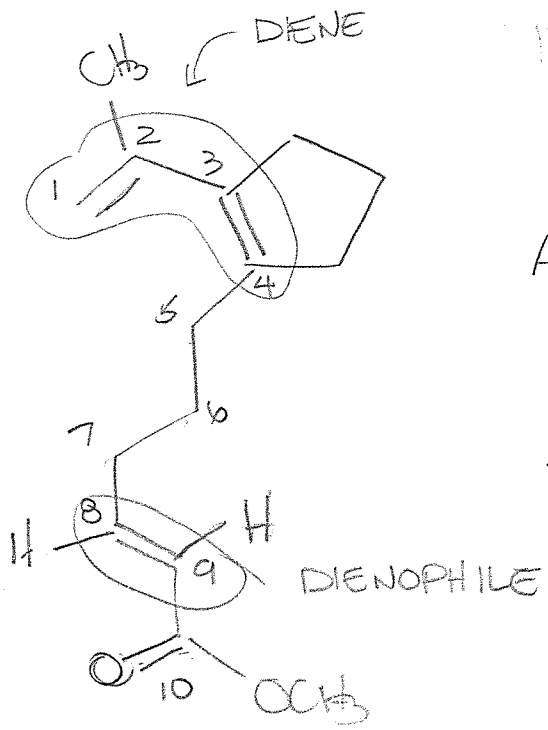
TETRASUB

4 THERMO PRODUCTS

17.



18.



A cyclohexene forms with the alkene forming between C₂-C₃ carbons of the diene

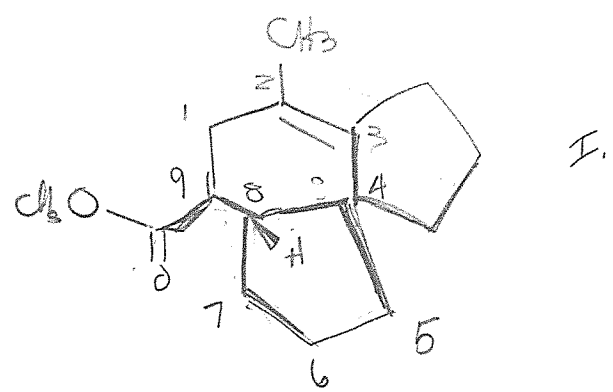
Two possible regioisomers may form.

C₁-C₈ and C₄-C₉
OR

C₁-C₉ and C₄-C₈

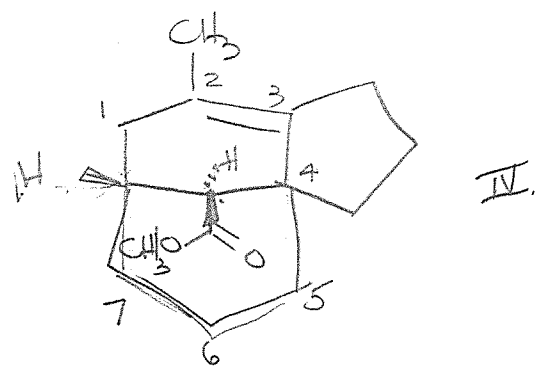
1B. (CONT'D)

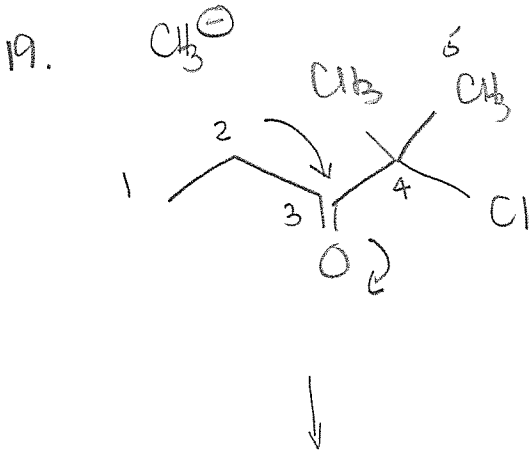
IF C_1-C_9 C_4-C_8



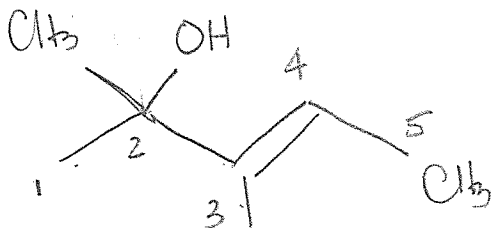
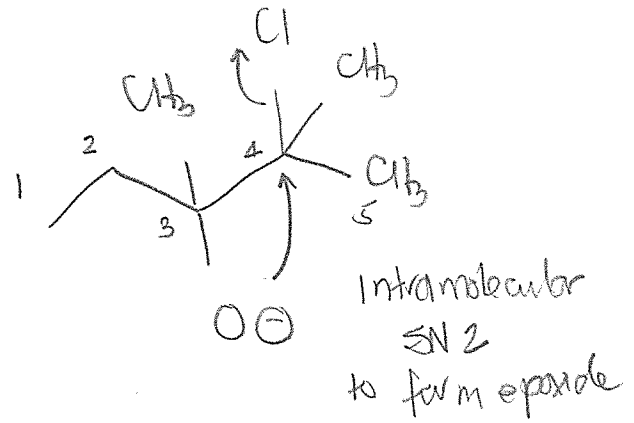
(C)

IF C_1-C_8 C_4-C_9

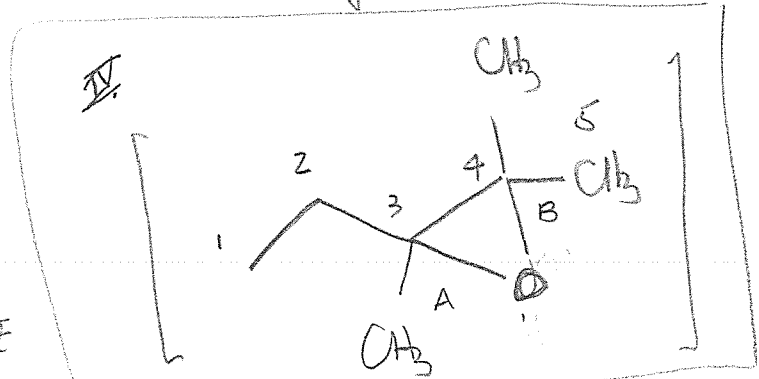




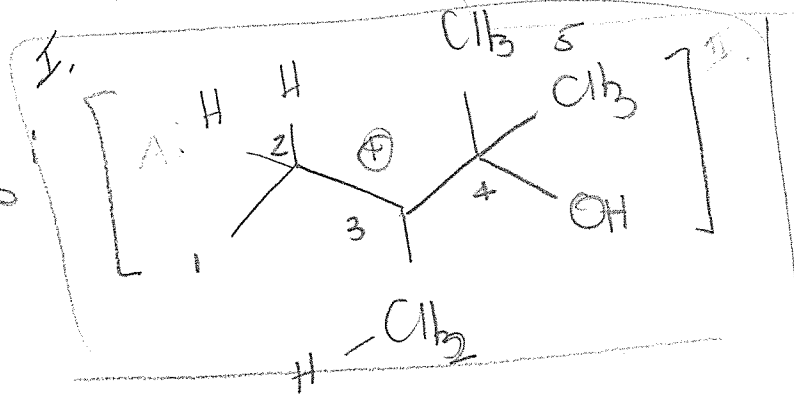
1. CH_3MgBr
 \longrightarrow
 2. H_2SO_4



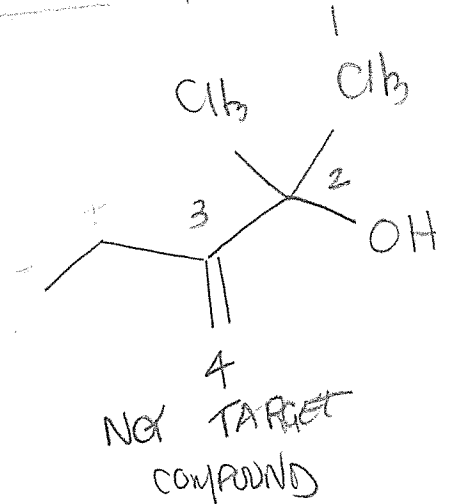
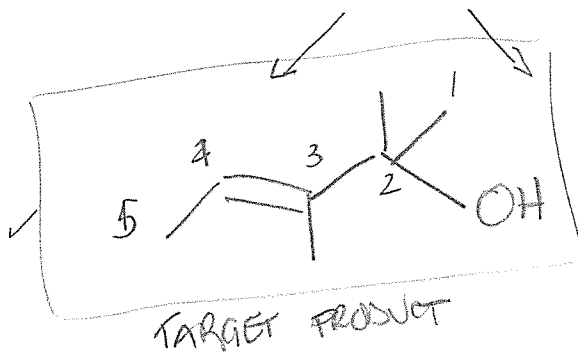
2-hydroxy-2,3-dimethyl-3-pentene



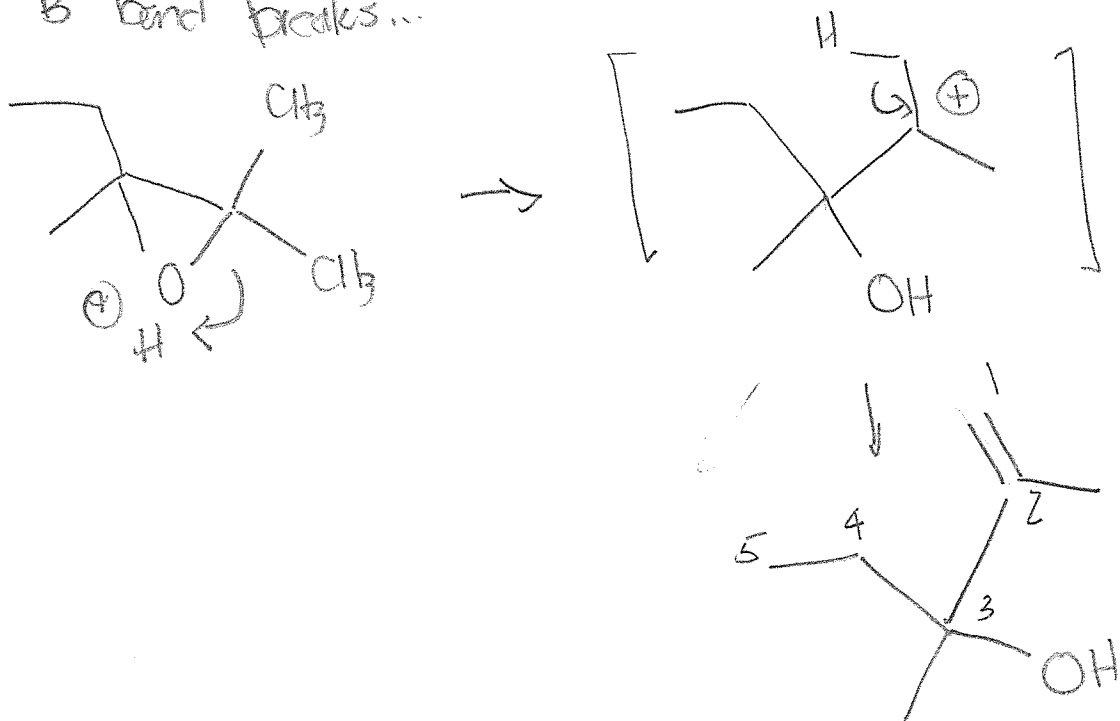
If A bond of epoxide breaks



(B)



If B band breaks...

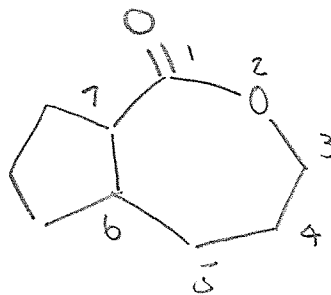


3-hydroxy-2,3-dimethyl-1-pentene
NOT TARGET COMPOUND

20. Ketones more reactive than esters.
least steric crowding on α -C most reactive

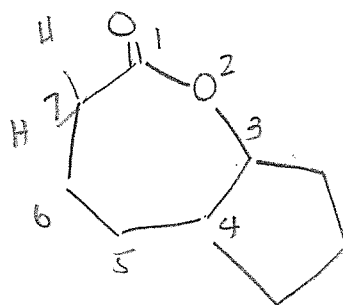
COMPARE TWO STRUCTURES AT A TIME, THEN ELIMINATE CHOICES AS YOU GO.

I.



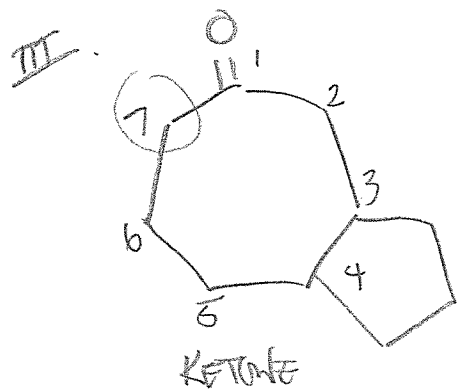
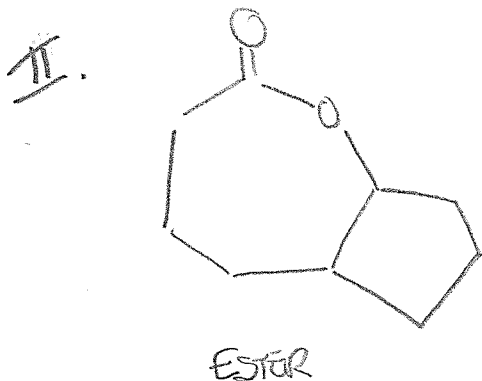
Both esters
II less sterically crowded at α -carbon

II.



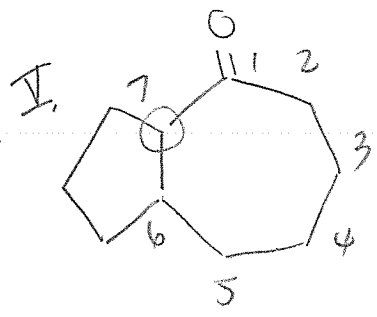
II > I
(eliminate C, e)

20. (CONT'D)



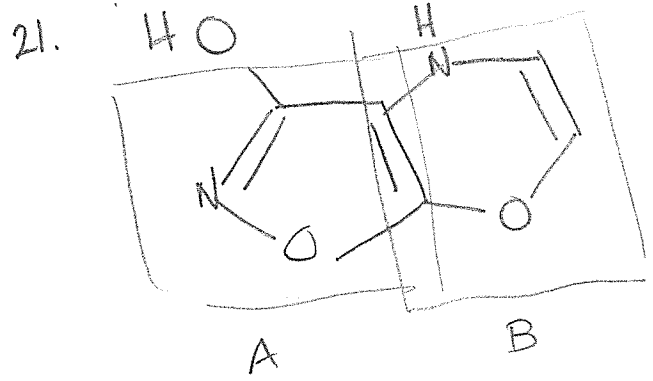
III > II
 (cannot eliminate
 (II > IV))

(A)

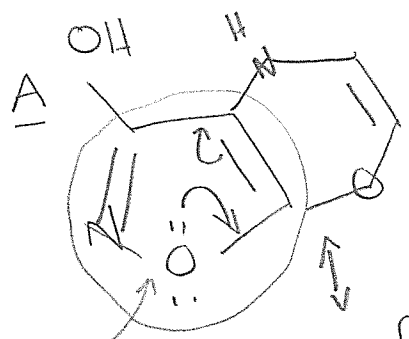


C₇ of III less
 sterically crowded than
 C₇ of IV
 III > IV
 (eliminate b,d)

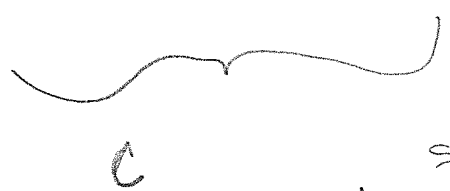
Choice a is the
 only viable choice



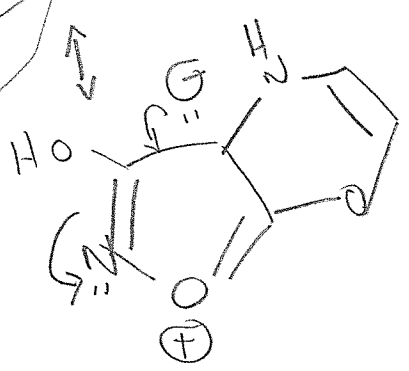
Consider A, and B
 independently, then consider C



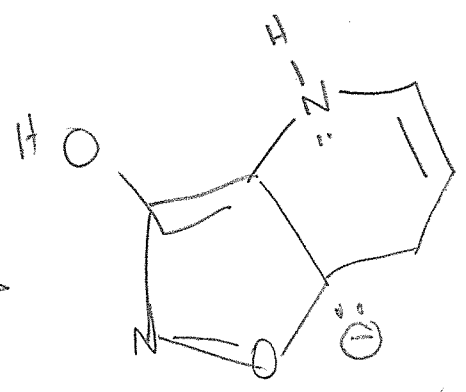
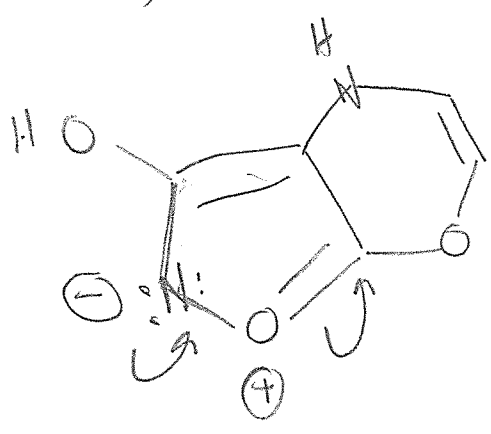
CYCLOC ✓
 PLANAR ✓



but can adopt
 sp² via resonance



21. (CONT'D)



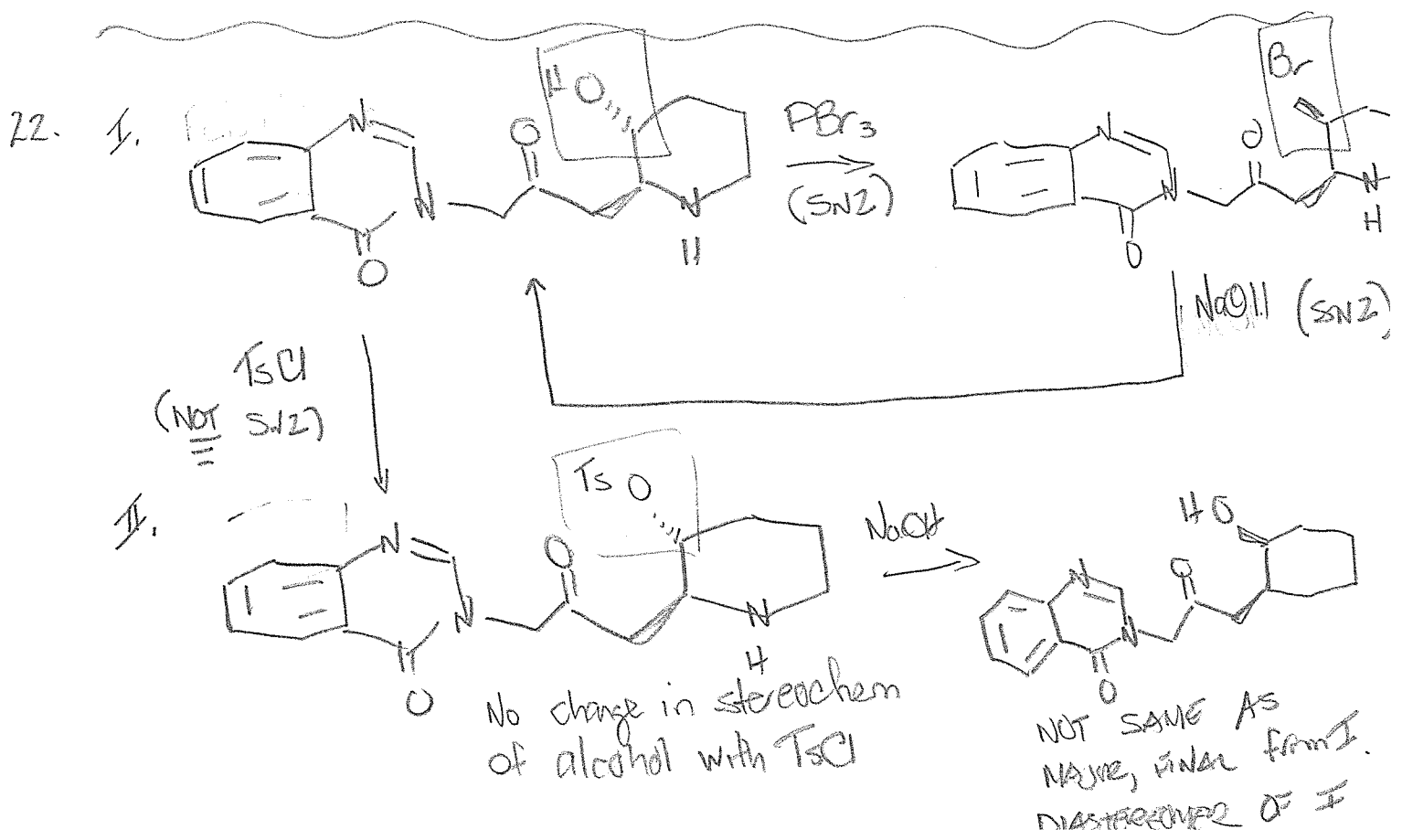
CONTINUOUS π ✓
 e^- start @ O and get all the way around back to O

$$4n + 2 = 6 \quad n = 1 \quad \checkmark$$

Use lone pair from O and $4e^-$ from two π bonds of ring

(B)

B ring is NOT aromatic, nor is A+B (i.e. C ring)



22. (cont'd)

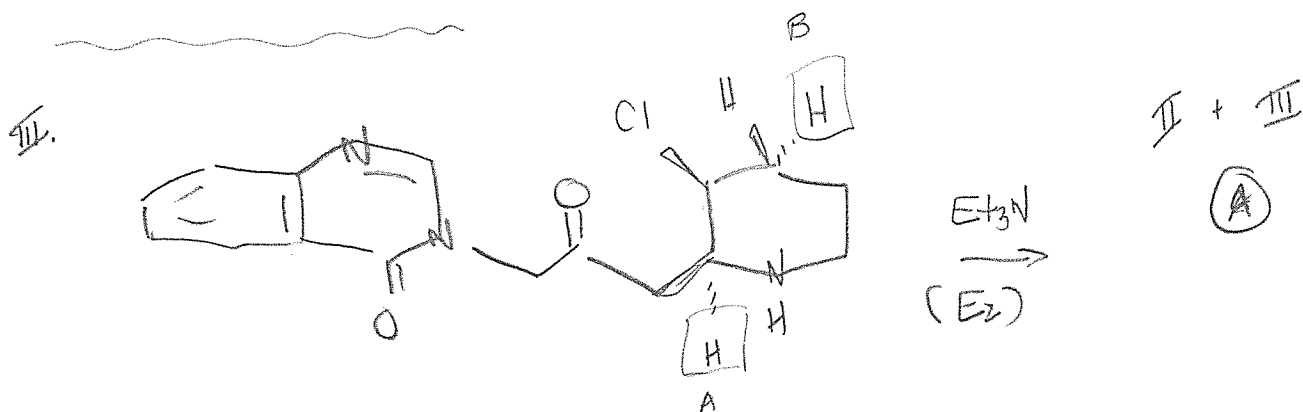
I. FALSE

II. TRUE

III. TRUE

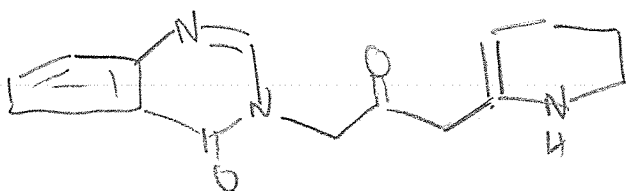
IV. FALSE

-32-



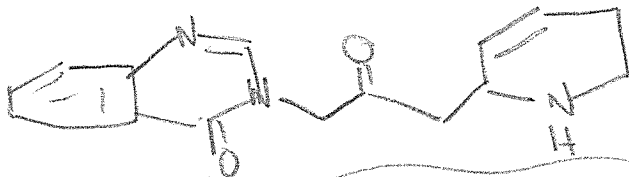
E₂ can occur via loss of either HA or HB

A:



TRI SUB
MAJOR TRANSO
PRODUCT

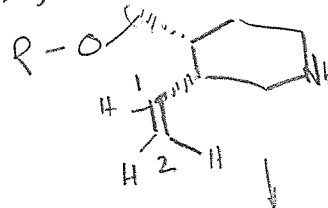
B:



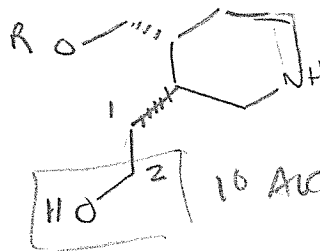
DI SUB

23. Reaction w/ 1. BH₃ 2. H₂O₂, NaOH occurs via ANTI MARK addition where final product puts OH on least SUB carbon of alkene.

I, II, IV will give 1° Alcohol



II will not. (eliminate b)



D

With NaBH₄, Alcoh

I. does not react ⇒ Ester do not react w/ NaBH₄ (eliminate a)

III + IV both will give 2° alcohol w/ NaBH₄

With 1) HgCl₂, H₂O 2) NaBH₄

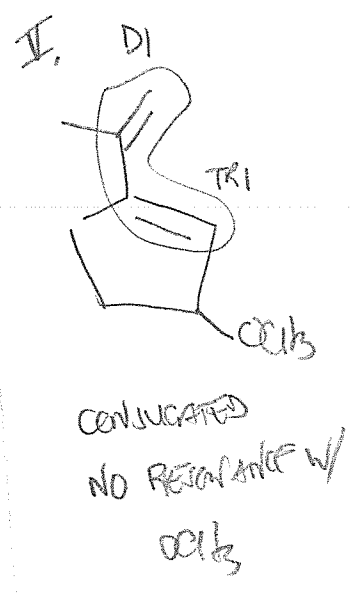
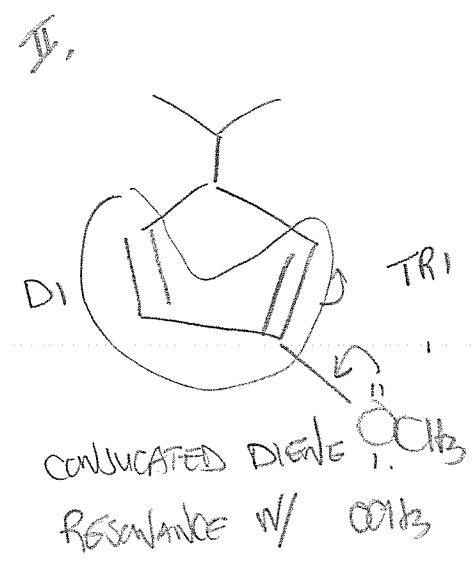
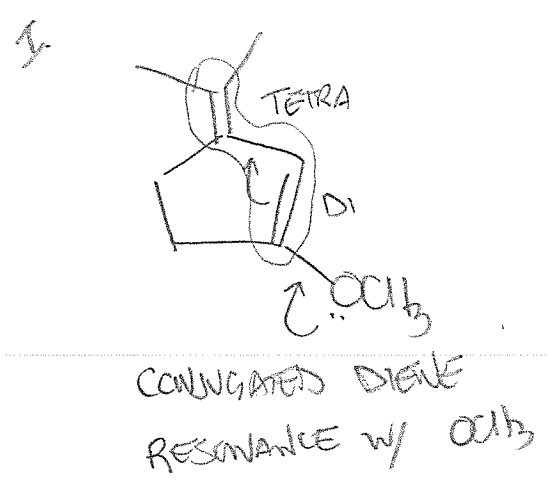
III give 3° Alcohol II. gives 2° Alcohol (eliminate c)

24. FOR STABILITY CONSIDER

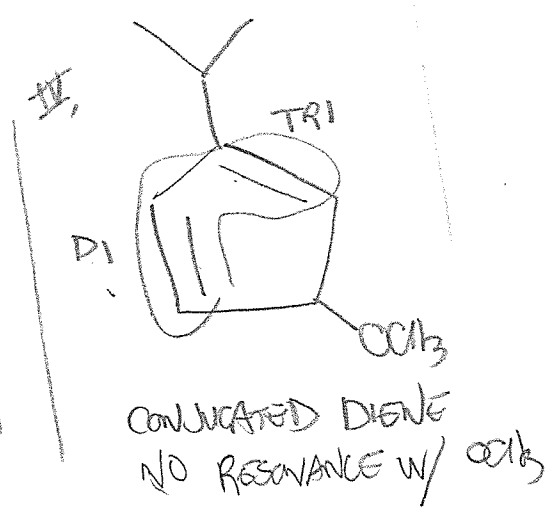
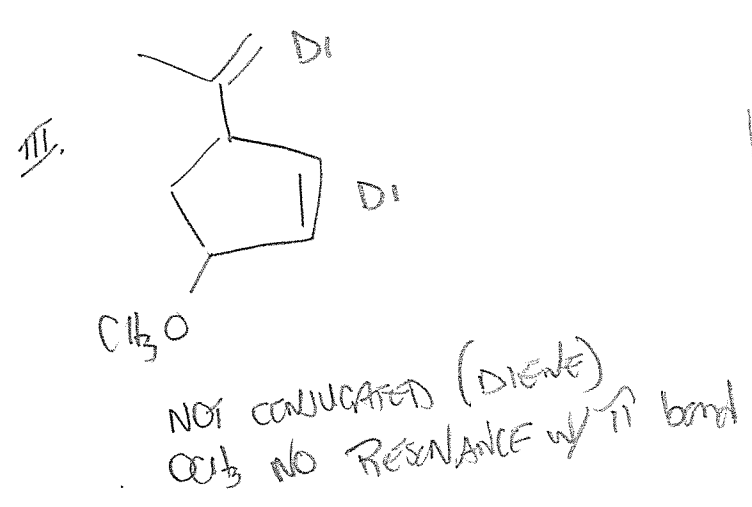
CONJUGATION (MORE CONJ., MORE STABLE)

RESONANCE w/ alkene and -O-C(=O)- (MORE RESONANCE, MORE STABLE)

SUBSTITUTION OF DOUBLE BOND (TETRA > TRI > DI > MONO)



I > II
(eliminate b)



(E)

II > III

II > IV IV > III
I > IV
(eliminate a, c, d)

25. META

DISUBSTITUTED
ONLY

only two substituents
on a benzene ring.

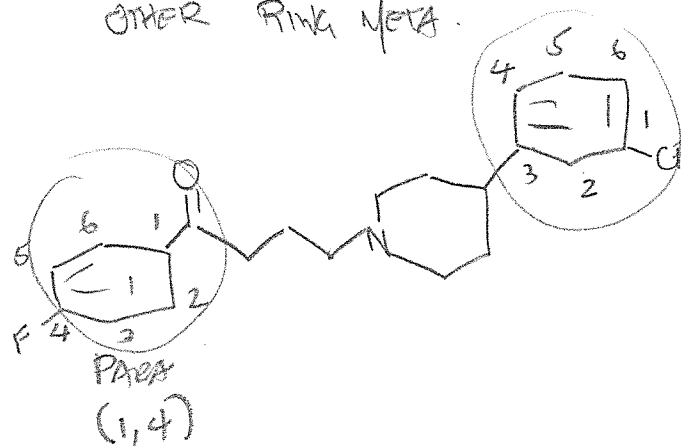
I. PARA

II. 3 SUBSTITUENTS
CANNOT BE
META

III. ONE RING PARA
OTHER RING META.

META (1,3)

IV. 3 SUBSTITUENTS
ON RING.



(B)