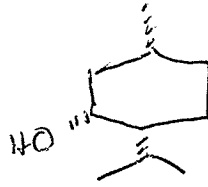


ISOMENTHOL

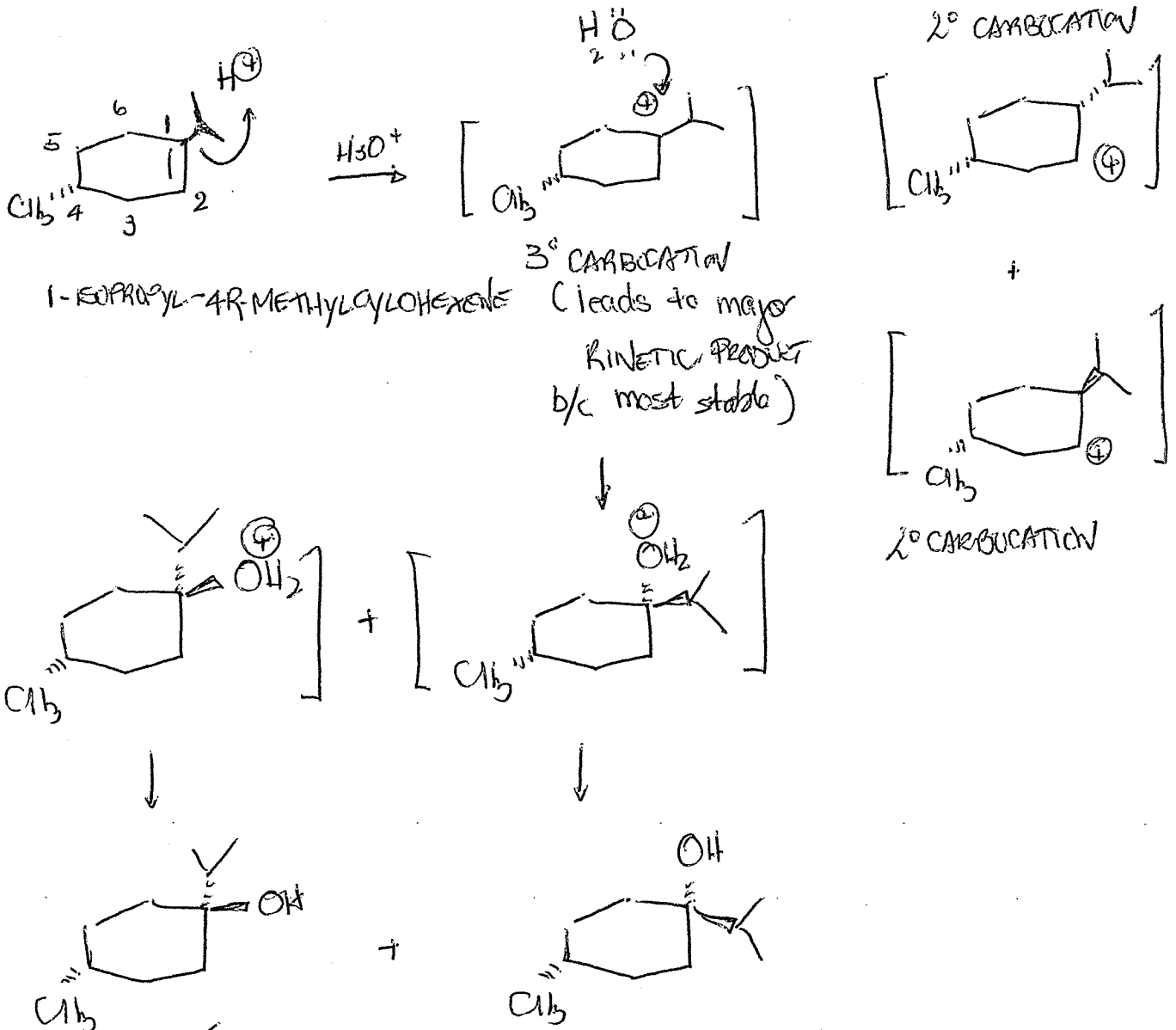


NEOMENTHOL



NEOISOMENTHOL

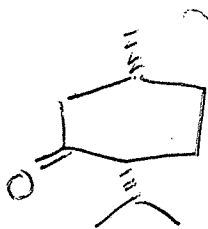
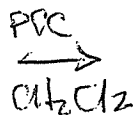
I.



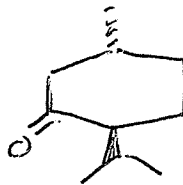
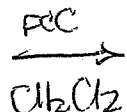
These are the major kinetic products
so I is FALSE

(CONT'D)

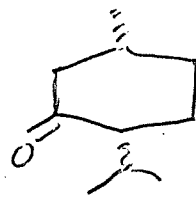
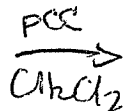
ISOMENTHOL



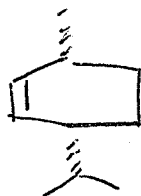
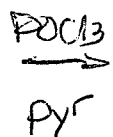
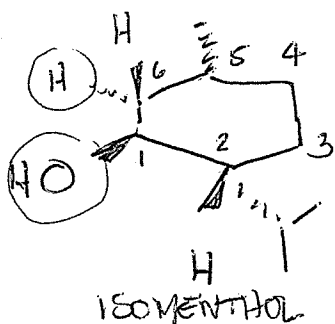
NEOMENTHOL



NEOISOMENTHOL



These are STEREOISOMERS of each other NOT the same product.
 II IS FALSE



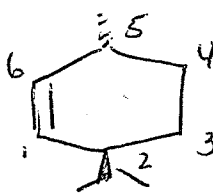
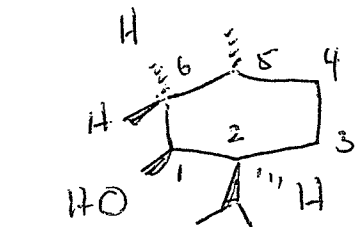
MAJOR THERMO PRODUCT

E₂ CANNOT occur across C₁-C₂ bond
 Only occurs across C₁-C₆ b/c OH and H must be trans

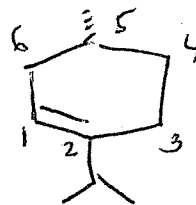
III is FALSE since major thermo products are NOT the same

MAJOR THERMO-DYNAMIC PRODUCT

MOST STABLE

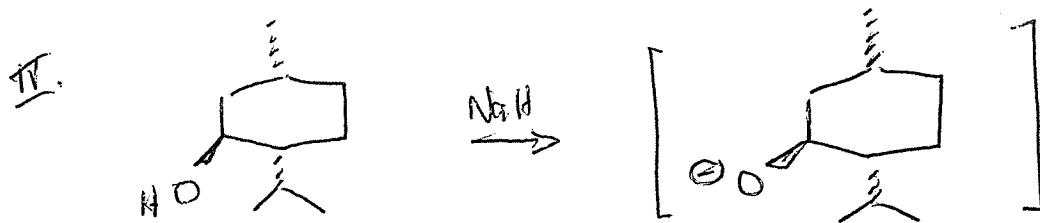


+



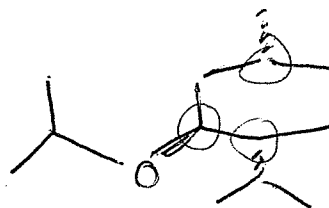
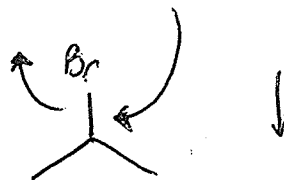
E₂ can occur across C₁-C₂ and C₁-C₆

1. (CONT'D)



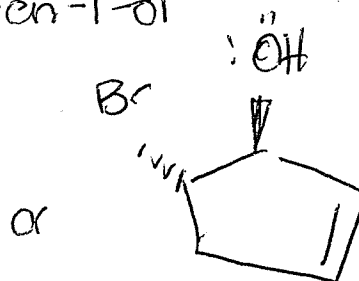
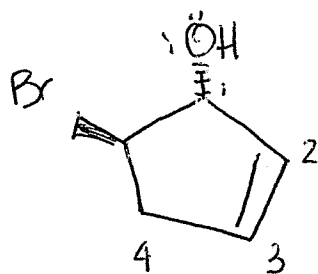
NO CORRECT ANSWER GIVEN

CREDIT FOR ALL



ONLY 3 CHIRAL CENTERS

2. trans-5-bromocyclopent-2-en-1-ol

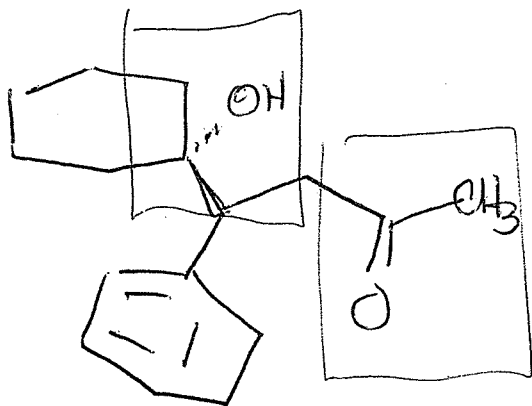


CONJUGATE ACID OF THE ALCOHOL IS THE STRUCTURE AFTER THE OH GROUP ACCEPTS A PROTON $\oplus\text{OH}_2$



(D)

TERTIARY ALCOHOL



METHYL
KETONE

TERTIARY
ALCOHOL

- ⊖ JONES
- ⊖ IODOFORM
- ⊕ LUCAS
- ⊖ Br₂/H₂O
- ⊖ KMnO₄

III

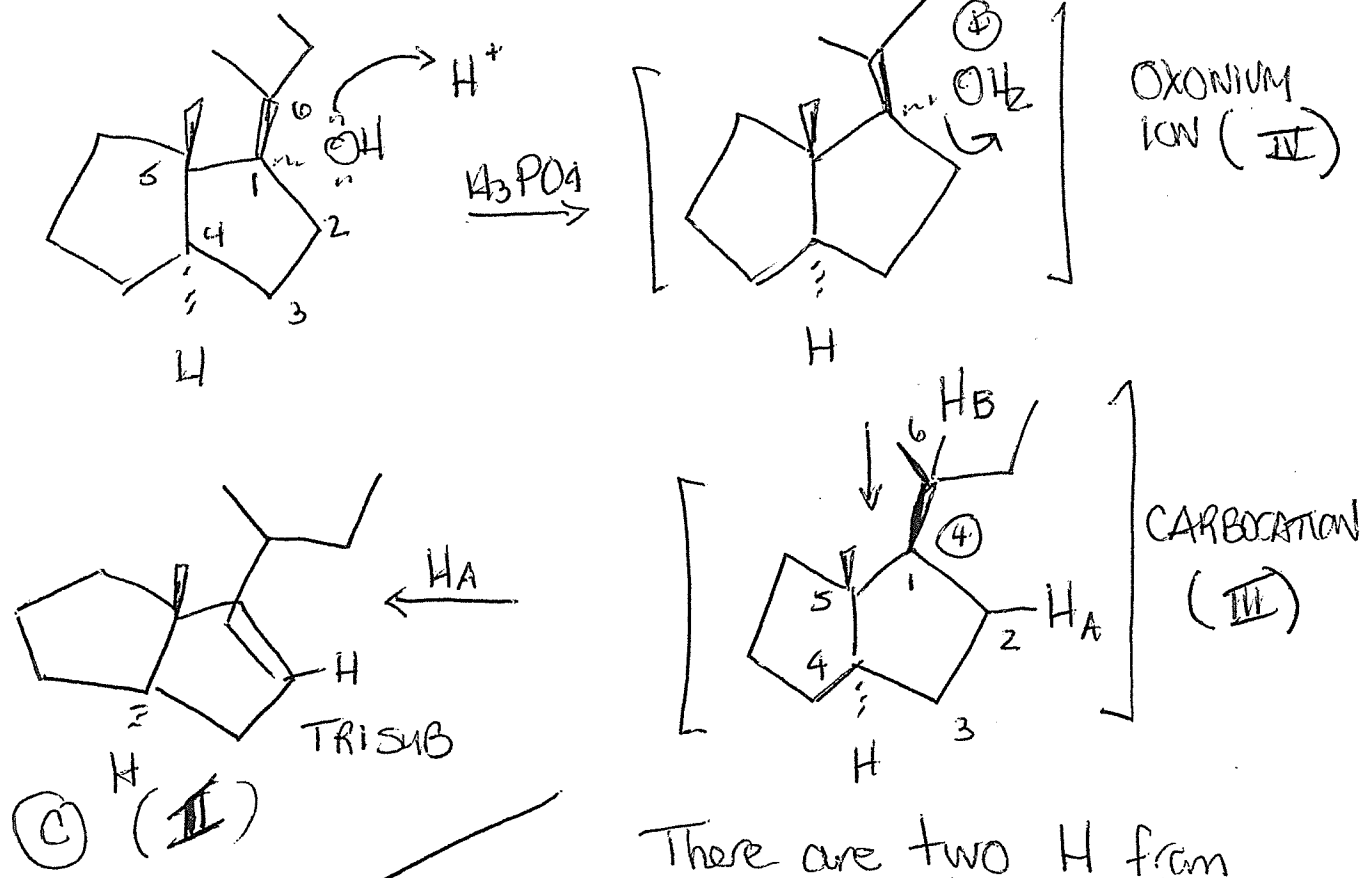
METHYL
KETONE

- ⊖ JONES
- ⊕ IODOFORM
- ⊖ LUCAS
- ⊖ Br₂/H₂O
- ⊖ KMnO₄

II

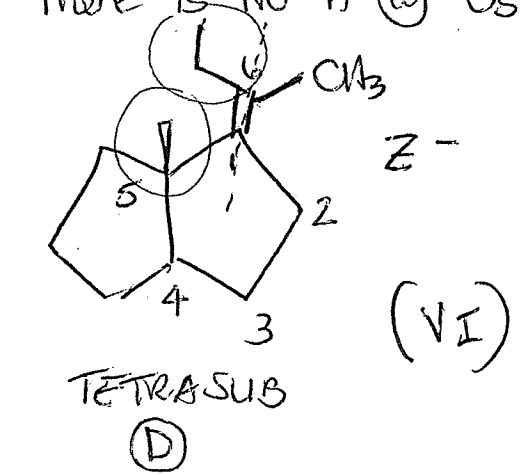
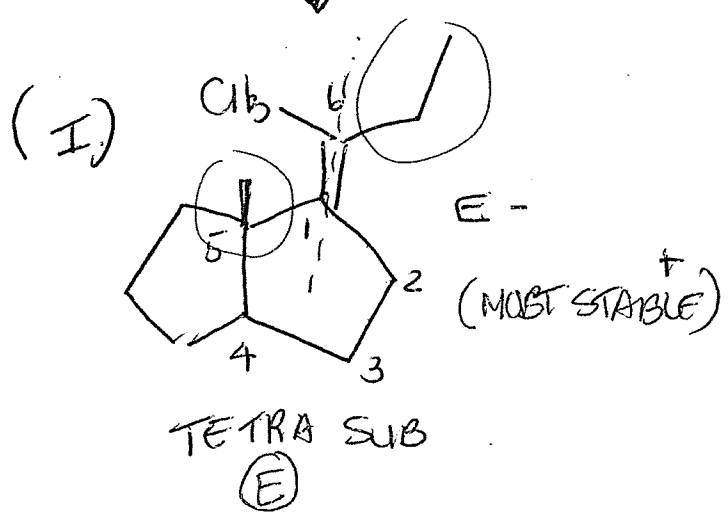
(C)

4. This is an E₁ mechanism. (A)

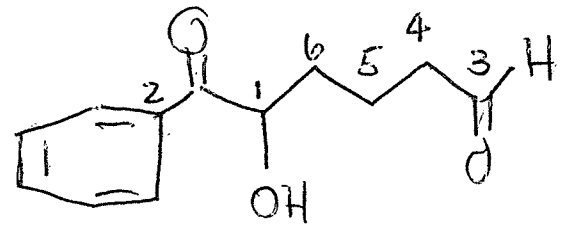
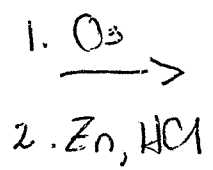
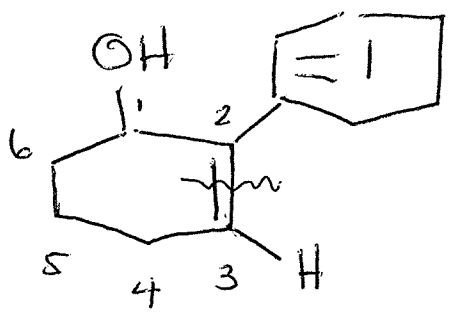


There are two H from C₂ (H_A) and C₆ (H_B) that can give up electrons to form alkene product. H_B gives rise to E⁻ and Z-alkene products

There is NO H @ C₅

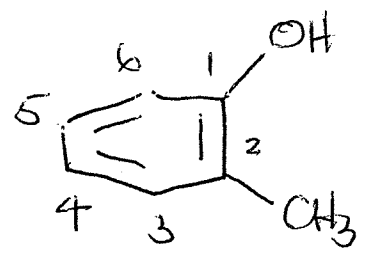


5.

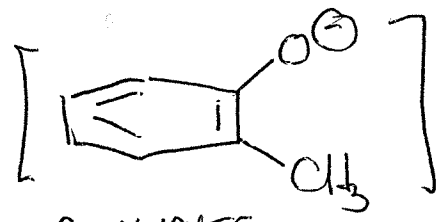


No correct answer given. Should be II.
 Credit for all.

6.



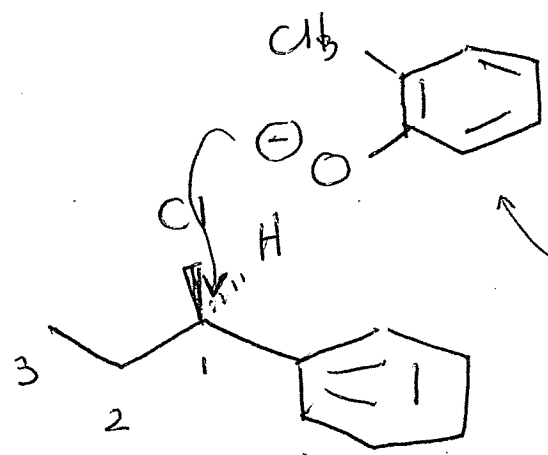
2-METHYLPHENOL



CONJUGATE BASE

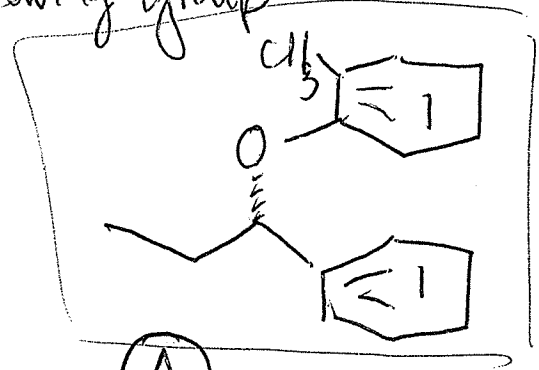
This is the Nu: in the S_N2 reaction with IR-chloro-1-phenylpropane

(WILLIAMSIN ETHER SYNTHESIS)



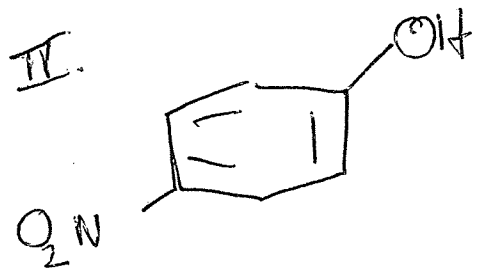
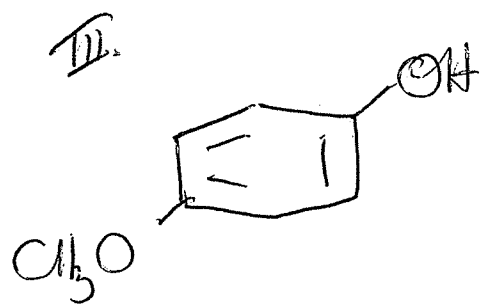
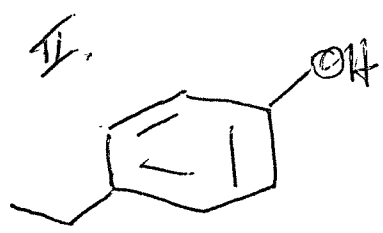
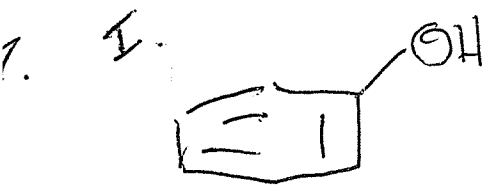
IR-chloro-1-phenylpropane

Nu: attacks from 180° away from Cl leaving group.

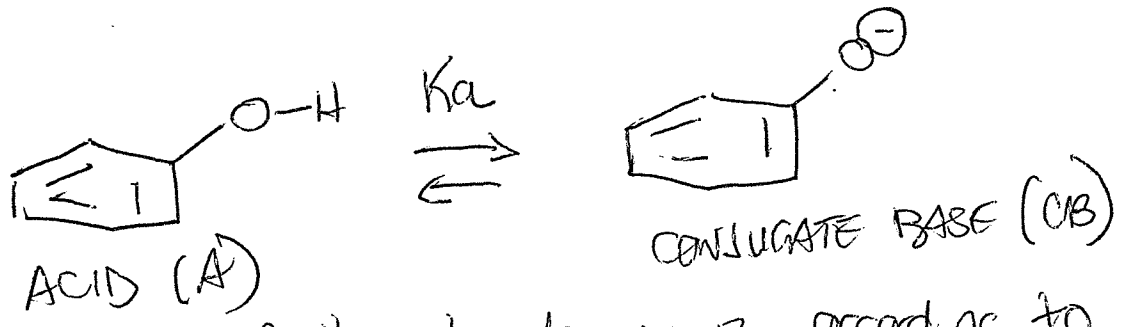


(A)

7.



MOST ACIDIC = LOWEST pKa



All four of the phenols ionize according to the scheme above. The more stable the CB, the higher the concentration of CB (i.e. $\uparrow [CB]$)

If $K_a = \frac{[CB]}{[A]}$ then $\uparrow [CB], \uparrow K_a$

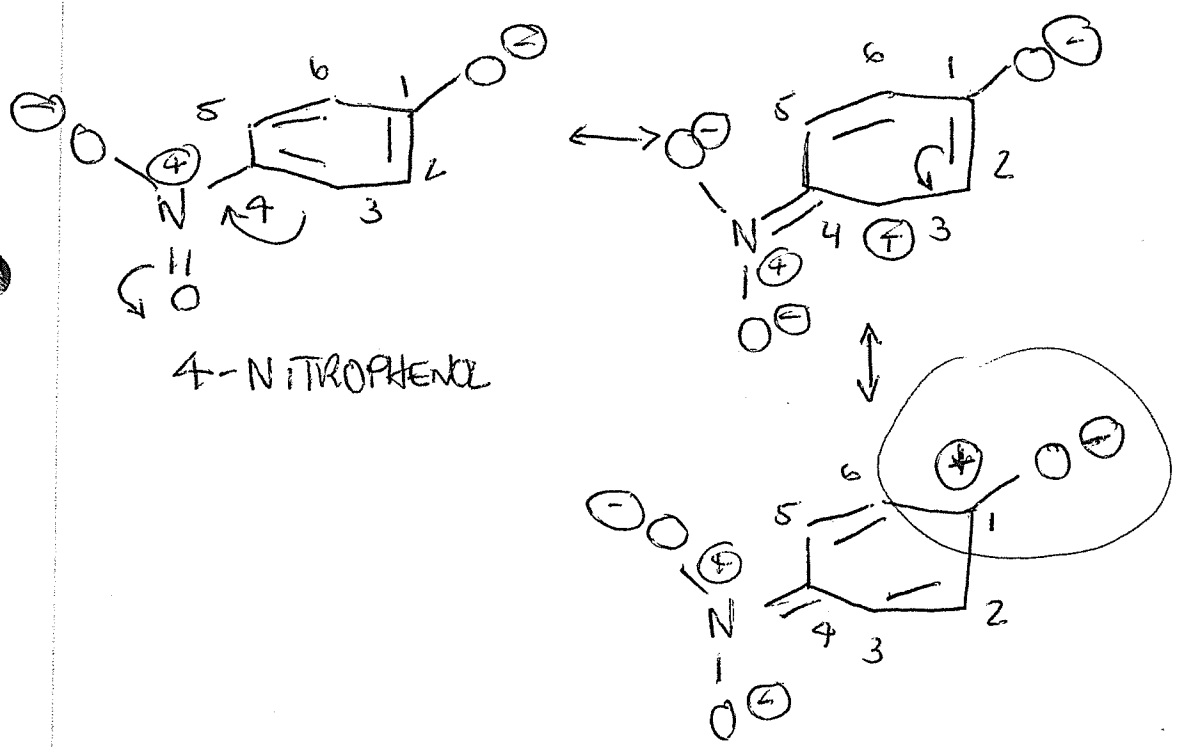
K_a is INVERSELY proportional to pKa $pKa = -\log K_a$

So, $\uparrow K_a, \downarrow pKa$ STRONGER ACID (MOST ACIDIC)

7. (CONT'D)

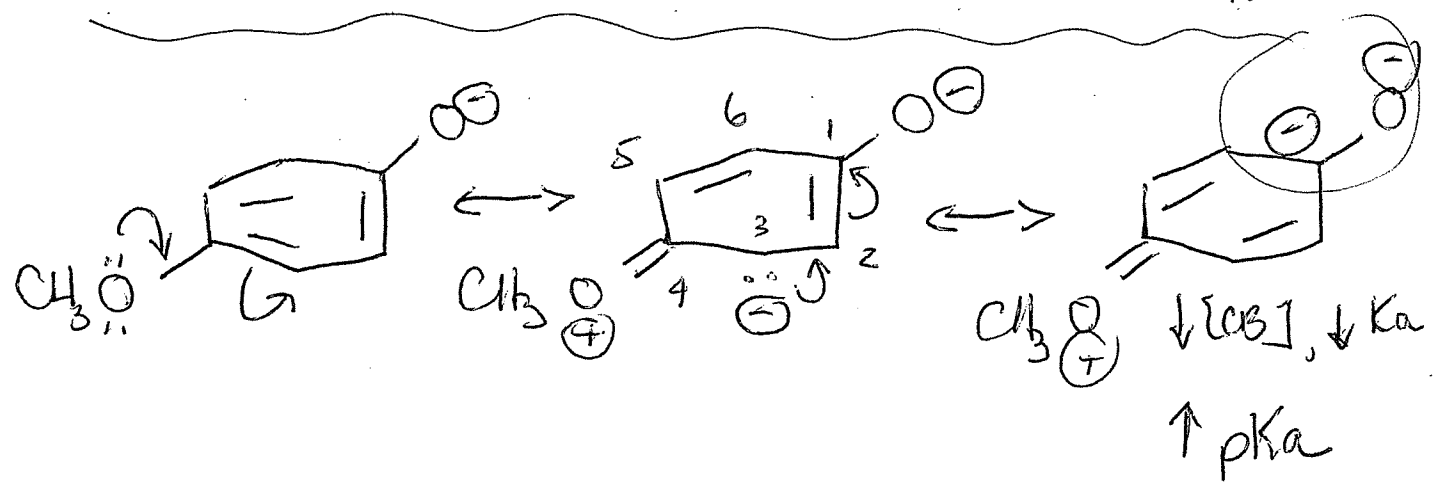
If the ring of the phenol has positive character (\oplus), it will stabilize the conjugate base (i.e. \oplus stabilizes \ominus of OB)

The substituents on the benzene ring can influence the \oplus or \ominus character of the ring via RESONANCE



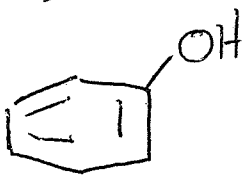
STABILIZING
 \uparrow [OB] \uparrow K_a
 \downarrow pKa

DESTABILIZING

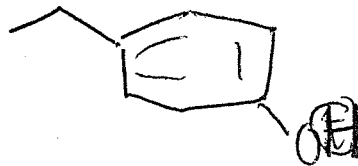


\downarrow [OB], \downarrow K_a
 \uparrow pKa

(CONT'D)



Phenol and Ethyl
Phenol do not
have a major effect
however the ethyl
group has a slight
"dehydrating" effect
(\ominus)



4-NITRO
(IV)

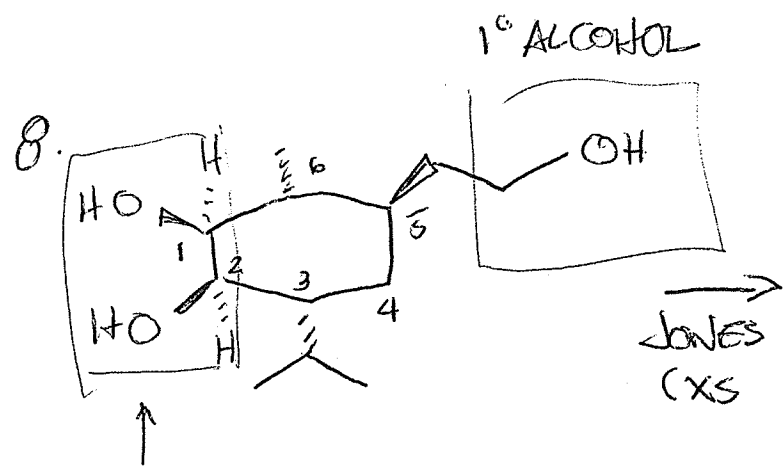
MOST STABILIZING
LOWEST pKa
MOST ACIDIC

4-METHOXY
(III)

MOST DE-STABILIZING
HIGHEST pKa
LEAST ACIDIC

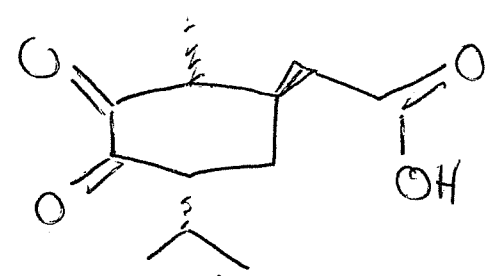
IV > I > II > III

(C)

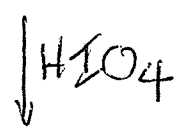


CIS-DIOL
(BOTH ARE 2°)

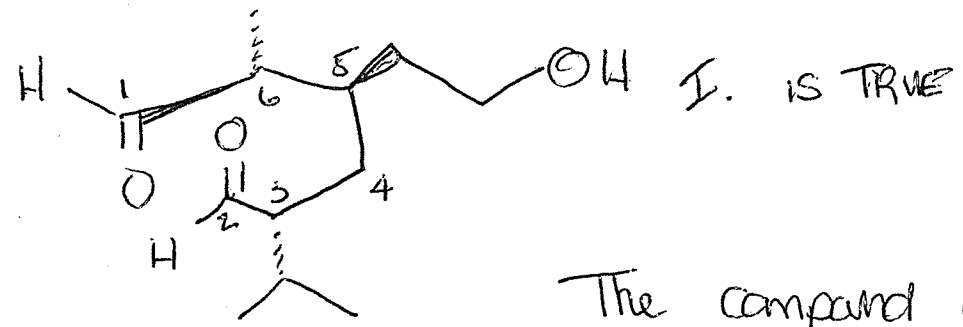
II IS FALSE



ONLY ONE PRODUCT IS FORMED
(Only one product forms w/ excess or one equiv)



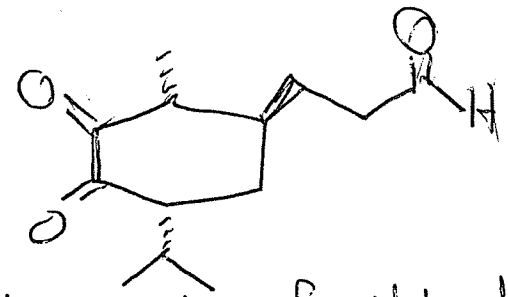
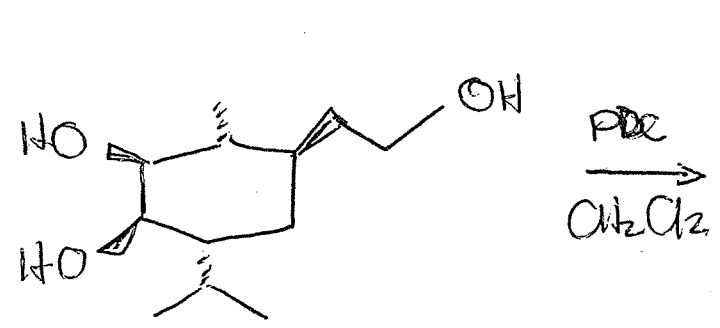
HIO₄ cleaves cis-diol to di-aldehyde. Nothing happens to the 1° Alcohol



- I. TRUE
- II. FALSE
- III. FALSE
- IV. TRUE

(E)

The compound contains
ONE 1° ALCOHOL
TWO 2° ALCOHOLS
III IS FALSE

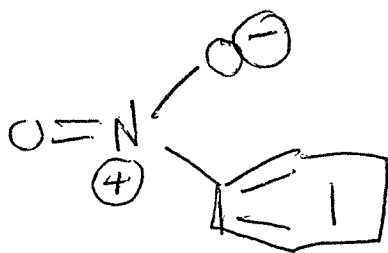


No H-atoms for H-bonding

At pH = 2

Any compound that contains an AMINE can undergo ion-dipole interactions. Only a) and b) contain amines so c) can be ruled out.

NOTE: -NO₂ IS NOT an AMINE



It does not ionize at pH = 2 but it does have formal charges that could participate in ion-dipole interactions

At pH = 7

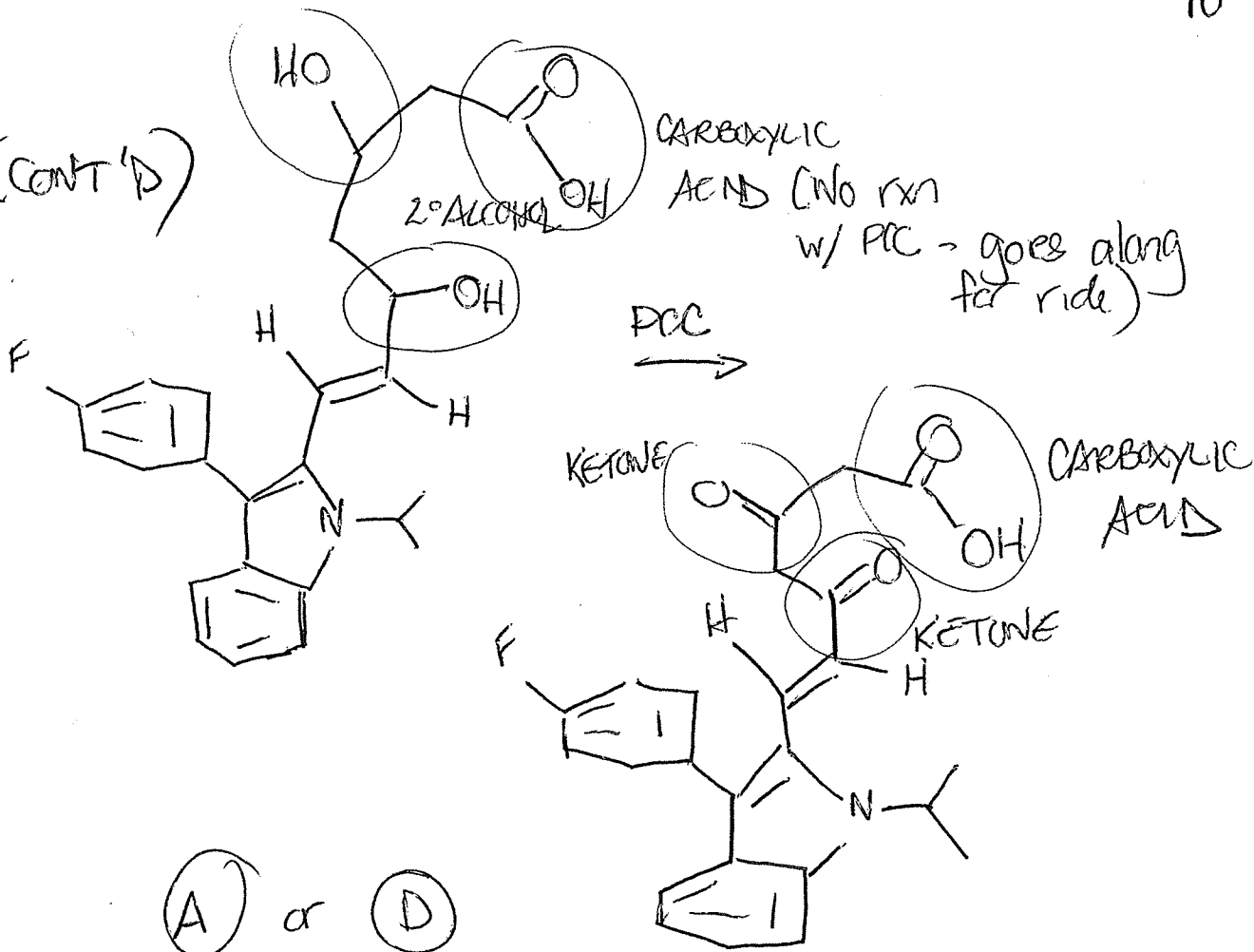
Any compound that contains a carboxylic acid (pKa ~ 4-6) will ionize and can participate in ion-dipole interactions. Phenols and alcohols do NOT IONIZE @ this pH. b) can be ruled out.

Both a) and d) contain E- alkenes.

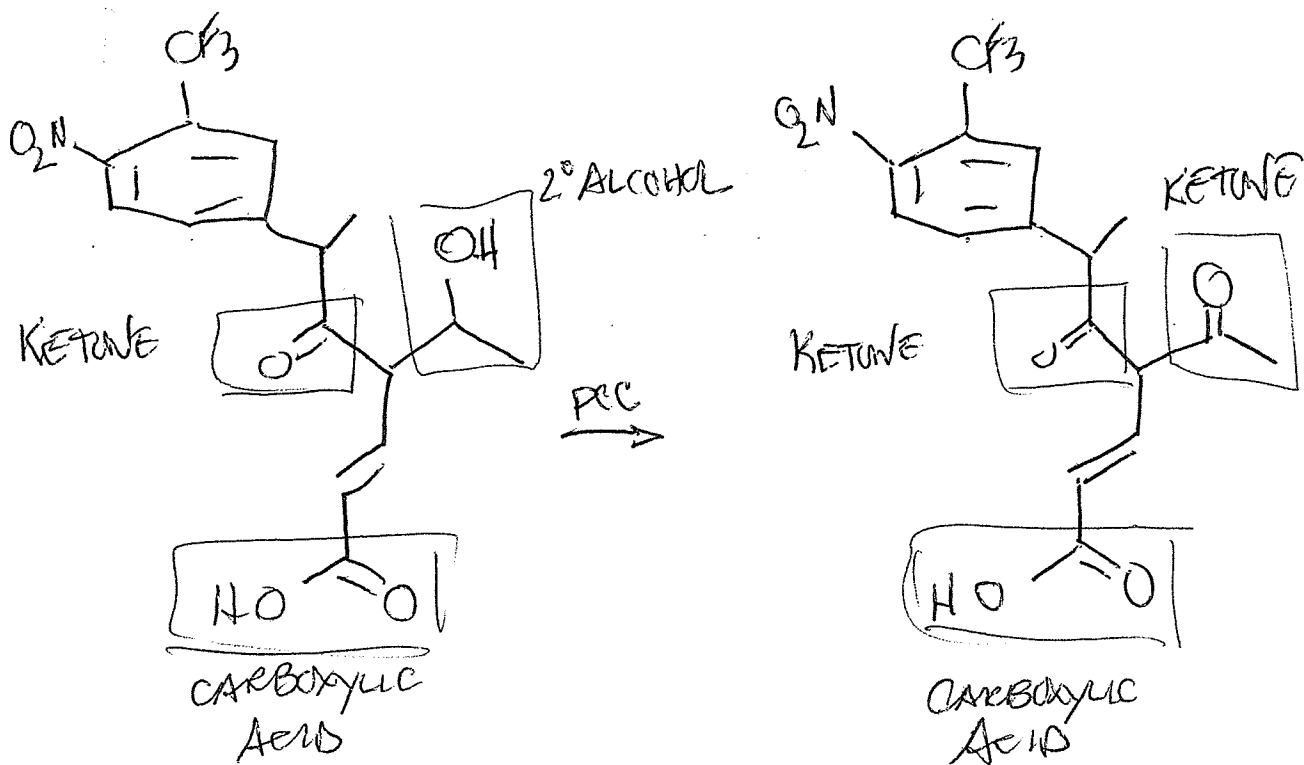
2° ALCOHOL

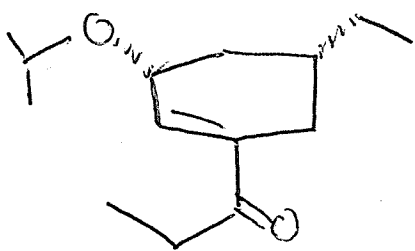
9. (CONT'D)

c)

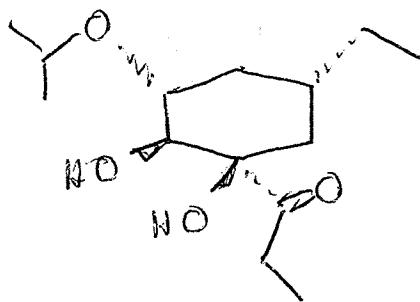


d)

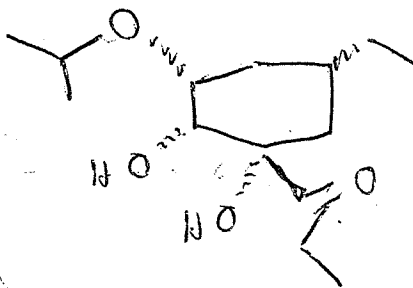




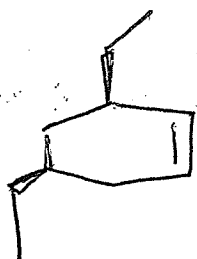
cold, basic
 $\xrightarrow{\text{KMnO}_4}$



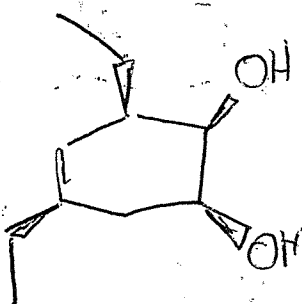
DIASTEREOMERS



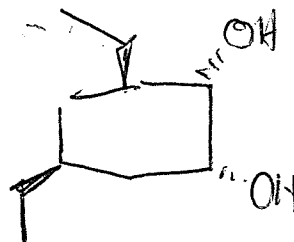
(C)



cold, basic
 $\xrightarrow{\text{KMnO}_4}$

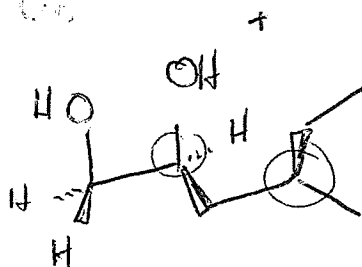
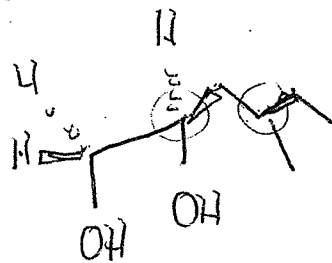
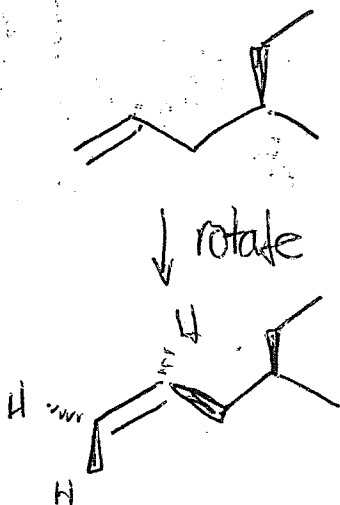


DIASTEREOMERS

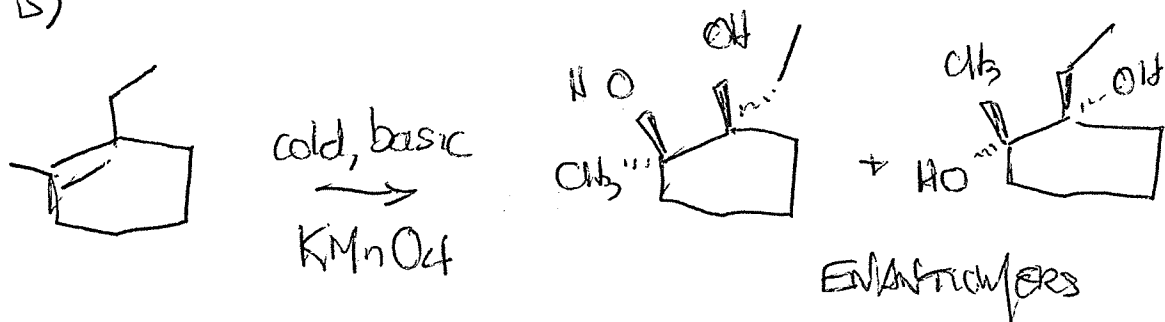


DIASTEREOMERS

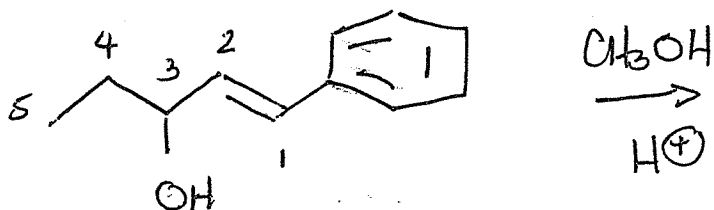
cold, basic
 $\xrightarrow{\text{KMnO}_4}$



10. (CONT'D)

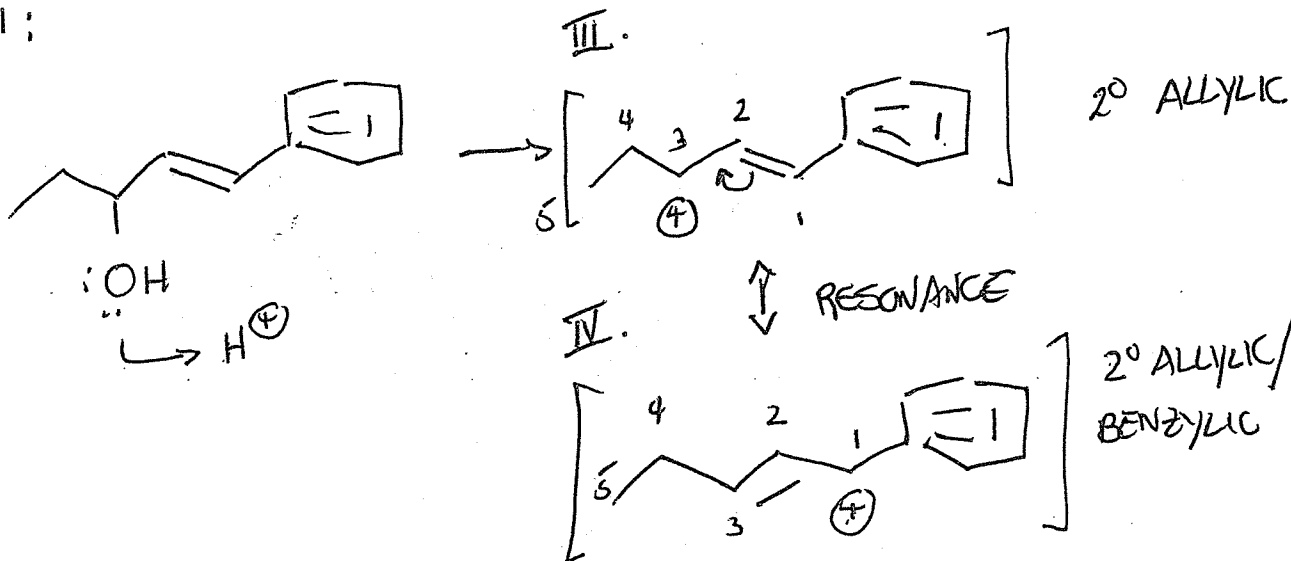


11.



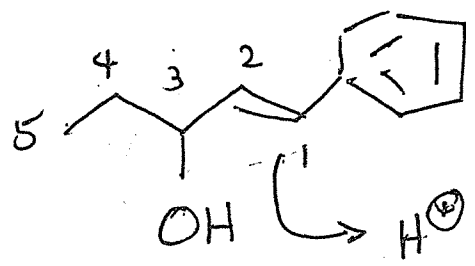
In the presence of H^+ and a Nu: (i.e. CH_3OH) the reaction can be $\text{S}_{\text{N}}1$ or Electrophilic addition

$\text{S}_{\text{N}}1$:

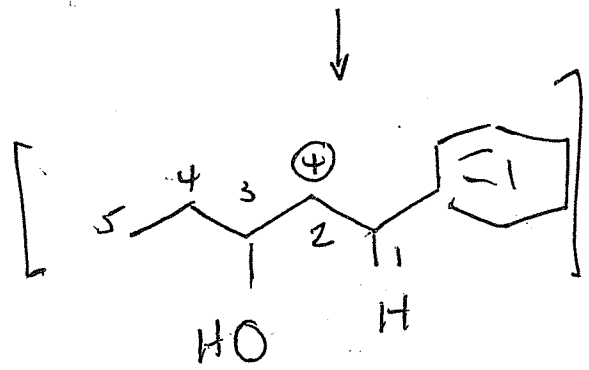


1. (cont'd)

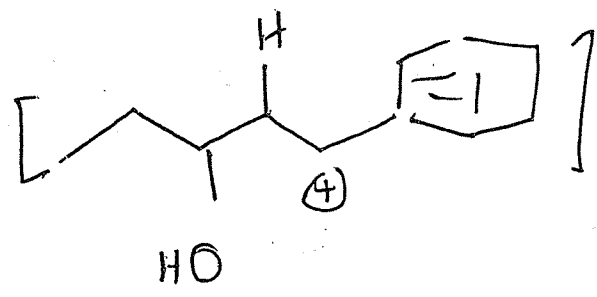
ELECTROPHILIC ADDITION



III.

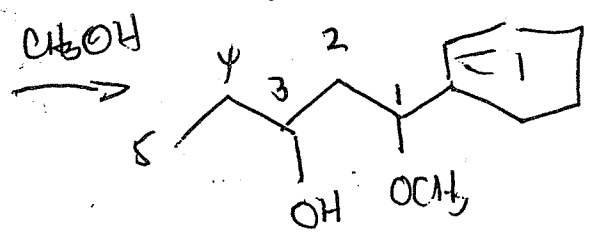


IV.

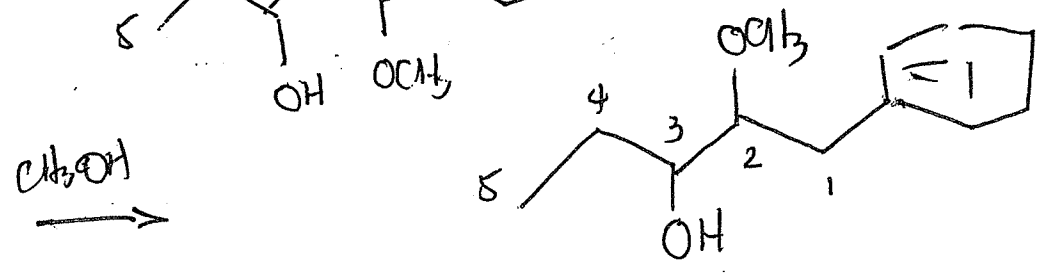


I, II, III & IV are carbocations, each that leads to a product. The major THERMODYNAMIC product(s) is the most stable product(s), regardless of the carbocation from which it is derived.

I.



II.

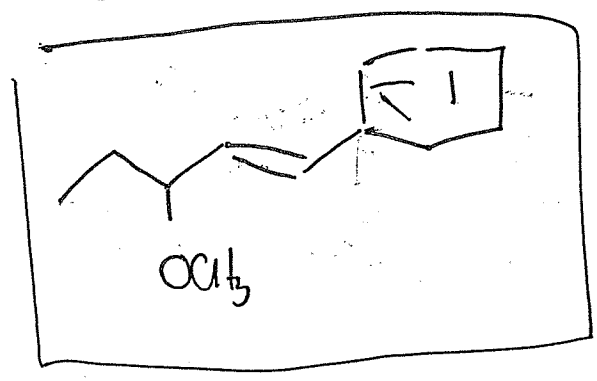
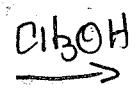


11. (cont'd)

CONJUGATED, DISUBSTITUTED

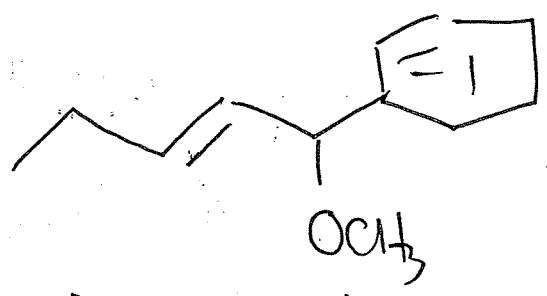
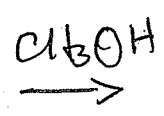
(D)

III



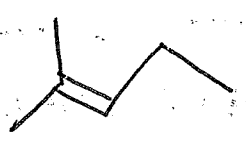
MOST STABLE
THERMO
PRODUCT

IV

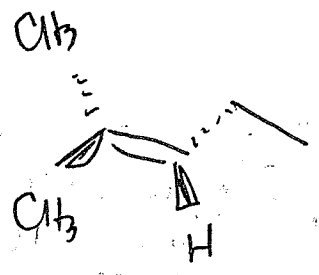


DISUBSTITUTED
NOT CONJUGATED

12. I.

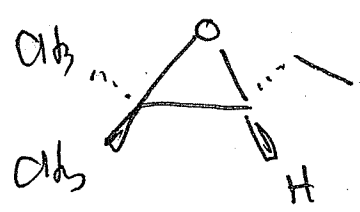


rotate →

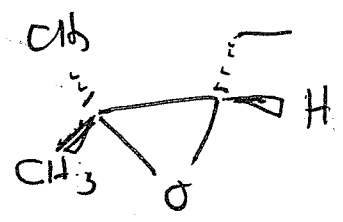


(TOP)

(BOTTOM)

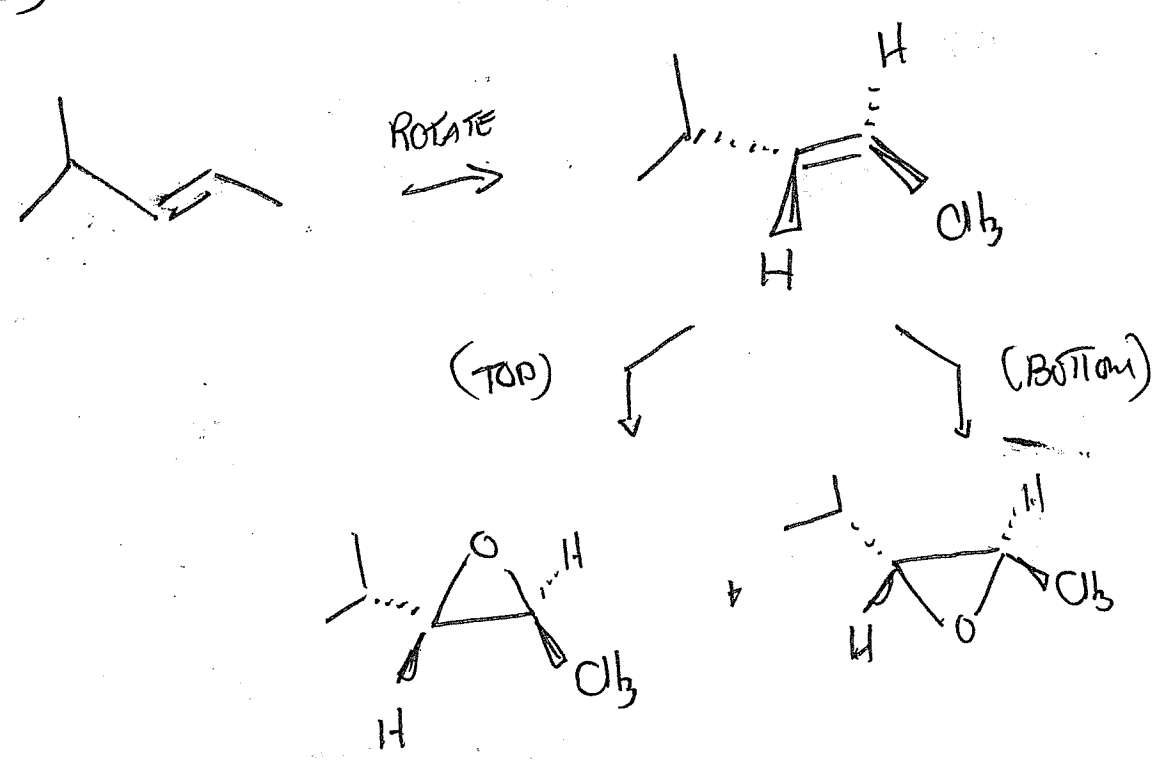


+



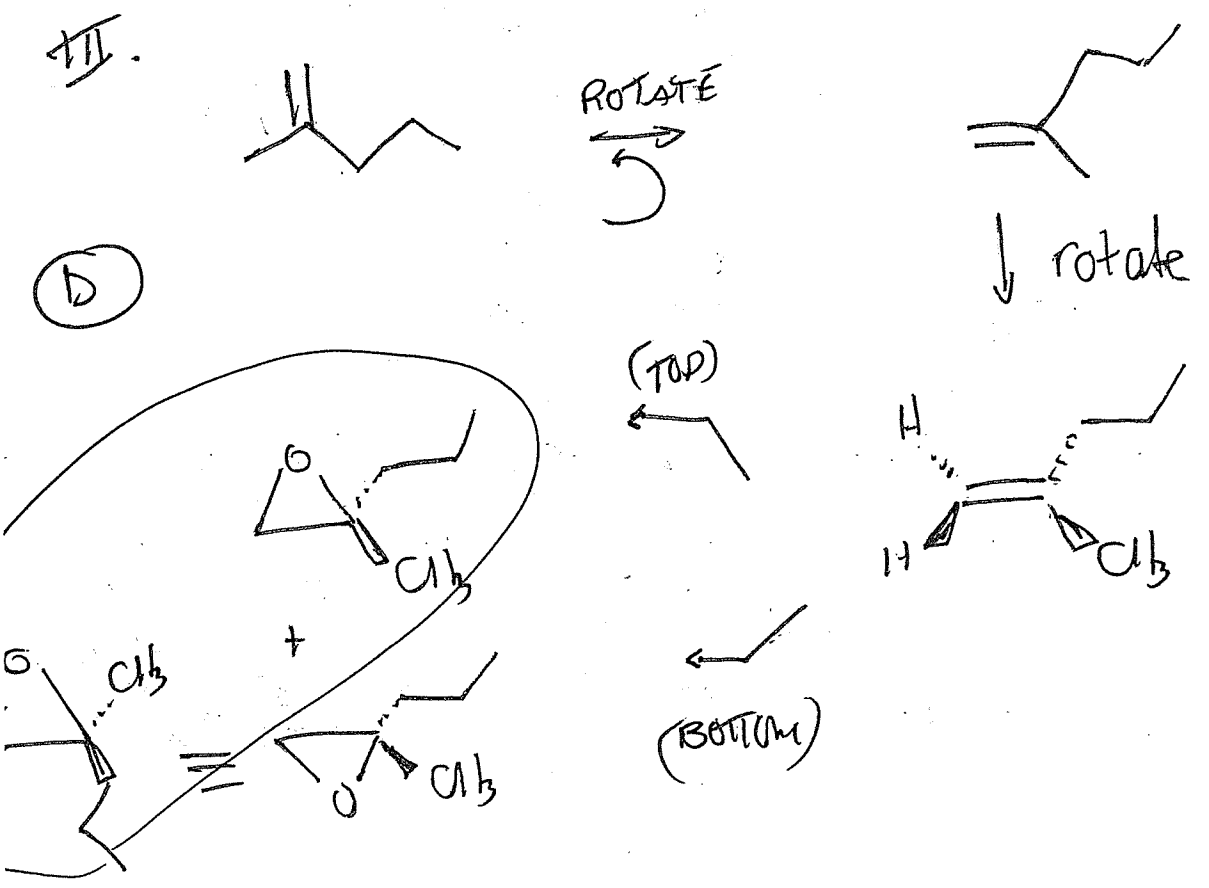
.. (CONT'D)

II.

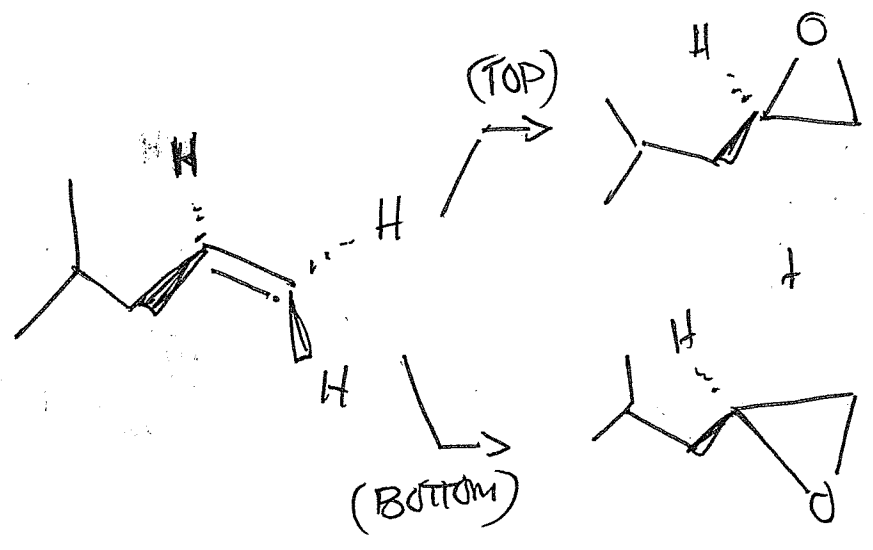


III.

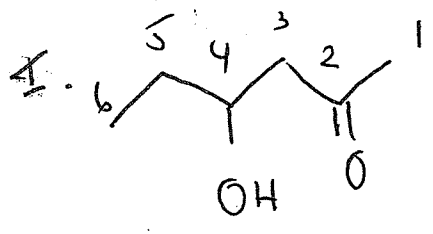
(D)



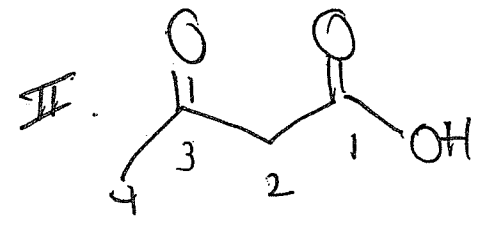
12. (cont'd)



13.

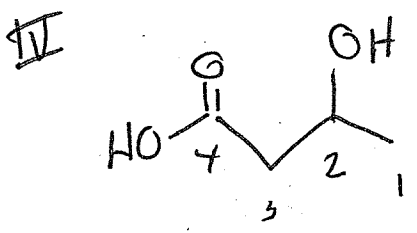


C₂: 2 oxygen
 C₄: 1 oxygen
 1 hydrogen

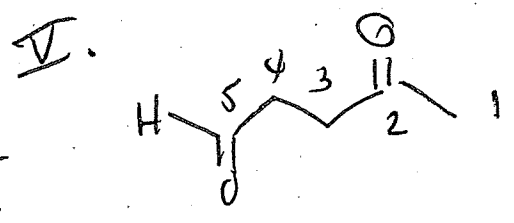


C₁: 3 oxygen
 C₃: 2 oxygen

II > I



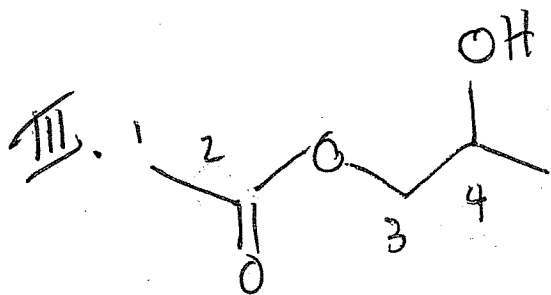
C₂: 1 oxygen
 1 hydrogen
 C₄: 3 oxygen



C₂: 2 oxygen
 C₅: 2 oxygen
 1 hydrogen

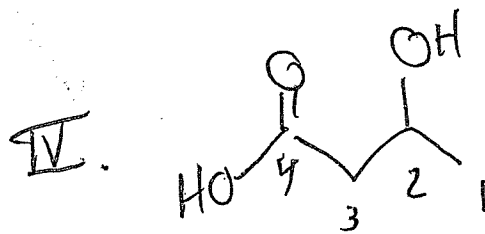
III = IV

3. (CONT'D)



C₂: 3 OXYGEN

C₄ 1 OXYGEN
1 HYDROGEN



C₄ 3 OXYGEN

C₂ 1 OXYGEN
1 HYDROGEN



(A)

4. At pH = 12, any ACIDIC FUNCTIONAL group with a pK_a < 10 will be ~100% ionized (i.e., in its conjugate base form)

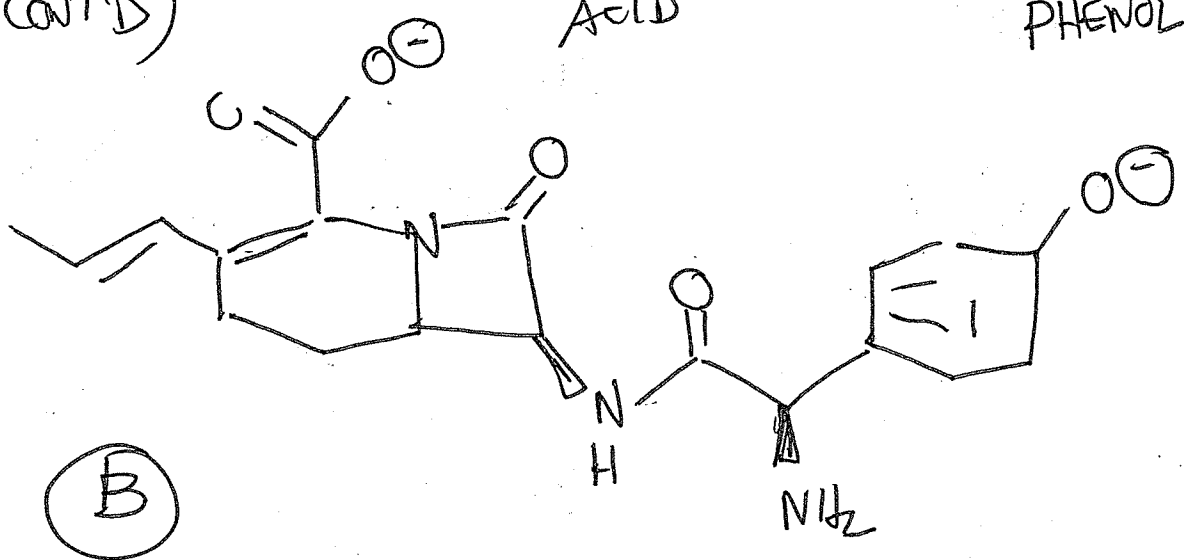
This means PHENOLS (pK_a ~ 8-10) and CARBOXYLIC ACIDS (pK_a ~ 4-6) will be ionized.

ALCOHOLS will NOT ionize at this pH b/c their pK_as 15-20.

14. (CONT'D)

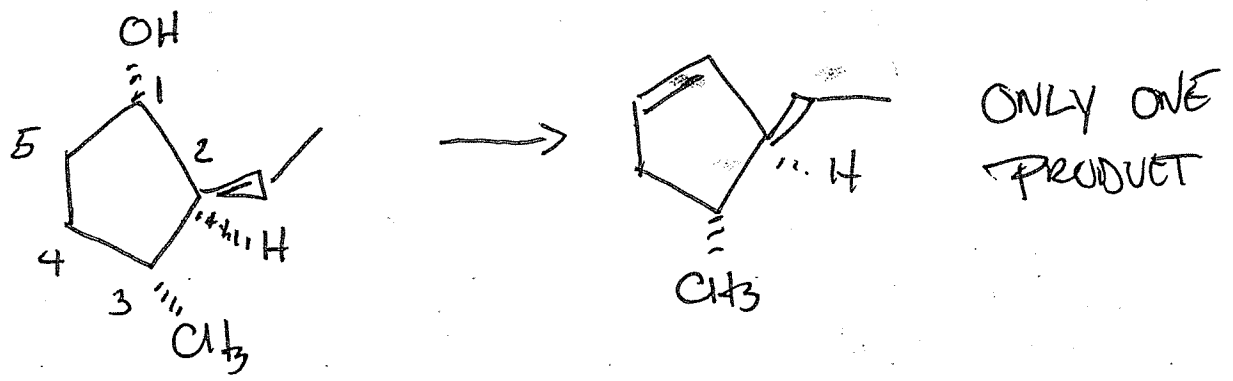
CONJUGATE ACID
OF CARBOXYLIC
ACID

CONJUGATE BASE OF
PHENOL



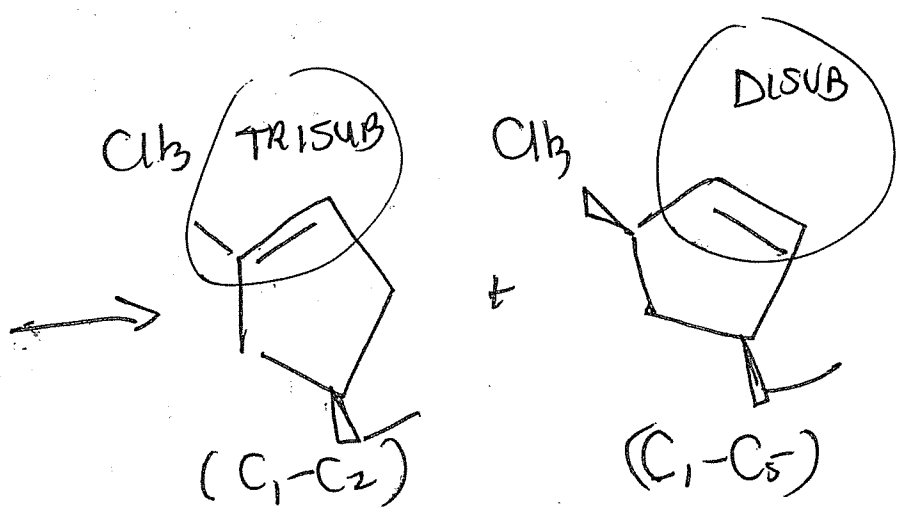
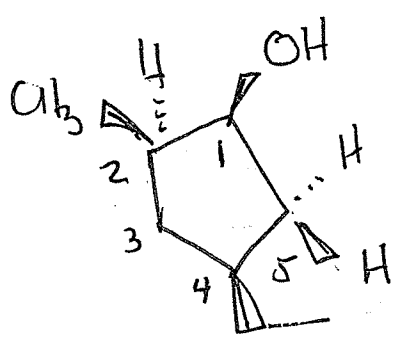
(B)

15. This is an E₂ reaction. OH group will become the LG, and it must be TRANS to H on adjacent sp³ carbon in order for E₂ to occur.



No E₂ across
C₁-C₂, only
C₁-C₅

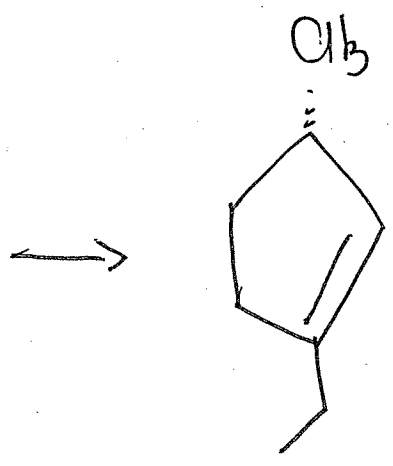
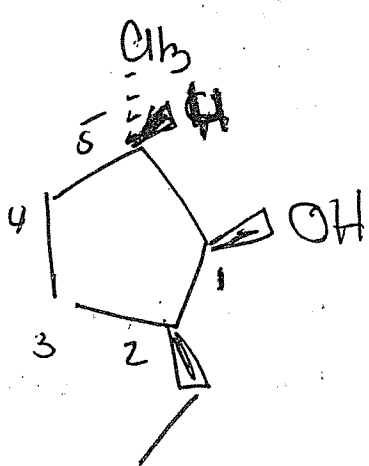
5. (CONT'D)



E₂ can occur across both C₁-C₂ and C₁-C₅

ONLY THERMO PRODUCT MORE STABLE

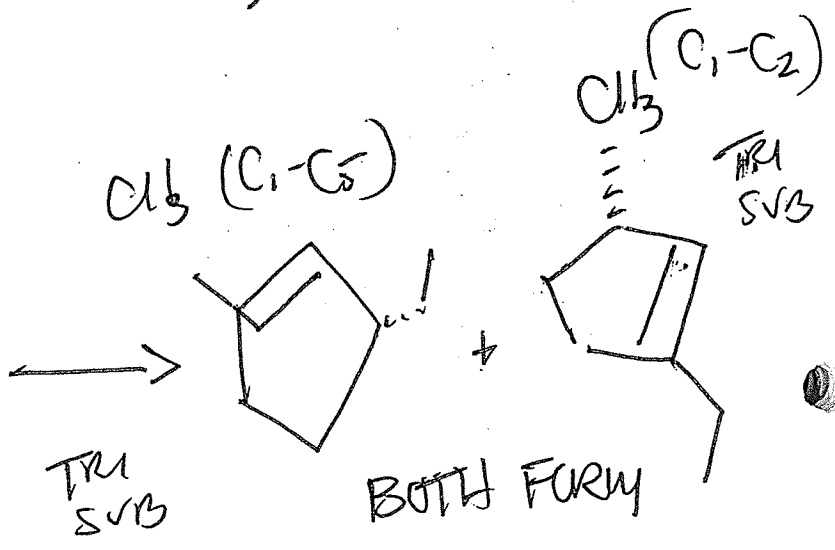
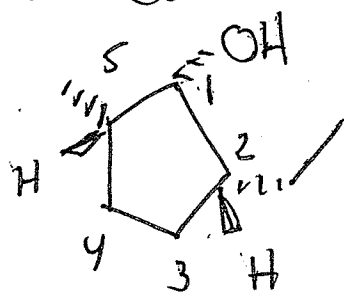
I.



ONLY ONE PRODUCT

E₂ only across C₁-C₂ not C₁-C₅

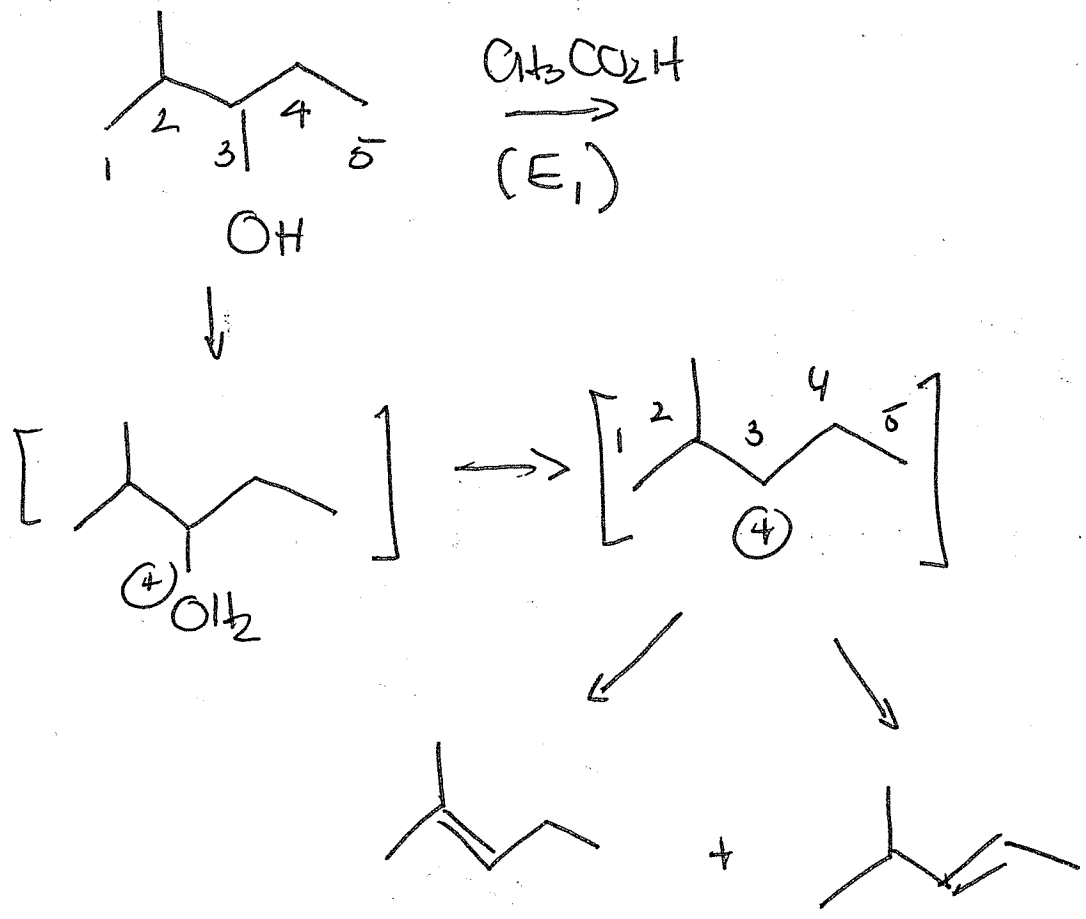
II.



BOTH FORM

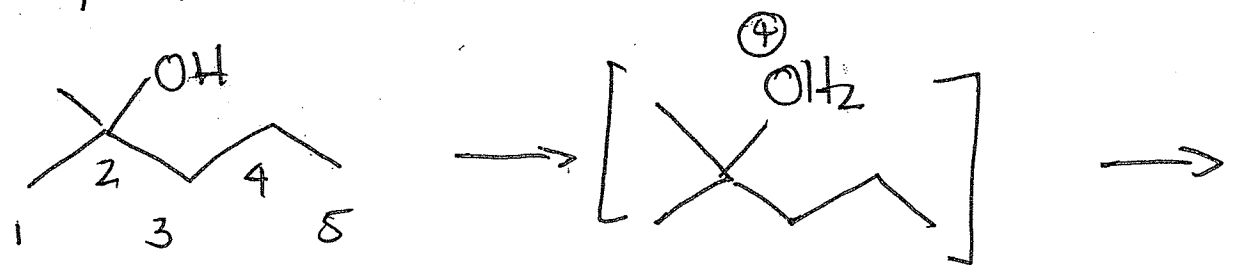
16. 2-METHYL-3-PENTANOL

I

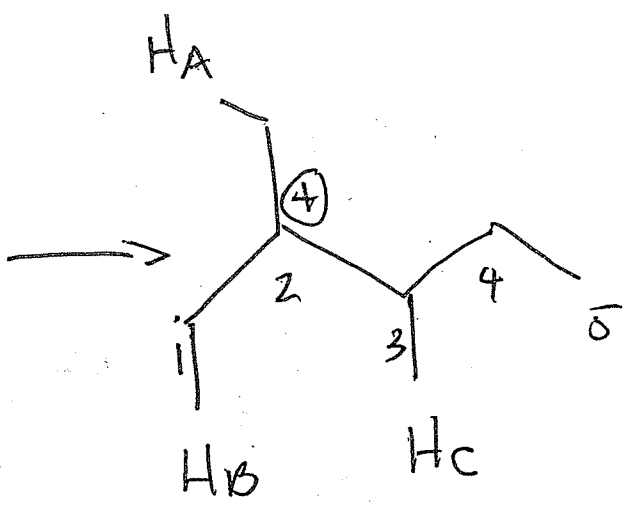
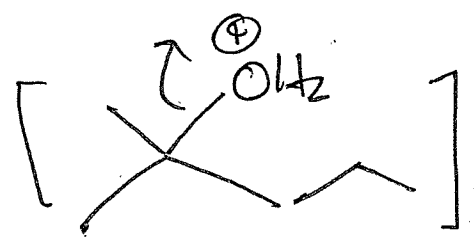


BOTH ARE KINETIC PRODUCTS
(DERIVED FROM SAME C⁺)

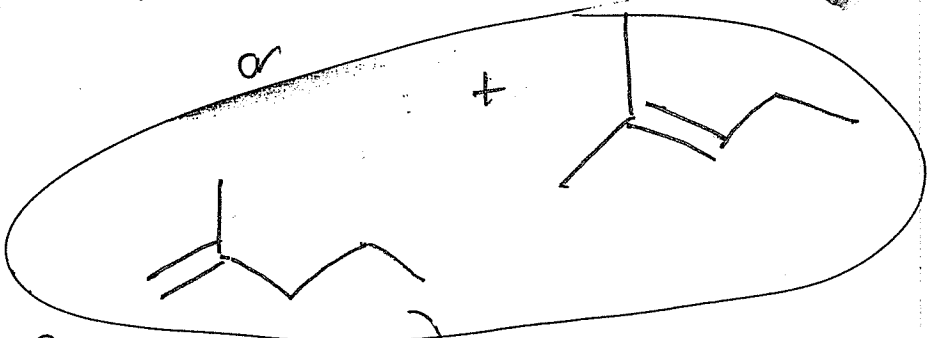
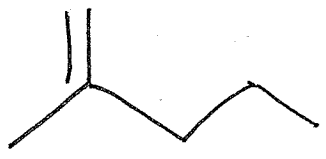
II. 2-METHYL-2-PENTANOL



(CONT'D)



There are 3 hydrogens on adj. sp^3 carbons. But HA and HB give SAME product



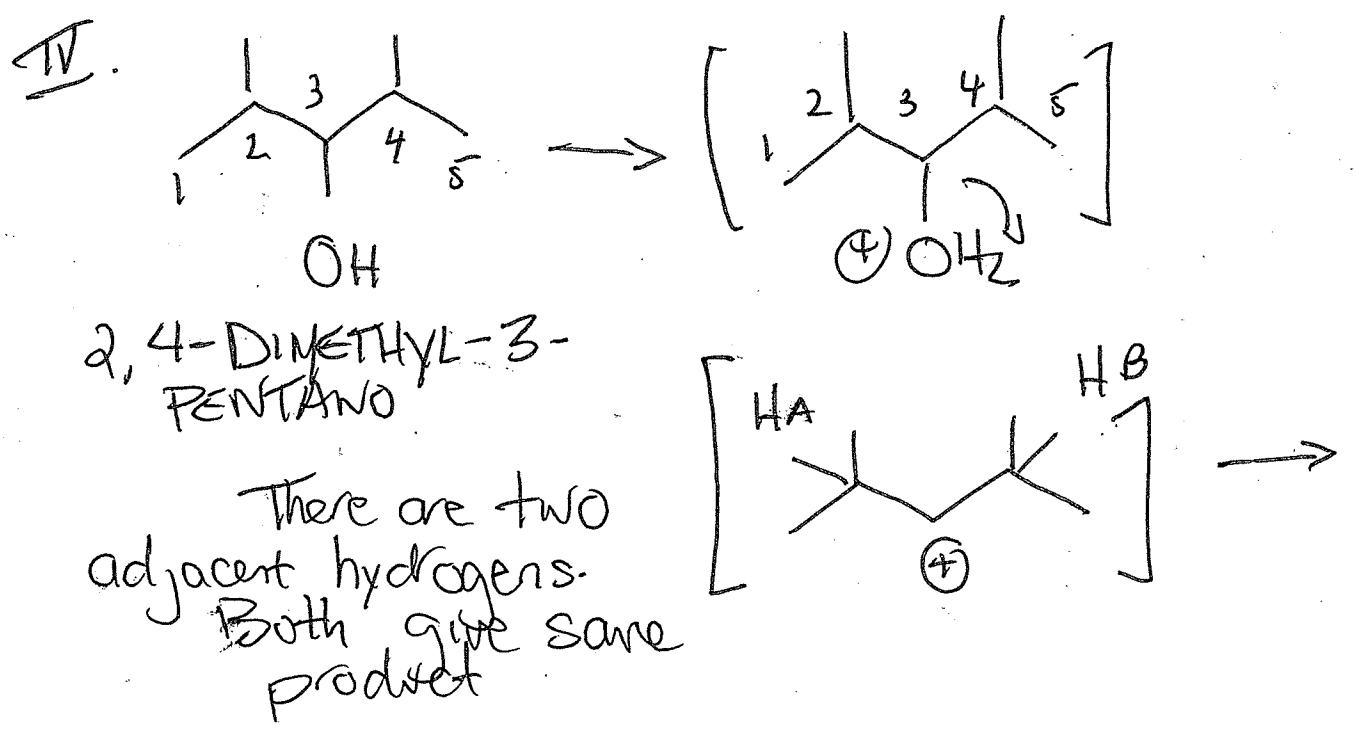
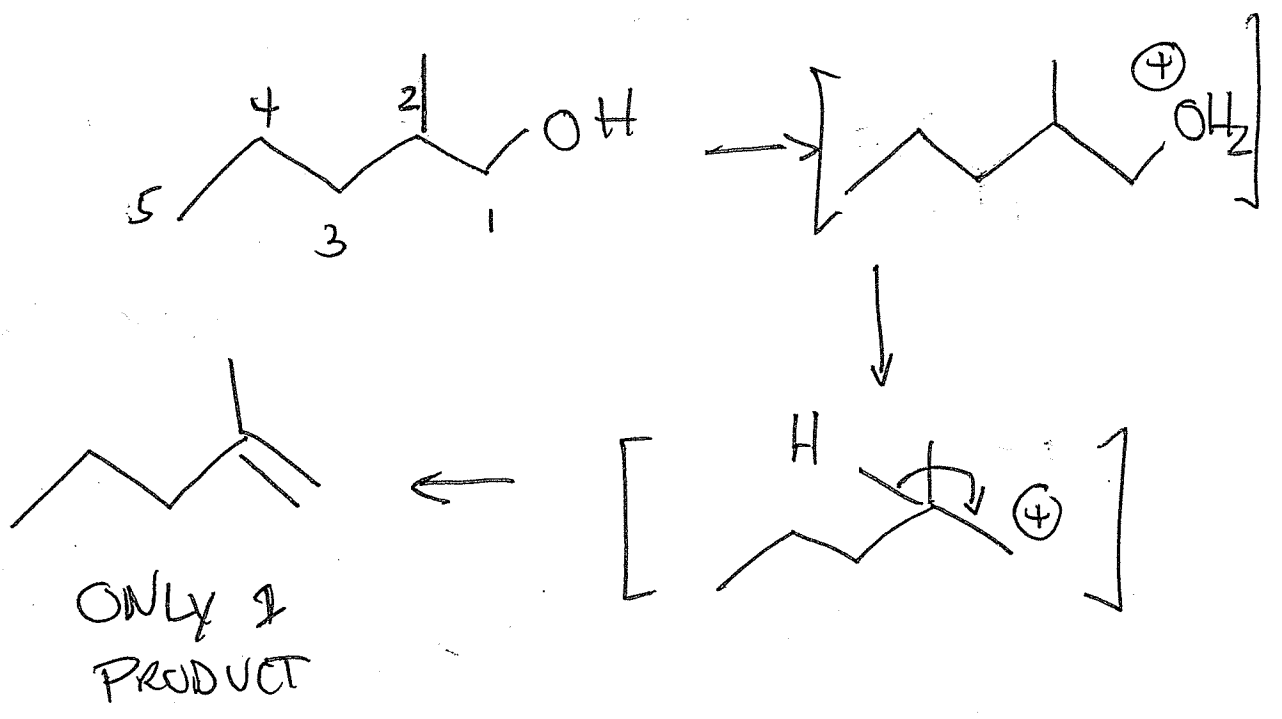
(These are same)

Two products derived from same carbocation

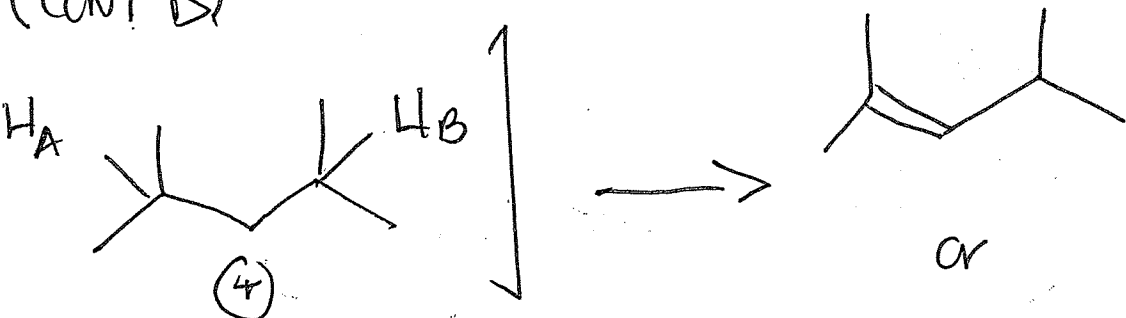
Two KINETIC PRODUCTS

16. (CONT'D)

III. 2-METHYL-1-PENTANOL



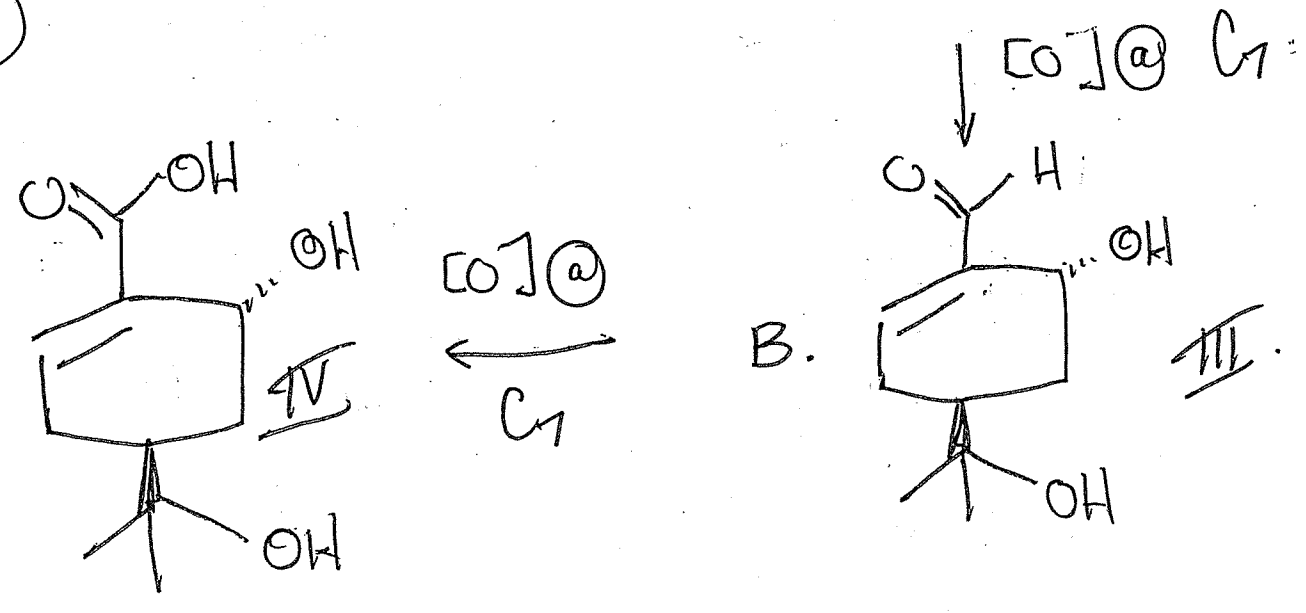
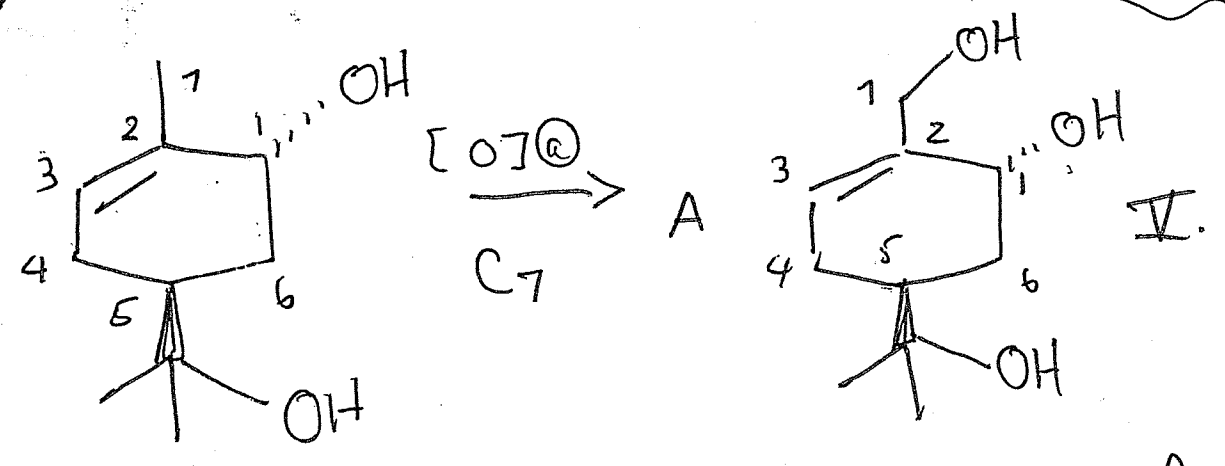
(CONT'D)



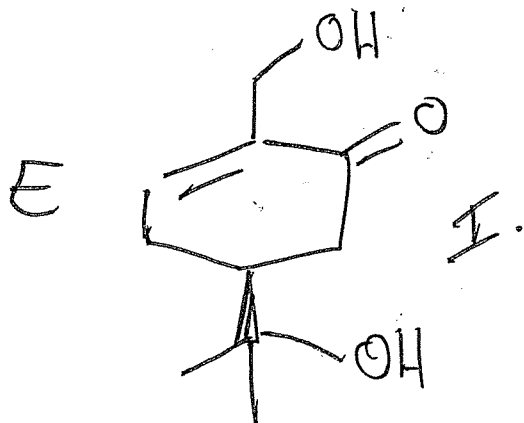
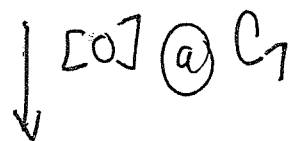
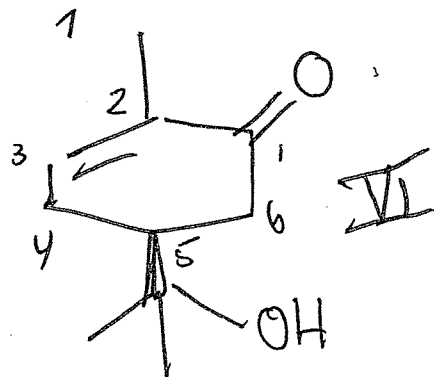
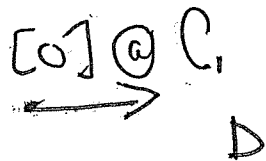
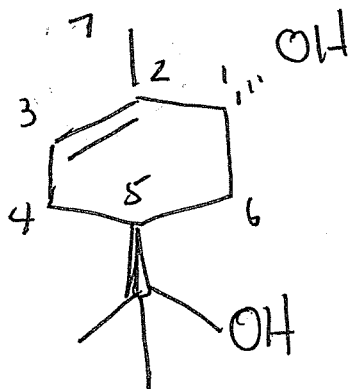
(B)

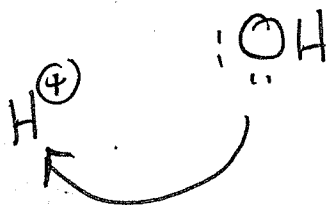
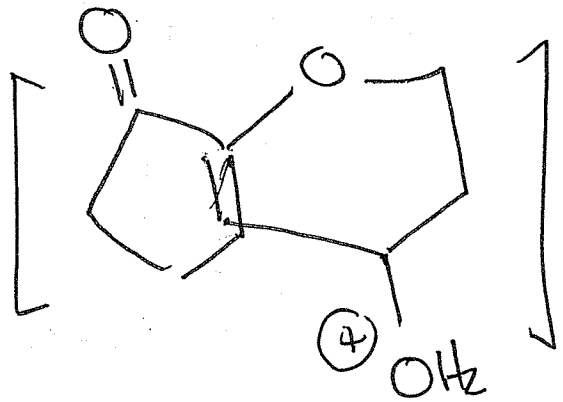
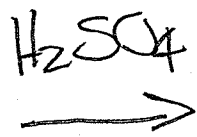
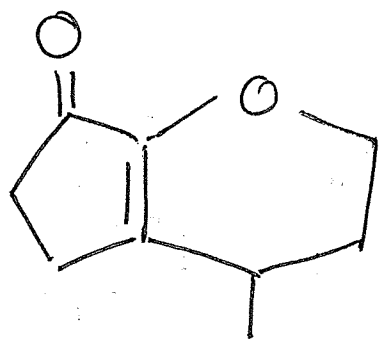


SAME PRODUCT



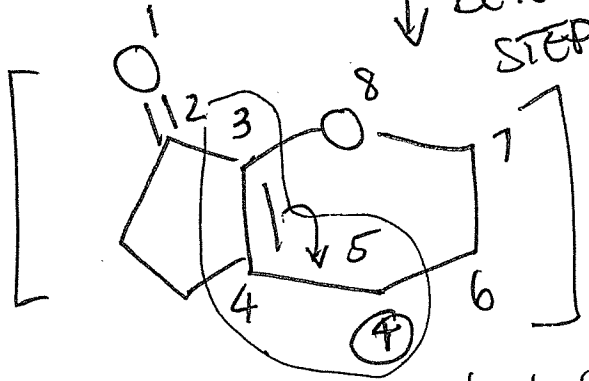
17. (CONT'D)



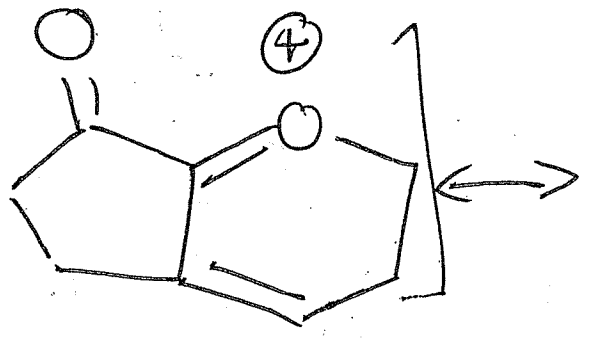


RATE DETERMINING STEP

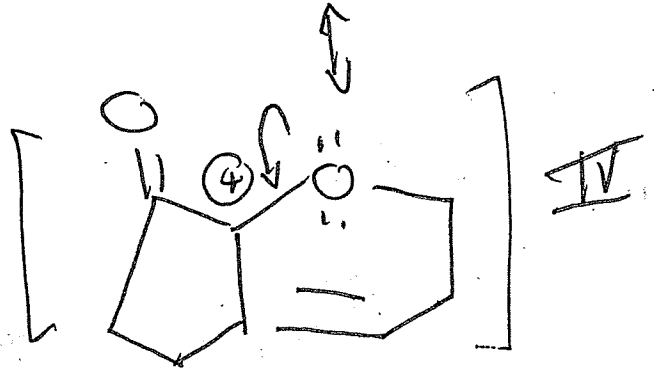
↓



RESONANCE INVOLVING C_3, C_4, C_5

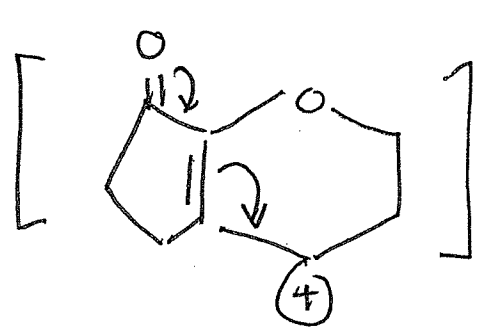


III



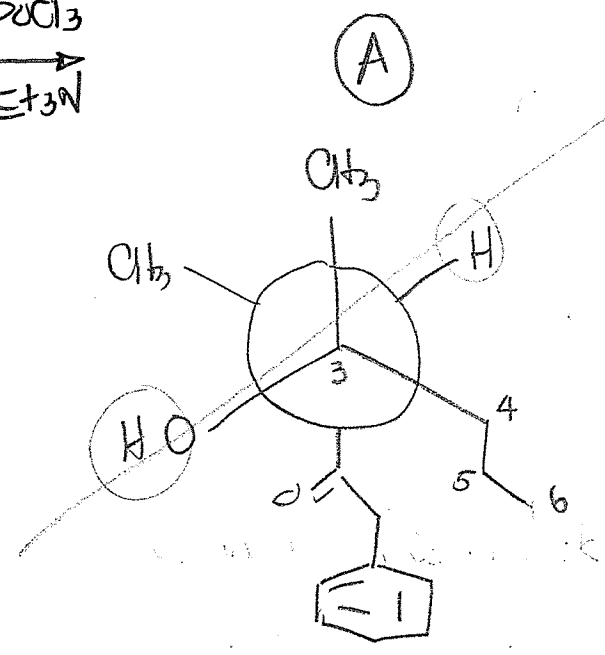
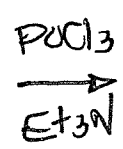
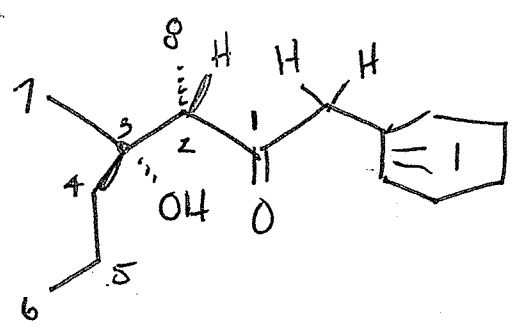
IV

18. (CONT'D)



This is NOT Allowed.
 If electrons will not move away from an electro negative oxygen

19.

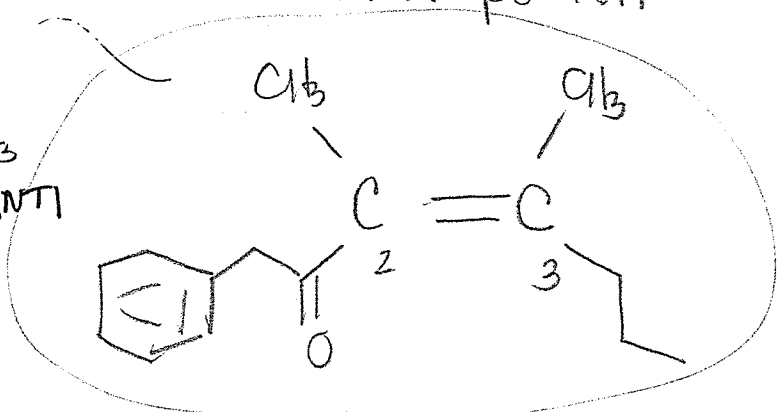


OH is the LG
 E2 can occur across
 C₃-C₄
 C₂-C₇
 C₂-C₃

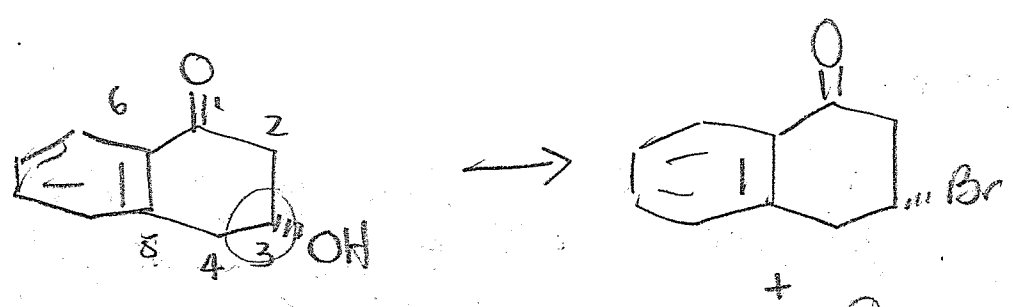
E2 across C₂-C₃
 will give THERMO product.

H and OH already in ANTI position

Newman projection must be across C₂-C₃ bond with H @ C₂ ANTI to OH @ C₃



20.

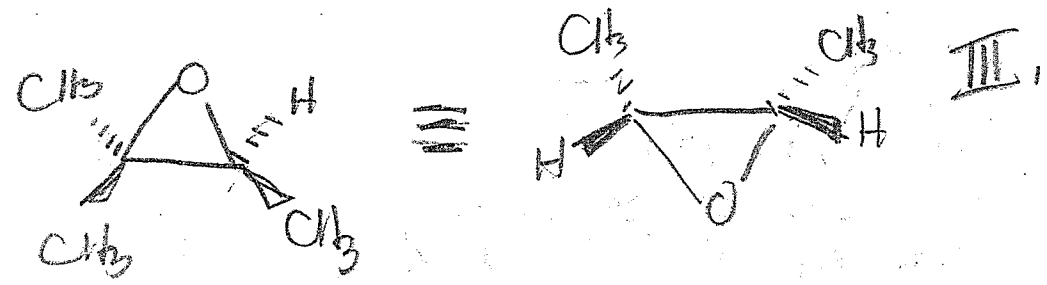
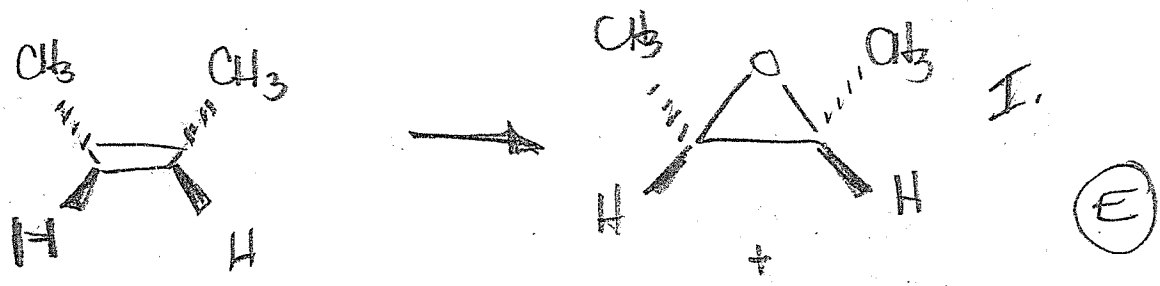


C₃ IS CHIRAL in starting material

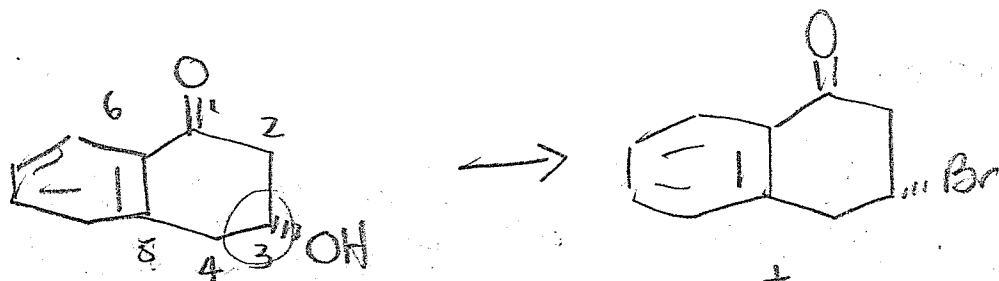
OH IS SUBSTITUTED with Br in product. Must be S_N1 or S_N2

Since Nu (Br) comes in from TOP + BOTTOM must be S_N1 only (A)

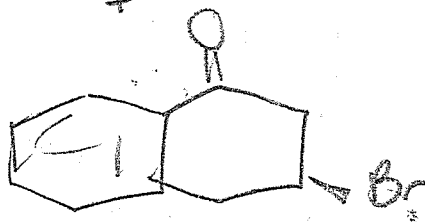
21.



O adds from TOP (I) and bottom (II) of alkene



C3 IS CHIRAL in starting material

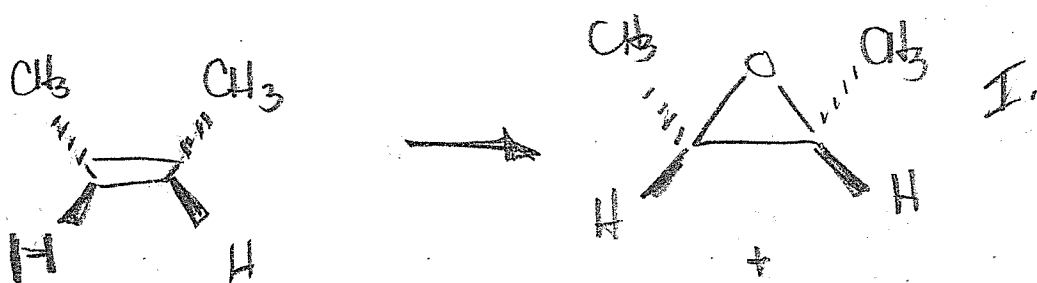


OH is SUBSTITUTED with Br in product.
Must be S_N1 or S_N2

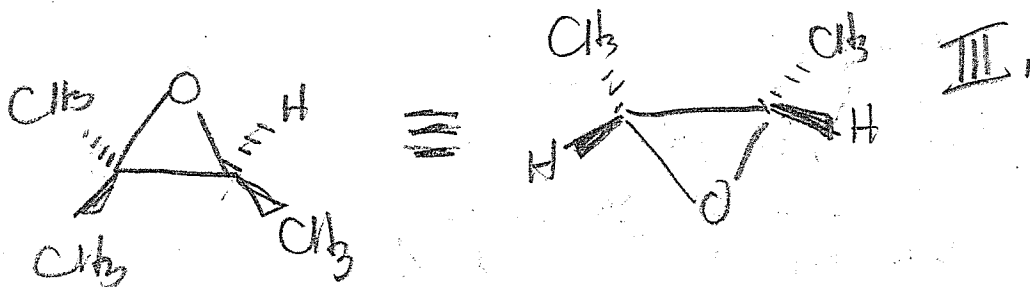
Since Nu (Br⁻) comes in from TOP + BOTTOM must be S_N1 only

(A)

173.

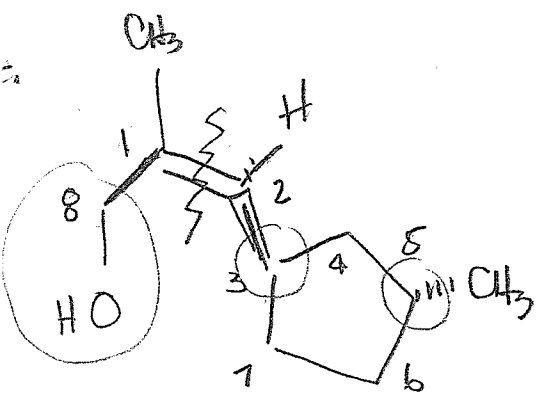


(E)

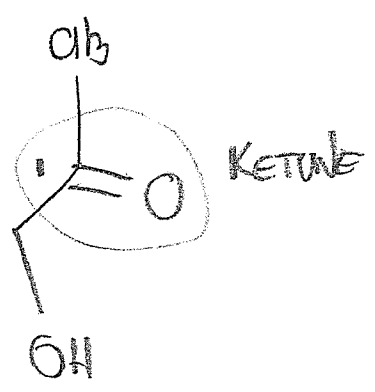


O adds from TOP (I) and bottom (III) of alkene

24.

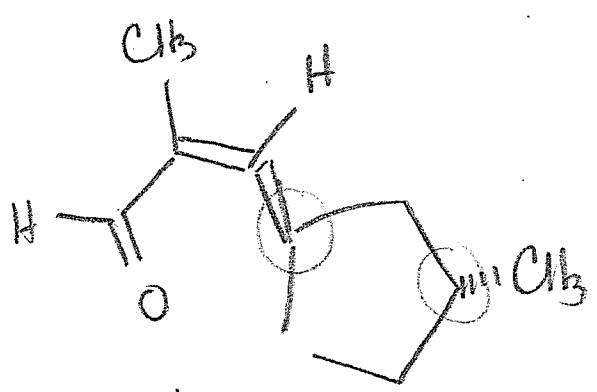
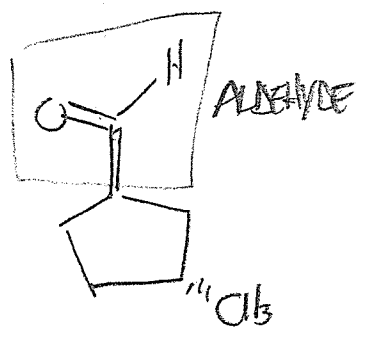


1, cold, basic KMnO_4
 \rightarrow
 2, HIO_4

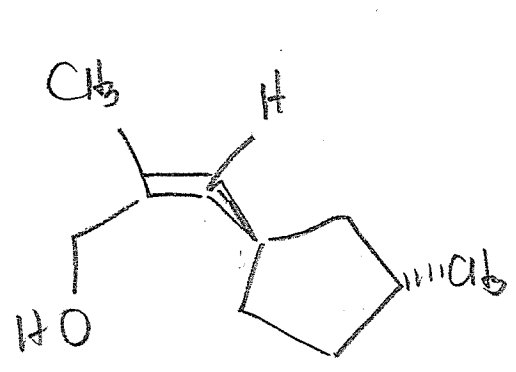


C_3 and C_5 are CHIRAL
TWO CHIRAL CENTERS

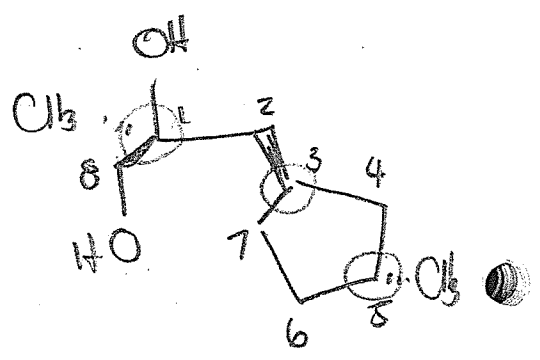
\downarrow PCC, CH_2Cl_2



Product has two
 chiral centers



H_3O^+
 \rightarrow



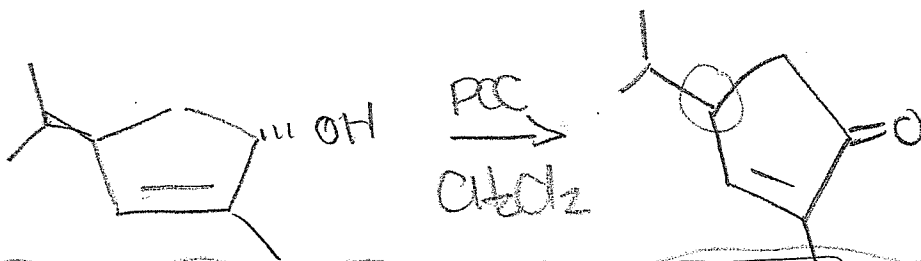
$\text{C}_1, \text{C}_3, \text{C}_5$ CHIRAL
 (3 CHIRAL CENTERS)

d) and e) provide two products after rxn with 1) cold, basic $KMnO_4$ 2) HIO_4

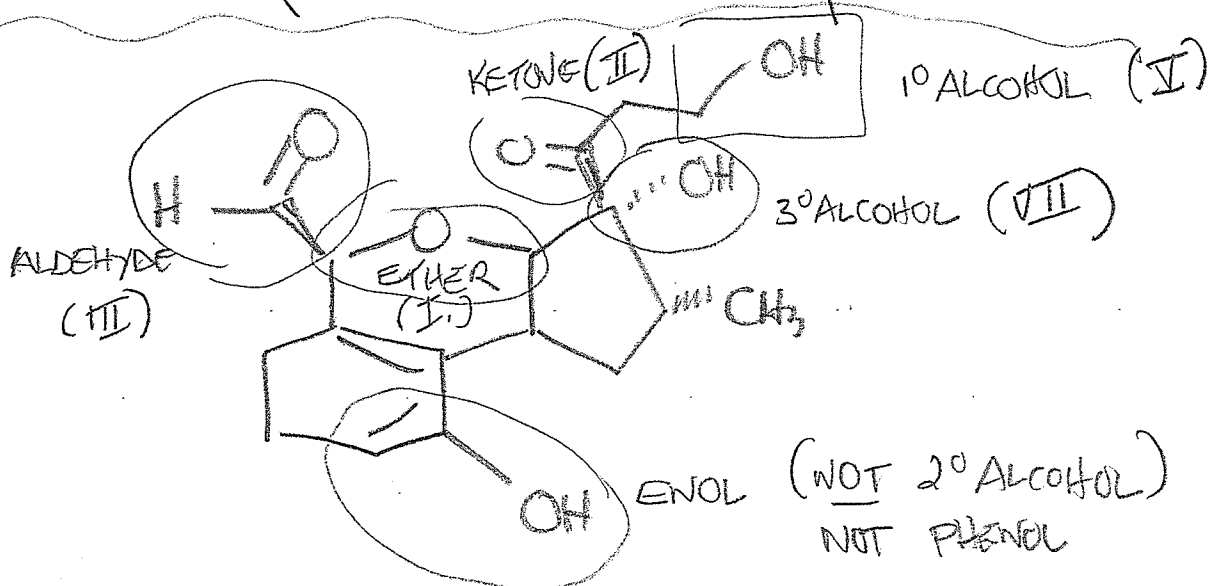
each one containing an ALDEHYDE (No Ketone)

b) contains only one chiral center

c) Rxn of c) with PCC, CH_2Cl_2 gives a product that contains only one chiral center



25.



I, II, III, V, VII

(E)