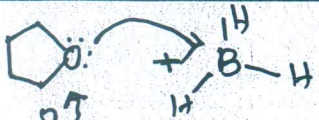
CH105
Tutorial 2: Model Answers

1.

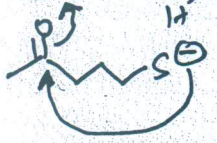
(a) II secondary allylic carbocation

(b) II both C and N in octect configuration

2.

(a) 

$n_O \rightarrow$ AO on B

(b) 

$n_S \rightarrow \pi^* C{=}O$

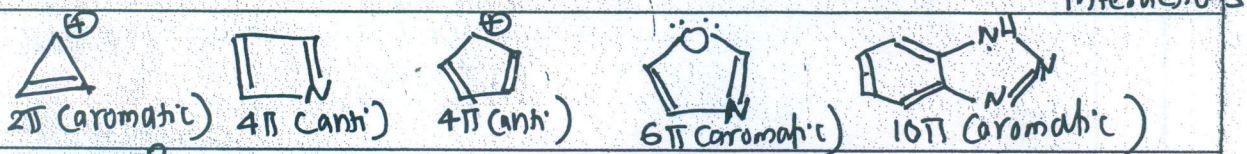
(c) $H_3N: + CH_3{-}I$

$n_N \rightarrow \sigma^*_{C-I}$

HOMO \ LUMO	σ^*	π^*	a → AO
σ	$\sigma\sigma^*$	$\sigma\pi^*$	σa
π	$\pi\sigma^*$	$\pi\pi^*$	πa
n	$n\sigma^*$	$n\pi^*$	na

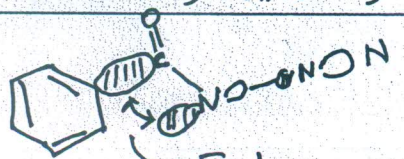
All possible HOMO-LUMO interactions

3.



2π (aromatic) 4π (anti) 4π (anti) 6π (aromatic) 10π (aromatic)

4.

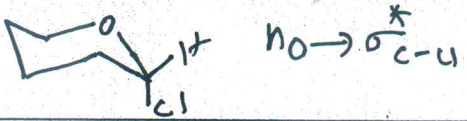


$\sigma_{C-C=O} \rightarrow \sigma^*_{N-N}$

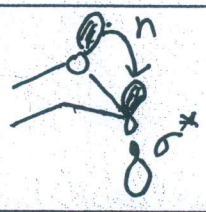
π type overlap

5.

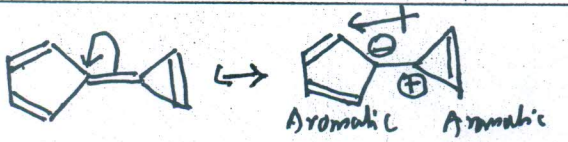
b is more stable than a



$n_O \rightarrow \sigma^*_{C-Cl}$

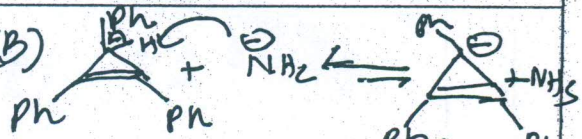


6

(A) 

Aromatic Aromatic

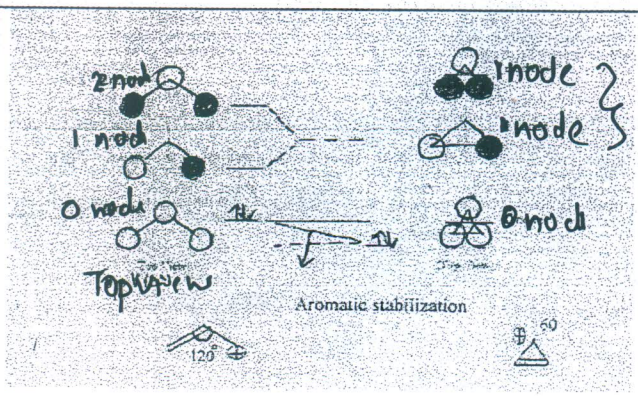
Dipole momnt 5.6D

(B) 

Ph Ph

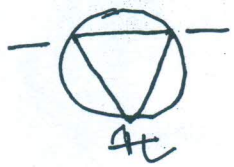
Antiaromatic

7



degennate orbitals

Net 1 AB interactions.



4t

8.

(11)

5] (a) Total Number of π electrons = $2 \times (3 \text{ double bonds}) = 6$

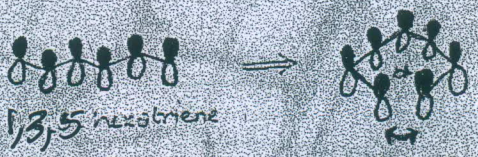
Total Number of occupied π orbitals = 3

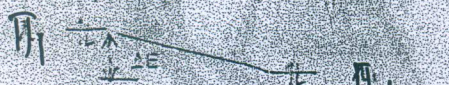
2 nodes — A_2 π_3 — HOMO

1 node — S π_2

0 node — A π_1

(b) In the case of benzene the lowest occupied orbital π_1 enjoys an additional stabilization due to favorable overlap as shown

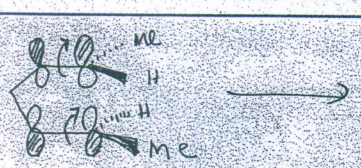




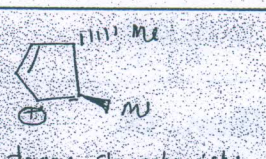
hexatriene benzene

9.

A)

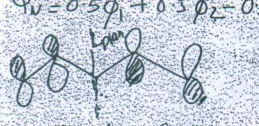


HOMO



trans stereochemistry

B) $\Psi_4 = 0.5\phi_1 + 0.5\phi_2 - 0.5\phi_4 - 0.5\phi_5$

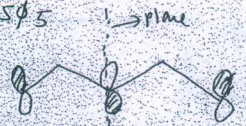


1 node (Ψ_2)

Antisymmetric (A)

Bonding orbital

Energy $\Psi_3 < \Psi_2$



2 nodes (Ψ_3)

Symmetric (S)

Non bonding orbital

10.

HOMO

LUMO

OR

LUMO

HOMO

CH105 Organic Chemistry
Tutorial-3 Model Answers

1. a) achiral, plane of symmetry & centre of symmetry

b) achiral, plane of symmetry

c) achiral, plane of symmetry

d) chiral, enantiomers

2. b) 2,4-dibromo pentane

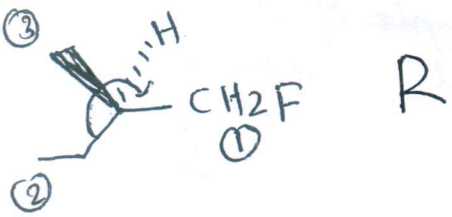
3. a) $-Cl > -SH > -OH > -H$

b) $-CH_2Br > -CH_2Cl > -CH_2OH > -CH_3$

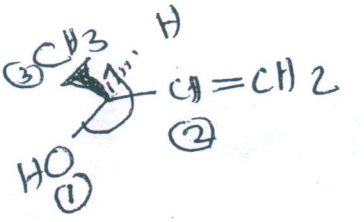
c) $-OH > -CHO > -CH_3 > -H$

d) $-C(CH_3)_3 > -CH=CH_2 > -CH(CH_3)_2 > H$

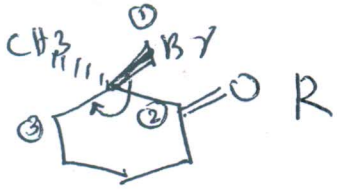
e) $OCH_3 > -N(CH_3)_2 > -CH_3 > -H$

7. a) 

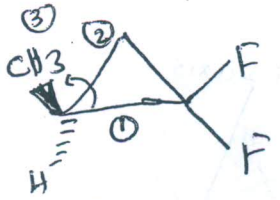
R

(b) 

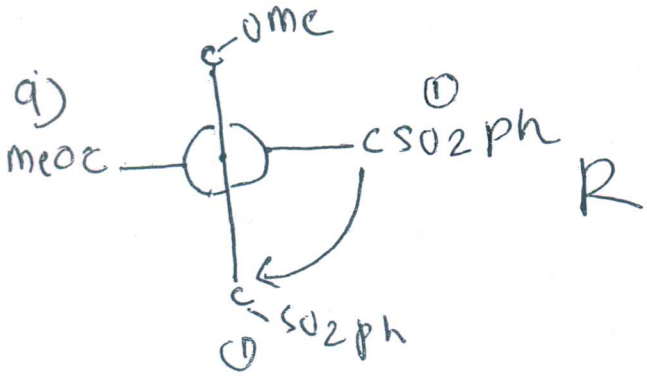
S

5. a) 

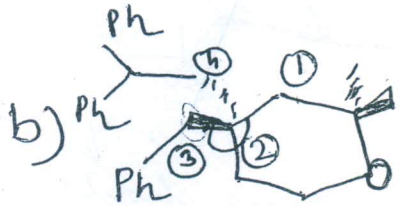
R

b) 

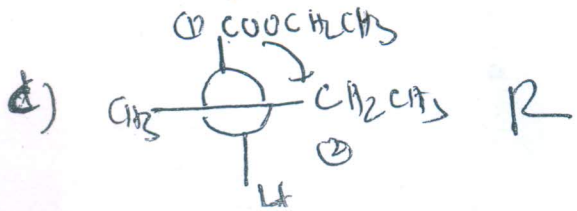
S

6. a) 

R

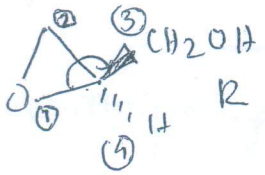
b) 

R

c) 

R

7. a) constitutional b) same c) Enantiomers

8. 

mix

* d + l = 100 %. l = 25 %.

d − l = 50 % d = 75 %.

ee = 50 %

$$ee = \frac{[\alpha]_{mix}}{[\alpha]_{pure}}$$

$$50\% = \frac{[\alpha]_{mix}}{+12} = +6^{0}$$

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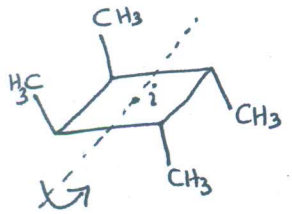
9. (a) 

C_2

σ

i

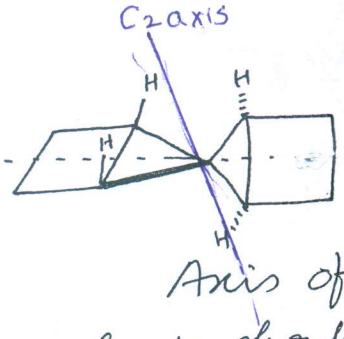
It is important to identify the inversion center (i)

Achiral

(b) Only C_2 axis

chiral

example of a chiral compound which is not asymmetric, but has a C_2 axis

(c) 

Axis of chirality

the emphasis should be given on

(i) the spiro ring junction

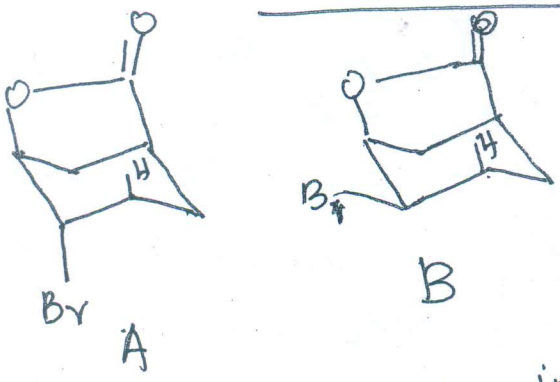
(ii) any of the ring junction carbon atoms between the three-membered and four-membered ring.

CH105 Tutorial 4

Conformational Analysis and Carbonyl Compounds

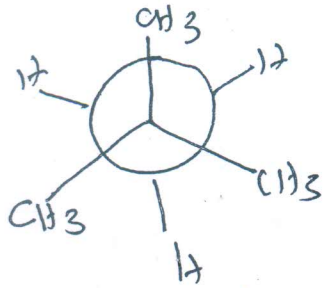
MODEL ANSWERS

1.



In A H and Br are in antiperiplanar configuration

2.

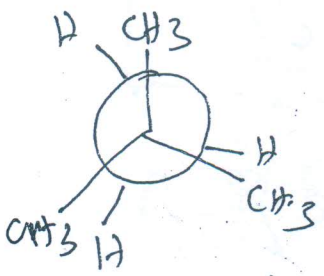


Staggered

most stable

↓

No eclipsing interaction

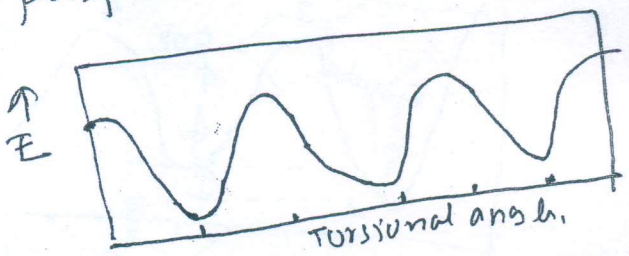


Eclipsed

least stable.

↓

3 CH3/H eclipsing



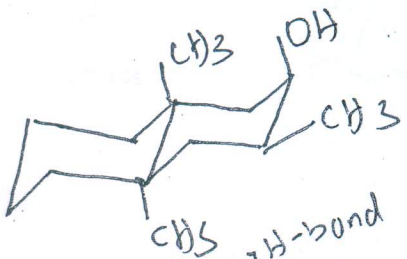
Therefore the barrier height will be 3.9 kcal/mol

↑

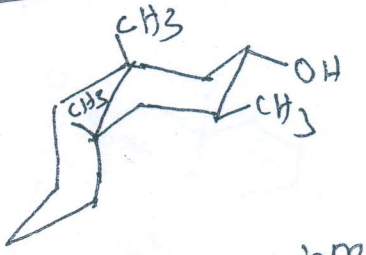
$3 \times 1.3 = 3.9$ kcal/

Homework problem: 2,2-dimethyl butane

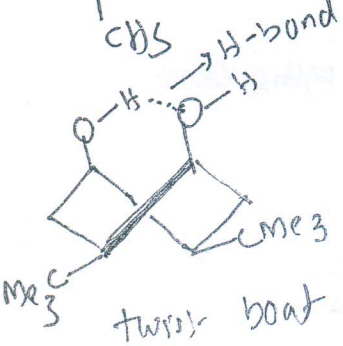
3. (a)



(b)

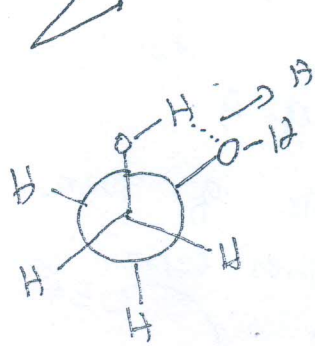


4. (a)

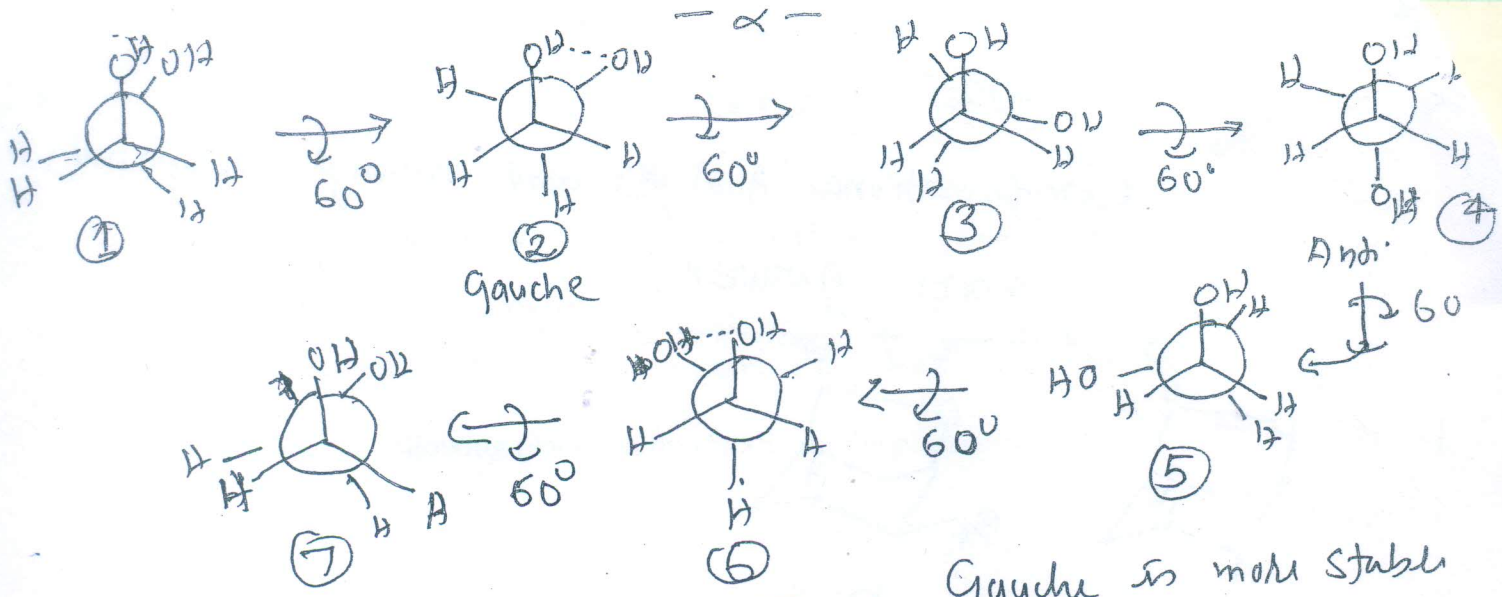


twist boat

(b)

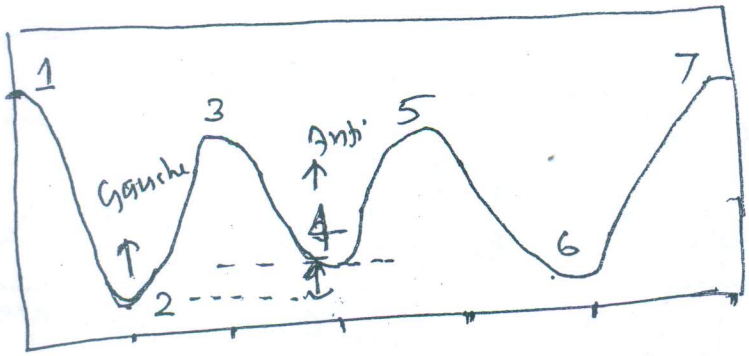


gauche

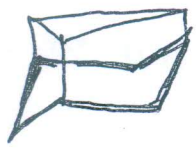


① ② ③ ④ ⑤ ⑥ ⑦

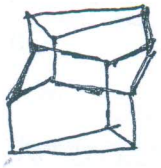
Gauche is more stable than anti due to H-bonding



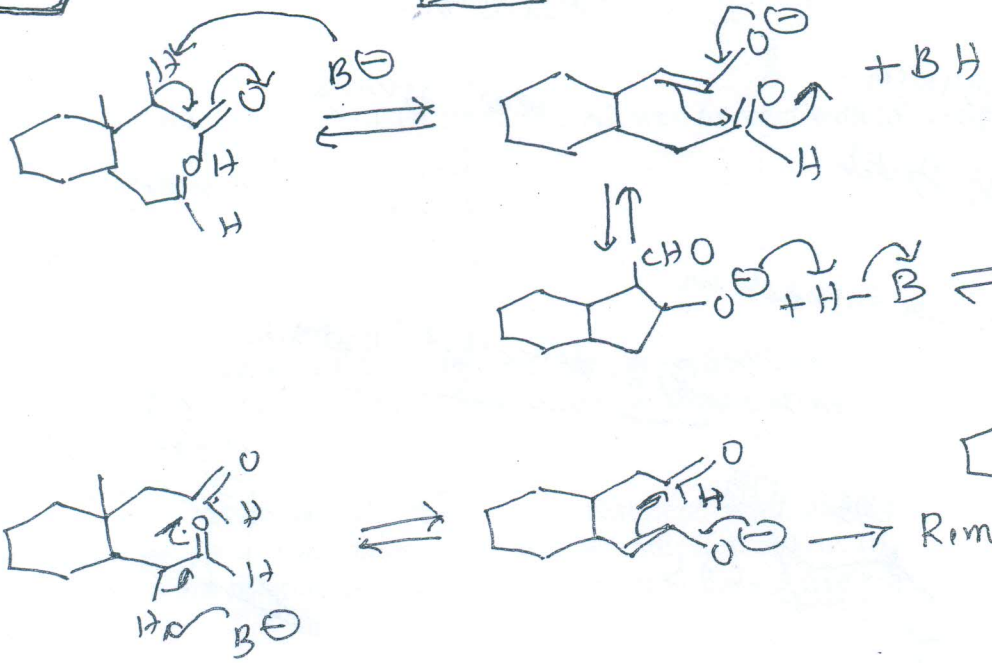
5. (a)



(b)



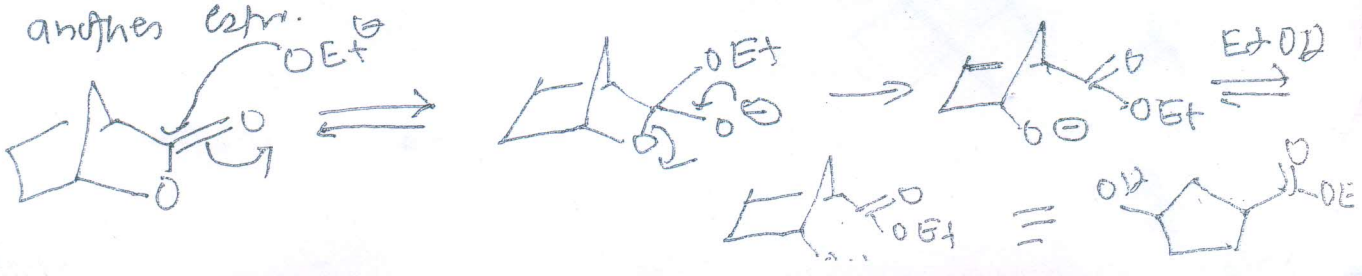
6. A.

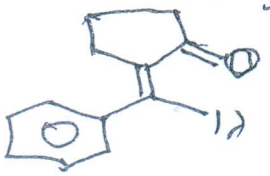


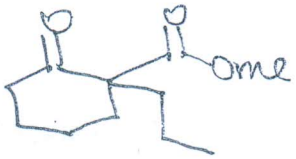
B.

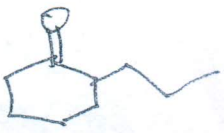
→ Remaining same as that of A

7. Example of trans-esterification: A cyclic ester (lactone) is converted into another ester.



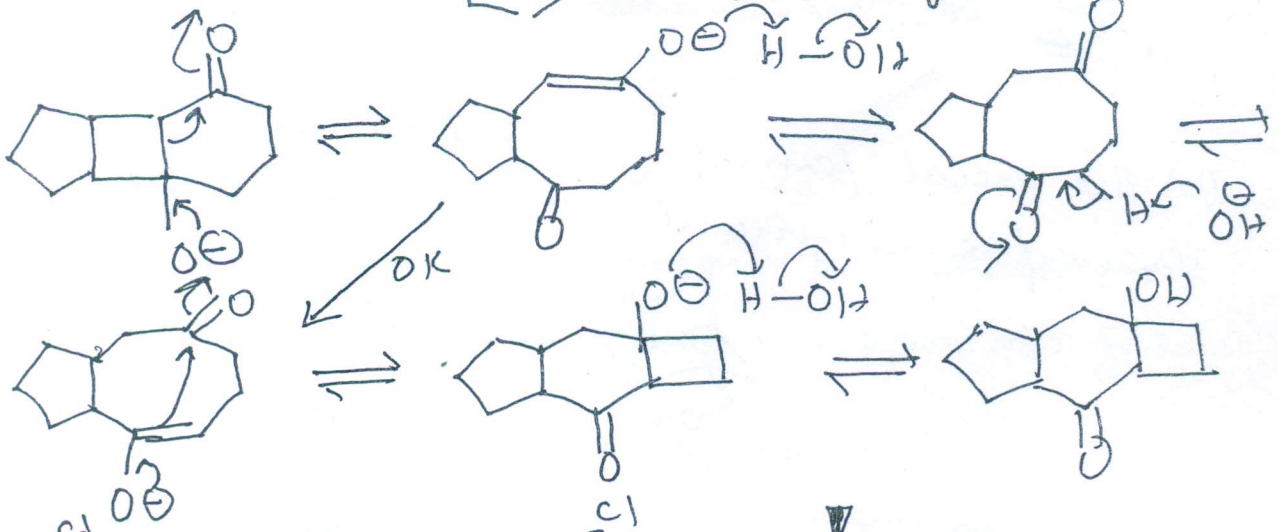
8. (I) 

(II) A 

B 

6 membered TS

Decarboxylation

9. 

10. 

Fraction I — Diastereomers — Fraction II

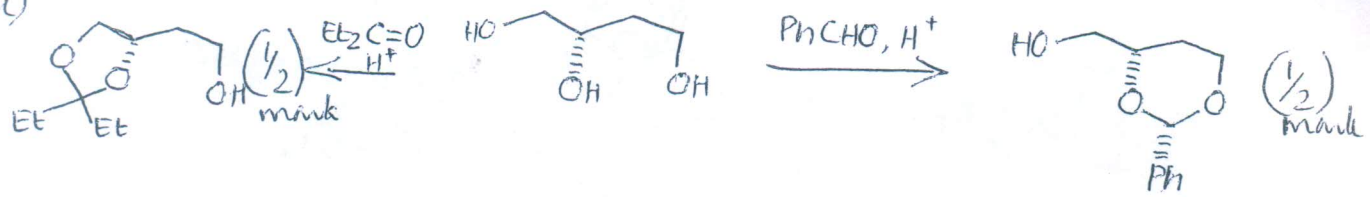
Enantiomers react ~~differently~~ at different rates with chiral compounds

Fraction II should be a mixture of acid where one enantiomer is in excess

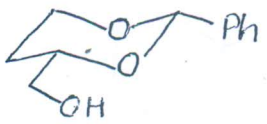
11. → Next page.

11.

(a)



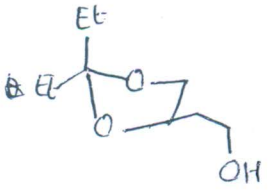
(b) The acetal formed with benzaldehyde is a strain-free six-membered ring as shown



both Ph and CH_2OH are equatorial

In the case of ketal, formed with diethylketone, the corresponding six-membered ring would have an axial 'Et' group, resulting in high 1,3-diaxial interaction.

This situation results in the formation of a five-membered ketal.



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any one of conformational drawing — (1)

justification of acetal with benzaldehyde by invoking 1,3-diaxial interaction (or gauche-butane) — (1)