

CH105: R.B. Sunoj

48A chem building

call 7173

02225767173

chem orbitals

org

inorg

25M

25M

1exam

1exam

4modules

Books:

Wade

Solomon

Morrison

Breice

Huckel theory - molecular orbital theory!



* orbitals are waves.

- bonding interactions
- antibonding interactions

→ M.O. by LCAO:-

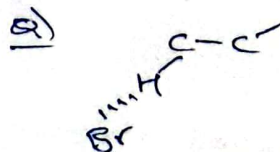
H₂ diagram:



same space;
separated by energy



in protonation;
which orbitals are involved.

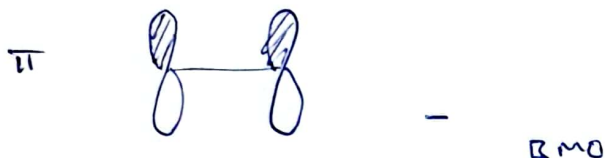


Here, which orbitals?

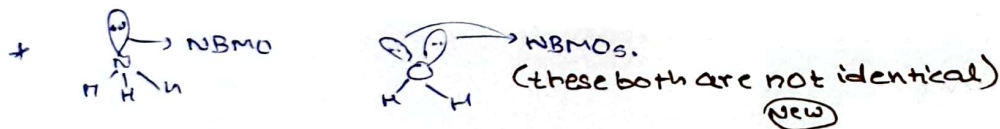
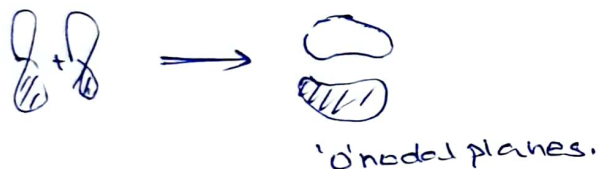
ethylene: types of m.o.s

we don't use hybridization here.

mixing AO of a single atom.

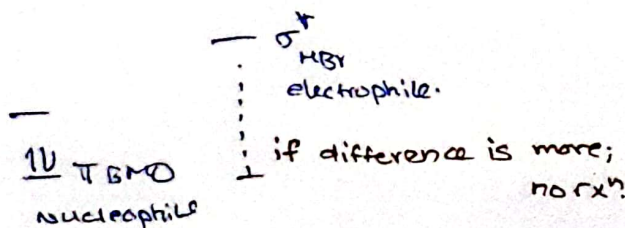
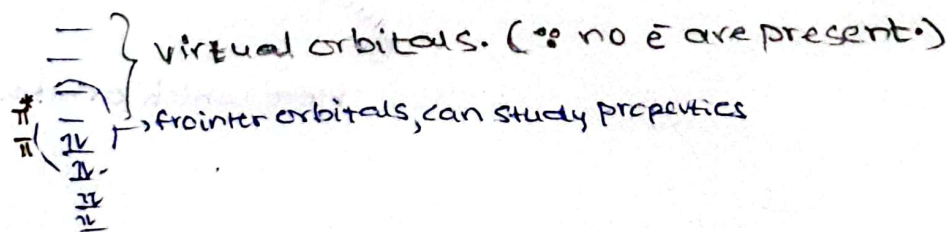
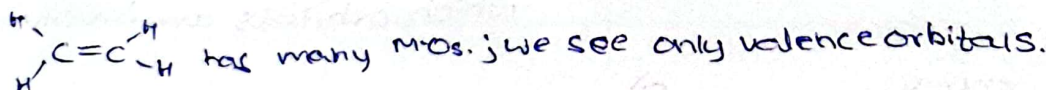


* for m.o.s nodal planes; don't count already existing nodal planes.



→ nucleophile:

have high energy filled non-bonding orbitals.



MO for allyl:



$$\Psi_{MO} = C_1\phi_1 \pm C_2\phi_2 \pm C_3\phi_3$$



ABMO



NBMO (LUMO)

no contribution.



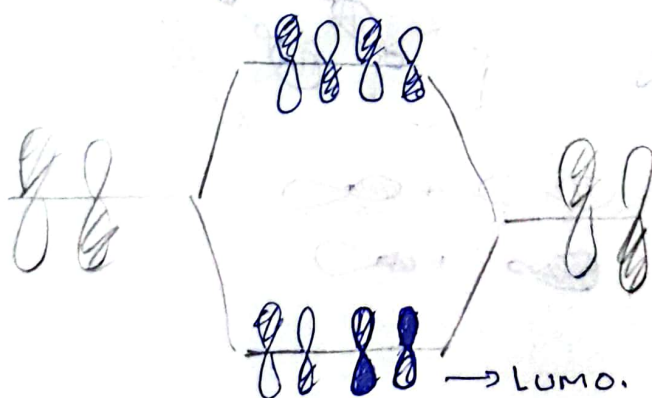
Bonding (HOMO)



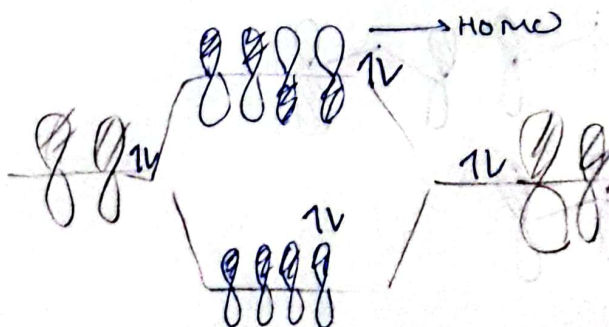
Will C-C lengths vary?

Symmetric

four C:



\therefore LUMO of butadiene; lower than LUMO of ethylene.



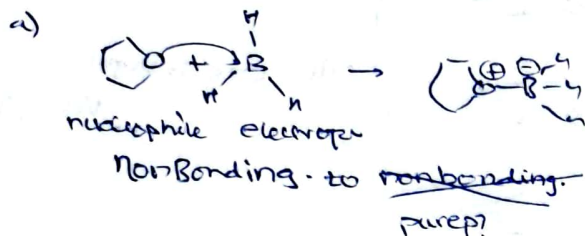
\therefore HOMO of butadiene more energetic than HOMO of ethylene.

Tut-1: 3 July 2019

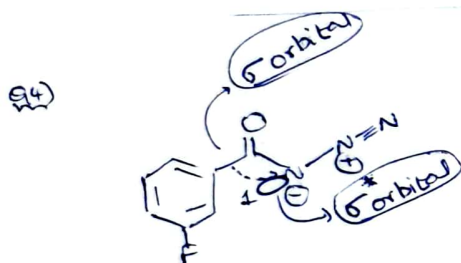
Q1) Which resonance structure, contributes more towards hybrid. & explain your choice.



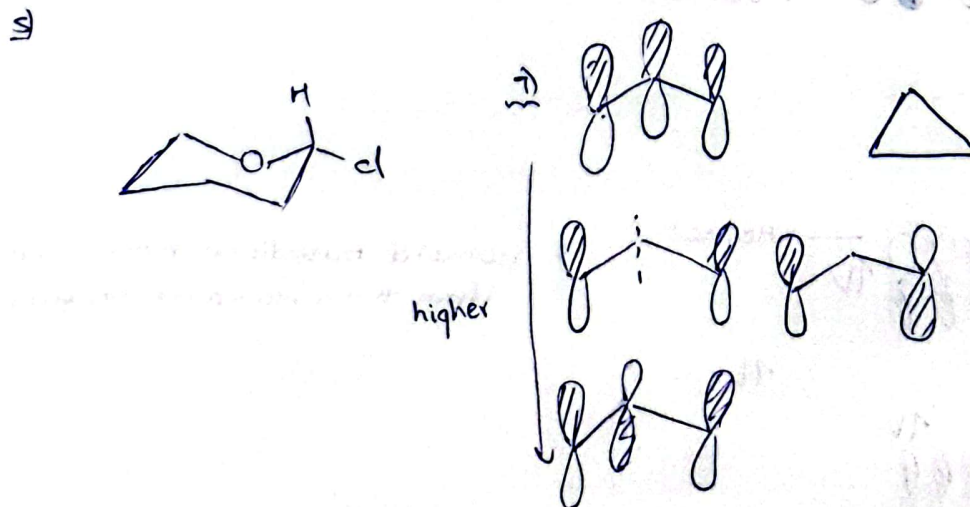
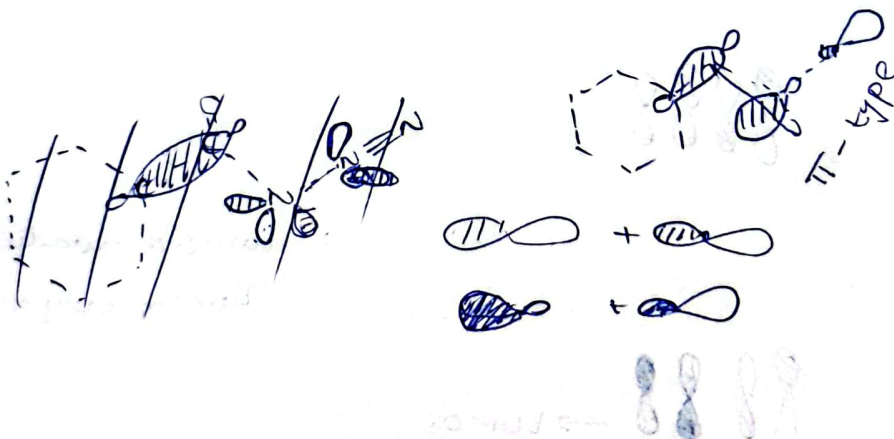
Q2) Identify nucleophile & electrophile.



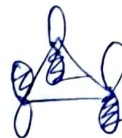
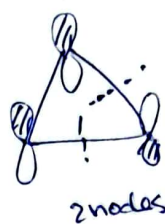
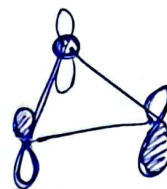
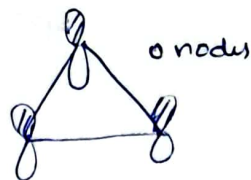
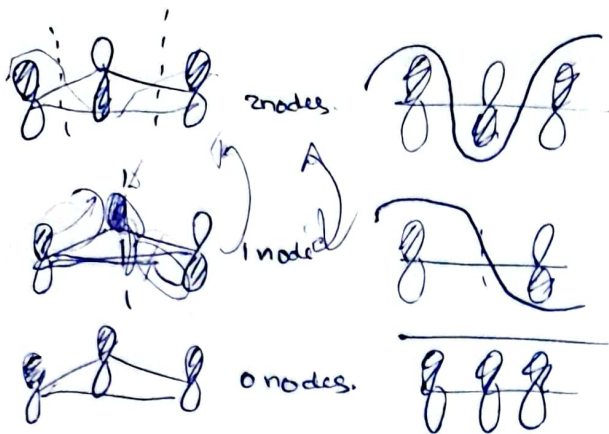
Tut-1



i) What type of bond is bre

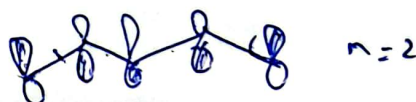
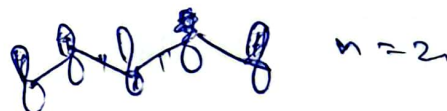
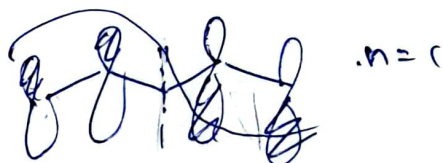
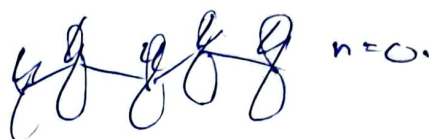


2

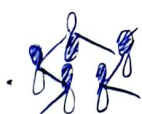
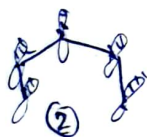
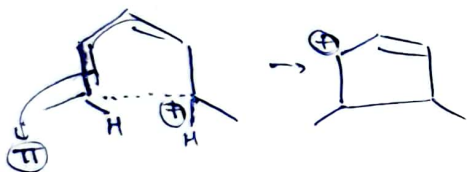


3 orbitals - 3 MOs

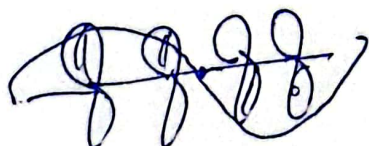
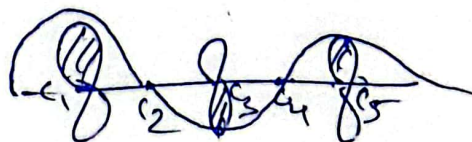
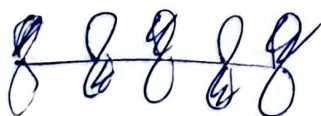
TUT-1



Q(A)

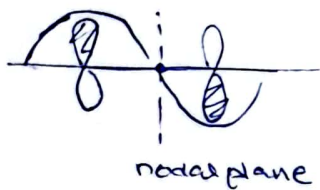


5 AO \rightarrow 5 MO



we increase the number of nodes by 1.

energy increases as node ↑.



M.O. 2.

nodal plane

variation principle
- coefficients are varied;
- energy is observed
- E minimized.

→ butadiene:

energy of HOMO of butadiene > HOMO of ethylene.

for mixing:

energy close.
symmetry match.

* "Resonance" → not a term of MO.



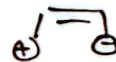
tut problem:

σ -bond; formed by
 π -type bond.

≠ no. of MO's are same as no. of A.O's.



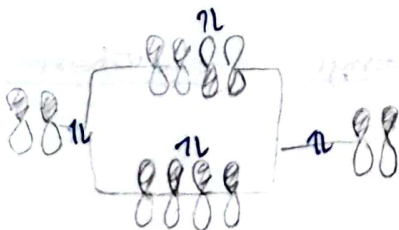
C_2-C_3 shorter one.
than C_1-C_2 .



by resonance concept.



coefficient $\frac{1}{\sqrt{2}}$ → i told wrong
to bharith.



* energies of molecular orbitals:- (using α, β)

↳ don't know value. like 1 rupee.

Huckel theory:-

- 1) σ, π interactions, don't exist.
- 2) only 1,2 interact. 1,3 don't interact.

* energies of M.O.s; in terms of integrals:-

- α (Coulomb integral) $i^{th} e^-$ with i^{th} nucl. $j^{th} e^-$ with j^{th} nucl.
the energy of each orbital before interaction is 'set equal' to α .
- β (resonance integral) $i^{th} e^-$ with j^{th} nucl.

for acyclic; linear conjugated.

$$\alpha + 2\beta \cos\left(\frac{\pi}{N+1} \cdot j\right)$$

Formulae

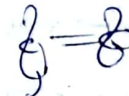
cyclic:



butadiene:

- $\alpha - 1.61\beta$
- $\alpha - 0.62\beta$
- $\alpha + 0.62\beta$
- $\alpha + 1.61\beta$

* For ethylene:



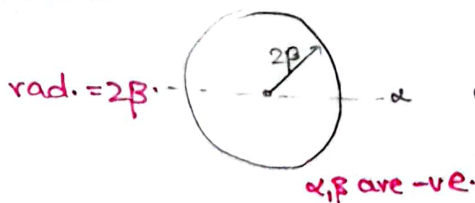
energy = $\alpha + \beta$
only 1 p. adjacent

For cyclic:

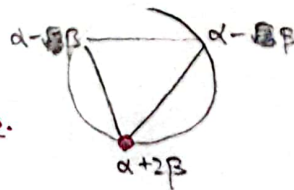
* extreme: $\alpha - 2\beta$ —
as, on both sides, p-orbitals.

$\alpha + 2\beta$ —

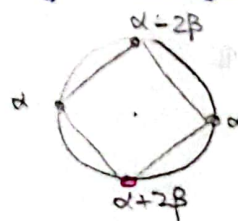
Frost:



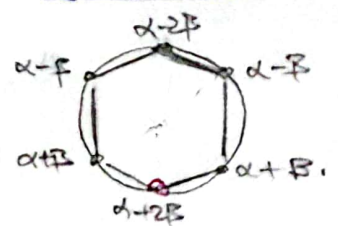
cyclopropenyl:



cyclobutenyl:



cyclohexenyl:



benzene

3-ethylene

$2 \times (\alpha + 2\beta)$

$+ 4(\alpha + \beta)$

$= 6\alpha + 8\beta$

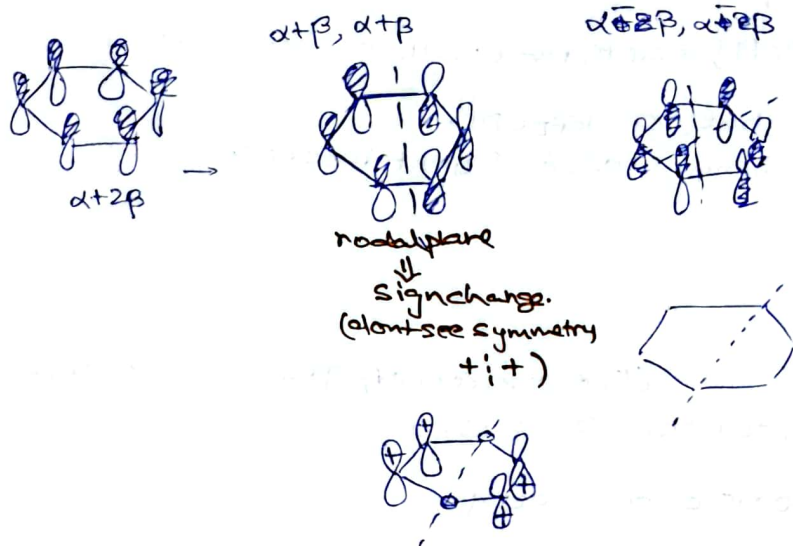
$= 6(\alpha + \beta)$

Take home:

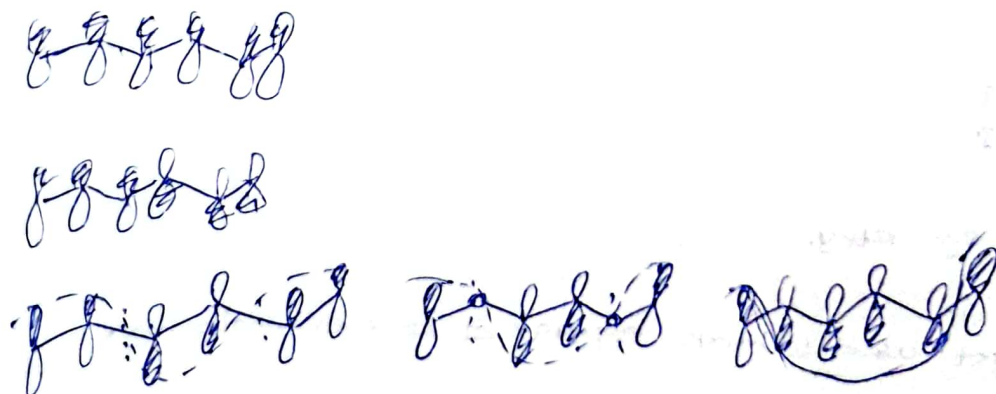
- 1) How to localize benzene double bonds?


- 2) a) Find out the structural distortion in benzene; when $1e^-$ is removed from it; making it a radical cation?
- b) is Jahn - Teller distn only for inorganics?

Benzene. M.O.



*



- *  PPL contains two circularly polarised light.
Right circularly polarised light...
{LCPL}.

polarised light is "chiral."

→ if passed in a chiral environment;

one of these two (say RCPL) reacts more with environment.

∴ right CPL slows down; but NOT LEFT CPL.

hence, phase of P. light rotates.

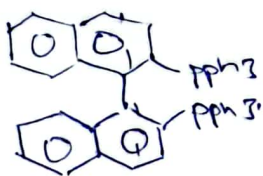
° Axis of chirality:-



(like at a center; groups are stretched)

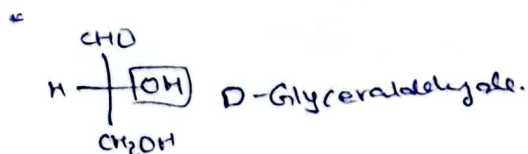
→ instead of center, we have an axis...

axis of symmetry.



axis of symmetry.

* asymmetric catalyst: used to make 99-99% of one enantiomer.



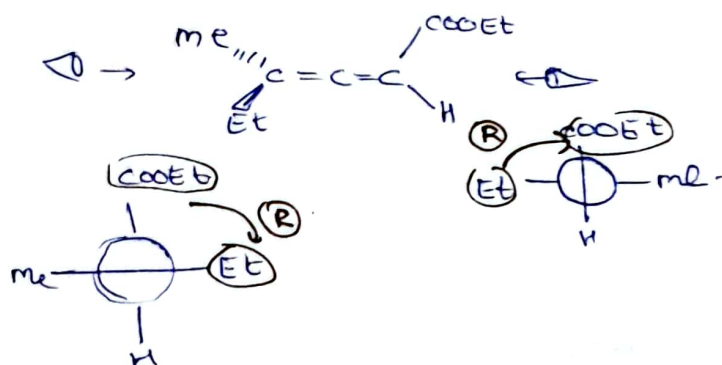
* we can digest, only D-sugars.
not L-sugars.

Homochirality: all the proteins in ~~world~~ are L-amino acids
(human world).

all the carbohydrates in
human body are D-sugars.



→ Absolute config. for axis of chirality :-

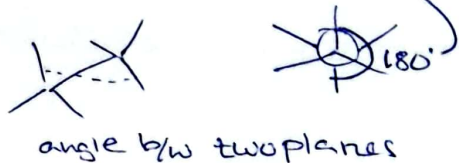


see from "highest preferred group on back; to highest priority group on closest carbon".

8/8/19

* enzyme shape changes; due to conformation changes; about
(molecules) single C-C bonds.

* dihedral angle



* energy values: (barrier height)

C-H
C-H eclips. 1 kcal/mol

C-H
C-CH₃ eclips. 1.3 kcal/mol

C-CH₃ 0.9 kcal/mol
C-CH₃ gauche

C-CH₃ 2.9 kcal/mol ~
C-CH₃ eclips.

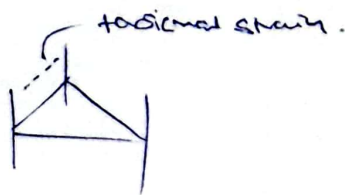
"Gauche interaction" (imp.)

Remember!

- rotational barrier:
- energy dif. b/w least & highest.
- don't ask, about which bond. find the worst guy.
- butane, means C₂-C₃ only na!

1) Torsional strain:-

bp-bp repulsion; by the virtue of rotation; or simply the structure of molecule.

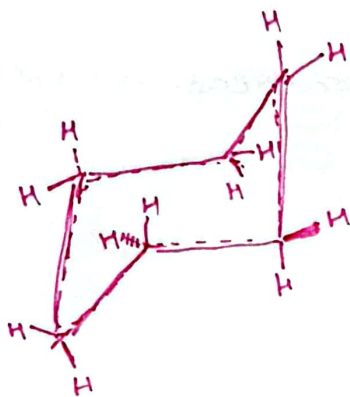


* benzene, when frozen, come in T-shape

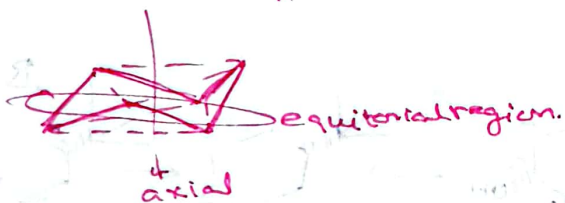
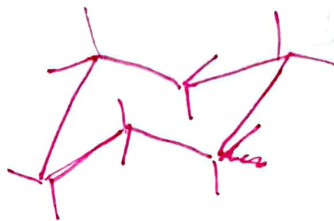
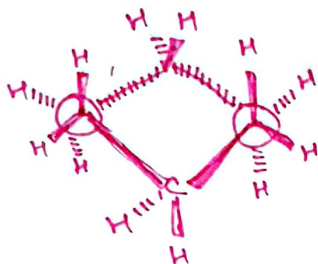
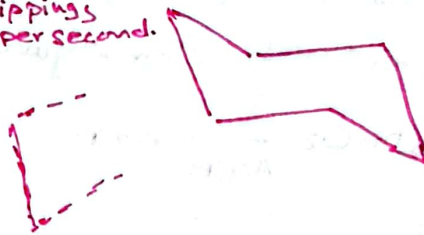


CH-π interaction.

CHAIR:



many flippings
per second.

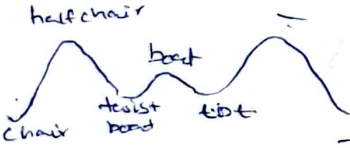


pseudorotation:-

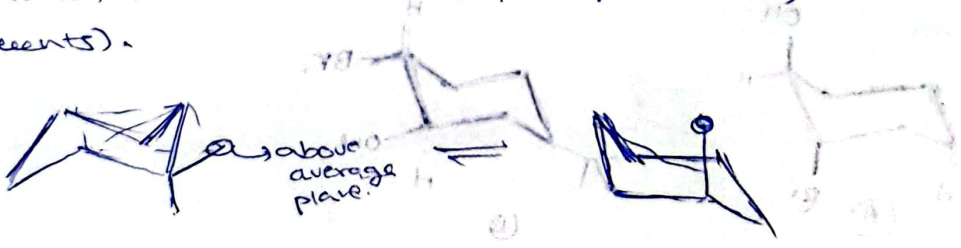


these
ups, become down & so...
So; we feel as if
ring turned by
60°

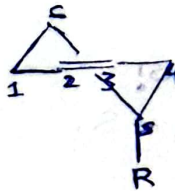
*



i) Groups; which lie above the average plane, remain so, after flipping.
(substituents).



* cyclohexene:-

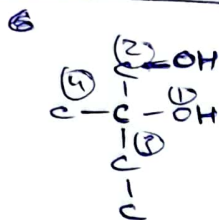
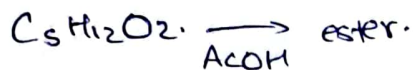


trans decalin → conformationally rigid.
cis decalin → conformationally flexible.

fused: c-c bonds shared.
bicyclic

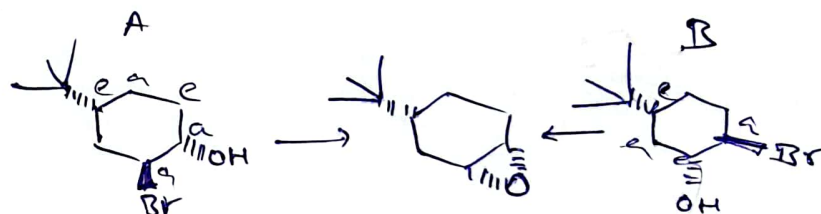
Solving session:-

- 3) An optically active alcohol has 'R' config. Upon treatment with AcOH; it forms esters with 'S' configuration.



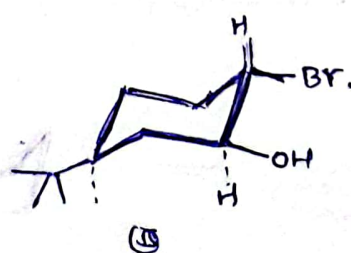
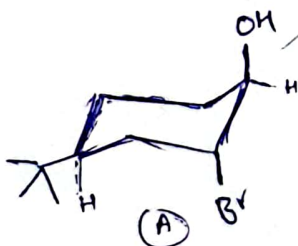
4)

Two bromocyclohexanols
one reacts much

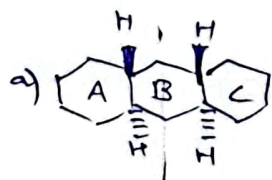


i) Provide suitable conformational drawings for A & B

ii) Which one would react faster & why?



5)

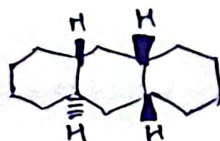


1) draw conformer.

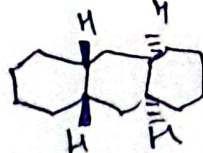
2) comment whether chiral or meso!

3) only for chiral centers, write R or S.

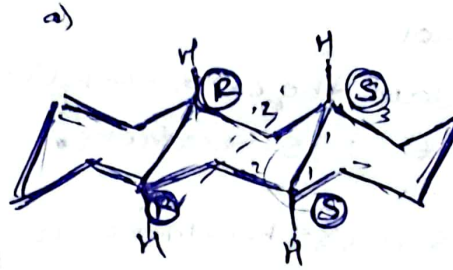
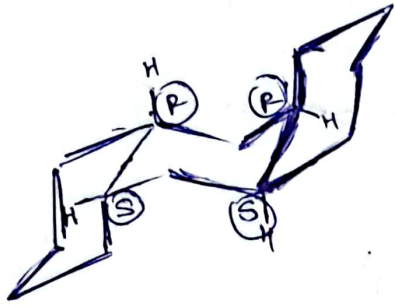
~~B)~~



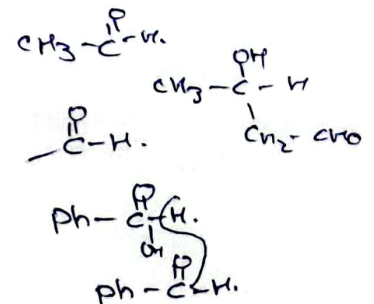
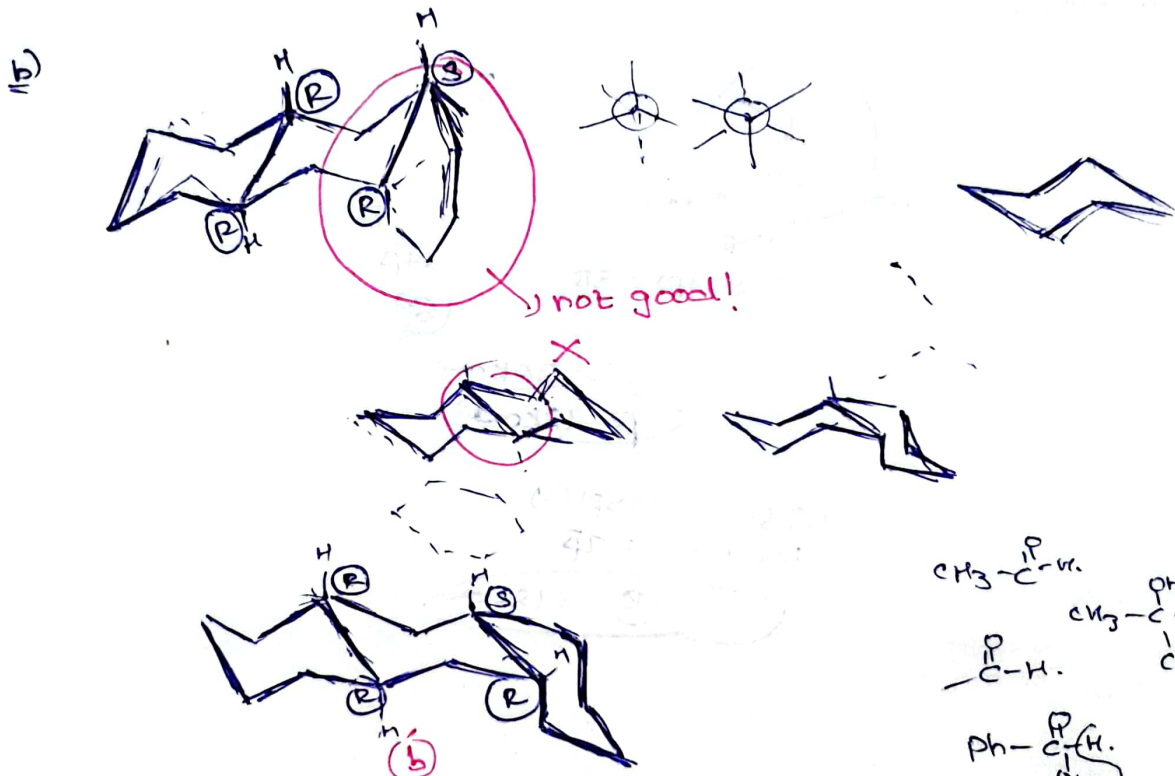
C)



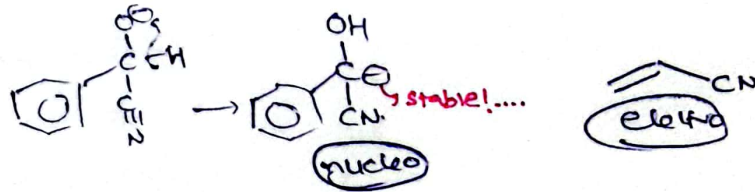
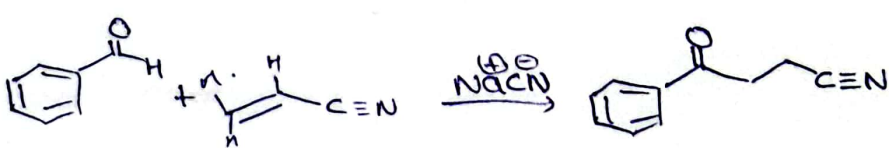
12/10



POS meso



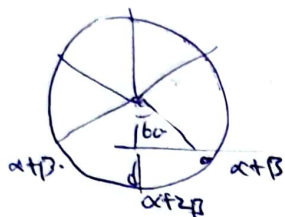
6)



Q7 The additional stabilisation in benzene in comp. to 3 C=C is 36 kcal/mol.

calculate the extra stabilisation in benzene wrt 1,3,5-hexatriene.

(energies in 1,3,5 hexatriene is $\begin{pmatrix} \alpha + 0.45\beta \\ \alpha + 1.25\beta \\ \alpha + 1.8\beta \end{pmatrix}$ in benzene



$$2(2\beta + \beta + \beta) = 8\beta$$

3 C=C.



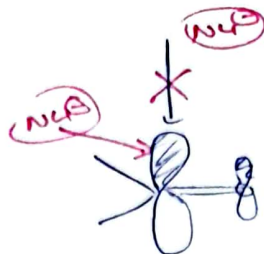
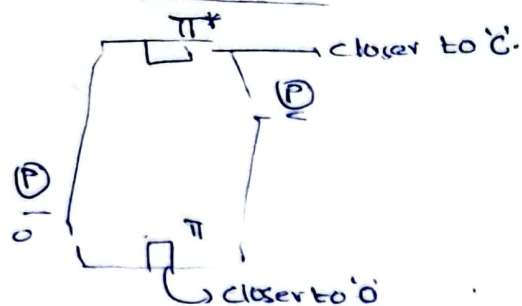
$$2\beta = 36 \text{ kcal}$$

$$\beta = 18 \text{ kcal}$$

1,3,5- (3-SP) (2) hexatriene = 7\beta

$$\beta = 18 \text{ kcal}$$

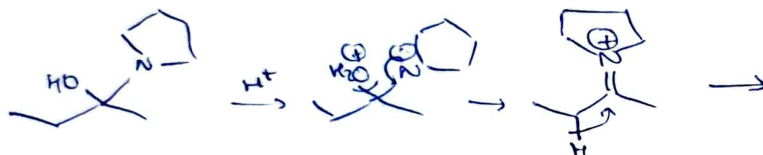
Carbonyl compounds:-



Mechanism:-

1) in any mechanistic step, don't use more than 3 arrows.

* enamine:-



* Grignard setbacks:-

-OH⁻ bad.
 $\equiv C-H$

Strong nucleophile (Grignard) \rightarrow 1,2 addition on $C=O$

Weak nucleophile (enolate) \rightarrow 1,4 addition

PART-2:- enol-enolate.

* Michael addition:

add enolate to (1,4) carbonyl

