14.07.17

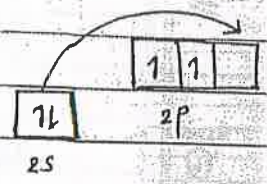
GENERAL CHEMISTRY

Page
Date : / /

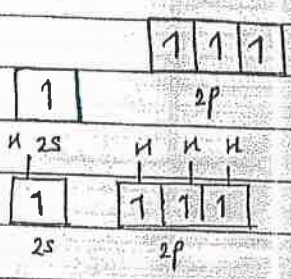
Carbon — Atomic no - 6

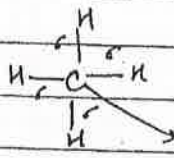
$1s^2 2s^2 2p^2$

Ground state



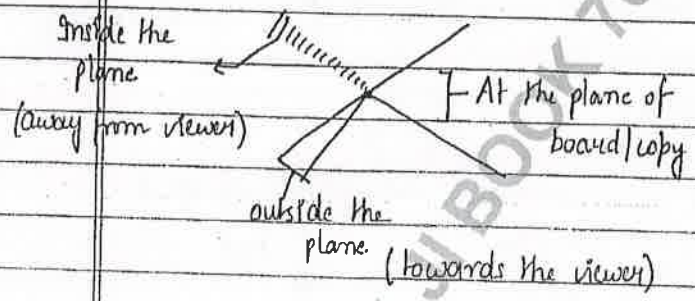
Excited state

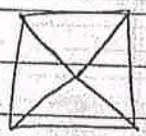




sp^3 [Tetrahedral]

$2V \Rightarrow V \perp V$

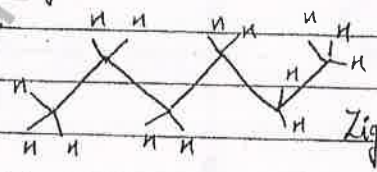




Square planar arrangement

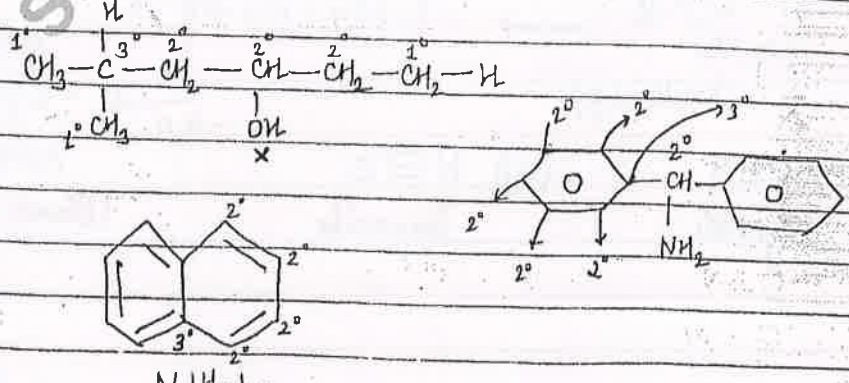
Catenation :

Self linking of C-atom is k/a as catenation (due to bond energy — strong bond).



Zig-Zag fashion chain

Ques.



Naphthalene

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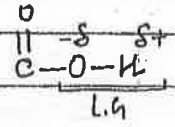
★ Acid & Acid derivative have leaving grp (unique)

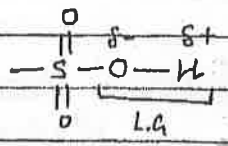
Active H → Acid Base reac^{n}. → Polar protic solvent

Page No.:
Date : / /

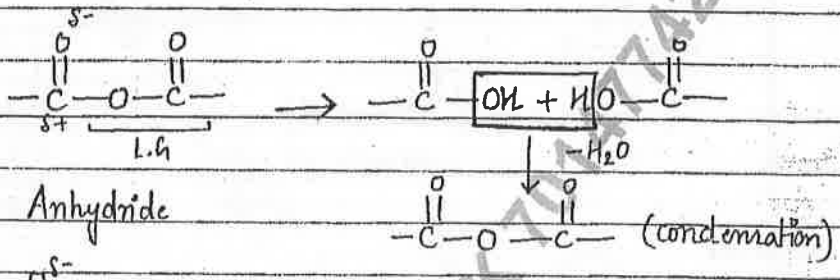
Functional group -

(I) 

Carbonylic acid

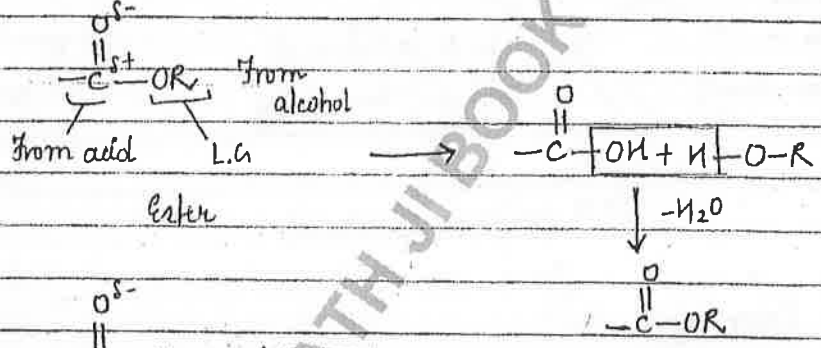
(II) 

Sulphonic acid

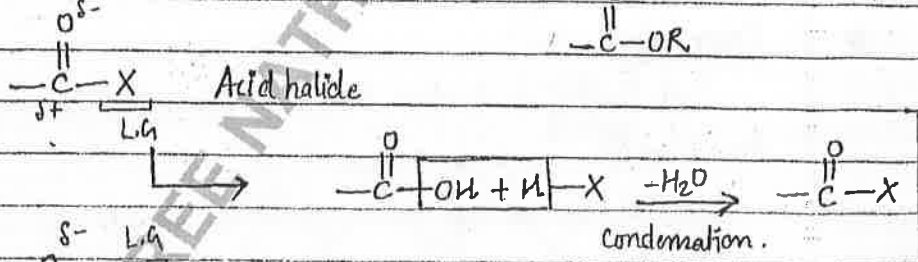
(III) 

Anhydride

(condensation)

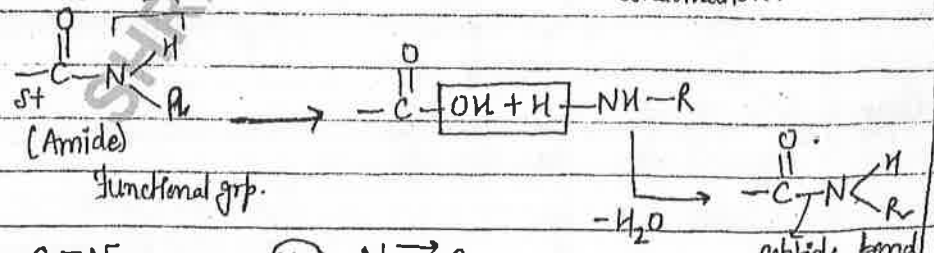
(IV) 

Ester

(V) 

Acid halide

condensation.

(VI) 

(Amide)

Functional grp.

peptide bond

(Biuret test)

(VII) $-C\equiv N$ Cyanide

(VIII) $N\rightleftarrows C$ Isocyanide

Acid & Acid derivatives. (Leaving group)

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Page No.:
Date : / /

(IX) $-\overset{\overset{O}{\|}}{C}-H$ Aldehyde

(X) $-\overset{\overset{O}{\|}}{C}-$ Ketone

carbonyl compounds.
no leaving group.

(XI) $-O-H$ Alcohol

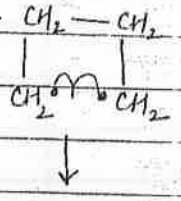
(XII) $-SH$ (Thioalcohol)

(XIII) $-NH_2$ Amine

(XIV) $-O-$ Ether

15.07.17

Degree of unsaturation - Index of H-deficiency (DU)

(1) $CH_2-CH_2-CH_2-CH_2 \xrightarrow{\Delta} CH_2-CH_2-CH_2-CH_2 \longrightarrow$ 

$-2H\ [1H_2]$

M.f → C_4H_{10}

G.f → C_nH_{2n+2}

(2) $CH_2-CH-CH_2-CH_3$ M.f = C_4H_{10} G.f = C_nH_{2n+2}

$2H \Rightarrow 1H_2$ DU = 1

$\xrightarrow{\Delta}$ $-2H\ (1H_2)$

$CH_2-CH-CH_2-CH_2$

$CH\equiv C-CH_2-CH_3$ M.f = C_4H_6 G.f = C_nH_{2n-2}

$2H \Rightarrow 1H_2$ DU = 1

$\xrightarrow{\Delta}$

$CH=C-CH_2-CH_3$

$CH\equiv C-CH_2-CH_3$ M.f = C_4H_6 G.f = C_nH_{2n-2}

$4H \Rightarrow 2H_2$ DU = 2

Acid & Acid derivatives (leaving group)

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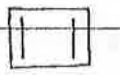
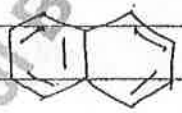
Page No.
Date

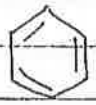
Key points-

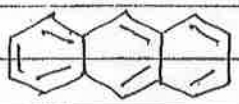
1. 1 Ring $= 2H = 1H_2$, $DU = 1$
2. 1 Double bond $= 2H = 1H_2$, $DU = 1$
3. 1 Triple bond $= 4H = 2H_2$, $DU = 2$

Ques	M.F	Alkane	
	C_2H_2	C_2H_6	$4H \Rightarrow 2H_2$, $DU = 2$
	C_2H_4	C_2H_6	$2H \Rightarrow 1H_2$, $DU = 1$
	C_3H_6	C_3H_8	$2H \Rightarrow 1H_2$, $DU = 1$ (C-C=C ring)
	C_4H_8	C_4H_{10}	$2H \Rightarrow 1H_2$, $D.U = 1$
	C_6H_6	C_6H_{14}	$8H \Rightarrow 4H_2$, $D.U = 4$
	$C_{10}H_{10}$	$C_{10}H_{22}$	$12H \Rightarrow 6H_2$, $D.U = 6$


(3)


(7) Naphthalene


(4)


(10) Anthracene

* Deficiency of H_2 molecule in given compd w.r.t acyclic alkane is DU.

Acyclic alkane-

$$DU = \frac{\text{No. of H-atoms in acyclic alkane} - \text{No. of H-atoms in given compd.}}{2}$$

→ D.U tells total no of double & triple bond in a compound.

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Curly hairs - disulphide bond ↑

Valine - 5C

Copro - 6C

Amide ≡ Peptide in Bi

Page No.:
Date : / /

Calculation of DU in heteroatom containing compd -

1. $C_4H_{10}O_x$ Alkane

$C_4H_{10} \Rightarrow C_4H_{10}$, DU = 0

2. $C_4H_8O_x$ – $C_nH_{2n+2} \Rightarrow C_4H_{10}$, DU = 1 [2H]

3. $C_4H_8O_x$ – $C_nH_{2n+2} \Rightarrow C_4H_{10}$, DU = 1 [2H]

4. C_5H_9N ($-H$) C_5H_8 ($-1H$) $\Rightarrow C_5H_{12}$, DU = 2 [4H]

ring 5. $C_5H_8O_2S_2F_2N_2$ ($+2H$, $-2H$) $C_5H_8 \Rightarrow C_5H_{12}$, DU = 2 [4H]

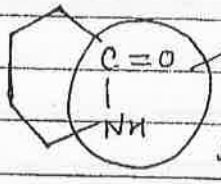
6. $CH\equiv C-\underset{\underset{C\equiv N}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH$ DU = 5 (2 triple (2+2) + 1 double) = 5

Concept -

N-family	O-family	F-family
N = –H	O – xx	f = +H
Eg N_2 = –2H	Eg – O_2 – xx, S_2 – xx	Eg – f_2 = +2H, Cl_2 = +2H

17.07.17

Some extra points -

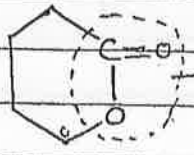
1. 

cyclic amide
Lactum
ring system.

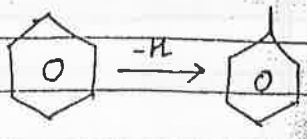
Nylon ≡ Amide

Eg Caprolactum – Nylon-6

Penicillin - cidal effect

2. 

cyclic ether

3. 

Same-Same

Phenyl

Ph / Φ

Ar / Aryl

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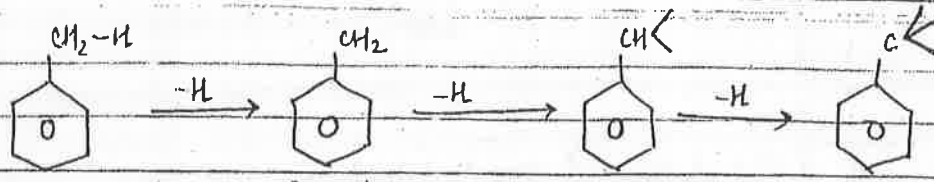
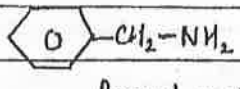
* Methylene containing form has 50% more resol content.

Page No.:
Date : / /

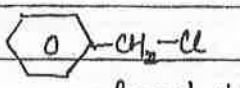
(IV)



Benzyl — Benzol — Benzo



Benzyl amide



Benzyl chloride

(V) $CH_2=CH-H \xrightarrow{-H} CH_2=CH-$

Alkene — Vinyl

Eg- $CH_2=CH-Cl$ Vinyl chloride

(VI) $CH_2=CH-CH_2-H \xrightarrow{-H} CH_2=CH-CH_2-$

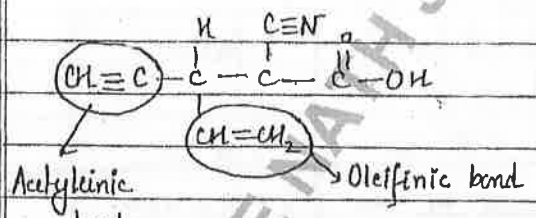
Allyl

Eg- $CH_2=CH-CH_2-OH$ Allylic alcohol

(VII) $CH_4 \xrightarrow{-H} CH_3 \xrightarrow{-H} *-CH_2- \xrightarrow{-H} CH\equiv$

Methane — Methyl — Methylene OR Methylidene — Methylidyne

Ques



Acetyleinic bond — Oleifinic bond

① DU 6
② No. of double bond 2
③ No. of triple bond 2
④ No. of Acetyleinic bond 1
⑤ No. of oleifinic bond 1
⑥ No. of π-bond 3
⑦ No. of σ bond 12

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IUPAC System

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2° Prefix	+	1° Prefix	+	Word Root	+	1° Suffix	+	2° Suffix
ive idea about bstituent (branch nt) in alphabetical rder with their sition.		Used only when compound is cyclic & in this case 'cyclo' prefix used.		How many C-atoms in P.C.C Eg- 1C - Meth 2C - Eth 3C - Prop..... 4C - But 5C - Pent 6C - Hex.		Give info abt double bond & triple bond (nature of hydrocarbon) (compd is saturated or unsaturated) in alphabetical order with their position. C-C → ane C=C → ene C≡C → yne $(C=C)_n$ → 'a' diene $(C\equiv C)_n$ → "a" diyene		Give info about principle functional group with their position.

(1) FORMAT OF IUPAC

Hexa-1,3-diene

Penta-1,4-diene.

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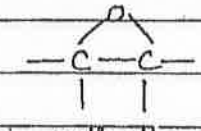
principle

(2) Selection of functional group -

→ If compd having a single functional grp then it considered as principle functional group of that compound.

Except- —O— (Ether),  (cyclic ether), —X (Halogen), —NO₂ (Nitro)

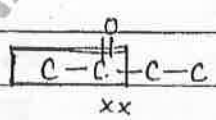
—N=O (Nitroso), —O—N=O (Nitrite)

→ If compd having more than one functional grp then select PFG acc to given IUPAC series.

In this case rest of F.G behave as substituents & their prefix are used.

3. Selection of principle C-chain (PCC) -

→ If PFG having Carbon then it considered as a first C- of PCC (except ketone).



→ If PFG not having Carbon then consider that carbon which to PFG is directly attached. In this case that C-atom covered by both side of other C-atom. (Including ketone)

Principle f.g > Multiple bond (= or ≡) > No. of C-atoms in PCC > No. of substituents

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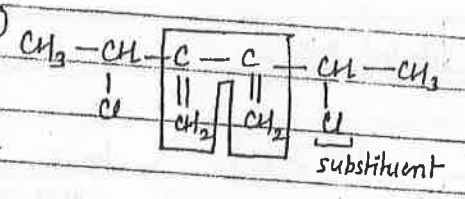
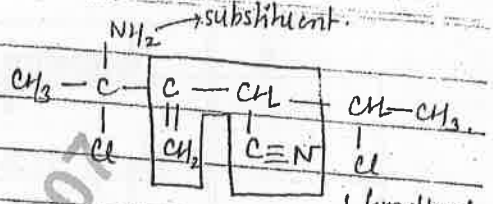
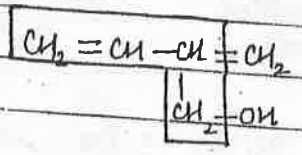
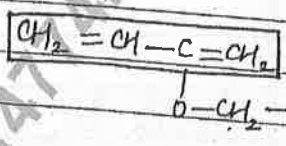
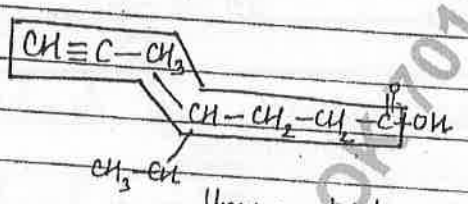
Date
Page

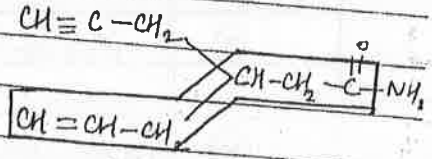
Ques ① 
substituent

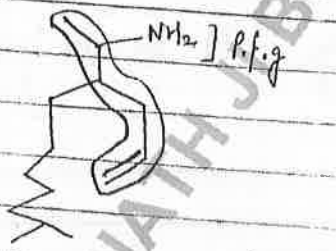
② 
substituent.
1. functional
2. m.b.

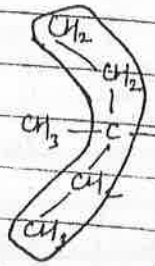
③ 

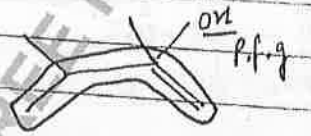
④ 

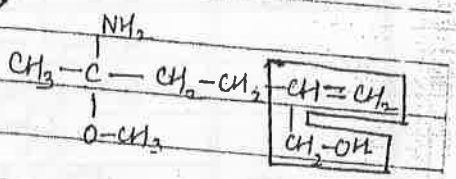
⑤ 
Unsymmetrical

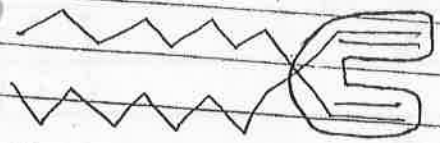
⑥ 
Symmetrical,

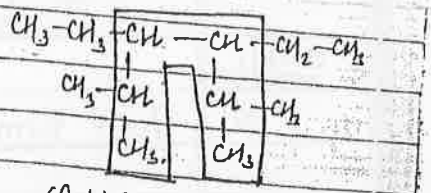
⑦ 
p.f.g

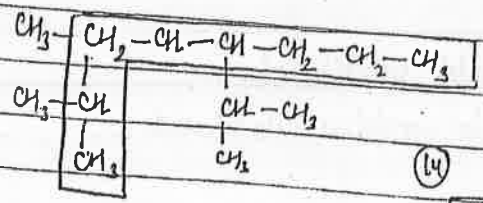
⑧ 
p.f.g.

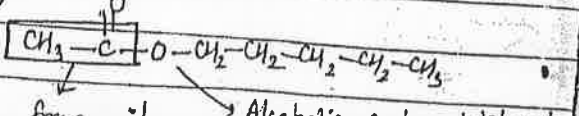
⑨ 
p.f.g

⑩ 

⑪ 

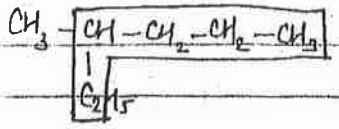
⑫ 
6C + 4S
6C + 3S
6C + 3Sub.

⑬ 
8C + 2S

⑭ 
from acid
Alcoholic part - substituent

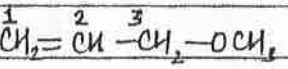
SHREE NATH JI BOOKS 7014711201

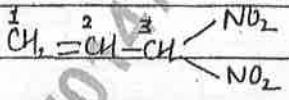
Date / /
Page
bill 10 out of 10 Student Notebooks

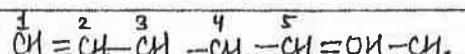
(15) 

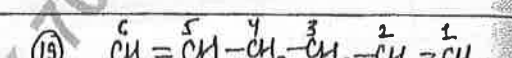
4. **Numbering in selected P.C.C -**

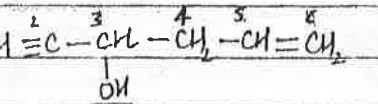
Pfg > M.B (any m.b) = or ≡ > =>≡ symmetrical condition > locants rule > Alphabetical order

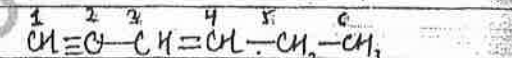
(16) 

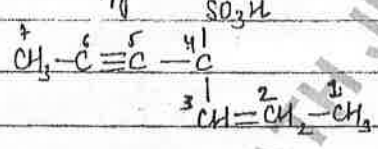
(17) 

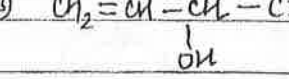
(18) 
unsymmetrical.

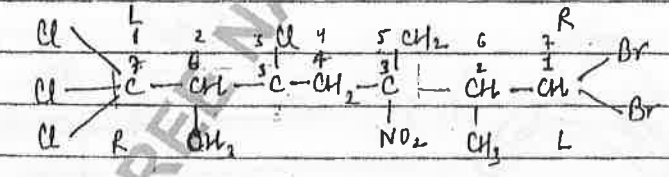
(19) 
symmetrical.

(20) 
Pfg.

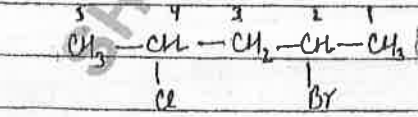
(21) 
unsymmetrical.

(22) 

(23) 

(24) 

Locants rule
L → R correct
1 1 1 2 3 5 5 6 7 = 36
R → L

(25) 

1 1 2 3 3 4 5 5 6 7 = 46

18.07.17

(5) **Use of numerical prefix -**

→ di, tri .... used for simple substituents.

→ Bis, tris, tetrakis used for complex substituents.

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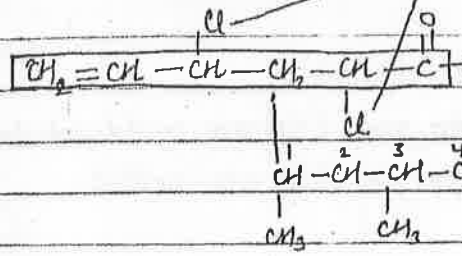
Date / /
Page

simple substituent.



→ complex substituent.

→ Substituted substituent is k/w as complex substituent.

In case of complex substituent first carbon is that carbon having free valency.

IUPAC name of complex substituent –

(26) $-\overset{1}{C}H(CH_3)-\overset{2}{C}H_2-\overset{3}{C}H_3$ [1-methyl propyl]
SEC-butyl

(27) $-\overset{1}{C}(CH_3)_2-\overset{2}{C}H_3$ [1,1 dimethyl ethyl]
tert-butyl

(28) $-\overset{1}{C}H_2-\overset{2}{C}H(CH_3)-\overset{3}{C}H_3$ [2 methyl propyl]
iso-butyl

(29) $-\overset{1}{C}H_2-\overset{2}{C}(CH_3)_2-\overset{3}{C}H_3$ [2,2-dimethyl propyl]
Neo-pentyl

(30) $-\overset{1}{C}H_2-\overset{2}{C}(CH_3)=\overset{3}{C}H_2$ [2-methyl prop-2-enyl]

(31) $-\overset{1}{C}H_2-\overset{2}{C}\equiv\overset{3}{C}-\overset{4}{C}H_3$ But-2-ynyl

(32) $-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2-NH_2$ 4 Amino but-2-enyl

1. $-CH_2-CH(CH_3)-CH_3$ (Isobutyl) — i-C, iso
2. ★ $-CH(CH_3)-CH_3$ Iso propyl or 2° propyl

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(6) **Alphabetical order of substituents -**

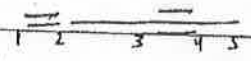
→ In case of simple substituents -

Cyclo, iso, neo (cin) are considered in alphabetical order rest all like di, tri, pri, sec, tert are avoided.

→ In case of complex substituents -

first alphabet decide alphabetical order.

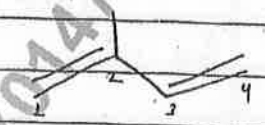
(33)



pent-1-en-3-yne

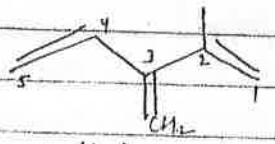
(a, e, i, o, u, y) → c xx

(34)



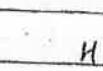
2-methyl-buta-1,3-diene

(35)



2-methyl-3-methylidene penta-1,4-diene

(36)

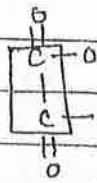


formic acid

single acid to undergo further oxidation forming $CO_2(g)$

Methanoic acid

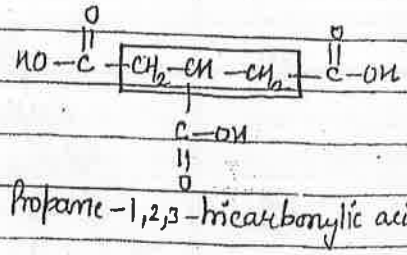
(37)



Oxalic acid

Ethan-1,2 dioic acid

(38)



Propane-1,2,3-tricarbonylic acid

(38) contd...

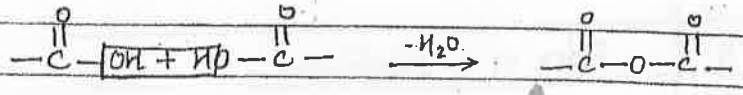
F.G	Suffix
$-COOH$	carbonylic acid
$-SO_3H$	sulphonic acid
$-COOR$	Alkyl carbonylate
$-COX$	Carbonyl halide
$-CONH_2$	Carbonamide
$-C\equiv N$	Carbonitrile
$-CHO$	Carbaldehyde.

SHREE NATH II BOOK 7014774207

Date / /
Page

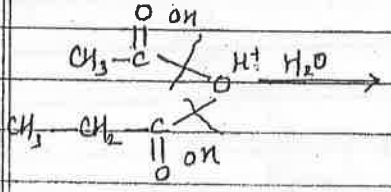
(37)

IUPAC name of Anhydride -



→ IUPAC of Anhydrides always given w.r.t their respective acids & follow alphabetical order rule.

(39)

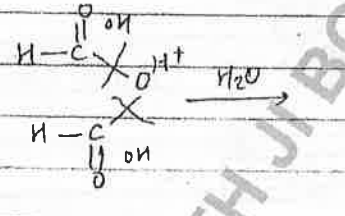


Methanoic acid

Ethanoic acid.

Ethanoic-Methanoic anhydride

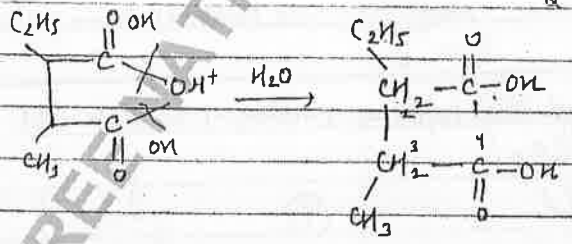
(40)



Methanoic anhydride.

2 moles

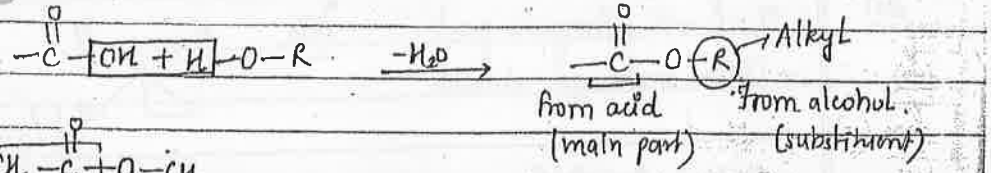
(41)



2-ethyl-3-methyl butan-1,4-dioic anhydride

(38)

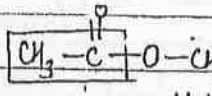
IUPAC name of ester -



From acid (main part)

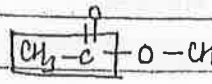
From alcohol (substituent)

(42)



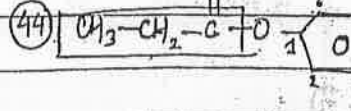
Methyl ethanoate

(43)



Chloro-methyl ethanoate

(44)



4-hydroxy phenyl propanoate

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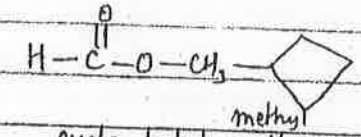
★ Samaan k saare I containing compds are antiseptic.

Date / /
Page

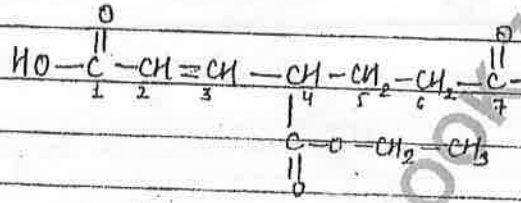
(45) 

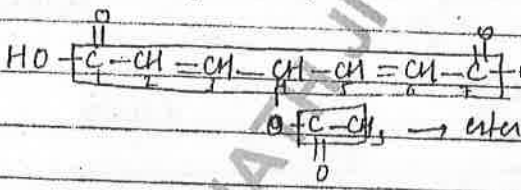
cyclo-butyl-methanoate

(91)

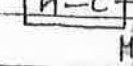
Ester as a substituent:-

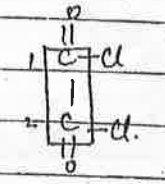
P	$-O-\overset{O}{\overset{\|}{C}}-R$ → subs → prefix Alkanoyl oxy (total no. of C-atoms.)
C	$-O-\overset{O}{\overset{\|}{C}}-O-R$ → subs → prefix Alkoxy carbonyl

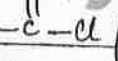
(46) 
4-Ethoxy-carbonyl-hep-2-en-1,7 dioic acid

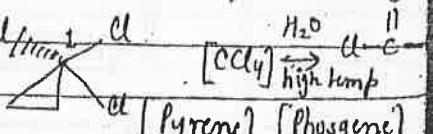
(47) 

4-Ethanoyl oxy hepta-2,5-dien-1,7-dioic acid

(48) 
Methanoyl chloride

(49) 
Ethanoyl 1,2 dichloride

(50) 
(Phosgene gas)
Chloro methanoyl chloride

(51) 

(52) $CHCl_3$ Anaesthisia
1,1,1-trichloromethane
Chloroform.

(53) CHI_3
1,1,1 tri-Iodo methane
(Iodoform) Antiseptic

1,1,1,1 tetrachloro methane

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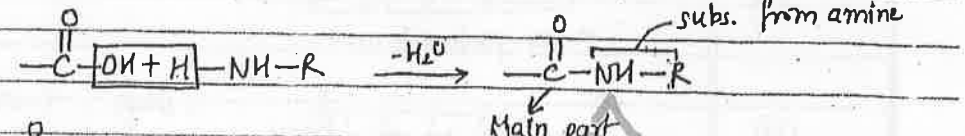
CCl_4 – used as fire extinguishers (old days)
– Phosgene formed at high temp (harmful)

Tetra-ethyl lead → Petrol for anti-knocking effect
carcinogenic

orange colour of petrol → ferrocene – Now-a-day used with petrol

(10)

IUPAC name of Amide –



(54) Methanamide

(55) N,N dimethyl ethanamide

(56) Ethane-1,2-diamide

(57) Ethane-nitrile

(58) 1-Amino methanoyl chloride

(59) Ethane 1,2 dinitrile

(60)* Methanal (formaldehyde) / Polymer industry.

(61) Ethan 1,2 di-al

(62) Butan-2-ol

(63) 3-keto-butane 1-al.

* Methanal is the ald. only used in polymer.
Bakelite – strongest polymer.

(64) 4-hydroxy butane-2-ol

19.07.17

(69) Mercapto, Formyl, Halo formyl, Chloro formyl, Amino, Hydroxy

4-Amino-5-Chloroformyl-3-Formyl-2-hydroxy-5-mercapto-Hex-3-enal-1-oic acid

If C-containing functional group not as a substituent then its Carbon not included in PCC, but in case of aldehyde & ketone, its C may be included in PCC. In this case "one" prefix is used.

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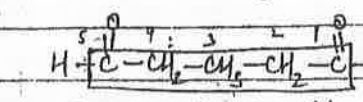
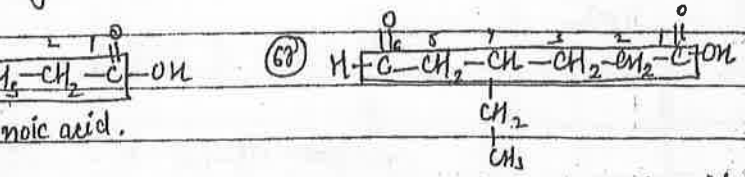
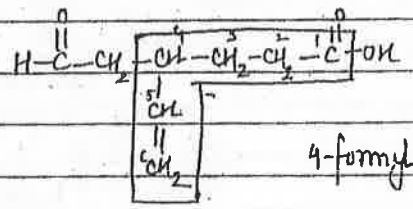
Ald → formyl — Same acam substituent to
oxo — If C-included in chain
(Prefix)

Date / /
Page

Special case for aldehyde & ketone-

(66) 
5-oxo-pentanoic acid.

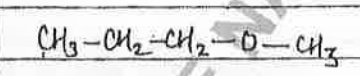
(67) 
4 ethyl - 6-oxo-hexan-1-oic acid

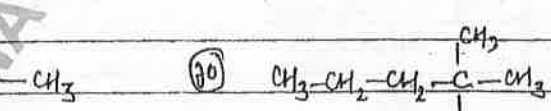
(68) 
4-formyl methyl hex-5-en-1-oic acid

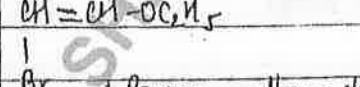
(11) Naming of ether-

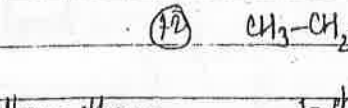
Ether can never be p.fg It always behave as a substituent & 'alkoxy' prefix is used.

→ All ethers are polar aprotic solvent.

(65) 
1-Methoxy propane

(70) 
2-methoxy-2-methyl pentane

(71) 
1 Bromo-2-ethoxy ethene

(72) 
1-ethoxy-methan-1-ol

(12) IUPAC name of cyclic ether-

In case of cyclic ether to give IUPAC name compound treated as a open chain compd. & in this case 'epoxy' prefix used.

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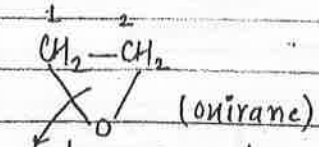
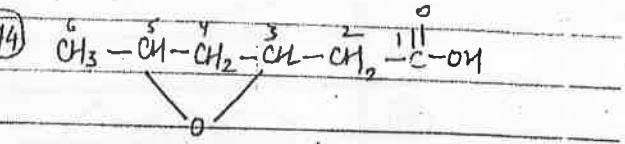
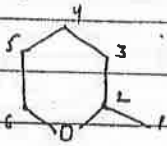
(73) 

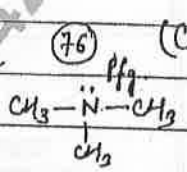
epoxy ring system
1,2 epoxy-ethane

(74) 

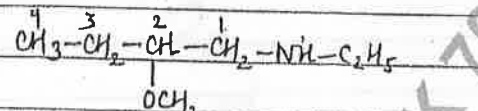
3,5 epoxy hexan-1-oic acid

(75) 

2,6 epoxy hexane

(76) 

N,N-dimethyl methanamine

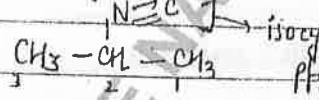
(77) 

N-ethyl-2-Methoxy butan-1-amine

(13)

IUPAC name of isocyanide-

→ In case of isocyanide even C-atom ~~not~~ in isocyanide, still we select PCC assuming that their is no-carbon in it.

(78) 

propan-2-isonitrile (old system)
2-carbyl-amino propane (new system)

IUPAC name of Cyclic compounds

Rule 1: If given compd is comb^{n} of open & closed chain hydrocarbon part then principle part is selected acc to given IUPAC series.

[Pfg > M.B > No. of C-atoms in PCC > Ring] (if C-atom equal same-same)

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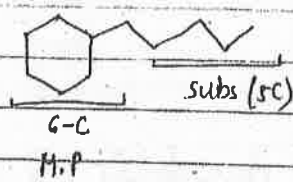
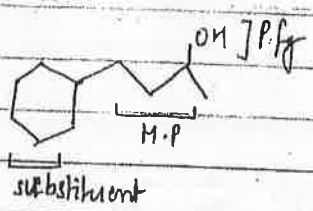
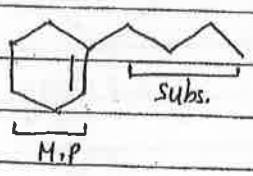
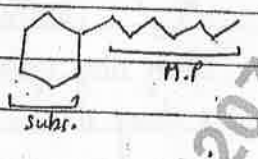
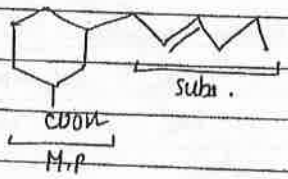
Page
bilk 10/10 Student Notebook

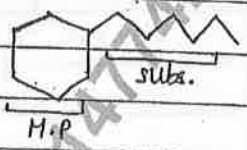
(79) 

(80) 

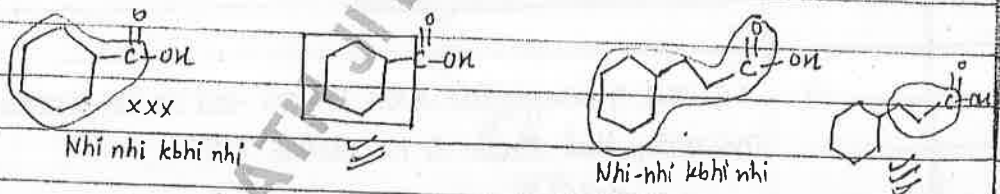
(81) 

(82) 

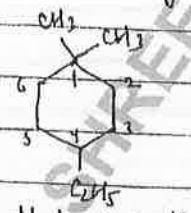
(83) 

(84) 

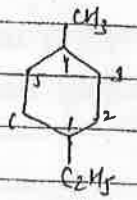
Rule 2: If Pfc directly attached to C-atom of ring then it considered as a part of ring, not a seperate part, but in case of ketone, it may be out inside a ring.



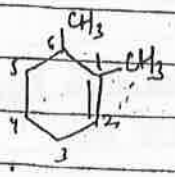
→ In case of cyclic compound "cyclo" prefix used.

(85) 

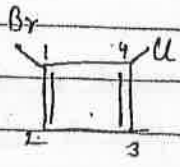
4 ethyl -1,1 dimethyl cyclohexane

(86) 

1-ethyl 4-methyl cyclohexane

(87) 

1,6 dimethyl hex-1-ene

(88) 

1-Bromo-4-Chloro cyclobuta-1,3 diene

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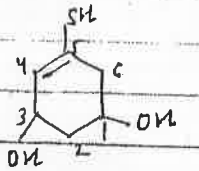
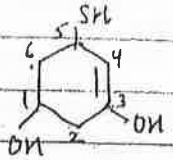
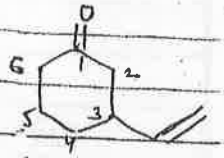
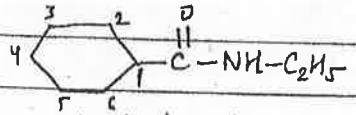
(89) 

5-mercapto cyclo hex-4-en-1,3-diol

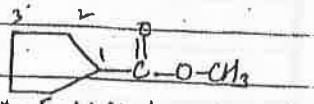
(90) 

(91) 

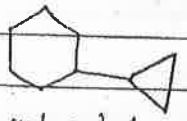
3-vinyl cyclo hexan-3-1-ol

(92) 

N-ethyl cyclohexan-1-carbonamide

(93) 

Methyl cyclopentan carboxylate

(94) 

1 cyclopropyl cyclohexane

(95) 

1,2 dicyclobutyl cyclobutane.

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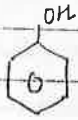
IUPAC name of Aromatic compound -

Rule 1 : Common name of some compounds has been retain ~~retain~~ written in IUPAC system

(96) 

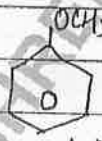
Benzene

(97) 

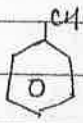
Phenol
Carbolic acid

(98) 

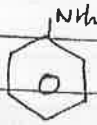
Toluene

(99) 

Anisole

(100) 

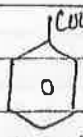
Benzaldehyde
(oil of bitter almonds)

(101) 

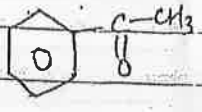
Aniline

(102) 

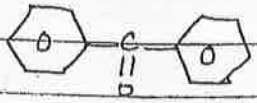
Nitrobenzene
(oil of mirbane)

(103) 

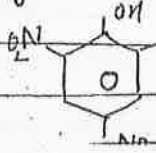
Benzoic acid
Benzene carboxylic acid

(104) 

Acetophenone

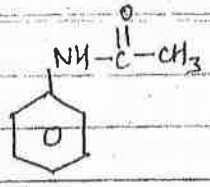
(105) 

Benzophenone

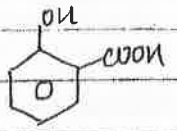
(106) 

Picric acid.

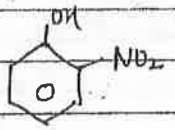
Date / /
Page

(107) 

Acetanilide

(108) 

Salicylic acid

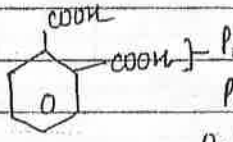
(109) 

o-nitrophenol

p-nitrophenol

Separated by steam distillation method

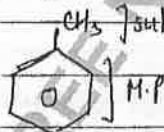
Rule 2 - If more than one principle functional grp ent then suffix is used acc to IUPAC rule.

(110) 

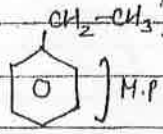
Phthalic acid

Benzene-1,2-dicarboxylic acid

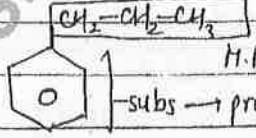
Rule 3 - If given compd is combination of open chain & closed chain hydrocarbon part then except ethyl & methyl benzene open chain part considered as a main part. In this case benzene behave as a substituent & phenyl prefix used.

(111) 

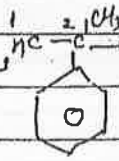
Methyl benzene

(112) 

ethyl benzene

(113) 

1-phenyl propane

(114) 

(tert butyl benzene)

2-methyl-2-phenyl propane

(115) 

1 Chloro-1-phenyl methane

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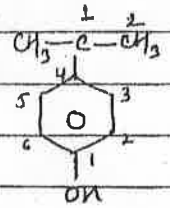
Date / /
Page

Rule 4: If any part having functional group then it is considered as main part.

(116)



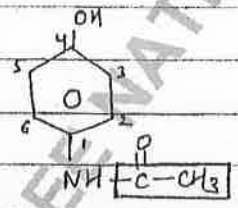
4 [1-methyl ethyl] Benzen-1-ol

OR 4-Isopropyl, Benzen-1-ol

Use of aspirin -

(i) Analgesic (pain ↓)
(ii) Antipyretic
(iii) Anti coagulation
(iv) Anti-inflammatory

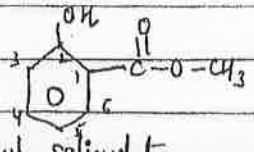
(118)



Paracetamol (PCM)

N-(4-hydroxyphenyl) ethanamide

(119)



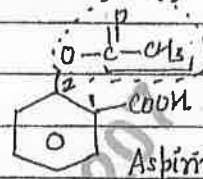
Methyl salicylate
(oil of winter green)

Use - Joint pain

Methyl-2-hydroxy benzene carboxylate

Acetoxy (-OAc)

2012



(117)

Aspirin

Acetyl Salicylic acid (Chemical name)

OR 2-Ethanoyl oxy benzene carboxylic acid.

OR 2-Acetoxy benzene Carboxylic acid

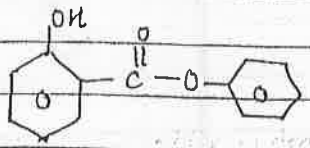
O-Acetoxy benzene carboxylic acid

Aspirin, Paracetamol } alcohol addicts should not used it (causes peptic ulcer)

Use of Paracetamol -

(i) Analgesic
(ii) Antipyretic
(iii) Anti-inflammatory

(120)



Salol

Use - Antiseptic

Action - Astringent

Phenyl-2-hydroxy benzene carboxylate

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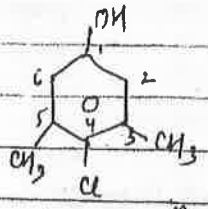
BCT → Terpineol

Phenol — Bioxylenol, Chloroxylenol

Date / /

Page

(121)



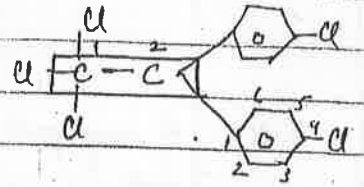
Chloroxylenol

Dettol - chloroxylenole + terpineol

4-chloro-3,5 dimethyl benzen-1-ol

Use - Antiseptic

(122)



1,1,1 trichloro-2,2-Bis [4-chlorophenyl] ethane

DDT

non-biodegradable

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if bonding pattern & connectivity changes then always structural mera

stereoisomerism. connectivity same.

20.07.17

ISOMERISM

ISOS — equal

MEROS — parts

→ Isomers are those which can be separated at room temp.
→ Isomerism is resultant factor of thermodynamic system "entropy".
→ Isomers always have same DU. (Isomers are diff compds)
→ Isomers are formed to stabilise a system.

→ Isomers are 2 diff. compounds (either physical or chemical properties diff)
→ Connectivity change (bonding pattern) – Structural isomerism.
→ Connectivity same – Stereoisomers.

→ Compounds having same molecular formula but diff connectivity, diff bonding pattern (structural isomerism) or diff 3-D relative arrangement (stereoisomerism) is k/a as isomers. & this phenomena is k/a as isomerism

→ Isomers have diff physical, chemical or both properties (enantiomers have same physical properties).

→ Isomerism is resultant of thermodynamic factor "entropy."

Classification

due to diff. connectivity / bonding pattern.

(A) Structural / constitutent isomerism

1. Chain isomerism
2. Position isomerism
3. Functional grp isomerism
4. Ring chain isomerism
5. Metamerism
6. Tautomerism

due to same connectivity

(B) Stereoisomerism

- Configuration
  - Geometrical isomerism
  - Optical isomerism
- Conformational — due to rotation around a single bond (pseudoisomers)

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Date / /
Page

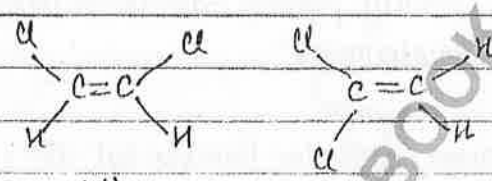
C_2H_6O ; DU = 0

→ $CH_3-CH_2-\overset{-\delta}{O}-\overset{+\delta}{H}$ (Alcohol) — Due to Active H → Hydrogen bonding (Liquid)
Give active metal test with Na
$H_2\uparrow$ (gur-gur)
(highly explosive)

→ CH_3-O-CH_3 (Ether)
→ No active H – No H-bonding (Gas phase)
→ No active H – does not give active metal test with Na (H_2 ✗✗) (no gur-gur)

→ Both compounds have diff physical & chemical properties so both are isomers.

Ques



(I) (II)

① Both are structural isomers
② Both are stereo-isomers

Structural isomerism
(due to diff connectivity, diff bonding pattern)

Chain isomerism –
Compound having same MF (same) functional group but different P.C.C or side chain.

Ques. ① $CH_3-CH_2-CH_2-CH_3$ (I) ; $CH_3-\underset{CH_3}{CH}-CH_3$ (II) — I & II ⇒ CI

② $CH_3-\underset{CH_3}{C}=CH_2$ (I) ; $CH_3-CH_2-CH=CH_2$ (II) — I & II → CI

③ $CH_3-\underset{CH_3}{C}=CH_2$ (I) ; □ (II) — I & II ✗→ CI

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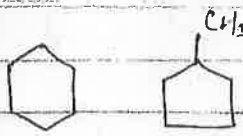
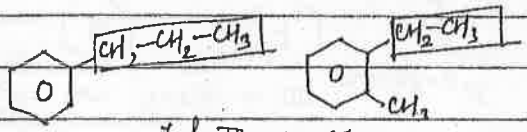
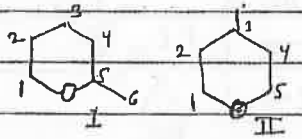
Chain chalti bdi toh chain isomerism.

Date / Page

④  I & II are CI

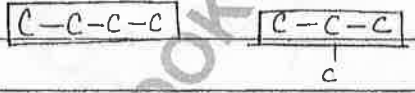
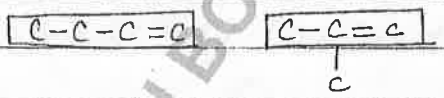
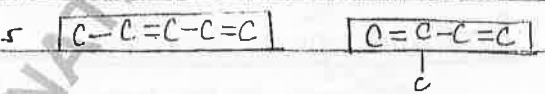
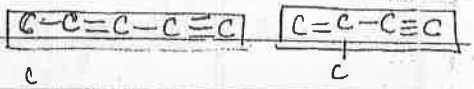
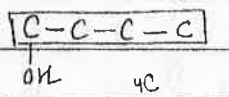
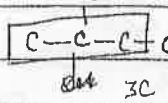
⑤  I & II are CI

⑥  I & II are CI

⑦ 

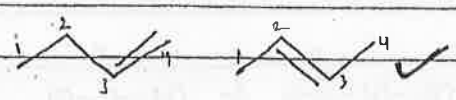
 Both are CI

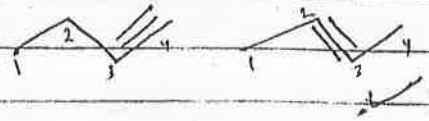
Ques How many min^m C-atom reqd to give CI for following compounds ?

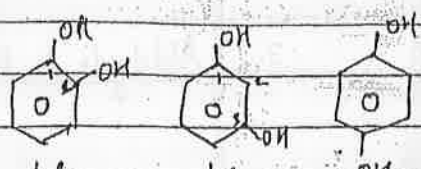
1. Alkane 4 
2. Alkene 4 
3. Alkyne 5 
4. Alkadiene 5 
5. Alkenyne 5 
6. Alcohol 4  4C  3C

II Position isomers -

Compound having same M.f, same f.g, same PCC or side chain but diff position of functional group, multiple bond & substituent.

Ques ① 

② 

③ 

1,2 Catechol 1,3 Resourcinol 1,4 Quinole

Kahi resource lgaya queen.

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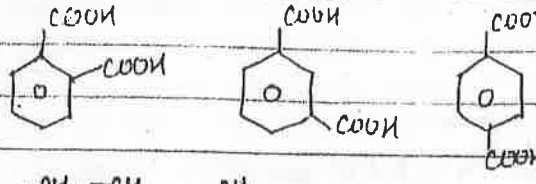
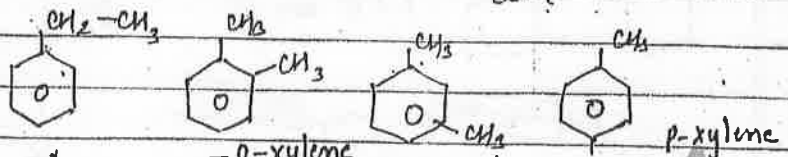
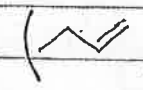
Ortho ↑ Phthalic acid — Meta ↑ iso-phthalic — Tere ↑ Tere-Phthalic acid

④  — all are PI

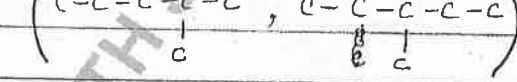
⑤ 

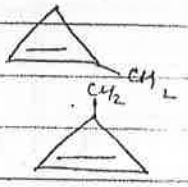
I & II → Chain. II & III
I & III → Chain II & IV } P.I
I & IV → Chain III & IV

Ques How many min^m C-atom reqd to give PI for following compds-

(A) Alkene - 4 

(B) Alkyne - 4 

(C) Alkane - 6 

(D) Cyclopropene 

III Functional group isomerism

Compd having same M.F but diff functional grp.

★ Following functional group give fg isomerism-

1. Acid & ester-

a. $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$ & $CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$ → fgI

2. Cyanide & Isocyanide-

$CH_3-C\equiv N$ & $CH_3-N\rightleftarrows C$ → fgI

3. Aldehyde & Ketone-

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H$ & $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ → fgI

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direct ring → Phenol
→ (OH)

of molecule more.

Date / / Page

1°, 2° & 3° Amines are diff f.g.

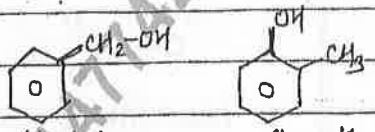
4. Keto & enol form- $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ & $CH_3-\overset{OH}{\overset{|}{C}}=CH_2$ → fg I

Keto form enol form

5. Nitro & Nitrite- CH_3-NO_2 $CH_3-O-N=O$ → fg I

Nitro Nitrite

6. Alcohol & Phenolic compds-



Alcoholic Phenolic

7. Nitro Alcohol & Ether-

CH_3-CH_2-OH & CH_3-O-CH_3

8. 1°, 2° & 3° Amines-

$CH_3-CH_2-CH_2-\ddot{N}H_2$ (I) 1° Amine — I — 2 active H

$CH_3-CH_2-\ddot{N}H-CH_3$ (II) 2° Amine — II — 1 active H

$CH_3-\ddot{N}(CH_3)-CH_3$ (III) 3° Amine — III — no active H

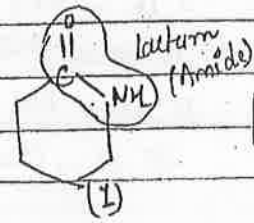
Ques ① $CH_3-CH_2-CH_2-CH_2-CH_3$ (I) DU=0 $CH_3-CH_2-CH_2-CH=CH_2$ (II) DU=1

Not isomers (DU → diff)

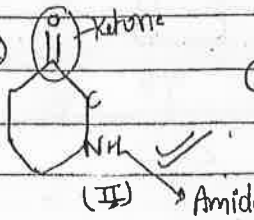
② $CH_3-C\equiv C-CH_3$ (I) (DU=2) $CH_2=CH-CH=CH_2$ (II) (DU=2)] Isomers (functional isomers)

③ $CH_3-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$ $CH_3-\underset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$] Functional grp Isomers.

④



Lactum (Amide) (I)



Ketone (II) → Amide.

⑤

Lactn

→ Ketone → Ether

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* fgI & RCl can never be LL & IL

Date / /
Page

Ques How many min^m C-atom reqd. to give f.gI for any compd?

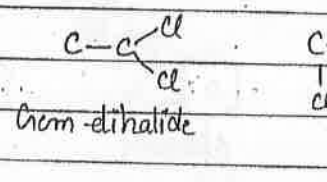
(1)

(CH_3-NO_2 , CH_3-ONO)

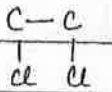
(H-CN , H-N≡C)

Ques Min^m C-atom reqd to give position isomers?

(2)



Gem-dihalide



Vicnal dihalide

IV Ring-chain isomerism

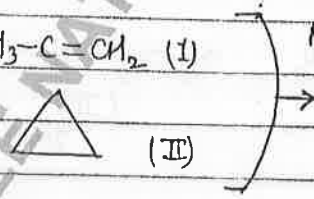
Compd having same M.F but diff mode of linking.

Open chain — Closed chain } cannot be membu of same homologous series

C–OH
C–C–OH
C=C–C–OH

Homologous

Ques C_3H_6 [DU=1]



(I) $CH_3-C=CH_2$

(II)

→ Ring chain isomers & fgI

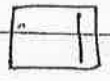
→ All RCl are fgI but vice-versa not true.

→ In case of RCl & fgI priority is given to RCl.

Ques C_4H_6 → D.U = 2

I $C-C\equiv C-C$ — I, III → fg

II $C=C-C=C$ — I, III → f.g, RCl

III  — I, IV → RCl, fgI

II, III → RCl, fgI } Non Hoc } diff

IV  — II, IV → RCl, fgI

III, IV → Chain Isomers

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Chain m compd hmosne bravency hota h.

Date / /
Page

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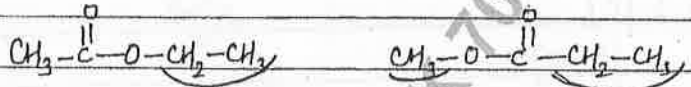
V **Metamers –**

Compd having same M.F but diff alkyl group attached at polyvalent functional group.

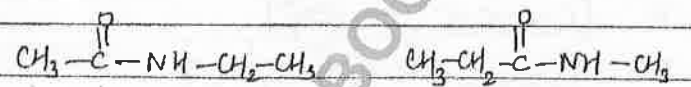
↓

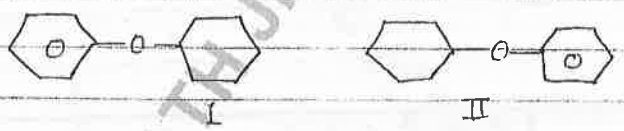
Bi/ Polyvalent functional group.

①  Inter-unit change

↓

only metamers.

②  Inter-unit change only metal.

③  Metamers – X

Identical / Homomers (same-same)

④ $CH_3-CH_2-CH_2-CH_2-O-CH_3$ (I) $CH_3-CH_2-CH_2-O-CH_2-CH_3$ (II)

Intra Inter unit change

Metamers.

⑤ $CH_3-CH_2-CH_2-CH_2-NH-CH_3$ (I)

$CH_3-CH_2-CH(CH_3)-NH-CH_3$ (II)

butyl, iso-butyl

Intra unit change.

Metamers as well as CI

When alkyl grp of one side remains unchanged. Then it can be CI & PI always.

⑥ $CH_3-CH_2-CH_2-CH_2-CH_2-\ddot{N}H_2$ (I)

$CH_3-CH_2-CH_2-CH_2-NH-CH_3$ (II)

$CH_3-CH_2-CH_2-NH-CH_2-CH_3$ (III)

I & II – fg I, I & III → fg I

II & III → Metamers (only)

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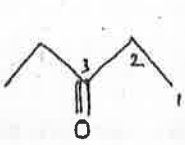


] Metamers & PI

Date / /

Page

Metamers.

- **Inter-unit change** → only metamers *(except Ketones)*
- **Intra-unit change** → Metamers may be CI & PI

Isomers form^{n} probability -

(I) Open chain hydrocarbon -

1. $1C \longrightarrow 1$ [C]
2. $2C \longrightarrow 1$ [C–C]
3. $3C \longrightarrow 1$ [C–C–C]
4. $4C \longrightarrow 2$ [C–C–C–C , C–C(C)–C]
5. $5C \longrightarrow 3$ [C–C–C–C–C , C–C(C)–C , C–C–C–C(C)]
6. $6C \longrightarrow 5$
7. $7C \longrightarrow 9$

[C–C–C–C–C–C , C–C–C–C–C(C) , C–C(C)–C–C–C , C–C–C(C)–C–C , C–C(C)–C–C]

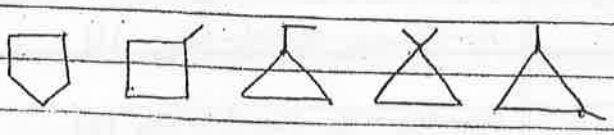
(II) Closed chain hydrocarbon -

$1C \longrightarrow X$

$2C \longrightarrow X$

$3C \longrightarrow 1 \longrightarrow$ 

$4C \longrightarrow 2 \longrightarrow$ 

$5C \longrightarrow 5 \longrightarrow$ 

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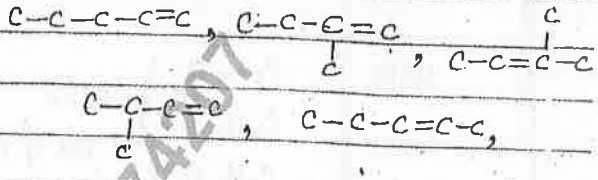
Date / /
Page

Ques How many structural isomers are possible with following molecular formula?

(i) C_5H_{10} Open - 5 Closed - 5

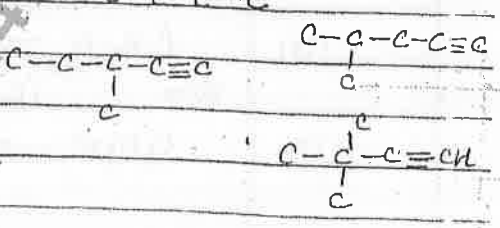
DU = 1



(ii) C_6H_{10} Open - 4 ~~Closed~~

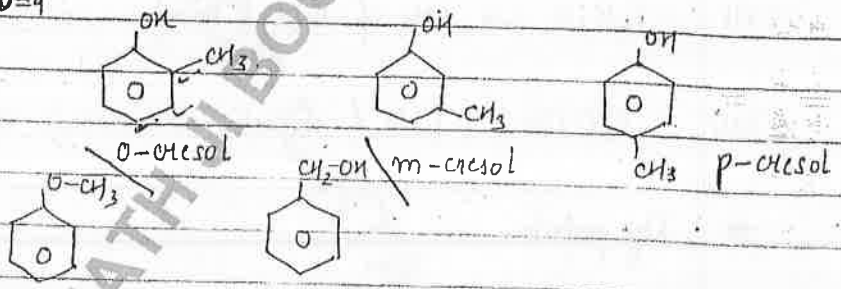
DU = 2

(no. of terminal alkynes)

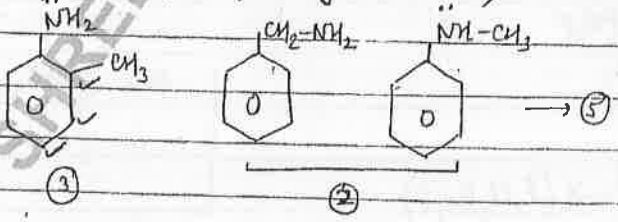


(iii) C_7H_8O (no. of benzoid iso)

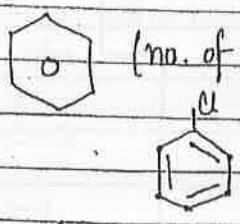
DU = 4



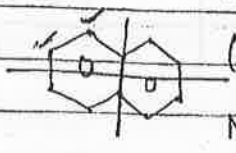
(iv) C_7H_9N (no. of benzoid isomers) DU → 4



(v) (no. of mono-chloro products)



(vi) (no. of mono-chloro product)



Naphthalene (2)

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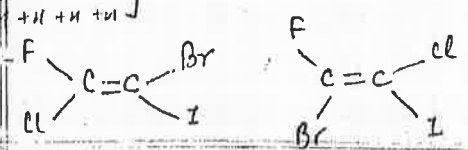
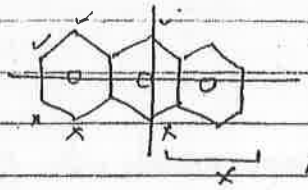
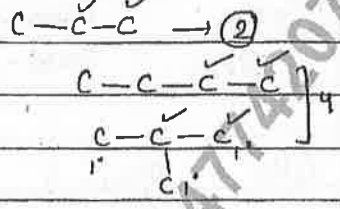
(xii) $C_2FClBrI$ } C_2H_4 → DU = 1 (3)



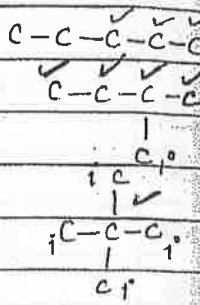
(viii)  No. of mono-chloro product ? (3)

Anthracene

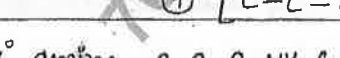
(viii) C_3H_8O, $C_4H_{10}O$, $C_5H_{12}O$ } DU = 0, No. of Alcohol (–OH)



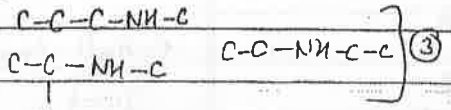
$C_5H_{12}O$ (8)



(ix) $C_4H_{11}N$ (DU = 0) $\xrightarrow{-1H}$ (C_4H_{10}) → No. of 1°, 3° amine (ix)

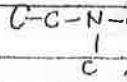
(4) 

(x) C_3H_9N → No. of 1°, 2°, 3° amine

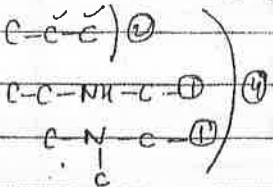


(3)

(xi) $C_4H_8O_2$ → (No. of Acid & ester)

total (8) 

(xii) $C_2FClBrI$ (No. of structural isomers) (x)



(4)

Key points-

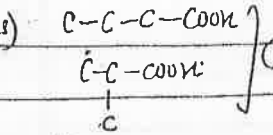
CH_3-	C_2H_5-	C_3H_7-	C_4H_9-	$C_5H_{11}-$
1	1	2	4	8

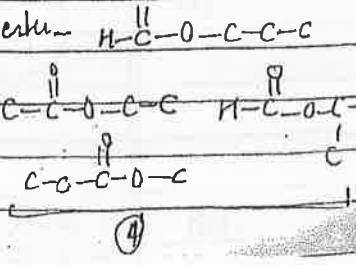
Free valency -

$-X$ (F, Cl, Br, I)

$-NH_2$, $-OH$ ..... etc

(xi) $C_4H_8O_8$ DU → 1

(no. of acids)  (1)

ester- 

(4)

Eg- $C_5H_{11}Cl$ → 8

$C_5H_{13}N$ → 1° Amine → 8

C_4H_9Cl → 4.

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Date / /
Page

26.07.17

(II) Stereo-isomerism -

CONFORMATIONAL ISOMERISM -

→ ∞ no. of stereo-isomers which are formed due to free rotation around a single bond is k/w as conformations & this isomerism is k/w as conformational isomerism.

→ Conformers also k/w as rotamers, & this isomerism is k/w as rotational isomerism.

→ Study of conformations on the basis of P.E is k/w as conformational analysis.

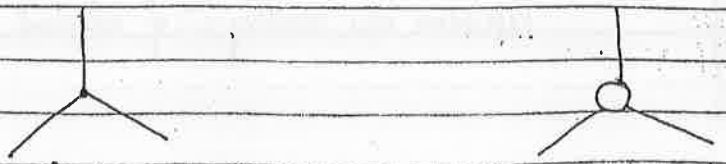
→ ~~Due~~ The energy needed for rotation around a single bond is available at room temp that's why conformers interconvertible to each other at room temp & not seperated & c/d pseudoisomers.

Representation of 3-D molecule:-

1. Newman's projection formula -
(front view / Back view)

→ Front view projection of 3D molecules is k/w as newman's projection formula.

→ C-C bond does not represent in this projection formula.



Front C - represented by dot Back C - represented by circle

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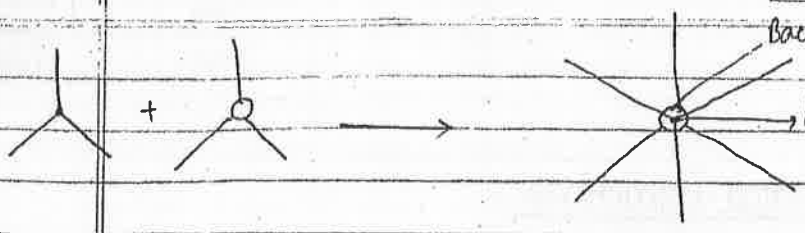
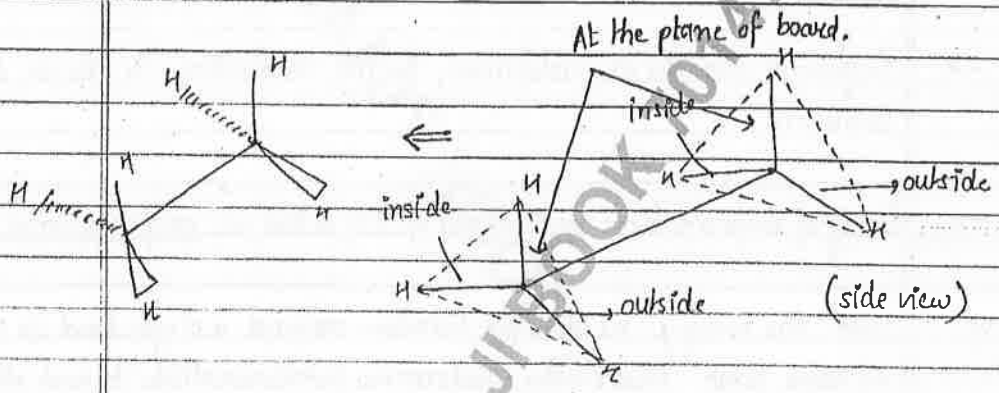


Newman's project formula.

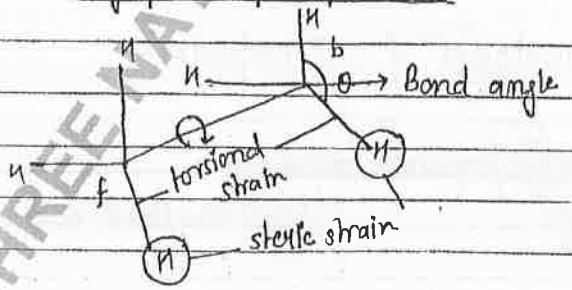
2. Saw-horse projection formula -
(side view projection of 3D molecules)

→ C–C bond represented in this projection.

1.



Stability factor of conformers



Steric strain (SS) -
Repulsion b/w atoms of group.

Torsional strain (TS) -
Repulsion b/w bonding e⁻ of adjacent atoms.

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$0^\circ \rightarrow$ Always eclipsed
$180^\circ \rightarrow$ Anti / Staggered.

Date / /
Page

Bond angle - The angle b/w 2 bond of a same atoms lying in same plane.

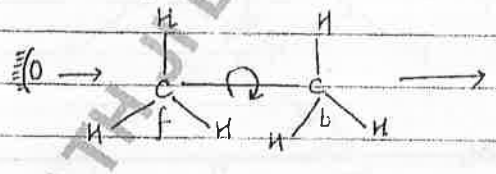
Dihedral angle - The angle b/w 2 bonds of adjacent atoms

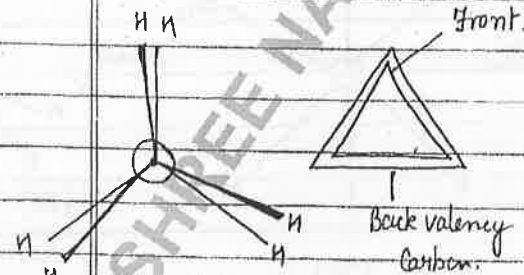
* During conformational isomerism B.A & Bond length remains same while dihedral angle changes.

Skew form -

∞ conformations in b/w eclipsed & staggered (Anti) form is k/w as skew forms.

Conformers of Ethane -

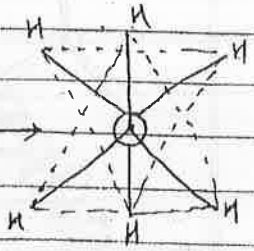




(Eclipsed form)

$\theta = (0^\circ, 120^\circ, 240^\circ, 360^\circ)$

→ Max^m S.S & T.S
→ Max^m inter-electronic repulsion
→ Max^m inter-electron energy
→ Min^m Stability



(Staggered form)

$(\theta = 60^\circ, 180^\circ, 300^\circ)$

→ Min^m S.S & T.S
→ Min^m inter-electron repulsion
→ Min^m inter-electron energy
→ Max^m stability

Energy order - Eclipsed > Skew > Staggered
Stability order - Staggered > Skew > Eclipsed

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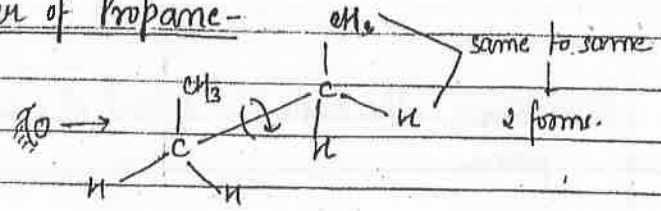
Date / /
Page

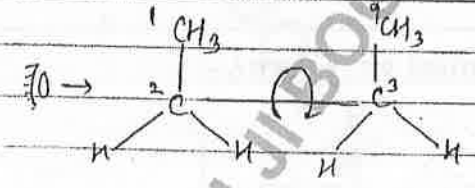
Conformer of Propane-

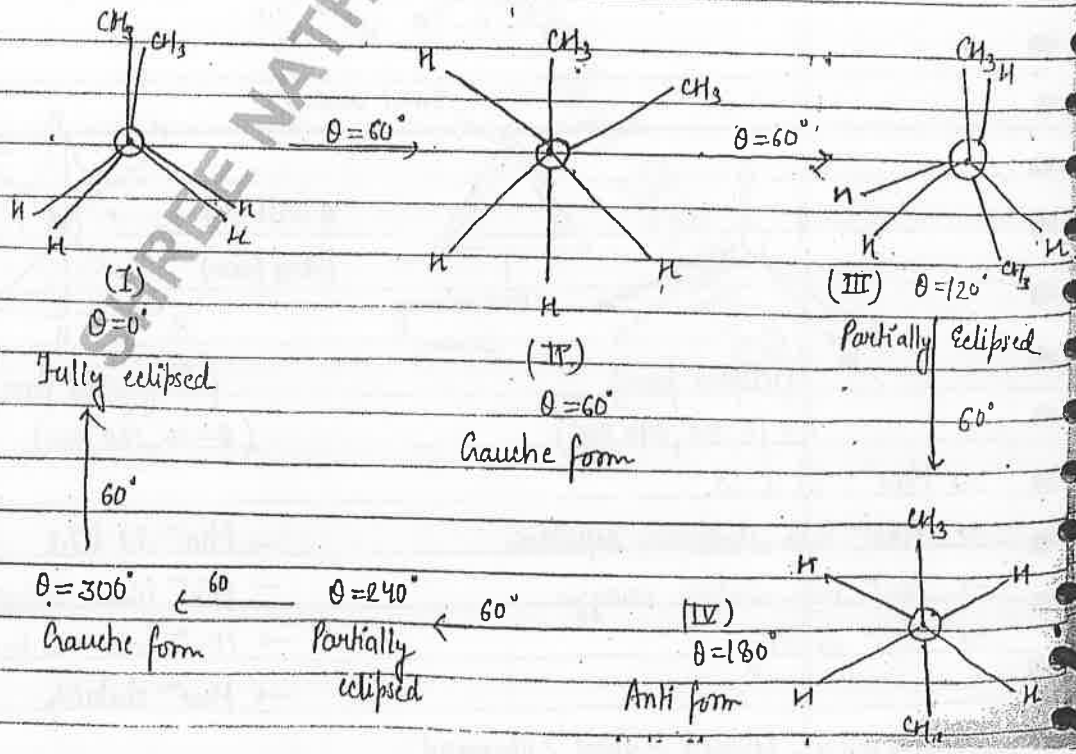


→ Conformers of Ethane, Propane & Butane $\left(CH_3\overset{1}{C}H_2-\overset{2}{C}H_2-CH_3\right)$ are same → same.

Energy order - Eclipsed > Skew > Staggered
Stability order - Staggered > Skew > Eclipsed.

Conformers of Butane-





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Anti → only formed 180°

Torsional strain + Steric strain → Vanderwaal repulsion

Date / Page

Conformational Analysis -

(1) Torsional strain -

$$\left.\begin{matrix} I \cong III \\ II \cong IV \end{matrix}\right\} - I > III > II > IV$$

(2) Stearic strain -

$$\left.\begin{matrix} I \neq III \\ II \neq IV \end{matrix}\right\} - I > III > II > IV$$

Energy order - Fully eclipsed > Partially eclipsed > Gauche > Anti

Stability order - Anti > Gauche > Partially eclipsed > Fully eclipsed.

28.07.17

Conformers -

Out of ∞ conformations which are formed at minimam point of energy profile curve, are conformers.

→ All conformers are confirmations but vice-versa not true. (Stable form)

→ Conformations of ethane = ∞

Conformer of ethane = 1 (Staggered)

→ Conformer of butane ($C-\underset{2}{C}-\underset{3}{C}-C$) = 3 (1 Gauche, +1 Anti)

Cos X Pair

Optically active 1 (mirror imag.

Judgement of stability -

1. Vanderwaal repulsion. (S.S & T.S) -

Staggered more stable > Eclipsed

2. Hydrogen bonding - Gauche form more stable than Anti form/Stagger

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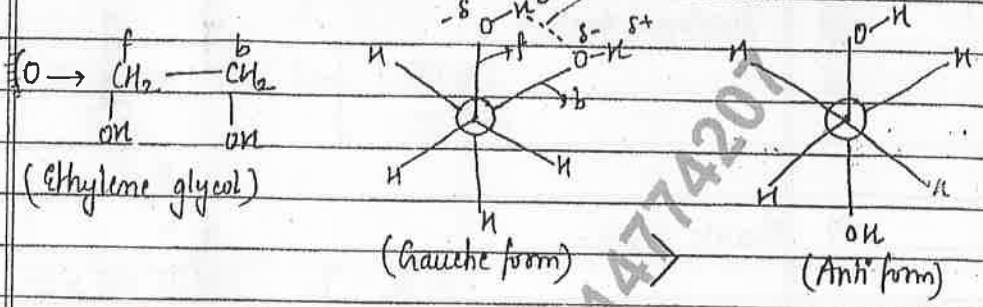
Max^m a.a remains in zwitter ion form.

Date / / Page

Gauche form may be more stable than Anti / Staggered form if following factors exist in Gauche form -

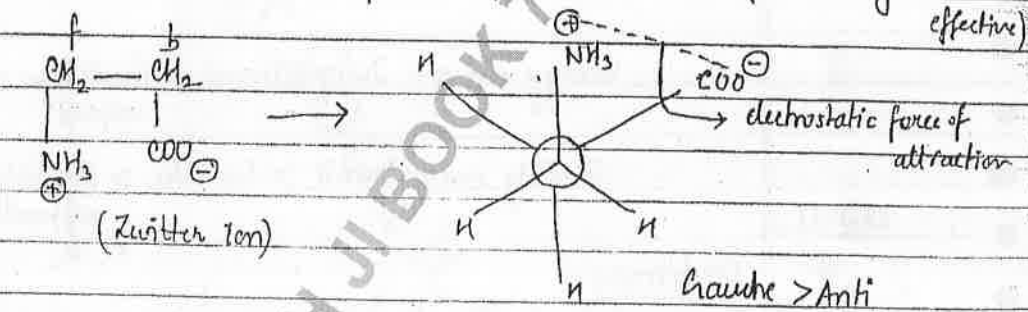
① Hydrogen bonding
② Electrostatic attraction

Eg - ①

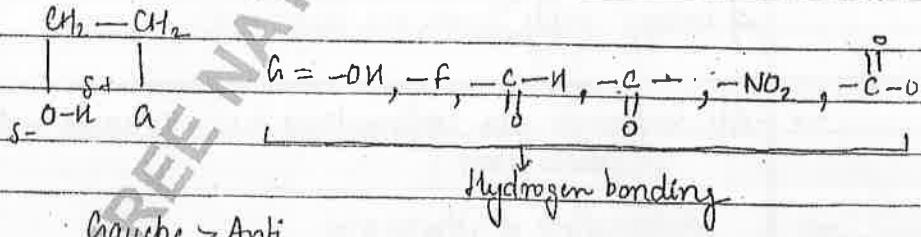


→ In case of eclipsed form repulsion is more (H-bonding is not so effective)

②

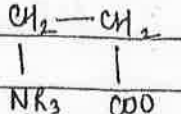


③



Gauche > Anti
(Stability)

④



Gauche > Anti
(electrostatic force of attraction)

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COOH
|
COOH

larger rings [illegible]

↳ like to

Date / /
Page

(5) CH_2-CH_2 (Succinic acid) $\xrightarrow{pH>7}$ ($pH=10$) Basic medium $\rightarrow$ $CH_2(COO^{\ominus})-CH_2(COO^{\ominus})$

Stability – Anti > Gauche

$\xrightarrow{pH<7}$ ($pH=3$) Acidic medium. $\rightarrow$ $CH_2(COOH)-CH_2(COOH)$

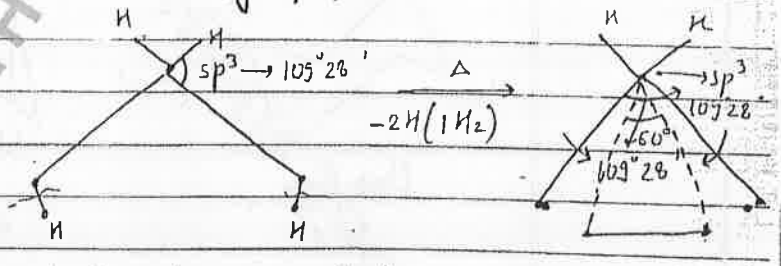
Stability – Gauche > Anti

Conformer of Cyclic ring –
Cycloalkane

→ Any cyclic compound have 3 type of strain –

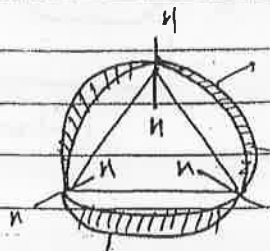
(i) Angle strain
(ii) Steric strain
(iii) Torsional strain.

① Cyclopropane



Real bond angle in propane → 105°28'
Bond angle in cyclopropane → 60°
Angle strain → 49°28'

	% p	% s	B.A
sp^3	75%	25%	105°28'
sp^2	66%	33%	120°
sp	50%	50%	180°



% p character ↑ → π-bond character ↑

σ bond behaves as π-bond

Dash-...Dash...Dash. Dash.

% p ↑ → % s ↓ → B.A ↓

$(\% p \propto \frac{1}{\text{B.A}})$

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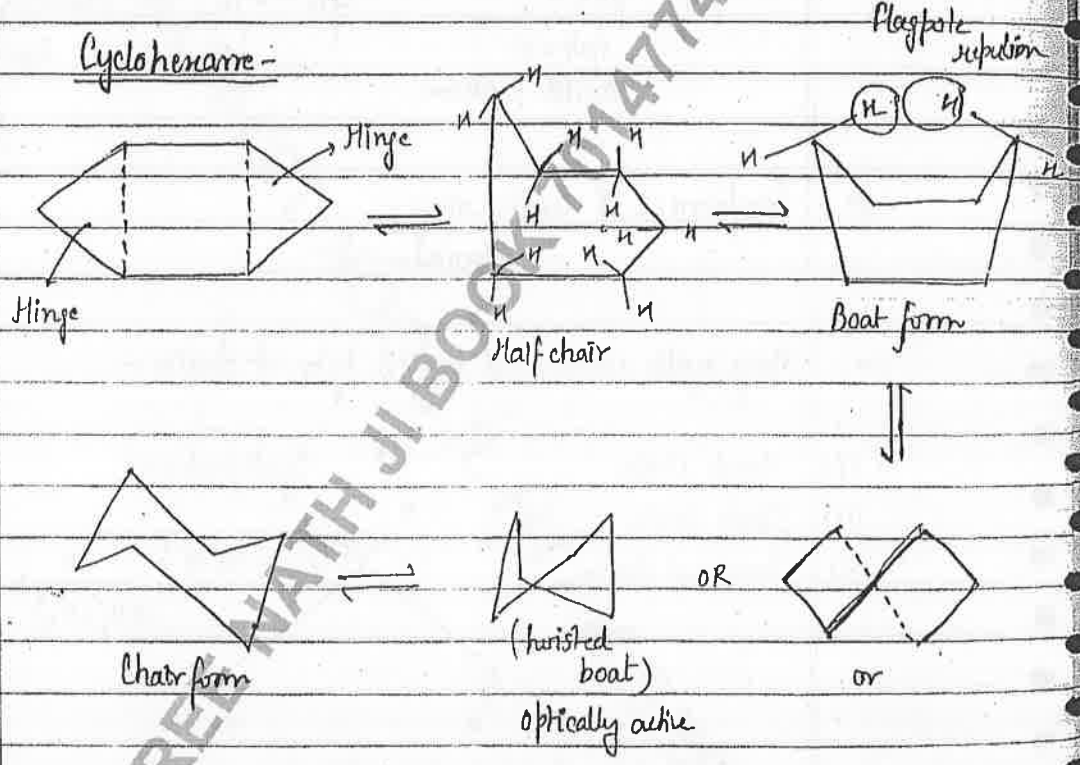
→ High angle strain, planar molecule
→ No flexibility
→ Cyclopropane does not form conformer

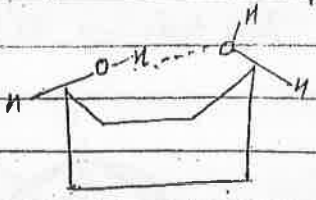
① Cyclopentane -
→ forms envelop at room temp. (appears like wave)
→ Highly unstable.

② Cyclohexane -



Stability - Chair form > Twisted boat > Boat form > Half chair

[Except →



> Twisted boat form

(H-bonding)

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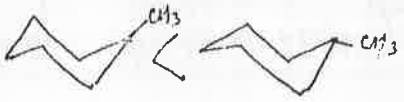
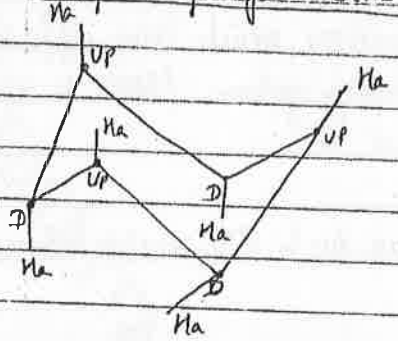
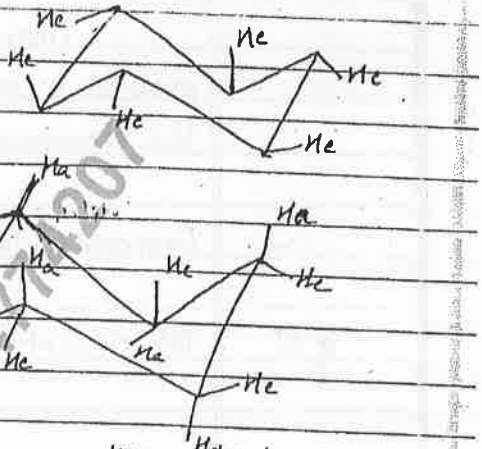
★ In case of cyclopentane (chair form) on bulky grp equatorial position par hona chahiye.

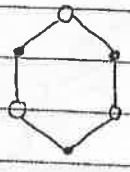


Date / Page

Chair form of cyclohexane -







O → UP
• → down

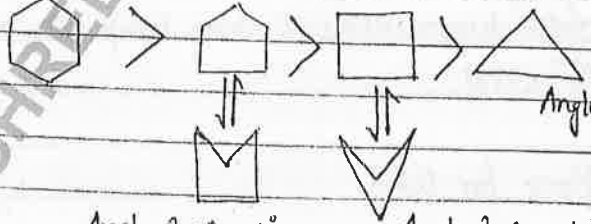
→ Most symmetric molecule
→ Thermodynamically stable molecule
→ Every C bear 2 ideal tetrahedral

Key points -

[UP-UP → cis
UP-down → trans
down-UP → trans]

→ Conformer of cyclohexane = 3 (1 chair + 2 twisted boat)
optically active

Stability of ring -



Angle strain = 49°

Angle strain = 1° → envelop like

Angle strain = 19° → V-shaped structure.

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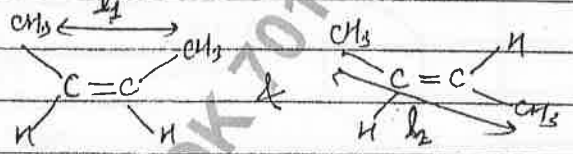
CONFIGURATIONAL ISOMERISM

Geometrical isomerism -

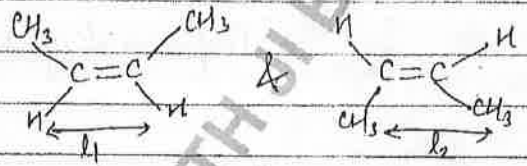
Those stereoisomerisms which have diff 3D relative arrangement around a restricted rotatory system (RRS) is k/w as G.I somers & this phenomena is k/w as GI.

→ Geometrical isomers occur due to diff aerial distance b/w terminal grps.

Eg ① $CH_3-CH=CH-CH_3$



Both are GI $l_1 \neq l_2$ (due to diff aerial distance)



$l_1 = l_2$ (due to same aerial distance)

No GI

→ G.I are not interconvertible at room temp, b/c a bond dissociation energy is 62 KCal.

≠ Conditions for GI -

Condition I. → Compound must has R.R.S /-nce of free rotation / Rigid system / hindered rotation / frozen rotation.

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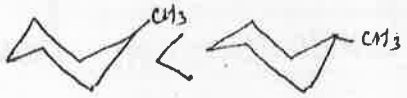
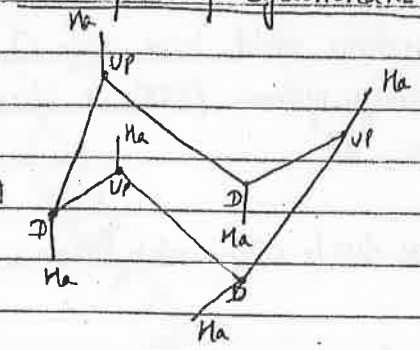
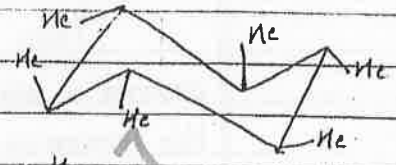
* In case of cyclohexane (chair form) in bulky grp equatorial position par hona chahiye.

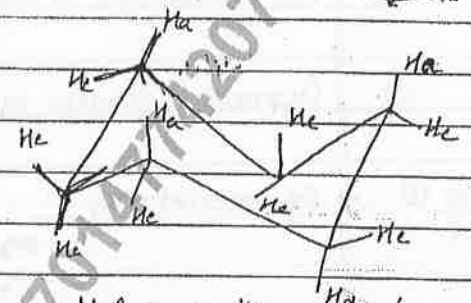


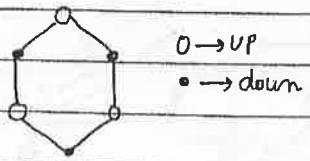
Date / /
Page

Chair form of cyclohexane -









→ Most symmetric molecule
→ Thermodynamically stable molecule
→ Every C bear a ideal tetrahedral

Key points -

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- UP-down → trans
- down-UP → trans

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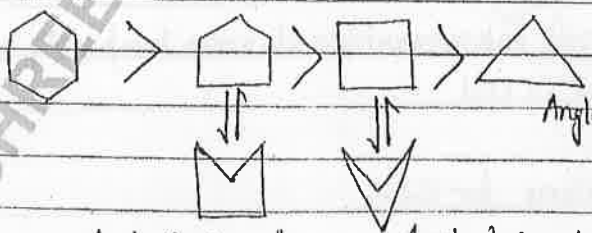
optically active

Stability of ring -



→ envelop like
V-shaped structure.

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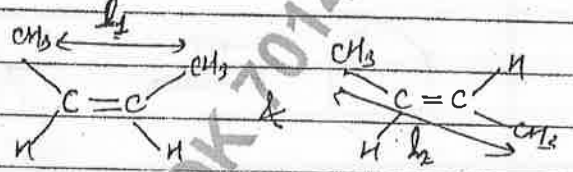

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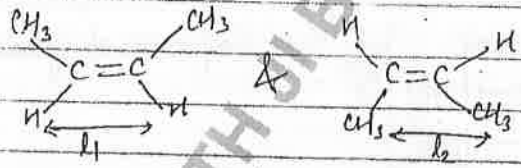

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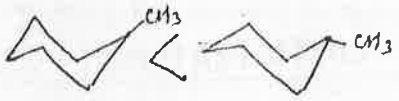
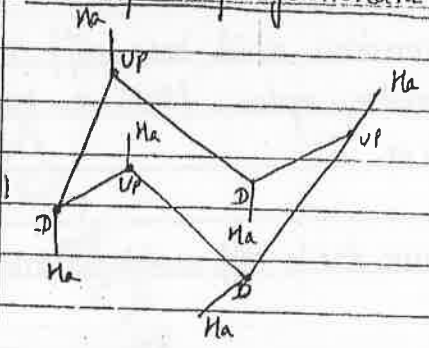
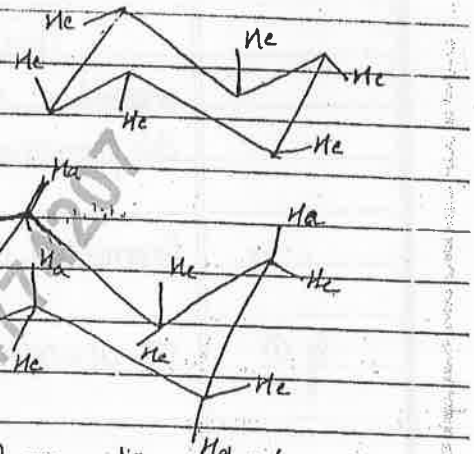
chahiye.

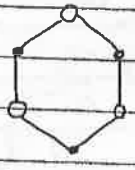


Date / /
Page

Chair form of cyclohexane-







O → UP
• → down

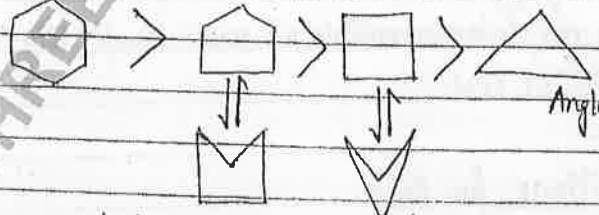
→ Most symmetric molecule
→ Thermodynamically stable molecule
→ Every C bear a ideal tetrahedral

Key points-

- UP-UP → cis
- UP-down → trans
- down-UP → trans

→ Conformer of cyclohexane = 3
(1 chair + 2 twisted boat)
optically active

Stability of ring-



Angle strain = 49°

Angle strain = 1°
Angle strain = 19°

→ envelop like
V-shaped structure.

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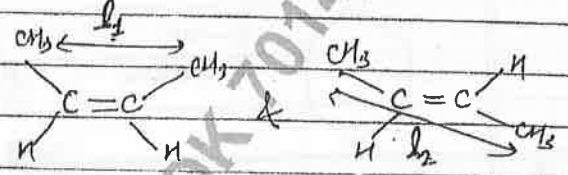
CONFIGURATIONAL ISOMERISM

Geometrical isomerism -

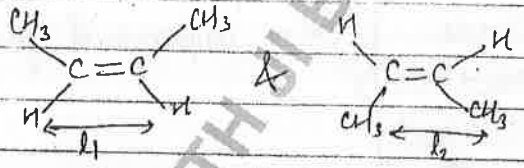
Those stereoisomerisms which have diff 3D relative arrangement around a restricted rotatory system (RRS) is k/w as G.Isomers & this phenomena is k/w as GI

→ Geometrical isomers occur due to diff aerial distance b/w terminal grps.

Eg ① $CH_3-CH=CH-CH_3$



Both are GI $l_1 \neq l_2$ (due to diff aerial distance)



$l_1 = l_2$ (due to same aerial distance)

No GI

→ G.I are not interconvertible at room temp, b/Cs ∴ bond dissociation energy is 62 KCal.

≠ Conditions for GI -

Condition I. → Compound must has R.R.S /-nce of free rotation / Rigid system / hindered rotation / frozen rotation.

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Isomers - (cont...)

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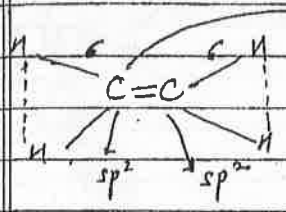
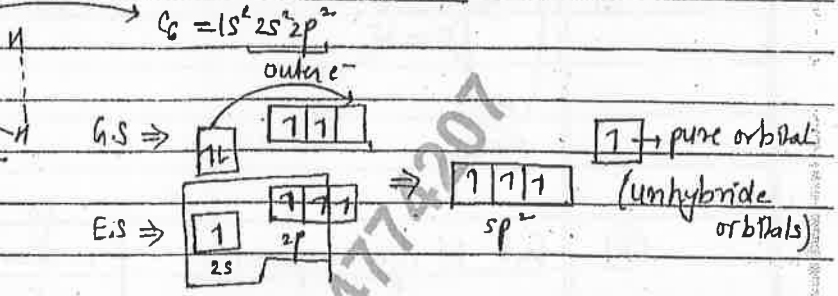
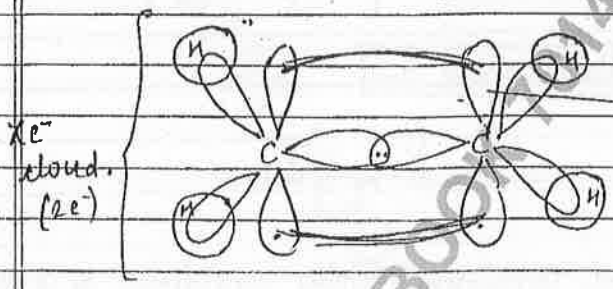
Type of R.R.s -

1. Double bonded RRS



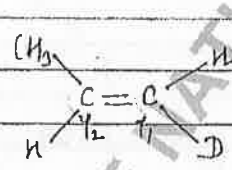
$C_6 = 1s^2 2s^2 2p^{2x}$





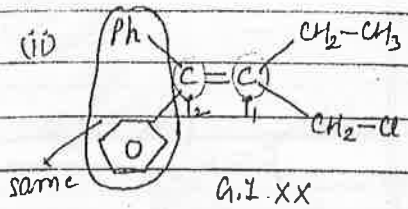
(A) GI in Alkene -

(i)



G.I ✓

(ii)

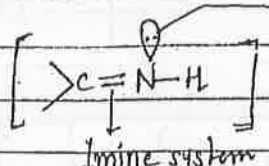


G.I. XX

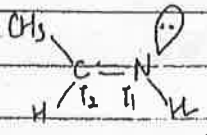
(iii)

G.I ✓

(B) G.I in Imine -

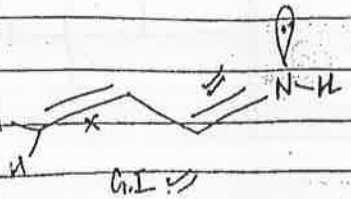


(4)



G.I ✓

(5)



G.I ✓

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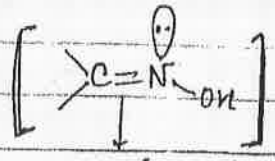
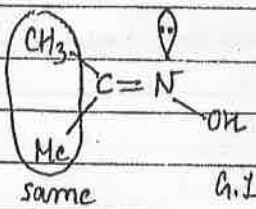
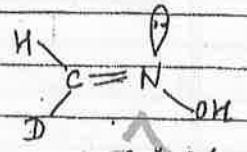
Date / Page

(C) G.I in oxime- 

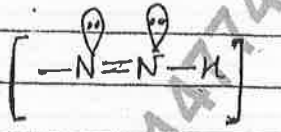
oxime system.

(6) 

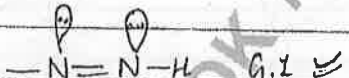
same G.I ✗✗

(7) 

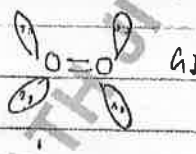
G.I ✓

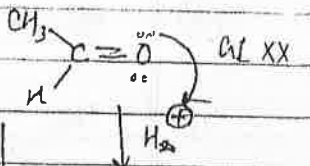
(D) G.I in Azo-compounds- 

Always show G.I

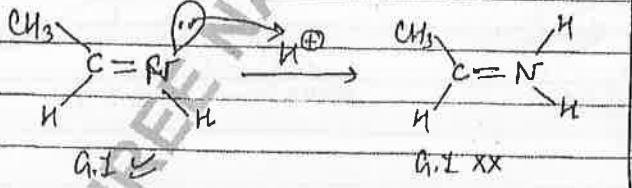
(8) N_2H_2 →  G.I ✓

→ In Geometrical isomerism isotopes considered as a diff atom.

(9) O_2 →  G.I ✗✗

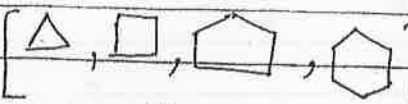
(10) 

G.I ✗✗

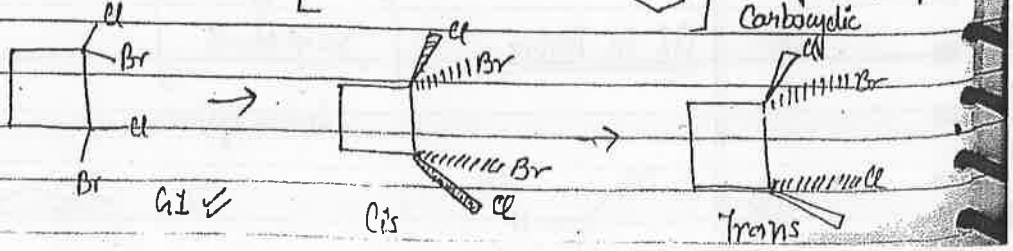
(11) 

G.I ✓ G.I ✗✗ G.I ✓

2. GI in Cycloalkane-

 Aliphatic compd.

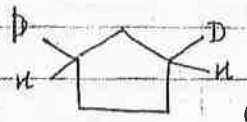
Carbocyclic

(12) 

G.I ✓ Cis Trans

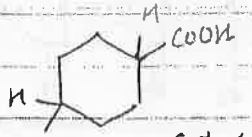
* 2 diff grps on diff terminals – G.I in cycloalkane

(13)



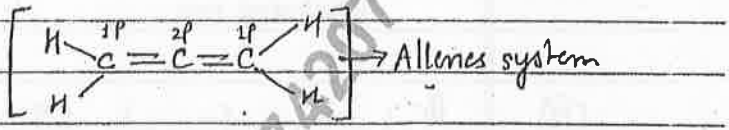
G.I ✓

(14)



G.I ✓

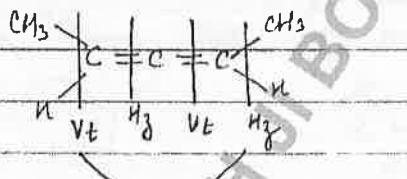
3. G.I in Allene –



→ Whenever 2 double bond continue ~~+nt~~ in an ~~atom~~ system then it is cld allene system.

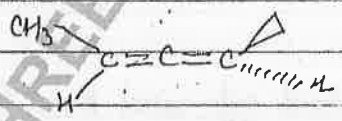
→ Whenever more than 2 double bond ~~+nt~~ in a system then it is cld cumulated dienes.

(15)



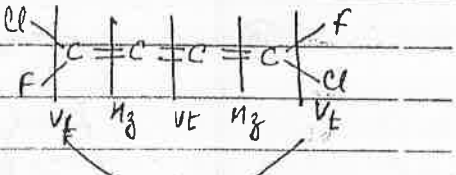
Tetrahedral environment

G.I XX



Axial distance same.

(16)



Square planar environment

G.I ✓

4. G.I in spiro compound –

Whenever 2 rings fused at same C-atom then it is cld spiro compound.

(Both rings are ⊥ to each other).

→ sp^3 Tetrahedral environment

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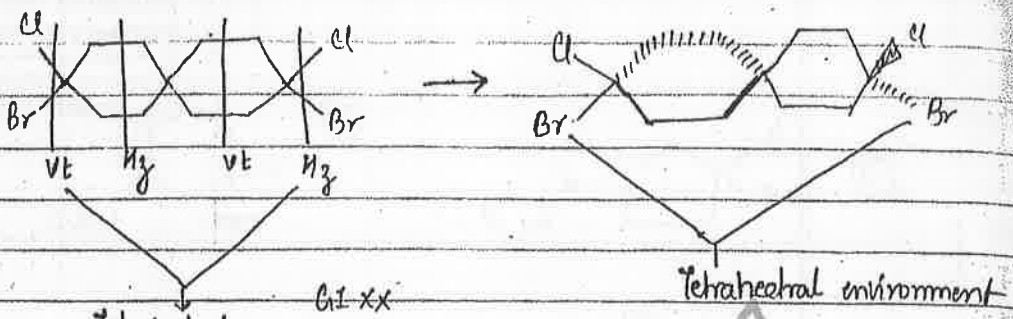
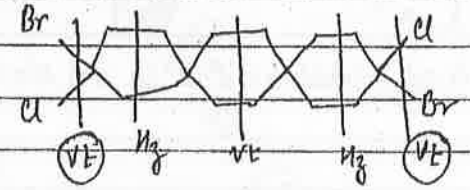
(19)



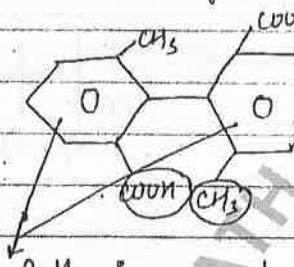
(18)



Square planar environ^{n}
↓
Compd gives G.I ✓

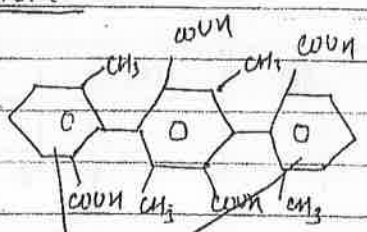
5. **G.I in Biphenyl & Triphenyl system –**

(19)



Both rings are Ieular
Tetrahedral env.
G.I ✗✗

(20).



Square planar env.
G.I ✓
(Both ring in same plane)

Condition 2 : At RRS Both terminal grp must be diff.

Condition 3 : At RRS both terminal valencies must be in a same plane. (square planar environment).

NOTE★ Alkynes will never give G.I, due to its linear structure, b/c in linear structure two 3-D arrangement not possible.

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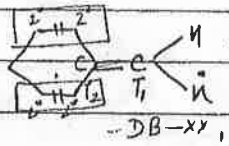
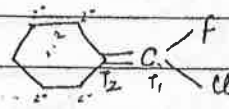
08.17

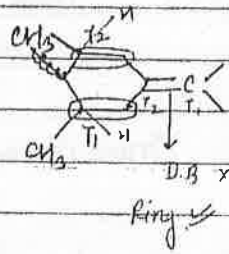
$R_1 - C \equiv C - R_2$

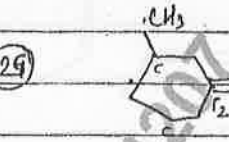
└ sp, linear, GI ✗

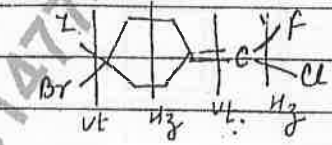
(20)  GI ✗✗

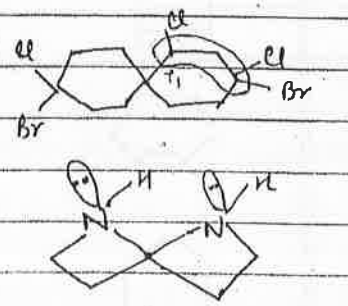
(21) 
DB — ✗✗, Ring ✗✗

(22)  G.I ✗✗

(23) 
D.B ✗✗
Ring ✓

(24) 
GI ✓
D.B ✓
Ring ✗✗

(25) 
G.I ✗✗
Tetrahedral env.
No GI

(26) 

(27)

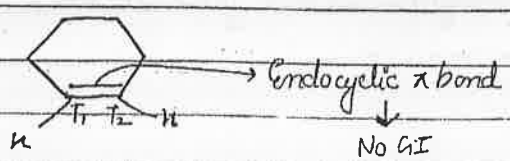
(28)

★ Key point -

→ Whenever terminal groups are diff then odd no double bond containing cumulated dienes (allene) & odd no. ring containing spirosystem gives GI, due to square planar environment.

→ If terminal groups are diff then even no. double bond containing allene system & even no. ring containing spirosystem, does not gives G.I due to tetrahedral environment (due to same aerial distance)

6. G.I in "Endo-cyclic π-bond- (Ring disc)



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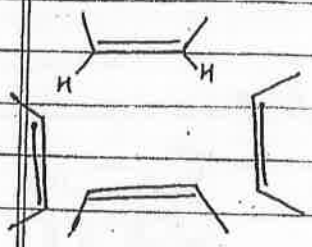
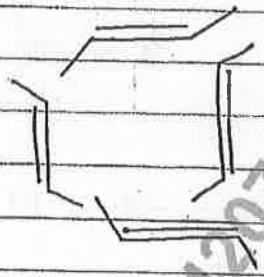
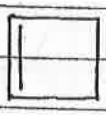
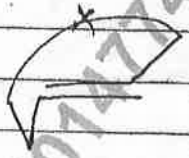
Cis in O. chem.



Trans in O. chem.



4C 



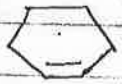
Trans not exist

No G.I ××

5C 

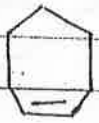
××× Trans does not exist

G.I ××

6C 

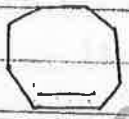
××× Trans does not exist

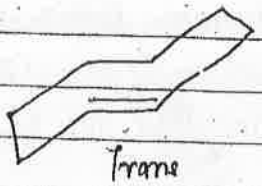
G.I ××

7C 

Trans does not exist

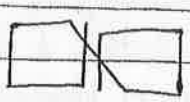
No. G.I ××

8C 



Trans

OR



NOTE :

1. In case of endocyclic π-bond trans that's why endocyclic π bond gives G.I after 7 membered ring.

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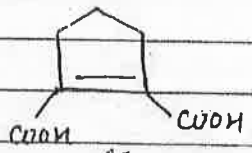
2. In case of endocyclic π-bond 8-11 membered ring -

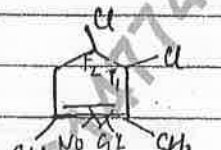
Cis > Trans

&

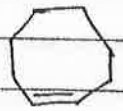
After 12 or 12 membered ring Trans > Cis

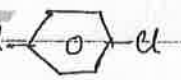
(29) 

GI xx

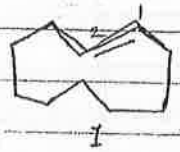
(30) 

double bond xx
Ring GI ≂
∴ GI ≂

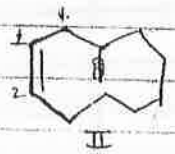
(31) 
GI ≂

(32) 

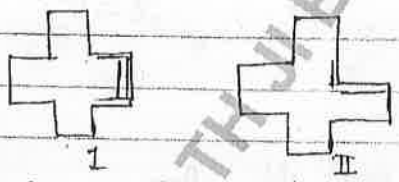
GI xx

(33) 

I
Both are GI



II

(34) 

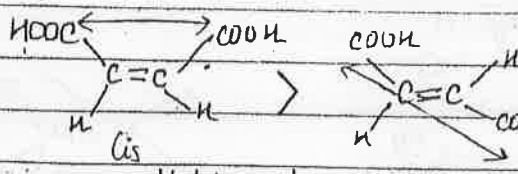
Cis
Trans
I & II are GI
I > II

Nomenclature system for GI

(I) Cis-Trans system -

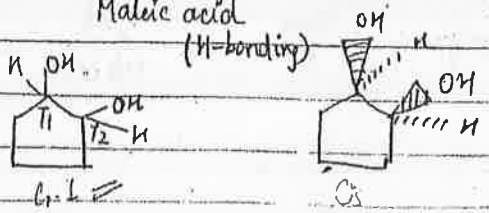
If 2 identical grp at RRS same-same. - Cis

If 2 identical grp at RRS opposite side - Trans

① 

Cis
Trans
Maleic acid
Fumaric acid

(H-bonding)

② 

Cis
Trans

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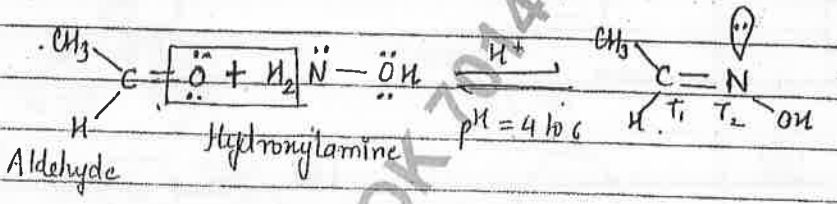
Date / /
Page

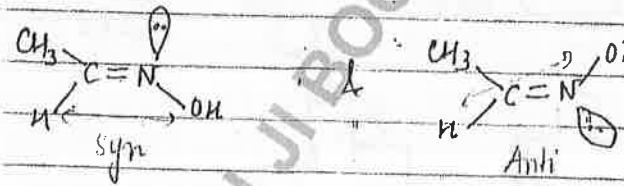
II Syn-Anti System-

→ Whenever one terminal or both terminal of RRI having L.P then syn-Anti system applied.

1. OXIMES -

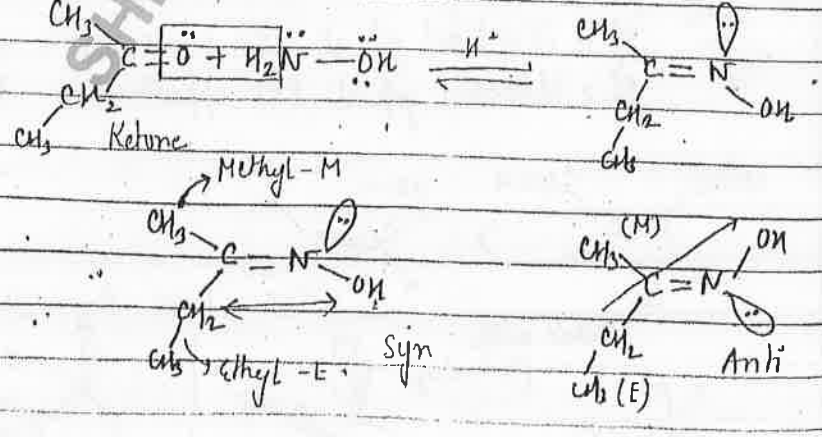
(A) Aldoxime -





→ If H & OH grp both are same side - Syn
→ If H & OH grp both are opposite side - Anti

(B) Ketoxime -



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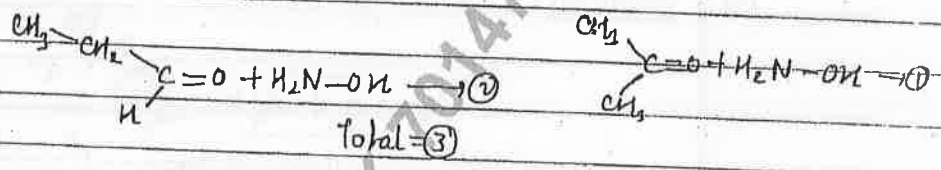
→ Unsymmetrical ketoxime gives G.I.

→ Alphabetically prefer alkyl grp & OH grp same side - Syn.

→ Alphabetically prefer alkyl grp & OH grp both opposite side - Anti

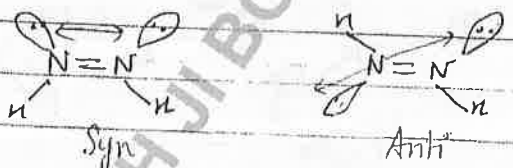
L.p the

Ques $\underbrace{C_3H_6O}_{DU=1}$, No. of oximes = ?



OH

2. AZO COMPOUNDS :



→ Both L.p same side - Syn

→ Both L.p opposite side - Anti

☆☆ III E-Z system -

(CIP rule) (Cohn, Ingold, Prelog)

→ Latest system

E → ENTGEGAN (Opposite side)

Z → Zeusseman (same side)

→ Whenever all 4 grps are diff at both terminal of R&S then the new system E-Z applied.

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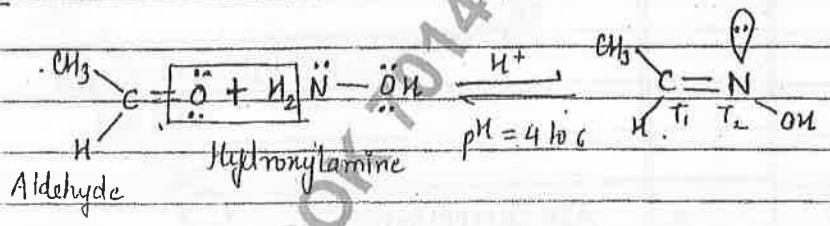
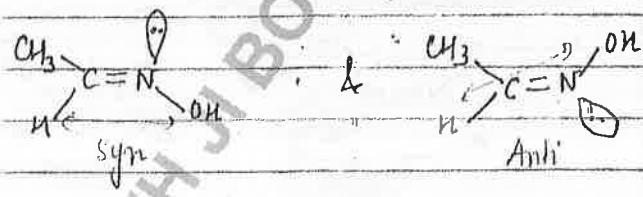
II Syn-Anti System-

→ Whenever one terminal or both terminal of RRI having L.P then syn-Anti system applied.

1. OXIMES-

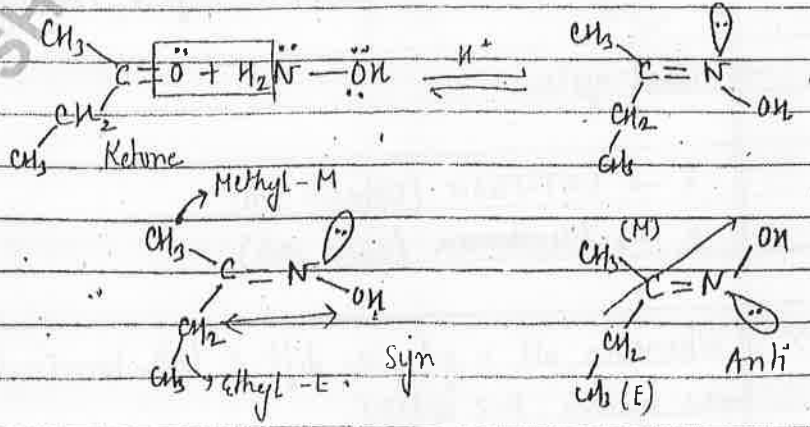
(A) Aldoxime-





→ If H & OH grp both are same side - Syn
→ If H & OH grp both are opposite side - Anti

(B) Ketoxime-



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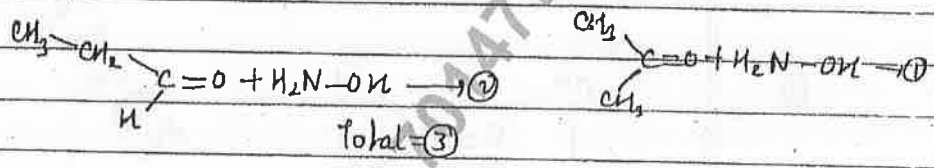
→ Unsymmetrical ketoxime gives G.I.

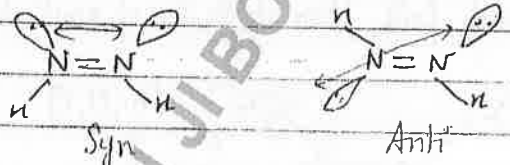
→ Alphabetically prefer alkyl grp & OH grp same side - Syn.

L.p rhs → Alphabetically prefer alkyl grp & OH grp both opposite side - Anti

Ques $\underset{DU=1}{C_3H_6O}$, No. of oximes = ?



OH 2. AZO COMPOUNDS :



→ Both L.p same side - Syn

→ Both L.p opposite side - Anti

III E-Z system -

(CIP rule) (Cohn, Ingold, Prelong)

→ Latest system

E → ENTGEGAN (Opposite side)

Z → Zeusseman (same side)

↔ Whenever all 4 grps are diff at both terminal of RES then the new system E-Z applied.

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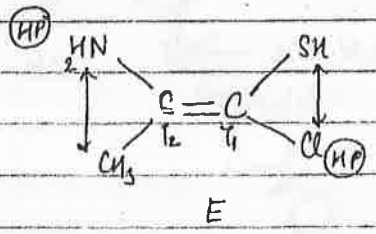
→ High priority (HP) grp same side → Z
High priority (H.P) grp opposite side → E

4.08.17

Priority rules -

Rule 1 : Priority of atoms or groups ∝ At no. of atom which are directly attached to terminal of R.R.S.

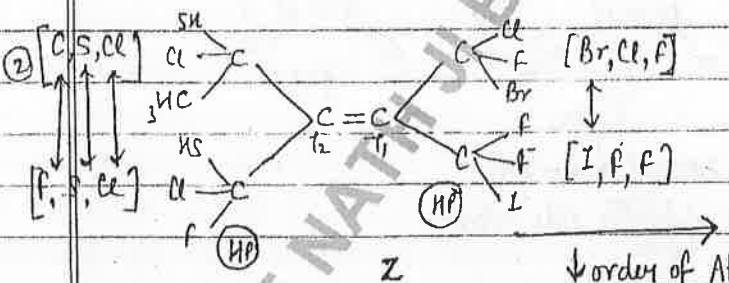
(1)



E

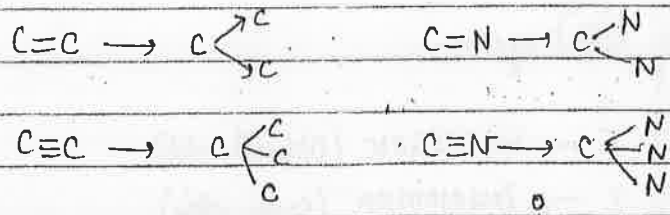
Rule 2 : If first rule fails then atomic no. of next atom considered.

(2)

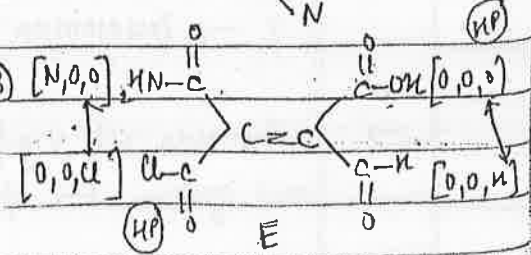


Z

Rule 3 : If multiple bonds are not then it considered as a -



(3)



E

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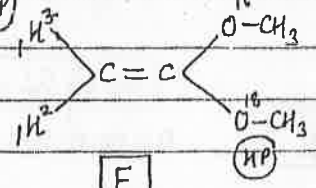
Date / /
Page

Rule-4 If isotopes ent, **Priority of isotopes ∝ At. mass**

(4) Tritium/ $_1H^3$ (HP)

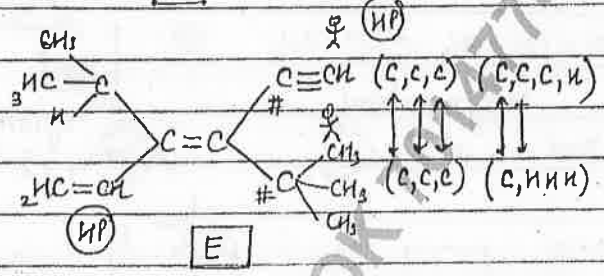
Deuterium/ $_1H^2$



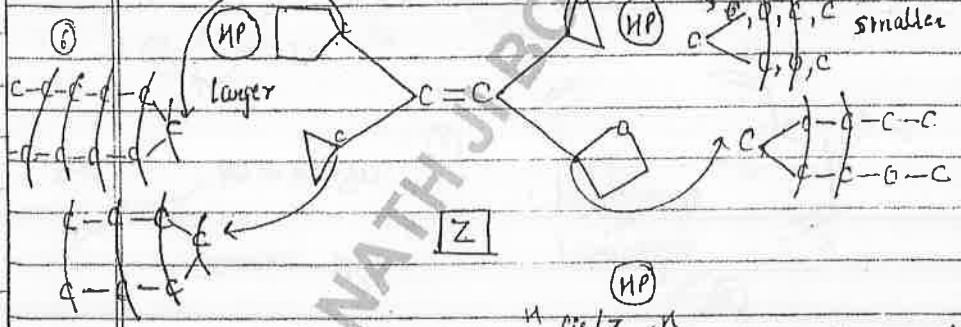
E

Attached

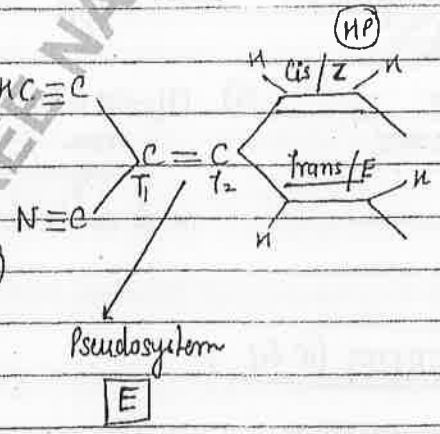
(5)



(6)



(7)



* In case of pseudosystem -

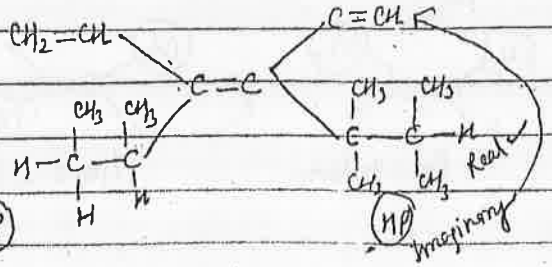
Priority rule -

Cis > Trans

Z > E

R > S

(8)



Concept -

Priority **Real > Imaginary structure**

HP
[0,0,0]
[0,0,H]

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Always total stereoisomers are not i.e optical + G.I

Date / /
Page

No. of Geometrical isomers –

Symmetrical system | Unsymmetrical system

n = even: $2^{n-1} + 2^{\frac{n}{2}-1}$

n = odd: $2^{n-1} + 2^{\frac{n-1}{2}}$

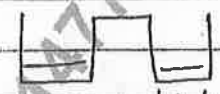
No. of G.I $= 2^n$

n = no. of site where G.I possible

① $CH_3-CH=CH-CH_2-C\equiv C-CH_3$

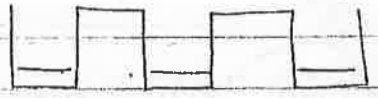
unsymmetrical

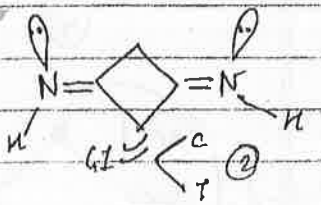
n = 1 $\quad 2^n = 2$

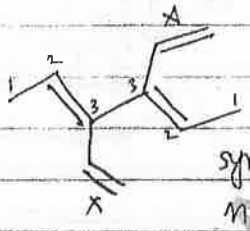
② 

symmetrical

$2^{2-1} + 2^{\frac{2}{2}-1} = 2+1 = 3$

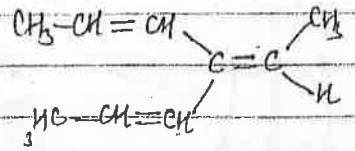
③ 

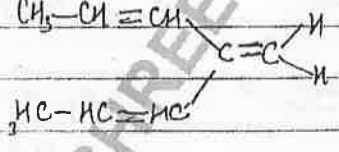
④ 

⑤ 

symmetrical.

n = 2 (even)

⑥ 

⑦ 

⑧ $CH_3-CH=CH-CH=C=C=CH-CH_2-CH_3$

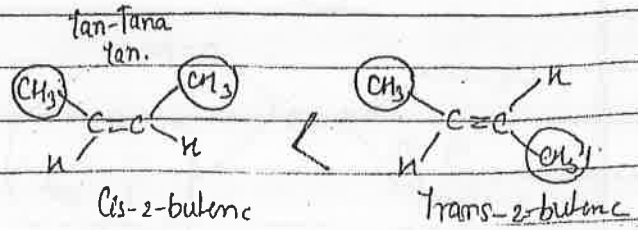
n = 2

unsymmetrical

no. of G.I $= 2^n = 2^2 = 4$

PROPERTIES OF G.I :

1. STABILITY –



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Date / /
Page

2. **DIPOLE MOMENT -**

Degree of polarity will be measured by dipole moment.

→ Dipole moment is a vector quantity.

Less EN + ⟶ More EN
(δ+) (δ−)

$CH \equiv CH$ $CH_2 = CH_2$ $CH_3 - CH_3$

↓ sp ↓ sp^2 ↓ sp^3

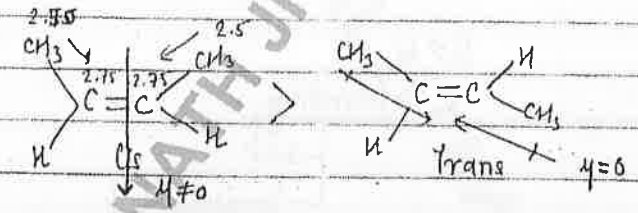
% s-char. = 50% % s char. = 33% % s char. = 25%.

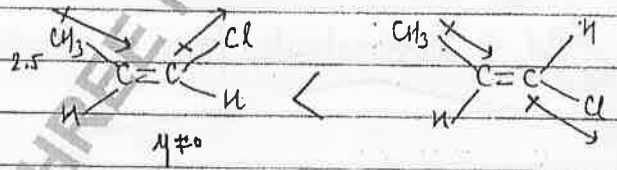
↓ ↓ ↓

Near to nucleus EN = 2.75 EN = 2.5

↓

Attraction ↑, EN ↑ = 3.25

① 

② 

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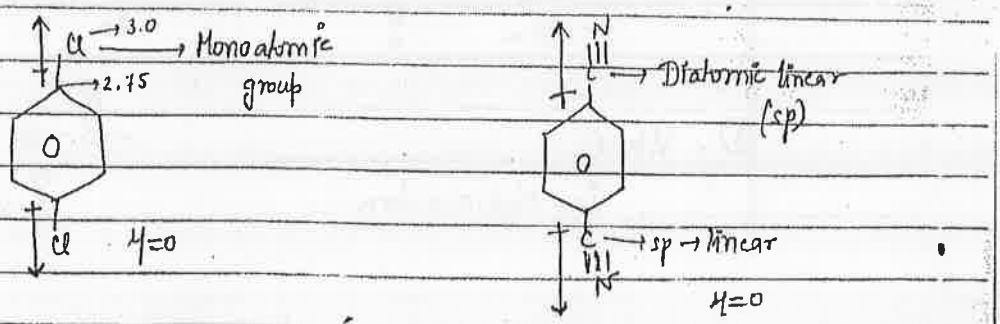
Dipole moment at para position of Benzene molecule -

③ 

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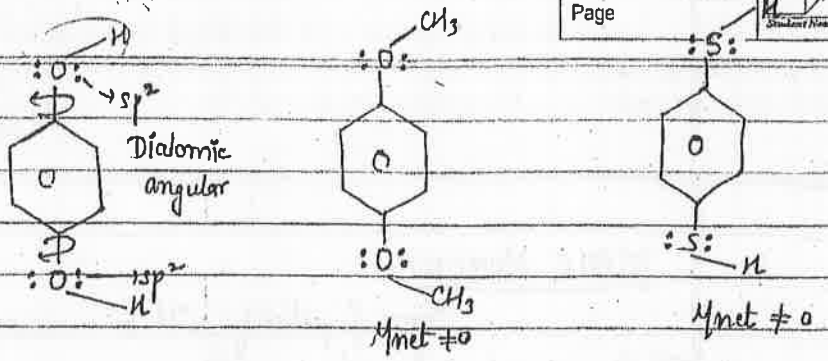
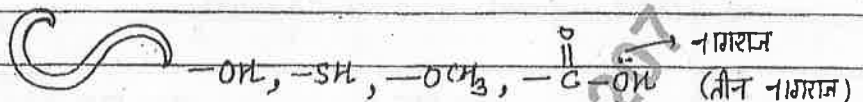
★ Cis Maleic & Trans Fumaric acid $\mu_{net} \neq 0$

★ Catechol, Resourcinol, Quinol - $\mu_{net} \neq 0$

Date / /
Page

④





→ Whenever diatomic angular group ~~not~~ at para-position of benzene molecule then angular grp forms infinite conformations around a single bond. In this case, $\mu_{net} \neq 0$ (non-zero).

3. # **Boiling point -**

Key points -

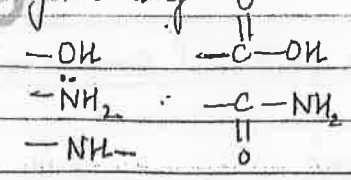
$B.P \propto$ Mol. wt (Mw)

$B.P \propto \frac{1}{\text{branching}}$

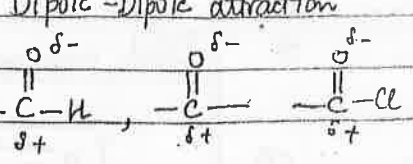
- S.A ↓
- Vanderwaal ↓

$B.P \propto$ Intermolecular force of attraction

① Hydrogen bonding

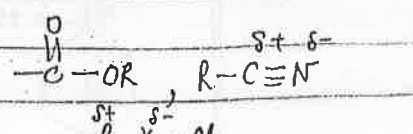


② Dipole-Dipole attraction



③ . V.W.F

Eg - Hydrocarbon



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Date / /
Page

Ques ① C–C–C–C–C > C–C–C(C)–C > C–C(C)(C)–C (Branching)

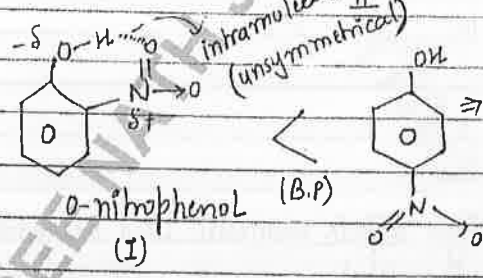
② C–Cl (I) C–Br (II) $CHBr_3$ (III) CBr_4 (IV) IV > III > II > I (M.wt)

③ ④ C–C–C–C–C ① C–C–C(OH)–C ⑤ C–C(=O)–C–C ④ C–C(C)–C–C

④ $R-C(=O)-NH_2$ > $R-C(=O)-OR$ (same Mw)

⑤ C–C–C(OH)–C(OH) (I) > C–C–C–C–OH (II)

⑥ C–C–C–C–NH_2 (I) < C–C–C–C–OH (II) → Hydrogen bonding (more effect in Alcohol)

⑦ 

o-nitrophenol (I) < p-nitrophenol (II)

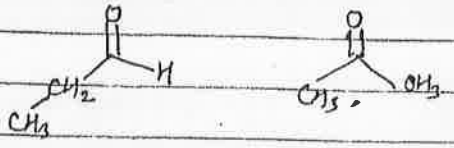
Can be seperated by steam distillation method. b/c → o-nitrophenol is steam volatile. (It can be seperated out of mix of H_2O)

⑧ 

$\mu \propto B.P$
$\mu \propto$ solubility $\propto$ viscosity

μ → Cis > trans

B.P → cis > trans

⑨ 

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$-C-C-C-$ hydrocarbon chain ↑ → solubility ↓

$CH_3-CH_2-NH_2 > CH_3CH_2OH$

Date / /

Page

4. **Melting point**

Key points -

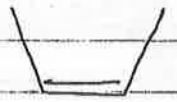
M.P ∝ H.wt

∝ Packing efficiency (Interlocking more)

∝ symmetry of molecule

∝ Branching.

(1)



cis

I

trans

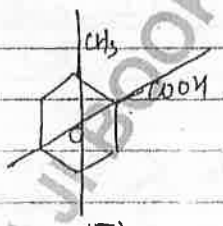
II

P.E : II > I

M.P : II > I

(2)

(I)



(II)

Symmetry - I > II

M.P - I > II

5. **Solubility -**

Cl having high dipole moment will be more soluble in polar solvent & Cl having less dipole moment will be more soluble in non polar solvent.

p-nitrophenol > o-nitrophenol

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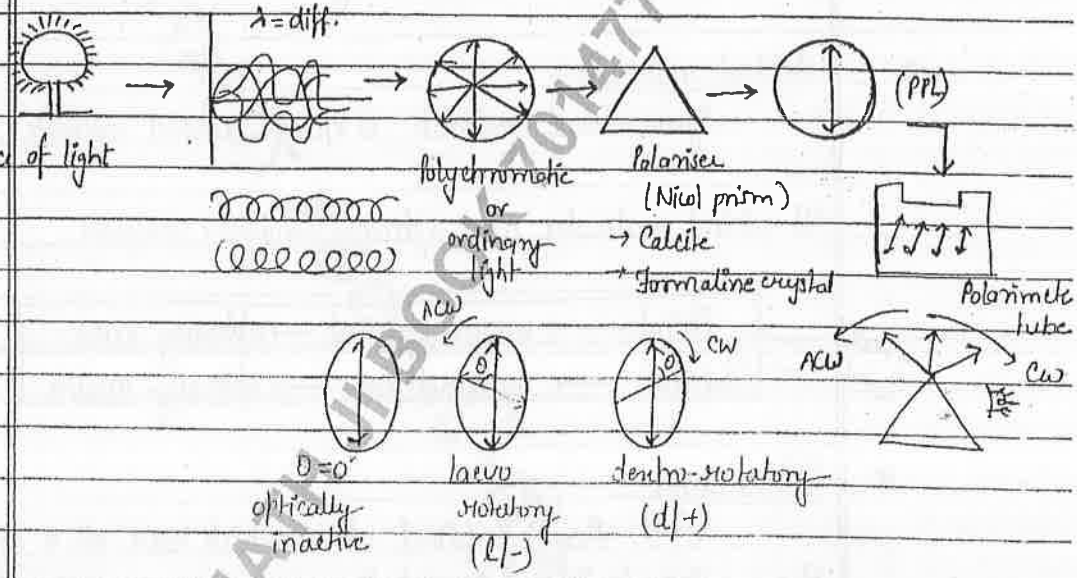
9.08.17

OPTICAL ISOMERISM :

Compound having same M.F, same structural formula but diff behaviour towards PPL are k/w as optical isomers & this phenomena is k/w as optical isomerism.

Polarimeter experiment -



Compounds is optically inactive due to 3 reasons -

→ Compound does not give optical isomerism - Achiral molecule
→ Compound give optical isomerism but optically inactive - Meso compound.
→ Compound may be equimolar mixture of 'd' & 'l' isomers.
(Racemic mixture)

Some important terms -

* Optical activity -

Tendency to rotate PPL.

* Optically active compounds -

Compds which are capable to rotate PPL.

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→ Sansaar k vo compds jo room temp pr ghum kr apni mirror image ni bnate hain vo optically active hote hain.

Date / /
Page

★ Optically inactive compd-
Compounds which are incapable to rotate PPL.

★ Chiral molecule-
Unsymmetrical molecule is k/w as chiral molecule.

→ All chiral molecules are optically active molecules.

★ Achiral molecule-
Symmetrical molecule is k/w as achiral molecule.

→ All achiral molecules are optically inactive molecule.

greek word
Chiral ⟶ unsymmetrical ⟶ optically active
Achiral ⟶ symmetrical ⟶ optically inactive

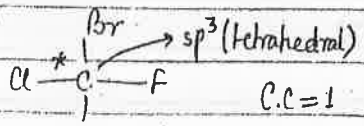
★ Chiral centre-
(C.C) Any sp^3 hybridised atom which have all 4 diff groups is k/w as C.C (asymmetric centre).

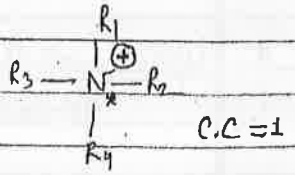
10.08.17

→ Chiral centre is not a necessary condition for a compound to be optically active (optical activity).

→ Generally if compd having only one chiral centre then compound is optically active (Except - Amine flipping)

Any sp^3 → (C, N, O, P, S)

(1) 

(2) 

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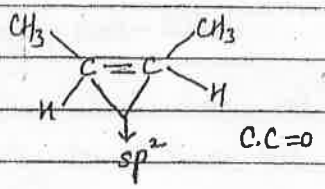
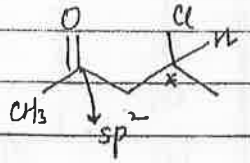
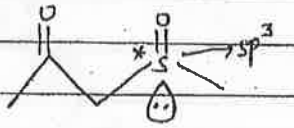
Chiral centre milte hain hmesha branen pr pr

Date / Page

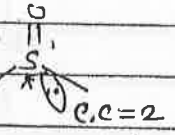
(3) 

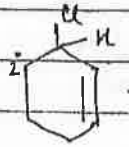
C.C = 0

(4) 

(5) 

C.C = 1

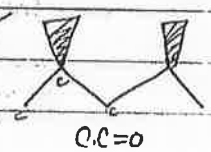
(6) 
C.C = 2

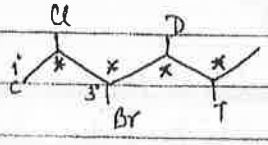
(7) 

C.C = 1

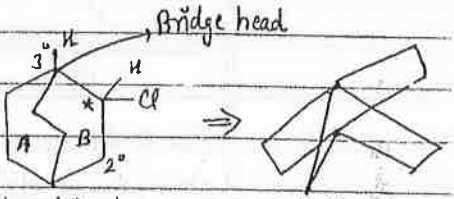
(8) 

C.C = 0

(9) 
C.C = 0

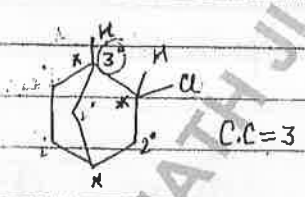
(10) 

C.C = 4

(11) 

(Bridge bicyclo compound)

Bridge head.

(12) 

C.C = 3

$C_8H_{14} \Rightarrow C_8H_{10} \Rightarrow 4H \Rightarrow 2H_2 \Rightarrow DU = 2$

(not bicyclo)

Conditions for Optical activity -

↓

for a molecule to be optically active

↓

Compound must be chiral or unsymmetrical

(Compound & its mirror image both are non-superimposable)

↓ Condition 1

If compd having only one chiral centre then chiral centre is sufficient condition for a molecule to be optically active (optical activity).

↓ Condition 2

If compd having more than one chiral centre then chiral centre is not a sufficient condition for a molecule to be optically active, in this case the whole molecule must be chiral or unsymmetrical * for a molecule to be chiral or unsymm

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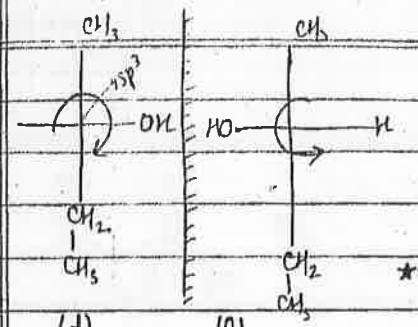
Date / /
Page

11.08.17

Eg ①



Symmetry elements –

(i) COS – Centre of symmetry
(ii) POS – Plane of symmetry
(iii) AOS – Axis of symmetry

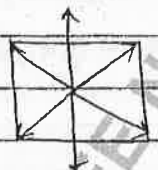
** for a molecule to be optically active COS & POS must be –nt.

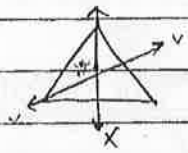
→ ** Compd & its mirror image both are non-superimposable Optically active compd.

Symmetry elements –

(1) Centre of symmetry (COS) –

It is an imaginary pt. situated at the centre of molecule, from the centre if we draw a straight line then they will meet at same atom, same distance but in opposite direc^{r} then molecule has COS.

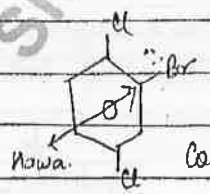
① 
COS ✓

② 

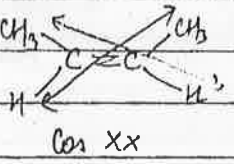
Cos XX

③ 

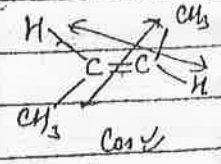
COS ✓

④ 

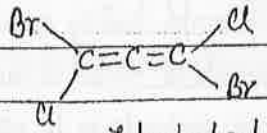
Cos XX

⑤ 

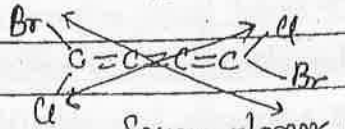
Cos XX
Cis

⑥ 

Cos ✓
Trans

⑦ 

Tetrahedral env.

⑧ 

Square planar env.
Cis ✓

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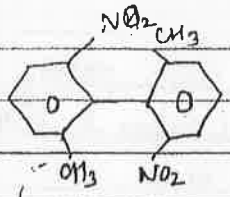
★ Tetrahedral envi. mein kbhi Cis nhi hta.

Date / /
Page

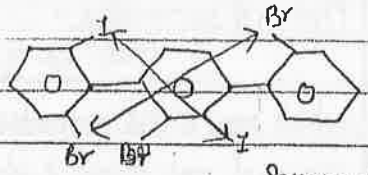
(9)



Tetrahedral envi.

Cis ✗✗

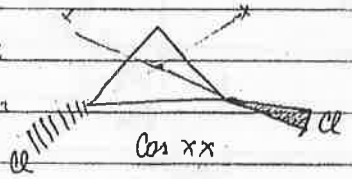
(10)



Square planar envi

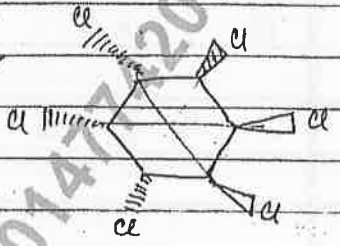
Cis ✓

(11)



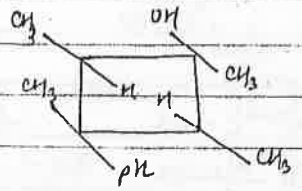
Cis ✗✗

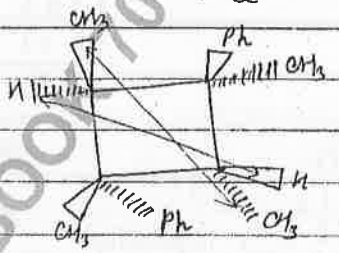
(12)



Cis ✓

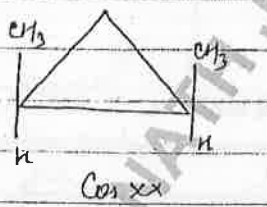
(13)





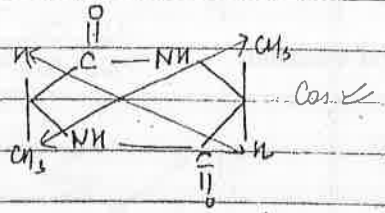
Cis ✓

(14)



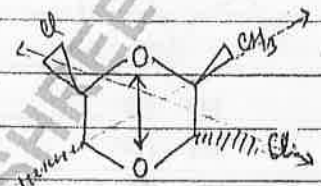
Cis ✗✗

(15)



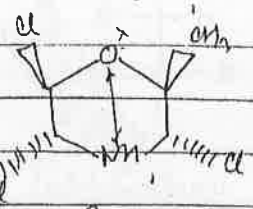
Cis ✓

(16)



Cis ✓

(17)



Cis ✗✗

★ Key points –

(1) Cis is -nt in odd no. atom containing ring.

(2) Cis is -nt in Cis isomers.

(3) Cis is -nt in all the molecules which can form tetrahedral environment.

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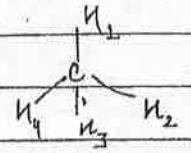
Date / /
Page

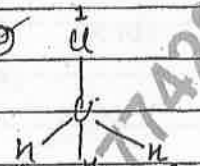
(2) **Plane of symmetry (POS)** – It is an imaginary plane, passing through a molecule which can bisect a molecule into 2 equal halves & both half are mirror image of each other. Such plane is k/w as POS.

(1) CH_4



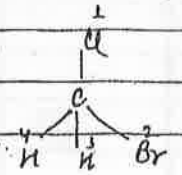
1,2 ⇒ 1 POS
1,3 ⇒ 1 POS
1,4 ⇒ 1
2,3 ⇒ 1
2,4 ⇒ 1
3,4 ⇒ 1
6 POS

(2)



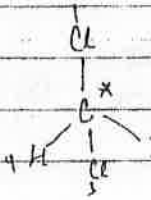
1,2 → POS
1,3 → POS
1,4 → POS

(3)



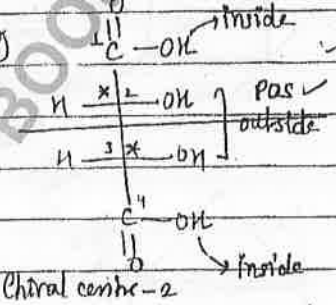
1,3 POS

(4)



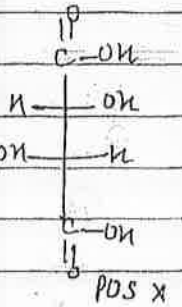
C.C = 1
Optically active
NO COS
NO POS
Chiral molecule

(5)



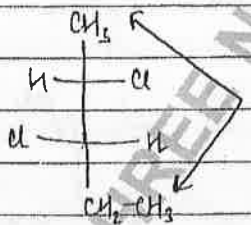
Chiral centre – 2
Meso tartaric acid.

(6)



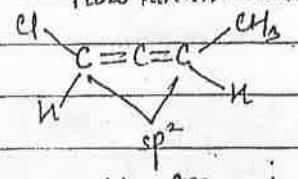
POS ✗
COS ✗
Optically active
d or l tartaric acid
Not mirror images.

(7)



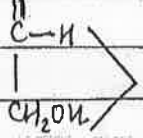
unsymmetrical
cmpd → optically active

(8)



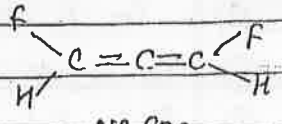
NO COS
NO POS
NO CC
*Chiral molecule
Optically active

(9)



unsymmetrical
cmpd
↓
optically active

(10)



NO COS
POS ✓

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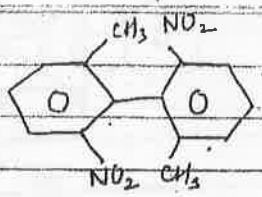
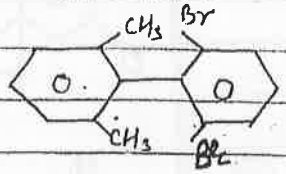
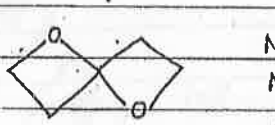
(11) 

NO COS
NO POS
NO CC
Chiral molecule

Tetrahedral envi.
Optically active

(12) 

POS ✓
Optically inactive

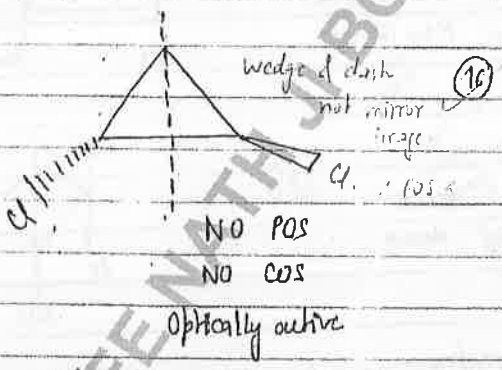
(13) 

NO COS
NO POS
NO CC
Chiral molecule
Optically active

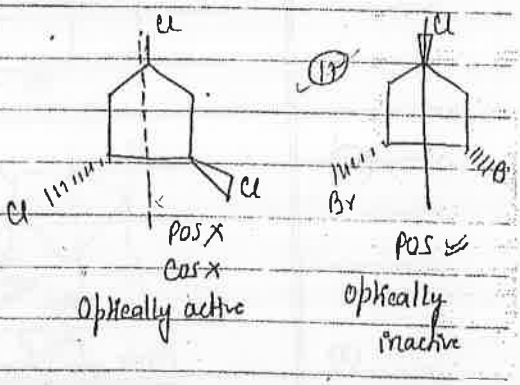
(14) 

not mirror image
∴ POS ✗
NO COS
NO POS
NO CC
Optically active

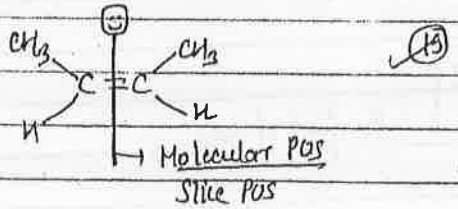
NOTE Chiral centre is not a necessary condition for a compd to be optically active.

(15) 

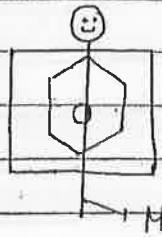
(16) wedge & dash not mirror image
POS ✗
NO POS
NO COS
Optically active

(17) 

POS ✗
COS ✗
Optically active

(18) 

Molecular POS
Slice POS

(19) 

Molecular POS
Total - (7)

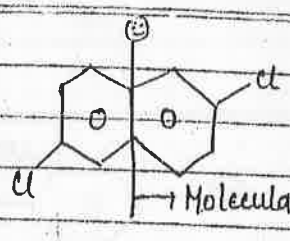
Molecular POS

→ Every planar molecule will have POS along the plane in which they exist. ∴ as molecular POS.

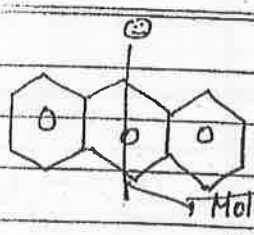
NOTE - Chair form = 3 POS Twisted boat - optically active.
Boat form = 2 POS
Half chair = 1 POS

Date / /
Page

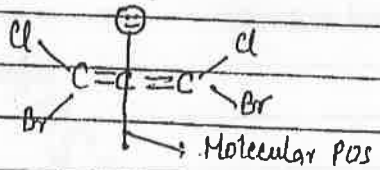
(20)



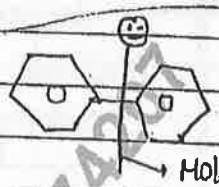
(21)



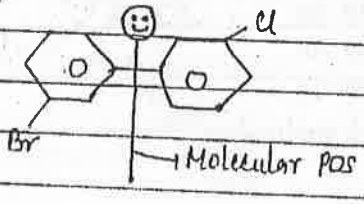
(22)



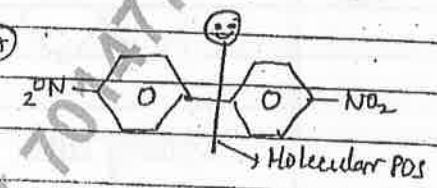
(23)



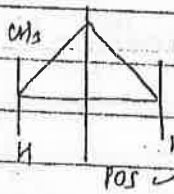
(24)



(25)

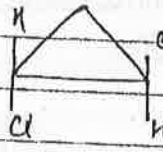


(26)



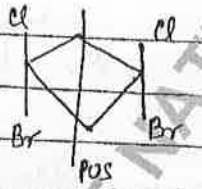
C.C = 2
Meso compd.

(27)



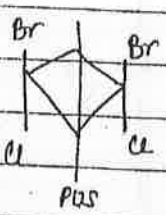
NO CAS
NO POS
optically achie

(28)



C.C X
Meso x

(29)



(3) Axis of symmetry -

If new image are obtained by rotation of a molecule by an angle 'θ' about axis passing through a molecule then it gets similar orientation, then molecule has AOS.

$$\theta = \frac{360}{n}$$

n → fold of axis

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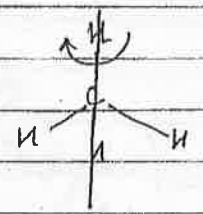
★ Sansaar ko harr ek planar molecule apne plane mein exist kta h.

Date / /
Page

NOTE For a molecule to be optically active COS & POS should be -nt.

(1)



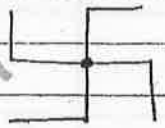
$C_3 \rightarrow AOS$

$n=3$

$\theta = 120°$

CH_4 molecule.

(2)

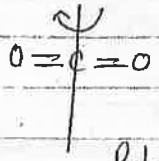


$C_4 \rightarrow AOS \rightarrow 4$

$n=4$

$\theta = 90°$

(3)



$C_2 \rightarrow AOS$

$\theta = 180°$

Polarimeter experiment

→ Optical activity of a molecule can be predicted at the plane of paper by -nce of COS & POS, but direc^n of Rotation & angle of rotation is experimental value & measured by polarimeter (dextro & laevo).

Specific rotation -

special

$$\alpha_{specific} = \frac{\alpha_{observed}}{l \cdot c}$$

l → length of polarimeter tube (taken in dm)

c → conc^n of sol^n (taken in gml^{-1})

→ Specific rotation gives information about optical strength of a molecule. Whenever length of polarimeter tube is 1 dm^3 & conc^n of sol^n is 1 gm/ml then the observed rotation is specific rotation.

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Data / /
Page

$\alpha_{observed} = \alpha_{specific} \times l \cdot c$

$\alpha_{specific} = constt$

$\therefore$ $\boxed{\alpha_{observed} \propto l \cdot c}$

Factors affecting angle of rotation ($\alpha_{observed}$) -

① Length of polarimeter tube -

$\alpha_{observed} \propto l$, $l \uparrow$, $\alpha_{observed} \uparrow$

② Conc^n of sol^n -

$\alpha_{observed} \propto c$, $c \uparrow$, $\alpha_{observed} \uparrow$

③ Solvent -

Solvent must be chemically & optically inert.

④ Temperature -

Polarimeter exp. carried out at room temp.

⑤ Source of light -

Generally Na lamp used. $\lambda = 589$ A°

MESO COMPOUND -

→ Optical isomers having chiral centre more than one, with symmetry elements (COS & POS) is Meso.

→* Meso compd give optical isomerism but optically inactive.

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NOTE: If compd having chiral centre (1 or more than one) then compd always give optical isomerism but may be optically active or inactive.

Date / / Page

(is symmetrical)

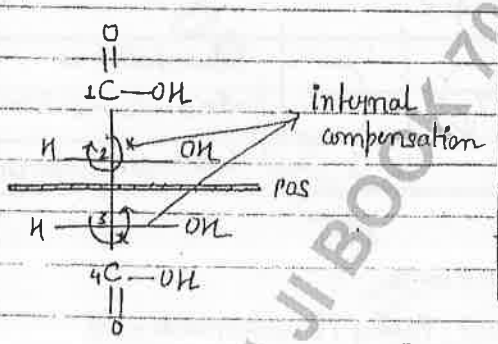
→* Mirror image of Meso-compound represent its identical molecule.

→* Meso compound is optically inactive due to internal compensation or intra-molecular neutralisation or molecular symmetry.

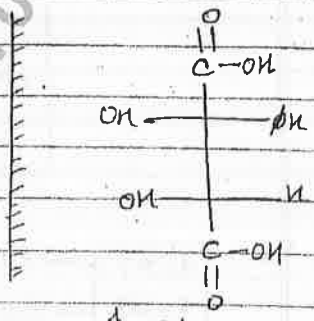
→ Meso is achiral compound.

→ Meso compd cannot have enantiomers.

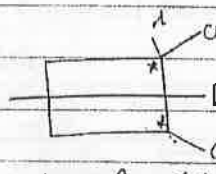
(1)



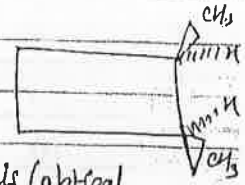
Meso-tartaric acid.
Nil rotation = 0
C.C = 2 } Meso
Symmetry }



(2)

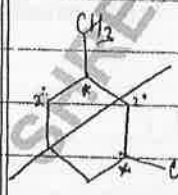


C.C = 2 } Meso
POS ✓ }
Given optical isomerism



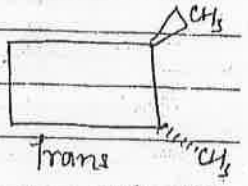
Cis (optical Meso isomerism)

(3)



POS ✓ }
C.C ✓ } Meso.
Give optical isomerism

17.08.17



Trans (NO POS) (0.A)

RACEMIC MIXTURE :

Equimolar mixture of 'd' & 'l' isomers is k/w as racemic mixture (Enantiomeric mixture)

→ Racemic mixture is a resolvable mixture, seperation of d & l isomers is k/w as optical resolution.

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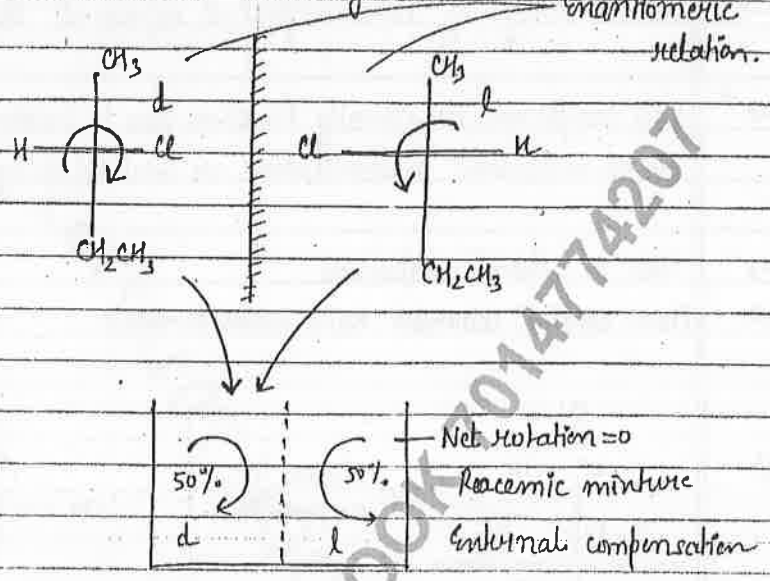
→ Racemic mixture is optically inactive due to external compensation or inter-molecular neutralization.



① d = 50% → R.M = 100%
l = 50% → Optical Purity / Enantiomeric excess = 0%
(O.P)

② d = 100% → R.M = 0%
l = 0% → O.P = 100%

③ d = 80% → R.M = 40%
l = 20% → O.P = 60%
Net rotation = dextro ↻

④ 20 g
d = 12g → R.M = 16g
l = 8g → O.P = 4g
Net rotation = d ↻

ENANTIOMERS -

→ Optically compd having non-superimposable mirror images of each other.

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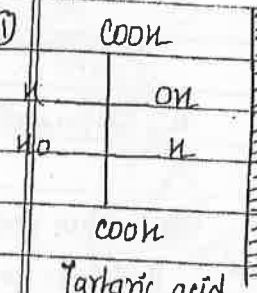
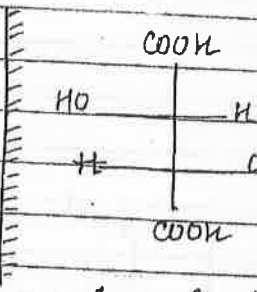
In inorganic, jaisaa k scale - isomers → diastereomers. hote hain.
↓
GI

Date / /
Page

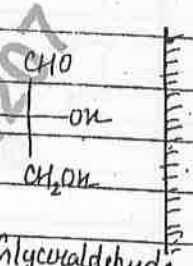
→ Enantiomers have diff behaviour towards each other.
→ Enantiomers have same physical property. (P.I)

① 

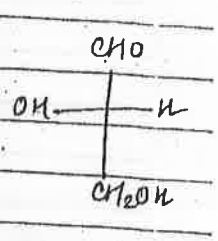
Tartaric acid (d/l)



I, II → Enantiomers

② 

Glycraldehyde



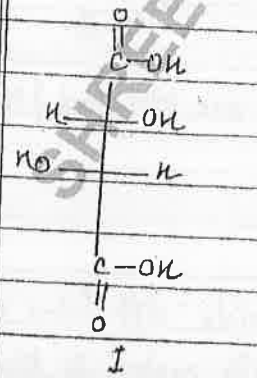
I & II are enantiomers

DIASTERIOMERS -

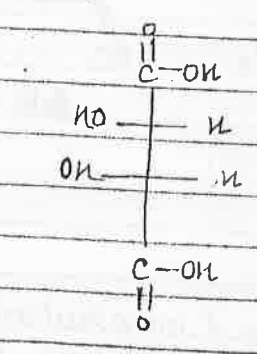
Stereoisomers which are not mirror images of each other. Diasteriomers can be 2 optical isomers, 2 G.I & 2 conformat

→ Diasteriomers can be 2 optically active compd, 2 optically inactive compd & one is optically active & other is optically inactive compd.

→ Diasteriomers have diff P.P & seperated by fractional distillation.

③ 

I

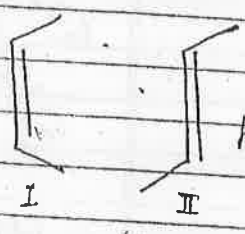


II

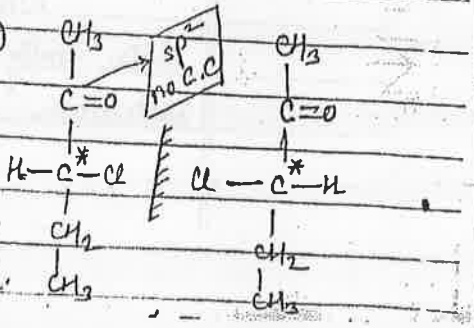
d/l tartaric acid (O.A)

Meso tartaric acid (O.I)

I & II diasteriomers

④ 

diasteriomers.

⑤ 

See only chiral centre.

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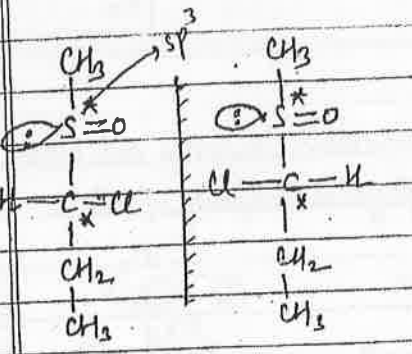
Min^m mol wt of Hydrocarbon for optical isomerism = 68.

Date / /
Page

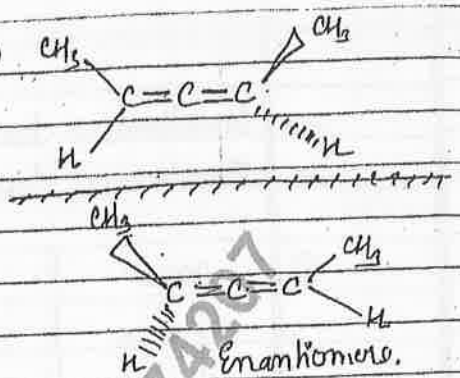
bill 10/10

(6)



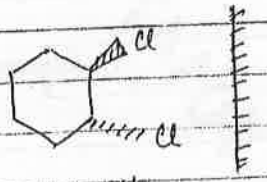
Diastereomers.

(7)



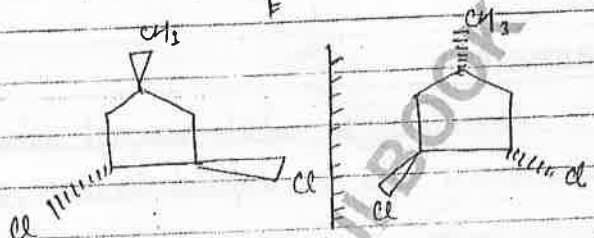
Enantiomers.

(8)



Use upper mirror.
Both are enantiomers.

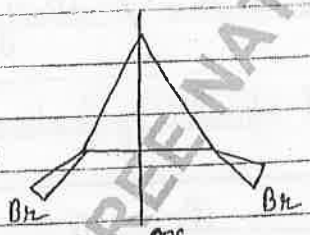
(9)



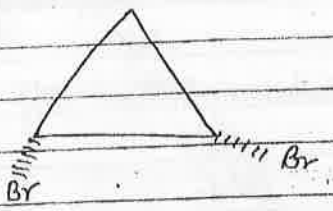
Both are enantiomers.

Mirror wedge ko dash aur dash ko wedge dikhata hai

(10)



POS
C.C
Meso (O.A)



Both are identical / Homomers.

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EPIMERS -

Whenever 2 monosaccharide diff from each other in their config around a single specific carbon is kno as epimers of each other.

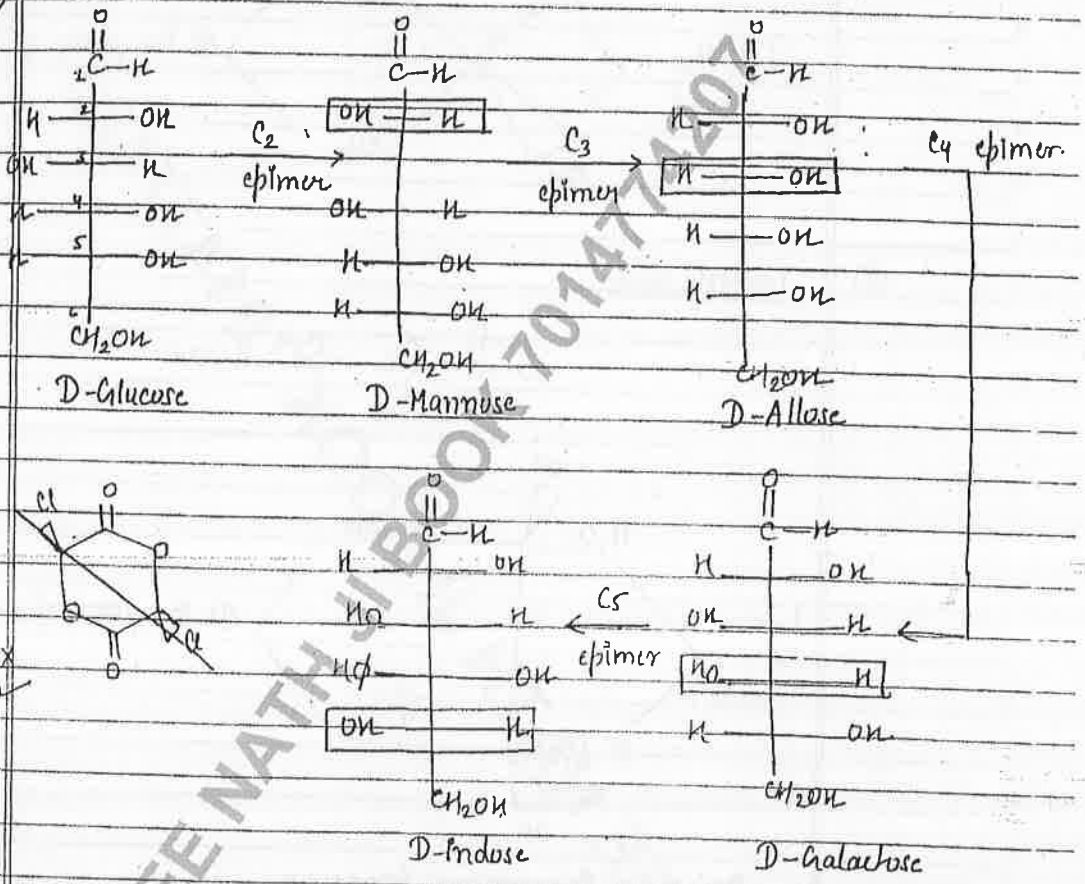
DPP- Q-8

12-13 → Slice.
16 → Meso.
17 → Pos.

Date / /
Page

→ All epimers are diastereomers but vice-versa not-true.

NEET-2015

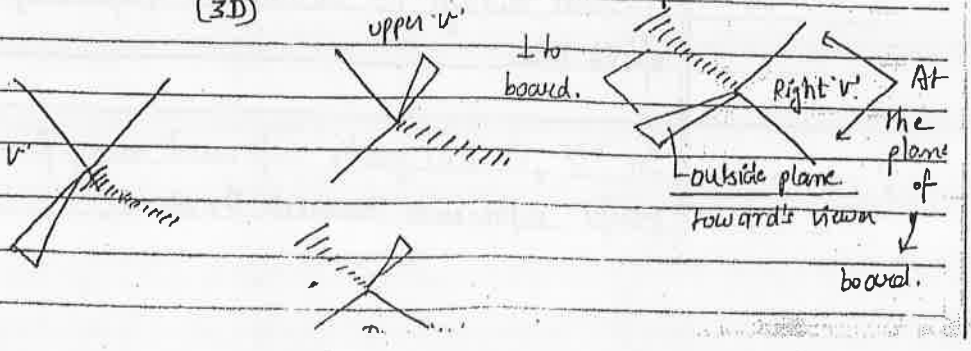


Q-34

Pos ✓

Representation of Optical isomers -

1 WEDGE-DASH FORMULA- (3D)



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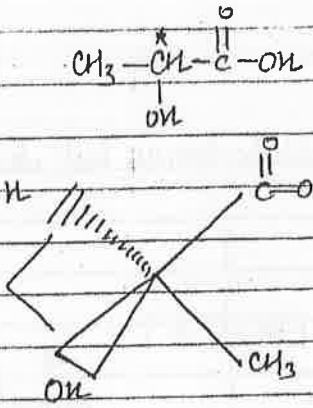
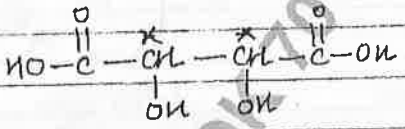
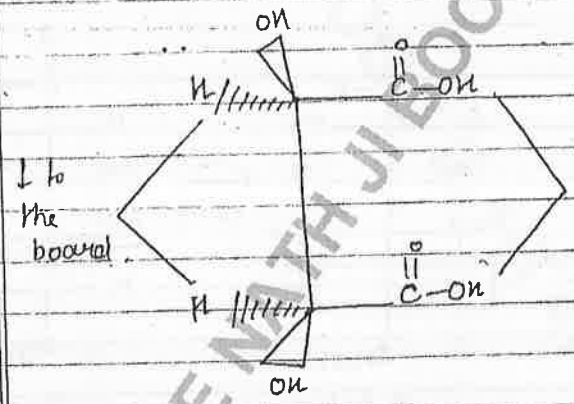
① Lactic acid -



② Tartaric acid -





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2. FISCHER PROJECTION FORMULA -
(2D)

→ Fischer projection is a 2 plane projection formula.

→ In it one is vertical plane & other is horizontal plane.
(only one) (one or more than one)

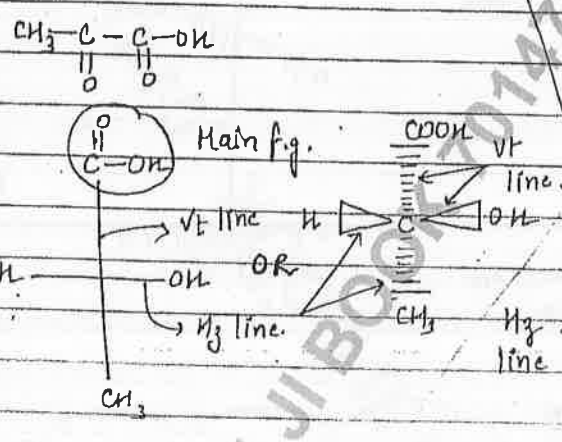
→ In it C-chain always in vertical line (Vt) & top-most f.g at top position of Vt line.

→ In FPF, Vt line groups represent away from the viewer, & Hz line groups represents towards the viewer.

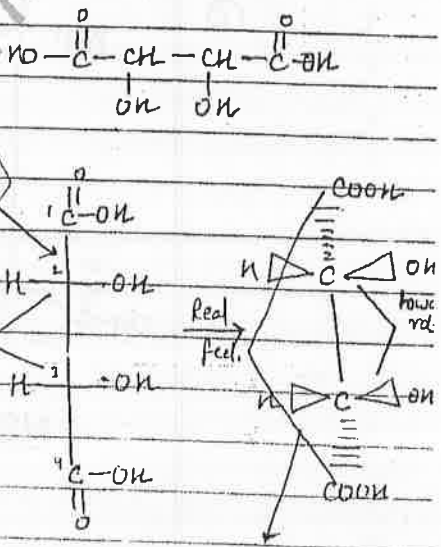
Date / /
Page

→ Fischer is a map of molecule.
→ Fischer projection represent tetravalency.
→ Fisher projection always formed in eclipsed form.

① Lactic acid-

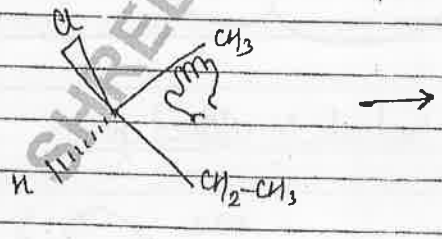


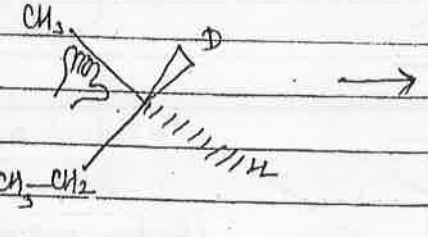
Tartaric acid-

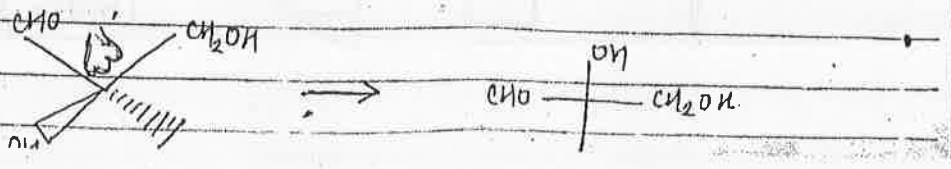


Conversion of diff projection formula-

1. Wedge Dash into fischer projection formula-

① 

② 

③ 

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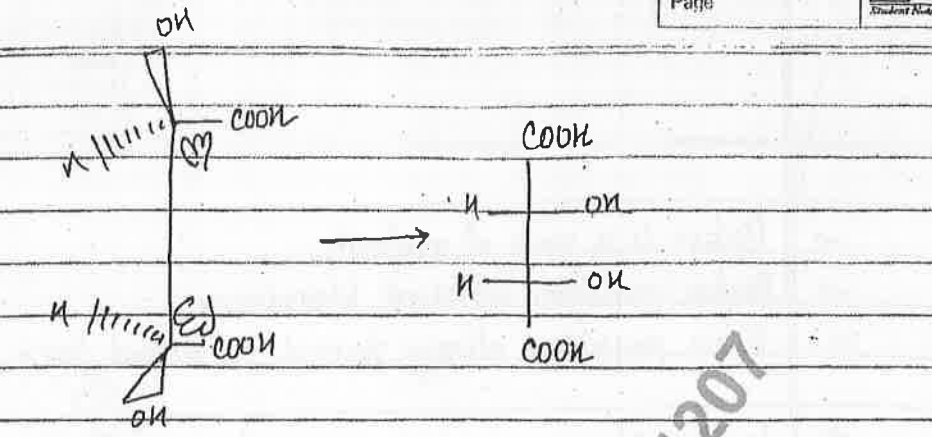
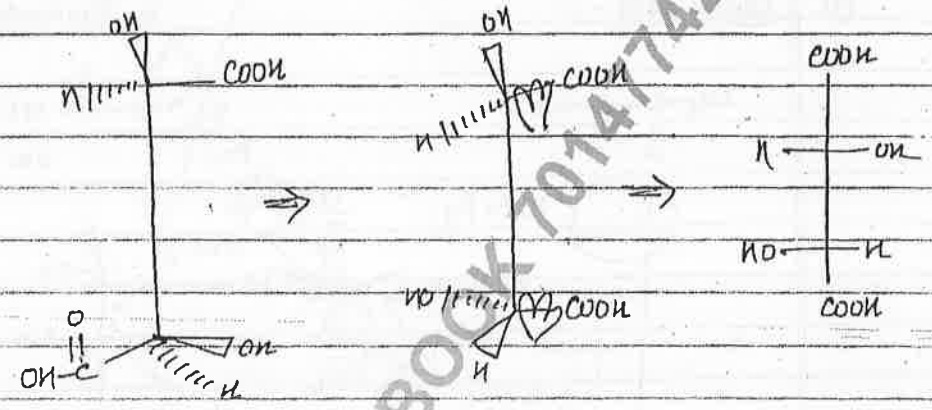
Always remain in
Glucose molecule - 100%. closed chain

Date / /

Page





NOTE

Jo 'V' board k plane m hoti
h usko jha s dhakka diya
jta h vha wedge
vala grp aa jta

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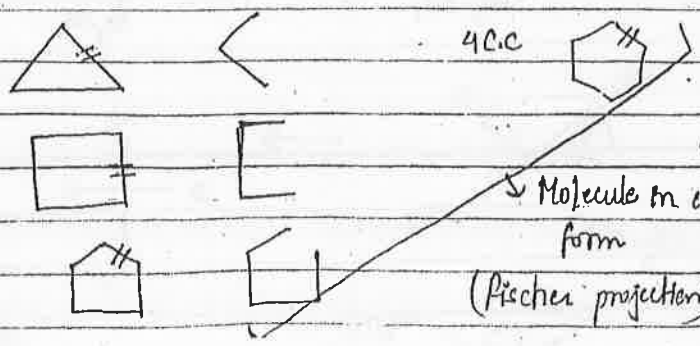
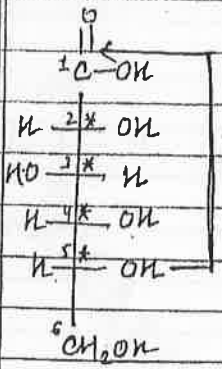
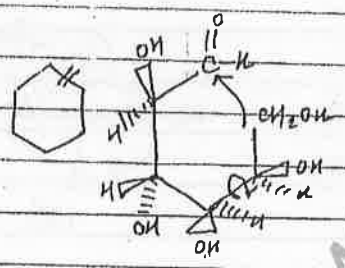
for diff chiral centre molecule in eclipsed form -



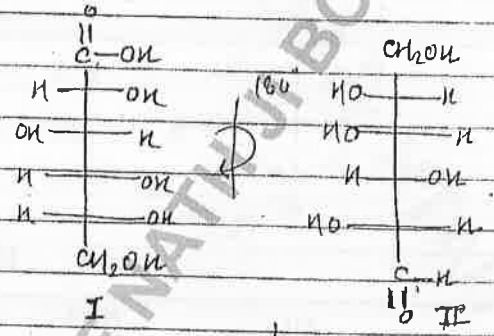




19.08.17

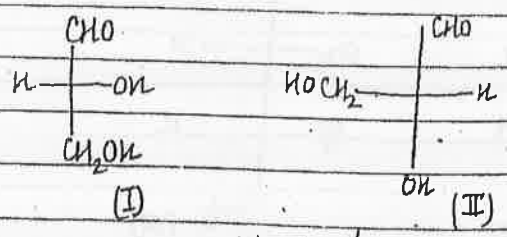
2. Fischer into fischer projection formula -

Statement 1 : If given Fischer projection formula rotated by 180° at the plane of paper then it represents its identical molecule.



Identical / homomer

Statement 2 : In given fischer projection formula any one unit kept fixed, rest all 3 units rotated in clockwise or anticlockwise direction then it represents its identical molecule.



Identical / homomer

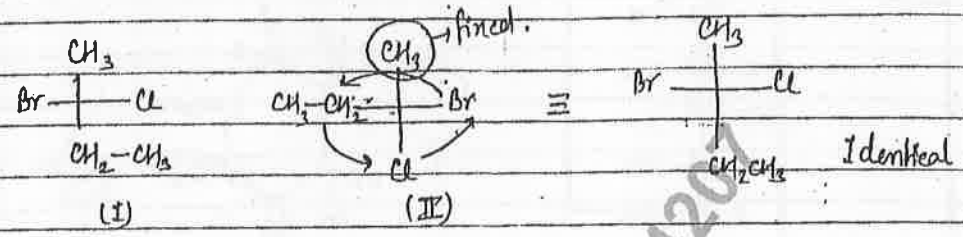
SREENATH'S BOOK 7044774207

Date / /

Page

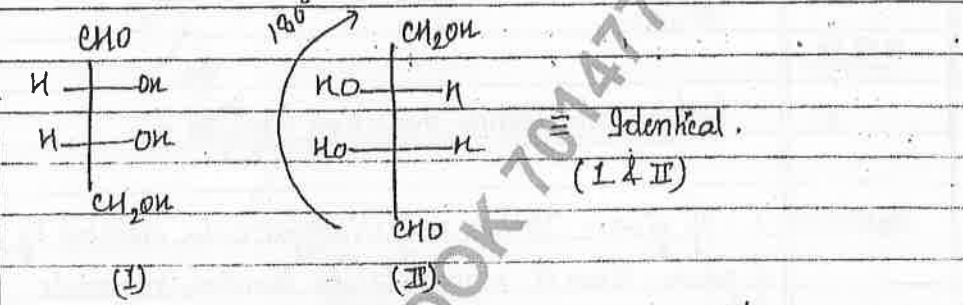
Ques Find out relation in given compds -

1.



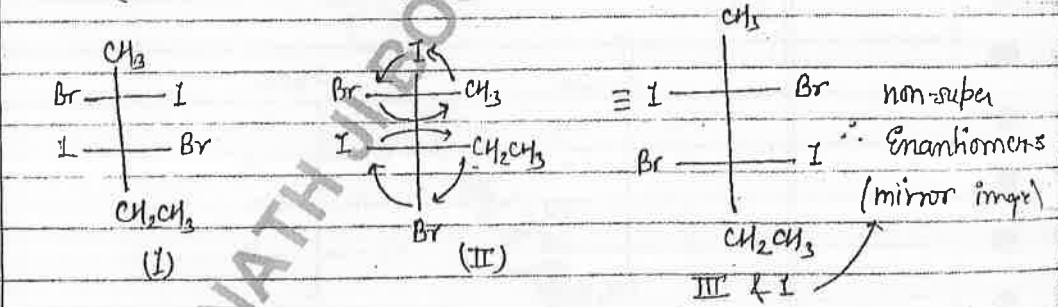
Identical

2.



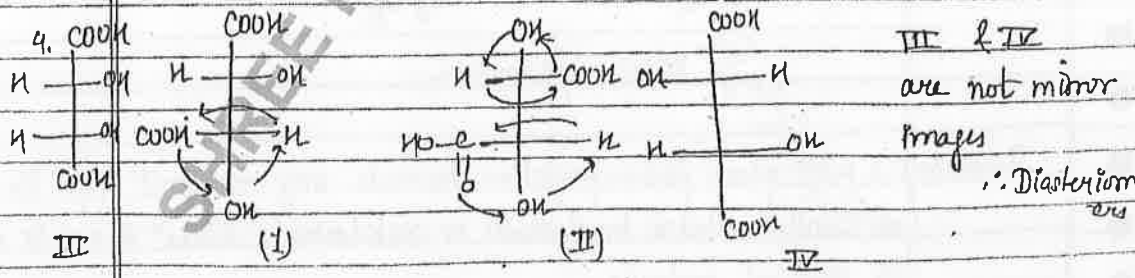
≡ Identical.
(I & II)

3.



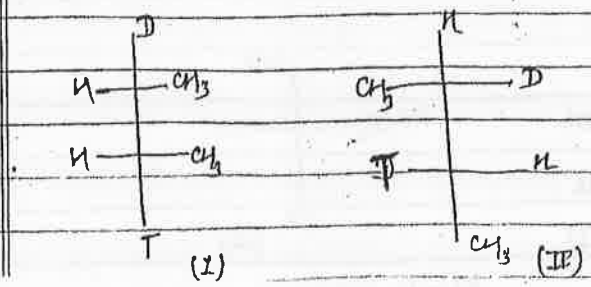
non-super
∴ Enantiomers
(mirror image)

4.



III & IV
are not mirror
images
∴ Diasteriomers

5.



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Date / /
Page

Given fischer
↓
Perfect fischer
↓
Super / non superimposable

If Superimposable → Identical

If non-super imposable → mirror image Enantiomers / If not mirror image Diastereomers

Config. of optical isomerisms -

1. D-L config. (Relative config)
2. R-S config (Absolute config)

1. D-L configuration -

CARBOHYDRATE -

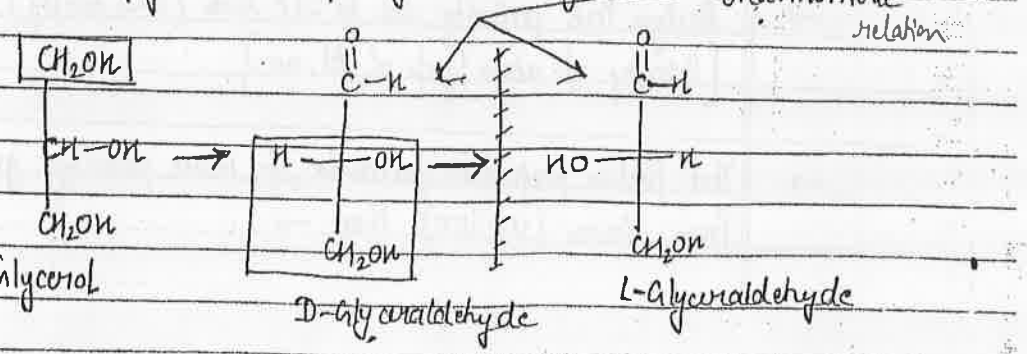
Polyhydroxy aldehyde or ketonic compd with min^m one C.C is klw as carbohydrate.

→ D & L config is standard relative config of glyceraldehyde. There is no relation with 'd' & 'l' isomers (optical activity).

→ D & 'L' config valid for carbohydrate, a.a & like-molecules.

→ D & 'L' have enantiomeric relation.

→ D & 'L' config not valid for symmetrical system.



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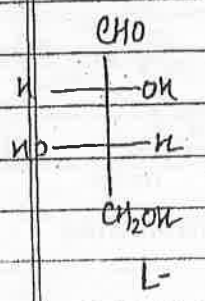
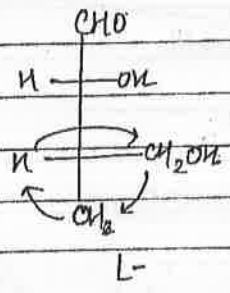
Date / /
Page

→ If at last C.C [-OH/NH_2] grp right side = D

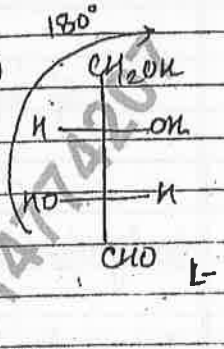
→ If at last C.C [-OH/NH_2] grp left side = L

① 

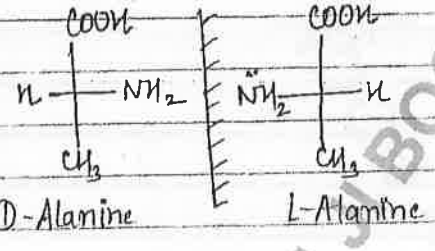
L-

② 

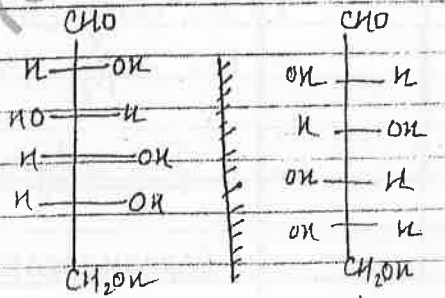
L-

③ 

L-

④ 

D-Alanine L-Alanine

⑤ 

D-Glucose L-Glucose

2. **R-S Configuration**

R → Rectus → Right side
S → Sinister → Left side

C.W, A.C.W → Give inform^n abt arrangement of units at C.C not rotation of PPL (d & l)

(A) **R-S config in fischer projection formula-**

→ Assign the priority acc. to CIP rule (E-Z config)
[Priority of atom/grp ∝ At. no.]

→ In fischer projection formula, if lower priority grp ④ int away from viewer (Vt line) then →

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Cis > Trans

E < Z.

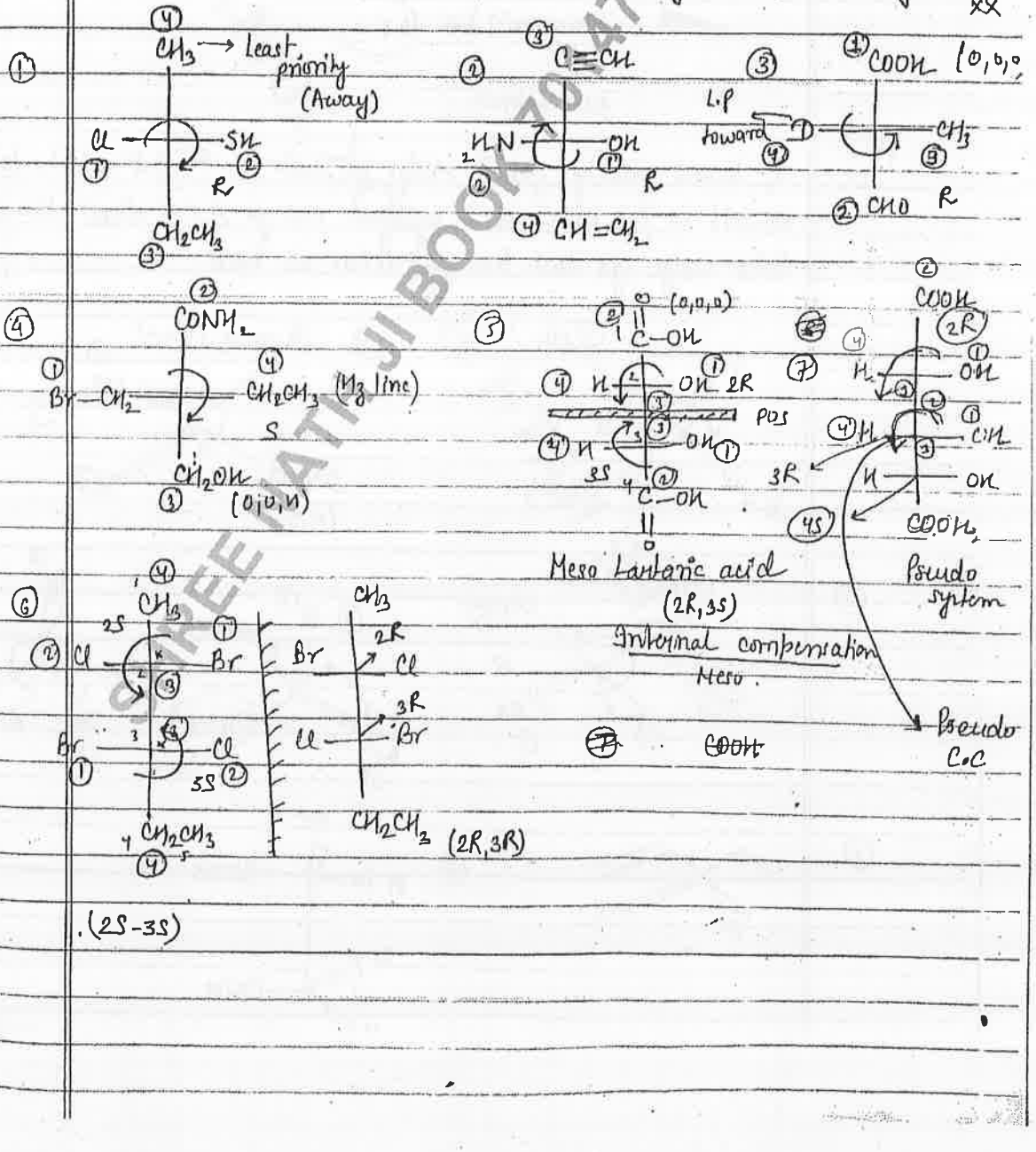
R > S

C.W ⇒ R A.C.W ⇒ S

→ If lowest priority grp ④ mt towards the viewer (H₂ line) then the real orientation just opposite to the observed orientation. (To ata h uska ulta kr deta hain)

Always go through → 1 → 2 → 3

If lowest priority ④ mt in b/w ignore it XX



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In case of pseudosystem -
priority R > S

Date / /
Page

(B) RS config in wedge-dash formula -

→ Rules of R-S config in Fischer & Wedge dash formula → same-same

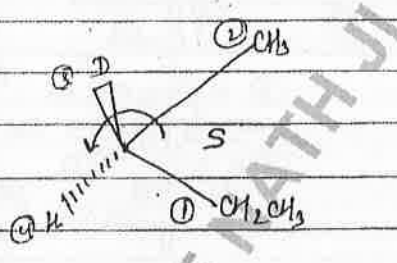
→ If lowest priority group ④ +nt at dash line then -

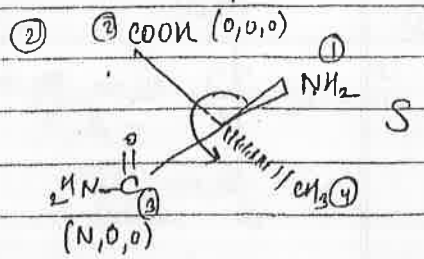
||||||| (Away) → C.W → R

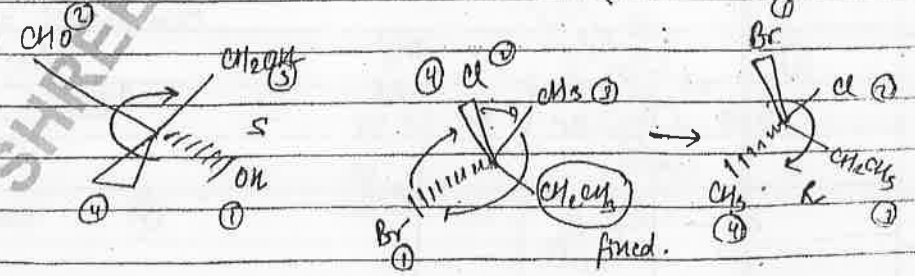
(towards) → A.C.W → S

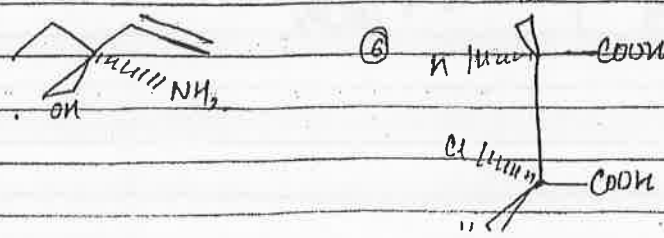
just opposite.

NOTE → If lowest priority grp ④ wedge ya dash line pr +nt nhi ho toh kisi ek unit ko fix krke rest 3 units ko C.W ya A.C.W direction main rotate krke wedge ya dash line par lekar ate hain.

① 

② 

③ 

④ 

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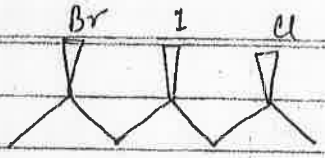
Date / /
Page

(7)

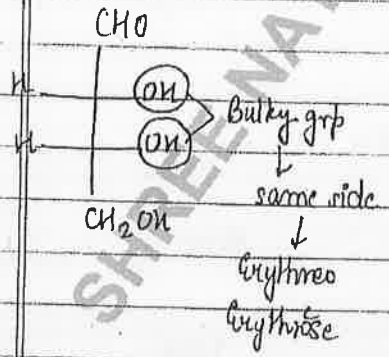


Relation b/w diff compounds -

	Compound 1	Compound 2	Relation
1.	R	R	Identical / Homomers
2.	S	S	Identical / Homomers
3.	R	S	Enantiomers
4.	RR	SS	Enantiomers
5.	RS	SR	Enantiomers. (If comp unsym) Meso (If comp symm)
6. ↓	RR	RS	Diastiomers

3. Threo & Erythro system -

(1)



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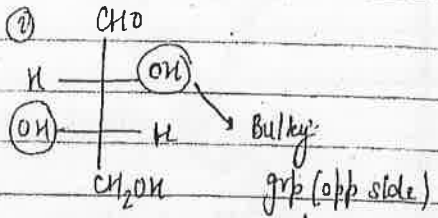

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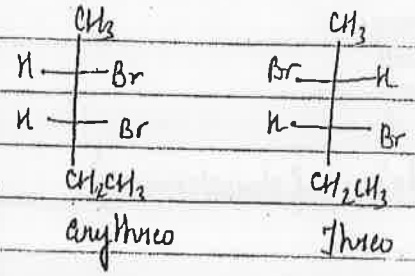

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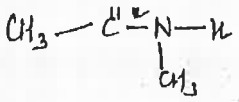
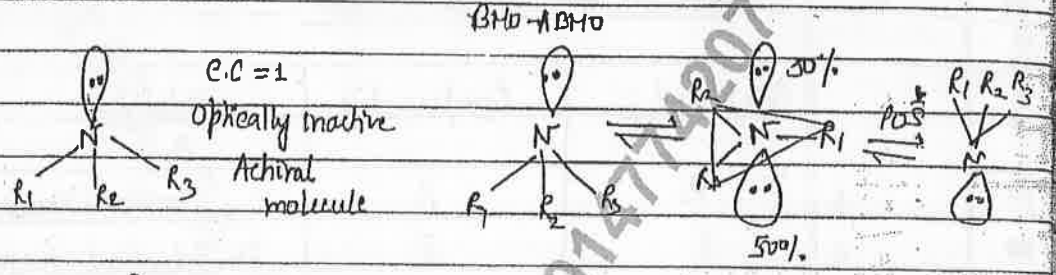


Date / /

Page

Amine flipping -

In case of amine nitrogen atom having C.C. but optically inactive due to amine flipping /umbrella inversion & in this case molecule is achiral.



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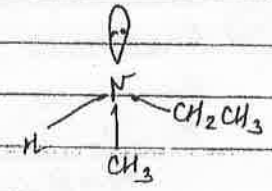
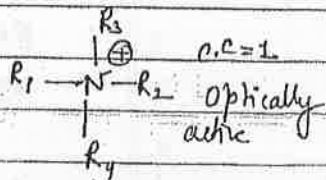


(3)



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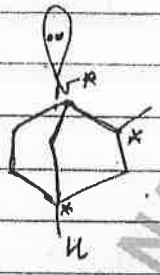

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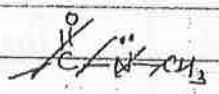

No. of optical isomers -

	No. of optically active	Meso.
Unsymmetrical compd →	2^n / n = no. of stereogenic unit (CL+OL)	zero.

(2^n → Total no. of stereoisomers)

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Date / /
Page

(2) Symmetrical compd n=even 2^{n-1} $2^{\frac{n}{2}-1}$

n=odd $2^{n-1} - 2^{\frac{n-1}{2}}$ $2^{\frac{n-1}{2}}$

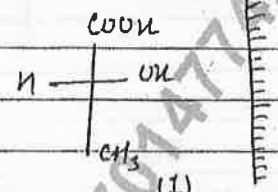
(1) $CH_3-\overset{*}{C}H-\overset{O}{\overset{\|}{C}}-OH$ (R3)
|
OH

unsymmetrical

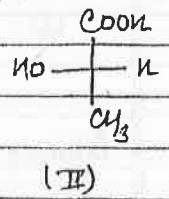
$n=1$

no. of stereo $= 2^n = 2^1 = 2$

(or)



(I)



(II)

(A) Total no. of optically ~~active~~ isomers = 2

(B) Total no. of optically active isomers = 2

(C) Total no. of meso = 0

(D) Total no. of enantiomeric pair = 1

(E) Total no. of Racemic mixture

(2) $CH_3-CH-CH-CH_3$
| |
Cl Br

unsymmetrical.

$n=2$

no. of stereo $= 2^n = 2^2 = 4$.

(3) $CH_3-CH-CH-CH_3$
| |
OH OH

(4) Glucose → no. of stereoisomers

(5) $CH_3-\underset{|}{\overset{Cl}{CH}}-CH=CH-CH_2CH_3$

(6) $CH_3-CH=CH-CH-CH-CH_3$
| |
OH OH

(7) Total no. of optical isomers = 4

Total no. of optically active isomers = 4

Total no. of meso = 0

Total no. of enantiomeric pair = 2

Racemic mixture.

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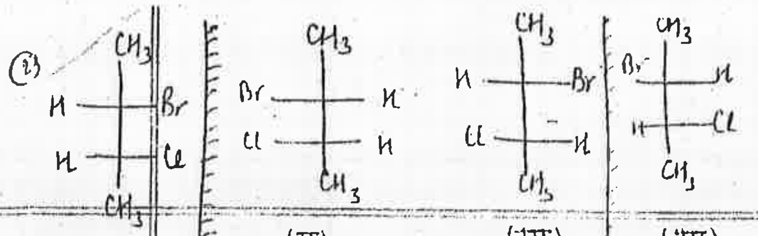
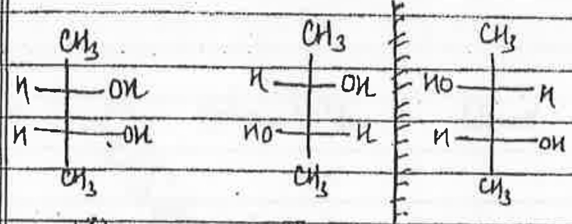
(2)



(I) (II) (III) (IV)

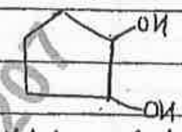
III (7) $CH_3-CH(Cl)-CH=CH-CH(Cl)-CH_3$

(3) Total no. of optical isomers = 3



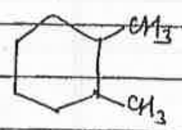
(I) II III

(8)

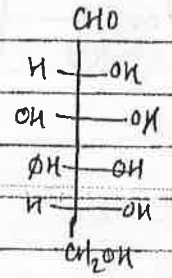


Total no. of stereo ?

(9)



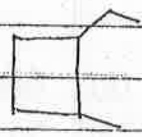
(4) Glucose



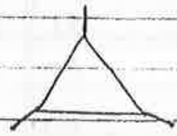
$n=4$

$2^n = 2^4 = 16$

(10)



(11)



(5) $CH_3-CH(Cl)-CH=CH-CH_2-CH_3$ (T_1, T_2)

C	R
C	S
T	R
T	S

unsymmetrical

$n=2$

Total no. of stereoisomers $= 2^n = 2^2 = 4$

n = no. of stereogenic unit (GI + OI)

(6) $CH_3-CH=CH-CH(OH)-CH(OH)-CH_3$

Total no. of stereo = 8

C	RR	C	SR
C	SS	T	RR
C	RS	T	SS
		T	RS
		T	SR

8

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Reaction Mech-I

STABILITY OF INTERMEDIATE [GIOC]

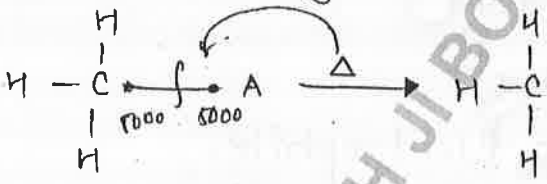
Reaction → intermediate ↑ → product.

↓ collision

↓ Bond Breaking

- C· {carbon free radical}
- C+ {carbocation}
- C⊖ {carbanion}
- Carbene
- Nitrene.

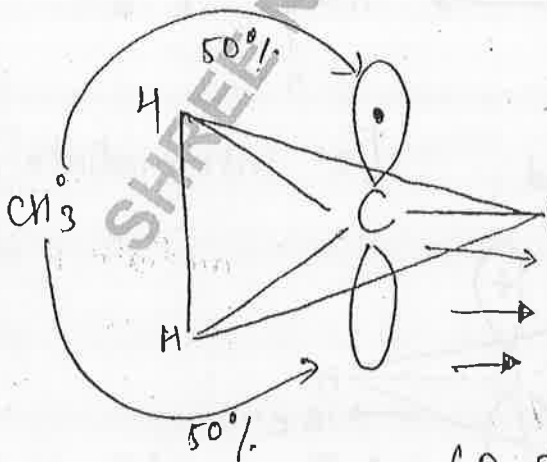
* Bond Breaking :-

① 

$E_{NC} = E_{NA}$

(Nonpolar)

(f.R. intermediate)



- 7e-
- Incomplete octate
- Katora Khali.

(f. R. intermediate)

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→ form by homolytic cleavage.

→ Incomplete octate.

→ stablisied by e^- Donating group.
(+I / +M / +H) (EDG)

→ hyb ⇒ sp^2

→ trigonal planar

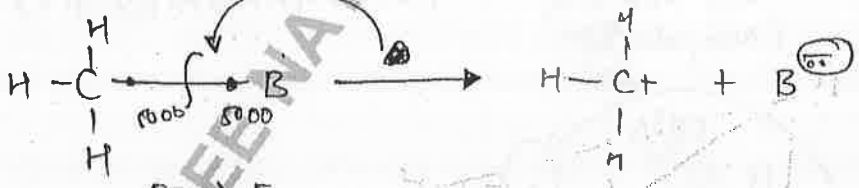
→ B.P ⇒ 3 (6 e^-)
U.P ⇒ 1 e^-
L.P ⇒ 0

→ highly unstable

→ More reactive

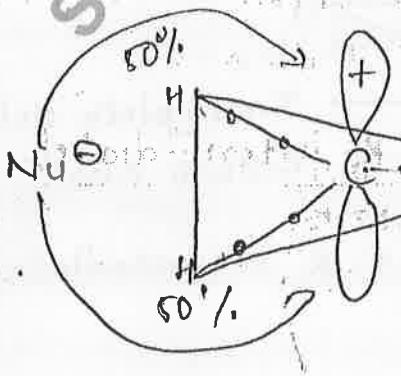
→ Behave as a Electrophile.

(2)



$E_{NB} > E_{NC}$
(Polar bond

[C^+ intermediate]



→ 6 e^-
→ Incompelete octate
→ katora khali

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→ formed by heterolytic cleavage

→ Incomplete octate

→ Stablisied by e^- Donating group (EDG)
(+I / +M / +H)

→ hyb ⇒ sp^2

→ Trigonal planar

→ B.P ⇒ 3 (6 e^-)
U.P ⇒ 0
L.P ⇒ 0

→ highly unstable

→ more reactive

→ Behave as a Electrophile

→ —H—— lewis base

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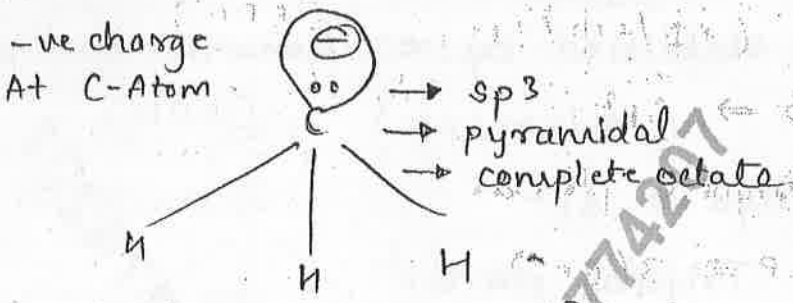
③ 

ENC > END
(polar bond)

(Anion intermediate)



[Carbanion intermediate] $R^{\ominus}$

→ form by heterolytic cleavage
→ complete octate
→ stablised by e^- withdrawing group.
[-I/-M/-H] (EWG)
→ hyb ⇒ sp^3
→ pyramidal
→ B.P ⇒ 3 ($6e^-$)
U.P ⇒ 0
L.P ⇒ 1 ($2e^-$)
→ highly unstable
→ more reactive
→ Behave as a nucleophile ($Nu^{\ominus}$)
↔ -II ——— lewis Acid.

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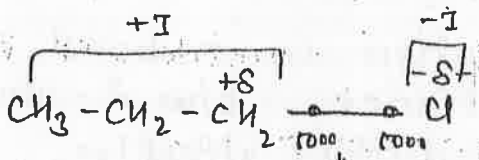
Inductive effect :-

Inductive :-



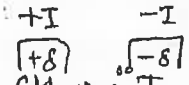
↓

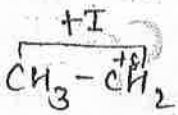
Induction of Dipole

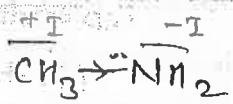
↓

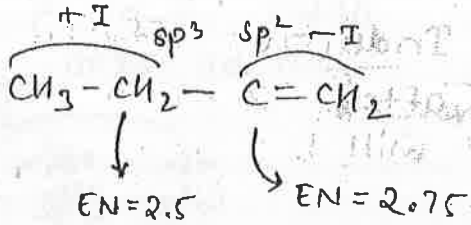
Inductive effect.

Reason → E_N Difference b/w two atom or groups.

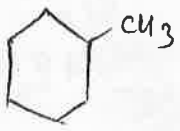
eg. ① 

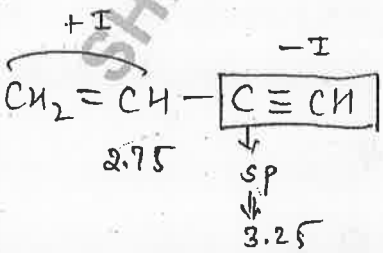
② 

③ 

④ 

⑤  ✗✗

⑥  ✗✗✗

⑦ 

⑧

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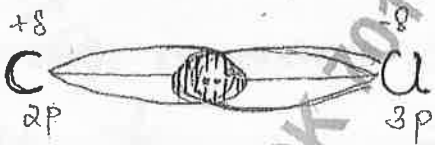
Important Note:-

1) Permanent effect :-

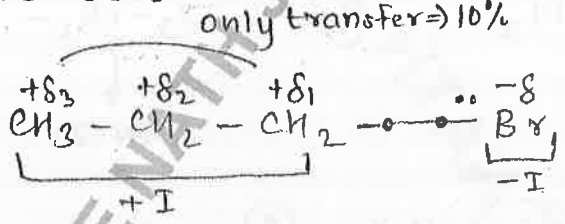
2) Inductive effect is a weak effect.

3) Partially polarisation in σ bond $e^{\ominus}$ due to EN diffence b/w 2-atoms or group is known as inductive effectiv.

★ 4) In Inductive effect $e^{\ominus}$ remain in same orbital.



5) Inductive effectiv is distance dependent after 3 or 4 carbon Inductive effect will be zero



$+\delta_3 < +\delta_2 < +\delta_1$

Dist. ↑

I-effect ↓

3 or 4 ⇒ 0

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b) Different hybridisied carbon →

$CH \equiv C - H$ > $CH_2 = C(H)(H)$ > $CH_3 - CH_3$

$CH \equiv C - H$	$CH_2 = C(H)(H)$	$CH_3 - CH_3$
Sp	Sp^2	Sp^3
%s ⇒ 50 %	%s ⇒ 33 %	%s ⇒ 25
%s ⇑	%s ⇓	
Near to Nucleus	EN = 2.75	EN ⇒ 2.5
Attractn force ↑		
EN = 3.25		

7) Standard I-effect of C-H bond ⇒ zero

(i) $CH_2 = \overset{-I}{CH} - \overset{+I}{CH_3}$
2.75

(ii) $\overset{+I}{CH_2} = CH - \overset{-I}{C \equiv CH}$
2.75 3.25

(iii) $\overset{-\delta}{CH_3} - \overset{+\delta}{Mg} - X$
$-I$

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* On the basis of C-H bond I-effect is of 2-types.

① + I effect (e⁻ Donating group)

② - I - effect (e⁻ Withdrowing group).

+I - effect →

Order of +I - effect →

Key point :- All anion + All Alkyl group (Saturated Alkyl group)

संसार के सारे Anion और सारे Alkyl group +I लगाते है।

except

$-C \equiv CH$ ⇒ Saturated alkyl group

$-CH=CH_2$

⇒ -I - effect.

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$\Rightarrow -\overset{\ominus}{C}H_2 > -\overset{\ominus}{N}H > -\overset{\ominus}{O} > -\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O} > <\overset{\delta+}{C}H(CH_3)-\overset{\delta+}{C}H_2-H^{+\delta} >$

E.N — Distance. — 3° Alkyl group

$-CH(CH_3)_2 > -CH_2-CH_3 > -CH_3$

2° alkyl group — 1° alkyl group

⇒ C-T > C-D > C-H

⇒ $C-T_3 > -CD_3 > -CH_3$

KINETIC ISOPOPIC EFFECT (K.I.E)

① C—H C~~~~H ⇒ max. Vibrath ⇒ Min. e- densin
$_1H^1$ n⇒0 max. SHM
⇓
Min. Donate.

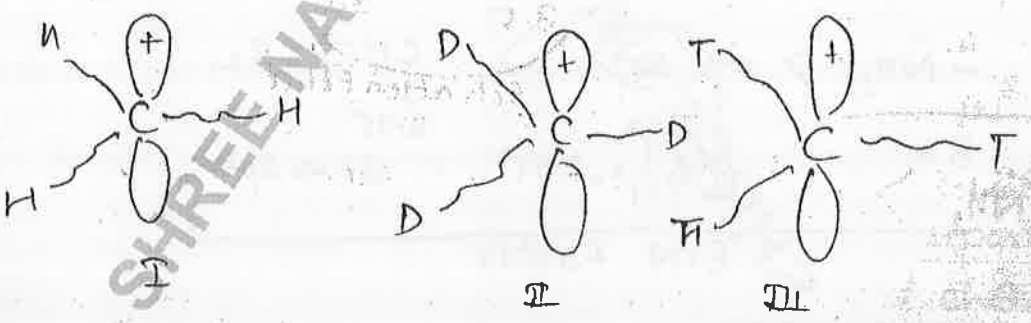
② C—D C~~~~D ⇒ Min. Vibrath ⇒ More e⁻ density
$_1H^2$ n=1 Min SHM
⇓
more Donate

③ C—T C~~~T ⇒ least vibrath ⇒ Max e. density
$_1H^3$ n=2 Least SHM
⇓
max Donate

Order ⇒ C-T > C-D > C-H

⇒ $C-T_3 > -CD_3 > -CH_3$

Q.



Stability C^+ ⇒ III > II > I

(KIE)

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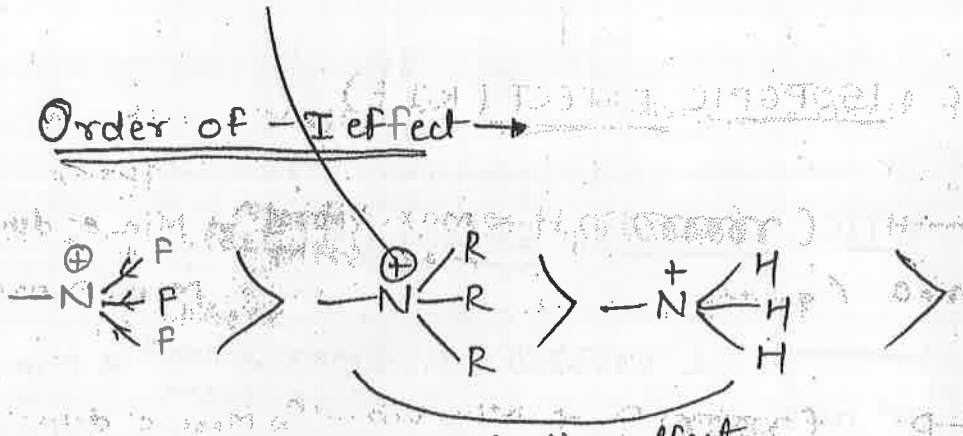
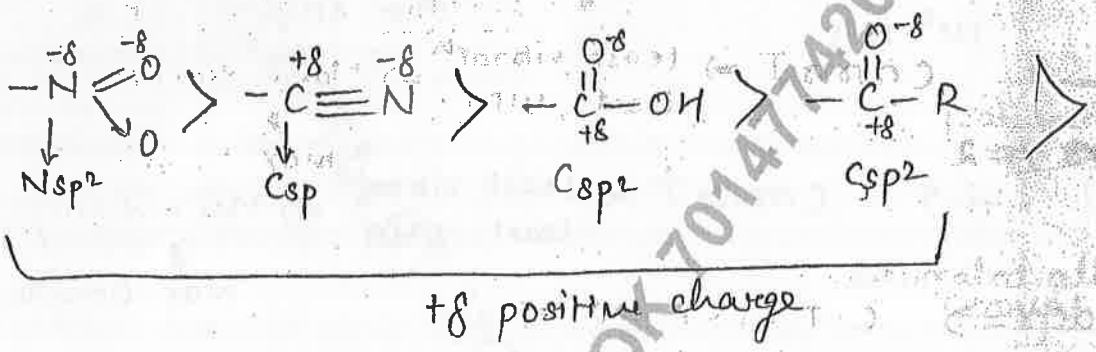
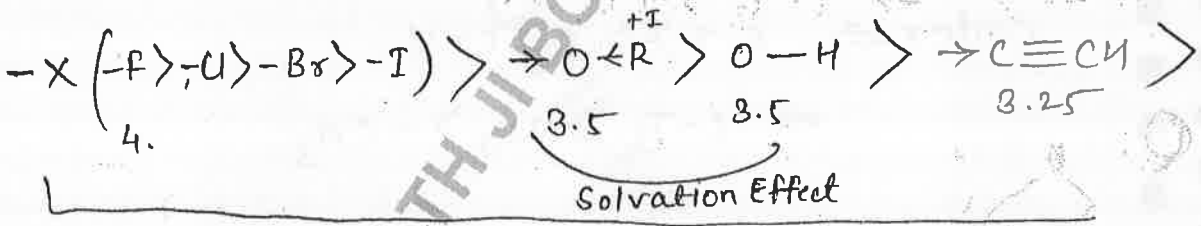
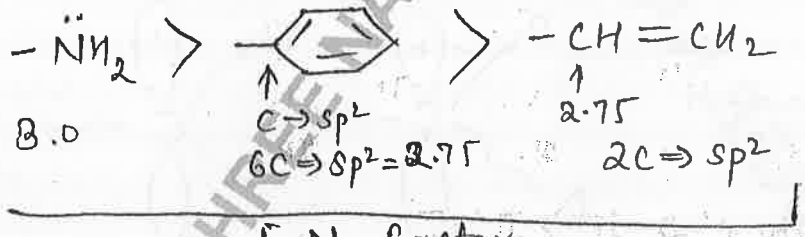
Order of −I effect →









KEY POINT

Complete ⊕ charge > +δ positive charge > EN factor.

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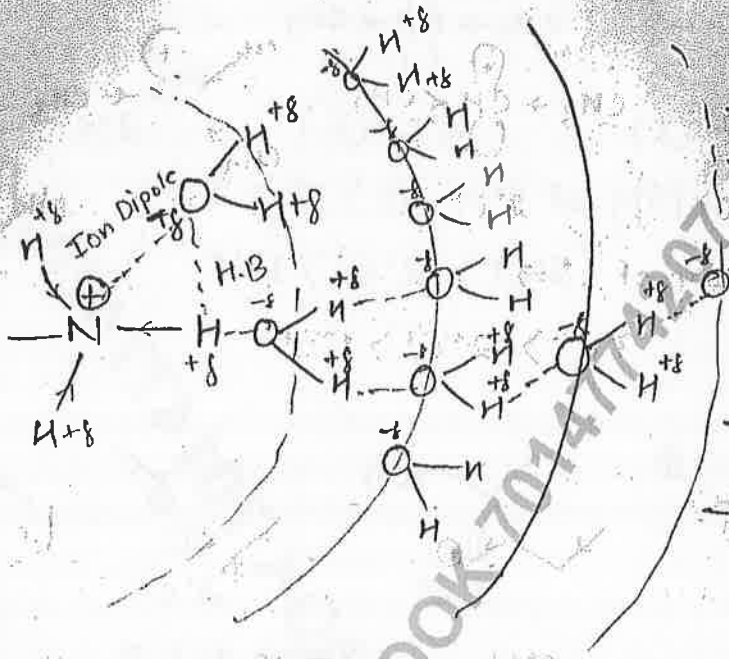
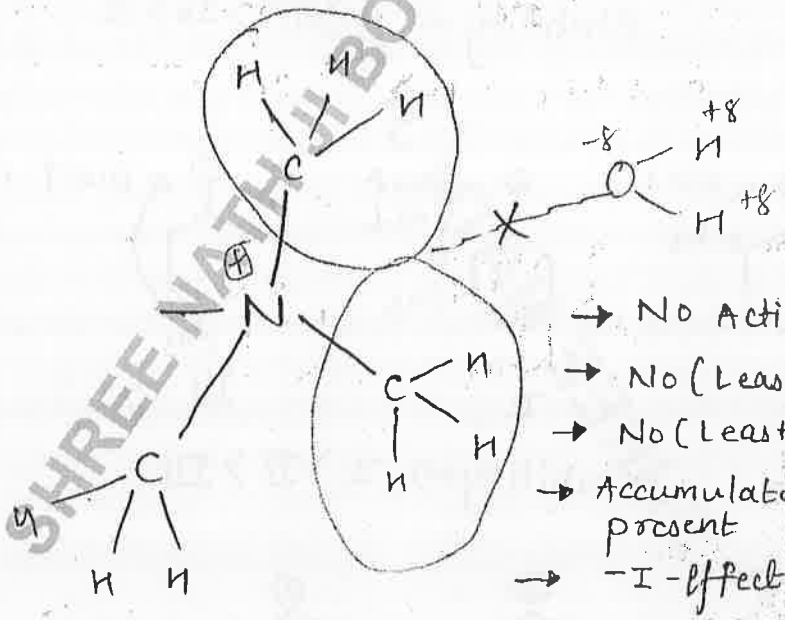
Explain

$-I$-effect of $-\overset{\oplus}{N}R_3$ > $-I$-effect of $-\overset{\oplus}{N}H_3$



→ Active H present
→ H.B present
→ max. solvatn ↑ (hydration)
→ max charge separation
→ No Accumulated charge
→ $-I$-effect ↓



→ No Active H
→ No (Least) solvation
→ No (Least) separation
→ Accumulated charge present
→ $-I$-effect ↑↑↑

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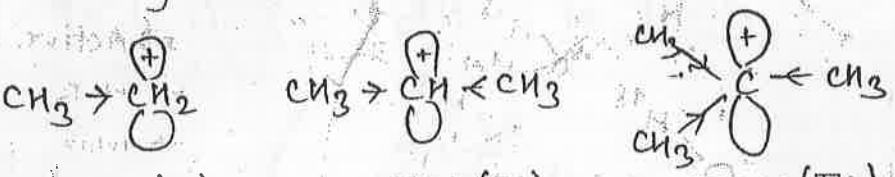
Application of Inductive effect :-

① Stability of carbo cation and freed radical.

Q.1. 

1° C+ (I) 2° C+ (II) 3° C+ (III)

Stability of C+ ⇒ III > II > I

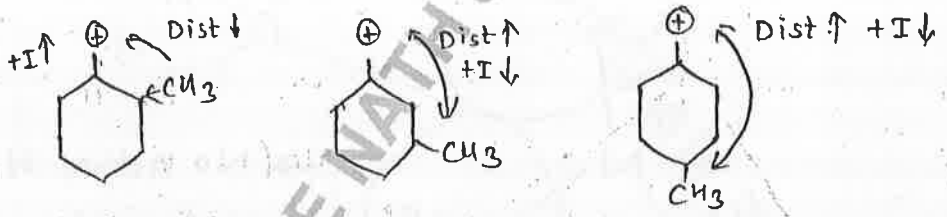
3° C+ > 2° C+ > 1° C+

Q.2. 

I II III IV

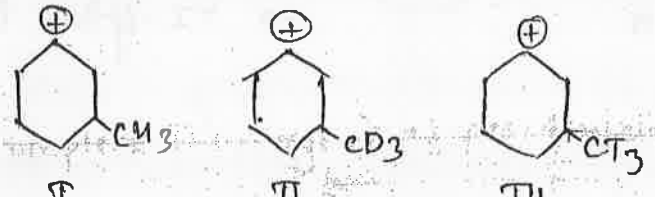
1° C+ 2° C+ 3° C+

Stability ⇒ IV > III > II > I

③ 

I II III

Stability ⇒ I > II > III

④ 

I II III

III > II > I

Reason : K I E

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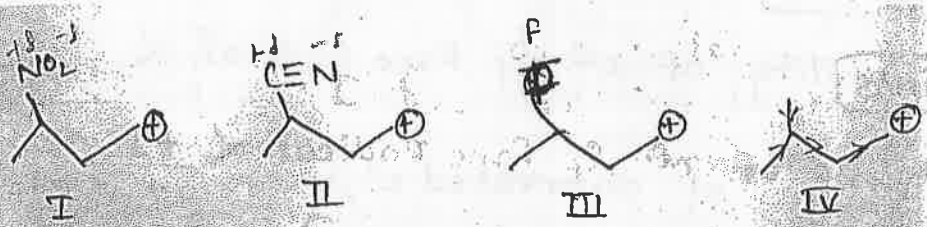
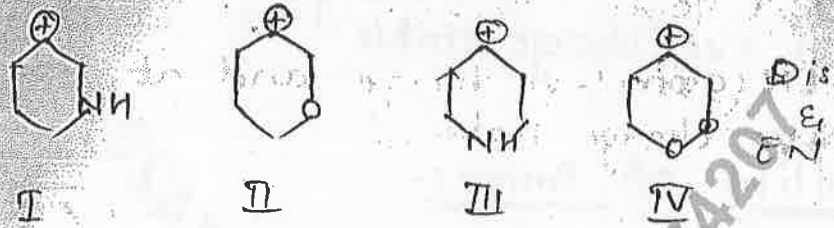
⑤ 

I II III IV

IV > III > II > I ✓

⑥ 

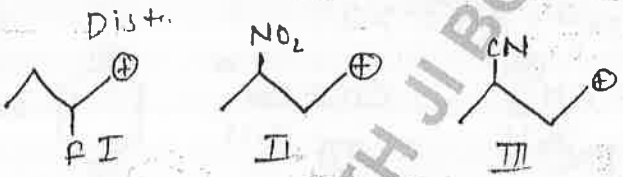
I II III IV

III > IV > I > II ✓

⑦ $CH_3-CH_2-CH_2-\overset{\oplus}{C}H_2$ $CH_2=CH-CH_2-\overset{\oplus}{C}H_2$ $CH\equiv C-CH_2-\overset{\oplus}{C}H_2$

I II III

I > II > III ✓

⑧ 

I II III

III > II > I ✓

⑨ $CH_3\rightarrow\dot{C}H_2$ $CH_3\rightarrow\dot{C}H\leftarrow CH_3$ $CH_3\rightarrow\dot{C}-CH_3$ (CH_3 on C)

I II III

III > II > I ✓

⑩ $CH_3-\overset{\oplus}{C}H_2$ $CH_2=\overset{\oplus}{C}H$ (2.7) Aryl cation $CH\equiv\overset{\oplus}{C}$ (3.2)

saturated C^+ | Unsaturated

I > II > III > IV ✓

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Key points

1) Stability of $c^{\oplus}$ & free Radical $\propto$ $\frac{+I \text{ effect}}{-I \text{ effect}}$

2) Stability of saturated c^{+} > stability of unsaturated c^{+}

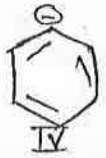
3) At more EN atom -ve charge and at less EN atom +ve charge stable.

2) Stability of Anion :-

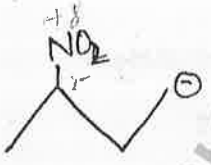
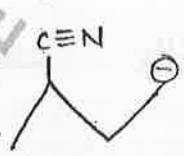
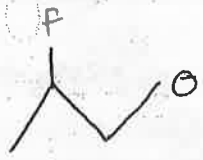
1) $CH_3^{\ominus}$ (I) $\quad CH_3-CH_2^{\ominus}$ (II, 1°C) $\quad CH_3-\overset{\ominus}{C}H-CH_3$ (III, 2°C) $\quad CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-\ominus$ (IV, 3°C)

I > II > III > IV ✓

$CH_3^{\ominus} > 1° > 2° > 3°$

2) $CH_3-CH_2^{\ominus}$ (I, 2.5) $\quad CH_2=CH^{\ominus}$ (II, 2.75) $\quad CH\equiv C^{\ominus}$ (III, 3.25) $\quad$  (IV, 2.75)

III > IV > II > I ✓

3)  (I) $\quad$  (II) $\quad$  (III) $\quad$  (IV)

I > II > III > IV ✓

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C^+ & C°

11) $\overset{\oplus}{C}H_3 > \overset{\oplus}{N}H_2 > \overset{\oplus}{O}H > \overset{\oplus}{F}$

(Same preciod)

⇓

(EN factor)

12) $\overset{\oplus}{I} > \overset{\oplus}{B}r > \overset{\oplus}{C}l > \overset{\oplus}{F}$

(Same group ⇒ Size factor)

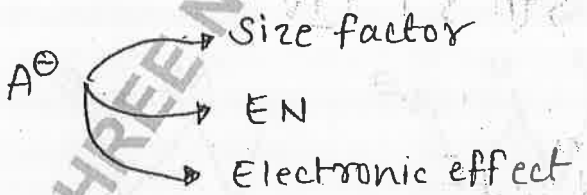
ANION :-

KEY POINT

① Stability of anion $\propto \frac{-I \text{ effect}}{+I \text{ effect}}$

② Stability of unsaturated anion > Stability of Saturated anion

③



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④ $CH_3^{\ominus} < NH_2^{\ominus} < OH^{\ominus} < F^{\ominus}$ (EN factor)

Stability of Anion ↑

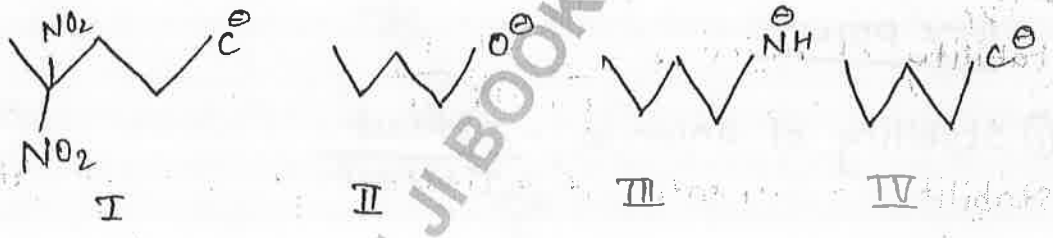
⑤ $F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}$ (Size factor)

Stability of Anion ↑

⑥

stab ⇒ II > I

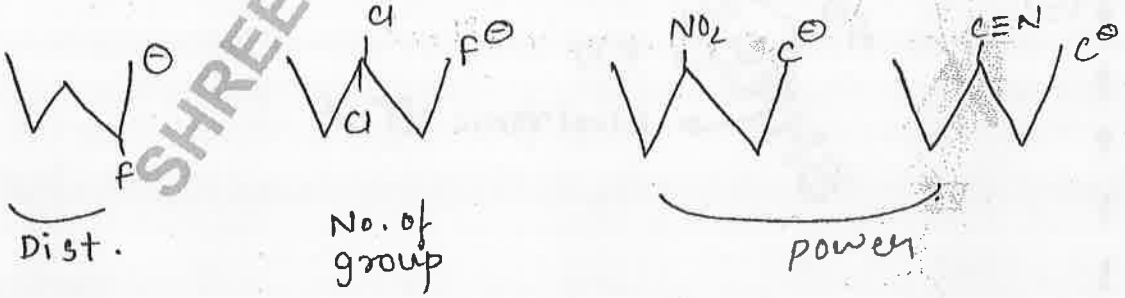
⑦



I II III IV

II > III > I > IV

⑧



Dist. No. of group power

Stabi ⇒ I > II > III > IV

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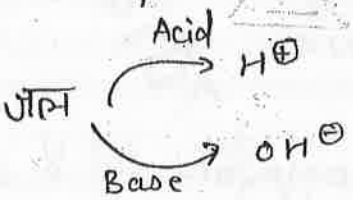
★ Oder of different stability factor in I-effect.

Distance factor > No. of group > Power

3. ACIDIC STRENGTH

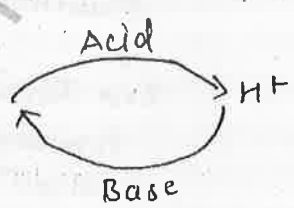
① Arrenius Concept →



eg: ① $H-Cl \rightleftharpoons H^+ + Cl^{\ominus}$ (Acid)

② $NaOH \rightleftharpoons Na^+ + \overset{\ominus}{O}H$ (Base)

② Bronstate & lower concept →



eg. $H-Cl \rightleftharpoons H^+ + Cl^{\ominus}$

$\ddot{N}H_3 \overset{H^+}{\rightleftharpoons} \overset{\oplus}{N}H_4$

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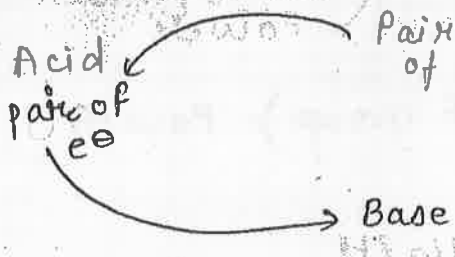
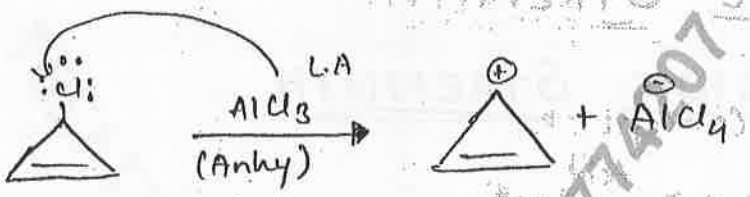
(3) Lewis Acid base theory:- सुखे में बेट कर बाते करता है।



eg.



संसार के सारे Anion base भी होते है और Nucleophile भी होते है.

H के साथ bond

$$H-A \underset{}{\overset{Ka}{\rightleftharpoons}} H^+ + A^\ominus \text{ (conjugated base)}$$

Anion
⇓
IF EWG present.
⇓
Stability of Anion ⇑
⇓
Rxn favours to forward direct^n ⇒ A.S ⇑ ⇒ Ka ⇑ ⇒ Pka ⇓

Ka ⇒ Acid dissociation const.

$$Ka \Rightarrow \frac{[H^+][A^\ominus]}{[HA]}$$

$[H^+] \uparrow \Rightarrow Ka \Uparrow \Rightarrow$ Strong Acid

$[H^+] \downarrow \Rightarrow Ka \Downarrow \Rightarrow$ Weak Acid

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$H-A \underset{}{\overset{K_a}{\rightleftharpoons}} H^{\oplus}\uparrow + A^{\ominus}$ (conjugated base)

Acid
S.A

Anion
W.B

संसार का हर Anion कोशिश है कि वह सब से पहले ACID/BASE Rxn kare.

$A^{\ominus}$ → Base ✓

→ Nucleophile Ex. $NaOH \rightleftharpoons Na^{+} + OH^{\ominus}$

① $HO^{\ominus} + H-O-\overset{O}{\overset{\|}{C}}-R \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{+}$ ($-H_2O$)

Acid-base rxn.

② $H_3C-Cl \xrightarrow{OH^{\ominus}} HO-CH_3 + Cl^{\ominus}$ ⇒ Sn^2-me

Key Point

Acidic strength ∝ Stability of Anion [conjucated base]

$\propto \frac{-I \text{ effect}}{+I \text{ effect}}$

$\propto K_a$

$\propto \frac{1}{PK_a}$

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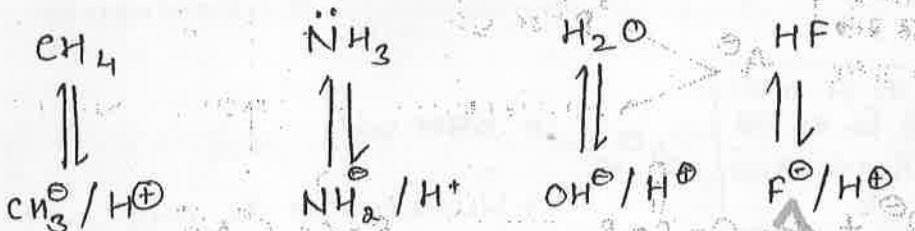
★ Acidic strength acc. to periodic table:-

(a) A.S in period →



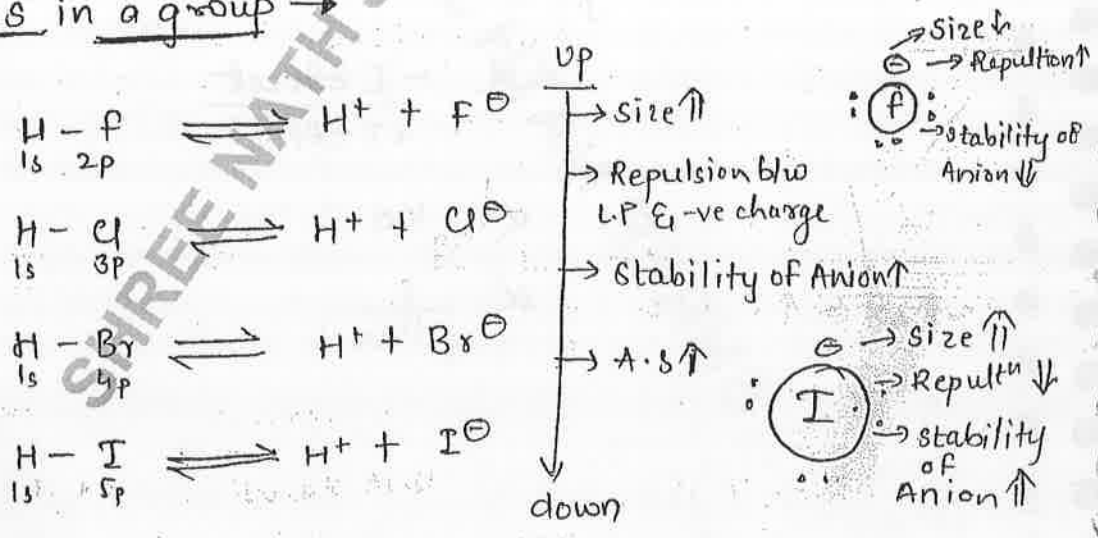
EN factor →
→ Stability of Anion ↑
→ A.S ⇑

A.S ⇒ H-F > H_2O > NH_3 > CH_4

Base ⇒ $CH_3^\ominus$ > $NH_2^\ominus$ > $OH^\ominus$ > $F^\ominus$

(b) Acidic strength acc. to group:-

(b) A.S in a group →



A.S ⇒ H-I > H-Br > H-Cl > H-F

Base ⇒ ~~$I^\ominus > Cl^\ominus > Br^\ominus > I^\ominus$~~
$F^\ominus > Cl^\ominus > Br^\ominus > I^\ominus$

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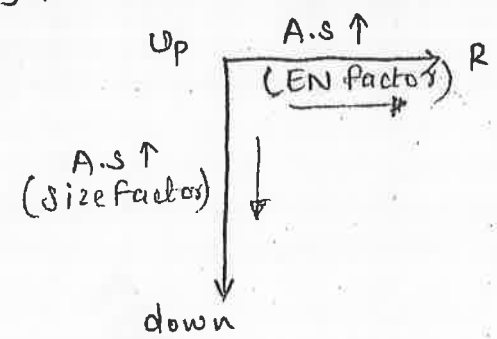
Key point →



Q.1 $CH\equiv CH$, H_2O, HBr, NH_3, HI

$CH\equiv CH^{\ominus}/H^+$ (3.25) ; $OH^{\ominus}/H^+$ (3.5) ; $H^+/Br^{\ominus}$; $NH_2^{\ominus}/H^+$ (3.0) ; $H^+/I^{\ominus}$

A.S ⇒ $HI > HBr > H_2O > \cancel{NH}\ CH\equiv CH > NH_3$

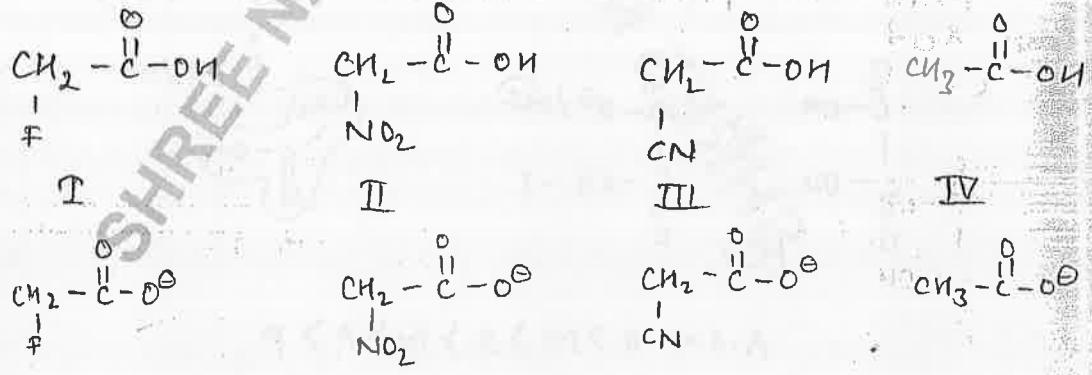
Q.2 $H-\overset{O}{\overset{\|}{C}}-OH$, $CH_3-\overset{O}{\overset{\|}{C}}-OH$, $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$

$H-\overset{O}{\overset{\|}{C}}-O^{\ominus}/H^+$; $CH_3\xrightarrow{+I}\overset{O}{\overset{\|}{C}}-O^{\ominus}/H^+$; $CH_3>CH_2\xrightarrow{+I\uparrow}\overset{O}{\overset{\|}{C}}-O^{\ominus}/H^{\oplus}$

max

I > II > III

Q.3



II > III > I > IV

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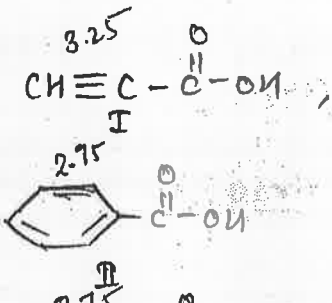
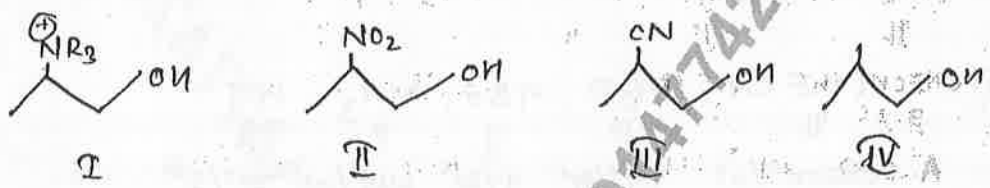
Q.4. 

A.S ⇒ I > II > III > IV

Q.5. 

A.S ⇒ I > II > III > IV

(6)

O → oxalic Acid (0C)

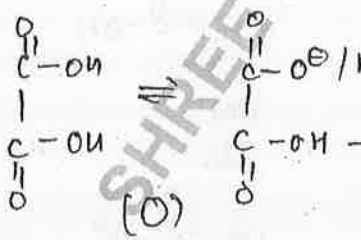
M → malonic Acid (1C)

S → Succinyl Acid (2C)

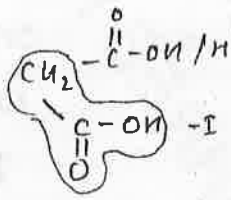
Gl → Glutamic Acid (3C)

A → Adipic Acid (4C)

P → Pimellic Acid (5C)



(O)



A.S ⇒ O > M > S > Gl > A > P

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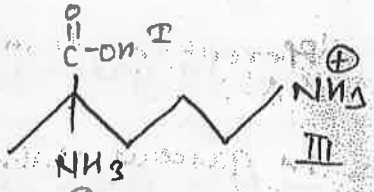
(7)



$\ddot{N}H_3$ $\ddot{P}H_3$
S=25% S=100%

A.S ⇒ I > II > III

$$\boxed{A.S \Rightarrow R-\overset{O}{\overset{\|}{C}}-OH \;>\; R-\overset{\oplus}{N}H_3}$$

4. Basic Strength of ~~Anion~~ Amine

संसार का हर एक Anion base भी होता है और Nu⊖ भी होता है

H के साथ Bond — Base

कीसी और के साथ — Nucleophile.

Base → Species which can donate lone pair on -ve charge to H^+ is known as base

[H^+ के साथ Bond बनाने tendency एक अच्छे Base की होती है].

(Base) (Conjugated Acid.

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Basic strength amine in different medium

① Basic strength of amine in gaseous state :-

① $\ddot{N}H_3 \rightleftharpoons NH_4^{\oplus}$ (with H^+) → Min stable cation → strong Acid

Ammonia

② $CH_3 \rightarrow \ddot{N}H_2 \rightleftharpoons CH_3 - \overset{\oplus}{N}H_3$ (with H^+)

e-density ↑, +I

1° Amine

③ $CH_3 \rightarrow \ddot{N}H \leftarrow CH_3 \rightleftharpoons CH_3 - \overset{H^+}{\underset{H}{N}} - CH_3$ (with H^+)

+I, +I

2° Amine

④ $CH_3 \rightarrow \ddot{N} \leftarrow CH_3$, CH_3 (+I, +I, +I) $\rightleftharpoons CH_3 - \overset{H^+}{\underset{CH_3}{N}} - CH_3$ (with H^+)

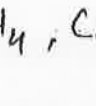
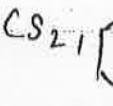
3° Amine

Max. stable cation

Weak conjugate Acid

B.S ⇒ 3° Amine > 2° Amine > 1° Amine > $\ddot{N}H_3$

② Basic strength of amine in case of non-polar medium.

[CCl_4, CS_2,  ,  , ---- etc]

Non-polar medium.

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B.S ⇒ 3° Amine > 2° Amine > 1° Amine > $\ddot{N}H_3$

(3) Basic strength of Amine in aqueous medium ***

(A) Basic strength of Amine in case of methyl Amine.

B.S ⇒ $CH_3-\ddot{N}H-CH_3$ > $CH_3-\ddot{N}H_2$ > $CH_3-\overset{\overset{CH_3}{|}}{\ddot{N}}-CH_3$ > $\ddot{N}H_3$

Dimethyl Amine — 1° Amine — 3° Amine

2° Amine

⇒ +I-effect ⇒ +I-effect ⇒ only +I effect ⇒ only solvat

⇒ Solvation ⇒ Solvation

In case of ($-CH_3$) / Methyl ⇒ छोटे वाला ⇒ 213

(B) Basic strength of Amine in case of ethyl Amine.

B.S $H_5C_2-\ddot{N}H-C_2H_5$ > $C_2H_5-\overset{\overset{C_2H_5}{|}}{\ddot{N}}:$ > $C_2H_5-\ddot{N}H_2$ > $\ddot{N}H_3$

C_2H_5

⇒ +I-effect (2) ⇒ +I-effect ⇒ +I-effect ⇒ only solvat^n

⇒ Solvation ⇒ Solvation

In case of ethyl (C_2H_5) ⇒ बड़ा वाला ⇒ 231

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Key point →

① B.S ∝ $\frac{+I \text{ effect}}{-I \text{ effect}}$

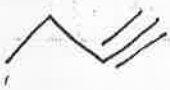
② B.S ∝ tendency donate lone pair to H^+

③ B.S ∝ Stability of cation ($-\overset{\oplus}{N}-$) / conjugated Acid
- +I-effect
- Solvatn effect.

Q.1

NH_2 sp^3 – 25%

$\ddot{N}H$ sp^2 – 83%



$\ddot{N}$ sp – %s ⇒ 50%

B.S ⇒ I > II > III

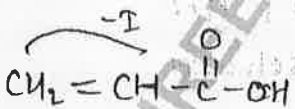
Q.2.

I

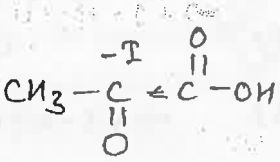
II

B.S ⇒ I > II

Q.3



I



II

A.S ⇒ II > I

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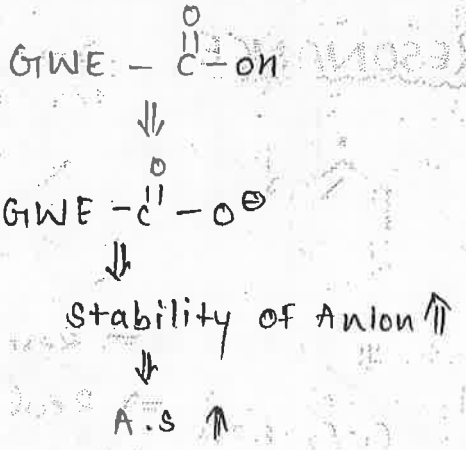
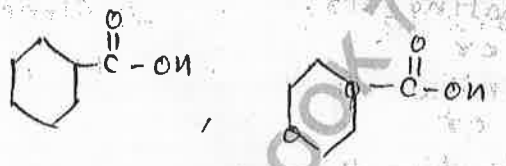
Key point →



Ex. 2017



* Deprotonation ⇒ generate conjugated base
* Protonation generates conjugated Acid.
* Strong Acid contain Weaker conjugate base
* Strong Base contain Weaker conjugated Acid.

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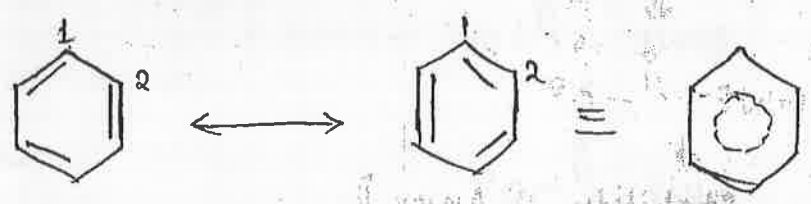
↷ ⇒ moving of 2e⁻

↶ ⇒ moving of 1 e⁻

⟷ ⇒ hypothetical

RESONANCE

⬡ → Robinson's circle



I ⟷ II ≡ B.L ⇒ 1.39 (1.4 Å)

I ⇒ $C_1 - C_2$ ⇒ 1.54 Å

II ⇒ $C_1 - C_2$ = 1.34 Å

Resonating str.
or
cannonical ||
or
Contributing ||

⇒ Resonating hybrid
⇒ Real str.
⇒ lowest energy
⇒ Max - stable
⇒ Almost explain all PP & CP of molecules.

① Hypothetical concept.

② Parmanent effect.

③ Generally resonance is stablising phenonmenon

④ In Resonance we can't change position of atom. It involve only de-localisat^n of $\pi e^{\ominus}$'s / lone pair / -ve charge / free radical and +ve charge.

Delocalisation → movable → Not fixed → Energy released ⇑ ⇒ stability ⇑

Localised ⇒ fixed e^- → energy released ⇓ ⇒ stability ⇓

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⑤ Resonance is a interamolecular ~~formulae~~ phenonmenon.

⑥ Atoms or orbital which are participate in Resonance must be in the samp plane [comp. must be planer or innerly planer only in resonance area]

⑦ In Resonance pure-p-orbital // Pure-d-orbitals are participated [unhybrid orbitals]

⑧ Hybride orbital never participate in Resonance.

⑨ All resonanting structure are hypothetical in nature while resonating hybride is real in nature.

⑩ More stable resonanting str. will give more contribut^{n} resonanting hybrido.

⑪ When properties of a molecules can not explain by single lewis dot str. even some time, we made more than 1 lewis dot str. that all str. Cannonical / Resonating / contributing str. but real str. is Resonating hybrid which can explain all PP & OP of molecule.

for a resonance comp. must have conjugated system

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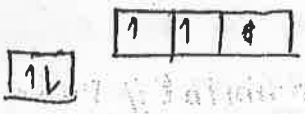
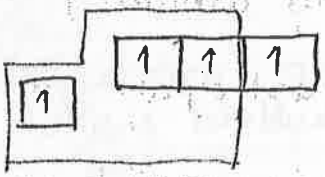
$C_6 \rightarrow 1s^2\ 2s^2\ 2p^2$

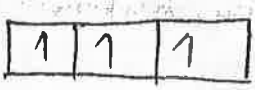
G.S ⇒



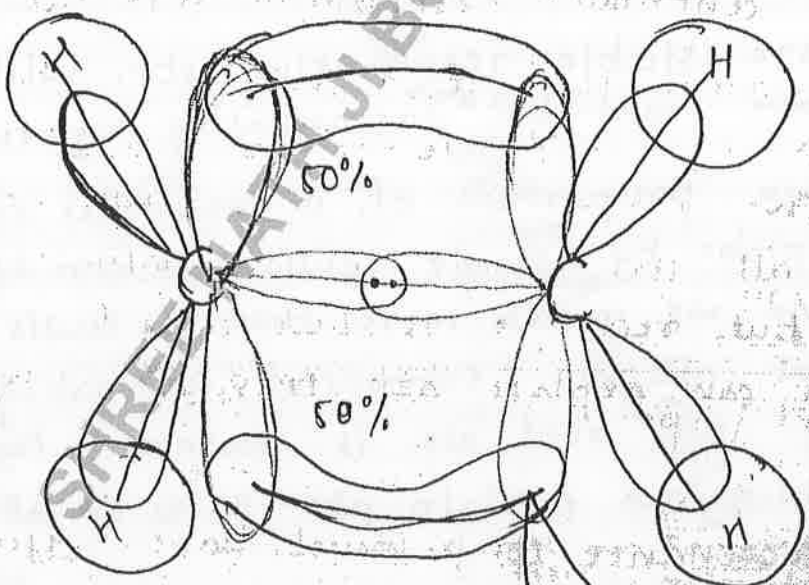
⇓

E.S ⇒





1 Pure P-orbital
unhybrid orbital



→ pure p-orbital
→ Weak bond
⇒ loosely bonded e⁰
⇒ side ways overlapping

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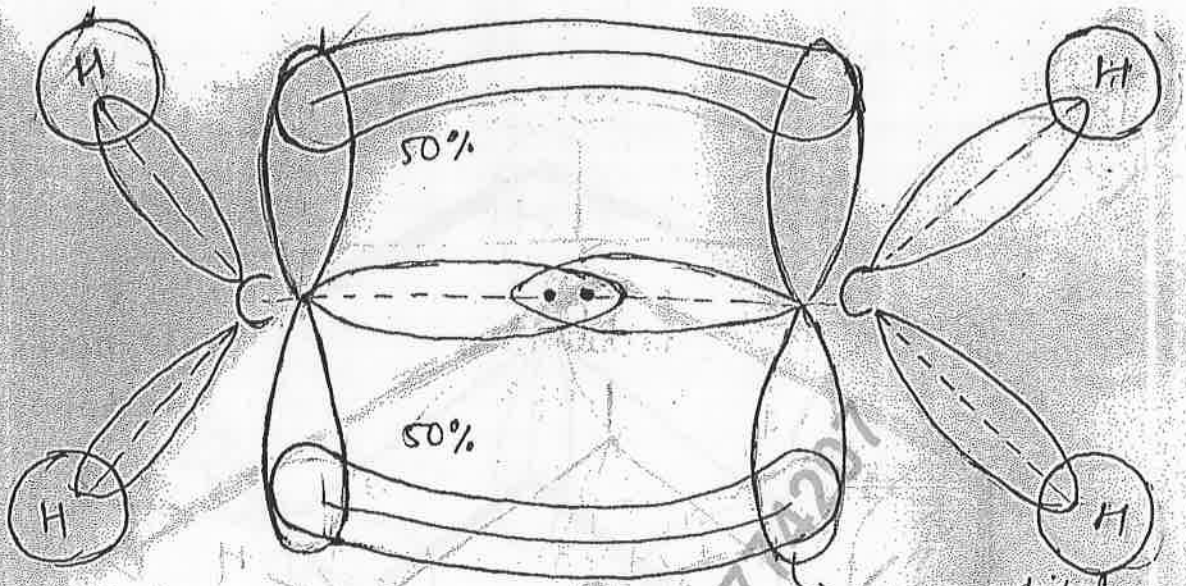

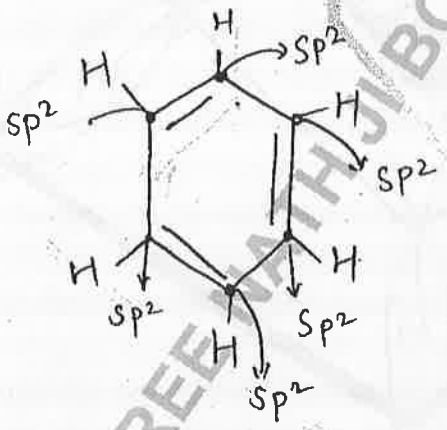

⇒ 6 pure p-orbital

⇒ 6 π e⁻ (3 π bond)

⇒ B.L ⇒ 1.39 Å

⇒ B.O ⇒ 1.5

⇒ e⊖ density ⇒ Same - 2

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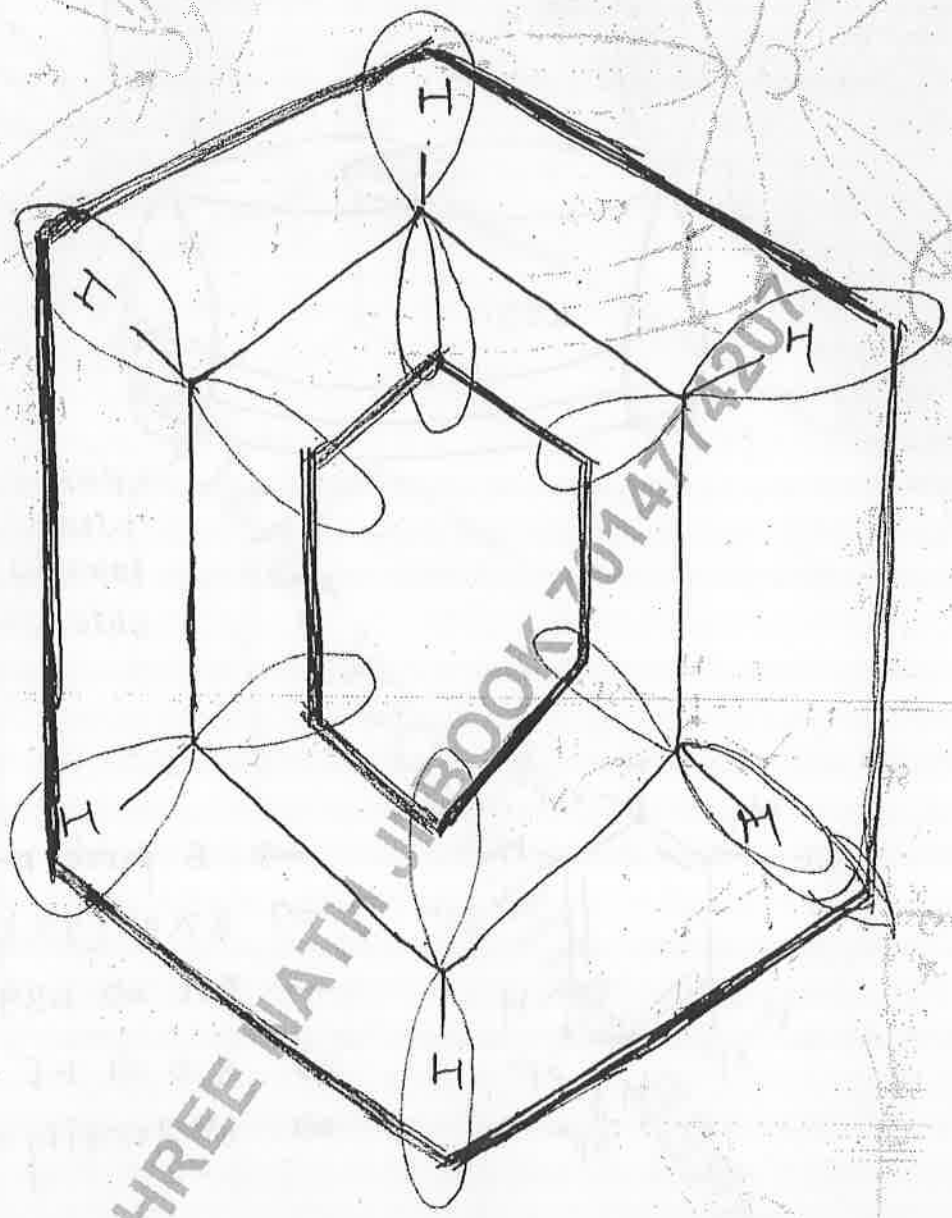

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Type of System :-

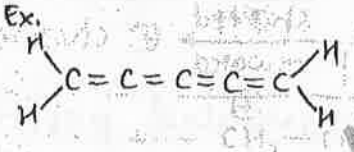
- conjugatory System
- Cumulated System
- Isolated System

→ planer system. with parallel-p-d orbital

→ Reso

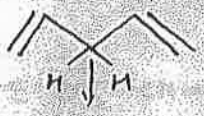
Ex.

Ex.



→ Reso

Ex.



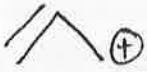
sp^3

isolated C → Non Planar

⇓

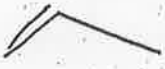
No Resonance.

Conjugatory System

1.  Reso

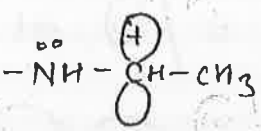
2.  Reso

3.  Reso

4.  Reso

Radical

5. 

6. 

7. vacant d-orbital (P, S, Cl)

ऐसे cation का सम्पर्क होता है कि उसका पड़ोसी lone pair valla ho;

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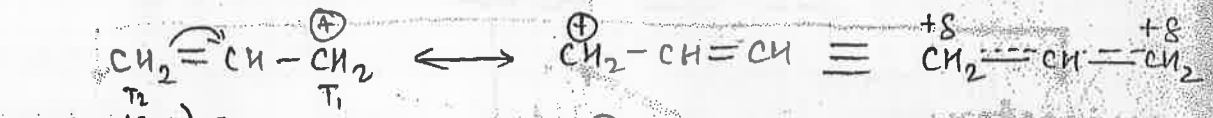
Condit^n for Resonance / Mesomeric Effect :-

1] Double Bond / ⊕ at conjugated position.



(Allylication) I

II

Hybrid Str.

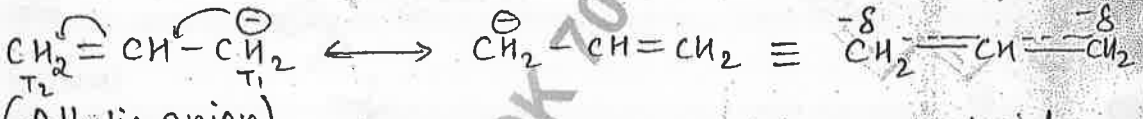
R.S ⇒ 2

2e⁻ e⁻

= shifted toward ⊕ charge

reason M.O.T

2] = / ⊖ at conjugated position



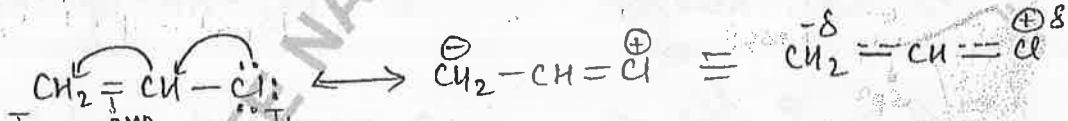
(Allylic anion)

Hybrid Str.

R.S ⇒ 2

⊖ shifted towards =

3] = / ⊕⊕ at conjugated position.



Vinyllic chloride

hybrid str

R.S = 2

L.P shifted toward =

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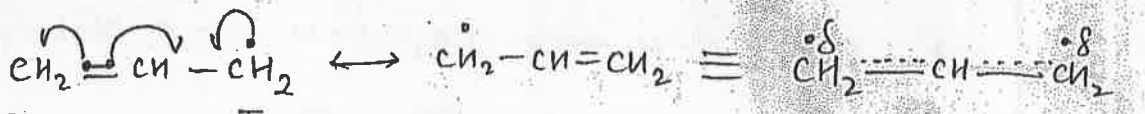
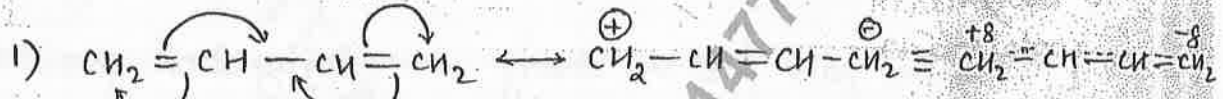
4] =/ free Radical at conjugated position.



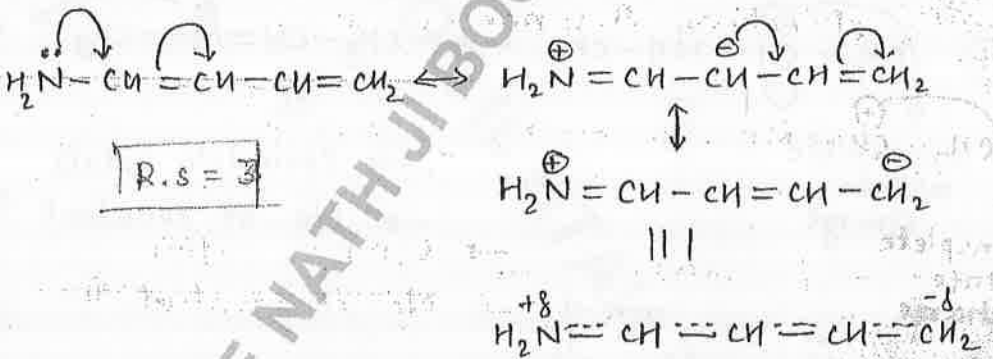
R.S => 2

5] =/ conjugated with DB.

1) 

(1,3-Butadiene)

Resonance ⇒ bidirectional.

ii) 

R.S = 3

+R/+M ⇒ Resonance / Mesomeric effect

⇓

Unidirectional

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iii) $CH_2=CH-CH=CH-\overset{\overset{O}{\|}}{C}-H$

$-M/-R$ effect.

→ $\overset{\oplus}{C}H_2-\overset{\overset{O}{\|}}{C}-H \longleftrightarrow CH_2=\overset{\overset{O^{\oplus}}{|}}{C}-H$ → Not possible

→ $CH_2=CH_2 \longleftrightarrow \overset{\oplus}{C}H_2-\overset{\ominus}{C}H_2$ → Not possible

→ $>C=O \longleftrightarrow >\overset{+}{C}-\overset{\ominus}{O} \equiv >\overset{\delta+}{C}=\overset{\delta-}{O}$ → possible

6.] lone pair / ⊕ ve charg at conjugated position.

→ IN case of cation this is maximum effective Resonance.

(i) $CH_3-\overset{\oplus}{C}H-\ddot{N}H-CH_3 \longleftrightarrow CH_3-CH=\overset{\oplus}{N}H-CH_3$

I II

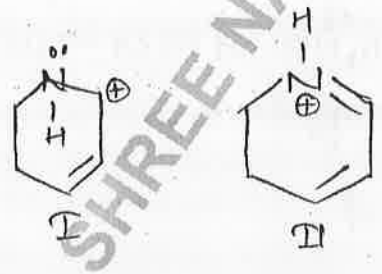
Incomplete octate charge

formal charge

→ Complete octate

→ No. of covalent ⇑

(ii)



I II

stability → II > I

(iii) $CH_3-\overset{\overset{O}{\|}}{\overset{\oplus}{C}}=\ddot{O}: \longleftrightarrow CH_3-C\equiv O^{\oplus}$

(Acyl cation)

Acyliniumin

Stab⇒ II > I

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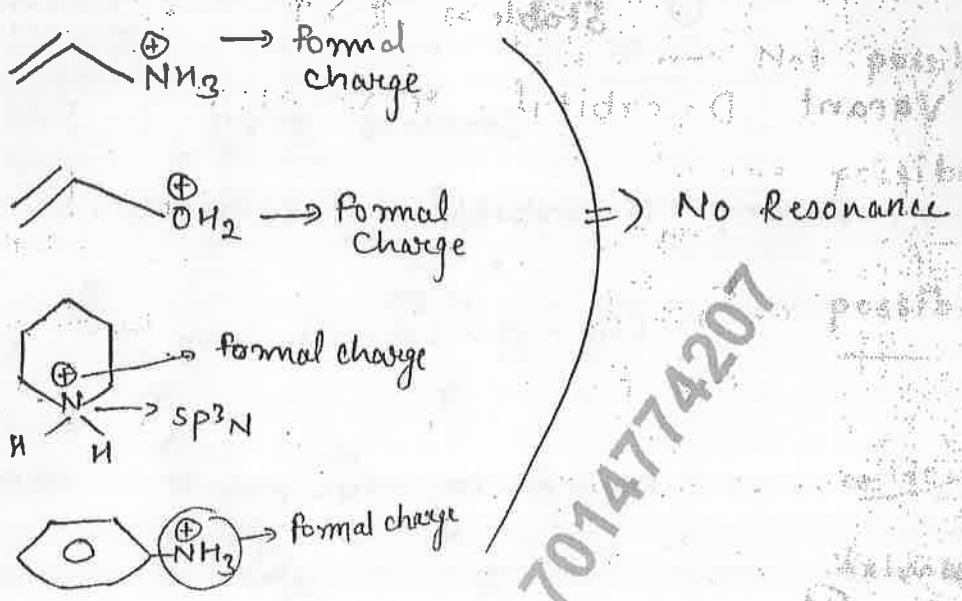
KEY POINT

1) formal charge never participate in Resonance.



2) Any compound must have 3 parallel p-orbital for resonance.

Ex.

3-pure p-orbital

3) for ions must have two parallel p-orbital.

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(iv) $CH_3-\overset{(+)}{C}H(O)-\ddot{O}-CH_3 \longleftrightarrow CH_3-CH=\overset{+}{O}-CH_3$

I II

Stable ⇒ II > I

7) Vacant D-orbital - resonance.

Repulsion

$CH_3-\ddot{O}-CH(\ominus)-CH_2-CH_3$

I

S & P
↓
Roobinhood of Chemistry

$CH_3-\ddot{O}-CH_2-\overset{\ominus}{C}H-CH_3$

−I α β γ

II

Stability ⇒ II > I

(i) $CH_3-\overset{(+)}{C}H(O)-\ddot{S}-CH_3 \longleftrightarrow CH_3-CH=\overset{\oplus}{S}-CH_3$

I II

Stab ⇒ II > I

(ii) $CH_2(\ominus)-\ddot{S}-CH_3 \longleftrightarrow CH_2=\overset{\ominus}{S}-CH_3$

I (vacant d-orbital) II

Stab ⇒ II > I

(iii) $CH_3-\overset{(+)}{C}H(O)-\ddot{P}(H)-CH_3 \longleftrightarrow CH_3-CH=\overset{\oplus}{P}(H)-CH_3$

I II

Stab ⇒ II > I

$CH_2(\ominus)-\ddot{P}(H)-CH_3 \longleftrightarrow CH_2=P(H)-CH_3$

(vacant d-orbital)

Stab ⇒ II > I

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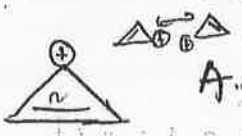
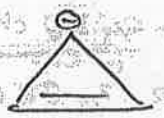
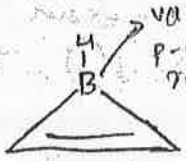
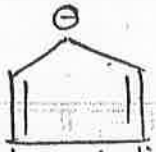
(1)  N.A.

(2)  N.A

(3)  A.

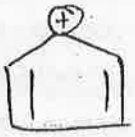
(4)  A.A

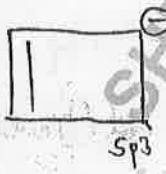
(5)  A

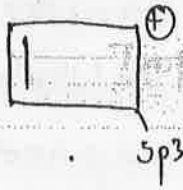
(6)  A

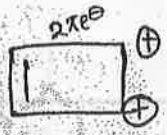
Cyclo Pentadiene Anion

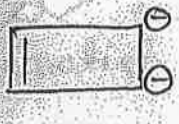
(7)  N.A

(8)  A.A

(9)  N.A

(10)  N.A

(11)  A

(12)  A

(13)  NA

(14)  A

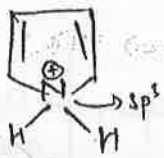
pyrole

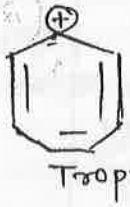
(15)  A

furan

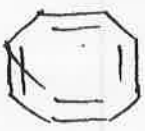
(16)  A

Thiophen

(17)  N.A

(18)  A

Tropolium cation

(19)  COT → cyclo octa tetraene

NA.

(20)  A

(21)  A

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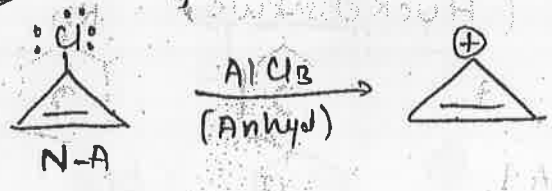
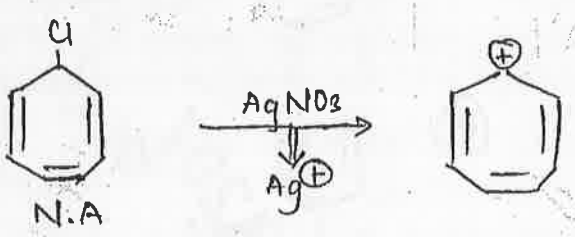
2014

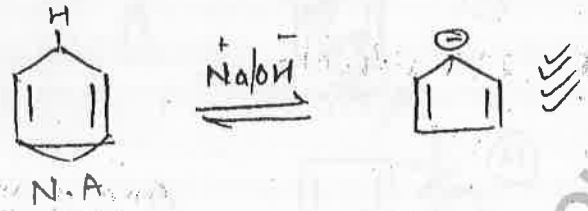
Q.1



Q.2



Q.3



Aromatic

- Comp. must be cyclic
- " " planer
- " " have cyclic reso. over the enitre cycle
- Comp. must follow Huckel's Rule

$(4n+2)\pi e^{\ominus}$

$n \Rightarrow 0, 1, 2, 3, 4, 5 \cdots 6 \cdots$ etc

Trick ⇒ $2\pi e^{\ominus}$, $6\pi e^{\ominus}$, $10\pi e^{\ominus}$, $14\pi e^{\ominus}$, $22\pi e^{\ominus}$ etc

Non Aromatic

- Out of Four if any one condn voileted then comp. behave as Non-Aromatic.

Anti Aromatic

- Comp. must be cyclic
- comp must be planer
- comp must have cyclic resonance
- Comp. must follow Huckel's Rule

$(4n)\pi e^{\ominus}$

$n = 1, 2, 3, 4, 5$ etc.

Trick ⇒ $4\pi e^{\ominus}$, $8\pi e^{\ominus}$, $12\pi e^{\ominus}$ etc.

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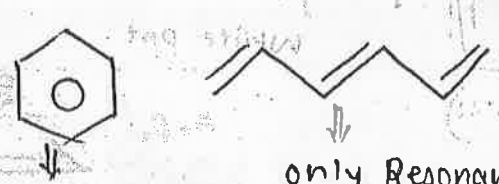
AROMACITY (Huckel's Rule)

① Aromatic comp. [A]

② Non-Aromatic comp [N.A]

③ Anti-Aromatic comp [A.A]

Ex.



Reso + extra Factor
Aromaticity

R.E = -36 kcal/mole

only Resonance

R.E = -22 kcal/mole.

Stability A > N.A > A.A

Comp. doesn't exit in Room temp in pure form.

Reson ⇒ MOT

- A: Cyclic Reso & All $e^{\ominus}$ in BMO
- N.A: Non-cyclic Reso & All $e^{\ominus}$ in BMO
- A.A: Cyclic Reso & But all $e^{\ominus}$ ABMO/NBMO

Application ⇒

① A A ⟶ A चाले ✓

② A.A ⟶ N.A चाले ✓

③ N.A ⟶ A चाले ✓

④ A ⟶ A.A ××× हट

⑤ A ⟶ N.A ××× हट

⑥ N.A ⟶ A.A ××× हट

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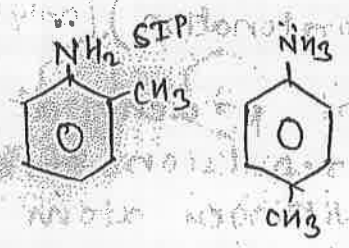
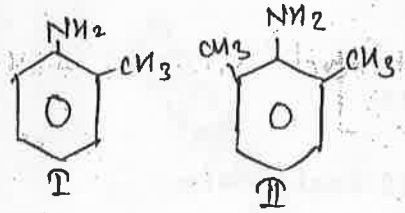
Q.1



B.S ⇒ II > I

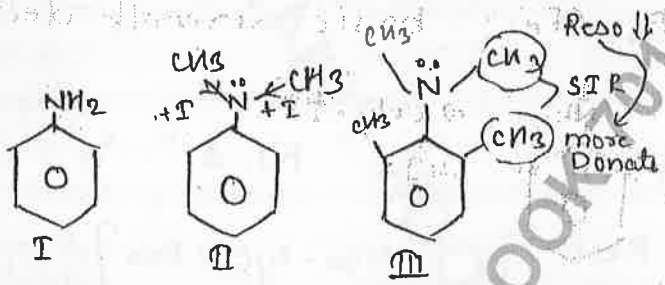
O-Toluidine P-Toluidine

Q.2



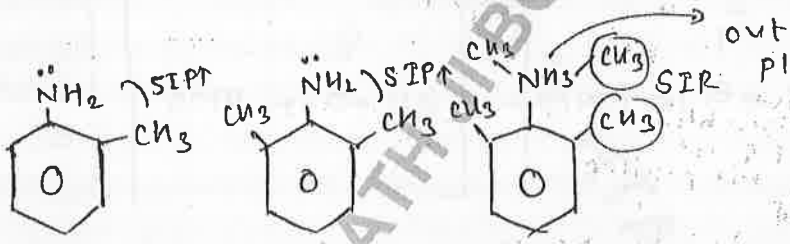
B.S ⇒ I > II

Q.3



B.S ⇒ III > II > I

Q.4



B.S ⇒ III > I > II

NH

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IMI

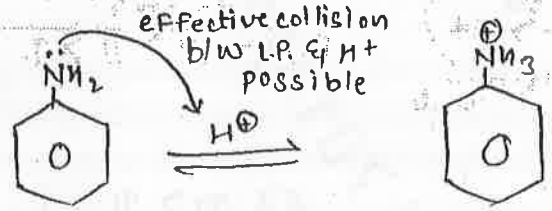
SIP (steric of inhibition of protonation) (only for aniline)

* Whenever ortho substituent present at aniline then due to steric repulsion effective collision b/w lone pair of Nitrogen atom & H^+ not possible, this effect is known as SIP.

* In case of ortho substituted aniline ~~orth~~ solvation effect observed.

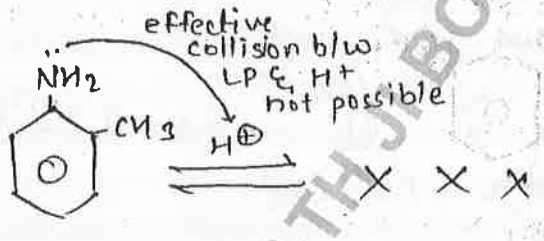
In case of SIP effect basic strength decreases

(i)



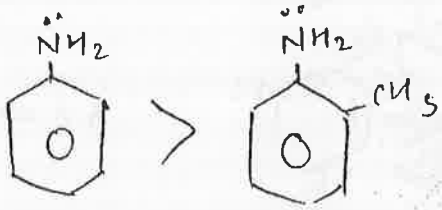
Aniline

(ii)



O-Toluidine

B.S ⇒



O-Toluidine.

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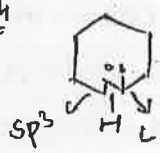
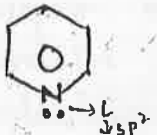
Q.4



Pyridine

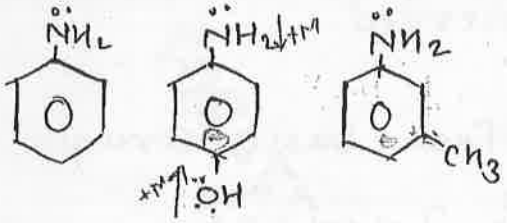


Pyrole

Aniline

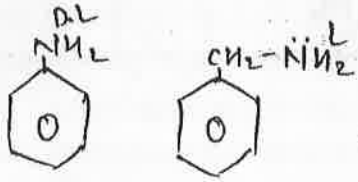
B.S ⇒ I > II > IV > III

Q.5.



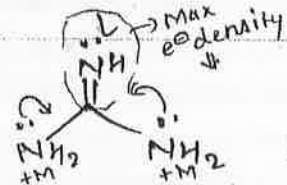
B.S ⇒ IV > II > III > I

Q.6

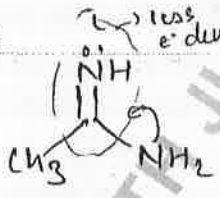


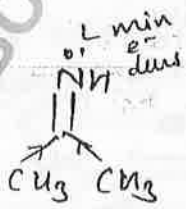
B.S III > II > I

Q.7



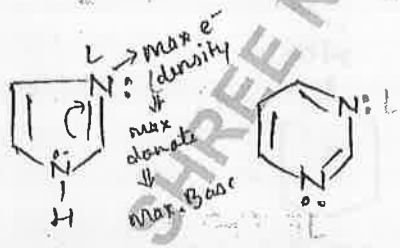
(guanidine)





B.S ⇒ I > II > III

Q.8



B.S ⇒ I > II

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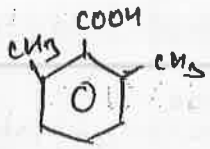
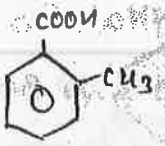
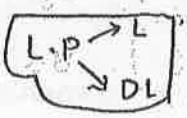
Q.4   A.S ⇒ I > II

Basic strength →

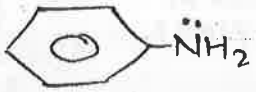
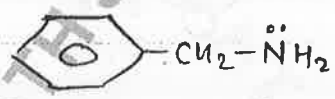
KEY POINT

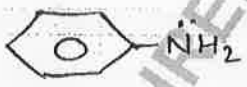
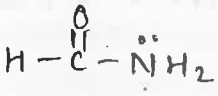
(I) B.S ∝ $\frac{1}{R.S}$  (B.S ⇒ L > D.L)

(II) B.S ∝ $\frac{1}{\%\ s\text{-character of Donor atom}}$

($\ddot{N}\ sp^3 > \ddot{N}\ sp^2 > \ddot{N}\ sp$)

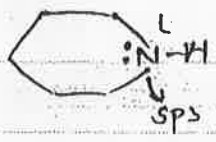
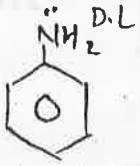
(III) B.S ∝ $\frac{+I\ /+M}{-I\ /-M}$

Q.1  I  II B.S ⇒ II > I

Q.2  Aniline  Amide

TB.S ⇒ I > II

Amide ↳ 2016 ⇒ Amide ⇒ Neutral comp.

Q.3   

B.S ⇒ III > II > I

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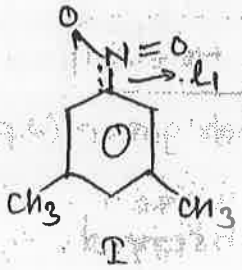
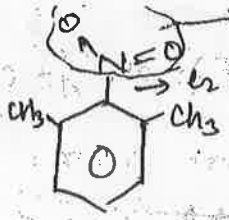
Q.5



I



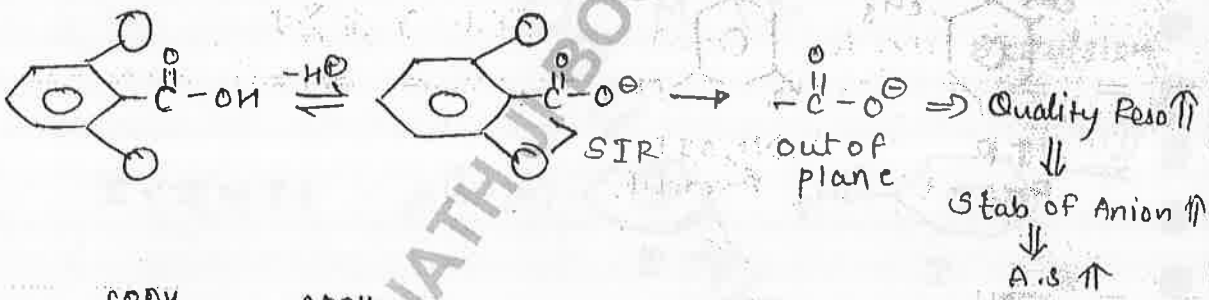
II

B.L ⇒ $l_2 > l_1$

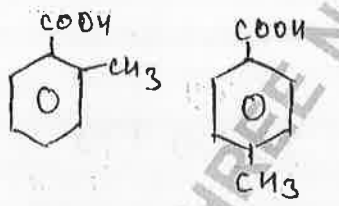
* ORTHO Effect [for only aromatic carboxylic acid]

→ ortho effect is the application of SIR.

→ ortho substituted aromatic carboxylic acid is more acidic than Para & Meta substituted carboxylic acid this effect is known as ortho effect.

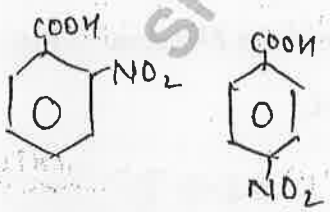


Q.1



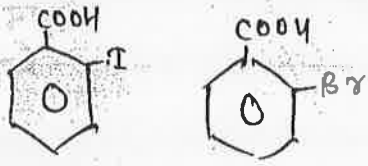
AS ⇒ I > II

Q.2



A.S ⇒ I > II

Q.3



A.S ⇒ I > II

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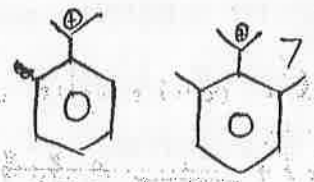
NOTE: $-H, -D, -T, -F, -OH$, $-C\equiv N$, $-C\equiv CH$ (Linear group (sp))

⇓

SIR effect Not observed.

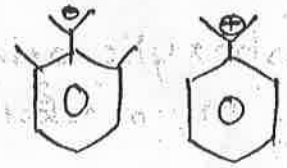
Q.1



SIR

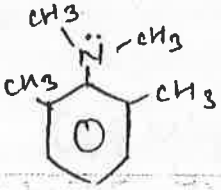
Stab ⇒ I > II

Q.2

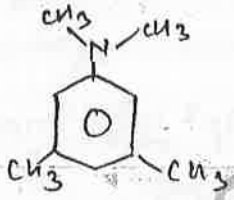


Stab ⇒ II > I

Q.3



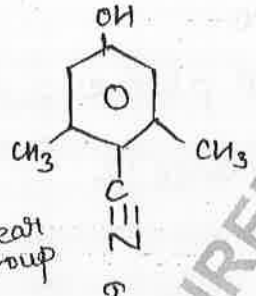
SIR Present



No SIR Present.

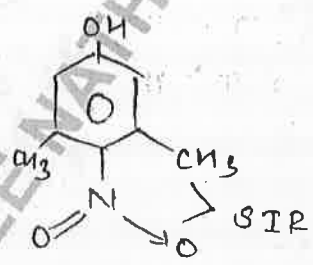
Stab ⇒ II > I

Q.4



Linear group

I



SIR

II

Stab ⇒ I > II

→ No S.I.R ⊕

⇓

Both +I & -M effect obs.

→ SIR ⊕

⇓

No -M effect

⇓

Onyl +I effect

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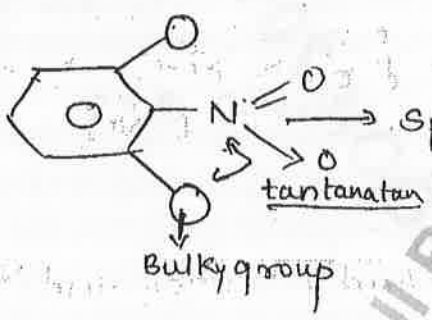
* SIR [Steric inhibition of Resonance].

Whenever bulky group ~~nt~~ at ortho posith of triangular group due to steric repulsion [बड़ा बड़ा टच] triangular group change its plane [out of plane] so tendency of Reso. with benzene decrease this effect is known as SIR.

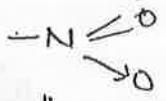
Concept →



⇓

Due to steric repulsion

⇓



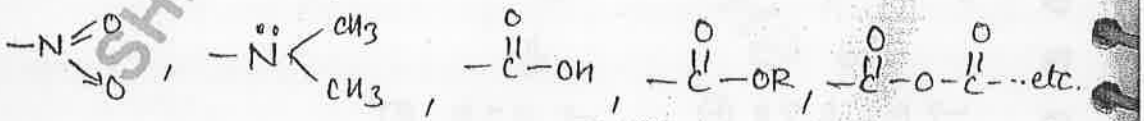
⇓

out of plane

⇓

Resonance ⇓

① All trigular group:-



⑪ Bulky group:- All triangular group + All Alkyl group

जूते मारने वाले.

eg (CH_3-, CH_3-CH_2- etc.

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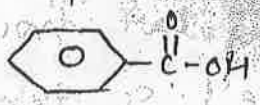
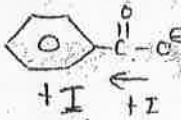
formic acid benzoic acid Acetic Acid.

(15) $H-\overset{O}{\overset{\|}{C}}-OH$ >  > $CH_3-\overset{O}{\overset{\|}{C}}-OH$

FBA

$H-\overset{O}{\overset{\|}{C}}-O^{\ominus}$  $CH_3\rightarrow\overset{O}{\overset{\|}{C}}-O^{\ominus}$

+I +I +I

Formic acid.

I > II > III

Solvatn effect

(i) A.S ⇒  > H_3O^{+} > $R-\overset{O}{\overset{\|}{C}}-OH$ > $\overset{\oplus}{N}H_4$ > $R-\overset{\oplus}{N}H_3$ > R-OH or CH≡CH

= -1.73

(ii) A.OS ⇒ Picric Acid > formic Acid > Benzoic Acid > Acetic Acid

(iii) A.S ⇒ $CH_3-OH > H_2O > R-OH$

Solvatn effect.

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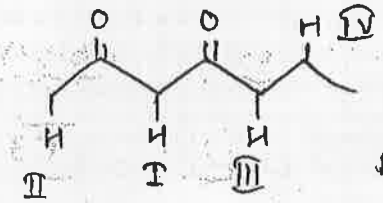
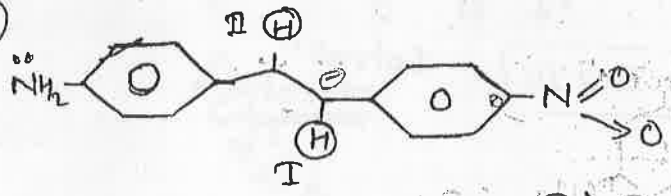
(11)



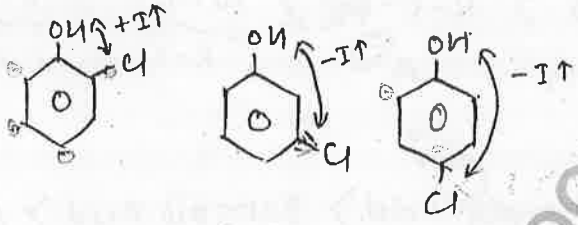
A·S ⇒ I > II > III > IV

(12)



A·S ⇒ I > II

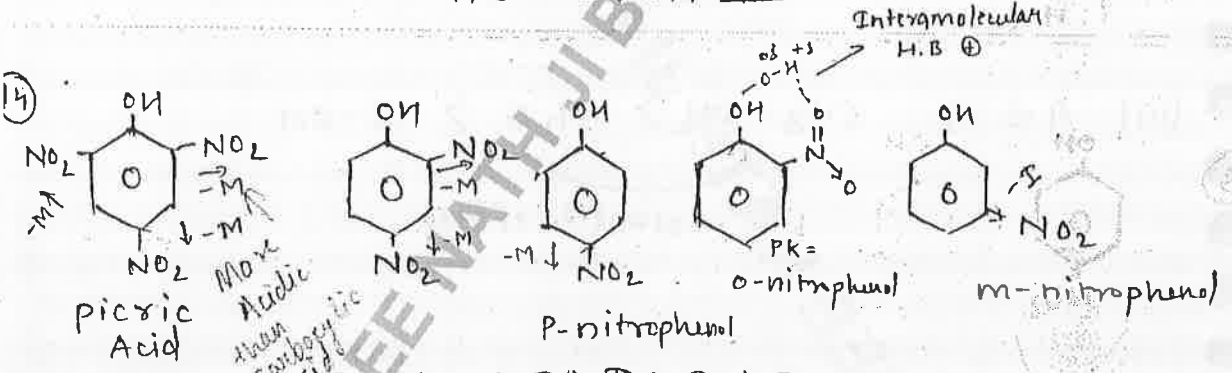
(13)



When same atom ⇒ I effect.

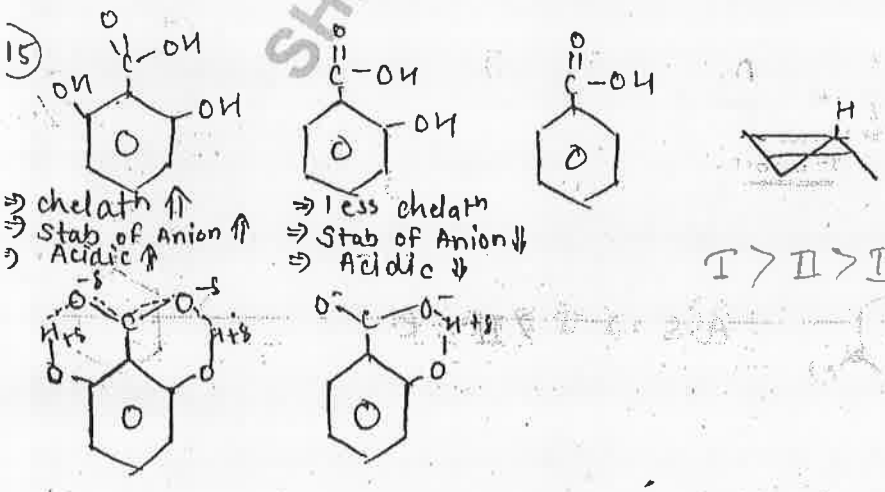
A·S ⇒ I > II > III

(14)



A·S. ⇒ I > II > III > IV > V

(15)



I > II > III

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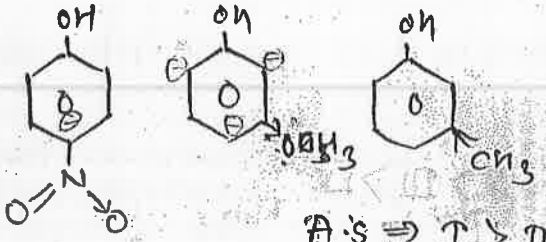
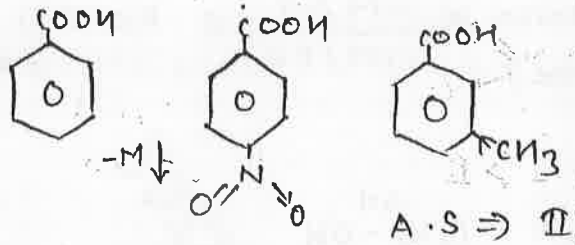
(5)



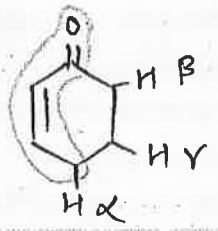
A·S ⇒ I > II > III

(6)



A·S ⇒ II > I > III

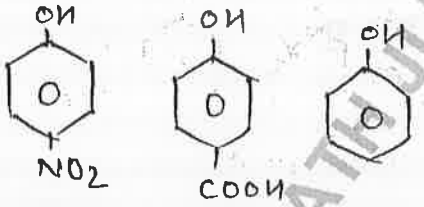
(7)



α > β > γ

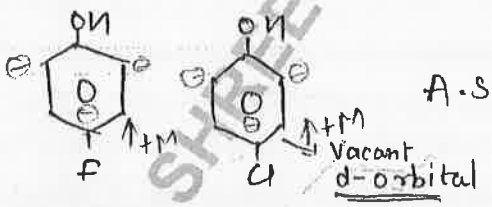
A·S ⇒ α > β > γ

(8)



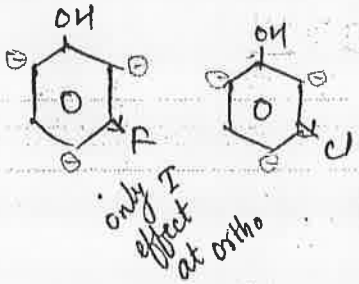
A·S ⇒ II > I > III

(9)



A·S ⇒ II > I

(10)



A·S ⇒ I > II

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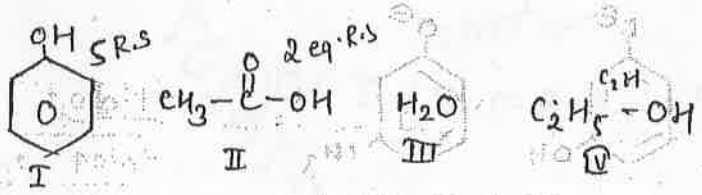
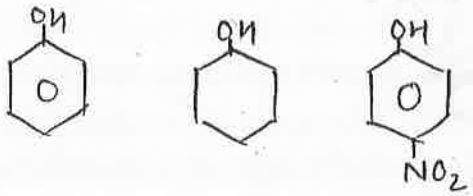
③ Acidic Strength :-

KEY POINT

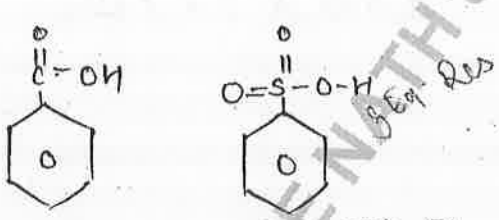
$$A.S \propto \text{Stability of Anion (conjugate Base)} \propto \frac{-M/-I}{+M/+I} \propto Ka \propto \frac{1}{PKa}$$

① 

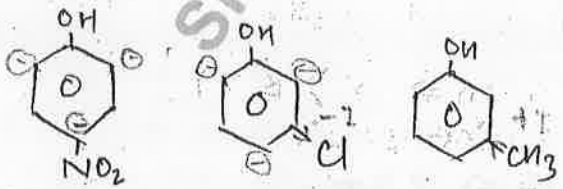
A.Stab ⇒ II > I > III > IV

② 

A.S ⇒ III > I > II

③ 

A.Stab ⇒ II > I

④ 

A.S ⇒ I > II > III

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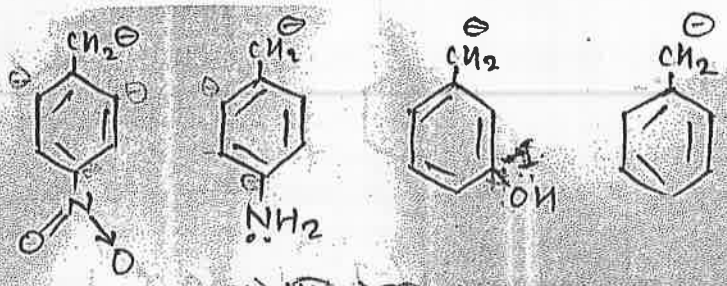
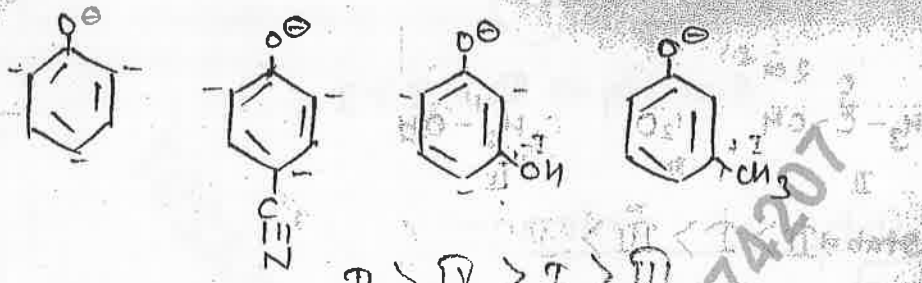
(5)



Stab ⇒ III > IV > II

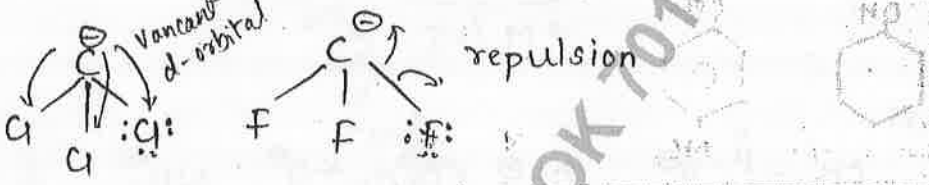
(6)



II > IV > I > III

Stab ⇒ II > III > I > IV

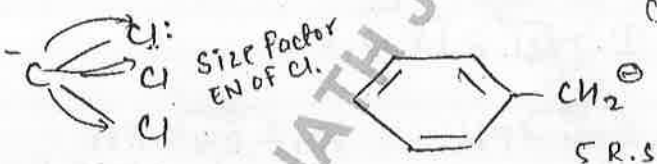
(7)



I > II

Stab ⇒ I > II

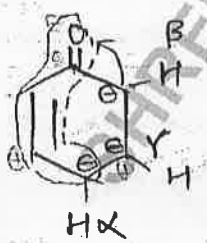
(8)



$ClO^{\ominus}$ pe -ne stable than

Stab ⇒ I > II

(9)



Stab of Anion ⇒ α > β > γ

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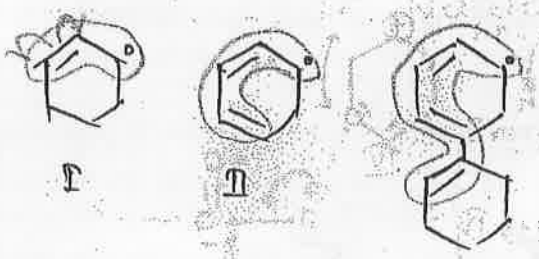
⑨



I II III

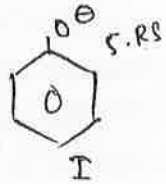
Stability ⇒ III > II > I

② Stability of anion :-

Key point

Stability of anion $\propto \frac{-M/-I}{+M/+I} \propto$ extent of Reso.

①



I

$CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}$ II 2 eq R.S

$OH^{\ominus}$ III 3.5

$C_2H_5 \xrightarrow{+I} O^{\ominus}$ IV 3.5

$NH_2^{\ominus}$ V 3.0

II > I > III > IV > V

Stab ⇒ II > I > III > IV > V

②

$Ph-\overset{\ominus}{C}H_2$

$Ph-\overset{\ominus}{C}H-Ph$

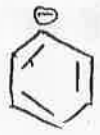
$Ph-\overset{\ominus}{C}H-Ph$ (Ph) max Res. max stable anion

Stab ⇒ III > II > I

③

$CH\equiv C^{\ominus}$ 3.25 sp

$CH_2=CH^{-}$

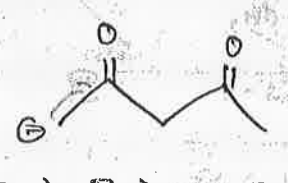


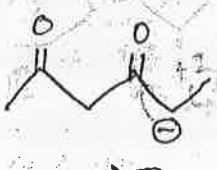
2.75 sp^2 $CH_2^{\ominus}$

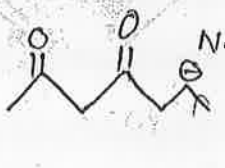
IV > Stab ⇒ I > IV > II > III

④

More ranalof H'







No reso

I > II Stab ⇒ I > II > III > IV

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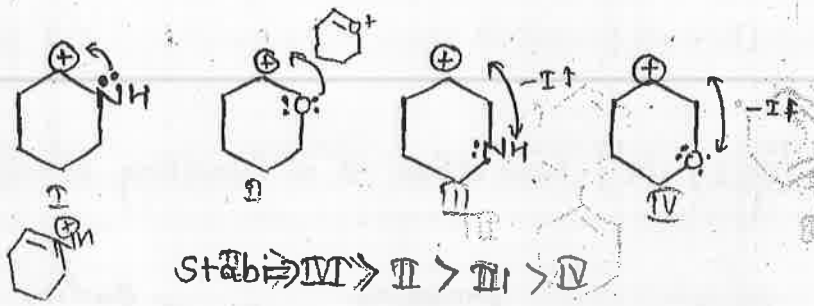
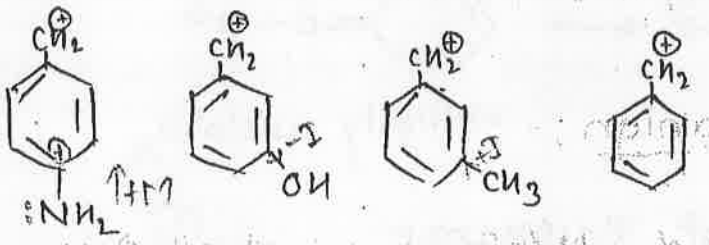
(4)



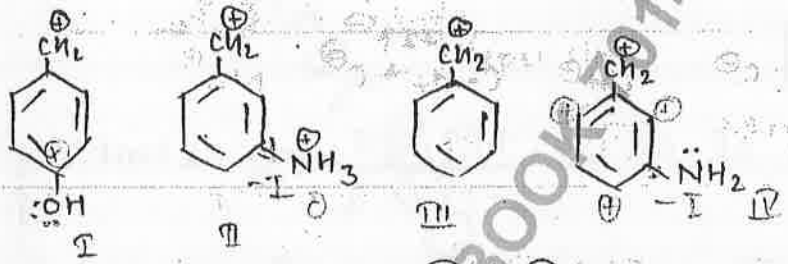
Stab ⇒ IV > II > III > I

(5)



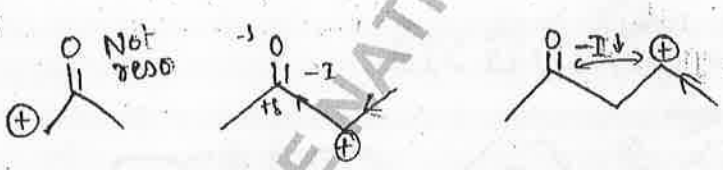
Stab ⇒ I > III > IV > II

(6)



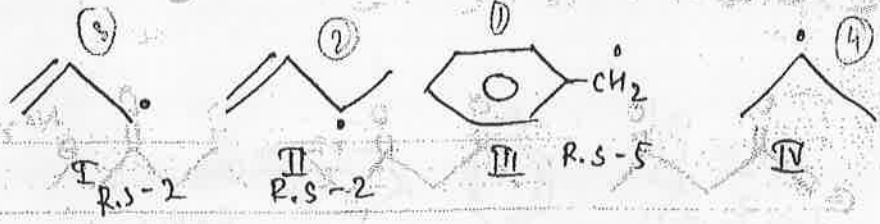
Stab ⇒ I > III > IV > II

(7)



III > II > I

(8)



III > II > I > IV

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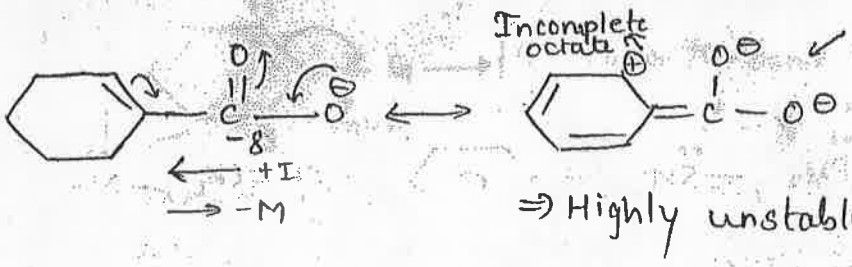
② $-\overset{O}{\overset{\|}{C}}-O^{\ominus}$ [+I/-M] Net effect ⇒ e⁻ Donating effect (+I > -M)



⇒ Highly unstable

Application of Resonance

1) Stability of $C^{\oplus}$ & $C^{\bullet}$ [Free Radical].

Key point

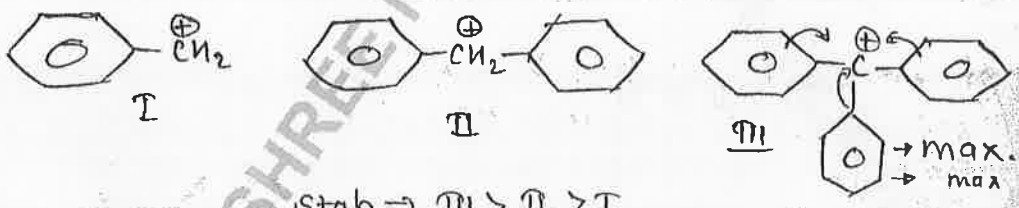
Stability of $C^{\oplus} \propto \frac{+M/+I}{-M/-I} \propto$ extent of Reso.

I)

IV > II > I > III

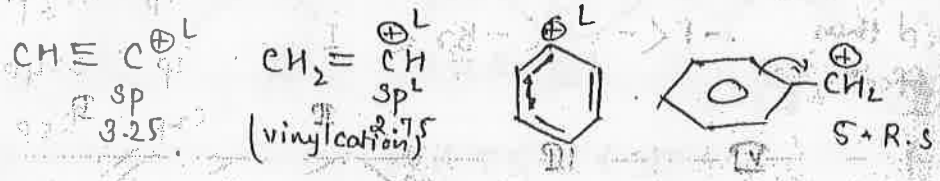
Stab ⇒ II > I > IV > III

II)



Stab ⇒ III > II > I

III)



II > Stab ⇒ IV > II > III > I

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(B)  → No vacant orbital ⇓ only -I effect

+M/-M Both → $-\ddot{P}H_2$, $-\ddot{S}H$,  , $-CH=CH_2$, $-\ddot{N}=O$ etc.

Comparision b/w Mesomeric & Inductive effect :

Generally Mesomeric effect is more effective than I-effect, but in case of two groups [halogen $[-\ddot{X}:]$, $-\overset{\overset{O}{\|}}{C}-O^{\ominus}$] I-effect is more effective then M-effect.

① $-\ddot{X}:$ [-I/+M] ⇒ Net effect ⇒ $e^{\ominus}$ withdrawing effect (-I > +M)

(A) order of -I effect ⇒ $-\underset{10000}{F} > -\underset{10000}{Cl} > -\underset{10000}{Br} > -\underset{10000}{I}$

(B) order of +M effect ⇒ $-\underset{9500}{f} > -\underset{7000}{Cl} > -\underset{3000}{Br} > -I$ C_4

(C) if Both effect (-I/+M) overlapped then net effect ⇒ ~~-f > -Cl > -Br > -I~~

$-f < -Cl < -Br < -I$

C_{2p} Cl_{3p}

C_{4p} Br_{4p}

C_{2p} I_{5p}

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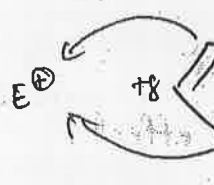
② -M/-R effects



All Polar π-bond + All vacant orbital containing grp

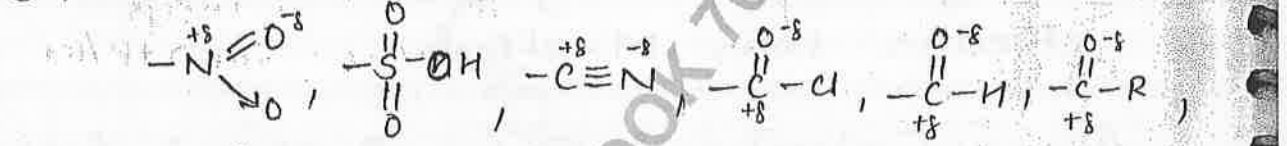
⇓

if Polar π-bond & Vacant orbital involve in Rcoo ⇒ -M/-R effect.

⇒ e-density ⇓
⇒ Deactivated ring
⇒ m-directing

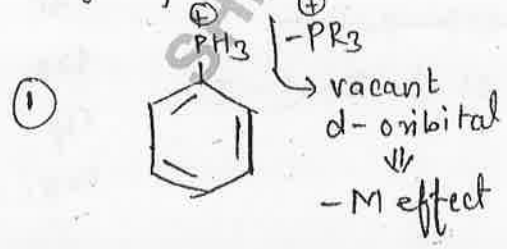
-M/-R groups:-

① polar π-bond →

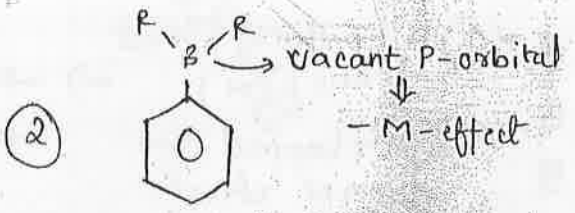


↓
Non polar π-bond (B.2F)

② Vacant orbital containing group ⇒



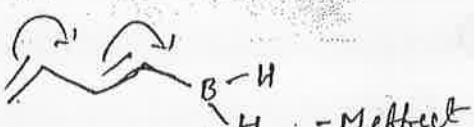
-M/-R



$B_5 \Rightarrow 1s^2\ 2s^2\ 2p^1$

G.S ⇒ ↑↓ | ↑ | ⇓

E.S ⇒ ↑↓ | ↑ | ↑ vacant p-orbital



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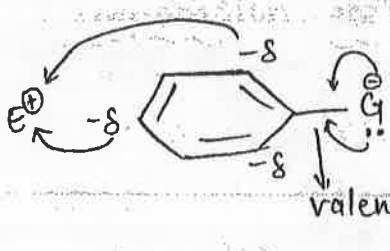
Types of Resonance / Mesomaric effect :-

① +M / +R effect → Electron relasing effect

② -M / -R effect → Electron withdrawing effect.

① +M / +R effect →



→ (All L.P containing + All -ve charge containing group)

⇓

if L.P & -ve charge involve in Reso ⇒ +R / +M

+M / +R groups ⇒

$-\overset{\ominus}{C}H_2$ (valency), $-\overset{\ominus}{N}H$, $-\overset{\ominus}{O}$, $-N(CH_3)_2$, $-\ddot{N}H-CH_3$, $-\ddot{N}H_2$, $-\ddot{O}H$, $-\ddot{O}CH_3$,

$-\ddot{N}H-\overset{O}{\overset{\|}{C}}-R$ (Exam), $-\ddot{O}-\overset{O}{\overset{\|}{C}}-R$, $-\ddot{X}:$ (All halogen) etc.

Ex.

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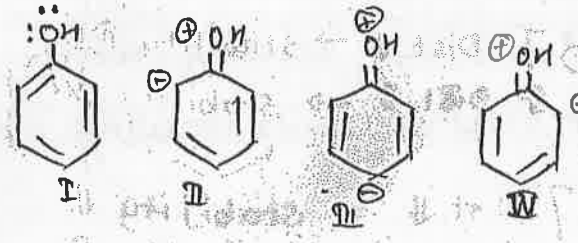
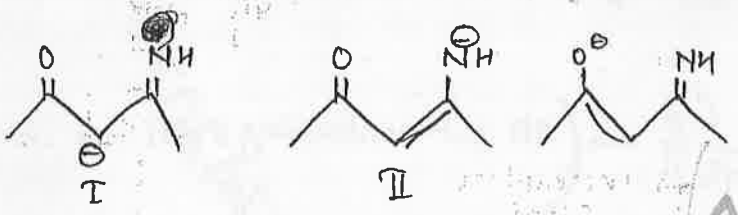
(4)



I II III IV

Stab ⇒ I > II = IV > III

(5)



I II

⇒ III > II > I

6) $CH_3 - \ddot{O} - CH = CH - CH = CH_2$

I

Dist ↓

$CH_3 - \overset{+}{O} = CH \leftarrow \overset{-}{C}H - CH = CH_2$

II

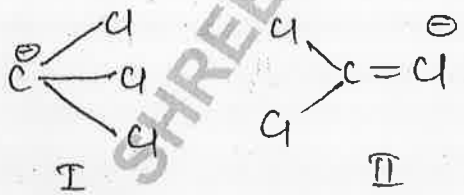
Stab ⇒ I > II > III

pist ↑

$CH_3 - \overset{+}{O} = CH - CH = CH - \overset{-}{C}H_2$

III

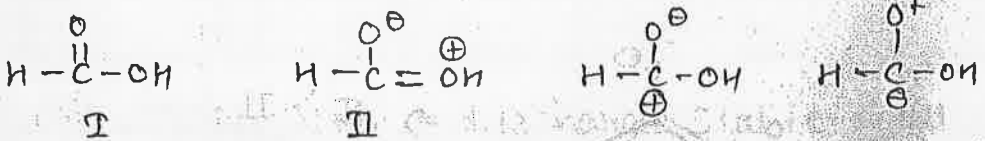
(7)



I II

Stab ⇒ ~~I > II > III~~ II > I

(8)



I II III IV

Stab ⇒ I > II > III > IV

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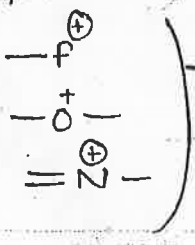
(4) Distance factor → (1) +/⊖] Dist ⇓ → stability ⇑
Dist ⇑ → stability ⇓

(2) +/+ , −/−] Dist ⇓ → stability ⇓
Dist ⇑ → stability ⇑

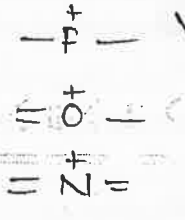
KEY POINT

(i)



→ incomplete octate ⇓ str. Not exist

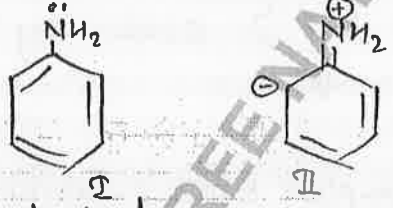
(ii)



⇒ complete octate (Formal charge) ⇓ स्टेबिलाइट

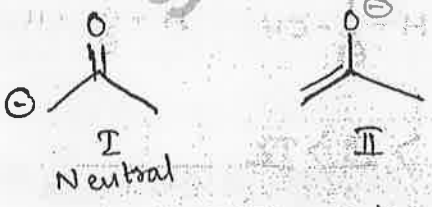
(1) $CH_2 = CH - \ddot{C}l:$ (I, Neutral) $\quad \overset{\ominus}{C}H_2 - CH = \overset{\oplus}{C}l$ (II) $\quad$ Stab ⇒ I > II

(2)



Neutral (I) (II) $\quad$ Stab ⇒ I > II

(3)



(I) Neutral (II) $\quad$ Stab ⇒ I > II

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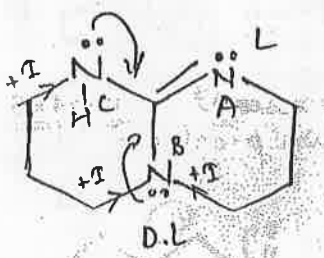
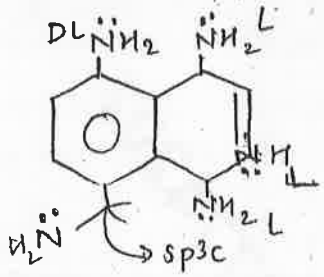
(9)

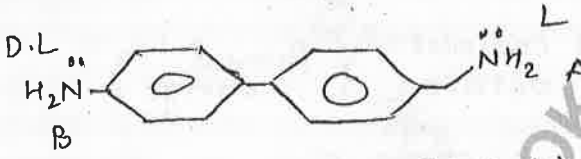


B.S ⇒ A > B > C

(10)



(11)



B.S ⇒ A > B

Stability of Resonating structure.

(1) Stability of non-polar R.S > stability of polar R.S

⇓

(2) Stability of polar R.S with complete octate > stability of polar R.S with incom octate.

⇓

(3) No. of covalent

(3) At more EN atom -ve charge stable & at less EN —11— +ve —11—

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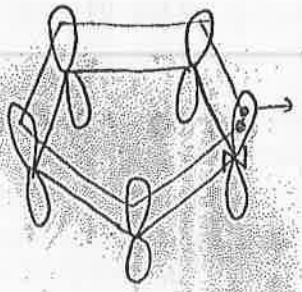
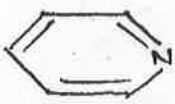
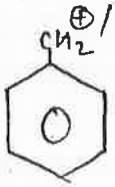
① 

Pyrole I ⇒ 

② 

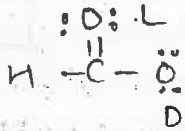
B.S ⇒ II > I

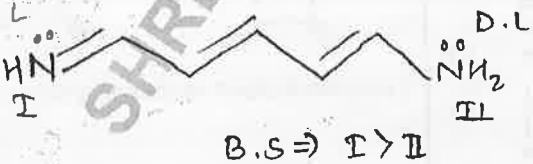
③ 
⊕/⊖/··/· ⇒ L → out of plane

④ 

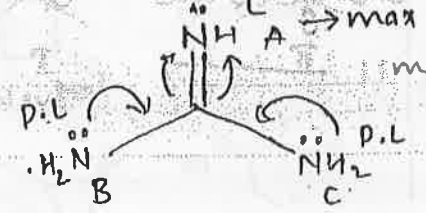
⊕/⊖/··/· ⇒ D.L

⑤ $CH_2 = \overset{\oplus}{C}H$ ⊕/⊖/··/· ⇒ L

⑥ 
⊕/⊖/··/· ⇒ D.L

⑦ 

B.S ⇒ I > II

⑧ 

→ max $e^{\ominus}$ density ↓ max. donate

(guanidine → superbase / strongest base)

B.S ⇒ A > B = C

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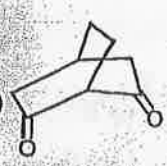
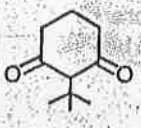
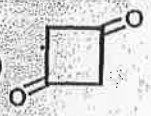
Q.3 In which of the following keto form is more dominating than enol form :

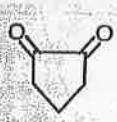
(1) 

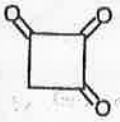
(2) 

(3) 

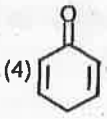
(4) All of these

Q.4 Which of the following has unstable enol form?

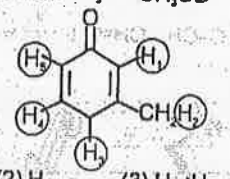
(1) 

(2) 

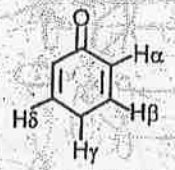
(3) 

(4) 

when it react with $CH_3O^{\ominus}/CH_3OD$



(1) H_1, H_5 (2) H_4 (3) H_3, H_2 (4) H_5, H_3

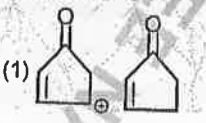
Q.7 

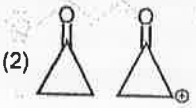
In the enolization of the given molecule, the H-atom involved is :

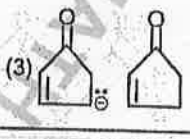
(1) δ-H (2) β-H

(3) γ-H (4) cannot be enolized

Q.8 Among the given pairs, In which pair second compound has less enol content than first compound ?

(1) 

(2) 

(3) 

(4) None of these

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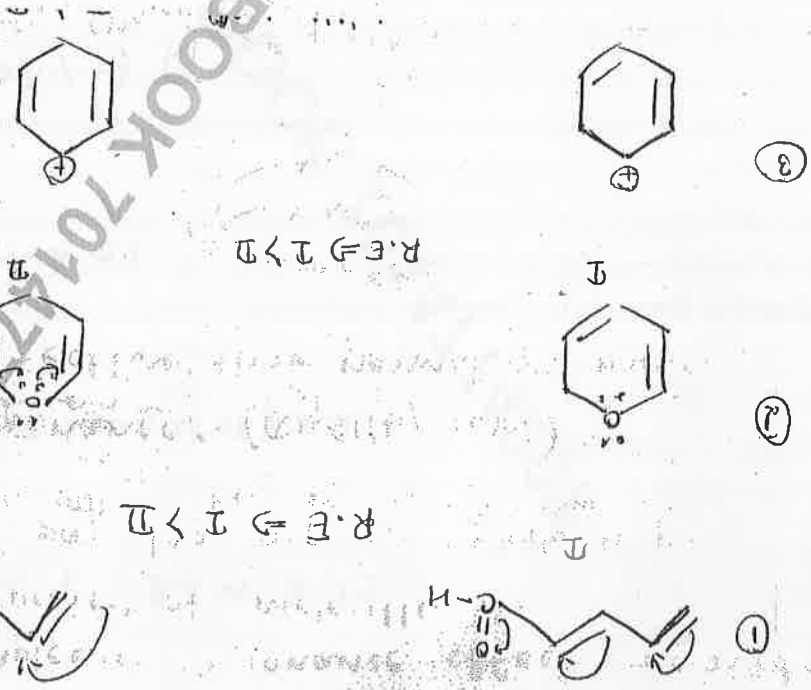
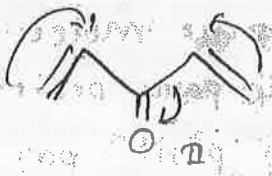


Extended Reso

cross conjugatn

① 

I



II

R.E ⇒ I > II

② 

I

II

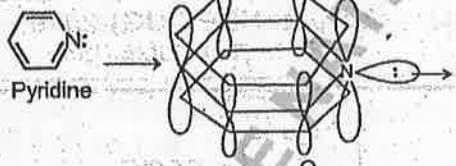
R.E ⇒ I > II

③ 

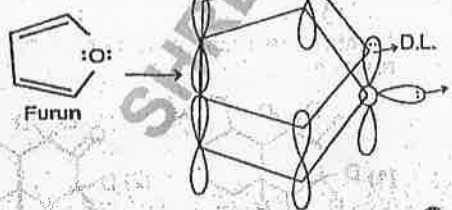
Stabilit of C⊕ ⇒ I > II

Localisied & Delocalised electron.

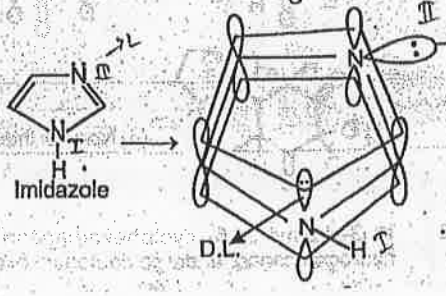
Orbital Diagram of organic compund

1. 

L.P. Localised [Out of Plane] [L.P tnt. in sp^2 hybrid orbital]

2. 

[tnt sp^2 hybrid orbital]

3. 

B.O ⇒ II > I

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KEY POINT

Phenol → charge separation
phenoxide → " distribution.

1) In linear molecular resonance effect observed at both terminal of a molecule.

2) In benzene molecule resonance effect observed at ortho, & para position of molecule

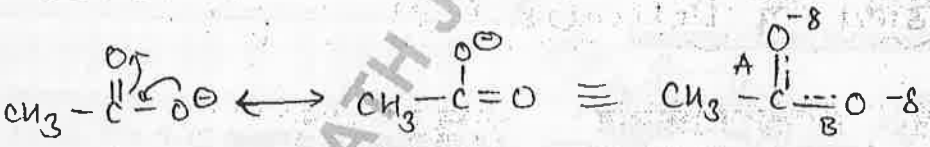
[Meta position par laga grp reso karta h para Meta position ya upar laga grp Para Uska koi effect nahi aata]

Equivalent Resonance :- (Quality reso.)

→ It more effective than normal resonance.

① $CH_3-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H^+$

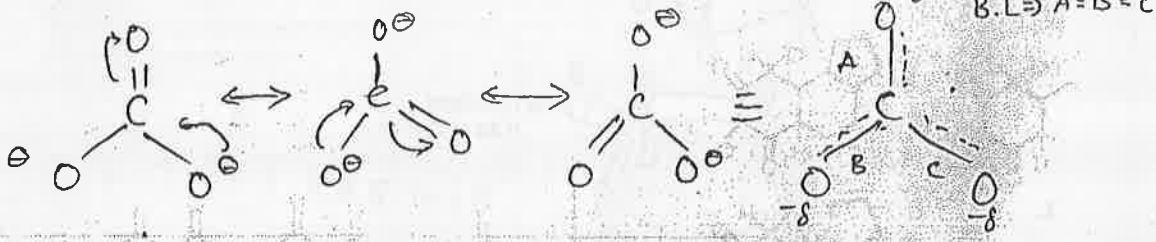
Acetic Acid — Acetate ion



R.S = 2 — hybrid

B.L ⇒ A = B

② $H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{-2}$



B.L ⇒ A = B = C

3 eq. ⇒ R.S

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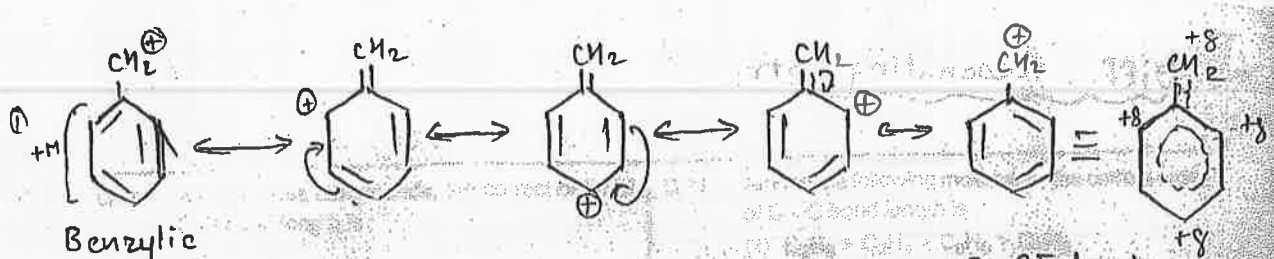
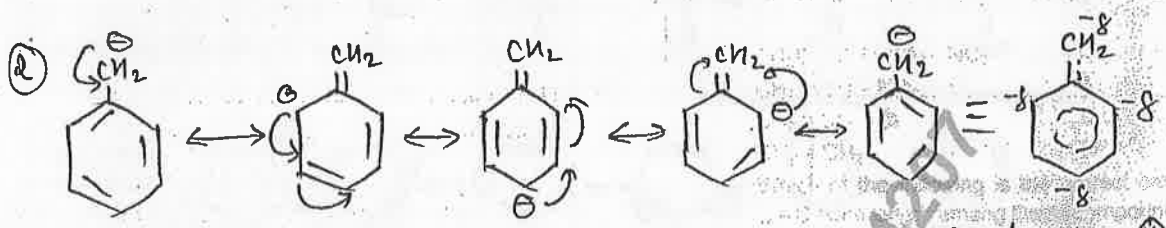
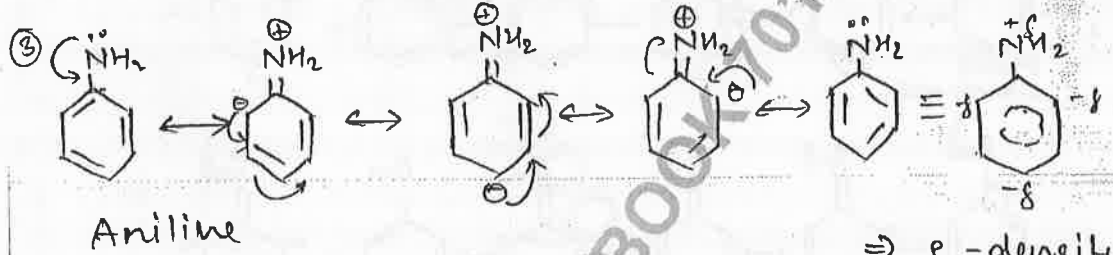


Benzylic cation

⇒ e⁻ density ⇓
⇒ Deactivated ring
⇒ m-directing

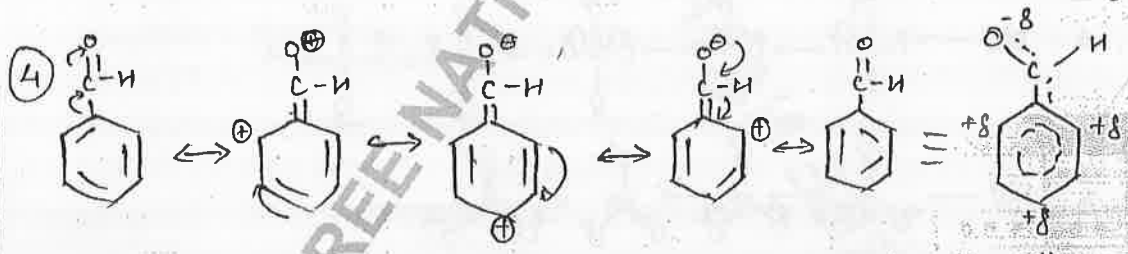


⇒ e-density ⇑
⇒ Activated Ring
⇒ o/-p-directing grp.

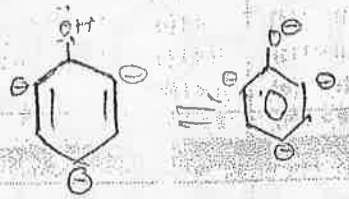


Aniline

⇒ e-density ⇑
⇒ Activated Ring
⇒ o/p directing grp.



⇒ e density ⇓
⇒ Deactivated
⇒ m-directing



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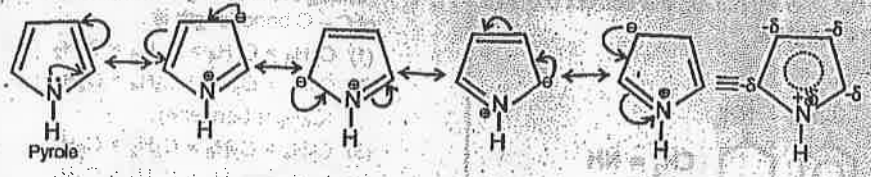
Diff. Resonating Str.

Diff. Resonating Structure :

R.S = 5

6π e⁻

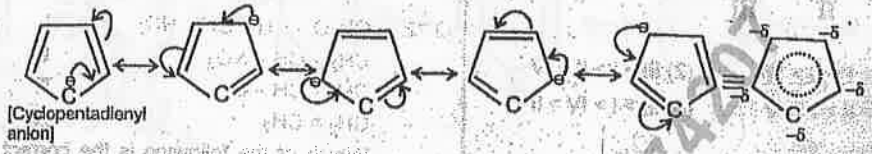
1.



Pyrole

Resonance contributors of pyrole ⇒ 5

2.

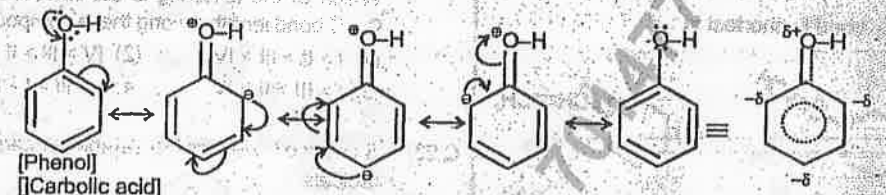


[Cyclopentadienyl anion]

4π e⁻ = 6

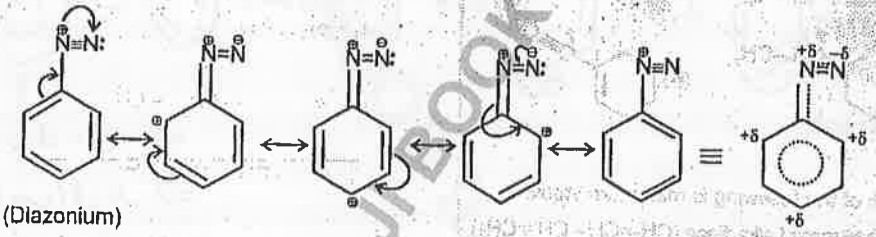
R.S = 5

3.



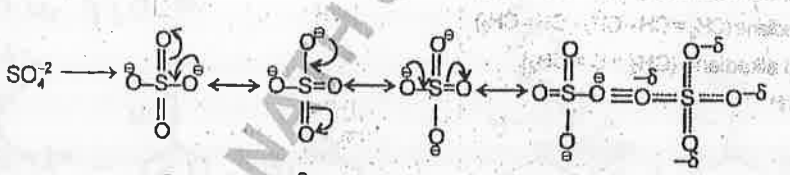
[Phenol]
[]Carbolic acid]

4.

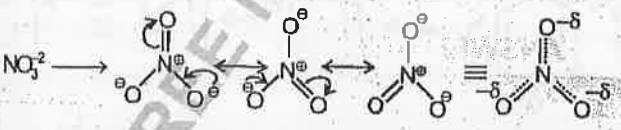


(Diazonium)

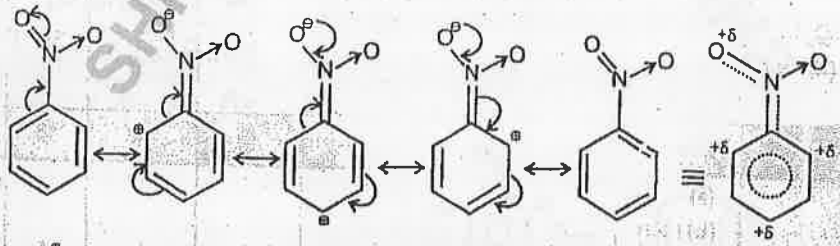
5.



6.



7.



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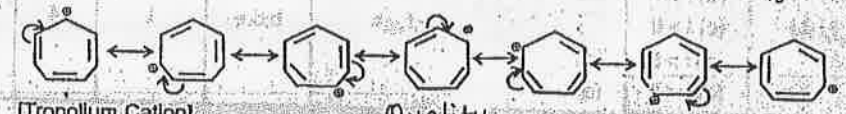

[Tropolium Cation]

Quality Reso.

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