compounds show electromeric effect only in presence of reagent.

General Organic Chemistry

Electronic displacement effects:

charges developed are permanent	charges developed are temporary
• Inductive effect (I)	• Electromeric effect
• Resonance effect (R)	• Inductomeric effect
• Hyperconjugation (C+H)	

Inductive effect: displacement of σ e's.

+I grp ← $\overset{\delta+}{C}H_3-\overset{\delta-}{Cl}$ -I grp

order of -I groups:

$-NF_3^+ > -NR_3^+ > -SR_2^+ > -NH_3^+ > -NO_2 >$
$-SO_3H > -CN > -\overset{\overset{O}{\|}}{C}-H > -\overset{\overset{O}{\|}}{C}- > -\overset{\overset{O}{\|}}{C}-OH > F$
$> -Cl > -Br > -I > -OR > -OH > -C\equiv H > -NH_2$
$> -Ph > -CH=CH_2 > H$; -I = 0

order of +I groups:

$-CH_2^{\ominus} > -NH^{\ominus} > -O^{\ominus} > -\overset{\overset{O}{\|}}{C}-O^{\ominus}$ > Alkyl grps
$> -D > -H$; +I = 0

Alkyl groups :- 3° > 2° > 1°

for the same degree: The longer the chain, ↑I

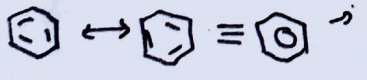
→ characteristics of I-effect:

i) I-effect is a relative effect
ii) I-effect is distance dependant.
iii) no I-effect in alkanes.

Resonance effect: delocalisation of Pi e⁻s

Resonance Hybrid.

i) canonical forms don't have real existence
Resonance hybrid is the most stable structure which actually exists.
ii) contains characteristics of all canonical forms.
iii) more stable canonical forms contribute more towards resonance hybrid.
iv) equally stable canonical forms contribute equally towards resonance hybrid.
v) more no. of resonating structures ↑ stability
vi) more is resonance energy, ↑ stability of resonance hybrid.



→ kekule structures

+R effect order:

$-CH_2^{\ominus} > -NH^{\ominus} > -O^{\ominus} > -NH_2 > -NH-R > NR_2$
$> OH > OR > -\overset{\overset{O}{\|}}{N}H-\overset{\overset{O}{\|}}{C}-CH_3 > -O-\overset{\overset{O}{\|}}{C}-CH_3 >$ 
$> -CH=CH_2 > -C\equiv C-H > -F: > -Cl: > Br: > I:$
$> -\overset{\oplus}{N}O > -N=O$

Hydrogen shows +ve (H+) electromeric effect

→ -R effect:

Identification: multiple bonds b/w atoms of different electronegativity.

$-NO_2 > -CN > SO_3H > -\overset{\overset{O}{\|}}{C}-H > -\overset{\overset{O}{\|}}{C}- > -\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$
$> -\overset{\overset{O}{\|}}{C}-OR > -\overset{\overset{O}{\|}}{C}-OH > -\overset{\overset{O}{\|}}{C}-NH_2 > -\overset{\overset{O}{\|}}{C}-O^{\ominus} >$
$C\equiv C-H > -Ph > -CH=CH_2 > -NO > -NO_2$

→ Rules for stability of resonating struc:-

i) max. no. of pi bonds max stability
ii) The structure in which octet of every atom is complete
iii) neutral structures > charged structure

→ Rules for stability of charged structures

i) opposite charges → closer
like charges → farther
ii) For elements of same period.
-ve charge is most stable on most e.n atom
For elements of same group:
-ve charge is most stable on biggest atom
iii) Linear conjugation is more stable than cross conjugation.

I → linear
II → cross.

→ Aromaticity:

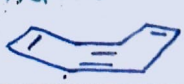
Aromatic > non-aromatic > Anti-aromatic
stable at room temp — unstable at room temp

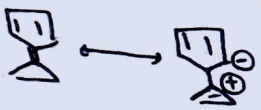
aromatic: diamagnetic
anti aromatic: paramagnetic

Aromatic	Anti-aromatic
→ cyclic	→ cyclic
→ every atom involved in delocalisation	→ every atom must be involved in delocalisation
→ planar	→ planar
→ sp^2 hyb	→ sp^2 hyb
Huckle's rule: no. of e⁻s involved in delocalisation = 4n + 2	no. of e⁻s involved in delocalisation = 4n

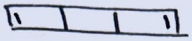
exceptions

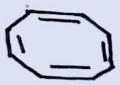

★ non-aromatic
COT → cyclo octa tetraene
· quasi-aromatic

actual structure: 
Tub shape structure

→  is rotation allowed around this bond
yes

Important reaction:

i) 2  dimerisation  non aromatic

ii)  Na →  Aromatic

→ **Annulenes**: cyclic conjugated polyenes

→  (4) Annulene →  (6)-Annulene

→  (8) Annulene →  (10)-Annulene

→  (12) Annulene → 
There is a CH_2-group which we can add due to which the CH_2 group is a little above the plane. but the compound maintains its aromaticity to a certain extent

→  or  (14)-Annulene

↑ partially aromatic due to there being significant space b/w hydrogen atoms to avoid steric hindrance to some extent

→ Hyperconjugation effect:

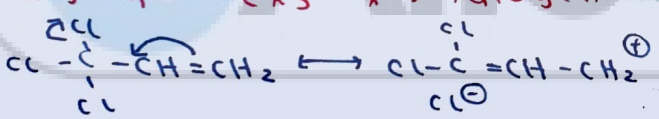
- No bond resonance → Baker-Nathan effect
→ Anchimeric effect.

sigma electrons are delocalised with multiple bonds (or e^-)

No of hyperconjugat structures = No. of α-Hydrogens

Reverse hyperconjugati

-H group ⇒ $-CX_3$ X >

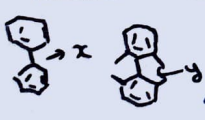


TH effect:
H > D > T

e^- releasing groups: +R > +H > +I

e^- drawing groups: -R > -H > -I

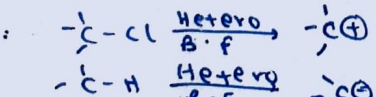
→ Steric Inhibition of Resonance:



b.l x > y. The 4 methy groups cause so much steric hindrance that the Ph-rings move to another plane so resonance doesn't take place

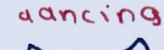
→ Intermediates:

a) Heterolytic Bond fission: 

b) Homolytic Bond fission: 

Is preferred when: → non-polar solvent → gaseous phase → high temps → presence of → presence of FRSF initiators ⇒ peroxide, O_2, $\overset{h\nu}{}$ → when e.n diff is very small.

→ Resonance and Hyperconjugation only affect ortho and meta.

→ cyclopropyl methyl carbocation  exceptionally stable due to bent p-orbital resonance or dancing resonance.

→ Heteroatom stabilised carbocation

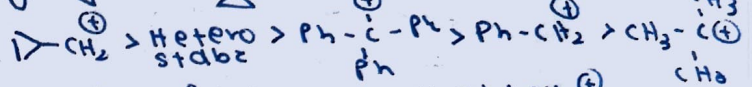
 very stable

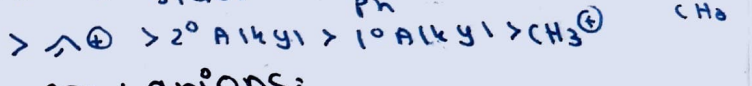
→ Bridge head carbocations:

⊕ Bredt's rule:
 According to this rule, planarity (sp2) is not possible at bridge head position of smaller bridge (bicyclic) rings (containg upto 7 atoms)

↗ not valid for fused rings.

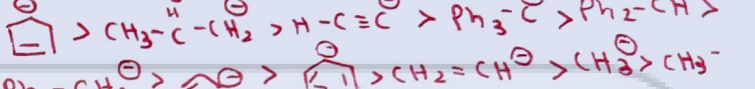
overall order:

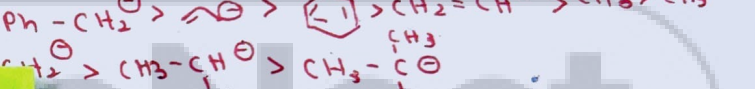


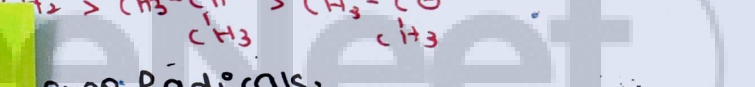


⇒ Carbanions:

EWG make more stable
ERG make less stable



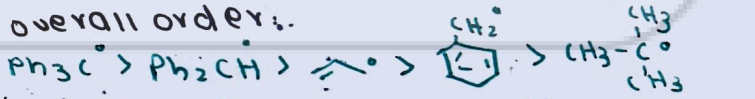




Free Radicals:

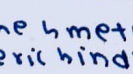
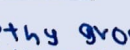
carbon atom having unpaired $e^\ominus$

overall order:



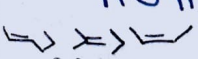
→ Stability of Alkene/Alkyne:

Stability ∝ Resonance
∝ Hyperconjugation

→  vs  → this one having only 1 sp2 hyb carbons, so ring strain is less due to having less tendency for B.A = 120° II > I

→ Heat of Hydrogenation:

HOH ∝ No. of double bonds

 (geminal) ← stability of Alkenes

 stability. III > II > I
HOH: I > II > III

Now HOH per molecule: II > III > I (experimental)
HOH per double bond: I > II > III

→ Stability of Alkanes:

For isomeric alkanes, as branching ↑ stability of alkane ↑

Heat of Combustion:

HOC ∝ 1/Stability of alkane
∝ No. of carbon atoms.

↑ first priority

Acidity of organic compounds:

- all organic compounds are weak acids

Acidity ∝ stability of C.B

E.W.G → Increase Acidity
E.R.G → decrease acidity

→ Acidity ∝ ·E·N ∝ B·L
along period, along group.

→ negative charge on more E·N atom is given more preference over stability

Note that: $CH_3-\overset{O}{\overset{\|}{C}}-OH$ >  for acidity

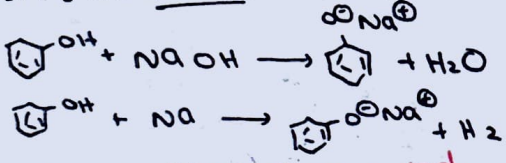
→ All alcohols are acidic in nature they react with highly electropositive metals to release H_2 gas.

→ Alcohols are neutral to litmus

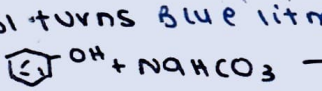
$R-OH + NaOH \longrightarrow$ no rxn
$R-OH + Na_2CO_3 \longrightarrow$ X no rxn.

except CH_3OH, all alcohols are less acidic than water.

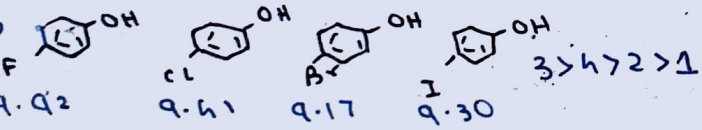
→ Acidity of Phenol:



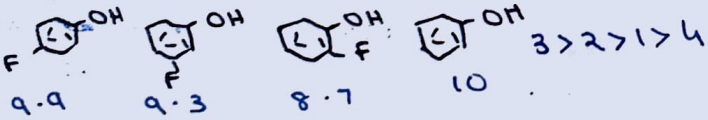
Phenol turns blue litmus red.



o-nitrophenol is less acidic than p-nitrophenol because acidic H is involved in intramolecular H-bonding.

→ 

3 > 4 > 2 > 1

→ 

3 > 2 > 1 > 4

→ carboxylic acids:

React with all 4: NaOH, Na, $NaHCO_3$, $NaNH_2$

Remember the DNP rule
Distance > Number > power for inductive effect.

→ Acidity of Benzoic acid:

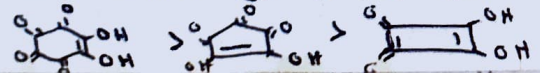
Orthoeffect:

any group present on the ortho position of benzoic acid, increases the acidity of that acid. due to S.I.R

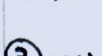
the groups CAN'T be -OH, -F (Too small)

→ Some special orders:

i) $H-\overset{O}{\overset{\|}{C}}-OH$ >  > $R-\overset{O}{\overset{\|}{C}}-OH$

ii) 

> picric acid > acetic acid

③ $CH_3-\overset{O}{\overset{\|}{C}}-(CH_2)-\overset{O}{\overset{\|}{C}}-CH_3$ >  > H_2O

↗ active meth comps

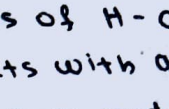
→ Rxns of $H-C\equiv C-H$

→ Reacts with all except NaOH, $NaHCO_3$

→ General order of Acidity:

react with NaOH ... dont x NaOH

sulphonic > carboxylic > Phenols > H_2O > R-OH

> C_2H_2 >  > $CH_3-\overset{O}{\overset{\|}{C}}-OH$

→ All sulphonic, carboxylic, picric acid, 2-4 dinitrophenol react with $NaHCO_3$

→ Basicity of organic compounds:

Nitrogen containing compounds behave as weak bases. $C^{1°}, 2°, 3°$ Amines

• amines behave both as lewis bases and bronsted bases

Basicity ∝ stability of C.A

In aqueous mediym:-

case-I : R-me

order of basicity: $2° > 1° > 3°$

case-II : R → any other alkyl grp

order of basicity: $2° > 3° > 1°$

In gaseous medium:

$3° > 2° > 1°$

→ Aromatic amines:

*Any aliphatic amine is more basic than a aromatic amine

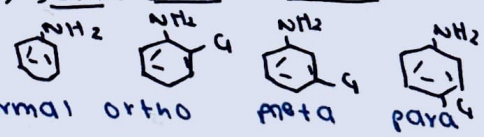
→ 

Guanidine, Amidine, Imine

Guanidine > Amidine > Imine

→ Amides are the least basic organic compounds, infact they are acidic due to stable C.B.

→ some special orders:

• 

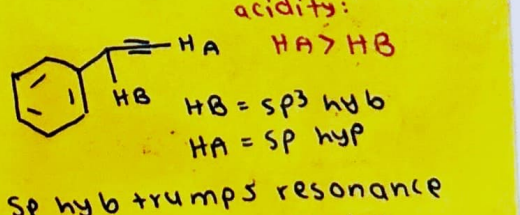
normal, ortho, meta, para

G → ome : p > m > o > m
G → OH : p > o > m > m
G → Cl : o > p > m > o

General order:

Guanidines > Amidines > aliphatic amines > Imines > aromatic amines > Amide

acidity:



HA > HB

HB = sp^3 hyb
HA = sp hyb

Sp hyb trumps resonance stabilization by a mile

for alkanes: C_nH_{2n+n}
Structural isomers: $2^{n-4}+1$

Isomerism

m: same m.F, diff S.F

i) Chain isomers → diff lengths of parent chain or ~~po~~ side chains


↗ chain isomers

ii) Position isomers → same length of parent chain and side chain but diff positions of substituents / F.G / multiple bond are called positional isomers

Chain isomerism > Position

iii) Functional Isomerism:

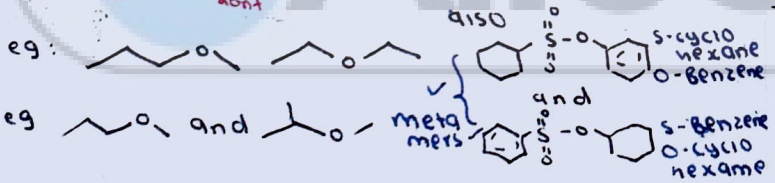
Two diff functional groups

eg:
- Alcohol and ether  & 
- Aldehydes and Ketones 
- 1°, 2°, 3° Amines and 1°, 2°, 3° Amide
- Carboxylic acids and esters
- Alkane, Alkyne, Cycloalkene
- Nitrile and Isonitrile CN & NC
- Alcohol and phenol
- Nitro and Nitrites CH_3-NO_2, $CH_3-O-N=O$

iv) Metamerism:

different types of groups around poly-valent functional group

→ Two metamers should have same F.G so they have ~~have~~ same functional isomerism.

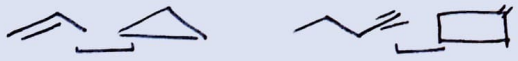
eg: 

eg

F.I > metamerism > Chain > Position

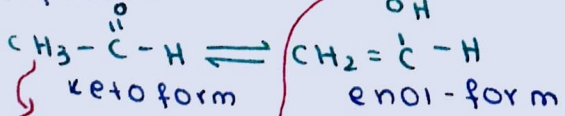
v) Chain-Ring Isomers

one → cyclic other → chain (acyclic)

eg 

vi) Tautomerism

Two tautomers are interconvertible into each other through transfer of acidic hydrogen / proton



→ i) Two tautomers are always in dynamic equilibrium with each other

ii) Tautomerism is a special case of F.I

iii) Tautomers ✗ resonating structures

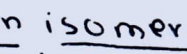
iv) Tatomer s (acidic or basic) as acid or base acts as a catalyst

v) Also known as alleloprotism / desmoprotism / Kryptomerism

Necessary conditions for Tautomerism:

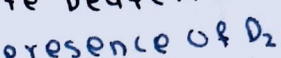
① Presence of -R group to make an acidic hydrogen

② Presence of ennolisable Hydrogen

 3 ennolisable H

note Deuterium exchange:

In presence of D_2O/OD^-, all ennolisable H are converted to deuterium



→ Stability of enol form:

generally keto > enol

% enol content ∝ stability of enol ← Aromaticity, Intramolecular H-bonding, Resonance

∝ Acidity of H

∝ 1/Polarity of keto: more polar solvent enol: less polar

% enol content order:

β-diketo comps with aromatic rings > β-diketo comps w/o aromatic rings > β-keto ester > β-di keto ester > normal aldehydes and ketones

→ Degree of unsaturation:

no. of bonds that need to be broken to convert a compound into a fully saturated compound (open chain, all single bonds)

→ for alkenes, alkynes

eg $C_6H_6 \rightarrow C_6H_{14}$ $\frac{14-6}{2} = 4$ ⇒ dou

→ for C-15 elements in comps

$C_5H_5N \rightarrow C_5H_{11}$ C_5H_{12} $\frac{12-4}{2} = 4$

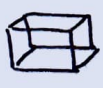
→ for C-16 elements in comps

$C_5H_5O \rightarrow C_5H_{11}$ $C_5H_{12}O$ $\frac{12-4}{2} = 3$

→ for C-17 elements in comps

$C_4H_5Cl \rightarrow C_4H_6$ C_4H_{10} $\frac{10-6}{2} = 2$

→ special cases:

→ Cubane:  C_8H_8 C_8H_{18} d.o.u = 5

→ Prismane:  C_6H_6 C_6H_{14} d.o.u = 4

→ Stereoisomerism:

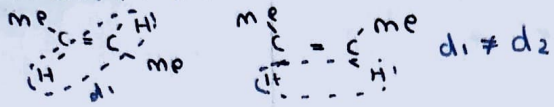
Phenomenon of compounds having same m.F and S.F, but differ due orientation of atoms in space

stereoisomers
- configurational
  - geometrical isomers
  - optical isomers
- conformations (↺)

Configurational	Conformational
• Two of these can be interconverted (rotation around pi X)	• Two of these can be interconverted (rotation around σ ✓)
• These can be seperated from each other	• These can't be seperated from each other

→ Geometrical Isomerism:

* distance blw two same groups in two G.I is different.



Rotation may be restricted due to:

① when there is multiple bond
② when single bond is part of ring

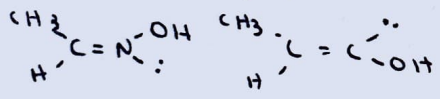
∴ show G.I rotation of bond in ring causes it to become distorted.

1) G.I in alkenes:

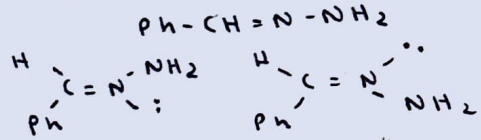
a) Restricted rotation
b) dist blw two same grp → diff
c) two groups on each double bonded carbon must be diff.

2) G.I in compounds containing C=N

a) oximes : $CH_3-CH_2-CH=N-OH$



b) Hydrazones

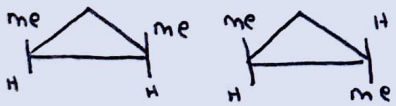


c) similarly with Imines ($CH_3-HC=NH$)

d) AZO comps ($C-N=N-$) (i.p show G.I)

3) G.I in cycloalkane

a) altleast two sp^3-C in ring
b) two o diff groups on each sp_3-C
c) distance criteria



4) G.I in cycloalkenes

C_3-C_4	only cis	no trans
C_8-C_{11}	Both cis+trans	cis > trans
C_{12} - Higher	Both cis+trans	trans > cis

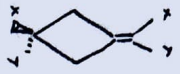
5) G.I in cumulenes

i) odd no. of d.b
ii) Two groups on terminal carbon ⇒ diff
iii) distance criterior.

6) G.I in spirocyclic compounds

i) odd no. of rings
ii) diff groups on each terminal carbon.
iii) distance criterion

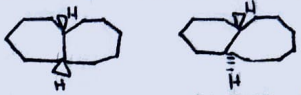
8) G.I in cycloalkylidenes



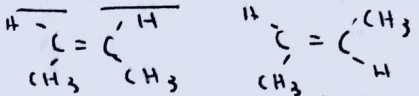
i) ring + d.b = odd
ii) diff groups on each term C.
iii) distance criterion

9) G.I in bicyclic compounds

→ each ring should atleast have 5 carbon



→ cis-trans nomenclature



→ Syn-Anti nomenclature:

(oximes, hydrazone, azo)

Oximes

Aldoxime: $R-C(H)=N-OH$ — Ketoxime: $R-C(R)=N-OH$

H-OH on same → syn
H-OH on diff → anti

→ E-Z nomenclature:

two priority groups on same side → Z
two priority groups on opp side → E

C.I.P rules:

① Atoms having higher atomic number gets ↑ priority
② same with isotopes
③ In case of double bond, move to the next atom until difference is obtained.
③ double bonded and triple bonded atoms are duplicated and triplicated
④ B.P > L.P
⑤ Z is given more priority in locants

Pseudo geometric Centre:

both groups on side of carbon are structurally same, but not stereochemically

→ No. of G.I:

case 1: molecule is not divisible in two part

no. of G.I = 2^n n = no. of geometric centre

case II: molecule is divisible in two parts

a) n = even → $2^{n-1} + 2^{\frac{n}{2}-1}$
b) n = odd → $2^{n-1} + 2^{\frac{n-1}{2}}$

Physical properties of G.I:

- Two d G.I are diastereomers of each other.
  ↳ not mirror images
- Two diastereomers have diff physical properties.

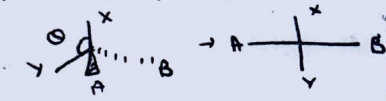
cis has more dipole moment than trans.

→ 3-D Representation of Organic comps:

i) Flying-wedge Representation:

out of the plane ← H–C···H → into the plane

ii) Fischer projection:



⊖ → on left solid wedge : left dashed : right
⊖ → on right solid wedge : right dashed : left

→ R-S Nomenclature:

a) Fischer : • assign priority based on C.I.P

4th priority on vertical line : 1→2→3 ⇒ a.c.ω → S
1→2→3 ⇒ ξ.ω (cc) → R

4th priority on Horizontal : 1→2→3 ⇒ a.c.ω → R
1→2→3 ⇒ ξ.ω (cs) → S

b) Flying Wedge:

4-B ⇒ ⊕ 3-B ⇒ ⊖ 2-B ⇒ ⊕ 1-B ⇒ ⊖
4-F ⇒ ⊖ 3-F ⇒ ⊕ 2-F ⇒ ⊖ 1-F ⇒ ⊕

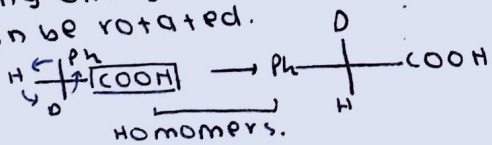
⊕ 1→2→3 ⇒ clockwise → R
1→2→3 ⇒ anti c.ω → S

⊖ 1→2→3 ⇒ clockwise → S
1→2→3 ⇒ anti c.ω → R

→ Rules for Handling fischer projection:

1) Rotating 180° in plane → homomers.
180° out of plane } stereoisomers
90° rotation }

2) Keeping one group constant, other 3 groups can be rotated.



→ Optical Isomerism:

optically active comp : compound which is capable of rotating plane of a plane polarised light.

Rotating plane towards Right : Dextrorotatory
Left : Laevorotatory

→ ⊖ depends on:

i) Length of tube : ⊖ ∝ l $[\alpha] = \frac{\ominus}{c \cdot l}$ | ⊖ = degree, l = d.m, c = g/ml

ii) Conc of soln : ⊖ ∝ c

$[\alpha]_D^{20}$ → 20 → temp (°C)
→ specific rotation
→ deuterium lamp

Stereoisomers which are non-superimposable m.I → enantiomers

mixture containing 2 enantiomers in equal amt :- racemic mix → optically inactive

→ Elements of symmetry:

Plane of symmetry : plane dividing molecule in two equal halves

Centre of symmetry :

C.O.S ⇒ 1

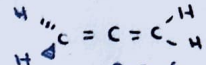
Chiral centre : Any atom attached to 4 diff groups.

Chiral molecule : • optically active
• non-superimposable over mirror image
• not elements of symmetry
• Resolvable

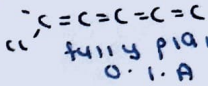
molecule having a chiral centre is not always chiral.

Optical activity in comps w/o chiral centre

a) Allenes/Cumulenes

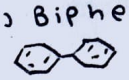


two P.O.S
0.I.A

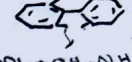


fully planar ∴ 1 P.O.S
0.I.A

b) Biphenyl comps



P.O.S ✓
0.I.A



Benzene goes out of plane due to S.H
∴ 0.A
not → OH, NH₂ (not bulky)

→ Calculation of no. of stereoisomers.

case I : not div into two halfs ∴ 2^n n = no. of S.C (C.C + O.C)

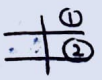
case I : div into two halves
- n = even → 2^{n-1} ✓
- n = odd : Pseudo centre ⇒ $2^{n-1} + 2^{\frac{n-1}{2}}$
- n = odd : Pseudo centre ✗ ⇒ 2^{n-1}

Pseudo chiral centre : ⓡ-C(a,b,c)-ⓢ

→ Enantiomeric excess :

$\frac{n(+) - n(-)}{n(+) + n(-)} \times 100\%$

eg: ⊕ enan = 20% rest 80% → Racemic
∴ ⊕ = 60% ⊖ = 40%



for enantiomers → completely opposite R,S

for diastereomers → one opp R,S

*In fischer projection:
always check : Horizontal P.O.S.

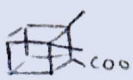
→ Properties of Enantiomers:

I) Physical properties:
Two enantiomers have similar physical properties, except direction of rotation of plane of ppl.

II) Chemical properties:
enantiomers show:
similar chemical interaction towards :- Achiral substance
different towards, Chiral substance

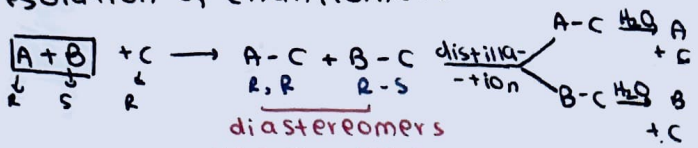
→ for rigid structures (exception)

despite having n = 2, Theoretically only its m.I and itself exists
$2^2 = 4$
∴ no. of S.I = 3



→ only 2 isomers (

Resolution of Enantiomers:



R S R

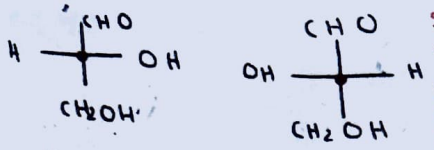
R, R R-S

diastereomers

diff physical properties

→ D, L configuration:

a) Reference comp: Glyceraldehyde

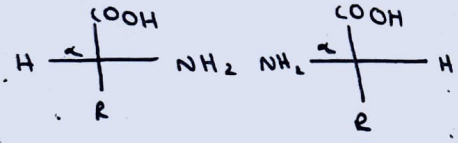


start from CHO and end at CH_2OH look at last chiral centre in line from CHO to CH_2OH

if OH lies Right to last chiral centre → D

if OH lies to left chiral centre → L

b) Reference: Amino acid

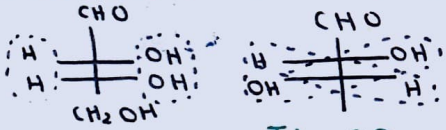


if NH_2 lies right to α → D

if NH_2 lies left to α → L

→ Erythro-Threo configuration:

used only for fischer proj.

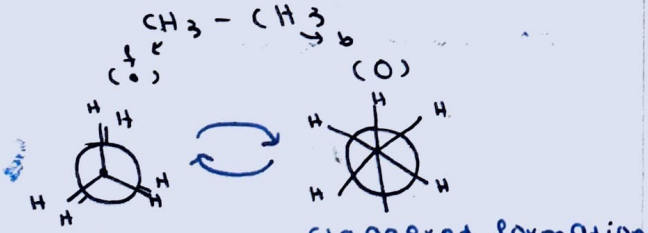


Erythro Threo

→ Conformational Isomerism:

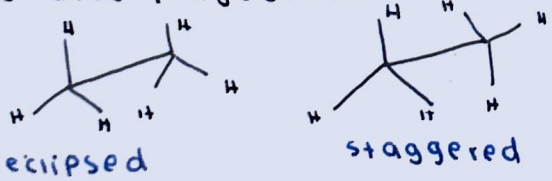
Two stereoisomers which can be turned into each other by rotation around C-C single bond are called conformers.

Newman projection



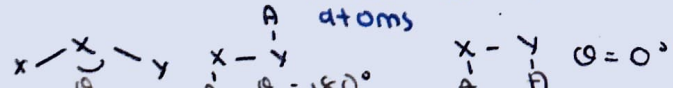
eclipsed formation — staggered formation

Sawhorse projection



eclipsed — staggered

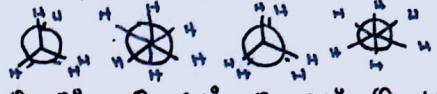
→ Dihedral angle: angle blw two bonds present on adjacent atoms



Stability of conformers depends on:

i) Torsional strain
ii) Steric hindrance
iii) Intramolecular H-bonding
iv) Gauche effect
v) Anomeric effect

→ Conformers of Ethane:

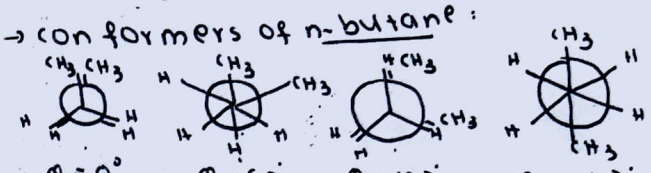


θ = 0° (e) θ = 60° (s) θ = 120° (e) θ = 180° (s)

→ All intermediate conformers → skew
→ There can be infinite conformers for a compound.

Stability: s > e

→ Conformers of n-butane:



θ = 0° fully eclipsed/syn-periplanner

θ = 60° Gauche/Anticlinar

θ = 120° partially eclipsed syn-clinar

θ = 180° fully staggered or anti-periplanar

Stability: IV > II > III > I

→ Conformers of Ethylene Glycol:

Gauche is most stable due to intramolecular H-bonding.

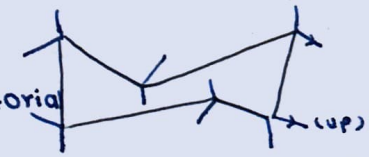
→ Conformers of cyclohexane:

chair Boat Twist boat

Stability: chair > twist > boat

→ Chair form:

vertical: axial
slanting: equatorial



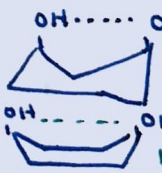
if two groups going up/down → cis
one is going up, the other down → trans

Ring flipping: any bulky group is preferred at an equatorial position

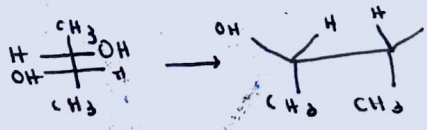
exceptions:

1,3 diol cyclohexane — cis > trans

1,4 diol cyclohexane — exists in boat form



→ Interconversion of Newman/Saw-horse to fischer:



→ keep ends down
→ keep H_2OH on respective sides

By default make eclipsed.

Then convert sawhorse to newman

Seperation Techniques

The purity of a compound is ascertained by determining its melting or boiling point most pure compounds have sharp melting and boiling points.

→ Crystallisation:

→ most commonly used
→ Based on difference in solubilities in a solvent
→ The impure comp is dissolved in a solvent in which it is sparingly soluble at room temp but appreciably soluble at high temp.
→ The solution is concentrated and cooled, pure compound crystallises out.

Impurities which impart colour to the soln are removed by adsorbing over activated charcoal. Repeated crystallisation is nessary for comparable solubilities

→ Distillation: used for:

i) volatile liquids from non-volatile imp.
ii) sufficient diff in boiling point

Chloroform and anilline

→ Fractional Distillation

→ not sufficient diff in b.p.t

Fractionating column: provides many surfa-ces for heat exchange b/w the ascending vapours and the descending condensed liq.

Each successive condensation and vaporisation unit in the fractionating column is called theoretical plate.

Crude oil in petroleum industry

→ Distillation under reduced pressure:

→ very high boiling points
→ which decompose at or below their bpt.

* A liquid boils at a temperature at which its vapour pressure is equal to external pressure.

Glycerol can be seperated from spent-lye in soap industry

→ Steam Distillation:

→ steam volatile and are immiscible with water.
→ The liquid boils when pressure due to organic liquid (p_1) and that due to water p_2) i.e $P = p_1 + p_2$ since p_1 is lower than p_2, the organic liq vapourised at lower temp than its b.p.t

Aniline from Aniline water mix

→ Differential Extraction

When an organic compound is present in an aqueous medium, it is seperated by shaking with an organic solvent in which is is more soluble than water.

Chromatography:

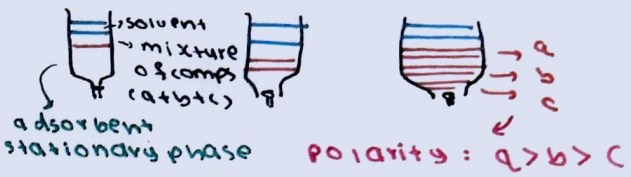
→ first used for seperation of coloured substances found in plants.

Adsorption chromatography:

diff comps are adsorbed on an adsorbent to diff degreers.
commonly used adsorbents: silica gel and alumina

column chromatography:

column of adsorbent: stationary phase



Thin layer Chromatography:

R_f = Distance moved by substance from base line (x) / Distance moved by solvent from base line (y)

Partition Chromatography:

↳ paper chromatography

•water trapped in chromatography paper acts as a stationary phase
•solvent acts as a mobile phase
→ used for isolating non-volatile mix.

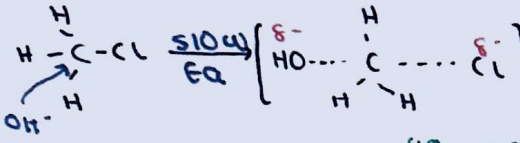
Reaction Mechanisms

→ Aliphatic Nucleophilic Substitution:

$CH_3Cl + OH^{\ominus} \xrightarrow{\text{substitution}} CH_3OH + Cl^{\ominus}$

Aliphatic $Nu^{\ominus}$

i) S_N2 mechanism: Substitution nucleophillic bimolecular



Rate of S_N2 ∝ 1/steric hindrance

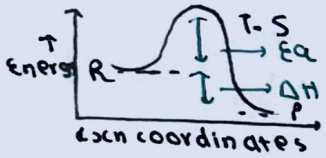
Slow process :- R.D.S → Rate determining step.

ultimately decides the rate of the rxn

Rate : $k[CH_3-Cl]^1[OH^-]^1$ overall order: 1+1 = 2

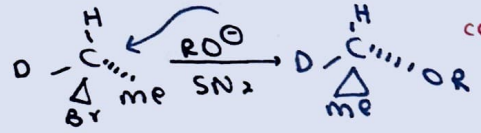
- one step process
- concerted reaction

→ Potential energy diagram:



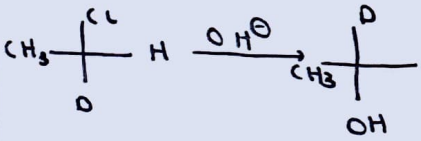
since $Nu^{\ominus}$ atks from behind, it has opposite configuration of reactant

⇒ Inversion of config.



config from R → S

when L.G at head



→ convert L.G for attacking group

→ flip groups at ends

ii) S_N1 mechanism

steps:

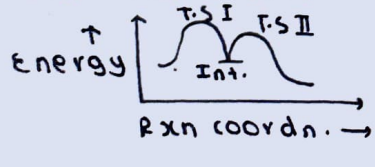
i) carbocation formed in presence of polar protic solvent RDS

ii) $Nu^{\ominus}$ atks on carbocation fast

Rate ∝ $[R-X]^1$

order = 1 = unimolecular = S_N1

more than 1 step → non-concerted.



→ Two enantiomers are formed

∴ S_N1 proceeds with racemisation

However it isn't 100% racemisation inversion product is formed more

Amount of racemisation ∝ stability of carbocation

Rate of S_N1 rxn ∝ 1/stability of $C^{\oplus}$

Rate of S_N1 and S_N2 both:

∝ Leaving group ability

L.G.A ∝ Acidity of C.A ∝ stability of -ve charge

→ Allylic, Benzylic :- ✓ S_N1 ✓ S_N2

→ Rate of S_N2 ∝ E.W.G groups

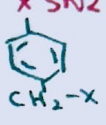
Rate of S_N1 ∝ E.R.G groups

→ Vinylic, Arylic :- ✗ S_N1 ✗ S_N2

→ Bridged Bicyclic :- ✗ S_N1 ✗ S_N2

overall order:

→ neo pentyl carbon: ✗ S_N1 ✗ S_N2



$NO_2-CH_2-X > CN-CH_2-X > R-\overset{O}{\overset{\|}{C}}-CH_2-X >$ $> X > CH_2-X > 1^{\circ} > 2^{\circ} > 3^{\circ}$

→ Reaction of Alcohol with HX:

$R-OH + HX \longrightarrow R-X + H_2O$

S_N1 → 2°, 3° Alc

S_N2 → 1° Alc (reacts by both)

Reactivity order :- Acid: HI > HBr > HCl

Alcohol: 3° > 2° > 1°

Reaction of 1° alcohol with conc HCl requires a reagent

$ZnCl_2$ + conc HCl → Lucas reagent

↓ know as Grooves process

Alcohol + $\xrightarrow[\text{conc HCl}]{ZnCl_2}$ Alkyl Chloride (Turbidity)

3° Alcohol - Immediate turbidity

2° Alcohol - slowly but without Heat

1° Alcohol - no turbidity without heat

in rxn of HBr and HI, The acids are generated Insitu.

$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$

$KI + H_3PO_4 \rightarrow KH_2PO_4 + HI$

→ Williamson Ether Synthesis

Alkyl halide + sodium Alkoxide → Ether + Sodium Halide

$R-X + Na^{\oplus}O^{\ominus}R \longrightarrow R-O-R + NaX$

→ Reaction of Alcohol with $SOCl_2$:

$R-OH + SOCl_2 \longrightarrow R-Cl + SO_2\uparrow + HCl\uparrow$

thionyl chloride

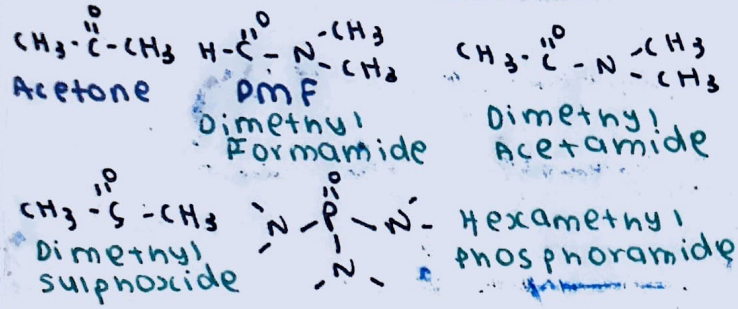
In absence of pyridine :- Retention of configuration

In presence of pyridine: Inversion of configuration

→ polar solvents

- polar protic: H attached to highly E.N atom
- polar aprotic: H is not attached to highly E.N atom

some polar aprotic solvents:



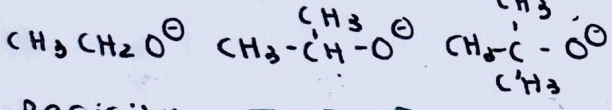
S_N1 → polar protic solvent
S_N2 → polar aprotic solvent

→ Nucleophilicity and Basicity

$OH^\ominus$ — atk on carbon → Nucleophile; atk on acidic H → Base

- -vely charge species are better nucleophile and better bases
- for the same donor atom, order of basicity and nucleophility is the same

exception:



Basicity: III > II > I
Nucleophilicity: I > II > III (steric hindrance)

→ Nucleophility along grp depends on solvent

→ polar protic: B → $F^- > Cl^- > Br^- > I^-$
N → $I^- > Br^- > Cl^- > F^-$

→ polar aprotic: B = N → $F^- > Cl^- > Br^- > I^-$

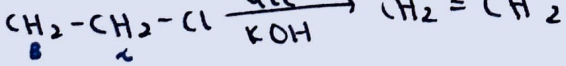
Remember:

$R-X + NaCN \rightarrow R-CN$
$R-X + AgCN \rightarrow R-NC$
$R-X + NaNO_2 \rightarrow R-O-N=O$
$R-X + AgNO_2 \rightarrow R-NO_2$

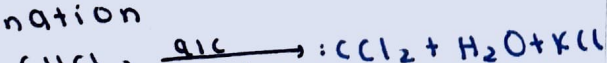
Ag has a highy affinity for X ★.

→ Elimination Reactions:

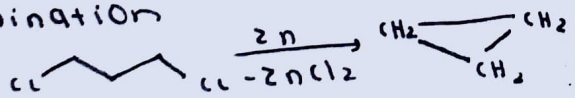
β-elimination



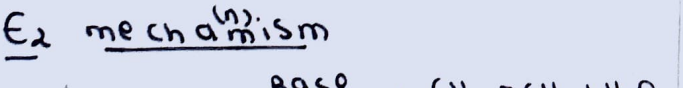
α-elimination

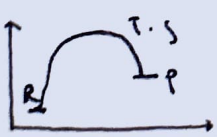


γ-elimination



→ E_2 mechanism





→ one step process
→ order: 2 (Bimolecular)

Hammond-Leffler postulate:
since T.S is closer to product in energy, the stability of T.S will depend on stability of product.

Saytzeff Rule:
alkene having more β-H is formed more as a product

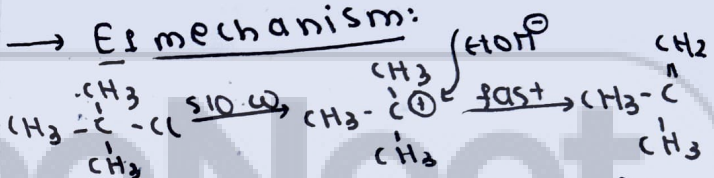
Hoffmann Elimination:
Rxns not following saytzeff rule
when: • poor L.G is present
• attacking base is bulky
• steric hindrance at β-carbon

→ stereochemistry:
Stereospecific: rxns in which stereochem of reactants defines the product.
for eg. E_2 reaction → anti elimination

K.I.E :- C-H bonds are easier to break than C-D bonds, so the one with C-H is faster. This is Kinetic Isotropic effect
Zaitseff > K.I.E

CAT cis→anti →Threo TAE Trans→anti →erythro

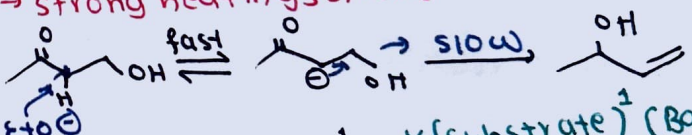
→ E_1 mechanism:



Reactivity order: 3° R-X > 2° R-X > 1° R-X

→ E_1CB mechanism:

→ presence of -M group KIE not possible
→ β-H → highly acidic
→ poor L.G should be present
→ strong heating, strong base.



Rate :- $K[C \cdot B]^1 \rightarrow K[\text{substrate}]^1[\text{Base}]^1$

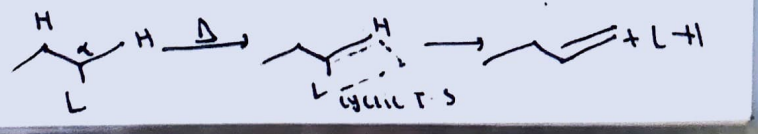
E_1, E_1CB → non-stereospecific
E_1, E_1CB → stereoselective

→ Ei: Elimination Intramolecular

→ β-elimination
→ occurs in presence of specific L.G

L.G :- $-O-\overset{O}{\overset{\|}{C}}-R$ (ester)
$-O-\overset{S}{\overset{\|}{C}}-SR$ (xanthate ester)
$-\overset{R}{\overset{R}{N^\oplus}}-R$ (amine oxide)

→ no base → only heating → stereospecific (syn)
→ T.S is Syn periplanner → Hoffmann product



Dehydration of Alcohols:

$CH_2-CH_2-OH \longrightarrow CH_2=CH_2$

i) dehydrating agent and Δ

conc H_2SO_4, Δ / H_3PO_4 — E_1 → carbocation rearrangement → saytzeff

Al_2O_3, Δ — E_2 → no rearrang

P_2O_5, Δ → saytzeff

ThO_2, Δ — E_2 → no rearrang.

WO_2, Δ → Hoffmann

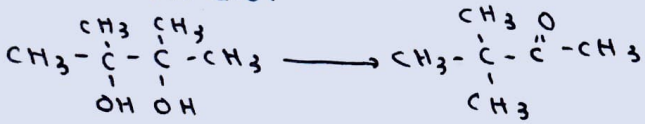
Denalogenation of Vic-dinalide:

i) Zn, Δ
ii) NaI, acetone

→ E_2 elimination
→ Anti elimination

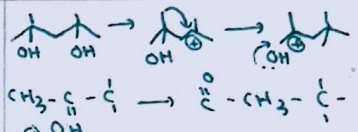
Pinacol-Pinacolone rearrangement

→ vic-diol

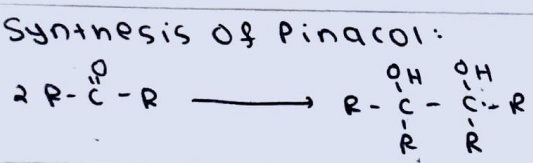


i) conc H_2SO_4

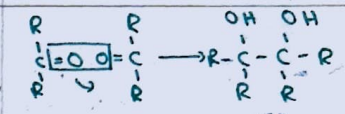
migratory apt:- -Ph > -H > $-CH_3$



Synthesis of Pinacol:

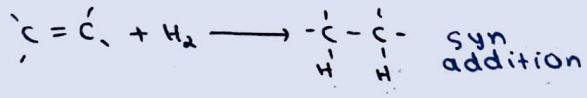


i) mg-Hg
ii) H_2O / H^+



Reduction: CO_2 → carboxylic acids → Aldehydes/Ketones → Alcohols → Hydrocarbons

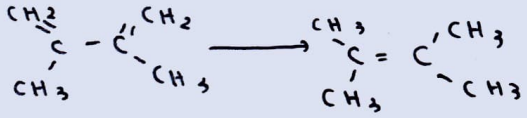
Catalytic hydrogenation of Alkenes:



i) Raney-Ni (Sabatier-Senderensrix)
ii) Pd / Pt
iii) $Pt O_2$ → Adam's catal-
iv) $(PPh_3)_3RhCl$ wilkinson's catalyst

Reactivity of alkene in catalytic hydrogenation ∝ 1 / no. of α-H

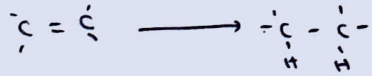
Hydrogenation of conjugated di-enes



i) H_2 (1 eq) / Pt
(more than 1 eq will cause normal hydrogenation)

Bring the double bond in middle.

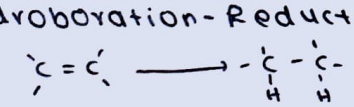
Diimide Reduction (Transfer hydrogenation)



$NH_2-NH_2 + H_2O_2 \rightarrow NH=NH$ → diimide

syn-addition

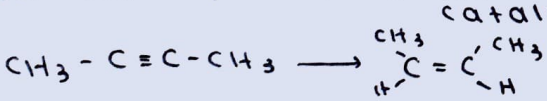
Hydroboration-Reduction



Diborane + THF (Tetra hydrofuran) + Acetic acid (step 2)

syn-addition

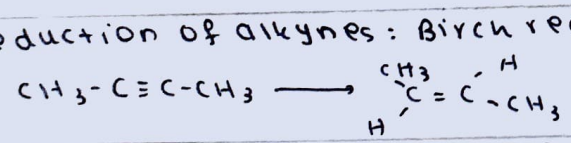
Reduction of Alkynes: Lindlar's catalyst



poisoned palladium catalyst
Pd + $BaSO_4$ / $CaCO_3$ / C / Sulphur / Isoquinoline

Cis-alkene

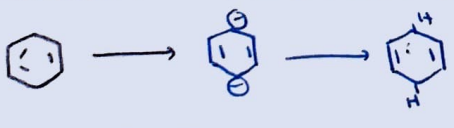
Reduction of alkynes: Birch reduction



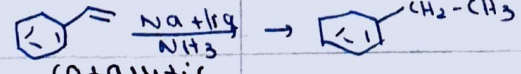
Na / Li + Liq NH_3

- trans-alkene
- Terminal alkynes can't be reduced by this.

Reduction of aromatic comps: Birch



i) Na + liq NH_3
ii) NH_3



put two out of three d.b opp to each other and -ve charge on opp sides

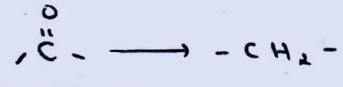
Reduction of Aromatic comps:- catalytic Hydrogenation

H_2 + Ni

very vigorous conditions req.

Reduction of Aldehyde/Ketone :-

i) TO hydrocarbone



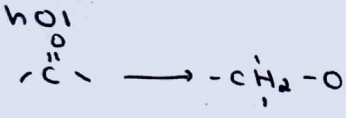
Clemenson rxn :- Zn-Hg + conc HCl

wolf-kischer rxn :- NH_2-NH_2 + $OH^{\ominus}$

mozingo reduction :-  (dithiol) + Raney Ni

Reduction with :- Red P + HHI

ii) TO alcohol



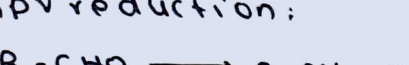
$LiAlH_4$, $NaBH_4$, B_2H_6, H_2 + catalyst

H_2 + catalyst → high P (> 1 atm)

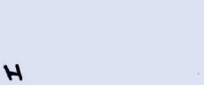
- $LiAlH_4$ can only reduce those C=C conjugated with ph-ring

mpv reduction :

$R-CHO \longrightarrow R-CH_2-OH$



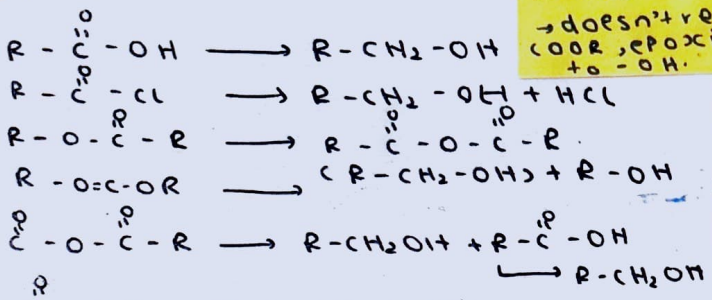
Aluminium isopropoxide + Isopropanol



meerwein-pondoff verley reduction.

Reduction of carboxylic acids and derivatives

Raney Ni in THF → doesn't reduce COOH, COOR, epoxide by acid to -OH.



	$LiAlH_4$	H_2 + catalyst	$NaBH_4$	B_2H_6
	✓	✓	✓	x
	✓	✓	x	x
	✓	✓	x	✓
	✓	✓	x	✓
	✓	✓	x	✓
	✓	✓	x	✓

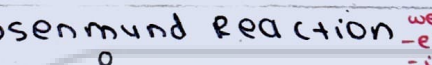
Rosenmund Reaction

we can't form formaldehyde as formyl chloride is unstable at room temp

Pd - $BaSO_4$ (Lindlar's catalyst)

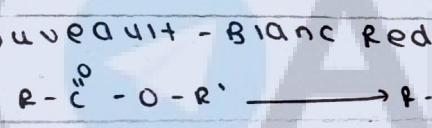
if it was pure, it would've been reduced to alcohols.

Bouveault-Blanc Reduction



Na + C_2H_5OH

Reduction of comps using Dibal-H

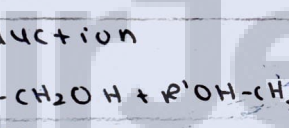


Dibal-H

-78°C

Diisobutyl Aluminium hydride.

Dibal-H can only reduce :-



Nitriles :

$R-C\equiv N \xrightarrow{[R]} R-CH_2-NH_2$

$LiAlH_4$, H_2/Pd, Na + C_2H_5OH

Isonitriles :

$R-N\equiv C \xrightarrow{[R]} R-NH-CH_3$

same as nitriles

Azide :-

$R-N_3 \xrightarrow{[R]} R-NH_2 + N_2\uparrow$

$LiAlH_4$, H_2/Pd.

Nitro-compounds

$R-NO_2 \xrightarrow{[R]} R-NH_2$

$LiAlH_4$, H_2/Pd, metal + acid

Imine :-

$R-CH=NH \xrightarrow{[R]} R-CH_2-NH_2$

$LiAlH_4$, H_2/Pd, $NaBH_4$

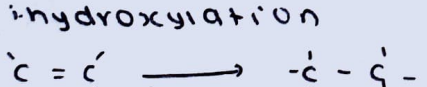
Oximes :

$R-CH=N-OH \xrightarrow{[R]} R-CH_2-NH_2 + H_2O$

$LiAlH_4$, H_2/Pd

Oxidation

a) Syn-dihydroxylation

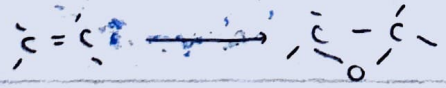


i) Bayers reagent cold and dil alk $KMnO_4$

ii) OSO_4 / $NaHSO_3$

syn-addition of 2-OH.

b) Epoxidation of Alkene :



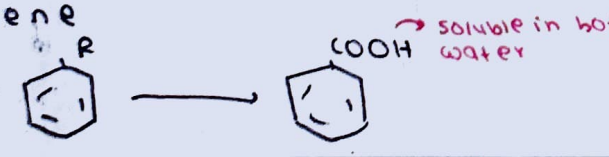
i) per acid (/ mCPBA)

ii) Ag + O_2 / Ag_2O

iii) $X_2 + H_2O \rightarrow$ Base

Rate of epoxidation 2-H-s.

Oxidation of side chain attached to benzene



soluble in hot water

i) Strong oxidising agent

R-group oxidised to COOH irrespective of length

R-group must have benzylic hydrogen.

Oxidation of Alkene using strong O.A

unsubstituted alkene ⇒ $\overset{H}{\overset{|}{}}\!\!>C=$ ⟶ $CO_2 + H_2O$

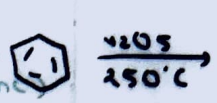
monosubstituted alkene $R-\overset{H}{\overset{|}{C}}=$ ⟶ $R-COOH$

disubstituted alkene $R-\overset{R}{\overset{|}{C}}=$ ⟶ $R-\overset{O}{\overset{\|}{C}}-R$

O.A :- acid $K_2Cr_2O_7$

acid $KMnO_4$

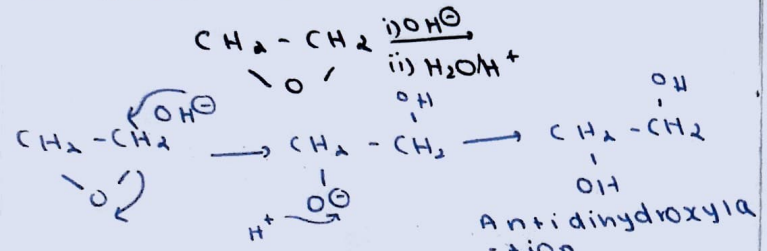
alk $KMnO_4$ cnot and cone)



$\xrightarrow[500°C]{V_2O_5}$ maleic anhydride

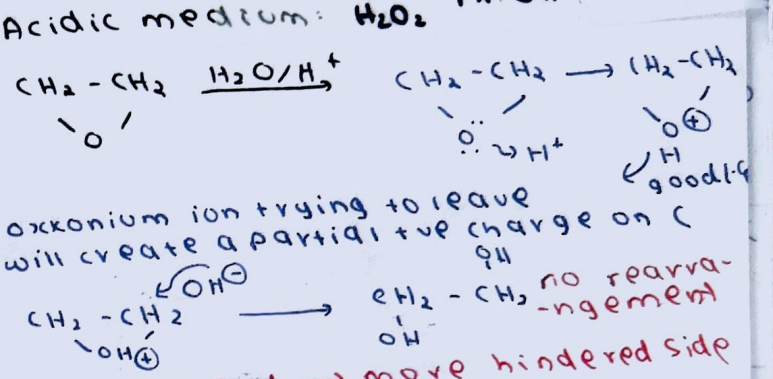
Epoxide Ring Opening:

a) Basic medium:



Basic medium → S_N2 → $Nu^{\ominus}$ attacks on less hindered side

Acidic medium:



Acidic → SN1 → more hindered side

Oxidation of Alcohols:

1° Alcohol :-

oxidising agents:
- Al(OMe)3, O=C1CCCCC1=O
- NBS
- collin's reagent

CH_2-OH —weak [O]→ $R-\overset{O}{\overset{\|}{C}}-H$ —strong [O]→ $R-COOH$

2° Alcohol :-

$R-\overset{OH}{\overset{|}{C}}H-R$ —weak (O)→ $R-\overset{O}{\overset{\|}{C}}-R$ —strong (O)→ $R-\overset{O}{\overset{\|}{C}}-R$

3° Alcohol :- strong [O] / weak (O) → No reaction

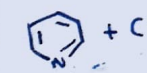
Strong [O]

1) Acidic $K_2Cr_2O_7$
2) Acidic $KMnO_4, \Delta$
3) Hot and alk $KMnO_4$
4) Jones Reagent
5) conc HNO_3 (not for alcohols)

3° alcohols with Cu at 300° undergo dehydration

weak [O]

i) PCC → pyridinium chlorochromate



ii) PDC → pyridinium dichromate (Corn forth reagent)

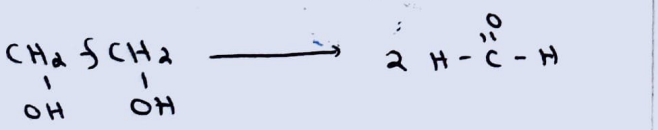
iii) Cu / 300°C

iv) MnO_2 (used for allylic and Benzylic alcohol

v) TSCl + DMSO + $NaHSO_3$ (Swerns oxidation

Oxidation of vic-diols

malaprade oxidation



Oxidising agent :-

HIO_4 (per-iodic acid)
or
$Pb(CH_3COO)_4$ lead tetra acetate
or
$NaIO_4$ (Criemux reagent)

- Break bond b/w to adjacent carbons and replace with OH
- Two OH on one carbon → unstable !

Oppenaur oxidation

$R-\overset{OH}{\overset{|}{C}}H-R \longrightarrow R-\overset{O}{\overset{\|}{C}}-R$

isopropanol.

opposite of MPV reduction
→ reversible

Oxidation of Aldehyde / Ketones:

- for aldehydes:

i) strong oxidising agent:

$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[O.A]{strong} R-\overset{O}{\overset{\|}{C}}-OH$

ii) Schiff's Reagent :-

↳ decolourises p-sonanilline

Aldehyde —Schiff's reagent→ pink/ magenta.

ii) Tollen's Reagent

$R-\overset{O}{\overset{\|}{C}}-H + (Ag(NH_3)_2)^{\oplus}OH^{\ominus} \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + NH_3 + H_2O\uparrow$

↓Ag Silver ppt

ketones X Aldehydes ✓

other comps:
- Aldehyde
- Hemi-acetals
- Formic acid
- α-Hydroxy Ketone

iii) Fehling's Test

Fehling soln A :- aq $CuSO_4$ (Cu^{2+}) | Fehling soln B: alk soln of Rochelles salt (Na-K tartarate)

$R-\overset{O}{\overset{\|}{C}}-H + Cu^{2+} + OH^{\ominus} \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + H_2O + Cu_2O\downarrow$ (Brick red)

- distinguish b/w alds and keton
- X aromatic aldehydes
- rest same as Tollen

Oxidation of Ketones

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3COOH + HCOOH$

Strong O.A
- acidic $KMnO_4$
- acidic $K_2Cr_2O_7$
- alkaline $KMnO_4$ (hot and conc)

Popoff's rule:- Bond blw longer alkyl group and carbonyl grp is broken.

Oxidation using SeO_2

oxidises CH_2 group α to carbonyl group

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$

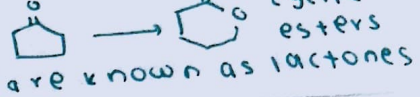
SeO_2, Δ

CH_2 of longer alkyl group is chosen.

Bayer-Villager oxidation.

$R-\overset{O}{\overset{\|}{C}}-R \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-R$

O.A:- • peracids • H_2SO_5, mCBPA, R-COOOH



cyclic esters are known as lactones

Grignard Reagent:-

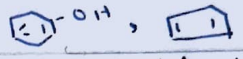
$R-X + Mg \xrightarrow[Ether]{Dry} RMgX$

$R-\overset{\oplus}{Mg}X \rightarrow$ highly polar ($R^{\ominus}$)

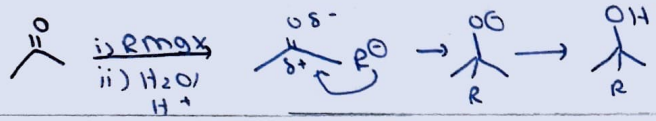
Grignar with compound containing acidic hydrogen

$CH_3MgBr + H_2O \longrightarrow CH_4$

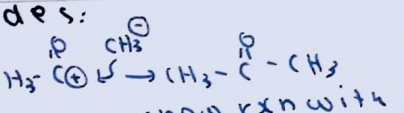
eg:- Acids, ROH, H_2O, $H-C\equiv C-H$, amide, $RCOOH$, $R-SO_3H$, HCl, $R-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-R$,



with Aldehydes and ketones:

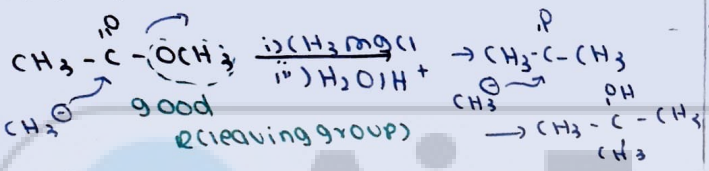


with acid chlorides:



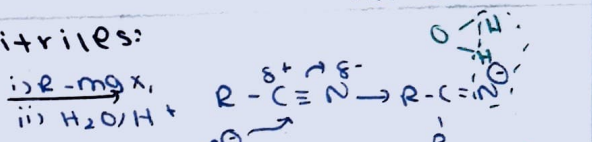
Chow rxn with carbonyl (comp)

with ester:-



good (leaving group)

with nitriles:



Imines are unstable in H_2O

Hydrocarbons

Alkanes:

Prep from carboxylic acid / Alcohol

$R-OH \longrightarrow R-CH_3$

$R-COOH \longrightarrow R-CH_3$

Red P + HI

6 moles of HI → COOH

2 moles of HI → OH

Decarboxylation:

$R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus} \longrightarrow R-H + Na_2CO_3$

$NaOH + CaO, \Delta$

- Soda lime degradation
- very stable carbanion (resonance) only needs heating to decarboxylate.

Kolbe's Electrolysis:-

$2R-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus} + 2H_2O \longrightarrow R-R + 2CO_2 + H_2 + NaOH$

- Electrolysis only alkanes containing even no. of C-atoms can be prepped.

F.R.S.R mechanism aq soln of sodium / potassium salt of carboxylic acid.

Corey-house synthesis:

$R_2CuLi + R-X \longrightarrow R-R + LiX + CuX$

R_2CuLi → Gilmann's reagent (like grignard)

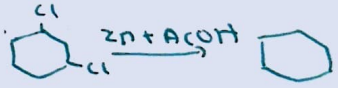
Synthesis of Gilmann's reagent:- $R-X + Li \longrightarrow R-Li + LiX$

$2R-Li + CuX \rightarrow R_2CuLi + LiX$

Reduction of Alkyl Halides:

$R-X \xrightarrow{(R)} R-H$

$LiAlH_4$, $NaBH_4$, Red P + HI, Zn + CH_3COOH (1 mole)

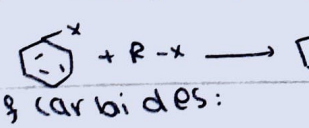


Wurtz Rxn / Wurtz-Fittig Rxn:

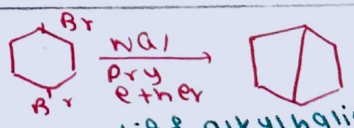
$2R-X + 2Na \longrightarrow R-R + 2NaX$ (X = Cl, Br, I)

Dry ether

Wurtz-Fittig:-



Na / dry ether.



if two diff alkyl halides are used, a number of products will be formed.

Hydrolysis of carbides:

i) $Al_4C_3 + H_2O \longrightarrow CH_4 + Al(OH)_3$

ii) $Be_2C + H_2O \longrightarrow CH_4 + Be(OH)_2$

FRSR Reaction:

$CH_4 + Cl_2 \xrightarrow{h\nu/\Delta} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$

$CH_4 + Cl_2$ (excess) $\xrightarrow{h\nu/\Delta} CCl_4$ (majors)

CH_4 (excess) $+ Cl_2 \xrightarrow{h\nu/\Delta} CH_3Cl$ (major)

Reactivity Order :-

a) Halogen :- $F_2 > Cl_2 > Br_2 > I_2$

reversible but made possible by HIO_3, HNO_3

chain initiation: $Cl-Cl \xrightarrow{h\nu} 2Cl\cdot$

chain propagation: free radicals attack on alkane

$H_3C-H + Cl\cdot \rightarrow \cdot CH_3 + HCl$

$CH_3\cdot + Cl-Cl \rightarrow CH_3Cl + Cl\cdot$

chain termination

$Cl\cdot + Cl\cdot \rightarrow Cl_2$

$CH_3\cdot + CH_3\cdot \rightarrow CH_3-CH_3$

b) Alkanes :-

$(CH_3)_3C-H > (CH_3)_2CH-H > CH_3-CH_2-H$

Reactivity selectivity

Cl :- 1 : 2 : 3 → 1 : 3.8 : 5

Br :- 1 : 2 : 3 → 1 : 82 : 1600

F :- 1 : 2 : 3 → 1 : 1 : 1

Allylic and Benzylic Halogenation

$CH_2=CH-CH_3 \xrightarrow[\text{or } NCS]{h\nu, Cl} CH_2=CH-CH_2Cl$

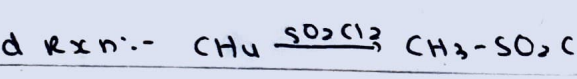
$+X_2 + h\nu, \Delta$

→ NBS, NCS

Halogenation at allylic pos via FRSR.

Nitration / Sulphonation of Alkane

$CH_4 \longrightarrow CH_3NO_2$



conc HNO_3

conc H_2SO_4

SO_2Cl_2, Δ

only straight chain alkanes having 6 C-atoms or more give sulphonation, H substituted by SO_2Cl

Reed Rxn :- $CH_4 \xrightarrow{SO_2Cl_2} CH_3-SO_2Cl$

Controlled oxidation

$2CH_4 + O_2 \xrightarrow[1100\,atm]{Cu/523K} 2CH_3OH$

$CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$

$2CH_3-CH_2 + 3O_2 \xrightarrow[Mn]{(CH_3CO)_2} 2CH_3COOH + 2H_2O$

$(CH_3)_3CH \xrightarrow{KMnO_4} (CH_3)_3OH$

Isomerisation

n-alkanes → branched alkanes

$AlCl_3 / HCl$

Aromatization :

$Cr_2O_3 / V_2O_5 / Mo_2O_3$, 773 K, 10-20 atm

Reaction with steam

$CH_4 + H_2O \xrightarrow{Ni, \Delta} CO + 3H_2$

Pyrolysis / Cracking :

C_6H_{14} (↓ FR rxn) → $C_6H_{12} + H_2$; $C_4H_8 + C_2H_6$; $C_3H_8 + C_2H_4$; $+ CH_4$

ex: $C_{12}H_{26} \xrightarrow[973K]{Pt, Pd, Ni} C_7H_{16} + C_5H_{10}$

dodecane

Alkenes :

Addition of H-X to Alkene (Cl, Br, I)

$CH_2=CH_2 \longrightarrow CH_2(H) - CH_2(X)$

HX (Cl, Br, I) (based on stability of carbocation so look out for that)

markonikove rule: carbocation → less H ; (-ve part of reagent is added to carbon having less Hydrogen

Addition of HBr to Alkene in presence of peroxide :-

$CH_3-CH=CH_2 + HBr \longrightarrow CH_3-CH_2-CH_2-Br$

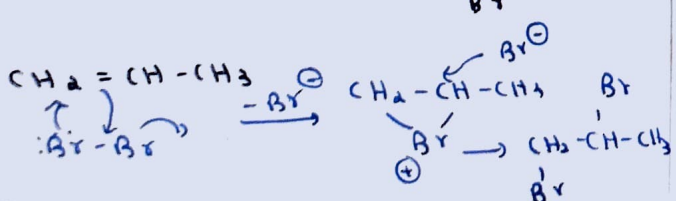
peroxide effect not observed in H-Cl, H-I → HCl → step 1 → endo ; HI → step 2 → endo

peroxide (R-O-O-R) + HBr

Formation of Anti markonikov product as major product in presence of peroxide → kharash effect

Addition of X_2 :

$CH_2=CH_2 + Br_2 \longrightarrow CH_2(Br) - CH_2(Br)$



Br_2, CCl_4 (solvent)

stereospecific → anti-addition.

Test of unsaturation → decolourise Br water

S_N1 mech → $Nu^\ominus$ attacks on more hindered side

ring formation rxns are always anti

$CH_3-CH=CH_2 \xrightarrow[\text{or } HOBr]{Br_2 + H_2O}$

$Br + H_2O$ / $HOBr$

$CH_3=CH-CH_2 \rightarrow CH_3-\overset{\overset{+}{Br}}{CH}-CH_2 \rightarrow CH_3-\underset{OH}{CH}-\underset{Br}{CH_2}$

Addition of X, X':-

$CH_3-CH=CH_2 \longrightarrow CH_3-\underset{Cl}{CH}-\underset{I}{CH_2}$

$X\ X'$

use markonikou's rule $I^{\delta\oplus}-Cl^{\delta\ominus}$

Acid catalysed hydration of Alkene

$CH_2=CH_2 + H_2O \longrightarrow CH_3-CH_2-OH$

H_2O / H^+

look out for carbocation rearrangement.

Hydroboration oxidation.

$CH_3-CH=CH_2 \longrightarrow CH_3-CH_2-\underset{OH}{CH_2}$

i) B_2H_6 / THF (H)
ii) $H_2O_2 + OH^\ominus \rightarrow OH$

No carbocation → No rearrangement → Anti markonikov.
Syn addition of H, OH (same side)

Oxy-mercuration - demercuration

$CH_2=CH_2 \longrightarrow \underset{H}{CH_2}-\underset{OH}{CH_2}$

i) $Hg(OAc)_2 + H_2O$ (→OH)
ii) $NaBH_4 \rightarrow H$

No carbocation → No rearrangement → markonik
Anti addition

Addition of cold and conc. H_2SO_4

$CH_2=CH_2 \longrightarrow \underset{H}{CH_2}-\underset{OSO_3H}{CH_2}$

$CH_3-CH_2-OSO_3H \xrightarrow{H_2O} CH_3-CH_2-OH.$

cold and conc H_2SO_4

look for most reactive (stable) $\oplus$ for reactivity.
use for seperating alkane-allene mixt
$R-CH=CH_2 \xrightarrow[\text{conc } H_2SO_4]{\text{cold}} R-\underset{OSO_3H}{CH}-CH_3$ → Δ back to water soluble original

Addition of Alcohol to Alkene

$CH_2=CH_2 \longrightarrow CH_3-\underset{OCH_3}{CH_2}$

CH_3OH / H^+

use markonikou's rule.

Addition of NOCl (Tildon's Reagent)

$CH_2=CH_2 \longrightarrow \underset{NO_2}{CH_2}-\underset{Cl}{CH_2}$

NOCl → Nitrosyl chloride
$NO^\oplus-Cl^\ominus$

No carbocation → No rearrangement
Anti addition
· atking from more hindered side, (SN1 mech)

Epoxidation of Alkene:

Ring opening :- basic → SN2 / acidic → SN1 like

Anti-dihydroxilation

→ carbenes: → neutral carbon intermediates acting as electrophiles

$:C(-H)(-H)$

singlet (1L CH_2) < (stability) Triplet (^1_1CH)

$H-\overset{\ominus}{C}-H$ (S=0, sm = 2×0+1 = 1) more repulsions

$H-\overset{\ominus}{C}(-H)=O$ (S=1, sm = 3)

But incase of backbonding is possible in carbenes, singlet is more stable

back bonding → singlet

→ Generation of carbenes:

$CH_3Cl \xrightarrow[\Delta]{\text{alc KOH}} {}^1_1CCl_2 + H_2O + Cl^-$

diazomethane $CH_2N_2 \xrightarrow{\Delta} :CH_2 + N_2\uparrow$

i) Addition of singlet carbene:

$CH=CH_2 \xrightarrow{1L\,CH_2} CH_2-CH_2$

Addition of Triplet carb:

$CH=CH_2 \xrightarrow{{}^1CH^\cdot} {}^1_1CH_2-{}^1_1CH_2$

$\rightarrow {}^1_1CH_2-CH_2$ (few moments later)

Stereochem:

$CH_3-C(CH_3)=C(H)-CH_3 \rightarrow$ meso

$CH_3-C(CH_3)=C(H)-CH_3 \rightarrow$ racemic

cis/trans alk $\xrightarrow{{}^1CH_2}$ 3 pro
cis alk $\xrightarrow{1L\,CH_2}$ 1 pro
trans alk $\xrightarrow{1L\,CH_2}$ 2 pro

Ozonolysis: Reductive / Oxidative

a) Reductive:

$>C=C< \longrightarrow >C=O + O=C<$

Reagent: i) O_3 ii) $Zn + H_2O$ / $(CH_3)_2S$

b) Oxidative:

Reagent: i) O_3 ii) H_2O

- unsubstituted - $CO_2 + H_2O$
- monosubstituted - carboxylic acid
- disubstituted - ketone

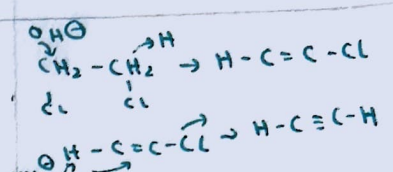
Alkynes:

i) Preparations:

a) Dehalogenation of vic-dihalide

$Cl-CH_2-CH_2-Cl \longrightarrow H-C\equiv C-H$

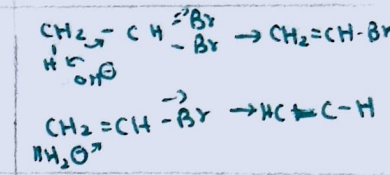
alk KOH / $NaNH_2$



b) Dehydrohalogenation of geminal dihalides

$CH_3-CH(Br)-Br \longrightarrow H-C\equiv C-H$

alk KOH / $NaNH_2$



c) Higher alkyne from lower alkenes

$H-C\equiv C-H \longrightarrow H-C\equiv C-CH_3$

i) $NaNH_2$ iii) CH_3-I

d) From Haloform (CHX_3):

$CHX_3 + 6Ag \longrightarrow H-C\equiv C-H + 6AgX$

Ag — Ionic reaction

e) From dehalogenation of terminal halides

$CH_3-C(Br)_2-C(Br)_2-CH_3 \longrightarrow CH_3-C\equiv C-CH_3$

Zn, Δ or NaI / Acetone

Chemical properties:

i) Addition of HX

$H-C\equiv C-H \longrightarrow H-C(Br)=C-H \longrightarrow H-C(Br)-C(Br)_2-H$

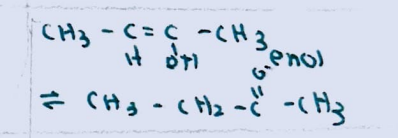
(same for addition of X_2)

HBr, excess — use Markonikov's rule

Addition of H_2O (Kucherov)

$CH_3-C\equiv C-CH_3 \xrightarrow[Hg^{2+}]{H_2O/H^+} CH_3-CH_2-C(=O)-CH_3$

H_2O/H^+, Hg^{2+}



v) Oxidation of Alkyne:

a) using Bayer's reagent:

$CH_3-C\equiv C-CH_3 \xrightarrow[dil\ KMnO_4]{cold\ and} H_3C-C(OH)=C(OH)-CH_3 \rightarrow CH_3-C(=O)-C(=O)-CH_3$

b) using strong O.A

- → acidic $K_2Cr_2O_7$
- → acidic $KMnO_4$
- → hot and conc alk $KMnO_4$

terminal: $H-C\equiv C-H \rightarrow CO_2$

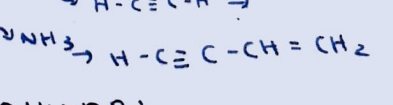
internal: $R-C\equiv C \rightarrow R-C(=O)-OH$

vi) Ozonolysis of Alkyne:

Reductive	Oxidative
i) O_3 ii) $Zn > H_2O$	i) O_3 ii) H_2O
a) Bayer's R.A	b) Strong O.A

Dimerisation of Terminal Alkyne:

$2H-C\equiv C-H \xrightarrow[or\ CuCl_2 + NH_4Cl]{NaNH_2} H-C\equiv C-CH=CH_2$



Trimerisation of Alkyne:

$3H-C\equiv C-H \xrightarrow[Tube,\ 873\ K]{red\ hot\ Fe}$ Benzene

$3CH_3-C\equiv C-H \xrightarrow[Tube,\ 873\ K]{red\ hot\ Fe}$ mesitylene

→ Alternate way to prep mesitylene

$3CH_3-C(=O)-CH_3 \xrightarrow[-3H_2O]{conc\ H_2SO_4}$

Interconversion of terminal and Internal Alkyne

$CH_3-C\equiv C-CH_3$ (internal) $\underset{ii}{\overset{i}{\rightleftharpoons}}$ $CH_3-CH_2-C\equiv CH$ (terminal)

i) $NaNH_2, \Delta$
ii) Alc KOH, Δ

→ $NaNH_2$ can atk non-acidic hydrogen due strength of base

chemical tests to distinguish blw terminal and internal alkynes.

① Ammonical cuprous chloride (Cu_2Cl_2)

$H-C\equiv C-H \xrightarrow[NH_4OH]{Cu_2Cl_2} C_2Cu_2$ (reddish brown)

$R-C\equiv C-R \xrightarrow[NH_4OH]{Cu_2Cl_2}$ NO rxn

② Using Tollen's reagent $[Ag(NH_3)_2]OH$

$H-C\equiv C-H \xrightarrow{\text{Tollen's reagent}} Ag_2C_2$ white ppt
× not silver mirror test ★

$R-C\equiv C-R \xrightarrow{\text{Tollens reagent}}$ NO rxn

Addition of H-X to conjugated diene

Reagent: HBr (1 eq)

$CH_2=CH-CH=CH_2 \xrightarrow{HBr} CH_2=CH-\overset{\oplus}{C}H-CH_3 \xrightarrow{Br^\ominus} CH_2=CH-\underset{Br}{CH}-CH_3$

resonance stabilized $\overset{\oplus}{C}$

$CH_2^\ominus-CH=CH-CH_2 \xrightarrow{Br^\ominus} CH_2-CH=CH-CH_2$ (Br)

Kinetic product

Thermodynamic product.

Kinetic	Thermodynamic
• 1,2-addition	• 1,4-addition
• fast	• slow
• unstable	• stable (more α-H)
• reversible	• Irreversible
• major at low Temp	• major at High Temp

Hydroformation of Alkene

i) $CH_3-CH=CH_2 \longrightarrow CH_3-\underset{CHO}{CH}-CH_3$ — i) $CO+H_2$, ii) $H[(CO)_4]$ — markonikove addn of CHO group.

ii) $CH_3-CH=CH_2 \longrightarrow CH_3-\underset{COOH}{CH_2}-CH_3$ — ii) i) $CO+H_2O$, ii) H^+ acid — same but for COOH group.

Miscellaneous:

1) $2H-C\equiv C-H + S \xrightarrow{\Delta}$ Thiophene

2) $H-C\equiv C-H \xrightarrow[BF_3+HgO]{CH_3OH\ (excess)} H-\underset{H}{C}=\underset{OCH_3}{C}-H \longrightarrow CH_3-\underset{OCH_3}{\overset{OCH_3}{C}}-H$ (acetal)

3) $H-C\equiv C-H \xrightarrow[Ba(N)_2]{H(CN)\ (1eq)} H-\underset{H}{C}=\underset{CN}{C}-H$ acrylonitrile

Halogen Derivatives

Preparation:

i) Reaction of Alcohol with Phosphorous Halides

1) $3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$ (inversion) — PX_3 is insitu — → S_N2 mech, → (X = Cl, Br, I)

2) $R-OH + \longrightarrow R-H$ — i) Red P + HI — → S_N2 mech
$R-OH + \longrightarrow R-Cl + POCl_3 + HCl$ — ii) PCl_5

ii) Borodine Hunsdicker reaction

$R-\overset{O}{\overset{\|}{C}}-OAg + X_2 \longrightarrow R-X + AgX + CO_2$ — i) CCl_4, Peroxide, $h\nu$ — X = Cl, Br; reactivity of R: 1° > 2° > 3°

Previous rxn but with X = F

$R-\overset{O}{\overset{\|}{C}}-OAg + \longrightarrow$ Esters — i) I_2 — simonini Rxn

Finkelstein rxn → for alkyl Iodides

$R-X + NaI \xrightarrow{S_N2} R-I + NaX$ — i) Acetone — → acts as a — NaI → covalent soluble in acetone; NaX → Ionic Insoluble → forms ppt

Swartz Reaction → used for alkyl fluorides

$R-X + mF \longrightarrow R-F + mX$

H_2O (gaseous phase)

AgX → Cl, Br, I

mF → heavy metal fluorides eg: Hg_2F_2, COF_2, AgF, SbF_5, etc.

Substitution Vs Elimination

	Substitution	Elimination
	• low temp → bc they are exo	• High temp → bc they are endo
	• small sized :- $Nu^{\ominus}$	• Bulky species → base
	• aqueous KOH	• alcoholic KOH
	• SN1 : 1° > 2° > 3°	• E1 : 3° > 2° > 1°
	SN2 : 3° > 2° > 1°	E2 : 3° > 2° > 1°

atks on C ← $Nu^{\ominus}$ $OH^{\ominus}$ → CH_3-CH_2-OH substitution

CH_2-CH_2-X

atks on H ← Base ($OH^{\ominus}$) → $CH_2=CH_2$ elimination

100% subs/elimination → very very rare

Ratio of subs:elimination can be adj.

1° R-X → substitution 3° R-X → elimination.

Preparation of Dihalides

carbonyl + PCl_5

$CH_3-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\underset{H}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-Cl + POCl_3$

PCl_5

1O → 2Cl

Trihalides:

→ Chloroform ($CHCl_3$)

$CCl_3-\overset{O}{\overset{\|}{C}}-H \longrightarrow CHCl_3 + H-\overset{O}{\overset{\|}{C}}-O^{\ominus}Na^{\oplus}$

$NaOH$

$CCl_3^{\ominus}$ → very good L.G

Stabilized by Back bonding.

Chemical properties of Chloroform:

① Oxidation of Chloroform

$CHCl_3 \xrightarrow[hv]{air} \underset{1}{COCl_2} + HCl$

i) air, sunlight

ii) C_2H_5OH

- 1 → phosgene (poisonous)
- 2 → Diethyl carbonate

* $O=C(Cl)(Cl) + \longrightarrow O=C(O-C_2H_5)(O-C_2H_5)$ (2)

② With Acetone

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CHCl_3 \longrightarrow CH_3-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CCl_3$

i) $OH^{\ominus}$

- Chloritane
- Chypnotic)

③ With HNO_3

$CHCl_3 + HNO_3 \longrightarrow CCl_3-NO_2$

HNO_3

Chloropicrin (Tear gas)

Alcohol and Ethers

i) Hydrolysis of R-X

$R-X \longrightarrow R-OH$

i) H_2O
ii) aq NaOH
iii) moist Ag_2O
iv) (aq) K_2CO_3
v) (aq) $AgNO_3$

→ aqueous is the important part.

ii) Hydrolysis of Ethers (acidic med)

$R-\ddot{O}-R' \xrightarrow{H_2O/H^+} R-OH + R'OH$

H_2O/H^+

SN1 ✓ R = 3°/2°/1°/Benzyl/Allyl

SN2 ✓ R = 1°

X doesn't take place in basic med

iii) Hydrolysis of Hemiacetals/Acetals

Hemiacetal: $\overset{H}{\underset{R}{\overset{OR}{\underset{|}{\overset{|}{C}}}}}-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-H + ROH$

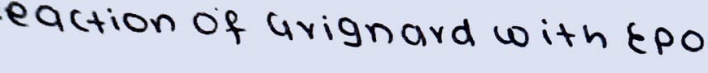
Acetal: $\overset{H}{\underset{R}{\overset{OR}{\underset{|}{\overset{|}{C}}}}}-OR \longrightarrow H-\overset{O}{\overset{\|}{C}}-R + 2ROH$

H_2O/H^+

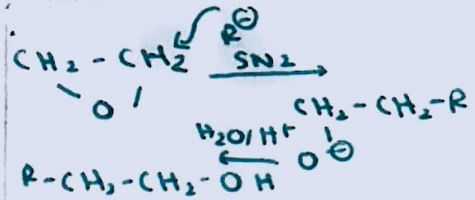
→ Break C-OR bond and add -OH.

→ add H to OR

iv) Reaction of Grignard with Epoxide



i) RMgX
ii) H_2O/H^+



Victormeyer Test: distinguishing b/w primary, secondary, tertiary alc.

$R-CH_2-OH \xrightarrow{HI} R-CH_2-I \xrightarrow{AgNO_2} R-CH_2-NO_2 \xrightarrow{HNO_2} R-\underset{\underset{N=O}{|}}{CH}-NO_2$

$R_2-CH-OH \xrightarrow{HI} R_2-CH-I \xrightarrow{AgNO_2} R_2-CH-NO_2 \xrightarrow{HNO_2} R-\underset{\underset{R}{|}}{\overset{\overset{N=O}{|}}{C}}-NO_2$

$R_3-C-OH \xrightarrow{HI} R_3-C-I \xrightarrow{AgNO_2} R_3C-NO_2 \xrightarrow{HNO_3}$ NO rxn

$R-\underset{\underset{N=O}{|}}{CH}-NO_2 \longrightarrow R-\underset{\underset{NOH}{||}}{C}-NO_2 \xrightarrow{NaOH}$ Red colour

(NOH → Nitrolic acid)

$R-\underset{\underset{N=O}{|}}{\overset{\overset{R}{|}}{C}}-NO_2 \longrightarrow$ doesn't tautomerise (pseudo nitrile) $\xrightarrow{NaOH}$ Blue colour

Reaction of ether with H - X

$R-\ddot{O}-R + HX \longrightarrow ROH + RX$ i) HX (1 mole)

$R-\ddot{O}-R + HX \longrightarrow 2R-X$ ii) HX (excess)

R = 3°/Allyl/Benzyl ⇒ S_N1

R = 2°/1° ⇒ S_N2

Williamson continous Etherification

$CH_3-CH_2-OH \longrightarrow H_2C=CH_2$ T = 473K (intramolecular dehydration)

$CH_3-CH_2-\boxed{OH}\,O\boxed{H}-CH_2-CH_3 \xrightarrow{T = 413\,K} Et-O-Et$ (intermolecular dehydration)

- unsymmetrical ethers cant be prepared
- 2°, 3° alcohols give alkenes in sig. amt even at low temp.

Diethyl ether on prolong exposure to air → Diethyl hydroxy peroxide

Aromatic Compounds

Electrophillic aromatic substitution:

Electrophites:- X^+ ⟶ Halogenation
NO_2^+ ⟶ Nitration
SO_3 ⟶ sulphonation
R^+ ⟶ Alkylation
$R-C\equiv O^+$ ⟶ Acylinium cation
NO^+ ⟶ Nitrosation.

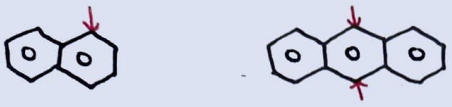
Sulphonation, Iodination are reversible rxn
∴ KIE → applicable
for the rest → not applicable

Factors affecting reactivity of Benzene:
- Stability of σ-complex
- e^- density on Benzene ring.

o/p-directing + Activating	m-directing + deactivating	o/p directing + deactivating
$-O^\ominus$, $-NH_2$, $-OH$, OR, $NH-C(=O)-R$, $-O-C(=O)-CH_3$, $-Ph$, $-CH=CH_2$, $-C\equiv CH$, etc.	$-NO_2$, $-SO_3H$, $-CN$, $-C(=O)-H$, $-C(=O)-$, $-C(=O)-OH$, $-C(=O)-Cl$, $-C(=O)-OR$, $-C(=O)-OC$, $-C(=O)-NH_2$, $NR_3^\oplus$, $NF_3^\oplus$, $-CX_3$.	+R → o/p directing −I → deactivating $-F$, $-Cl$, $-Br$, $-I$ $-\ddot{N}=O$, $-S(=O)-HO$, $-(CH_2)-X$, $-(CHX_2)$

Rules for attack of electrophile:-
- more deactivating > less deactivating (when both are m-directing)
- more activating > less activating
- Activating > Deactivating
- o/p directing > meta directing

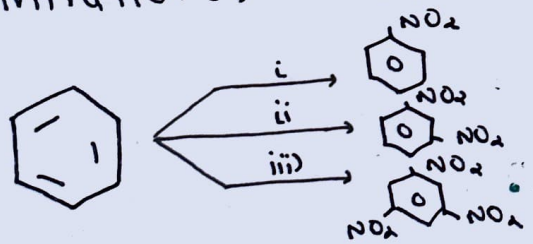
attack position for napthalene:- anthracene:-



General:
- in most cases of o vs p, para gets attacked.

Nitration	Sulphonation	Halogenation	Friedel craft Alkylation	Friedel craft Acylation
• conc $HNO_3 + H_2SO_4$ nitrating mix. • Fuming HNO_3 • N_2O_5 • $[NO_2]^+[BF_4]^-$	• conc H_2SO_4 • oleum → $H_2S_2O_7$ sulphonation, conc H_2SO_4, dil H_2SO_4, desulphonation, SO_3H	• X_2 + lewis acid • $AlCl_3$, BF_3, $FeCl_3$ ✱ $TiCl_4$, $ZnCl_2$	a) $R-Cl + AlCl_3$ ✱ carbocation rearr ✓ $ZnCl_2$, $FeCl_3$ ✗ no rearr. b) Alkene + acid b) R-OH + acid	• $R-C(=O)-Cl + AlCl_3$ • $R-C(=O)-O-C(=O)-R + AlCl_3$ • $R-C(=O)-OR + AlCl_3$ • $R-C(=O)-OH$ + (conc H_2SO_4, conc H_3PO_4, PPA)

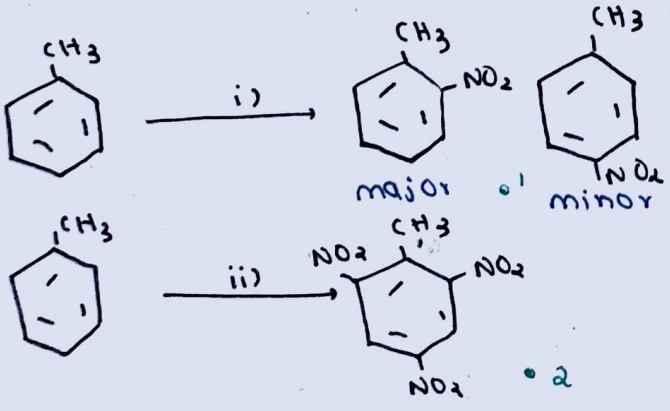
1.) Nitration of Benzene:



- i) Nitrating mix → 60°C
- ii) Nitrating mix → 120°C
- iii) Nitrating mix → 150°C /6hr) + fuming HNO_3 100°C

- → Sym-Trinitro Benzene.

2.) Nitration of Toulene



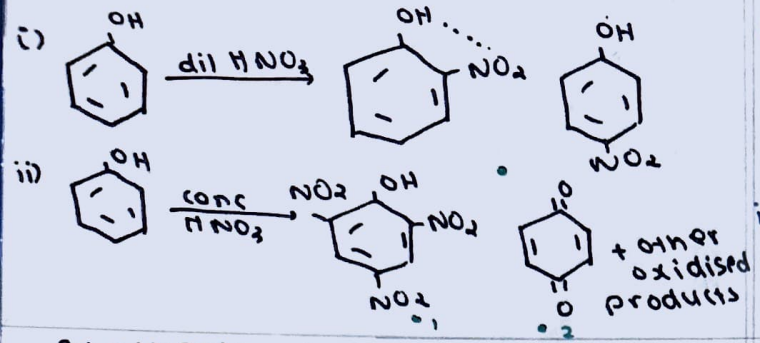
i) conc HNO_3 + H_2SO_4

- why o instead p:
  → less S.H due to me
  → +I of me most at ortho

ii) Fuming HNO_3

- Trinitro toulene.

3. Nitration of phenol.



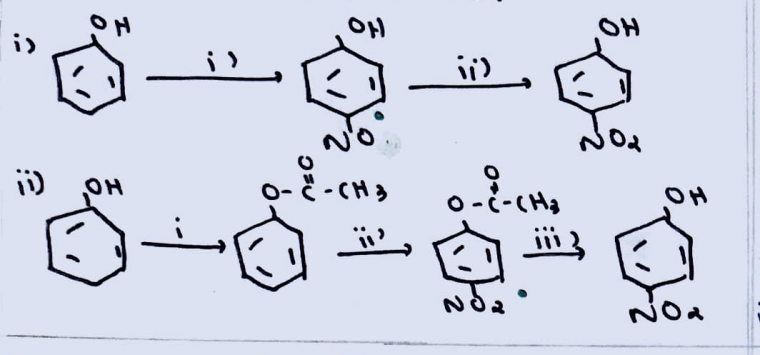
i) dil HNO_3
OH being very activating can even react with dil HNO_3

ii) conc HNO_3.

due to intra H-B, ortho > para.

- picric acid
- Benzoquinone

4. Synthesis of p-nitrophenol:



i) $NaNO_2 + HCl$ (HNO_2 prepped insitu)

ii) conc HNO_3 (acts as an oxidising agent)

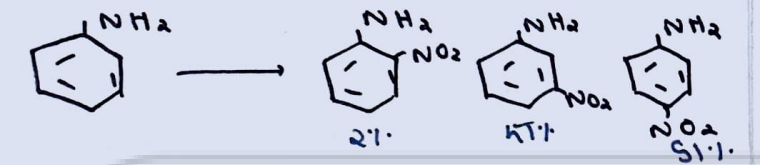
i) $CH_3-\overset{O}{\overset{\|}{C}}-Cl$ (Acylation)

ii) conc HNO_2

iii) H_2O / H^+

- The NO^+ carboca-tion formed has a high affinity for para position.
- why was there mono nitration:-
  → SH at ortho
  → less activation of OCOP.

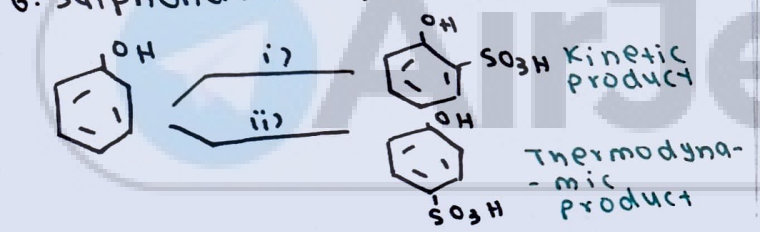
5. Nitration of Anilline



i) HNO_3

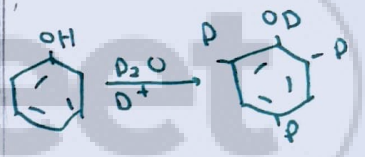
i) reason for signi. meta Nitro:-
$NH_2 \rightarrow NH_3^+ \rightarrow$ meta directing

6. Sulphonation of phenol:

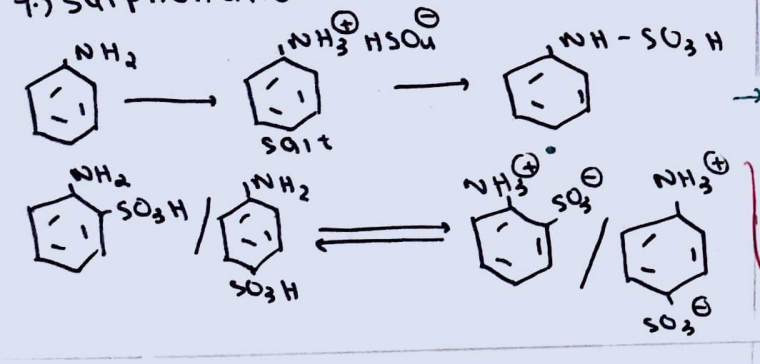


i) conc H_2SO_4, 25°C

ii) conc H_2SO_4, 125°C

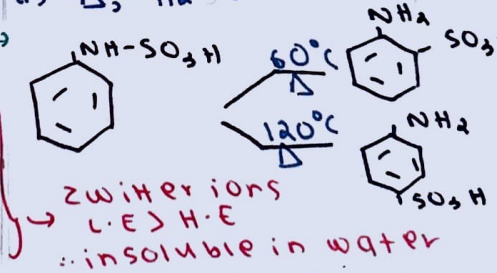


7.) Sulphonation of Anilline



i) conc H_2SO_4

ii) Δ, - Ha_2O



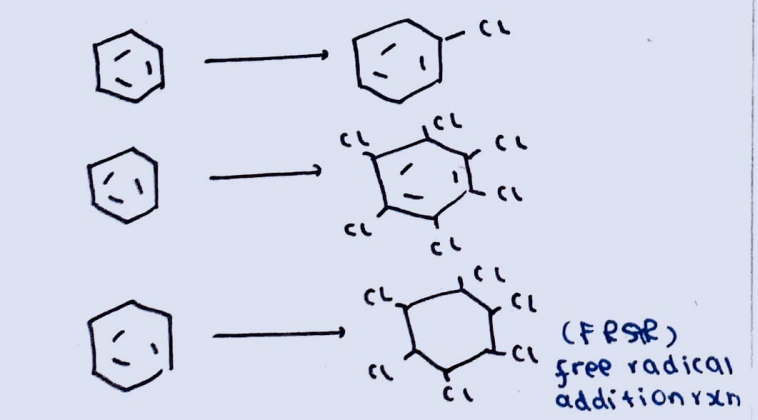
- sulphamic acid.

orthanillic acid
Kinetic product

sulphanilic acid
Thermody product

zwitter ions
↳ L.E > H.E
∴ insoluble in water

8.) Halogenation:



i) $Cl_2 / AlCl_3$

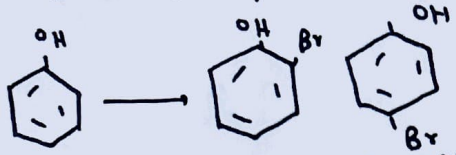
ii) Cl_2 excess + $AlCl_3$

iii) Cl_2 + UV light

- known as
  → Gammaxene
  → Lindane
  → 6/6 C
  → Benzene Hexa chloride
- used as an insect-icide

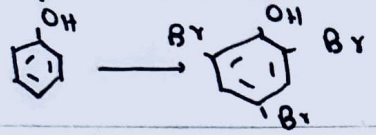
Halogenation of Phenol:

a) In presence of non-polar solvent:



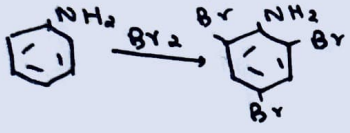
- Br_2 in $CHCl_3$, CCl_4, CS_2, etc. → monon bromo product
- Br_2 in H_2O and other polar solvents → Tribomo products

b) In presence of polar solvent:

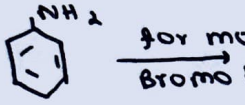


Halogenation of Aniline ✱

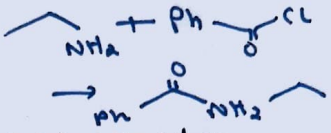
- Br_2
- gives white ppt.

i) 

NH_2 being a very activating group causes tribromination

ii) 

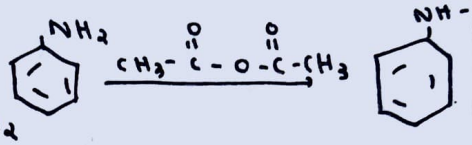
for mono Bromo product → convert NH_2 → $NH-\overset{O}{\overset{\|}{C}}-CH_3$



→ Benzoylation of an amine is known as:-

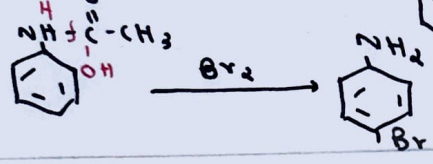
first step:- acylation (acid chloride/anhydride)

second step:- form acetanilide:-



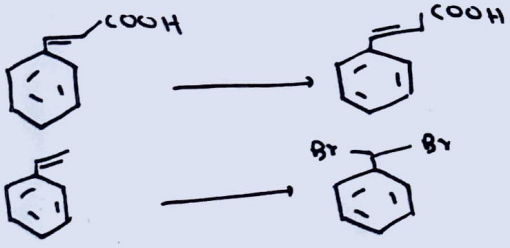
→ schotten Baumann rxn

third stem -



+ CH_3COOH.

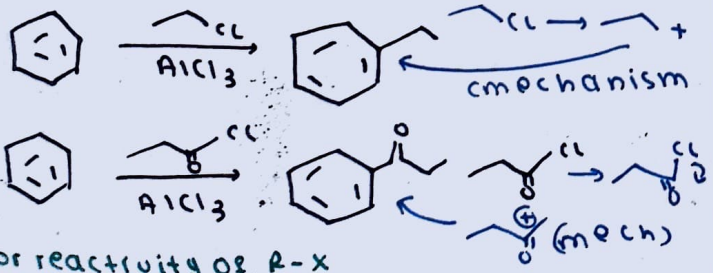
Iodination of Benzene:



Br_2 is presence of HIO_3 and HNO_3 → reversible reaction.

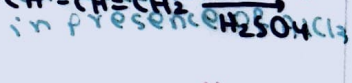
Friedel craft Reactions:

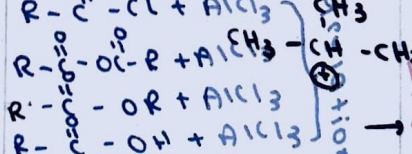
- dont take place on highly activated benzene
- dont take place on highly deactivated Benzene
- alkylation can lead to polyalkylated benzene



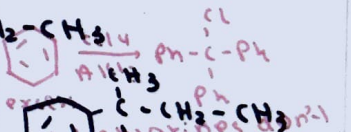
$R-Cl + AlCl_3 \rightarrow C_6H_6 + CH_3-CH-CH_2-CH_3$ (alkylation)

Rearrangement of carbocation in presence of $AlCl_3$





why doesn't it take place with Ph-OH

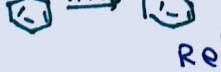


can be chlorines don't get replaced due to steric

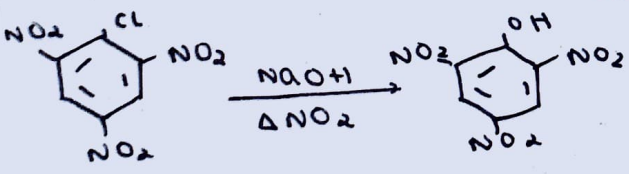
for reactivity of R-X

$R-Cl > R-Br > R-I$ (since $AlCl_3 \rightarrow$ L.A it will react with most L.B which is Cl^-)

S_NAr_2 mechanism:



Phenol uses up $AlCl_3$ ∴ no ⊕

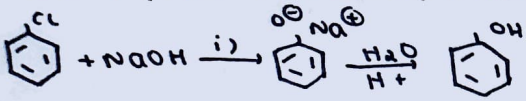


Reagents:- NO_2, Δ

- This rxn is only possible due to Nitro making the rxn suitable for nucleophile attk
- e⁻ density on Benzene ∝ Leaving group ability
- Rate: $R[Ar-X]^1[Nu^\ominus]^1$

Benzyne mechanism:

Dow's process for preparation of phenol



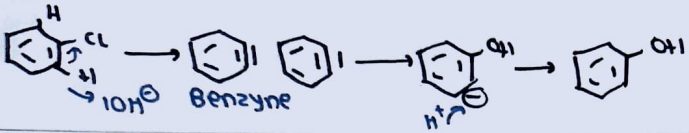
i) NaOH / H_2O H^+

ii) KNH_2, NH_3

iii) $NaNH_2$, NH_3

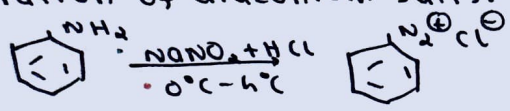
- Benzyne is aromatic
- The triple bonded C are sp^2 hyb
- In Benzyne mechs we only look at inductive effects of groups.

mechanism:-

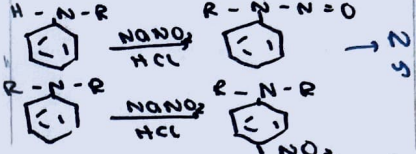


S_NAr1 mechanism :- only for diazonium salts

Preparation of diazonium salts:



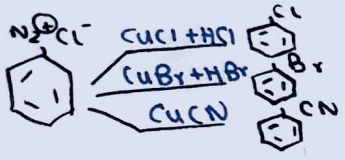
- $NaNO_2 + HCl$ (0°-5°C)



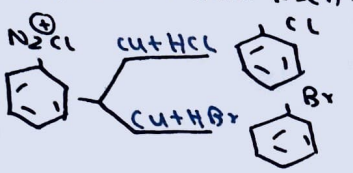
- ice cold temp to prevent diazonium salt from decomposing

N-nitrosoamine yellow, oily liquid.

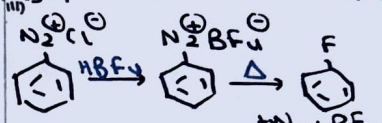
i) Sandmeyers Rxn



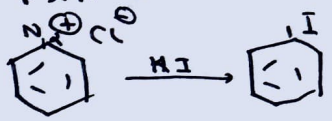
ii) Gattermann Rxn



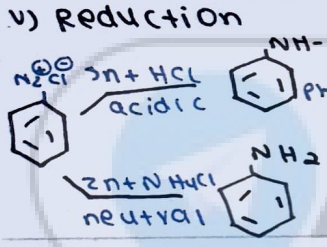
iii) Balz-Schieman Rxn



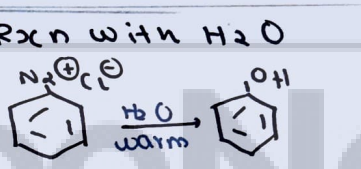
iv) Rxn with KI

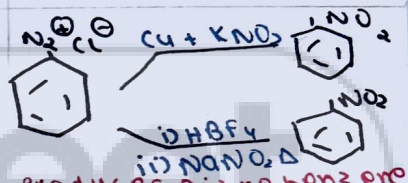


v) Reduction



Rxn with H_2O



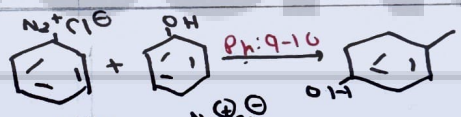


produces nitrobenzene in good yield.

Coupling Rxns:-

- Strong +R group is required.
- Basic medium favours OH
- Acidic medium favours NH_2.
- Aromatic diazonium salts are more stable than aliphatic
- doesn't take place on a deactivating benzene.

with phenol :-



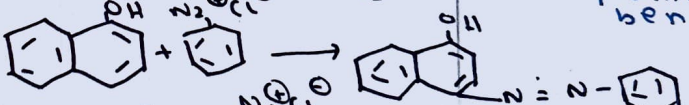
p-hydroxy Benzene (orange dye)

with Aniline :-

yellow dye

p-amino azo benzene.

with α-Napthol:

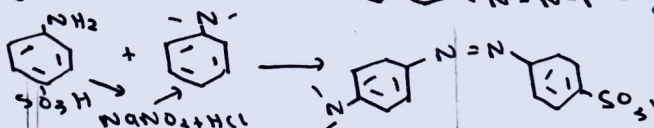


Red dye.

with β-Napthol :

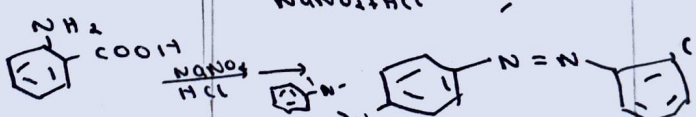
orange dye

with sulphanilic acid

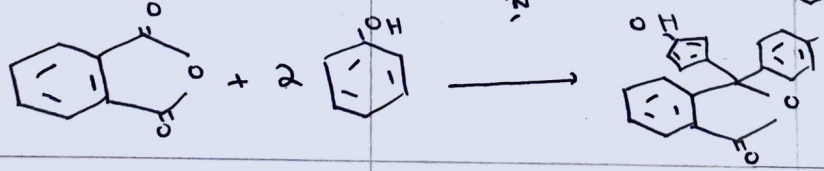


methyl orange

with h :-

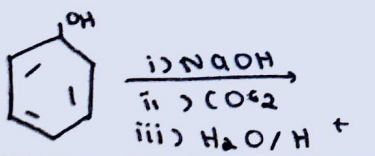


methyl red.



Phenolphthalein

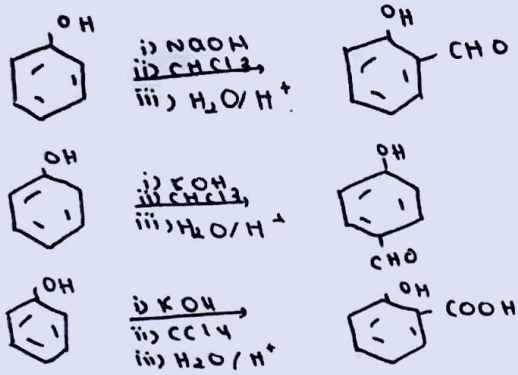
Kolbe-Schmidth Rxn:



i) NaOH
ii) CO_2
iii) H_2O/H^+

- if ortho position is blocked, go ahead with para.

Reimer-Tiemann Rxn (formylation)

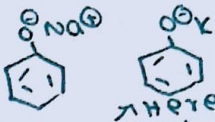


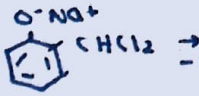
i) NaOH
$CHCl_3$
H_2O/H^+

ii) KOH
$CHCl_3$
H_2O/H^+

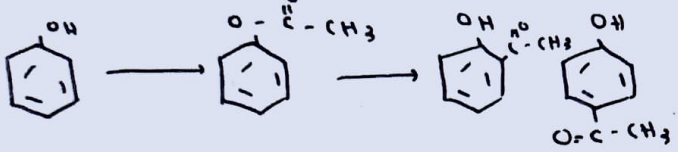
iii) KOH / NaOH
CCl_4
H_2O/H^+

electrophile :-
carbene $:C(Cl)Cl$
→ (neutral)





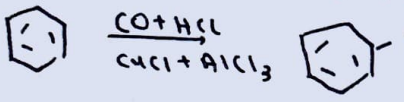
Fries rearrangement.



1) i) $CH_3-\overset{O}{\overset{\|}{C}}-Cl$
ii) $AlCl_3$
2) $AlCl_3$

ortho → Thermo dynamic pro.
para → kinetic pro

Gattermann Koch Rxn: → fails with $-NH_2$, $-NO_2$, etc. (variation of F.C rxn)

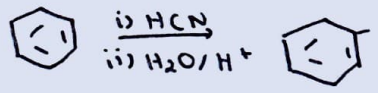


i) CO + HCl
ii) CuCl, $AlCl_3$

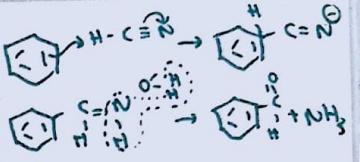
$CO + HCl \xrightarrow{CuCl} H-\overset{O}{\overset{\|}{C}}-Cl$ (unstable)

$H-\overset{O}{\overset{\|}{C}}-Cl \rightarrow H-C^{\oplus}=O$

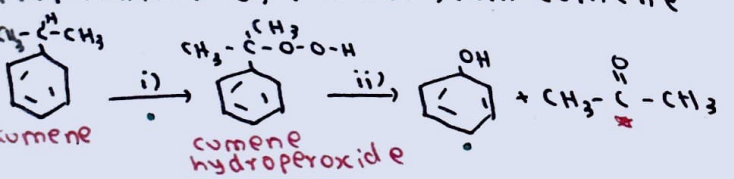
Gattermann Formylation → variation of F.C ∴ fails with $-NH_2$, $-NO_2$, etc.



i) HCN
ii) H_2O/H^+



Preparation of phenol from cumene



i) O_2 (air)
ii) H_2O/H^+

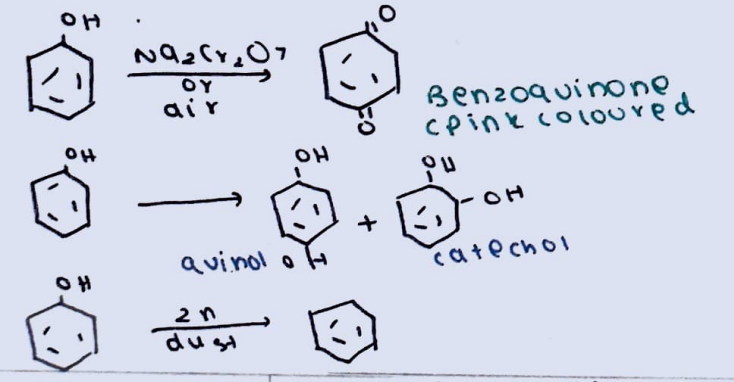
i) first step is FRSR
ii) Ph migrates in 2nd step formation
migrating tendency ∝ e⊖ density.

Preparation of phenol from Benzene sulphonic acid.

i) conc H_2SO_4 / oleum (cor)
ii) NaOH, Δ (fusion)
iii) NaOH, — Na_2SO_3
iv) NaOH
v) H_2O/H^+

iii step occurs through the Benzyne mechanism

Oxidation and reduction of phenol



i) $Na_2Cr_2O_7$ / air

i) $K_2S_2O_8$

Elb's Reaction

i) Zn dust

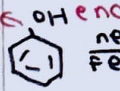
Litmus Test

also phenols

Blue → Red

Neutral $FeCl_3$ Test

(all compounds having enol give this test)



$[Fe(OC_6H_5)_3]$

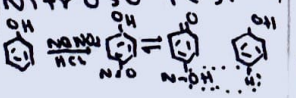
Phthalein dye test

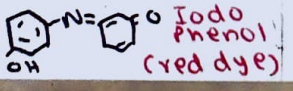
Phenol + Phthalic anhydride

⇒ Phenolphthalein

Basic → pink Acidic → ∅

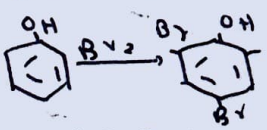
Liebermann Nitroso Test





Iodo Phenol (red dye)

Bromine water test

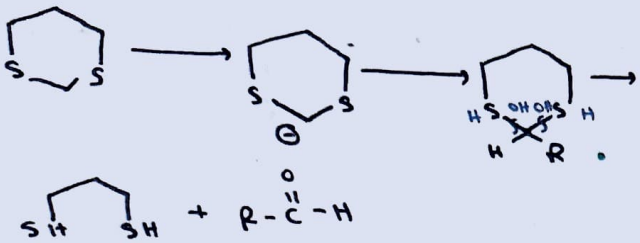


white ppt.

Carbonyl Compounds

Methods of preparation:-

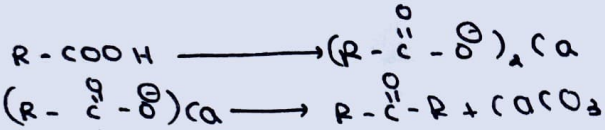
1). From 1,3-Dithiane



i) BuLi
ii) R-X
iii) H_2O/H^+

Thioacetal

2.) dry distillation of calcium salt of carboxylic acid



i) $Ca(OH)_2$
ii) $\Delta, -CaCO_3$

$CaCO_3$ gets deposited as a solid and carbonyl comp gets collected as gas.

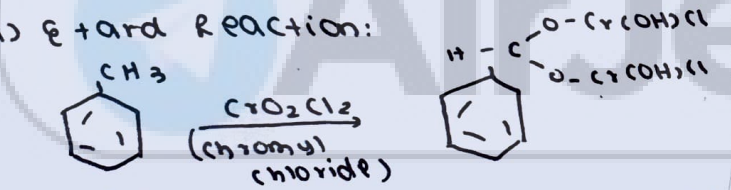
3.) Reaction of acylchloride with organometallic compound.

organometallic comp
→ dialkyl lithium cuprate (Gilmann's Reagent)
→ Dialkyl cadmium (R_2Cd)

Grignard reagent cant be used as the rxn won't stop at ketone and would be taken to alcohol.

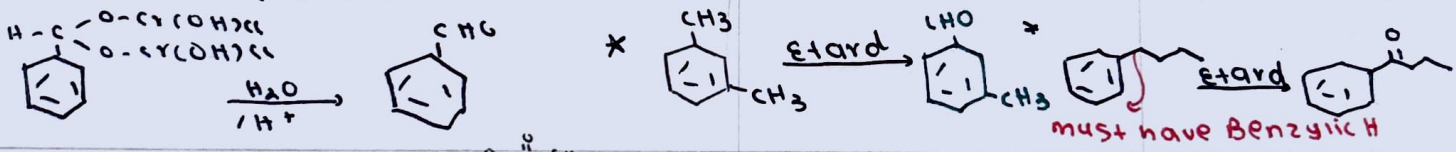
Preparation of Benzaldehyde:

a) Etard Reaction:



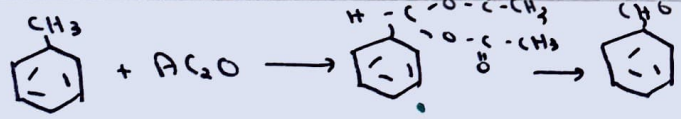
i) CrO_2Cl_2
ii) H_2O/H^+

- Rare reaction in which coordination (oxidation) no. of Cr is +4
- FRSR reaction



must have Benzylic H

b)

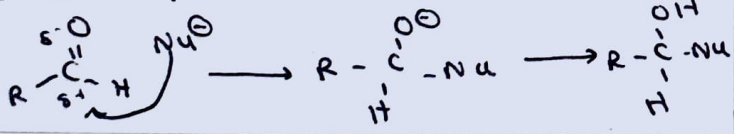


i) CrO_3
ii) H_2O/H^+

- Benzal diacetate

Chemical properties:

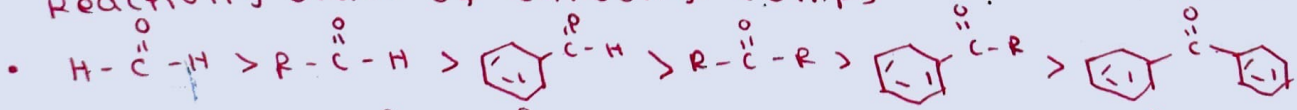
i) Nucleophillic addition rxn



first step → slow
second step → H_2O/H^+

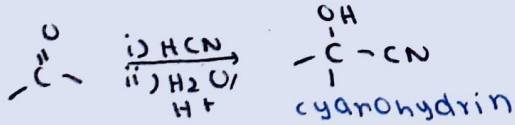
→ Tetrahedral intermediate

Reactivity order of carbonyl comps



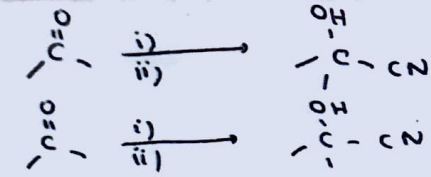
- Any cyclic ketone > open chain ketone

ii) Addition of HCN:



i) HCN
ii) H_2O/H^+

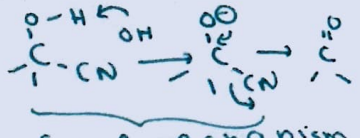
- This reaction is very slow in presence of pure HCl
- it is carried out in presence of NaCN, KCN or HCN with a small amount of base



i) NaCN ii) H_2O/H^+

ii) HCN/$OH^\ominus$ ii) H_2O/H^+

This rxn is reversible



E 1 cB mechanism

Reactions of Cyanohydrin:

1) RCN $\xrightarrow{\text{"}}$ Inter mediate $\xrightarrow{\text{"}}$ $R-\overset{O}{\overset{\|}{C}}-OH + NH_3$ ✱

$-CN \xrightarrow[\Delta]{H_2O/H^+} -COOH$

can also give
- H_2O/H^+
- H^+
- dilute acid

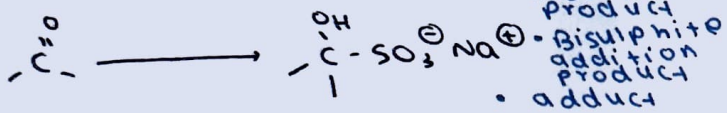
$H_2O/H^+ + \Delta$

Intermediate = $R-\overset{O}{\overset{\|}{C}}-NH_2$

ii) $R-CN \longrightarrow R-CH_2-NH_2$

H_2/Ni

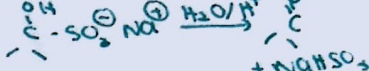
Addition of $NaHSO_3$:



- crystalline product
- Bisulphite addition product
- adduct

$NaHSO_3$

- rxn is reversible



- used for seperation and purification of aldehydes and ketones
- sterically hindered ketones don't give this rxn

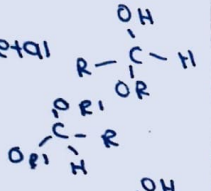
Addition of Alcohol:

$R-\overset{O}{\overset{\|}{C}}-H + R'OH \longrightarrow$ Hemiacetal (1 mole)

$R-\overset{O}{\overset{\|}{C}}-H + R'OH \longrightarrow$ acetal (2 moles)

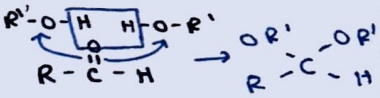
$R-\overset{O}{\overset{\|}{C}}-R + R'OH \longrightarrow$ Hemiketal (1 mole)

$R-\overset{O}{\overset{\|}{C}}-R + R'OH \longrightarrow$ ketal (2 moles)



for 1 mole alcohol :-

for 2 moles alcohol :-



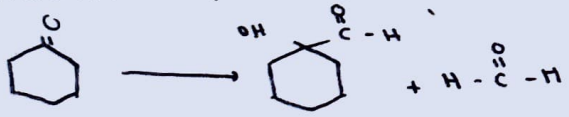
same with aldehydes and ketones

- All those rxns are done in presence of a dry acid
reason: aq acid will lead to hydrolysis c
- if treated with H_2O/H^+ they will all return to their starting materials
- Hemiacetals, Hemiketals

Aldehyde / Ketone + 2 moles alcohol

- Acetals, Ketals are stable in Basic medium
- Hemiacetals, Hemi ketals also go back to starting materials with $OH^\ominus$ medium
- Acetals are used as protecting groups in organic chemistry
- They are used to protect more reactive functional group in presence of less reactive functional group.
- only cyclic hemiacetals / ketals are stable can be seperated.

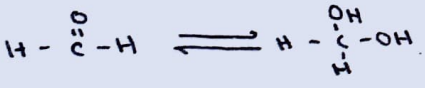
Addition of Acetylide ion:



i) $H-C\equiv C^\ominus Na^\oplus$
ii) H_2O/H^+
iii) H_2 / Pd-sulphur
iv) O_3
v) Zn-H_2O

Both OH and C^{1p}-H in the product will not react due to formation of highly strained ring.

Addition of water:

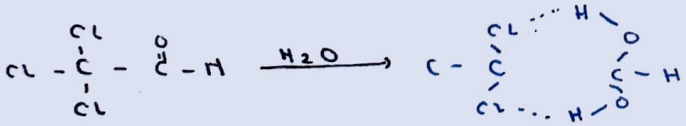


H_2O/H^+

most reactive ⇒ formaldehyde

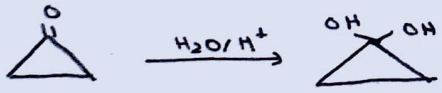
Some compounds actually forming stable hydrates:

i) Chloral:



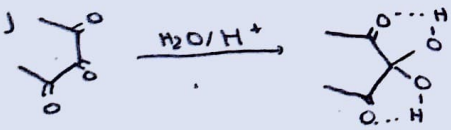
Stable due to intra molecular H-bonding.

ii)



Ring strain of cyclopropane ketone is very high (60° strain)

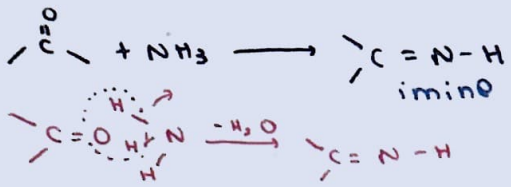
iii)



H-bonding

Nucleophillic Addition followed by Elimination:

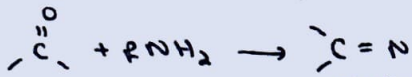
1) Reaction with ammonia



in presence of acid
ph: 4-6 (not too acidic)

- formaldehyde gives $>C=NH$ Imine
- aldehyde → aldimines
- ketones → ketimines

2) Reaction with 1° Amine ($R-NH_2$)

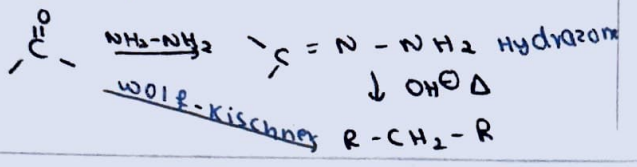


yellow in colour

3) Reaction of Hydroxyl amine (NH_2-OH)

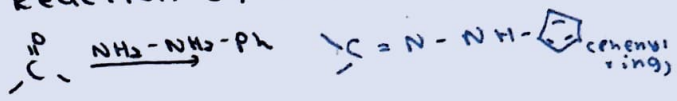
Aldoxime / Ketoxime

4) Reaction of Hydrazine (NH_2-NH_2)

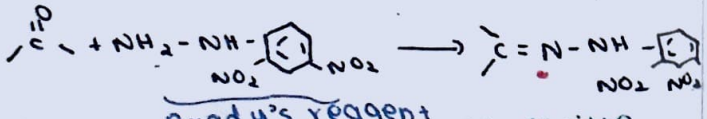


Wolff-Kischner: $R-CH_2-R$

5) Reaction of phenyl Hydrazine



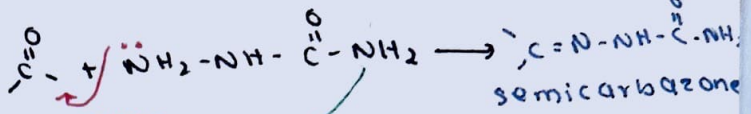
6) Addition of 2,4-dinitro phenyl Hydrazine



- Product ⇒ red
- This rxn is used to distinguish carbonyl compounds from other compounds.
- Known as Brady's test or 2,4 D-NP test.

Brady's reagent: 2,4-Dinitro phenyl Hydrazone

7) Addition of semi-carbazyde

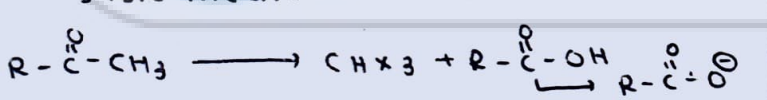


attacker

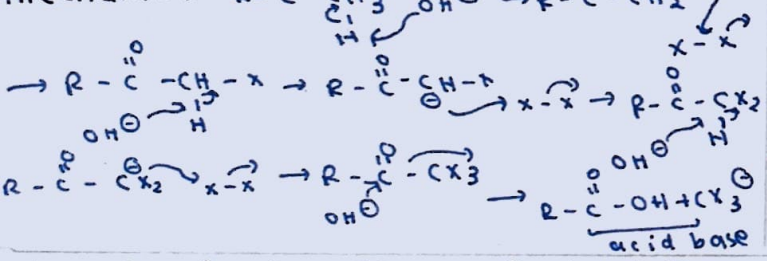
won't attack as its lone pairs are involved in resonance

Halogenation of Carbonyl compounds

a) Basic medium: (Haloform Rxn)



mechanism:



- Halogenation in presence of a base is known as base promoted halogenation. As base is consumed in this rxn.

- abstraction of α-H in base presence to form enolate ion, is R.D.S

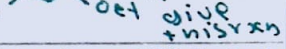
i) α-carbinols $R-\underset{OH}{CH}-CH_3$ only compounds having
ii) C_2H_5OH iii) $CH_3-\underset{OH}{CH}-CH_3$ $-C(=O)-CH_3$ can give this rxn
iv) Resorcinol
v) active meth compound

i) $NaOH + X_2$
or
$NaOX$
$X = Cl, Br, I$

vi) Phloroglucirol
vii) $Ph-C(=O)-CH_2-X$, $R-C(=O)-CH_2-X$, $R-C(=O)-CX_3$

- $R-C(=O)-CH_3$
- $R \neq NH_2, OH, OR, O-C(=O)-R$
- $R = H$, alkyl, Ph, $-C(=O)-R$, $-C(=O)-H$

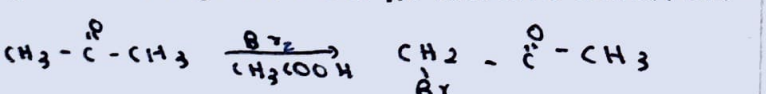
Haloform rxn:-
Iodoform test
CHX_3 → yellow



X does not give this rxn

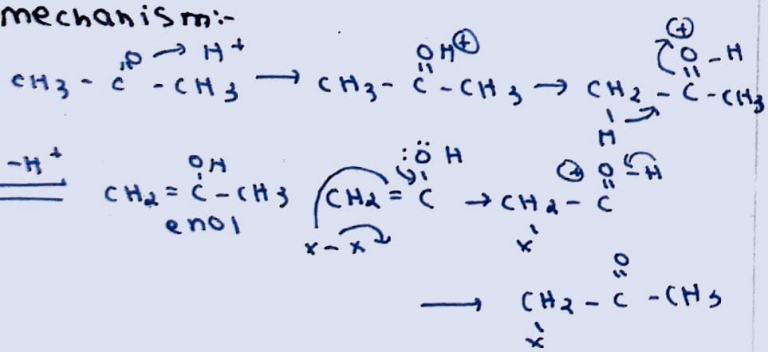
- multiple halogenation takes place in basic medium due to H becoming more acidic

b) α-Halogenation in acidic medium:



X_2 and acid

mechanism:-



- in acidic medium, multiple halogenation never takes place due to very unstable +ve charge

- halogenation occurs on longer alkyl grp incase of unsymmetrical ketone due to more stability of enol form and more α-H

Aldol condensation

• reaction only given by aldehydes and ketones having α-Hs.

Basic medium: self-aldol condensation / cross-aldol condensation

i) dil Alkali (10%)
ii) Δ, $-H_2O$

condensation goes through with E1cB.

self:

aldol rxn: $2CH_3-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\underset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H$

β-hydroxy aldehyde or aldol

condensation: $CH_3-\underset{OH}{CH}-CH_2-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-CH=CH-\overset{O}{\overset{\|}{C}}-H$

α-β-unsaturated carbonyl compound

Simple method:

$CH_3-\overset{H}{\overset{|}{C}}=\boxed{O\ H-\overset{H}{\overset{|}{C}}-}\ \overset{O}{\overset{\|}{C}}-H \rightarrow CH_3-CH=C-\overset{O}{\overset{\|}{C}}-H$

remove O from E^+ and 2H from $Nu^\ominus$

• The concept of removing α-Hs is because it is more acidic due to resonance. But if there is a more acidic Hs remove that.
• aldehydes → ↑ E^+
ketones → ↑ $Nu^\ominus$

Cannizzaro rxn:

• given by aldehydes w/o any α-H

self-canizzaro:-

$2H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{[R]} CH_3OH$; $2H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{[O]} H-\overset{O}{\overset{\|}{C}}-O^\ominus\ Na^\oplus$

disproportionation rxn

i) 50% alkali (< 50%)
∴ → Δ
rate :- $k[H-\overset{O}{\overset{\|}{C}}-H]^2[OH]^1$

E^+ aldehyde → oxidised
less E^+ aldehyde → reduced
KIE ⇒ applicable.

self-cannizzaro with > 50% alkali

$H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{OH^\ominus} H-\underset{OH}{\overset{O^\ominus}{C}}-H \xrightarrow{OH^\ominus} H-\underset{O^\ominus}{\overset{O^\ominus}{C}}-H$ ⇒ di anion

$H-\underset{O^\ominus}{\overset{O^\ominus}{C}}-H \rightarrow H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{slow} H-\overset{O}{\overset{\|}{C}}-O^\ominus + H-\underset{H}{\overset{O^\ominus}{C}}-H \xrightarrow{H_2O} H-\overset{O}{\overset{\|}{C}}-O^\ominus + CH_3OH$

i) > 50% alkali

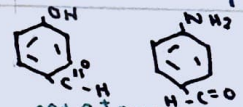
Rate :- $k(H-\overset{O}{\overset{\|}{C}}-H)^2(OH)^2$
4th order rxn.

Benzil-Benzillic acid rearrangement

$Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow{OH^\ominus} Ph-\underset{Ph}{\overset{OH}{C}}-\overset{O}{\overset{\|}{C}}-OH$

$Ph-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow{OH^\ominus} Ph-\underset{OH^\ominus}{\overset{O}{C}}-\overset{O}{\overset{\|}{C}}-Ph \rightarrow Ph-\underset{Ph}{\overset{O^\ominus}{C}}-\overset{O}{\overset{\|}{C}}-OH \rightarrow Ph-\underset{Ph}{\overset{OH}{C}}-\overset{O}{\overset{\|}{C}}-O^\ominus \xrightarrow{H_2O/H^+} Ph-\underset{Ph}{\overset{OH}{C}}-\overset{O}{\overset{\|}{C}}-OH$

Note for cannizzaro: i) $CCl_3-\overset{O}{\overset{\|}{C}}-H$ — CCl_3 will leave as soon as OH attks

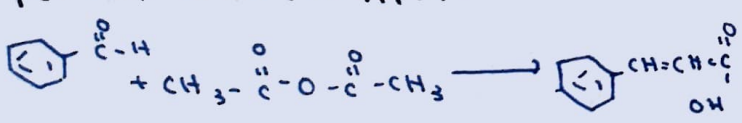


not E^+ enough

dont give cannizzaro

ii) $CH_3-\underset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-H$ doesn't give aldol gives cannizzaro.

Perkin condensation:



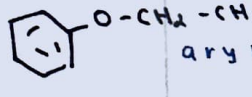
• acid anhydride having atleast two α-H with salt of carboxylic acid of sodium or potass

• condensation of aromatic aldehyde
• same way as aldol just hydrolyse end product.

Claisen rearrangement

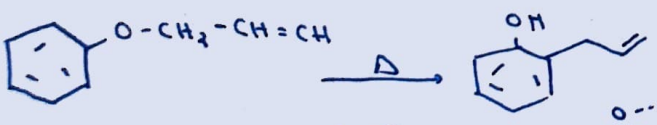
→ given by aryl allyl ethers and allyl vinyl ethers.

Reagent: Δ

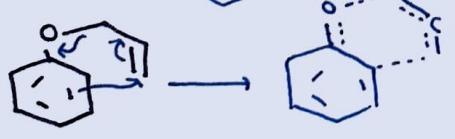


aryl vinyl ether.

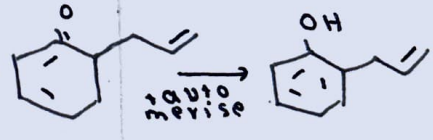
$CH_2=CH-O-CH_2-CH=CH_2$
allyl vinyl ether



mechanism



six membered cyclic T.S



Claisen-Ester condensation

self:

$2CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \longrightarrow CH_3-\underset{OC_2H_5}{\overset{O}{\overset{\|}{C}}}-CH_2-\overset{O}{\overset{\|}{C}}-$

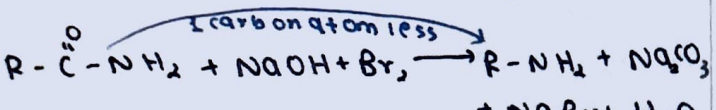
$CH_3-\overset{O}{\overset{\|}{C}}-O-\boxed{C_2H_5\ H}-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5$

C_2H_5ONa — salt should match with ester

Rxn is given by esters having α-Hydrogen.

Hoffmann Bromamide Rearrangement

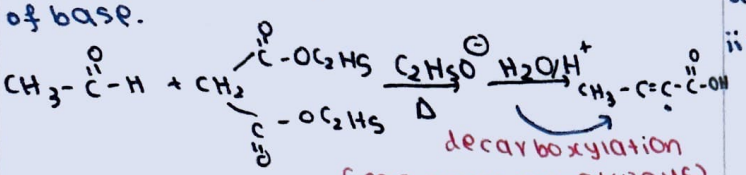


$NaOH + Br_2$ or $NaOBr$ or $KOBr$ or $KOH + Br_2$

- stable intermediate: $R-\overset{O}{\overset{\|}{C}}-N$ → Nitrene
- migration → R.D.S
- more $e^{\ominus}$ rich comp will migrate. stereochem doesn't change during migration.

Knoevenagel condensation

condensation of aldehydes and ketones with active methylene comps in presence of base.



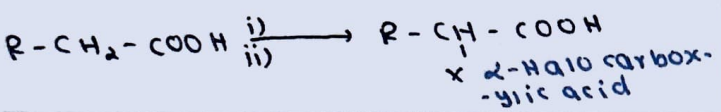
i) salt matching active meth-comp

ii) H_2O / H^+ (hydrolysis)

- crotonic acid
- follow same trick as aldol condensation by taking acidic H from active meth-comp and then hydrolysis.

Hell-Volhardt-Zelinsky Rxn:

This rxn is given by carboxylic acids having α-H.



i) Red P + X_2 (Br, Cl)

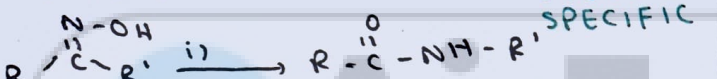
ii) H_2O / H^+

Halogenation can take place on the remaining H (even more acidic) check the options.

Beckmann Rearrangement:

in this Rxn, Ketoximes on treatment with dehydrating agents are converted to N-substituted amides

STEREO SPECIFIC



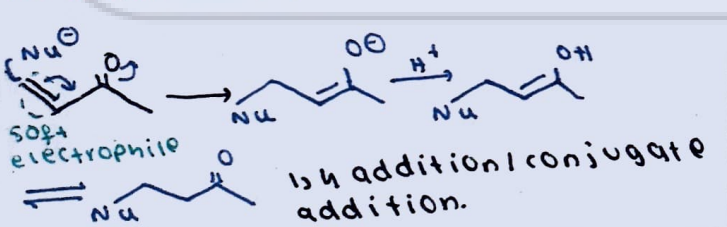
i) dehydrating agent such as conc H_2SO_4, H_3PO_4, etc.

- alkyl group ANTI to OH group will migrate from C → N.
- aldoximes on treatment with D.A give Nitriles

Conjugated addition to α-Bunsaturated carbonyl compounds:

conjugate addition is a characteristic of alkenes conjugated with EWG

An alkene conjugated with an E.W.G behaves as E⊕ centre. Generally alkenes → Nu⊖



1,4 addition / conjugate addition.

1,2 addition / Direct addition

Factors affecting 1,4 and 1,2 addition:

Reaction conditions:

conjugate addⁿ	Direct addⁿ
• Thermodynamically controlled	• Kinetically controlled
• product formation slow and irreversible	• product formation fast and reversible
• more stable	• less stable
• major at high temp	• major at low temp
• long Rxn hours	• short rxn hours.

Structural factor:

more reactive comps like aldehydes, acid chlorides: hard electrophiles

less reactive comps like ketones, amides, esters: soft electrophiles

Nature of Nucleophile

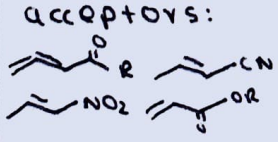
- Hard $Nu^{\ominus}$: more $e^{\ominus}$ den, small, more E.N.

Hard	Border line	Soft
$H^{\ominus}$, $F^{\ominus}$, ROH, $RO^{\ominus}$, $R-NH_2$, $LiAlH_4$ (always 1,4 addⁿ)	$CN^{\ominus}$, $R-NH_2$, R_2NH	RSH, PH_3, $FS^{\ominus}$, R_2CuLi, $NaBH_4$

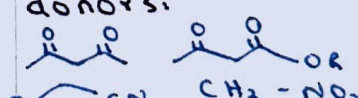
Michael Addition

1,4 addition of reactive carbanions (ennaates / active meth comps) to α-Bunsat. comps.

acceptors:

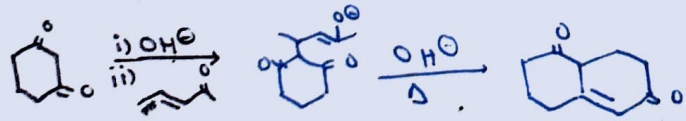


donors:

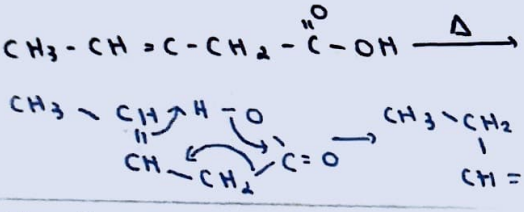


Michael addition followed by intramolecular aldol condensation : Robinson annulation

eg:



Decarboxylation of β-γ unsaturated comp.

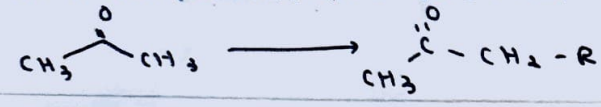


→ Δ

→ use mechanism

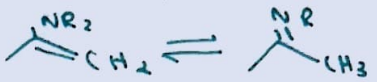
Stork-Enamine Rxn:

This rxn is used for alkylation of carb-only compounds at α-position.

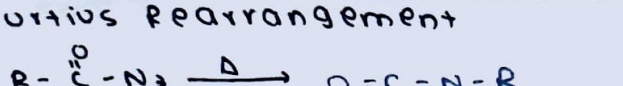


→ $R-NH_2$, H^+
→ R-X

This rxn involves formation of enamine

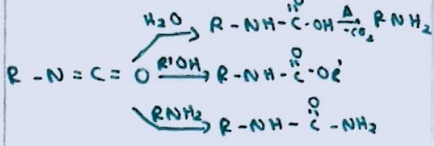


Curtius Rearrangement

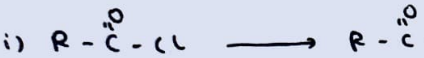


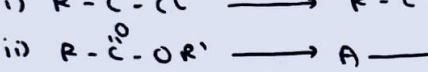
Acyl azide

Δ



Preparation of Acyl azide

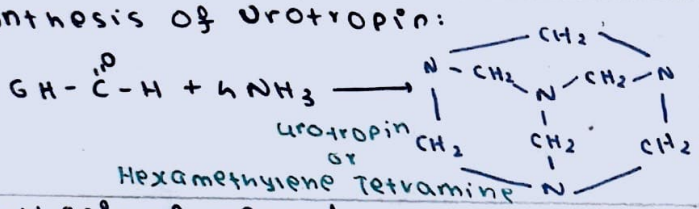
i) 

ii) 

i) NaN_3

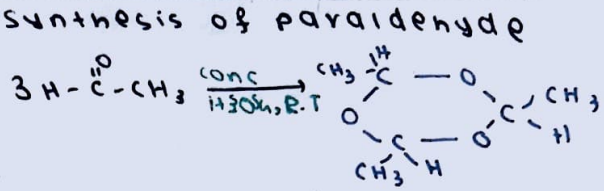
ii) $NH_2 \xrightarrow[-NH_2]{} HNO_2$

Synthesis of Urotropin:

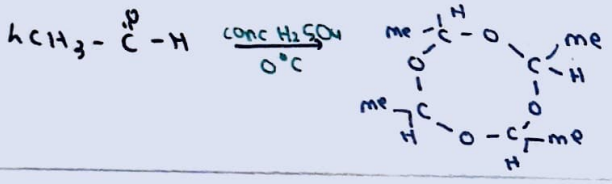


Urotropin or Hexamethylene Tetramine

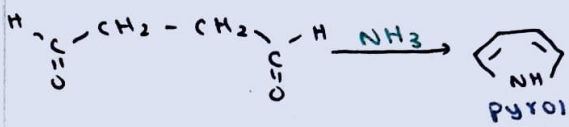
Synthesis of paraldehyde



Synthesis of metaldehyde:



Synthesis of pyrrol:

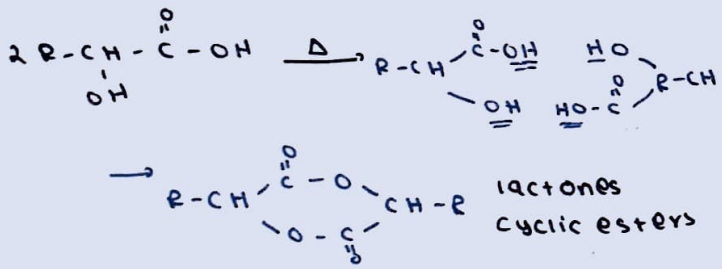


Pyrol

Carboxylic Acids and Derivatives:-

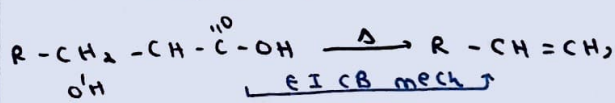
→ Dehydration → Decarboxylation
→ Dehydration + Decarboxylation

Heating of α-Hydroxy carboxylic acid



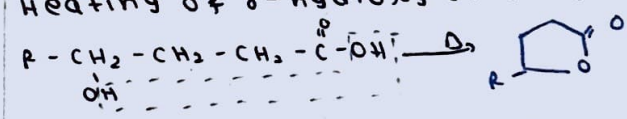
lactones
cyclic esters

Heating of β-hydroxy carboxylic acid



E1cB mech

Heating of γ-hydroxy carboxylic acid



Esterification:

① Carboxylic acid + alcohol → Ester + water

- reversible
- can only take place in acidic m.
- acid acts as a catalyst
- cant take place in basic medium

mech 1:- OH → acid H → alcohol

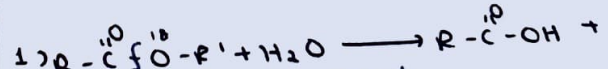
mech 2:- OH → alcohol H → acid

* → only when stable carbocation from alcohol.

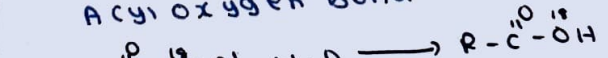
② Acid chloride $\xrightarrow[\text{Pyridine}]{\text{Alcohol}}$ Ester + HCl

③ Acid anhydride + Alcohol → ester + acid.

Ester hydrolysis:

1) 

Acyl oxygen bond

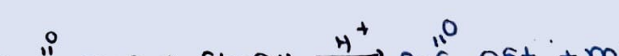
2) 

Alkyl oxygen bond

Reversible → acidic medium

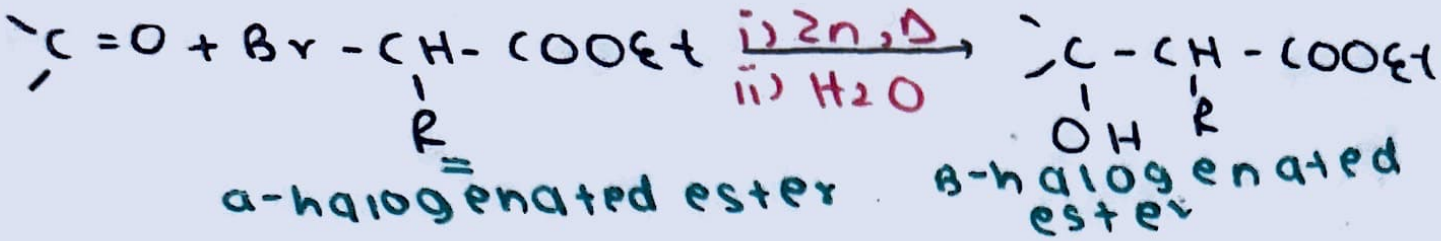
Irreversible → basic medium

Trans-Esterification:



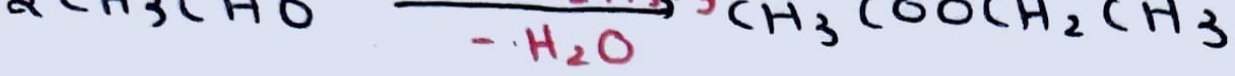
converting one ester to other

Reformatsky Reaction:



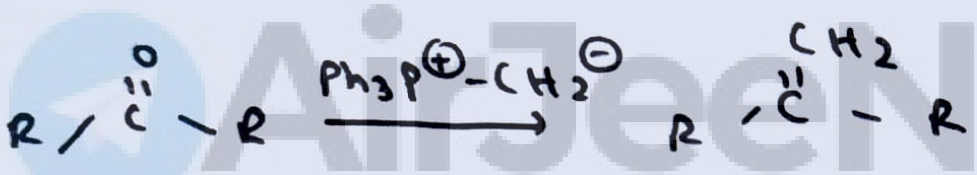
Tischenko Reaction:

forming esters from aldehyde.

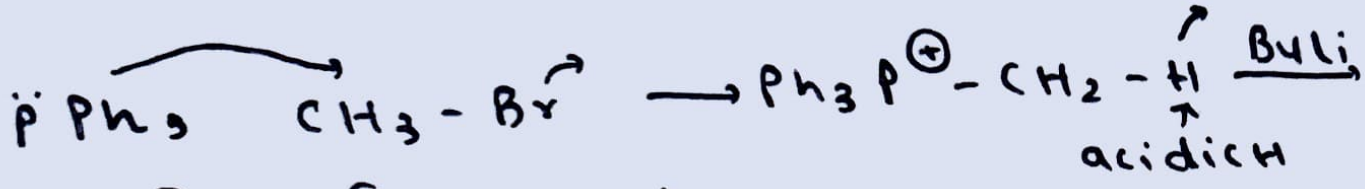


Wittig Reaction:

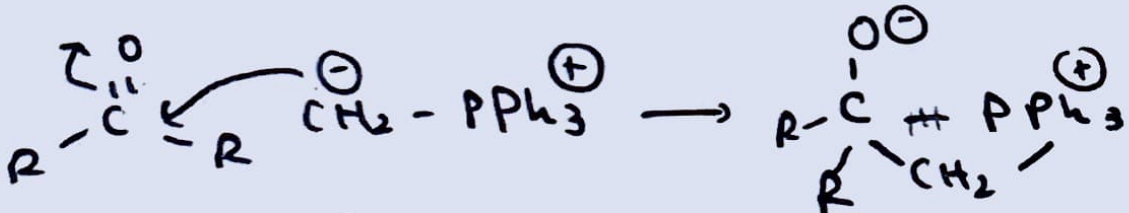
carbonyl ⟶ alkene

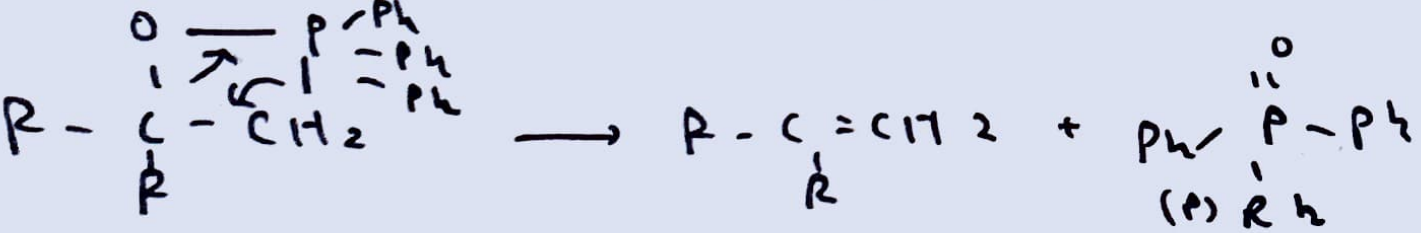


formation of ylide:



$Ph_3P^{\oplus}-CH_2^{\ominus}$ ⟶ ylide





Amide + P_2O_5 → Nitrile

Amines

Hoffmann Ammonolysis:

$R-X + NH_3 \longrightarrow R-NH_2 + R_2-NH + R_3N + R_4N^{\oplus}X^{\ominus}$

This rxn is carried out in presence of small amount of base to neutrq. HX.

$CH_3I \xrightarrow{NH_3} A \xrightarrow{OH^{\ominus}} B$

$NH_2-CH_2+HI \xrightarrow[\text{acid+base}]{} CH_2-NH_3^{\oplus}I^{\ominus} \xrightarrow{OH^{\ominus}} CH_3-NH_2$

Schmidt Rearrangement:

$R-\overset{O}{\overset{\|}{C}}-OH + HN_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-N_3$

Acyl azide → Then, Curtius.

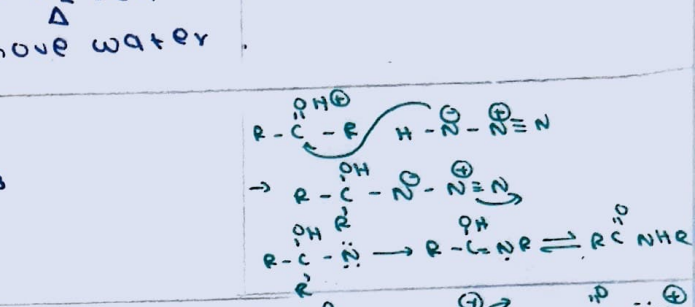
conc. H_2SO_4, Δ, remove water

Hydrazoic acid

Schmidt Rearrangement in Ketones:

$R-\overset{O}{\overset{\|}{C}}-R \longrightarrow R-\overset{O}{\overset{\|}{C}}-NHR$

HN_3



Cosen rearrangement:

$R-\overset{O}{\overset{\|}{C}}-NH-OH \longrightarrow R-NH_2$

conc H_2SO_4

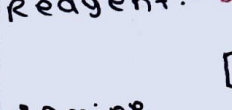
$R-\overset{O}{\overset{\|}{C}}-NH-OH_2^{\oplus} \longrightarrow R-\overset{O}{\overset{\|}{C}}-\ddot{N}H^{\oplus}$

$R-\overset{O}{\overset{\|}{C}}-\ddot{N}:$ Nitrene now

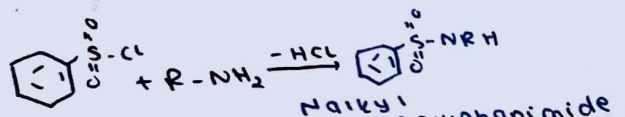
Hoffmann Bromamide D.

Hinsberg Test: used to distinguish as well as seperate 1°, 2°, 3° amines.

Reagent:- Benzene sulphonyl chloride

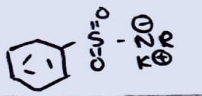


1° Amine



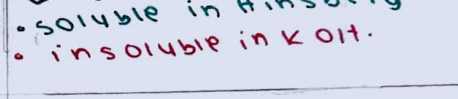
Naiky! Benzene sulphanimide

KOH



- soluble in Hinsberg's
- soluble in KOH

2° Amine



- soluble in Hinsberg
- insoluble in KOH.

3° Amine:

NO rxn.

Mustard oil Test: used to distinguish blw primary, secondary and tertiary ami.

Reagent:- CS_2,

1° Amino:-

$R-NH_2 + CS_2 \longrightarrow \underbrace{R-N=C=S}_{\text{isothiocyanates (mustard oil like smell)}} + H_2S \xrightarrow{HgCl_2}$ (HgS Black ppt)

2° Amine:-

$R_2NH + CS_2 \longrightarrow R_2N-\overset{SH}{\overset{|}{C}}=S$

- soluble in CS_2
- But no mustard oil smell

Δ → no rxn.

3° Amine:-

→ No rxn

→ not soluble

Carbyl Amine Test:

$R-NH_2 + CHCl_3 + \underset{(alc)}{KOH} \xrightarrow{\Delta} R-NC + KCl + H_2O$

- $CHCl_3$ + alcoholic KOH
- only given by 1° Amine
- carbenes formed
- R-NC has foul smell.

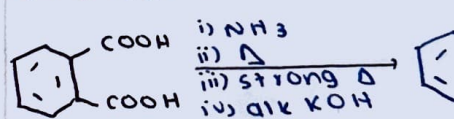
Rxn with HNO_2:-

1° Amine $\xrightarrow{HNO_2} [R-N_2^{+}] \longrightarrow R-OH + N_2\uparrow$

2° Amine $\xrightarrow{HNO_2} R-\underset{R}{N}-N=O$ yellow-oily liquid

3° Amine $\xrightarrow{HNO_2}$ NO rxn

Gabriel Pthalamide Rxn:



i) NH_3
ii) Δ
iii) strong Δ
iv) alk KOH
v) R-X
vi) H_2O/H^{+}

$+ NH_2-R$

no aromatic amines can be prepped like this.

Rxn with Tildon's Reagent

$R-NH_2 \xrightarrow{NOCl} [R-N_2^{+}] \longrightarrow R-Cl + N_2\uparrow$

Arndt-Eistert Rxn:

$R-COOH \xrightarrow[\text{ii) } CH_2N_2 \text{ iii) } Ag_2O \text{ iv) } H_2O/H^{+}]{\text{i) } SOCl_2} R-CH_2-COOH$

(carbene is formed)

Hydrolysis of Isonitrile

$R-N\equiv C \xrightarrow[H^{+}]{H_2O/} R-NH_2 + H-\overset{O}{\overset{\|}{C}}-OH$

Oxidation of Amines:

1° Amine [O]

$R-CH_2-NH_2 \xrightarrow{[O]} R-C(=NH)-H$

$R-\underset{R}{\overset{H}{C}}-NH_2 \xrightarrow{[O]} R-\underset{R}{C}=NH$

$R_3C-NH_2 \xrightarrow{[O]} R_3C-NO_2$

2° Amine:

$R-NH-R \xrightarrow{[O]} R-\overset{R}{\overset{|}{N}}-\overset{R}{\overset{|}{N}}-R$

$R-NH-R \xrightarrow{\text{per acid}} R-\underset{R}{N}-OH$

3° Amine: $\xrightarrow{[O]}$ no rxn

$\xrightarrow[\text{acid}]{\text{per}} R_3N \longrightarrow O$

Reductive Amination carbonyl → Amines

$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NH_3} R-\overset{NH}{\overset{\|}{C}}-H \xrightarrow[Pt]{H_2/} R-CH_2-NH_2$

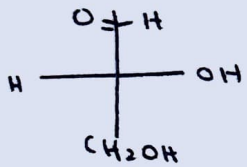
Biomolecules

Carbonydrates: according to old definition 'Hydrates of carbon'
because of general formula: $C_n(H_2O)_n$

limitations: • not are carbonydrates can be represenent in that formula
• There are compounds which are not carbonydrates that don't fit in this formula
eg:- Sucrose → X in formula
rhamanose → $C_6H_{12}O_5$ X formula
HCHO → $C(H_2O)$ ✓ formula

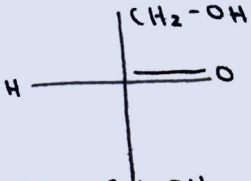
modern definition: Polyhydroxy aldehy--des or ketones / compounds which produce polyhydroxy aldehydes or ketones upon hydrolysis.

Aldotriose:



D-(+)-> Glyceraldehyde

Ketotriose:



Dihydroxy ketone.

NOte:- Ketone group is present on second carbon.

• all naturally occuring carbohydrates → +D configuration

Carbonydrates

- Sugar
  - • sweet in taste
  - • crystalline.
  - • water soluble
  - monosaccharides
  - oligo saccharides
- Non-sugar
  - • not-sweet
  - • Amorphous
  - • Insoluble in water
  - ↓ polysaccharide

Monosaccharides: • a carbonydrate that can't be hydrolysed further.

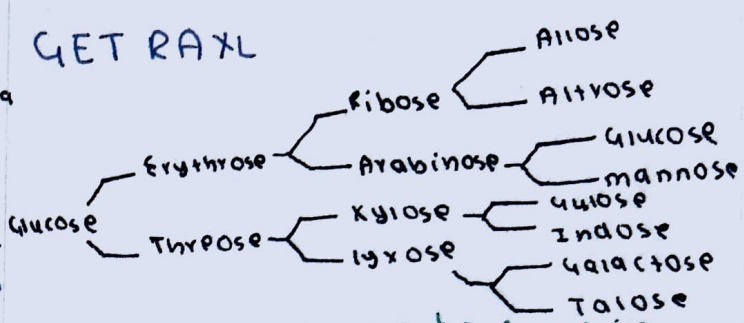
• about 20 monosaccharides are known to occur in nature
eg: glucose, fructose, ribose.

Oligosaccharides: yield two-ten mono saccharides on hydrolysis.

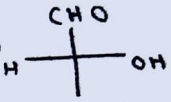
• The most common → dissaccharides
One molecule sucrose → 1 Glucose + 1 fructose
One mole maltose → 2 Glucose

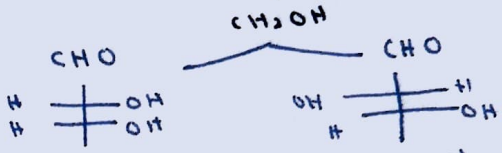
Polysaccharides: carbonydrates which yield a large number of monosaccharide units on hydrolysis.
• not sweet in taste.
ex:- starch, cellulose, glycogen, gums, etc.

GET RAXL



All altrome gladly make gums in giant tanks.

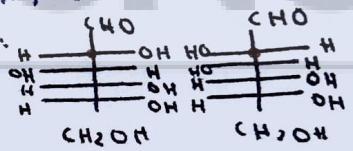
start from  glyceraldehyde (simplest sugar



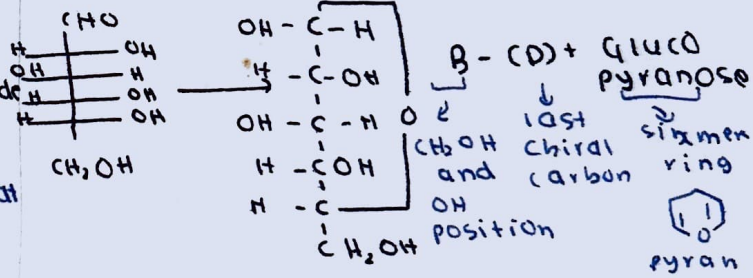
Erythrose Threose.

→ keep adding H—OH in similar way.

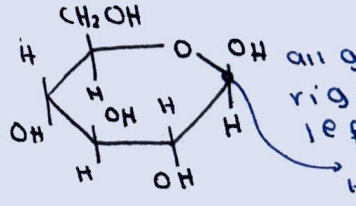
→ Epimers:
sugars which differ from each other in configuration only at one carbon.

eg:  C2 epimers.

→ Cyclic structure of Glucose:



α → CH_2OH and OH → diff side
β → CH_2OH and OH → same side

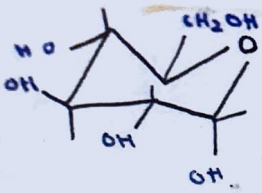


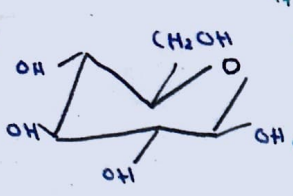
β-D-Glucopyranose.

→ α-D Glucopyranose and β-D Gluco--pyranose are anomers of each other

Two sugars having opp. configuration on anomeric carbon.

Chair form:



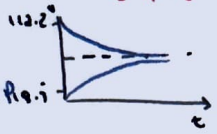


if OH is down, choose the pos, whether axial or equatorial, whichever is down.

α-D(+) Gluco-pyranose β-(D+)-Glucopyranose

→ Mutarotation:

α-D-GLP [α] = +112.2° β-D-GLP → [α] = +18.7°



α-D-GLP ⇌ (H₂O) open chain ⇌ β-D GLP

β-D GLP ⇌ (H₂O) open chain ⇌ α-D GLP

definition: when either anomer of Glucose in dissolved in water, the optical rotation of the solution changes and then become constant after some time.

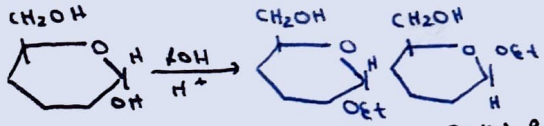
It occurs due to establishment of eq. blw two forms of Glucose.

α = 36.1 β = 64.1

All monosaccharides and disaccharide (except sucrose) → show mutarotation
→ reducing sugars.

Sucrose and polysaccharides:
→ don't show it
→ non-reducing sugar

→ Formation of Glycosidic bond:

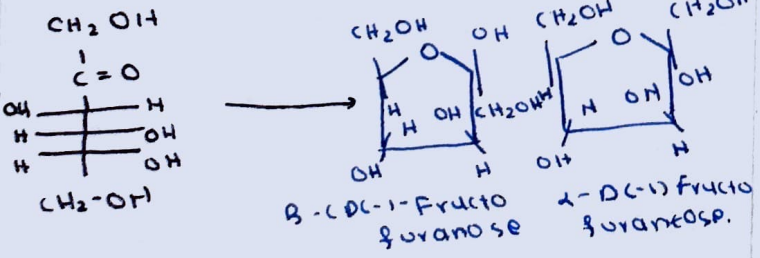


α-D Gluco Pyranose (hemiacetal sugar) → Ethyl α-(D(+)) Glucopyranoside (acetal sugar) + Ethyl β-(D(+)) Glucopyranoside (acetal sugar)

α > β instability

due to anomeric effect (Back bonding in empty p-orbital.

→ Cyclic structure of fructose:



β-(D(-)-Fructo furanose α-D(-) fructo furanose.

Fructose :-
- Ketonexose
- laevorotatory
- naturally exists as five membered ring

Preparation of Glucose:

i) Hydrolysis of sucrose (Inversion of cane sugar)

$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{invertase}]{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

sucrose (dextrorotatory) → glucose dextrorotatory + fructose laevorotatory

This hydrolysis can only take place in acidic medium.

dextrorotation of Glucose is < levorotation of fructose.

ii) Hydrolysis of starch.

$(C_6H_{10}O_5)_n \longrightarrow nC_6H_{12}O_6$

starch → glucose

Chemical properties of Glucose:

1.) Glucose $\xrightarrow[\text{/reducing agent}]{NaBH_4}$ $CH_2OH(CHOH)_4CH_2OH$ sorbitol

2.) $CHO(CHOH)_4CH_2OH \xrightarrow[OH^\ominus]{HCN}$ $CH(CN)OH(CHOH)_4CH_2OH$ Glucose cyanohydrin

$\xrightarrow{NH_2OH}$ $CH=N-OH(CHOH)_4CH_2OH$ oxime of glucose.

3.) oxidation of Glucose

$CHO(CHOH)_4CH_2OH \xrightarrow[\text{Tollens / Fehling's / Benedict's}]{Br_2 \text{ water}}$ $COOH(CHOH)_4CH_2OH$ Gluconic acid.

The sugars which reduce Tollen's reagent and Fehling's soln^n are known as reducing sugars → All monosacs. (Aldose, Ketose)

4.) Glucose $\xrightarrow[HNO_3]{conc}$ $COOH(CHOH)_4COOH$ [saccharic acid]

5.) Acetylation of Glucose.

Glucose → $(CH(O-\overset{O}{\overset{\|}{C}}-CH_3)_4CH_2-O-\overset{O}{\overset{\|}{C}}-CH_3$

6.) methylation of Glucose.

Glucose $\xrightarrow[Ag_2O \text{ or } Me_2SO_4]{MeI}$ $(H-C-OMe)_4CH_2OMe$ → not a reducing sugar as it is a ketal

7.) Glucose $\xrightarrow[(5 \text{ eq})]{HIO_4}$ $5O=C-OH + H-\overset{O}{\overset{\|}{C}}-H$

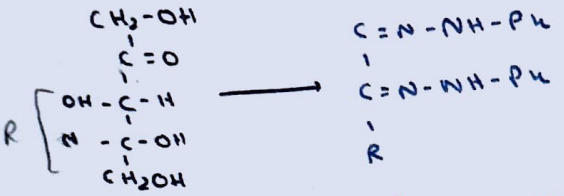
8) Glucose $\xrightarrow[+HI \text{ (4 moles)}]{Red\ P}$ n-hexane

9.) Glucose $\xrightarrow[(yeast)]{zymase}$ $2C_2H_5OH + 2CO_2\uparrow$

10) Glucose + phenyl Hydrazine

$O=C-H(H-C-OH)_4CH_2OH \xrightarrow[-NH_3]{3PhNH-}$ $H-C=N-NH-Ph$ $C=N-NH-Ph$ $(CHOH)_3$ CH_2OH Glucosazone/osazone of Glucose

Ozasone formation of fructose:



Osazone of glucose, mannose, fructose is the same.

Only reducing sugars form osazone

Osazone formation → Rxn of open chain structures.

→ Ene-diol Rearrangement / Epimerisation

Glucose, mannose, Fructose $\xrightarrow{OH^\ominus}$ Glucose + Fructose + mannose.

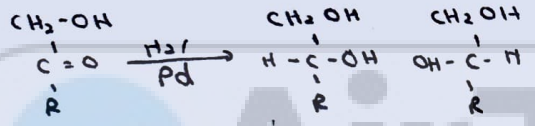
→ Chain elongation: (Killiani-Fischer synthesis)

Fructose: $\xrightarrow[ii)\ H_2O/H^+]{i)\ OH^\ominus, HCN} \xrightarrow[Pd.BaSO_4]{H_2} \xrightarrow{H_2O/H^+}$ Aldonexose + NH_3

→ Chain shortening:

Aldohexone:- $\xrightarrow[water]{Br_2} \xrightarrow[\text{Basic salt}]{Base} \xrightarrow{H_2O_2} \xrightarrow{Fe^{3+}}$ Aldo pentose

→ Reduction of Fructose:



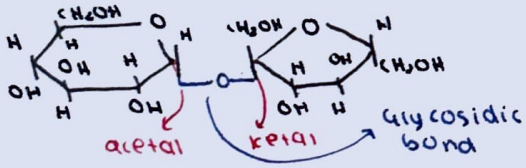
→ Disaccharides

i) Sucrose:

Sucrose

α-D Glucose — C_1-OH anomeric

β-D-Fructose — C_2-OH anomeric



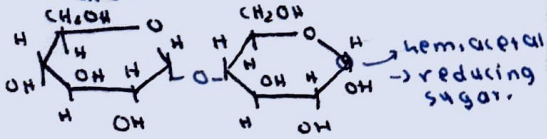
acetal, ketal, Glycosidic bond

ii) Maltose:

Maltose:

α-D Glucose — C_1-OH

α-D-Glucose — C_4-OH



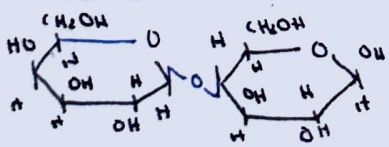
Hemiacetal → reducing sugar.

iii) Lactose:

Lactose:

β-D-Glucose — C_4-OH

β-D-Galactose — C_1-OH



iv) Cellulose: 2 β-D Glucose

(C_4-C_4) linkage

Polysaccharides

1.) Starch:

Starch

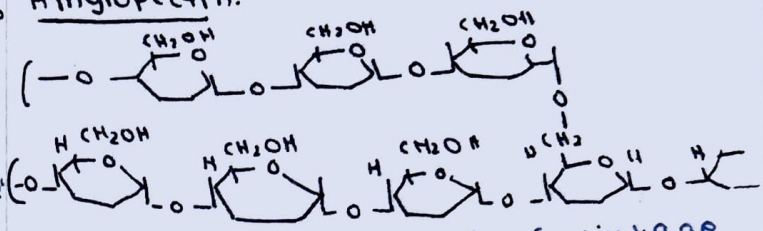
Amylose: 20:1, water soluble, linear polymer, violet coloured complex with I_2, less degree of polymerisation

Amylopectin: 80:1, water insoluble, Branched structure, Blue-black complex with I_2, more degree of polymerisation

Amylose: linear polymer of α-D Glucose

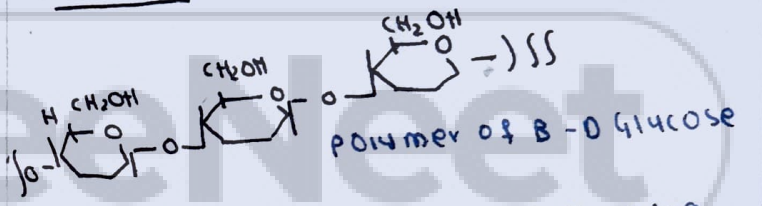
(C_1-C_4) linkage

Amylopectin:-



(28-30) units, C_1-C_6 linkage for branching

Cellulose:



polymer of β-D Glucose

Glycogen: Animal starch → Branching starts after 5-6 units of monomer

→ Tests for carbohydrates:

1) Molisch Test:-

→ given by all carbs

Reagent:- α-Naphthol + Ethanol / Resorcinol

- carbohydrate first dissolved in molisch reagent
- conc H_2SO_4 added dropwise
- Bluish-red ring is formed in the middle
- soln turns violet on standing.

2.) Barfoed Test:

used to distinguish b/w monosaccharides and disaccharides.

Reagent:- Cu(II) Acetate + AcOH

monosac $\xrightarrow{\text{within 2 min}}$ Cu_2O Brick red ppt.

Dis sac $\xrightarrow[\text{slower (10 mins)}]{\text{acid}}$ Cu_2O

$$R-\overset{O}{\overset{\|}{C}}-H + Cu^{2+} + 2H_2O \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + Cu_2O\downarrow$$

Chair form:

3.) Seliwanoff's Test:

Used to distinguish b/w aldose and ketose sugar.

Reagent:- Resorcinol + conc HCl

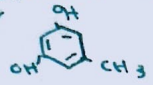
Ketose sugar ⟶ Cherry red

Aldose sugar ⟶ Faint pink (very slow)

4.) Bial's Test:

only used for pentose sugar.

Reagent:- Orcinol + $FeCl_3$ + HCl



Pentose sugar —reagent→ Blue colour (always)

Hexose sugar —reagent→ Red, green brown

5.) Iodine Test:-

Starch on treatment with Iodine produces deep blue colour.

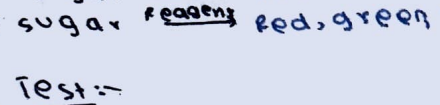
Amino Acids

All naturally occuring acids:-

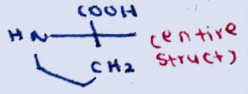
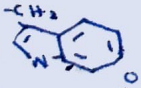
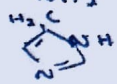
⟶ α-amino acid.

⟶ L-configuration

⟶ optically Active except Glycine.



(Neutral)

Name of amino acids:		- R	one letter code
1. Glycine	Side chain contains only carbons and Hydrogen	H	G
2. Alanine		$-CH_3$	A
3. Valine		$(H_3C)_2CH-$	V
4. Leucine		$(H_3C)_2CH-CH_2$	L
5. Isoleucine		$H_3C-CH_2-CH(CH_3)-$	I
6. Proline		 (entire struct)	P
7. Serine	Side chain has alcoholic group.	$HO-CH_2$	S
8. Threonine		$H_3C-CHOH$	T
9. Cysteine	Side chain consains Sulphur	$HS-CH_2$	C
10. Methionine		$H_3C-S-CH_2-CH_2$	M
11. Phenyl Alanine	Aromatic Amino acids	$C_6H_5-CH_2$	F
12. Tyrosine		$p(HO)-C_6H_4-CH_2-$	Y
13. Tryptophan			W
14. Asparagine	Side chain containing amide F.G	$H_2N-\overset{O}{\overset{\|\|}{C}}-CH_2-$	N
15. Glutamine		$H_2N-\overset{O}{\overset{\|\|}{C}}-CH_2-CH_2$	Q
16. Aspartic acid	Acidic Amino acids	$COOH-CH_2-$	D
17. Glutamic acid		$HOOC-CH_2-CH_2$	E
18. Lysine	Basic Amino Acids	$NH_2-(CH_2)_4-$	K
19. Arginine		$HN=C(NH_2)-NH-(CH_2)_3-$	R
20. Histidine		 Imidaz-ole ring.	H

Preparation of Glucose:

Essential Amino Acids

I ⟶ Isoleucine
LOVE ⟶ Lysine
LUCY ⟶ Leucine
VERY ⟶ valine
MUCH ⟶ methionine
PLEASE ⟶ Pheny Alanine
TRY ⟶ Tryptophan
TO ⟶ Threonine
HELP ⟶ Histidine
ARGENTLY ⟶ Arginine.

Non-essential Amino acids

ALMOST ⟶ Alanine
ALL ⟶ Aspartic acid
GIRLS ⟶ glycine
GO ⟶ Glutamine
CRAZY ⟶ cystiene
AFTER ⟶ Asparagine
GETTING ⟶ glutamic acid
TELE ⟶ Tyrosine
SERIES ⟶ serine
PROMOTION ⟶ proline

In aqueous medium, structure of amino acid will depend upon pH of medium

$-COOH \longrightarrow pKa = 2$

$-NH_3^{\oplus} \longrightarrow pKa = 9$

I $pH < 2$ ⟶ $R-CH(COOH)-NH_3^{\oplus}$

II $pH > 9$ ⟶ $R-CH(COO^{\ominus})-NH_2$

III $2 < pH < 9$ ⟶ $R-CH(COO^{\ominus})-NH_3^{\oplus}$ ⟶ zwitter ion

⟶ Isoelectronic point:

The pH at which there is no net charge on the amino acids, i.e amount of +ve charge = amount of -ve charge

I ⟶ For neutral amino acids:

$$PI = \frac{pKa \text{ of } NH_3^{\oplus} + pKa \text{ of } COOH}{2}$$

II ⟶ For acidic amino acids:

$$PI = \frac{pKa \text{ of } COOH + pKa \text{ of side chain}}{2}$$

III ⟶ For Basic amino acids:

$$PI = \frac{pKa \text{ of } NH_3^{\oplus} + pKa \text{ of side chain}}{2}$$

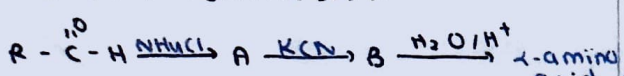
⟶ Electrophoresis: process of seperation of amino acids on basis of P.I values

⟶ Synthesis of Amino Acids:

1) From α-carboxylic acids

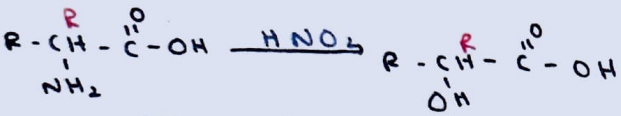
$R-CH_2-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[+Br_2]{Red\ P} A \xrightarrow{NH_3} B \xrightarrow[H^+]{H_2O} C \Rightarrow$ α-amino

2.) Strecker's synthesis:-



→ Chemical properties:

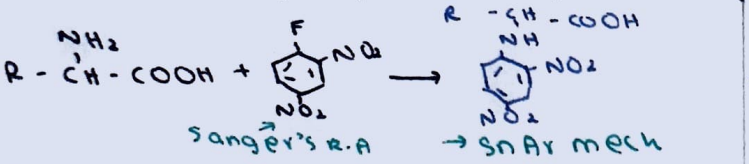
i) Rxn with HNO_2:



2 Inversion → 1 retention

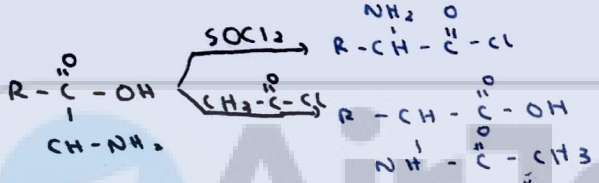
→ neighbouring group participation
→ 2 times S_N2
→ formation of unstable ring
→ extremely fast rate of rxn

ii) Rxn with sanger's reagent:



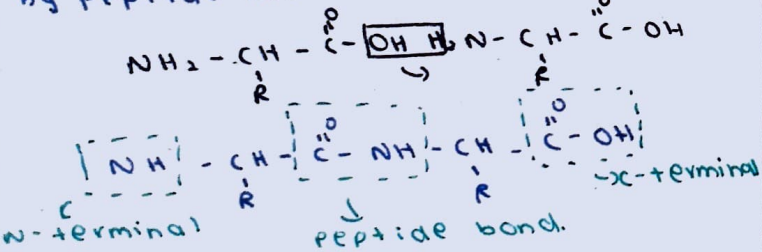
→ This rxn is used to detect n-terminals of protein.

iii)



Proteins:

Proteins are the polymer units in which various amino acids are joined together by peptide bonds

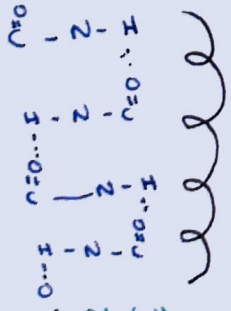


Structure of Proteins:

i) Primary structure:-
- simplest structure

ii) Secondary structure

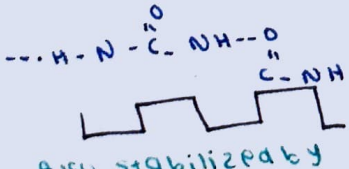
α-Helix structure



Stabilized by H-bonds

β-pleated structure

various polypeptide chains arranged in the form of sheets



Also stabilized by H-bonds.

iii) Tertiary structure

When α-Helical structure of proteins is further coiled, we get tertiary structure

→ also stabilized by H-bonds and bisulphide linkages

iv) Quaternary structure

arrangement of various polypeptide chains in proteins.

→ Denaturation of Proteins:

proteins having particular biological activity → native proteins
(only in quaternary structures)

Denaturation:-
Breakage of various H-bonds and di-sulphide linkages when subjected to change in pH.
After denaturation, protein loses its biological activity.

→ Fibrous proteins:-
- various polypeptide chains run parallel to each other.
- water insoluble proteins.

eg:- Keratin, Fibrin

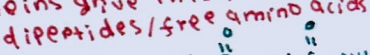
→ Globular proteins:
various polypeptide chains arranged in form of spheres.
- water soluble proteins.

eg: Albumin, Insulin.

Tests for Proteins:

i) Biuret Test → proteins give this test not dipeptides/free amino acids

Protein $\xrightarrow[\text{ii) NaOH}]{\text{i) } CuSO_4}$ violet colour



compounds containing any 2 of these F.G give +ve Biuret test

Proteins ✓ Amino acids ✗

ii) Xanthroproteic Test:
amino acids containing aromatic ring ✓

Protein $\xrightarrow[\text{HNO}_3]{\text{conc}}$ yellow $\xrightarrow{NaOH}$ orange

iii) Ninhydrin Test:
dye ↙
Protein → violet pink
2° Amines: Proline → yellow

iv) Sakaguchi Test:
used to detect arginine unit

Protein $\xrightarrow[\text{ii) NaOBr}]{\text{i) 2-Naphthol}}$ reddish brown

v) Millon's Test:
detects proteins with phenolic OH group

Protein $\xrightarrow[\text{acid}]{\text{nitrous}}$ white ppt $\xrightarrow{Hg(NO_3)_2}$ red ppt

Vitamins:

Fat soluble: → insoluble in water
A, D, E, K stored in liver and adipose (fat storing tissues)

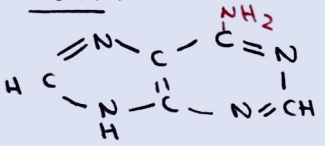
water soluble: must be supplied regularly as they get excreted readily. (except B_{12})

A_1 ⟶ xerophthalmia, and night blindness
B_1 ⟶ Beri-Beri ⟶ B_1 = Thiamine
B_2 ⟶ cheilosis, digestive disorders → B_2 → Ribo flavin
B_6 ⟶ convulsions B_6 → Puridoxine
B_{12} ⟶ pernicious anaemia
C ⟶ Scurvy C → Ascorbic acid.
D ⟶ Rickets, osteomalacia
E ⟶ Increase fragility of RBCs and muscular weakness.
K ⟶ Increased blood clotting time.

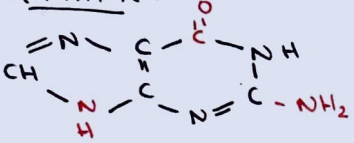
Nucleic acids:

↳ pentose sugar + Phosphoricacid + nitrogen base.

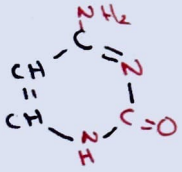
Adenine:



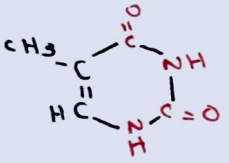
Guanine:



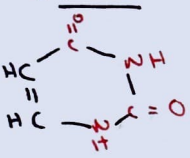
Cytosine:



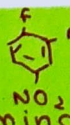
Thymine:



Uracil:

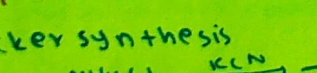


→ sanger's reagent:



used to detect n-terminals of of protein.

- strecker synthesis



- secondary structures: α-helix structure and β-pleated sheets.
- Fibrous proteins: → water I.S
  Keratin, fibroin
- Globular proteins:- water S
  Albumin, Insulin.

Practical Organic Chemistry

Organic Qualitative Analysis:

1.) Lassaign's Test: for detection of N, S, X

organic compound $\xrightarrow[\text{Heat}]{Na}$ molten mixture

i) dis H_2O → Lassaign's extract
ii) Filter

if N is present: $N + C + Na = NaCN$
if S is present: $S + Na \longrightarrow Na_2S$
if N, S both present: $Na + S + N + C \longrightarrow NaSCN$
if X is present: $Na + X \longrightarrow NaX$

Test for N:

$$NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6]$$
$$FeSO_4 \xrightarrow{H_2SO_4} Fe_2(SO_4)_3$$
$$Na_4[Fe(CN)_6] + Fe_2(SO_4)_3 \longrightarrow Fe_4[Fe(CN)_6]_3 \ *$$

Ferric ferrocyanidee (Prussian blue)

Test for S:

$$Na_2S + Pb(CH_3COO)_2 \longrightarrow PbS$$ (black ppt)
$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS] \ *$$ violet ppt

if N, S both present:

$$3NaSCN + FeCl_3 \longrightarrow [Fe(SCN)_3]$$ Blood red colour

Test for X:

$NaCl \xrightarrow{AgNO_3} AgCl \xrightarrow{NH_4OH}$ soluble
$NaBr \xrightarrow{AgNO_3} AgBr \xrightarrow{NH_4OH}$ sparingly sol.
$NaI \xrightarrow{AgNO_3} AgI \xrightarrow{NH_4OH}$ Insoluble

Nitrogen and sulphur must be removed before testing Halogen, as they interfere
done by adding dilute HNO_3

Detection of Phosphorous:

organic comp containing Phosphorous $\longrightarrow Na_2O_2 \longrightarrow Na_3PO_4$

$$Na_3PO_4 \xrightarrow{HNO_3} H_3PO_4$$
$$H_3PO_4 + (NH_4)_2SO_4 + HNO_3 \longrightarrow (NH_4)_3PO_4 \cdot 12MoO_3 + NH_4NO_3$$

canary yellow ppt *

Organic Quantitative Analysis

Estimation of carbon and hydrogen:

organic compound $\xrightarrow[\Delta]{CuO}$ products

$C \xrightarrow[\Delta]{CuO} CO_2$
$H \xrightarrow[\Delta]{CuO} H_2O$

CO_2 (absorbs CO_2) $\xrightarrow{KOH}$ $KOH + CO_2$ ↑ y gm; $H_2O \xrightarrow{\text{anhy } CaCl_2}$ $CaCl_2 + H_2O$ ↑ b g; x gm, a gm

44 g CO_2 → 12 g C
(y − x) g → ? $\frac{12}{44}(y-x)$ (mole concept)

Estimation of Nitrogen:

i) Kjeldahl's method
can't be used when:- i) Nitrogen in ring ii) N attached to O $-N=N-$ iii) In azo comps

organic compound $\xrightarrow[H_2SO_4]{conc.}(NH_4)_2SO_4 \xrightarrow{NaOH} NH_3$

Duma's method for estimation of N:

$C_xH_yN_z \xrightarrow[\Delta]{CuO} CO_2 + H_2O + N_2 + \text{Oxides of N}$ (Cu)

$CO_2, H_2O, N_2 \xrightarrow{\text{conc KOH}} H_2O, N_2 \xrightarrow{\text{anhy } CaCl_2} N_2 \rightarrow PV = nRT$

Carius method for P, S, X:

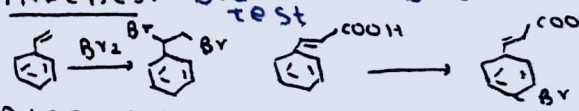
For P:-
org comp $\xrightarrow{HNO_3} H_3PO_4 \xrightarrow[\text{mix}]{\text{magnesia}*} Mg(NH_4)PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + NH_3$
* $MgCl_2 + NH_4Cl + NH_4OH$
222 g $Mg_2P_2O_7$ → 62 g P (magnesium pyro phosphate)
x g → ? $\frac{62}{222}x$ — $Mg_2P_2O_7$: x gm

For S:-
org comp $\xrightarrow{HNO_3} H_2SO_4 \xrightarrow[BaCl_2]{\text{excess}} BaSO_4 \rightarrow$ x gm

For X:-
org comp + $AgNO_3 \longrightarrow AgX \rightarrow$ x gm

Tests of Functional groups:

Alkenes: • Br_2 water • Bayer test



Alcohols:

• sodium metal test (self exp).
• CAN Test ($(NH_4)_2Ce(NO_3)_6$):
Alcohols + CAN → red colour ↓ disapps after some time
Note: Phenols + CAN → Brown-Black (not considered a test)
• $K_2Cr_2O_7$ Test:

$$R\text{-}CH_2\text{-}OH + Cr_2O_7^{2-} \longrightarrow R\text{-}COOH + Cr^{3+}$$
orange → green

Halogens

i) Bielstien's Test
org comp + Cu → CuX_2 (green flame)
→ Type of Halogen can't be detected
→ urea, Thiourea ✓
ii) Alcoholic $AgNO_3$
Alkyl halide which can form stable $C^{\oplus}$ → AgX

Amines

using diethyl oxalate
$R\text{-}NH_2$ → solid comp due to H-bond
$R_2\text{-}NH$ → liquid
$R_3\text{-}N$ → X reacn

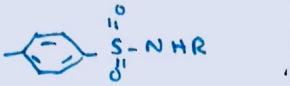
Ethers

i) Iodine soln
Ethers + I_2 soln → violet due to complex form.
ii) Ziesel-Alkoxy method
Ether + conc HI → Alkyl Iodide + HgCl₂ → orange ppt

Chemistry in Everyday Life

Drugs:
- low molecular mass (100 - 500 u)
- most drugs used as medicines are potential poisons.
- "use of chemicals for therapeutics ⇒ chemotherapy.

Pharmacological effects:-
- analgesics → pain killing effects
- antiseptics → killing or arresting growth of microorganisms

Chemical Structures:
Sulphonamides have:- 

Molecular Targets:
Drugs usually interact with carbs, lipids, proteins, nucleic acid.

Drug - Target Interaction:
enzymes :- biological catalysts
communication systems:- receptors
carrier proteins: carry polar molecules across cell-membrane.
Nucleic acids: coded genetic info for cell
Lipids, carbs: structural parts of cell memb.

Catalytic enzyme of actions:
i) I function: Hold substrate in place
↳ through ionic bonds, H-bond, van-der vaal.

ii) II function: provide f.g that will attack the substrate

Drug-Enzyme Interaction:
Basically drug vs enzyme

i) Competitive inhibitors: Drug takes place of substrate in the active system.

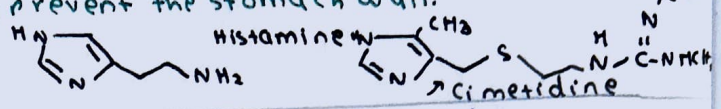
ii) Drug gets into the "allosteric site", which changes the shape of active site

Receptors as Drug Targets:
- messages b/w two neurons are communicated through certain chemicals
- These chemicals are recieved at the binding sites of receptor proteins.
- To accomodate a messenger, shape of receptor site changes
- Drugs that bind to receptor site and inhibit its natural function → antagonists.
- Drugs that mimic the natural messenger by switching on receptor, → agonists.

Therapeutic Action of Different Drugs

Antacids:
excessive hydrogen carbonate can make the stomach alkaline and trigger the secretion of more acid
- metal hydroxides → insoluble → better as it doesn't increase pH above neutrality
- They only treat symptoms, not the cause

Breakthrough → Histamine
- Histamine, secretion of pepsin and hydrochloric acid. stimulates
- Drug Cimetidine (Tegamet) was designed to prevent the stomach wall.



Antihistamines:
potent vasodilator
- smooth muscle in bronchi and gut → contract
- other muscles such as blood vessel walls → relax.
- Histamine is responsible for nasal congestion associated with common cord and allergic response to pollen.

eg:- Brompheniramine (Dimetapp)
Terfenadine (seldane)

"why dont antihistamines affect acid secretion in the stomach"
antiallergic and antacid drugs work on different receptors.

Tranquilizers: neurologically active drugs
- essential component of sleeping pills
- if level of noradrenaline is low for some reason, signal-sending activity ↓ ∴ ⇒ depression.
- antidepressant drugs inhibit the enzyme which catalyse the degradation of noradrenaline

Analgesics: ⟺ non-narcotic (non-addictive) / narcotic
- reduce or abolish pain without causing impairment of consciousness, mental confusion, incoordination or paralysis.

→ non-narcotic:-
examples:- aspirin, paracetamol.

→ aspirin inhibits synthesis of prostaglandins which stimulate inflammation in tissue
- also relieve skeletal pain due to arthritis
- also antipyretic
- prevent platelet coagulation ∴ good in prevention of heart atk.

→ narcotic:-
morphine * in poisonous doses :- stupor, coma, convulsions, death
also called opiates

Antibiotics: low toxicity ✓✓
"an antibiotic now refers to a substance produced partly/wholly by chemical synthesis which in low conc inhibits or destroys microorga-

- German biologists investigates Arsenic based structures for syphillis
- The first elective antibacteria agent, Prontosil.

Bactericidal	Bacteriostatic
Penicillin	Erythromycic
Aminoglycoside	Tetracycline
Ofloxacin	Chloramphenol

Braad spectrum: Ampicillin, Amoxycillin, Chloramphenic
narrow spectrum: Penicillin vancomycin, ofloxacin.
Aysidazirine → toxic towards certain strains of cancer cells

Antiseptics:
dettol: chloroxylenol + terpineol
tincture of iodine:- 2-1. percent soln of Iodine in alcohol.
Boric acid for eyes.
0.2 % phenol → antiseptic
0.1 % phenol → disinfectant
chlorine (0.2 to 0.4 ppm) and also SO_2 in low conc → disinfectants

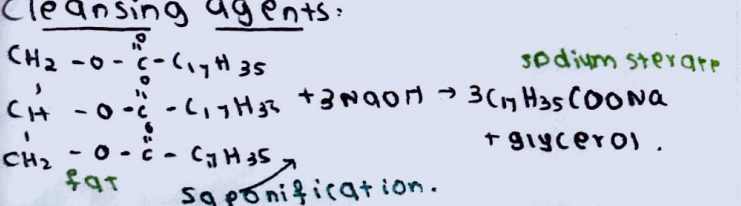
- **Antifertility drugs:**
  - essentially a mixture of synthetic estrogen and progesterone derivatives.
    - ↳ suppresses ovulation.
  - eg: Norethindrone (norestrol, ethyle-strad-iol.)
    - ↳ the estrogen derivative used is -

- **Artificial sweetening agents:** (550 times sweeter than cane sugar)
  - saccharin: ortho-sulphoben-zimide
  - aspartame: 100 times sweeter than sugar
    - ↳ limited to cold food and drinks
  - alitame: controlling sweetness of food is difficult.
  - sucralose: trichloro derivative of sucrose resembles sugar and tastes like it

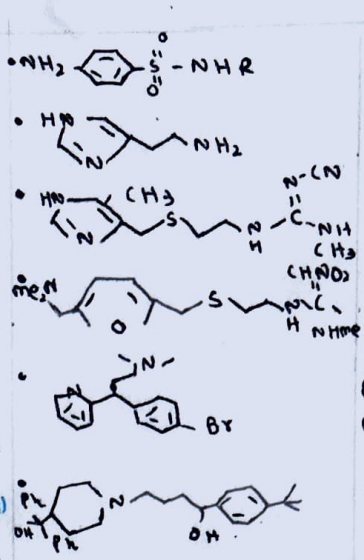
- **Food Preservatives:** (most common: table salt, sugar, vegetable oils and sodium benzoate.)
  - prohibit microbial growth.
  - salts of sorbic acid and propanoic acids

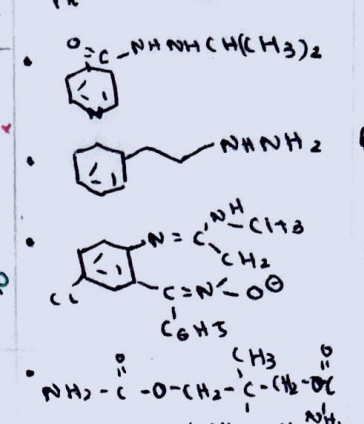
- **Antioxidants in Food:**
  - Butylated hydroxy toulene and butylated hydroxy anisole. → added to butter.
    - ↓
    - sometimes these both are used with citric acid.
  - sulphur dioxide and sulphite are useful anti-oxidants for wine and beer, sugar syrups and cut, peeled, dried fruits.

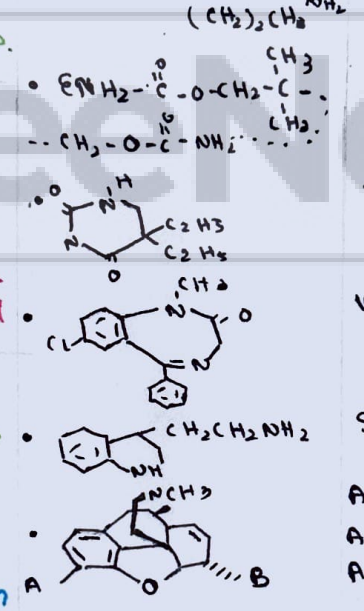
Cleansing agents:

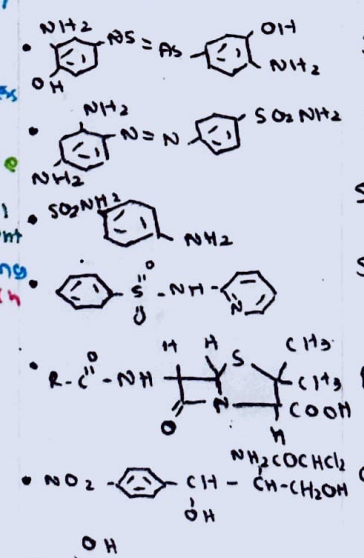


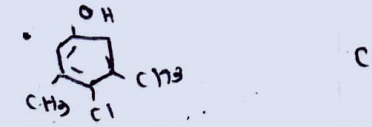
- only sodium and potassium salts are soluble in water and used for cleaning purposes.
- potassium soaps are soft to skin.
- Toilet soaps: better grade fats + to remove excess alkali
- Soaps floating in water: heating tiny air bubbles before hardening.
- Transparent soaps: made by dissolving soap in ethanol and the evaporating excess solvent
- Shaving soaps: contain glycerol to prevent drying. rosin is added, forming sodium rosinate which lathers well.

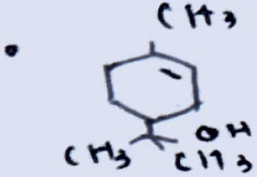


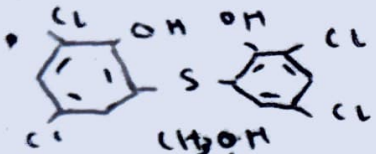


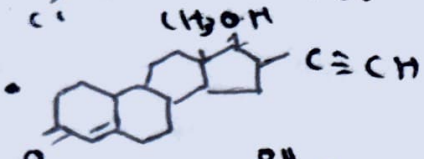


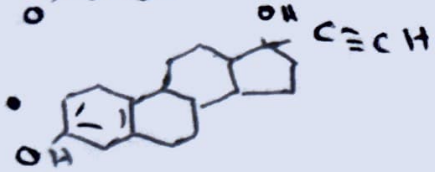






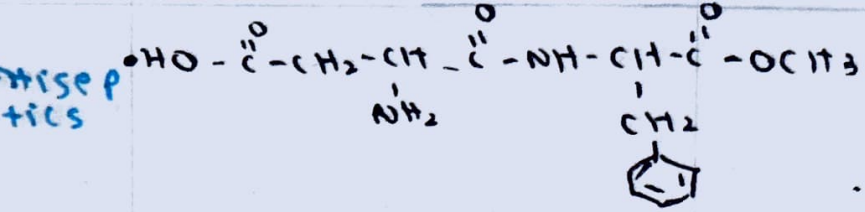




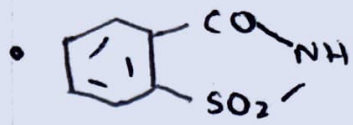


Terpineol.
Bithionol.
} Antiseptics

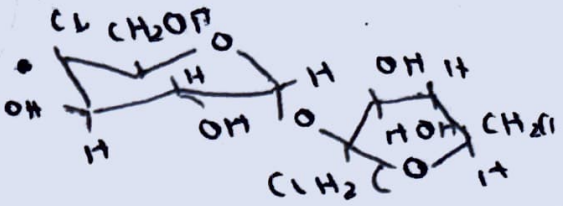
Norethindrone
Ethynlestradiol.
(Novestrol)
} Antifertility drugs



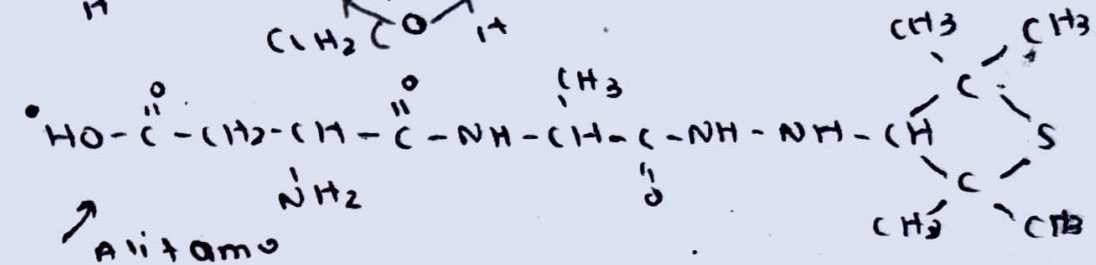
Aspartame



Saccharin



Sucralose

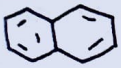


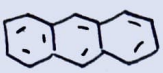
Alitame

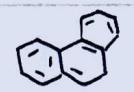
Low conc → Antiseptics

Common Names

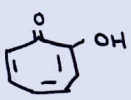

Benzene

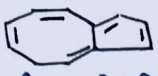

Napthalene


Anthracene


Phenathrene


Tropone


Tropolone

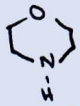

Azulene


THF

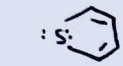

Piperidine


Pyran


Pyrrolidine


morpholine


Furan


Thiophene

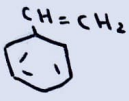

Pyrrol

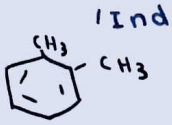

Pyridine

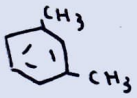

Benzopyrol / Indole


Chloro Benzene

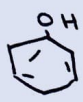

Toulene

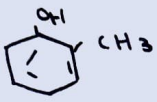

Styrene

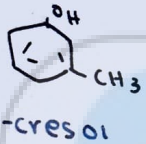

O-Xylene

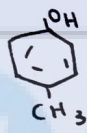

m-xylene


p-xylene

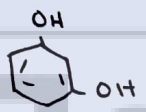

Phenol / carbolic acid


O-Cresol

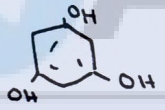

m-Cresol


p-Cresol


Catechol

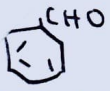

Resorcinol

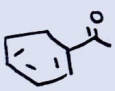

Quinol / Hydraquinone

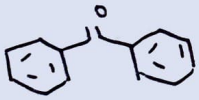

Phloroglucinol

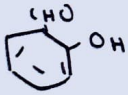

Anisole


Phenetol

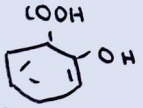

Benzaldehyde / oil of Bitter almonds

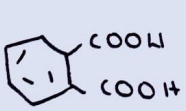

Acetophenone


Benzophenone


Salicaldehyde


Benzoic acid


Salicylic acid


Pthalic acid

Isophalic acid

Terpthalic acid

Acetyl Salicylic acid or Aspirin.

Methyl Salicylate / Oil of wintergreen

Benzo nitrile

Benzoyl Chloride

Benzamide

Acetanilide

Paracetalmol

Phthalic annydride

Sulphanilic acid

Orthanilic acid

Anthranilic acid

Saccharine

α-Napthol

β-Napthol

Coumarine

Isopropyl Benzene / Cumene

O-Toluidine

Nitro benzene / oil of mirbane

O-phenylene diamine

Mesitylene

Caprolactum

Mesityl oxide

Trinitro toulene

→ Gammaxene
→ Lindane
→ 6,6,6
→ Benzene Hexachloride

Pyragallol

Methyl orange

Methyl red

Phenolpthalein

Iodo phenol

Benzoquinone

Hinsberg reagent
Benzene Sulphonyl chloride

→ Carboxylic acids:

HCOOH - Formic Acid

CH_3COOH - Acetic acid

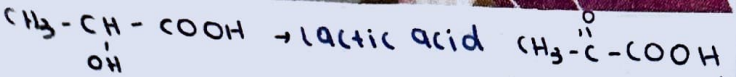
CH_3-CH_2COOH - Propionic acid

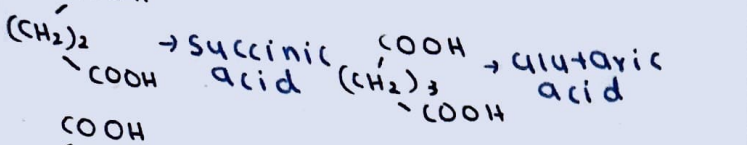
$CH_3CH_2CH_2COOH$ - Butyric acid

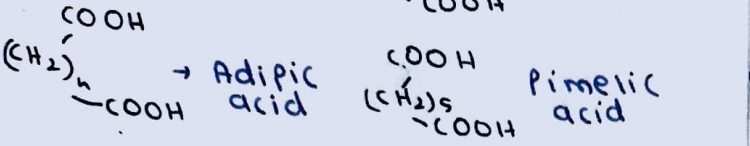
$CH_3CH_2CH_2CH_2COOH$ - valeric acid

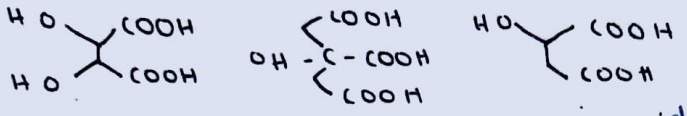
$CH_3CH_2CH_2CH_2CH_2COOH$ - caproic acid

$CH_3CH_2CH_2CH_2CH_2CH_2COOH$ - Enanthic acid





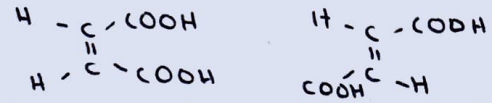


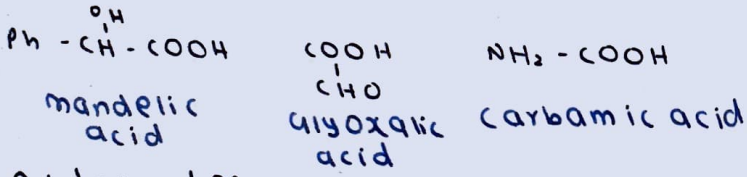


$CH_2 = CH - COOH$ ⇒ Acrylic acid

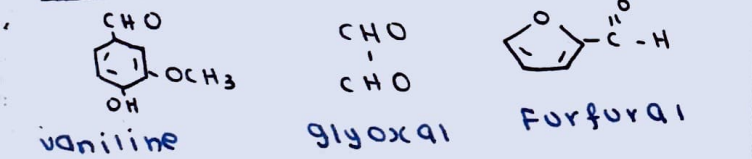
$CH_3 - CH = CH - COOH$ ⇒ Crotonic acid

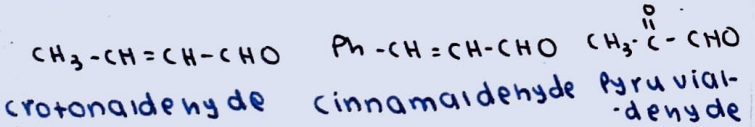
$Ph - CH = CH - COOH$ ⇒ Cinnamic acid

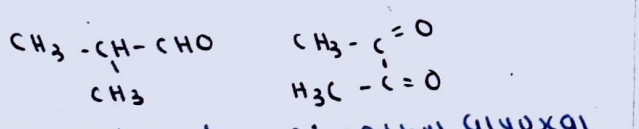




Aldehydes:







Miscellaneous Names:

CH_4 - marsh gas

$CH_2 = C = CH_2$ → Allene

$CHCl_2 - CHCl_2$ → westron

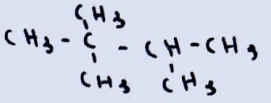
$ClCH = CCl_2$ → westrosol

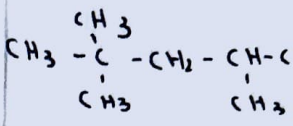
$CH_3-C(=O)-CH_2-C(=O)-OEt$ ethyl acetoacetate or acetoacetic ester (AAE)

$CH_2 = CH - CN$ → Acrylonitrile or vinyl cyanide

CH_3OH → wood spirit

$CH_3 - CH_2 - OH$ → grain alcohol





Polymers

Classification:

→ Based on: **Source**

- **Natural**: cellulose, natural rubber, Gutta percha, starch, etc
- **Semi synthetic**: • vulcanised rubber • cellulose acetate (rayon) • cellulose nitrate (Gun cotton)
- **Synthetic**: • Nylon • polythene

→ Based on: **Structure**

- **Linear**: →no branching →closely packed →high density high tensile strength → All fibres
- **Branched**: →Branches of linear chain →poor packing →low density and tensile strength → L.D.P, Amylo-pectin
- **Cross-linked**: →cross links blw polymers. →extremely hard. →very high tensile strength → Bakelite → vulcanised rubber.

→ Based on: **mode of polymerisation**

- **Chain growth / Addition**: →no elimination of small molecule
  - Homopoly: same-same, polythene
  - copolymers: diff, Styrene Butadiene Rubber
- **condensation / step-growth polymer**: →small molecules such as H_2O, ROH eliminated

eg:- Nylon-6,6

→ Based on: **intermolecular forces:**

a) **Elastomers:** → vanderwaal forces

acquired when stress is applied.

→ High elasticity - less tensile strength
eg:- Buna-S, Buna-N, SBR, Natural rubber

b) **Fibres:** → H-bonding
- very high tensile strength eg: Nylon 6,6

c) **Thermo plastics:**
Intermediate intermolecular forces such as dipole-dipole
These polymers can be melted and recasted multiple times.
eg: Polythenes, PVC (Polyvinyl chloride)

d) **Thermosetting polymers:**
→ contain crosslinks
→ can only be melted once and after recasted become infusible
eg:- Melanine, Bakelite.

mech of chain growth polymerisation:

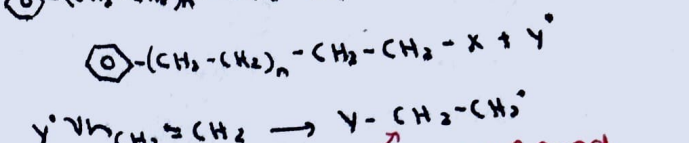
→ free radical initiators like (peroxide, O_2)

Steps: →chain initiation
→chain propagation
→chain termination

1) The two end groups donot affect the physical properties of polymer if chain insufficiently large.

→chain termination can also occur by disproportionation

2) **chain transfer agent:**



CCl_4 → general chain transfer agent

3) **chain inhibitors** → To stop the growth of chains.
ex:- phenol, Aniline, Benzoquinone

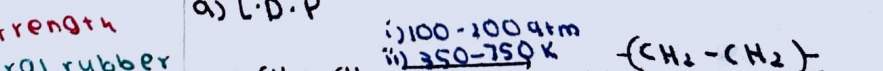
→ **cationic polymerisation:**
→proceeds via carbocation intermediate
→ Lewis acids like ($BF_3 + H_2O$) used.
How to end chain?
1st way:- adding $Nu^{\ominus}$
2nd way:- By elimination

→ **Anionic polymerisation:-**
→occurs in presence of $nu^{\ominus}$ (strong)
→active site can't terminate itself.
→ It always remains.

→ **Examples:**

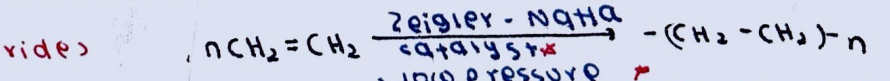
1) Polythene — low density / High density

a) L.D.P



→ Highly branched
→ chemically inert.
→ Insulator of electricity
→ Tough, Hard and Flexible
→used in making toys, squeeze bottles, etc.

b) H.D.P



→ Linear structure
→ Chemically inert
→ Harder than L.D.P
→used for making buckets, dustbins

2) Teflon:

$n(CF_2=CF_2) \xrightarrow[\text{catalyst: per sulphate}]{\text{polymerisation}} -(CF_2-CF_2)_n-$

tetrafluoro ethane — Teflon

3) Poly-acrylo nitrile

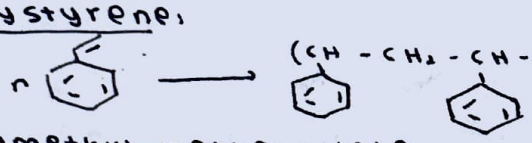
$n(CH_2=CHCN) \xrightarrow[\text{peroxide}]{\text{catalyst:}} (-CH_2-\underset{CN}{CH})_n$

Acrylonitrile — P.A.N

4) Poly vinyl chloride

$n(CH_2=\underset{Cl}{CH}) \longrightarrow -(CH_2-CH)_n-Cl$

5) Polystyrene:



6) Polymethyl methacrylate:

$CH_2=\underset{CH_3}{C}-COOCH_3 \longrightarrow (CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}})_n$

(methyl methacrylate) — PMMA

7) Nylon 6-6:-

$NH_2-(CH_2)_6-NH_2 + HO-C(=O)-(CH_2)_4-C(=O)-OH$

hexamethylene diamide (HMDA) — Adipic acid

$\downarrow$

$(NH-(CH_2)_6-NH-C(=O)-(CH_2)_4-C(=O)-)_n$

Nylon-6,6

8) Nylon 6-10:-

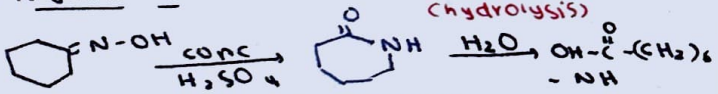
$H_2N-(CH_2)_6-NH_2 + HO-C(=O)-(CH_2)_8-C(=O)-OH$

HMDA — sebacic acid

$\downarrow$

$(NH-(CH_2)_6-NH-C(=O)-(CH_2)_8-C(=O)-)_n$

9) Nylon-6:



caprolactum

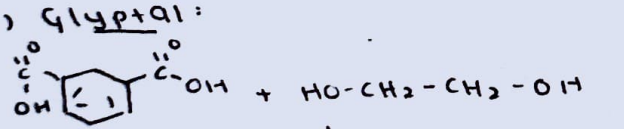
$\xrightarrow[\text{polymerisation}]{\Delta} (C(=O)-(CH_2)_5-NH)_n$

10) Terylene or Dacron:

$OH-C(=O)-C_6H_4-C(=O)-OH + HO-CH_2-CH_2-OH$

$\longrightarrow (C(=O)-C_6H_4-C(=O)-O-CH_2-CH_2-O)_n$

11) Glyptal:

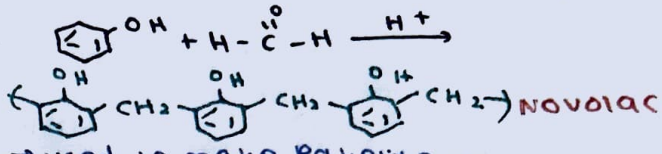


$\downarrow$

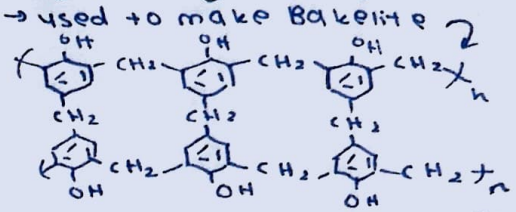
$(C(=O)-C_6H_4-C(=O)-O-CH_2-CH_2-O)_n$

* Resins:

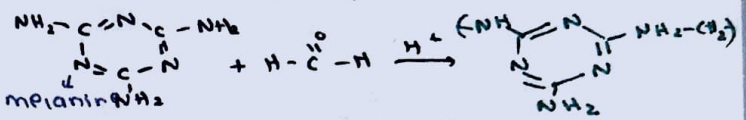
a) phenol-formaldehyde resin



→ used to make Bakelite



b) melanine-formaldehyde resin:



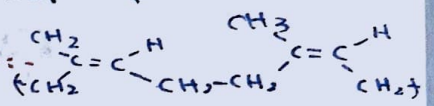
c) Urea Formaldehyde Resin:

$NH_2-C(=O)-NH_2 + H-C(=O)-H \longrightarrow (NH_2-C(=O)-NH-CH_2)_n$

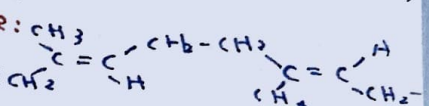
* Rubber: Natural polymer of isoprene

$CH_2=\underset{CH_3}{C}-CH=CH_2$ isoprene

cis poly isopropene:



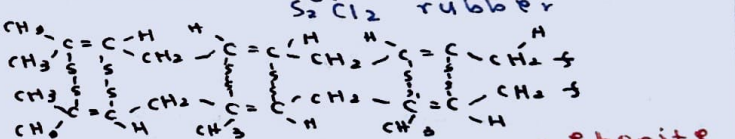
Trans poly isopropene: Gutta percha



- natural rubber in unfit due to:
  - becomes brittle at high Tempt
  - can be attacked by moisture
  - soluble in non polar solvent

vulcanisation:

Natural rubber $\xrightarrow[\text{or } S_2Cl_2]{S,\Delta}$ Vulcanised rubber



S): Sulphur :- tyre rubbers 25-1 → ebonite rods

Synthetic rubber:

- Buna-S or SBR (Styrene Butadiene rubber)

$CH_2-CH=CH-CH_2-\underset{C_6H_5}{CH}-CH_2$

- Buna-N

$CH_2=CH-CH=CH_2 + CH_2=CH-CN$

- Neoprene: $(CH_2-\underset{Cl}{C}=CH-CH_2)_n$
- Butyl rubber.

$(CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{C}=CH-CH_2)$

* Biodegradable Polymers:

1) Poly-β hydroxy butyrate-co-β-hydroxy valerate

$(O-\underset{CH_3}{C}H-CH_2-C(=O)-O-\underset{C_2H_5}{CH}-CH_2-C(=O))_n$

2) Nylon-2-Nylon-6

$(NH-CH_2-C(=O)-O-NH-CH_2-CH_2-CH_2-CH_2-C(=O))_n$