ITC
Enduring Value

classmate

ECO KIDS

Notebook

# INDEX

NAME: K. Sreeman Reddy STD.: ____ SEC.: ____ ROLL NO.: 207118 SUB.: Chemistry

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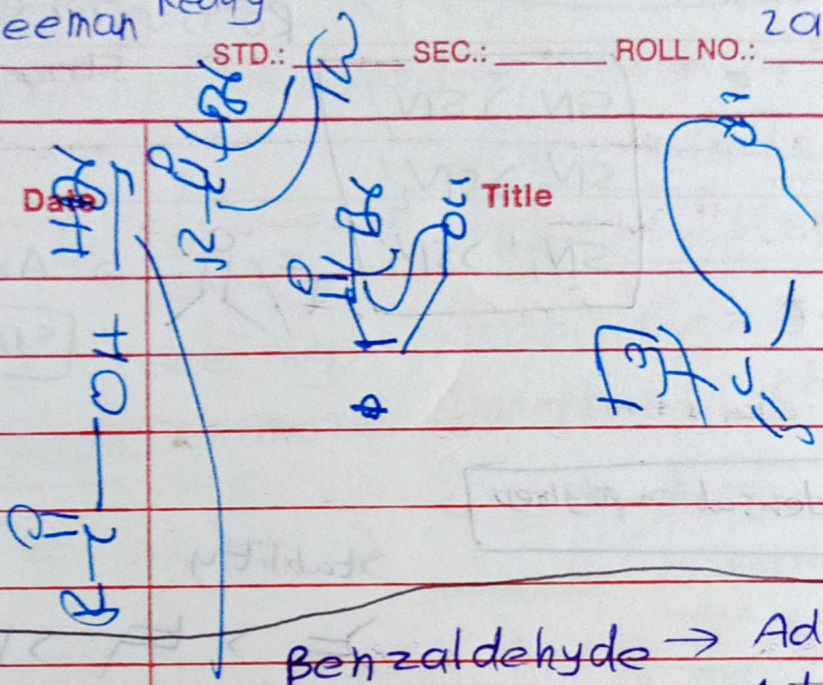
| | | | | |



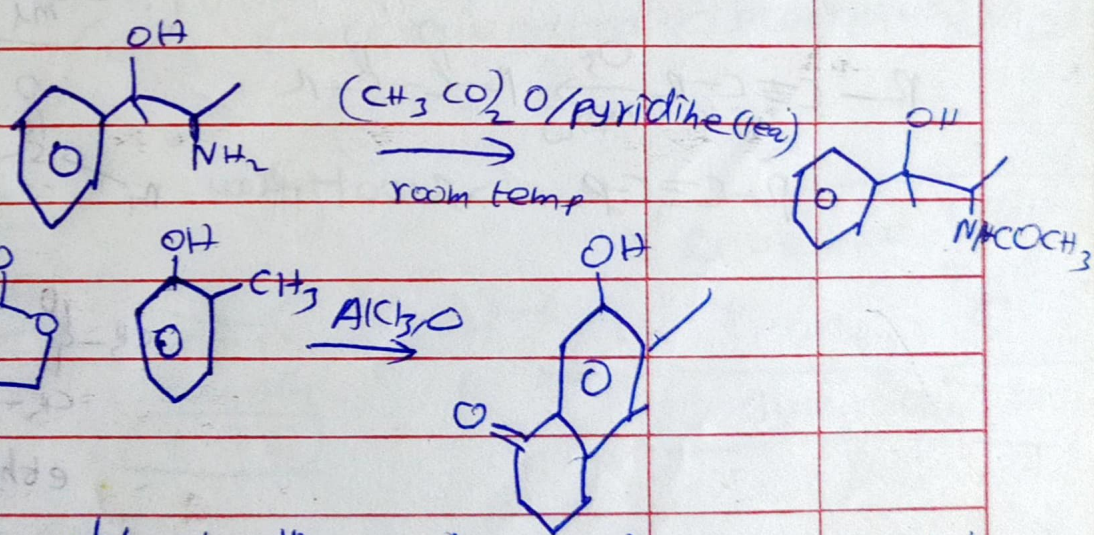
Benzaldehyde → Adsorbate

Alumina → Adsorbent (like silica gel)

Aceto nitrile → Mobile phase

V, Zn, Fe, Cu ⇒ Zn has lowest atomisation

$\Delta S = C \ln\left(\frac{T_2}{T_1}\right)$




T The plot of $\psi$ vs r for various azimuthal numbers shows peak shifting towards higher n value

F According to wave mechanics, the ground state angular momentum is equal to $\frac{h}{2\pi}$

| S. No. | Date | Title | Page No. | Teacher's Sign / Remarks |
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1° halide $\xrightarrow{\text{dil NaOH}}$ $S_N2$

2° halide $\xrightarrow{\text{aq NaOH}}$ $S_N2$

1° allylic, 2° allylic, 1° benzylic, 2° benzylic $\rightarrow$ $S_N1$

1° $S_N2$ $\xrightarrow{OH^-}$ (polar aprotic solvent)

2° $S_N2$

1° allylic, 2° allylic, Phenylic, 2° benzylic $\rightarrow$ $S_N2$

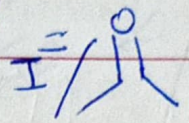
$S_N1 > S_N1'$

$S_N2 > S_N2'$

$S_Ni' > S_Ni$

$RO^-$ is stronger Nu than $OH^-$

strong base than $OH^-$

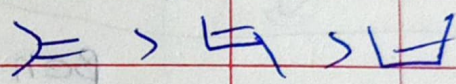


→ Anti

syn for 1°, 1°

**Step growth = Condensation polymers**

Stability



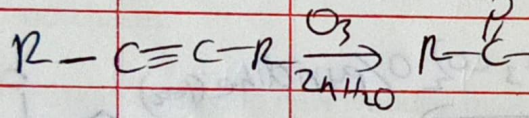
β-napthol → α position

electrophile will attack

$\alpha_{specific} = \frac{\alpha}{c \times l}$

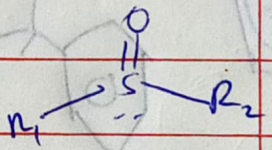
$l$ = decimeters

$c = \frac{g}{ml}$

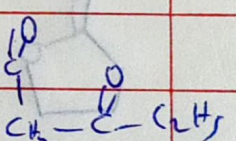


$R-C\equiv C-R \xrightarrow[2H_2O]{O_3} R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R$

$R-C\equiv C-R \rightarrow RCOOH + RCOOH$



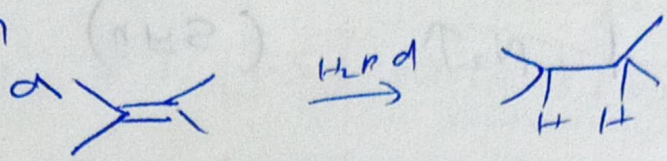
is O.A



ethyl aceto acetate

# Alkanes (Paraffins)

1) preparation (only syn)

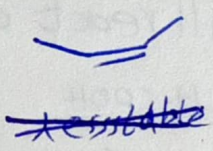
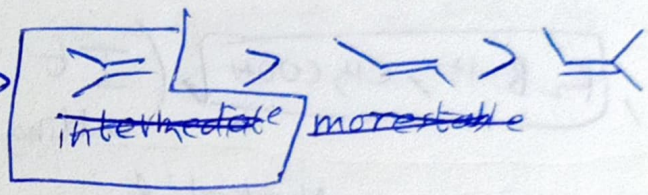



Reagents: $H_2Pt$, $H_2Pd$, $H_2Ni$, $H_2$ Raney Ni, $H_2PtO_2$, $Rh(PPh_3)Cl$ (Homogenous), Pd–C

H–O·H ∝ $n_\pi$ → Only syn

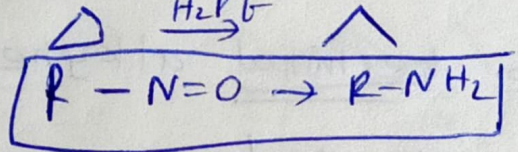
∝ $\frac{1}{\text{stabilit.}}$ → Rate : stericfactor

★ While seeing stability of double bond conjugation is more important than Hyperconjugation

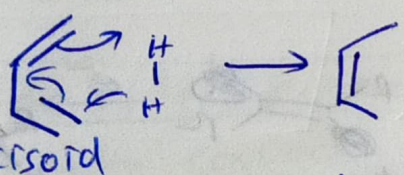
Rate: = > ≡ >  > 


| | | |
|---|---|---|
| S | CSM | TSR |
| U.S | CSE | TST |
| S | CAR | TAM |
| U.S | CAT | TAE |

⇒ △ behave in many cases like alkene



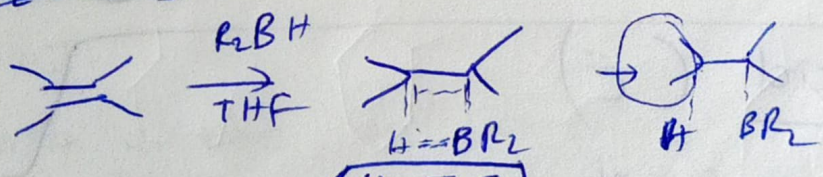

$R-NO_2 \rightarrow R-NH_2$

★ ⇒ 

(only for conjugated cis compound)

~~1) $2CH_4 + O_2 \xrightarrow{Cu/573K}$~~

2) HBO :

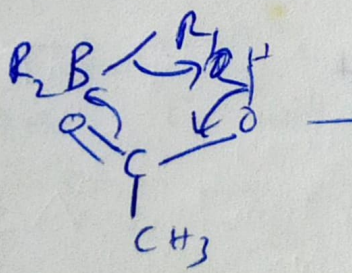



4-T·S

Reagent = $R_2BH$ / THF

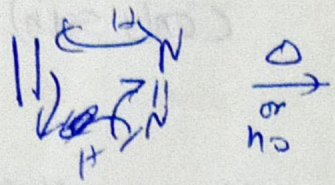
syn, Stericfactor

6-T·S




$R_2B(OCOCH_3) \rightarrow B(OCOCH_3)_3$ + RH

→ It reacts very fastly with R–CH=O, R–CO–R, R–COOH

⇒  (syn)

Reagent → $N_2H_2$ ($N_2H_4 + H_2O_2$)

⇒ Instead of $CH_3COOH$, $H_2O_2$ ~~may~~ will give OH

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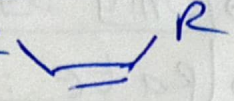
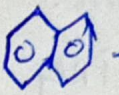
$R-C\equiv C-R \longrightarrow$ 

Reagents $H_2$ – Pd $BaSO_4$ or ($CaCO_3$ or  +S), $H_2$–$Ni_2B$(P-2)

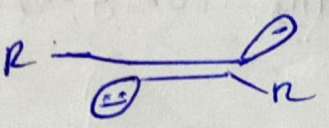
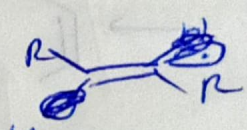
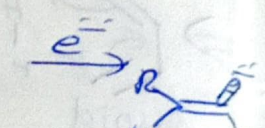
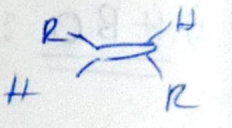
(Lindlar's catalyst)

, $R_2B-H$, $CH_3COOH$ (It will react only once as after adding $CH_3COOH$ we will not add it again

$R-C\equiv C-R \xrightarrow[\text{Li/NH}_3\text{ or}]{\text{Na or K or Li}} R\diagup\!=\!\diagdown R$ ( $R-C\equiv CH \xrightarrow[\text{liq NH}_3]{\text{Na}} R-C\equiv C^{\ominus}$ no reduction)

→ It can't reduce terminal alkyne But

Na, $NH_3$ + $(NH_4)_2SO_4$ can reduce:

$R-C\equiv C-R \xrightarrow{e^-}$  ① →  ②  ③ 

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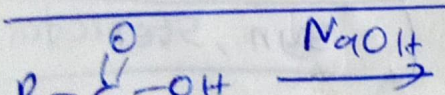
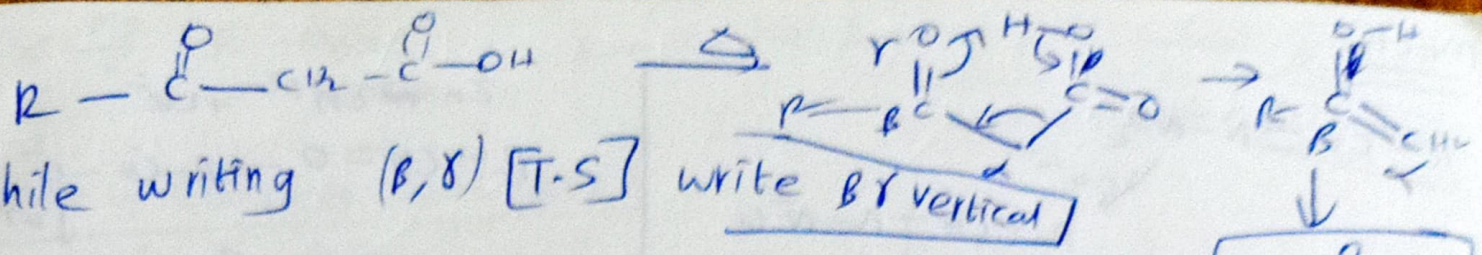
From Carboxylic acid ($\bar{e}$)



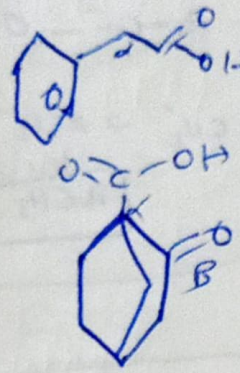
$R-\overset{\ominus}{C}(=O)-O^- \longrightarrow R^{\ominus} + H_2O \rightarrow RH$

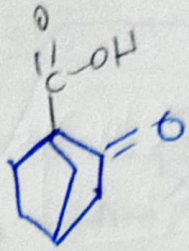
→ Intra molecular



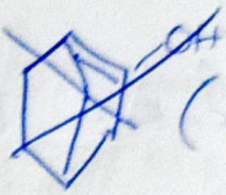
→ While writing (β, γ) [T.S] write β γ vertical

→ Benzene donot undergo β, γ decarboxylation





but



(not isolated)

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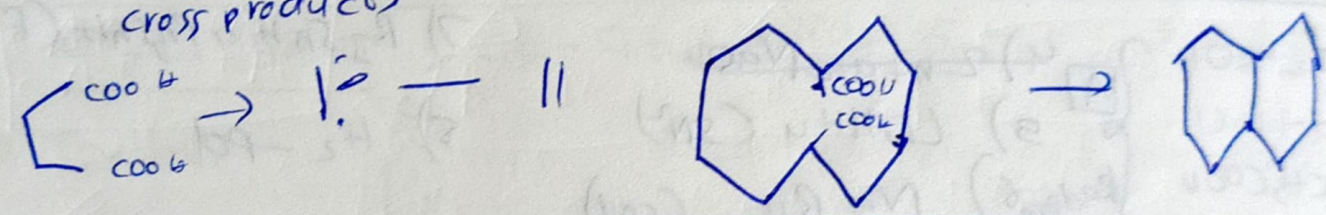
**Kolbe's electrolysis** (C·)

$R-COO-Na/K \xrightarrow[H_2O]{\text{electrolysis}} R-R + CO_2 + NaOH + H_2$ or $R-R + Na_2CO_3 + H_2$

Oxd pot $RCOO^- > OH^-, H^+ > Na^+$

$R\cdot$, $RCOO\cdot$, $2R\cdot$ ⟶ alkene + alkane, $R\cdot \xrightarrow{-e} R^+ \rightarrow ROH$

cross products



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**Aldehydes/ketones → R–H**

1) Zn Hg conc HCl
Clemmenson Red (C·)

2) $N_2H_4$/base/Δ
Wolf-Kischer Red

3) i) $C^{SH}_{SH}$, $H^+$ ii) $H_2$/Raney Ni
Mozingo method

4) Red P / HI

→ In Clemmenson alkene will isomerise.

$R-OH \xrightarrow{\text{clemmenson}} R-Cl$

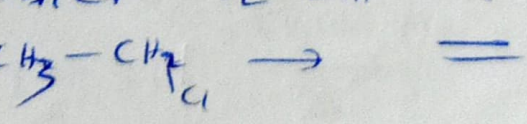
$R-O-R \rightarrow RCl$

$Ph-OH \rightarrow PhX$

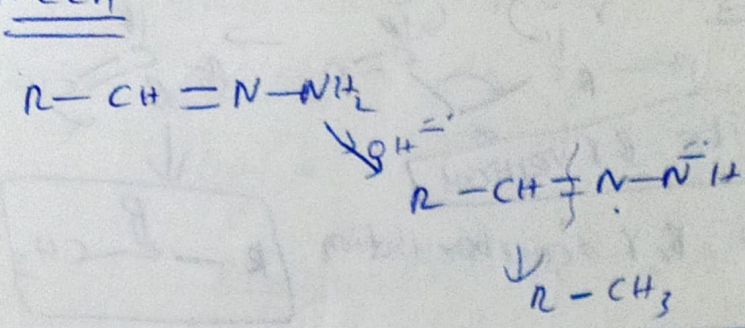
$R-NO_2 \rightarrow R-NH_2$

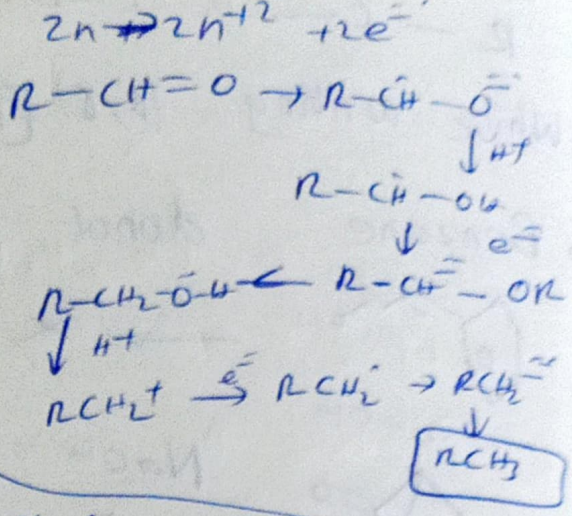
$R-NO \rightarrow R-NH_2$

→ In wolf kisher E$_L$ can occur

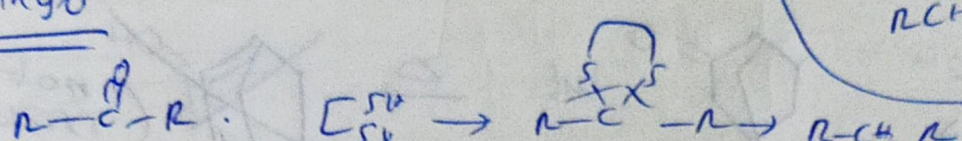


## Mech

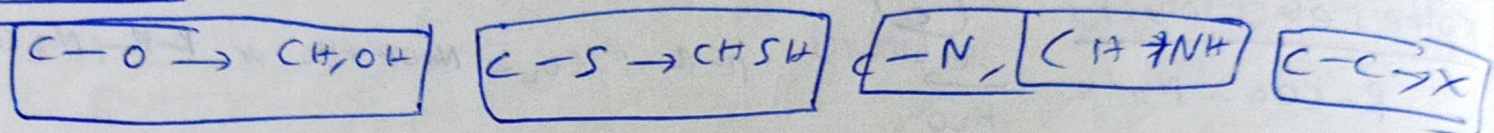




## Mozingo



## Red P + HI



Ex: $R-CH_2OH \rightarrow RCH_3$, $R-OR \rightarrow RH$, $RCHO \rightarrow RCH_3$, $R-\overset{O}{\overset{\|}{C}}-R \rightarrow RCH_2R$

## From alkyl halides

1) $Na + C_2H_5OH$
2) $Zn + dil\ HCl$
3) $Zn + CH_3COOH$
4) $Zn + aq\ NaOH$

A

~~4) Zn + aq NaOH~~
5) $LiAlH_4$ ($SN^2$)
6) $NaBH_4$ ($SN^1$)

Radical

7) $R_3SnH$ or $Ph_3SnH$ ($ER_S$)
8) $H_2$ – Pd

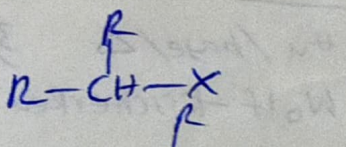
$R-CH_2-X$

$LiAlH_4$ ($SN_2$)
$NaBH_4$ ($SN^1$)
$Ph_3SnH$ ($FR-S$)
~~$NaC_2H_5OH$~~ A

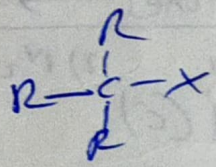
$R-CH_3$

Norrxn

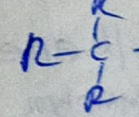
$R-CH_3$



$R-CH_2R$



Alkene ($E_2$)



$R_3CH$

$R-X \xrightarrow{Mg} R-MgX$ Grignard

$R-X \xrightarrow{Li} RLi \xrightarrow{CuX} R_2CuLi$ Gilmann reagent

→ **Corey Cousee synthesis**

$R_2CuLi \xrightarrow[SN_2]{R-X} R-R$

$CH_2=CH-R \xrightarrow[\text{Grignard}]{\text{gilmann}}$ ✓ ✗

$Ph-X \xrightarrow[\text{grignard}]{\text{gilmann}}$ ✓ ✗

→ **Wurtz**: $R-X + Na + R-X \longrightarrow R-R$ $(C^{+} + C^{-})$ ~~retrieved~~

→ Symmetrical only → disproportionation possible

→ **Fittig**: $Ph-X + Na + Ph-X \rightarrow Ph-Ph$

→ **Wurtz-Fittig** $Ph-X + Na + R-X \rightarrow R-Ph$

**Frankland rxn** $R_2Zn + R-X \rightarrow R-R$

**Ullmann Rxn** $R-X \xrightarrow{Cu} R-R$

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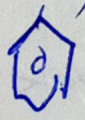
→ $C_1-C_4$ gases, $C_5-C_{17}$ Liquids, from $C_{18}$ Solids

⇒ Toulene  is Polar molecule but non polar solvent

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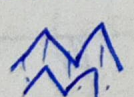
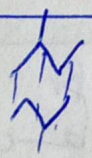
B-P  >  >  (Vanderwalls forces & Surface area)

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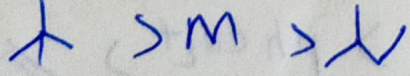
M.P  It depends on packing fraction

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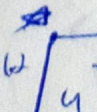
→ **Controlled oxidation** (A)

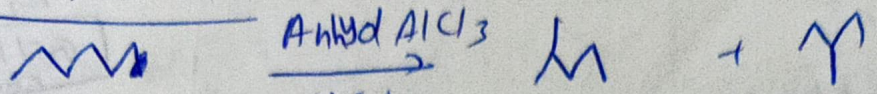
1) $2CH_4 + O_2 \xrightarrow[100\,atm]{Cu\ 523K} 2CH_3OH$

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

3) $2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3COOH$

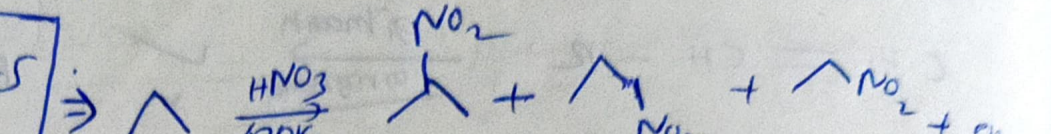
4)  $\xrightarrow[\text{Oxidn}]{KMnO_4}$ 

→ Isomerisation




→ $CH_4 + H_2O$ (steam) $\xrightarrow[\Delta]{Ni} CO + 3H_2$

tBuOCl
$SO_2Cl_2$
$CBrCl_3$
$CCl_4$
→ FR-S




i.e it can break

## Halogenation

→ Br can both form radical radily & react readily

→ F is highly reactive. Cl is reactive, Br is selective

1 : 3·8 : 5

1 : 82 : 1600

→ Preparation of AF

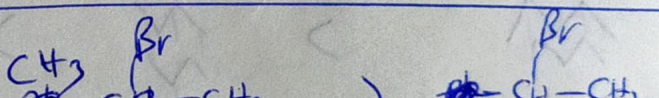
Swarts

$R-Cl/Br/I \xrightarrow[\text{or } SbF_3,\ SbF_5,\ CoF_3,\ Ag_2F_2]{AgF} R-F + AgX$

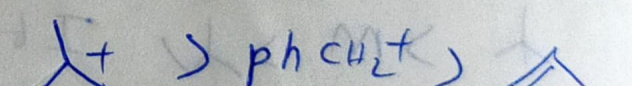
Finkelstein rxn

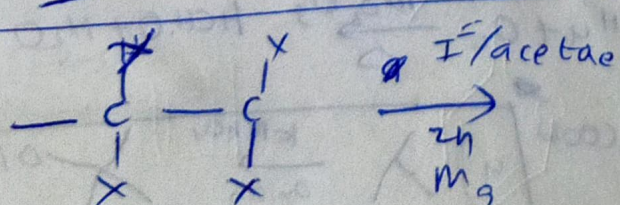
$R-Cl/Br \xrightarrow[\text{acetone}]{KI \text{ or } NaI} R-I + KX \text{ or } NaX$

## Stability of $C^+$

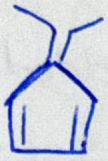
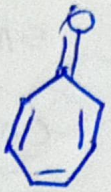


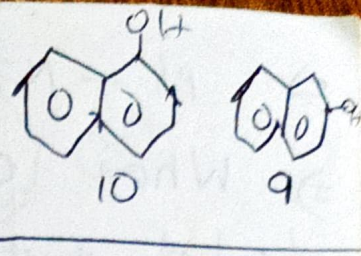

O
A
R+conjugation
H
I

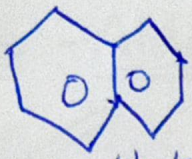


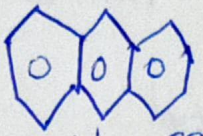



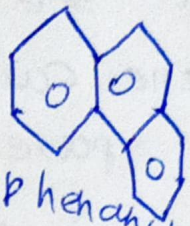
Note (Random)

1)  → N.A  →  A




2) 
Napthalene (3)


Anthracene (4)


Phenanthrene (5)

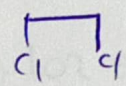
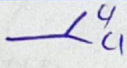
R-E = B C N C A C P

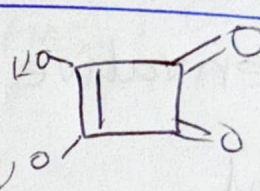
$(R-E)_{peri\,ng}$ = B > N > A > P

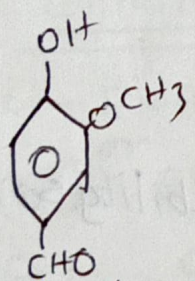
3) △ → SPS

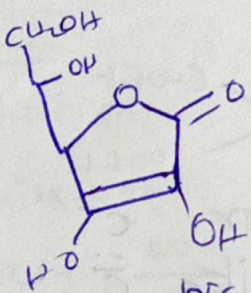
$NH_4(CNO) \xrightarrow{\triangle} H_2N-\overset{O}{\overset{\|}{C}}-NH_2$

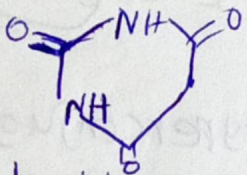
---

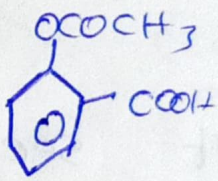
4) Vicinal  Geminal 


= squaric acid

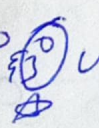
⇒ 
Vanillin


Ascorbic acid


barbituric acid


Aspirin

⇒ $FeCl_3$ test only phenols (not aliphatic alcohols)

⇒ In williamson's ether synthesis  will yield alkene

⇒ R-OR + HI → atleast one is 3° ⇒ $S_N1$

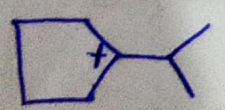
R-OR + aq HI → ROH + RI ROH + HI → RI + $H_2O$

P 1° → $S_N2$ P 2° 2° also $S_N2$

~~P 2°~~ P, 3°, 3°, 3°, 1°, 3° → $S_N1$

| ROR + $\frac{HI}{anhy}$ | $S_N2$ |
|---|---|
| ROR | $\xrightarrow{conc\,HI}$ RI + RI |

(instead of migration)

⇒  Here expansion takes place

⇒ Ph – N=N – Ph can show geometrical isomerism

⇒ When organometallic compounds are added we should first see acid base rxn. Especially if it is active methelene carbon.

⇒ Migrating power ($\bar{e}$ density)

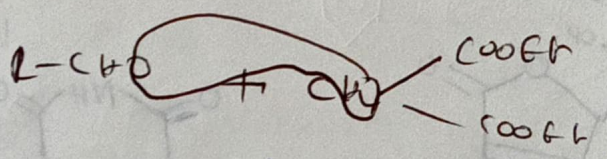
Ph-OCH$_3$ ) Ph-Me ) Ph-Cl > Ph-Br > Ph-CN > Ph-NO$_2$

⇒ In SN, cation is formed because of solvent after forming intimate ion pair

→ Aromatic alcohols and aromatic amides give $FeCl_3$ test

→ Acid derivative and diketo are soluble in hot aq $NaOH$

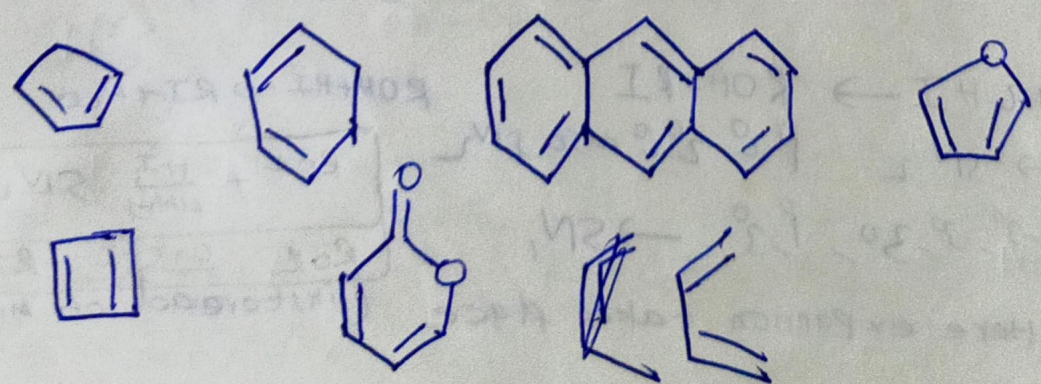
→ Knoevengal

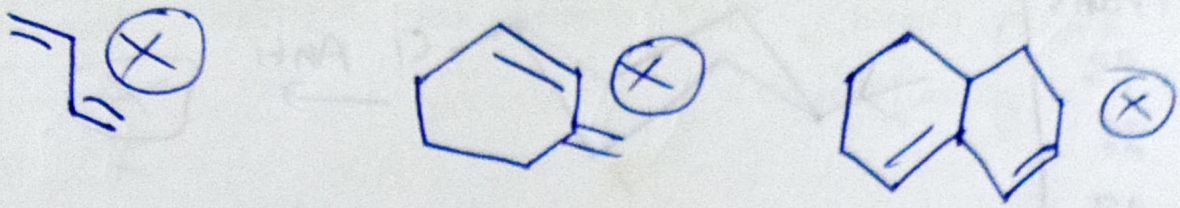



→ Don't see Hyperconjugation for '$\bar{C}$' stability. So Hyper conjugation will never destabilise $\bar{C}$.

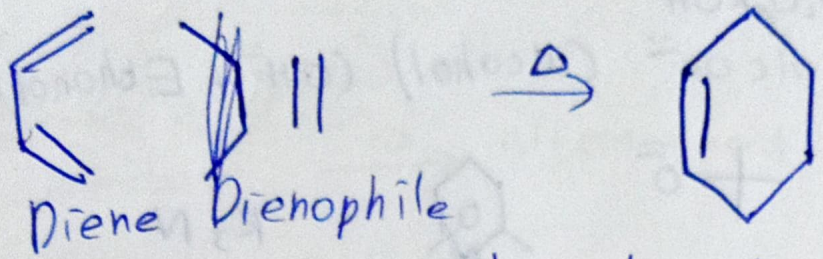
→ we should not see <u>hyperconjugation</u> for rate of $E_2$. (also in 3membered Et rxn)

⇒ The following compounds ~~rec~~ act as "diene" in Diels – Alder rxn.





## Diels -Alder rxn




Diene Dienophile

→ Aromatic compounds ~~do not~~ give diels -alder rxn.

Ozonolysis - rate ≈ ē density

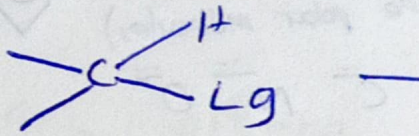
$OSO_4$, $KMnO_4$, rate: steric factor

## Alkenes (Oletins)

~~Pre~~ Elimination

α - Elimination

(1,1) or - Elimination




(carbene) (electro phile)

Ex: $CHCl_3 \xrightarrow[\Delta]{KOH} \ddot{C}Cl_3 \rightarrow \ddot{C}Cl_2$

→ Leaving groups

$RSO_3^{=} > I^{=} > Br^{=} > Cl^{=}$

Poor L.g $H^{=}$ $R^{=}$ $NH_2^{=}$

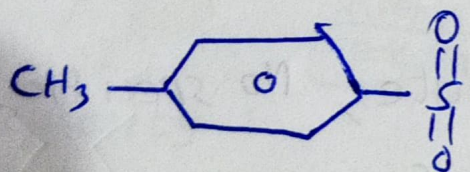
$OH^{=}$ $RO^{=}$ $phO^{=}$ $F^{=}$ → $E_2$ also possible.

$E_1$ $E_2$ $E_1CB$

moderate $-\overset{+}{N}Me_3$ $-\overset{+}{S}Me_2$

$E_1 \times E_2 \checkmark E_1CB$

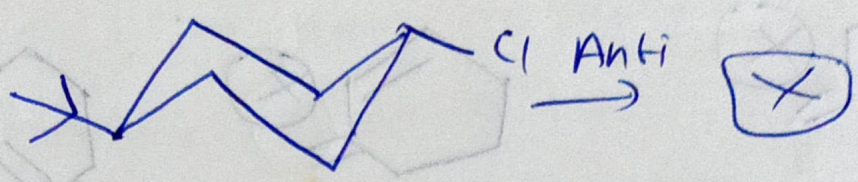
good lg $RSO_3^{=} > I^{=} > Br^{-} > Cl^{-}$




$-OTs$ (OTosyl) (p-toluene sulphonate)

Sulphonates are good lgs than halides

| | Cis | Trans |
|---|---|---|
| 1,2 | ae, ea | aa, ee |
| 1,3 | a,a, ee | ae, ea |
| 1,4 | ae, ea | aa, ee |




bases

Weak : $H_2O$, $D_2O$, ROH

strong bases : $alcOH^{\ominus}$ (alcohol) ($OH^{\ominus}$ + Ethanol)

(L-B-B)

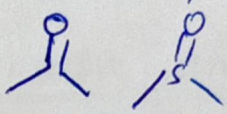
Bulky bases + $O^{\ominus}$

$R_3N$

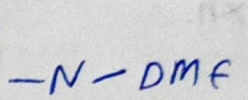
## Solvents

Polar solvents: $H_2O$, ROH, $D_2O$, RCOOH, $NH_3$

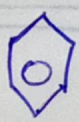
Polar aprotic solvents:



DMSO



DMF

non-polar solvents $CCl_4$,  , R-O-R, $CH_2Cl_2$

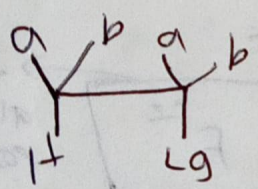
(They may be polar molecules)

Nucleophiles → Ex: $C^{\ominus}$ $N^{\ominus}$ $O^{\ominus}$

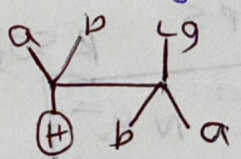
S.A > $CH_3OH/H_2O$ > W.A

↓ conjugates are mostly $Nu^{\ominus}$

↓ conjugates of W.A mostly bases

→ 

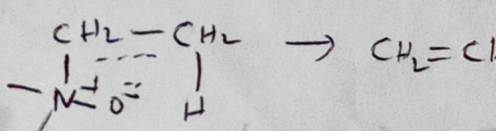

Syn-periplanar




(Anti-periplanar

## Cope elimination (or cope rearrangement) (only syn) (Ei(1))

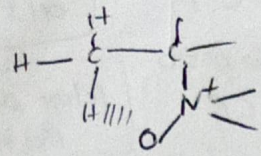
N-oxide $\xrightarrow{\Delta}$ alkene + hydroxy amine




⇒ Molecularity : 1, order : 1, no intermediate, No specific solvent

⇒ If conjugation is possible it will form or else Hoffmann alkene

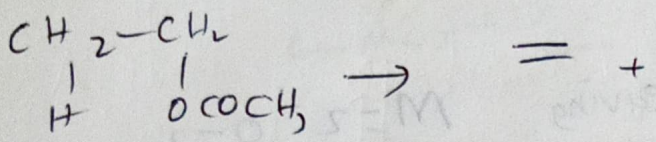
=> 5-membered cyclic transition state (nearly planar)



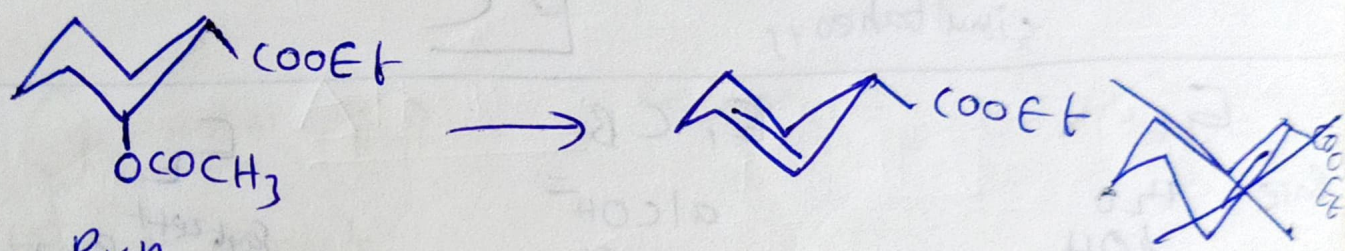
Preparation $R_3\ddot{N} \xrightarrow[\text{or } H_2SO_5 \text{ or } RCO_3H]{H_2O_2} R_3\overset{+}{N}-\ddot{O}:$

**Pyrolysis of ester**

ester $\xrightarrow{\Delta}$ alkene + acid (Hoffmann & cis for acyclic Saytzeff if cyclic



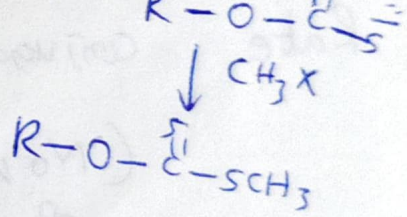
8-11-18

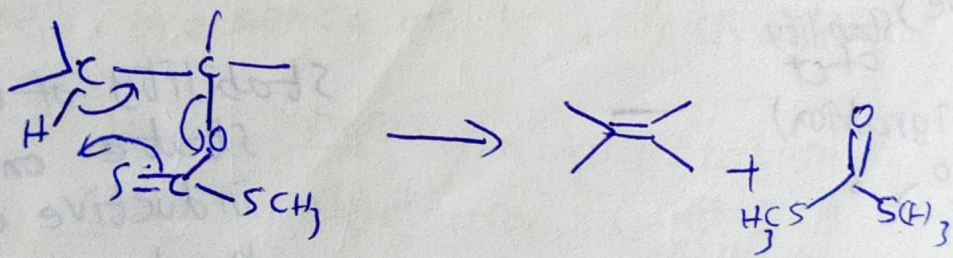


**Chugaev Rxn**

S-ester xanthate $\xrightarrow{\Delta}$ alkene

$R-OH \xrightarrow[NaH \text{ or } Na]{\text{base}} R\ddot{O}: \xrightarrow{S=C=S}$





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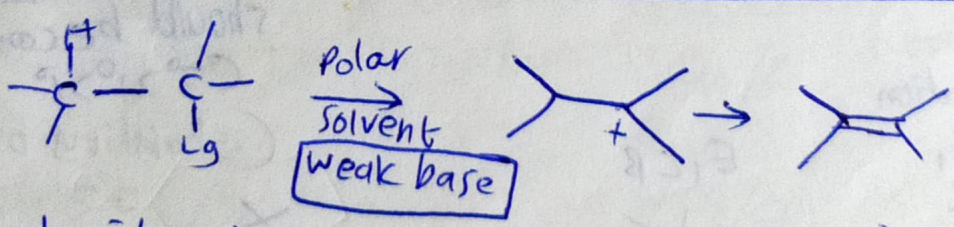
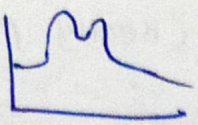
E1

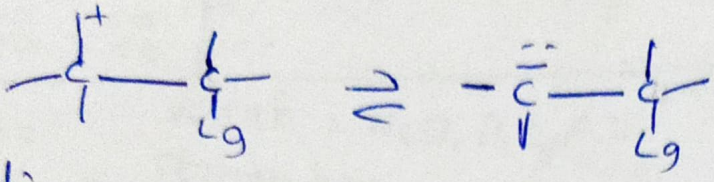


1) Molecularity 1
2) rate law = k[substrate]$^1$
3) Order = 1
4) Solvent polar

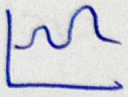


Rate of E2 → heaver to E1 (Stable alkene)
→ heaver to E1CB (Most Acid Proton)

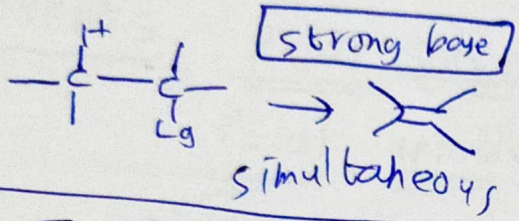
## E1CB



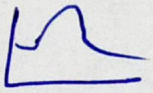
1) Acidic proton 2) Moderate leaving 3) M = 1 4) O = 2 (-R or Poly halo)



## E2




→ Good leaving M = 2 O = 2



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## E1

Base: $H_2O$, KOH, $D_2O$

Rearrangement: $C^+$ (✓)

Rate: Conjugate) Stability of $C^+$ (No migration) $3^0 > 2^0 > 1^0$

Deuterium incorporation: E1 ✗ $no\ C^-$

## E1CB

alcoH$^-$, $NH_2^-$, $RO^-$

$C^-$ (✓)

$R^- + D_2O \rightarrow R\text{-}D$

Deuterium incorporation: E1CB ✓

## E2

Saytzeff: L.B.B $OH^-$ $NH_2^-$ $CH_3O^-$ $C_2H_5O^-$

S.B → Hoffmann: B-B

✗ no intermediate

Stability of transition state only inductive double bond character should be considered $C^{3^0} > 2^0 > 1^0$ (stability of alkene)

Deuterium incorporation: ✗ $no\ C^-$

isotopic effect $\Rightarrow \frac{k_H}{k_D} \propto 7\text{-}1$ for $E_2$ reaction.

→ only $F^-$ give hoffmann product among halogens

9-11-18

Hoffmann alkene : Alkene connected to less no. of substituents

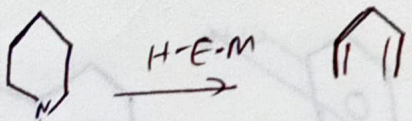
Hoffmann elimination

$R-NH_2 \xrightarrow{Ex\,CH_3I} R-NHCH_3$

$R-\overset{+}{N}(CH_3)_2\,I^- \leftarrow R-N(CH_3)_2$

$\downarrow AgI \qquad R-\overset{+}{N}(CH_3)_2\,OH^-$

→ H-E-M



Reagent = $CH_3I/AgOH/\Delta$

→ Dehydration of Alcohols

Reversible

alkene stability

$2^0/3^0$ $E_1$

$E_2$ $1^0$ (primary $c^+$ is not formed)

→ Alkene isomerisation

In the presence of $H^+$ or $(AlCl_3\ \Delta)$

→ 10-11-18

$R-OH \xrightarrow{base}$ no dehydration

$R-OH \xrightarrow{base}$ dehydration (If E1CB is possible)

| | | |
|---|---|---|
| → Conc $H_2SO_4/\Delta$ | similar | $AlPO_4/\Delta$, $P_2O_5/\Delta$, $P_4O_{10}/\Delta$, $Al_2O_3/\Delta$, $WO_3/\Delta$, $ThO_2/\Delta$, $POCl_3/\Delta$ |
| → Conc $H_3PO_4/\Delta$ | | |
| → Conc $H^+/\Delta$ | | |
| → $KHSO_4/\Delta$ | | |

stable alkene

Hoffmann

Random

→ For $C^{+}$ stability 'H' is not applicable

SARRI order for $C^{+}$

→ Assymetric ; except Cl

→ Dissimetric ; all

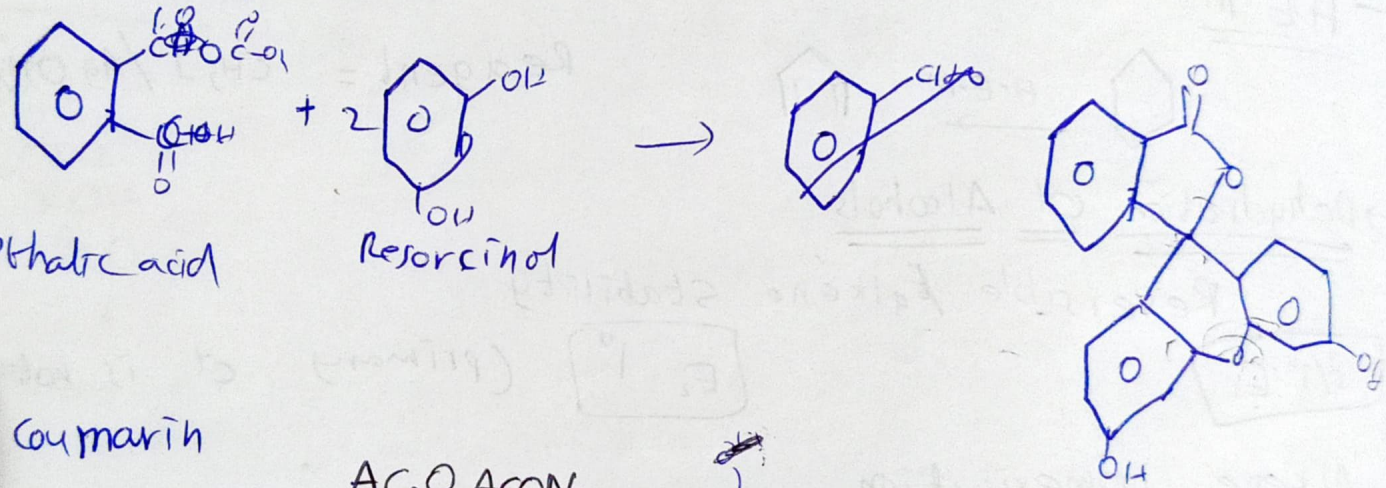
→ Methanal = formaldehyde

Methanoic acid = formic acid

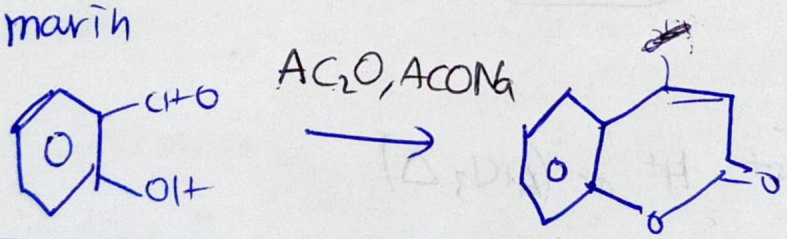
→ Alcohol give cerric ammonium test.

→ Luca's reagent = Conc. HCl + Anhydrous $ZnCl_2$

→ Fluorescein




→ Coumarin




---

1,2

→ RLi

$RMgX$

$LiAlH_4$

$NaBH_4$

1,4

eholate

Enamine

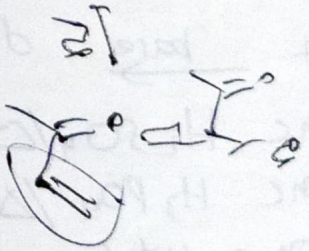
Nitrogen $Nu^{-}$s

Sulphur $Nu^{-}$s

$CN^{-}$

$R_2CuLi$ or $RMgX$ $CuX$

Halogens, Alcohols / Na + ethanol, $H_2$ / Pd



## Aldol

condensation in Basic $P > 2^\circ > 3^\circ$

addition in Basic $3^\circ > 2^\circ > 1^\circ$

addition in acidic & condensation $3^\circ > 2^\circ > 1^\circ$

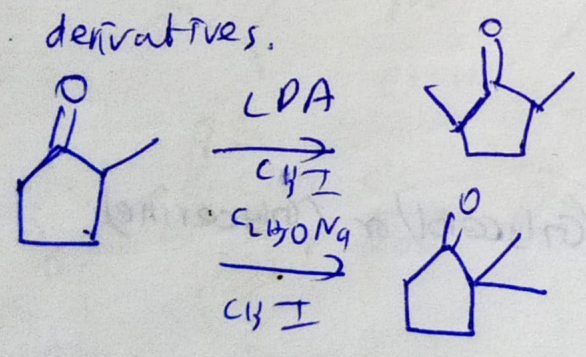
Phenyl hydrazone = ph – NH – $NH_2$

→ In acidic medium electrophile will be substituted the

→ $CH_3-\underset{OH}{\underset{|}{CH}}-\underset{O}{\overset{\|}{C}}-OH$ lactic acid

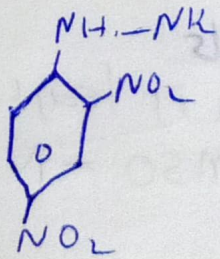
→ $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{SeO_2} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}H$

→ ketones & aldehydes are more reactive towards $N_u^-$ rxn than acid derivatives.

→ 


$1^\circ > 2^\circ > 3^\circ$ (logical)

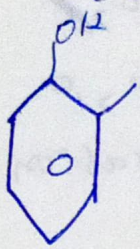
~~$3^\circ > 2^\circ > 1^\circ$~~

→ Borsh reagent = 

→ hydrazines

hydrazone means after reacting with ketone.

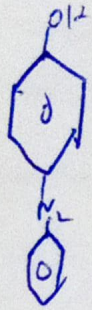
→  p-cresol.

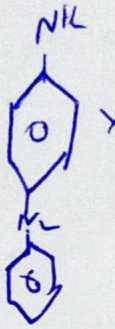
 catechol

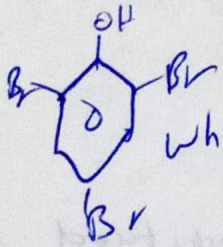
cis

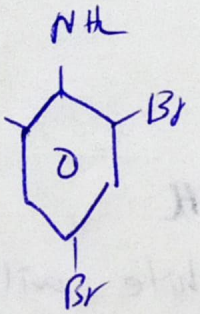
m-Resorcinol

p- Hydroquinone.

→  orange

 Yellow

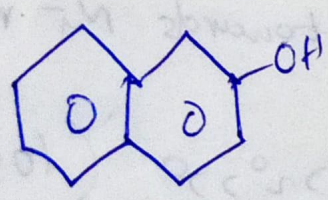
→  white ppt

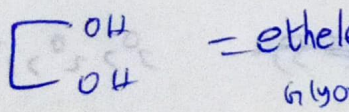
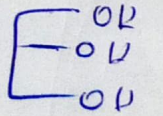
 white ppt

→ $PhN_2^+ \xrightarrow{H_3PO_2} ph-H$

$ph\,N_2^+ \xrightarrow{EtOH} ph-H$

→ $Ph-N_2^+-Cl^- \xrightarrow{Zn/HCl} ph-NH_2$

→  → $CCl_4$ is called pyrene

→  = ethelene Glycol or Glyoxal  (Glycerol) or (Glycerine)

→ All ketals are acetals

→ For aniline ortho is least basic (in general)

POSM - OH PMSO - $NH_2$ (like $CH_3$)

PSOM - OMe

(logical)

SPMO - X

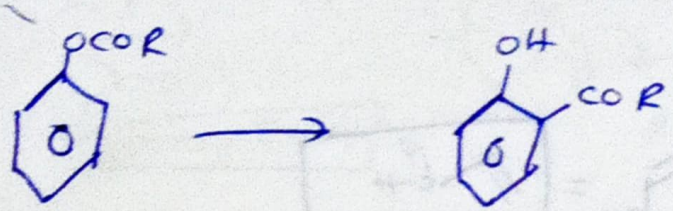
SMPO - $NO_2$ $COOCH_3$

Rate of Nucleophilic substitution

$RCOX > RCOOCOR > RCHO > RCOR > RCOOR > RCONH_2$

## Fries rearrangement

High Temp = Thermodynamic = H-bonding




2 1 3 Me (Mahendra Singh Dhoni)

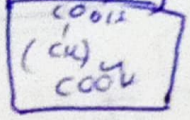
2 3 1 Et (Sachin)

glucopyranose = 2-4 DNP (−)

$H_2NOH$ +

tollens +

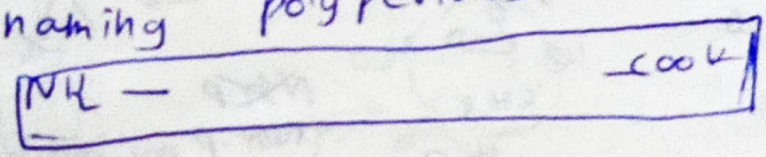
$NaHSO_3$ (−ve)

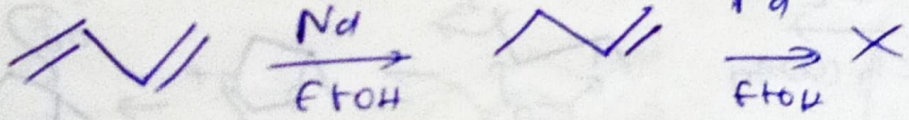


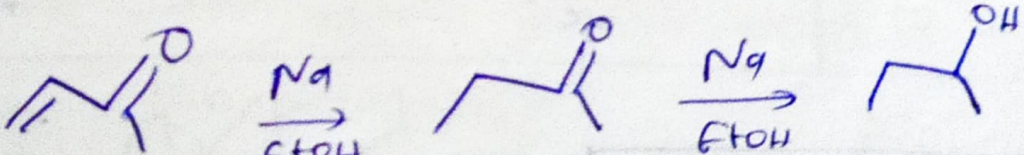

adipic acid =

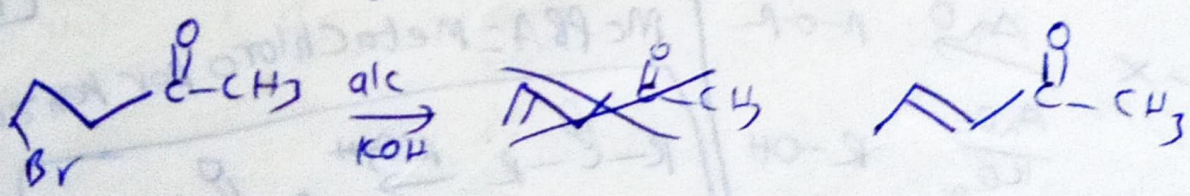
OMSGAP
0 1 2 3 4 5

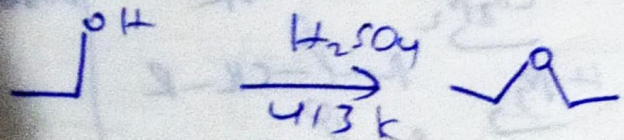
While naming polypeptides

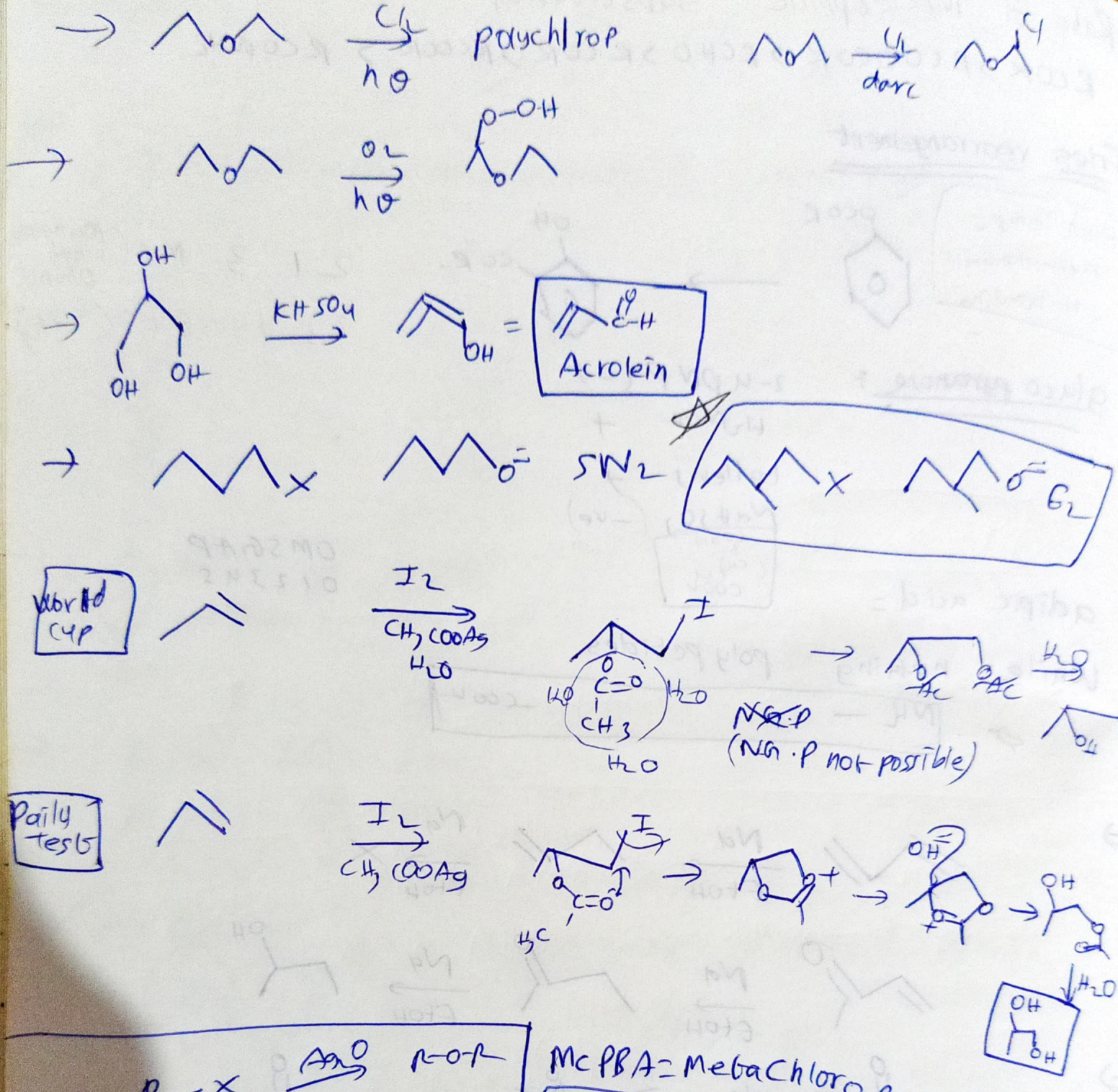


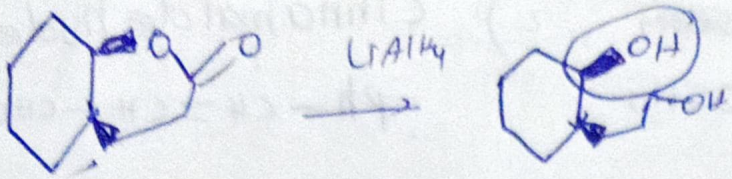

⇒ 

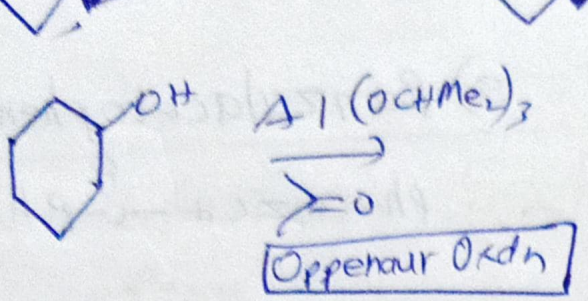



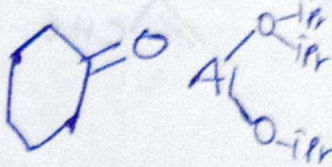

⇒ 

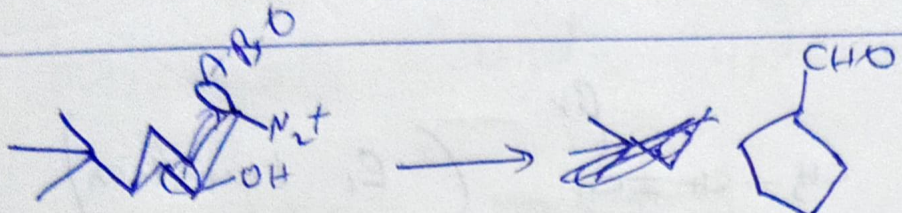

⇒ 


Cl2
hυ
polychlorop
Cl2
dark
O2
hυ
OH
OH
OH
KHSO4
Acrolein
SN2
Cl2
World
CYP
I2
CH3COOAg
H2O
I
C=O
CH3
H2O
H2O
H2O
(NGP not possible)
Daily tests
I2
CH3COOAg
OH
H3C
OH
H2O
OH
R–X
Ag2O
R–O–R
Ag2O
H2O or
moist Ag2O
Ag(OH)
R–OH
McPBA = Metachloro per benzoic acid
RCO3H
CH2N2
H+ N3
Bayer Villeger
Oxidation

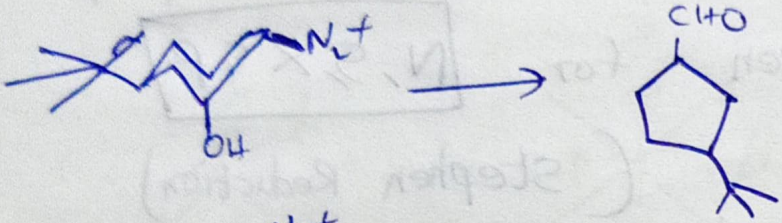


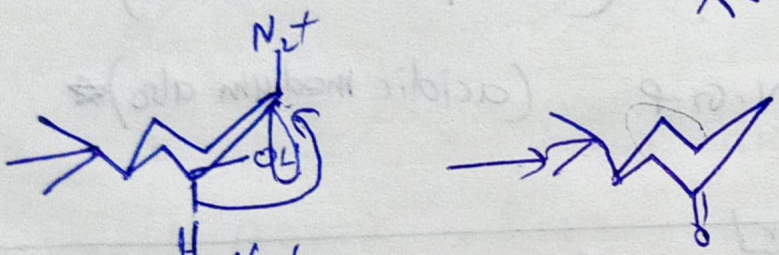



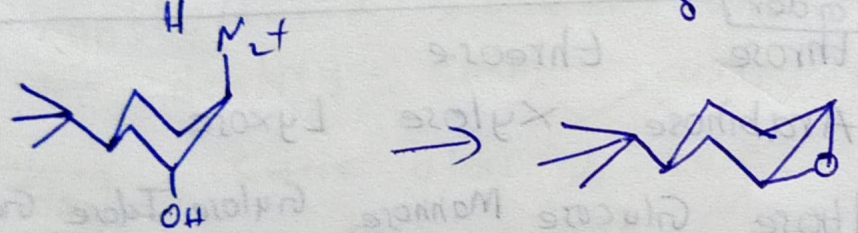

migration ✓



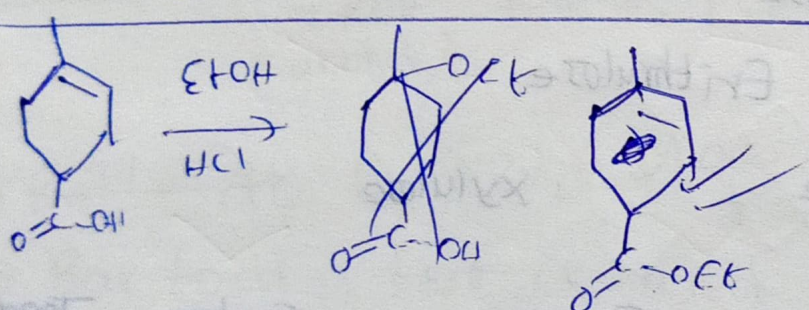

migration ✓

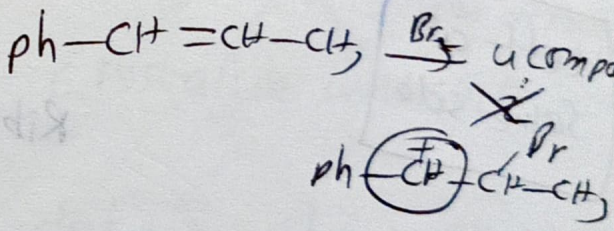



His migrated

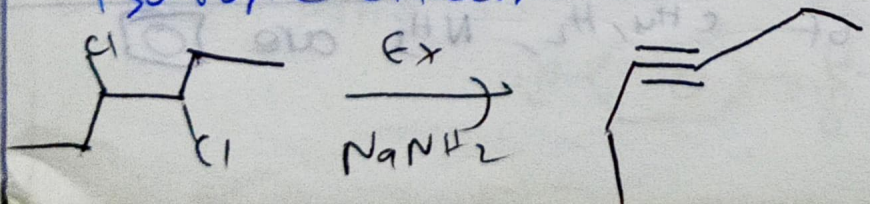



Only parallel bonds can donate to anti-bonding orbitals

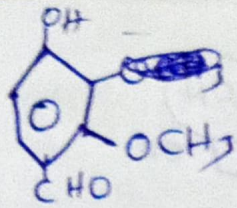



Iodoation, Sulphonation, Nitrosoation & ph-$N_2^+$ (coupling rxns) have iso-topic effect.



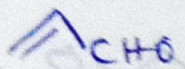
**Random**

1) Vanillin = 

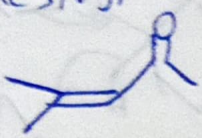
2) Cinnamaldehyde

$Ph-CH=CH-CHO$

3) Acrolein

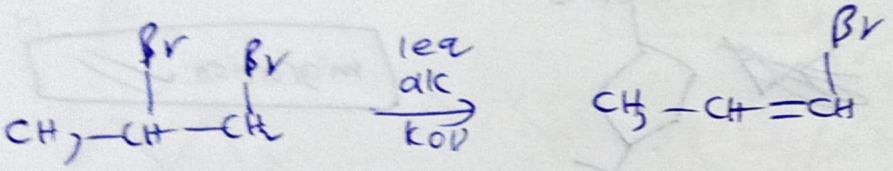


4) Mesityl Oxide



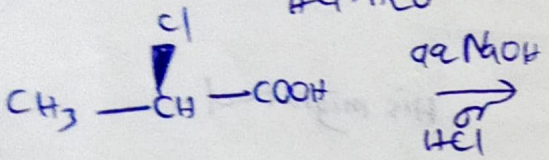
5) Benzalacetophenone

$Ph-CH=CH-\overset{O}{\overset{\|}{C}}-Ph$

$\Rightarrow$  ( $E_1$ transition)

$\Rightarrow$ Lassaigne's test is given for **N, S, X & P**

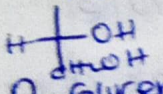
$\Rightarrow$ $R-C\equiv N \xrightarrow[HCl \cdot H_2O]{Sn\,Cl_2} R-\overset{O}{\overset{\|}{C}}-H$ ( Stephen Reduction)

$\Rightarrow$  N·G·P (acidic medium also)

---

All are D in this order

Erythrose threose



D-Glyceraldehyde

Ribose Arabinose Xylose Lyxose

Allose Altrose Glucose Mannose Gulose Idose Galactose

Erithrulose

Left all same side

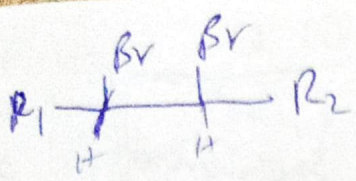
Ribulose Xylulose

Psicose Fructose Sorbose Tagatose

---

No. of optical isomers of $CH_4$, $H_2$, $NH_3$ are 0

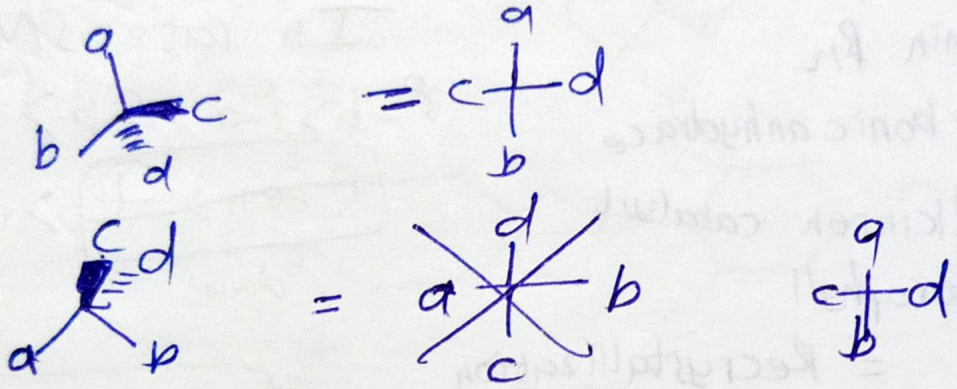
(Not 1)




$\xrightarrow[Mg \text{ or } Zn]{I^-, \text{acetone}}$ $E_2$

$E_1$ ($i^{0}$)

→ In ~~Opening~~ Drawing fischer diagram's open only "horizontally" and upper one is changed




→ $CH_3N{=}$⟨ $\xrightarrow{NaBH_4}$ $CH_3.NH-$⟨

urea
BMX
SLN

→ Xanthoproteic, Biuret and Ninhydric test are used to identify amino acids.

ose Talose → Ceric ammonium test

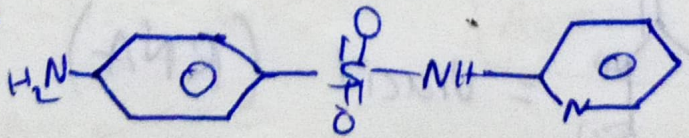
$2ROH + (NH_4)_2[Ce(NO_3)_6] \longrightarrow 2NH_4NO_3 + [Ce(NO_3)_4(ROH)_2]$

(alcohols) ✓ — Pink or red

→ ~~$Ba^{2+}$ do~~ $Ba(NO_3)_2$ does not crystalise with $H_2O$.

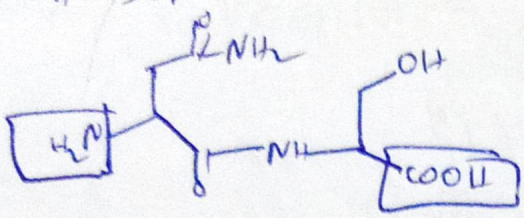
→ Barfoed test is used to detect the presence of monosaccharide (reducing sugars) in solutions.

→ Sulpha pyridine

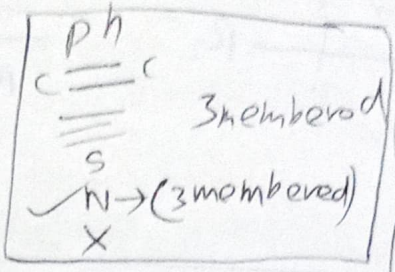


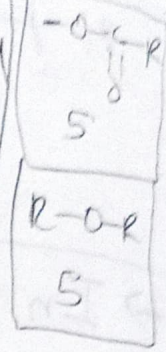

carbohydrates
BBB
SIM

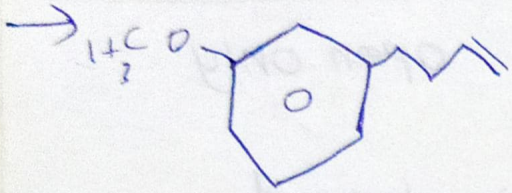
→ Asn - Ser



NGP

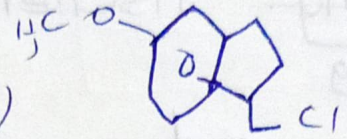



→ 


$Cl_2/CCl_4$

2) $AlCl_3$ (Anhyd)




→ $C_o$ – Vitamin $B_{12}$

Zn – Carbonic anhydrace

Rh – Wilkinson catalyst

$M_g$ – Chlorophyll

$H_2O$ : Sugar = Recrystallization

→ $H_2O$ : Aniline = steam distillation

$H_2O$ : Toluene = Differential extraction

In rate $SN_1$

$3^\circ\text{-b} > 3^\circ\text{-a} > 2^\circ\text{-b} > 2^\circ\text{a} > 1^\circ$

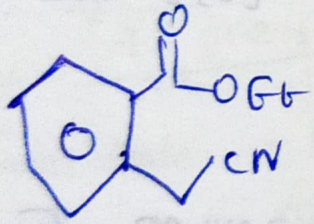
~~1° ben > 1°~~ > 1°-a > $2^\circ$

(double)

In Freidel Craft rxn

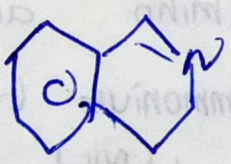
rate ~~Cl~~ > Cl > Br > I

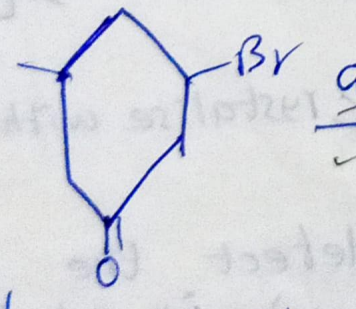
(like $SN_1$ or)

→ 

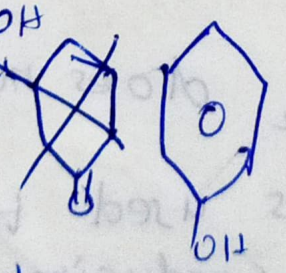

i) $NH_4Cl$

ii) DIBAL-H



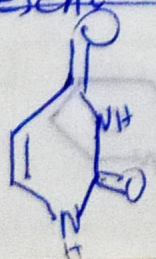

→ 


alcKOH



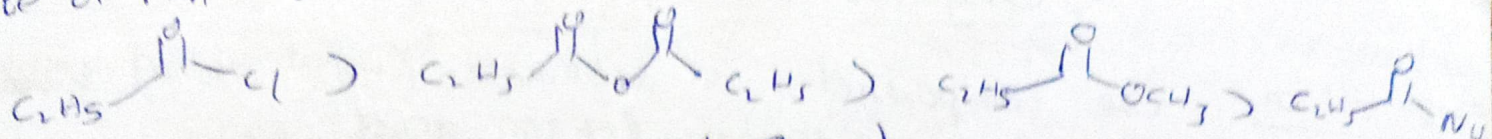

(Take excess granted)

→ ~~PAN is present in pho~~

→ 


= Uracil (RNA)

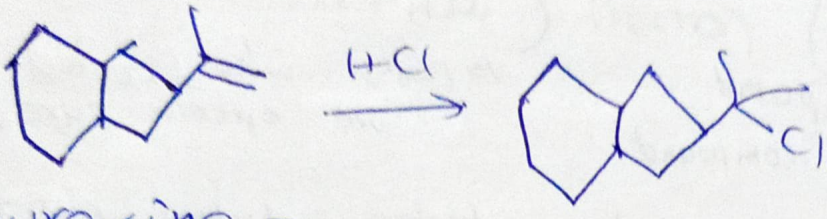
→ Rate of rxn with $LiAlH_4$



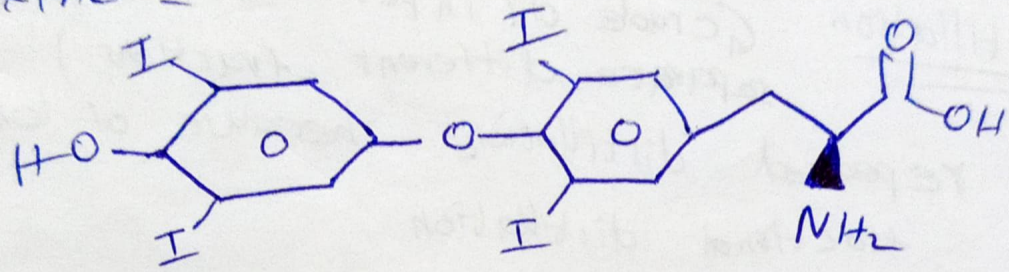
→ Ester test - Aspartic acid (Asp)

→ pthalein dye test - Tyrosine (Tyr) (Phenols give pthalein dye test)

→ ~~Proline doesn't give ninhydrin test.~~ (doubt)

→ 

→ Thyroxine =

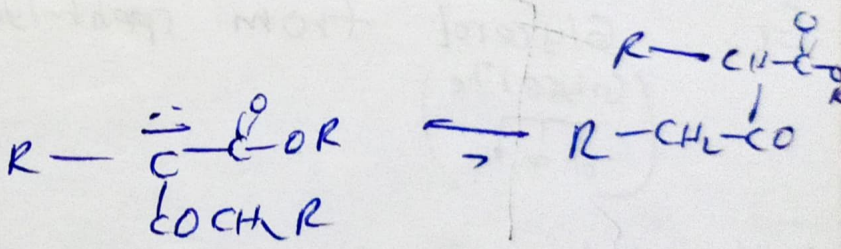


$SN_2 > SN_2'$

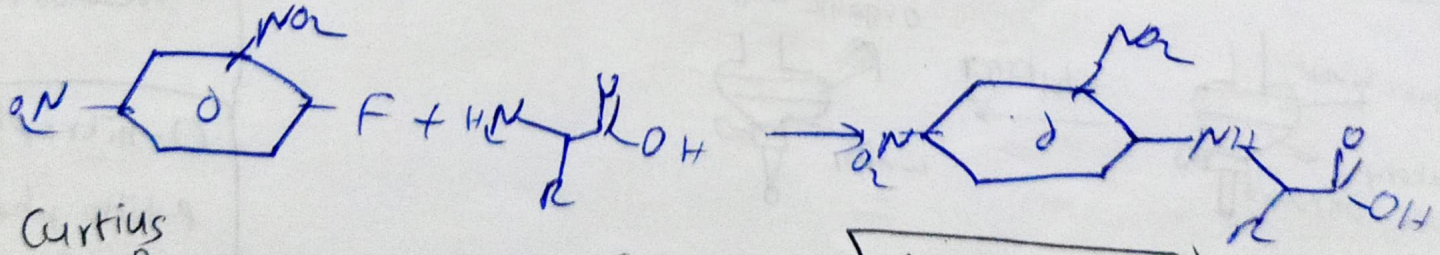
$SN_1' > SN_1$

→ $2R-CH_2-\underset{\underset{O}{\|}}{C}-OR \xrightarrow[ROH]{ROMg} R-CH_2-\underset{\underset{O}{\|}}{C}-\underset{k}{CH}-\underset{\underset{O}{\|}}{C}-OR + ROH$

Claisen ester condensation occurs if in $\alpha$ 2 hydrogens are present because



→ Rxn with sanger's reagent



→ Curtius

$R-\underset{\underset{O}{\|}}{C}-NH_2 \rightarrow R-N=C=O$

→ Wolf

$R-\underset{\underset{O}{\|}}{C}-CH_2 \rightarrow R-C=C=O$

$AgOH - SN_1$

# Organic - basic principles

**Sublimation:** One compound is sublimable (vapour ⇌ solid) & other is not. Ex: Camphor + Benzoic acid

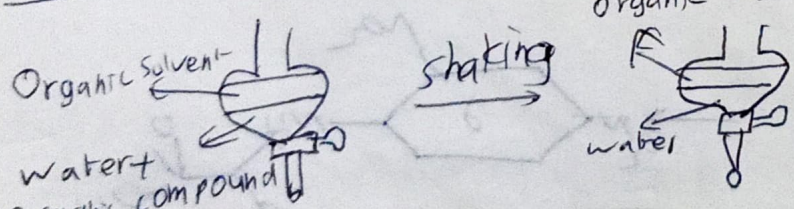
**Crystallation:** A → hot water-soluble & cold water insoluble
B → soluble
first heated then cooled Ex: Benzoic acid

**Distillation:** ($CHCl_3$ + PhNH$_2$) (BT > 30°) ($HCCl_3$ + PhH)
A = Volatile compound
B = Non-volatile compound
vapours when cooled we obtain pure A

**Fractional distillation** (crude oil in petroleum industry) (BT < 30°)
separate different fractions)
repeated distillation because of long fractional distillation.

**Distillation under reduced pressure** (If they decompose)
N.B - B > decomposition temperature
B.P is decreased by decreasing pressure.
Ex: Glycerol from spent-lye (in soap industry)
(Glycerine)

**Differential extraction**




Aniline + water
Steam distillation

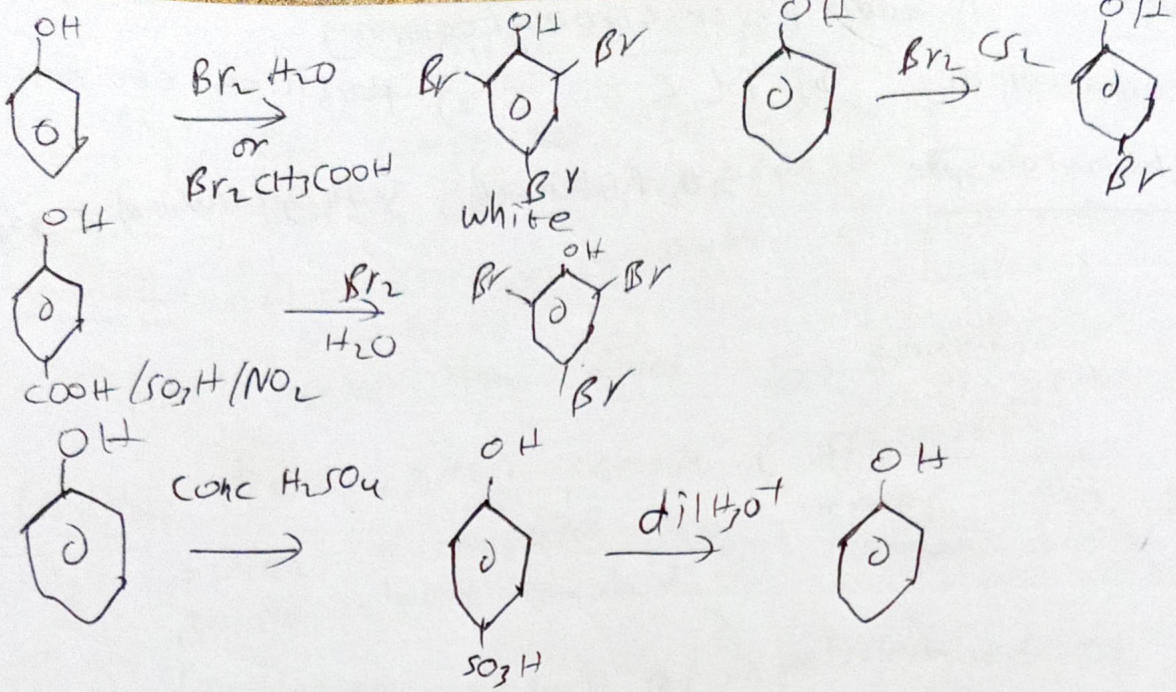
O-nitrophenol
p-nitro phenol
Fractional distillation

Chromatography

1) Adsorption chromatography

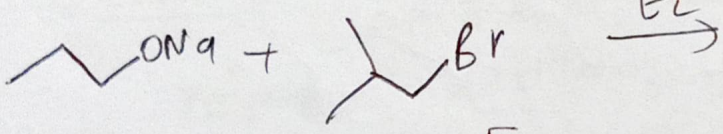
1) a) Column chromatograph  b) T.L.C  2) Partition chromatography

1) Adsorption chromatography : $SiO_2$ (Silica gel) & $Al_2O_3$ (Alumina) = adsorbents

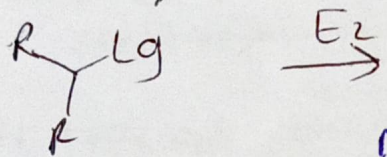




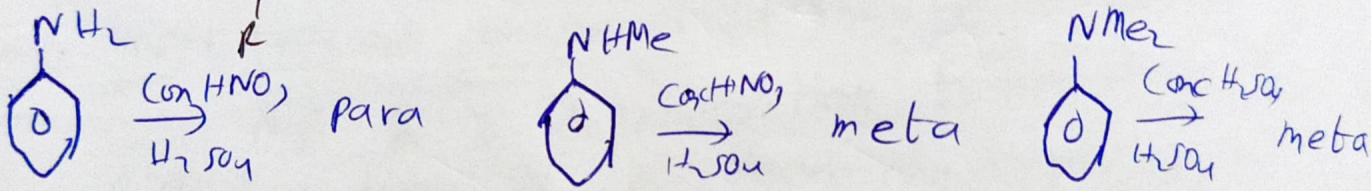


→ 

$E_2$

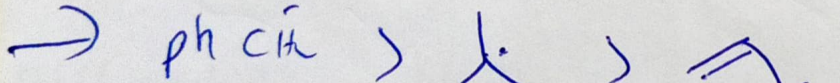
→ $CH_3O^-$ + 

$E_2$

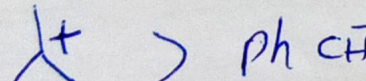
→ 

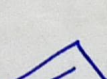

→ Rate of cannizaro = rate of $Nu^-$ attack

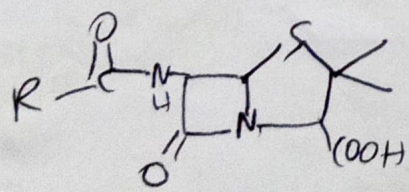
→ $R-NH_2$ $\xrightarrow[KOH]{CHCl_3}$ $R-NC$ rate ∝ Basic strength

→ 

>  > 

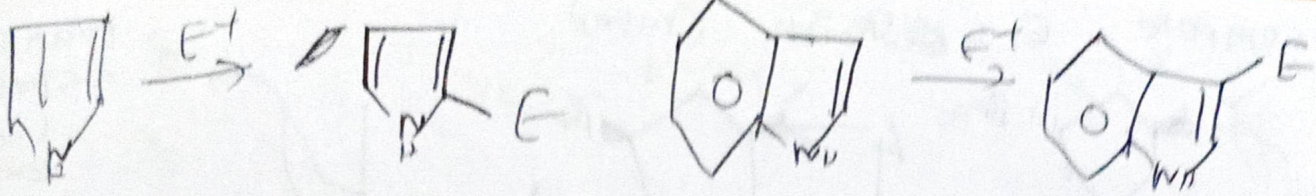


> ph $CH_2$ > 

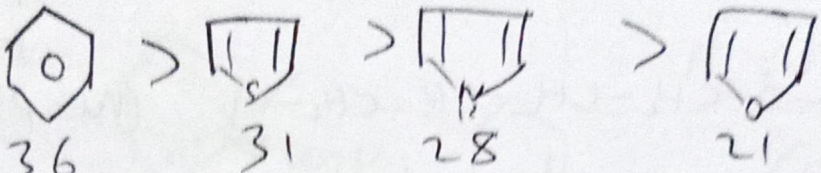

→ 

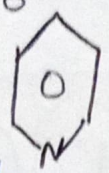
= Penicillin

→ Ether = soluble in conc $H_2SO_4$

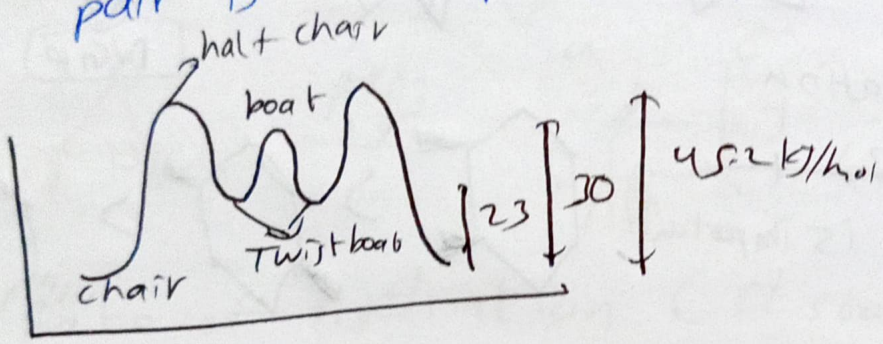
→ 

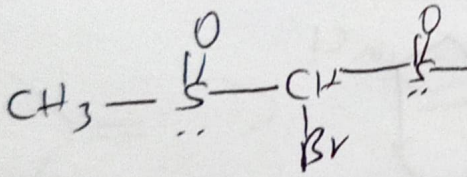
rate of EAS  Pyrole > furan > thiophene > benzene

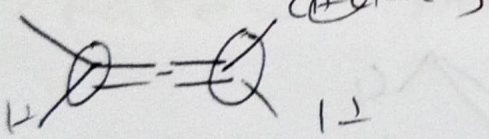
Resonance Energy 

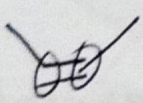

 = 32

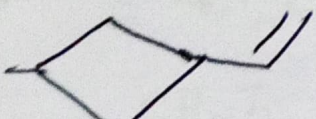
→ Lone pair is better Nucleophile than =

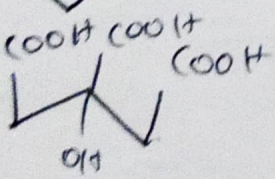
→ 

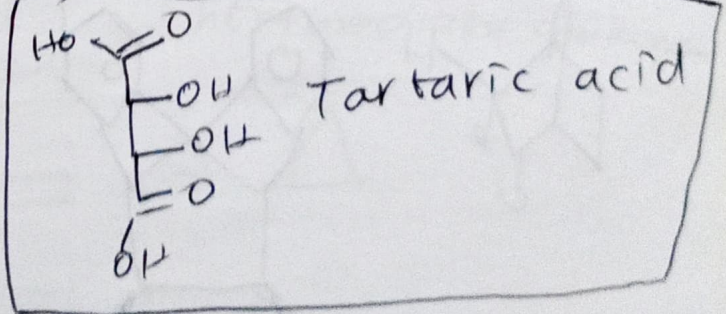

→  No. of chiral centre ≠ 1 = 3

→  No. of stereogenic centres = 3

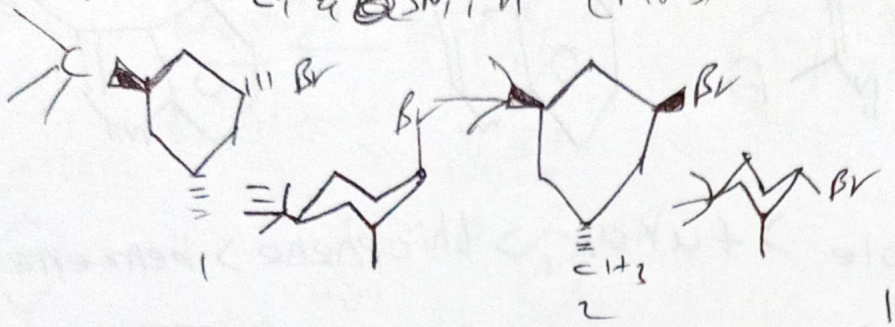
→  No. of stereo genic centres = 2

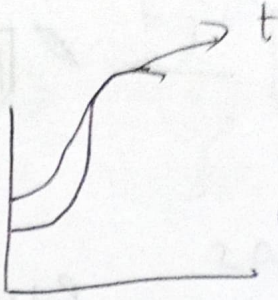
→  (3bromo cyclobutyl) ethene

→  = citric acid

 Tartaric acid

→ compare $E_1$ & $SN_1$ in (rates)




1 > 2 ($E_1$)

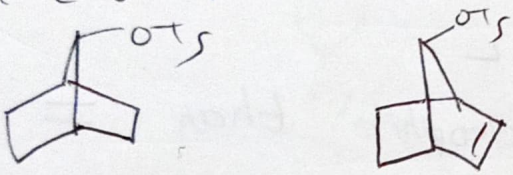
1 > 2 ($SN_1$)

(NGP as solvolysis)

1 > 2 ($SN_2$)

→ $CH_3-O-CH_2-CH_2-CH_2-CH_2-Cl$

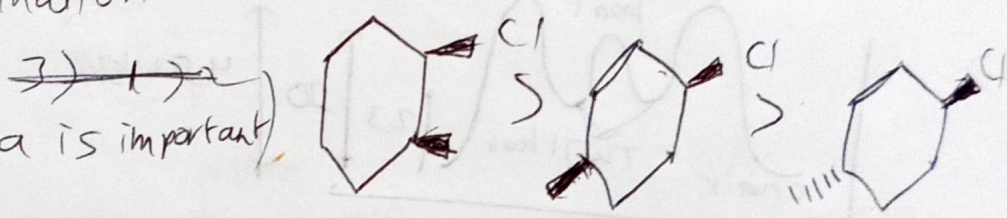
→ rate of $Nu^-$ attack




3 >> 2 > $SN_1$

NGP

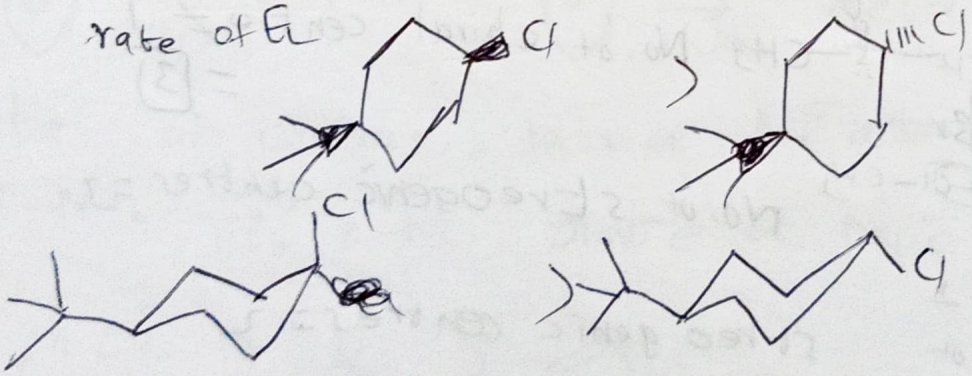
→ Rate of elimination




(Ea is important)

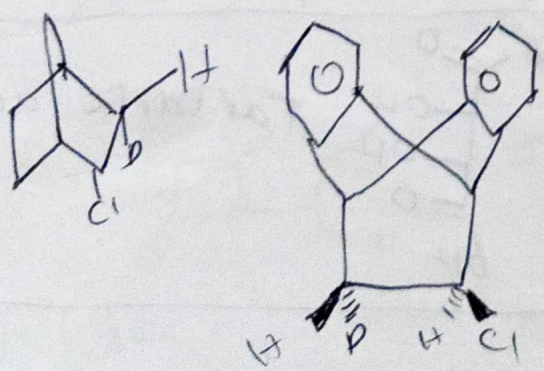
→

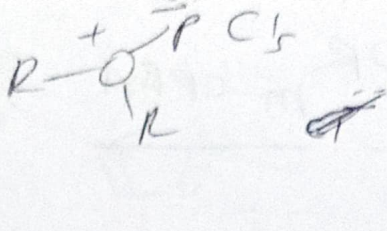
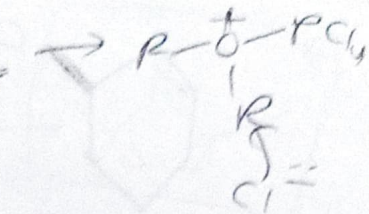
rate of $E_2$




→ Rate of dehydro halogenation means generally $E_2$

→

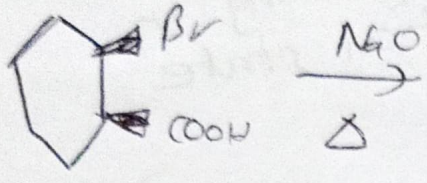


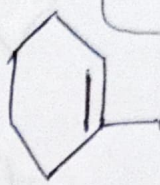
→ R–O–R + $PCl_5$ →  → 

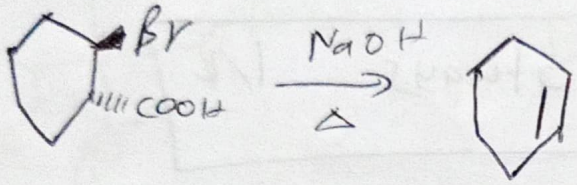
$Cl-R + R-OPCl_4$

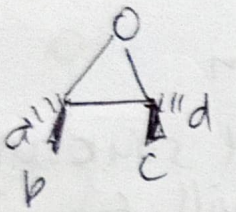
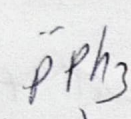
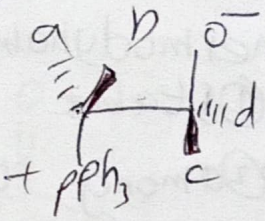
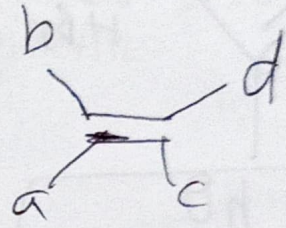
↓ SM

$Cl-R + R-Cl$

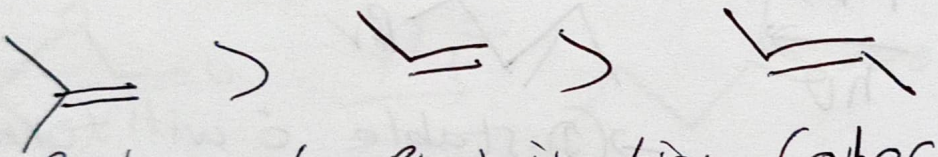
→ 

 (conjugation)

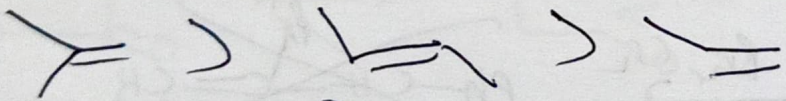


→    → 

→ Rate of hydration ($C^+$ stability)



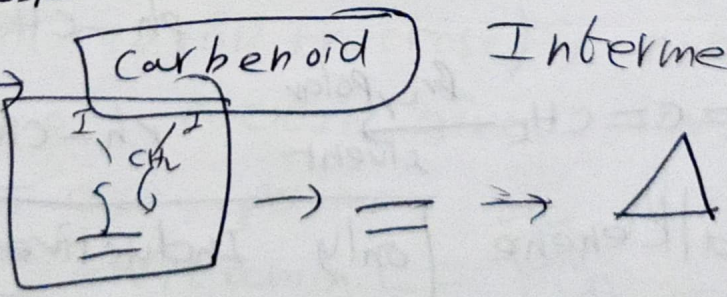
→ Rate of Bromination (electron density)
(as $C^+$ is not formed only inductive)

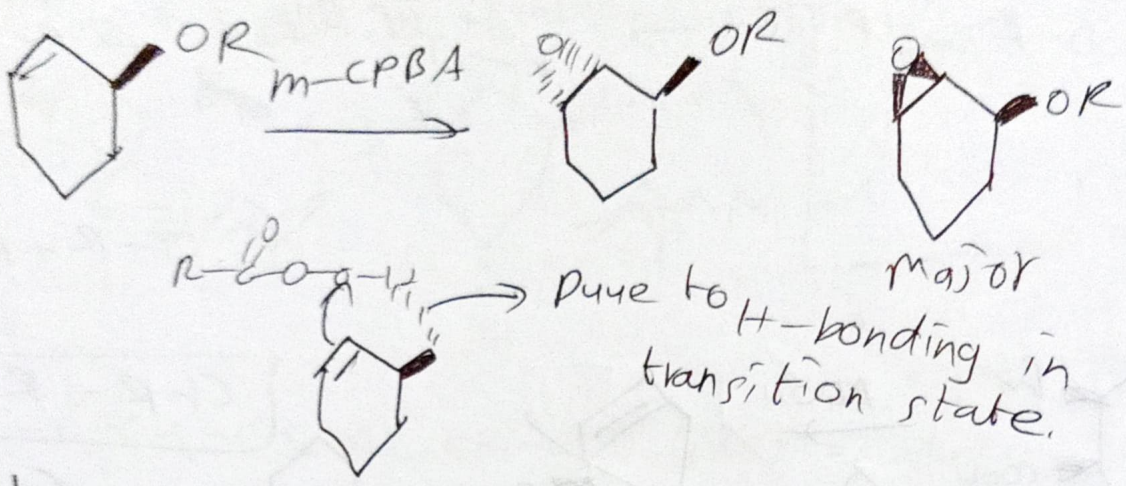


→ $CH_2N_2$ $\xrightarrow[RO-R]{\Delta}$ $CH_2$

→ $CH_2I_2$ $\xrightarrow{Zn}$ carbenoid

Intermediate carbenoid



→ 



→ Due to H-bonding in transition state.

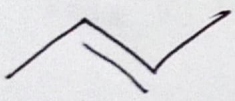
→ 

1 eq
HBr

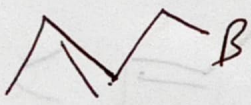
Kinetic always 1/2

Thermodynamic
→ ① Stable ĉ will form
→ ② among its canonical structures stable alkene will form,

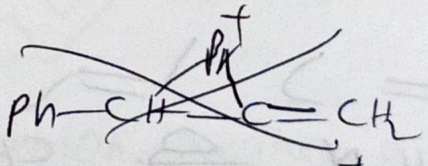
☆ $Br_2$ hθ
F.R.S
at aryl & allyl

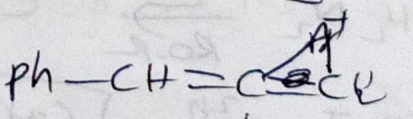
→ 

NBS
hθ

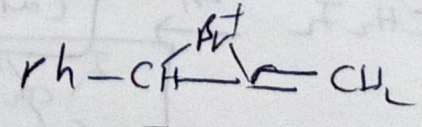


→ ① stable ĉ will form
→ ② stable alkene

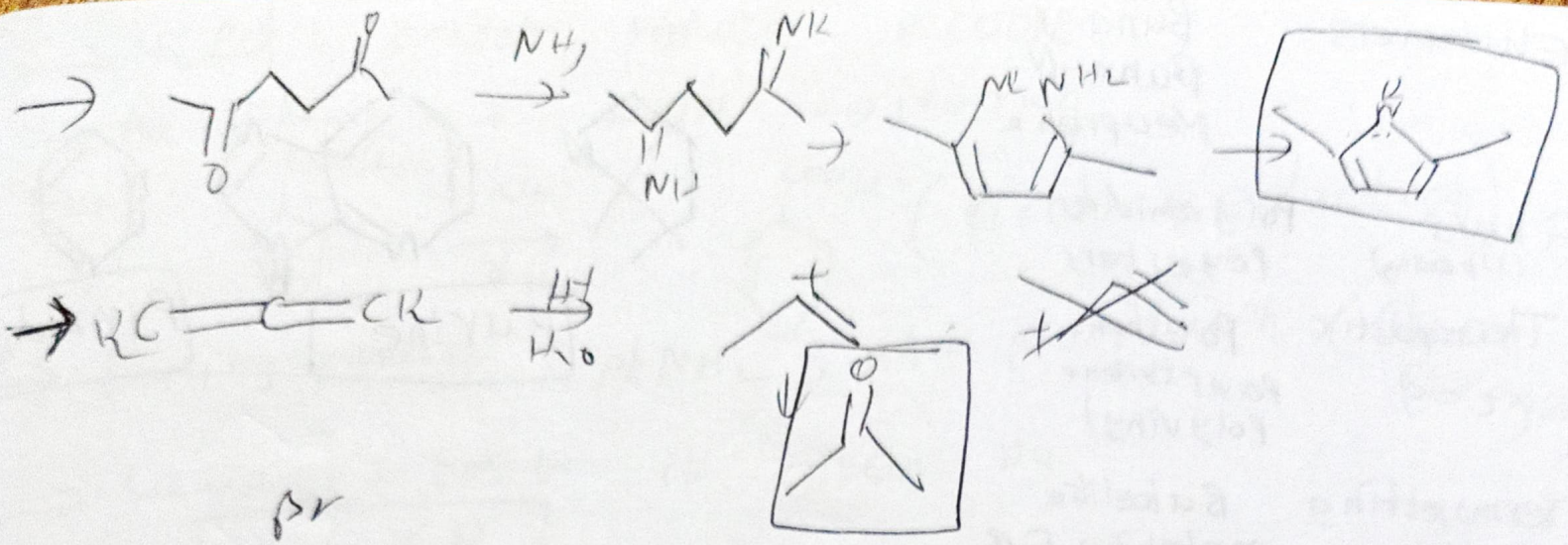
→ Ph—CH=C=CH₂ $\xrightarrow{Br_2\ CCl_4}$ 

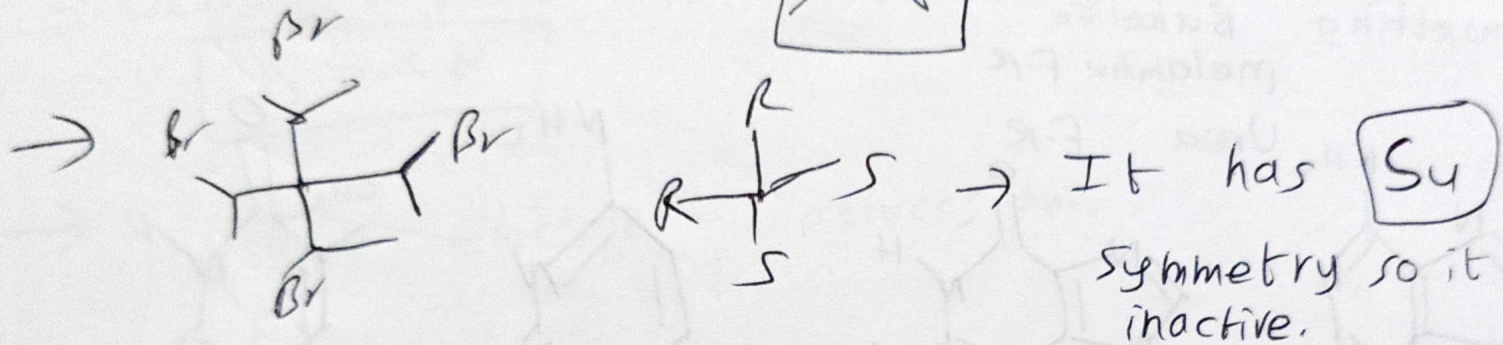
(only Induct

→ Ph—CH=C=CH₂ $\xrightarrow[\text{solvent}]{Br_2,\ \text{Polar}}$ 

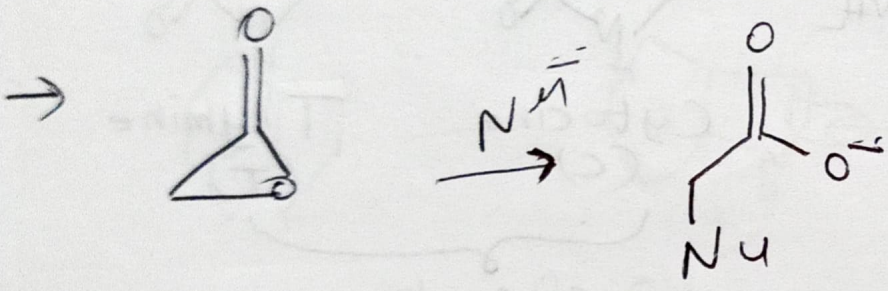

→ Normal alkehene only Inductive

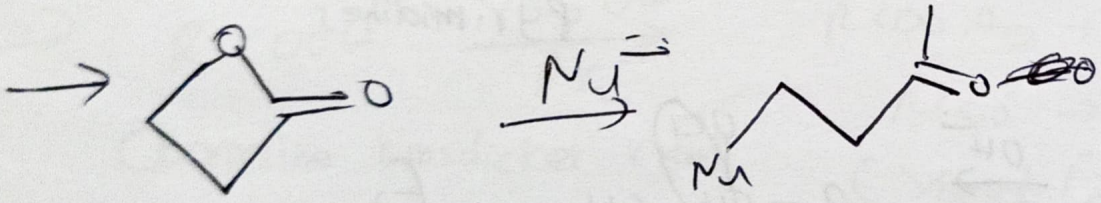


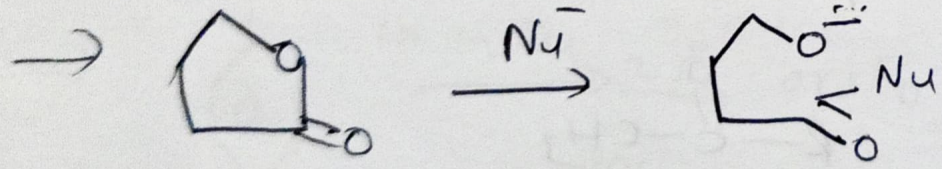




→ It has Sᵤ symmetry so it is inactive.





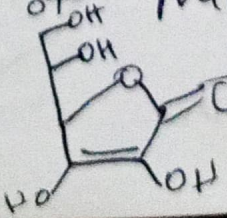


→ glycoside = actals at anomeric carbon

→ Sucrose (αD Glucose + βD Fructose) is not invert sugar. Hydrolysis of sucrose gives invert sugar

→ Nucleic acids are polymers of Nucleotides

→ Ascorbic acid = Vitamin C =

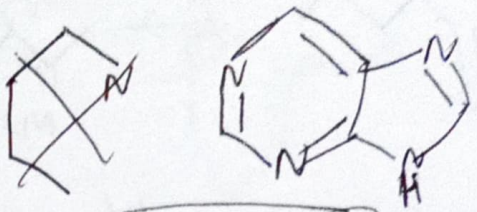


Elastomers · Buna-S
Buna-N
Neoprene

Fibers (H bonding) — Polyamides, Polyesters

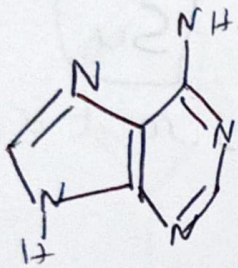
Thermoplastic (C=C) — Polythene, Polystyrene, Polyvinyl

Thermosetting — Bakelite, melamine F-R, Urea F-R

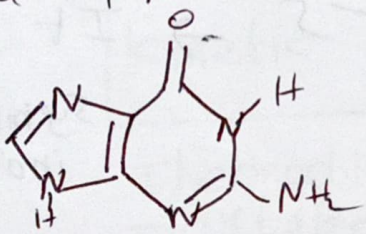


Purine.

Pyrimidine

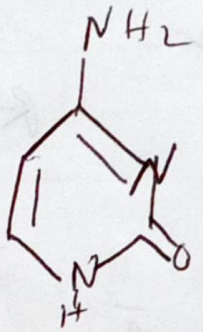


Adenine (A)

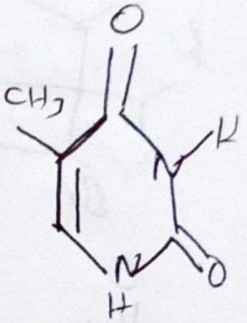


Guanine (G)

Purines

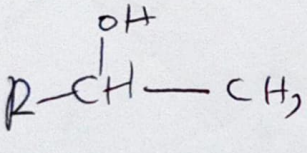


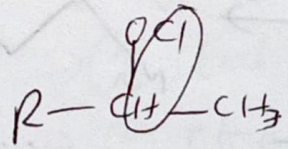
Cytocine (C)



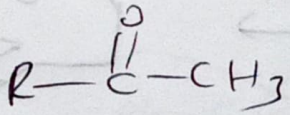
Thymine (T)

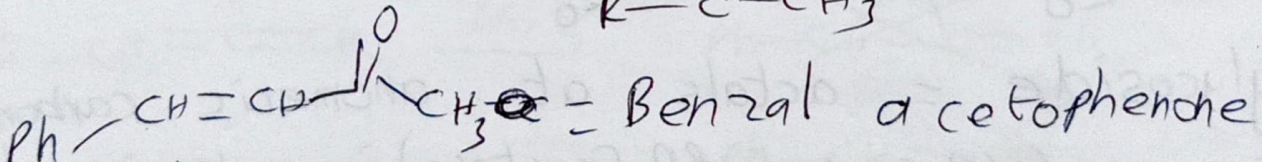
Pyrimidines



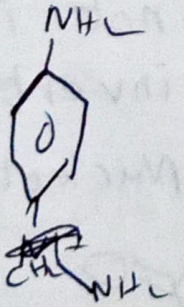


$E_2$





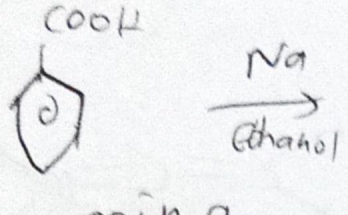
= Benzal acetophenone



= (p-aminomethyl)aniline

→ $H_2Pd$ cannot reduce RCOOH

→ Na : Ethanol + COOH → No rxn

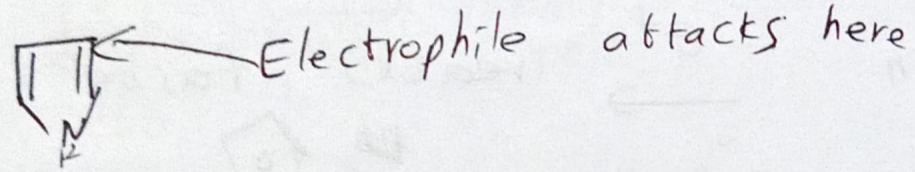
Ex: 

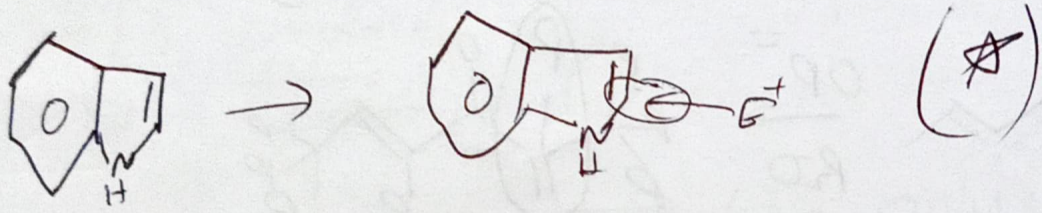
(Birch reduction)

→ ~~Boiling point~~ $PhNH_2 > Ph-\ddot{N}=\ddot{N}-Ph$ (Basic strength)

→ Lassaigh's test is given by

NSXP

→ 

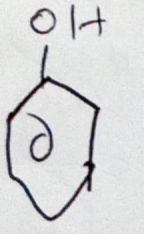
(*)

→ $RCOOH \xrightarrow[Br_2]{AgOH}$ $RCOOAg + Br_2$

$RCOO^- \rightarrow R^- \; Br_2 \rightarrow R-Br$

(Borodine hunsdicker rxn)

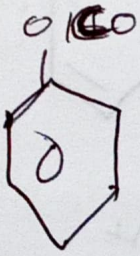
(Yield $1^\circ > 2^\circ > 3^\circ$ steric factor)

→ 

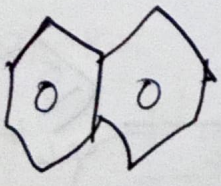
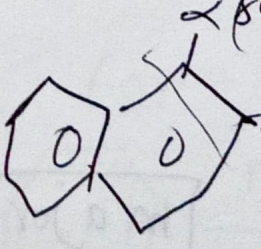
$\xrightarrow{conc\ H_2SO_4}$ $25^\circ$ → ortho

$\xrightarrow{100^\circ C}$ para

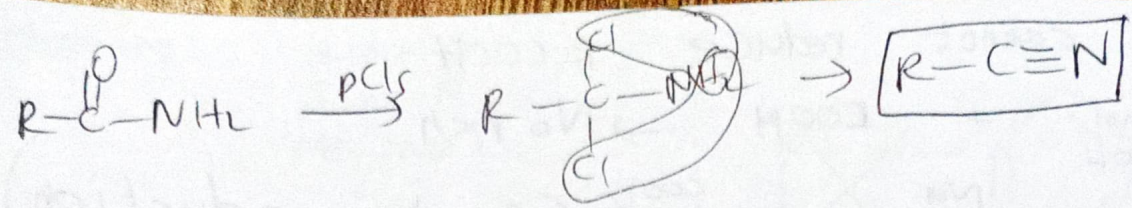
(steric factor)

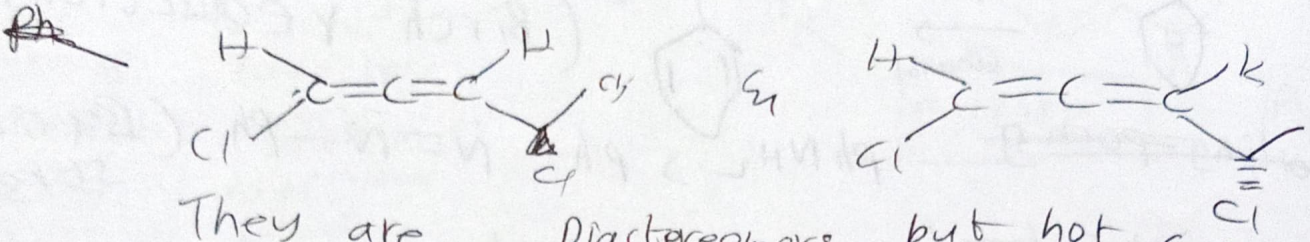


Fries → rearrangement → low Temp → H ortho + (H-bond)

→ 
$\xrightarrow{conc\ H_2SO_4}$ 

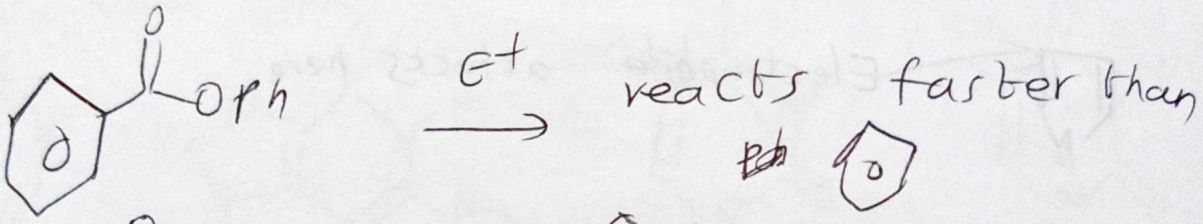
→ Thermodynamic

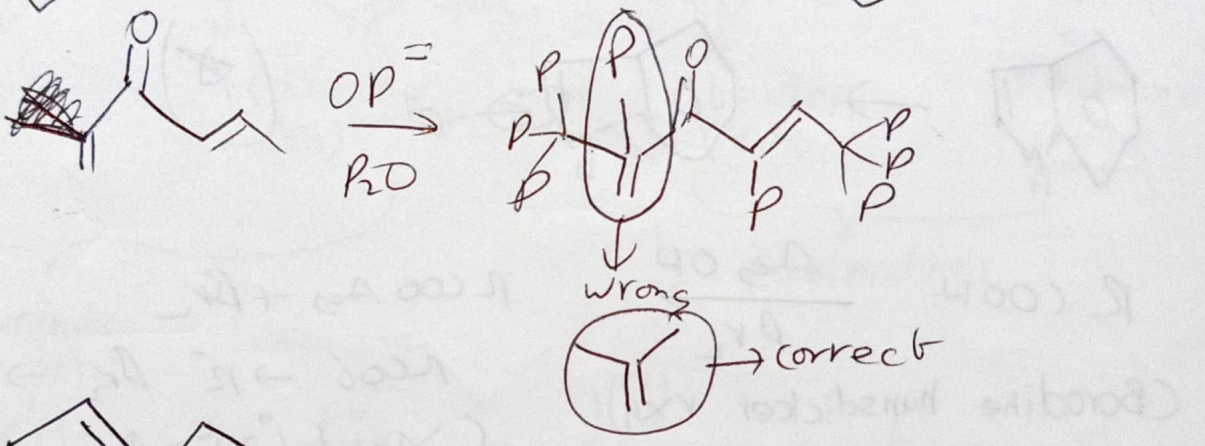
→ 

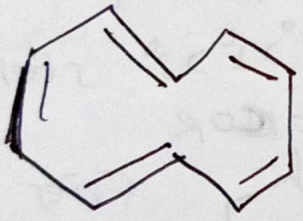
→ 

They are Diastereomers but hot G-I

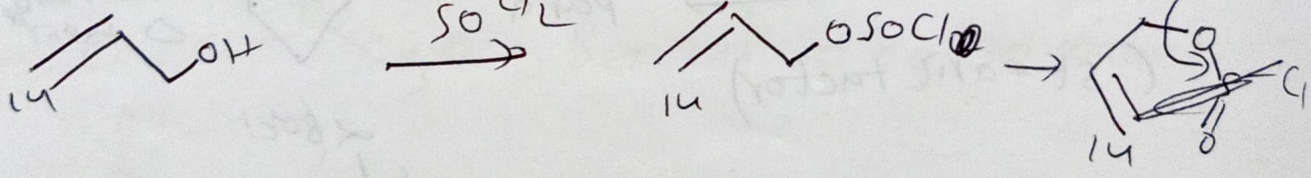
All G-Isomers are Diastereomers.

→ 

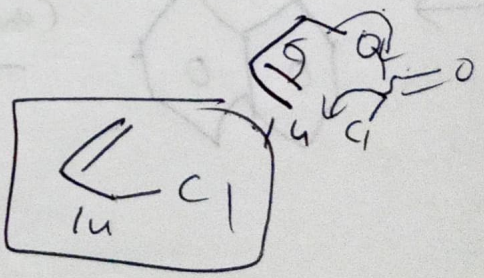
→ 

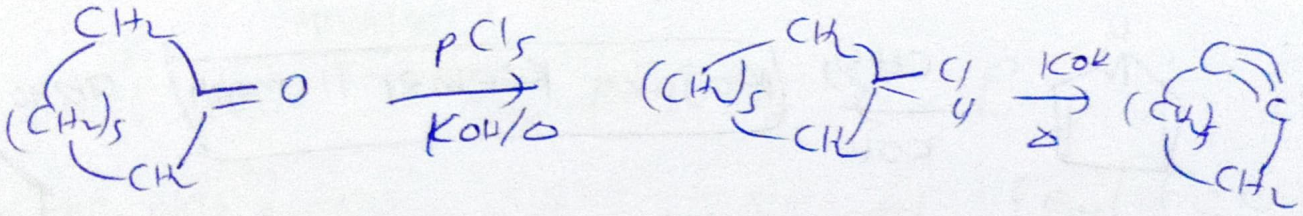
→ 

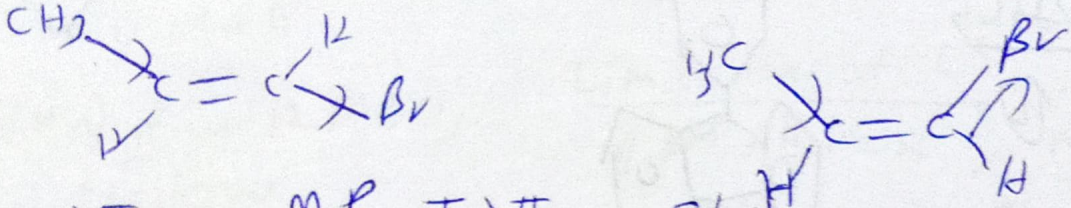
→ N·A

→ 

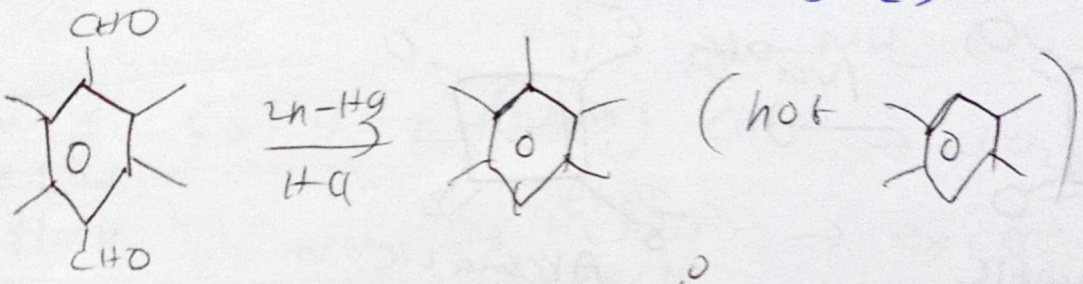
major SN1'

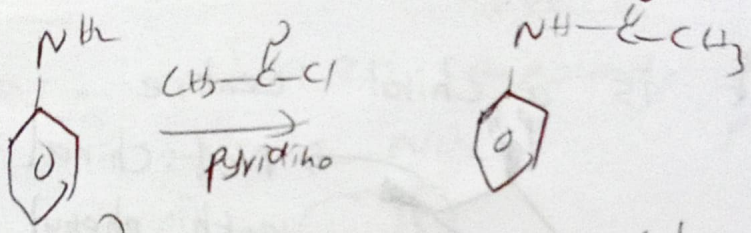


→ 

→ 

M I > II  M.P I > II  Solubility I > II  stability I > II

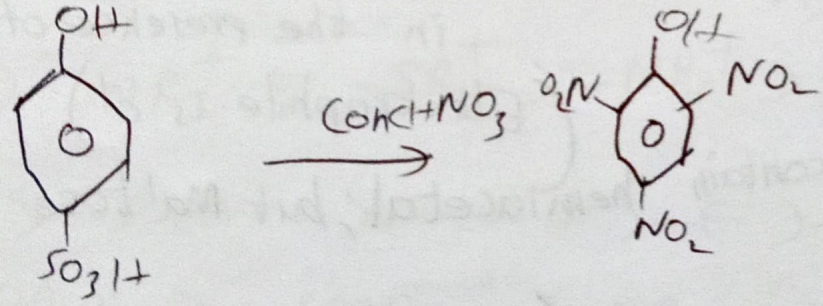
→ 

→ 

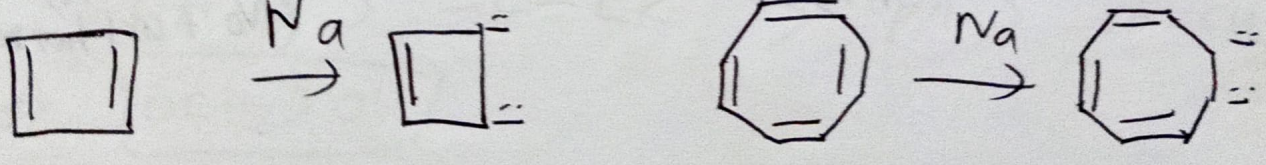
→ $CH_3-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$ is the only ester which gives Iodoform.

→ acid near $NH_2$ is more acidic (In amino acids)

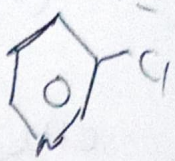
→ amin near COOH is less basic

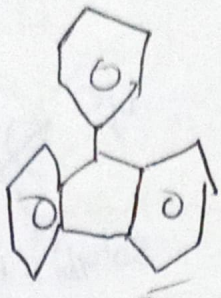
→ 

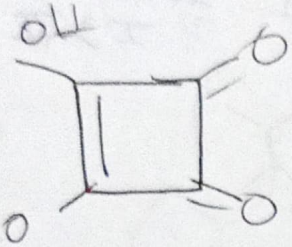
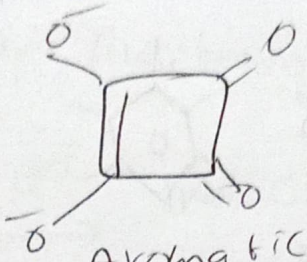
→ In general Ipso only for $SO_3H$/COOH

→ 

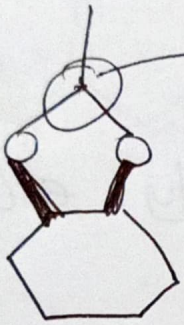
→  $\xrightarrow[KOH]{CHCl_3}$ Major = Kremer Tiemann abnormal =

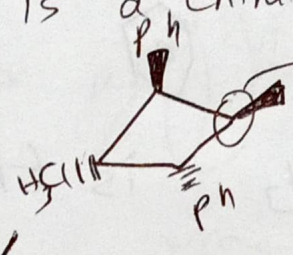


→ $Ph_3CCl \xrightarrow[\text{benzene}]{AlCl_3}$ 

→  $\xrightarrow{NaOH}$ 

Aromatic Aromatic

→  It is a chiral centre

 Not chiral because both phenyl R,R or S,S

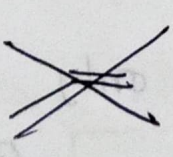
→ Chain isomers = different main chain

→ positional isomers = same main chain

→ Friedal cratt reaxn = any electrophile generated in the presence of Lewis acid.

(Electrophile is $c^+$)

→ Sucrose doesnot contain hemiacetal, but Maltose & lactose contains

→ $CH_3-C\equiv CH \xrightarrow[liq\ NH_3]{Na}$  $-\equiv-$ (Acid Base) (No further rxn)

# Analysis

→ Lassaigh's test ~~O~~, N, S, X, P

$Na_4[Fe(CN)_5NOS]$ violet

$Fe(SCN)_3$ red

$Fe_4[Fe(CN)_6]_3$ Prussian blue

Limitations of L-T

1) ~~ph~~ ph $N_2X$, $N_2\uparrow$
2) $ph-N=N-ph$ $N_2\uparrow$
3) $H_2N-NH_2$ (no C)

→ Duma's method $C_xH_yN_2 + \left(2x+\frac{y}{2}\right) CuO \rightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2$

→ Kjeldhal's $NH_3 \rightarrow$ then $H_2SO_4$ reacts → excess is back titrated.

Limitations - 1) azo compounds ~~ph~~ $N_2$ + $ph-N=N-ph$
2) $\phi-NO_2$
3) 

Inductive effect (permanent): distance dependence dominates

(-I) $O^- > COO^- > -CR_3 > -CHR_2 > CH_2R > CH_3 > D$

(-I) $-NR_3^+ > -SR_2^+ > -NH_3^+ > -NO_2 > -SO_2R > -CN$

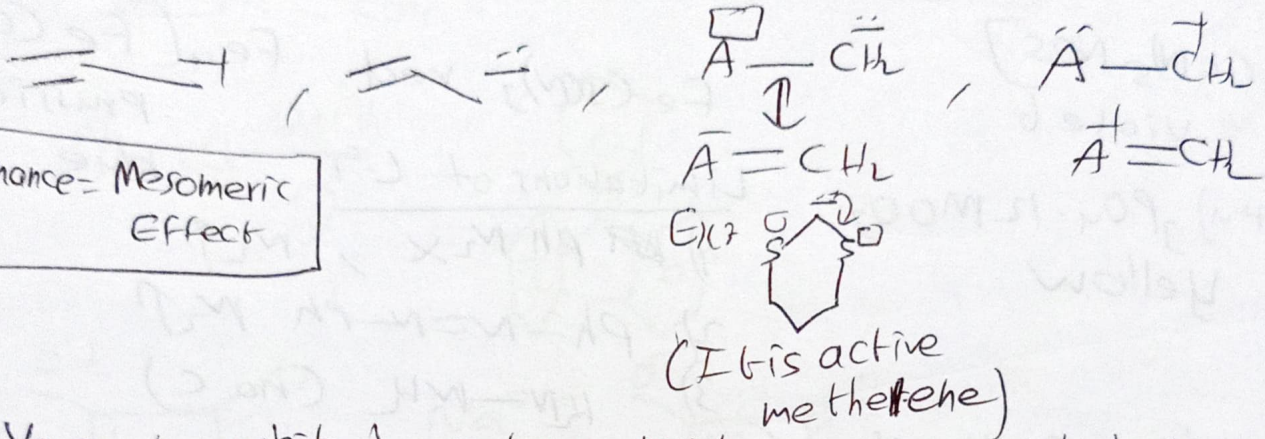
$> -SO_2Ar > -COOH > -F > -Cl > -Br > -I >$

$-OAr > -COOR > -OR > -COR > -SH > SR$

$> OH > -C\equiv CR > -ph > -CH=CH_2$

$\Rightarrow$ ~~A~~ $OCH_3 > OH$

**Resonance** : The delocalisation of $e^-$ density among $\pi$ orbitals is called resonance.



Resonance = Mesomeric Effect

(It is active methylene)

→ Vacant orbital prefers mainly pure orbital if it is possible.

→ Ortho effect for $-COOH$, $-NR_2$, $-SO_3H$, $-NO_2$

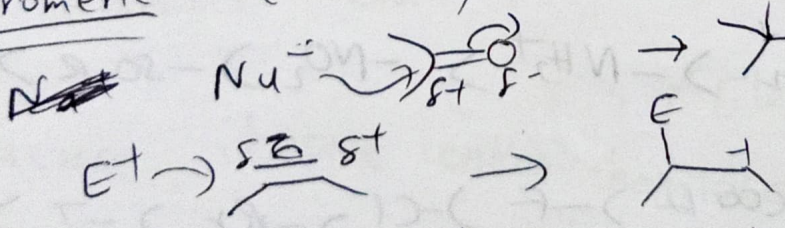
→ If both double bond & lone pair are present ⟹ dominates

Ex; $-\ddot{N}=O$ (−R) $-\overset{\overset{O}{\|}}{\underset{\underset{:}{}}{S}}-OH$ (−R)

**Inductomeric** : Due to polarisation (Temporary)

$H_2O$: $\overset{\delta+}{Br}-Br^{\delta-}$ (In polar medium $E^+$ generates)

**Electromeric** : (Temporary)



**Hyperconjugation**: It is the $\sigma$ delocalisation

→ Count hyperconjuation in all resonance structures & add

*Radical is stabilised by both +R & −R & also +I (−I destabisise)

## Heat of hydrogenation

1) h.oh $\propto$ n $\pi$-bonds

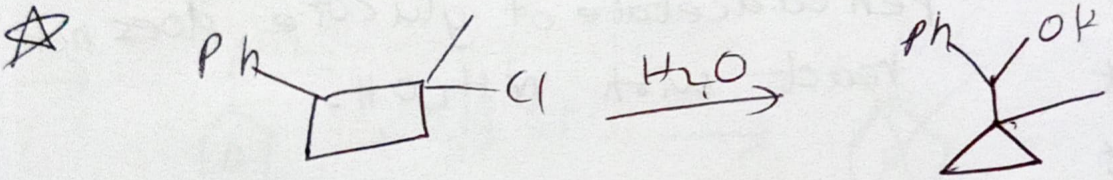
$\propto \frac{1}{\text{stability of alkene}}$

## Heat of combustion

h.o.c $\propto$ mol wt (mol wt same)

$\propto \frac{1}{\text{stability of isomer}}$

$\propto$ surface area (isomers of alkane.




## stability

$3^\circ$ benzyl > $3^\circ$ allyl > $2^\circ$ benzyl > $2^\circ$ allyl > $\overset{+}{>}$

> $1^\circ$ benzyl > $1^\circ$ allyl > $3^\circ > 2^\circ > 1^\circ$

Sucrose — $\alpha$ D Glucose – $\beta$ D Fructose

Lactose — $\beta$ D Galactose – $\beta$ D Glucose

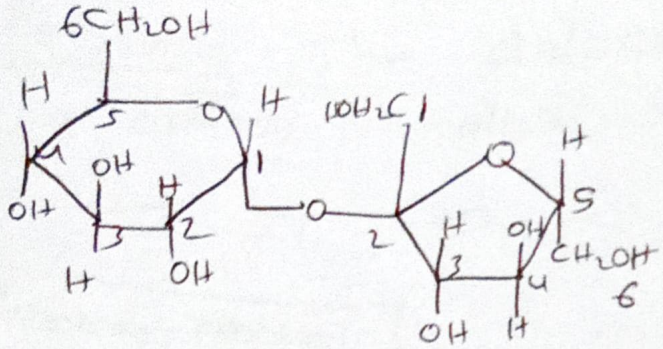
Maltose — $\alpha$ D Glucose – $\alpha$ D Glucose

Amylose — $(\alpha$ D Glucose$)_n$

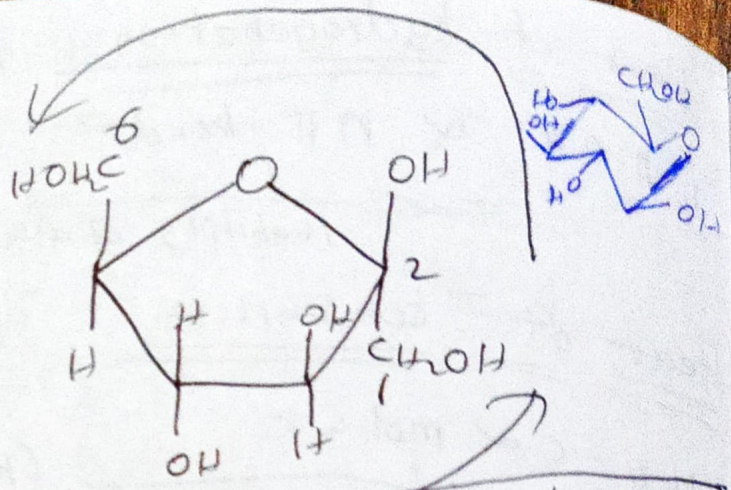
Amylopectin — $(\alpha$ D Glucose$)_n$ (branching C1–C6)

Cellulose — $(\beta$ D Glucose$)_n$

Glycogen $\cong$ Amylopectin (more branched than amylo



∝D-Glucose



βD Fructose

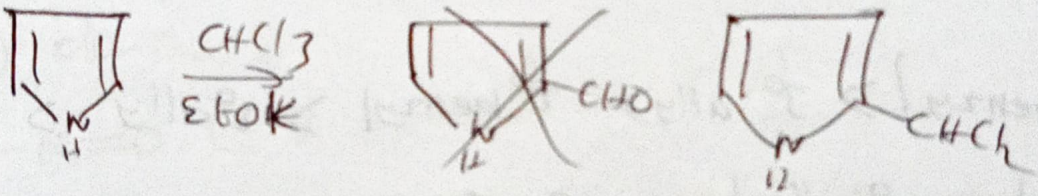
Invertase = ∝D-Glucse + βD fructose

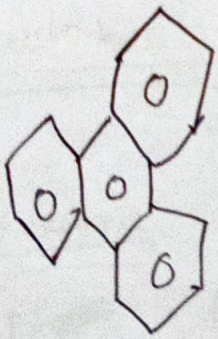
Fructose does not react with $Br_2H_2O$

Glucose does not give

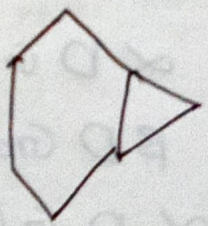
1) 2,4-DNP test
2) Schiff's test
3) $NaHSO_3$ test

Pentaacetate of glucose does not react with $NH_2OH$.

→ 

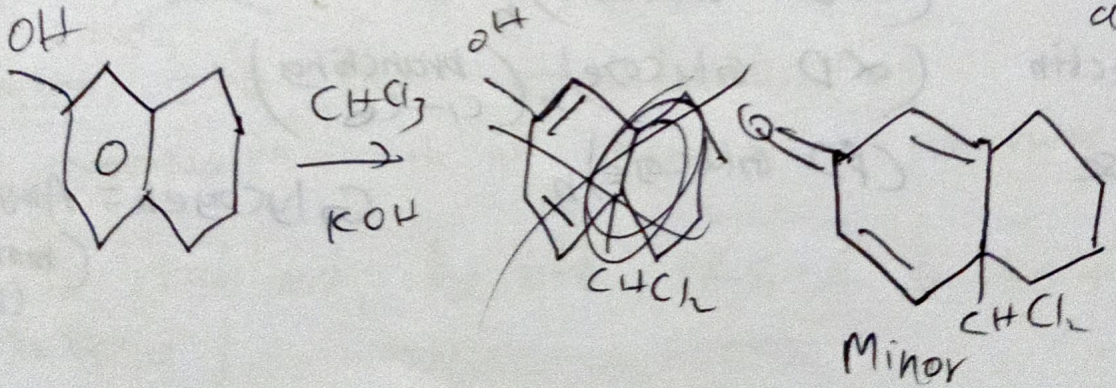
→ 

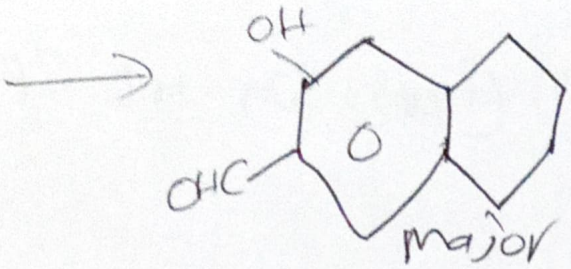
= Triphenylene →

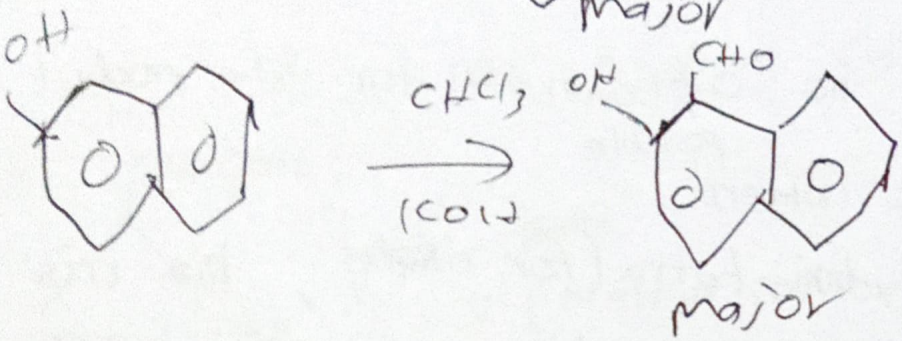


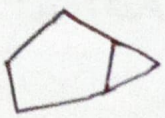
Cis & Trans both exists

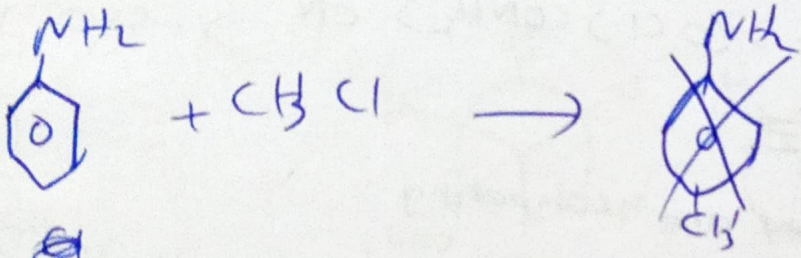
Trans = Optically active

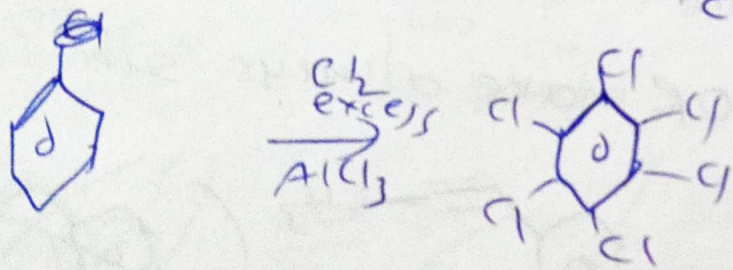
→ 

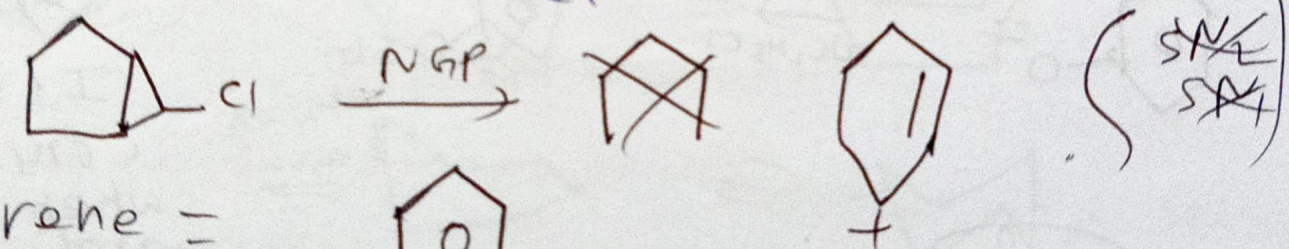


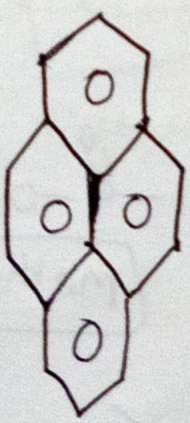




→  Geometrical isomers not possible only cis

→ 

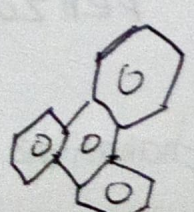

→ 


→ 

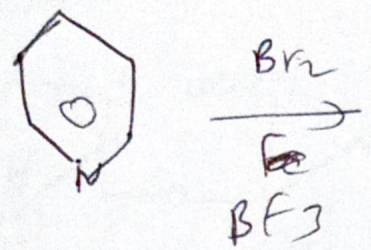

→ Pyrene = 

No. of resonances = 6

→ ethylene = =

→ Triphenylene = 

9

→ 

(This is not F-C rxn)

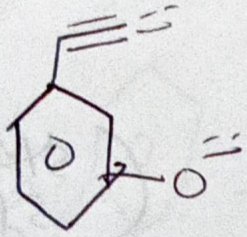
→ If they asked no. of isomers for the product possible
then count all possible isomers.

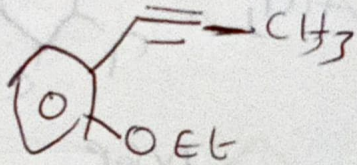
→ In nomenclature di, tri, tetra (for simple), bis tris (for complex) are not considered in alphabetical order.
But neo & iso are considered.

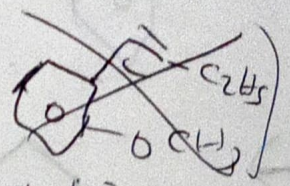
→ COOH > $SO_3H$ > COOR > COCl > $CONH_2$ > CN > -CHO > C=O > OH > $NH_2$ > = > ≡

↓ If they are competing

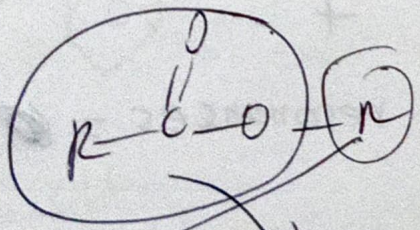
→ X, $NO_2$, NO, OR are always substituents

→ 

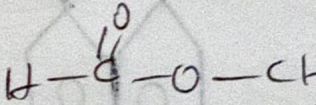
1) $CH_3Cl$
2) $C_2H_5Cl$


( 

It is not considered when no. of products are asked

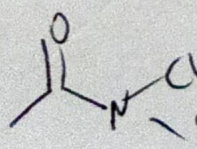
→ 

alkyl alkanoate.

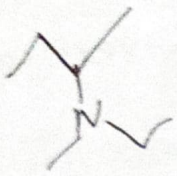


Methyl formate

→ ph-$CH_2$ benzyl ph-CH< benzal ph-C< Benzo

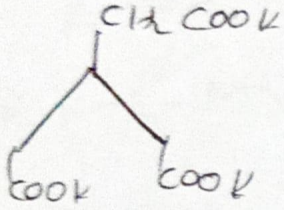
→ 

(N,N) dimethy ethanamide.



= N ethyl N methy Butan 2-amine.

$CH_3-CN$ = ~~Ne~~ Methyl cyanide = Ethane nitrile.

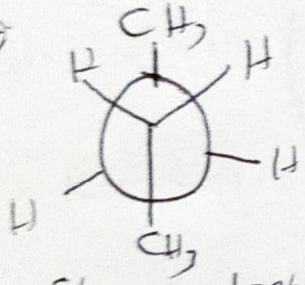



→ ~~(1,3)~~

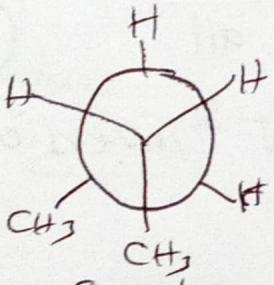
2-(methyl carboxy) - ~~(1,3) dicar~~ propane - (1,2) dicarboxylic acid

or

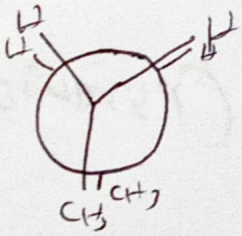
2-(hydroxy oxo ethyl) propane - (1,2) dioic acid

→ 

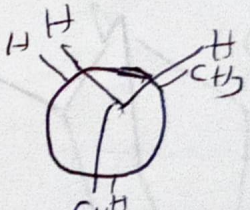
Staggered = ahtr



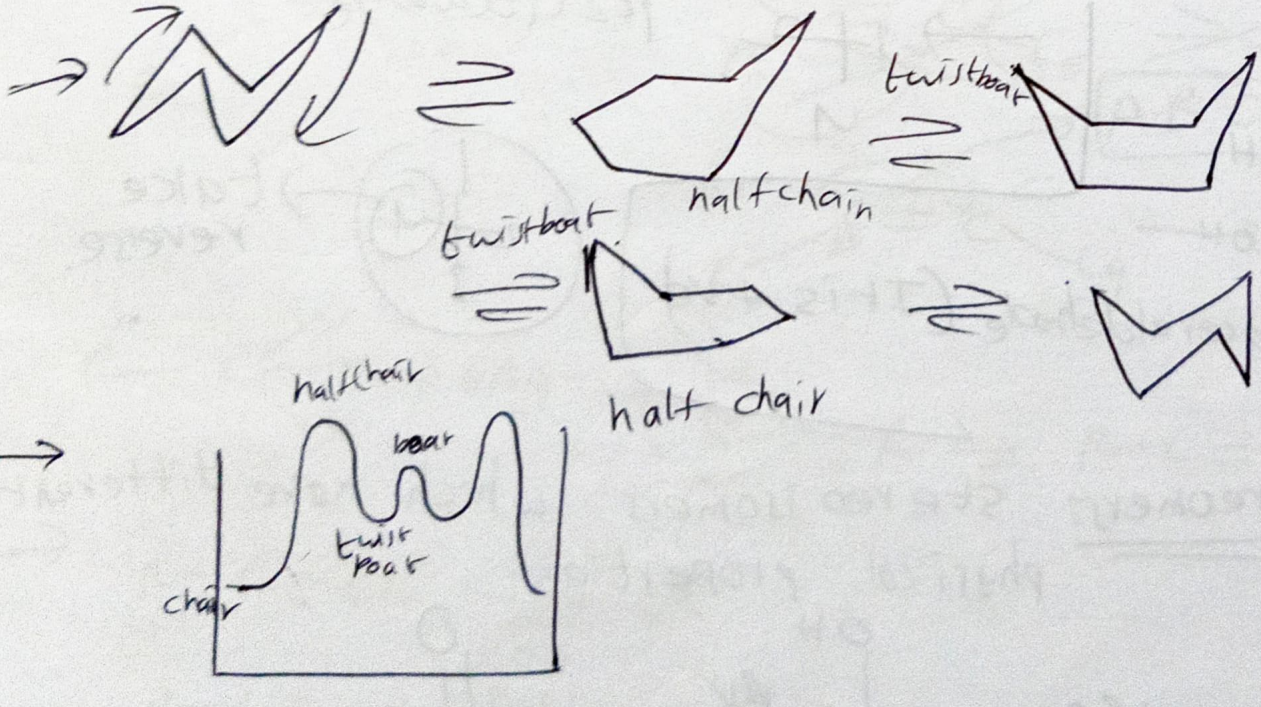
gauche



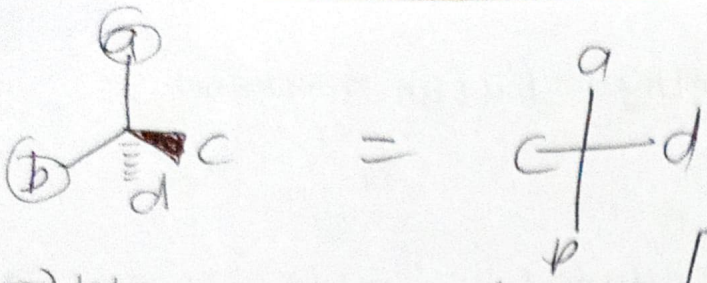
fully edipsed



partially eclipsed

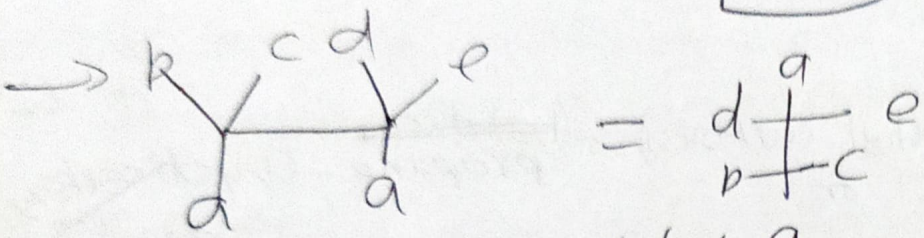
→ 


→ 



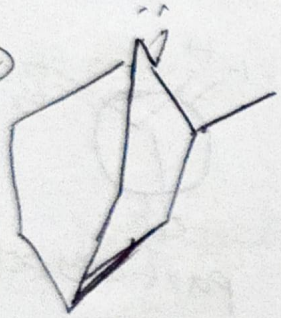

(we should open vertically

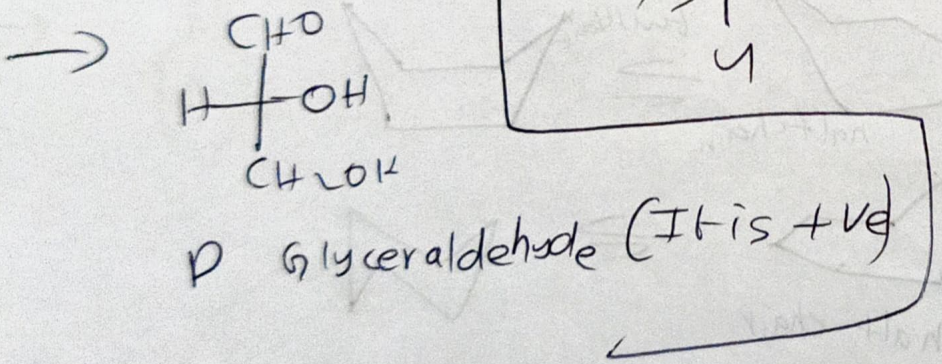
→ we can robabe 180°




→ Prissimetric = It lacks a all other except axis of symmetry

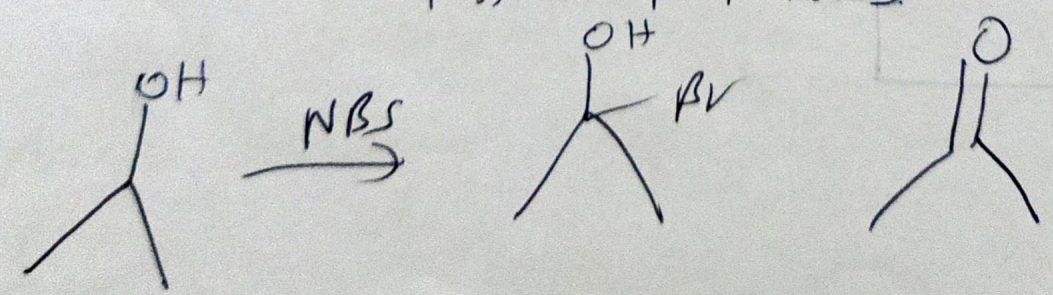
→ Assymetric = It lacks all (A= all)

→ 
(pyramidal inversion)

→ 


D Glyceraldehyde (It is +Ve)

→ <u>Diastereomers:</u> stereo isomers which have different physical properties

→ 

→ Meso compound is an inactive compound having more than 1 chiral compound.

→ In general lone-pair – hybrid
empty orbital – pure
radical – hybrid

→ $R-NH_2 \xrightarrow{CH_3MgX} R-\ddot{N}H^-$ (only once)

→ $R-\overset{O}{\overset{\|}{C}}-NH \xrightarrow{RMgX} R-\overset{O}{\overset{\|}{C}}-\ddot{N}^-$

## Alkynes

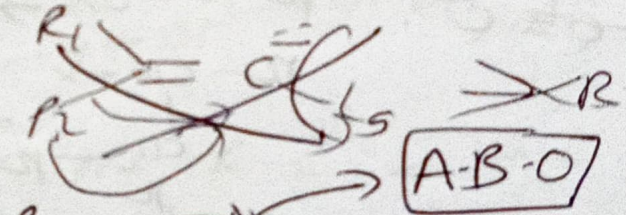
$R-\underset{X}{CH}-\underset{X}{CH}-R \xrightarrow[NaNH_2]{alc.KOH} R-C\equiv CR$

(vicinal dihalides)

$R-CH_2-\underset{X}{\overset{X}{C}}-R \xrightarrow[\Delta]{base} R-C\equiv C-R$

(Geminal)

$R_1R_2C=C(H)(lg) \xrightarrow{base}$




$R_1R_2C=C(lg) \rightarrow R-C\equiv C-R$

$R-CX_3 + 6Ag + R \rightarrow R-C\equiv C-R$

→ $R-C\equiv CH_2 \xrightarrow[\text{or } KOH]{NaOH} X$

$R-C\equiv CH \xrightarrow{NaNH_2} R-C\equiv C^-$

→ $R-C\equiv C^-R \xrightarrow{2HX}$ $R-CH_2-\underset{X}{\overset{X}{C}}-R$

$R-C\equiv CX \xrightarrow{HX} R-C=CX_2$

$R-C\equiv C-R \xrightarrow[H_2O]{HBr}$ $R-\overset{Br}{C}=\overset{Br}{C}-R \Rightarrow R-\underset{Br}{CH}-\underset{Br}{CH}-R$

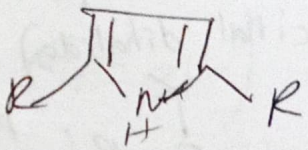
→ $2HC\equiv CH \xrightarrow[NH_4Cl]{CuCl}$ $H_2C=CH-C\equiv CH$

$3HC\equiv CH \xrightarrow[NH_4Cl]{CuCl}$ $H_2C=CH-C\equiv C-CH=CH_2$

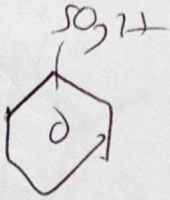
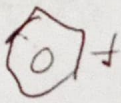
→ $CH_3-CH_2-C\equiv CH \xrightarrow[\Delta]{alc\,KOH}$ $CH_3-C\equiv C-CH_3$

→ $CH_3-C\equiv C-CH_3 \xrightarrow{NaNH_2}$ $CH_3-CH_2-C\equiv C^{-}\,Na^{+}$

→ Conjugate alkyne

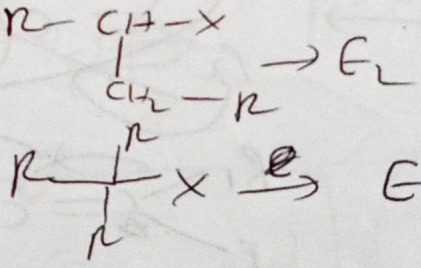
$R-C\equiv C-C\equiv C-R \xrightarrow{NH_3}$ 

(similarly $H_2O, H_2S$)

→  $\xrightarrow{dil\,H^+}$  $+\ H_2SO_4$

→ $R-C\equiv C^{-}$.

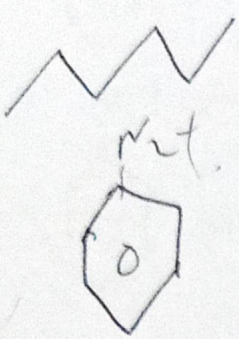
$R-CH_2X \Rightarrow$



→  $\xrightarrow[H_2O]{Br_2}$ ✓

alc KOH ✗

# Aromatic compounds

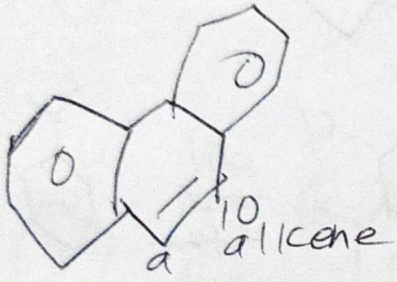


$\xrightarrow{Cr_2O_3 \text{ or } Mo_2O_3 \text{ or } V_2O_5}$



$\xrightarrow[\text{or } C_2H_5OK]{H_3PO_2}$

→ isotopic effect: Nitrosoation
coupling rxn
Iodoation ~~SE~~
Sulphonation





= Arenium ion or Wheland or complex

→ Halogenation: $Br_2$ + Lewis A ($AlCl_3, FeCl_3, BF_3$ e.t.c)
$Br_2$ + Fe or Al

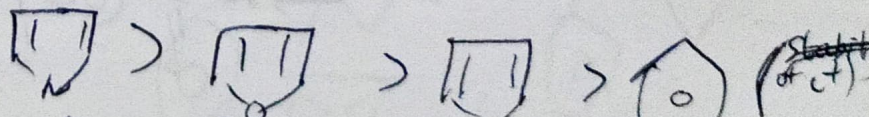
→ F-C Rnx $R-X$ or $R-\overset{O}{\overset{\|}{C}}-X$ + L.A

→ among halogens see (+R)

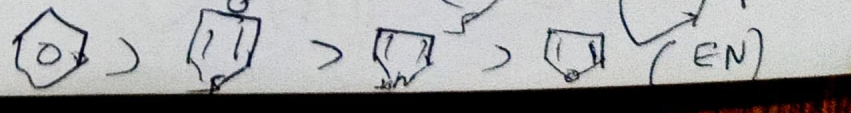
→ Deactivating but +R

$-C\equiv CH$, $-NO_2$, $-X$, $-CH_2Cl$ ($-I, +H$), $-CH_2OH$ ($-I, +H$),

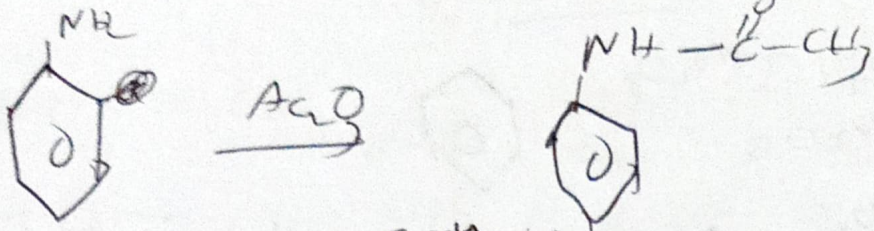

→ Rate of EAS.



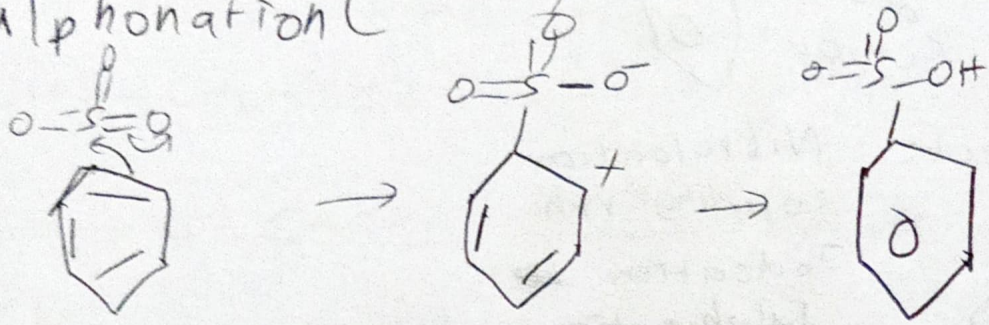

Resonance Energy



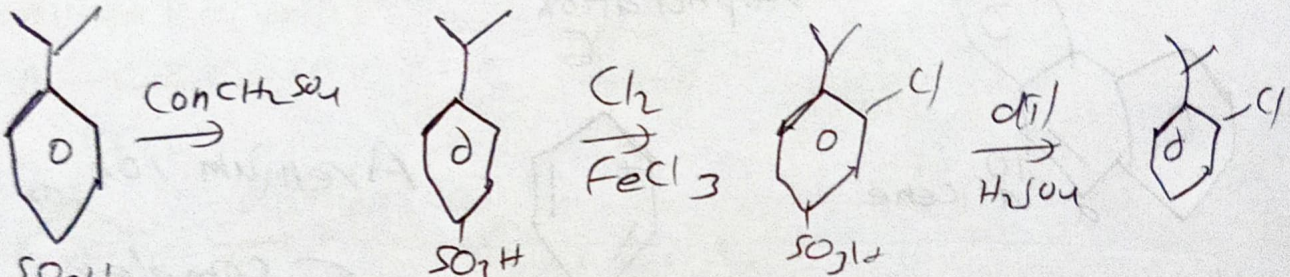
→ Ph is an activating group

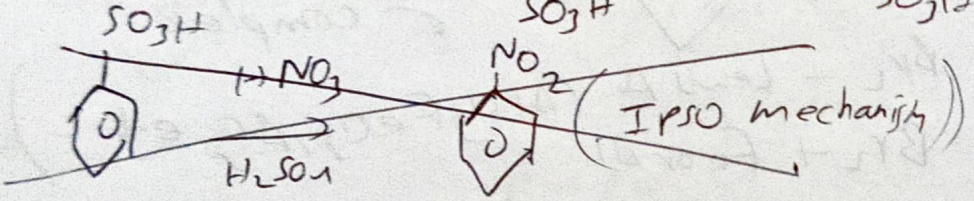
→ 

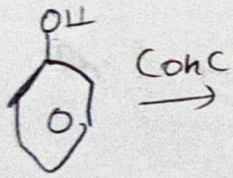
→ Sulphonation (conc $H_2SO_4$)

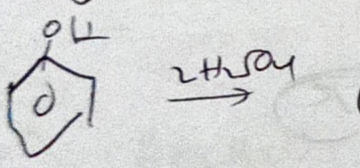


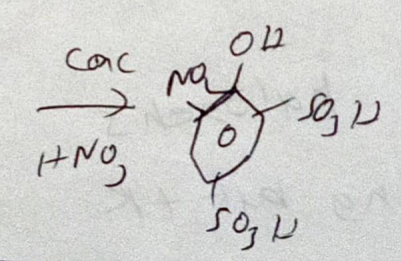
Use:



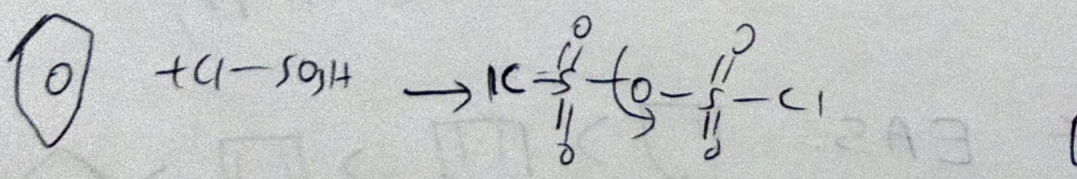
→ 

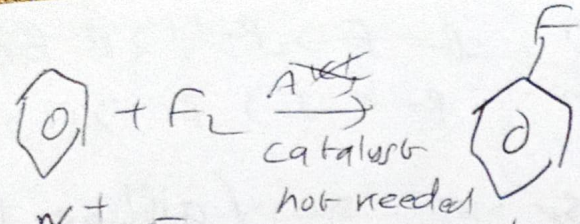
→ 

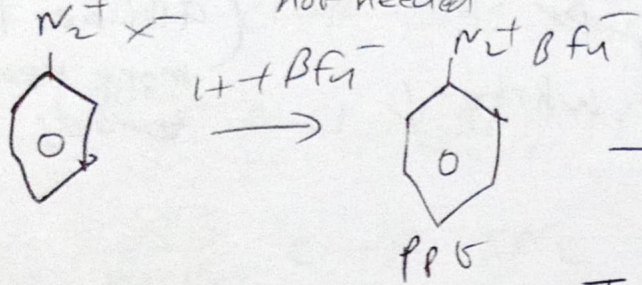
→ 

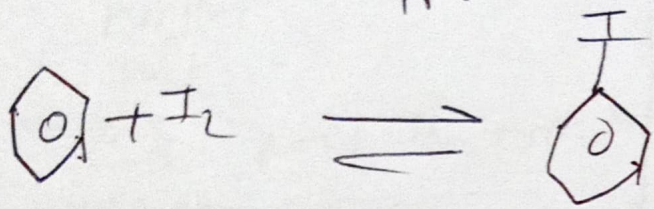


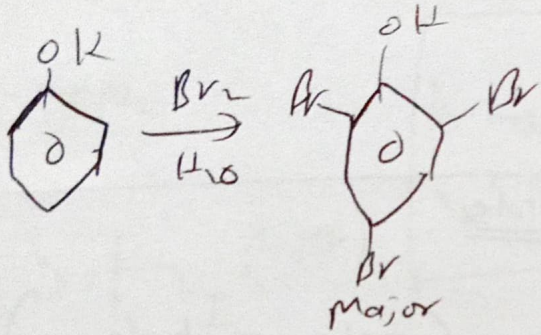
→ Sulphonation = steric factor

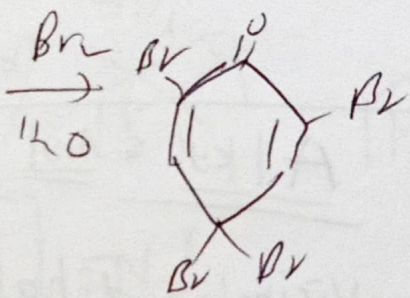
→ 

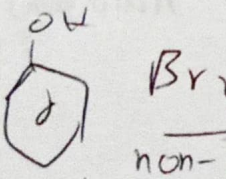
→  (highly exothermic)

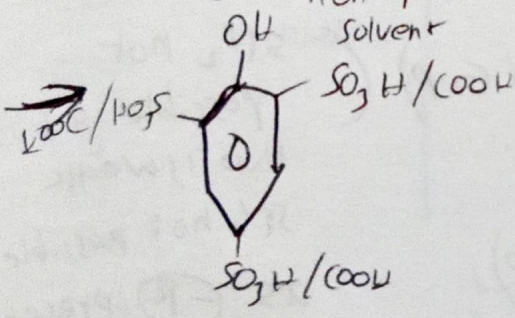
→  (Balz-Schiemann Rxn)

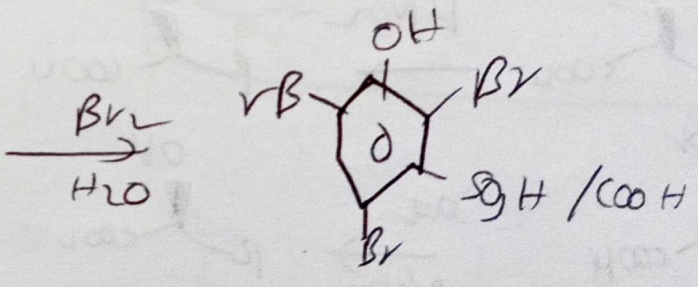
→ 

→ 

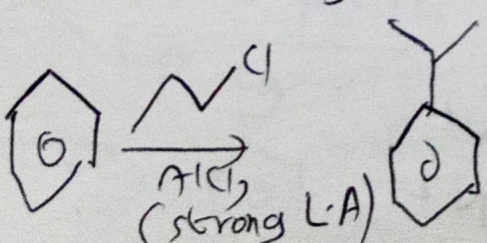


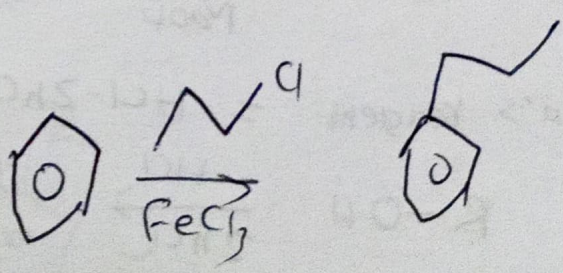
→ 



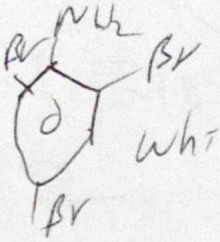


→ In F-C rxn $C^+$ is not generated but migration is granted





Rate of F-C alkylation: R–F > R–Cl > R–Br > R–I
acylation: R–C(=O)–I > Br > Cl > F

→  $\xrightarrow[\text{or } H_2O]{Br_2 \text{ non-polar}}$  white ↓

(aniline is more reactive towards EAS)

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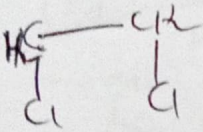
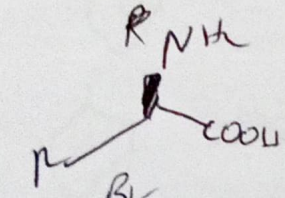
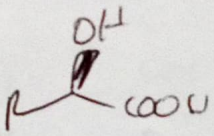
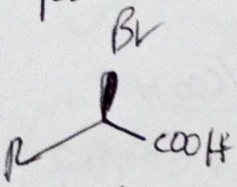
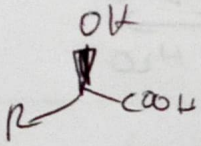
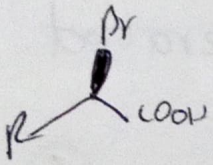
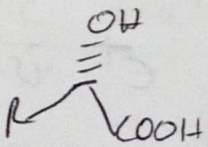
## Alkyl & Aryl halides

→  = Vicinal dihalide (only 2 halogens)

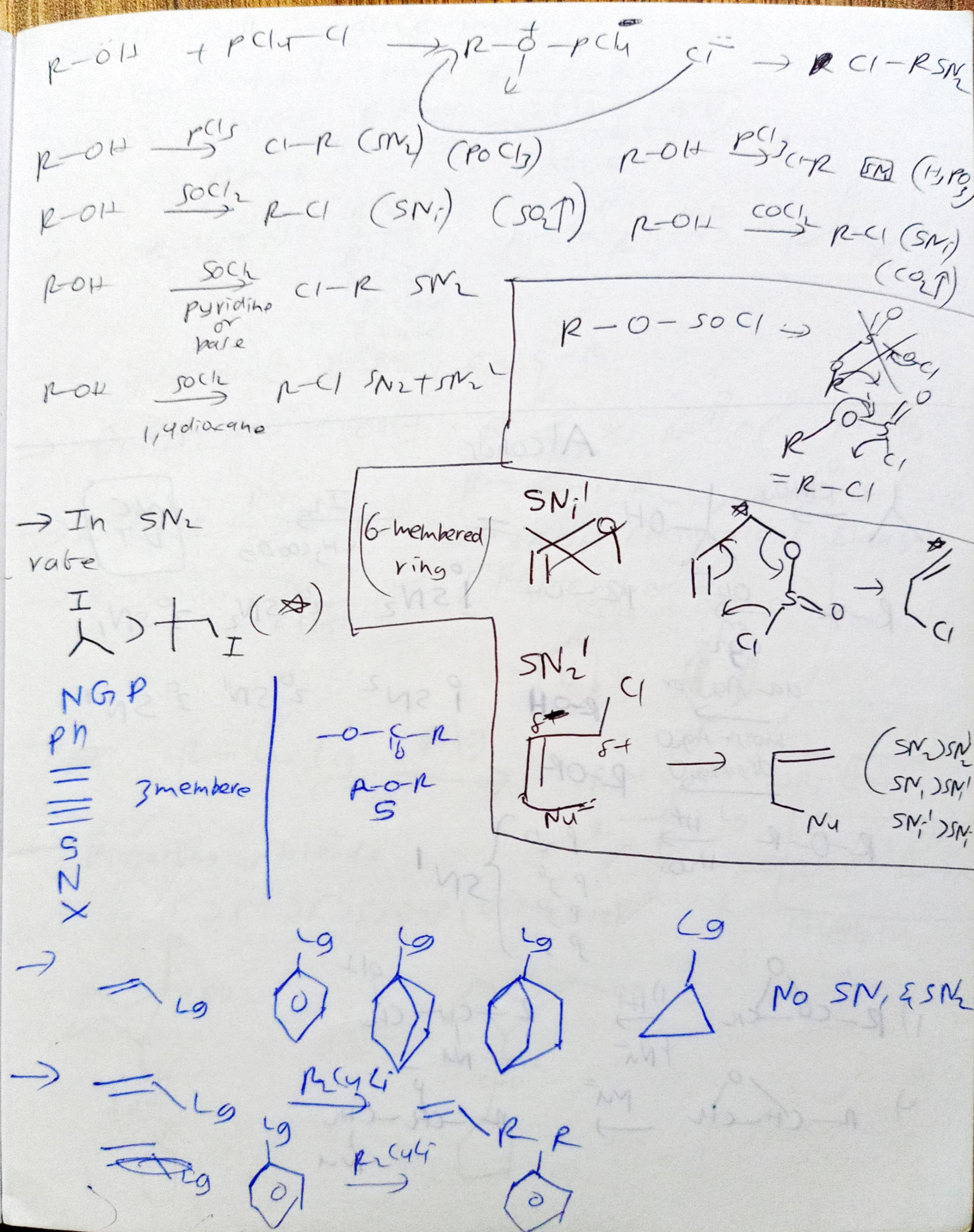
→  $\xrightarrow{HNO_2}$  (NGP) ( $S_N2$ not possible as $H_2O$ is weak $S_N1$ not possible as ⊖ is present)

→  $\xrightarrow[NaOH]{aq}$  (NGP)

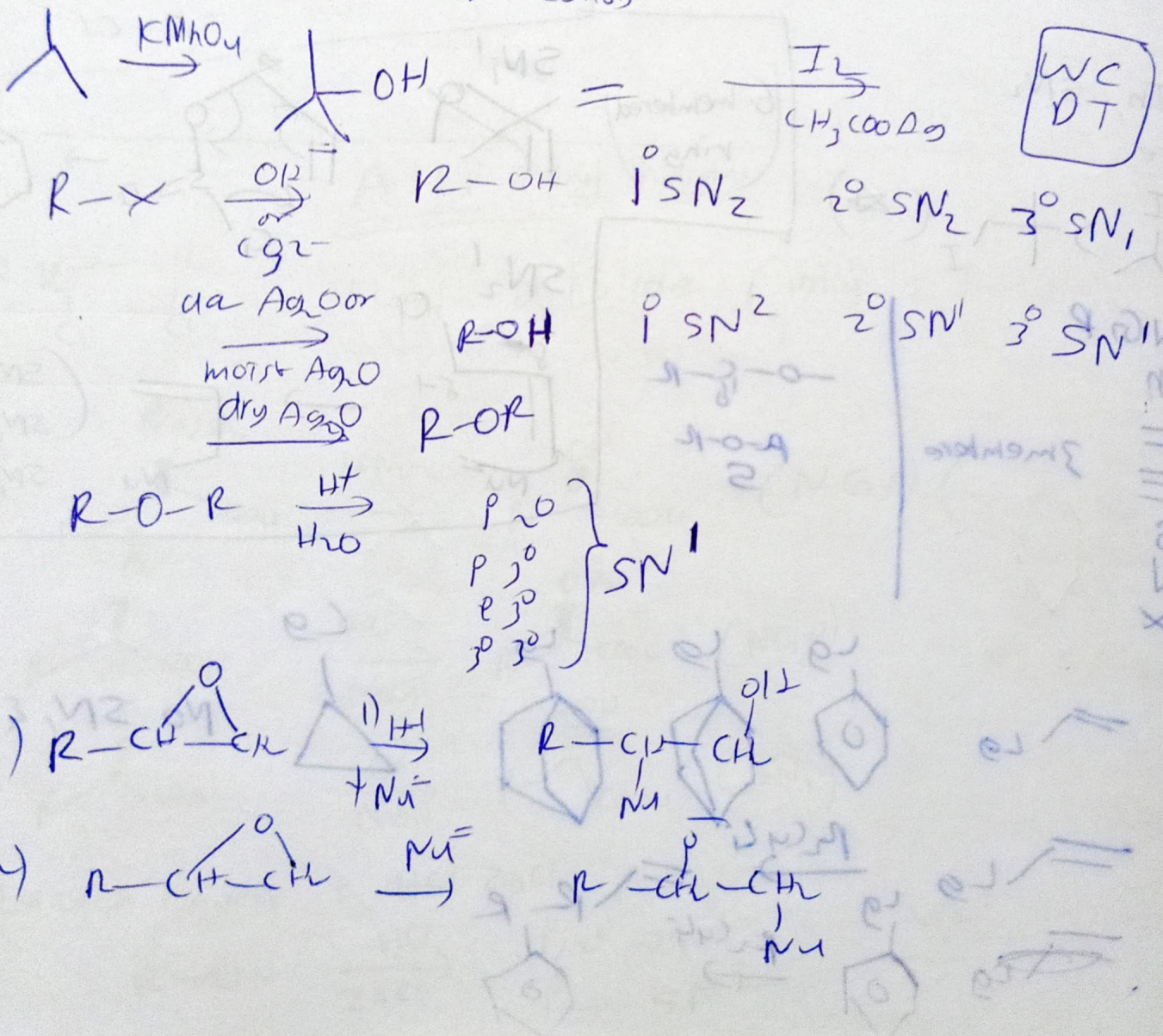
→  $\xrightarrow[NaOH]{conc}$  ($S_N2$)

→ Luca's reagent = $HCl\text{-}ZnCl_2$

$R\text{–}\ddot{O}H \xrightarrow[ZnCl_2]{HCl}$ 3°, 2° → $S_N1$; 1° – $S_N2$


R–OH + PCl4–Cl → R–O–PCl4
Cl⁻ → R–Cl – SN2
R–OH → PCl5 → Cl–R (SN2) (POCl3)
R–OH → PCl3 → Cl–R SN2 (H3PO3)
R–OH → SOCl2 → R–Cl (SNi) (SO2↑)
R–OH → COCl2 → R–Cl (SNi) (CO2↑)
R–OH → SOCl2 / pyridine or base → Cl–R SN2
R–OH → SOCl2 → R–Cl SN2 + SN2'
1,4 dioxane
R–O–SOCl →
= R–Cl
6-membered ring
SNi'
→ In SN2 rate
I > I (*)
NGP
Ph
S
N
X
3 membere
–O–C(=O)–R
A–O–R
S
SN2'
Nu
SN2 > SN2'
SNi > SNi'
SNi' > SNi
Lg
No SNi & SN2
R2CuLi
R2CuLi

# Alcohols


KMnO4
OH
I2
CH3COOAg
WC
DT
R–X
OH
or
CgZ–
R–OH
1° SN2
2° SN2
3° SN1
dil Ag2O or
moist Ag2O
dry Ag2O
R–OH
1° SN2
2° SN1
3° SN1
R–OR
R–O–R
H+
H2O
P 1°
P 1°
P 2°
P 3°
3° 3°
SN1
1) R–CH–CH2
1) H+
+N4
R–CH–CH2
OH
N4
2) R–CH–CH2
M+
R–CH2–CH2
N4

NaBH4 will reduce imine.

$R-\overset{O}{\overset{\|}{C}}-OH + RLi \rightarrow R-\overset{O}{\overset{\|}{C}}-R$ (2 times A-D)

→ With amide $RMgX$ (1 time)

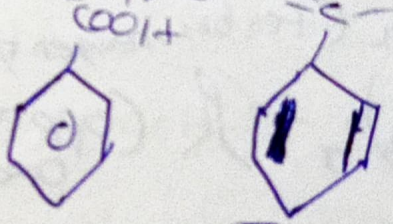
amine

→ $R-C\equiv N \xrightarrow[RLi,\ R_2CuCd,\ R_2CuLi,\ R_2Zn,\ RMgX]{RMgX}$ $R-\overset{=N}{\overset{|}{C}}-R \xrightarrow{H_2O}$ $R-\overset{O}{\overset{\|}{C}}-R$

→ $R-\overset{O}{\overset{\|}{C}}-NR_2 \xrightarrow{RMgX}$ $R-\overset{O^-}{\overset{|}{\overset{\|}{C}}}-R$ (R)

→ DiBAL-H = only $R-\overset{O}{\overset{\|}{C}}-X$, $R-\overset{O}{\overset{\|}{C}}-OR$, $R-CN$, $R-\overset{O}{\overset{\|}{C}}-NR_2$, $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$

→ $R-\overset{O}{\overset{\|}{C}}-OR \xrightarrow[EtOH]{Na}$ $R-CH_2OH + ROH$ (Bouvelent Blank)

→ $R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[EtOH]{Na}$ ✕ (Remember 

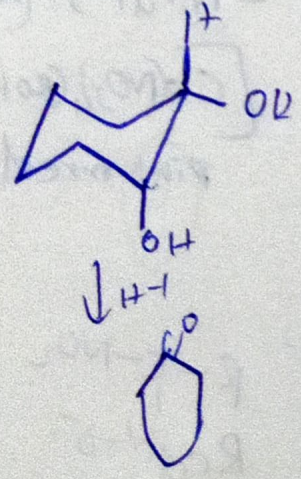
)

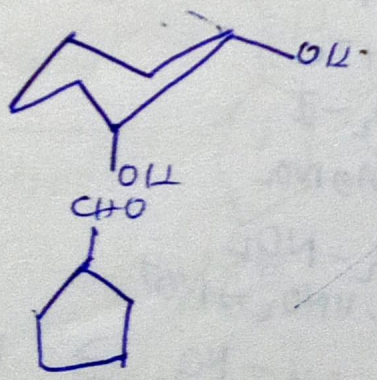
→ ☆ $R-\overset{O}{\overset{\|}{C}}-lg \xrightarrow{Mg}$ $R-\overset{O^-}{\overset{|}{C}}-lg$ (R, R, G) → $R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R$

→ $R-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}}-R$ Acyloin

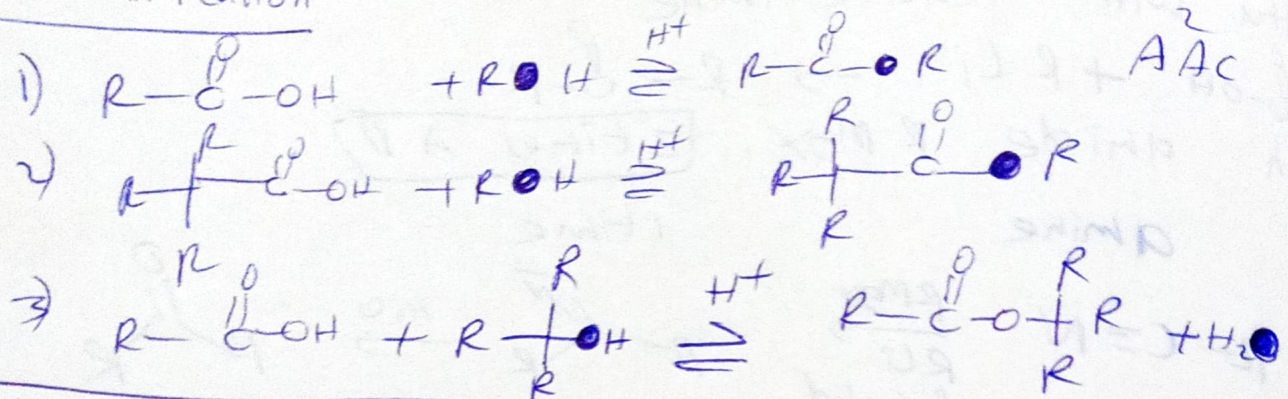
→ Migrating aptitude

$H^- > Ph^- > R^- > 3^\circ > 2^\circ > 1^\circ$ (octet care)



# Esterification

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$R-CH_2OH \rightarrow RCHO$

$R_2CH-OH \rightarrow R_2C=O$

i) Cu or Ag or Au △ (300°C)

ii) PCC Non-polar solvent

iii) PDC non polar solven

iv) $CrO_3$, Jones reagent $(Cr_2O_3)$

v) $FeSO_4-H_2O_2$ (Fenton's reagent)

vi) $Al(OCH(CH_3)_2)_3$ + (oppenaur oxdn)

vii) $X_2OH^-$

viii) $(COCl)_2$ DMSO (Swern Oxdn)

ix) $MnO_2$ (allylic & benzylic)

→ V.M.T = R.B.C (Victor Mayer test)

$R-CH_2OH \rightarrow RCOOH$

$R_2CH-OH \rightarrow R_2C=O$

i) $KMnO_4$ ($H^+/OH^-$)

ii) $K_2Cr_2O_7$ H+

iii) $H_2CrO_4$

iv) Jones reagent aq

v) PCC $H_2O$

vi) PDC $H_2O$

$2ROH + (NH_4)_2[Ce(NO_3)_6]$

$\rightarrow 2NH_4NO_3 + Ce(NO_3)_4(ROH)_2$

pink → red

$R-CH_2OH$

↓ PBr

$R-CH_2-Br$

↓ $AgNO_2$

$R-CH_2-NO_2$

↓ $HNO_2 \rightarrow NO^+$

$R-CH(NO)-NO_2 \rightleftharpoons R-C(=N-OH)-NO_2 \xrightarrow{NaOH} R-C(=N-O^-)-NO_2$

Red

$R_2CHOH \xrightarrow{P+I_2} R_2CH-I \xrightarrow{AgNO_2} R_2CH-NO_2 \xrightarrow{HNO_2}$ $R_2-\underset{\underset{NO}{|}}{C}-NO_2$

Pseudonitrolic acids

Blue

$R_3C-OH \xrightarrow{P+I_2} R_3C-I \xrightarrow{AgNO_2} R_3C-NO_2 \xrightarrow{HNO_2}$ Colourless

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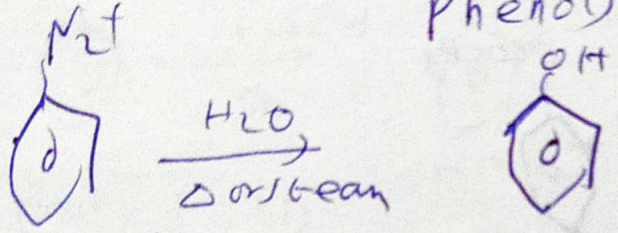
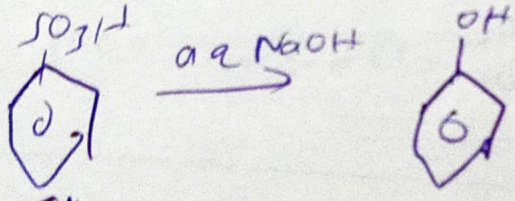
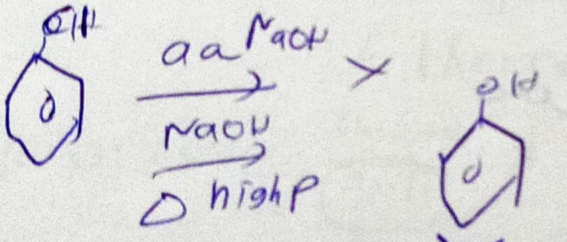
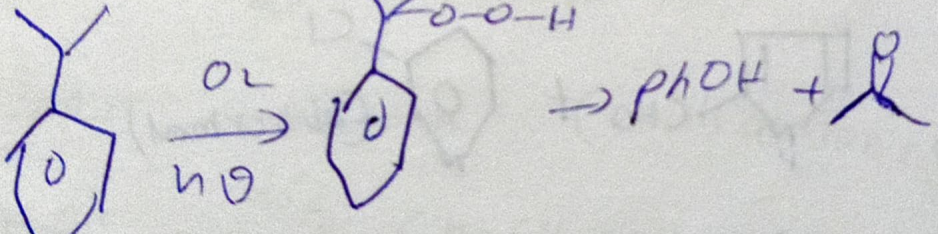
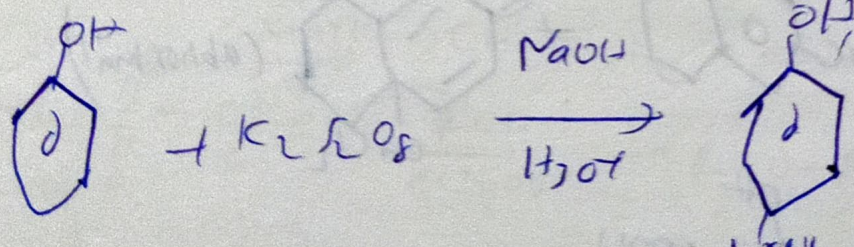
Phenols

1)  ($ArSN_1$)

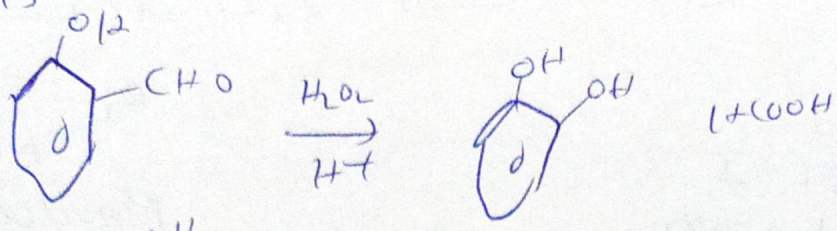
2) 

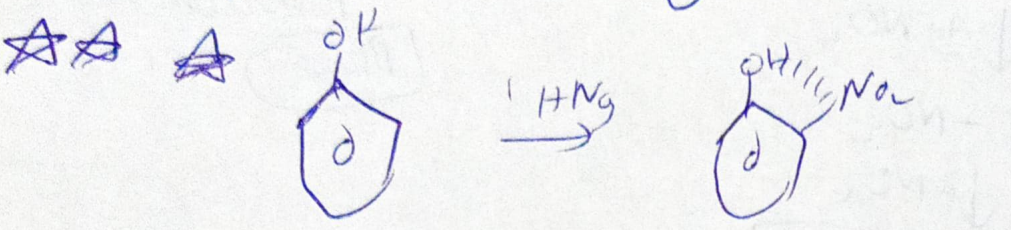
3)  (Dow's Process)

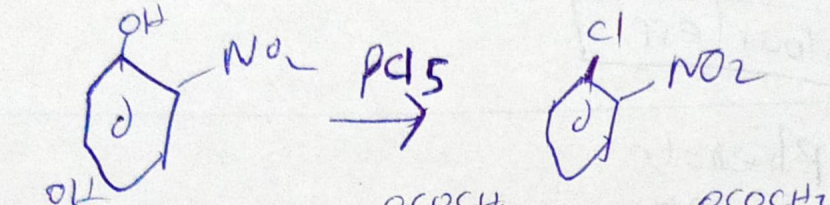
4) 

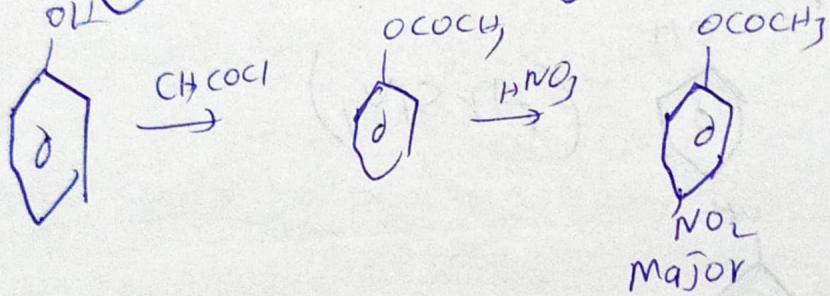
5) 

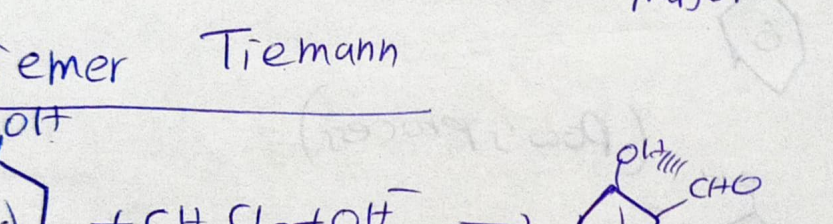
Dakin's







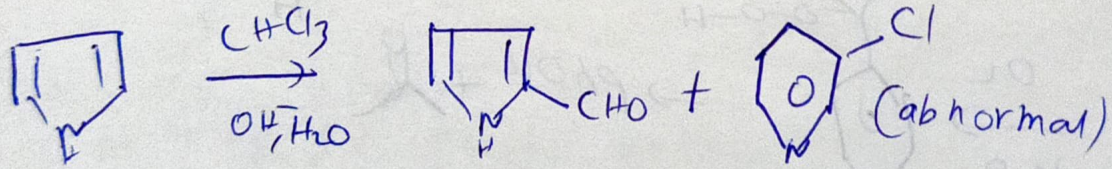




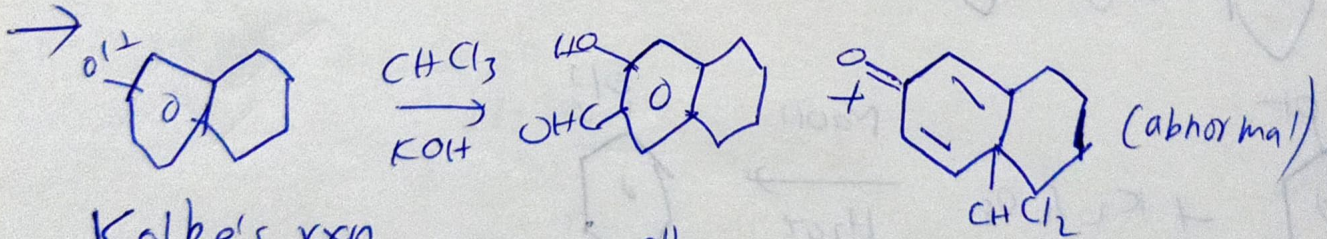
Major

→ Riemer Tiemann



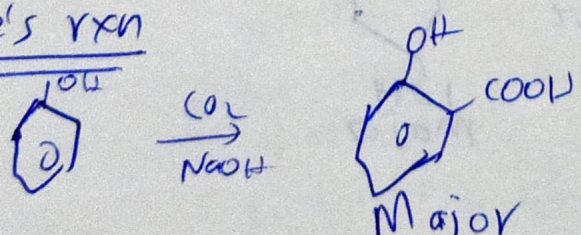


(abnormal)

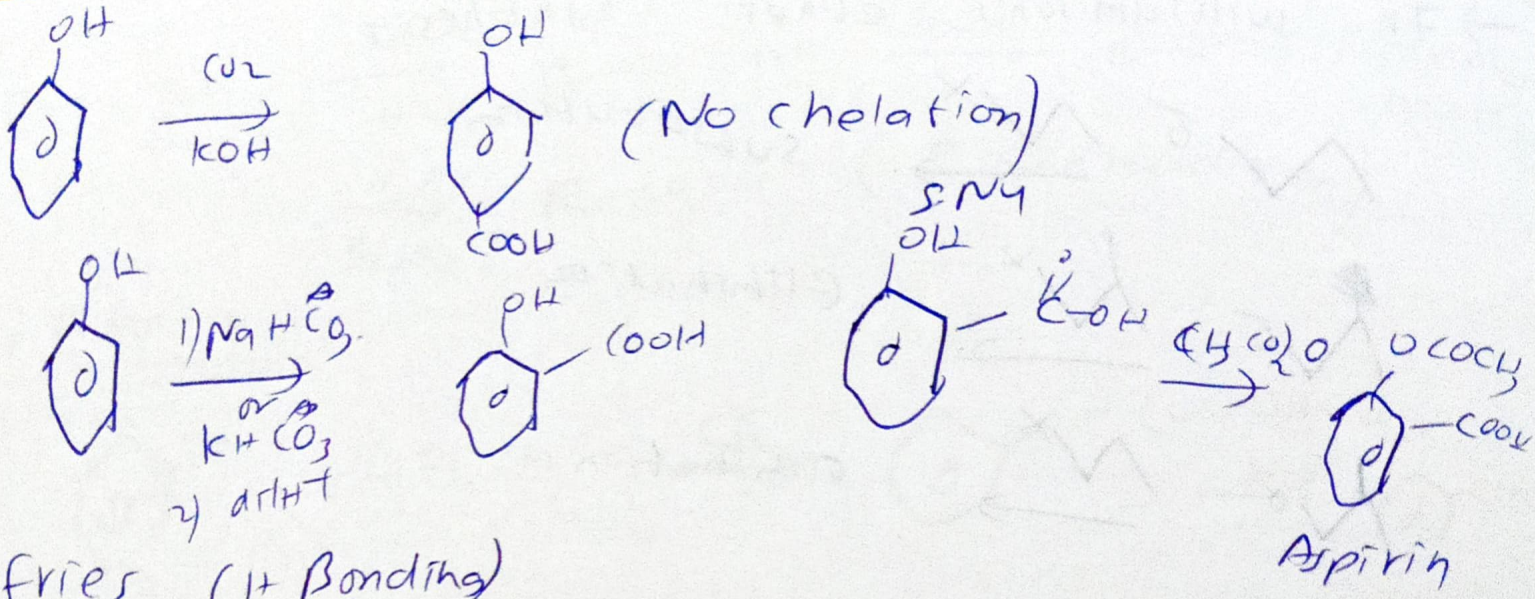


(abnormal)

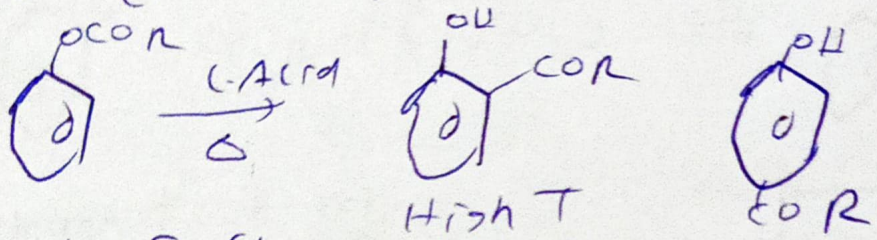
Kolbe's rxn



Major




→ fries (1+ Bonding)




Neutral $FeCl_3$

$PhOH + FeCl_3 \rightarrow [Fe(OPh)_6]^{3-}$

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## Ethers

1) $R-CH=CH_2 \xrightarrow[ROH]{Hg(OAc)_2} R-\underset{OR}{CH}-CH_2-HgOAc \xrightarrow{NaBH_4} R-\underset{OR}{CH}-CH_3$

2) $RO^- + RX \rightarrow R-O-R$ (Williamson's).

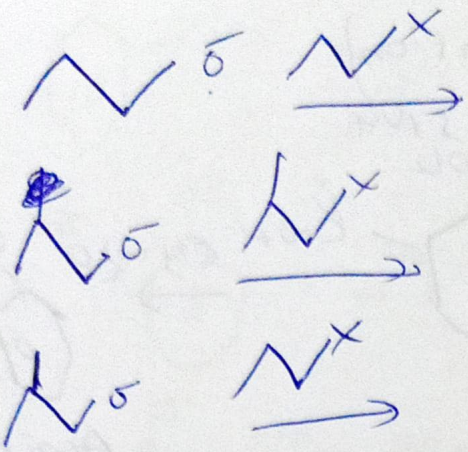
$CH_3CH_2OH \xrightarrow[413K]{140^\circ C} CH_3CH_2OCH_2CH_3$

$\xrightarrow[443K]{140^\circ C} CH_2=CH_2$

3) $R-O-\overset{O}{\overset{\|}{C}}-OR \xrightarrow[aq\,NaOH]{R'OH} R-O-R'$

Ethers are soluble in cold conc $H_2SO_4$

→ In Williamson's ether synthesis



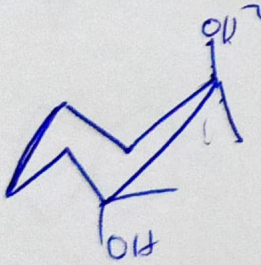

## Aldehydes & Ketones

electronic factor ald > ket

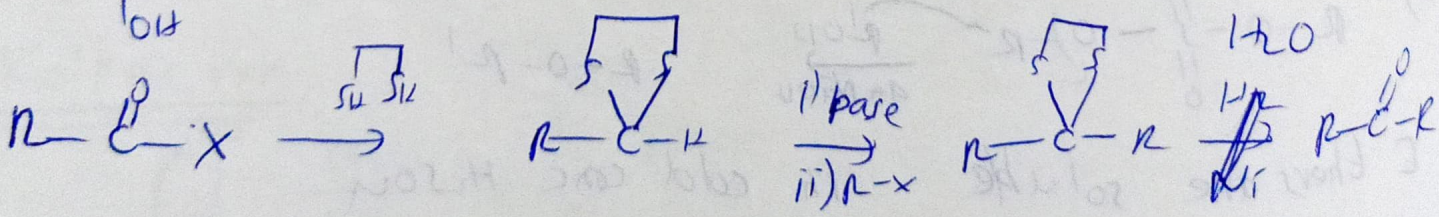
steric factor ald > ket

$KMnO_4$ $HCOOH$ / $\begin{matrix}COOH\\|\\COOH\end{matrix}$ $\longrightarrow$ $CO_2$

$=C=O$ $\xrightarrow{O_3}$ $HCHO + CO_2$ (~~Generally in reductive $CO_2$ is not pr~~)



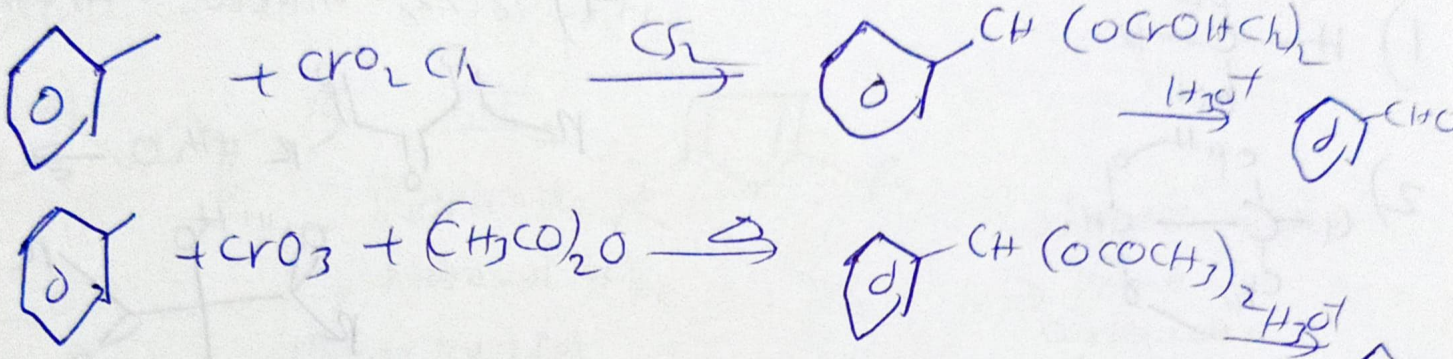

$\xrightarrow{H^+}$ No migration



→ $R-C\equiv N \xrightarrow[HCl]{SnCl_2} R-CH=NH \xrightarrow{H_3O^+} R-CH=O$ (Stephen reduction)

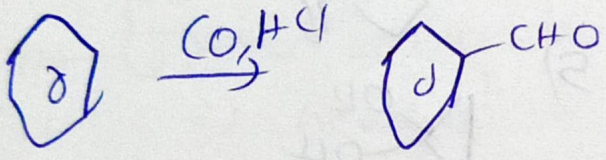
→ $R-\underset{O}{\overset{\|}{C}}-X \xrightarrow[BaSO_4]{H_2Pd} R-CH=O$ (Rosenmund rxn)

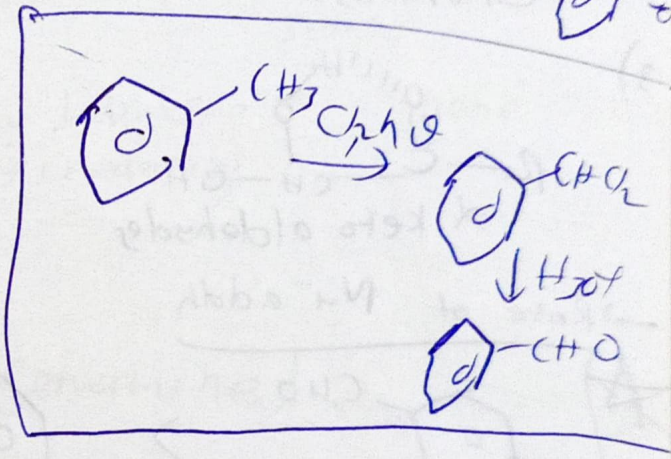
## ~~Etard~~ Etard rxn





## Gattermann-Koch rxn

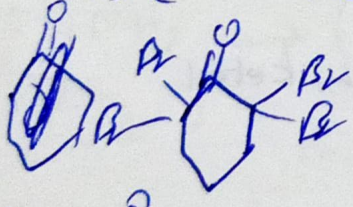




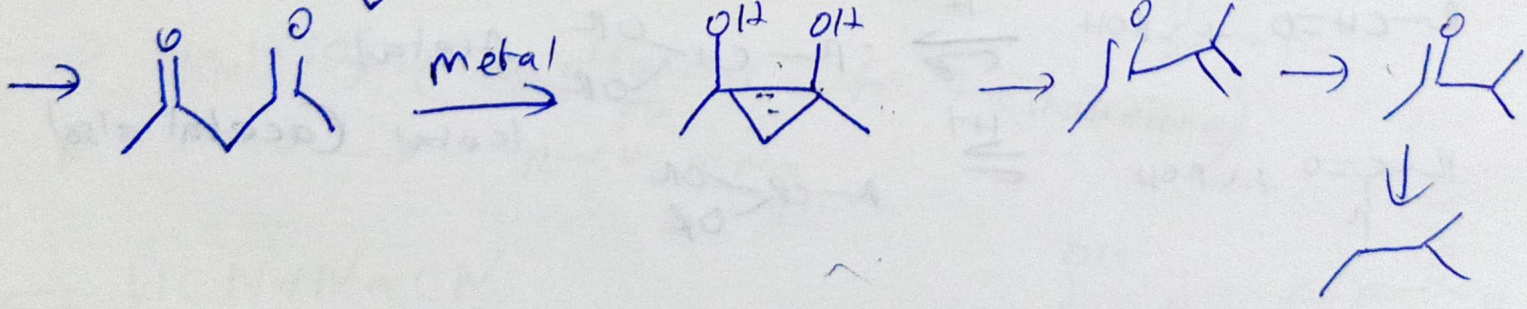
→ With metal aldehydes & ketones dimerise

→ $CH_3-\underset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[CH_3COOH]{Br_2} CH_2(Br)-\underset{O}{\overset{\|}{C}}-CH_3$

→ In basic medium poly halogenation occurs



acidic medium mono.



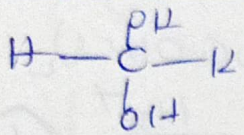
Rate of $Nu^-$ addn

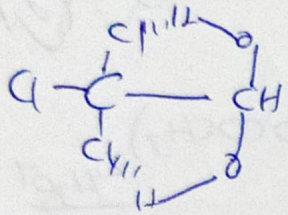
$CCl_3CHO > HCHO > RCHO > PhCHO > RCOR > RCOPh > PhCOPh$

$Nu^-$ attack

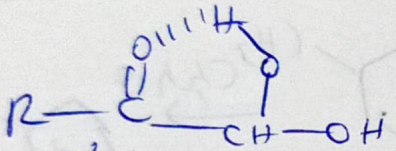
$RCOX > RCOOCOR > RCHO > RCOR > RCOOR > RCONH_2$

## Hydrate stable cases

1) 

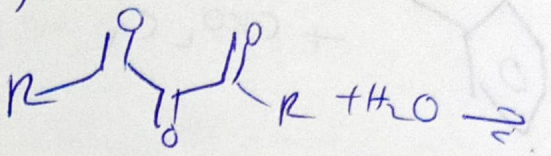
2) 

Chloral hydrate

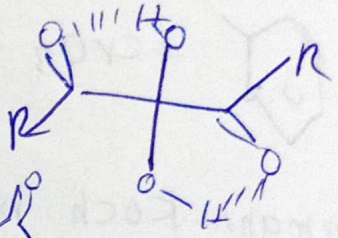
3) 

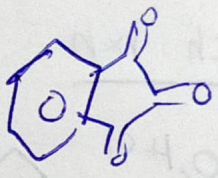
α keto aldehydes

4) 1,2,3,- triketo compounds

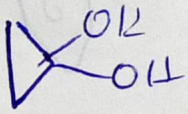


Ex:

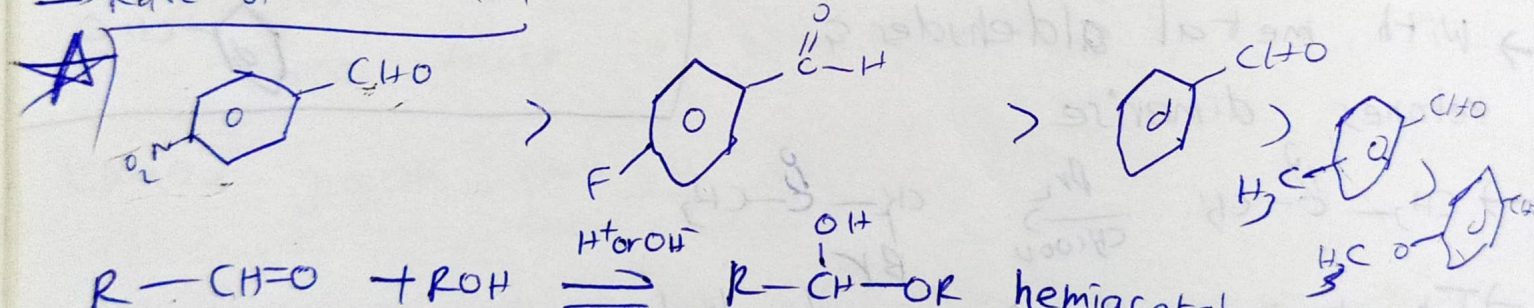




5)



→ Rate of $Nu^-$ addn



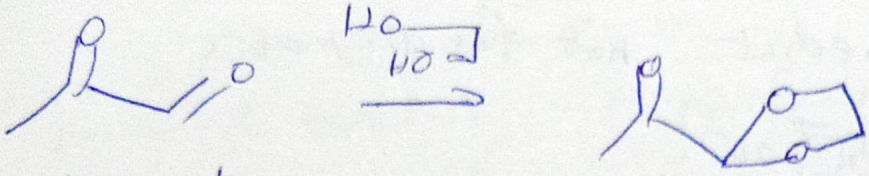
$R-CH=O + ROH \underset{}{\overset{H^+ \text{ or } OH^-}{\rightleftharpoons}} R-CH(OH)-OR$ hemiacetal

$R_2C=O + ROH \overset{H^+ \text{ or } OH^-}{\rightleftharpoons} R_2C(OH)-OR$ hemiketal

$R-CH=O + 2ROH \overset{H^+}{\rightleftharpoons} R-CH(OR)_2$ Acetal

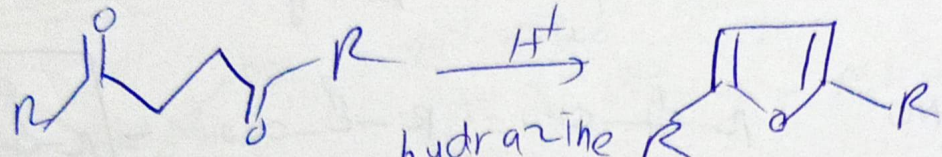
$R_2C=O + 2ROH \overset{H^+}{\rightleftharpoons} R_2C(OR)_2$ Ketal (Acetal also)

→ ketones react to a very less extent.

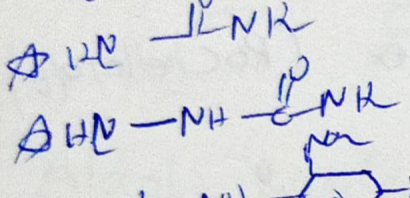


→ cyclic hemiacetals 5, 6, 7

→ 1,4 diketo → aromatic

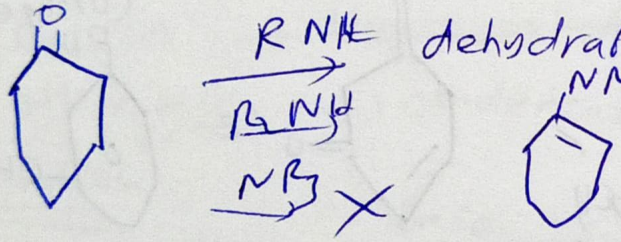


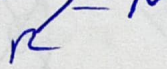
- hydrazine → hydrazone
- hydroxyl amine → oxime
- carbazid → carbazone
- semi → semi



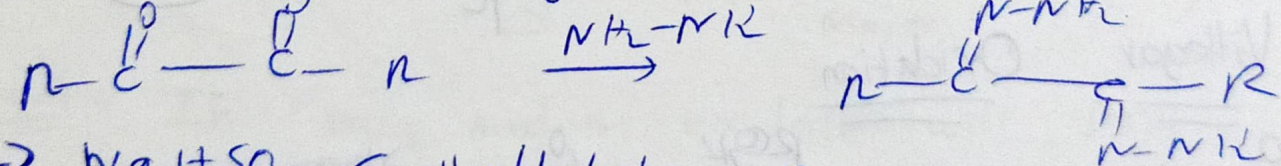
→ 2,4 dinitro phehy hydrazine (Brady's reagent)

→ (H+ is needed)

→ 

Schiff's base = imine = 

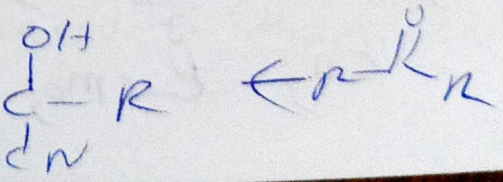
$HCHO + NH_3 \rightarrow (CH_2)_6N_4$ Urotropine.



→ $NaHSO_3$ (all aldehydes & few methylketones)

$R-CHO \rightarrow R-\underset{OH}{\overset{SO_3Na}{CH}}$

→ HCN + NaCN

$R-CHO \rightarrow R-\underset{OH}{\overset{CN}{CH}}$ , 

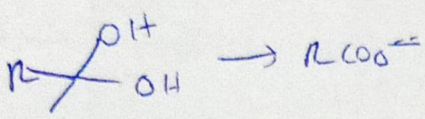
→ Aldehydes are oxidised by $HNO_3$, $KMnO_4$, $CrO_3$

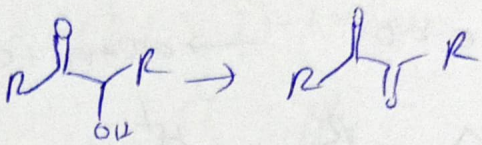
→ Fehling's & Benedict not for aromatic

→ Tollen's $[Ag(NH_3)_2]^+ OH^-$

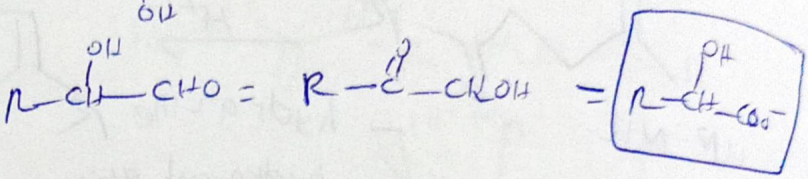
$R-CHO \rightarrow RCOO^-$

$HCOOH \rightarrow CO_2$ or $CO_3^{2-}$





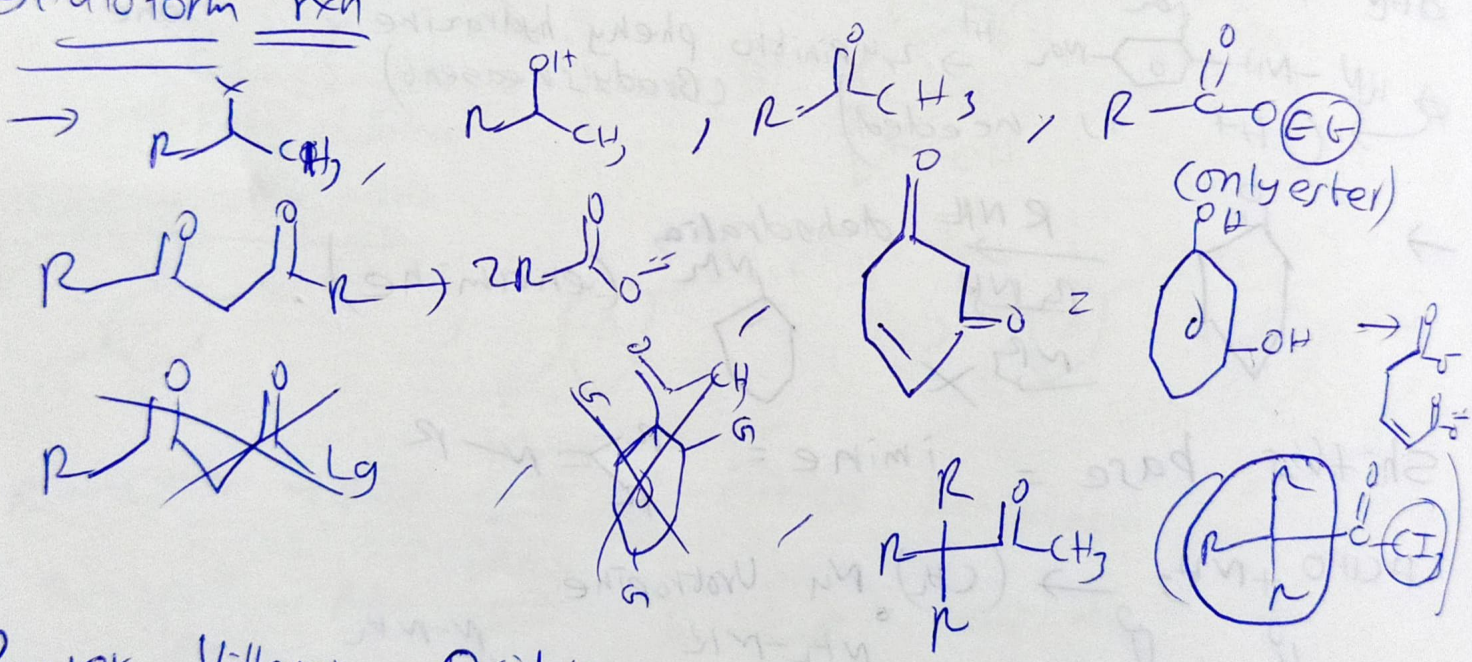
$R-NHOH \rightarrow R-NO$



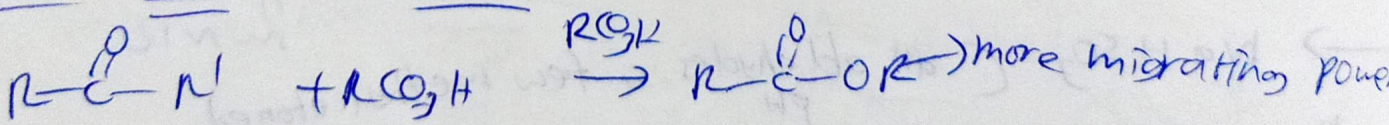
→ Fehling's A = $CuSO_4$.

Fehling's B = copper tartarate complex (Rochelle salt)

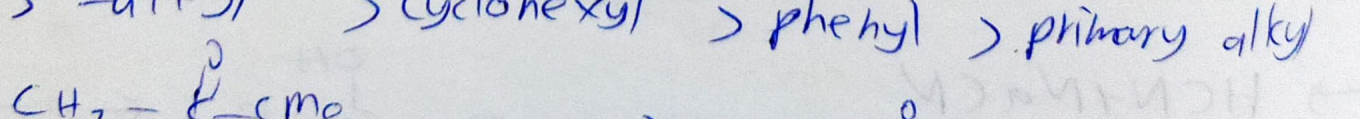
→ Haloform rxn

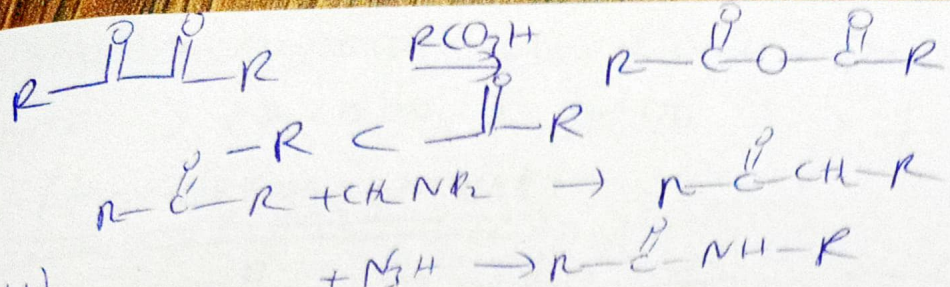



Bayer Villegar Oxidation



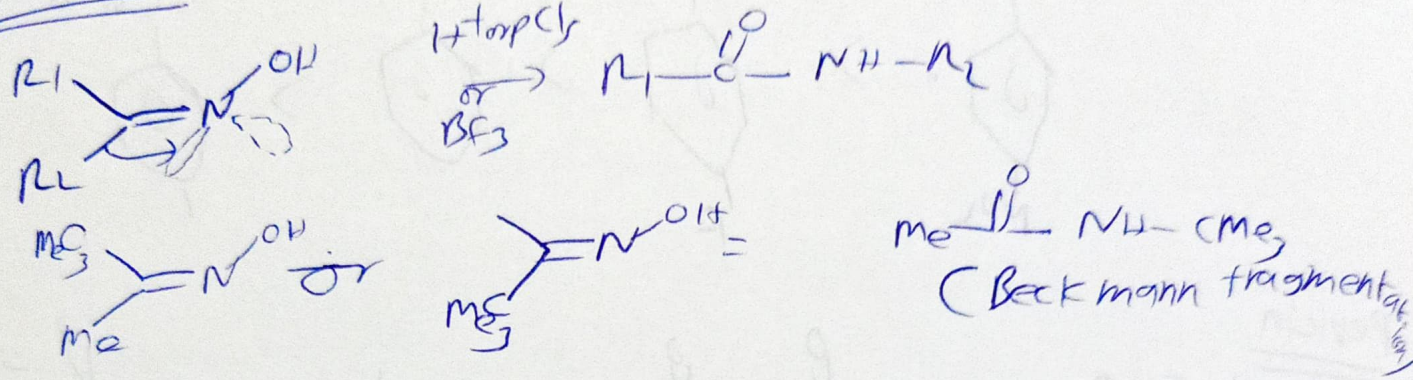
$1^\circ$ > $3^\circ$-alkyl > cyclohexyl > phenyl > primary alkyl





→ (Smidth) rxn

## Beck mann rearrangement



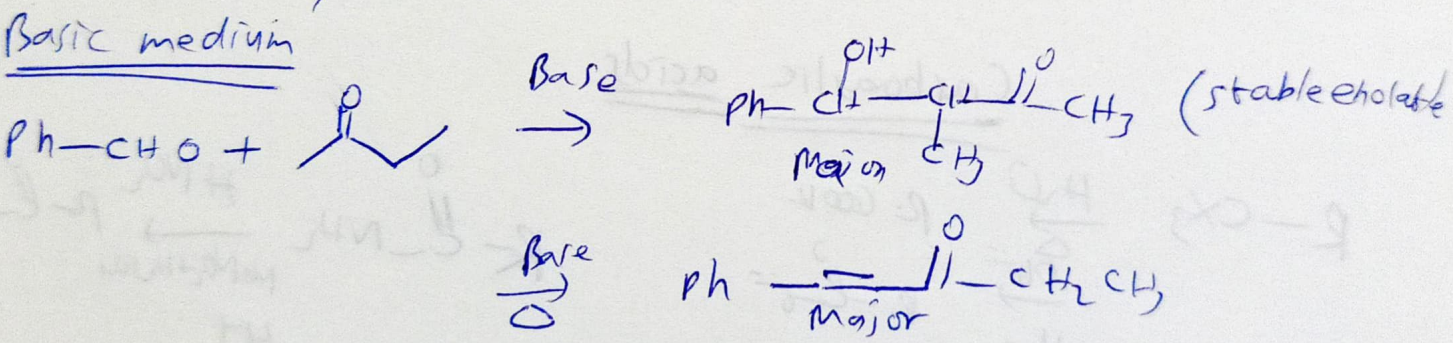
## Aldol condensation

Base → aldol

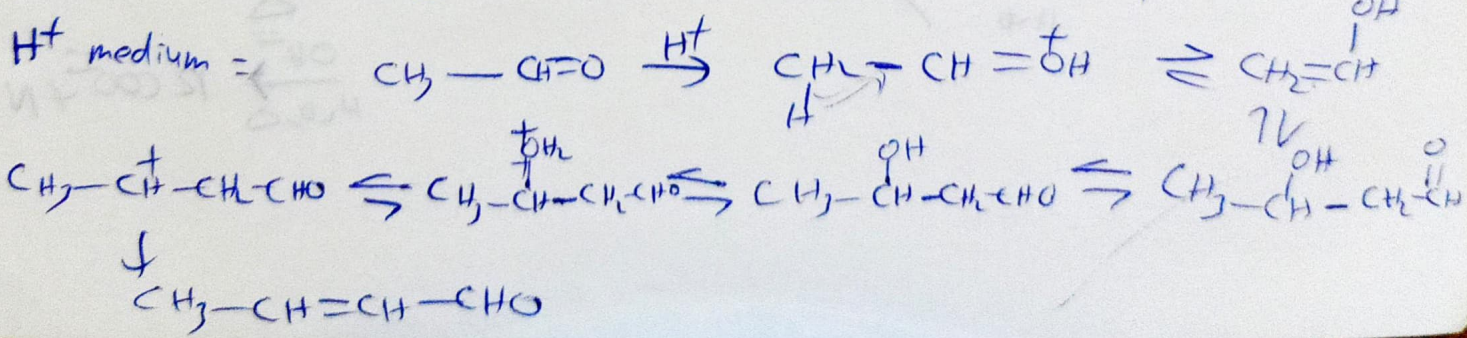
Base/Δ → ~~Unsaturated cond~~ condensation

H+ or H+/Δ → condensation

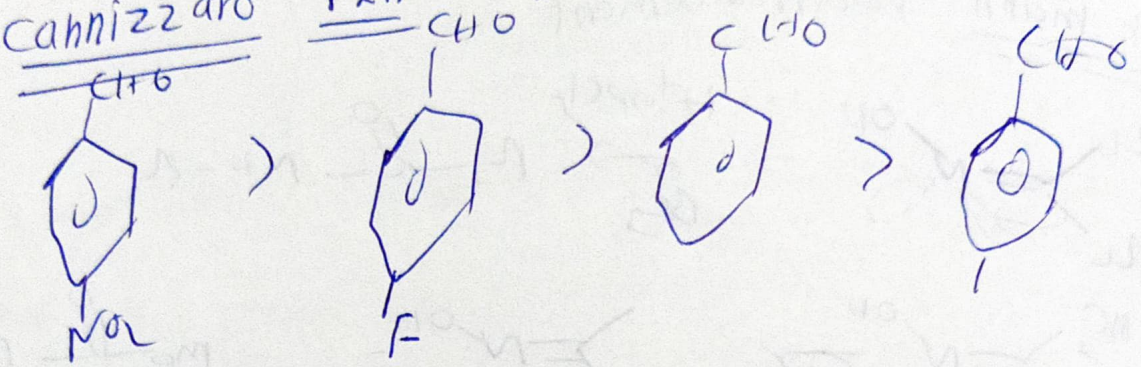
### Basic medium



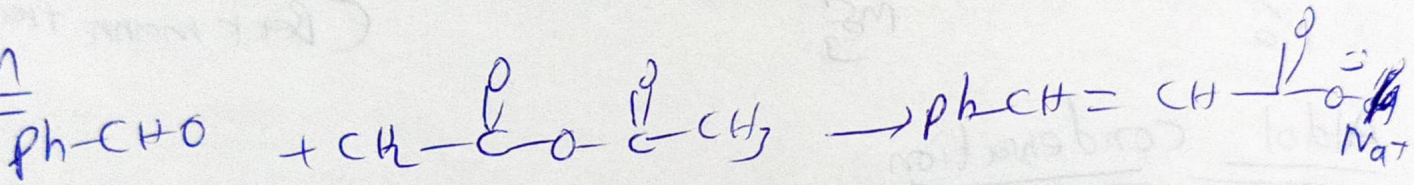
**Mech:** In basic medium enolate will form



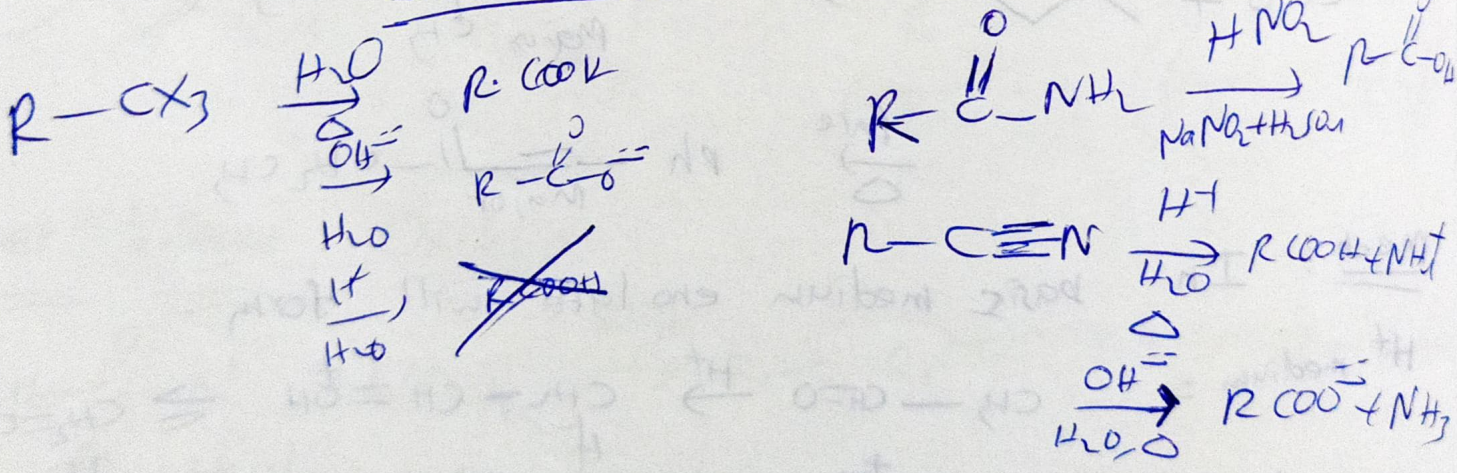
Rate of cannizzaro rxn = rate $N_u^-$ adn



Perkin



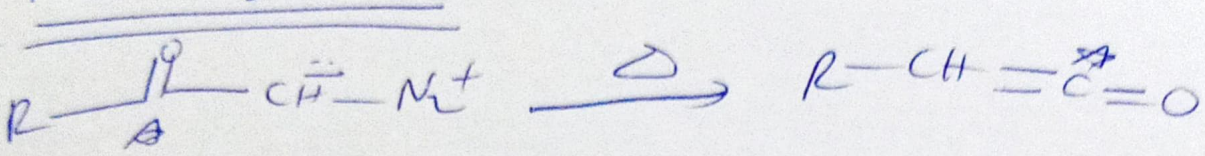
Carboxylic acids



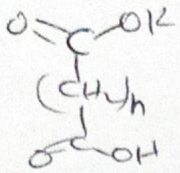
$HCOOH > CH_3COOH > CH_3CH_2COOH > \text{C}_6\text{H}_5\text{COOH} > \text{C}_6\text{H}_5\text{CH}_2\text{COOH}$

$CH_3OH > CH_3CH_2OH > \text{C}_6\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{CH}_2\text{OH}$

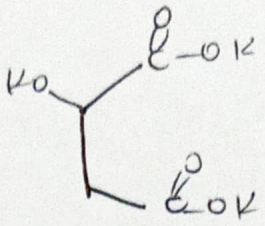
**Wolff rearrangement:**



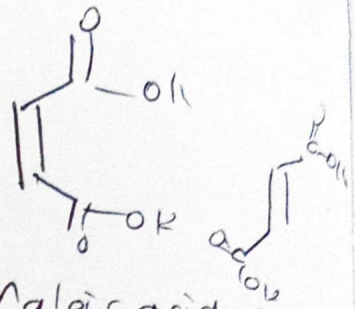
# Common names



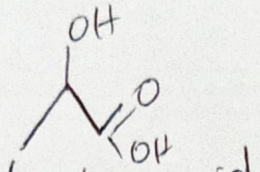
h=0 Oxalic acid
h=1 Malonic acid
h=2 Succinic acid
3 Glutaric acid
4 Adipic acid
5 Palmetic acid



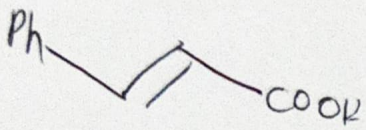
Malic acid



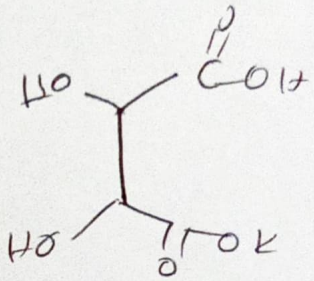
Maleic acid fumeric acid



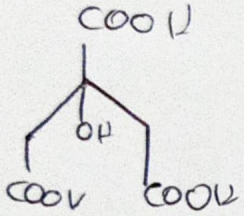
Lactic acid



cenamic acid

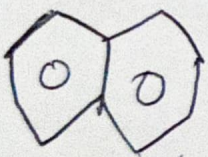


tartaric acid

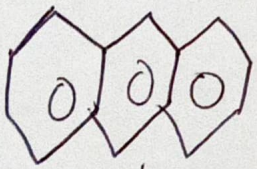


citric acid

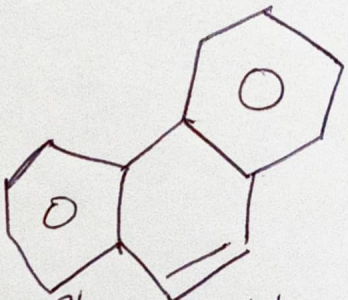
$CH_2Cl_2$ – Methylene chloride



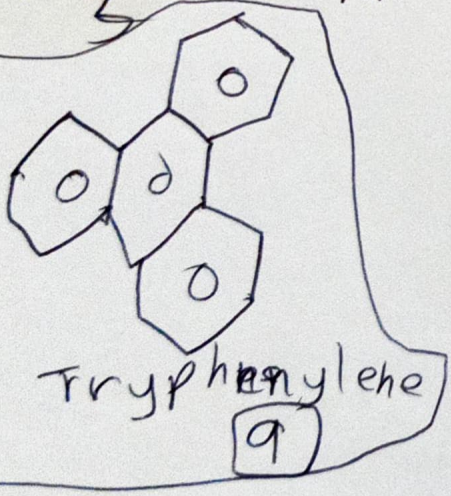
Naphthalen
2



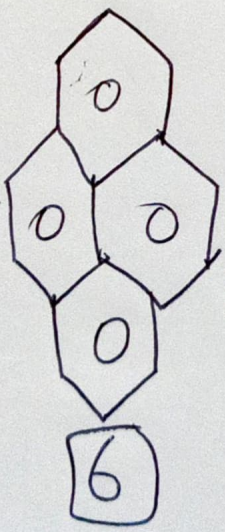
Anthracene
4



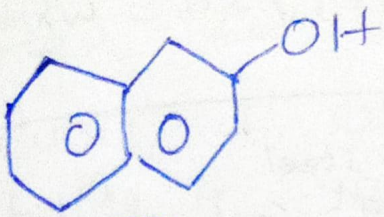
Phenanthene
5



Tryphenylene
9

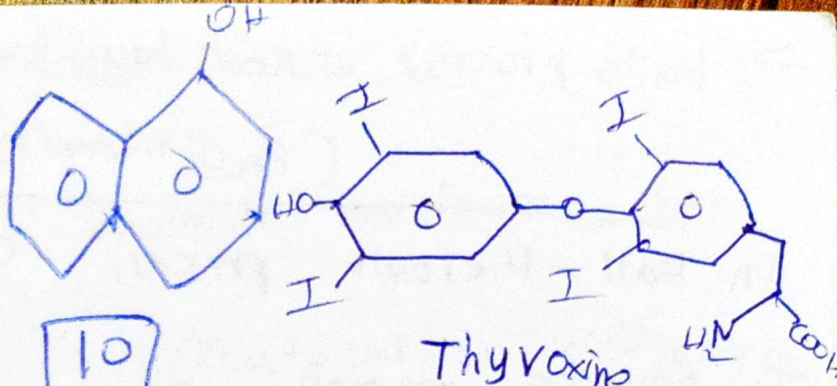


Pyrene
6



9

β-naphthol

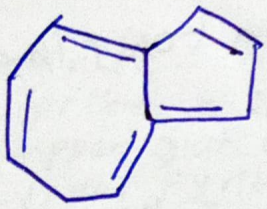


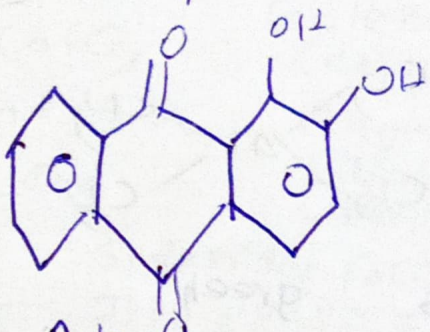
10

α-naphthol

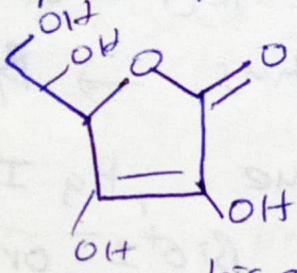
Thyroxine.

→ Azulene

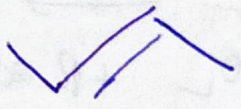




Alizarin

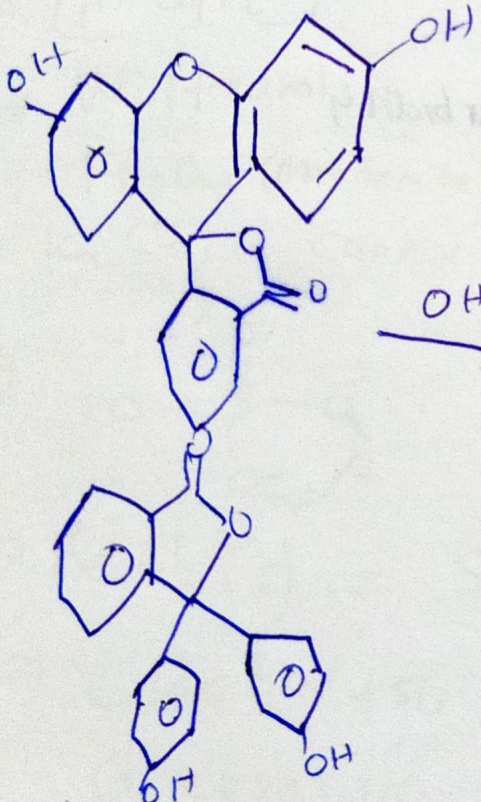


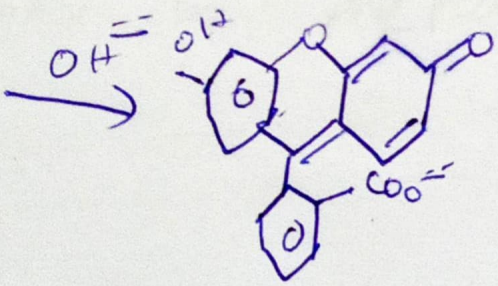
Ascorbic acid



Crotonic acid

Fluoroscein





Phenapthalin

Random / Inorganic

→ Be & Mg do not react with hydrogen directly so to prepare

$2MgCl_2 + LiAlH_4 \rightarrow 2MgH_2 + LiCl + AlCl_3$

$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$

→ Be doesn't react even with hot water. Mg reacts with boiled water. Others react even with cold water.

→ In asbestos mineral, double strand (contains), silicates (chain) (Amphiboles). ($(Si_2O_5)^{2-}$, $(Si_4O_{11})^{6-}$, $(Si_6O_{17})^{10-}$)

→ $Ba^{+2}$ does not crystallise with water molecules.

→ In the hall-herhoult process aluminium is formed at carbon cathode.

→ $d_{x^2-y^2}$ & $d_{z^2}$ are directly facing the ligands in octahedral complexes.

→ NaH, CsH, $CaH_2$ e.t.c are ionic or salt like hydrides. (Not metallic)

→ A cylinder of compressed $H_2$ weighs 30 times of petrol tank (same energy) (Pg-287 NCERT)

→ For storing $H_2$ > NaNi5, Ti-$TiH_2$ & Mg-$MgH_2$ e.t.c

→ PAN is present in photo chemical smog.

→ If DO < 6ppm growth of fish get inhibited

→ In cold water DO ~~≤ 10ppm~~ can reach 10 ppm.

→ for clean water B.O.D ≤ 5ppm

for highly polluted water B.O.D ≥ 17 ppm.

→ Eu > Ce > Ho > N (atomic radii)

→ $CF_2Cl_2$ is not present in photochemical smog

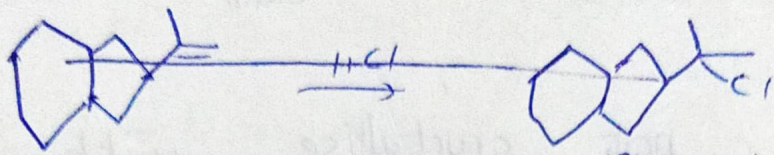
→ $SO_2$ causes stiffness of flower buds

→ The carat statements w.r.t $K^+$ ions, that are abundant in cell fluids are

✓ 1) they activate enzymes ✓ 2) They participate in the oxidation of glucose to produce ATP

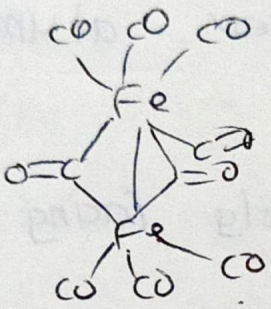
✓ 3) Along with sodium ions, they are responsible for the transmission of nerve signals.

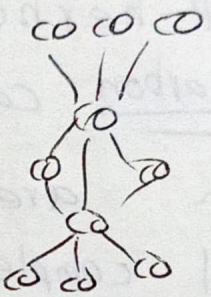
→

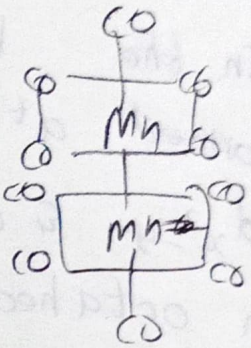


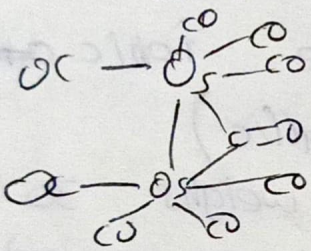
→ As, Sb, Se, Te, Ag, Au, Pt are present in anode mud in the electrolytic refining of copper.

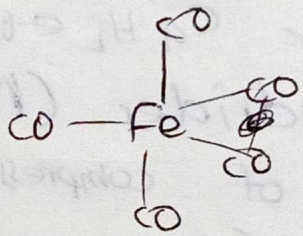
→











Chromium doesn't form neutral binuclear CO compound

→ $BeH_2$ & $MgH_2$ are polymeric and covalent

→ For dilution always add ~~water~~ acid to water

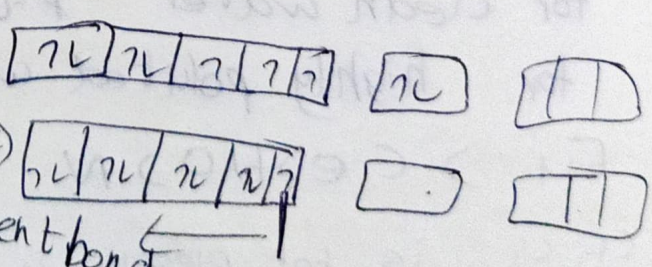
→ $CaF_2$ is ppt

→ radii – Sc > Zn > V > Fe

→ Glass ($SiO_2$) is etched by using HF.

→ $[CO_2(CO)_x]$ $x \neq 9$

$x = 8$



→ Sodium ions are found primarily on the outside of cells, being located in plasma and in the interstitial fluid which surrounds the cells. (NOKIA)

→ The potassium ions are the most abundant cations with in the cell fluids.

→ All enzymes that utilise ATP in phosphate transfer require magnesium as the cofactor

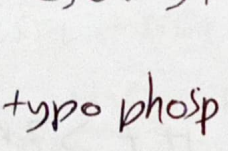
→ The calcium conc in plasma is regulated at 100 mg/L

→ Extent of hydrolysis

$$PCl_5 > SiCl_4 > AlCl_3 > MgCl_2 > CCl_4$$

→ Thermal stability

$$CsOH > RbOH > KOH > NaOH > LiOH$$

→ Hypophosphinic acid = 

($PbO_2$ is very strong $Mn \rightarrow KMnO_4$)

→ $KI + H_2SO_4 \rightarrow SO_2 + I_2$

$KI + HNO_3 \rightarrow NO_2 + I_2$

(acidic) $KI + KMnO_4 \rightarrow Mn^{2+} + I_2$

$KI + K_2Cr_2O_7 \rightarrow Cr^{3+} + I_2$

$KI + H_2O_2 \rightarrow I_2$

$KI + CuSO_4 \rightarrow Cu_2I_2 + I_2$

$PbO_2 + KI \rightarrow I_2$

(In alkaline ~~$IO_3^-$~~ $\rightarrow MnO_2 + IO_3^-$)

$KI + FeCl_3 \rightarrow I_2$

→ In graphite there are no unpaired electrons

→ Silicon exhibit more catenation power in halides than in hydrides due to $p\pi - d\pi$ nature.

→ $2NH_3 + 3NaOCl \rightarrow N_2 + 3NaCl + 3H_2O$

$2NH_3 + NaOCl$ (in gelatin) $\rightarrow H_2N-NH_2$ (prep for hydrazine).

→ ~~et~~ E.A $O^- > O > O_2^{2-} > O^{2-}$

→ Heamatite ($Fe_2O_3$), Magnetite ($Fe_3O_4$) Ileminite ($FeTiO_3$), Chromite ($FeCr_2O_4$), pyrolusite (impurity manganese ore) can be separated by magnetic separation.

→ pH of $MgCl_2 > BeCl_2$

→ $BF_3 \xrightarrow{Al_2Cl_6 \text{ or } Al_2Br_6}$ $BCl_3$ or $BBr_3$ + $AlF_3$

→ $NH_2-\overset{O}{\overset{\|}{C}}-NH_2 + 2H_2SO_4 \rightarrow CO_2 + H_2N SO_3H + NH_4HSO_4$

→ $H_3PO_2$ & $H_3PO_3$ do not act an oxidising agent

→ NO reacts with KOH (but it is neutral)

→ $H_2SO_4$ oxidises $HBr_2$ & HI

→ E.A $\boxed{S > Se > Te > Po > O}$

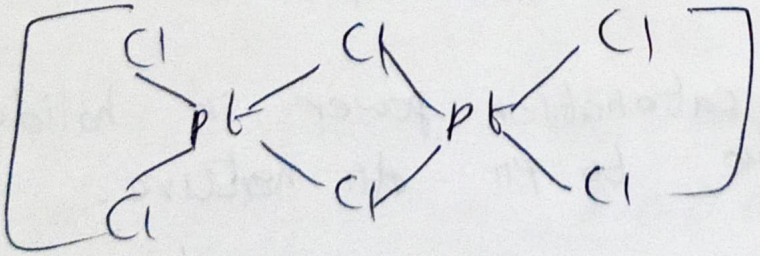
→ I.P Sc > Y > La & ~~Hf~~ Zr > Ti $H^+ > Zr > Ti$

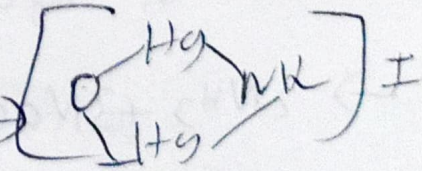
→ $Fe(ClO_4)_2 \xrightarrow{\Delta}$ ~~$Fe^{+3}$~~ $Fe_2O_3 + Cl^-$

→ $2ClO_2 + 2NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O$

→ $SO_2$, $H_2O_2$, $Na_2S_2O_3$ & $H_3PO_2$ are used as antichlor in textile industry

→ $2CuSO_4 + K_4[Fe(CN)_6] \rightarrow Cu_2[Fe(CN)_6] + 2K_2SO_4$ (chocolate Brown)

→ 

→ $NH_4^+ + NaOH + K_2HgI_4$ (Nessler's reagent) → 

Iodide of Millon's base (Brown)

$\boxed{HgI_2 = \text{red ppt}}$

→ $Cu(SCN)_2 \xrightarrow{SO_2}$ white
Black

→ $KMnO_4 + H_2 \rightarrow MnO$

→ Tin A Poling
Mercury B Distillation
Copper C Liquation
Silver D Electrolytic refining

A C D
B
A D
D

→ $H_2S + SO_2 \rightarrow S$ (colloidal)

→ $H_2S + HNO_3 \rightarrow S$ (colloidal)

→ $MnS \xrightarrow[+H_2O]{H_2O} Mn(OH)_2 + 2H_2S$

→ $MnS + 2HCl \rightarrow MnCl_2 + H_2S$
soluble

(soluble but MnS will not ppt as $S^{-2}$ ccc tow (common ion effect)

→ $NaNO_3 + 4Zn + 7NaOH \rightarrow 4Na_2[ZnO_2] + 2H_2O + NH_3$ (Nascent H is produced)

$3NaNO_3 + 8Al + 5NaOH + 2H_2O \rightarrow 8Na[AlO_2] + 3NH_3$

Excellent results - with Devardas alloy (45% Al, 5% Zn, 50% Cu)

→ Decomposition of $H_2O_2$
Catalysts: Dust, Finely divided metals, $SiO_2$, $Al_2O_3$, $MnO_2$
-ve catalysts (used in storage): acetanilide, Urea, glycerol, $H_3PO_4$, $Na_3PO_4$, $Na_2SnO_2$

→ $S^{2-} + [Fe(CN)_5NO]^{2-} \rightarrow [Fe(CN)_5NOS]^{4-}$

→ $PH_3$ is rotten fish smell.

→ In Iodometric titration (Basic Permanganate ✗ acidid Permanganate ✓)

→ $FeS_2$ = fools gold → Argentite $Ag_2S$

→ $CuSO_4$ is soluble in water

→ heating is used to remove hardness when bicarbonates are present.

→ Calamine = $ZnCO_3$

Dolomite = $MgCO_3 \cdot CaCO_3$

Zinc Blende or Sphalarite ZnS

Cassiterite = Tin stone = $SnO_2$

Kadinite = $Al_2(OH)_4Sn_2O_5$

Cuprite = $Cu_2O$

Copper glance = $Cu_2S$

Copper pyrites = $CuFeS_2$

Malachite = $CuCO_3 \cdot Cu(OH)_2$

Azurite = $2CuCO_3 \cdot Cu(OH)_2$

Galena = $PbS$

Cerrusite = $PbCO_3$

Anglesite = $PbSO_4$

Litharge = $PbO \cdot PbSO_4$

Canarkite = $PbO \cdot PbSO_4$

Siderite = $FeCO_3$

Iron pyrites = $FeS_2$

---

→ With $K_4[Fe(CN)_6]$ $Zn^{2+}$, $Cu^{2+}$, $Cd^{2+}$ will give ppt.

→ $[Ma_3b_2c]$ n (G.I) = 3, n (C-I) = 3

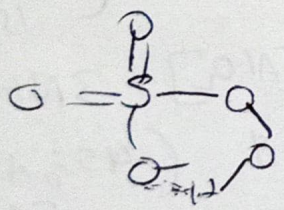
→ Wolframite magnetic

$Fe_3O_4$ (Magnetite) "

Tinstone — ~~non~~ non magnetic

$MnO_2$ (Pyrolusite)

→ $K_2CO_3$ cannot be prepared by solvay process

→ 

→ $BeCl_2(s)$ = $SP_3$ hybridised

→ Electrolysis of NaCl (molen) gives Na

Electrolysis of NaCl (aq) gives $NaOH + H_2 + Cl_2$

→ Gold is insoluble conc. $HNO_3$

→ Gold, platinum, iridium, rhodium do not react with $HNO_3$ but they dissolve in Aqua regia ($3HCl + 1HNO_3$)

→ Halls process = Red bauxite ($Fe_2O_3$ impurity)

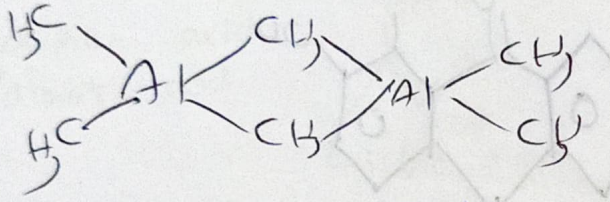
Serpeck's process = White bauxite

In Hall-Heroult process Carbon lining (steel) = cathode

graphite = anode ($C_{(s)} \rightarrow CO_{(g)}$)

In Bauxite generally $Fe_2O_3$, $SiO_2$ & $TiO_2$ are present as impurities

→



Max atoms in a plane = ~~8~~ = 10

→ $Cu_2CO_3$ is green.

→ $MnO_2$ —fusion→ $K_2MnO_4$

$N_2O_3$ = no. of l.p = 8

→ $Na_2O_2$ + Red litmus → ~~Blue~~ white ($H_2O_2$ bleaches)

→ $Co[Hg(SCN)_4]$ Blue, $HgI_2$ = red

→ $BiI_3$ = black, $Bi^{+}I^{-}$ orange turbidity

→ Butane LPG methane CNG

# Chemical Bonding

$SiF_6^{2-}$ → Valency = 4
→ covalency = 6

$NO_3^-$ → valency = 5
→ covalency = 4

→ Kossel Lewis Theory (Octet theory)

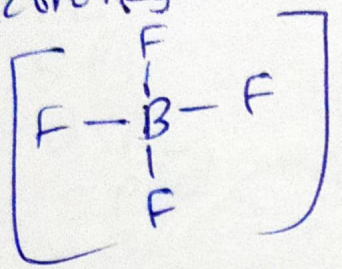
→ Formal charge Vs Oxidation number

In formal charge the electrons of a bond are given to both atoms equally.

In oxidation number both are given to more electronegative atom

$F.C = N_V - 2\times N_{LP} - \frac{1}{2} N_{BP}$

Ex:



F.C ⇒ F = 0, B = −1

O.N ⇒ F = −1, B = +3

(When all bonds are equivalent) $\cos\theta = \frac{S}{S-1} = \frac{P-1}{P}$

⇒ Lattice energy

$|\Delta H| \propto \frac{1}{r_+ + r_-}$

Hydration energy

$|\Delta H| \propto \frac{1}{r_+} + \frac{1}{r_-}$

→ Solubility

LiF < LiCl < LiBr < LiI

CsF > CsCl > CsBr > CsI

$\% = 16\Delta + 3.5\Delta^2$

$\Delta \cong 1.7 \Rightarrow 50\%$

$O^{-2}$, $OH^-$, $F^-$ → smaller anions

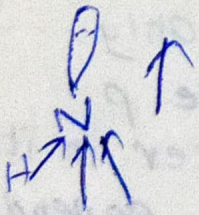
$Cl^-$, $Br^-$, $I^-$, $CO_3^-$, $SO_4^{-2}$, $PO_4^{-3}$, $CrO_4^{-2}$ → Larger anions

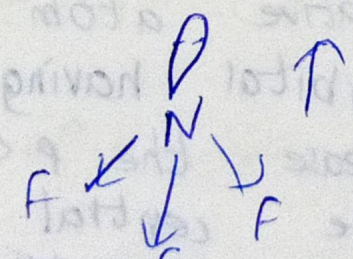
⇒ CsF → ionic  LiI → covalent.

Dipole movement

$D = \frac{1}{3} \times 10^{-29}$ C-m $= 3.3 \times 10^{-30}$ C-m  & $1D = 10^{-18}$ esu-cm

% ionic character $= \frac{\mu_{exp}}{\mu_{cal}} \times 100$  ($\mu_{cal} = \mu_{ion}$)





repulsions

LP−LP > LP−BP > BP−BP

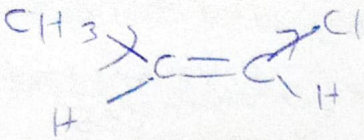
(Ex: $P_4O_{10}$ > $P_4O_6$)

$N_2O_3$ no. of $L_P = 8$

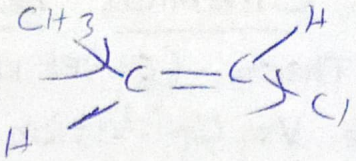
M $NH_3 > NCl_3 > NF_3$

$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$

$CH_3Cl > CH_3F > CH_3Br > CH_3I$



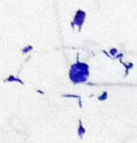
$M_1$

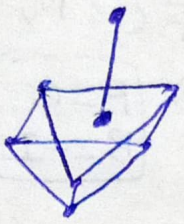


$M_2$

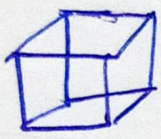
$M_2 > M_1$

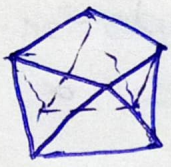
## Co-ordination-7



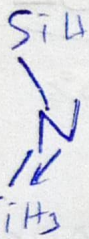


## C-N-8





or dodecahedron (All triangles)



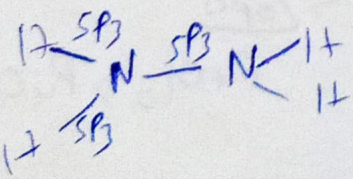
$SiH_3 \longrightarrow SiH_3 \longrightarrow$ Triangular planar.

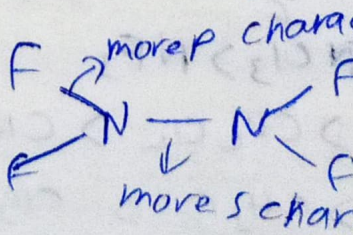
## C-N-5

→ Lone pairs occupy equatorial position because it minimizes repulsions

→ more electronegative atoms occupy axial position

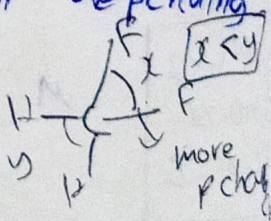
**Bent's rule**: more electronegative atom not only prefers to stay in the orbital having more p character but also can increase the p character in its attached orbital from the central atom depending on the circumstance





more p character

more s character



$(d_{N-N})_{N_2H_4} > (d_{N-N})_{N_2F_4}$

$(d_{C-C})_{C_2H_6} > (d_{C-C})_{C_2F_6}$

$(d_{O-O})_{O_2H_2} > (d_{O-O})_{O_2F_2}$

| | | |
|---|---|---|
| SP | S+P$_z$ | ($Ed_{x^2-y^2} > Ed_{z^2}$) |
| SP$_2$ | S+P$_z$+P$_x$ or P$_y$ | |
| SP$_3$ | S+P$_x$+P$_y$+P$_z$ | |
| dSP$_2$ | $d_{x^2-y^2}$ + S+P$_x$+P$_y$ | |
| sp$^3$d (T·BP) | (S+P$_x$+P$_y$) + (P$_z$+$d_{z^2}$) | |
| sp$^3$d$_2$ | (S+P$_x$+P$_y$+P$_z$)+$d_{x^2-y^2}$+$d_{z^2}$ | |
| sp$^3$d$^3$ | (S+P$_x$+P$_y$+P$_z$) + $d_{x^2-y^2}$ + $d_{z^2}$ + $d_{xy}$ (☆) | |
| SP$_3$d (S·P) | S+P$_x$+P$_y$+P$_z$+$d_{x^2-y^2}$ | |

$CO^+$ bond length is decreased due to charge develop

→ According to V·B·T $BCl_3$ angle is 90°

$d^2sp^3$ $(n-1)d_{x^2-y^2}+(n-1)d_{z^2}+nS+P_x+P_y+P_z$

(☆) $d_3S$ (tetrahedral) $d_{xy}+d_{xz}+d_{yz}+S+$[redacted]

→ $Co^{+3}$ → stable in strong field

$Co^{+2}$ → stable in weak field

→ Bond angle POP > P SP (Back bonding or partial double bond character)

SOS > SSS

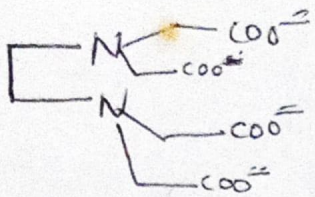
→ M·O $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma 2P_z < \pi 2P_x = \pi 2P_y < \pi^* 2P_x = \pi^* 2P_y < \sigma^* 2P_z$

(upto N) $\sigma 1s < \sigma^* 1s < \sigma 2s <$ [$\pi 2P_x = \pi 2P_y < \sigma 2P_z$] $< \pi^* 2P_x = \pi^* 2P_y < \sigma^* 2P_z$

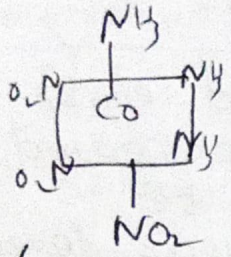
# Co-ordination Compounds

inner orbital ⇒ low spin
Ex: $Ni(CO)_4$ ($sp^3$)

Secondary Valency = C-N

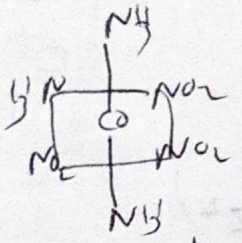



= EDTA




fac

achiral




mer-planar

merplane

## i) Linkage Isomerism

$-NO_2$ $-O-NO$ $-ONO$

$-NCS$ $-SCN$

$[Co(NH_3)_5-ONO]$ red

$[Co(NH_3)_5-NO_2]$ yellow

## ii) Co-ordination Isomerism

cation ⇄ anion

$[Cr(NH_3)_6][Co(CN)_6]$

$[Cr(NH_3)_5CN][Co(NH_3)(CN)_5]$

## iii) Ionisation isomerism

$[Co(NH_3)_5SO_4]Br$ $[Co(NH_3)_5Br]SO_4$

## iv) Solvate Isomerism

$[Cr(H_2O)_6]Cl_3$

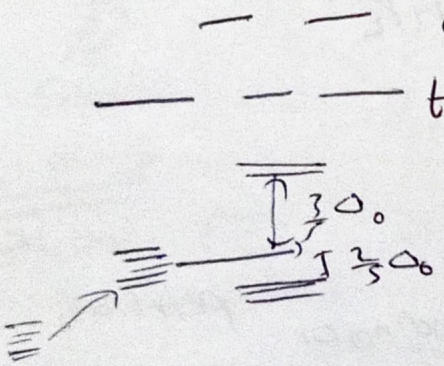
$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$

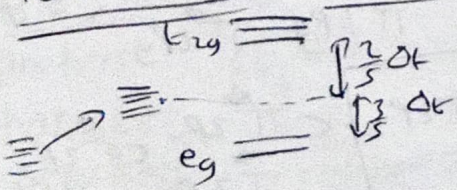
$Co^{+3}$ → stable in strong ligand

$Co^{+2}$ → stable weak

## Octahedral Complexes




## Tetrahedral complexes ($\Delta_t = \frac{4}{9}\Delta_o$) (No pairing takes place)




Nitro-O = nitrito
Nitro-N or nitro

$Cu^{+2} + NH_3 \rightleftharpoons Cu(NH_3)^{+2}$ $K_1$

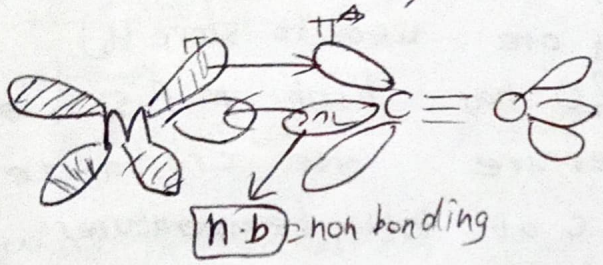
$[Cu(NH_3)]^{+2} + NH_3 \rightleftharpoons [Cu(NH_3)_2]^{+2}$ $K_2$

$K_1 > K_2 > K_3 > K_4$

→ EDTA is used in the treatment of lead poision

→ cisplatin prevents growth of tumours $[Pt(NH_3)_2Cl_2]$

→ Cyanocobalamine ($B_{12}$) = anti pernicious anamia factor

→ 


in the synergic bond electron is donated to $\pi^*$ orbital of CO.

## $H_2$ & its compounds

→ $H_2$ reactivity is very low compared to halogens

→ Preparation

Lab

1) $Zn_{(s)} + 2H^+ \rightarrow 2H^{+2} + H_{2(g)}$

2) $2Al + 2NaOH \rightarrow Na_2ZnO_2 + H_2$

Commercial

1) $H_2O \xrightarrow{\text{electrolysis}}$

2) $Ba(OH)_2 \xrightarrow{\text{electrolysis}}$ (99.95%)

3) $NaCl \xrightarrow{\text{electrolysis}} NaOH + H_2 + Cl_2$

4) $C_nH_{2n+2} + n\,H_2O \xrightarrow[Ni]{1270^oC} nCO + (3n+1)H_2$

$CO + H_2$ = Water gas = syn gas

⇒ $CO_{(g)} + H_2O_{(g)} \xrightarrow[\text{catalyst}]{673} CO_{2(g)} + H_{2(g)}$ (water-gas shift rxn)

$CO + N_2$ = Producer gas

$CO + H_2 + CH_4 + CO_2$ = Coal gas

⇒ Hydrogenation of vegetable oils using Nickel as catalyst gives edible fats.

⇒ Dihydrogen is used in the manufacture of vanaspati fat by the hydrogenation of polyunsaturated vegetable oils like soya bean, cotton seed, etc

**Hydride** → Ionic or saline ($NaH, CsH$) (some have covalent character: $LiH, BeH_2, MgH_2$) → Polymeric
→ covalent or molecular
→ Metallic or Non-stoichiometric

Ionic → Crystalline, non-volatile, non-conducting

Covalent → Volatile

**Metallic** → (7, 8, 9) do not form hydrides
→ Except Ni, Pd, Ce & Ac all metal lattices are changed.
→ Some like Pd, Pt can store a large volume of $H_2$ (They are used to store $H_2$)

**$H_2O$** → $\angle HOH = 104.5°$ → $H_2O$ has high M-P & & ~~low~~ high B.P
→ At atmospheric pressure ice crystallizes in the hexagonal form & at low temperatures it condenses to cubic form.

**Hard water** → Soap contains $C_{17}H_{35}COO^-Na$ which will ppt, $Ca(\text{stearate})_2$ or $Mg(\text{stearate})_2$
→ It is unsuitable for laundry and biler

Temporary → $Mg(HCO_3)_2$, $Ca(HCO_3)_2$

i) Boiling
$M(HCO_3)_2 \longrightarrow M(OH)_2\downarrow + 2CO_2\uparrow$

ii) Clark's method
$M(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$

**Permanent** → $MgSO_4$, $MgCl_2$ & $CaCl_2$, $CaSO_4$

i) Treatment with washing soda:
$MCl_2 + Na_2CO_3 \longrightarrow MCO_3\downarrow + 2NaCl$ & $MSO_4 + Na_2CO_3 \rightarrow MCO_3\downarrow + Na_2SO_4$
ppt ppt

ii) Calgon's method: $Na_2[Na_4(PO_3)_6]$ (Polyposphate of Na)

$$M^{2+} + [Na_4(PO_3)_6]^{-2} \longrightarrow 2Na^+ + [Na_2M(PO_3)_6]^{-2}$$

iii) Ion-exchange method: (zeolite / permutit process)

$2NaZ + M^{2+} \longrightarrow MZ_2 + 2Na^+$ ($Z = Al SiO_4$)

Permutit/zeolite is said to be exhausted when

all the sodium in it is used up It can be reused.

$M Z_2 + 2NaCl \longrightarrow 2NaZ + MCl_2$

iv) Synthetic resins method: (more efficient than zeolite process)

They catain large molecules $SO_3H$ & alkyl groups. $RSO_3H$ reacts with NaCN to form R Na

$2RNa + M^{2+}_{(aq)} \longrightarrow R_2M(s) + Na^+$ (can be regenarated - NaCl)

Pure de-ionised water is obtained when (cation exchange)

$2RH + M^{2+} \longrightarrow MR_2 + 2H^+$ (acid)

anion exchanger

$RNH_2 + H_2O \longrightarrow RNH_3^+ X^- + OH^-$ (neutralises $H^+$)

$X^- = Cl, HCO_3, SO_4$ e.t.c

$H_2O_2$ → used in pollution control treatment of domestic & industrial effluents.

Prep 1) $BaO_2 \cdot 8H_2O + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2 + 8H_2O$

(evaporation under reduced pressure)

2) electrolytic oxidation of acidified sulphate solutions at high current density

$2H^+SO_4 \xrightarrow{\text{electrolysis}} HO_3SOOSO_3H \xrightarrow{\text{Hydrolysis}} 2HSO_4^- + 2H^+ + H_2O_2$

→ $P_2O_2$ can also be prepared

$K_2S_2O_8 + 2P_2O \longrightarrow 2KPSO_4 + P_2O_2$

Hot H

3) industrial 2ethyl anthra quihol ⇌ $H_2$ at Oxidised product

Very pale blue-colour → 1% $H_2O_2$ is prepared → 30% after distillation under reduced pressure → 85% distillation under reduced pressure. The remaining is frozen to freeze $H_2O$.

$MnO_4^- \xrightarrow{\text{acidic}} Mn^{2+}$ → stored in wax-lined glass or plastic in dark

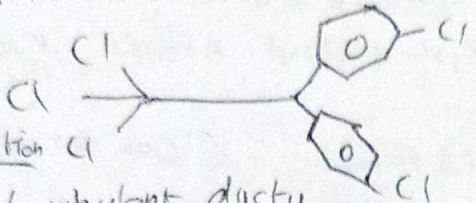
$MnO_4^- \xrightarrow{\text{basic}} MnO_2$ → Uses - hair bleach · mild disinfectant

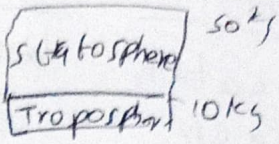
→ manfacture of Sodium Perborate & per carbonate (high quality detergents)

→ bleaching agent for textiles, paper pulp, leather, oil, fats e.t.c.

# Environmental Chemistry

→ DDT, plastic, heavy metals, many chemicals, nulear wastes are difficult to remove.






Atmospheric pollution

Tropo sphere → turbulent, dusty zone, much water vapour & clouds.

Strato sphere → $N_2$, $O_2$, $O_3$ & little water vapour.

Tropospheric pollution → 1) Gaseous → N, S oxides, $H_2S$, $O_3$, hydro carbons
2) Particulate → dust, mist, fumes, smoke
smog

## Gaseous air pollutants

a) Oxides of S → Produced when sulphur containg fosil fuel burnt

→ $SO_2$ Causes respiratory diseauses e.g Asthma, bronchitis, emplysema

→ $SO_2$ causes stiffness of flower buds which eventually fall off

→ particulate pollutants catalyse

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

→ $SO_2 + O_3 \rightarrow SO_3 + O_2$ & $SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$

b) Oxides of N

→ $N_2$ & $O_2$ react at high altitudes when lightning strikes

→ In auto mobiles' cumbustion $N_2$ & $O_2$ cobine to form NO

$$N_{2(g)} + O_{2(g)} \xrightarrow{1483} 2NO_{(g)}$$

$NO_{(g)}$ reacts with air

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_2$$

It will react even faster with $O_{3(g)}$.

→ irritant-red haze - in the traffic due to oxides of Nitrogen

→ High conc $NO_2$ damage the leaves of plants and retard

the rate of photosynthesis.
→ $NO_2$ is a lung irritant & leads to an acute respiratory disease in children.
→ $NO_2$ is harmful to various textile fibres and metals.

c) Hydrocarbons : formed by incomplete combustion of fuel used in automobiles. Carcinogenic
→ They harm plants by causing ageing, breakdown of tissues and shedding of leaves, flowers and twigs.

d) Oxides of C
i) CO - highly toxic, produced as a result of incomplete combustion of C. ~~300~~ Carboxy haemoglobin is 300 times more stable than oxy-haemglobin complex.
→ Oxygen deficiency causes headache, weak eysight, nervousness & cardiovascular disorder.
→ In pregnant women who smoke - spontaneous abortions - deformed babies.

ii) $CO_2$ - released - respiration, burning of fossil fuels, decomposition of limestone during the manufacture of cement, volcanic erruptions.
→ major contributor to Global warming.

Global warming and Green house effect
→ $CO_2$, CH4, $O_3$, CFCs cause G.W. also (water vapour, $N_2O$)
→ Greenhouses are transparent to sun light & opaque to infrared rays
→ Methane is produced when vegetation is burnt

or digested or rotted in the absence of oxygen.

→ CFCs - used in air conditioning - damage $O_3$ layer

→ large amount of $CH_4$ - released - paddy fields - coal mines, from rotting garbage dumps & by fossil fuels.

→ Increa in T - increases - dengue, malaria, yellow fever sleeping sickness etc.

Acid rain → Generally $(pH)_{rain} = 5.6$ if $(pH)_{rain} < 5.6$ it is called acid rain.

→ Particulate matter catalyses

$$2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4 \text{ (g) } 4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

→ Ammonium salt also formed and can be seen as an atmospheric haze (aerosol of the particles)

→ Causes respiratory ailments in human beings.

2) Particulate pollutants ex: smoke, dust, mist, fumes

→ P.P bigger than 5 Mm are likely to lodge in the nasal passage, whereas particles about 1 Mm enter into lungs easily

→ Lead interferes with the development & maturation of red blood cells.

Smog : (Smoke + fog)

Reducing Smog (classical smog)

→ cool, humid climate

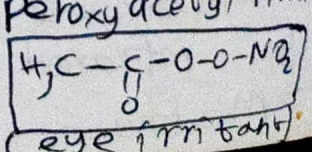
→ Smoke + fog + $SO_2$

2) Oxidising Smog (Photochemical smog)

→ warm, dry & sunny climate

→ $O_3 + NO$, $H_2C=CH-CH=O$ acrolein, farmaldehyde, hydrocarbons, Peroxyacetyl Nitrate

($O_3$ eye irritant)



$NO \rightarrow NO_2$ hv $NO + O$

$O_2 + O \rightarrow O_3$

$NO + O_3 \rightarrow NO_2 + O_2$

because of this chain rxn $NO_2$, $O_3$ concentration ↑

$NO_2$ & $O_3$ oxidise hydrocarbons → acrolein, HCHO, PAN

→ $O_3$ & NO irritate nose & throat and their high conc causes headache, chest pain, dryness of the throat cough & difficulty.

→ Photo Chemical smog leads to cracking of rubber & damages plant life.

→ It also causes corrosion of metals, stones, building materials

→ P.C.S can be controlled by reducing $NO_2$.

stratospheric pollution

→ $O_3$ protects from – UV ($\lambda \approx 255nm$) – which causes melanoma (skin cancer)

→ $O_2 \xrightarrow{UV} O + O$

$O_2 + O \xrightarrow{UV} O_3$

$O_3 \rightarrow O_2 + O_{(g)}$ (decomposes)

Dynamic eqbn will be there.

→ Freons (CFCs) are depleting $O_3$ layer.

→ $CF_2Cl_2 \xrightarrow{UV} \boxed{Cl} + \dot{C}F_2Cl$ (chlorine radical is catalyst)

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow \boxed{Cl} + O_2$

Ozone Hole

$ClO + NO_2 \rightarrow ClONO_2$

$Cl + CH_4 \rightarrow CH_3 + HCl$

$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$

$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$

$HOCl \xrightarrow{h\theta} OH + Cl$

$Cl_2 \xrightarrow{h\theta} \boxed{2Cl}$

→ Effects: ageing of skin, cataract, sunburn, skin cancer, killing of many phytoplanktons, damage to fish producting

→ Paints & fibres also damaged

**Water pollution** : i) Pathogens & ii) Organic wastes iii) Chemical pollutants

ii) Oraganic wastes (domestic sewage & animal excreta) (In cold water DO can reach 10 ppm)

→ Organic wastes contain bacteria which consume DO.

→ If DO < 6ppm growth of fish get inhibited.

→ aquatic green plants ↑ DO during morning & ↓ at night.

→ If too much organic matter is added only aherobic bacteria can survive.

**B.O.P** : The amount of $O_2$ required by bacteria to break down the organic matter present in a certain volume of a sample of water. Clean water BOD < 5ppm

BOD > 17ppm ⇒ highly polluted water.

→ fertilizers - phosphates - increase algae - covers the surface - fish will die

This lass of biodiversity is known as Eutrophication

**Fluoride:**

1ppm good

$3(Ca_3(PO_4)_2) \cdot Ca(OH)_2$

$3(Ca_3(PO_4)_2) \cdot CaF_2$

2ppm - mottling of teeth

10ppm - very harmful

**Lead** : 50ppb

**Sulphate** 500ppm

**Nitrate** 50ppm methemoglobinemia (blue baby syndrome)

| | ppm |
|---|---|
| Fe | 0.2 |
| Al | 0.2 |
| Mn | 0.05 |
| Pb | 0.05 |
| Cu | 3 |
| Zn | 5 |
| Cd | 0.005 |

**Green Chemistry**

i) Dry cleaning earlier $C_2Cl_4$ was used

→ $liq.O_2$ is now used for dry cleaning.

→ $H_2O_2$ is used for the purpose of bleaching clothes

ii) Earlier $Cl_2$ was used for bleaching, now $H_2O_2$ is used

iii) $CH_2=CH_2 + O_2 \xrightarrow[PdCl_2/CuCl_2]{\text{Catalyst}} CH_3-CHO$ (90%)

# Halogens

⇒ F-F bond enthalpy weak → ① Repulsion between lone pairs
→ ② No multiple bonding as no d-orbitals

$Cl-Cl > Br-Br \geq F-F > I-I$

→ But still $E^\circ$ value is more for flouring (H-E & B.D.E)
(Electrong G.E is more for $Cl_2$)

→ $CaF_2$ is insoluble
(Only $BeF_2$ is soluble among $MF_2$)

→ Rxn with water

$2F_2 + 2H_2O \rightarrow 4H^+ + 4F^- + O_2$ (Ozonised oxygen)

$X_2 + H_2O \rightarrow HX + HOX$ $(X = Cl, Br)$

$4H^+ + 4I^- + O_2 \rightarrow 2I_2 + 2H_2O$

HOCl will give nascent oxygen & used as bleaching agent

$F_2$ = Yellow
$Cl_2$ = Greenish Yellow
$Br_2$ = red
$I_2$ = Violet

Complementary colours are absorbed for HOMO to LUMO transition

→ Rxn with $H_2$

HX is formed - ~~acidic~~ acidic strength

$HI > HBr > HCl > HF$

(Bond dissociation energy is important) not E-N

Rxn with $O_2$

→ $OF_2$ & $O_2F_2$ (flourides) are flourinating agents

$P_4 + 3O_2F_2 \rightarrow PF_6 + 3O_2$

$I > Cl > Br$ (Stability) (Middle Row anamoly)

→ $Cl_2O$, $ClO_2$, $Cl_2O_6$ & $Cl_2O_7$ → highly reactive oxidising agents — explode

→ $ClO_2$ is used as bleaching agent for paper pulp

→ $Br_2O$, $BrO_2$, $BrO_3$ exists only at high temp.

→ $I_2O_4$, $I_2O_5$ & $I_2O_7$ decompose on heating ($I_2O_5$ - CO estimation)

→ Rxn with metals → they form halides

→ Rxn with halogens → central atom will be large size

→ They are more reactive than halogens (except flourine)

Chlorine Prep: → $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

→ $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

Deacon's process: $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

Electrolytic process: Conc $NaCl \xrightarrow{electrolysis} NaOH + H_2 + Cl_2$

$P_4 + 6Cl_2 \rightarrow 4PCl_3$, $S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$

$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 \cdot H_2O$ (bleaching powder)

Bleaching powder = $Ca(OCl)_2 \cdot CaCl_2 \cdot Ca(OH)_2 \cdot 2H_2O$

$Cl_2 + H_2O \rightarrow HCl + HOCl$ $HOCl \rightarrow HCl + (O)$ (Permanent bleach action & Oxidising property)

($SO_2$ has temporary bleaching action ↓ due to reducing nature it converts into sulphuric acid)

$H_2S + Cl_2 \rightarrow 2HCl + S$ $Na_2S_2O_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl + S$

HCl $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

$H_2O + HCl \rightleftarrows H_3O^+ + Cl^-$ $K_a = 10^7$ $NH_3 + HCl \rightarrow NH_4Cl$ (white fume)

$3HCl + 1HNO_3$: aqua regia.

$Au \rightarrow AuCl_4^-$

$Pt \rightarrow [PtCl_6]^{-2}$

Oxo acids

| HOF | HOCl | HOBr | HOI |
|---|---|---|---|
| | $HOClO$ | – | – |
| | $HOClO_2$ | $HOBrO_2$ | $HOIO_2$ |
| | $HOClO_3$ | $HOBrO_3$ | $HOIO_3$ |

$HClO > HBrO > HIO$ (electronegativity)

~~HOClO~~

$HClO_4 > HClO_3 > HClO_2 > HClO$

$ClO_3^- + 6I^- + 6H_2SO_4 \rightarrow Cl^- + 6HSO_4^- + 3I_2 + 3H_2O$

→ $2AgClO_3 + Cl_2 \rightarrow 2AgCl + 2ClO_2 + O_2$

→ $2NaClO_2 + Cl_2 \rightarrow 2NaCl + 2ClO_2$

→ $2ClO_2 + 2NaOH \rightarrow NaClO_2 + NaClO_3 + H_2O$

$2ClO_2 + Na_2O_2 \rightarrow 2NaClO_2 + O_2$

## Interhalogen compounds

$XX'$, $XX_3'$, $XX_5'$, $XX_7'$ (X = large size, X' = smaller size)

→ IF is unstable → $ICl_3$ exists as $I_2Cl_6$

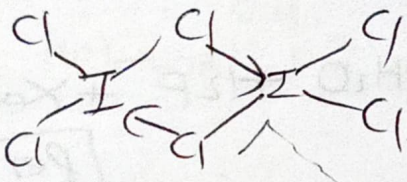
→ Only ClF is gas others being liquids or gases.

→ They are reactive due to polar nature.

→ they undergo hydrolysis to produce oxo acids & HX'.

$V + 3ClF_3 = VF_6(g) + 3ClF(g)$ (Flourinating agents)

$V(s)$

→ $I_2Cl_6$ = 

→ $Na_2S_2O_3 + 5H_2O + 4Cl_2 \rightarrow 2NaHSO_4 + 8HCl$ (Br also same)

## Noble Gases

He, Ne, Ar, Kr, Xe, Rn

→ Sparingly soluble in water → only weak dispersion forces so, low melting and boiling points because the only type of interato → It has an unusual (Helium) property of diffusing through most commonly used laboratory materials such as rubber, glass or plastics.

→ $O_2 \rightarrow O_2^+ \approx Xe \rightarrow Xe^+$ $\quad Xe + PtF_6 \rightarrow Xe^+PtF_6^-$

→ He, Ne, Ar → no compounds

$Xe + F_2 \rightarrow XeF_2(s)$ (excess)

$Xe + 2F_2 \rightarrow XeF_4(s)$ (1:5 ratio)

$Xe(g) + 3F_2(s) \rightarrow XeF_6(s)$ (1:20)

$XeF_2$, $XeF_4$, $XeF_6$ sublime readily

→ Power ful flourinating agents

$2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2(g)$

$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$

$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

(through $XeOF_4$, $XeO_2F_2$)

$XeF_6$ → distorted octahedral structure

→ $XeF_2 + PF_5 \rightarrow [XeF]^+[PF_6]^-$

$XeF_4 + SbF_5 \rightarrow [XeF_3]^+[SbF_6]^-$

$XeF_6 + MF \rightarrow M^+[XeF_7]^-$ (M = Na, K, Rb or Cs)

→ Melting point $XeF_2 > XeF_4 > XeF_6$

→ $XeO_3$ is explosive

→ $XeO_3 + 2XeF_4 \rightarrow 3XeOF_4$

→ $XeO_3 + XeOF_4 \rightarrow 2XeO_2F_2$

→ $2XeF_6 + 16OH^- \longrightarrow 8H_2O + 12F^- + XeO_6^{4-} + Xe + O_2$

(Strongly alkaline)

Perxenate ion

→ $Ba_2XeO_6 + 2H_2SO_4 \rightarrow XeO_4 + 2BaSO_4 + 2H_2O$

↳ $Xe + 2O_2$ (unstable so decomposes)

→ $2Na_4XeO_6 + 8HCl \longrightarrow 8NaCl + 2XeO_3 + 4H_2O + O_2$

→ $XeF_2$ is not flouride ion acceptor

# d & f block

→ Zn, Cd, Hg are not transition metals

Cr $3d^5 4s^1$
Cu $3d^{10} 4s^1$

Zr
Nb $4d^4 5s^1$
Mo
Tc $4d^6 5s^1$
Ru $4d^7 5s^1$
Rh $4d^8 5s^1$
☆ Pd $4d^{10} 5s^0$
Ag $4d^{10} 5s^1$
Cd ~~$4d^{10} 5s^2$~~

Y Zr | Nb Mo Tc Ru Rh Pd Ag Cd ☆

La Hf Ta W Re Os Ir | Pt | Au | Hg

→ Greater horizontal similarities & less group similarities.

→ Nearly all transitions elements display high tensile strength, ductility, malleability, high thermal & electrical conductivity & metallic lustre (except Zn, Cd, Hg & Mn)

→ Melting & boiling points are least for Zn, Cd & Hg & highest in the middle of the row

→ Enthalphy of atomisation is least for Zn, Cd & Hg & highest in the middle of the row.

→ As we go down M.P, B.P & $\Delta H_{atomisation}$ incrases (sizes are almost same but charge is different)

→ For same charged ions radius ↓ as we go → (poor shielding effect of d)

→ radii of 4d are gregter than 3d but 4d ≈ 5d (Zr 160pm, Hf 159pm)

→ density ↑ as we go → ⇒ 1st I. Enthalpy decreases slowly along the group

→ 2 & 3. I.E's increase at a fasterrate as go →

→ Unipositive ions have $d^n$ configurations with no 's' electrons.

→ Cr & Cu 2nd I.E is high.

→ Oxidation states generally defer by 1

→ In p block heavier elements prefer low oxidation state
d-block " " higher oxidation state
$Cr_2O_4^{-2}$ is oxidising agent $MoO_3$ & $WO_3$ are stable.

→ Lower oxidations states (zero also) when a complex compound with ligands capable of π-acceptor character ($Fe(CO)_5$, $Ni(CO)$

→ $M^{2+} \rightarrow M$ ; $E^\circ$ value is +ve only for cupper

→ $Cr^{+2}$ is reducing, $Mn^{3+}$ is oxidising agent

→ Only oxidising acids oxidise Cu, normal mineral acid don't evolve $H_2$ with Cu. ($HNO_3$, $H_2SO_4$)

→ $Ti^{2+}$, $V^{2+}$, $Cr^{2+}$ are strong reducing agents

→ $Mn^{3+}$ $Co^{3+}$ are strong oxidising agents.

→ $Fe^{+2}$ is more stable than $Fe^{+3}$

→ Higher oxidation states are shown with $O_2F_2$

→ ~~$CuI_2$~~ does not exist as $Cu^{+2}$ oxidises $I^-$ to $I_2$

→ Flourides are instable in their low oxidation states. $2Cu^{2+} + 4I^- \rightarrow Cu_2I_2 + I_2$

→ $2Cu^{+} \rightarrow Cu^{+2} + Cu$ ($Cu^{+2}$ is much more hydrated)

→ ferates (VI) $(FeO_4)^{2-}$ are formed in alkaline medium & decompose to $Fe_2O_3$ & $O_2$.

→ highest Mn fluoride is $MnF_4$

$[MO_4]^{n-}$ $M = V^{+5}, Cr^{+6}, Mn^{+5}, M^{+6}, Mn^{+7}$

→ Most of them are paramagnetic

→ Spin only ⇒ $\mu = \sqrt{n(n+4)}$ B.M

→ Catalytic properties are due to multiple oxidation states and to form complexes

→ $V_2O_5(s)$ is used in contact process

→ They increase its concentration at the surface & weakens their bonds which decreases the bond energy & activation energy.

(-)ve $2I^- \longrightarrow 2I + S_2O_8^{-2} \xrightarrow{Fe^{3+}} I_2 + 2SO_4^{2-}$

→ Interstitial compounds → high melting points, higher than pure metals.

→ they are very hard, some borides approach diamond

→ conductors & chemically inert.

Alloys ⇒ homogeneous → if radius is within 15%

Brass (Cu - Zn) Bronze (Cu Sn)

→ $Mn_2O_7$ covalent green oil.

→ $CrO_3$, $V_2O_5$ have low melting points. (covalent)

→ $V_2O_5 \xrightarrow{OH^-} VO_4^{3-}$ $V_2O_5 \xrightarrow{H^+} VO_2^+$

→ $Cr_2O_3$ & $V_2O_5$ are amphoteric

→ $K_2Cr_2O_7$ $K_2Cr_2O_7 + H_2SO_4 + H_2O_2 \longrightarrow CrO_5$

$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

soluble

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$ ($K_2Cr_2O_7$ - orange red)

crystallises

→ by changing pH we can convert dichromates & chromates.

→ $Na_2Cr_2O_7$ is hygroscopic so not a primary standard.

$K_2Cr_2O_7$ is a primary standard.

→ $Cr_2O_7^{2-} + H_2S \rightarrow S + Cr^{+3}$

($K^+ MnO_4^-$ - purple, $Mn^{2+}$ - pale pink)

*$MnO_4^-$

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

(black) pyrolusite dark green

Commercially

$MnO_2 \xrightarrow[\text{or } KOH + O_2]{KOH,\ HNO_3} MnO_4^{2-} \xrightarrow[\text{Oxidn}]{\text{Electrolytic}} MnO_4^-$

laboratory

$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

(Peroxy borates etc can also be used)

$2K\,MnO_4 \xrightarrow{573K} K_2MnO_4 + MnO_2 + O_2$

→ manganate is paramagnetic with 1 unpaired electron

⇒ $H_2S \longrightarrow S\downarrow$ ⇒ $Fe^{+2}$ (green) → $Fe^{3+}$ (yellow)

acidic $n=5$

neutral & slightly basic $n=3$

strong basic $n=1$

⇒ Used in bleaching of wool, cotton & silk & for decolourisation of oils.

→ $Fe^{+2}$ is more stable due to thermodynamic reasons

→ $Co^{3+}$ & $Mn^{3+}$ (highest) are very strong oxidising agents

# F-block

Lanthanoids
Actinoids

+3 is the most stable & common to all oxidation state.

In +3 state their common E-C is $4f^n$

→ Radii of $M^{3+}$ decreases regularly.

→ Shielding of f-f electrons < d-d

→ Eu has highest radii

→ La (II) & Ln (III) are generally predominant.

→ $Ce^{4+}$ (Noble gas configuration) (strong oxidant)
$Eu^{2+}$ ($f^7$) (Reducing agent) & $Yb^{2+}$ ($f^{14}$) (RA)

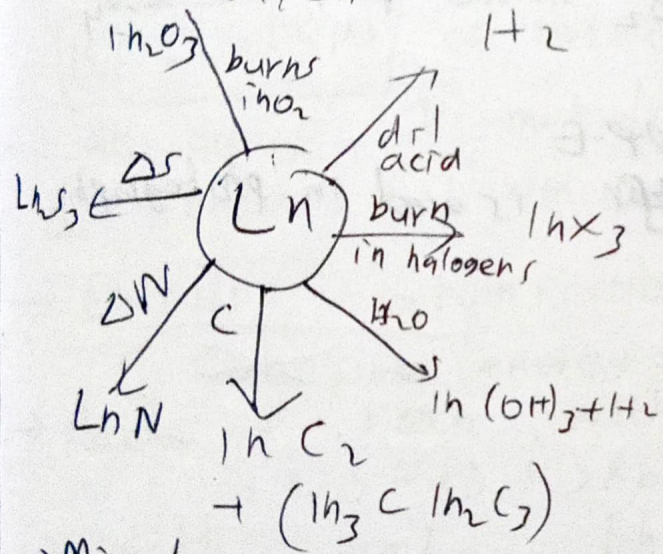
$Tb^{+4}$ ($f_7$) (OA), $Sm^{2-}$ (R-A)

→ samarium is steel hard. (other 1000 - 1200K)
M.P of samarium = 1623K

→ $La^{+3}$, $Lu^{+3}$, $Gd^{+3}$ are colourless the remaining being coloured.

→ higher atomic number Ln behave like Al

→ $E^\circ Ln/Ln^{+3}$ ∈ [-2.2 to -2.4] except $E^\circ_{Eu} = 2V$




Misch metal = 95% Ln + 5% Iron + traces of S, C, Ca & Al.
to produce bullets, shell & lighter flint.

→ Mixed oxides of Lanthanoids are employed as catalysts in petroleum cracking.

→ Some Ln oxides are used in phosphors in T.V & similar fluorescing surfaces.

## Actinoids

→ The end members can be prepared only in nanogram.

→ size is decreased for atoms & $M^{3+}$ like Ln.

→ Actinoid contraction > lanthanoid contraction

→ +3 & +4 ions tend to hydrolyse.
→ They are highly reactive, especially when finely divided
→ With water gives a mixture of oxides & hydride and combination with most non metals takes place at moderate temperature. HCl reacts with all of them.
→ They are slightly affected by $HNO_3$ (oxide layer is formed)
→ Reacts with alkalies.
→ The second half of actinoids are similar to Lanthanoids. The first half is almost simila except with oxidation states.

Uses of P & F block

→ $V_2O_5$ is used as catalyst to oxidise $SO_2$ in the prep of $H_2SO_4$
→ $Al(Et)_3 + TiCl_4$ to make HDP-E
→ light sensitive properties of AgBr is used in photographic industry.

# 1st Group

Density $Cs > Rb > Na > (K) > Li$ EN M.P B.P

→ Density

| | |
|---|---|
| Li | Crimson Red |
| Na | Golden |
| K | Violet |
| Rb | Red violet |
| Cs | Blue Violet |
| Be | ✗ |
| mg | ✗ |
| Ca | Brick red |
| Sr | crimson red |
| Ba | Apple Green |

| | EN | M.P | B.P |
|---|---|---|---|
| Li | 1.0 | 181 | 1347 |
| Na | 0.9 | 98 | 881 |
| K | 0.8 | 63 | 766 |
| Rb | 0.8 | 39 | 688 |
| Cs | 0.7 | 28.5 | 705 |

As we go down metallic bonding weakens & M.P & B.P ↓

→ At Normal temperatures all Group I metals adopt BCC type of lattice. (C.N = 8)

→ All group 1 metals can be cut easily with a knife. Lithium is harder among them.

→ Enthalpy atomisation is low for Group 1 metals.
(Cohesive energy = $-\Delta H_{atom}$)

→ Rate of rxn with $H_2$
Li > Na > K > Rb > Cs

→ With water thermodynamically Li reacts more feasible. But kinetics dominate here. Li has high melting point, others melt during the reaction with water & due to more area they react vigorously.

→ Rxn with air
Li → $Li_2O$
$Na_2O_2$
$KO_2$
$RbO_2$
$CsO_2$

$MO_2 \rightarrow \frac{1}{2}M_2O + \frac{3}{4}O_{2(g)}$
Unstable | stable
↓
stable $M_2O$ unstable

→ L-E change in $O^{-2}$ dominates (small)

So large → $O_2^-$ atoms

Solubility

$CsOH > RbOH > KOH > NaOH > LiOH$

$Cs_2CO_3 > Rb_2CO_3 > \ldots > Li_2CO_3$

~~$CsHCO_3 > \ldots > LiHCO_3$~~

$KHCO_3 > NaHCO_3$

Thermal stability

$CsOH > \ldots > LiOH$ ($\because$ $Cs^+$ $OH^-$)

$Cs_2CO_3 > Rb_2CO_3 > \ldots > Li_2CO_3$

$CsHCO_3 > \ldots > LiHCO_3$

→ In NaI, KI, RbI if $I_2$ is dissolved $I_3^-$ is formed.

→ Among $Cs^+$, $Mg^{2+}$, $Mg^{2+}$ form an acetate complex

→ $M + NH_3 \rightarrow$ ~~$M(NH_2)_2 + H_2$~~ $\Rightarrow$ $[M(NH_3)_y]^+ [e(NH_3)_y]^+$

→ $Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$

→ With $Na_2CO_3$

| Ca<br>Ba<br>Ag | ~~Zn~~ $Mg^{2+}$<br>$Zn^{2+}$<br>$Cu^{2+}$<br>$Pb^{2+}$ | $Fe^{+3}$<br>$Al^{+3}$<br>Sn |
|---|---|---|
| ↓ forms ppt of $CO_3^{-2}$ | ↓ forms basic carbonate & releases $CO_2$ | ↓ forms ppt of $CO_3^{-2}$ & immediately hydrolyse to release $CO_2$ |

| Amophoteric oxides | Metals |
|---|---|
| BeO | Be |
| $Ga_2O_3$ $Al_2O_3$ | Al |
| ZnO | Zn |
| SnO, $SnO_2$ | Sn |
| PbO, $PbO_2$ | Pb |
| $Cr_2O_3$ | Ge |
| $MnO_2$ ~~$FeO_3$~~ $V_2O_5$ | |
| $As_2O_3$ $Sb_2O_3$ | $TeO_2$ $PoO_2$ |

→ $Na_2CO_3 + SO_2 + S \rightarrow Na_2S_2O_3 + CO_2$

→ $MgCl_2 \cdot 6H_2O \Rightarrow MgO$

→ $CaCl_2 \cdot 6H_2O \Rightarrow CaCl_2$

→ $MgO + C + Cl_2 \rightarrow MgCl_2 + CO$

## Group-2

→ Ionic size $Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$ (mobility $Ba^{+2} > Be^{2+}$)

→ Be & Mg are kinetically inert to water and air due the formation of oxide film.

→ $M + X_2 \rightarrow MX_2$

$(NH_4)_2BeF_4 \Rightarrow BeF_2$ $\quad BeO + C + Cl_2 \rightleftharpoons BeCl_2 + CO$

→ Upon heating except Be others form $MH_2$

$BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$

→ $M + NH_3 \rightarrow M(NH_3)_6 \Rightarrow \boxed{M(NH_2)_2}$ (they give amides)

→ $[Be_4O(R_6)]$ $\quad i + N{=}N{=}\overset{-}{N} \Rightarrow$ Basic Beryllium Nitrate / acetate ($R = CH_3COO$)

→ $CaC_2 + N_2 \rightarrow CaNCN + C$

→ $BeCl_2 \rightarrow$ solid state polymo

$\rightarrow$ vapour monomer or dimer

Size of $\boxed{OH^- > O^{2-}}$

→ $MgCl_2 \cdot 2H_2O \rightarrow MgO + 2HCl + H_2O$ (HCl: excess)

# III A

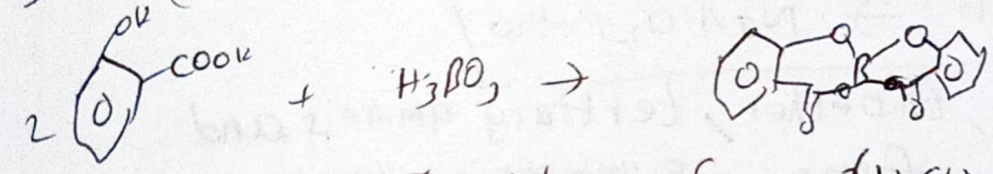
$Na_2B_4O_7 \cdot 10H_2O$ = Borax or Prismatic Borax  $5H_2O$ = Octahedral or Jeweller's borax

$[Na_2B_4O_5(OH)_4] \cdot 8H_2O$

$Na_2B_4O_7 \cdot 4H_2O$ = Kernite

→ In $(AlH_3)_n$  C.N of Al = 6

| | Z |
|---|---|
| B | 2 |
| Al | 1.9 |
| Ga | 1.6 |
| In | 1.7 |
| Tl | 1.8 |

→ 

→ $2AlCl_3 \cdot 6H_2O \rightleftharpoons Al_2O_3 + 6HCl + 9H_2O + 6HCl \rightarrow 9H_2O + 6HCl$

Prep of $AlCl_3$

$Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO$

or

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$

$2Al + 3Cl_2 \rightarrow 2AlCl_3$

→ $Na_2[B_4O_5(OH)_4] + 5H_2O \rightleftharpoons 2B(OH)_3 + 2NaB(OH)_4$

→ Borazine $(B_3N_3H_6)$ Unlike benzene adds HCl on the double bond.

or

Borzole

$B_2H_6 + 2NH_3 \xrightarrow{120^\circ C} B_2H_6 \cdot 2NH_3$

~~$B_2H_6$~~ $3(B_2H_6 \cdot 2NH_3) \xrightarrow{200^\circ C} B_3N_3H_6 + 12H_2$

$B_2H_6 + 2NH_3 \xrightarrow{200^\circ C} B_3N_3H_6$

1 : 2 Proportion

$nB_3N_3H_6 \xrightarrow{200^\circ C} (BN)_{3n} + 3nH_2$

$Na_2B_4O_7 + 2NH_4Cl \xrightarrow[\text{not}]{\text{Red}} 2BN + B_2O_3 + 2NaCl + 4H_2O$

$H_3BO_3 + 2KHF_2 \rightarrow K[BF_4] + 2H_2O + 2KOH$

acid  acid  base

→ Nidoboranes $(B_nH_{n+4})$ are quite stable

→ $AlCl_3 + 3H_3O^+ \rightarrow [Al(OH)_6]^{3+} + 3HCl$

$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl$

$AlCl_3 + 3NaOH \rightarrow Al(OH)_3 + 3NaCl$

$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$

→ With CO, ether, thioether, tertiary amines and pyridine $B_2H_6$ forms symmetric cleavage

$B_2H_6 + 2X \rightarrow [BH_4^-] + [B_2H_2X_2]^+$

→ Radius of Ga > Al

→ $B_2H_6 + CH_3OH \rightarrow BH(OCH_3)_2 + B(OCH_3)_3 + H_2$

→ $BX_3 + 3H_2O \rightarrow H_3BO_3 + 3HX$ (X = Cl, Br, I

→ $4BF_3 + 12H_2O \rightarrow 4H_3BO_3 + 12HF$

$12HF + H_3BO_3 \rightarrow 3H^+ + 3[BF_4]^- + 9H_2O$

$4BF_3 + 3H_2O \rightarrow H_3BO_3 + 3H^+ + 3BF_4^-$

→ $3SiCl_4 + 4Al \rightarrow 3Si + 4AlCl_3$

crystalline

$SiO_2 + Na_2CO_3 \rightleftharpoons Na_2SiO_3 + CO_2$

# 4th group

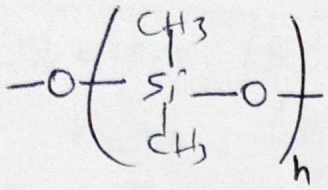
→ Ge expands when it forms the solid

→ $CH_4$ highly reducing nature $PbH_4$ = stable

→ Catenation C >> Si > Ge ≃ Sn > Pb

| | |
|---|---|
| C | 2.5 |
| Si | 1.8 |
| Ge | 1.8 |
| Sn | 1.8 |
| Pb | 1.9 |

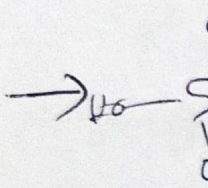
→ Silicones



$Sn^{4+}$ is stable

$Pb^{4+}$ is stable.

→ $C + H_2O \rightarrow CO + H_2$ watergas or syn gas (better) $2C + O_2 + 4N_2 \rightarrow 2CO + 4N_2$ Producer gas

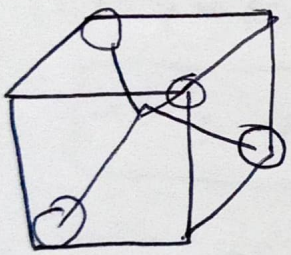


silicic acid

→ Fullerenes are aromatic

→ quartz is a piezo-eletric material

→

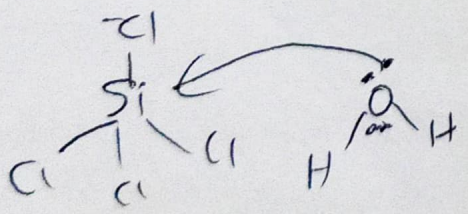


$S_4$ → symmetry is present

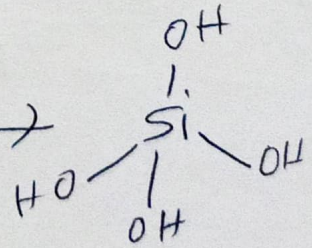
→ $3SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 2H_2SiF_6$ or $H_2SiO_3 + 2HSiF$

→ CO = neutral oxide

→



→



→ $CCl_4 + H_2O$ (vapour) $\rightarrow COCl_2 + 2HCl$

→ Diamond is better thermal conductor than graphite

$SiO_2 + HF \rightarrow SiF_4 + HF \longrightarrow H_2SiF_6$

$6SiF_4 + 4H_2O \rightarrow H_4SiO_4 + 2H_2SiF_6$

orthosilicic acid — Fluoro silicic acid

→ $Sn(C_2O_4) \xrightarrow{\Delta} SnO + CO + CO_2$

$2Na_2SnO_2 + O_2 \longrightarrow 2Na_2SnO_3$

→ $SnCl_2 \cdot 2H_2O \rightarrow Sn(OH)Cl + HCl + H_2O$

(excess HCl current)

→ $SnCl_2$ is a strong reducing agent.

$HgCl_2 \longrightarrow Hg_2Cl_2 \rightarrow Hg$

$FeCl_3 \rightarrow FeCl_2$

$CuCl_2 \rightarrow Cu_2Cl_2$

$AuCl_3 \longrightarrow Au$

$I_2 \longrightarrow I^-$

# (5) Nitrogen Family

→ Stability $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

→ Reducing nature $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$

→ among halides

(Stability) fluoride > chloride > Bromide > Iodide

$\overset{-3}{N}\overset{+1}{Cl}_3 + 4H_2O \rightarrow NH_3 + 3HOCl$ or $(NH_4OH + 3HOCl)$

$\overset{+3}{P}\overset{-1}{Cl}_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

$AsCl_3 + 3H_2O \rightleftharpoons H_3AsO_3 + 3HCl$

$SbCl_3 + H_2O \rightleftharpoons SbOCl\downarrow + 2HCl$

$BiCl_3 + H_2O \rightleftharpoons BiOCl\downarrow + 2HCl$

| | |
|---|---|
| N | 3-0 |
| P | 2-1 |
| As | 2-0 |
| Sb | 1-9 |
| Bi | 1-0 |

→ Lewis acidity $N\ddot{I}_3 > NBr_3 > NCl_3 > \ddot{N}F_3$

→ $\underset{\text{excess}}{8NH_3} + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$

→ As & Sb are metalloids

→ N - Max covalency 4. P → $PF_6$

→ N - also can't form $d\pi - p\pi$ bonds like in $R_3P=O$ or $R_3P=CH_2$.

→ Trihalides except $BiF_3$ are covalent.

→ with metals they form nitrides, phosphides, arsenides, antimonides, magnesium bismuthide

→ Ammonia is dried by CaO. But not with Conc $H_2SO_4$, anhydrous $CaCl_2$ & $P_4O_{10}$

→ 1 Vol of $H_2O$ can dissolve 1000 vol of $NH_3$.

Soluble in excess of

Ni (6)
Cr (6)
Co (6)
Cu (4)
Cd (4)
Zn (4)
Ag (2)

Ppt only

$Fe^{+3}$
$Fe^{+2}$
$Al^{+3}$
$Mn^{+2}$

→ $N_2O$ & NO are neutral

→ very pure nitrogen

$$Ba(N_3)_2 \longrightarrow Ba + 3N_2$$

→ $N_2O$, NO, $N_2O_4$, $N_2O_5$ — colourless solids; $N_2O_3$, blue solid; $NO_2$, brown gas

→ Ostwald's process

$$4NH_3(g) + 5O_2(g) \xrightarrow[500^\circ C,\ 4\text{ bar}]{Pt/Rh\ gauge\ catalyst} 4NO(s) + 6H_2O(g)$$

$$2NO + O_2 \rightleftharpoons 2NO_2$$

→ $$3NO_2 + H_2O(l) \longrightarrow 2HNO_3(aq) + NO$$

| | | | |
|---|---|---|---|
| V. Dil | Mg Mn | $H_2 + M.N$ | Be, Al, Cr, Fe, Co become passive with conc $HNO_3$ |
| | Al Zn Sn Fe | $NH_4NO_3 + M.N$ | |
| Dil | Hg Pb Cu Ag (to+1) | $NO + M.N$ | |
| | Fe Zn Sn | $N_2O + M.N$ | |
| | | $NH_4NO_3 + Sn(NO_3)_2$ | |
| Conc | Hg Pb Cu Ag Zn (to+2) | $NO_2 + M.N$ | |
| | Sn | $NO_2 + H_2SnO_3$ | |

→ $$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$$

Brown ring

→ $$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$$

$$2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl$$

$$2NH_3 + 3CaOCl_2 \rightarrow N_2 + 3H_2O + 3CaCl_2$$

$$2NH_3 + 3NaOCl \rightarrow N_2 + 3H_2O + 3NaCl$$

$$2NH_3 + 3CuO \longrightarrow 3Cu + 3H_2O + N_2$$

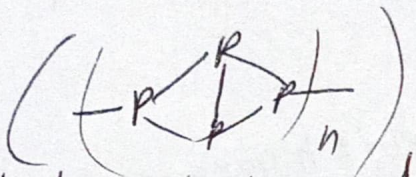
$$2NH_3 + 3PbO \longrightarrow 3Pb + 3H_2O + N_2$$

Stability: Black > Red > white

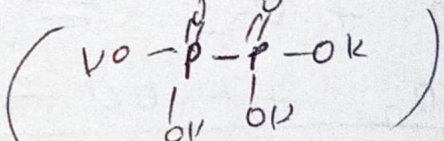
White phosphorous → insoluble in water but soluble in carbon disulphide. & glows in dark

$P_4$ (white) + NaOH + $H_2O$ → $PH_3$ + $NaH_2PO_2$

$P_4 + 5O_2 \longrightarrow P_4O_{10}$ (dense white fumes with air)

Red phosphorous  insoluble in both water & $CS_2$. It does not glow in dark

$(P_4)_n$ (red) + alkali → $HuP_2O_6$



Black: optained by heating Red at high P.q.

→ Pure $PH_3$ is non inflammable but if it contains impurities like $P_2H_4$ or $P_4$ vapours it is inflammable

To purify it is absorbed in HI

$PHuI + KOH \longrightarrow KI + H_2O + PH_3$ pure.

→ It ($PH_3$) explodes in contact with traces of oxidising agents. Homes signal = $Ca_3P_2$ + $CaC_2$ + $H_2$

$PCl_3$

$P_4 + 6Cl_2 \longrightarrow 4PCl_3$ / $P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$

$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$ with acid & alcohol $H_3PO_3$

$PCl_5$

$P_4 + 10Cl_2$ (excess) $\longrightarrow 4PCl_5$

$P_4 + 10SO_2Cl_2 \longrightarrow 4PCl_5 + 10SO_2$

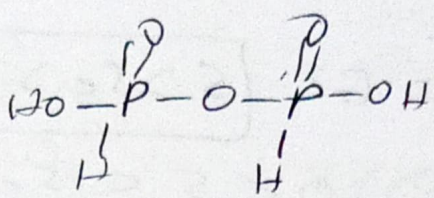
$PCl_5 + H_2O \longrightarrow POCl_3$

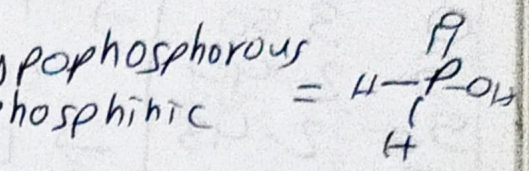
$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$

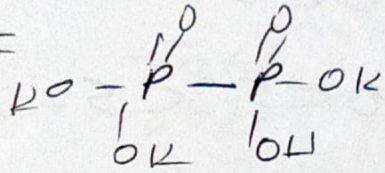
Red P + $H_2O$ → $H_3PO_2$ + $PH_3$

with alcohol & acid it gives $POCl_3$

In solid state $[PCl_4]^+[PCl_6]^-$
tetrahedral octahedral

Pyrophosphorous = 

Hypophosphorous phosphinic = 

Hypo phosphoric = 

→ P–H bond has strong reducing properties

→ Oxoacids in ~~to~~ oxidation state intermediate tend to disproportionate in both H+ & OH⁻.

For N they disproportionate in acid solution

$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

→ $HNO_3$ on long standing

$4HNO_3 \rightarrow 2H_2O + 4NO_2 + O_2$

→ $NH_2OH + HNO_2 \rightarrow N_2O + 2H_2O$

→ $2NH_3 + 3NaOCl \rightarrow N_2 + 3NaCl + 3H_2O$

$2NH_3 + NaOCl$ (in gelatin) $\rightarrow H_2N-NH_2$

→ $PCl_5 + SO_2 \rightarrow POCl_3 + SOCl_2$

$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

$2PCl_5 + H_2SO_4 \rightarrow SO_2Cl_2 + 2POCl_3 + 2HCl$

$6PCl_5 + P_4O_{10} \rightarrow 10POCl_3$

$PCl_5 + CO_2 \rightarrow X$

$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 + 3H_2SO_4$

$6AgNO_3 + PH_3 + 3H_2O \rightarrow 6Ag + 6HNO_3 + H_3PO_4$

$1S\,CaO + 4P_4 \rightarrow 5Ca_3P_2 + 3P_2O_5$

Haber's process

$CaCO_3 \rightarrow CaO + CO_2$

$CaO + H_2O \rightarrow Ca(OH)_2$

$CO_2 + NH_3 \rightarrow (NH_4)_2CO_3$

$CO_2 + NaHCO_3 \rightarrow Na_2CO_3$

$(NH_4)_2CO_3 + NaCl \rightarrow NH_4Cl$

$HNO_3$ decompose in sunlight

$HNO_3 \xrightarrow{h\nu} NO_2 + O_2 + H_2O$

B.P of $SF_4 > SF_6$

# Group -16 - Oxygen family

| | |
|---|---|
| O | 3.50 |
| S | 2.44 |
| Se | 2.48 |
| Te | 2.01 |
| Po | 1.76 |

→ The size of O atom is exceptionally small.

→ E.G.E $S > Se > Te > Po > O$

M.P $O < S < Se < Po < Te$

B.P $O < S < Se < Po < Te$

→ The stability of +6 oxd no. decreases down & +4 oxdn increased

→ Acidic strength $H_2Te > H_2Se > H_2S > H_2O$

→ Except water other hydrides ↑ reducing property

(Reducing strength) $H_2Te > H_2Se > H_2S > H_2O$

$\Delta H_f$ is +ve for $H_2Se$ & $H_2Te$

→ $O_3$ is the oxide of oxygen of type $EO_2$.

→ Amongst hexahalides, hexafluorides are the only stable halides. All hexafluorides are gaseous in nature.

→ Among tetrafluorides $SF_4$ is a gas, $SeF_4$ a liquid & $TeF_4$ a solid

→ All elements except Se form dichlorides & dibromides. (Middle Row anamoly)

→ stability of halides $F^- > Cl^- > Br^- > I^-$

→ Dimeric halides undergo disproportionation

$2Se_2Cl_2 \rightarrow SeCl_4 + 3Se$

a prep

i) $2KClO_3 \xrightarrow[heat]{MnO_2} 2KCl + 3O_2$

2) $2Ag_2O \rightarrow 4Ag + O_2$ $\quad 2Pb_3O_4 \rightarrow 6PbO + O_2$

$2HgO \rightarrow 2Hg + O_2$ $\quad 2PbO_2 \rightarrow 2PbO + O_2$

3) $2H_2O_2 \rightarrow 2H_2O + O_2(g)$

4) Electrolysis of water.

→ Colourless & Odourless & Paramagnetic

→ Dioxygen directly reacts almost all element (except Au, Pt & noble gases).

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$

$2HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$ (Deacon's process)

→ $CO, NO, N_2O$ are neutral oxides.

→ Ozone is an allotrope of $O_2$.

Prep

$3O_2 \rightarrow 2O_3$

silent electrical discharge → 10% ozone will form.

$O_3$ is
Pale blue gas
Dark blue liquid
Violet black solid

→ $O_3$ liquifies first

→ $PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$

$2Ag + O_3 \rightarrow Ag_2O + O_2$

$2Hg + O_3 \rightarrow Hg_2O + O_2$

$2I^- + H_2O + O_3 \rightarrow 2OH^- + I_2 + O_2$

→ Ozone is estimated with hypo with liberated $I_2$.

→ Ozone is used as oxidising agent in the manufacture of pottasium permanganate.

# S

Yellow rhombic ($\alpha$) sulphur (most stable) $\xrightarrow{369K}$ monoclinic ($\beta$) sulphur

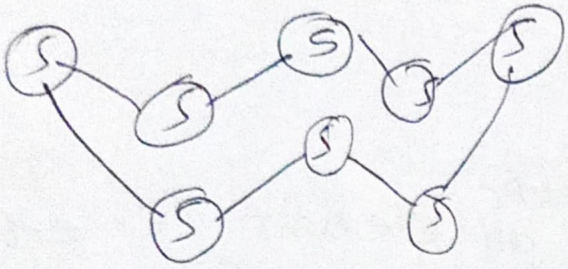
insoluble in water

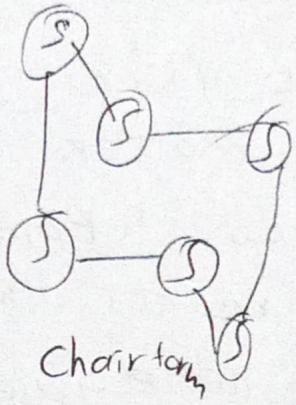
readily soluble in $CS_2$

soluble in $CS_2$

Transition temperature

In both $\alpha$ & $\beta$ $S_8$ molecules are present





Chair form

At high temp $S_2$ is dominant (paramagnetic)

## $SO_2$

colourless gas with pungent smell

dioxides are more stable than trioxides

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$$

$$SO_2(g) + H_2O \rightleftharpoons H_2SO_3$$

$$SO_2(g) + Cl_2(g) \xrightarrow{\text{charcoal}} SO_2Cl_2 \text{ (sulphuryl chloride)}$$

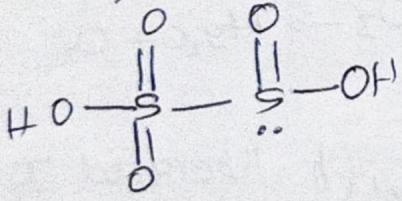
$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

$$Fe^{3+} + SO_2 \rightarrow Fe^{2+} + SO_4^{2-}$$

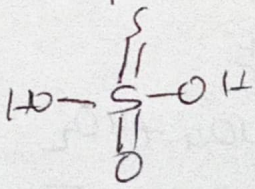
$$SO_2 + MnO_4^- \rightarrow SO_4^{2-} + Mn^{2+}$$

## Oxo acids

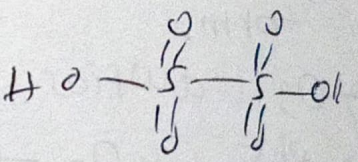
Pyrosulphurous or Disulphurous



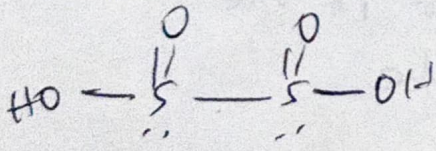
Thiosulphuric acid



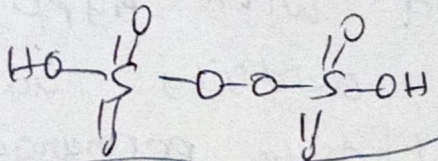
Dithionic acid



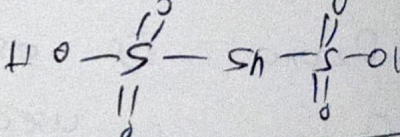
Dithionous

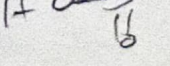


Peroxo disulphuric acid



Poly thionic acid



 = Peroxomono sulphuric acid or Caro's acid

$H_2SO_4$ — contact process

Acid should be added to water slowly

colourless dense oily liquid

i) $S \xrightarrow{\text{burning}} SO_2$

ii) $SO_2 + \frac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$

iii) absorption of $SO_3$ in $H_2SO_4$.

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (oleum)

→ It is used to prepare more valatile acids.

$2MX + H_2SO_4 \rightarrow 2HX + M_2SO_4$ (X = F, Cl, $NO_3$) (HX: volatile)

$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11H_2O$

→ Hot & conc sulphuric acid is moderalely oxidising agent. (Intermediate between $H_3PO_4$ & $HNO_3$)

→ $Na_2SO_3 + S \xrightarrow{\Delta} Na_2S_2O_3$

→ $Na_2SO_3 \longrightarrow$

$2KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 2MnO_2 + 3Na_2SO_4 + 2KOH + 3S$

$n_f =$

$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$

→ $SO_2$ is more stable than $SO_3$ (that's why it is hard to prepare it)

→ $SeO_2$ dimerises (polymerises), $SO_3$ trimerises & polymerises.

$SO_2$ only monomer

$SeO_2$ gas monomer

$SeO_2$ only exists as chains in solid form

# Physical Chemistry

## Stoichiometry

⇒ No. of eq may not be equal in successive rxn because n factor of a particular compound may be different in different rxns

⇒ In basic medium $I^- + MnO_4^- \longrightarrow IO_3^-$

⇒ In a cidic medium ($HNO_3$)

$K_2CrO_4 + HNO_3 \rightarrow Cr_2O_7^{-2}$ (not $CrO_4^{2-}$)

$2CrO_4^{2-} \xrightarrow{+2H^+} Cr_2O_7^{-2} + H_2O$

⇒ Bleaching powder $Ca(OCl)_2$ or $CaOCl_2$ is converted to $Cl^-$

($Ca(OCl)_2$: $n=4$; $CaOCl_2$: $n=2$)

⇒ $KMnO_4$

| $H^+$ | Neutral | $OH^-$ |
|---|---|---|
| 5 | 3 | 1 |

⇒ $dG = Vdp - SdT + \Sigma \mu_i dn_i$

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{P,T,n'} = \left(\frac{\partial V}{\partial n_j}\right)_{S,V,n'}$$

⇒ $S_{solution} > S_{solvent}$

$\Delta H_{solution} = \Delta H_{solvent}$

for electron

$\lambda = \sqrt{\frac{150}{V}}$

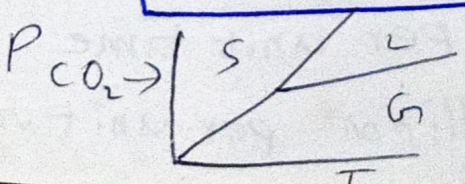
$\lambda$ = in $A^0$

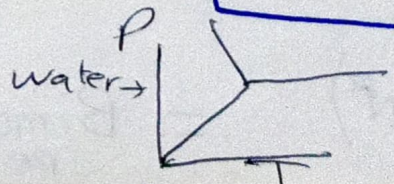
V = Volt

⇒ Claussius claperyon equation

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$ → for a transition

$$\frac{d\ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}$$



# States of matter

→ Dispersion or London forces $\frac{1}{r^6}$ (Energy)

→ Dipole – Dipole $\frac{1}{r^3}$ (not rotating)

$\frac{1}{r^6}$ (rotating)

→ Dipole – Induce dipole $= \frac{1}{r^6}$

→ Gas laws $PV = \text{constant}$ (Boyle

$\frac{V}{T} = \text{constant}$ (charles)

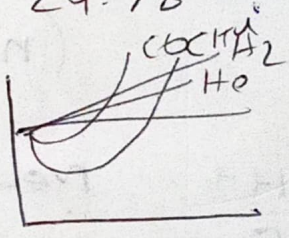
$\frac{P}{T} = \text{constant}$ (Gay lussac's law)

→ Vapour can be directly liquified. (Vapour ≠ gas)

→ At STP 22.7 L mol⁻¹

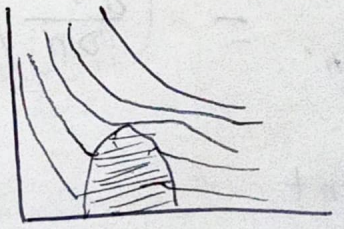
→ SATP (1 bar 298.15) 24.78

→ $PV = \frac{1}{3} mNc^2$ →




→ $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$ a, b are independent of T.

→ $Z = \frac{V_{real}}{V_{ideal}}$ →



$V_c = 3b = 12 V_m \times N_a$

$T_b = \frac{a}{Rb}$ $T_i = \frac{2a}{Rb}$

$T_c = \frac{8a}{27Rb}$

$P_c = \frac{a}{27b^2}$

$V_c = 3b$

→ $Z_1 = \sqrt{2}\pi\sigma^2\bar{u}(N^*)$ = No. of collisions made by a single molecule with other molecules per unit time.

→ $Z_{11} = \frac{1}{2}(Z_1 N^*)$ = Bimolecular collision per unit volume per unit time

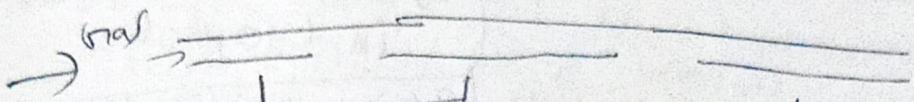
$$= \frac{1}{\sqrt{2}} \pi \sigma^2 \bar{v} (N^*)^2$$

$$Z_{12} = \pi \sigma_{12}^2 \sqrt{\frac{8kT}{\pi M}} N_1 N_2$$

$$\lambda = \frac{1}{\sqrt{2} \pi \sigma^2 N^*}$$

$\phi$ =

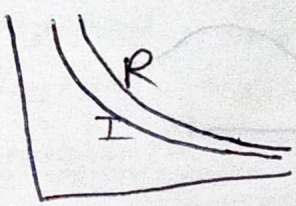
$T_2$ relaxation time $= \frac{1}{2_1} = \sqrt{2} \pi \sigma^2 \bar{v} N^*$




$m_1 \propto P_s$

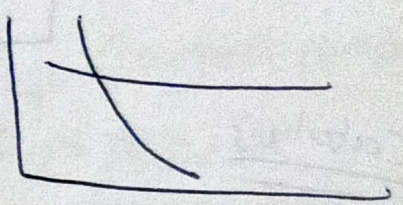
$m_2 \propto P_0 - P_s$

→ $T > T_B$




$T = T_B$

$T < T_B$



# Surface chemistry

→ Gas/Gas interface is not possible

→ Water vapours are absorbed by CaCl adsorbed by silica gel

→ OS C6 OHC6

→ Physisorption at low temp may convert into chemisorption at high temp

→ Easily liquefyable (with highe critical Temp) are readily adsorbed.

(lower the gold no, more the protective power)

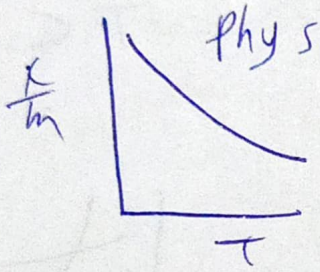
Tyndall effect more in Lyophobic

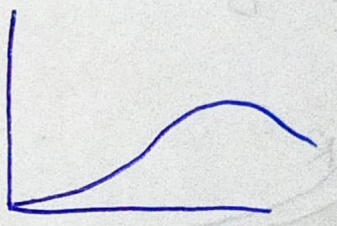
During purification all impurities are not removed (ex: electrolytes)

Phy: (10-40 kJ) Chem: (80-240 kJ)

→ $\frac{x}{m} = kp^{\frac{1}{n}}$ (Freundlich isotherms)

→ At high pressure saturation is obtained (Freundlich isotherms fails)



## Catalysis

$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$

**Promoter**: Enhances the activity of a catalyst.

**Poison**: Poisons decrease the activity of a catalyst.

**Inhibitor** = opposite to catalyst

## Langmuir's Isotherms (Uni-Chemisorption)

$\frac{x}{m} = \frac{ap}{1+bp}$

$\theta$ = fraction of active sites occupied.

rate of adsorption $= k_A p(1-\theta)$

rate of desorption $= k_d \theta$

$\theta = \frac{V}{V_{mono}}$

$\frac{x}{m} \propto \theta \Rightarrow \frac{x}{m} = \frac{ap}{1+bp}$

$\Delta G^{\circ}_{ads} = -RT \ln\left(\frac{k_a}{k_d}\right)$

$V = V_{mono}\left(\frac{P}{1+K_{eq}P}\right)$

$\frac{1}{V} = \frac{1}{V_{mono}}\left(\frac{1+K_{eq}P}{P}\right)$

$$\boxed{\frac{1}{V} = \frac{K_{eq}P}{V_{mono}} + \frac{1}{V_{mono}P}}$$

→ Enzyme catalysis is homogeneous catalysis

→ milk = liquid fat in water

→ hydrophilic → less surface tension

hydrophobic → nearer to water.

$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$ when the reactants & the catalyst are in same phase - homogeneous catalysis.

$2SO_{2(g)} + O_2 \xrightarrow{NO(g)} 2SO_{3(g)}$ (lead chamber process)

$CH_3COOCH_{3(g)} + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(aq) + CH_3OH(aq)$

$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{H_2SO_4(l)} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$

Heterogeneous → $2SO_2 + O_2 \xrightarrow{Pt(s) \text{ or } V_2O_5(s)} 2SO_{3(g)}$ (contact process)

$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{Pt(s)} 4NO_{(g)} + 6H_2O_{(g)}$

Vegetable oil $s(l) + H_2(g) \xrightarrow{Ni(s)}$ vegetable ghee

$2H_2(g) + O_2(g) \xrightarrow{\Delta} 2H_2O(l)$

→ Gold no. : mg of protective colloid required to stop colour change of 10ml of gold sol from red to violet by adding 1ml of 10% NaCl soln. (It is a measure of protective power)

→ $4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$ (Deacons process)

→ Flocculating value. - $(Na^+) > (Ca^{2+}) > Al^{3+}$

→

# Thermodynamics

**Intensive**

| x | x |
|---|---|

$x$

**Extensive**

| $x_1$ | $x_2$ |
|---|---|

$x = x_1 + x_2$

**1st law**

$\Delta U = q + w = q - pdv$

$H = U + PV$

$C = \frac{dq}{dT}$

$C_m = \frac{dq}{n dT}$

**zeroth law**

$T_a = T_b$ & $T_b = T_c$

$\Rightarrow T_a = T_c$

$C_{p,m} - C_{v,m} = R$ (for ideal gas)

$C_{p,m} = aT^3$ (very low temp)

$G = H - TS$

For a rxn $\Delta H = \Delta U + \Delta n_g RT$

$\Delta H(T_2) = \Delta H(T_1) + (T_2 - T_1)\Delta_r C_p$

**2nd law**

$\Delta S = \frac{q_{rev}}{T}$

$\Delta S_{trans} = \frac{\Delta H_{Trans}}{T_{Trans}}$

It is constant for a process

$\Delta S = C \ln\left(\frac{T_1}{T_i}\right)$

$$\Delta S = nR \ln \frac{V_f}{V_i} + nC_V \ln \frac{T_f}{T_i}$$

or

$$\Delta S = nR \ln \frac{P_i}{P_f} + nC_p \ln \frac{T_f}{T_i}$$

**Trouton's rule**

$\frac{\Delta H_{vap}(T_b)}{T_b} \approx 85\ JK^{-1}$ almost same for all liquids (except H-bonded liquids). The entropy change is same since all gases have same volume.

⇒ The surroundings are so extensive that they remain at constant pressure regardless of any events taking place in the system.

3rd law

The entropies of all perfectly crystalline substances are the same at T=0.

That value is defined as zero.

$$\Delta G = -T\Delta S_{Total}$$

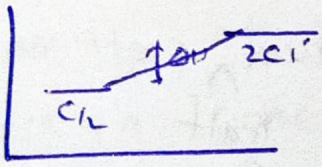
⇒ Beckmann thermometer to measure low temperature.

⇒ OH combustion

⇒ ~~OH combustion~~ ethane > ethyne & Cyclohexane > Benzene (more number of $H_2O$ · ~~OH~~ dominated)

⇒ Lavoiser & Laplace law

$A \rightarrow B \Rightarrow \Delta H$ then $B \rightarrow A \Rightarrow -\Delta H$

⇒ 


$Ea_f = \Delta H$

$Ea_b = 0$

⇒ $dG = vdp - ST$ (reversible process)

⇒ $\Delta G_m = V_m \Delta P$ (at constant T)

⇒ $\Delta S = nC_v \ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{V_f}{V_i}\right) = nC_p \ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{P_i}{P_f}\right)$ (for any process.

⇒ standard state means ⇒ 1 atm, any temperature (may not be 25°)

→ The SI unit of $\Delta H^0$ for a reaction is J/mole

→ A real gas is expanded ~~abt~~ below its inversion temperature (free expansion)

i) $q=0$ $w=0$ $\Delta U=0$ $\Delta T<0$ $\Delta S_{sys}>0$, $\Delta S_{surr}=0$

# Electro Chemistry

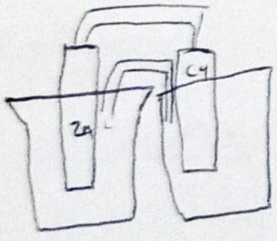
→ A large no. of metals, NaOH, $Cl_2$, $F_2$ are produced by electrochemical methods.

**Daniel Cell**

$Cu^{2+} + 2e^- \longrightarrow Cu_{(s)}$ 0.34

$Zn^{+2} + 2e^- \longrightarrow Zn_{(s)}$ −0.76

$Cu^{+2} + Zn_{(s)} \longrightarrow Zn^{+2} + Cu_{(s)}$ 1.1




→ Salt bridge is not needed if only 1 solution is used as both electrolytes.

→ The potential of individual half cell cannot be measured.

→ In a Galvanic cell ex. daniel cell → Cu → cathode → +ve

Cu → anode → −ve

In electrolytic cell →

$M_{(s)} \mid M^{+n}_{(aq)} \mid\mid A^{+m}_{(aq)} \mid A_{(s)}$ $E_{cell} = E_{right} - E_{left}$

**Nerst eqn** $M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$

$$E_{(M^{n+}/M)} = E^{\circ}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \left[\frac{[M]}{[M^{n+}]}\right]$$

R = 8.314 F = 96487

$aA + bB \rightarrow cC + dD$

$$E = E^0 - \frac{RT}{nF} \ln \left[ \frac{[C]^c [D]^d}{[A]^a [B]^b} \right]$$

$\Delta G = -nFE$

## Conductance

$R = \rho \frac{l}{a} \Rightarrow G = K \frac{A}{l} \Rightarrow G = \frac{K}{G^*}$

$G^* = \frac{1}{a}$ = cell constant (not measured directly)

$1S = 1 ohm^{-1} = mho$ $\quad [K] = Sm^{-1} = \frac{1}{100} S cm^{-1}$

→ Kappas can be added.

$K = Sm^{-1}$ $\quad c = mol\,m^{-3}$

$\Lambda_m = Sm^2 mol^{-1}$

$$\Lambda_m = \frac{K}{c}$$

$$\Lambda_m = \frac{K(Sm^{-1})}{1000\ m^{-3} \times \text{molarity}\ (mol\,l^{-1})}$$

$$\Lambda_m\ (S cm^2 mol^{-1}) = \frac{K \times 1000}{C\ (\frac{m}{l})}$$

→ Conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between 2 electrodes with unit area & at a distance of unit length. (Conductivity decreases with decreare in conc. but $\Lambda_m$ increases)

$[K] = S cm^{-1}$

For strong electrolytes $= \Lambda_m = \Lambda_m^0 - A c^{\frac{1}{2}}$ for weak $\quad \alpha = \frac{\Lambda_m}{\Lambda_m^0}$

# Kinetics

→ Diamond → Graphite (very slow)

→ precipitation of AgCl is very fast (irrev)

→ rusting is a slow process.

→ $\text{rate} = \frac{1}{n_A}\frac{dC_A}{dt}$ ($n_A$ = stoichiometric co-eff for reactants $n_A < 0$)

$A + B \rightarrow C + D$ (K)

$2A + B \rightarrow 2C + D$ ($\frac{K}{2}$)

units of $K = \frac{C^{1-n}}{t}$

$[R] = [R]_0 - kt$ → zeroth

$kt = \ln \frac{[R]_0}{[R]}$

Ex

1) $2NO + O_2 \longrightarrow 2NO_2 \Rightarrow k[NO]^2[O_2]$

2) $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$ $\quad k[CHCl_3][Cl_2]^{\frac{1}{2}}$

3) $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$ $\quad r = k[CH_3COOC_2H_5]^1[H_2O]^0$

Ex: $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ $(M=1)$ $\quad 2NO + O_2 \rightarrow 2NO_2$ $(M=3)$

$2HI \longrightarrow H_2 + I_2$ $(M=2)$

⇒ slow step is called rate determining step.

⇒ $2H_2O_2 \xrightarrow[OH^-]{I^-} 2H_2O + O_2$ $\quad r = k[H_2O_2][I^-]$

→ catalyst concentration is constant

$H_2O_2 + I^- \rightarrow H_2O + IO^-$

$H_2O_2 + IO^- \rightarrow H_2O + I^- + O_2$

## zero order

1) $2NH_{3(g)} \xrightarrow[Pt]{1130} N_{2(g)} + 3H_2$

2) $2HI \xrightarrow[\text{gold surface}]{} H_2 + I_2$

3) $H_2 + Cl_2 \xrightarrow{UV} 2HCl$

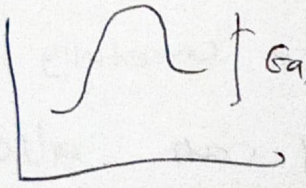
## first order

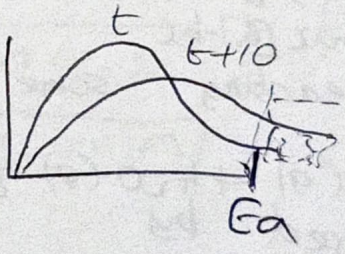
1) Radioactive decay

2) $CH_3\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_2O$ —— $CH_3COOH + C_2H_5OH$ (pseudo 1st order)

## Arrhenius theory

$k = A e^{-\frac{Ea}{RT}}$



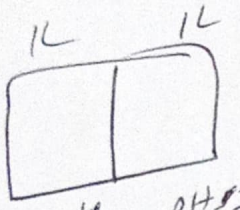

## Collision theory

$Rate = P Z_{AB} e^{-\frac{Ea}{RT}}$

P = orientation factor (p may be > 1)

## Random

→ $CH_3COOH + NaOH$, $HCN + KCN$, $CH_3COOH + NH_3$, $CH_3COO^-Na^+ + HCl$, $NH_4Cl + NaOH$, $NH_3 + HCl$ are all buffers.

→ 


If 1 mole of [HA] is added & the membrane can allow HA to pass through it.

⇒ Then don't take $\frac{1}{2}$ of HA will go to 1 & other half will go to 2 & then they dissociate. After dissociation HA will be same but not before.

→ $aA + bB \rightarrow cC + dP$ in this type of reactions

$[A_0] - ax \quad [B_0] - bx$

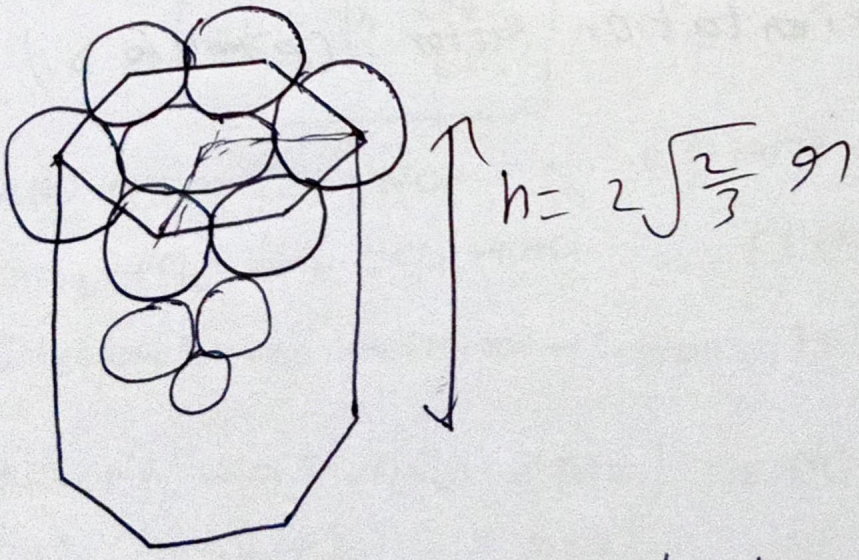
while reacting some of A & B write carefully

→ $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $[CO_2]$ can also be increased by

1) decreasing total volume ($T = C_{ons}$)

$[CO_2] = \frac{n}{V}$

2) By increasing P ($T = cons$)

→ 


→ Equilibrium constant also depends on total pressure for heterogeneous equilibrium.

$\Delta G^\circ = f(T)$ for gases $\Delta G^\circ = f(T, P)$ for solids, liquids

→ In vapour $(d)_{liq} = (d)_{pure\ liq}$

" $(d)_{gas} = (d)_{pure\ gas}$

→ when $\frac{r_+}{r_-} = \frac{2-\sqrt{2}}{\sqrt{2}}$ ⇒ anion touches 18 ions

→ $HA + NaOH \rightleftharpoons NaA + H_2O$ $\left(K_a(HA) = 2\times10^{-5}\right.$

50ml 50ml
0.12 0.06

~~0.0~~ 3m mole 3m $HA \rightleftharpoons H^+ + A^-$

$0.03 - x$ $x$ $0.03 + x = 2\times10^{-5}$

$$\frac{x(x+0.03)}{0.03-x} = 2\times10^{-5}$$

$x = 0.01M$

(S) 1) Humans - Troposphere clouds - Troposphere

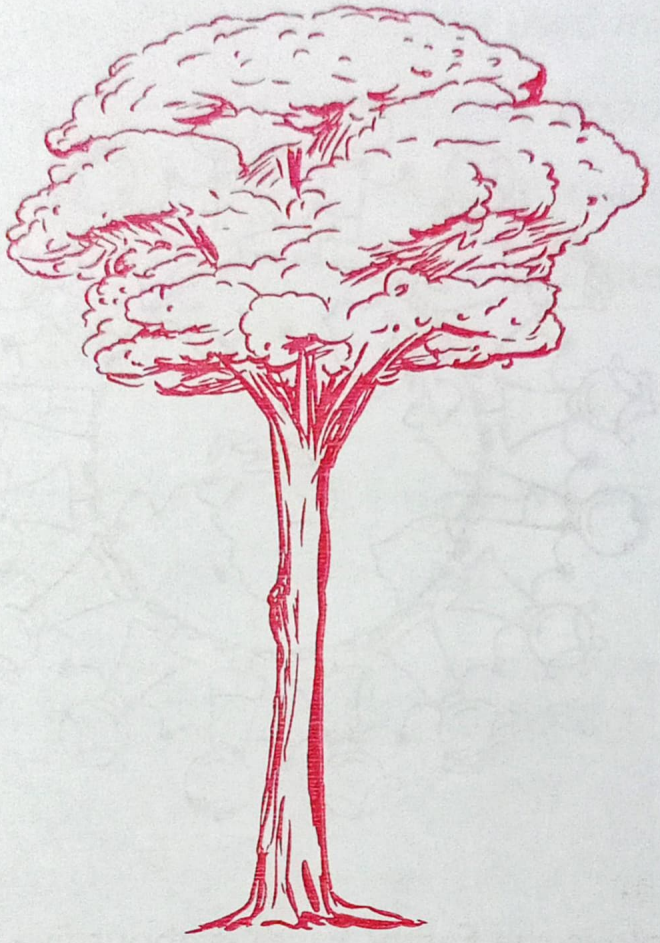
(S) 2) ethyl formate + $CH_3-\underset{OH}{CH}-CH_2-CH_2$ : $CH_3-\underset{OH}{CH}-CH_2-CH_2-NHCHO$

$H-\overset{O}{C}-OEt$

(A) 3) $\frac{NO}{N}$

# Did you know?

4) β D Glucose in amylopectin branching due to $C_1$ to $C_6$ glycosidic linkage



The tallest tree on Earth is called Hyperion and measures 379.1 feet.

The Earth's moon is called Luna. It is the brightest object in the sky after the sun.

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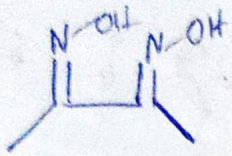
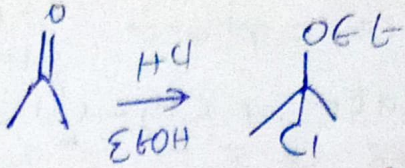
DMG = Dimethyl Glyoxime




# Earth Facts!

KRR!- 9966012021

How old is the Earth? Earth is about five billion years old! There are more than seven billion people on Earth and the number keeps increasing every day.

The distance between the Earth and the sun is 150 million kilometres.

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