Alkanes

→ C_nH_{2n+2}
→ Paraffin – less reactive
→ Chy found in coal mines & many types

Prep:

① Unsaturated hydrocarbon

catalytic hydrogenation

C=C or C≡C + H_2 → (Ni/Pt/Pd/Raney Ni) → C–C

C=C → (H_2/Ni, 200°c) → C–C
C≡C → (H_2/Ni, 300°c) → C–C
Sabatier & Sadanes Rx

Raney Ni: Ni/Al+NaOH → Ni powder

SYN addition of H occurs # Exceptions

② From alkyl halides R–X

i. Reduction of alkyl halides

(i) metal + acid: Zn + HCl, Zn + CH_3COOH → RX + H_2 → RH + HX (Libera H_2)
(ii) Red P + HI [शक्तिशाली Reducing agent]
(iii) $LiAlH_4$, $NaBH_4$ [H⁻]
(iv) Zn–Cu couple in C_2H_5OH
(v) Al+Hg couple in C_2H_5OH

ii. Wurtz Rx^n : Free Radical Mech.

→ Higher alkanes & symmetrical alkanes x form
→ When 2 alkyl halides di 3 products form

$CH_3I + CH_3I$ → (Na dry ether) → $CH_3–CH_3$

iii. Frankland Reagent [Zn dry ether]

R–X + Zn + X–R → (dry ether) → R–R + ZnX_2

Frankland Reagent: $R_2Zn + ZnX_2$ — organo metallic

iv. Corey House Synthesis

R–X → (Li) → R–Cu–Li → (R–X) → R–R'

CuX → R_2CuLi — Gilman Reagent – Li dialkyl Cu

→ used for prep^n of alkanes & add no of C
→ Carbanion Intermediate

③ Carboxylic acid

i. Soda-lime decarboxylation

NaOH : CaO = 3:1

Saturated mono carboxylic's Salt of Na/K → (NaOH, CaO) → alkane

$R–C(=O)–O^-Na^+$ → (NaOH, CaO) → R–H + CO_2↑ + Na_2CO_3

- Step-down process
- Carbanion Intermediate

→ Rate of decarboxylation ∝ stability of carbocation
→ If –COOH grp are ⊕ at on some carbon then decarboxylation occurs on simple heating

ii. Kolbe's Electrolysis Kolbe's Electrolysis

→ Electrolysis of saturated mono carboxylic acid salts

$2R–C(=O)–O^-Na^+$ → (H_2O, Electrolysis) → R–R + $2CO_2$ + 2NaOH + H_2

→ Free Radical M
→ pH rises after
→ CH_4 not C_2H_6

$R'COONa + R''COONa$ → (H_2O, Electrolysis) → R–R' + R''–R'' + R'–R''

$CH_3COO^-Na^+$ → (H_2O, Electrolysis) → $CH_4 + CO_2 + H_2$

$RCOO^-Na^+$ → (H_2O, Electrolysis) → R–R + CO_2 + H_2

$RCH_2COO^-Na^+$ → (H_2O, Electrolysis) → R–CH=CH–R + CO_2 + H_2 — give good yield

④ Grignard (R⁻)

i. takes away active Hydrogen & forms alkane

R–Mg–X + H–OH → RH
H–OR
H–NH–R

Zerewitinoff method used to find the no. of active H in compound

ii. R + alkyl halide → forms higher alkane

$R^{\delta+}$ ..... $X^{\delta-}$ → R–R'

⑤ Aldehyde, Ketone, Carboxylic acid, acid derivatives

R–OH → (Red P, HI, 150°C) → R–H + H_2O + I_2
R–CHO → (HI) → R–CH_3 + H_2O + I_2
R–C(=O)–R' → (HI) → R–CH_2–R'
R–COOH → (HI) → R–CH_3
R–C(=O)–Cl → (HI) → R–CH_3
R–C(=O)–O–et → (HI) → R–CH_3

सभी RO bond तोड़ते हैं R–H

⑥ Aldehyde, Ketones

i. Clemmensen reduction Clemmensen reduction

R–C(=O)–H → (Zn–Hg/HCl) → R–CH_3
R–C(=O)–R → (Zn–Hg/HCl) → R–CH_2–R

Acidic Reduction

ii. Wolf-Kishner Reduction Wolf-Kishner reduction

R–C(=O)–H → (NH_2NH_2, KOH) → R–CH_3
R–C(=O)–R → (NH_2NH_2, KOH) → R–CH_2–R

Basic Reduction

Physical Prop:

→ C_1–C_4 – gas, Pentane C_5–C_{17} – liq, ≥C_{18} – solid
→ neopentane gas
→ BP ∝ mol. wt ∝ 1/branching
→ alkane has its even no. of carbon have more MP than neighbours
→ They are insoluble in water, non polar, Vanderwaal force
→ packing effect

→ गर्म पड़ोसी मारे ठंड से ठिठुरे

$-CO_2$ $-H_2O$ $CO_2 + H_2O$

0 1 2 3 4 5
O M S O A P

Chemical prop.

1. Substitution

a. Halogenation :-

$R-H + H-X \xrightarrow{h\nu} R-X + H-X$

$\rightarrow CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$ (excess)

$\rightarrow CH_4 + Cl_2 \longrightarrow CH_3Cl$ (excess)

Reagent :- $F_2 / Cl_2 / Br_2 / I_2 \longrightarrow$ UV Lst $h\nu$ temp (250-400°C) Peroxide

Reactivity

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

Reacts even in dark

Enthalpy

Requires Lst Energy $3^\circ H > 2^\circ H > 1^\circ H$

don't react at Room temp - Reversible process

Free Radical Mechanism

3 step process

Chain initiation - Endothermic $\rightarrow$ Cl

Chain propagation - Exothermic $\rightarrow$ $CH_3^\circ + Cl$

Chain termination - Endothermic $\rightarrow$ CH_3Cl, CH_3Cl

HNO_3 / HIO_3 - oxidising agent

Chlorination & Bromination :- Same $3^\circ > 2^\circ > 1^\circ$ product

non selective, selective

Fluorination :- 1, 2, 3 products halogenated

$CH_4 + F_2 \longrightarrow$ carbon + HF [high explosive]

Black

$CH_4 + F_2 \xrightarrow[\text{inert gas}]{N_2 \text{ gas}} CH_3F + HF$

Iodination :- $CH_4 + I_2 \rightleftharpoons CH_3I + HI$

- Reversible Process, Slow Process, HNO_3 / HIO_3 OA

b. Nitration : Free Radical Substitution

- all possible nitroalkanes r formed.

- H is Replaced by NO_2

$CH_3CH_2CH_3 \xrightarrow[400-450^\circ C]{HNO_3} CH_3CH_2CH_2NO_2$, $CH_3CH_2NO_2$, CH_3NO_2, $CH_3CH(NO_2)CH_3$

c. Sulphonation :- High temp

Oleum $H_2S_2O_7$ (Mix of SO_3 + conc H_2SO_4) fuming H_2SO_4

- H is Replaced by SO_3H

d. Chloro sulphonation (Reeds Rx) (RSO_2Cl)

$(Cl_2 + SO_2)$ in Ⓟnce of $h\nu$

$C_3H_8 + SO_2 + Cl_2 \xrightarrow{h\nu} CH_3H_7SO_2Cl + HCl$

$\downarrow H_2O$

$C_3H_7SO_3H$

2. Combustion :-

complete combustion

$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$

$\Delta H = -ve$ Exothermic

Incomplete Combustion

$CH_4 + O_2 \longrightarrow C + 2H_2O$ (carbon black)

$\Delta > \square > \square$

$HOC \propto$ no of C $\propto \frac{1}{\text{Branching}} \propto \frac{1}{\text{Size of Ring}}$

3. controlled Oxidation

$CH_4 + O_2$ (alkane) $\xrightarrow[100\text{ atm}, 523K]{\text{Red Hot / Fe / Cu tube}} CH_3OH$ (alcohol)

$CH_4 + O_2 \xrightarrow[\Delta]{MO_2O_3} HCHO$

$CH_3CH_3 + O_2 \xrightarrow{Mn(CH_3COO)_2} CH_3-\overset{O}{\overset{\|}{C}}-OH$

Mn-diacetate

$\xrightarrow{KMnO_4} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$

3 alkane

4. Isomerization

Strength chain $\xrightarrow[HCl]{\text{Anhydrous } AlCl_3}$ Branch chain Isomer

$CH_3(CH_2)_6CH_3 \xrightarrow[HCl]{\text{Anhy. } AlCl_3} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\underset{CH_3}{CH}-CH_3$

Iso-octane

5. Aromatization

alkane (6C ormos) $\xrightarrow[10-20\text{ atm}, 773\text{ atm}]{Cr_2O_3 / V_2O_5 / MoO_3} \boxed{O}$

$C_6H_{14} \longrightarrow \boxed{O}$

6. Pyrolysis

$\rightarrow$ cracking of hydrocarbon 773K

$CH_4 \xrightarrow{''} C + 2H_2$

$CH_3CH_3 \xrightarrow{''} CH_2=CH_2 + H_2$

$CH_3CH_2CH_3 \xrightarrow{''} CH_3CH=CH_2 + H_2$

$CH_2 + CH_2 + CH_2$

$\rightarrow$ Kerosene

$\downarrow$

dodecane

$\downarrow$

$C_{12}H_{26} \xrightarrow{\Delta} C_7H_{16} + C_5H_{10} + \text{other}$

heptane, pentane

$\rightarrow CH_4 + Cl_2 \longrightarrow CH_3Cl$ (excess)

$CH_4 + Cl_2 \longrightarrow CCl_4$ (excess)

$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$

$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$

$C_nH_{2n-1} + \frac{(3n-1)}{2}O_2 \longrightarrow nCO_2 + (n-1)H_2O$

7. Rx^n c̄ Steam

$CH_4 + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2$ Syn gas

$\rightarrow$ volatile $\propto \frac{1}{BP}$

$1^\circ H = 1$

$2^\circ H = 3.8$

$3^\circ H = 4.5$

Alkenes

method of prep :-

1. alkyne → alkene

Catalytic Hydrogenaⁿ c̄ Poison catalysts

(i) syn addition of H_2 → gives cis-alkenes

- Lindlar catalysts H_2, Pd-C, $CaCO_3$, quinoline/$Pb(CH_3COO)_2$
- Rosen must " H_2, Pd-C, $BaSO_4$, quinoline/"
- P_2 Catalysts H_2, Ni_2B (Nickel Boride)

(ii) Anti-addition of H_2 :- gives trans alkenes

- Birch Reduction: Na, liq NH_3 Trans

not valid in terminal alkyne.

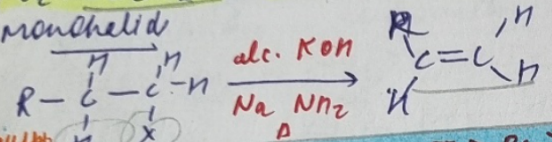
$R-CH_2-C\equiv CH \xrightarrow{''} R-C\equiv C^-Na^+ + NH_4^+$

2. alkyl halide

→ alkyl halide $\xrightarrow[\text{or } NaNH_2/\Delta]{\text{alc KOH}}$ alkene

- Dehydrohalogenaⁿ, B-eliminaⁿ,
- E_2 Mechanism, endothermic

monohalide



$R-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-H \xrightarrow[\Delta]{\text{alc. KOH}} R-C=C-H$ (H, H)

quiz

Rate of dehydrohalogenaⁿ :- I > Br > Cl
3 alkyl > 2 alkyl > 1 alkyl

Satzeff - Major - more α H

Hoffman - Minor - less α H

Dihalide :- Vicinal Halides :- $R-\underset{X}{CH}-\underset{X}{CH_2}$

Dehydrohalogenaⁿ

$R-\underset{X}{CH}-\underset{X}{CH_2} \xrightarrow[300°C]{\text{Zn dust}/\Delta} R-CH=CH_2 + ZnX_2$

$\underset{X}{CH_2}-CH_2-\underset{X}{CH_2} \xrightarrow{\text{Zn dust}}$ Δ cycloalkene

1,3-dihalide

geminal dihalides :- $R-CH(X)_2$

$R-CH(X)_2 \xrightarrow{Zn} R-CH=CH-R + 2ZnX_2$

3. Alcohol : Removal of H_2O & dehydraⁿ

B-eliminaⁿ, E_1-Mech., endothermic process

- carbocation intermediate

$\xrightarrow[\Delta]{Al_2O_3}$ $\xrightarrow[(H_2SO_4),(H_3PO_4)]{\text{mineral acid}}$ Temp is an imp factor

Rate of Dehydraⁿ :- 3° alcohol > 2° alcohol > 1° alcohol

Carbocation : Rearrange : product
Banega Hoga payega

1° alcohol 95% H_2SO_4 → alkene

2° alcohol 60% H_2SO_4 → alkene

3° alcohol 30% H_2SO_4 → alkene

Carbocation Rearrangement

H-shift > phenyl shift > alkyl shift

→ carbocaⁿ causes Ring contracⁿ / Expansion

4 memb → 5 memb, 6 memb. ← 7 memb

2-3 Bond तोड़ो
1-3 तो जोड़ो
1 Ka Chang Do Pe

4. aldehyde / Ketone

Wittig Rxⁿ : Wittig Reagent Phosphorus yield

$R-C(R)=O + PPH_3=C(R)_2 \longrightarrow R-C(R)=C(R)_2$ (R/H)

aldehyde/Ketones alkene $+ PPH_3=O$

5. carboxylic acid / Kolbe's Rxⁿ

$2CH_3COO^-Na^+ \xrightarrow[\text{Electrolysis}]{H_2O} CH_3CH_3 + 2CO_2 + 2NaOH + H_2$

anode cathode

6. Ester (Pyrolysis)

Ester $\xrightarrow[\text{glass wool}]{\text{liq } NH_2}$ alkene

$R-\overset{O}{\overset{\|}{C}}-O-R' \rightarrow$ alkyl alkene

alkenoid carboxylic acids

Physical prop :-

1. C_1-C_3 → gas
C_4-C_{20} → liq
$> C_{20}$ → solid

2. colourless & odourless → Except Ethene
faintly sweet smell colourless

3. Insoluble in H_2O but soluble in nonpolar solvent

4. BP α Mult α $\frac{1}{\text{Branches}}$

5. MP α Mult

Trans MP > Cis MP
↓
Packing efficiency

Saytzeff / Zeitsev Rule :- more substituted alkene is major product as more α-H

Hoffman Rule :- Less substituted alkene is minor product less α H.

Chemical Rxn

1. Addition Rxn

i. ⊕n of H_2

catalytic hydrogenan

$R-CH=CH-R' \xrightarrow[Ni, Pt/Pd, Raceb]{H_2} R-CH_2-CH_2-R'$ + Heat

Heat of hydrogen

Syn Adn		
CSM –	cis alkene + Syn addn	→ Meso
CAR –	——— + Anti "	→ Racemic Mix (Enation)
TAM –	Trans alkene + Anti "	→ Meso
TSR –	Trans + Syns	→ Racemic

PDS

ii ⊕n of X_2

alkene $\xrightarrow[CCl_4]{X_2}$ vicinal dihalide (alkene)

$C=C \xrightarrow[CCl_4]{Br_2} C-C \rightarrow C-C$ (Br, Br, Br, Br)

anti ⊕n

nonpolar medium, vicinal dihalide, → cyclic halonium ion.

Reactivity $F_2 > Cl_2 > Br_2 > I_2$

$CH_3-C=C-CH_3 \xrightarrow[CCl_4]{Br_2}$ (CAR)

Enationmic Pair

Racemic Mix

$CH_2=CH_2 \xrightarrow[aq\ NaCl]{Br_2}$

polar medium

Br, Cl, OH (ingos)

Test for saturan

$CH_2=CH_2 + Br_2/CCl_4$ (Brown colour) → CH_2-CH_2 (Br, Br) colourless

iii ⊕n of HX

→ ⊕n of HX unsymmetrical alkene takes place

By MK Rule → X attach to C have less H

Ionic Rule

→ AMK ⊕n of Peroxide ⊕n of HBr takes place

Free radical opposite to MK Rule

$CH_3CH=CH_2 \xrightarrow[CCl_4]{HBr} CH_3-CH-CH_3$ (Br) MK Rule

HBr, Peroxide

HBr, CCl

HBr, Pero: $CH_3-C-C-C$ (Br, C)

HCl, Pero, MK: $CH_3-C-C-C$ (Cl, C)

HBr, CCl: $C-C-C-C$ (Br, C)

* HBr only show
* HCl & HI does

iv. Addn of H_2O (hydrate) H^+OH^-

Carbocation → Rearrange → produce

Banao Karo pao

MK Rule

v. ⊕n of Hypohalous acid (HOX) OH^- X^+

Reactivity: HOCl > HOBr > HOI

$OH-X^+ + R-CH=CH_2 \rightarrow R-CH-CH_2$ (⊕) → $R-CH(Cl)-CH_2-OH$

vi ⊕n of sulphuric acid

conc H_2SO_4 (H^+ SO_4^-)

$R-CH=CH_2$ + conc H_2SO_4 → $R-CH-CH_2$ → $R-CH(OSO_3H)-CH_3$

dil H_2SO_4 (H^+ OH^-)

$R-CH=CH_2$ + dil H_2SO_4 → $R-CH(OH)-CH_3$

vii Hydroformylation / ono Rxn (CHO)

$R-CH=CH_2 \xrightarrow[CO\ catalyst]{CO + H_2} R-CH_2-CH_2-CHO$; $R-CH(CHO)-CH_3$

2. Oxidation Rxn

① complete Oxidan

$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \rightarrow nCO_2 + (n+1)H_2O$

$C_nH_{2n} + \left(\frac{3n}{2}\right)O_2 \rightarrow nCO_2 + nH_2O$

$C_nH_{2n-2} + \left(\frac{3n-1}{2}\right)O_2 \rightarrow nCO_2 + (n-1)H_2O$

② Oxidan c̄ acidic $KMnO_4$ / $K_2Cr_2O_7$ → Strong oxidizing agent

2π Bond Tut Hot $KMnO_4$

$R-CH=CH_2 \rightarrow RCHO + HCHO$ → RCOOH, HCOOH, $H_2O + CO_2$

③ Oxidan c̄ alkaline $KMnO_4$ / cold $KMnO_4$

* Bayer's Reagent → OH ant Syn ⊕n Racto H

$R-CH=CH_2 \xrightarrow[KMnO_4]{alk.} R-CH(OH)-CH_2(OH)$ (Pink) glycol

Syn ⊕n

Test for saturan

→ alk. $KMnO_4$ (Pink colour) $\xrightarrow{decolorises}$ Brown ppt (glycol + MnO_2)

④ Oxidan c̄ OsO_4 (Osmium Tetraoxide)

→ Syn ⊕n

$R-CH=CH_2 \xrightarrow[H_2O]{OsO_4} R-CH(OH)-CH_2(OH)$

Syn ⊕n: H_2, Bayer's Reagent, OsO_4/H_2O

anti ⊕n: X_2, HOX

3. Ozonolysis

Reductive ozonolysis $\xrightarrow[Zn, H_2O]{O_3, CCl_4}$ 2 Rx^n 1. Ozonide form 2. Cleavage of ozonide by Zn/H_2O

Oxidative ozonolysis $\xrightarrow[H_2O]{O_3, CCl_4}$ $KMnO_4$ Hot or H^+

$$\text{C=C} \xrightarrow{O_3} \text{C(O)C(O)O} \xrightarrow[H_2O]{Zn} ZnO + \text{C=O} + \text{C=O}$$

$$CH_3-CH=CH_2 \xrightarrow[Zn, H_2O]{O_3} CH_3-\overset{O}{\overset{\|}{C}}-H + HCHO$$

RO

$$CH_3-CH=CH_2 \xrightarrow[H_2O]{O_3} CH_3CHO + HCHO$$

OO

CH_3COOH $HCOOH$ $CO_2 + CO_2$

4. Substitution Rx^n

Double Bond से जुड़ा C के बाद वाला C

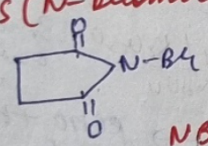
Chlorinan^n :- Free Radical Substitution.

$$CH_2=CH-CH_3 + Cl_2 \xrightarrow[773K]{500°C} CH_2=CH-CH_2Cl$$

$$CH_2-CH_3 + Cl_2 \xrightarrow[773K]{500°C} CH_2-CH_3$$

Bromina^n :- Free Radical Substitution

NBS (N-Bromo Succinamide) is needed



$$CH_2=CH-CH_3 \xrightarrow{NBS} CH_2=CH-CH_2Br$$

$$CH_2-CH_3 \xrightarrow{NBS} Br-CH-CH_3$$

6. Isomerization

→ High Temp & Pressure $AlCl_3$

7. Polymerization

$$n(CH_3-CH=CH_2) \longrightarrow (CH_3CHCH_3)_n$$

From diols

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

glyoxal

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

From questions

→ G.I is shown by restricted rotation around C=C

→ Reactivity of hydrogen atom attached to carbon atom in an alkene 3° > 2° > 1°.

→ Ethylene Bromide = CH_2Br | CH_2Br.

Alkynes

→ C_2H_2 → $H-C\equiv C-H$ → acetylene

— welding torch : oxyacetylene → fuel

Prep

1. From alkyne

(i) $\bar{c}$ Birch Reagent Na/liq NH_3

$R-C\equiv CH \xrightarrow[\text{liq. } NH_3]{Na} R-C\equiv C^- \xrightarrow{R^-X} R-C\equiv C-R'$

(ii) $\bar{c}$ grignard Reagent

$R-C\equiv CH + R'MgX \longrightarrow R'H + R-C\equiv C^{\ominus}$

$\downarrow R^+-X$

$R-C\equiv C-R'$

2. From alkyl halids

$R-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}$ + alc KOH ⟶ $R-CH=CH$

$\downarrow NaNH_2$

$R-C\equiv CH$

gen-halides

$R-\underset{X}{CH}-\underset{X}{CH_2}$ + alc KOH ⟶ $R-CH=\underset{X}{CH} \xrightarrow{NaNH_2} R-C\equiv CH$

Vic-halids

3. From carboxylic acids

Kolbe's Reaction

$CH_2-COO^-Na^+$ ‖ $CH_2-COO^-Na^+$ $\xrightarrow[\text{Electrolysis}]{H_2O}$ $CH\equiv CH + 2CO_2 + 2NaOH + H_2O$

Anode, Cathode

4. Prep for Ethyne / acetylene

(a) Lab Method

$CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

(b) Pure acetylene

chloroform / iodoform + Ag Pd → alkyne

$CHI_3 + 6Ag + CH_3I_3 \longrightarrow CH\equiv CH + 6AgI$

Physical Prop — C_2-C_4 — gas

C_5-CH — liq

$> C_{12}$ → solid

BP ∝ MP ∝ Mwt ∝ $\frac{1}{\text{Branching}}$

Chemical Prop :-

(1) Addition of H_2

Catalytic Hydrogenation

$R-C\equiv C-R \xrightarrow[Ni, Pt, Pd, Raney\ Ni]{H_2} R-CH_2-CH_2-R$

$\xrightarrow[CaCO_3,\ quinoline]{H_2 / Pd-C}$ alkens cis

Lindlar catalyst lead acetate

$\xrightarrow[\text{Rosenmund}]{BaSO_4,\ Pd-CH_2}$ cis alkene

$\xrightarrow[P_2\ catalysts]{Ni_2B}$ cis alkene

$\xrightarrow[\text{Liq } NH_3]{Na}$ Trans alkene

Birch Reduction

(2) Addition of X_2

MI $CH_3-C\equiv CH \xrightarrow[CCl_4]{Br_2} CH_3-\overset{Br}{C}\equiv \underset{Br}{CH} \xrightarrow[CCl_4]{Br_2} CH_3-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}-H$

MII — In ⊕nce of lewis acid

$R-C\equiv CH \xrightarrow[FeX_3]{X_2} R-\overset{X}{C}=\underset{X}{CH} \xrightarrow[FeCl_3]{X_2} R-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-H$

Double Bond + OH = enol

(3) Addⁿ to HX

H^+X^-

$R-C\equiv CH + HX \longrightarrow R-\overset{X}{\underset{X}{C}}-CH_3$ (MK pule)

(4) Addⁿ HOX

$OH^-\ X^+$

$R-C\equiv Cl + HOCl \longrightarrow R-\overset{OH}{\underset{OH}{C}}-CHCl_2$

$\downarrow$

$R-\overset{O}{C}-CHCl_2$

(5) Addⁿ of H_2O (Hydrⁿ)

Kucherov's Reaction, nucleophilic ⊕ⁿ

— Heavy metals. Pb, Hg.

[1% $HgSO_4$ + 4% H_2SO_4]

$CH\equiv CH + H_2O \xrightarrow{\text{"}} CH_2=CH-OH \rightleftharpoons CH_3-\overset{O}{C}-H$ (enol)

$CH-C\equiv CH \xrightarrow{\text{"}} CH_3-\underset{OH}{C}=CH_2 \rightleftharpoons CH_3-\overset{O}{C}-CH_3$

(6) Oxidation Rxⁿ

(1) complete Oxidation

$C_nH_{2n-2} + \frac{3(n-1)}{2}O_2 \longrightarrow nCO_2 + (n-1)H_2O$

(2) Oxidaⁿ $\bar{c}$ acidic $KMnO_4$ / Hot $KMnO_4$ / acidic $K_2Cr_2O_7$

$CH_3-\overset{OH}{\underset{OH}{C}}\equiv\overset{OH}{\underset{OH}{C}}-H \xrightarrow{\text{"}} 2(CH_3-\overset{O}{C}-OH) + H-COOH$

$CO_2 + H_2O$

(3) $\bar{c}$ Bayer's Reagent

$C-C\equiv CH \xrightarrow[KMnO_4]{alk} CH_3-\overset{O}{C}-\overset{O}{C}-OH$

इतना strong NH₃ है कि सारे bond तोड़ दे

(7) Ozonolysis

Reductive: $\xrightarrow[Zn, H_2O]{O_3}$

Oxidative: $\xrightarrow[H_2O]{O_3}$

$CH_3-\overset{O}{C}\equiv\overset{O}{C}H$

$\xrightarrow[Zn\ H_2O]{O_3} CH_3-\overset{O}{C}-\overset{O}{C}-H$

$\xrightarrow[H_2O]{O_3} CH_3-\overset{O}{C}-\overset{O}{C}-H$

$CH_3COOH + HCOOH$

$CO_2 + H_2O$

⑧. Substitution Rx:

a. Sodium acetylide

$H-C\equiv C-H \xrightarrow{NaNH_2} H-C\equiv C^{\ominus}Na^{\oplus} \xrightarrow{NaNH_2} Na^{\oplus}C^{\ominus}\equiv C^{\ominus}Na^{\oplus} + H_2$

H_2 gas nikal Raha E.

b. Cu acetylide

$R-C\equiv C-H + Cu_2Cl_2 + NH_4OH \rightarrow R-C-CCu + NH_4Cl + H_2O$

ammonical cuprous chloride

Red ppt

c. Ag Acetylide

$R-C\equiv CH + AgNO_3 + NH_4OH \rightarrow R-C-CAg + NH_4NO_3 + H_2O$

ammonical $AgNO_3$

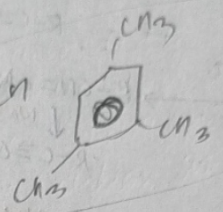
Tollen Reagent

Silver white ppt

⑨ Cyclic Polymerisation

$3HC\equiv CH \xrightarrow[\text{quartz tube}]{\text{Red Hot Fe, Cu tube}}$ 

$H_3C-CH\equiv CH$



⑩ Isomerisation

1° alkyne

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

2° alkyne

$CH_3-C\equiv C-CH_3 \xrightarrow[\Delta]{NaNH_2} CH_3-CH_3-C\equiv C^{-}Na^{+}$

OH का +M ज्यादा होता है OR से

$(CH_3)_3C-C(CH_3)-CH_3$

$CH_3-C(CH_3)_2-C(CH_3)-CH_3$

From question

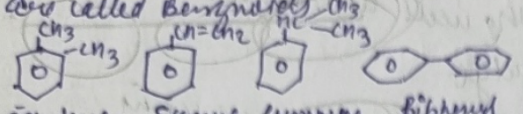
→ correct order of acidic nature of alkynes

$CH\equiv CH > CH_3-C\equiv CH > CH_3C\equiv CCH_3$

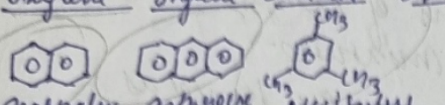
Arenes

$(4n+2)\pi$

- cyclic, planar, should follow Hucklerful
→ shows electrophilic substitution Reaction
→ Aromatic compounds contains Benzene Rings are called Benzenoids



oxylene Styrene Cumene Biphenyl



naphthalene anthracene Mesitylene

i. alkane → Benzene (Aromatization)

n-Hexane $\xrightarrow[Mo_2O_3/V_2O_5]{Cr_2O_3/Al_2O_5}$

ii. alkyne → Benzene (cyclic Polymerisation)

$3CH\equiv CH \xrightarrow[\text{tube}]{\text{Red Hot Fe/Cu}}$

iii. Alkyl Halide : free Radical

Wurtz Fittig Rx

$+ CH_3-Cl \xrightarrow[\text{ether}]{Na\ \text{dry}}$

Fittig Rx

$\xrightarrow[\text{ether}]{Na\ \text{dry}}$

iv. Phenol (Reduction)

$\xrightarrow[\Delta]{Zn\ \text{dust}} + ZnO$

v. aldehyde Ketone

Clemenson Reduction

$\xrightarrow{Zn-Hg/HCl}$

Wolf-Kishner Reduction

$\xrightarrow[OH^-]{NH_2NH_2}$

vi. carboxylic → Benzene

Soda-lime decarboxylation

$\xrightarrow{NaOH : CaO} + Na_2CO_3$

vii. grignard Reagent

$\xrightarrow{H-OH}$

$\xrightarrow{H-OCH_3}$

viii. Diazonium salt

$\xrightarrow[\text{or } HCOOH + C_2H_5OH]{H_3PO_2 \text{ or } SnCl_2 + NaOH} + N_2\uparrow + HCl\uparrow$

Physical prop : ① Insoluble liq.
② insoluble in H_2O & density is less than H_2O
③ used as a solvent
④ Burns c smoky / sooty flame

Chemical Rx :

1. catalytic Hydrogenation : complete Hydrogenation

$\xrightarrow{H_2/Ni}$

2. Birch Reduction / Birch Reduction

- partial Hydrogenation

$\xrightarrow{Na/liq\ NH_3}$

3. Addition of X_2 Free Radical Substitution

$\xrightarrow[h\nu]{3Cl_2}$

Benzene then Cl 666
gammaxene
lindane
powerful insecticide

4. electrophilic substitution

Step-1 Electrophilic generation

$E-Nu \xrightarrow{\text{catalyst}} E^{\oplus} + Nu^{\ominus}$

Step-2 Attack of electrophilic organic of carbocation

$\xrightarrow{E^+}$ $\xrightarrow{E^+}$ $\xrightarrow{Nu^-}$

i. Nitration $\boxed{\text{conc. } HNO_3 + \text{con } H_2SO_4}$

nitrating mixture

$\xrightarrow{''}$ $\xrightarrow{''}$ $+ NO_2$

Role of H_2SO_4 is to provide electrophile

ii. Sulphonation - SO_3H

$\xrightarrow[\text{or Fumis } H_2SO_4(SO_4)]{H_2S_2O_7\ (\text{oleum})}$

$\xrightarrow{''}$ $+$

iii. Halogenation

$\xrightarrow[AlCl_4^- \quad Cl^+]{AlCl_3 + Cl_2}$

$\xrightarrow[Cl^+ + FeCl_4^-]{FeCl_3 + Cl_2}$

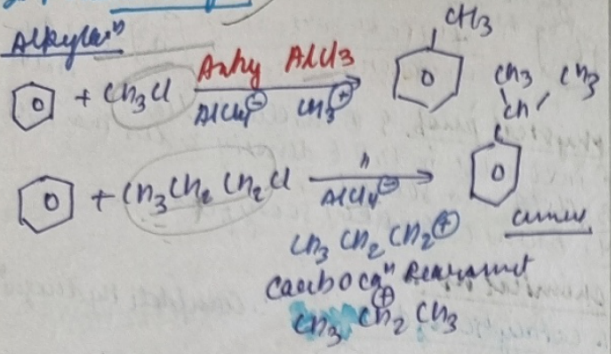
Q.

$\xrightarrow{Cl_2/h\nu}$

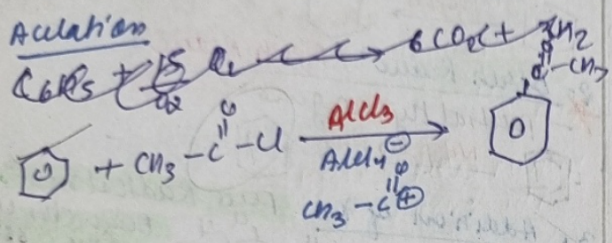
$\xrightarrow{AlCl_3/Cl_2}$

5. Friedel Craft

Alkylation



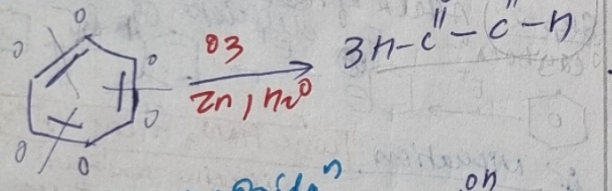
Acylation



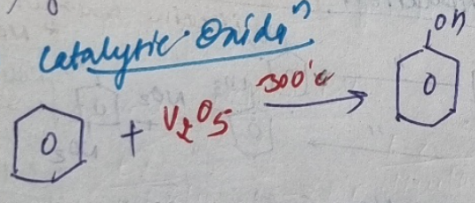
6. Combustion

$$C_6H_5 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$$

7. Ozonolysis



8. Catalytic Oxidation



* Benzene is more reactive towards electrophilic substitution
* NaNH2 will distinguish 1- butyne & 2-butyne.
* Nitration of Benzene using nitrating mixture-
  - Sigma complex is formed as intermediate
  - Nitric acid acts as base
  - In sigma complex one of the carbon is sp^3 hybridised

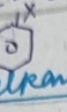
→ Coal tar is the main source of aromatic compds.
→ Benzene doesn't go addition Rxn as π e⁻ of Benzene Ring are delocalised
→ C–C Bond length in Benzene 1.39Å
→ Nitro group is meta directing because it lose e⁻ density at ortho & para pos
→ –Cl is o,p directing but deactivates ring for electrophile substitution
→ order of electrophillic substitution
- phenol > Benzene > Chloro Benzene > Benzoic acid

Haloalkanes & Haloarenes

⇒ In Haloalkane :- Halogen is attached sp^3 carbon.

- Allylic halide —  or $-C=C-C-X$
- Benzylic halide 

⇒ In Haloarene : Halogen attach to sp^2 carbon.

- Vinylic halide :- $-C=C-X$
- Aryllic halide :- 

Preparation : 1. from alkane [Halogen]

$R-H + Cl_2 \xrightarrow{h\nu} R-Cl + HCl$ (Excess)

2. alkene → alkyl halides

⊕ⁿ of X_2: $CH_2=CH_2 \xrightarrow{Br_2/CCl_4} CH_2-CH_2$ (Br, Br) vicinal dihalides

⊕ⁿ of HX (MK Rule): $CH_3-CH=CH_2 \xrightarrow{HBr} CH_3-CH(Br)-CH_3$

3. alkyne → alkyl halide

⊕ⁿ of X_2: $CH_3-C\equiv CH + Cl_2 \xrightarrow{CCl_4} CH_3-C(Cl)_2-CH_3$

⊕ⁿ of H-X: $CH_3-C\equiv CH + HCl \rightarrow CH_3-C(Cl)=CH_2$

4. Alkyl halide → alkyl halide

$R-Cl$ or $R-Br \xrightarrow{NaI/\text{acetone}} RI$ [Finkelstein Rxn]

$R-Cl/Br \xrightarrow{AgF,\ Hg_2F_2,\ COF_2,\ SbF_3} R-F$ [Swarts Rxn]

5. Alcohol → alkyl halide

① $R-OH + HX \xrightarrow{ZnCl_2} R-X + H_2O$

$R-OH_2^{\oplus} \rightarrow R^{\oplus} + H_2O$ → carbocation formation

Reactivity : 3° alcohol > 2° alcohol > 1° alcohol

High Reactive ← HI > HBr > HCl → Less Reactive

HCl + $ZnCl_2$ — Lucas Reagent

1° alcohol + LR → 30 min turbidity

2° alcohol + LR → 5 min turbidity

3° alcohol + LR → Immediate turbidity

② $R-OH + NaBr + H_2SO_4 \rightarrow R-Br + NaHSO_4 + H_2O$

③ $R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$

$R-OH + PCl_3 \rightarrow R-Cl + H_3PO_4$

PBr_3/PI_3 → less stable

mixture $(P+Br_2)/(P+I_2)$

$ROH \xrightarrow{Red\ P/Br_2} RBr$

$ROH \xrightarrow{Red\ P/I_2} RI$

④ $R-OH + SOCl_2 \xrightarrow{Pyridine} R-Cl + SO_2\uparrow + HCl\uparrow$

⑤ aldehyde & Ketone

$R-\underset{\underset{O}{\|}}{C}-OH + PCl_5/PBr_5 \rightarrow R-\underset{\underset{Cl}{|}}{C}-H + POCl_3$

$R-\underset{\underset{O}{\|}}{C}-OR + PCl_5/PBr_5 \rightarrow R-\underset{\underset{Cl}{|}}{\underset{\underset{H}{|}}{C}}-R + POCl_3$

⑥ carboxylic acid → alkyl halide (Hunsdiecker Rxn)

$R-\underset{\underset{O}{\|}}{C}-O^{-}Ag^{+} \xrightarrow{X_2} R-X + CO_2 + AgX$

silver salt of carboxylic acid

X_2 = CCl_4 → $R-Cl$; Br_2 or I_2 → $R-Br$ / $R-I$

Physical Prop :-

→ CH_3Cl, CH_3Br, CH_3I → gas at Room temp (Rest → Liquid & solid)

→ Alkyl halides have higher B.P & Mol. mass

alkane, polar, non-polar, dipole-dipole, London forces

B.P ∝ M.P ∝ 1/Branching

B.P = nearly same as alcohol & ether because of high mass

MP ≥ Para isomers (packing efficiency due to Symmetry)

density :- R-F, R-Cl → lighter than H_2O; R-Br, R-I → higher than H_2O

HI > HBr > HCl > HF

solubility :- although polar but very slightly soluble (insoluble) in H_2O because they don't form H-bond in H_2O

Chemical Prop. 1. Nucleophilic Substitution

$R-\overset{\delta+}{X} + Nu^{\ominus} \rightarrow R-Nu + X^{\ominus}$

Halide ion is substituted by nucleophilic (alkoxide, cyanide, ...)

S_N1	S_N2
→ unimolecular	→ Bimolecular
→ Depends on alkyl halide	→ Depends on alkyl halide & Nu⊖
→ 2 Step Process	→ 1 Step Process
→ weak nucleophile (solvent)	→ Strong Nucleophile
→ carbocation formation	→ Pentavalent transition state (anion)
→ Rate ∝ [Alkyl halide]	→ Rate ∝ [Alkyl halide][Nucleophile]
→ 1st order Rxn	→ 2nd order Rxn
→ Racemization (Retension) (more Inversion)	→ Inversion (Walden Inversion)
→ Polar protic solvent	→ Polar aprotic solvent
→ Allyl, 3° > 2° > 1°, Benzyl	1° > 2° > 3°
→ carbocation intermediate	→ no Intermediate
→ favoured by weak & low conc of nucleophile	→ favoured by Strong & high conc of Nu

Factors affecting Nucleophilicity

- Anion is stronger nucleophile than neutral
- Basicity ∝ Nucleophilicity (in same period)
- Nucleophilicity ∝ 1/EN (in same group)
- Basicity ∝ 1/Stability
- Stable → no charge, better leaving group

$F^- > Cl^- > Br^- > I^-$ (Basic Strength)

$F^- < Cl^- < Br^- < I^-$ (Leaving Strength)

→ Solvent

Polar Protic

→ H is connected to more EN atom (F, O, N)

H_2O, ROH, Ph-OH, □OH, ⬡OH

→ It solvate cation & anion.

→ [illegible]

→ Strong nucleophil – weak Nu (solvent)

Polar aprotic

→ H is not connected to more EN

DMSO :- Dimethyl Sulphoxide

$CH_3-\overset{O}{\overset{\|}{S}}-CH_3$

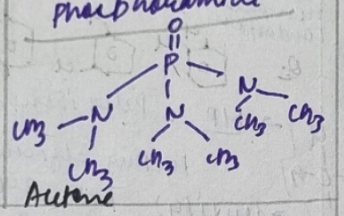
DMF :- Dimethyl formoxide

$H-\overset{O}{\overset{\|}{C}}-N(CH_3)_2$

DMA :- Dimetyl acetamide

$CH_3-\overset{O}{\overset{\|}{C}}-N(CH_3)_2$

HMPA : Hexa Methyl Phosphoramide



Acetone

→ for Bulky Base (+ O^-) Hoffman alkene are major products

→ comparison SN_1, SN_2, E_1, E_2 & H weak

Alkyl Halides :- SN^2 – PA – ~~[illegible]~~ Stero Nu

2 SN_1 – PP – low temp – weak Nu
SN_2 – PA – ~~[illegible]~~ – Strong
E_1 – PP – High temp – ~~[illegible]~~ weak
E_2 – PA – High temp, Strong

3° SN_1 – PP low temp weak
E_1 – PP High temp weak
E_2 – PA High temp Stron.

Strong Nu

CH_3O^-, alcoh ($C_2H_5O^-$)

$NaNH_2$,

tert Butoxide (+ O^-) Hoffman alkene

Eg of SN_1 & SN_2

R–X + KCN (Ionic Band) $\xrightarrow{\Delta}$ R–C≡N cyanide

R–X + AgCN (Covalent Band) $\xrightarrow{\Delta}$ R–N≡C isocyanide

R–X + KNO_2 (Ionic Band) $\xrightarrow{\Delta}$ R–O–N=O

R–X + $AgNO_2$ (Covalent Band) $\xrightarrow{\Delta}$ R–NO_2

2. elimination Rx

E_1 – alkene Base

→ unimolecul Elimina
→ 2 Step Rxⁿ
→ 1st order

Rate ∝ [alkyl Halides]

3° > 2° > 1°

→ carbocation intermediate
→ good leaving grp
→ polar protic solvent
→ Racemisation

SN^1 → low temp → ≤ 25°C
E_1 → high temp → ≥ 50°C
w/w 25°C – 50°C
SN_1 & E^1 Both occurs

E_2 alkene Anex

→ Bimolecular Elimina
→ 1 Step Rx
→ 2nd order

Rate ∝ [alkyl halide] [nucleophile]

3 > 2 > 1

→ no intermediate
→ good leaving grp
→ polar aprotic solvent
→ anti-Eliminaⁿ

Rate of Rxⁿ ∝ Stability of alkene

Rxⁿ c̄ metals

① Wurtz Rxⁿ
ⓐ wurtz
ⓑ Fitting
ⓒ wurtz fitting

alkyl halide

② Fridal craft Rxⁿ
ⓐ alkylation
ⓒ acylation

③ Reduction to fin alkane
ⓐ preparation of alkane

R^- grignard

a. nucleophilic ⊕ⁿ
b. nu ⊕nd eliminate
→ agr leaving grp

2 mole grignard lagta H

* In SN_1 on chiral centers, there is inversion more than Retention leading to partial racemization.

→ The least Reactive alkyl chloride towards substitution Rxⁿ is Vinyl chloride.

c. acid Base R^- H^+
d. Nucleophilic substitution. (SN_2)

→ Grignard

acid Base > Nu addition > Nu ⊕nd elimination

Halogens

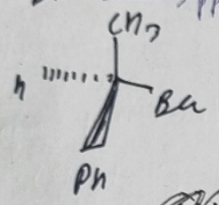
→ Dipole Moment

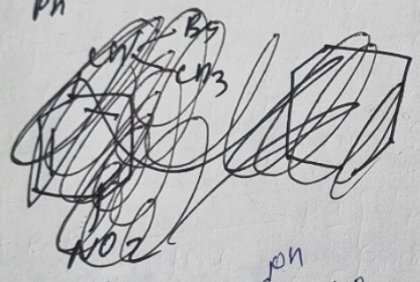
$CH_3Cl > CH_3F > CH_3Br > CH_3-I$

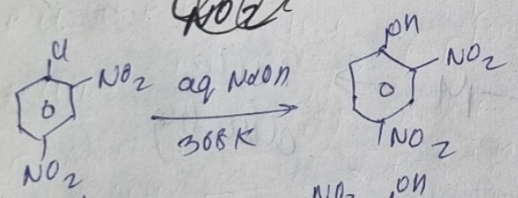
→ Dichloromethane is liquid at Room temperature.

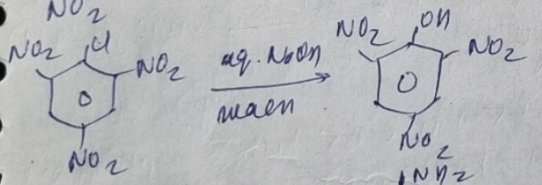
→ Chloroform

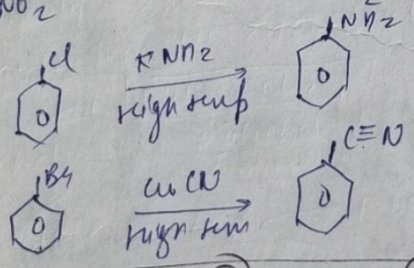
- is oxidised by air in ⊕nce of light to phosgene gas
- is used in production of freon Refrigerant R-22
- DDT contains 5 Cl atoms → pp- dichloro, diphenyl trichloroethane

→  gives max Racemised product

→ 





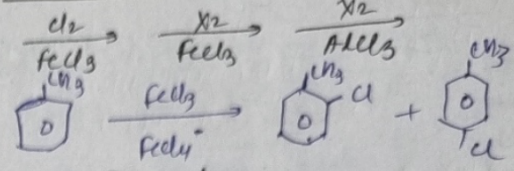
→ 

	②	③
Halogenation		Wurtz
Nitration		Filtig
Sulphonate		Wurtz Rx filtig Rx
Fridel Crafts		

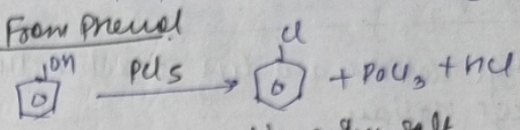
Aryl halide :-

GMP.

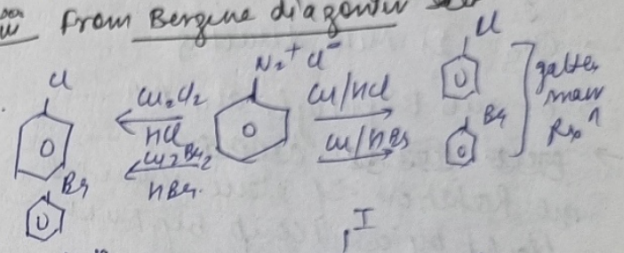
i From Benzene Chalogenation

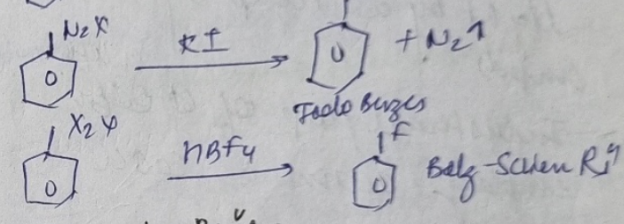


ii From Phenol



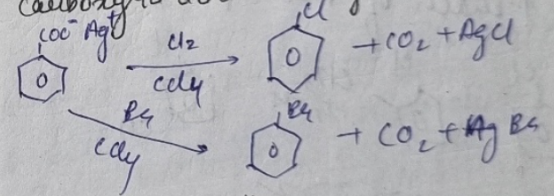
iii From Benzene diazonium salt





iv Hunsdicker Rx :-

carboxylic acid — aryl halide



Chemical Rx

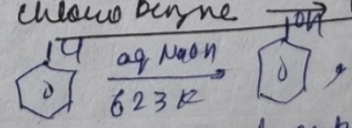
1. nu. Substitution
2. "Elephilic Rx"
3. Rx c̄ metals

→ Aryl Halid are less Rx toward nu substitution

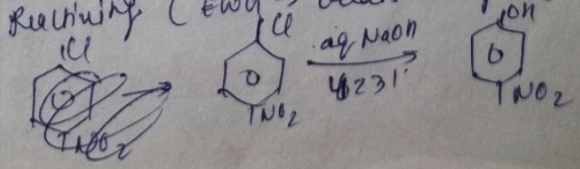
① Becoz of Halogen atom

② after Removal of Halide ion, phenyl cation is unstable

→ Chloro Benzene → Phenol

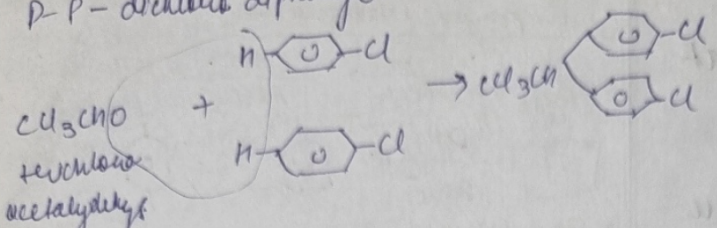


⊕n of EWG at ortho/para reses Reactivity (EWG → creates e- deficiency)



DDT :-

P-P- dichloro diphenyl trichloroethane.



→ aryl halides are less Reactive than alkyl halides

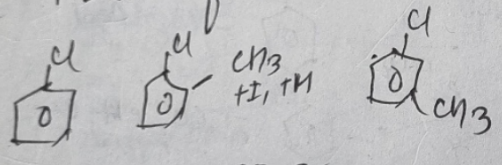
→ CH_3 is meta directing

→ o-sub Biphenyl are OA.

→ no Rotation of plane polarised light by a comp by meso cmpds

→ Industrial prep of chloroform $CHCl_3$ employ acetone & CaOCl

↑ order of Nucleophilic subs.



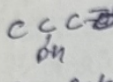
1 > 3 > 2

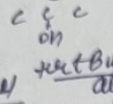
—M → meta directing

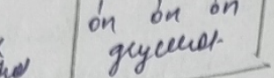
Alcohol, Phenol & Ethers

→ Hydrogen atom is replaced by OH gp in aliphatic chain
→ H atom is replaced by OH group in aromatic hydrocarbon
→ Hydrogen atom is replaced by OR group in aliphatic / aromatic hydrocarbon
→ In normal, Allylic, Benzylic alcohol OH is attached to sp^3 carbon.
→ In vinylic, Phenol alcohol is attached to sp^2 carbon.

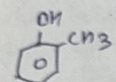
Alcohol

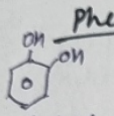

Sec-Butyl alcohol

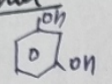

tert-Butyl alcohol

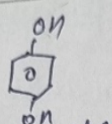

glycerol

Phenol

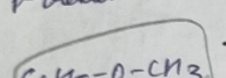

o-cresol
m-cresol
p-cresol

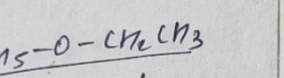

Catechol


Resorcinol


quinol or hydroquinone

Ether


Anisol

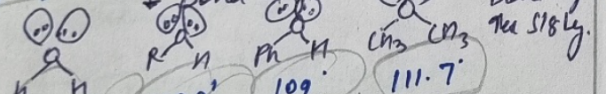

phenetole

Structure of functional group

Alcohol → O atom → 2 Bond & 2 lp → 4 → sp^3 hybridised

Bond angle → 109.5° = 109°28'

But acc^n to lp-lp theory lp-lp repulsion is max. ∴ Bond angle ↓ → In ether Bond angle ↑ slightly.


104.5° 108.9° 109° 111.7°

Prep

(1) alkene → alcohol

3° alkene: $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{H^+/KMnO_4} \underset{CH_3}{\overset{CH_3}{C}}(OH)-CH_3$

$CH_3-CH=CH_2 \xrightarrow{H^+/KMnO_4} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3$

(2) alkene → alcohol

(i) acidic hydration (MCCH) Markovnikov rule

$CH_3-CH=CH_2 \xrightarrow[H_2O]{H^+} CH_3-\underset{H}{\overset{OH}{C}}-CH_3$ (MK rule)

carbocation forms

(ii) alkene → alcohol Hydro boration (AMK)

$CH_3-CH=CH_2$ (alkene) $\xrightarrow{BH_3/THF\ or\ B_2H_6}$ $B(CH_2-CH_2CH_3)_3$

$\xrightarrow[NaOH]{H_2O_2/OH^-}$ $CH_3CH_2CH_2OH$ (alcohol)

$\xrightarrow{H_2O/H^+}$ $CH_3CH_2CH_3$ (alkane)

(iii) OMOM (Oxymercuration demercuration) MK Rule

-NO-Rearrangement

$-CH_2CH=CH_2 \xrightarrow[ii)\ NaBH_4,OH^-]{i)\ Hg(OAc)_2,H_2O} CH_3CH_2CH_2OH$

3. Alkyl halide → alcohol (MK Rule)

$R-X \xrightarrow[\text{or moist } Ag_2O]{aq.\ KOH} R-OH + HX$ (S_N2)

S_N2 dominant

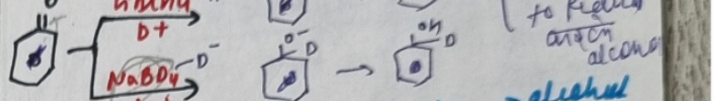
4. aldehyde / ketone (Reduction)

$>C=O \xrightarrow{Red^n} >C-OH$

i $\xrightarrow{H_2}$ Ni, Pt, Pd, Raney Ni, ii $LiAlH_4$, $NaBH_4$, iii $Na + EtOH$

Birch Reduction

iv. NaH (Deuterium Reduction)



- aldehyde
- ketone
- carbonyl to Reduce aromatic alcohol

5. carboxylic acid & derivatives → alcohol

(LiAlH4) Reduction → LiAlH4 gives $4H^-$

$R-\underset{O}{\overset{\|}{C}}-OH \xrightarrow[H^+]{LiAlH_4} RCH_2OH$

$R-\underset{O}{\overset{\|}{C}}-Cl \rightarrow RCH_2OH$

$R-CO-OR \rightarrow R-CH_2OH$

$LiAlH_4$: Expensive Reducing agent. So, 1st acid is converted to ester then Reduction of ester taking mild catalytic hydrogenation

$R-\underset{O}{\overset{\|}{C}}-OH \xrightarrow{R'OH} R-\underset{O}{\overset{\|}{C}}-O-R' \xrightarrow[\text{catalyst}]{H_2} RCH_2OH + R'OH$

6. Ester → alcohol (hydrolysis)

more EN atom less EN Deuterium
less EN atom more EN Deuterium

$R-\underset{O}{\overset{\|}{C}}-\underset{H}{\overset{OH}{O}}-R' \xrightarrow{H_2O} R-\underset{O}{\overset{\|}{C}}-OH + R'-OH$

$CH_3-\underset{O}{\overset{\|}{C}}-O-C_2H_5 \xrightarrow{H_2O} CH_3-\underset{O}{\overset{\|}{C}}-OH + C_2H_5OH$

7. 1° amine → alcohol.

$R-NH_2 \xrightarrow[\text{in } HNO_2]{NaNO_2+HCl} RN_2^+Cl^- \rightarrow R^+ + N_2\uparrow + Cl^-$

carbocation forms & Rearrangement occurs

8. Grignard → alcohol

$R-\underset{O}{\overset{\|}{C}}-H + R'MgX \rightarrow R-\underset{H}{\overset{OH}{C}}-R \xleftarrow{H_2O} R-\underset{H}{\overset{O^-}{C}}(R')-MgX$ (aldehyde)

$R-\underset{O}{\overset{\|}{C}}-R + R'MgX \rightarrow R-\underset{R'}{\overset{OH}{C}}-R \xleftarrow{H_2O} R-\underset{R'}{\overset{O^-}{C}}(R)-MgX$ (ketone)

$RMgX + H-\underset{O}{\overset{\|}{C}}-OR \rightarrow H-\underset{R}{\overset{OH}{C}}-R \xleftarrow{} H-\underset{R}{\overset{O^-}{C}}(OR)-MgX$

R_2CHOH

Formaldehyde → 1°
normal aldehyde → 2°
ketone → 3°

Physical Prop: - alcohol undergoes H-Bonding

→ BP ∝ Mol wt ∝ 1/branching

C-C-C (OH) < C-C-C (OH) < C-C-C (OH OH OH)

more OH groups → more H-Bond → higher BP

→ BP of ether is less than alcohol (no H-Bonding)

→ BP of alcohol is less than carboxylic acid (forms dimer)

Solubility: lower alcohols (1st 3 members) are in H_2O (H-Bonding)

solubility ∝ 1/molecular mass, no of soda chain

If molecular mass is same ∝ COOH > OH > ROR

OR OH

Chemical Rxn

Breaking of OH Bond	Breaking of OR Bond
→ alcohol acts as nucleophile	→ protonated alcohol acts as electrophile
→ can give H^+ due to polar protic nature of H Bond	
1. Acidity of alcohol	1. Rxn ∵ HX
2. Rxn ∵ metals	2. Rxn ∵ $SOCl_2$ (Darzen Rxn)
3. Esterification	3. Rxn ∵ PCl_5, PCl_3
a. alkylation	4. Dehydration of alcohol
b. acetylation	
c. Benzoylation	
4. Rxn ∵ aldehyde, Ketone	
5. Rxn ∵ grignard	

1. Acidic nature of Alcohol

→ Alcohol can give H^+ - due to polar nature of H Bond

→ Acidic nature ∝ −M ∝ −I ∝ 1/+M ∝ 1/+I ∝ +1/+H

→ alcohol is less acidic than H_2O

$R-O-H$; $H-O-H$; $H-O^-$ not stable

$R-O^-$ unstable

+I of R unstable

→ alcohol acts as Base

Bronsted acid & donate H^+: $R-OH + B^- \rightarrow R-O^- + HB$

Bronsted base & accept H^+: $R-OH + H^+ \rightarrow R-\overset{\oplus}{O}H_2$

2. Le-Chat Rxn ∵ metals

$R-OH + Na/K/Al \longrightarrow R-O^-Na^+ + \frac{1}{2}H_2\uparrow$

3. Esterification

Acid + alcohol → carboxylic acid / acid chloride / acid anhydride → Ester

$R'-\overset{O}{\overset{\|}{C}}-OH + ROH \overset{H^+}{\rightleftharpoons} R'-\overset{O}{\overset{\|}{C}}-O-R + H_2O$ (Ester + acid)

$R'-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + ROH \overset{H^+}{\rightleftharpoons} R'-\overset{O}{\overset{\|}{C}}-O-R + RCOOH$

$Ph-OH$

$\rightarrow ROH + Ph-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[\text{or conc NaOH}]{\text{Pyridine}} HCl + Ph-\overset{O}{\overset{\|}{C}}-OR$

Pyridine reacts ∵ HCl & forms stable product therefore the yield of Le-Chatelier principle

a. acetylation (⊕ ion of $(CH_3-\overset{O}{\overset{\|}{C}}-$ group to alcohol)

$CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3OH \overset{H^+}{\rightleftharpoons} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$

b. alkylation

⊕ ion of $(CH_3-$ group to alcohol)

$R-OH + Na \longrightarrow R-O^- + \frac{1}{2}H_2\uparrow \xrightarrow{R'-X} R-O-R'$

c. Benzoylation Schotten Baumann Rxn

⊕ ion of $(Ph-\overset{O}{\overset{\|}{C}}-)$ group to alcohol

$Ph-\overset{O}{\overset{\|}{C}}-Cl + C_2H_5OH \longrightarrow Ph-\overset{O}{\overset{\|}{C}}-O-C_2H_5$

4. Rxn ∵ aldehyde / Ketone

$R-\overset{O}{\overset{\|}{C}}-H$ aldehyde $+ 2ROH \longrightarrow R-\underset{H}{\overset{OR}{\overset{|}{\overset{|}{C}}}}-OR$ (acetal) $\xleftarrow{ROH} R-\underset{H}{\overset{OR}{\overset{|}{\overset{|}{C}}}}-OH_2^+$ (hemiacetal) $\xleftarrow{H^+} R-\underset{H}{\overset{OR}{\overset{|}{\overset{|}{C}}}}-OH$

$R-\overset{O}{\overset{\|}{C}}-R$ ketone $+ 2ROH \longrightarrow R-\underset{RO}{\overset{RO}{\overset{|}{\overset{|}{C}}}}-R$ (ketal) $\xleftarrow{H^+} R-\underset{RO}{\overset{RO}{\overset{|}{\overset{|}{C}}}}-OH$ (hemiketal)

5. Rxn ∵ grignard

$R^-Mg^+X + R-OH \longrightarrow R'-H + RO^-Mg^+X$

1. Rxn ∵ HX

$R-\ddot{O}-H + H^+X^- \longrightarrow R-\overset{\oplus}{O}H_2 \rightarrow R-X + H_2O$

RCH_2OH ↓ Conc HCl $\xrightarrow{ZnCl_2}$ RCH_2Cl Turbidity (30 min)

R_2CHOH + Conc HCl $\xrightarrow{ZnCl_2}$ R_2CHCl Turbidity (5 min)

R_3COH + Conc HCl $\xrightarrow{ZnCl_2}$ R_3CCl Turbidity @ once

conc. HCl + $ZnCl_2$ = Lucas Reagent

2. Rxn ∵ PCl_5 & PCl_3

$R-OH + PCl_5 \longrightarrow POCl_3 + RCl + HCl$

$R-OH + PCl_3 \longrightarrow H_3PO_3 + RCl$

3. Rxn ∵ $SOCl_2$ Darzen Rxn

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

4. Dehydration of Alcohol (Ex mechanism)

$\xrightarrow[\Delta]{conc\ H_2SO_4}$ $\xrightarrow[\Delta]{H_3PO_4}$ $\xrightarrow[\Delta]{Al_2O_3}$ alcohol → alkene

Reactivity order of dehydration

3° alcohol > 2° alcohol > 1° alcohol

→ C_2H_5OH + $conH_2SO_4$ — 100°C $C_2H_5-HSO_4$; 140°C $C_2H_5-O-C_2H_5$ (williamson synthesis); 170°C $CH_2=CH_2$

II. oxidation of alcohols

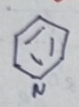
$R-CH_2-OH \xrightarrow[H^+/K_2Cr_2O_7]{H^+/KMnO_4}$ strong O.A (carboxylic Acid)

If we want aldehyde

$R-CH_2OH \xrightarrow{CrO_3} R-CHO$

If we want aldehyde in good yield

$R-CH_2OH \xrightarrow[\text{Pyridine chloro (PCC) chromate}]{PCC} R-CHO$



$O=\overset{O}{\overset{\|}{Cr}}-Cl$ (O⁻)

पहला

1° $\xrightarrow{H^+KMnO_4 / H^+K_2Cr_2O_7}$ acid

$\xrightarrow{CrO_3}$ aldehyde

$\xrightarrow{PCC}$ aldehyde (good yield)

2° $\xrightarrow{H^+/KMnO_4}$ Ketone $\xrightarrow{\Delta\Delta}$ acid

$\xrightarrow{CrO_3}$ Ketone $\xrightarrow{\Delta\Delta}$ acid

3° $\xrightarrow{\text{normal cond}^n}$ no oxidaⁿ

$\xrightarrow{H^+/KMnO_4 \text{ or } H^+/K_2Cr_2O_7 \text{ & high temp}}$ acid c̄ low no. of carbon

1.1 oxidation c̄ Cu/300°C

$CH_3CH_2OH \xrightarrow{Cu/300°C} CH_3CHO + H_2$

$CH_3-CH(OH)-CH_3 \xrightarrow{Cu/300°C} CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + H_2$

$CH_3-C(CH_3)_2-OH \xrightarrow{Cu/300°C} CH_3-C(CH_3)=CH_2 + H_2O$ (olefin)

1.2 oxidaⁿ c̄ HIO_4

→ vicinal OH, → vicinal C=O, vicinal C=O & OH

$CH_2(OH)-CH_2(OH) \xrightarrow{HIO_4} HCHO$ & $HCHO$

$CH_3-\overset{O}{\overset{\|}{C}}-CH(OH)-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{HIO_4} CH_3COOH$

$H-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CHO$

Pinacole - Pinaclone Rearrangement

$CH_3-C(CH_3)(OH)-C(CH_3)(OH)-CH_3$ (Pinacole) $\xrightarrow[H^+]{conc\ H_2SO_4}$ $CH_3-C(CH_3)(OH)-C(CH_3)(OH_2)-CH_3$

$CH_3-C(CH_3)(OH)-C(CH_3)(CH_3)-CH_3$ (Pinaclone) ↓ $CH_3-C(CH_3)(OH)-C(CH_3)(CH_3)-CH_3$ (Rearrang ⊕ no stabilized)

$CH_3-C(=O)-C(CH_3)(CH_3)-CH_3$ ↑ $CH_3-C(OH)(CH_3)-C(CH_3)(CH_3)-CH_3$

Test of Alcohol

1. Lucas Test :- Distinguish 1°, 2°, 3°
2. Victor Mayer Test :- RBC 1° 2° 3°

1° alcohol → Red colour

2° alcohol → Blue colour

3° alcohol → No colour

$RCH_2OH \xrightarrow{Pt\ I_2} RCH_2I \xrightarrow{AgNO_2} RCH_2NO_2 \xrightarrow{HNO_2}$ Red colour

$R_2CHOH \xrightarrow{Pt\ I_2} R_2CHI \xrightarrow{AgNO_2} R_2CHNO_2 \xrightarrow{HNO_2}$ Blue colour

$R_2COH \xrightarrow{Pt\ I_2} R_3CI \xrightarrow{AgNO_2} R_2CNO_2 \xrightarrow{HNO_2}$ colourless

3. dichromate Test

only distinguishe 3°

1° alcohol $\xrightarrow[\text{orange}]{H^+/K_2Cr_2O_7}$ Cr^{+3} green + acid

2° alcohol $\xrightarrow{\quad''\quad}$ Cr^{+3} green + Ketone

3° alcohol $\xrightarrow{\quad''\quad}$ no oxidaⁿ

4. Test for alcoholic grp

$R-OH \xrightarrow{Na} RO^-Na^+ + \frac{1}{2}Na^+$

$R-OH \xrightarrow{PCl_5} R-Cl + POCl_3 + HCl$ ↓ $+NH_3$ → NH_4Cl (white fume)

Methanol & Ethanol

Methanol :- Wood spirit
- prepared by destructive distillation of wood (old Method)

Modern Method :- catalytic hydrogen of CO.

$CO + 2H_2 \xrightarrow[\substack{200-300\,atm \\ 573-673K}]{ZnO + Cr_2O_3} CH_3OH$

- colourless liq & very high poisonous

Ethanol :- commercial by fermentation.

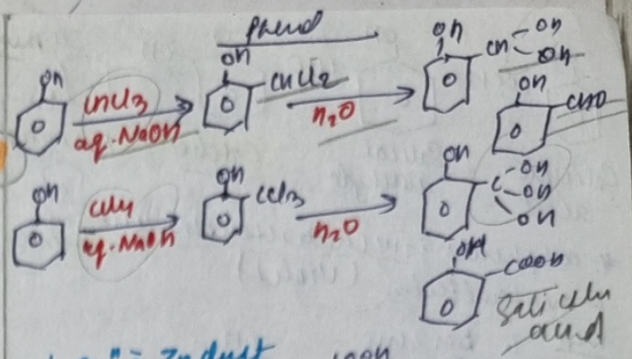
$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}}$ glucose + fructose

glucose & fructose $\xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$

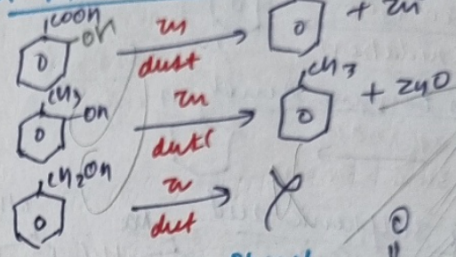
→ C_2H_5OH is made unfit for drinking by mixing $CuSO_4$ (to give colour) & pyridine is also added known as denaturation of alcohol.

→ **Wine making** :-

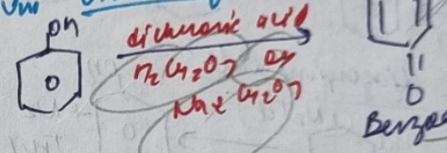
grapes → Ripen → when grapes crushed
↓ sugar & yeast
sugar ↑ yeast ↑
↓ sugar meets enzymes
↓ fermentation starts (in -nce of air



vi. Rxn c̄ Zn dust

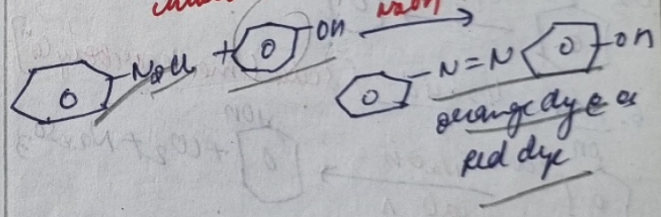


viii. Oxidation of Phenol



viii. Coupling Rxn

Phenol + Benzene diazonium chloride $\xrightarrow[\text{Medium}]{\text{Basic}}$ dye formation P-hydroxy azobenzene



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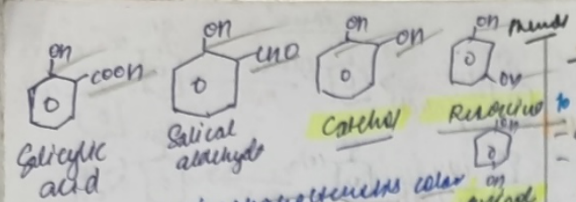
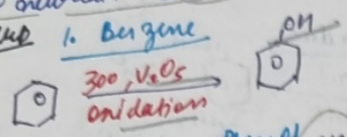
* In Rolbe's Rxn electrophile used is CO_2

* BP
$CH_3CH_2OH > CH_3OCH_3 > CH_3CH_2CH_3$

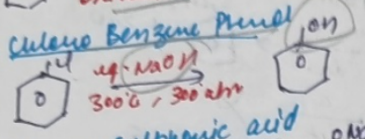


* all phenols give characteristics color $\bar{c}$ neutral $FeCl_3$ (Violet)

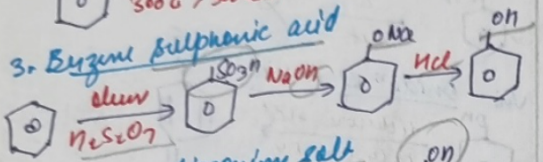
Rxn 1. Benzene



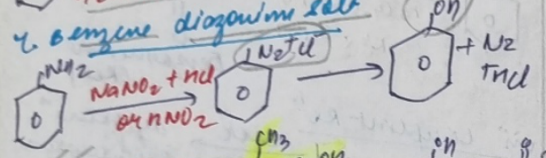
2. Chloro Benzene Phenol



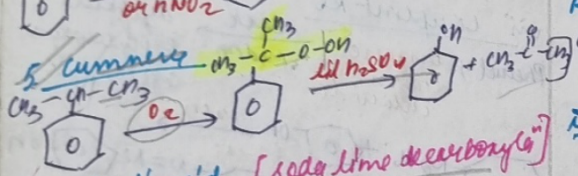
3. Benzene sulphonic acid



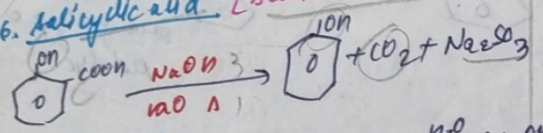
4. Benzene diazonium salt



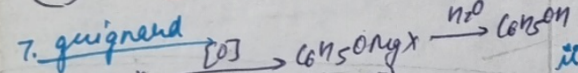
5. Cumene



6. Salicylic acid [soda lime decarboxylation]



7. Grignard

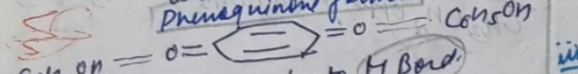


Physical prop

→ Phenol attains PINK on exposure to air/light

↓ due to oxidation

Phenoquinone formation



- solubility in H_2O due to H Bond
- Phenol is less soluble than alcohol because of large Hydrocarbon part in phenol.
- due to intermolecular H-Bond phenol has relatively high B.P than other molecules of same molecular mass

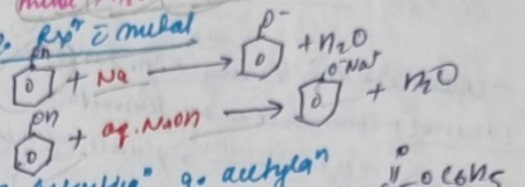
Chemical Rxn

- due to Breakdown of O-H Bond

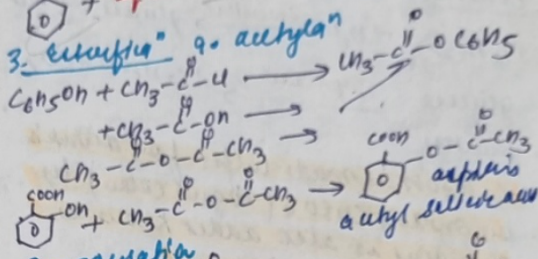
1. Acidity of Phenol
- due to Resonance stabilized phenoxide ion.
- EWG ↑ - ↑

Phenol > H_2O > alcohol — acidic character

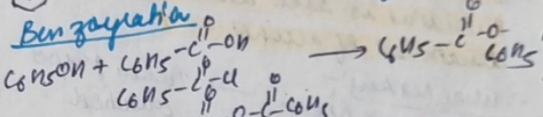
2. Rxn $\bar{c}$ metal



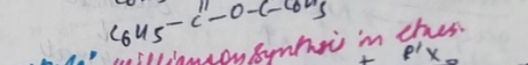
3. Esterification a. acetylation



Benzoylation

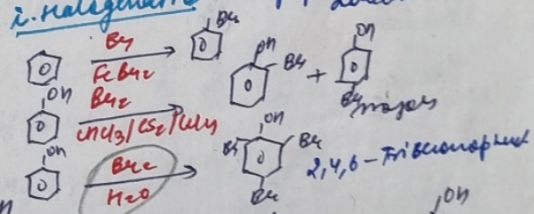


Alkylation Williamson synthesis in ether

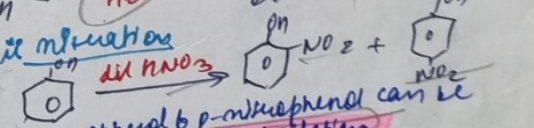


Chemical Rxn due to benzene Ring

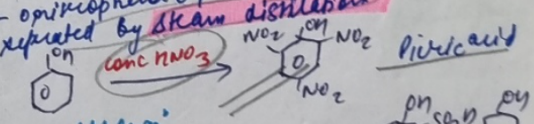
i. Halogenation - OH grp is ortho para directive



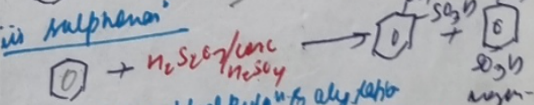
ii. Nitration



- o-nitrophenol & p-nitrophenol can be separated by steam distillation



iii. Sulphonation



iv. Friedel craft alkylation & alkylation

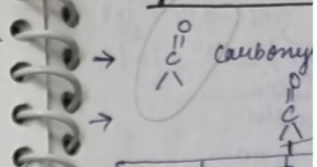
why $AlCl_3$

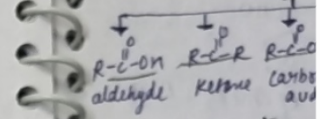
v. Riemer - Tiemer Rxn Reimer/Feimer Rxn

Phenol + Chloroform dil NaOH → aldehyde at O-position of phenol

(Back)

aldehyde, ketone, Ca...





Common Naming

aldehyde

→ HCHO → Formald...

→ CH_3CHO → acetalde...

→ Benzaldeh...

→ $CH_2CH-CHO$ — Acro...

→ — pthala...

→ $CH_3-CH(Br)-CH_2-C(=O)-$

β-Bromobutyral...

→ $CH_3-CH(OCH_3)-CH$

α-Methoxypropio...

→ $CH_3-CH(CH_3)-CH$

iso butyraldeh...

→ nucleo... electro...

Preparation:

1. ~~Hydrocarbon~~

a. $R-CH=CH_2$ unbranched alkene

$R-C(R)=CH_2$

b. Hydration o...

$CH\equiv CH + H_2O$ ethyne

$CH_3-C\equiv CH + H_2O$

ethyne hydration → a...

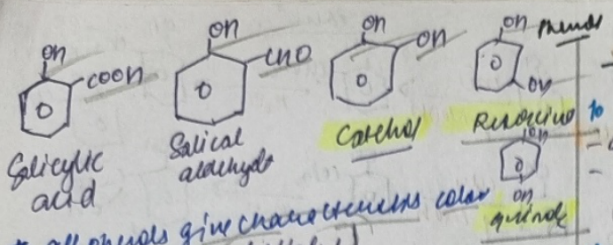
other alkyne → "

c. Hydroboration

BH_3

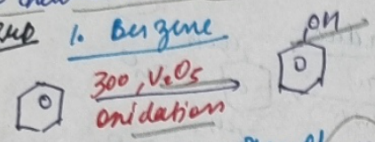
THF, H_2O_2/O...

$R-C\equiv CH$ B_2H_2 H_2O_2

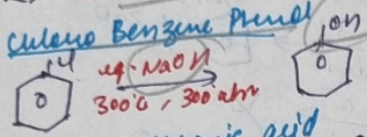


* all phenols give characteristics color $\bar{c}$ neutral $FeCl_3$ (Violet)

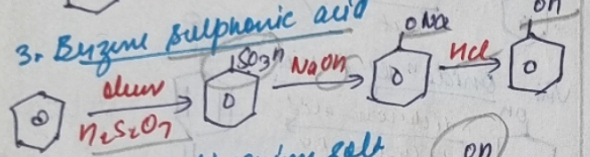
Prep 1. Benzene



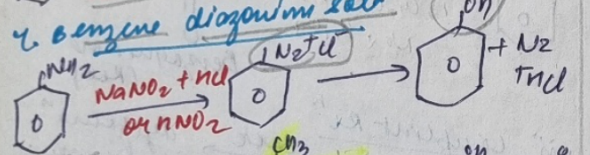
2. Chloro Benzene Phenol



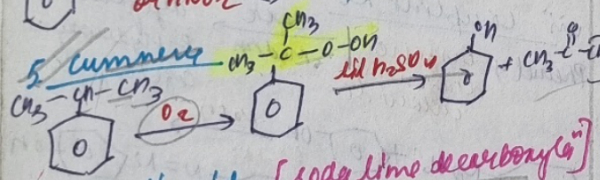
3. Benzene sulphonic acid



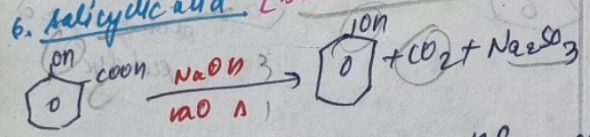
4. Benzene diazonium salt



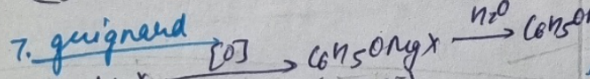
5. Cumene



6. Salicylic acid [soda lime decarboxylation]



7. Grignard

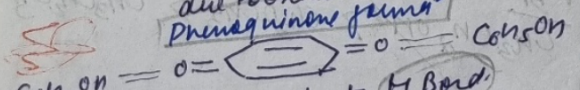


Physical prop

→ Phenol attains PINK on exposure to air & light

↓ due to oxidation

Phenoquinone formation



- Solubility in H_2O due to H Bond.
- Phenol is less soluble than alcohol becoz of large Hydrocarbon part in phenol.
- due to intermolecular H-Bond phenol has relatively high B.P than other molecules of same molecular mass

Chemical Rx

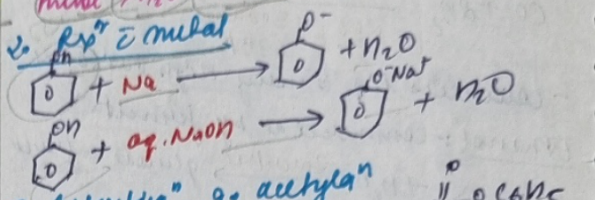
- due to Breakdown of O-H Bond

1. Acidity of Phenol

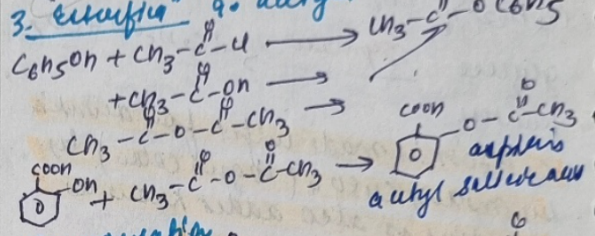
- due to Resonance stabilized phenoxide ion.
- EWG ↑ = ↑

Phenol > H_2O > alcohol — acidic character

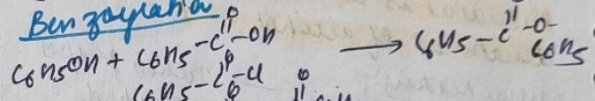
2. Rx $\bar{c}$ metal



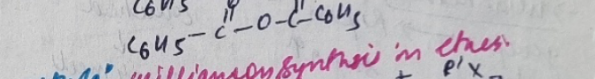
3. Esterification a. acetylation



Benzoylation

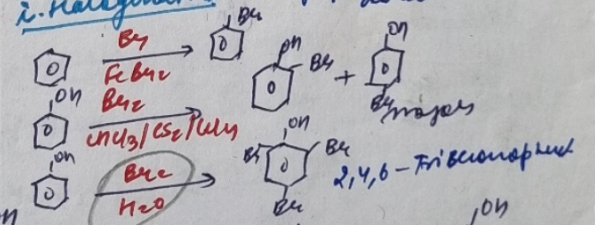


Alkylation Williamson synthesis in ether

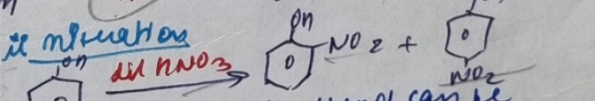


Chemical Rx due to benzene Ring

i. Halogenation - OH grp is ortho para directing



ii. Nitration



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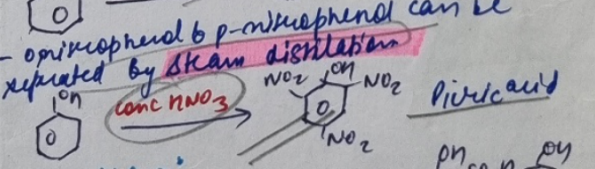
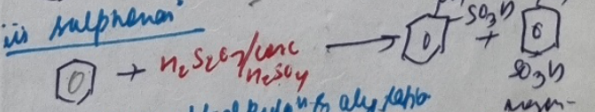


iii. Sulphonation



iv. Friedel craft alkylation & alkylation

why $AlCl_3$

v. Riemer - Tiemer Rx Reimer/Feimer Rx

Phenol + Chloroform $\xrightarrow{\text{dil NaOH}}$ aldehyde at O-position of phenol

(Back)

aldehyde, ketone, carboxylic acid

→ carbonyl grp (oxo grp)

→

R-C(=O)-OH aldehyde | R-C(=O)-R ketone | R-C(=O)-OH carboxylic acid | R-C(=O)-X acyl halide | R-C(=O)-NH2 amide | R-C(=O)-O-C(=O)-R ester | amydride

common Naming

aldehyde	ketone
→ HCHO → Formaldehyde	→ $CH_3-C(=O)-CH_3$ acetone
→ CH_3CHO → acetaldehyde	→ Acetophenone
→ Benzaldehyde	→ Propiophenone
→ $CH_2=CH-CHO$ Acrolein	
→ Phthaldehyde	→ Benzophenone
→ $CH_3-CH(Br)-CH_2-CHO$ β-Bromobutyraldehyde	→ $CH_3-CH(CH_3)-C(=O)-CH(CH_3)-CH_3$ Diisopropylketone
→ $CH_3-CH(OCH_3)-CHO$ α-Methoxypropionaldehyde	
→ $CH_3-CH(CH_3)-CHO$ iso butyraldehyde	

→ $C^{\delta+}=O^{\delta-}$ — nucleophile (Lewis Base)

→ $C^{\oplus}$ — electrophile (Lewis acid)

Preparation:

1. Hydrocarbon → oxides

a. Hydrocarbon

$R-CH=CH_2$ unbranched alkene —O_3, Zn, H_2O→ $R-CHO + HCHO$ aldehyde

$R-C(R)=CH_2$ —O_3, Zn, H_2O→ $R-C(=O)-R + HCHO$ ketone + aldehy

b. Hydration of alkyne (MK Rule) Hydrate

$CH\equiv CH + H_2O$ (Ethyne) —dil H_2SO_4, 1% $HgSO_4$→ $CH=CH \leftrightarrow CH_2=CH-OH$ (enol)

$CH_3-C\equiv CH + H_2O$ → $CH_3-C(OH)=CH_2$ → $CH_3-C(=O)-CH_3$ (Tautomerism)

Ethyne —hydration→ acetaldehyde

other alkyne → ketone

c. Hydroboration of alkyne (AMK Rule)

$R-C\equiv CH$ —BH_3, THF, H_2O_2/OH^- or B_2H_6, H_2O_2/OH^-→ $R-C(OH)=CH_2$ → $RCH=CH$ (OH) ⇌ $R-CH_2-C(=O)-H$

1° alkyne → Aldehyde

other alkyne → ketone

2. From alcohol

1° alcohol —[O]→ aldehyde

→ RCH_2OH —$K_2Cr_2O_7$, H+→ RCHO → RCOOH

→ RCH_2OH —CrO_3, Pyridine→ RCHO [milder O.A]

→ RCH_2OH —PCC, CH_2Cl_2 or PDC→ RCHO + H_2O

or $(COCl)_2 + H_2SO_4$ → Swern Reagent in acetone

- good yield of aldehyde

2° alcohol —[O]→ ketone

→ $R-CH(Ph)-R$ —$KMnO_4/H^+$, $K_2Cr_2O_7/H^+$→ $R-C(=O)-R$

→ $R-CH(Ph)-R$ —PCC, CH_2Cl_2 or PDC or $CrO_3 + H_2SO_4$→ ketone

3. Oxidn of alkene (dehydrogen)

CH_3-CH_2-OH —Cu/300°C, Ag 300°C→ CH_3-CHO + H_2 gas

$CH_3-CH(OH)-CH_3$ —Cu 300°→ $CH_3-C(=O)-CH_3$

$CH_3-C(CH_3)(OH)-O-CH_3$ —Cu 300°→ $CH_2=C(CH_3)-CH_3$ isobutylene

4. a. from alkyl halides

1° $R-CH_2-X$ —DMSO→ RCHO

2° $R-CH(X)-R$ —DMSO→ $R-C(=O)-R$

DMSO = $CH_3-S(=O)-CH_3$ Dimethyl sulphoxide

b. Hydrolysis of gem dihalides

1. Terminal gem halides → hydrolysis → Aldehyde

CH_3CHCl_2 —aq KOH→ $CH_3CH(OH)_2$ → $CH_3-C(=O)-H$

2. Non Terminal gem halides → hydrolysis → Ketone

$CH_3-C(H)(Cl)-CH_3$ —aq KOH→ $CH_3-C(OH)_2-CH_3$ → $CH_3-C(=O)-CH_3$

Hydrolysis of carbonyl derivatives

$R-CH=N-OH$ (aldoxime) —H_2O/H^+→ $R-CHO + NH_2OH$

$R-C(R)=N-OH$ (Ketoxime) —H_2O/H^+→ $R-C(=O)-R + NH_2OH$

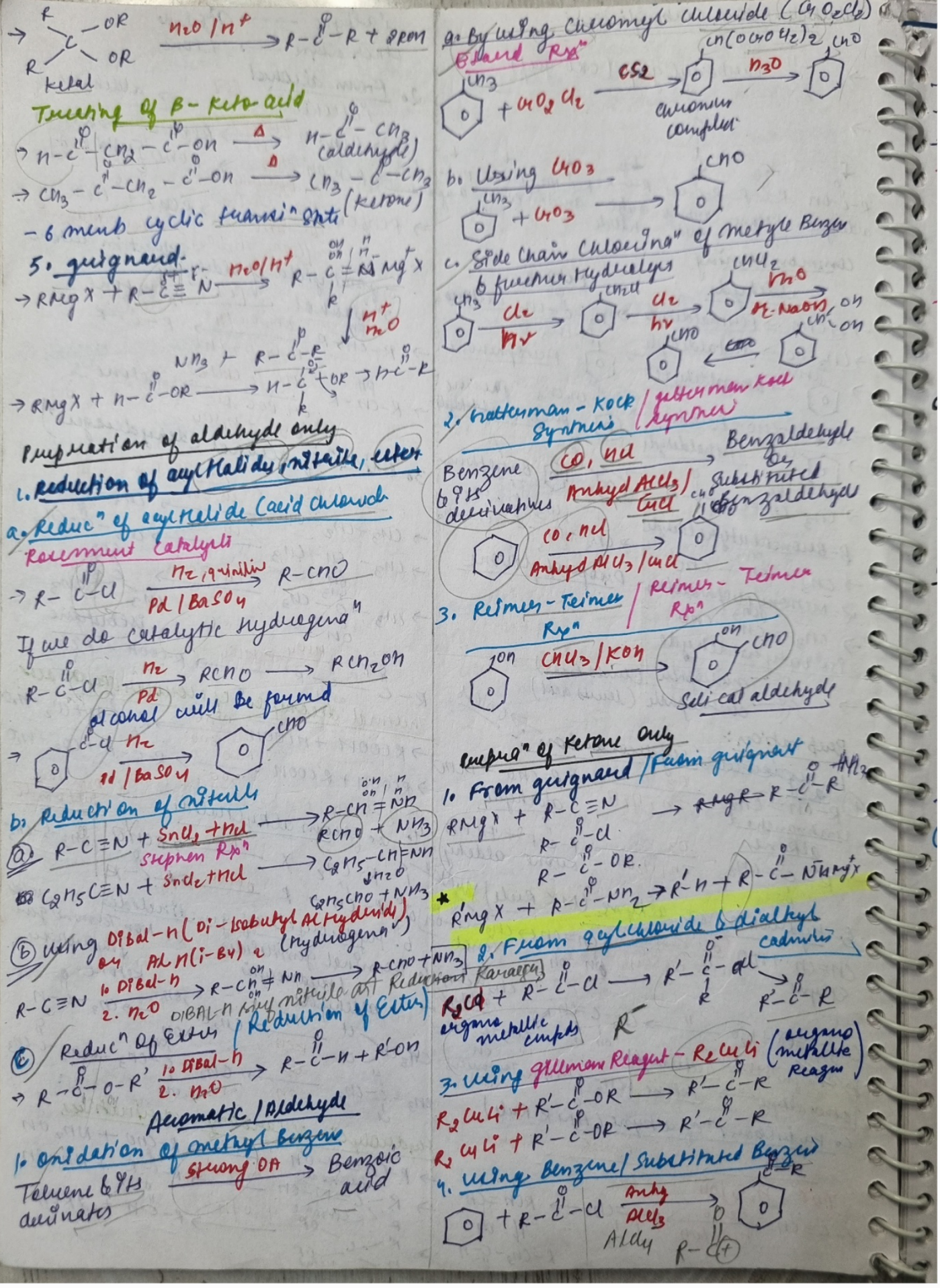
$R-C(OR)(H)-OR$ (acetal) —H_2O/H^+→ $R-C(=O)-H + 2ROH$

Thermal decompn of monocarboxylic acid

$R-COOH + HCOOH$ —MnO, 300°, Δ→ $R-C(=O)-H + CO_2 + H_2O$

$R-COOH + R'COOH$ —MnO, 300°, Δ→ $R-C(=O)-R + CO_2 + H_2O$

(Ca or Mn or Ni salt) Peak CO_2



Physical Prop

→ only methanal (HCHO) formaldehyde - gas

→ $C_2 - C_{11}$ → liq

→ C_{12} onward → solid

→ BP ∝ Mult

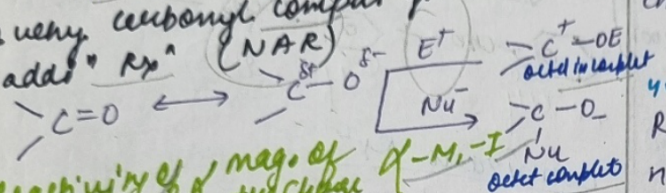
Alcohol > carbonyl comp > Alkane / Ethane

Intermolecular H Bonding | polar dipole-2 interac^n | non-polar London force instancous induced dipole

→ Solubility ∝ $\frac{1}{Mult}$

$C_1 \rightarrow C_3$ carbonyl compds are soluble in H_2O Becoz of H bonding.

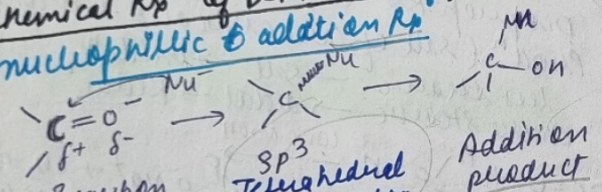
Q. why carbonyl compds gives nucleophilic addi^n Rx^n (NAR)



Reactivity of NAR ∝ mag. of +ve charge ∝ -M, -I

Chemical Rx^n of Both aldehyde & Ketone

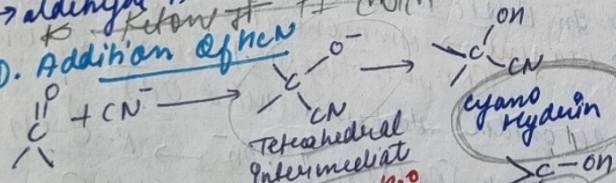
nucleophillic addition Rx^n



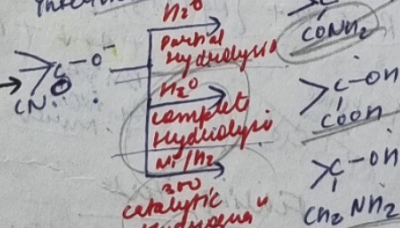
- nucleophillic attack is ⊥
- Hybridiza^n → $Sp^2 \rightarrow Sp^3$

→ aldehyde is more Reactive than ketone.

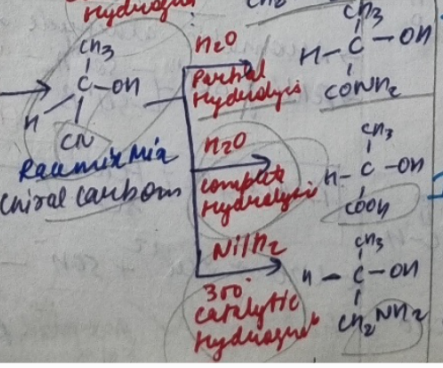
1. Addition of HCN



Q. >=O + HCN →



Q. CH_3 >C=O + HCN →



2. Rx of $NaHSO_3$ (Na H Sulphite)

$NaHSO_3 \rightleftharpoons Na^+ + HSO_3^-$

$HSO_3^- \rightleftharpoons H^+ + SO_3^{-2}$

>C=O + SO_3^{-2} ⇌ >C(OH)-SO_3^- Na^+

↓ dil HNO_3, dil H_2SO_4, H_3O^+

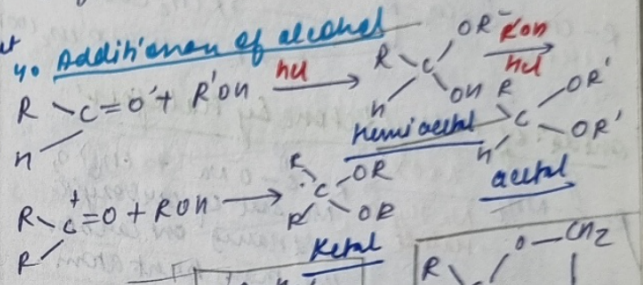
carbonyl compds

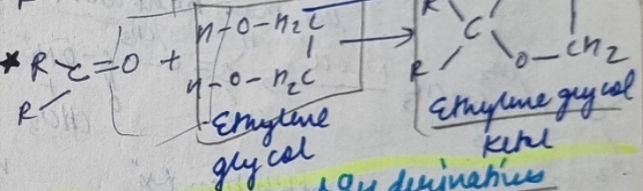
3. Addition of grignard

$CH_3MgI + CH_3-C(=O)-H \rightarrow CH_3-C(O^-)(CH_3)-H \rightarrow CH_3-C(OH)(CH_3)-CH_2$

$CH_3MgI + CH_3-C(=O)-OCH_3 \rightarrow CH_3-C(OH)(CH_3)-CH_2$

4. Addition of alcohol





5. Addition of NH_3 & its derivatives

Condensa^n Rx^n (Removal of H_2O)

>C=O + H_2N-Z → >C=N-Z

Z	Reagent name	Product	
H	Ammonia	>C=N-H	imine
R	Amine	>C=N-R	substituted imine (Shiff Base)
NH_2	Hydrazine	>C=N-NH_2	Hydrazone
-OH	Hydroxyamine	>C=N-OH	Oxime
-NH-⟨O⟩	phenyl hydrazine	>C=N-NH-⟨O⟩	phenyl hydrazone
-NH-⟨O⟩-NO_2	2,4-dinitro-phenyl hydrazine	>C=N-NH-⟨O⟩-NO_2	2,4-dinitro-phenyl hydrazone (2,4 DNP)
-NH-C(=O)-NH_2	Semicabazide	>C=N-NH-C(=O)-NH_2	Semicarbazone

6. Reduction to hydrocarbon

R-CHO $\xrightarrow{H_2 / Ni/Pt/Pd}$ RCH_2OH

R-C(=O)-R $\xrightarrow{4AlH_4 \text{ or } NaBH_4}$ R-CH(OH)-R

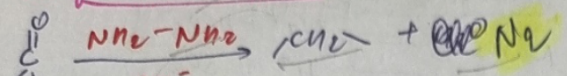
7. Reduction to Hydrocarbon

Clemenson Reduction

C(=O) $\xrightarrow{Zn-Hg / HCl}$ CH_2 + H_2O

aldehyde ketone

Wolf – Kishner Reduction



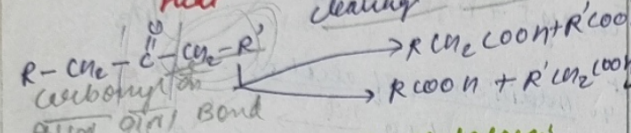
① Oxidation of Aldehyde

R–CHO (aldehyde) —oxidising agent→ R–COOH (carboxylic acid)

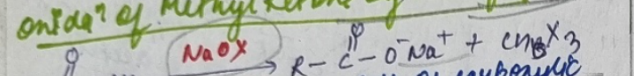
- Strong O.A: HNO_3, $KMnO_4$, $K_2Cr_2O_7$
- Tollen Reagent, Fehling sol^n — Mild oxidising agent

Oxidation of Ketone

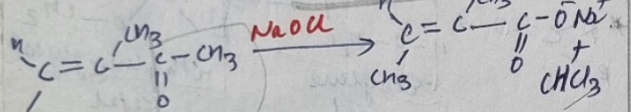
Ketone —Strong O.A, Heat, C–C Bond cleaving→ mixture of carboxylic acid



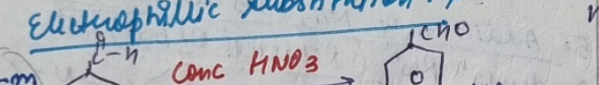
Oxidation of Methyl Ketone by Haloform



Na salt of carboxylic acid having one carbon less than parent atom.



Electrophillic Substitution Rx^n

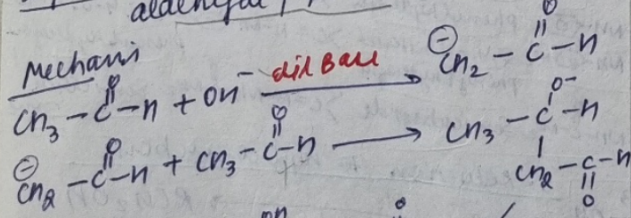


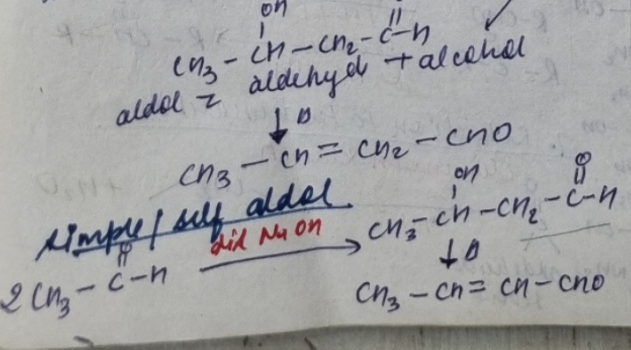
Aldol – Condensation Rx^n (med α–H)

Step-1 → formation of carbanion.

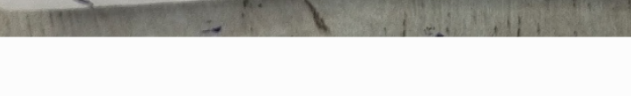
Step-2 → carbanion attacks on other aldehyde / ketone.

Mechanism

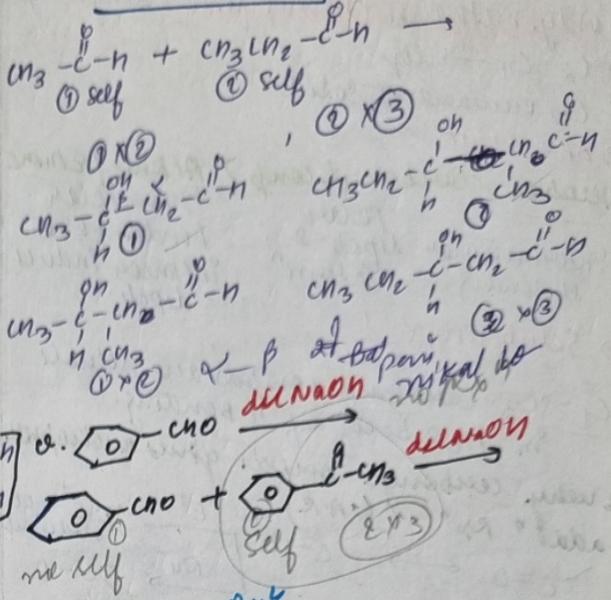


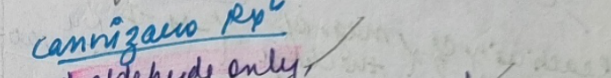


Simple / self aldol



mixed aldol / mixed aldol



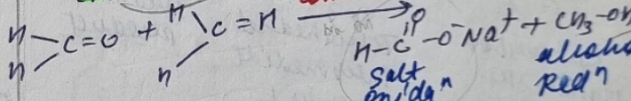


Cannizaro Rx^n

- → aldehyde only
- → no α–H
- → Disprop Rx^n (oxid^n & Red^n)
- → Prod^n (salt of carboxylic acid + Alcohol)

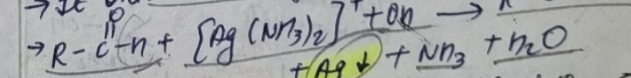
less steric → Salt → Oxidn

more steric → Alcohol → Reduc^n



Tollen Test / Silver Mirror Test

- → In Basic Medium
- → Reagent → Ammonical Silver Nitrate $[NH_4OH + AgNO_3] \rightarrow [Ag(NO_3)_2]^{\oplus}OH^{\ominus}$
- → It oxidises aldehyde (Mild OA)

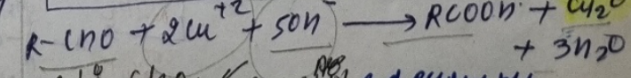


Ketone ❌ Aliphatic aldehyde ✓ Aro Aldehyde ✓

Fehling Test

- → Aromatic aldehyde ❌ doesn't give this test
- → Fehling sol^n — Sol^n A – aq. sol^n of $CuSO_4$; Sol^n B – Rochelle salt (Na–K Tartarate)

Aldehyde + Fehling Soln → Reddish Brown ppt



Ali CHO ✓ Aro CHO ❌ Red Brown ppt

Carbonylic acid

$-\overset{O}{\overset{\|}{C}}-OH$ → due to this carbonylic acid is acidic in nature

Carbonyl grp

$-\overset{O}{\overset{\|}{C}}-\ddot{O}H$

This carbon is less electrophillic than carbonyl group due to +M effect of Oxygen

Common Naming

Monoc

HCOOH – Formic acid

CH_3CH_2COOH – Propionic

$(CH_3)_2CHCOOH$ – isobutyr

Dicarbonylic acid

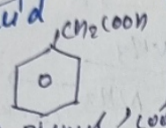
glutaric acid — Oxalic acid

Adipic acid

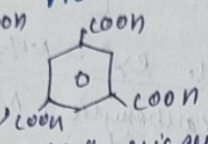
Pimeric acid

$HO-\overset{CH_2-COOH}{\overset{|}{C}}-COOH$ (with CH_2-COOH)

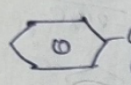
citric acid



phenyl acetic acid



trimesic acid



COOH Benzoic acid

Preparation :-

1. alkene → carbonylic (oxidation) (oxidative ozonolysis)

i. $RCH=CHR' \xrightarrow[H_2O]{O_3} RCHO + R'CHO$ ($RCHO \rightarrow HCOOH$, $R'CHO \rightarrow HCOOH$)

ii. $RH=CHR' \xrightarrow[2)\ H_3O^+]{1)\ con\ KMnO_4/OH^-} RCOOH + R'COOH$

2. alcohol → acid oxidation

i alcohol $\xrightarrow{H^+ / K_2Cr_2O_7}$ $KMnO_4$ / Acid / Basic / Neutral; Jones Reagent ($CrO_3 + H_2SO_4$) → Acid / RCOOH

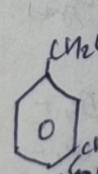
3. aldehyde → acid oxidation

$RCHO \xrightarrow{\text{Strong O.A}}$ $\xrightarrow{\text{mild O.A}}$ — Tollen's Reagent, Fehling Reagent

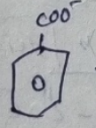
$RCHO \xrightarrow{''} RCOO^- \xrightarrow{H^+} RCOOH$ oxidation

4. alkyl Benzene → acid

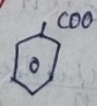
Alkyl Benzene $\xrightarrow{\text{Vigorous oxidation}}$ H_2CrO_4 (chromic acid) → Benzoic acid; $KMnO_4$ (Acidic / Basic)

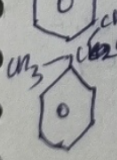


$\xrightarrow{KMnO_4/OH^-}$



$\xrightarrow{H_3O^+}$





$\xrightarrow{''}$



→ no oxidation, no α-H

see α-H

α-H dipha

→ Alkyl group must have one α-H

→ product of oxidation will always be Benzoic acid. irrespective of side chain

→ Rate of Benzoic acid formation

methyl Benzene > 1° alkyl Benzene > 2° alkyl Benzene > 3° alkyl Benzene (no Rxn)

5. grignard

$RMgX + O=C=O$ (CO_2) dryice $\xrightarrow{ether} R-\overset{O}{\overset{\|}{C}}-O^-Mg^+X \xrightarrow{H_3O^+} R-\overset{O}{\overset{\|}{C}}-OH$

6. nitrile acid

$R-C\equiv N$ $\xrightarrow{\text{partial Hydrolysis}}$ $R-\overset{O}{\overset{\|}{C}}-NH_2$ amide

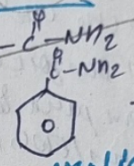
$R-C\equiv N$ $\xrightarrow{\text{complete Hydrolysis}}$ $R-\overset{O}{\overset{\|}{C}}-OH + NH_3$

acidic hydrolysis

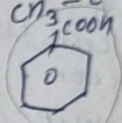
H^+ → acts as catalyst

7. amide

$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H_3O^+} CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_2$

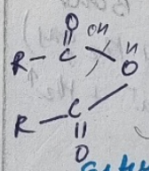


$\xrightarrow{H_3O^+}$



8. acylhalides & anhydrides

$R-\overset{O}{\overset{\|}{C}}-Cl$ — H_3O^+ → acidic hydrolysis RCOOH; H_2O / H^+ H_2SO_4; H_2O / OH^- → Basic Hydrolysis $RCOO^-$ $\xrightarrow{H_3O^+}$ RCOOH



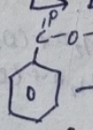
$\xrightarrow{H_3O^+} R-\overset{O}{\overset{\|}{C}}-OH + R-\overset{O}{\overset{\|}{C}}-OH$

9. Ester → acid

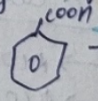
Hydrolysis

→ acidic Hydrolysis → carbonylic acid

→ Basic Hydrolysis → carboxylate $\xrightarrow{H_3O^+}$ carbonylic acid



$\xrightarrow{H_3O^+}$



$+ C_2H_5OH$

Physical Prop :-

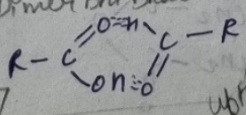
→ alliphatic carbonylic acid upto 4 carbon → colourless liq

– higher carbon → waxy solid

B.P ∝ Mwt

carbonylic acid (intermolecular) H Bond > alcohol (intermolecular) H-Bond > carbonyl comp dipole-2

Dimer BH Bnatn



Solubility ∝ $\frac{1}{Mwt}$

alliphatic carbonylic acid upto 4 carbon → miscible in H_2O due to Hydrogen Bond c̄ H_2O

Chemical Properties :-

1. Acidity in carboxylic acid

$R-\overset{O}{\overset{\|}{C}}-OH + H_2O \rightleftharpoons H_3O^+ + R-\overset{O}{\overset{\|}{C}}-O^-$ ⟷ $R-\overset{O}{\overset{\|}{C}}=O$

(Equivalent resonance ⟷ Identical)

Anion ← stable

Carboxylic acid is more acidic than phenol

Carboxylate ion → Eqⁿ Resonance

Phenoxide → Resonance

EWG = ↑ acidity = −M, −I

EDG = ↓ acidity = +M, +H, +I

Increasing acidity order

$Ph < I < Br < Cl < F < CN < NO_2 < CF_3$

$HCOOH > CF_3COOH > CH_3COOH > CH_2ClCOOH$

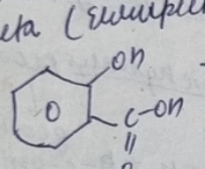
$> NO_2CH_2COOH > NC-CH_2-COOH >$

$F-CH_2COOH > ClCH_2COOH > Br CH_2Br >$

$HCOOH > ClCH_2CH_2COOH > C_6H_5COOH >$

$C_6H_5CH_2COOH > CH_3COOH > CH_2CH_2COOH$

Ortho effect :- o-substituted Benzoic acid is stronger acid than para & meta (irrespective of substituents / EWGs / EDGs)



Intermolecular H-Bond

Chemical Rxⁿ :- cleavage of O–H Bond

1. Rxⁿ with active metal (Liberate H_2 gas)

$2RCOOH + Na \longrightarrow RCOO^-Na^+ + H_2\uparrow$

(Na, K, Li)

2. Rxⁿ with Alkali

$2RCOOH + CaO \longrightarrow (RCOO)_2Ca + H_2O$

$RCOOH + NaOH \longrightarrow RCOO^-Na^+ + H_2O$

3. Rxⁿ with bicarbonate & carbonate

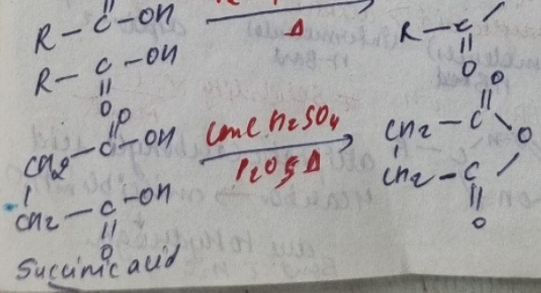
$RCOOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$

$RCOOH + Na_2CO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$

Rxⁿ with C–OH Bond Break

1. anhydride form

$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{P_2O_5 / \text{conc } H_2SO_4} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ (anhydride)



Succinic acid

2. Esterification

alcohol / phenol + carboxylic acid / carboxylic acid derivatives $\xrightarrow{\text{conc. } H_2SO_4,\ HCl \text{ gas}}$ Ester

$R-\overset{O}{\overset{\|}{C}}-OR$ (acid, alcohol)

3. Reaⁿ with PCl5

$RCOOH \xrightarrow{PCl_5} R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$

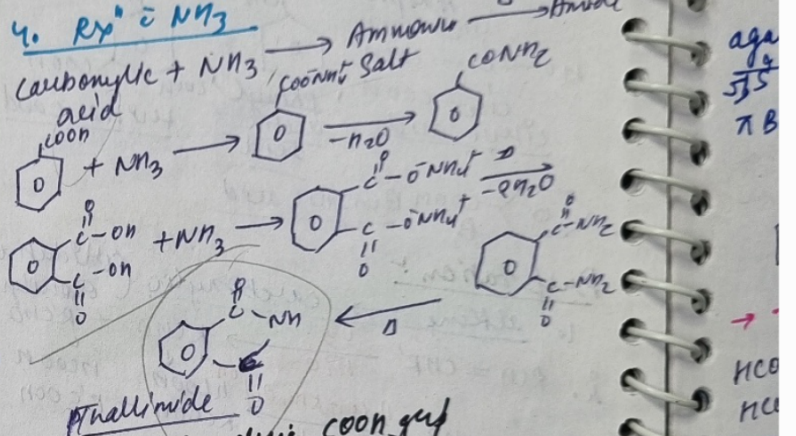
$\xrightarrow{PCl_3} R-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$

$\xrightarrow{SOCl_2} R-\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$ (Darzen Process)

$\xrightarrow{SO_2Cl_2} R-\overset{O}{\overset{\|}{C}}-Cl + SO_3 + HCl$

4. Rxⁿ with NH_3

Carboxylic acid + NH_3 → Ammonium salt → Amide



Phthalimide

Rxⁿ involving COOH group

1. Reduction

$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[B_2H_6 \text{ / } BH_3/THF]{LiAlH_4 \text{ / } H_3O^+} RCH_2OH$

$NaBH_4$ → doesn't reduce carbonyl grp

2. Decarboxylation

$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[3:1]{NaOH : CaO} R-H + Na_2CO_3$

3. Schmidt Rxⁿ

Hydrazoic acid + Carboxylic acid → Sulphuric acid

$R-\overset{O}{\overset{\|}{C}}-OH + N_3H \xrightarrow{H_2SO_4} R-NH_2 + N_2 + CO_2$ (gas)

4. Hunsdiecker Rxⁿ / Hunsdiecker Rxⁿ

$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{Ag_2O} R-\overset{O}{\overset{\|}{C}}-O^-Ag^+ \xrightarrow[CCl_4]{Br_2} R-Br + AgBr + CO_2$

Substitution Rx° in Hydrocarbon part

① Carbonylic acid → must have α-H

$R-CH_2COOH \xrightarrow[2.\ H_2O]{1.\ X_2 / RedP} R-CH(X)-COOH$ (α-Halo carbonylic acid)

X = Cl, Br

HVZ – Hell – Volhard Zelinsky Rx

$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H_2O \text{ excess}]{Red\ P + Cl_2} CH_2Cl-\overset{O}{\overset{\|}{C}}-OH$

$CH_3-\overset{O}{\overset{\|}{C}}-OH \xleftarrow{\Delta} CHCl_2-\overset{O}{\overset{\|}{C}}-OH$

again Ring pr directed on 5 atoms & π Bond pr

−M = Meta directing
+M = O, P directing

Ring – Substitution

$\xrightarrow[+\ conc\ H_2SO_4]{conc\ HNO_3}$ (COOH, NO_2)

→ Tollen & Fehling soln / Tollen

$HCOOH + Ag_2O \rightarrow CO_2 + Ag\downarrow$ (Silver mirror)

$HCOOH + 2CuO \rightarrow CO_2 + Cu_2O$ Red ppt

only formic acid reduce Tollen / Fehling

$HCOOH + HgCl_2 \rightarrow CO_2 + \underset{\text{white ppt}}{Hg_2Cl_2} + HCl$

1. alkene → ond "
2. alcohol → ond "
3. aldehyde → ond "
4. alkyl benzene → ond "
5. Grignard → CO_2 addition.
6. nitrile → hydrolysis
7. amide → hydrolysis
8. acyl halide & anhydride → hydrolysis
9. ester → hydrolysis

$H_3O^+ / \underset{OH^-}{H_2O}$

① O_3/H_2O ② $KMnO_4$ & H_3O^+ ③ $KMnO_4/NaOH$ ④ CrO_3 in H_2SO_4 Jones Reagent ⑤ Tollen / Fehling reagent ⑥ $H^+/K_2Cr_2O_7$ ⑦ PCC/CH_2Cl_2 ⑧ PDC/CH_2Cl_2

GNP – carboxylic acid

→ Reimer – Tiemann Rx carbene neutral electrophile ortho ε

Haloform Test CH_3 ईं

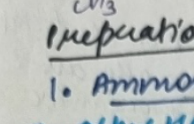
I_2 + KOH or NaOH,

↓ oxidise कर $\frac{H\ की}{SIR}$

X

Amines

Structure of Amines



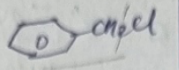
→ due to this lp it is lewis base & act as nucleophile

Sp^3 — 108

Preparation

1. Ammonolysis

R—X



a. alkyl Halide / Benzyl Halides

$NH_3 + R_{\delta+} — X_{\delta-} \longrightarrow RNH_3^+X^- \xrightarrow[\text{Strong Base}]{NaOH} RNH_2 + NaX + H_2O$

ethanolic sol^n of NH_3

$RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4N^+X^-$

1° amine, 2° amine, 3° amine, 4° amine

Dead :- mixture of 1°/2°/3°/4° amine is formed.

If NH_3 is in excess only 1° amine is main product

b. Alcohol

$ROH + NH_3 + Al_2O_3 \longrightarrow$ all 3 amine r formed

$ROH \xrightarrow[Al_2O_3]{NH_3} RNH_2 \xrightarrow[Al_2O_3]{NH_3} R_2NH \xrightarrow[Al_2O_3]{NH_3} R_3N$

$\downarrow NH_3, Al_2O_3$

quarternary amine is not formed

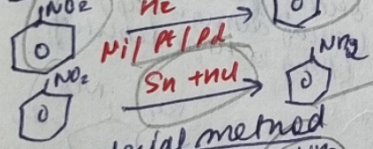
NH_3 in excess — 1° amine is major products

2. Reduction

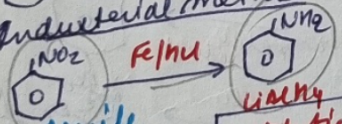
a. nitro comp :- ① → catalytic hydrogen^n ; → metal + acid

Fe + HCl preferred as gives HCl

① Lab method



② Industrial method



b. nitrile

nitrile $\xrightarrow[\text{catalytic hydrogen}^n]{LiAlH_4}$ 1° amine

$R-C\equiv N \xrightarrow[\text{Na/Hg/C}_2H_5OH \text{ reagent}]{H_2/Ni/Pt/Pd} R-CH_2NH_2$

$R-C\equiv N \xrightarrow[\text{Na/Hg/C}_2H_5OH \text{ solvent}]{LiAlH_4} R-\underset{H}{N}-CH_2O$ 2° amine

$R-N\equiv C \xrightarrow[\text{Na/Hg/C}_2H_5OH \text{ solvent}]{H_2/Ni/Pt/Pd} R-\underset{H}{N}-CH_2O$ 2° amine

c. amide

$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4} R-CH_2NH_2$

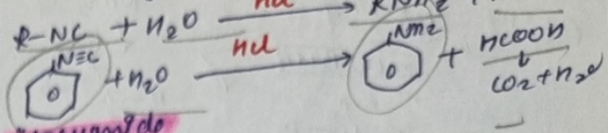
d. oxime

$R-CH=N-OH \xrightarrow{LiAlH_4} RCH_2NH_2$

3. Hydrolysis

Acidic Hydrolysis

$R-NC + H_2O \xrightarrow{HCl} RNH_2 + HCOOH$



isocyanide

Basic Hydrolysis

$R-N=C=O + H_2O \xrightarrow{KOH} RNH_2 + K_2CO_3$

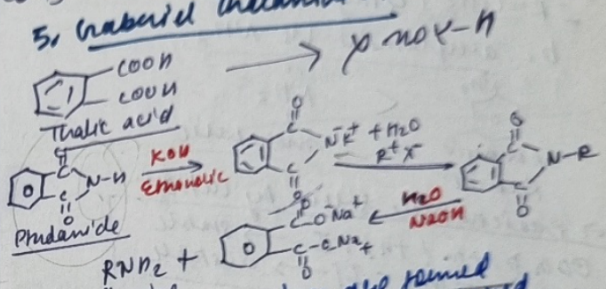
isocyanate

4. Grignard

$RMgX + Cl-NH_2 \longrightarrow R-NH_2 + Mg^+XCl^-$

$C_6H_5Br + Cl-NH_2 \longrightarrow C_6H_5-NH_2 + Mg^+BrCl^-$

5. Gabriel Thalamide Rx



Thalic acid

Phthalamide

RNH_2 + 1° amine

pure aliphatic amines are formed

aromatic amines can't be prepared — Bulk, — Double Bond character.

6. Hoffman Bromamide / Hoffman Bromamide

amide + Ethanolic / aq sol^n of NaOH + Br_2 → 1° amine + Na_2CO_3 + NaBr + H_2O

migra^n of alkyl / aryl from carbonyl carbon of of amide to N takes place

products has one carbon less than reactant

$CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{ethanolic sol}^n]{Br_2 + NaOH} CH_3NH_2 + Na_2CO_3 + NaBr + H_2O$

amide

7. Schmidth - Rx

Sulphuric acid, carboxylic acid, hydrazoic acid

$R-\overset{O}{\overset{\|}{C}}-OH + N_3H \xrightarrow{\text{conc } H_2SO_4} R-NH_2 + N_2\uparrow + CO_2\uparrow$

Physical Prop :-

① Solubility → lower aliphatic amines r soluble in H_2O due to H Bond in H_2O

1° amine > 2° amine > 3° amine

2-αH, 1-αH, 0-αH

② BP α Mult

Alcohol > Amine [comparable molecules]

strong H Bond — more EN

1° amine > 2° amine > 3° amine

→ Amine is Reactive Be CO_2

① diff in EN of NSH

② ⊕nce of lp on Nation (Basic nature)

3. Basic nature

a. Alkanamine Vs Ammonia

RNH_2 > NH_3

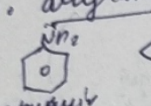
Lone Pair

In gas phase Basic nature $R_3N > R_2NH > RNH_2 > NH_3$ (+I Effect)

In aq. phase depend on: ① I effect, ② Steric hind., ③ Hydration energy

- $R=CH_3$ (Methyl Substituted) – 2° > 3° > 1° > NH_3
- $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- $R=C_6H_5$ (Ethyl Substituted) – 2° > 1° > 3° > NH_3

b. arylamine Vs NH_3



4-butyl-1-naphthylamine

NH_3 more basic

→ Basic nature shown by cation:

EDG → +m / +H / +I → stable

EWG → −m / −I / → unstable

Chemical Rxn

1. Acid-Base Rxn

$R-NH_2 + HCl \longrightarrow RNH_3^+Cl^-$

$2R-NH_2 + H_2SO_4 \longrightarrow (RNH_3^+)_2SO_4^{-2}$

2. Alkylation

$R-NH_2 + R-X \xrightarrow{Rxn} R_2NH \xrightarrow{Rxn} R_3N \xrightarrow{Rxn} R_4N^+X^-$

3. acylation

{Aliphatic / Benzene 1°/2° amine} + acid chloride / acid anhydride → Amide

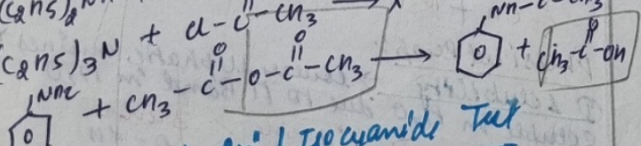
(Electron donating Group)

nucleophilic substitution Rxn

$C_6H_5NH_2 + CH_3-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow C_6H_5-NH-\overset{O}{\overset{\|}{C}}-CH_3$

$(C_6H_5)_2NH + Cl-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow (C_6H_5)_2-N-\overset{O}{\overset{\|}{C}}-CH_3$

$(C_6H_5)_3N + Cl-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow X$ (No α-H)



4. Carbylamine Rxn / Isocyanide Test

Carbylamine Rxn / Isocyanide Test

→ Both aliphatic & aromatic 1° amine give +ve

$R-NH_2 + CHCl_3 + KOH \xrightarrow{\Delta} R-N\equiv C + 3KCl + 3H_2O$

Isoorganic → Organic

K, OH

alkyl isocyanide or carbylamine

very bad smell foul smell

$C_6H_5NH_2 + CHCl_3 + KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$

Phenyl isocyanide

→ 2° / 3° amine don't give this test

→ Intermediate → Carbene → $[:CCl_2]$ (neutral intermediate)

5. Rxn with nitrous acid [HNO_2, $NaNO_2$ + HCl]

$R-NH_2 + HNO_2 \longrightarrow R_2^+N^- \xrightarrow{H_2O} R-OH + N_2\uparrow + HCl$

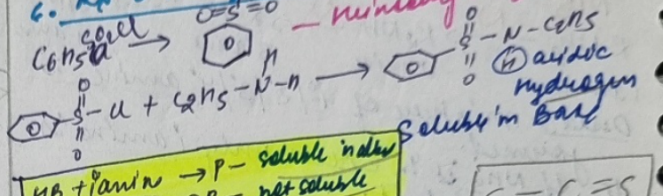
1° amine

$R_2NH + HNO_2 \longrightarrow R_2N-NO$ yellow oily substance

Liebermann nitrous Test — N-nitrosoamine

$R_3N + HNO_2 \longrightarrow R_3NH\,NO_2$ soluble in H_2O

6. Rxn with Benzene sulphonyl chloride



Hinsberg Reagent

Alkaline hydrolysis

Soluble in Base

NB + 1° amine → P – soluble in alkali

NB + 2° amine → P – not soluble

NB + 3° amine → P – Y

7. Hoffman Mustard oil Rxn

Hoffmann mustard oil Rxn

$RNH_2 + CS_2 \longrightarrow R-NH-\overset{S}{\overset{\|}{C}}=SH \xrightarrow{HgCl_2}$ mercuric Cl

$R_2NH + CS_2 \longrightarrow R_2N-\overset{S}{\overset{\|}{C}}=SH \xrightarrow{HgCl_2}$ Hg

$R_3N + CS_2 \longrightarrow X$

$R-N=C=S$ isothiocyanate mustard oil smell

CS_2 + 1° amine → $HgCl_2$ → isothiocyanate

CS_2 + 2° amine → precipitate

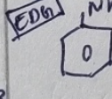
CS_2 + 3° amine → No

$S=C=S$

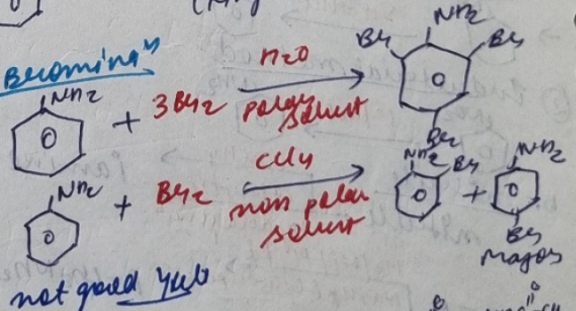
Benzene Rxn

Electrophilic substitution Rxn

EDG → +m → ortho / para directing (powerful activating group) (Ring is high dense)



1. Bromination

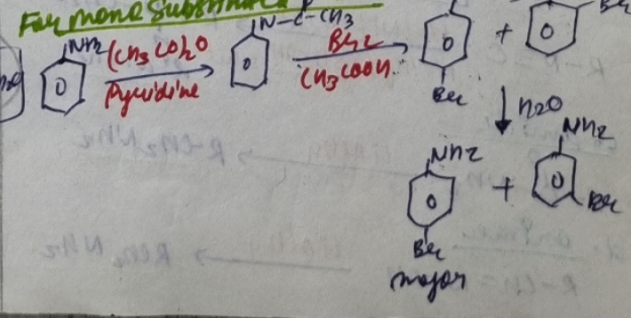


Polar solvent

Non polar solvent

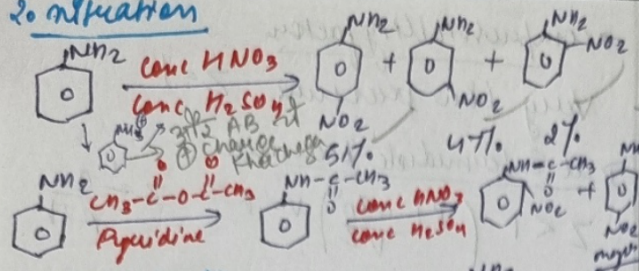
not good Yield

For mono substituted aniline

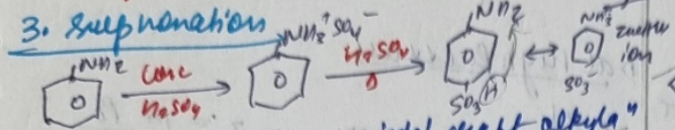


Major

2. Nitration



3. Sulphonation



aniline doesn't give friedal craft alkyla" on acylation as it form salt ē H_2O_3

Diazonium salt

$C_6H_5N_2^+Cl^-$ → Benzene diazonium chloride

$C_6H_5N_2^+HSO_4^-$ → Benzene diazene hydrogen sulphate

→ 1° aliphatic amine → highly unstable due to Resonance
2° aliphatic amine →

Prep^n :-

Diazotization :-

$C_6H_5-NH_2$ (amine) $\xrightarrow[HNO_2\ \Delta]{NaNO_2 + HCl}$ $C_6H_5N_2^+Cl^- + NaCl$

Physical prop :-

→ Benzene diazonium chloride — colourless.

→ soluble ē H_2O & stable in cold but when it warm it React ē H_2O

$C_6H_5N_2^+Cl^- \xrightarrow[warm]{H_2O} C_6H_5OH$

Benzene diazonium fluoroborate is H_2O insoluble

Chemical Ry^n

1. Displacement of N_2

Sandmeyer Ry^n

$C_6H_5N_2^+Cl^-$

- Cu_2Cl_2/HCl (cuprous chloride) → $C_6H_5Cl + N_2\uparrow$
- Cu_2Br_2/HBr → $C_6H_5Br + N_2\uparrow$
- $CuCN/HCN$ → $C_6H_5CN + N_2\uparrow$ (nitrile group)

Gattermann

$C_6H_5N_2^+X^-$

- Cu/HCl → C_6H_5Cl
- Cu/HBr → C_6H_5Br

Cu → Cu powder

Sandmeyer Ry^n me Better Yield than gattermann

$C_6H_5N_2^+Cl^- + KI \longrightarrow C_6H_5I + N_2\uparrow$

$C_6H_5N_2^+Cl^- + HBF_4 \longrightarrow C_6H_5F + N_2\uparrow$

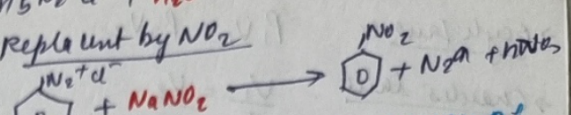
$C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2\uparrow + H_3PO_3 + HCl$

$C_6H_5N_2^+Cl^- + CH_3CH_2OH \longrightarrow C_6H_6 + N_2 + CH_3CHO + HCl$

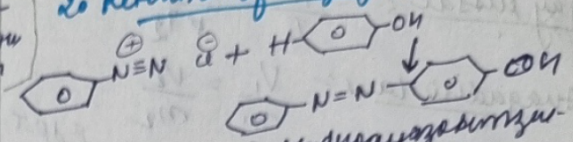
Replacement by OH^-

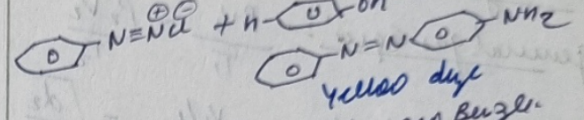
$C_6H_5N_2^+Cl^- + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$

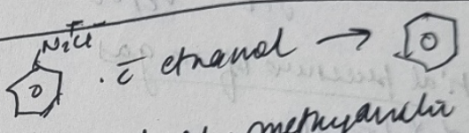
Replacement by NO_2



2. Retention of diazo grp — coupling Ry^n







→ Aniline & N-methylaniline can be chemically distinguished by CH_3I / KOH

→ Hinsberg Reagent is $C_6H_5SO_2Cl$

→ 3° amines are most Basic in gas phase

