ExamsRoad.com

Organic Chemistry

GOC

● Electronic Effect : → ● Inductive effect $-C-C-C-\overset{\delta+}{C}\rightarrow\overset{\delta-}{X}$ • Permanent, Partial displacement of electron pair towards more electronegative. [• Not at electron]

- Inductive effect] Permanent effect
- Resonating effect
- Hyperconjugation
- Mesomeric effect] Temporary.

• Arises due to EN difference, Alkanes are nonpolar. • It is a distance dependent effect.
• I effect works till the 3rd Carbon of Chain, after that its negligible.
• Since σ electrons are displaced partially, hence partial charges are created.

● I effect [e^- donating] [e^- withdrawing]
- +I effect
- −I effect

● EN with S character ~~$sp^2 > sp$~~ $sp > sp^2 > sp^3$

• −I effect $-\overset{+}{N}R_3 > -\overset{+}{S}R_2 > -\overset{+}{N}H_3 > -NO_2 > -SO_3H > -CN$ $-CHO > -COOH > F > Cl > Br > I > OR > OH > -C\equiv CH > NH_2 > C_6H_5 > -H$

• +I effect $-\overset{\ominus}{O} > -COO^{\ominus} > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2-CH_3 > -CH_3 > -D > -H$

● Exception $\overset{\delta-}{CH_3-CH_2-CH_2}\leftarrow\overset{\delta+}{Mg}X$ [Here Mg is a metal which is electropositive and thus it gives electron. This alkyl group has to accept the electron.]

● +I groups (Alkyl groups are generally +I groups) Primary < Secondary < Tertiary

- $-CH_3$
- $-CH_2-CH_3$
- $-CH_2-CH_2-CH_3$

+I effect (∝ No of C) ↓

● If a group is overall −ve, it shows +I, no matter what $O^- > COO^-$ ⁄⁄⁄⁄⁄C(=O)O⁻ Na⁺

If a group has overall +ve, it's +I group → EN: $O^+ > O^-$ EN: $\underset{sp^2}{O^+} > \underset{sp^2}{N^+} > \underset{sp^3}{O} > \underset{sp^3}{N}$ $sp^2 > sp^3$

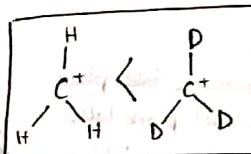
● −I effect (more EN elements)

- $F-CH_2-$
- $F-\overset{F}{CH}-$
- $F-\overset{F}{\underset{F}{C}}-$

−I effect ↓

• If a group has overall +ve charge after octate $[H_3O^{\oplus} / NH_4^{\oplus}]$
• High EN elements like O/N can accumulate +ve charge. But without octate, it is highly unstable. $[CH_3-\overset{+}{\ddot{O}}:]$

~~Application of I effect~~


Since +I of D > +I of H^+

● Application of I effect
• Stability of Carbocation $R_2-\overset{R_1}{\underset{R_3}{C^{\oplus}}}(3°) > R_1-\underset{R_2}{C^{\oplus}}(2°) > R_1-C^{\oplus}(1°) > \overset{\oplus}{C}H_3$ $[sp^2]$
• Stability of Carbanion $R_1-\overset{R_2}{\underset{R_3}{C^{\ominus}}}(3°) < \overset{R_1}{\underset{R_2}{}}C^{\ominus}(2°) < R_1-C^{\ominus}(1°) < \overset{\ominus}{C}H_3$ $[sp^3]$

● Bond Cleavage ● Homolytic bond cleavage : $A \frown B \xrightarrow[\text{or } \Delta]{h\nu} \dot{A} + \dot{B}$ [Both neutral] [When diff in EN is negligible]
• Heterolytic bond cleavage: $A \frown B \xrightarrow{(pps)} \overset{\oplus}{A} + \overset{\ominus}{B}$ [EN: A < B]

● Solvent
- → Non polar ($\mu = 0$) e.g. CCl_4, benzene
- → Polar solvent
  - → Polar protic (Can form H bond) (Can donate proton) [Contains HF/H-O, H-N]
  - → Polar aprotic (Can't form H bond) (Can't donate proton) e.g. Acetone, $H-\overset{O}{C}-N\langle^{CH_3}_{CH_3}$ [Dimethylformamide]

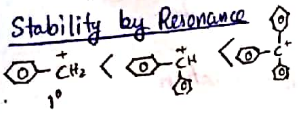
● Reaction Intermidiate
- Carbocation $-\overset{+}{C}-$ (+ve on C)
- Carbanion $-\overset{-}{C}-$ (−ve on C)
- Free radical $-\dot{C}-$ (single e^- on C)
- Carbene $H-\ddot{C}-H$ [lp on C with incompl't octate]
- Nitrene $R-\ddot{N}:$ [lp on N]
- Benzyne [Benzen w/ one triple bond]

Also known as Baker-Nathan effect or No bond resonance or σ−π conjugate

● Carbocation Stability can be explained by • Resonance • Hyperconjugation • Inductive effect
• For Hyperconjugation: there should be a sp^3 C containing at least one H adjacent to a sp^2 C $[\overset{\oplus}{C}H_2-C\langle H$ → Alpha C [Adjacent to C^+] → Alpha H [Adjacent to C]
• Stability » $3° > 2° > 1° > \overset{\oplus}{C}H_3$
$-\overset{\oplus}{C}-$ → sp^2 (Trigonal planner, Bond Angle = 120°)
• Vacant p orbitals →

Relative order: Resonance > Hyperconjugation > Inductive

Stability by Resonance


1°

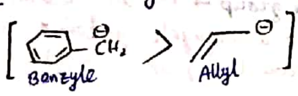
• 0 π bond on C → sp^3 (All single bond)
• 1 π bond on C → sp^2 (A double bond)
• 2 π bonds on C → sp (A triple or two double bond)

$\underset{(sp^2)}{CH_2}=\underset{(sp^2)}{CH}-\underset{(sp^3)}{CH_3}$
$\underset{(sp^3)}{CH_3}-\underset{(sp^3)}{CH_2}-\underset{(sp^2)}{\overset{\ominus}{C}H_2}$

● Carbanion ● Stability can be described by → ● Resonance ● Inductive effect [Stability → 1° > 2° > 3°]

$-\overset{\ominus}{C}-$ sp^3 (Tetra (Pyramidal)

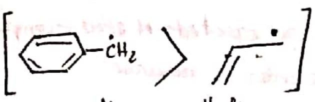
[Benzyle > Allyl]



● Free Radicals ● Stability can be explained by → ● Resonance ● Hyperconjugation ● Inductive effect.

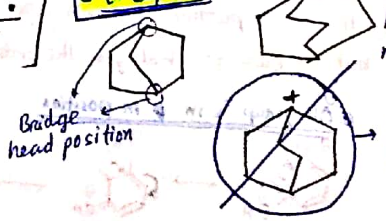
$-\dot{C}-$ sp^2 (Trigonal Planar)

[Benzylic > allylic]



$[3° > 2° > 1° > \dot{C}H_3]$

● Exception

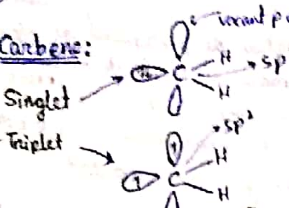


[If there is a free radical at bridge head position, its hybridization is sp^3 [co-planarity is not possible]

At bridge head position, carbocation isn't formed because of lack of co-planarity.

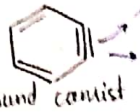
Q

Carbene:



Stability: [Triplet > Singlet]
Due to more e–e repulsion]

Benzyne



π bond due to hybridised orbital overlapping

- Only compound consist of π bond due to hybridised orbital overlapping
- These π e's do not participate in resonance.
- Phenol is more acidic than alcohol
- Stability decreases with increasing charge density.
- Aliphatic amines are more basic than aromatic amines. ($R-\ddot{N}H_2$ > $\phi-\ddot{N}H_2$)
- EWG increases acidic character
- EDG decreases acidic nature.

Exception

$C-C-\overset{\ominus}{C}$ (I) with NO_2 — [F has weak –I effect than NO_2 but (II) will be more stable since F is in a closer distance w/ $C^{\ominus}$]

$C-C-\overset{\ominus}{C}$ (II) with F

Resonance

- When resonance takes place, the stability of molecule becomes higher.
- Bond length becomes unexpected.
- Different Lewis structures are possible but imaginary. Real structure can't be drawn, resonating structures.

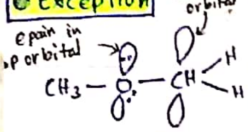
Stability: Aromaticity > Equal resonance > Resonance > Hyperconjugation > Inductive Effect [A,E,R,H,I]

When resonance takes place

Only in conjugated system (‖ p orbitals w/ π e⁻)

Conjugates » • $=-\oplus$ • $=-\ominus$ • $=-\odot$ • $=-=$ • $=-=$
• $(\cdot\cdot)-\oplus$ • $(-)$ — (vacant d orbital)

Exception



[Here resonance takes place in 2 parallel p orbitals. Normally resonance takes place b/w 3 parallel p orbitals]

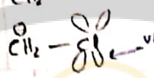
$CH_3-\ddot{O}-\overset{\ominus}{C}H_2 \leftrightarrow CH_3-\overset{+}{O}=CH_2$

[Because of shifting electron, +ve charge develops over oxygen atom, oxygen can form 2 bonds normally but it can form 3rd bond by giving its lone pairs in contribution along with +ve charge which will be present on the oxygen. Covalency = 3]

-ve charge and vacant d orbital

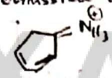
$\overset{\ominus}{C}H_2-Cl \longleftrightarrow CH_2=Cl^{\ominus}$ (II) — $\overset{\ominus}{C}H_2-F \longleftrightarrow CH_2=F$ (I)

[Considering Inductive effect. Stability of I > II but since chlorine has vacant d orbital, it forms resonating structure and thus becomes more stable.



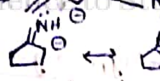
• $\overset{\ominus}{C}H_2-CF_3$; $\overset{\ominus}{C}H_2-CCl_3$ (I) (II) [Here d orbital is not adjacent so resonance doesn't take place. only –I effect is operating]
[(I) > (II)]

• Any structure violating the fundamental rule of structure writing is not permissible as RS.


$\overset{\oplus}{N}H_3$ → Not an RS cos max valency of N is 3. [non polar thus stable]

• like or unlike charges of adjacent carbons make the structure highly unstable thus cannot be RS.
[$\overset{\oplus}{C}H_2-\overset{\ominus}{C}H_2-CH=CH_2$; $\overset{\ominus}{C}H_2-\overset{\oplus}{C}H-CH=CH_2$; $\overset{\ominus}{C}H_2-\overset{\oplus}{C}H-\overset{\ominus}{C}H-\overset{\oplus}{C}H_2$; $\overset{\oplus}{C}H_2-\overset{\ominus}{C}H-\overset{\oplus}{C}H-\overset{\ominus}{C}H_2$]

Relative Stability of Resonating Structure

1. The more covalent bonds a structure has, more stable it is; $H_2C=CH-CH=CH_2$ (More Stable) ⟷ $H_2\overset{\ominus}{C}-CH=CH-\overset{\oplus}{C}H_2$ (6e⁻)
2. Atom which have complete valance shell of electrons are more stable; $H_3C-\ddot{O}-\overset{\oplus}{C}H_2$ (6e⁻) ⟷ $H_3C-\overset{\oplus}{O}=CH_2$ (8e⁻) (More stable)
3. Charge seperation decreases stability:  [I > II > III]
4. -ve charge if present in more EN atom are more stable; 

Electromeric Effect

It is a temporary delocalisation of π-electron in compounds. Occurs only when a reagent is added and vanishes when the attacking reagent is removed.

Mesomeric Effect: For the ~~moment~~ permanent polarisation of a group conjugated with a π bonds, delocalisation of π-e's occurs consecuently, and this type of π-e's delocalisation in the conjugate system is called mesomeric effect or conjugate effect.

(+M) $CH_2=CH-CH=CH-\ddot{N}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH-CH=\overset{\oplus}{N}H_2$

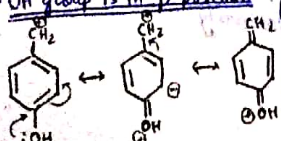
+M donor group → The first atom linked to a conjugate system should have lone pair.

→ The group which completely transfer the electron to conjugate system through resonance is called +M group.

(–M) → Group which completely withdraws the electrons from conjugate system is called –M group.
→ There is unsaturation in between 1st and 2nd atom

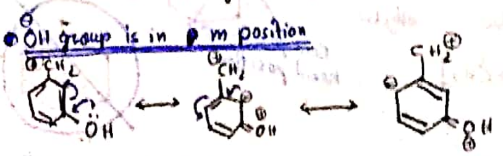
- In Inductive effect only partial displacement of electrons, so partial charges are created; M effect → complete.
- Normally M effect is predominant over I effect but in case of halogen, the order is reverse.

ÖH group is in p position



[This means that if there is a group which is present in para position (say OH).
Then its +M and –M effect reaches to the group (CH_2)]

ÖH group is in m position



[Here +M effect will also work in m position but it will not affect +ve charged Carbocation $\overset{\oplus}{C}H_2$]

Hyperconjugation • In resonance only π electrons participate but σ electrons do not participate, but in hyperconjugation σ electrons also are involved. • In case of hyperconjugation if any +ve charge which is directly connected with a sp^3 carbon having at least one CH, then σ electron pair of CH bond sacrifices and shifts towards next carbon to form π bond.

$-\overset{H}{C}-\overset{\oplus}{C}H_2 \longleftrightarrow -\overset{H^\oplus}{C}=CH_2$ [This is called σ-p overlap or σ-p resonance]

• The $H^\oplus$ remains without having any body, it is known as no bond resonance, it is also called Baker-Nathan effect.

$-\overset{H}{C}-CH=CH_2 \longleftrightarrow -\overset{H^\oplus}{C}=CH-\bar{C}H_2$ [Here sp^3 carbon directly connected with double bond]

• Hyperconjugation is possible only when an sp^3 carbon with at least one CH bond is directly connected w/ C. • Having vacant p • bonded P • Half filled • Not fullfilled

• Only carbocations and free radicals, alkenes show hyperconjugation, not carbanion

No of α H → no of Hydrogen on α C (adjacent Carbon)
[No of α Hydrogen ∝ Stability]

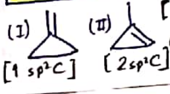
Rules of Stability [A > E > R > H > I] (E → Electromeric effect)
A → Aromaticity; R → Resonance
H → Hyperconjugation; I → Inductive effect

Important Points
+I effect $-D > -H$
+I effect $-CD_3 > CH_3$
+HC effect $-CD_3 < CH_3$
Bond energy $C-D > C-H$

[3 membered ring never wants to be sp^2 with 60° instead of the desired 120°, it increases angle strain]

Exception $CCl_3-\overset{\oplus}{C}H-CH_3$ (I) ; $CCl_3-CH_2-\overset{\oplus}{C}H_2$ (II)
According to no of α-H, (I) should be more stable than (II), but NO!! [Because of −I effect of CCl_3, the stability of (I) is less. The same −I effect is less prominent in case (II) since the dist. of Cl_3 group from carbocation is more in case of (I).

Exception A > E > R > H > I
Inspite of having less α-H, stability of (I) > (II)
[Inspite of having less α-H, stability of (I) > (II) cos angle strain is more in more in (II)]


(I) [1 sp^2C] (II) [2 sp^2C]

Heat of Hydrogenation
$\Delta H \propto \frac{1}{\text{stability of Alkene}}$

$H-\overset{H}{\underset{H}{C}}-CH=CH_2$
• C=C longer than expected
• C−C shorter than expected
• C−H involved in hyperconjugation. (longer than usual)

$CH_2=CH_2 \xrightarrow[H^+/Br^-]{HBr} [\overset{\oplus}{C}H_2-\underset{Br}{CH_2}] \xrightarrow{Br^\ominus} \underset{Br}{CH_2}-\underset{H}{CH_2}$

Electromeric Effect • It is a temporary effect that arises as per the demand of the reagent.
• As soon as the reagent is consumed, the effect vanishes.
• $CH_2=CH-CH=CH_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH-\overset{\oplus}{C}H_2$ — This bond is shorter than single σ bond.

Acidic Strength (Aromatic Acids)

(Benzoic Acid)
• If EWG grp is present in o/m/p in benzoic acid, the acid becomes stronger than Benzoic Acid.
• If ERG (E releasing G) grp is present in o/m/p in benzoic acid, it becomes weaker than Benzoic Acid.

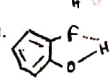
Dipole Moment
$\overset{\delta+}{A}\longrightarrow\overset{\delta-}{B}$
$\mu = q \cdot d$ (dist in m; Charge in C)

Points to RMbee
• All aliphatic Alcohols are weaker acids than H_2O, CH_3OH is an **exception**.
• As the degree of Alcohol increases, the strength goes on decreasing.
• Inorganic acids are very strong, formic acid is weaker than aliphatic acids. **[Exception]**
• Phenol is more acidic than aliphatic alcohol and H_2O.
• All aliphatic alcohols are weaker than acids but CH_3OH is an **Exception**.

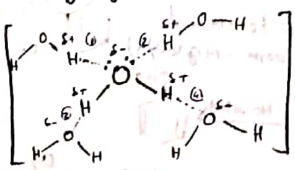
Aro > Meso > Reso > Hyper > Electro > Inductive

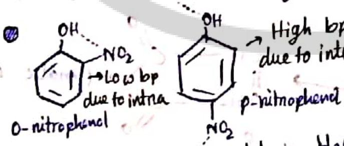
Hydrogen Bonding: [F, O, N — H ····· F, O, N] • H-bond strength → F > O > N
$\overset{+\delta}{H}-\overset{-\delta}{F}\cdots\overset{+\delta}{H}-\overset{-\delta}{F}$ [10 kcal/mol] $H-O\cdots H-O$ [7 kcal/mol]
$H-N\cdots H-N$ [5 kcal/mol]
• No hydrogen bond in solid state.

Hydrogen Bond
- Intermolecular [eg. H−F···H−F, H−F···H−O−H]
- Intramolecular [eg.]



• Intermolecular H-bonding increases boiling point.
• H_2O, H.bond = 4

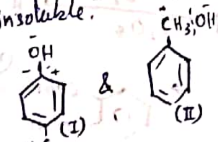




Alcohols have HB not ethers
C_2H_5 H bonded w/ O — Alcohol
CH_3-O-CH_3 No HB cos H are bonded with C — ether

• Molecules with HB is soluble in H_2O, without HB, insoluble.

Q $CH_3-CH_2-CH_2-OH$ & $CH_3-\underset{OH}{\overset{+}{C}H}-CH_3$
In this, the C_2H_5 will decrease the + a lil bit, so • elimination of OH is difficult. i.e. H bond will stay. (High b.p.)
In this 2 CH_3 will decrease the + more, so escape of OH is easier, i.e • OH will H bond escape, so will H bond (Low b.p)

Q

(I) & (II)
In (I) the bond is difficult to break. In (II) the + on CH_3 will cause Resonance so it is easier for OH to escape.

HB in Amines
$CH_3-CH_2-NH_2$ (2H) & $(CH_3)_2NH$ (1H)
Accordingly properties.

More than 1 OH on a C is not allowed
$CH_3-CH(OH)_2 \rightarrow CH_3-CHO + H_2O$
$CH_3-C(OH)_3 \rightarrow CH_3-\overset{O}{C}-OH + H_2O$
$C(OH)_4 \rightarrow O=C=O + 2H_2O$
HB is helping the breaking

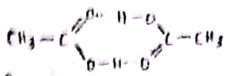
Q $CH_3-CH(OH)-NH_2$
Possibilities: $CH_3-CHO + NH_3$ ✓ ; $CH_3-CH=NH + H_2O$ ✗
[This one will not form cos H_2O is a better acid than NH_3, so it will be more stable]
Leaving tendency ∝ Acidic character

Exception Stable with 2OH
$Cl-\overset{Cl}{\underset{Cl}{C}}-CH(OH)_2$
Not HB (Polar-Polar) Due to Polar Polar attraction, it is stable.

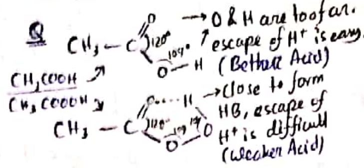
• $CH_3-\overset{O}{C}-COOH \xrightarrow{\Delta} X$
• $CH_3-\underset{\beta}{C}-CH_2-COOH \xrightarrow{\Delta} CH_3-\overset{O}{C}-CH_3 + CO_2$
$CH_3-CH(COOH)_2 \xrightarrow{\Delta} CH_3-CH_2-COOH$
• $CH_2(COOH)_2 \xrightarrow{\Delta} O=C=C=C=O$ [C_3O_2] Carbon Suboxide
$\rightarrow O=C=C=C=O$ (Ox. no +2, 0, +2)

(a) Q  $\xrightarrow{\Delta}$ Ph–CH_3 [1st CO_2 is going cos of heat, 2nd one cos there is double bond at β position]

- CA always form dimer



[They become very heavy and they have very high bp]

Q 

→ O & H are too far, escape of H^+ is easy (Better Acid)

→ Close to form HB, escape of H^+ is difficult (weaker Acid)

- HF forms dimer (H_2F_2) Strong Acid $\Delta H_{neut} = -13.7$

$HF + NaOH \longrightarrow NaF + H_2O$

$H{-}F \cdots H{-}F + NaOH \rightarrow NaHF_2$

Although very weak acid, it has numerically highest $\Delta H_{neut} = -18.4$

[Cos it forms HB w/ H_2O, thus the processes of neut and hydration both occur at once, causing more energy release]

- HF dissolves glass [$HF + SiO_2$]

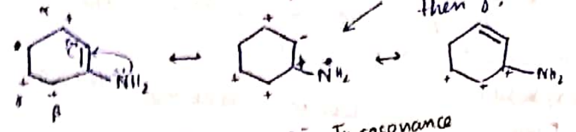
- **Mesomeric Effect:** Resonance → $CH_2{=}CH{-}CH{=}CH_2$ | Meso → $CH_2{=}CH{-}\ddot{N}H_2$

+M [$-\ddot{O}H$, $-\ddot{O}-CH_3$, $-\ddot{N}H_2$, –Ph] → Ring activating [$-\ddot{N}H_2 > -\ddot{O}H > -\ddot{O}CH_3$]

[–Ph > $-CH{=}CH_2$]

–M [NO_2, CHO, COOH, NH_3^+] → Ring deactivating.

e withdrawing (+ve charge or unsaturation)

Q 

α is most stable, then β, then γ.

- **Stability of Carbocation:** (a) $CH_3-CH_2^+$ (b) $\ddot{N}H_2-CH_2^+$

b/w (a) and (b), (b) is more stable cos, the lone pair on $\ddot{N}H_2$ will completely nullify the +ve charge.

Q (a) $\ddot{N}H_2-CH{=}CH-\overset{+}{C}H_2 \leftrightarrow \overset{+}{N}H_2{=}CH-CH{=}CH_2$ ← stabilising

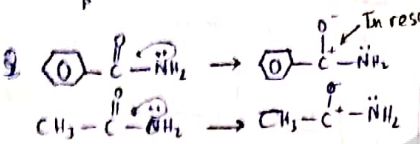
(b) $CH_2{=}C(\ddot{N}H_2)-\overset{+}{C}H_2 \leftrightarrow \overset{-}{C}H_2-C(NH_2)-CH_2^+$ ← destabilising

- **Acidic Nature of OH**

$CH_3 \rightarrow CH_2 \rightarrow \bar{O}\,H^+$

$CH_2{=}CH-\bar{O}\,H^+$

–ve in 2nd one is in resonance thus more acidic

Q 

In resonance

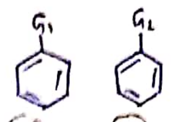
The +ve charge in the 2nd one will pull the lone pair on NH_2 but the +ve charge will be in resonance. So the removal of lone pair from 1st one is easier. More Basic (1)

Q $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$

$CH_2{=}CH-\ddot{N}H_2$

In first the O–C bond is polar, the O helps the transfer of electrons pair. In second the C–C bond is almost non polar.

- **Aromatic Compounds (EAS)**

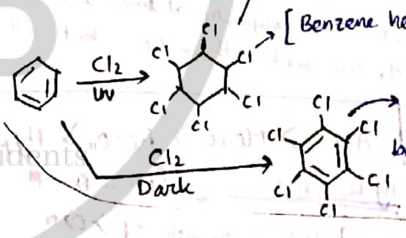


(+M) Ring Activating, O-P director | (–M) Ring Deactivating, M director

- Reduction of di-azonium salt: $PhN_2Cl \xrightarrow[H_2O]{H_3PO_2}$ Ph–H $+ H_3PO_3$

- $PhSO_3H \xrightarrow{NaOH} PhSO_3Na \xrightarrow{NaX} PhX + Na_2SO_4$; $\xrightarrow{H_2O}$ PhOH

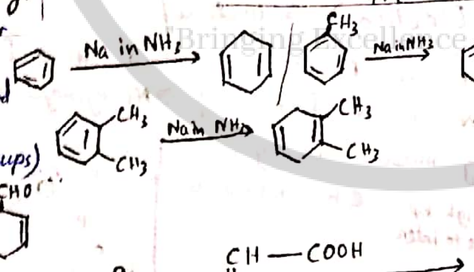
- Catalytic Reduction: benzene $\xrightarrow[\text{or } H_2/Pt]{H_2/Ni}$ cyclohexane



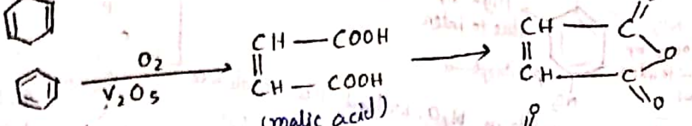
Also known as 666 [$C_6H_6Cl_6$] and gamaxin [Benzene hexa chloride] (BHC)

[Hexa chloro benzene (HCB)]

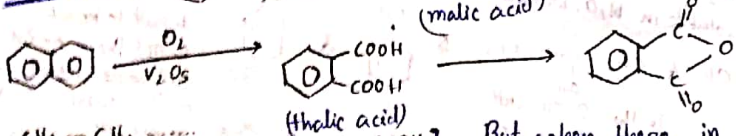
- **Birch Reduction** (Makes π bonds || and gets close to +M and further from –M groups)



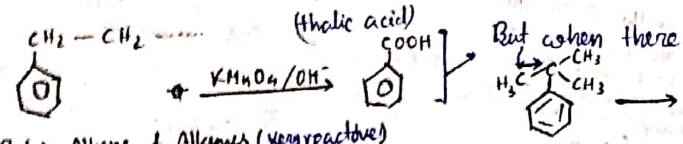
- **Oxidation:**



(malic acid) (malic anhydryte)

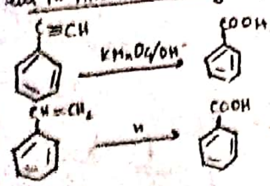


(thalic acid) (Tnalic anhydrate)



But when there is no benzylic hydrogen → Benzene ring will get oxidised.

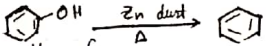
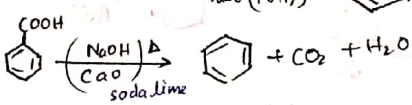
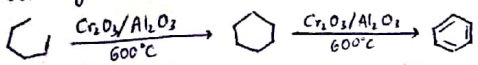
But in Alkene & Alkynes (very reactive)



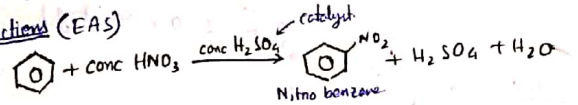
- All +M groups are ortho-para directing and ring activating
- All –M groups are meta directing and ring deactivating

Exception: All halogens are ortho-para directing cos they are all +M groups, but due to their high –I effect, they are ring deactivating group

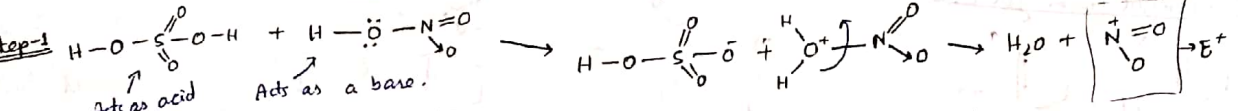
Preperation

- $CH \equiv CH$ passed over thru red-hot iron/Cu tube under high T and P, $3CH \equiv CH \xrightarrow[\text{tube (P\&T)}]{\text{iron}}$ 
- Phenol heated with Zn dust. 
- Decarboxylation of Na or K salt of benzoic acid, 
- 

Other Reactions (EAS)

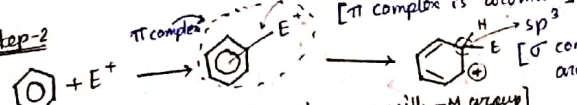
- **Nitration:** 

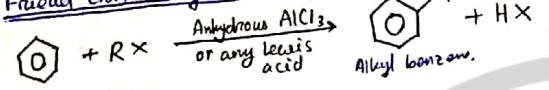
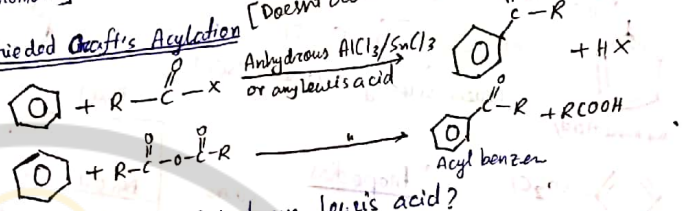
Every Electrophilic Aromatic Substitution (EAS) follows →
(i) Generation of E^+
(ii) Formation of σ complex through π complex (rds)
(iii) Loss of H^+ from the sp^3 hybridised C of σ complex

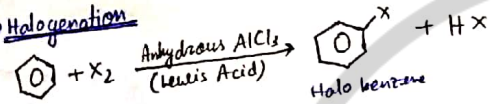
- **Step-1** 

→ Why H_2SO_4 acts as acid not HNO_3

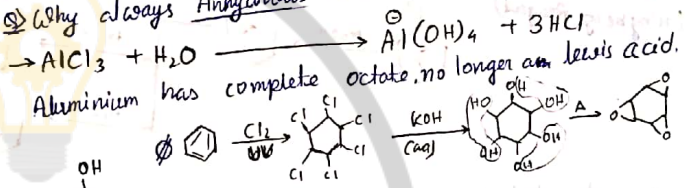
On removal of H^+, H_2SO_4 gives a resonatically more stable conjugate base.

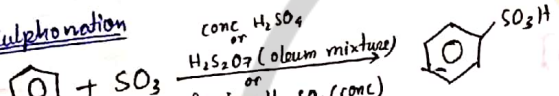
- **Step-2** 

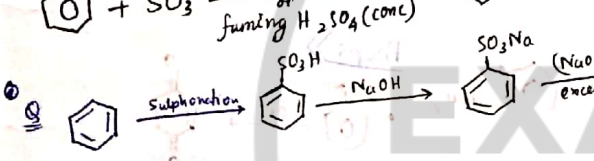
- **Friedel Craft's Alkylation** [Doesn't occur with −M group] 
- **Friedel Craft's Acylation** [Doesn't occur with −M group] 

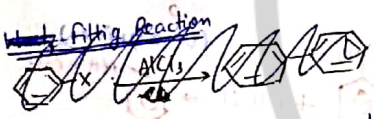
- **Halogenation** 

Why always Anhydrous Lewis acid?

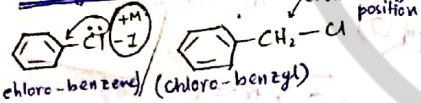


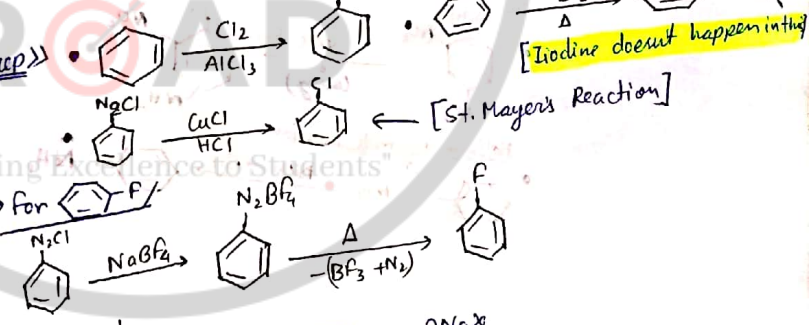
- **Sulphonation** 



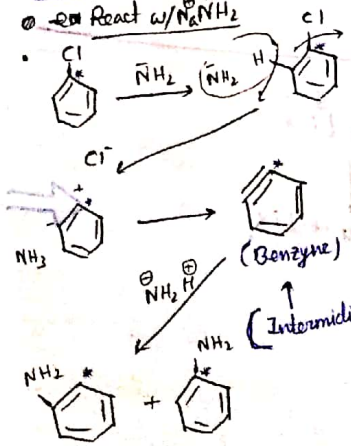
- **Fitting Reaction** 

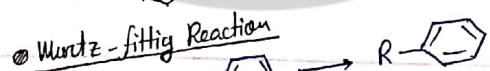
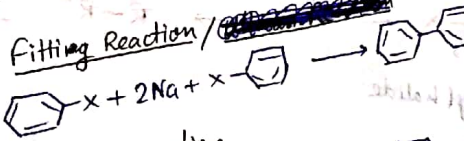
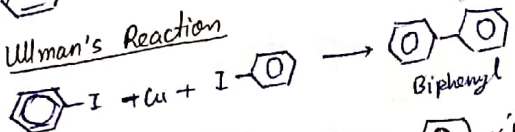
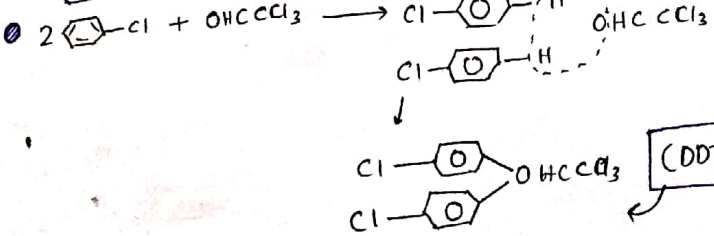
Halogen Compounds of Aromatics

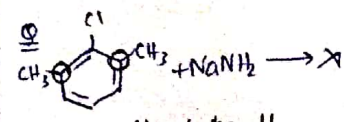


Prep: 

Properties (Chemical)

- React w/ $NaNH_2$ 

- **Wurtz-fitting Reaction** 
- **Fitting Reaction** 
- **Ullman's Reaction** 
- 



because there's no H adjacent to Cl

ALKANE

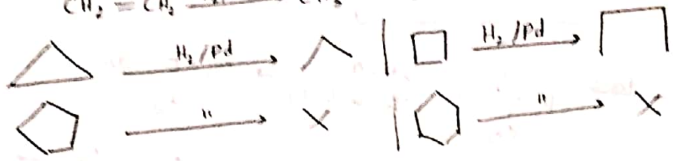
due to large surface area.

- General form → C_nH_{2n+2}
- b.p (symmetric > asymmetric)
  C-C-C-C-C   C-C-C-C-C
- Fuel → octane no (petrol)
  cetane no (diesel)
- Also called paraffins
- Used as fuels [CH_4 (85%) → CNG]
- mp → $C_4 > C_3$ | $C_4 > C_6, C_5$ (less repulsion)
- Nonpolar
- b.p → (st. chain > branched)
- LPG contains Butane / Isobutane

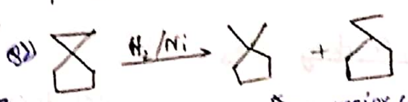
PREP → (Reduction alkene & alkyne) → $CH\equiv CH \xrightarrow{H_2/Pd} CH_2=CH_2 \xrightarrow{H_2/Ni} CH_3-CH_3$

$CH_2=CH_2 \xrightarrow{H_2/Ni} CH_3-CH_3$

- From unsaturated (cyclic) →



[Cos in 3,4 member chain, angle strain is high, but 5,6 are stable]

Q))  ← major cos symmetric

- $>C=O$ → Zn-Hg / HCl (clemmensen reduction); P/HI (Best reducer); NH_2NH_2 / Base (Wolff-Kishner reduction) → $>CH_2$

only this can reduce — only by P/HI:
[RCOOH → $R-CH_3$
RCOCl → $R-CH_3$]

- Reduction of Alkyl halide → $CH_3-CH_2-Cl \xrightarrow[\text{or } Zn/HCl]{LiAlH_4 \text{ or } NaBH_4} CH_3-CH_3$

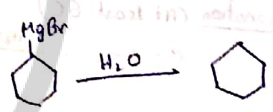
LiAlH₄		NaBH₄		Zn/HCl	
P/S	Alkane	P	X	P/S/T	Alkane
T	Alkene	S/T	Alkane		

Q)) $CH_3-C(CH_3)(Cl)-CH(Cl)-CH_2-Cl \xrightarrow{LiAlH_4} CH_3-C(CH_3)=CH-CH_3$ (T, S, P)

$\xrightarrow{NaBH_4} CH_3-CH(CH_3)-CH_2-CH_2-Cl$

- From Grignard Reagent

$RMgX + S-H / O-H / N-H / CH\equiv C-H \longrightarrow R-H$

Q)) 

- Decarboxylation

$CH_3COOH \xrightarrow[\text{lime}]{\text{Soda}} CH_4$ (NaOH, CaO ← absorbs water)

Mech: $CH_3COO-H + \overset{\ominus}{HO}\overset{\oplus}{Na} \xrightarrow{-H_2O} CH_3COONa + NaOH \rightarrow CH_4 + Na_2CO_3$

- Wurtz reaction

$R-X + 2Na + X-R \xrightarrow[\text{ether}]{\text{dry}} R-R + 2NaCl$ [CH_4 can't be formed, CH_3-CH_3 is best produced]

Mech: $CH_3-Cl + 2Na + Cl-CH_3$ → $R^{\ominus}Na^{\oplus} + X^{\ominus}Na^{\oplus}$ (salt)

$2Na \longrightarrow 2Na^+ + 2e^-$

Another prep: $R-X \xrightarrow{2e^-} \overset{\ominus}{R} + \overset{\ominus}{X}$ (carbanion) → $R^{\ominus}$, $Na^{\oplus}$

(SN2) Nucleophile $R^{\ominus}$: $\overset{\delta+}{R}-\overset{\delta-}{X} \longrightarrow R-R + NaX$

Ex)) $CH_3CH_2Cl + 2Na + CH_3CH_2Cl \longrightarrow CH_3CH_2CH_2CH_3$

[Halogen bonded with double bonded C can't leave.]

$Na \longrightarrow Na^+ + e^-$

$CH_3CH_2Cl \longrightarrow CH_3\overset{\ominus}{C}H_2 + Cl^{\ominus}$ → $Na^{\oplus}$ → NaCl

$CH_3-\dot{C}H_2 + \dot{C}H_2-CH_3 \longrightarrow$ [$CH_3-CH_2-CH_2-CH_3$] main product

$CH_3-\dot{C}H_2$ → $\dot{C}H_3-CH_3 \longrightarrow$ [CH_3-CH_3] By product

H· → $H-CH_2-\dot{C}H_2 \rightarrow H_2\dot{C}-\dot{C}H_2 \longrightarrow$ [$CH_2=CH_2$] By product

● **Kolbe's Electrolysis:** CH_3COONa, CH_2COONa (aq) $\xrightarrow{\text{Electrolysis}}$ CH_3-CH_3 (Anode) + CO_2 + $NaOH$ + H_2 (Cathode)

[Turn to previous note] Afterwards...

Continuing chemical properties

● **Combustion** $CH_4 + O_2$ (suff) $\longrightarrow CO_2 + H_2O$

$CH_4 + O_2$ (insuff) $\longrightarrow C + H_2O$ / $\longrightarrow CO + H_2O$

$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$ ← General equation of comb of hydrocarbon

$CH_4 + O_3 \longrightarrow$ (cyclic intermediate with HO, HO, H, H, C) $\longrightarrow HCHO$

$CH_4 \xrightarrow{1600°C,\ O_2} HC\equiv CH$

● **Only if 3° C is there** $(CH_3)_3C-H \xrightarrow[(1\%\ \text{alkaline})]{KMnO_4} (CH_3)_3C-OH$

● **Pyrolysis / Cracking** $CH_3-CH_2-CH_3 \xrightarrow{\Delta} CH_2-CH_2 + \dot{C}H_3 \longrightarrow CH_2=CH_2 + CH_4$ (H)

● **Isomerisation** $C-C-C-C \xrightarrow[\Delta]{AlCl_3/HCl} C-C(-C)-C$

● **Aromatisation** (6C) $\xrightarrow[600°C]{Cr_2O_3+Al_2O_3}$ benzene; $\xrightarrow[600°C]{Cr_2O_3+Al_2O_3}$ naphthalene

(7C) $\xrightarrow{\text{"}}$ toluene

Mechanism: $\xrightarrow{\Delta}$ $\cdot CH_2-CH_2\cdot$ $\longrightarrow$ $\xrightarrow{\Delta}$

● **Nitration** $CH_3-CH_3 \xrightarrow{HNO_3} CH_3CH_2NO_2 + CH_3NO_2$ [Reaction as well as cleavage]

$CH_3-CH_2-CH_3 \xrightarrow{HNO_3} CH_3CH_2CH_2NO_2 + CH_3-CH(NO_2)-CH_3 + CH_3CH_2NO_2 + CH_3NO_2$

● **Sulphonation** (At least 6C) $C-C-C-C-C-C \xrightarrow{H_2SO_4} C-C-C-C-C-C$ (SO_3H at any carbon)

$C-C-C \xrightarrow{H_2SO_4} \times$ Not for 3°C

$C-C(-C)-H \xrightarrow{\text{"}} C-C(-C)-SO_3H$

ALKENE

- General formula → C_nH_{2n} • Also known as olefins • Stable by resonance or hyperconjugation
- Stability → trans > cis (in open chain) & cis > trans (in closed chain)

PREPS »

Reduction of Alkyne: $CH_3-C\equiv C-CH_3$

- Lindlar cat. ← H_2/Pd, $BaSO_4$ → $CH_3-HC=CH-CH_3$ (Poison, restricts single bond formation by further reaction)
- H_2/Pd, $CaCO_3$ → [Cis]
- Li in NH_3 → [trans]
- Na in NH_3 → [trans]
- B_2H_6 → [cis]
- P2 cat, Ni_2B → [cis]

Dehydration of Alcohol [Reactivity [3° > 2° > 1°]]

$CH_3-CH_2-OH \xrightarrow{(E1)} CH_2=CH_2$

- $Al_2O_3/350°$, H_2SO_4 /170°
- Hoffman → $POCl_3$/Pyridine
- H_3PO_4
- H^+, $KHSO_3$ → Best reagent

Mechanism: $H_2SO_4 \rightarrow H^+ + HSO_4^-$

$CH_3-CH_2-\ddot{O}-H \rightarrow CH_3-CH_2-\overset{+}{O}(H)-H$

$CH_3-CH_2 + H_2O$ (catalyst H_2SO_4)

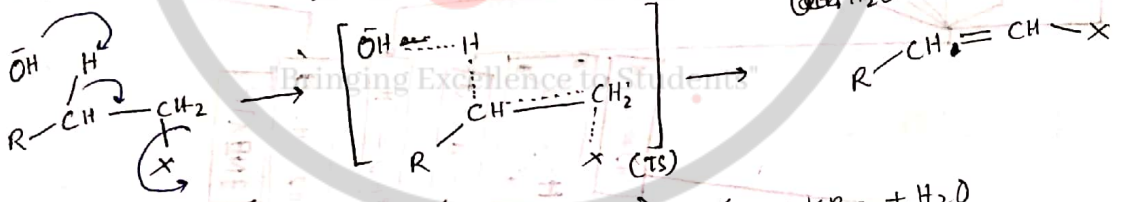
$CH_2=CH_2 + H^+$

$HSO_4^- + H^+ \rightarrow H_2SO_4$

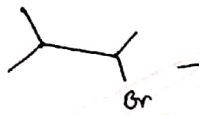
Dehydrohalogenation [Reactivity : 3° > 2° > 1°]

$R-CH_2-CH_2-X \xrightarrow[\Delta\ (E_2)]{KOH\ (alc)} R-CH=CH_2 + KX + H_2O$

Mechanism »



Base



alc KOH → [Hoffman] [less subs] + [Saytjeff] [More subs] + KBr + H_2O

- Loss of H takes place from βC with more H
- Loss of electron takes place from βC with less H.

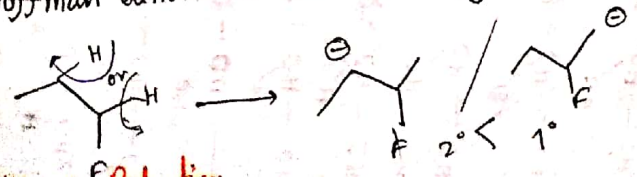
Base → Small base [eg. $\bar{O}H$] → Saytjeff is major

Bulky base [e.g. ] → Hoffman is major as its harder to reach the βC with less H

[ ← Threshold for bulky base, anything bigger is bulky]

→ If leaving group is −F, $-NMe_3$, $-SMe_2$ → Hoffman is major no matter what!!

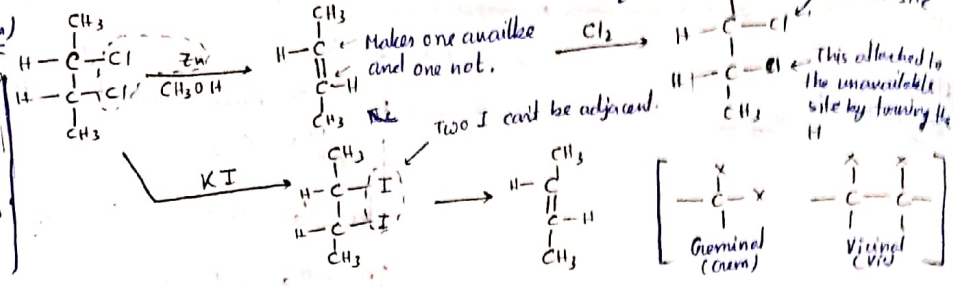
→ Hoffman elimination occurs through a 'TS' formation which behaves like an carbocation



Kolbe's Electrolysis: $CH_2-COONa$ / $CH_2-COONa$ (aq) $\xrightarrow{\text{⚡}}$ $CH_2=CH_2 + CO_2 + NaOH + H_2$

vicinal

From dihalides (Dehalogenation)



$CH_2=CH_2-C\equiv CH \xrightarrow{H_2/Pd}$

$CH_2=CH-CH=CH_2$

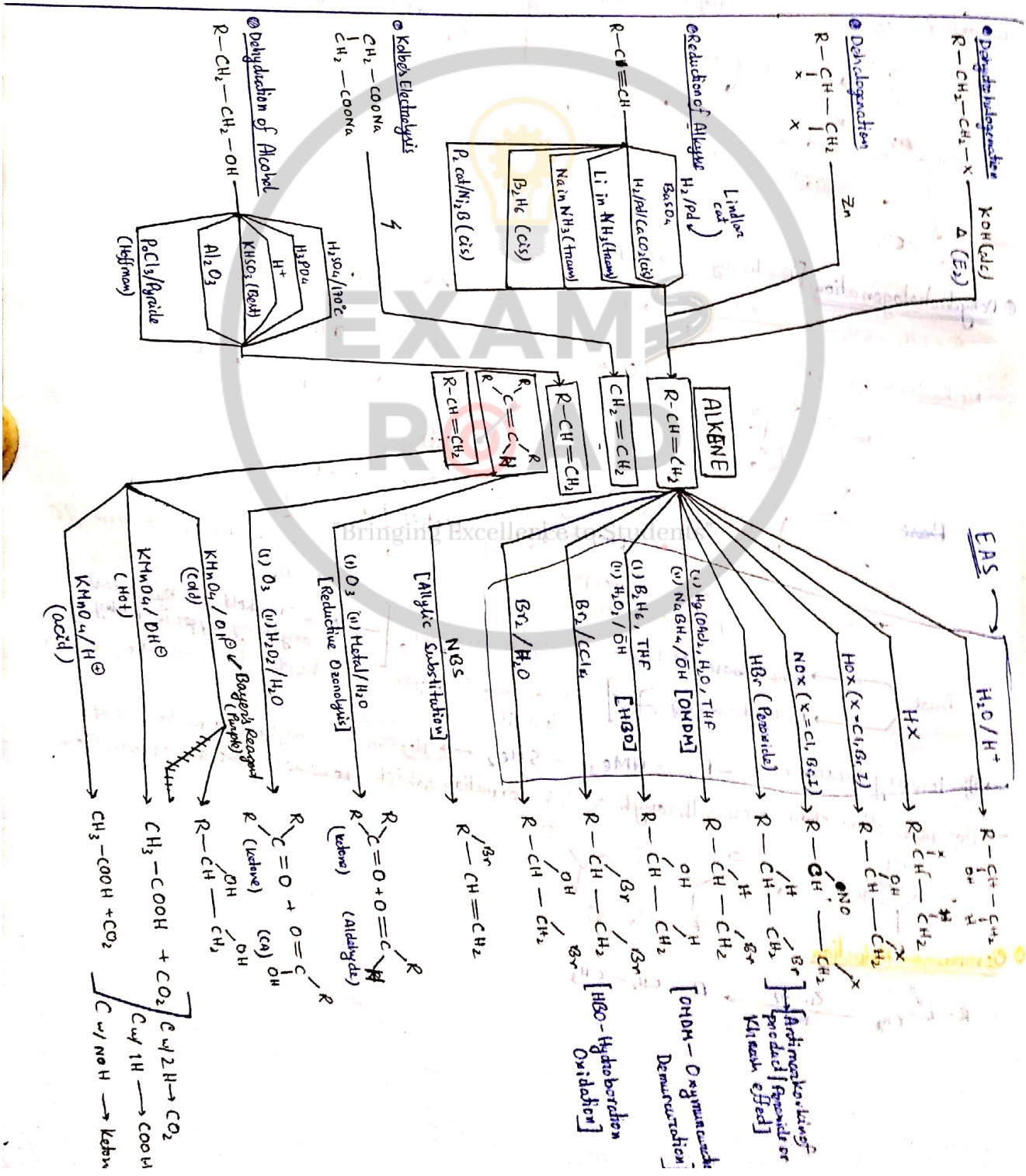
Although reactivity of '=' is more than '≡', breaking the '≡', gives a conjugated product (=, –, =)

Reactions of Alkane

$R-CH=CH_2 \xrightarrow{H_2O/H^+} R-CH(OH)-CH_2-H$

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

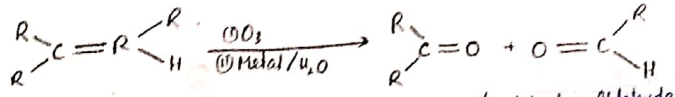
EAS



Ozonolysis

Oxidative / Reductive

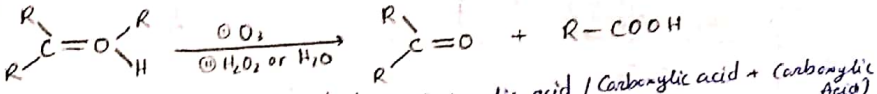
Reductive Ozonolysis:



Products → Ketone + Ketone / Ketone + Aldehyde / Aldehyde + Aldehyde

*Next page

Oxidative Ozonolysis



Products → Ketone + Ketone / Ketone + Carboxylic acid / Carboxylic acid + Carboxylic Acid

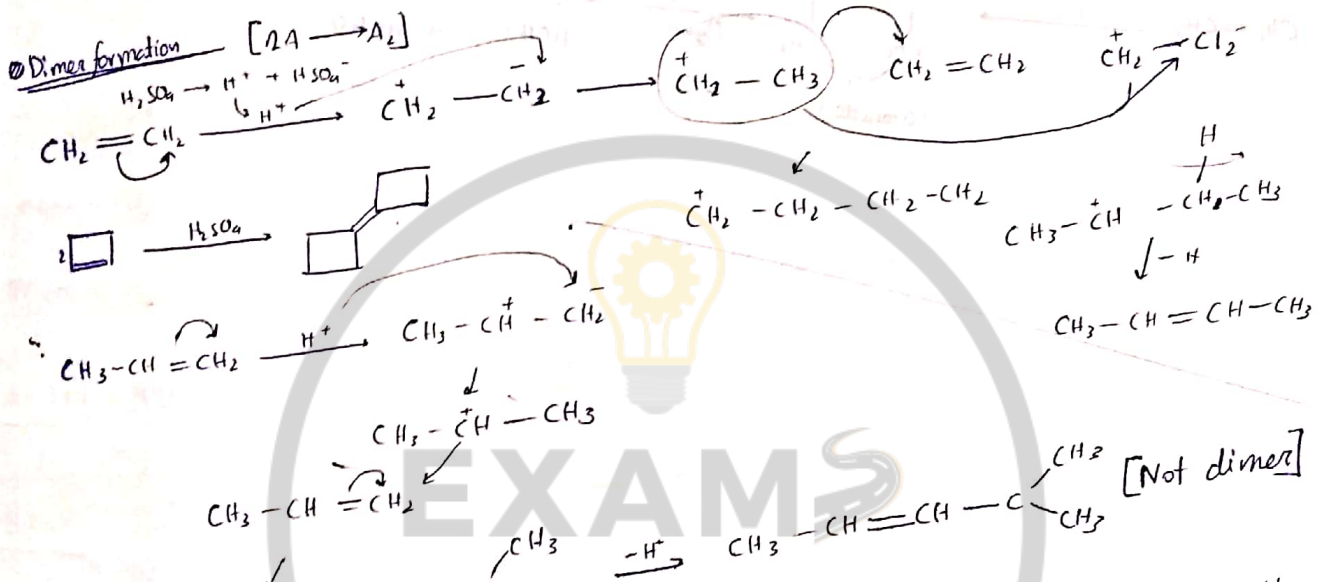
[The first step is same, if aldehyde is formed, it is converted to CA]

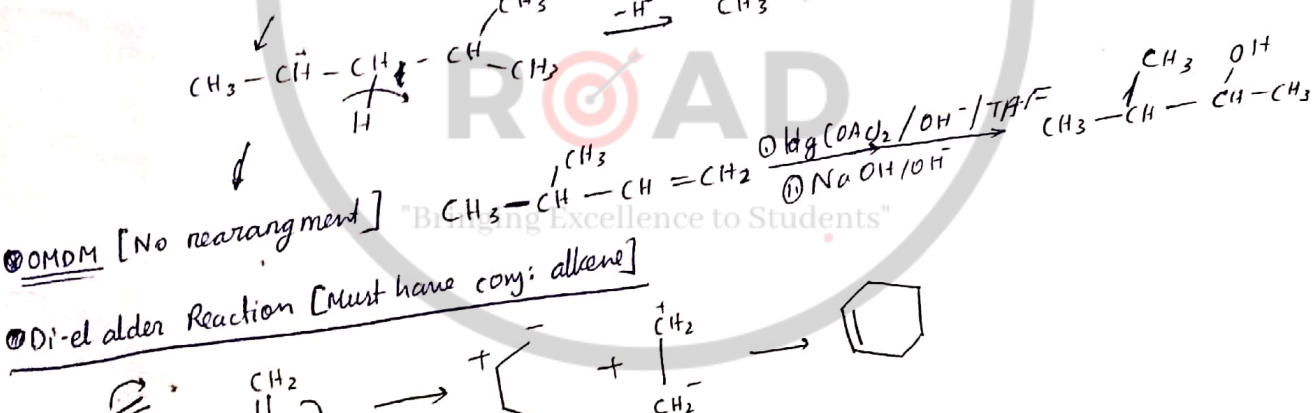
(Markovnikov's Rule)

When an unsymmetrical reagent is allowed to react with an unsymmetrical alkene, positive part of the re-agent combines with double bonded C having more no of H, and negative part of the reagent will combine with the other double bonded carbon. [Doesn't hold if EWG are attached]

ø HOCl → H + O − Cl → H − Ö + Cl ø HOF → H − O + F → H − Ö + F⁻ ø NOCl → Cl + N=O → Cl⁻ + N̊O

Dimer formation [A + A → A₂]

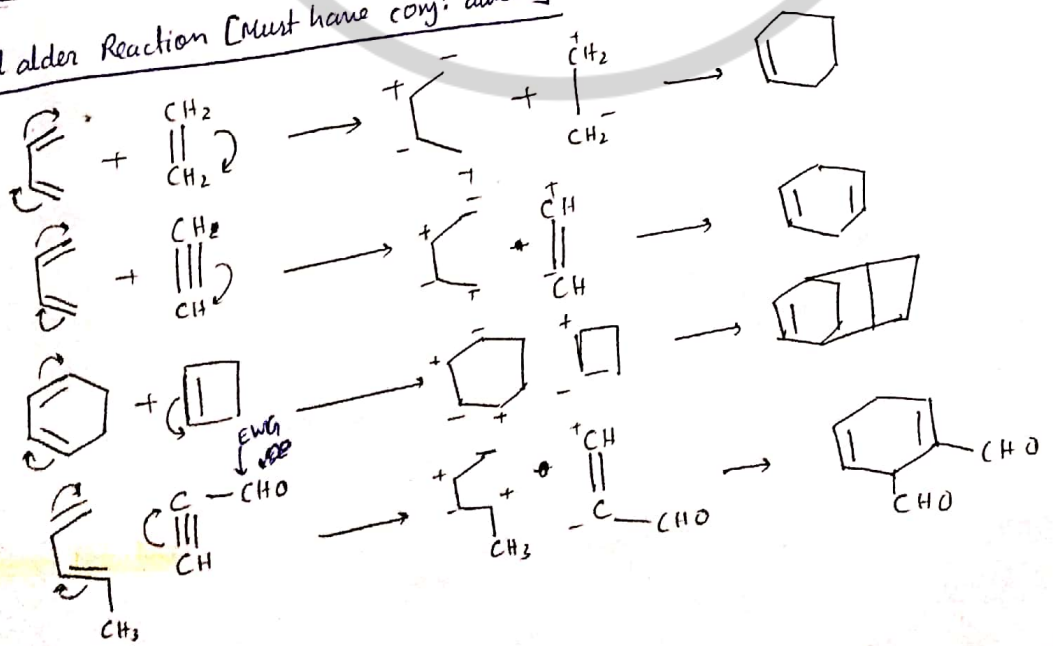




[Not dimer]

OMDM [No rearrangement]

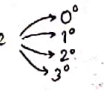
Di-el alder Reaction [Must have conj: alkene]

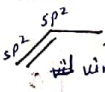


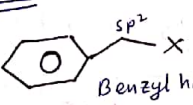
Alkyl & Aryl Halides → (Ar–X / Ph–X)

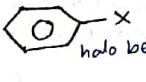
(R–X) ←

Alkyl halide → 0° 1° 2° 3°


allyl halide

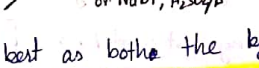

vinyl halide


Benzyl halide


halo benzene / Aryl halide

Preps

From Alcohol:

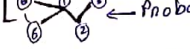
- $R-OH \xrightarrow{PX_3 \text{ or } HX} R-X$
- 
- $R-OH \xrightarrow{P+I_2} R-I$
- $R-OH + PCl_5 \rightarrow RCl$
- $ROH \xrightarrow{SOCl_2} RCl$ ← best as both the by products are gases.

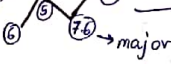
Halogenation of Hydrocarbon:

- $R-H \xrightarrow[h\upsilon]{X_2} R-X + HX$

Relative yield = Reactivity factor × Probability factor (No of eqv H)

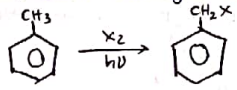
$Cl_2 \rightarrow 1^\circ : 2^\circ : 3^\circ = 1 : 3.8 : 5$ | $Br_2 \rightarrow 1^\circ : 2^\circ : 3^\circ = 1 : 82 : 1600$

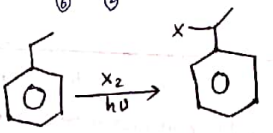

← Probability factor

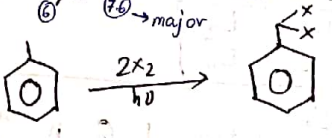

→ Relative yield

major

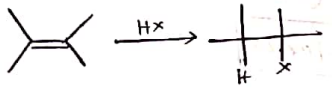
Side chain halogenation:



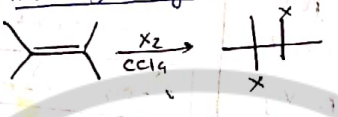


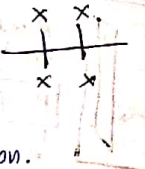


Addition of Hydrogen halide:

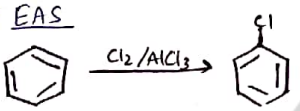


Addition of Halogen to Alkene, Alkyne

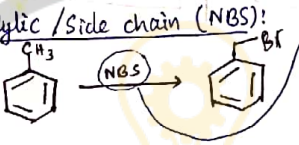




EAS



Allylic / Side chain (NBS):



Allylic substitution thru free radical formation.

Reactions

Nucleophilic Substitution Reactions:

carbanion

Nucleophiles:

- **Charged Nucleophiles:** In general anions. e.g. H^-, $\ddot{O}H^-$, $C^{\ominus}$, $Cl^{\ominus}$ etc.
- **Neutral Nucleophiles:** Central atom w/ lone pair e.g. $H-\ddot{O}-H$, $R-\ddot{O}-H$, $R-\ddot{O}-R$, $\ddot{N}H_3$, $R-\ddot{N}H_2$, $H-\ddot{S}-H$ etc.
  - → Hydrocarbons containing double / triple bond behave as nucleophiles. e.g. alkene, alkyne, benzene.
- **Ambient Nucleophiles:** Species w/ 2 nucleophilic centres, one is due to lone pair of e^- and other is due to negative charge are known as ambient nucleophiles e.g. $:\ddot{C}\equiv\ddot{N}$, $\ddot{O}-\ddot{N}=O$
  - → Organometallic compounds act as nucleophiles. All Nu^- are Lewis base
  - → Neutral organic compounds in which carbon is bonded with more electronegative atom by double or triple bond behaves as E^+ and Nu^-. Alkyl cyanide, aldehyde, ketone etc. act both as E^+ and Nu^-

Nucleophilicity: → ($RS^- > CN^- > I^- > RO^- > OH^- > Br^- > C_6H_5O^- > Cl^- > Me_3N$)

- → The reactivity of nucleophile is called as its nucleophilicity.
- → A nucleophile in which central atom has negative charge is a stronger nucleophile than a similar species without a negative charge. ($\ddot{O}H^- > H-\ddot{O}-H$) ($\bar{C}H_3 > \bar{N}H_2 > \bar{O}H > \bar{F}$)
- → Nucleophilicity decreases on moving from left to right in the periodic table.
- → Nucleophilicity increases on moving down the group of the periodic table due to decrease in EN : ($I^- > Br^- > Cl^- > F^-$)

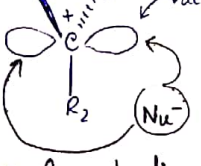
Nucleophilicity $\propto \frac{1}{\text{EN of central Atom}}$

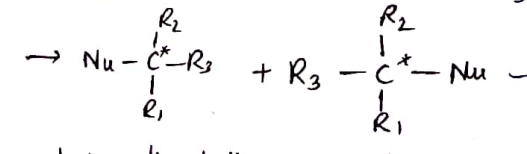
SN1: → Heterolytic bond cleavage occurs ($R-X \rightarrow R^+ + X^-$) in polar solvent → 1st order [$r = k[RX]$]

Mecha > • Step 1: Formation of carbocation: $R-X \xrightarrow{(RDS)} R^+ + X^-$ ← leaving group,

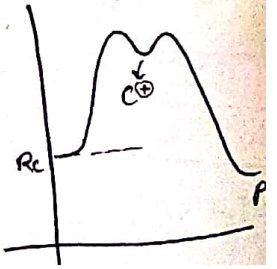
• Step 2: $Nu^- + R^+ \rightarrow$ (Nu–R) + (R–Nu) → Retention of config / Inversion of config

Carbocation →


← vacant p orbital,



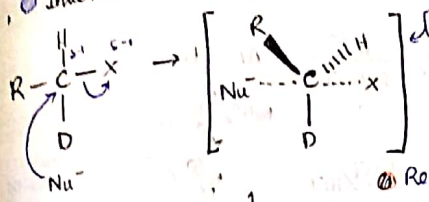
Both carbons are chiral and the molecules and enantiomers of each other (both optically active)



- **Racimisation:** As retention and inversion both occurs, forming racemic mixture
- **Reactivity:** Benzyl > 3° > 2° > 1° > CH_3X | R–I > R–Br > R–Cl > P–F
- Polar protic solvents favour SN1 & E1 mechanism.

SN2 : $r = k[RX][Nu^-]$ ● Reaction occurs in single step, through transition state [TS]

● Inversion of configuration will always take place. ● Nu^- attacks from opposite side of X



● TS is a state of simultaneous Bond making (C-Nu^-) and breaking (C-X). It contains partial bond, It is highly unstable.

● Reactivity $\propto \frac{1}{\text{Steric Hinderance}}$ ● Reactivity: $CH_3X > 1° > 2° > 3° >$ Benzyl

$R-I > R-Br > R-Cl > R-F$

● TS is less stable than rxn intermediate

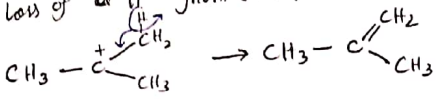
● Non polar or polar aprotic solvent favours SN2 or E2 mechanism. ● In TS, C has penta covalency.

E1: ● $r = k[RX]$ ● Two step reaction

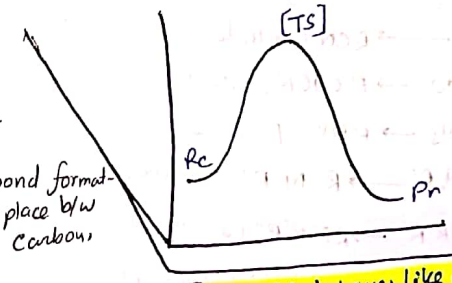
dehydrohalogenation or 1,2-elimination

● Step 1: C^+ formation, $R-X \longrightarrow R^+ + X^-$

● Step 2: Loss of H^+ from adjacent to(C^+) position,

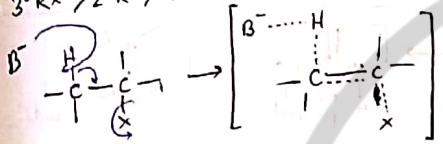


● Double bond formation takes place b/w α and β Carbon.



● Reactivity ∝ TS stability [Here TS behaves like an alkene, TS stability ∝ no of α-H]

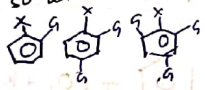
E2: ● $r = [RX][Base]$ ● Single step through TS. ● Reactivity: $3° RX > 2° RX > 1° RX$



● Weaker base is better leaving group.

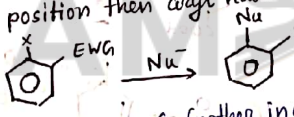
● Aryl halides can undergo SnAr or Benzyne mechanism. It doesn't give SN1 or SN2, why?

In S_N2, Nu^- always approaches from opposite side of leaving group, here the π e^- cloud repeals the Nu^-. There is also partial double bond character b/w C and X, so unbreakable.

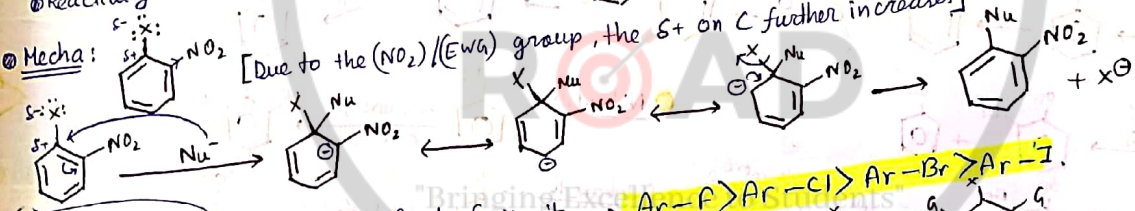


SnAr: If EWG is attached ortho/para, or both position then aryl halide undergoes SnAr.

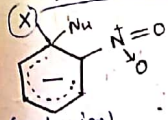
● Reactivity: $R-I > R-Br > R-Cl < R-F$



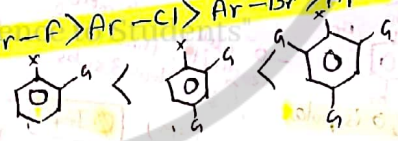
● Mecha: [Due to the (NO_2)/(EWG) group, the δ+ on C further increases]



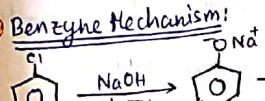
Due to the −I effect of X, it makes the carbanion further stable Thus



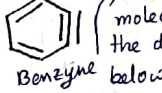
$Ar-F > Ar-Cl > Ar-Br > Ar-I$.



Benzyne Mechanism:



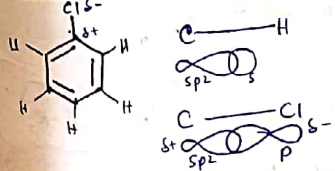
● No EWG / EDG
or ● EWG at meta
or ● EDG at ortho/para



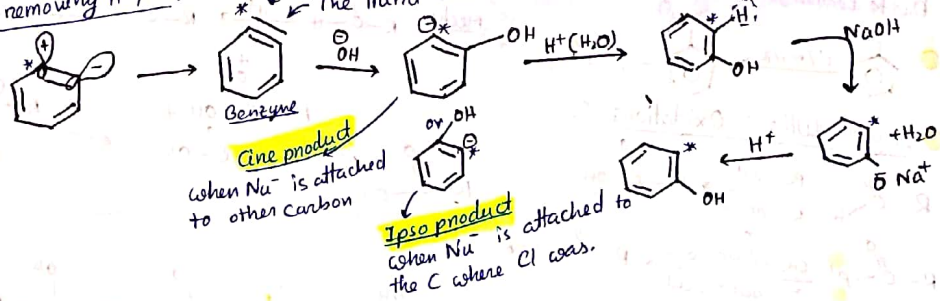
Benzyne

The sp^2-sp^2 π e^-s are in the molecular plane which doesn't affect the delocalised π e^- cloud above and below the plane, Thus still AROMATIC

● Mecha: [H at the ortho position is most acidic because of −I of X]

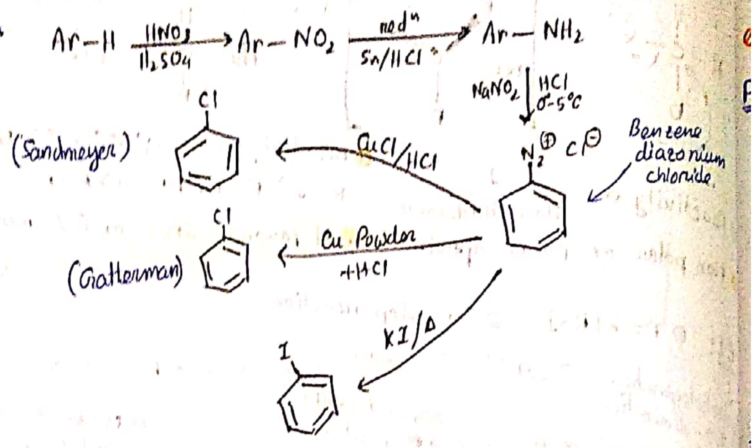


After removing H^+, Cl^-,

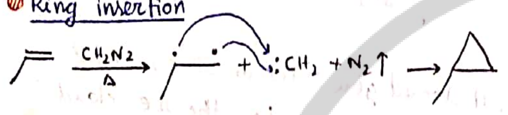


- $RX + \overset{\ominus}{O}H \longrightarrow R-OH + X^-$ (Alcohol)
- $RX + H_2O \longrightarrow R-OH$ (Alcohol)
- $RX + \overset{\ominus}{O}R' \longrightarrow ROR' + X^-$ (Ether) — Williamson synthesis
- ~~$RX + C^-$:~~
- $RX + \overset{\ominus}{C}\equiv CR' \longrightarrow R-C\equiv CR'$ (Alkyne)
- $RX + I^- \longrightarrow RI$ (Alkyle iodide)
- $RX + CN^- \longrightarrow RCN$ (Nitrile)
- $RX + R'COO^- \longrightarrow R'COOR$ (Ester)
- $RX + :NH_3 \longrightarrow RNH_2$ (1° amine)
- $RX + :NH_2R' \longrightarrow R-NHR'$ (2° amine)
- $RX + :NHR'R'' \longrightarrow RNR'R''$ (3° amine)
- $RX + \bar{S}H \longrightarrow RSH$ (Thiol)/Mercaptan
- $RX + \bar{S}R' \longrightarrow RSR'$ (Thioether)/sulphide
- $RX + ArH + AlCl_3 \longrightarrow ArR$ (Alkyl benzene) — FCA

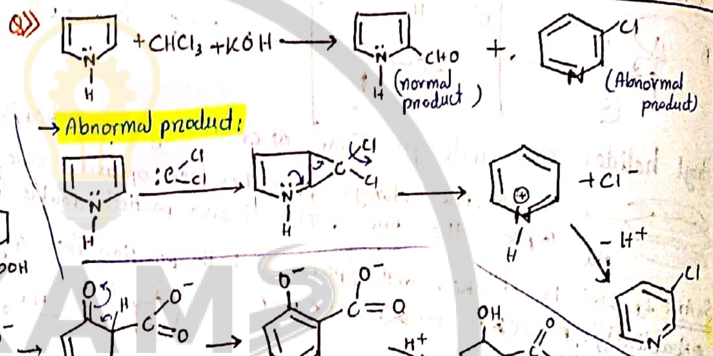
Aryl halide prep from Diazonium Salts:



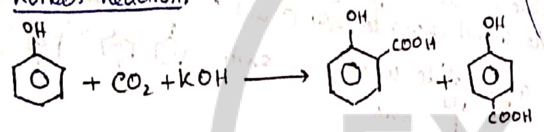
Ring insertion



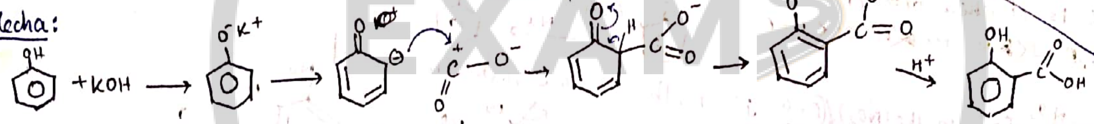
Q)



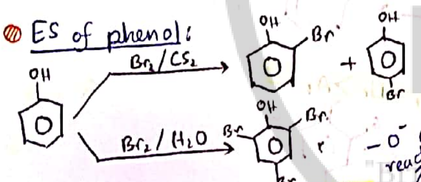
Kolbe's Reaction:



Mecha:

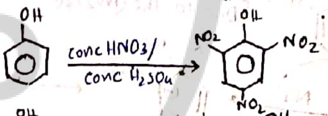


ES of phenol:

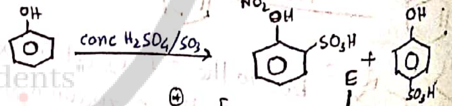


$-O^-$ will provide more reactivity. thus goes thru 3 subs (+M) — Imp

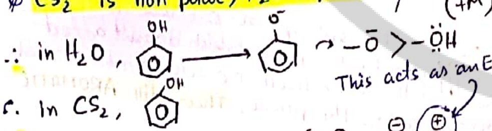
Nitration:

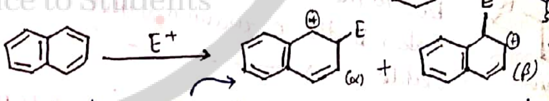


Sulphonation:



CS_2 is non polar, H_2O is polar





This σ complex has no RS without disturbing ⌬/Aromaticity

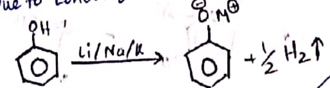
This sigma complex has 2 RS without disturbing ⌬/Aromaticity (more stable)

In H_2O, $Br_2 + H_2O \longrightarrow H^{\oplus}Br^{\ominus} + HO\overset{\oplus}{Br}$

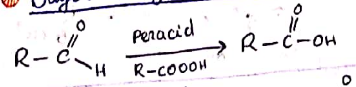
In CS_2, $\overset{\delta-}{Br}-\overset{\delta+}{Br}$ Due to London force

$Br^{\oplus}$ is better E^+ than $Br^{\delta+}$. Thus 3 subs in H_2O

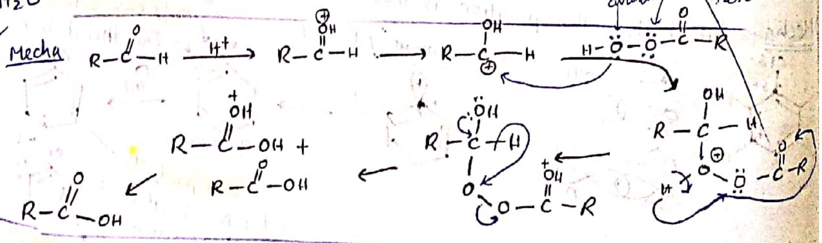
BUT, In case of sulphonation ($-SO_3H$), α is more stable due to steric hinderance

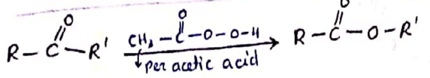


Bayer-Villiger Oxidation:

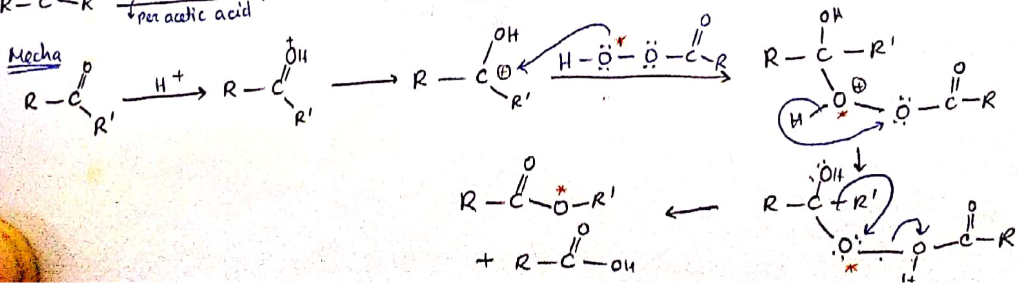


Mecha





Mecha



Alcohol

PREPS >>

From Alkene:

- $H_3C-C(CH_3)=CH_2 \xrightarrow{H_3O^+}$ (Markovnikov's Rule) (w/ rearrangement) $\rightarrow H_3C-C(OH)(CH_3)-CH_3$
- $\xrightarrow[(ii)\ NaBH_4\ (Mark's)]{(i)\ Hg(OAc)_2,\ H_2O}$ (w/o rearrangement) [OMDM]
- $\xrightarrow[(ii)\ H_2O_2/OH^-]{(i)\ BH_3/THF}$ (Anti Mark) (w/o rearr) [HBO]
- $\xrightarrow{HCO_3H/HOH}$ (Anti hydroxylation)
- $\xrightarrow{\text{Cold alk } KMnO_4}$ (Bayer's Reagent) or Syn hydroxylation OsO_4/aq Na_2SO_3
- $\xrightarrow[(ii)\ Zn-Cu\ (red^n)]{(i)\ CO+H_2\ [Co_2(CO)_8]}$ (Oxo process only for terminal alkenes)

From Alkyl Halides:

- $R-X \xrightarrow[S_N1\ or\ S_N2]{HOH/NaOH} R-OH$
- $R-X \xrightarrow[\text{(Hydrolysis } S_N2)]{\text{Moist } Ag_2O} R-OH$
- $\xrightarrow[or\ Ag_2O/HOH]{HOH/NaOH}$

From Aldehydes and Ketones:

- $\xrightarrow[or\ NaBH_4\ or\ Na/EtOH\ or\ Al(Me_2CHO)_3 \leftarrow [MPV\ red^n]]{LiAlH_4}$
- $\xrightarrow[(ii)\ H_3O^+]{(i)\ R_2-MgX}$

From CA and CA derivatives:

- $\xrightarrow[(ii)\ H_2O/H^+\ (Red^n)]{(i)\ LAH\ (excess)}$ $+HCl$
- $\xrightarrow[(ii)\ H_3O^+]{(i)\ R\ MgX\ (2\ moles)}$
- $\xrightarrow{NaBH_4}$
- $\xrightarrow[(ii)\ H^+]{(i)\ LAH}$
- $\xrightarrow[(ii)\ H^+]{(i)\ BH_3/THF}$
- $\xrightarrow{H_2/Pt\ or\ Ni}$
- $\xrightarrow{H_2/Pd-C}$

From 1° alkyl amines:

$R-CH_2CH_2NH_2 \xrightarrow{HNO_2} R-CH_2CH_2^+ \rightleftharpoons R-CH^+-CH_3$

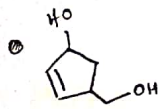
$\downarrow OH^-$ (E1) $\rightarrow CH_2=CH_2$

$\downarrow OH^-$ $\rightarrow R-OH$

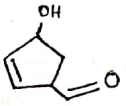
$\downarrow Cl^-$ $\rightarrow R-Cl$

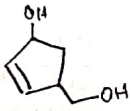
PROPS >>

- $R-CH_2-CH_2-OH \xrightarrow{Na} RCH_2CH_2O^-Na^+ + \frac{1}{2}H_2\uparrow$
- $R-OH \xrightarrow{Al} Al(O-R)_3 + \frac{3}{2}H_2\uparrow$
- $R-OH \xrightarrow[or\ Me_2SO_4]{CH_2N_2} R-O-CH_3$
- $R-CH_2CH_2OH \xrightarrow[H^+,\ \Delta]{R_1(CO)OH} R_1-C(=O)-O-CH_2CH_2R + H_2O$ [Esterification]
- $R-CH_2-OH \xrightarrow[\text{[Oppenauer's oxd}^n\text{]}]{Al(Me_3CO)_3/Me_2CO} R-CH_2-CHO$
- $R-OH \xrightarrow[ZnCl_2,\ \Delta]{HCl/anhyd} RCl$ [Lucas Test] — 1° → No turbidity; 2° → Turb in 5min; 3° → Insta Turb.
- $R-OH \xrightarrow[SN1,\ \text{(Retention of conf)}]{PCl_3,\ PCl_5} R-Cl$
- $R-OH \xrightarrow[Inert]{SOCl_2} RCl$ [In absence of pyridine, Retention of conf] [In presence " " , inversion "]
- $R-CH_2-CH_2-OH \xrightarrow[3°,2° \rightarrow E1;\ 1° \rightarrow E2]{H^+\ (Dehydration)} R-CH=CH_2$
- $R-CH_2OH \xrightarrow{KMnO_4/OH^-} R-CH_2-COO^-$
- $R-CH_2OH \xrightarrow{PCC/CH_2Cl_2} RCH_2CHO$
- $RCH_2CH_2OH \xrightarrow[CrO_3/H_2SO_4]{PCC/H_2O\ or} RCH_2COOH$
- $R-CH_2OH \xrightarrow[\text{(Dehydg)}]{Cu\ or\ Ag\ /300°C} R-CHO$
- $R-CH_2OH \xrightarrow{TsCl} R-CH_2OTs$ [Tosylation]
- $R-CH_2CH_2OH \xrightarrow[\text{(reduction)}]{P/HI} R-CH_2CH_3$
- $R-CH_2CH_2OH \xrightarrow{HO-OSR_1} RCH_2CH_2OSO_2R_1$
- $RCH_2CH_2OH \xrightarrow[R_1-CO-Cl]{} R-COO-CH_2CH_2R$ (Acylation)

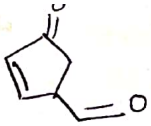


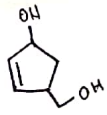
PCC/CH_2Cl_2 (Collin's Reagent)
(Oxidation of 1° alcohol)



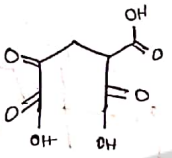


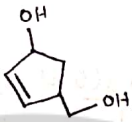
(i) CrO_3 in Acetic Acid
(ii) H_2O/H^+
(Oxd^n of 2° alcohol)



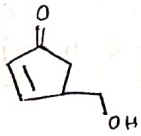


$KMnO_4/OH^-$
Δ



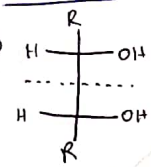


$(Me_3CO)Al$
(only 2° alcohol)



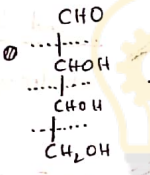
[Oppenauer's Oxidation]

Oxidation:



HIO_4 (1 mole)

$R-CHO$ + $R\,CHO$



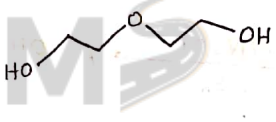
HIO_4 (3 moles)

$3\,H-COOH + HCHO$

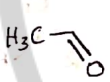
Dehydration of ethylene glycol and glycerol:

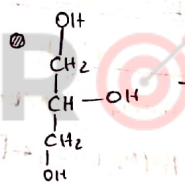
conc. H_2SO_4
$(-2H_2O)$

H_3PO_4
$(-H_2O)$

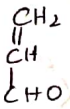


Anhyd $ZnCl_2$
$(-H_2O)$

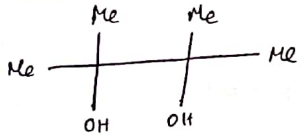




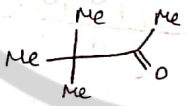
$KHSO_4/\Delta$
$(-2H_2O)$

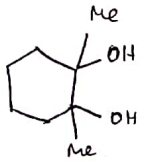


Pinacol Pinacolone Rearrangement:

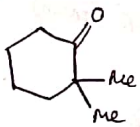


H^+/Δ

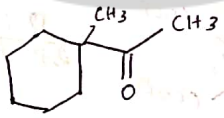




H^+/Δ



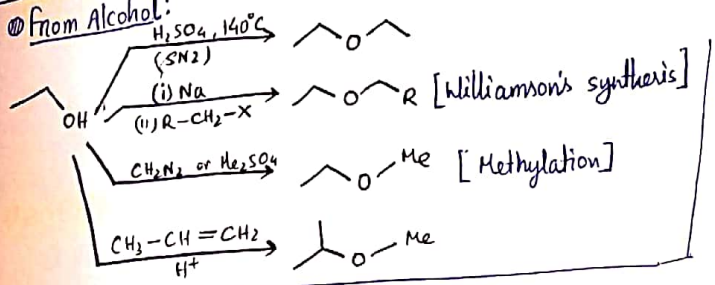
+



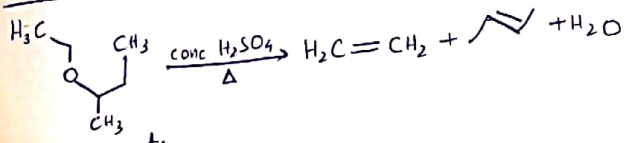
ETHER (Referred as alkyl derivatives of alcohols)

PREPS

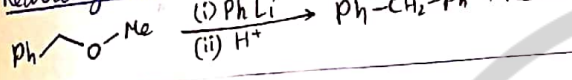
From Alcohol:



Dehydration Reaction:

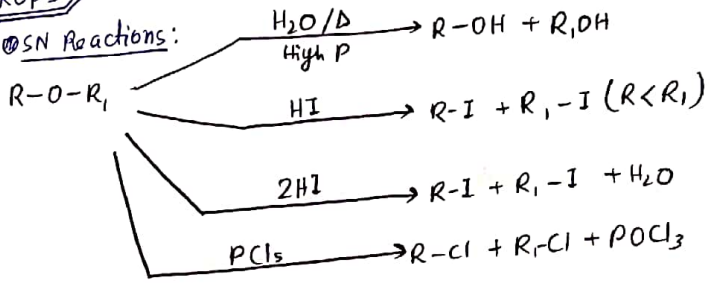


Rearrangement:

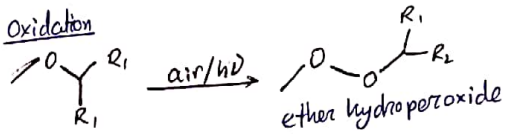


PROPS

SN Reactions:

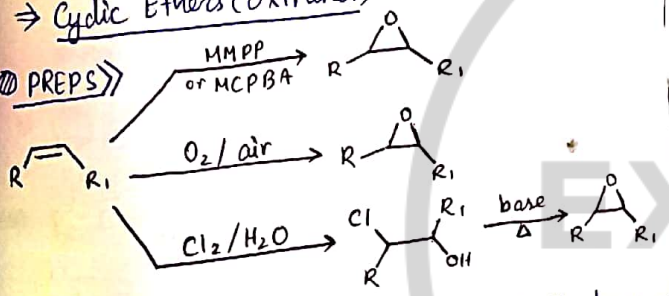


Oxidation

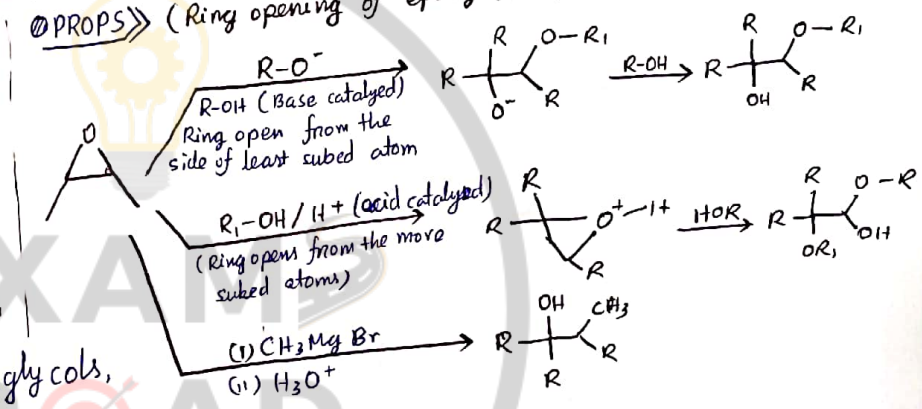


⇒ Cyclic Ethers (Oxiranes)

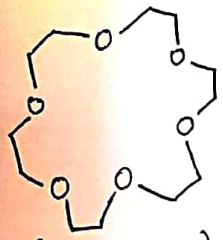
PREPS



PROPS (Ring opening of epoxy ethers)



- Crown ethers are cyclic polymer of ethylene glycols,
  e.g. 18-crown-6 (18 denotes the sum of total no. of C and O atoms in the ring while 6 denotes no of O atoms)



(18-crown-6)

Phenols

PREPS

- (i) $CH_3-\underset{Cl}{CH}-CH_3/AlCl_3$ (ii) O_2/air (iii) H_3O^+ → [Cumene process]
- (i) NaOH/300°C, 300 atm (ii) H_2O/H^+ → [Benzyne mechanism]
- H_2O, Δ → [DOW's process]
- (i) NaOH / fusion, 350 °C (ii) H^+

PROPS

- Reaction due to cleavage of O-H bond:
  - Alc. $FeCl_3$ → $[Fe(OPh)_6]^{3-}$ (Blue or violet colour)
  - $NaOH$ or Na → O^-Na^+
  - $R-\overset{O}{\overset{\|}{C}}-Cl/Py$ or $(RCO)_2O/Py$ [Acylation] → Anhy. $AlCl_3$, R (Fries reagent)
  - $Me_2SO_4/NaOH$ or CH_2N_2 → o-Me [Methylation]
- Reaction due to cleavage of C-O bond:
  - PCl_3/Δ or PCl_5/Δ or $SOCl_2/\Delta$ → Cl
  - P_2S_5 → SH
  - NH_3, Anhy $ZnCl_2$, 300°C → NH_2 + H_2O
- Reactions due to aromatic ring:
  - 20% HNO_3 → NO_2 + NO_2 [Mononitration]
  - HNO_3 (conc) / H_2SO_4/Δ → O_2N, NO_2 [Polynitration]
  - Br_2/CCl_4 or Br_2/CS_2 → Br + Br
  - Br_2/H_2O / $Br_2/AcOH$ → Br, Br, Br
  - H_2SO_4, 25°C → SO_3H
  - H_2SO_4, 100°C → SO_3H
- HNO_2 (Nitrosation) → NO → (Blue) → [which changes to red on adding NaOH]

Carboxylic Acid & Derivatives

- General formula → Saturated : $C_nH_{2n}O_2$, Unsaturated : $C_nH_{2n-1}COOH$

- PREPS :

i) By oxidation of alcohol, aldehyde, ketone :

(a) $RCH_2OH \xrightarrow[\text{or } KMnO_4/H^+ \text{ or } OH^- \text{ or } CrO_3/H^+]{K_2Cr_2O_7/H^+} R-CHO \xrightarrow{[O]} R-COOH$

(b) $R_2CH-OH \xrightarrow{[O]} R_2C=O \xrightarrow[\text{heating}]{\text{prolong}} R-COOH$

ii) By oxidation of Alkene:

(a) $R-CH=CH-R' \xrightarrow[(ii)\ H_2O,\ \Delta]{(i)\ KMnO_4} R-COOH + R'-COOH$

(b) Carbonylation: $CH_2=CH_2 + CO + H_2O \xrightarrow[300°-400°C]{H_3PO_4} CH_3CH_2COOH$

iii) From Alkyne: (Ozonolysis) → (a,b)

(a) $CH\equiv CH + 3[O] + H_2O \xrightarrow{\text{alk } KMnO_4} 2HCOOH$

(b) $R-C\equiv CH + 3[O] + H_2O \xrightarrow{\text{alk } KMnO_4} R-COOH + HCOOH$

(c) $CH\equiv CH + H_2O + [O] \xrightarrow{\text{Cromic acid}} CH_3-COOH$

iv) Hydrolysis of trihalogen derivatives:

$R-CX_3 \xrightarrow{H_2O} [R-C(OH)_3] \xrightarrow{-H_2O} R-COOH$ (unstable)

v) Carbonation of Grignard Reagent:

$R-Mg-X + O=C=O \longrightarrow O=C(R)(OMgX) \xrightarrow[H_2O]{H^+} R-COOH + Mg(X)OH$

vi) Hydrolysis of cyanide:

$R-C\equiv N + H_2O \xrightarrow{H^+} R-COOH + NH_3$

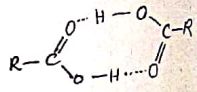
vii) Hydrolysis of CA derivatives:

(a) $R-COCl \xrightarrow{H_2O} R-COOH + HCl$

(b) $R-CONH_2 \xrightarrow{H_2O} R-COOH + NH_3\uparrow$

(c) $R-COOR' \xrightarrow{H_2O} R-COOH + R'OH$

(d) $R-CO-O-CO-R \xrightarrow{H_2O} 2R-COOH$

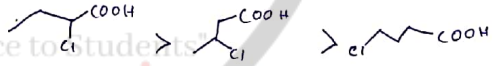
- Physical Properties: ∅ Molecules are polar and show intermolecular hydrogen bonding. 

∅ C_1-C_4 are highly soluble in water due to hydrogen bonding.

∅ The bp of CA is higher than alcohol due to presence of hydrogen bonding. It exist is dimeric form

- Chemical Properties: ∅ Acidic strength $\propto -I$ effect ∅ Acidic strength $\propto \frac{1}{+I \text{ effect}}$

$RCOOH > H-OH > R-OH > CH\equiv CH > NH_3 > RH$



- Chemical Reactions:

∅ $R-COOH \xrightarrow{PCl_5} R-COCl + POCl_3 + HCl$

∅ $R-COOH \xrightarrow{SOCl_2} R-COCl + SO_2 + HCl$

∅ $R-COOH \xrightarrow[\Delta]{HNH_2\ (NH_3)} R-CONH_2 + H_2O$

∅ $R-COOH \xrightarrow{C_2H_5-OH} R-COO-C_2H_5 + H_2O$

∅ $R-COOH \xrightarrow{R'COOH} R-CO-O-CO-R$

∅ $R-COOH \xrightarrow[CaO,\ 710°]{RCOOH} R_2C=O$

∅ $R-COOH \xrightarrow[Br_2]{Ag_2O/CCl_4} R-Br + CO_2 + AgBr$ [Hunsdicker Reaction]

∅ $R-COOH \xrightarrow{LiAlH_4} R-CH_2-OH + H_2O$

∅ $R-COOH \xrightarrow{CH_2N_2} R-COO-CH_3 + N_2\uparrow$

∅ $R-COOH \xrightarrow[\Delta,\ H_3PO_3]{CH_2=C=O} R-CO-CH_2-CO-CH_3$

∅ $R-COOH \xrightarrow[\Delta,\ \text{conc } H_2SO_4]{N_3H} R-NH_2 + CO_2 + N_2$ [Schmidt Reaction]

∅ $R-CH_2-COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Cl_2 \text{ or } Br_2,\ \text{Red P}} R-CH(Br)-COOH \xrightarrow{Br_2} R-C(Br)_2-COOH$ [Hell Volhard Zelinsky Reaction]

- Identification: ∅ Aqueous solution turns blue litmus red.

∅ Aqueous solution of the acid with $NaHCO_3$ gives effervescence of $CO_2\uparrow$ and $RCOONa$

$R-COOH + NaHCO_3 \longrightarrow R-COONa + H_2O + CO_2\uparrow$

∅ On heating be with alcohol, fruity smell is formed.

$RCOOH + ROH \underset{}{\overset{H^+}{\rightleftharpoons}} RCOOR + H_2O$

(ester)

fruity smell

Acid Derivatives

Acid Halide: $R-C(=O)-X$

PREPS: $R-C(=O)-OH + PCl_5 / SOCl_2 / PCl_3 \rightarrow R-C(=O)-Cl$

Chemical Properties:

- $R-C(=O)-Cl \xrightarrow{H_2O} R-C(=O)-OH + HCl$
- $R-C(=O)-Cl \xrightarrow{(NH_3)\ HNH_2} R-C(=O)-NH_2 + HCl$
- $R-C(=O)-Cl \xrightarrow{C_2H_5-OH} R-C(=O)-O-C_2H_5 + HCl$
- $R-C(=O)-Cl \xrightarrow{R-C(=O)-ONa} R-C(=O)-O-C(=O)-R + NaCl$
- $R-C(=O)-Cl \xrightarrow[(S)]{H_2/Pd\text{-}BaSO_4} R-C(=O)-H + HCl$ [Rosenmund's Reaction]
- $R-C(=O)-Cl \xrightarrow[anhy\ AlCl_3]{} C_6H_5-C(=O)-R + HCl$ [Friedel-Crafts Reaction]
- $R-C(=O)-Cl \xrightarrow{NaN_3} R-NH_2$ [Curtius Degradation]
- $R-C(=O)-Cl \xrightarrow[H_2O]{RMgX} R-C(=O)-R + MgX_2$

Acid Anhydride: $R-C(=O)-O-C(=O)-R$

PREPS:

- $CH_3-C(=O)-OH + CH_2=C=O \xrightarrow{AlPO_4} Me-C(=O)-O-C(=O)-Me$
- $2\ Me-C(=O)-OH \xrightarrow[-H_2O]{P_2O_5} Me-C(=O)-O-C(=O)-Me$

PROPS:

- $(RCO)_2O \xrightarrow{H_2O} 2\ RCOOH$
- $(RCO)_2O \xrightarrow{PCl_5} R-C(=O)-Cl$
- $R-C(=O)-O-C(=O)-R \xrightarrow{NH_3} R-C(=O)-NH_2 + HO-C(=O)-R$
- $R-C(=O)-O-C(=O)-R \xrightarrow{LAH} R-CH_2-OH$
- $(RCO)_2O \xrightarrow{C_2H_5OH} R-C(=O)-O-C_2H_5 + RCOOH$

Amide: $R-C(=O)-NH_2$

PREPS:

- $R-C(=O)-Cl + NH_3 \rightarrow R-C(=O)-NH_2 + HCl$
- $R-C(=O)-OH + NH_3 \xrightarrow{\Delta} R-C(=O)-NH_2 + H_2O$
- $R-C\equiv N + H-OH \rightarrow R-C(OH)=NH \xrightarrow{tauto} R-C(=O)-NH_2$ [Partial hydrolysis of cyanide]

PROPS:

- $R-C(=O)-NH_2 \xrightarrow{LAH} R-CH_2-NH_2$
- $R-C(=O)-NH_2 \xrightarrow[Br_2+KOH]{OBr^- \text{ or}} R-NH_2 + K_2CO_3 + KBr$ [Hofmann Bromamide degradation Reaction]
- $R-C(=O)-NH_2 \xrightarrow{H_2O} R-C(=O)-OH$
- $R-C(=O)-NH_2 \xrightarrow{P_2O_5} R-C\equiv N$
- $R-C(=O)-NH_2 \xrightarrow{POCl_3} R-C\equiv N$

Ester: $R-C(=O)-O-R$

PREPS:

- $R-C(=O)-OH \xrightarrow{ROH} R-C(=O)-O-R + H_2O$
- $R-C(=O)-Cl \xrightarrow{ROH} R-C(=O)-OR + HCl$
- $2\ R-CHO \xrightarrow[\Delta]{Al(OC_2H_5)_3} R-C(=O)-O-R + H_2O$ [Tischenko Reaction]

PROPS:

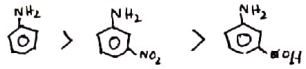
- $R-C(=O)-OR \xrightarrow{H_2O} R-C(=O)-OH$
- $R-C(=O)-OR \xrightarrow[H_2O]{2\ RMgX} R-C(R)(OH)-R$
- $R-C(=O)-OR \xrightarrow[\Delta, NaOH]{NaOC_2H_5} R-C(=O)-CH_2-C(=O)-O-R$ (β keto ester) [Claisen Ester Condensation]
- $R-C(=O)-OR \xrightarrow{NH_3} R-C(=O)-NH_2$
- $R-C(=O)-OR \xrightarrow{LAH} R-CH_2-OH + ROH$
- $R-C(=O)-OR \xrightarrow[R'-OH]{} R-C(=O)-O-R' + R-OH$ [Trans Esterification]

AMINE

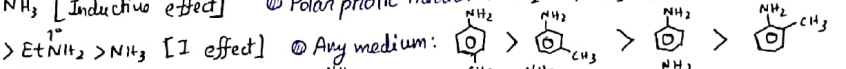
Basicity: Polar protic medium: $2^\circ > 1^\circ > 3^\circ > NH_3$ [Due to solvation effect]

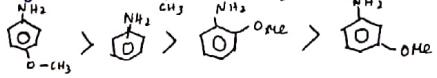
Non polar medium: $3^\circ > 2^\circ > 1^\circ > NH_3$ [Inductive effect]

Non polar medium: $Et_3^{3^\circ}N > Et_2^{2^\circ}NH > Et^{1^\circ}NH_2 > NH_3$ [I effect]

Any medium: 

Polar protic medium: $Et_2^{2^\circ}NH > Et_3^{3^\circ}N > Et^{1^\circ}NH_2 > NH_3$ [Solvation effect]

Any medium: 

Any medium: 

PREPS»

$R-X \xrightarrow{NH_3} R-NH_2$ [If NH_3 is excess, R_2NH, R_3N and $R_4N^+HX^-$ will be formed as well]

Reduction in acidic medium/catalytic rxn:

(a) $R-NO_2 \xrightarrow[Sn/HCl \text{ or } Fe/HCl \text{ or } Pd-C/EtOH]{H_2+Ni \text{ or } Pt} R-NH_2$

(b) $Ph-NO_2 \xrightarrow{"} Ph-NH_2$

$R-NC \xrightarrow[LAH]{Pt \text{ or } Ni \text{ or}} R-NH-CH_3$

$Ph-CN \xrightarrow{LAH} Ph-CH_2-NH_2$

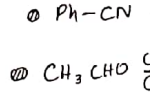
$R-\underset{\underset{NH_2}{|}}{\overset{\overset{O}{||}}{C}} \xrightarrow[(i)\ P_2O_5\ (ii)\ LiAlH_4]{LAH} R-CH_2-NH_2$

$CH_3CHO \xrightarrow[(ii)\ N_2/Ni]{(i)\ NH_3} CH_3-CH_2-NH_2$ [Reductive Amination]

$R-\underset{\underset{Cl}{|}}{\overset{\overset{O}{||}}{C}} \xrightarrow[(ii)\ \Delta\ (iii)\ 2OH^-/H_2O]{(i)\ NaN_3} RNH_2$ [Curtius reaction]

$R-COOH \xrightarrow{HN_3/conc.H_2SO_4} RNH_2$ [Schmidt reaction]

Phthalimide $\xrightarrow[(iii)\ 2KOH/H_2O]{(i)KOH\ (ii)RX} RNH_2$ [Gabriel Phthalimide Synthesis]



PROPS»

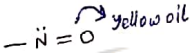
$R-NH_2 + Ph-\underset{\underset{Cl}{|}}{\overset{\overset{O}{||}}{C}} \xrightarrow{NaOH} HN(R)-\underset{\underset{Ph}{|}}{\overset{\overset{O}{||}}{C}}$ [benzyl alkyl amine] [Schotten-Baumann Reaction]

$R-NH_2 + CHCl_3 + KOH \longrightarrow RNC$ [Carbylamine Reaction] [only 1° Amine]

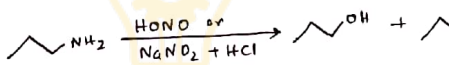
$C_2H_5NH_2 + COCl_2 \longrightarrow C_2H_5NCO$ (Carbonyl chloride → Ethyl isocyanide)

$PhNH_2 \xrightarrow[(0-5)^\circ C]{NaNO_2/HCl} Ph-N_2^+Cl^-$ [Diazotisation]

$Ph-NH-CH_3 + NaNO_2/HCl \longrightarrow Ph-N(CH_3)-N=O$ (yellow oil)

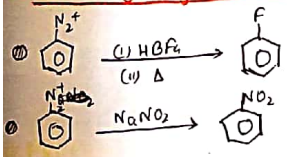


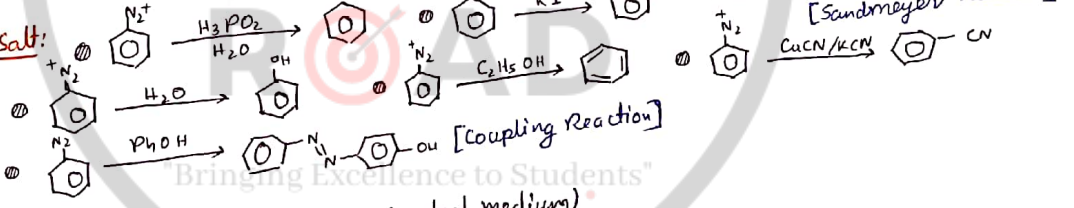
$C_2H_5NH_2 + CH_3CHO \longrightarrow C_2H_5N=CHCH_3$ [Schiff's base]



$R_3N \xrightarrow[HX]{NaNO_3} R_3N^+HX^- + R_3N^+-N^+=OX^-$

Reaction of Aryl Diazonium Salt:





Reduction Reactions:

$Ph-NO_2 \xrightarrow[H_2O]{Zn/NH_4Cl} Ph-NH-OH$ (neutral medium)

$Ph-NO_2 \xrightarrow[8[H]]{Zn/NaOH \text{ in } CH_3OH} Ph-N=N-Ph$

$Ph-NO_2 \xrightarrow{LAH} Ph-N=N-Ph$

$ArN=NAr \xrightarrow{\text{mild reduction}} ArNH-NHAr$ (Azo → Hydrazo)

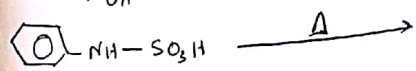
$ArN=NAr' \xrightarrow[(ii)\ OH^-]{(i)\ SnCl_2, H_3O^+} ArNH_2 + Ar'NH_2$

$Ph-NO_2 \xrightarrow{Sn/NaOH} PhNH-NH-Ph$

Rearrangement Reactions:

$Ph-\underset{\underset{NO}{|}}{N}-R \xrightarrow[(ii)\ OH^-]{(i)\ H^+} ON-Ph-NH-R$ [Fischer Hepp rearrangement]

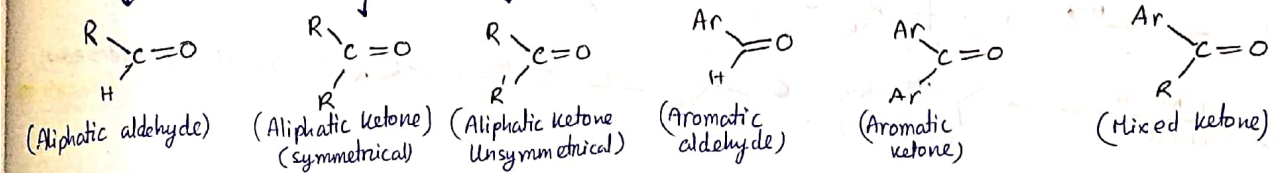
$PhNHOH \xrightarrow[(ii)\ OH^-]{(i)\ H^+} p\text{-}HO-Ph-NH_2$ [Phenyl hydroxyl amine rearrangement]



$Ph-NH-NH-Ph \xrightarrow{H_3O^+} H_2N-Ph-Ph-NH_2$ [Benzydine Rearrangement]

Aldehyde & Ketone

Carbonyl compounds



(Aliphatic aldehyde) (Aliphatic ketone (symmetrical)) (Aliphatic ketone Unsymmetrical) (Aromatic aldehyde) (Aromatic ketone) (Mixed ketone)

PREPS

- From Alkanes: $R-CH=CH_2 \xrightarrow[H_2O/H^+]{O_3/Zn} R-CHO + O=CH_2$ [Reductive ozonolysis]
- $R-CH=CH_2 \xrightarrow[[Co_2(CO)_8]]{CO+H_2} R-CH_2-CH_2-CHO$ [Only for terminal alkenes]
- $R-CH=CH_2 \xrightarrow[air/Cu_2Cl_2]{PdCl_2/H_2O} R-C(=O)-CH_3$ [Wackers process]
- From Alkynes: $R-C\equiv CH \xrightarrow{H_2O/HgSO_4/H_2SO_4} R-C(=O)-CH_3$ [Hydration]
- $R-C\equiv CH \xrightarrow[H_2O_2/OH^-]{R_2BH} R-CH_2-CHO$ [Hydroboration]
- From alcohols: $R-CH_2-OH \xrightarrow[300°C]{Cu \text{ or } Ag} R-CHO$ [Dehydrogenation]
- $R-CH_2-OH \xrightarrow[CH_2Cl_2]{PCC} R-CHO$
- $R-CH_2-OH \xrightarrow[(Fenton's\ Reagent)]{FeSO_4+H_2O_2} R-CHO$
- $R-CH_2-OH \xrightarrow{X_2/H_2O} R-CHO$
- $R-CH_2-OH \xrightarrow{CrO_3/AcOH} R-CHO$
- $R-CH_2-OH \xrightarrow{[(CH_3)_3CO]_3Al} R-CHO$ [Oppenauer oxidation]
- From CAD: $R-C(=O)-Cl \xrightarrow{H_2/Pd-BaSO_4} R-CHO$ [Rosenmund]
- $R-C(=O)-Cl \xrightarrow[or\ (t\text{-}BuO)_3AlHLi]{DIBAL-H} R-CHO$
- $R-C(=O)-Cl \xrightarrow{R_2'Cd} R-C(=O)-R'$
- $R-C(=O)-Cl \xrightarrow{R_2'CuLi} R-C(=O)-R'$
- $R-C(=O)-OR \xrightarrow{DIBAL-H} R-CHO$
- $R-C\equiv N \xrightarrow{DIBAL-H} R-CHO$ [Stephen's Reduction]
- $R-C\equiv N \xrightarrow{SnCl_2/HCl} R-CHO + NH_4^+$
- From Alkyl benzene: $Ph-CH_3$ (toluene) $\xrightarrow[(ii)\ H_3O^+]{(i)\ CrO_2Cl_2} Ph-CHO$ [Etard reaction]
- $Ph-CH_3 \xrightarrow[(ii)\ AcOH\ (iii)\ H_3O^+]{(i)\ CrO_3 \text{ in } Ac_2O} Ph-CHO$
- $Ph-CH_3 \xrightarrow[560°C]{Air/MnO} Ph-CHO$
- From Benzene: $\xrightarrow{R-C(=O)-Cl,\ Anhyd\ AlCl_3}$ [Friedel craft's acylation]
- $\xrightarrow[or\ ZnCl_2]{CO/HCl,\ Anhyd\ AlCl_3}$ [Gatterman-Koch]
- $\xrightarrow{HCN/HCl,\ Anhyd\ HCl}$ [Gatterman aldehyde synthesis]

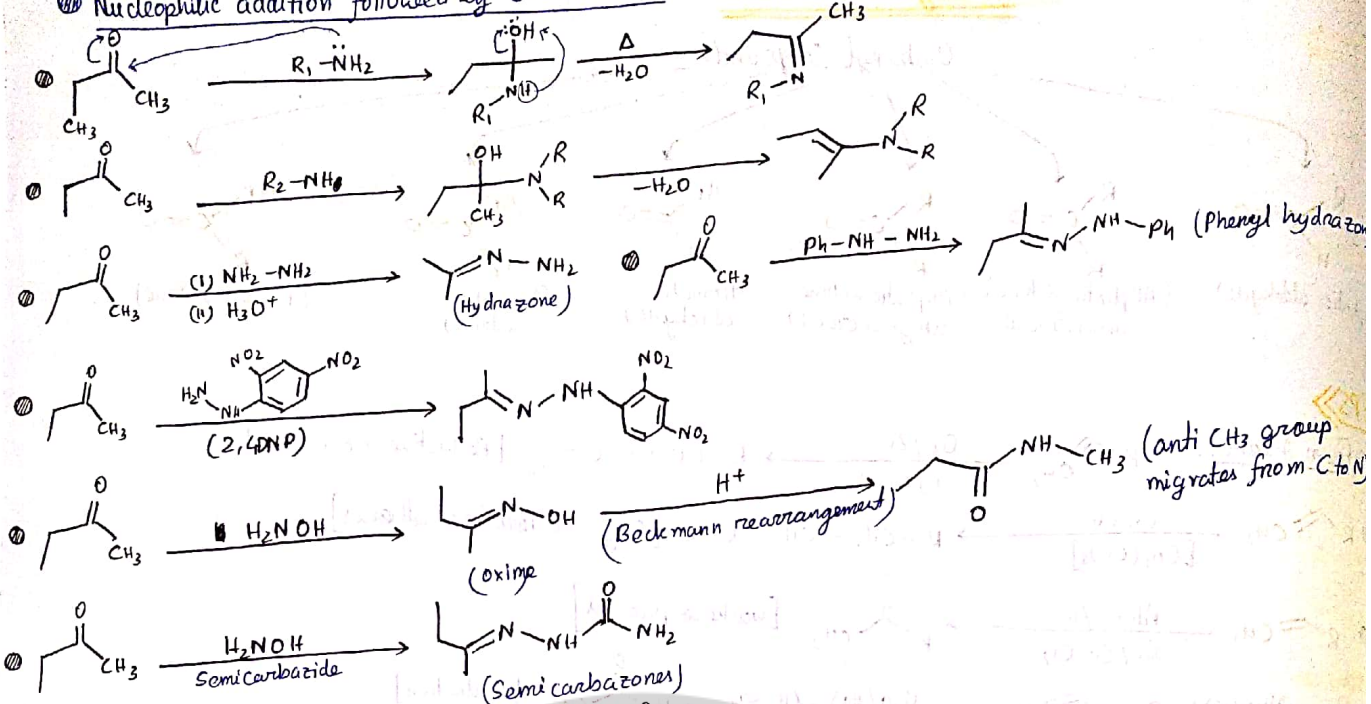
PROPS

- Reactions due to $>C=O$ group:
- Nucleophilic addition: $R-CHO \xrightarrow[NaCN+H_2SO_4]{HCN \text{ or}} R-CH(OH)-CN$ (cyanohydrin) (Reaction is accelerated by base and retained by acid)
- $R-CHO \xrightarrow{NaHSO_3} R-CH(ONa)-SO_3H \rightleftharpoons R-CH(OH)-SO_3Na$
- $R-CHO \xrightarrow[OH^-]{R_1-OH} R-CH(OH)-OR_1$ (Hemiacetal)
- $R-CHO \xrightarrow[dry\ HCl]{R_1-OH} R-CH(OR_1)-OR_1$

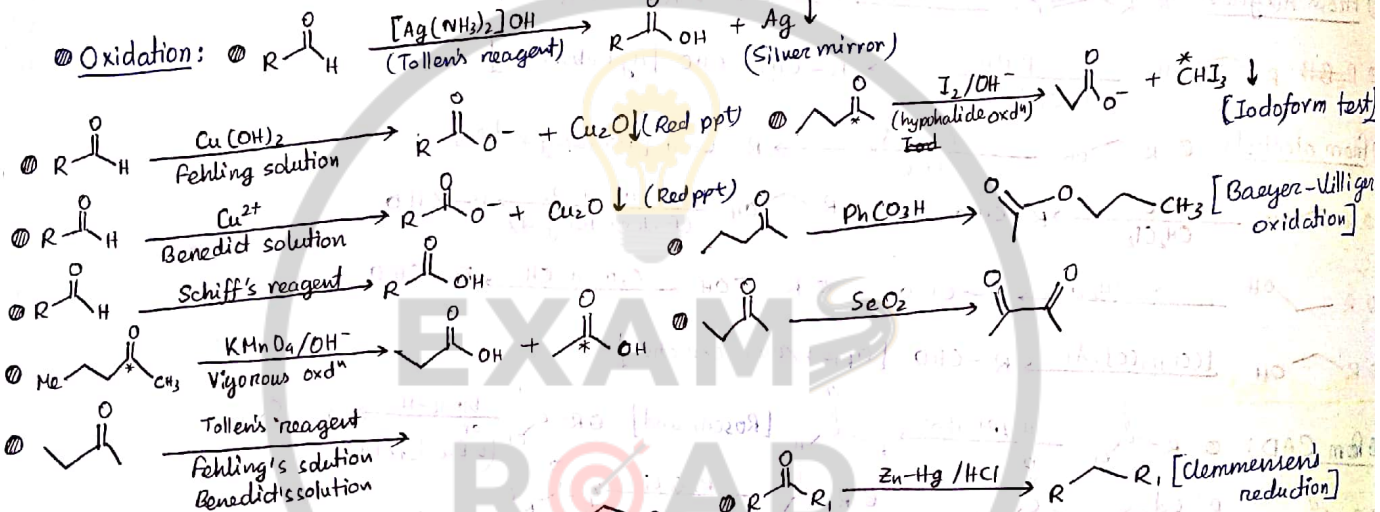
Open chain acetals are stable only in case of aldehyde while for ketones only cyclic acetals exist, and acetals get hydrolysed to give aldehyde or ketone in aq. acid)

- $R-CHO \xrightarrow{R_1-MgX} R-CH(OMgX)-R_1 \xrightarrow{H_3O^+} R-CH(OH)-R_1 + Mg(OH)Cl$
- $R-CHO \xrightarrow{H_2O} R-CH(OH)-OH$ (Gem-diols)
- $R-CHO \xrightarrow{Na-C\equiv C-R_1} R-CH(ONa)-C\equiv C-R_1 \xrightarrow{H_3O^+} R-CH(OH)-C\equiv C-R_1$

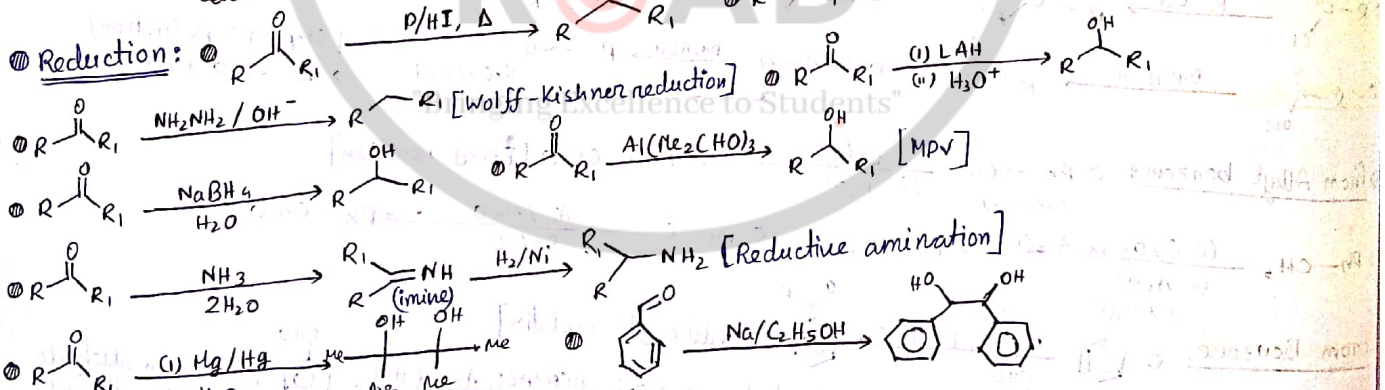
Nucleophilic addition followed by elimination:



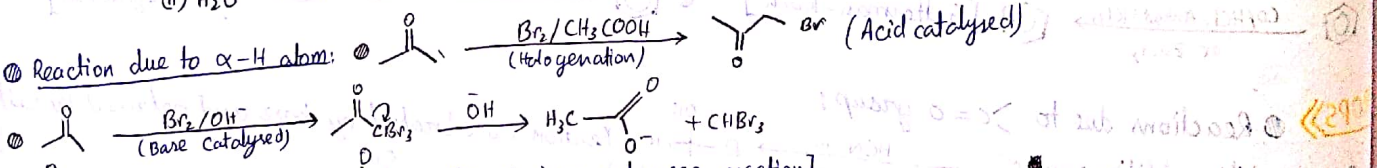
Oxidation:



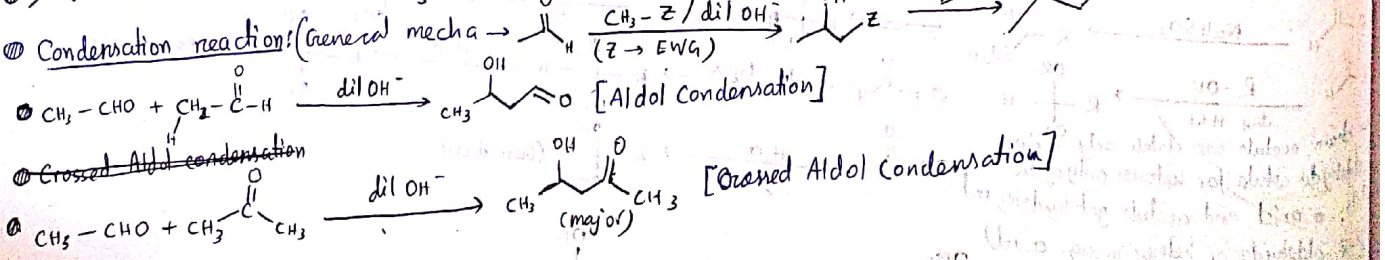
Reduction:



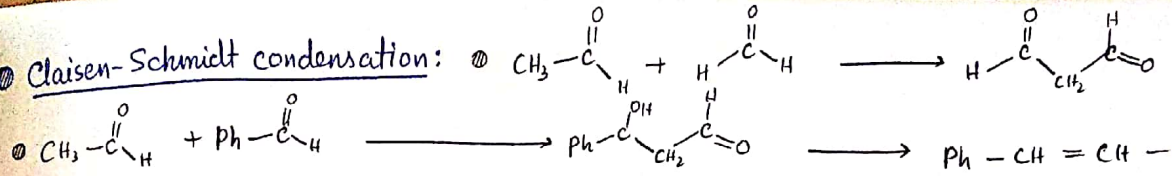
Reaction due to α-H atom:



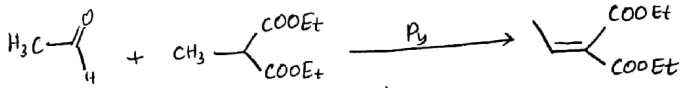
Condensation reaction: (General mecha →



Claisen-Schmidt condensation:

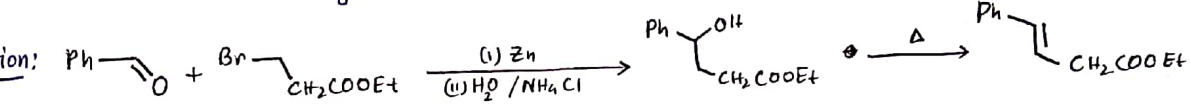


Knoevenagel's reaction:

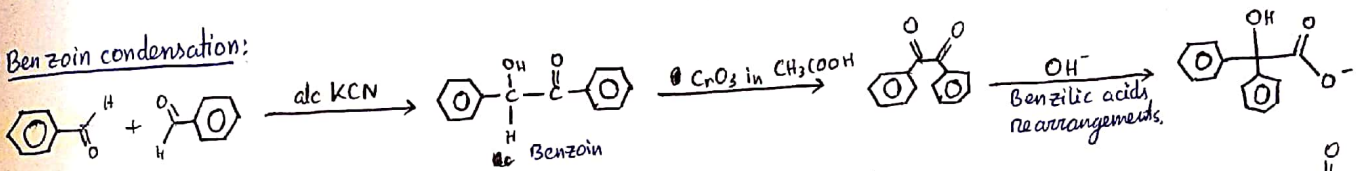


(reactive methylene comp)

Reformatsky reaction:



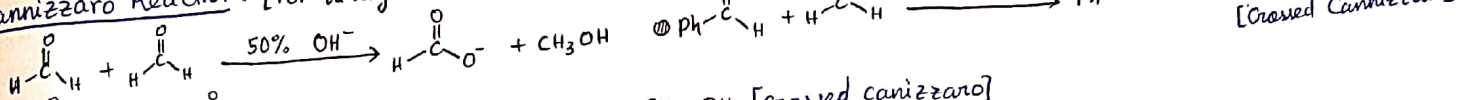
Benzoin condensation:



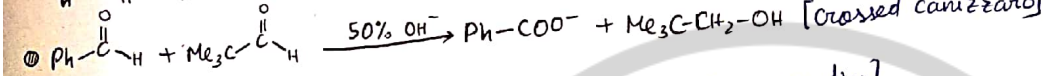
Benzoin

Benzilic acids rearrangements.

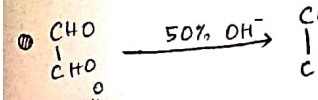
Cannizzaro Reaction: [for aldehyde w/o α-H atom]



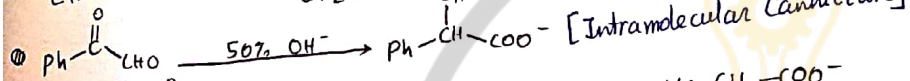
[Crossed Cannizzaro]



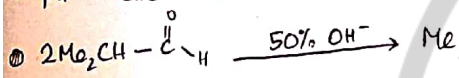
[Crossed cannizzaro]



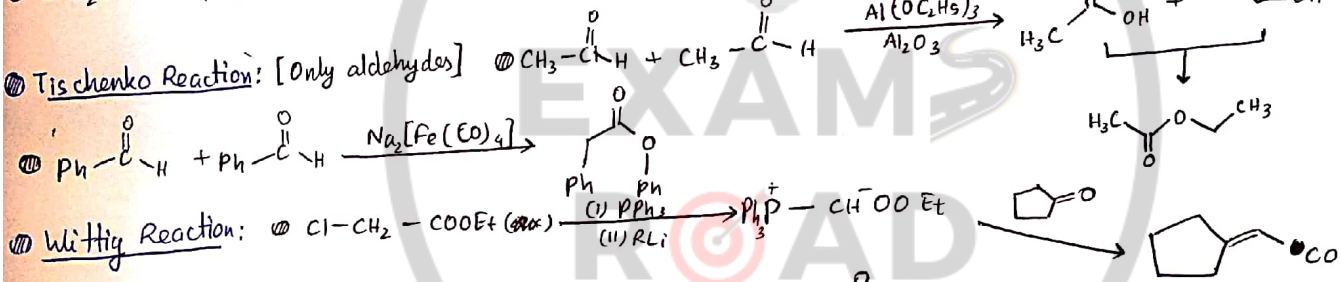
[Intramolecular Cannizzaro reaction]



[Intramolecular Cannizzaro]

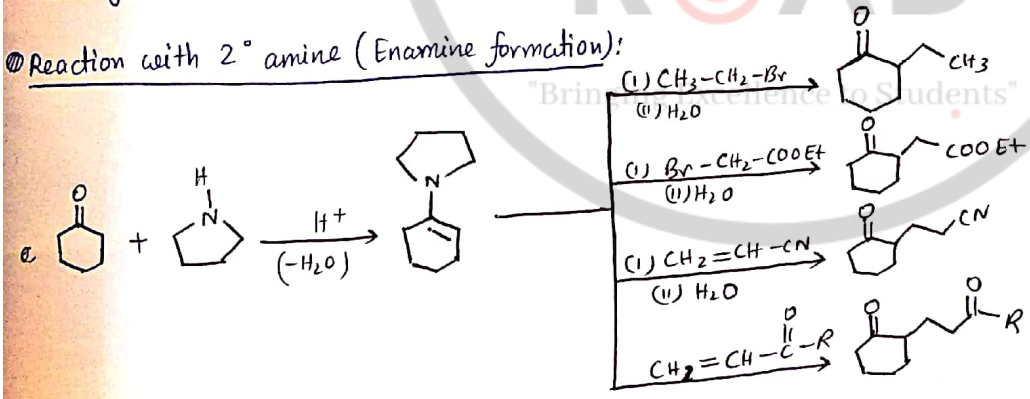


Tischenko Reaction: [Only aldehydes]

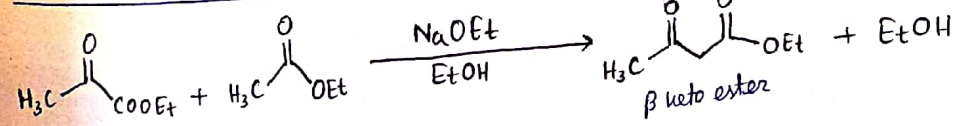


Wittig Reaction:

Reaction with 2° amine (Enamine formation):



Claisen Condensation:



β keto ester