Organic Chemistry Short Notes.

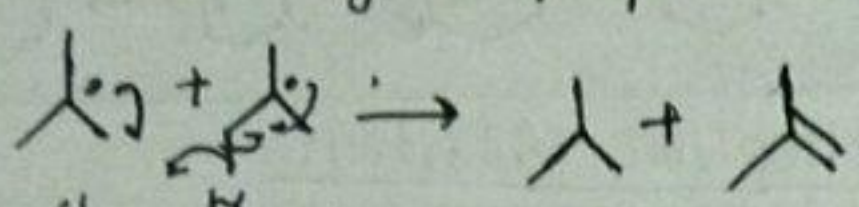
1) Wurtz Reaction ÷ Na / Et_2O.

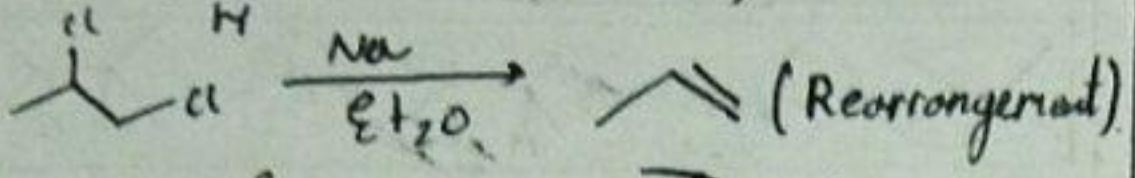
- Free Radical Intermediate → A) Combination, B) Disproportionation, C) Rearrangement.

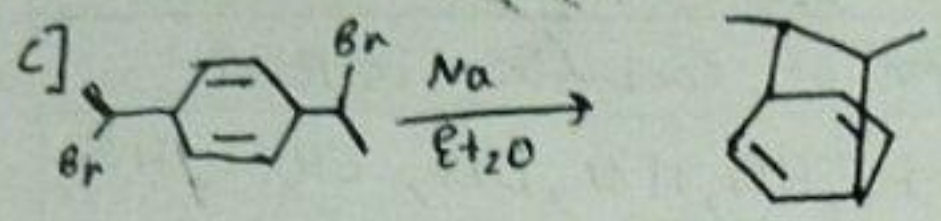
[* $2R-X + Na \longrightarrow R-R + NaX$]

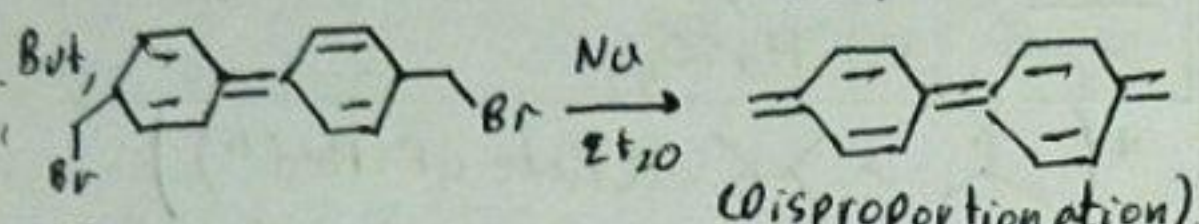
* ~~Bond~~ ROR: $C-I > C-Br > C-Cl > C-F$.

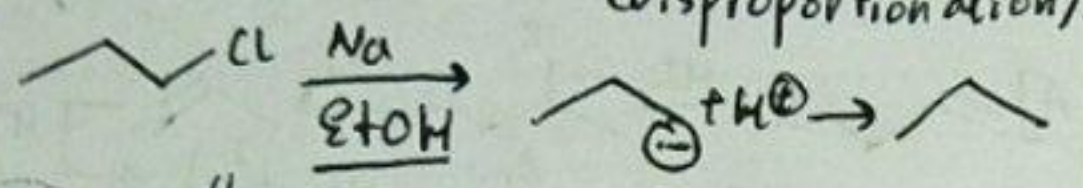
* 3° Radicals Never combine. Instead they Disproportionate.

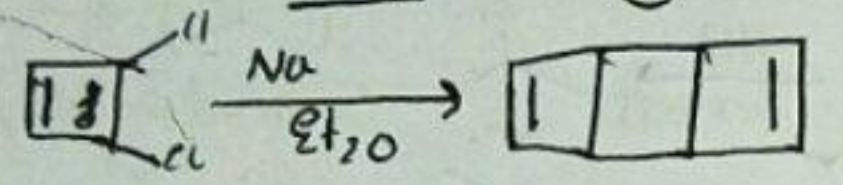
A] 

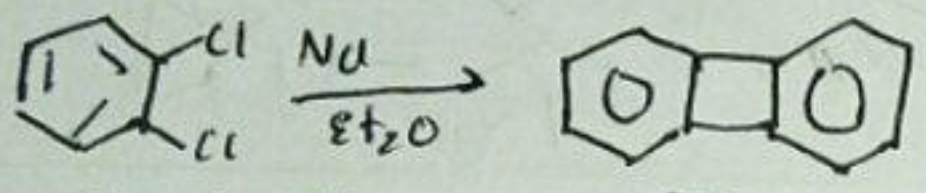
B] 
(Rearrangered)

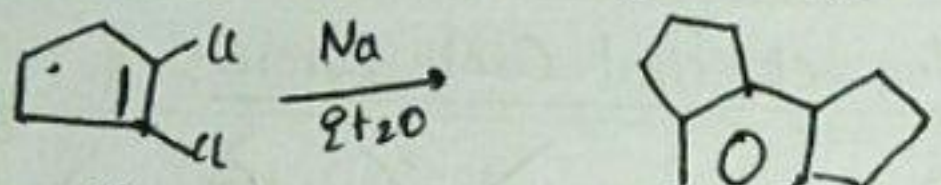
C] 

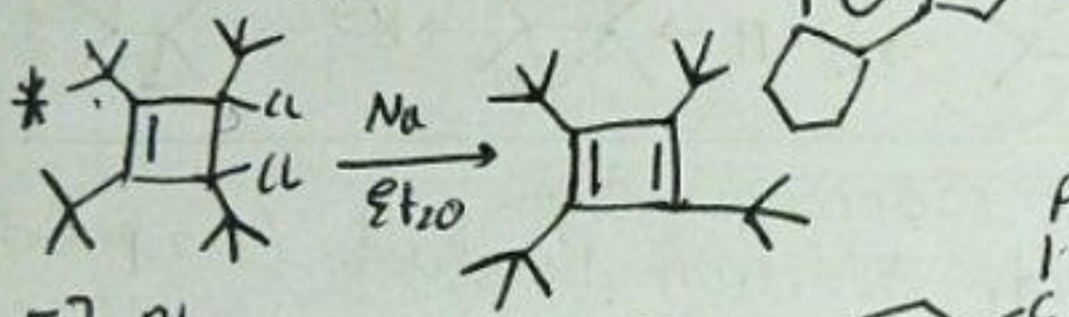

(Disproportionation)

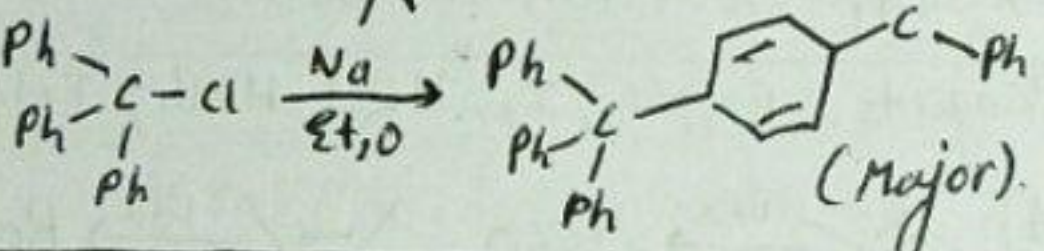
D] 

E] 







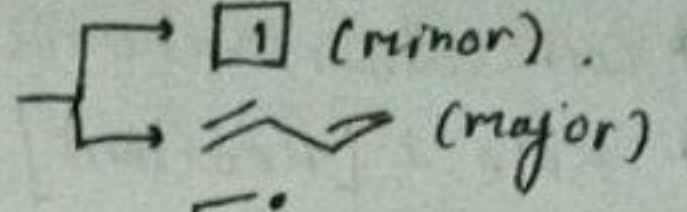
F] 
(Major)

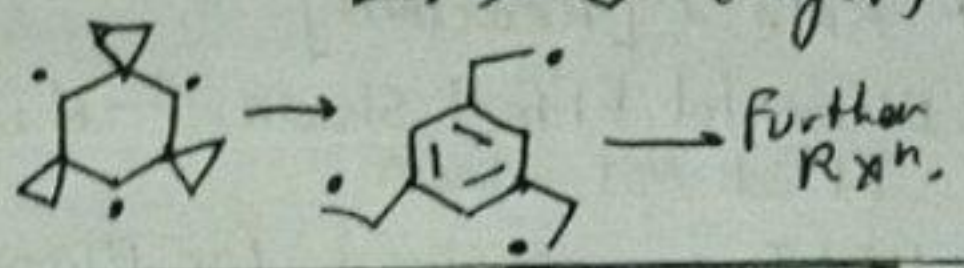
2) Kolbe's Electrolysis ÷ $NaOH, e^- / H_2O$

$$2RCOO^{\ominus}Na^{\oplus} + 2H_2O \xrightarrow{Elec} R-R + 2CO_2 + 2H_2 + 2Na^{\oplus} + 2OH^{\ominus}$$

* Free Radical Intermediate ÷ Same as Wurtz.

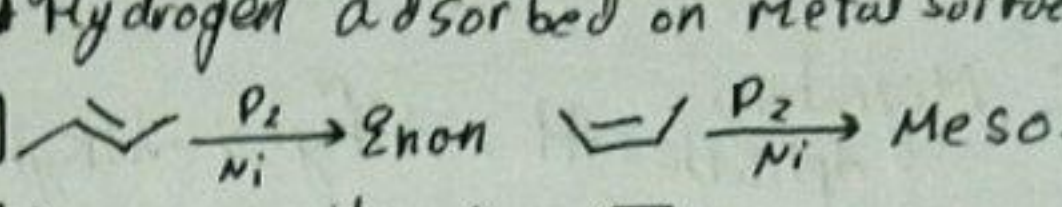
* moles of gas Released = 3 + (R-R, if Et, Pr, Bu).

A] 
[1] (minor).
(major)

B] 
Further Rxn.

3) Hydrogenation ÷ $H_2 / Pt, Pd, Ni$

* Syn addition * Concerted Mechanism.
* Hydrogen adsorbed on metal surface.

A] 
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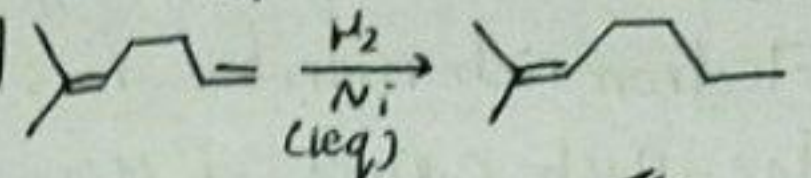
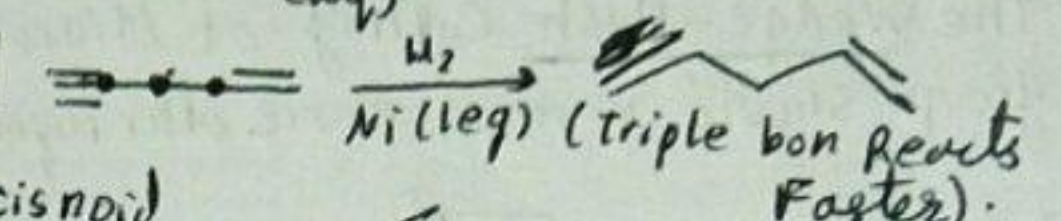
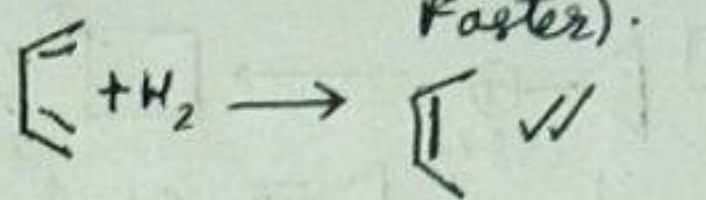
B] 
(1eq)

C] 
(Triple bon Reacts Faster).

* cisnoid Alkenes show 1-4 Addition ÷ 

4) Transfer Hydrogenation ÷ NH_2-NH_2 / H_2O_2

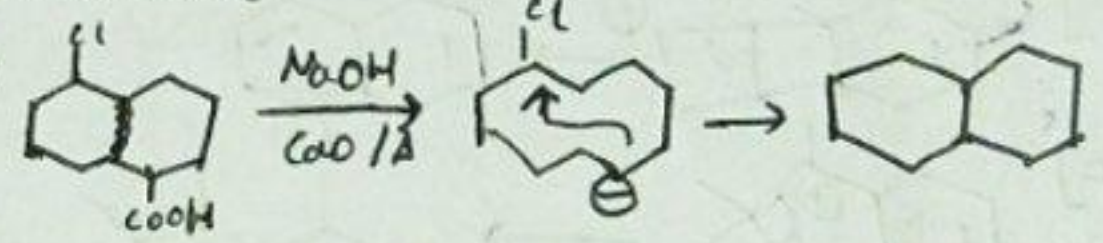
* $NH=NH$ is hydrogenating agent (Bolky)
* only C-C unsaturation is Reduced by it

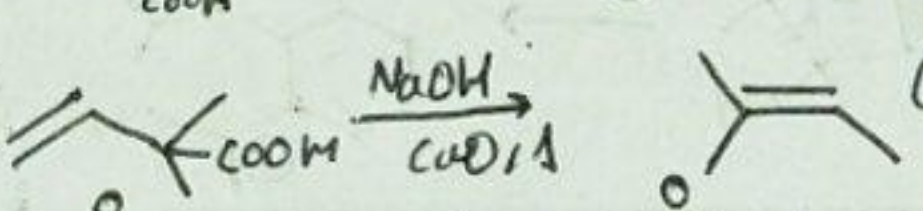
$$R_1-C\equiv C-R_2 \xrightarrow{NH=NH} \underset{H}{\overset{R_1}{}}\!\!>\!\!=\!\!<\underset{H}{\overset{R_2}{}} + N_2(\uparrow)$$

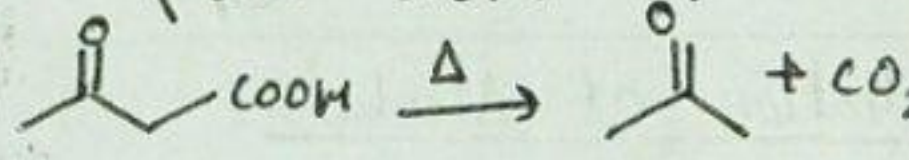
* It does not do 1-4 Addition.

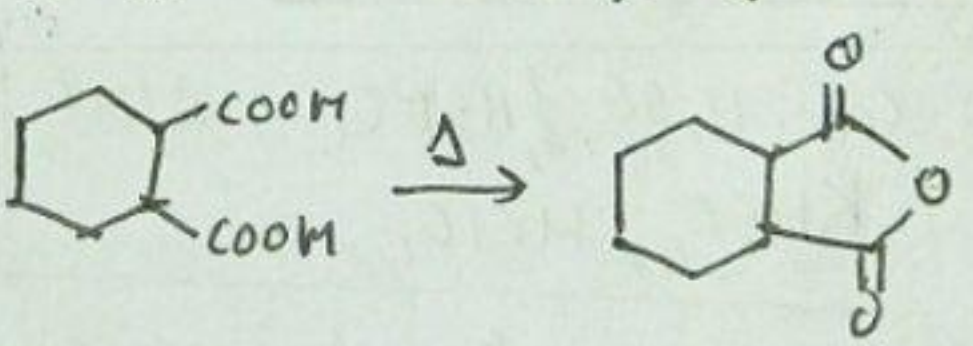
5) Soda Lime Decarboxylation ÷ NaOH/CaO, Δ

* carbanion intermediate ÷ RORa stability of carbanion.

A] 

B] 
(Resonance).

C] 

D] 

6) E_1 Elimination Mechanism.

⇒ C-X bond strength < C-H bond strength.

* Carbocation Mechanism. (2-step)
* Rate ∝ [Reactant]^1
* Elemental Effect Shown. β-H isotopic Effect Not Shown.
* HEAT is required for Elimination.
* Every subsequent ⊕ should be more stable than the previous ones.

** Migratory Aptitude: -H > -Aryl > -Alkyl.

→ More Electron rich migrates first.

→ The Wedge-Dash Config of Migrating group should remain same after migration.

*A] (48-1) → (47-1) ↔ (2-54-) (2-54-).

B] NH_2/OH → NH_2/OH.

[even 7mem → 8mem]

C] Ring Contraction. (6,5) ↓ (5,6).

D]

E]

F]

7) Dehydration of Alcohols.

Reagent: Conc. H_2SO_4, H_3PO_4, $\Delta/H^⊕$, $KHSO_4$, $HClO_4$..

R-$\overset{⊕}{O}H_2$ is an Intermediate too

* Formation of Carbocation → R.D.S.
* Saytzeff Alkene is formed.
* no. of T.S = no. of I + 1

A] conc. H_2SO_4

B] (β-naphthol)

C] (no reso in ⊕ because 6 mem OP)

D]

8) Electrophillic Addition.

* Formation of Carbocation is RDS.

Reagents: HI, HBr, HCl, DBr, $CH_3OH/H^⊕$, $H_3O^⊕$, Dil. H_2SO_4.

*(> (Rate of Redn))

A] HI

B] HBr (excess) (Gem-dihalide).

C] HBr

9) Non-classical Carbocation.

* no rearrangement.
* Anti Addition Product. (1-2 product)

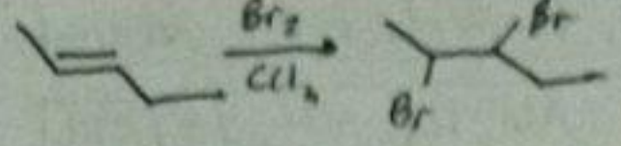
Reagents: Br_2, Cl_2, I_2, HOCl, HOBr, ICl, IBr,

A] Br_2/CCl_4 → Meso ; Br_2/CCl_4 → Racemic

B] Rate of Reaction: Alkene > Alkyne.

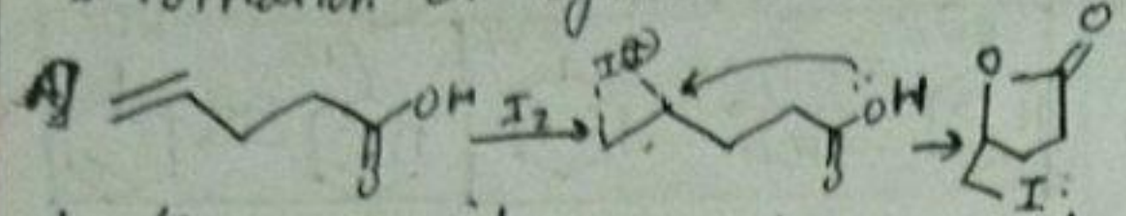
C] HCl/CCl_4 (As ⊕ > ⊕, no reso initially).

* The Nucleophile Attacks the position where more stable C⊕ is formed.

D]  (RM not formed as 50-50 ja nai)

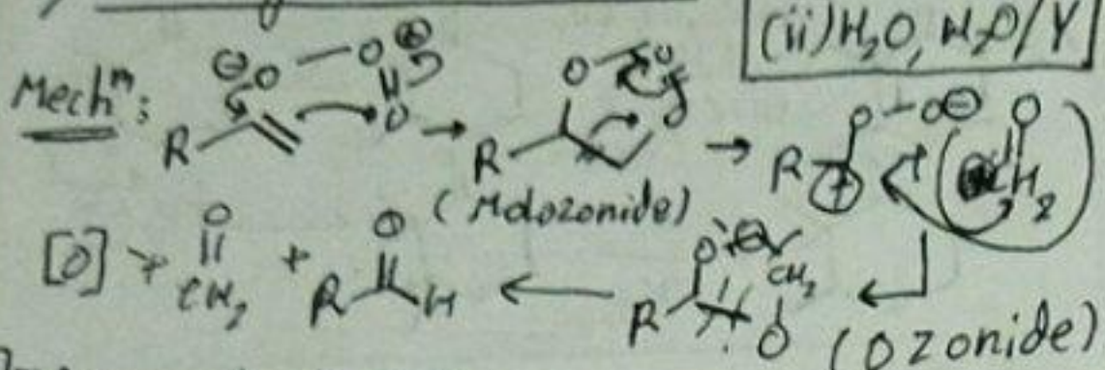
10) Iodolactization ÷ I_2/CCl_4

* Formation of cyclic ester.

A] 

*5/6 membered ring must be formed.

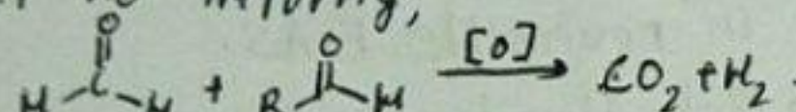
11) Ozonolysis of Alkenes ÷ $\xrightarrow[(ii)H_2O,\ H_2O/Y]{(i)O_3}$

Mechⁿ: 

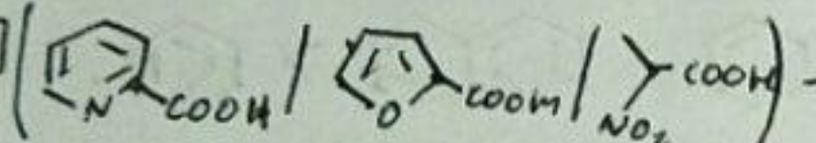
[I] If impurity Present: Zn, PPh_3, $S(CH_3)_2$

$Zn/PPh_3/S(CH_3)_2 \xrightarrow{[O]} ZnO / OPPh_3$ & $OS(CH_3)_2$

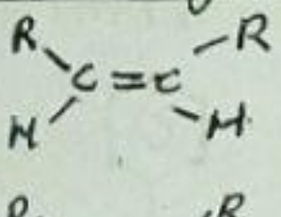
II] If no impurity,

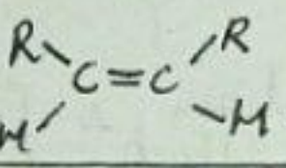


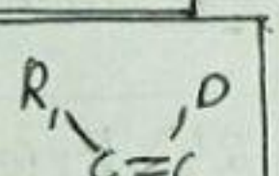
* Decarboxylation > Dehydration

A]  $\xrightarrow{\Delta}$ Decarboxylation

12) Catalytic Hydrogenation of Alkynes

Lindlar's Catalyst: $R-C\equiv C-R \xrightarrow[Pd-CaCO_3]{H_2}$ 

Rosenmund catalyst: $R-C\equiv C-R \xrightarrow[Pb-BaSO_4]{H_2}$ 

Birch Reduction ÷ $R_1-C\equiv C-R_2 \xrightarrow[EtOH]{Na,\ liq.\ NH_3}$ 

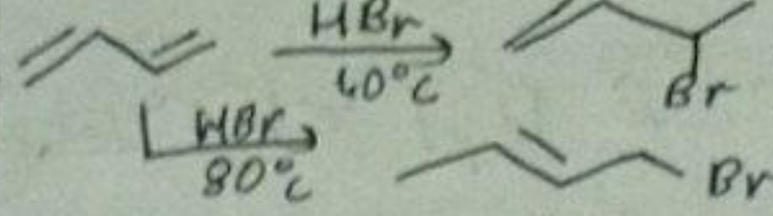
* Terminal Alkynes form Salt on Reaction with Na/liq. NH_3

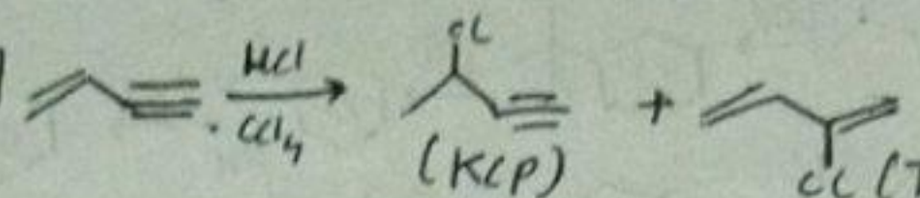
$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2(\uparrow)$

$R-C\equiv CH + NaNH_2 \longrightarrow R-C\equiv C^{\ominus}\ Na^{\oplus}$

This is further used to increase Chain length in organic Synthesis.

13) 1-2 v/s 1-4 Addition.



A] 

14) Ionic Carbides

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

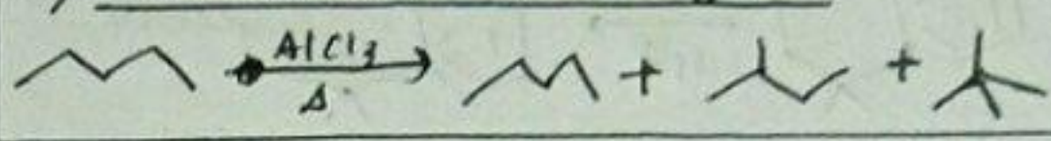
$Be_2C + H_2O \longrightarrow Be(OH)_2 + CH_4$

$Mg_2C_3 + H_2O \longrightarrow Mg(OH)_2 + C_3H_4$.

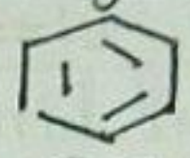
$Li_2C_2 + H_2O \longrightarrow LiOH + C_2H_2$

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

15) Isomerisation via $AlCl_3$, Δ



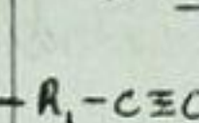
16) Polymerisation of Alkynes.

$3(CH\equiv CH) \xrightarrow[\text{Red hot tube.}]{Cu/\Delta}$  (or Fe/Δ).

$4(CH\equiv CH) \xrightarrow[\Delta]{Ni(CO)_4}$ 

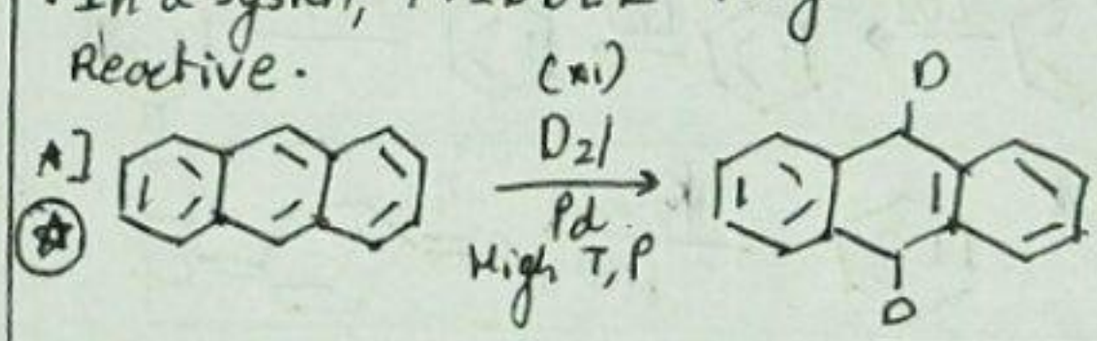
* Via Free Radical Mechanism.

17) Ozonolysis of Alkynes.

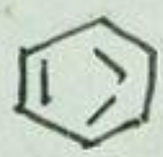
$R_1-C\equiv C-R_2 \xrightarrow[Zn]{O_3}$  $\xrightarrow{[O]}$ $R_1-COOH + R_2-COOH$.

18) Reduction of Aromatic Compounds.

*In a system, MIDDLE Ring is most Reactive.

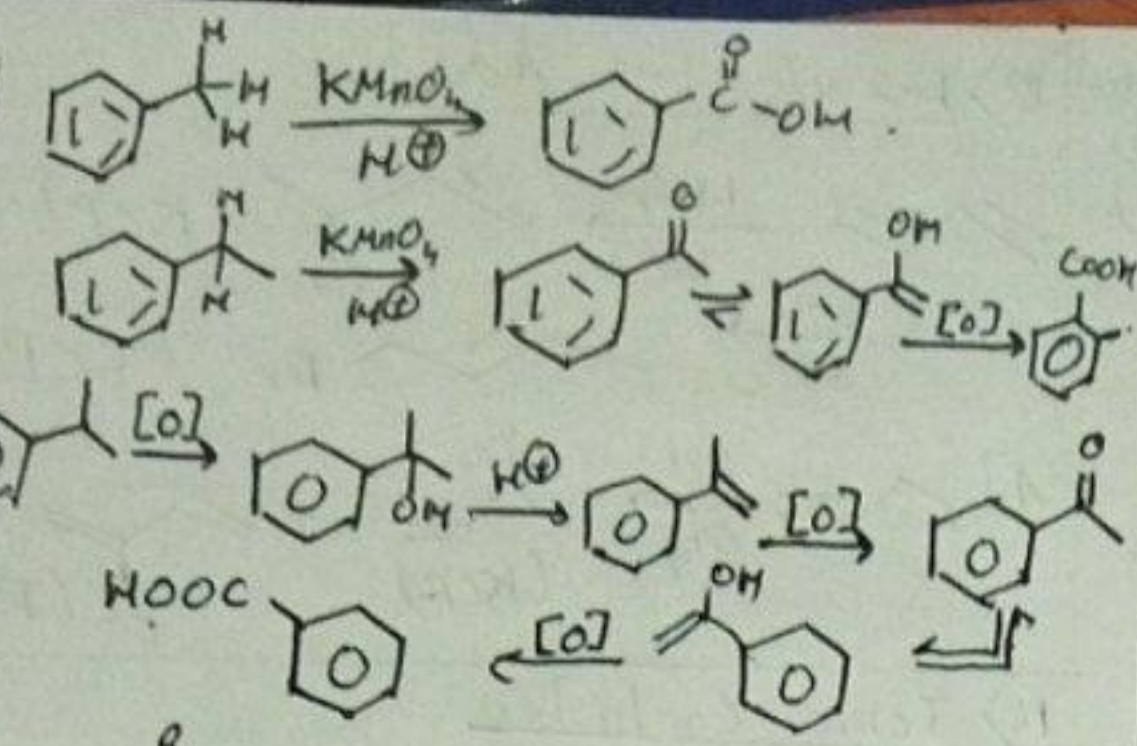
A] 

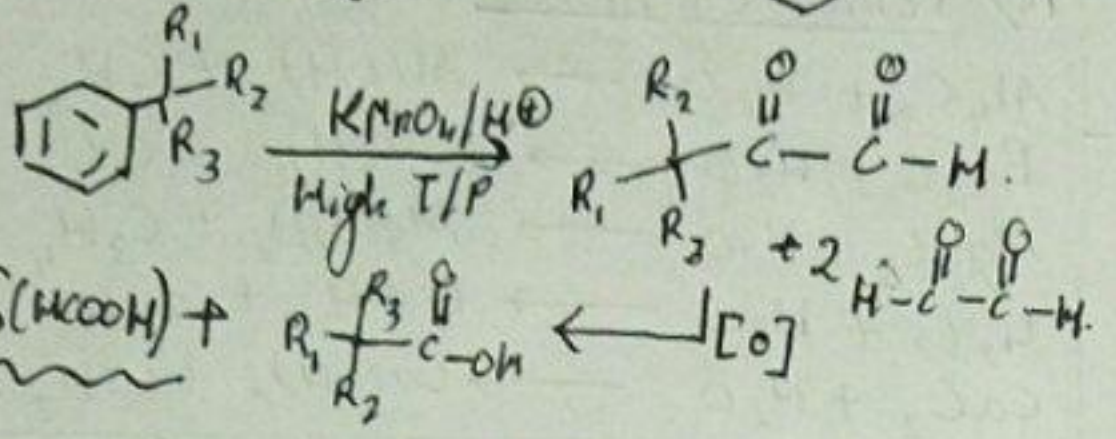
19) Oxidation via $KMnO_4/H^{\oplus}$.

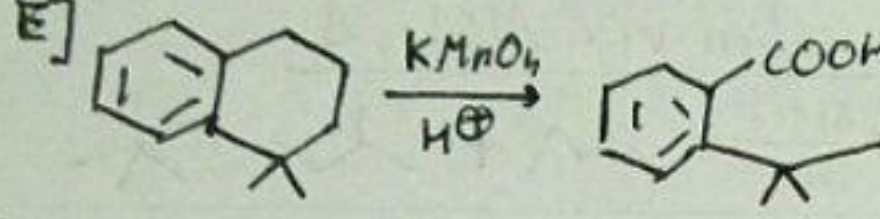
A]  $\xrightarrow[\text{Room Temp}]{KMnO_4/H^{\oplus}}$ no rxn.

B] $R_1-CH=CH-R_2 \xrightarrow[H^{\oplus}]{KMnO_4} R_1-COOH + R_2COOH$

* $KMnO_4/H^{\oplus}$ can oxidise ketones too.

C] 

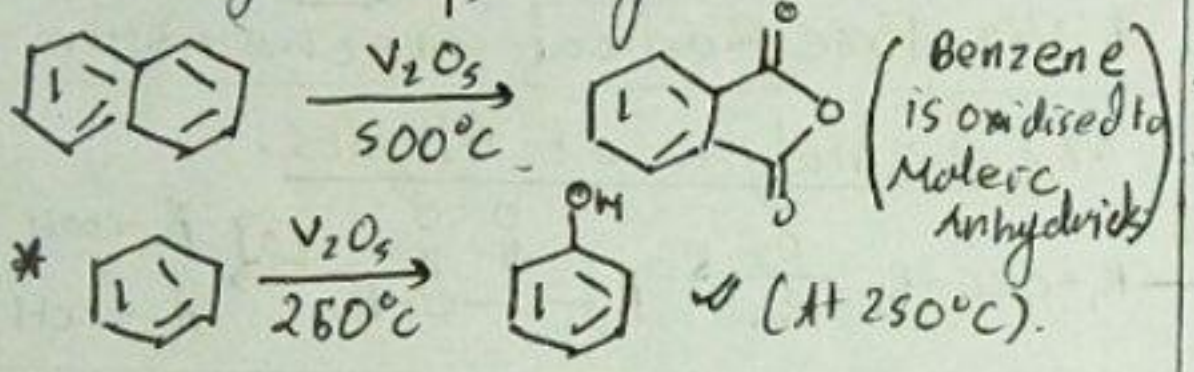
D] 

E] 

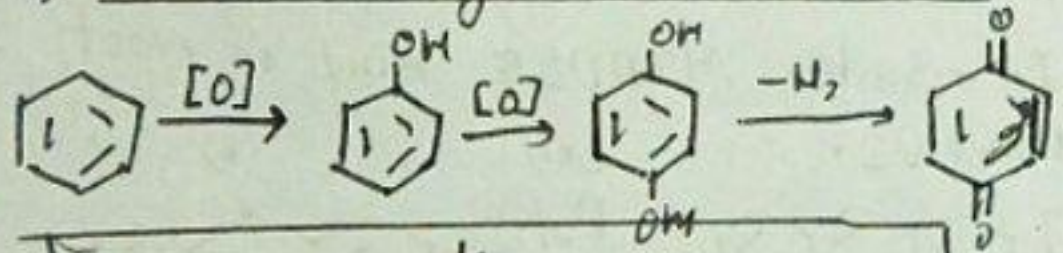
* The more e⁻ rich ring is oxidised first. ~~Ebar~~.

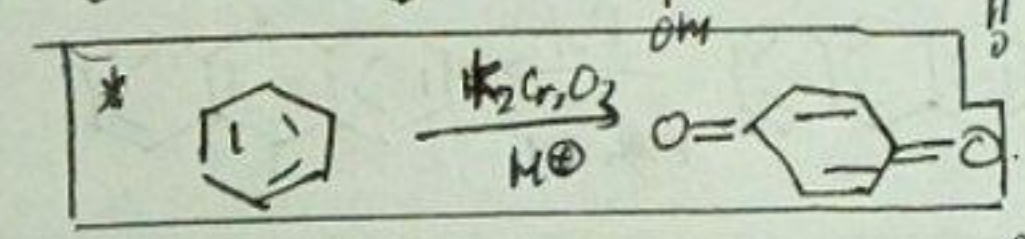
20) Oxidation by V_2O_5 / 500°C.

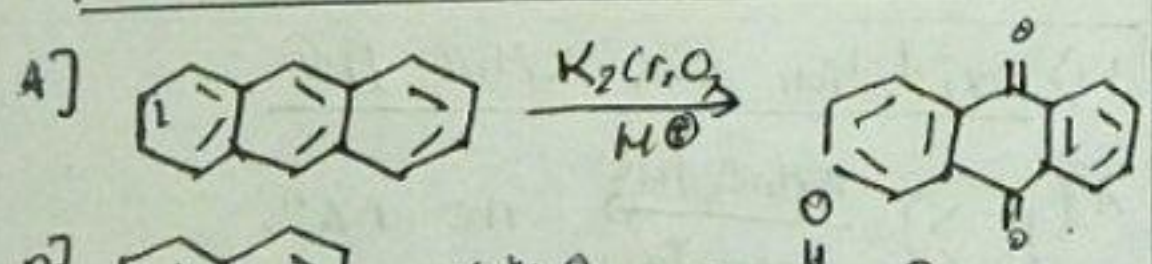
* At high temp, Anhydride is formed.

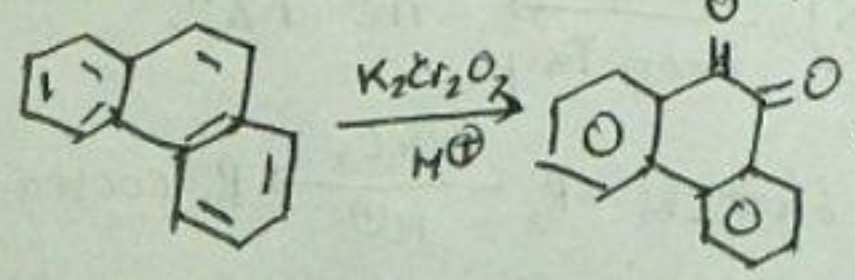


21) Oxidation by $K_2Cr_2O_7$ / M⊕.





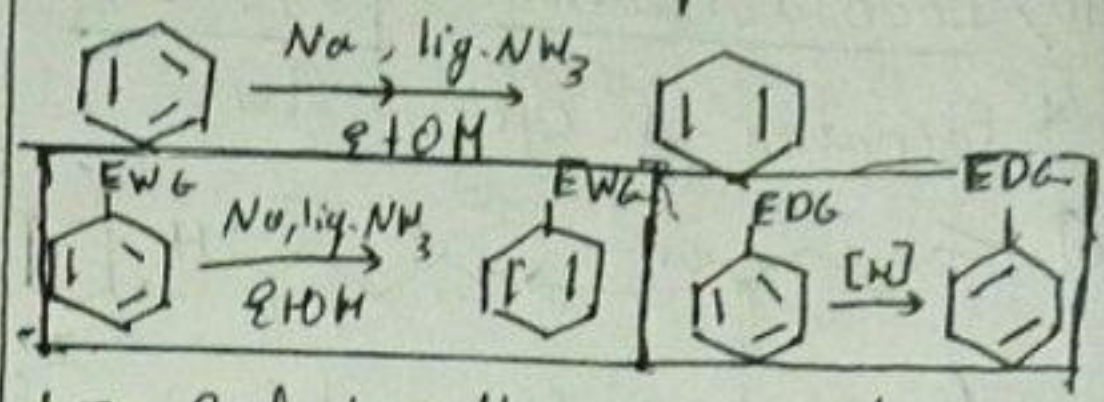
A] 

B] 

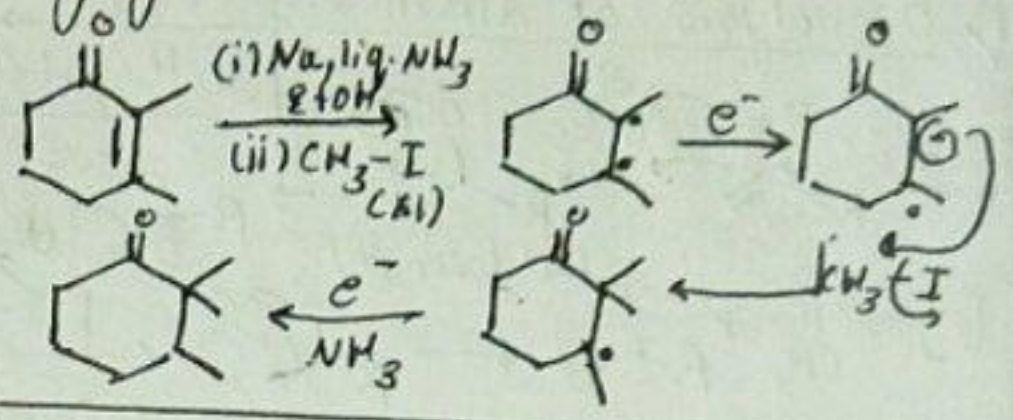
22) Birch Reduction of Aromatic Comp.

Reagent: Na, liq. NH_3 / EtOH

*1 Birch Reduction Requires 2 moles.



* In Reduction, the more e⁻ deficient Ring gets reduced first.

A] 

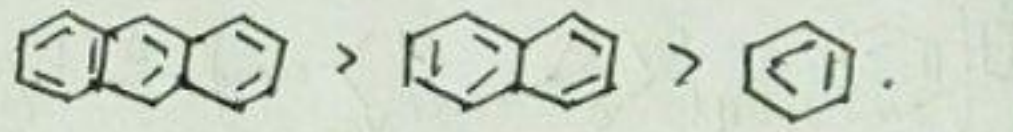
23) Electrophilic Aromatic Substitution.

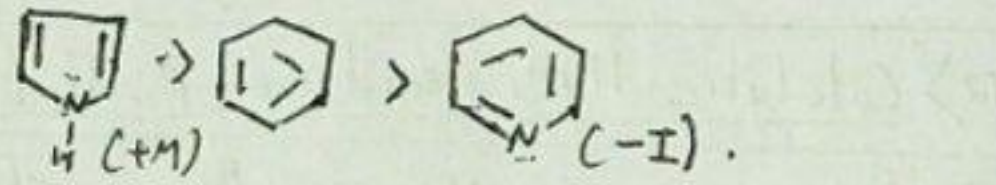
a) Formation of σ complex is RDS.

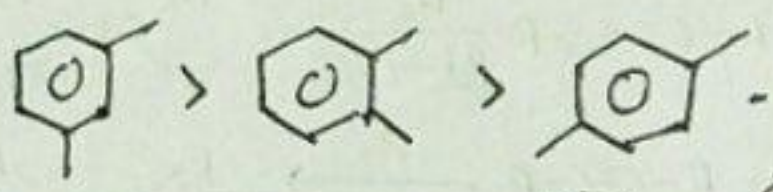
b) β-H isotopic Effect is not shown except in reversible EAS.

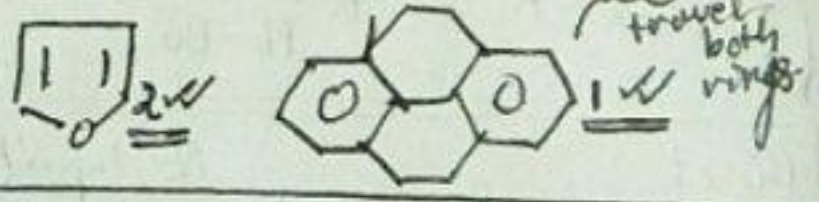
c) EWG → Meta Director
EDG → o-p Director (Para > ortho).

Rate of EAS :-

A] 

B] 

C] 

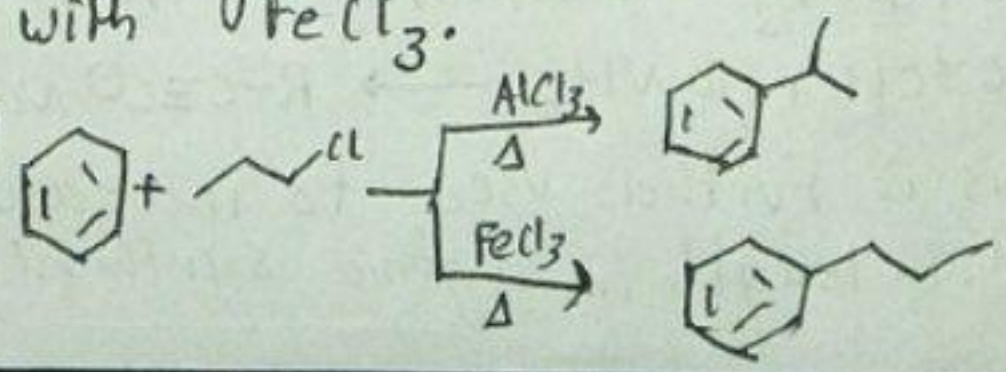
Position of Attack :- 

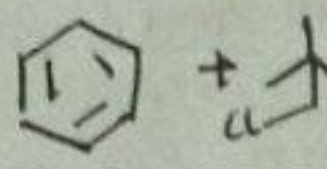
24) Friedel Craft Alkylation.

a) Lewis Acids like BF_3, AlX_3, FeX_3 are used.

b) carbocation → Rearrangement.

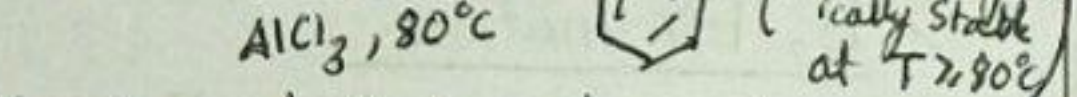
c) Rearrangement doesn't take place with $FeCl_3$.

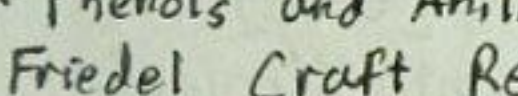
A] 

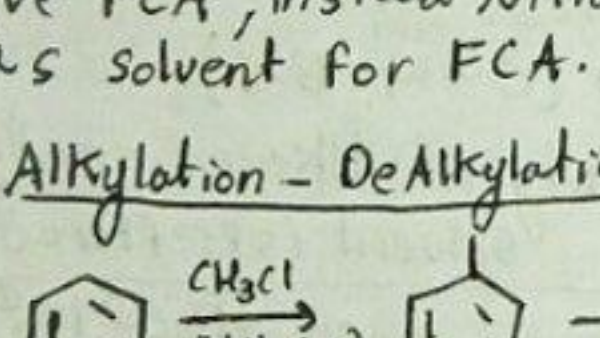
B]  $\xrightarrow[H_2O]{AlCl_3}$ no rxn (H_2O Destroys catalyst).

* In oxidation of cyanide with $KMnO_4$
$H^{\oplus}$, HNO_2 is released $\xrightarrow{[O]} HNO_3 \xrightarrow{\Delta} N_2O_5 + H_2O$

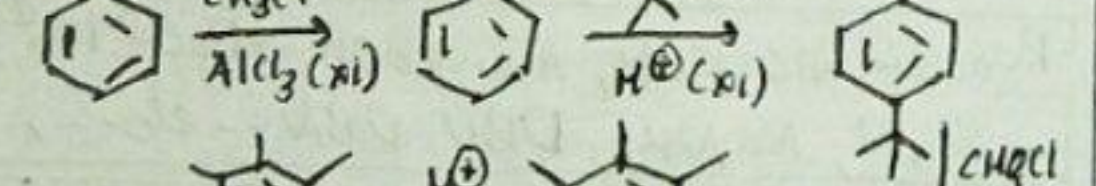
Deactivating +÷ $-Cl$, $-Br$, $-I$, $-C{=}CH_2$,
OP-Director $-N{=}O$, $-\overset{O}{\overset{\|}{S}}-OH$.

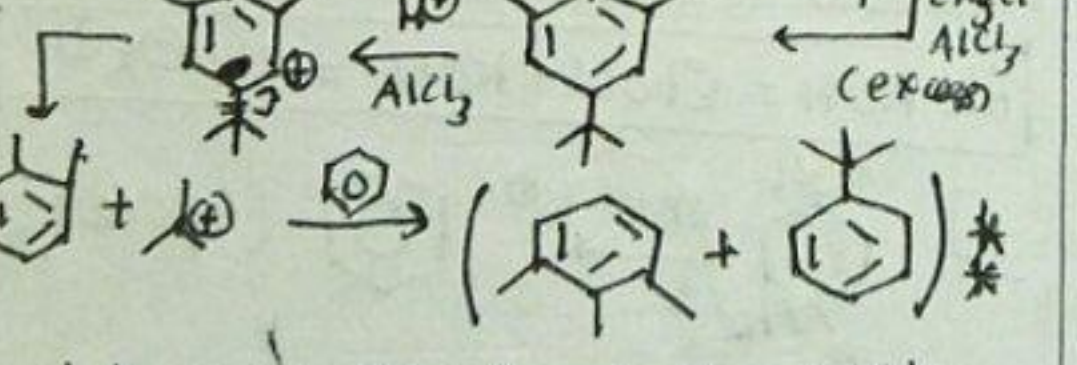
C] (i) 
(Easy cleavage)

(ii)  (Hard cleavage)
↳ Rearrangement not possible.

D] 

Reagent (Sketchell Rxn): $AlCl_3/H^{\oplus}$.

E]  (Stable $C^{\oplus}$ Formed).

F] 
(Thermodynamically Stable at T > 80°C)

* Phenols and Aniline do not Give Friedel Craft Reactions.
* Benzene Rings with EWG also do not Give FCA, instead Nitrobenzene is used as solvent for FCA.

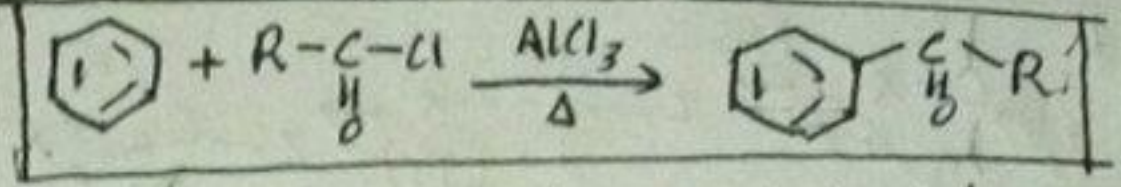
G] Alkylation - DeAlkylation ÷ $HCl/AlCl_3$

Ex÷

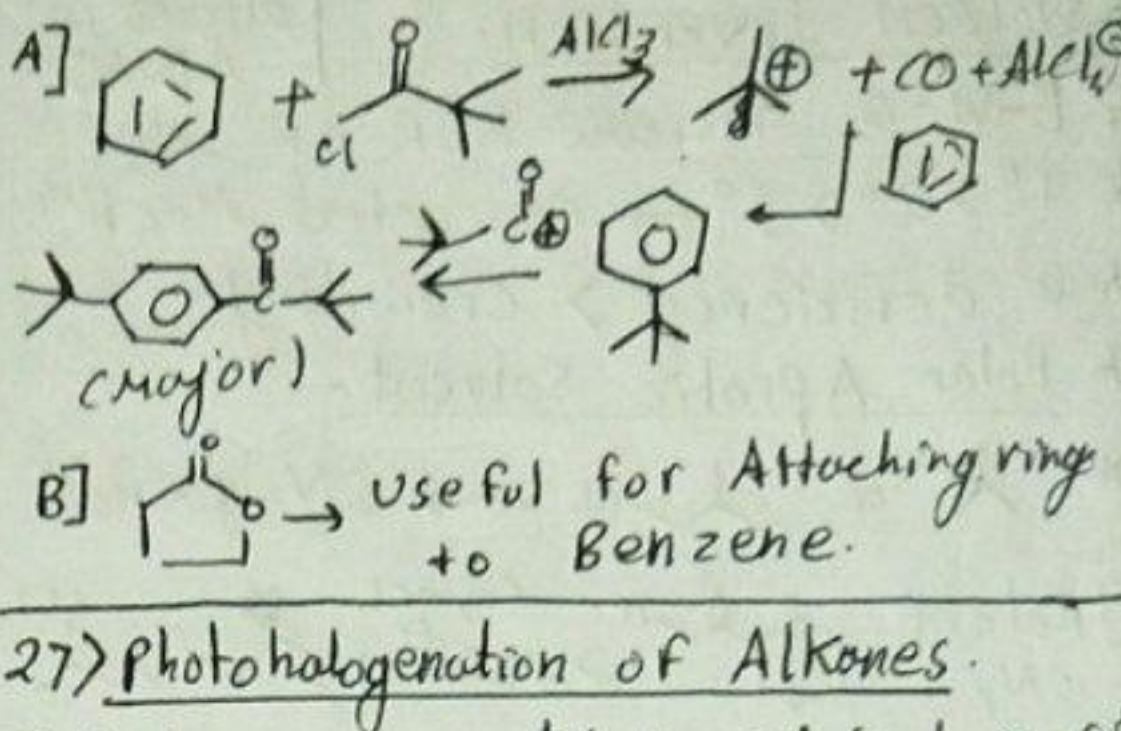
* Friedel Craft Alkylation is Reversible.
Hence, Rate of EAS ÷ $C_6H_6 > C_6D_6 > C_6T_6$.

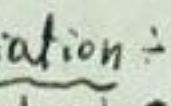
* Pd-C, catalyst of Hydrogenation, Performs Aromalization by Removing H_2.

26) Friedel Craft Acylation.



* no rearrangement, no polyAcylation.
* It is Irreversible in nature.

A] 

B]  → useful for Attaching ring to Benzene.

27) Photohalogenation of Alkanes.

Initiation ÷ $X-X \xrightarrow{h\nu} 2\dot{X}$ (endo, Para(↑))

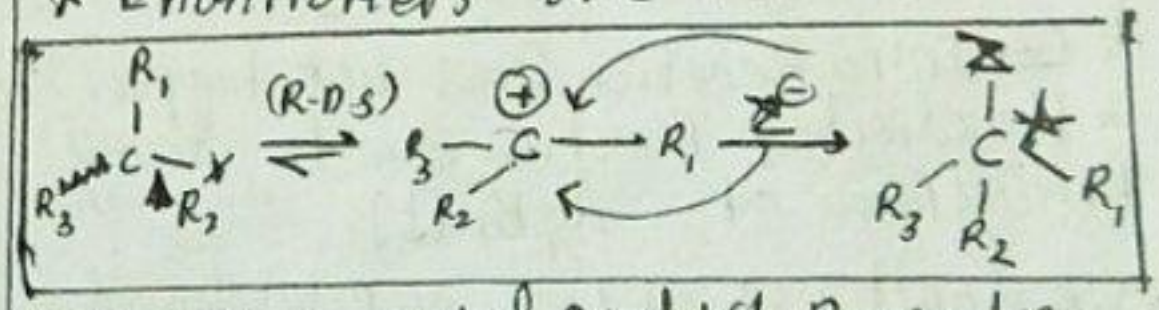
Propagation ÷ $\dot{X} + CH_3-H \longrightarrow \dot{C}H_3 + HX$ (RDS)
↓ exo or endo, Para = const
$\dot{C}H_3 + X-X \longrightarrow CH_3X + \dot{X}$

Termination ÷ $\dot{X} + \dot{C}H_3 \longrightarrow CH_3-X$
exo, Para(↓) $\dot{X} + \dot{X} \longrightarrow X-X$.
$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$.

* β-H Isotopic effect is shown.
* $F_2 >> Cl_2 > Br_2 > I_2$ → endo
(highly exo) ↙ ↘ Selective; 1 : 80 : 1600.
~~Selective~~ Reactive: 1 : 3.8 : 5

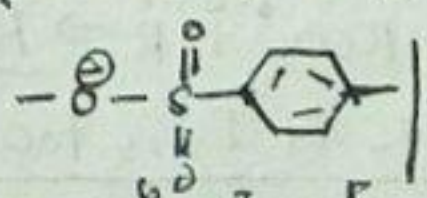
28) S_N1 Reactions. [Rate ∝ [substrate]]

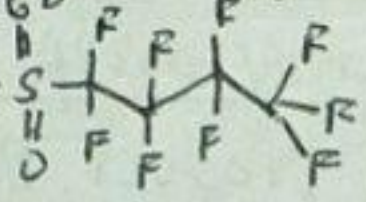
* Carbocation is formed.
* Enantiomers are Formed.



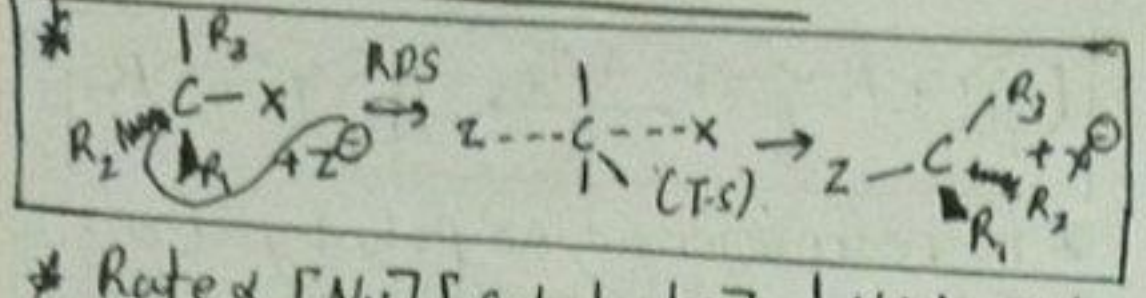
* Slightly Inverted product Dominates.
* Polar Protic Solvent is preffered.

L.G.A → {$-OTf > -OTs$.}

$-OTs$ = 
$-OTf = -O-\overset{O}{\overset{\|}{\underset{O}{S}}}-CF_3$.

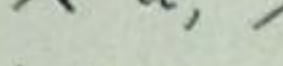
$-ONf$ =  (Nonaflate).

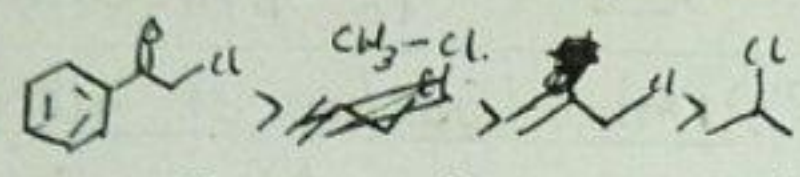
29) S_N2 Reactions. ÷



* Rate ∝ [Nu] [substrate]
* Walden Inversion.

Nucleophile attacks in ABMO.

* E-W-G increase ROR of S_N2.
* 1° > 2° > 3° → Concerted Mechm.
* e⁻ deficiency > crowding.
* Polar Aprotic Solvent.
*  → S_N2 jaanai

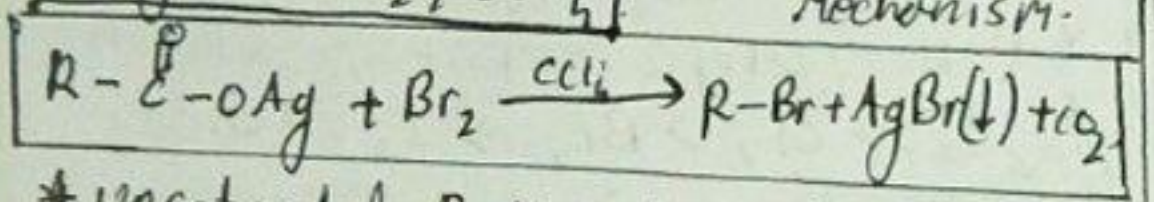
A] Rate of S_N2 ÷ 

Nucleophilicity: $I^\ominus > Br^\ominus > Cl^\ominus > F^\ominus$ (Protic).
$F^\ominus > Cl^\ominus > Br^\ominus > I^\ominus$ (Aprotic)

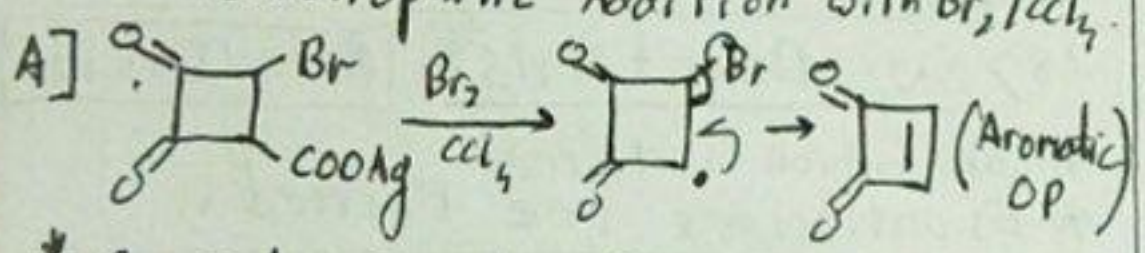
V. Product → $\frac{r_{SN}}{r_{net}} = \frac{K_1[\text{substrate}]}{K_1[\text{substrate}] + K_2[\text{substrate}][Nu]}$

30) Hunsdiecker Reaction.

Reagent: Br_2/CCl_4 → Free Radical Mechanism.



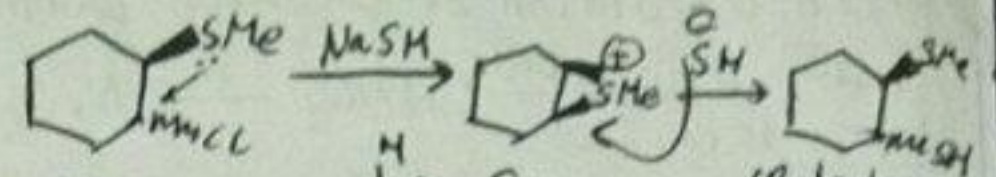
* Unsaturated R is not preffered as it Gives electrophilic Addition with Br_2/CCl_4.

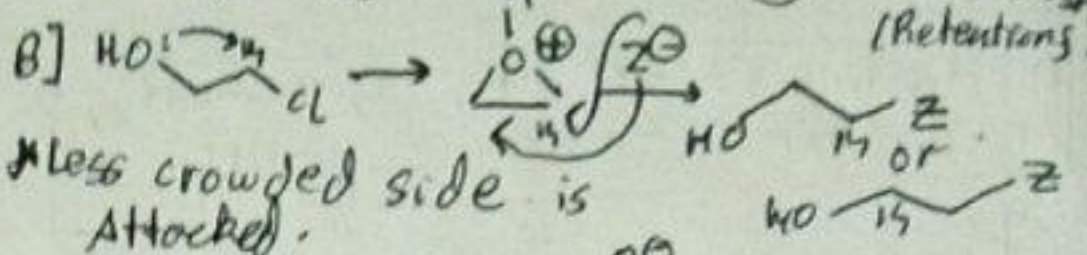
A] 

* ~~Cor~~ Intra Reaction Does not happen in Hunsdiecker Reaction due to strong Driving force of AgBr(↓).
* we don't use Cl_2/CCl_4 as polyhalogeration happens.
* If we use I_2/CCl_4 ÷
  a) 1:1 Ration → Normal Product.
  b) 2:1 Ratio → $RCOO^\bullet + {}^\bullet R \rightarrow$ RCOOR.
  since, cleavage of I_2 is too slow.

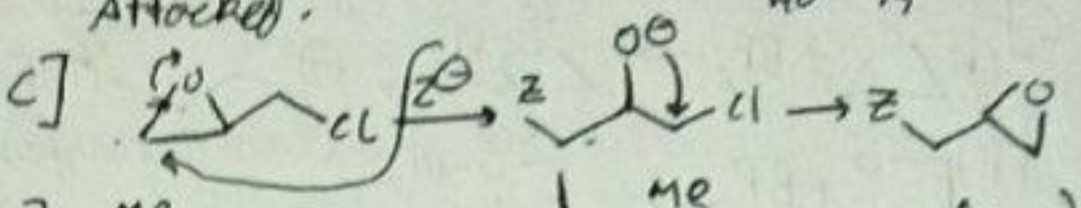
31) Neighbouring Group Participation

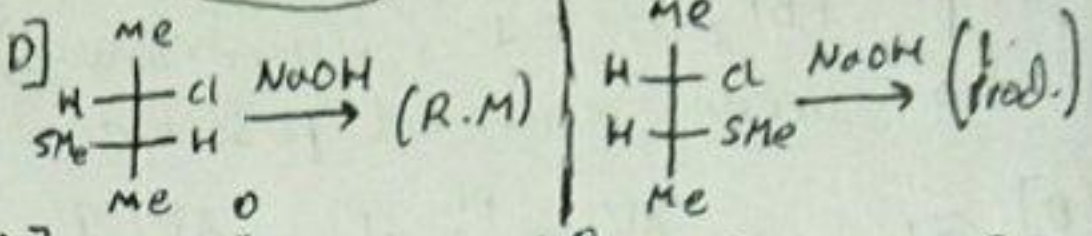
* Retention Product Dominates.
* 600-3000 times faster than next Nu.
* Z and L.G must be in Anti posn.
  NGP is not observed in compounds with Z and L.G in syn Posn.

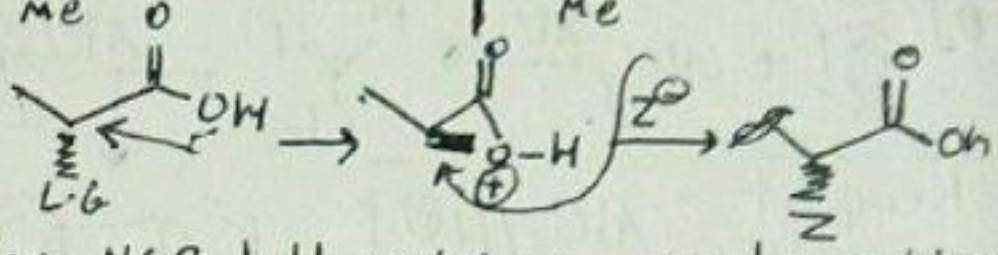
A] 

B] 

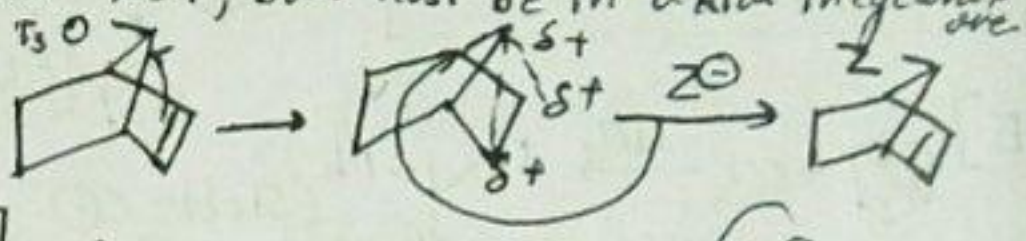
* Less crowded side is Attacked.

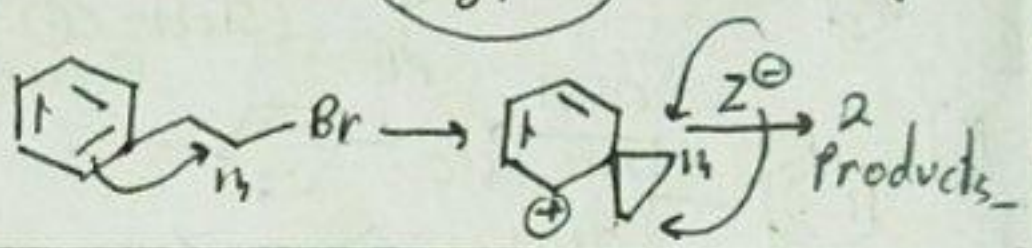
C] 

D] 

E] 

* For NGP, both must be in axial in cyclohexane

F] 

G] 

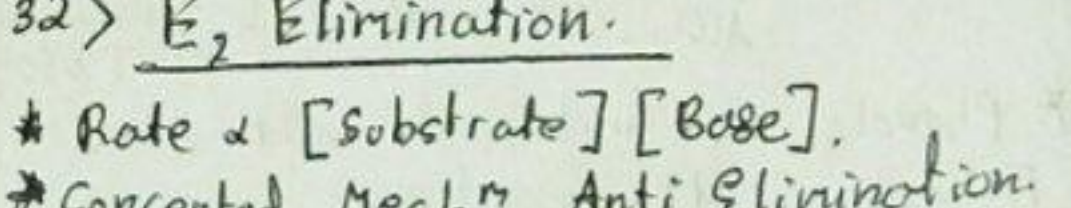
32) E_2 Elimination.

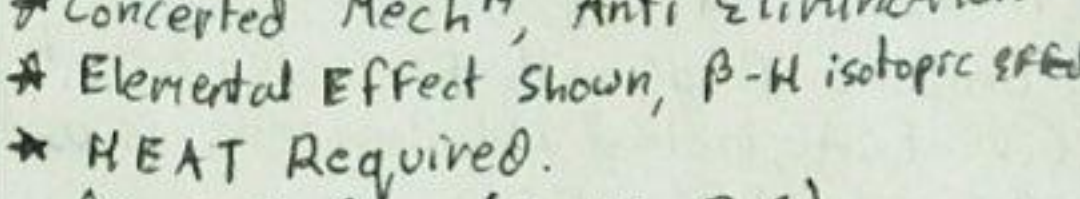
* Rate ∝ [Substrate] [Base].
* Concerted Mechm, Anti Elimination.
* Elemental Effect Shown, β-H isotopic effect
* HEAT Required.
* (C-X B.S) = (C-H B.S).
* ROR ∝ Stability of Alkene Formed.
* Polar Protic Solvent is preffered.

Bases ÷ Alc. KOH, Alc. NaOH, $tBuO^\ominus K^\oplus$, Et_3N, $NaNH_2$, DBU, DBN --- etc --

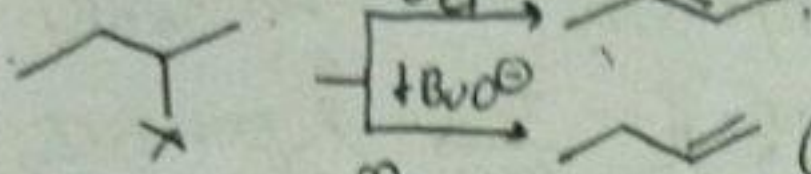
Alc KOH = EtOH + KOH = $EtO^\ominus K^\oplus$

A]

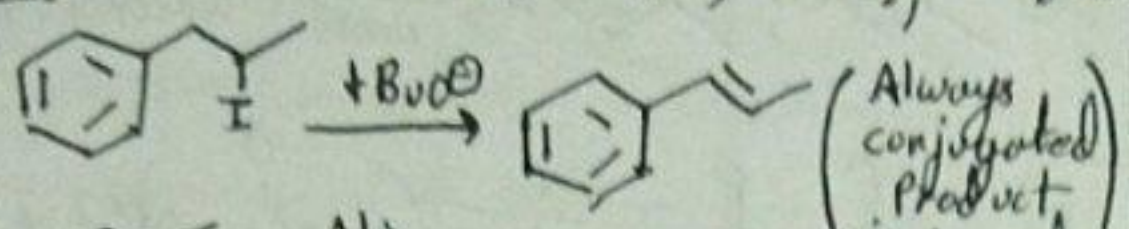
B] 

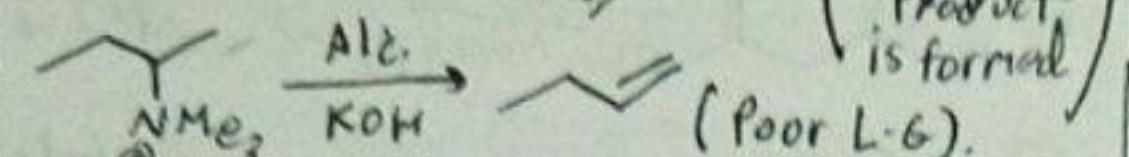
C] 

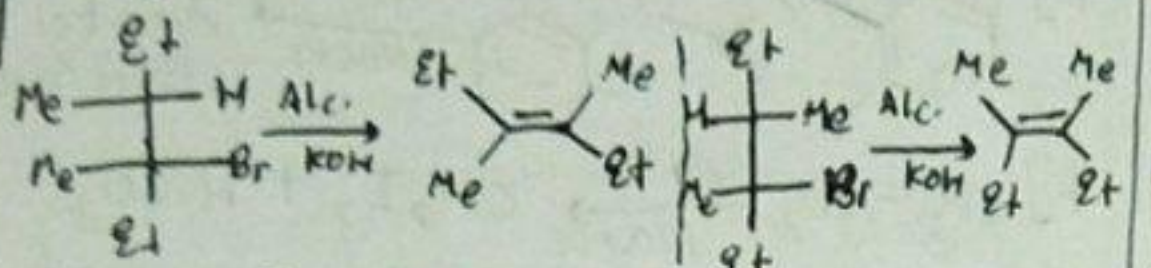
* Since ring flip is not possible, S_N2 is preffered over E_2 for ①.

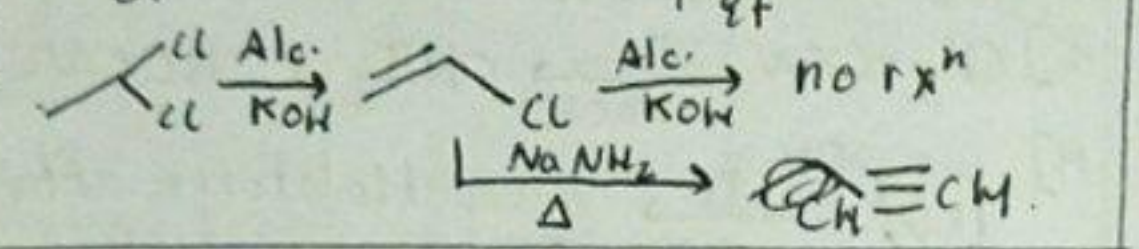
* 
(Saytzeff).
(Hoffmann).

Poor L.G ÷ F, $\overset{\oplus}{N}Me_3$, $\overset{\oplus}{N}H_3$, $-\overset{\oplus}{S}Me_2$, $-\overset{\oplus}{S}H_2$ etc

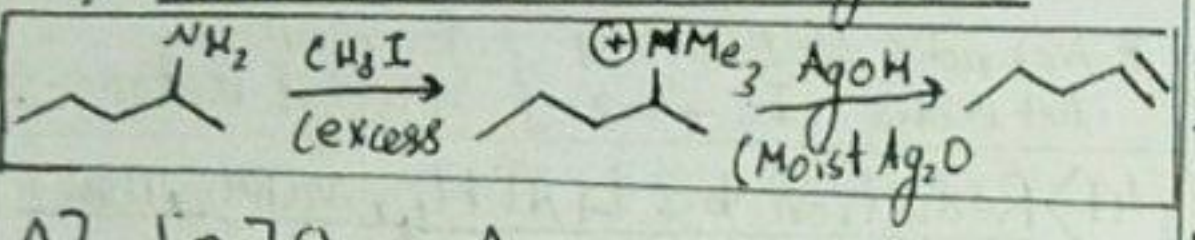
D] 
(Always conjugated Product is formed)

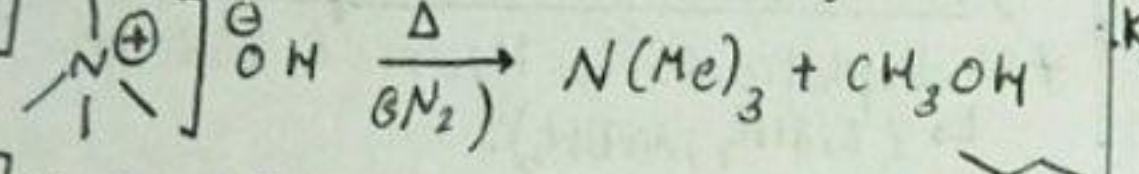
E] 
(Poor L.G).

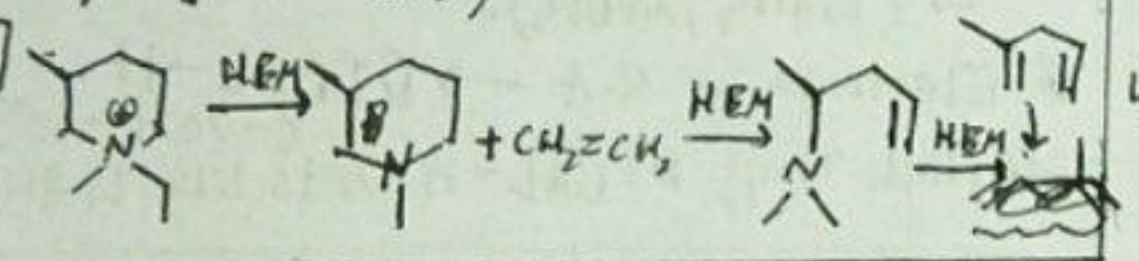
F] 

G] 

33) Hoffmann Exhaustive Methylation.



A] 

B] 

34) Grignard Reagent. (organometallic)

I] Acid Base Rxn is Fastest.

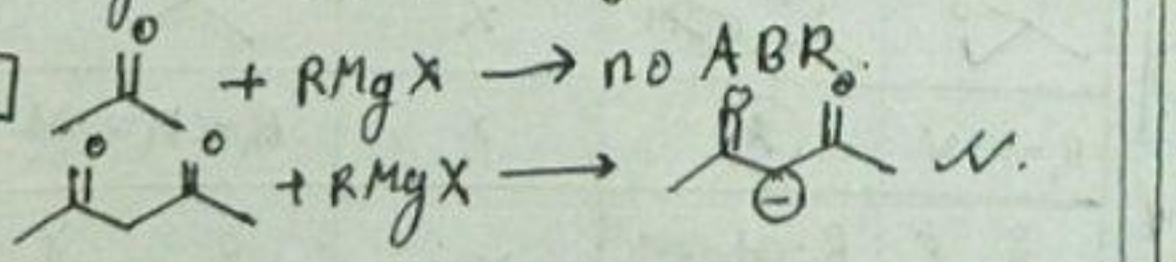
A] $Ph-Mg-Br + HO-CH_2-CH_2-OH \longrightarrow 2\times(Ph).$

B] $Ph-Mg-Br + NH_4Cl \longrightarrow 2\times(Ph)\cdot[NH_3 + NCl]$

II] Formation of Grignard (Free Radical)

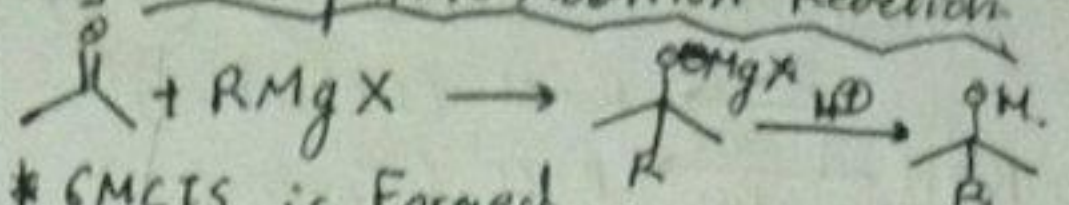
$$R-X + Mg \xrightarrow{Et_2O} R-Mg-X$$

* we don't use polar protic solvent as Grignard is destroyed.

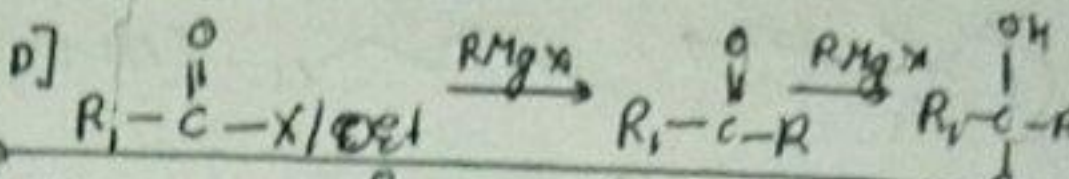
C] 

P.T.O

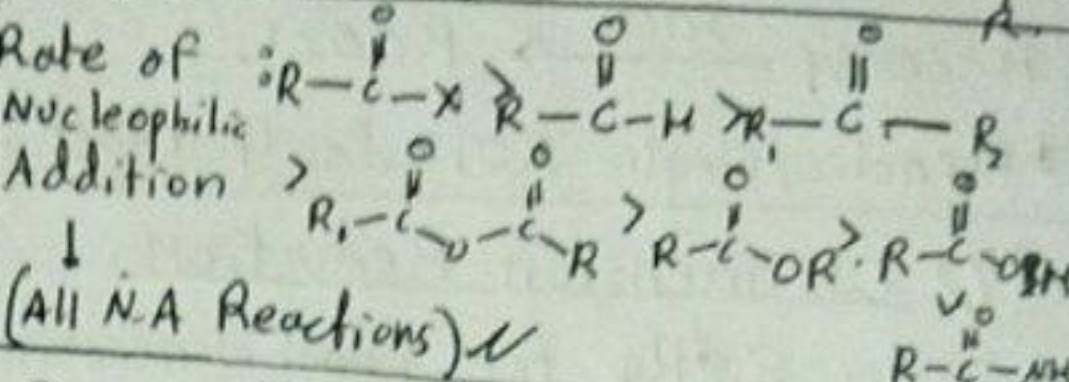
III] Nucleophillic Addition Reaction

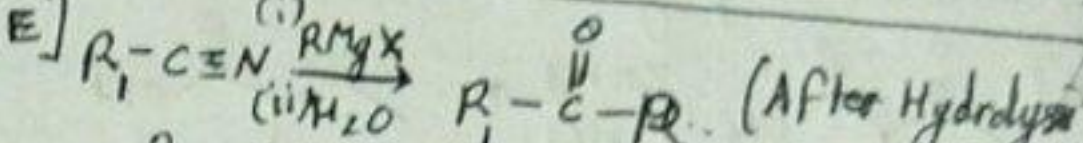


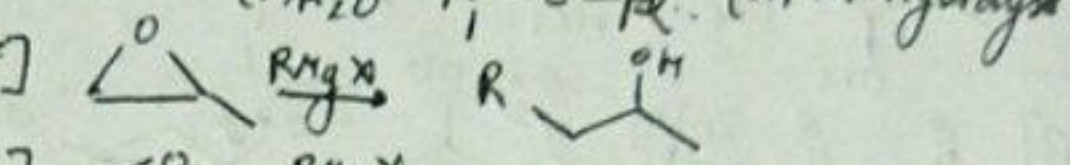
* CMCIS is Formed.

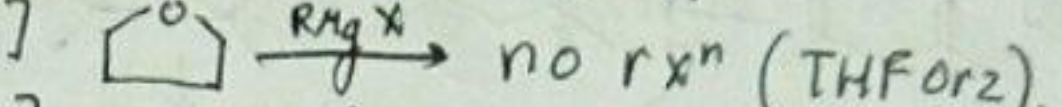
D] 

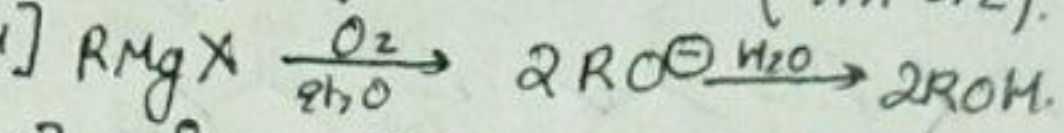
Rate of Nucleophilic Addition ↓ (All N.A Reactions) ✓

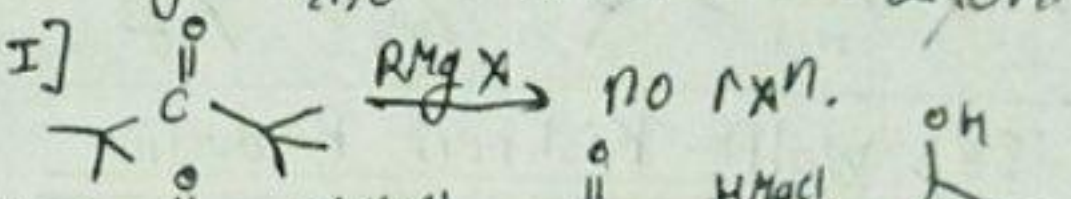


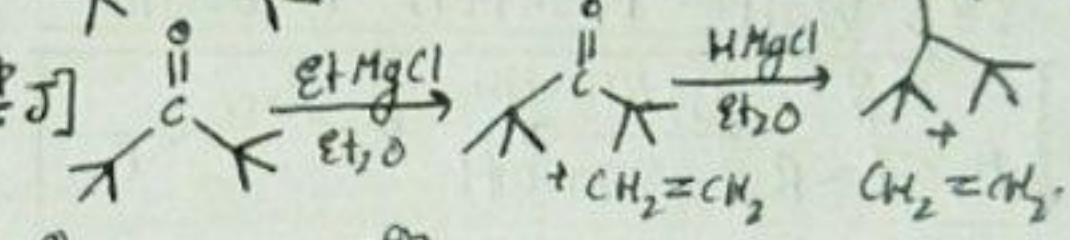
E] 
(After Hydrolysis)

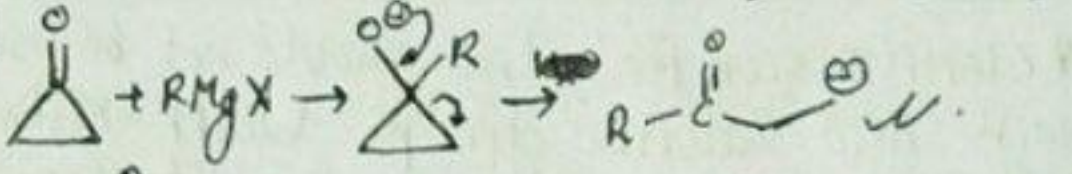
F] 

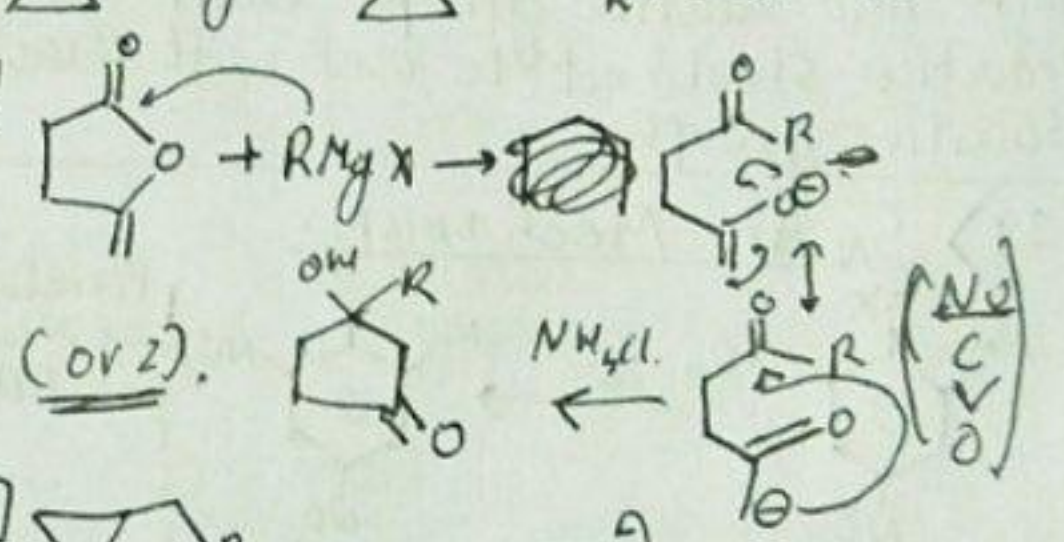
G] 

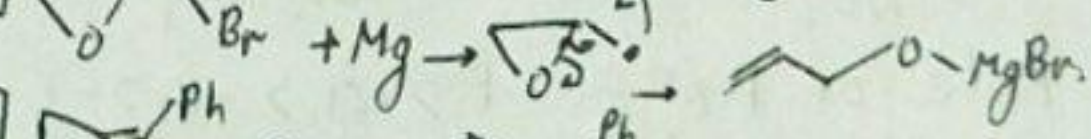
H] 

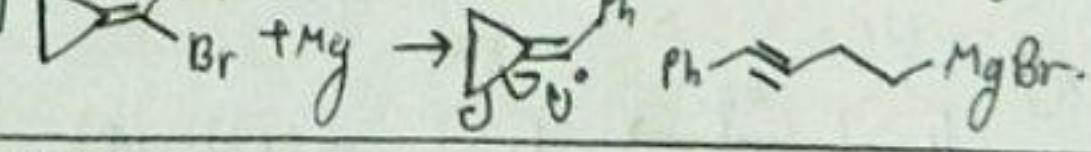
I] 

J] 

K] 

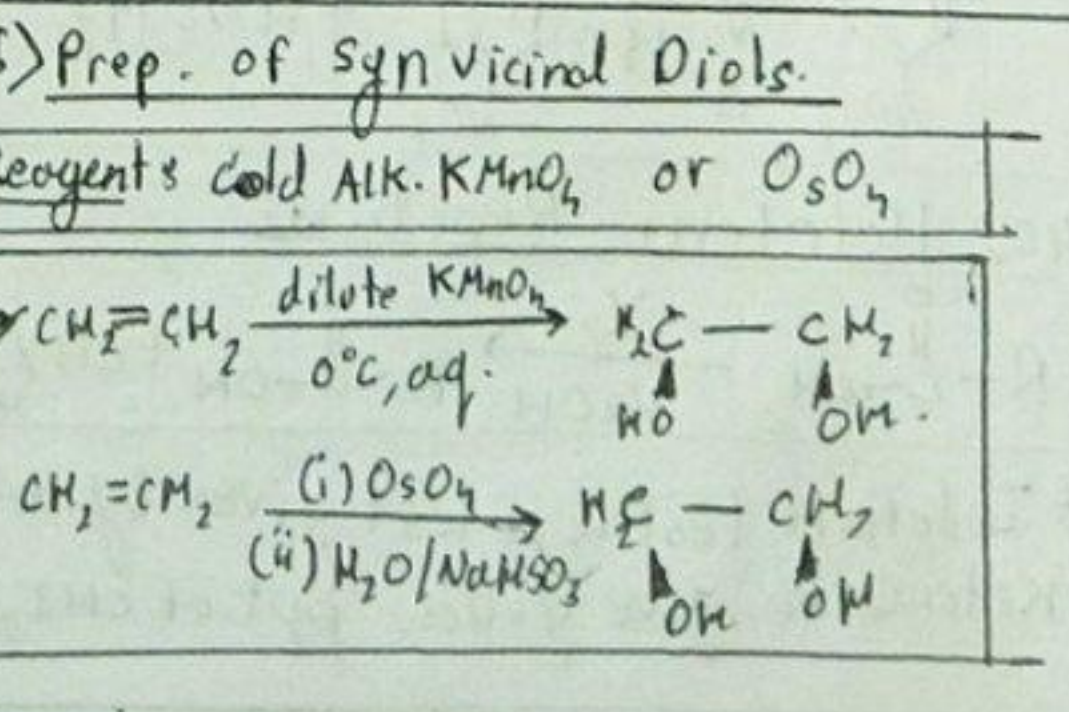
L] 

M] 

N] 

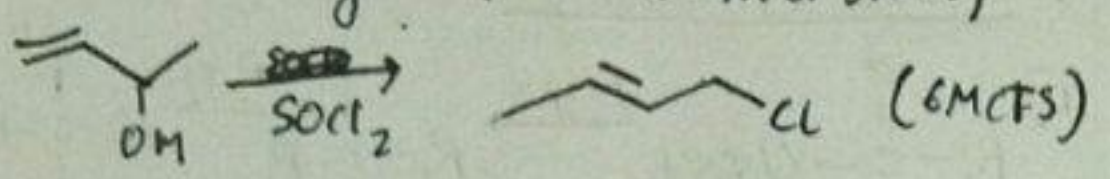
35) Prep. of syn vicinal Diols.

Reagents cold Alk. $KMnO_4$ or OsO_4



36) Darzen's Reaction. → (SN_i)

ROH $\xrightarrow[\text{Py.}]{SOCl_2}$ R-Cl (Retention)*
ROH $\xrightarrow{SOCl_2}$ R-Cl (Inversion)

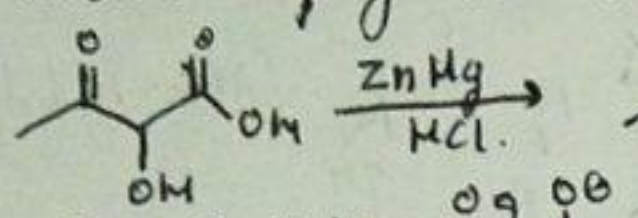


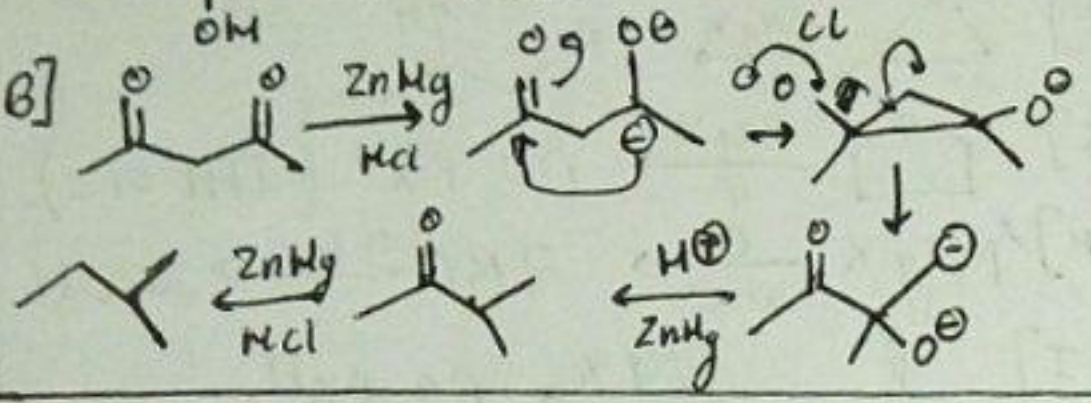
R-COOH $\xrightarrow{SOCl_2}$ RCOCl.

* Pheaolic/Vinylic ROH don't react.

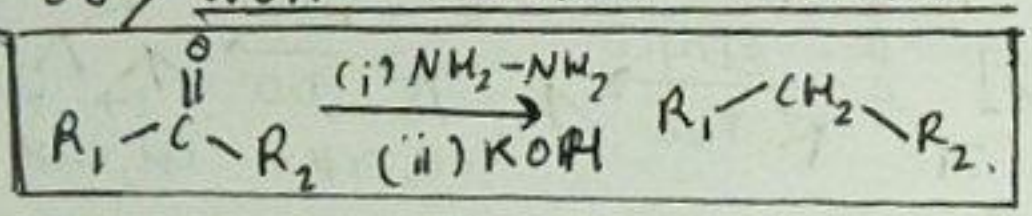
37) Clemmension Reduction.

* 2moles Zn/Hg for ~~1mol~~ clemmension

A] 

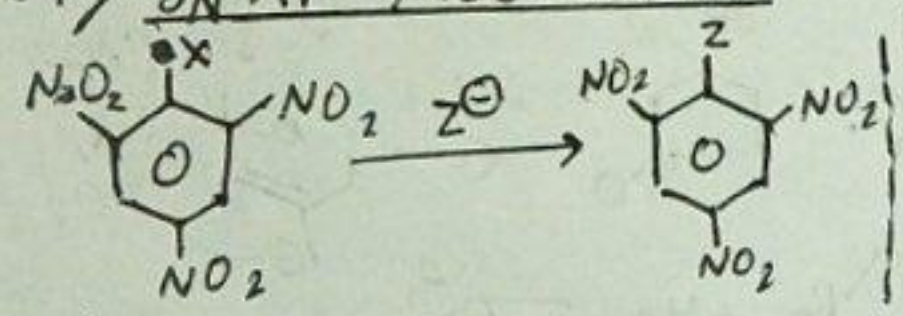
B] 

38) Wolff-Kishnerr Reduction



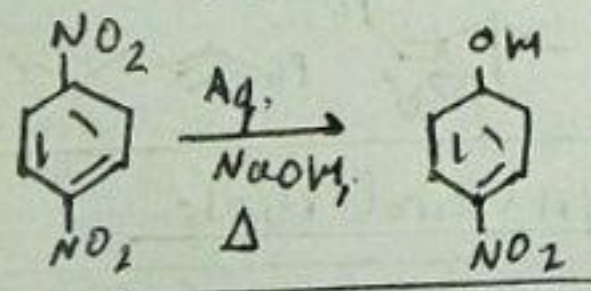
* clemmension Reduction should not be used with Acid Sensitive groups. Wolff-Kishner Reduction should not be used with Base Sensitive groups.

39) S_NAr Mechanism.

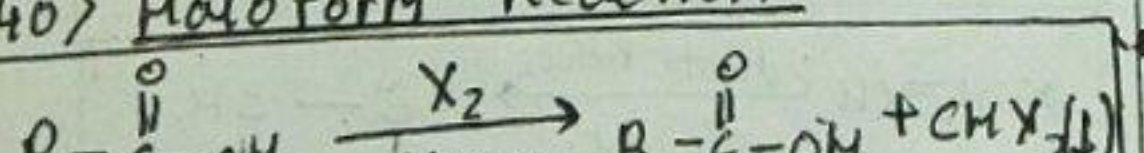


Formation of M complex is RDS.

Rate of R_xn ÷ -F > -Cl > -Br > -I

A] 

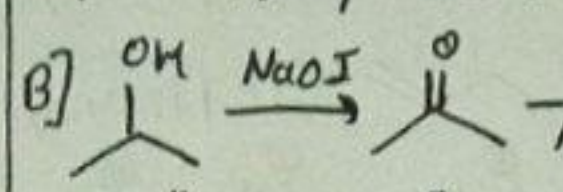
40) Haloform Reaction.

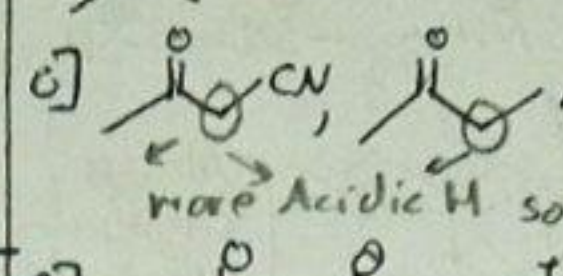


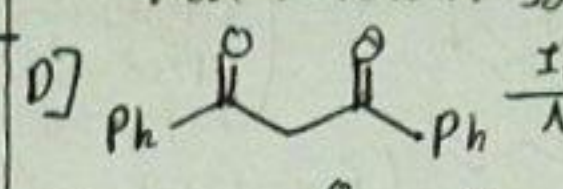
* Iodoform test is a test given by methyl Ketones to give yellow ppt of CHI_3.

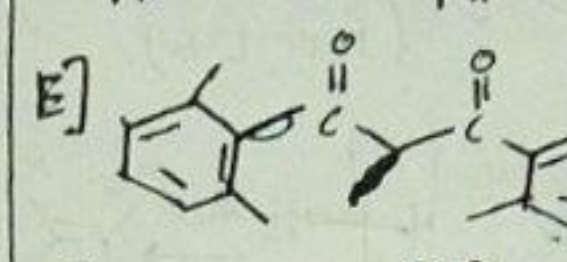
* RDS is formation of first carbanion.

A] 

B] 

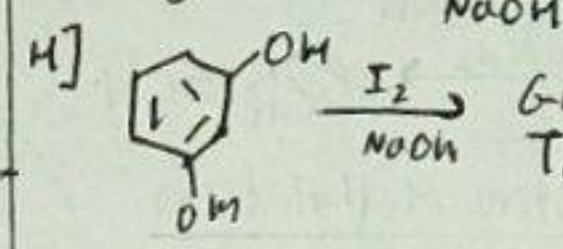
C] 

D] 

E] 

F] $CH_3-NO_2 \xrightarrow[NaOH]{I_2} CH_2I_3 + HNO_3$

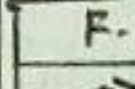
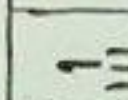
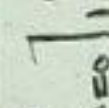
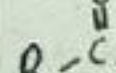
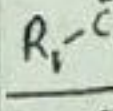
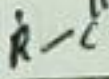
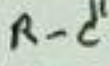
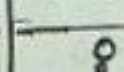
G] $CH_3-C\equiv N \xrightarrow[NaOH]{I_2} CHI_3 + HOCN.$

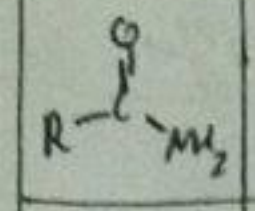
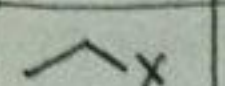
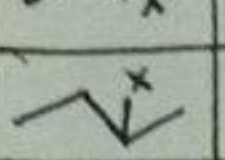
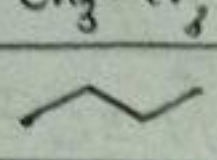
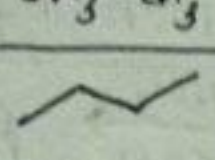
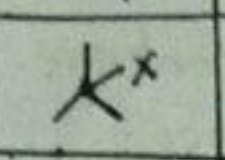
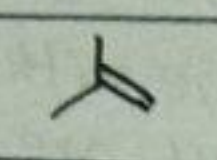
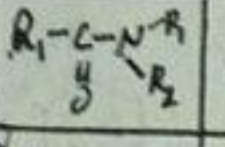
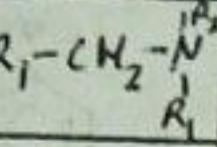
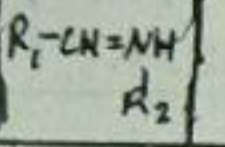
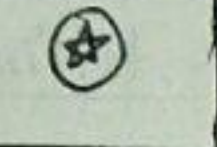
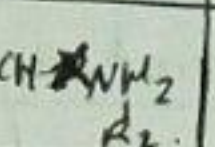
H] 

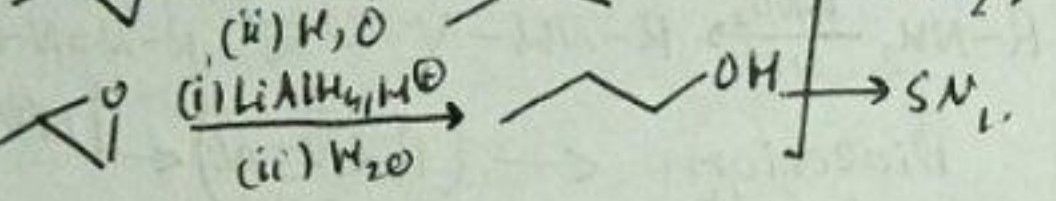
* Net moles NaOH → 4
  Net moles I_2 → 3
  ] for one methyl ketone.

41) Reduction by $LiAlH_4$, $NaBH_4$, DIBAL-H

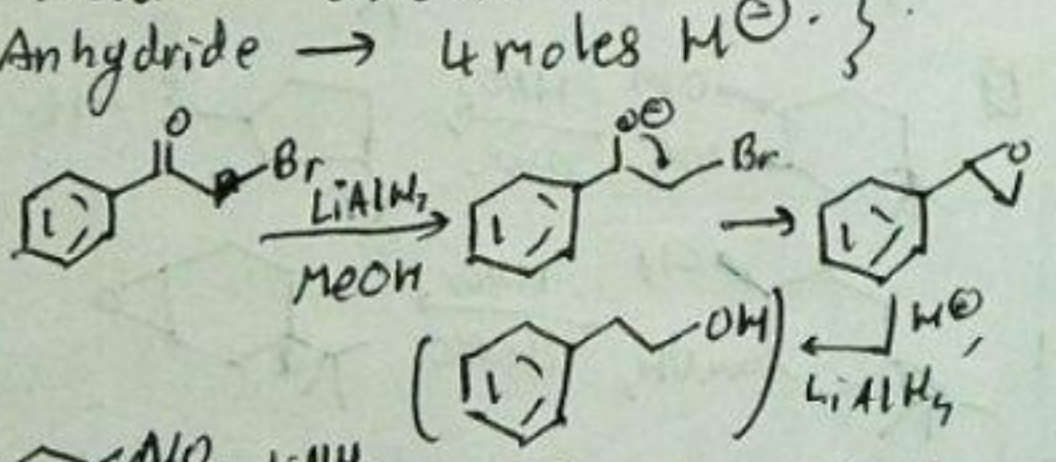
* Nucleophilic R.A, Hydride Donor.
  ↳ ($LiAlH_4$, $NaBH_4$).
* Electrophilic R.A → DIBAL-H. (-70°, -40°).
* At High Temp, DIBAL-H Acts like $LiAlH_4$.

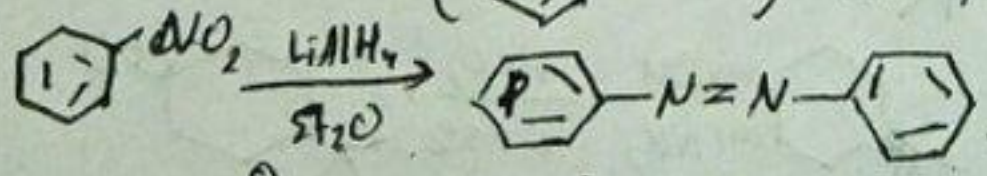
F.G.	$LiAlH_4$	$NaBH_4$	DiBAL-H.
	×	×	×
	×	×	×
			×
		×	
		×	
			
		×	
		×	
		×	
		X	

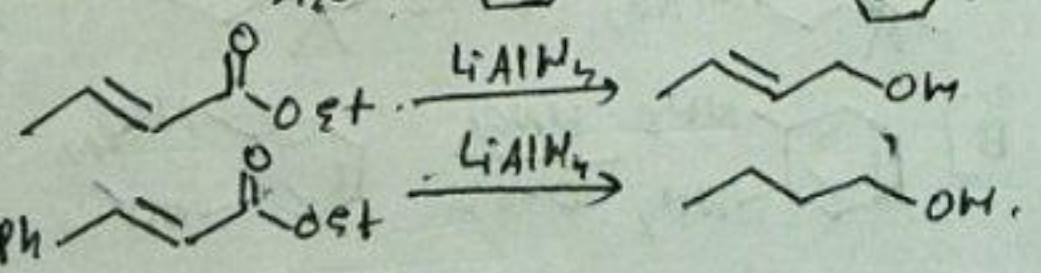
	R-C≡N	X	R-CH=NH
	CH_3-CH_3	CH_3-CH_3	X
			X
		X	X
$R-NO_2$	$R-NH_2$	X	X
$R-N_3$	$R-NH_2+N_2$	X	X
$R-N=N-OH$	$R-NH_2$	X	X
$Ph-NO_2$	$Ph-N=N-Ph$	X	X
		X	X
$R-O-R$	X	X	X
			X

A] 

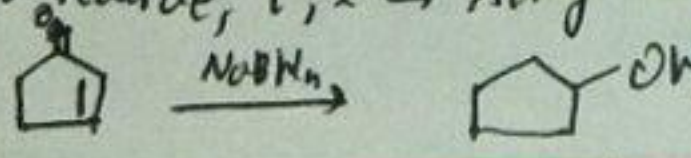
B] Acid → 3 moles $H^{\ominus}$.
Anhydride → 4 moles $H^{\ominus}$.

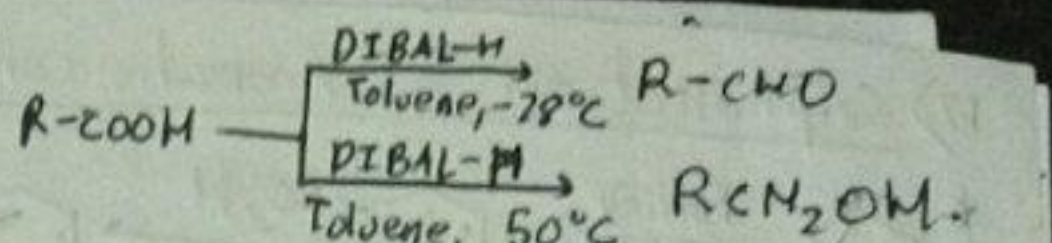
C] 

D] 

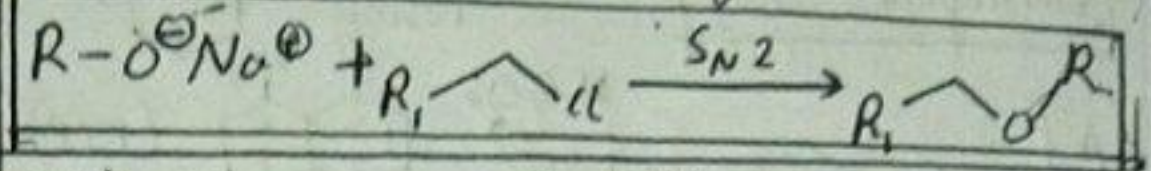
E] 

F * $NaBH_4$ Reduces, Aldehyde, Ketone, Imines, Acid Halide, 1°, 2° → Alkyl Halide.

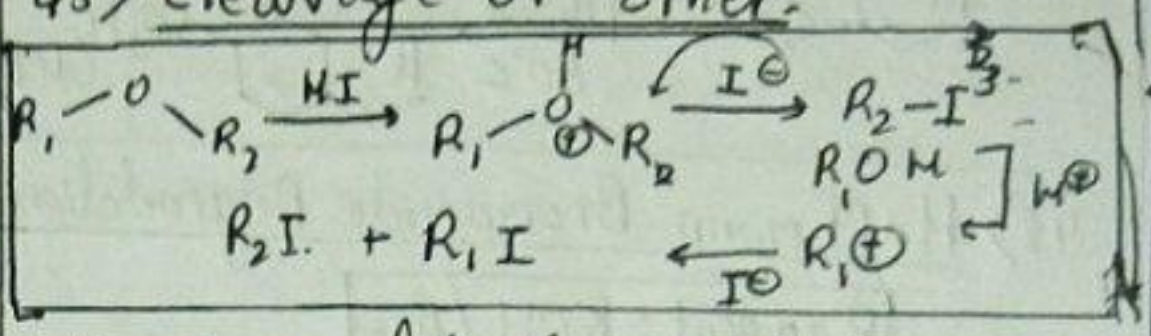
F] 

G] 

42) Williamson's Ether synthesis.



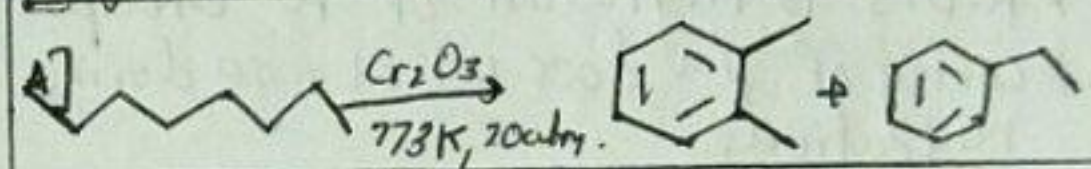
43) Cleavage of Ether.



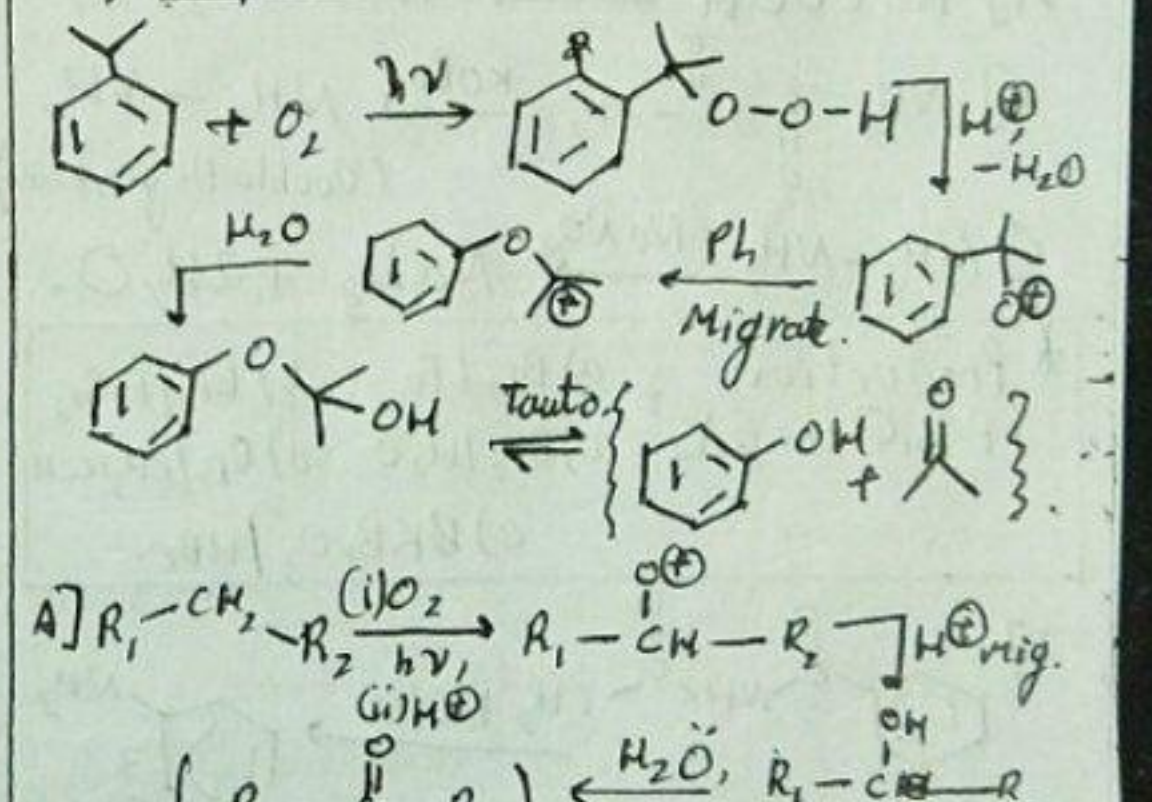
* May proceed by S_N1 or S_N2.
* First Attack will be on less crowded
* Most Stable C⊕ leaves fastest.

44) Aromatization:

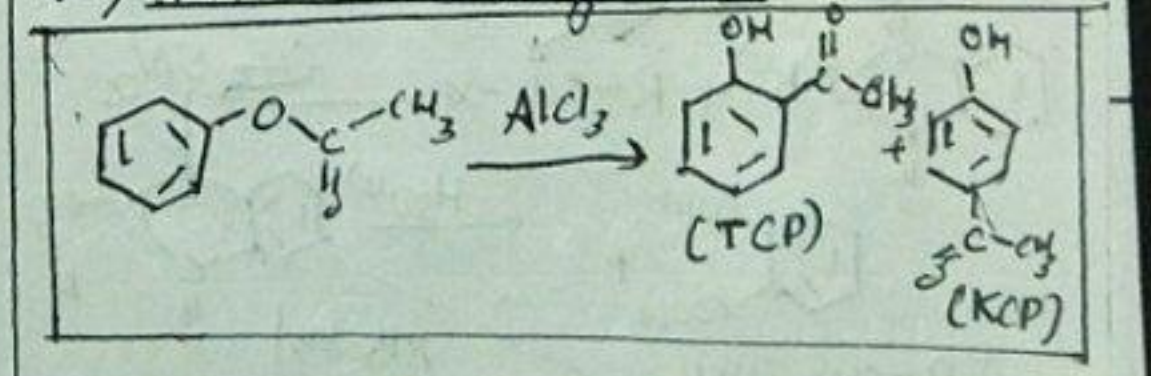
Reagents: Cr_2O_3 of Al_2O_3 / MO_2O_3 / V_2O_5

A] 

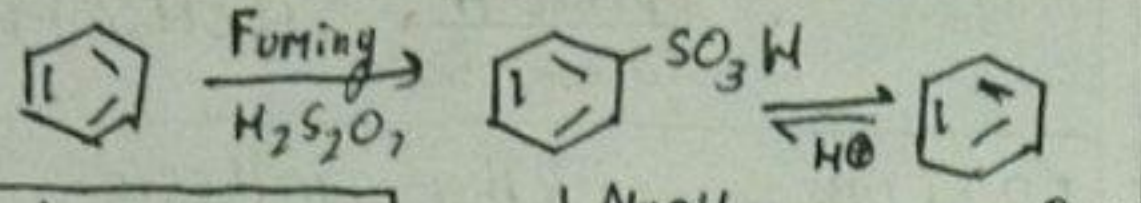
45) Preperation of Phenol from Cumene.



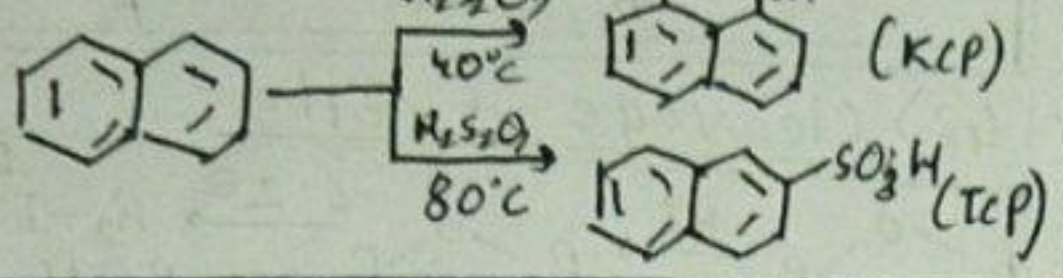
46) Fries Rearrangement.



47) Sulphonation of Aromatic comp.

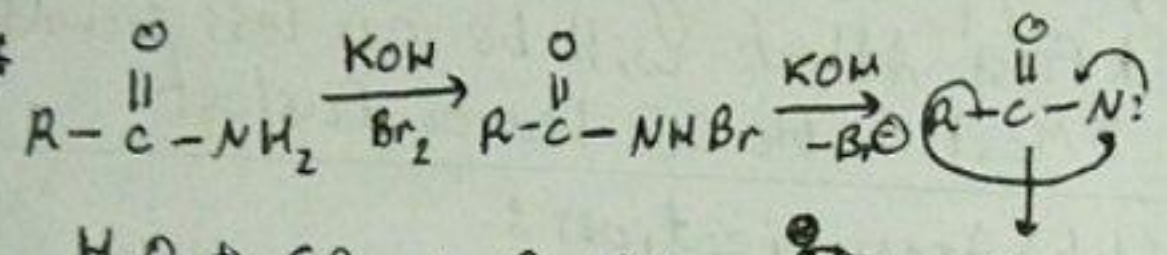
* 

Electrophile: SO_3.

*I. A] 

48) Hoffmann Bromamide Degradation.

Reagent: KOH / Br_2

D. * 

E. $H_2O + CO_2 + R-NH_2 \xleftarrow[H_2O]{\ominus OBr} R-N=C=O$

* R.D.S is migration of R- Group.

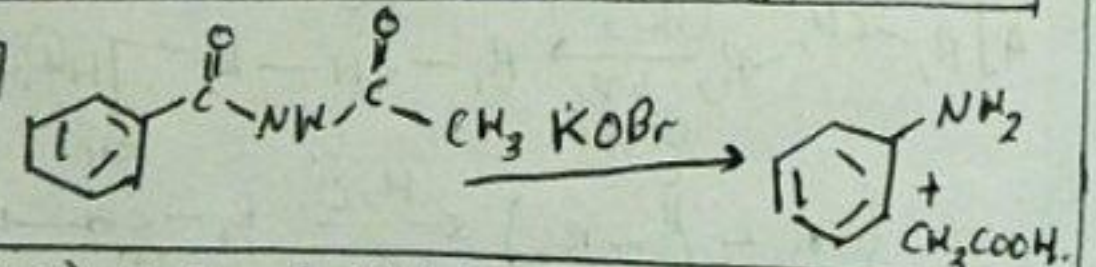
F. * Config of 'R' does not change during migration.

A] $R-COOH \xrightarrow{NH_3} R-CONH_2 + H_2O$.

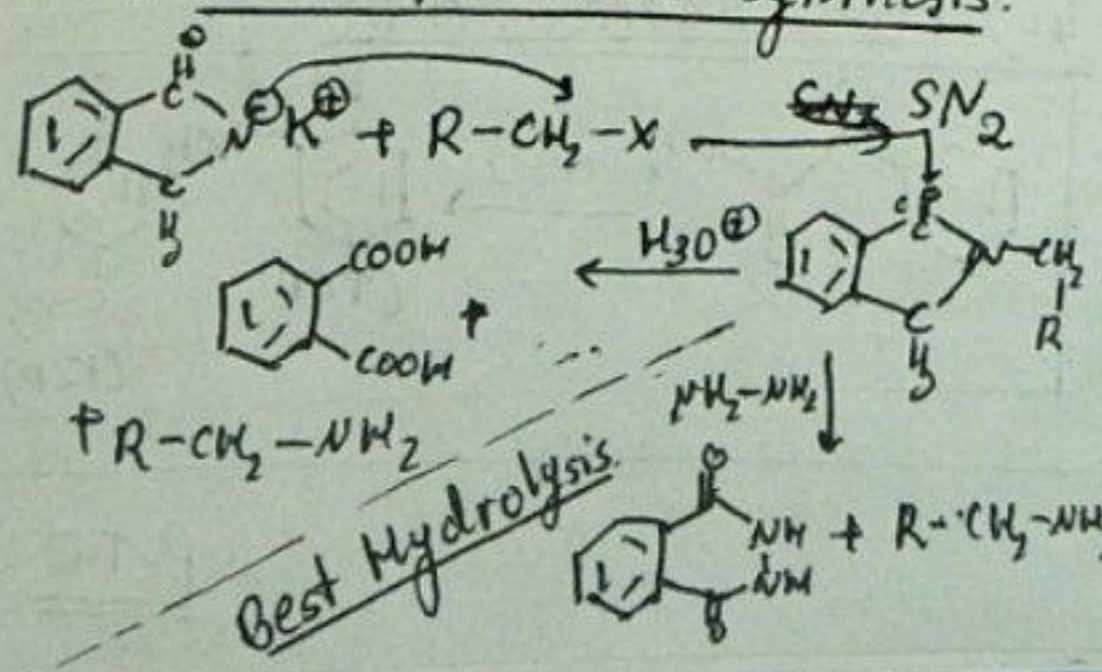
B] $NH_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{KOBr} NH_2-NH_2$ (Double Degradation)

C] $NH_2-NH_2 \xrightarrow{NaNO_2} NaN_3 + 2H_2O$.

* Production of $Br^{\oplus}$ for EAS: a) Br_2/Fe b) $Br_2/FeBr_3$ c) Br_2/H_2O d) Br_2/CH_3COOH e) $BKBrO_3/HBr$.

D] 

49) Gabriel Phtalamide Synthesis.



Best Hydrolysis

* SN_2 → Inversion in config.

50) Carbamyl Test.

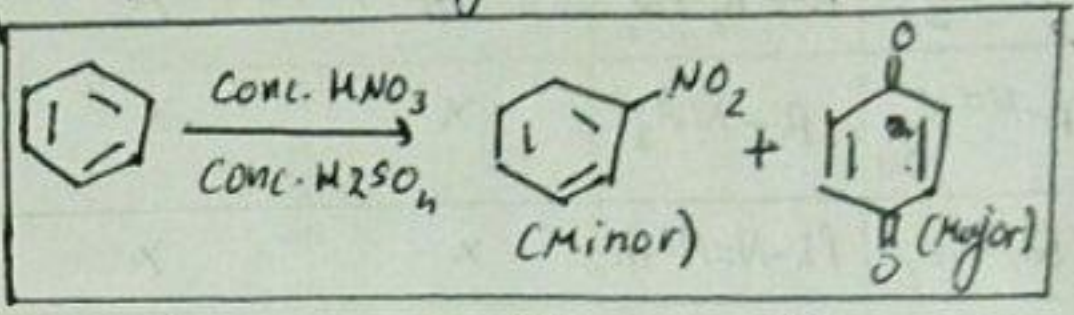
* It is Given by only 1° Amines.

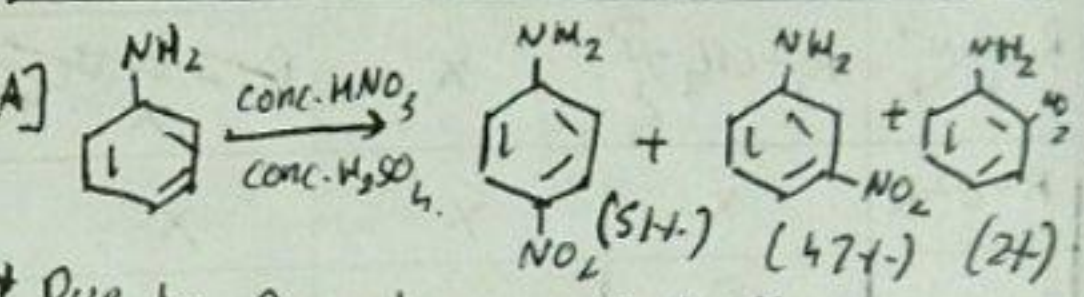
$R-\ddot{N}H_2 \xrightarrow[KOH]{CHCl_3} R-\overset{\oplus}{N}\equiv C\ominus$

* RDS : Rxn of 1° Amine with Carbene.

* 3 moles of KOH are used.

51) Nitration by conc. HNO_3/H_2SO_4.



A] 

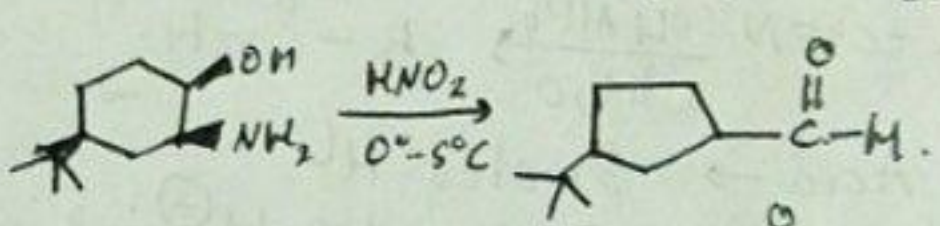
* Due to formation of Anilinium.

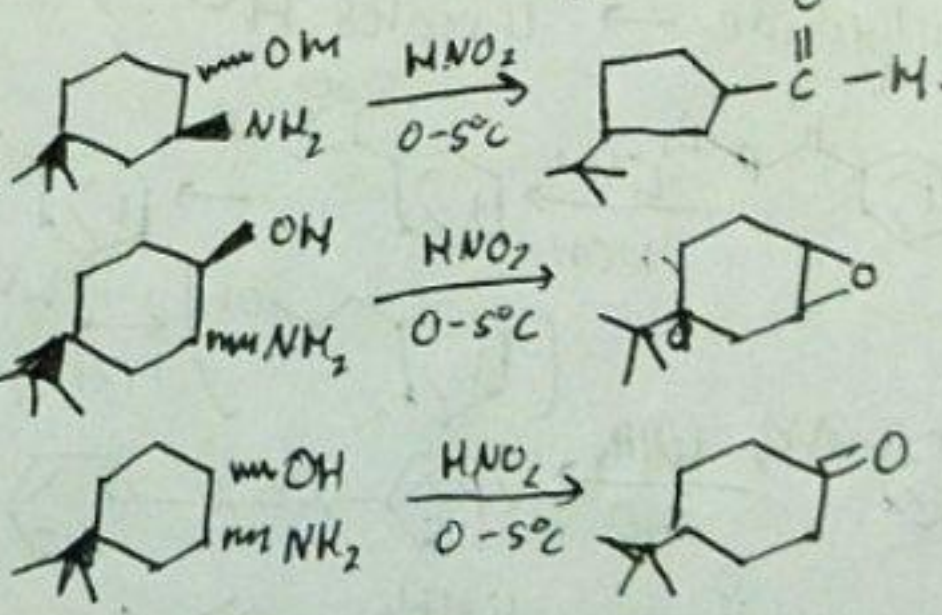
52) Diazotization. :

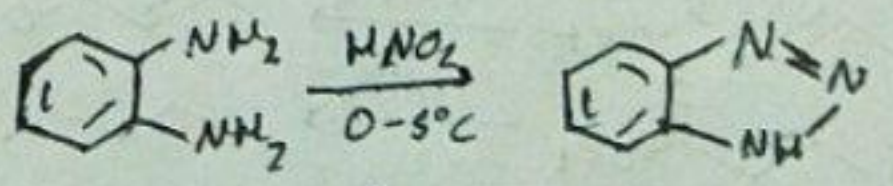
$R-NH_2 \xrightarrow[HCl]{NaNO_2} R-NH-N=O \underset{\text{Tauto.}}{\rightleftharpoons} R-N=N-OH$

$R-\overset{\oplus}{N}\equiv N: \; Cl^{\ominus}$ (Diazonium Salt.) $\xleftarrow{H^{\oplus}}$ $R-NH-N=O$

I] If Aliphatic, $R-\overset{\oplus}{N}\equiv N \rightleftharpoons R^{\oplus} + N_2\uparrow$

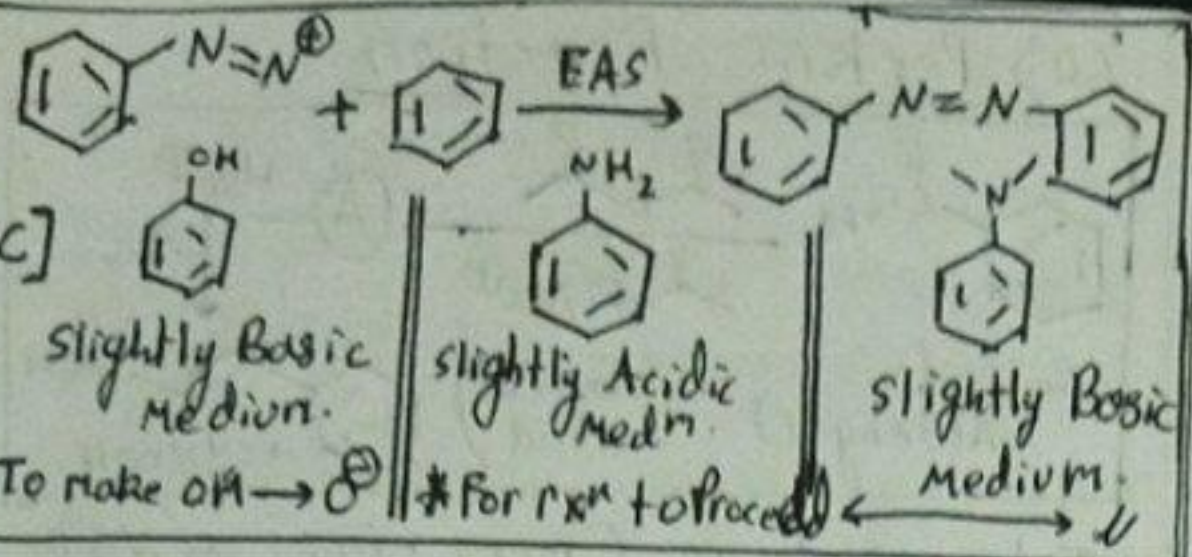
A] 

B] 

B] 

II] If Aromatic, ($Ph-N\equiv N^{\oplus}Cl^{\ominus}$ is stable at 0-5°C)

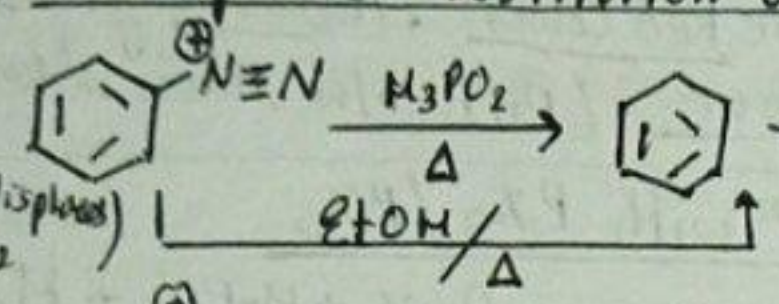
P-T-O

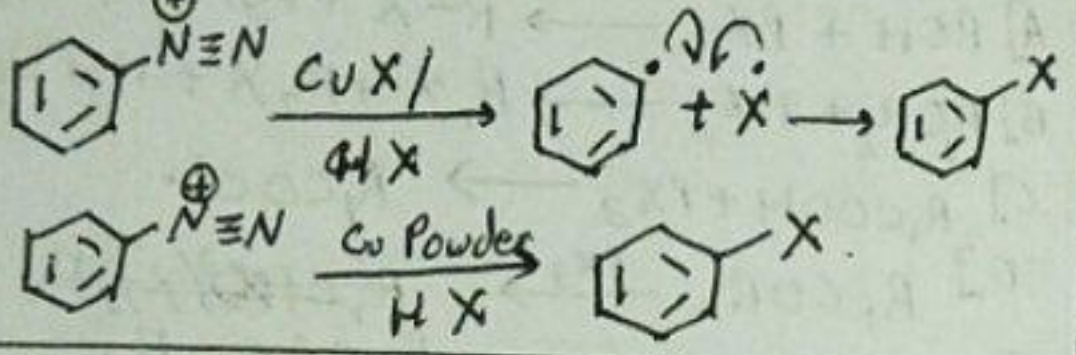


* Mesityline also gives Diazonium Coupling.

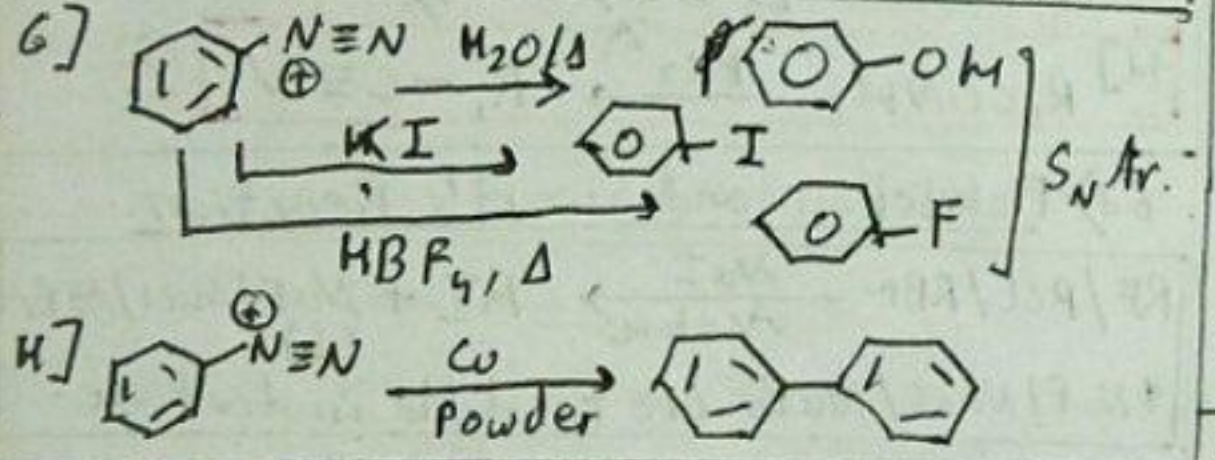
* Faster Rxn is EWG on Diazonium salt. And EDG on Ring to be EAS'd.

III] Nucleophilic Substitution of Diazonium

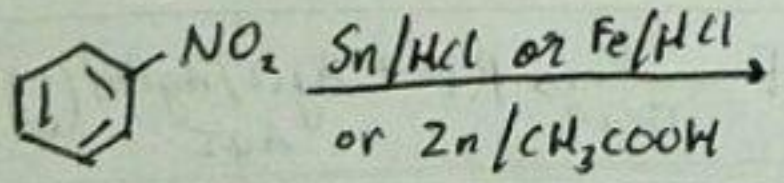




E → Free Radical Mech → Sandmeyer Rxn → Faster with EDG.
F → SNAr Mech → Gattermann Rxn → Faster with EWG.



53) Reduction in Acidic Medium.



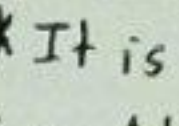
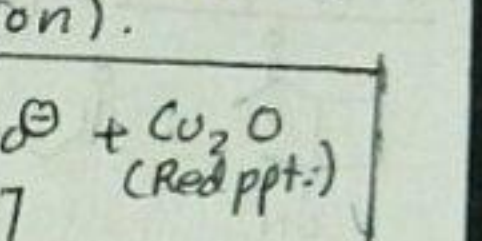
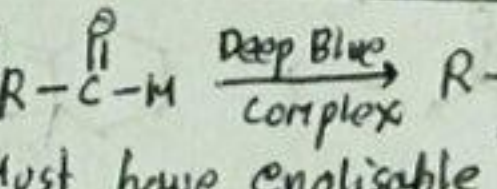
54) Tollen's Reagent.

÷ $[Ag(NH_3)_2]^+OH^-$ ⊖ Age⁻ khata OH aajata

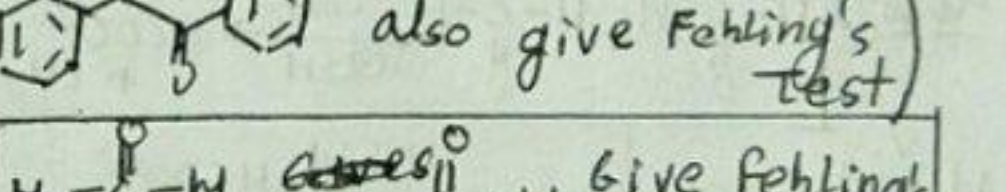
$R-\overset{O}{\overset{\|}{C}}-H + Ag_2O \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + 2Ag(\downarrow)$ (Silver Mirror)

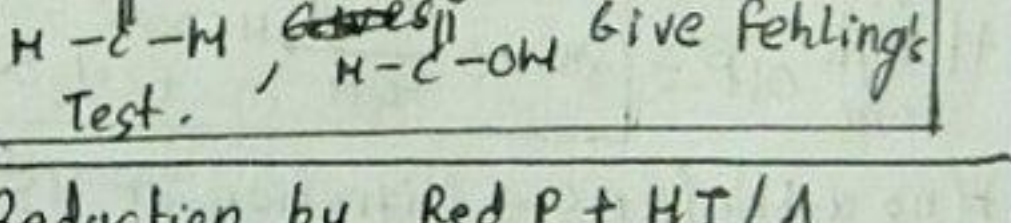
* Tollen's Test / Silver Mirror Test.

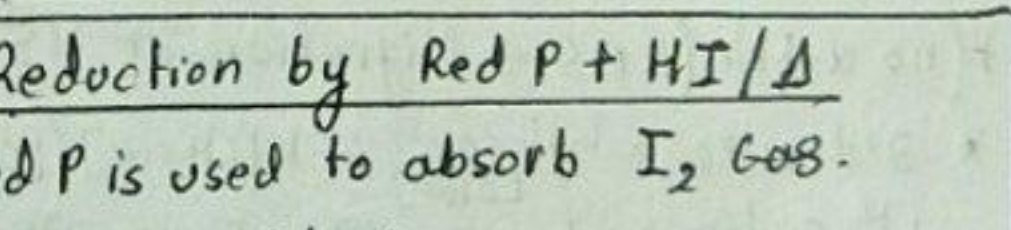
A] $H-C\equiv C-H + Ag^{+2} \xrightarrow{\text{Tollens}} Ag-C\equiv C-Ag.$

$R-\overset{O}{\overset{\|}{C}}-H$, $H-\overset{O}{\overset{\|}{C}}-H$, $H-\overset{O}{\overset{\|}{C}}-OH$, CH_2Cl_2, CH_3Cl_3, , Hemiacetal, , , Give tollen's Test.

* Tollen's Test is a Basic Medium test.

B] 

C] 

D] 

55) The Fehling's Solution.

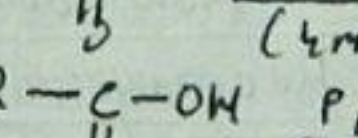
* It is a Basic Medium Test.

* = Alkaline $CoSO_4$ + Sodium Potassium Tartarate (Rochelle's Salt). (Deep Blue Solution).

P $R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\text{complex}]{\text{Deep Blue}} R-\overset{O}{\overset{\|}{C}}-\ominus + Cu_2O$ (Red ppt.)

[Must have enolisable 'H']

* Rate of Rxn ∝ Rate of Formation of end.

* ( also give Fehling's test)

* eff. $H-\overset{O}{\overset{\|}{C}}-H$, ~~Ketones~~ $H-\overset{O}{\overset{\|}{C}}-OH$ Give Fehling's Test.

56) Reduction by Red P + HI / Δ

* Red P is used to absorb I_2 Gas.

A] $R-CH_2-OH \xrightarrow[(2\ Moles)]{P/HI} R-CH_3$.

B] $R-\underset{H_3}{C}-H \xrightarrow[(4\ moles)]{P/HI} R-CH_3$.

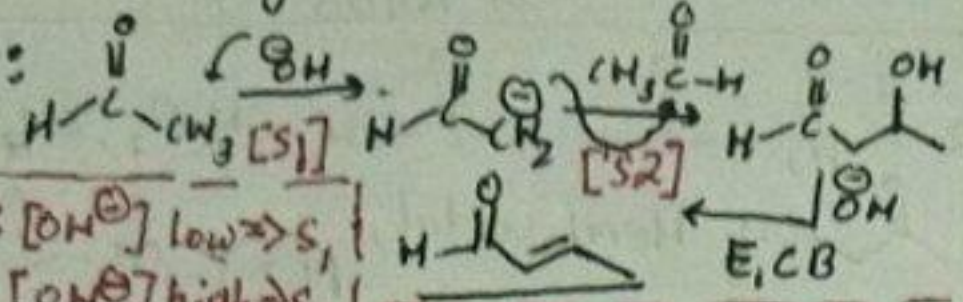
C] $R-\underset{H_3}{C}-OH \xrightarrow[(6\ moles)]{P/HI} R-CH_3$.

57) Aldol Condensation.

* Reagents: dil NaOH, dil KOH, NaH, $Ba(OH)_2$.

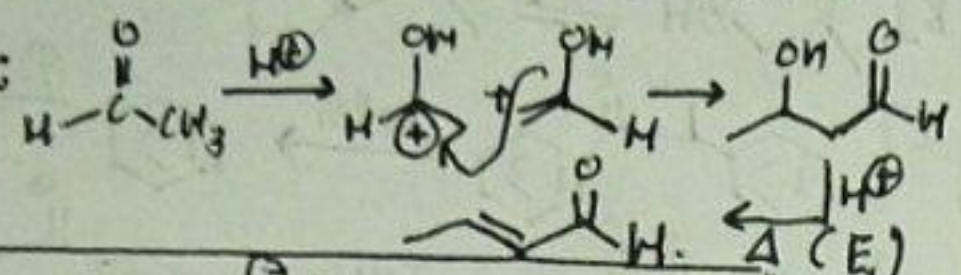
P.T.O

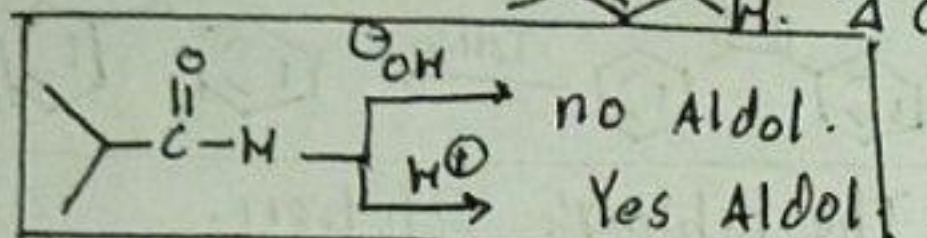
* Aldol has 3 Types → Self, Crossed, Cyclisation] 2 reds → Acidic, Basic.

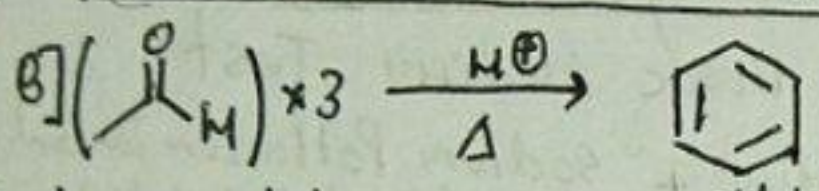
Mechⁿ : 

*RDS : $[OH^{\ominus}]$ low ⇒ S_1 | $r = K[CH_3CHO][OH^{\ominus}]$
$[OH^{\ominus}]$ high ⇒ S_2 (moderate level) | $r = K[CH_3CHO]^2[OH^{\ominus}]$

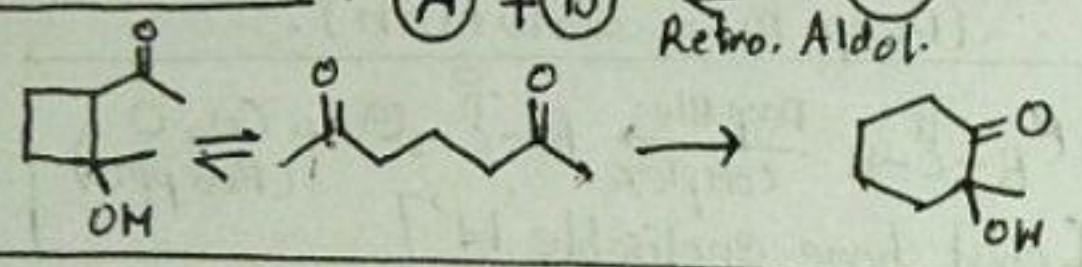
* has order 2 at low conc. $OH^{\ominus}$ and has order 3 at moderate conc. $OH^{\ominus}$.

$H^{\oplus}$ Mech: 

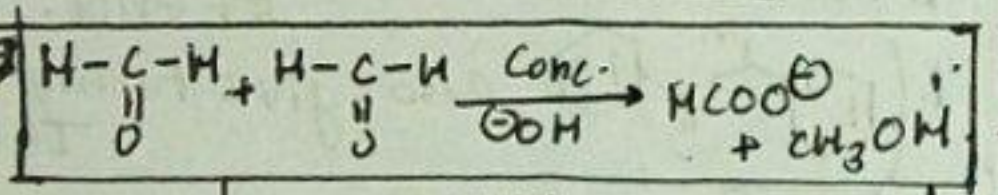
A] 

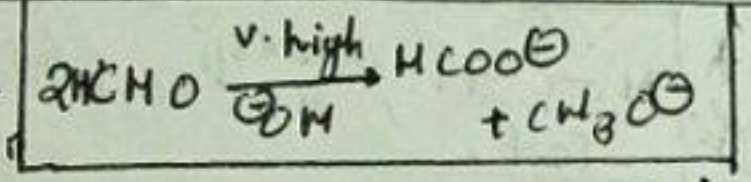
B] 

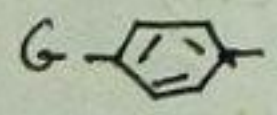
Retro Aldol ÷ (A) + (B) ⇌ (C) (Aldol / Retro. Aldol.)



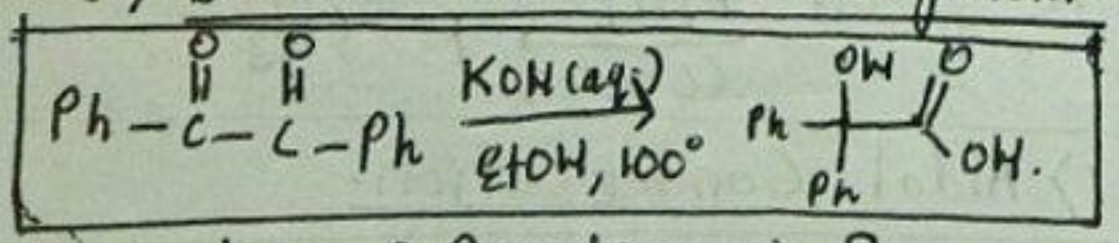
58) Cannizzaro Reaction.



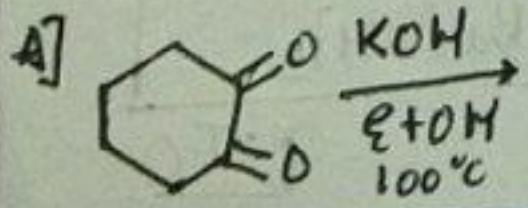
At high conc. $OH^{\ominus}$ ÷ 

* (no α-H). (RDS ÷ Migration of $H^{\ominus}$.)
* 3rd order ÷ high conc. $[OH^{\ominus}]$ ÷ $K[CH_3CHO]^2[OH^{\ominus}]$
  4th order ÷ v. high $[OH^{\ominus}]$ ÷ $K[CH_3CHO]^2[OH^{\ominus}]^2$.
*  If G is +M the it will not show Cannizaro.

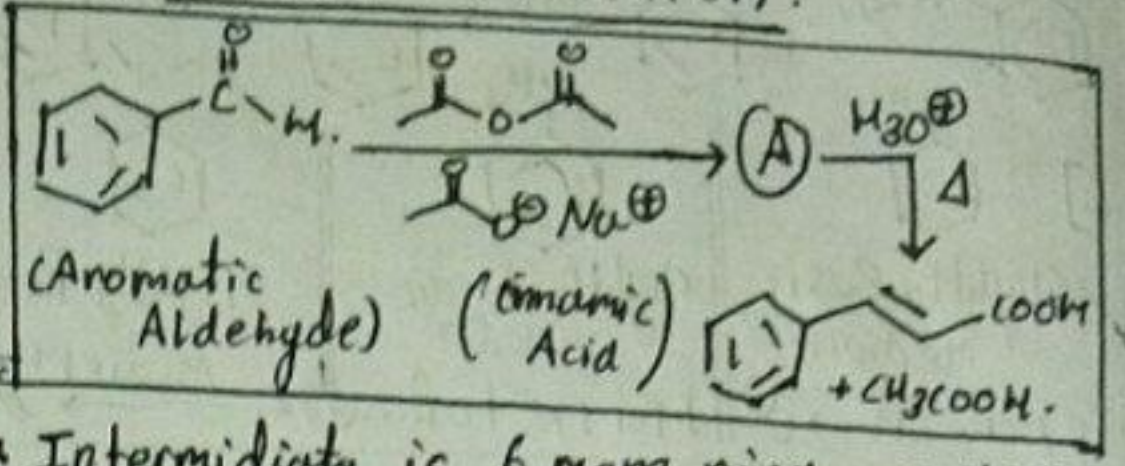
59) Benzil Benzillic Rearrangement.



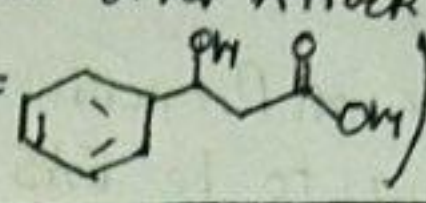
* Order of Reaction is 2.

A] 

60) Perkin Reaction.



* Intermidiate is 6 mem ring. as NGP happens after Attack on $PhCHO$.

(A) = 

61) Seliwinoff test.

Ketoses give Red colour. Aldoses give Pink Colour. (Diff b/w Aldose nd ketose)

62) Rxⁿ with PX_3 / PX_5

A] $ROH + PX_3 \longrightarrow R-X + H_3PO_3 + HX$

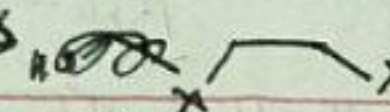
B] $R_1OR_2 + PX_3 \longrightarrow R_1X + R_2X + H_3PO_4$

C] $R_1COOH + PX_3 \longrightarrow R_1COCl$.

D] $R_1COR_2 \xrightarrow{PX_3} R_1C(X)_2R_2$

E] $R_1COOR_2 \xrightarrow{PX_3} R_1COCl + R_2-Cl$.

F] $(R_1CO)O(COR_2) \xrightarrow{PX_3} R_1COX + R_2COX$.

G] 

H] $R_1CONH_2 \xrightarrow{PX_3} R_1-C\equiv N$. ☆

63) Finkelstien and Swart's Reaction.

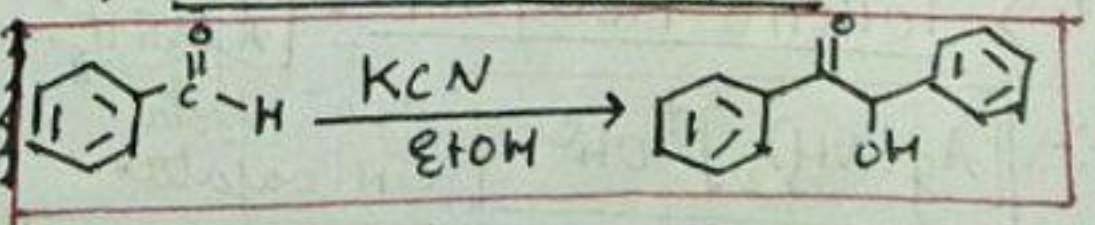
$RF/RCl/RBr \xrightarrow[Acetone]{NaI} RI + NaF/NaCl/NaBr\downarrow$

* NaF/NaCl/NaBr are Insoluble in Acetone.

* CoF_2, Hg_2F_2, Sb_2F_3, SbF_3, AgF in aq. medium are used is Swartz Reaction.

$RCl/RBr/RI + AgF \xrightarrow[medn]{aq.} RF + AgCl/AgBr/AgI\downarrow$

64) Benzoin Condensation.



* Carbonyl of Attacker Remains.
* KCN acts as catalyst.
* Order of Reaction is 3.

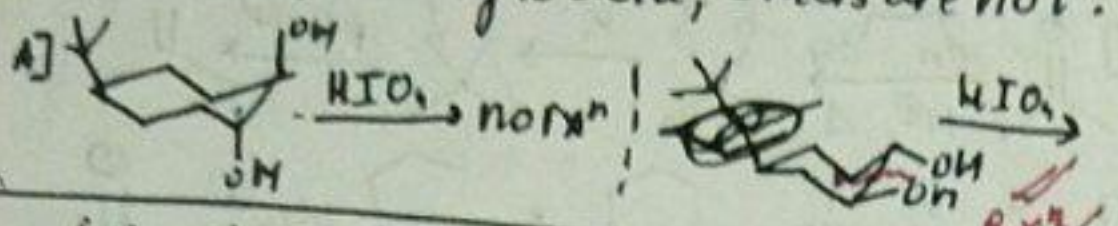
P.T.O.

65) Malaprade Reaction.

$[HIO_4 + 2H_2O \longrightarrow H_5IO_6]$.

* Vicinal Diols, Amine (1°, 2°), Ketone, ~~COOH~~, ~~Carboxylic Acids~~ Epoxides are oxidised one step up.

* 3° Amines, carboxylic acid, ethers are not.

A] 

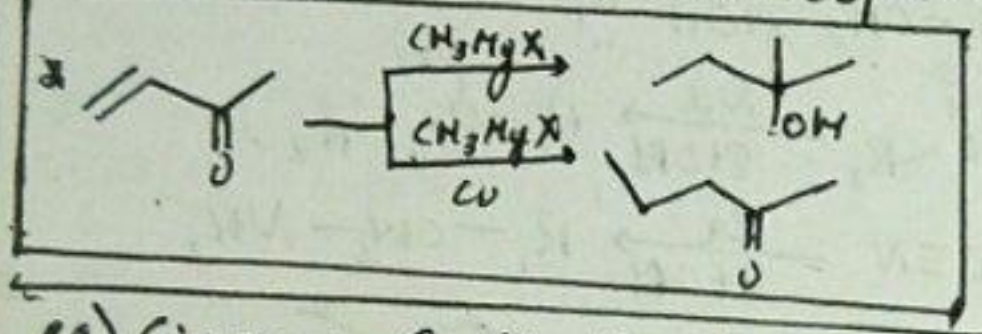
66) Stephen Reduction.

$R-C\equiv N \xrightarrow[HCl]{SnCl_2} R-CH=NH \xrightarrow{H_3O^{\oplus}} R-\overset{O}{\overset{\|}{C}}-H.$

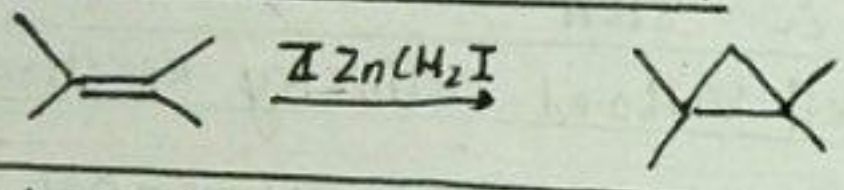
67) Soft Grignard Reagent.

R-Na, R-Li → Hard Nucleophide.

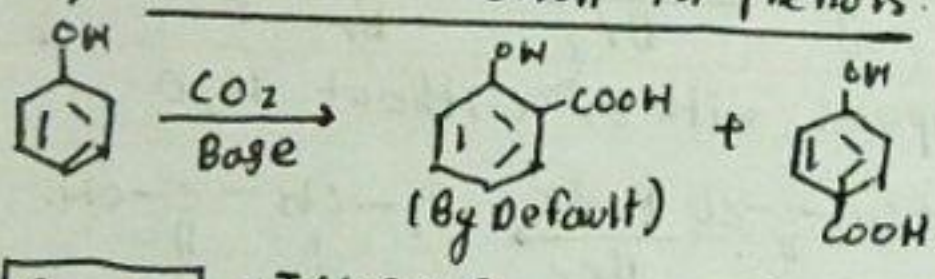
R_2CuLi, R_2Cd → Soft. Nucleophile.



68) Simmons Smith Reaction.



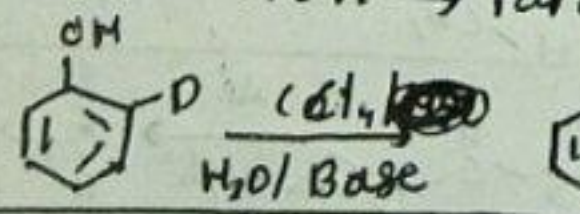
69) Kolbe's Reaction For phenols.



Base = KOH
- T < 60° → Para (KCP)
- 60°C < T < 150°C → ortho (TCP)
- T > 150° → Para (H bond breaks)

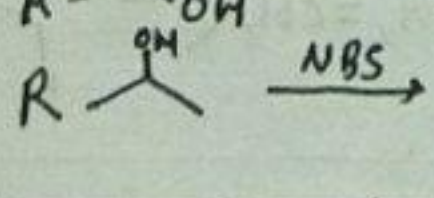
T ≯ 50°C
- KOH → Para
- NaOH → ortho
- LiOH → Para

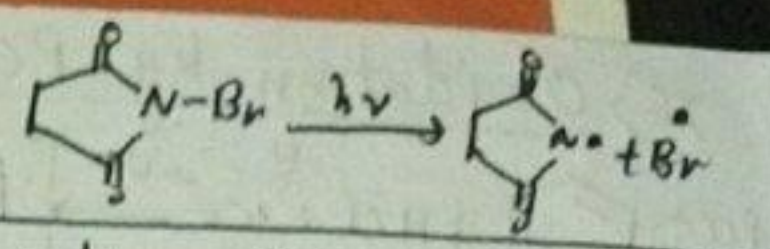
Due to size of $Li^+(aq.)$

A] 

70) NBS / hν.

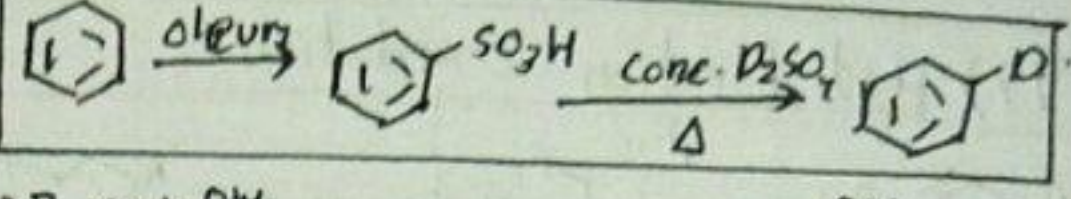
* Pure NBS is inert. But usually contains impurities of (Br_2, HBr.) → Source.

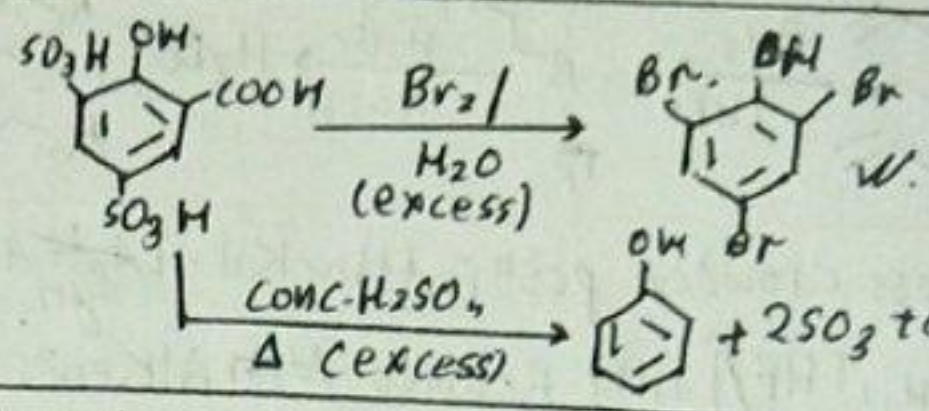
* Oxidising Nature :- 

* halogenation (Allylic posn) 

71) Desulphonation of organic compounds.

Reagent : (H_2SO_4/Δ), (HCl/H_2O/Δ), (HCl/$AlCl_3$, Δ)



A] 

72) Williamson's Esterification Reaction

$R_1-\overset{O}{\overset{\|}{C}}-OH + H\overset{18}{O}R_2 \xrightarrow[\Delta]{H^{\oplus}} R_1-\overset{O}{\overset{\|}{C}}-\underset{18}{O}R$

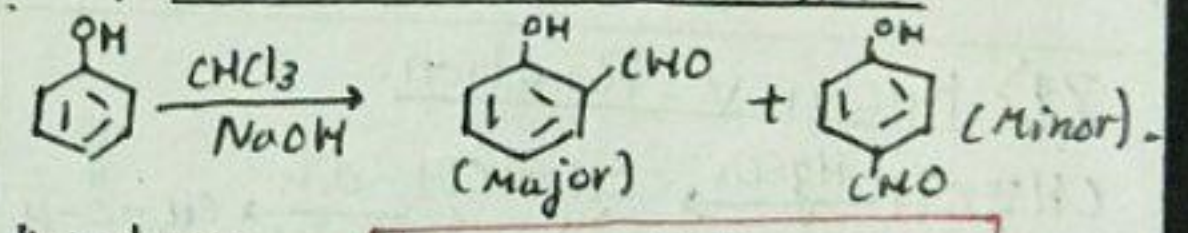
(Rate of Esterification $\propto \frac{1}{size}$)

73) Trans - Esterification.

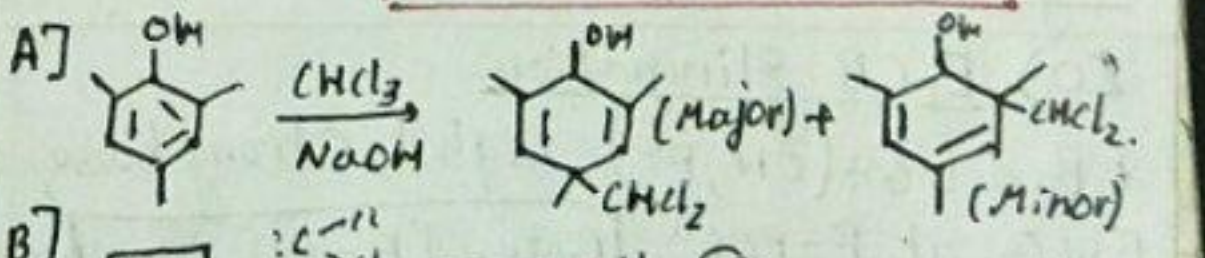
$R_0-\underset{H}{\overset{O}{\overset{\|}{C}}}-OR_1 + R_2OH \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}} R-\underset{H}{\overset{O}{\overset{\|}{C}}}-OR_2 + R_1OH$

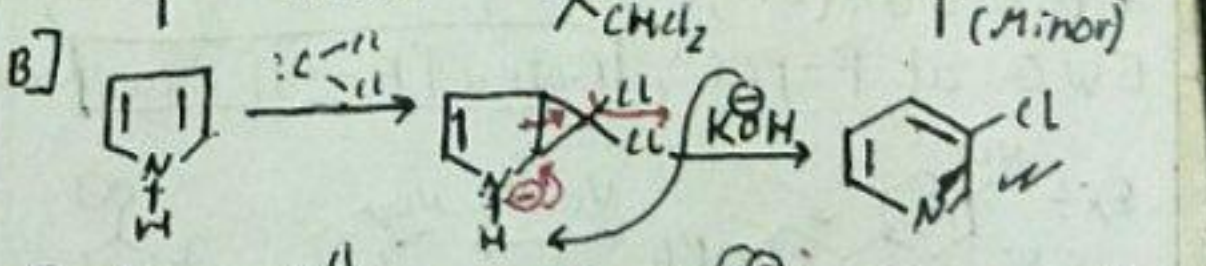
* this Rxn is Faster in Acidic Medm.

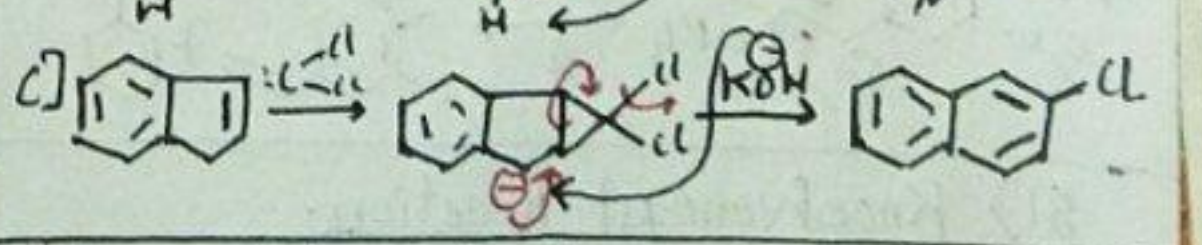
74) Riemer - tiemann Reaction.



* Carbene intermediate ; $\left(\frac{o}{p}\right)_{NaOH} > \left(\frac{o}{p}\right)_{KOH} > 1$

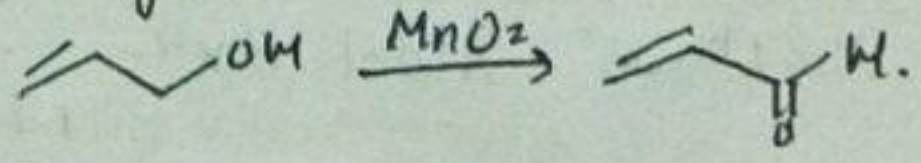
A] 

B] 

C] 

75) oxidation by MnO_2.

* It only oxidises Allylic and benzylic Aldehydes to Ketones.

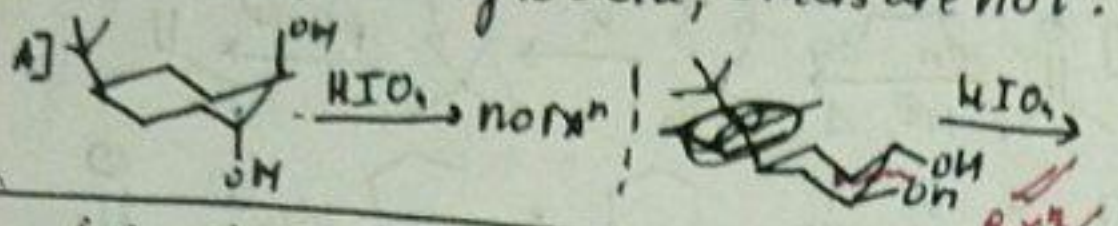


65) Malaprade Reaction.

$[HIO_4 + 2H_2O \longrightarrow H_5IO_6]$.

* Vicinal Diols, Amine (1°, 2°), Ketone, ~~COOH~~, ~~Carboxylic Acids~~ Epoxides are oxidised one step up.

* 3° Amines, carboxylic acid, ethers are not.

A] 

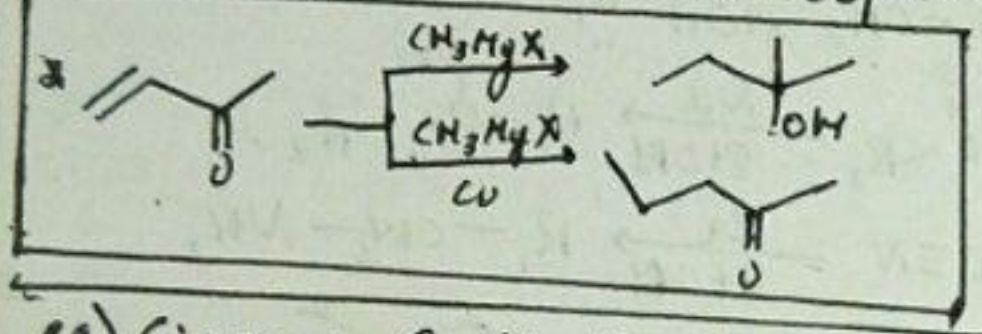
66) Stephen Reduction.

$R-C\equiv N \xrightarrow[HCl]{SnCl_2} R-CH=NH \xrightarrow{H_3O^{\oplus}} R-\overset{O}{\overset{\|}{C}}-H.$

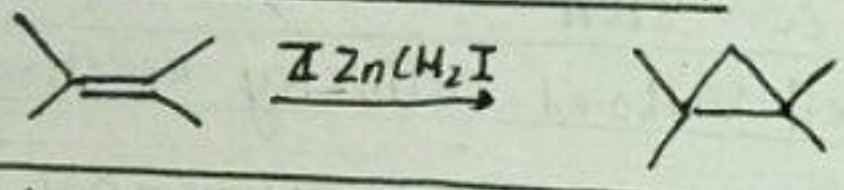
67) Soft Grignard Reagent.

R-Na, R-Li → Hard Nucleophide.

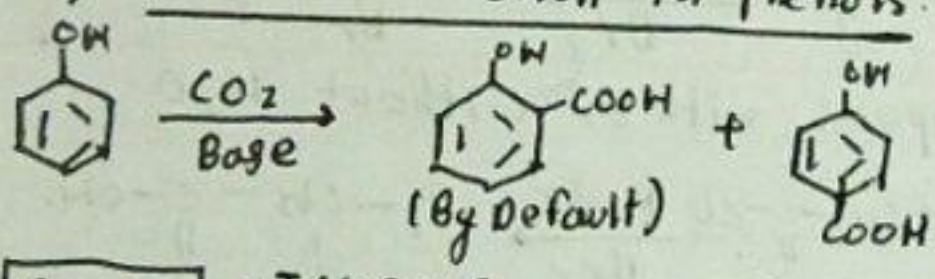
R_2CuLi, R_2Cd → Soft. Nucleophile.



68) Simmons Smith Reaction.



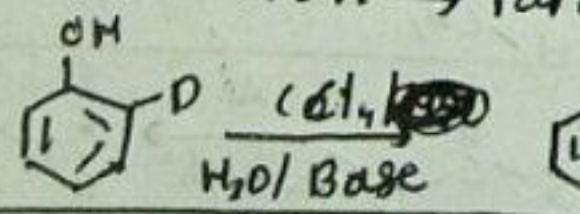
69) Kolbe's Reaction For phenols.



Base = KOH
- T < 60° → Para (KCP)
- 60°C < T < 150°C → ortho (TCP)
- T > 150° → Para (H bond breaks)

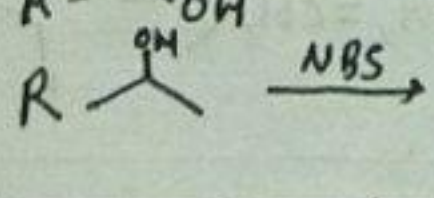
T ≯ 50°C
- KOH → Para
- NaOH → ortho
- LiOH → Para

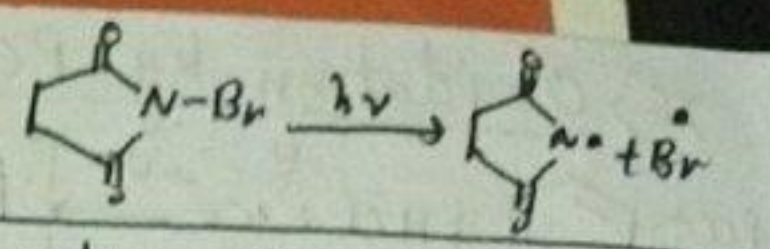
Due to size of $Li^+(aq.)$

A] 

70) NBS / hν.

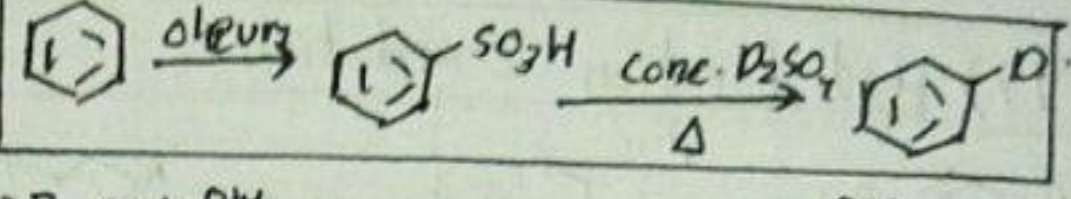
* Pure NBS is inert. But usually contains impurities of (Br_2, HBr.) → Source.

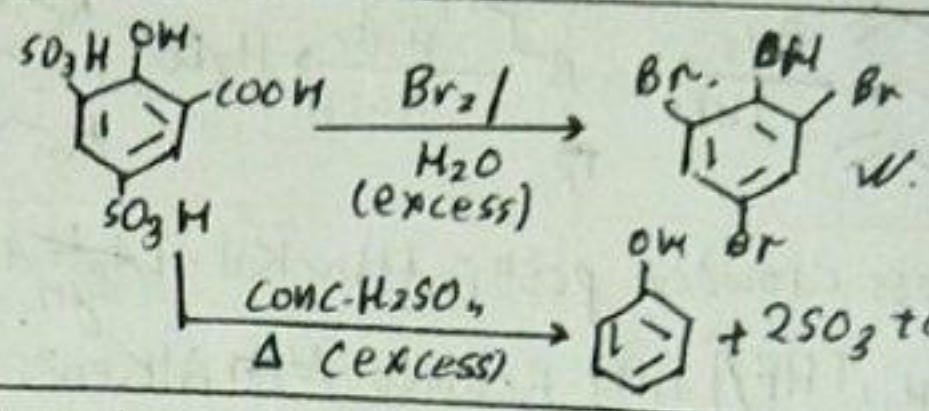
* Oxidising Nature :- 

* halogenation (Allylic posn) 

71) Desulphonation of organic compounds.

Reagent : (H_2SO_4/Δ), (HCl/H_2O/Δ), (HCl/$AlCl_3$, Δ)



A] 

72) Williamson's Esterification Reaction

$R_1-\overset{O}{\overset{\|}{C}}-OH + H\overset{18}{O}R_2 \xrightarrow[\Delta]{H^{\oplus}} R_1-\overset{O}{\overset{\|}{C}}-\underset{18}{O}R$

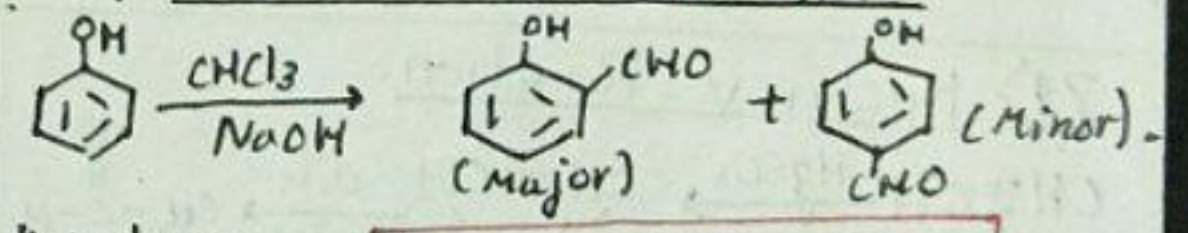
(Rate of Esterification $\propto \frac{1}{size}$)

73) Trans - Esterification.

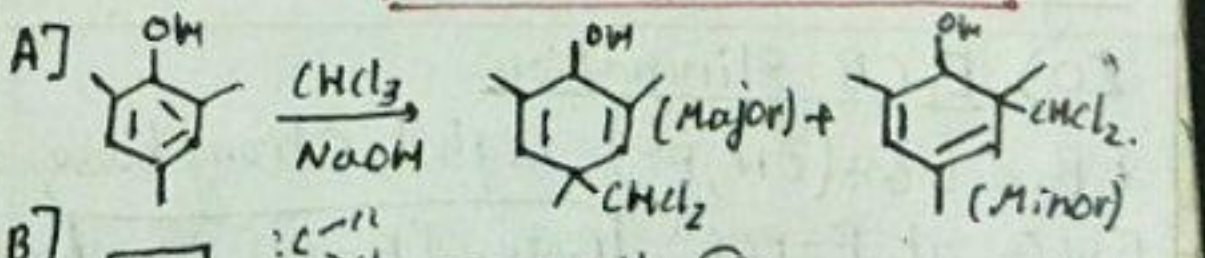
$R_0-\underset{H}{\overset{O}{\overset{\|}{C}}}-OR_1 + R_2OH \underset{}{\overset{H^{\oplus}}{\rightleftharpoons}} R-\underset{H}{\overset{O}{\overset{\|}{C}}}-OR_2 + R_1OH$

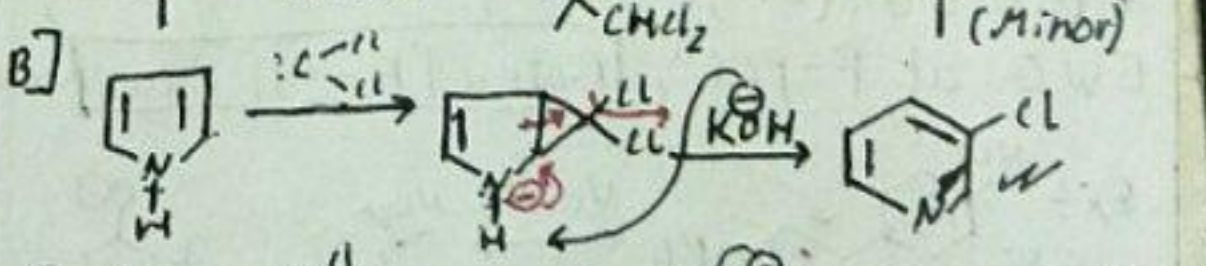
* this Rxn is Faster in Acidic Medm.

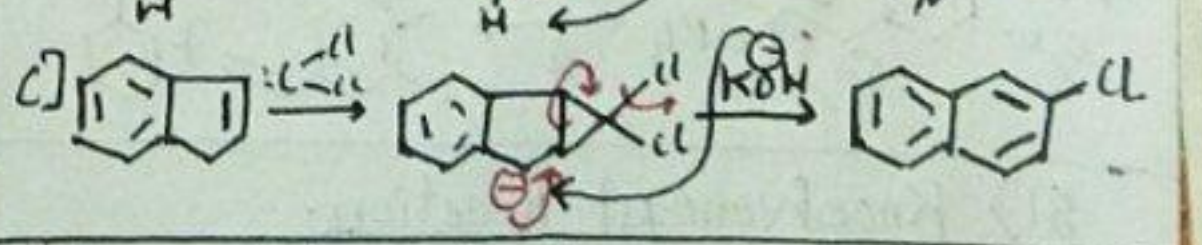
74) Riemer - tiemann Reaction.



* Carbene intermediate ; $\left(\frac{o}{p}\right)_{NaOH} > \left(\frac{o}{p}\right)_{KOH} > 1$

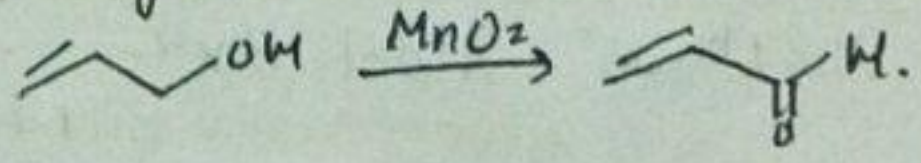
A] 

B] 

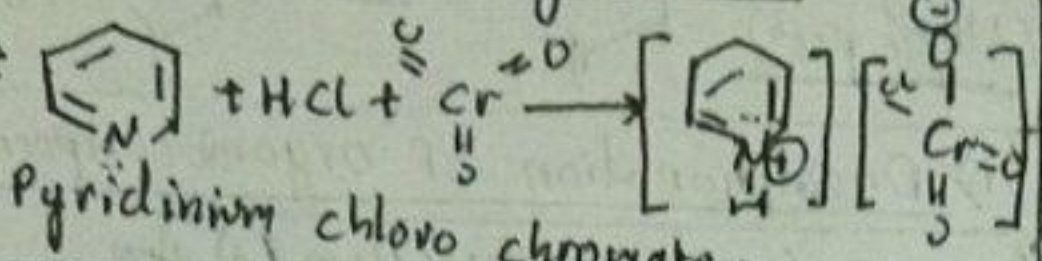
C] 

75) oxidation by MnO_2.

* It only oxidises Allylic and benzylic Aldehydes to Ketones.



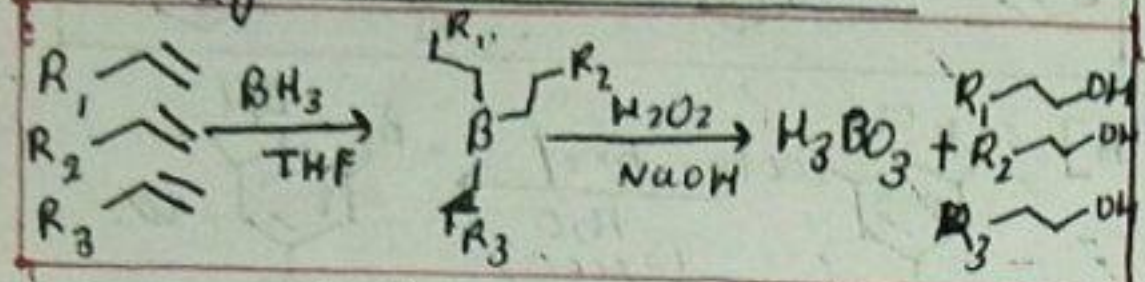
76) Oxidation by PCC.

PCC ÷ 

↳ Pyridinium chloro chromate.

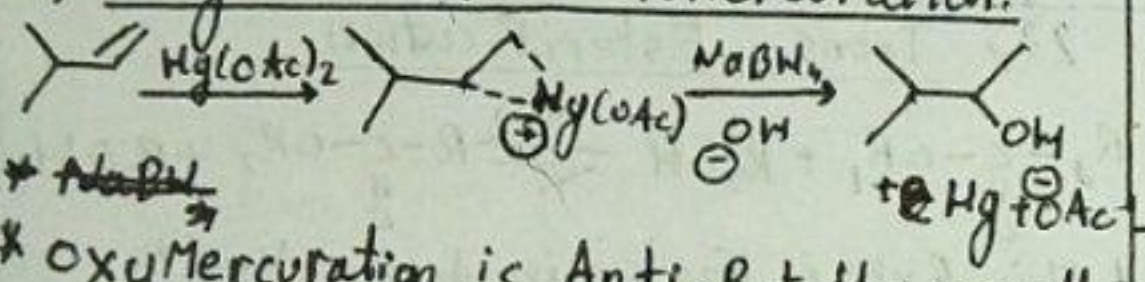
$RCH_2OH \xrightarrow{PCC/CH_2Cl_2} RCHO$ ↗ 1°, ↘ 2°

77) Hydroboration oxidation.



* less crowded posⁿ is Attacked. [~~Anti~~ Addⁿ syn.
* $(BH_3, THF / CH_3COOH)$ only Reduces ~~Alkin~~ Alkenes Alkynes and carboxylic Acids
* Rate of Reduction: Acid > Aldehyde/Ketone > Alkyne > Alkene (As it is an Electrophillic Reducing Agent)

78) OxyMercuration Demercuration.



* ~~NaBH4~~
* OxyMercuration is Anti. But the overall Rⁿ may be syn or anti..

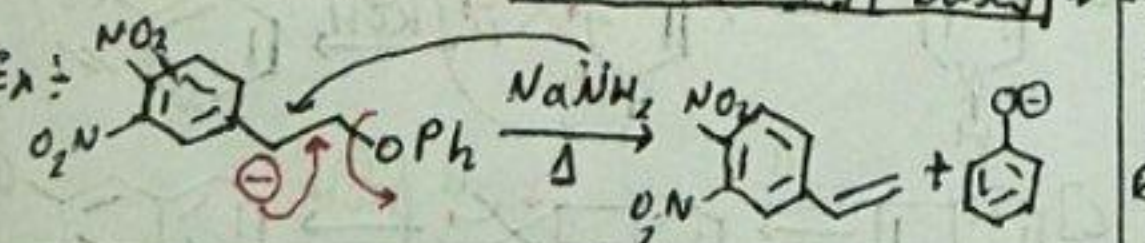
79) Kuchirov Reaction.

$CH\equiv CH \xrightarrow{HgSO_4} CH=CH \xrightarrow[H_2SO_4]{dil.} CH_3-C(=O)-H + Hg^{+2}$

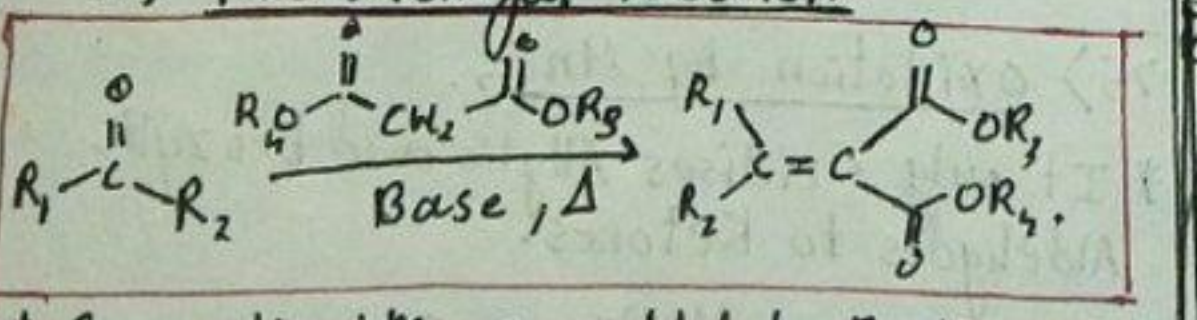
* $HgSO_4$ is catalyst.

80) E1CB Elimination.

* Bad L-G ÷ ($^{\ominus}OH$, $F^{\ominus}$), high T, strong base, EWG at β-posⁿ, Rate ∝ [R-X] [Base]

Ex ÷ 

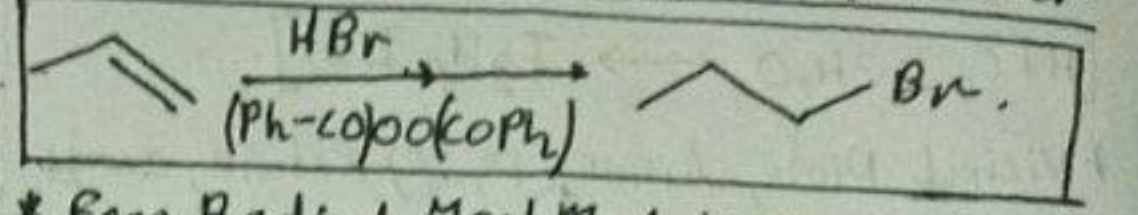
81) Knoevenegal Reaction.



* Same Mechᴹ as Aldol Rxⁿ.

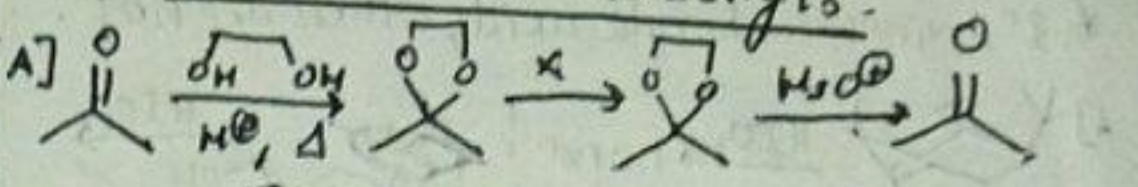
P-T.o.

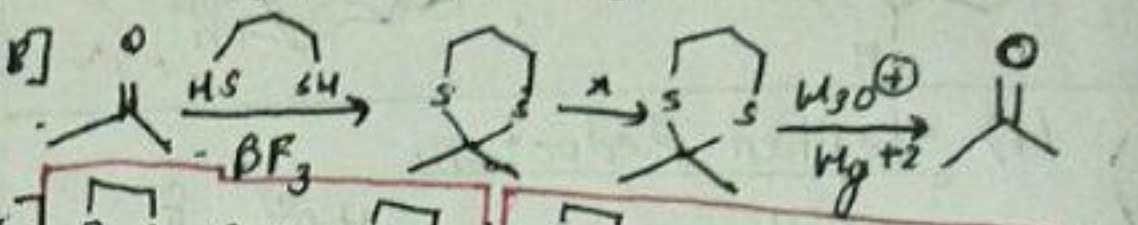
82) Peroxide Effect / Khorash effect.

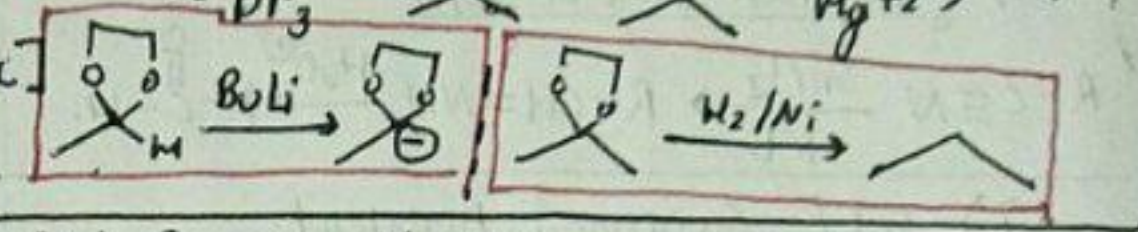


* Free Radical Mechᴹ, Anti-Markonikov Prod.

83) Protection of Carbonyls.

A] 

B] 

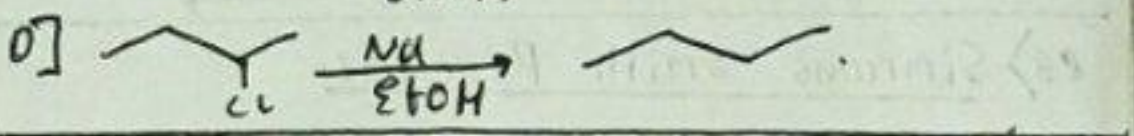
C] 

84) Bouveault-Blanc - Reduction.

A] $R_1-C(=O)-OR_2 \xrightarrow[EtOH]{Na} R_1-CH_2-OH + R_2-OH.$

B] $R_1-C(=O)-R_2 \xrightarrow[EtOH]{Na} R_1-CH(OH)-R_2.$

C] $R_1-C\equiv N \xrightarrow[EtOH]{Na} R_1-CH_2-NH_2$

D] 

85) Hell Volhard Zelinsky Reaction.

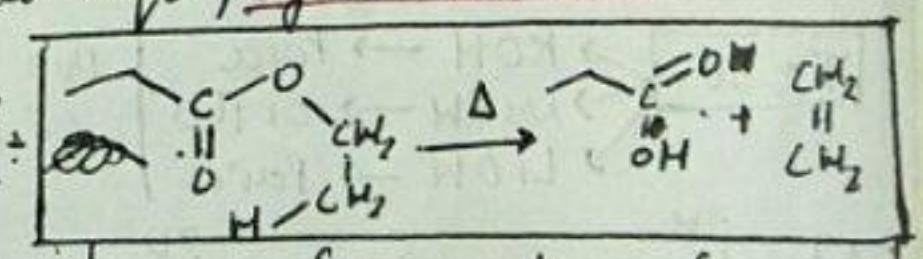
$R_1-CH_2-C(=O)-OH \xrightarrow[Br_2]{Red\,P} R_1-CH(Br)-C(=O)-OH.$

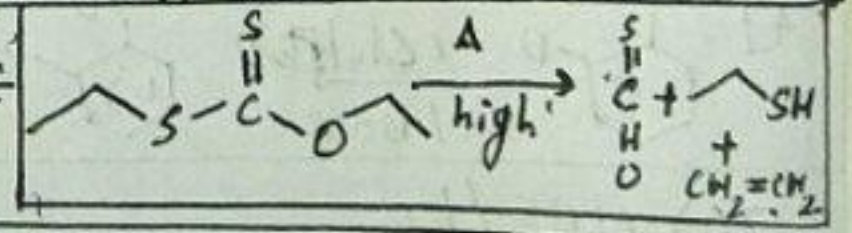
* Happens, with or without H_2O.

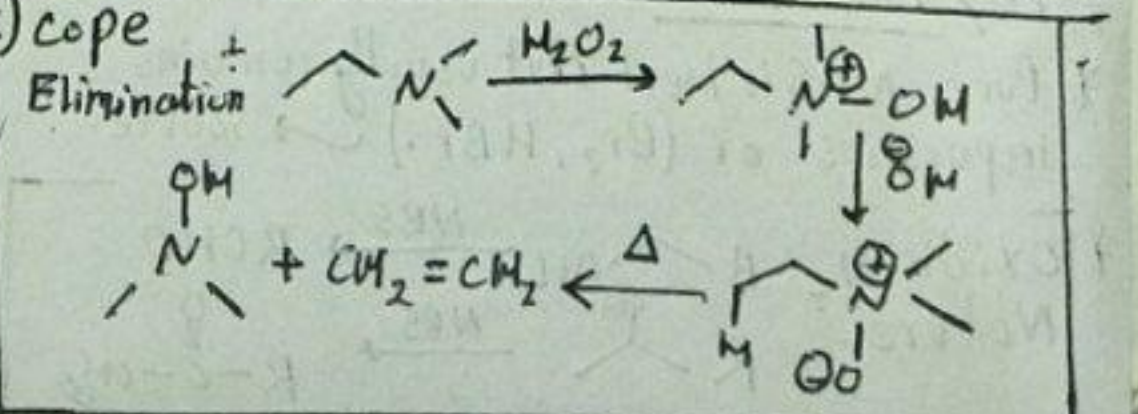
A] $R_1-CH_2-C(=O)-Cl \xrightarrow[Br_2]{Red\,P} R_1-CH(Br)-C(=O)-OH.$

86) E_i Elimination.

* only heat reqd, syn elimination.

A) Pyrolysis of Esters ÷ 

B) Pyrolysis of Xanthates ÷ 

C) Cope Elimination ÷ 

87) Wolff Rearrangement

Mechm: $R-\overset{\overset{O}{\|}}{C}-\overset{\oplus}{N}=\overset{\ominus}{N}=N \xrightarrow{\Delta} R-C(=O)-\ddot{N} + N_2(T)$

$\rightarrow R-N=C=O$ (isocynate)

$R-N=C=O \xrightarrow{H_2O} RNH_2 + CO_2(T)$

A] $R-\overset{\overset{O}{\|}}{C}-X \xrightarrow[(iii)\,H_2O]{(i)\,HN_3,\ (ii)\,\Delta} R-NH_2 + N_2(T) + CO_2(T)$ [Schmidt Degragation]

B] $R-CH=C=O \xrightarrow{P} R-CH_2-\overset{\overset{O}{\|}}{C}-X$

P = HCl → X = Cl | P = H_2O → X = −OH

P = NH_3 → X = NH_2 | P = NH_2R → X = −NHR.

P = ROH → X = OR | R = CH_3COOR → X = $-OOCH_3C$

C] $R-C(=O)-NH-NH_2 \xrightarrow[(ii)\,\Delta]{(i)\,NaNO_2/HCl} R-N=C=O$ [Curtius Degradation]

D] $R-C(=O)-HN-O-C(=O)-R' \xrightarrow{\ominus OH} R-N=C=O$ [Lossen Degradation]

E] $R-\overset{\overset{O}{\|}}{C}-OH \xrightarrow[(iv)\,H_3O^{\oplus}]{(i)\,SOCl_2,\ (ii)\,CH_2-NH_2,\ (iii)\,\Delta} R-CH_2-\overset{\overset{O}{\|}}{C}-OH$ [Arndt-Eistert Rx]

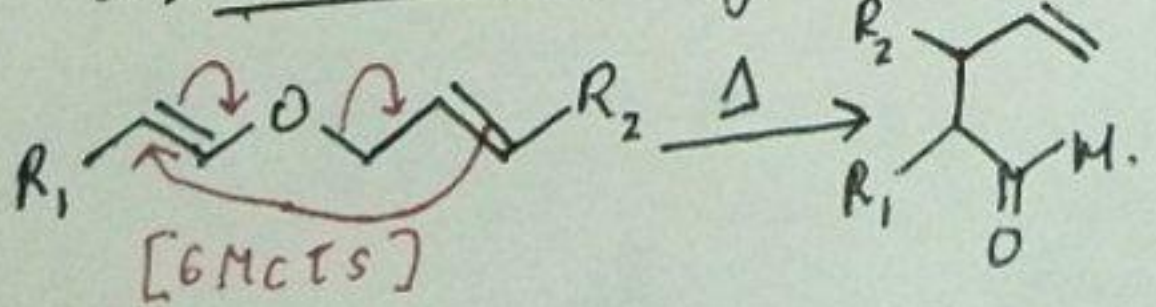
88) Beckmann Rearrangement

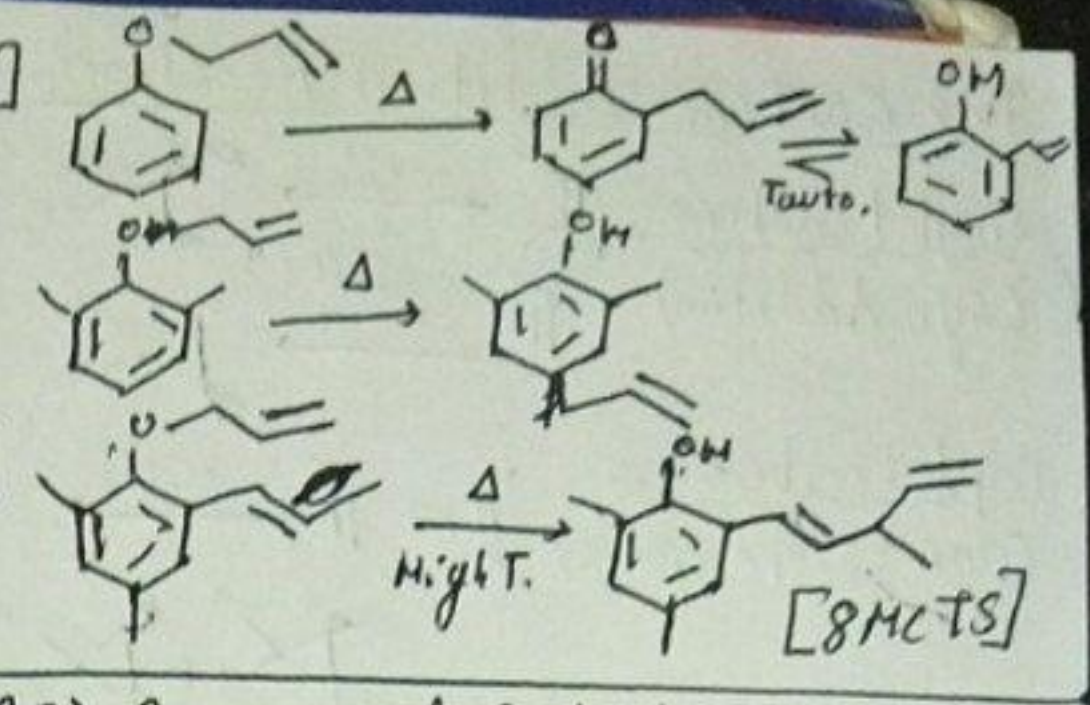
$R_1-C(=N-OH)-R_2 \xrightarrow{(i)\,conc\ H_2SO_4,\ (ii)\ HgCl_2}$ $R_1-\overset{\oplus}{C}=N-R_2$ → $R_1-\overset{\overset{O}{\|}}{C}-NH-R_2$ → $R_1-\overset{\overset{O}{\|}}{C}-OH + R_2-NH_2$ ($H_3O^{\oplus}$)

A] $Ph-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[High\ T]{\Delta} Ph-C\equiv N$.

$Ph-NH-\overset{\overset{O}{\|}}{C}-H \xrightarrow[High\ T]{\Delta} Ph-\overset{\oplus}{N}\equiv C\overset{\ominus}{}$

89) Claisen Rearrangement.



A] 

90) Rosenmund Reduction.

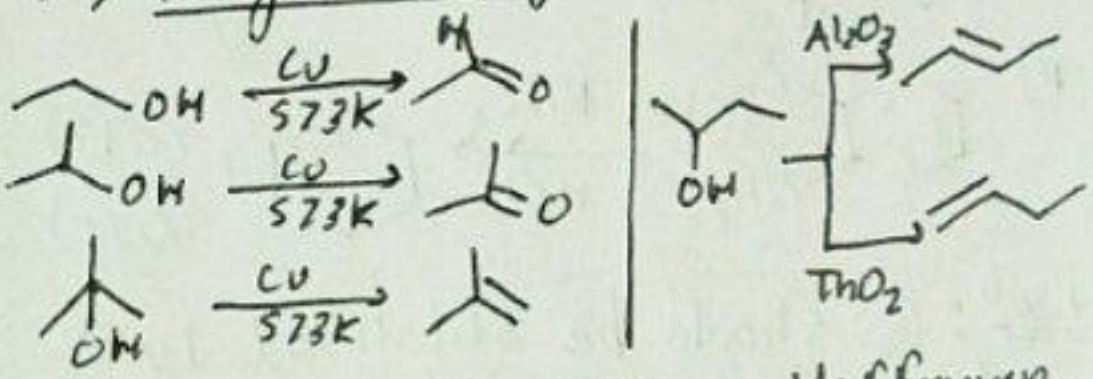
$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[BaSO_4]{H_2/Pd} R-CH=O$.

* Also Reduces triple bond to Double bond
* Also Reduces NO_2 to NH_2.

91) Corey-house Synthesis.

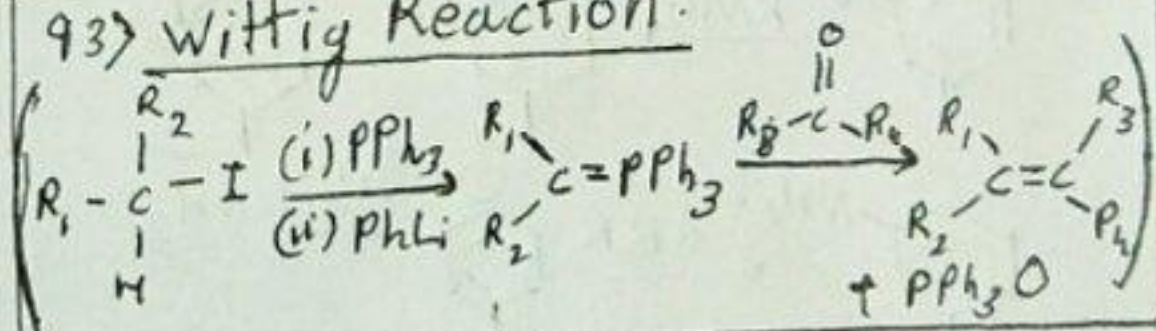
$R-X + Li/Et_2O \rightarrow R-Li \xrightarrow{Cu-I} R_2CuLi \xrightarrow{R'-X} R-R'$

92) Dehydration by Al_2O_3 / ThO_2 / Cu.

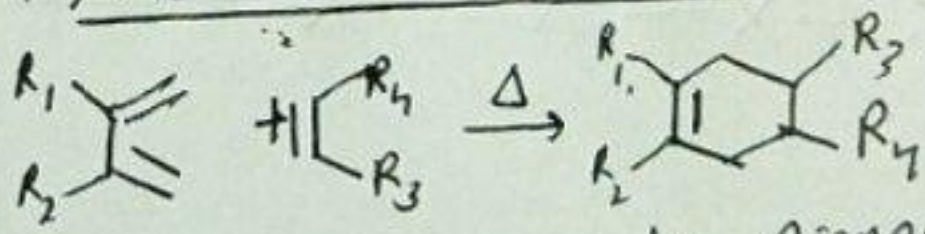


* Al_2O_3 → Saytzeff, ThO_2 → Hoffmann.

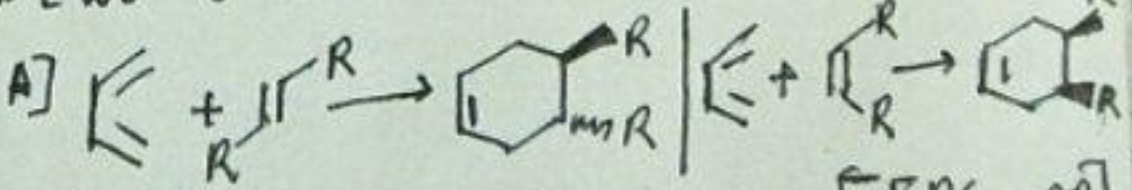
93) Wittig Reaction.

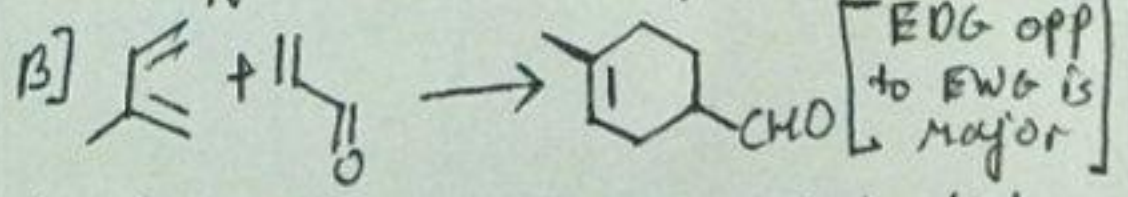


94) Diel's Alder Reaction.



* EDG should be Attched to Dienes.
* EWG should be Attatched to dienophile.

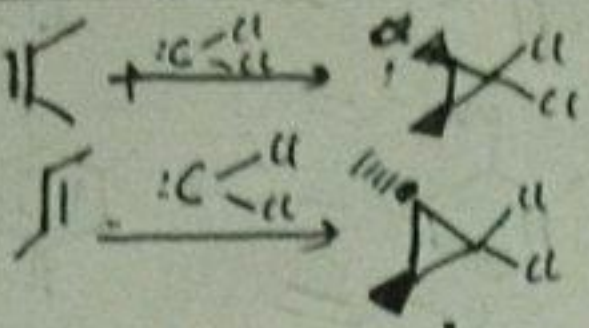
A] 

B] 

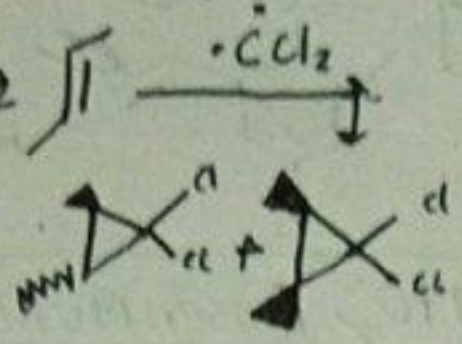
* only Cisoid Alkenes Give Diels Alder.

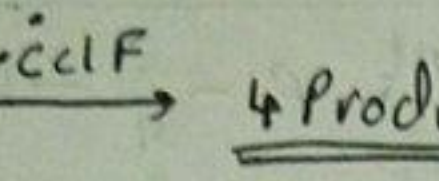
95) Carbene Addition Reaction.

singlet carbene ∴ (Syn Addition)



Triplet carbene ∴ (non-stereospecific)

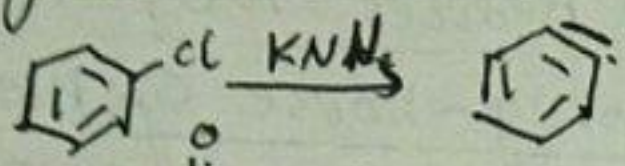


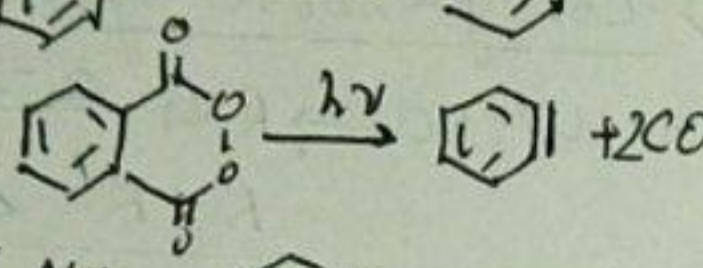
A] 

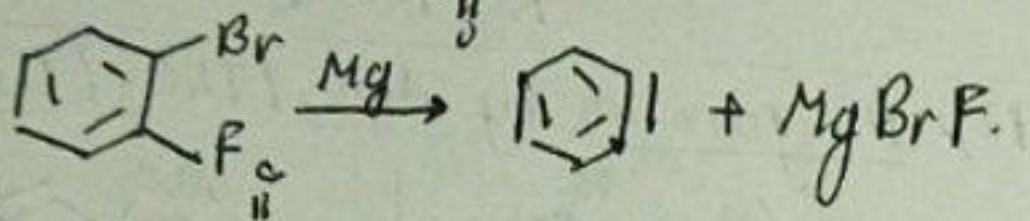
4 Products ☆

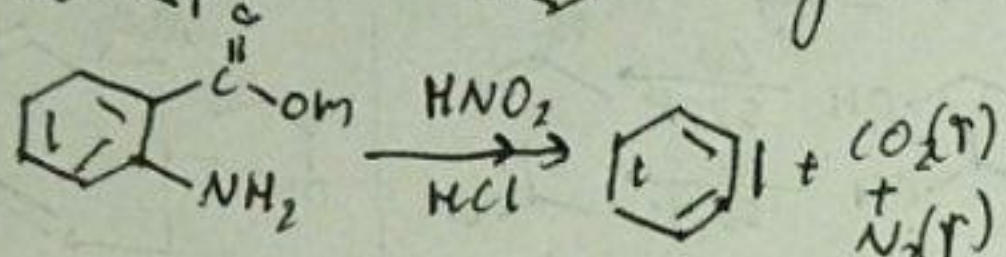
96) Benzyne Mechanism.

methods to Prepare Benzene

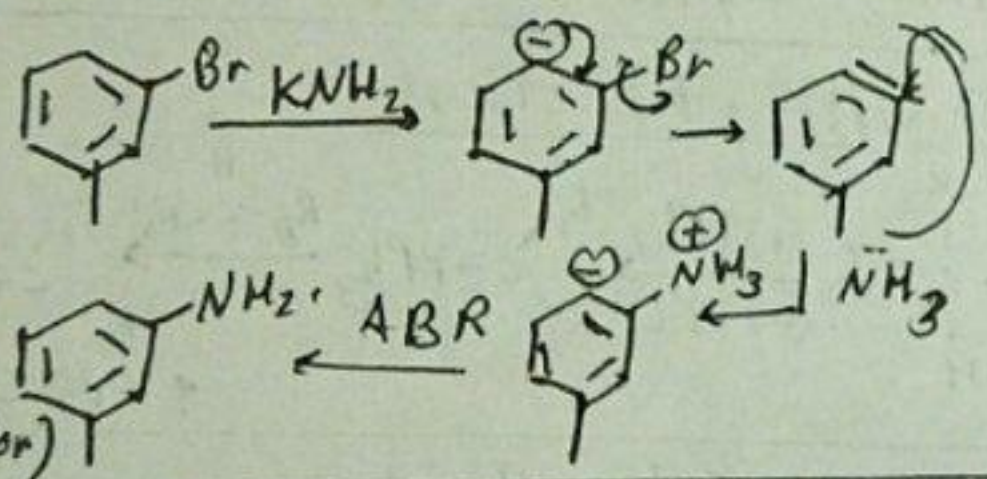
1] 

B] 

C] 

D] 

Rxn: ⊖ should be Stabalised by ▣ Inductive Effect.

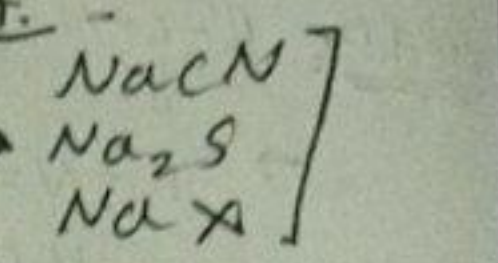
Ex: 

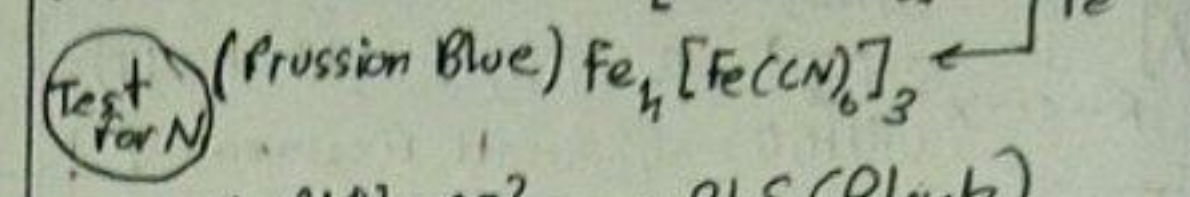
(Major)

ABR

Missed Parts in POC

1) Lassaigne's Test.





Test for N

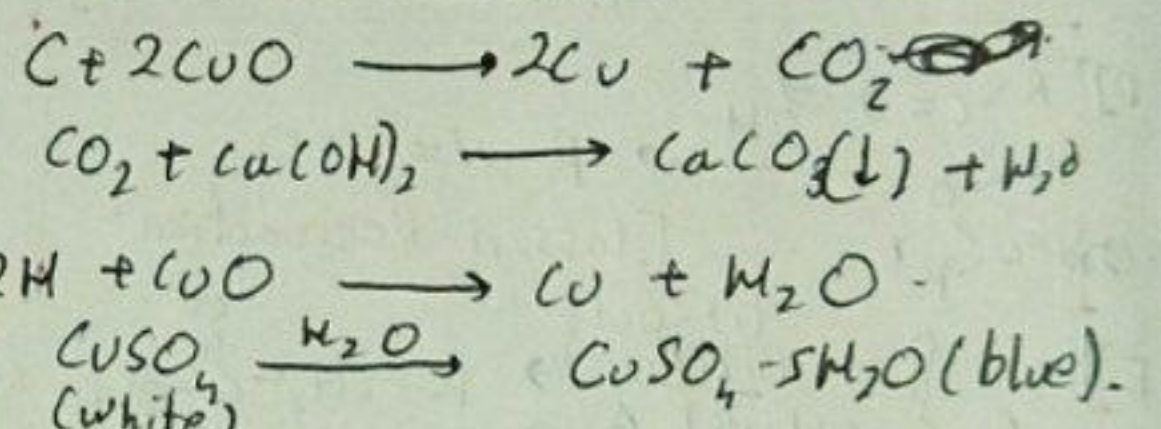
Test for S

IP both N, S → Khooni lal via SCN

Test for X

Test for Phosphorus

2) Detection of C, H:



* NH_2-NH_2, NH_2-OH, HN_3, $CH_3-\overset{\oplus}{N}\equiv N\,Cl$ do not give lassaigne's test ▣ bcoz we don't have carbon.

* $Ph-\overset{\oplus}{N}\equiv N\,Cl^{\ominus}$ also does not give Lassaigne's Test as on heating Diazo linkage goes BOOM BOOM!

— X — X — X — X ——