Basics

a) $-I$ series [~~can be~~ list ~~+M~~]

$-\overset{+}{N}F_3 > -\overset{+}{N}R_3 > -\overset{+}{S}R_2 > -\overset{+}{N}H_3 > -NO_2 > -SO_3H > -CN >$

$-COOH > -F > -Cl > -Br > I > -OR > -OH > C\equiv CH >$

$-NH_2 > -$ Benzene $>$ ene $> H$

b) $+I$ series

$-\overset{\ominus}{C}H_2 > -\overset{\ominus}{N}H > -\overset{\ominus}{O} > -COO\overset{\ominus}{} > 3^\circ R > 2^\circ R > 1^\circ R$

Nomenclature priority

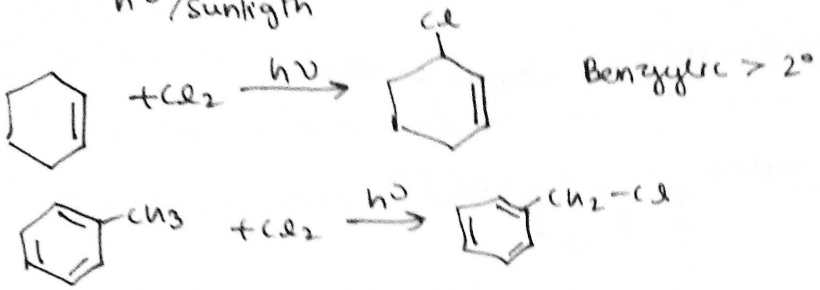
$-COOH > SO_3H > -\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}- > -COOR > -COX > CONH_2$

$> -CN > -NC > -CHO > \diagup C=O > -OH > -SH > -NH_2$

$> \diagup C=C\diagdown > -C\equiv C- > -OR > -NO_2 > X$

Alkane

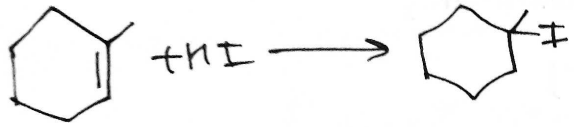
$R \xrightarrow[h\upsilon/\text{Sunlight}]{\text{U.V light}} R\text{-}Cl$



2) Alkene

$CH_3-CH=CH_2 + HBr \xrightarrow[\text{MARKOWNIKOFFS}]{} CH_3-\underset{Br}{CH}-CH_3$

$CH_3-CH=CH_2 + HBr \xrightarrow[\text{peroxide}]{H_2O_2} CH_2-CH_2-CH_2-Br$



3) Alkyne

$CH_3-C\equiv CH + H_2 \xrightarrow[\text{S/Quinoline}]{\text{Pd-Basou}} CH_3-CH=CH_2$

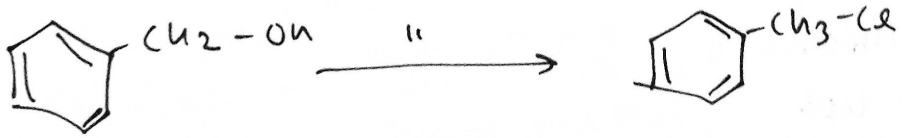
Lindlars catg.

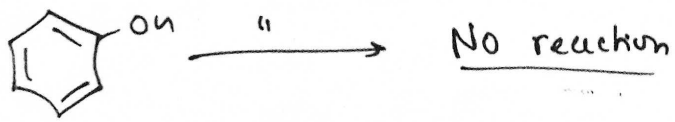
$CH_3-C\equiv CH + H_2 \xrightarrow[Ni\ /Pd\ /Pt]{} CH_3-CH_2-CH_3$

4) Alcohols

$CH_3-CH_2-OH \xrightarrow{PCl_5\ /PCl_3/SOCl_2} CH_3-CH_2-Cl$

$CH_3-\underset{\underset{OH}{|}}{CH_2}-CH_3 \xrightarrow{''} CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3$





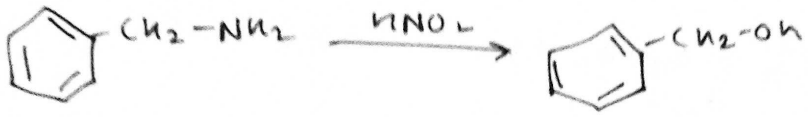
No reaction

5) Primary amine

a

$CH_3-CH_2-NH_2 \xrightarrow[\text{or } HNO_2]{NaNO_2 + HCl} CH_3-CH_2-OH$

$CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3 \xrightarrow{NaNO_2 + HCl} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$



6) Oxidation

a) MOA

$CrO_3 \cdot 2Py$ (Collins reagent)

PCC · in CH_2Cl_2 (pyridinium chlorochromate)

PDC (pyridinium dichromate)

CrO_3 + acetone (Jones reagent)

1) 1° alcohol ⟶ aldehyde

2) 2° alcohol ⟶ Ketones

3) 3° alcohol ⟶ No rct

$CH_3-CH_2OH \xrightarrow{oxy} CH_3-CHO$

$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{oxy} CH_3-\underset{\underset{O}{||}}{C}-CH_3$

b) SOA

$CrO_3 + H_2SO_4$ (Jones reagent)

$H^+ / K_2Cr_2O_7$

$H^+ / KMnO_4$

1) 1°/2° alcohol ⟶ acid

aldehyde ⟶ acid

Ketone ⟶ acid

i) $CH_3CH_2OH \xrightarrow[\Delta]{KMnO_4} CH_3-COOH$

ii) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \longrightarrow CH_3-COOH + HCOOH$

; Reduction

H_2/Pt, H_2/Pd, H_2/Ni → red^n to all except COOH, R-CONH$_2$, R-COOR'

$LiAlH_4$ reduces to all except C=C, C≡C

$NaBH_4$ reduces R-CHO, $R-\underset{\underset{O}{\|}}{C}-R$

a) $CH_3-CHO \xrightarrow[\text{or } LiBH_4]{NaBH_4} CH_3-CH_2-OH$

b) $CH_3-COOH \xrightarrow{"} CH_3-CH_2-OH$

c) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{"} CH_3-\underset{\underset{OH}{|}}{CH_2}-CH_3$

8) Nucleophic substitution reaction

CH_3-CH_2-Cl

- $\xrightarrow{aq\ KOH}$ CH_3-CH_2-OH [NaOH for cyclic compounds]
- $\xrightarrow{alc\ KCN}$ CH_3-CH_2-CN
- $\xrightarrow{NH_3}$ $CH_3-CH_2-NH_2$
- $\xrightarrow{alc\ AgCN}$ CH_3-CH_2-NC
- $\xrightarrow{AgNO_2}$ $CH_3-CH_2-NO_2$
- $\xrightarrow{KNO_2}$ CH_3-CH_2-ONO

$CH_3-CH_2-X + NaI \xrightarrow[\text{finkel stein}]{\text{dry ether}} CH_3-CH_2-I$

X = Cl, Br

$CH_3-CH_2-X \xrightarrow[\text{Swarts reaction}]{AgF/CoF/HgF} CH_3-CH_2-F$

ambidental nucleophile

CN^- & NC^-

NO_2^- & ONO

SCN^- & NCS

9) Elimination Reaction

$CH_3-CH_2-Cl \xrightarrow{\text{alc KOH}} CH_2=CH_2 + HCl + H_2O$

$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{\text{alc KOH}} CH_3-CH=CH_2$

$CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[\text{saytzeus rule}]{\text{alc KOH}} CH_3-CH=CH-CH_3$

$CH_3-CH_2-OH \xrightarrow[\text{443 K}]{H^+} CH_2=CH_2$

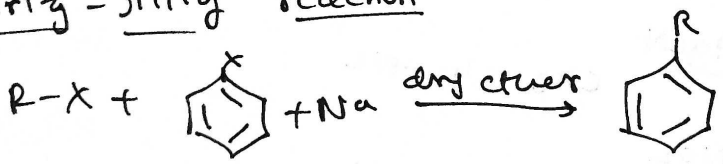
$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[\text{443 K}]{H^+} CH_3-CH=CH_2$

$CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[\text{443 K}]{H^+} CH_3-CH=CH-CH_3$

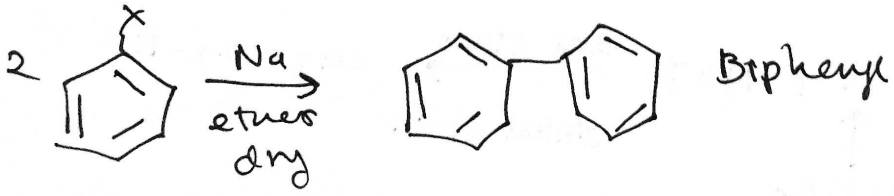
10) a) Wurtz reaction

$2R-X + 2Na \xrightarrow{\text{dry ether}} R-R + 2NaX$

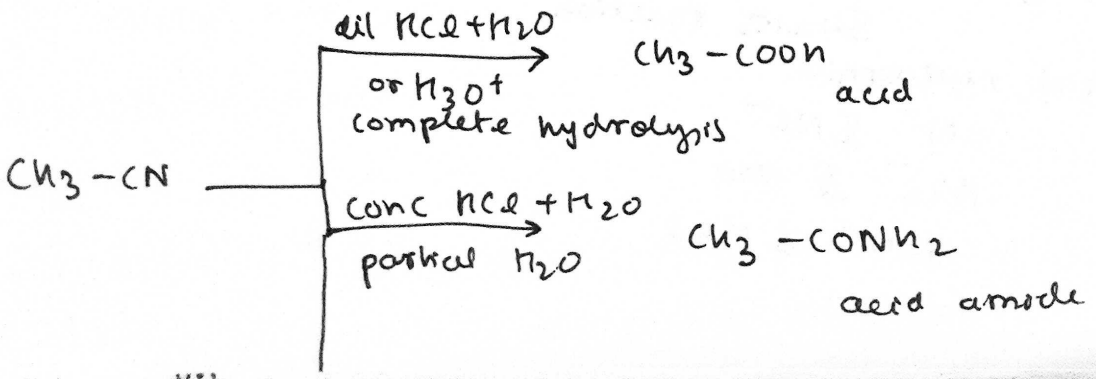
b) Wurtz - fitting reaction



c) Fitting reaction



11) HB [common path]



$SnCl_2 + HCl$ → CH_3-CHO aldehyde
(H_3O^+, Stephens rcdn)

$LiAlH_4$ → $CH_3-CH_2-NH_2$ amine

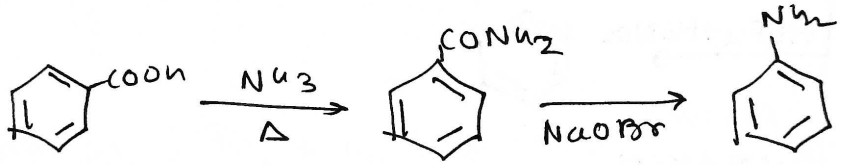
12) $CH_3-COOH + NH_3 \longrightarrow CH_3-COONH_4 \xrightarrow{\Delta} CH_3-CONH_2$

OR

$CH_3-COOH + NH_3 \xrightarrow{\Delta} CH_3-CONH_2$

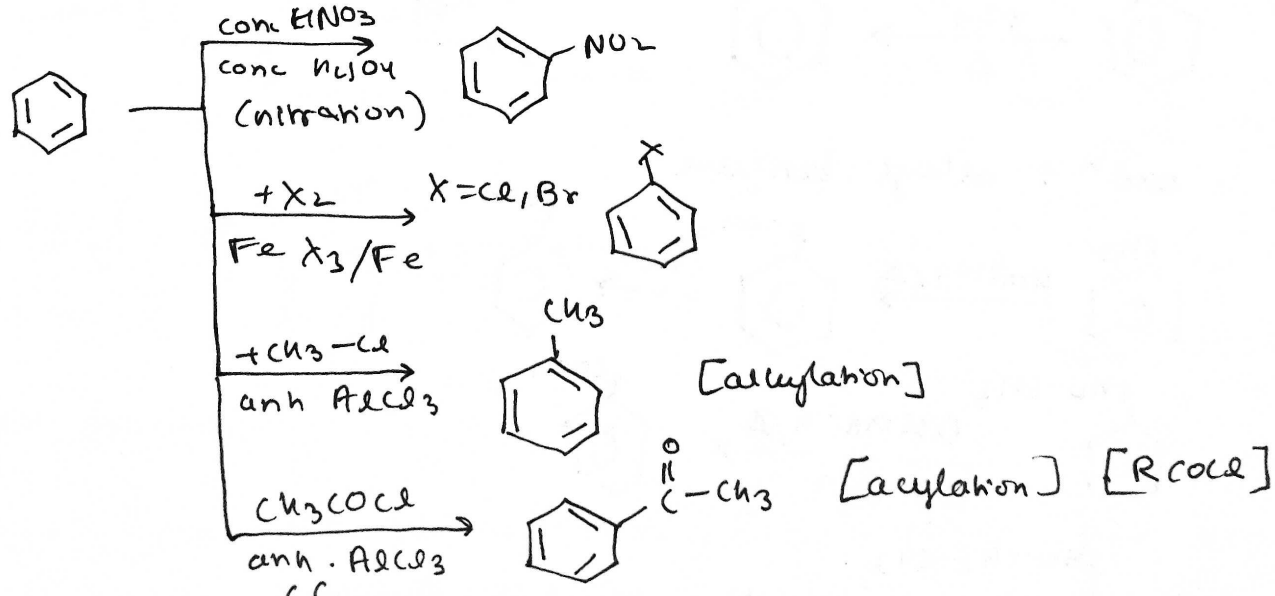
13) Hoffmans Bromoamide reaction

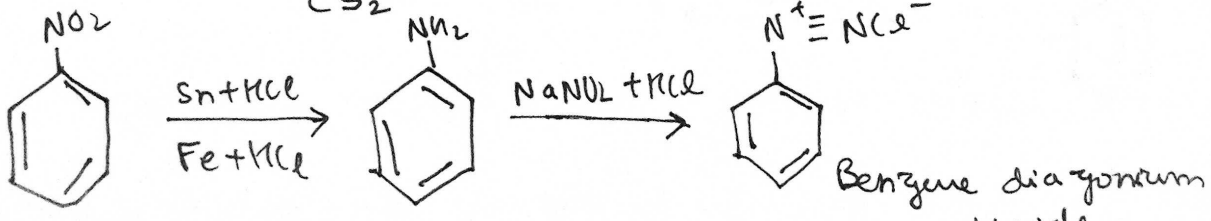
$CH_3-CONH_2 \xrightarrow[\text{or } NaOBr]{Br_2 + KOH} CH_3-NH_2$



Benzamine

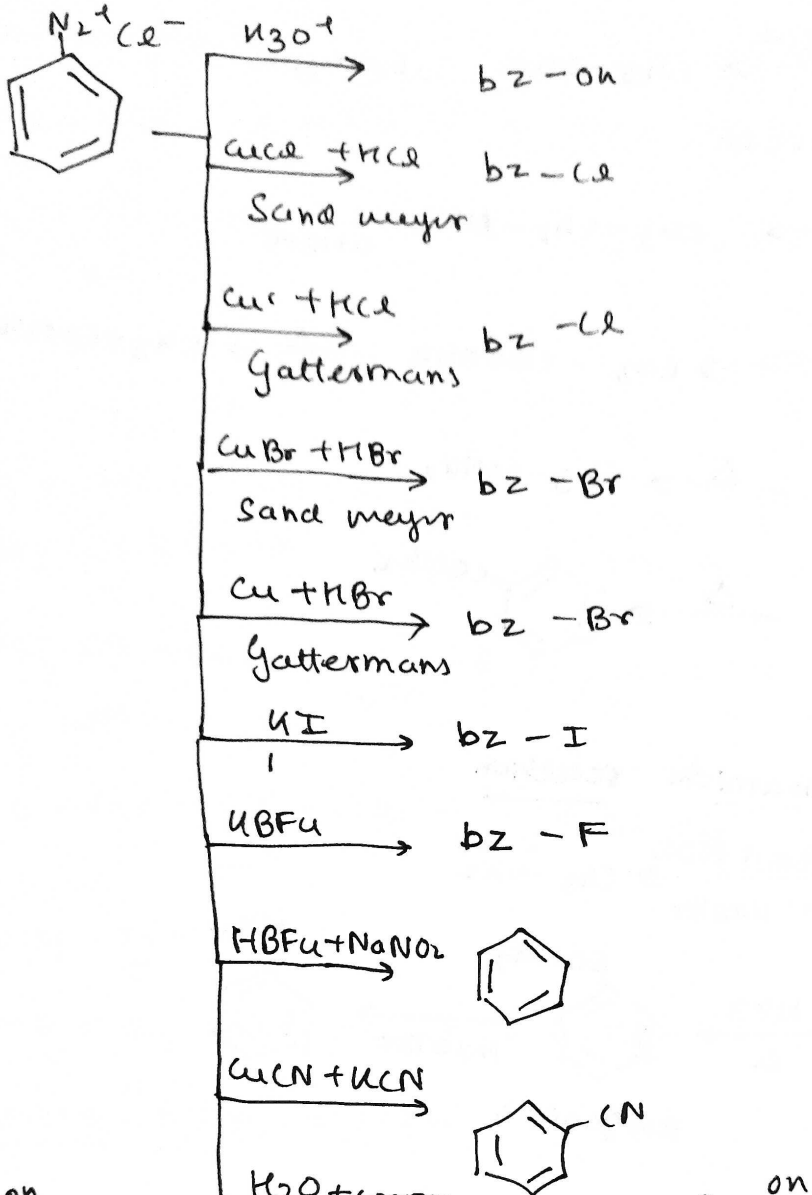
14) electrophilic substitution reaction





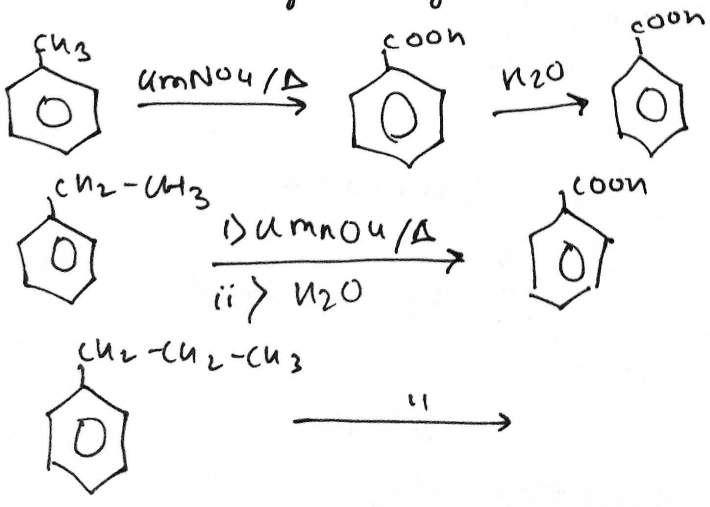
Benzene diazonium chloride

16

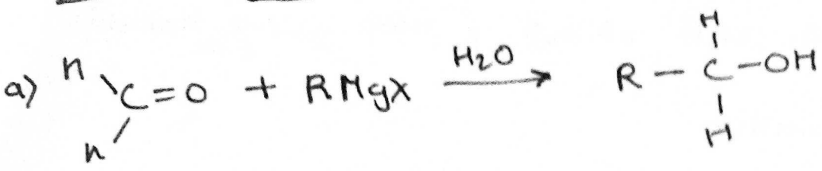


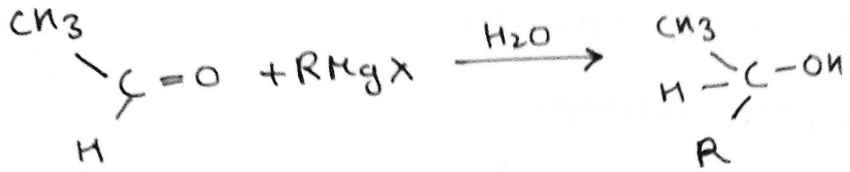
17)

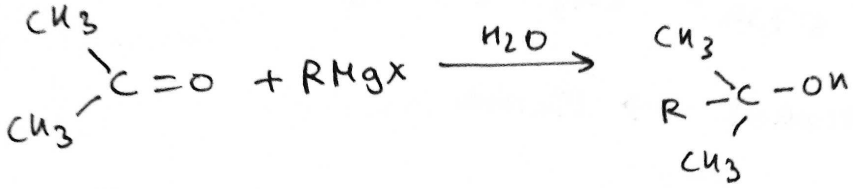
18) oxdn + alkyl benzene



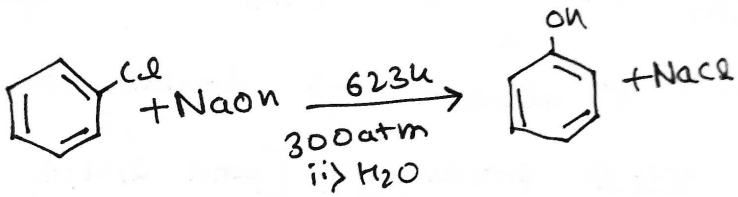
alcohols from carbonyl compounds — Misc

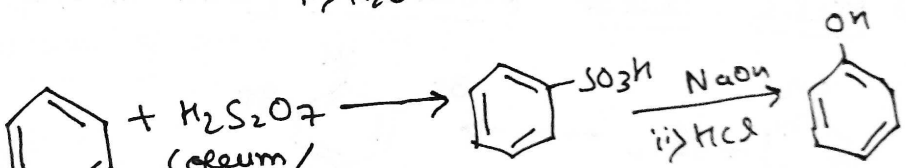
a) 

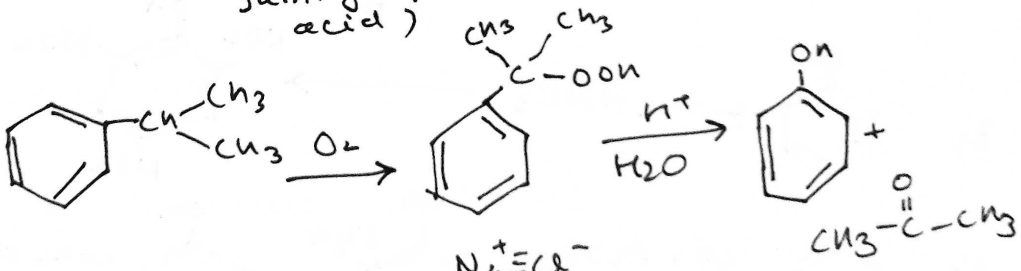
b) 

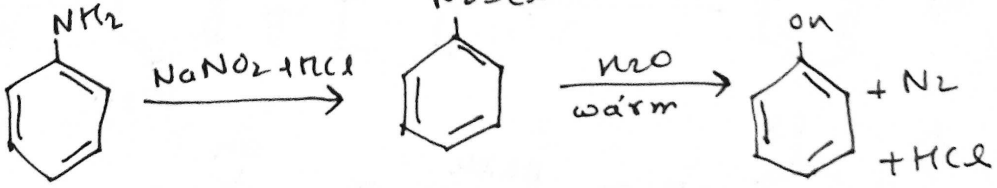
c) 

20) Phenol production

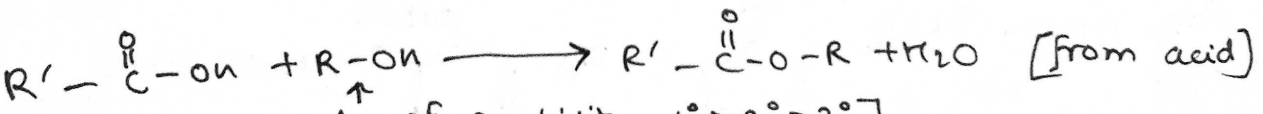
[from chloro benzene] a) 

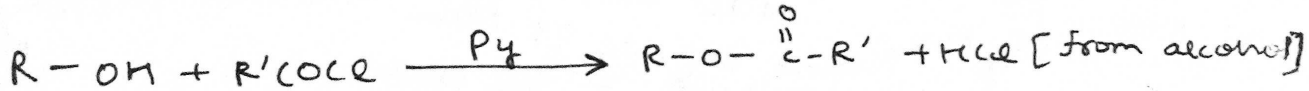
[from benzene sulphonic acid with oleum] b) 

[from cumene] c) 

[from BDC] d) 

21) Ester production

a) 

b) 

c) 

[from acid anhydride]

d) $RX + R'COONa \longrightarrow R-COOR' + NaX$ [from alkyl halide] aliphatic

- Kolbes proc

22) Catalytic dehydrohalogenation

a) $R-CH_2-OH \xrightarrow[573K]{Cu} R-CHO + H_2$

1° alcohol → aldehyde

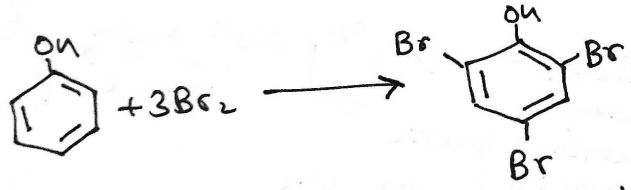
b) $R-\underset{\underset{OH}{|}}{CH}-R' \xrightarrow[573K]{Cu} CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

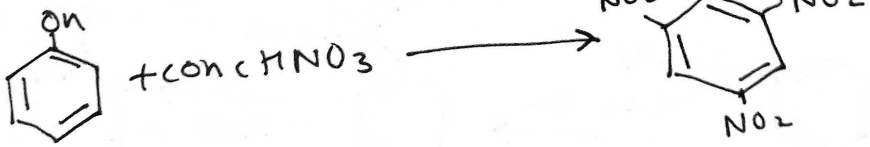
2° alcohol → Ketone

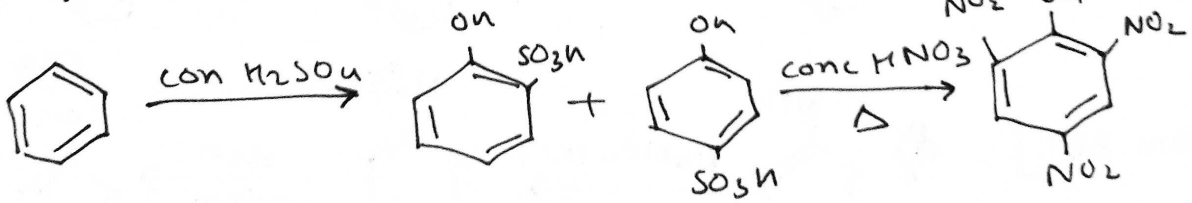
c) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow[573K]{Cu} CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + H_2O$

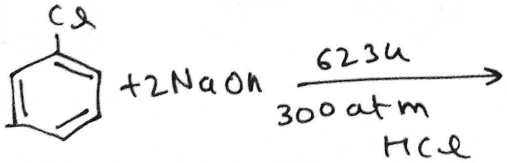
3° alcohol → double bond [Saytzeffs rule]

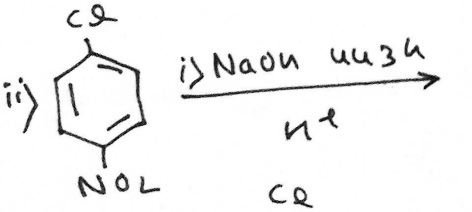
23) Picric acid production [and 2,4,6 tribromo phenol]

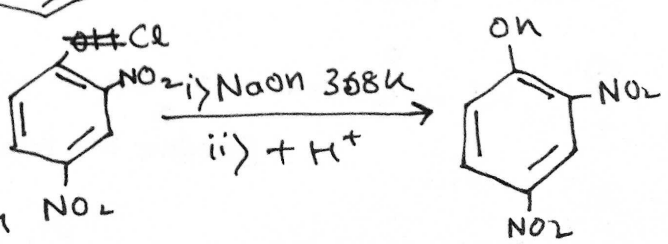
a) 

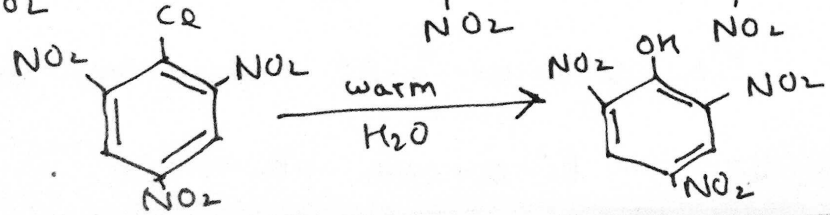
b) 

c) 

d) i) 

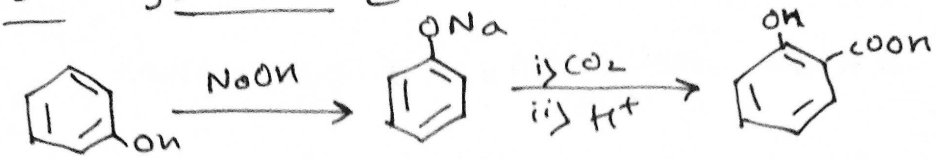
ii) 

iii) 

iv) 

Salicylic acid formation [and salicylaldehyde]

a) [Kolbes process]



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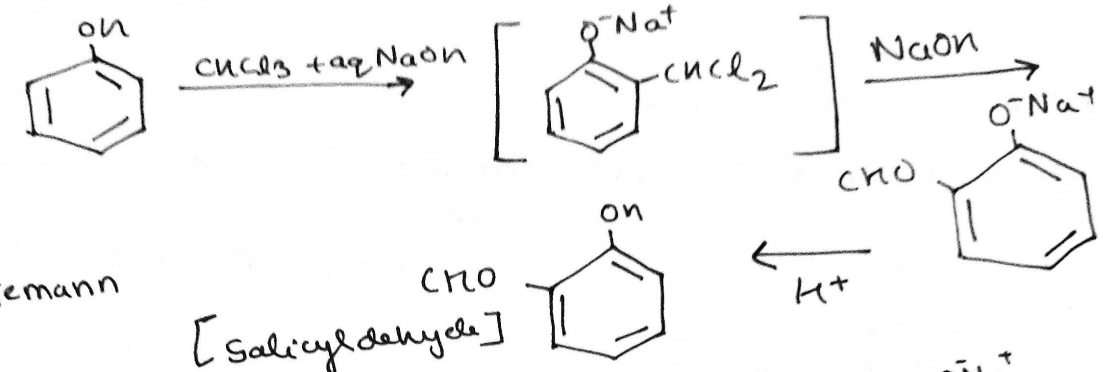

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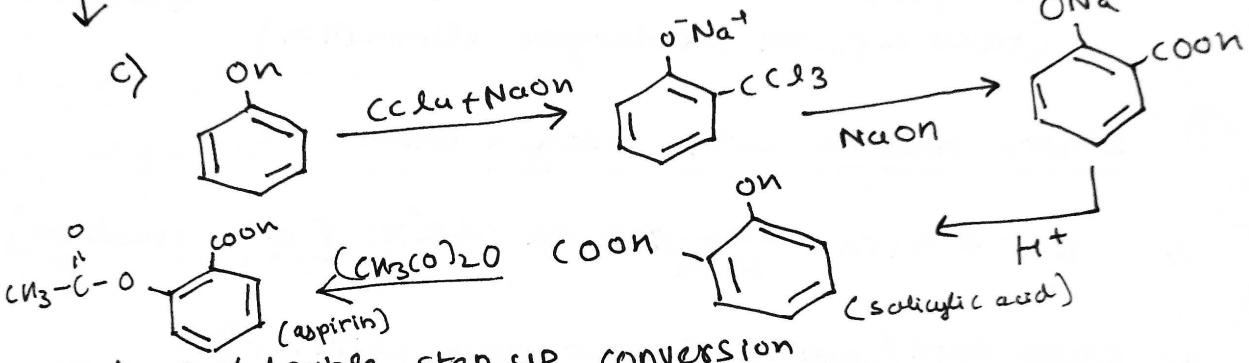


25) Step-down / double step up conversion

i) 

ii) $R-X + Na-C\equiv C-R' \longrightarrow R-C\equiv C-R' + NaX$

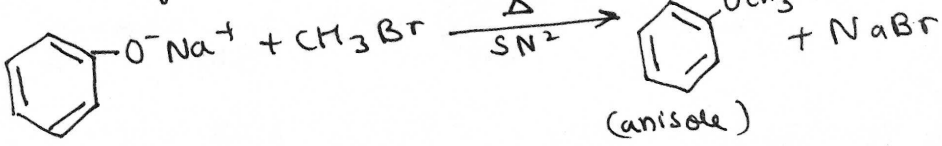
26) Ether production a) (Williamson synthesis)

i) $R-X + R'-\ddot{O}Na \longrightarrow R-\ddot{O}-R' + NaX$

alkyl halide always 1°

ii) $R'-\underset{\displaystyle R''}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}-O^- Na^+ + R'''-Br \xrightarrow[SN^2]{\Delta} R'-\underset{\displaystyle R''}{\overset{\displaystyle R}{\underset{|}{\overset{|}{C}}}}-O-R'''$

iii) anisole production [aryl halides less rct towards SN reaction]



b) By dehydration of alcohols (SN2, 1° preferance)

$$2R\text{-}OH \xrightarrow[413K]{\text{conc } H_2SO_4} R\text{-}O\text{-}R + H_2O$$

Limits of williamson synthesis

a) R-X always 1°

b) R-X always smallest

c) if R-X is 3° and reacted for example [alkene forms]

$$C_2H_5O^-Na^+ + CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\text{-}Br \longrightarrow C_2H_5OH + CH_3\text{-}\underset{CH_3}{\overset{CH_2}{\overset{\|}{C}}} + NaBr$$

$C_2H_5O^-Na^+$ ↓ strong base (takes a proton; undergoes elimination)

27) ethers reacting with halogen acids

i) $R\text{-}OR' + HX \xrightarrow[373K]{} R\text{-}OH + R'X$ [R' is smaller]

ii) excess acid [alcohol further reacts with HX]

$$R\text{-}OH + HX \longrightarrow R\text{-}X + H_2O$$

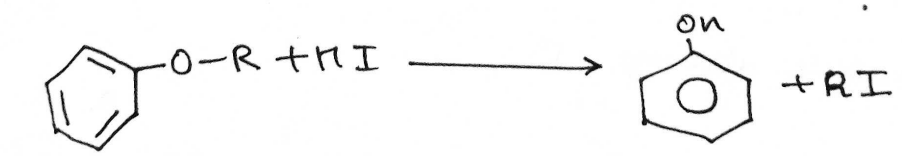
iii) 3° ether [SN1 mechanism]

↑ use SN1 instead of SN2

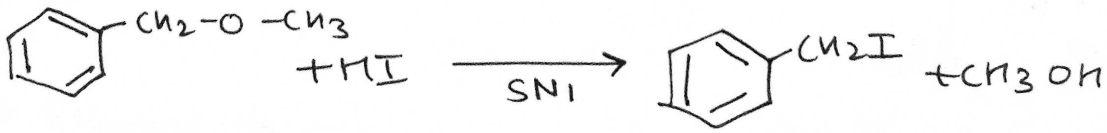
$$[3^\circ \text{ alkyl}]\text{-}O\text{-}CH_3 + HI \xrightarrow[SN1]{373K} [3^\circ \text{ alkyl}]\text{-}I + CH_3\text{-}OH$$

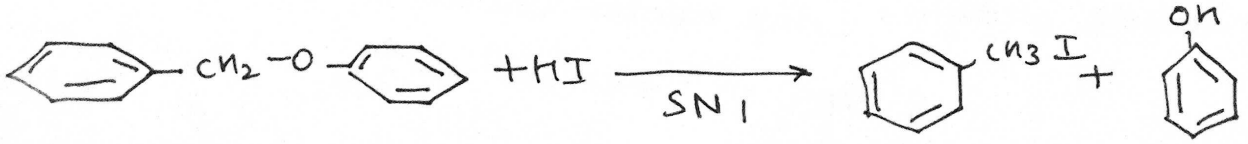
↓

iv) wherever alkyl aryl ether are present phenols must form



[anisole if R = CH_3]





28) Alcohol production

i) from alkene [using H_3O^+]

markownikow addition

ii) from alkene [using $(BH_3)_2$]

$$CH_3-CH=CH_2 + (BH_3)_2 \xrightarrow[H_2O_2]{H_2O,\,OH} CH_3-CH_2-CH_2-OH$$

mechanism → markownikow addition outcome ÷ kharash effect

29) Aldehyde production

a) ozonolysis of alkene

$$CH_3-CH=CH_2 \xrightarrow[ii)\ Zn+H_2O]{i)\ ozone} CH_3-CHO + HCHO$$

$$CH_3-CH=CH-CH_3 \xrightarrow[ii)\ Zn+H_2O]{i)\ ozone} CH_3-CHO + CH_3CHO$$

ethanal

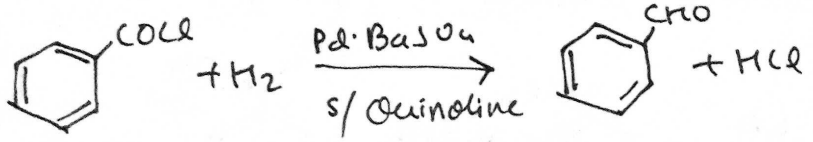
b) hydrolysis of alkyne [only produces ethanal]

$$CH\equiv CH \xrightarrow[H_2SO_4\,HgSO_4]{H_2O} H-\underset{OH}{\overset{OH}{C}}=CH_2 \xrightarrow{H_2O} H-\underset{OH}{\overset{OH}{C}}-CH_3 \xrightarrow{-H_2O} CH_3-CHO$$

c) Rosenmunds reduction

$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[S/Quinoline]{Pd\cdot BaSO_4} R-\overset{O}{\overset{\|}{C}}-H + HCl$$

(acid chloride)



benzoyl chloride

* cannot produce methanal because methanoyl chloride is unstable

d) [STEPHANS REDUCTION]

$$R-CH_2-CN \xrightarrow{SnCl_2+HCl} \underset{\text{imine}}{R-CH_2-CH=NH} \xrightarrow{H_3O^+} \underset{\text{aldehyde}}{R-CH_2-CHO}$$

e) DIBAL-H reduction

i) alkane nitrile

$$R-CH_2-CN \xrightarrow[ii)\ H_2O]{i)\ DIBAL-H} R-CH_2-CHO + NH_3$$

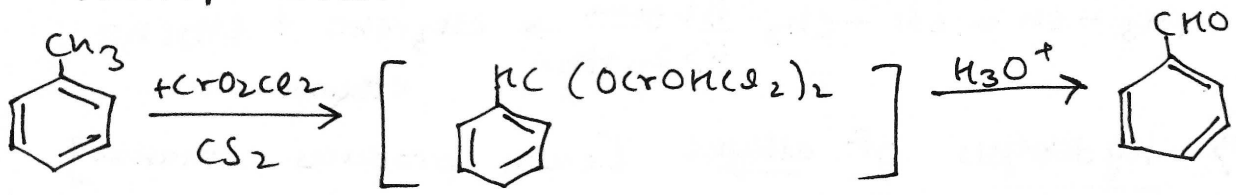
ii) ester...

$$R-CH_2-COO-R' \xrightarrow[ii)\ H_2O]{i)\ DIBAL-H} \underset{\displaystyle R}{\underset{|}{CH_2}}-CHO$$

$$CH_3-(CH_2)_9-COO-C_2H_5 \xrightarrow[ii)\ H_2O]{i)\ DIBAL-H} CH_3-(CH_2)_9-CHO$$

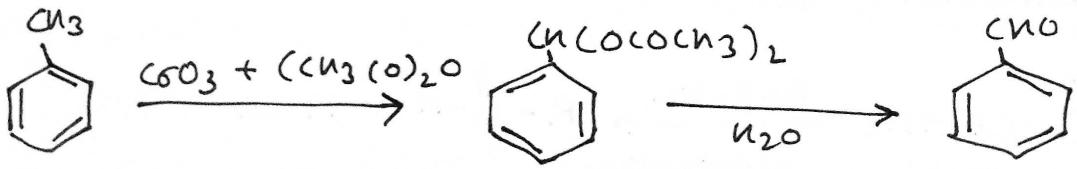
f) Etards reaction [Benzaldehyde production]

i) Chromyl chloride CrO_2Cl_2 then H_3O^+

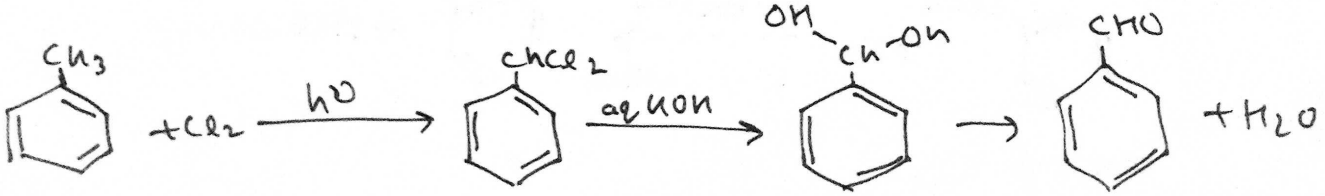


brown coloured complex

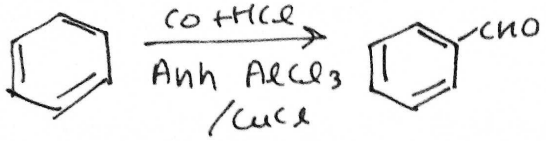
ii) Chromic oxide



g) Chlorine substitution followed by hydrolysis

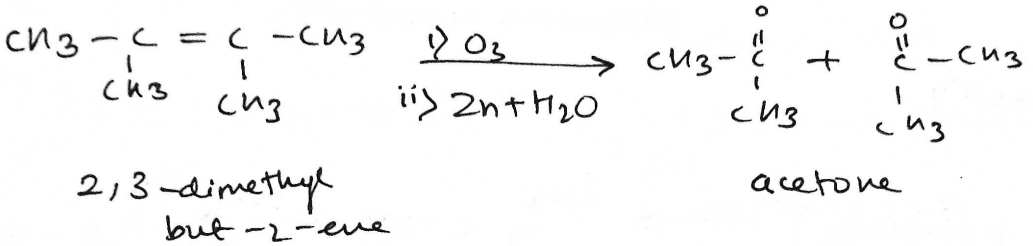


h) Gatterman Koch reaction



3o) Ketone Production

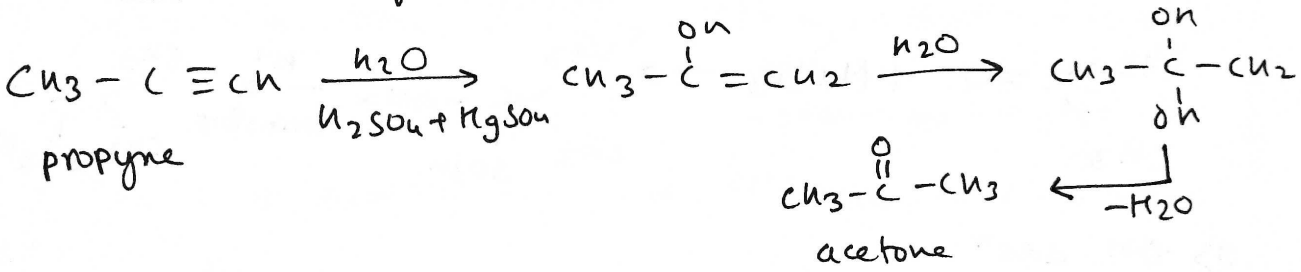
a) Ozonolysis of alkenes [2° alkenes]



2,3-dimethyl but-2-ene

acetone

b) hydrolysis of alkyne



propyne

acetone

c) from acid chloride [RMgX + CdCl2]

grignards reagent

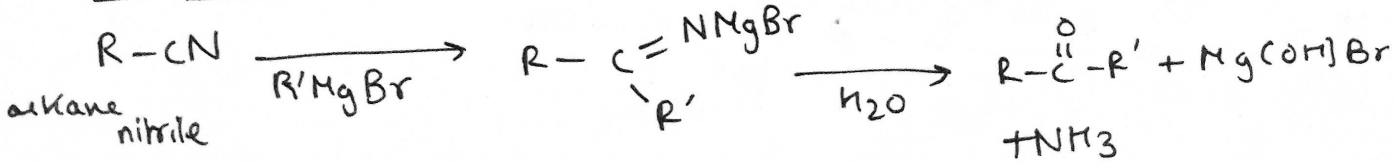
dialkyl cadmium

acid chloride

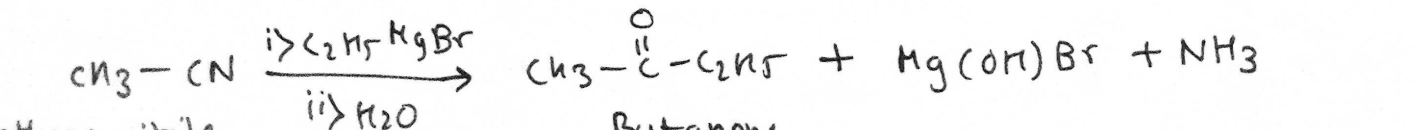
ketone

Not preffered as C=O reacts with RMgX to give 3° alc

d) from alkane nitrile



alkane nitrile

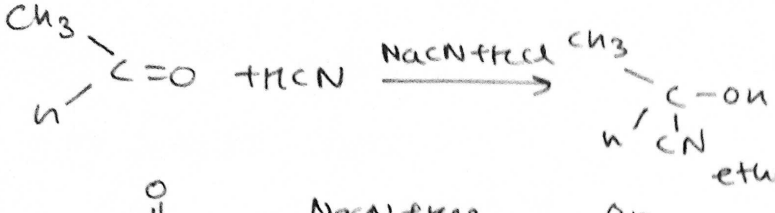


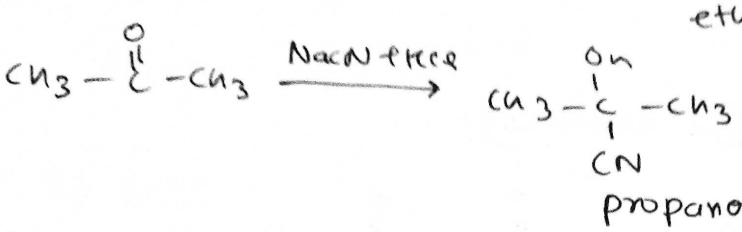
ethane nitrile

Butanone

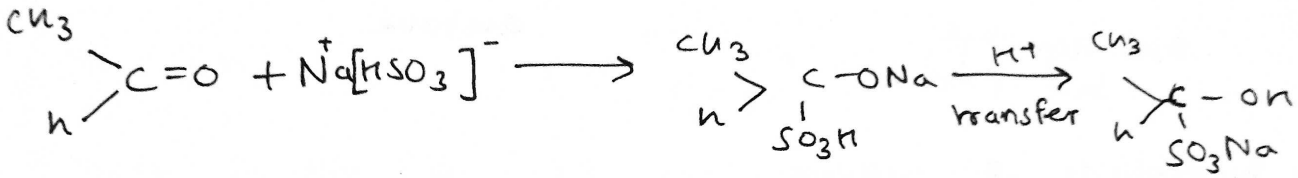
3) Nucleophilic addⁿ rectⁿ

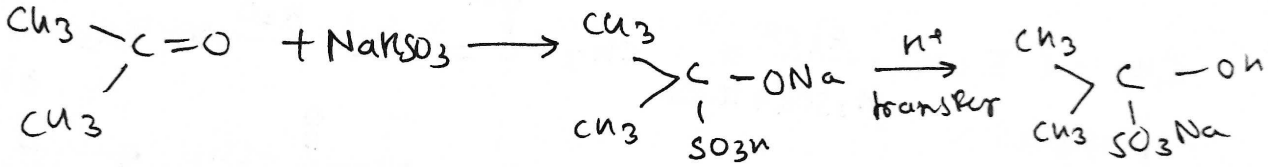
1) HCN addⁿ :





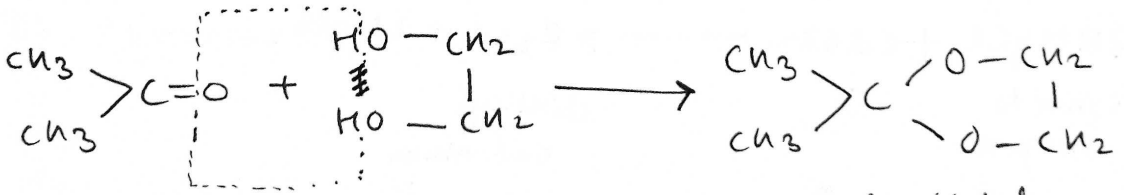
2) $NaHSO_3$ addⁿ :



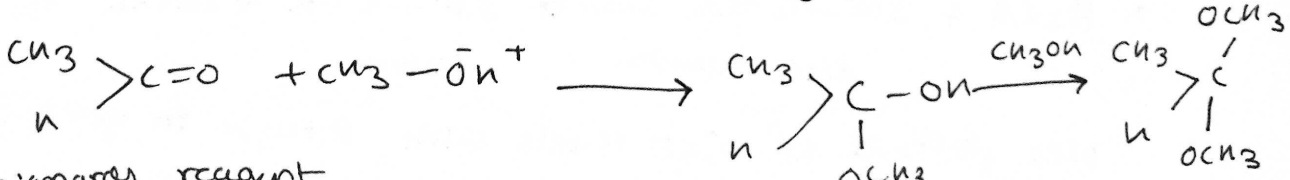


3) -OH addⁿ

* Ketones wont react with monohydric alcohol rather with dihydric alcohol

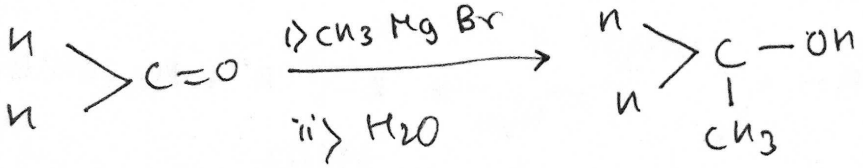


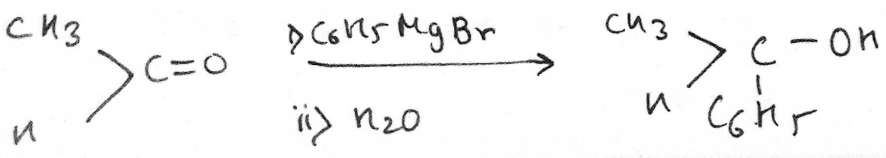
cyclic ketal

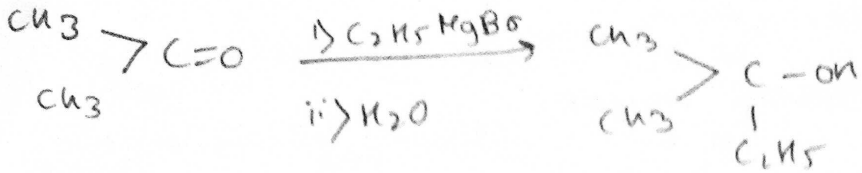


hemiacetal → acetal

4) Grignards reagent

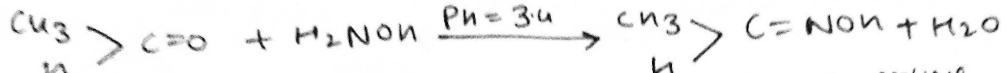


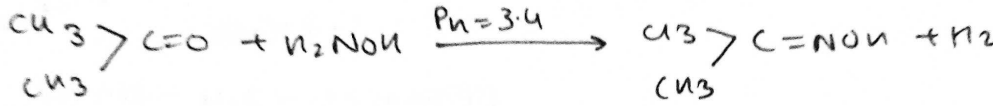




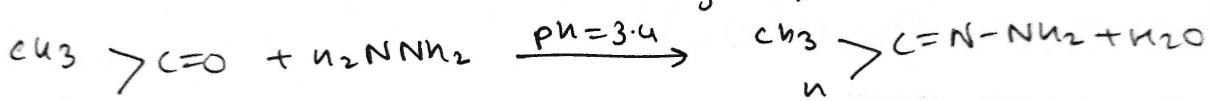
3) Nucleophilic addn followed by elimination of water

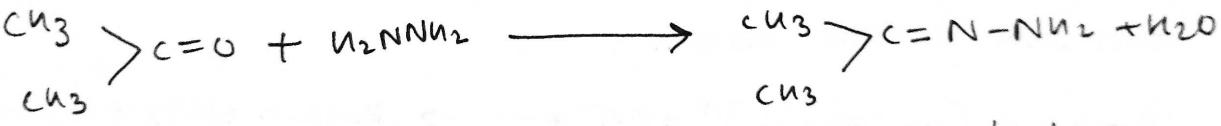
i) hydroxy amine $[NH_3 \xrightarrow[+OH]{-H} H_2N-OH]$ hydroxyl amine



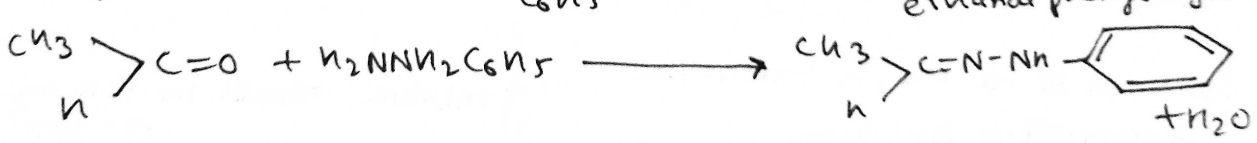


ii) hydrazine $[NH_3 \xrightarrow[+NH_2]{-H} H_2N-NH_2]$ hydrazine

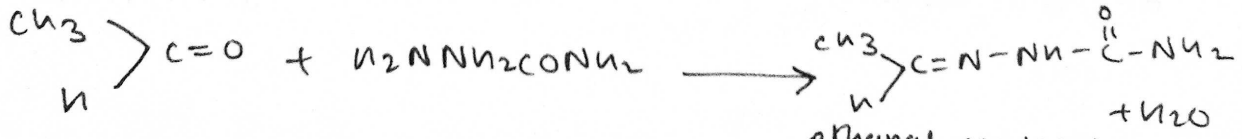


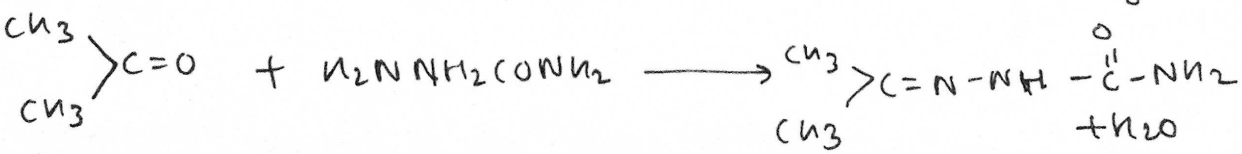


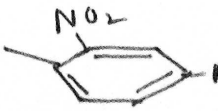
iii) phenyl hydrazine $[H_2NNH_2 \xrightarrow[C_6H_5]{-H} H_2NNHC_6H_5]$



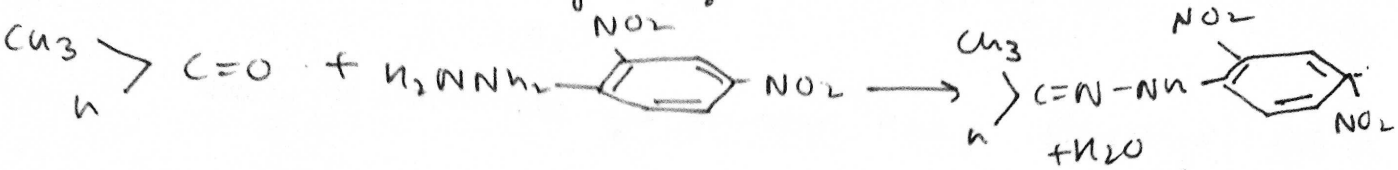
iv) Semicarbazide $[H_2NNH_2 \xrightarrow[+CONH_2]{-H} H_2NNHCONH_2]$



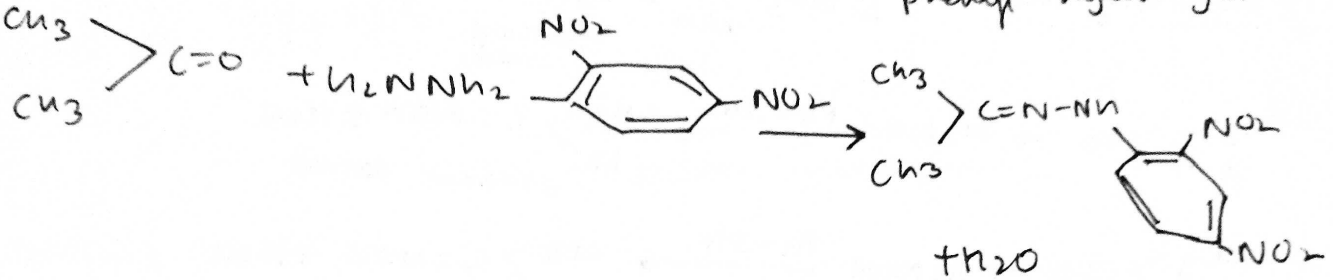


v) 2,4-DNP $[H_2N-NH_2$  $]$

Brady's reagent



ethanal - 2,4 - dinitro phenyl hydrazone



propanone - 2,4 - dinitro phenyl hydrazone

33) Oxidation of aldehyde / ketone

i) Tollens reagent $[Ag(NH_3)_2]^+$

Ketone doesn't react

aldehyde gives COOH, terminal alkyne ($\equiv CH$), formic acid do react with Tollens reagent

$$R-CHO + [Ag(NH_3)_2]^+ + OH^- \longrightarrow R-COOH + NH_3 + H_2O + Ag$$

ii) Oxidation with Fehling reagent

Solution B → Na, K tartarate

Solution A → Aq $CuSO_4$

3 mixture results in Fehling reagent

Ketone doesn't react

aldehyde react, not benzaldehyde, also terminal alkyne formic acid

$$R-CHO + Cu(OH)_2 + OH^- \longrightarrow R-COO^- + \underset{\text{reddish brown}}{Cu_2O} + H_2O$$

Reduction reaction <34

i) Clemmensons Redn

$CH_3-CHO \xrightarrow[HCl]{Zn\cdot Hg} CH_3-CH_3$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[HCl]{Zn\cdot Hg} CH_3-CH_2-CH_3$

ii) Wolff - Kishner

$>C=O + H_2N\,NH_2 \longrightarrow >C=N-NH_2 \xrightarrow[KOH/]{glycol} >CH_2$

$CH_3-CHO \xrightarrow[i)KOH/glycol]{H_2NNH_2} CH_3-CH_3$

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[i)KOH/glycol]{H_2NNH_2} CH_3-CH_2-CH_3$

35) Iodoform test (haloform reaction)

→ aldehydes with $(CH_3-\overset{O}{\overset{\|}{C}})$ group & with $(CH_3-\underset{OH}{CH})$ group

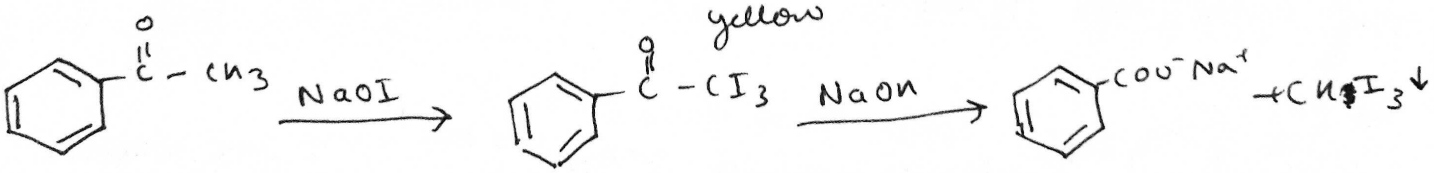
→ C=C is ~~tra~~ unaffected

→ $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \xrightarrow[NaOH+HI]{NaOI} ~~CH_3~~\ CI_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

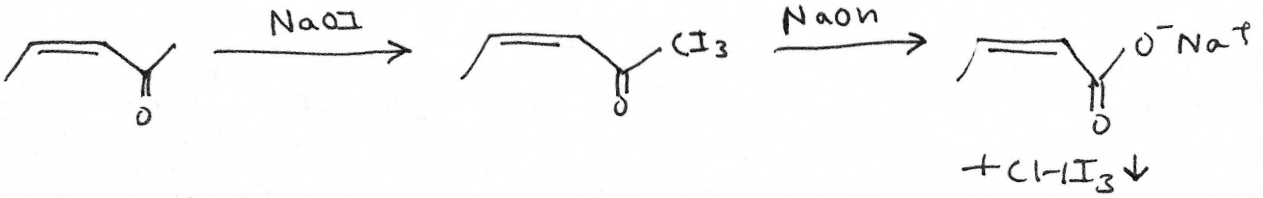
$\downarrow NaOH$

$CHI_3\downarrow + CH_3CH_2-COO^-Na$

iodoform yellow



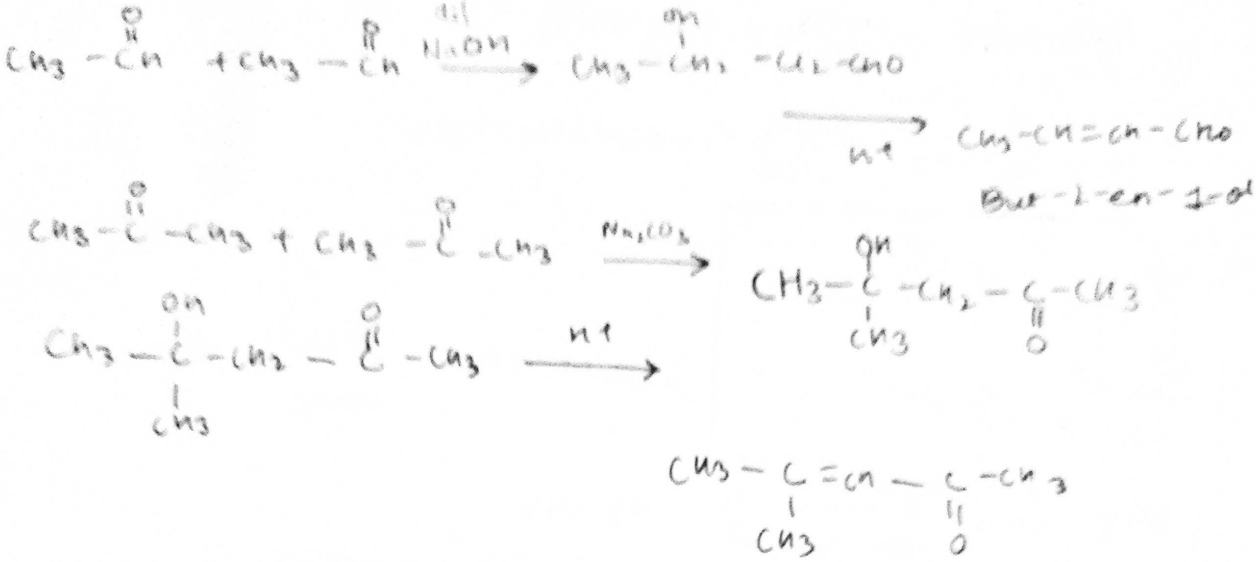
$CH_3-\underset{OH}{CH}-CH_2-CH_3 \xrightarrow{NaOI} CI_3-\underset{OH}{CH}-CH_2-CH_3 \xrightarrow{NaOH} CHI_3 + CH_3-CH_2-COO^-Na^+$



* only aldehyde to respond is ~~ace~~ acetaldehyde (ethanal)

36 i) Aldol condensation

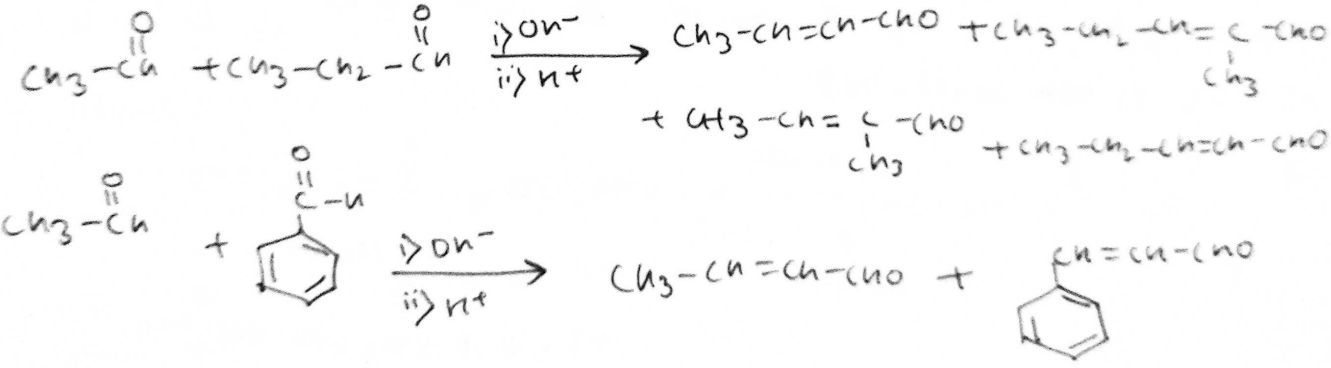
* Aldehyde / ketone should have minimum 1 α-hydrogen



ii) Cross-Aldol condensation

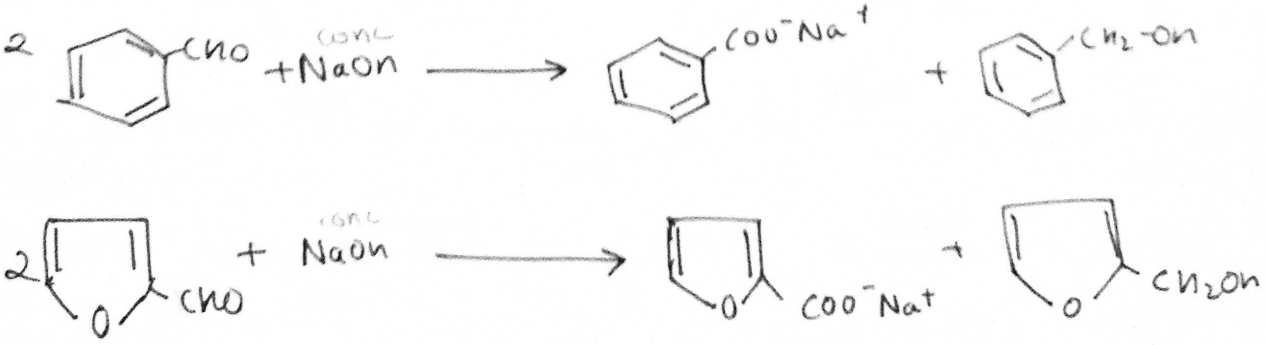
4 methyl pent-3-en-2-one

* -CHO with one α-hydrogen and other not having α-hydrogen yields 2 products



37 Cannizzaros reaction

→



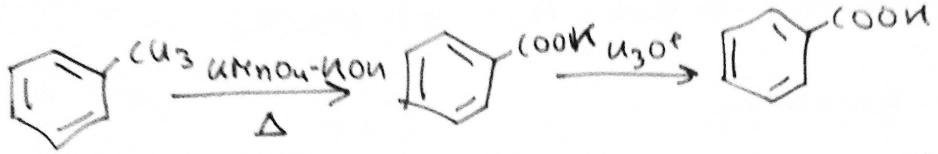
* those -CHO not having α-hydrogen undergo. This is a disproportional reaction where 1 gets oxidised other gets reduced

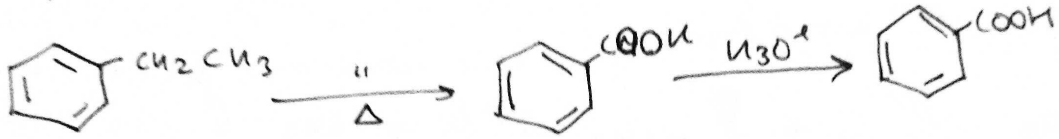
36) Production of acid

1) from 1° alc & aldehydes

$RCH_2OH \xrightarrow[2)\ H_3O^+]{\text{Dalkaline } KMnO_4} RCOOH$

2) from alkylbenzenes

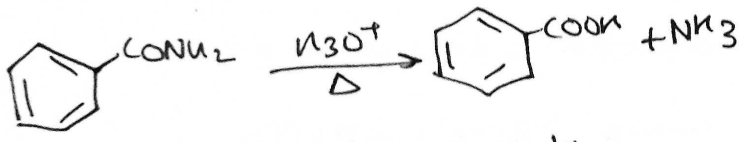




3) From nitriles and amides

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

$R-CONH_2 \xrightarrow[\Delta]{H_3O^+} CH_3COOH + NH_3$



4) from grignards reagents

$R-MgX + C(=O)=O \xrightarrow{\text{dryether}} R-\overset{O}{\overset{\|}{C}}-O^-Mg^+X \xrightarrow{H_3O^+} RCOOH$

5) from acyl halides and anhydrides

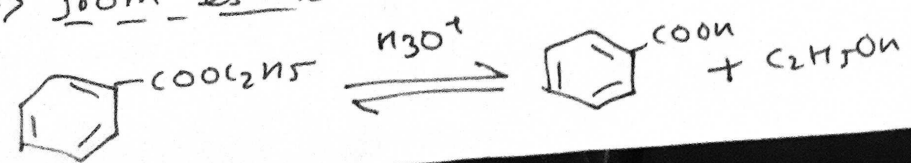
$R-COCl \xrightarrow{H_2O} RCOOH + Cl^-$

$R-COCl \xrightarrow{OH^-/H_2O} RCOO^- + Cl^- \xrightarrow{H_3O^+} RCOOH$

$(C_6H_5CO)_2O \xrightarrow{H_2O} 2C_6H_5COOH$

$C_6H_5COOCOCH_3 \xrightarrow{H_2O} C_6H_5COOH + CH_3COOH$

6) from esters



$CH_3CH_2CH_2COOC_2H_5 \underset{NaOH}{\rightleftharpoons} CH_3CH_2CH_2COONa + C_2H_5OH$

$\downarrow H_3O^+$

$CH_3CH_2CH_2COOH$

39) Acidity of acids (R-COOH)

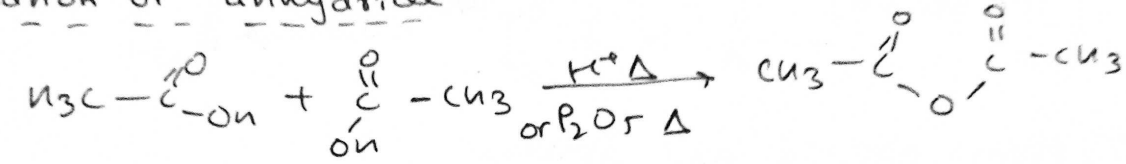
$RCOOH + Na \longrightarrow RCOO^-Na^+ + \frac{1}{2}H_2$

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

$RCOOH + NaHCO_3 \longrightarrow RCOO^-Na^+ + H_2O + CO_2$

40) C-OH bond breaking

i) formation of anhydride



ii) Esterification

$R-COOH + R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} RCOOR' + H_2O$

iii) Reactions with PCl_5, PCl_3 and $SOCl_2$

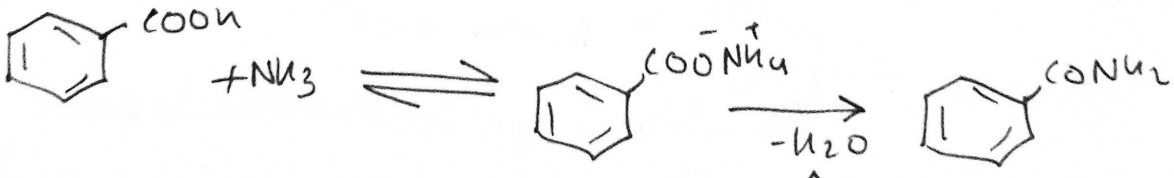
$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

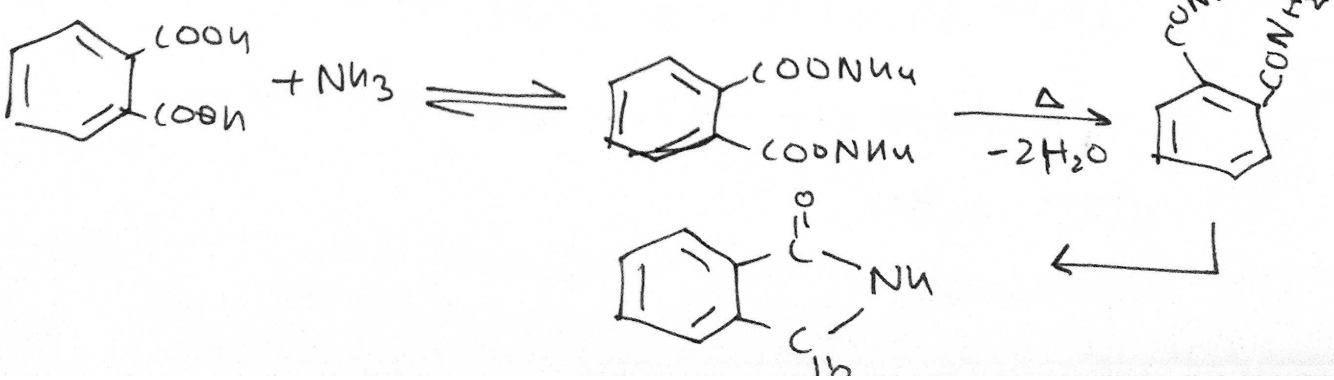
$R\,COOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3$

$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$

iv) Ammonia

$CH_3COOH + NH_3 \rightleftharpoons CH_3COONH_4 \xrightarrow[-H_2O]{\Delta} CH_3CONH_2$





4) Redⁿ, decarboxylation & halogenation

i) $RCOOH \xrightarrow[ii)\ H_3O^+]{i)\ B_2H_6} R-CH_2-OH$

ii) $RCOONa \xrightarrow[\Delta]{NaOH+CaO} RH + Na_2CO_3$

iii) [Hell Volhard & Zelinsky reaction]

$R-CH_2-COOH \xrightarrow[ii)\ H_2O]{i)\ X_2 / \text{Red phosphorus}} R-\underset{\underset{X}{|}}{CH}-COOH$

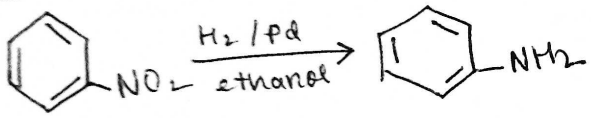
$X = Cl, Br$

* COOH, CHO are meta directing

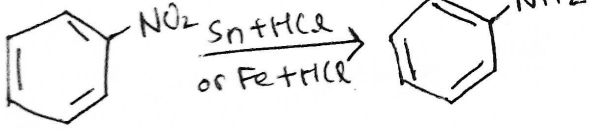
42) Amine production

I) NO_2 redn

i)



ii)



II) Ammonolysis of alkyl halides

i) $RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4\overset{+}{N}X^-$

ii) $NH_3 + R-X \longrightarrow R-\overset{+}{N}H_3X^-$

iii) $R-\overset{+}{N}H_3X^- + NaOH \longrightarrow R-NH_2 + H_2O + \overset{+}{N}a\ X^-$

ii) & iii) → 1° amine produced

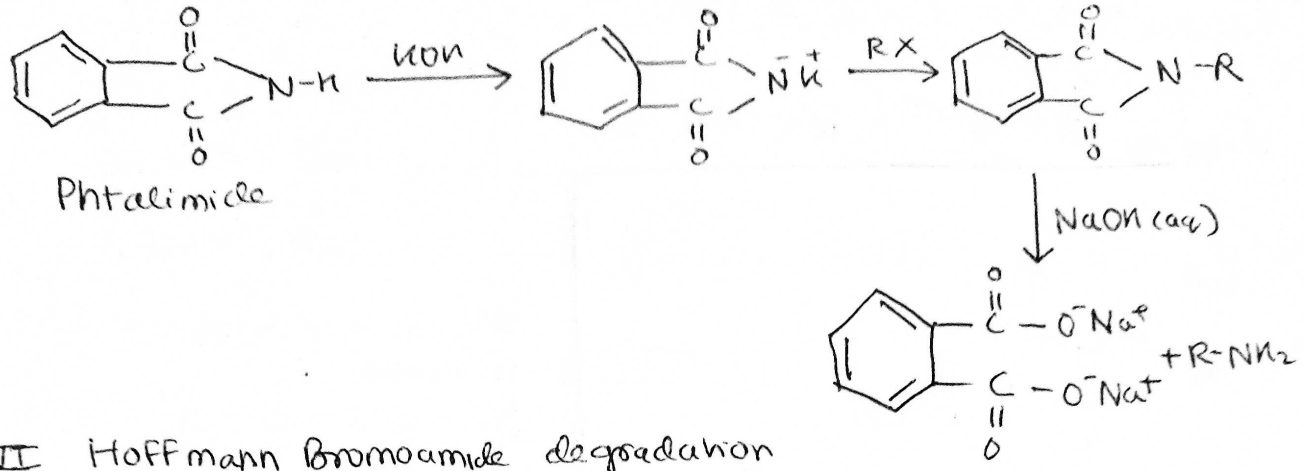
III) Redⁿ of Nitriles

$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5OH]{H_2/Ni} R-CH_2-NH_2$

IV Redⁿ of amides

$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[ii)\ H_2O]{i)\ LiAlH_4} R-CH_2-NH_2$

V GABRIEL PHTALIMIDE



VI Hoffmann Bromoamide degradation

$$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

4) CHEMICAL REACTIONS OF AMINES :

I) ACYLATION

$$C_2H_5-\underset{\underset{C_2H_5}{|}}{N}-H + Cl-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Base} HCl + C_2H_5-\underset{\underset{C_2H_5}{|}}{N}-\overset{O}{\overset{\|}{C}}-CH_3$$

$$C_6H_5-\underset{\underset{H}{|}}{\ddot{N}}-H + CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow C_6H_5-\underset{\underset{H}{|}}{\ddot{N}}-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3COOH$$

$$CH_3NH_2 + C_6H_5COCl \longrightarrow CH_3NHCOC_6H_5 + HCl$$

II Carbylamine reaction

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$$

only 1° cyclic & straight chain show this test

III Nitrous acid

a) $R-NH_2 + HNO_2 \xrightarrow{NaNO_2+HCl} R-\overset{+}{N}_2Cl^- \xrightarrow{H_2O} R-OH + N_2 + HCl$

aliphatic

b) $C_6H_5-NH_2 \xrightarrow[273-278K]{NaNO_2 + HCl} C_6H_5-\overset{+}{N}_2Cl^- + NaCl + 2H_2O$

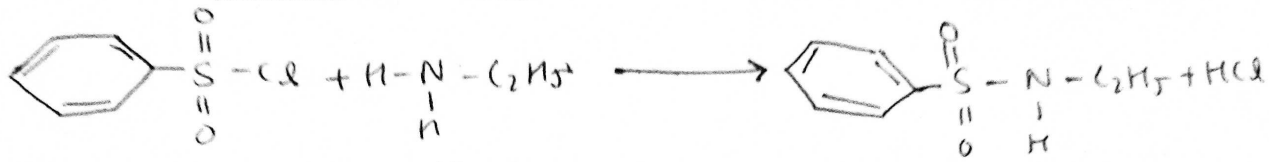
aniline

IV) acyl sulponyl chloride

Benzene sulphonyl chloride ($C_6H_5SO_2Cl$)

HINSBERG TEST

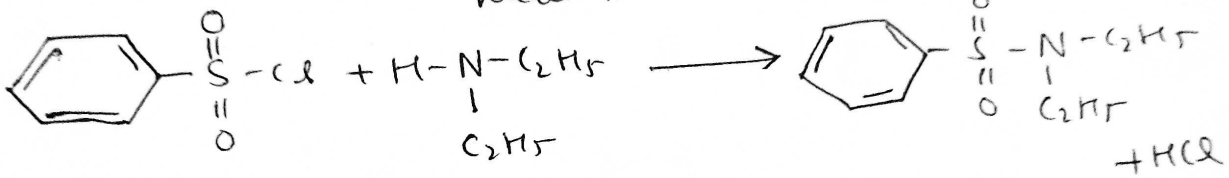
a)



(1°) 1° amine

soluble in basic medium → N-ethyl benzene sulphonamide

b)



(2°)

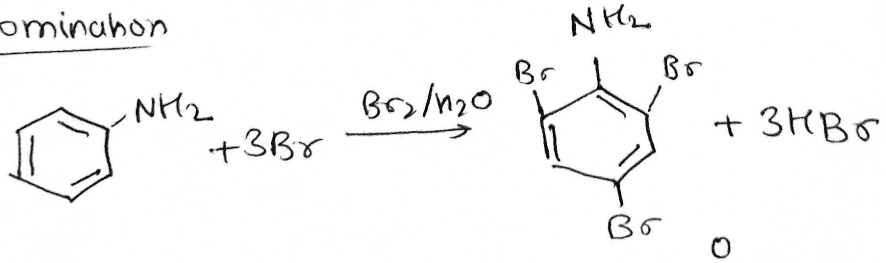
not soluble in basic medium → N,N-diethyl benzene sulphonamide

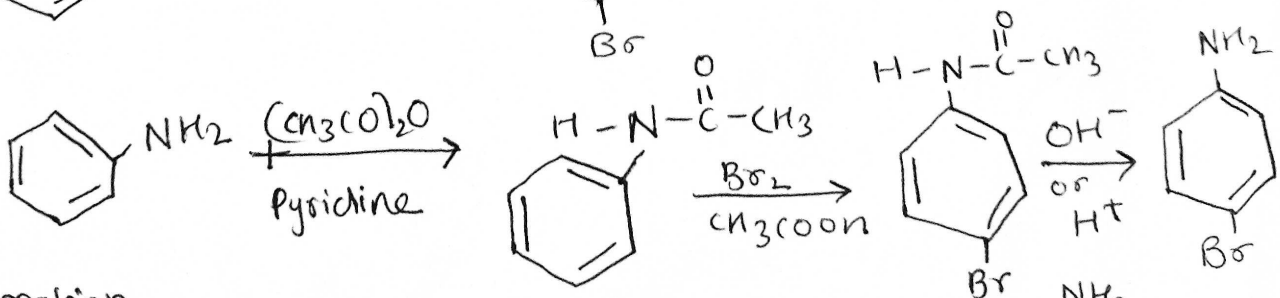
c)

3° amines dont give

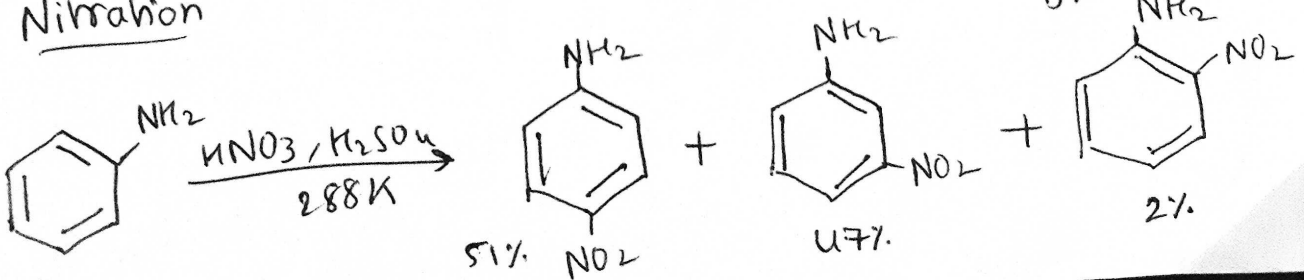
V) Electrophilic substitution

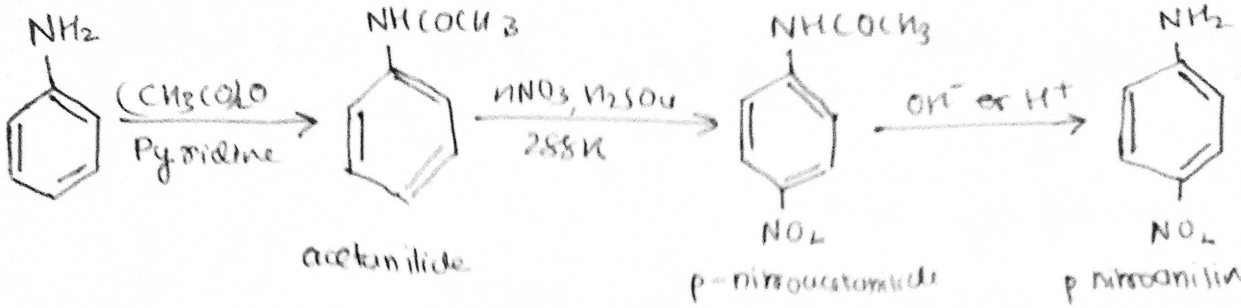
i) Bromination





ii) Nitration



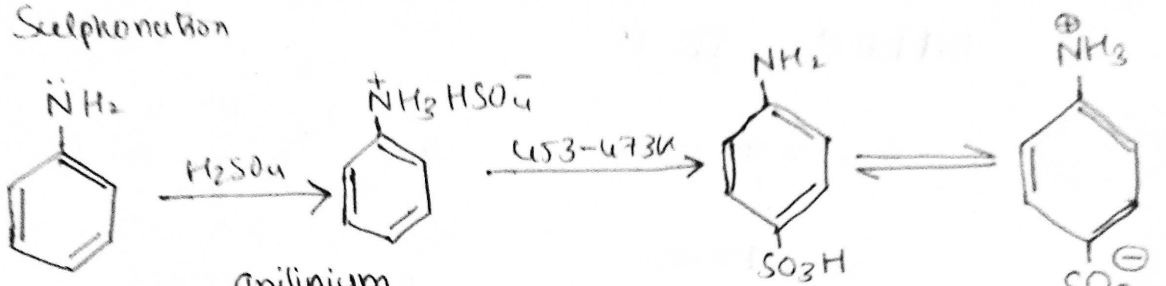


acetanilide

p-nitroacetanilide

p nitroaniline

iii) Sulphonation

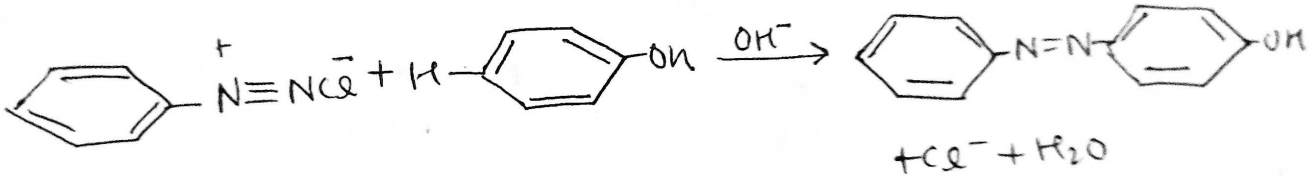


anilinium hydrogensulphate

sulphanilic acid

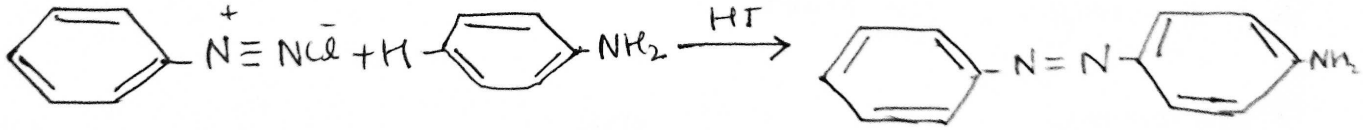
zwitter ion

4) Coupling reaction of diazo group



+Cl⁻ + H2O

p-hydroxyazobenzene (orange dye)



+Cl⁻ + H2O

p-aminoazo benzene (yellow dye)

5) Azonium dichloride ~~or~~ reactions