CONTENTS

1. ALKANES

Catalytic Hydrogenation — Formation

Free Radical substitution

2. ALKENES

Elimination — Formation

Oxidation

Reduction

Electrophilic Addition

1) FRS	4) NS
2) EA	5) NA
3) ES	

3. ARENES

A) Benzene

Electrophilic substitution

B) Methylbenzene

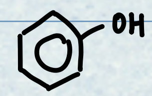
Free radical substitution

Oxidation

Electrophilic substitution

$K_2Cr_2O_7$: alcohols & aldehydes

$KMnO_4$: C=C ; side chain [O] for



4. HALOGEN DERIVATIVES

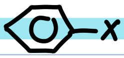
A) H-X

Nucleophilic substitution
Electrophilic addition
free radical substitution (alkanes)
electrophilic substitution (benzene)
] formation

Nucleophilic substitution (SN)

- Hydrolysis
- Step-up reaction
- Acid hydrolysis
- Basic hydrolysis
- Reduction
-

Elimination

B) 

Electrophillic substitution
- Nitration
- Halogenation
- Friedel- Crafts Alkylation

5. HYDROXYL COMPOUNDS

A) Alcohols

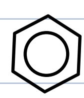
Electrophillic addition
Nucleophillic Substitution
Reduction of Aldehydes, carboxylic acids
Reduction of ketones
Hydrolysis of esters
] formation

Combustion
Redox
Condensation
] RO-H

Nucleophillic substitution
Elimination
Oxidation
Tri-iodomethane test
] R-OH

B) Phenol

Redox
Neutralisation
Condensation
] OH

Electrophillic substitution
- Nitration
- Halogenation
] 

6. CARBONYL COMPOUNDS

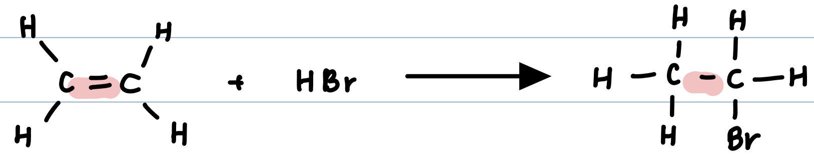
- alcohol oxidation (1° → aldehyde, 2° → ketone)] formation
- oxidative cleavage of alkenes] formation
- nucleophillic addition
- Acid hydrolysis] cyanohydrin reactions
- Basic hydrolysis] cyanohydrin reactions
- Reduction] cyanohydrin reactions
- Condensation (2,4-DNPH)
- Oxidation (Aldehydes only)
  - inorganic oxidising agents
  - Tollen's reagent
  - fehling's solution
- Reduction (1° ← aldehyde, 2° ← ketone)
- Tri-iodomethane Test

7. CARBOXYLIC ACID & DERIVATIVES

- oxidation] formation
- Hydrolysis] formation

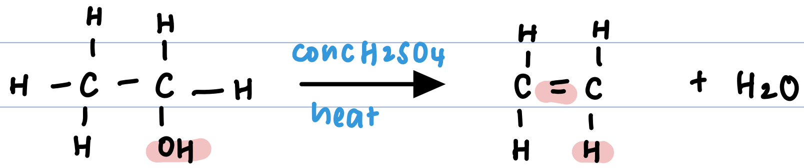
Reactions

Addition



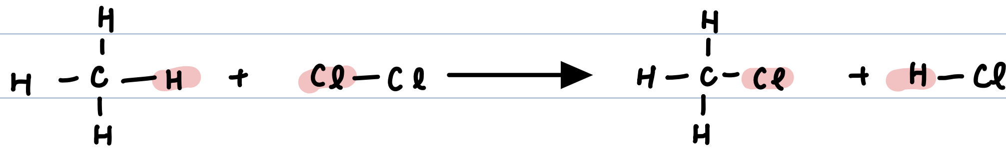
alkene
break π bond
unsat → sat

Elimination

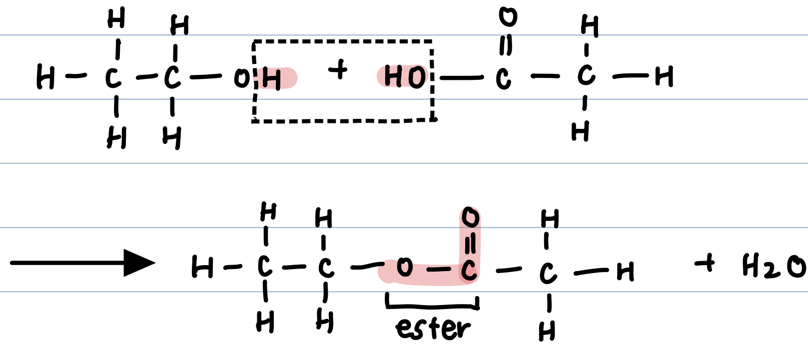


(alcohol)
π bond formed

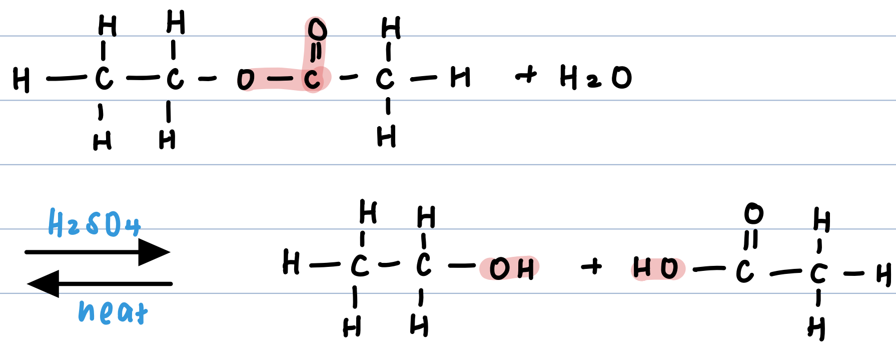
Substitution



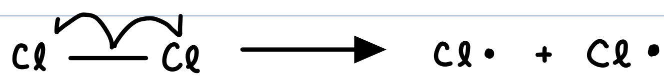
Condensation



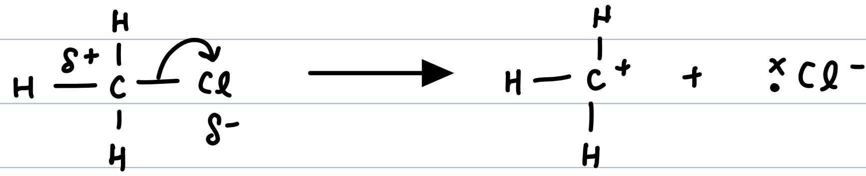
Hydrolysis



Homolytic Bond Fission



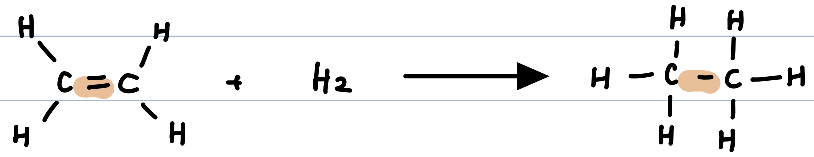
Heterolytic Bond Fission



ALKANES

reduc^n of alkene

Catalytic hydrogenation



formation

H₂ gas, Ni catalyst, heat

H_2 gas, Pt or Pd catalyst, room temp

Free radical substitution

1) Initiation

$Cl-Cl \xrightarrow[\text{heat}]{\text{UV light}} Cl\bullet + Cl\bullet$

greenish-yellow Cl_2 decolourised
reddish-brown Br_2 decolourised

limited $Cl_2(g)$ or $Br_2(l)$
UV light or heat

2) Propagation

$Cl\bullet + CH_4 \longrightarrow \bullet CH_3 + HCl$

$\bullet CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\bullet$

3) Termination

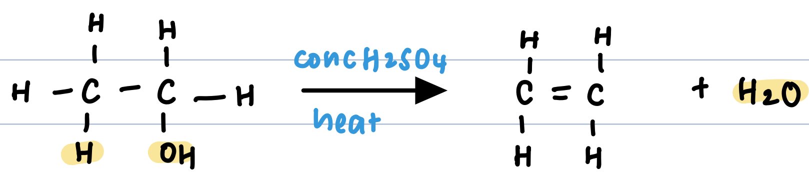
$Cl\bullet + Cl\bullet \longrightarrow Cl_2$

$Cl\bullet + \bullet CH_3 \longrightarrow CH_3Cl$

$\bullet CH_3 + \bullet CH_3 \longrightarrow CH_3CH_3$

ALKENES

Elimination

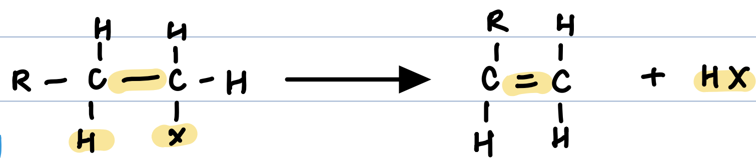


xs conc H_2SO_4

170 °C

adjacent C atoms

Elimination



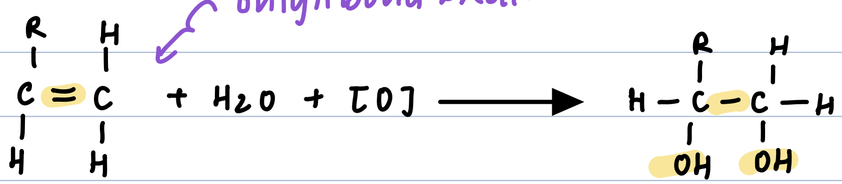
ethanolic NaOH

heat

formation (alcohol) / (halogenoalkane)

Mild oxidation

only π bond break



diol

$KMnO_4(aq)$

$NaOH(aq)$ / $H_2SO_4(aq)$

cold

acidic: purple $KMnO_4$ decolourised

alkaline: purple $KMnO_4$ decolourised, brown ppt MnO_2 formed

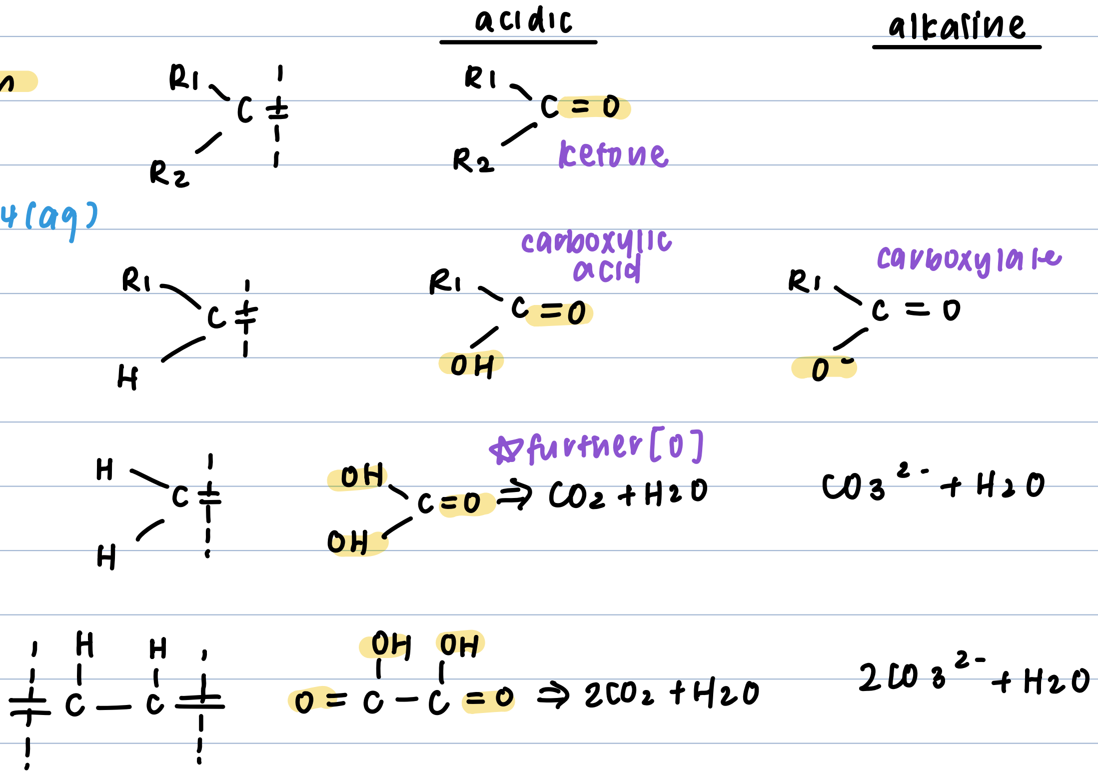
BOTH

strong oxidation

$KMnO_4$ (aq)

NaOH (aq) / H_2SO_4 (aq)

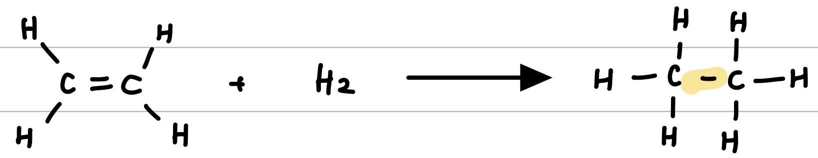
☆ Heat



Reduction

H_2 gas, Ni catalyst, heat

H_2 gas, Pt or Pd catalyst, room temp

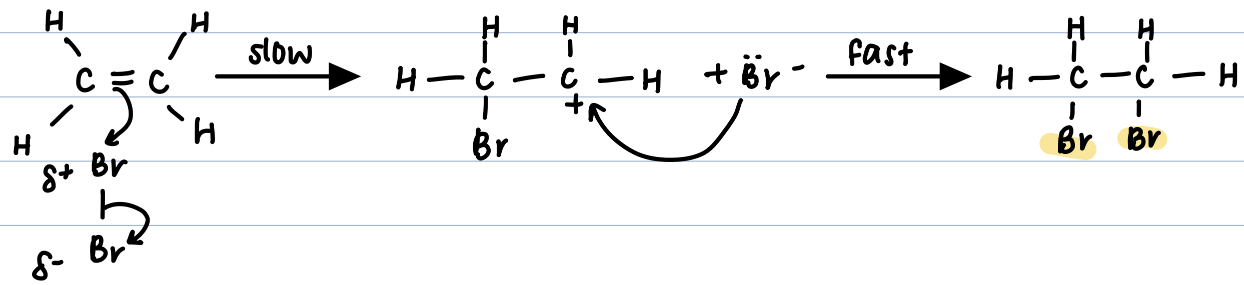


☆ to prevent free-radical sub

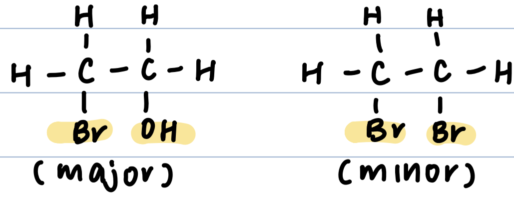
Br_2 in CCl_4, in the dark

orange-red bromine decolourised

Electrophilic addition

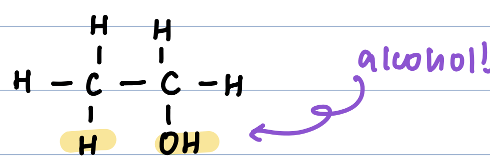


Br_2(aq) + H_2O (large xs)



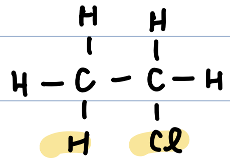
conc H_2SO_4, 0°C (or cold)

followed by boiling w H_2O or steam



H_2O and H_3PO_4 catalyst, 300°C, 65 atm – industrial method

δ^+ δ^-
HCl(g)



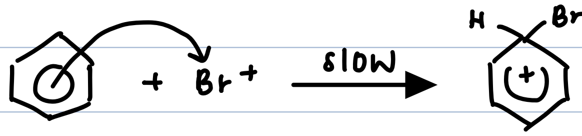
ARENE

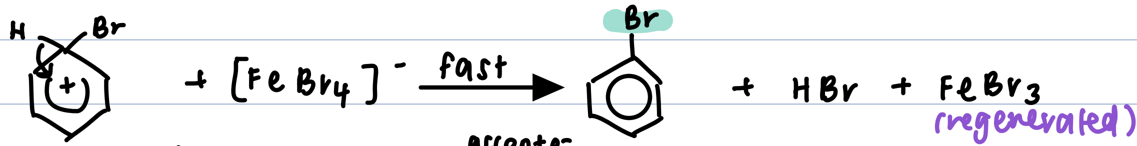
(benzene) ✗ oxidation ✗ Addition (harsh)

Electrophilic substitution

A) Halogenation

$Br_2 + FeBr_3 \longrightarrow [FeBr_4]^- + Br^+$ (electrophile)





(prevent partial hydrolysis in water) lewis acid catalyst

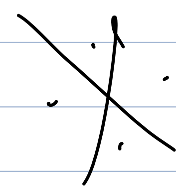
Br_2, anhydrous $FeBr_3$ or $AlBr_3$ or Fe, room temp

reddish-brown Br_2 decolourised & white fumes of HBr observed

B) Nitration

$HNO_3 + 2H_2SO_4 \longrightarrow H_3O^+ + 2HSO_4^- + NO_2^+$

∴ same



conc HNO_3, conc H_2SO_4, 55 °C

yellow liquid

C) Friedel-Crafts Alkylation

$CH_3Br + AlBr_3 \longrightarrow [AlBr_4]^- + CH_3^+$

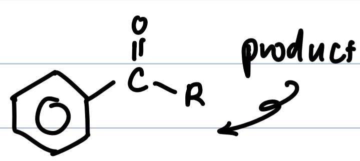
∴ same

RX, anhydrous AlX_3 or FeX_3 (X = Cl / Br), room temp

D) Friedel-Crafts Acylation

$R-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \longrightarrow [AlCl_4]^- + R-\overset{O}{\overset{\|}{C}}^+$

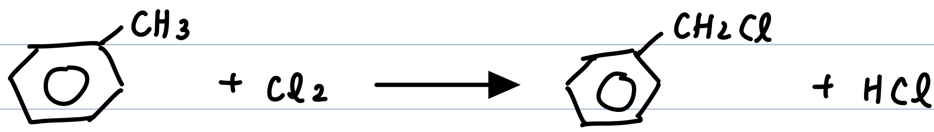
∴ same



$R-\overset{O}{\overset{\|}{C}}-X$, anhydrous AlX_3 or FeX_3, room temp

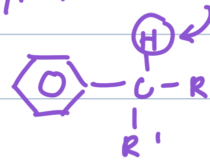
(Methylbenzene) - side chain reactions

Free radical substitution (like alkanes)



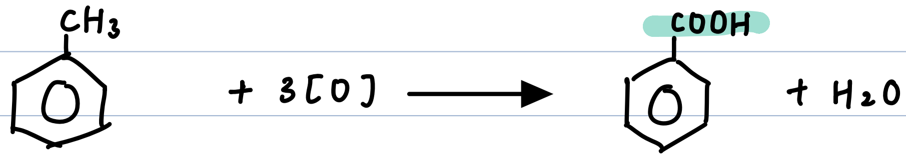
limited $Cl_2(g)$ or $Br_2(l)$
UV light or heat

☆ benzylic H must be present



Oxidation (like alkenes)

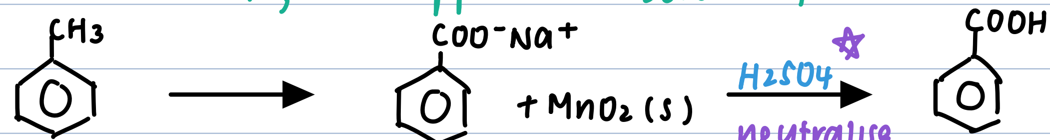
acidic :



$KMnO_4(aq)$, $H_2SO_4(aq)$, Heat

☆ purple $KMnO_4$ decolourised, white ppt of benzoic acid

alkaline :



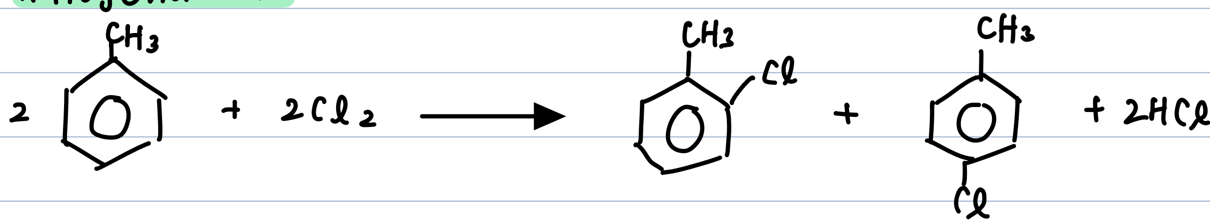
neutralise by dilute acid!

$KMnO_4(aq)$, $NaOH(aq)$, Heat

purple $KMnO_4$ decolourised, brown ppt of MnO_2

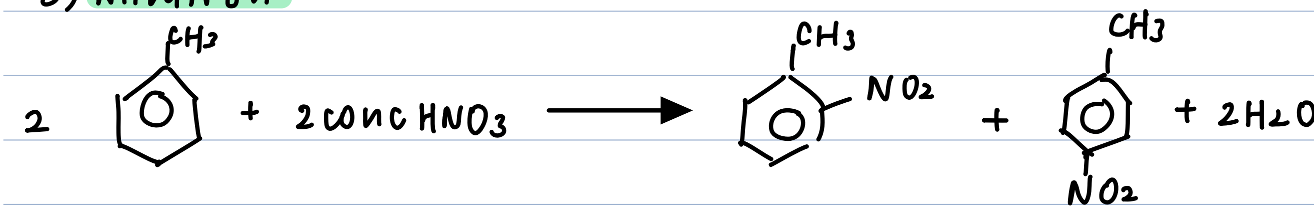
Electrophilic substitution (like benzene)

A) Halogenation

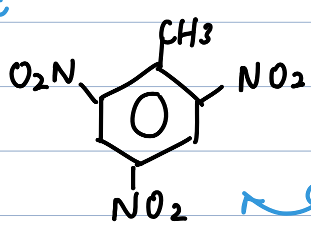


anhydrous AlX_3 or FeX_3, room temp, dark

B) Nitration



conc HNO_3, conc H_2SO_4, 30°c



higher temp

HALOGEN DERIVATIVES H-X , 

Nucleophilic substitution of Alcohols

$3R-OH + PX_3 \longrightarrow 3RX + H_3PO_3$ — PX_3, heat

☆ cannot PBr_5/PI_5 — not stable.

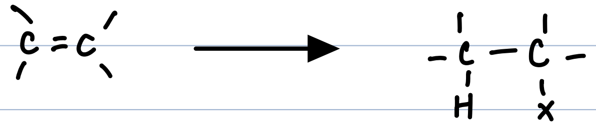
$R-OH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$ — PCl_5 white fumes

$R-OH + SOCl_2 \longrightarrow RCl + SO_{2(g)} + HCl_{(g)}$ — $SOCl_2$ white fumes

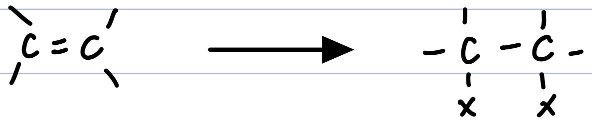
will escape to atmosphere : preferred!

$R-OH + HX \longrightarrow RCl + H_2O$ — HX, heat

Electrophilic addition of alkenes (in alkenes)

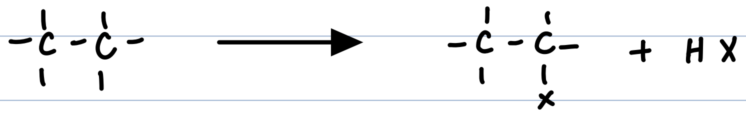


HX



X_2 in CCl_4, in the dark

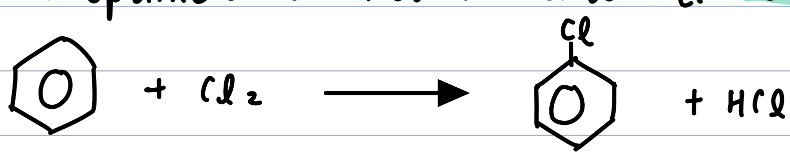
Free radical substitution of alkanes (in alkanes)



$X_{2(g)}$ UV light / Heat

☆ not recommended, ↓ yield.

Electrophilic substitution in benzene (in benzene)

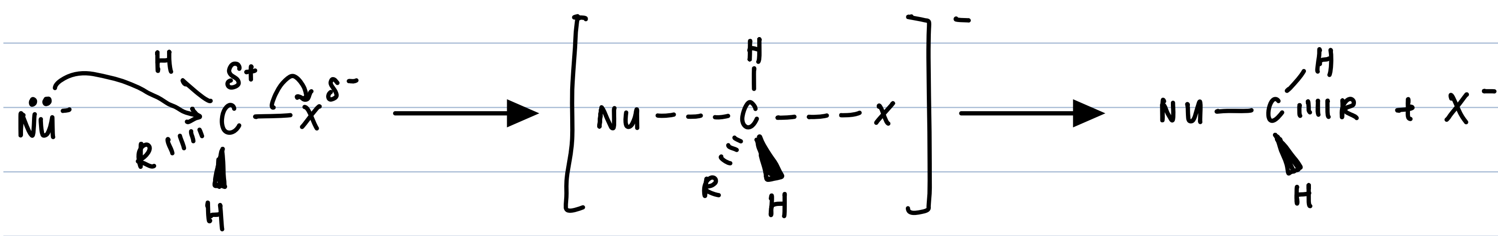


$AlCl_3$ (Lewis acid catalyst)

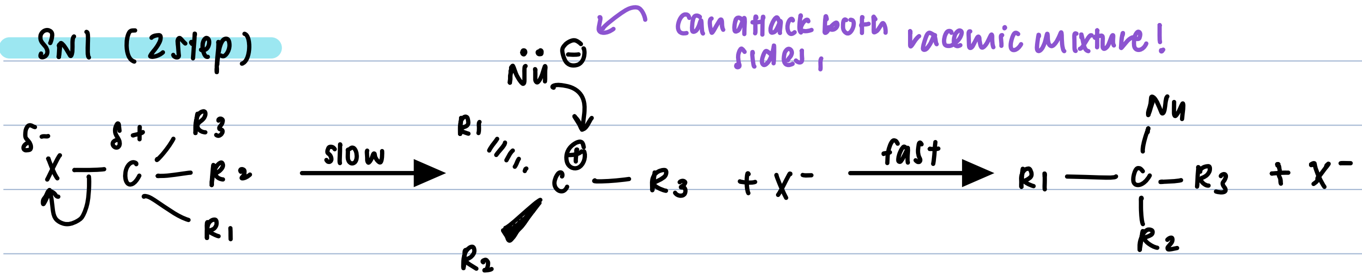
formation

Nucleophilic substitution (SN)

SN 2 (1 step)



SN1 (2 step)



Types of nucleophilic substitution

A) Hydrolysis to form alcohols

$R-X + OH^- (aq) \rightarrow R-OH + X^-$

$NaOH (aq)$ or $KOH (aq)$, heat OH^- is the Nu

B) Step-up reaction to form nitrile (H-C≡N)

$R-X + CN^- \rightarrow R-CN + X^-$

ethanolic KCN or ethanolic NaCN, heat CN^- is the Nu

C) Acid hydrolysis of nitrile to form carboxylic acids (COOH)

$R-CN + H^+ + 2H_2O \rightarrow RCOOH + NH_4^+$

$H_2SO_4 (aq)$, heat

D) Basic hydrolysis of nitriles to form carboxylate salts (COO^-)

$R-CN + OH^- + H_2O \rightarrow RCOO^- + NH_3$

$NaOH (aq)$, heat

E) reduction of nitriles to form primary amines (CH_2NH_2)

$R-CN + 4[H] \rightarrow R-CH_2NH_2$

$LiAlH_4$ in dry ether

$R-CN + 2H_2 \rightarrow R-CH_2NH_2$

$H_2 (g)$, Ni catalyst, heat

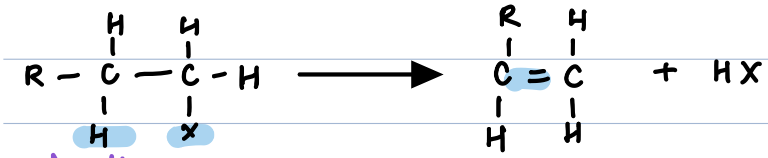
F) ________________ to form amines (NH_2)

$R-X + NH_3 \rightarrow RNH_2 + HX$

excess conc NH_3, heat NH_3 is the Nu

↳ to prevent polyalkylation

Elimination to form alkenes

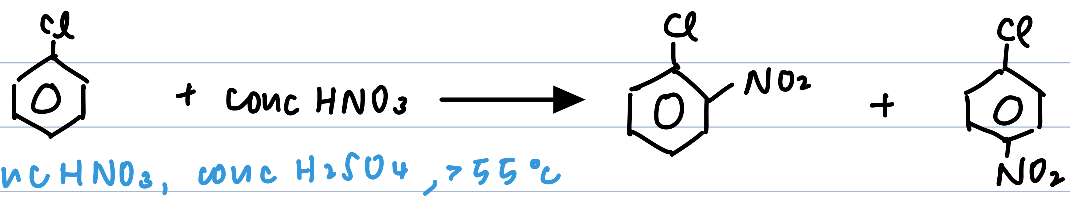


* adjacent carbon atoms

ethanolic NaOH, heat

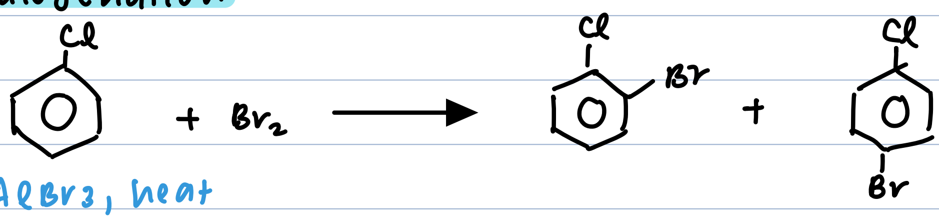
Electrophilic substitution of halogenoarene (in arenes)

Nitration



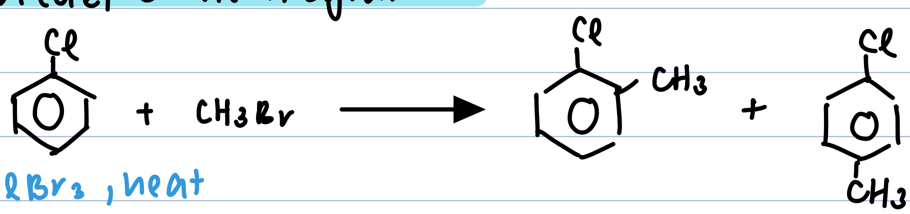
conc HNO_3, conc H_2SO_4, >55 °C

Halogenation



$AlBr_3$, heat

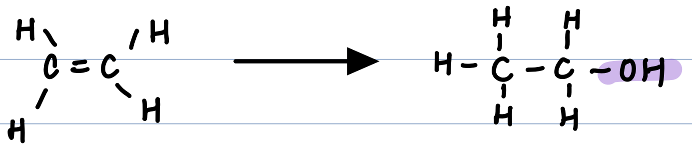
Friedel-Crafts Alkylation



$AlBr_3$, heat

HYDROXYL COMPOUNDS   –OH – Alcohol

Electrophilic addition of alkene



conc H_2SO_4 at 0°C, followed by boiling water

industrial method: H_3PO_4, 300 °C, 65 atm

formation

Nucleophilic substitution of Halogenoalkanes

$CH_3CH_2Br + OH^- (aq) \rightarrow CH_3CH_2OH + Br^-$

NaOH (aq) or KOH (aq), heat

Reduction of Aldehydes (C(=O)–H), carboxylic acids (C(=O)–OH) to give 1° alcohols

$CH_3-C(=O)-H + 2[H] \rightarrow CH_3-C(OH)(H)-H$

$CH_3-C(=O)-OH + 4[H] \rightarrow CH_3-C(OH)(H)-H + H_2O$

Reduction of ketones (R–C(=O)–R) to give 2° alcohols

$CH_3-C(=O)-CH_3 + 2[H] \rightarrow CH_3-C(OH)(H)-CH_3$

	H_2 ; Ni, heat	$NaBH_4$	$LiAlH_4$ dry ether
Alkene	✓	✗	✗
Carbonyls	✓	✓	✓
Carboxylic Acids	✗	✗	✓

Hydrolysis of esters (C(=O)–O)

$H-CH_2-C(=O)-O-CH_2-CH_2-H + H_2O \rightleftharpoons H-CH_2-C(=O)-OH + HO-CH_2-CH_2-H$

(δ+ on C, δ− on O)

H_2SO_4 (aq), heat

Combustion

$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

O_2

formation

Redox

$$R-OH + Na \longrightarrow RO^-Na^+ + \frac{1}{2}H_2$$

Na

Effervescence (H_2) → gas extinguishes lighted splint with 'pop'

Condensation with carboxylic acids (COOH) to produce ester ($C(=O)-O$)

$$RO-H + R'-C(=O)-OH \rightleftharpoons R'-C(=O)-O-R + H_2O$$

conc H_2SO_4, heat

→ ☆ small amount OK!

→ catalyst

→ dehydrating agent

Condensation with acyl chlorides ($C(=O)-Cl$) to produce esters ($C(=O)-O$)

$$R-C(=O)-Cl + H-OR' \longrightarrow R-C(=O)-OR' + HCl$$

alcohol

white fumes (HCl)

RO-H

Nucleophilic substitution

R-OH ↓

$$3R-OH + PX_3 \longrightarrow 3RX + H_3PO_3$$

PX_3, heat

☆ cannot PBr_5/PI_5: not stable.

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

PCl_5 white fumes

$$R-OH + SOCl_2 \longrightarrow RCl + SO_2(g) + HCl(g)$$

$SOCl_2$ white fumes

will escape to atmosphere: preferred!

$$R-OH + HX \longrightarrow RX + H_2O$$

dry HCl, $ZnCl_2$, heat : RCl

NaBr, conc H_2SO_4, heat : RBr

Elimination

☆ 2°, 3° alcohol → >1 alkene product

alcohol dehydrate to give alkenes, –OH, –H removed from adjacent carbons

$$CH_3CH_2OH \longrightarrow CH_2=CH_2 + H_2O$$

excess conc H_2SO_4 at 170°C

industrial method: pass alcohol vapour over Al_2O_3 catalyst @ 350°C

oxidation

☆ 1° and 2° only !

primary → carboxylic acids

$$RCH_2OH + 2[O] \longrightarrow RCOOH + H_2O$$

$KMnO_4$ (aq), H_2SO_4 (aq), heat — purple $KMnO_4$ decolourised

$K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat — orange $K_2Cr_2O_7$ turned green

Primary → aldehydes

$$RCH_2OH + [O] \longrightarrow RCHO + H_2O$$

$K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat w immediate distillation

secondary → ketones

$$CH_3-CH(OH)-CH_3 + [O] \longrightarrow CH_3-C(=O)-CH_3 + H_2O$$

$KMnO_4$ (aq), H_2SO_4 (aq), heat — purple $KMnO_4$ decolourised

$K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat — orange $K_2Cr_2O_7$ turned green

Tri-iodomethane Test (Iodoform Test) (oxidisation)

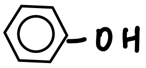
To identify:

$$CH_3-CH(OH)-R$$

$$CH_3-CH(OH)-R + 4I_2 + 6OH^- \longrightarrow R-C(=O)-O^- + CHI_3 + 5I^- + 5H_2O$$

I_2 (aq), NaOH (aq), warm → to prevent yellow ppt from dissolving

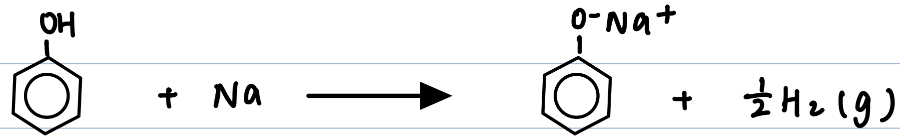
yellow ppt (CHI_3) formed



phenols

– OH

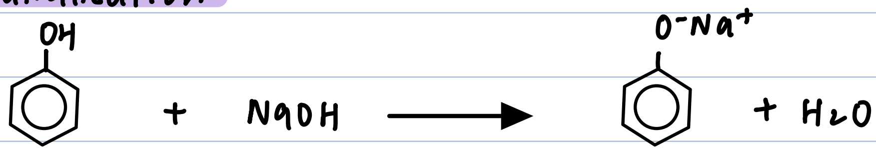
Redox



Na

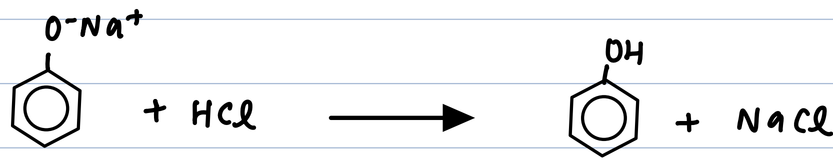
colourless gas (H₂) extinguishes lighted splint with 'pop'

Neutralisation



NaOH(aq) / Na

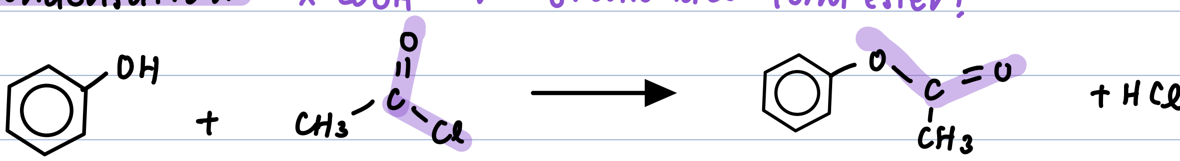
reversed!



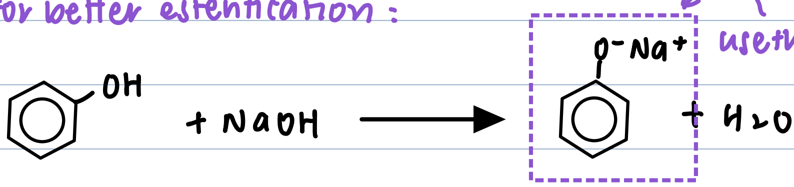
	Neutralisation		Redox
	Na_2CO_3 / $NaHCO_3$	NaOH(aq)	Na
Alcohol	✗	✗	✓
Phenol	✗	✓	✓
Carboxylic Acid	✓	✓	✓

Condensation

(alcohol) ✗ COOH ✓ acyl chlorides form ester!



✲ For better esterification :

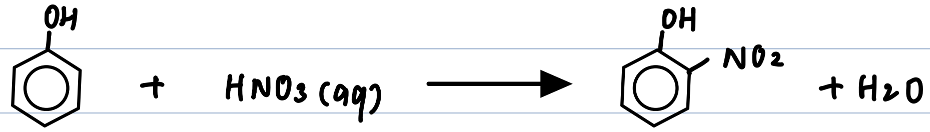


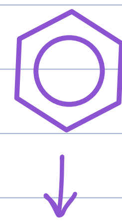
use this instead!

(Neutralisation)

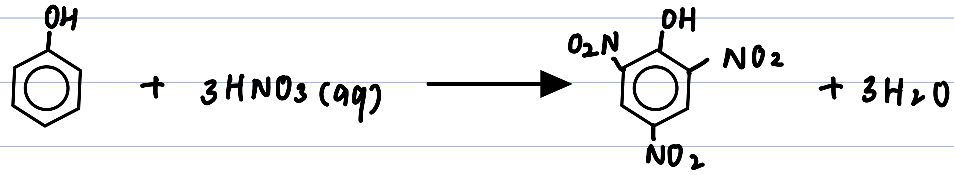
CH_3COCl

Electrophillic substitution (Nitration)





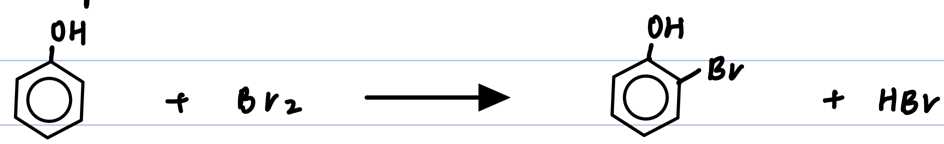
HNO_3 (aq)



conc HNO_3

yellow solid (2,4,6-trinitrophenol) formed

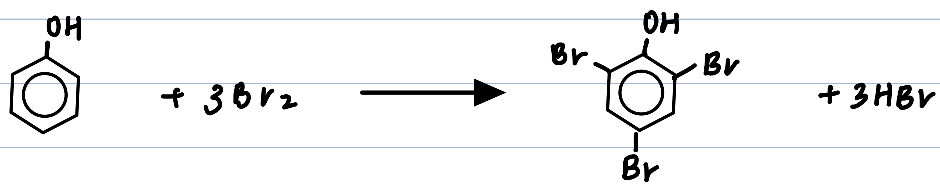
Electrophillic substitution (Halogenation)



Br_2 (l) in CCl_4

orange-red bromine decolourised

steamy white fumes (HBr)



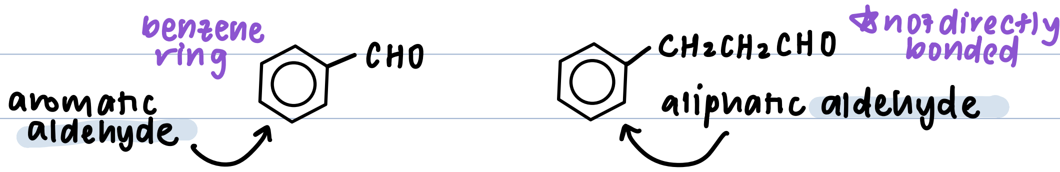
Br_2 (aq)

orange-red bromine decolourised

white ppt (2,4,6-tribromophenol) formed

CARBONYL COMPOUNDS

→ aldehydes $H-\overset{O}{\overset{\|}{C}}-R$ / ketones $R'-\overset{O}{\overset{\|}{C}}-R$



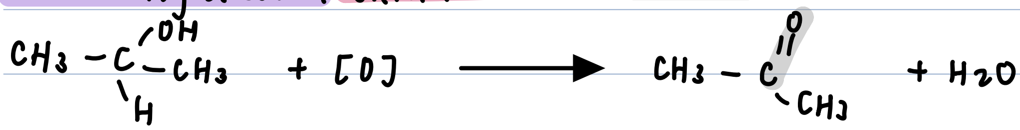
Primary alcohol oxidation → aldehydes

$RCH_2OH + [O] \longrightarrow RCHO + H_2O$

$K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat w immediate distillation → prevent further oxidation

orange $K_2Cr_2O_7$ turns green

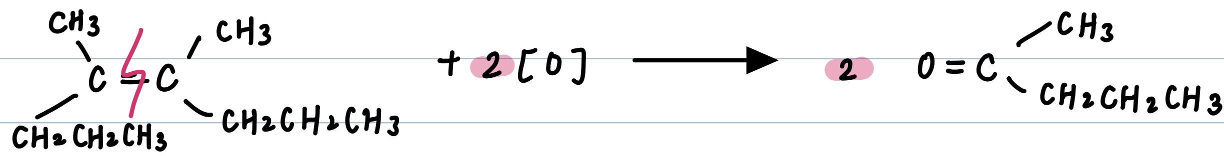
secondary alcohol oxidation → ketones



$KMnO_4$ (aq), H_2SO_4 (aq), heat — purple $KMnO_4$ decolourised

$K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat — orange $K_2Cr_2O_7$ turned green

Oxidative cleavage of alkenes → ketones



$KMnO_4$ (aq), H_2SO_4 (aq), heat

✲ must have 2 R groups!

$=C$ R H → 1 R will form carboxylic instead!

formation

Nucleophilic addition

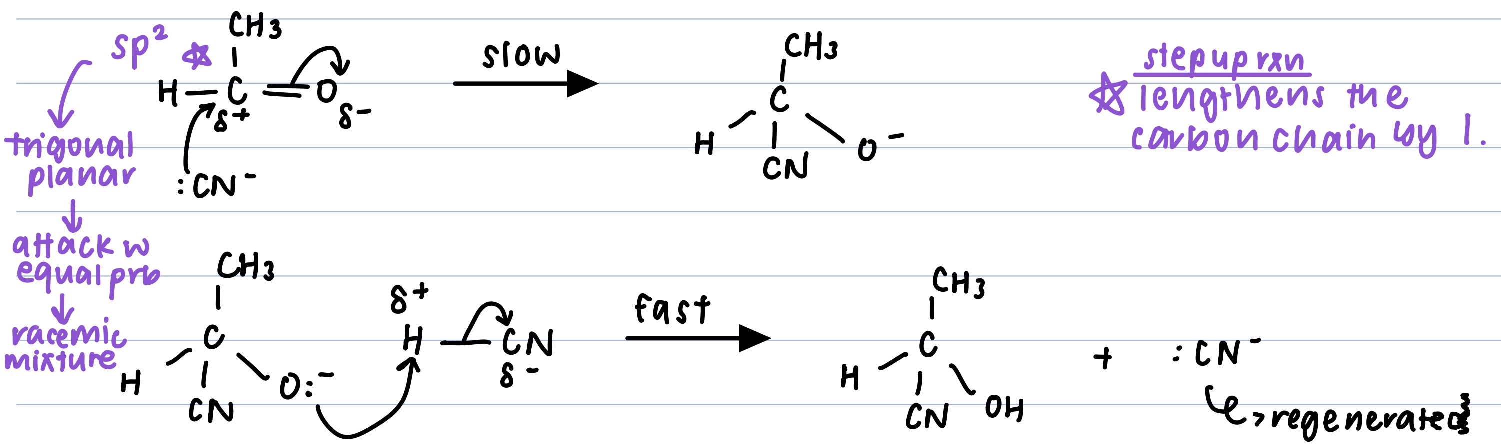
HCN + trace NaCN (aq), 10°C – 20°C

OR

HCN + trace NaOH (aq), cold

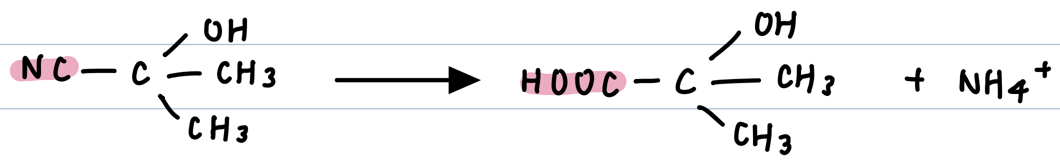
$NaCN \longrightarrow Na^+ + CN^-$

$HCN + NaOH \longrightarrow Na^+ + CN^- + H_2O$



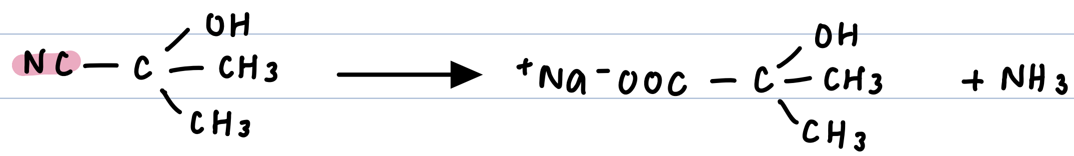
Cyanohydrin Reactions

Acid Hydrolysis → carboxylic acids



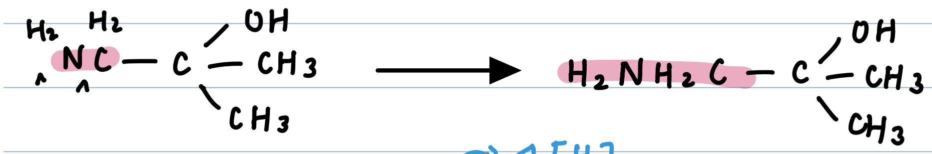
H_2SO_4 (aq), heat

Basic hydrolysis → carboxylate ions ($COO^- Na^+$)



NaOH (aq), heat

Reduction → primary amines (CH_2NH_2)



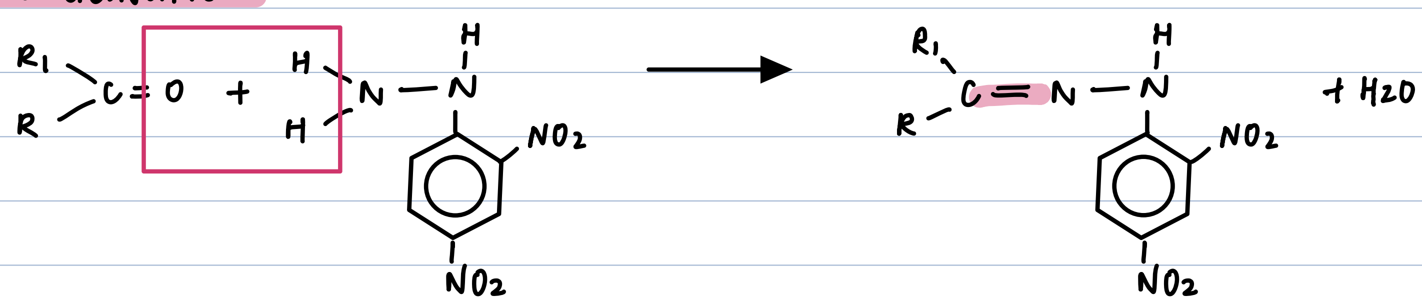
$LiAlH_4$ in dry ether → 4[H]

OR

H_2 (g), Ni catalyst, heat → 2 H_2

☆ aldehyde > ketone — more R groups, steric hindrance

Condensation



2,4-DNPH, warm — dinitrophenylhydrazine

orange ppt formed

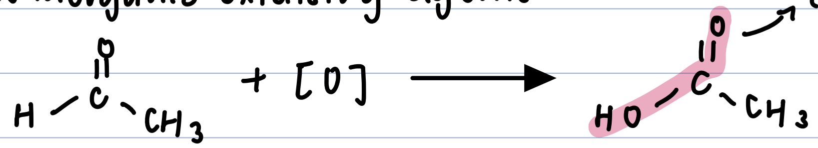
☆ distinguishing test for carbonyl group

(x) between ketones & aldehydes!

Oxidation (Aldehydes)

★★ distinguishing test between aldehydes & ketones bc ketones r resistant to oxidation.

1) w inorganic oxidising agents

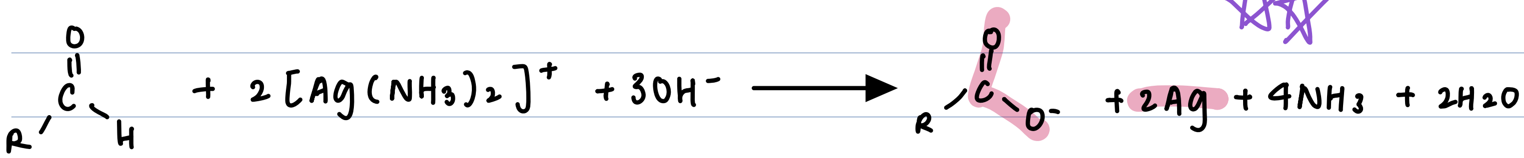


carboxylic!

$KMnO_4$ (aq), H_2SO_4 (aq), heat — purple decolourised

$K_2Cr_2O_7$ (aq), H_2SO_4 (aq), heat — orange → green

2) with Tollen's reagent

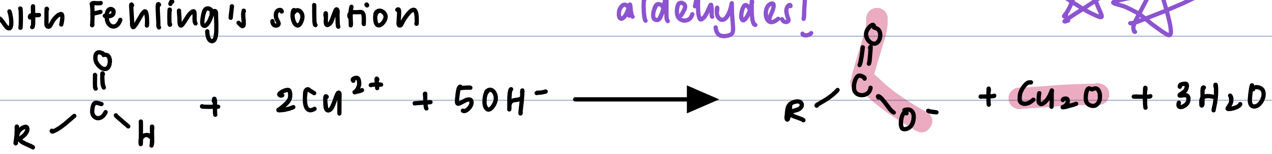


★★

Tollen's reagent, warm — silver mirror (Ag) formed

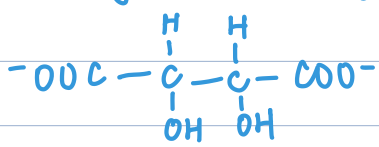
★ distinguishing test between aliphatic & aromatic aldehydes!

3) with Fehling's solution



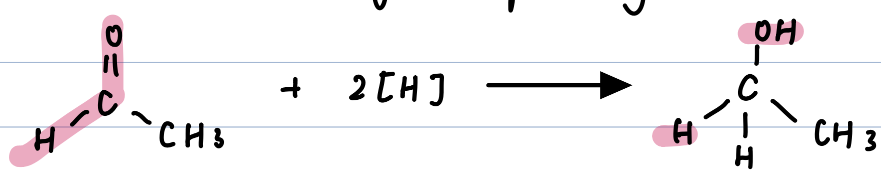
★★

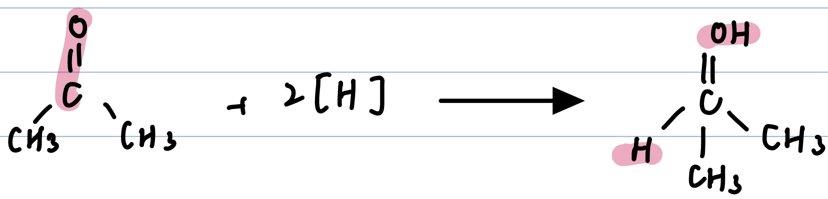
Fehling's solution, warm — reddish brown ppt (Cu_2O) formed



Reduction

Aldehyde → primary alcohol   ketone → secondary alcohol





$LiAlH_4$ in dry ether OR

$NaBH_4$ OR

H_2, Ni catalyst, heat

↳ use H_2 instead of [H]!!

Tri-iodomethane Test

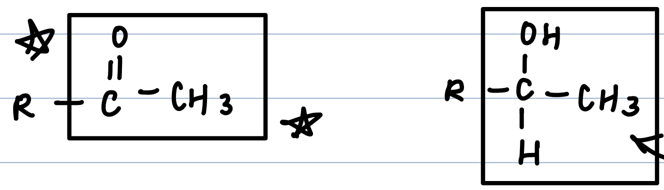
$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3I_2 + 4OH^- \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^- + CHI_3 + 3I^- + 3H_2O$$

(CHI_3: yellow ppt)

Iodine (aq), NaOH (aq), warm

yellow ppt formed

☆ distinguishing test for methyl carbonyls & methyl alcohols



methyl alcohol from hydroxyl!

CARBOXYLIC ACIDS & DERIVATIVES

Primary alcohol oxidised → aldehydes → carboxylic acids

CH_3CH_2OH (ethanol) $\xrightarrow[\text{heat w distillation}]{K_2Cr_2O_7(aq),\ H_2SO_4(aq)}$ CH_3CHO (ethanal) $\xrightarrow[\text{heat w distillation}]{K_2Cr_2O_7(aq),\ H_2SO_4(aq)}$ CH_3COOH (ethanoic acid) (or $KMnO_4$)

CH_3CH_2OH (ethanol) $\xrightarrow[\text{heat under reflux}]{KMnO_4(aq),\ H_2SO_4(aq)}$ CH_3COOH (ethanoic acid) (or $K_2Cr_2O_7$)

purple $KMnO_4$ decolourise

orange $K_2Cr_2O_7$ turns green

Oxidation of alkenes. → ☆ only $R_1(H)C=C$!!

$$(CH_3)(H)C=C(CH_2CH_3)(H) + 4[O] \longrightarrow CH_3CO_2H + CH_3CH_2CO_2H$$

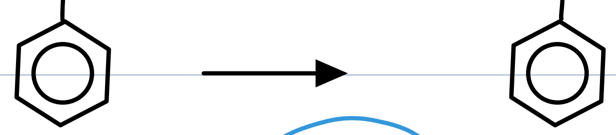
(ethanoic acid + propanoic acid)

$KMnO_4(aq)$, $H_2SO_4(aq)$, heat

purple $KMnO_4$ decolourise

Oxidation of Alkylbenzene

CH_3 $COOH$

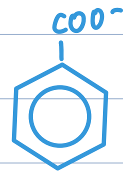


$KMnO_4$ (aq), H_2SO_4 (aq), heat

purple $KMnO_4$ decolourise

white ppt (benzoic acid)

can be NaOH alkaline medium, just need to H_2SO_4 it after.



Hydrolysis of esters (need H_2O)

↳ acidic → reversible — H_2SO_4, heat — $CH_3-C(=O)-O-CH_3 + H_2O \rightleftharpoons CH_3-C(=O)-OH + CH_3OH$

↳ basic → irreversible — NaOH/KOH, heat — " $CH_3C(=O)-O^-Na^+ \xrightarrow{H_2SO_4} CH_3-C(=O)-OH$

Hydrolysis of acid chlorides / acyl chlorides

$CH_3-C(=O)-Cl + H_2O \longrightarrow CH_3-C(=O)-OH + HCl$

white fumes

Hydrolysis of nitriles

↳ acidic — H_2SO_4, heat

↳ basic — NaOH/KOH, heat

↑ Formations

Reactions ↓

Redox

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

Na, RT

Acid-base / Neutralisation

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

" $+ NaHCO_3 \longrightarrow$ " $+ H_2O + CO_2$

2 " $+ Na_2CO_3 \longrightarrow$ 2 " $+ H_2O + CO_2$

NaOH/$NaHCO_3$/Na_2CO_3, RT

☆ distinguish btwn alcohol & COOH

Condensation of alcohol

$R-C(=O)-OH + HO-R' \rightleftharpoons R-C(=O)-OR + H_2O$

Alcohol, conc H_2SO_4 catalyst, heat

Condensation of acyl chloride

$$R-\overset{O}{\overset{\|}{C}}-Cl + HO-R \longrightarrow R-\overset{O}{\overset{\|}{C}}-OR + HCl$$

ROH at RT

$$R-\overset{O}{\overset{\|}{C}}-Cl + H-\underset{}{\overset{H/R}{\overset{|}{N}}}-H/R \longrightarrow R-\overset{O}{\overset{\|}{C}}-\overset{H/R}{\overset{|}{N}}-H/R + HCl$$

NH_3 , 1°/2° amine (must have H) RT

Nucleophilic acyl substitution

$RCOOH + \underline{PCl_5} \xrightarrow{RT} RCOCl + POCl_3 + HCl$

3 " $+ \underline{PCl_3} \xrightarrow{heat}$ " $+ H_3PO_3$

" $+ \underline{SOCl_2} \xrightarrow{RT}$ " $+ SO_2 + HCl$

reduction of COOH to form 1° alcohols

$$R-\overset{O}{\overset{\|}{C}}-OH + [H] \longrightarrow R-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-H$$

$LiAlH_4$ in dry ether

[esters] < hydrolysis < COOH, OH ; reduction

distinguishing test :

① hydrolyse → COOH

② Test for OH / COOH

OH ↓ I_2 NaOH

COOH ↓ aq Br