Alkanes

Halogenation

Type: free radical substitution
Condition: UV radiation

Overall: $CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$

Initiation: $Cl_2 \xrightarrow{UV} 2Cl\cdot$

Propagation: $CH_4 + Cl\cdot \longrightarrow \cdot CH_3 + HCl$

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

Termination: $\cdot CH_3 + Cl\cdot \rightarrow CH_3Cl$

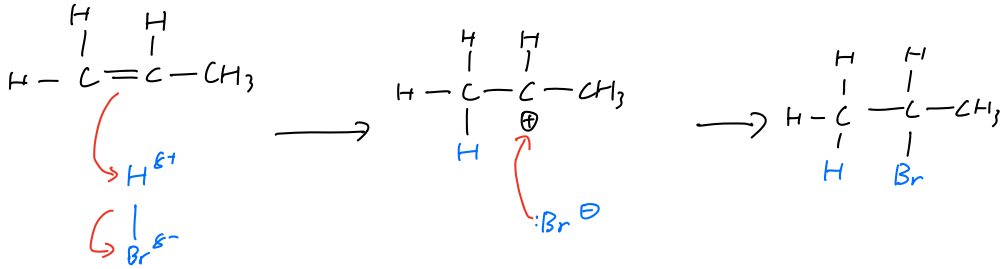
$Cl\cdot + Cl\cdot \rightarrow Cl_2$

$\cdot CH_3 + \cdot CH_3 \rightarrow C_2H_6$

Alkenes

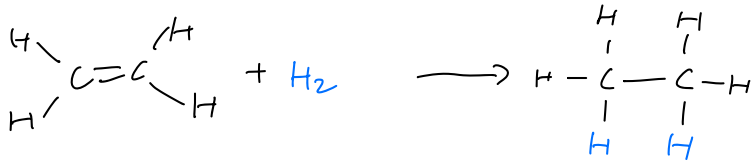
Halogen / hydrogen halide addition

Type: electrophilic addition
Conditions: RTP / no catalyst



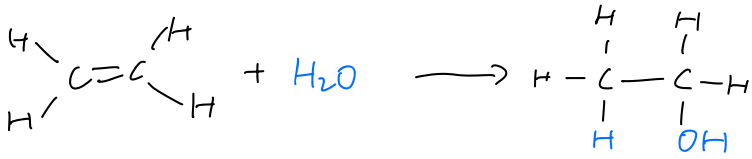
Hydrogenation

Condition: Ni catalyst, high temperature and pressure



Hydration

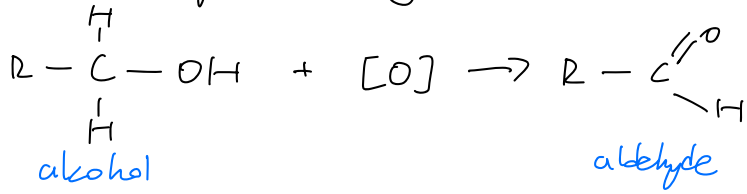
Condition: steam, H_3PO_4 catalyst



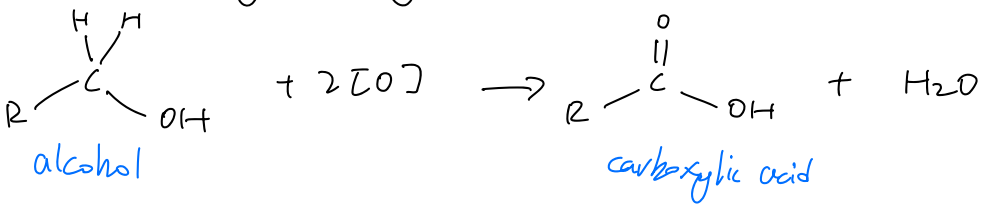
Alcohols

Oxidation reactions of primary alcohols

Condition: gentle heating + distillation + $K_2Cr_2O_7 / H^+$

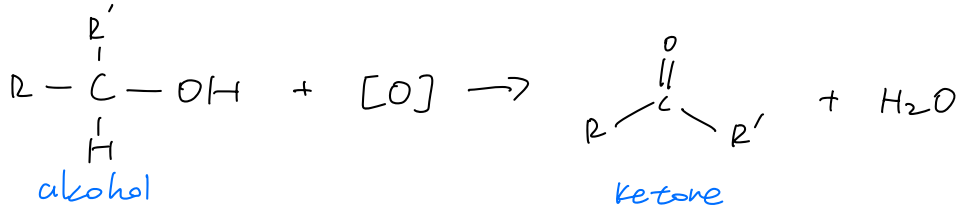


Condition: strong heating + reflux + excess $K_2Cr_2O_7 / H^+$



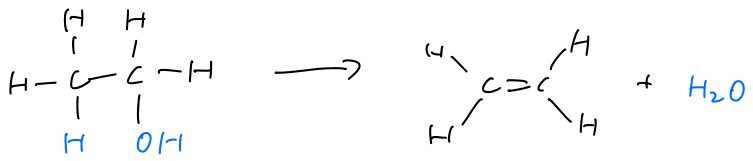
Oxidation reactions of secondary alcohols

Condition: heated under reflux



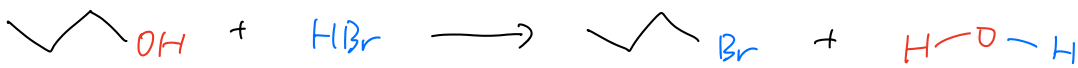
Dehydration of alcohols

Condition: conc. H_2SO_4, heat under reflux



Substitution with halides

Condition: reflux, conc. acid catalyst

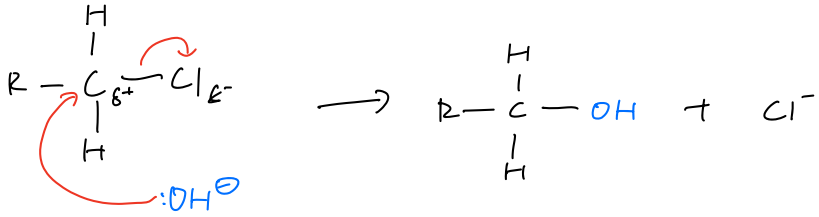


$R-OH + NaX \longrightarrow R-X + NaHSO_4 + H_2O$

Haloalkanes

Hydrolysis

Type : nucleophilic substitution
Condition: NaOH, reflux



Breakdown of ozones (CFC)

Initiation : $CF_2Cl_2 \xrightarrow{UV} \cdot CF_2Cl + Cl\cdot$

Propagation: $Cl\cdot + O_3 \longrightarrow \cdot ClO + O_2$

$\cdot ClO + O \longrightarrow O_2 + \cdot Cl$

Overall: $O_3 + O \longrightarrow 2O_2$

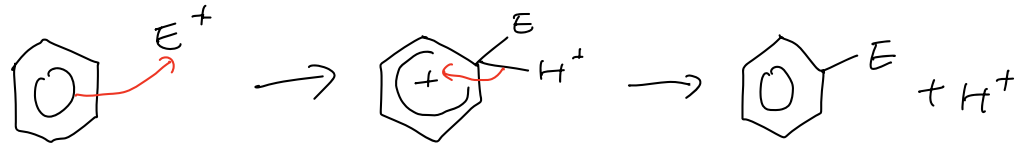
Breakdown of ozones (NO·)

Propagation: $NO + O_3 \longrightarrow \cdot NO_2 + O_2$

$\cdot NO_2 + O \longrightarrow O_2 + \cdot N$

Aromatic compounds

Electrophilic substitution mechanism



Nitration of benzene

Conditions: H_2SO_4 catalyst, warm (50°C / 70°C for further substitution), conc. HNO_3

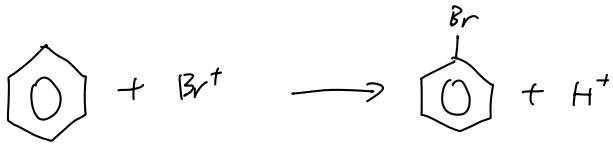
$$H_2SO_4 + HNO_3 \rightarrow NO_2^+ + HSO_4^- + H_2O$$

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

Halogenation

Conditions: Need halogen carrier catalyst e.g. $AlCl_3$, $FeBr_3$

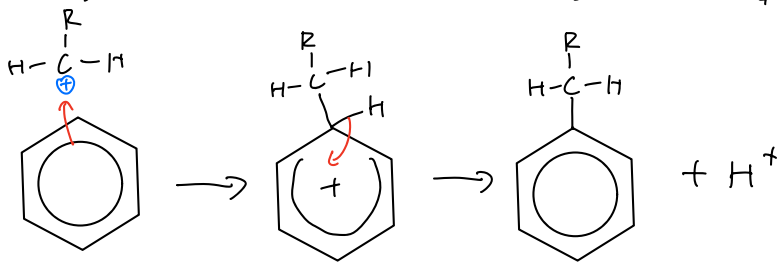
$$Br_2 + FeBr_3 \rightarrow FeBr_4^- + Br^+$$



$$H^+ + FeBr_4^- \rightarrow FeBr_3 + HBr$$

Alkylation

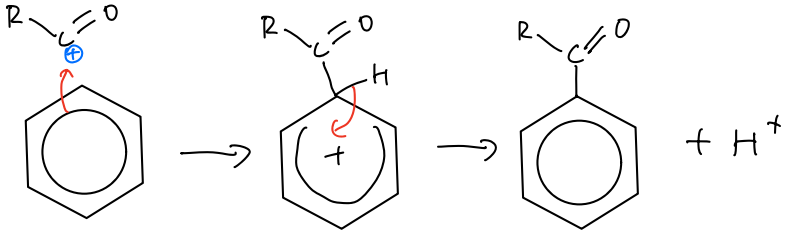
$AlCl_3 + R-CH_2-Cl \longrightarrow R-CH_2^+ + AlCl_4^-$



$H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$

Acylation

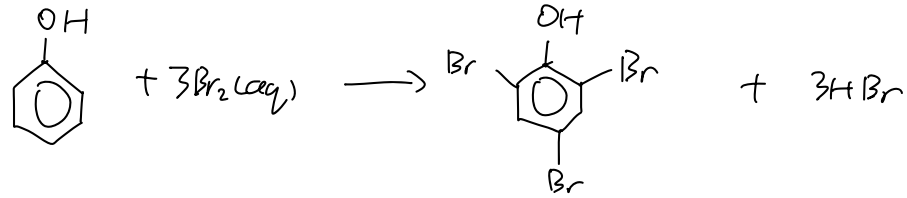
$R-COCl + AlCl_3 \longrightarrow R-C^+(=O) + AlCl_4^-$



$H^+ + AlCl_4^- \longrightarrow AlCl_3 + HCl$

Bromination of phenol

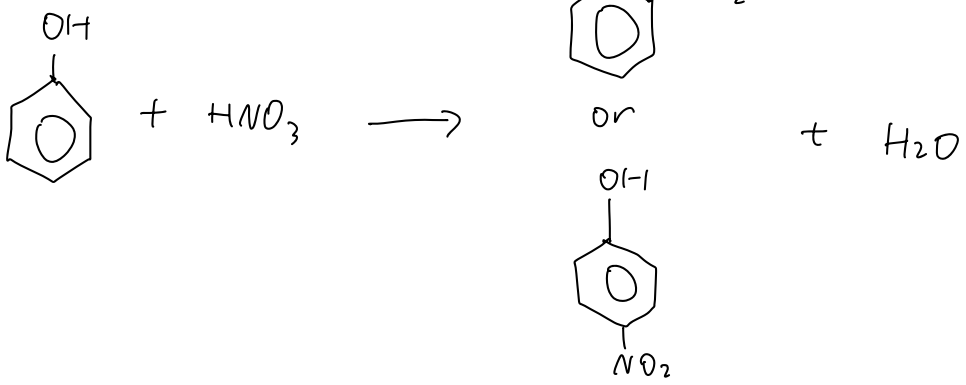
Conditions: $Br_2(aq)$, RTP, no halogen carrier needed



white ppt

Nitration of phenol

Condition: dilute nitric acid, RTP



Directing groups

deactivating

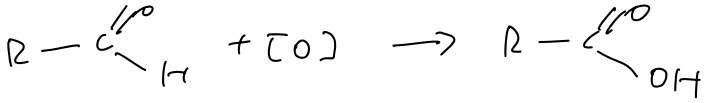
2/4-directing: $-Cl$, $-CH_3$, $-OH$, $-NH_2$, ...

3-directing: $-COOH$, $-NO_2$, ...

Carbonyl compounds

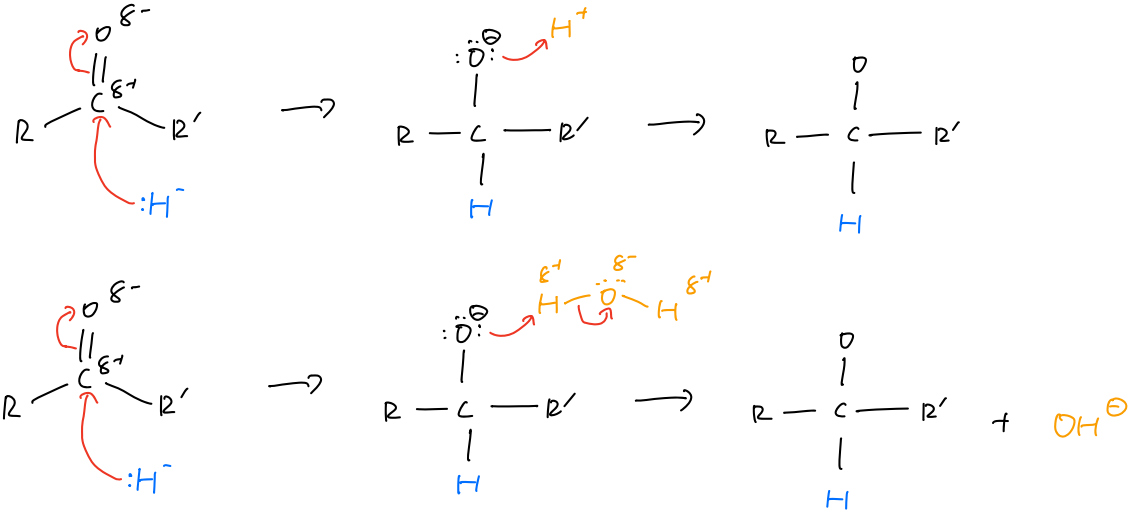
Oxidation of aldehydes

Condition: reflux, $Cr_2O_7^{2-}/H^+$

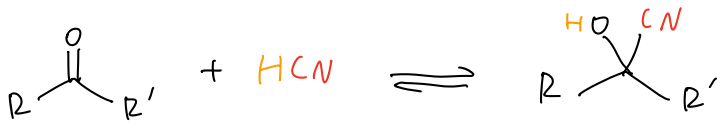


Reduction of carbonyl compounds

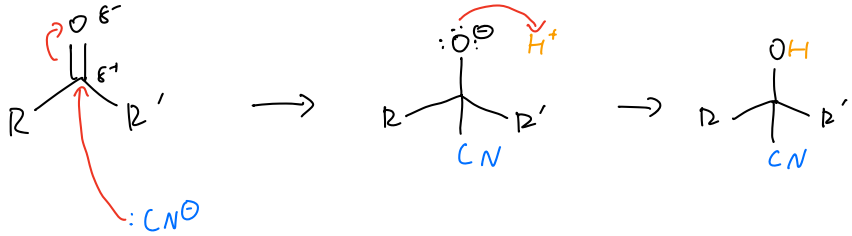
Reagent: $NaBH_4$ / $LiAlH_4$ (provides H^-)
Conditions: reflux, water or ethanol solvent

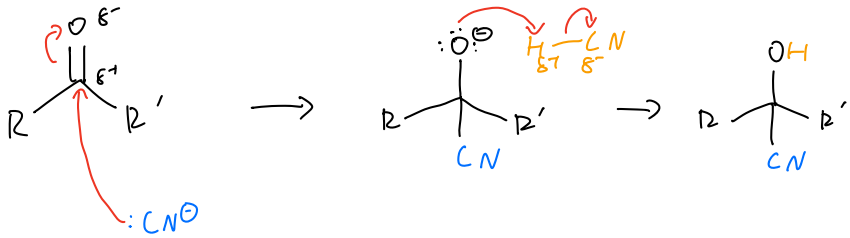


Reaction with HCN



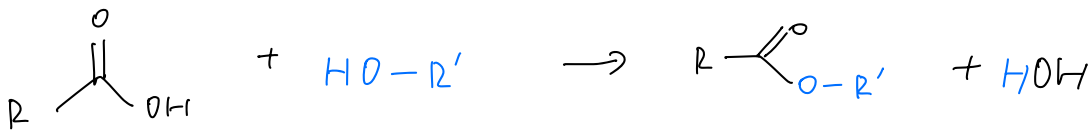
Reaction with $NaCN / H^+$



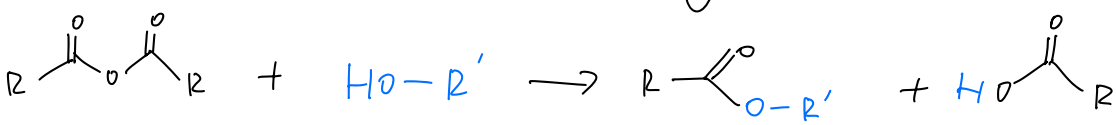


Esterification

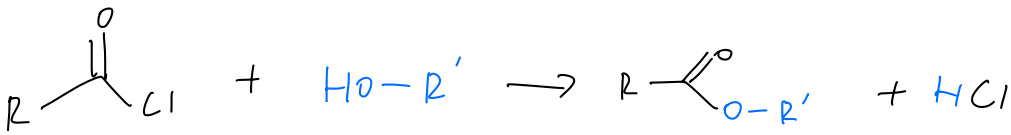
Conditions: conc. H_2SO_4, reaction mixture warmed



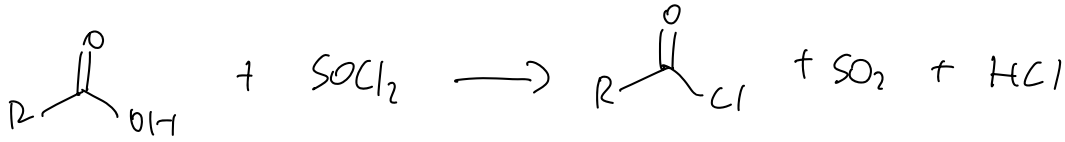
Conditions: non-aqueous solvent + heating



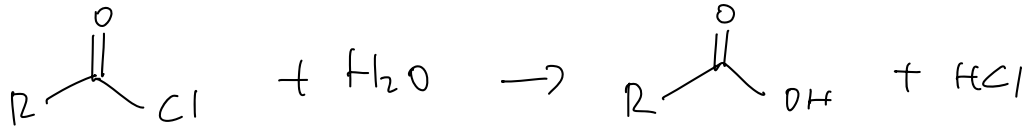
* much faster rate + higher yield
* phenol only esterify with acid anhydride / acyl chloride



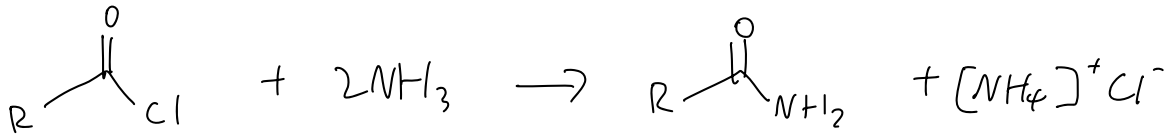
Acyl Chloride formation

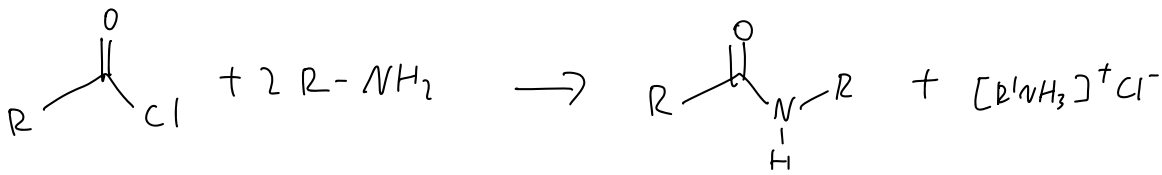


Conversion back to carboxylic acid



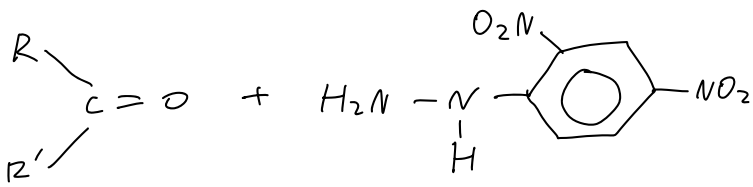
Amide formation

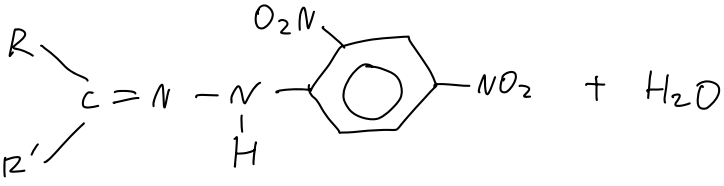




2,4-DNP

Aldehyde / ketones only



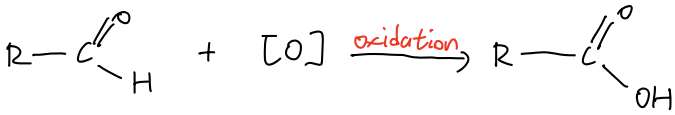


Orange / yellow precipitate

Tollen's reagent

Aldehyde only, need to warm

$$Ag^+_{(aq)} + e^- \xrightarrow{\text{reduction}} Ag_{(s)}$$



Acid hydrolysis of esters

Conditions: reflux, dilute aqueous acid

Alkaline hydrolysis of esters

Conditions: reflux, $OH^-_{(aq)}$

* Irreversible

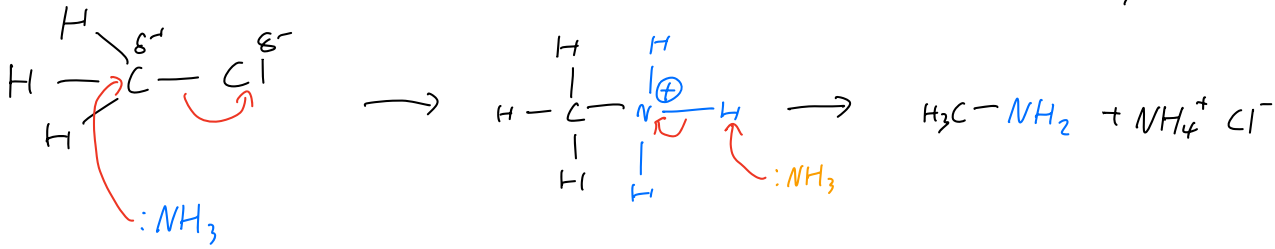
Reactions summary

Reactant	Aldehyde	Ketone	Carboxylic acid	Acyl chloride
$NaBH_4$	✓	✓	×	×
$NaCN/H^+$ or HCN	✓	✓	×	×
H_2O	×	×	×	✓
ROH	×	×	✓	✓
Ammonia	×	×	×	✓
Amine	×	×	×	✓
2,4-DNP	✓	✓	×	×
Tollen's reagent	✓	×	×	×
Na_2CO_3	×	×	✓	×
Na	×	×	✓	×

Nitrogen compounds

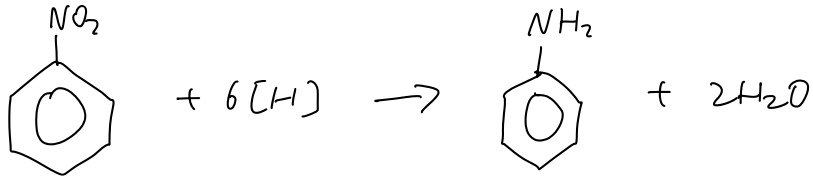
Amine formation

Condition: react haloalkenes with excess ethanolic ammonia / amine

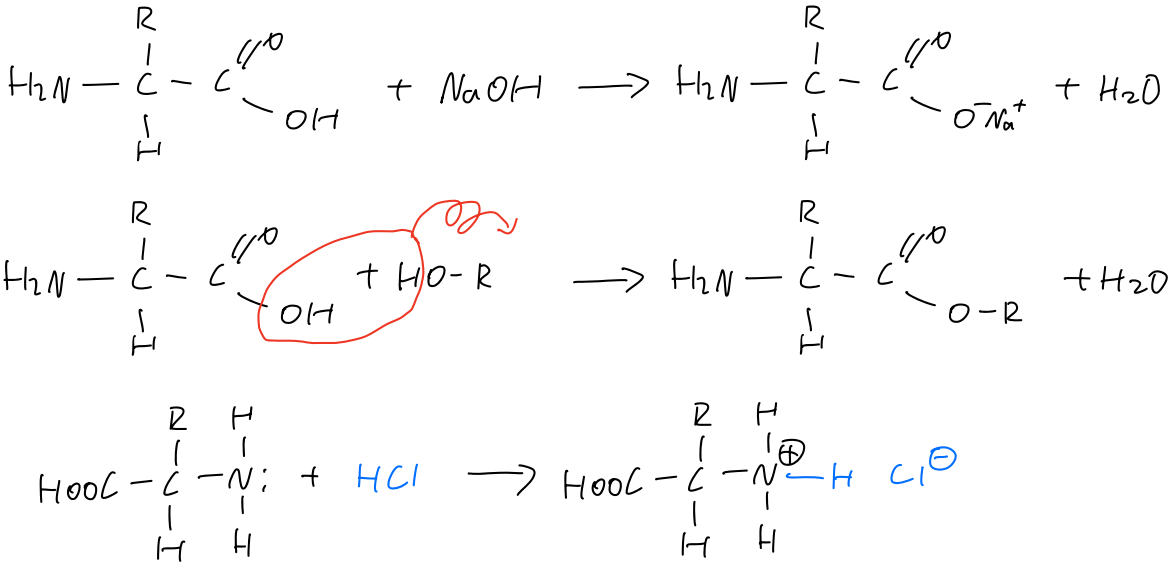


Aromatic amine formation

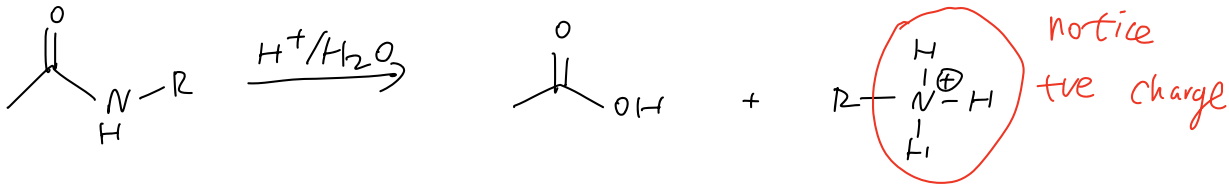
Condition: Tin / Conc. HCl



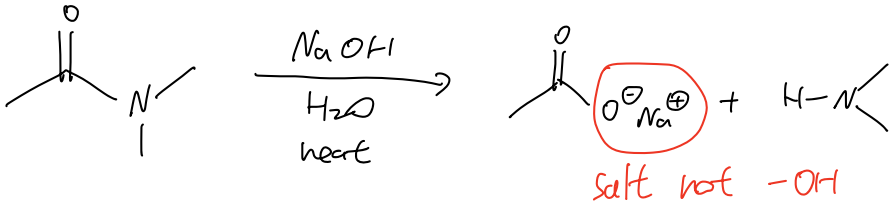
Amino acid reactions



Acid hydrolysis of amides



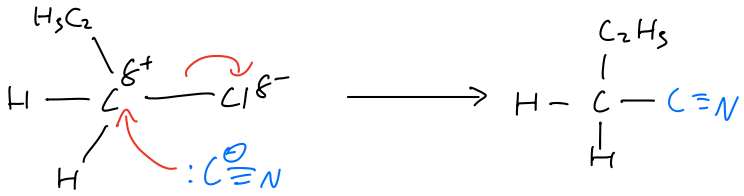
Basic hydrolysis of amides



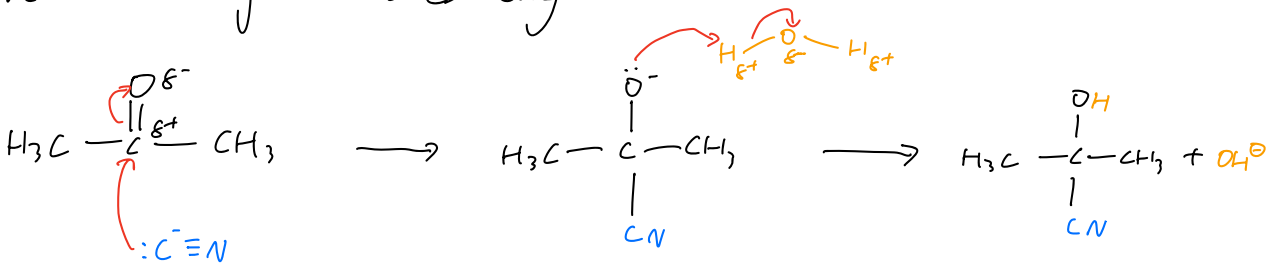
Carbon - carbon bond formation

Nitrile formation

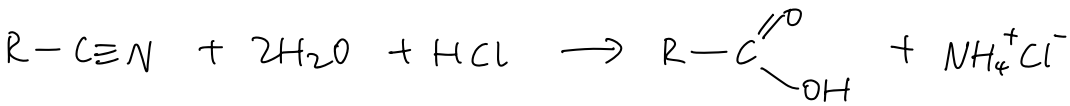
Condition: heat under reflux ; NaCN/KCN in ethanol



Condition: aldehydes / ketones only



Acid hydrolysis of nitriles



Reduction of nitriles

Condition: Ni catalyst