### **Alkanes Combustion**

**REACTANTS:** Alkane and O<sub>2</sub> (oxygen)

**CONDITIONS:** Excess of Oxygen (for complete combustion)

PRODUCT(S): Carbon Dioxide and Water

**REACTION TYPE: Combustion** 

 $C_5H_{12} + 80_2 \longrightarrow 5CO_2 + 6H_2O$ 

REACTION: (example of pentane)

Alkane

Oxygen

Carbon Dioxide Water

- When excess oxygen is present complete combustion occurs so carbon dioxide and water are the only products.
- Incomplete combustion of alkanes occurs when oxygen becomes a limiting reagent, leading to the formation of carbon monoxide (CO) and solid carbon particulates (soot).



### **Alkanes Free Radical Substitution**

**REACTANTS:** Alkanes and Halogen **CONDITIONS:** U.V (ultraviolet) light

PRODUCT: Halogenoalkane

**REACTION TYPE:** Free Radical Substitution

REACTION: (example of methane) Alkane Chlorine Chloroalkane Hydrogen

#### **NOTES:**

• Chain reaction, occurring in three steps - initiation, propagation and termination. See mechanism.

Halide

- U.V light is required to homolytically split halogen molecule, forming two radical species.
- Further substitution can occur, forming di, tri and tetra halogenoalkanes.



### ·Halogenoalkanes Substitution (OH<sup>-</sup>)

**REACTANTS:** Halogenoalkane and Sodium Hydroxide, *NaOH* (for OH ions)

**CONDITIONS:** Heat under reflux, Aqueous ('aq' - water present)

**PRODUCT(S):** Alcohol and Halide Ion (sodium halide salt if sodium hydroxide used)

**REACTION TYPE:** Nucleophilic Substitution, *Hydrolysis* 



- Rate of reaction is determined by strength of carbon-halogen bond (carbon-flourine bond is strongest giving slowest rate; carbon-iodine bond is weakest, giving fastest rate).
- Rate of hydrolysis can compared using aqueous silver nitrate (AgNO<sub>3</sub>) within the reaction mixture and timing how long it takes to form precipitate (CI = **white** ppt, Br = **cream** ppt and I = **yellow** ppt).
- Reaction must be carried out in **aqueous conditions**, otherwise an elimination can occur.

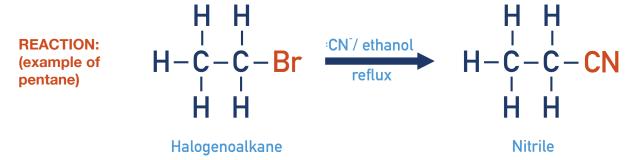


## ·Halogenoalkanes Substitution (CN<sup>-</sup>) ·

**REACTANTS:** Halogenoalkane and Sodium *or Potassium* Cyanide (NaCN *or KCN*) **CONDITIONS:** Heat under reflux, Ethanolic (ethanol as the solvent, **no water present**)

**PRODUCT(S):** Nitrile and Halide Ion (*forms salt with Na*<sup>+</sup> *or K*<sup>+</sup>)

**REACTION TYPE:** Nucleophilic Substitution



- Rate of reaction is determined by strength of carbon-halogen bond (carbon-flourine bond is strongest, giving slowest rate; carbon-iodine bond is weakest, giving fastest rate).
- Reaction must be carried out in ethanolic conditions (in ethanol, no water present), otherwise an alcohol is likely to form rather than the nitrile.
- Reaction is heated under reflux to ensure no volatile substances are lost.



## Halogenoalkanes Substitution (NH<sub>3</sub> and amines)

**REACTANTS:** Halogenoalkane and Ammonia (NH<sub>2</sub>)

**CONDITIONS:** Heat\*, Ethanolic (ethanol as the solvent, **no water present**)

**PRODUCT(S):** Amine and Ammonium Halide Salt **REACTION TYPE:** Nucleophilic Substitution

REACTION: (example of bromoethane)



Halogenoalkane

### **Amine**

### **NOTES:**

- Reaction must be carried out in ethanolic conditions (in ethanol, no water present), otherwise an alcohol is likely to form rather than the amine.
- \*A sealed container (to stop ammonia escaping) containing reactants is heated.
- The amine formed in the reaction is actually a stronger base than ammonia and an ammonium-alkyl salt may be formed. The amine can be obtained by adding sodium hydroxide to the mixture forcing the alkyl-ammonium ion to 'release' a H<sup>+</sup> ion and become a neutral molecule.
- Rate of reaction is determined by strength of carbon-halogen bond (carbon-flourine bond is strongest, giving slowest rate; carbon-iodine bond is weakest, giving fastest rate).
- If an amine is used instead of ammonia, a secondary amine can be formed. For example, the reaction of butylamine with 2-bromoethane:

 $\mathsf{CH_3CH_2CH_2CH_2NH_2} + \mathsf{CH_3CH_2Br} \to \mathsf{CH_3CH_2CH_2CH_2NHCH_2CH_3} \ (ethylbutylamine) + \mathsf{HBr}$ 

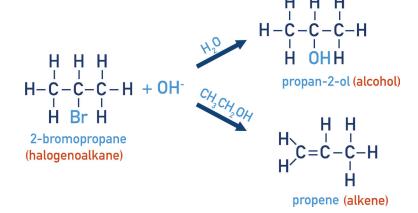


### ·Halogenoalkanes Substitution and Elimination (OH<sup>-</sup>)

**REACTANTS:** Halogenoalkane and Potassium Hydroxide (for OH<sup>-</sup> ions)

CONDITIONS: Heat under reflux, Ethanolic or Aqueous\*
PRODUCT(S): Alcohol and Alkene (possible mixture of both)
REACTION TYPE: Nucleophilic Substitution and Elimination

REACTION(S): (example of 2-bromopropane)



- Halogenoalkanes can react with hydroxide (OH<sup>-</sup>) ions in both substitution and elimination reactions.
- If substitution occurs an alcohol is formed, whereas if elimination occurs an alkene is formed.
- The solvent used can help ensure more of one product is formed than the other, although final product mixture can still contain both the alcohol and alkene.
- If a hot aqueous solvent is used, more alcohol forms.
- If a hot ethanolic solvent is used, more alkene forms.
- Primary alcohols are more likely to undergo substitution tertiary alcohols are more likely to undergo elimination.
- Higher temperatures and a more concentrated solution of hydroxide ions favour elimination.



## Alkenes Addition (HBr)

**REACTANTS:** Alkene and Hydrogen Bromide (HBr)

**CONDITIONS:** Hydrogen Bromide Gas or (concentrated) Hydrobromic Acid

PRODUCT(S): Bromoalkane

**REACTION TYPE:** Electrophilic Addition

**REACTION:** (example of ethene)

**Bromoalkane** 

- For unsymetrical alkenes, there will be two possible products from the electrophilic addition.
- Stability of the carbocation intermediate in the mechanism will determine which product will made more readily (major product) and which product will be made less readily (minor product). See mechanism.



# **Alkenes Addition (Br<sub>2</sub>)**

**REACTANTS:** Alkene and Bromine (Br<sub>9</sub>)

**CONDITIONS:** Bromine Liquid (pure Br<sub>2</sub>) or Bromine Water (Br<sub>2</sub>(aq))

PRODUCT(S): Dibromoalkane

**REACTION TYPE:** Electrophilic Addition, *Bromination* 

REACTION: (example of ethene)

**Alkene** 

Dibromoalkane

- Double bond in alkene polarises the bromine molecule to form an electrophile (Br<sup>δ+</sup>) that starts the reaction.
- Reaction can be used to test for the presence of an alkene. A sample is mixed with bromine water, if the bromine water turns colourless (from orange brown) an alkene is present in the sample.



### Alkenes Hydration (to alcohol)

**REACTANTS:** Alkene and Steam (H<sub>2</sub>O<sub>(a)</sub>)

CONDITIONS: Heat and Acid Catalyst (Phosphoric Acid, HaPO)

PRODUCT(S): Alcohol

REACTION TYPE: Electrophilic Addition, (acid catalysed) Hydration

REACTION: (example of ethene)

$$H = C = C \xrightarrow{H} \xrightarrow{H_2O/H^+} H = C - C - H$$
Alkene
Alcohol

- Acid catalyst is required to form hydroxonium ion (H<sub>3</sub>O<sup>+</sup>) ion that is able to act as an electrophile to start the reaction.
- For unsymetrical alkenes, there will be two possible products from the electrophilic addition.
- Stability of the carbocation intermediate in the mechanism will determine which product will made more readily (major product) and which product will be made less readily (minor product). See mechanism.



### Alkenes Hydrogenation (to alkane)

**REACTANTS:** Alkene and Hydrogen, H<sub>2</sub>

CONDITIONS: Approximately 150°C and Nickel (solid) Catalyst

PRODUCT(S): Alkane

**REACTION TYPE:** Addition, *Hydrogenation* 

REACTION: (example of ethene)

$$H = C = C \xrightarrow{H} \xrightarrow{H_2(g) / Ni(s)} H = C - C - H$$
Alkene
Alkane

### **NOTES:**

Hydrogen is 'added' across the double bond - addition reaction and the hydrocarbon becomes saturated (from unsaturated (alkene)).



## Alkenes Oxidation (to form diol)

**REACTANTS:** Alkene and (dilute) Potassium Manganate (VII)

**CONDITIONS:** Cold Temperature, Acidic Conditions

PRODUCT(S): Diol

**REACTION TYPE:** Oxidation

REACTION: (example of ethene)

- Oxidation reaction must be carried out in cold temperature with dilute potassium manganate to
  ensure the diol doesn't get further oxidised and split in two (forming two carbonyl containing molecules).
- Colour change of the acidified potassium mangangante (VII) (purple to colourless), can be used
  as a test to show a double bond is present (although the bromine water test is simpler and more
  specific).



### **Alcohols Oxidation**

**REACTANTS:** Alcohol (primary or secondary) and Acidified Dichromate ions (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> / H<sup>+</sup>)

CONDITIONS: Heat\*, Acid Catalyst (sulfuric acid (HaSOa))

PRODUCT(S): Aldehyde, Ketone or Carboxylic Acid (see below)

**REACTION TYPE:** Oxidation

REACTIONS: (example of primary and secondary alcohol)

- \*Primary alcohols form aldehydes and carboxylic acids when heated with an oxidising agent. To isolate aldehyde, distill aldehyde from reaction mixture as soon as it is formed. To obtain carboxylic acid, heat under reflux to ensure full oxidation of aldehydes already formed.
- Secondary alcohols form ketones and are unable to be further oxidised. Tertiary alcohols are unable
  to be oxidised at all.
- Oxidising agents can be repesented as [O].



## Alcohols Halogenation (PCI<sub>5</sub>)

REACTANTS: Alcohol and (solid) Phosphorus (V) Pentachloride (PCI<sub>2</sub>)

**CONDITIONS:** Pure alcohol (no water must be present) **PRODUCT(S):** Chloroalkane and HCl (white fumes)

**REACTION TYPE:** Halogenation

REACTIONS: (example of ethanol)

- PCI<sub>5</sub> reacts vigorously with -OH groups, producing white misty fumes of HCI. Due to this, the sample
  of alcohol being halogenated must be pure containing no water or other molecules with an -OH
  group.
- The reaction can be used to test for an alcohol (positive result is observation of misty white fumes).



### Alcohols Halogenation (KBr)

**REACTANTS:** Alcohol and 50% (concentrated) H<sub>2</sub>SO<sub>4</sub> and Potassium Bromide, KBr **CONDITIONS:** (concentrated) H<sub>2</sub>SO<sub>4</sub>, Warm Temperature (for distillation of product)

**PRODUCT(S):** Bromoalkane **REACTION TYPE:** Halogenation

REACTIONS: (example of ethanol)

- KBr and H<sub>2</sub>SO<sub>4</sub> react together to form HBr that reacts with the alcohol to form the bromoalkane.
- Bromoalkane is isolated from the reaction mixture by distillation.



### Alcohols Halogenation (Iodine and Red Phosphorus)

**REACTANTS:** Alcohol, Red Phosphorus and Iodine (I<sub>2</sub>)

**CONDITIONS:** Heat under reflux (distillation to isolate product)

PRODUCT(S): lodoalkane
REACTION TYPE: Halogenation

REACTIONS: (example of ethanol)

### **NOTES:**

Red phosphorus and iodine react together to form phosphorus (III) triiodide that reacts with the alcohol to form the iodoalkane.

$$2P + 3I_2 \rightarrow 2PI_3$$
 then  $3ROH + PI_3 \rightarrow 3RI + H_3PO_3$ 

Final product is isolated from reaction mixture by distillation.



## Alcohols Elimination (to alkenes)

**REACTANTS:** Alcohol

CONDITIONS: Heat, Acid Catalyst (concentrated H<sub>2</sub>SO<sub>4</sub> or concentrated H<sub>3</sub>PO<sub>4</sub>)

PRODUCT(S): Alkene

**REACTION TYPE:** Elimination, dehydration

REACTION: (example of ethene)

- Acid catalyst provides H<sup>+</sup> ion to start reaction and is reformed at the end when a H<sup>+</sup> ion is released by reacting molecule.
- Water molecule is removed, **dehydration reaction**.



# Ketones Reduction (LiAIH<sub>4</sub>)

**REACTANTS:** Ketone and LiAlH<sub>4</sub> (reducing agent)

**CONDITIONS:** Dry Ether

**PRODUCT(S):** Secondary Alcohol **REACTION TYPE:** Reduction

**REACTION:** 

$$R-C \nearrow 0 \qquad \qquad R-C-H \qquad \qquad R^1 \qquad \qquad R^1$$
Ketone (Secondary)

Alcohol

- Ketones form secondary alcohols when reduced.
- LiAlH<sub>4</sub> is a reducing agent able to provide hydride (:H<sup>-</sup>) ions that are needed for the reduction of carbonyls. The reaction must be carried out in dry ether as LiAlH<sub>4</sub> reacts vigorously with water.
- The hydrogens added in reduction reactions are often shown as [H].



## ·Aldehydes Reduction (LiAIH<sub>a</sub>) ·

**REACTANTS:** Aldehyde and LiAlH<sub>4</sub> (reducing agent)

CONDITIONS: Dry Ether PRODUCT(S): Primary Alcohol REACTION TYPE: Reduction

**REACTION:** 

- Aldehydes form primary alcohols when reduced.
- LiAlH<sub>4</sub> is a reducing agent able to provide hydride (:H<sup>-</sup>) ions that are needed for the reduction of carbonyls. The reaction must be carried out in dry ether as LiAlH<sub>4</sub> reacts vigorously with water.
- The hydrogens added in reduction reactions are often shown as [H].



## **Hydroxynitriles Formation (from carbonyls)**

**REACTANTS:** Carbonyl (aldehyde or ketone) and KCN (in acid)

PRODUCT(S): Hydroxynitrile

**REACTION TYPE:** Nucleophilic Addition

**REACTION:** 

$$R - C \xrightarrow{R^1} \xrightarrow{KCN(aq) / H_2SO_4(aq)} R - C = N$$

Carbonyl Group

Hydroxynitrile

- HCN is sometimes written as the reactant, but HCN is very reactive and dangerous. By using KCN in dilute acid, the same product can be formed as with HCN.
- If a chiral carbon centre is formed in the product, the final product mixture will be **racemic**, containing both enantiomers in a 50:50 ratio. This is because carbonyl groups are planar and there is equal chance of the :CN<sup>-</sup> nucleophile attacking the carbonyl group from above or below the plane producing two possible enantiomers in equal amounts.



### **Carboxylic Acids Acid-Base Reactions**

Carboxylic acids are able to act as weak acids and react with bases as any weak acid does

$$2 \times \underset{R}{\overset{\circ}{\text{C}}} \underset{OH}{\overset{\circ}{\text{OH}}} + Zn \longrightarrow \underset{R}{\overset{\circ}{\text{C}}} \underset{O}{\overset{\circ}{\text{O}}} Zn^{2+} + H_2$$

$$Carboxylic \ Acid \qquad Metal \qquad Zinc \ Carboxylate \qquad Hydrogen \qquad (salt)$$

$$R \xrightarrow{\overset{\circ}{\text{C}}} \underset{OH}{\overset{\circ}{\text{O}}} + NaOH \longrightarrow \underset{(salt)}{\overset{\circ}{\text{C}}} \underset{(salt)}{\overset{\circ}{\text{C}}} \underset{(salt)}{\overset{\circ}{\text{C}}} + H^{\bullet} \underset{(salt)}{\overset{\circ}{\text{C}}}$$

### **NOTES:**

 Salts formed by carboxylic acids are (usually) highly soluble in water and can be a useful source of conjugate bases for making buffer systems.



## Carboxylic Acids Reduction (to alcohols using LiAIH<sub>4</sub>)

**REACTANTS:** Carboxylic Acid and LiAlH<sub>4</sub> **CONDITIONS:** Dry ether (room temperature)

**PRODUCT(S):** Primary Alcohol **REACTION TYPE:** Reduction

**REACTION:** 

$$R-C \xrightarrow{O} OH \xrightarrow{\text{LiAlH}_4} R-C-OH$$

Carboxylic Acid

(primary) Alcohol

### **NOTES:**

• LiAlH<sub>4</sub> is used as the reducing agent as NaBH<sub>4</sub> isn't powerful enough to reduce the carboxylic acid.

Reducing agent can be represented as [H] when writing the reaction:

$$RCOOH + 4[H] \rightarrow RCH_2OH + H_2O$$

• Reaction must be carried out in dry ether (no water present) as LiAlH, reacts vigorously with water.



### ·Carboxylic Acids Substitution (to acyl chlorides)

REACTANTS: Carboxylic Acid and Phosphorus (V) Pentachloride, PCI<sub>5</sub>

**CONDITIONS:** Cold Temperature to Room Temperature

PRODUCT(S): Acyl Chloride

**REACTION TYPE:** Nucleophilic Substitution

REACTION:

$$R-C_{OH}^{0} + PCl_{5} \longrightarrow R-C_{Cl}^{0} + POCl_{3} + HCl$$

Carboxylic Acid

**Acyl Chloride** 

- White misty fumes of HCl are released, making this a useful reaction to identiy a carboxylic acid.
- The acyl chloride can be isolated from the reaction mixture using fractional distillation.



### Esters Esterification (carboxylic acid and alcohol)

**REACTANTS:** Carboxylic Acid and Alcohol

CONDITIONS: Heat under reflux and (concentrated) Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>) catalyst

PRODUCT(S): Ester

**REACTION TYPE:** Condensation, Esterification

REACTION:  $R-C \stackrel{\bigcirc{}0}{OH} + R^1-OH \stackrel{H_2SO_4(aq)}{\longrightarrow} R-C \stackrel{\bigcirc{}0}{\bigcirc} R^1 + H_2O$ Carboxylic Acid Alcohol Ester Water

### **NOTES:**

 Reaction is reversible (see hydrolysis of esters), so a (concentrated) acid catalyst is needed to force the position of equilibrium to the formation of ester.



### **Esters Hydrolysis**

**REACTANTS:** Ester

CONDITIONS: Warm, Aqueous (with dilute acid or alkali)

PRODUCT(S): Carboxylic Acid (or carboxylate salt) and Alcohol

**REACTION TYPE:** Hydrolysis

**REACTION(S):** 

$$R-C \xrightarrow{0}_{0-R^{1}} \xrightarrow{OH_{(aq)}^{-}} R-C \xrightarrow{0}_{0^{-}} + R^{1}-OH$$

Ester Carboxylate Ion Alcohol

$$R-C \xrightarrow{0 \atop 0-R^1} \xrightarrow{H^+_{(aq)}} R-C \xrightarrow{0 \atop 0-H} + R^1-OH$$

Ester Carboxylic Acid Alcohol

- If alkaline (OH) conditions are used, a carboxylate ion is formed and can be isolated by adding a dilute
  acid.
- Fats and oils are tri-esters and can be broken down into three fatty acid molecules (carboxylic acids) and one alcohol molecule (glycerol) by hydrolysis.
- Biodisel can be made by the reaction of oil (tri-ester) with methanol in the presence of an acid catalyst, forming methyl esters that can be used as a diesel fuel.



## Acyl Chlorides Addition-Elimination (H<sub>2</sub>0)

**REACTANTS:** Acyl Chloride and H<sub>2</sub>O **PRODUCT(S):** Carboxylic Acid and HCl

**REACTION TYPE:** Nucleophilic Addition-Elimination, *Hydrolysis of acyl chloride* 

REACTION:  $R \stackrel{O}{\subset} Cl \stackrel{H_2O}{\longrightarrow} R \stackrel{O}{\subset} OH + HCI$ 

Acyl Chloride Carboxylic Acid

### **NOTES:**

 Acyl chlorides are highly reactive and the reaction is vigorous, with heat given off (exothermic) and fumes of HCl released.



## Acyl Chlorides Addition-Elimination (alcohol)

**REACTANTS:** Acyl Chloride and Alcohol

PRODUCT(S): Ester and HCI

**REACTION TYPE:** Nucleophilic Addition-Elimination, Esterification

REACTION:  $R = C \setminus Cl$   $R = C \setminus Cl$ Acyl Chloride  $R = C \setminus Cl$   $R = C \setminus Cl$   $R = C \setminus Cl$ Ester

### **NOTES:**

Ester formed (esterification) has a sweet, fruity smell.



# Acyl Chlorides Addition-Elimination (NH<sub>3</sub>)

**REACTANTS:** Acyl Chloride and Ammonia

**PRODUCT(S):** Amide and Ammonium Chloride (salt) **REACTION TYPE:** Nucleophilic Addition-Elimination

**REACTION:** 

- Ammonia produces a primary amide and ammonium chloride salt when reacted with acyl chlorides.
- Primary amines produce a secondary amide and an alkyl ammonium chloride salt when reacted with acyl chlorides.
- Secondary amines produce a tertiary amide and an alkyl ammonium chloride salt when reacted with acyl chlorides.



### Acyl Chlorides Addition-Elimination (amine)

**REACTANTS:** Acyl Chloride and Amine (primary)

PRODUCT(S): (Secondary) Amide and Alkyl Ammonium Chloride

**REACTION TYPE:** Nucleophilic Addition-Elimination

### **NOTES:**

- Primary amines produce a secondary amide and an alkyl ammonium chloride salt when reacted with acyl chlorides.
- Secondary amines produce a **tertiary amide** and an alkyl ammonium chloride salt when reacted with acyl chlorides.
- Butylamine with ethanoyl chloride:

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> + CH<sub>3</sub>COCI → CH<sub>3</sub>CONHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> (N-butylethanamide) + HCI



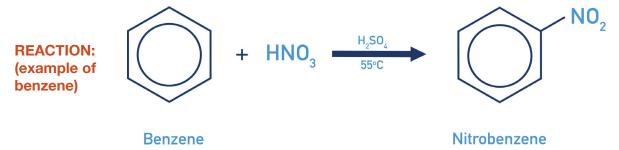
# Benzene Nitration (adding NO<sub>2</sub>)

REACTANTS: Benzene and (concentrated) Nitric Acid (HNO<sub>2</sub>)

CONDITIONS: (Concentrated) Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>)

PRODUCT(S): Nitrobenzene

**REACTION TYPE:** Electrophilic Substitution, *Nitration* 



### **NOTES:**

Nitronium ion is formed by the reaction of concentrated nitric acid with concentrated sulfuric acid.

$$HNO_3 + H_2SO_4 \longrightarrow H_2NO_3^+ + HSO_4^-$$

$$H_2NO_3^+ \longrightarrow NO_2^+ + H_2O$$

Nitronium Ion

H<sup>+</sup> ion removed from benzene ring combines with hydrogen sulfate (HSO<sub>4</sub><sup>-</sup>) ion to reform catalyst H<sub>2</sub>SO<sub>4</sub>.



## Benzene Acylation (with acyl chlorides)

**REACTANTS:** Benzene and Acyl Chloride **CONDITIONS:** Warm and AlCl<sub>3</sub> catalyst **PRODUCT(S):** (Aromatic) Ketone

**REACTION TYPE:** Electrophilic Substitution, *Acylation (Friedel Crafts)* 

#### NOTES:

Acylium (RCO+) ion is formed by reacting an acyl chloride with a halogen carrier (AlCl<sub>3</sub>).

H<sup>+</sup> ion removed from benzene ring combines with [AlCl<sub>4</sub>]<sup>-</sup> to reform AlCl<sub>3</sub> catalyst and form HCl.
 HCl. + AlCl<sub>3</sub>

Halogen Carrier

## **Benzene Alkylation (with halogenoalkanes)**

**REACTANTS:** Benzene and Halogenoalkane **CONDITIONS:** Warm and AlCl<sub>3</sub> (or AlBr<sub>3</sub>) catalyst

PRODUCT(S): Alkylbenzene

**REACTION TYPE:** Electrophilic Substitution, *Alkylation (Friedel-Crafts)* 



### **NOTES:**

• Alkyl (R+) ion is formed by reacting an acyl chloride with a halogen carrier (AlCl<sub>2</sub>).

H<sup>+</sup> ion removed from benzene ring combines with [AlCl<sub>4</sub>] to reform AlCl<sub>3</sub> catalyst and form HCl.

### Nitriles Reduction (to form primary amine)

**REACTANTS:** Nitrile and Reducing Agent - LiAlH<sub>4</sub>, or Hydrogen gas (H<sub>2</sub>(g)) **CONDITIONS:** Dry ether\* (if using LiAlH<sub>4</sub>), Nickel catalyst (if using H<sub>2</sub>(g))

PRODUCT(S): Amine

**REACTION TYPE:** Reduction, *Hydrogenation* 

**REACTION:** 

R-C≡N

or H<sub>2</sub>(g) / Ni

LiAlH,

R-CH<sub>2</sub>-NH<sub>2</sub>

**Nitrile** 

**Amine** 

- If H<sub>2</sub>(g) and a nickel catalyst is used, the reaction is an example of catalytic hydrogenation.
- \*Dry ether must be used with LiAIH<sub>4</sub> (LiAIH<sub>4</sub> reacts violently with water). To obtain the amine as a final product, dilute acid must be added to the inital product from reduction.

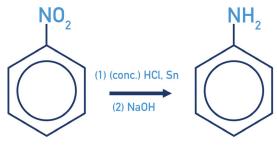


### Nitroarenes Reduction (to form aromatic amines)

REACTANTS: Nitroarene and (concentrated) Hydrochloric Acid (HCI), followed by NaOH

CONDITIONS: Tin catalyst PRODUCT(S): Aromatic Amine REACTION TYPE: Reduction

REACTION: (example of nitrobenzene)



**Nitroarene** 

Phenylamine

### **NOTES:**

When reacted with concentrated HCl, the nitroarene will form an ammonium ion -NH<sub>3</sub><sup>+</sup>. The aromatic amine can be obtained by adding dilute sodium hydroxide (to form -NH<sub>3</sub>).



### Polymers Condensation (from dicarboxylic acids and diols)

**REACTANTS:** Dicarboxylic Acid and Diol

PRODUCT(S): Polyester

**REACTION TYPE:** Condensation Polymerisation

Repeating Unit

- Polymer formed is a polyester due to ester link between one dicarboxylic acid group and one diol group.
- Condensation polymerisation as water is released when polymer is formed.
- Polyesters are broken apart into dicarboxylic acids and diols by hydrolysis reactions (addition of water) which means they are biodegradable (unlike addition polymers).



## **Phenol Bromination (Br<sub>2</sub>)**

**REACTANTS:** Phenol and Bromine water (Br<sub>2</sub>(aq))

PRODUCT(S): 2,4,6-tribromopenol

**REACTION TYPE:** Electrophilic Substitution, *Bromination* 

REACTION: (example of phenol)

Here are the second of the

Phenol 2,4,6-tribromophenol

- Bromine water changes from orange-brown to colourless and a white precipitate forms.
- Unlike with benzene, no halogen carrier catalyst is needed for the bromination of phenol. This
  is due to the increased electron density in the delocalised electron ring (from the -OH group),
  making phenol more reactive than benzene.

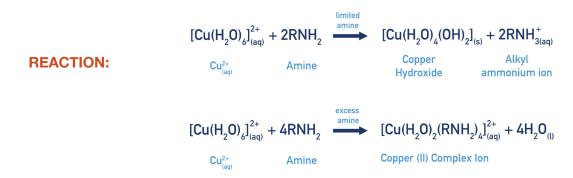


### **Amines Acting as Bases (with Cu<sup>2+</sup>(aq))**

**REACTANTS:** Amine and Copper (II) lons (Cu<sup>2+</sup>)

PRODUCT(S): Copper (II) Hydroxide and [Cu(RNH<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>

**REACTION TYPE:** Acid-Base, Ligand Substitution



- When added dropwise, amine acts a base. The nitrogen atom in amine has a lone pair of electrons that can act as a base and accept a H<sup>+</sup> ion from a water ligand in [Cu(H<sub>2</sub>O)<sub>e</sub>]<sup>2+</sup> aqua complex ion, forming blue, solid percipitate of Cu(OH)<sub>2</sub>.
- If higher amounts of amine are used, ligand substitution occurs and four amine groups swap places with four water ligands in aqua complex. Blue precipitate formed above redissolves.
- Butylamine with [Cu(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup>:

$$4\text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{NH}_{2} + [\text{Cu}(\text{H}_{2}\text{O})_{6}]^{2+} \rightarrow [\text{Cu}(\text{H}_{2}\text{O})_{2}(\text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{NH}_{2})_{4}]^{2+} + 4\text{H}_{2}\text{O}$$



### · Amines Acting as Bases (with acids)

**REACTANTS:** Amine and Acid

PRODUCT(S): Alkyl Ammonium Salt

**REACTION TYPE:** Acid-Base

REACTION: 
$$R-N-H$$
 + HCl  $\longrightarrow$   $\begin{bmatrix} H \\ R-N-H \end{bmatrix}$  Cl Amine Acid Alkyl ammonium salt

### **NOTES:**

Nitrogen atom in amine has lone pair of electrons that can act as a base and accept a H<sup>+</sup> ion
in an acidic solution, forming an alkyl ammonium salt (with the negative ion from the acid).

• Butylamine with hydrochloric acid:

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub> + HCI → [CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>NH<sub>3</sub>]<sup>+</sup>Cl<sup>-</sup> (butylammonium chloride)



## Amines Acting as Bases (with H<sub>2</sub>0)

**REACTANTS:** Amine and Water

PRODUCT(S): Alkyl Ammonium Ion and Hydroxide Ion (OH)

**REACTION TYPE:** Acid-Base

REACTION:  $R-N_{H}^{-H} + H_{2}^{-0} \longrightarrow R-N_{H}^{-H} + OH_{H}^{-1}$ Amine Water Alkyl Hydroxide ammonium ion

- Nitrogen atom in amine has lone pair of electrons that can act as a base and accept a H<sup>+</sup> ion from a water molecule, forming an alkyl ammonium ion and a hydroxide ion.
- Butylamine with water:

$$\mathbf{CH_{3}CH_{2}CH_{2}CH_{2}NH_{2}} + \mathbf{H_{2}O} \rightarrow \mathbf{[CH_{3}CH_{2}CH_{2}CH_{2}NH_{3}]^{+}} + \mathbf{[OH]^{-}}$$

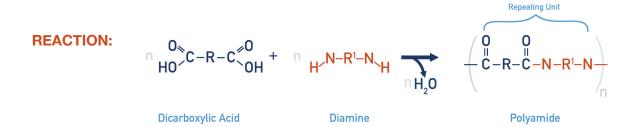


### Polymers Condensation (from dicarboxylic acids and diamines)

**REACTANTS:** Dicarboxylic Acid and Diamine

**PRODUCT(S):** Polyamide

**REACTION TYPE:** Condensation Polymerisation



- Polymer formed is a polyamide due to the amide group in the repeating unit (formed when one dicarboxylic acid reacts with a diamine).
- Condensation polymerisation as water is released when polymer is formed.
- Polyesters are broken apart into dicarboxylic acids and diamines by hydrolysis reactions (addition of water), which means they are biodegradable (unlike addition polymers).



### Amino Acids Condensation Polymerisation (form proteins)

**REACTANTS:** Amino Acids

**PRODUCT(S):** Polyamide (polypeptide)

**REACTION TYPE:** Condensation Polymerisation

**REACTION:** 

**Amino Acid** 

### Polyamide

- Polymer formed is a polyamide, often referred to as a polypeptide in biology.
- Polyamide chains formed by amino acids are used in nature to make up proteins.
- DNA is a 'code' used by organisms to give the correct amino acid sequence for a particular protein. A section of DNA that codes for a given protein is called a gene.

