A S CHEMISTRY

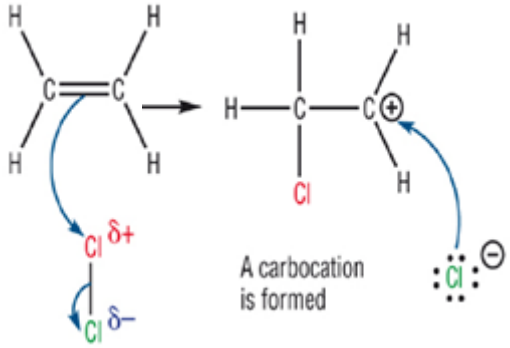
Summary of mechanisms

Type of reaction:

electrophilic addition

Electrophiles:

$H^{\delta+}$ in H_2 (Ni catalyst needed), $H^{\delta+}$ in H-X; $X^{\delta+}$ in X_2; $H^{\delta+}$ in $H_2O_{(g)}$ (conc H_3PO_4 cat needed); $H^{\delta+}$ in NH_3; $H^{\delta+}$ in H_2SO_4

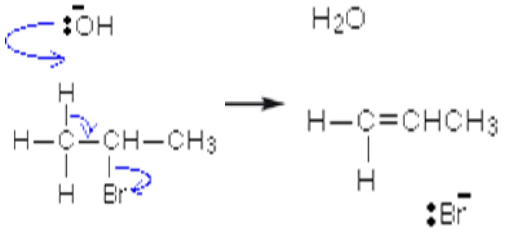


Type of reaction:

Elimination reaction

Examples:

Reaction of RX with hot, ethanolic metal hydroxide:



A S CHEMISTRY

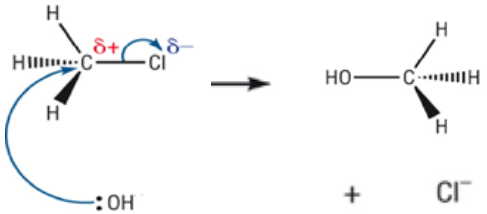
Summary of mechanisms

Type of reaction:

Nucleophilic subsitution/hydrolysis

Examples:

Haloalkanes with aqueous metal hydroxide (OH^- is the nucleophile); ethanol solvent required as haloalkanes do not mix with water.



Haloalkane with cyanide ion to produce a nitrile R-CN. Useful reaction as the chain length increases by one carbon atom.

Haloalkane with excess ammonia in ethanol under pressure. The product is a primary amine:

$R\text{-}X + 2NH_3 \rightarrow R\text{-}NH_2 + NH_4^+X^-$

A 2 CHEMISTRY

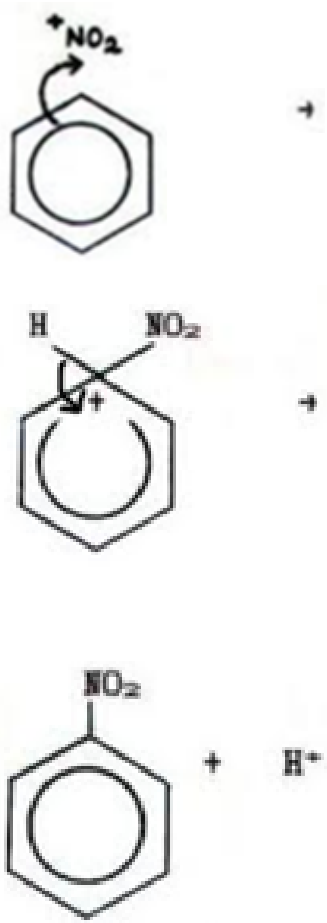
Nitration of Benzene

Type of reaction:

electrophilic substitution

Electrophile:

NO_2^+



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Nitration of Benzene

Formation of electrophile:

Concentrated nitric acid reacts with concentrated sulfuric acid catalyst at 55°C:

$HNO_3 + H_2SO_4 \rightarrow$

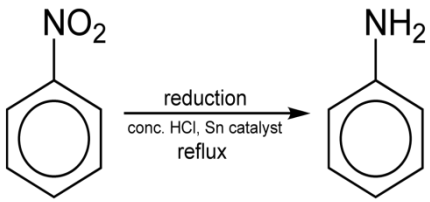
$H_2NO_3^+ + HSO_4^-$

$H_2NO_3^+ \rightarrow NO_2^+ + H_2O$

Reduction of nitrobenzene to phenylamine:

$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$

NOTE: Using tin and conc HCl produces the salt $C_6H_5NH_3^+Cl^-$. $NaOH_{(aq)}$ is added to remove the salt and form phenylamine



A 2 CHEMISTRY

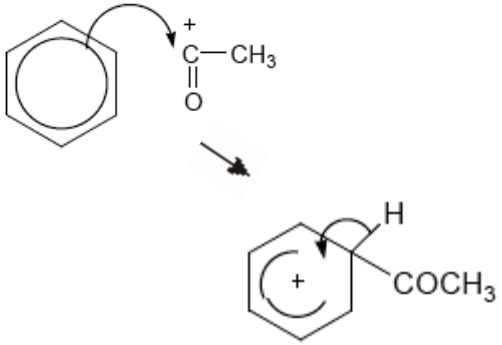
Friedel-Crafts Acylation

Type of reaction:

electrophilic substitution

Electrophile:

$RC^{+}=O$



Note: if you are asked to add an alkene to the benzene ring, you need to add HCl first to create a haloalkane. The haloalkane will then react with the carrier $AlCl_3$ to produce an electrophile:

$CH_2=CH_2 + HCl \rightarrow CH_3CH_2Cl$

$CH_3CH_2Cl + AlCl_3 \rightarrow$
$CH_3CH_2^{+} + AlCl_4^{-}$

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Friedel-Crafts Acylation

Formation of electrophile:

$AlCl_3/FeBr_3$ Halogen carrier in warm conditions (Al has only 6 electrons in $AlCl_3$ and can accept 2 more electrons forming a co-ordinate bond with Cl^-)

$AlCl_3 + RCOCl \rightarrow$

$AlCl_4^- + RC^{+}=O$

Example equation for acylation of benzene:

$C_6H_6 + CH_3COCl \rightarrow$

$C_6H_5COCH_3 + HCl$

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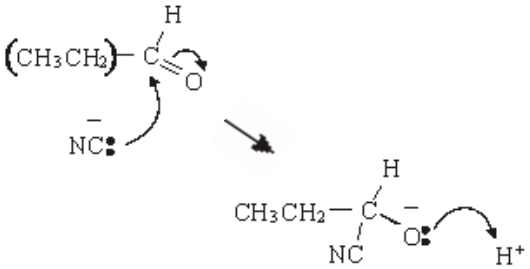
Type of reaction:

nucleophilic addition

Nucleophile:

$^-$:CN



$CH_3CHO + HCN \rightarrow CH_3CH(OH)CN$

Note: HCN is highly toxic and has to be prepared in situ. It is created by reacting KCN with dilute HCl which produces HCN.

Further reaction:

The 2-hydroxypropanenitrile can be reacted with dilute HCl, which produces 2-hydroxypropanoic acid (lactic acid) and ammonium chloride:

$CH_3CH(OH)CN + HCl + 2H_2O \rightarrow CH_3CH(OH)COOH + NH_4Cl$

Chain lengthening

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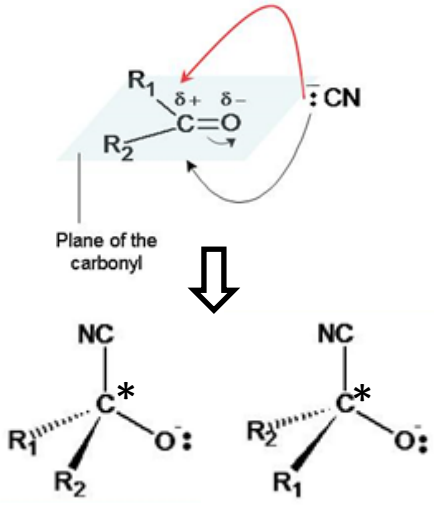
Optical activity

The reaction produces a racemic mixture as the nucleophile can attack from above or below the planar >C=O group with equal likelihood:



Importance or reaction:

Chain length greater

Optical isomers produced

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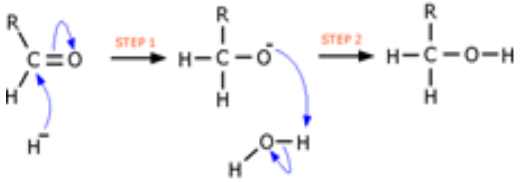
Reduction of carbonyls

Type of reaction:

Nucleophilic addition.

Nucleophile:

$H:^-$



Equation:

$RCHO + 2[H] \rightarrow RCH_2OH$

The reaction will also turn ketones into secondary alcohols.

The reducing agent is $NaBH_4$ in warm aqueous solution or $LiAlH_4$ in dry ether which are represented as 2[H] in the equation. The first H is produced by the reducing agent, the second one by the solvent.

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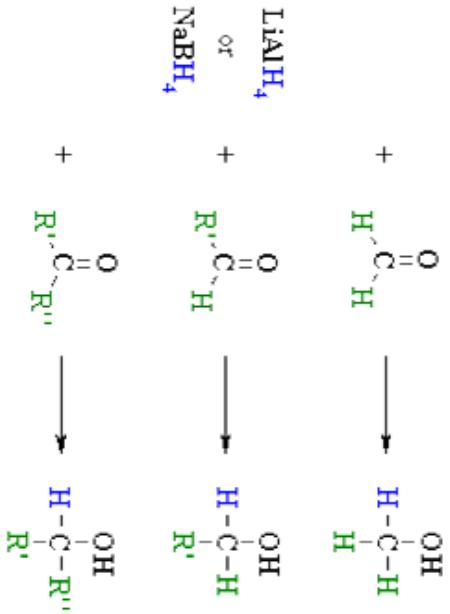
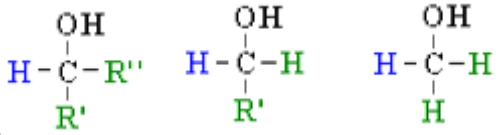
Reduction of carbonyls

Formation of alcohols:



Optical isomers formed?



Yes if R'& R" differ	No	No

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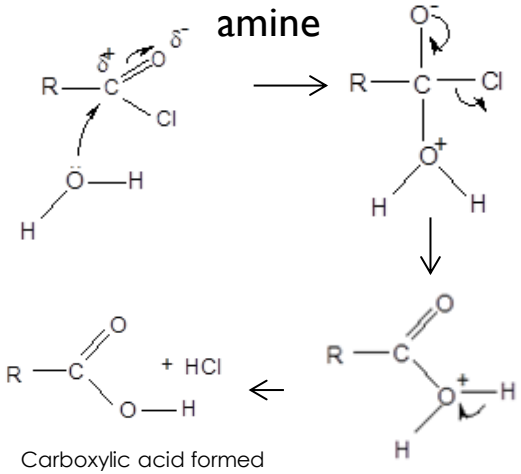
Type of reaction:

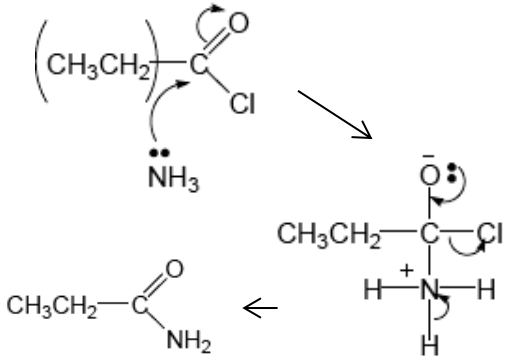
nucleophilic addition-elimination reaction

Nucleophiles:

water, ammonia, alcohol, amine



Carboxylic acid formed



1° amide formed

Acylation

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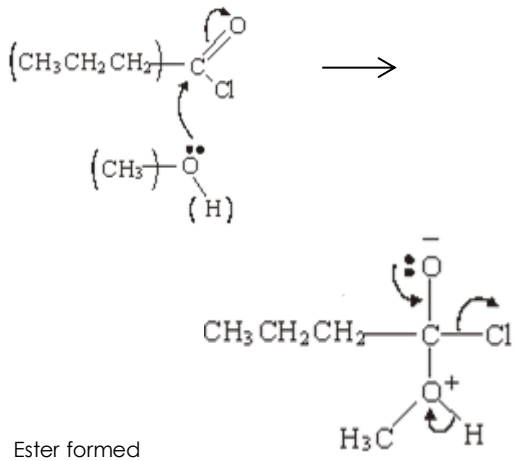
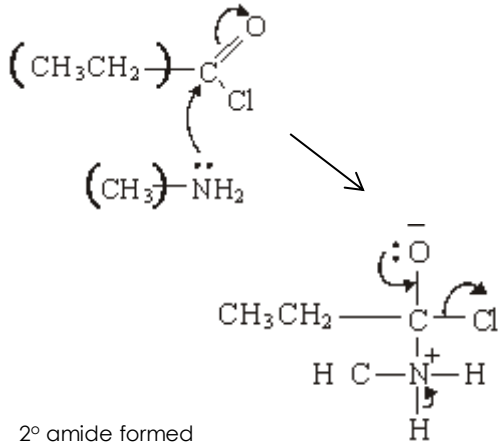


Ester formed



2° amide formed

Naming acyl chlorides:

Alkanoyl chloride. E.g. ethanoyl chloride is CH_3COCl; propanoyl chloride is CH_3CH_2COCl

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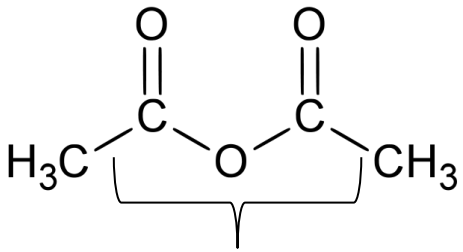
General formula:

RCOOCR'

Examples:

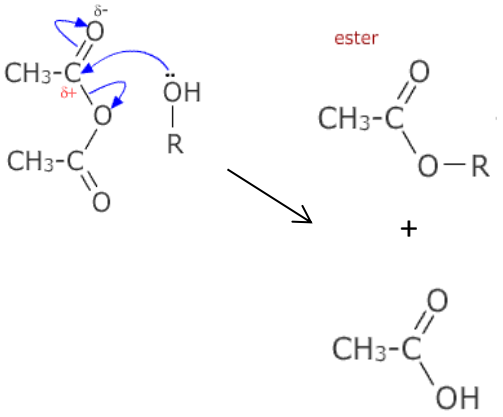
Ethanoic anhydride



Anhydride group

Reactions:

Anhydrides react in the same way as acyl chlorides.



Acid Anhydrides

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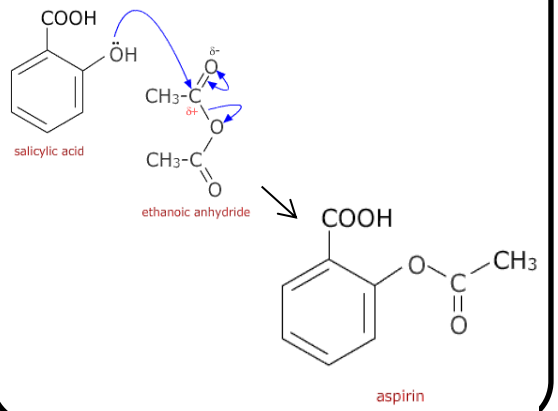
Reasons for using acyl chlorides and acid anhydrides:

Reactions are faster, produce a better yield and occur at lower temperatures.

Reasons for acid anhydrides instead of acyl chlorides:

Acid anhydrides are cheaper, less corrosive, less reactive with water and produce a safer by-product (which is ethanoic acid rather than hydrogen chloride). The reaction is also slower than with acyl chlorides and therefore easier to control on a large scale in industry.

An important synthesis reaction using ethanoic anhydride:



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General formula:

Primary amine: RNH_2

Secondary amine: RR'NH

Tertiary amine: RR'R''N

Examples:

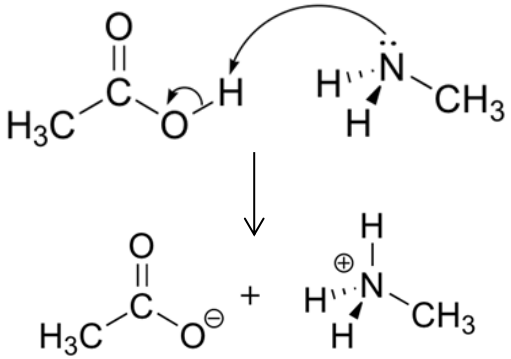
Ethylamine $CH_3CH_2NH_2$

Ethylmethylamine $CH_3CH_2(CH_3)NH$

Trimethylamine $(CH_3)_3N$

Type of reaction:

Acid-base reaction (methylammonium salt formed)



(Methylammonium ethanoate)

Amines

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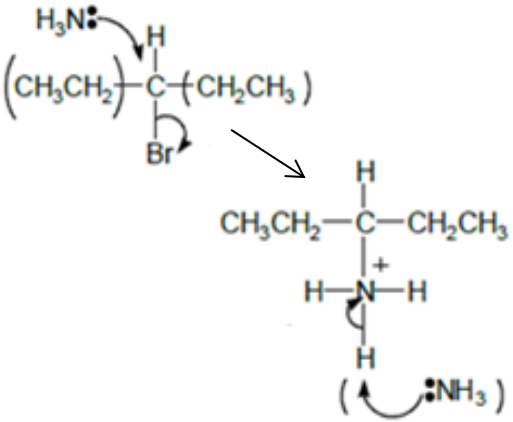
Forming amines:

Nucleophilic substitution



Note:

Excess ammonia + haloalkane → mainly primary amine + ammonium salt

If ammonia is not used in excess, further substitution reactions will take place and a mixture of 1°, 2°, 3° and quarternary amines will be formed. The amines need to be separated by fractional distillation.

Forming 1° amines:

Reduction of nitriles

1. $RX + {}^{-}CN \rightarrow R\text{-}CN + X^{-}$
2. $R\text{-}CN + 2H_2 \rightarrow R\text{-}CH_2NH_2$

Step 1 requires cyanide ions in aqueous ethanol

Step 2 requires a Nickel catalyst