Electrophilic Substitution

ckchemistry.co.uk

ckchemistry.co.uk

Example equations

$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$

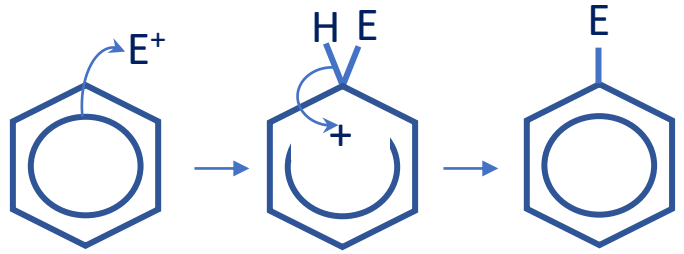
$C_6H_6 + CH_3Cl \rightarrow C_6H_5CH_3 + HCl$

$C_6H_6 + CH_3COl \rightarrow C_6H_5OCH_3 + HCl$

Which functional groups?

Arenes:
Electrophiles accept electrons from the delocalised electron ring and substitute a H atom which is lost as H^+

Mechanism



E^+ = the electrophile, e.g. Cl^+, NO_2^+, CH_3^+

Important notes

Formation of electrophile using $AlCl_3$
$AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$
$AlCl_3 + CH_3Cl \rightarrow AlCl_4^- + CH_3^+$

Formation of NO_2^+ electrophile
$H_2SO_4 + HNO_3 \rightarrow NO_2^+ + H_2O + HSO_4^-$

Phenol does not require a catalyst to react with halogens and only requires dilute HNO_3 for nitration – multiple substitutions occur

Reagents/conditions

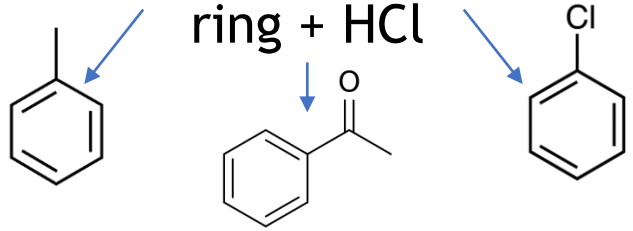
Halogen
Haloalkane
Acyl Chloride

Use a 'halogen carrier' catalyst: $AlCl_3$ (or $FeBr_3$)

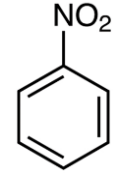
Nitration: Conc H_2SO_4 and conc HNO_3, below 55°C to prevent further substitutions

Products of the reaction

Substituted benzene ring + HCl



Nitrobenzene and water



Reduction

Example equations

$CH_3CHO + 2[H] \rightarrow CH_3CH_2OH$

$CH_3COCH_3 + 2[H] \rightarrow CH_3CHOHCH_3OH$

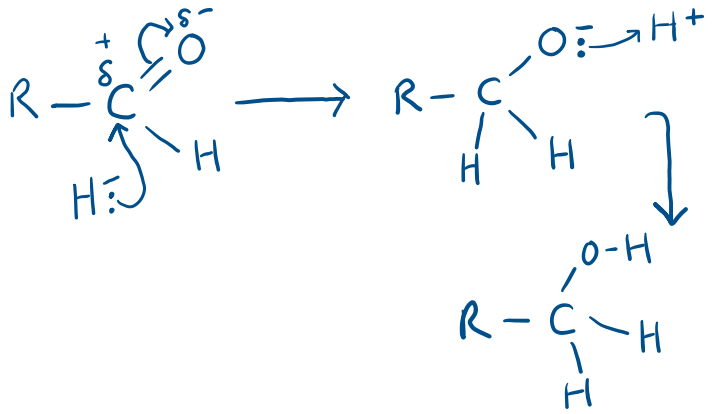
$CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2NH_2$

Which functional groups?

Aldehydes or ketones:
Form primary or secondary alcohols
Nitriles: form amines
Nitrobenzene: forms aminobenzene

Mechanism*

**Only C=O addition mechanism needed*



ckchemistry.co.uk

Important notes

The reducing agents $LiAlH_4$ or $NaBH_4$ provide **hydride ions**, H^-. These attack the δ+ carbon.
$LiAlH_4$ is a **strong reducing agent** that can reduce nitriles and carboxylic acids as well as ketones and aldehydes. $NaBH_4$ only reduces aldehydes and ketones.

Reagents/conditions

Aldehyde/ketone: $NaBH_4$ or $LiAlH_4$, ether solvent, followed by dilute acid (to provide H^+ ions)
Nitrile: $LiAlH_4$ as above or H_2 with nickel catalyst
Nitrobenzene: Tin and concentrated HCl

Products of the reaction

For C=O reduction primary or secondary alcohols are made (you can't make an aldehyde from a carboxylic acid).

For –CN and $–NO_2$ amines are made.

Elimination

Example equations

$CH_3CH_2Br \rightarrow CH_2CH_2 + HBr$

$CH_3CH_2OH \rightarrow CH_2CH_2 + H_2O$*

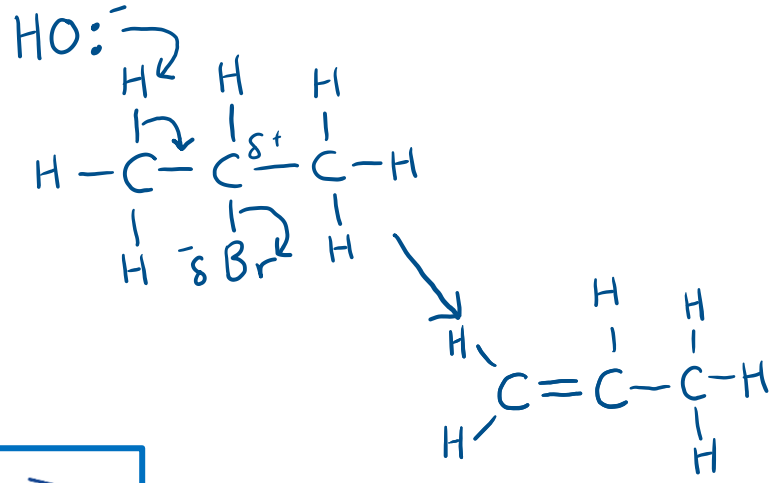
**This is more commonly known as dehydration*

Which functional groups?

Haloalkanes:
Molecule loses H from the carbon adjacent to the C-Hal bond, then loses the halogen atom to form a C=C bond

Mechanism*

**Needed for AQA*



Important notes

Elimination is the opposite to an addition reaction. OH^- ions act as a **base** to remove H^+ from carbon adjacent to C-Hal bond.
The solvent is important: KOH/NaOH in aqueous solvent will result in nucleophilic substitution to produce an alcohol from a haloalkane.

Reagents/conditions

Haloalkanes:
KOH or NaOH dissolved in ethanol, heated under reflux
Alcohols (dehydration):
Heated with concentrated H_2SO_4 or H_3PO_4

Products of the reaction

The product is always an **alkene** plus a small molecule.
Different structural isomers can form: H^+ can be removed from either side of the C-Hal. For example, 2-bromobutane could produce but-1-ene or but-2-ene (which also has stereoisomers!).

Condensation

Example equations

$CH_3COOH + CH_3CH_2OH \rightarrow CH_2COOCH_2CH_3 + H_2O$

$CH_3COCl + CH_3CH_2OH \rightarrow CH_2COOCH_2CH_3 + HCl$

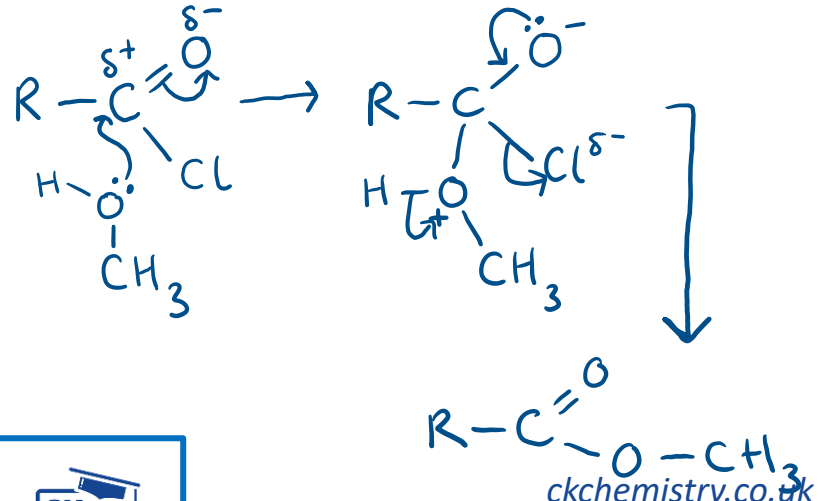
$CH_3COCl + CH_3NH_2 \rightarrow CH_2CONHCH_3 + HCl$

Which functional groups?

Alcohol and carboxylic acid
Alcohol and acyl chloride
Amine and acyl chloride
These molecules join together by loss of a small molecule such as H_2O or HCl. The products are esters or amides.

Mechanism*

**Acyl chloride mechanism needed for AQA*



Important notes

Reaction between carboxylic acids and alcohols is **reversible** so lower yield.

Acyl chlorides are **highly reactive** so give a higher yield, but you have to keep them away from water (they will react to form RCOOH) and the reaction produce fumes of HCl.

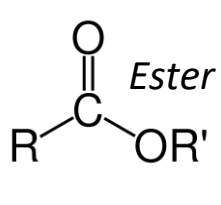
Reagents/conditions

Alcohol and carboxylic acid: reflux with a catalyst of conc H_2SO_4

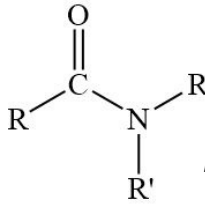
Acyl chloride with amine or alcohol: room temperature, dry ether solvent

Products of the reaction

Organic products are **esters** or **amides**.
The reaction also produces a small molecule – usually water or HCl.



Ester



Amide
(R' and R'' can be H or carbon)

Hydrolysis

Example equations

$CH_2COOCH_2CH_3 + H_2O \rightarrow CH_3COOH + CH_3CH_2OH$

$CH_2COOCH_2CH_3 + NaOH \rightarrow CH_3COONa + CH_3CH_2OH$

$CH_2COONHCH_3 + NaOH \rightarrow CH_3COONa + CH_3NH_2$

Which functional groups?

Esters or amides:
Bond between C=O carbon and O (ester) or N (amide) breaks to form two organic molecules
(Also haloalkanes and nitriles – see right)

Other examples

Haloalkanes: in hot water or aqueous NaOH the C-Hal bond breaks to produce an alcohol (nucleophilic substitution)
Nitriles: the CN bond can be broken using either hot dilute acid or alkali, to form a carboxylic acid and ammonia.

Important notes

Hydrolysis = breaking bonds using water
Acid hydrolysis: the acid acts as a catalyst and the reaction is reversible
Alkaline hydrolysis: NaOH is a reagent and the reaction goes to completion – the carboxylate salt is formed

Reagents/conditions

Acid hydrolysis: dilute acid
Alkaline hydrolysis: dilute aqueous NaOH
Both require reflux

Products of the reaction

Acid hydrolysis:
Ester: RCOOH + ROH
Amide: RCOOH + RNH_3^+

Alkaline hydrolysis:
Ester: $RCOO^-$ + ROH
Amide: $RCOO^-$ + RNH_2