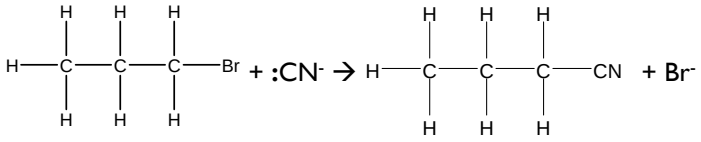
6.2.4 Carbon–carbon bond formation

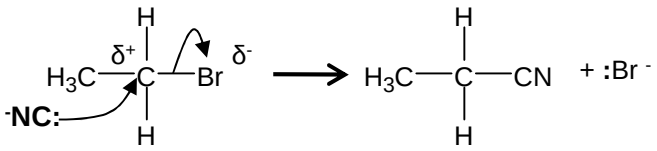
Various reactions are used the involve formation of a C–C bond in synthesis to increase the length of a carbon chain

Nucleophilic substitution of haloalkanes with cyanide ions

Change in functional group: haloalkane → nitrile
Reagent: KCN dissolved in **ethanol/water mixture**
Conditions: Heating under reflux
Mechanism: Nucleophilic substitution
Type of reagent: Nucleophile, $:CN^-$



1-bromopropane butanenitrile

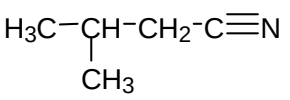


This reaction increases the length of the carbon chain (which is reflected in the name) In the above example butanenitrile includes the C in the nitrile group.

Naming Nitriles

Nitrile groups have to be at the end of a chain. Start numbering the chain from the C in the CN

CH_3CH_2CN : propanenitrile



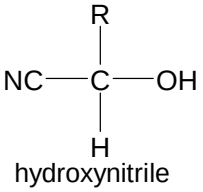
3-methylbutanenitrile

Note the naming: but**ane**nitrile and not butannitrile.

Addition of hydrogen cyanide to carbonyls to form hydroxynitriles

Reaction: carbonyl → hydroxynitrile
Reagent: sodium cyanide (NaCN) and dilute sulfuric acid.
Conditions: Room temperature and pressure
Mechanism: nucleophilic addition

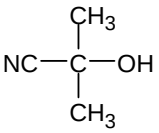
The NaCN supplies the nucleophilic CN^- ions. The H_2SO_4 acid supplies H^+ ions needed in second step of the mechanism



hydroxynitrile

CH_3COCH_3 + HCN → $CH_3C(OH)(CN)CH_3$

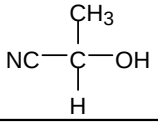
2-hydroxy-2-methylpropanenitrile



When naming hydroxy nitriles the CN becomes part of the main chain

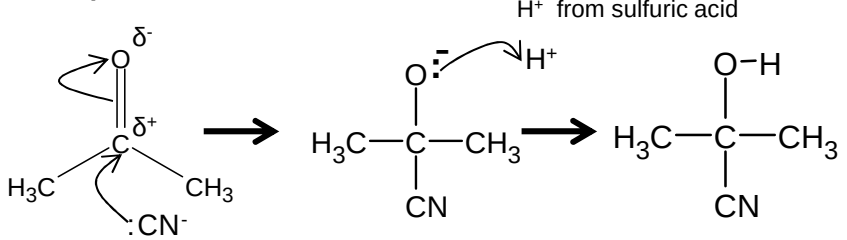
CH_3CHO + HCN → $CH_3CH(OH)CN$

2-hydroxypropanenitrile



We could use HCN for this reaction but it is a toxic gas that is difficult to contain. The KCN/NaCN are still, however, toxic, because of the cyanide ion.

Nucleophilic Addition Mechanism



The nitriles made in the previous two reactions can then be converted into other functional groups by the following reactions

Preparing amines from nitriles

Reduce **nitrile to amine** by using **$LiAlH_4$ in ether** or by reducing with H_2 using a Ni catalyst

$CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2NH_2$

This is a reduction reaction

Preparing carboxylic acids from nitriles

Hydrolysing nitriles by reacting them with strong acids will produce a carboxylic acid

$CH_3CH_2CN + H^+ + 2H_2O \rightarrow CH_3CH_2CO_2H + NH_4^+$

This is a hydrolysis reaction

C-C bonds can be added to aromatic compounds through the Friedal Craft's Reactions met in 6.1.1 aromatic compounds

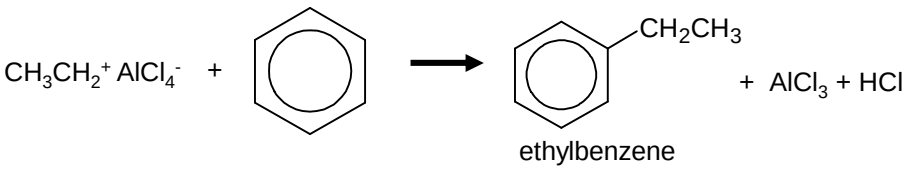
Friedel Crafts Alkylation

Change in functional group: benzene → alkylbenzene
Reagents: chloroalkane in the presence of anhydrous aluminium chloride catalyst
Conditions: heat under reflux
Mechanism: Electrophilic substitution

Any chloroalkane can be used RCl where R is any alkyl group Eg $-CH_3$, $-C_2H_5$. The electrophile is the R^+.

Formation of the electrophile.
$AlCl_3 + CH_3CH_2Cl \rightarrow CH_3CH_2^+ AlCl_4^-$

Overall Equation for reaction



ethylbenzene

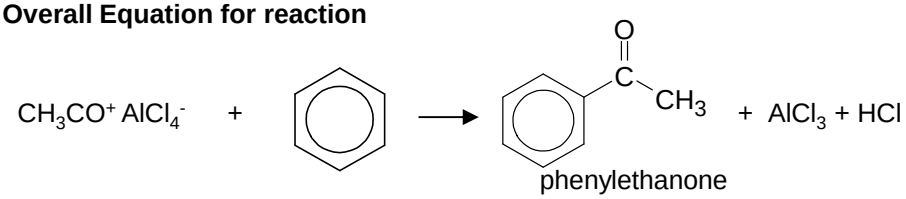
Friedel Crafts Acylation

Change in functional group: benzene → phenyl ketone
Reagents: acyl chloride in the presence of anhydrous aluminium chloride catalyst
Conditions: heat under reflux (50^OC)
Mechanism: Electrophilic substitution

Any acyl chloride can be used RCOCl where R is any alkyl group e.g. $-CH_3$, $-C_2H_5$. The electrophile is the RCO^+.

Equation for Formation of the electrophile.
$AlCl_3 + CH_3COCl \rightarrow CH_3CO^+ AlCl_4^-$

Overall Equation for reaction



phenylethanone

These are important reactions in organic synthesis because they introduce a reactive functional group on to the benzene ring