Organic Chemistry (AS)

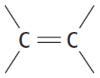
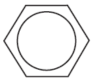
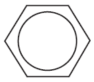
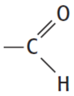
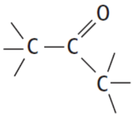
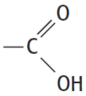
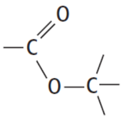
Structure of functional group	General formula	Name of an example	Structural formula of the example
alkenes, 	C_nH_{2n}	ethene	$CH_2{=}CH_2$
arenes, 	C_6H_5—	benzene	
halogenoalkanes, —X, where X = F, Cl, Br, I	$C_nH_{2n+1}X$	chloromethane	CH_3Cl
alcohols, —OH	$C_nH_{2n+1}OH$	methanol	CH_3OH
aldehydes, 	$C_nH_{2n+1}CHO$	ethanal	CH_3CHO
ketones, 	$C_nH_{2n+1}COC_mH_{2m+1}$	propanone	CH_3COCH_3
carboxylic acids, 	$C_nH_{2n+1}COOH$	ethanoic acid	CH_3COOH
esters, 	$C_nH_{2n+1}COOC_mH_{2m+1}$	ethyl ethanoate	$CH_3COOC_2H_5$
amines, —NH_2	$C_nH_{2n+1}NH_2$	methylamine	CH_3NH_2
nitriles, —C≡N	$C_nH_{2n+1}CN$	ethanenitrile	CH_3CN

Table 14.2 Some common functional groups.

Alkane (saturated hydrocarbon):

- **Combustion** (complete and incomplete)
- **Free-radical substitution**
- **Cracking** (elimination): alkane → alkene + alkane (no oxygen, high temperature, zeolite catalyst)

Alkene (unsaturated hydrocarbon):

- **Addition** (electrophilic addition):
    - Hydrogen (H_2 (g)): CH2=CH2 + H2 → CH3CH3 (140℃, Ni catalyst)
    - Steam (H2O (g)): CH2=CH2 + H2O → CH3CH2OH (330℃, 6MPa, H3PO4)
    - Hydrogen Halides (HX (aq)): CH2=CH2 + HBr → CH3CH2Br (conc. HX, r.t.p.)
    - Halogens (X2 (aq)): CH2CH2 + Br2 → CH2BrCH2Br (r.t.p.
        - Test for the presence of C=C bond (decolourisation of Br2)

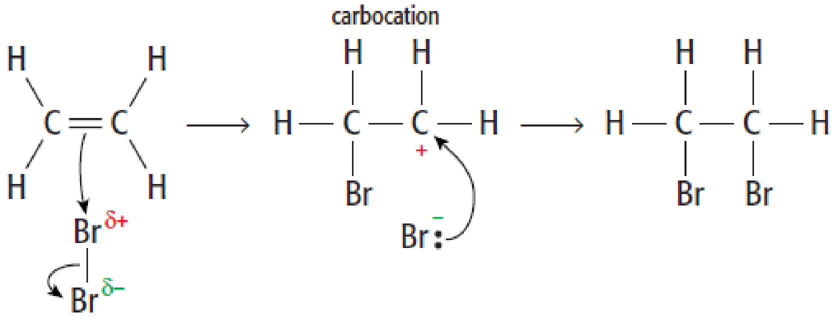
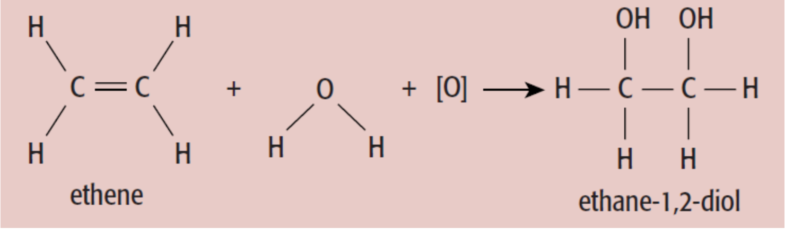


Figure 15.16 The mechanism of electrophilic addition of bromine to ethene.

- **Oxidation**:
  - Cold Dilute Acidified Manganate(VII) Solution (KMnO4)



  - Hot Concentrated Acidified Manganate(VII) Solution (KMnO4)

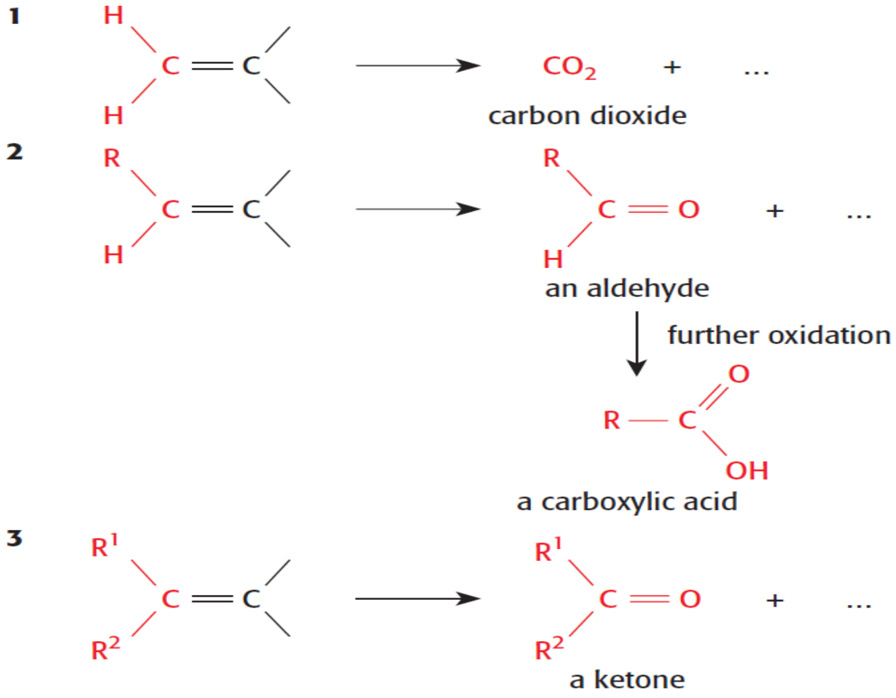


Figure 15.17 Oxidation with hot, concentrated manganate(VII) solution.

- Addition Polymerisation

Halogenoalkane:

- **Subsitution** (nucleophilic substitution):
  - Aqueous Alkali (OH$^-$ (aq)): CH3CH2Br + NaOH → CH3CH2OH + NaBr / CH3CH2Br + H2O → CH3CH2OH + HBr (Heated under reflux)
    - Alcohol produced
  - KCN (CN$^-$ (in ethanol)): CH3CH2Br + CN$^-$ → CH3CH2CN + Br$^-$ (heated under reflux)
    - Addition of carbon atom
    - Nitrile produced
  - Ammonia (NH3 (in ethanol)): CH3CH2Br + NH3 → CH3CH2NH2 + HBr (heated)
    - Alkylamine produced
- Mechanism:

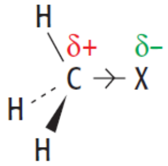


Figure 16.3 The carbon–halogen bond is polarised.

- Primary Halogenoalkane (S$_N$2): S stands for substitution, N stands for nucleophilic, 2 is the rate of reaction; depends on both conc. of halogenoalkane and hydroxide ions present.

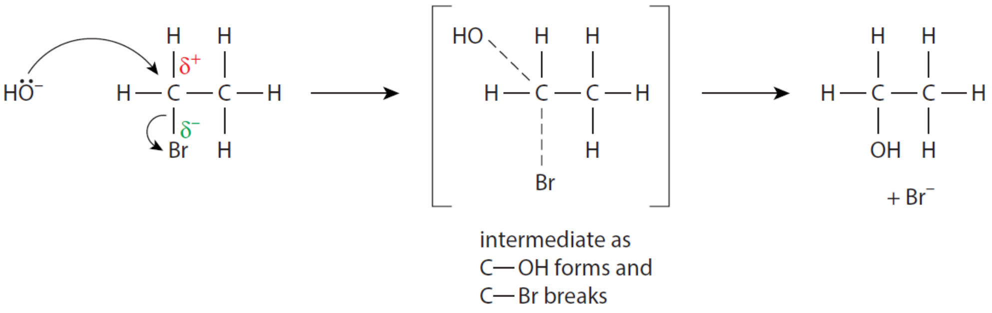

intermediate as C—OH forms and C—Br breaks

Figure 16.4 The mechanism of nucleophilic substitution in a primary halogenoalkane.

- Tertiary halogenoalkanes (S$_N$1): two-step mechanism, where a carbocation is produced, due to the stability of the carbocation – due to the inductive effect of the alkyl groups attached to the C atom; depends on only the conc. of the halogenoalkane (slow-step)

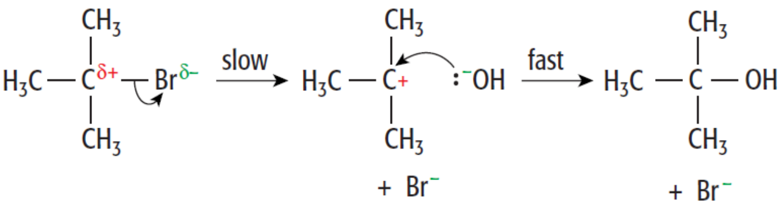
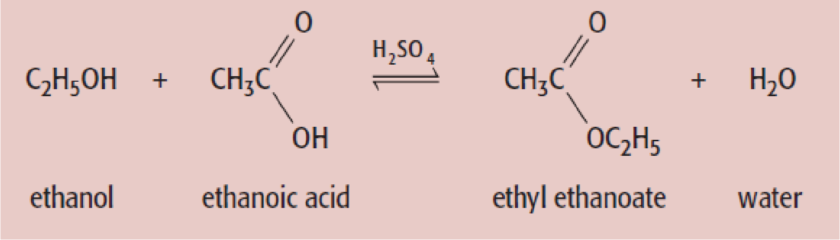


Figure 16.6 The mechanism of nucleophilic substitution in a tertiary halogenoalkane.

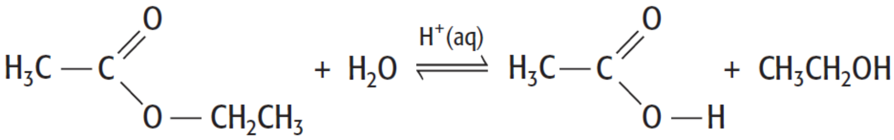
  - Secondary halogenoalkane (S_N1 and S_N2)
- **Elimination**: CH3CHBrCH3 + NaOH(ethanol) → CH2=CHCH3 + H2O + NaBr
  - Ethanolic sodium hydroxide as the reagent
  - HBr eliminated from the 2-bromopropane
  - Propene produced

Alcohol:

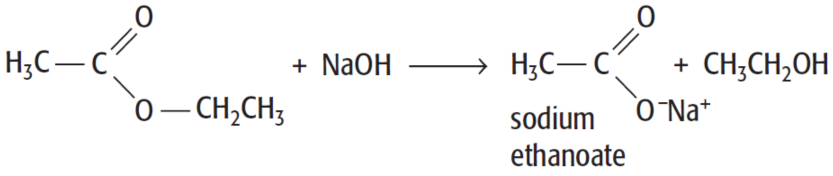
- Hydrogen bonding causes the higher boiling point than expected compared to other organic molecules with similar relative molecular masses.
- **Combustion**: C2H5OH + 3O2 → 2CO2 + 3H2O
- **Substitution** (forming halogenoalkane (nucleophilic substitution)):
  - CH3CH2OH + HCL → CH3CH2Cl + H2O
    - Chloroalkane produced
    - Occur due to the partial positive charge of the C atom bonded to the hydroxyl group
    - Carbon atom open to nucleophilic attack (by the partially negative halogen atom in the hydrogen halide)
    - Dry HCl(g) made *in situ*: NaCl + H2SO4 → NaHSO4 + HCl
  - C2H5OH + SOCl2 → C2H5Cl + HCl(g) + SO2(g)
    - Sulfur dichloride oxide as the reagent
  - C2H5OH + PCl5 → C2H5Cl +HCl(g) + POCl3
    - At room temp.
    - Phosphorus halides as the reagent
    - Test for hydroxyl group: steamy fumes of HCl observed
  - 3C2H5OH + PCl3 → 3C2H5Cl + H3PO3
    - Requires heating
    - Phosphorus (III) chloride as the reagent
  - 3C2H5OH + PI3 → 3C2H5I + H3PO3
    - Requires heating with the alcohol
    - Phosphorus (III) halide made *in situ* using red phosphorus and bromine or iodine
- **Substitution with sodium metal**: C2H5OH + Na → $C2H5O^{-}Na^{+}$ + H2(g)
  - O-H bond in the alcohol breaks instead of C-O
  - Sodium alkoxide produced - basic ionic compound (sodium ethoxide in the ex.)
  - H2 gas given off
- **Esterification**: CH3CH2COOH + CH3CH2OH ↔ CH3CH2COOC2H5 + H2O
  - Ethyl propanoate produced
  - Reagents heated under reflux with a strong acid catalyst (conc. H2SO4)
  - Esters produced usually have sweet, fruity smell
  - Esters used in artificial flavouring, perfumes and solvents



- **Hydrolysis of Esters**:
  - With an acid (H2SO4) – catalyst: Reverses the preparation of an ester from an alcohol and a carboxylic acid.
    - Reaction will be reversible and an equilibrium mixture is established.

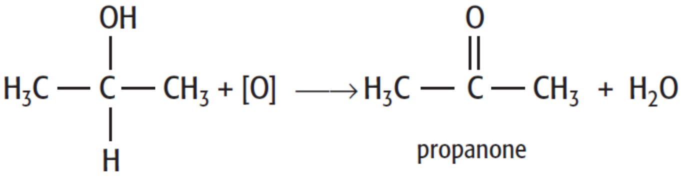


  - With an alkali (NaOH(aq)): fully hydrolysed
    - An alcohol and the sodium salt of the carboxylic acid produced

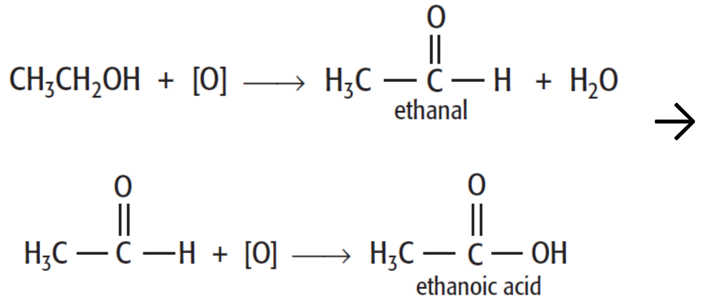


- **Dehydration** (Elimination): CH3CH2OH → CH2=CH2 + H2O
  - Heating required
  - Catalyst: Al2O3 (s) - powder or H2SO4
  - Alkene produced

- **Oxidation** (using potassium dichromate(VI) solution, K2Cr2O7, acidified with dilute H2SO4 – Orange Cr2O7^{2-}(aq) reduced to green Cr^{3+}(aq), warming of reaction mixture required):
  - Tertiary alcohol: No change, remains orange
  - Secondary alcohol: Oxidised to form a ketone, turns green



  - Primary alcohol: Oxidised to an aldehyde (distillation), where further oxidation forms carboxylic acid – achieved by reflux with excess acidified potassium dichromate(VI):



$$CH_3CH_2OH + [O] \longrightarrow \underset{\text{ethanal}}{H_3C-\overset{\overset{O}{||}}{C}-H} + H_2O \rightarrow$$

$$H_3C-\overset{\overset{O}{||}}{C}-H + [O] \longrightarrow \underset{\text{ethanoic acid}}{H_3C-\overset{\overset{O}{||}}{C}-OH}$$

Nitrile:

- **Hydrolysis**: CH3CH2CN + HCl + 2H2O → CH3CH2COOH + NH4Cl
  - Alkanenitrile to carboxylic acid
  - Refluxed with dilute HCl
- **Reduced to an amine** (NH2): –CN + 4[H]→ –CH2NH2
  - Na & ethanol

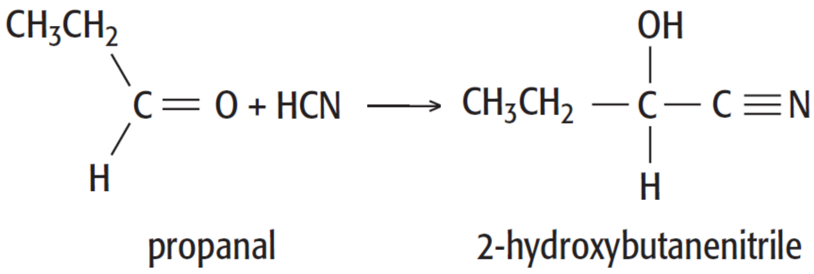
Carboxylic Acid:

- **Dissociation**: CH3COOH(aq) ↔ $CH3COO^-$(aq) + H^+(aq)
  - alkanoate ions produced
- **Neutralisation** (Alkali): CH3COOH + NaOH → CH3COONa + H2O
- **Reactive metals**: 2CH3COOH + Mg → (CH3COO)2Mg + H2
  - Salt (magnesium ethanoate) and H2(g) produced
- **Carbonates**: 2CH3COOH + K2CO3 → 2CH3COOK + H2O + CO2
  - Salt (potassium ethanoate), H2O and CO2 produced
- **Reduction**: CH3COOH + 4[H] → CH3CH2OH + H2O
  - Reducing agent: LiAlH4 (lithium tetrahydridoaluminate) – dry ether at r.t.p (v. Reactive)
  - Primary alcohol produced

Aldehyde & Ketone:

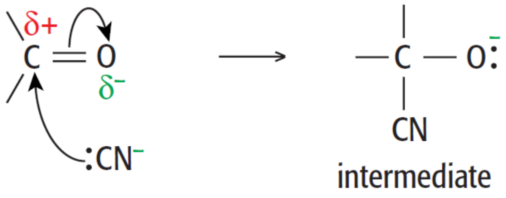
- **Reduction** (reducing agents: NaBH4 (sodium tetrahydridoborate) Or LiAlH4 (lithium tetrahydridoaluminate)):
  - Aldehyde + reducing agent → primary alcohol
    - CH3CHO + 2[H] → CH3CH2OH
      - Ethanal into ethanol
  - Ketone + reducing agent → Secondary alcohol
    - CH3COCH3 + 2[H] → CH3CH(OH)CH3
      - Propanone into propan-2-ol
- (Warming the aldehyde or ketone with an aqueous alkaline solution of sodium tetrahydridoborate)

- (Adding lithium tetrahydridoaluminate dissolved in a dry ether, such as diethyl ether, at r.t.p. As it reacts vigorously with water and a more powerful reducing agent compared to sodium tetrahydridoborate)
- **Nucleophilic addition with HCN** (The HCN is generated in situ (in the reaction vessel) by the reaction of sodium cyanide, NaCN, and dilute sulfuric acid):

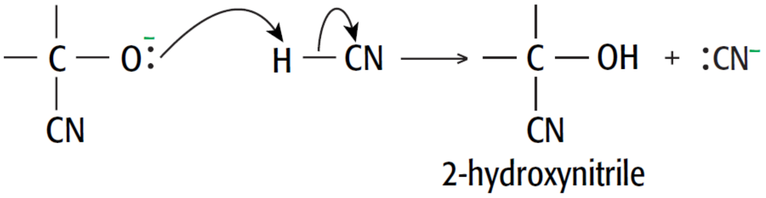


  - Increases the length of the hydrocarbon chain
- Mechanism of Nucleophilic addition:

First step

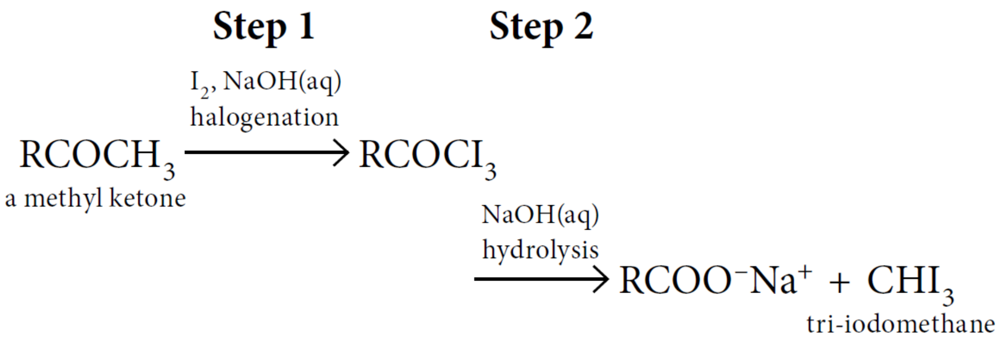


Second step

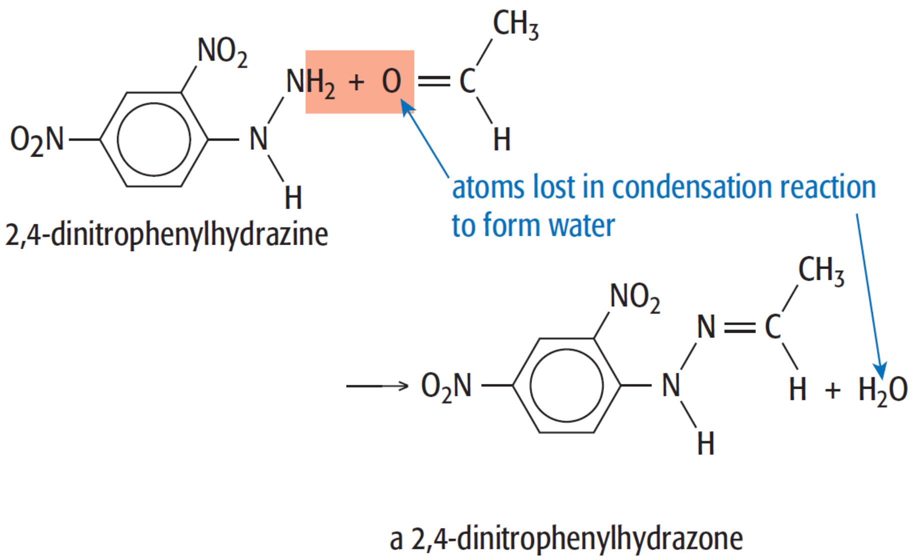


Testing for the carbonyl group:

- **Tri-iodomethane** (Alkaline iodine solution test): Formation of yellow ppt. with methyl ketones, compounds containing CH3CO- group or secondary alcohol (CH3CH(OH)-) due to its oxidation into ketone (reagent: alkaline solution of iodine; warmed together with the substance being tested):



- **Tollen's reagent**: Colourless to silver 'mirror' formation for aldehyde
- **Fehling's solution**: Clear blue turns to opaque red/orange as ppt. of copper(I) oxide forms throughout the solution for aldehyde
- **2,4-DNPH** (2,4-dinitrophenylhydrazine) – condensation reaction: A deep-orange ppt. is formed when ketone or aldehyde is present



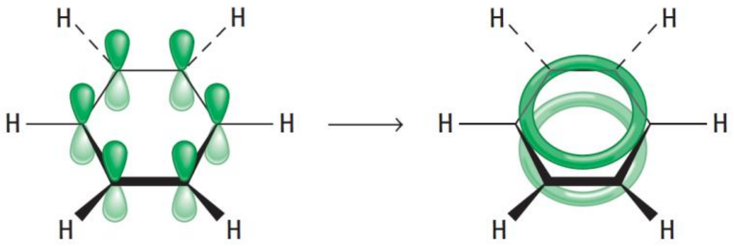
C=C → Electrophilic addition

C=O → Nucleophilic addition

Organic Chemistry (A-level)

Benzene:

- Organic hydrocarbons containing one or more benzene rings are called arenes. In general, compounds of benzene are known as aryl compounds or aromatic compounds; an example is chlorobenzene, which is one of the halogenoarenes. The simplest arene is benzene itself (C6H6)
- Benzene molecule is a planar, perfectly symmetrical molecule
- Each carbon atom in the hexagonal ring is sp2 hybridised sharing:
  - one pair of electrons with one of its neighbouring carbon atoms
  - one pair of electrons with its other neighbouring carbon atom
  - one pair of electrons with a hydrogen atom
- All three are σ (sigma) bonds; leaves one electron to spare contributing to a π (pi) bond – delocalised
- The π bonding is formed by the overlap of carbon p atomic orbitals, where the lobes form a ring of delocalised electrons above and below the plane of the carbon atoms.



overlap of p orbitals produces a ring of delocalised electrons above and below the plane of benzene's carbon atoms

Figure 25.4 The π bonding in benzene. The three bond angles around each of the sp^2 hybridised carbon atoms are 120°.

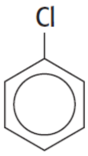
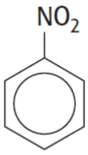
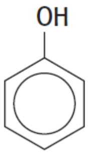
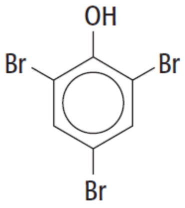
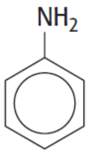
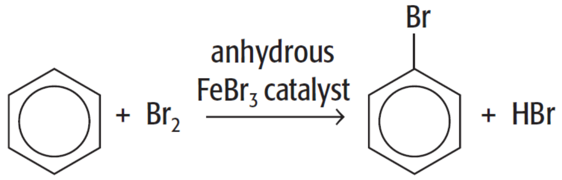
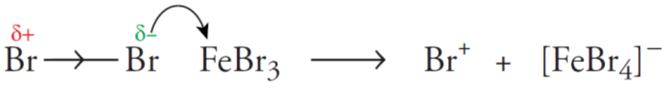
Skeletal formula of aryl compound	**Name**
	chlorobenzene
	nitrobenzene
	phenol
	2,4,6-tribromophenol: note the numbering of the carbon atoms in the benzene ring to describe the position of each substituted group (see page 193)
	phenylamine

Table 25.2 The names of some aryl compounds. The phenyl group can be written as C_6H_5; e.g. the structural formula of phenylamine is $C_6H_5NH_2$.

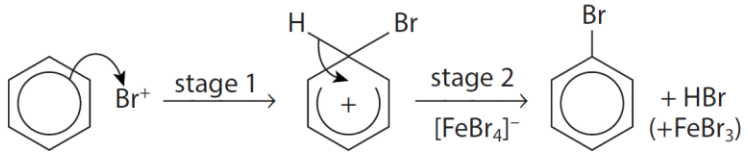
- **Substitution** (Cl & Br) – Electrophilic substitution:



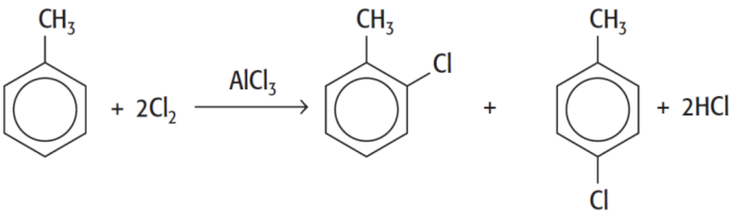
  - The Br2 molecule forms a dative (co-ordinate) bond with Iron (III) bromide by donating a lone pair of electrons from one bromine atom into an empty 3d orbital in the iron. This draws electrons from the other bromine atom in the Br2 molecule making it partially positive, creating the electrophile (Br^+):



  - The Br+ cation and the 'electron-rich' benzene ring are attracted to each other, as the mechanism (electrophilic substitution) shows:



    - Mechanism done at r.t.p & FeCl3, AlCl3 and FeBr3 (halogen carriers) catalyst
  - Another example:

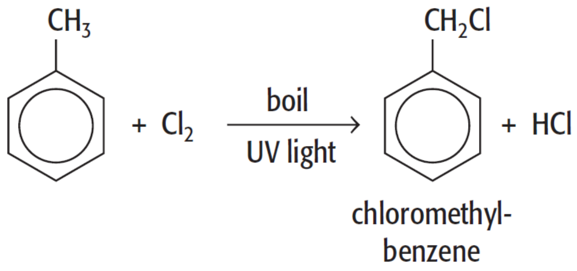


2-chloromethyl-benzene

4-chloromethyl-benzene

    - When we halogenate alkylarenes, the halogen atom substitutes into the benzene ring at positions 2 or 4. While in excess chlorine gas, we can form 1-methyl-2,4,6-trichlorobenzene (2 and 6 positions in substituted arenes are equivalent)
    - The C-X bond in halogenoarenes is stronger than the C-X bond in a halogenoalkane, as one of the lone pairs on the halogen atom overlaps slightly with the π bonding system in the benzene ring, hence giving the C-X bond a partial double bond character

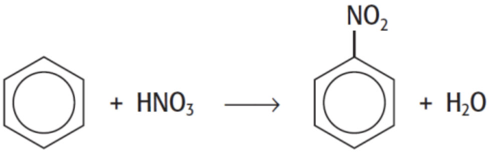
- **Free-radical substitution** (Cl & Br) into the alkylbenzene side-chain:
  - In excess chlorine, eventually all three of the hydrogen atoms will be replaced by chlorine atoms



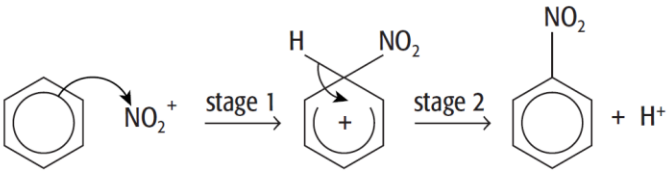
- **Nitration** – Electrophilic substitution:
  - Conc. HNO3 & conc. H2SO4 to create the electrophile – nitronium ion ($NO2^+$ ion):

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

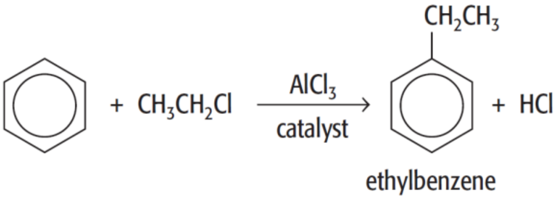
  - Reflux with benzene at 55℃ to make nitrobenzene:

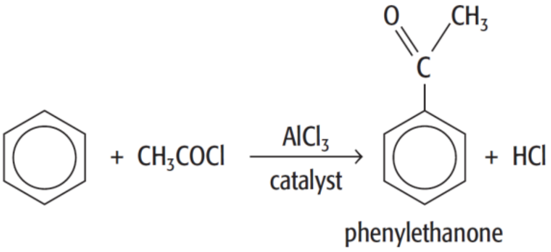


  - Mechanism (In stage 1, $NO2^+$ is attracted to the high electron density of the π bonding system inn benzene; a pair of electrons donated to $NO2^+$, forming a new covalent bond, disrupting benzene's ring of electrons (4 π bonding electrons and a positive charge spread over 5 carbon atoms. In stage 2, C-H bond breaks heterolytically, H^+ ion leaves the system, restoring the full delocalised ring.):

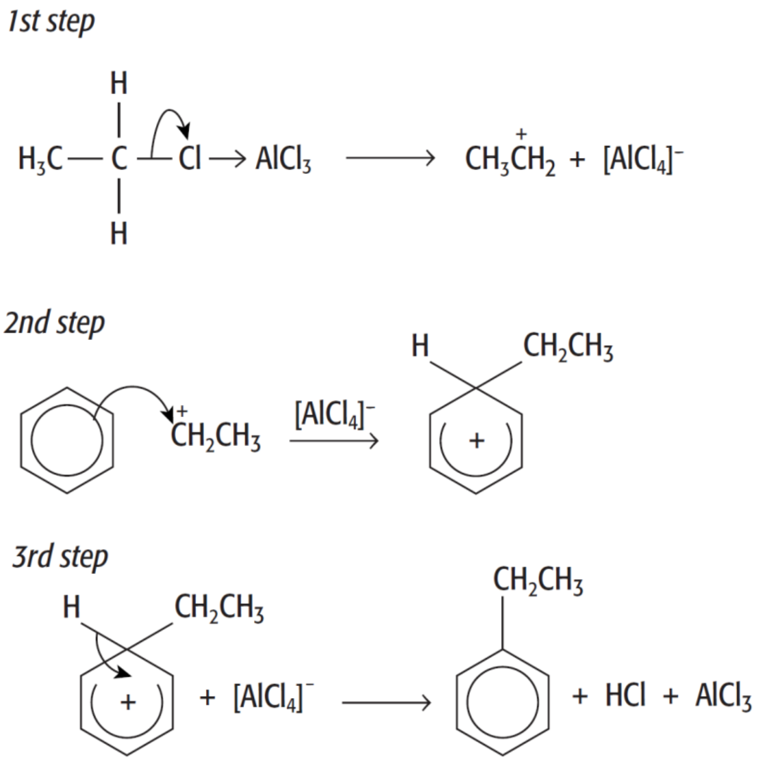


  - Further nitration yields 1,3,5-trinitrobenzene
- **Alkylation or Acylation** (Friedel-Crafts reaction):
  - Friedel-Crafts reactions result in **the introduction of a side-chain** into a benzene ring, also called alkylation or acylation reactions





- Mechanism:



- **Oxidation of the side-chain:**
  - Alkylarenes' alkane side-chain can be oxidised form carboxylic acid.
  - Reagent and conditions:
    - Reflux, alkaline potassium manganate(VII) then acidified with dilute H2SO4
    - Reflux, potassium dichromate(VI) then acidified with dilute H2SO4

Phenol:

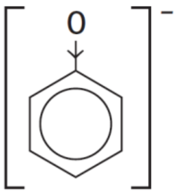
- Phenol, C6H5OH, a crystalline solid that melts at 43℃, due to its hydrogen bonding, however, its non-polar benzene ring causes only a slight solubility in water
- Weakly acidic (however still stronger than water or alcohol):

$$C_6H_5OH(aq) \rightleftharpoons \underset{\text{phenoxide ion}}{C_6H_5O^-(aq)} + H^+(aq)$$

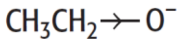
Weak acid	Dissociation in water	pK_a at 25 °C
phenol	$C_6H_5OH(aq) \rightleftharpoons C_6H_5O^-(aq) + H^+(aq)$	10.0
water	$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$	14.0
ethanol	$C_2H_5OH(aq) \rightleftharpoons C_2H_5O^-(aq) + H^+(aq)$	16.0

Table 25.3 Comparing the acidity of phenol, water and ethanol.

- Phenol's conjugate base (the phenoxide ion, $C6H5O^-(aq)$), has its negative charge spread over the whole ion as one of the oxygen's lone pairs overlaps with the delocalised π bonding system, hence reducing the charge density of the $C6H5O^-(aq)$ compared with $OH^-(aq)$ or $C2H5O^-(aq)$; therefore $H^+(aq)$ ions are less attracted to the phenoxide than hydroxide or ethoxide ions, making phenoxide less likely to re-form the undissociated molecules
    - Phenol ionises to form a stable negative ion, so the position of equilibrium lies further to the right-hand side
    - Ethanol is the weakest acid due to the electron-donating alkyl group attached to the oxygen atom in the ethoxide ion, concentrating more negative charge on the oxygen atom, which more readily accepts H^+ ions (equilibrium lies further to the left-hand side)

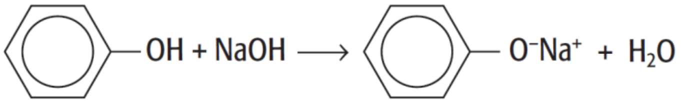


phenoxide ion,
with negative
charge spread over
the whole ion

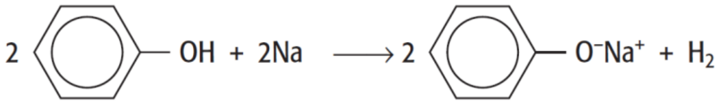


ethoxide ion, with
negative charge
concentrated on
the oxygen

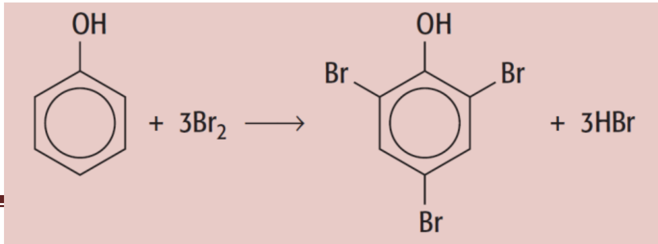
- **Breaking of OH bond:**
    - Slightly soluble in water, but dissolves well in **alkaline solutions (NaOH)**:
        - Sodium phenoxide salt is soluble in water



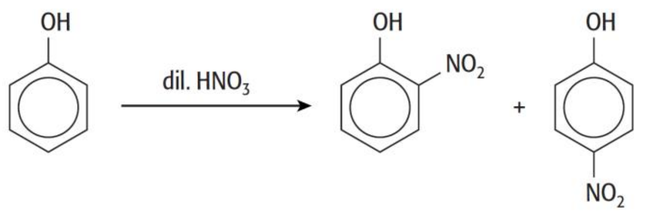
- Reacts vigorously with **Na(s)**:
    - H2 gas released (effervescence) & Sodium phenoxide salt produced



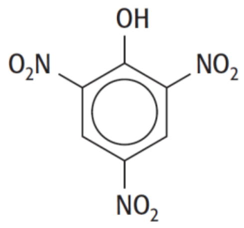
- **Electrophilic Substitution into benzene ring:**
    - Phenol reacts with electrophiles more readily than benzene
    - The overlap of one of the lone pairs of electrons on the oxygen atom in the OH group with the π bonding system increases the electron density of the benzene ring in phenol. This makes the benzene ring more open to attack from electron-deficient electrophiles
    - **Substitution** (Cl & Br) at r.t.p (a white ppt. forms):



- **Nitration with dilute nitric acid** at r.t.p:

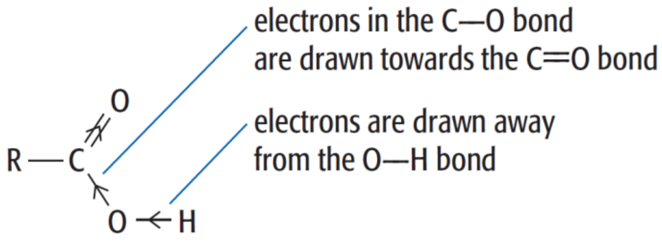


OR

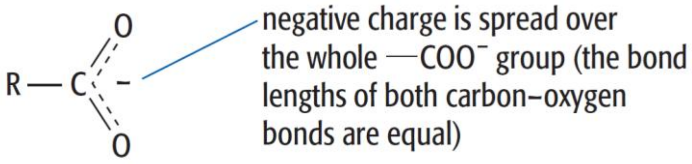


Carboxylic Acids:

- **Neutralisation** (Alkali): CH3COOH + NaOH → CH3COONa + H2O
    - Carboxylate salt produced (Sodium ethanoate)
- **Dissociation:**
    - CH3COOH(aq) ↔ CH3COO^{-}(aq) + H^{+}(aq)
        - Alkanoate ions produced
        - Considered as weak acids (equilibrium lies well over to the left-hand side), however are still stronger than alcohols
        - The O-H bond in the carboxylic acid is weakened by the carbonyl group, C=O:



- Carboxylate ion stabilised by the delocalisation of electrons around the –COO^{-} group (spreading out the negative charge on the ion), reducing its charge density, hence less likely to bond with an H^{+}(aq) ion to reform the undissociated acid molecule:



- Electron-withdrawing groups (halogens) bonded to the carbon atom next to the –COOH group make the acid stronger:
    - Electron-withdrawing groups further weaken the O H bond in the undissociated acid molecule
    - Electron-withdrawing groups extend the delocalisation of the negative charge on the COO– group of the carboxylate ion (pulling of

negative charge further from O^-), making it less likely to bond with H^+ (aq) ions

- E.g. CCl3COOH which has three strongly electronegative Cl atoms all withdrawing the electrons from the –COOH group, weakening the O-H bond more than the other acids; once it is broken the resulting anion would be stabilised more effectively, making it less attractive to the H^+ (aq) ions
- E.g. CH3COOH is the weakest acid, due to its electron-donating nature:
  - It strengthens the O-H bond in the acid's –COOH group
  - It donates negative charge towards the $–COO^-$ group of the carboxylate ion, making it more prone to accept H^+

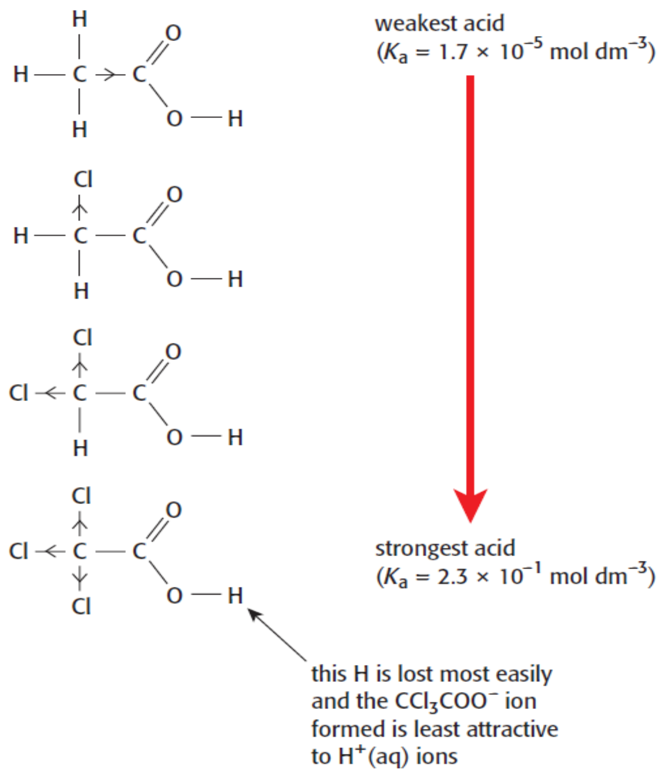


Figure 26.2 The more electron-withdrawing groups on the C atom in the COOH group, the stronger the acid.

- **<u>Oxidation Of HCOOH (methanoic acid):</u>**

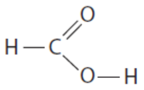


Figure 26.3 The displayed formula of methanoic acid.

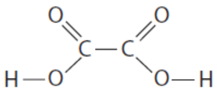


Figure 26.4 The displayed formula of ethanedioic acid.

- Special cases of carboxylic acids which can undergo further oxidation
- Oxidation will occur with strong oxidising agents:
  - Reflux with alkaline potassium manganate(VII) then acidified with dilute H2SO4 (decolourising the purple solution)
  - Reflux with potassium dichromate(VI) then acidified with dilute H2SO4 (solution turns from orange to green)

- Oxidation will occur with milder oxidising agents:
    - Fehling's and Tollen's – same positive results as test for adehydes

$$\underset{+2}{\text{HCOOH}} \xrightarrow{\text{oxidation}} \underset{+4}{\text{CO}_2} + 2\text{H}^+(aq) + 2e^-$$

oxidation number

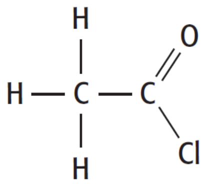
$$\text{HCOOH} + [\text{O}] \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$$

- **Oxidation Of (COOH)2 (ethanedioic acid):**
    - Oxidised by only strong oxidising agents
    - The reaction is often used to standardise potassium manganate(VII) solution:
        - A standard solution of ethanedioic acid is acidified with dilute sulphuric acid, warmed and titrated with potassium manganate(VII) solution from the burette
        - Decolourisation of potassium manganate(VII) solution can be observed until the end-point when a trace of pale pink remains
    - An example of an autocatalysis reaction, where Mn2$^+$ (the product) acts as the catalysis for that reaction

$$2\text{MnO}_4^- + 6\text{H}^+ + 5\text{H}_2\text{C}_2\text{O}_4 \longrightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$$

- **Nucleophilic substitution, forming acyl chlorides:**
    - Replacement of carboxylic acid's –OH with a Cl atom:
    - Reagents and conditions:
        - Phosphorus(V) chloride (r.t.p.):

$$\text{CH}_3\text{COOH} + \text{PCl}_5 \longrightarrow \text{CH}_3\text{COCl} + \text{POCl}_3 + \text{HCl}$$



ethanoyl chloride

- Phosphorus(III) chloride (heating required):

$$3\text{CH}_3\text{COOH} + \text{PCl}_3 \longrightarrow 3\text{CH}_3\text{COCl} + \text{H}_3\text{PO}_3$$

- Sulfur dichloride oxide (r.t.p.):

$$\text{CH}_3\text{COOH} + \text{SOCl}_2 \longrightarrow \text{CH}_3\text{COCl} + \text{SO}_2 + \text{HCl}$$

Acyl Chlorides:

- Acyl chlorides are more reactive than carboxylic acid, hence are more used in compound synthesis:

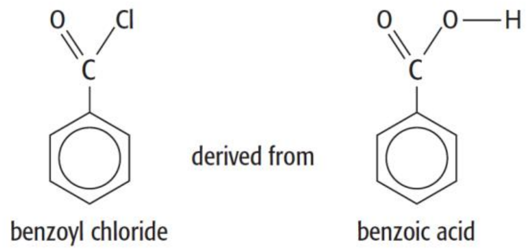
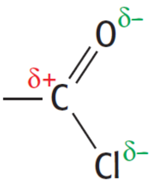


Figure 26.5 Benzoyl chloride is the acyl chloride derived from benzoic acid.

- The carbonyl carbon has electrons drawn away from it by electronegative atoms (O and Cl), giving it a large partial positive charge, open to nucleophiles:



- Reactions will cause C-Cl bond to break; HCl(g) to be given off as white fumes:
  - Where HZ can be water, an alcohol, ammonia or an amine (contains either an oxygen or nitrogen atom with a lone pair that can be donated – nucleophile)

$$ROCl + HZ \longrightarrow ROZ + HCl$$

- **Hydrolysis (r.t.p.)**:
  - A lone pair on the oxygen atom in water initiates the attack on the δ+ carbonyl carbon atom

$$CH_3CH_2COCl + H_2O \longrightarrow CH_3CH_2COOH + HCl$$

propanoyl chloride → propanoic acid

  - Carboxylic acid and HCl(g) forms

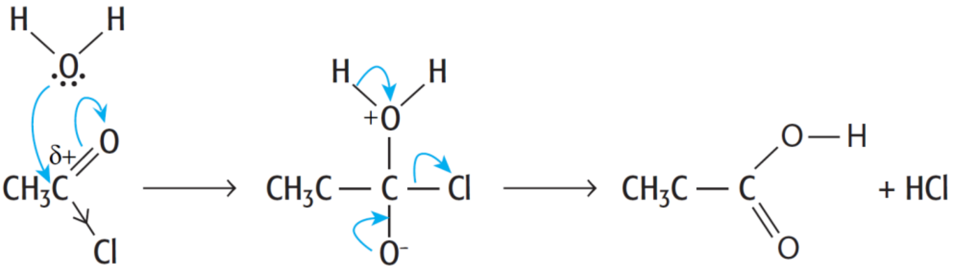
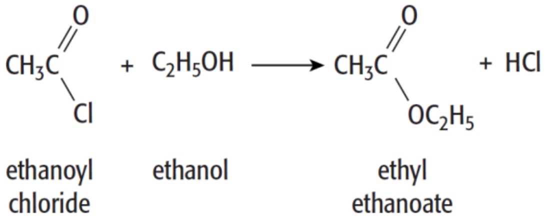
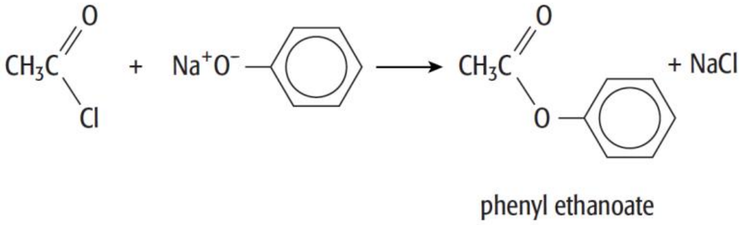


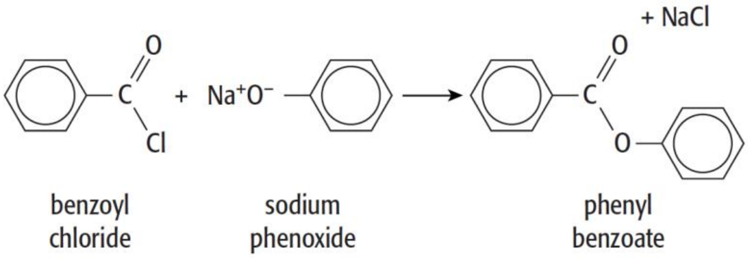
Figure 26.6 The condensation (addition-elimination) mechanism of hydrolysis of ethanoyl chloride.

- The ease of hydrolysis: acyl chloride > chloroalkane > aryl chloride
  - Acyl chloride has a more δ+ carbon compared to chloroalkane, due to the attachment of an oxygen atom to the chlorine bonded carbon
  - Aryl chloride will not undergo hydrolysis due to the overlapping of p orbitals of the Cl atom to the delocalised p electrons in the benzene ring
- **Esterification:**
  - When acyl chlorides reacts with alcohols or phenol, esters (and HCl) formed
  - Reaction will occur more quickly and go to completion compared to that of carboxylic acid + alcohols:

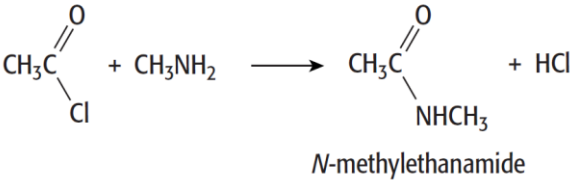


- To produce phenyl esters (+ phenol), acyl chlorides must be used, warmed and in the presence of a base (NR with carboxylic acid); where in the initial reaction, phenoxide ion (C6H5O$^-$) will form to act as the nucleophile to attack the acyl chloride:





- **<u>Nucleophilic substitution with amines:</u>**
  - Amines with a lone pair of electrons acts as a nucleophile and attacks the carbonyl carbon atom in acyl chlorides (reaction is vigorous and a substituted amide formed):



Amines:

- Three classes of amine: primary (NH2 group bonded to an alkyl or aryl group, e.g. ethylamine (C2H5NH2) or phenylamine (C6H5NH2)), secondary (two alkyl or aryl groups attached to an NH group, e.g. dimethylamine (CH3)2NH), tertiary (three alkyl or aryl groups attached to the same nitrogen atom, e.g. trimethylamine (CH3)3N)
- Ammonia and amines act as bases due to the lone pair of electrons on the nitrogen atom (donation of the lone pair to a H$^+$ ion, forming a co-ordinate (dative) bond)
- **<u>Reaction with dilute acids</u>** (HCl in the example):

For ammonia:

$$NH_3 + HCl \longrightarrow \underset{\text{ammonium chloride}}{NH_4{}^+Cl^-}$$

For a primary amine:

$$CH_3NH_2 + HCl \longrightarrow \underset{\text{methylammonium chloride}}{CH_3NH_3{}^+Cl^-}$$

ethylamine > ammonia > phenylamine

STRONGEST BASE ⟷ WEAKEST BASE

- The strength of ammonia and amines as bases depends on the availability of the lone paur of electrons on their N atom to bond with an H^+ ion
    - Ethylamine > ammonia due to the ethyl group's electron-donating nature, releasing more electrons towards the N atom
    - Ammonia > phenylamine due to the overlapping of the p orbitals on the nitrogen atom with the π bonding system in the benzene ring, causes the lone pair to delocalise into the benzene ring: benzene ring's electron-withdrawing nature
- **<u>Formation of ethylamine:</u>**
    - Ammonia (NH3 (in ethanol)) (excess) (hot)+ bromoethane, to avoid formation of secondary and tertiary amines

$$CH_3CH_2Br + NH_3 \longrightarrow \underset{\text{ethylamine}}{CH_3CH_2NH_2} + HBr$$

- Bromomethane + KCN (potassium cyanide); reduced by adding of hydrogen to the ethanenitrile (passing of the nitrile vapour and H2(g) over a nickel catalyst / LiAlH4 in dry ether)

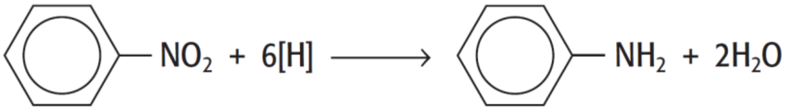
$$\underset{\text{bromomethane}}{CH_3Br} + CN^- \longrightarrow \underset{\text{ethanenitrile}}{CH_3CN} + Br^-$$

$$CH_3CN + 4[H] \longrightarrow \underset{\text{ethylamine}}{CH_3CH_2NH_2}$$

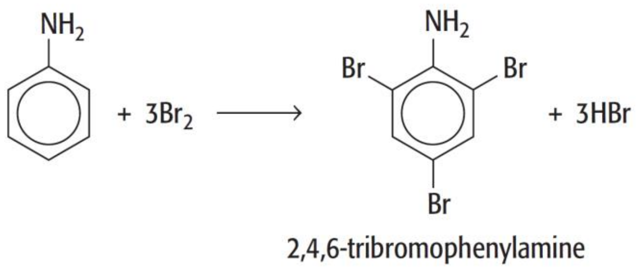
- Reduction of amides to amines, by using LiAlH4 in dry ether catalyst

$$\underset{\text{ethanamide}}{CH_3CONH_2} + 4[H] \longrightarrow \underset{\text{ethylamine}}{CH_3CH_2NH_2} + H_2O$$

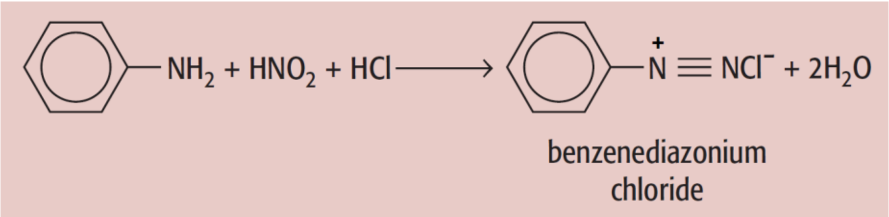
- **<u>Formation of phenylamine:</u>**
    - Reduction of nitrobenzene, by heating nitrobenzene with tin (Sn) and concentrated hydrochloric acid (separation of phenylamine from reacting mixture using steam distillation:



- **Electrophilic substitution of Br(aq) into phenylamine:**
  - A white ppt. forms
  - The nitrogen in the –NH2 group has a lone pair of electrons that can be delocalosed into the benzene ring, increasing the electron density of the ring, hence more prone to electrophile attacks (reaction similar to that of phenols)



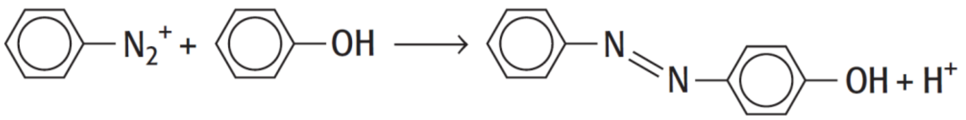
- **Diazotisation:**
  - Used in the synthesis of dyes
  - First step (must be kept below 10°C due to the instability of the diazoniium salt – decomposes easily giving N2(g) at higher temperatures):



    - Phenylamine + nitrous acid (nitric(III) acid) → diazonium salt
    - The positive charge on the diazonium ion (C6H5N2$^+$) is on the nitrogen atom shown with four bonds
    - Nitrous acid can be bade using sodium nitrite (sodium nitrate(III)) and dilute HCl:

$$NaNO_2 + HCl \longrightarrow \underset{\text{nitrous acid}}{HNO_2} + NaCl$$

  - Second step:



    - Diazonium ion reacts with an alkaline solution of phenol in a coupling reaction
    - The positively charged diazonium ion acts as an electrophile, substituting into phenol at the 4 position
    - An orange dye – very stable – is formed, called an azo dye, or diazonium dye

  - The delocalised π bonding system extends between the two benzene rings through the NN group
- Using alternative aryl compounds to phenol:

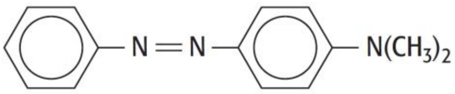
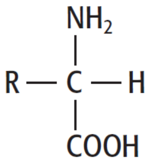


Figure 27.8 A molecule of a yellow azo dye. Instead of phenol, C_6H_5OH, the reactant used in the coupling reaction is $C_6H_5N(CH_3)_2$.

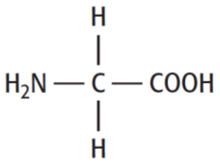
Amino acids:



$$\begin{array}{c} NH_2 \\ | \\ R-C-H \\ | \\ COOH \end{array}$$

Figure 27.9 The general structure of a 2-amino-carboxylic acid.

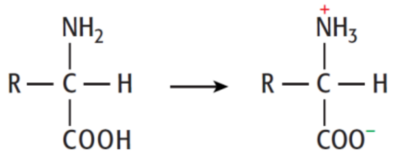
- The general structure: RCH(NH2)COOH
- Examples of amino acids: glycine (aminoethanoic acid) (R group: H atom) (simplest amino acid); alanine (2-aminopropanoic acid) (R group: -CH3)



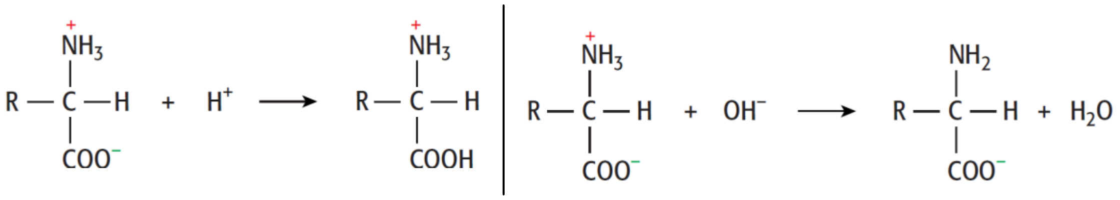
$$\begin{array}{c} H \\ | \\ H_2N-C-COOH \\ | \\ H \end{array}$$

glycine (aminoethanoic acid)

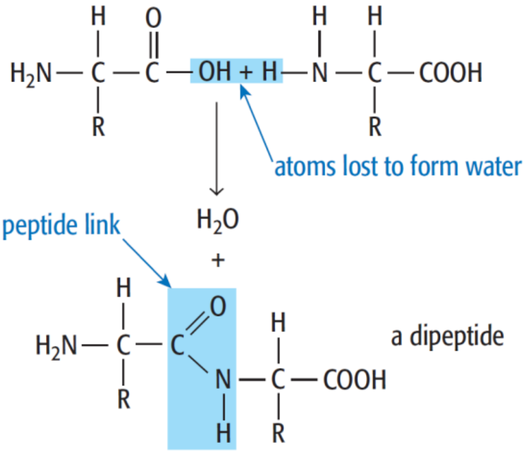
- The R group can be acidic (e.g. containing another –COOH group), basic (e.g. containing another –NH2 group) or neutral (e.g. where R is an alkyl group)
- Interactions between the molecules within amino acids are possible due to its basic –NH2 group and its acidic –COOH group (forming a zwitterions as it carries two charges):



- Zwitterion creates relatively strong intermolecular force due to their ionic nature (carrying two charges); they are crystalline solids that are soluble in water
- Solutions of amino acids are amphoteric, buffer solutions:



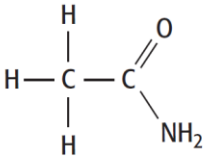
- Two amino acids reacted together will create a dipeptide (condensation reaction – elimination of a small molecule when the reactant molecules join together):



  - The amide link between the two amino acids are also called a peptide link
  - The dipeptide product still has an –NH2 group and –COOH at its ends, hence the reaction can continue forming polypeptides and then proteins

Amides:

- Structural formula: CONH2, e.g. CH3CONH2

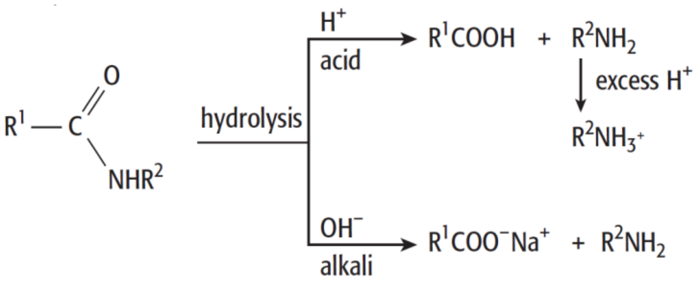


ethanamide

- Amides are neutral compounds unlike amines, due to the presence of the electron-withdrawing oxygen atom in the amide group, hence the unavailability of lone pair on the amide's nitrogen to donate to electron deficient species, such as H^+ ions
- **Formation of amides:**
  - $CH_3COCl + NH_3 \longrightarrow CH_3CONH_2 + HCl$
    - Ethanoyl chloride with conc. NH3(aq) producing ethanamide
  - $C_3H_7COCl + C_2H_5NH_2 \longrightarrow C_3H_7CONHC_2H_5 + HCl$
    - Primary amide with an acyl chloride producing a substituted amide
    - Excess amines will react with HCl forming a salt (e.g. $C2H5NH3^+Cl^-$)
  - Both reactions are in r.t.p.; white fumes of HCl forms
  - The italic letter N is used in naming substituted amides to denote which alkyl (or aryl) group or groups are bonded to the nitrogen atom, e.g. N-ethylbutanamide, C3H7CONHC2H5, the ethyl (C2H5-) group has replaced an H atom in the amide group. If the H atom on the nitrogen in this molecule is replaced by another alkyl or

aryl group, two N's are used in the name, e.g. C3H7CON(C2H5)2 is called N,N-diethylbutanamide

- **Hydrolysis:**
  - Substituted amides (-CONH-):
    - Reflux with, e.g. HCl(aq) or NaOH(aq):



    - The product of hydrolysis with acid yields a carboxylic acid (R^1COOH) and a primary amine (R^2NH2); excess acid in the reaction will react with amine to form ammonium salt, e.g. $R^2NH3^+Cl^-$ with excess HCl
    - The product of hydrolysis with an alkali, the product are sodium salt of the carboxylic acid ($R^1COO^-Na^+$) and the primary amine (R^2NH2)
  - Unsubstituted amide (RCONH2):
    - Same reactions and products, except ammonia will be produced instead of primary amines, and ammonium salts during excess of acid