WJEC A2 Organic Chem

UNIT 4.1-4.4

IGC HK Exam

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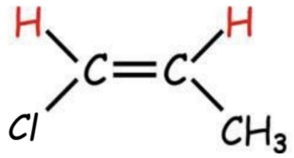
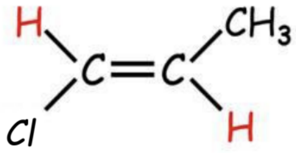
Isomerism

Sterioisomer

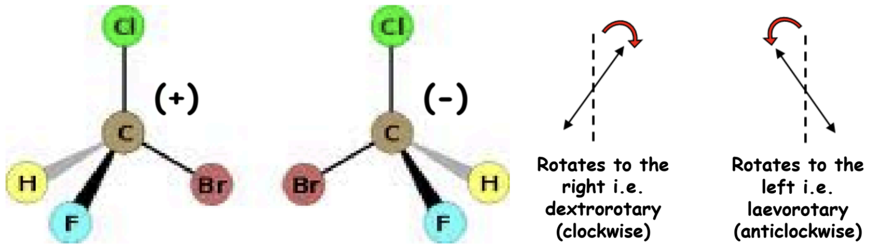
Geometric Isomer (E-Z Isomer)

z - isomer which has two higher priority substituents on the same side of the carbon-carbon double bond or planar ring plane, z.
ε - isomer which has two substituents on the opposite side of the carbon-carbon double bond or ring planar, ε.



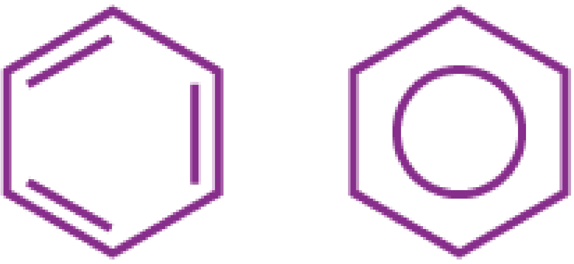


Optical Isomer (Enantiomers)



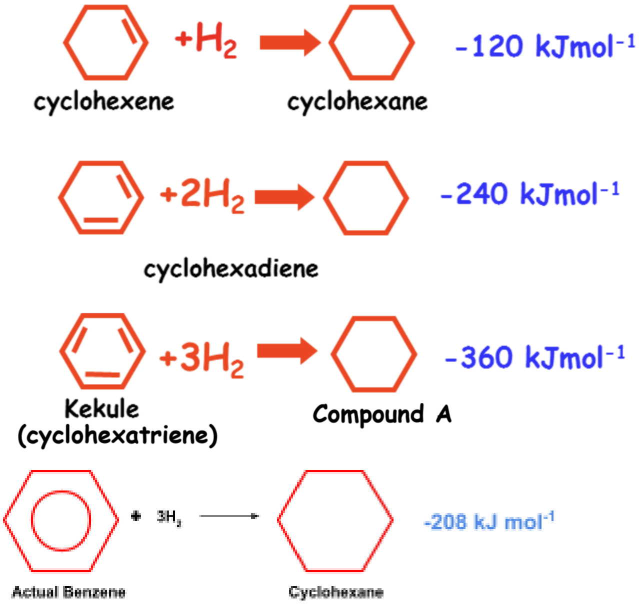
- Non-superposable mirror images → Have line of symmetry
- Molecules possesses chiral center
- Racemic Mixture → Equimolar solution of both isomers
- Different isomer will rotate the plane of polarised light to opposite direction

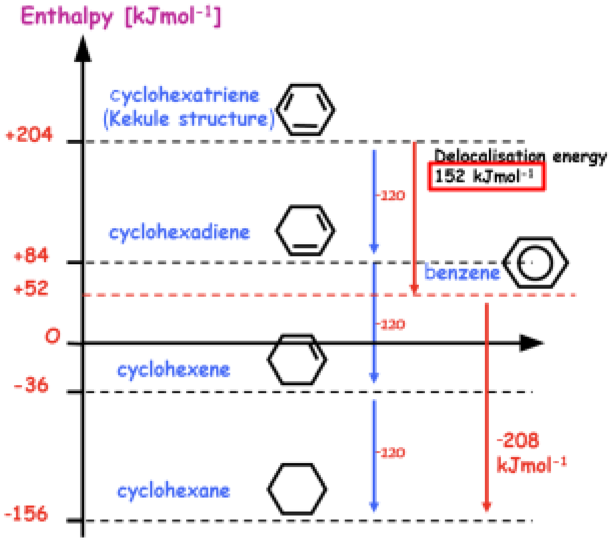
Aromaticity – Benzene



Proof of Kekule Structure vs Actual Structure

1. Enthalpy of Hydrogenation Data





   - 152 kJ mol^{-1} is Delocalisation energy / Stabilisation energy
   - **<u>Enthalpy of hydrogenation of benzene is less exothermic than Kekule Structure</u>**
   - There are <u>delocalised pi (π) bonding</u> system in Actual structure → delocation energy

2. Mean Bond Enthalpy Data
   - Actual bond enthalpy of Benezne is less than Kekule Stucure
   - This suggest other types of bond are formed
3. Do not carry out addition reaction → Substitution only
4. Less isomer found
5. Bond Length (All C–C bond length are identical in Benzene)

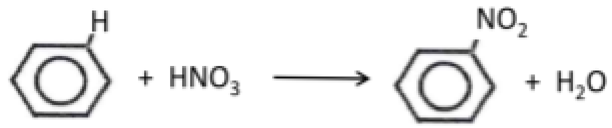
   C – C in cyclohexane > C – C in benzene > C – C in cyclohexene

   C-C cyclohexane = 0.15nm
   C⎓C benzene = 0.14nm
   C=C cyclohexene = 0.13nm

Reaction of Benzene — Electrophilic Substitution

Nitration of Benzene

Overall reaction:



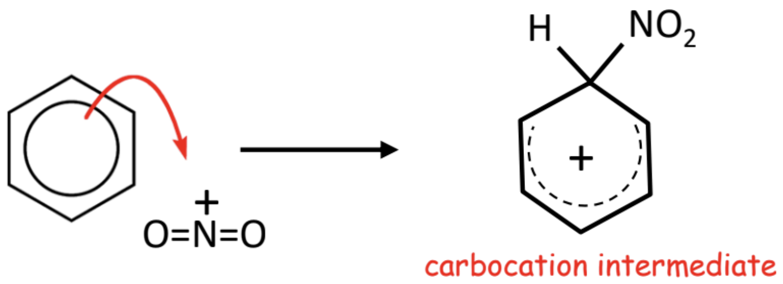
Conditions:
50°C-60°C
concentrated sulfuric(VI) acid
concentrated nitric(V) acid

Step 1 – Generation of Electrophile

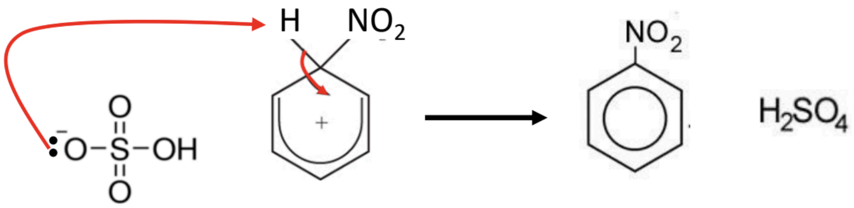
$$2H_2SO_4 + HNO_3 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

nitronium ion **hydronium ion**

Step 2 – Attack of Electrophole on Benzene Ring



Step 3 – Abstraction of Proton & Regeneration fo Catalyst

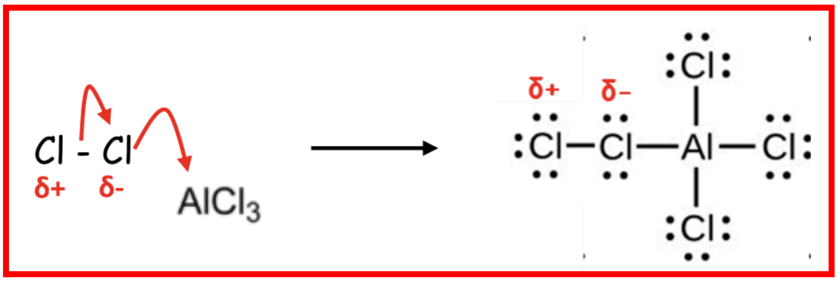


Halogenation of Benzene

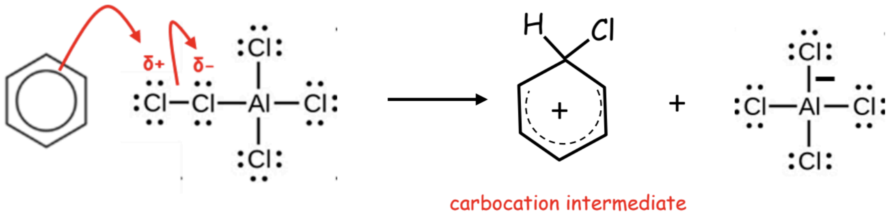
Overall reaction:

Conditions:
Room temperature
Absence of light
Anhydrous conditions (prevents hydrolysis of halogen carrier)
Presence of a halogen carrier e.g. $AlCl_3$ or $FeCl_3$

Step 1 – Generation of Electrophile



Step 2 – Attack of Electrophile on Benzene Ring



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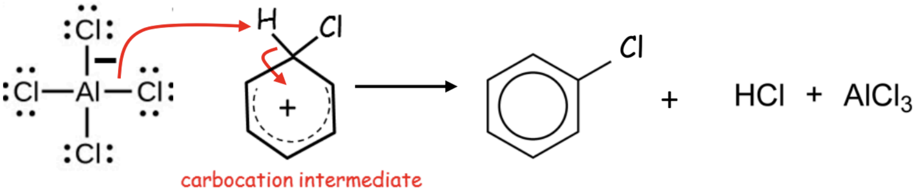
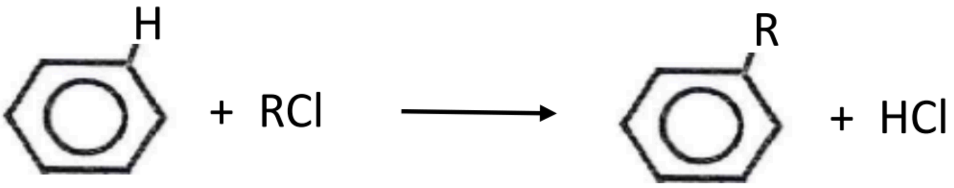


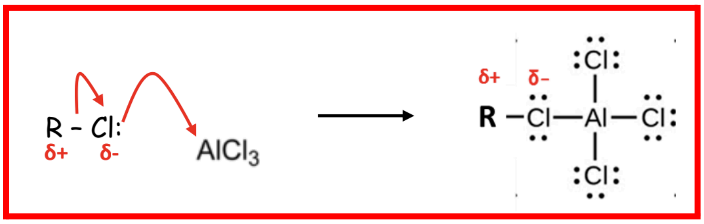
Alkylation

Overall Reaction:

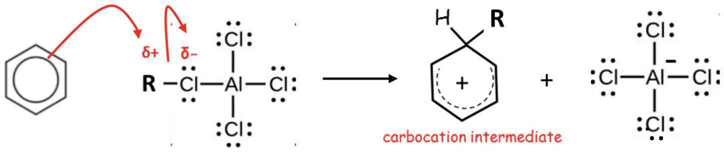


Conditions:	Room temperature Anhydrous conditions (prevents hydrolysis of halogen carrier) Presence of a halogen carrier e.g. $AlCl_3$ or $FeCl_3$ The appropriate halogenoalkane

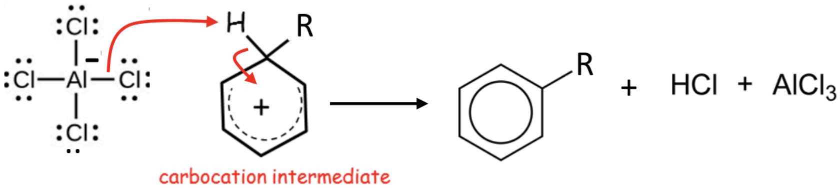
Step 1 – Generation of Electrophile



Step 2 – Attack of Electrophile on Benzene Ring



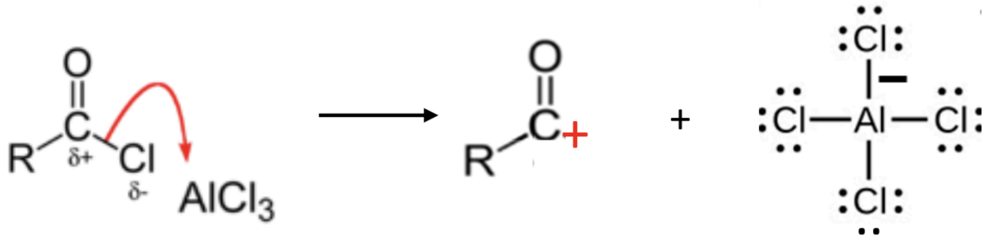
Step 3 – Abstraction of Proton & Regeneration fo Catalyst

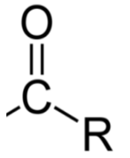


Acylation (Friedel–Crafts)

Conditions: Approx. 60°C for about 30 minutes
Presence of $AlCl_3$ as the catalyst
A mixture of an acyl chloride:
e.g. ethanoyl chloride (CH_3COCl) and benzene

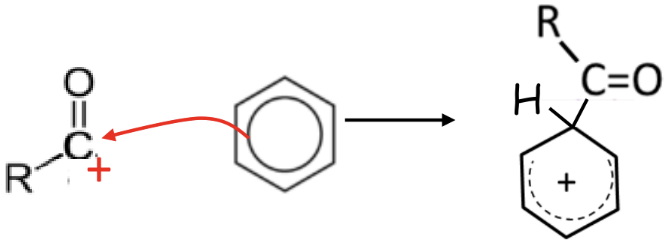
Step 1 – Generation of Electrophile





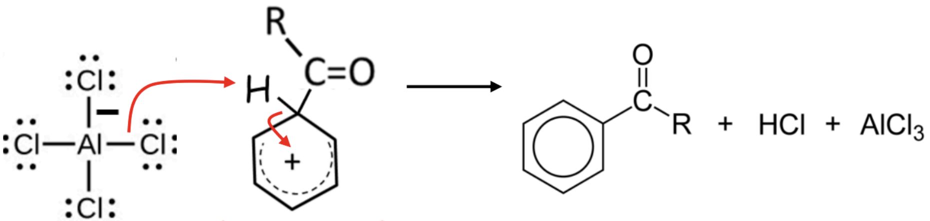
alkanoyl group

Step 2 – Attack of Electrophile on Benzene Ring



carbocation intermediate

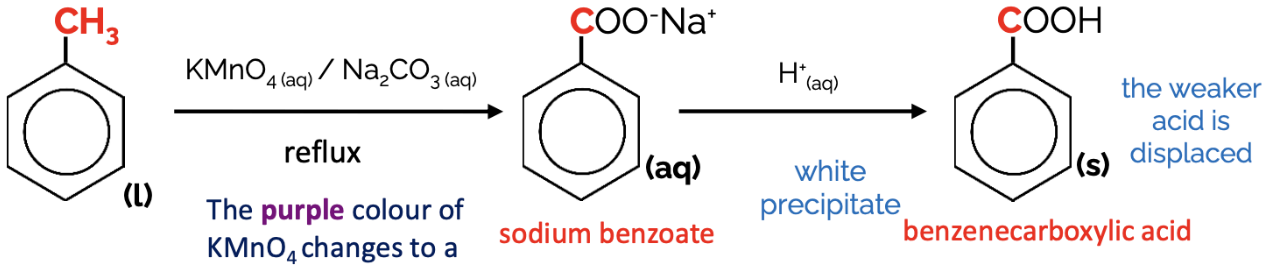
Step 3 – Abstraction of Proton & Regeneration fo Catalyst



carbocation intermediate

Oxidation of Alkyl Side of Benzene Ring

Conditions: **Reflux followed by acidification.**
Potassium manganate(VII) solution made *alkaline* with sodium carbonate,
acts as an oxidising agent.



The **purple** colour of $KMnO_4$ changes to a **dark brown** precipitate of MnO_2.

sodium benzoate

white precipitate

benzenecarboxylic acid

the weaker acid is displaced

The free carboxylic acid can be liberated by adding a dilute solution of a strong acid.

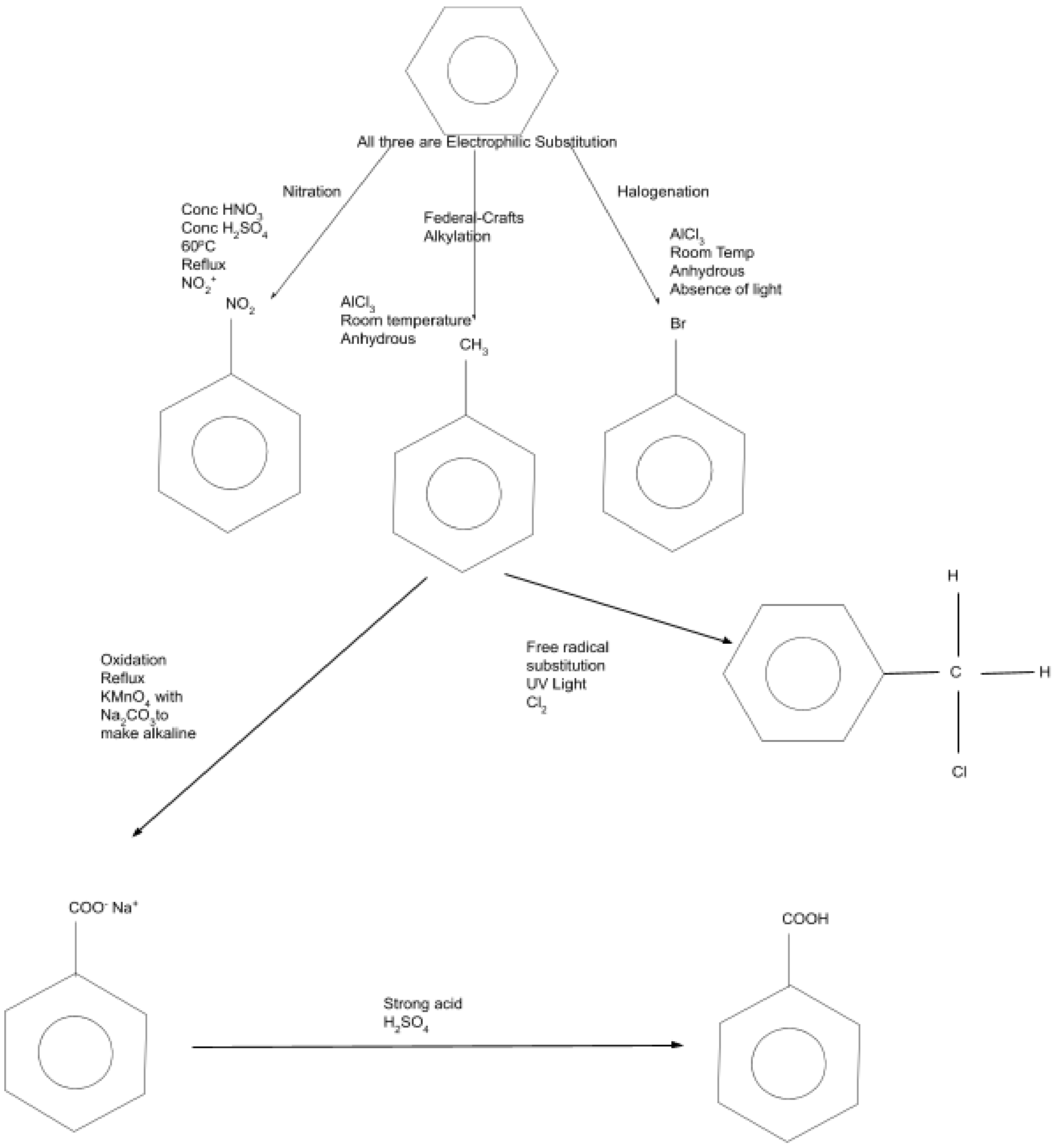
Comparison of the Reactions of 1-Chlorobutane and Chlorobenzene with $OH^-_{(aq)}$

- Chlorobenzene is more difficult to Nucleophilic Substitution compared to 1-Chlorobutane

Because:

I. Repels the attacking OH^- nucleophile away from carbon atom C_1.
II. Strengthens the C–Cl bond giving the bond some π bonding character.

Summary reaction of benzene



Reminder Question Key Terms:
Mechanism: Free Radicle Substitution, Electrophilic Addition / Substitution, SN
Type of reaction: Nitration, Acylation, Alkylation

Alcohol

Industrial Preparation of Alcohol from Alkenes

Conditions: 300°C
60-70atm
phosphoric (V) acid on a silica gel (catalyst)

The mechanism is not required.

Other Method of Alkene to Alcohol:

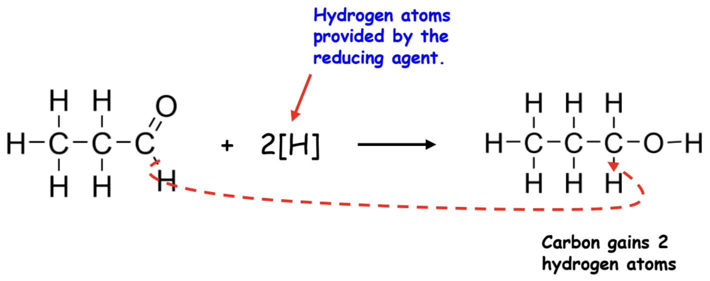
- Electrophilic Addition (and Hydrolysis) to form Alcohol

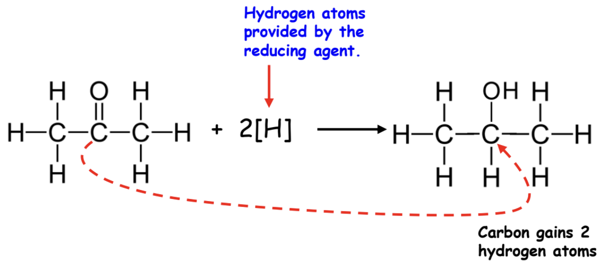
Nucleophilic Substitution from Halogenoalkane to Alcohol

Conditions: aqueous NaOH
reflux
mutual solvent (e.g. propanone)

Reduction from Carbonyl Compound (Aldehyde & Ketone) – Nucleophilic Addition

Conditions: aqueous $NaBH_4$ (sodium borohydride/tetrahydridoborate (III))
room temperature
separation of alcohol by fractional distillation





Reduction from Carboxylic Acid

Conditions: $LiAlH_4$ (lithium aluminium hydride/tetrahydridoaluminate (III)) in a dry ether solvent
room temperature
sulfuric acid

Fermentation from Sugar

Conditions: yeast ("zymase")
no air (anaerobic conditions)
optimum temperature and pH for the yeast
separation of ethanol by fractional distillation

Fermentation of glucose	
Advantages	- Renewable material - Low cost
Disadvantages	- Low atom economy - Low yield - Greenhouse gas emission - Purification and separation are expensive
Direct hydration of ethene	
Advantages	- More pure product → Higher yield - High atom economy - No toxic / harmful product
Disadvantages	- Non renewable raw material (crude oil) - High pressure requires → Can be dangerous + expensive

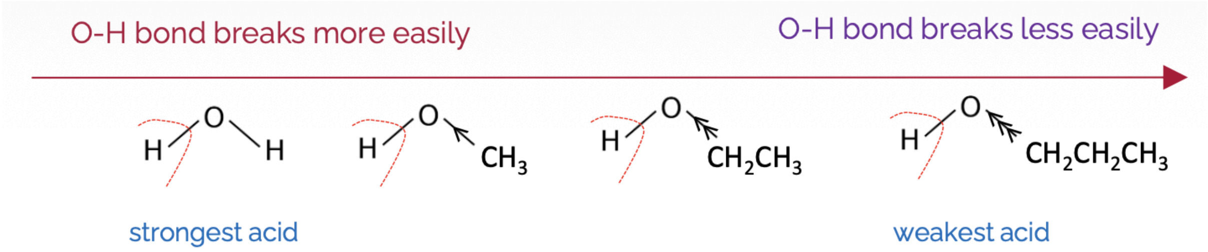
Chemical Properties of Alcohol

Alcohol Acidic Character

- Alcohol react slowly with sodium to evolve hydrogen gas
- Alcohol react in a similar way to water, i.e. alcohol have some acidic character
- Alcohol are weaker acid than water

Observation:

- Colourless gas forms (H_2 Gas)
- White solid forms $CH_3CH_2O^-Na^+$



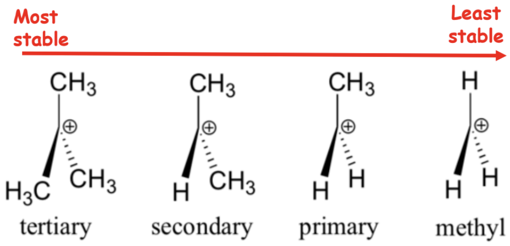
- Longer the carbon chain, the inductive effect (pushing the electron) is stronger
- The O–H bond is strengthened if electron being donated to O–H
- *Easier to break O–H bond, stronger acidic character (as it can donate* H^+*)*

Summary

- Alkyl groups have an electron donating (pushing) inductive effect. This increases the electron density in the O-H bond.
- The bond is therefore strengthened when compared to that in water and breaks less easily. This makes all alcohols weaker acids than water.
- As the length of the carbon chain increases, the inductive effect increases in magnitude. This further strengthens the O-H bond and reduces the acid character.

Oxidation of Alcohol – AS Chemistry

Elimination of Alcohol – AS Chemistry



Conversion of Alcohol to Halogenoalkane

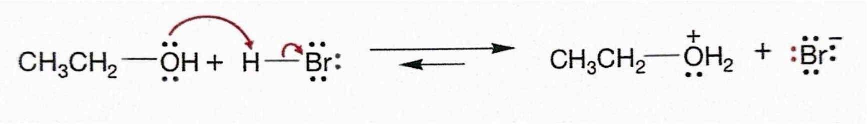
- Alcohols do not undergo nucleophilic substitution with Cl^- or Br^- ions <u>alone</u>.
- OH^- group of the alcohol is highly basic and is a very poor leaving group

Bromination

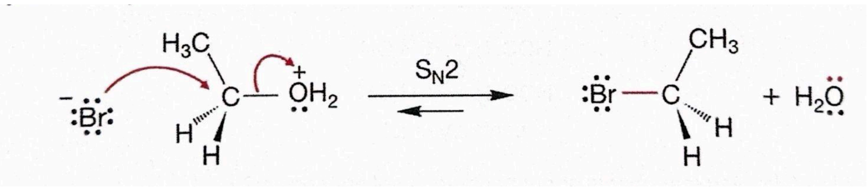
Step 1 – HBr Generated "in situ" from H_2SO_4 and KBr

$$H_2SO_4 + KBr \longrightarrow KHSO_4 + HBr$$

Step 2 – Propagation of OH group



Step 3 – Nucleophilic Attack



Overall Reaction

$$CH_3CH_2CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2CH_2Br + H_2O$$

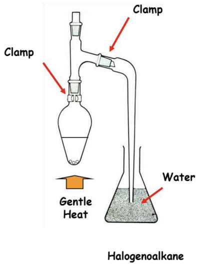
Chlorination

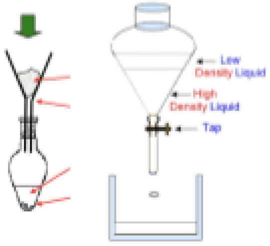
$$CH_3CH_2CH_2CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2CH_2CH_2Cl + H_2O$$

Conc HCl and $ZnCl_2$ act as catalyst

Practical Skill for Chlorination of Alcohol

1. The alcohol is shaken in a stoppered flask with concentrated hydrochloric acid and anhydrous $ZnCl_2$ at room temperature
   The anhydrous $ZnCl_2$ act as a catalyst because it is a dehydrating agent, absorbing the water as it is formed
2. The halogenoalkane formed as the top immiscible layer it is removed using a separating funnel
3. Excess sodium carbonate solution is added to the halogenoalkane to neutralise any remaining acid and shake. The stopper needs to be removed at regular intervals.
4. The halogenoalkane is again separated from the water layer using a separating funnel.
5. Anhydrous sodium sulfate is added to absorb any water
6. The mixture is filtered to remove the sodium sulfate
7. The halogenoalkane is collected by distillation



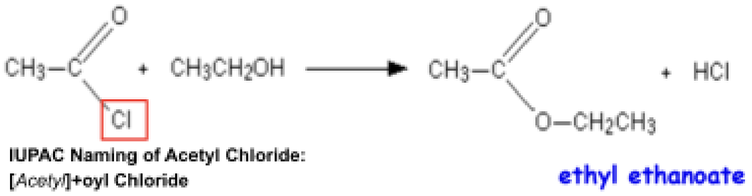


Purification of Organic Products (by removing acid impurities) – Practical

- Place the impure distillate in a separating funnel
- Add sodium carbonate/sodium hydrogencarbonate solution
- Stopper and shake
- Release pressure
- Separate the layers
- Add anhydrous magnesium sulfate/sodium sulfate/calcium chloride
- Until the liquid is clear/no longer cloudy
- Decant the liquid/filter off solid

Conversion to Ester with Carboxylic Acid – AS

Conversion to Ester from Acetyl Chlorides – Nucleophilic Addition Elimination



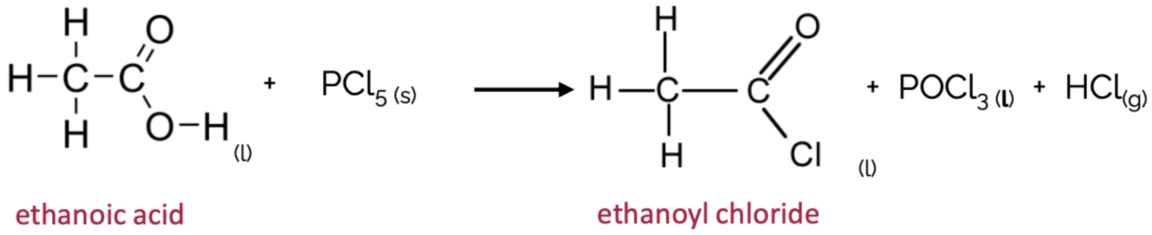
Conditions:

- Acyl chloride
- Ice bath
- Fractional distillation (to separate the ester from the reaction mixture)

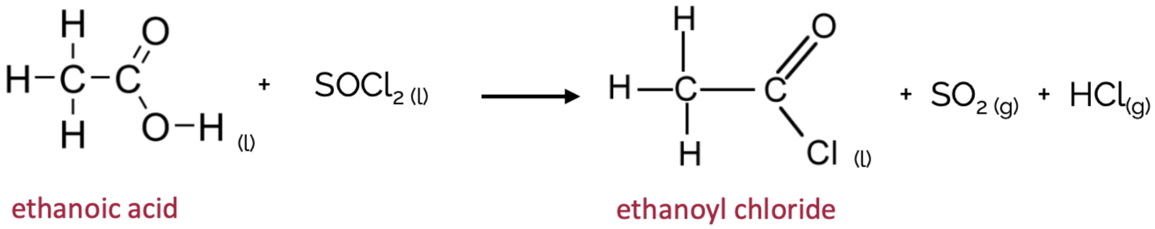
- Ethanoyl chloride reacts instantly with ethanol
- It is very exothermic reaction and HCl (steamy acidic gas is given off)
- The alcohol must be added dropwise with cooling → reduce the vigour of the reaction

Preparation of acyl chloride

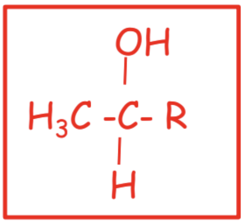
1. **PCl_5**



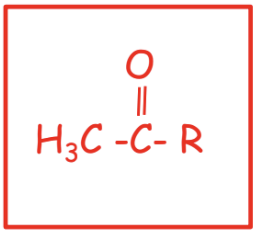
2. **$SOCl_2$**



Iodoform Reaction



$H_3C-\overset{OH}{\underset{H}{C}}-R$



$H_3C-\overset{O}{\overset{\parallel}{C}}-R$

Reagents:	Iodine and sodium hydroxide solution (or potassium iodide and sodium chlorate(I) solution}
Method:	Add the $NaOH_{(aq)}$ dropwise to the $I_{2\ (aq)}$ until the orange-brown colour disappears. Add 2-3 drops of the compound under test.
Observations:	Yellow crystals of triiodomethane (iodoform), CHI_3, slowly form. These crystals often have an antiseptic smell.

Physical Properties of Alcohol

Melting and Boiling Points

MP BP increase as the carbon length increase

Comparing Butane, Chloroethane and Propan-1-ol

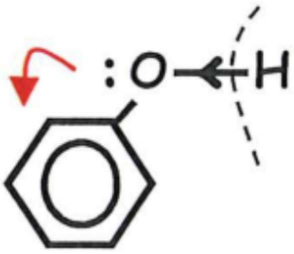
Butane – Non polar (only weak vdw)
Chloroethane – C–Cl bond is polar (permanent dipole)
Propan-1-ol – H and O lone pair can form Hydrogen bond

Solubility in Water

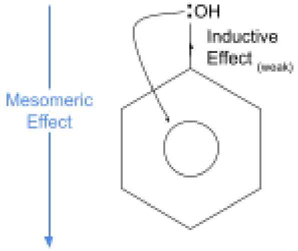
Shorter carbon chain alcohol are soluble in water
As they can form hydrogen bond with water

Longer carbon chain: solubility decrease
As the chain length increase, a larger proportion of the molecule becomes nopn-polar and cannot form hydrogen bond with water

Phenol



The lone pair of electrons on the oxygen atom is delocalised into the pi system of the ring. → Increasing electron density on ring
This weakens the O–H bond.

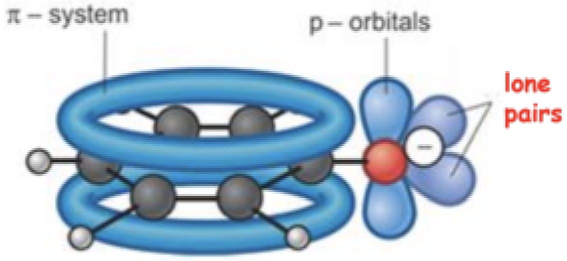


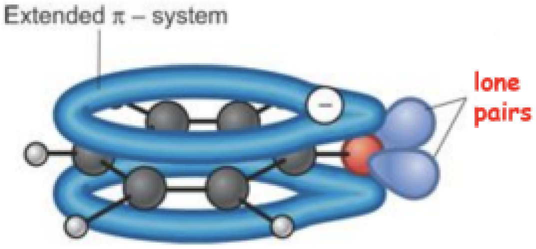
Mesomeric Effect

- Electronegative oxygen atom draws the electron towards itself in C–O bond (inductive)
- <u>A lone pair of electrons on oxygen delocalised into the ring (mesomeric effect)</u>
- Mesomeric Effect > Inductive Effect

Acidic Character (O–H bond strength so H^+ can be released)

- Phenol is a stronger acid compared to alcohol
    I. The delocalisation of the lone pair into the ring, <u>reduces electron density in O–H bond</u>, this **weakens the O–H bond**
    II. The phenolate ion is stabilised by the delocalisation of the negative charge into the ring (shown in image below) [the p orbital interact with the ring]





Phenoxide is more stable than it should be

Solubility in Water

Phenol is moderately soluble in water
One pair of the lone pair is inside of the ring, so less chance of forming H-bond with water

Acidic Character cont.

Acid character: [Carboxylic Acid > Phenol > Alcohol]

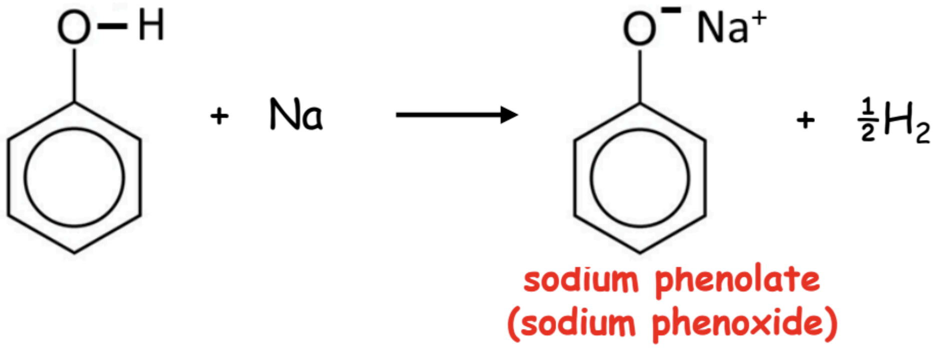
Carboxylic Acid: Has **negative inductive effect** so C=O and O–H bond is weakened
Phenol: Lone pair on Oxygen is **delocalised into ring** so O–H bond is weakened
Alcohol: Has **positive inductive effect** *(from the CH_2 group attached to O–H)* which strengthened the O–H bond

Phenol is a weak acid

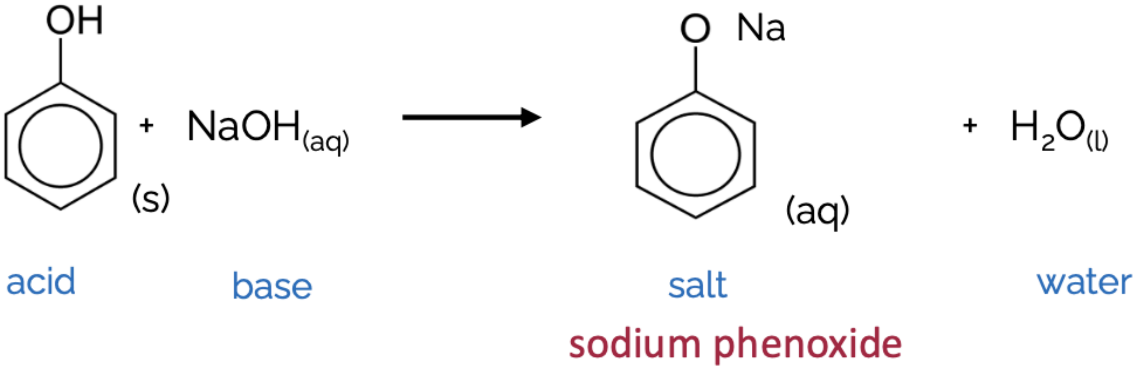
Reaction of Phenol

With Sodium Metal

<u>Molten</u> phenol release a proton when sodium is added



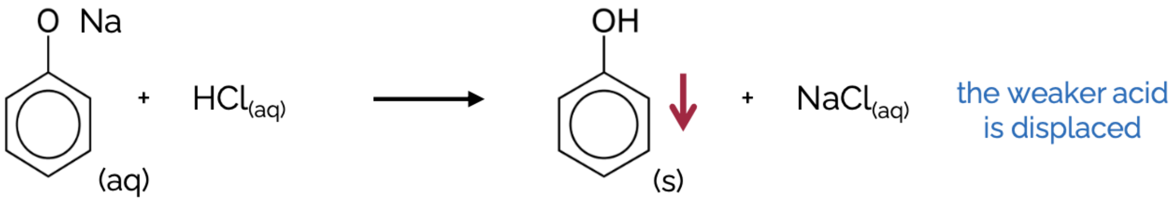
With NaOH

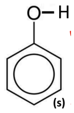


When NaOH is added, the phenol readily dissolves into solution forming ionic salt
<u>This confirms that phenol has acidic character</u>

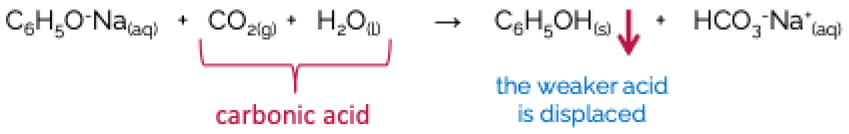
Note: Sodium phenolate has charge but sodium phenoxide does not

Followed by addition of HCl



- HCl is a stronger acid →  precipitates
- HCl is a stronger acid than Phenoxide (O Na) ion

Followed by addition of CO_2



$$C_6H_5O^-Na_{(aq)} + \underbrace{CO_{2(g)} + H_2O_{(l)}}_{\text{carbonic acid}} \rightarrow \underbrace{C_6H_5OH_{(s)}\downarrow}_{\text{the weaker acid is displaced}} + HCO_3^-Na^+_{(aq)}$$

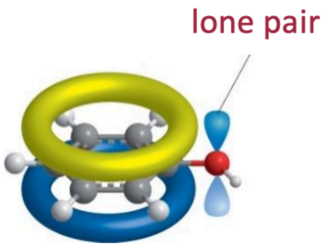
- Shows carbonic acid is stronger acid than phenol

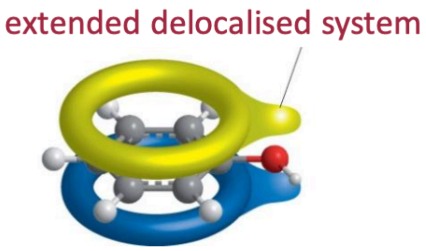
Followed by Sodium Carbonate or Sodium Hydrogencarbonate

- Na_2CO_3 and $NaHCO_3$ are not a strong enough acid than phenolate

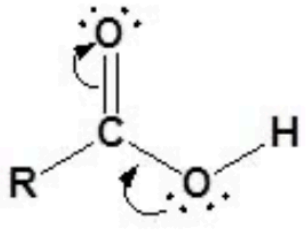
Esterification

- **Phenol will not react directly with carboxylic acid to form esters**
  Because:
  I. Phenol - the lone pair on the oxygen of phenol is delocalised into the benzene ring thereby reducing its availability for nucleophilic attack



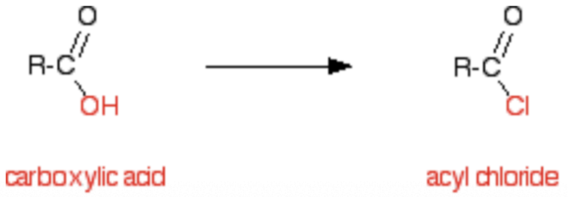


  II. Carboxylic acid - conjugation of the lone pair on oxygen in the –OH group with the π bond of the adjacent –C=O group reduces the electropositive character of the C in the –C=O group. This means a stronger nucleophile than phenol is required.



Esters from phenol <u>can only be made from acetyl chloride</u>

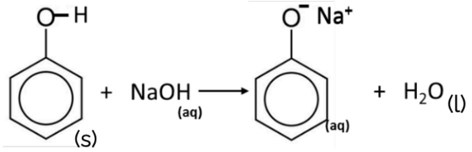
i. Convert the carboxylic acid into an acyl chloride using either **$SOCl_2$** or **PCl_5**.



See 4.3 Alcohols p22 & 4.5 Carboxylic acids later

more reactive

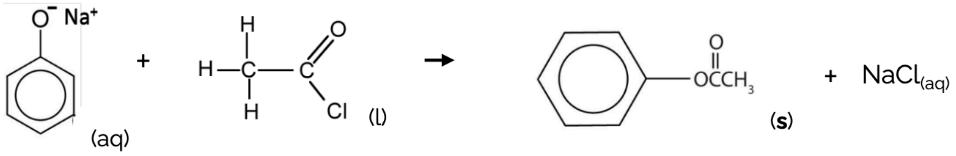
ii. Dissolve phenol in **sodium hydroxide solution** to create the phenolate ion.



The phenolate ion has a full negative charge and thus, is a much more powerful nucleophile.

sodium phenolate

iii. Shake the sodium phenolate with the acyl chloride and the reaction will occur at room temperature to produce the ester as a white solid in suspension.



ethanoyl chloride

phenyl ethanoate

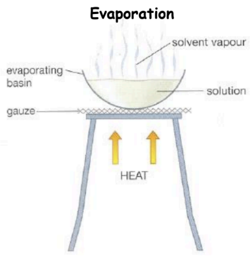
ester

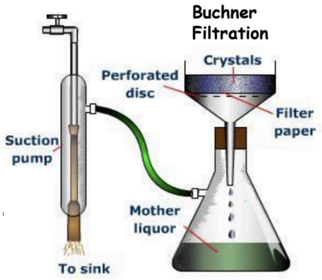
Chemical Properties compared with Benzene

- Both react with electrophiles and undergo substitution reactions
- In phenol delocalisation of the oxygen electron pair into the ring, increases the electron density in the π bonding system → electrophiles will attack phenol far more readily than benzene

Purification of the Product by Recrystallisation

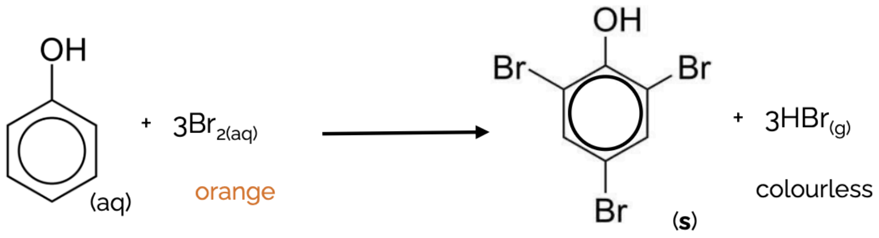
1. Filter and collect the crude product.
2. Dissolve the compound in the minimum quantity of hot solvent. (Hot filter if any solid insoluble impurities are visible.)
3. Evaporate the solvent until crystals are about to form. (Glass rod test.)
4. Place into a crystallising dish, cover with filter paper (excludes dust) and allow it to slowly crystallise.
5. Pour off surplus liquid (this contains soluble impurities).
6. Wash with a small quantity of ice cold solvent to remove surface impurities.
7. Dry crystals between pieces of filter paper.



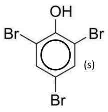


- The purified crystal can be checked by comparing it to the melting point

Bromination of Phenol



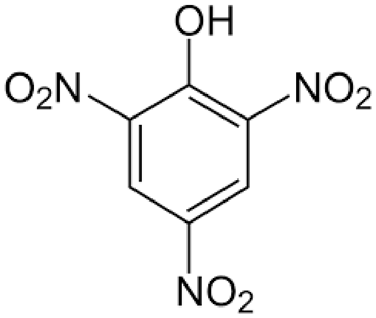
Conditions:	Bromine water Room temperature (no catalyst required)



- White precipitate

- Colour change from yellow-orange to colourless
- Test for phenol

Reaction with nitric(V) acid solution (HNO_3)



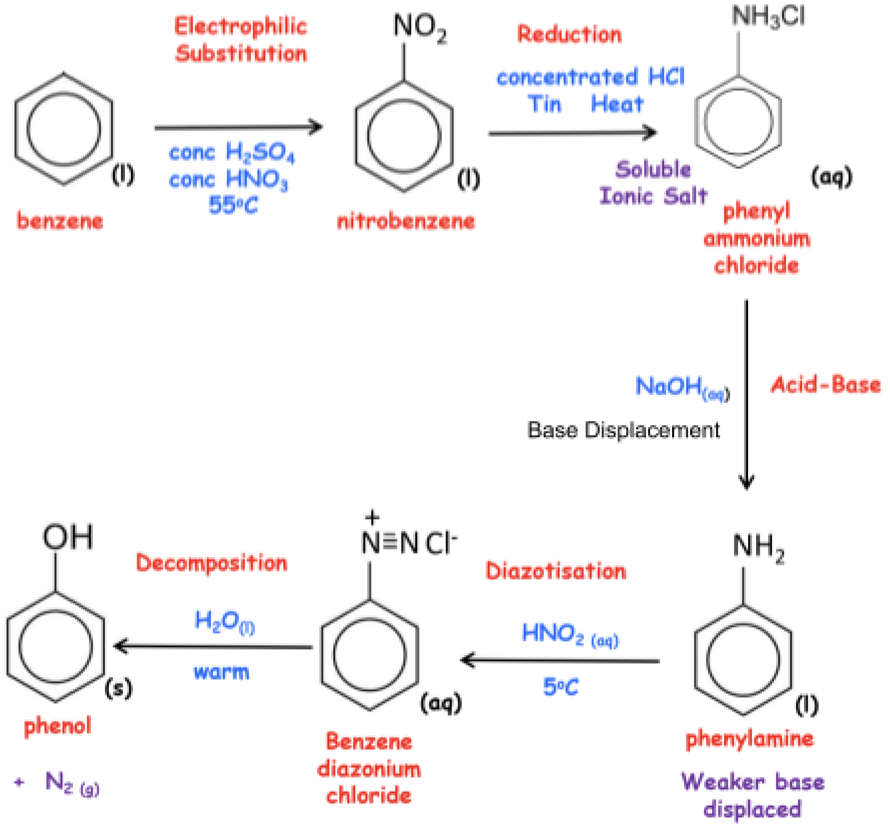
2,4,6–trinitrophenol

Conditions:

- Concentrated HNO_3 with dilute HNO_3
- No catalyst
- Room Temperature

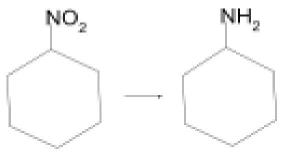
$$3HNO_3 + C_6H_5OH \rightarrow C_6H_2(NO_3)_3OH + 3H_2O$$

Preparation of Phenol in Lab

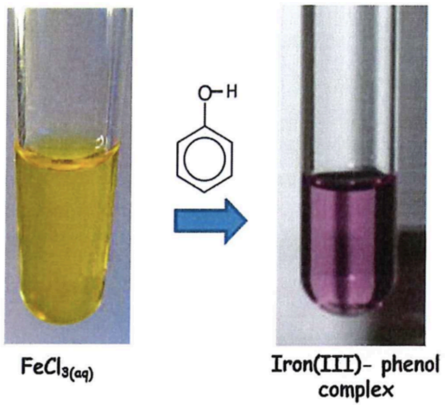


NO_2 to NH_2

- Tin and concentrated HCl
- Followed by NaOH

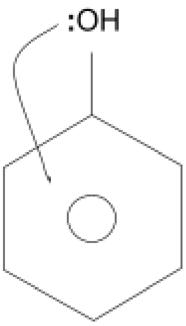


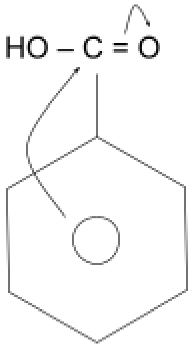
Test for Phenol



Phenol

Phenol – Has delocalise lone pair on oxygen, increase electron density on ring
Benzene – Delocalised pi electron bonding system
Benzoic Acid – Conjugation of C=O pi electron with the pi system on the ring <u>reduce electron density</u>

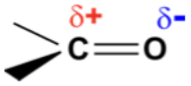




Aldehyde and Ketone

Preparation of Carbonyl Compounds – Oxidation – AS

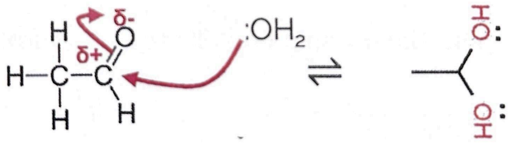
Polarity of Carbonyl Group



- Double bond in alkene has no polarity → Alkene are non-polar
- C=O bond is highly polarised → Aldehyde and Ketone are polar molecules

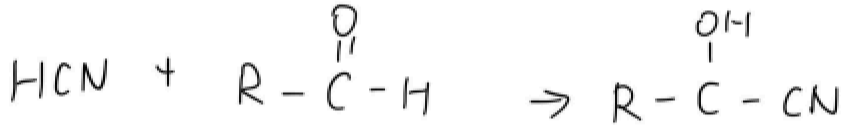
Physical Properties

- Aldehyde and Ketone have higher melting point compared to alkene
- Carbonyl compound have better solubility as their ability to form H-bond with water and forming a diol (which can form more H bond)
- Solubility decrease as the carbon chain increase



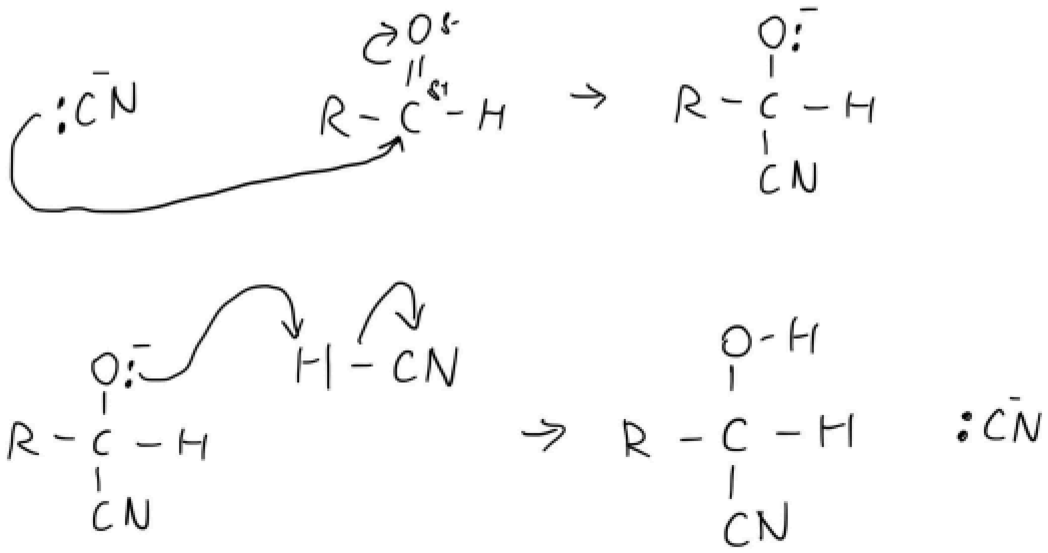
Nucleophilic Addition

1. Aldehyde and HCN

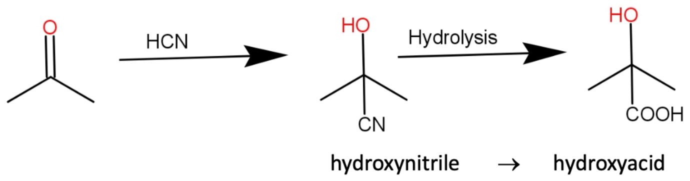


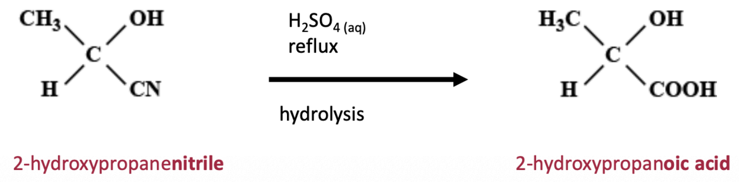
$$HCN + R-\overset{O}{\overset{\|}{C}}-H \rightarrow R-\overset{OH}{\overset{|}{C}}-CN$$

Mechanism:



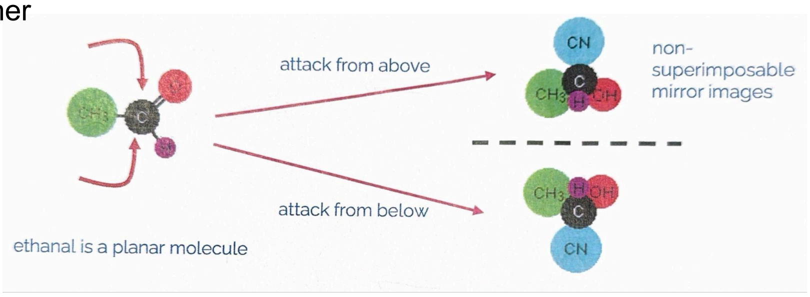
Generation of hydroxyacid





Notes:

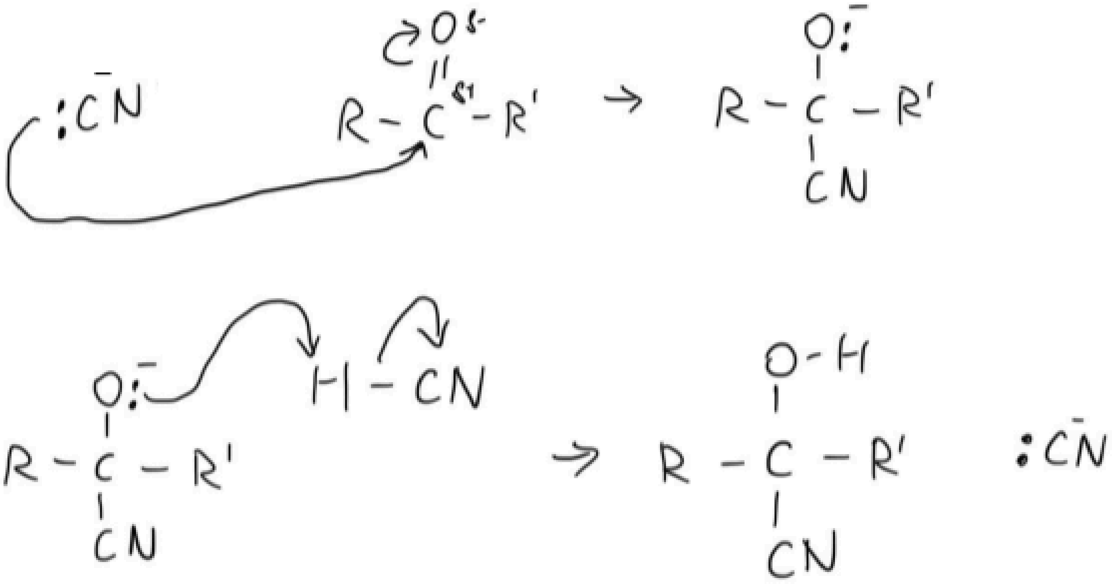
- Aldehyde may have optical isomer
- Ketone do NOT have optical isomer



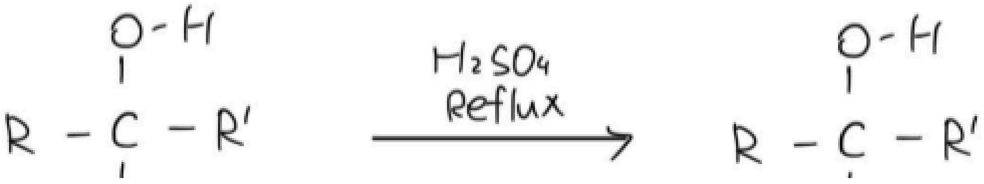
2. Ketone with HCN (identical with aldehyde)

$$HCN + R-\overset{\overset{O}{\|}}{C}-R' \rightarrow R-\overset{\overset{OH}{|}}{C}-CN$$

Mechanism:



CN to Carboxylic Acid

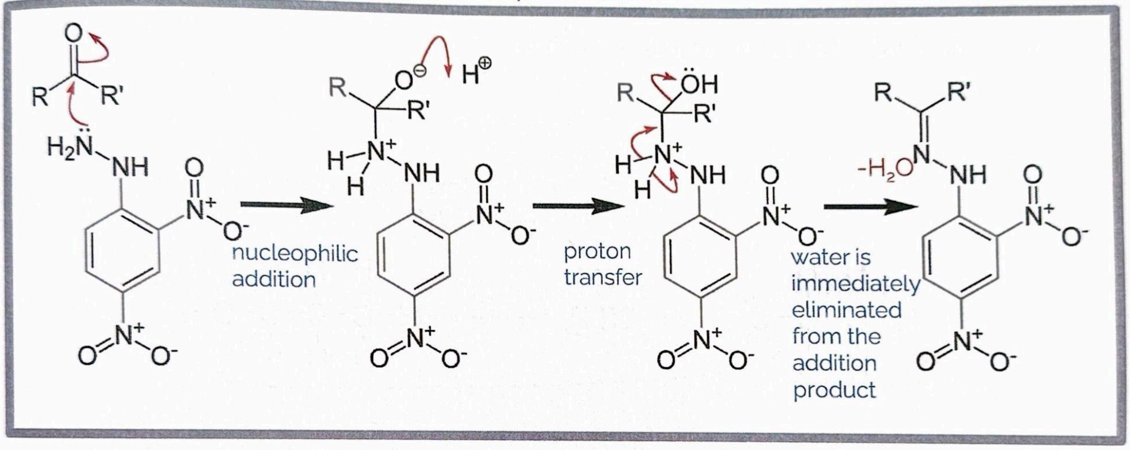


Test for Carbonyl Compound – 3 Tests

2,4–DNPH (Brady’s Reagent)

Reagent: 2,4-dinitrophenylhydrazine (2,4-DNPH) in alcohol solvent
Observation: Immediate formation of a heavy yellow orange precipitate
<u>Test for present of Aldehyde or Keytone</u>

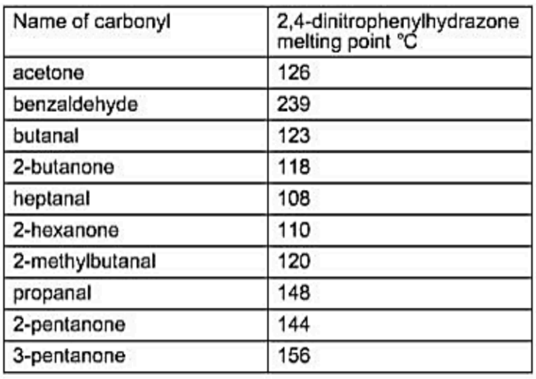
Reaction mechanism – <u>not</u> required for the specification



N.B. *You <u>are</u> required to know that this is a* **nucleophilic addition** followed by the **elimination** of water i.e. a nucleophilic **condensation** reaction.

Identifying the Exact Compound

- Add a few drops of aldehyde or ketone into Brady’s reagent (2,4-DNPH)
- Recrystalise
- A bright orange or yellow ppt shows present of carbon-oxygen double bond
- Use the melting point apparatus to measure the melting point of the prepared derivative and compare the values to the table of data



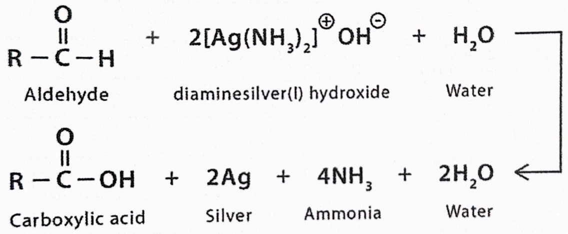
Name of carbonyl	2,4-dinitrophenylhydrazone melting point °C
acetone	126
benzaldehyde	239
butanal	123
2-butanone	118
heptanal	108
2-hexanone	110
2-methylbutanal	120
propanal	148
2-pentanone	144
3-pentanone	156

Tollen’s Reagent

- To distinguish between aldehyde or ketone
- Aldehyde form silver mirror

Method:

1. Add a few drops of Tollens reagent to a clean test tube
2. Add a few drops of suspected aldehyde and warm the test tube gently
3. A silver mirror (or grey precipitate) is formed with aldehyde
4. No silver mirror with ketone



Fehling Solution (Copper (II) Sulphate and Potassium tartrate)

Similar method

A dark red precipitate is formed with an aldehyde

The blue solution remans with a ketone

All aldehyde give classic brick-red precipitate expect phenylmethanal