

BENZENE (Notes)

30 Hydrocarbons

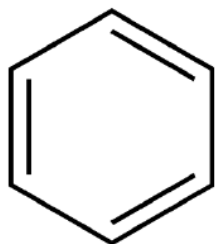
30.1 Arenes

Learning outcomes

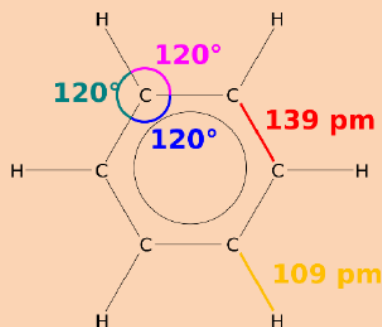
Candidates should be able to:

- 1 describe the chemistry of arenes as exemplified by the following reactions of benzene and methylbenzene:
 - (a) substitution reactions with Cl_2 and with Br_2 in the presence of a catalyst, $AlCl_3$ or $AlBr_3$, to form halogenoarenes (aryl halides)
 - (b) nitration with a mixture of concentrated HNO_3 and concentrated H_2SO_4 at a temperature between $25^\circ C$ and $60^\circ C$
 - (c) Friedel–Crafts alkylation by CH_3Cl and $AlCl_3$ and heat
 - (d) Friedel–Crafts acylation by CH_3COCl and $AlCl_3$ and heat
 - (e) complete oxidation of the side-chain using hot alkaline $KMnO_4$ and then dilute acid to give a benzoic acid
 - (f) hydrogenation of the benzene ring using H_2 and Pt/Ni catalyst and heat to form a cyclohexane ring
- 2 describe the mechanism of electrophilic substitution in arenes:
 - (a) as exemplified by the formation of nitrobenzene and bromobenzene
 - (b) with regards to the effect of delocalisation (aromatic stabilisation) of electrons in arenes to explain the predomination of substitution over addition
- 3 predict whether halogenation will occur in the side-chain or in the aromatic ring in arenes depending on reaction conditions
- 4 describe that in the electrophilic substitution of arenes, different substituents direct to different ring positions (limited to the directing effects of $-NH_2$, $-OH$, $-R$, $-NO_2$, $-COOH$ and $-COR$)

Benzene and its compounds



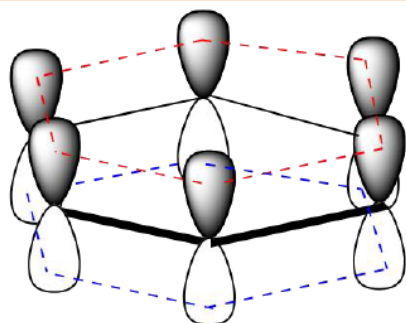
Benzene was first discovered in 1825 by Michael Faraday and Kekulé proposed the original structure for benzene as shown in fig. The structure consists of a planar, hexagonal ring of carbon atoms, with a hydrogen atom joined to each carbon atom. This structure has alternating single and double bonds between the carbon atoms. A systematic name for this molecule would be cyclohexa-1,3,5-triene or 1,3,5-cyclohexatriene.



The structure of benzene is nowadays better represented as in Figure. Each carbon atom seems to form just three bonds – two to C atoms and one to an H atom.

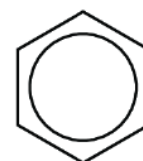
The remaining electrons form a delocalised system of six electrons – this is represented by the circle in the centre of the structure. These six electrons are not localised between individual carbon atoms in double bonds but instead are spread over the whole ring.

The ring of electrons is formed when p orbitals of each carbon overlap parallel (side to side) to form a π delocalised system



π electrons delocalized around the ring, above and below the plane

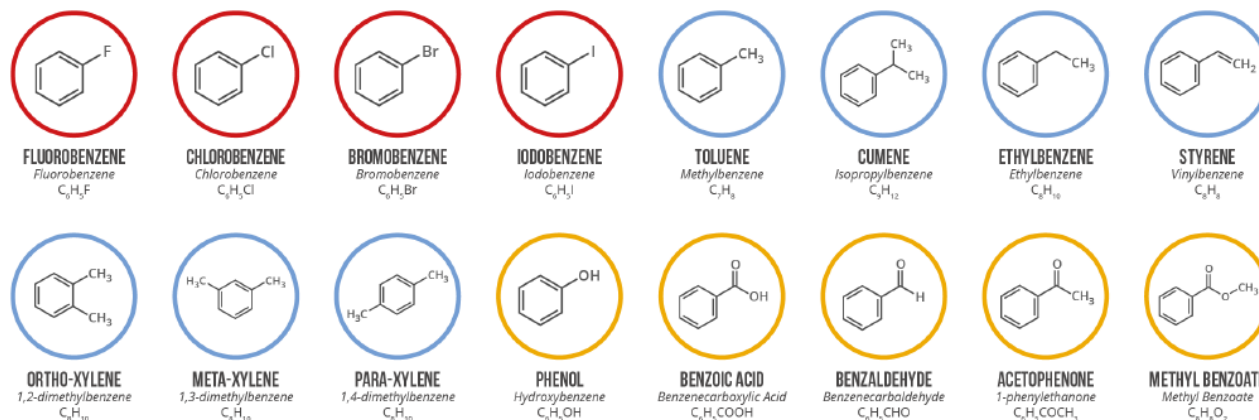
so benzene can be drawn as shown below

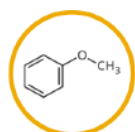


Sigma and Pi bonds in benzene

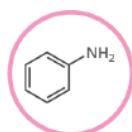
In benzene each carbon atom is joined to two other similar carbon atoms. Each carbon atom uses the sp^2 hybrids to form sigma bonds with two other carbons and one hydrogen atom. So there are 12 sigma bonds. Know each carbon atom contains unhybrid P orbital as shown above, these p orbitals form three pi bonds. So there are total 6 (C-C) sigma bonds and 6 (C-H) sigma bonds. Benzene also has 3 (C=C) pi bonds. So, there are 12 total sigma bonds and 3 pi bonds in benzene.

However, the π bonds formed are not localised between pairs of carbon atoms as in an alkene C C bond. Instead, the π bonds in benzene spread over all six carbon atoms in the hexagonal ring. The six electrons in the π bonds are said to be **delocalised**.

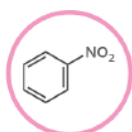




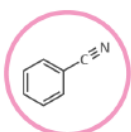
ANISOLE
Methoxybenzene
 $C_6H_5OCH_3$



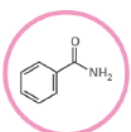
ANILINE
Aminobenzene
 $C_6H_5NH_2$



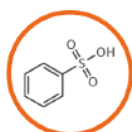
NITROBENZENE
Nitrobenzene
 $C_6H_5NO_2$



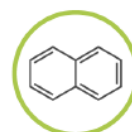
BENZONITRILE
Benzonitrile
 C_6H_5CN



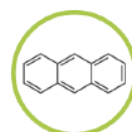
BENZAMIDE
Benzamide
 $C_6H_5CONH_2$



BENZENESULFONIC ACID
Benzenesulfonic Acid
 $C_6H_5SO_3H$



NAPHTHALENE
Naphthalene
 $C_{10}H_8$



ANTHRACENE
Anthracene
 $C_{14}H_{10}$

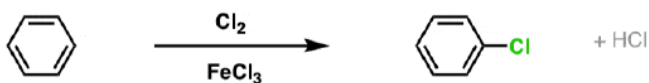
1 describe the chemistry of arenes as exemplified by the following reactions of benzene and methylbenzene:

- substitution reactions with Cl_2 and with Br_2 in the presence of a catalyst, $AlCl_3$ or $AlBr_3$, to form halogenoarenes (aryl halides)
- nitration with a mixture of concentrated HNO_3 and concentrated H_2SO_4 at a temperature between $25\text{ }^\circ\text{C}$ and $60\text{ }^\circ\text{C}$
- Friedel–Crafts alkylation by CH_3Cl and $AlCl_3$ and heat
- Friedel–Crafts acylation by CH_3COCl and $AlCl_3$ and heat
- complete oxidation of the side-chain using hot alkaline $KMnO_4$ and then dilute acid to give a benzoic acid
- hydrogenation of the benzene ring using H_2 and Pt/Ni catalyst and heat to form a cyclohexane ring

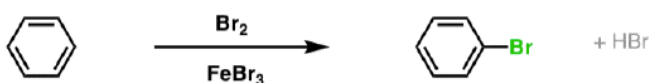
Electrophilic substitution with chlorine or bromine

Benzene reacts with chlorine and bromine by electrophilic substitution reaction in the presence of catalyst like aluminum chloride, Iron (III) chloride or iron. Aluminum bromide is used when benzene reacting bromide. Iron is not a catalyst because it reacts with small amount of chlorine or bromine and form iron (III) chloride $FeCl_3$ or iron (III) bromide $FeBr_3$.

Chlorination:



Bromination:

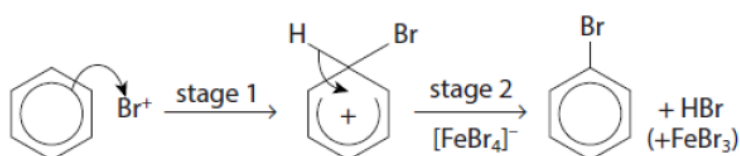


Mechanism of electrophilic substitution reaction

The delocalization of electron in the benzene ring repel bromine – bromine bond when bromine molecule approaches the benzene ring. Iron bromide helps in the polarization of bromine bond, and bromine bond broken as shown below.

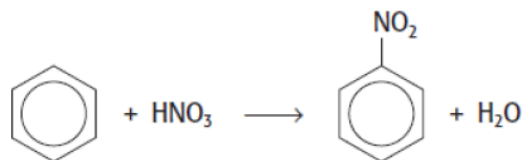


positive end of the bromine molecule act as the electrophile. The Br^+ cation and the 'electron-rich' benzene ring are attracted to each other.



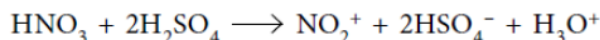
Nitration of Benzene

Nitration refers to the introduction of the NO_2 group into a molecule

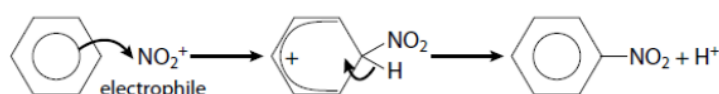


4

NO_2^+ is the electrophile. This nitronium ion (or nitryl cation) is made from a mixture of concentrated nitric acid and concentrated sulfuric acid:

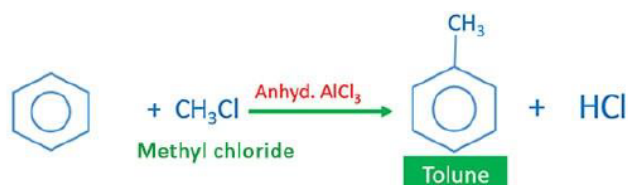


The mechanism is as



Friedel-Crafts alkylation and acylation by CH_3Cl , CH_3COCl and AlCl_3 and heat

Friedel-Crafts reactions result in the introduction of a side-chain into a benzene ring. They are also called alkylation or acylation reactions.



Importance of AlCl_3

In Friedel craft alkylation, AlCl_3 behaves as a catalyst. AlCl_3 helps to start the reaction and after the reaction, it is generated again.



Mechanism of Friedel Craft Alkylation Reaction of Benzene

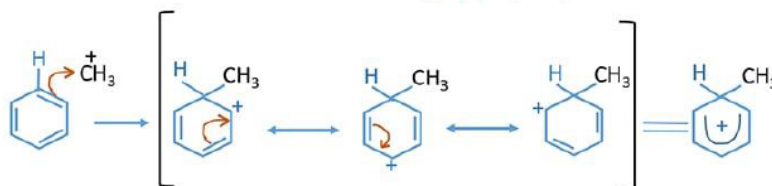
This reaction mechanism contains three steps. An alkyl carbonium ion is generated as the electrophile to start the reaction. Anhydrous aluminium chloride helps to formation of alkyl carbonium ion (electrophile). This reaction is an electrophilic substitution reaction.

Step 1. Formation of electrophile

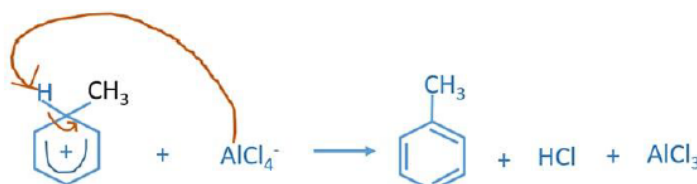


Step 2. Benzene ring attacks electrophile

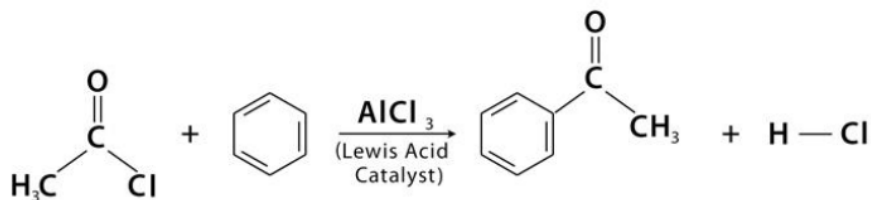
Benzene ring attacks the methyl carbocation (electrophile) to form intermediate carbocation



Step 3. Intermediate carbocation loses a proton to AlCl_4^-



Friedel–Crafts acylation

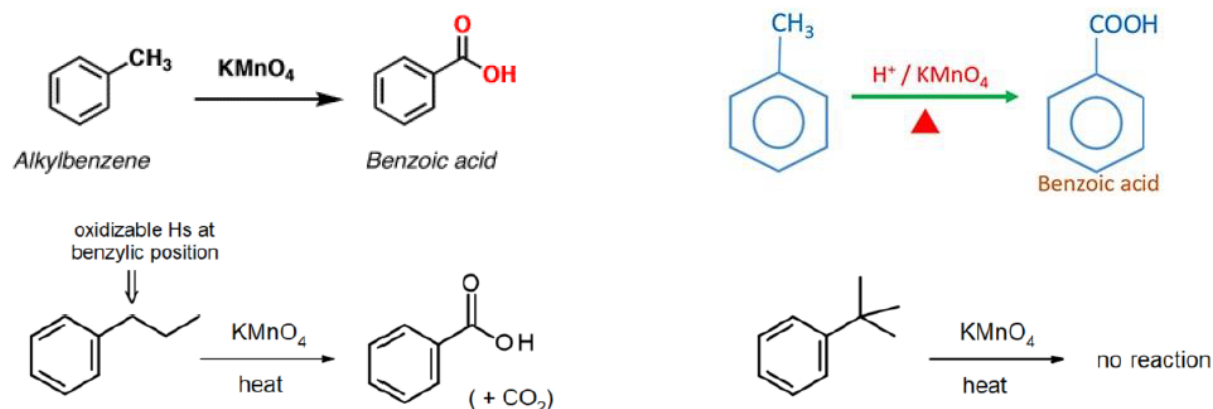


5

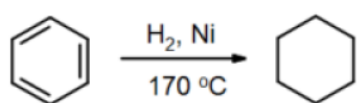
Mechanism of Friedel Craft acylation Reaction of Benzene Activity. Draw the Mechanism for the above reaction.

complete oxidation of the side-chain using hot alkaline KMnO_4 and then dilute acid to give a benzoic acid

methylbenzene produces benzoic acid when refluxed with alkaline potassium manganate(VII), and then acidified with dilute sulfuric acid, or another strong oxidizing agent such as acidified potassium dichromate(VI):



hydrogenation of the benzene ring using H_2 and Pt/Ni catalyst and heat to form a cyclohexane ring



under high temperature and pressure, benzene can be converted into cyclohexane. Pt or Ni is used as catalyst.

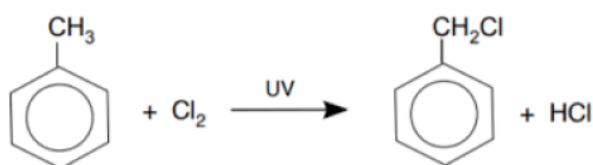
2 describe the mechanism of electrophilic substitution in arenes:

- as exemplified by the formation of nitrobenzene and bromobenzene
- with regards to the effect of delocalisation (aromatic stabilisation) of electrons in arenes to explain the predomination of substitution over addition

3 predict whether halogenation will occur in the side-chain or in the aromatic ring in arenes depending on reaction conditions

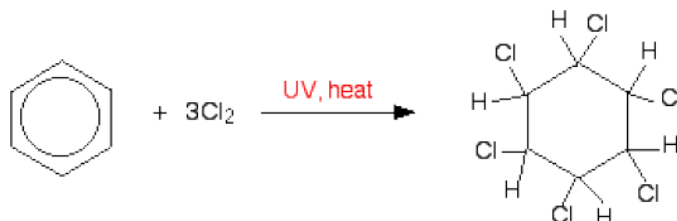
will halogenation occur in the side-chain or in the aromatic ring

- If chlorine or bromine react with boiling methylbenzene in the absence of a catalyst but in the presence of UV light, substitution happens in the methyl group rather than the ring.



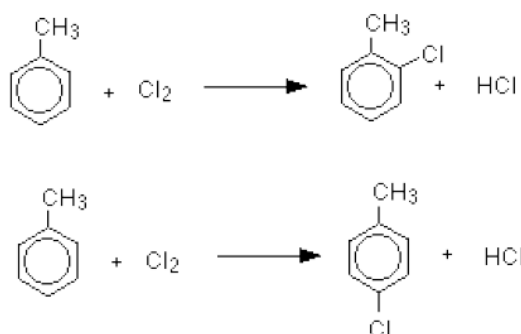
In the presence of ultraviolet light (but without a catalyst present), hot benzene will also undergo an *addition* reaction with chlorine or bromine. The ring delocalisation is permanently broken and a chlorine or bromine atom adds on to each carbon atom.

For example, if you bubble chlorine gas through hot benzene exposed to UV light for an hour, you get 1,2,3,4,5,6-hexachlorocyclohexane.



- Benzene reacts with chlorine or bromine in the presence of a catalyst, replacing one of the hydrogen atoms on the ring by a chlorine or bromine atom.

The reactions happen at room temperature. The catalyst is either aluminium chloride (or aluminium bromide if you are reacting benzene with bromine)



NOTE: electron-donating methyl group

remember electron donating groups activate 2 and 4 position of benzene ring.

electron-withdrawing

electron withdrawing groups activate 1, 3, and 5 position of benzene ring

Electron-donating group	Electron-withdrawing
$-\text{NH}_2, -\text{NHR}$ or $-\text{NR}_2$	$-\text{NO}_2$
$-\text{OH}$ or $-\text{OR}$	$-\text{N}^+\text{H}_3$
$-\text{NHCOR}$	$-\text{CN}$
$-\text{CH}_2, -\text{alkyl}$	$-\text{CHO}$
$-\text{Cl}$	$-\text{COOH}, -\text{COOR}$

When we halogenate methylbenzene or other alkylarenes, the halogen atom substitutes into the benzene ring at positions 2 or 4. These positions are 'activated' by any electron-donating groups bonded directly to the benzene ring.

Further nitration of the nitrobenzene produces 1,3-dinitrobenzene and 1,3,5-trinitrobenzene as nitro group is electron withdrawing.

4 describe that in the electrophilic substitution of arenes, different substituents direct to different ring positions (limited to the directing effects of $-\text{NH}_2$, $-\text{OH}$, $-\text{R}$, $-\text{NO}_2$, $-\text{COOH}$ and $-\text{COR}$)
explain the difference in reactivity between a halogenoalkane and a halogenoarene as exemplified by chloroethane and chlorobenzene

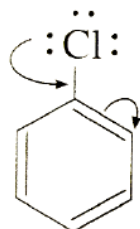
Reactivity difference between halogenoalkane and halogenoarenes

Halogenoarenes are less reactive than halogenoalkanes.

7

Explanation

Stabilization by resonance : The electron pair of halogen atom in halogenoarene, is in conjugation with the π electrons of the benzene ring. Thus, the C-X bond has partial double bond character. As a result of this, C-X bond in haloarene is shorter and hence stronger than that of haloalkane. So it is difficult to break C-X bond in haloarenes compared to haloalkanes, therefore, it is less reactive.



Polarity of the C-X bond : In aryl halide C-X bond is less polar than in alkyl halides. More polar the bond, more reactive it will be, so alkyl halides are more reactive than aryl halides