AROMATIC - BENZENE

Benzene, C_6H_6, is one of the most important organic molecules known because it is representative of a large variety of molecules known as aromatic compounds. Benzene is a colourless, highly flammable liquid, good solvent for fuels and oils.

STRUCTURE OF BENZENE

Arenes are hydrocarbons that contain one or more benzene rings.

The benzene molecule is an example of a resonance hybrid which has two resonance forms. In the Kekule structures,(German chemist Friedrich August Kekule`, 1865), the six carbon atoms form a ring of alternate single and double bonds:

However, modern physical methods, such as X-ray and electron diffraction, show that the benzene molecule is flat, i.e. planar, with a regular hexagonal arrangement of the carbon atoms, all six carbon-carbon bond lengths being identical (0.139 nm). The carbon-carbon bond length is thus seen to be intermediate between the carbon-carbon single bond length (0.154 nm) and the carbon-carbon double bond length (0.134 nm).

Benzene does not behave chemically as a typical unsaturated compound, and one of its most characteristic reaction is the replacement of one of it hydrogen atoms with another atom or group of atoms, i.e. a substitution reaction (see later notes). Because **all of the carbon atoms** in the benzene molecule react in the same way, they must be **chemically equivalent** to each other.

It is in general more stable than would be expected for a compound which could be accurately represented by a single Kekule structure. This stability is reflected in the observed heat of hydrogenation of benzene:

$$\underset{\text{benzene}}{C_6H_{6\,(l)}} \quad + \quad 3\ H_{2\,(g)} \quad \longrightarrow \quad \underset{\text{cyclohexane}}{C_6H_{12\,(l)}} \qquad \Delta H \quad = \quad -208\ \text{kJ mol}^{-1}$$

which compares with a value of 360 kJ mol^{-1} calculated on the basis of a Kekule structure with its three carbon-carbon double bonds. The observed heat of hydrogenation of cyclohexene (one double bond only) is 120 kJ mol^{-1} ...

$$\underset{\text{cyclohexene}}{C_6H_{10\,(l)}} \quad + \quad H_{2\,(g)} \quad \longrightarrow \quad \underset{\text{cyclohexane}}{C_6H_{12\,(l)}} \qquad \Delta H \quad = \quad -120\ \text{kJ mol}^{-1}$$

so that if benzene could be correctly represented by a Kekule structure (three alternate double bonds), its heat of hydrogenation for three carbon-carbon double bonds would be expected to be 3 x 120 = 360 kJ mol^{-1}. Thus benzene is 360 - 208 = 152 kJ mol^{-1} more stable than would be expected for a compound with a Kekule structure of three alternate double bonds, and this extra stability is known as the **resonance energy**. The resonance energy is measured by the difference between the calculated and the observed heat of hydrogenation: the greater the resonance energy, the more stable the compound.

The concept of resonance accounts satisfactorily for most of the observed properties of benzene, including its great stability, the six identical carbon-carbon bond lengths and the observed heat of hydrogenation. The cyclic 6-electron arrangement confers a special stability in the form of a large resonance energy.

The structure of the benzene molecule may be described in terms of molecular orbital theory. Each of the six carbon atoms makes use of three equivalent sp^2 hybrid orbitals to form three σ-bonds, two to carbon and one to hydrogen, at an angle of approximately 120° to each other as in ethene:

The remaining unhybridized 2p orbital of each carbon atom is at right angles to the plane of the ring of six carbon atoms and sideways overlap of these orbital to form π-bonds can occur equally well between carbon atoms 1 and 2, 3 and 4, 5 and 6, or between 2 and 3, 4 and 5, and 1 and 6:

The p orbitals overlap to give two electron clouds above and below the plane of the ring. The six π-electrons are accommodated in three delocalized π-orbitals, each molecular orbital containing two electrons. This is to say that the p-orbitals overlap all around the benzene ring structure to give a continuous π-bond around the nucleus, usually summarized as a double ring doughnut of electron density:

Aromatic Derivatives

Several functional groups can be attached to a benzene ring ...

halogen: bromobenzene

hydroxyl: phenol
(antiseptic)

amino: aniline
(used in dyes)

cyano: benzonitrile

carboxylic acid: benzoic acid
(food preservative)

ester: methyl benzoate

aldehyde: benzaldehyde
(artificial flavouring)

ketone: acetophenone
(hypnotic drug)

methoxy: anisole
(used in perfumes)

ethoxy: phenetole

methyl: toluene
(methyl benzene)

sulphonic acid: benzenesulphonic acid

alkene: ethenylbenzene
(styrene –> polystyrene)

nitro: nitrobenzene

methyl 2-hydroxy benzoate, (methyl salicylate: oil of wintergreen flavour)

4-hydroxy-3-methoxy benzaldehyde: vanillin –> vanilla flavour

1,4-dichlorobenzene: insecticide

naphthalene: crystalline solid, mp 80 ^{O}C, moth balls, insecticide.

When benzene is treated as a substituent, it is given the name “phenyl”, (C_6H_{5-})

The general ‘rule’ is that if the alkyl chain is greater than six carbons, the benzene ring is treated as a substituent and it is a phenylalkane.

If the chain is less than six carbons, it is named as a benzene derivative, i.e. it is an alkyl benzene (such as ethylbenzene).

Example: Example: 2-phenyl octane (2-methyl propyl)- benzene

ISOMERS

Aromatic compounds with more than one substituent on the benzene ring can exist as positional isomers. A total of three different isomers are possible:
Example: 1,2-dimethylbenzene 1,3-dimethylbenzene 1,4-dimethylbenzene
(ortho– dichlorobenzene) (meta– dichlorobenzene) (para– dichlorobenzene)

The common name for the:
1,2- orientation is ortho, abbreviation: o –
example: o– nitromehtylbenzene:

1,3- substitution is meta, abbreviation: m –
example: m– chlorobenzoic acid:

1,4- substitution is para, abbreviation: p –
example: p– methylphenylamine:

If the two substituents are different, one of them is deemed the ‘root’ group, in the order of precedence:
— COOH, — OH, — CH_3 , — halogen, — NO_2
Example: 3-hydroxybenzoic acid, 4– methylphenol,

2,4– dinitrochlorobenzene 2,4,6– trichlorophenol (the antiseptic TCP)

MANUFACTURE

1. from coal: distillation of coal tar
2. from distillation of petroleum

Physical Properties of Arenes

Benzene and most alkylbenzenes are strongly oily-smelling colourless liquids, immiscible with , and less dense than water. They are non-polar, and the only intermolecular bonding is due to induced dipoles of van-der-Waals forces. Their boiling points are similar to those of the equivalent cycloalkanes, and increase with relative molecular mass as expected.

Reactions of Arenes

Benzene and methylbenzene (toluene) are components of many brands of unleaded petrol. In sufficient oxygen, they burn completely to carbon dioxide and steam:

$$C_6H_6 \quad + \quad 7\,½\,O_2 \longrightarrow 6CO_2 \quad + \quad 3H_2O$$

In the presence of insufficient oxygen, arenes burn with a very smoky flame, because much soot is produced due to the high C:H ratio.

$$C_6H_6 \quad + \quad 1\,½\,O_2 \longrightarrow 6C_{(s)} \quad + \quad 3H_2O$$

ELECTROPHILIC SUBSTITUTION IN BENZENE

Benzene has a high electron density, ∴ of the π-electron cloud; ∴ it is susceptible to electrophilic attack to form a carbocation intermediate. When benzene reacts with a suitable electrophilic species, X, that group replaces a hydrogen on the benzene ring:

$$\text{Ph - H} \xrightarrow{E^+ X^-} \text{Ph - E} \quad + \quad HX$$

In this reaction, the group E is a cation, the replacement of H by E is a substitution and benzene is aromatic, thus this process is called ***electrophilic aromatic substitution***

If benzene underwent normal addition reactions, the resulting product would not have delocalised π-bond, this would result in benzene would lose the added stability that is obtained from delocalisation, i.e. the resonance energy.

CHEMICAL REACTIONS OF BENZENE

At room temperature benzene is inert to acids, H_2, Br_2, oxidising agents such as $KMnO_4$, unlike other conjugated alkenes.

1. Reaction with HBr or Br_2 in the absence of other reagents

Benzene is a very weak Lewis base (recall: Def. Lewis base is an electron pair donor).
To function as a Lewis base, benzene must donate the π-electrons, but these are 'tied-up' in the aromatic cloud that gives benzene its special stability.

Both HBr and Br-Br are insufficiently strong Lewis acids to react. The loss of resonance energy associated with this donation of electrons by benzene precludes its reaction, thus benzene is normally unreactive with hydrogen halides, HX and with halogens, X_2.. However, the HX or X_2 may be activated by Lewis acids such as FeX_3 or AlX_3 to become a powerful electrophile.

2. Reaction with a halogen, X_2, in the presence of a Lewis acid: $FeBr_3$ or $AlCl_3$

$$\mathbf{F_2} \quad > \quad \mathbf{Cl_2} \quad > \quad \mathbf{Br_2} \quad > \quad \mathbf{I_2}$$

(explosive) (endothermic)

Overall reaction:

$$Br_2 \quad + \quad C_6H_6 \quad \longrightarrow \quad C_6H_5Br \quad + \quad HBr \qquad \Delta H \ = \ -\text{ ve}$$

Transition metals, (and aluminium), with halogens react as follows:

$$2\ Fe \quad + \quad 3\ Br_2 \quad \longrightarrow \quad 2\ FeBr_3$$

Iron is a transition metal possessing incompletely filled 3d - orbitals, thuerefore Fe can obtain a pair of lone electrons from the bromine molecule. $FeBr_3$ is electron deficient, there are 6 e^- associated with Fe, .: to complete its octet, it pulls the lone pairs of electrons on the bromine, .: polarising the halogen resulting in the hetrolysis of the X – X bond; and thus $FeBr_3$ is a Lewis acid.

When $FeBr_3$ (often referred to as Halogen Carrier) - a Lewis acid, comes in close proximity to the diatomic bromine, the closest bromine takes on a negative charge, i.e. a dipole is induced, thus inducing a positive charge on the other bromine:

$$FeBr_3 \quad + \quad \overset{\delta-}{:Br} — \overset{\delta+}{Br} \quad \longrightarrow \quad Br^{+1} \quad + \quad FeBr_4^{\,-}$$

The function of the catalyst, $FeBr_3$ (or $AlCl_3$) is to withdraw electrons from the bond between the bromine atoms, i.e. to polarize the bromine molecule leading to heterolysis of the molecule, in order that the positively charged bromine atom can attack the benzene ring (∴ $FeBr_3$ is a Lewis acid).

The electrophile, the brominium ion, Br^+, attacks the benzene ring, this is the SLOW STEP of the reaction. The C_6H_6 ring, donates a pair of electrons to the Br^+, forming a C — Br bond and leaving a positive charge on the ring:

This carbocation intermediate, sometimes called the **Wheland intermediate**, is resonance stabilized, since the positive charge can be delocalized by the adjacent π-bonds. A total of three resonance forms can be drawn which differ only in their electronic distribution and the actual structure of the ion is a resonance hybrid of these forms:

The carbocation intermediate is, :. more stable than any of the contributing structures.

Since the aromatic character of C_6H_6 , (i.e. the six delocalized π-electrons which adds stability) has been disrupted in the formation of the intermediate (since the delocalization can only now spread over the rest of the five atoms), hence a proton is expelled, (FAST), from the Wheland intermediate to regenerate the aromatic ring:

The hydrogen ion, a proton, is easily lost, because the reformation of the aromatic ring is an exothermic process, since the delocalized π-electron system over the six carbon atoms is now retained.

The name given to this entire mechanism is **Electrophilic Aromatic Substitution**.

Similar reaction with $AlCl_3$, generates the aluminum complex, also containing Br^+ ion:

$$AlCl_3 \quad + \quad Br — Br \xrightarrow{\qquad} AlCl_3Br^{-1} \quad + \quad Br^{+1}$$

Note: Further substitution of the halogeno benzene is difficult, since the halogen substituent deactivates the benzene ring. Similar reaction for other halogens: Cl_2 as for benzene is observed, but iodine does not react. Also, halogenation is not reversible.

The **potential energy diagram** for the halogenation of benzene is:

3. NITRATION

Benzene does not react with nitric acid, even with concentrated. But a mixture of **concentrated nitric acid and concentrated sulphuric acid below 60°C** ('nitrating mixture') converts benzene to nitrobenzene - a pale yellow oil.

The active electrophilic species is the nitryl cation (nitronium ion), NO_2^{+1}, which forms in the presence of $H_2SO_{4(aq)}$:

$HNO_{3(aq)}$ can dissociate in two ways:

(1) $HNO_3 \longrightarrow H^{+1} + NO_3^{-1}$ (2) $HNO_3 \rightleftharpoons OH^{-1} + NO_2^{+1}$

$H_2SO_{4(aq)}$ can dissociate to form:

$$H_2SO_4 \longrightarrow H^{+1} + HSO_4^{-1}$$

The $H^{+1}_{(aq)}$ formed by the H_2SO_4 removes the OH^{-1} in equilibrium (2) forming H_3O^{+1}

$$2\,H_2SO_4 + OH^{-1} \longrightarrow H_3O^{+1} + 2\,HSO_4^{-1}$$

$\therefore$ the equilibrium in (2) is displaced to the right, hence in the presence of sufficient H_2SO_4, the nitronium ions are present. Thus the function of the concentrated H_2SO_4 appears to be to produce the highly reactive nitronium ion, NO_2^{+1}, from the nitric acid.

The nitryl cation, NO_2^{+1}, is an electrophile which is attracted to the delocalised π-electron system in benzene to form the unstable Wheland intermediate:

This is followed by th expulsion of a proton, which retains the stable delocalised ring system:

The reason why the C – H bond breaks in preference to the C – N bond is because there is the possibility of the p-orbitals overlapping with the — NO_2 group into the benzene ring.

The H^{+1} formed reacts with the HSO_4^{-1} reforming H_2SO_4.:

$$H^{+1} + HSO_4^{-1} \longrightarrow H_2SO_4$$

Evidence that the nitronium ion is the actual electrophilic reagent under these conditions is provided by spectroscopic studies of a solution of $HNO_{3(aq)}$ in pure H_2SO_4 indicates the presence of the NO_2^{+1} ion.

This reaction is useful as a synthetic route as the nitro-group can be readily reduced to the amino-group, – NH_2:

$$C_6H_6 \xrightarrow[c.H_2SO_4]{c.HNO_3} \underset{\text{nitrobenzene}}{C_6H_5NO_2} \xrightarrow{Sn/c.HCl} \underset{\text{aniline}}{C_6H_5NH_2}$$

If C_6H_6 is heated above 60°C, with concentrated HNO_3 and concentrated H_2SO_4, then 1,3 dinitrobenzene - pale yellow crystals - is formed.
This is $\because$ above 60°C, the HSO_4^{-1} ion dissociates to form :

$$HSO_4^{-1} \longrightarrow H^{+1} + SO_4^{-2}$$

Hence, greater quantities of H^{+1} are present, which react with OH^{-1} from equilibrium (2), $\therefore$ more of the electrophile, the nitryl ion is produced, thus quicker attack by the NO_2^{+1}, yielding the 1,3-dinitrobenzene, (m-dinitro benzene):

4. SULPHONATION

If C_6H_6 is boiled with concentrated H_2SO_4 for several hours, then benzenesulphonic acid is produced.

$$C_6H_6 \quad + \quad H_2SO_4 \longrightarrow C_6H_5SO_3H \quad + \quad H_2O$$

The details of the mechanism are less well known than the previous examples.
H_2SO_4 can dissociate in two ways:

(1) $H_2SO_4 \longrightarrow H^{+1} + HSO_4^{-1}$

and to a very small extent:

(2) $H_2SO_4 \rightleftharpoons OH^{-1} + HSO_3^{+1}$

Heating above 60°C and boiling for several hours, it is thought that the equilibrium (2) is favoured and attack by the electrophile HSO_3^{+1} occurs, producing the unstable Wheland intermediate :

Loss of hydrogen ion the usual manner regenerates the aromatic ring with transfer of the H^{+1} to OH^{-1} produced in equilibrium (2): $H^{+1} + OH^{-1} \longrightarrow H_2O$

<u>Sulphonation is industrially important in two respects</u>:

1. The incorporation of sulphonic acid groups into the molecules of dyes helps to make the dyes water soluble.
2. The sodium salts of arylsulphonic acids incorporating long alkyl chains on the ring are important anionic detergents.

Sulphonic acids are used in detergents, which are water-soluble salts of long-chain sulphonic acids as $CH_3(CH_2)_{11}C_6H_4SO_3^{-1}Na^{+1}$.

Heating above 250°C, produces benzene-1,3-disulphonic acid:

5. FRIEDEL - CRAFTS' REACTIONS

This involves reactions of the C_6H_6 ring with an alkyl or an acyl halide in the presence of a suitable catalyst - typically $AlCl_3$ or $FeCl_3$ (Lewis Acids) - referred to as alkylation (with an alkyl halide) or acylation (with an acid halide) – these are synthetically important routes.

A) ALKYLATION

$$C_6H_6 \quad + \quad R — X \longrightarrow C_6H_5 – R \quad + \quad HX$$

An alkyl side chain may be introduced into the C_6H_6 ring by reacting C_6H_6 with a halogenoalkane ($^{\delta+}R\text{-}X^{\delta-}$ have a permanent dipole) in the presence of anhydrous $AlCl_3$ as a catalyst or Halogen Carrier:

$$AlCl_3 \quad + \quad {}^{\delta-}X — R^{\delta+} \longrightarrow AlCl_3\,X^{-1} \quad + \quad R^{+1}$$

$AlCl_3$ is electron deficient, being a covalent molecule, there are only 6 electrons associated with it ∴ in order to complete its octet, it pulls the lone pairs of electrons on the halogen in the halogenoalkane, thus inducing a dipole (i.e. polarising the R-X bond, leading to heterolysis:

$$AlCl_3 \quad + \quad \overset{\delta-}{I} - \overset{\delta+}{CH_3} \longrightarrow AlCl_3{:}I^{-1} \quad + \quad CH_3^{+1}$$

The function of the $AlCl_3$ catalyst is to form a highly polarised complex with the alkyl halide in which the carbon atom attached to the halogen carries a fractional positive charge.

The electrophilic alkyl group produced then reacts with the nucleophilic benzene ring to form a carbocation from which a proton is expelled to give the product, toluene:

The proton expelled reacts with the anion: $H^{+1} + AlCl_3I^{-1} \longrightarrow AlCl_3 + HI_{(g)}$

Stable addition compounds such as $AlCl_3I^{-1}$ can be isolated ∴ **proof for this mechanism**.

This is **not** a good method for preparing homologs of C_6H_6, because further substitution takes place immediately, because the **product is usually more reactive than C_6H_6, (because of the activating effect of an electron-releasing alkyl group on the C_6H_6 ring)**, so that further alkylation occurs to give a mixture of products: 1,2- , 1,4- , and 1,6- dimethyl benzene.

Note: The side chain, no matter what its length is readily oxidised to an acid group by boiling with an oxidizing agent such as acidified $KMnO_4$ or $K_2Cr_2O_7$ ——————> C_6H_5COOH (benzoic acid)

B) ACYLATION

Side chains alkanes may also be introduced by using an acid chloride (an alkanoyl halide, example: CH_3COCl - ethanoyl chloride) in the presence of a halogen carrier.

The **main advantage** of the acylation reaction is that the first acyl group introduced into the ring has a **deactivating effect,** so that further acylation is effectively prevented.

The mechanism of the acylation reaction is similar to that of the alkylation reaction and involves a complex of the acid chloride with the $AlCl_3$:

$$AlCl_3 + \overset{\delta+}{CH_3CO} — \overset{\delta-}{Cl} \longrightarrow AlCl_4^{-1} + CH_3CO^{+1}$$

the electron deficient $AlCl_3$ attracts lone pairs of electrons on the Cl – polarising bond – leading to heterolytic fission – producing the electrophile — which goes on to attack the π-electron density of the benzene ring:

Proton expulsion results, the product is acetophenone or phenyl ethanone

And the H^{+1} ion expelled reacts with the $AlCl_4^{-1} \longrightarrow HCl + AlCl_3$ (regenerated).

Here polysubstitution does not take place, ∵ the product is less reactive than C_6H_6, ∴ a good yield of product is obtained.

The ketones produced by this method can easily be reproduced by Zn + c.HCl to ethylbenzene, which can be dehydrogenated to styrene – this can be polymerised to polystyrene :

$$C_6H_6 \xrightarrow{AlCl_3+CH_3COCl} C_6H_5COCH_3 \xrightarrow[4[H]]{Zn+c.HCl} C_6H_5CH_2CH_3 \xrightarrow{ZnO/600^\circ C} C_6H_5CH_2 = CH_2$$

↓

polystyrene

ADDITION REACTIONS OF BENZENE

When benzene reacts with electrophiles, it always undergoes substitution. There are two ways in which it can be forced to undergo addition reactions.

In general addition reactions do not occur to any great extent, in fact benzene shows inactivity to addition reaction, because this would require the destruction of the π– electron cloud which induces extra stability to the benzene ring, i.e. loss of stability would occur.

1. Addition of hydrogen: Ni catalyst, high T, high P $\xrightarrow{3\ H_2}$ **cyclohexane**

2. Addition of X_2: in bright sunlight, i.e. UV light, .: a free radical mechanism is indicated,
3 molecules of X_2 add on to the benzene ring. $\longrightarrow$
1,2,3,4,5,6-hexahalogeno cyclohexane

Example: BHC: 'benzene hexachloride'**,** was once used as an organochlorine insecticide. (The molecule of BHC contains six chiral centres, and so there are many optical isomers that could be formed. The biologically active one is called gamma – BHC, or gammexane)

Substitution in the side chain

Methylbenzene and other alkylbenzenes very readily undergo radical substitution with chlorine or bromine in the presence of UV light, (just like alkanes). As in th ecase of alkanes, substitution occurs only in the during the reaction, and not in the ring.

Example:

$$C_6H_5CH_3 \quad + \quad Cl_2 \longrightarrow C_6H_5CH_2Cl \quad + \quad HCl$$

Oxidation of the side chain

When alkylbenzenes are treated with hot alkaline potassium manganate(VII), oxidation of the whole side chain occurs, leaving the closest carbon atom to the ring as a carboxylic acid group.

Example:

$$C_6H_5CH_3 \longrightarrow C_6H_5COOH$$

Benzoic acid (or benzenecarboxylic acid)

$$C_6H_5CH_2CH_2CH_3 \longrightarrow C_6H_5COOH \quad (+\ CH_3COOH)$$

Assignment

In the following question you should use reactions of hex-1-ene, cyclohexane and benzene to illustrate your answer, indicating the possible mechanism of each reaction you describe:

Some reactions are said to be 'saturated', other 'unsaturated'. Explain what these terms mean both in terms of reaction and structure. In what ways do aromatic compounds fit into either of these classifications?