Aromatic - Benzene

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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. Benzene is a highly dangerous substance, causing anaemia and cancer on prolonged exposure to its vapour. At one time it was used as a solvent, but its use is now restricted. It is still added to some brands of unleaded petrol, however, to increase their anti– knock rating.

Manufacture

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

Structure of the benzene ring

Arenes are hydrocarbons that contain one or more benzene rings.
The benzene ring 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). All the bond angles in benzene are 120^0.

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:

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

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} :

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

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

Compounds that contain rings of delocalised electrons are sometimes called **aromatic compounds**. The name was originally coined for certain natural products that had strong, pleasant aromas, such as almond oil, clove oil, oil of wintergreen, thyme oil and vanilla bean oil. All of these oils contained compounds whose structures were found to include a benzene ring.

Several functional groups can be attached to a benzene ring :

halogen: bromobenzene

hydroxyl: phenol
(antiseptic)

amino: aniline
Phenylamine (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 °C, moth balls, insecticide.

Pyridine, C_5H_5N: pyridine ring occurs in the vitamin niacin

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 (ortho– dichlorobenzene) 1,3-dimethylbenzene (meta– dichlorobenzene) 1,4-dimethylbenzene (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)

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:

$$C_6H_6 \quad + \quad 7\tfrac{1}{2}\,O_2 \quad \longrightarrow \quad 6CO_2 \quad + \quad 3H_2O$$

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.

$$C_6H_6 \quad + \quad 1\tfrac{1}{2}\,O_2 \quad \longrightarrow \quad 6C_{(s)} \quad + \quad 3H_2O$$

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:

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

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-electron cloud, this would result in benzene losing the added stability that is obtained from delocalisation, i.e. the resonance energy.

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 a halogen, X_2, in the presence of a Lewis acid: $FeBr_3$ or $AlCl_3$

Overall reaction:

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

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.

2. 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.

Equation:

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.

Equation:

3. 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 $C_6H_6 + R—X \longrightarrow C_6H_5 - R + HX$

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

$$C_6H_6 + CH_3—X \longrightarrow C_6H_5 - CH_3 + HX$$

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- dimethylbenzene.

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.

Example:

$$C_6H_6 + CH_3CO—X \longrightarrow C_6H_5 - OCCH_3 + HX$$

acetophenone
or phenyl ethanone

Here polysubstitution does not take place, $\because$ the product is less reactive than C_6H_6, $\therefore$ 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

Assignment

1. In the following question you should use reactions of cyclohexene, cyclohexane and benzene to illustrate your answer:

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? Describe two tests you could perform to distinguish the three compounds.

2. How would you prepare the following starting with benzene:

a. 2-phenylbutane b. Chlorobenzene c. Nitorbenzene