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BASIC CONCEPTS OF AROMATIC COMPOUNDS

Rohit Saini* and Sanchit Srivastav

Department of Pharmacy IEC Group of Institutions, Gr. Noida (UP).

*** Corresponding Author: Rohit Saini**
Department of Pharmacy IEC Group of Institutions, Gr. Noida (UP).

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ABSTARCT
Aromatic compounds also called as arenes. These are the chemical compounds that contain conjugated planar ring systems having delocalization of pi electron clouds rather than discrete alternating single and double bonds. Typical aromatic compounds are benzene and toluene and satisfy the Hückel's rule. When the functional group or any substituent, in aromatic compounds is directly attached to the benzene ring, it is a called nuclear substituted compound and is named as the derivatives of benzene under the IUPAC system. Aromatic compounds where the functional group is present in the sidechain of the ring are called sidechain substituted compounds and compounds are named as the phenyl derivatives of the corresponding aliphatic compounds. Only one kind of monosubstituted derivatives is possible in benzene rings as all six hydrogen atoms are equivalent. In the formulation of various drugs, medicines and chemical are having its own importance of aromatic nucleus. Aromatics are the backbone for the chemical industry, research and developments. In addition to this various natural products are also having aromatics in their molecule. Aromatics are the proven and extremely powerful tool in the field of medical science and discovery.

KEYWORDS: Aromaticity, Aromatics, Benzene, Huckel's rule, Homocyclic compounds, Heterocyclic compounds, Halogenation, Nitration, Electrophilic substitution.

1. BASIC CONCEPTS OF AROMATIC COMPOUND

1.1 INTRODUCTION

Aromatic compounds are the substances that consist of one or more rings that contain alternating single and double bonds in its chemical structure.

In organic chemistry, the term **aromaticity** describes a cyclic (ring-shaped), planar (flat) molecule which have a ring of resonance bonds that exhibits more stability than other geometric or connective arrangements with the same set of atoms. Aromatic molecules are more stable and do not easily break apart and react with other substances. Aliphatic compounds are also organic compounds but they are not aromatic—they might be cyclic, but only aromatic rings have special stability (low reactivity).[1]

A ring is said to be aromatic if it has a loop of π electrons. Thus, the rings in 2, 4, 5, and 7 are aromatic. Aromatic compound is a compound whose molecule contains one or more aromatic rings. Thus, 2, 4, 5, and 7 are aromatic compounds.[2]

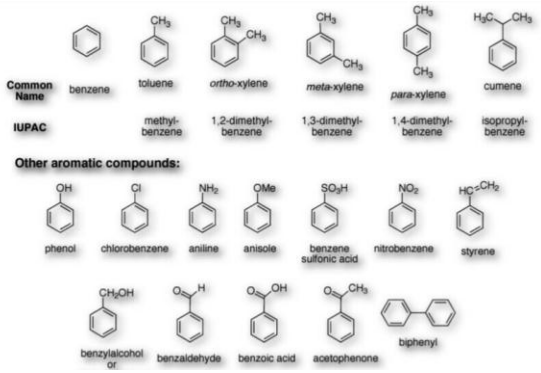


Fig1. Aromatic compounds

2. TYPES OF AROMATIC COMPOUNDS

2.1 Homocyclic compound

Benzene, is an example of homocyclic compound and other annulenes (cyclodecapentaene) having general formula of C_nH_n (n = even number) like cyclotetradecaheptaene.

2.2 Heterocyclic compound

A heterocyclic compound or ring structure has atoms of at least two different elements as members ring(s).[3] Heterocyclic aromatics (heteroaromats) or compounds

containing at least one atom other than carbon in their rings. This can lessen the ring's aromaticity, and thus (as in the case of furan) increase its reactivity. Examples of heterocyclic compound are pyridine, pyrazine, imidazole, pyrazole, oxazole, thiophene, and their benzannulated analogs (like benzimidazole). The number of π-electrons is 6 in all these examples, due to the π electrons from the double bonds as well as the two elections from any lone pair that is in the p-orbital that is in the plane of the aromatic π system. For example, the five sp2-hybridized carbons in pyridine in which each have a p-orbital that is perpendicular to the plane of the ring, and each of these p-orbitals contains one π-electron. Additionally, the nitrogen atom has only one electron in a p-orbital and it is also sp2-hybridized, which adds up to 6 p-electrons, it makes pyridine aromatic. The lone pair on the nitrogen is not part of the aromatic π system. Pyrrole and imidazole contain heteroatoms and both have five membered aromatic rings. In pyrrole, each of the four sp2-hybridized carbons contributes one π-electron, and the nitrogen atom is also sp2-hybridized and contributes two π-electrons from its lone pair, which occupies a p-orbital. In imidazole, both nitrogens are sp2-hybridized; the one in the double bond contributes one electron and the one which is not in the double bond and is in a lone pair contributes two electrons to the π system.[4]

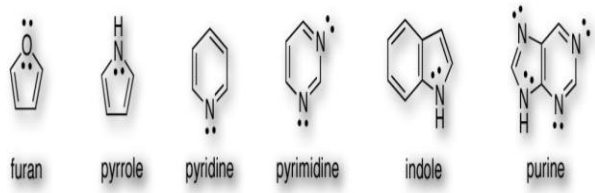


Fig2. Heterocyclic compounds

3. KEKULE STRUCTURE

Kekule did the most famous work on the structure of benzene. In 1865 Kekule published a paper in French (for he was then still in Francophone Belgium) suggesting that benzene consist of a cyclic, planer structure of six carbon with alternate double bond and single bond.[5]

Most chemists were accept this structure quickly, since Kekule's structure accounted for most of the known isomeric relationships of aromatic chemistry. Only one isomer of benzene exists and disubstituted compounds have three isomers were explained through hexagonal structure.[6]

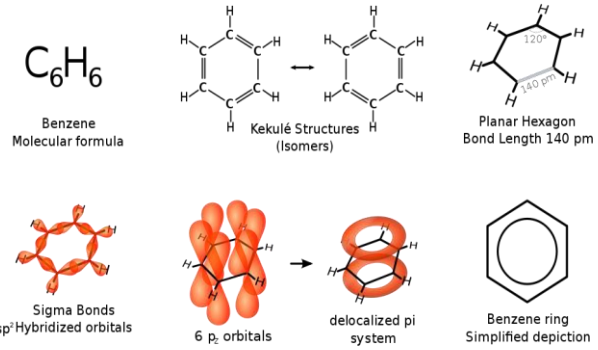
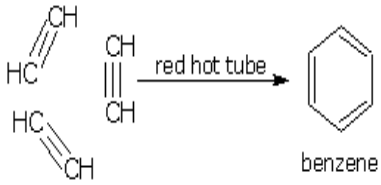


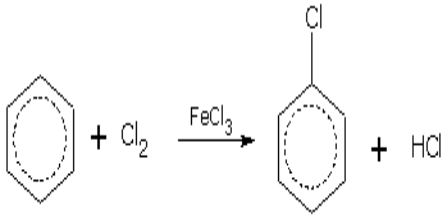
Fig 3. Kekule structure of Benzene

4. PREPARATION OF SOME AROMATIC COMPOUNDS (SCHEMES)

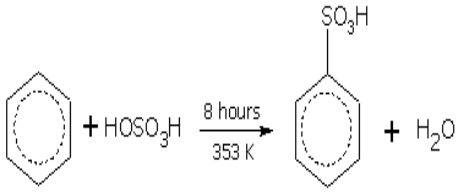
(1) By passing acetylene through red-hot tube.[7]



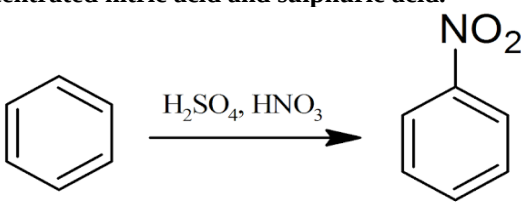
(2) Direct Halogenations as Aryl chlorides and aryl bromides are generally prepared from arenes by reaction with chlorine or bromine in the presence of a catalyst such as FeCl3, FeBr3 or AlCl3.[8]



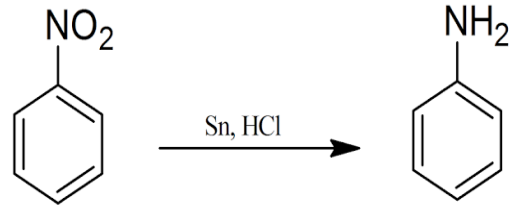
(3) Direct Sulphonation. When benzene is heated with concentrated sulphuric acid at 353 K for 8 hours, sulphonic acid is formed.[9]



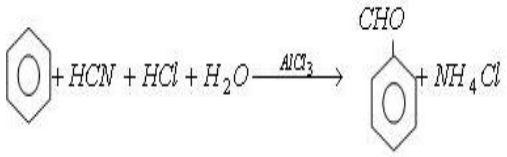
(4) Nitration of an aromatic compound is usually carried out by heating it with a mixture of concentrated nitric acid and sulphuric acid.[10]



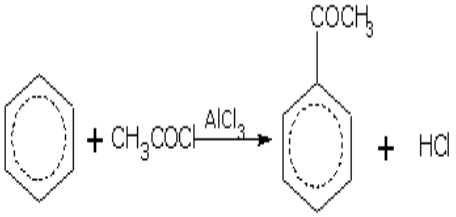
(5) Preparation of aromatic amine by reduction of Nitro Compounds.[11]



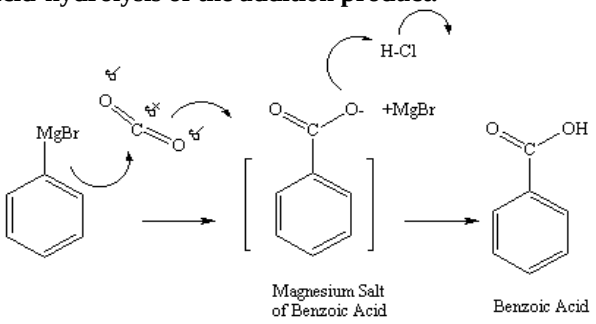
(6) The treatment of benzene with HCN, HCl and H2O in the presence of AlCl3 catalyst gives Benzaldehyde.[12]



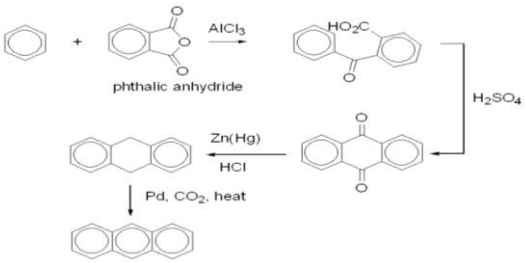
(7) Preparation of Acetophenone by Friedal-Crafts Acylation. This involves the treatment of benzene with acetyl chloride or acetic anhydride in the presence of aluminium chloride. [13]



(8) Preparation of Benzoic acid by reaction of phenyl magnesium bromide with carbon dioxide followed by acid-hydrolysis of the addition product. [14]



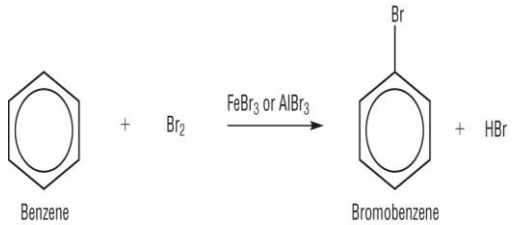
(9) Haworth Synthesis of Anthracene. Anthracene is made up of three benzene rings, was confirmed by Haworth synthesis. Benzene is treated with phthalic anhydride and aluminium chloride to form *o*-benzoylbenzoic acid. This on heating with concentrated sulphuric acid dehydrates to 9, 10-anthraquinone which on distillation with zinc dust is reduced to anthracene.[15]

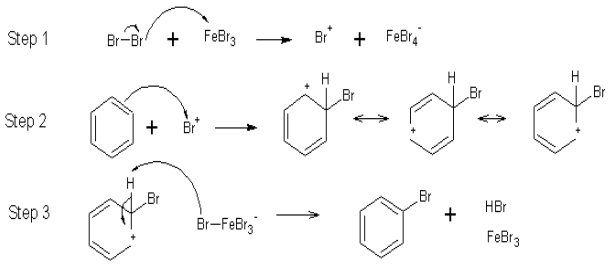


5. REACTIONS OF AROMATIC COMPOUND WITH MECHANISM

(1) Halogenations (reaction and mechanism)

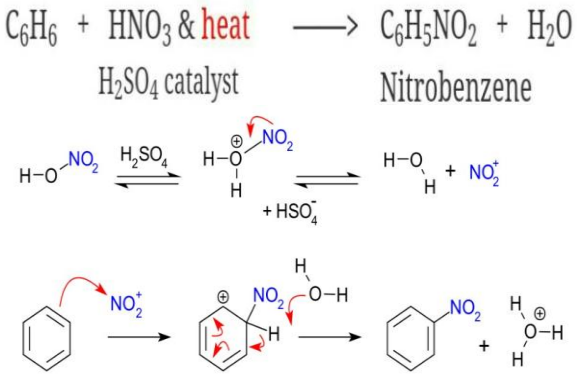
Benzene reacts with chlorine or bromine in the presence of FeCl3 or AlCl3 at room temperature to form chlorobenzene.[16],[17]





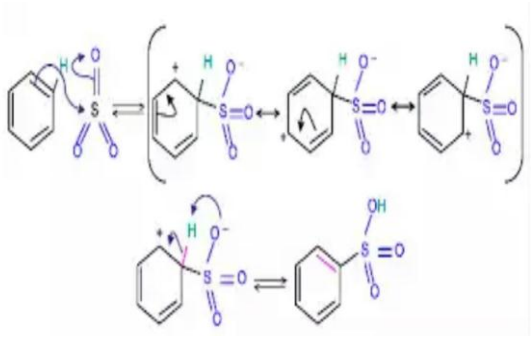
(2) Nitration (reaction and mechanism)

Benzene reacts with concentrated nitric acid in the presence of concentrated sulphuric acid to form nitrobenzene.[18], [19]



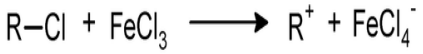
(3) Sulphonation (reaction and mechanism)

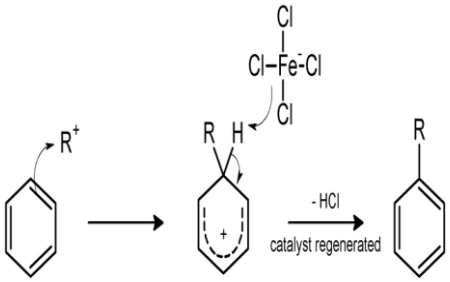
Benzene reacts with concentrated sulphuric acid or fuming sulphuric acid at room temperature to give benzenesulphonic acid. [20], [21]



(4) Friedal-Crafts Alkylation (reaction and mechanism)

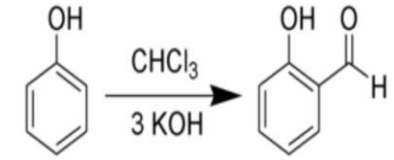
Benzene reacts with alkyl halides in the presence of ferric chloride to form alkyl benzenes.[22]

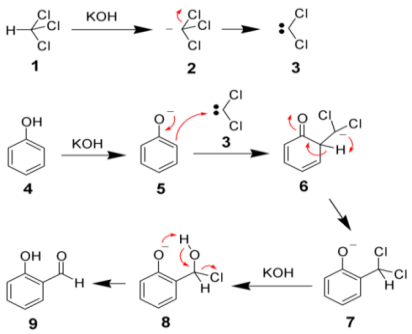




(5) Reimer-Tiemann (reaction and mechanism)

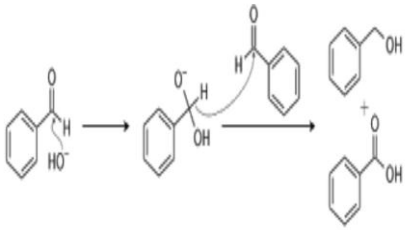
This reaction involves the treatment of phenol with chloroform in aqueous sodium hydroxide solution followed by acid hydrolysis. Salicyaldehyde is formed.[23], [24]

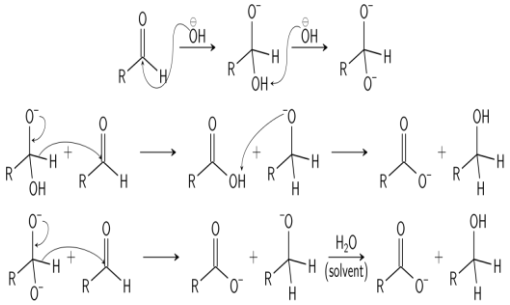




(6) Cannizzaro (reaction and mechanism)

The Cannizzaro reaction involves the treatment of an aldehyde with concentrated NaOH or KOH. The aldehyde undergoes an oxidation reduction.[25], [26]





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