PREPARATION OF CYCLOALKANES via:

1) DIELS-ALDER REACTION: A conjugated diene and alkene form cyclohexene. Relative alkenes called dienophiles have electron attracting group on their unsaturated carbons .

The reaction above can be considered as 1,4-addition of an olefine (ethene) to a conjugated diene(1,3-butadiene) and such is called [4+2] cycloaddition reaction.

Diels Alder reaction is a [4+2] cycloaddition reaction- in this case, the new molecule is formed from a conjugated 4pi-electron system on the one hand and a 2pi electron system on the other hand. Other examples are as follows, involving derivatives of the cycloaddition product;

1) ELECTROCYCLIC REACTION

This is an intramolecular cyclisation of polyenes

CHEMICAL PROPERTIES OF CYCLIC HYDROCARBONS

Most reactions of cyclic hydrocarbons are similar to those of acyclic alkanes and alkenes. E.g cycloalkanes undergo heat or light-induced halogination in a manner similar to the halogenation reaction of the acyclic alkanes.

Cycloalkenes also exhibit the same reactions as their acyclic counterparts.

Other derivatives behave like acyclic hydrocarbon in their reactivity.

However, cyclopropane is unique among the cyclic hydrocarbons in its reactions with halogens.cyclopropane undergoes ring opening much more easily than we might expect for a molecule that has only C-C single bond. This occur in cyclopropane easily because of its high strain , the release of strain energy provides the driving force for the ring opening process.

a) halogenation reaction of cyclopropane

b) hydrogenation reaction

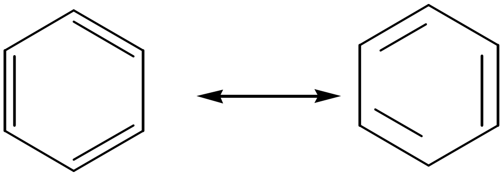
Above reactions show how cyclopropane behaves like an alkene.. ring opening reaction of cyclobutane requires higher temperature and more severe reaction conditions than those for cyclopropane. Cycloalkanes with ring sizes greater than four are completely resistant to ring opening reaction.

AROMATIC HYDROCARBON

BENZENE AND AROMATICITY

Aromatic compounds are compounds containing benzene ring or closely related ring. By aromaticity, it implies that the Pi-electrons are delocalized over the entire ring system and they are stabilized by the Pi-electron delocalization called RESONANCE. For instance, Benzene is represented by the Kekule structure.

RESONANCE STRUCTURE OF BENZENE



In fact, benzene is a hybrid of two equal energy (Kekule) structures, differing only in the location of the double bond. In the structures of Benzene above, the six bond angles are equal (120^0), hybridization is sp2 and planar from x-ray analysis. The bonding in benzene is a multicenter bonding or delocalized bonding. The pie-electrons in the benzene is delocalized and not restricted to any carbon atom- a kind of multicenter bonding or delocalized bonding. The two canonical forms exist. The implication of the parameter highlited above is an indication that the double bonds in benzene is unlike that found in alkene. In fact experiment has shown that benzene does not undergo addition reaction, expected in a a C-C double bond in alkene.

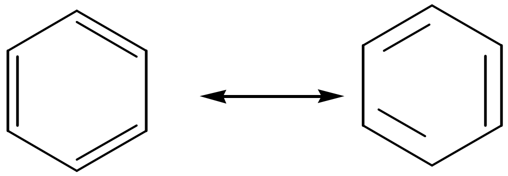
Benzene- a colourless compound, boiling point of 80o c was first isolated by Michael Faraday in1825 from the oily residue collected in the illumin along gas lines of London. The molecular formula is C_6H_6. For comparison , a saturated alkane of six carbon atoms has the molecular formula C_6H_{14} and saturated cycloalkane of six carbon atom has molecular formula of C_6H_{12}.

Considering benzene's high degree of unsaturation, one might expect it to be highly reactive and to exhibit reactions characteristics of alkenes and alkynes. However, this is not so, benzene does not undergo addition, oxidation and reduction reactions, characteristics of alkenes and alkynes. E.g it does no decolorizes bromine water, not oxidized by KMnO4 or Chromic acid (CrO3) under conditions that readily oxidizes alkenes and alkynes. Infact, benzene undergoes substitution reaction just like alkanes.

STRUCTURES OF BENZENE

Kekule's model;

In 1865, Kekule proposed that the six carbon of benzene are arranged in a six-membered ring with on hydrogen attached to each carbon. To maintain the then established tetravalency of carbon , Kekule further proposed that the ring contains three double bonds that shift back and forth so rapidly that the two forms (1a and 1b below) cannot be separated.



The model above is called Kekule's structure.

The Kekule's structure was found to be consistent with many experimental observations.

HOME PRACTICE: If benzene contain three double bonds, why does it not show reaction typical of alkene?

BONDING IN BENZENE

Each carbon atom is sp2 hybridizes and is sigma bonded and is sigma bonded to two other carbon atoms and one hydrogen atom. These sigma bonds comprised the skeleton of the molecule. Each C atom has one electron in a p-orbital at right angle to the plane of the ring. These p-orbitals overlap equally with each of the two adjacent p-orbital to form a pie-electron system parallel to and above and below the plane of the ring. The six p-electrons in the pi-system are associated with six carbon atoms. They are therefore more delocalized and this accounts for the great stability and large resonance energy of aromatic rings.ie,

The unusual properties of benzene collectively known as aromatic characters are;-

- thermal stability
- substitution rather than addition reaction with polar reagents such as HNO3, H_2SO_4 and Br_2. The unsaturated bonds in the ring is preserved in this reaction
- resistance to oxidation by aq KMnO4 or HNO3
- unique NMR spectra.

CALCULATING THE RESONANCE ENERGY

The observed heat of combustion of benzene is -3301.6KJ/mol. Theoretical values are calculated for C6H6 by adding the contributions from each bond obtained experimentally for other compounds. E.g C=C is -492.5KJ/mol, C-C is -206.3KJ/mol and -225.9KJ/mol for C-

H. these data can be used to calculate the heat of combustion for benzene. The difference between this value and the experimental value gives the resonance energy. For example, in benzene, there are; 6 C-H bonds, 3 C-C bonds, 3 C=C bonds.

6 C-C bonds = (6x -225.9) KJ/mol = -1355.4KJ/mol

3 C-C bonds = (3x -206.3) KJ/mol = - 618.9 KJ/mol

3 C=C bonds = (3x -492.5)KJ/mol = -1477.5KJ/mol

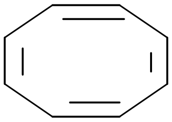
Calculated value = total ΔH_c = -3451.8KJ/mol

Experimental value = <u>- 3301.6KJ/mol</u>

Difference = <u>150.2KJ/mol</u>

This difference is the resonance energy of benzene. Hence , the resonance energy =150.2KJ/mol.

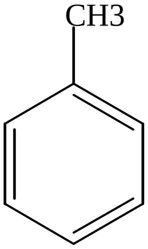
HOME PRACTICE;-

Given the cyclooctatetraene  , calculate the enthalpy of combustion of the various bonds and hence the resonance energy ; assuming the experimentally enthalpy of combustion of cyclooctatetraene is -4581.5KJ/mol.

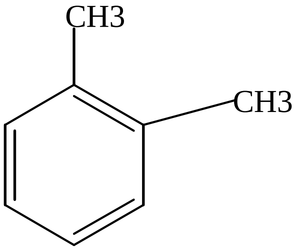
[C-H = -225.9KJ/mol, C-C = -206.3KJ/mol and C=C is -492.5KJ/mol]

NUMENCLATURE

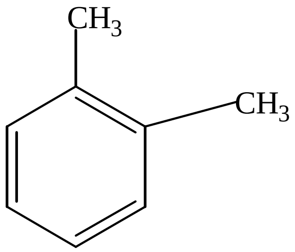
a) monosubstituted benzene;-



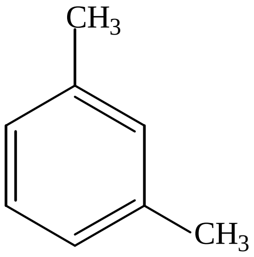
b) Disubstituted Benzene;



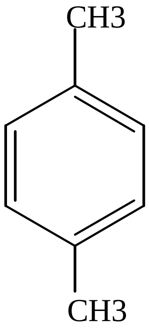
When two substituents are on benzene ring; three structural isomers are possible, based on the position of the substituent on the benzene ring e.g.



ortho



meta



para

HOME PRACTICE1. Give the structural formula for ;

a) 2,4,6- tribromoaniline

b) m-toluene sulphonic acid

c) p-bromobenzaldehyde

PROOF OF AROMATICITY

For an organic compound to be aromatic , it must be;

a) cyclic b) planar c) possess delocalized pi-electrons and d) obey Huckel’s rule of 4n+2= Π –electrons.

AROMATICITY AND HUCKEL’S RULE

Huckel’s rule (1931) for aromaticity states that if the number of pi-electrons is equal to 4n+2, where n equals zero or a whole number integer, the compound is aromatic. This rule applies to C-containing monocyclics in which each carbon is capable of being sp2 hybridized to provide a p-orbital for extended pi-bonding. The rule has been extended to unsaturated heterocyclic compounds and fused ring compounds.

AMINES AND DERIVATIVES

Amines are the principal organic base which are structurally equivalent to ammonia OR put simply a derivative of ammonia in which one or more of its H atom is replaced by alkyl group(s).
Amines are classified as primary (1^0), secondary (2^0) or tertiary (3^0) depending on the number of H atom replaced by alkyl on NH_3
At times, the H atom may be replaced by a benzyl or aryl or phenyl group (Aromatic amine)
To some extent, 1^0, 2^0 and 3^0 amines share some common physical and chemical properties, though the difference in the environment of the N atom is each class brings about some major difference.
Note that the general formula of amines is $C_nH_{2n+1}NH_2$ or RNH_2. The functional group is $–NH_2$ (amine group).

NOMENCLATURE OF AMINE

Nomenclature of amines is based on that of aliphatic side chain i.e according to the alkyl group attached to the nitrogen, the general suffix –amine is used .

GENERAL CHARACTERISTICS OF AMINE

PHYSICAL PROPERTIES

Generally, amines have fishy odour and are basic specifically, they are Lewis base, an electron-pair donor. Amines smell like ammonia, though less pungently.
There is less evidence of hydrogen bonding in the amines than in alcohol even though they exhibits trend in physical properties like boiling points and solubility. Low molecular weight amines are soluble in water and this has been attributed to the formation of H-bonds between the amine and water molecule. i.e
Amines are basic. More basic than ammonia i.e

The K_b of NH_3 is 1.8×10^{-5} while the K_b of CH_3NH_2 is 5.0×10^{-4}

Due to the basicity of amine, it is soluble in aqueous mineral acids, this distinguishes amine from ammonia and other classes of organic compounds. Amine are as well nucleophilic. The basicity and nucleophilicity of amine is due to the presence of unshared pair of electrons on the nitrogen atom.

The amine, salts formed from the reaction between amine and mineral acid is odourless, water-soluble crystalline solids with the usual characteristics of ionic compounds. Amine salts like ammonium salts, are readily decomposed by alkalis to regenerate the amines i.e

The properties above make it easy to separate amines from mixtures with other organic compounds.
(2) Reaction with Nitrous Acid (HNO_2)

(a) Ice-cold aqueous solution of $NaNO_2$ mixed with ice-cold aqueous or ethanolic solution of 1^0amine at 0^0c and the mixture treated with cold HCL gives effervescence and N_2 gas is quantitatively evolved.

They yield of N_2 (g) in the reaction above is quantitative hence its effervescence serves a chemical test to distinguish 1^0 amines from 2^0 and 3^0 which do not evolve N_2 under the same condition.

(b) The 2^o react under the same condition above to form yellow in soluble oily product, nitrosamines. No N_2 gas is evolved The nitrosamines are decomposed by boiling dilute mineral acids to give the amine salts from which the original amine can be regenerated by neutralization with a strong base..