

UNIT I

Benzene and its derivatives

Sub Topic: Structure of benzene



RAFFLES
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Presented by

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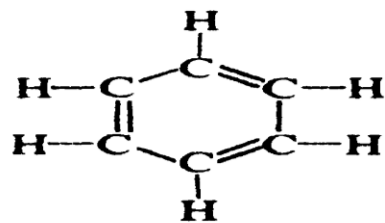
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Benzene has the molecular formula C₆H₆. From its elemental composition and molecular weight, benzene was known to contain six carbon atoms and six hydrogen atoms. The question was: how are these atoms arranged?

In 1858, August Kekule (of the University of Bonn) had proposed that carbon atoms can join to one another to form chains. Then, in 1865, he offered an answer to the question of benzene: these carbon chains can, sometimes be closed, to form rings.

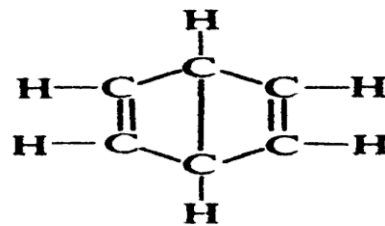
Kekulé's structure of benzene was one that we would represent today as I.



I
Kekulé formula



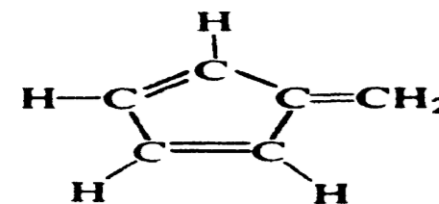
IV



II
"Dewar" formula



V



III

Other structures are, of course, consistent with the formula C₆H₆: for example, II-V. Of all these, Kekulé's structure was accepted as the most nearly satisfactory;

Benzene yields only one monosubstitution product, C_6H_5Y .

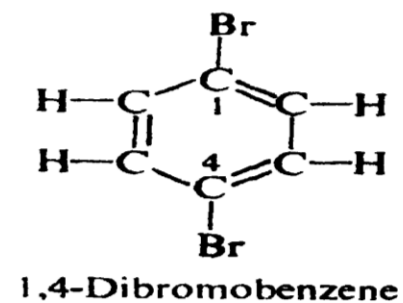
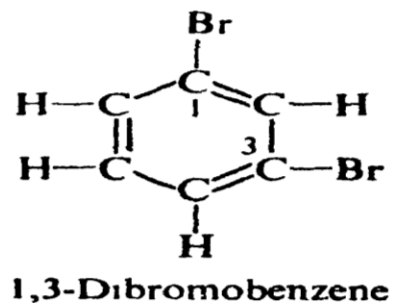
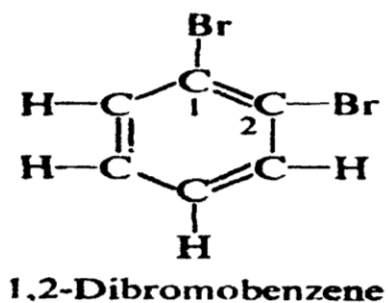
Only one bromobenzene, C_6H_5Br , is obtained when one hydrogen atom is replaced by bromine; similarly, only one chlorobenzene, C_6H_5Cl , or one nitrobenzene, $C_6H_5NO_2$, etc., has ever been made. This fact places a severe limitation on the structure of benzene: each hydrogen must be exactly equivalent to every other hydrogen, since the replacement of any one of them yields the same product.

Structure V, for example, must now be rejected, since it would yield two isomeric monobromo derivatives, the 1-bromo and the 2-bromo compounds; all hydrogens are not equivalent in V. Similar reasoning shows us that II and III are likewise unsatisfactory. (How many monosubstitution products would each of these yield?) I and IV, among others, are still possibilities, however.

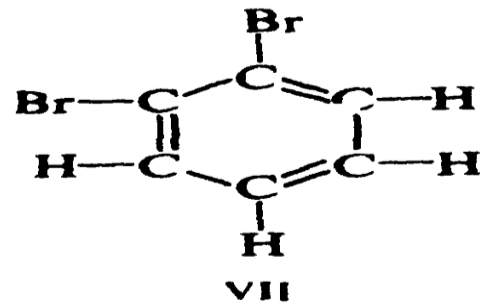
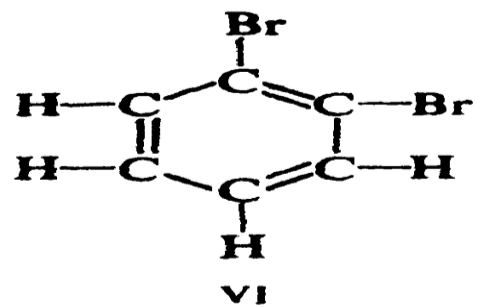
Benzene yields three isomeric disubstitution products, $C_6H_4Y_2$ or C_6H_4YZ .

Three and only three isomeric dibromobenzenes, $C_6H_4Br_2$, three chloronitrobenzenes, $C_6H_4ClNO_2$, etc., have ever been made. This fact further limits our choice of a structure; for example, IV must now be rejected. (How many disubstitution products would IV yield ?)

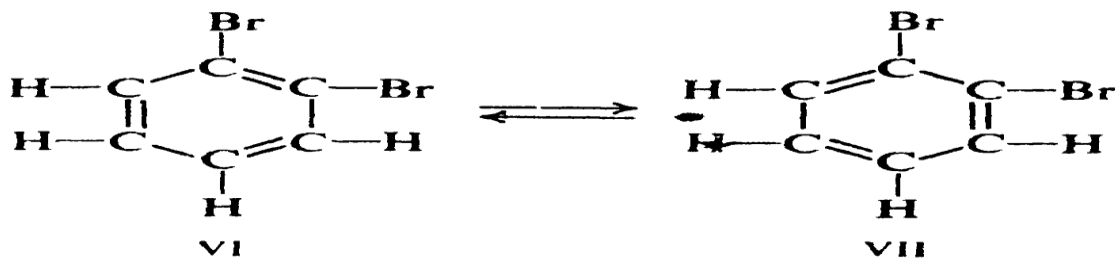
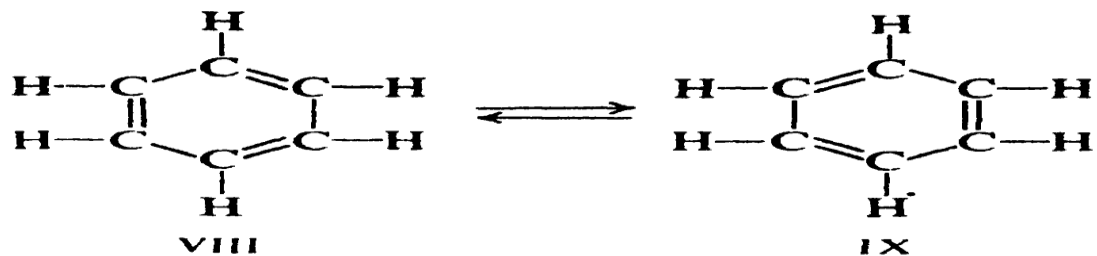
At first glance, structure I seems to be consistent with this new fact; that is, we can expect three isomeric dibromo derivatives, the 1,2- the 1,3-, and the 1,4-dibromo compounds shown:



Closer examination of structure I shows, however, that *two* 1,2-dibromo isomers (VI and VII), differing in the positions of bromine relative to the double bonds, should be possible:

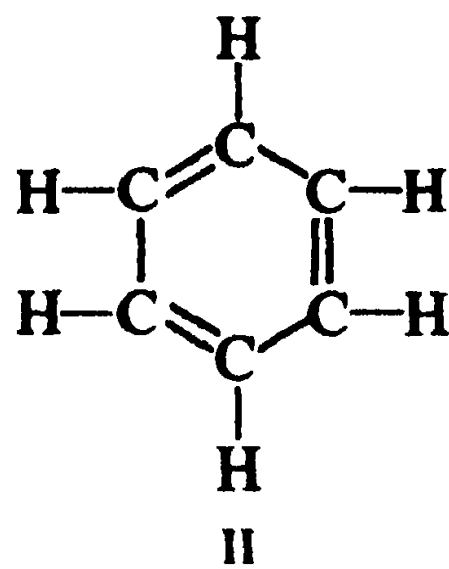
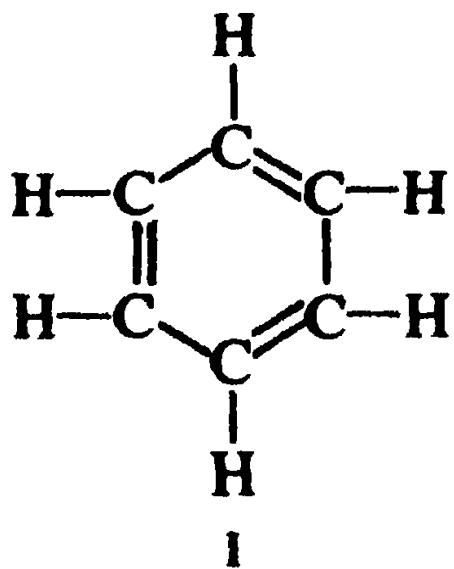


But Kekulé visualized the benzene molecule as a dynamic thing: “. . . the form whirled mockingly before my eyes . . .” He described it in terms of two structures, VIII and IX, between which the benzene molecule alternates. As a consequence, the two 1,2-dibromobenzenes (VI and VII) would be in rapid equilibrium and hence could not be separated.)

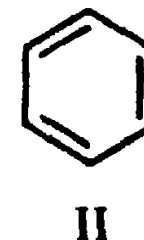
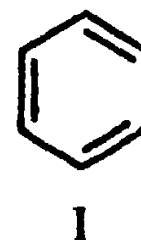


Resonance structure of benzene

The Kekule structure of benzene, while admittedly unsatisfactory, was generally used by chemists as late as 1945. The currently accepted structure did not arise from the discovery of new facts about benzene, but is the result of an extension or modification of the structural theory; this extension is the concept of resonance



or



The Kekule structures I and II, we now immediately recognize, meet the conditions for π -resonance:

structures that differ only in the arrangement of electrons

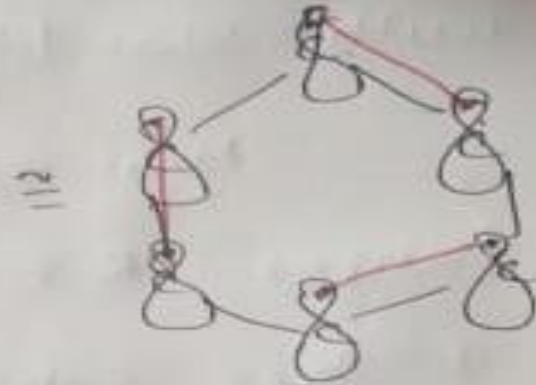
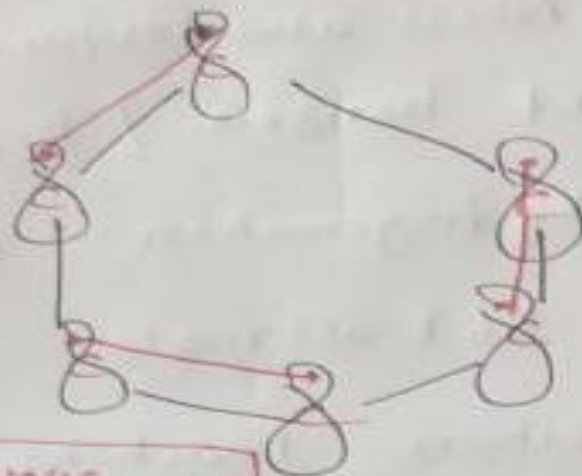
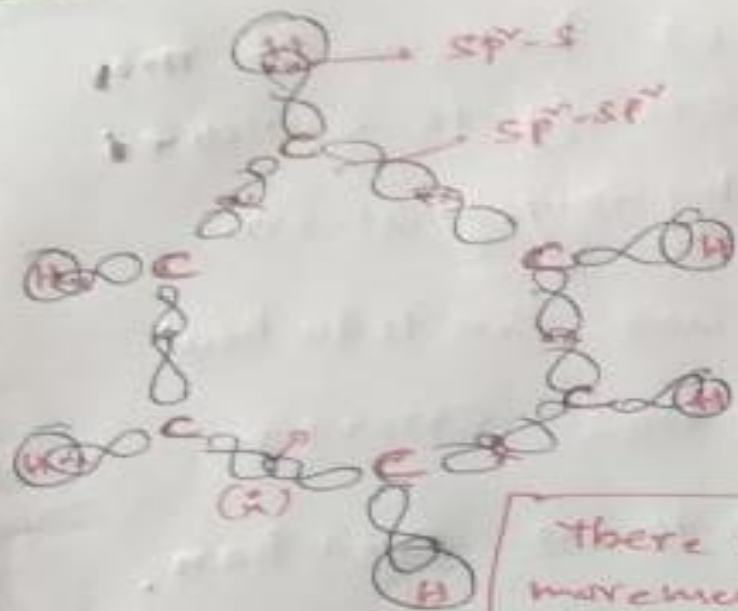
Benzene is a hybrid I and II since I and II are exactly equivalent and hence of exactly the same stability, they make equal contributions to the hybrid.

And, also since I and II are exactly equivalent, stabilization due to resonance should be large.

Orbital picture of benzene

A more detailed picture of the benzene molecule is obtained from a consideration of the bond orbitals in this molecule.

Since each carbon is bonded to three other atoms, it uses sp^2 orbitals. These lie in the same plane, that of the carbon nucleus, and are directed toward the corners of an equilateral triangle. If we arrange the six carbons and six hydrogens of benzene to permit maximum overlap of these orbitals, we obtain the structure shown in Figure



There is Continuous movement in e^- s from one carbon to other carbon \therefore called delocalised e^- s.

m.o.:



delocalised e^- s.

Creates π aromatic

System Above and below the plane of

Ring system. | Due to the delocalisation and movement in molecule creates the energy due to displacement of e^- s. phenomenon called Resonance. and energy called as

Resonance energy. due to this energy benzene does not give up like Alkenes and Alkynes.



|||



|||



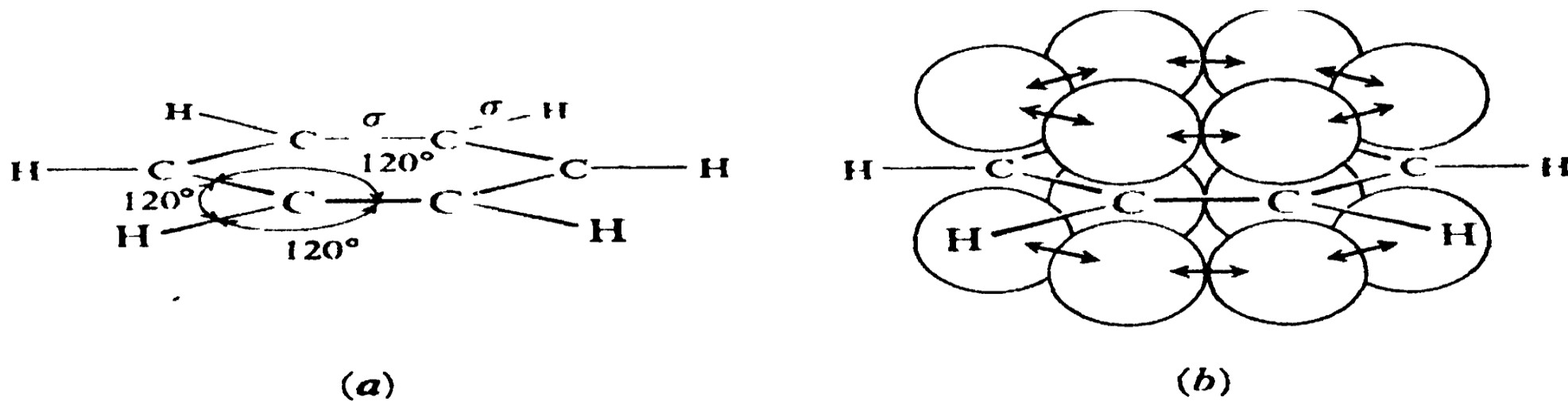


Figure 10.2. Benzene molecule. (a) Only σ bonds shown. (b) p orbitals overlap to form π bonds.

Benzene is a flat molecule, with every carbon and every hydrogen lying in the same plane. It is a very symmetrical molecule, too, with each carbon atom lying at the angle of a regular hexagon; every bond angle is 120° . Each bond orbital is cylindrically symmetrical about the line joining the atomic nuclei and hence, as before, these bonds are designated as σ bonds.

There are still six electrons to be accounted for. In addition to the three orbitals already used, each carbon atom has a fourth orbital, a p orbital. As we know, this p orbital consists of two equal lobes, one lying above and the other lying below the plane of the other three orbitals, that is, above and below the plane of the ring; it is occupied by a single electron. the orbital of any one carbon atom overlaps equally well the p orbitals of both carbon atoms to which it is bonded. The result (see Fig. 10.3) is two continuous doughnut-shaped electron clouds, one lying above and the other below the plane of the atoms.

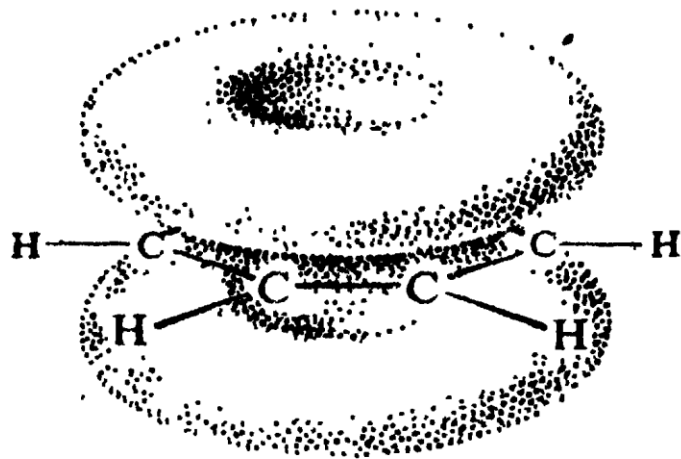


Figure 10.3. Benzene molecule. π clouds, above and below plane of ring.

it is the overlap of the p orbitals in both directions, and the resulting participation of each electron in several bonds that corresponds to our description of the molecule as a resonance hybrid of two structures. Again it is the delocalization of the n electrons their participation in several bonds that makes the molecule more stable.

To accommodate six electrons, there must be three orbitals. Their sum is, however, the symmetrical π clouds we have described.

The orbital approach reveals the importance of the planarity of the benzene ring. The ring is flat because the trigonal (sp^2) bond angles of carbon just fit the 120° angles of a regular hexagon; it is this flatness that permits the overlap of the p orbitals in both directions, with the resulting delocalization and stabilization.

The facts are consistent with the orbital picture of the benzene molecule. X-ray and electron diffraction show benzene (Fig. 10.4) to be a completely flat, symmetrical molecule with all carbon-carbon bonds equal, and all bond angles 120° .

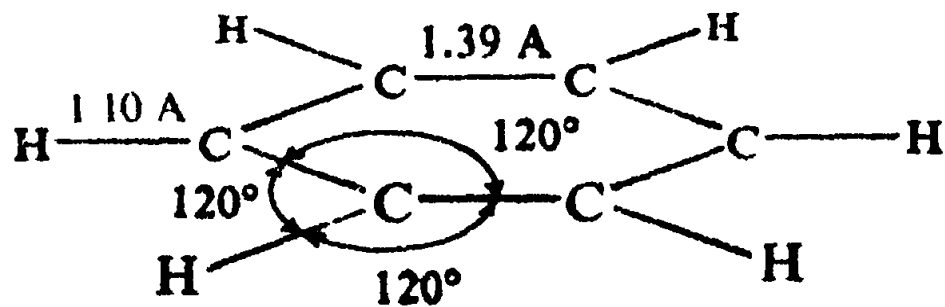


Figure 10.4. Benzene molecule: shape and size.

Despite delocalization, the π electrons are nevertheless more loosely held than the sigma electrons. The π electrons are thus particularly available to a reagent that is seeking electrons: the typical reactions of the benzene ring are those in which it serves as a source of electrons for electrophilic (acidic) reagents. Because of the resonance stabilization of the benzene Ring, these reactions lead to substitution, in which the aromatic character of the benzene ring is preserved

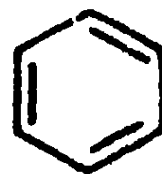
Representation of the benzene ring

For convenience we shall represent the benzene ring by a regular hexagon containing a circle (I); it is understood that a hydrogen atom is attached to each angle of the hexagon unless another atom or group is indicated.



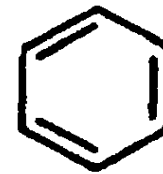
I

means a hybrid of



II

and



III

I represents a resonance hybrid of the Kekule structures II and III. The straight lines stand for the σ bonds joining carbon atoms. The circle stands for the cloud of six delocalized π electrons. I is a particularly useful representation of the benzene ring, since it emphasizes the equivalence of the various carbon-carbon bonds. The presence of the circle distinguishes the benzene ring from the cyclohexane ring, which is often represented today by a plain hexagon.

Stability of the benzene ring.

The most striking evidence of this stability is found in the chemical reactions of benzene.

(a) Benzene undergoes substitution rather than addition.

Kekule's structure of benzene is one that we would call "cyclohexatriene." We would expect this cyclohexatriene, like the very similar compounds, cyclohexadiene and cyclohexene, to undergo readily the addition reactions characteristic of the alkene structure.

As the examples in Table show, this is not the case; under conditions that cause an alkene to undergo rapid addition, benzene reacts either not at all or very slowly.

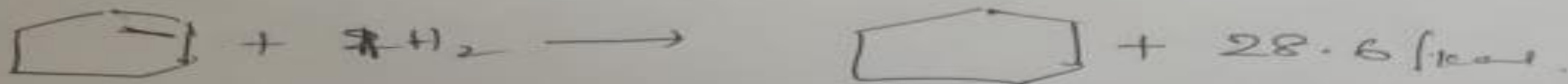
Table 10.1 *CYCLOHEXENE vs. BENZENE*

Reagent	Cyclohexene gives	Benzene gives
KMnO₄ (cold, dilute, aqueous)	Rapid oxidation	No reaction
Br₂/CCl₄ (in the dark)	Rapid addition	No reaction
HI	Rapid addition	No reaction
H₂ + Ni	Rapid hydrogenation at 25°, 20 lb/in.²	Slow hydrogenation at 100–200°, 1500 lb/in.²

In place of addition reactions, benzene readily undergoes a new set of reactions, all involving substitution.

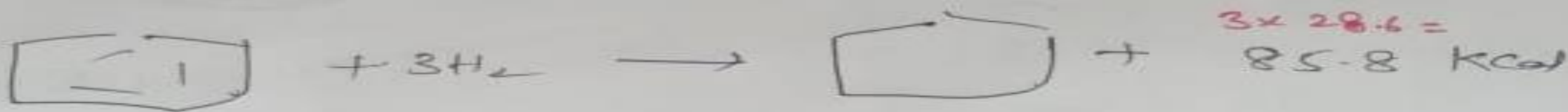
Stability of the benzene ring. Heats of hydrogenation

Heats of hydrogenation and combustion of benzene are lower than expected, that heat of hydrogenation is the quantity of heat evolved when one mole of an unsaturated compound is hydrogenated. In most cases the value is about 28-30 kcal for each double bond the compound contains. It is not surprising, then, that cyclohexene has a heat of hydrogenation of 28.6 kcal and cyclohexadiene has one about twice that (55.4 kcal.) We might reasonably expect cyclohexatriene to have a heat of hydrogenation about three times as large as cyclohexene, that is, about 85.8 kcal. Actually, the value for benzene (49.8 kcal) is 36 kcal less than this expected amount. This can be more easily visualized, perhaps, by means of an energy diagram (Fig. 10.1), in which the height of a horizontal line represents the potential energy content of a molecule. The broken lines represent the expected values, based upon three equal steps of 28.6 kcal. The final product, cyclohexane, is the same in all three cases.



+ Observed: 55.4 kcal/mole.

$$\text{difference: } 57.2 - 55.4 = \underline{1.8 \text{ kcal/mole}} \\ \text{R.E.}$$



Benzene + observed = 49.8 kcal.

$$\text{difference} = 85.8 - 49.8 = \boxed{36 \text{ kcal.}}$$

R.E. →

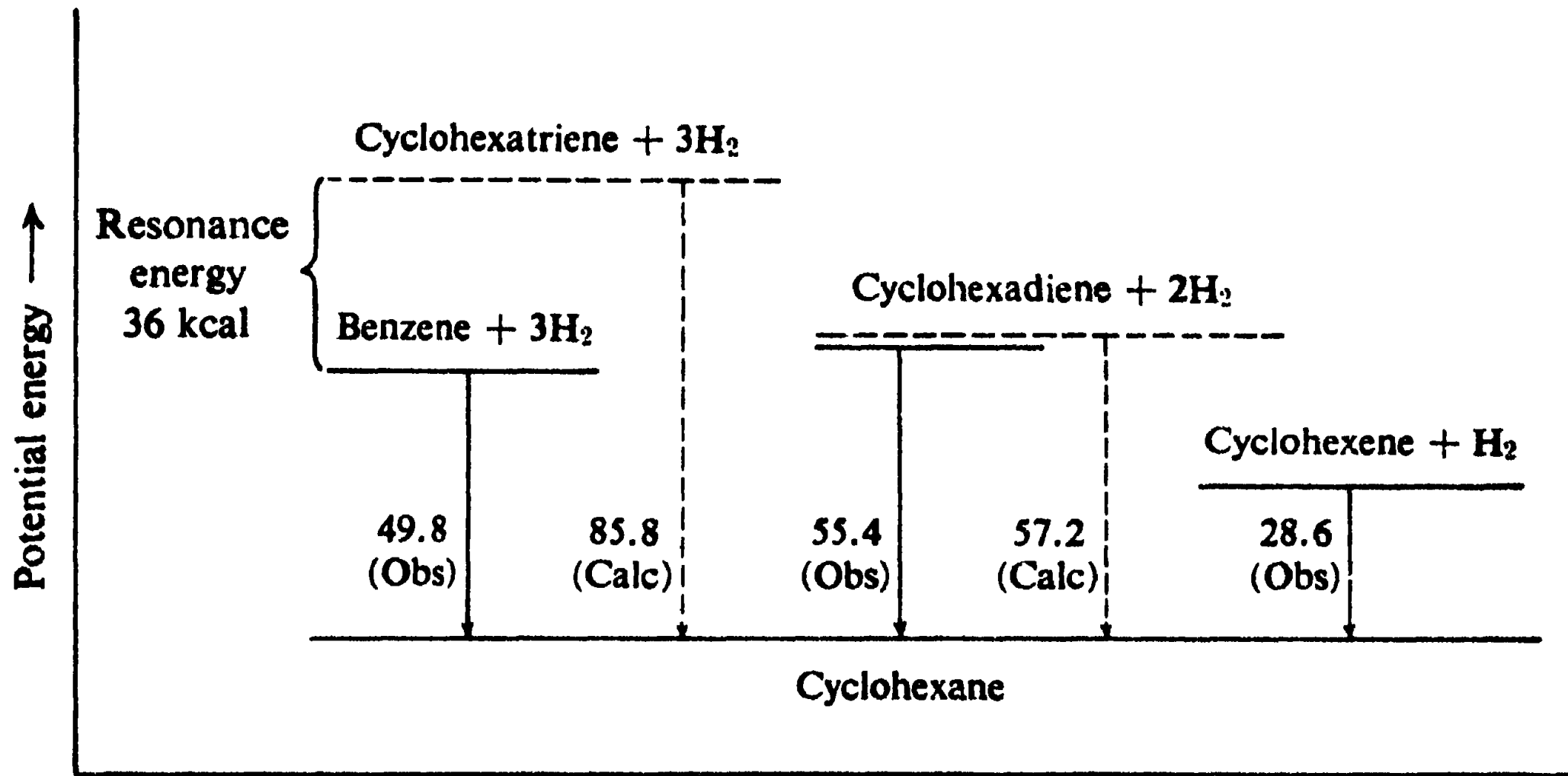


Figure 10.1. Heats of hydrogenation and stability: benzene, cyclohexadiene, and cyclohexene.

Aromaticity

Aromatic compounds are those that resemble benzene. But just which properties of benzene must a compound possess following points

- Aromatic compounds are compounds whose molecular formulas would lead us to expect a high degree of unsaturation
- Compounds possess the cyclic rings in their structures
- Possess the alternative double and single bonds in the structures
- which are resistant to the addition reactions generally characteristic of unsaturated compounds
- Instead of addition reactions, aromatic compounds undergo electrophilic substitution reactions like those of benzene.

Modern concept of aromaticity or Huckle's rule

A molecule must satisfy **Hückel's rule**, and contain a particular number of π electrons.

Hückel's rule:

- An aromatic compound must contain $4n + 2 \pi$ electrons ($n = 0, 1, 2,$ and so forth).
- Cyclic, planar, and completely conjugated compounds that contain $4n \pi$ electrons are especially unstable, and are said to be *antiaromatic*.

Benzene is aromatic and especially stable because it contains 6 π electrons. Cyclobutadiene is **antiaromatic** and especially unstable because it contains 4 π electrons.

$$4n+2= 6$$

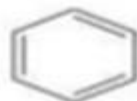
$$4n=6-2$$

$$4n=4$$

$$n=1$$

Benzene is aromatic

Benzene
An aromatic compound



$$4n + 2 = 4(1) + 2 = 6 \pi \text{ electrons aromatic}$$

Cyclobutadiene
An antiaromatic compound



$$4n = 4(1) = 4 \pi \text{ electrons antiaromatic}$$

$$4n+2= 4$$

$$4n=4-2$$

$$4n=2$$

$$n=1/2$$

Huckel's Rule:

~~Anthracene~~ Naphthalene



$$4n + 2 = 10$$

$$4n = 10 - 2 = 8$$

$$n = \underline{2} \checkmark$$

No. of ~~π~~ π numbers

∴ Aromatic

Also $n=2$ indicates
size of the ring is

Case of Aromatic Compounds.



Cyclopentadienyl cation

$$4n + 2 = 4$$

$$n = \underline{1/2} = 0.5$$

n is integer ∴

Non Aromatic

Anthracene



$$4n + 2 = 14$$

$$4n = 14 - 2 = 12$$

$$n = \underline{3} \checkmark$$

n - number

∴ Aromatic Compound.



cyclopentadienyl Anion

$$4n + 2 = 6$$

$$4n = 6 - 2 = 4$$

$$n = \underline{1} \checkmark$$

Aromatic.



Pyrazole

$$4n + 2 = 6$$

$$4n = 4$$

$$n = \underline{1}$$

Aromatic

Quinoline



$$C_{10}H_7N = 10$$

Iso Quinoline



$$C_{10}H_7N = 10$$

Indole



$$C_{10}H_7N = 10$$

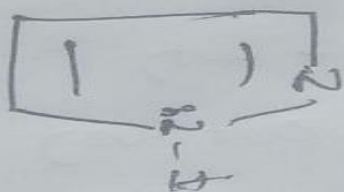


Pyran



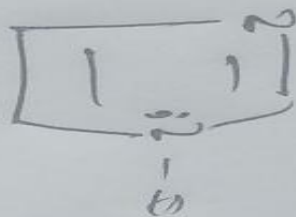
Thiophene

Pyrazole



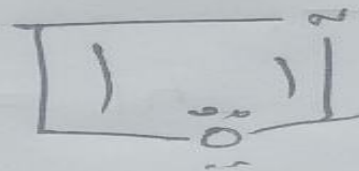
$$C_4H_4N_2 = 6$$

Imidazole



$$C_4H_4N_2 = 6$$

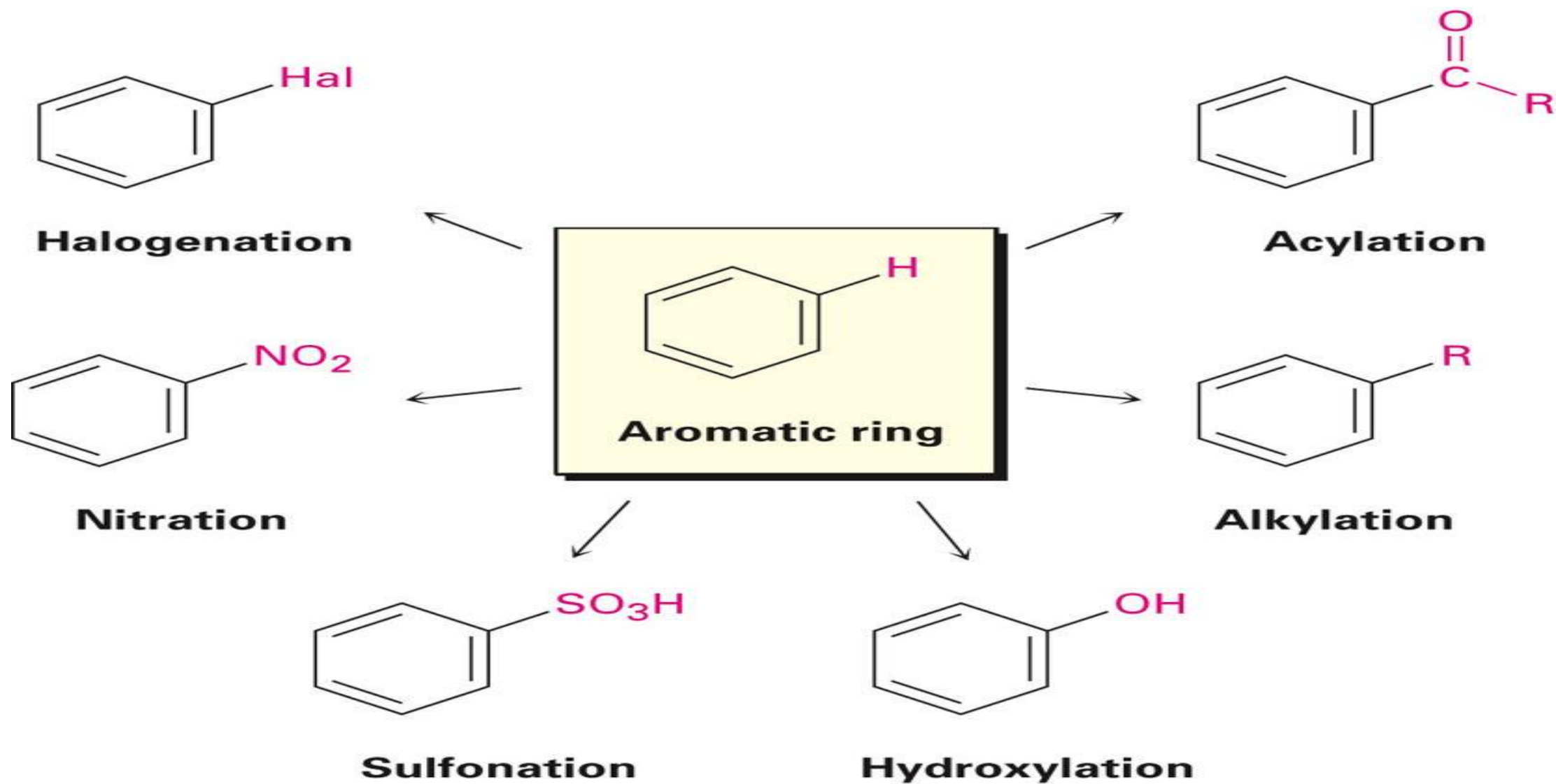
oxazole



Reactions of Benzene and Its Derivatives

- Benzene **does not** undergo electrophilic addition
- It undergoes electrophilic aromatic substitution maintaining the aromatic core
- Electrophilic aromatic substitution replaces a proton on benzene with another Nucleophile

Electrophilic Aromatic Substitution

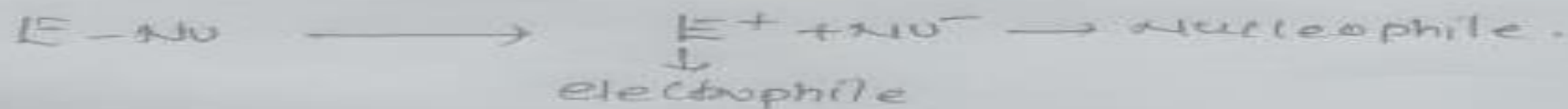


General electrophilic aromatic substitution of benzene:



Mechanism:

i) Generation of electrophile.



ii) Formation of stable carbocation.



iii) Removal of proton:

