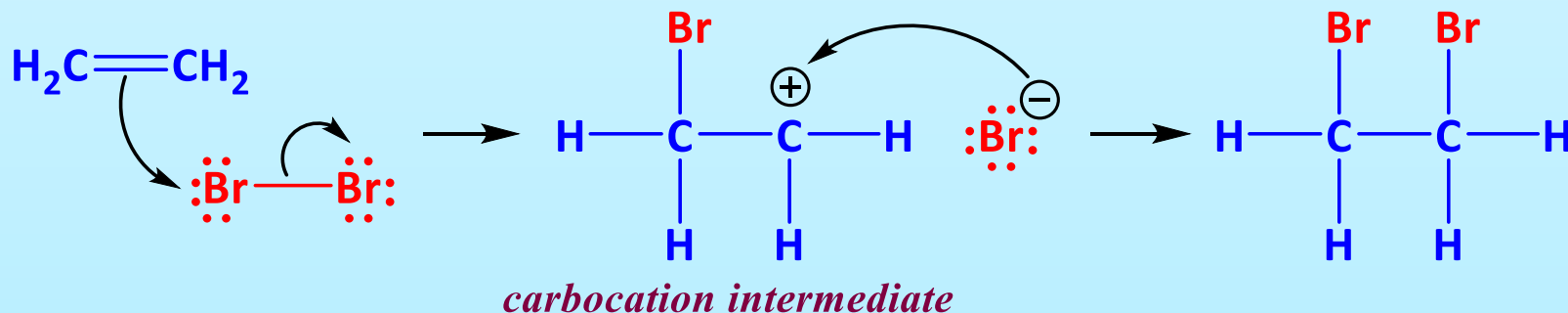# Mechanism of halogen addition

➢ **A possibility of the addition of bromine or chlorine to an alkene is one that involves the formation of a *carbocation***

carbocation intermediate

➢ **Although this mechanism is similar to the one for the addition of H-X to an alkene, it does not explain one important fact**
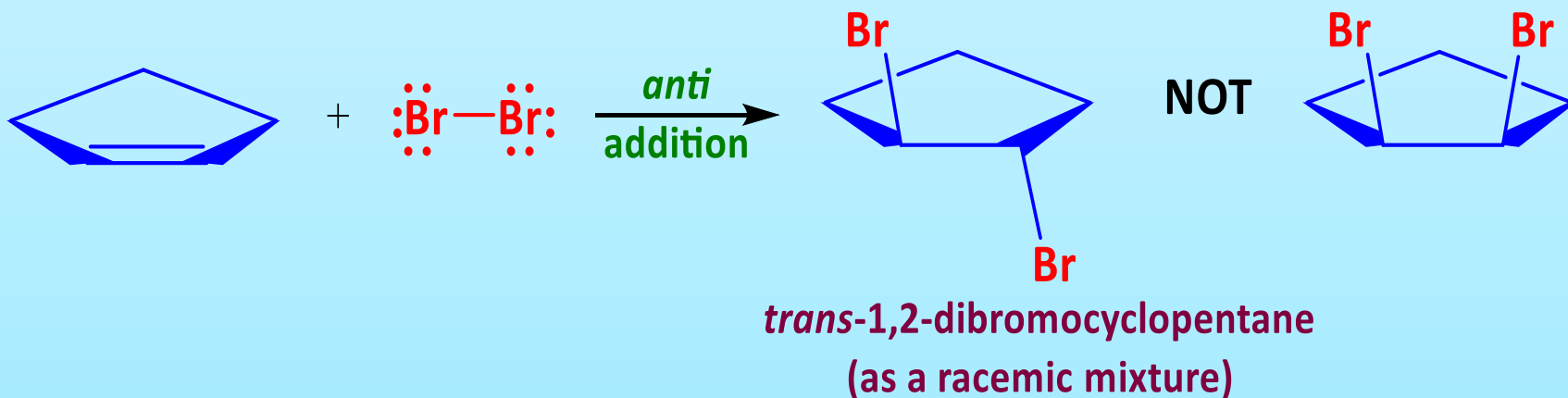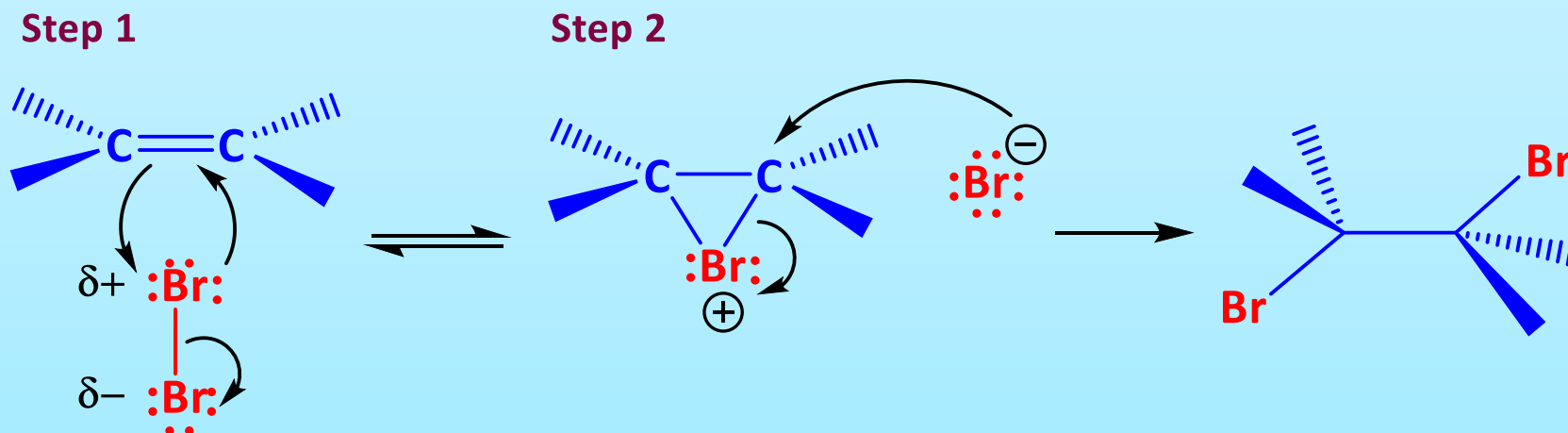
Mechanism of halogen addition

➤ **The addition of bromine to an alkene occurs in an *anti* fashion, i.e. *anti* addition**

➤ **The addition of bromine to cyclopentene produces *trans*-1,2-dibromocyclopentane**

trans-1,2-dibromocyclopentane
(as a racemic mixture)

Mechanism of halogen addition

➢ **A mechanism that explains *anti* addition is one in which a bromine molecule transfers a bromine atom to the alkene to form a cyclic *bromonium ion* and a bromide ion**

Step 1   **Step 2**

Mechanism of halogen addition

Step 1

➢ **As a bromine molecule approaches an alkene, the electron density of the alkene π electrons repels electron density of the closer bromine**

➢ **This polarizes the bromine molecule making the closer bromine atom electrophilic**

➢ **The alkene donates a pair of electrons to the closer bromine causing displacement of the distant bromine atom**

Mechanism of halogen addition

➢ **As this occurs, the newly bonded bromine atom, due to its size and polarizability, donates an electron pair to the carbon atom that would otherwise be a carbocation**

➢ **This stabilizes the positive charge by delocalization**

➢ **The result is a bridged (or cyclic) bromonium ion which is produced as an intermediate and a bromide ion as the other product**

Mechanism of halogen addition

Step 2

➢ **The bromide anion then attacks at the back side of one carbon (or the other) of the bromonium ion in an S_N2 reaction**

➢ **This causes the ring to open up and results in the formation of a vicinal dibromide**

➢ **The overall outcome is that the additions occur from either side of the original double bond resulting in a *trans* arrangement**
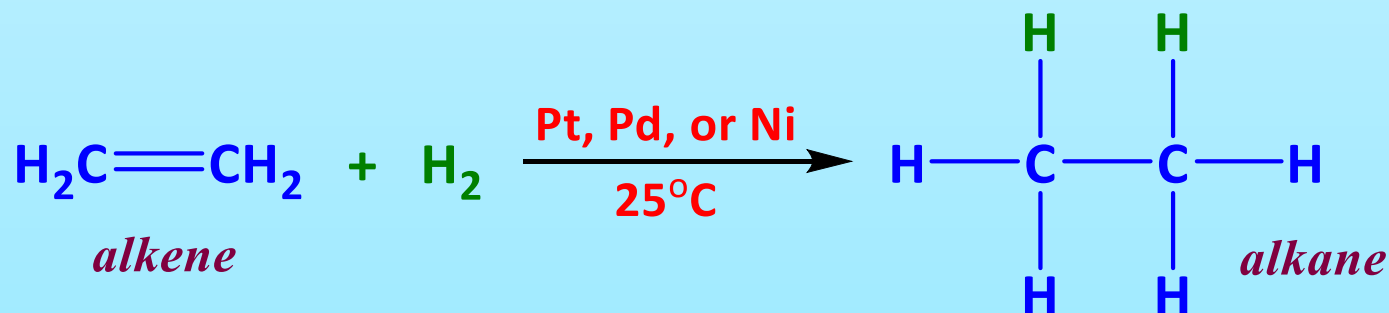
Mechanism of halogen addition

➢ **The process is shown below for the addition of bromine to cyclopentene**

Cyclic
bromonium ion

trans-1,2-dibromocyclopentane
(as a racemic mixture)
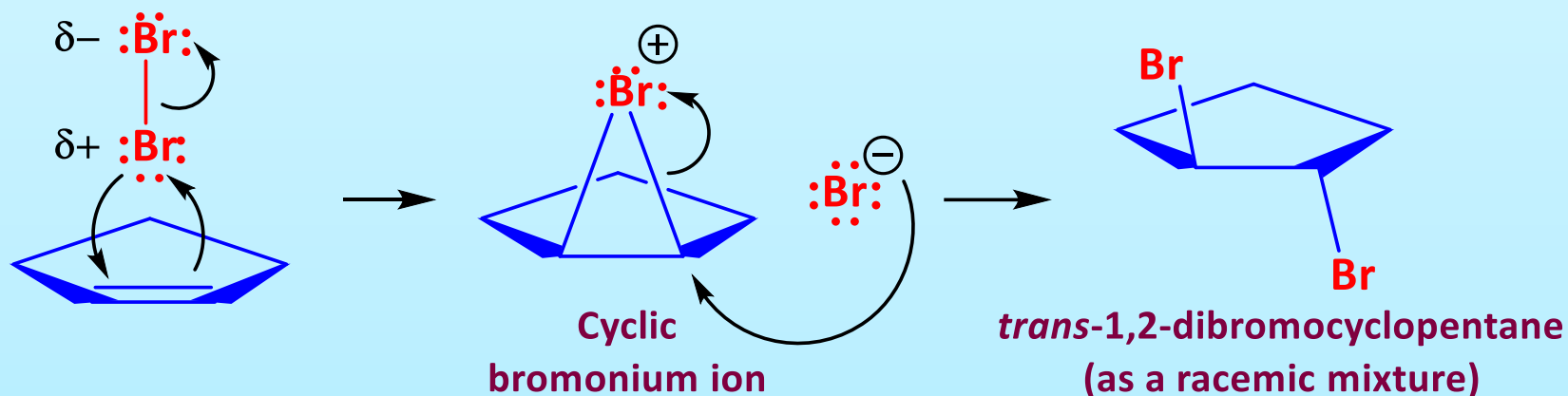
➢ **Attack at either carbon of the cyclopentene bromonium ion is symmetric – the result is that the product is a racemic mixture**
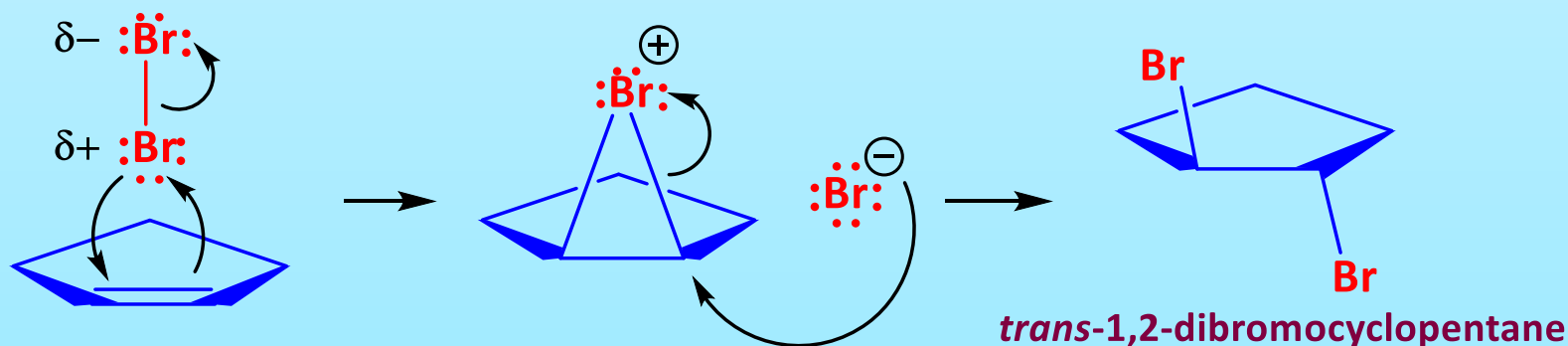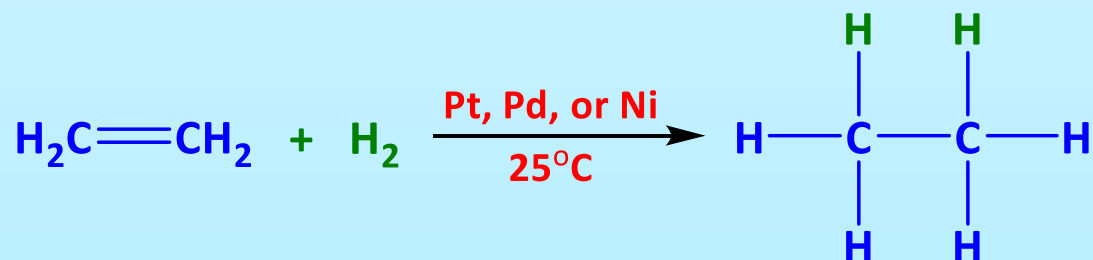
Hydrogenation of alkenes

➢ **We saw earlier that when alkenes (and alkynes) are treated with hydrogen gas in the presence of a catalyst (like Pd, Pt or Ni), a hydrogenation reaction take place**

➢ **The π bond in the double bond is converted into a σ bond and this results in the formation of an alkane**

$$H_2C = CH_2 \ + \ H_2 \quad \xrightarrow[25^OC]{Pt, \ Pd, \ or \ Ni} \quad H - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - H$$

*alkene*   *alkane*

Hydrogenation of alkenes

➢ **In these reactions, both hydrogen atoms are added to the double from the same side or face (i.e. *syn* addition) whereas the addition of bromine is said to be in an *anti* fashion**

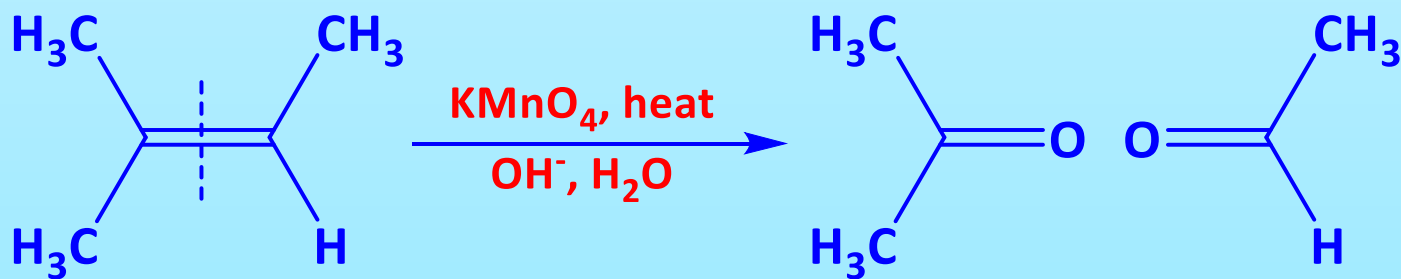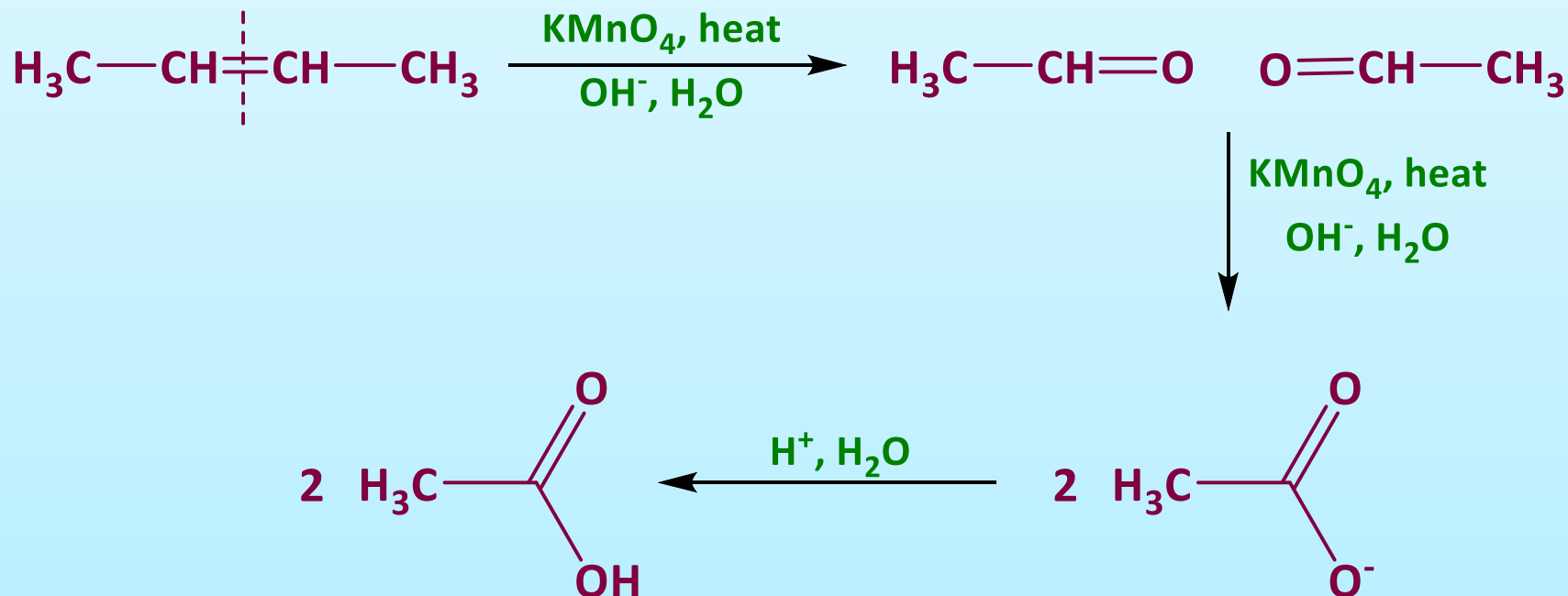$$H_2C=CH_2 \ + \ H_2 \ \xrightarrow[\text{25}^\text{o}\text{C}]{\text{Pt, Pd, or Ni}} \ H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$$

trans-1,2-dibromocyclopentane

Oxidation of alkenes

➢ **Alkenes also undergo reactions in which the double bond is oxidized, i.e. oxygen atoms are added across the double bond**

➢ **Potassium permanganate ($KMnO_4$) and osmium tetroxide (OsO_4) for example are used to oxidize the alkenes to give *1,2-diols* called *glycols***


1,2-diol or glycols
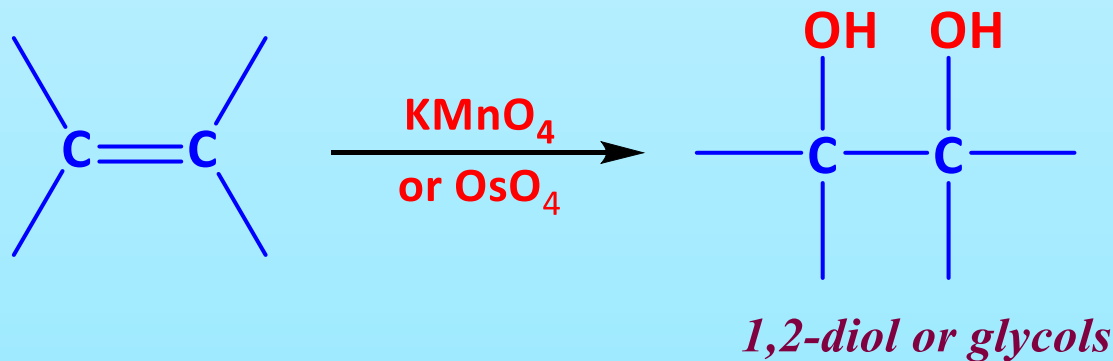
Oxidation of alkenes

➢ **A very important requirement in these reactions is that the reaction has to be conducted at a low (cold) temperature**

➢ **At elevated temperatures, the alkene will undergo oxidative cleavage – in this case, the alkene is split where the double bond is and the resultant fragments are oxidized separately to salts of carboxylic acids or ketones**

Oxidation of alkenes

$$H_3C - CH = CH - CH_3 \xrightarrow[\text{OH}^-, \text{H}_2\text{O}]{\text{KMnO}_4, \text{heat}} H_3C - CH = O \quad O = CH - CH_3$$

$\downarrow \text{KMnO}_4, \text{heat} \quad \text{OH}^-, \text{H}_2\text{O}$

$$2 \ H_3C - \overset{\displaystyle O}{\underset{\displaystyle OH}{C}} \xleftarrow{\text{H}^+, \text{H}_2\text{O}} 2 \ H_3C - \overset{\displaystyle O}{\underset{\displaystyle O^-}{C}}$$

$$\begin{array}{c} H_3C \\ H_3C \end{array} = \begin{array}{c} CH_3 \\ H \end{array} \xrightarrow[\text{OH}^-, \text{H}_2\text{O}]{\text{KMnO}_4, \text{heat}} \begin{array}{c} H_3C \\ H_3C \end{array} = O \quad O = \begin{array}{c} CH_3 \\ H \end{array}$$

Aromatic hydrocarbons

➢ **So far, all the hydrocarbon compounds that were encountered are classified as *aliphatic***

➢ **These compounds were: alkanes, cycloalkanes, alkenes and cycloalkene and alkynes**

H_3C—CH_2–CH_2—CH_3 H_3C—CH=CH—CH_3 H_3C—C≡C—CH_3
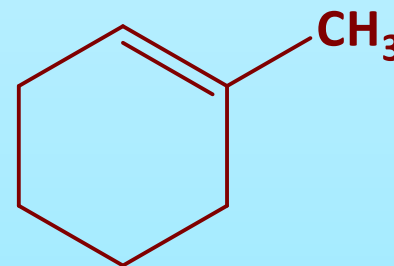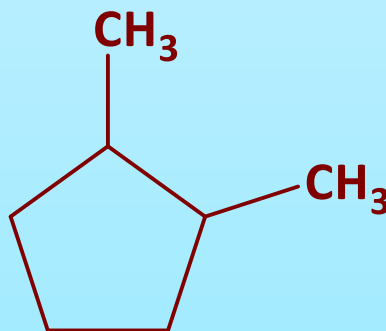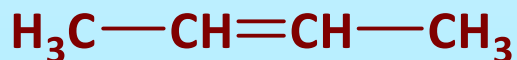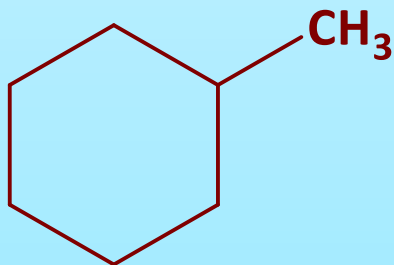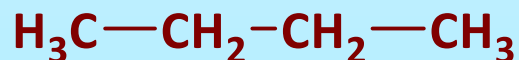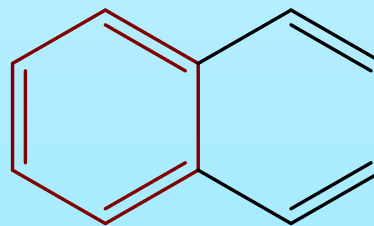
Aromatic hydrocarbons

➢ **The second class of compounds that are hydrocarbons are *aromatic* compounds**

➢ **These are compounds that possess a ring structure of benzene and other molecular structures that resemble benzene in electronic configuration and chemical behaviour**
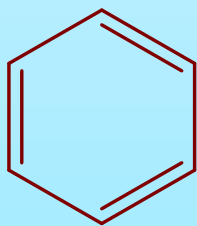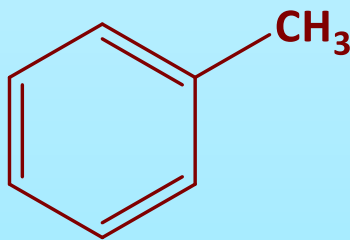
benzene   *methylbenzene*   *naphthalene*
                         (toluene)

Aromatic hydrocarbons

➢ **There are other compounds that, at first glance, bear little appearance to benzene, but have a basic similarity in electronic configuration**

➢ **At this stage we will just interpret aromatic character in terms of the benzene ring structure, since this definition does incorporates most of the commonly encountered aromatic substance**

Aromatic hydrocarbons

➢ **In the early days of organic chemistry, the word aromatic was used to describe fragrant substances such as benzaldehyde (from cherries, peaches, and almonds) and toluene (from Tolu balsam)**

➢ **It was soon realized, however, that substances grouped as aromatic behaved in a qualitatively different manner from most other organic compounds**

Aromatic hydrocarbons

➢ **Benzene, the simplest member of this class of compounds, was first isolated in 1825 from oily residue left by the illuminating gas used in London street lamps**

➢ **Today we use the term aromatic to refer to the class of compounds composed of benzene and its structural relatives**

➢ **Many compounds isolated from natural sources are aromatic in part, including benzene, benzaldehyde, and toluene complex compounds such as estrone (the female steroidal hormone and morphine (pain killer)**

Aromatic hydrocarbons
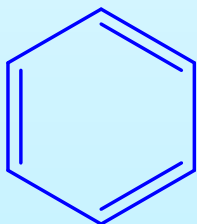
benzene
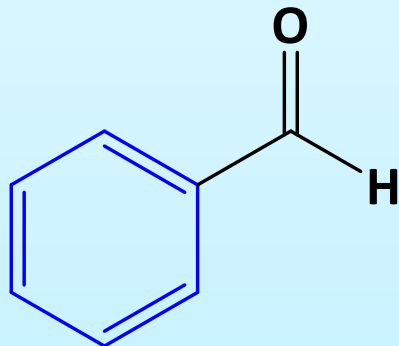
benzaldehyde
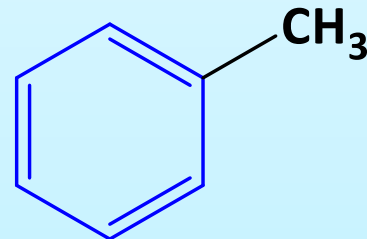
toluene
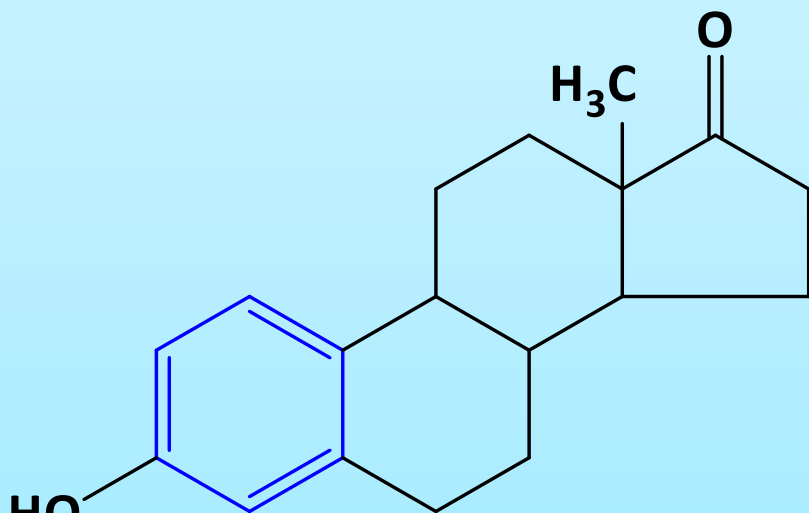
estrone
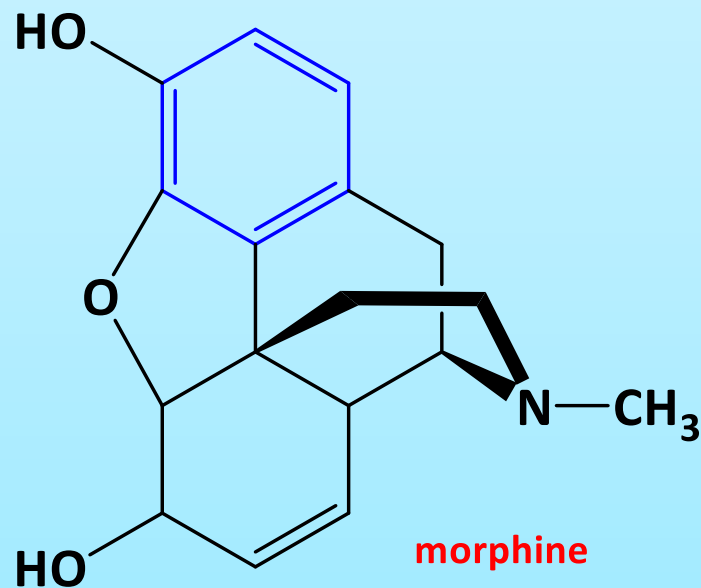
morphine

Aromatic hydrocarbons

➢ **Most synthetic drugs used medicinally are also aromatic**

➢ **The local anesthetic procaine and the tranquillizer diazepam (valium) are two of many examples**
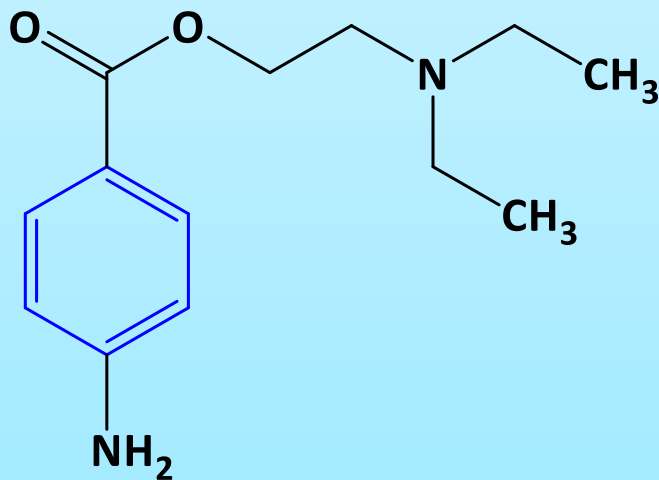

procaine
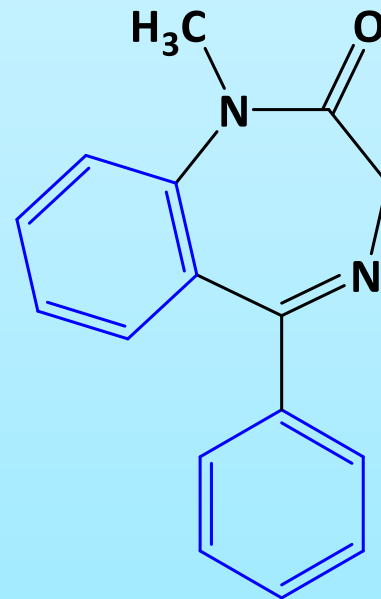
Diazepam

Structure of benzene

Structure of benzene

➢ **Following its isolation in 1825 by Michael Faraday, the molecular formula of benzene was deduced to be C_6H_6 – this posed a huge challenge for chemists of the day**

➢ **In 1866, August Kekulé used his then recently published structural theory of matters to propose a structure for benzene – specifically he proposed a ring comprised of alternate double and single bonds**
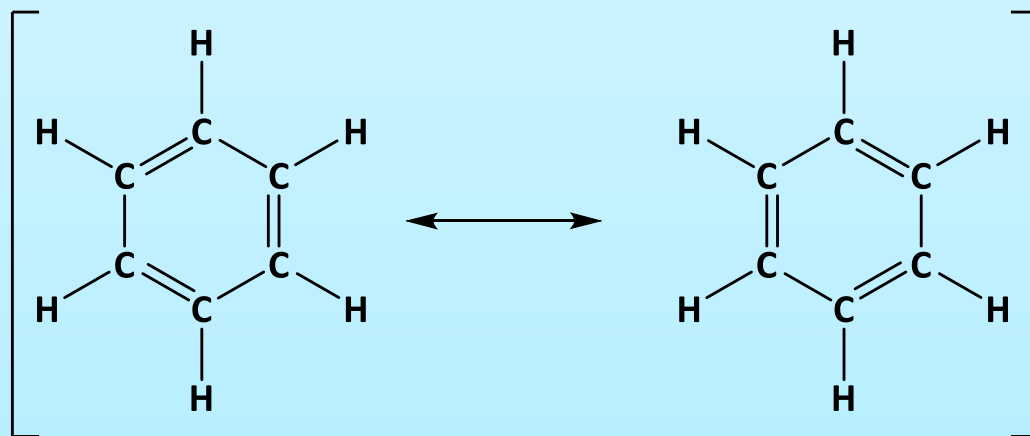
Structure of benzene
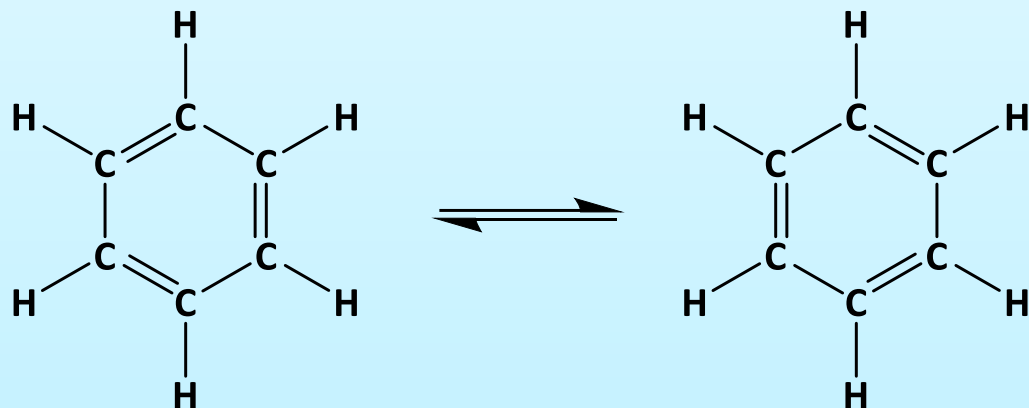
➢ **Kekulé described the exchange of double and single bonds to be an equilibrium process**

➢ **Over time this view was refined by the advent of the resonance theory and the molecular orbital concept of delocalization**
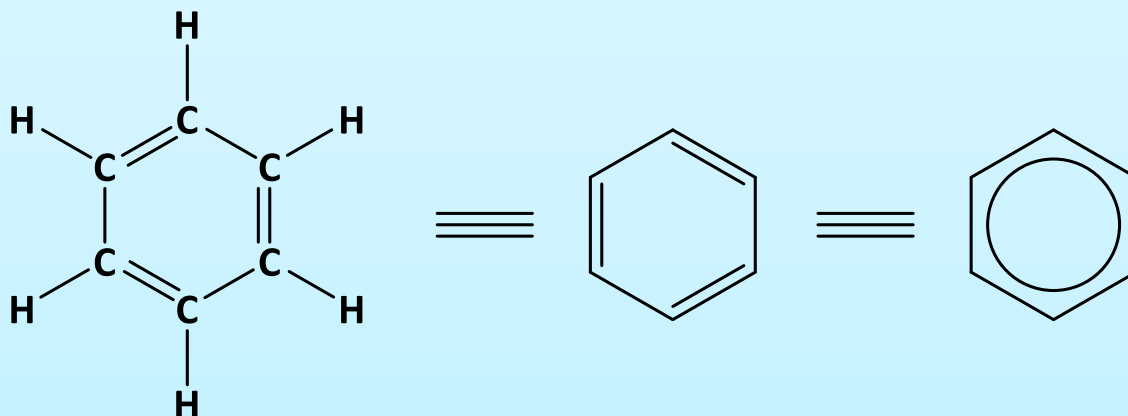
Structure of benzene

➢ **The two drawings are now viewed as resonance structures and not as in an equilibrium process**

➢ **Because of this rapid 'conversion' between the two forms, the structure is sometimes written as a cyclohexane ring with a circle in it**

Structure of Benzene

➢ **Resonance is not a motion of electrons, but rather, resonance is the way that chemists deal with the inadequacy of bond-line drawing**

➢ **Specifically, each drawing alone is inadequate to describe the structure of benzene**

Structure of benzene

➢ **The problem is that each C—C bond is neither a single bond nor double bond, nor is it vibrating back and forth between the two states**

➢ **Instead, each C—C bond has a bond order of 1.5 (1.39Å), exactly midway between a single bond and a double bond**

➢ **To avoid drawing resonance structures, benzene is often drawn as explained earlier, a cyclohexane ring with a circle in it**
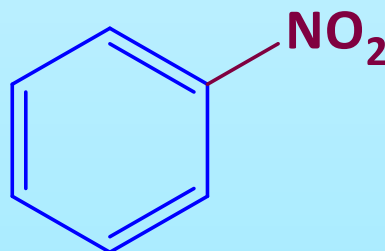
Nomenclature

Monosubstituted derivative of benzene

➢ **Monosubstituted derivatives of benzene are named systematically using benzene as the parent and listing the substituent as a prefix**

➢ **For example**
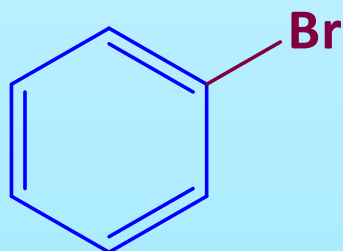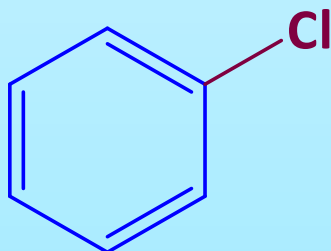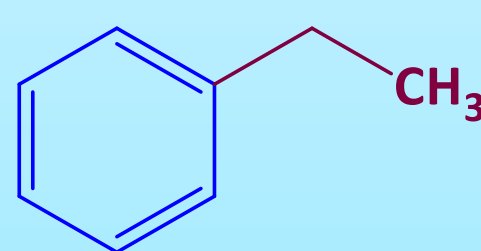

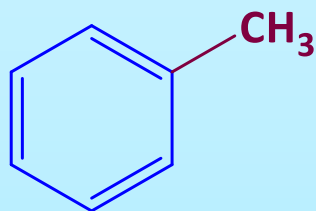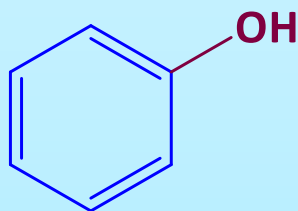Bromobenzene   Chlorobenzene   Nitrobenzene   Ethylbenzene

Nomenclature
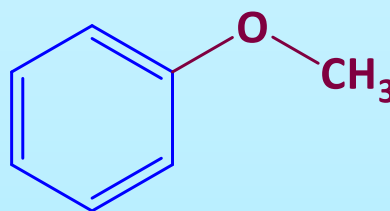
Monosubstituted derivative of benzene

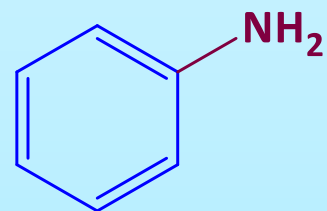➢ **The following are some monosubstituted aromatic compounds that have common names accepted by IUPAC…**
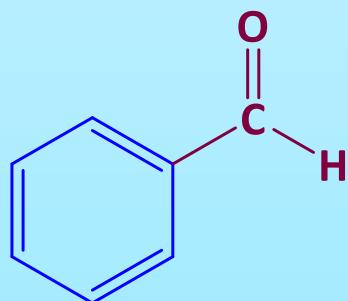

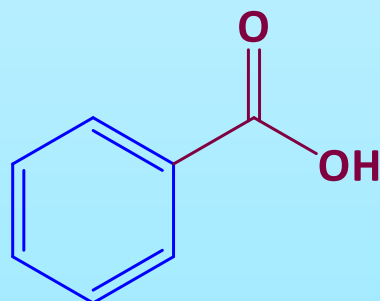Toluene   Phenol   Anisole   Aniline
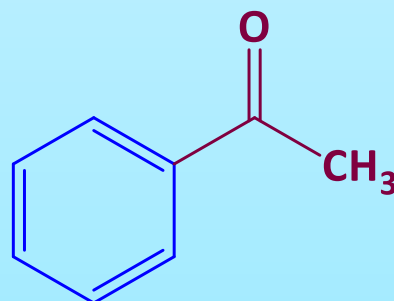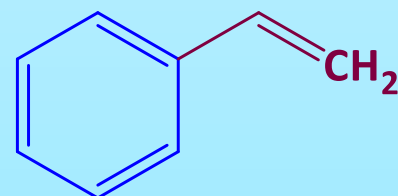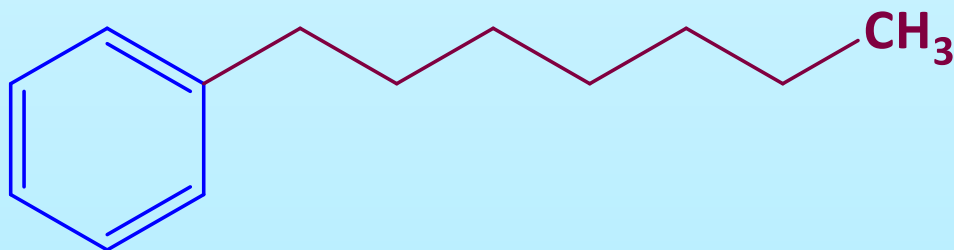
Benzaldehyde   Benzoic acid   Acetophenone   Styrene

Nomenclature

➢ **If a substituent is larger than the benzene ring (i.e. if the substituent has more than six carbon atoms), then the benzene ring is treated as the substituent and is called a phenyl group**

1-Phenylheptane and NOT heptylbenzene

➢ **The presence of the phenyl group is often indicated by the letters Ph or with the Greek phi (φ)**

Nomenclature

Tetraphenyl cyclopentadienone
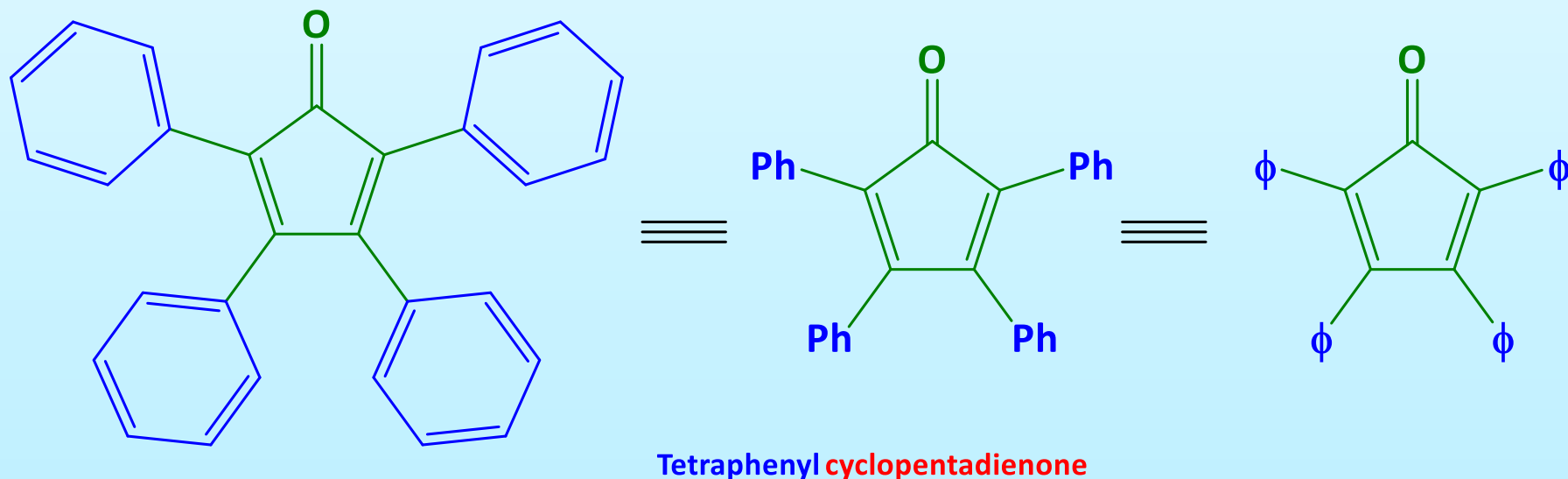
➢ **Phenyl groups bearing substituents are sometimes indicated with the letters Ar, indicating the presence of an aromatic ring, for example phenol is represented as Ar-OH and benzaldehyde is represented as Ar-CHO**

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Nomenclature

Disubstituted derivative of benzene

➢ **Dimethyl derivatives of benzene are called xylene and there are three constitutionally isomeric xylenes**

|		
o-Xylene	*m*-Xylene	*p*-Xylene
1,2-dimethylbenzene	1,3-diemthylbenzene	1,4-dimethylbenzene
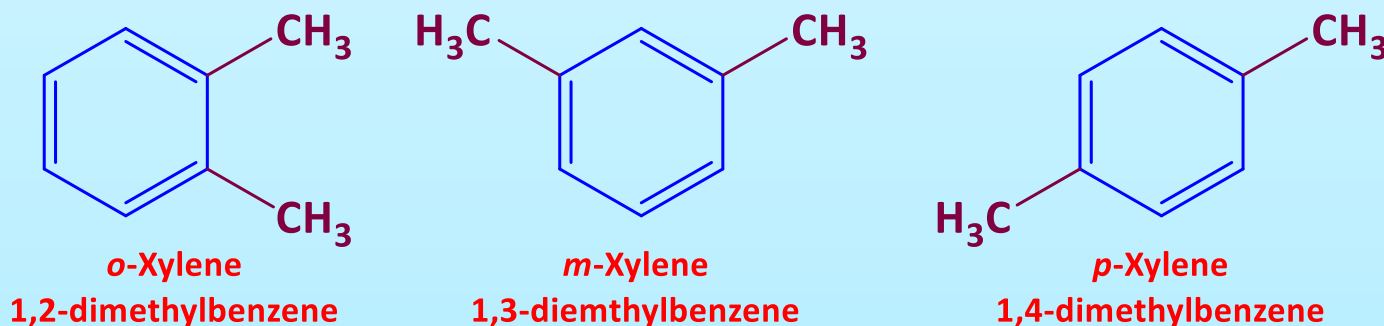
➢ **These isomers differ from each other in the relative positions of the methyl groups and can be named in two ways: (1) using the descriptors *ortho, meta* and *para...or***
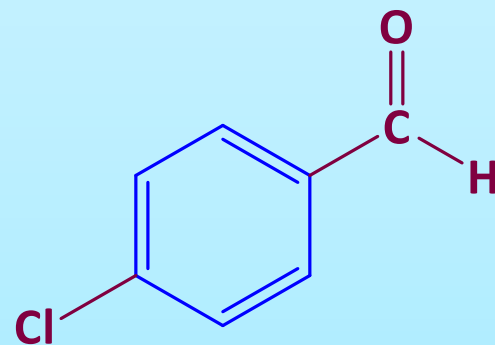
Nomenclature

> ...(2) using locants (i.e. 1,3 is the same as *meta*)

> Both methods can be used when the parent is the same name
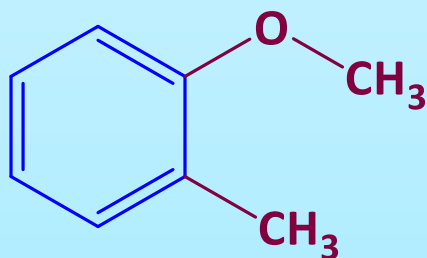
ortho-methylanisole
2-methylanisole
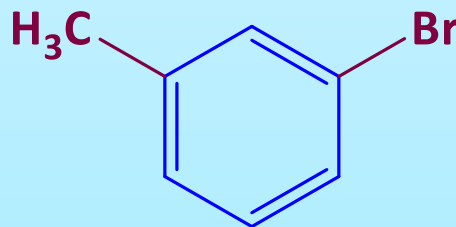
meta-bromotoluene
3-bromotoluene

para-chlorobenzaldehyde
4-chlorobenzaldehyde

Nomenclature

Polysubstituted derivatives of benzene

➢ **The descriptors *ortho, meta* and *para* cannot be used when naming an aromatic ring bearing three or more substituents**

➢ **In such a case, locants are required – i.e. each substituent is designated with a number to indicate its location on the ring**

➢ **When naming a polysubstituted benzene ring, follow the same four-step process used for naming alkanes, alkenes and alkynes and alcohols**
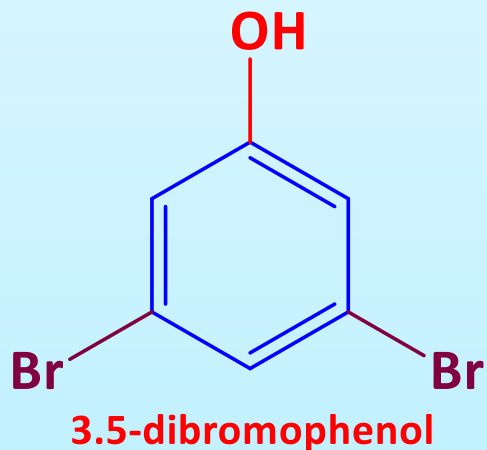
Nomenclature to aromatic chemistry

That is…

1. **Identify and name the parent compound**
2. **Identify and name the substituent**
3. **Assign a locant to each substituent**
4. **Arrange the substituent alphabetically**

➢ **When identifying the parent, it is acceptable (and common practice) to choose a common name – consider the following**

Nomenclature to aromatic chemistry

3.5-dibromophenol

➢ **This compound could certainly be named as a trisubstituted benzene**

➢ **However, it is much more efficient to name the parent as phenol rather than benzene and to list the two bromine atoms as substituents**

Nomenclature to Aromatic Chemistry

➢ **The choice to name this compound as a phenol dictates that the carbon atom connected to the OH group must receive the lowest locant (number 1)**

➢ **When a choice exists, place numbers so that the second substituent receives the lowest possible number**

INCORRECT

3-Bromo-6-chlorophenol

CORRECT

5-Bromo-2-chlorophenol

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