Ministry of Higher Education and Scientific Research
Al-Mustaqbal University College
Department of Pharmacy

Organic Chemistry

The Second Stage

LEC 1 : Aromatic Compound

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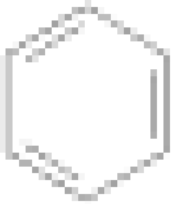
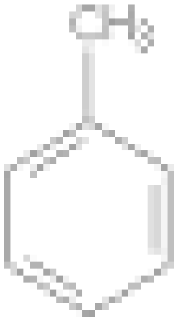
Aromatic compounds

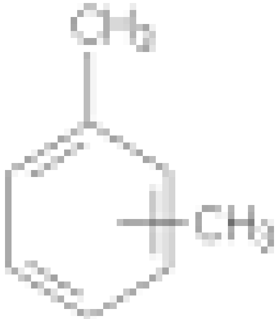
are those chemical compounds (most commonly organic) that contain one or more rings with pi electrons delocalized all the way around them. In contrast to compounds that exhibit aromaticity, aliphatic compounds lack this delocalization. The term "aromatic" was assigned before the physical mechanism determining aromaticity was discovered, and referred simply to the fact that many such compounds have a sweet or pleasant odour; however, not all aromatic compounds have a sweet odour, and not all compounds with a sweet odour are aromatic. Aromatic hydrocarbons, or arenes, are aromatic organic compounds containing solely carbon and hydrogen atoms. The configuration of six carbon atoms in aromatic compounds is called a "benzene ring", after the simple aromatic compound benzene, or a phenyl group when part of a larger compound.



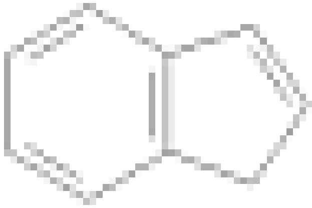
benzene



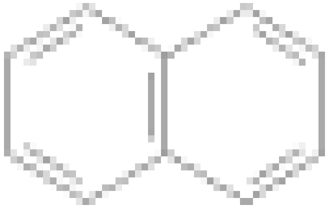
toluene



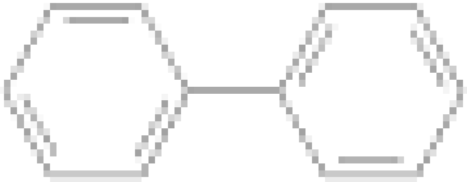
o-, *m*-, *p*-xylene



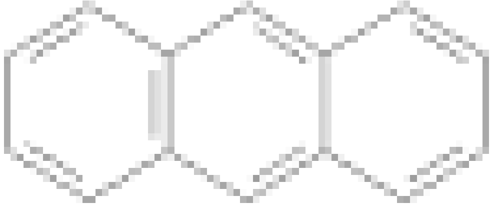
indene



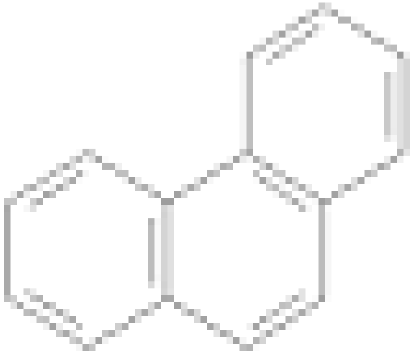
naphthalene



biphenyl

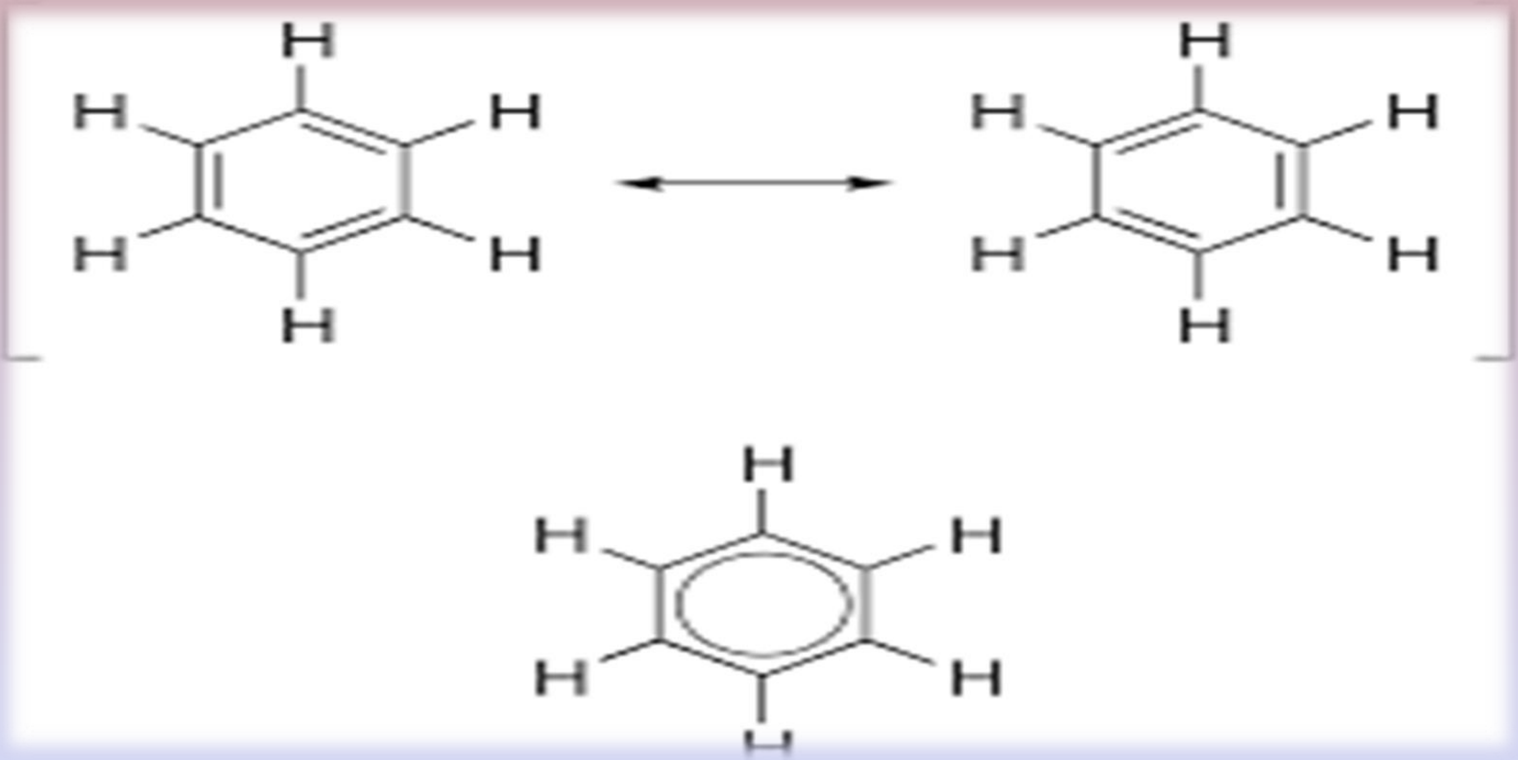


anthracene



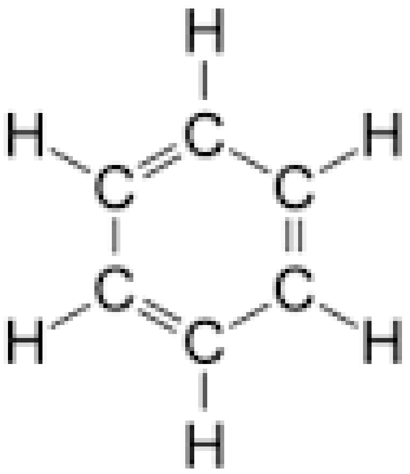
phenanthrene

Not all aromatic compounds are benzene-based; aromaticity can also manifest in heteroarenes, which follow Hückel's rule (for monocyclic rings: when the number of its π electrons equals $4n + 2$, where $n = 0, 1, 2, 3, \ldots$). In these compounds, at least one carbon atom is replaced by one of the heteroatoms oxygen, nitrogen, or sulfur. Examples of non-benzene compounds with aromatic properties are furan, a heterocyclic compound with a five-membered ring that includes a single oxygen atom, and pyridine, a heterocyclic compound with a six-membered ring containing one nitrogen atom

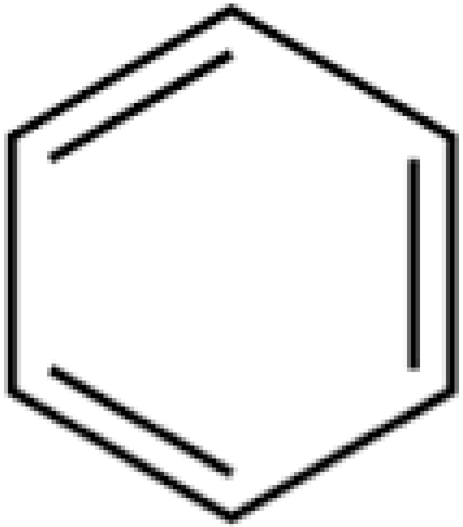


Benzene ring model

Benzene, C_6H_6, is the least complex aromatic hydrocarbon. The nature of its bonding was first recognized by August Kekulé in the 19th century. Each carbon atom in the hexagonal cycle has four electrons to share. One goes to the hydrogen atom, and one to each of the two neighbouring carbons. This leaves one electron to share with one of the two neighbouring carbon atoms, thus creating a double bond with one carbon and leaving a single bond with the other, which is why some representations of the benzene molecule portray it as a hexagon with alternating single and double bonds.



(1)



(2)

Other depictions of the structure portray the hexagon with a circle inside it, to indicate that the six electrons are floating around in delocalized molecular orbitals the size of the ring itself. This represents the equivalent nature of the six carbon–carbon bonds all of bond order 1.5; the equivalency is explained by resonance forms. The electrons are visualized as floating above and below the ring, with the electromagnetic fields they generate acting to keep the ring flat.

General properties of aromatic hydrocarbons:

They display aromaticity

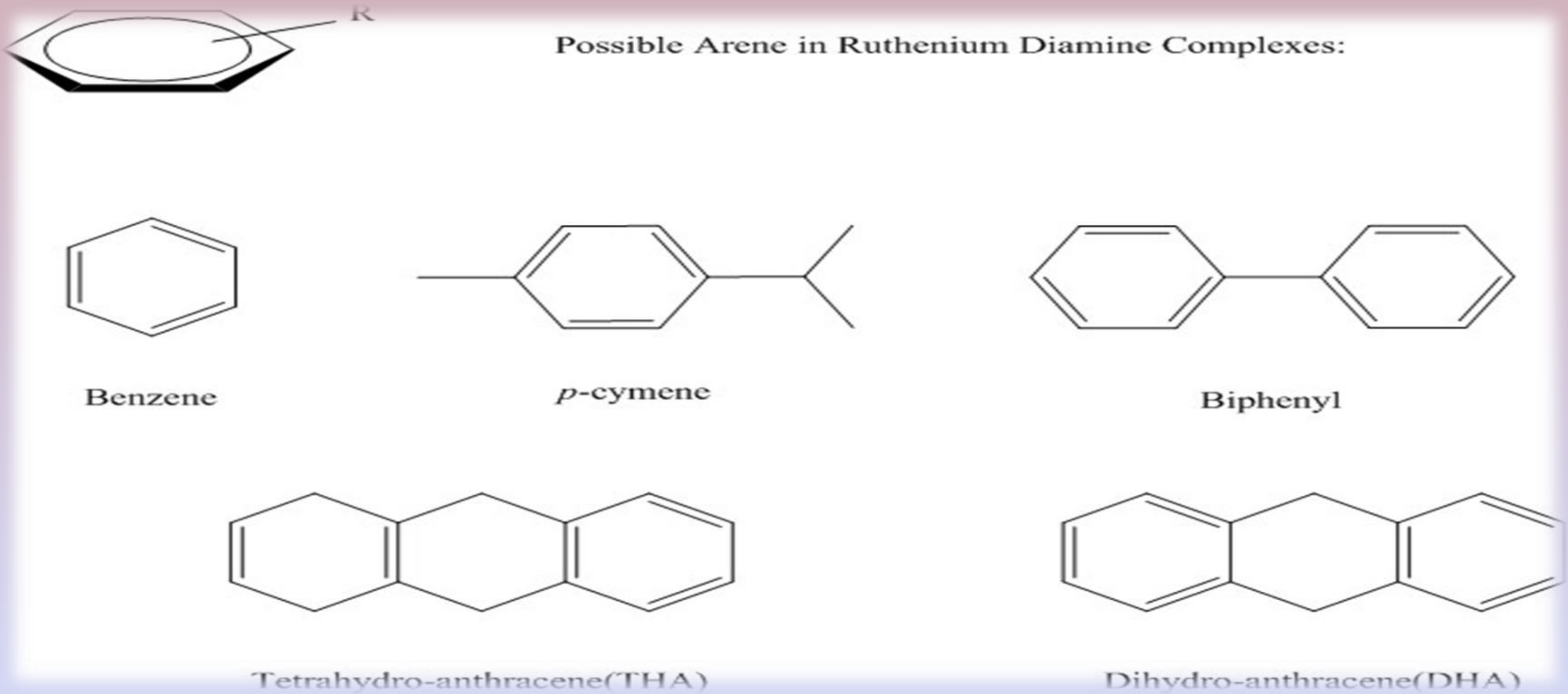
The carbon–hydrogen ratio is high

They burn with a strong sooty yellow flame because of the high carbon–hydrogen ratio

They undergo electrophilic substitution reactions and nucleophilic aromatic substitutions

Arene synthesis

A reaction that forms an arene compound from an unsaturated or partially unsaturated cyclic precursor is simply called aromatization. Many laboratory methods exist for the organic synthesis of arenes from non-arene precursors. Many methods rely on cycloaddition reactions. Alkyne trimerization describes the [2+2+2] cyclization of three alkynes, in the Dötz reaction an alkyne, carbon monoxide and a chromium carbene complex are the reactants. Diels–Alder reactions of alkynes with pyrone or cyclopentadienone with expulsion of carbon dioxide or carbon monoxide also form arene compounds. In Bergman cyclization the reactants are an enyne plus a hydrogen donor.

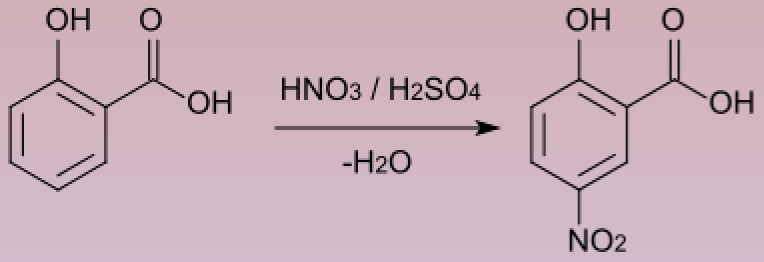


Reactions

Aromatic ring systems participate in many organic reactions.

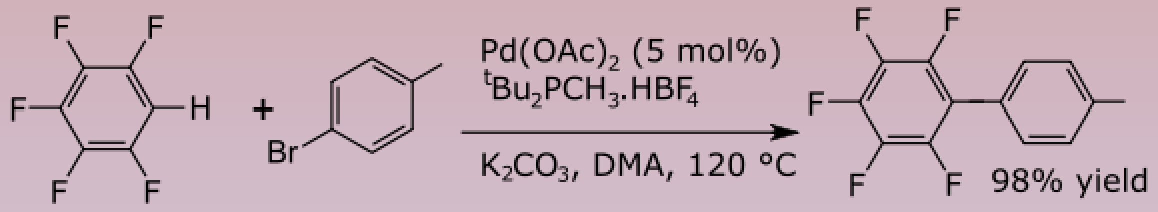
Aromatic substitution

In aromatic substitution one substituent on the arene ring, usually hydrogen, is replaced by another substituent. The two main types are electrophilic aromatic substitution when the active reagent is an electrophile and nucleophilic aromatic substitution when the reagent is a nucleophile. In radical-nucleophilic aromatic substitution the active reagent is a radical. An example of electrophilic aromatic substitution is the nitration of salicylic acid

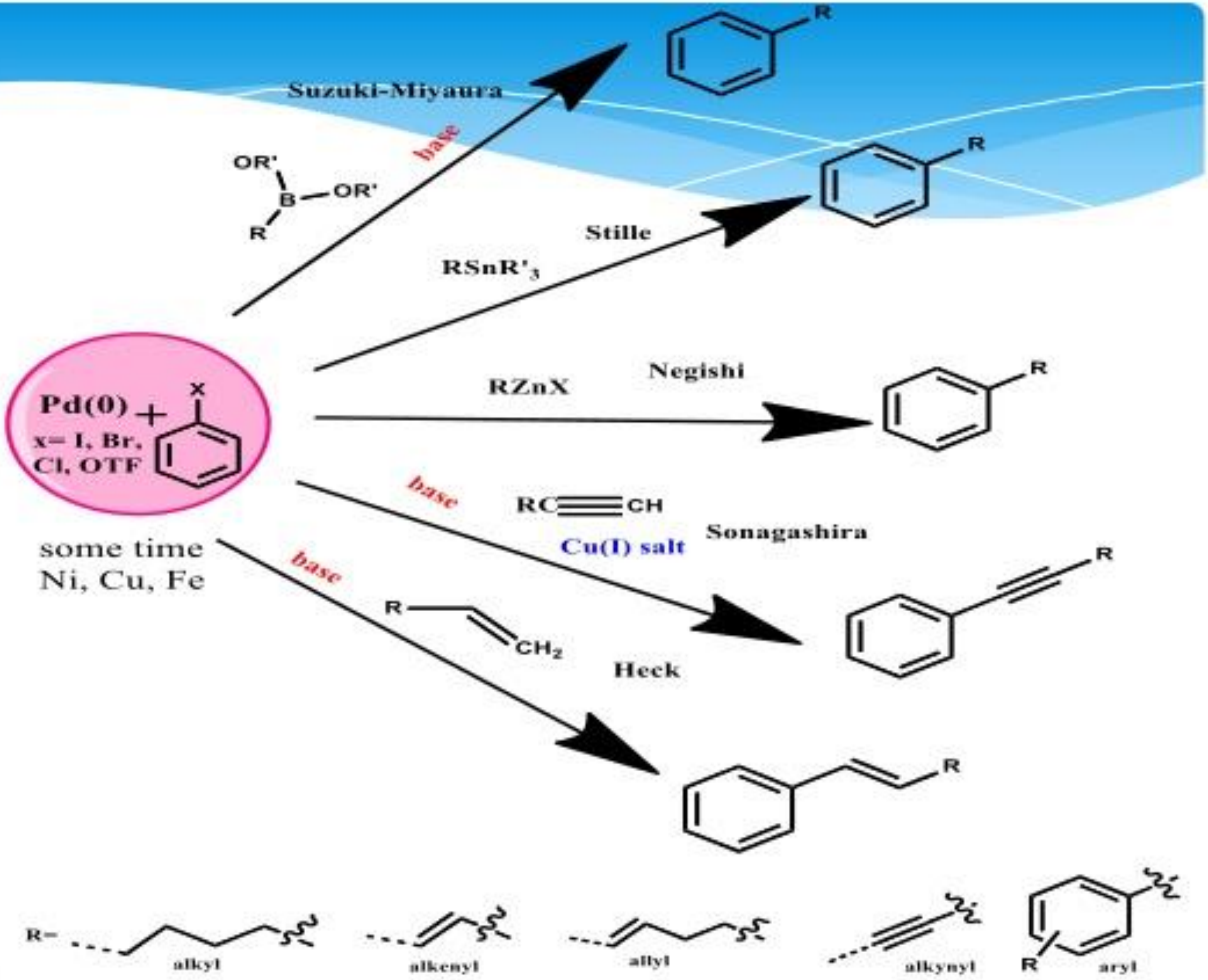


Coupling reactions

In coupling reactions a metal catalyses a coupling between two formal radical fragments. Common coupling reactions with arenes result in the formation of new carbon–carbon bonds e.g., alkylarenes, vinyl arenes, biraryls, new carbon–nitrogen bonds (anilines) or new carbon–oxygen bonds (aryloxy compounds). An example is the direct arylation of perfluorobenzenes

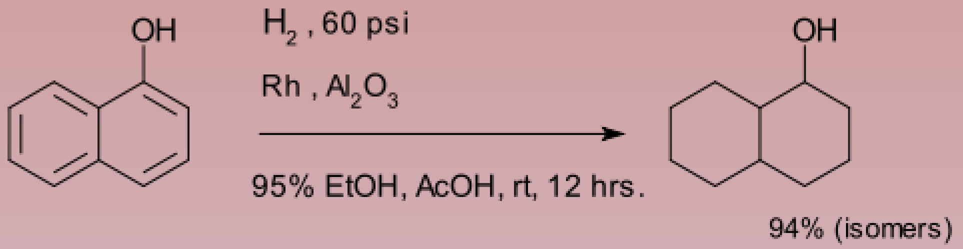


C-C coupling reactions

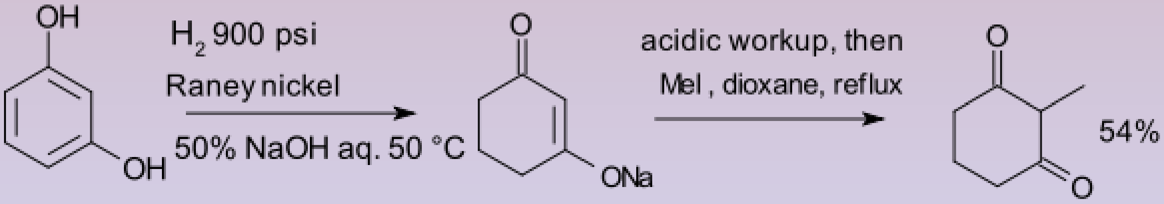


Hydrogenation

Hydrogenation of arenes create saturated rings. The compound 1-naphthol is completely reduced to a mixture of decalin-ol isomers



The compound resorcinol, hydrogenated with Raney nickel in presence of aqueous sodium hydroxide forms an enolate which is alkylated with methyl iodide to 2-methyl-1,3-cyclohexandione

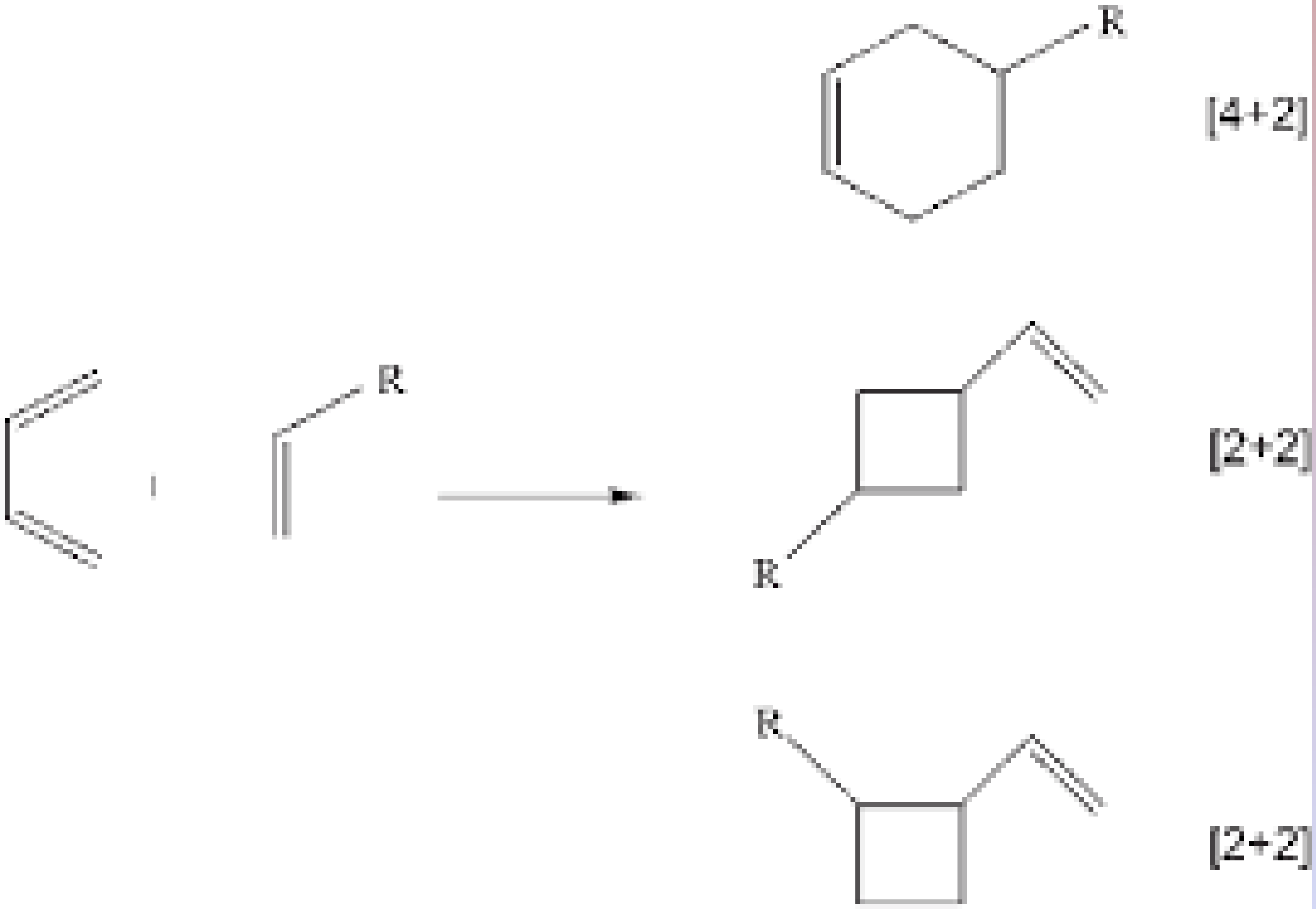


Cycloadditions

Cycloaddition reaction are not common. Unusual thermal Diels–Alder reactivity of arenes can be found in the Wagner-Jauregg reaction. Other photochemical cycloaddition reactions with alkenes occur through excimers.

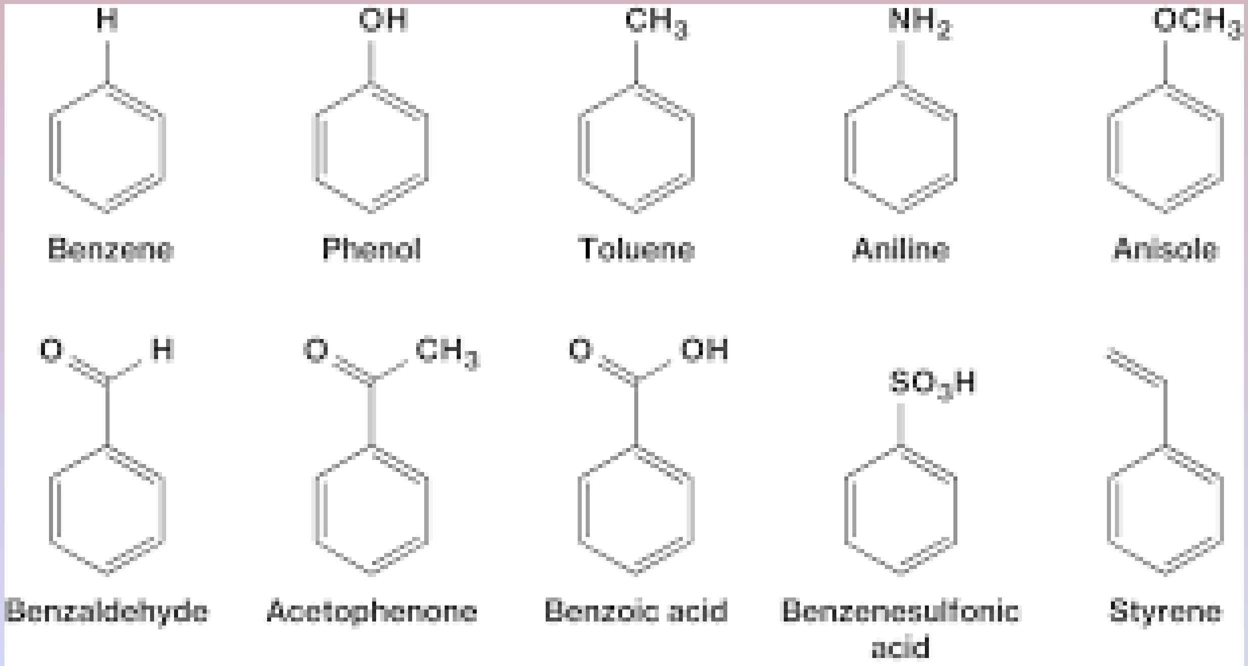
Dearomatization

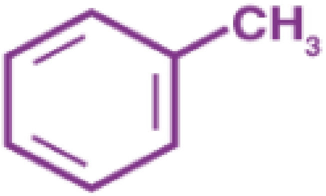
In dearomatization reactions the aromaticity of the reactant is permanently lost.



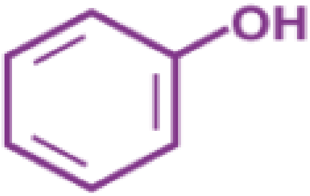
Benzene and derivatives of benzene

Benzene derivatives have from one to six substituents attached to the central benzene core. Examples of benzene compounds with just one substituent are phenol, which carries a hydroxyl group, and toluene with a methyl group. When there is more than one substituent present on the ring, their spatial relationship becomes important for which the arene substitution patterns ortho, meta, and para are devised. For example, three isomers exist for cresol because the methyl group and the hydroxyl group can be placed next to each other (ortho), one position removed from each other (meta), or two positions removed from each other (para). Xylenol has two methyl groups in addition to the hydroxyl group, and, for this structure, 6 isomers exist.

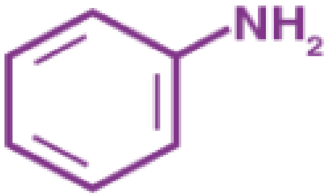




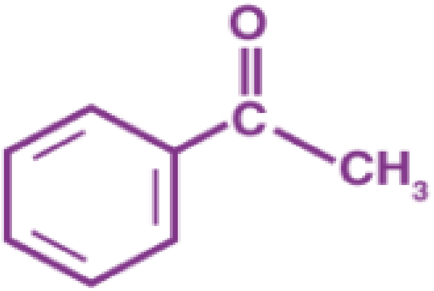
Toluene



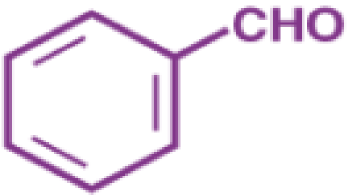
Phenol



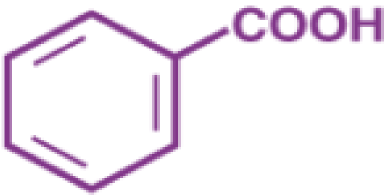
Aniline



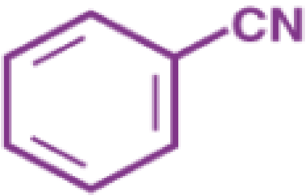
Acetophenone



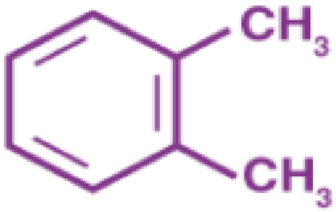
Benzaldehyde



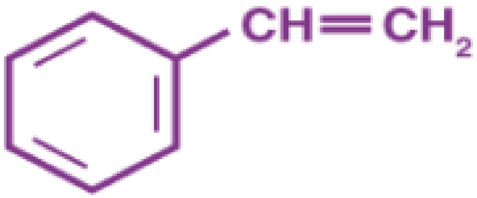
Benzoic acid



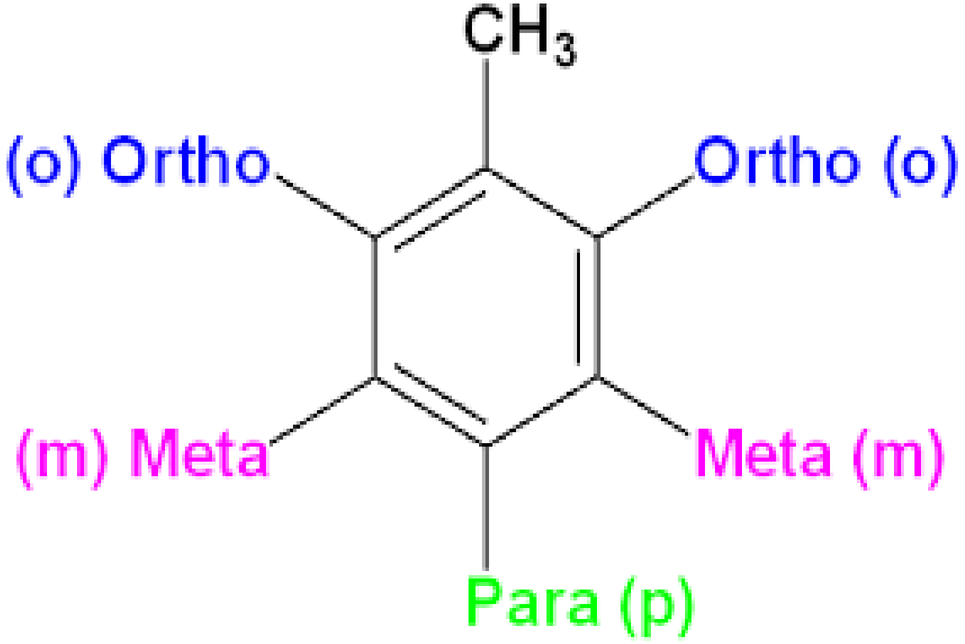
Benzonitrile

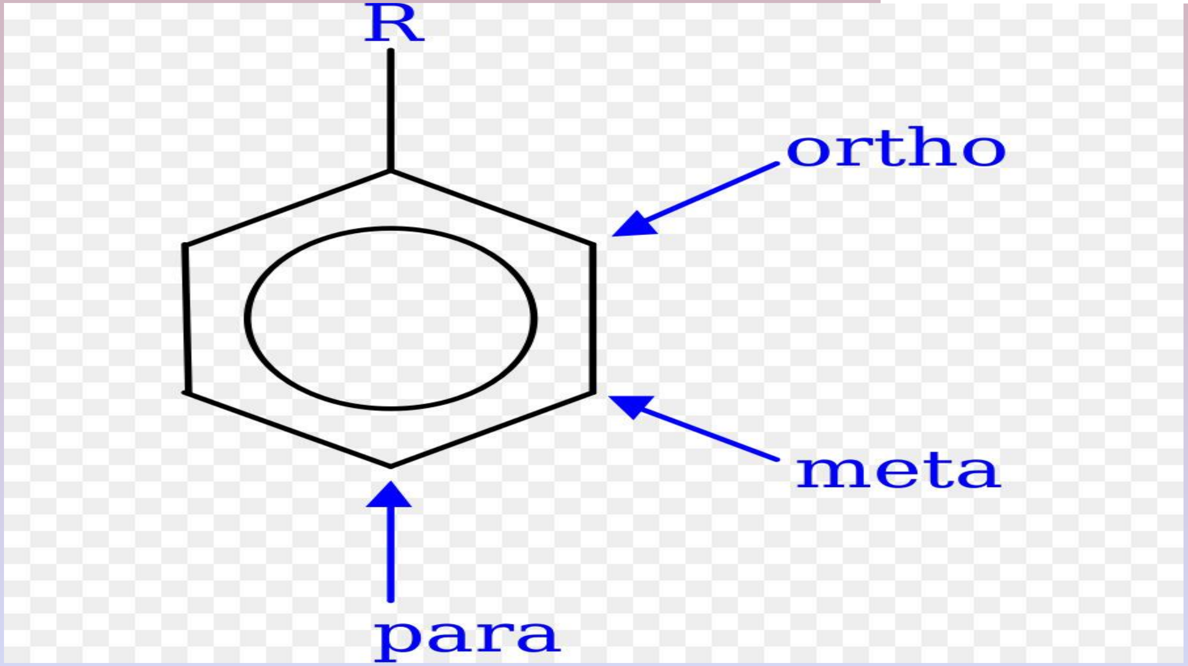


Ortho-xylene



Styrene


CH_3
(o) Ortho
Ortho (o)
(m) Meta
Meta (m)
Para (p)


R
ortho
meta
para