UNIT-III(SEM-I)

hydrocarbon

Ball-and-stick model of the methane molecule, CH_4. Methane is part of a homologous series known as the alkanes, which contain single bonds only.

In organic chemistry, a **hydrocarbon** is an organic compound consisting entirely of hydrogen and carbon.[1]:620 Hydrocarbons are examples of group 14 hydrides. Hydrocarbons are generally colourless and hydrophobic; their odor is usually faint, and may be similar to that of gasoline or lighter fluid. They occur in a diverse range of molecular structures and phases: they can be gases (such as methane and propane), liquids (such as hexane and benzene), low melting solids (such as paraffin wax and naphthalene) or polymers (such as polyethylene and polystyrene).

In the fossil fuel industries, *hydrocarbon* refers to naturally occurring petroleum, natural gas and coal, or their hydrocarbon derivatives and purified forms. Combustion of hydrocarbons is the main source of the world's energy. Petroleum is the dominant raw-material source for organic commodity chemicals such as solvents and polymers. Most anthropogenic (human-generated) emissions of greenhouse gases are either carbon dioxide released by the burning of fossil fuels, or methane released from the handling of natural gas or from agriculture.

Types

As defined by the International Union of Pure and Applied Chemistry's nomenclature of organic chemistry, hydrocarbons are classified as follows:

1. Saturated hydrocarbons, which are the simplest of the hydrocarbon types. They are composed entirely of single bonds and are saturated with hydrogen. The formula for acyclic saturated hydrocarbons (i.e., alkanes) is C_nH_{2n+2}.[1]:623 The most general form of saturated hydrocarbons, (whether linear or branched species, and whether with or without one or more rings) is $C_nH_{2n+2(1-r)}$, where r is the number of rings. Those with exactly one ring are the cycloalkanes. Saturated hydrocarbons are the basis of petroleum fuels and may be either linear or branched species. One or more of the hydrogen atoms can be replaced with other atoms, for example chlorine or another halogen: this is called a substitution reaction. An example is the conversion of methane to chloroform using a chlorination reaction. Halogenating a hydrocarbon produces something that is not a hydrocarbon. It is a very common and useful process. Hydrocarbons with the same molecular formula but different structural formulae are called structural isomers.[1]:625 As given in the example of 3-methylhexane and its higher homologues, branched hydrocarbons can be chiral.[1]:627 Chiral saturated hydrocarbons constitute the side chains of biomolecules such as chlorophyll and tocopherol.[2]
2. Unsaturated hydrocarbons, which have one or more double or triple bonds between carbon atoms. Those with one or more double bonds are called alkenes. Those with one double bond have the formula C_nH_{2n} (assuming non-cyclic structures).[1]:628 Those containing triple bonds are called alkyne. Those with one triple bond have the formula C_nH_{2n-2}.[1]:631

3. Aromatic hydrocarbons, also known as arenes, which are hydrocarbons that have at least one aromatic ring. 10% of total nonmethane organic carbon emission are aromatic hydrocarbons from the exhaust of gasoline-powered vehicles.[3]

The term 'aliphatic' refers to non-aromatic hydrocarbons. Saturated aliphatic hydrocarbons are sometimes referred to as 'paraffins'. Aliphatic hydrocarbons containing a double bond between carbon atoms are sometimes referred to as 'olefins'.

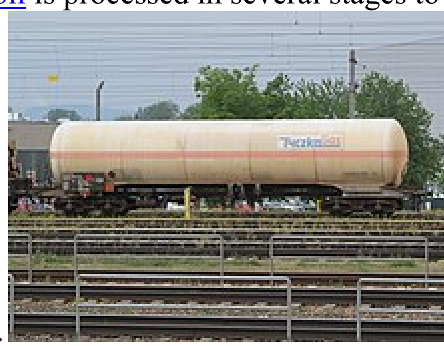
Variations on hydrocarbons based on the number of carbon atoms

Number of carbon atoms	Alkane (single bond)	Alkene (double bond)	Alkyne (triple bond)	Cycloalkane	Alkadiene
1	Methane	—	—	—	—
2	Ethane	Ethene (ethylene)	Ethyne (acetylene)	—	—
3	Propane	Propene (propylene)	Propyne (methylacetylene)	Cyclopropane	Propadiene (allene)
4	Butane	Butene (butylene)	Butyne	Cyclobutane	Butadiene
5	Pentane	Pentene	Pentyne	Cyclopentane	Pentadiene (piperylene)
6	Hexane	Hexene	Hexyne	Cyclohexane	Hexadiene
7	Heptane	Heptene	Heptyne	Cycloheptane	Heptadiene
8	Octane	Octene	Octyne	Cyclooctane	Octadiene
9	Nonane	Nonene	Nonyne	Cyclononane	Nonadiene
10	Decane	Decene	Decyne	Cyclodecane	Decadiene
11	Undecane	Undecene	Undecyne	Cycloundec	Undecadiene

				ane	
12	Dodecane	Dodecene	Dodecyne	Cyclododecane	Dodecadiene

Usage

Oil refineries are one way hydrocarbons are processed for use. Crude oil is processed in several stages to form desired hydrocarbons, used as fuel and in other products.



Tank wagon 33 80 7920 362–0 with hydrocarbon gas at Bahnhof Enns (2018)

The predominant use of hydrocarbons is as a combustible fuel source. Methane is the predominant component of natural gas. C^{6} through C^{10} alkanes, alkenes, cycloalkanes, and aromatic hydrocarbons are the main components of gasoline, naphtha, jet fuel, and specialized industrial solvent mixtures. With the progressive addition of carbon units, the simple non-ring structured hydrocarbons have higher viscosities, lubricating indices, boiling points, solidification temperatures, and deeper color. At the opposite extreme from methane lie the heavy tars that remain as the *lowest fraction* in a crude oil refining retort. They are collected and widely utilized as roofing compounds, pavement material (bitumen), wood preservatives (the creosote series) and as extremely high viscosity shear-resisting liquids.

Some large-scale non-fuel applications of hydrocarbons begin with ethane and propane, which are obtained from petroleum and natural gas. These two gases are converted either to syngas or to ethylene and propylene respectively. Global consumption of benzene in 2021 is estimated at more than 58 million metric tons, which will increase to 60 million tons in 2022.[4]

Hydrocarbons are also prevalent in nature. Some eusocial arthropods, such as the Brazilian stingless bee, *Schwarziana quadripunctata*, use unique cuticular hydrocarbon "scents" in order to determine kin from non-kin. This hydrocarbon composition varies between age, sex, nest location, and hierarchal position.[5]

There is also potential to harvest hydrocarbons from plants like *Euphorbia lathyris* and *E. tirucalli* as an alternative and renewable energy source for vehicles that use diesel.[6] Furthermore, endophytic bacteria from plants that naturally produce hydrocarbons have been used in hydrocarbon degradation in attempts to deplete hydrocarbon concentration in polluted soils.[7]

Reactions

The noteworthy feature of saturated hydrocarbons is their inertness. Unsaturated hydrocarbons (alkanes, alkenes and aromatic compounds) react more readily, by means of substitution, addition, polymerization. At higher temperatures they undergo dehydrogenation, oxidation and combustion.

Substitution

Main article: Substitution reaction

Of the classes of hydrocarbons, aromatic compounds uniquely (or nearly so) undergo substitution reactions. The chemical process practiced on the largest scale is the reaction of benzene and ethene to give ethylbenzene:

$C_6H_6 + C_2H_4 \rightarrow C_6H_5CH_2CH_3$

The resulting ethylbenzene is dehydrogenated to styrene and then polymerized to manufacture polystyrene, a common thermoplastic material.

Free-radical substitution

Main article: Free-radical halogenation

Substitution reactions occur also in saturated hydrocarbons (all single carbon–carbon bonds). Such reactions require highly reactive reagents, such as chlorine and fluorine. In the case of chlorination, one of the chlorine atoms replaces a hydrogen atom. The reactions proceed via free-radical pathways, in which the halogen first dissociates into a two neutral radical atoms (homolytic fission).

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$

all the way to CCl_4 (carbon tetrachloride)

$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$
$C_2H_4Cl_2 + Cl_2 \rightarrow C_2H_3Cl_3 + HCl$

all the way to C_2Cl_6 (hexachloroethane)

Addition

Main article: Addition reaction

Addition reactions apply to alkenes and alkynes. In this reaction a variety of reagents add "across" the pi-bond(s). Chlorine, hydrogen chloride, water, and hydrogen are illustrative reagents.

Addition polymerization

Main article: Polyolefin

Further information: Addition polymer

Alkenes and some alkynes also undergo polymerization by opening of the multiple bonds to produce polyethylene, polybutylene, and polystyrene. The alkyne acetylene polymerizes to produce polyacetylene. Oligomers (chains of a few monomers) may be produced, for example in the Shell higher olefin process, where α-olefins are extended to make longer α-olefins by adding ethylene repeatedly.

Hydrogenation

Main article: Hydrogenation

Metathesis

Some hydrocarbons undergo *metathesis*, in which substituents attached by C–C bonds are exchanged between molecules. For a single C–C bond it is alkane metathesis, for a double C–C bond it is alkene metathesis (olefin metathesis), and for a triple C–C bond it is alkyne metathesis.

High-temperature reactions

Cracking

Main article: Cracking (chemistry)

Dehydrogenation

Main article: Dehydrogenation

Further information: Steam reforming

Pyrolysis

Main article: Pyrolysis

Combustion

Main article: Combustion

Combustion of hydrocarbons is currently the main source of the world's energy for electric power generation, heating (such as home heating) and transportation.[8][9] Often this energy is used directly as heat such as in home heaters, which use either petroleum or natural gas. The hydrocarbon is burnt and the heat is used to heat water, which is then circulated. A similar principle is used to create electrical energy in power plants.

Common properties of hydrocarbons are the facts that they produce steam, carbon dioxide and heat during combustion and that oxygen is required for combustion to take place. The simplest hydrocarbon, methane, burns as follows:

In inadequate supply of air, carbon black and water vapour are formed:

And finally, for any linear alkane of n carbon atoms,

Partial oxidation characterizes the reactions of alkenes and oxygen. This process is the basis of rancidification and paint drying.

Benzene burns with sooty flame when heated in air:

Origin

Natural oil spring in Korňa, Slovakia

The vast majority of hydrocarbons found on Earth occur in crude oil, petroleum, coal, and natural gas. Since thousands of years they have been exploited and used for a vast range of purposes.[10] Petroleum (lit. 'rock oil') and coal are generally thought to be products of decomposition of organic matter. Coal, in contrast to petroleum, is richer in carbon and poorer in hydrogen. Natural gas is the product of methanogenesis.[11][12]

A seemingly limitless variety of compounds comprise petroleum, hence the necessity of refineries. These hydrocarbons consist of saturated hydrocarbons, aromatic hydrocarbons, or combinations of the two. Missing in petroleum are alkenes and alkynes. Their production requires refineries. Petroleum-derived hydrocarbons are mainly consumed for fuel, but they are also the source of virtually all synthetic organic compounds, including plastics and pharmaceuticals. Natural gas is consumed almost exclusively as fuel. Coal is used as a fuel and as a reducing agent in metallurgy.

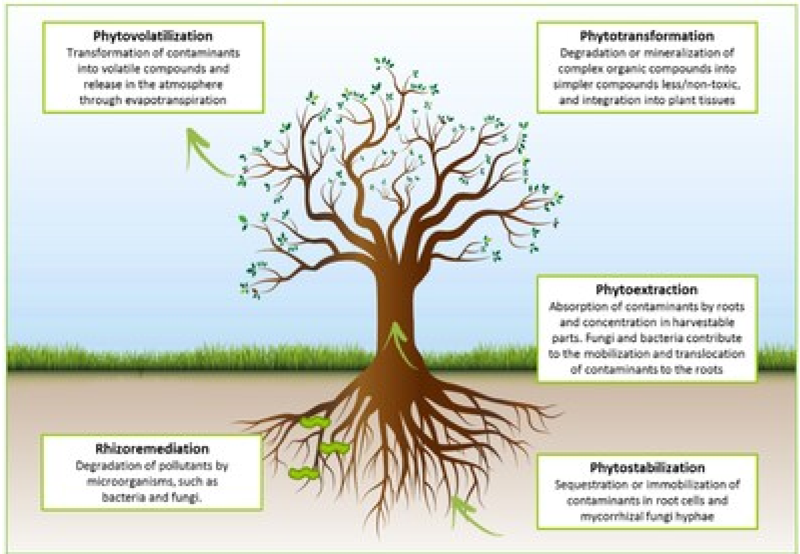
A small fraction of hydrocarbon found on earth, and all currently known hydrocarbon found on other planets and moons, is thought to be abiological.[13]

Hydrocarbons such as ethylene, isoprene, and monoterpenes are emitted by living vegetation.[14]

Some hydrocarbons also are widespread and abundant in the Solar System. Lakes of liquid methane and ethane have been found on Titan, Saturn's largest moon, as confirmed by the *Cassini–Huygens* space probe.[15] Hydrocarbons are also abundant in nebulae forming polycyclic aromatic hydrocarbon compounds.[16]

Environmental impact

Burning hydrocarbons as fuel, which produces carbon dioxide and water, is a major contributor to anthropogenic global warming. Hydrocarbons are introduced into the environment through their extensive use as fuels and chemicals as well as through leaks or accidental spills during exploration, production, refining, or transport of fossil fuels. Anthropogenic hydrocarbon contamination of soil is a serious global issue due to contaminant persistence and the negative impact on human health.[17]



Mechanisms involved in hydrocarbon phytoremediation[18]

When soil is contaminated by hydrocarbons, it can have a significant impact on its microbiological, chemical, and physical properties. This can serve to prevent, slow down or even accelerate the growth of vegetation depending on the exact changes that occur. Crude oil and natural gas are the two largest sources of hydrocarbon contamination of soil.[19]

Bioremediation

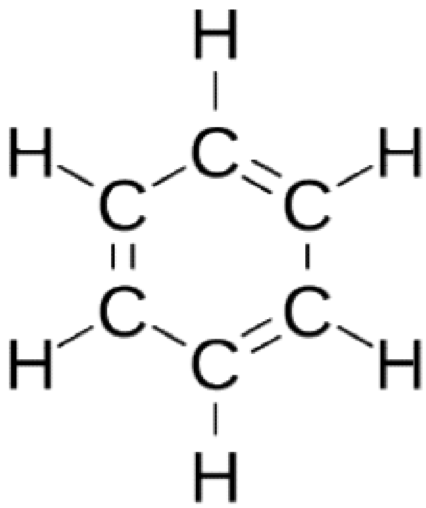
Bioremediation of hydrocarbon from soil or water contaminated is a formidable challenge because of the chemical inertness that characterize hydrocarbons (hence they survived millions of years in the source rock). Nonetheless, many strategies have been devised, bioremediation being prominent. The basic problem with bioremediation is the paucity of enzymes that act on them. Nonetheless, the area has received regular attention.[20] Bacteria in the gabbroic layer of the ocean's crust can degrade hydrocarbons; but the extreme environment makes research difficult.[21] Other bacteria such as *Lutibacterium anuloederans* can also degrade hydrocarbons.[22] Mycoremediation or breaking down of hydrocarbon by mycelium and mushrooms is possible.[23][24]

Safety

Main article: Hydrocarbon poisoning

Hydrocarbons are generally of low toxicity, hence the widespread use of gasoline and related volatile products. Aromatic compounds such as benzene and toluene are narcotic and chronic toxins, and benzene in particular is known to be carcinogenic. Certain rare polycyclic aromatic compounds are carcinogenic. Hydrocarbons are highly flammable.

"Arene" redirects here. For other uses, see Arene (disambiguation).



2D model of a benzene molecule. The carbon "ring" is what makes benzene "aromatic".

Aromatic compounds or **arenes** usually refers to organic compounds "with a chemistry typified by benzene" and "cyclically conjugated."[1] The word "aromatic" originates from the past grouping of molecules based on odor, before their general chemical properties were understood. The current definition of aromatic compounds does not have any relation to their odor. Aromatic compounds are now defined as cyclic compounds satisfying Hückel's Rule. Aromatic compounds have the following general properties:

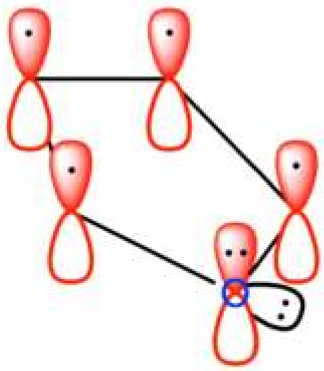
- Typically unreactive
- Often non polar and hydrophobic
- High carbon-hydrogen ratio
- Burn with a strong sooty yellow flame, due to high C:H ratio
- Undergo electrophilic substitution reactions and nucleophilic aromatic substitutions[2]

Arenes are typically split into two categories - benzoids, that contain a benzene derivative and follow the benzene ring model, and non-benzoids that contain other aromatic cyclic derivatives. Aromatic compounds are commonly used in organic synthesis and are involved in many reaction types, following both additions and removals, as well as saturation and dearomatization.

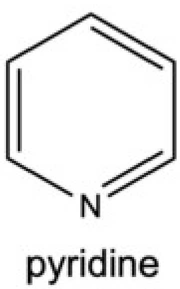
Heteroarenes

[edit]

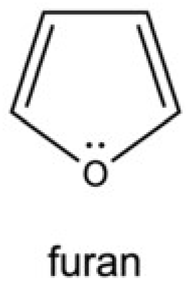
Heteroarenes are aromatic compounds, where at least one methine or vinylene (-C= or -CH=CH-) group is replaced by a heteroatom: oxygen, nitrogen, or sulfur.[3] Examples of non-benzene compounds with aromatic properties are furan, a heterocyclic compound with a five-membered ring that includes a single oxygen atom, and pyridine, a heterocyclic compound with a six-membered ring containing one nitrogen atom. Hydrocarbons without an aromatic ring are called aliphatic. Approximately half of compounds known in the year 2000 are described as aromatic to some extent.[4]



Electron flow through p orbitals for the heterocycle furan[5]



Line bond structure of the heterocycle pyridine[5]



Line bond structure of the heterocycle furan[5]

Applications

[edit]

Aromatic compounds are pervasive in nature and industry. Key industrial aromatic hydrocarbons are benzene, toluene, Xylene called BTX. Many biomolecules have phenyl groups including the so-called aromatic amino acids.

Benzene ring model

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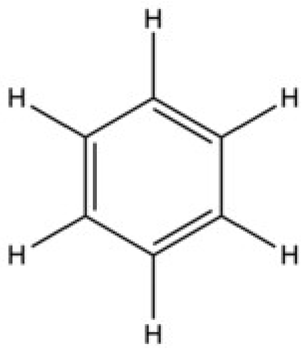
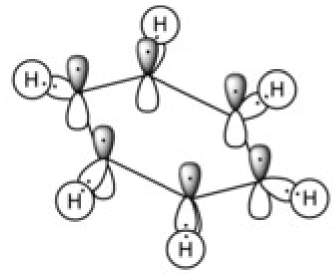
Main article: Aromaticity



Line bond structure of benzene[5] 

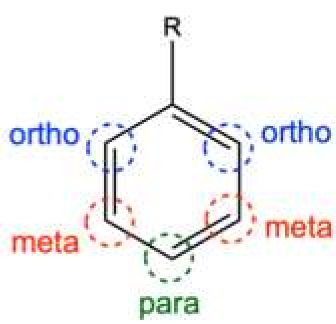
Electron flow through p orbitals showing the aromatic nature of benzene[5]

Benzene, C_6H_6, is the least complex aromatic hydrocarbon, and it was the first one defined as such.[6] Its bonding nature was first recognized independently by Joseph Loschmidt and August Kekulé in the 19th century.[6] Each carbon atom in the hexagonal cycle has four electrons to share. One electron forms a sigma bond with the hydrogen atom, and one is used in covalently bonding to each of the two neighboring carbons. This leaves six electrons, shared equally around the ring in delocalized pi molecular orbitals the size of the ring itself.[5] This represents the equivalent nature of the six carbon-carbon bonds all of bond order 1.5. This equivalency can also explained by resonance forms.[5] The electrons are visualized as floating above and below the ring, with the electromagnetic fields they generate acting to keep the ring flat.[5]

The circle symbol for aromaticity was introduced by Sir Robert Robinson and his student James Armit in 1925 and popularized starting in 1959 by the Morrison & Boyd textbook on organic chemistry.[7] The proper use of the symbol is debated: some publications use it to *any* cyclic π system, while others use it only for those π systems that obey Hückel's rule. Some argue that, in order to stay in line with Robinson's originally intended proposal, the use of the circle symbol should be limited to monocyclic 6 π-electron systems.[8] In this way the circle symbol for a six-center six-electron bond can be compared to the Y symbol for a three-center two-electron bond.[8]

Benzene and derivatives of benzene

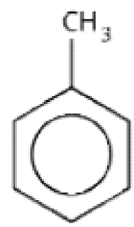
[edit]



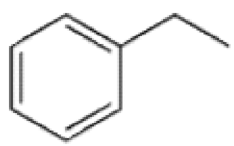
Substitution nomenclature of benzene[5]

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.[9] When reacting to form more complex benzene derivatives, the substituents on a benzene ring can be described as either activated or deactivated, which are electron donating and electron withdrawing respectively.[9] Activators are known as ortho-para directors, and deactivators are known as meta directors.[9] Upon reacting, substituents will be added at the ortho, para or meta positions, depending on the directivity of the current substituents to make more complex benzene derivatives, often with several isomers. Electron flow leading to re-aromatization is key in ensuring the stability of such products.[9]

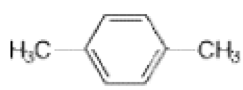
For example, three isomers exist for cresol because the methyl group and the hydroxyl group (both ortho para directors) can be placed next to each other (*ortho*), one position removed from each other (*meta*), or two positions removed from each other (*para*).[10] Given that both the methyl and hydroxyl group are ortho-para directors, the ortho and para isomers are typically favoured.[10] Xylenol has two methyl groups in addition to the hydroxyl group, and, for this structure, 6 isomers exist.[*citation needed*]

- **Representative arene compounds**
  - 

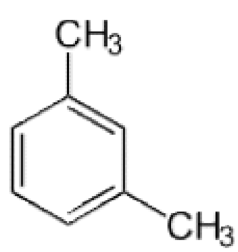
Toluene

  - 

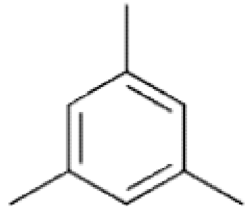
Ethylbenzene

  - 

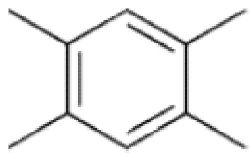
p-Xylene

  - 

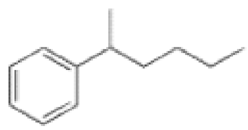
m-Xylene

- 

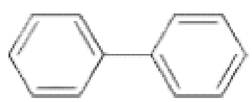
Mesitylene

- 

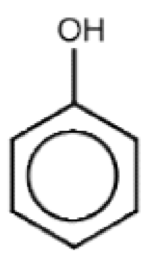
Durene

- 

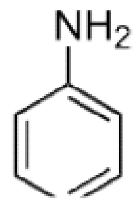
2-Phenylhexane

- 

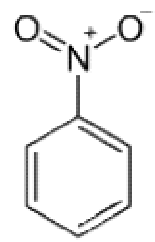
Biphenyl

- 

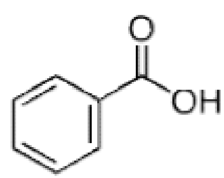
Phenol

- 

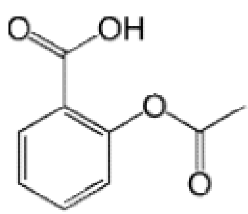
Aniline

- 

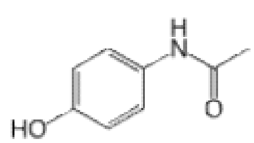
Nitrobenzene

- 

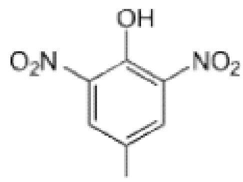
Benzoic acid

- 

Aspirin

- 

Paracetamol

- 

Picric acid

Arene rings can stabilize charges, as seen in, for example, phenol (C_6H_5–OH), which is acidic at the hydroxyl (OH), as charge on the oxygen (alkoxide $–O^-$) is partially delocalized into the benzene ring.

Non-benzylic arenes

[edit]

Although benzylic arenes are common, non-benzylic compounds are also exceedingly important. Any compound containing a cyclic portion that conforms to Hückel's rule and is not a benzene derivative can be considered a non-benzylic aromatic compound.[5]

Monocyclic arenes

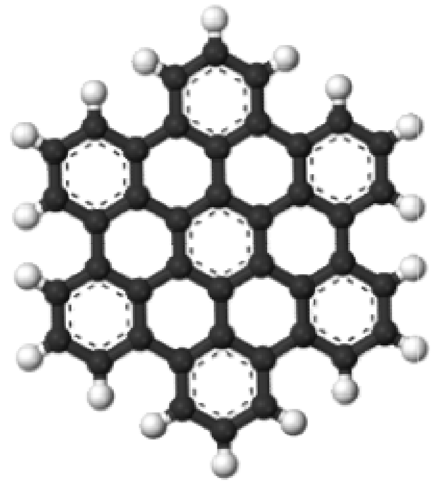
[edit]

Of annulenes larger than benzene, [12]annulene and [14]annulene are weakly aromatic compounds and [18]annulene, Cyclooctadecanonaene, is aromatic, though strain within the structure causes a slight deviation from the precisely planar structure necessary for aromatic categorization.[11] Another example of a non-benzylic monocyclic arene is the cyclopropenyl (cyclopropenium cation), which satisfies Hückel's rule with an n equal to 0.[12] Note, only the cationic form of this cyclic propenyl is aromatic, given that neutrality in this compound would violate either the octet rule or Hückel's rule.[12]

Other non-benzylic monocyclic arenes include the aforementioned heteroarenes that can replace carbon atoms with other heteroatoms such as N, O or S.[5] Common examples of these are the six-membered pyrrole and five-membered pyridine, both of which have a substituted nitrogen[13]

Polycyclic aromatic hydrocarbons

[edit]

 Hexabenzocoronene is a large polycyclic aromatic hydrocarbon.

Main article: Polycyclic aromatic hydrocarbon

Polycyclic aromatic hydrocarbons, also known as polynuclear aromatic compounds (PAHs) are aromatic hydrocarbons that consist of fused aromatic rings and do not contain heteroatoms or carry substituents.[14] Naphthalene is the simplest example of a PAH. PAHs occur in oil, coal, and tar deposits, and are produced as byproducts of fuel burning (whether fossil fuel or biomass).[15] As pollutants, they are of concern because some compounds have been identified as carcinogenic, mutagenic, and teratogenic.[16][17][18][19] PAHs are also found in cooked foods.[15] Studies have shown that high levels of PAHs are found, for example, in meat cooked at high temperatures such as grilling or barbecuing, and in smoked fish.[15][16] They are also a good candidate molecule to act as a basis for the earliest forms of life.[20] In graphene the PAH motif is extended to large 2D sheets.[21]

Reactions

[edit]

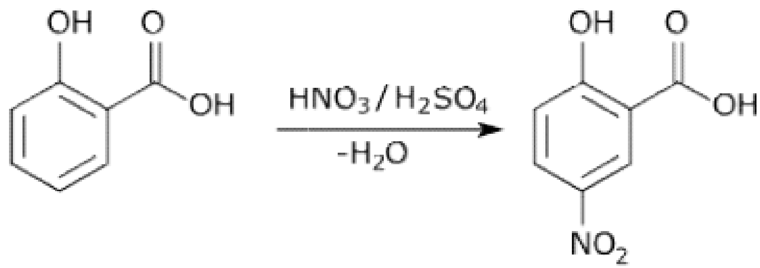
Aromatic ring systems participate in many organic reactions.

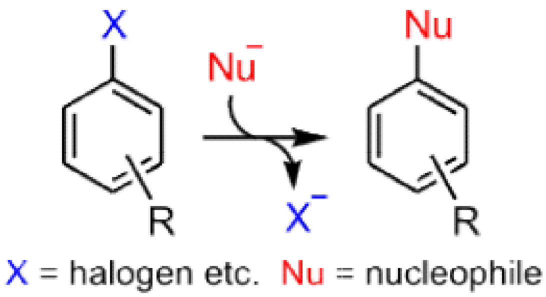
Substitution

[edit]

In aromatic substitution, one substituent on the arene ring, usually hydrogen, is replaced by another reagent.[5] 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.[22][23]

An example of electrophilic aromatic substitution is the nitration of salicylic acid, where a nitro group is added para to the hydroxide substituent:



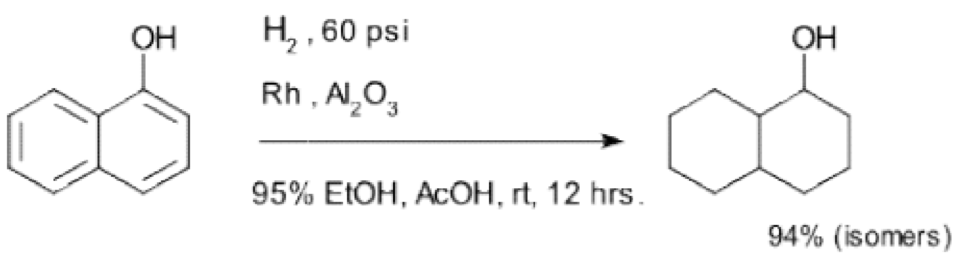


[Nucleophilic aromatic substitution](#) involves displacement of a leaving group, such as a halide, on an aromatic ring. Aromatic rings usually nucleophilic, but in the presence of electron-withdrawing groups aromatic compounds undergo nucleophilic substitution. Mechanistically, this reaction differs from a common S_N2 reaction, because it occurs at a trigonal carbon atom (sp^2 hybridization).[24]

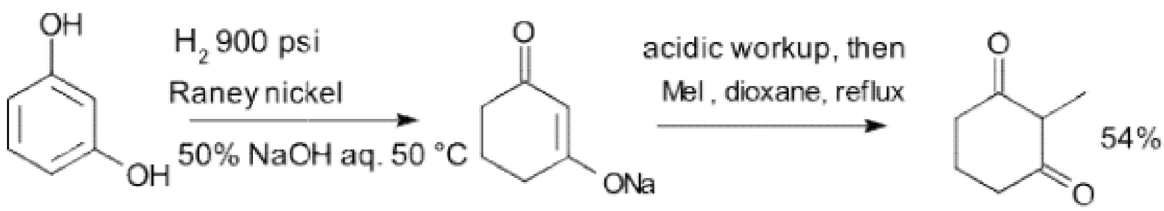
Hydrogenation

[edit]

Hydrogenation of arenes create saturated rings. The compound 1-naphthol is completely reduced to a mixture of decalin-ol isomers.[25]



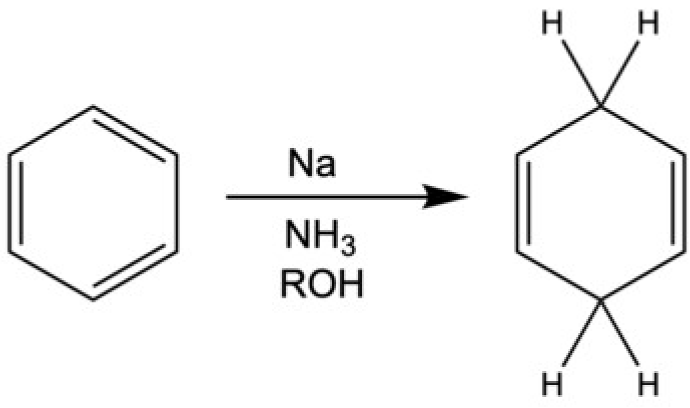
The compound resorcinol, hydrogenated with Raney nickel in presence of aqueous sodium hydroxide forms an enolate which is alkylated with methyl iodide to 2-methyl-1,3-cyclohexandione:[26]



Dearomatization

[edit]

In dearomatization reactions the aromaticity of the reactant is lost. In this regard, the dearomatization is related to hydrogenation. A classic approach is Birch reduction. The methodology is used in synthesis.[27]



Dearomatization of benzene through the Birch reduction[28]