PHA284

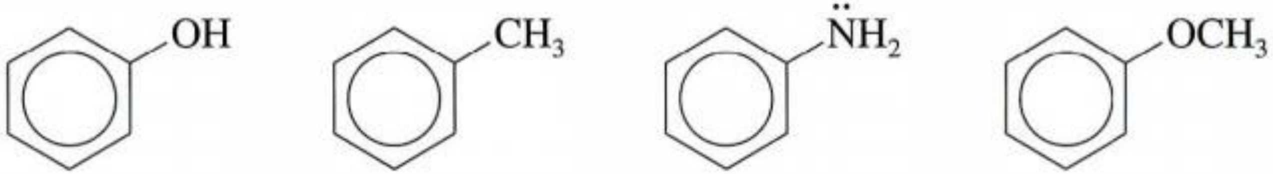
Organic Chemistry II

Ankara University
Faculty of Pharmacy
Department of Pharmaceutical Chemistry

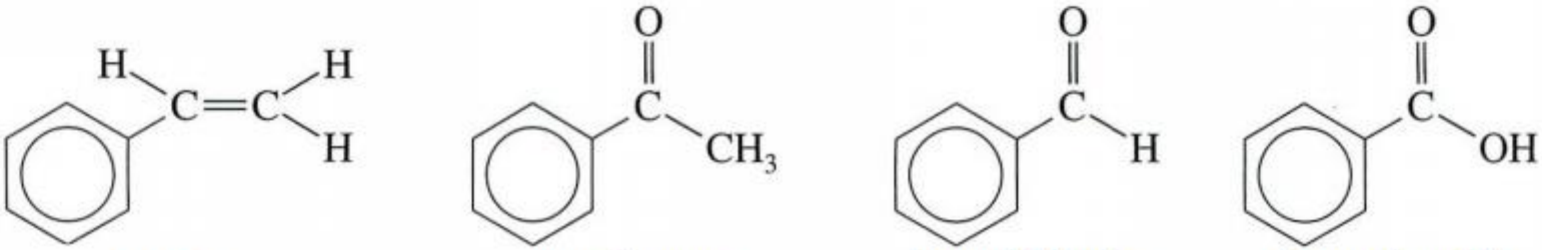
Nomenclature of Aromatic Compounds

Nomenclature

The following compounds are usually called by their historical common names, and almost never by the systematic IUPAC names:



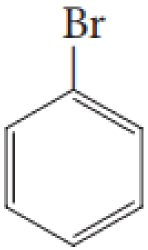
common name: phenol (benzenol) toluene (methylbenzene) aniline (benzenamine) anisole (methoxybenzene)



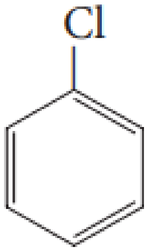
common name: styrene (vinylbenzene) acetophenone (methyl phenyl ketone) benzaldehyde benzoic acid

Nomenclature

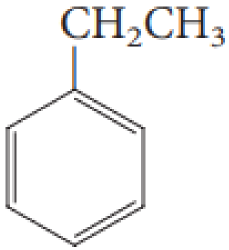
- Monosubstituted benzenes, that do not have common names accepted by IUPAC, are named as derivatives of benzene.



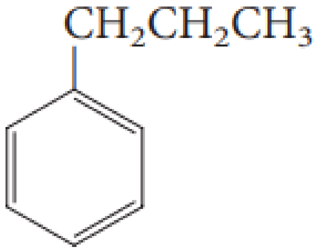
bromobenzene



chlorobenzene



ethylbenzene

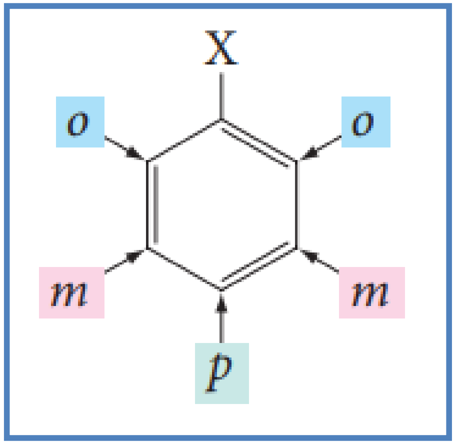


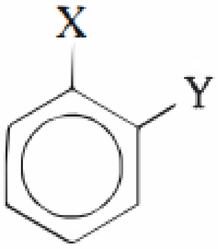
propylbenzene

Nomenclature

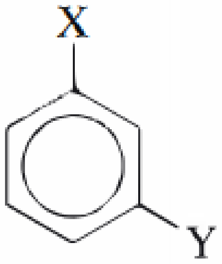
Disubstituted benzenes are named using the prefixes **ortho-, meta-,** and **para-** to specify the substitution patterns.

These terms are abbreviated ***o-, m-,*** and ***p-***.

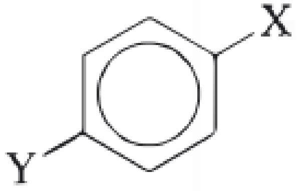




1,2 or ortho

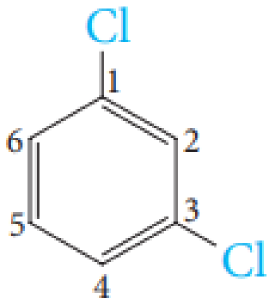


1,3 or meta

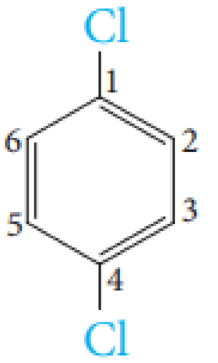


1,4 or para

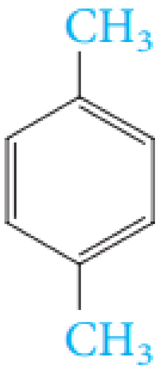
Nomenclature



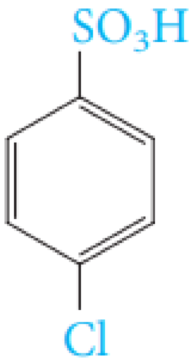
meta-dichlorobenzene



para-dichlorobenzene



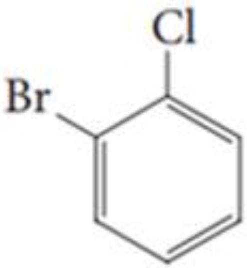
para-xylene



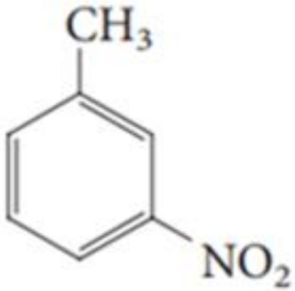
para-chlorobenzenesulfonic acid

Nomenclature

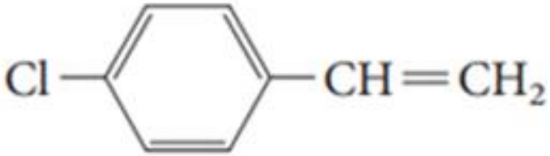
- The prefixes ortho-, meta-, and para- are used even when the two substituents are not identical.



o-bromochlorobenzene
(note alphabetical order)



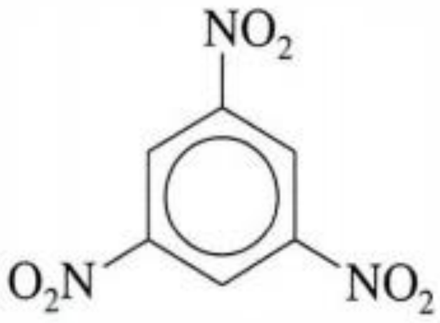
m-nitrotoluene



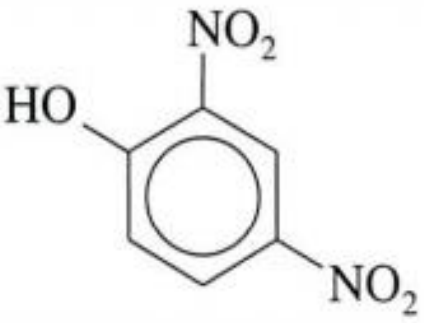
p-chlorostyrene

Nomenclature

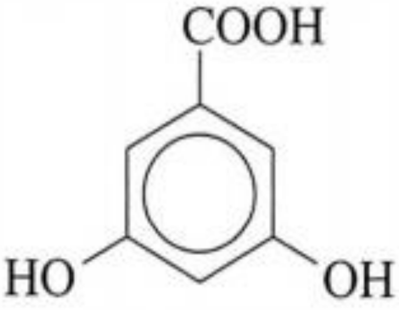
- With three or more substituents on the benzene ring, numbers are used to indicate their positions.



1,3,5-trinitrobenzene



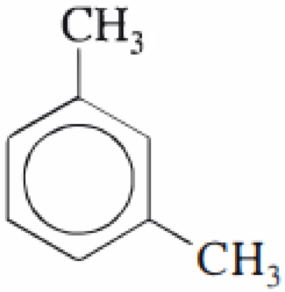
2,4-dinitrophenol

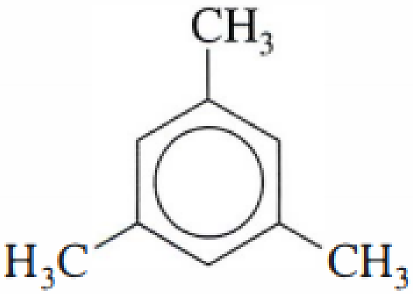


3,5-dihydroxybenzoic acid

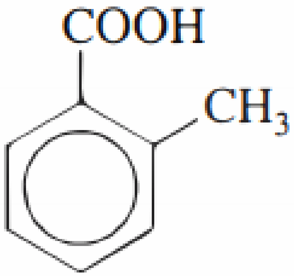
Nomenclature

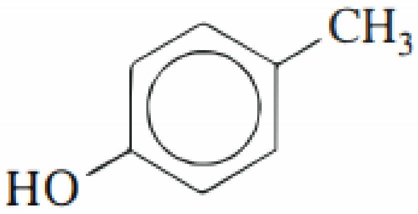
- Many disubstituted benzenes (and polysubstituted benzenes) have historical names.





common name:	*m*-xylene	mesitylene
IUPAC name:	1,3-dimethylbenzene	1,3,5-trimethylbenzene



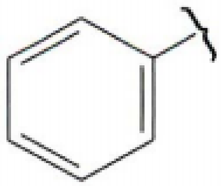


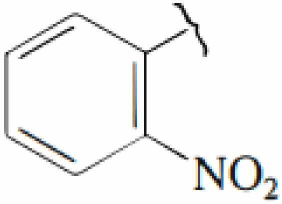
common name:	*o*-toluic acid	*p*-cresol
IUPAC name:	2-methylbenzoic acid	4-methylphenol

Nomenclature

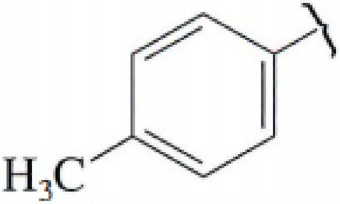
An **aryl group**, abbreviated **Ar**, is the aromatic group that remains after the removal of a hydrogen atom from an aromatic ring. The phenyl group, **Ph**, is the simplest aryl group.

Examples of aryl groups

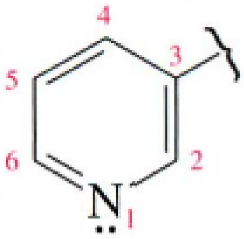

the phenyl group



the *o*-nitrophenyl group



the *p*-tolyl group



the 3-pyridyl group

Examples of the use of a generic aryl group

$\mathrm{Ar{-}MgBr}$
an arylmagnesium bromide

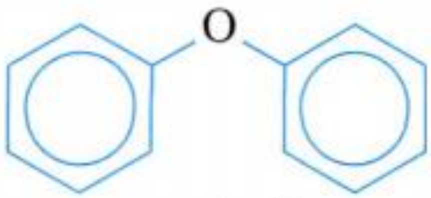
$\mathrm{Ar_2O}$ or $\mathrm{Ar{-}O{-}Ar'}$
a diaryl ether

$\mathrm{Ar{-}NH_2}$
an arylamine

$\mathrm{Ar{-}SO_3H}$
an arylsulfonic acid

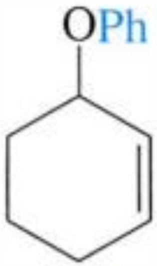
Nomenclature

- The phenyl group is used in the name just like the name of an alkyl group, and it is often abbreviated «**Ph**» in drawing a complex structure.



or Ph_2O

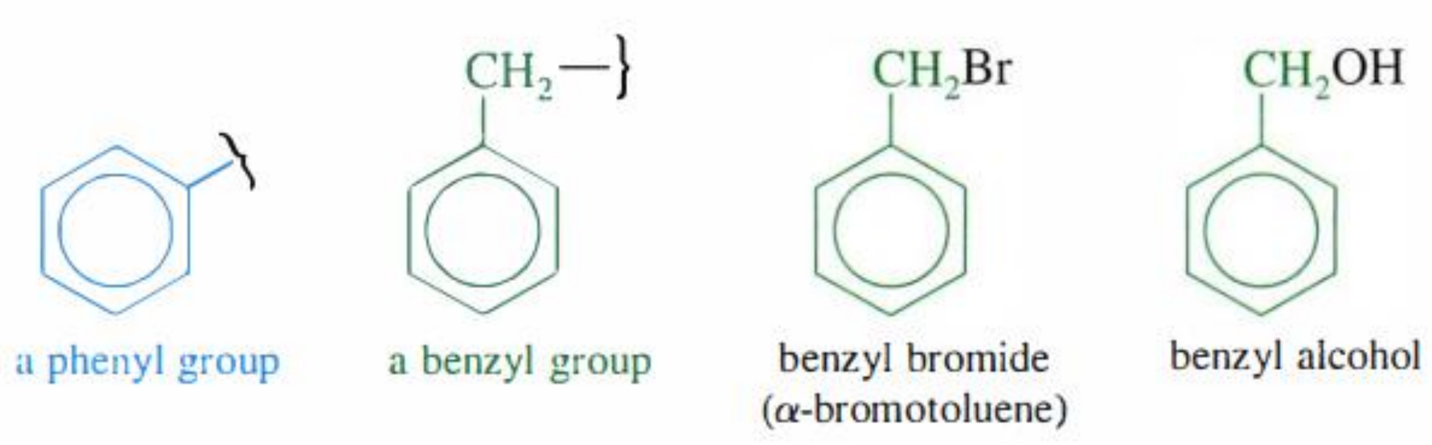
diphenyl ether

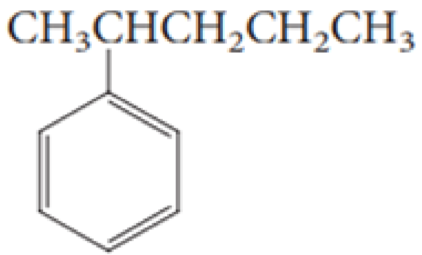


3-phenoxycyclohexene

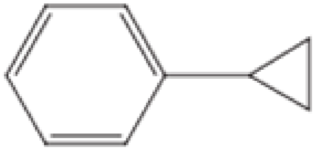
Nomenclature

- The seven-carbon unit consisting of a benzene ring and a methylene (-CH_2) group is often named as a benzyl group.

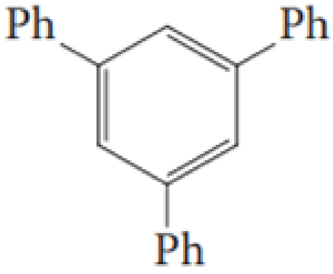




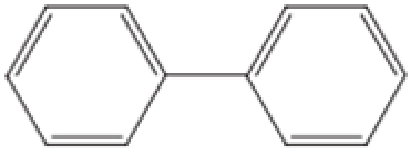
2-phenylpentane
(or 2-pentylbenzene)



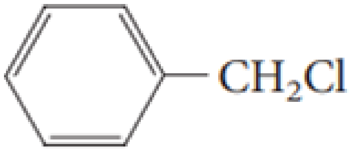
phenylcyclopropane
(or cyclopropylbenzene)



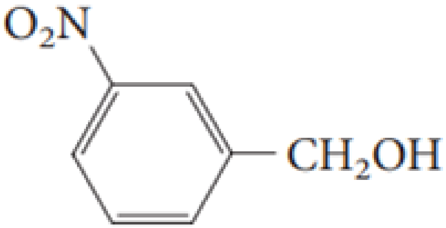
1,3,5-triphenylbenzene



biphenyl



benzyl chloride

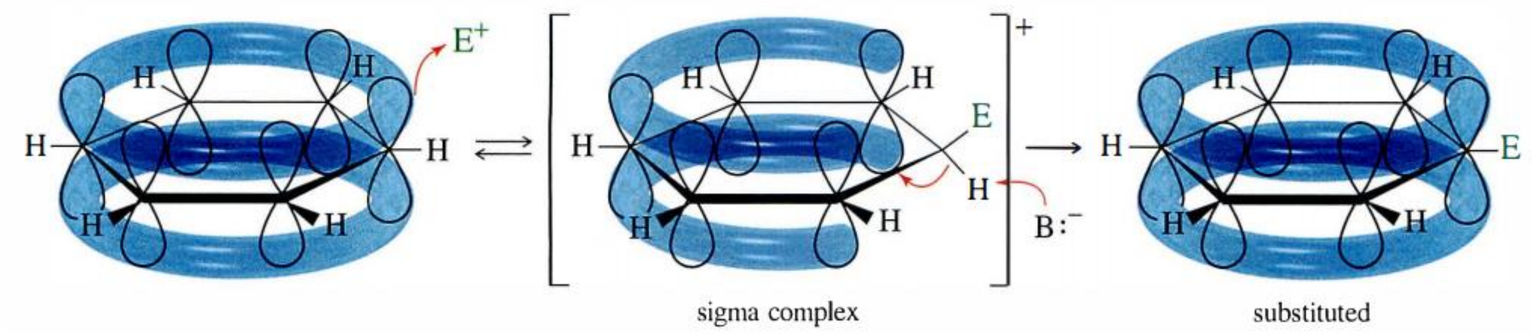


m-nitrobenzyl alcohol

Reactions of Aromatic Compounds

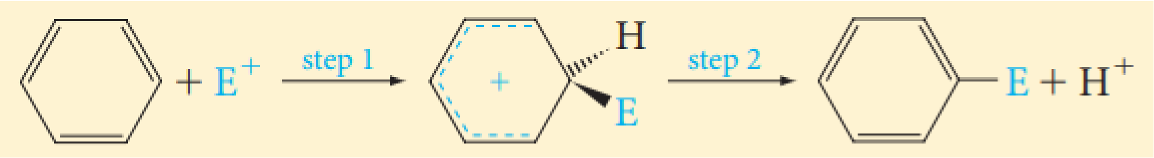
Electrophilic Aromatic Substitution

Like an alkene, benzene has clouds of pi electrons above and below its sigma bond framework. Although benzene's pi electrons are in a stable aromatic system, they are available to attack a strong electrophile to give a carbocation.

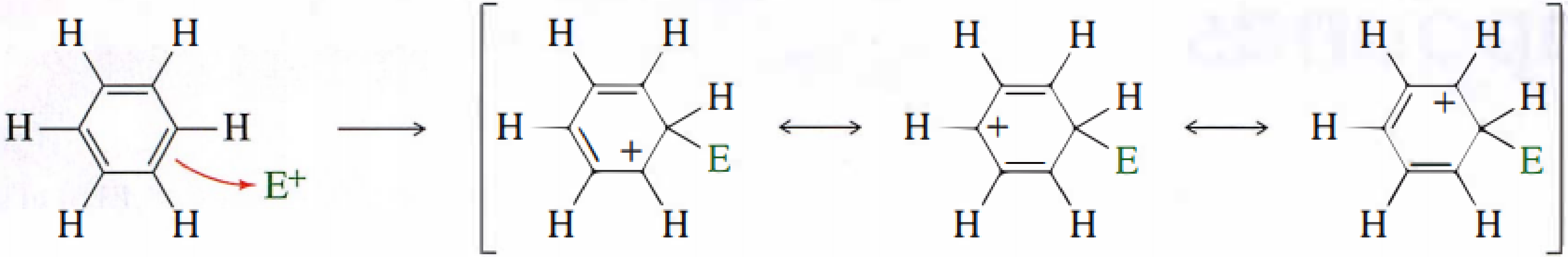


The overall reaction is the substitution of an electrophile (E^+) for a proton (H^+) on the aromatic ring: **electrophilic aromatic substitution**.

Electrophilic Aromatic Substitution

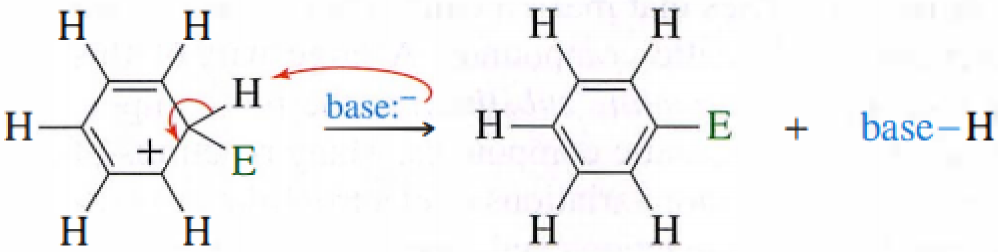


Step 1: Attack on the electrophile forms the sigma complex.



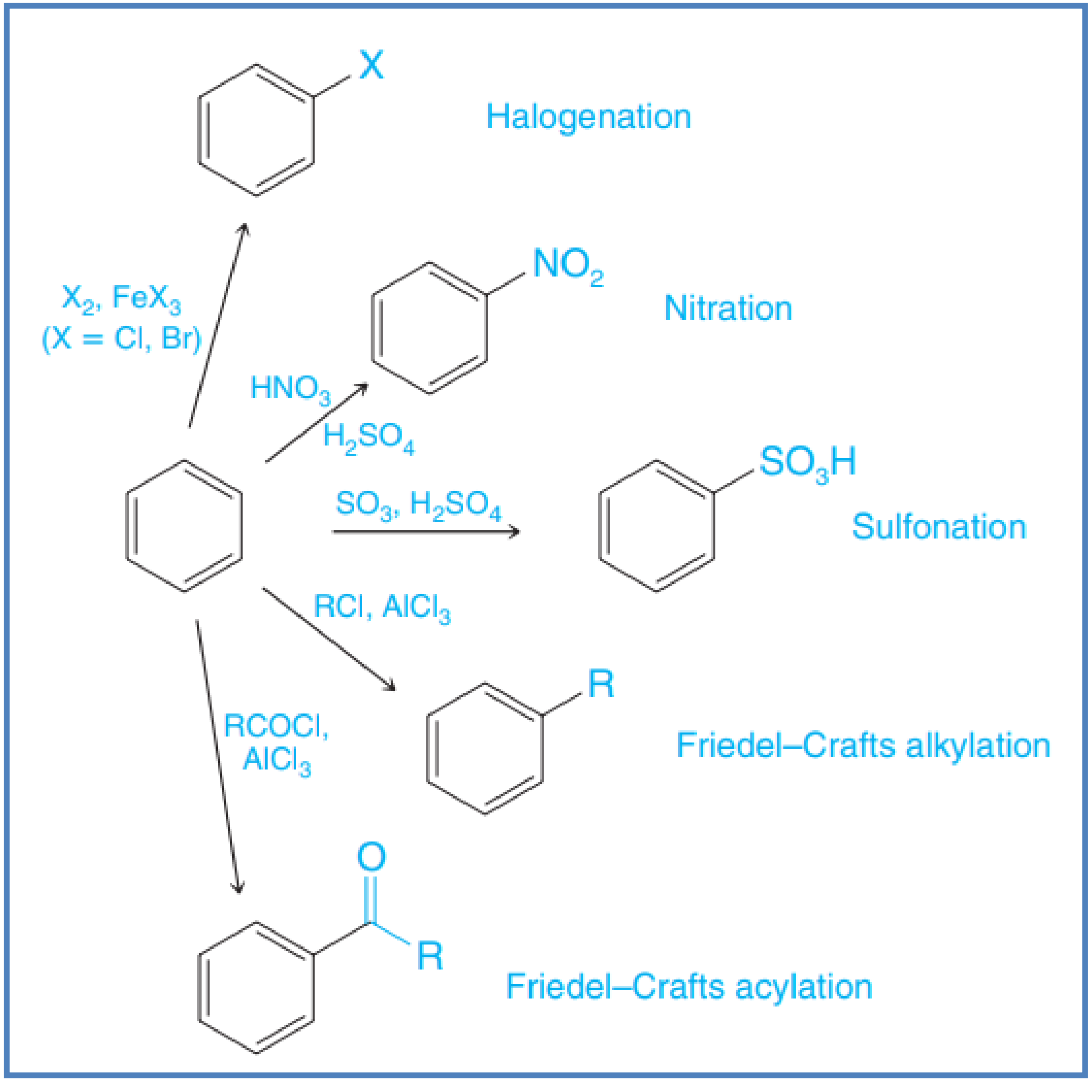
sigma complex (arenium ion)

Step 2: Loss of a proton regains aromaticity and gives the substitution product.



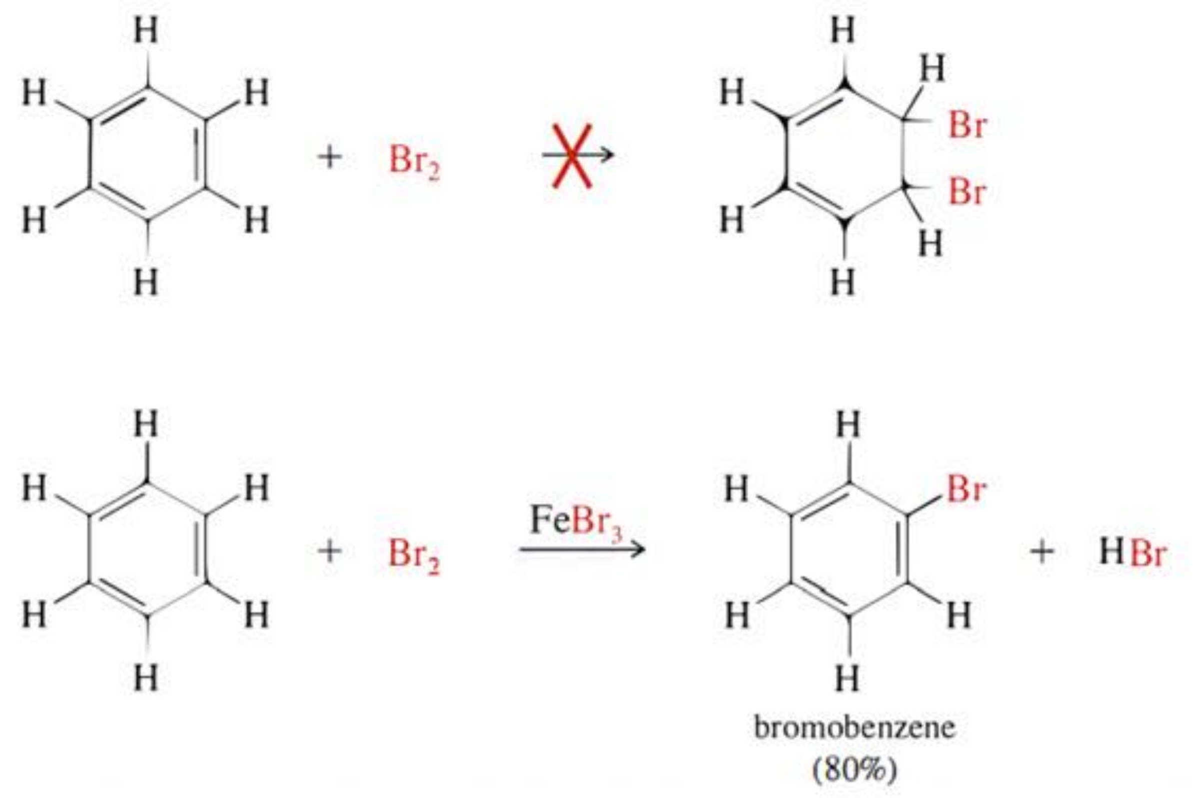
Electrophilic Aromatic Substitution

Electrophilic aromatic substitutions



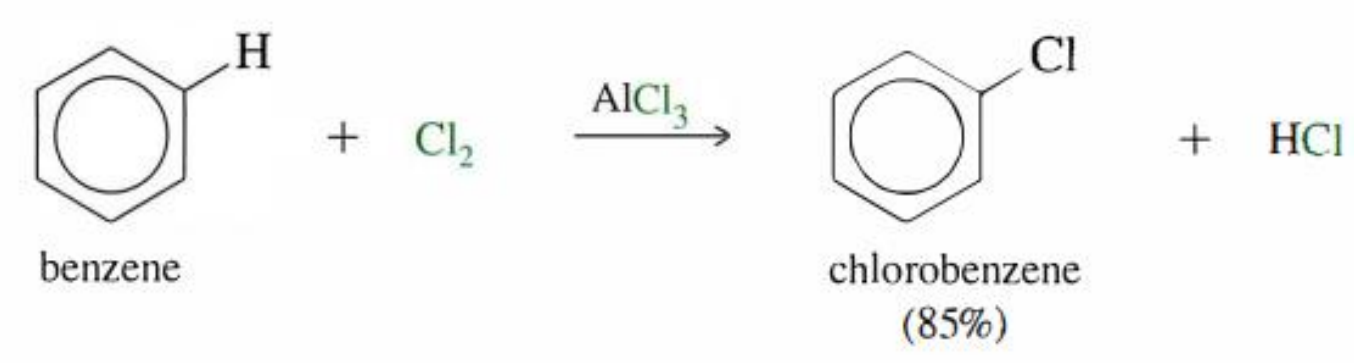
1) Halogenation of Benzene

Bromination of Benzene:

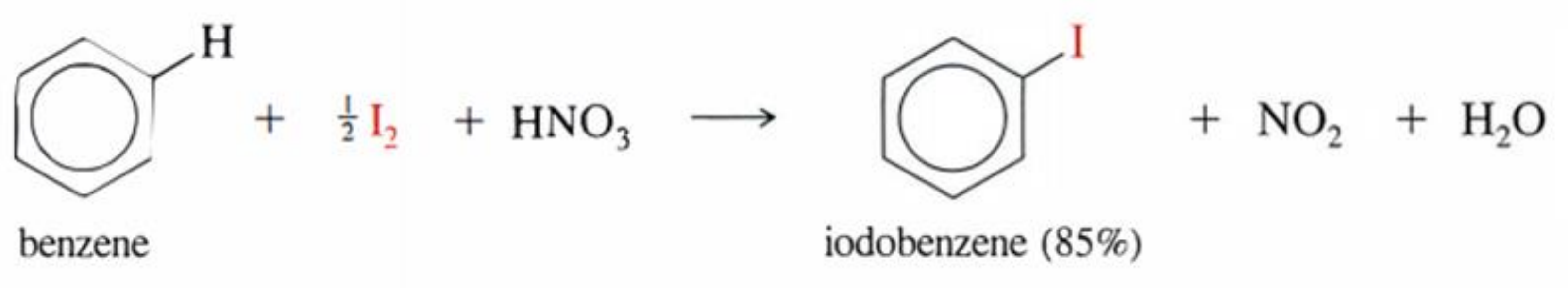


Chlorination of Benzene

Chlorination of benzene works much like bromination, except that aluminum chloride ($AlCl_3$) is most often used as the Lewis acid catalyst.

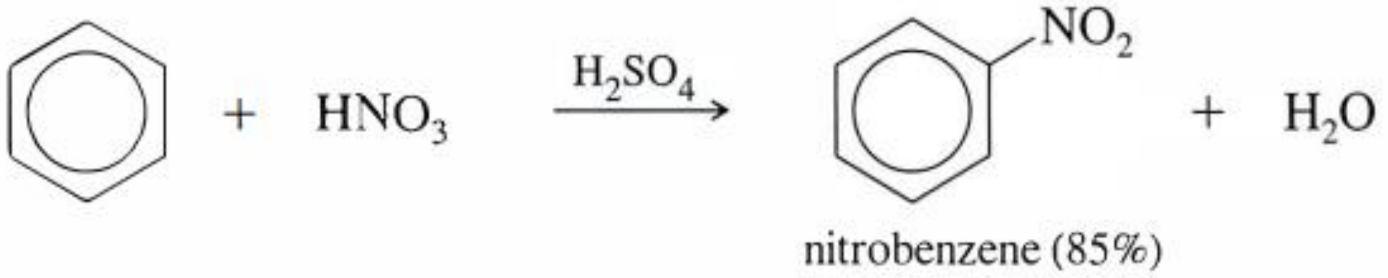


Iodination of Benzene



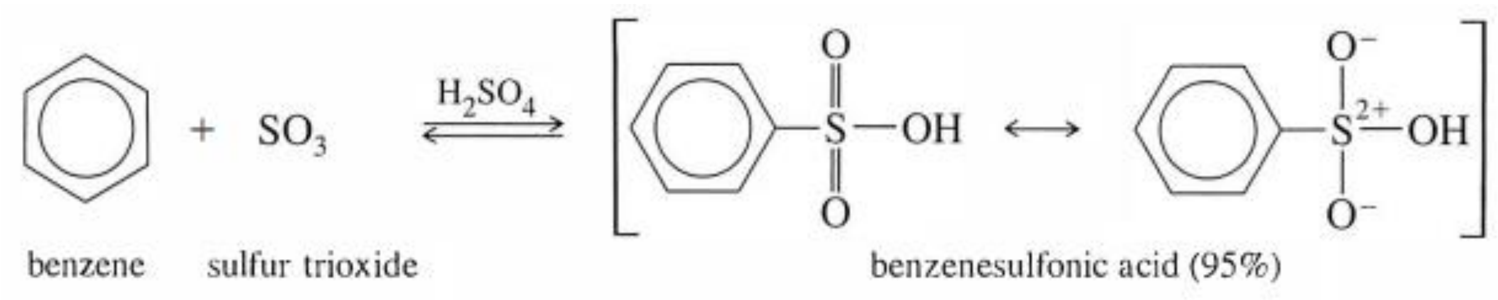
2) Nitration of Benzene

Benzene reacts with hot, concentrated nitric acid to give nitrobenzene. A safer and more convenient procedure uses a **mixture of nitric acid and sulfuric acid**.

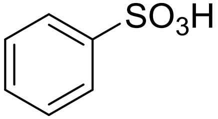


3) Sulfonation of Benzene

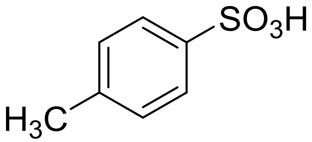
Arylsulfonic acids (general formula Ar-$S0_3H$) are easily synthesized by sulfonation of benzene derivatives, an electrophilic aromatic substitution using sulfur trioxide ($S0_3$) as the electrophile.



Arylsulfonic acids



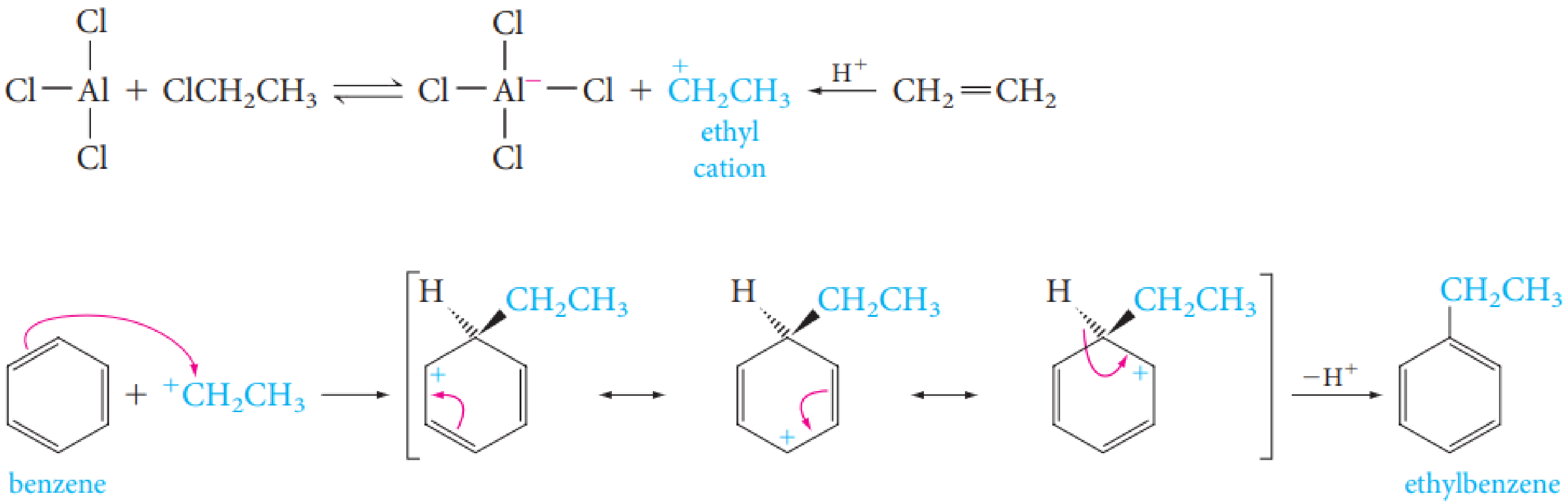
benzenesulfonic acid



4-methylbenzenesulfonic acid
p-Toluenesulphonic acid
4-Toluenesulfonic acid
p-TsOH

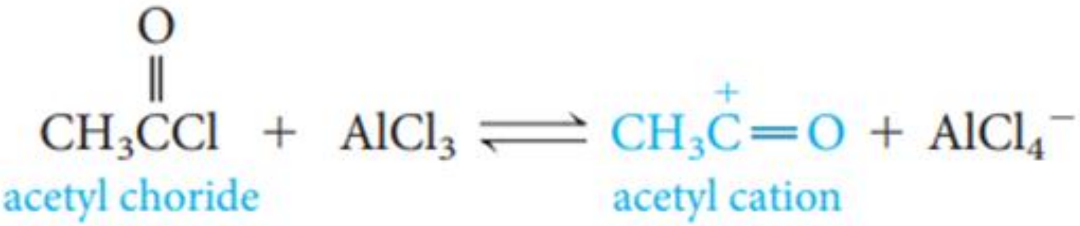
4) Alkylation and Acylation

- Alkylation of aromatic compounds is referred to as the Friedel– Crafts reaction, after Charles Friedel (French) and James Mason Crafts (American), who first discovered the reaction in 1877.

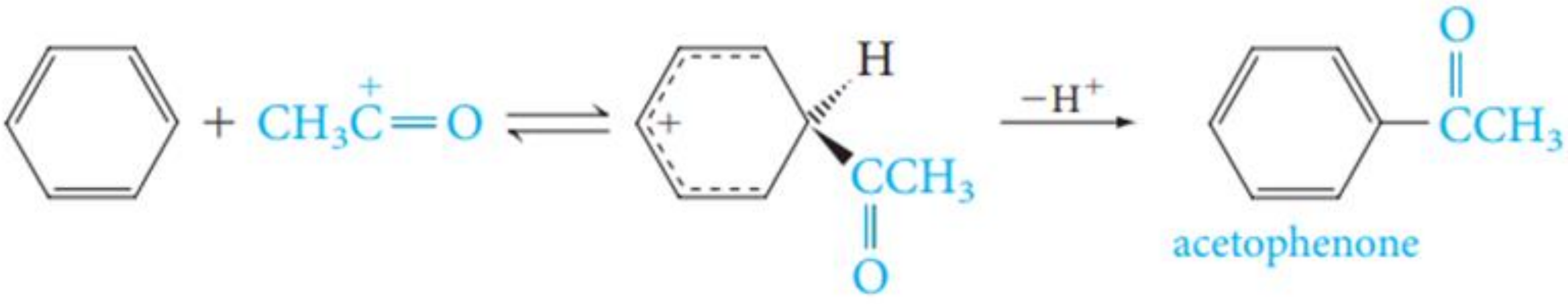


Friedel–Crafts Acylation

- Friedel–Crafts acylations occur similarly. The electrophile is an acyl cation generated from an acid derivative, usually an acyl halide.



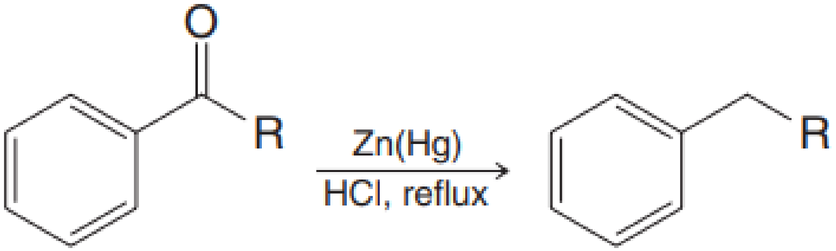
$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}Cl} + \mathrm{AlCl_3} \rightleftharpoons \mathrm{CH_3\overset{+}{C}{=}O} + \mathrm{AlCl_4^-}$$



The Clemmensen Reduction

One general method for reducing a ketone to a methylene group—called the Clemmensen reduction.

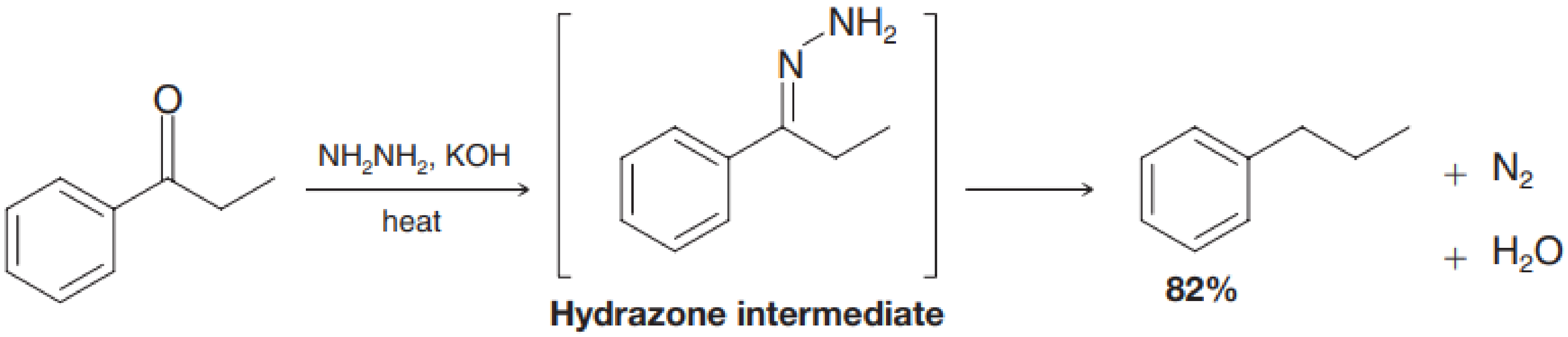
In general,



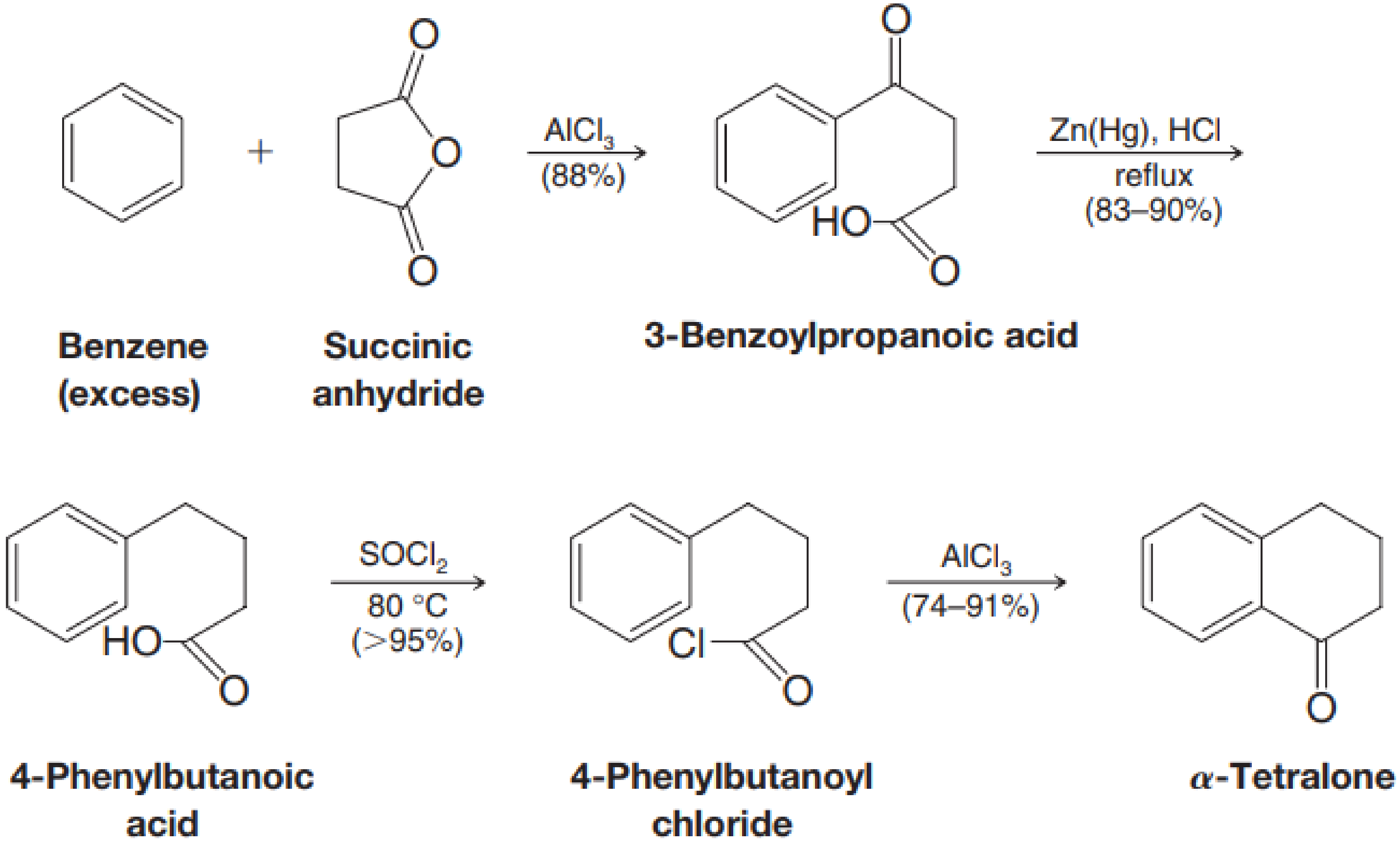
The Wolff–Kishner Reduction

Another method for reducing a ketone to a methylene group is the Wolff–Kishner reduction.

Ethyl phenyl ketone can be reduced to propylbenzene by the Wolff–Kishner reduction as follows:

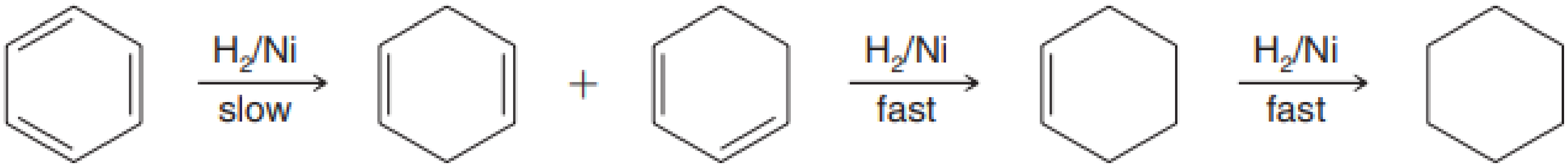


Synthetic application;



Reduction of Aromatic Compounds

- Hydrogenation of benzene under pressure using a metal catalyst such as nickel results in the addition of three molar equivalents of hydrogen and the formation of cyclohexane.

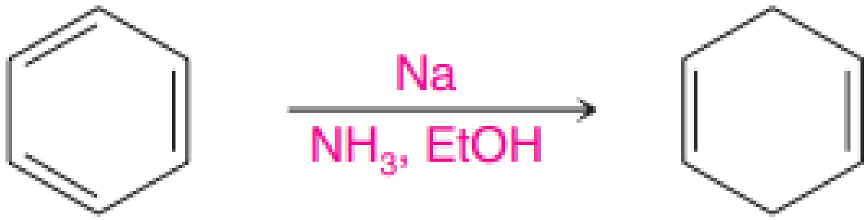


Benzene **Cyclohexadienes** **Cyclohexene** **Cyclohexane**

Reduction of Aromatic Compounds

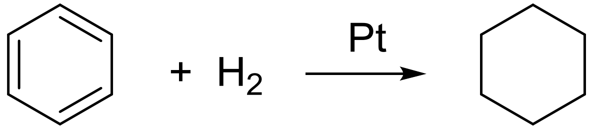
Birch reduction

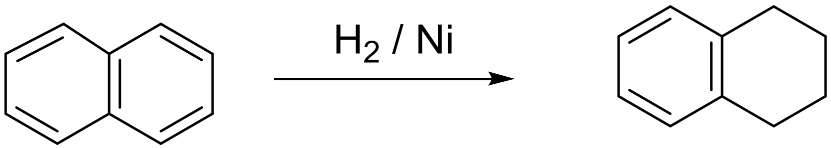
- Benzene can be reduced to 1,4-cyclohexadiene.
- This reaction is called the Birch reduction, after A. J. Birch, the Australian chemist who developed it.



Benzene **1,4-Cyclohexadiene**

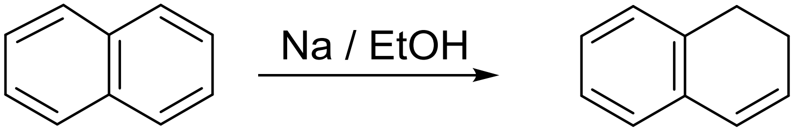
Reduction of Aromatic Compounds





naphthalene

1,2,3,4-tetrahydronaphthalene



1,2-dihydronaphthalene

References

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