Organic Chemistry

Benzene and Aromatic compounds (2)

by

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Expected Outcomes

In the completion of this chapter, student will have the ability to:

- Compare and identify aromatic, antiaromatic and nonaromatic compounds

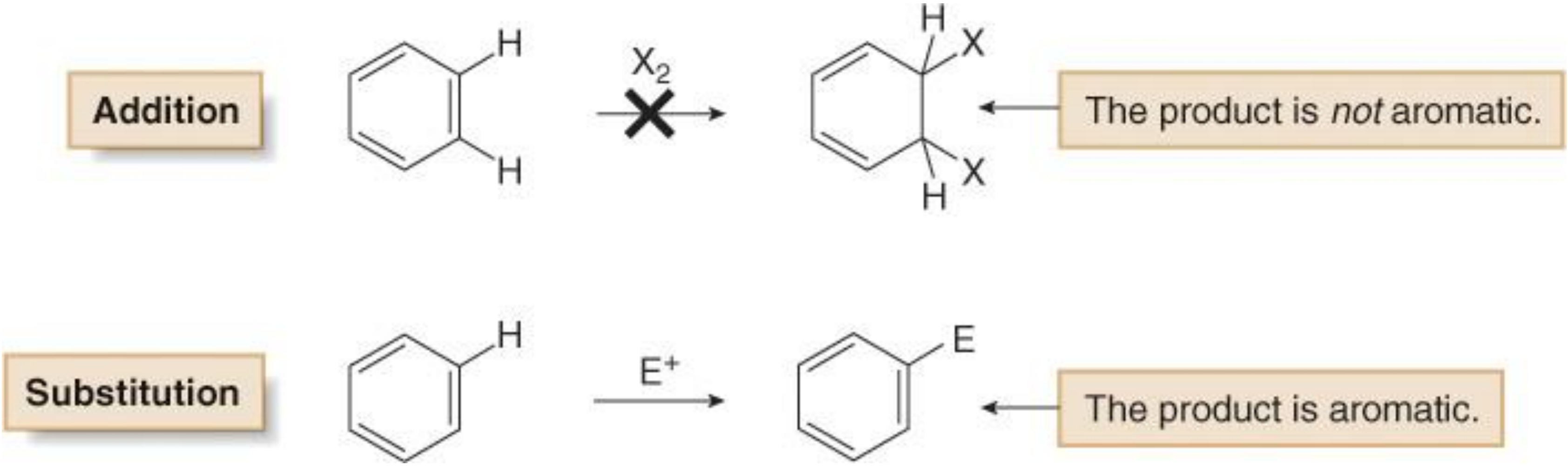
Contents

- Benzene structure
- Nomenclature
- Huckel's rule

Electrophilic Aromatic Substitution

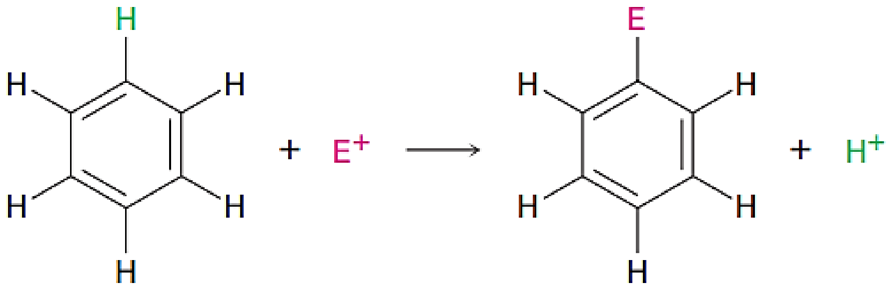
Background

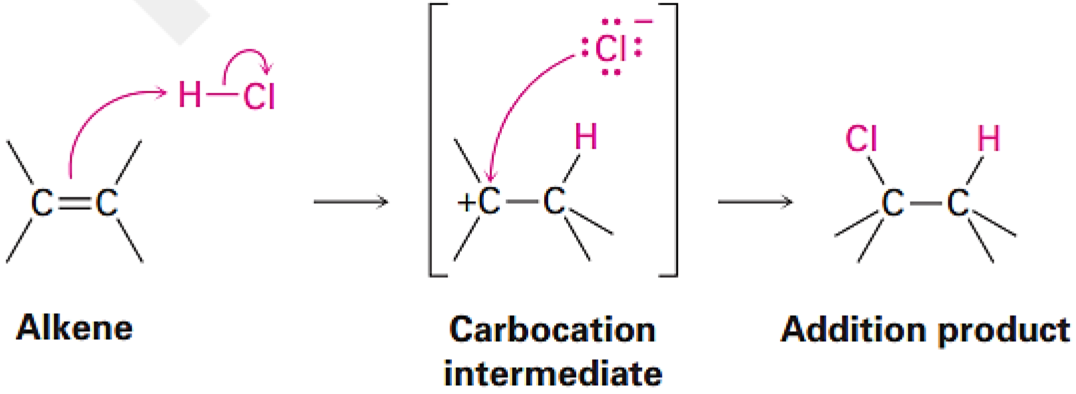
- Benzene does not undergo addition reactions like other unsaturated hydrocarbons, because addition would yield a product that is not aromatic.
- Substitution of a hydrogen keeps the aromatic ring intact.
- There are five main examples of electrophilic aromatic substitution.



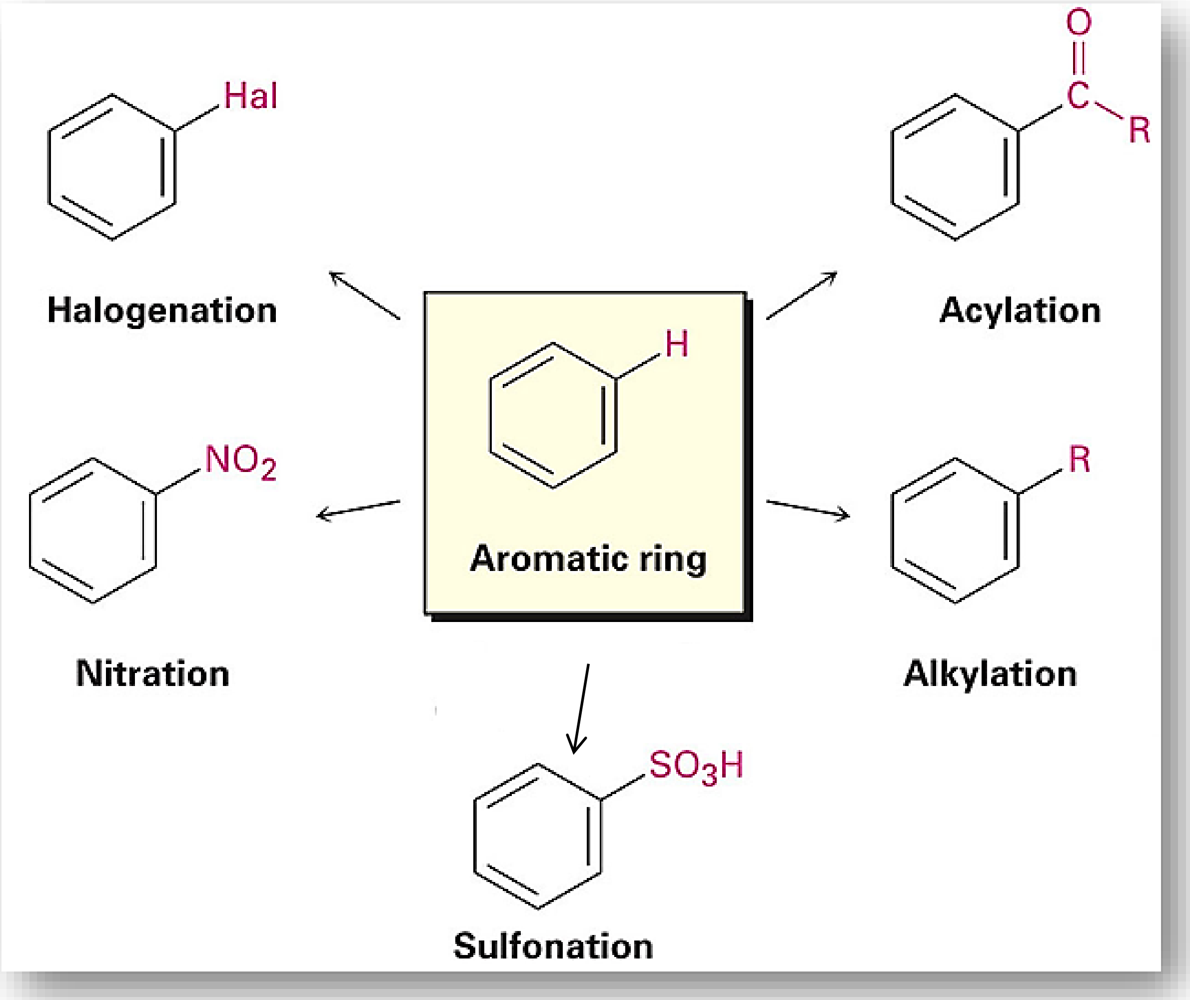
Reactions of Aromatic Compounds: Electrophilic Substitution

The most common reaction of aromatic compounds is **electrophilic aromatic substitution**, a process in which an electrophile (E^+) reacts with an aromatic ring and substitutes for one of the hydrogens:

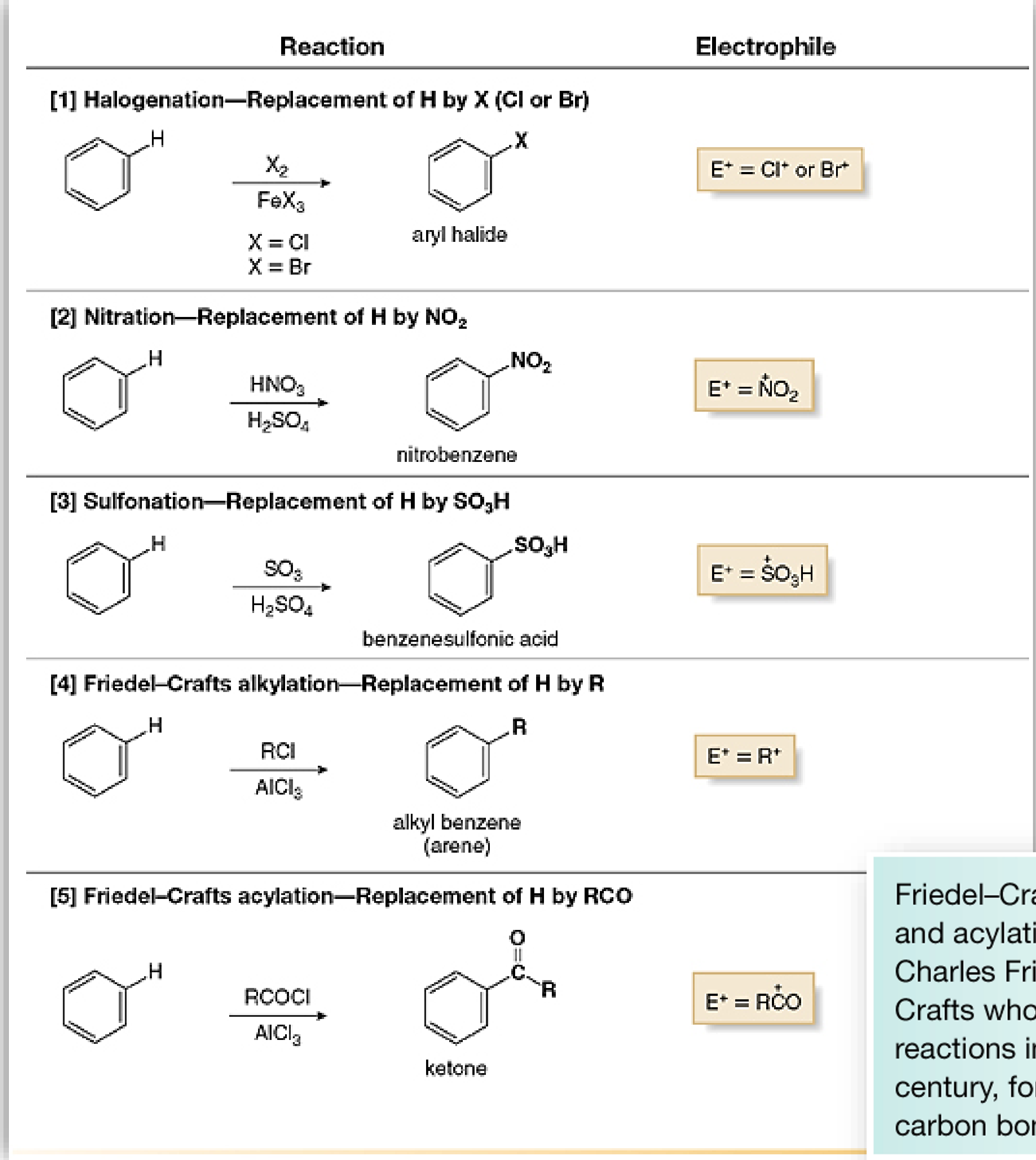




Electrophilic Aromatic substitution



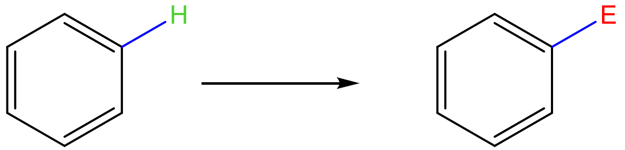
Five examples of electrophilic aromatic substitution



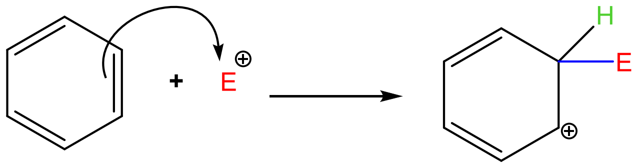
Reaction			Electrophile
[1] Halogenation—Replacement of H by X (Cl or Br)			
H	$\xrightarrow[FeX_3]{X_2}$ X = Cl X = Br	X aryl halide	$E^+ = Cl^+$ or Br^+
[2] Nitration—Replacement of H by NO_2			
H	$\xrightarrow[H_2SO_4]{HNO_3}$	NO_2 nitrobenzene	$E^+ = \overset{+}{N}O_2$
[3] Sulfonation—Replacement of H by SO_3H			
H	$\xrightarrow[H_2SO_4]{SO_3}$	SO_3H benzenesulfonic acid	$E^+ = \overset{+}{S}O_3H$
[4] Friedel–Crafts alkylation—Replacement of H by R			
H	$\xrightarrow[AlCl_3]{RCl}$	R alkyl benzene (arene)	$E^+ = R^+$
[5] Friedel–Crafts acylation—Replacement of H by RCO			
H	$\xrightarrow[AlCl_3]{RCOCl}$	O, C, R ketone	$E^+ = R\overset{+}{C}O$

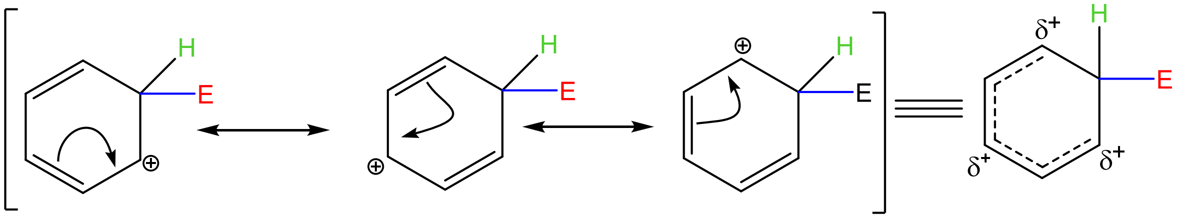
Friedel–Crafts alkylation and acylation, named for Charles Friedel and James Crafts who discovered the reactions in the nineteenth century, form new carbon–carbon bonds.

General Mechanism of Electrophilc Substitution Reaction



1- Addition of the elcrtophile ($E^{\oplus}$) to form a carbocation

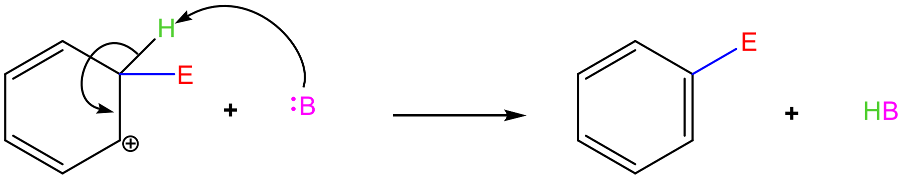




(Resonance-stablized carbocation)

(Hybrid)

2- Loss of a proton to re-form the aromatic ring



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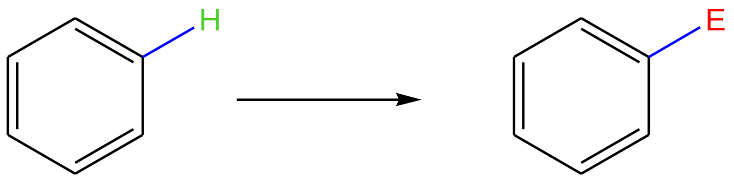
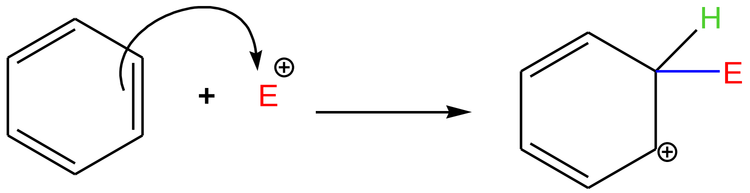
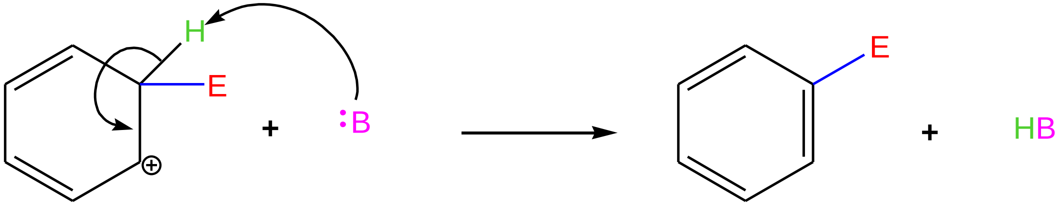


1- Addition of the elcrtophile ($\overset{\oplus}{E}$) to form a carbocation



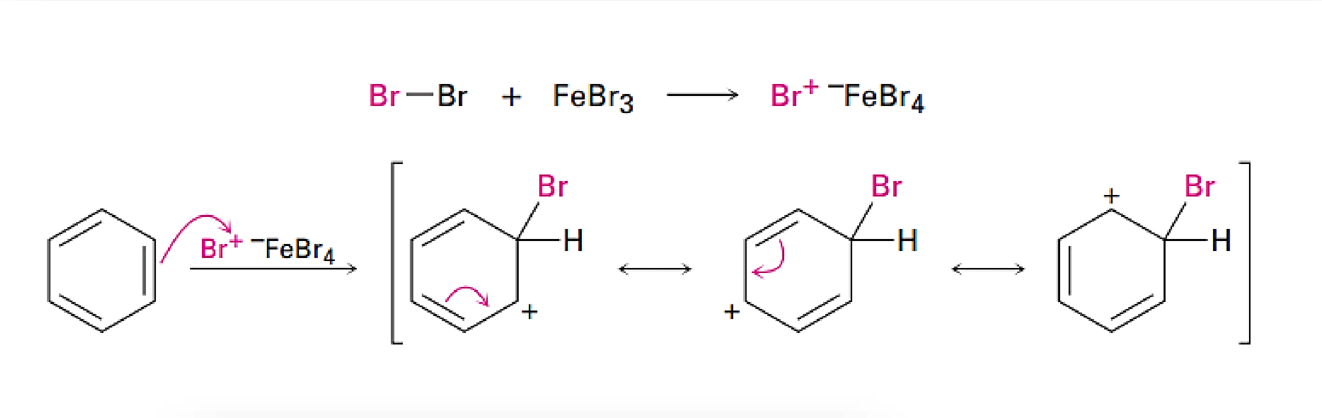
2- Loss of a proton to re-form the aromatic ring



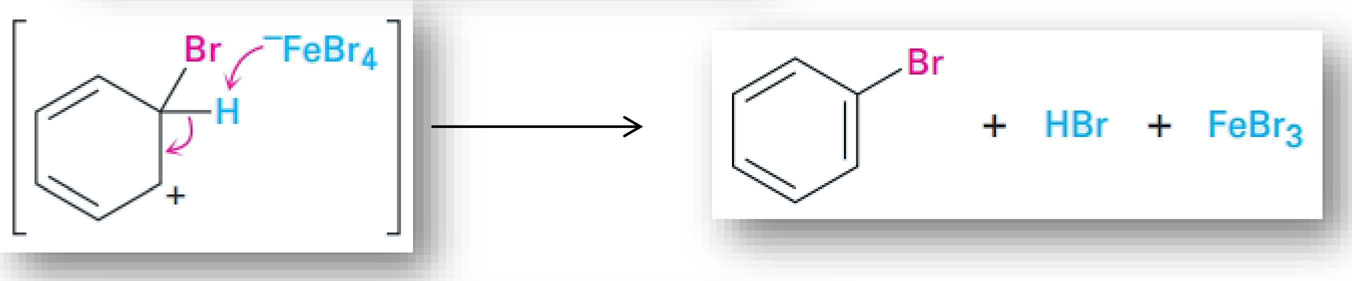
Halogenation of Benzene

- Benzene's π electrons participate as a Lewis base in reactions with Lewis acids
  - **Lewis acid:** **electron pair acceptor**
  - **Lewis base:** **electron pair donor**
- The product is formed by loss of a proton, which is replaced by a halogen

Bromination Reaction

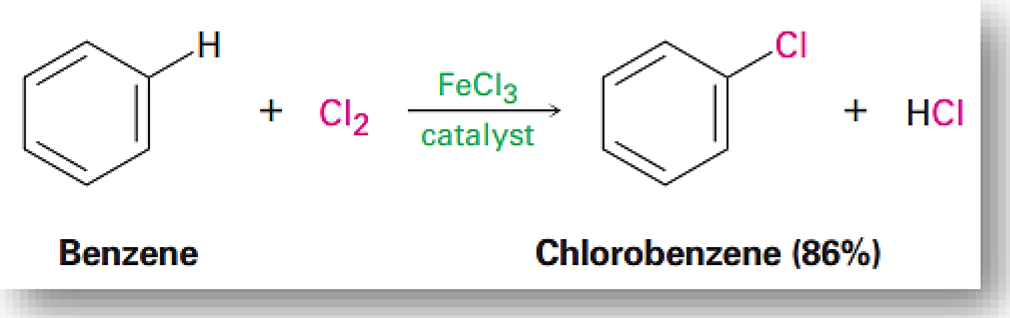


An electron pair from the benzene ring attacks the positively polarized bromine, forming a new C–Br bond and leaving a nonaromatic carbocation intermediate.

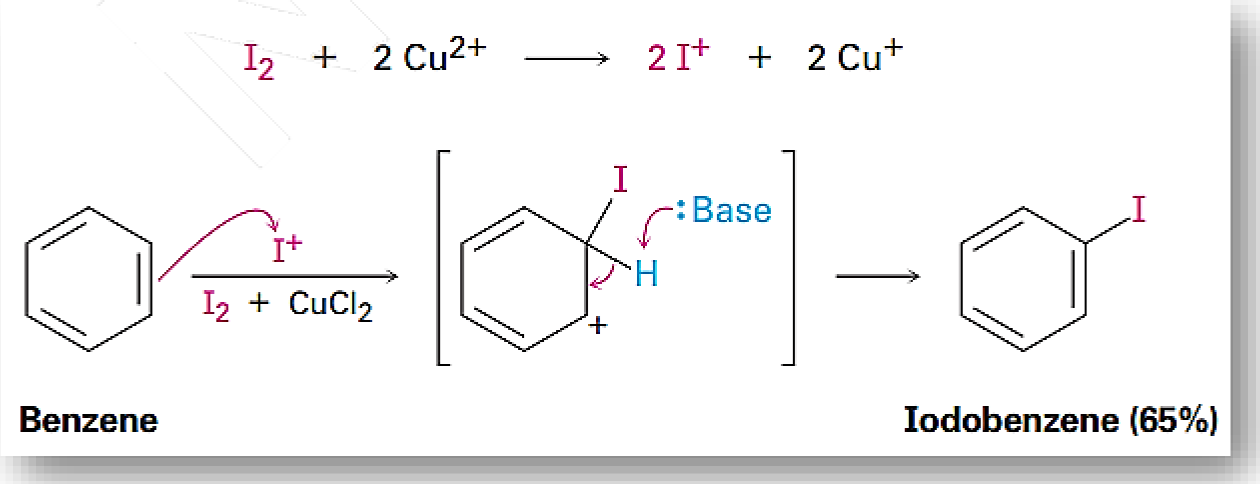


A base removes H^+ from the carbocation intermediate, and the neutral substitution product forms as two electrons from the C–H bond move to re-form the aromatic ring.

Chlorination Reaction



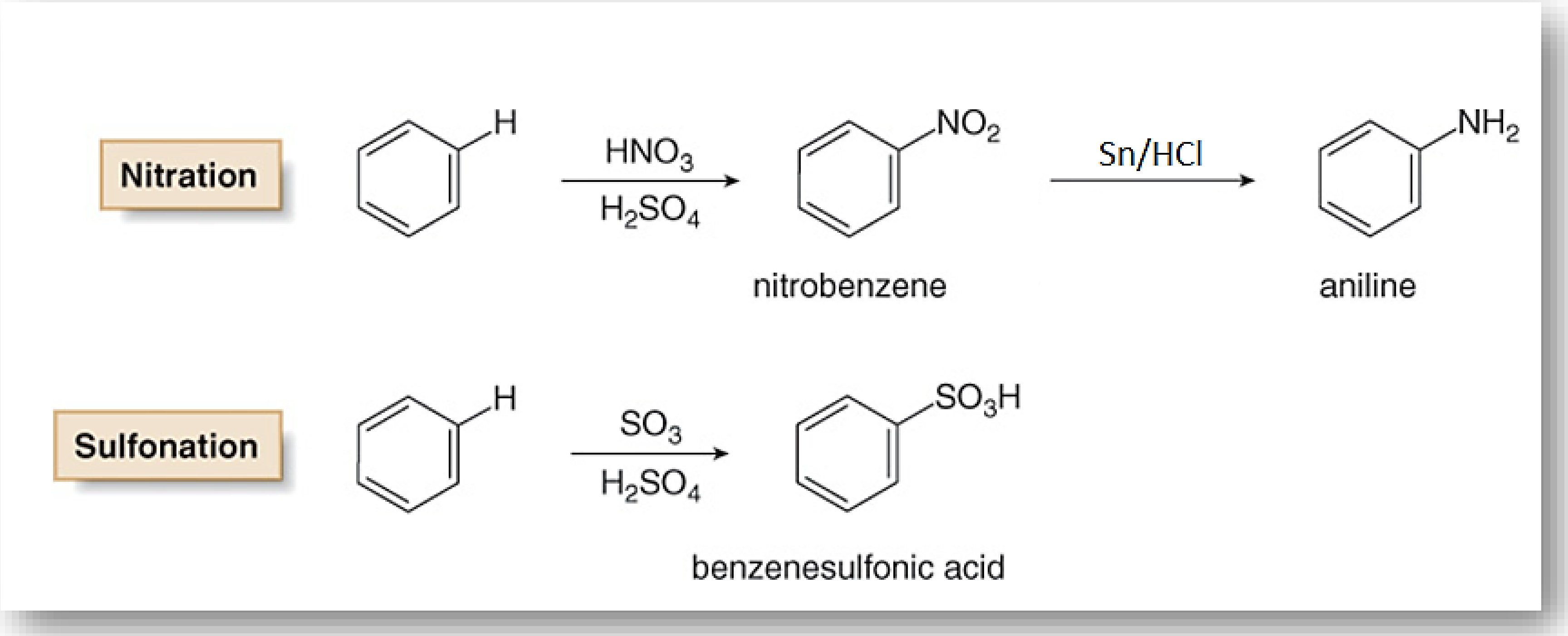
Iodination Reaction



Electrophilic Aromatic Substitution

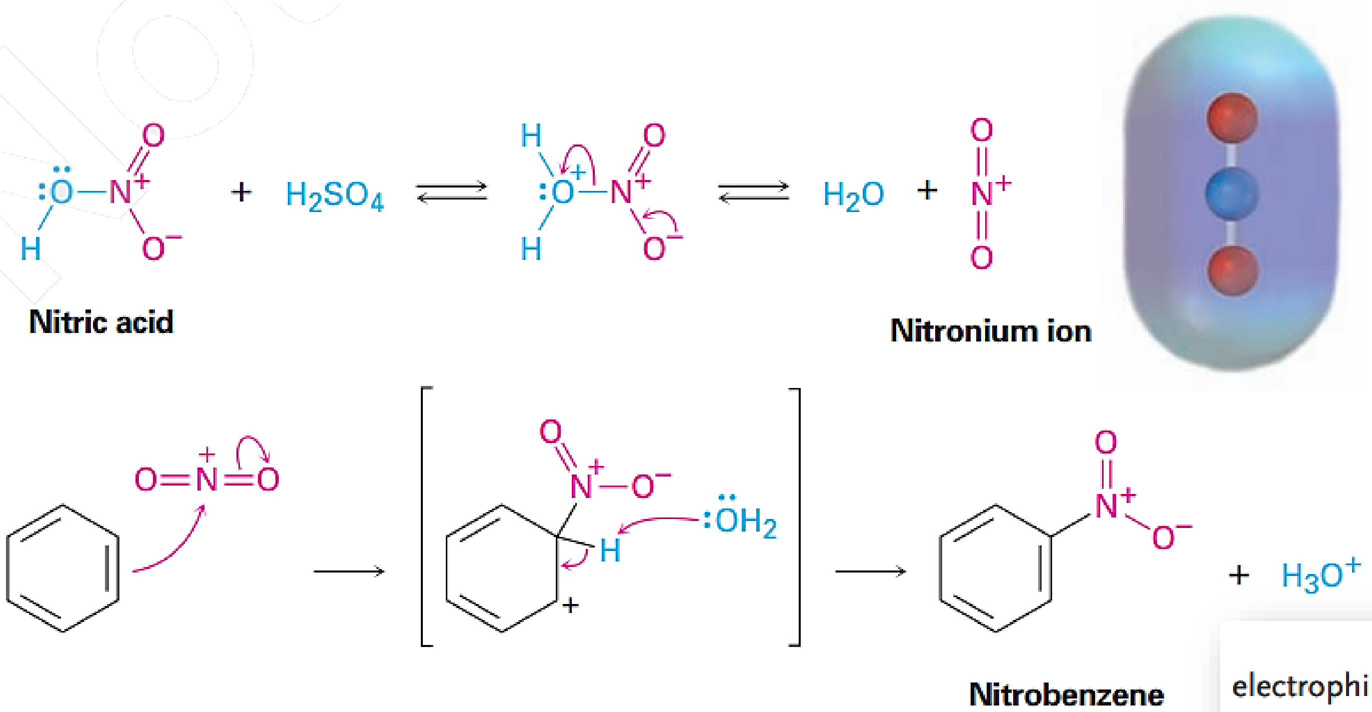
Nitration and Sulfonation

- **Nitration** and **sulfonation** introduce two different functional groups into the aromatic ring.
- Nitration is especially useful because the nitro group can be reduced to an NH_2 group.



Aromatic Nitration

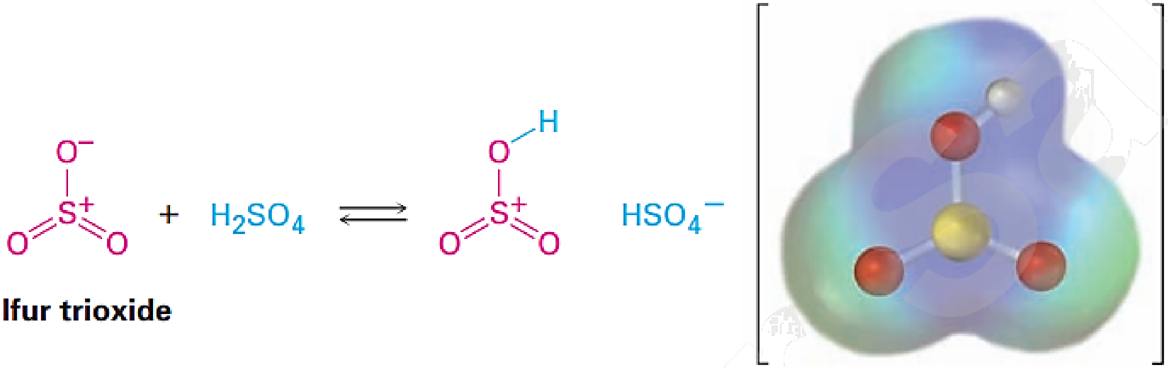
Aromatic rings can be nitrated by reaction with a mixture of concentrated nitric and sulfuric acids. The electrophile is the nitronium ion, NO_2^+, which is generated from HNO_3 by protonation and loss of water. The nitronium ion reacts with benzene to yield a carbocation intermediate, and loss of H^+ from this intermediate gives the neutral substitution product, nitrobenzene.



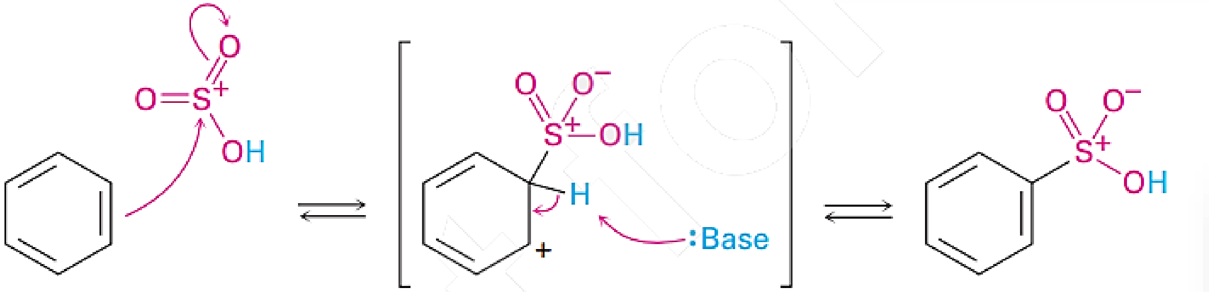
The mechanism of electrophilic nitration of an aromatic ring. An electrostatic potential map of the reactive electrophile NO_2^+ shows that the nitrogen atom is most positive (blue).

Aromatic Sulfonation

Aromatic rings can be sulfonated in the laboratory by reaction with fuming sulfuric acid, a mixture of H_2SO_4 and SO_3. The reactive electrophile is either $HSO_3{}^+$ or neutral SO_3, depending on reaction conditions, and substitution occurs by the same two-step mechanism seen previously for bromination and nitration.



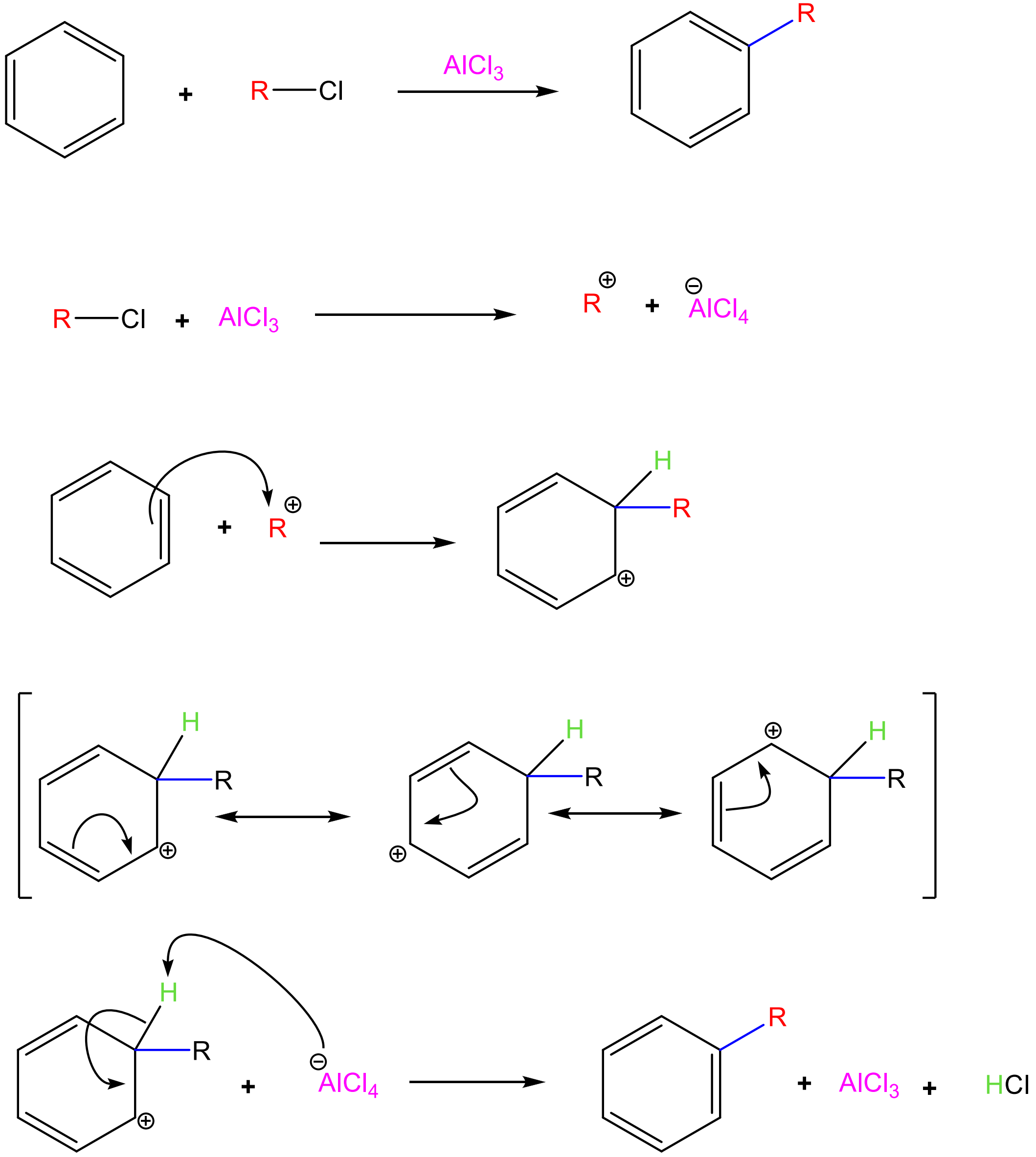
Sulfur trioxide



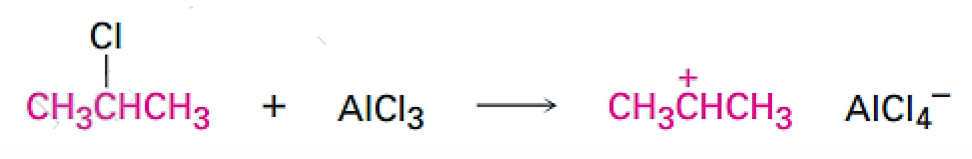
Benzenesulfonic acid

The mechanism of electrophilic sulfonation of an aromatic ring. An electrostatic potential map of the reactive electrophile $HOSO_2{}^+$ shows that sulfur and hydrogen are the most positive atoms (blue).

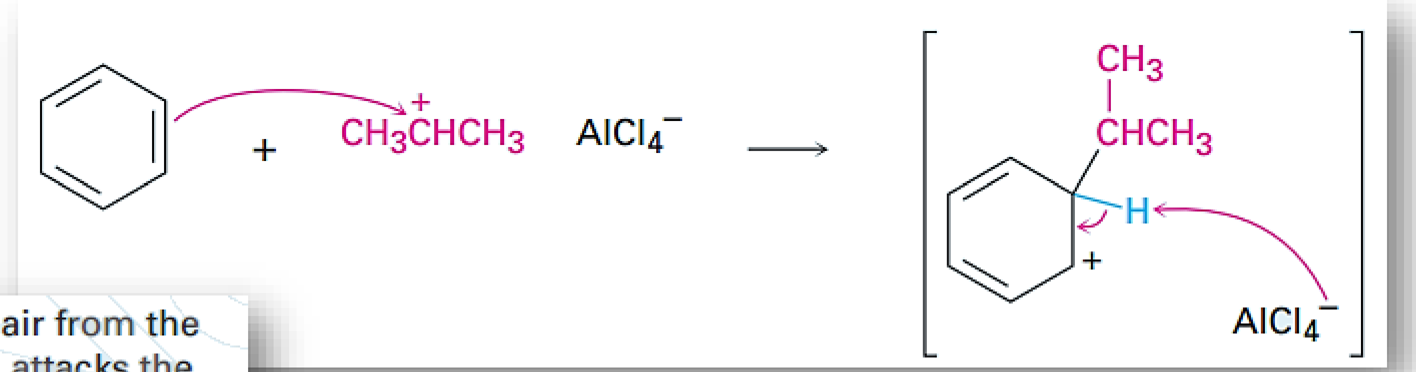
Freidel Crafts Acylation



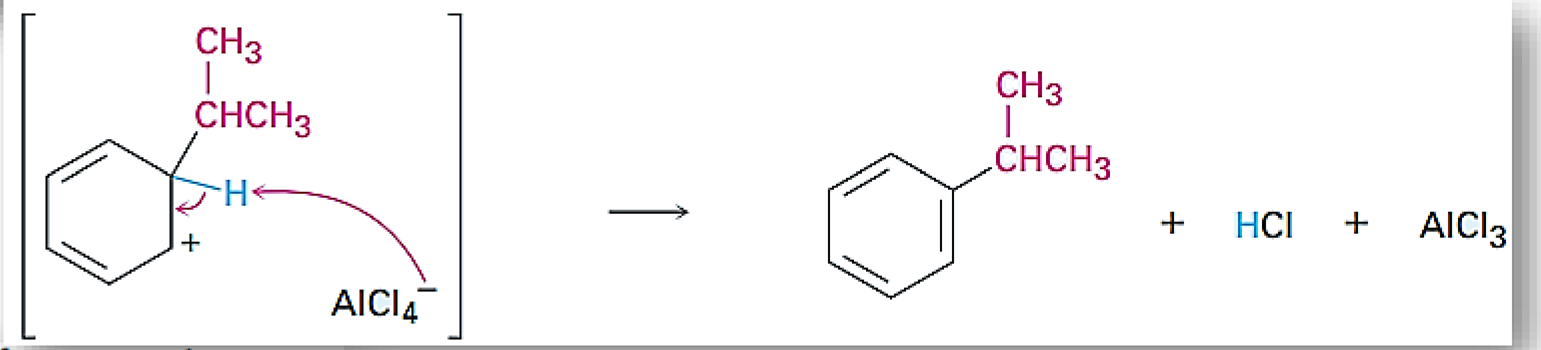
Friedel-Crafts Alkylation



$$CH_3\overset{\overset{\displaystyle Cl}{|}}{C}HCH_3 + AlCl_3 \longrightarrow CH_3\overset{+}{C}HCH_3 \quad AlCl_4^-$$

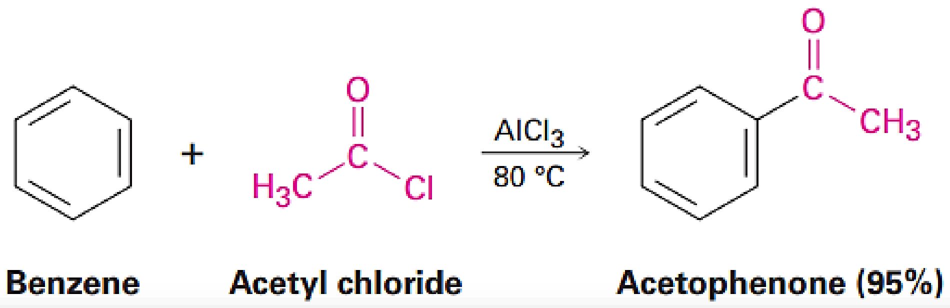


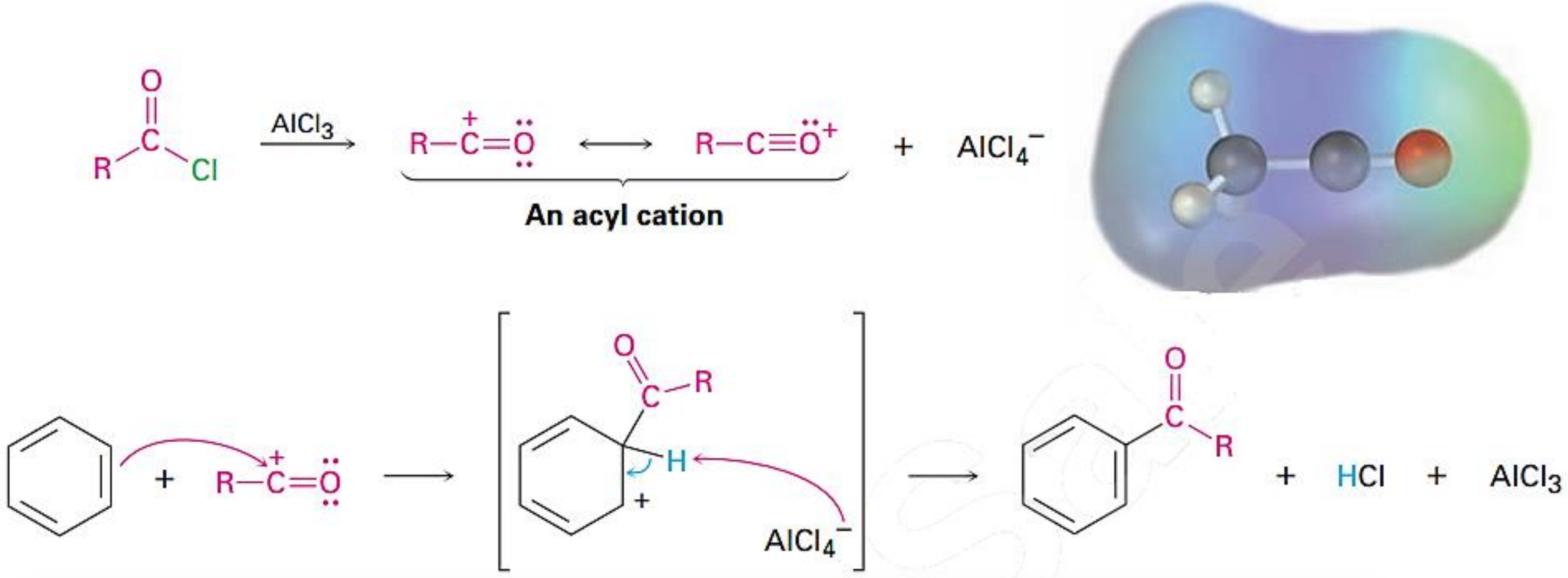
An electron pair from the aromatic ring attacks the carbocation, forming a C–C bond and yielding a new carbocation intermediate.



Loss of a proton then gives the neutral alkylated substitution product.

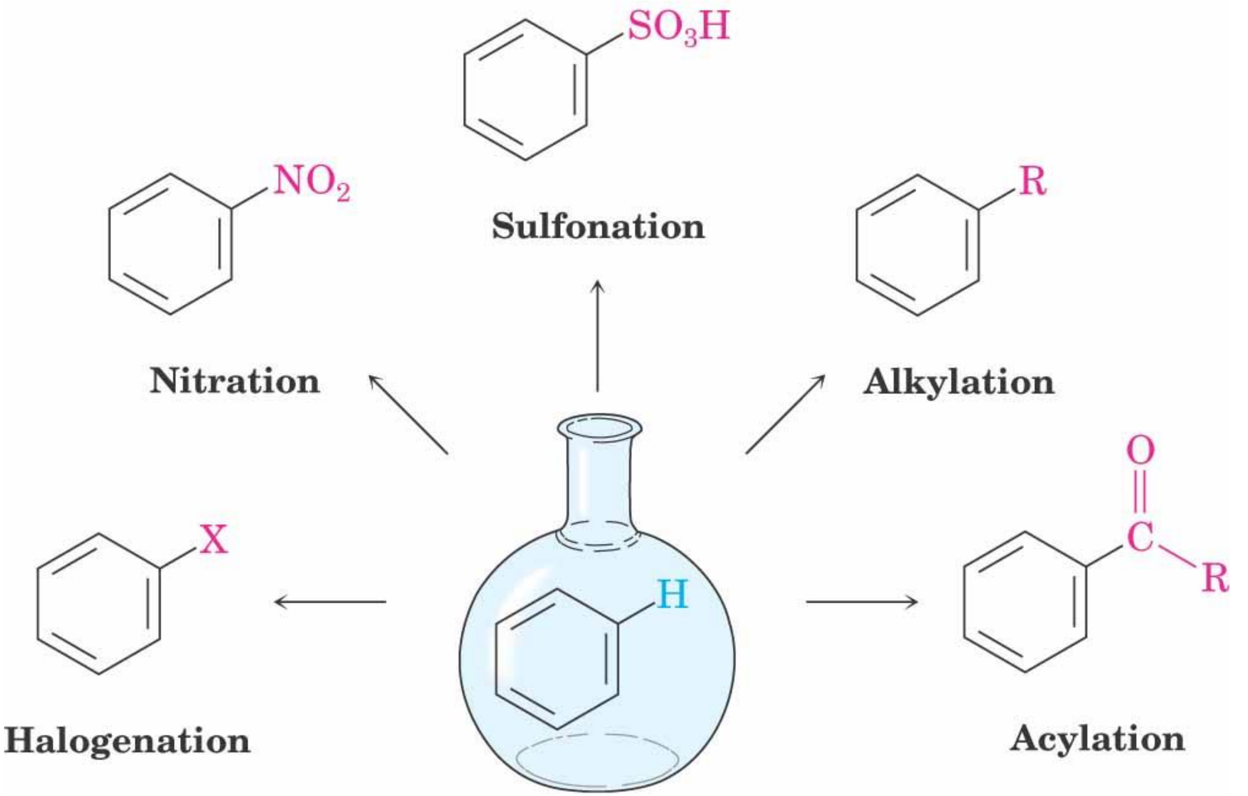
Friedel-Crafts Acylation





Mechanism of the Friedel–Crafts acylation reaction. The electrophile is a resonance-stabilized acyl cation, whose electrostatic potential map indicates that carbon is the most positive atom (blue).

Orientation of Benzene



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Substituent Effects in Substituted Aromatic Rings

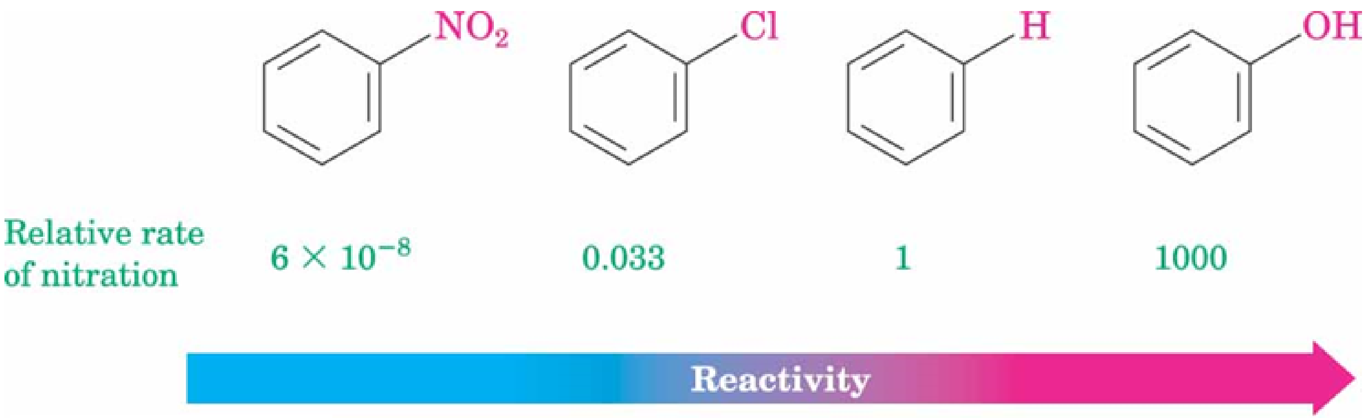
A substituent present on an aromatic ring affects:

- the reactivity of the aromatic ring
- the orientation of the reaction

Substituents affect the reactivity of the aromatic ring

Substituents may

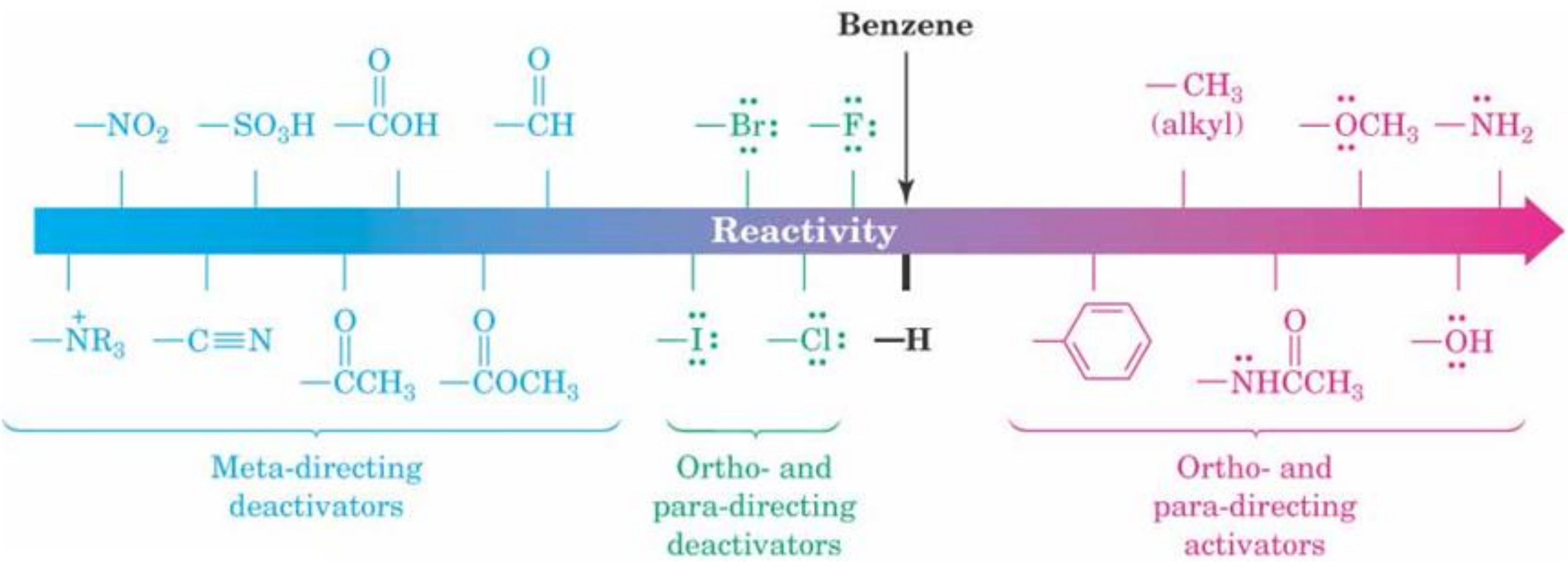
- activate the ring, make it (much) more reactive than benzene or
- deactivate the ring, make it (much) less reactive than benzene



Classification of Substituent Effect

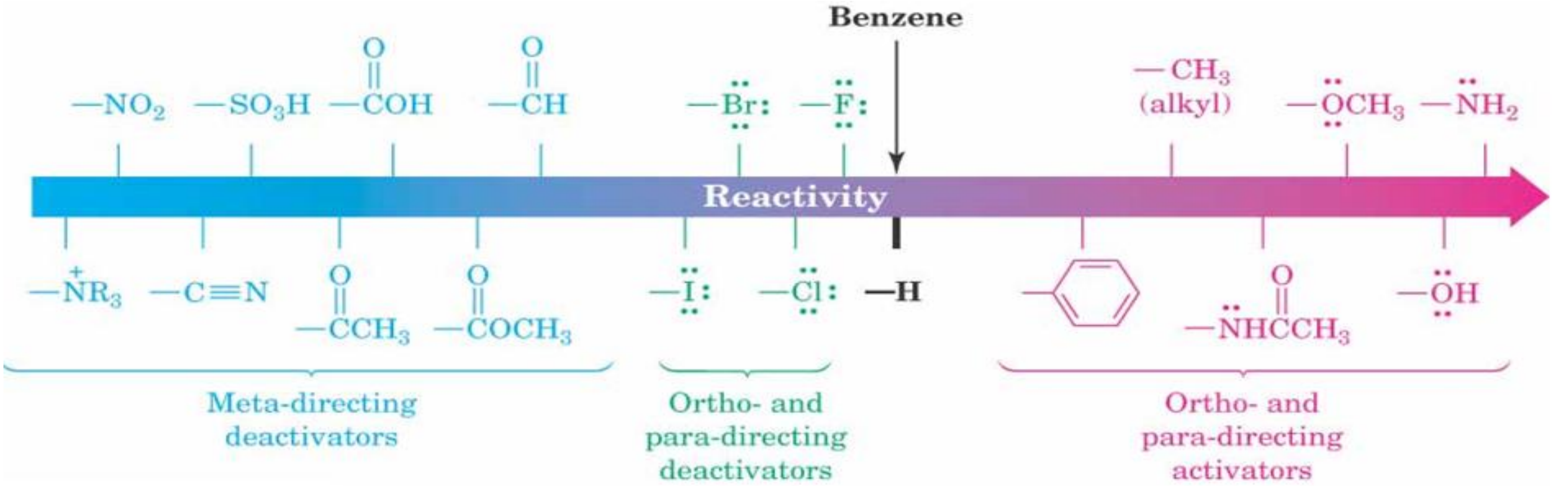
Substituents can be classified as:

- ortho- and para-directing activators,
- ortho- and para-directing deactivators, and
- meta-directing deactivators

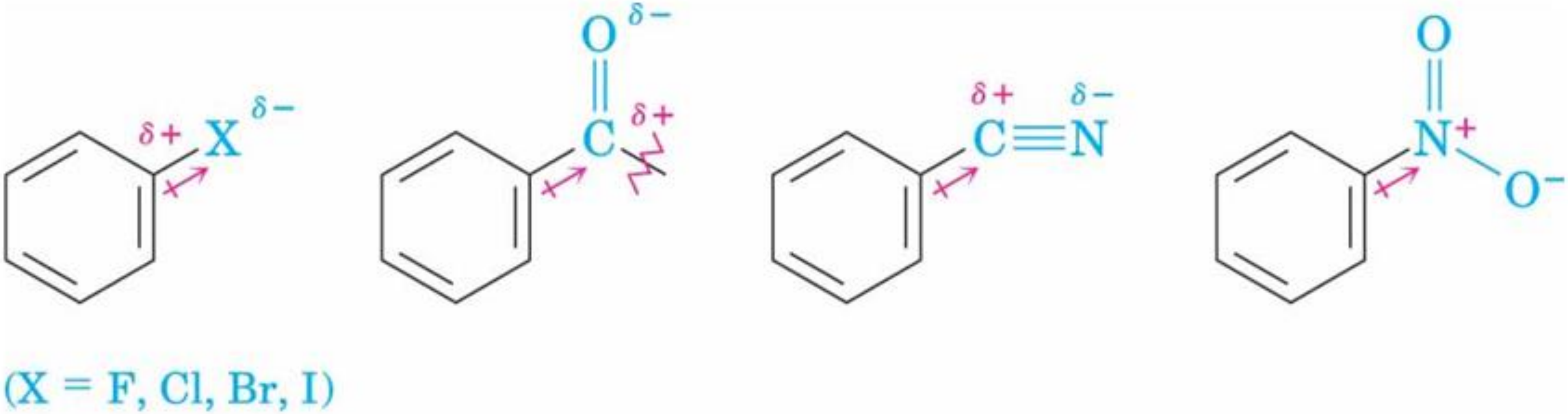


The directing effects of the groups correlate with their relativities:

- All meta-directing groups are strongly deactivating
- Most ortho- and para-directing groups are activating
- Halogens are unique being ortho- and para-directing but weakly deactivating

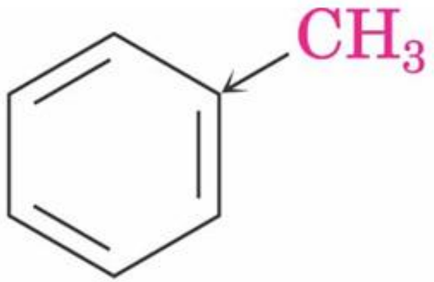


- Halogens, C=O, C≡N, and NO_2 inductively *withdraw* electrons through σ bond connected to ring



The groups attached to the aromatic rings are inductively electron-withdrawing because of the polarity of their bonds.

- Alkyl groups inductively *donate* electrons



Alkyl group; inductively electron-donating

Summary of Substituent Effects in Aromatic Substitution

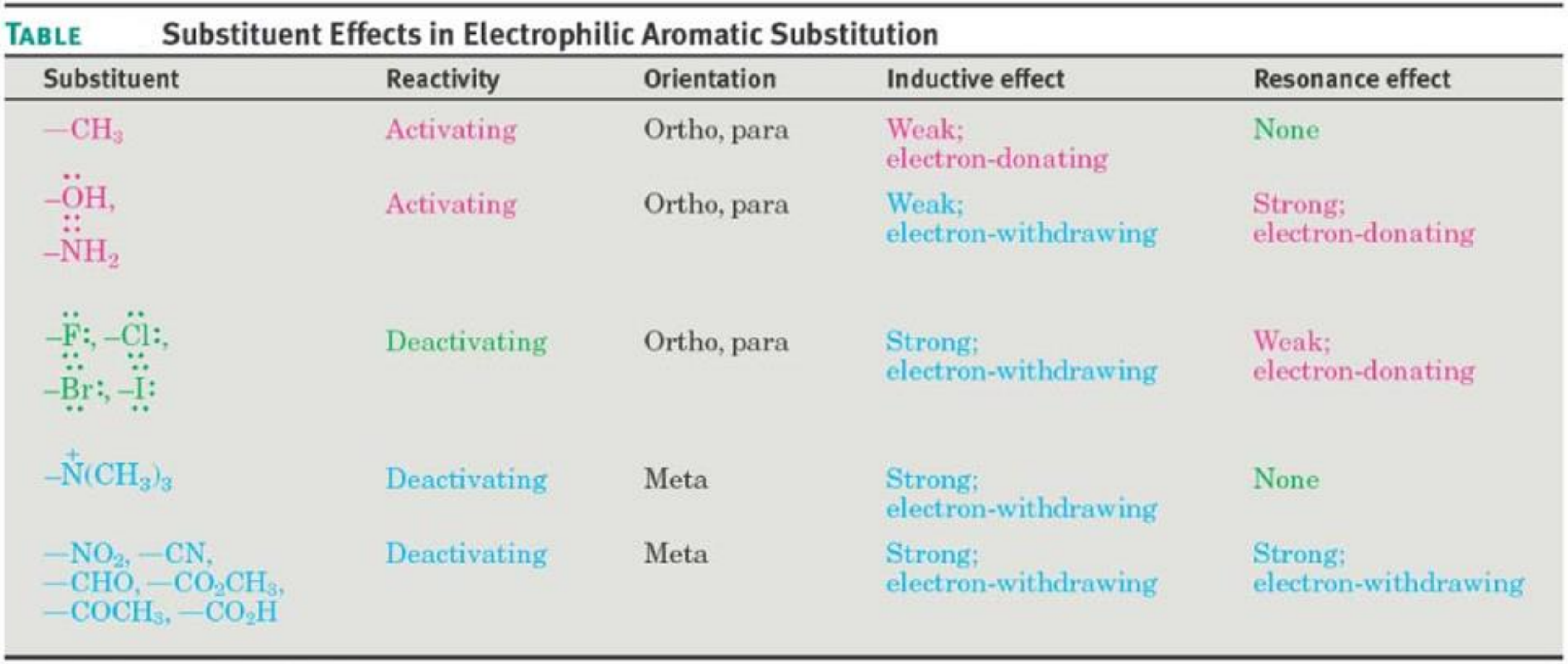


TABLE **Substituent Effects in Electrophilic Aromatic Substitution**

Substituent	Reactivity	Orientation	Inductive effect	Resonance effect
$-CH_3$	Activating	Ortho, para	Weak; electron-donating	None
$-\ddot{O}H$, $-\ddot{N}H_2$	Activating	Ortho, para	Weak; electron-withdrawing	Strong; electron-donating
$-\ddot{F}:$, $-\ddot{Cl}:$, $-\ddot{Br}:$, $-\ddot{I}:$	Deactivating	Ortho, para	Strong; electron-withdrawing	Weak; electron-donating
$-\overset{+}{N}(CH_3)_3$	Deactivating	Meta	Strong; electron-withdrawing	None
$-NO_2$, $-CN$, $-CHO$, $-CO_2CH_3$, $-COCH_3$, $-CO_2H$	Deactivating	Meta	Strong; electron-withdrawing	Strong; electron-withdrawing