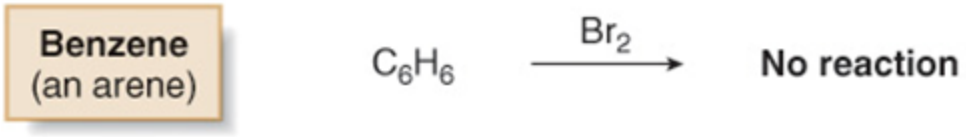
Benzene and Aromatic Compounds

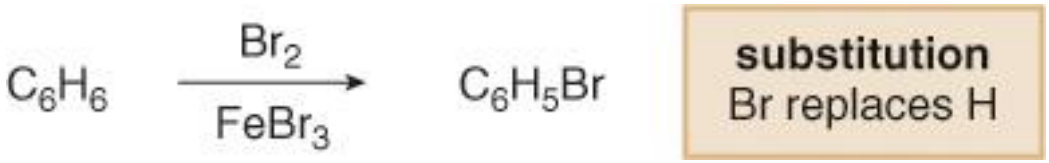
Chapter 15
Organic Chemistry, *8th Edition*
John McMurry

Background

- Benzene (C_6H_6) is the simplest aromatic hydrocarbon (or arene).
- Four degrees of unsaturation.
- It is planar.
- All C—C bond lengths are equal.
- Whereas unsaturated hydrocarbons such as alkenes, alkynes and dienes readily undergo addition reactions, benzene does not.



- Benzene reacts with bromine only in the presence of $FeBr_3$ (a Lewis acid), and the reaction is a substitution, not an addition.

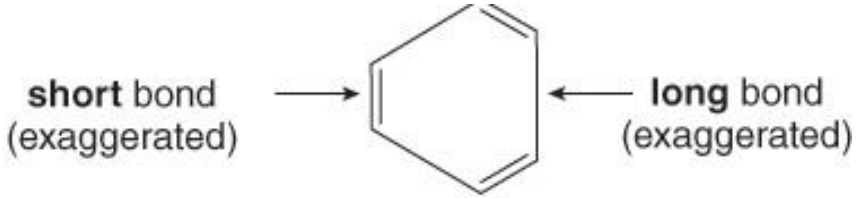


Background

- August Kekulé (1865) proposed that benzene was a rapidly equilibrating mixture of two compounds, each containing a six-membered ring with three alternating π bonds.

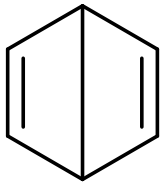
Kekulé description: An equilibrium

This structure implies that the C–C bonds should have **two different lengths**.



- three short bonds
- three long bonds

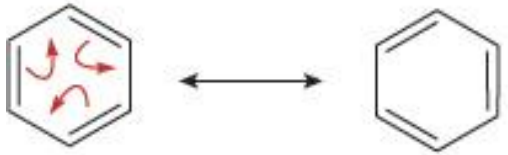
- All C—C bond lengths are equal!



James Dewar: the Dewar benzene was prepared in 1962 but it is not stable and it converts to benzene

The Structure of Benzene: Resonance

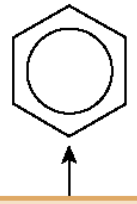
- The true structure of benzene is a resonance hybrid of the two Lewis structures.



The hybrid

The electrons in the π bonds are **delocalized** around the ring.

Some texts draw benzene as a hexagon with an inner circle:



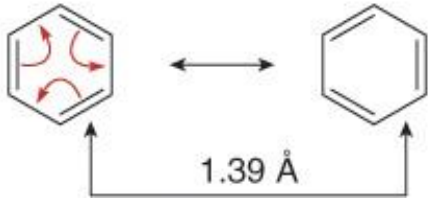
The circle represents the **six π electrons,** distributed over the six atoms of the ring.

CH_3-CH_3

1.53 Å

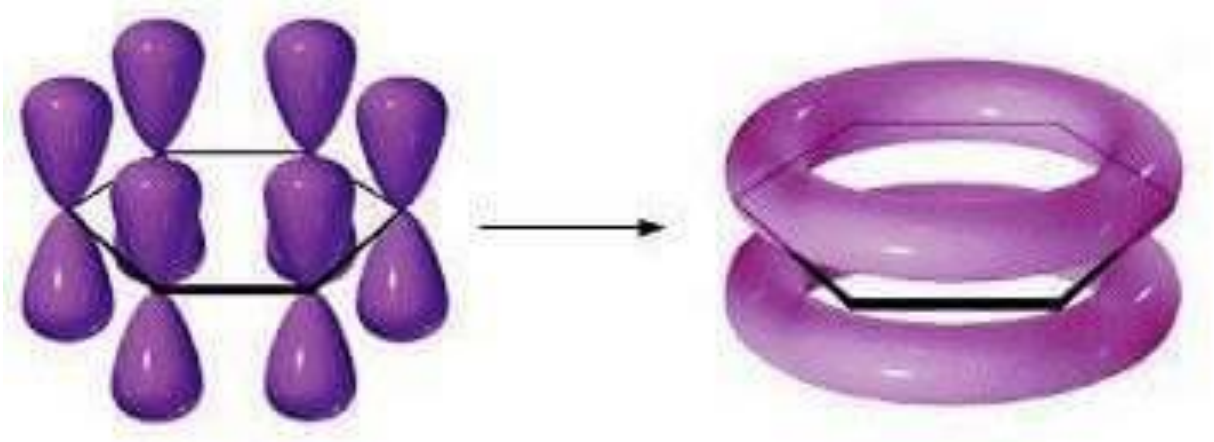
$CH_2=CH_2$

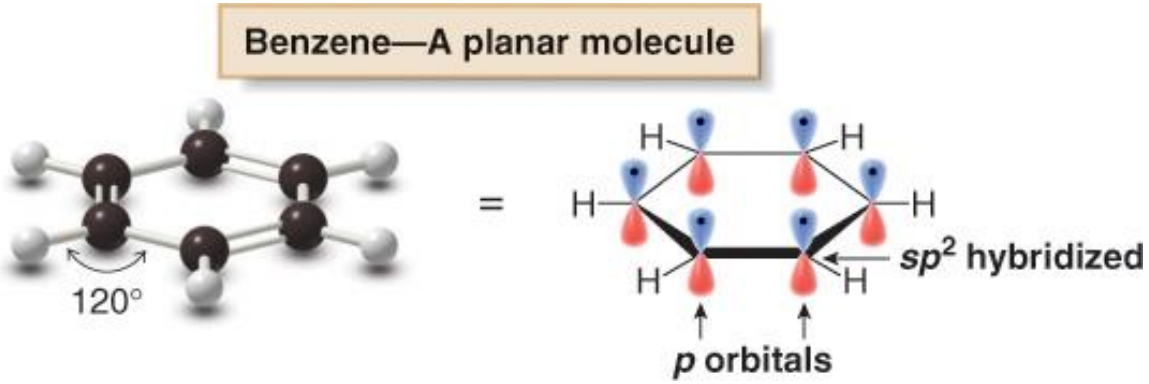
1.34 Å



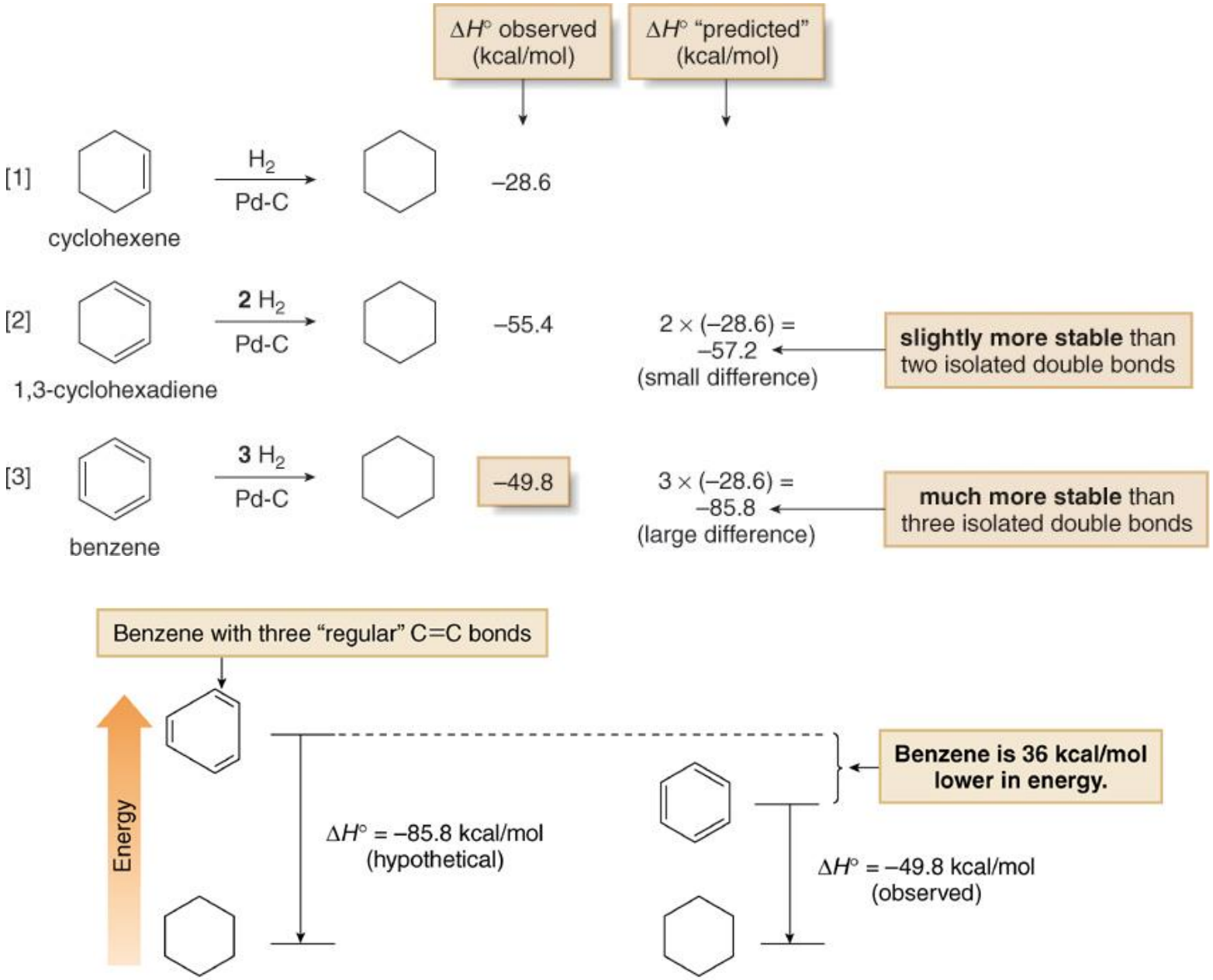
The C–C bonds in benzene are equal and intermediate in length.

The Structure of Benzene: MO



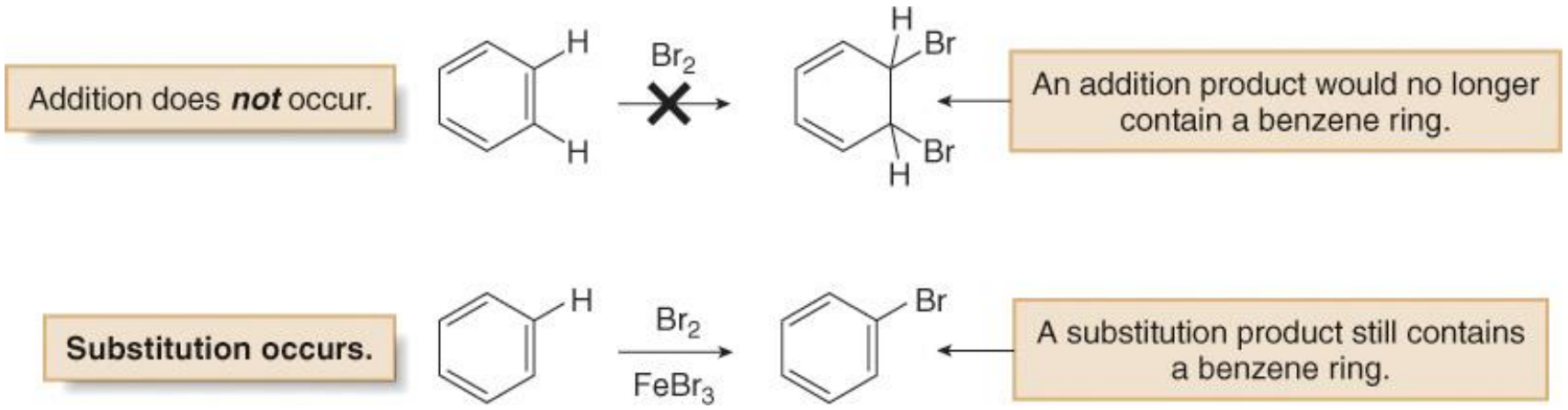


Aromaticity – Resonance Energy



Stability of Benzene - Aromaticity

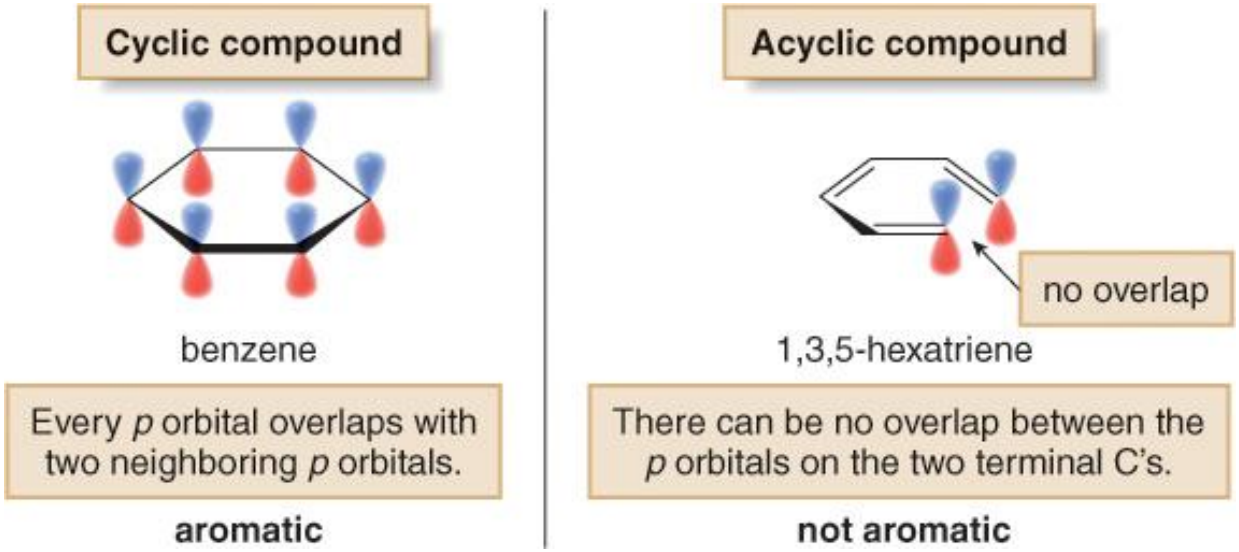
- Benzene does not undergo addition reactions typical of other highly unsaturated compounds, including conjugated dienes.



The Criteria for Aromaticity

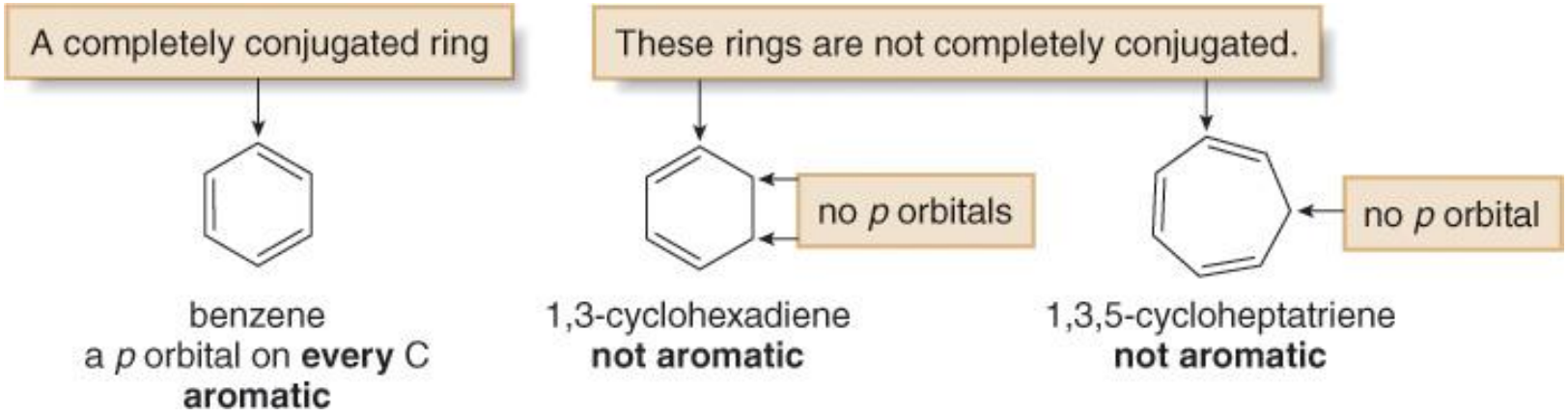
Four structural criteria must be satisfied for a compound to be aromatic.

[1] A molecule must be cyclic.

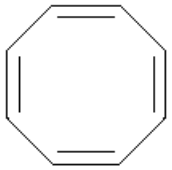


The Criteria for Aromaticity

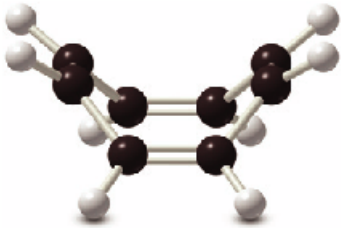
[2] A molecule must be completely conjugated (all atoms sp^2).



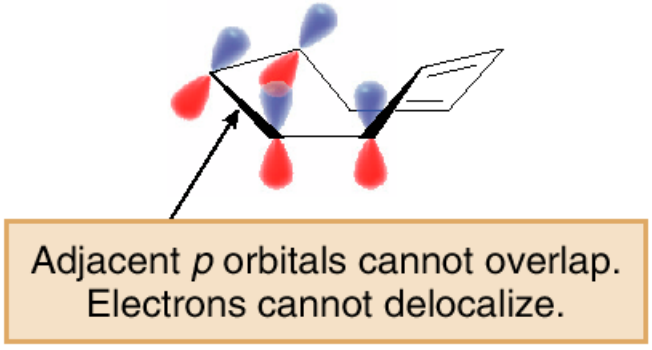
[3] A molecule must be planar.



cyclooctatetraene
not aromatic



a tub-shaped,
eight-membered ring



The Criteria for Aromaticity—Hückel's Rule

[4] A molecule must satisfy Hückel's rule.

- An aromatic compound must contain $4n + 2$ π electrons (n = 0, 1, 2, and so forth).
- Cyclic, planar, and completely conjugated compounds that contain $4n$ π electrons are especially unstable, and are said to be *antiaromatic.*

Benzene
An aromatic compound

$4n + 2 = 4(1) + 2 =$
6 π electrons
aromatic

Cyclobutadiene
An antiaromatic compound

$4n = 4(1) =$
4 π electrons
antiaromatic

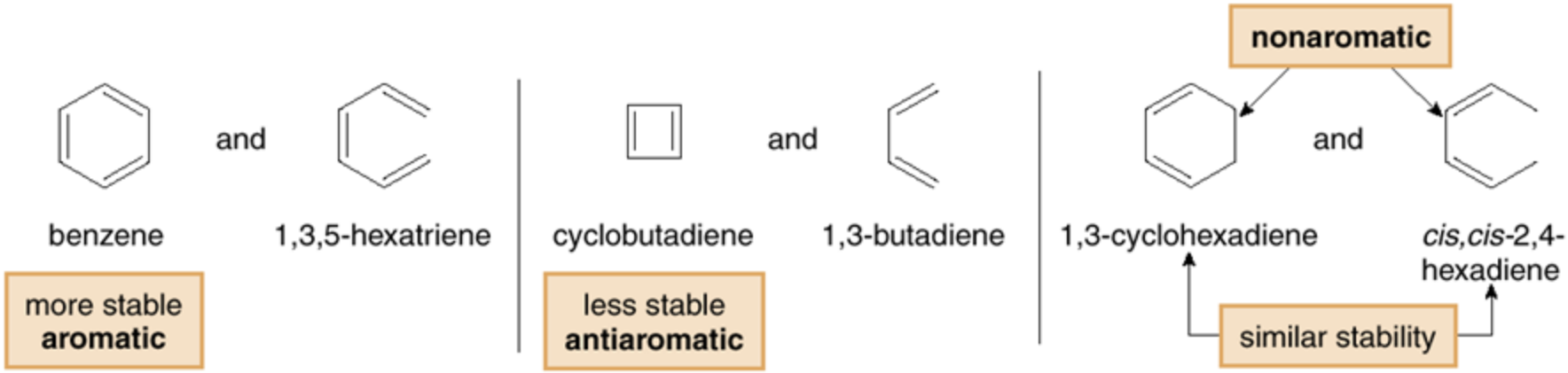
Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

Table 17.2 **The Number of π Electrons That Satisfy Hückel's Rule**

n	$4n + 2$
0	2
1	6
2	10
3	14
4, etc.	18

The Criteria for Aromaticity—Hückel's Rule

1. Aromatic—A cyclic, planar, completely conjugated compound with $4n + 2$ π electrons.
2. Antiaromatic—A cyclic, planar, completely conjugated compound with $4n$ π electrons.
3. Not aromatic (nonaromatic)—A compound that lacks one (or more) of the following requirements for aromaticity: being cyclic, planar, and completely conjugated.

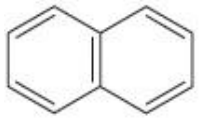


Examples of Aromatic Rings

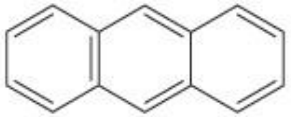
Cyclooctatetraene
8 π electrons

planar
antiaromatic

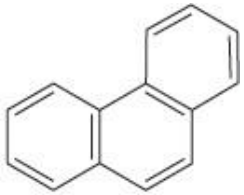
puckered
nonaromatic



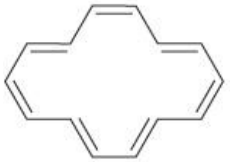
naphthalene
10 π electrons



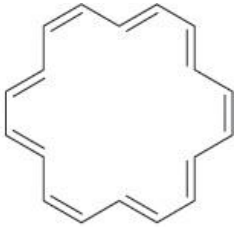
anthracene
14 π electrons



phenanthrene
14 π electrons

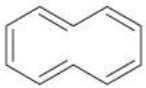


[14]-annulene
$4n + 2 = 4(3) + 2 =$
14 π electrons
aromatic



[18]-annulene
$4n + 2 = 4(4) + 2 =$
18 π electrons
aromatic

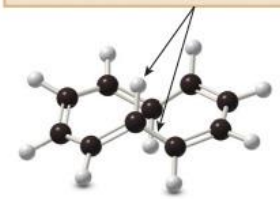
[10]-Annulene fits Hückel's rule, but it's **not planar**.



[10]-annulene
10 π electrons
not aromatic

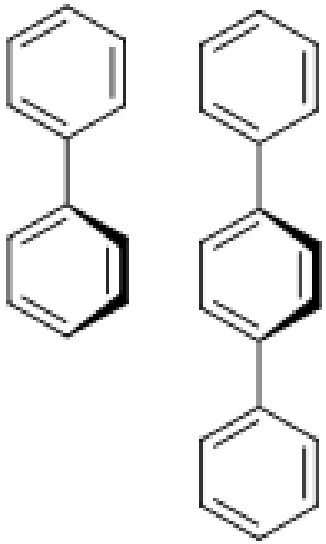
=

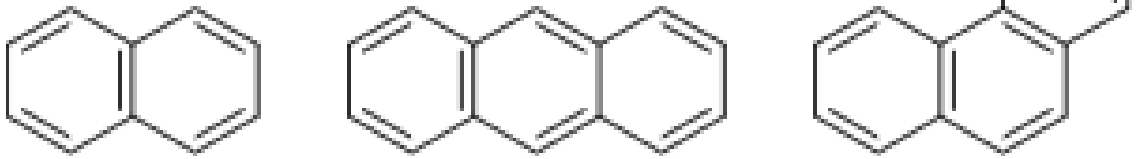
The molecule puckers to keep these H's further away from each other.



3-D representation

Polycyclic Aromatic Hydrocarbons





biphenyl terphenyl naphthalene anthracene phenanthrene

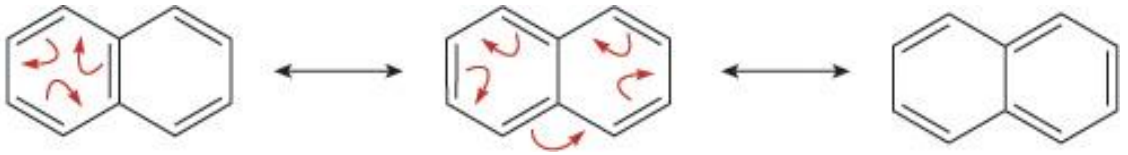
No interactions between rings

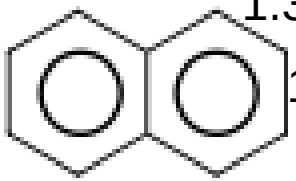
61 kcal/mol

84 kcal/mol

92 kcal/mol

Three resonance structures for naphthalene





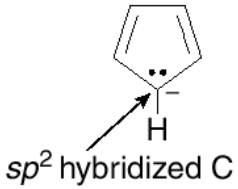
Other Aromatic Compounds

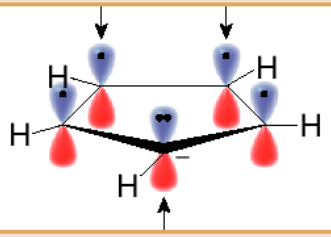
cyclopentadiene
not aromatic
$pK_a = 15$

cyclopentadienyl anion
aromatic
a stabilized conjugate base

The cyclopentadienyl anion

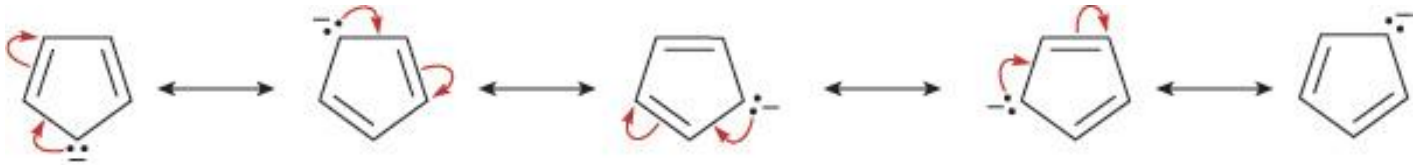
The ring is completely conjugated with **6 π electrons**.





The lone pair resides in a *p* orbital.

- **The cyclopentadienyl anion is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons.**



Other Aromatic Compounds

cyclopentadienyl anion
- **6** π electrons
- contains $4n + 2$ π electrons

aromatic

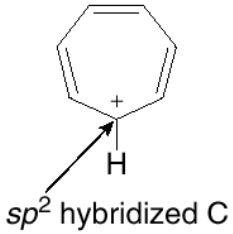
cyclopentadienyl cation
- **4** π electrons
- contains $4n$ π electrons

antiaromatic

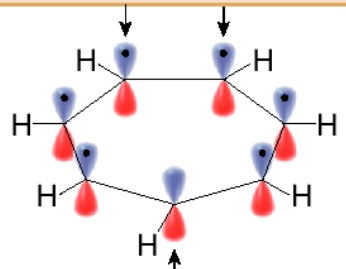
cyclopentadienyl radical
- **5** π electrons
- does not contain either $4n$ or $4n + 2$ π electrons

nonaromatic

The tropylium cation



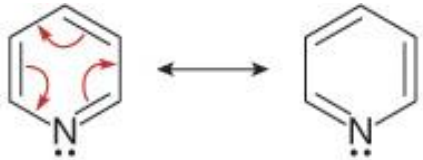
The ring is completely conjugated with **6 π electrons**.



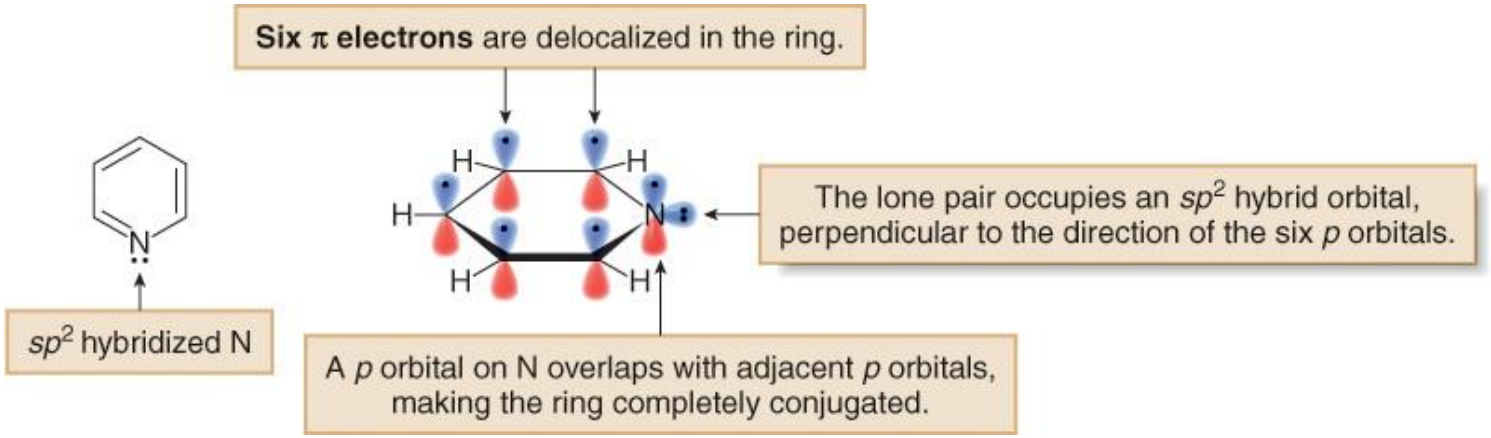
One *p* orbital is vacant.

- The tropylium cation is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons delocalized over the seven atoms of the ring.

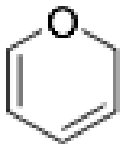
Aromatic Heterocycles



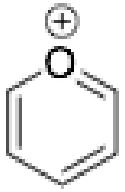
two resonance structures for pyridine
6 π electrons



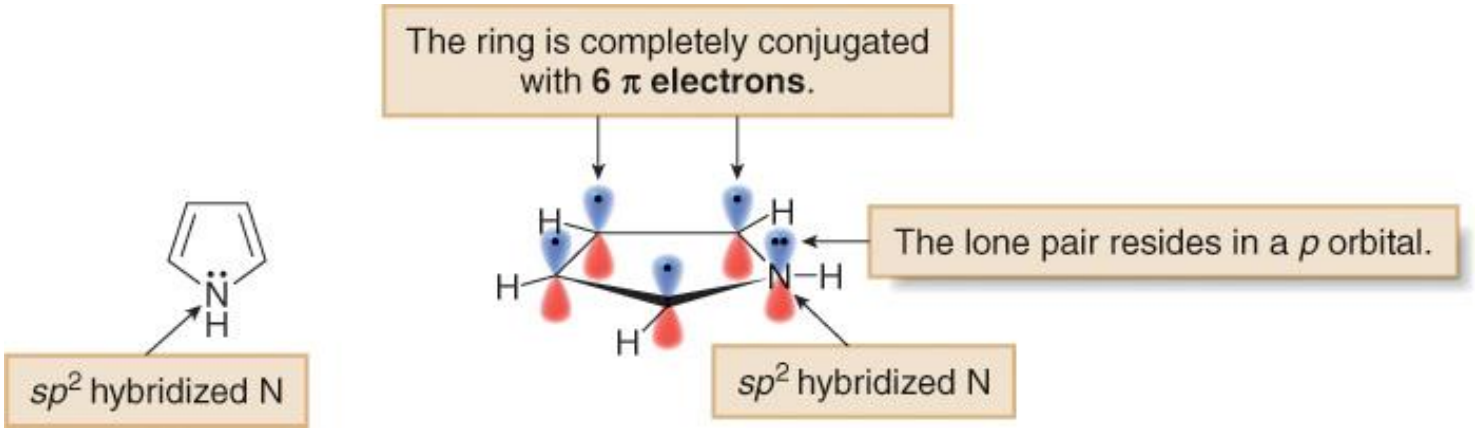
2H-pyran
4 π electrons
nonaromatic

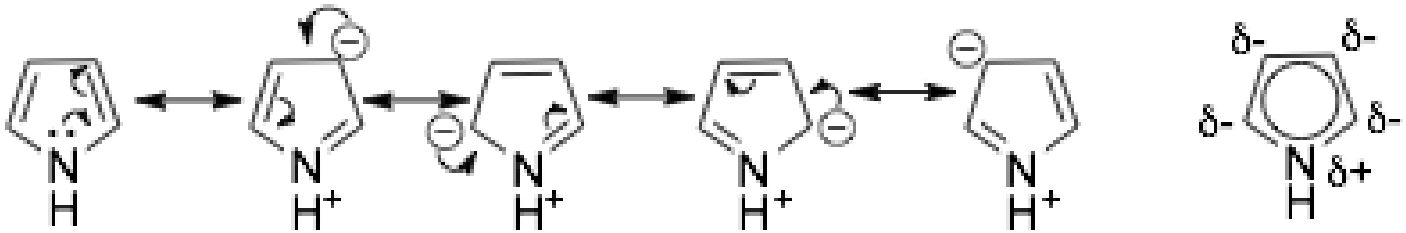


2H-pyrilium ion
6 π electrons
aromatic



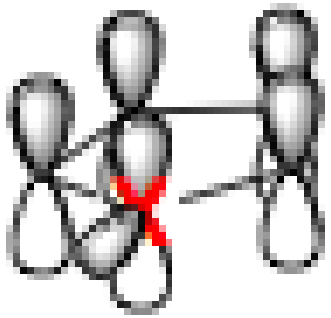
Aromatic Heterocycles



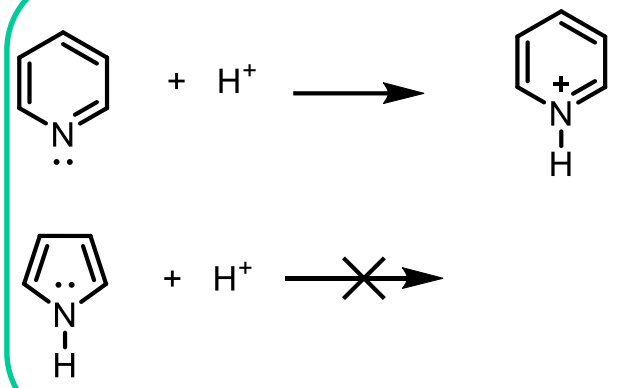


furan

thiophen

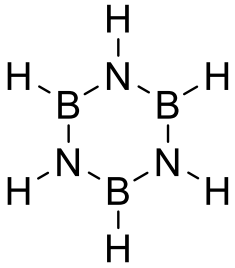


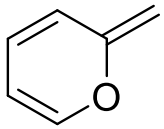
Aromatic Heterocycles

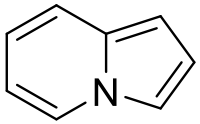


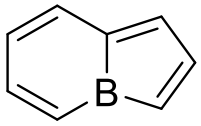
pyridine is basic and nucleophilic the pyrrole is not

Other examples



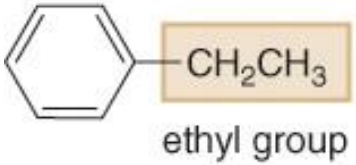






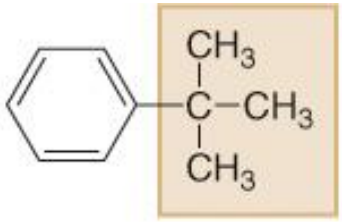
Nomenclature: 1 Substituent

Systematic:



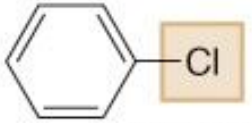
ethyl group

ethylbenzene



tert-butyl group

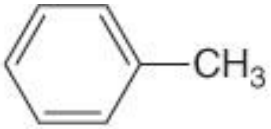
tert-butylbenzene



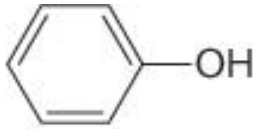
chloro group

chlorobenzene

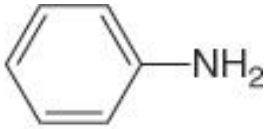
Common:



toluene
(methylbenzene)



phenol
(hydroxybenzene)

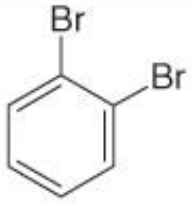


aniline
(aminobenzene)

Nomenclature: 2 Substituents

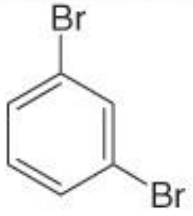
Identical:

1,2-disubstituted benzene
ortho isomer



1,2-dibromobenzene
o-dibromobenzene

1,3-disubstituted benzene
meta isomer



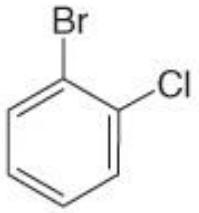
1,3-dibromobenzene
m-dibromobenzene

1,4-disubstituted benzene
para isomer

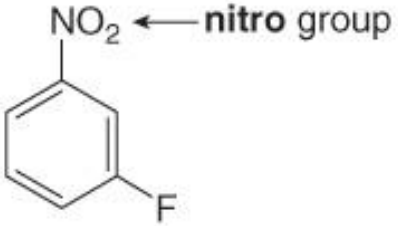
1,4-dibromobenzene
p-dibromobenzene

Different:

Alphabetize two different substituent names:

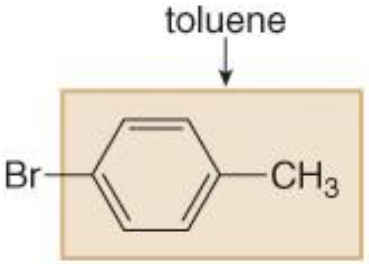


***o*-bromochloro-benzene**

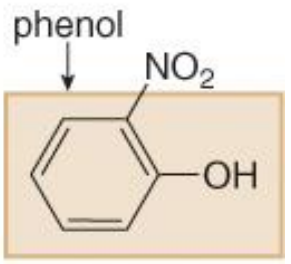


***m*-fluoronitro-benzene**

Use a common root name:



***p*-bromo**toluene

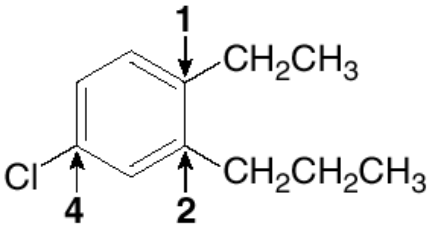


***o*-nitro**phenol

Nomenclature: 3 or More Substituents

Examples of naming polysubstituted benzenes

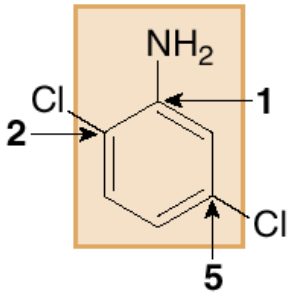
[1]



- Assign the lowest set of numbers.
- Alphabetize the names of all the substituents.

4-chloro-1-ethyl-2-propylbenzene

[2]

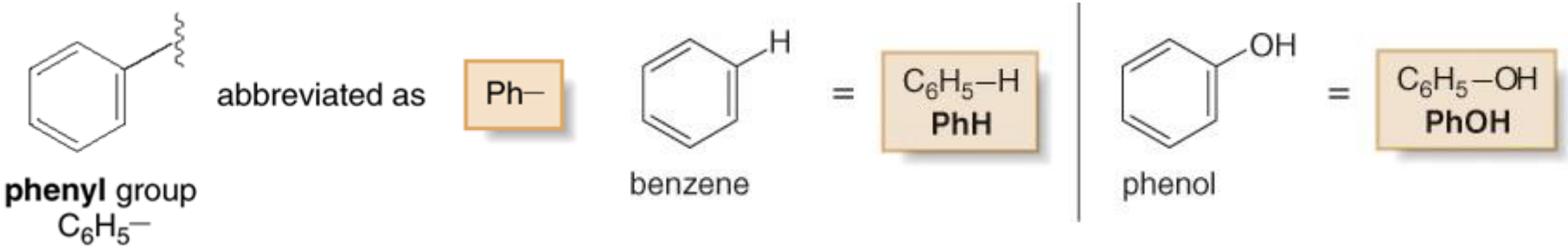


- Name the molecule as a derivative of the common root **aniline.**
- Designate the position of the NH_2 group as "1," and then assign the lowest possible set of numbers to the other substituents.

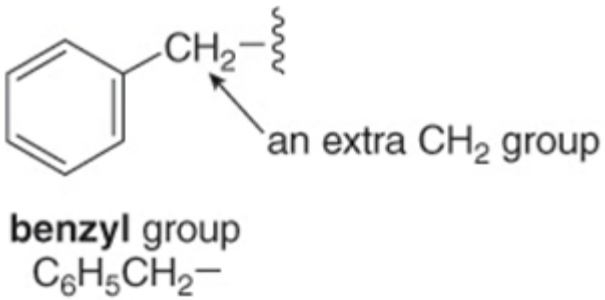
2,5-dichloroaniline

Nomenclature

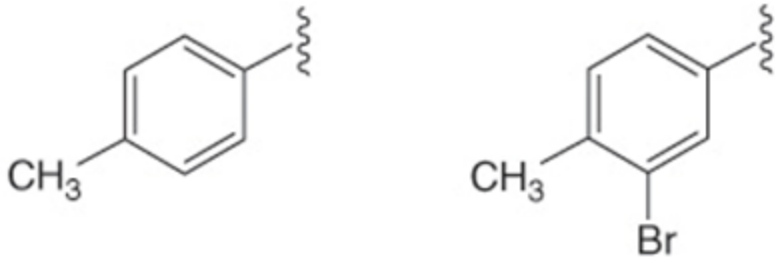
- A benzene substituent is called a phenyl group, and it can be abbreviated in a structure as "Ph-".



- The benzyl group:



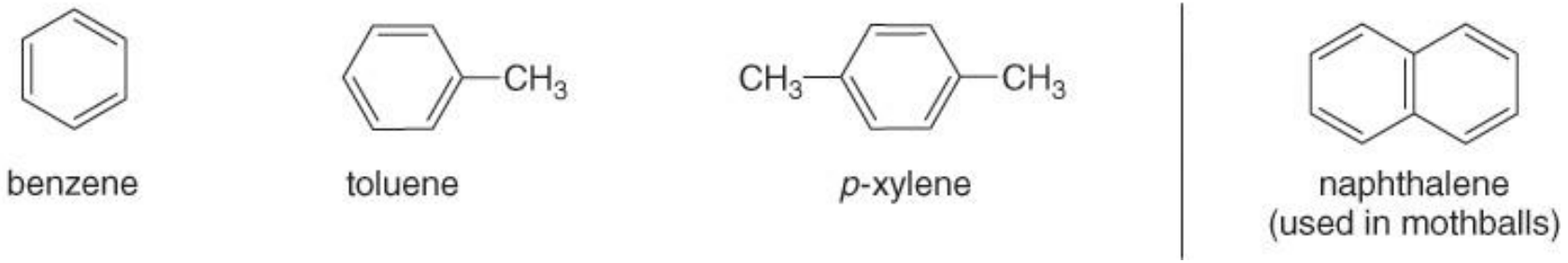
- Aryl groups:



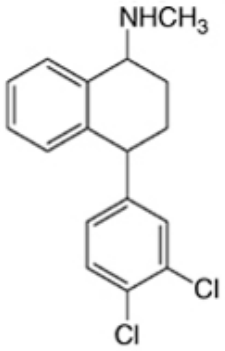
Interesting Aromatic Compounds

- Benzene and toluene, are obtained from petroleum refining and are useful starting materials for synthetic polymers.
- Compounds containing two or more benzene rings that share carbon—carbon bonds are called polycyclic aromatic hydrocarbons (PAHs). Naphthalene, the simplest PAH, is the active ingredient in mothballs.

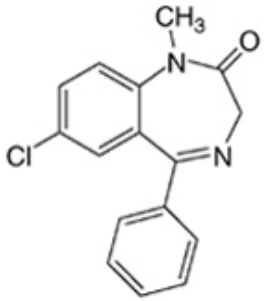
The components of the gasoline additive BTX



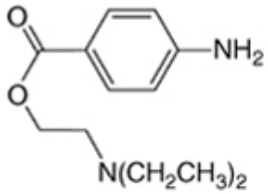
Interesting Aromatic Compounds



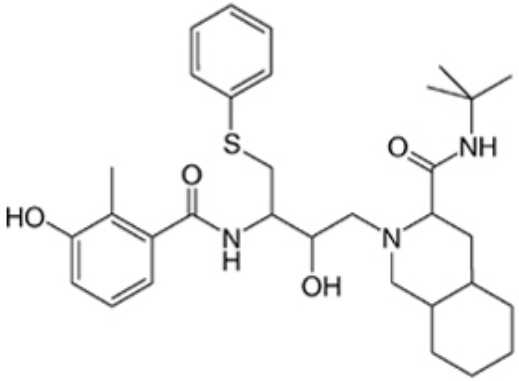
- Trade name: **Zoloft**
- Generic name: **sertraline**
- Use: a psychotherapeutic drug for depression and panic disorders



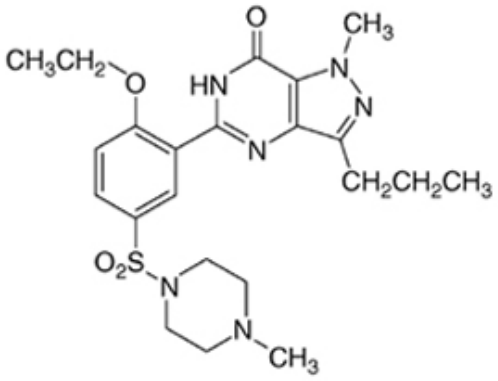
- Trade name: **Valium**
- Generic name: **diazepam**
- Use: a sedative



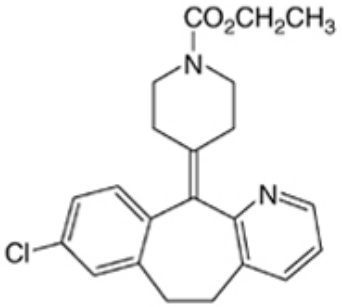
- Trade name: **Novocain**
- Generic name: **procaine**
- Use: a local anesthetic



- Trade name: **Viracept**
- Generic name: **nelfinavir**
- Use: an antiviral drug used to treat HIV



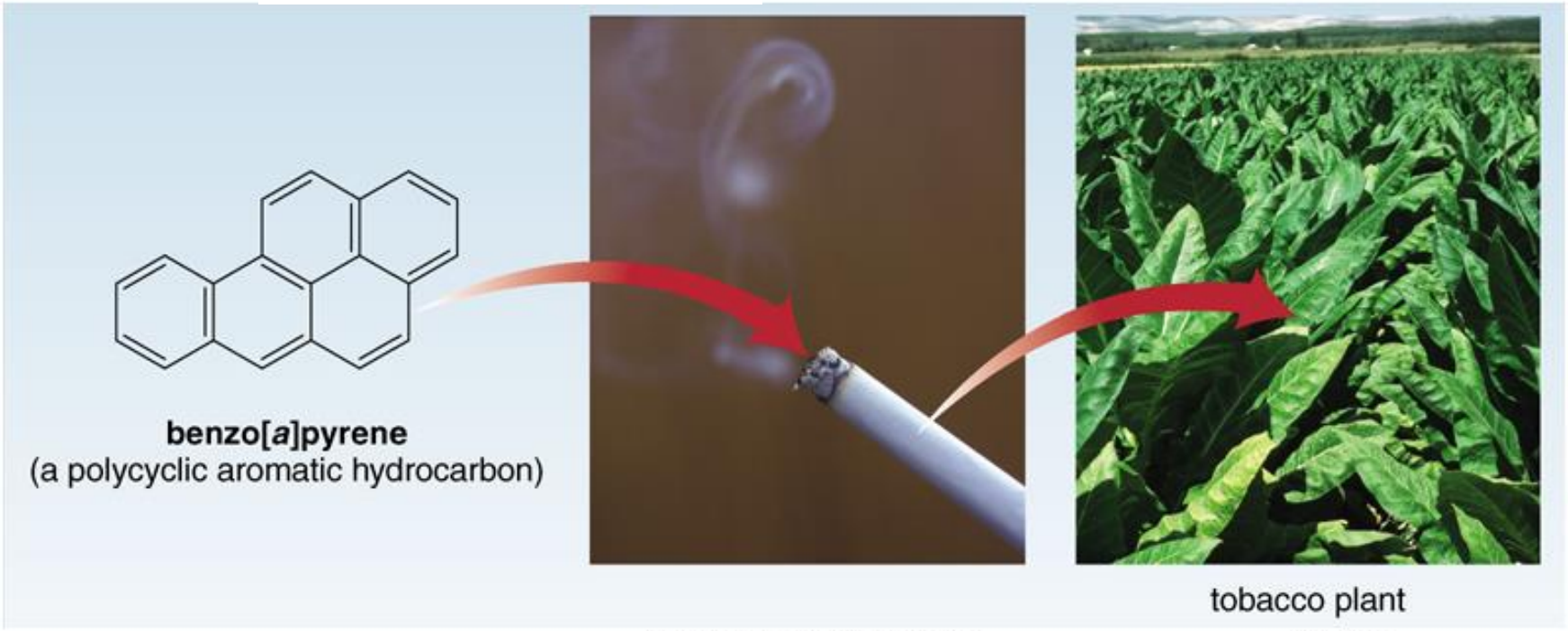
- Trade name: **Viagra**
- Generic name: **sildenafil**
- Use: a drug used to treat erectile dysfunction



- Trade name: **Claritin**
- Generic name: **loratadine**
- Use: an antihistamine for seasonal allergies

Interesting Aromatic Compounds

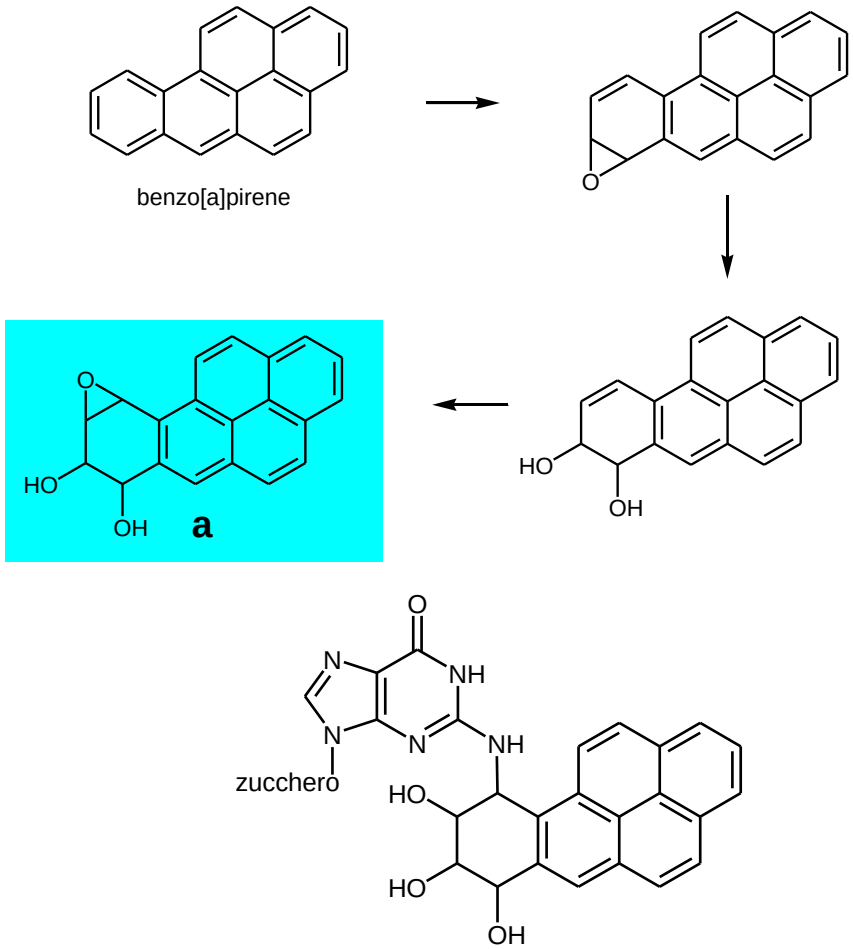
- Benzo[*a*]pyrene, produced by the incomplete oxidation of organic compounds in tobacco, is found in cigarette smoke.



- When ingested or inhaled, benzo[a]pyrene and other similar PAHs are oxidized to carcinogenic products.

Benzo[a]pyrene

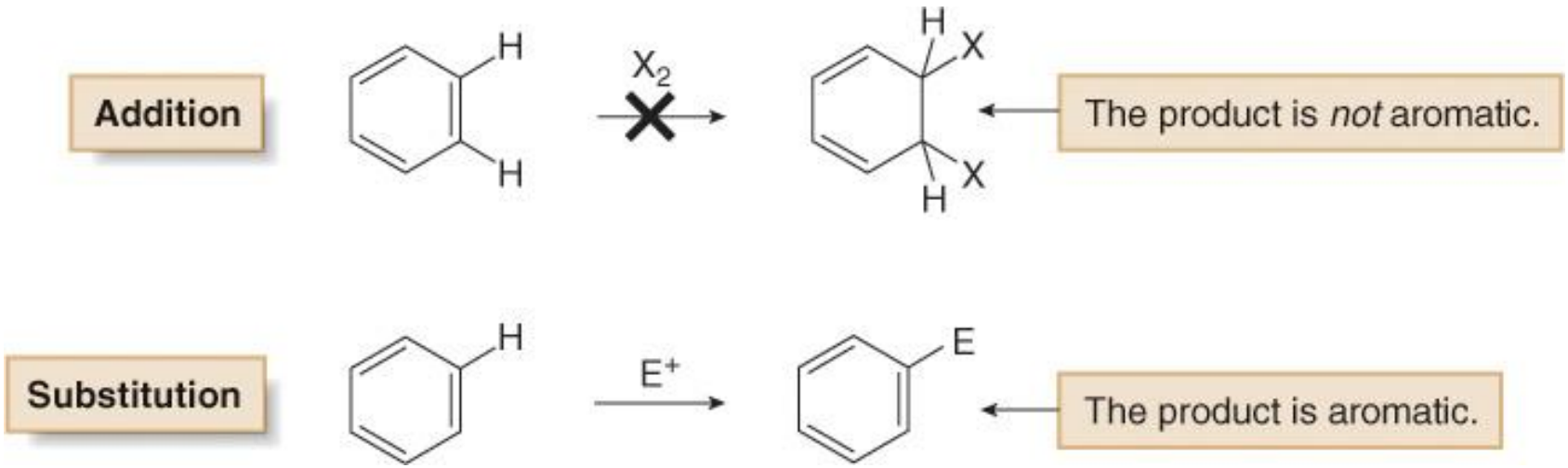
The metabolic degradation of PAHs involves their transformation into hydroxylated compounds that, being more soluble in water, are more easily eliminated. In the process can also form the derivative **a** which it is believed to be responsible for carcinogenic activity because it degrades the DNA forming covalent adducts with guanine.



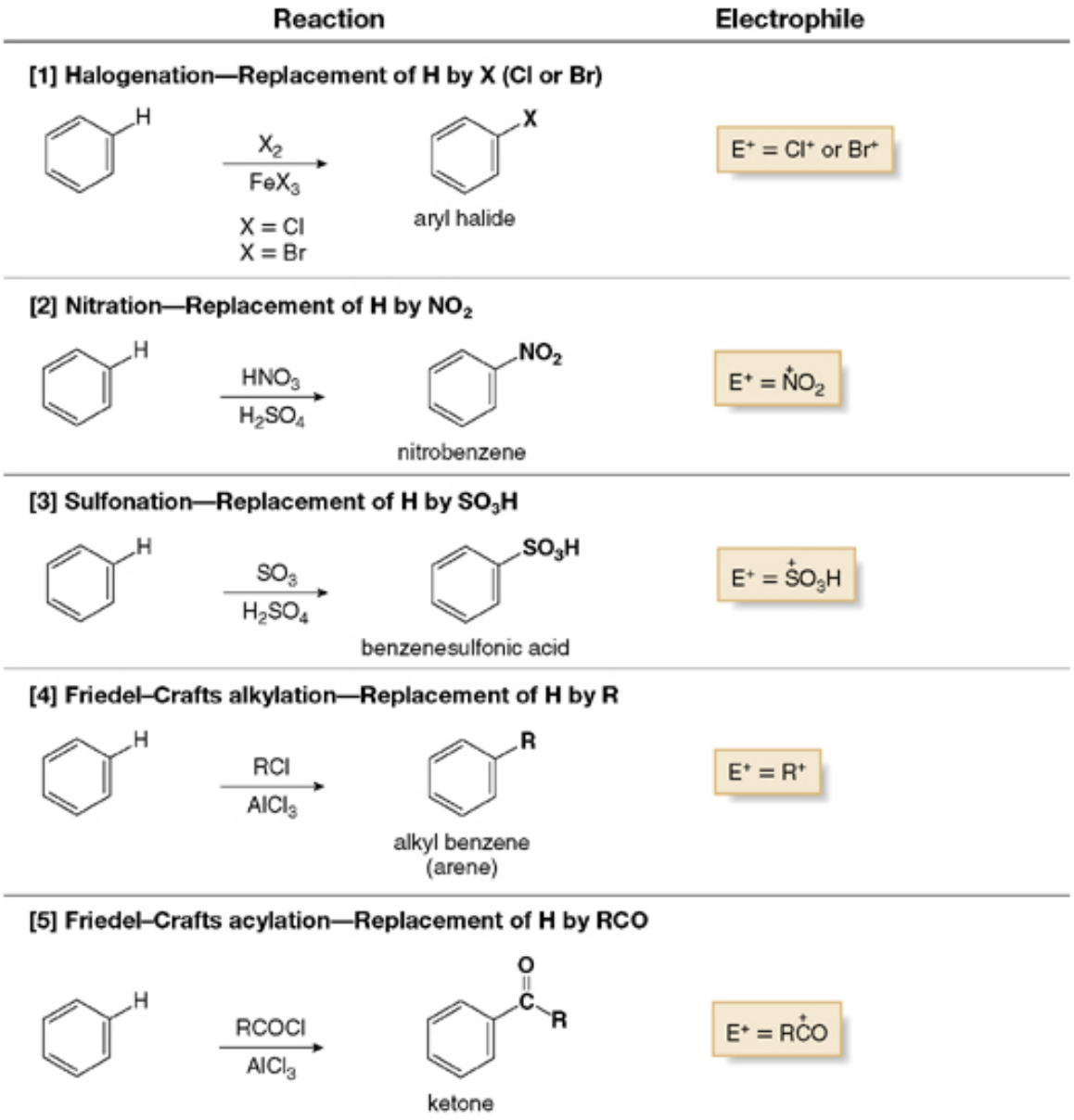
Electrophilic Aromatic Substitution

Chapter 16
Organic Chemistry, *8th Edition*
John McMurry

Introduction



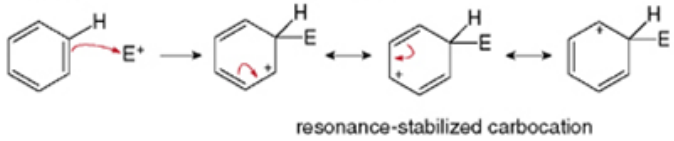
Introduction



Mechanism

Mechanism 18.1 General Mechanism—Electrophilic Aromatic Substitution

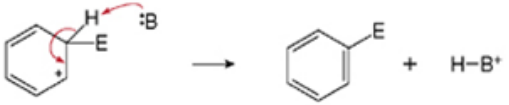
Step [1] Addition of the electrophile (E^+) to form a carbocation



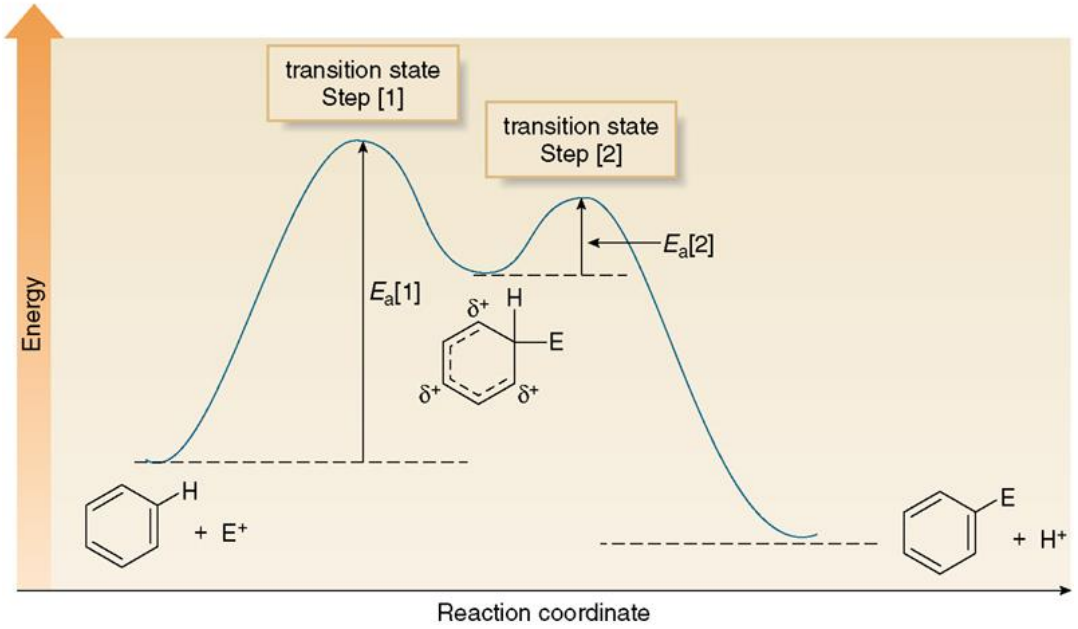
resonance-stabilized carbocation

- Addition of the electrophile (E^+) forms a new C–E bond using two π electrons from the benzene ring, and generating a carbocation. This carbocation intermediate is not aromatic, but it is resonance stabilized—**three resonance structures can be drawn.**
- Step [1] is rate-determining because the aromaticity of the benzene ring is lost.

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



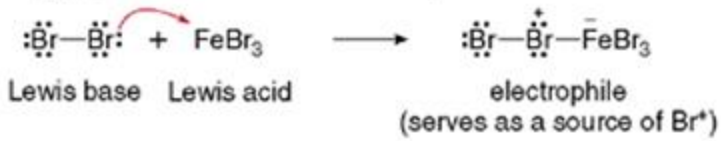
- In Step [2], a base (B:) removes the proton from the carbon bearing the electrophile, thus re-forming the aromatic ring. This step is fast because the aromaticity of the benzene ring is restored.
- Any of the three resonance structures of the carbocation intermediate can be used to draw the product. The choice of resonance structure affects how curved arrows are drawn, but not the identity of the product.



Halogenation

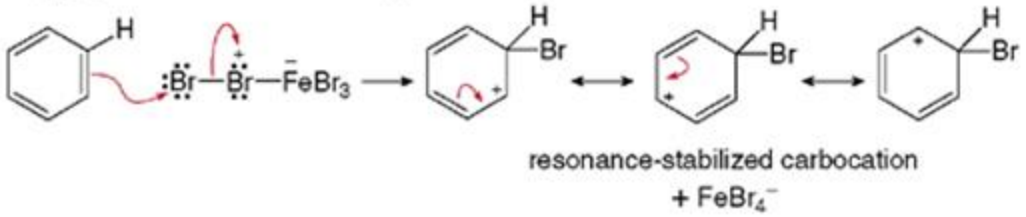
Mechanism 18.2 Bromination of Benzene

Step [1] Generation of the electrophile



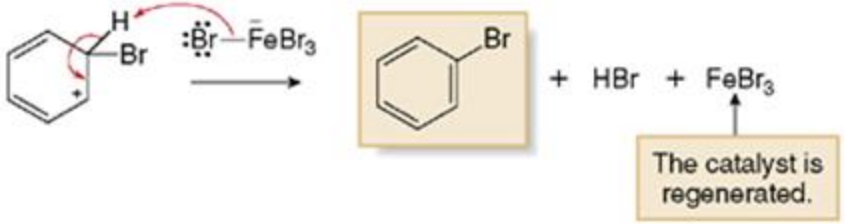
- Lewis acid–base reaction of Br_2 with $FeBr_3$ forms a species with a weakened and polarized Br – Br bond. This adduct serves as a source of Br^+ in the next step.

Step [2] Addition of the electrophile to form a carbocation



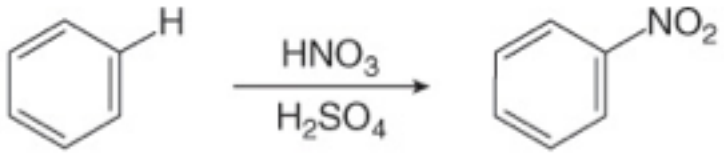
- Addition of the electrophile forms a new C – Br bond and generates a carbocation. This carbocation intermediate is resonance stabilized—**three resonance structures can be drawn.**
- The $FeBr_4^-$ also formed in this reaction is the base used in Step [3].

Step [3] Loss of a proton to re-form the aromatic ring



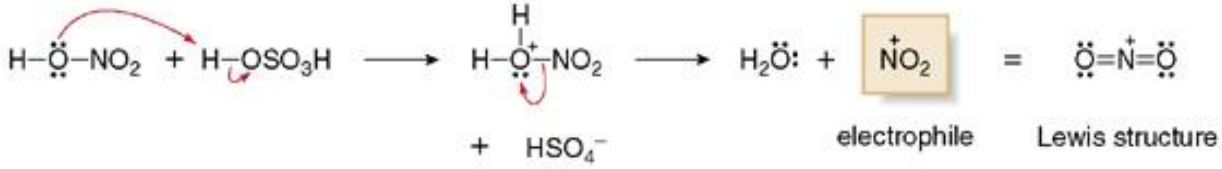
- $FeBr_4^-$ removes the proton from the carbon bearing the Br, thus re-forming the aromatic ring.
- $FeBr_3$, a catalyst, is also regenerated for another reaction cycle.

Nitration



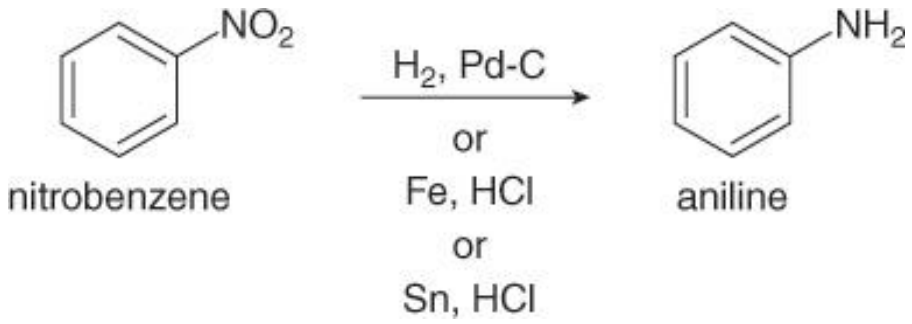
nitrobenzene

Mechanism 18.3 **Formation of the Nitronium Ion ($^+NO_2$) for Nitration**



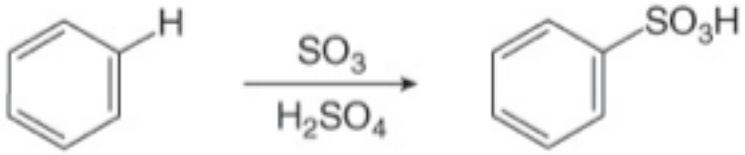
Nitro Group Reduction

Aromatic nitro groups (NO_2) can readily be reduced to amino groups (NH_2) under a variety of conditions.



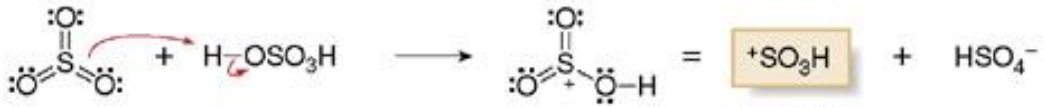
Sulfonation

Sulfonation



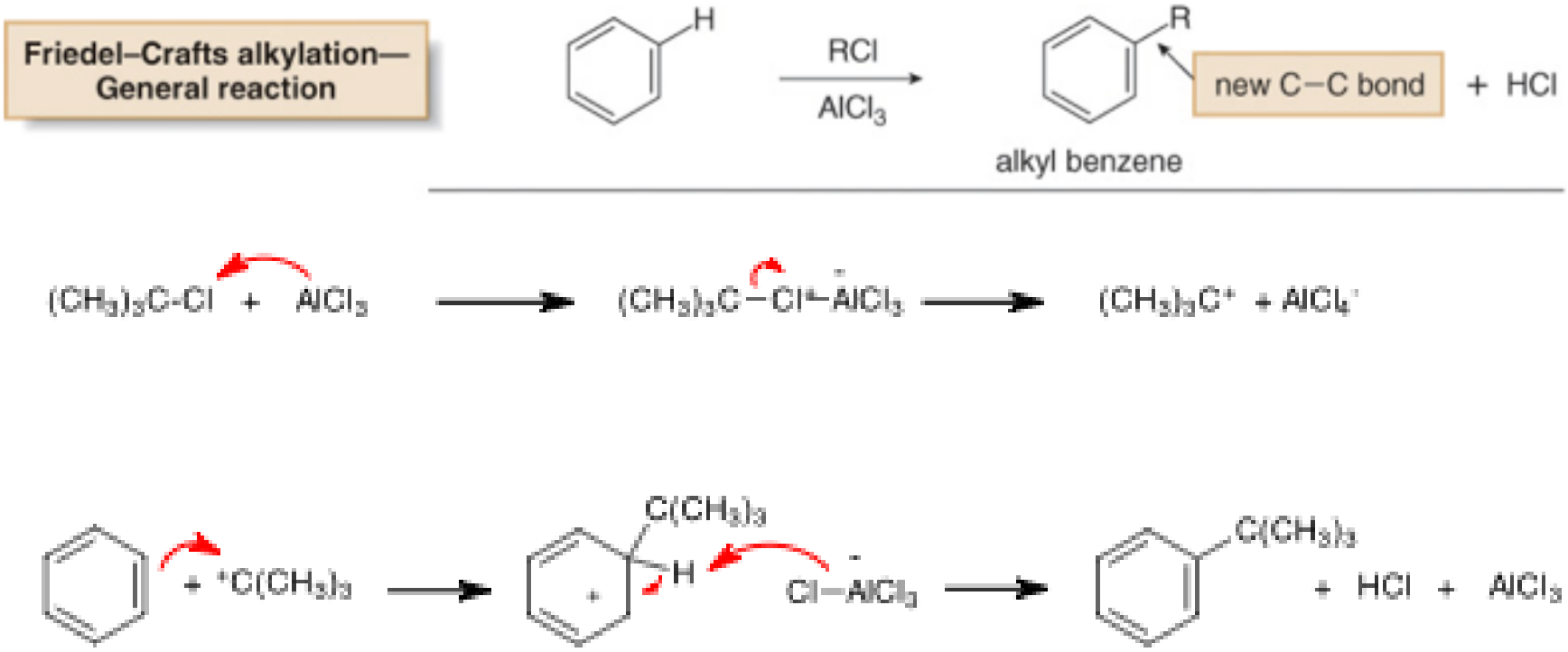
benzenesulfonic acid

Mechanism 18.4 **Formation of the Electrophile $^{+}SO_3H$ for Sulfonation**



electrophile

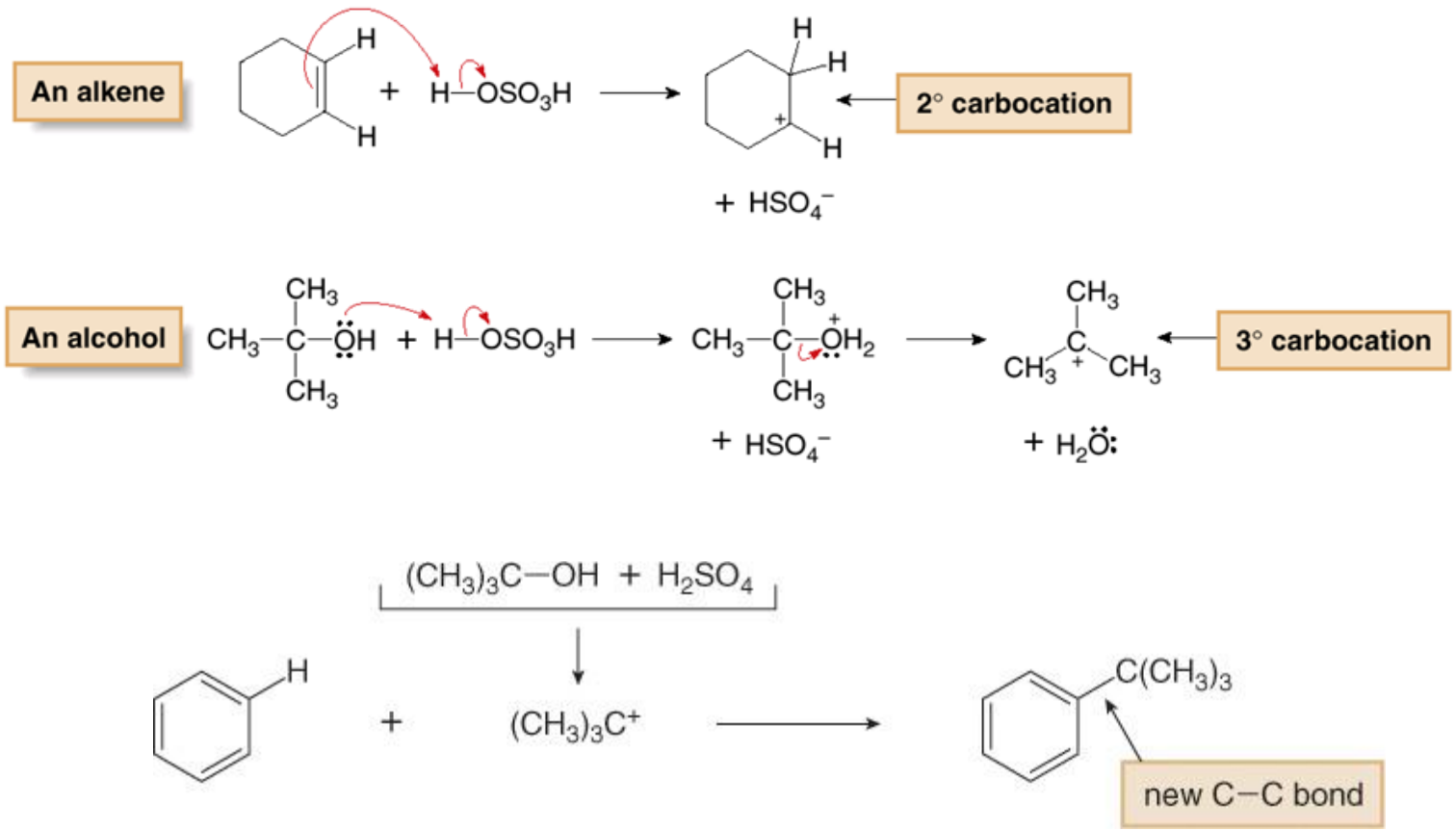
Friedel-Crafts Alkylation



Best with 2ry and 3ry halides

Friedel-Crafts Alkylation

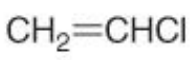
Other functional groups that form carbocations can also be used as starting materials.



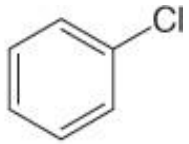
Limitations

[1] Vinyl halides and aryl halides do not react in Friedel-Crafts alkylation.

Unreactive halides in the Friedel–Crafts alkylation

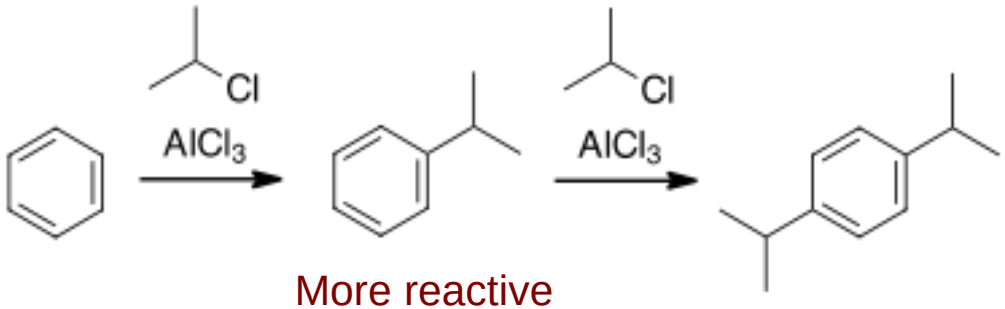


vinyl halide



aryl halide

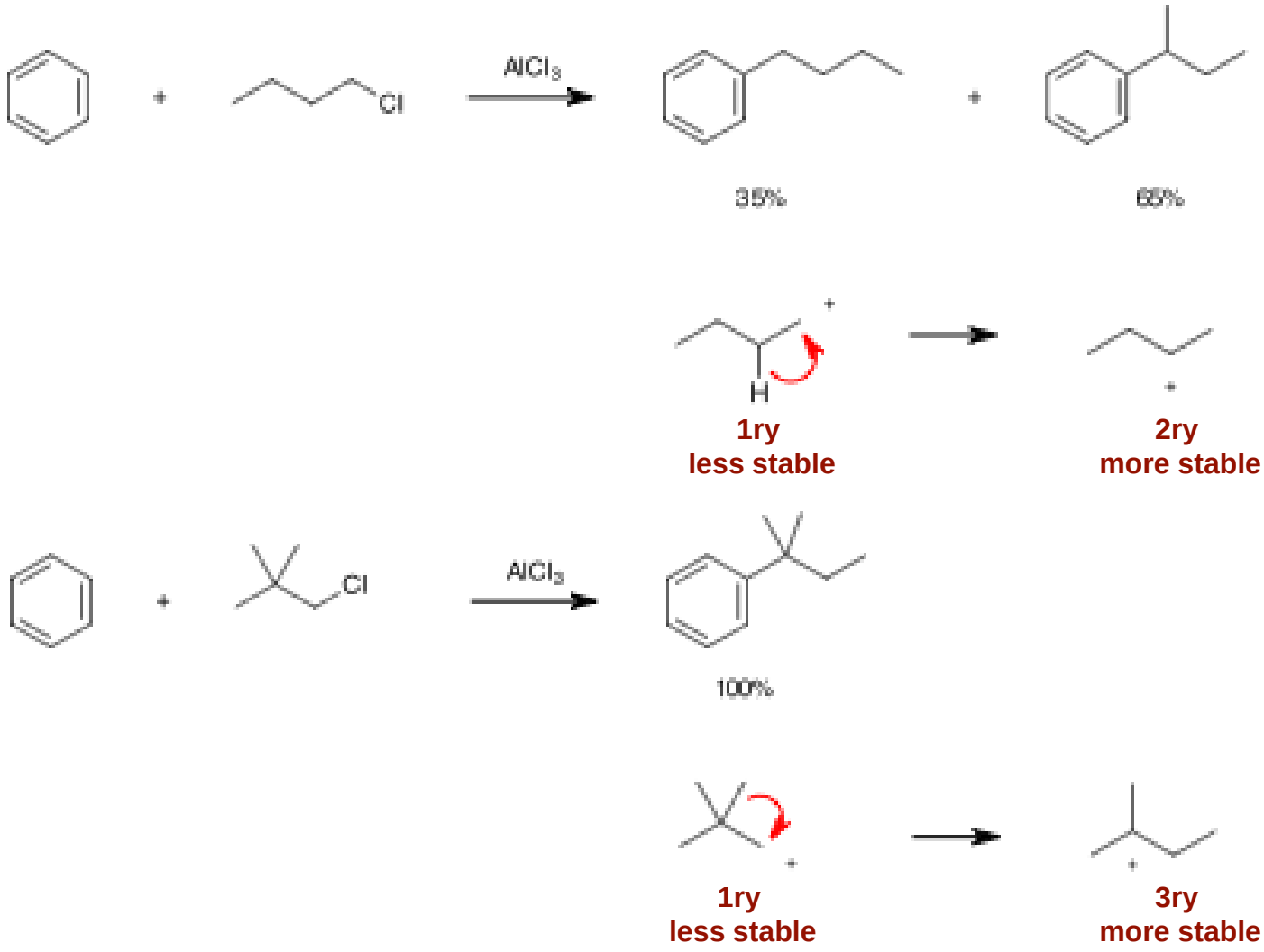
[2] Disubstituted products are obtained in F.-C. alkylations, but not in acylations.



More reactive than benzene

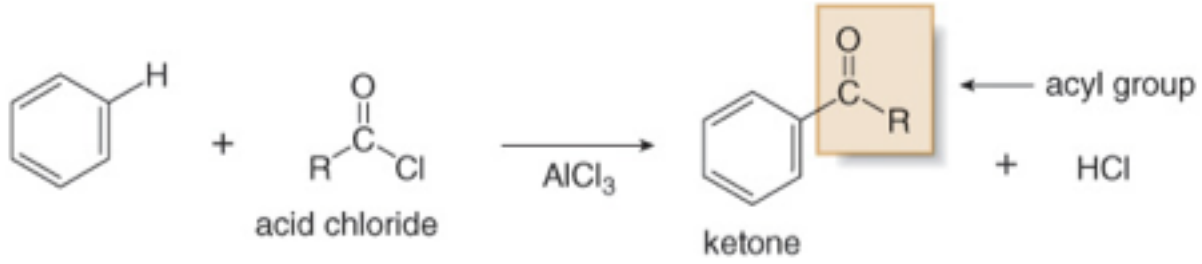
Limitations

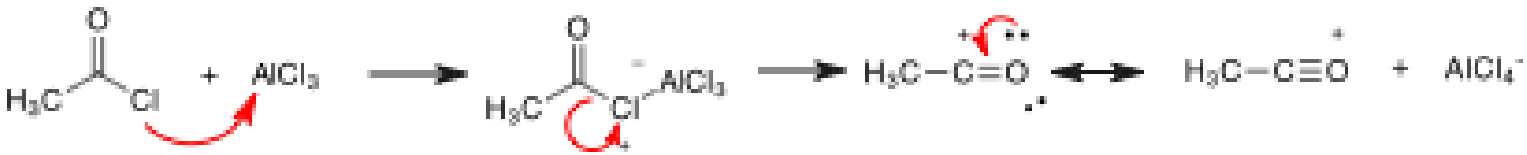
[3] Rearrangements can occur.

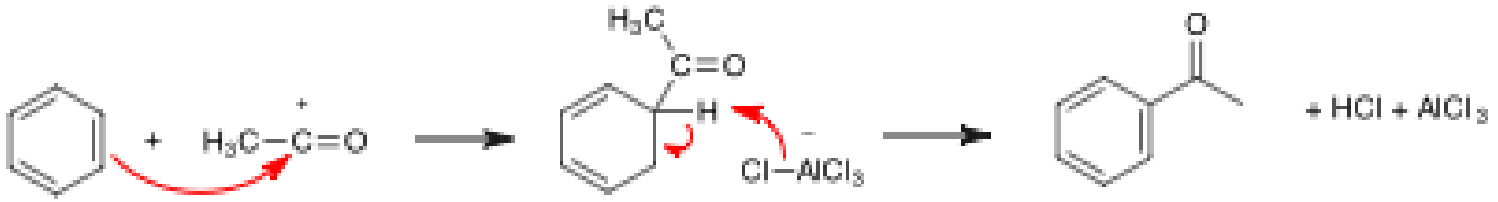


Friedel-Crafts Acylation

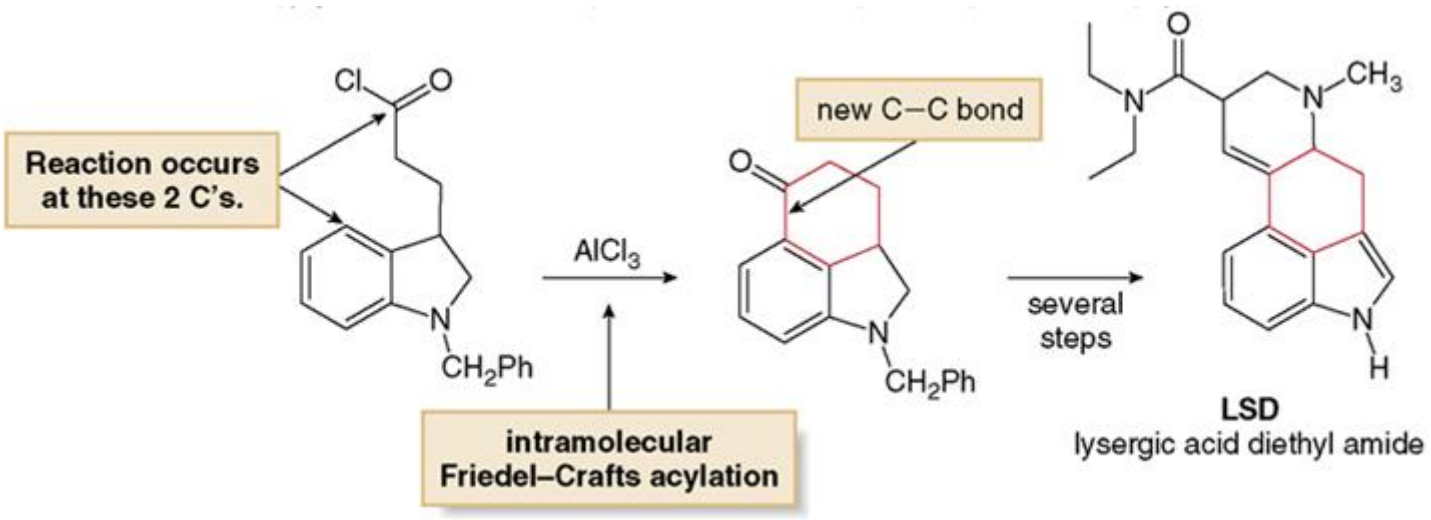
Friedel–Crafts acylation—General reaction



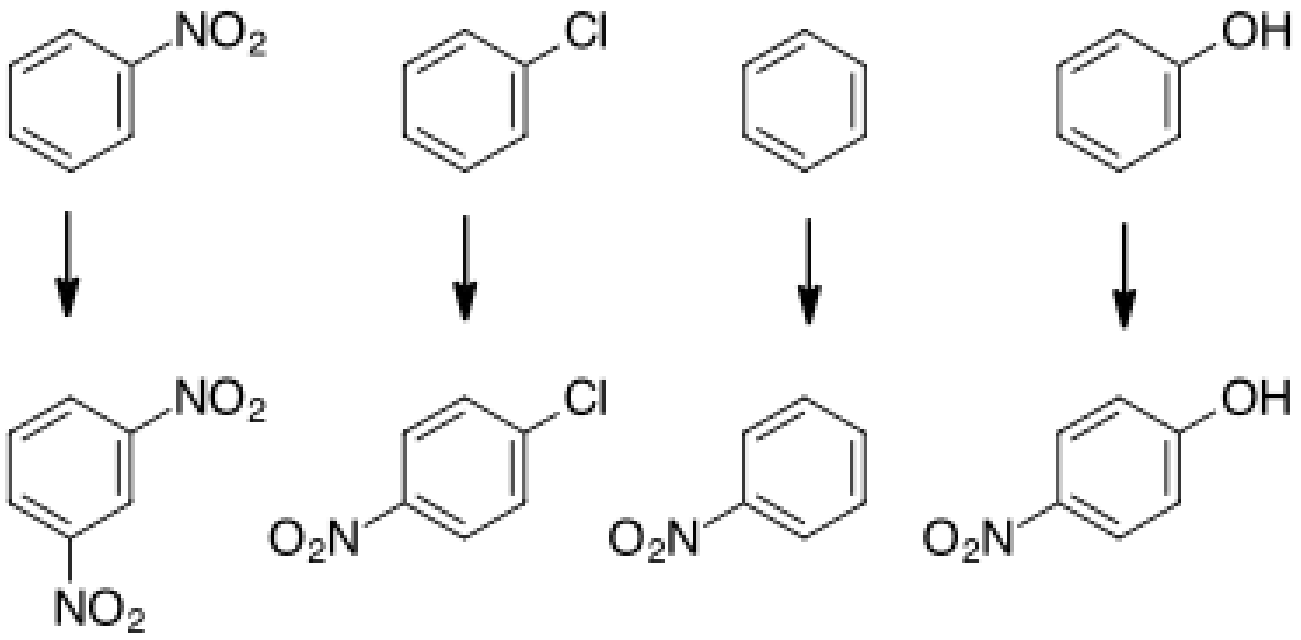




intramolecular Friedel-Crafts reactions.



Nitration of Substituted Benzenes



Relative rates	6 x 10^{-8}	0.033	1	1000

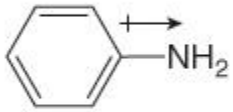
Substituents modify the electron density in the benzene ring, and this affects the course of electrophilic aromatic substitution.

Substituted Benzenes

Inductive effects (through σ bonds):

- Atoms more electronegative than carbon—including N, O, and X—pull electron density away from carbon and thus exhibit an electron-withdrawing inductive effect.
- Polarizable alkyl groups donate electron density, and thus exhibit an electron-donating inductive effect.

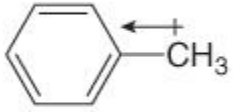
Electron-withdrawing inductive effect



- I

- N is **more electronegative** than C.
- N inductively withdraws electron density.

Electron-donating inductive effect



+ I

- Alkyl groups are **polarizable**, making them electron-donating groups.

- I	$-NH_3^+$ $-CF_3$	$-NH_2$, -NHR $-NR_2$	-OH -OR	-F -Cl -Br -I	-CHO -COR -COOH -COOR	-CN	SO_3H SO_2R	$-NO_2$
+ I	$-CH_3$ -Alkyl $-SiR_3$							

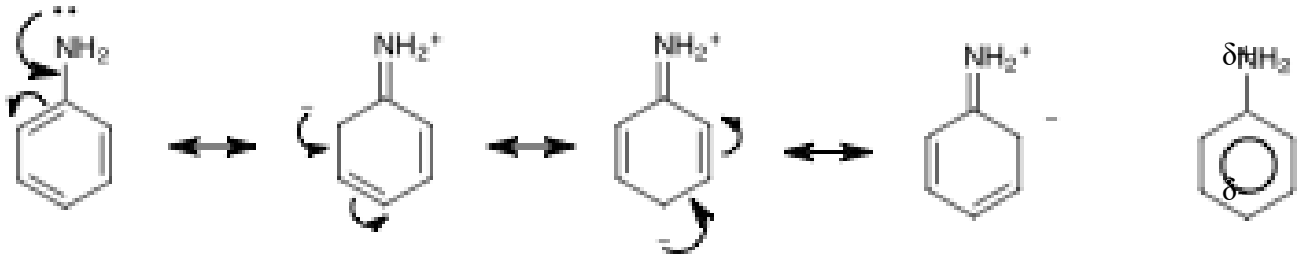
Inductive effects (through σ bonds):

- *I*	$-NH_3^+$ $-CF_3$	$-NH_2$, -NHR $-NR_2$	-OH -OR	-F -Cl -Br -I	-CHO -COR -COOH -COOR	-CN	SO_3H SO_2R	$-NO_2$
+ *I*	$-CH_3$ -Alkyl $-SiR_3$							

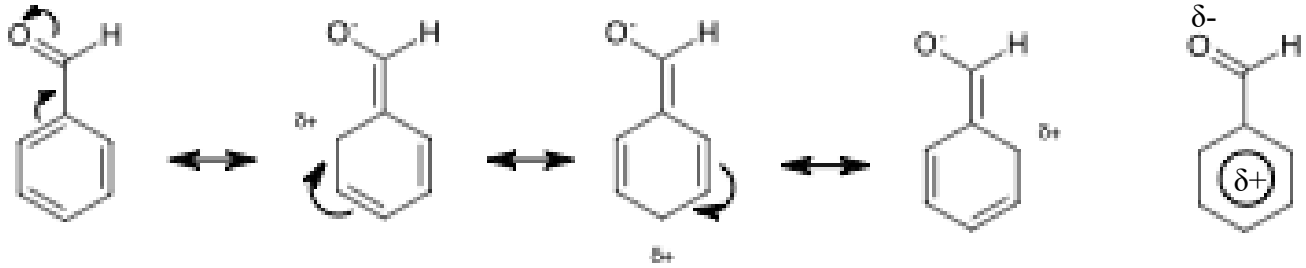
Substituted Benzenes

Resonance effects (through π bonds) are only observed with substituents containing lone pairs or π bonds.

- Substituents containing lone pairs are electron donating **(+ R)**



- Substituents –Y=Z (C_6H_5-Y=Z), where Z is more electronegative than Y are electron accepting **(- R)**



Substituted Benzenes: Activation

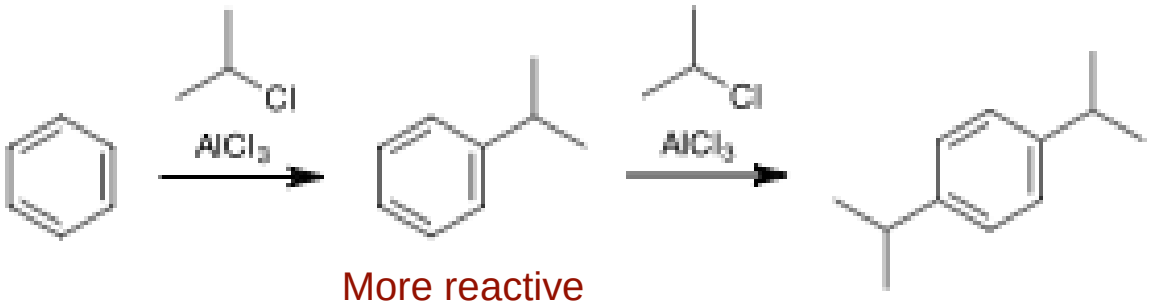
		+ R			- R			
		+R > -I		-I >+R				
- I	$-NR_3^+$ CF_3	$-NH_2$, -NHR $-NR_2$	-OH -OR	-F -Cl -Br -I	-CHO -COR -COOH -COOR	CN	SO_3H SO_2R	$-NO_2$
+ I	$-CH_3$ -Alkyl $-SiR_3$							

- Substituents that increase the electron density on the ring activate the ring towards electrophiles. Substituents that decrease the electron density on the ring deactivate the ring towards electrophiles.
- To predict whether a substituted benzene is more or less electron rich than benzene itself, we must consider the net balance of both the inductive and resonance effects.

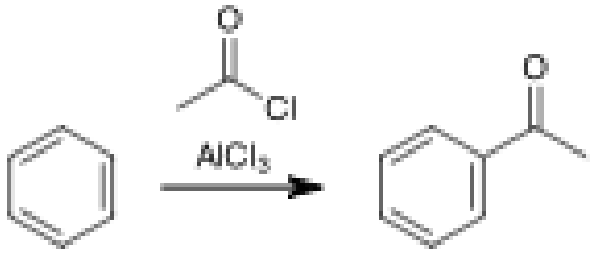
Resonance effects (through π bonds) are only observed with substituents containing lone pairs or π bonds.

		+ R			- R			
		+R > -I		-I >+R				
- I	$-NR_3^+$ CF_3	$-NH_2$, -NHR $-NR_2$	-OH -OR	-F -Cl -Br -I	-CHO -COR -COOH -COOR	CN	SO_3H SO_2R	$-NO_2$
+ I	$-CH_3$ -Alkyl $-SiR_3$							

Substituted Benzenes: Activation



More reactive
than benzene



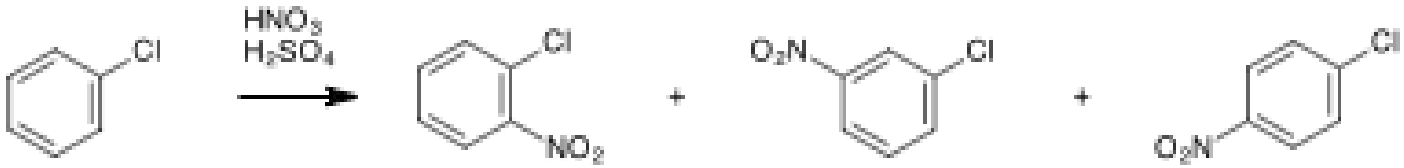
Less reactive
than benzene

Substituted Benzenes: Orientation

+R > -I (-OR, -NR_2): activating, o- p- directing

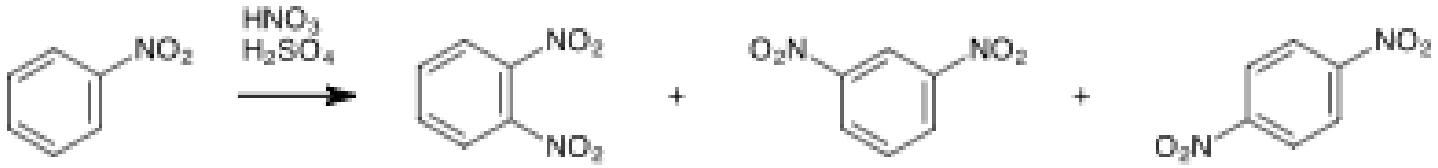
30% traces 70%

-I > +R (-F, -Cl, -Br, -I): deactivating, o- p- directing



35% traces 65%

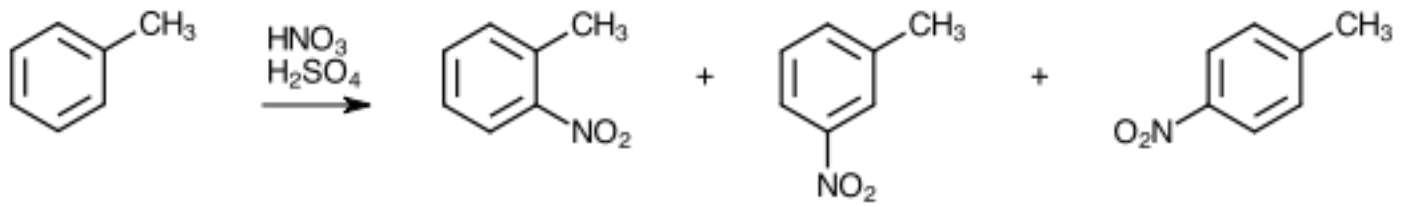
-I, -R (-NO_2, -SO3H, -CN, -COR): deactivating, m- directing.



5% 90% 5%

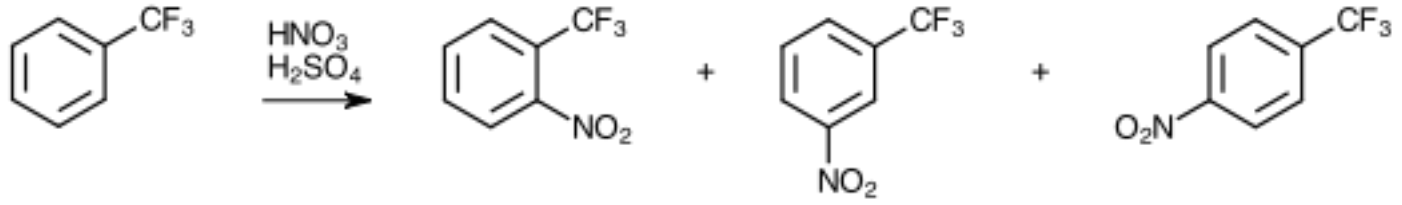
Substituted Benzenes: Orientation

+ I: activating, -o -p directing (same as + R)



58% 5% 37%

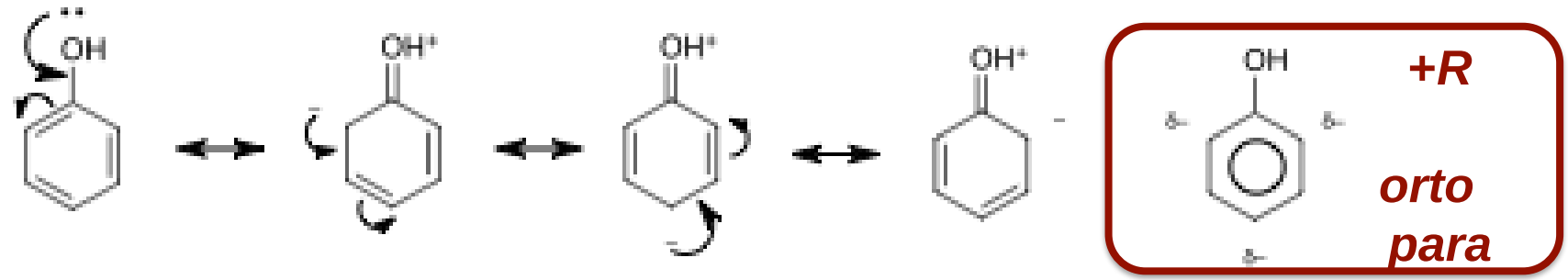
- I: deactivating, -m directing (same as - R)

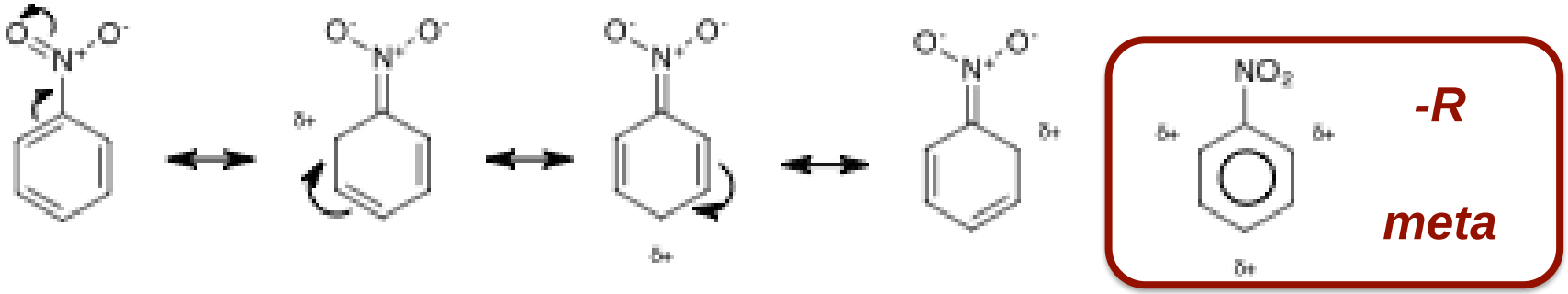


6% 91% 3%

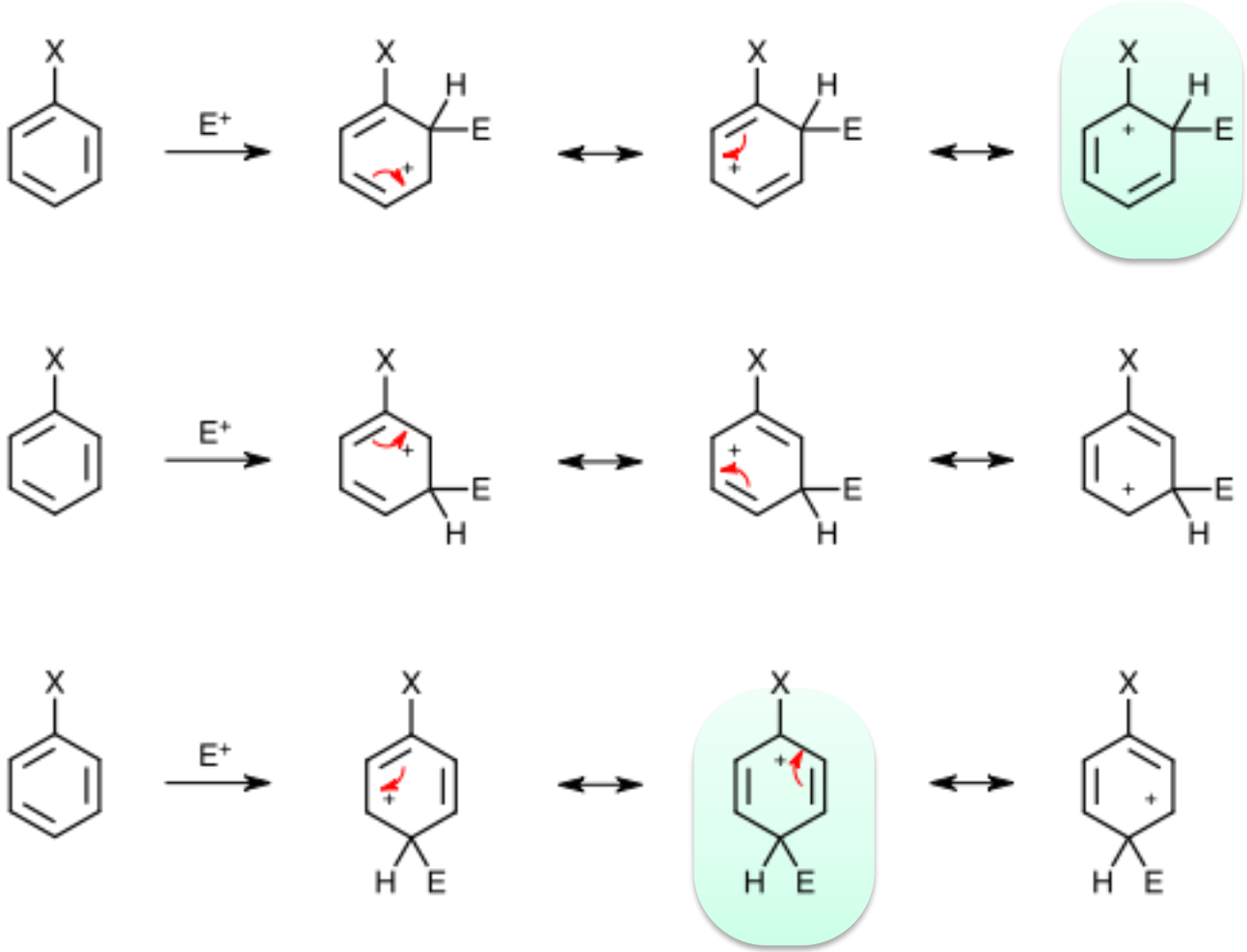
Substituted Benzenes: Orientation

The new group is located either ortho, meta, or para to the existing substituent. The resonance effect of the first substituent determines the position of the second incoming substituent





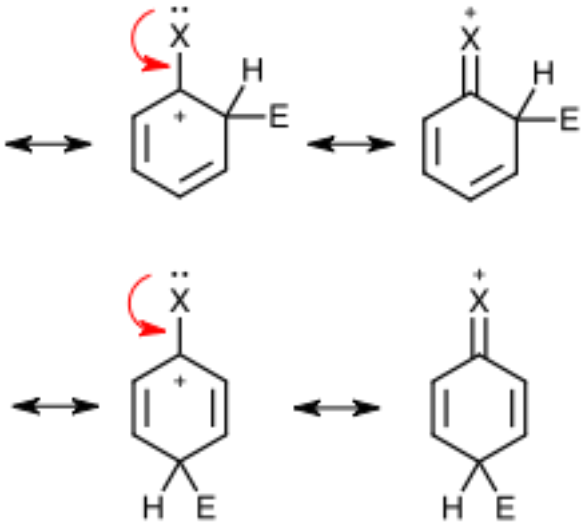
Substituted Benzenes: Orientation



Substituted Benzenes: Orientation

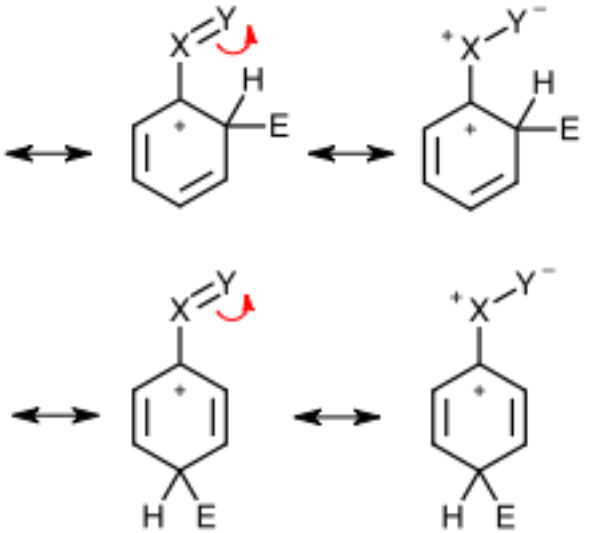
+ R

-o, -p intermediates are resonance stabilised



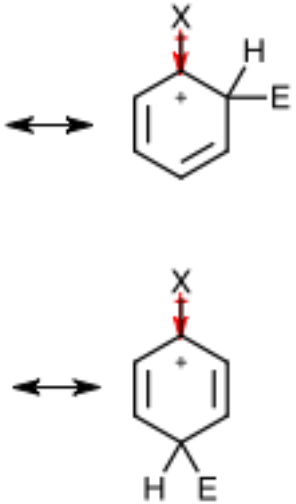
- R

-o, -p intermediates are resonance destabilised



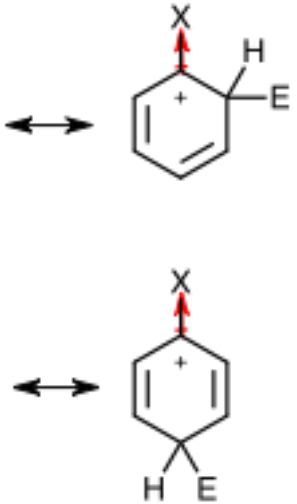
+ I

-o, -p intermediates are inductively stabilised

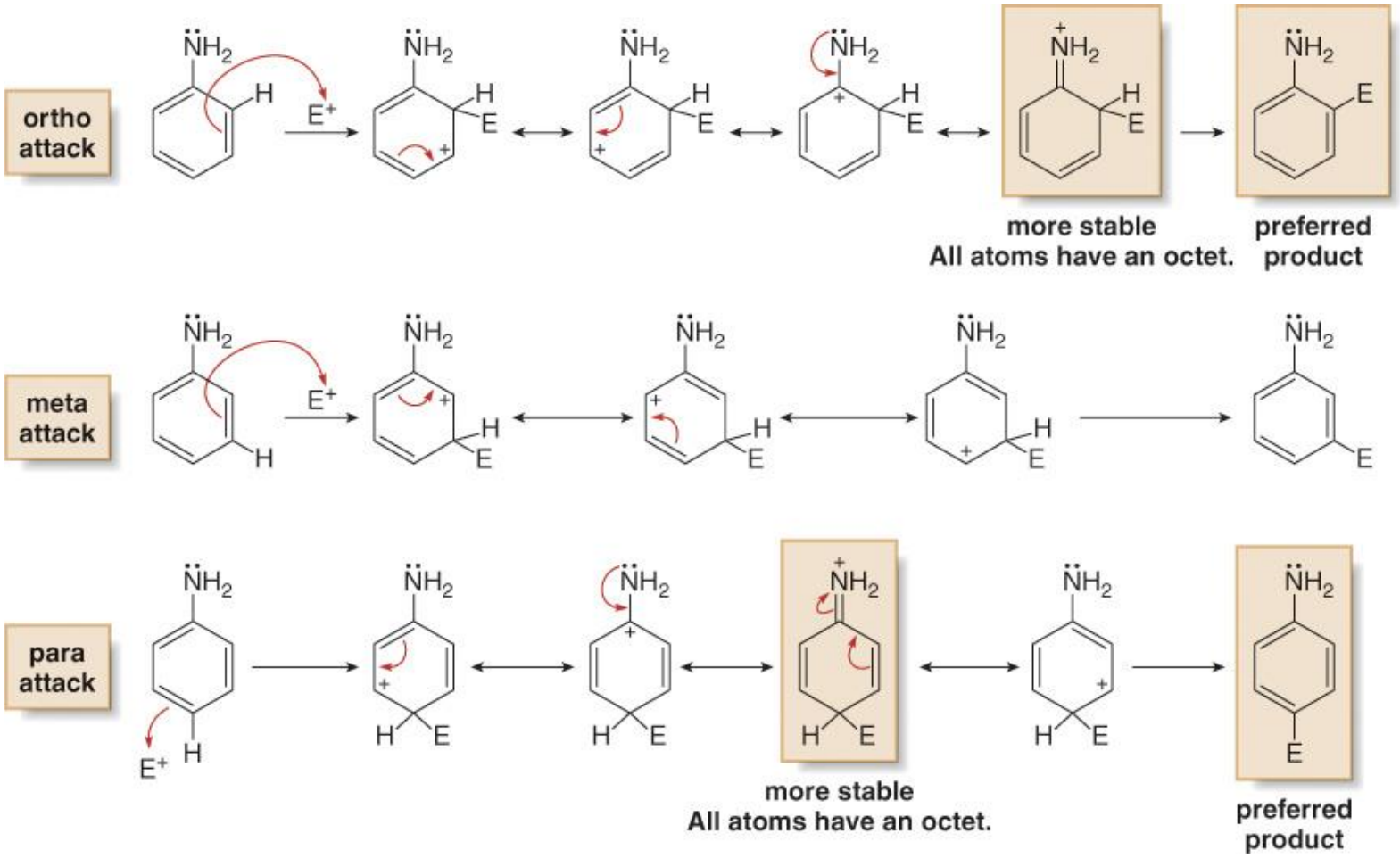


- I

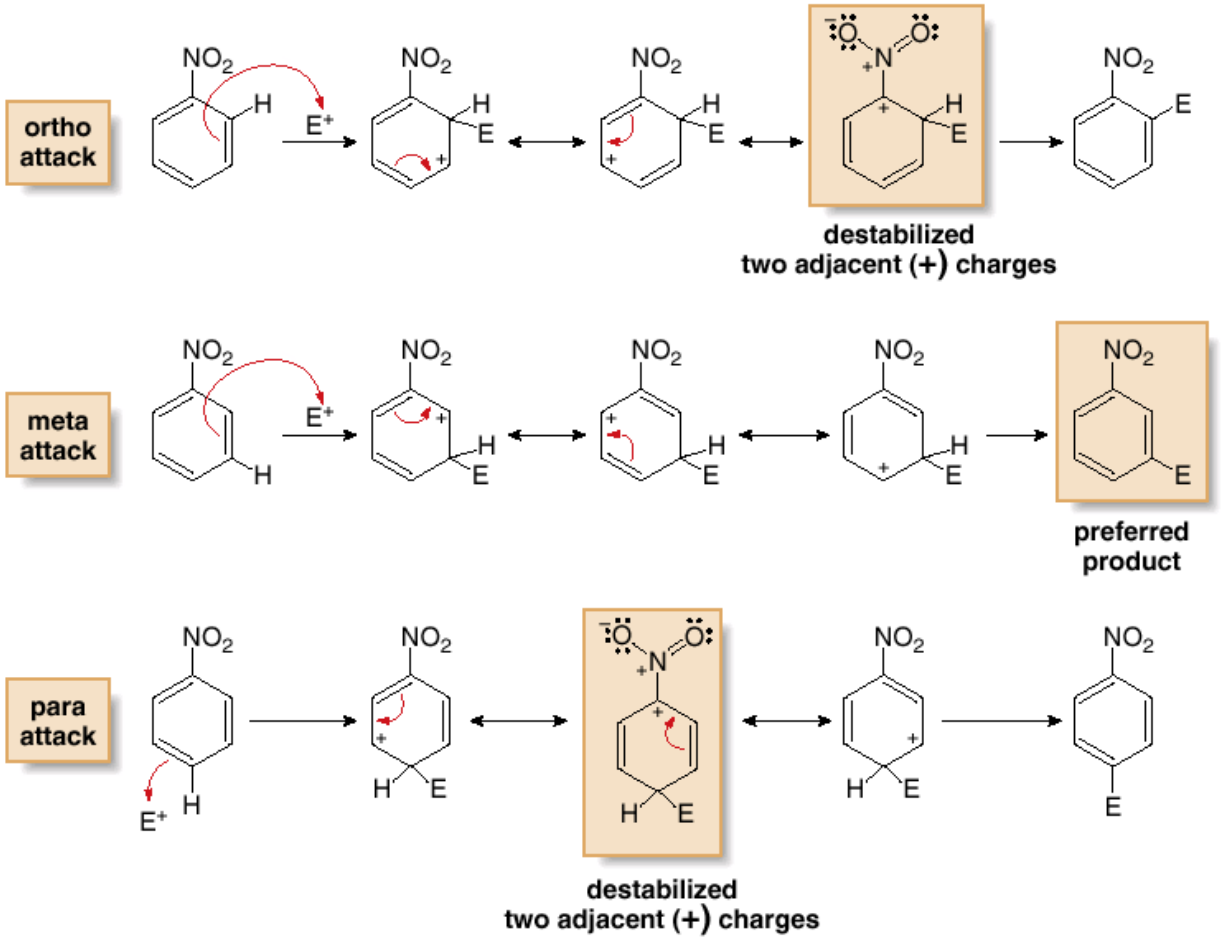
-o, -p intermediates are inductively destabilised



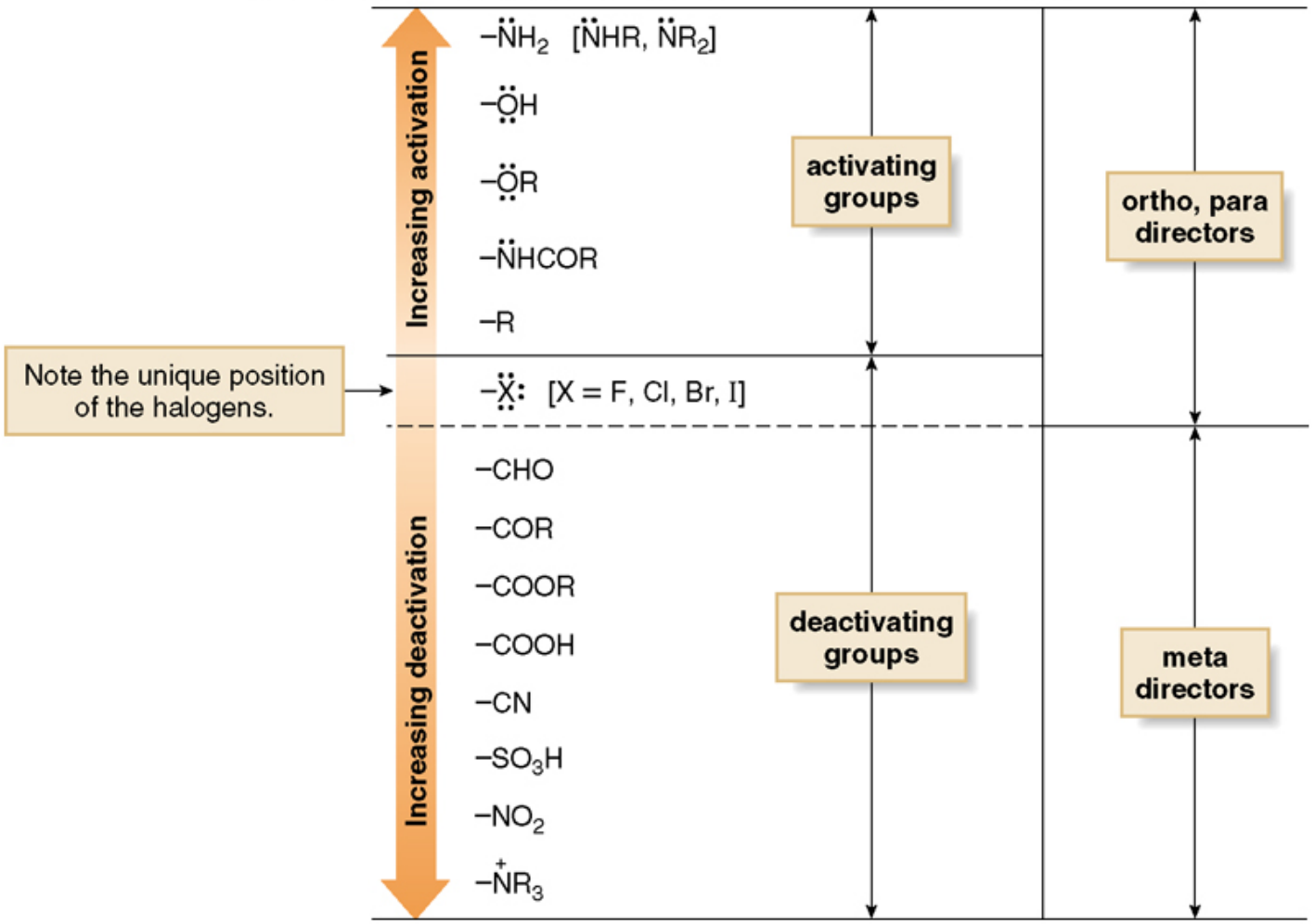
Substituent Effects. Alternative Explanation



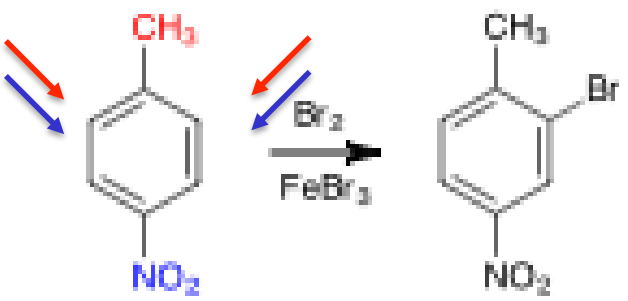
Substituent Effects. Alternative Explanation

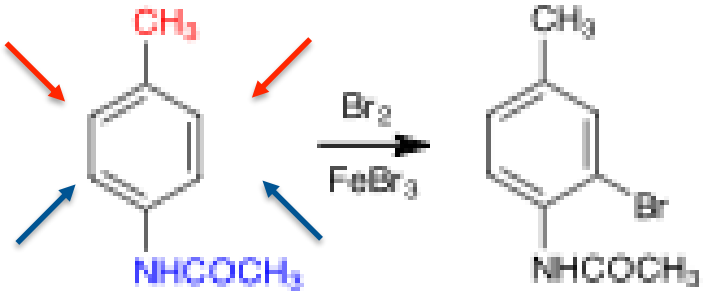


Substituent Effects. Summary

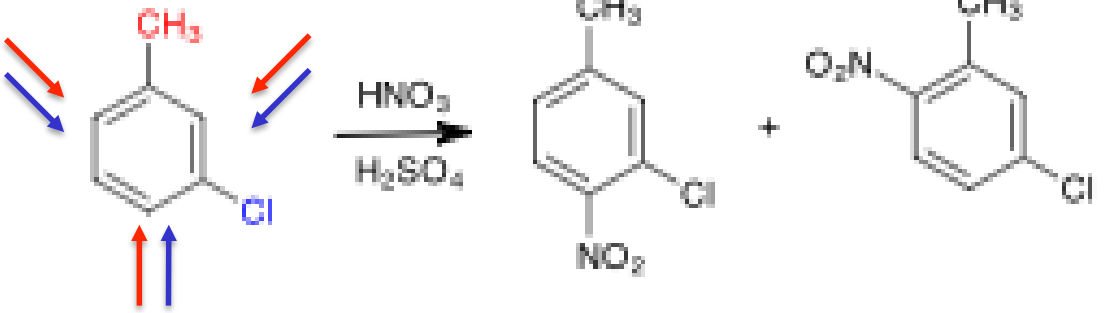


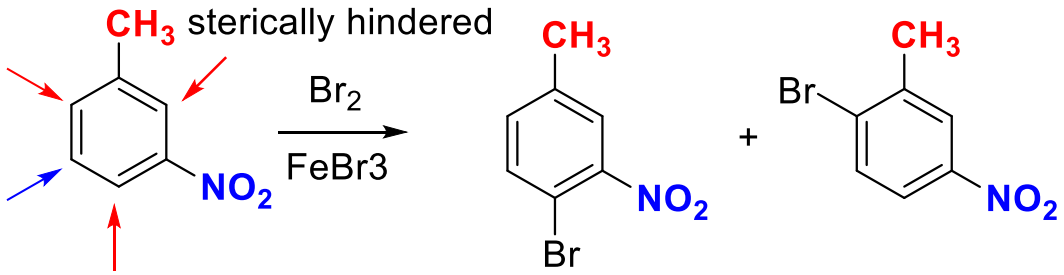
Disubstituted Benzenes



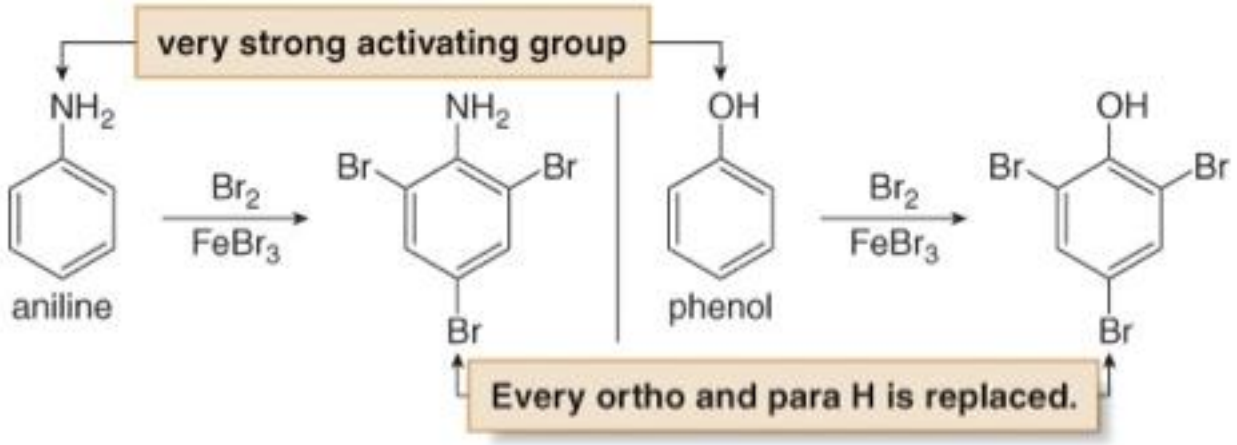


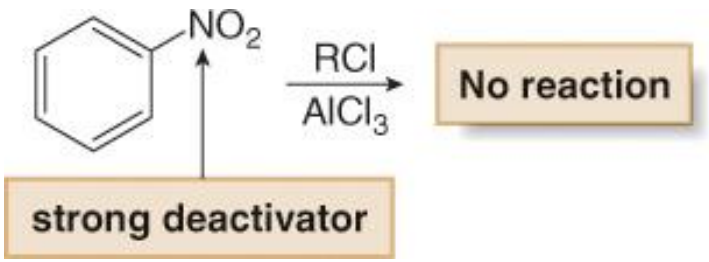
sterically hindered



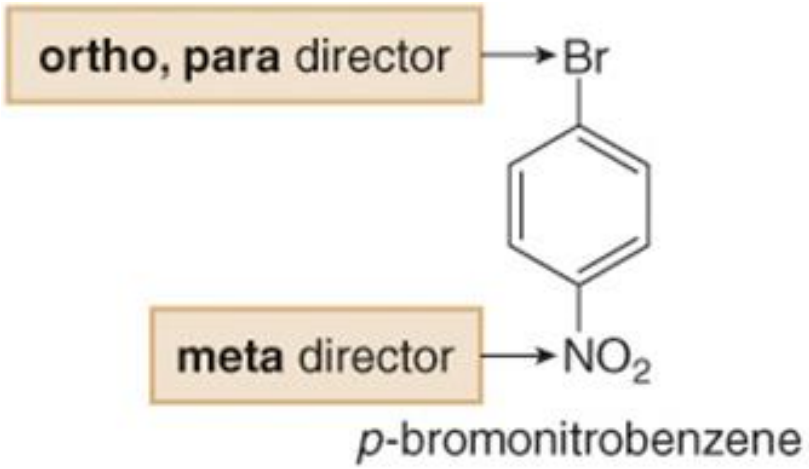


Further Examples





Synthesis of Polysubstituted Benzenes



p-bromonitrobenzene

Synthesis of Polysubstituted Benzenes

Pathway [1]: Bromination before nitration

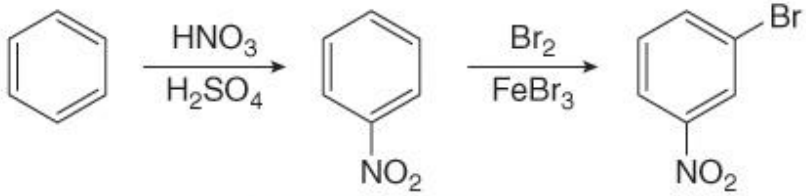
ortho, para director

para product

The ortho isomer can be separated from the mixture.

This pathway gives the desired product.

Pathway [2]: Nitration before bromination

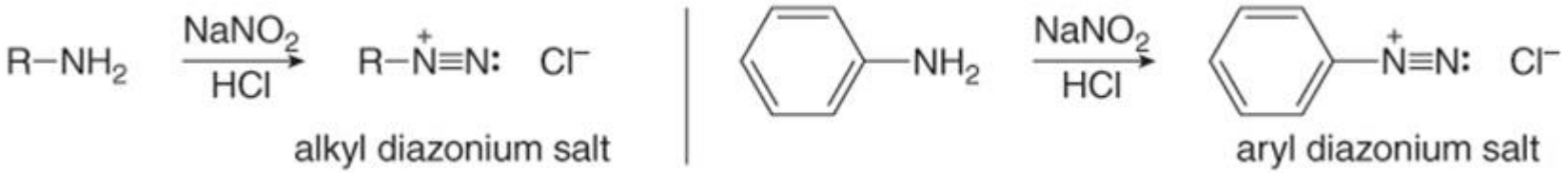


meta director

meta isomer

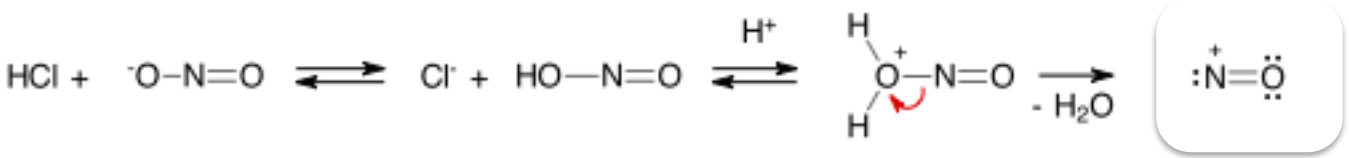
This pathway does NOT form the desired product.

Reaction of Amines with Nitrous Acid



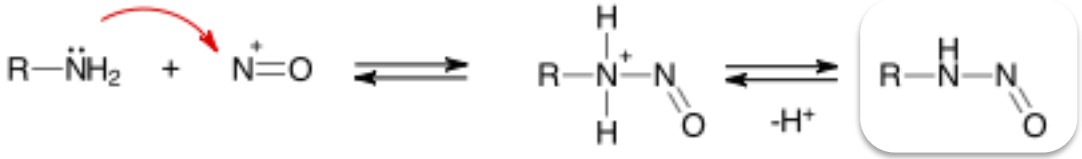
Reaction of Amines with Nitrous Acid

1. generation of the electrophile



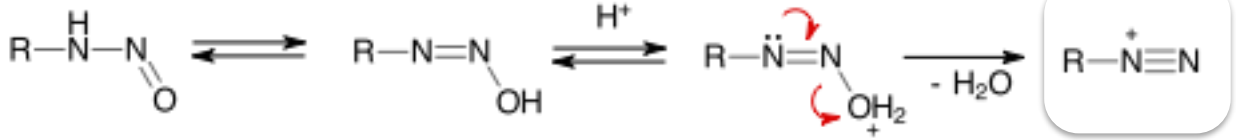
nitrosonium ion

2. nitrosation



N-nitrosamine

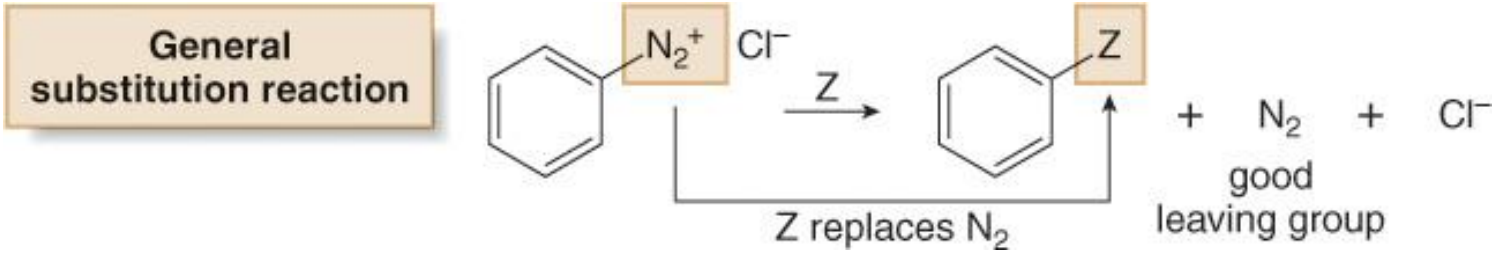
3. acid-catalysed elimination



diazonium ion

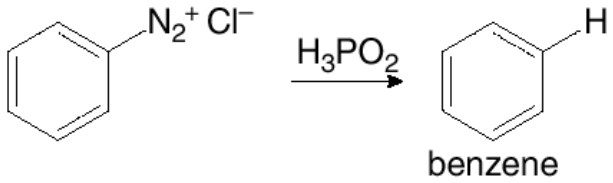
Substitution Reactions of Aryl Diazonium Salts

- Alkyl diazionium salts are unstable and decompose giving carbocations and N_2
- Aryl diazonium salts react with a variety of reagents to form products in which a nucleophile Z replaces N_2, a very good leaving group.
- The mechanism of these reactions varies with the identity of Z.



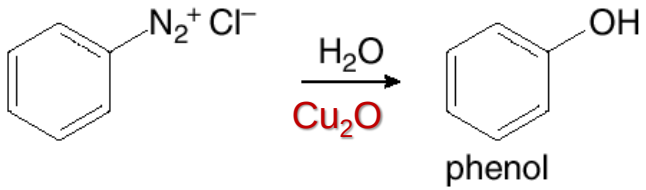
Substitution Reactions of Aryl Diazonium

Substitution by H—Synthesis of benzene



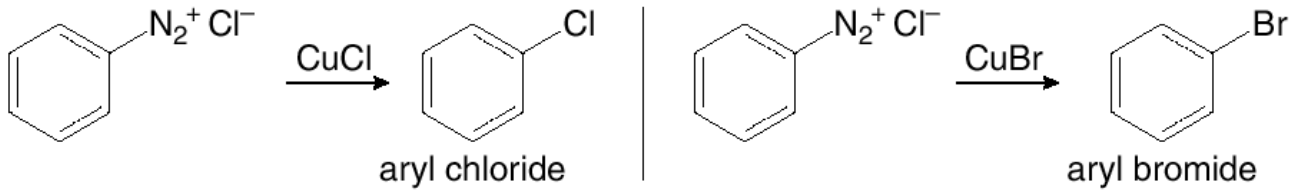
A diazonium salt reacts with hypophosphorus acid to form benzene. This reaction is useful in synthesizing compounds that have substitution patterns that are not available by other means.

Substitution by OH—Synthesis of phenols



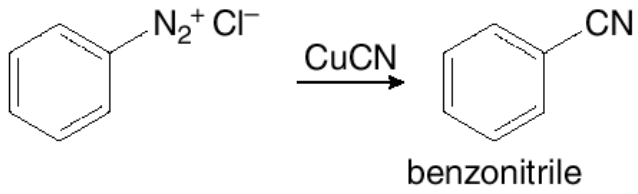
Substitution Reactions of Aryl Diazonium

Substitution by Cl or Br—Synthesis of aryl chlorides and bromides



This is called the Sandmeyer reaction. It provides an alternative to direct chlorination and bromination of the aromatic ring using Cl_2 or Br_2 and a Lewis acid catalyst.

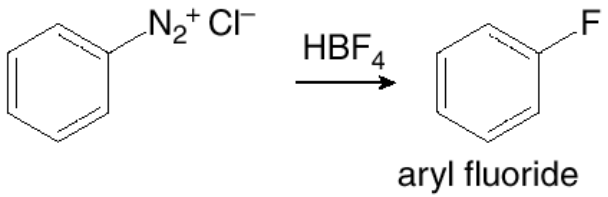
Substitution by CN—Synthesis of benzonitriles



Since the cyano group can be converted into a variety of other functional groups, this reaction provides easy access to a wide variety of benzene derivatives.

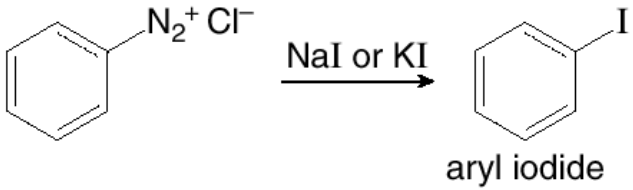
Substitution Reactions of Aryl Diazonium Salts

Substitution by F—Synthesis of aryl fluorides



This is a useful reaction because aryl fluorides cannot be produced by direct fluorination with F_2 and a Lewis acid catalyst.

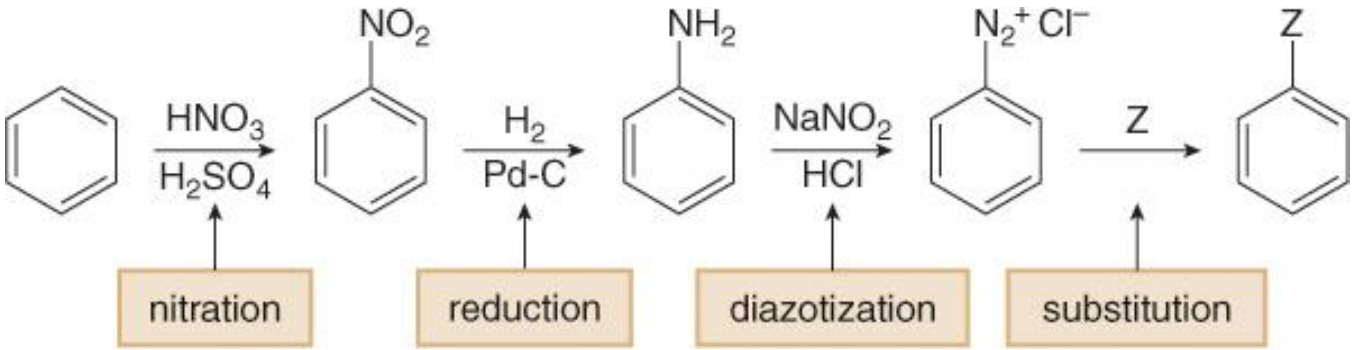
Substitution by I—Synthesis of aryl iodides



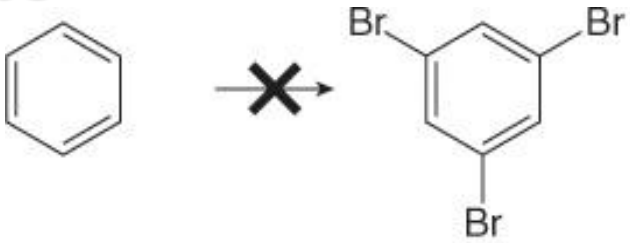
This is a useful reaction because aryl iodides cannot be produced by direct iodination with I_2 and a Lewis acid catalyst.

Substitution Reactions of Aryl Diazonium Salts

Diazonium salts provide easy access to many different benzene derivatives. Keep in mind the following four-step sequence, because it will be used to synthesize many substituted benzenes.

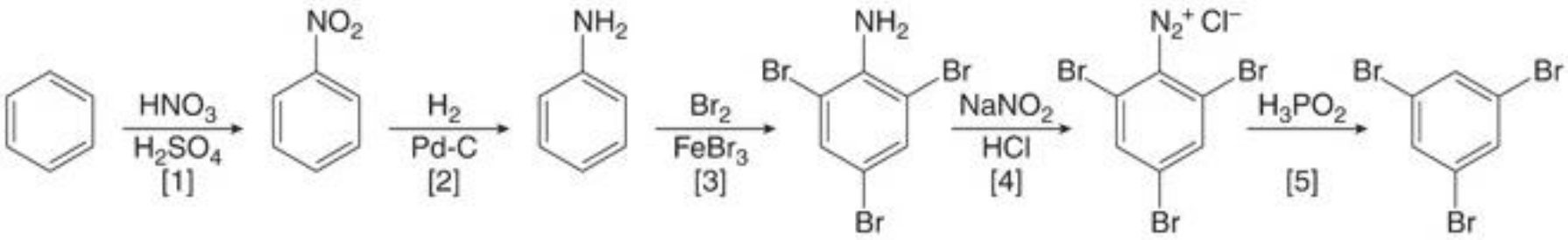


Substitution Reactions of Aryl Diazonium Salts



1,3,5-tribromobenzene

The Br atoms are ortho, para directors located meta to each other.

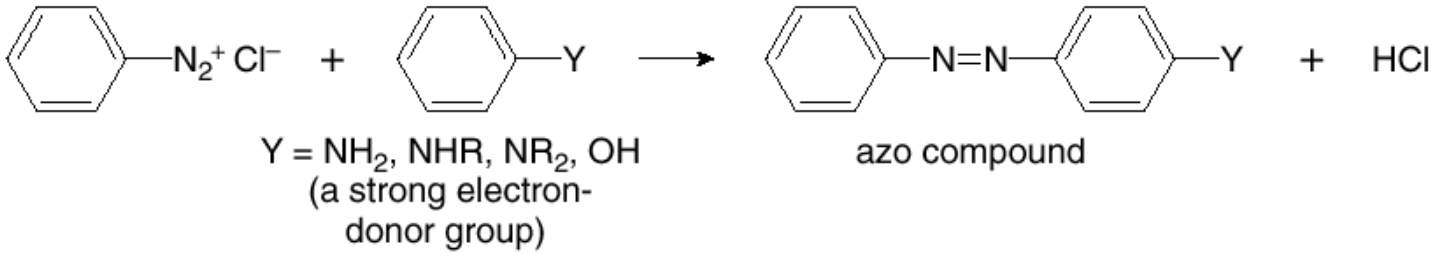


- Nitration followed by reduction forms aniline ($C_6H_5NH_2$) from benzene (Steps [1] and [2]).
- Bromination of aniline yields the tribromo derivative in Step [3].
- The NH_2 group is removed by a two-step process: diazotization with $NaNO_2$ and HCl (Step [4]), followed by substitution of the diazonium ion by H with H_3PO_2.

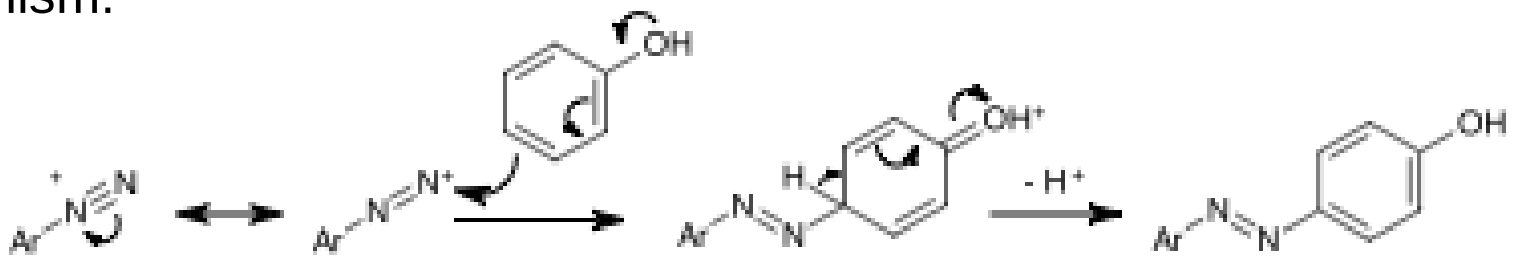
Coupling Reactions of Aryl Diazonium Salts

- When a diazonium salt is treated with an aromatic compound activated by a strong electron-donor group, a substitution reaction takes place giving an azo compound.

Azo coupling



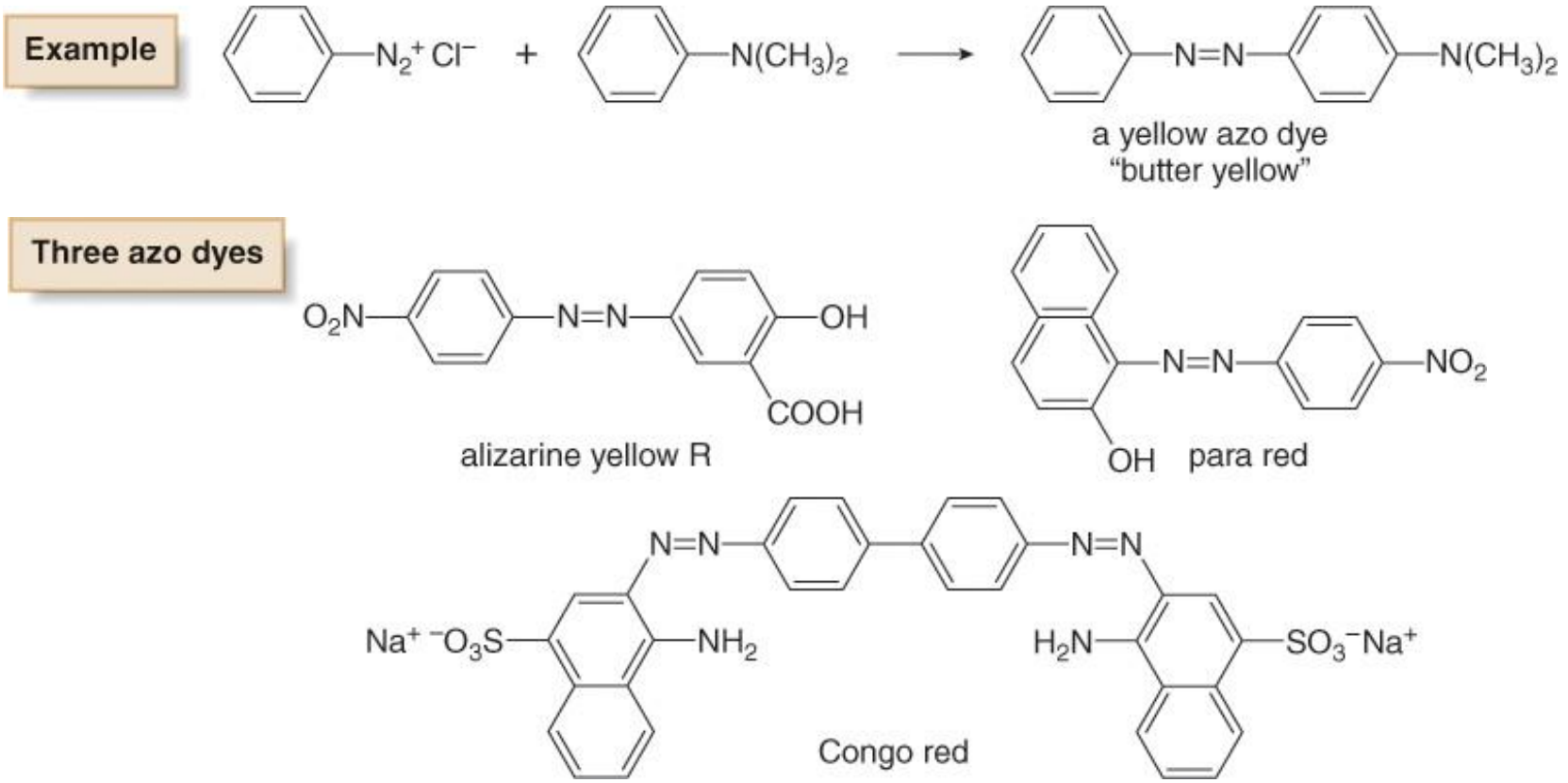
Mechanism:



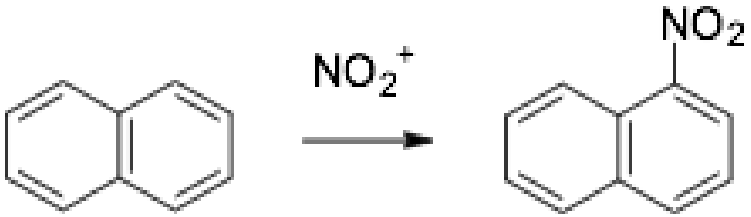
The para position is preferred for steric reasons

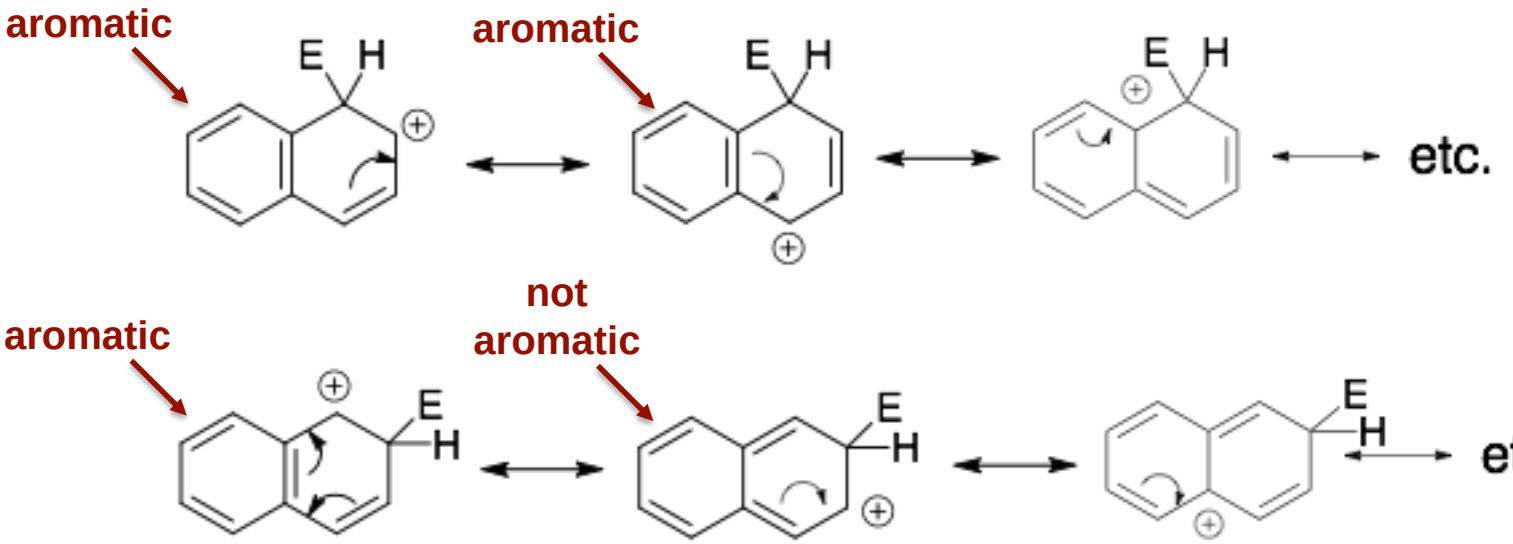
Azo Dyes

- Azo compounds are highly conjugated, rendering them colored. Many of these compounds are synthetic dyes. Butter yellow was once used to color margarine.

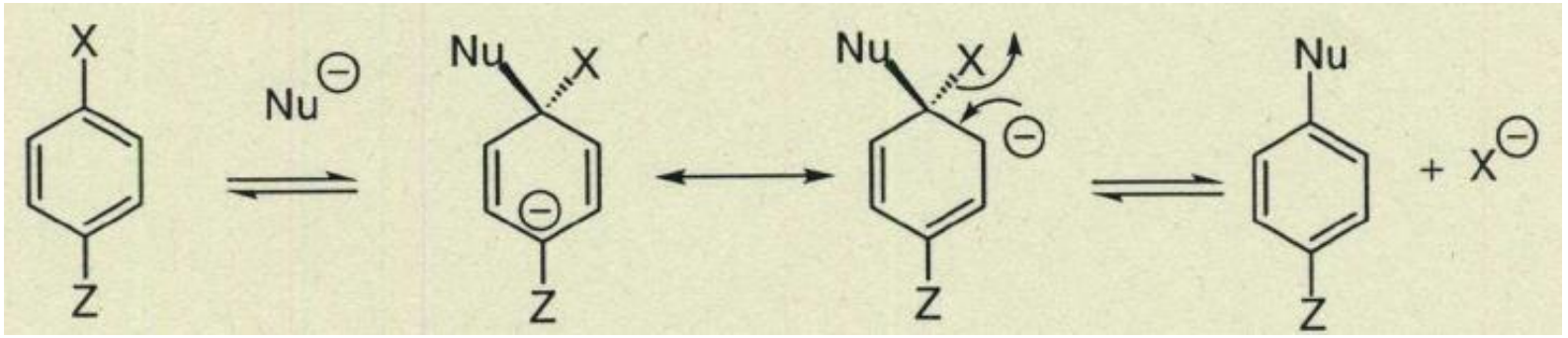


S_EAr in Polyciclic Aromatic Compounds



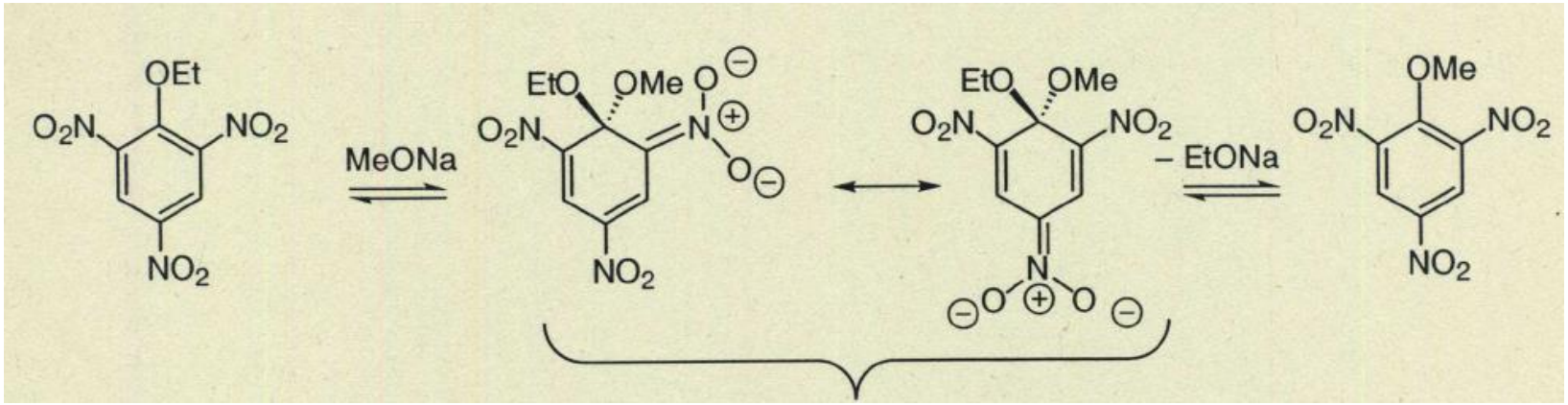


Nucleophilic Aromatic Substitutions, S_NAr



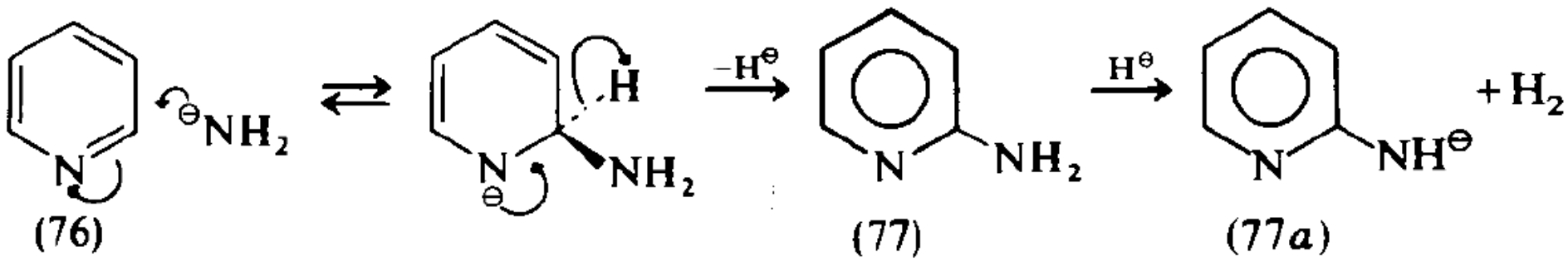
Z = Electron Accepting Substituent (sigma or π: NO_2, CN, N_2^+, SO_2R)
X = Leaving Group

Example



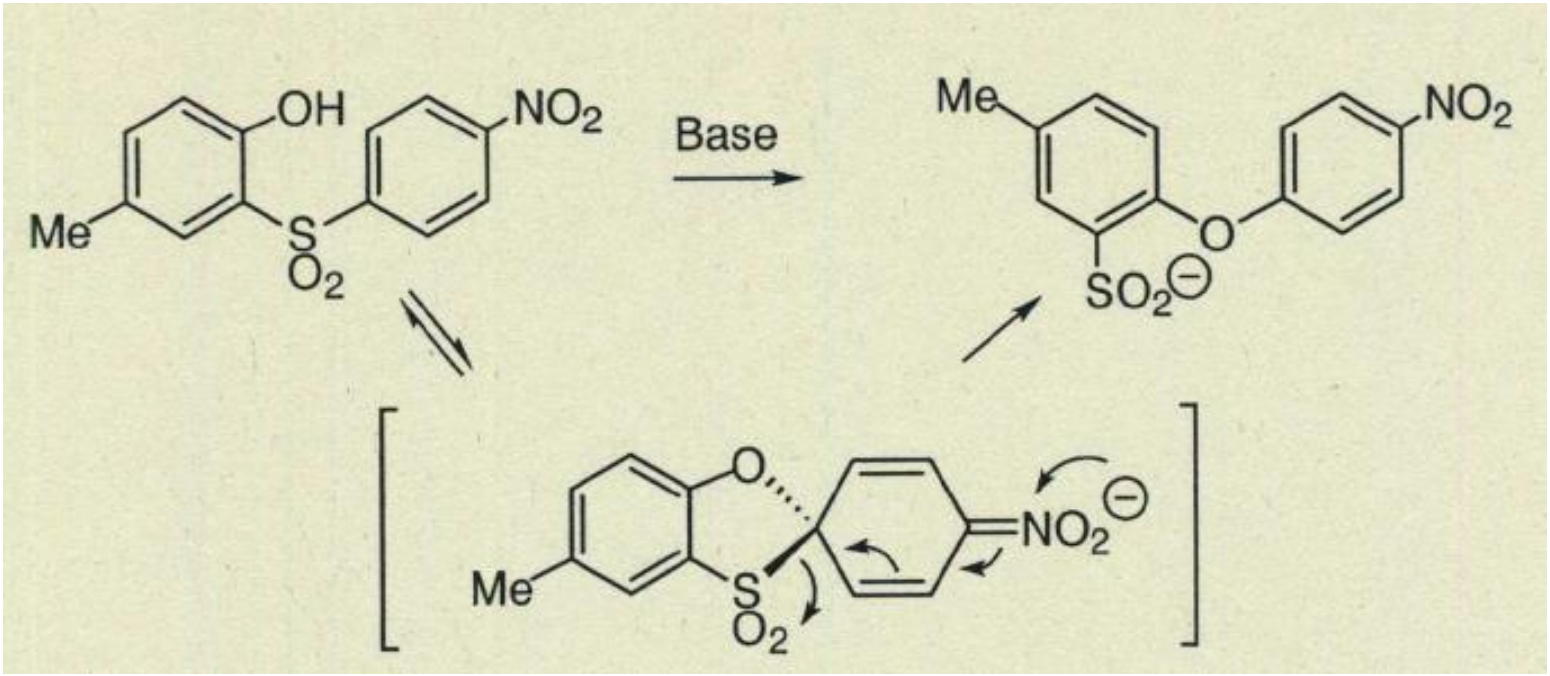
Examples of S_NAr

1)



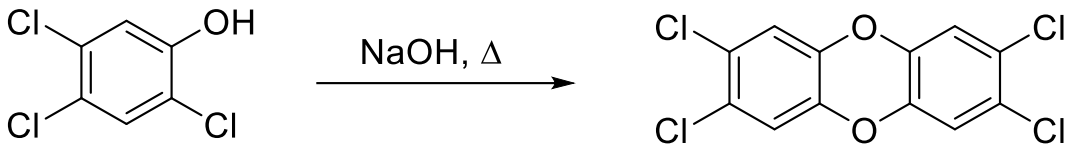
(76) (77) (77a)

2)



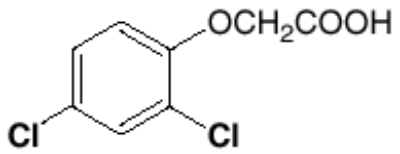
Examples of S_NAr

3)

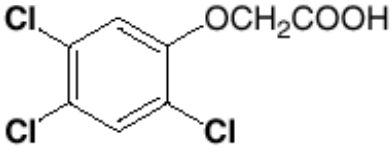


2,3,7,8-tetraclorodibenzo-*p*-diossina (TCDD)

Herbicides were used extensively during the Vietnam War to defoliate dense jungle areas. The concentration of certain herbicide by-products in the soil remains high today.

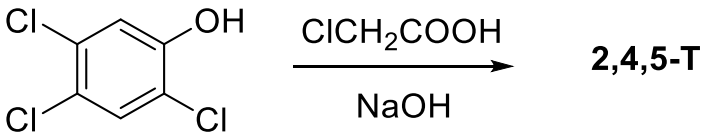


2,4-D
2,4-dichlorophenoxy-acetic acid herbicide



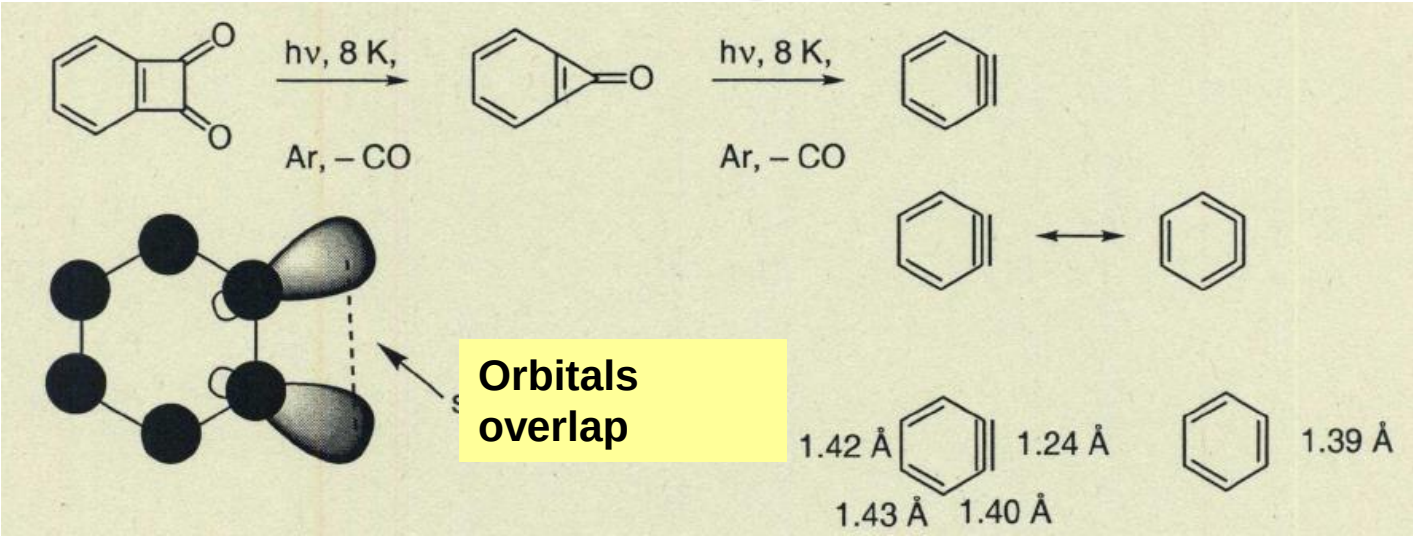
2,4,5-T
2,4,5-trichlorophenoxy-acetic acid herbicide

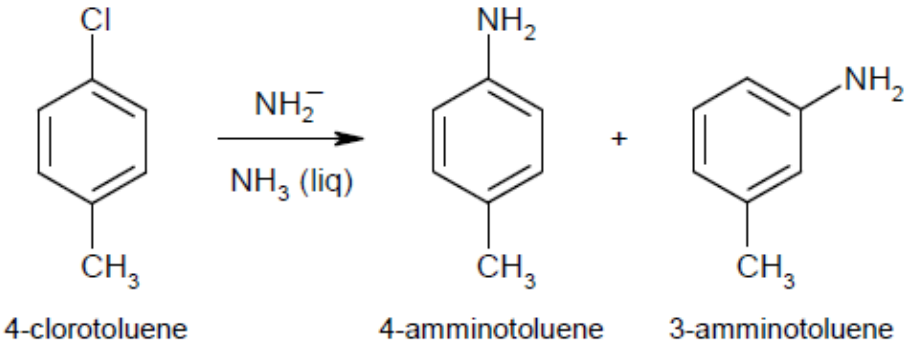
the active components in **Agent Orange**, a defoliant used in the Vietnam War

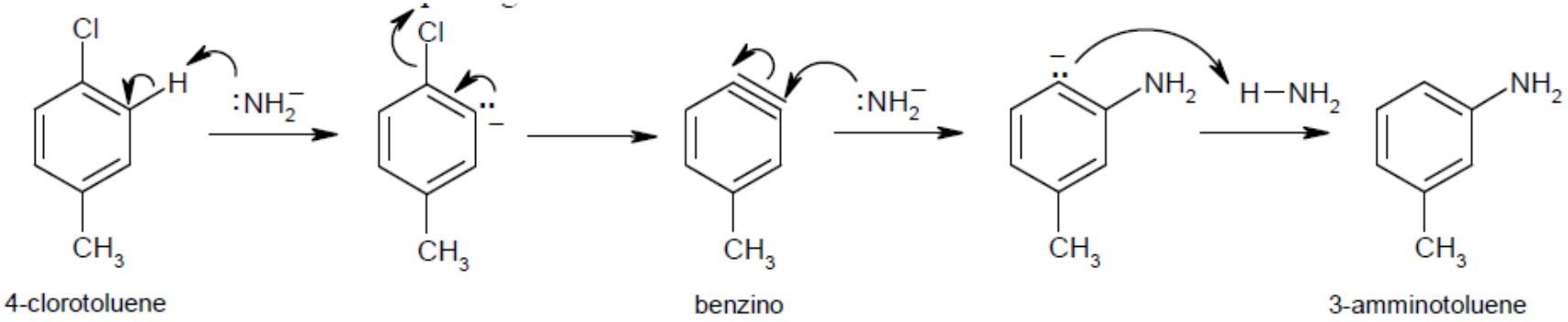


2,4,5-T

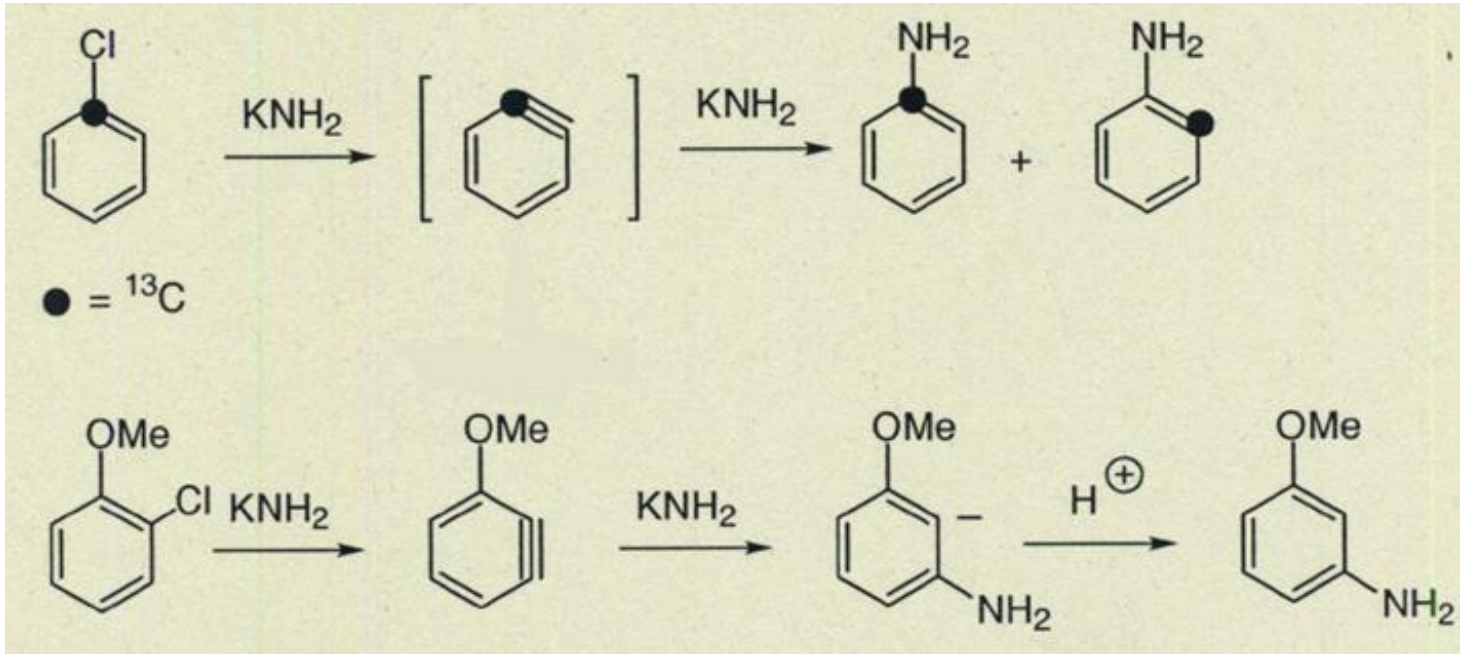
Benzyne


hν, 8 K,
Ar, – CO
hν, 8 K,
Ar, – CO
Orbitals overlap
1.42 Å
1.24 Å
1.39 Å
1.43 Å
1.40 Å


Cl
CH3
NH2−
NH3 (liq)
NH2
NH2
CH3
CH3
+
4-clorotoluene
4-amminotoluene
3-amminotoluene

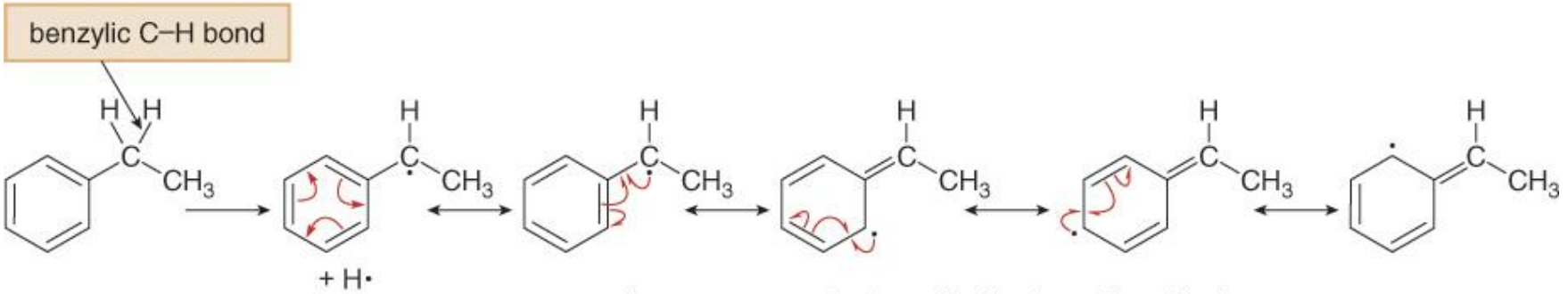

Cl
H
:NH2−
Cl
CH3
CH3
:NH2−
NH2
H—NH2
NH2
CH3
CH3
CH3
4-clorotoluene
benzino
3-amminotoluene

Benzyne

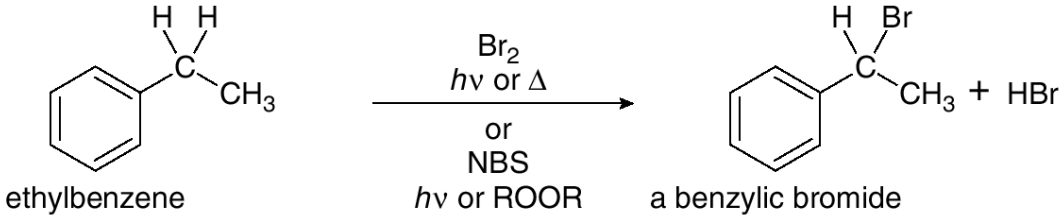


Side Chain Reactivity: Radical Halogenation

Benzylic C—H bonds are weaker than most other sp^3 hybridized C—H bonds, because homolysis forms a resonance-stabilized benzylic radical.



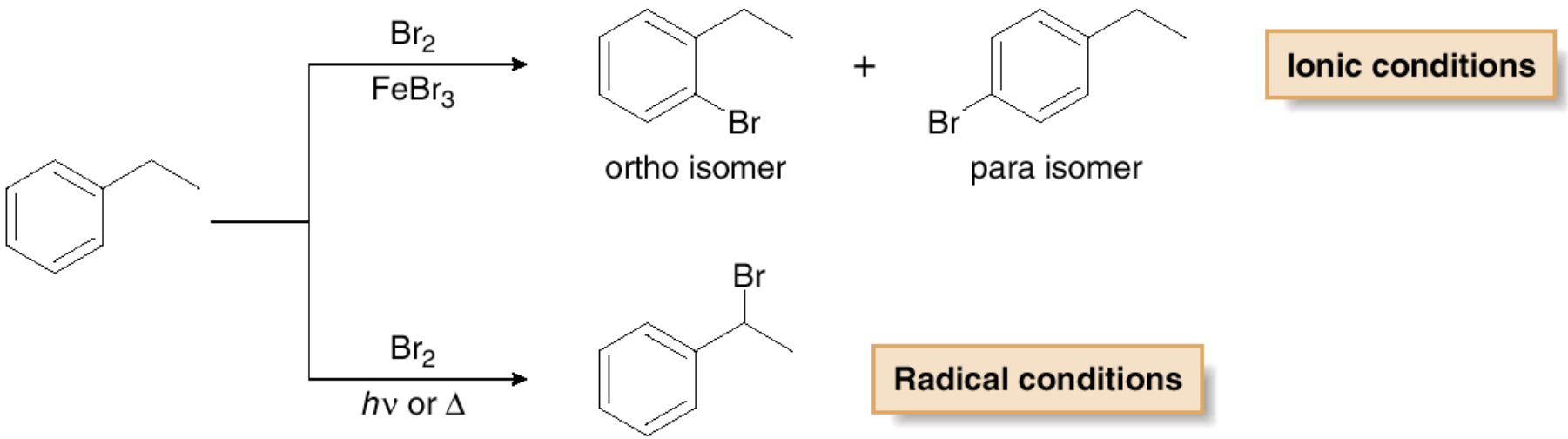
five resonance structures for the benzylic radical



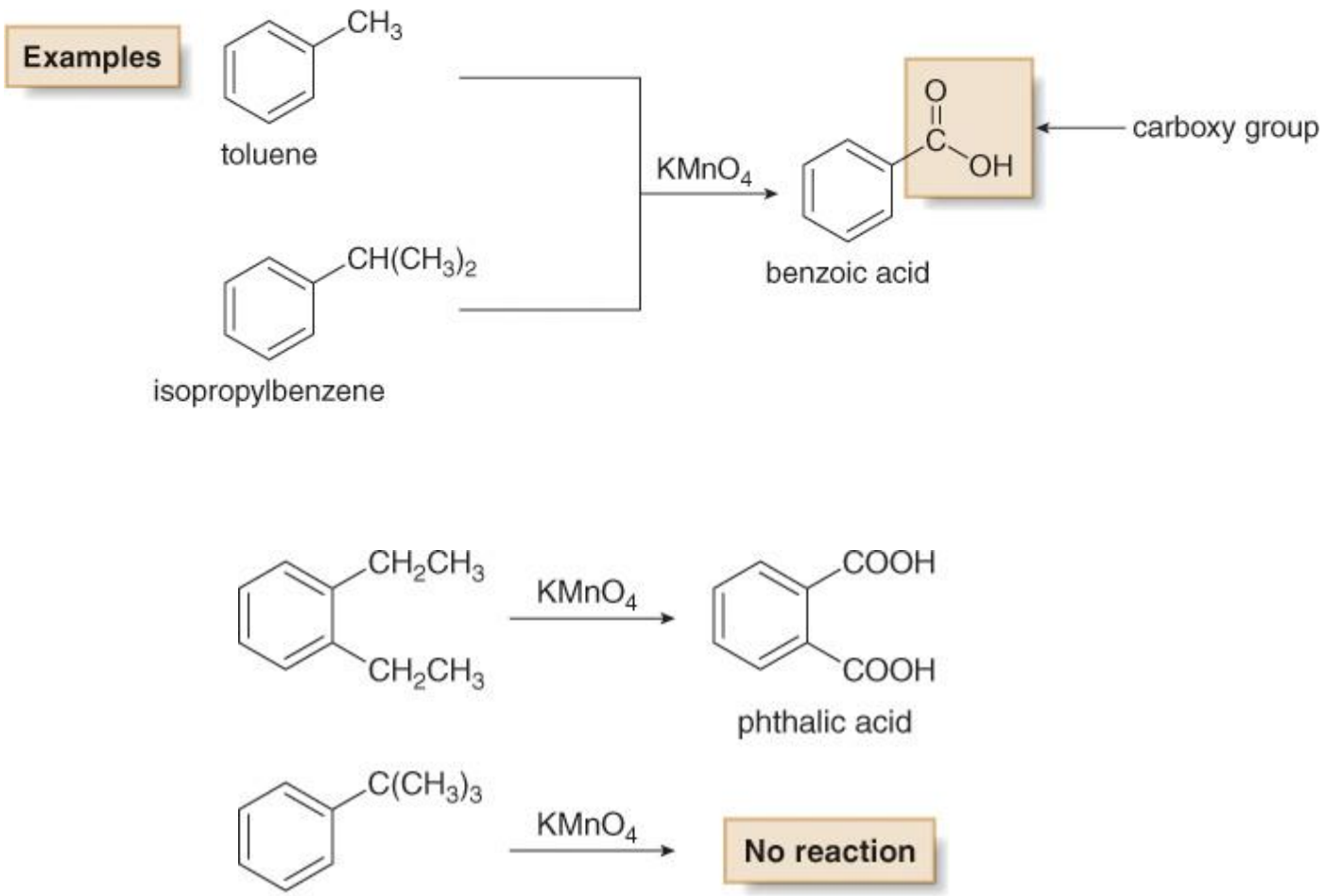
ethylbenzene — a benzylic bromide

radical conditions

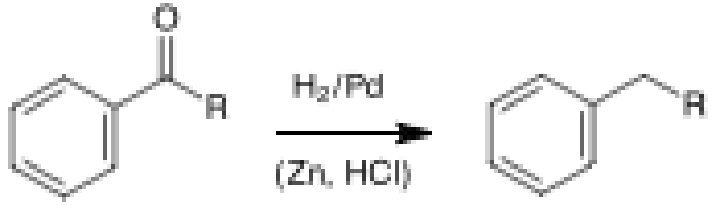
Side Chain Reactivity

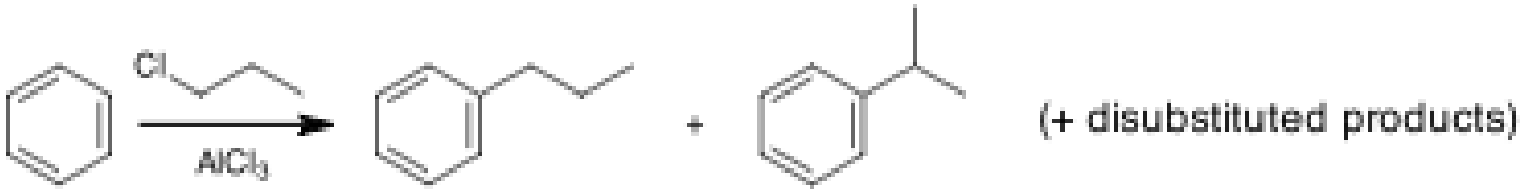


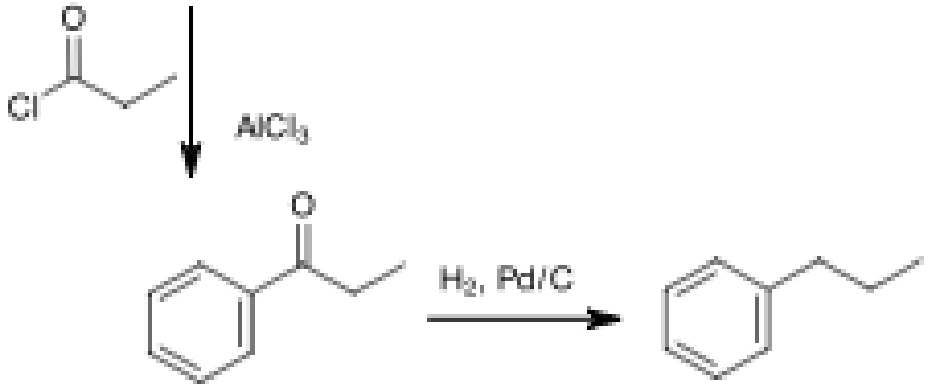
Side Chain Reactivity: Oxidation



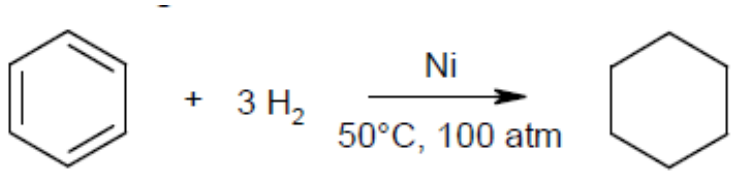
Side Chain Reactivity: Reduction







Reduction of Benzene



- Benzene reduction requires strong conditions. In milder conditions it is possible to reduce a double bond without reducing the benzene ring