

CHAPTER 11

**AROMATICITY AND BENZENE;
ELECTROPHILIC AROMATIC
SUBSTITUTION (REVIEW)**

Nomenclature of Benzene Derivatives

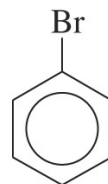
- Benzene is the parent name for some monosubstituted benzenes; the substituent name is added as a prefix



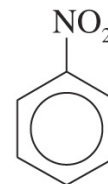
Fluorobenzene



Chlorobenzene

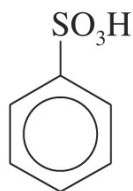


Bromobenzene

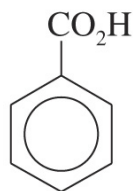


Nitrobenzene

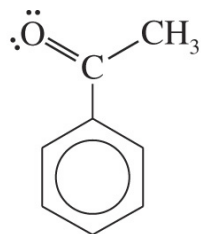
- For other monosubstituted benzenes, the presence of the substituent results in a new parent name



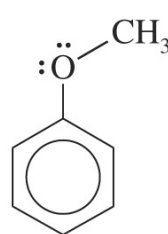
Benzenesulfonic acid



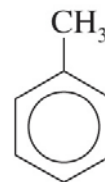
Benzoic acid



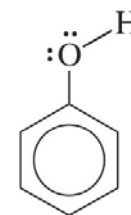
Acetophenone



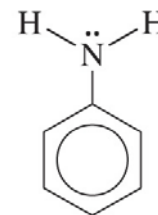
Anisole



Toluene

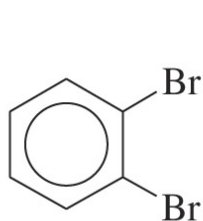


Phenol

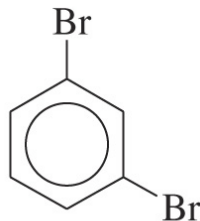


Aniline

When **two** substituents are present their position may be indicated by the prefixes *ortho*, *meta*, and *para* (*o*, *m* and *p*) or by the corresponding numerical positions



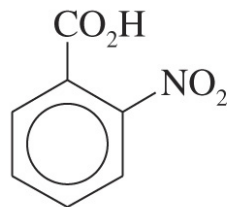
1,2-Dibromobenzene
(*o*-dibromobenzene)
ortho



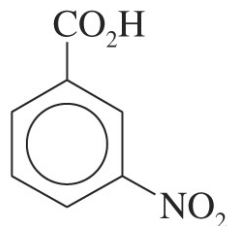
1,3-Dibromobenzene
(*m*-dibromobenzene)
meta



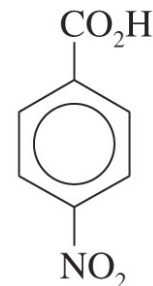
1,4-Dibromobenzene
(*p*-dibromobenzene)
para



2-Nitrobenzoic acid
(*o*-nitrobenzoic acid)

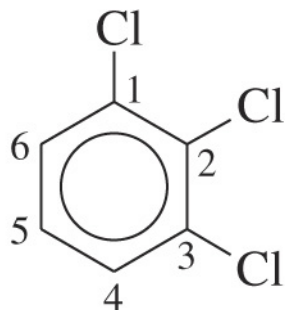


3-Nitrobenzoic acid
(*m*-nitrobenzoic acid)

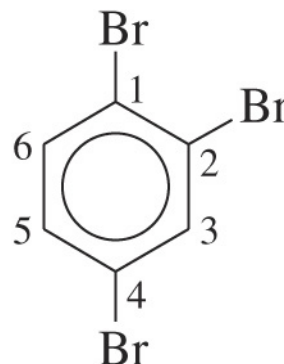


4-Nitrobenzoic acid
(*p*-nitrobenzoic acid)

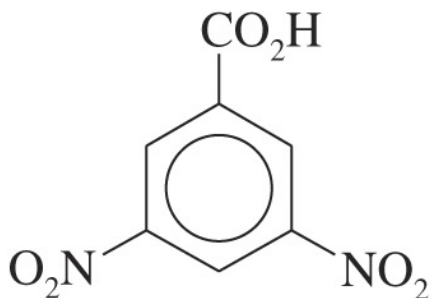
Numbers must be used as locants when more than two substituents are present



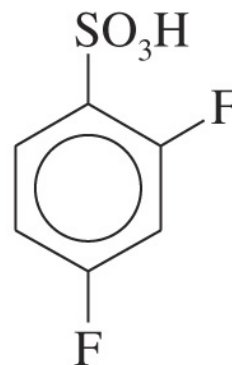
1,2,3-Trichlorobenzene



1,2,4-Tribromobenzene
(not 1,3,4-tribromobenzene)



3,5-Dinitrobenzoic acid



2,4-Difluorobenzenesulfonic acid

AROMATICITY

THE HUCKEL RULE

AROMATICITY

HÜCKEL $4n+2$ RULE

Prediction: Compounds that have $4n+2$ pi electrons in a cyclic array will be aromatic.

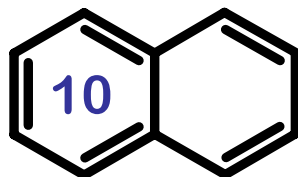
$4n+2$ series = 2, 6, 10, 14, 18, 22, 26, 30 etc.

The rule was derived by observation of

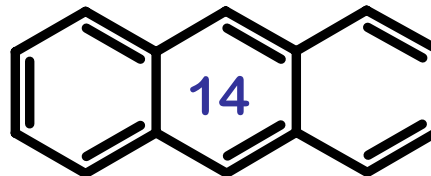
POLYCYCLIC AROMATIC COMPOUNDS



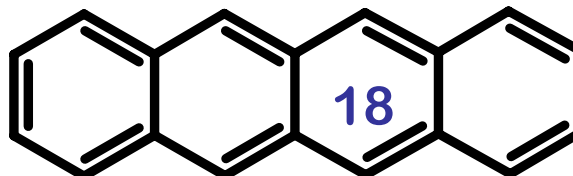
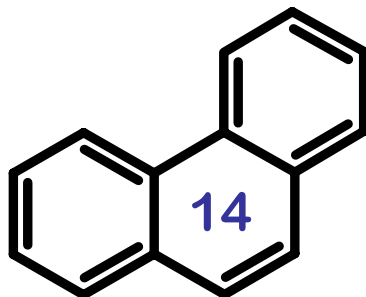
benzene



naphthalene



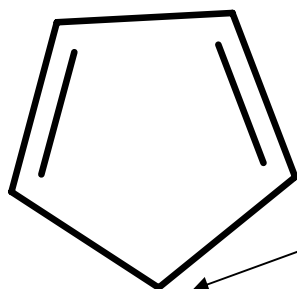
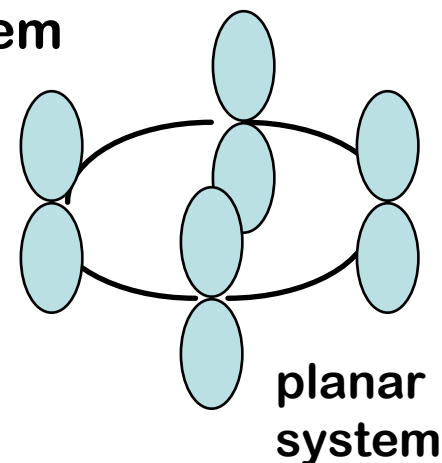
anthracene



Aromatic Compounds Have Special Properties

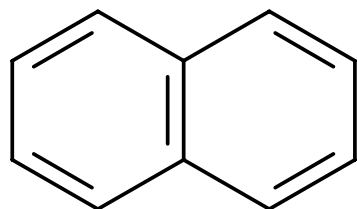
Aromatic compounds:

- 1) Must be cyclic and fully conjugated
- 2) Must have $4n+2$ π electrons in the system
- 3) Must have the entire system planar
- 4) Each atom of the ring must have a p orbital perpendicular to the ring

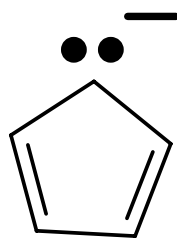


Sp³- no p orbital
Not aromatic

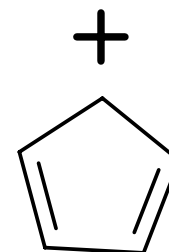
Examples



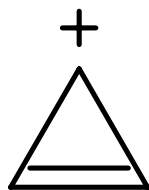
10 pi electrons
Aromatic



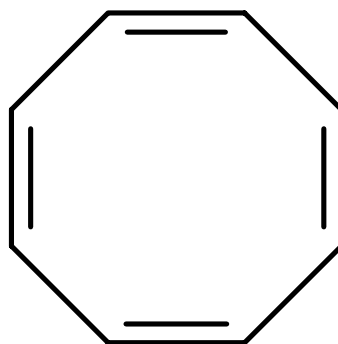
6 pi electrons
Aromatic



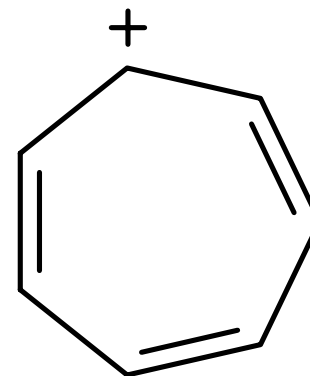
4 pi electrons
Not aromatic



2 pi e → Ar

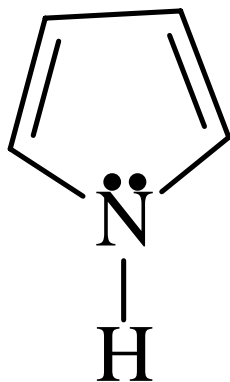


8 pi e → not Ar

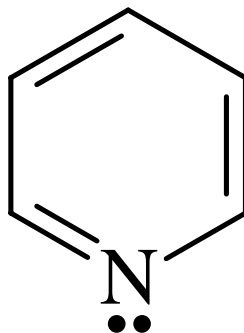


6 pi e → Ar

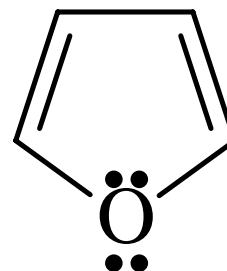
More Examples



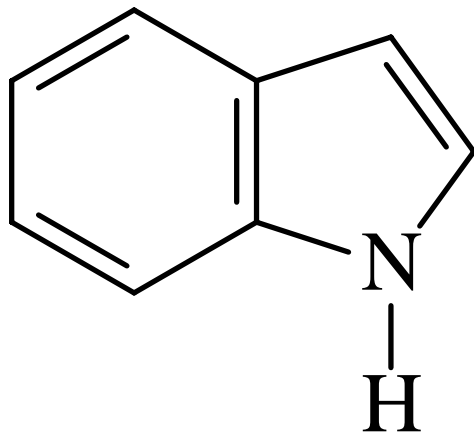
6 pi e \rightarrow Ar



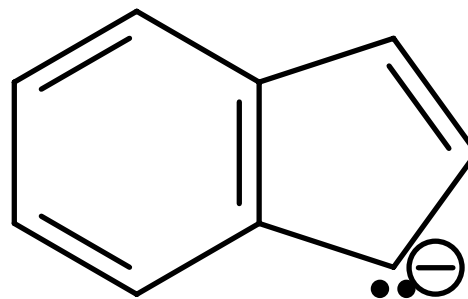
6 pi e \rightarrow Ar



6 pi e \rightarrow Ar

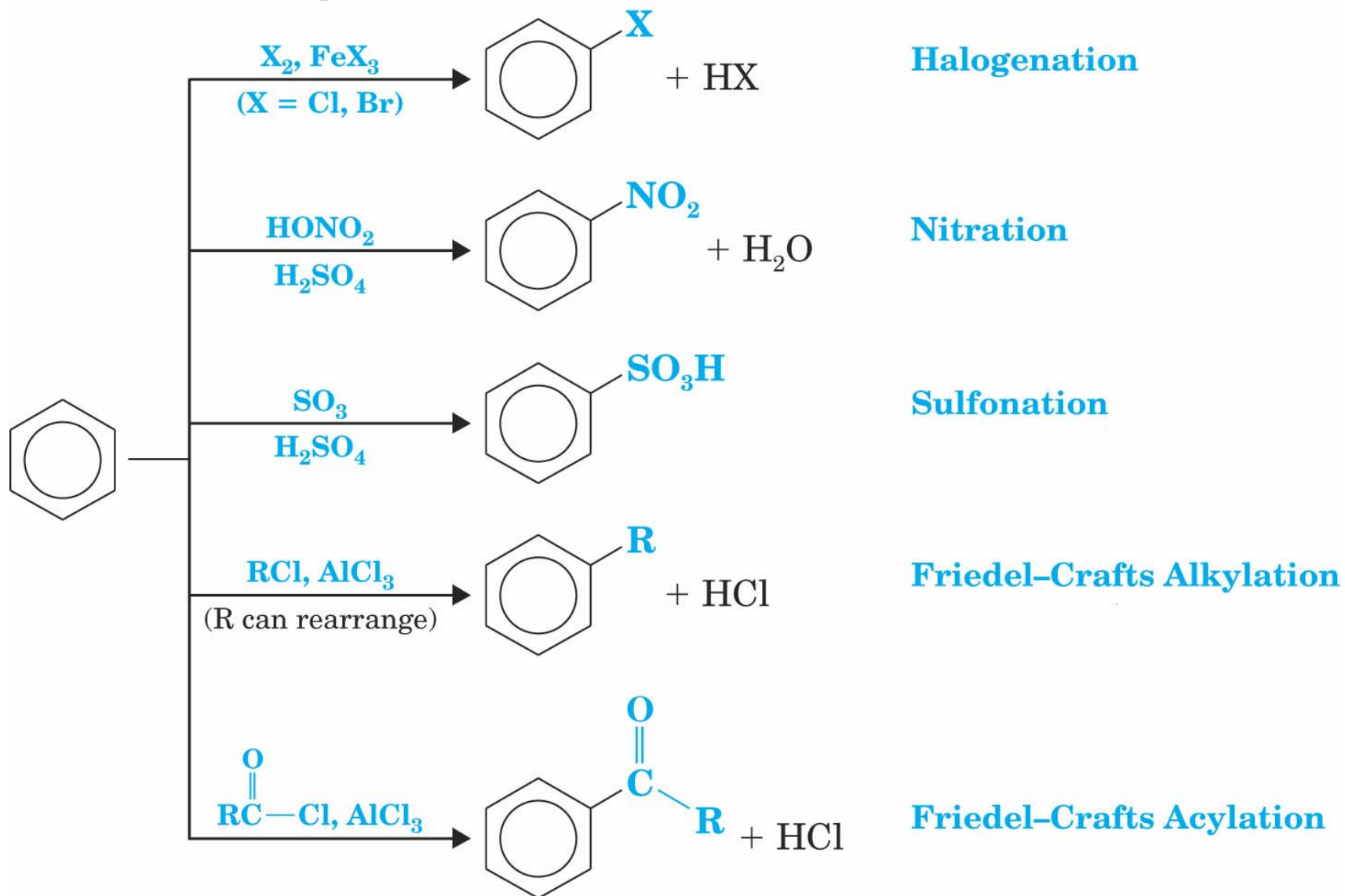


10 pi e \rightarrow Ar

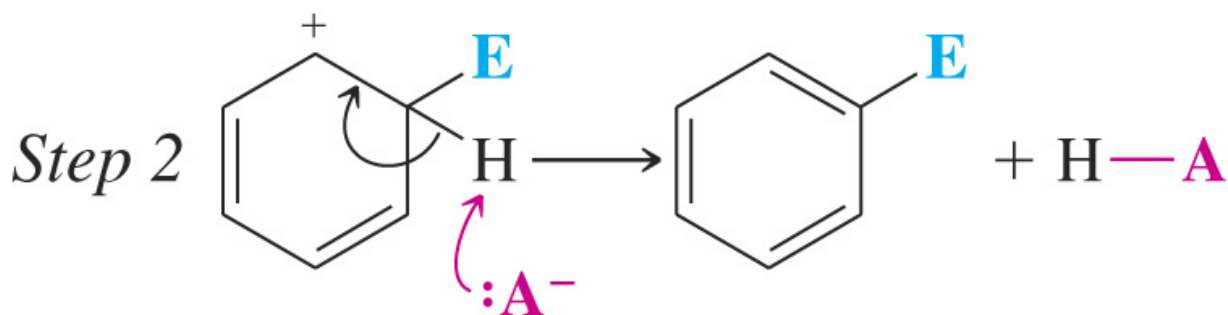
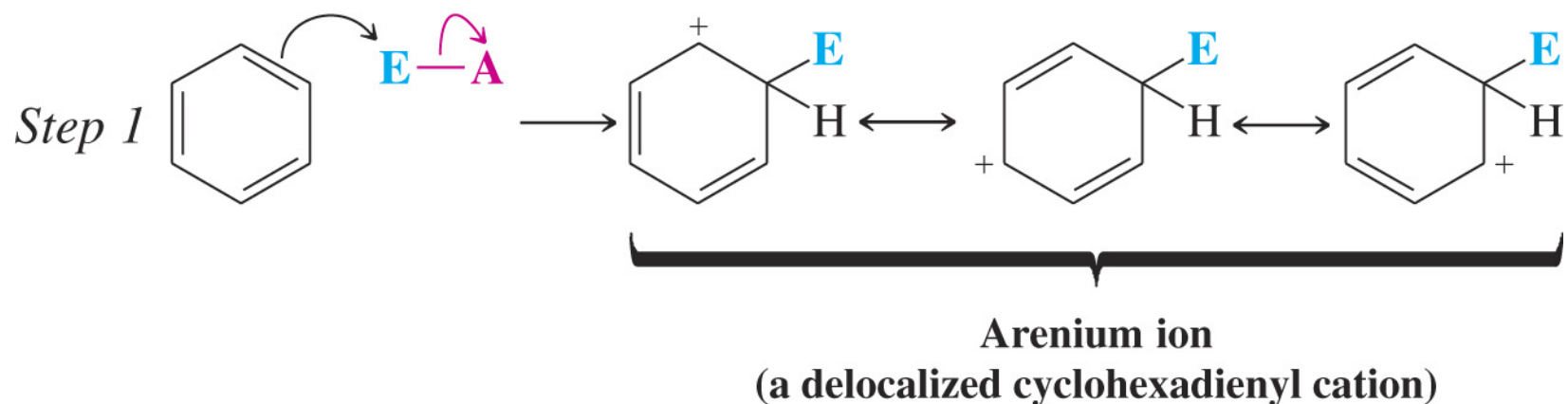


10 pi e \rightarrow Ar

Electrophilic Aromatic Substitution







A General Mechanism for Electrophilic Aromatic Substitution:

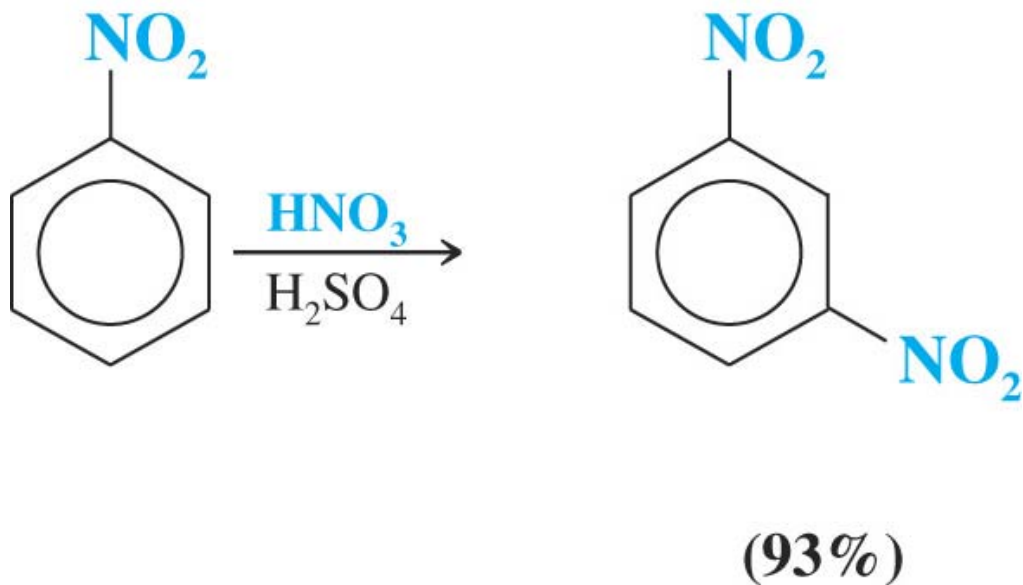
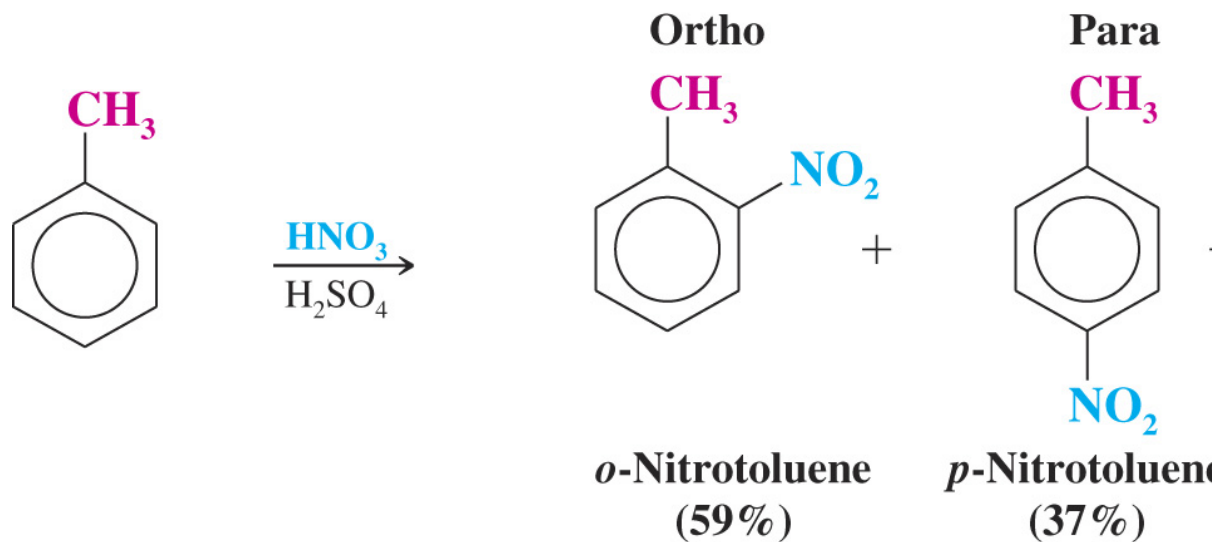


The Second Substitution

Table 11.5 Effect of the first substituent on the second substitution

	<i>o,p</i> -Directors	<i>m</i> -Directors (All Deactivating)	
 increasing activation 	$-\ddot{\text{N}}\text{H}_2, -\ddot{\text{N}}\text{HR}, -\ddot{\text{N}}\text{R}_2$	$-\overset{\text{O}}{\parallel}{\text{C}}\text{R}$	 increasing deactivation 
	$-\ddot{\text{O}}\text{H}$	$-\text{CO}_2\text{R}$	
	$-\ddot{\text{O}}\text{R}$	$-\text{SO}_3\text{H}$	
	$-\overset{\text{O}}{\parallel}{\text{N}}\text{HCR}$	$-\text{CHO}$	
	$-\text{C}_6\text{H}_5$ (aryl)	$-\text{CO}_2\text{H}$	
	$-\text{R}$ (alkyl)	$-\text{CN}$	
	$-\ddot{\text{X}}:$ (<i>deactivating</i>)	$-\text{NO}_2$	
		$-\text{NR}_3^+$	

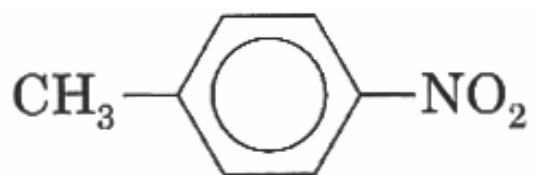
Examples



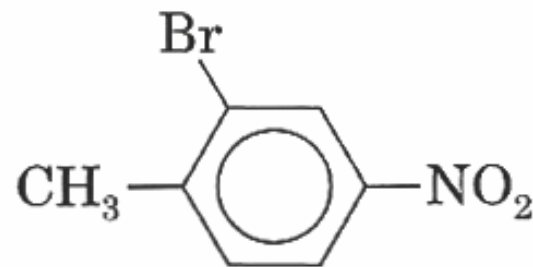
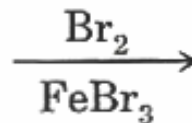
The Third Substitution

1. If two substituents direct an incoming group to the same position, that will be the principal position of the third substitution.

ortho to CH₃ and meta to NO₂

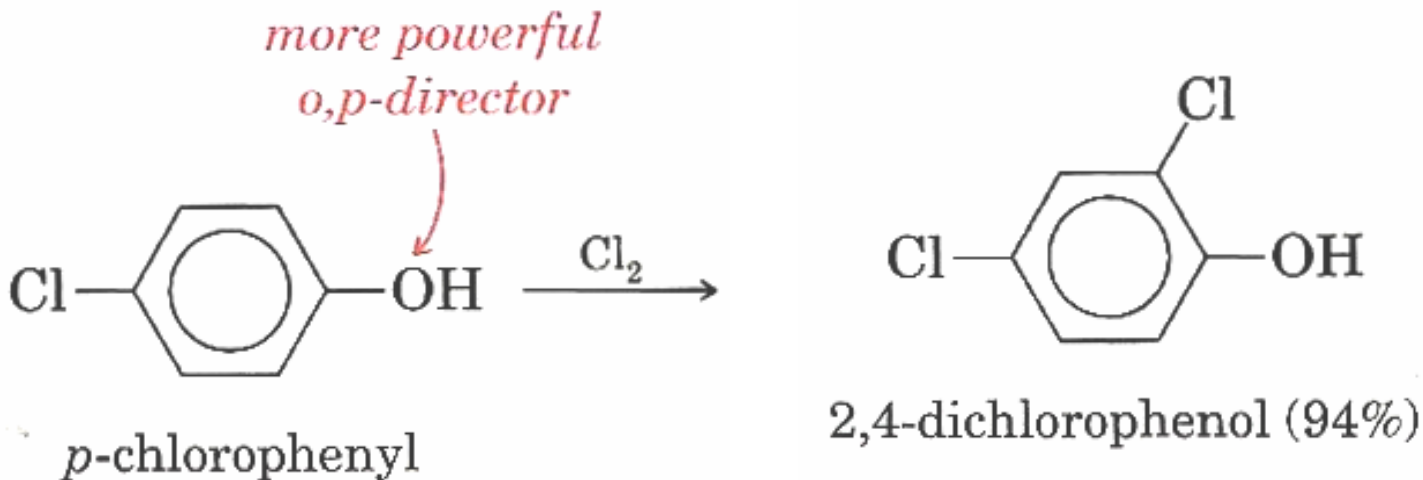


p-nitrotoluene

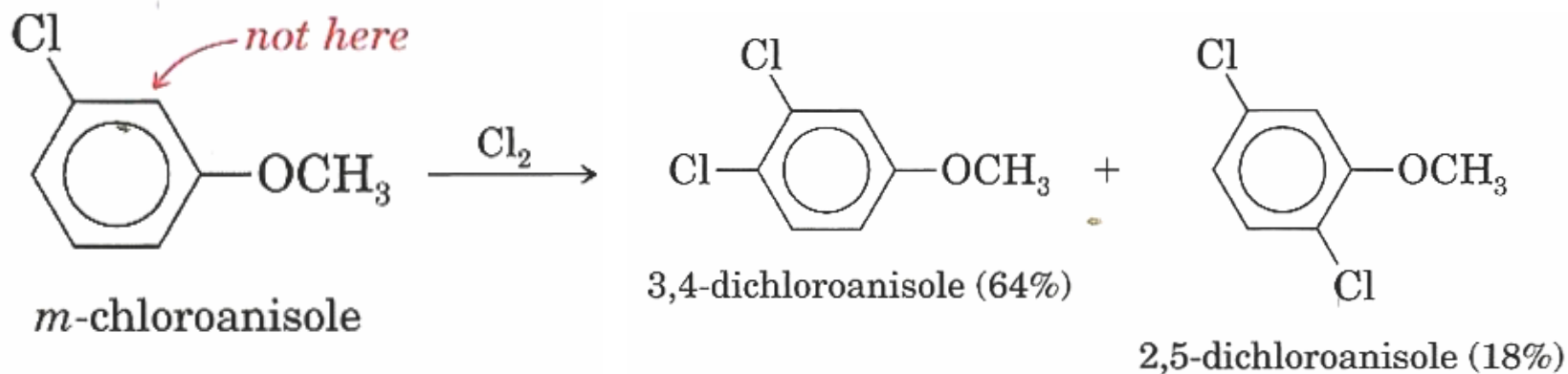


2-bromo-4-nitrotoluene (90%)

2. If two groups conflict in their directive effects, the more powerful activator (Table 11.5) will exert the predominant directive effect.

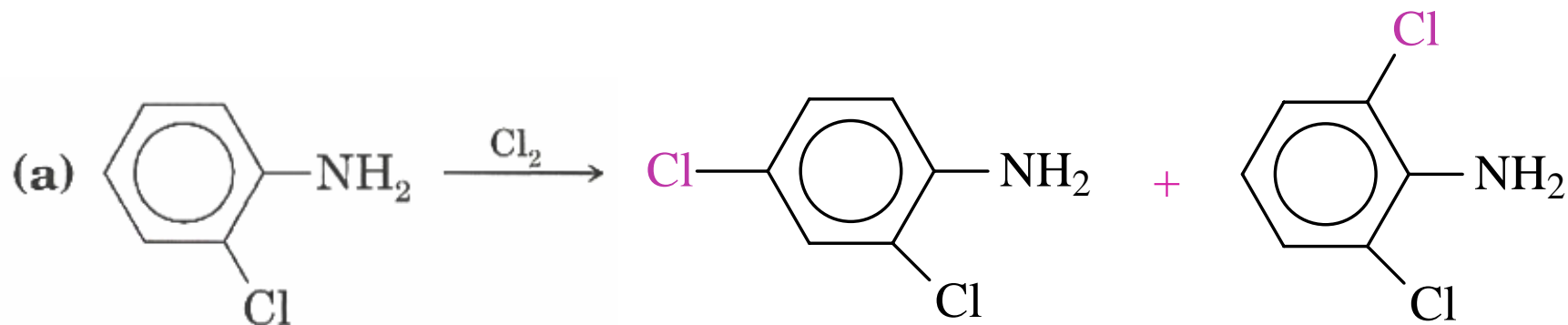


3. If two groups on a ring are **meta** to each other, the ring does not usually undergo substitution at the position between them, even if the ring is activated.
- **The lack of reactivity at this position is probably due to steric hindrance.**



4. If two deactivating groups are on the ring, regardless of their positions, it may be difficult to effect a third substitution.

EXAMPLES



MORE EXAMPLES

