
Benzene and other aromatic compounds: electrophilic substitution reactions

22.1 The structure of benzene and other aromatic compounds

Planar hexagon with bond lengths in between C–C and C=C



benzene

Cyclic delocalization of 6 π electrons explains the unusual stability of benzene



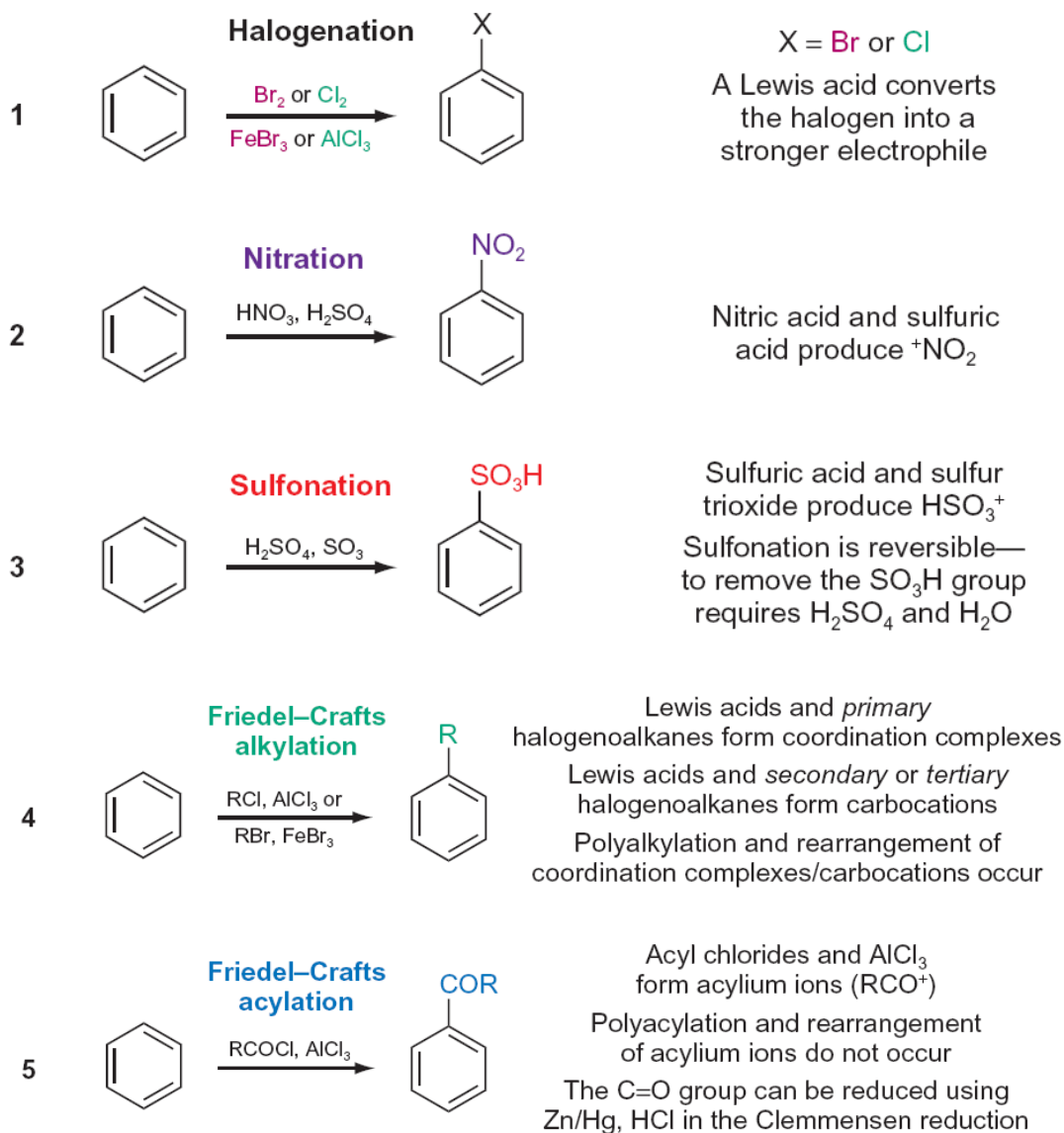
Kekulé structure of benzene

Benzene has $(4n + 2)$ π electrons (where $n = 1$) and it is aromatic

- Aromatic compounds are cyclic, planar, and have an uninterrupted ring of π electrons.
- According to Hückel's rule, the number of π electrons in an aromatic monocyclic compound must be equal to $4n + 2$, where $n = 1, 2, 3$, etc.
- Aromatic compounds can be neutral or charged, and heteroatoms can be part of the ring.
- Antiaromatic compounds are cyclic, planar, and have an uninterrupted ring of $4n$ π electrons.
- Frost circles provide a convenient way of determining the number of molecular orbitals, and their relative energies, in aromatic or antiaromatic compounds.

22.2 Electrophilic substitution reactions of benzene

- Benzene reacts with electrophiles in **electrophilic substitution reactions**. Another atom, or group of atoms, replaces a hydrogen atom on the benzene ring, and the product retains the stable aromatic ring.
- There are five important electrophilic substitution reactions of benzene.



- These reactions are useful in synthesis as a way of introducing reactive groups into a benzene ring.

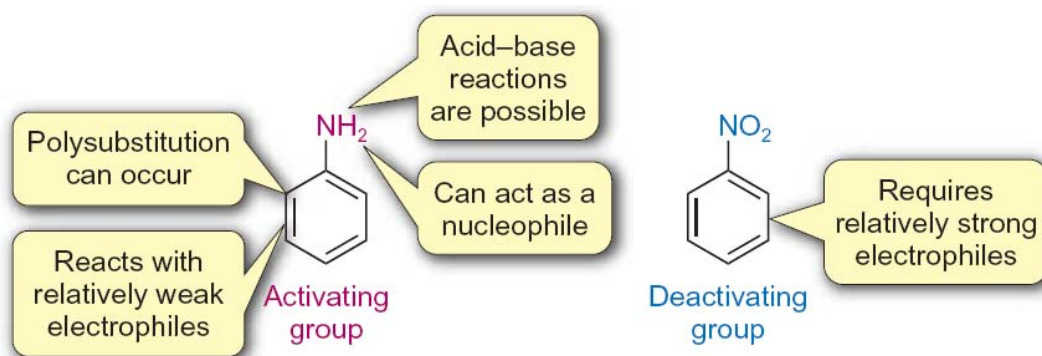
22.3 Reactivity of substituted benzenes in electrophilic

- Activating groups direct electrophiles to the 2- and 4-positions. The larger the activating group on the ring, the greater the proportion of attack at the 4-position.
- Deactivating groups direct electrophiles to the 3-position, except for the halogens, which direct electrophiles to the 2- and 4-positions.

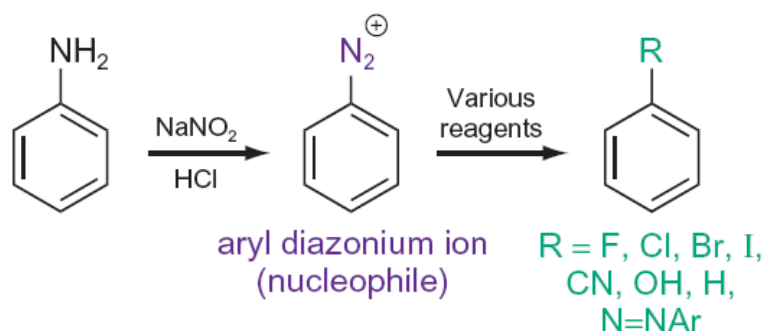
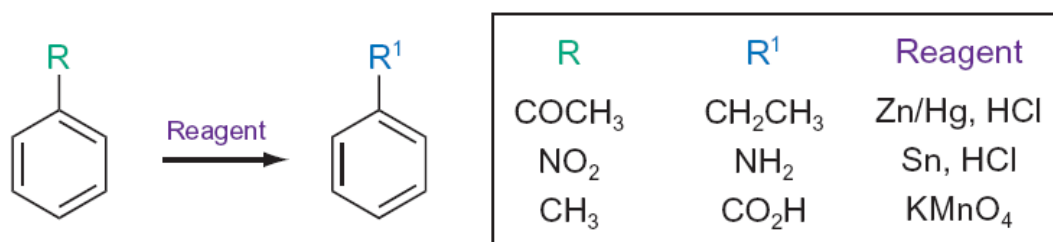
	Substituents	Electronic effects	
2,4-directing activators	-NH ₂ , -NHR, -NR ₂	+M > -I	↑ Increasingly more reactive than benzene to electrophiles
	-OH, -OR	+M > -I	
	-NHCOR, -OCOR	+M > -I	
	-Ph, -CH=CH ₂	+M, +I	
	-R	+I	
	-H		benzene
2,4-directing deactivators	-Cl, -Br, -I	-I > +M	↓ Increasingly less reactive than benzene to electrophiles
3-directing deactivators	-CHO, -COR	-M, -I	
	-CO ₂ H, -CO ₂ R	-M, -I	
	-SO ₃ H	-M, -I	
	-NO ₂	-M, -I	

22.4 The synthesis of substituted benzenes

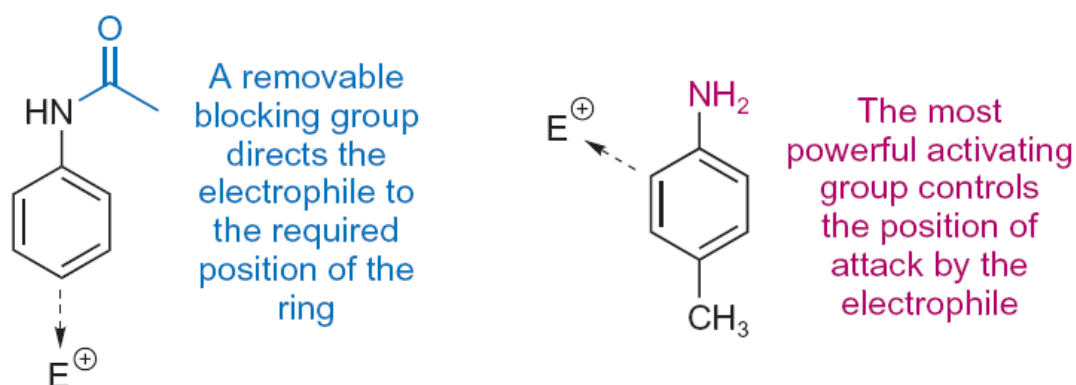
- You need to consider the following factors when planning syntheses of substituted benzenes by electrophilic substitution reactions.



- The following reactions are used to transform substituents on benzene rings.



- Regioselective formation of di- and trisubstituted benzenes is possible.

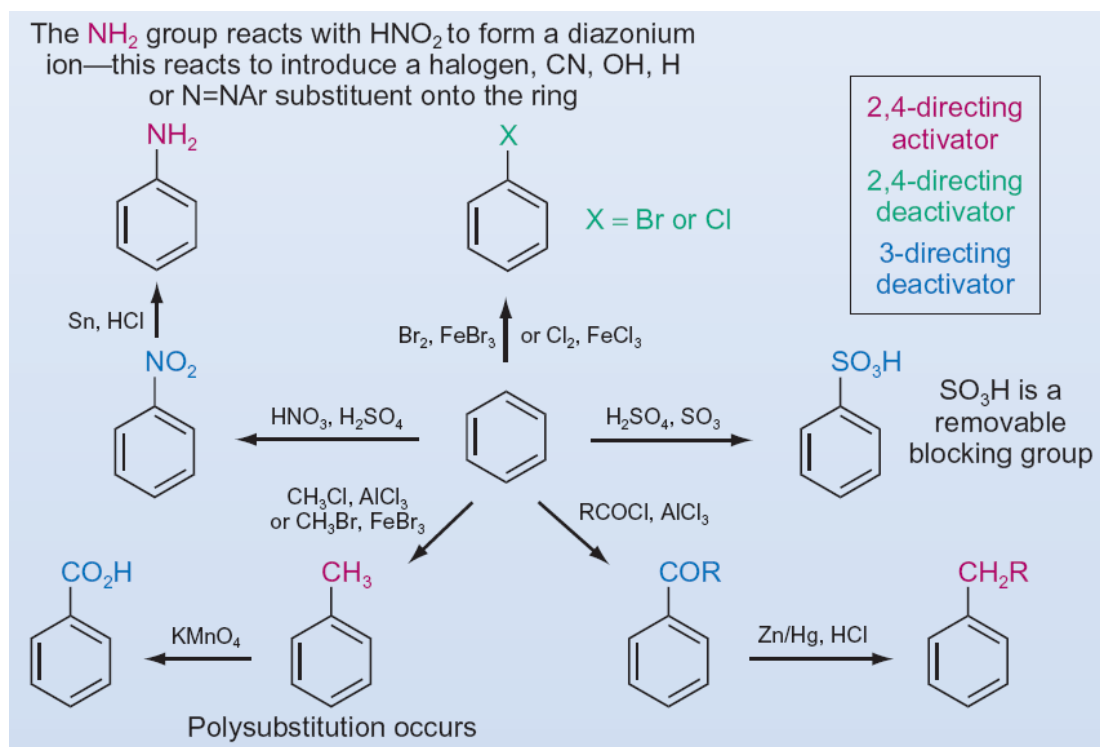


Learning outcomes

By the end of this chapter you should be able to do the following.

- Know what aromatic, antiaromatic, and nonaromatic compounds are and give examples of each.
- Understand why benzene reacts in electrophilic substitution reactions.
- Give reagents and write reaction mechanisms to explain how benzene undergoes halogenation, nitration, sulfonation, Friedel–Crafts alkylation, and Friedel–Crafts acylation.

- Classify substituents on benzene rings as either 2,4-directing activators, 2,4-directing deactivators, or 3-directing deactivators.



- Understand how the electronic and steric effects of substituents on benzene rings influence the rates and regioselectivities of electrophilic substitution reactions.
- Describe how substituents on benzene rings can be converted into other substituents by redox reactions or by forming diazonium ions.
- Design efficient syntheses of polysubstituted benzenes from benzene.