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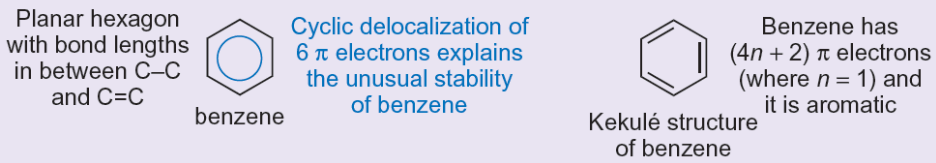
Benzene and other aromatic compounds: electrophilic substitution reactions

22.1 The structure of benzene and other aromatic compounds

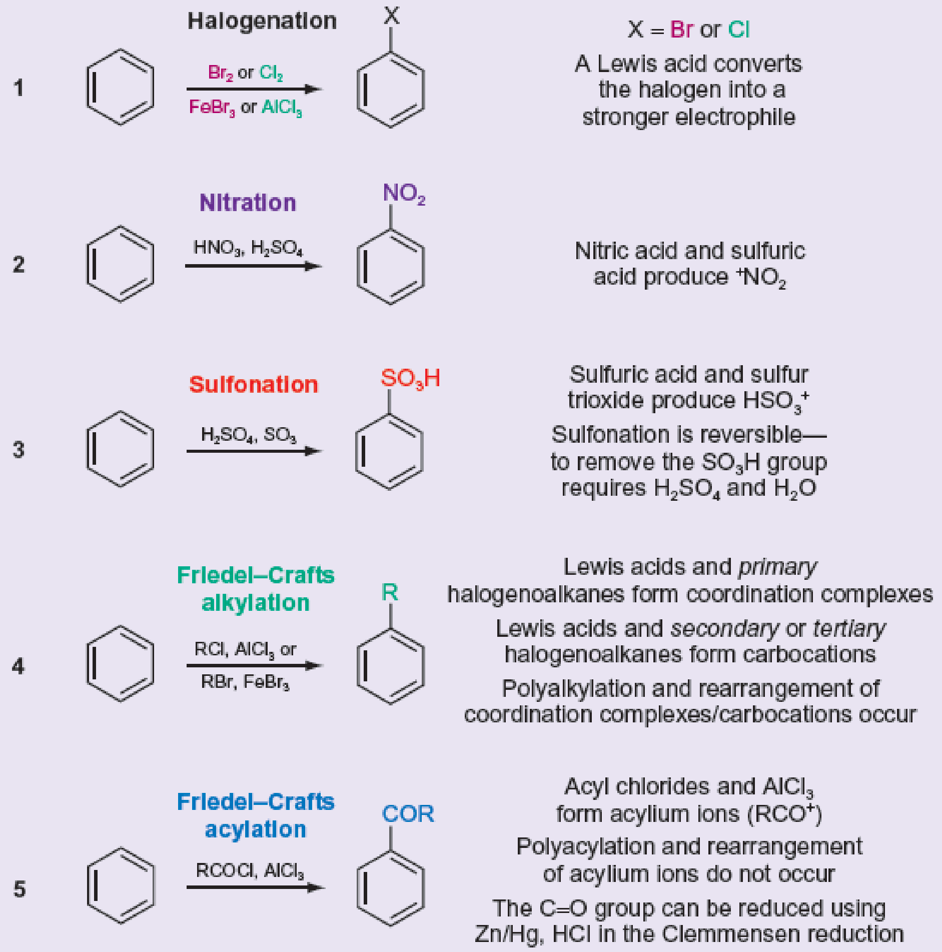


- Aromatic compounds are cyclic, planar, and have an uninterrupted ring of π electrons.
- According to Hückel's rule, the number of π electrons in an aromatic monocyclic compound must be equal to $4n + 2$, where $n = 1, 2, 3$, etc.
- Aromatic compounds can be neutral or charged, and heteroatoms can be 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.

For a practice question on this topic, see question 1 at the end of this chapter (p.1052).

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 onto a benzene ring.

For a practice question on this topic, see question 2 at the end of this chapter (p.1095).

22.3 Reactivity of substituted benzenes in electrophilic substitutions

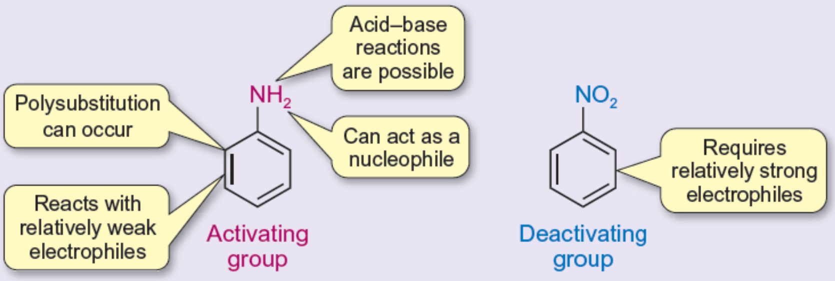
- Activating groups direct electrophiles to the 2- and 4-positions. The larger the activating group on the ring, the greater the proportion of attack at the 4-position.
- Deactivating groups direct electrophiles to the 3-position, except for the halogens, which direct electrophiles to the 2- and 4-positions.

	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	
	$-CO_2H$, $-CO_2R$	−M, −I	
	$-SO_3H$	−M, −I	
	$-NO_2$	−M, −I	

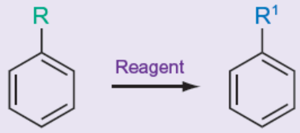
For a practice question on this topic, see question 2 at the end of this chapter (p.1052).

22.4 The synthesis of substituted benzenes

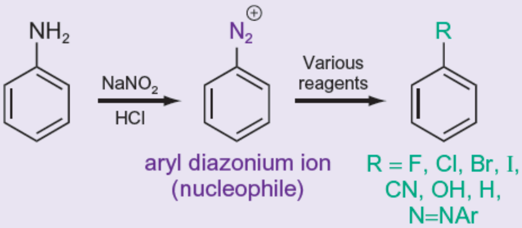
- You need to consider the following factors when planning syntheses of substituted benzenes by electrophilic substitution reactions.



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



R	R^1	Reagent
$COCH_3$	CH_2CH_3	Zn/Hg, HCl
NO_2	NH_2	Sn, HCl
CH_3	CO_2H	$KMnO_4$



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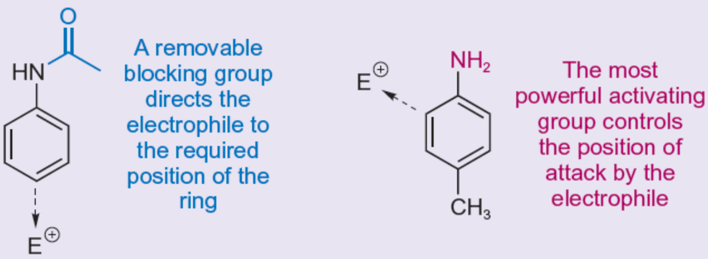
- Regioselective formation of di- and trisubstituted benzenes is possible.



For practice questions on this topic, see questions 3–5 at the end of this chapter (pp.1052–1053).

Concept review

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 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.