Chapter 5.
Aromatic Compounds

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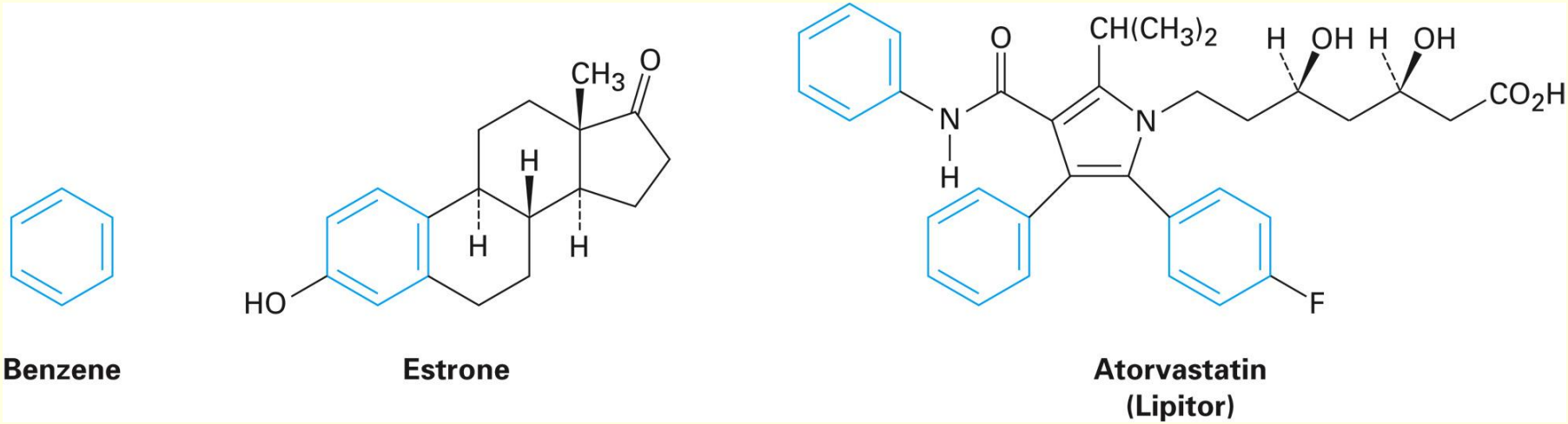
Aromatic Compounds

- *Aromatic* was used to described some fragrant compounds in early 19th century
- Current: distinguished from *aliphatic* compounds by electronic configuration
- What is aromatic or aliphatic? Aromatic and aliphatic both are organic compound. Aromatic compounds having benzene ring is a typical chemical structure that contains six carbon atoms, cyclically bonded with alternating double bonds. whereas the aliphatic does not have benzene rings.



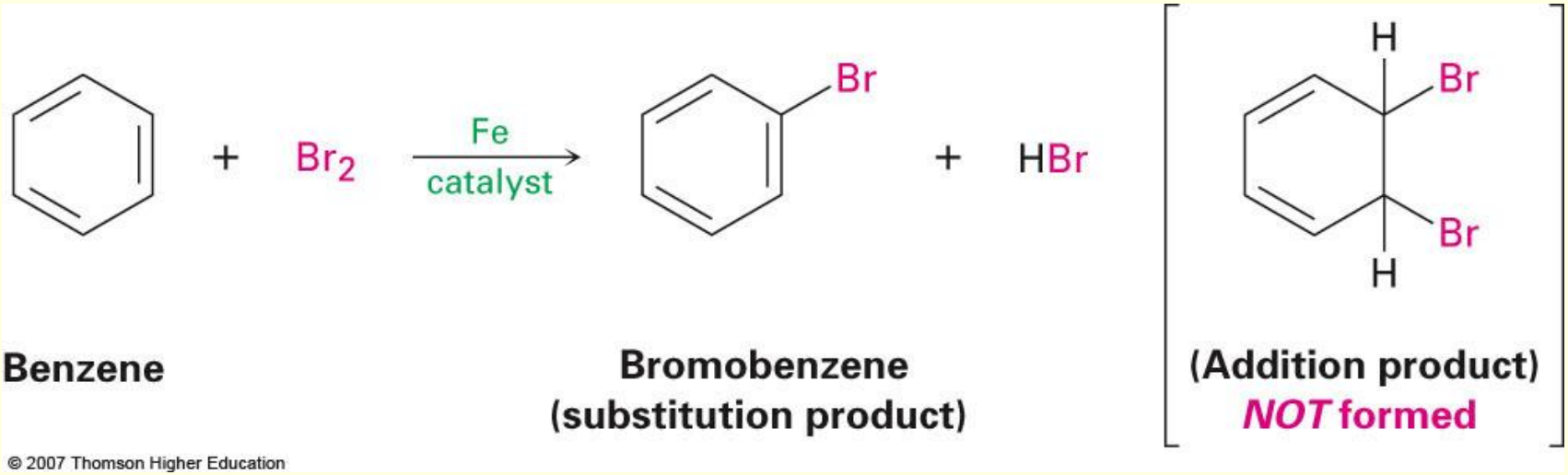
Why this Chapter?

- Aromatic rings are a common part of many organic structures and are **particularly important in nucleic acid** chemistry and in the **chemistry of several amino acids**.

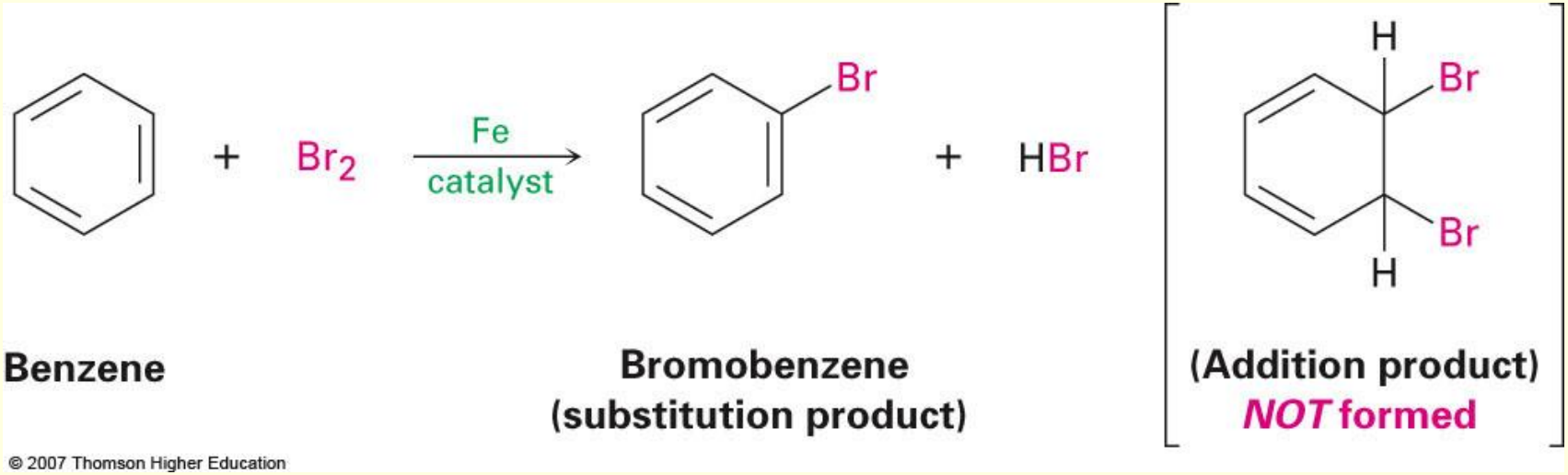
- In this chapter, we'll find out how and why **aromatic** compounds are **different from such apparently related compounds as alkenes.**

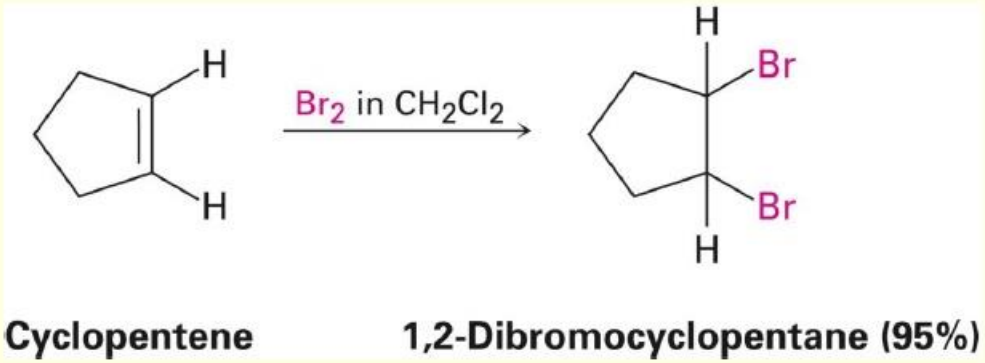
5.1 Structure of Benzene

- Benzene reacts slowly with Br_2 to give bromobenzene (where Br replaces H)
- This is substitution rather than the rapid addition reaction common to compounds with C=C, suggesting that in benzene there is a higher barrier



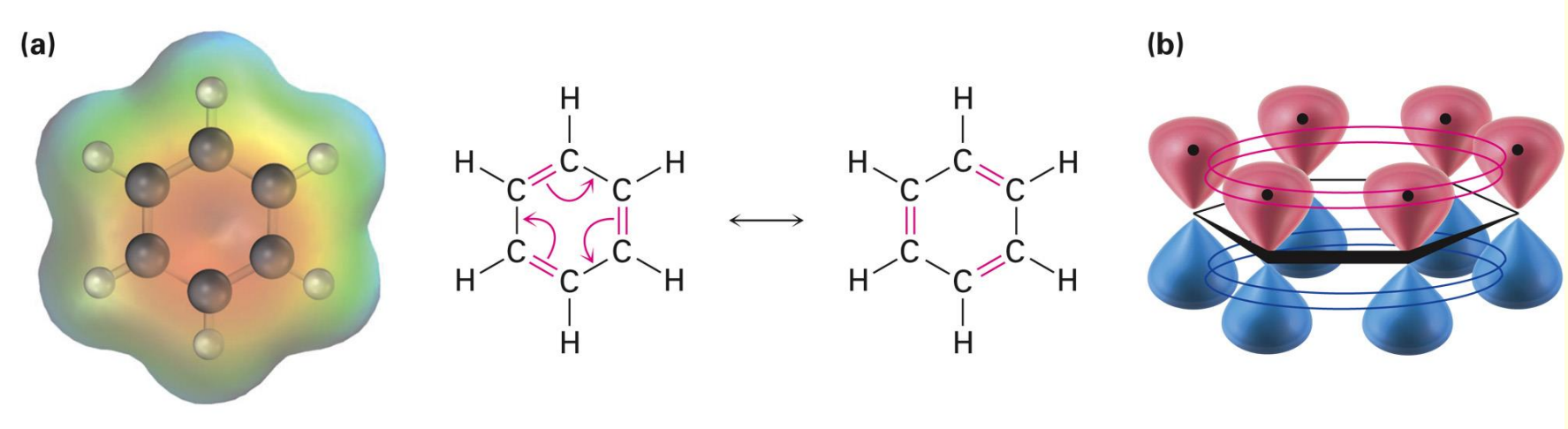
Cyclohexene, for instance, reacts rapidly with Br_2 and gives the addition product 1,2-dibromocyclohexane, but benzene reacts only slowly with Br_2 and gives the *substitution* product C_6H_5Br.





Benzene's Unusual Structure

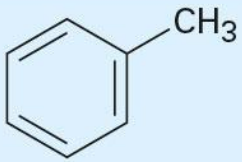
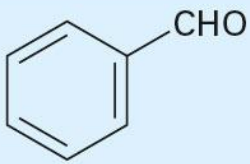
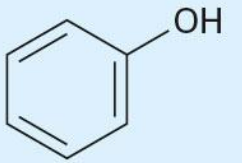
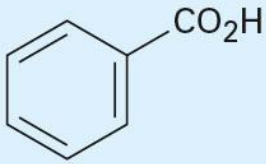
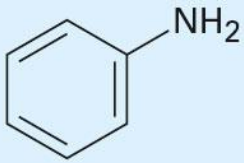
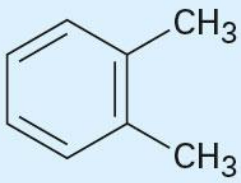
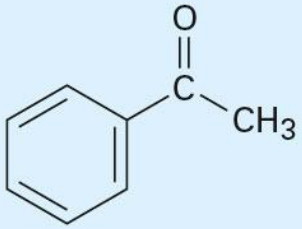
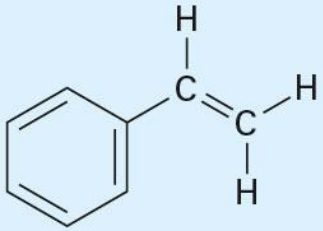
- All its C-C bonds are the same length: 139 pm — between single (154 pm) and double (134 pm) bonds
- Electron density in all six C-C bonds is identical
- Structure is planar, hexagonal
- C–C–C bond angles 120°
- Each C is sp^2 and has a *p* orbital perpendicular to the plane of the six-membered ring



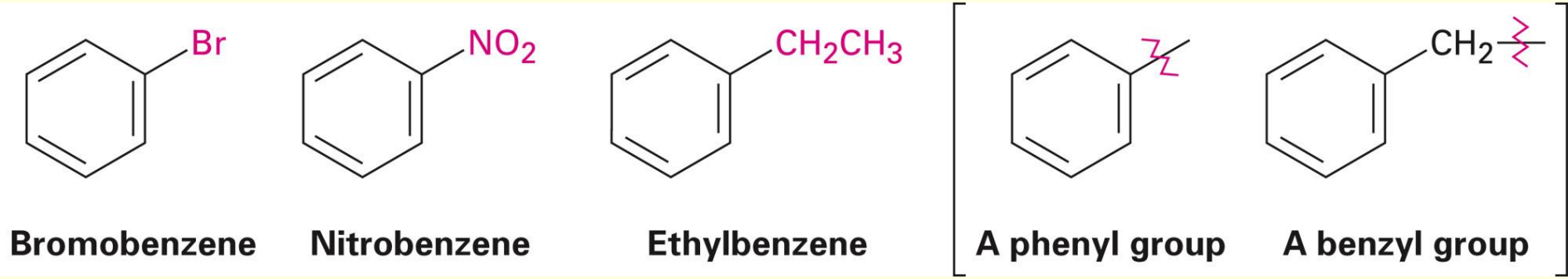
5.2 Naming Aromatic Compounds

Many common names (toluene = methylbenzene; aniline = aminobenzene)

Table 5.1 Common Names of Some Aromatic Compounds

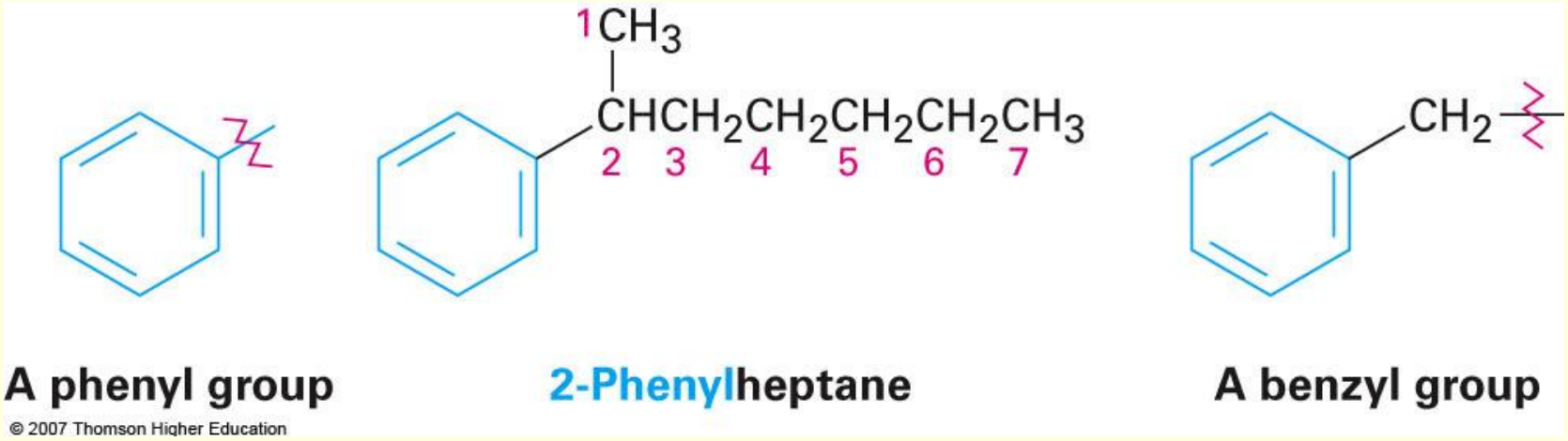
Structure	Name	Structure	Name
	Toluene (bp 111 °C)		Benzaldehyde (bp 178 °C)
	Phenol (mp 43 °C)		Benzoic acid (mp 122 °C)
	Aniline (bp 184 °C)		*ortho*-Xylene (bp 144 °C)
	Acetophenone (mp 21 °C)		Styrene (bp 145 °C)

- Monosubstituted benzenes systematic names as hydrocarbons with *–benzene*
  - C_6H_5Br = bromobenzene
  - $C_6H_5NO_2$ = nitrobenzene, and $C_6H_5CH_2CH_3$ is ethylbenzene



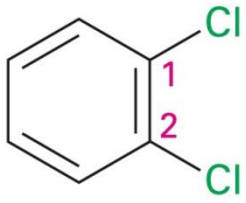
The Phenyl Group

- When a benzene ring is a substituent, the term **phenyl** is used (for -C_6H_5)
  - You may also see "Ph" or "ϕ(Greek phi)," in place of "C_6H_5"
- "**Benzyl**" refers to "-$C_6H_5CH_2$"

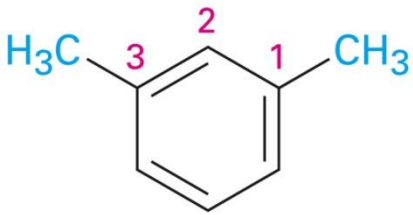


Disubstituted Benzenes

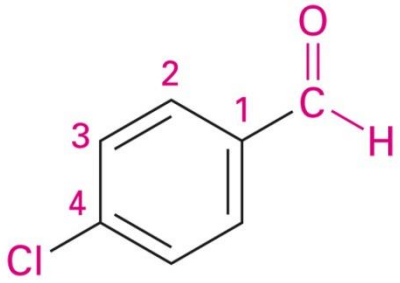
- Relative **positions** on a benzene ring
  - ***ortho- (o)*** on adjacent carbons (1,2)
  - ***meta- (m)*** separated by one carbon (1,3)
  - ***para- (p)*** separated by two carbons (1,4)
- Describes reaction patterns (“occurs at the para position”)



***ortho*-Dichlorobenzene**
1,2 disubstituted



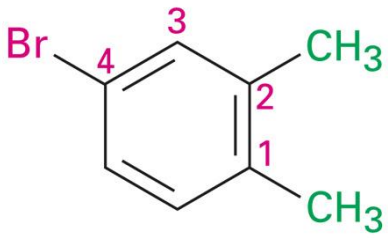
***meta*-Dimethylbenzene**
(*meta*-xylene)
1,3 disubstituted



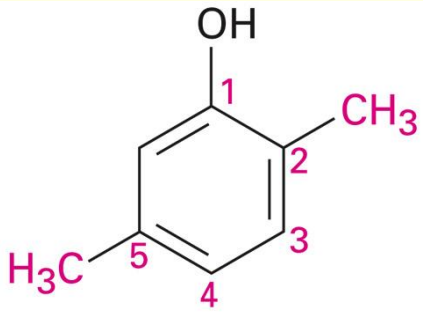
***para*-Chlorobenzaldehyde**
1,4 disubstituted

Naming Benzenes With More Than Two Substituents

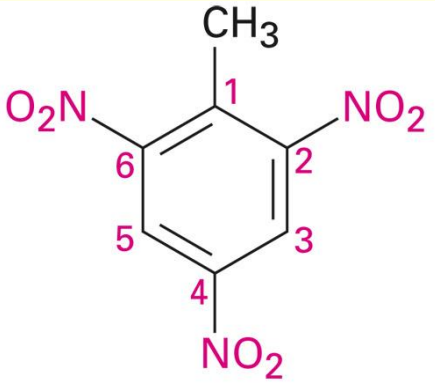
- Choose numbers to get **lowest possible values**
- List substituents alphabetically with hyphenated numbers
- Common names, such as “toluene” can serve as root name (as in TNT)



4-Bromo-1,2-dimethylbenzene



2,5-Dimethylphenol



2,4,6-Trinitrotoluene (TNT)

TNT

2,4,6-trinitrotoluene

$C_6H_2(NO_2)_3CH_3$

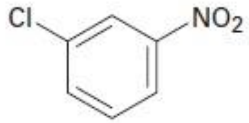
분류	2종 폭발물	상온 상태	황색 고체
분자량	227.13 g/mol	밀도	1.654 g/cm^3
인화점	240 °C	폭속	6.9 km/s
위력계수	1.00(기준)	산소 평형	-73.96%
CAS : 118-96-7			
[전문 정보 펼치기·접기]			

트라이나이트로톨루엔[1](tri-nitro-toluene)은 약자인 TNT라는 이름으로 잘 알려져 있는 폭약이다. 노란색을 띄고 있으며 화학 합성에서 시약으로 종종 쓰이기도 한다. 강한 폭발력을 가진 동시에 매우 둔감하고 다루기 쉬워 오래전부터 군용 폭약으로 널리 사용되었으며 이 때문에 폭발물의 폭발력을 비교하는 기준으로도 사용되고 있다.[2]

Worked Example 5.1

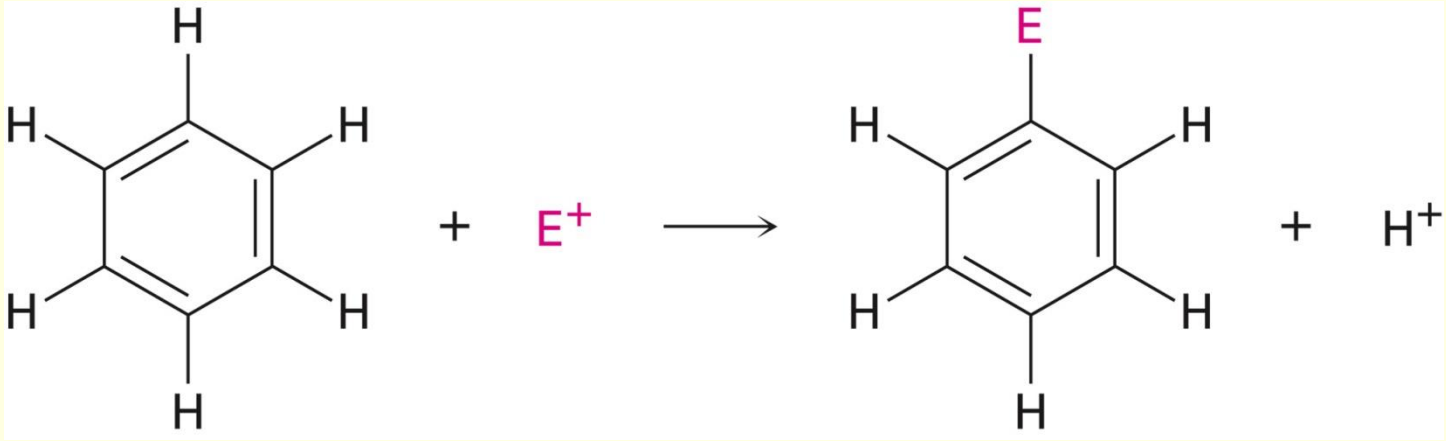
Naming an Aromatic Compound

What is the IUPAC name of the following compound?



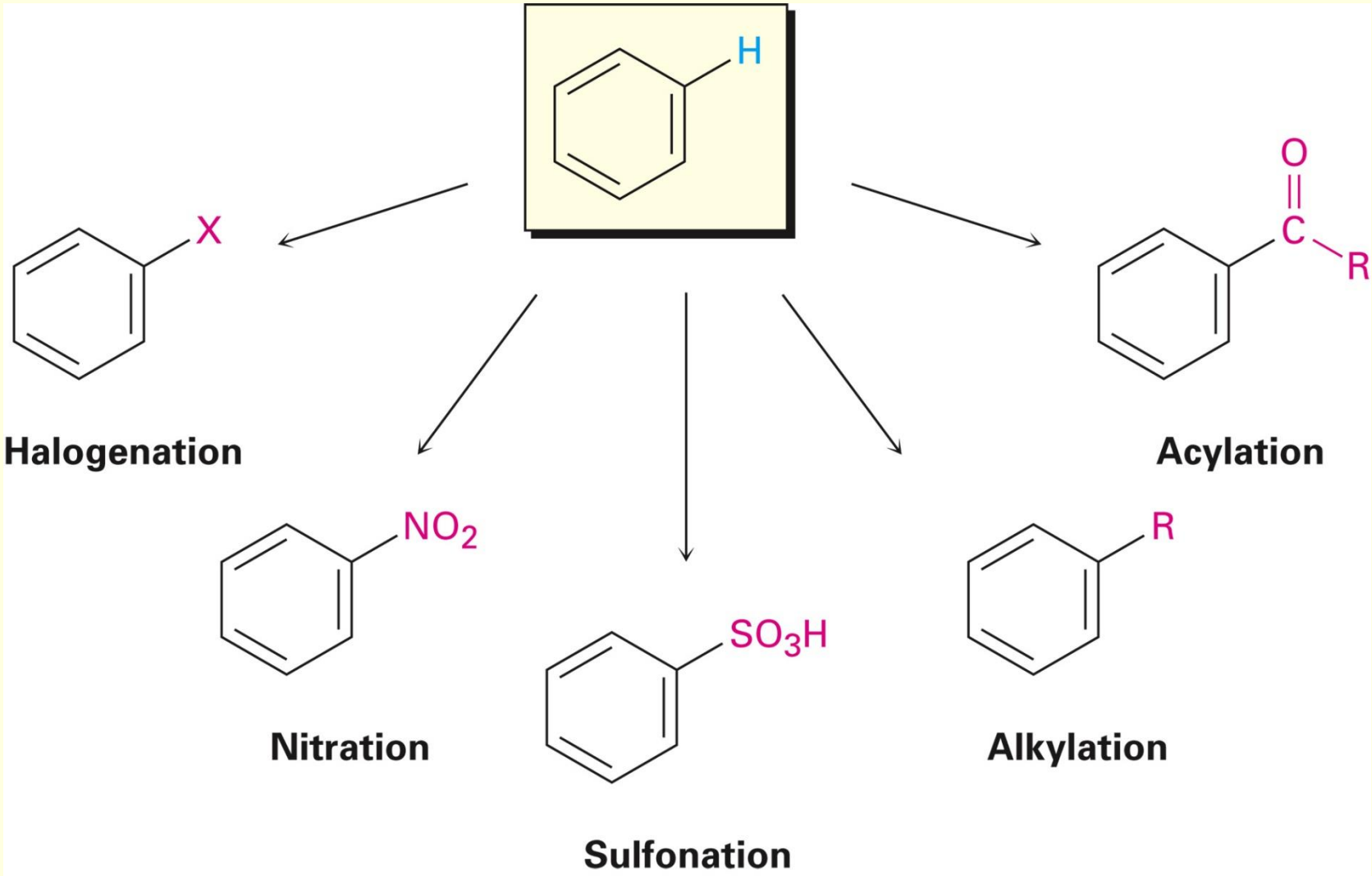
Solution Because the nitro group ($-NO_2$) and chloro group are on carbons 1 and 3, they have a meta relationship. Citing the two substituents in alphabetical order gives the IUPAC name *m*-chloronitrobenzene.

5.3 Electrophilic Aromatic Substitution Reactions: Bromination

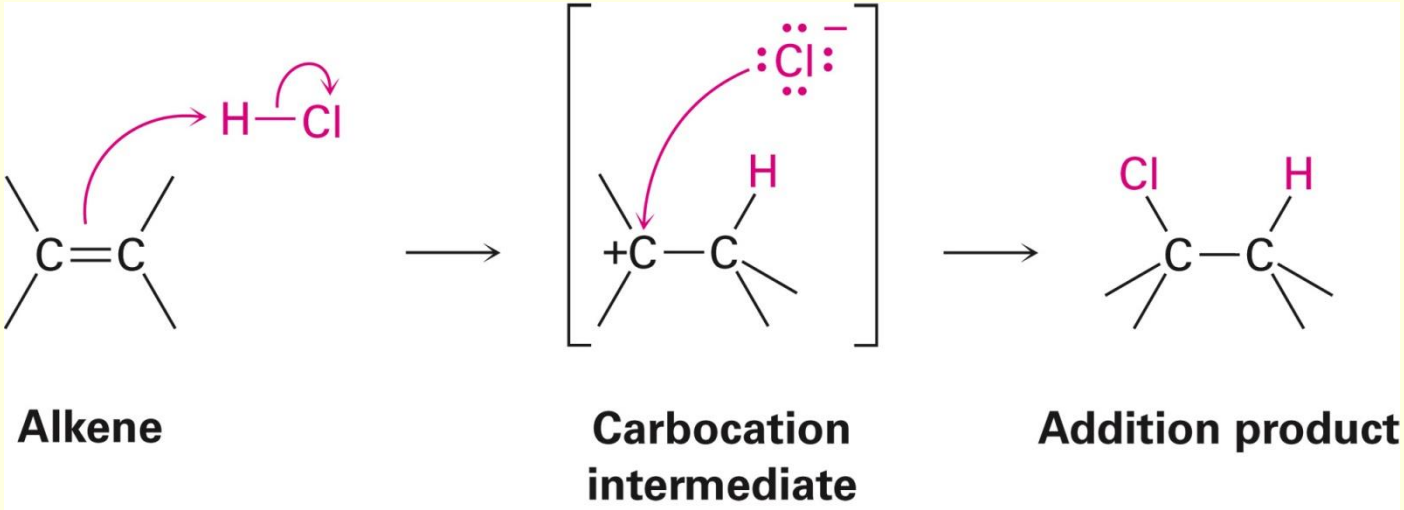


Electrophilic aromatic substitution reaction: an electrophile (E^+) reacts with an aromatic ring and substitutes for one of the hydrogens.

Some electrophilic aromatic substitution reaction

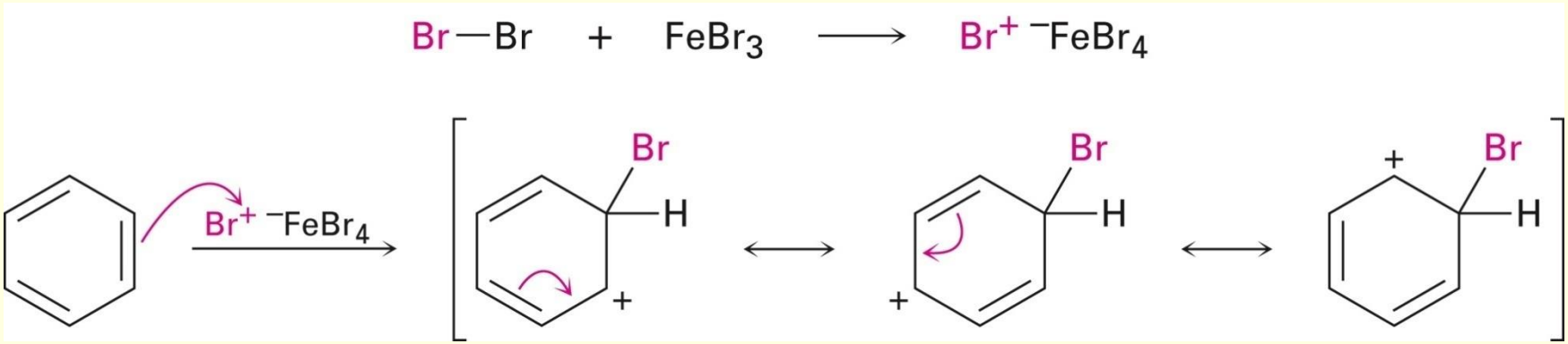


Electrophilic addition reactions of **alkenes**



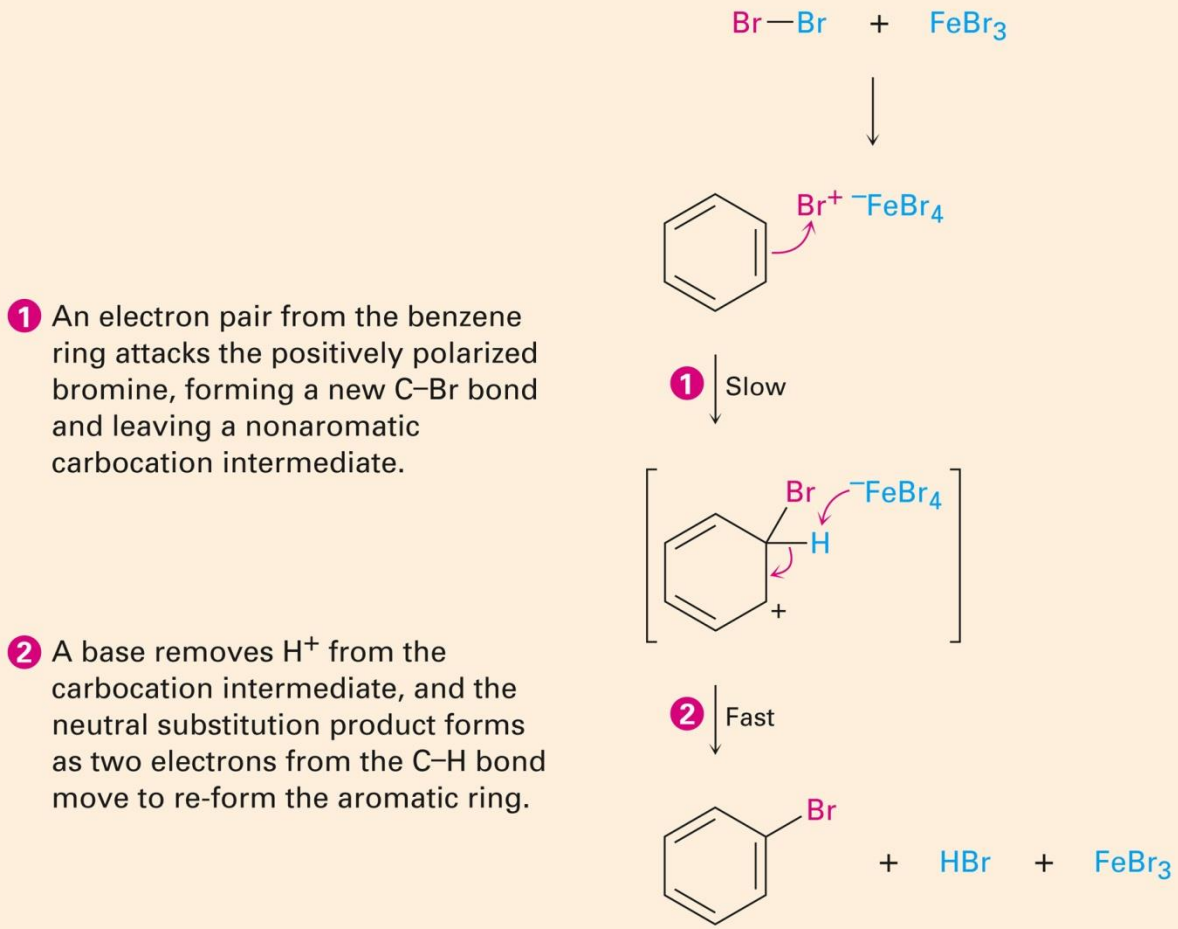
Mechanism of bromination

- The addition of bromine occurs in two steps
- In the first step the π electrons act as a nucleophile toward Br_2 (in a complex with $FeBr_3$)
- This forms a cationic addition **intermediate** from benzene and a bromine cation
- **Intermediate**: **Hybrid of three resonance forms**

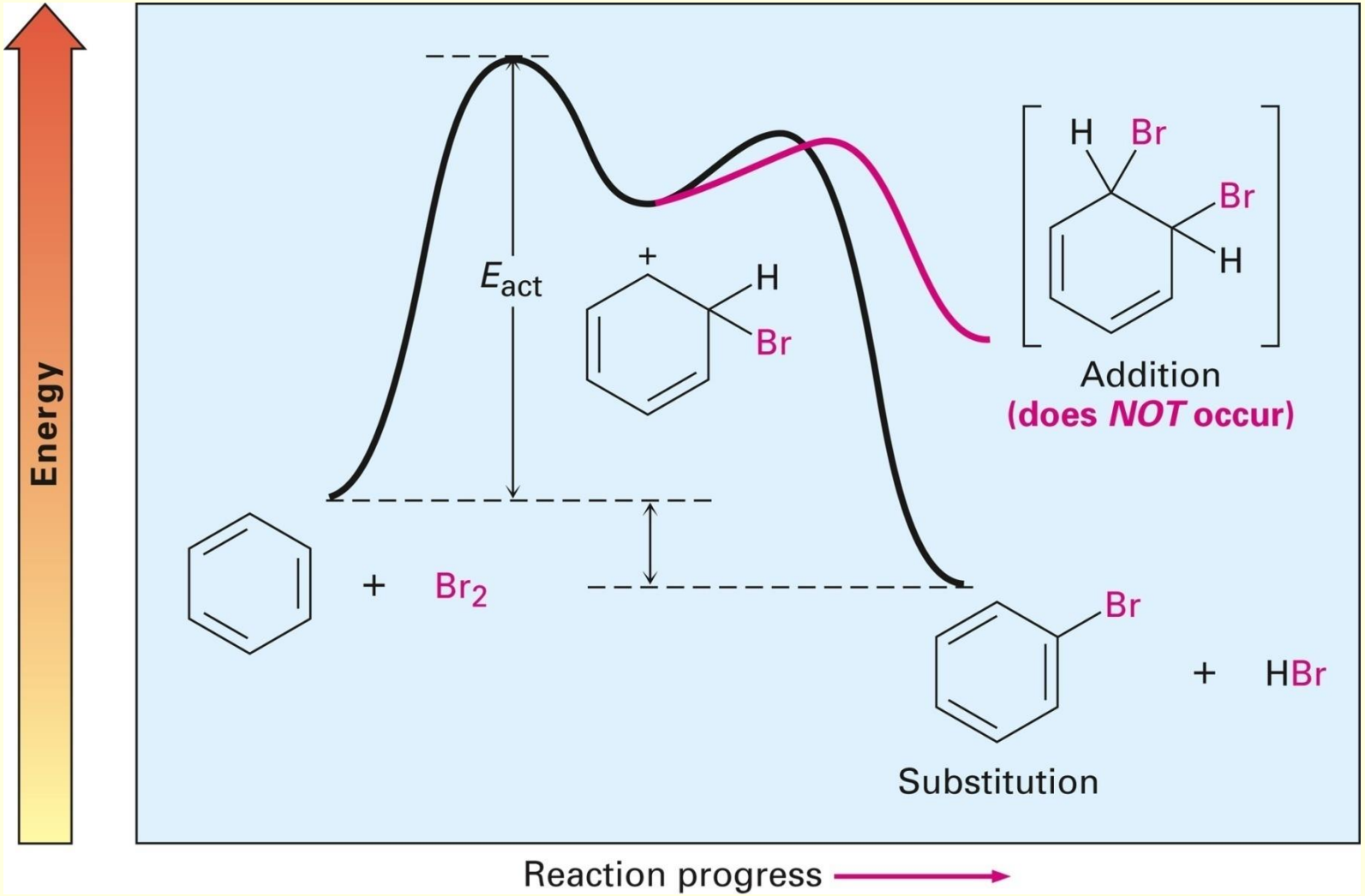


- The cationic addition intermediate transfers a proton to $FeBr_4^-$ (from Br^- and $FeBr_3$)
- This restores aromaticity (**in contrast with addition in alkenes)**

Mechanism

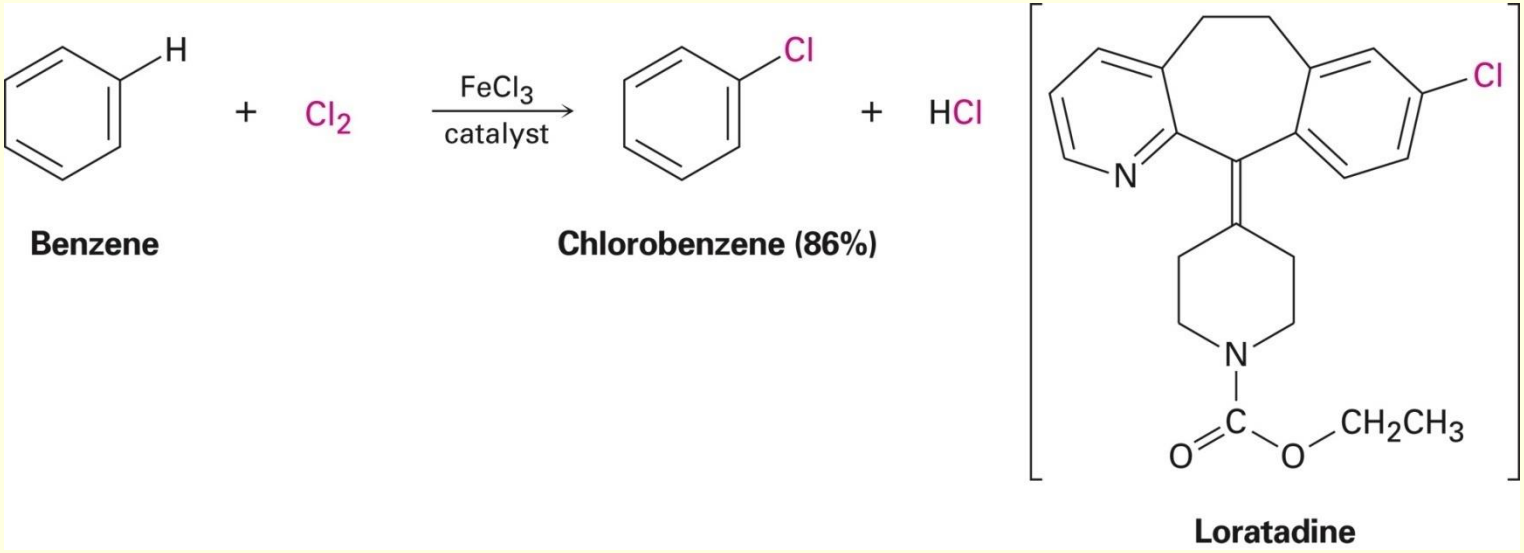


Energy diagram

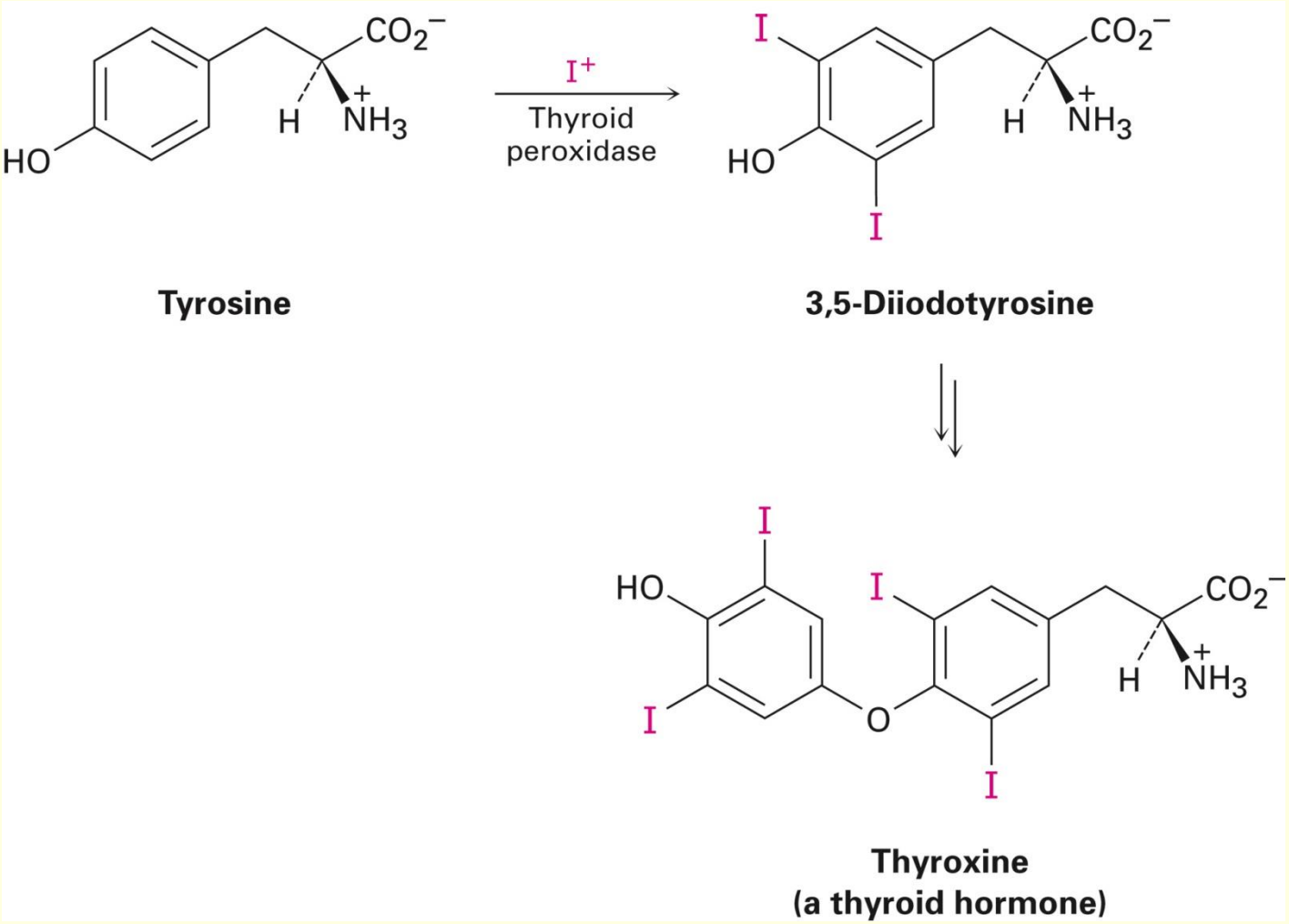


5.4 Other Electrophilic Aromatic Substitution Reactions

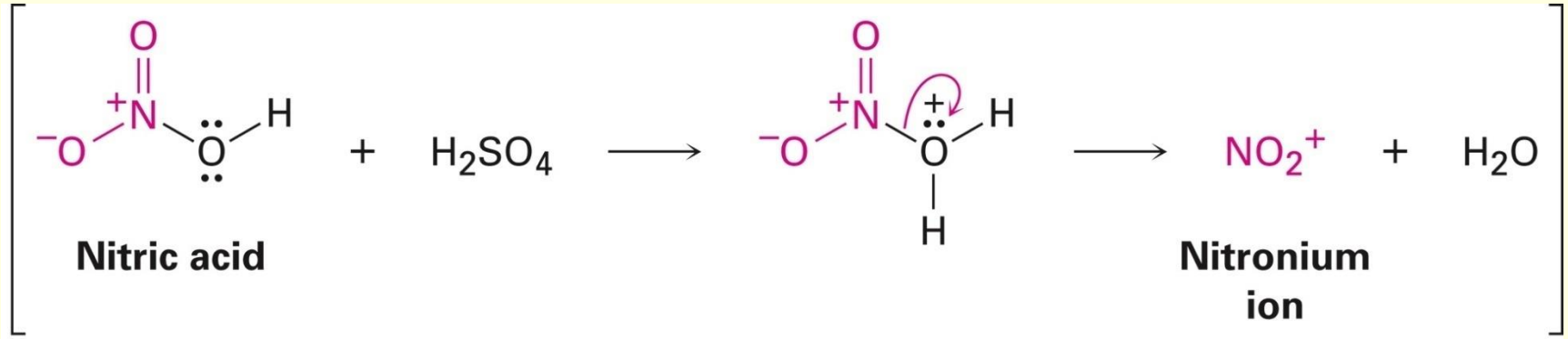
- **Chlorination and Iodination**
- Chlorine and iodine (but not fluorine, which is too reactive) can produce aromatic substitution with the addition of other reagents to promote the reaction
- Chlorination requires $FeCl_3$



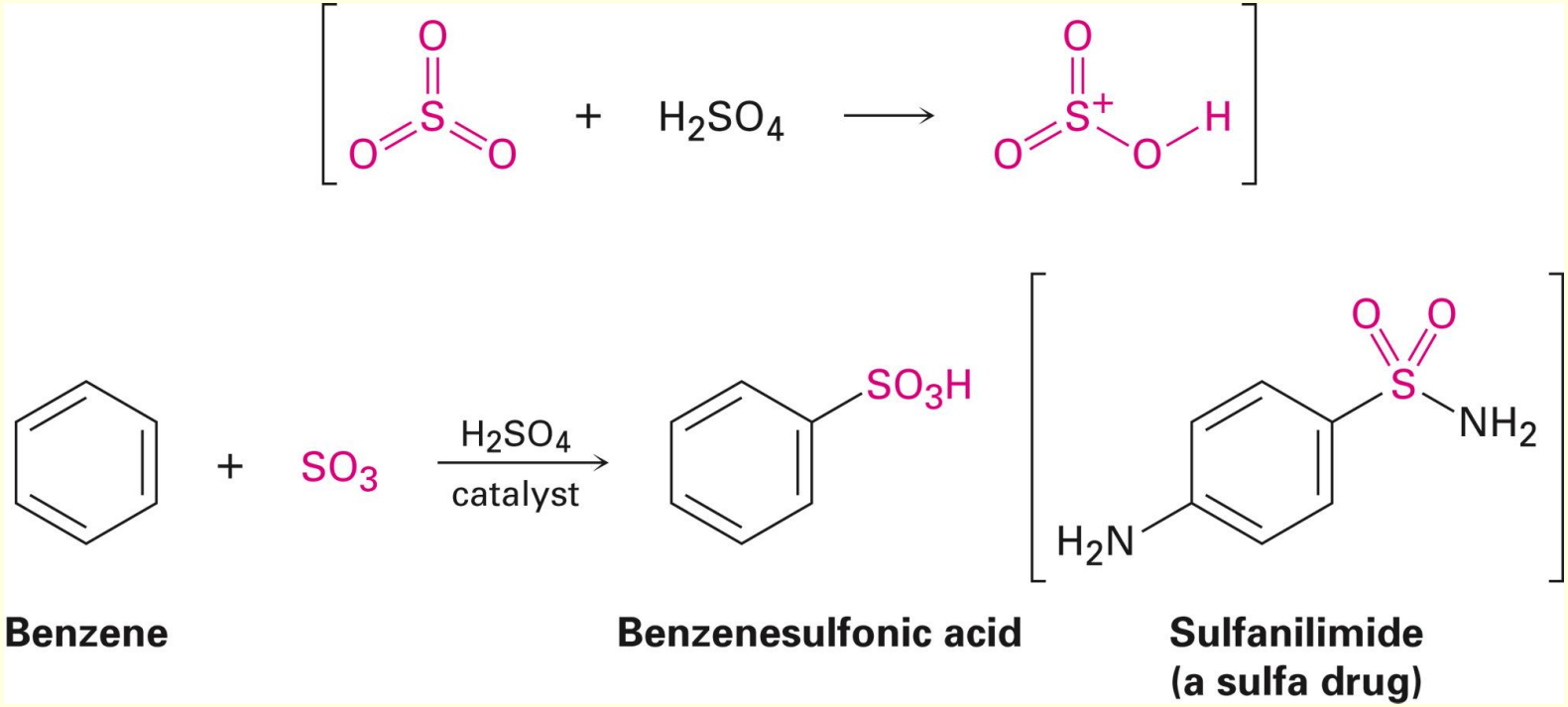
Biosynthesis of thyroxine, a thyroid hormone involved in regulating growth and metabolism.



- **Nitration**
- The combination of nitric acid and sulfuric acid produces **NO_2^+ (nitronium ion)**
- The reaction with benzene produces **nitrobenzene**
- The nitro-compound can be **reduced** by reagents such as iron, tin, or $SnCl_2$ to yield **amino-compound.**



- **Sulfonation**
- Substitution of H by SO_3 (sulfonation)
- Reaction with a mixture of sulfuric acid and SO_3
- Aromatic sulfonation is a key step in the synthesis of such compounds as the sulfa drug family of antibiotics.



Worked Example 5.2

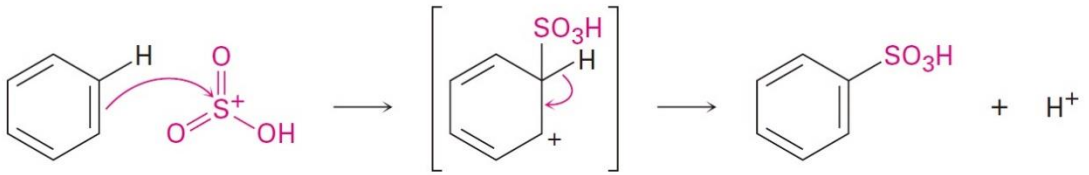
Writing the Mechanism of an Electrophilic Aromatic Substitution Reaction

Show the mechanism of the reaction of benzene with fuming sulfuric acid to yield benzenesulfonic acid.

Strategy

The reaction of benzene with fuming sulfuric acid to yield benzenesulfonic acid is a typical electrophilic aromatic substitution reaction, which occurs by the usual two-step mechanism. An electrophile first adds to the aromatic ring, and H^+ is then lost. In sulfonation reactions, the electrophile is HSO_3^+.

Solution



Carbocation intermediate