

Chapter 7 Arenes

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Problems

Answers

Organic compounds are roughly classified into two groups; aliphatic compounds and aromatic compounds.

Aromatic hydrocarbons, sometimes referred to as **arenes**, are important compounds which form the basis of aromatic compounds. Benzene is the most important and fundamental among aromatic compounds. Benzene was detected in coal gas and its structure was determined by Kekulé. Because benzene and most of its derivatives have specific odor and this is the reason why the name aromatic is given to these.

Arenes and their derivatives are important as the starting compound for a variety of organic compounds. Since these were obtained from coal, organic chemical industry was once essentially equal to coal industry. Since the middle of the 20th century, however, these were obtained from petroleum, and hence organic chemical industry is now based on petrochemical industry.

Study on the properties and reactions of arenes and their derivatives played the key role to develop theoretical organic chemistry.

7.1 Properties and nomenclature of arenes

Benzene, the representative aromatic hydrocarbons and its alkyl derivatives are liquids with characteristic odor. Naphthalene and anthracene, which are formed by ring condensation of benzene rings, are highly crystalline. Naphthalene, for instance, is crystalline to sublime easily. Thus, it was used as a proofing agent for cloth.

The stability of aromatic compounds is most clearly demonstrated by the difference in the reactivity of benzene vs. cyclohexene. Though cyclohexene behaves as a typical alkene, the reactivity of benzene is substantially different. The low reactivity of benzene is due to their aromaticity.

Table 7.1 Comparison of properties between benzene and cyclohexene

reaction (reagent)	benzene	cyclohexene
oxidation (aq. KMnO_4)	no reaction	rapid oxidation
reduction (H_2 + catalyst)	addition under vigorous condition	addition under mild condition
bromination (Br_2 in CCl_4)	no reaction	rapid addition
addition of HBr	rapid addition	rapid addition

(a) Benzene and alkylbenzenes

Representative arenes are benzene and its alkyl derivatives, alkylbenzenes. Alkylbenzenes include toluene with one methyl group and xylenes with two methyl groups. Use of common names is generally admitted for these arenes. However, it is possible to name these as alkyl-substituted benzenes. Three regioisomers exist for xylenes.

[Example]

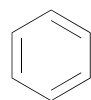
toluene \rightarrow methylbenzene

p-xylene \rightarrow 1,4-dimethylbenzene

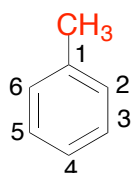
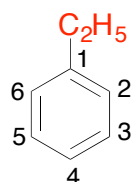
Examples of some representative arenes are given in Table 7.2.

Table 7.2 Some representative arenes

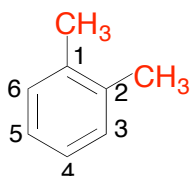
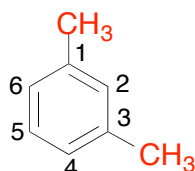
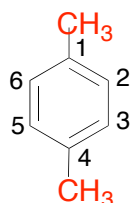
name	molecular formula	structural formula	m.p. (b.p.) ($^{\circ}\text{C}$)
benzene	C_6H_6	C_6H_6	5.533 (80.099)
toluene	C_7H_8	$\text{CH}_3\text{C}_6\text{H}_5$	-94.99 (110.626)
ethylbenzene	C_8H_{10}	$\text{C}_2\text{H}_5\text{C}_6\text{H}_5$	-94.98 (136.19)
<i>o</i> -xylene	C_8H_{10}	<i>o</i> - $(\text{CH}_3)_2\text{C}_6\text{H}_4$	-25.18 (144.41)
<i>m</i> -xylen	C_8H_{10}	<i>m</i> - $(\text{CH}_3)_2\text{C}_6\text{H}_4$	-47.89 (139.10)
<i>p</i> -xylene	C_8H_{10}	<i>p</i> - $(\text{CH}_3)_2\text{C}_6\text{H}_4$	13.26 (138.35)
isopropylbenzene (cumene)	C_9H_{12}	<i>iso</i> - $(\text{CH}_3)_2\text{CHC}_6\text{H}_5$	-96.02 (152.39)



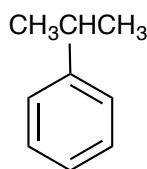
benzene

toluene
methylbenzene

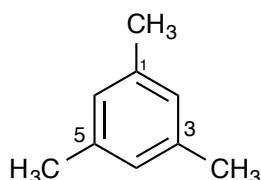
ethylbenzene

*o*-xylene
1,2-dimethylbenzene*m*-xylene
1,3-dimethylbenzene*p*-xylene
1,4-dimethylbenzene**Exercise 7.1** Naming of alkylbenzenes

Name cumene and mesitylene as an alkylbenzene.



cumene



mesitylene

Answer

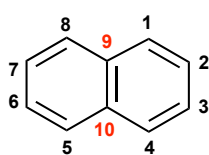
isopropylbenzene 1,3,5-trimethylbenzene

(b) Condensed ring aromatic hydrocarbons

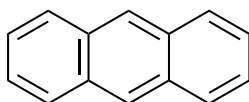
There are some aromatic hydrocarbons, named condensed ring aromatic hydrocarbons, in which two or more benzene rings share one side. Most of these have common names, and use of these common names is allowed in the systematic nomenclature. This type of compounds has many isomers depending on the number of benzene rings condensed and the number and position of shared sides. Naphthalene is the simplest among these compounds.

Compounds in which two sides are shared include two isomers, anthracene and phenanthrene.

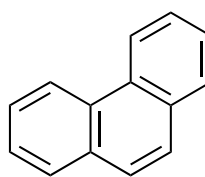
Biphenyls, in which two benzene rings are combined by a single bond, may be regarded as a benzene derivative in which a hydrogen atom of a benzene ring is replaced by a benzene ring. Hence, biphenyl is not a condensed ring aromatic compound.



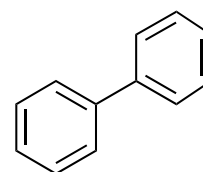
naphthalene



anthracene



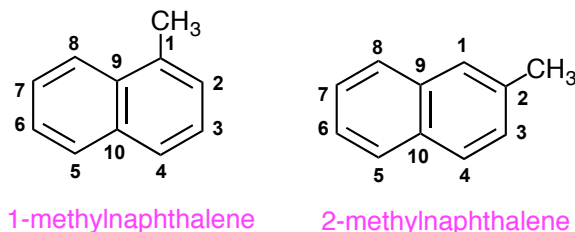
phenanthrene



biphenyl

The locants of condensed aromatic hydrocarbons are determined regardless of the presence or absence of substituents. For this reason, the locant of the carbon atom which bears only one substituent is not necessarily 1 (one).

[Example]



7.2 Structure of arenes

(a) Structure of benzene, naphthalene, and biphenyl

The most interesting aspect of the structure of a benzene ring is its carbon-carbon bond length. The carbon-carbon bond length of ethane is 0.154 nm. This value is the standard length of simple single bond made of two sp^3 hybridized carbon atoms. The carbon-carbon bond length of ethylene is 0.1339 nm, which is the standard length of pure double bond made of two sp^2 hybridized carbon atoms.

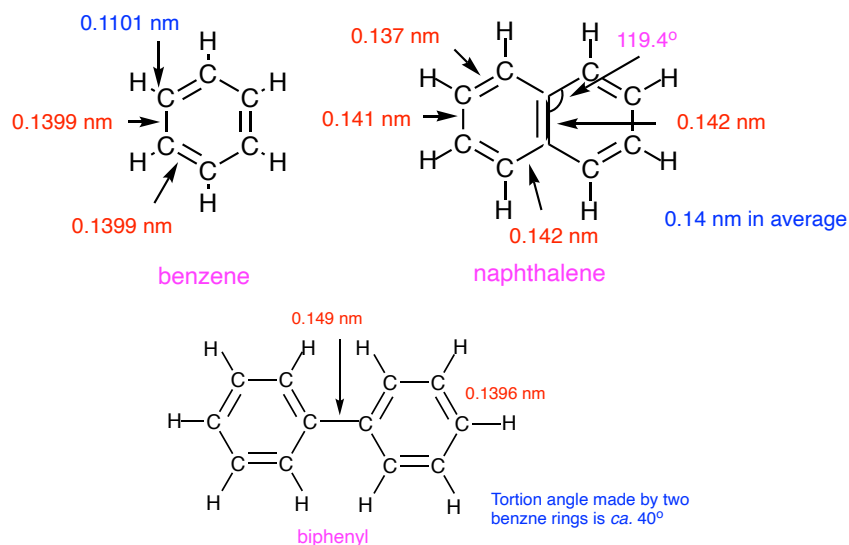


Figure 7.1 The carbon-carbon bond length in benzene, naphthalene, and biphenyl

On the other hand, the carbon-carbon bond length of naphthalene is not completely averaged, and some are longer and some shorter. Longer and shorter bonds alternatively appeared, and the bond shared by two benzene rings is longer.

In the case of biphenyl, the benzene rings are nearly regular hexagon, but two benzene rings do not exist in a common plane, but these are twisted by ca. 40° .

(b) Aromaticity

(1) Aromaticity based on heat of reaction

When the property of a benzene ring is discussed, it should be compared with an hypothetical

molecule 1,3,5-cyclohexatriene, composed with three single bonds (such as that of ethane) and three double bonds (such as that of ethylene). Addition of bromine does not take place with benzene but it should occur to 1,3,5-cyclohexatriene. Let us compare the stability of benzene and the hypothetical molecule.

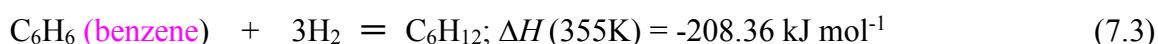
To make a quantitative comparison, it is advisable to use the heat of reaction accompanied by the hydrogenation of them. The hydrogenation of cyclohexene with 1 mole of hydrogen is exothermic and the heat of reaction is expressed by Eq. 7.1.



If the three double bonds of cyclohexatriene are essentially identical with that of cyclohexene, its heat of hydrogenation is expected to be three times of that of cyclohexene.



However, the observed value for the heat of hydrogenation of benzene is less than the expected value by 150 kJ mol^{-1}



This discrepancy is explained that, by the stabilization due to the resonance, the energy associated with a benzene ring is less than *ca.* 150 kJ mol^{-1} as compared with that of 1,3,5-cyclohexatriene which is composed of normal single and double bonds. The reduced energy by this stabilization is named **resonance energy** (Figure. 7.2).

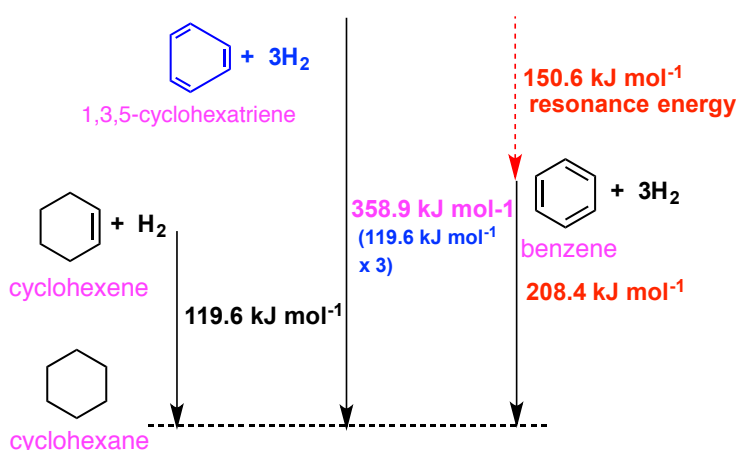


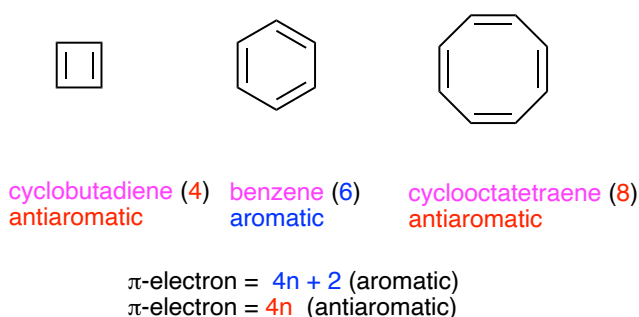
Figure 7.2 Resonance energy of a benzene molecule

(2) Hückel rule

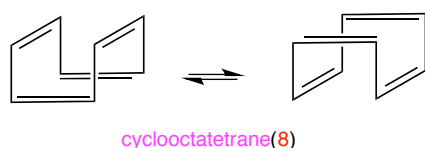
In 1930's, soon after the birth of quantum mechanics, a German physicist Erich Hückel (1896-1980) proposed a theory to handle with unsaturated compounds by means of quantum mechanics. The basis of his theory is π -electron approximation to focus only π -electrons of unsaturated

compounds. This method can relatively easily be applicable to aromatic compounds with high symmetry and it was possible to calculate the energy of molecules even in these days when use of computers is not yet possible. The method, summarized as **Hückel molecular orbital theory (HMO)**, was actively employed.

According to this theory, monocyclic aromatic hydrocarbons such as benzene which has $4n + 2$ π -electrons are stable, in other words, they have aromaticity. Those which has $4n + 2$ π -electrons are stable, in other words, they have aromaticity. On the other hand, compounds with $4n$ π -electrons are unstable, and in other words, they have **antiaromaticity**. These predictions are named **Hückel rule** or **($4n + 2$) rule**. Benzene has six π -electrons which correspond to the case when $n = 1$ for $4n + 2$. To the contrary, both cyclobutadiene and cyclooctatetraene do not belong to $4n + 2$, but to $4n$ ($n = 1$ and 2 , respectively). Hence it was believed that these could not exist as stable entities. In fact, both of them do not exist in the day of Hückel.

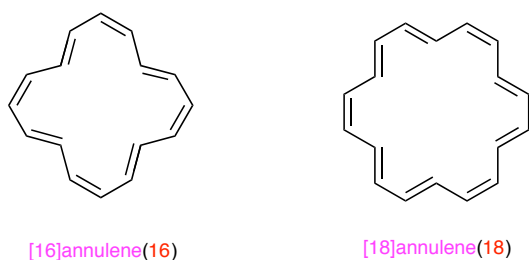


Later, cyclooctatetraene was synthesized and proved to be stable. It seems as if the compound violates the Hückel rule. It was shown that the compound is not a planar, cyclic conjugated system. Rather, it has a non-planar bath-tub structure. Moreover, a ring inversion like that of cyclohexane is associated with this compound. In a word, there is no violation of Hückel rule. The compound is out of scope of Hückel rule.



(3) Nonbenzenoid aromatic compounds

If Hückel rule is correct, any cyclic conjugated system with $4n + 2$ π -electrons should have aromaticity even if these are not six-membered. In fact, it was found that [16]annulene with $4n = 16$ π -electrons is antiaromatic, while [18]annulene with $4n + 2 = 18$ π -electrons is aromatic,



Furthermore, ionic species also exhibit aromaticity if ever they have $4n + 2 \pi$ -electrons. Among the ionic species, cyclopropenyl ion with 2 π -electrons, cyclopentadienylide ion with 6 π -electrons and cycloheptatrienyl ion with 10 π -electrons are aromatic, while cyclopropenylide ion with 4 π -electrons, cyclopentadienyl ion with 4 π -electrons and cycloheptatrienide ion with 8 π -electrons are antiaromatic, Aromatic compounds composed of rings other than benzene are named **nonbenzenoid aromatic compounds**.

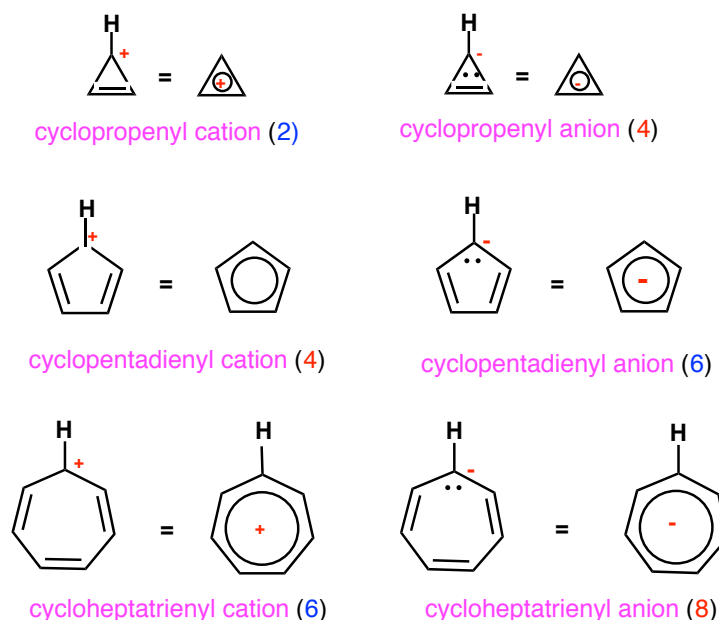


Figure 7.3 Aromaticity and antiaromaticity of ionic species
(Values in parentheses are the number of π -electrons)

Point: Aromaticity

Aromaticity: Specific stability associated with the cyclic conjugated system such as arenes.

Hückel rule:

If the number of π -electrons of monocyclic conjugated system is:

$4n + 2$; aromatic (stable)

$4n$; antiaromatic (unstable)

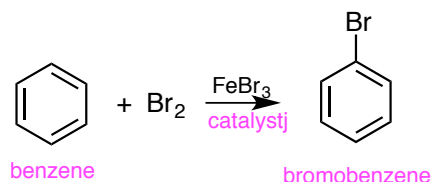
7.4 Reactions of arenes

(a) Electrophilic aromatic substitution of benzene

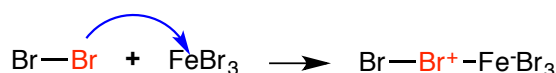
(1) Halogenation

As described before, the most characteristic feature of the reactivity of aromatic hydrocarbons is the fact that no electrophilic addition takes place (such as addition of bromine to ethylene) which is usually observed for compounds with double bonds.

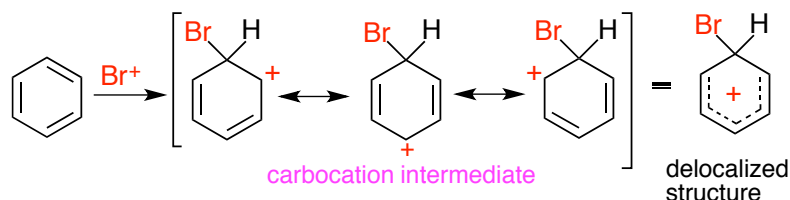
However, if benzene is reacted with bromine in the presence of iron(III) bromide (FeBr_3), one hydrogen atom of benzene is replaced by a bromine atom to give bromobenzene. In other words, substitution, rather than addition, takes place.



In this reaction, FeBr₃ plays a very important role. FeBr₃, a Lewis acid, combines with bromine by coordination bond, to enhance the electrophilicity of bromine.

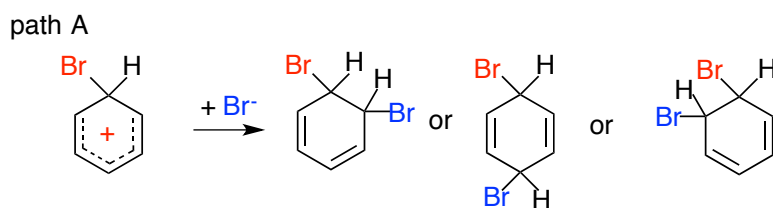


Thus, the activated bromine attacks the π-electrons of benzene as an electrophile, to yield carbocation intermediate which corresponds to the addition product of Br⁺ with benzene. The rightmost structure is often employed which emphasize the role of delocalization.



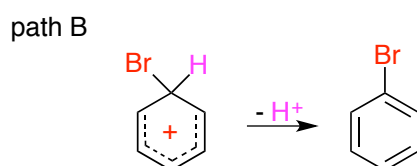
This carbocation intermediate shown above has three resonance structures, and consequently more stable than the standard carbocation.

If a bromide anion combines with the carbocation, a dibromide shown below will be formed (path A).



It is clear, however, that the dibromide lost the stability associated with cyclic conjugation of benzene.

On the other hand, loss of a hydrogen atom from the reactive intermediate, bromobenzene will be formed in which the cyclic conjugation of benzene is recovered (path B). What occurs is path B which is energetically favorable.



Such substitutions as bromination of benzene in which electrophiles attack π-electron or electron-rich center are named **electrophilic substitution**. The process of aromatic electrophilic substitution

is conveniently envisaged in the reaction coordinate (Figure 7.4), in which the horizontal axis represents the progress of the reaction and the vertical axis represents the energy of the system.

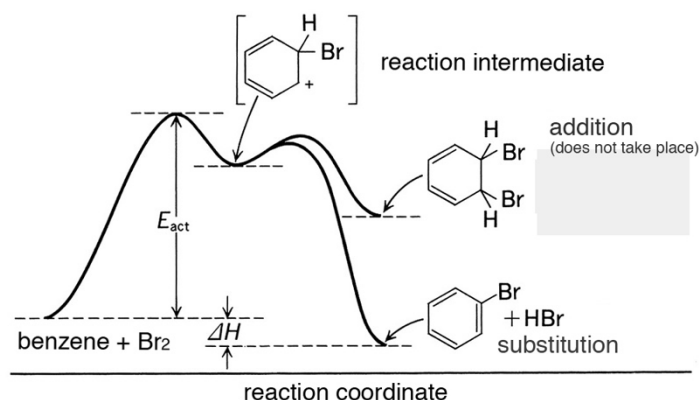
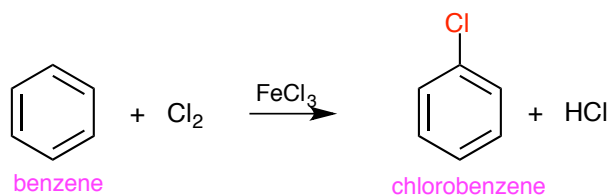


Figure 7.4 Reaction coordinate of the reaction between benzene and bromine.

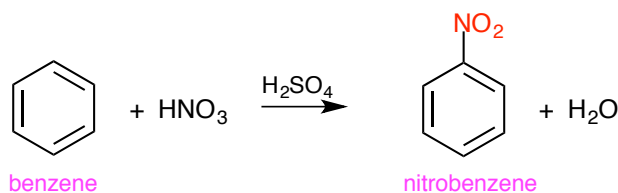
E_{act} : activation energy; ΔH : heat of reaction

Chlorination of benzene with chlorine and FeCl_3 is also important like the bromination. These are altogether named halogenation.



(2) Nitration

The reaction between benzene and a mixture of conc. sulfuric acid and conc. nitric acid (mixed acid) to introduce a nitro group in benzene is named **nitration**. This is one of the most important electrophilic substitution of benzene as a means to introduce nitrogen functionality into the ring.



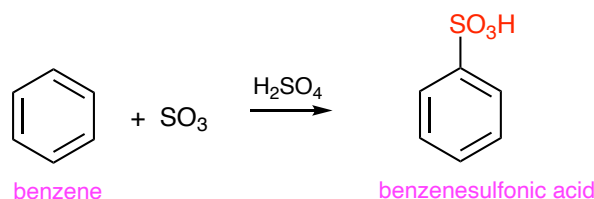
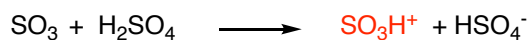
The role of sulfuric acid is not merely as a dehydrating agent but it generates nitronium ion (nitroyl ion) NO_2^+ which acts as an electrophilic reagent.



(3) Sulfonation

In sulfonation, a sulfonyl group is introduced into a benzene ring by the reaction between benzene

and conc. sulfuric acid. By this method a functional group containing sulfur can be introduced. The electrophilic reagent is SO_3 or SO_3H^+ generated from the following reaction.



Point: Aromatic electrophilic substitution

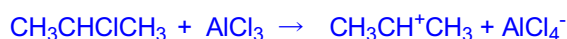
These reactions proceed as indicated below.

- (1) An electrophilic reagent attacks π -electron of the benzene ring
- (2) Formation of a carbocation intermediate
- (3) Recovery of aromaticity by removal of the proton

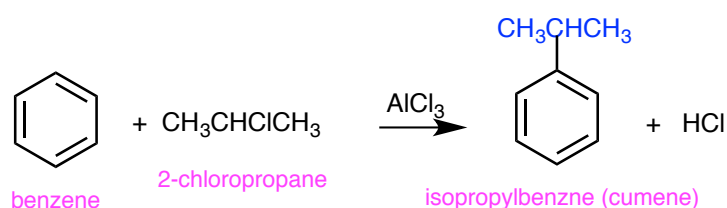
(4) Friedel-Crafts reaction (alkylation)

The carbon atom of alkyl halides is slightly positive (Ch. 4.1), but it is not enough to attack benzene as an electrophile to cause an electrophilic substitution. Aluminum chloride AlCl_3 , a strong Lewis acid, can deprive a halogen atom from alkyl halides to enhance its electrophilicity (you can assume that formally a carbocation is formed)

For instance, isopropyl chloride (2-chloropropane) yields a carbocation $\text{CH}_3\text{C}^+\text{HCH}_3$.

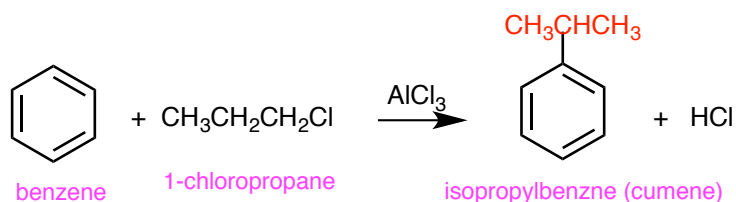


If this reaction is carried out in benzene, an isopropyl group will be introduced into benzene. This type of reaction is rather popular, and a variety of alkyl groups is introduced into benzene rings.



This reaction is named **Friedel-Crafts reaction** after the names of discoverers, Charles Friedel (1832-1899) and James Mason Crafts (1839-1917). Friedel-Crafts reaction is one of a few reactions that can form carbon-carbon bonds.

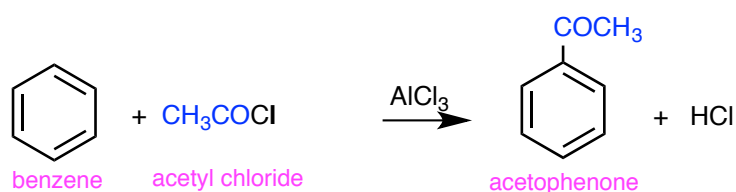
Interestingly, propyl chloride ($\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$) also gives the same product.



It is believed that the primary carbocation generated from propyl chloride rearranges to a more stable secondary carbocation, which reacted with benzene.

(5) Friedel-Crafts reaction (acylation)

By the reaction benzene and acetyl chloride CH_3COCl in the presence of aluminum chloride $AlCl_3$, an acetyl group CH_3CO- is introduced into the benzene ring. This is also Friedel-Crafts reaction, and is named **Friedel-Crafts acylation** to differentiate this reaction from the alkylation described in the previous session.



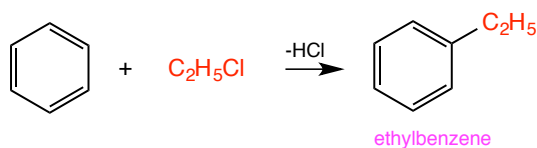
Exercise 7.2 Friedel-Crafts reaction

The reaction between benzene and the following reagents are attempted. Predict the products.

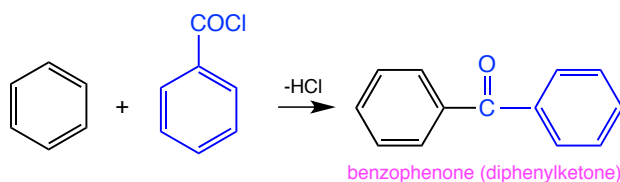
(a) ethyl chloride (chloroethane) CH_3CH_2Cl , (b) benzoyl chloride C_6H_5COCl

Answer

(a) ethylbenzene; $C_6H_6 + CH_3CH_2Cl \rightarrow C_6H_5CH_2CH_3 + HCl$



(b) benzophenone: $C_6H_6 + C_6H_5COCl \rightarrow C_6H_5COC_6H_5 + HCl$



(b) Nitration of substituted benzenes

(1) Nitration of toluene

Toluene also suffers from aromatic electrophilic substitution. Let us consider nitration of toluene.

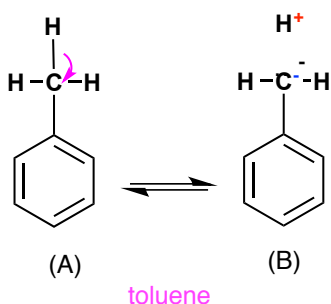
There arise two questions.

- (i) In comparison, which is more reactive, benzene and toluene? (reactivity)
- (ii) In which position the nitro group is introduced relative to the methyl group? (orientation)

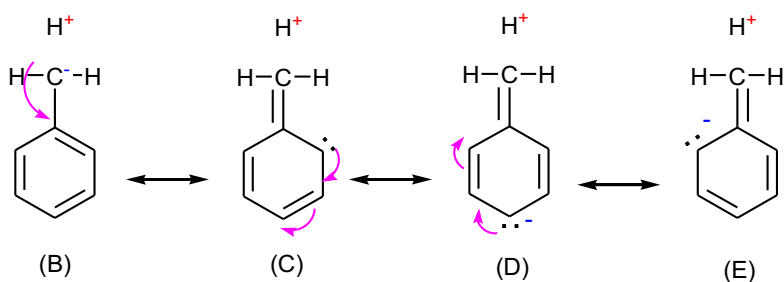
According to the experiment in which an equal amount of benzene and toluene is nitrated, the amount of nitrated toluene is 25 times as much as that of nitrated benzene. The reactivity of toluene toward electrophilic reagents is 25 times as large as that of benzene. In other words, the reactivity of benzene is enhanced by the methyl group. To summarize, a methyl group is an **activating group** to activate benzene in aromatic electrophilic substitution. As will be seen later, there are other groups which enhance the reactivity of benzene. A methyl group is rather weak one.

(2) The role of methyl group: activation

As is the case with toluene, when a methyl group is bonded to a conjugated system (in this case, benzene), a structure (B) in which one of the hydrogen atoms of the methyl group is dissociated as proton contributes to a very small extent.



For resonance formula (B), there are resonance formulas (C) and (E) in which the negative charge is moved from methyl carbon atom to the *o*-carbon atom of the benzene ring, and another resonance formula (D) in which the negative charge is moved from methyl carbon atom to the *π*-carbon atom of the benzene ring. These are also helpful to stabilize the structure (B).



This type of phenomenon in which a part of π -electron of methyl group conjugates with the π -electron of unsaturated bonds is named **hyperconjugation**.

(3) The role of methyl group: orientation

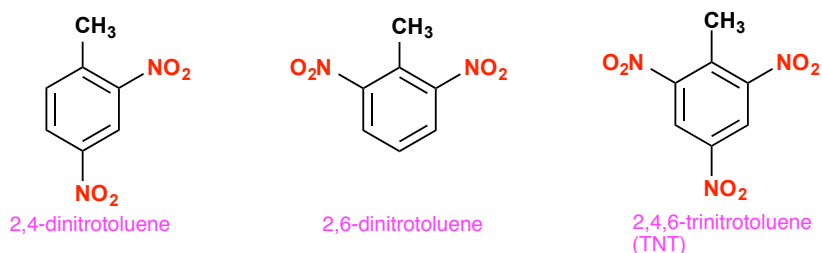
By means of hyperconjugation, the methyl group of toluene exhibits electron-donating property and hence is an activating group. The electron density is increased at the *o*- and *p*-carbon atoms by hyperconjugation. Almost all products of nitration are *o*- and *p*-nitrotoluene. Such groups as a methyl group are named an ***o*, *p*-directing group**.

Exercise 7.3 Nitration of toluene

By adjusting the reaction condition of nitration of toluene, it is possible to introduce two or three nitro groups. Predict the structures of di- and trinitrotoluenes.

Answer

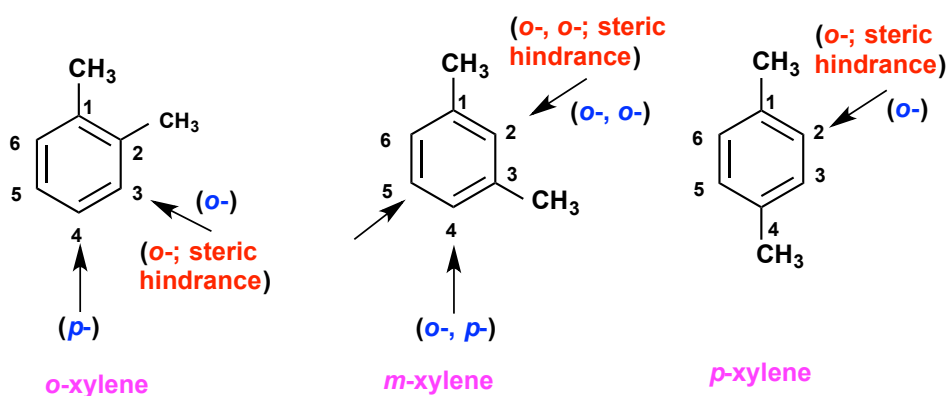
Since a methyl group is *o*-, *p*-directing, nitro groups will be introduced mainly in *o*- and *p*-positions. As for dinitro compounds, 2,4- and 2,6-dinitrotoluene and as for trinitro compounds, 2,4,6-trinitrotoluene are mainly formed. 2,4,6-trinitrotoluene is an explosive and is also known as TNT.

**(4) Nitration of other arenes**

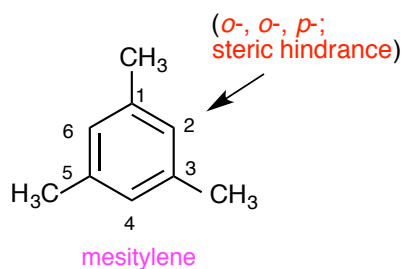
It is useful to study the nitration of such arenes as xylenes and mesitylene which have two or more methyl groups. For *o*-xylene, C³ and C⁴ may be nitrated. C³ is activated by one methyl group while this position is overcrowded by the adjacent methyl group. On the other hand, C⁴ is activated by one methyl group and there is involved no steric strain. Hence nitration takes place exclusively at this position.

For *m*-xylene, C² and C⁴ may be nitrated. Though C² is activated by two methyl groups, this position may be difficult to nitrate because of excessive steric congestion. C⁴ is activated by *o*- and *p*-methyl groups and may relatively easily be nitrated.

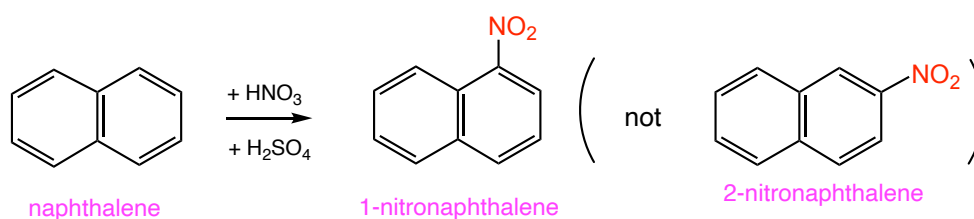
For *p*-xylene, only C² will be nitrated. Most of the experimental results agree with the prediction.



The case of mesitylene is interesting. The only possible position for nitration, C², is sterically congested (sandwiched by two methyl groups). However, this position is activated by three methyl groups. Thus, the nitration is very easy.



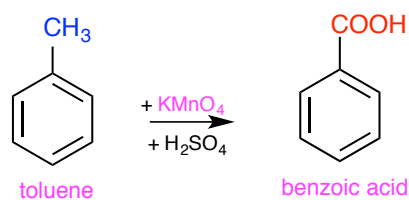
As compared with the reactivity of benzene, that of naphthalene is higher. For instance, under the same condition, naphthalene is nitrated 400 times as fast as benzene. Substitution takes place at C¹.



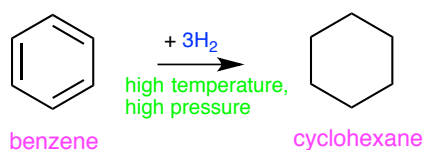
Kenichi Fukui (1918-1998), the 1st Japanese recipient of Nobel Prize in chemistry, theoretically explained with the aid of quantum chemistry (Frontier Orbital theory) the reason why C¹ rather than C² is nitrated.

(c) Other reactions

Alkenes are readily oxidized and the double bonds are cleaved. Under a similar condition (potassium permanganate acidified with sulfuric acid), benzene is not oxidized. However, alkyl side chains of benzene are oxidized by potassium permanganate acidified with sulfuric acid.

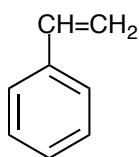


In the presence of catalyst, hydrogenation of alkenes proceeds in a mild condition (room temperature, 1 atm) Benzene is also hydrogenated to yield cyclohexane. However, more severe reaction condition is required (for instance, 100 -200 °C, 100 atm).

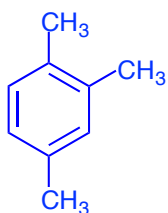


Problems**7.1**

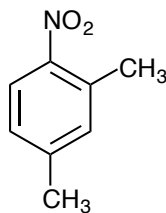
Name the following aromatic compounds.



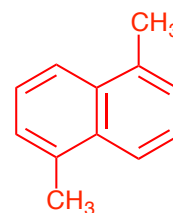
(a)



(b)



(c)



(d)

7.2

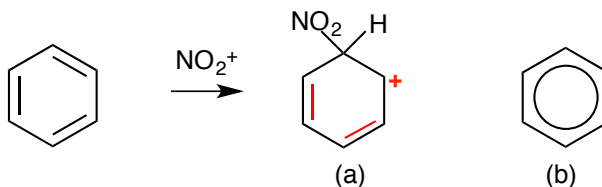
Draw the structures of the following aromatic compounds.

- methoxybenzene (anisole)
- 1,3,5-benzenetriol
- trans*-1,2-diphenylethylene
- 4,4'-dimethylbiphenyl

7.3

If NO_2^+ attacks benzene, (a) is formed.

- Draw the resonance structures other than (a).
- To emphasize the delocalization of π -electrons, benzene is often represented as (b), not as the Kekulé structure. Draw the structure of (a) in a manner like (b)

**7.4**

Draw the reaction formulas for the reaction between benzene and each of the following reagents under a mild condition. If reactions do not take place, explain the reason why.

- Br_2 (with FeBr_3)
- Br_2
- HNO_3 (with H_2SO_4)
- SO_3 (with H_2SO_4)
- $\text{C}_2\text{H}_5\text{Br}$ (with AlBr_3)
- $\text{C}_2\text{H}_5\text{COCl}$ (with AlCl_3)
- H_2 (with Pt catalyst, ambient temperature and pressure)

7.5

Nitrobenzene is formed by the reaction between benzene and a mixture of conc. HNO_3 and H_2SO_4 .

- Explain how nitric acid is cleaved into ions. Draw the dissociation of nitric acid into ions

- (2) Draw the structure of the product if the nitric acid is added to the double bond.
- (3) Explain the reason why nitrobenzene, rather than the compound predicted in (2), is obtained.

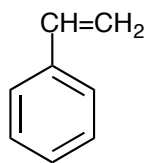
7.6

Heat of hydrogenation of cyclohexene is 120 kJ mol^{-1} (exothermic). On the other hand, the heat of formation of benzene is 208 kJ mol^{-1} (exothermic). Estimate the resonance energy of benzene.

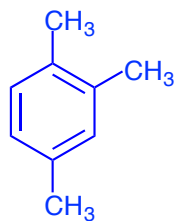
7.7 Guess the structures of mononitro compounds of three isomers of xylene.

Answers

7.1

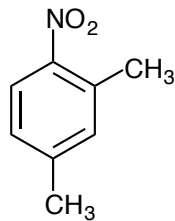


(a)

styrene
(vinylbenzene)

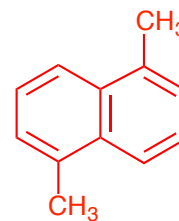
(b)

1,2,4-trimethylbenzene



(c)

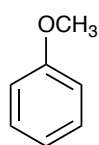
2,4-dimethylnitrobenzene



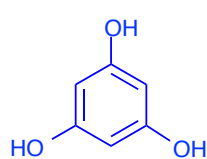
(d)

1,5-dimethylnaphthalene

7.2

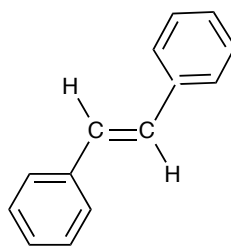


(a)

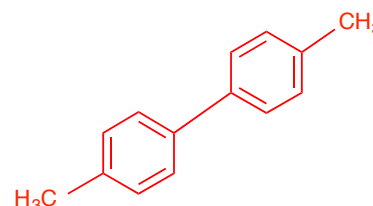
methoxybenzene
(anisole)

(b)

1,3,5-benzenetriol



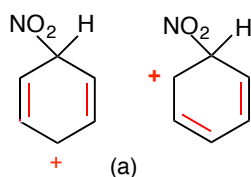
(c)

trans-1,2-diphenylethylene

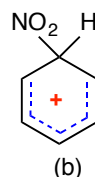
(d)

4,4'-dimethylbiphenyl

7.3



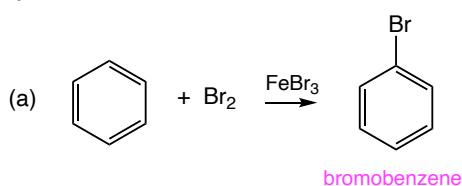
(a)

(a) Localization model: charges are localized at *o*- and *p*-positions.

(b)

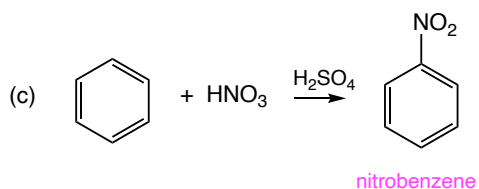
(b) Delocalization model: charges are delocalized at *o*-, *m*- and *p*-positions.

7.4

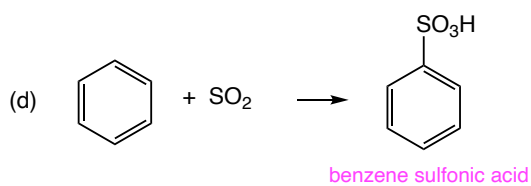


bromobenzene

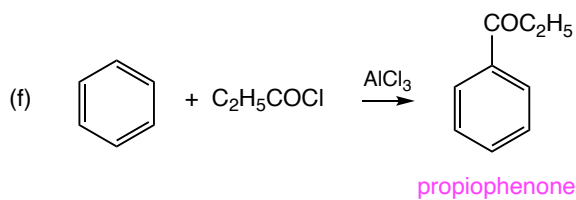
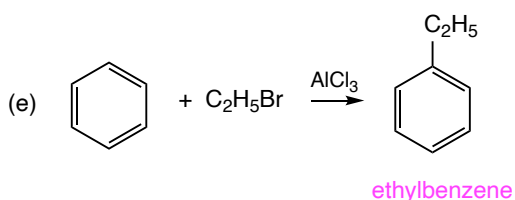
(b) An addition reaction takes place only by irradiation of light.



nitrobenzene

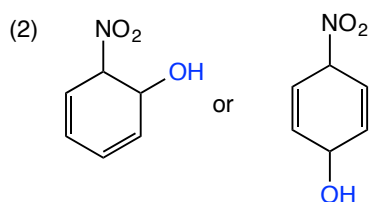
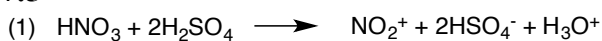


benzene sulfonic acid



(g) No reaction takes place at ambient temperature and pressure.

7.5



(3) Compounds written in (2) lost the resonance energy.

7.6

See Ch. 7.2 (b)

7.7

