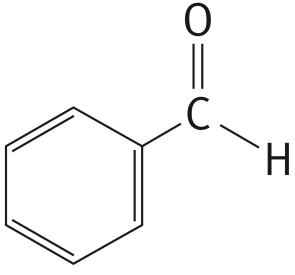
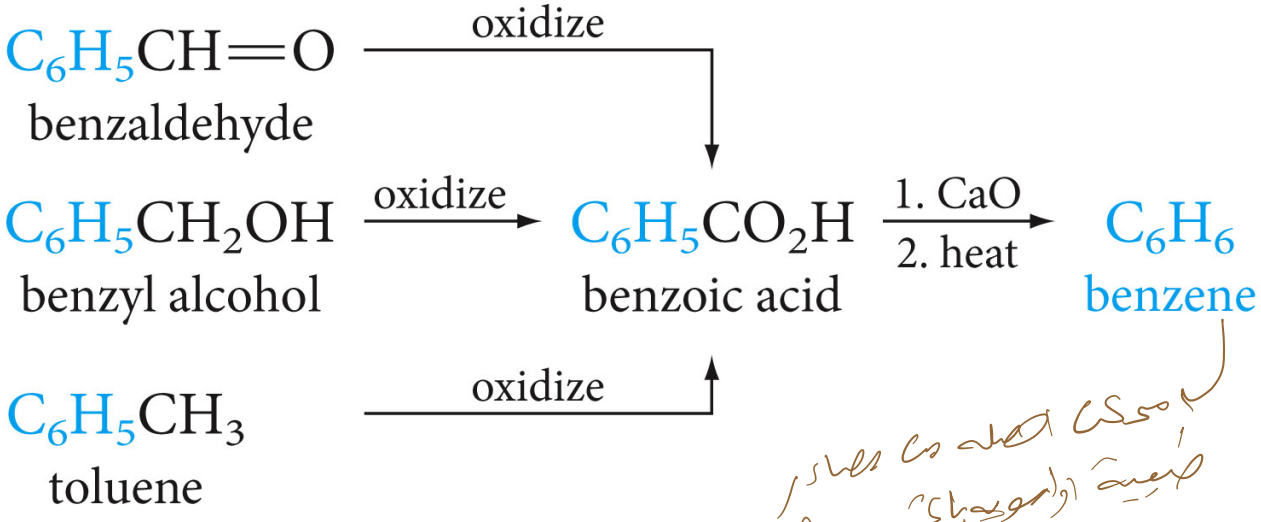
Chapter 4: Aromatic Compounds



benzaldehyde

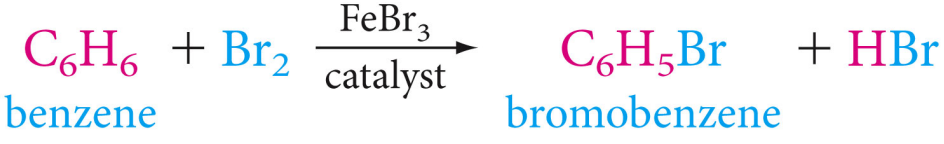
Bitter almonds are the source of the aromatic compound benzaldehyde

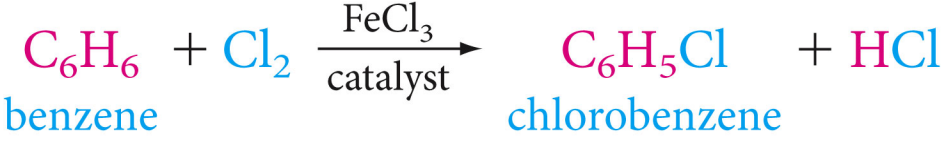
Sources of Benzene



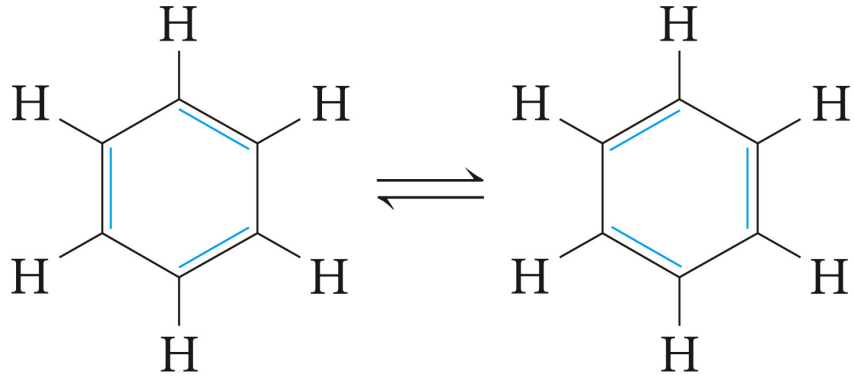
Some Facts About Benzene

Reacts mainly by substitution

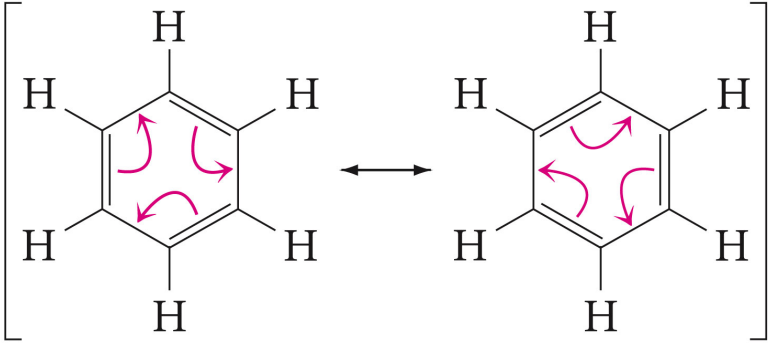




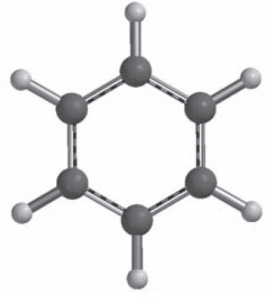
Friedrich August Kekule'

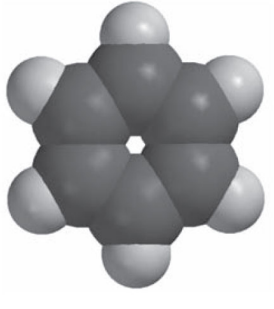


the Kekulé structures for benzene

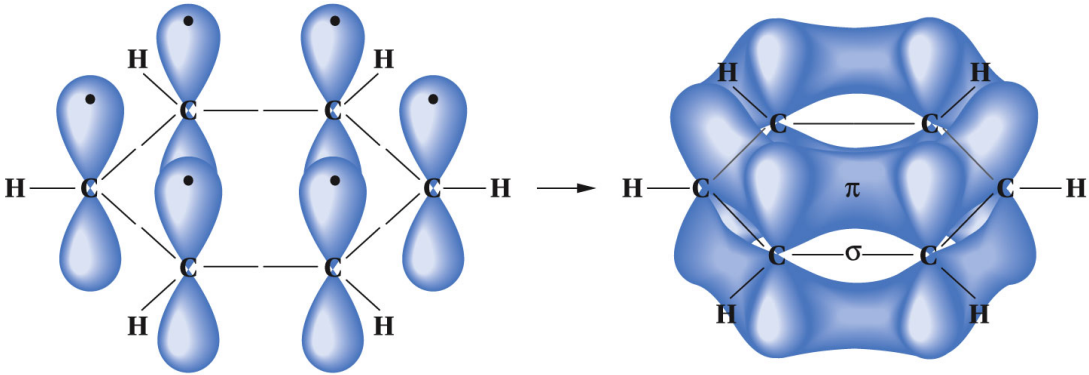


Benzene is a resonance hybrid of these two contributing structures.

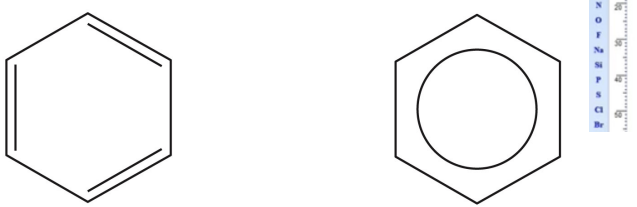


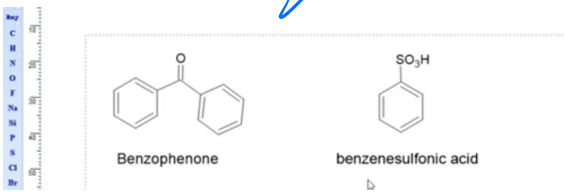


The Orbital Model for Benzene



Symbols for Benzene

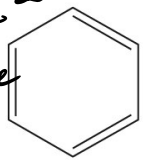




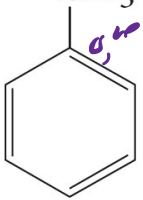
Kekulé derevative delocalized pi cloud

Nomenclature of Aromatic Compounds

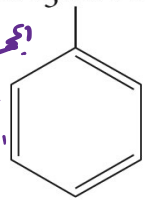
Monosubstituted benzenes with common names



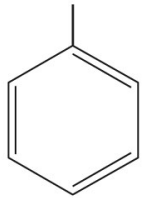
benzene



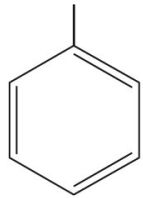
toluene



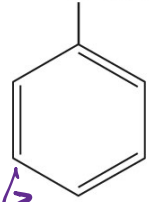
cumene



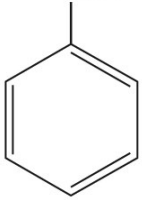
styrene



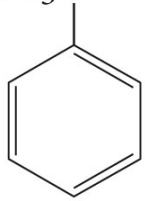
phenol



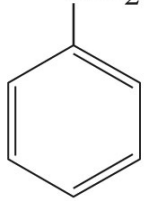
anisole



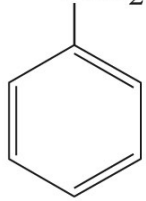
benzaldehyde



acetophenone

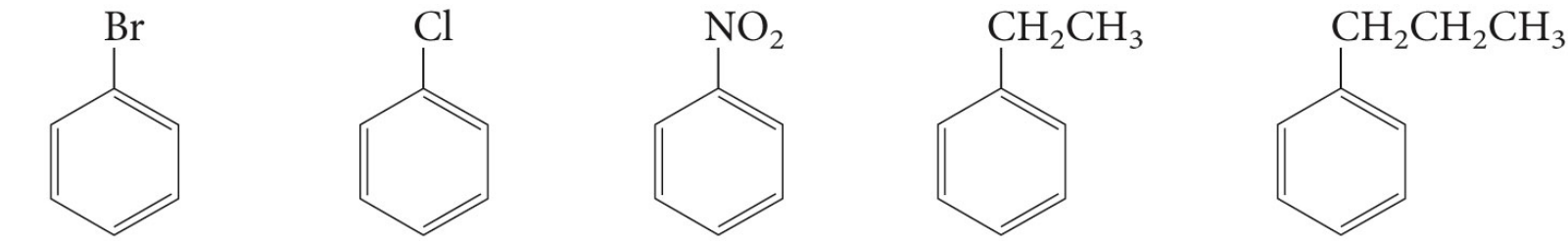


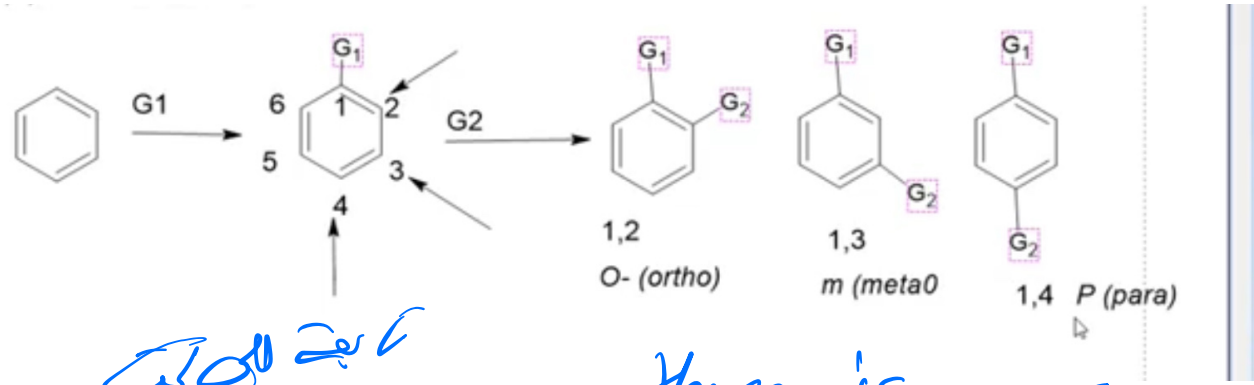
benzoic acid



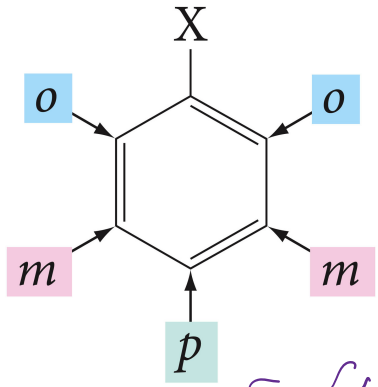
aniline

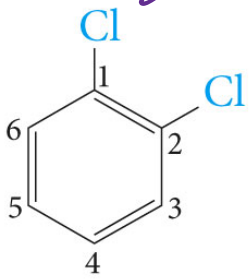
Monosubstituted benzenes that do not have common names



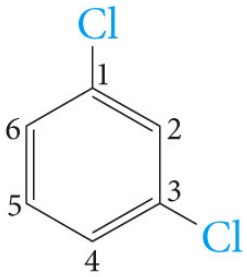


When two substituents are present, we use prefixes *ortho*-, *meta* -, and *para-,* usually abbreviated as o-, m-, and p-, respectively.

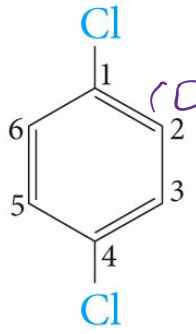




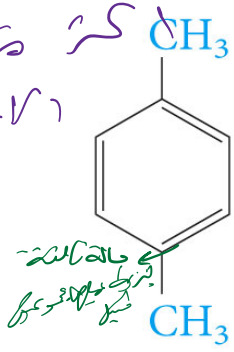
ortho-dichloro-benzene



meta-dichloro-benzene



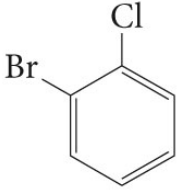
para-dichloro-benzene



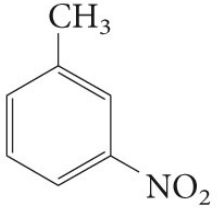
para-xylene**

Common name

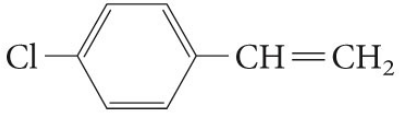
para-chlorobenzene-sulfonic acid



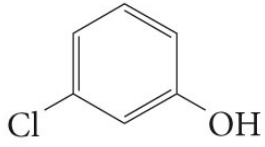
o-bromochlorobenzene
(note alphabetical order)



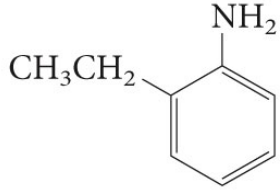
m-nitrotoluene



p-chlorostyrene

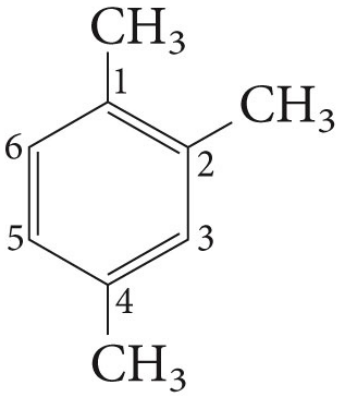


m-chlorophenol

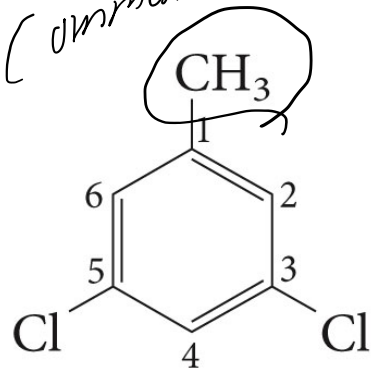


o-ethylaniline

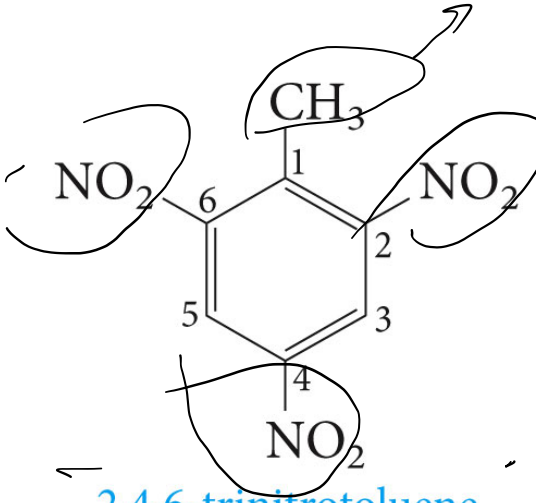
For more than two substituents, their positions are designated by numbering the ring.



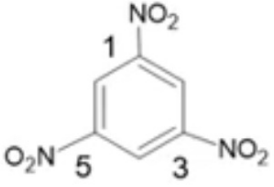
1,2,4-tri-methylbenzene



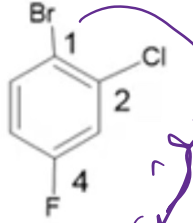
3,5-dichlorotoluene



2,4,6-trinitrotoluene (TNT)

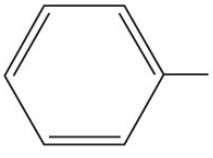


1,3,5-trinitrobenzene

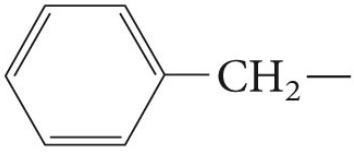


1-bromo-2-chloro-4-flourobenzene

Aromatic hydrocarbons, as a class called Arenes (Ar) the aryl groups are therefore aromatic substituents.

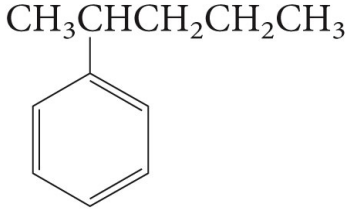
C_6H_5— or 

phenyl group

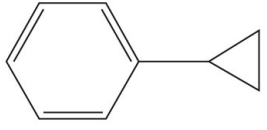
$C_6H_5CH_2$— or 

benzyl group

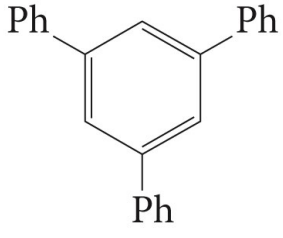
The symbol Ph is sometimes used as an abbreviation for phenyl group



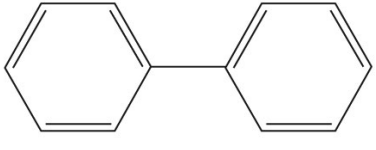
2-phenylpentane
(or 2-pentylbenzene)



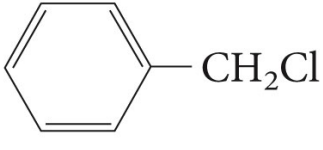
phenylcyclopropane
(or cyclopropylbenzene)



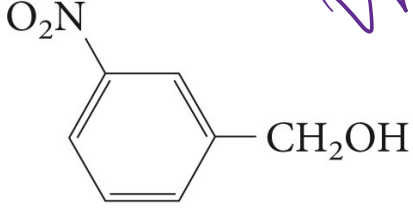
1,3,5-triphenylbenzene



biphenyl

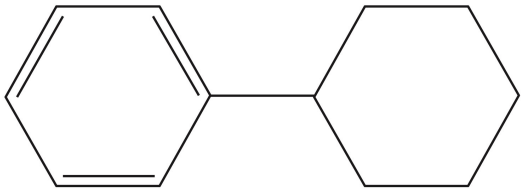


benzyl chloride

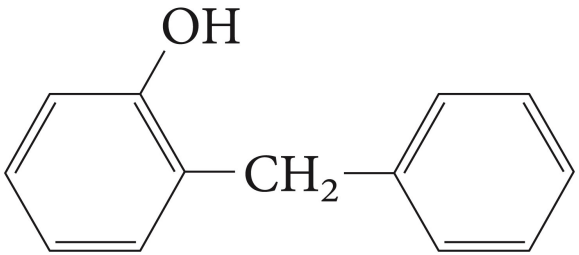


m-nitrobenzyl alcohol

Name the following structures

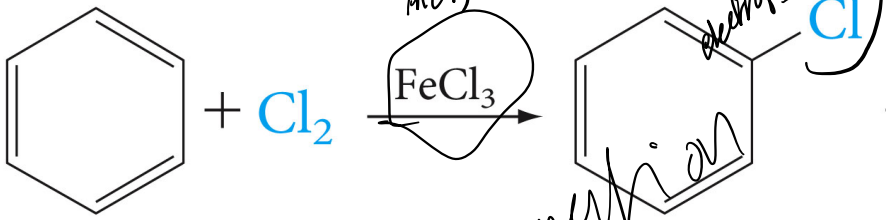


cyclohexylbenzen
phynil cyclohexan

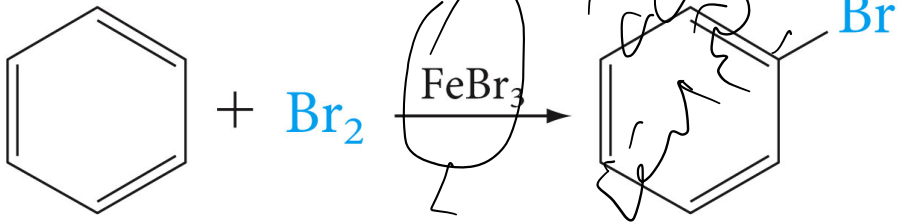


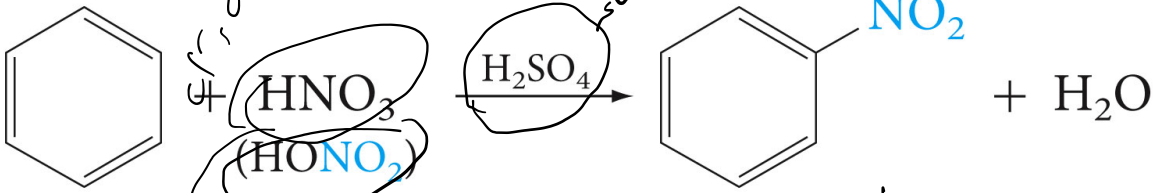
o-benzyl phenol

Electrophilic Aromatic Substitution

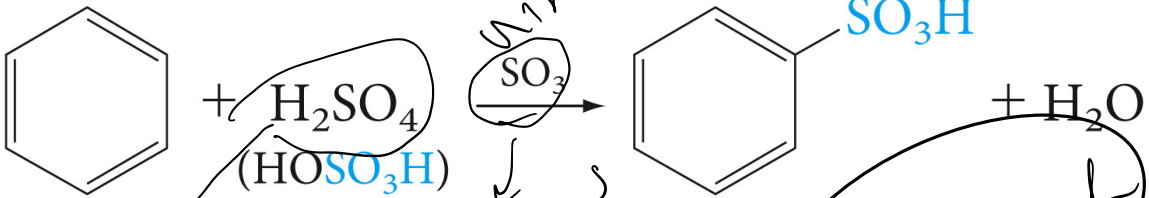


1- Halogenation

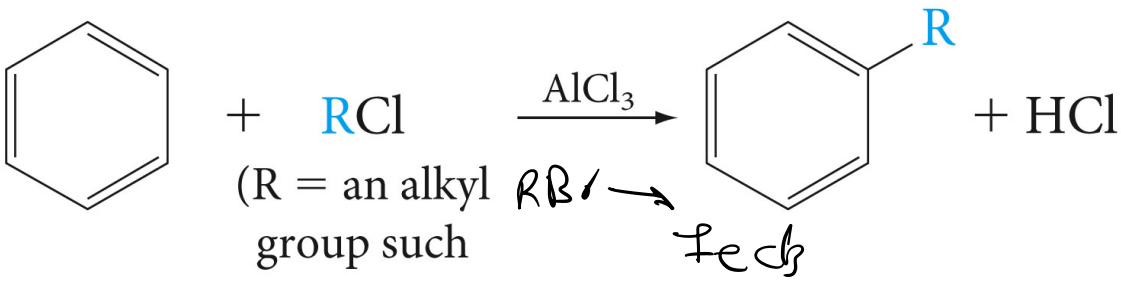




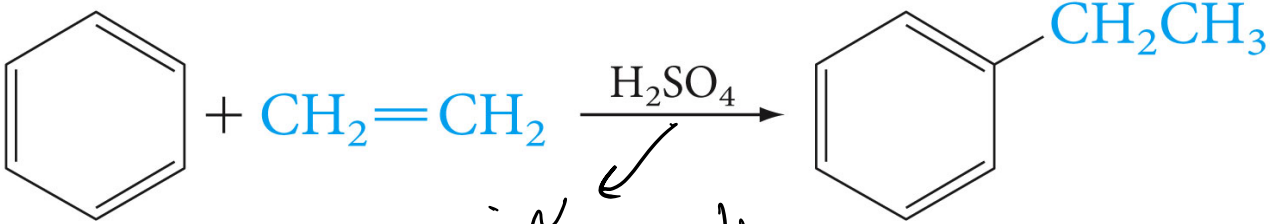
2- Nitration of benzene

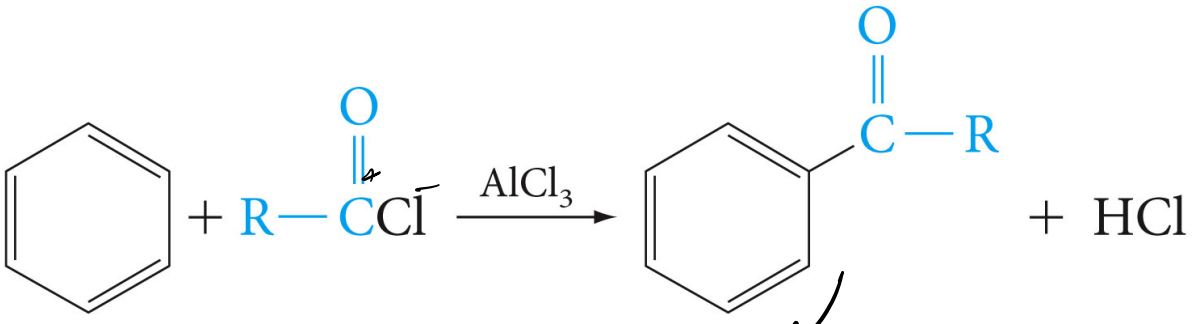


Sulfonation



4- alkelation





5 acelation

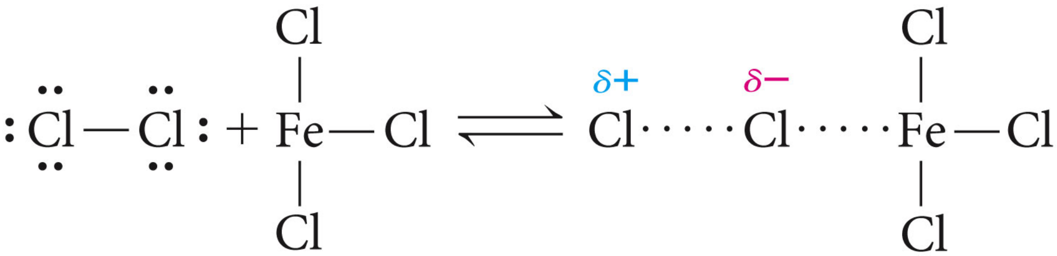
کیتون

کتون اروماتیک

عبارت است از حلقه بنزن

دراسة الخطوات التفصيلية لتفاعل ال electrophilic

The Mechanisms of Electrophilic Substitutions



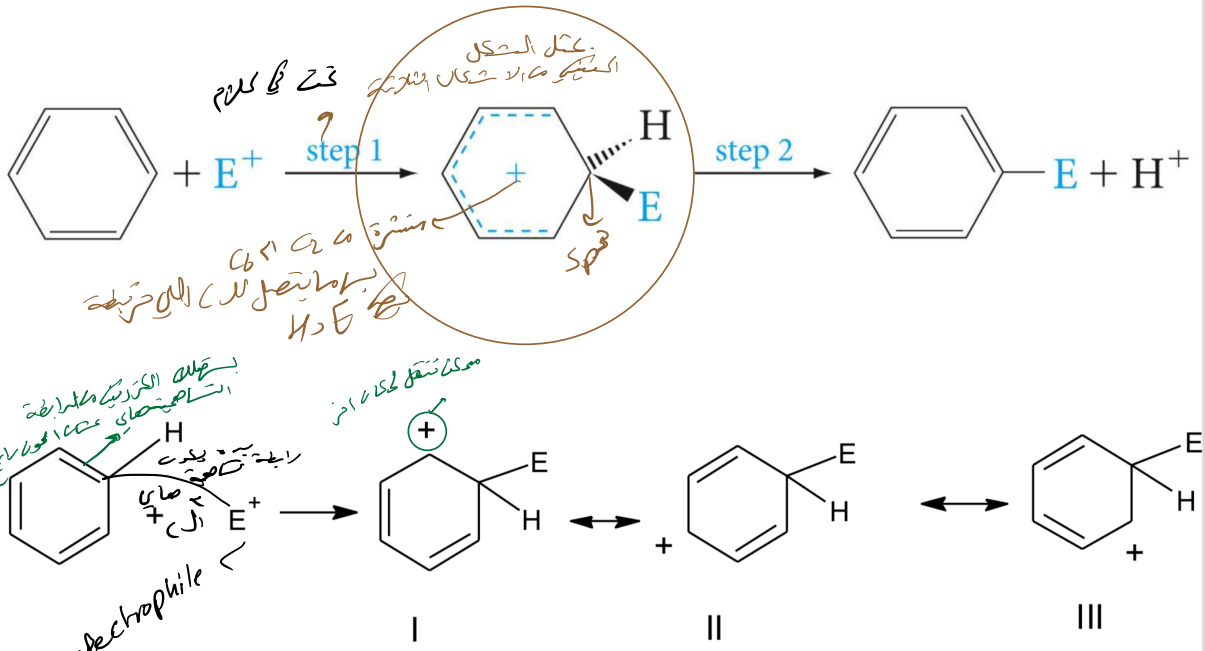
weak electrophile

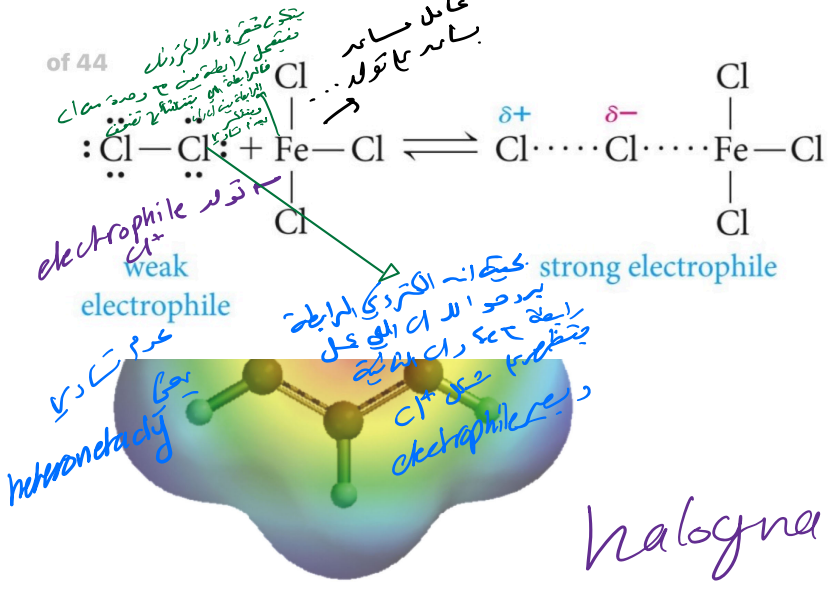
strong electrophile

13:04 Sat 20 Nov

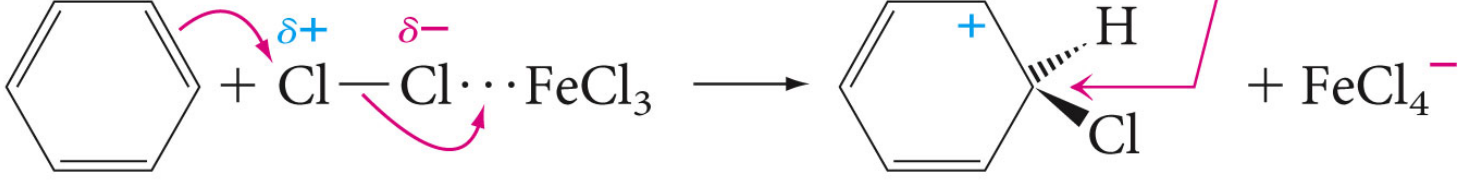
Chapter_4-modified

The Mechanisms of Electrophilic Substitutions

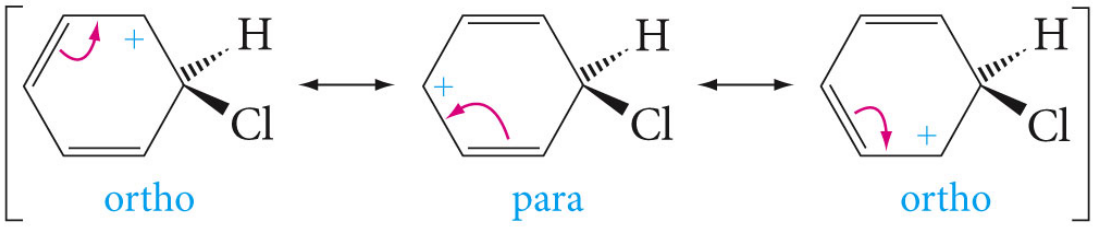




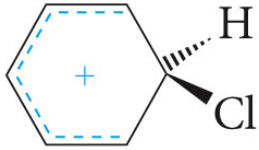
This carbon is sp^3-hybridized; it is bonded to *four* other atoms, and has no double bond to it.



a benzenonium ion (a carbocation)



resonance forms of a benzenonium ion



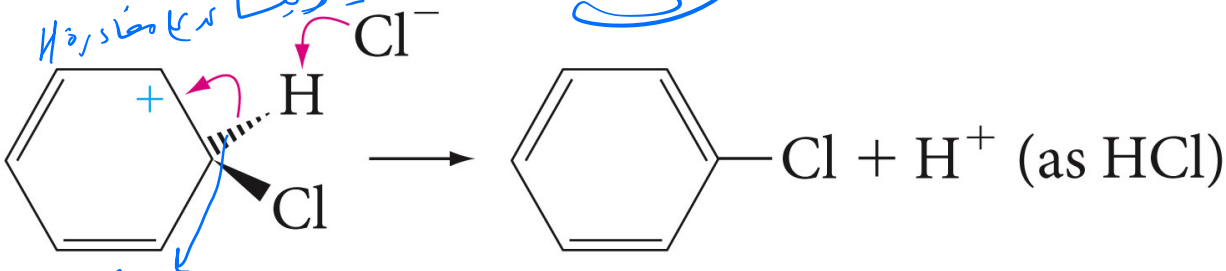
composite representation of the benzenonium ion resonance hybrid

صاحِ فطوة بطيئة

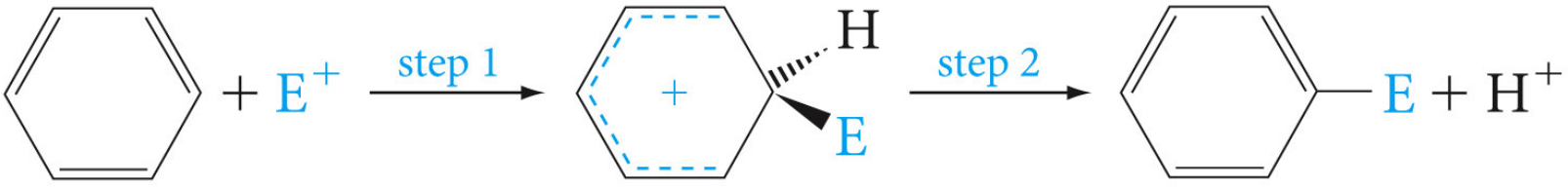
صاحِ فطوة بطيئة

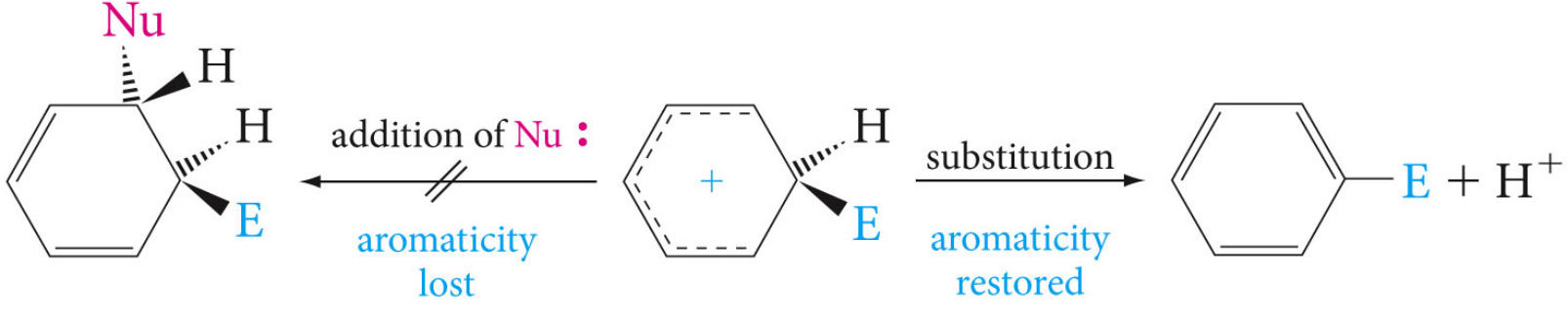
3 خطوات

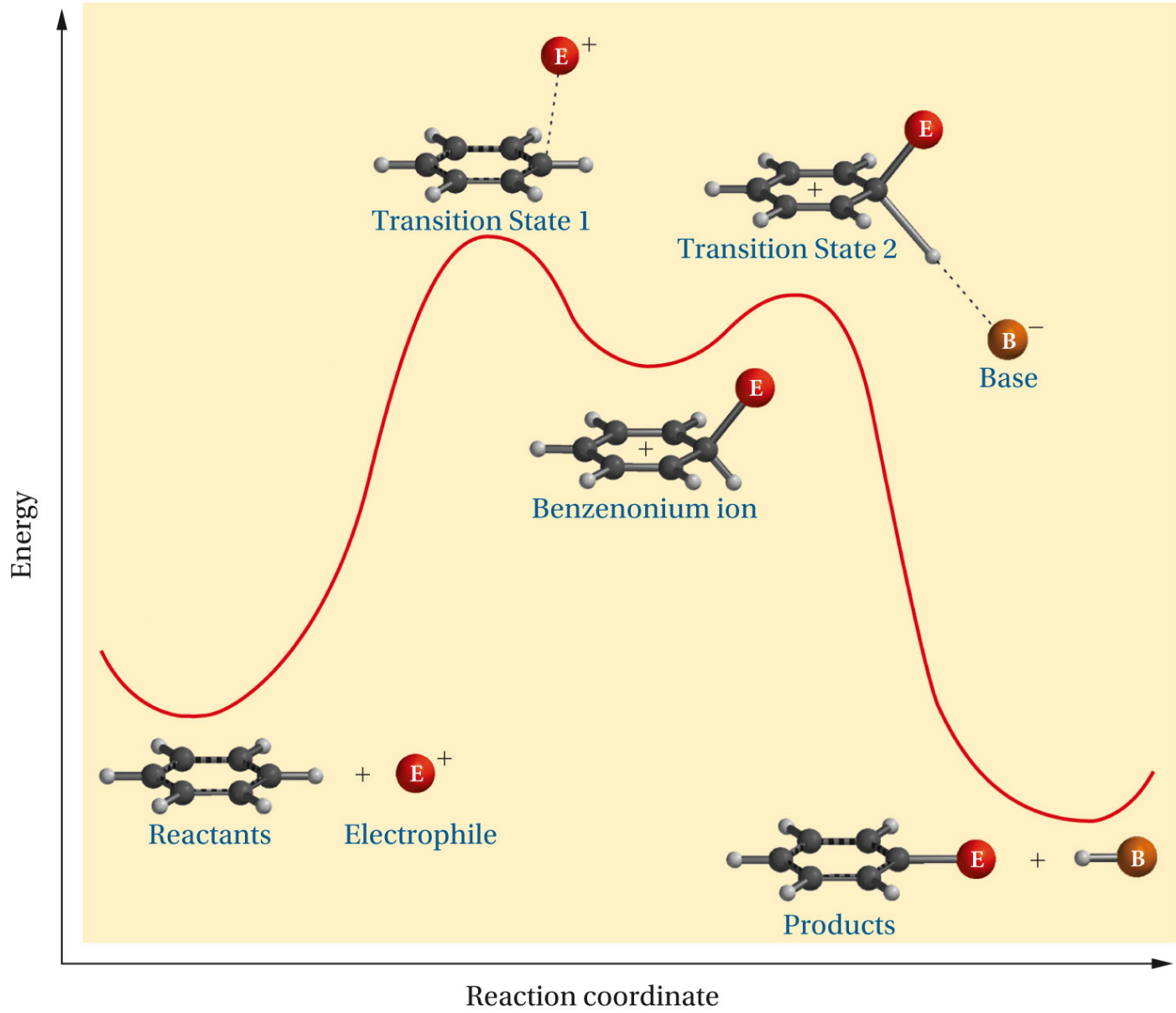
بتيجي وبتاخد بروتون من المذيب



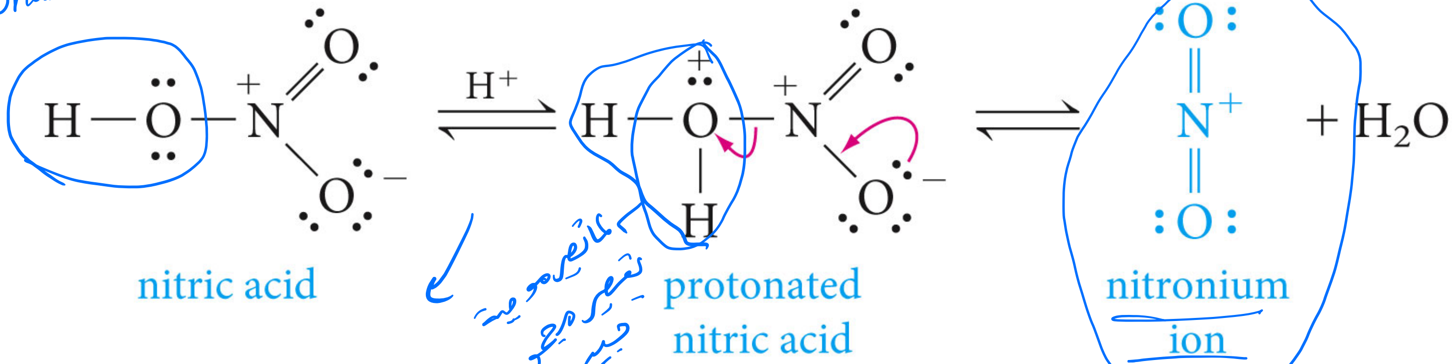
الإلكترونات الرابطة بتكون رابطة تساهمية وبيه فقدت

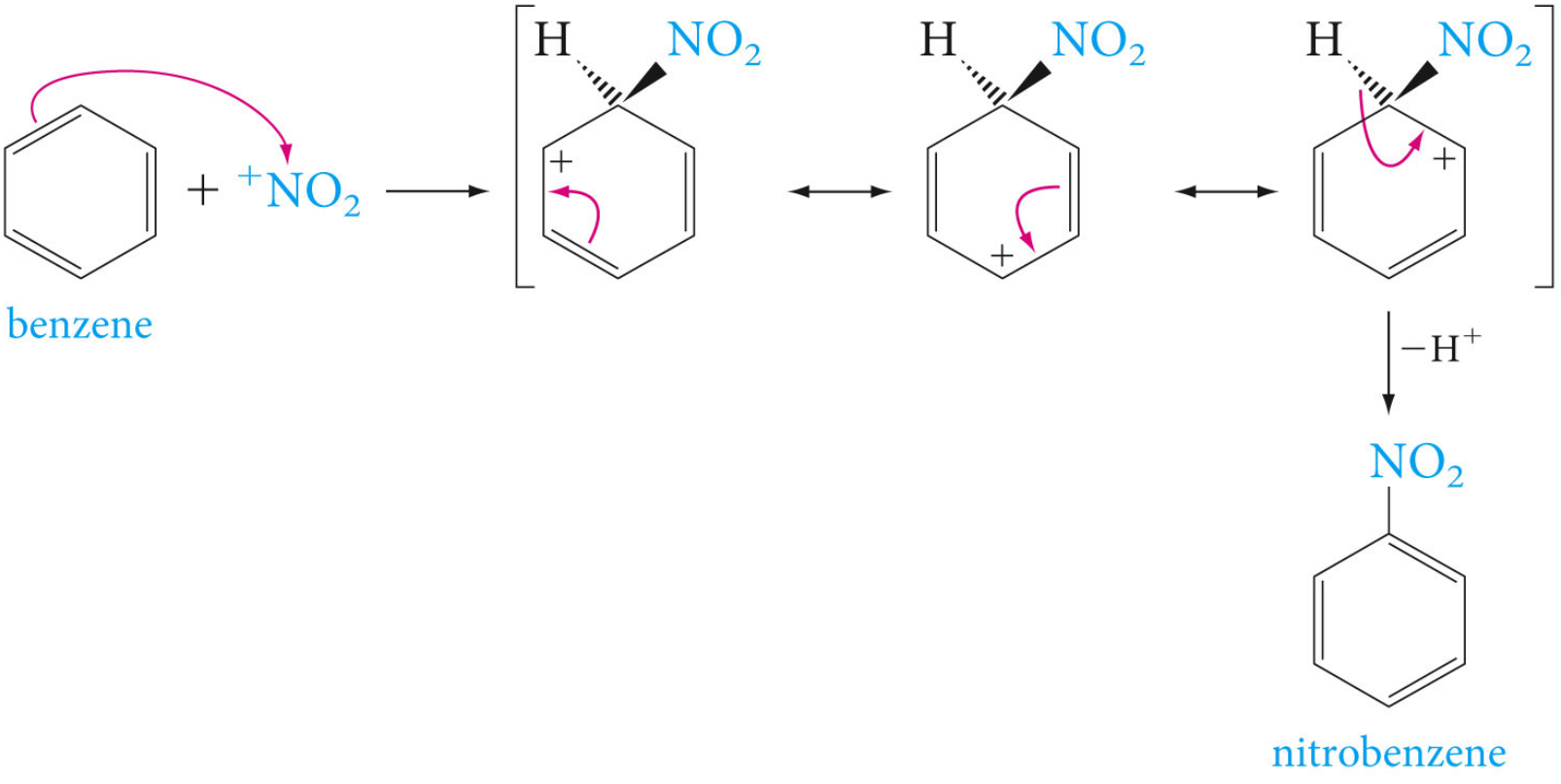

+ E+
step 1
H
E
+
step 2
E + H+


Nu
H
H
E
addition of Nu :
aromaticity
lost
H
E
+
substitution
aromaticity
restored
E + H+


Energy
Reaction coordinate
E
+
Transition State 1
E
+
Transition State 2
B
−
Base
E
+
Benzenonium ion
Reactants
+
E
+
Electrophile
E
+
B
Products

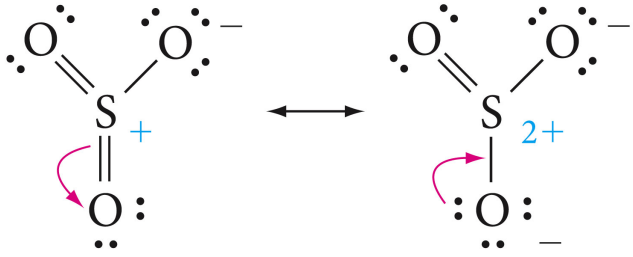
Nitration

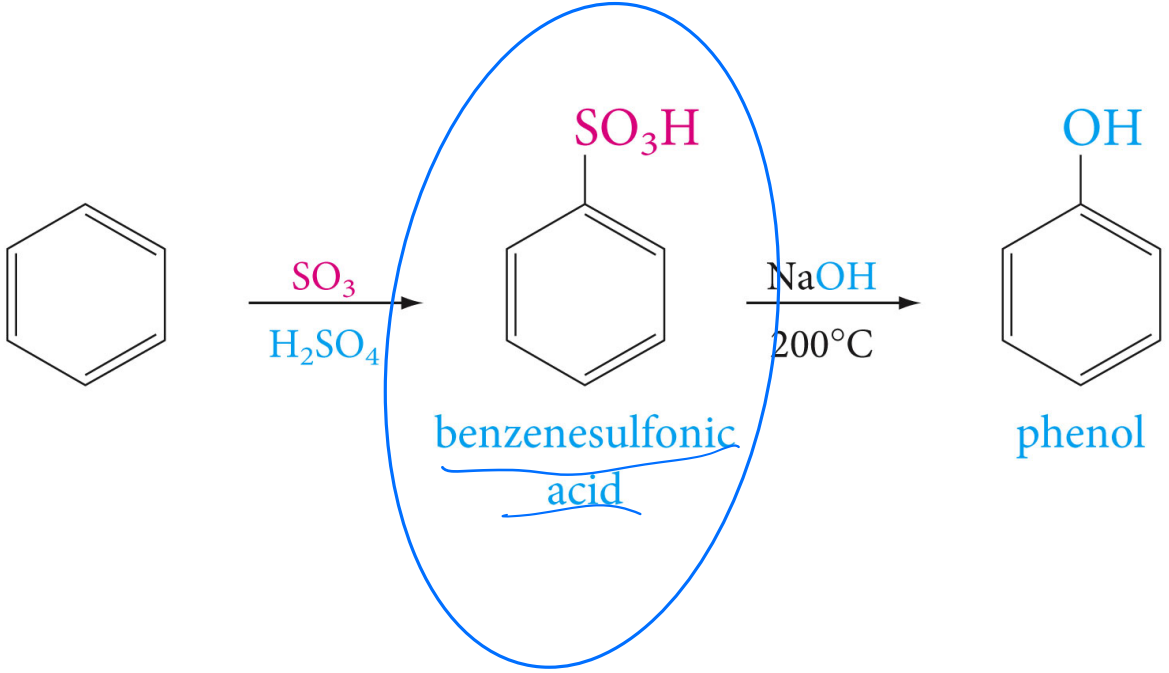



benzene
+ +NO2
H
NO2
+
H
NO2
+
H
NO2
+
−H+
NO2
nitrobenzene

sulfonation

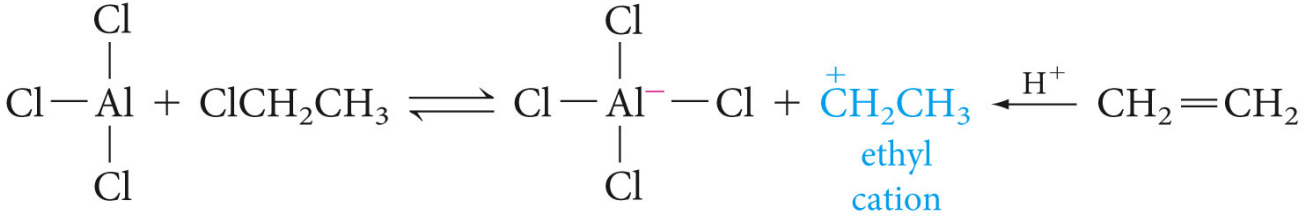
$$H{-}OSO_3H \rightleftharpoons H^+ + {}^-OSO_3H.$$

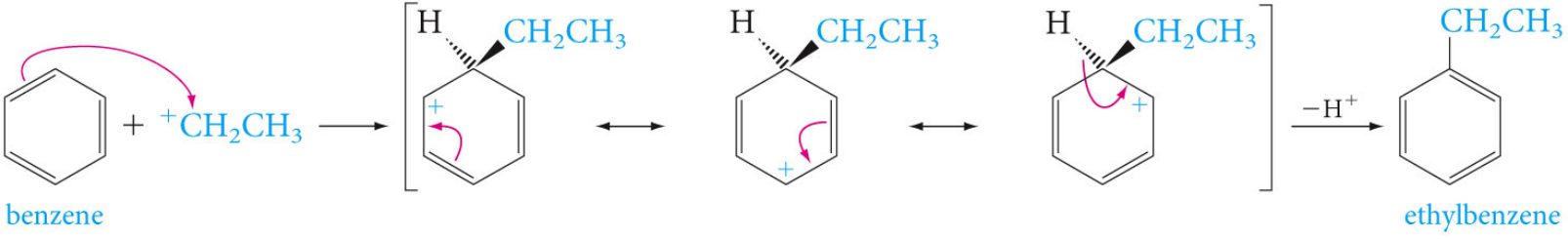


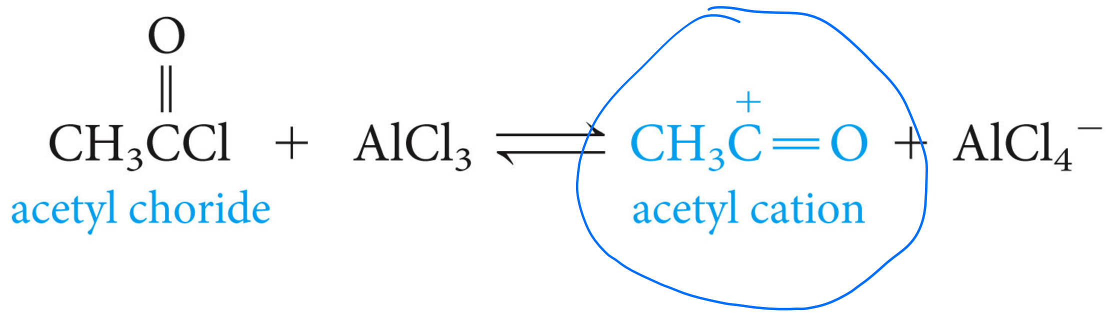


Alkylation and Acylation (Friedel-Crafts reaction)

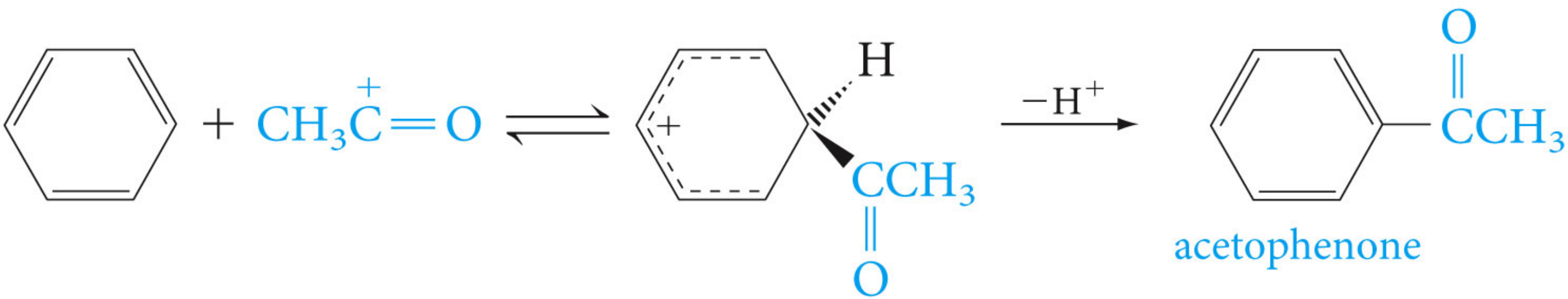
تتفاعل بنزين مع هاليد الكيل بوجود حامل حامض Alkyl...





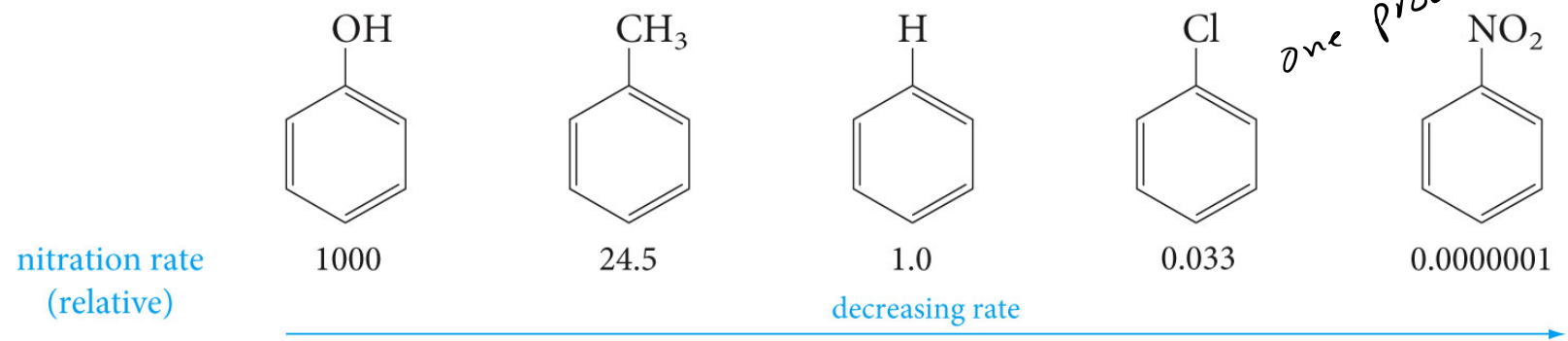


acetyl choride
acetyl cation



−H+
acetophenone

Ring-Activating and ring-Deactivating Substituents



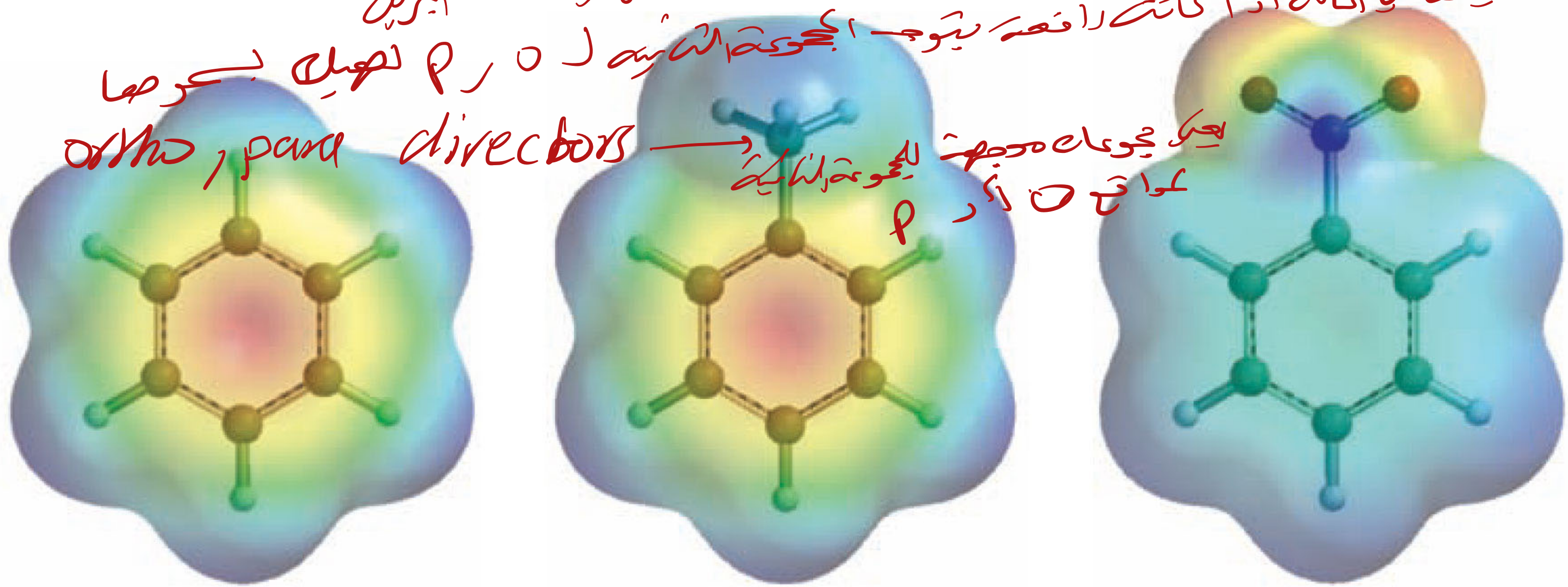
طبعاً لنعلم انه المجموعة الاولى طبيعاً توجه o , p , m حسب صفة المجموعة الاولى

ممكن نفهم انه تسحب الكترونات ، ممكن تكون دافعة للالكترونات

يعني تدفع e باتجاه حلقة البنزين وبتزيد الكثافة الالكترونية لحلقة البنزين

في هاي الحالة اذا كانت دافعة بتوجه المجموعة الثانية لـ o , p لتصل بنسميها

ortho , para directors →



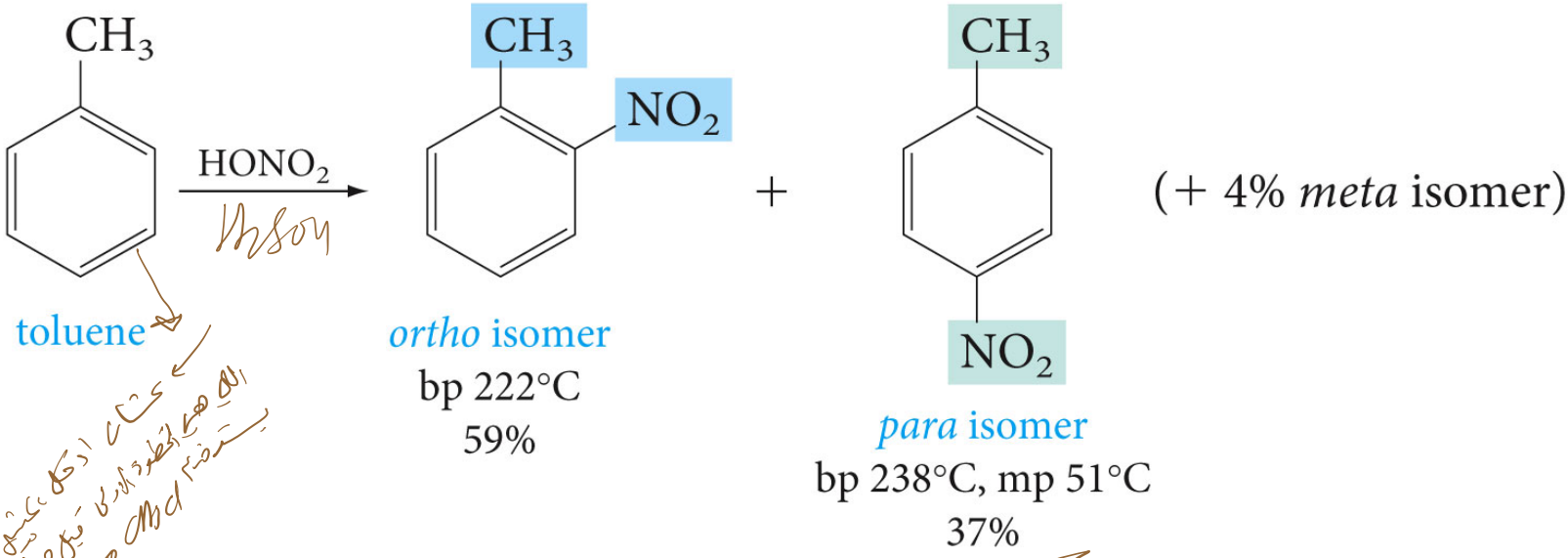
هدا مجموعات موجهة للمجموعة الثانية على o أو p

الفرق الآخر انه تكون المجموعة ساحبة للـ e يعني تسحب e من حلقة البنزين باتجاهها وبالتالي بتقلل من الكثافة الالكترونية لحلقة البنزين في هاي الحالة بتوجه لـ m

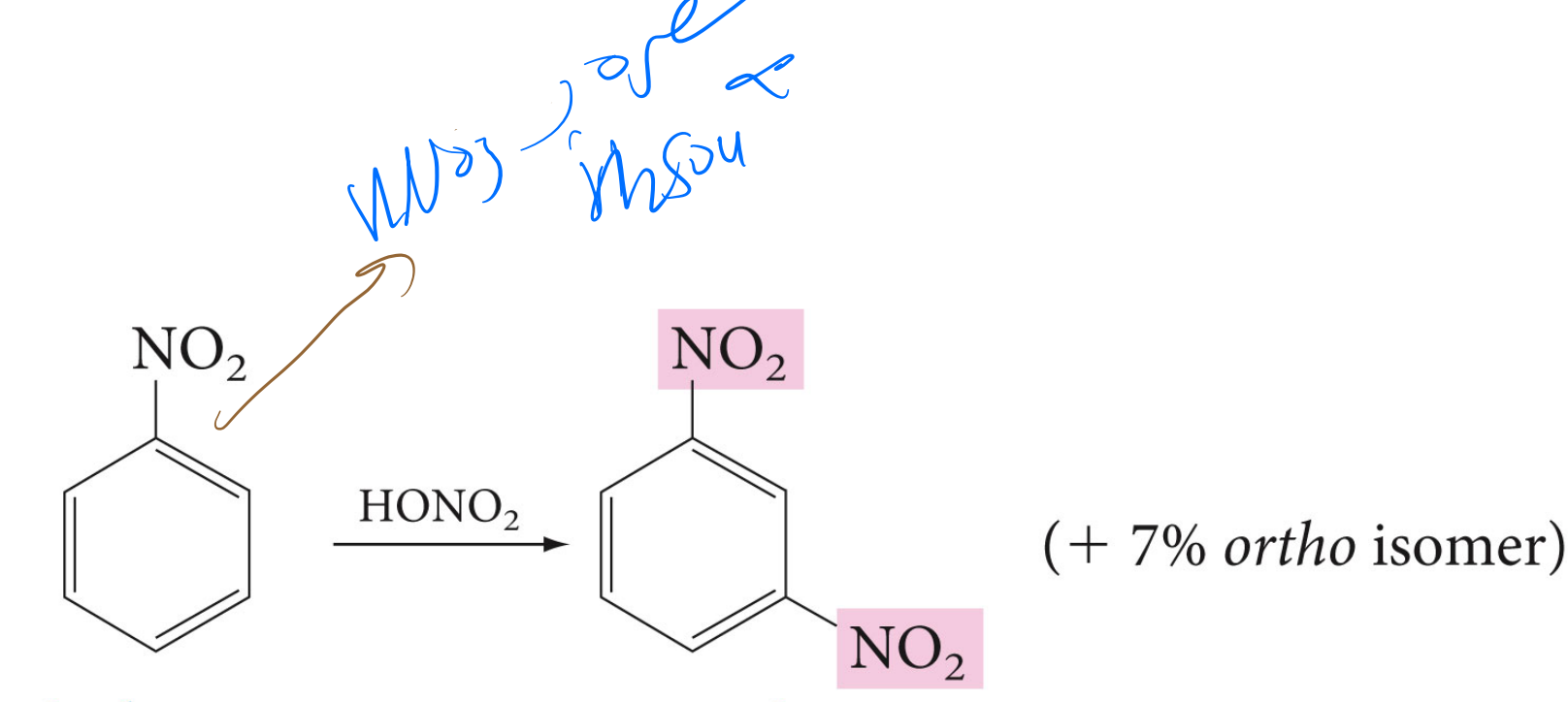
وبنسميها m-directors

طبعاً كيف بدي اعرف نوع المجموعة حسب جدول موضح

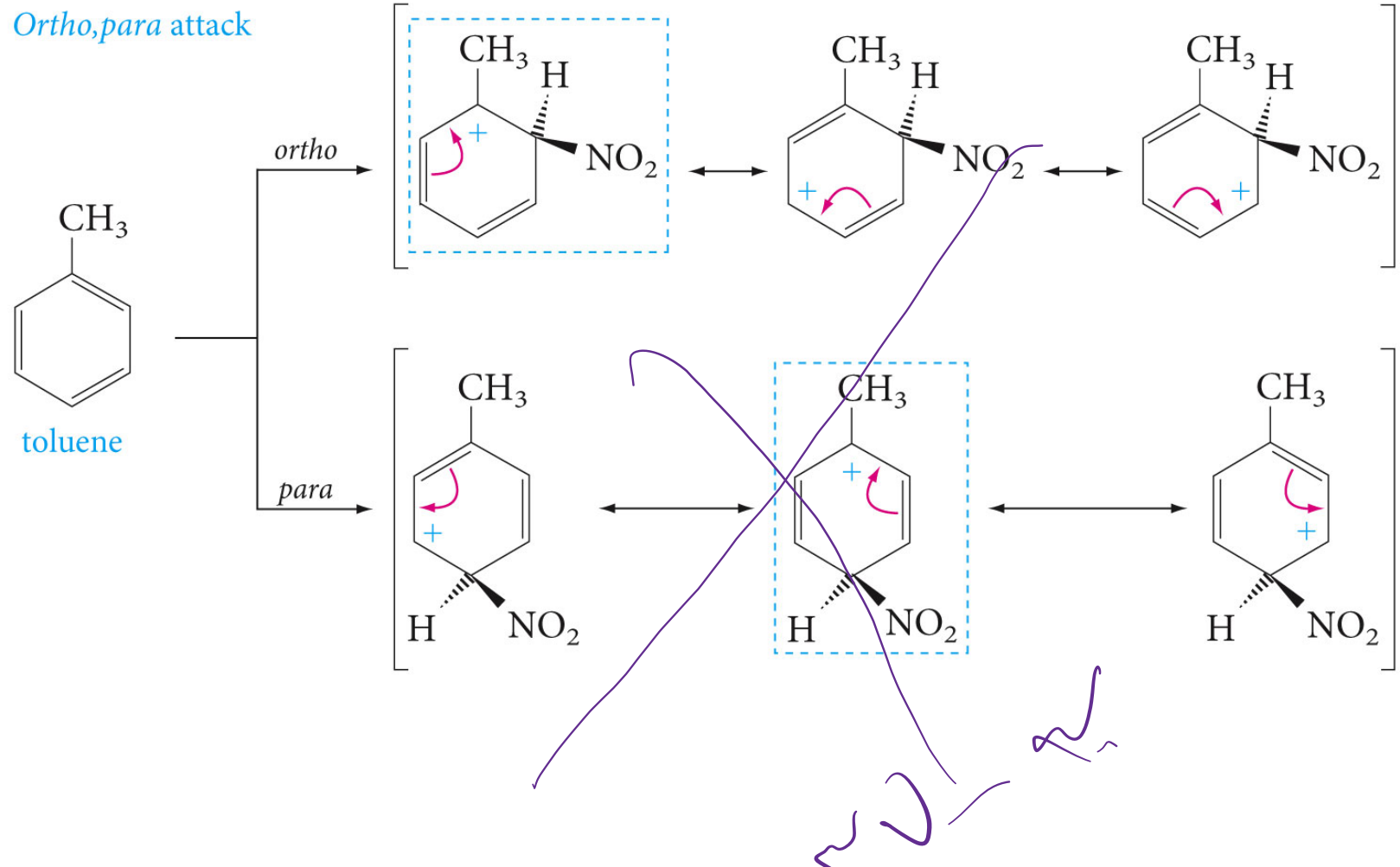
Ortho, *Para*-Directing and *Meta*-Directing Groups



2 isomers


NO2
HONO2
NO2
NO2
nitrobenzene
meta isomer
mp 89°C
93%
(+ 7% ortho isomer)

Ortho, *Para*-Directing Groups



Meta attack

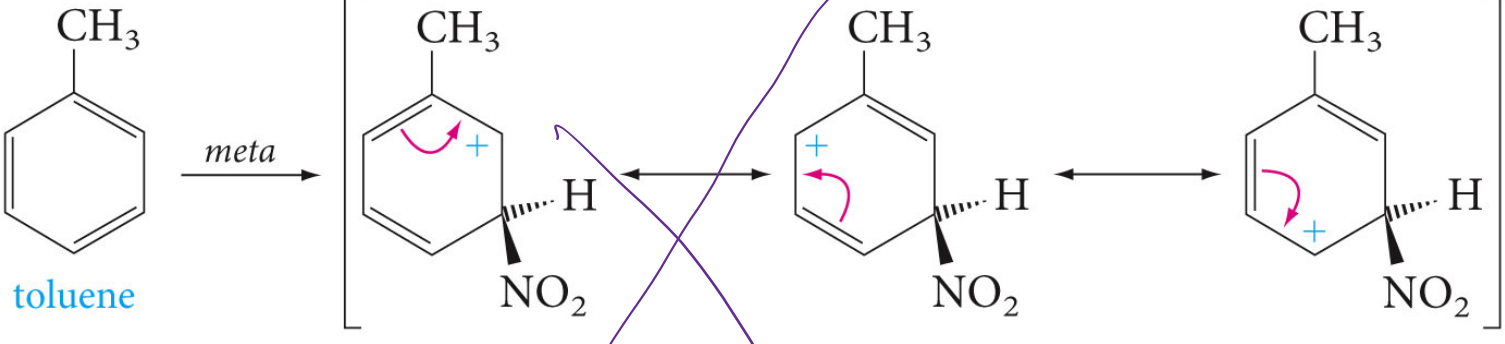
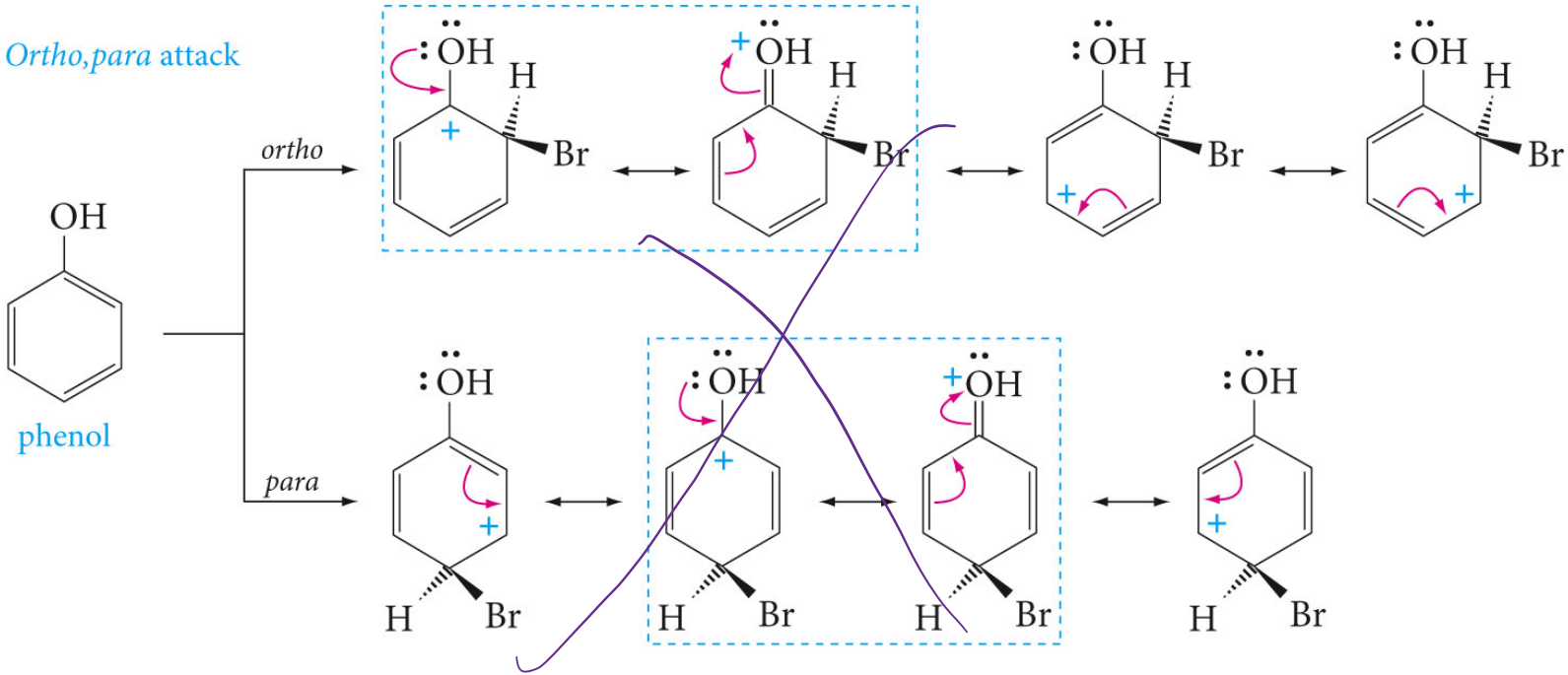


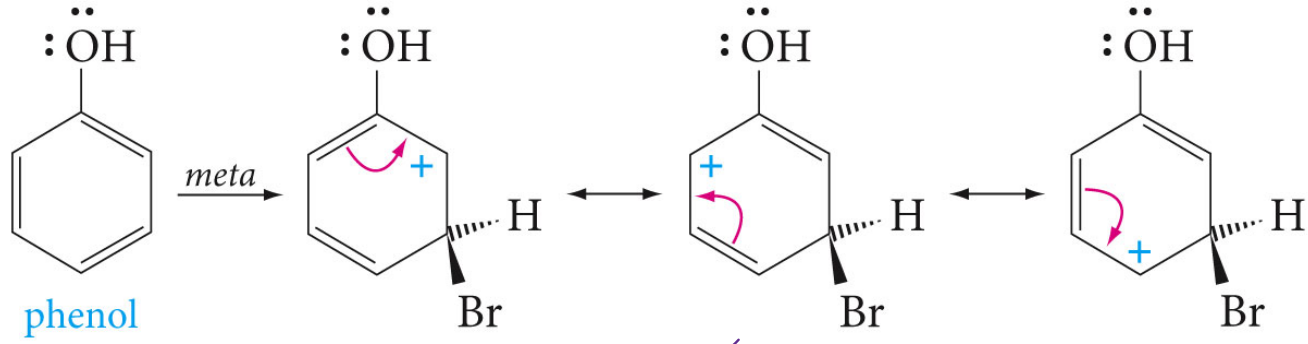
Table 4.1 Directing and Activating Effects of Common Functional Groups (Groups are Listed in Decreasing Order of Activation)

	Substituent group	Name of group	
Ortho,Para-Directing	$-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$	amino	Activating
	$-\ddot{O}H$, $-\ddot{O}CH_3$, $-\ddot{O}R$	hydroxy, alkoxy	
	$-\ddot{N}HC(=O)-R$	acylamino	
	$-CH_3$, $-CH_2CH_3$, $-R$	alkyl	
	$-\ddot{F}:$, $-\ddot{Cl}:$, $-\ddot{Br}:$, $-\ddot{I}:$	halo	Deactivating
Meta-Directing	$-C(=O)-R$	acyl	
	$-C(=O)-\ddot{O}H$	carboxy	
	$-C(=O)-\ddot{N}H_2$	carboxamido	
	$-C(=O)-\ddot{O}R$	carboalkoxy	
	$-S(=O)(=O)-\ddot{O}H$	sulfonic acid	
	$-C\equiv N:$	cyano	
	$-N^{+}(=O:)-\ddot{O}:^{-}$	nitro	

$-\ddot{F}:$ $-\ddot{O}H$ $-\ddot{N}H_2$

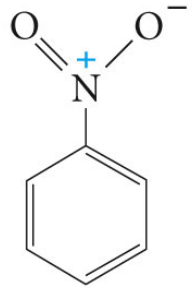

Ortho,para attack
OH
phenol
ortho
para
:OH
H
Br
+OH
+

Meta attack



phenol

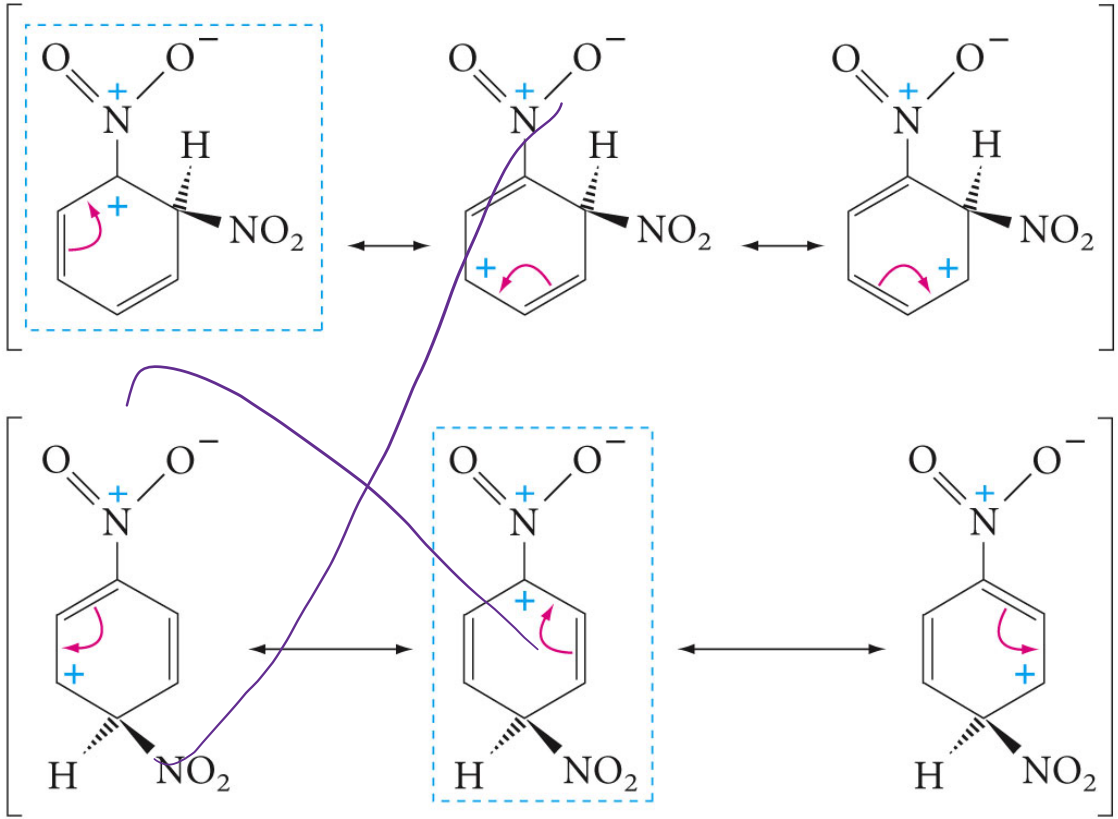
Ortho,para attack



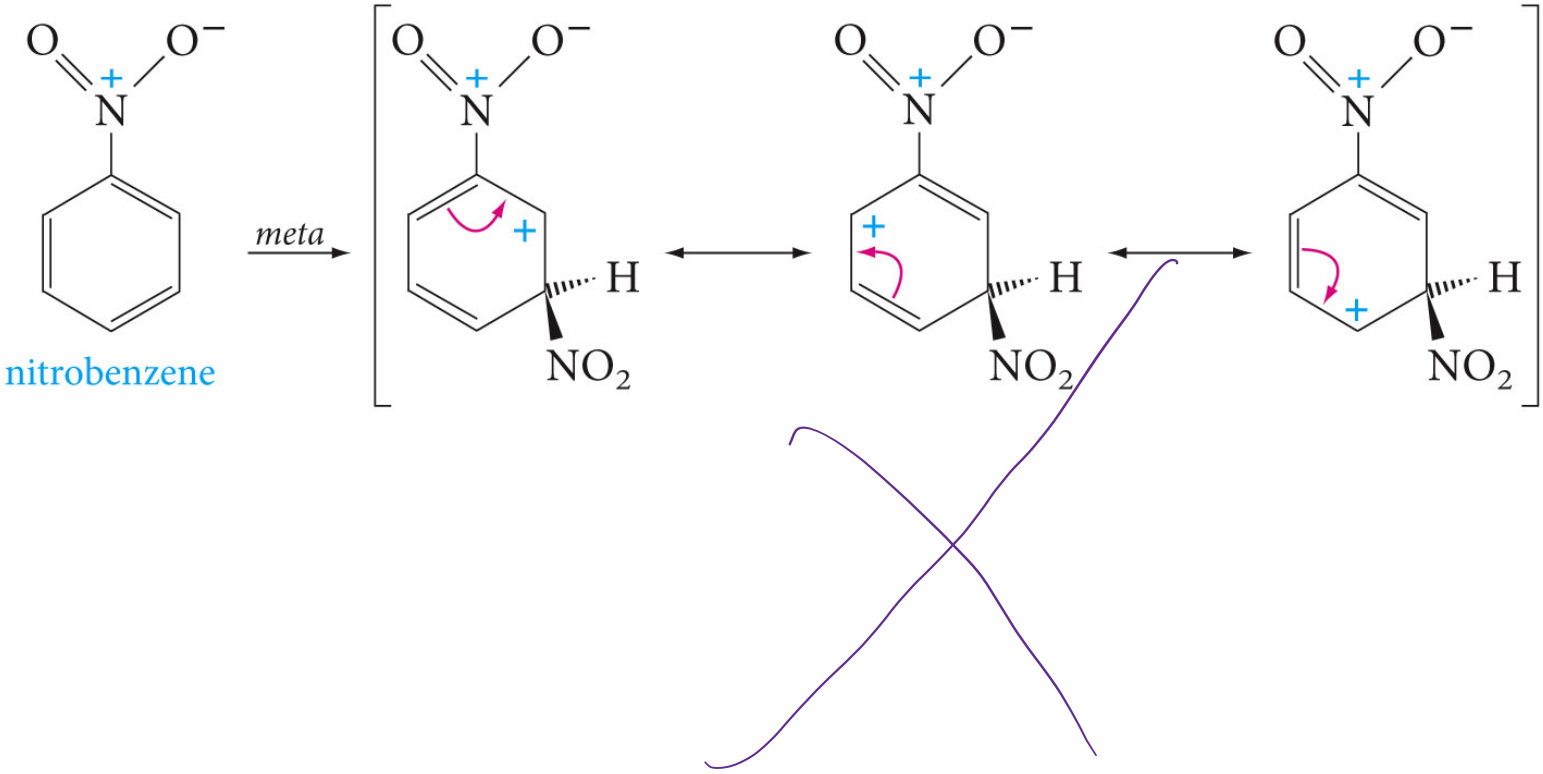
nitrobenzene

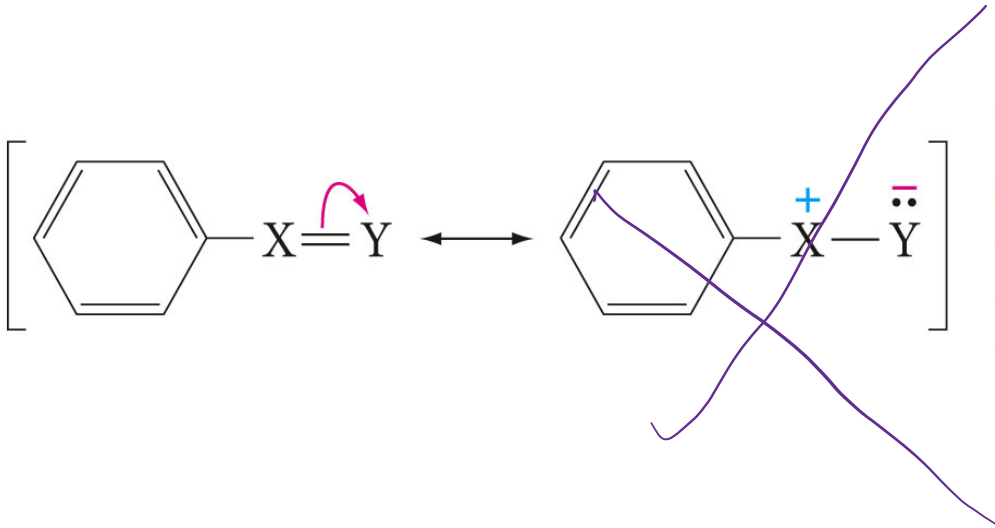
ortho

para



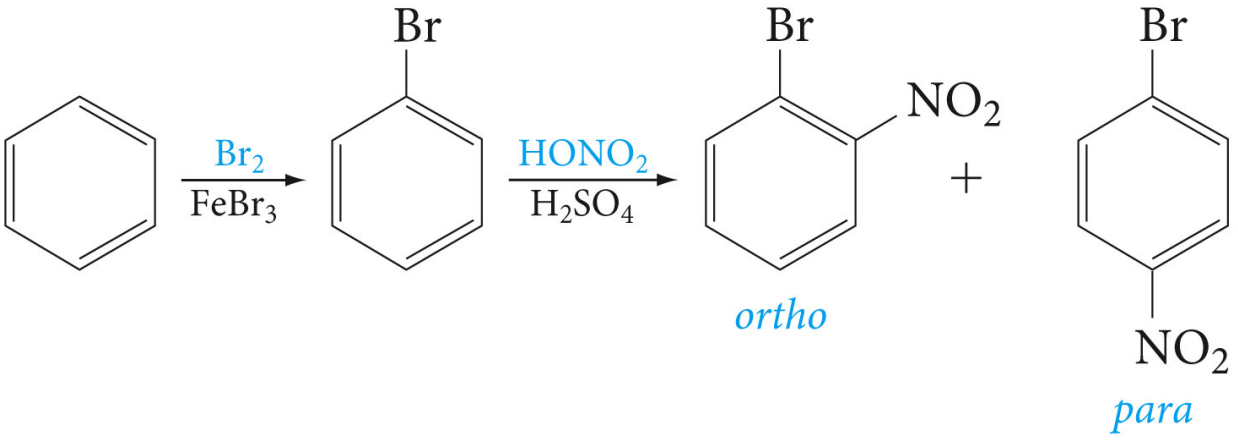
Meta attack

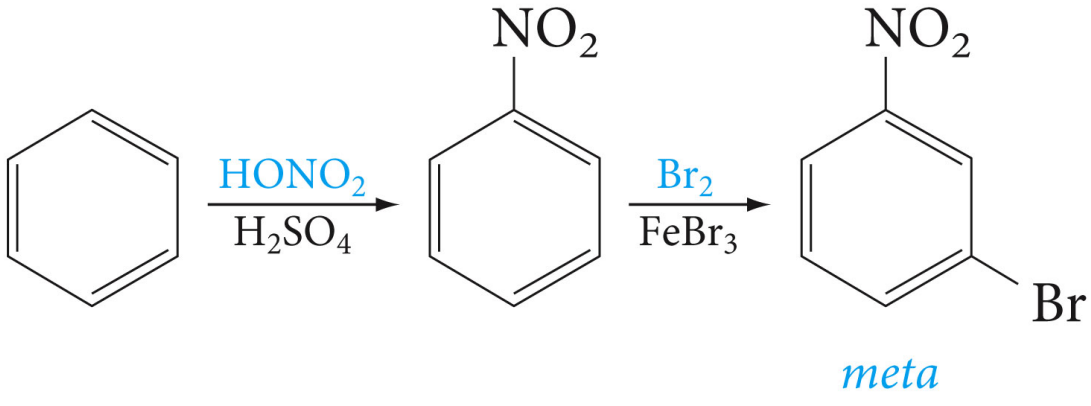




Y is an electron-withdrawing atom such as oxygen or nitrogen; atom X carries a positive charge in one of the resonance contributors.

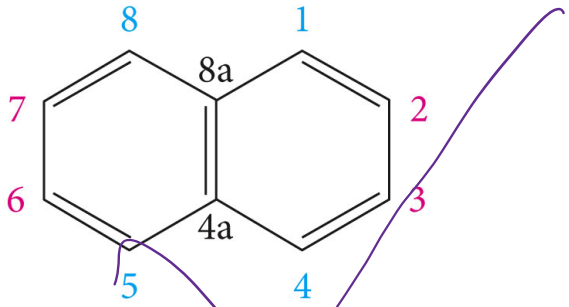
Importance of Directing Effects in Synthesis





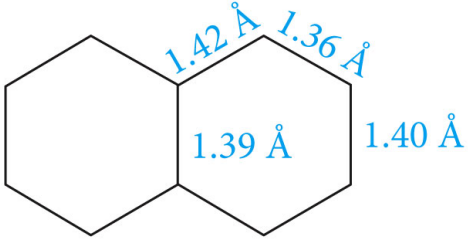
meta

Polycyclic Aromatic Hydrocarbons

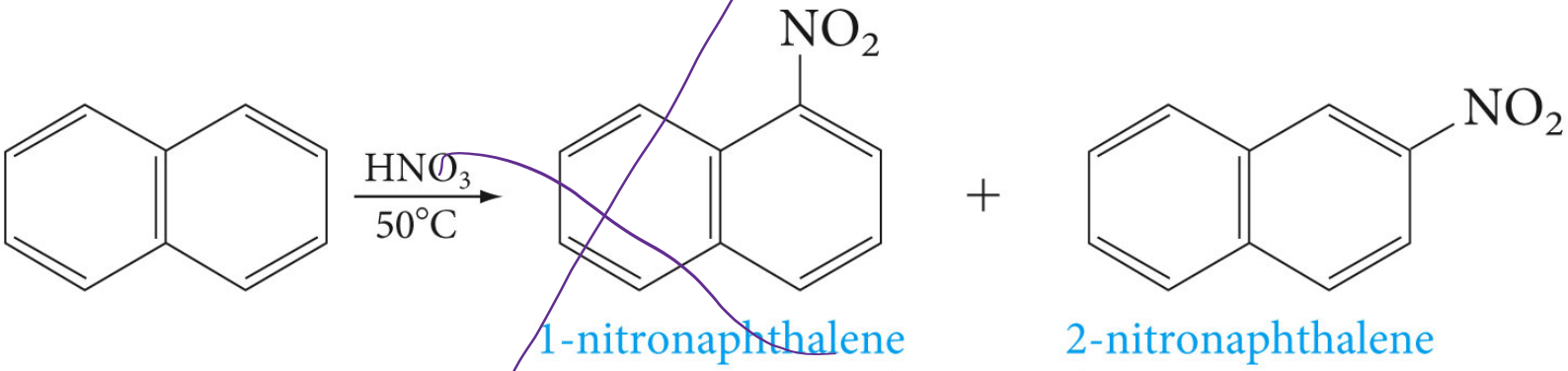


naphthalene

mp 80°C



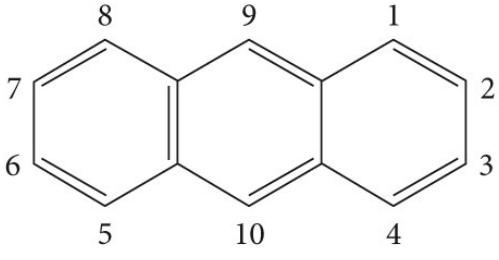
bond lengths in naphthalene



1-nitronaphthalene + 2-nitronaphthalene

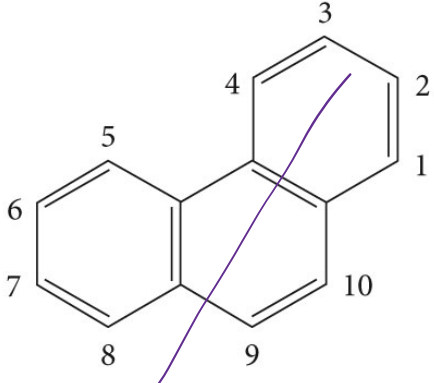
(ratio 10:1)

Fused polycyclic hydrocarbons



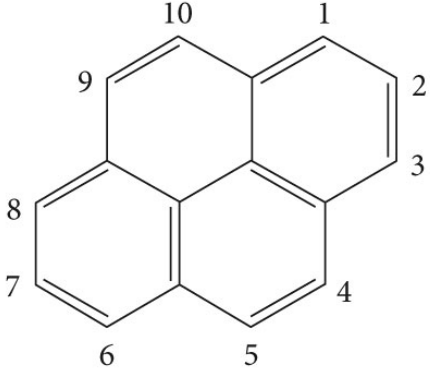
anthracene

mp 217°C



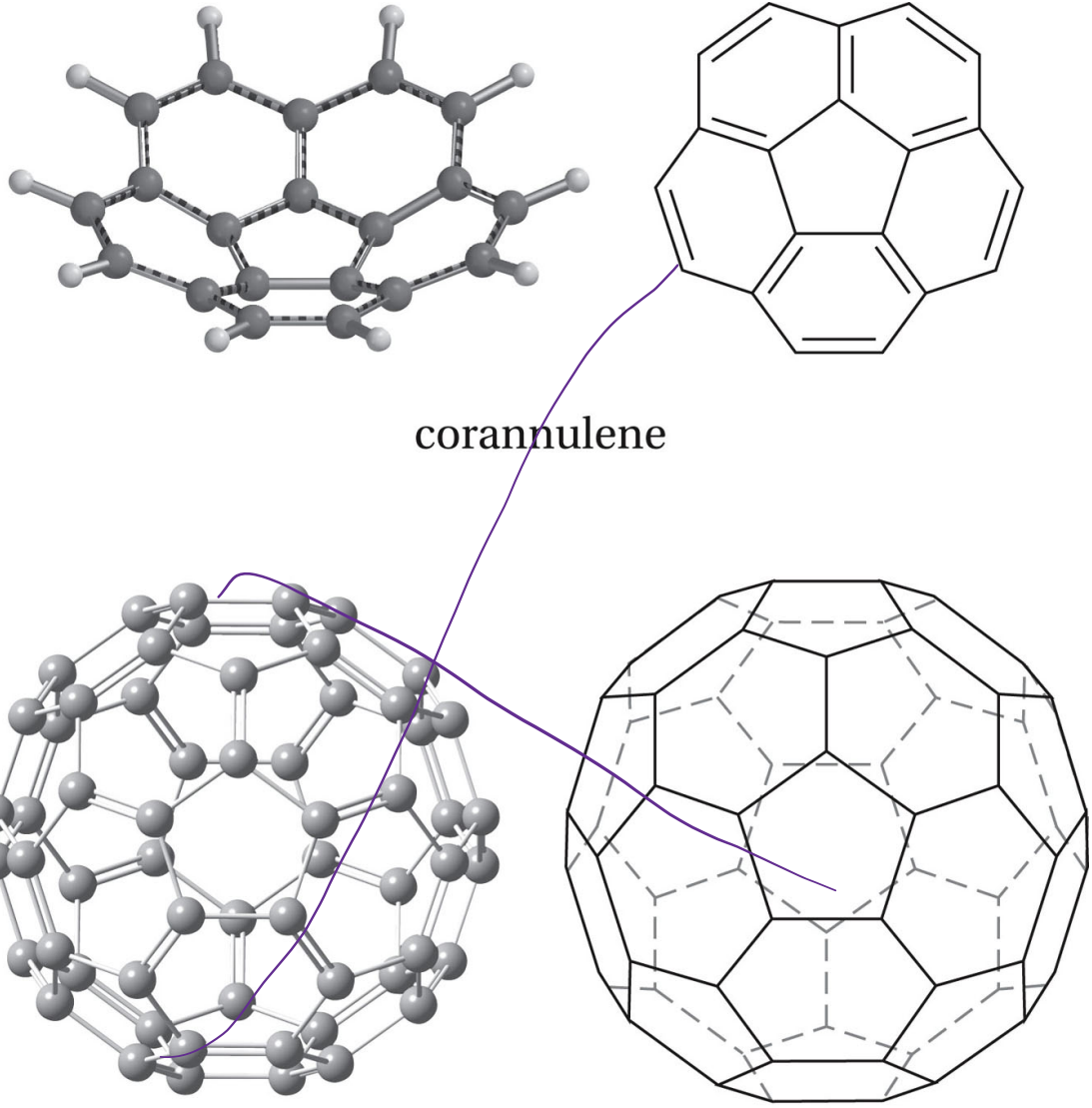
phenanthrene

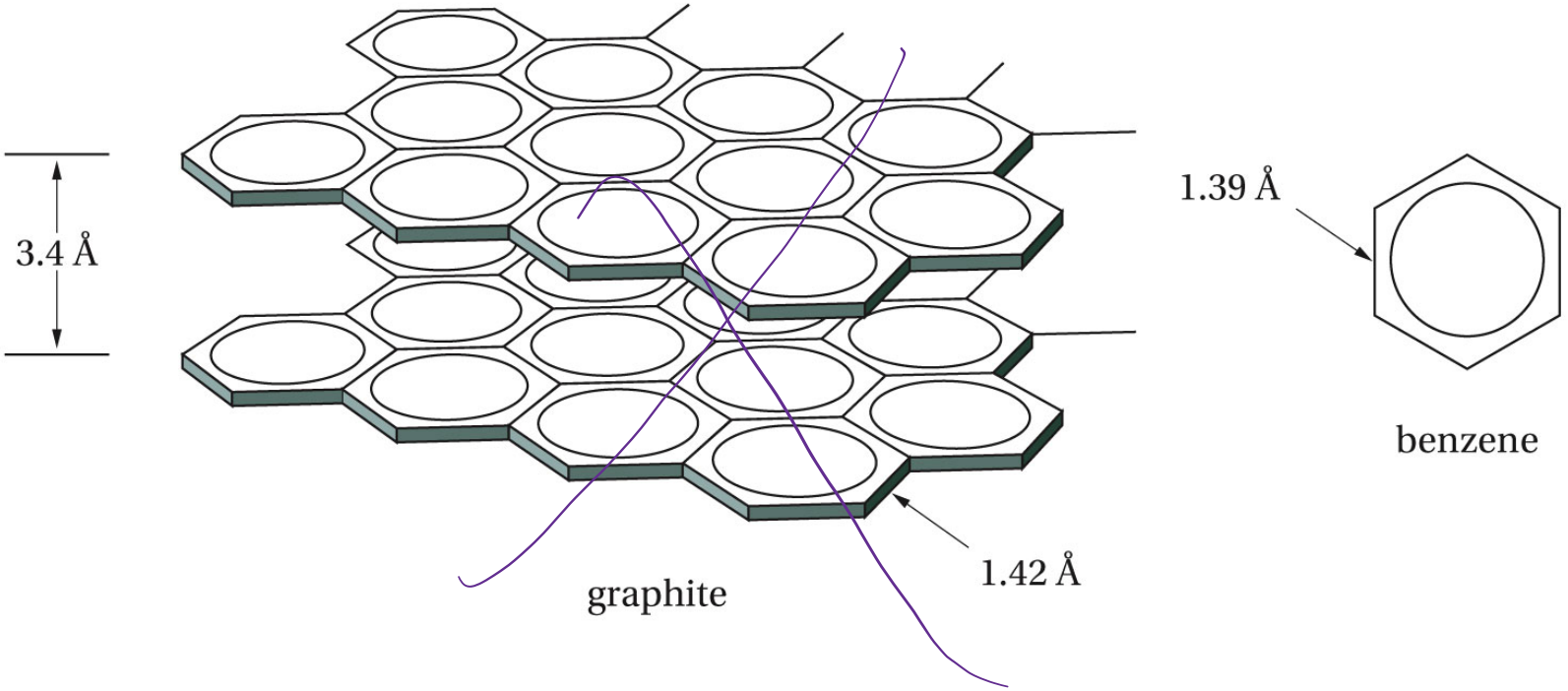
mp 98°C

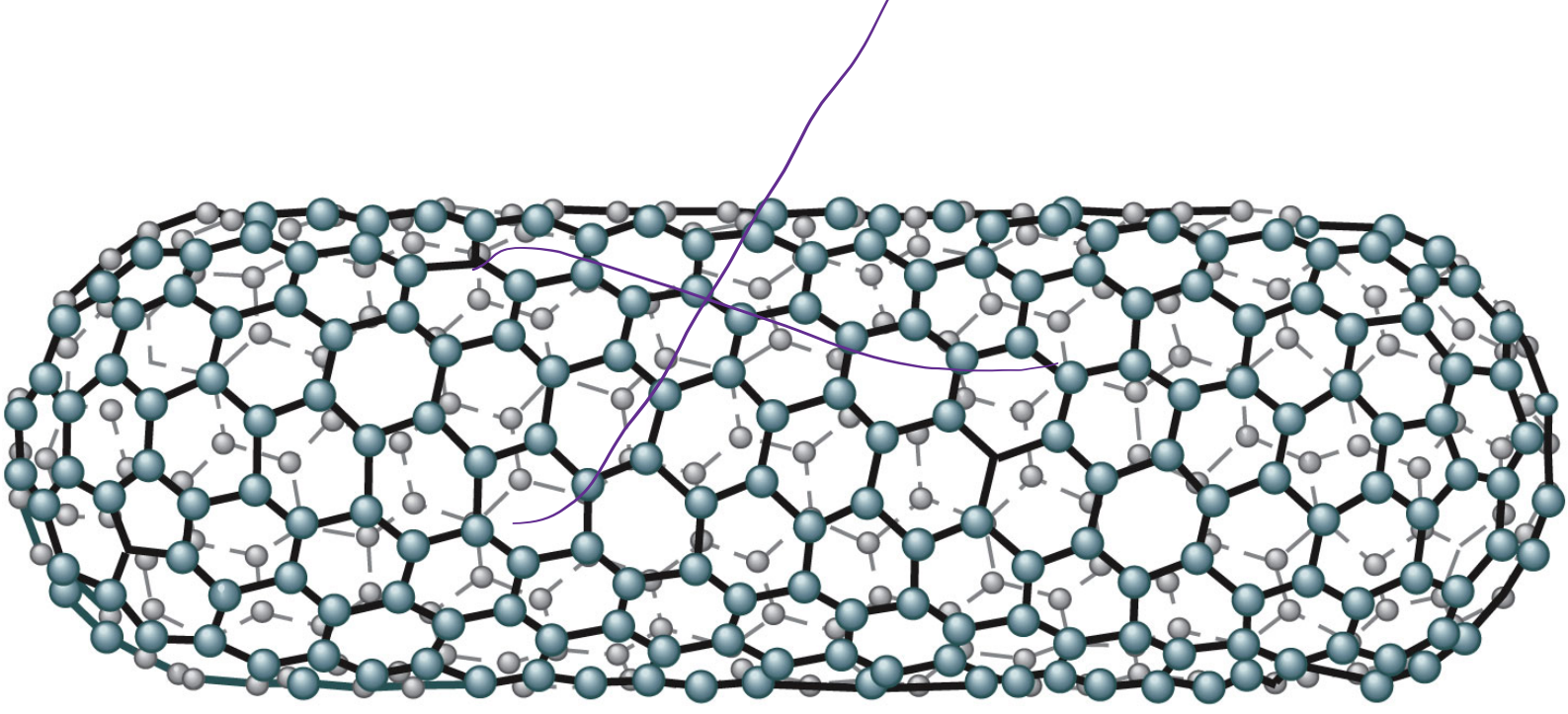


pyrene

mp 156°C


corannulene
C_{60} (the pi bonds are not shown)


3.4 Å
1.39 Å
benzene
1.42 Å
graphite



Carbon nanotube[1]