Benzene and Aromatic Compounds

Chapter 15

Organic Chemistry, *8th Edition*

John McMurry

Background

- Benzene (C_6H_6) is the simplest aromatic hydrocarbon (or arene).
- Four degrees of unsaturation.
- It is planar.
- All C—C bond lengths are equal.
- Whereas unsaturated hydrocarbons such as alkenes, alkynes and dienes readily undergo addition reactions, benzene does not. (substitution)

Benzene (an arene)

$$C_6H_6 \xrightarrow{Br_2} \text{No reaction}$$

- Benzene reacts with bromine only in the presence of $FeBr_3$ (a Lewis acid), and the reaction is a substitution, not an addition.

$$C_6H_6 \xrightarrow[FeBr_3]{Br_2} C_6H_5Br$$

lewis acid

substitution
Br replaces H

Background

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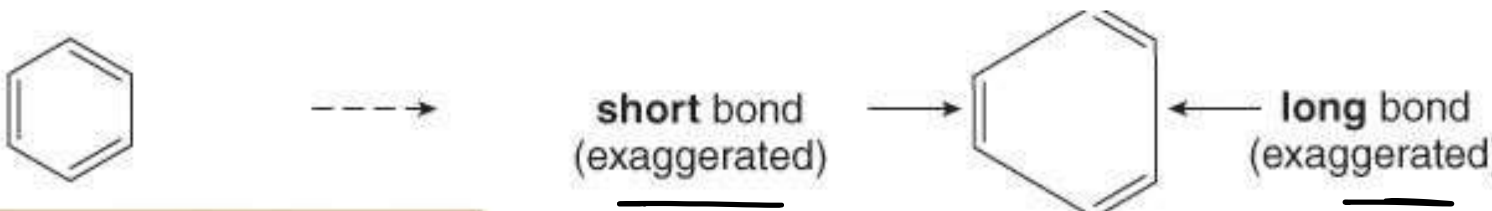
- August Kekulé (1865) proposed that benzene was a rapidly equilibrating mixture of two compounds, each containing a six-membered ring with three alternating π bonds.

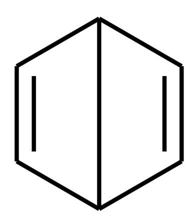
Kekulé description: An equilibrium



This structure implies that the C–C bonds should have **two different lengths**.

- three short bonds
- three long bonds

- All C—C bond lengths are equal!



James Dewar (1967) : the Dewar benzene was prepared in 1962 but it is not stable and it converts to benzene

1. Which of the following statements about benzene is true?

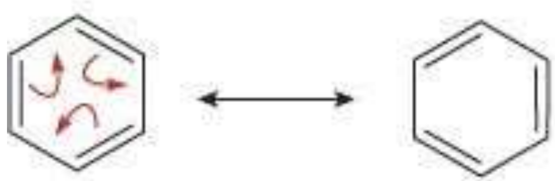
A. Benzene is a saturated hydrocarbon.
B. Benzene undergoes addition reactions.
C. Benzene has five degrees of unsaturation.
D. Benzene undergoes substitution reactions.

2. Which of the following statements about the structure of benzene is *not* true?

A. Benzene is planar.
B. Benzene has three short double bonds alternating with three longer single bonds.
C. The electrons in the pi bonds are delocalized around the ring.
D. Benzene has six pi electrons.

The Structure of Benzene: Resonance

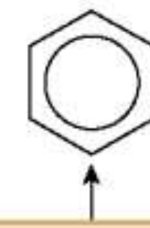
- The true structure of benzene is a resonance hybrid of the two Lewis structures.



The hybrid

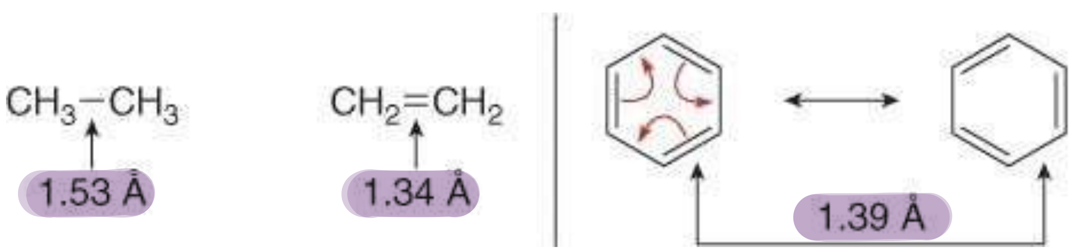
The electrons in the π bonds are **delocalized** around the ring.

Some texts draw benzene as a hexagon with an inner circle:



6π The circle represents the **six π electrons,** distributed over the six atoms of the ring.

6C

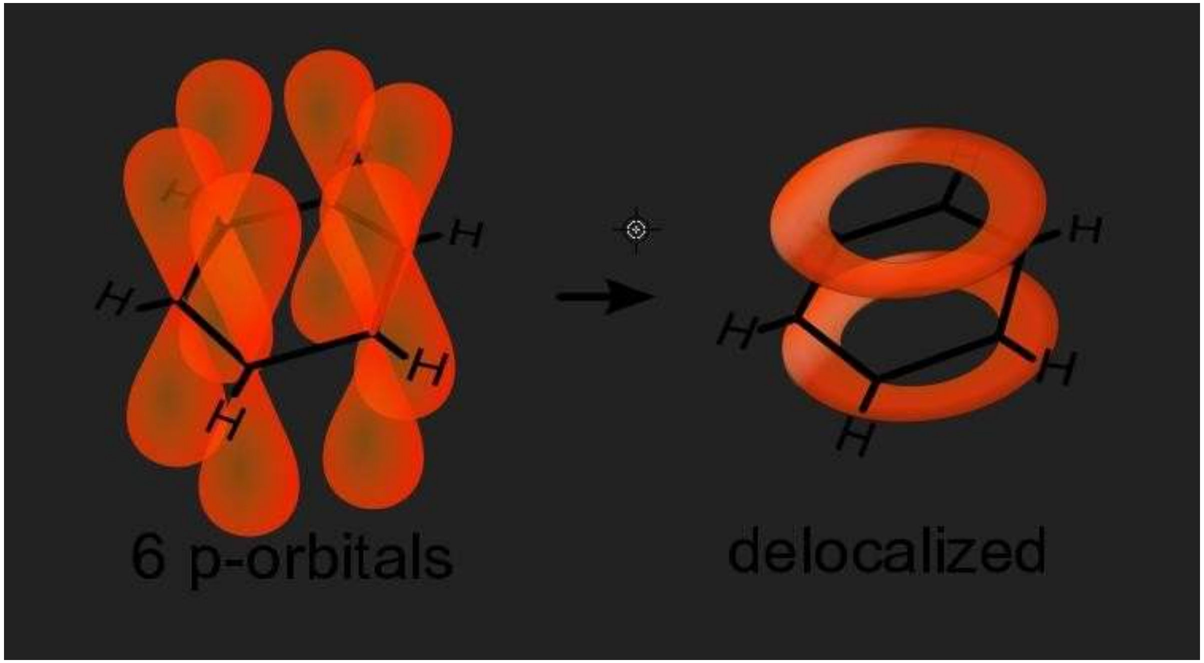


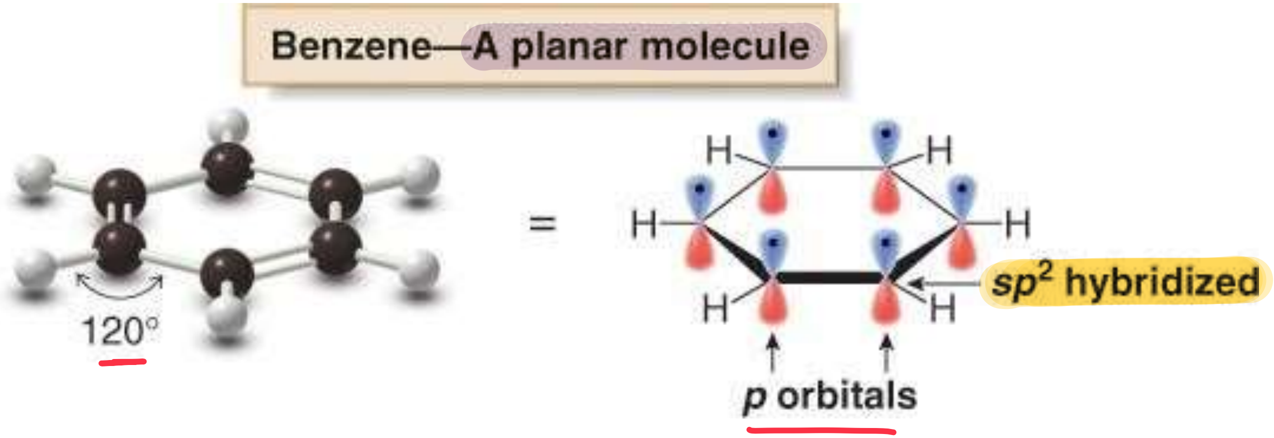
The C–C bonds in benzene are equal and intermediate in length.

4.18. Which statement about benzene is TRUE?

- **a.** All six hydrogens in benzene are chemically equivalent.
- **b.** Benzene decolorizes bromine solutions.
- **c.** The molecule is planar, and each carbon is at the corner of a regular hexagon.
- ***d.** Both a and c are true.
- **e.** Both b and c are true.

The Structure of Benzene: MO



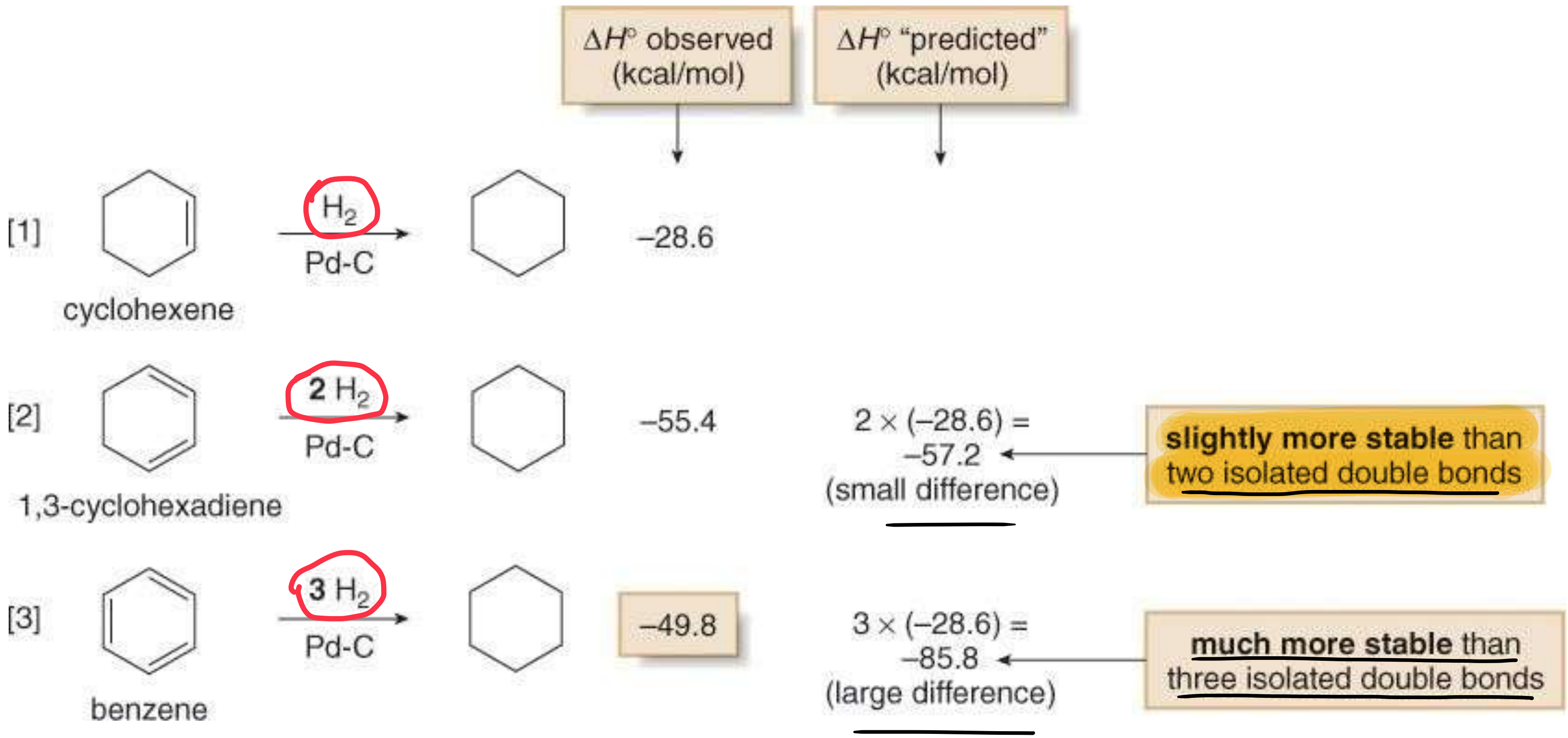


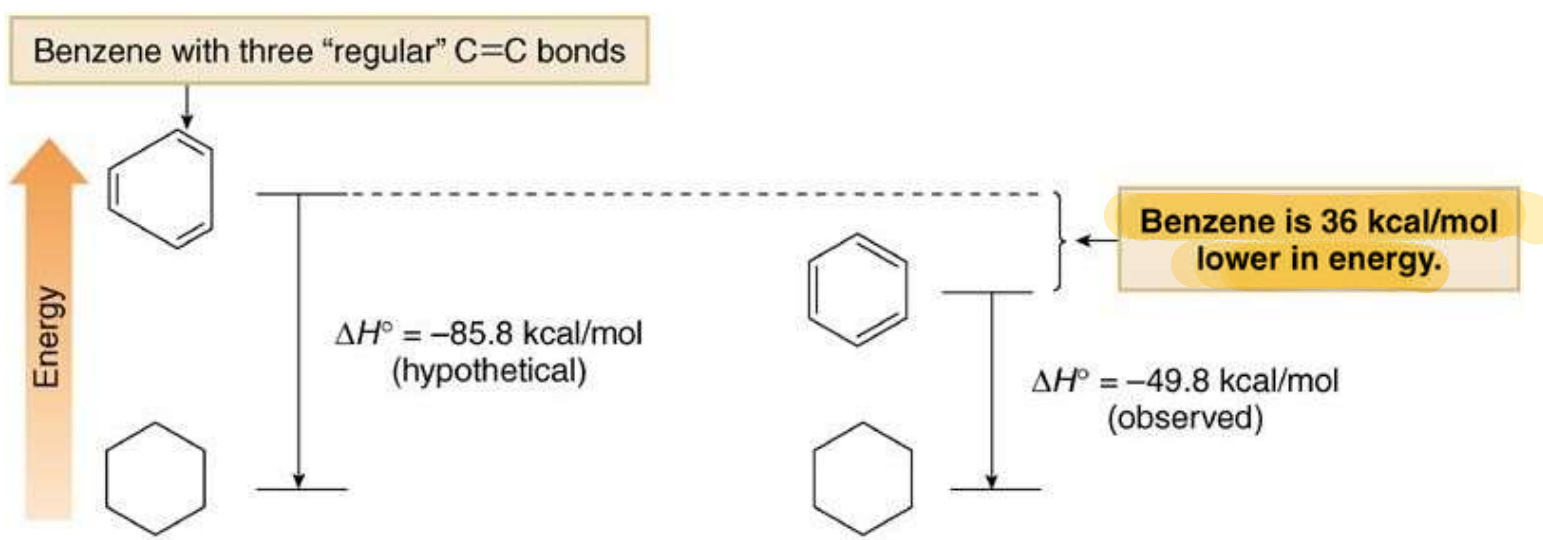
What is the hybridization of carbon atom in ?benzene structure

:Select one

- a. sp^2
- b. sp^3
- c. sp
- d. sp^3d

Aromaticity – Resonance Energy

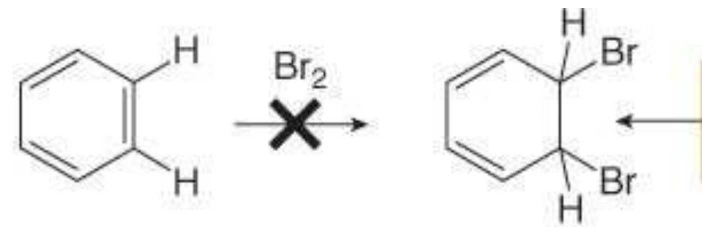




Stability of Benzene - Aromaticity

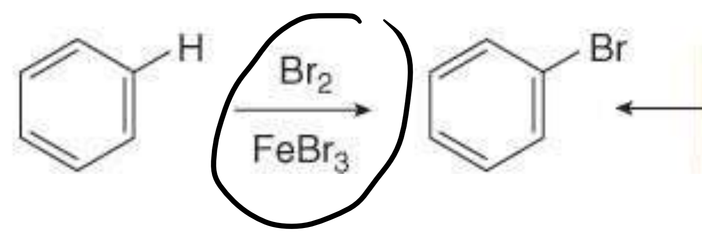
- Benzene does not undergo addition reactions typical of other highly unsaturated compounds, including conjugated dienes.

Addition does *not* occur.



An addition product would no longer contain a benzene ring.

Substitution occurs.



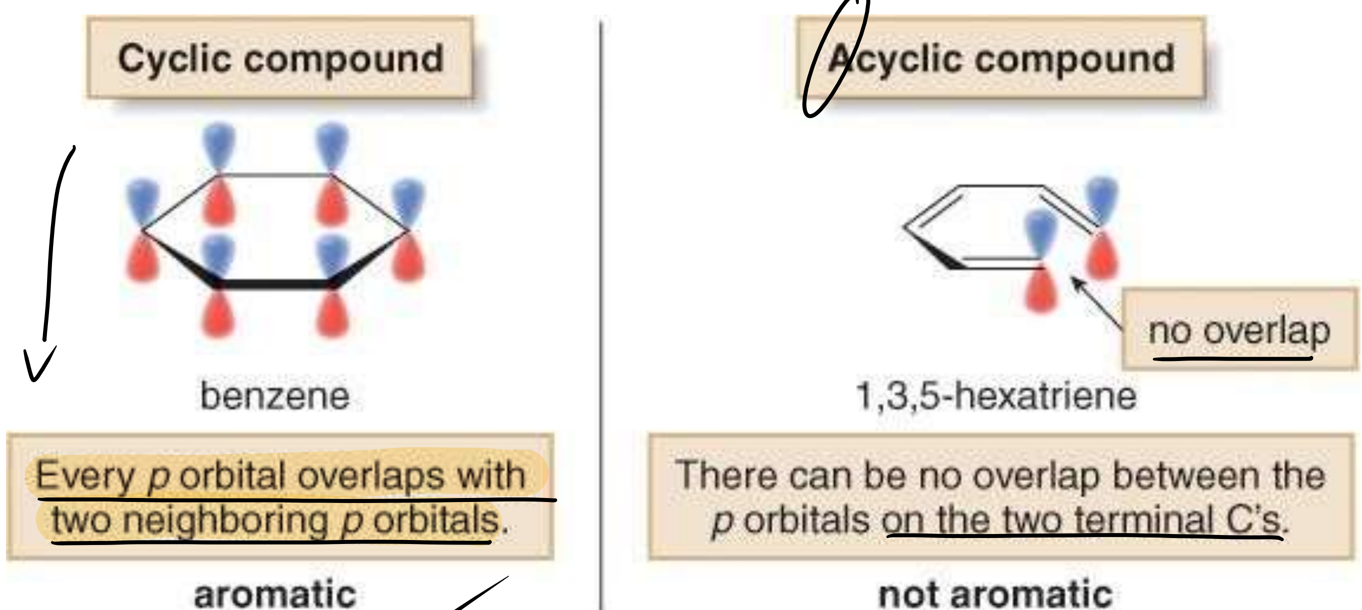
A substitution product still contains a benzene ring.

The Criteria for Aromaticity

cyclic
planner
conjugated

Four structural criteria must be satisfied for a compound to be aromatic.

[1] A molecule must be cyclic.



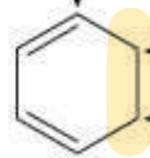
The Criteria for Aromaticity

[2] A molecule must be completely conjugated (all atoms sp^2).

A completely conjugated ring

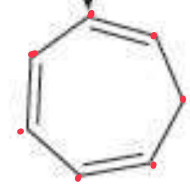
benzene
a *p* orbital on **every** C
aromatic

These rings are not completely conjugated.



no *p* orbitals

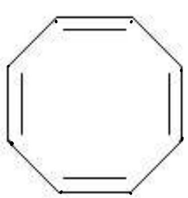
1,3-cyclohexadiene
not aromatic



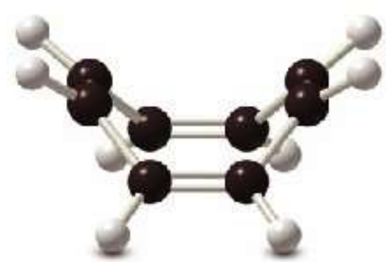
no *p* orbital

1,3,5-cycloheptatriene
not aromatic

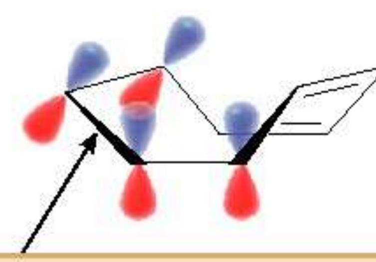
[3] A molecule must be planar.



cyclooctatetraene
not aromatic



a tub-shaped, eight-membered ring



Adjacent *p* orbitals cannot overlap.
Electrons cannot delocalize.

The Criteria for Aromaticity—Hückel's Rule

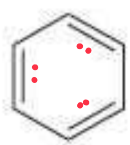
[4] A molecule must satisfy Hückel's rule.

= dots number

- An aromatic compound must contain $4n + 2$ π electrons (n = 0, 1, 2, and so forth).
- Cyclic, planar, and completely conjugated compounds that contain $4n$ π electrons are especially unstable, and are said to be *antiaromatic*.

Benzene
An aromatic compound

3π

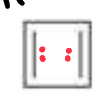


$4n + 2 = 4(1) + 2 =$
6 π electrons
aromatic

odd number of π cloud electrons

Cyclobutadiene
An antiaromatic compound

2π



$4n = 4(1) =$
4 π electrons
antiaromatic

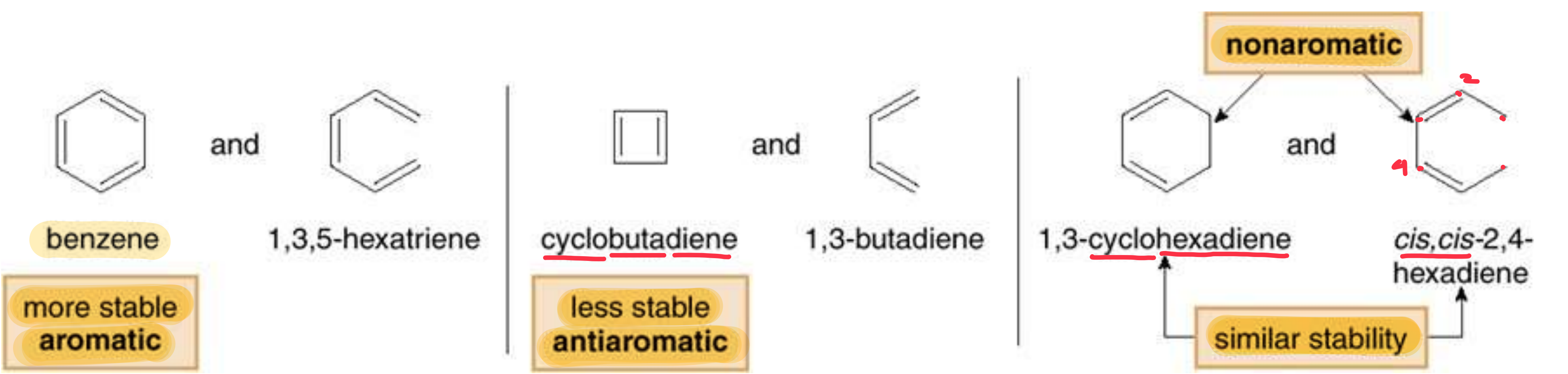
$4n+2=4$
$n=\frac{1}{2}$

Table 17.2 The Number of π Electrons That Satisfy Hückel's Rule

n		$4n + 2$	
0	⟷	2	✓ $4n+2=2$ $n=0$
1	⟷	6	✓ $4n+2=6$ $n=1$
2	⟷	10	✓ $4n+2=10$ $n=2$
3	⟷	14	✓ $4n+2=14$ $n=3$
4, etc.	⟷	18	✓ $4n+2=18$ $n=4$

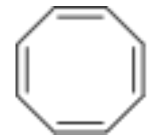
The Criteria for Aromaticity—Hückel's Rule

1. Aromatic—A cyclic, planar, completely conjugated compound with $4n + 2$ π electrons.
2. Antiaromatic—A cyclic, planar, completely conjugated compound with $4n$ π electrons.
3. Not aromatic (nonaromatic)—A compound that lacks one (or more) of the following requirements for aromaticity: being cyclic, planar, and completely conjugated.



Examples of Aromatic Rings

Cyclooctatetraene
8 π electrons



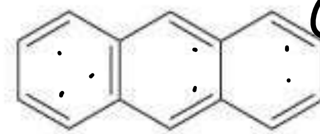
planar
antiaromatic 4n

متجعد

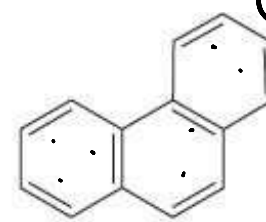
puckered
nonaromatic

$4n + 2 = 18$
$n = \frac{7}{2}$

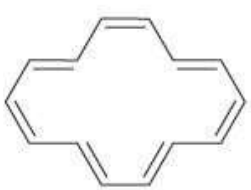
naphthalene
10 π electrons



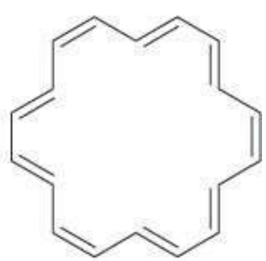
anthracene
14 π electrons



phenanthrene
14 π electrons

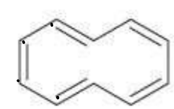


[14]-annulene
$4n + 2 = 4(3) + 2 =$
14 π electrons
aromatic



[18]-annulene
$4n + 2 = 4(4) + 2 =$
18 π electrons
aromatic

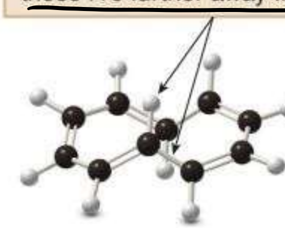
[10]-Annulene fits Hückel's rule, but it's **not planar**.



[10]-annulene
10 π electrons
not aromatic

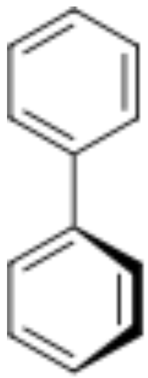
=

The molecule puckers to keep these H's further away from each other.



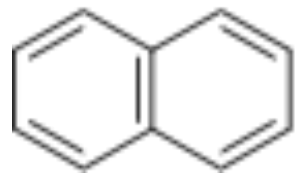
3-D representation

Polycyclic Aromatic Hydrocarbons

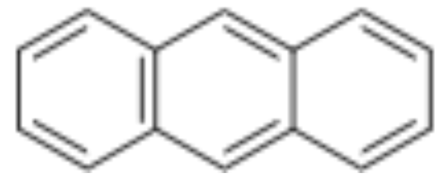


biphenyl

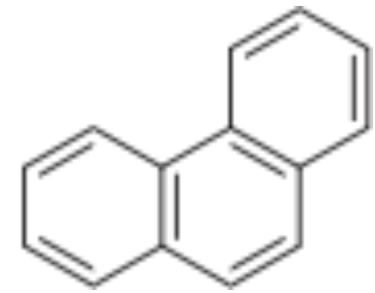
terphenyl



naphthalene



anthracene



phenanthrene

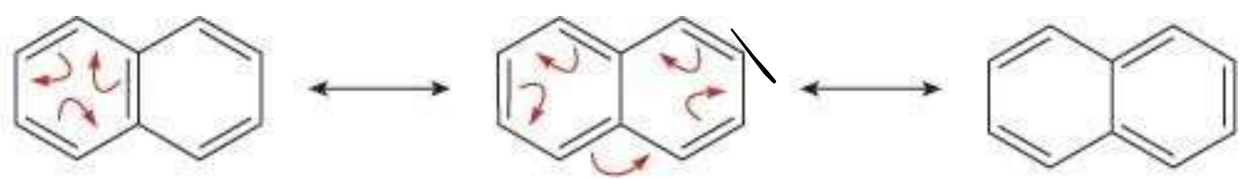
No interactions between rings

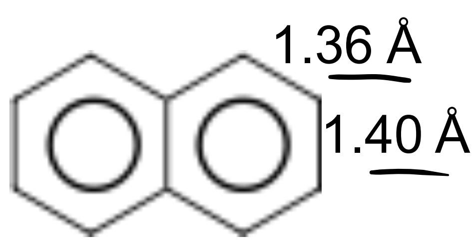
61 kcal/mol

84 kcal/mol

92 kcal/mol

Three resonance structures for naphthalene





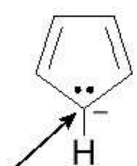
Other Aromatic Compounds

cyclopentadiene
not aromatic
pK_a = 15

cyclopentadienyl anion
aromatic
a stabilized conjugate base

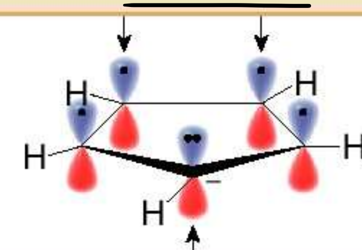
The cyclopentadienyl anion

aromatic



sp^2 hybridized C

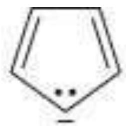
The ring is completely conjugated with **6 π electrons**.



The lone pair resides in a *p* orbital.

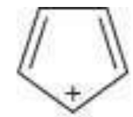
- The cyclopentadienyl anion is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons.

Other Aromatic Compounds



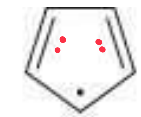
cyclopentadienyl anion
- **6** π electrons
- contains $4n + 2$ π electrons

aromatic



cyclopentadienyl cation
- **4** π electrons
- contains $4n$ π electrons

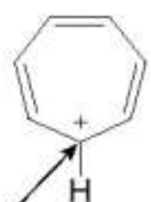
antiaromatic



cyclopentadienyl radical
- **5** π electrons
- does not contain either $4n$ or $4n + 2$ π electrons

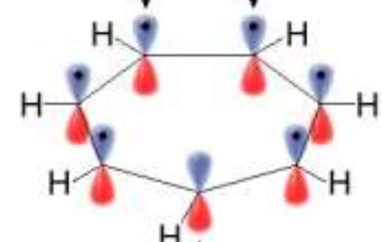
nonaromatic

The tropylium cation



sp^2 hybridized C

The ring is completely conjugated with **6 π electrons**.



One *p* orbital is vacant.

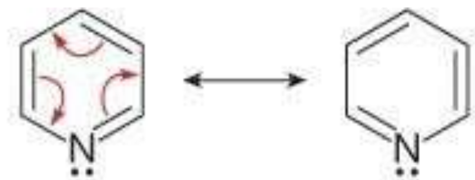
فلك فارغ

- The **tropylium cation** is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons delocalized over the seven atoms of the ring.

6π electrons 7C

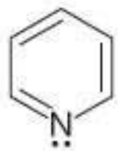
غير متجانسة

Aromatic Heterocycles

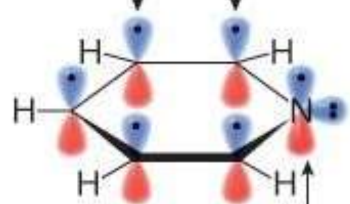


two resonance structures for pyridine
6 π electrons

Six π electrons are delocalized in the ring.



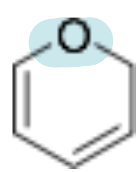
sp^2 hybridized N



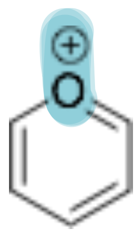
The lone pair occupies an sp^2 hybrid orbital, perpendicular to the direction of the six *p* orbitals.

A *p* orbital on N overlaps with adjacent *p* orbitals, making the ring completely conjugated.

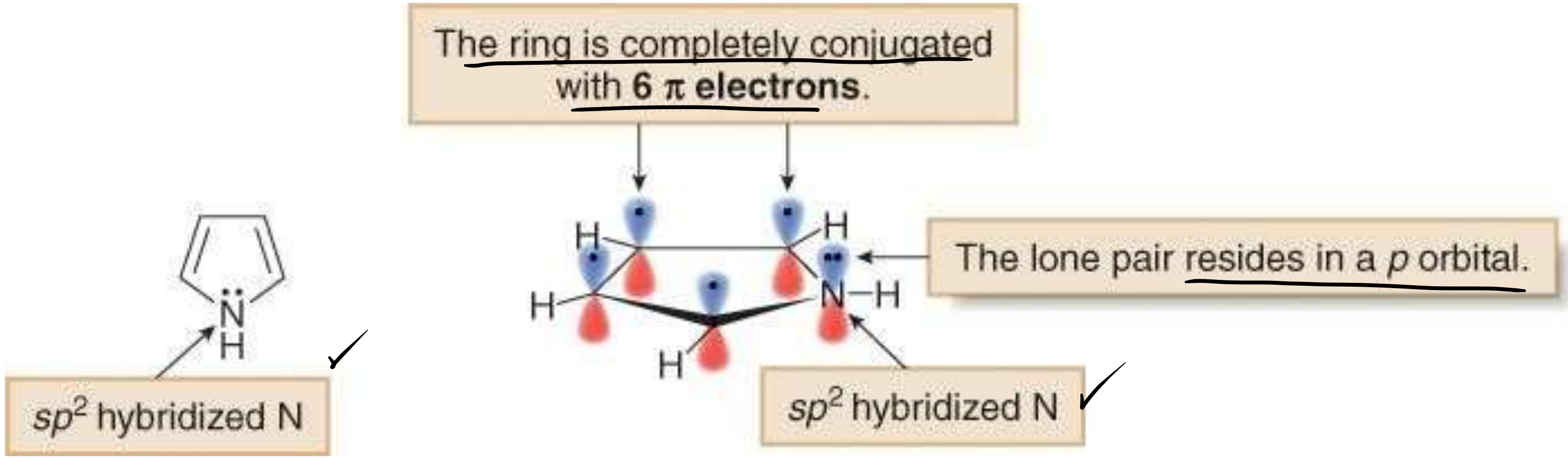
2H-pyran
4 π electrons
nonaromatic

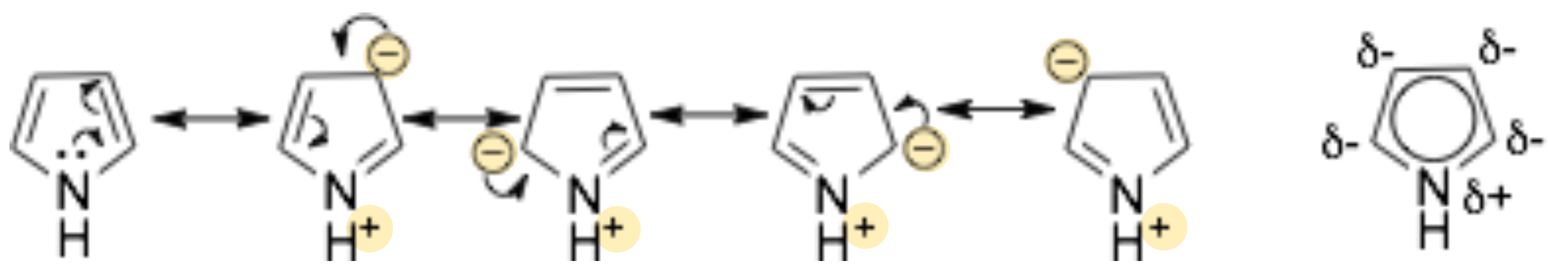


2H-pyrilium ion
6 π electrons
aromatic

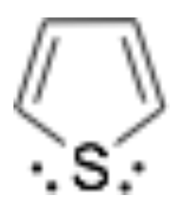


Aromatic Heterocycles





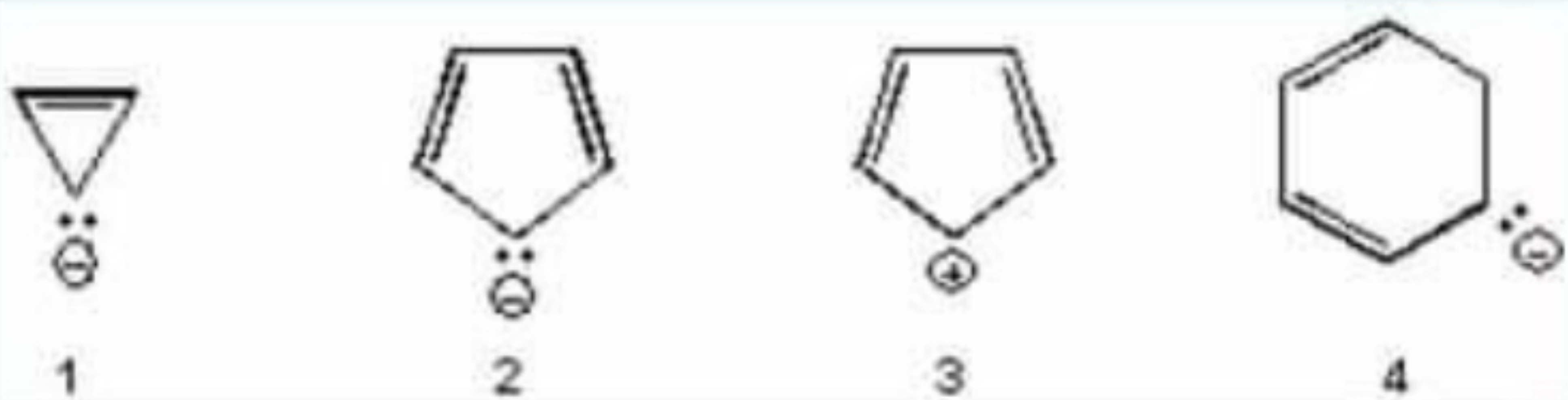
furan



thiophen

* ?Which of the following ions is aromatic

(1 نقطة)



1

2

3

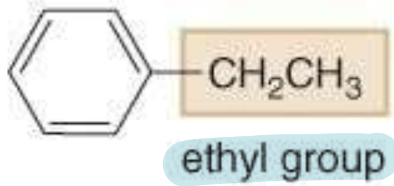
4

start
sunday
16/ Nov /2025

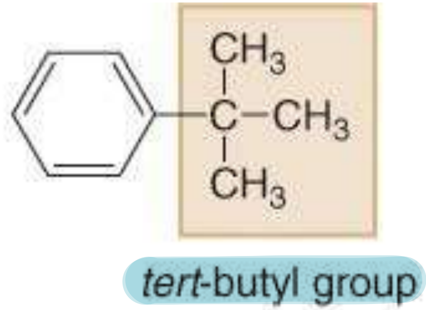
بديل

Nomenclature: 1 Substituent

Systematic:



ethylbenzene

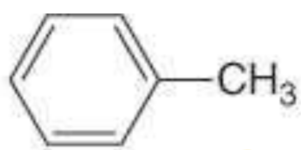


tert-butylbenzene

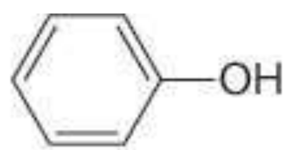
chlorobenzene

Common:

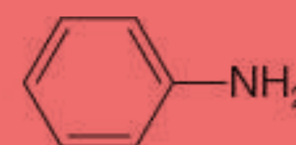
حفظ



toluene
(methylbenzene)



phenol
(hydroxybenzene)



aniline
(aminobenzene)

4.2. Which of the following structures accurately represents toluene?

*a. 

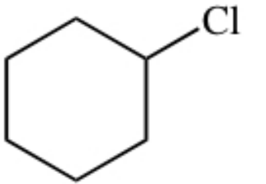
b. 

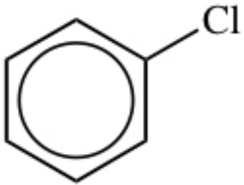
c. 

d. 

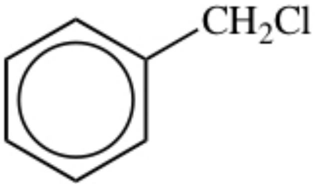
e. 

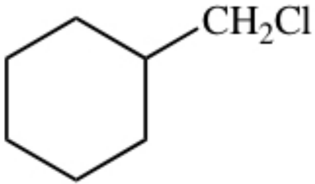
4.1. The structure of chlorobenzene is correctly represented by:

a. 

*b. 

c. 

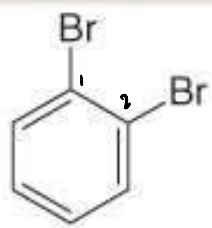
d. 

e. 

Nomenclature: 2 Substituents

Identical:

1,2-disubstituted benzene **ortho isomer**	1,3-disubstituted benzene **meta isomer**	1,4-disubstituted benzene **para isomer**



1,2-dibromobenzene
o-dibromobenzene

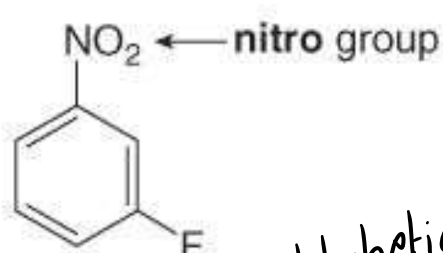
1,3-dibromobenzene
m-dibromobenzene

1,4-dibromobenzene
p-dibromobenzene

Different:

Alphabetize two different substituent names:

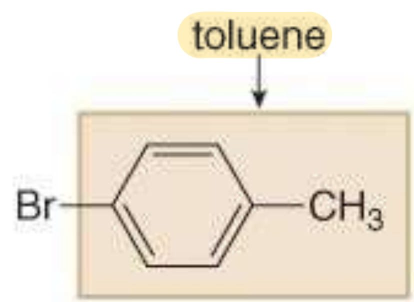
o-bromochloro-
benzene



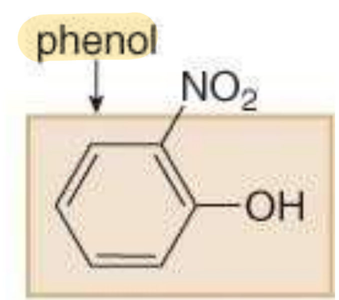
m-fluoronitro-
benzene

alphabetic order

Use a common root name:



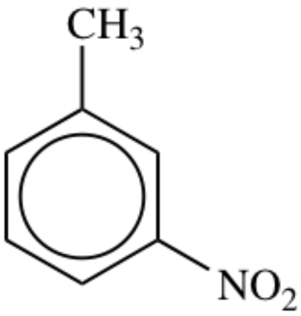
p-bromo**toluene**



o-nitro**phenol**

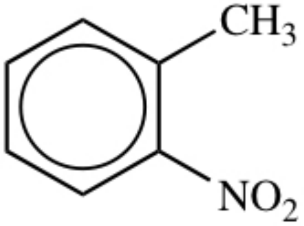
4.6. Which of the following molecules is *m*-nitrophenol?

a.

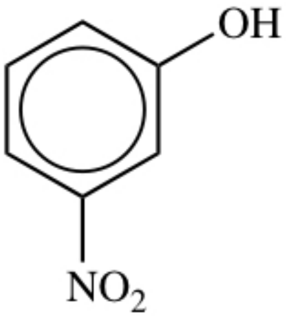


b.

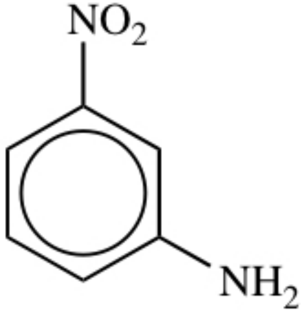
c.



***d.**



e.



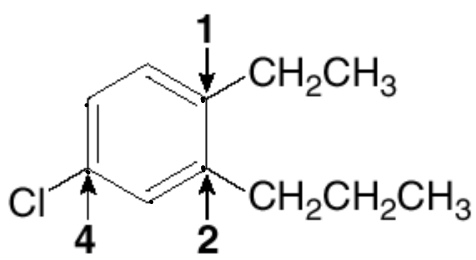
4.4. What dibromobenzene can form *only one* tribromobenzene?

a. *o*-dibromobenzene **b.** *m*-dibromobenzene ***c.** *p*-dibromobenzene
d. cumene **e.** styrene

Nomenclature: 3 or More Substituents

Examples of naming polysubstituted benzenes

[1]



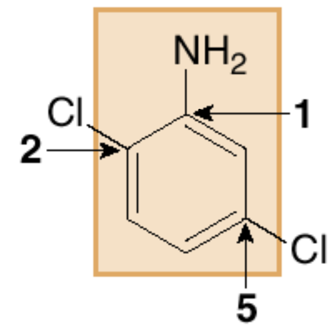
1 • Assign the lowest set of numbers.

2 • Alphabetize the names of all the substituents.

4-chloro-1-ethyl-2-propylbenzene

تفرعات
رتبناهم
أبجديًا

[2]

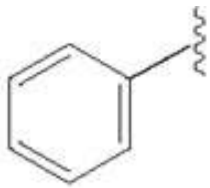


- Name the molecule as a derivative of the common root **aniline.**
- Designate the position of the NH_2 group as "1," and then assign the lowest possible set of numbers to the other substituents.

2,5-dichloroaniline

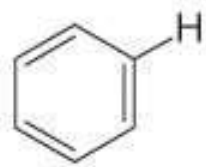
Nomenclature

- A benzene substituent is called a phenyl group, and it can be abbreviated in a structure as “Ph-”.



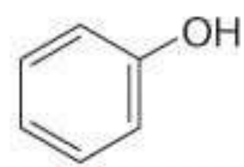
phenyl group
C_6H_5-

abbreviated as Ph–



benzene

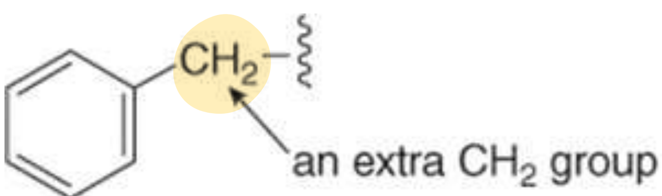
= C_6H_5-H
PhH



phenol

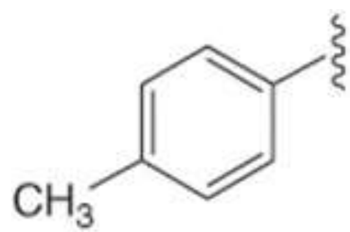
= C_6H_5-OH
PhOH

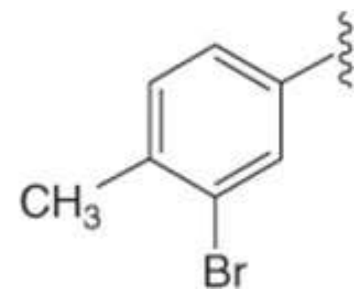
- The benzyl group:



benzyl group
$C_6H_5CH_2-$

- Aryl groups:

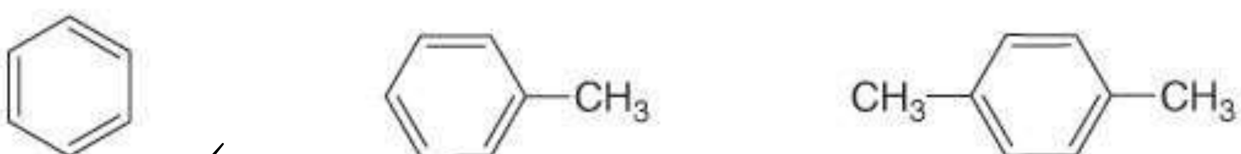




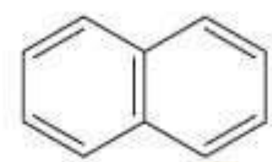
Interesting Aromatic Compounds

- Benzene and toluene, are obtained from petroleum refining and are useful starting materials for synthetic polymers.
- Compounds containing two or more benzene rings that share carbon—carbon bonds are called polycyclic aromatic hydrocarbons (PAHs). Naphthalene, the simplest PAH, is the active ingredient in mothballs.

The components of the gasoline additive BTX



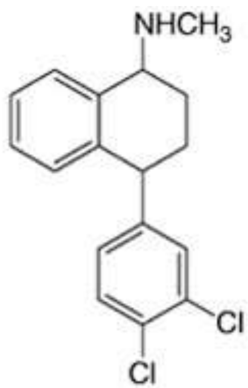
benzene | toluene | *p*-xylene



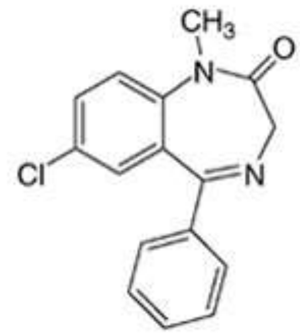
naphthalene (used in mothballs)

اطلاع
مش حفظ

Interesting Aromatic Compounds

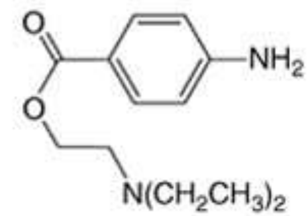


- Trade name: **Zoloft**
- Generic name: **sertraline**
- Use: a psychotherapeutic drug for depression and panic disorders



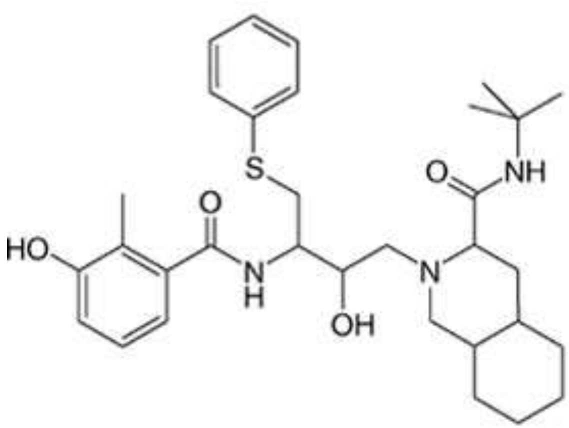
- Trade name: **Valium**
- Generic name: **diazepam**
- Use: a sedative

مهدئ



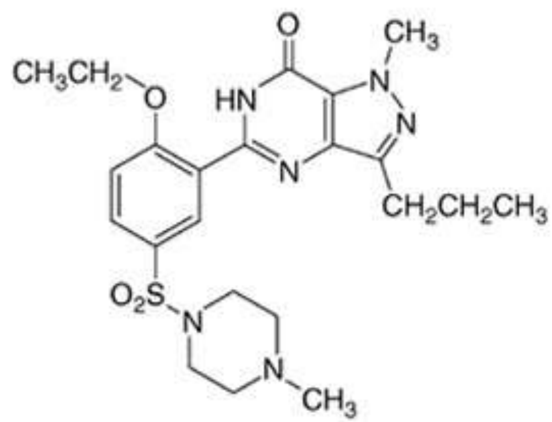
- Trade name: **Novocain**
- Generic name: **procaine**
- Use: a local anesthetic

مخدر



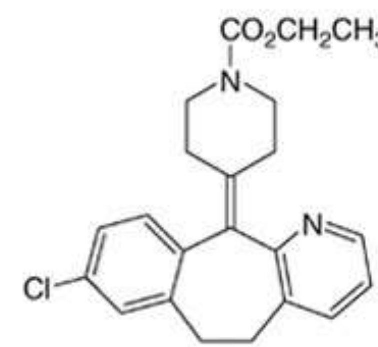
- Trade name: **Viracept**
- Generic name: **nelfinavir**
- Use: an antiviral drug used to treat HIV

مضاد فيروسات



- Trade name: **Viagra**
- Generic name: **sildenafil**
- Use: a drug used to treat erectile dysfunction

منشط الانتصاب

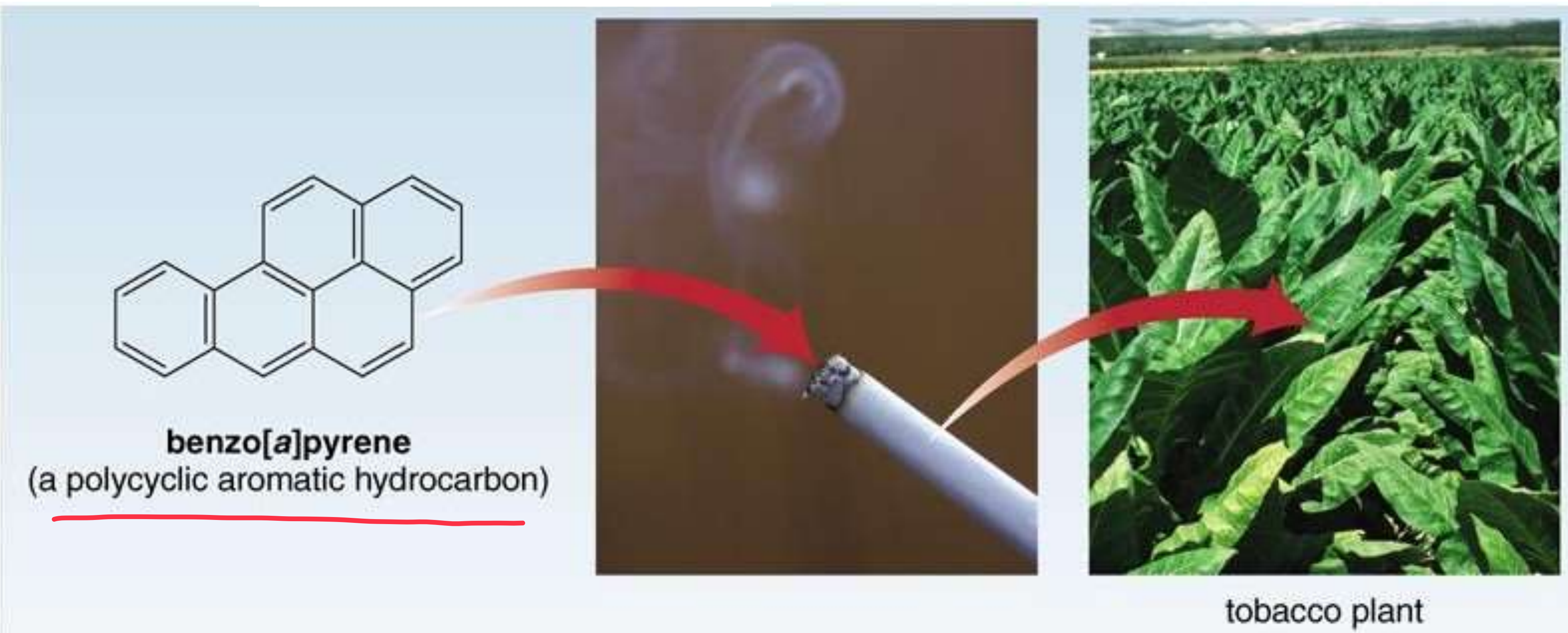


- Trade name: **Claritin**
- Generic name: **loratadine**
- Use: an antihistamine for seasonal allergies

حساسية موسمية

Interesting Aromatic Compounds

- Benzo[a]pyrene, produced by the incomplete oxidation of organic compounds in tobacco, is found in cigarette smoke.



© David Young-Wolff/PhotoEdit © Corbis

- When ingested or inhaled, benzo[a]pyrene and other similar PAHs are oxidized to carcinogenic products.

مواد مسرطنة

نقص

electro - deficient

+

Electrophilic Aromatic Substitution

Chapter 16

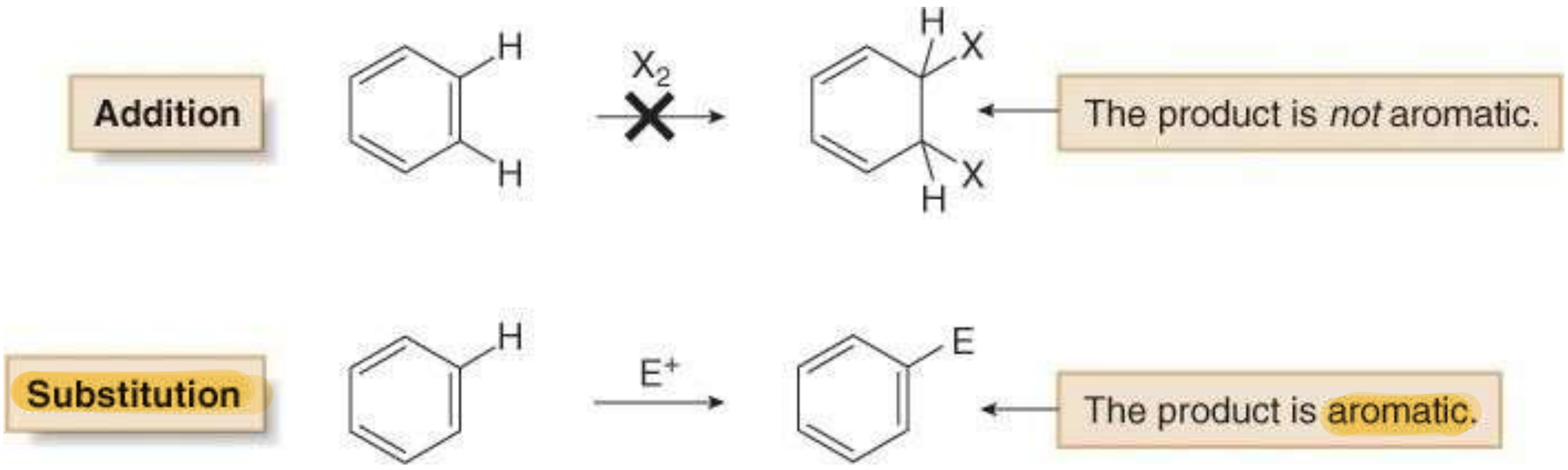
Organic Chemistry, *8th Edition*

John McMurry

https://youtu.be/ubtvxTvdWjA?si=e3l5WUtSr2C5QXN9

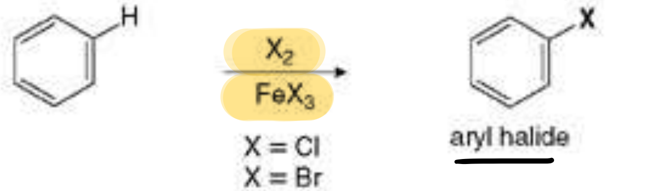
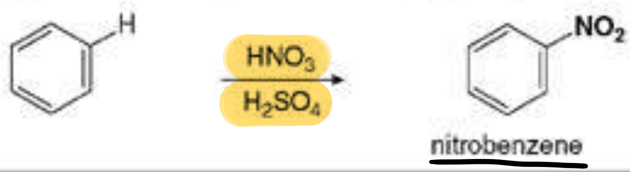
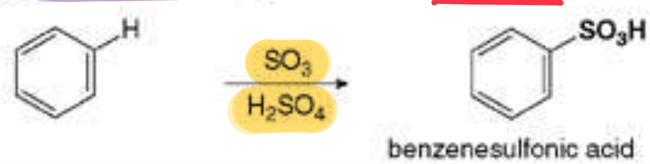
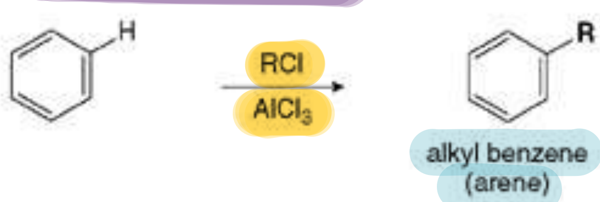
easy explanation

Introduction



catalyst حفظ ال

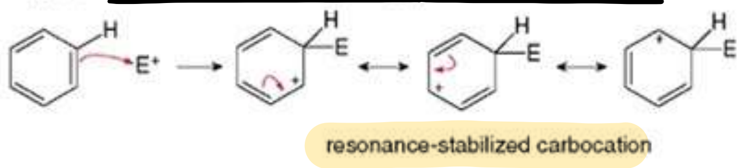
Introduction

Reaction	Electrophile
[1] **Halogenation**—Replacement of H by X (Cl or Br)	
	$E^+ = Cl^+$ or Br^+
[2] **Nitration**—Replacement of H by NO_2	
	$E^+ = \overset{+}{N}O_2$
[3] **Sulfonation**—Replacement of H by SO_3H	
	$E^+ = \overset{+}{S}O_3H$
[4] **Friedel–Crafts alkylation**—Replacement of H by R	
	$E^+ = R^+$
[5] **Friedel–Crafts acylation**—Replacement of H by RCO	
	$E^+ = R\overset{+}{C}O$

Mechanism

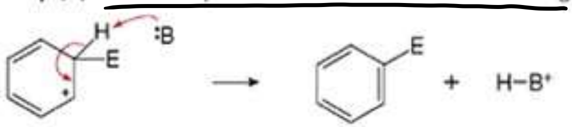
Mechanism 18.1 General Mechanism—Electrophilic Aromatic Substitution

Step [1] Addition of the electrophile (E^+) to form a carbocation



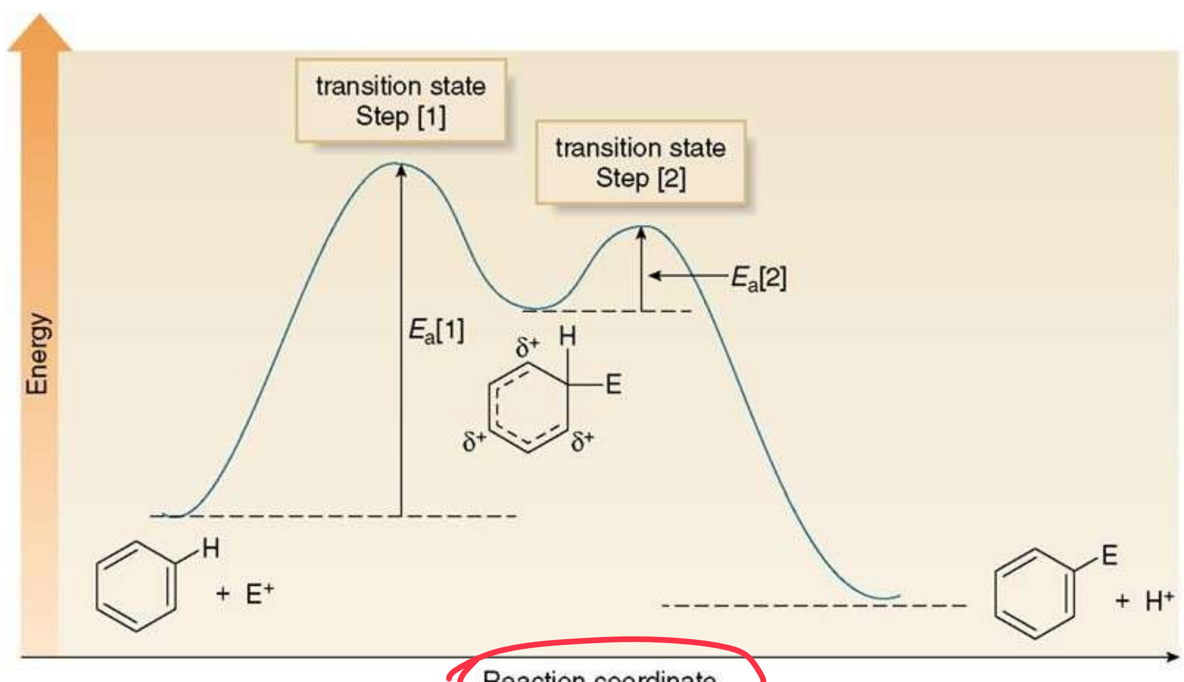
- Addition of the electrophile (E^+) forms a new C–E bond using two π electrons from the benzene ring, and generating a carbocation. This carbocation intermediate is not aromatic, but it is resonance stabilized—**three resonance structures can be drawn.**
- Step [1] is rate-determining because the aromaticity of the benzene ring is lost.

Step [2] Loss of a proton to re-form the aromatic ring



stable compound

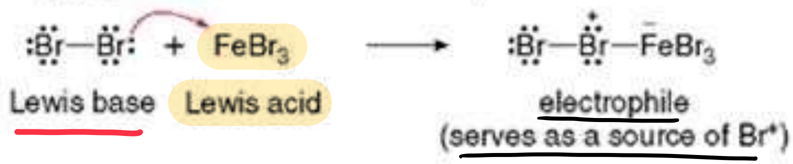
- In Step [2], a base (B:) removes the proton from the carbon bearing the electrophile, thus re-forming the aromatic ring. This step is fast because the aromaticity of the benzene ring is restored.
- Any of the three resonance structures of the carbocation intermediate can be used to draw the product. The choice of resonance structure affects how curved arrows are drawn, but not the identity of the product.



Halogenation

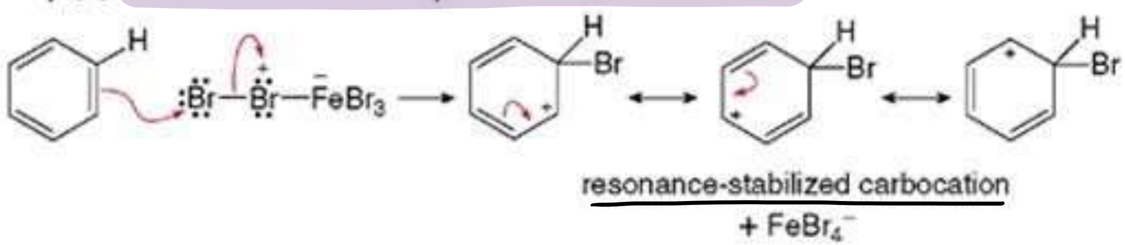
Mechanism 18.2 Bromination of Benzene

Step [1] Generation of the electrophile



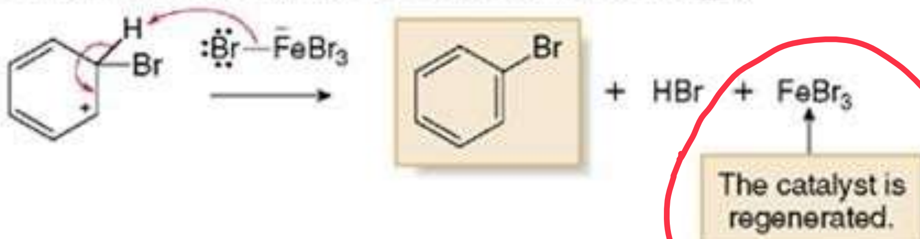
- Lewis acid–base reaction of Br_2 with $FeBr_3$ forms a species with a weakened and polarized Br–Br bond. This adduct serves as a source of Br^+ in the next step.

Step [2] Addition of the electrophile to form a carbocation



- Addition of the electrophile forms a new C–Br bond and generates a carbocation. This carbocation intermediate is resonance stabilized—**three resonance structures can be drawn.**
- The $FeBr_4^-$ also formed in this reaction is the base used in Step [3].

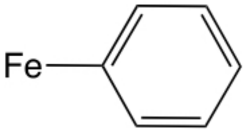
Step [3] Loss of a proton to re-form the aromatic ring

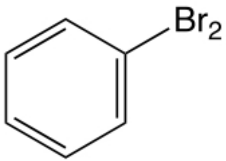


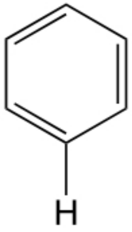
- $FeBr_4^-$ removes the proton from the carbon bearing the Br, thus re-forming the aromatic ring.
- $FeBr_3$, a catalyst, is also regenerated for another reaction cycle.

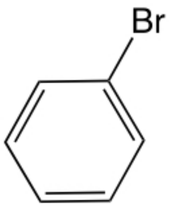
https://youtu.be/nP4-tAAGDVc?si=hTknRL9OzJ7MRa1i

EXAMPLE: Which of the following is a correct product of benzene substitution reaction with Br_2?

a) 

b) 

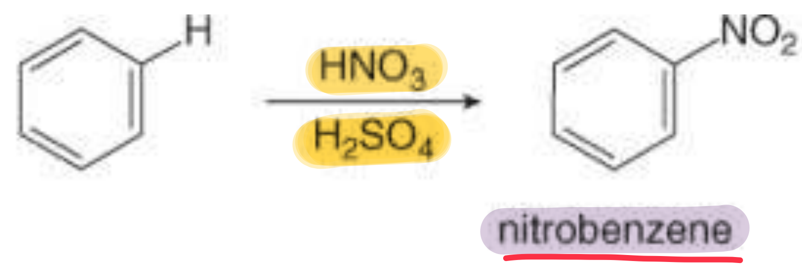
c) 

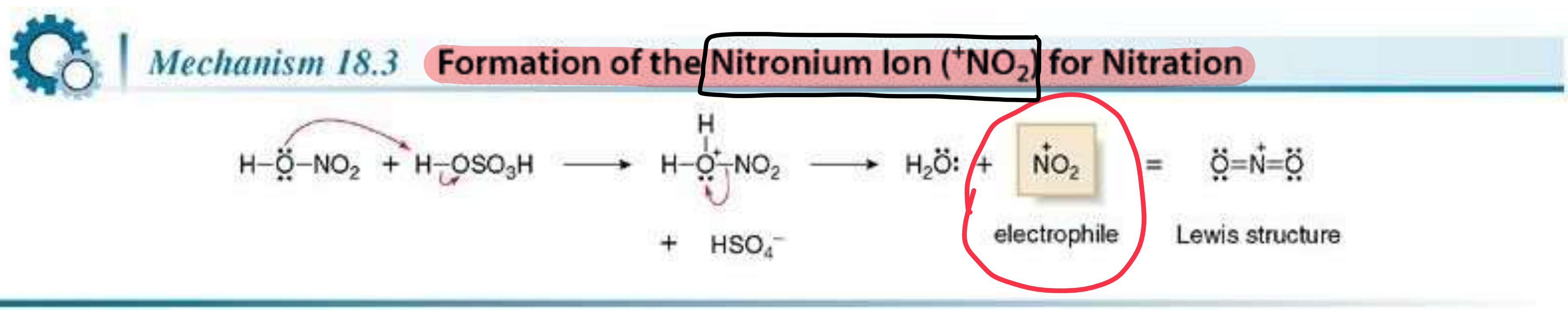
d) 

d

Nitration

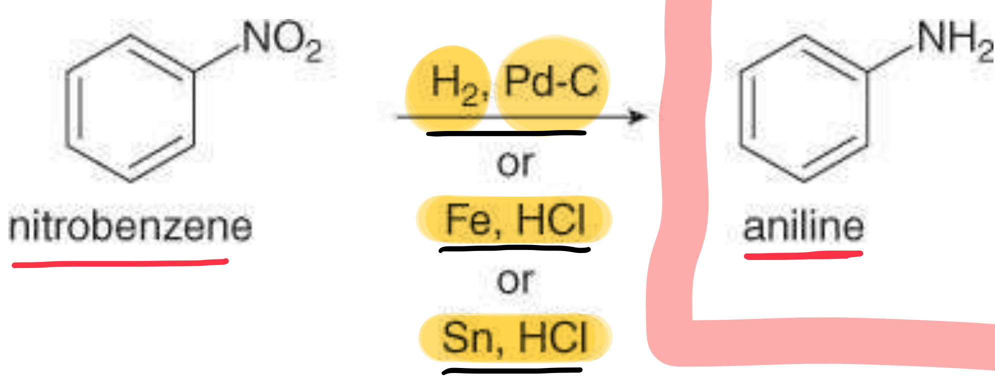
Final products



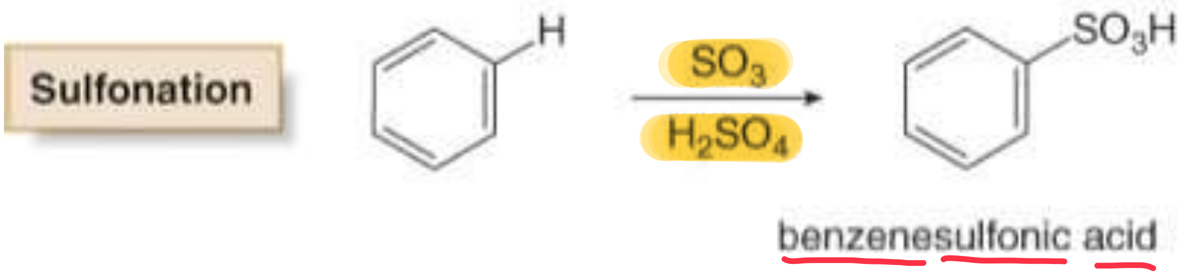


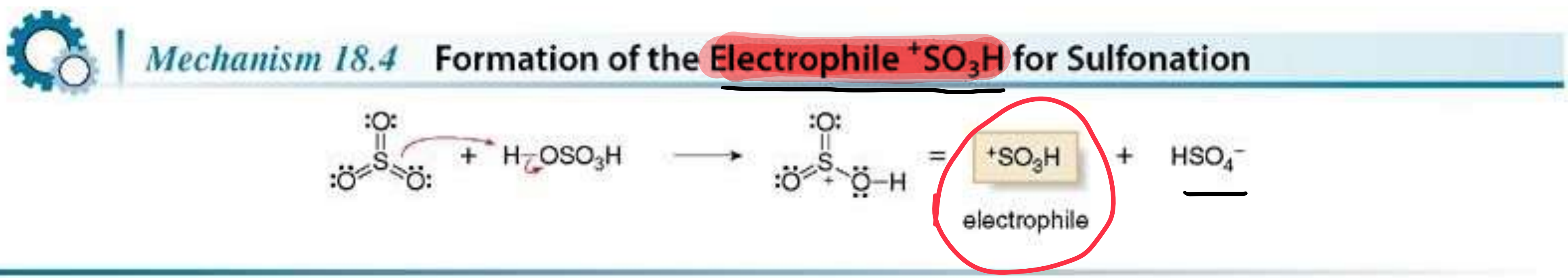
Nitro Group Reduction

Aromatic nitro groups (NO_2) can readily be reduced to amino groups (NH_2) under a variety of conditions.

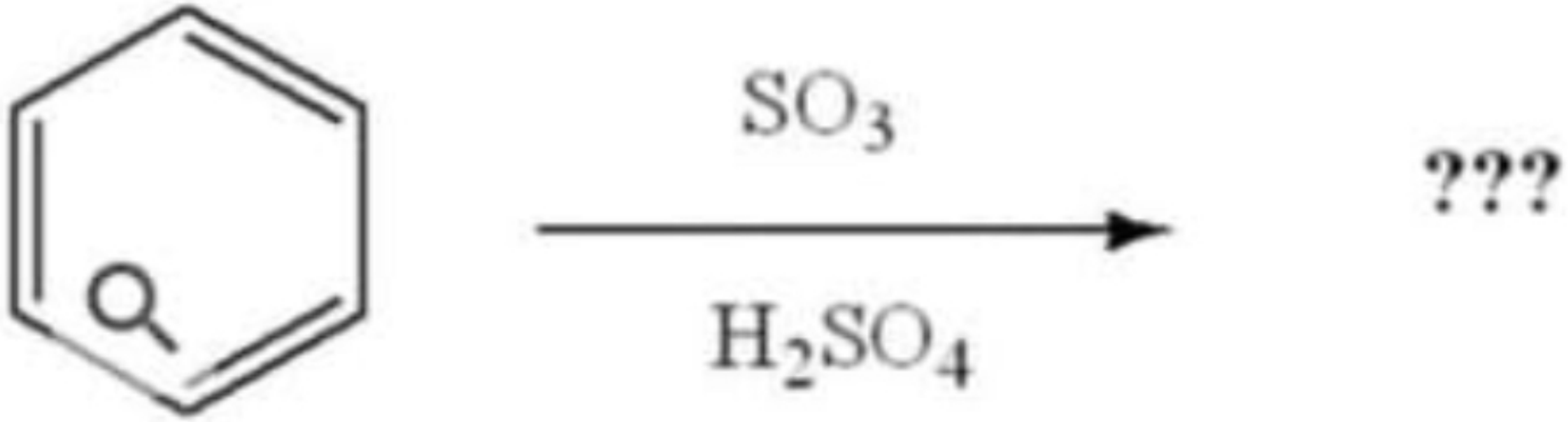


Sulfonation





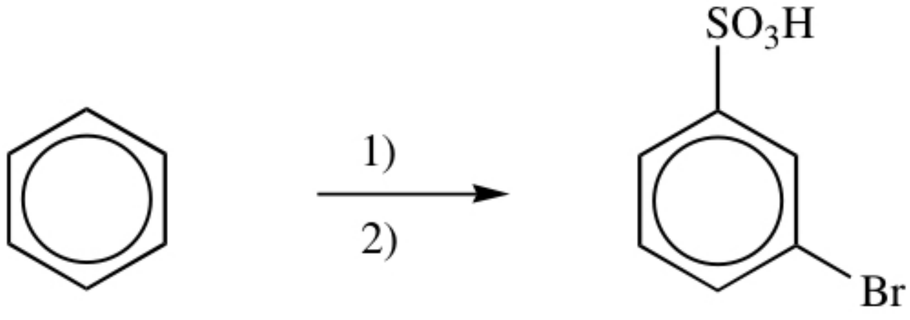
What is the name of the mechanism resulted ?from the following reaction



:Select one

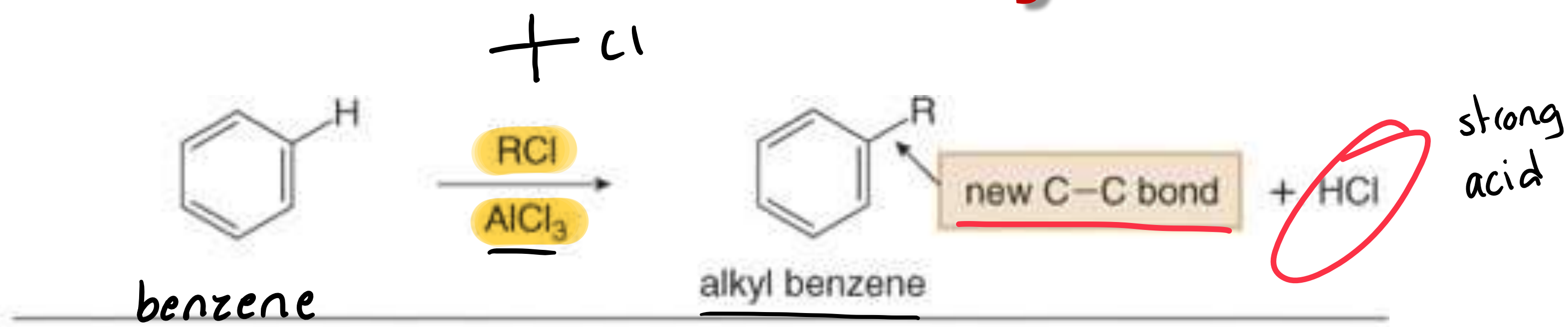
- a. Electrophilic aromatic substitution reaction
- b. Nucleophilic aromatic addition reaction
- c. Nucleophilic aromatic substitution reaction
- d. Electrophilic aromatic addition reaction

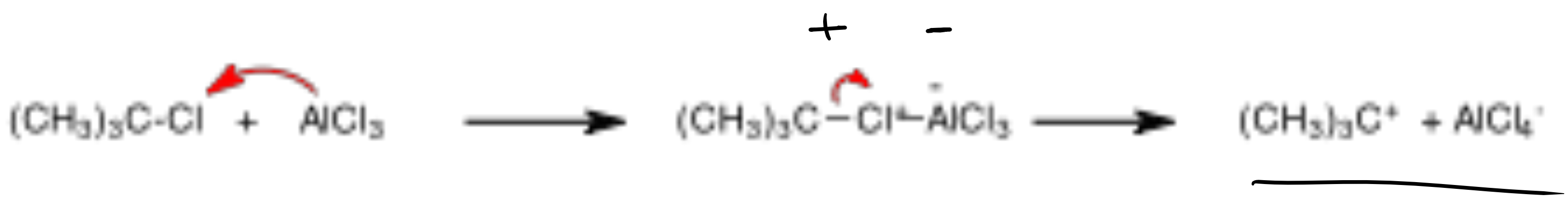
4.42. Which is the best reaction sequence to synthesize *m*-bromobenzenesulfonic acid from benzene?

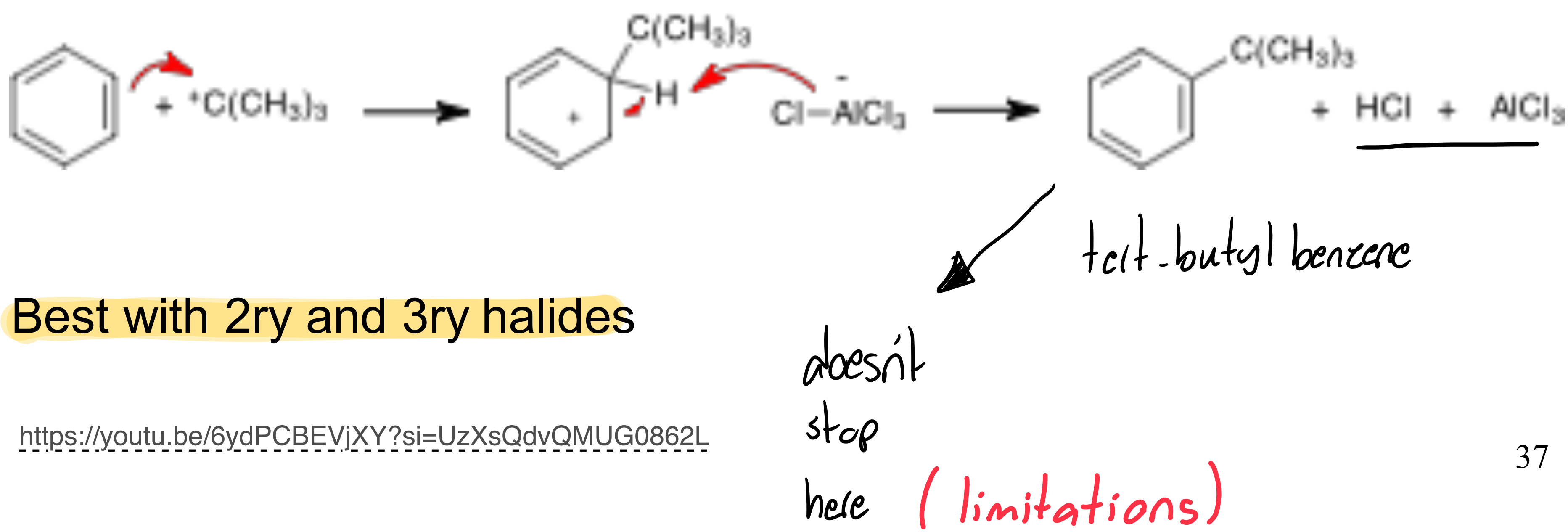


a. 1) Br_2, $AlBr_3$, 2) H_2SO_4, SO_3
***b.** 1) H_2SO_4, SO_3 2) Br_2, $AlBr_3$
c. 1) ethene, HF, 2) Br_2, $AlBr_3$
d. 1) CH_3Cl, $AlCl_3$, 2) Br_2, $AlBr_3$
e. 1) Br_2, $AlBr_3$, 2) CH_3COCl, $AlCl_3$

Friedel-Crafts Alkylation





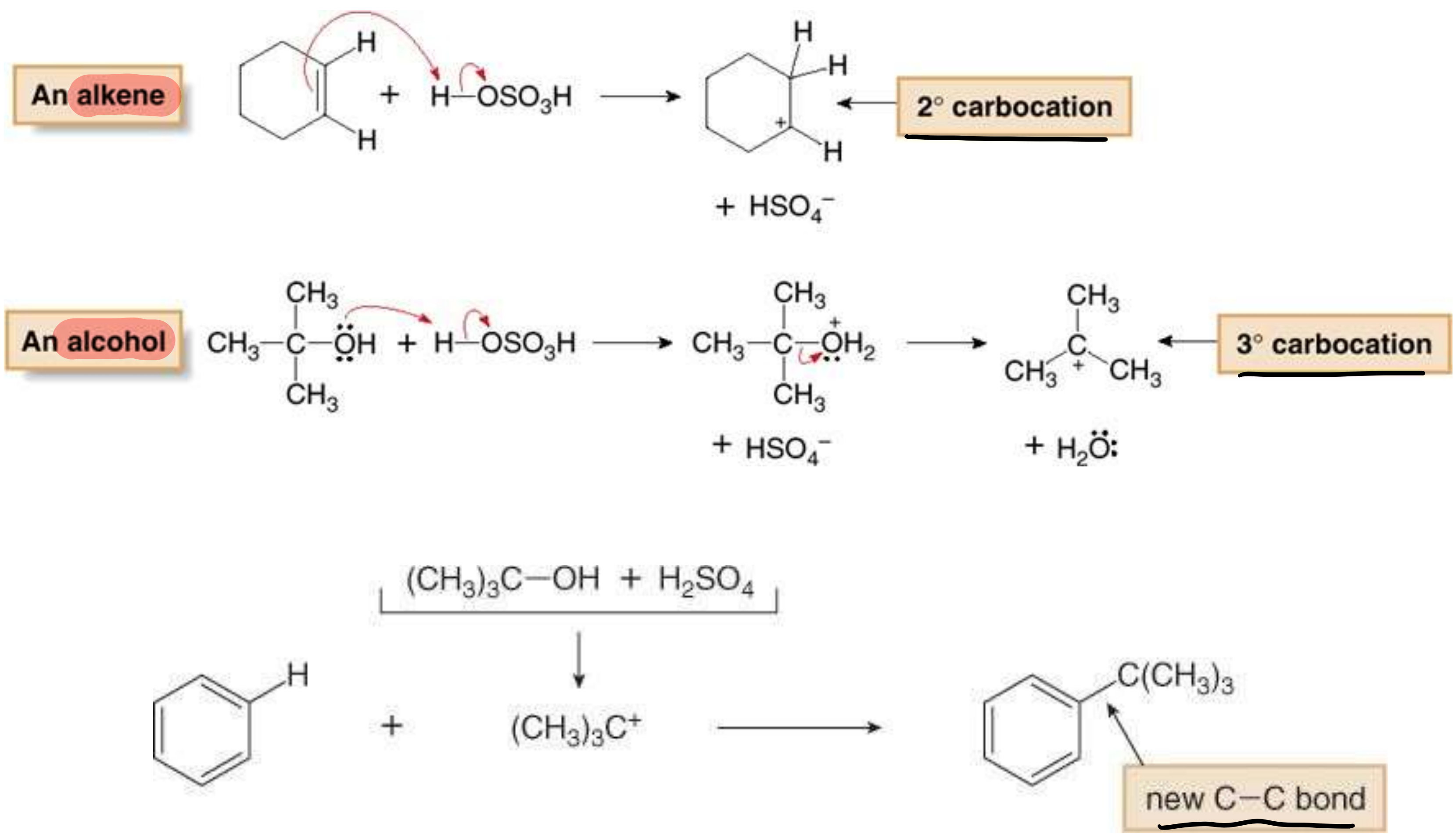


Best with 2ry and 3ry halides

https://youtu.be/6ydPCBEVjXY?si=UzXsQdvQMUG0862L

Friedel-Crafts Alkylation

Other functional groups that form carbocations can also be used as starting materials.



unreactive halides

Limitations

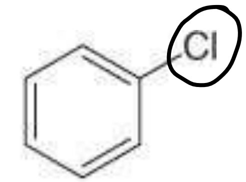
[1] Vinyl halides and aryl halides do not react in Friedel-Crafts alkylation.

Unreactive halides in the Friedel–Crafts alkylation

$CH_2{=}CHCl$

vinyl halide

chloromethene



aryl halide

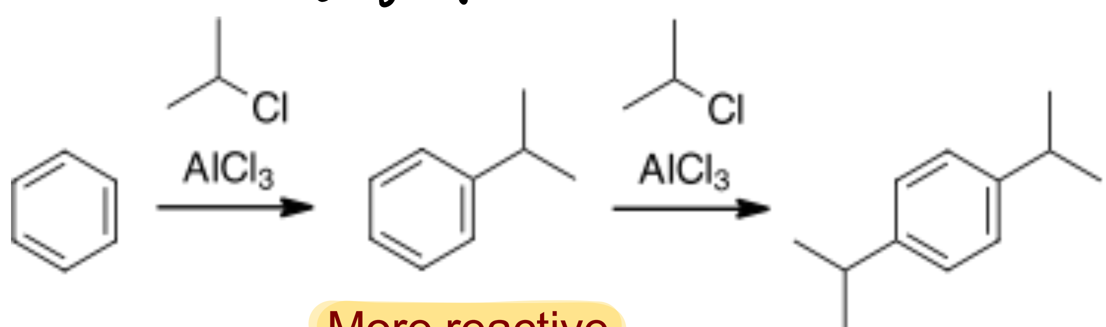
chlorobenzene

[2] Disubstituted products are obtained in F.-C. alkylations but not in acylations.

-limitations-

polyalkylations can occur.

tert-butyl group



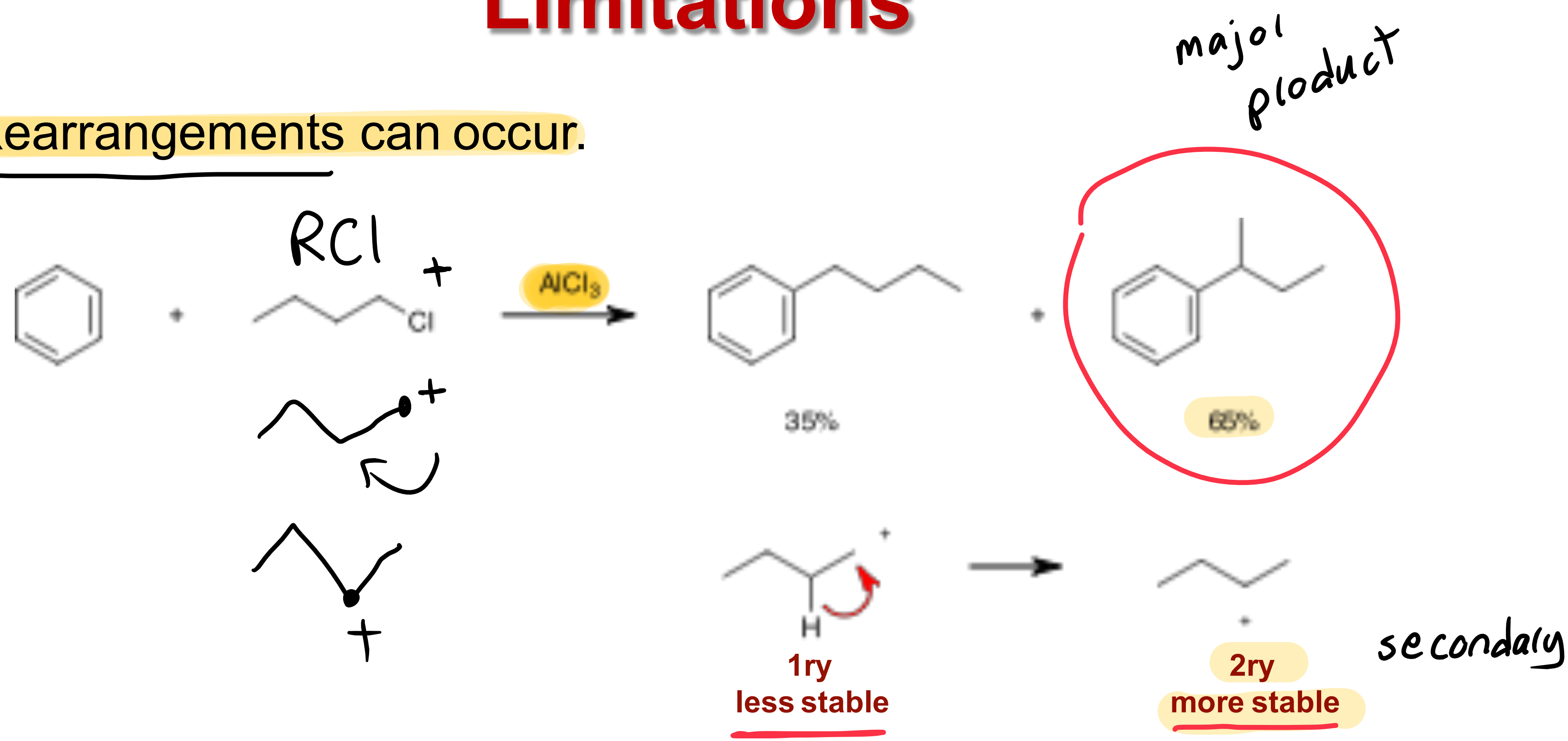
More reactive than benzene

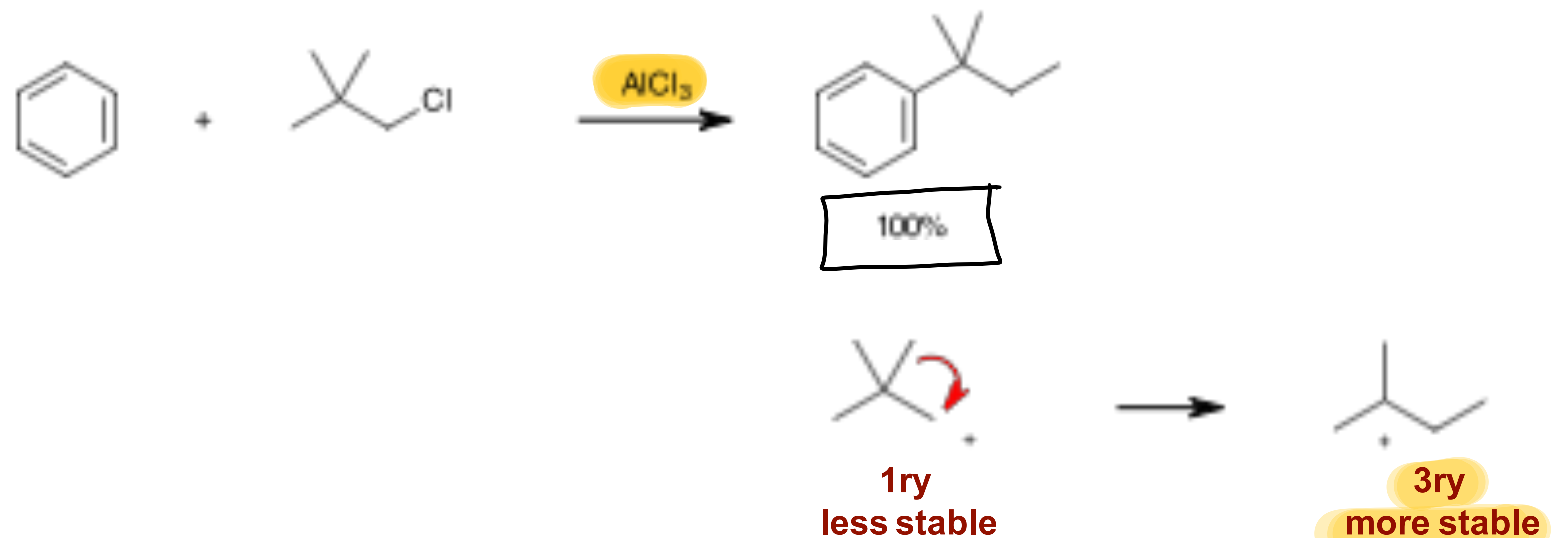
(tert-butyl benzene)

Final product

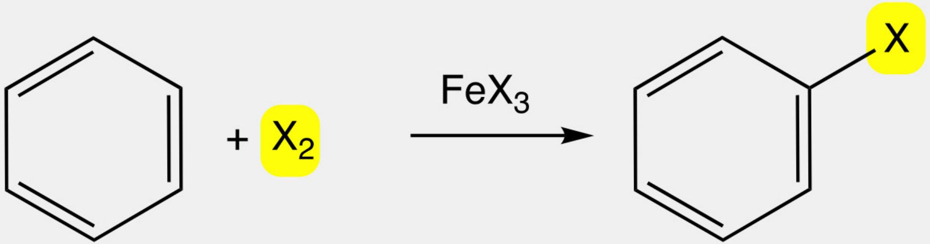
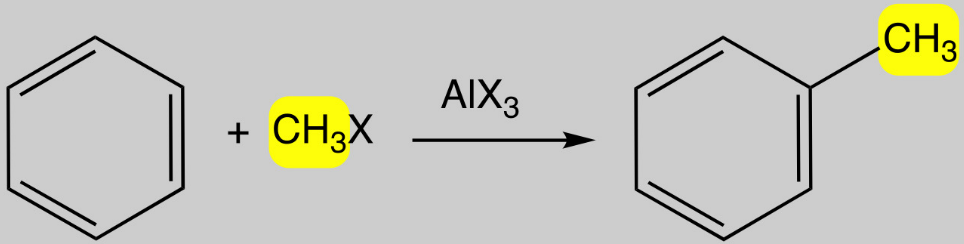
Limitations

[3] Rearrangements can occur.

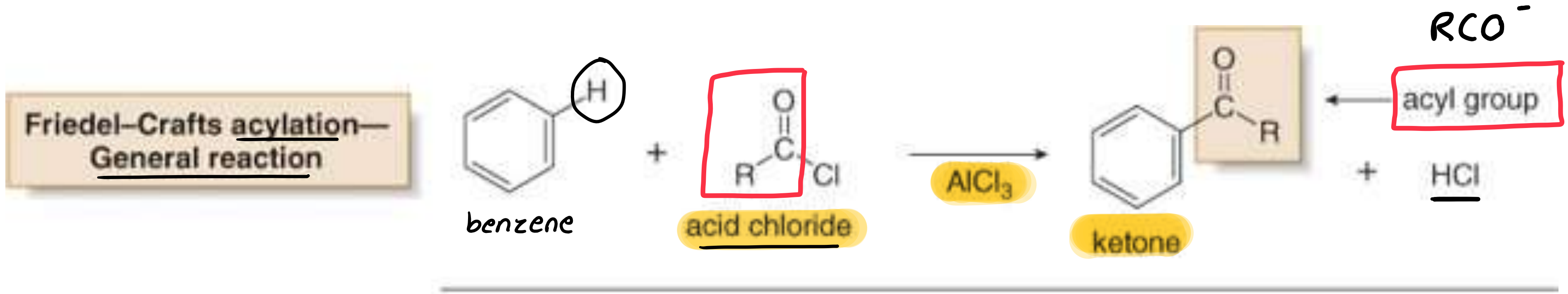


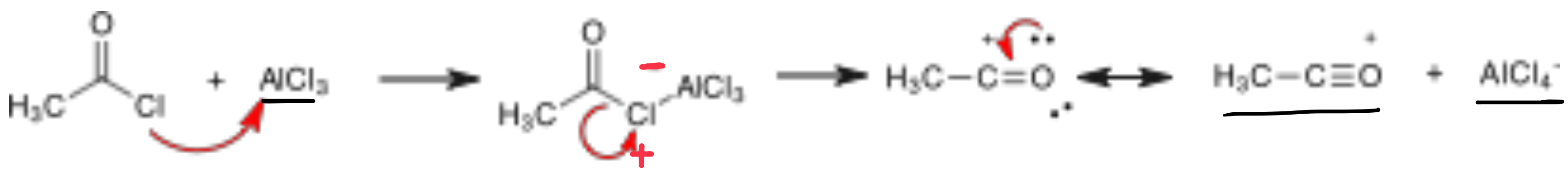


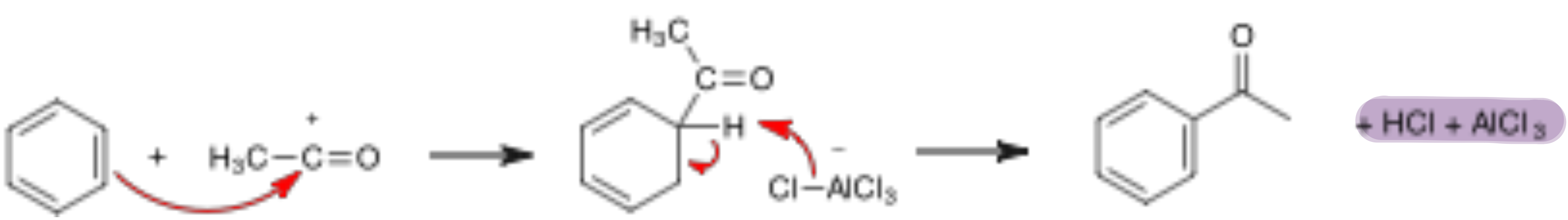
Summary of Benzene Reactions

Reaction	Reagent	Catalyst	Example
Halogenation	Halogen X_2	FeX_3	
Friedel Crafts Alkylation	Alkyl halide CH_3X	AlX_3	

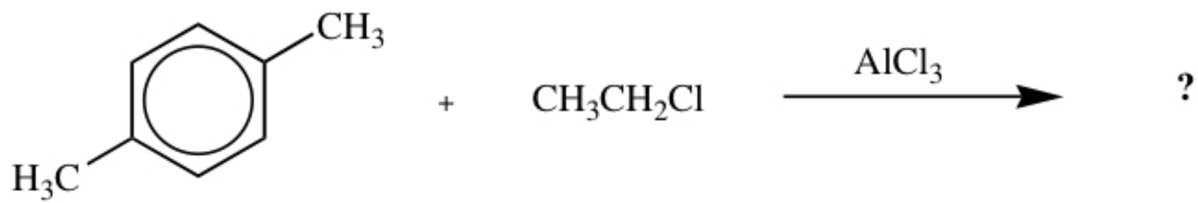
Friedel-Crafts Acylation

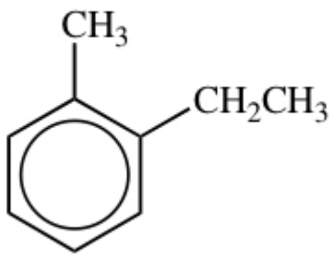


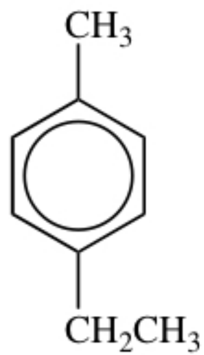


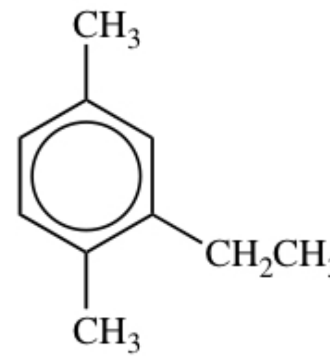


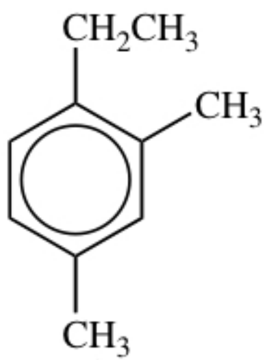
4.36. The expected product from the following reaction is:

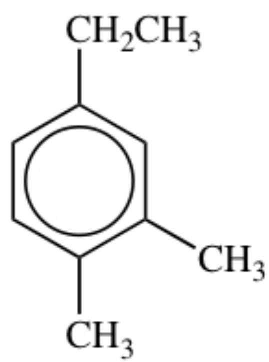


a. 

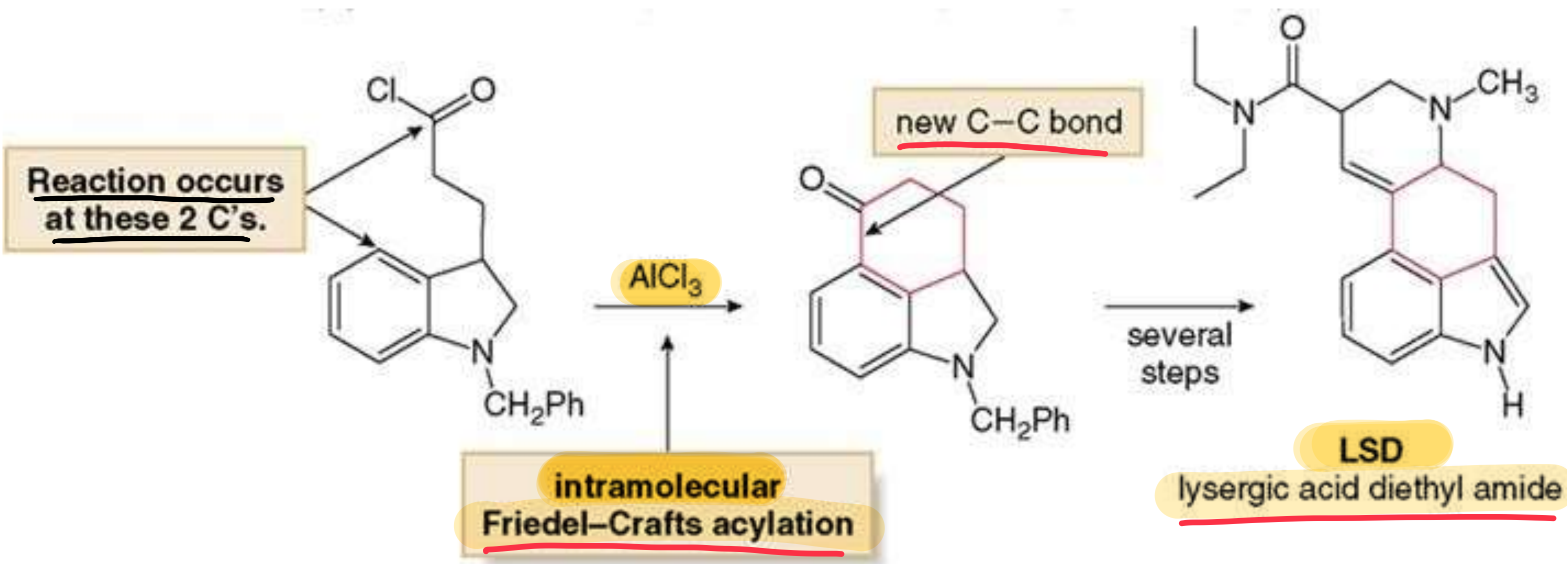
b. 

*c. 

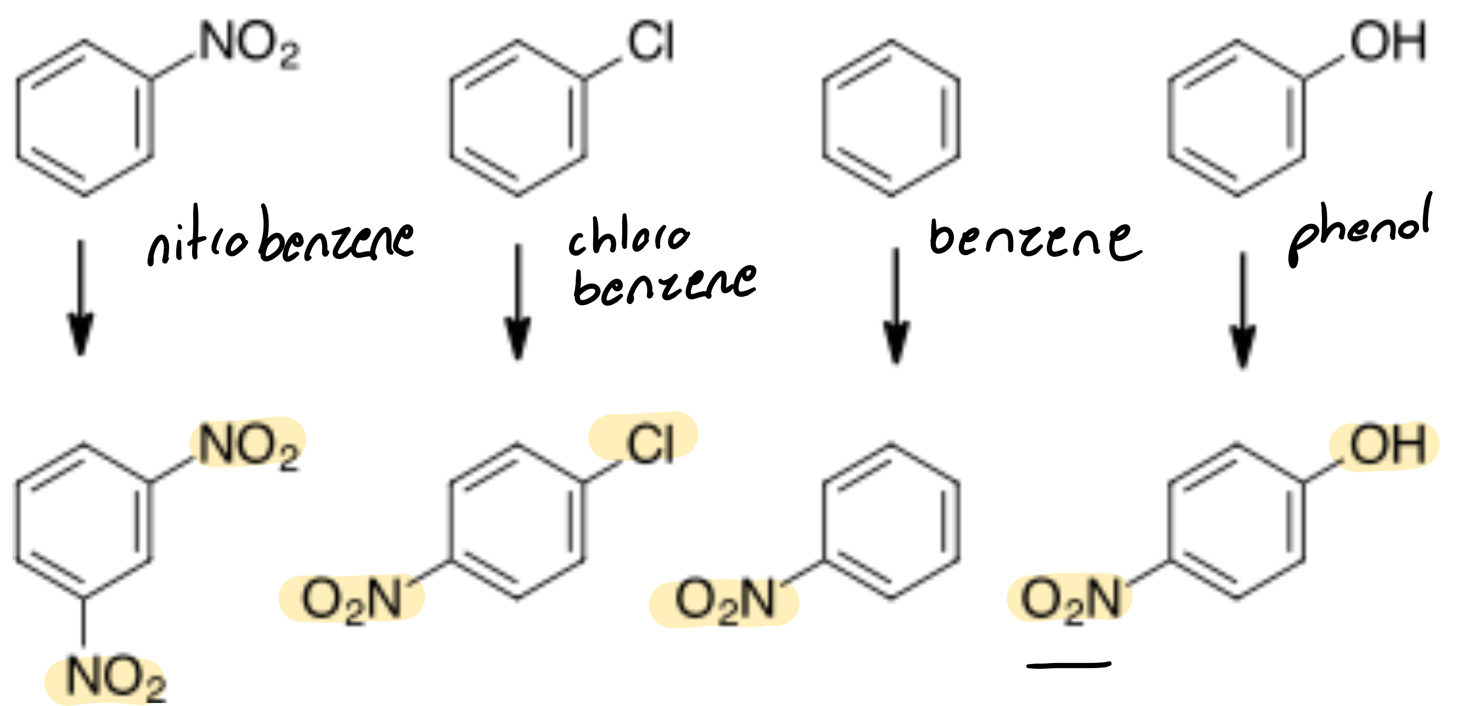
d. 

e. 

intramolecular Friedel-Crafts reactions.



Nitration of Substituted Benzenes



	NO2 / NO2	Cl / NO2	NO2	OH / NO2
Relative rates	6×10^{-8}	0.033	1	1000

Substituents modify the electron density in the benzene ring, and this affects the course of electrophilic aromatic substitution.

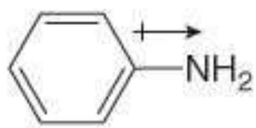
Substituted Benzenes

Inductive effects (through σ bonds):

single

- Atoms more electronegative than carbon—including N, O, and X—pull electron density away from carbon and thus exhibit an electron-withdrawing inductive effect.
- Polarizable alkyl groups donate electron density, and thus exhibit an electron-donating inductive effect.

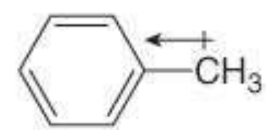
Electron-withdrawing inductive effect



-I

- N is **more electronegative** than C.
- N inductively withdraws electron density.

Electron-donating inductive effect



+I

- Alkyl groups are **polarizable,** making them electron-donating groups.

- I	$-NH_3^+$, $-CF_3$	$-NH_2$, $-NHR$, $-NR_2$	-OH, -OR	-F, -Cl, -Br, -I	-CHO, -COR, -COOH, -COOR	-CN	SO_3H, SO_2R	$-NO_2$
+ I	$-CH_3$, -Alkyl, $-SiR_3$							

primary secondary

inductive (σ) sigma < −I, +I

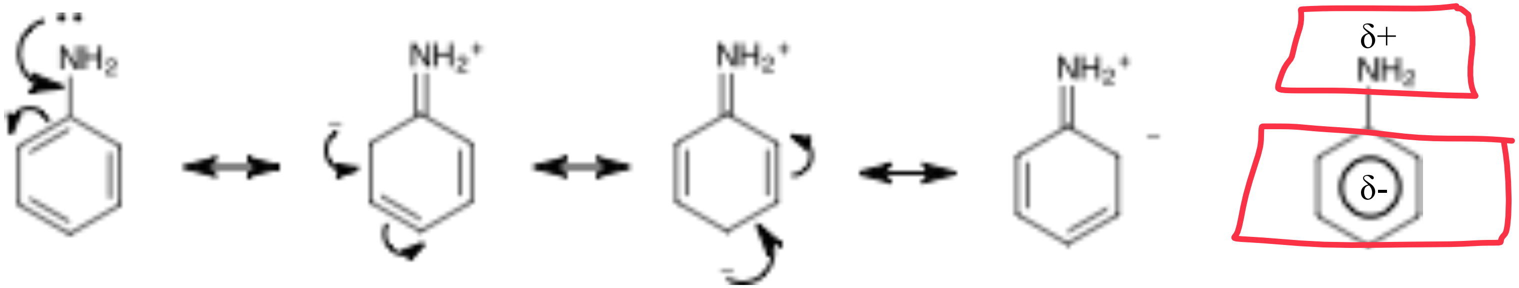
resonance (π) < −R, +R

Substituted Benzenes

Resonance effects (through *double* π bonds) are only observed with substituents containing lone pairs or π bonds.

- Substituents containing lone pairs are electron donating **(+ R)**

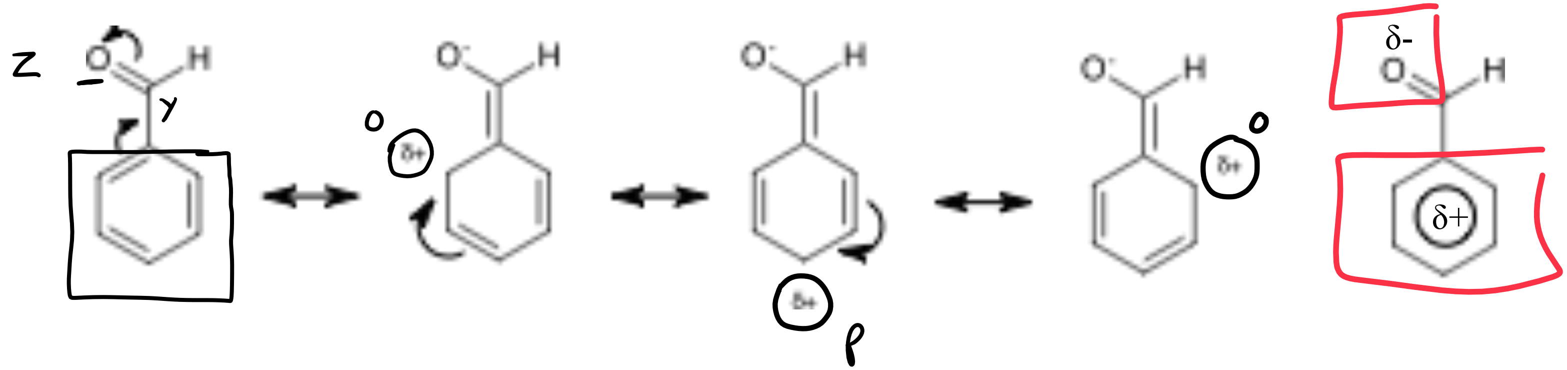
  - ortho/para director
  - activate the ring



($-CHO$, $-COOH$, $-NO_2$, $-SO_2R$)

- Substituents –Y=Z (C_6H_5-Y=Z), where Z is more electronegative than Y are electron accepting **(- R)** (electron withdrawing)

  - meta directing
  - deactivate the ring



Substituted Benzenes: Activation

		+ R			- R			
		+R > -I		-I >+R				
- I	$-NR_3^+$ CF_3	$-NH_2$, -NHR $-NR_2$	-OH -OR	-F -Cl -Br -I	-CHO -COR -COOH -COOR	CN	SO_3H SO_2R	$-NO_2$
+ I	$-CH_3$ -Alkyl $-SiR_3$							

حالوجينات
-I > +R
+R > -I
activate
deactivate
ortho/para director

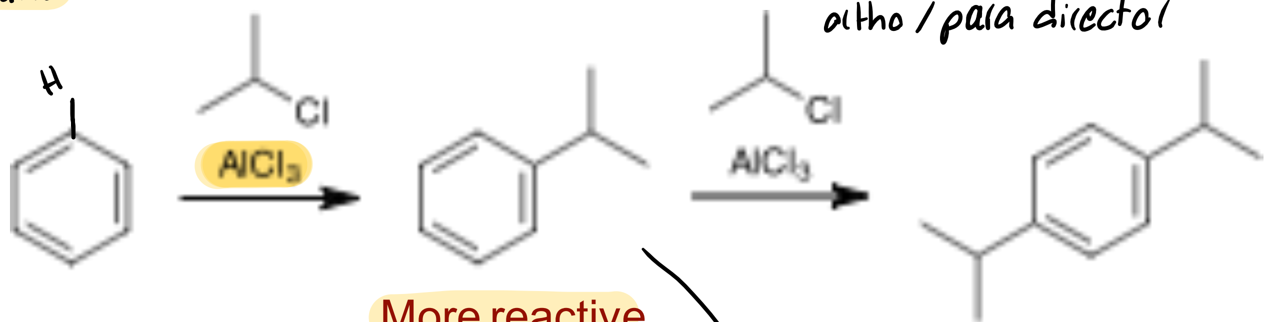
- Substituents that increase the electron density on the ring activate the ring towards electrophiles. Substituents that decrease the electron density on the ring deactivate the ring towards electrophiles.
- To predict whether a substituted benzene is more or less electron rich than benzene itself, we must consider the net balance of both the inductive and resonance effects.

Substituted Benzenes: Activation

- Friedal crafts alkylation

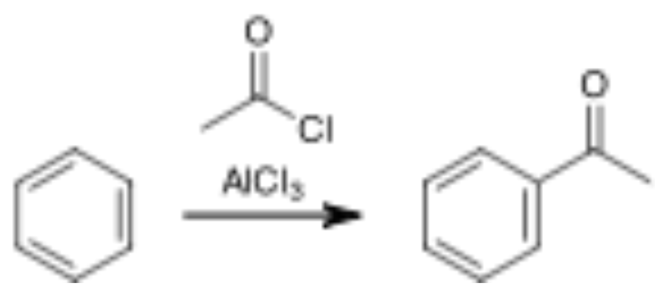
Alkyl group ortho / para director

رح نستبدل ذرة H بـ tert-butyl group



More reactive than benzene

tert-butyl benzene

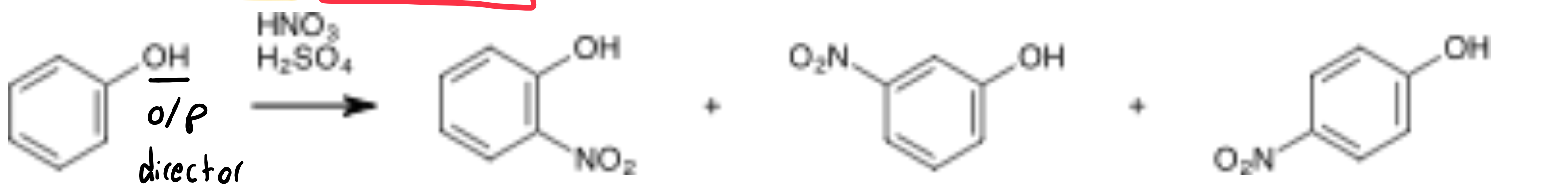


Less reactive than benzene

Substituted Benzenes: Orientation

ميل / توجيه

+R > -I (-OR, -NR2): activating, o- p- directing

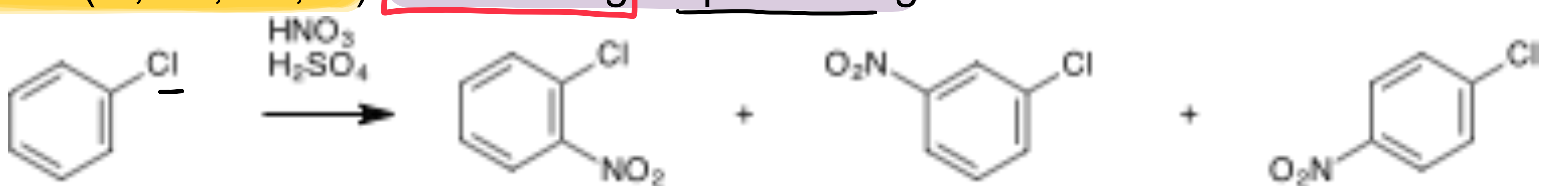


o/p director

strong activator

30% | traces | 70% para

-I > +R (-F, -Cl, -Br, -I): deactivating o- p- directing

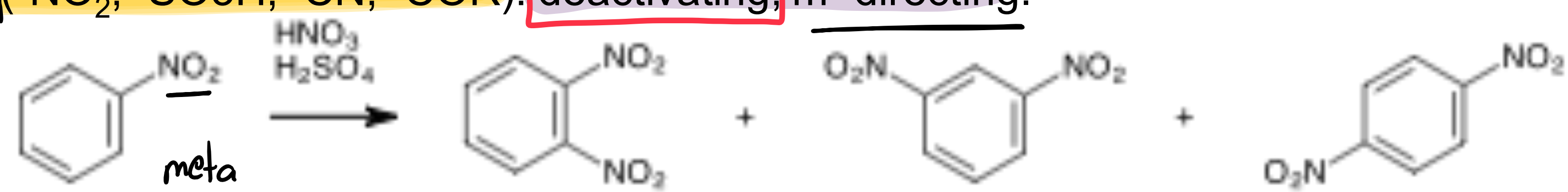


هالوجينات

o/p director

35% | traces | 65%

-I, -R (-NO_2, -SO3H, -CN, -COR): deactivating, m- directing.

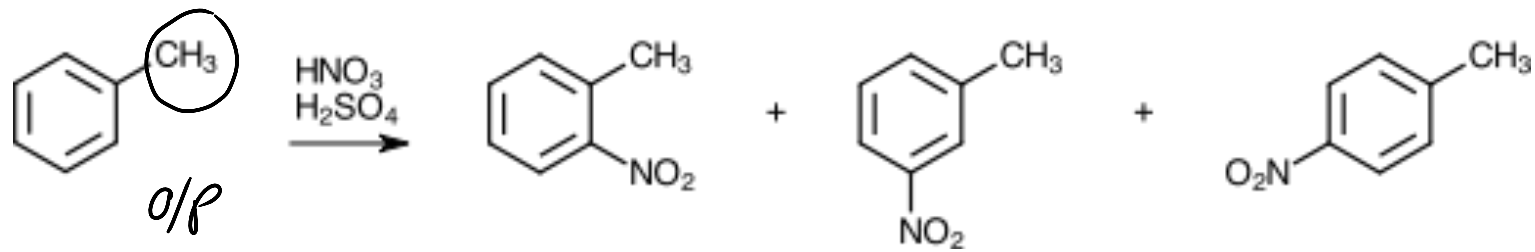


meta director

5% | 90% | 5%

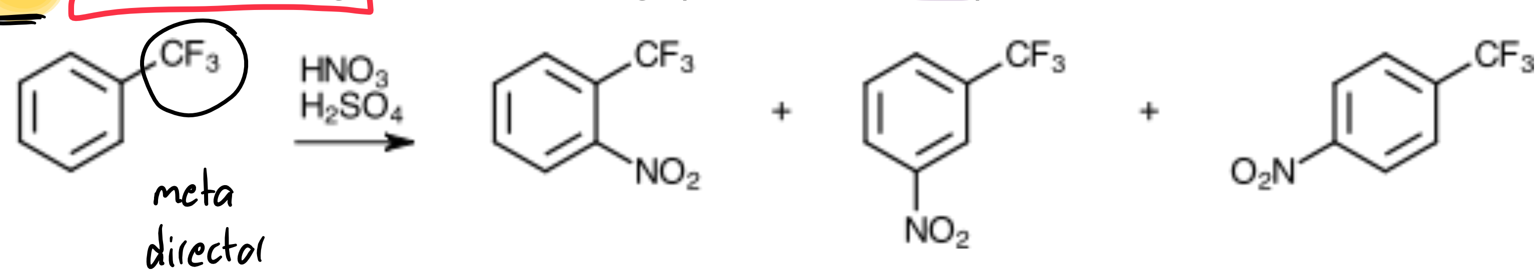
Substituted Benzenes: Orientation

+ I: activating, -o -p directing (same as + R)



58% ortho 5% 37%

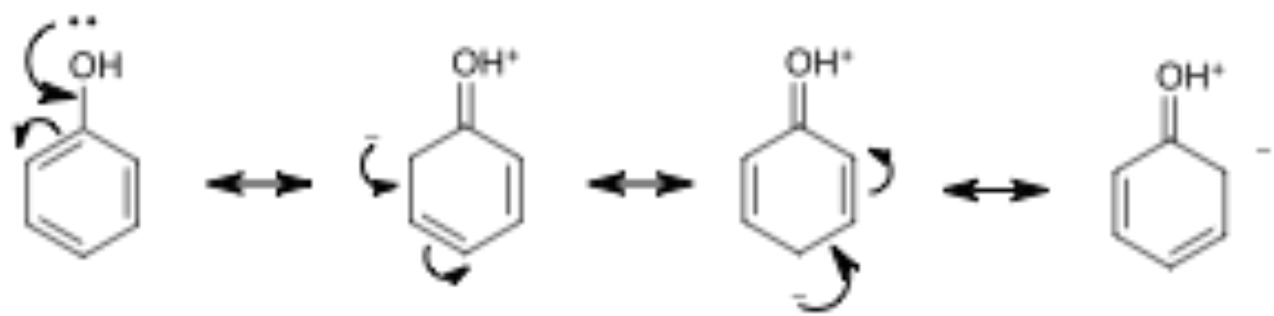
- I: deactivating, -m directing (same as - R)

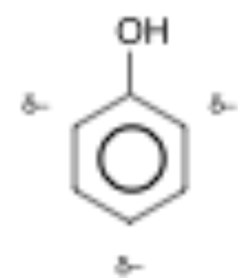


6% 91% 3%

Substituted Benzenes: Orientation

The new group is located either ortho, meta, or para to the existing substituent. The resonance effect of the first substituent determines the position of the second incoming substituent

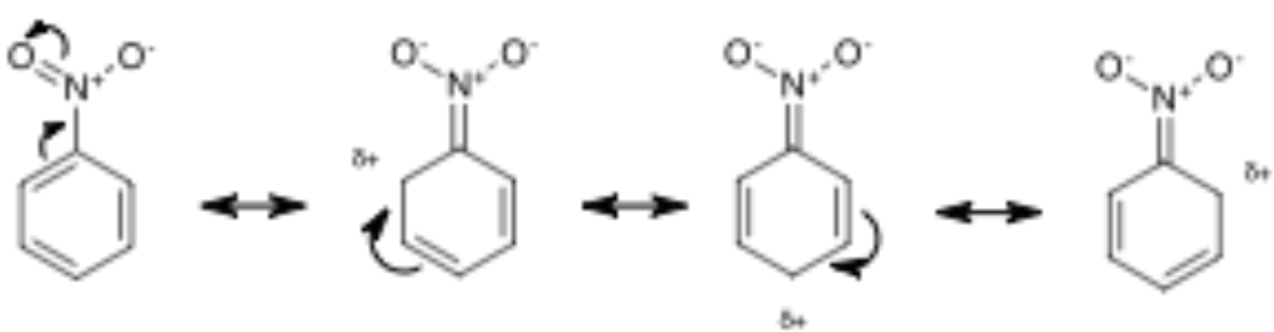


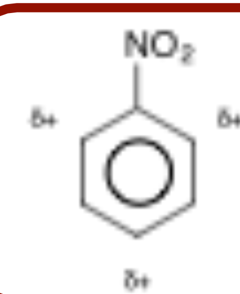


+R

orto

para

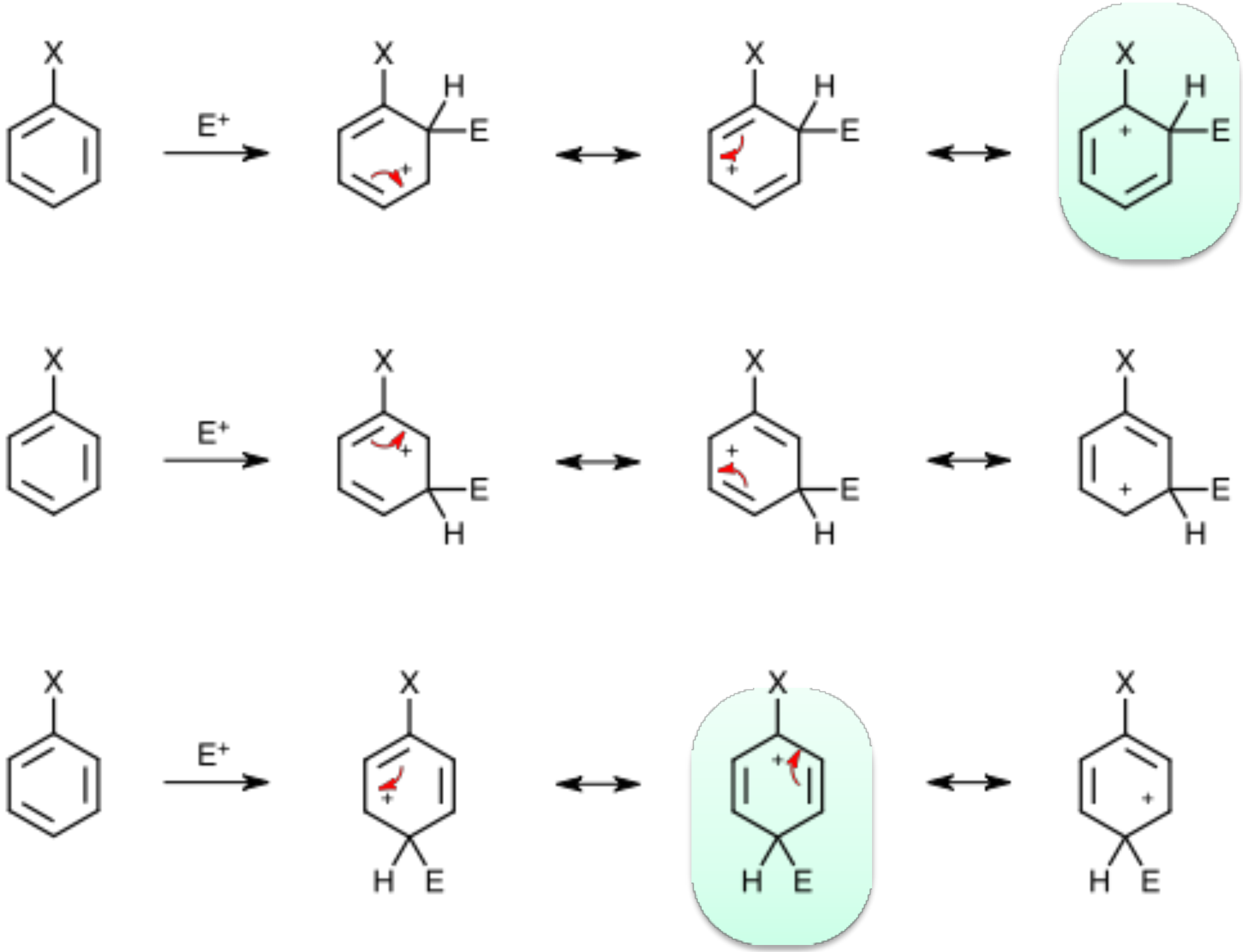




-R

meta

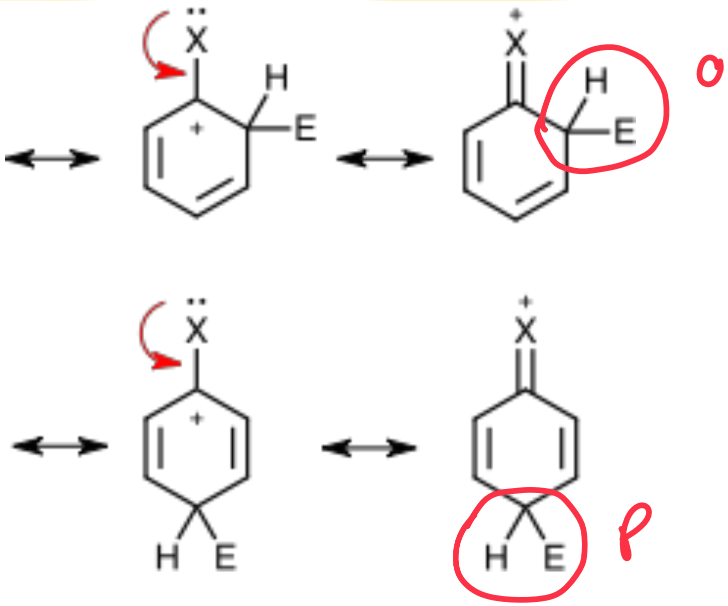
Substituted Benzenes: Orientation



Substituted Benzenes: Orientation

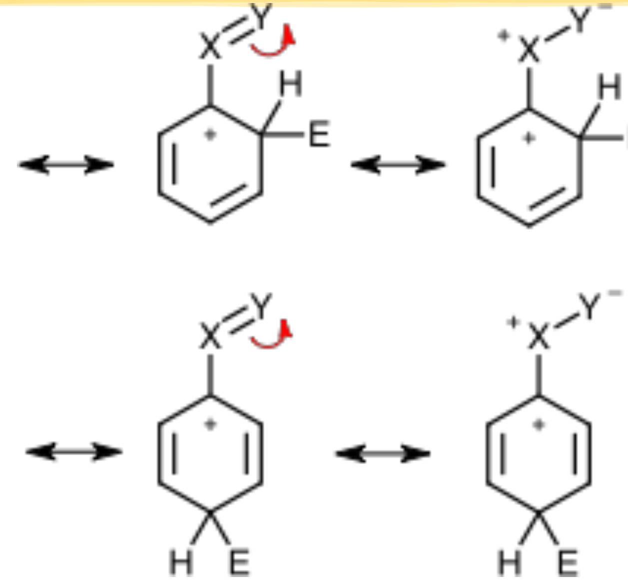
+ R

-o, -p intermediates are resonance stabilised



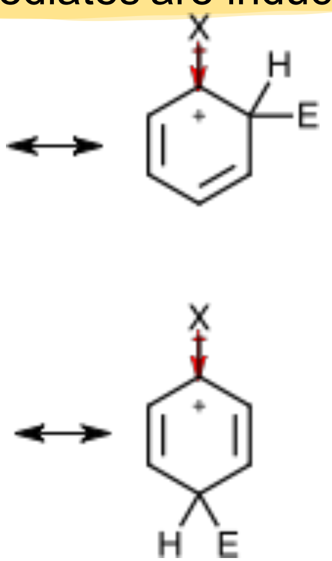
- R

-o, -p intermediates are resonance destabilised



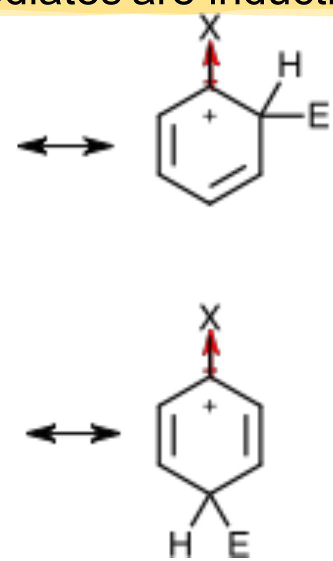
+ I

-o, -p intermediates are inductively stabilised



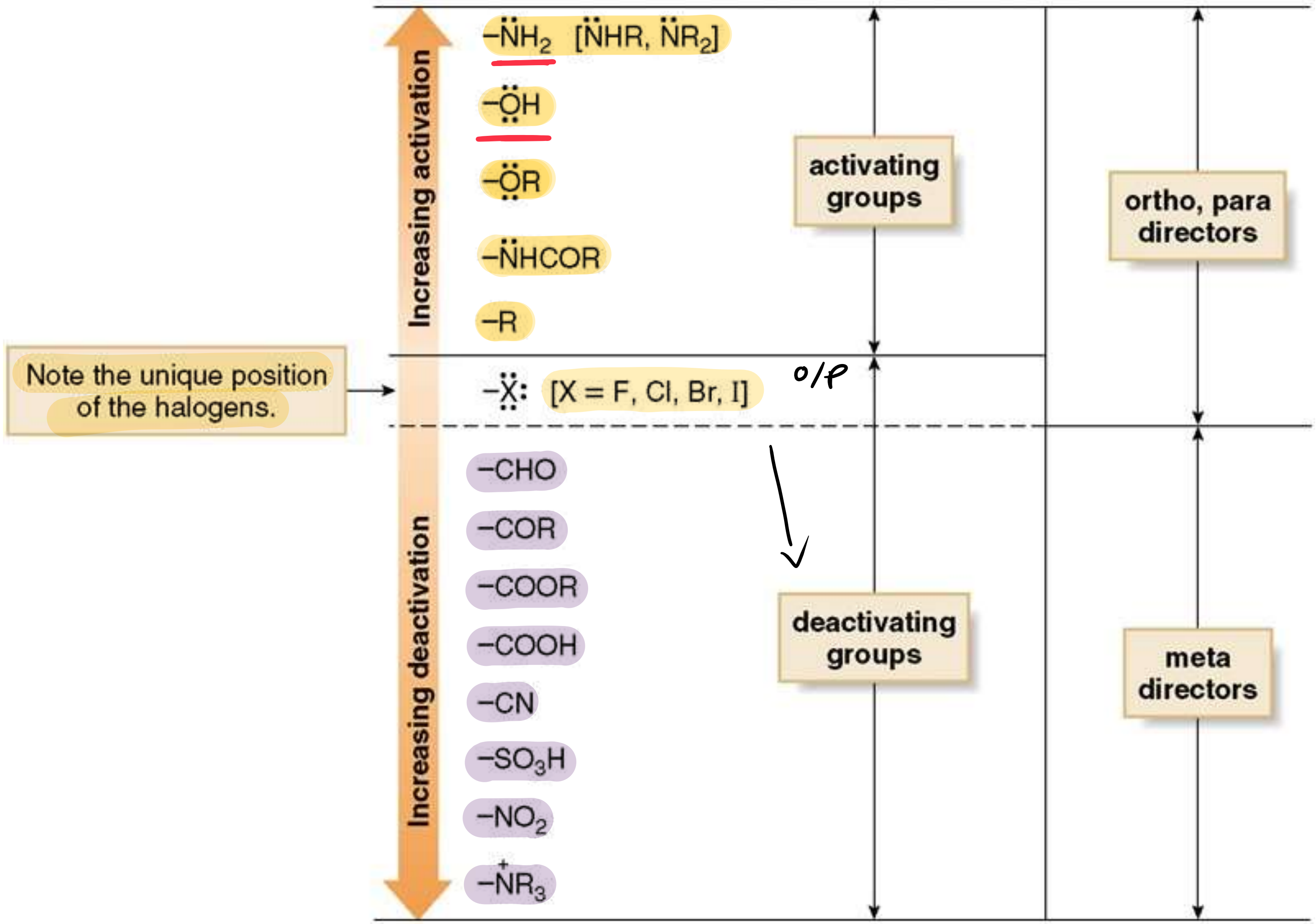
- I

-o, -p intermediates are inductively destabilised



حفظ + تمييز بينهم

Substituent Effects. Summary

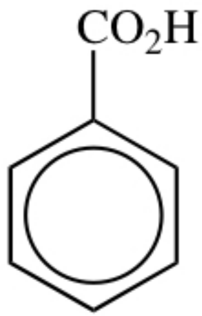


4.23. Which of the following groups is a *meta* director?

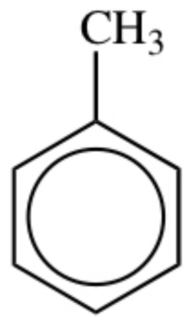
a. $-Cl$ ***b.** $-CHO$ **c.** $-OCH_3$ **d.** $-OH$ **e.** $-Ar$

4.24. In electrophilic aromatic substitution reactions, which of the following molecules are considered to be less reactive than benzene?

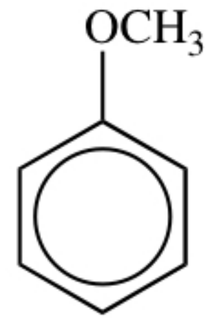
***a.**



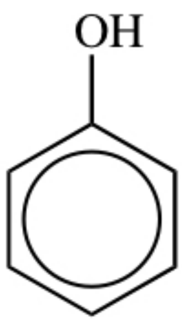
b.



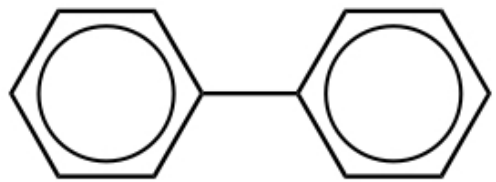
c.



d.



e.



4.25. Which of the following groups are *ortho*, *para*-directing?

a. $—CO_2CH_3$ **b.** $—CONH_2$ **c.** $—SO_3H$

d. $—\overset{+}{N}H(CH_3)_2$ ***e.** $—SCH_3$

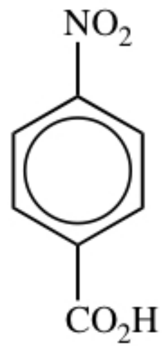
4.26. Among the following groups, which ones are *meta*-directing?

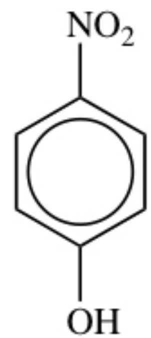
1. $-Cl$ 2. $-NO_2$ 3. $-SO_3H$ 4. $-CH_3$ 5. $-COCH_3$

a. 1 and 4 **b.** 1, 2 and 3 ***c.** 2, 3 and 5
d. 2 and 5 **e.** 1 and 2

4.27. Which of the following molecules is the *most* reactive toward electrophilic aromatic substitution?

a. 

b. 

c. 

***d.** 

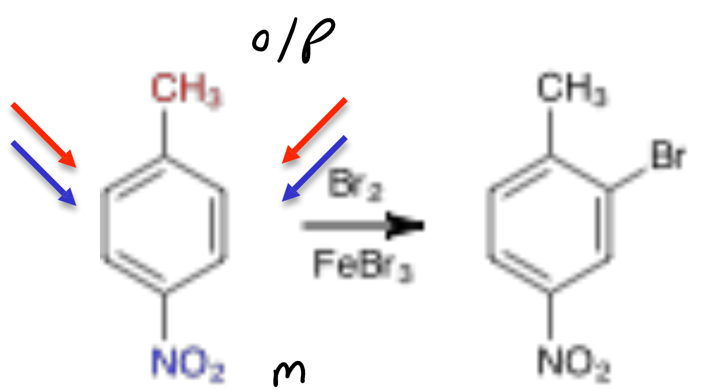
e. 

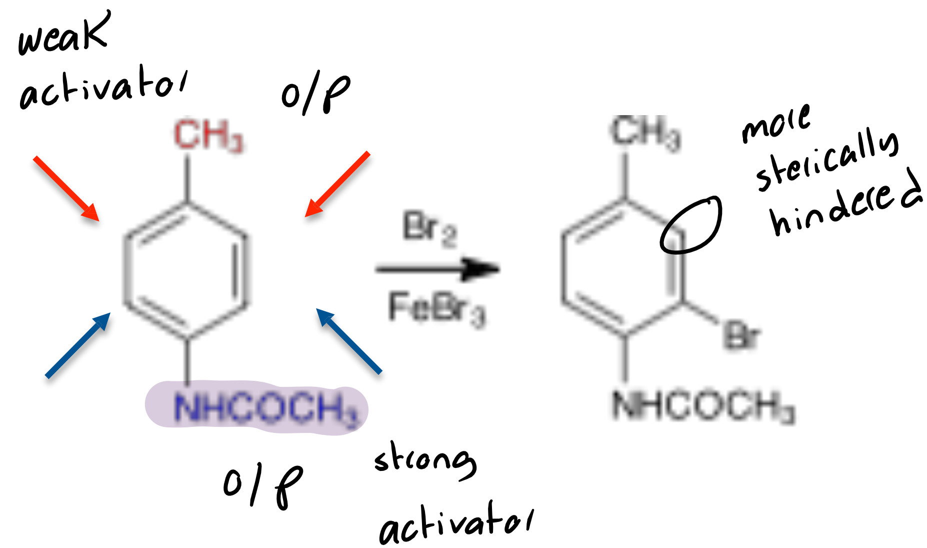
4.28. Which group is both *ortho*, *para*-directing and ring-deactivating?

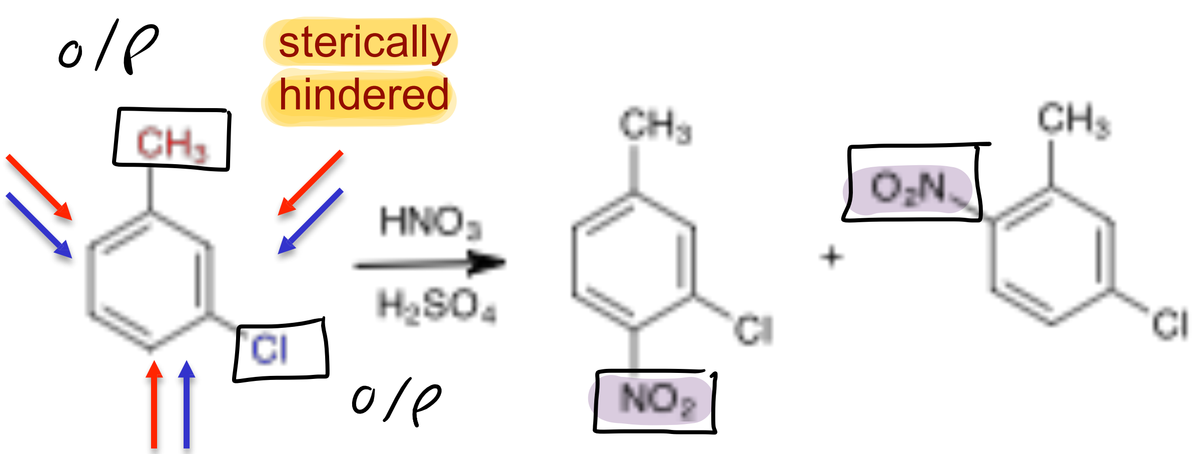
***a.** $-Br$ **b.** $-Ar$ **c.** $-NO_2$ **d.** $-CHO$ **e.** $-OCH_3$

متعدد التفرعات

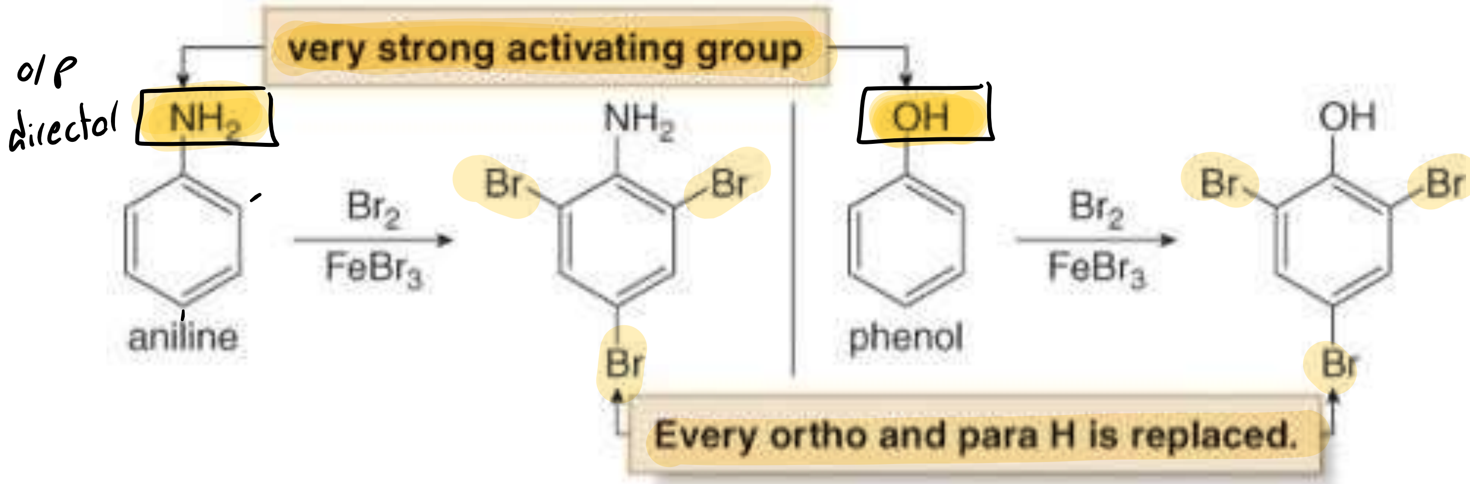
Disubstituted Benzenes

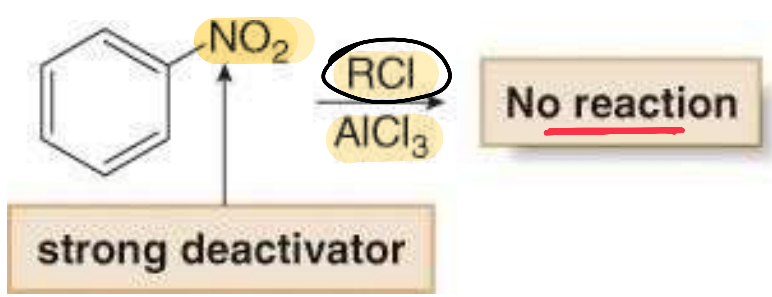




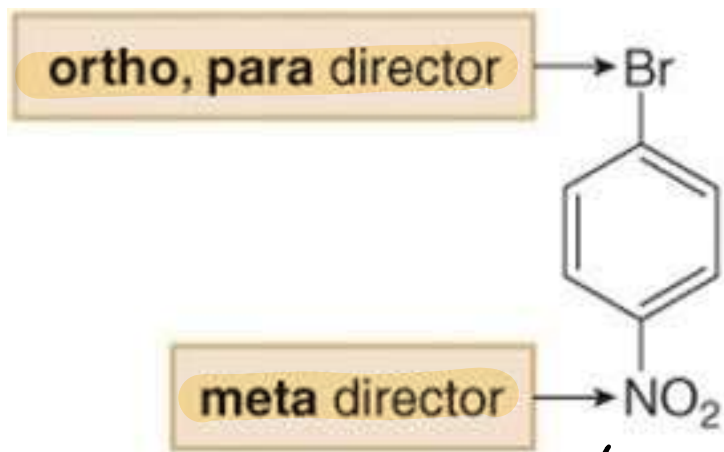


Further Examples





Synthesis of Polysubstituted Benzenes

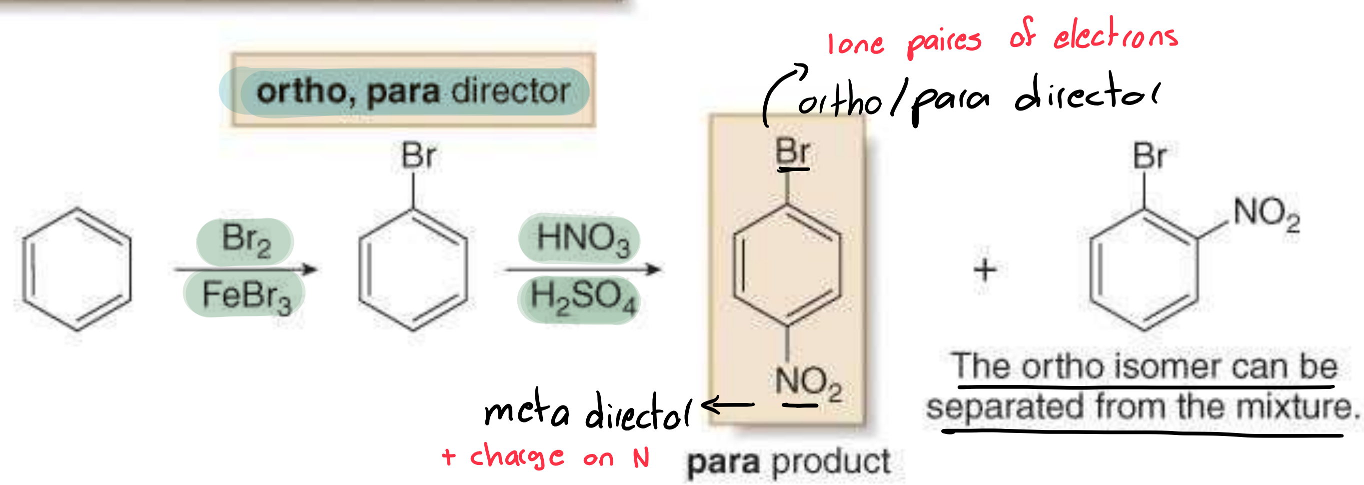


p-bromonitrobenzene

Sunday 23/Nov/2025

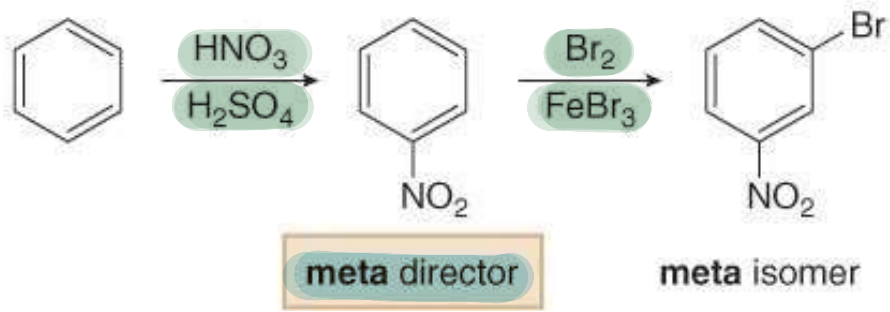
Synthesis of Polysubstituted Benzenes

Pathway [1]: Bromination before nitration



This pathway gives the desired product.

Pathway [2]: Nitration before bromination



This pathway does NOT form the desired product.

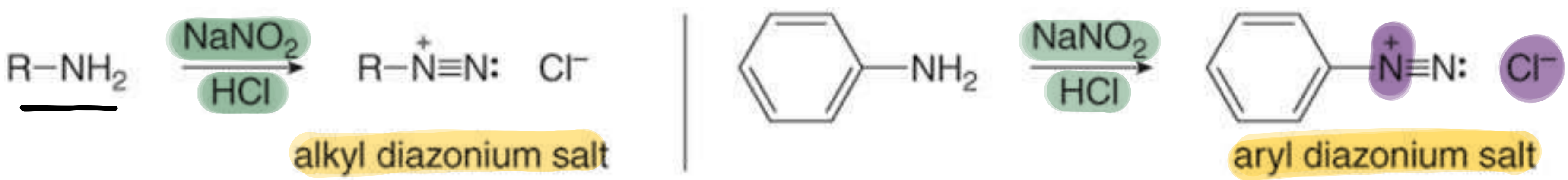
Reaction of Amines with Nitrous Acid

$NaNO_2 + HCl \rightarrow HNO_2 \rightarrow H_2O + NO^+ + Cl^-$

nitrosonium ion

HNO_2 very reactive

NO^+ can react with 1°/2° amines / Not 3°

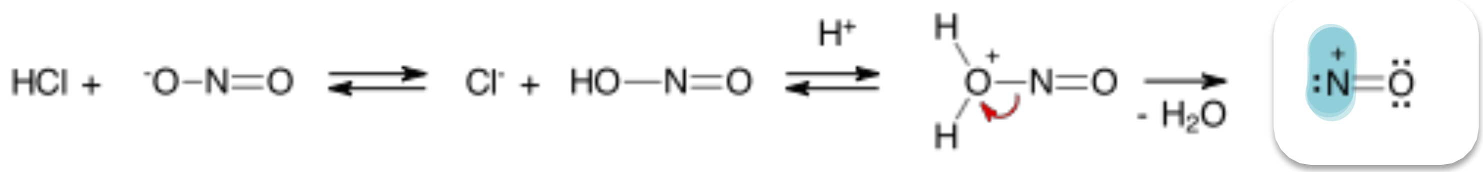


Aniline

Reaction of Amines with Nitrous Acid

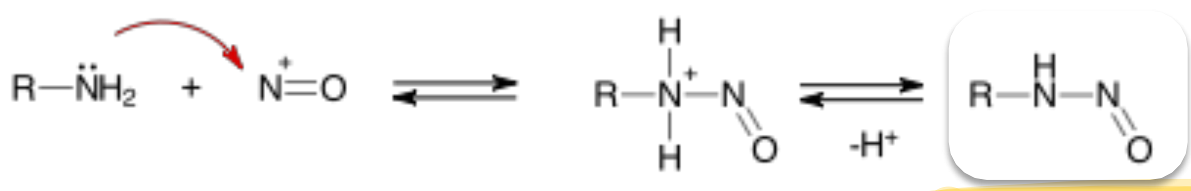
HNO_2

1. generation of the electrophile



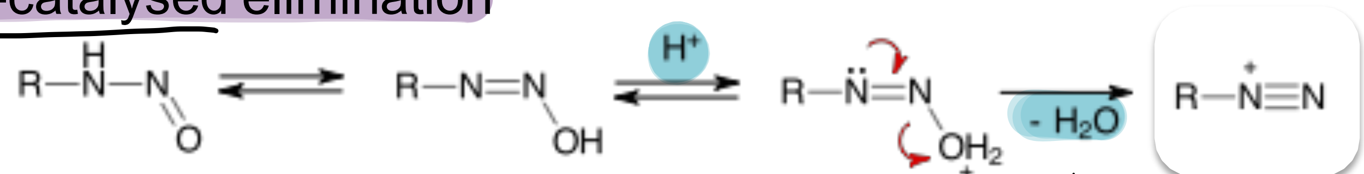
nitrosonium ion

2. nitrosation



N-nitrosamine

3. acid-catalysed elimination

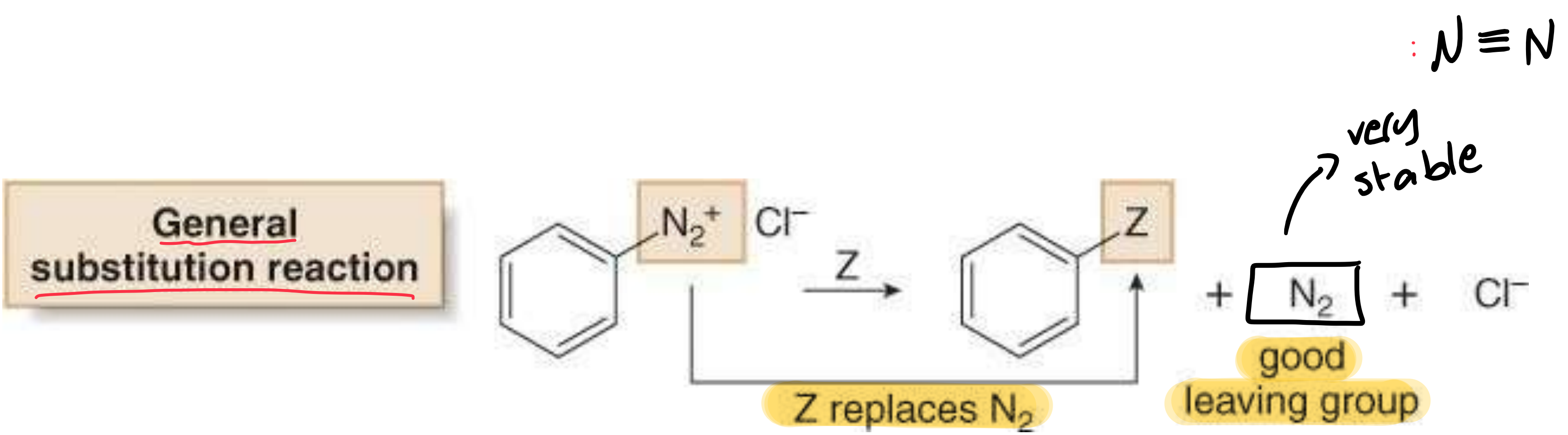


diazonium ion

عملية الحذف

Substitution Reactions of Aryl Diazonium Salts

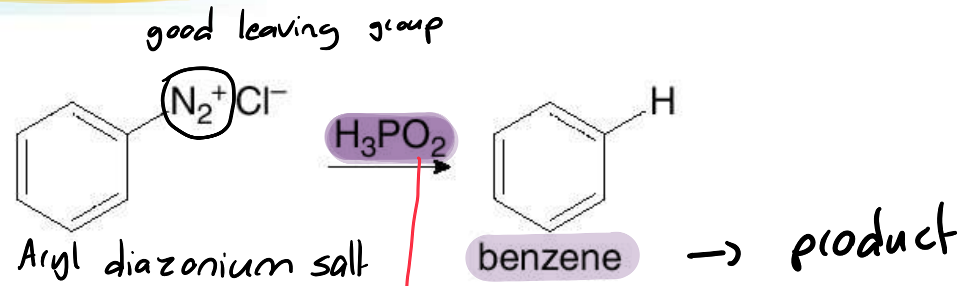
- Aryl diazonium salts react with a variety of reagents to form products in which a nucleophile Z replaces N_2, a very good leaving group.
- The mechanism of these reactions varies with the identity of Z.



https://youtu.be/kFNMB3rY9Ls?si=7ce0zqe0CZPdB20E

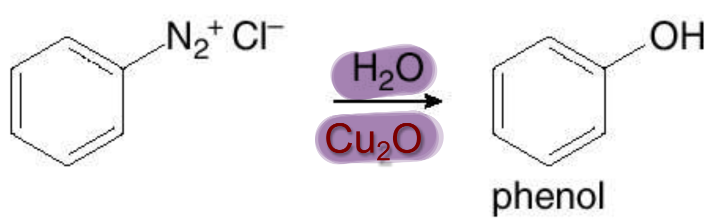
Substitution Reactions of Aryl Diazonium

Substitution by H—Synthesis of benzene



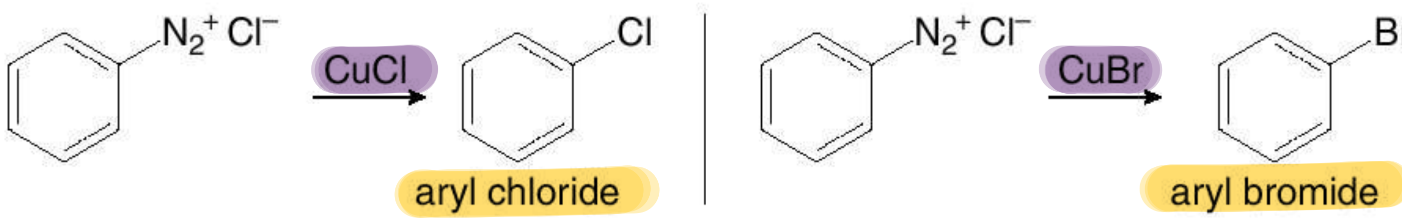
A diazonium salt reacts with hypophosphorus acid to form benzene. This reaction is useful in synthesizing compounds that have substitution patterns that are not available by other means.

Substitution by OH—Synthesis of phenols



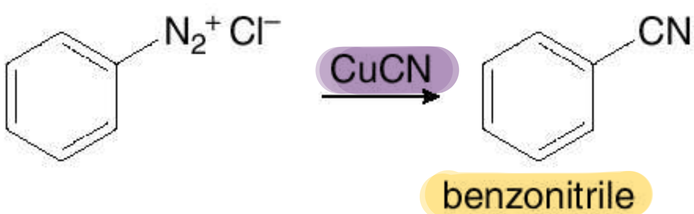
Substitution Reactions of Aryl Diazonium

Substitution by Cl or Br—Synthesis of aryl chlorides and bromides



This is called the Sandmeyer reaction. It provides an alternative to direct chlorination and bromination of the aromatic ring using Cl_2 or Br_2 and a Lewis acid catalyst.

Substitution by CN—Synthesis of benzonitriles

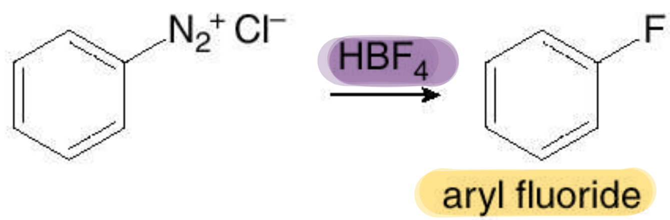


CN

Since the cyano group can be converted into a variety of other functional groups, this reaction provides easy access to a wide variety of benzene derivatives.

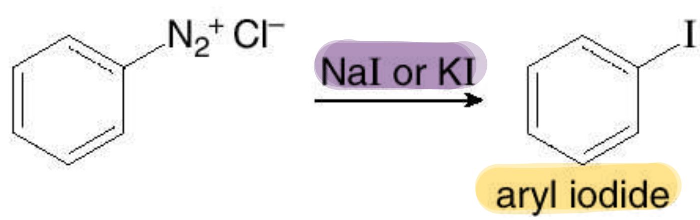
Substitution Reactions of Aryl Diazonium Salts

Substitution by F—Synthesis of aryl fluorides



This is a useful reaction because aryl fluorides cannot be produced by direct fluorination with F_2 and a Lewis acid catalyst.

Substitution by I—Synthesis of aryl iodides



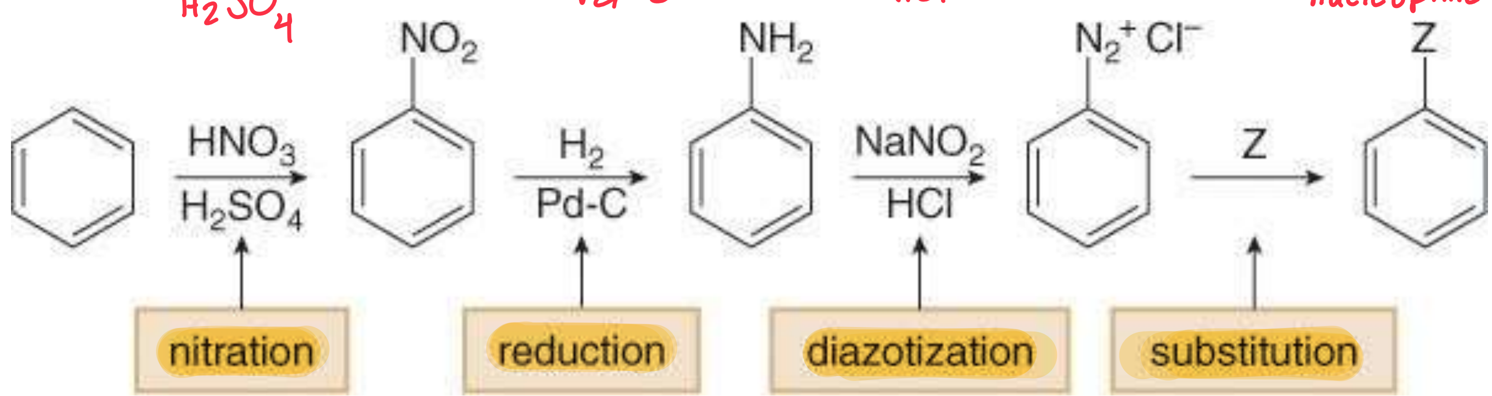
This is a useful reaction because aryl iodides cannot be produced by direct iodination with I_2 and a Lewis acid catalyst.

Substitution Reactions of Aryl Diazonium Salts

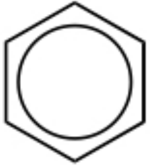
Diazonium salts provide easy access to many different benzene derivatives. Keep in mind the following four-step sequence, because it will be used to synthesize many substituted benzenes.

nitration reduction diazotization substitution

benzene $\xrightarrow[H_2SO_4]{HNO_3}$ nitrobenzene $\xrightarrow[Pd-C]{H_2}$ Aniline $\xrightarrow[HCl]{NaNO_2}$ diazonium salt $\xrightarrow[\text{nucleophile}]{Z}$ products



4.35. What is the name of the major product from the following sequence of reactions?

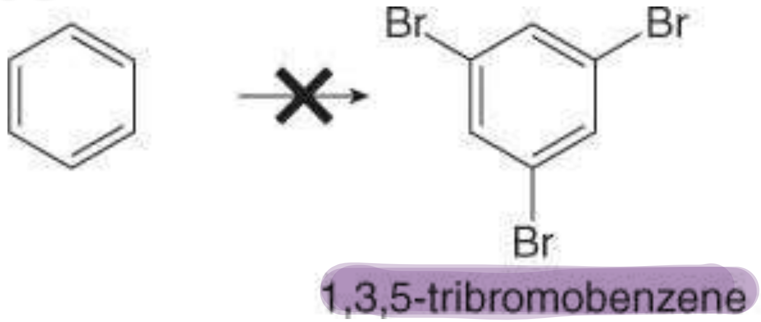


1) SO_3, H_2SO_4
2) NaOH, 200ºC

?

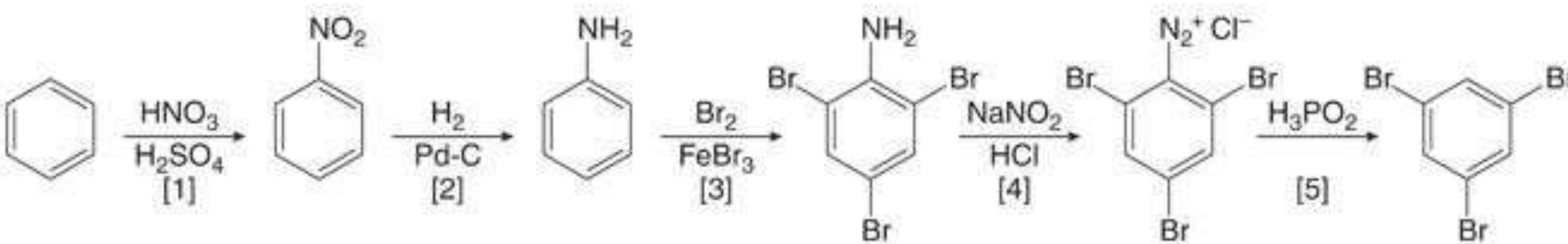
a. aniline **b.** anisole **c.** benzoic acid
***d.** phenol **e.** toluene

Substitution Reactions of Aryl Diazonium Salts

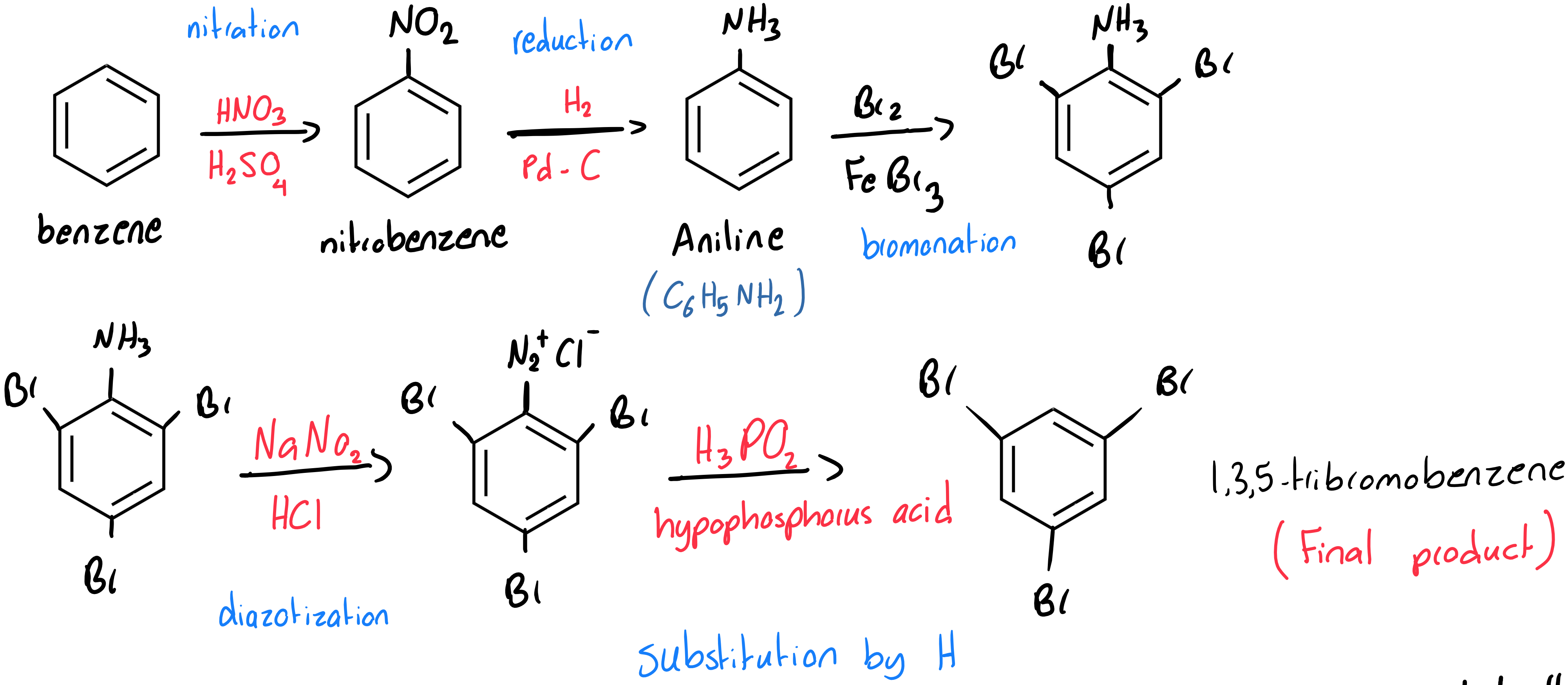


The Br atoms are ortho, para directors located meta to each other.

Aniline



- Nitration followed by reduction forms aniline ($C_6H_5NH_2$) from benzene (Steps [1] and [2]).
- Bromination of aniline yields the tribromo derivative in Step [3].
- The NH_2 group is removed by a two-step process: diazotization with $NaNO_2$ and HCl (Step [4]), followed by substitution of the diazonium ion by H with H_3PO_2.



- التسلسل -

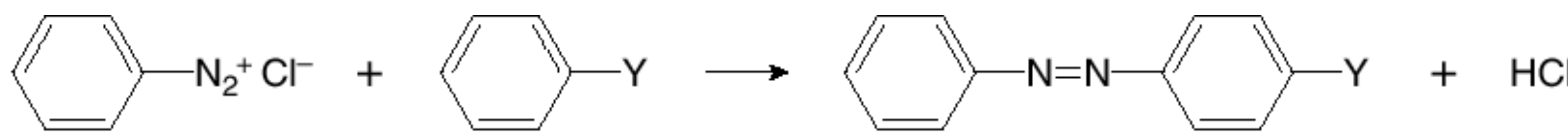
nitration → reduction → bromonation → diazotization → substitution

Coupling Reactions of Aryl Diazonium Salts

- When a diazonium salt is treated with an aromatic compound activated by a strong electron-donor group, a substitution reaction takes place giving an azo compound.

nucleophilic

Azo coupling

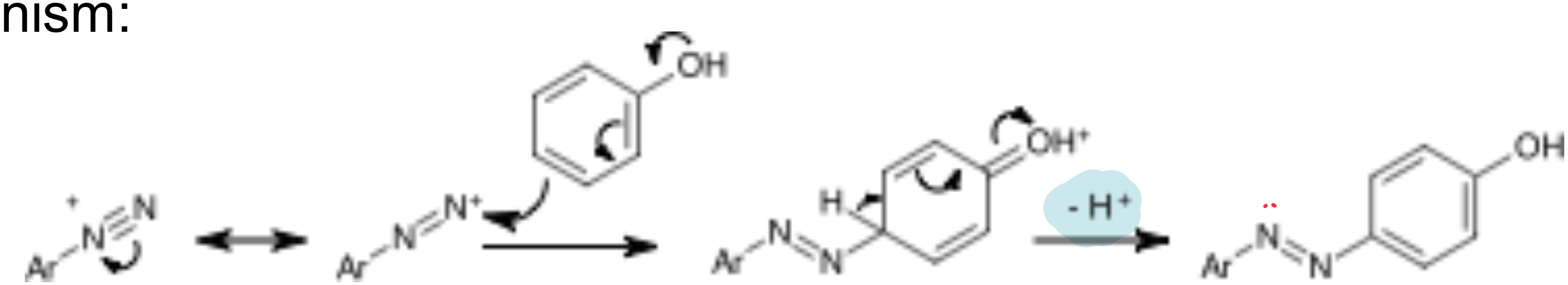


weak electrophile

Y = NH_2, NHR, NR_2, OH (a strong electron-donor group)

azo compound

Mechanism:



trans isomer

The para position is preferred for steric reasons

Azo Dyes

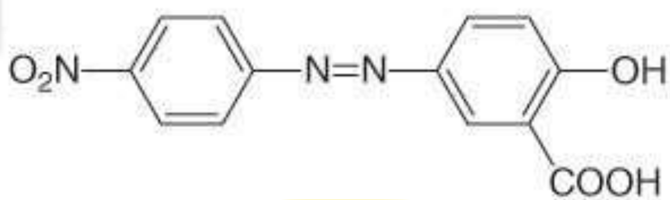
- Azo compounds are highly conjugated, rendering them colored. Many of these compounds are synthetic dyes. Butter yellow was once used to color margarine.

Example

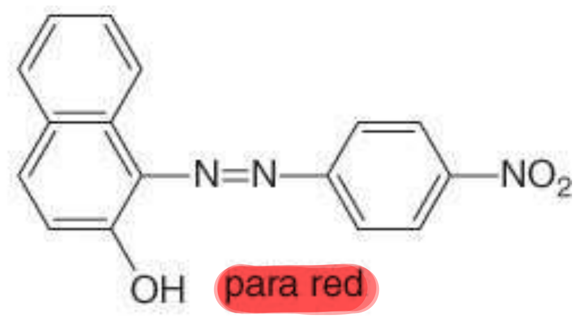
diazonium salt   secondary amine

a yellow azo dye
"butter yellow"

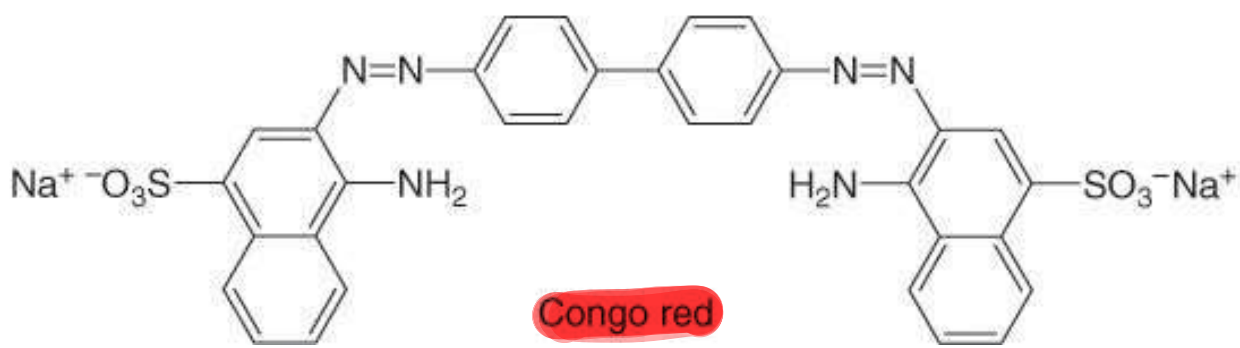
Three azo dyes



alizarine yellow R



para red



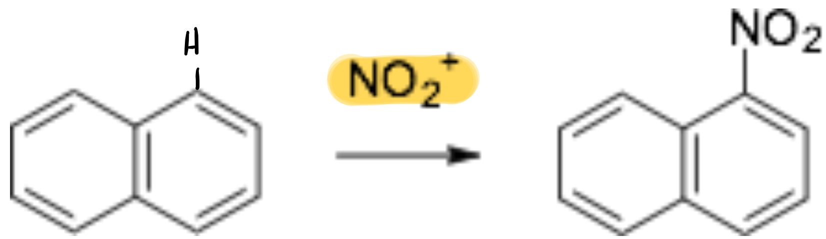
Congo red

متعددة حلقات

S_EAr in Polyciclic Aromatic Compounds

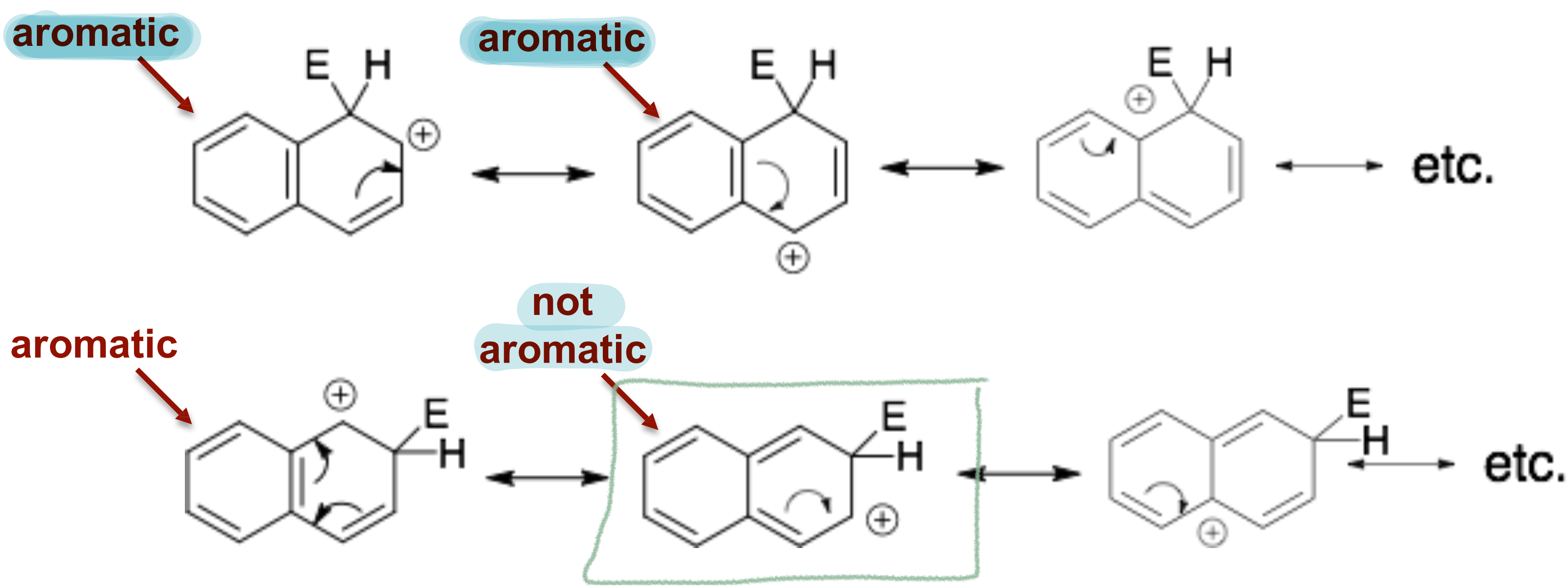
selectrophilic electrophilic aromatic compounds (substitution)

محبة للأنتقائية

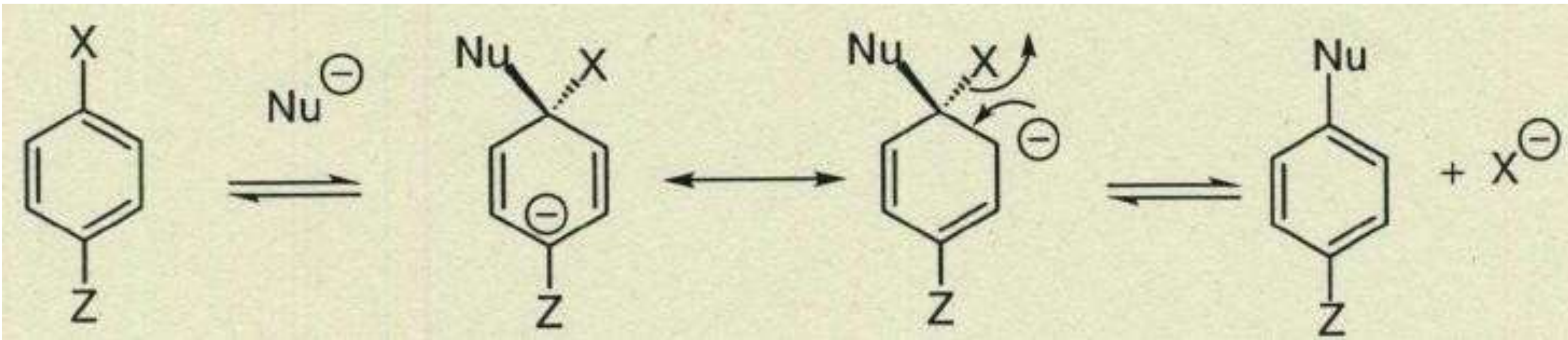


naphthalene

→ ليش هذا الموقع بالذات ؟! resonance structures keep both rings aromatic

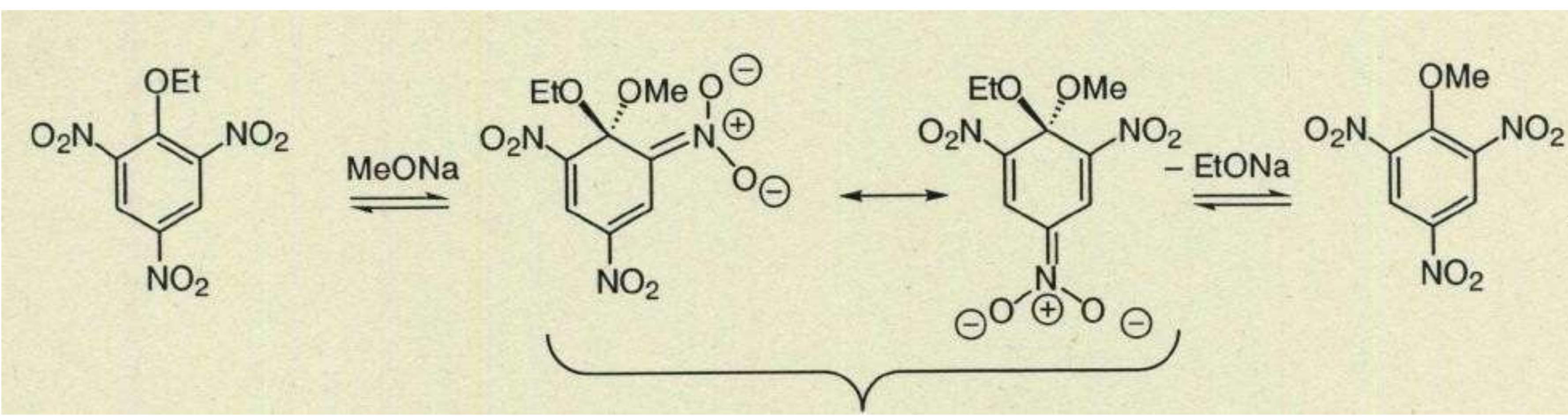


Nucleophilic Aromatic Substitutions, S_NAr



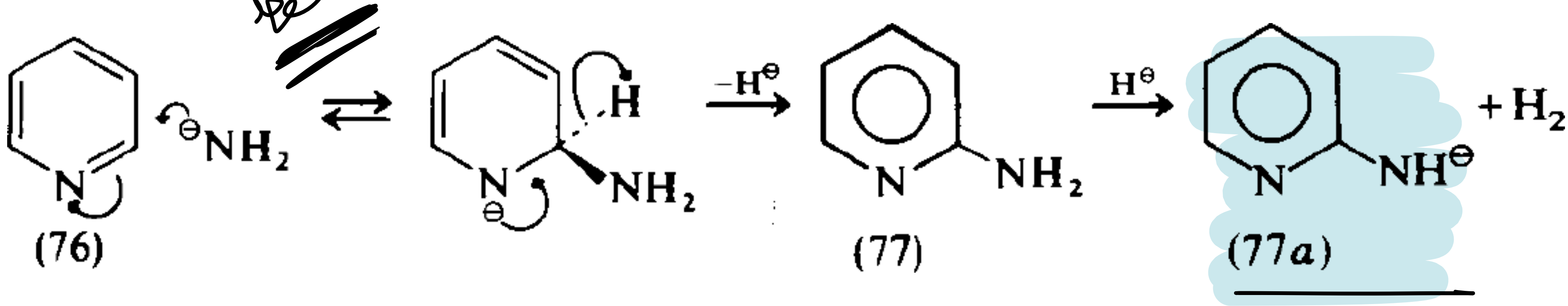
Z = Electron Accepting Substituent (sigma or π: NO_2, CN, N_2^+, SO_2R)
X = Leaving Group

Example

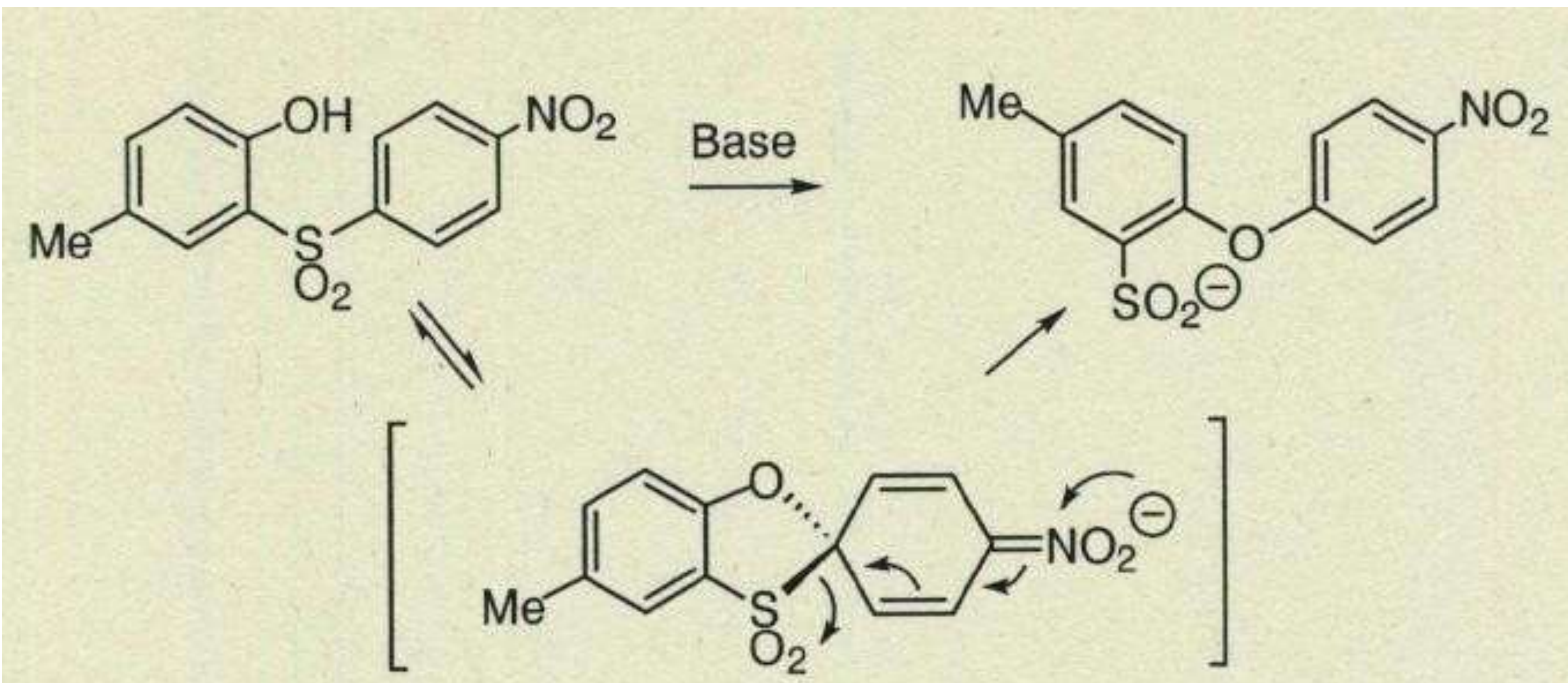


Examples of S_NAr

1)

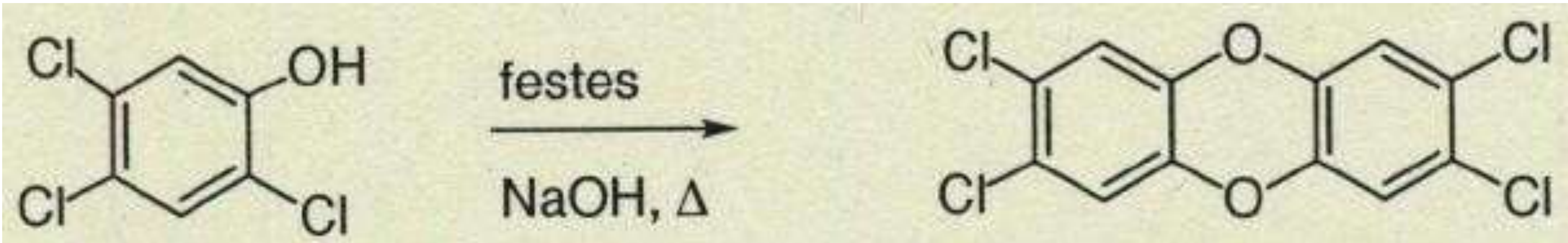


2)

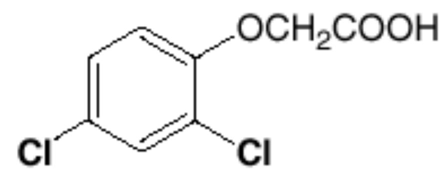


Examples of S_NAr

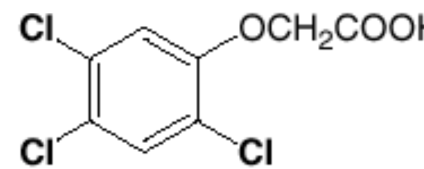
3)



Herbicides were used extensively during the Vietnam War to defoliate dense jungle areas. The concentration of certain herbicide by-products in the soil remains high today.

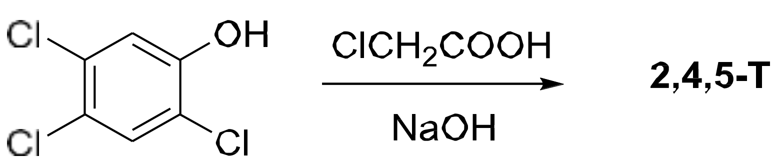


2,4-D
2,4-dichlorophenoxy-acetic acid
herbicide



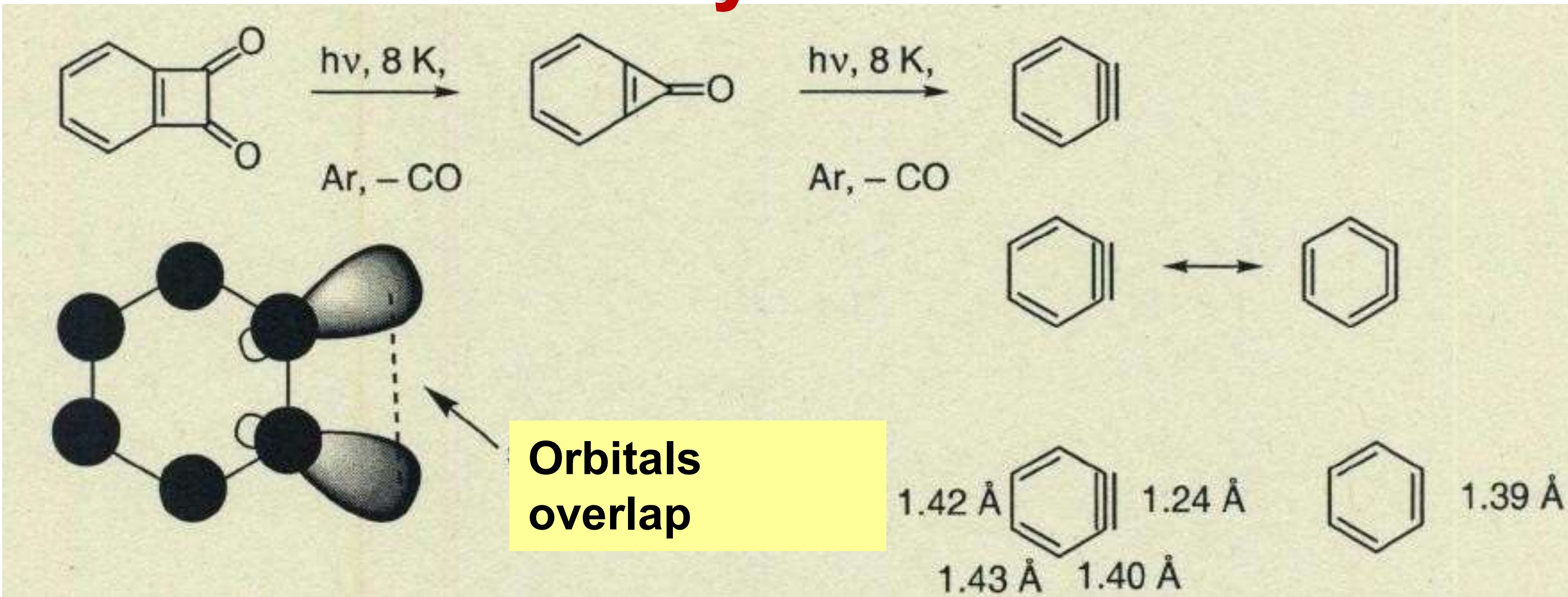
2,4,5-T
2,4,5-trichlorophenoxy-acetic acid
herbicide

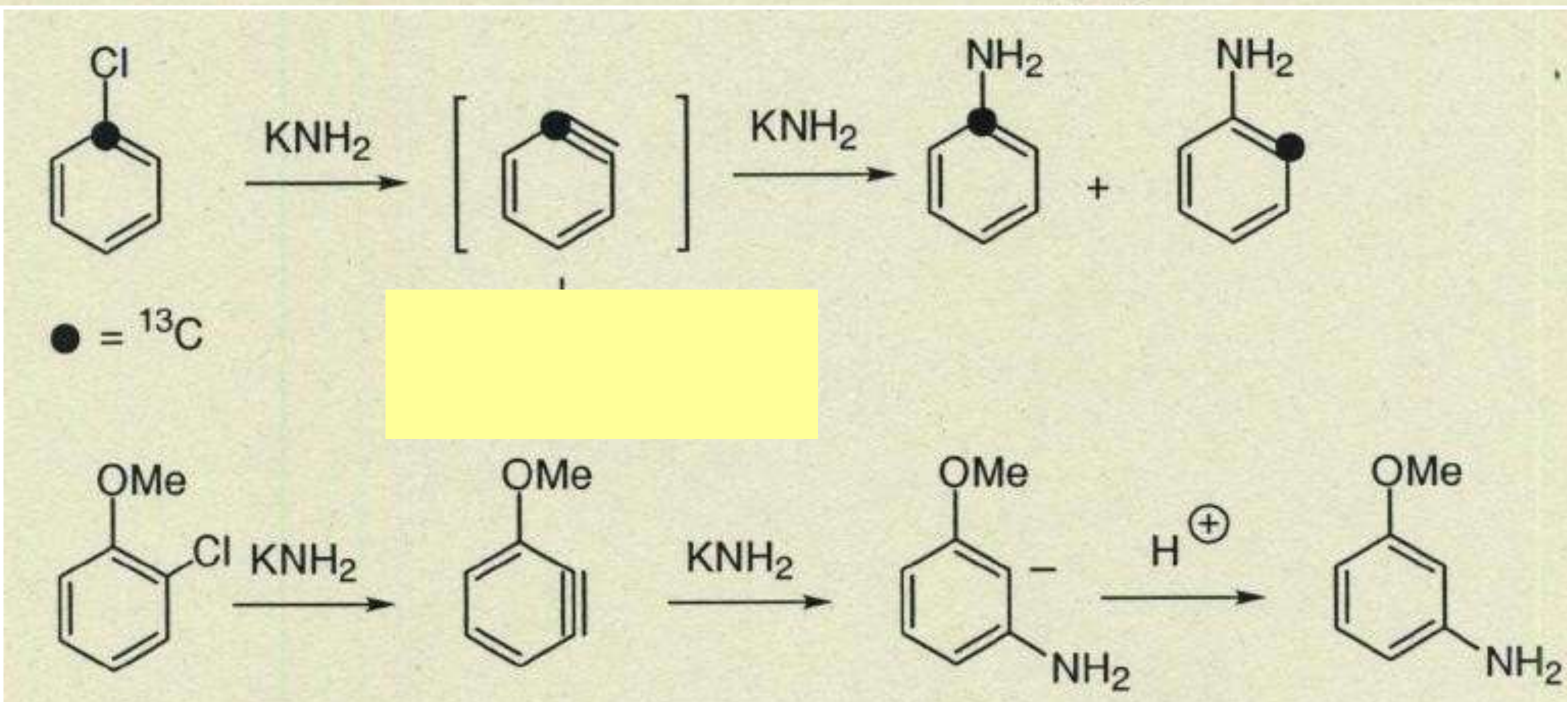
the active components in **Agent Orange**, a defoliant used in the Vietnam War



لذكر

Benzyne

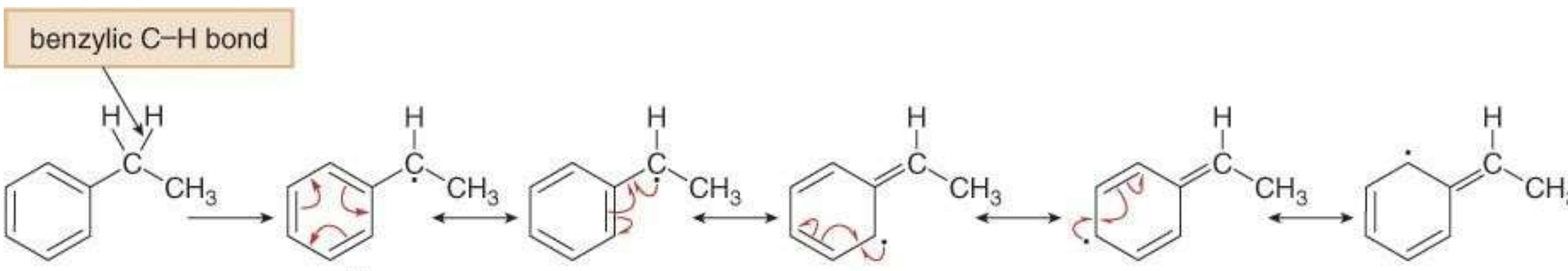




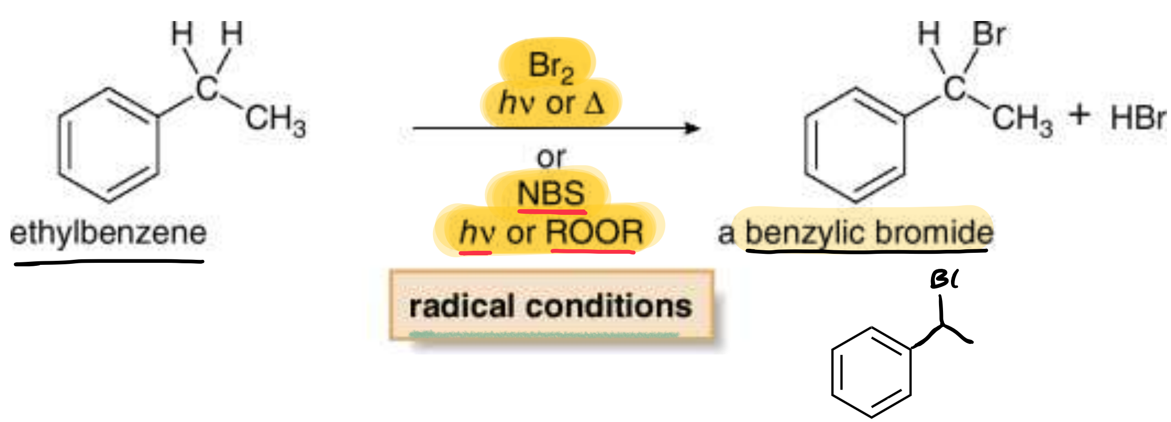
Side Chain Reactivity: Radical Halogenation

Benzylic C—H bonds are weaker than most other sp^3 hybridized C—H bonds, because homolysis forms a resonance-stabilized benzylic radical.

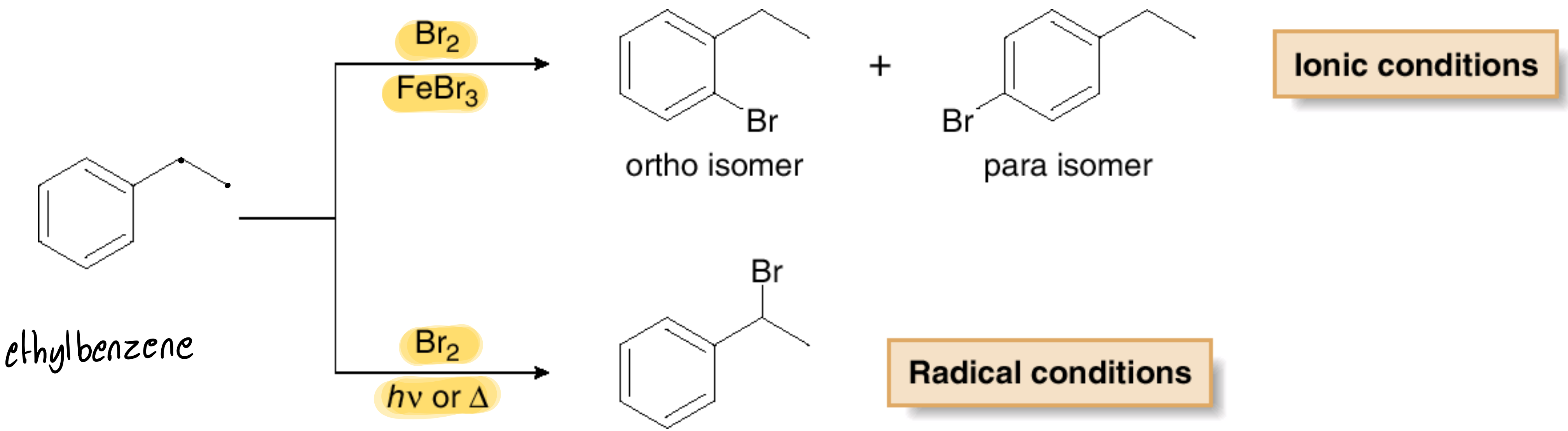
(تحلل متجانس)



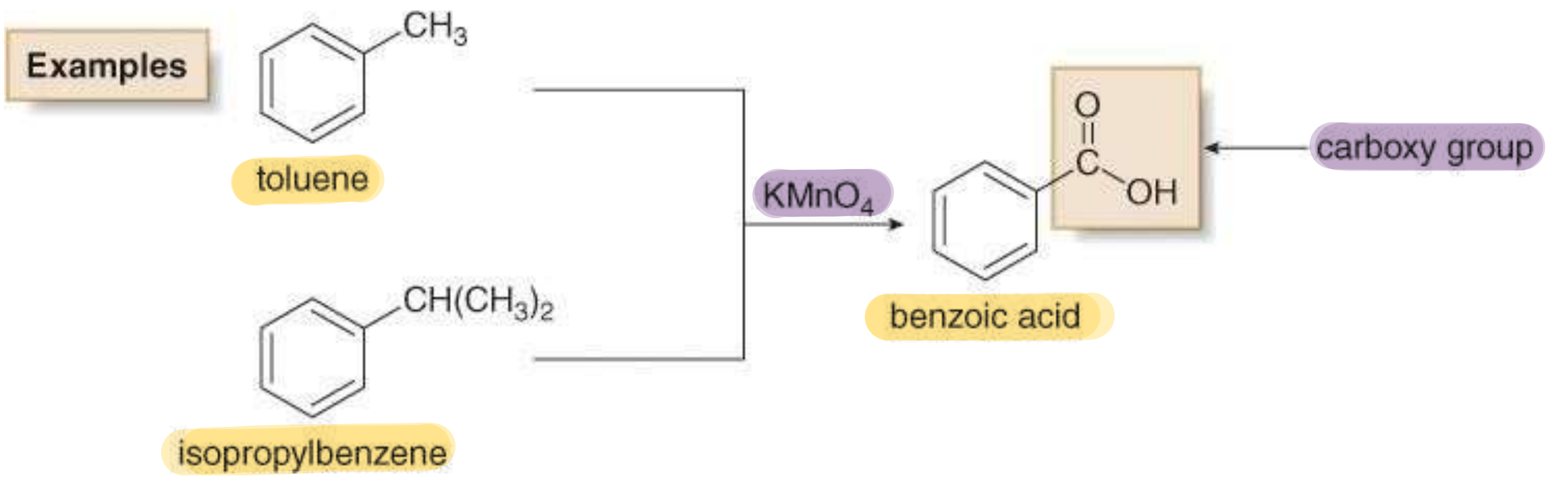
five resonance structures for the benzylic radical

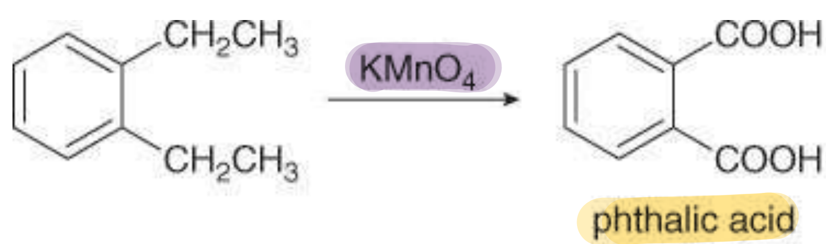


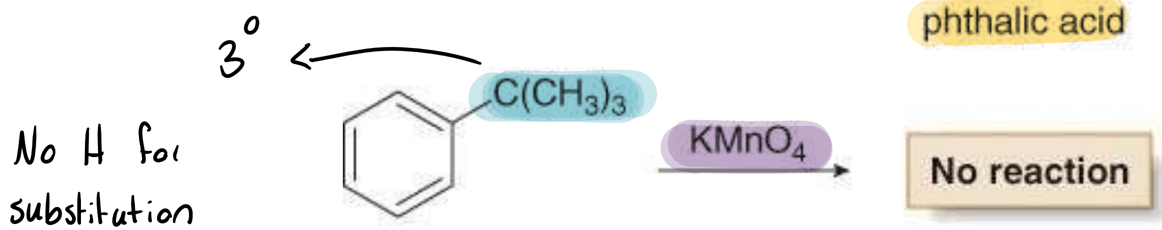
Side Chain Reactivity



Side Chain Reactivity: Oxidation



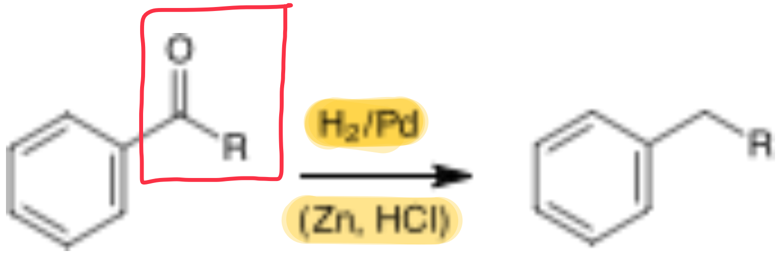


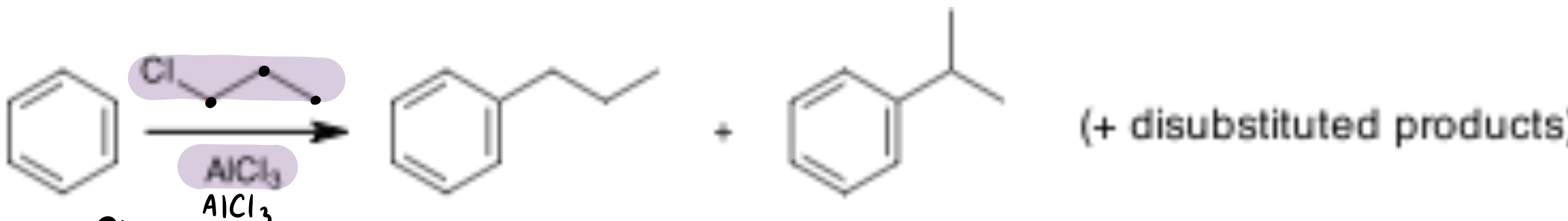


Side Chain Reactivity: Reduction

friedel-craft acylation

acyl group





the friedel-crafts alkylation

minor product

major product