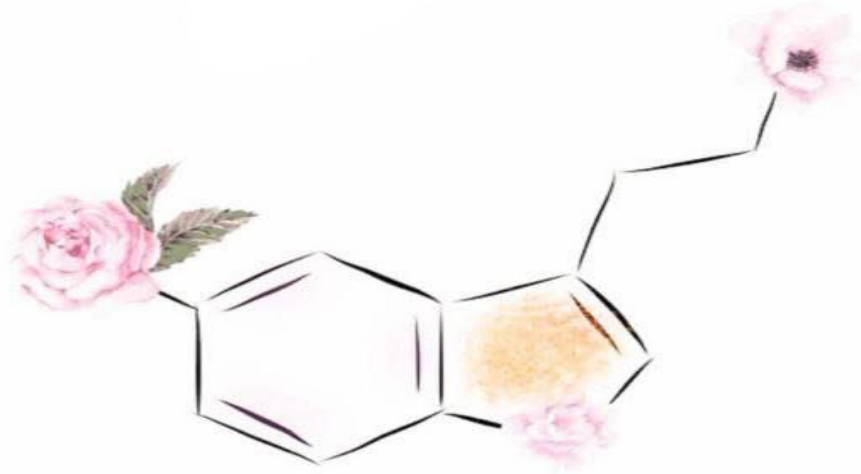


Date:

29/12/2023



لجان الدفقات



تفريغ عضويه 1



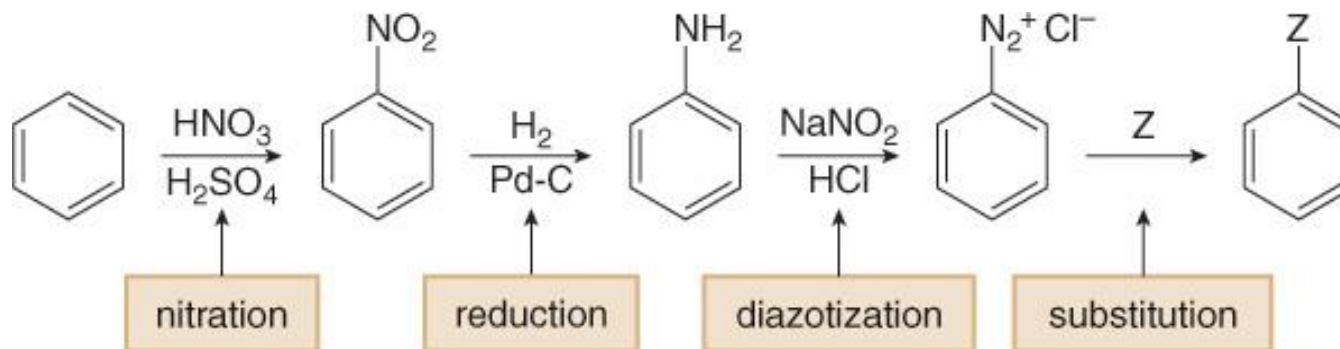
Benzene and Aromatics: موضوع المحاضرة

رقم المحاضرة : (١٥)

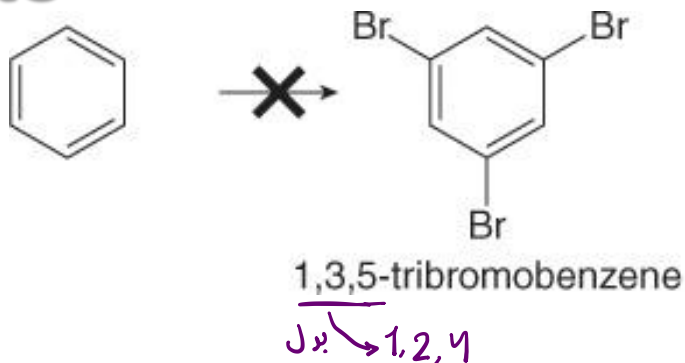
Gufran Khaseeb : إعداد الصيدلانية

Substitution Reactions of Aryl Diazonium Salts

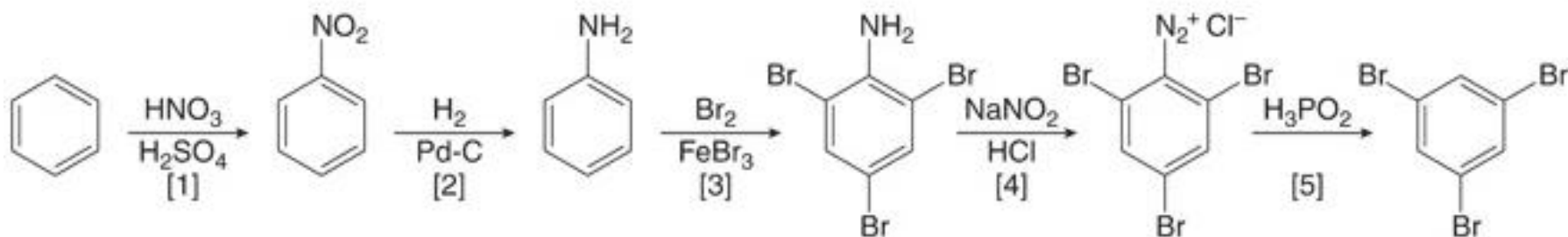
Diazonium salts provide easy access to many different benzene derivatives. Keep in mind the following four-step sequence, because it will be used to synthesize many substituted benzenes.



Substitution Reactions of Aryl Diazonium Salts



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



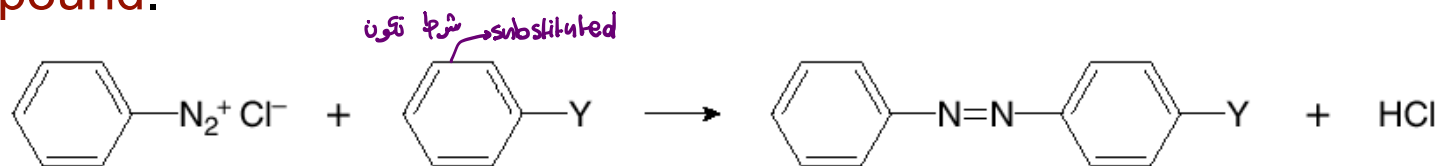
- Nitration followed by reduction forms aniline ($C_6H_5NH_2$) from benzene (Steps [1] and [2]).
- Bromination of aniline yields the tribromo derivative in Step [3].
- The NH_2 group is removed by a two-step process: diazotization with $NaNO_2$ and HCl (Step [4]), followed by substitution of the diazonium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

Coupling Reactions of Aryl Diazonium Salts

بربطه موكبين (aryl system)

- 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**.

Azo coupling

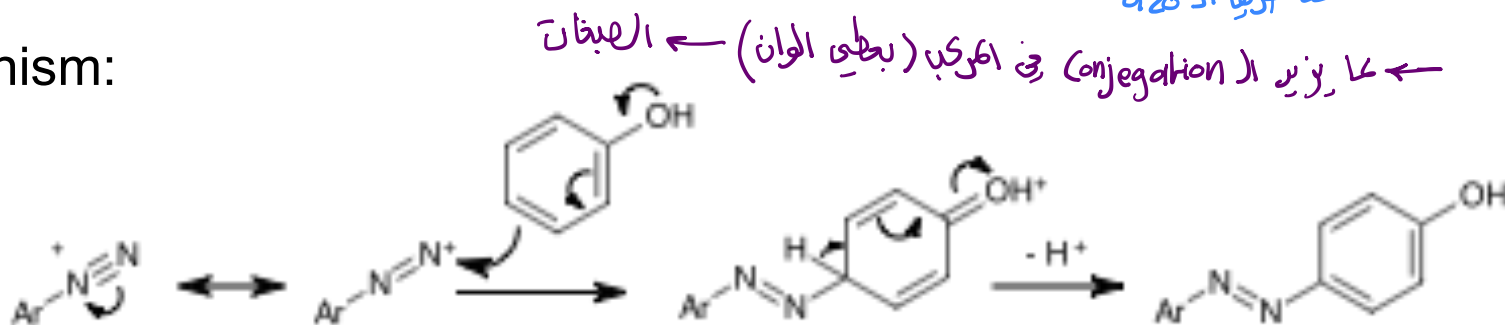


$Y = \text{NH}_2, \text{NHR}, \text{NR}_2, \text{OH}$
 (a strong electron-donor group)
 مشتقات الامينو او hydroxy

azo compound

حبي اوكسان (N=N)
 حلقين البنزين جازو conjugated
 عند طريقه الازو

Mechanism:

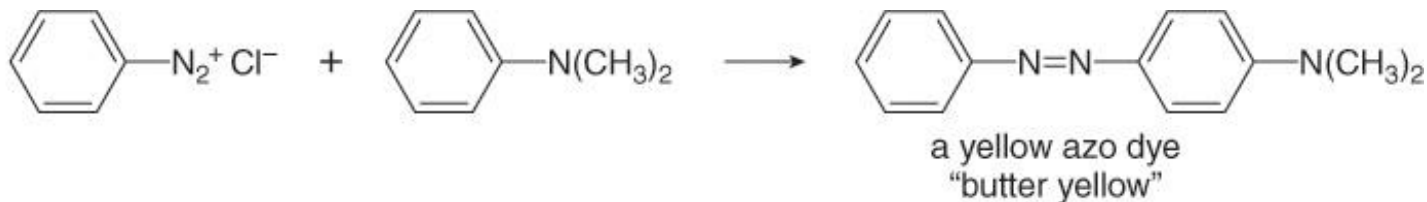


The para position is preferred for steric reasons

Azo Dyes

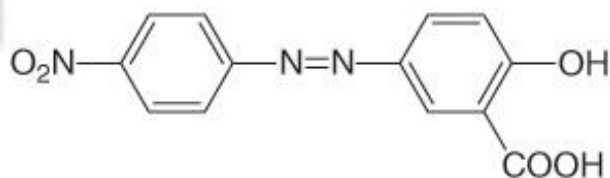
- Azo compounds** are highly conjugated, rendering them colored. Many of these compounds are synthetic dyes. Butter yellow was once used to color margarine.

Example

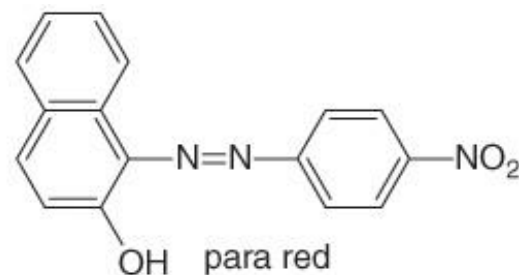


Three azo dyes

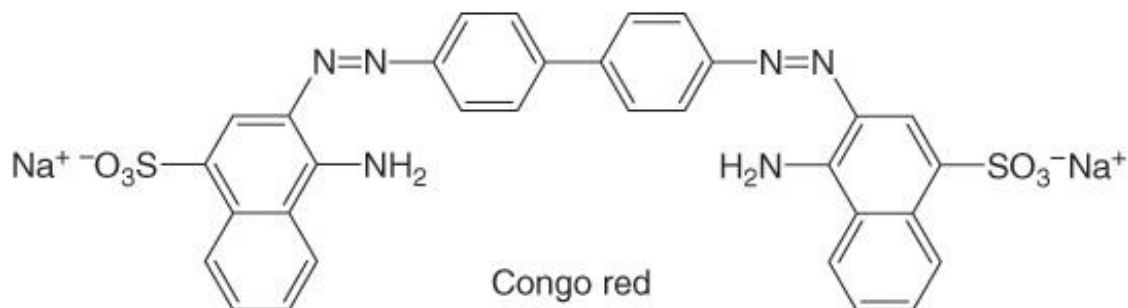
increase the conjugation



alizarine yellow R

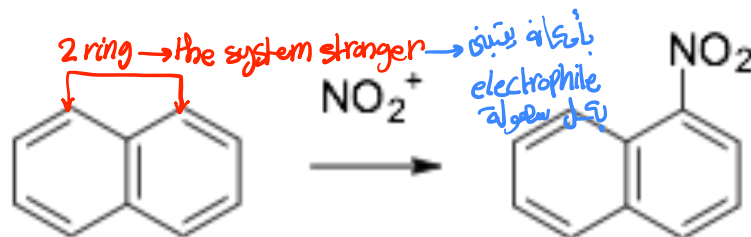


para red

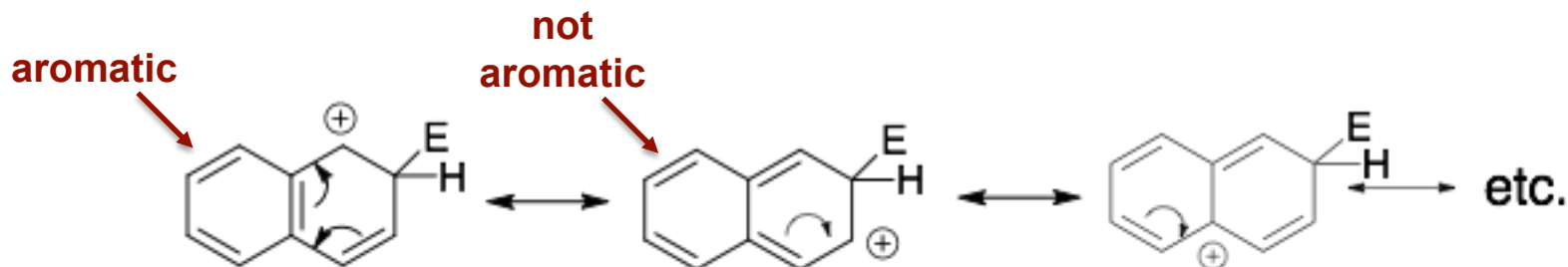
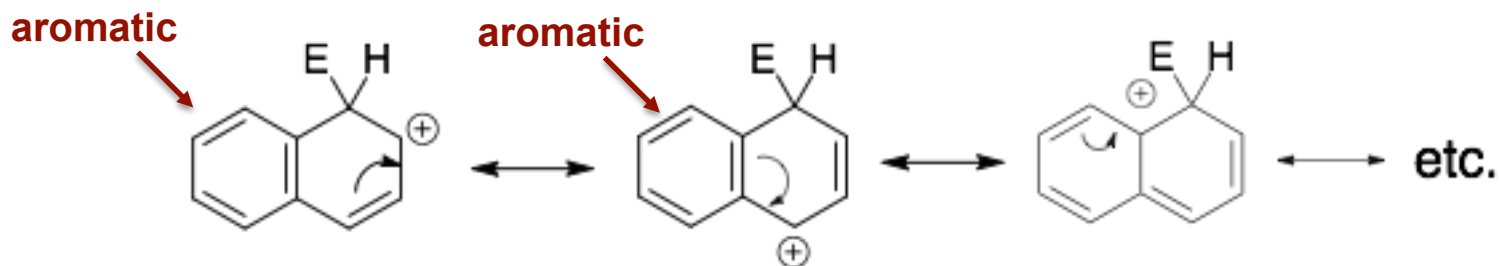


Congo red

S_EAr in Polycyclic Aromatic Compounds

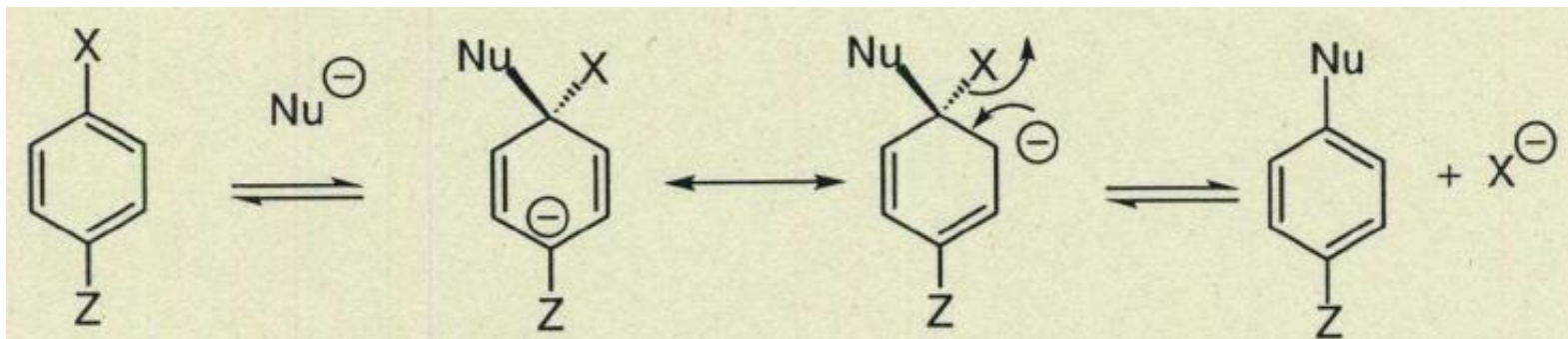


- عند وجود حلقتين بنزين
 متفاعل ومرة منهم كأيضا substitution كامل
 - عند وجود حلقتين يتخفف (-ve charge) ← التفاعل يكون اسهل



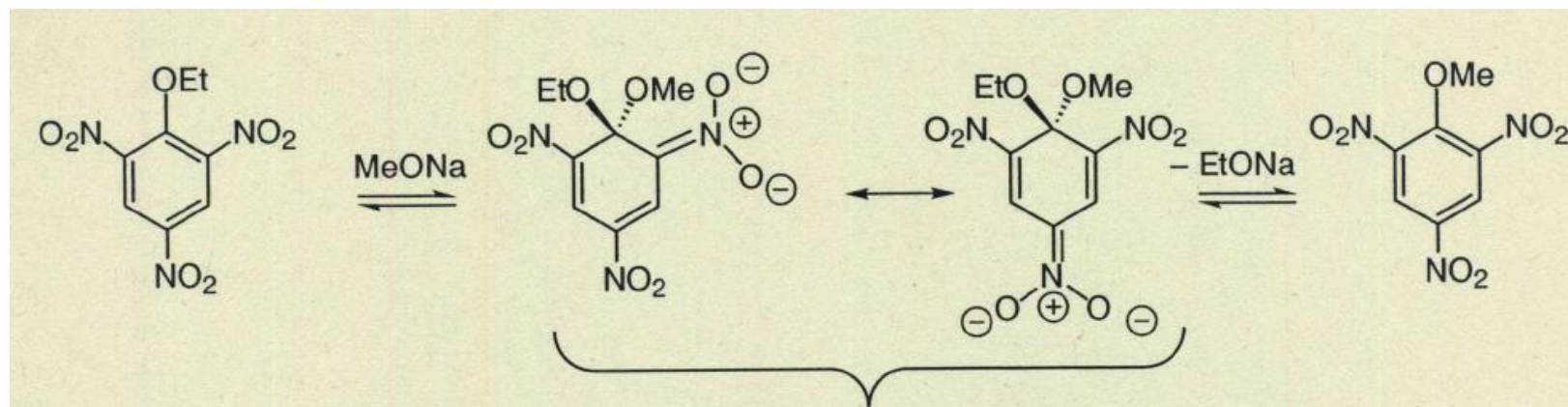
(مشت وطلوب details)

Nucleophilic Aromatic Substitutions, S_NAr



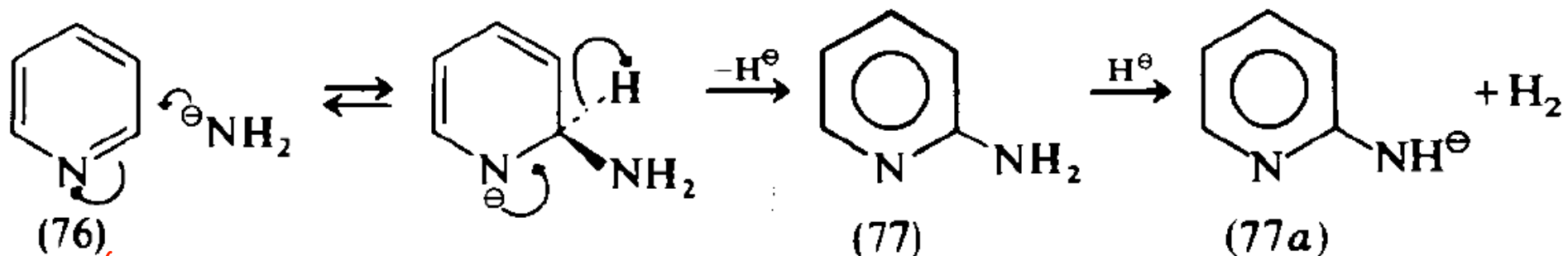
Z = Electron Accepting Substituent (sigma or π : NO_2 , CN , N_2^+ , SO_2R)
 X = Leaving Group

Example



Examples of S_NAr

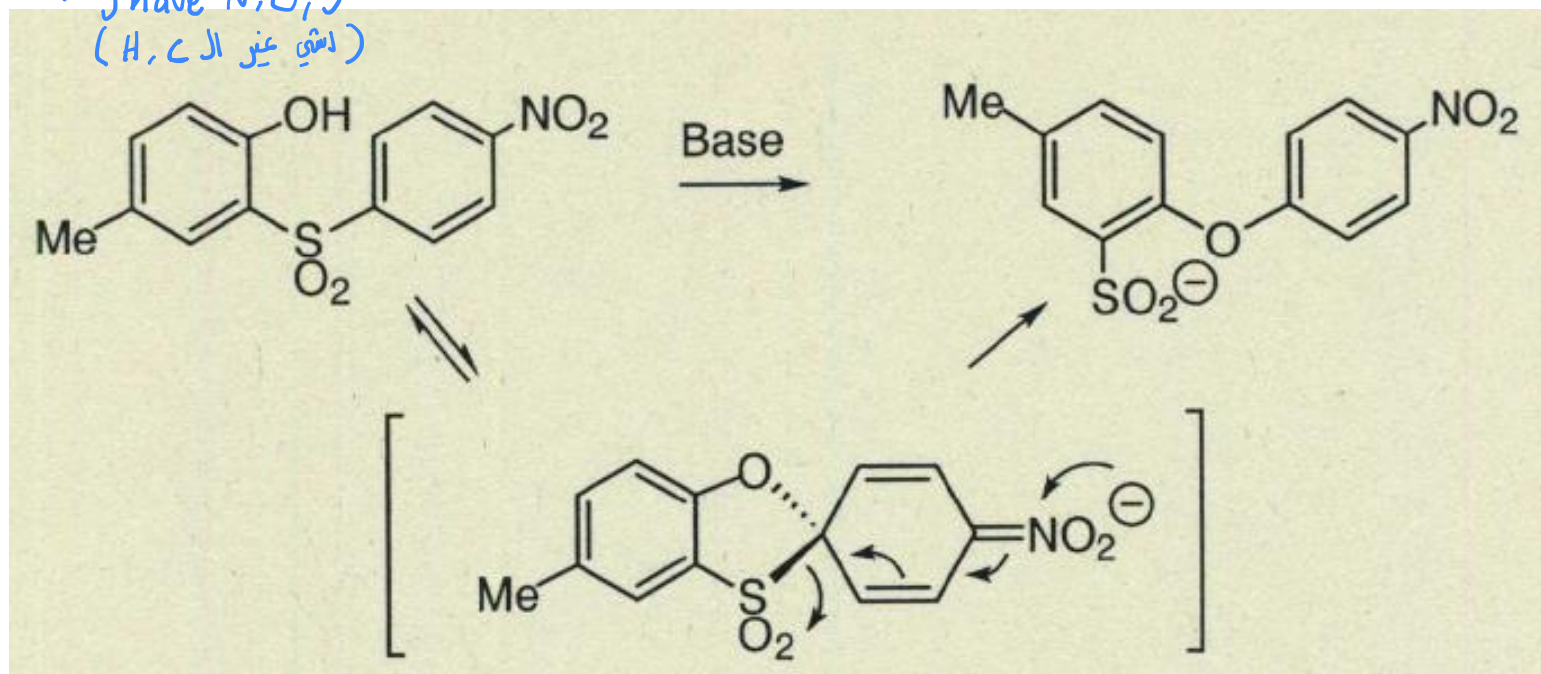
1)



(heterocyclic system)

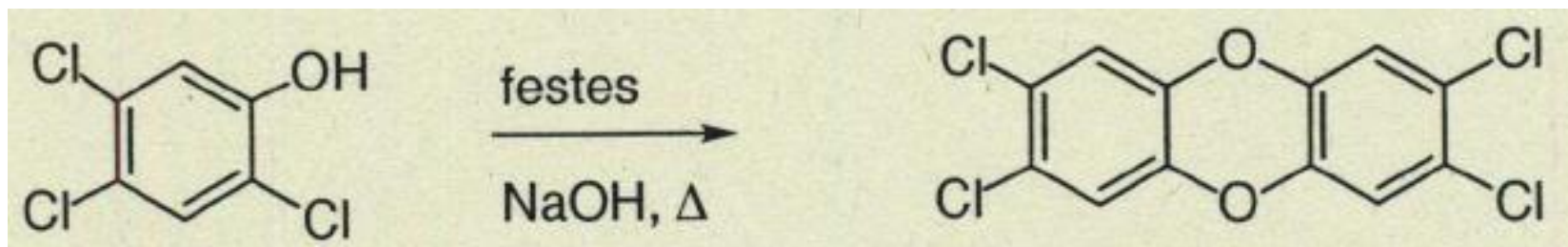
مختلف
ring have N, O, S
(اشي غير ال C, H)

2)

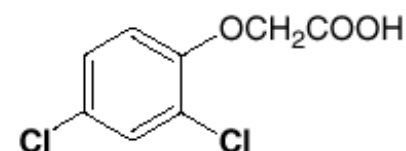


Examples of S_NAr

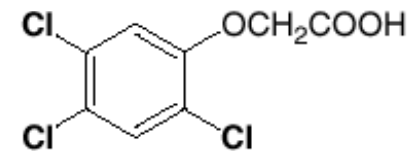
3)



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.

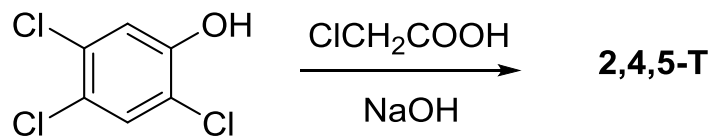


2,4-D
2,4-dichlorophenoxy-
acetic acid
herbicide

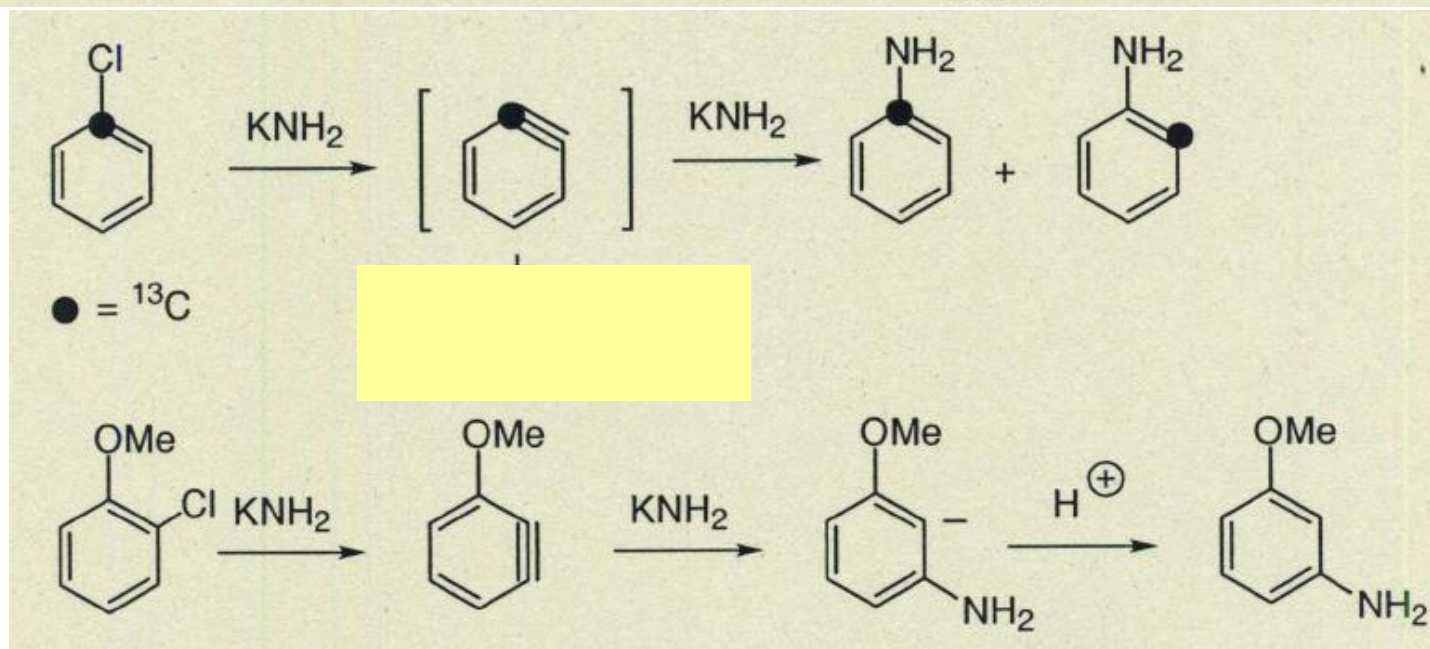
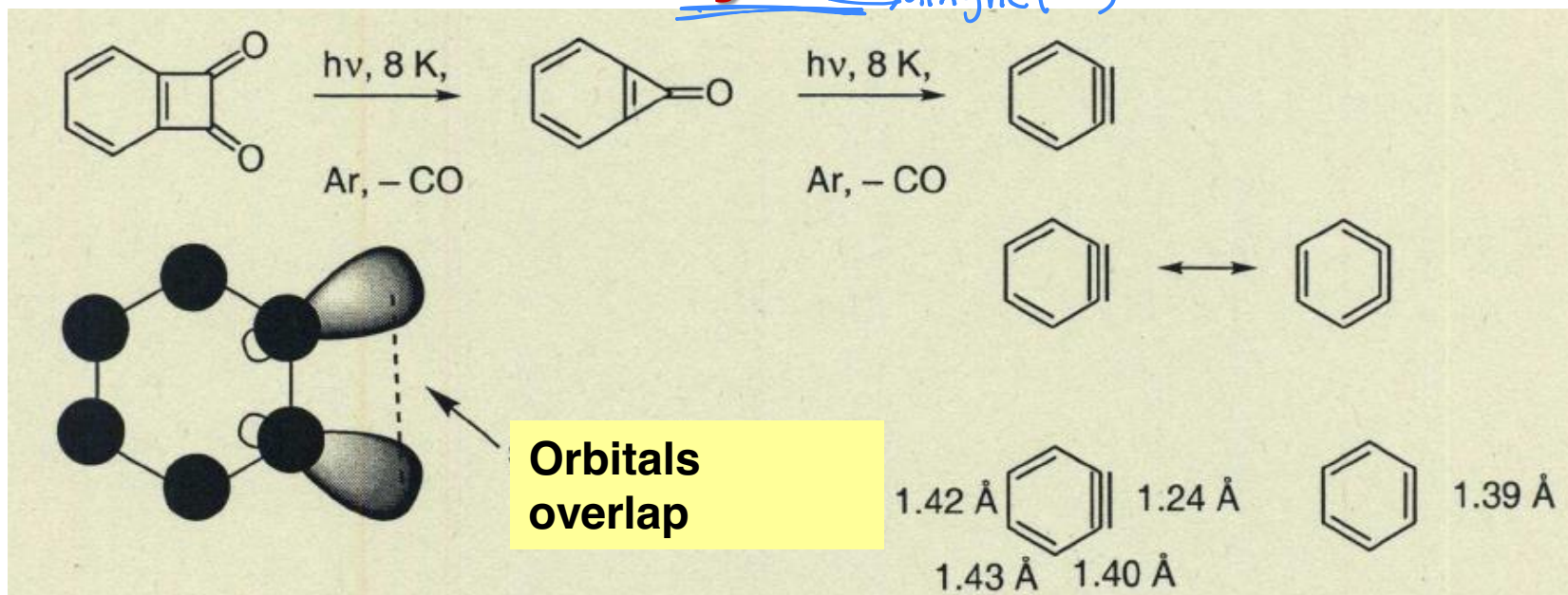


2,4,5-T
2,4,5-trichlorophenoxy-
acetic acid
herbicide

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



Benzyne $\rightarrow$ alkyne ($\equiv$)



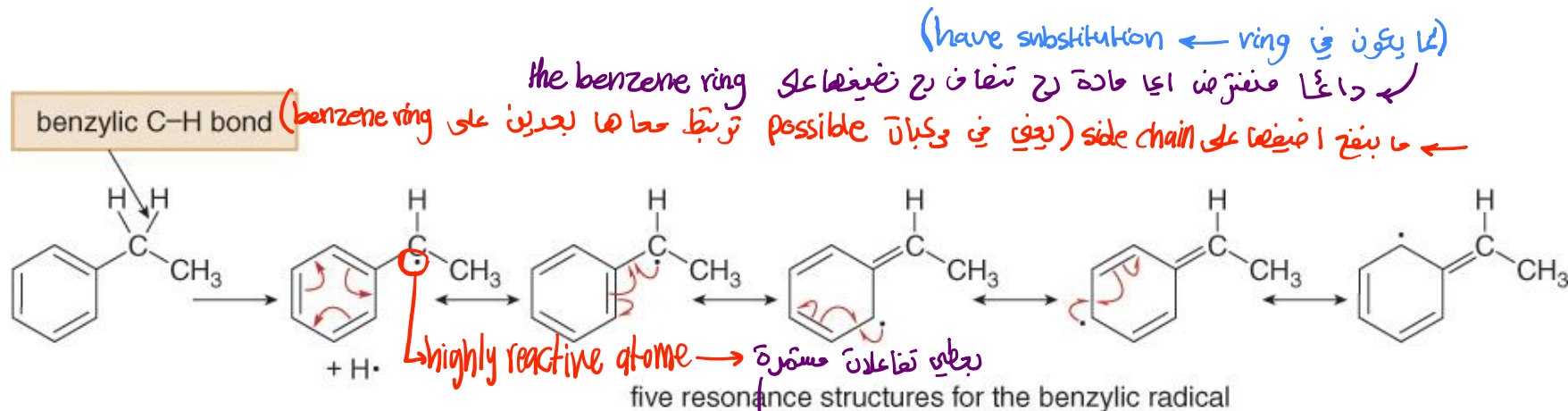
Side Chain Reactivity: Radical Halogenation

عند وجود رابطة متعادلة في مداره الاخير ونزعنا منه π وتكونت π (it will be not save reaction)
 highly reactive $\rightarrow$ give a side reaction (this will unacceptable)

متطرف (نقرفا عن طبيعي)

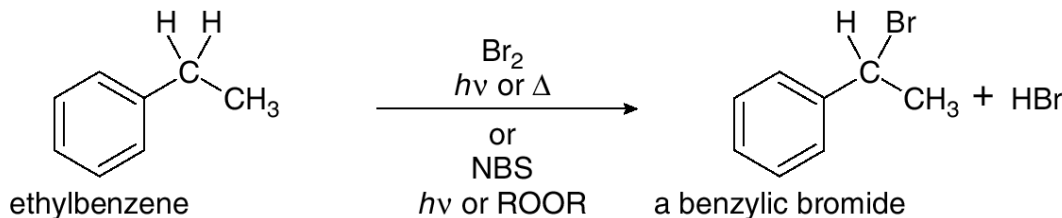
داخل اجسامنا it can lead to break down of the DNA and lead to cancers

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



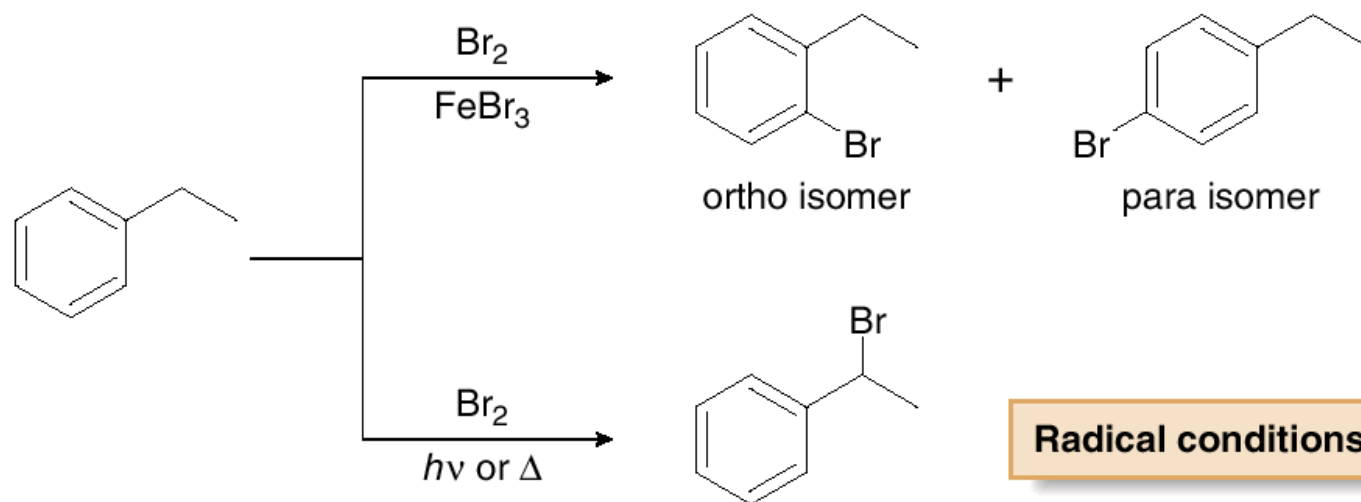
and give a highly reactive

ring then can add the substitution and Br at the side chain



radical conditions

Side Chain Reactivity

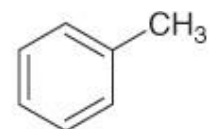


Ionic conditions

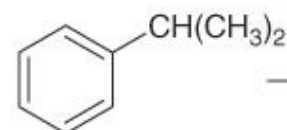
Radical conditions

Side Chain Reactivity: Oxidation

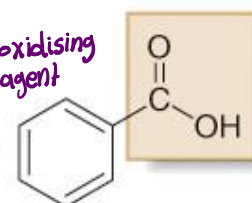
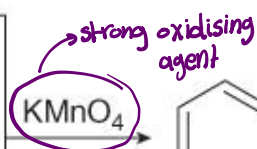
Examples



toluene

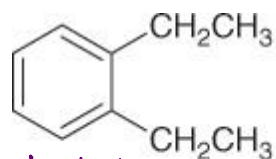


isopropylbenzene

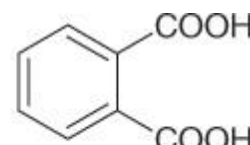


benzoic acid

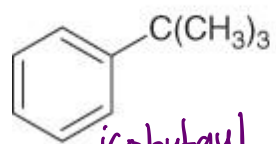
carboxy group



diethyl benzene



phthalic acid



isobutyl



No reaction

because there is a quaternary carbon → في مرتبة 4
H

Side Chain Reactivity: Reduction

← تحويل side chain باستخدام Conditions سابقاً

