Polynuclear Aromatic Hydrocarbons

Prepared by

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الفرقة الثالثة تربية كيمياء عام
العام الدراسي ٢٠٢٢-٢٠٢٣

اعداد
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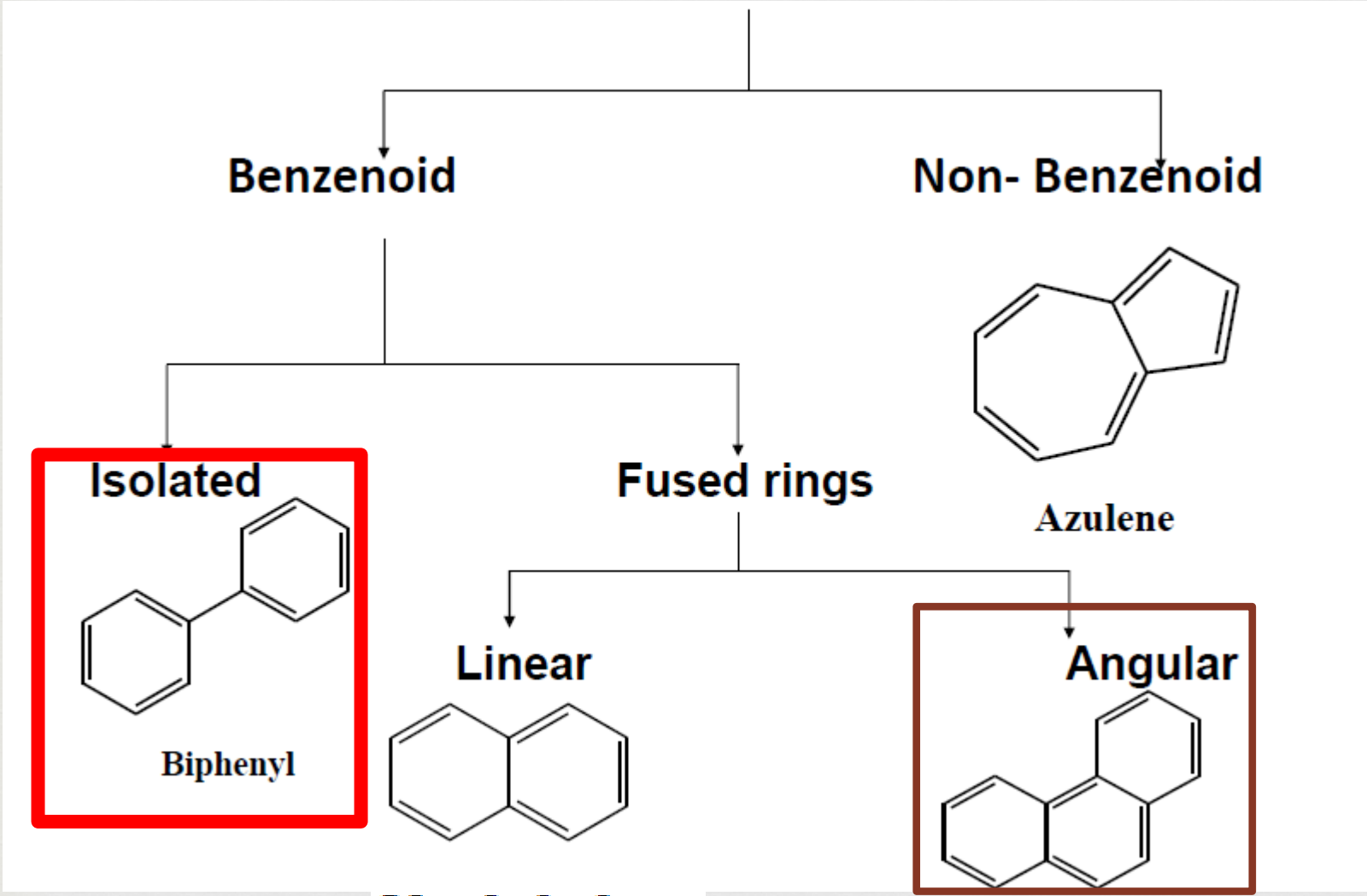
المدرس بكلية العلوم – جامعة جنوب الوادي

Polynuclear Hydrocarbons



- Contents

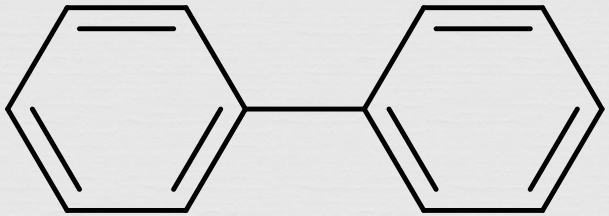
1- Isolated systems

- Biphenyl
- Biphenylderivatives
- Benzoine
- Benzil

2- Fused systems

- Naphthalene
- Anthracene
- phenancethracene

1- Isolated rings
a) Biphenyl



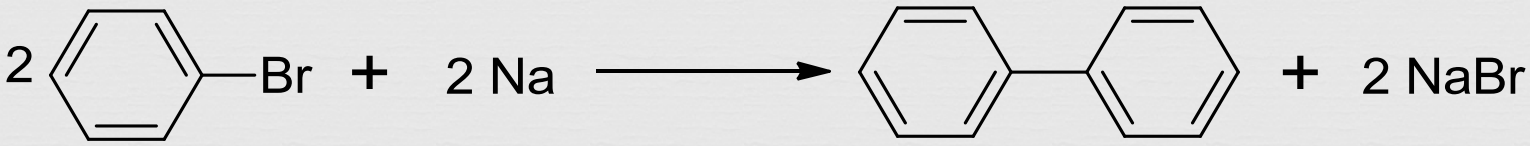
(i) Properties:

1- **Crystalline solid**

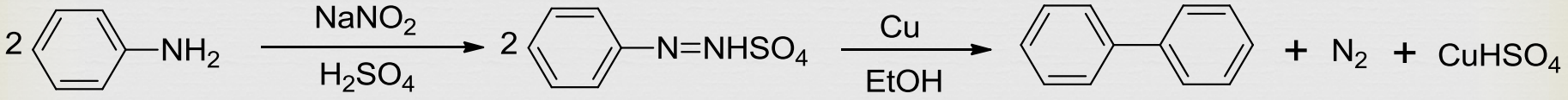
2- m. p. 71 C

(ii) Preparation of biphenyl

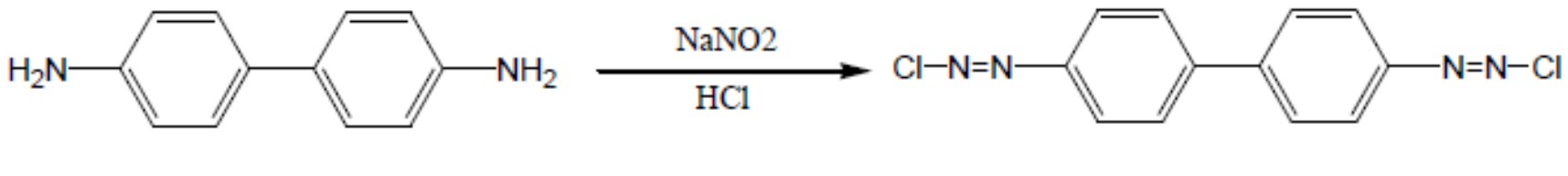
1- By Fittig reaction



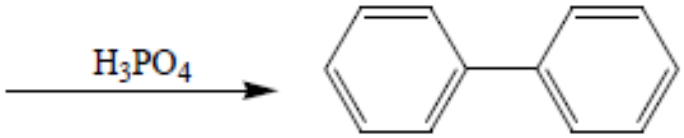
2- From benzene diazonium sulphate



3- From benzidine

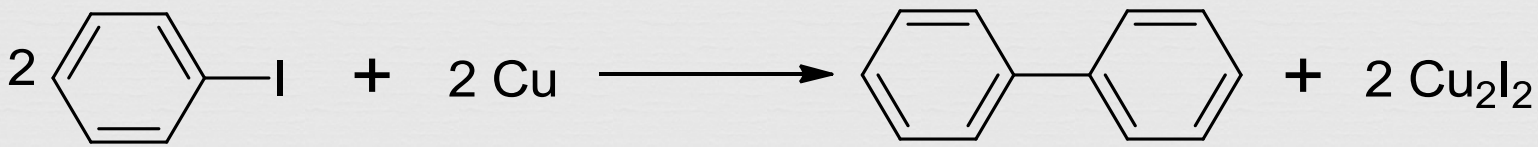


Benzidine



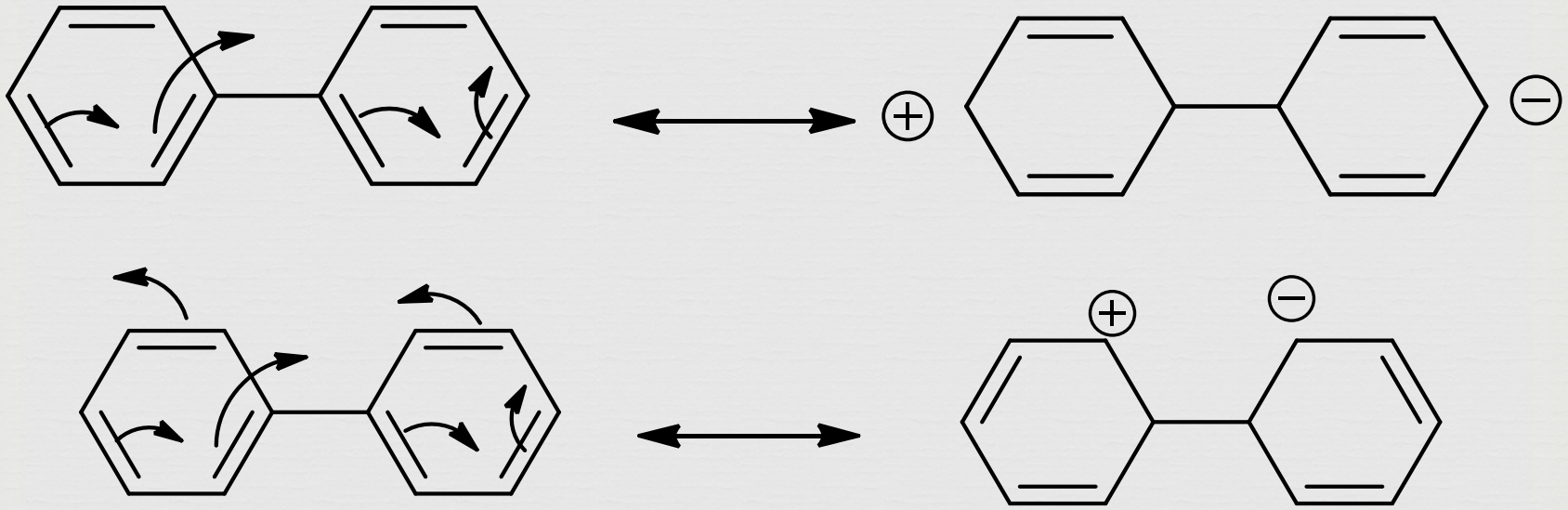
Biphenyl

4- Ulmann reaction

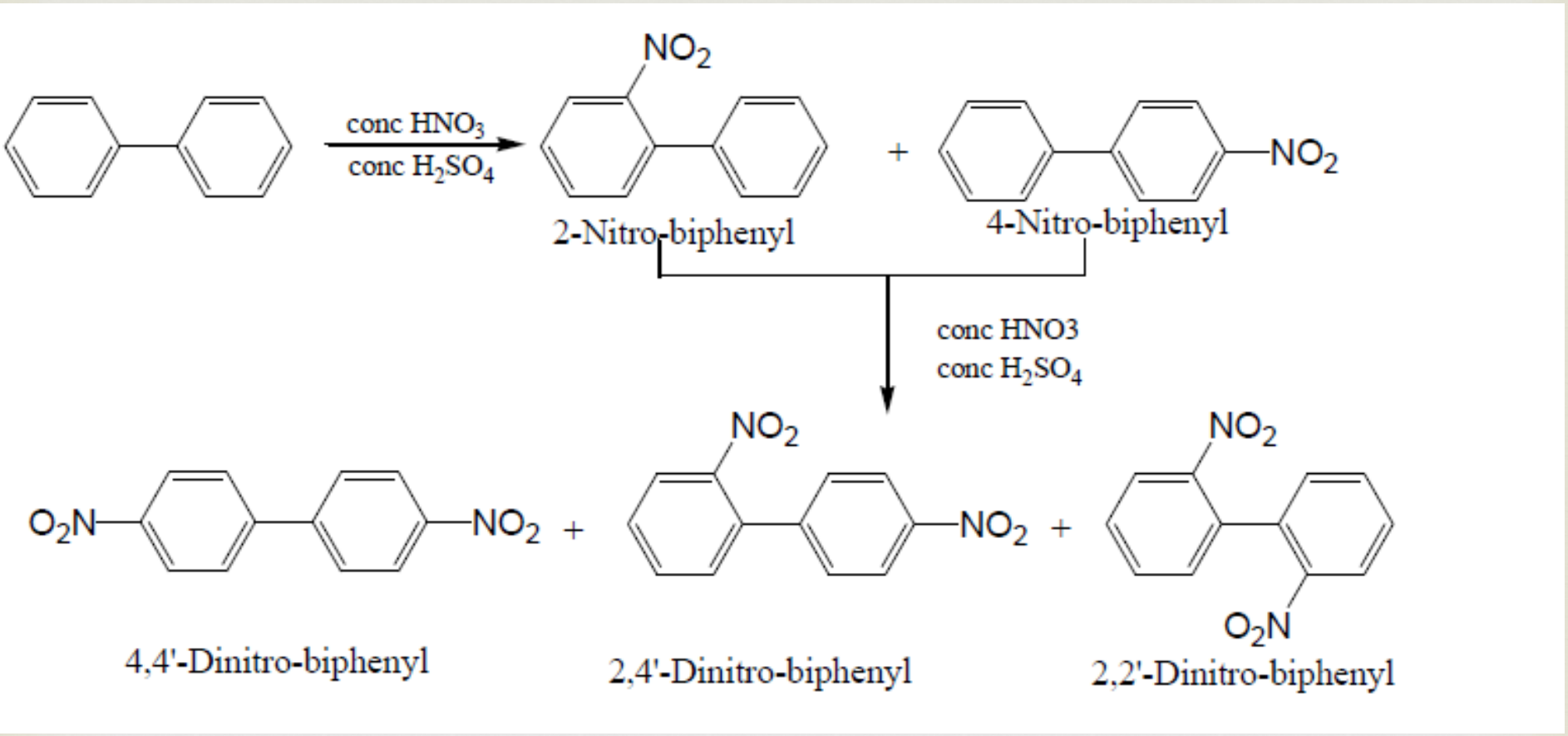


(iii) Reactions of biphenyl

A- Substitution reactions



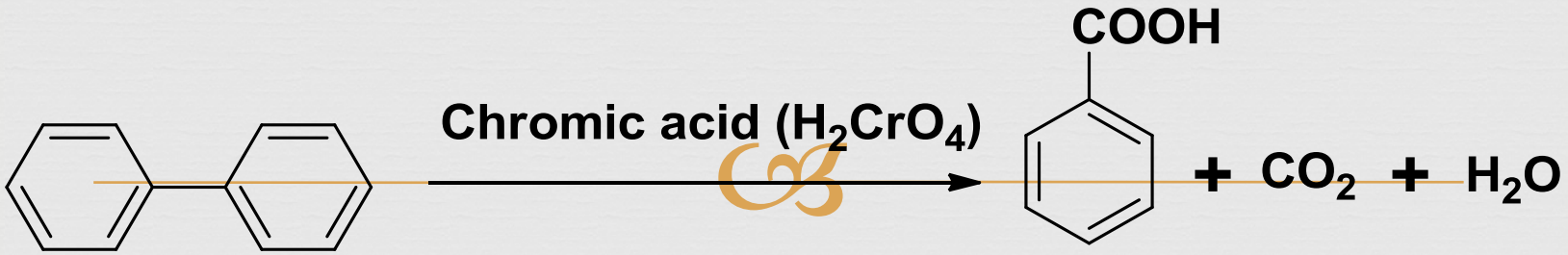
In biphenyl one ring act as electron donating group and the other act as electron withdrawing group



The electrophilic substitution occurs in 4- position (major) and 2- position (minor) due to steric effect of other benzene ring.

The 2nd substitution occurs in the empty ring in 2 or 4- position.

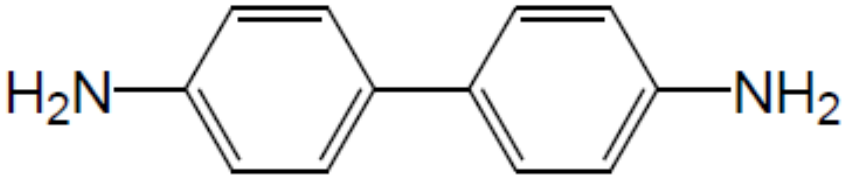
B) Oxidation



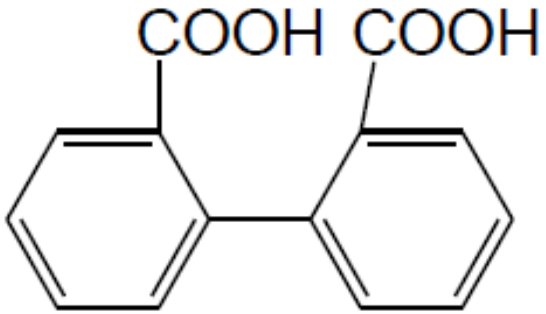
C) Ozonolysis

Biphenyl derivatives

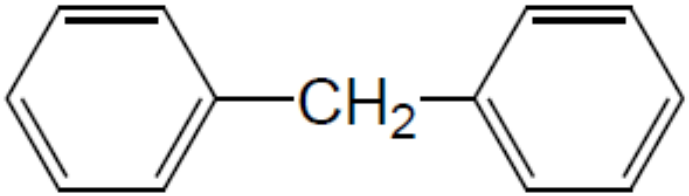
(1) Benzidine (4, 4`-diaminobiphenyl)



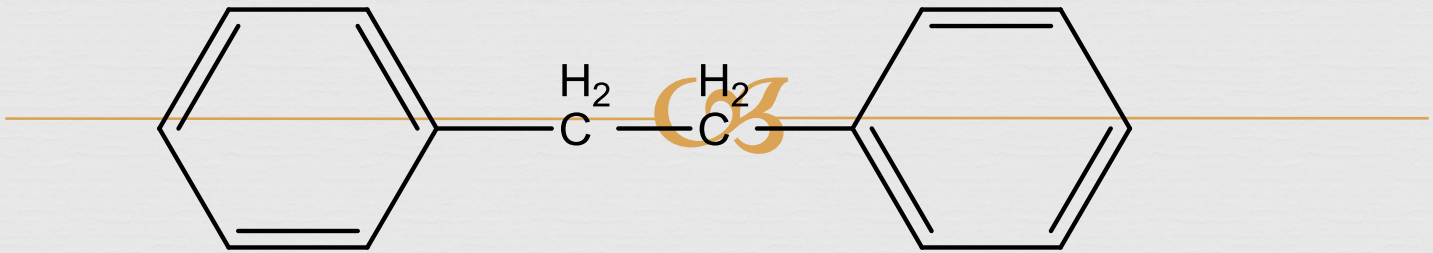
(2) Diphenic acid



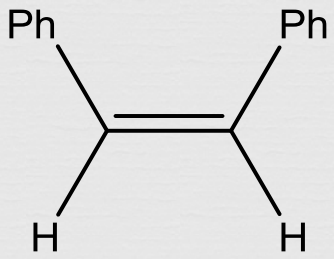
(3) Diphenyl methane



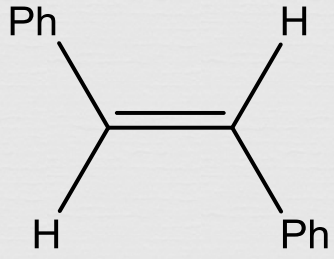
(4) 1,2-diphenylethane



(5) Stilbene and isostilbene



Isostilbene (cis diphenylethylene)

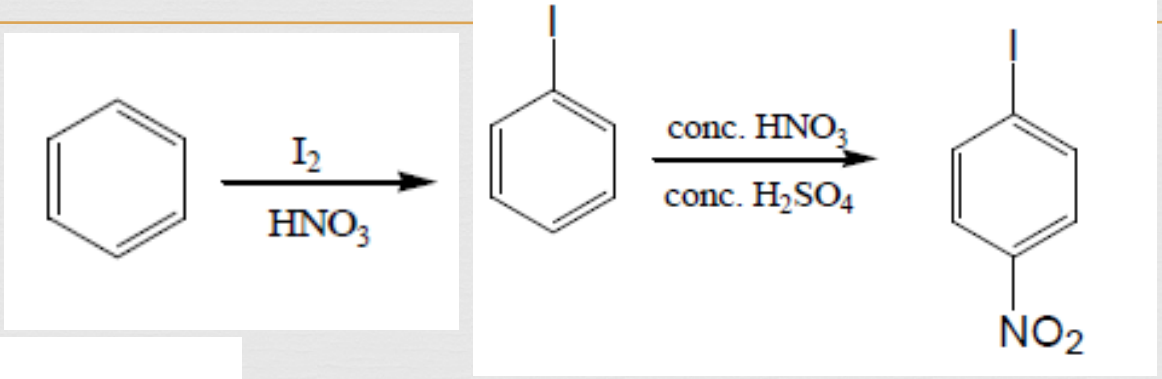


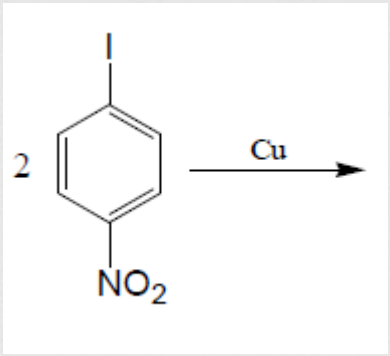
Stilbene (trans diphenylethylene)

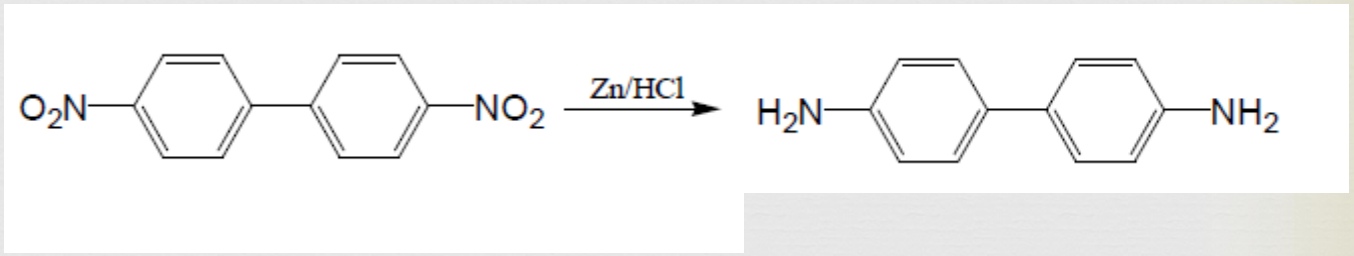
Benzidine

1- Q. Show how could you prepare benzidine from benzene?

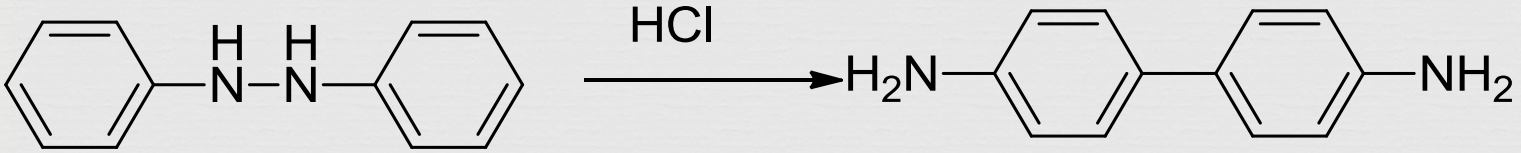
- Answer







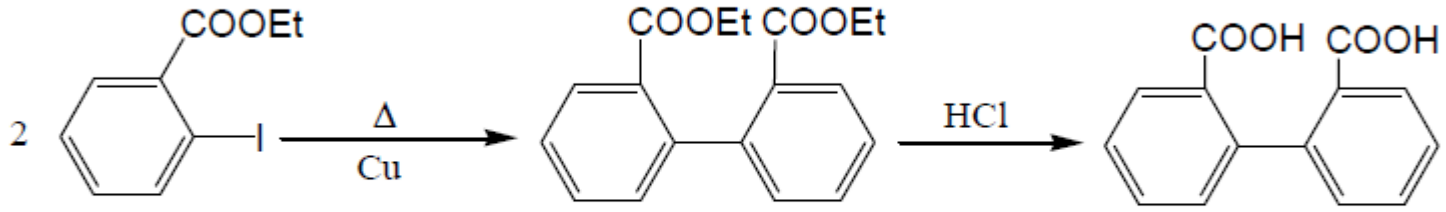
2- from hydrazobenzene through benzidine rearrangement



Diphenic acid : it is a solid , m.p. 229°

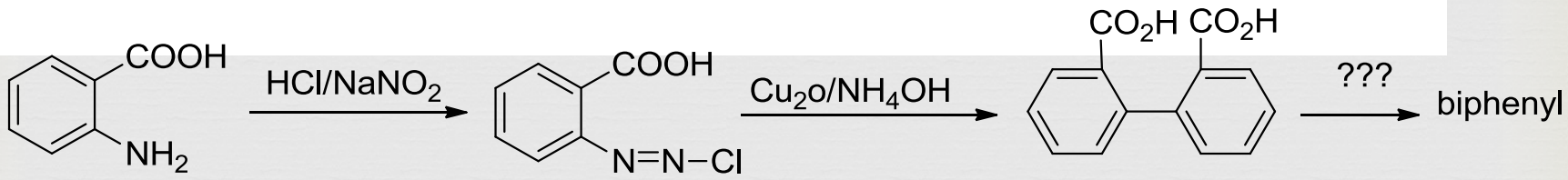
Prepreation

1- By Ulmann reaction

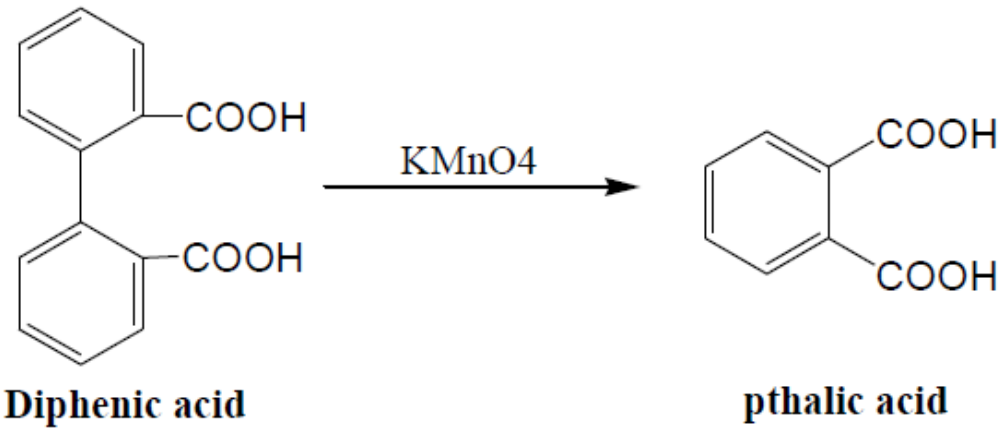


biphenyl- 2,2'- dicarboxylic acid
(Diphenic acid)

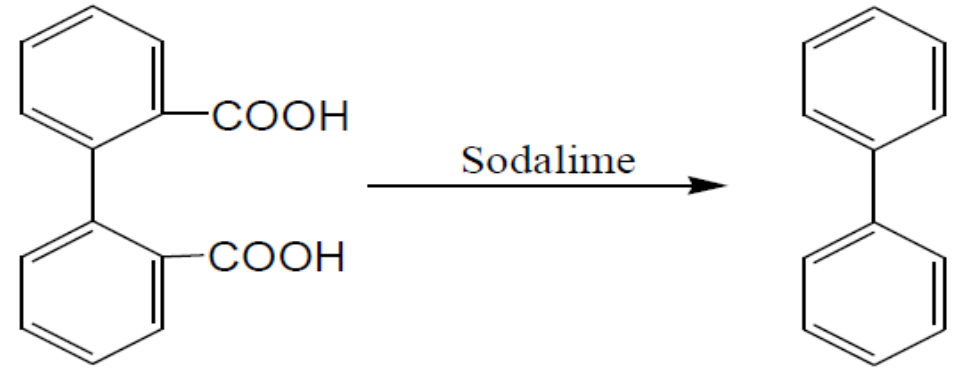
2- Via anthranilic acid



The chemical reactions



Diphenic acid **pthalic acid**

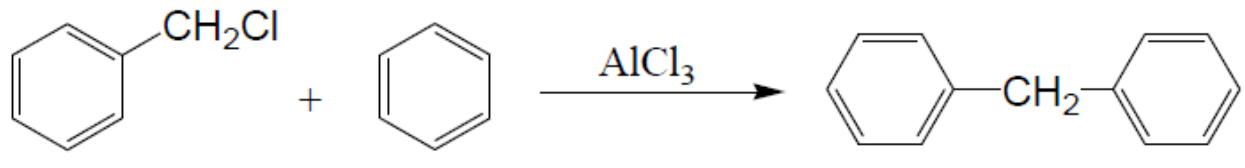


Diphenic acid **biphenyl**

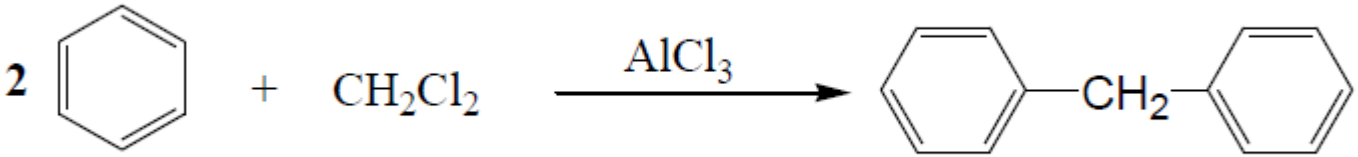
Diphenylmethane

- preparation

1- By Friedle crafts

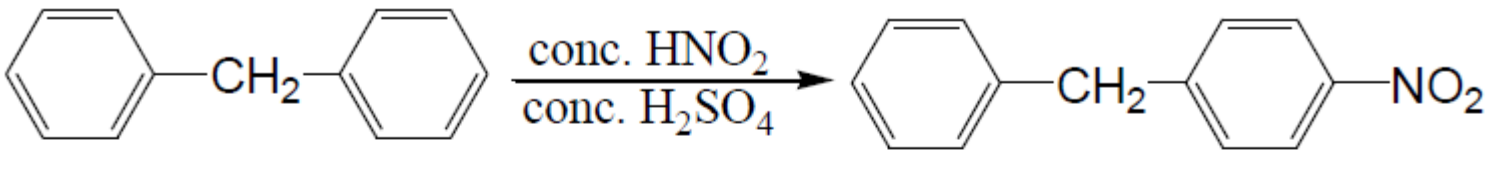


Benzyl chloride **Diphenyl methane**

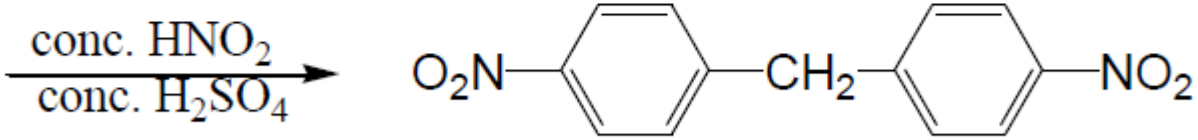


- **Reactions**

Nitration



Diphenyl methane **1-benzyl-4-nitrobenzene**



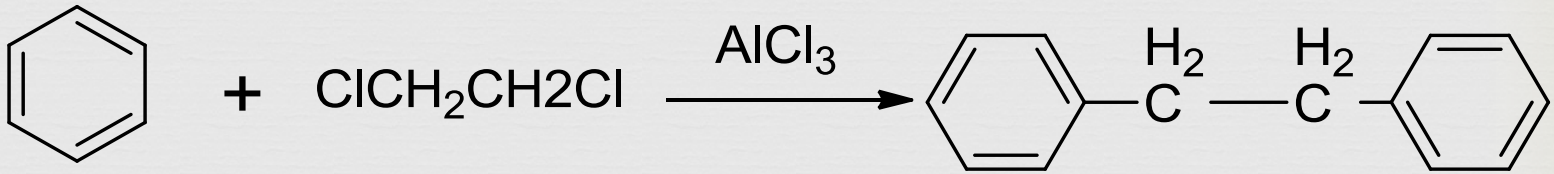
bis(4- nitrophenyl)methane

1,2-Diphenylethane

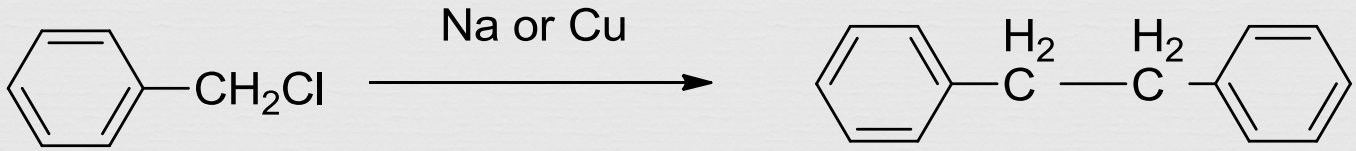
It is a white solide, m.p. 52°

- **preparation**

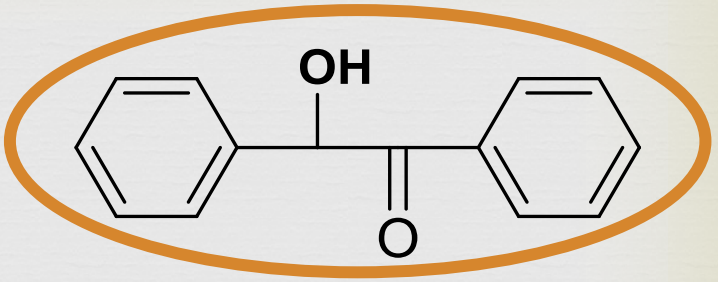
1- By Friedle crafts

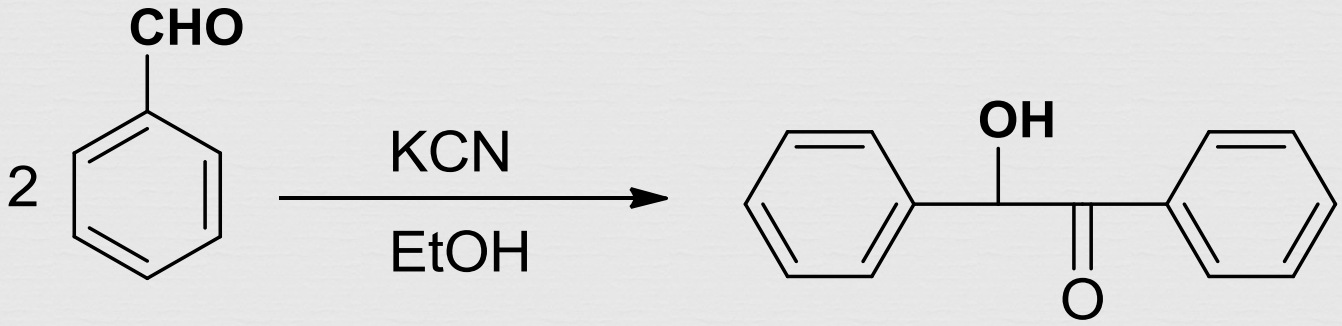


2- By Fittig or Ulmann

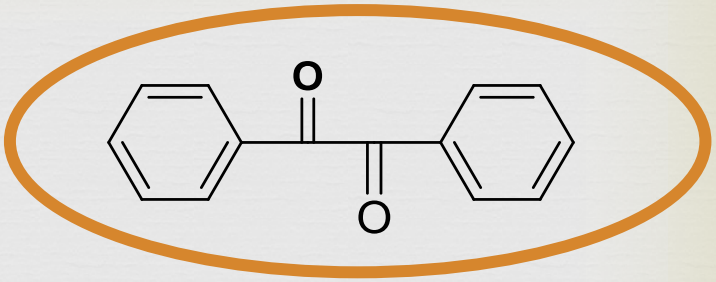


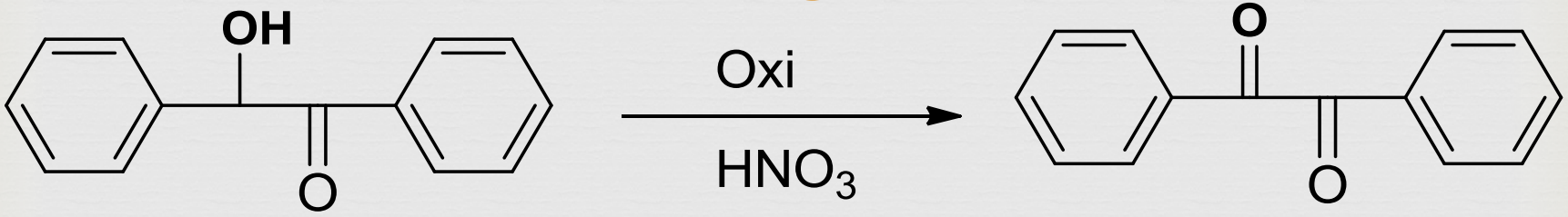
Benzoin





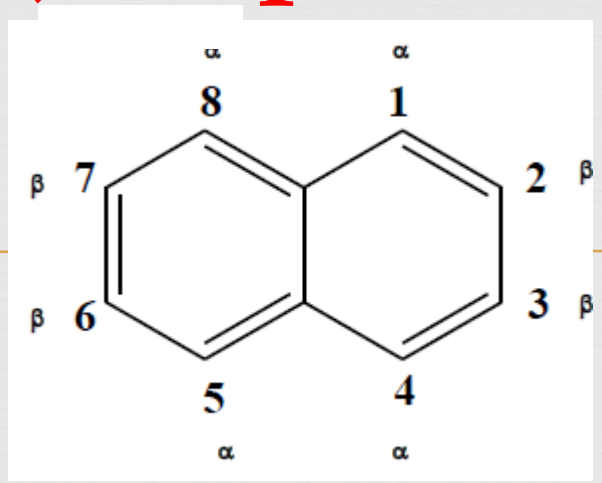
Benzil

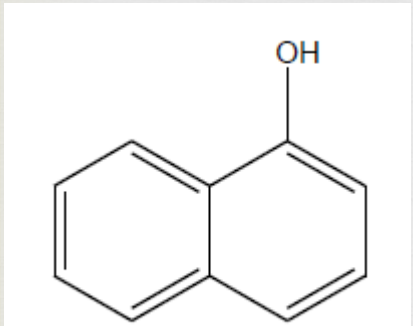




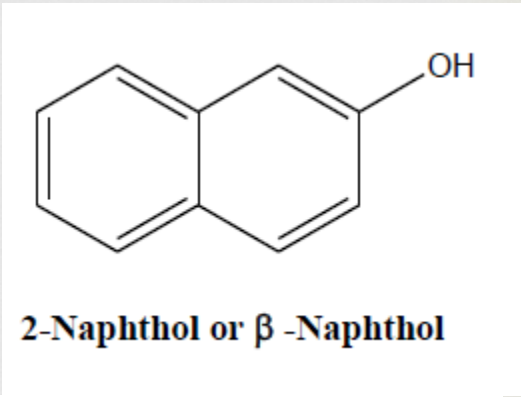
Condensed systems
Or
fused systems

(i) Naphthalene

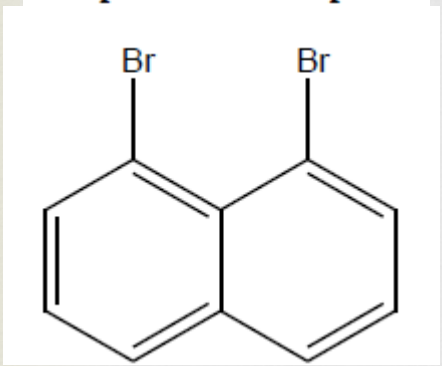




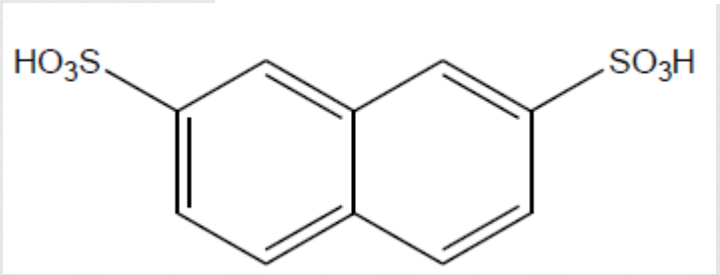
1-Naphthol or α-Naphthol



2-Naphthol or β -Naphthol

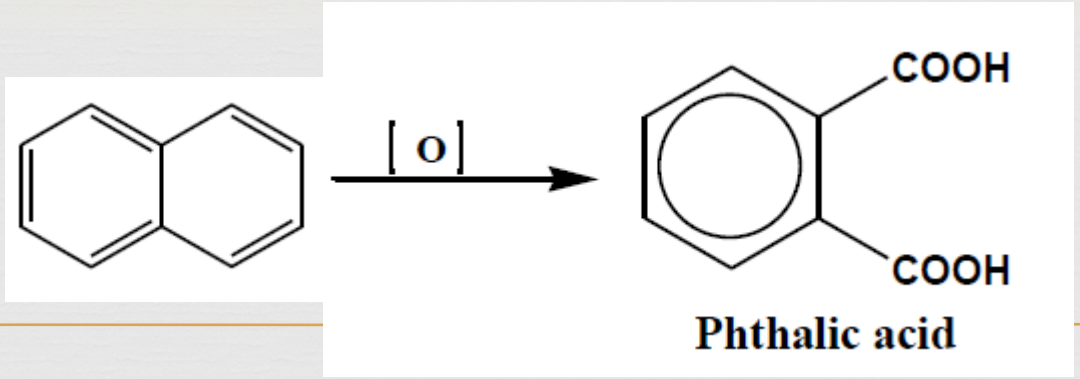


1,8- Dibromo-naphthalene

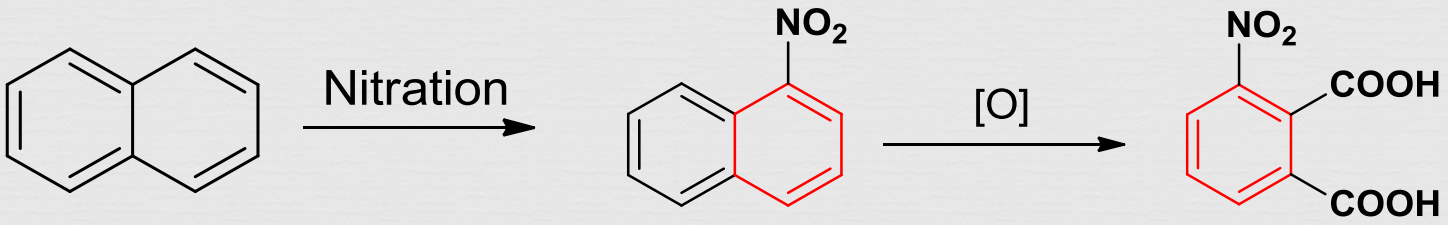


Naphthlene-2,7-disulfonic aci

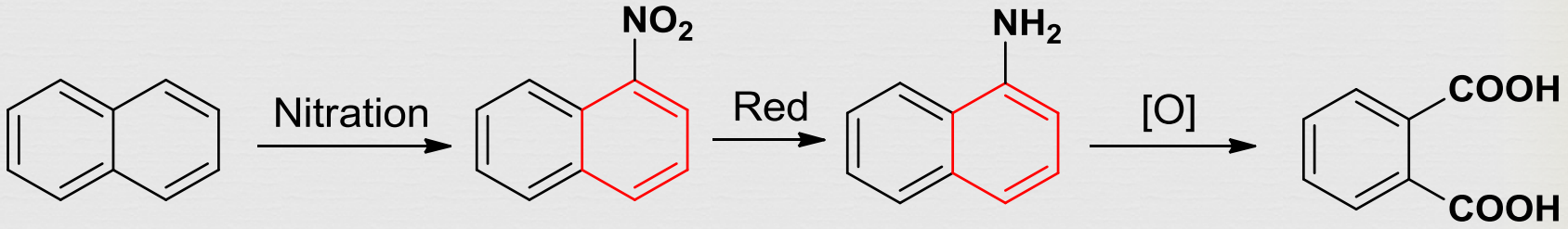
oxidation



a)

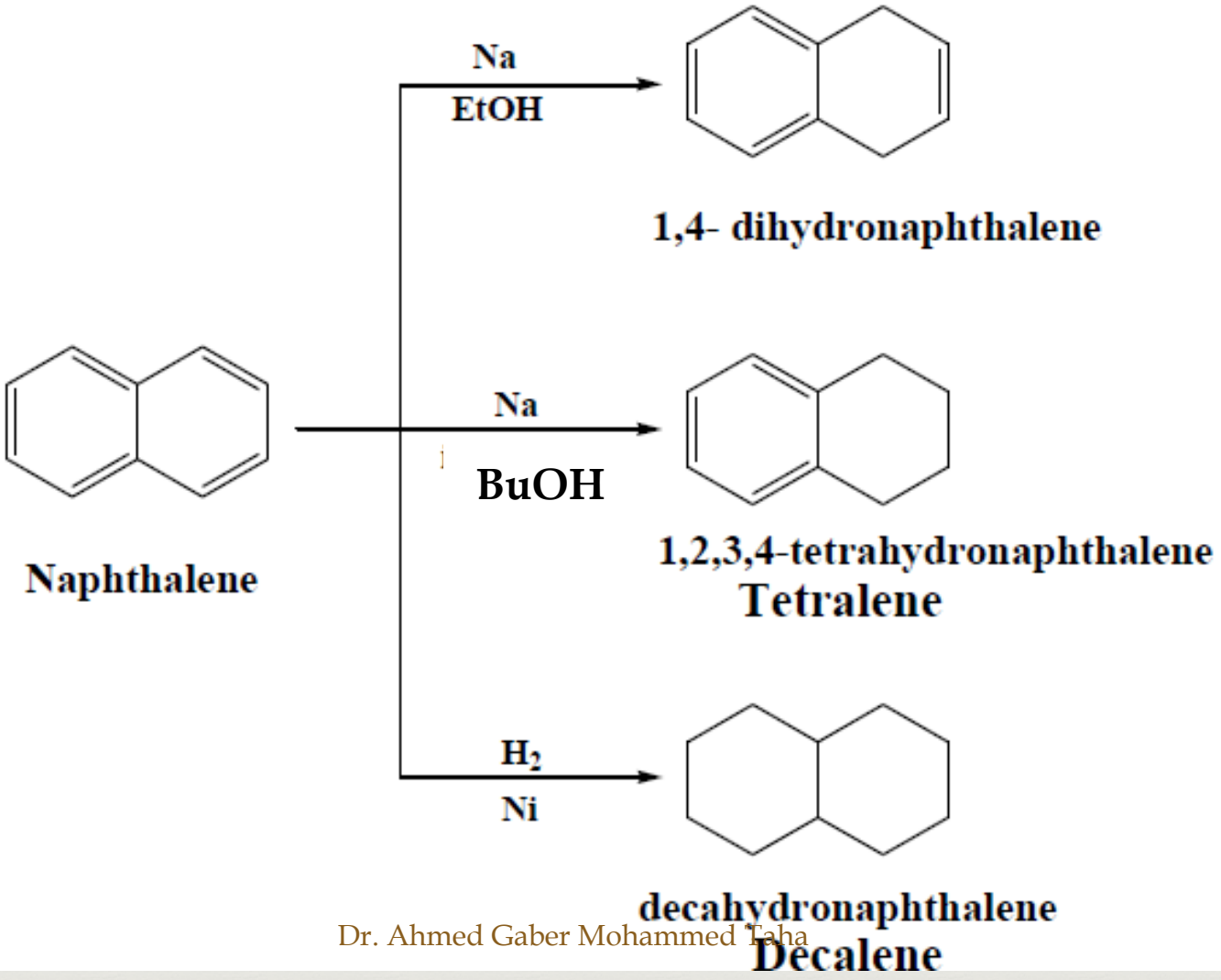


b)

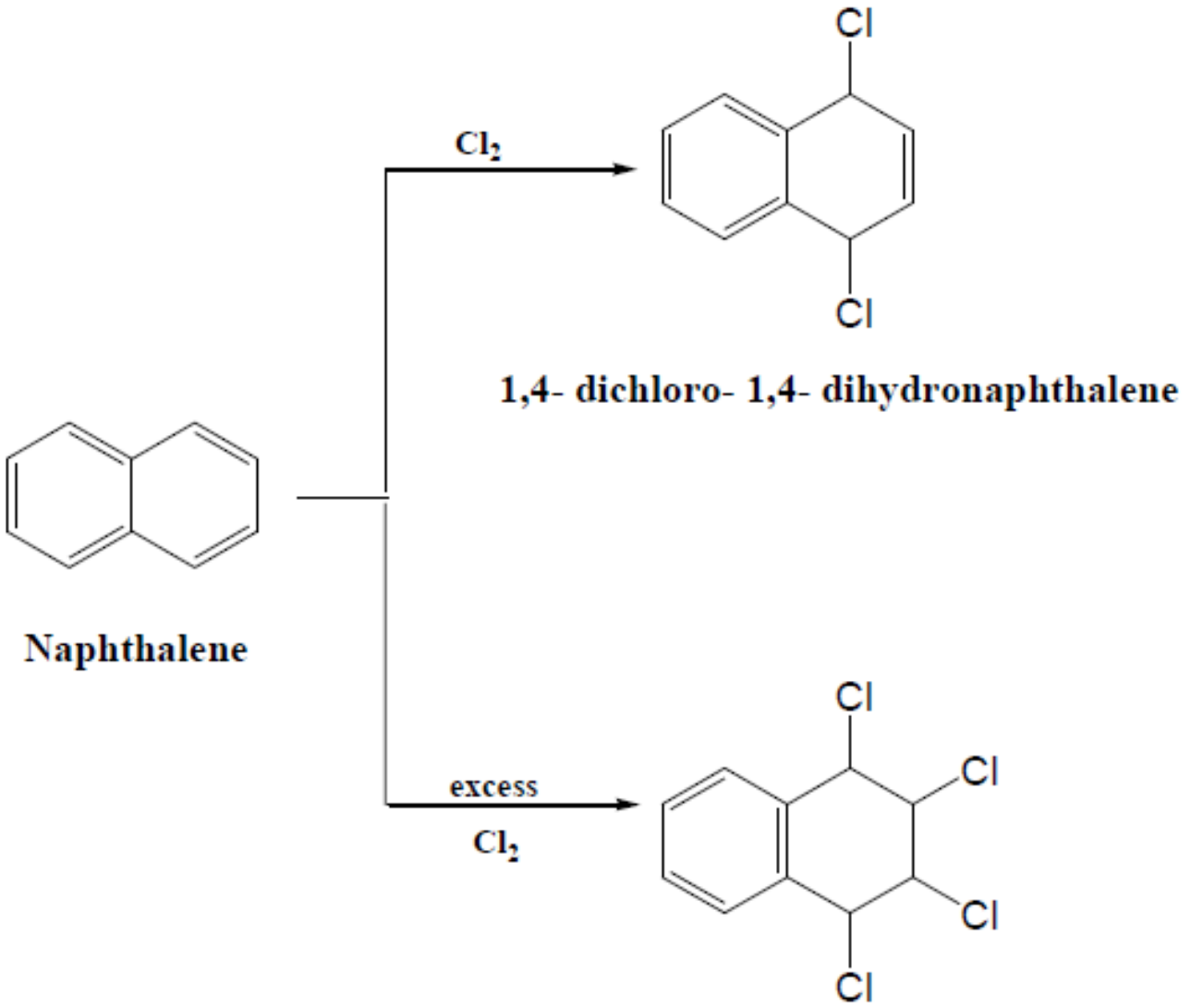


Chemical Reactions of naphthalene

1. Reduction



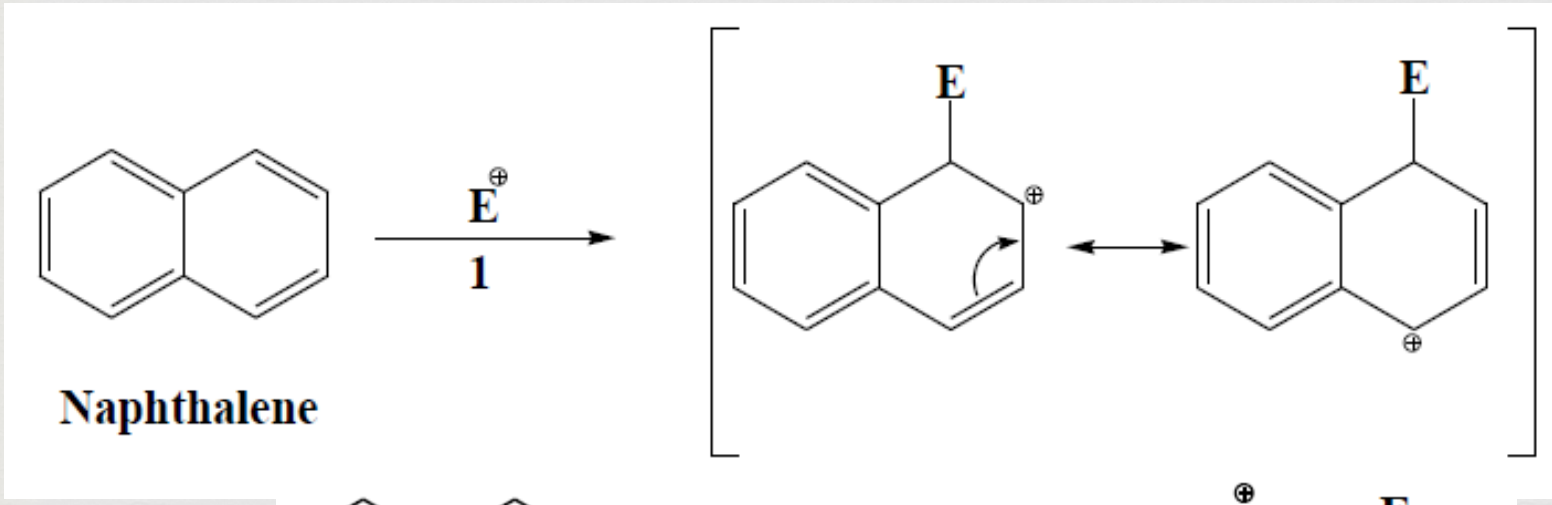
3. Addition of Cl_2



4. Electrophilic substitution reaction

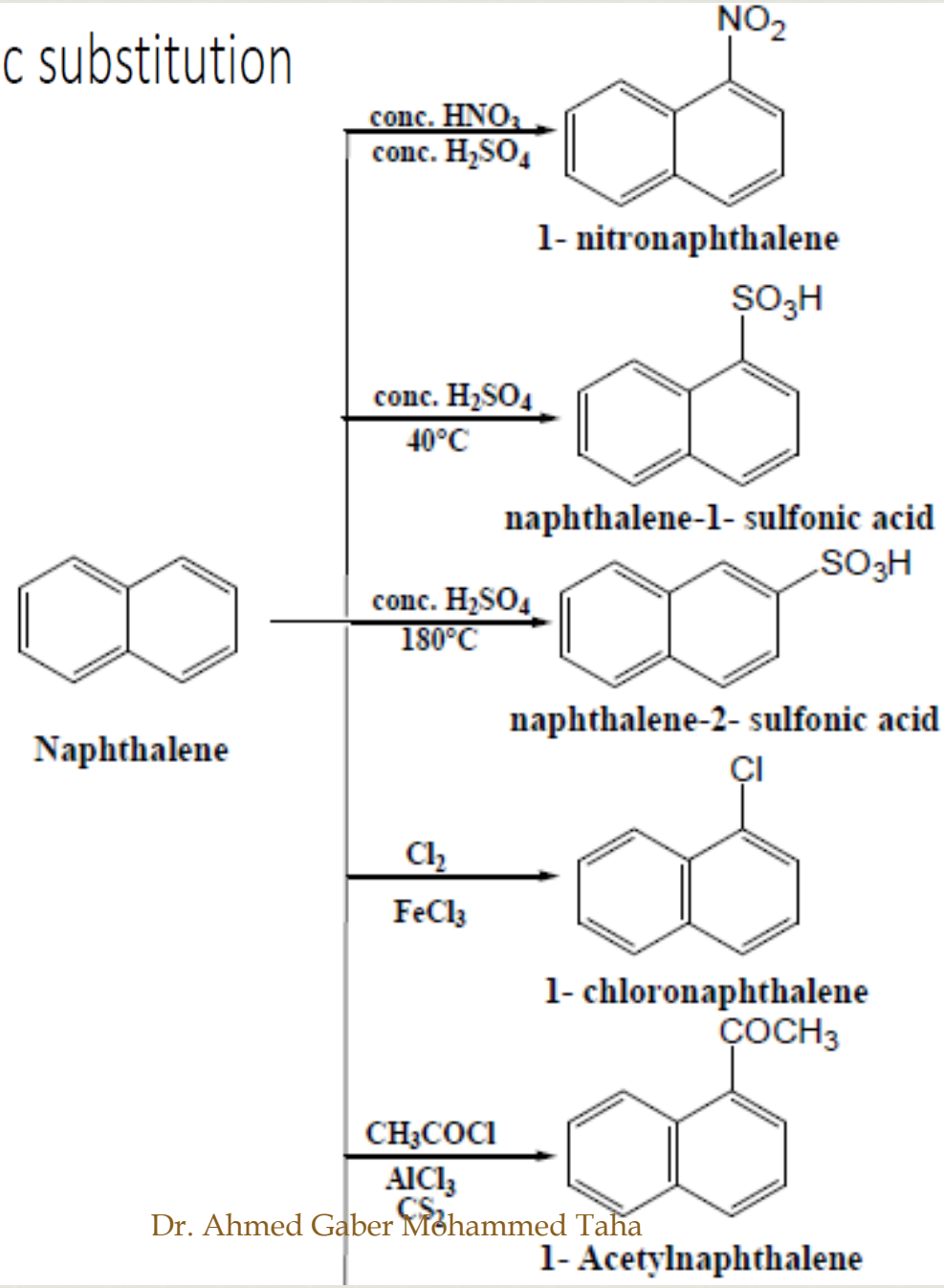
Q: Naphthalene udergoes electrophilic substitution at position 1 not 2. Explain

At position 1; carbocation intermediate stabilize by two resonance



So carbocation is more stable postion 1 than 2

Examples of electrophilic substitution



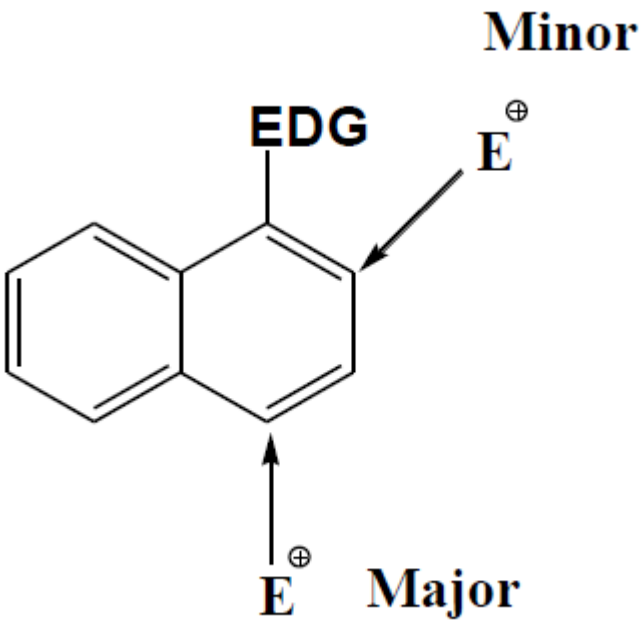
Substituted naphthalene

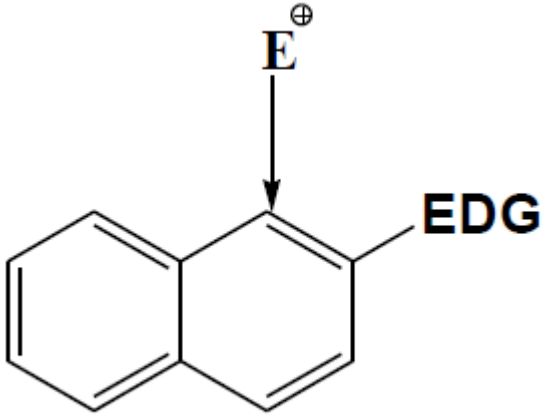
- Activating groups direct the electrophile to the same ring, while deactivating groups direct it to the other ring.

Electrodonating groups (EDG)
NH2, -OH, OR, Alkyl, Cl, Br

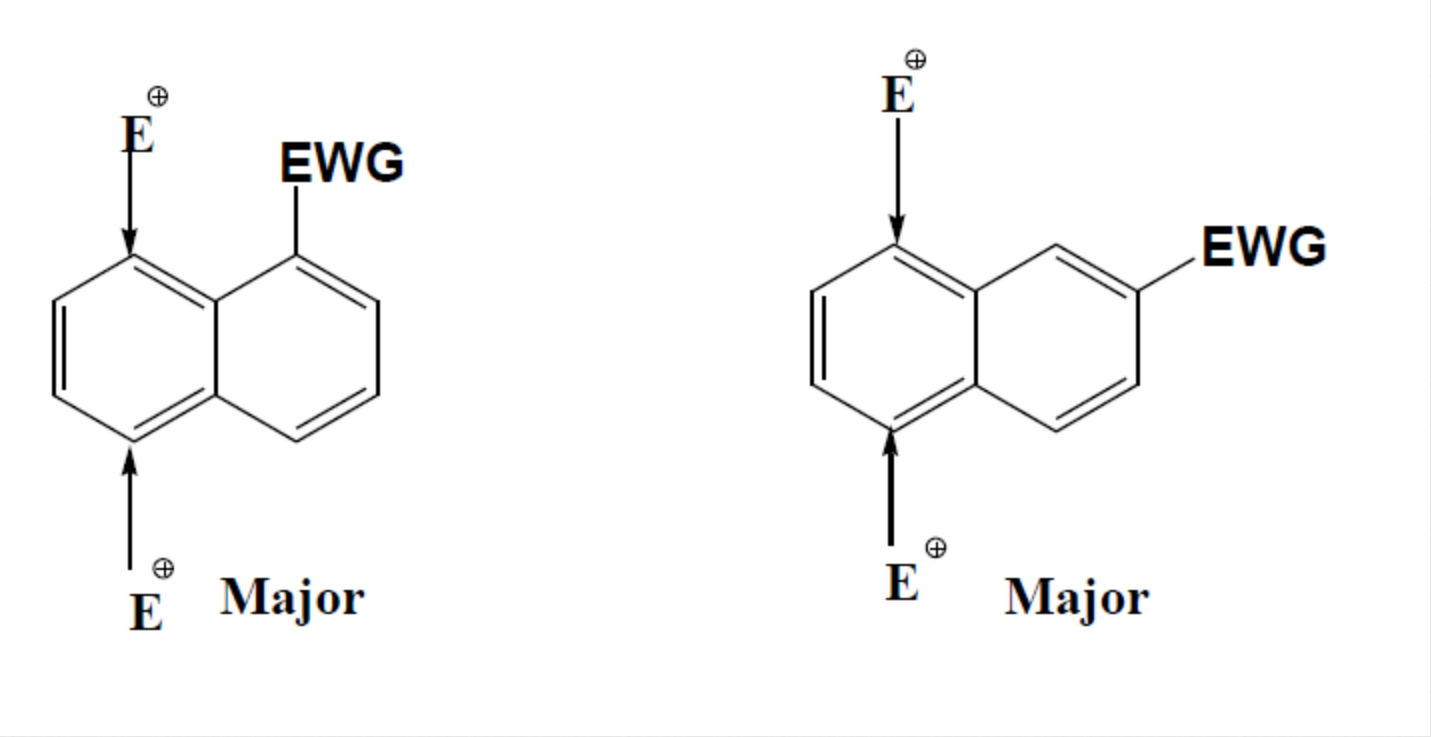
Electrowithdrawing grou (EWG)
NO2, SO3H, CO, COOH,

Homonuclear attack

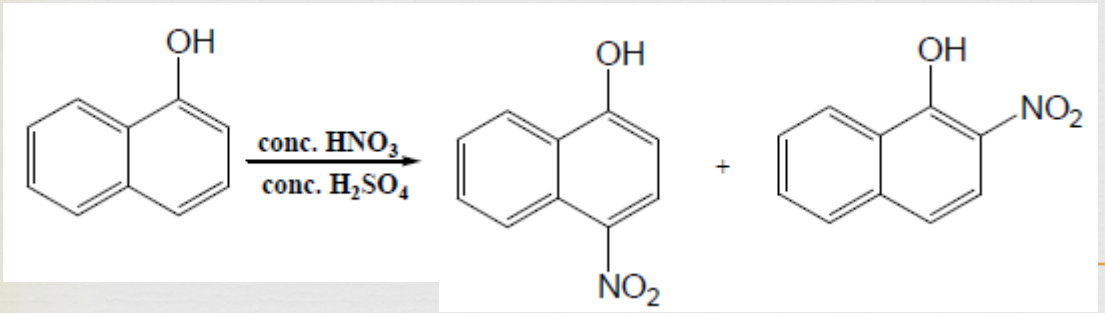




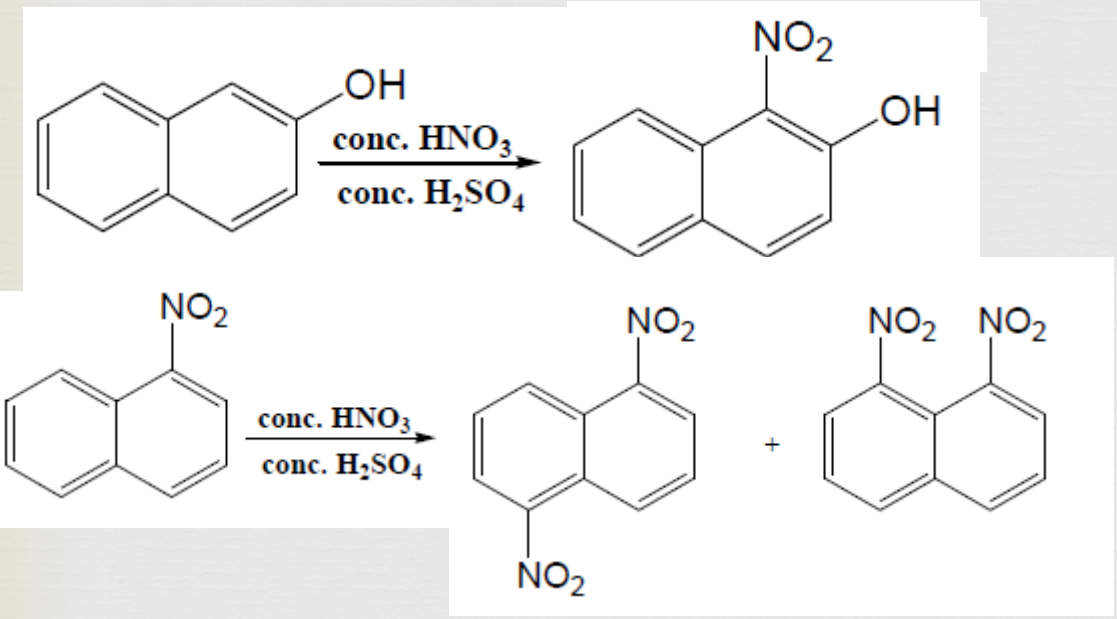
Heteronuclear attack



Examples

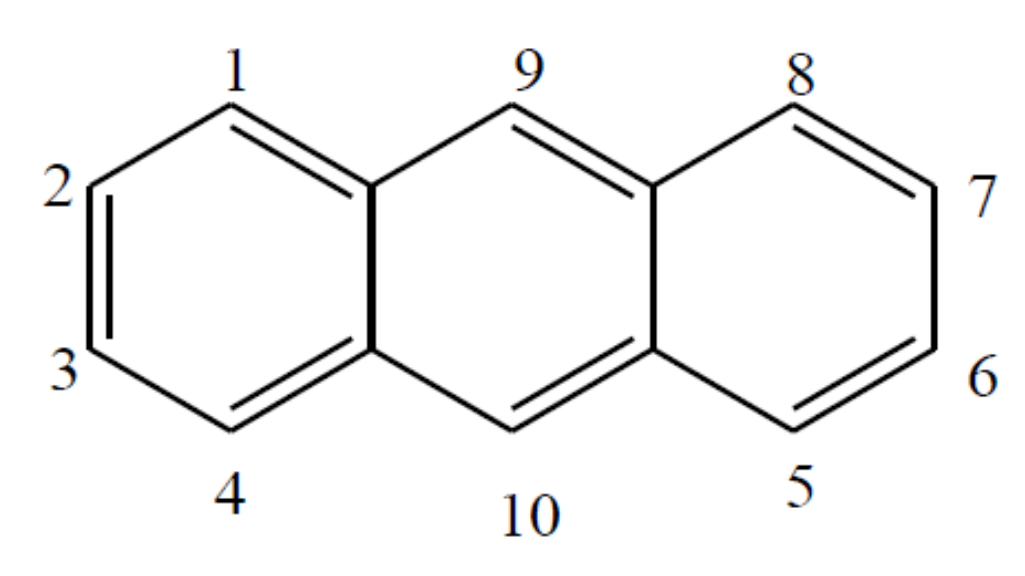


Major



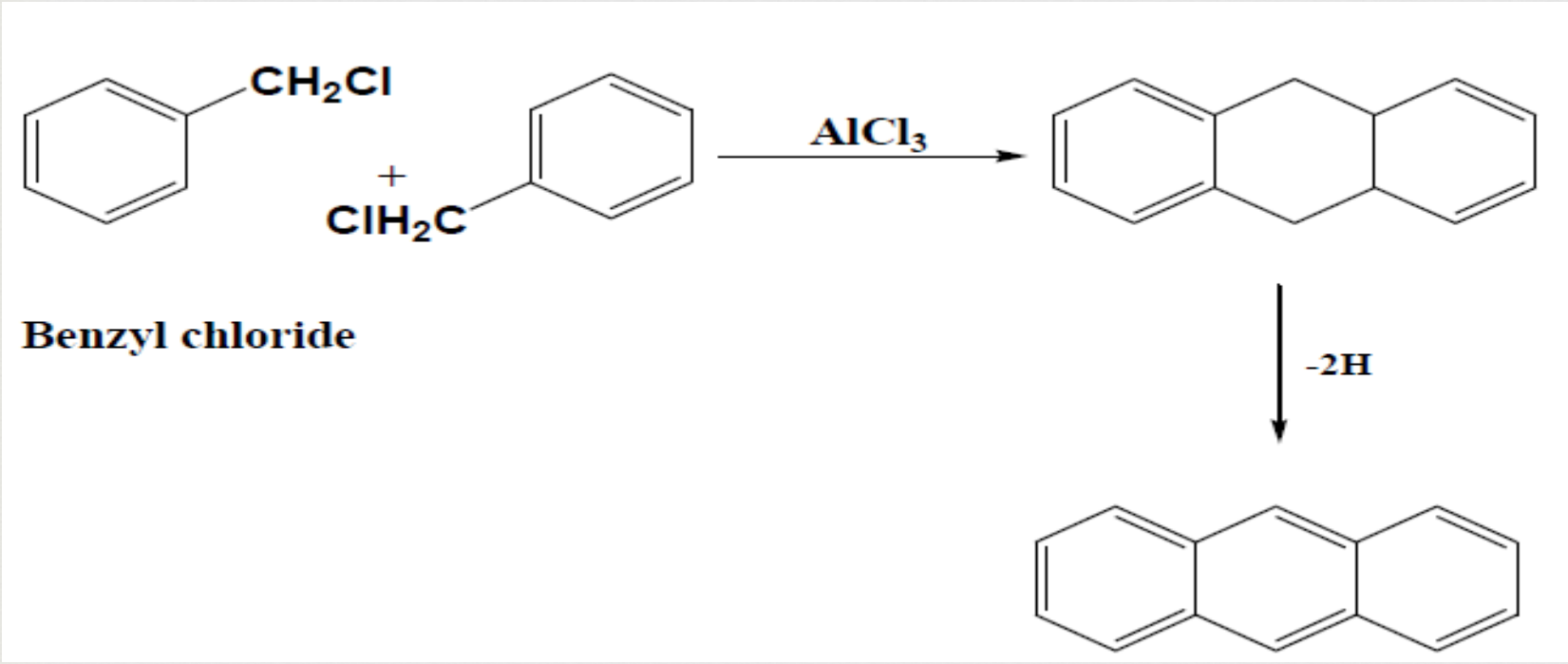
Major **Minor**

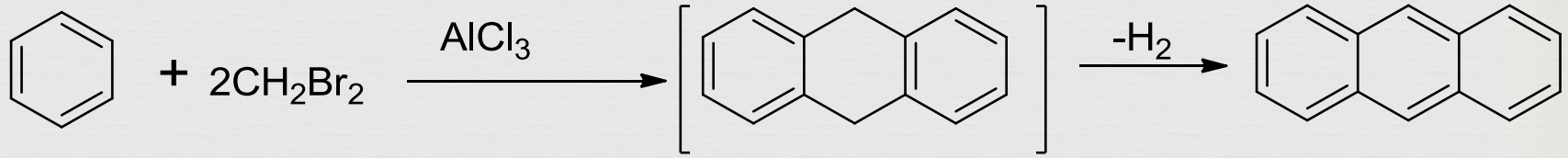
Anthracene



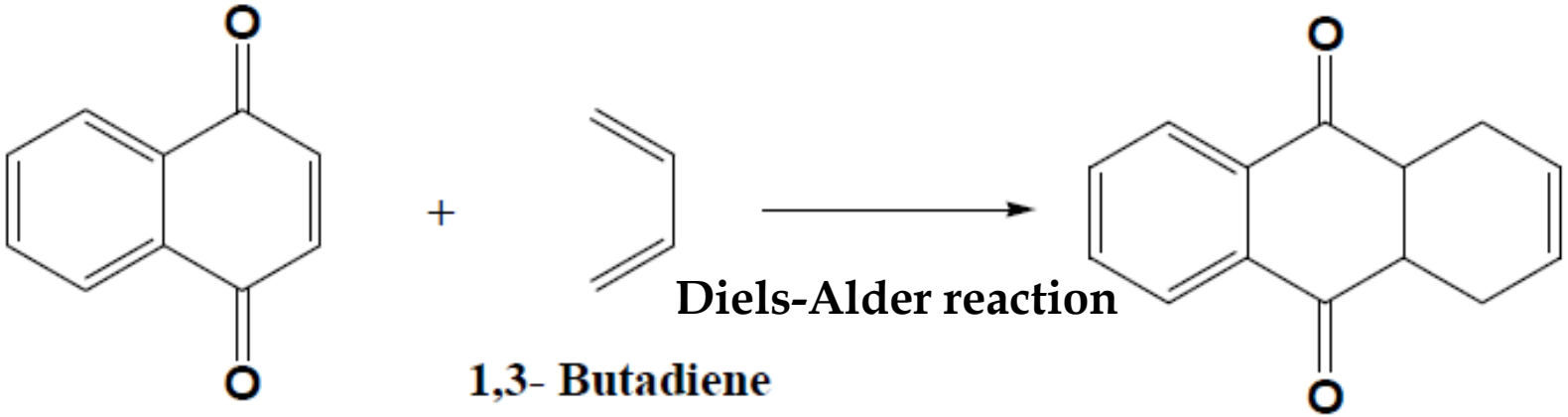
Synthesis of anthracene

1- Friedl Crafts



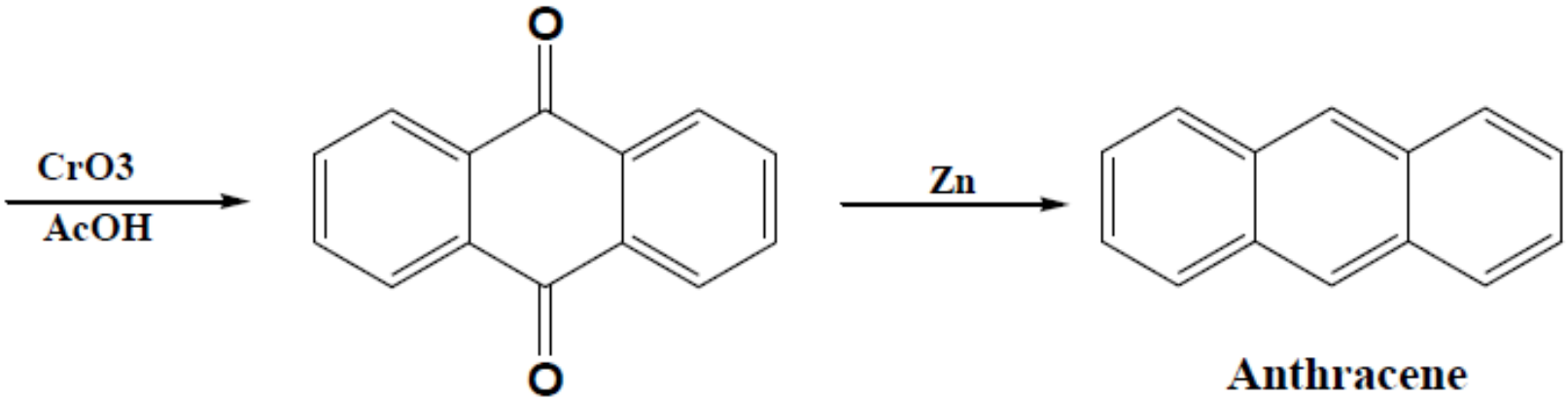


- 3. From 1,4- Naphthoquinone



1,4- Naphthaquinone

1,3- Butadiene

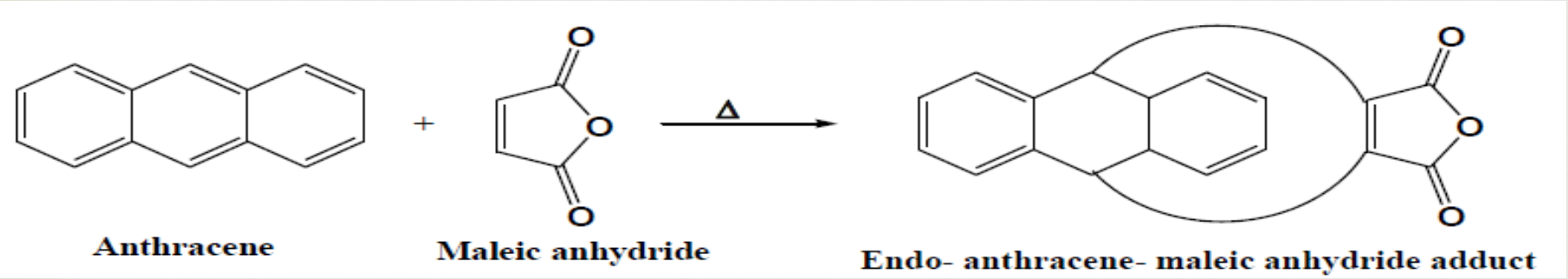


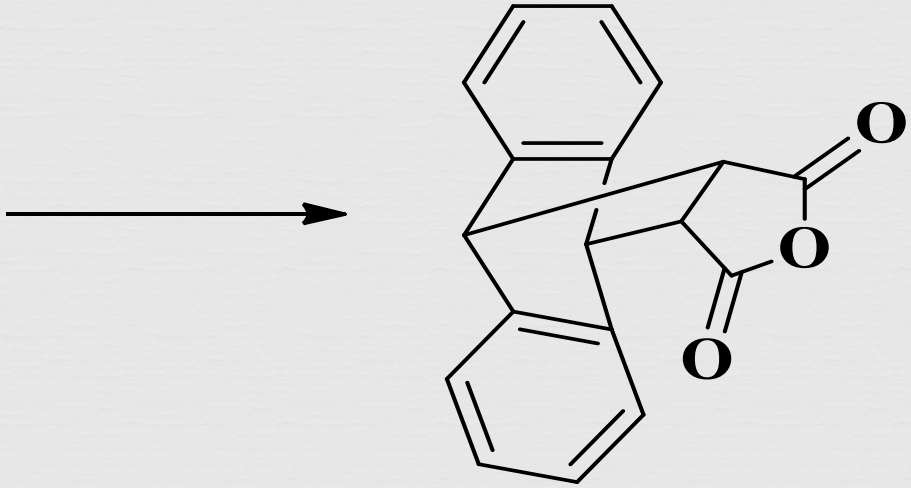
9,10- anthraquinone

Anthracene

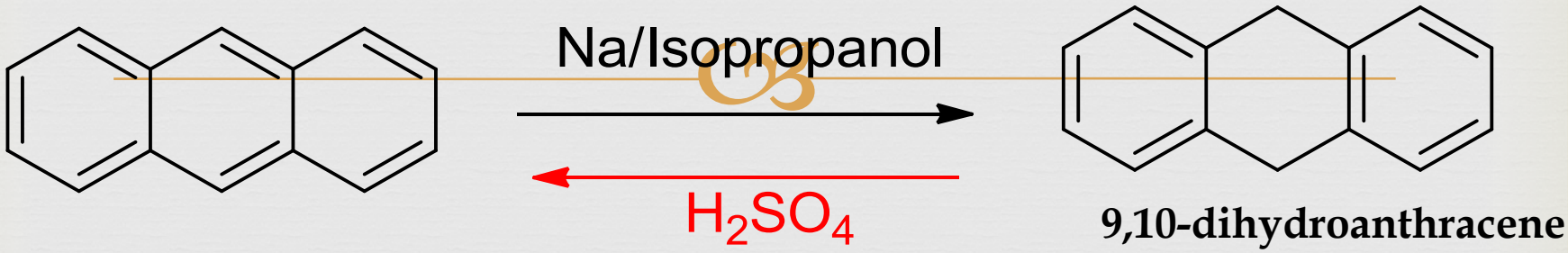
Chemical reactions

1) Diels -Alder

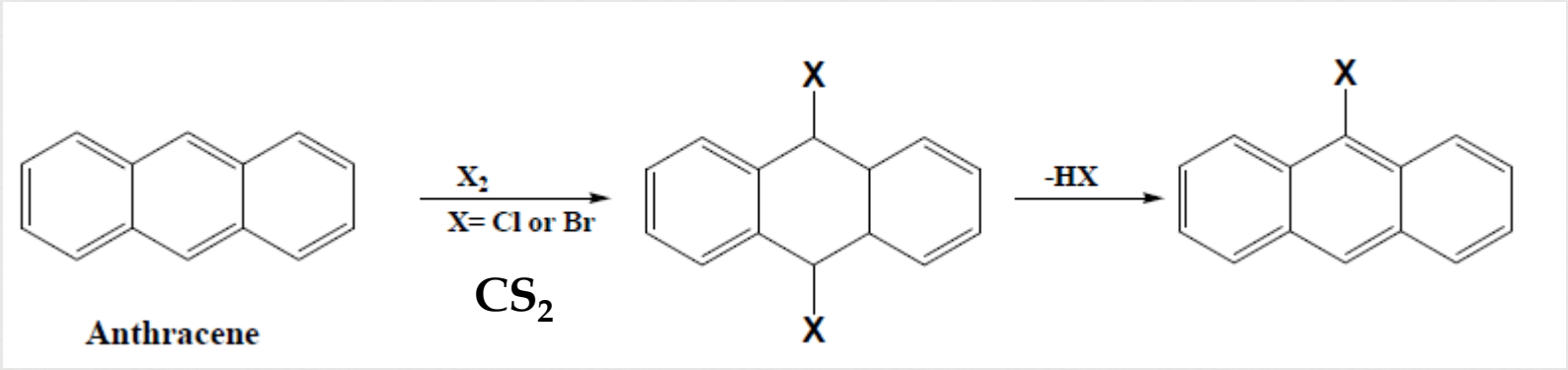




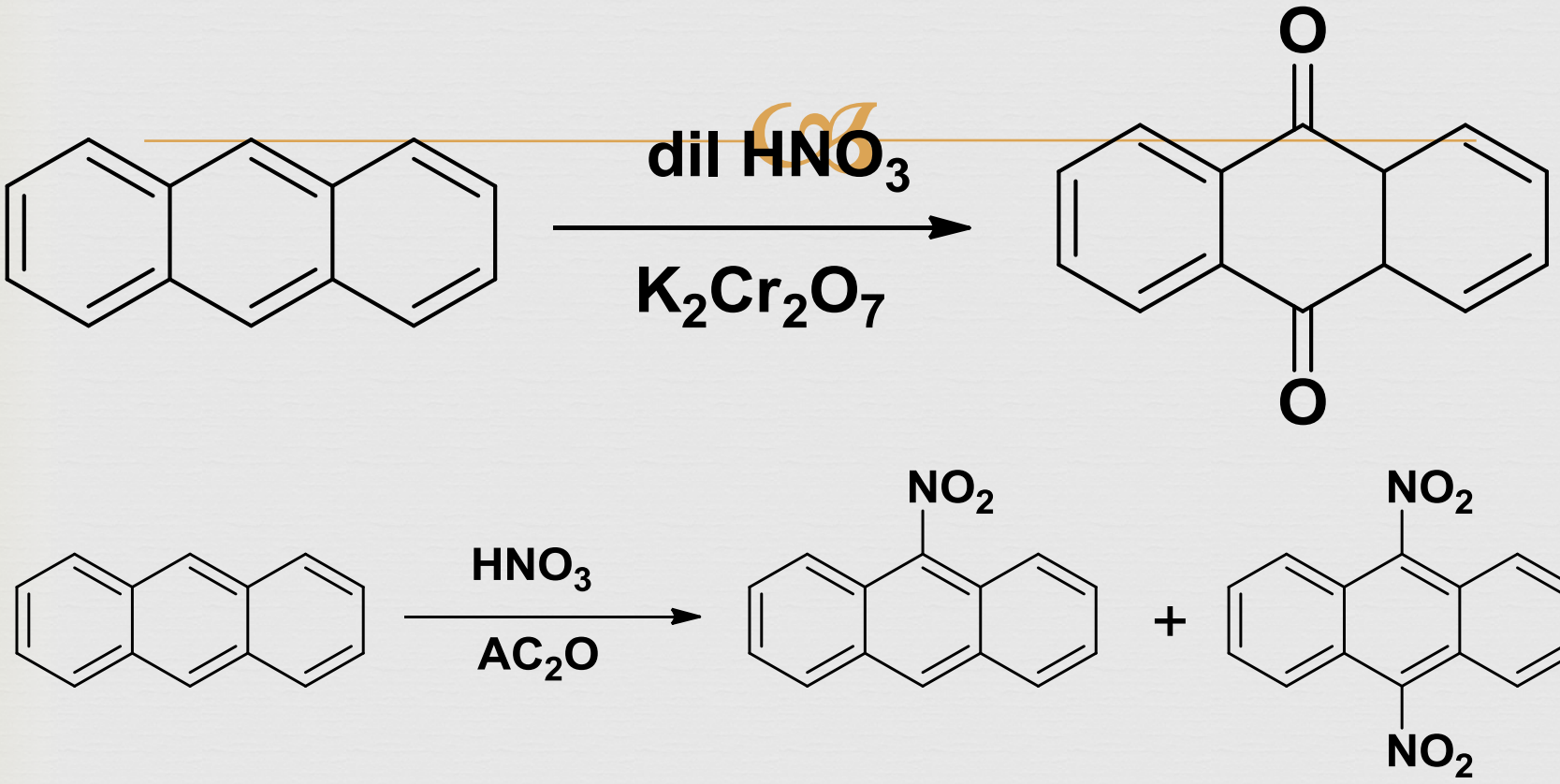
2) Reduction of anthracene



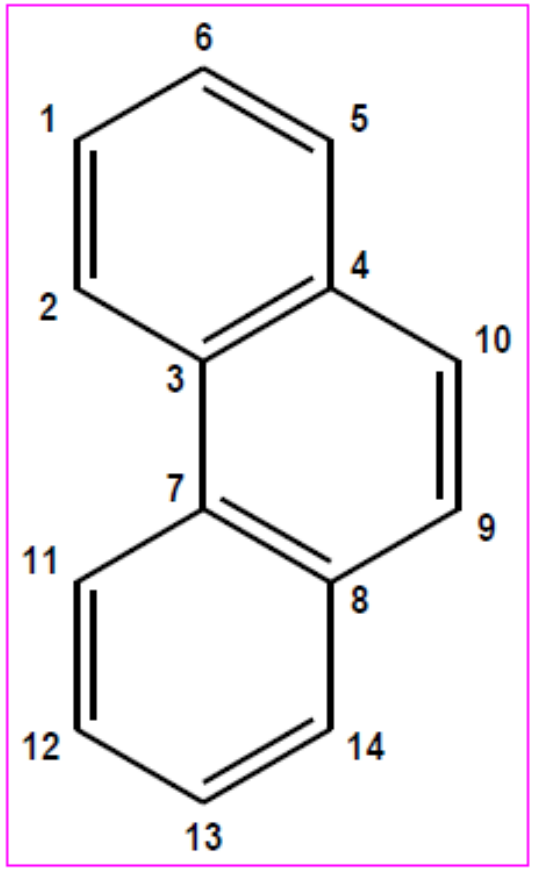
3) Halogenation of anthracene

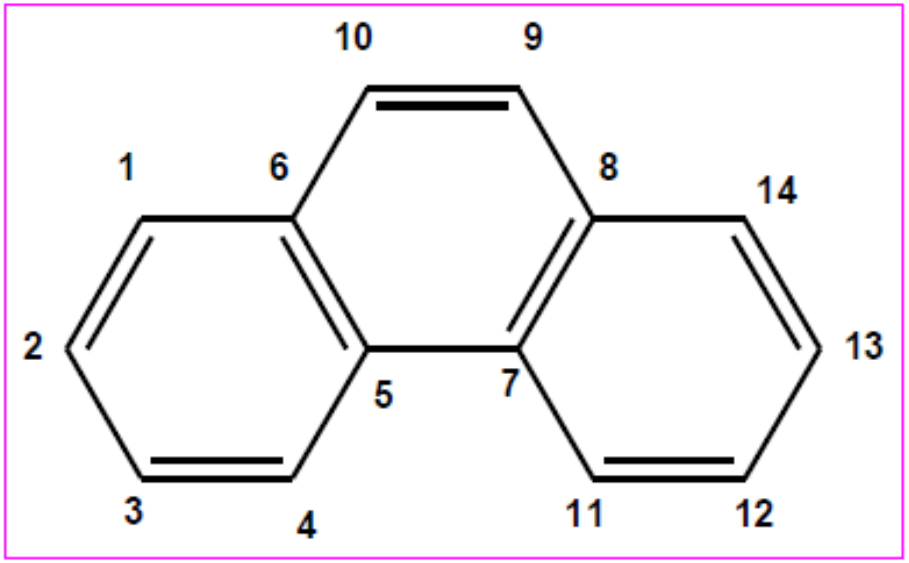


5) Nitration of anthracene



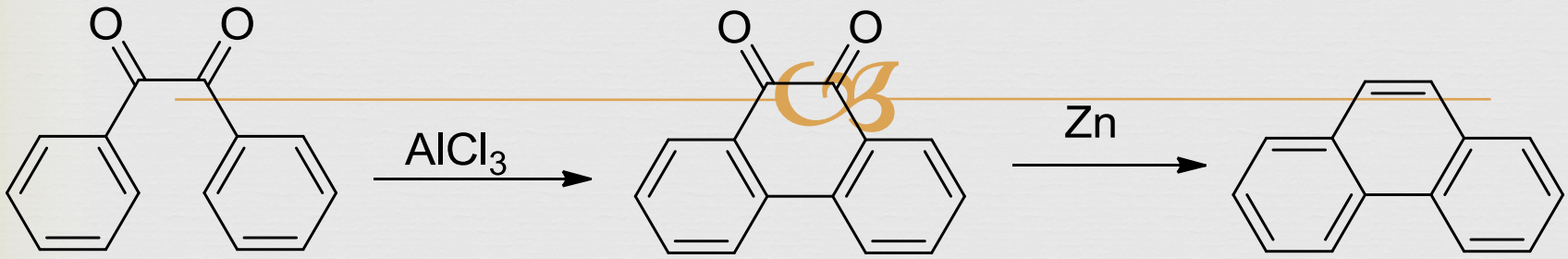
Phenanthrene





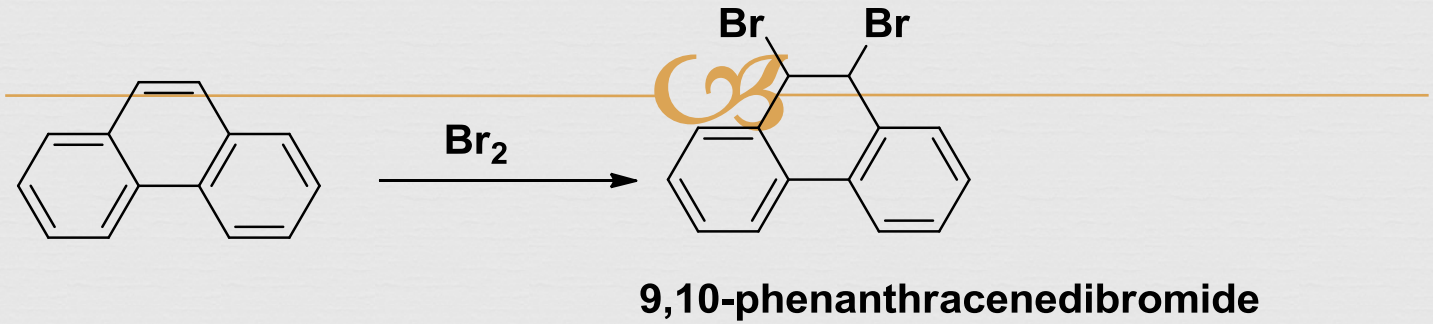
Preparation of phenanthrene

1- By benzil



Chemical reactions:

1) Brominatin reaction



9,10-phenanthracenedibromide