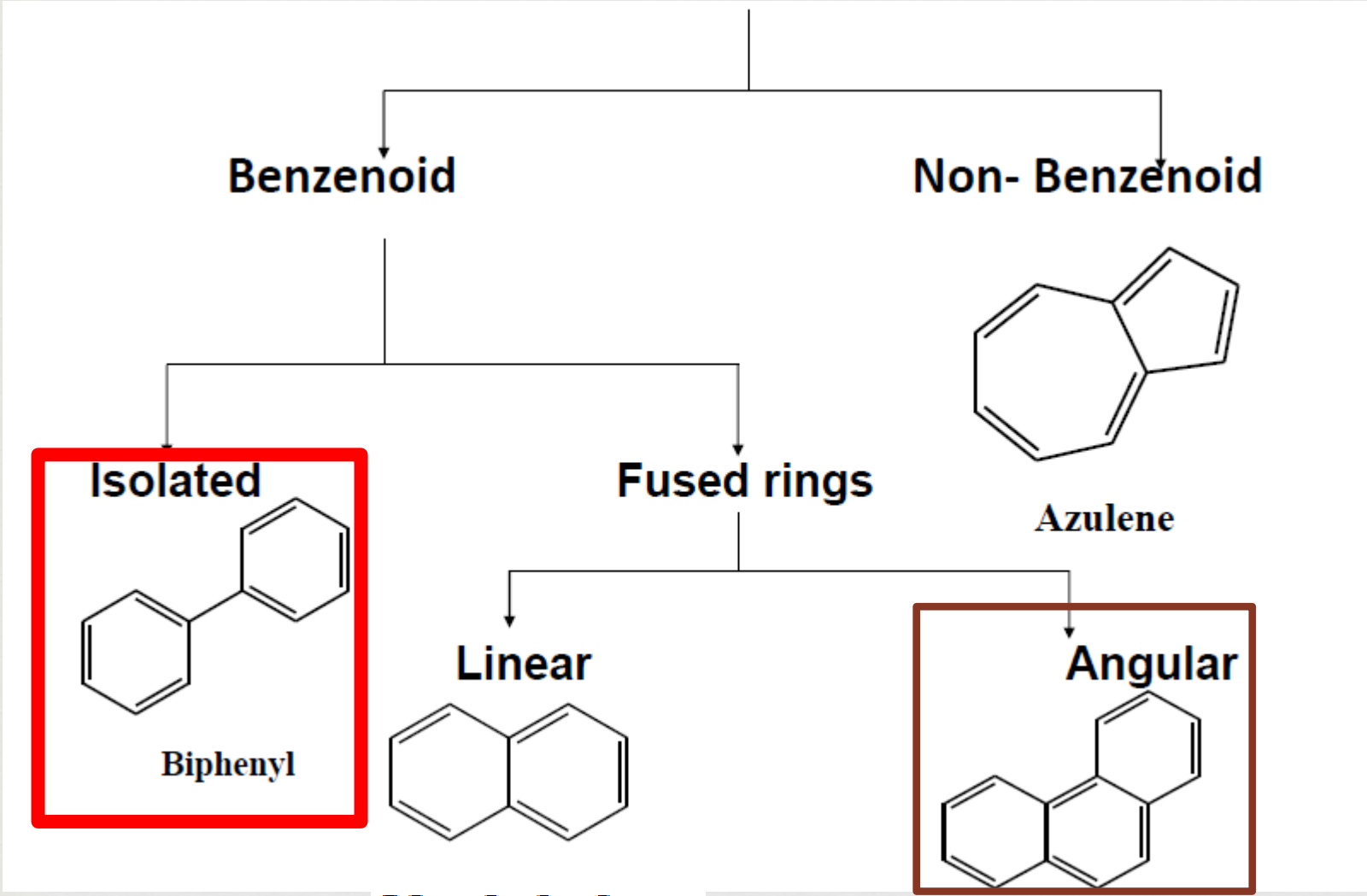
Polynuclear Aromatic Hydrocarbons

Prepared by

Dr. Ahmed Gaber Mohammed Taha

Polynuclear Hydrocarbons



- Contents

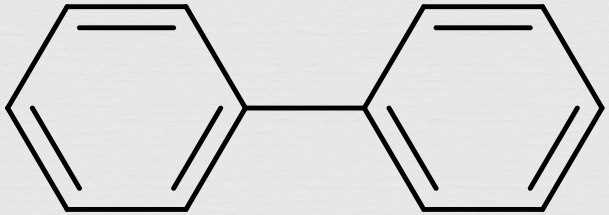
1- Isolated systems

- Biphenyl
- Biphenylderivatives
- Benzoine
- Benzil

2- Fused systems

- Naphthalene
- Anthracene
- phenancethracene

1- Isolated rings
a) Biphenyl



(i) Properties:

1- **Crystalline solid**

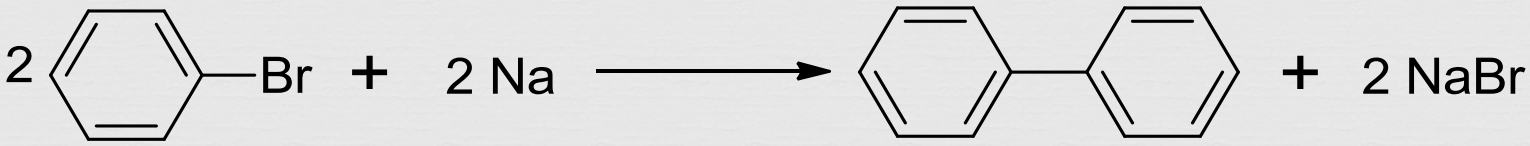
2- m. p. 71 C

3- Insoluble in water but soluble in ethanol or ether

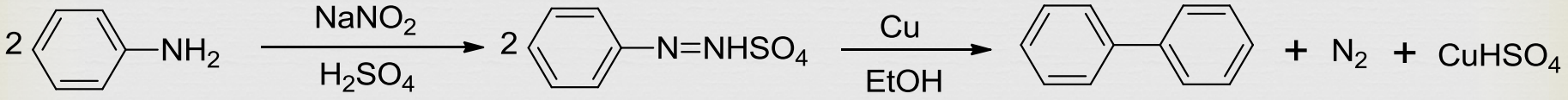
4- Occurs in small quantities in coal tar

(ii) Preparation of biphenyl

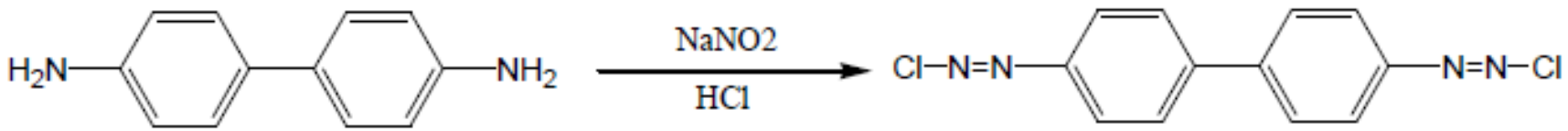
1- By Fittig reaction



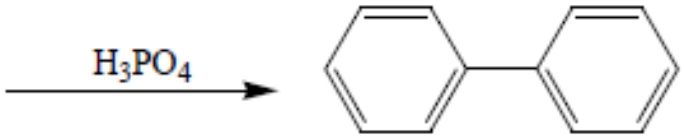
2- From benzene diazonium sulphate



3- From benzidine

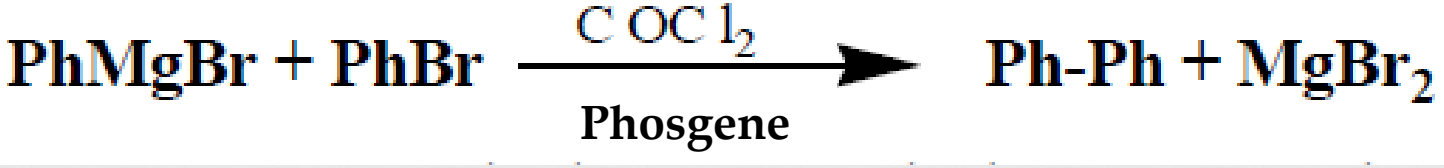


Benzidine

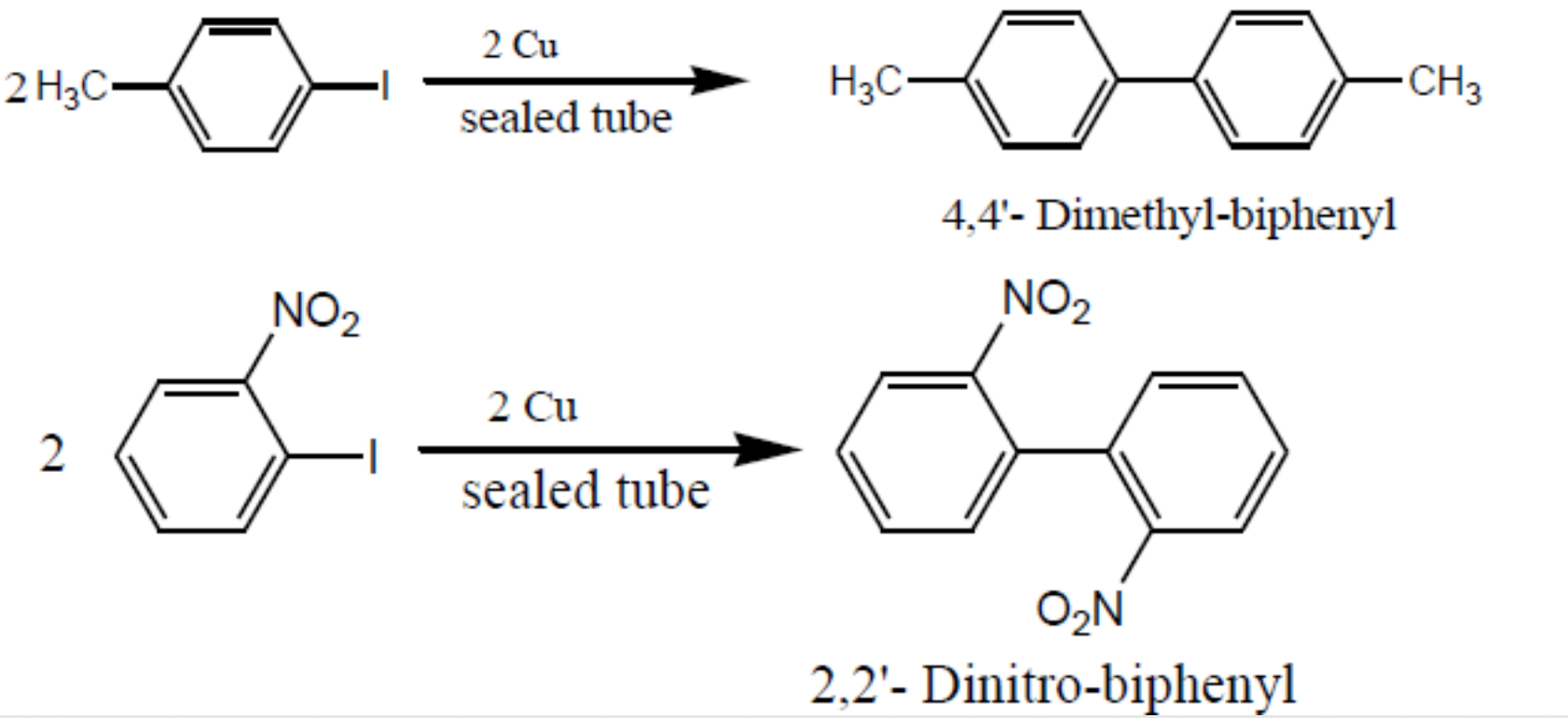


Biphenyl

4- By using arylmagnesium halid

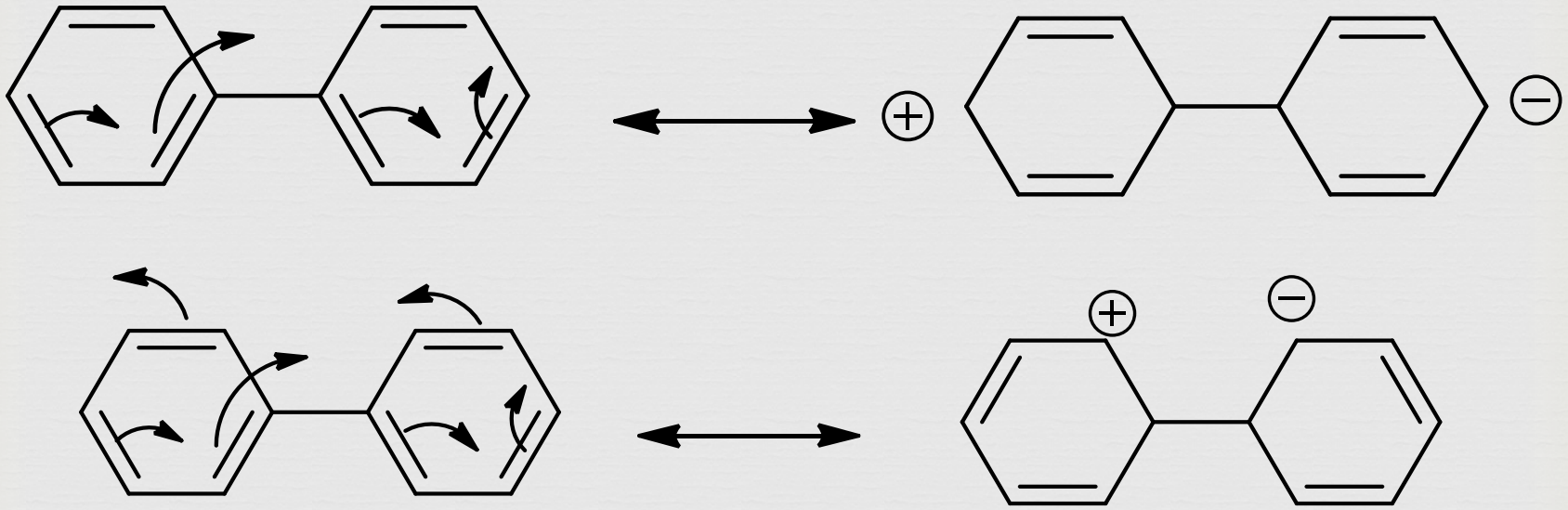


5- Ulmann reaction

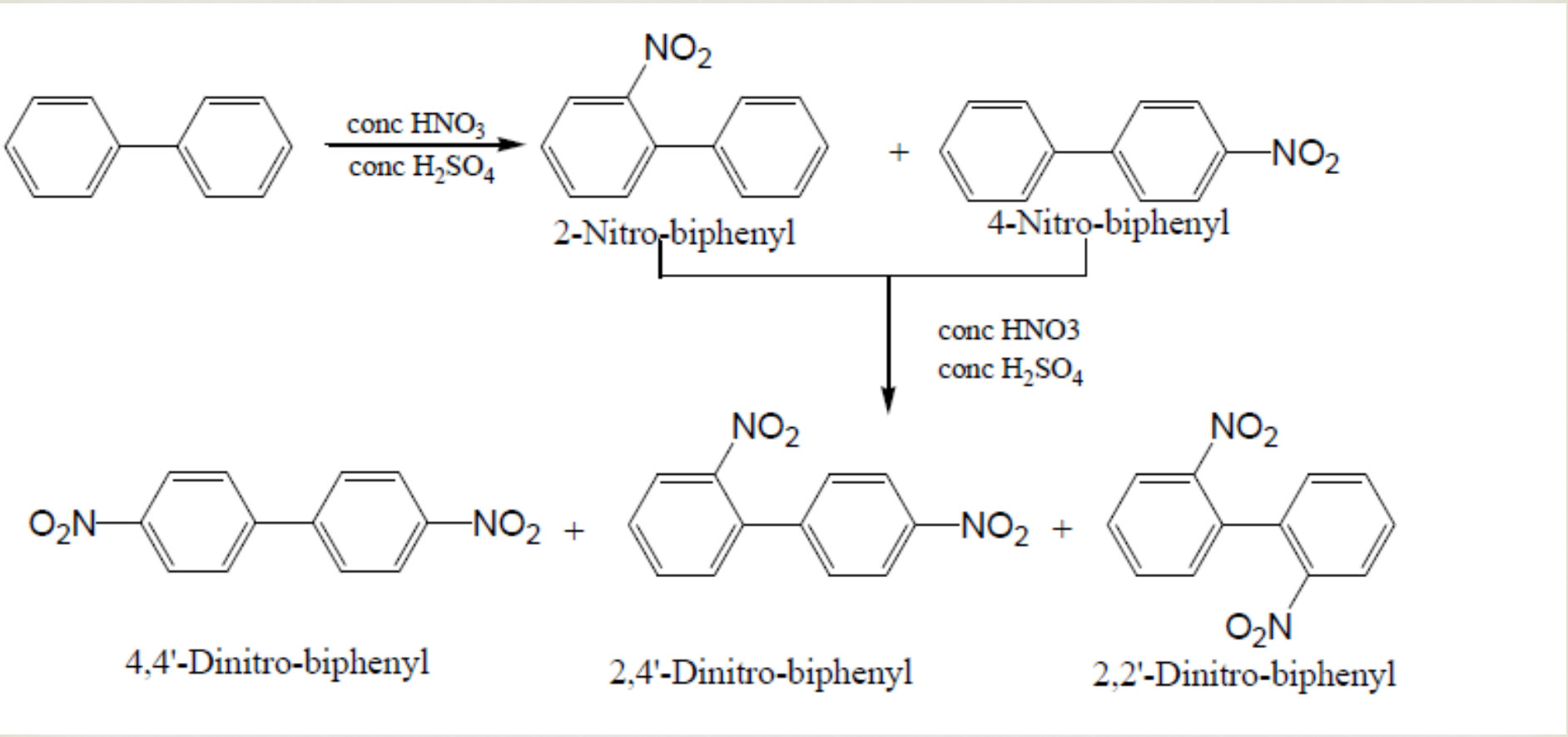


(iii) Reactions of biphenyl

A- Substitution reactions



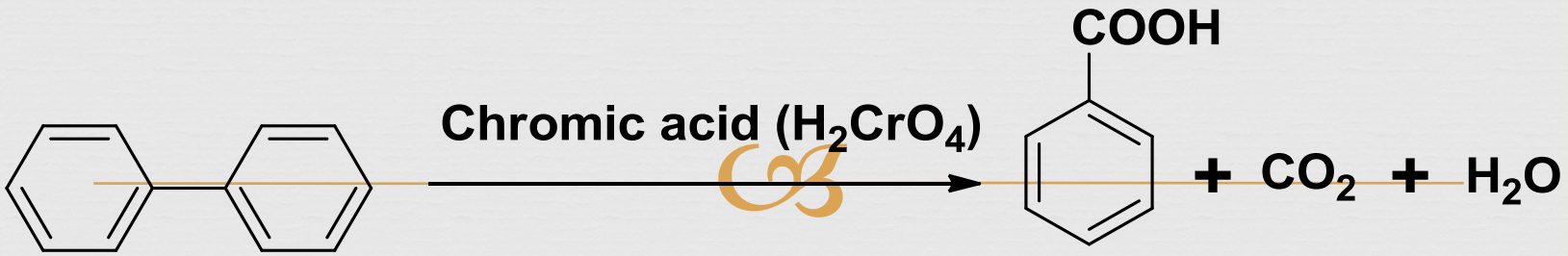
In biphenyl one ring act as electron donating group and the other act as electron withdrawing group



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

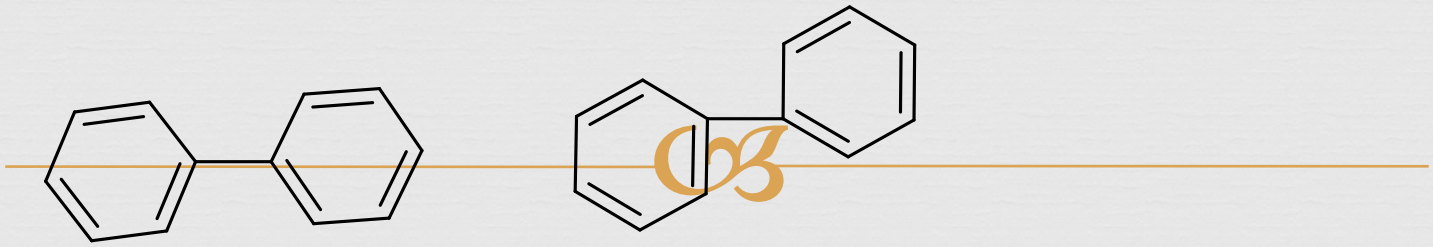
The 2nd substitution occurs in the empty ring in 2 or 4- position.

B) Oxidation

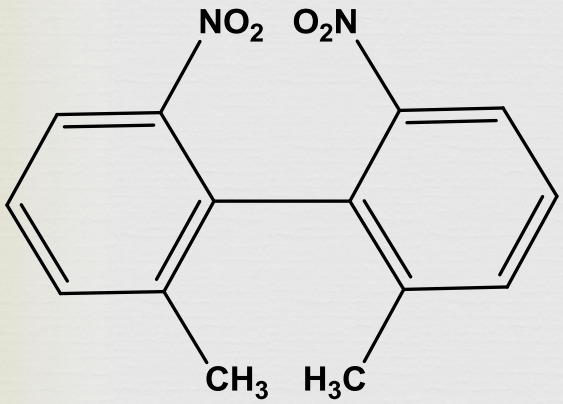


C) Ozonolysis

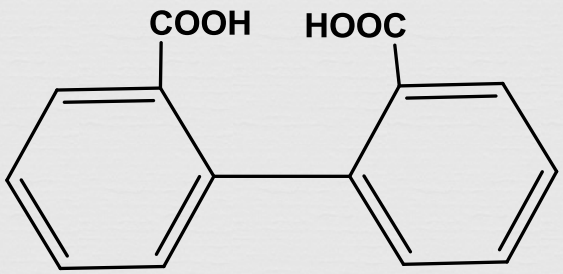
Stereochemistry of biphenyl



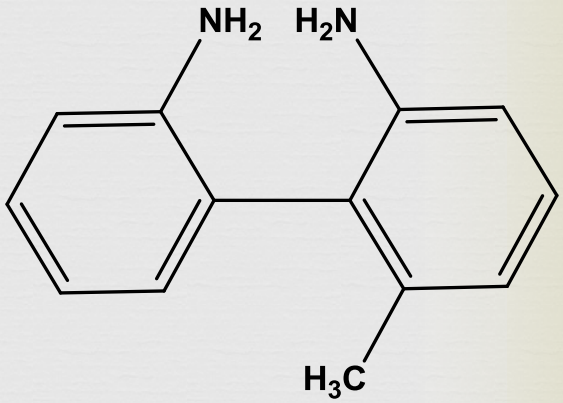
This rotation is restricted if :
A- at least three of the postions 2,2′, 6 and 6′ are occupied
B- two sbustitents large enough are introduced in the 2, 2′ positions



6,6′ -dinitro-2,2′-dimethyldiphenyl



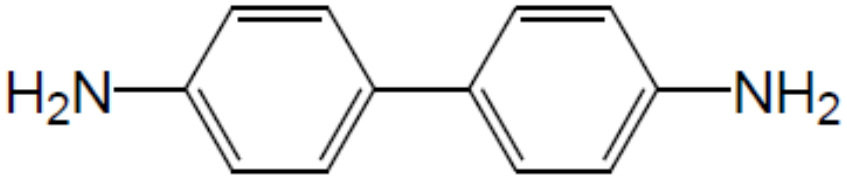
Diphenyl-6,6-dicarboxylic acid



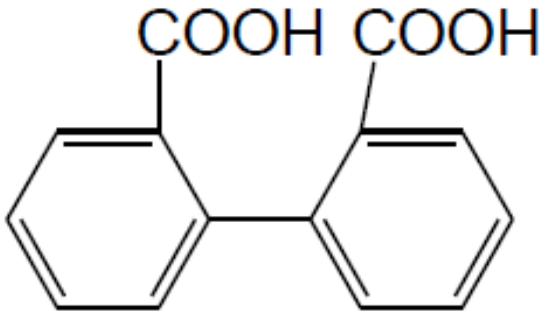
2,2′ -diamino-6-methyldipheny

Biphenyl derivatives

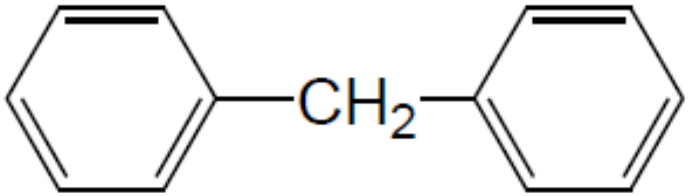
(1) Benzidine (4, 4`-diaminobiphenyl)



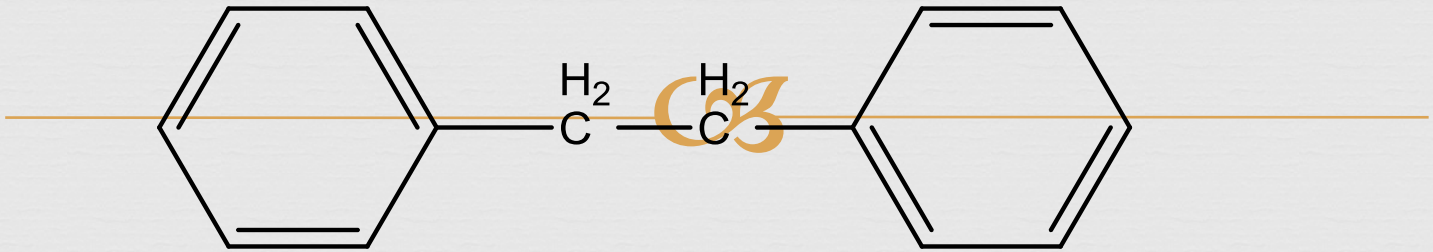
(2) Diphenic acid



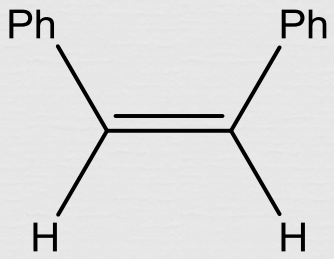
(3) Diphenyl methane



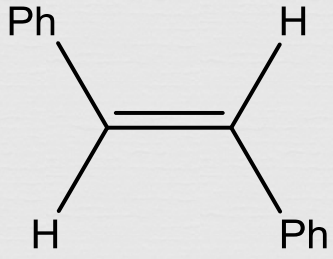
(4) 1,2-diphenylethane



(5) Stilbene and isostilbene



Isostilbene (cis diphenylethylene)



Stilbene (trans diphenylethylene)

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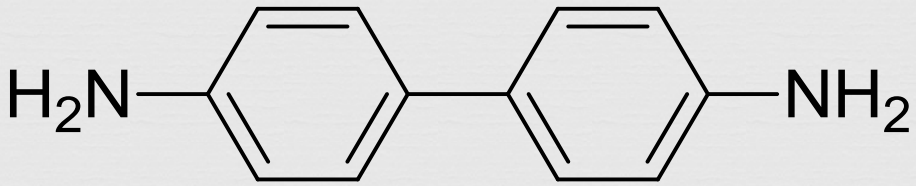
Benzidine

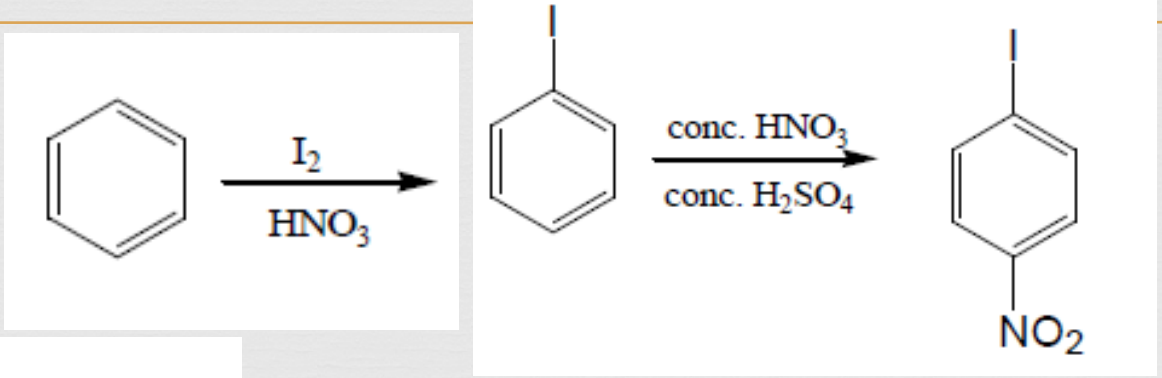
- 1- colourless solid.
- 2- m.p. 127°.
- 3-soluble in hydrochlorides.
- 4- used in the preparation of azo-dyes.

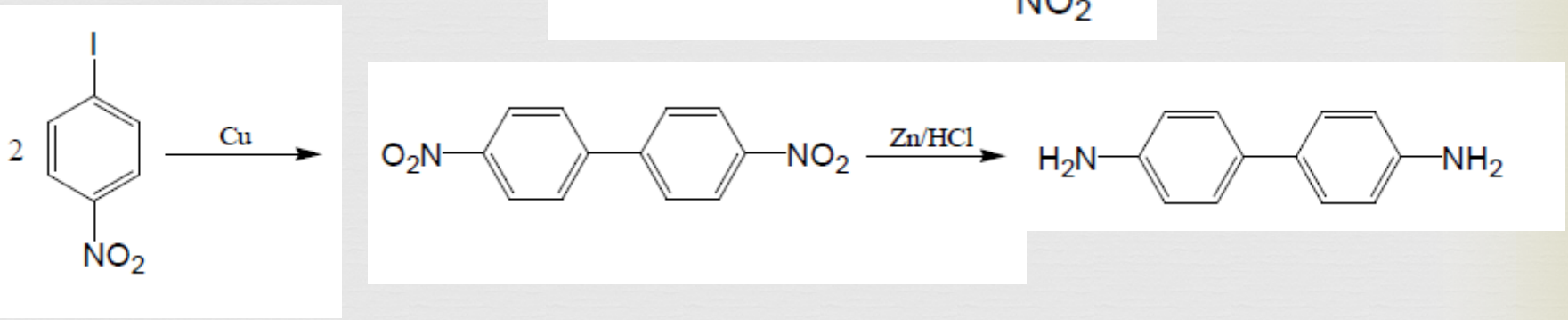


Benzidine

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

- Answer



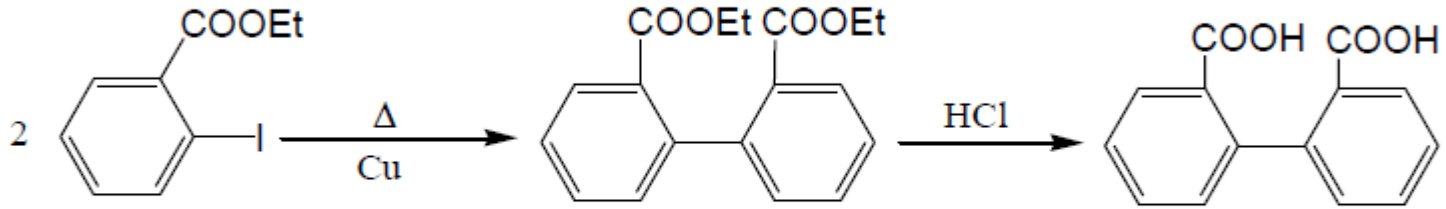


2- from hydrazobenzene through benzidine rearrangement

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

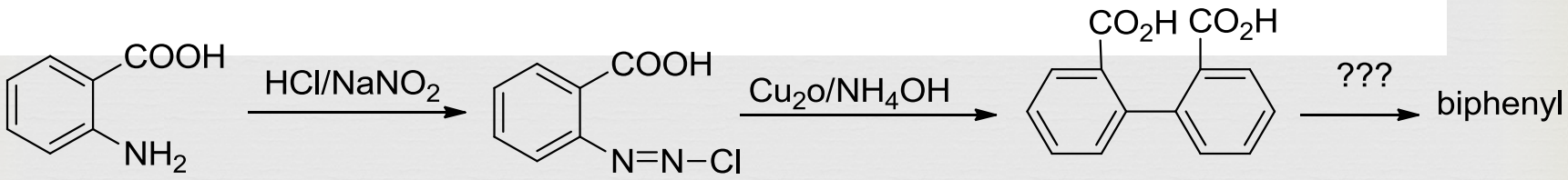
Prepreation

1- By Ulmann reaction

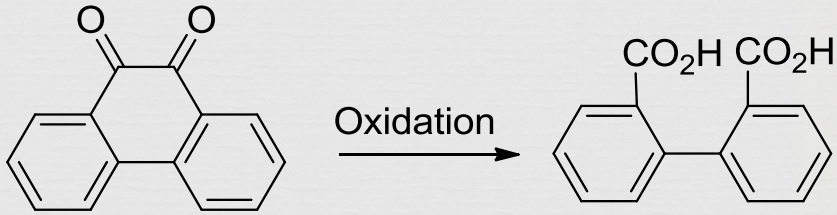


biphenyl- 2,2'- dicarboxylic acid
(Diphenic acid)

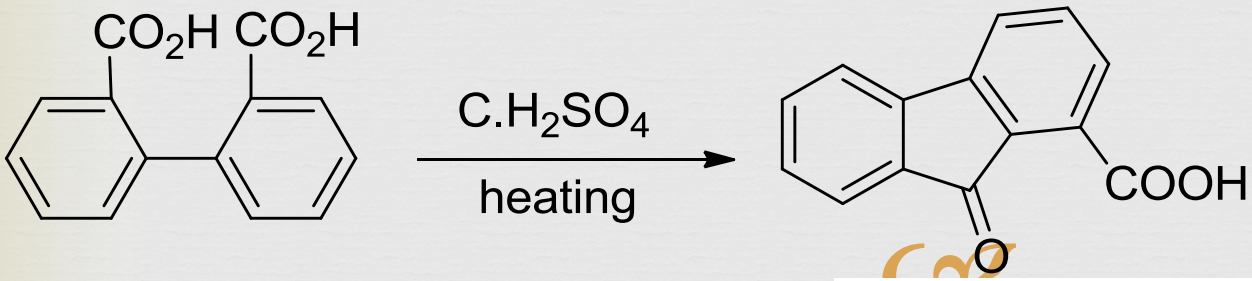
2- Via anthranilic acid



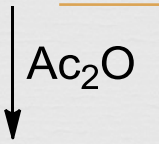
3- By oxidation of phenanthraquinone

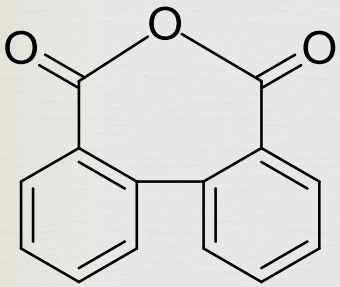


The chemical reactions

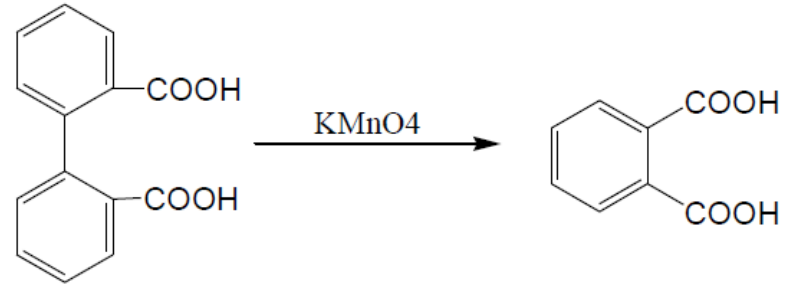


9-Fuorenone-2-carboxylic aci

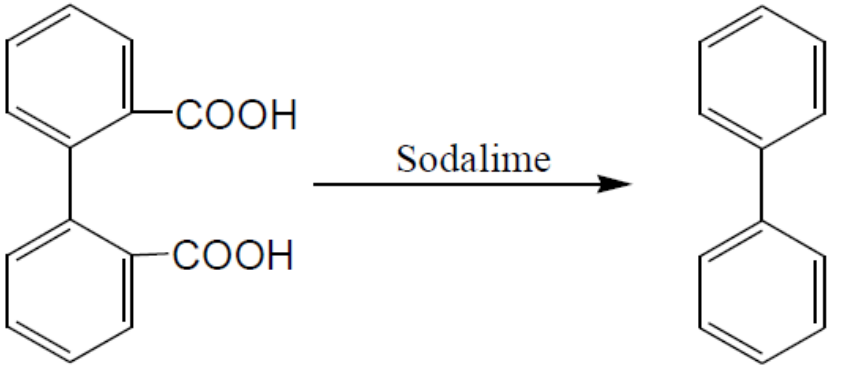




Diphenic anhydride



Diphenic acid **pthalic acid**



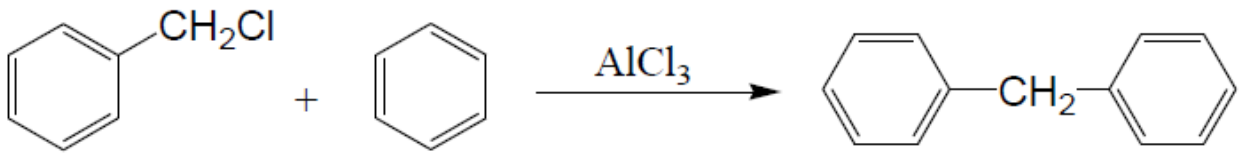
Diphenic acid **biphenyl**

Diphenylmethane

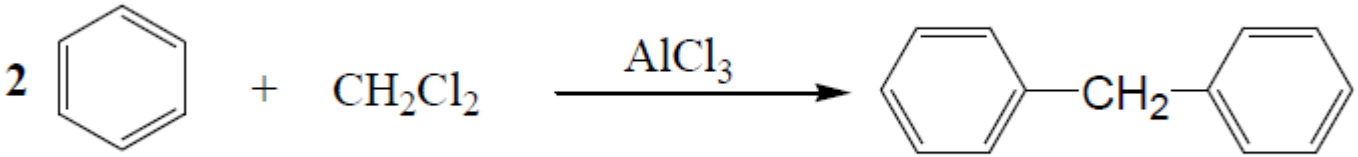
It is crystalline solid, m.p. 26 °

- preparation

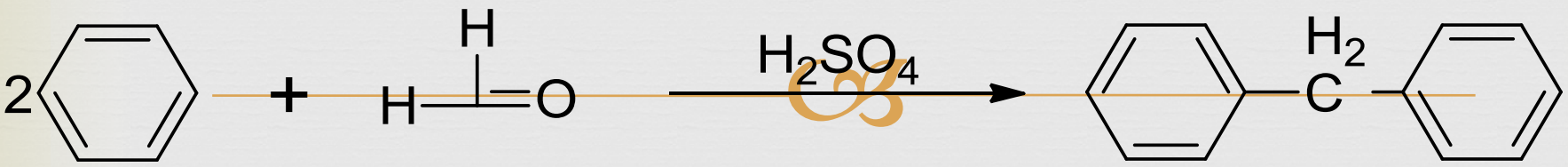
1- By Friedle crafts



Benzyl chloride **Diphenyl methane**



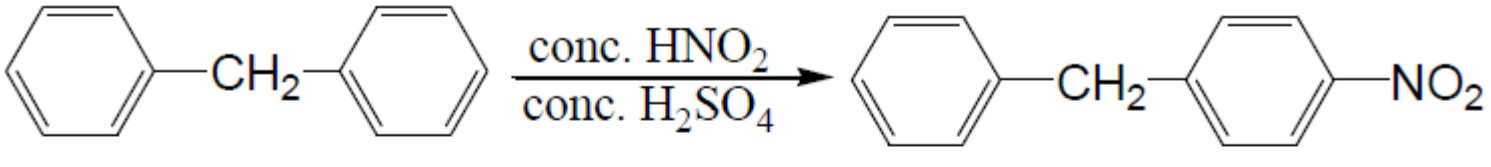
2- By condenzation one molecule of formaldehyde with two molecules of benzene in the presence of sulfuric acid.



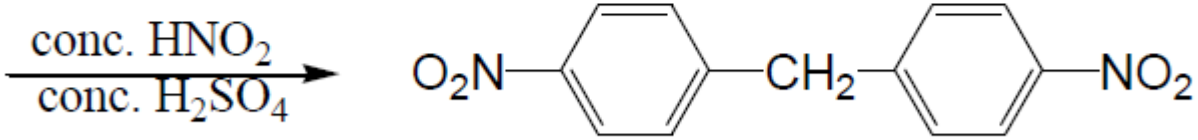
3- By heating benzophenone with hydroiodic acid and red phosphorous.

- **Reactions**

a) Nitration

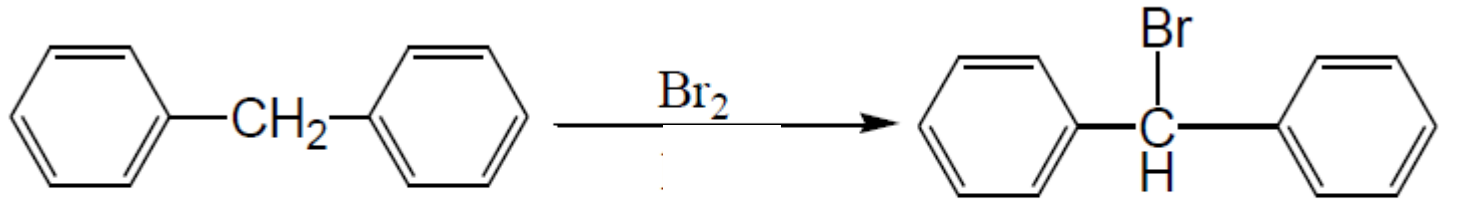


Diphenyl methane **1-benzyl-4-nitrobenzene**



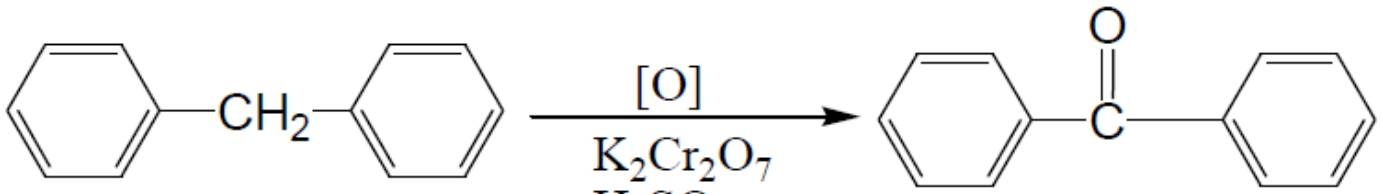
bis(4- nitrophenyl)methane

2) Brominating



Diphenyl methane **Diphenylmethylbromide**

3) Oxidation



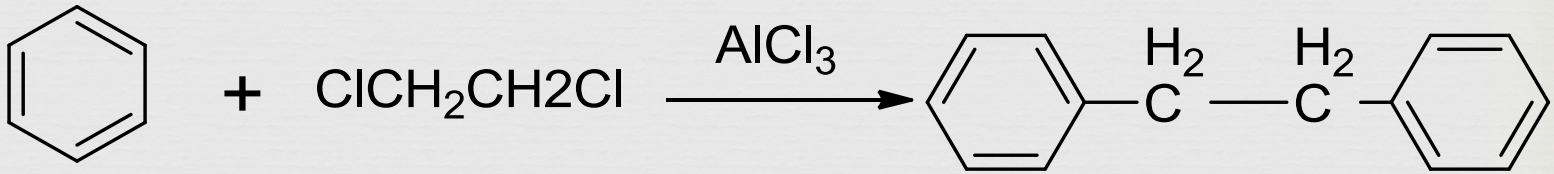
Diphenyl methane **benzophenone**

1,2-Diphenylethane

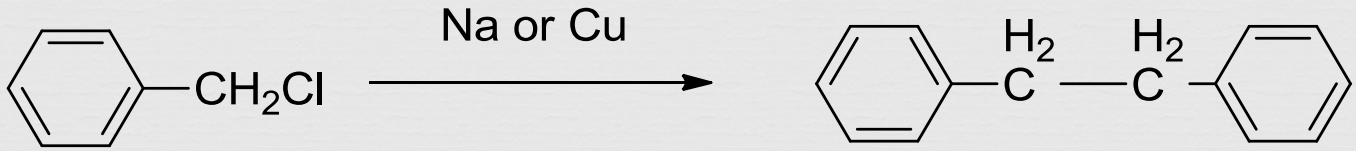
It is a white solide, m.p. 52°

- **preparation**

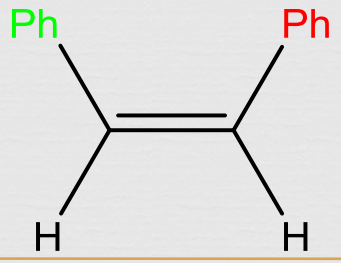
1- By Friedle crafts



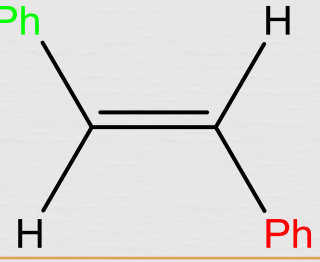
2- By Fittig or Ulmann



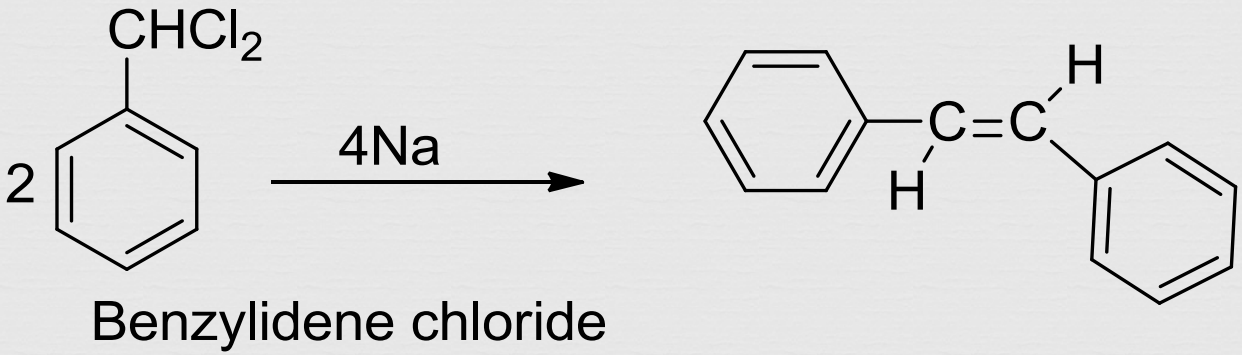
Stilbene and isostilbene



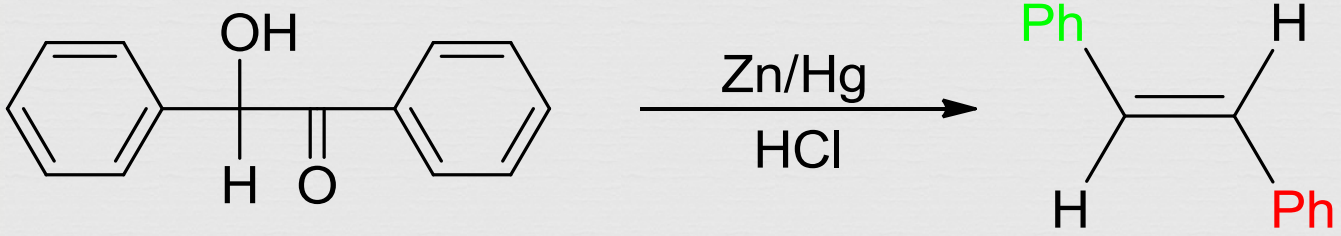
Isostilbene, cis, m.p. 145 C



Stilbene, trans, m.p. 124 C, more stable

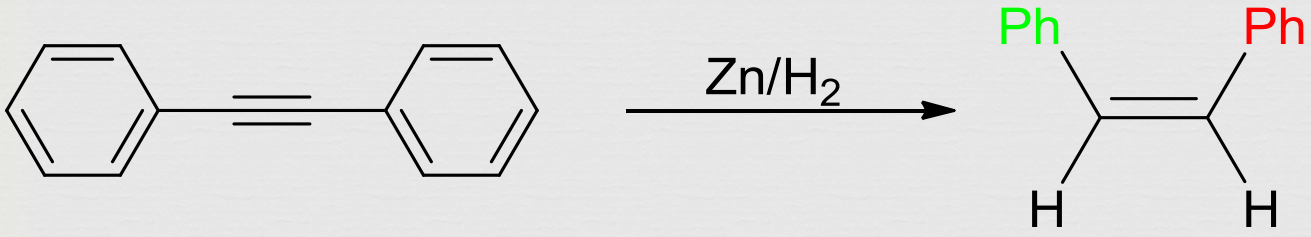


Benzylidene chloride



benzoine

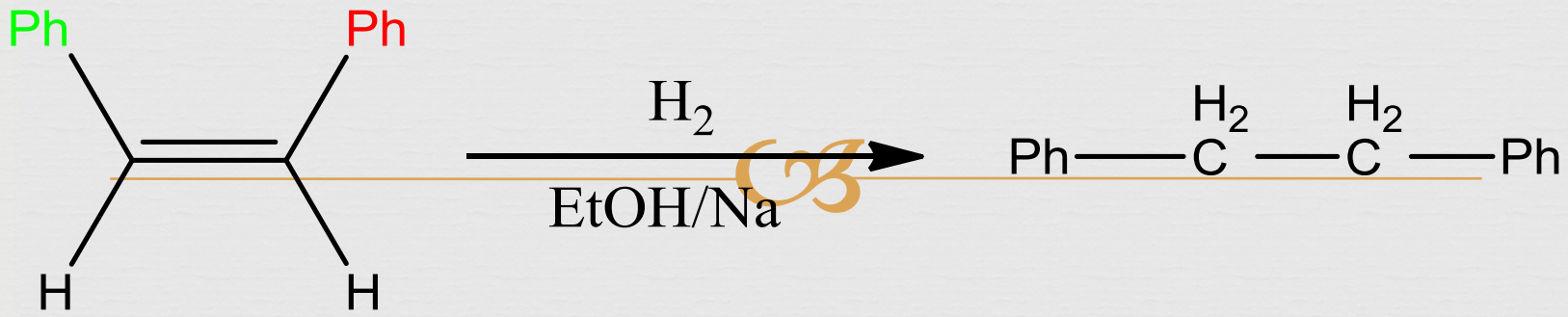
isostilbene



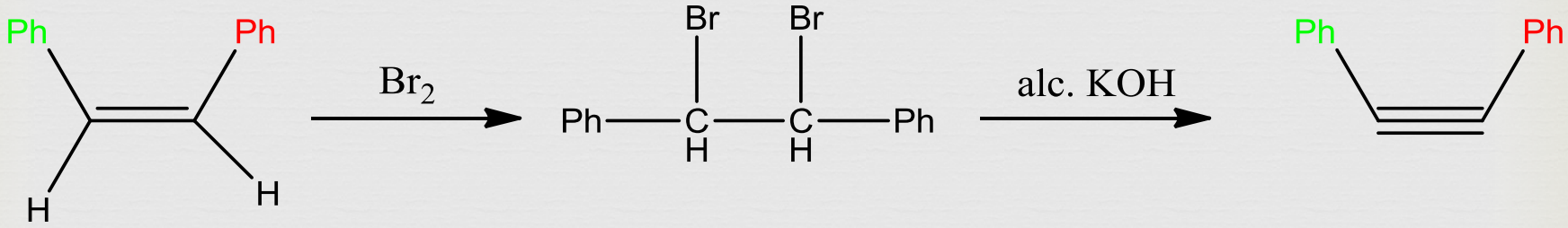
Diphenylacetylene (Tolan)

Reactions

1)



2)



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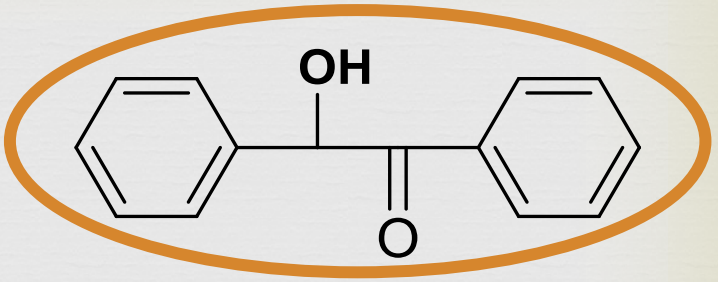
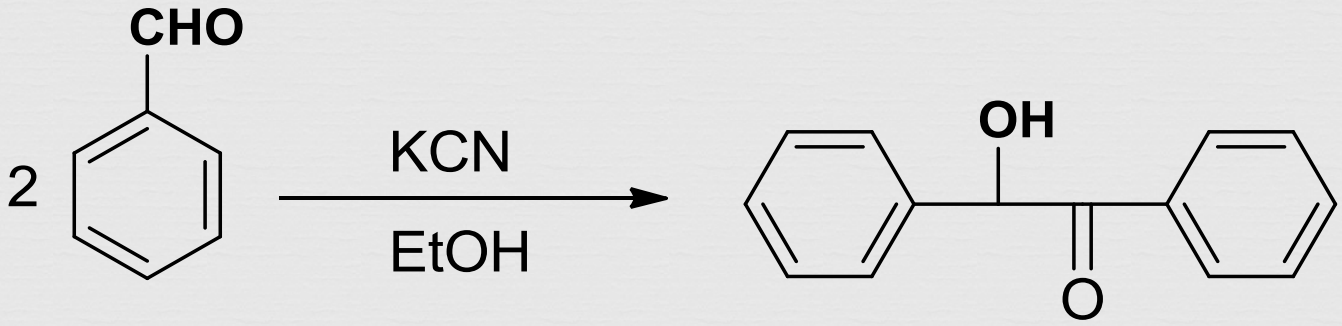
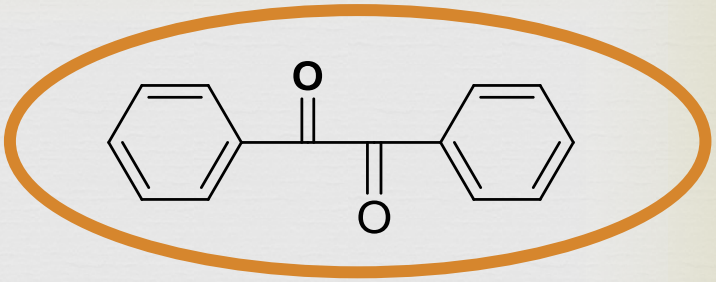
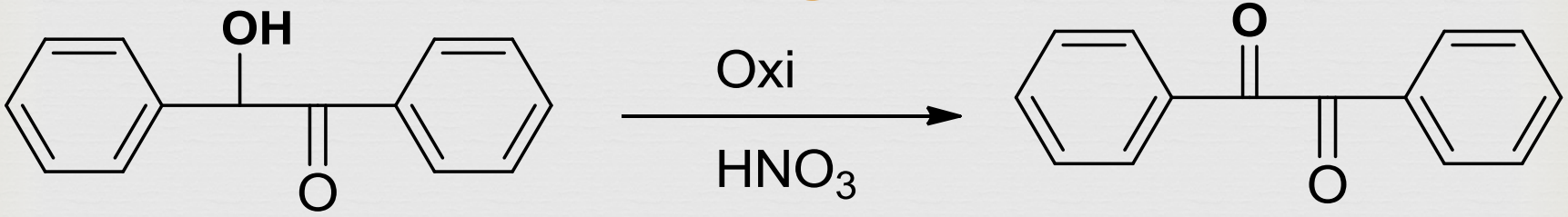
Benzoin



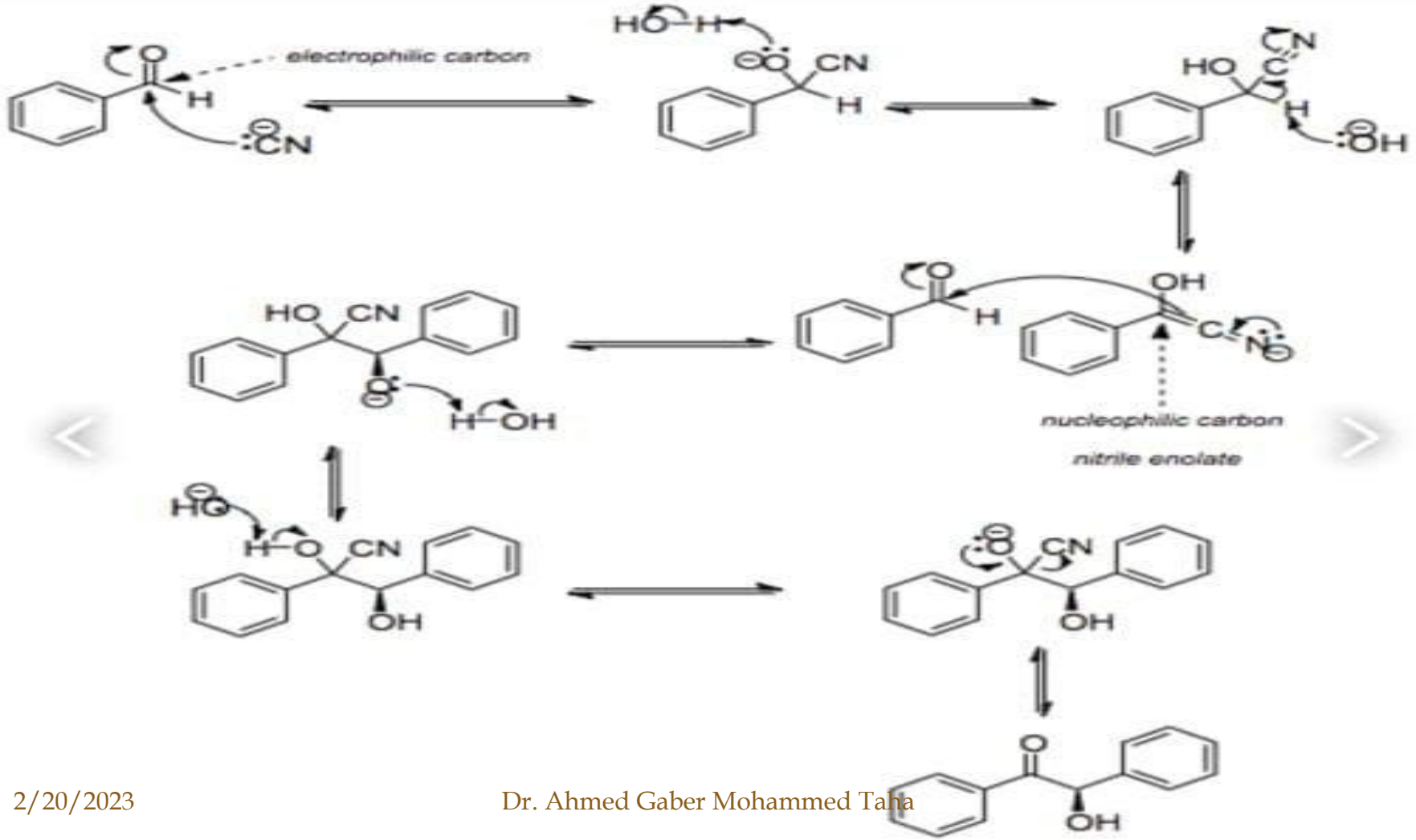


Benzil





Reaction Mechanism اعيد كتابته



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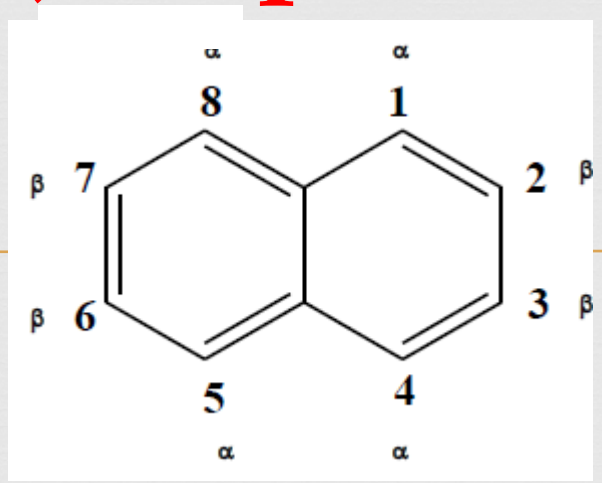
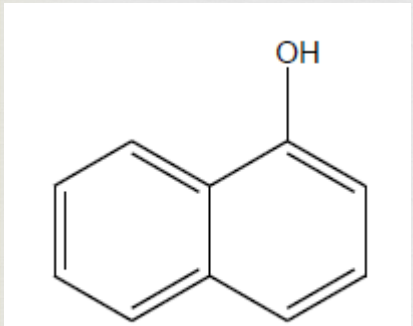
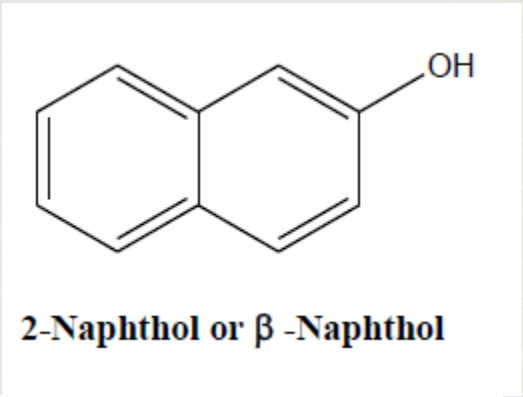
Condensed systems
Or
fused systems

(i) Naphthalene

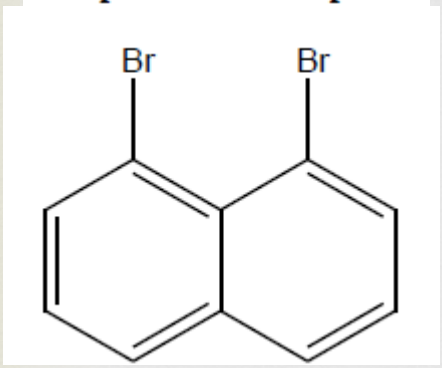




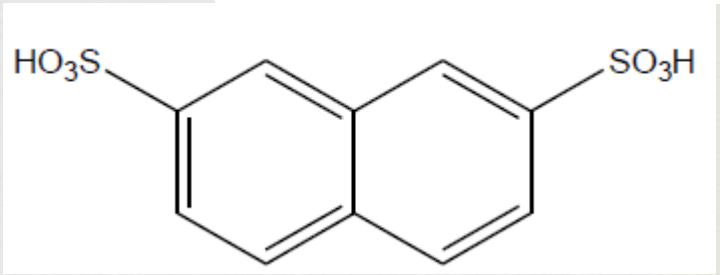
1-Naphthol or α-Naphthol



2-Naphthol or β -Naphthol

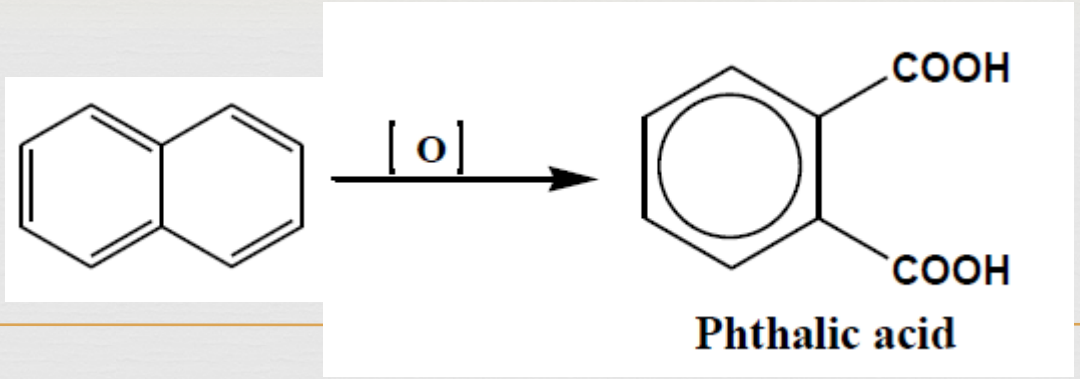


1,8- Dibromo-naphthalene

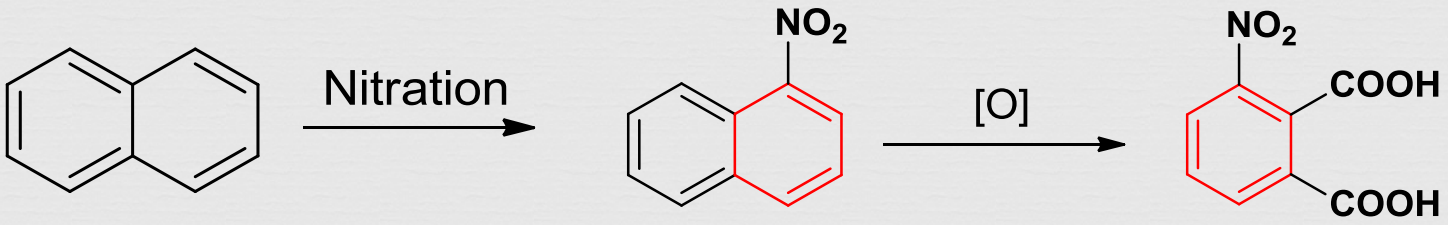


Naphthlene-2,7-disulfonic aci

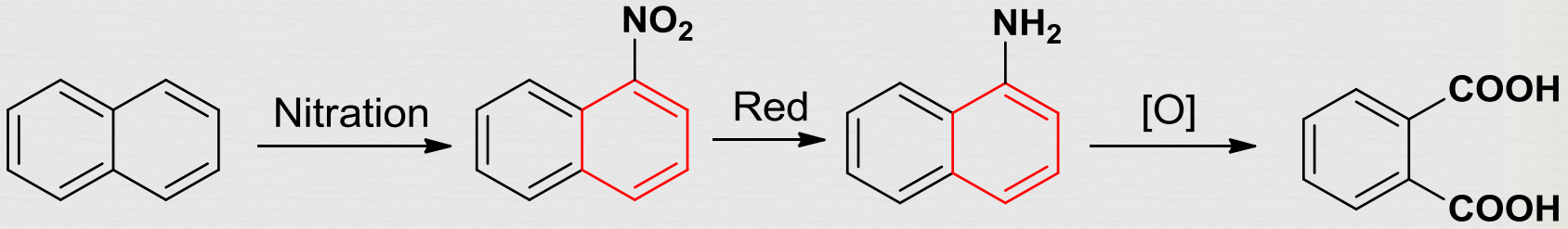
oxidation



a)

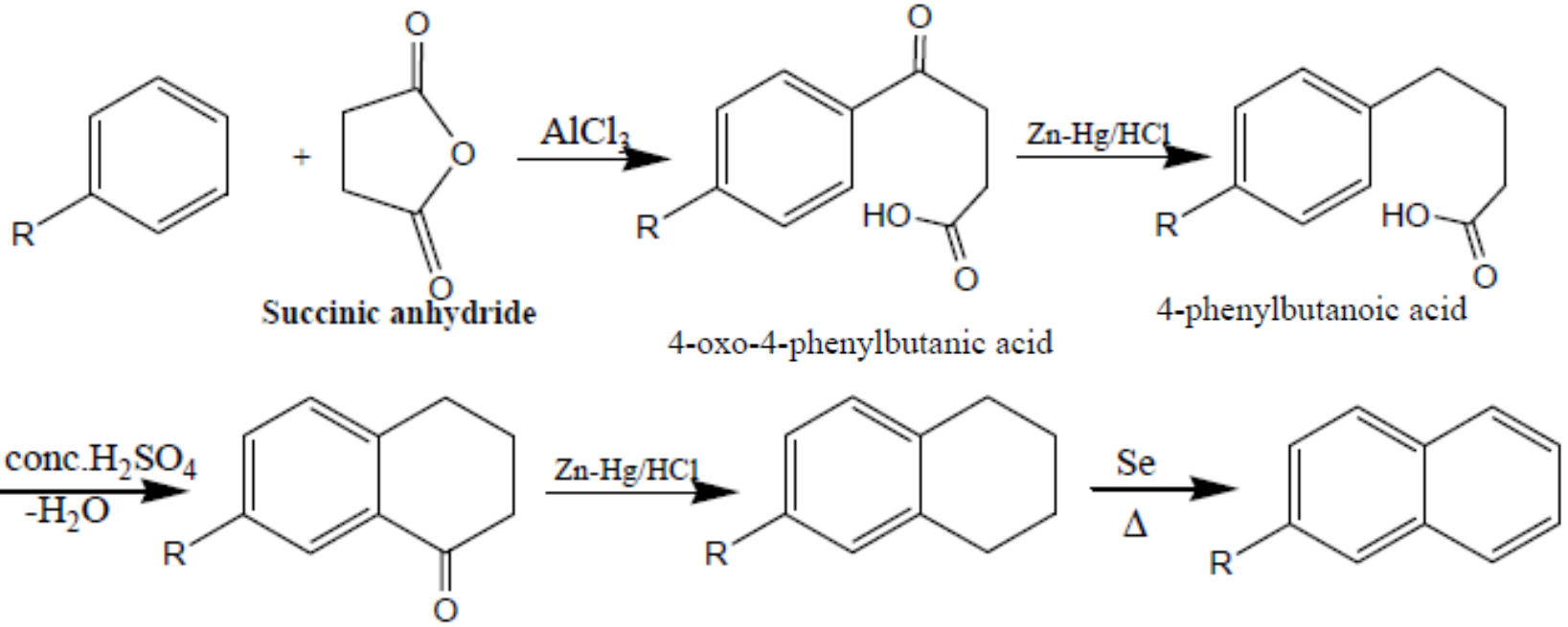


b)



Synthesis of naphthalene

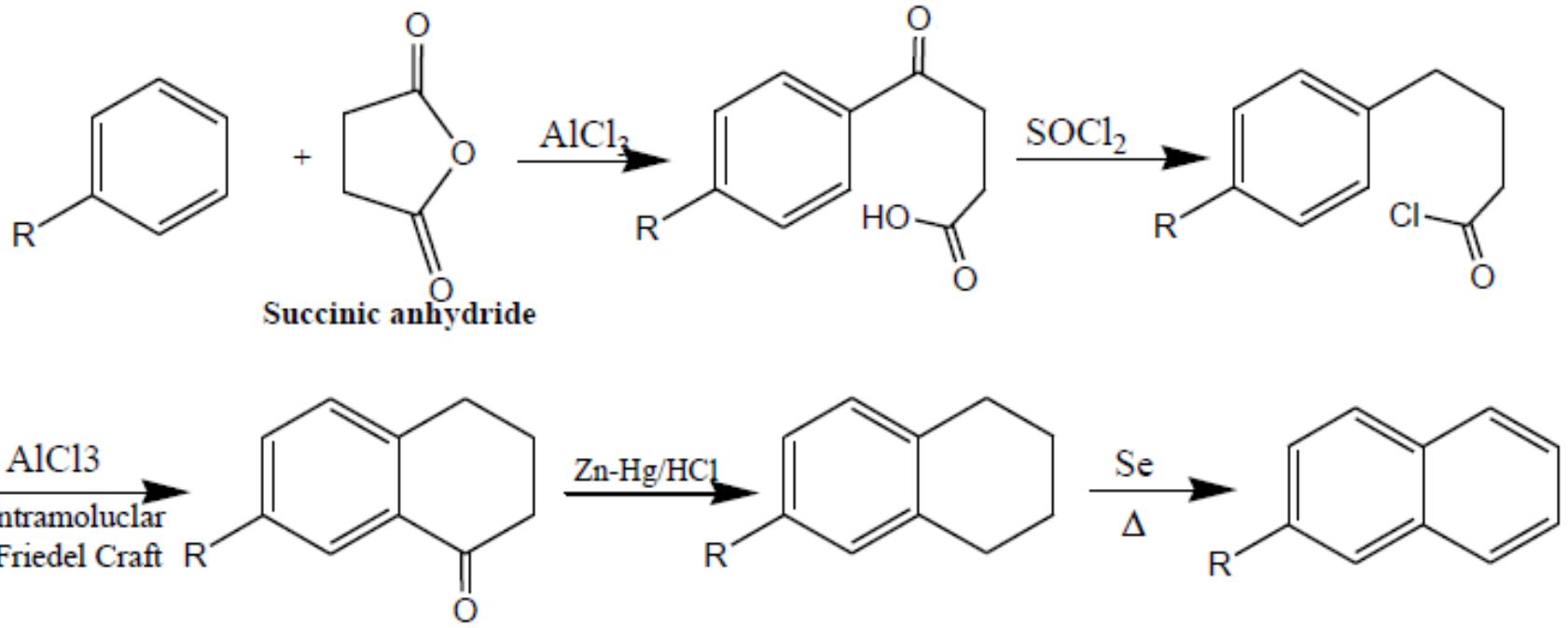
1- Howarth method



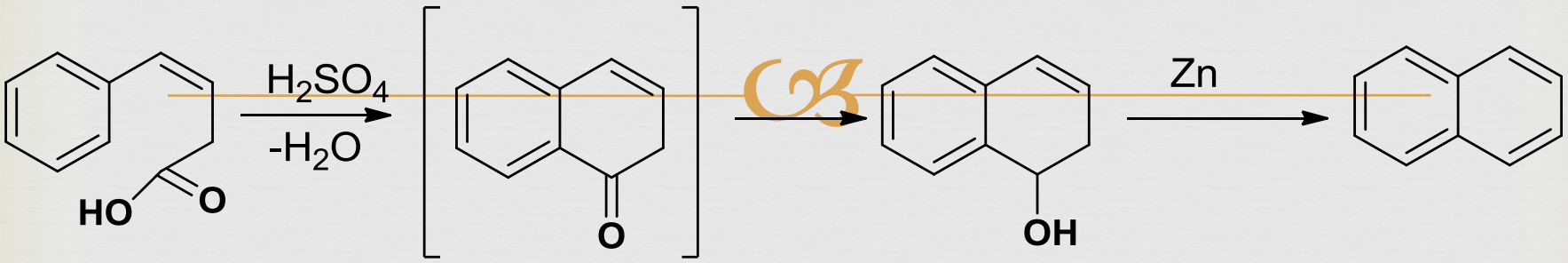
1-tetralone

Se = selenium

Other way of cyclization

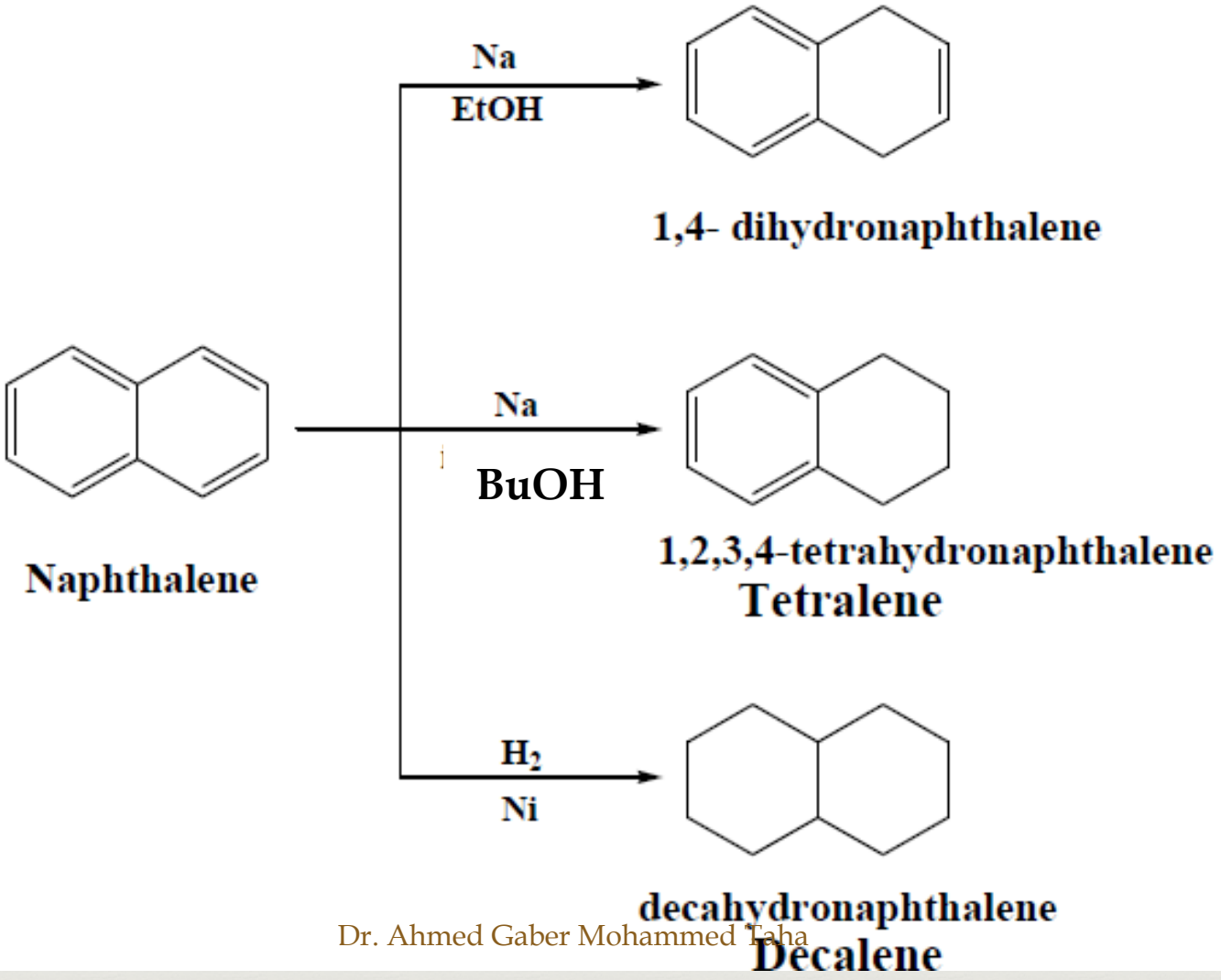


2- Via the reaction of **4-phenylbut-3-enoic acid** **β-Benzylidene-3-propenpoic acid** with sulphuric acid .

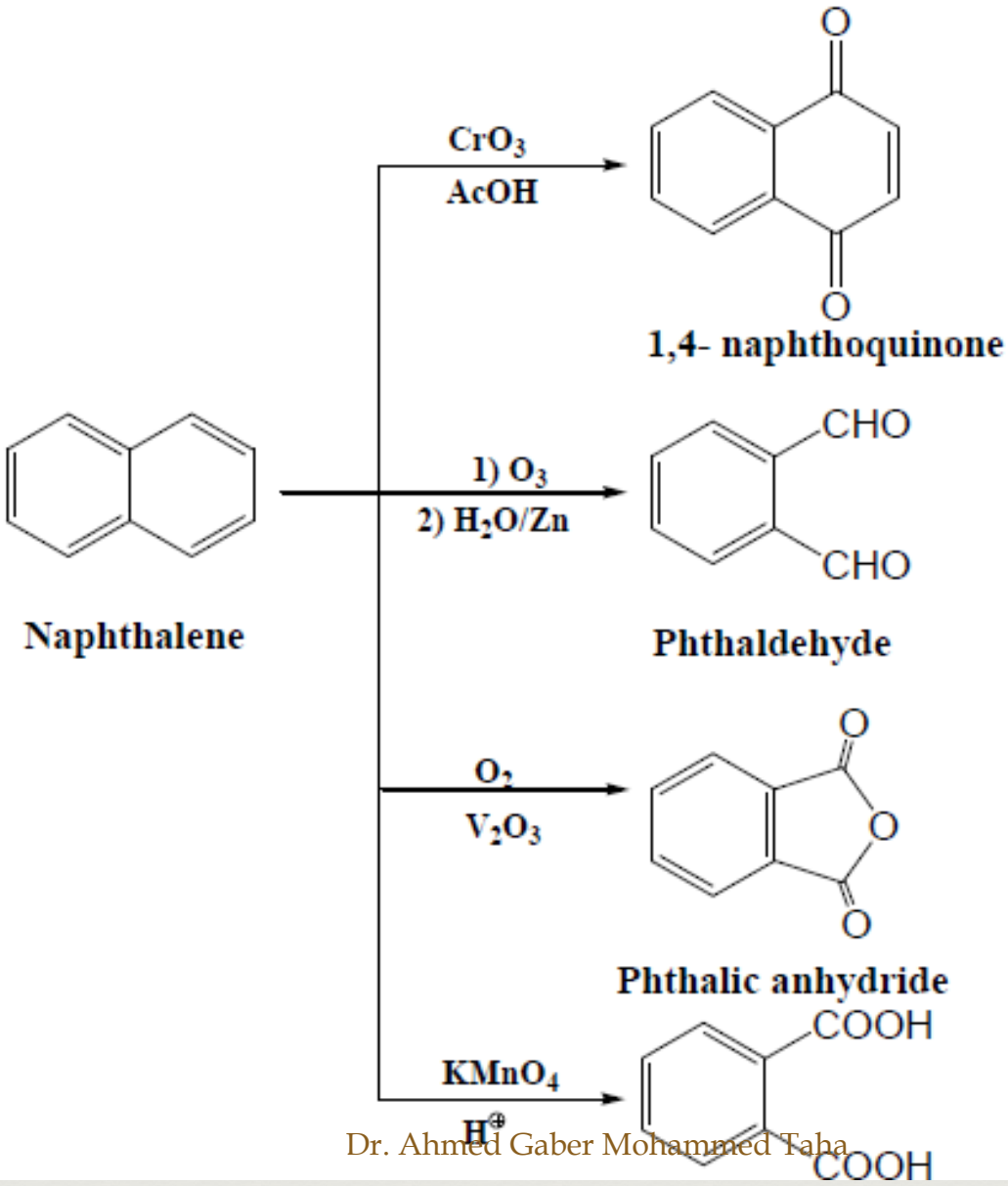


Chemical Reactions of naphthalene

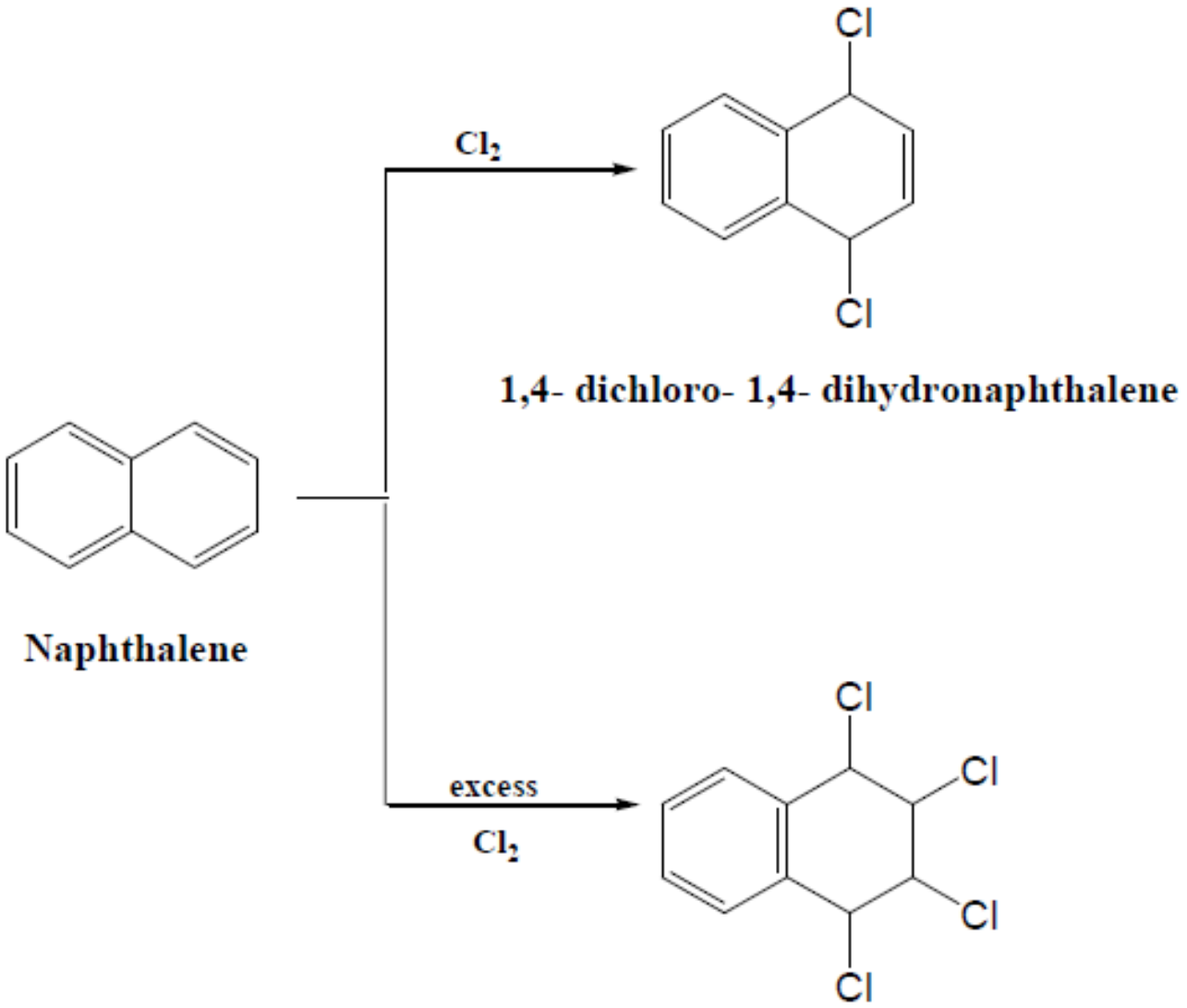
1. Reduction



2. Oxidation


CrO3
AcOH
1,4- naphthoquinone
1) O3
2) H2O/Zn
Naphthalene
Phthaldehyde
O2
V2O3
Phthalic anhydride
KMnO4
H⊕

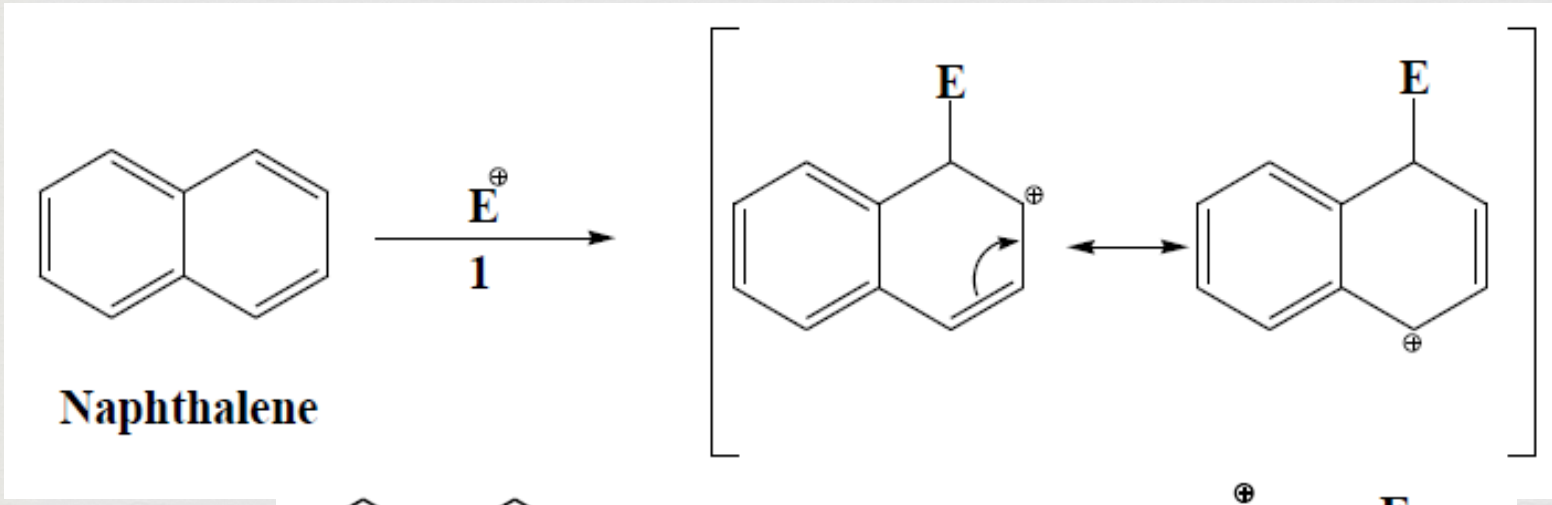
3. Addition of Cl_2

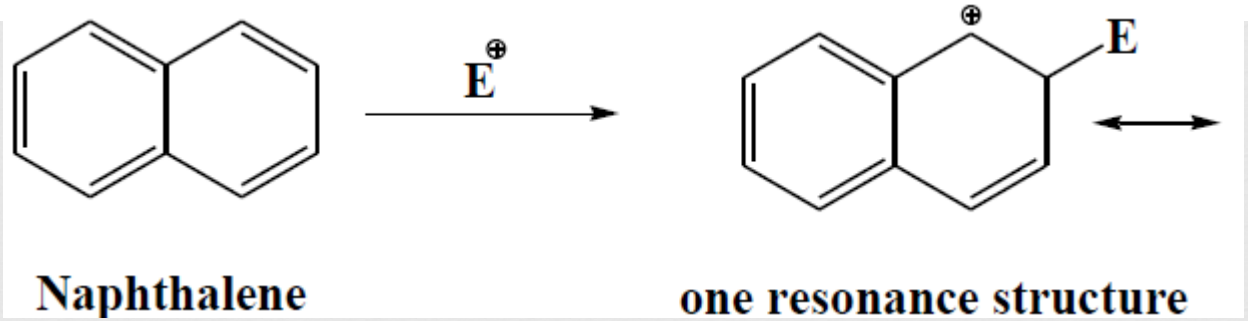


4. Electrophilic substitution reaction

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

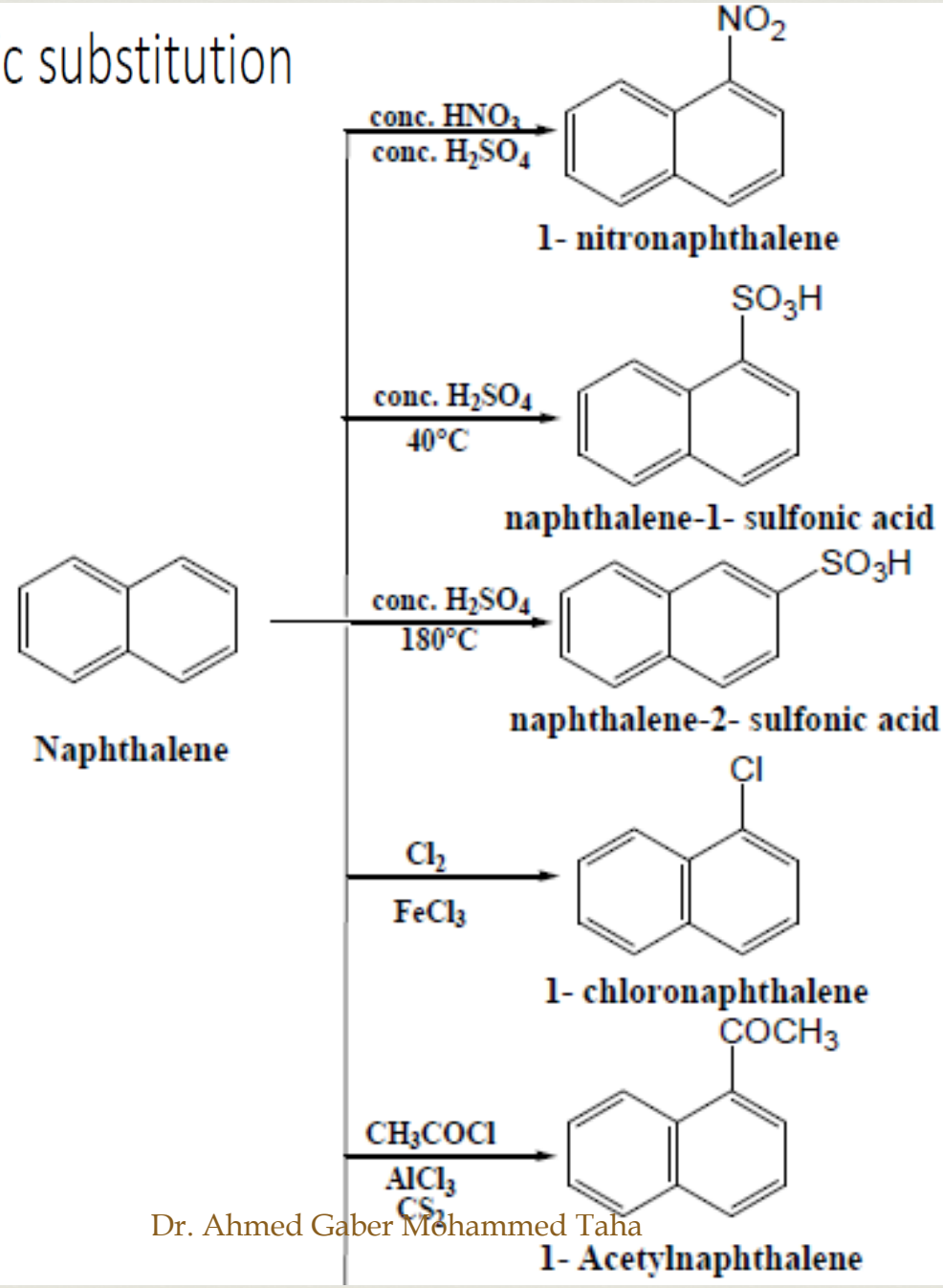
At position 1; carbocation intermediate stabilize by two resonance





So carbocation is more stable postion 1 than 2

Examples of electrophilic substitution



المحاضرة ٥

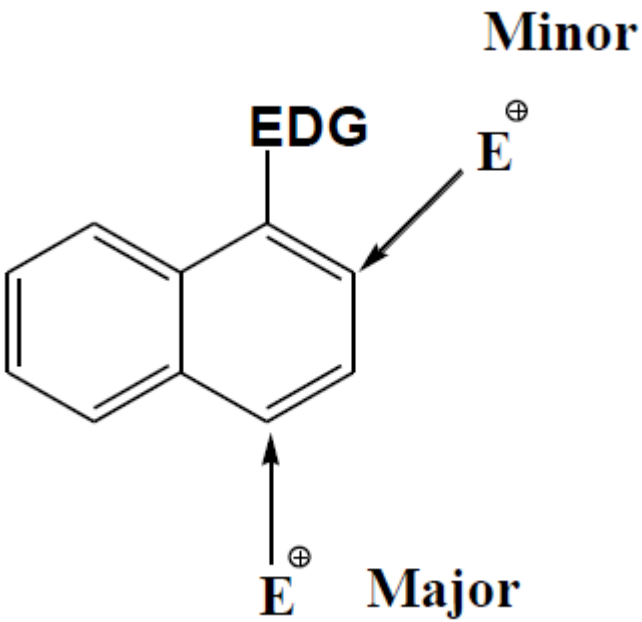
Substituted naphthalene

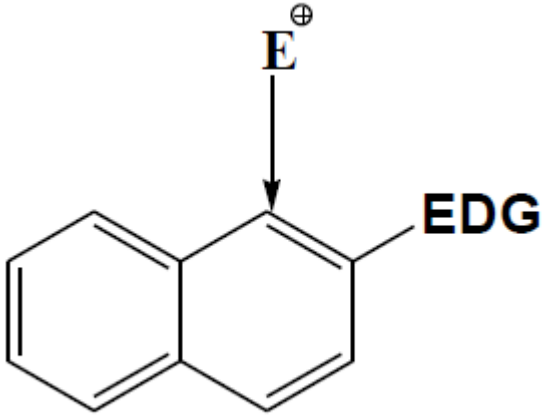
- Activating groups direct the electrophile to the same ring, while deactivating groups direct it to the other ring.

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

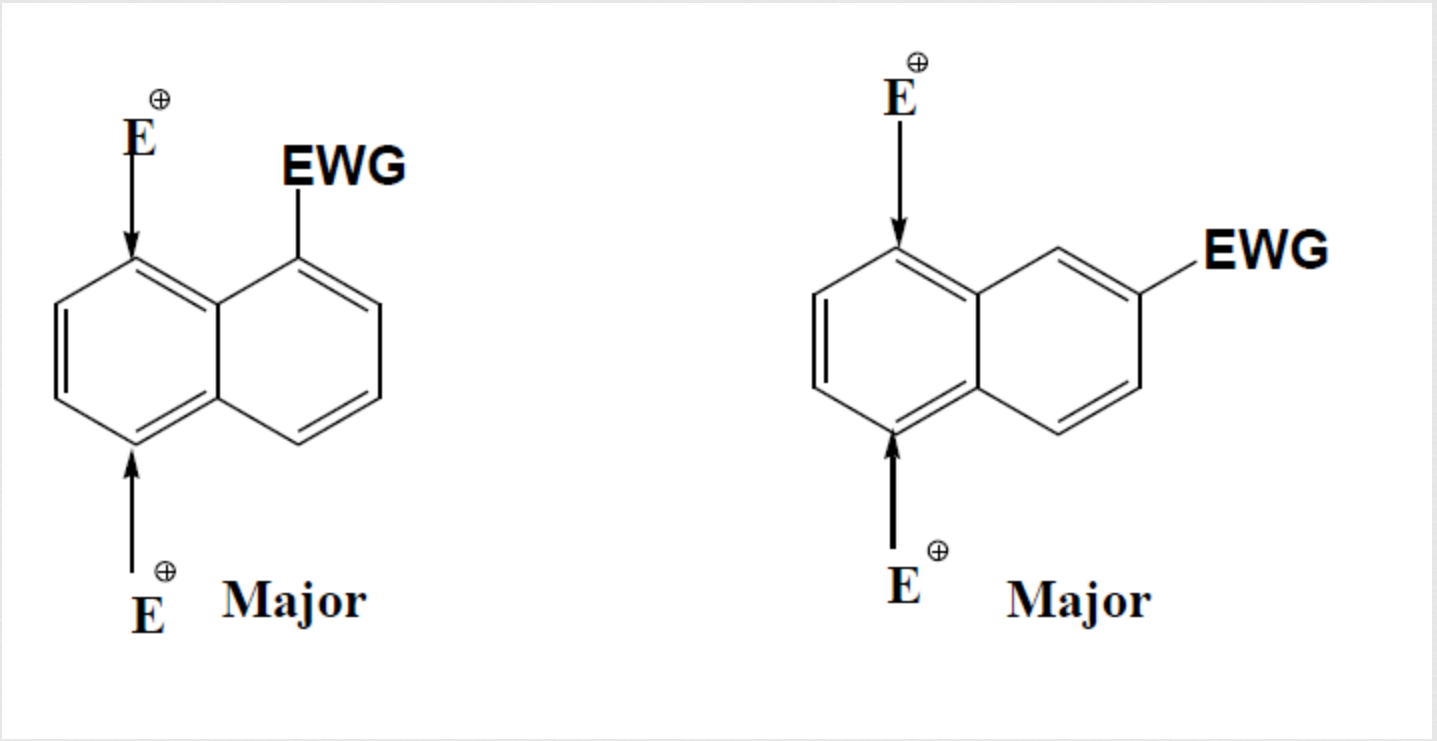
Electrowithdrawing grou (EWG)
NO2, SO3H, CO, COOH,

Homonuclear attack

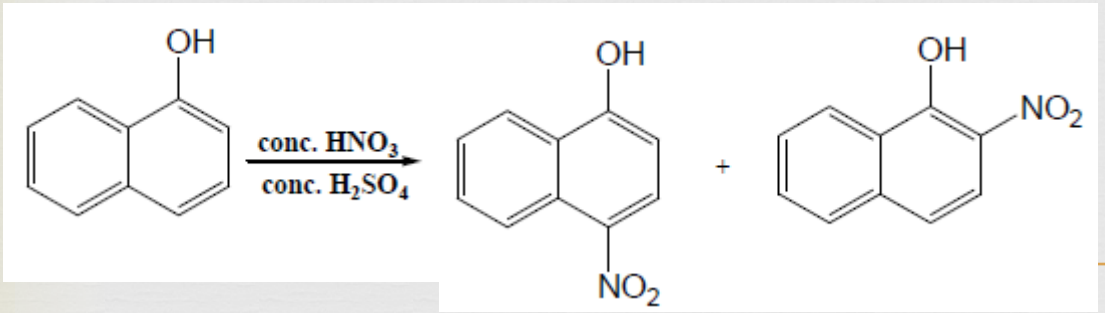




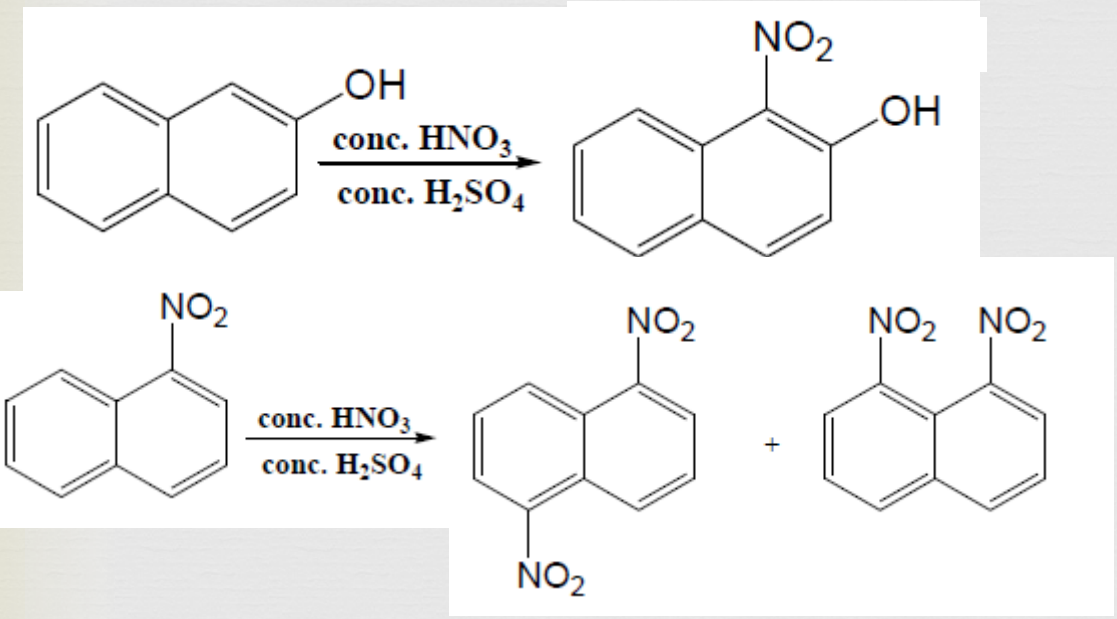
Heteronuclear attack



Examples



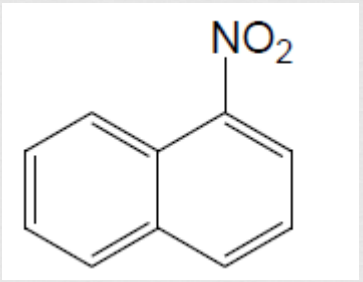
Major

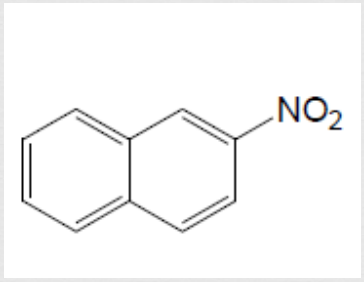


Major **Minor**

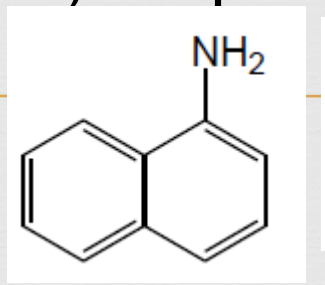
- Naphthalene derivatives

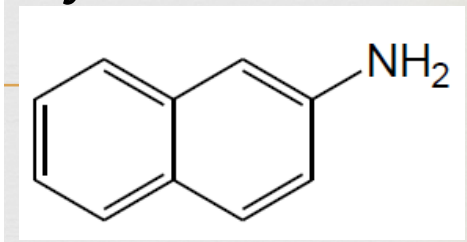
1) Nitronaphthalene



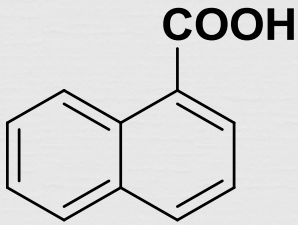


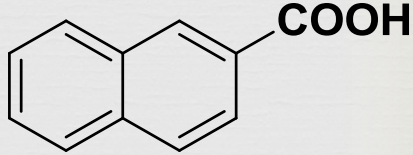
3) Naphthylamines



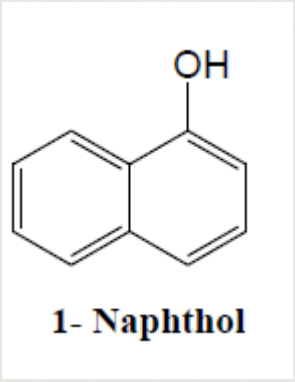


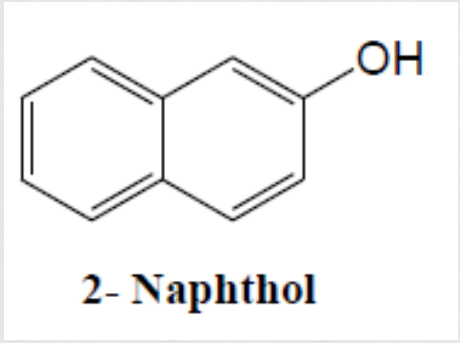
4) Naphthylene carboxylic acid



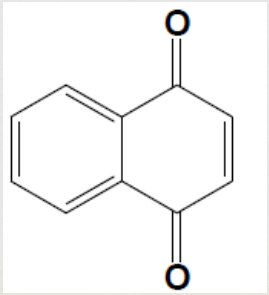


2) Naphthols



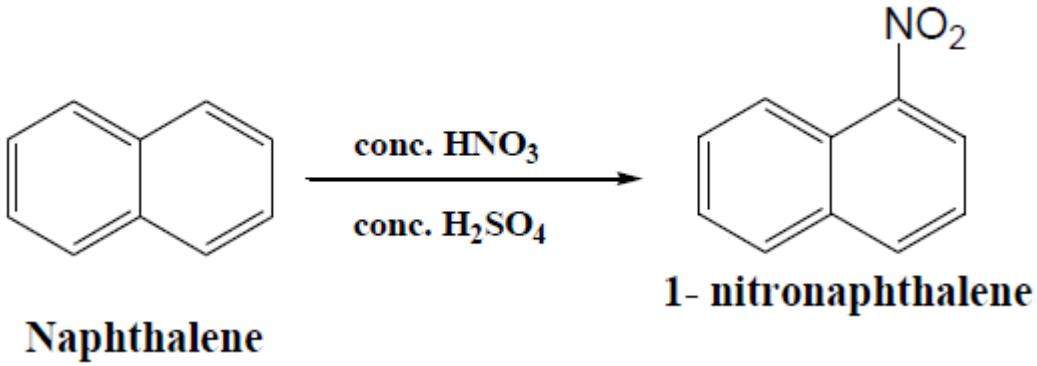


5- naphthoquinone

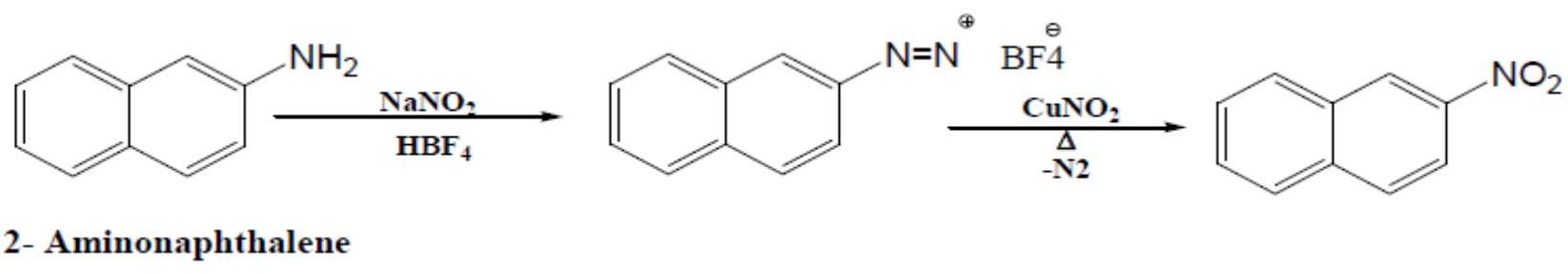


Nitronaphthalene

A- prepared by direct nitration



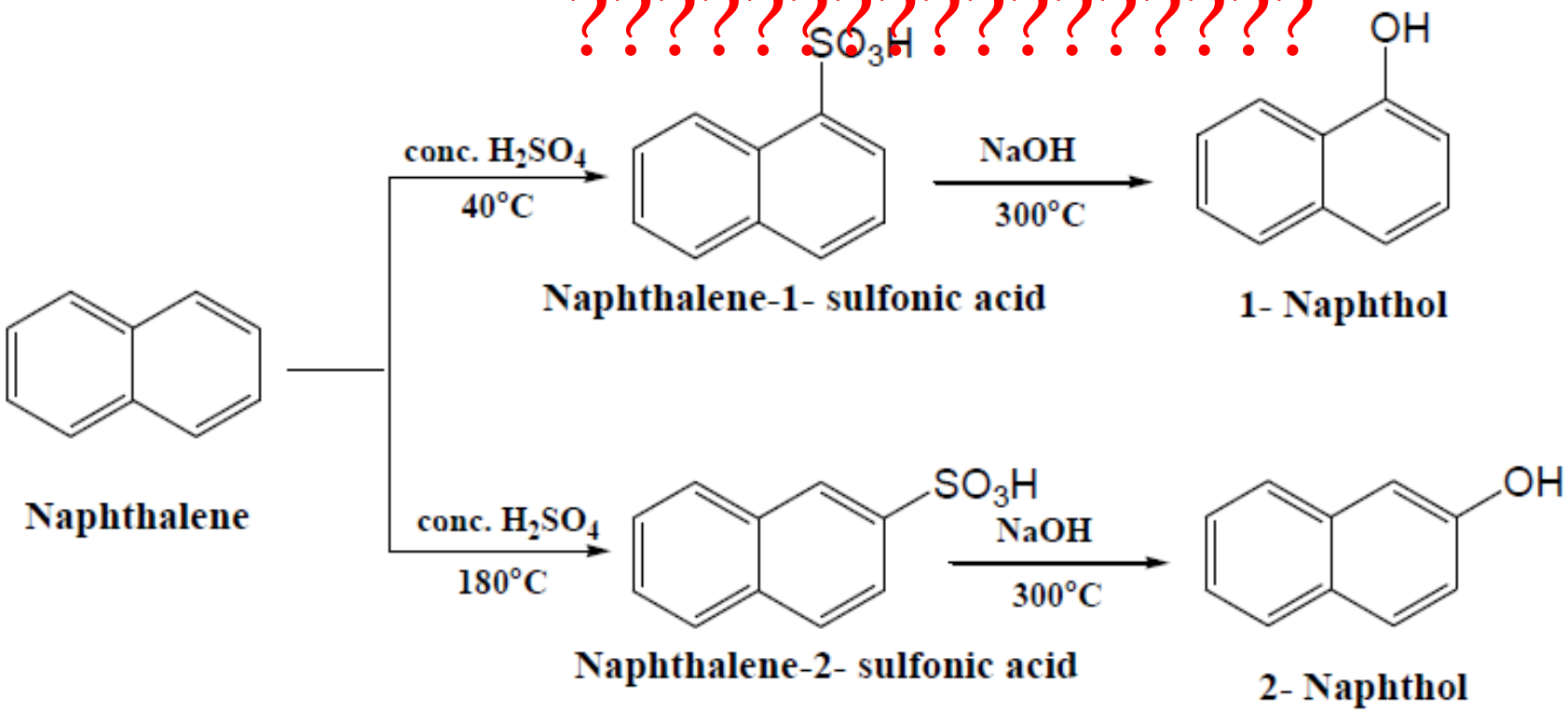
B- prepared by indirect nitration



Naphthols

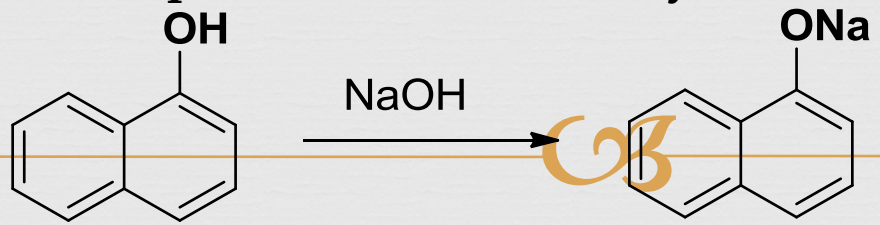
- **Preparation:**

??????????????????

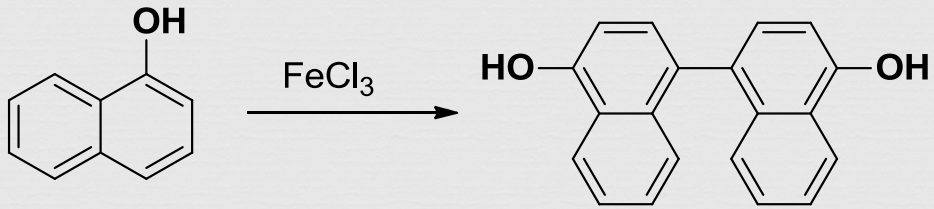


Reactions

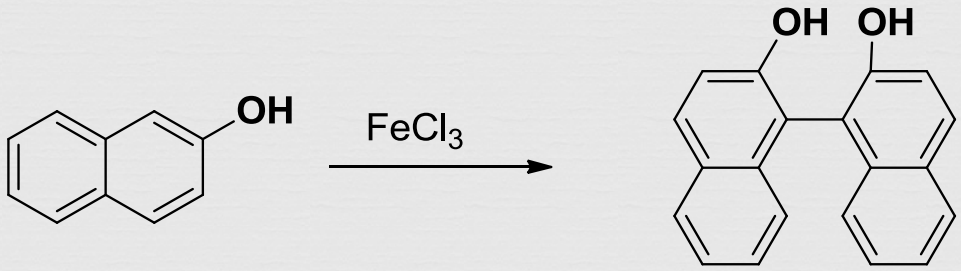
1- The reaction of naphthols with sodium hydroxide



2- The reaction of naphthols with ferric chloride

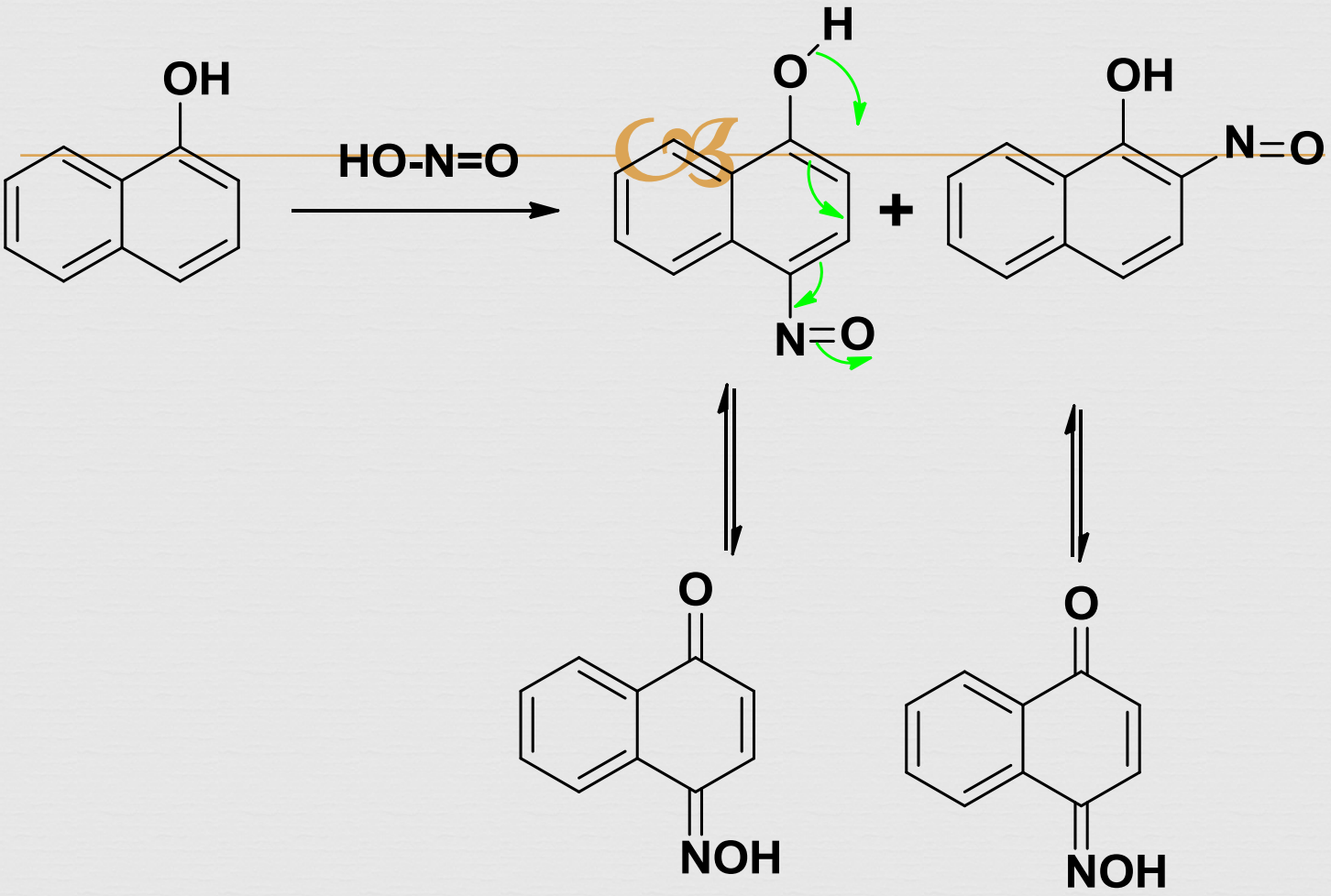


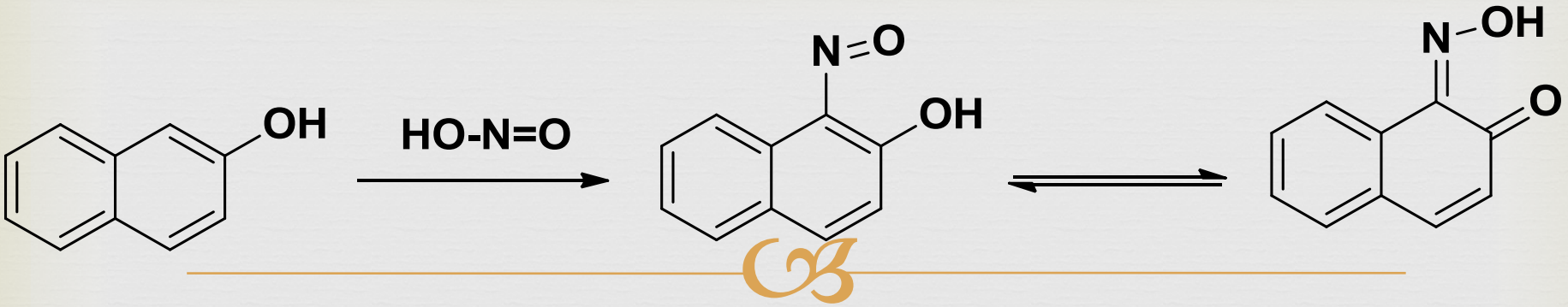
4,4-bis-1-naphthol or α-dinaphthol



2,2-bis-2-naphthol or β-dinaphthol

3- The reaction of naphthol with nitrous acid

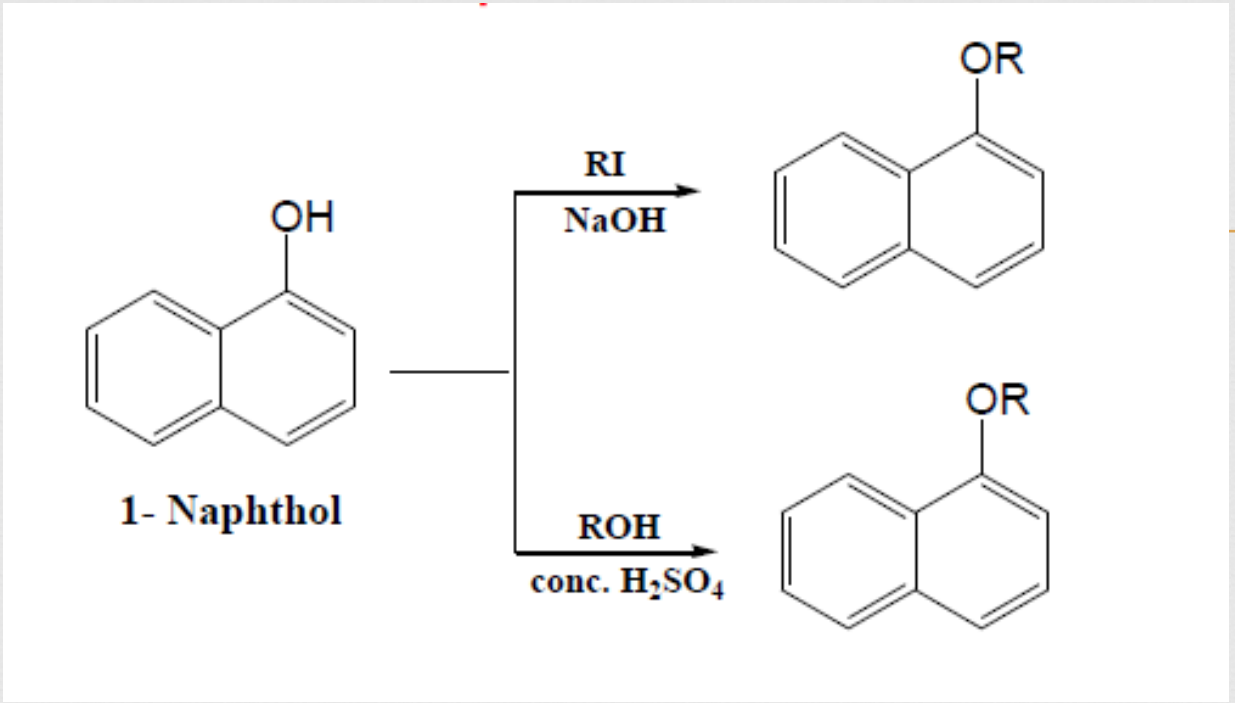




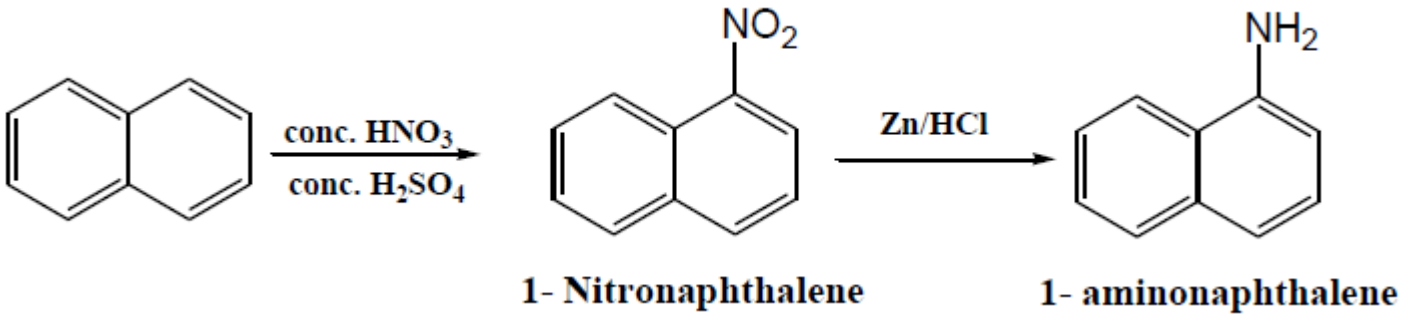
4- With diazonium salt

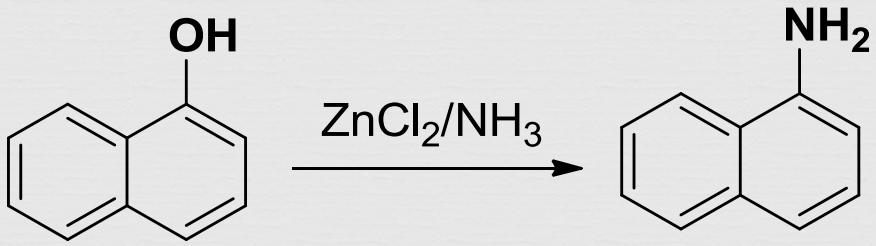
1-naphthol ?????????

5- conversion of naphthols to naphthyl ether

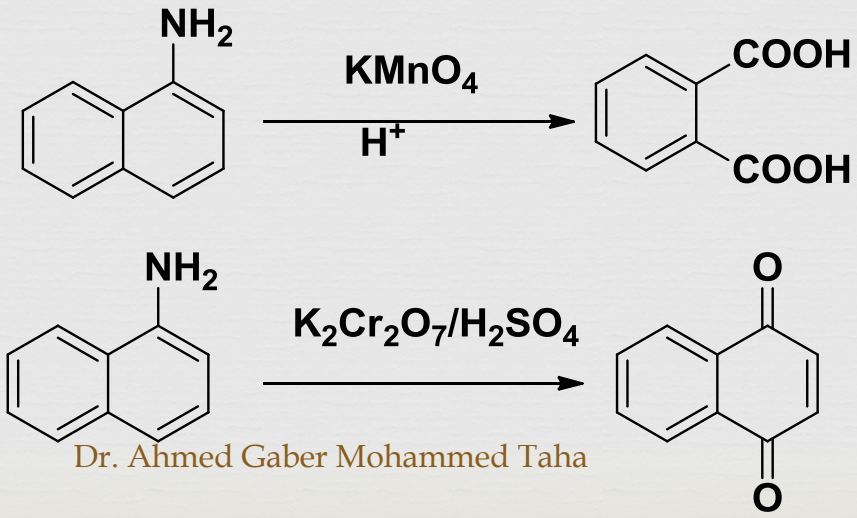


Naphthylamines



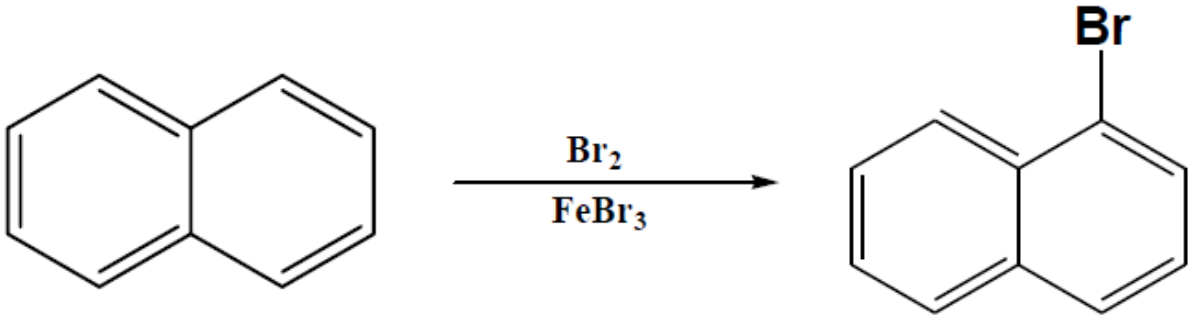


Oxidation of 1-naphthylamine



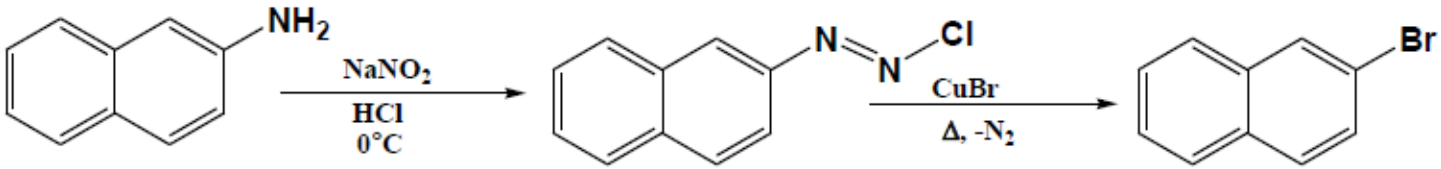
Halogenated naphthalene

- A) Preparation of 1- halogented naphthalene



1- bromonaphthalene

- B) Preparation of 2- halogenated naphthalene via Sandemeyer



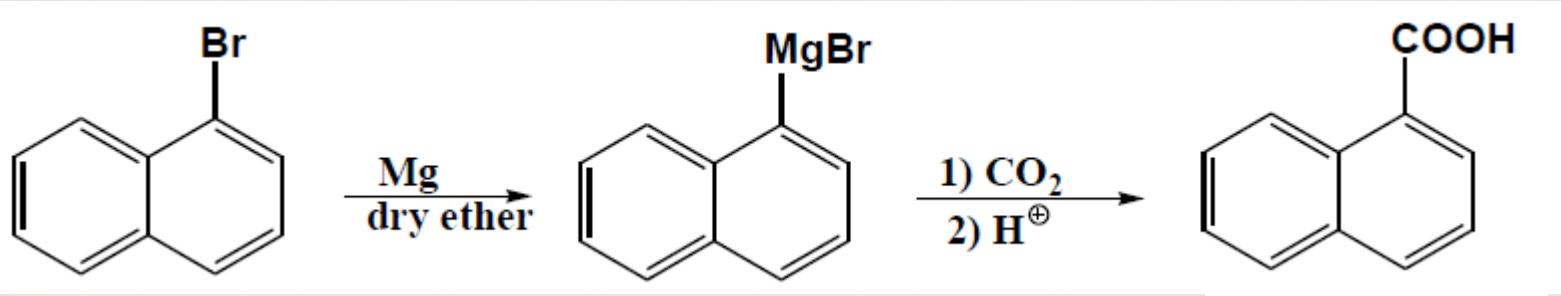
2-Naphthylamine

المحاضرة ٦

Naphthylene carboxylic acid

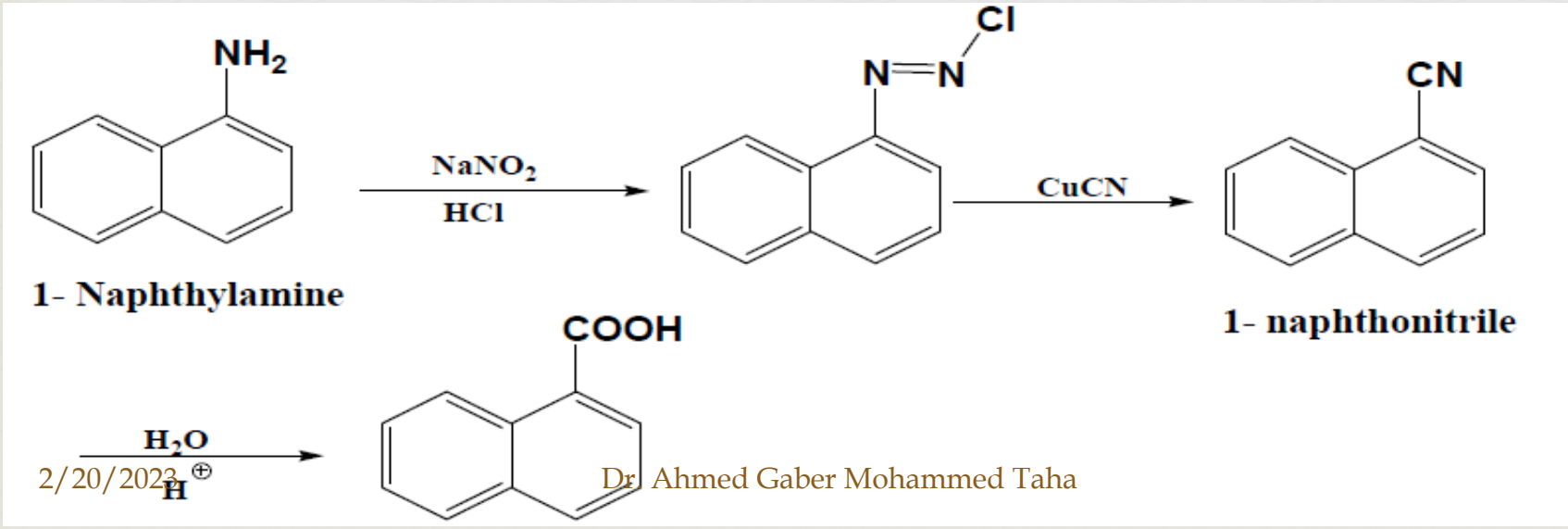
Preparation

1- From naphthyl 1 or 2-magnesium bromide



1- Naphthoic acid

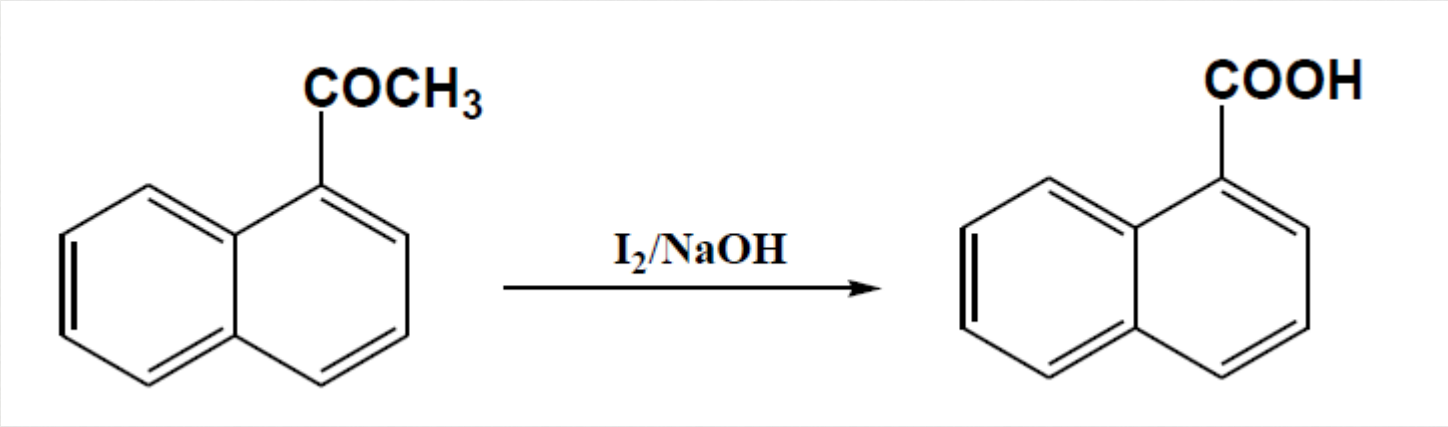
2- From naphthylamine



1- Naphthylamine

1- naphthonitrile

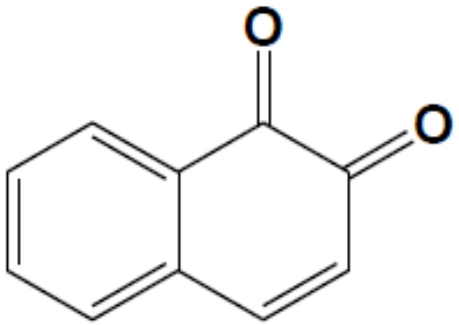
3- From acetylacetophenone



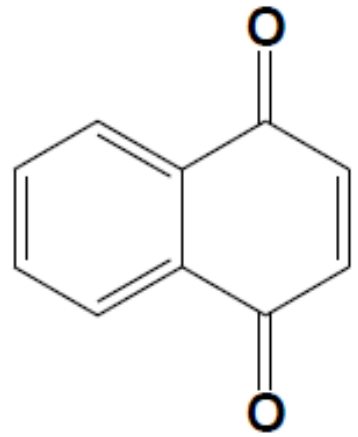
The same methods in case of 2-naphthoic acid

Naphthoquinones

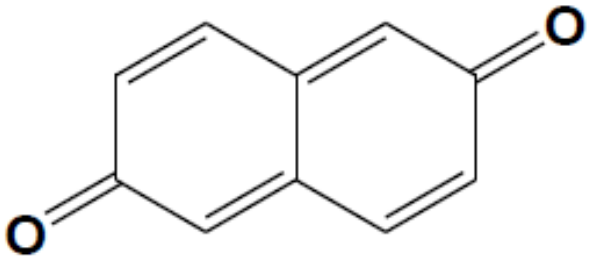
- There are six possible naphthaquinones, but only common are 1,2; 1,4; 2,6- naphthaquinones



1,2- Naphthaquinone



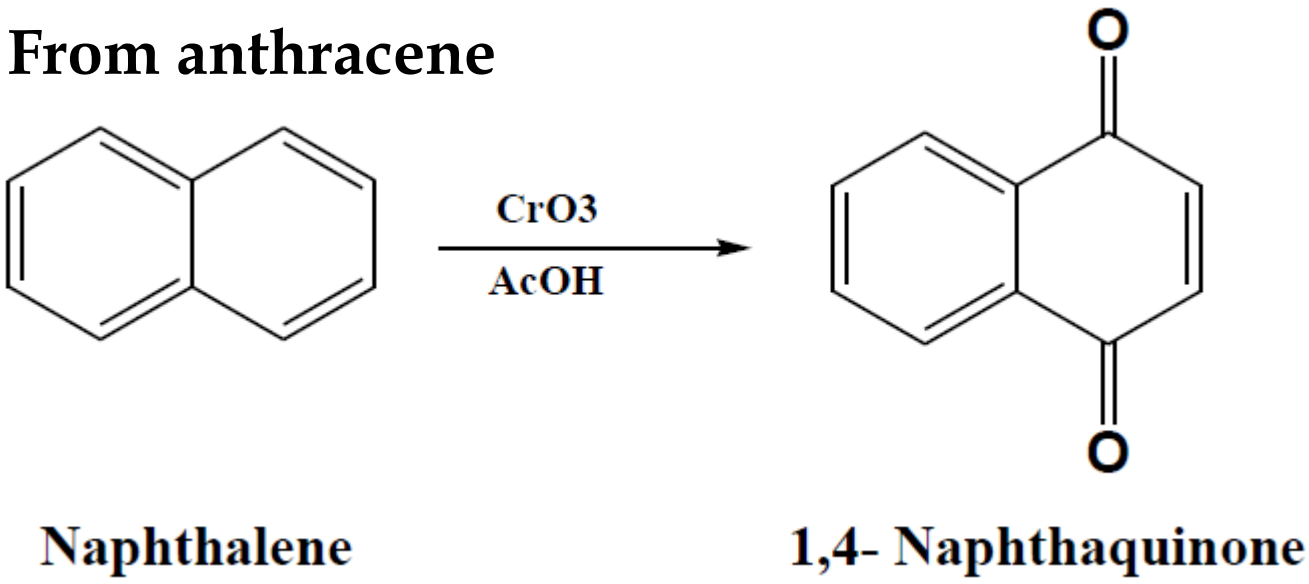
1,4- Naphthaquinone



2,6- Naphthaquinone

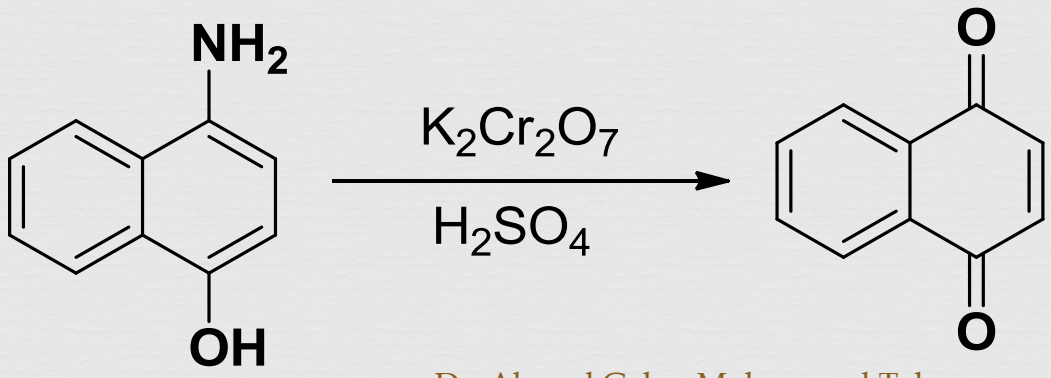
1,4- Naphthaquinone:

A- From anthracene

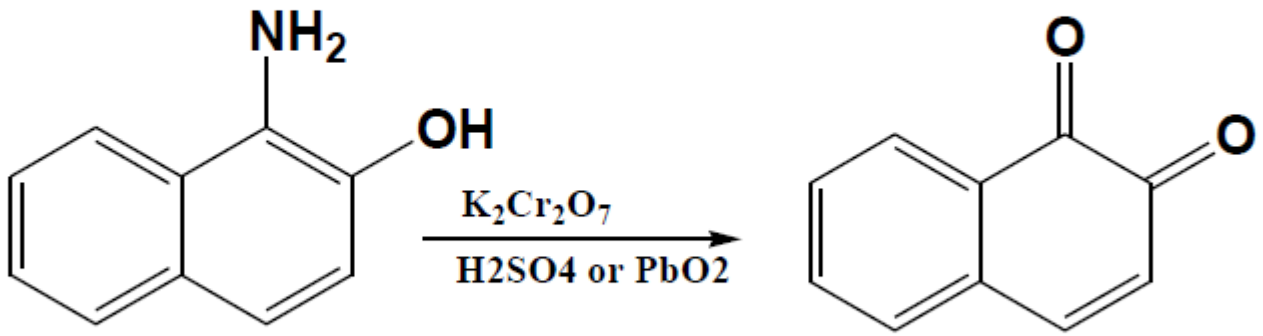


Naphthalene **1,4- Naphthaquinone**

2- From 1,4-diamino or dihydroxyl or aminohydroxylnaphthalene

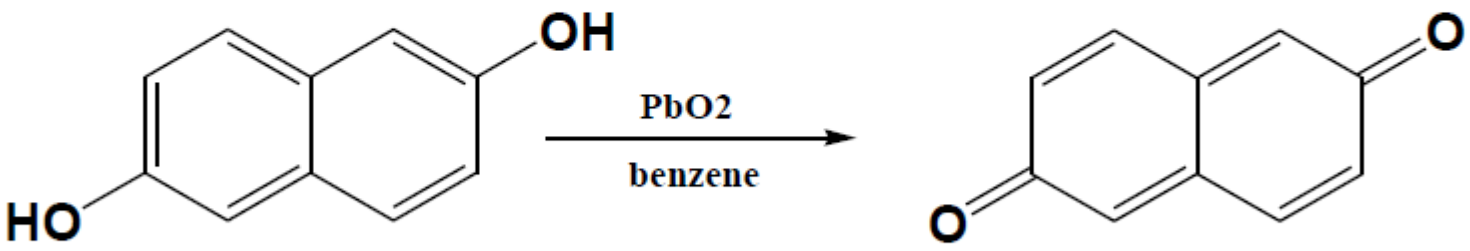


1,2- Naphthaquinone:



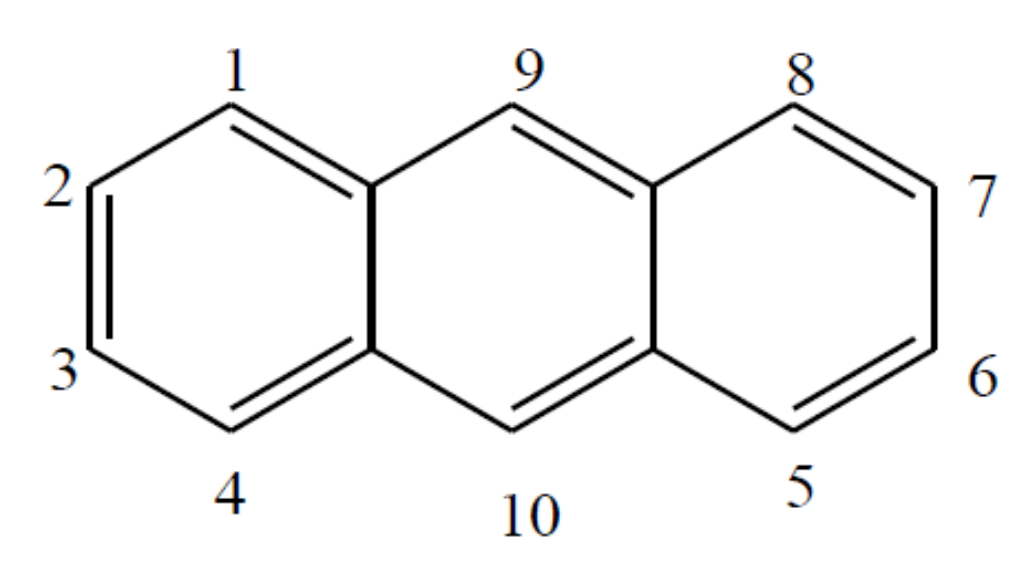
1- Amino- 2-naphthol **1,2- Naphthaquinone**

2,6- Naphthaquinone:



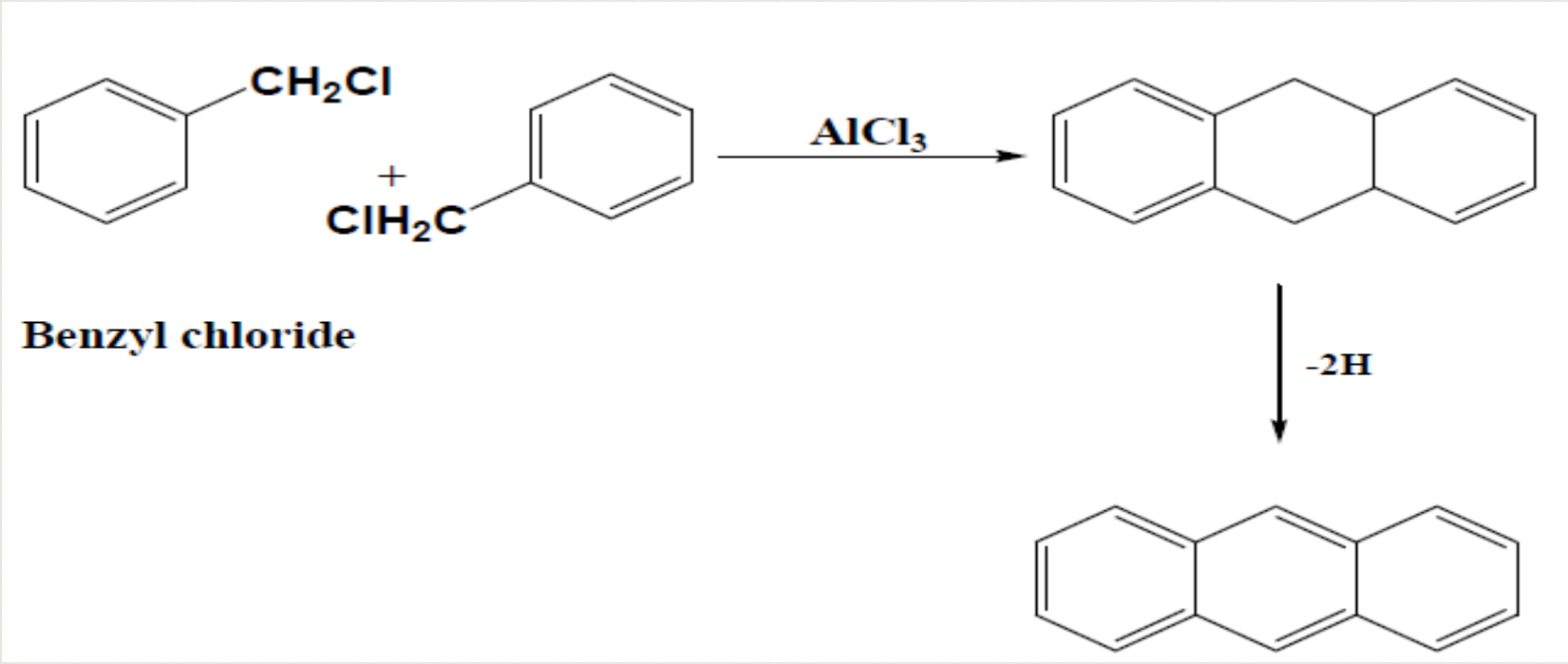
2,6- dihydroxynaphthalenel **2,6- Naphthaquinone**

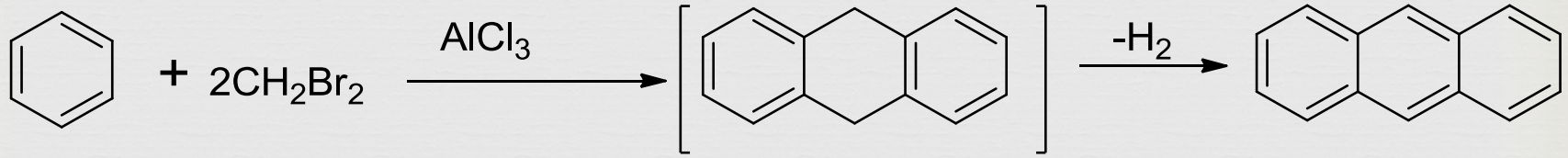
Anthracene



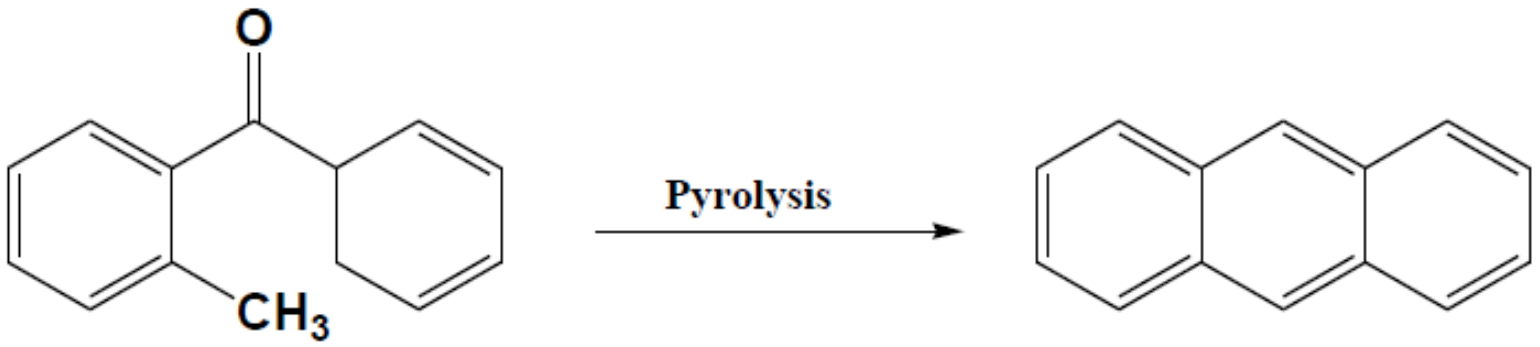
Synthesis of anthracene

1- Friedl Crafts





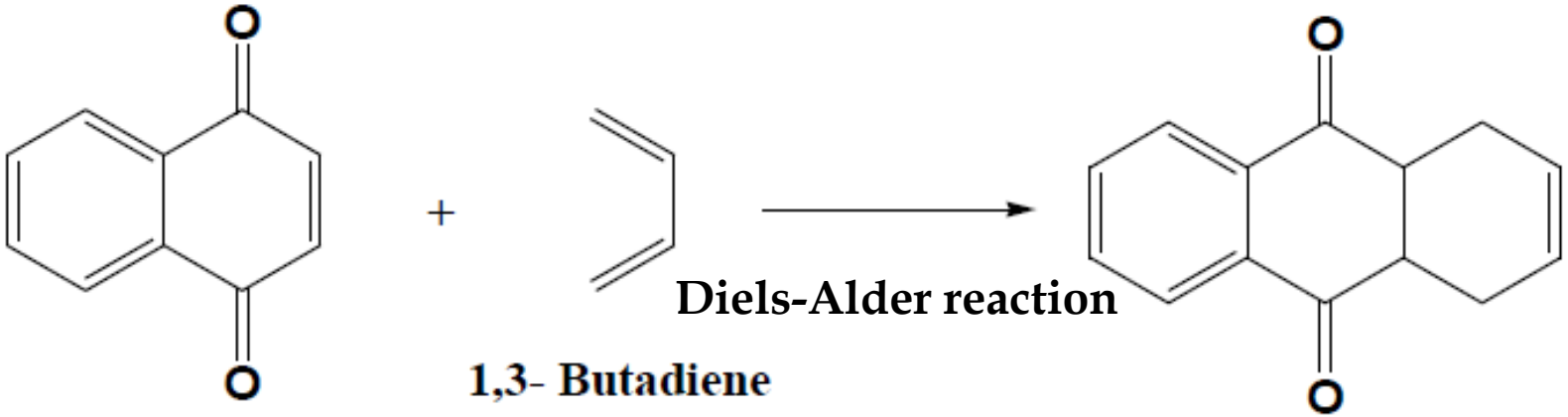
- 2. Elbe reaction



o- Methyl- benzenophenone
or o- Benzoyl- toluene

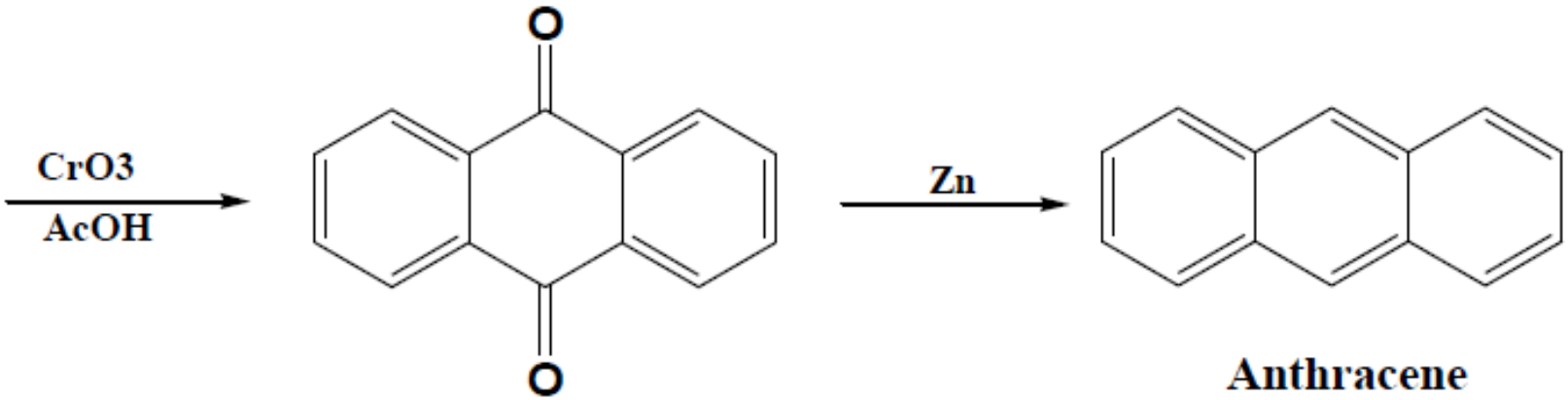
Anthracene

- 3. From 1,4- Naphthoquinone



1,4- Naphthaquinone

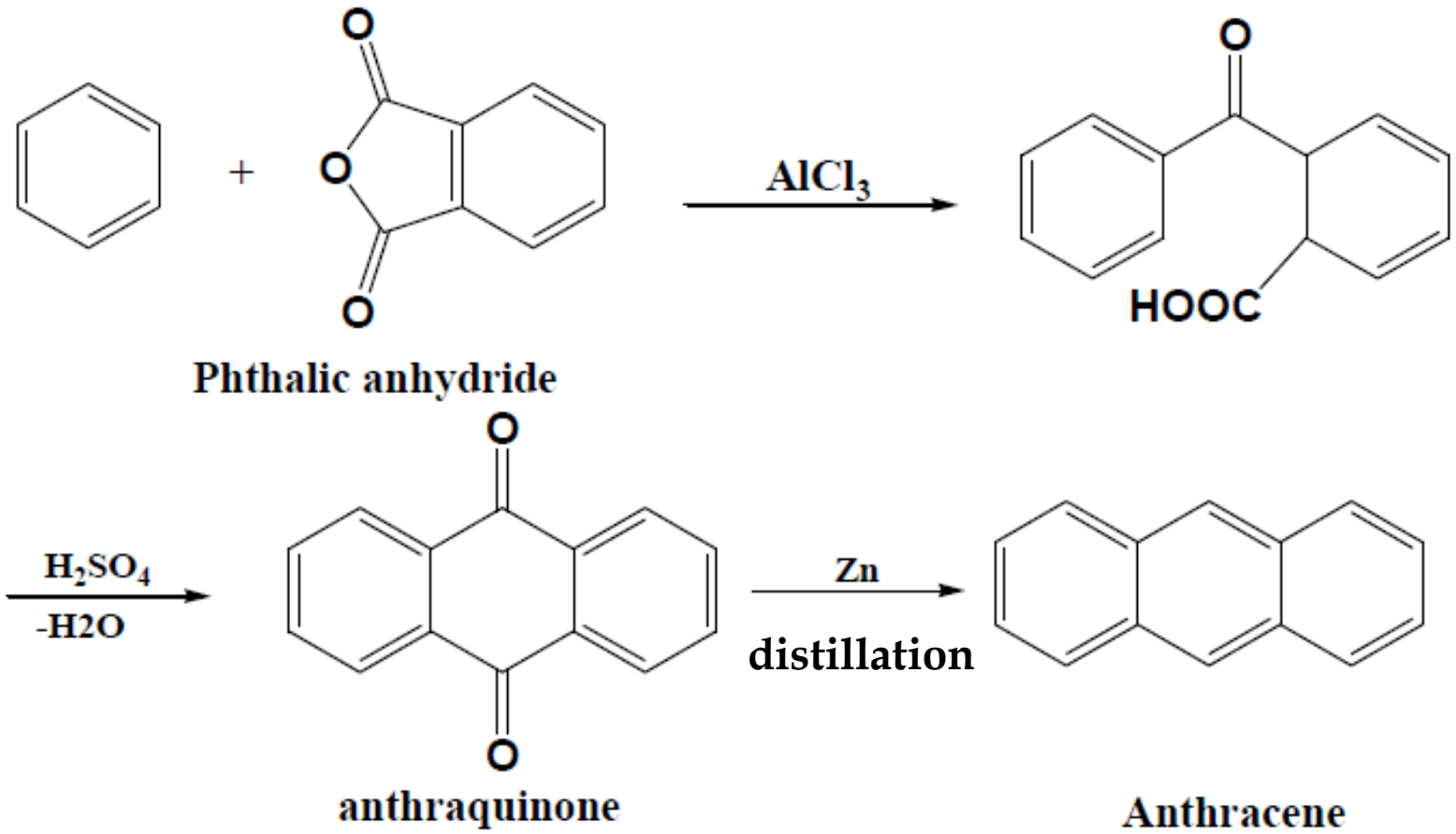
1,3- Butadiene



9,10- anthraquinone

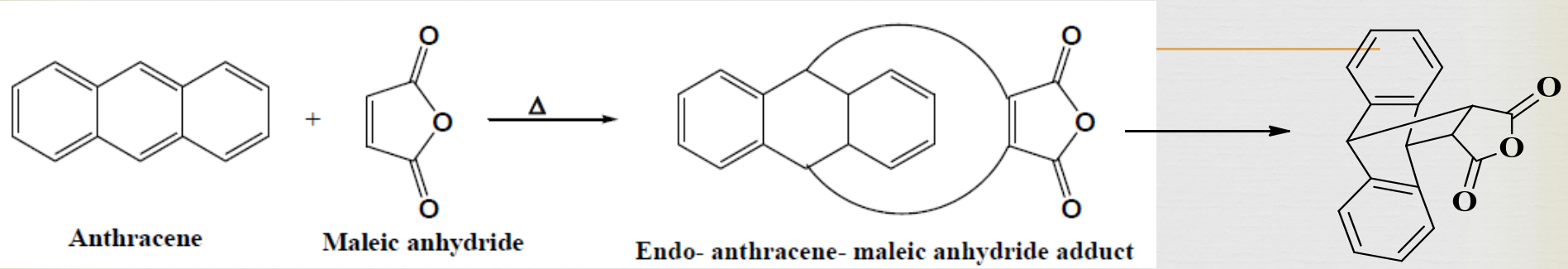
Anthracene

- 4. From benzene and phthalic anhydride

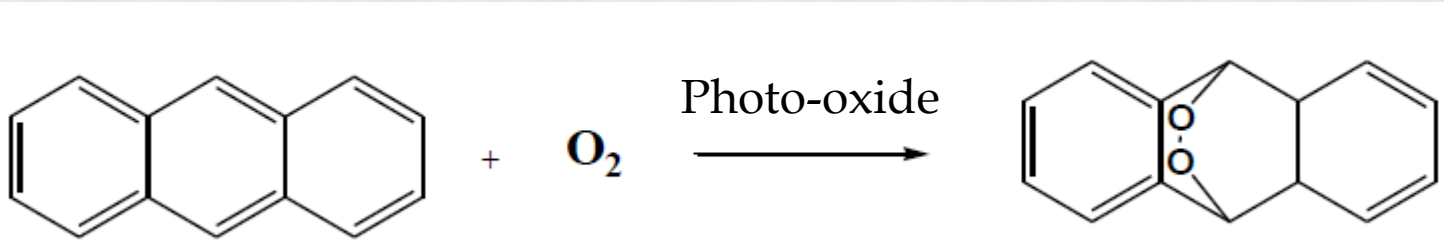


Chemical reactions

1) Diels -Alder

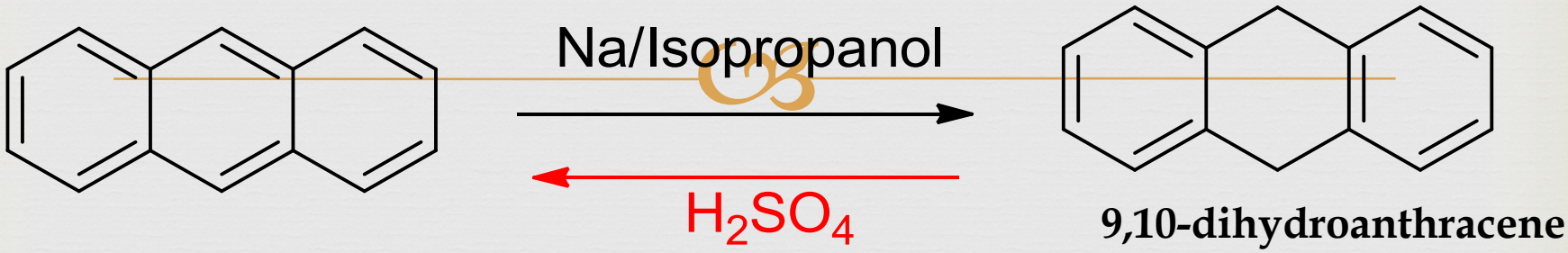


2) Addition of one molecule of O_2

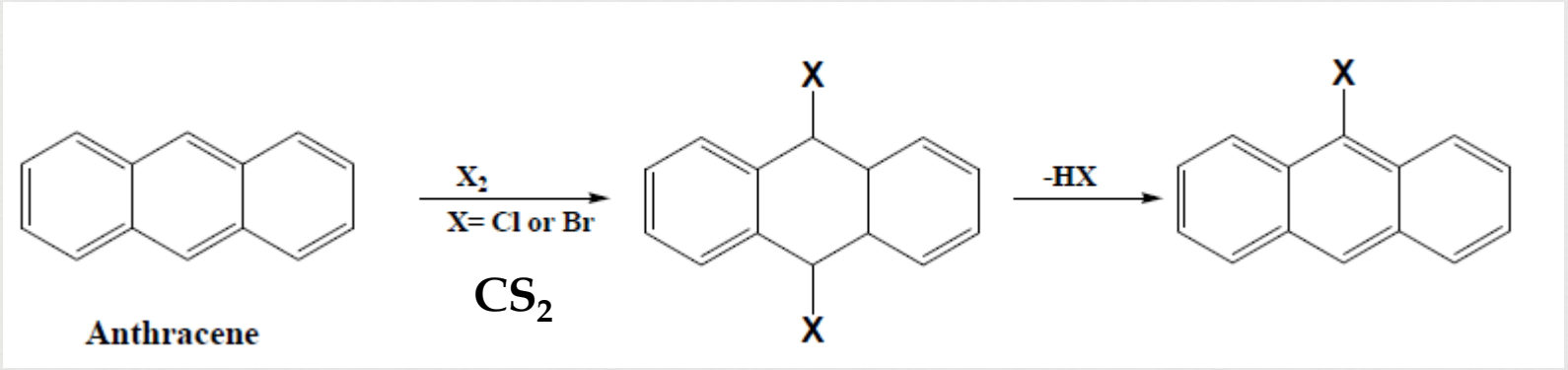


Anthracene peroxide

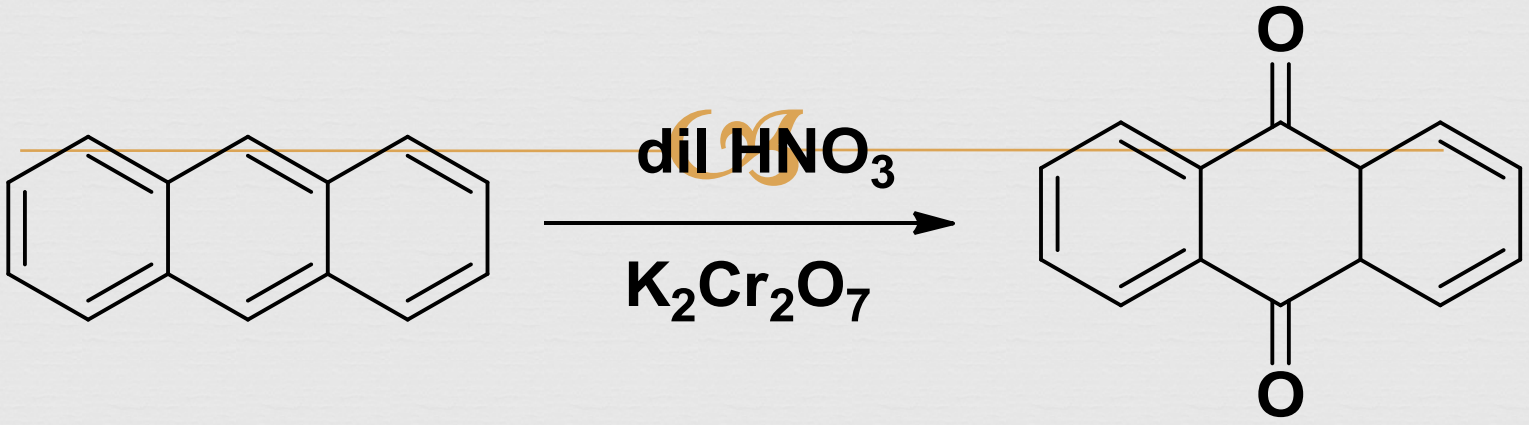
3) Reduction of anthracene

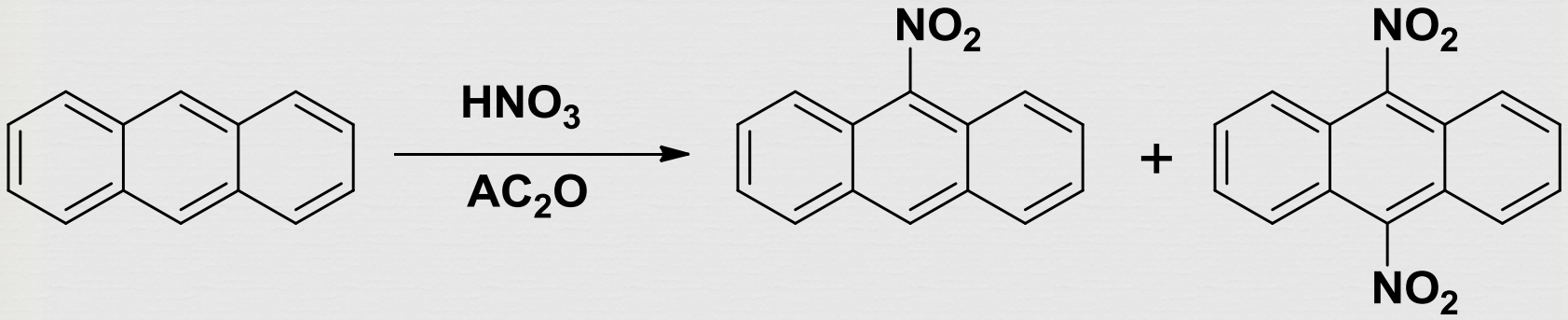


4) Halogenation of anthracene



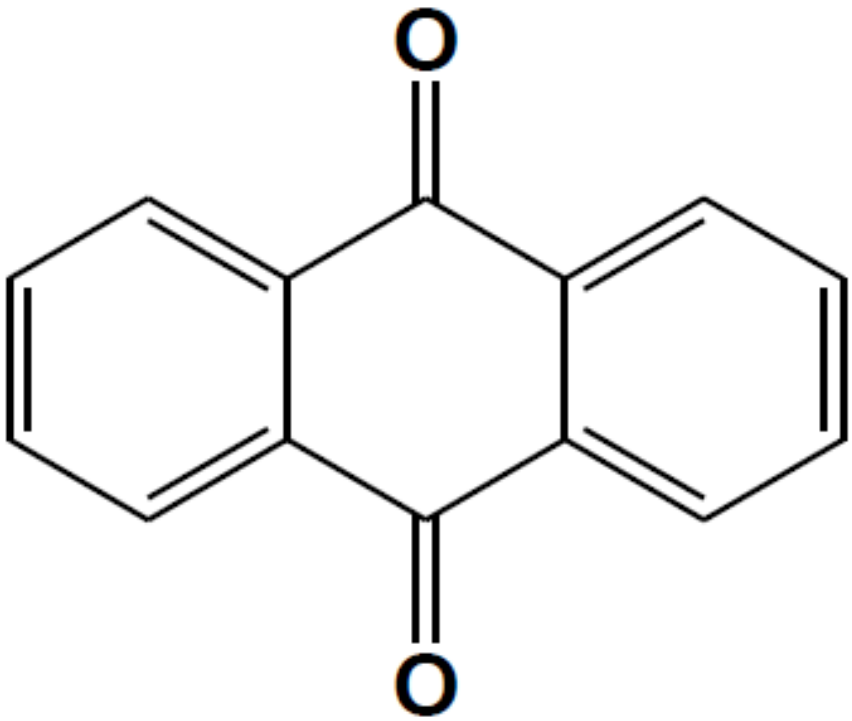
5) Nitration of anthracene





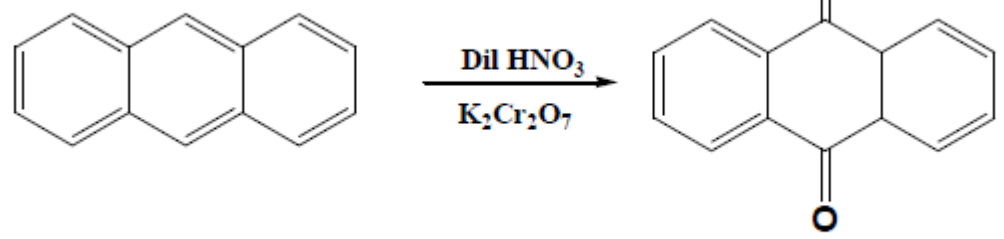
المحاضرة ٧

Anthraquinone



Preparation

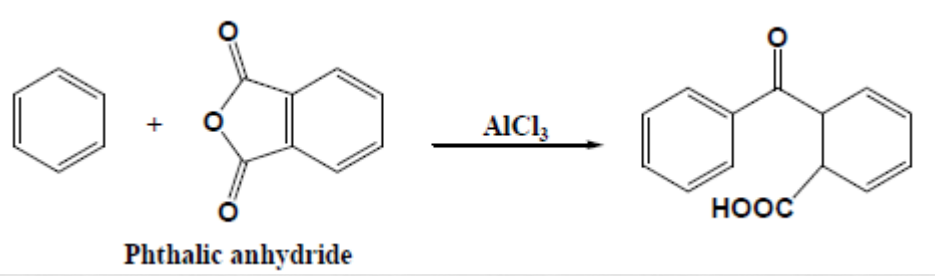
1- Oxidation of anthracene



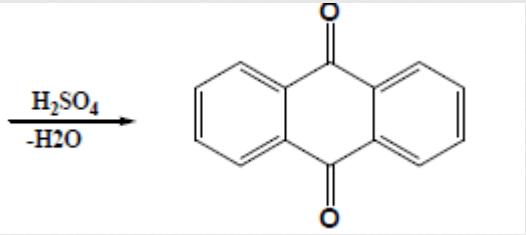
Anthracene

9, 10- Anthraquinone

2- Friedl crafts

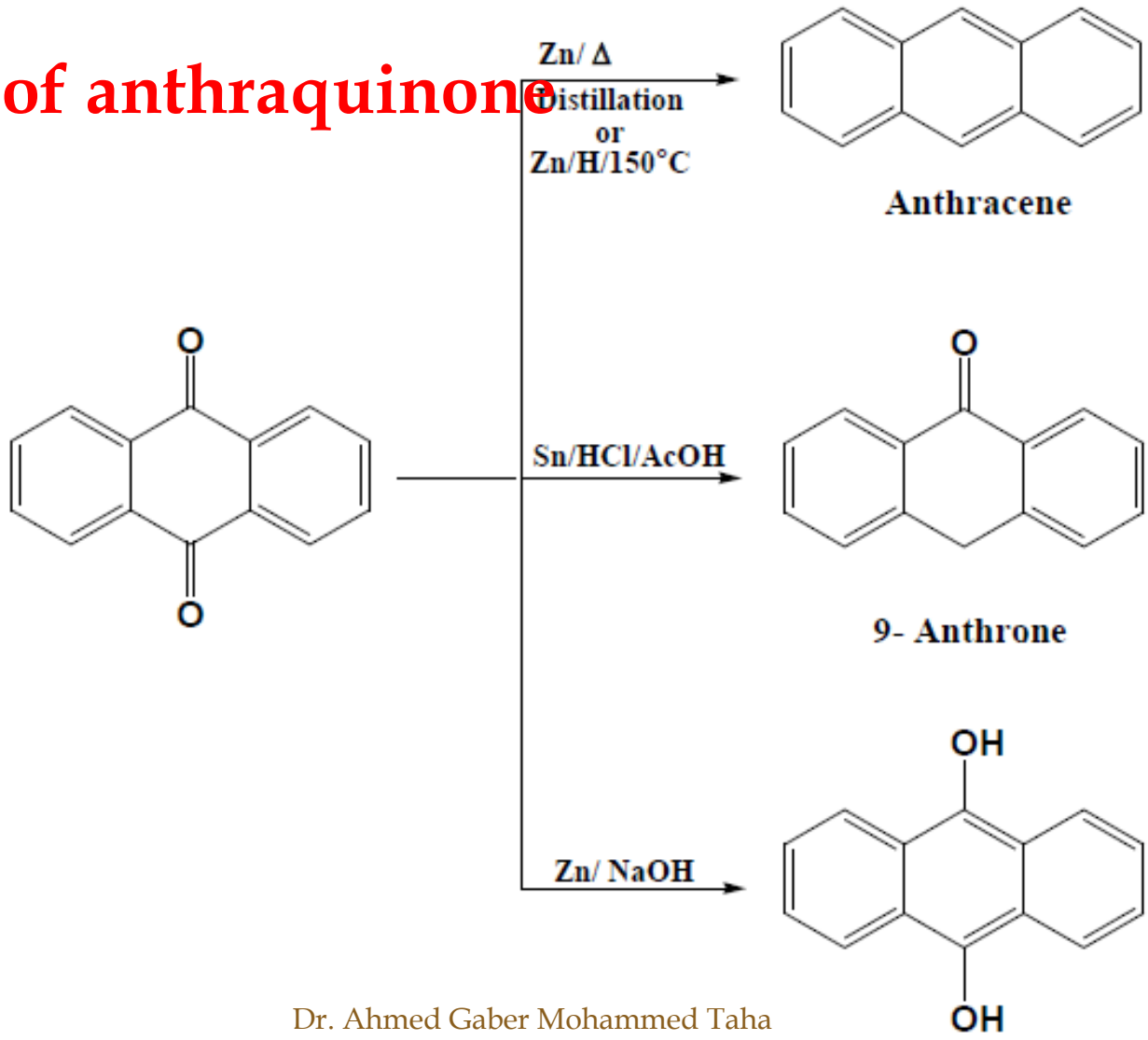


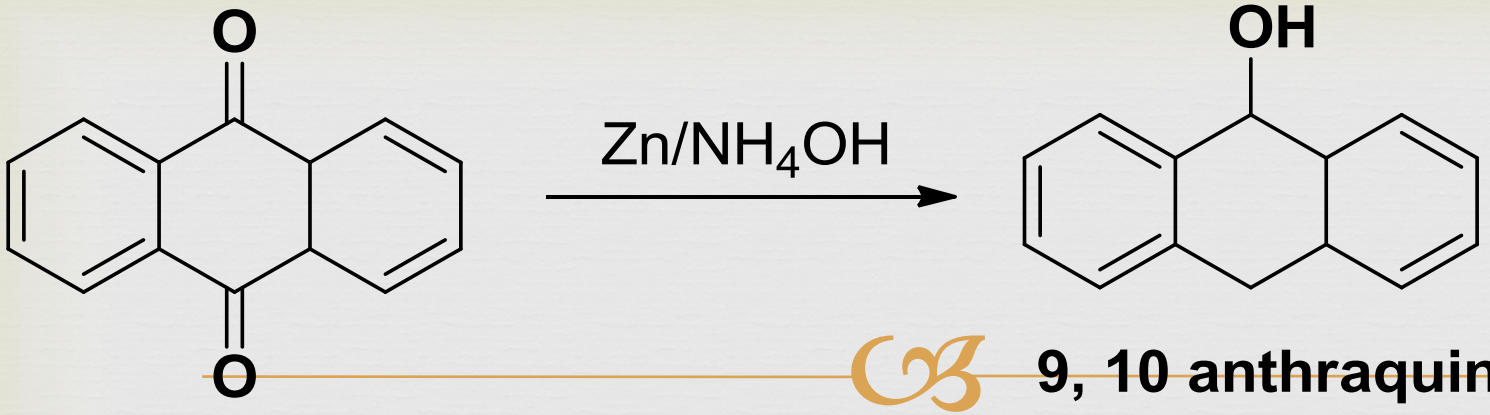
Phthalic anhydride



Chemical reactions

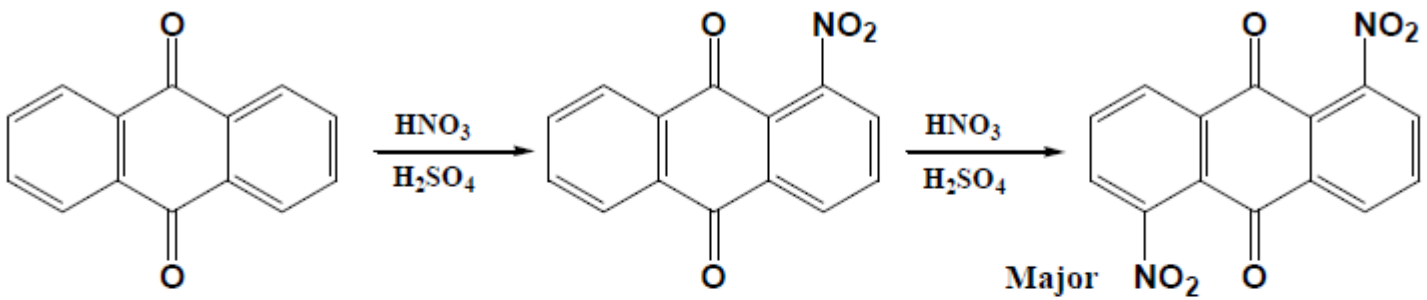
Reduction of anthraquinone





9, 10 anthraquinol

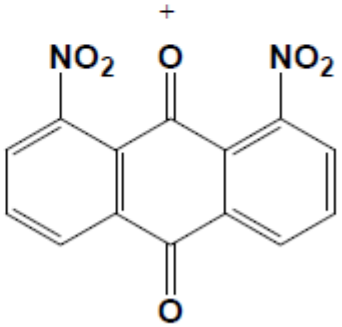
Nitration



1- nitro-9,10- anthraquinone

1,5- dinitroanthraquinone

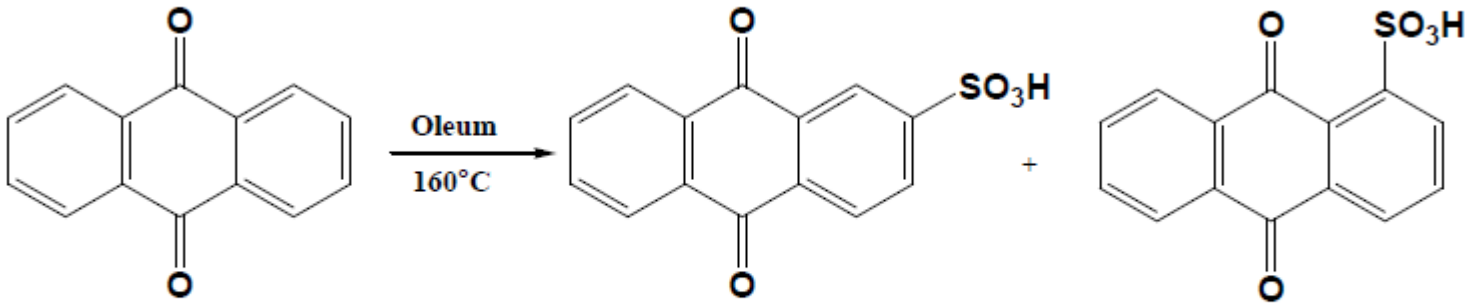
+



1,8- dinitroanthraquinone

+ with traces of 1,6 and 1,7

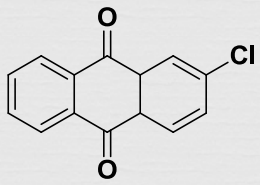
- **Sulphonation**

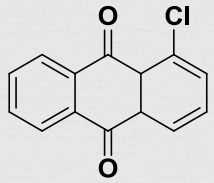


Anthraquinone-2-sulfonic acid

Major

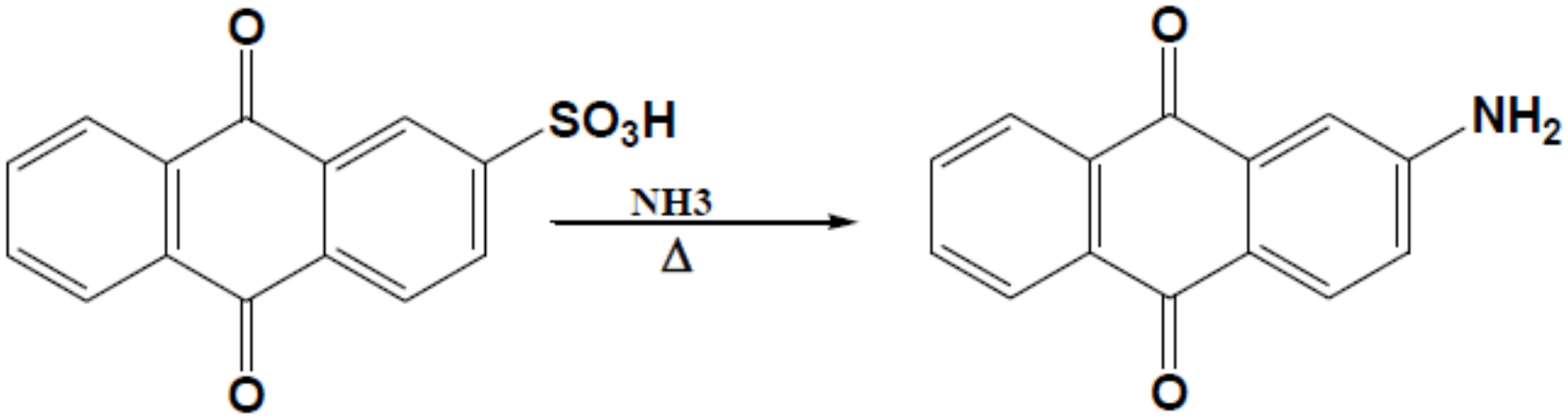
small





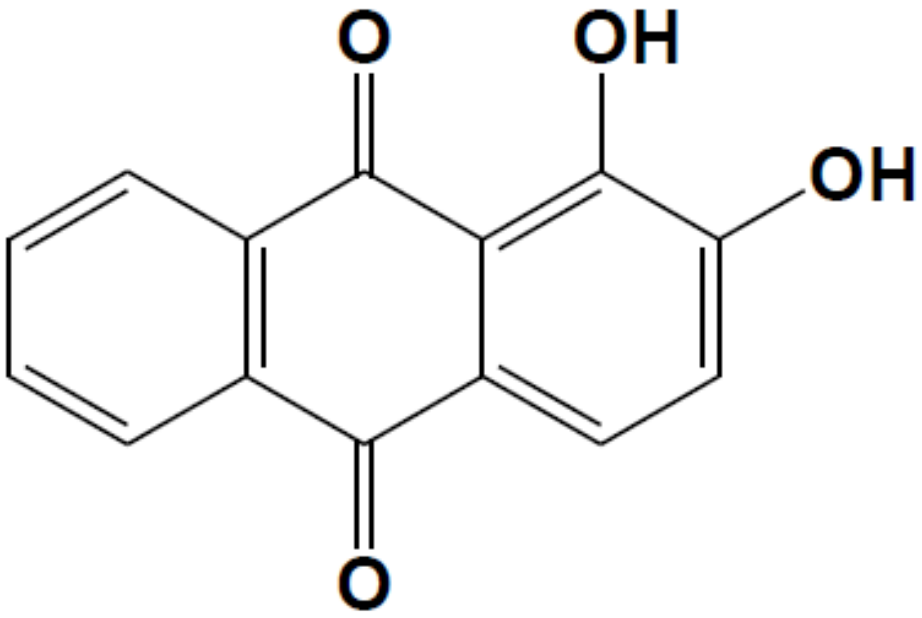
Anthraquinone does not undergo Friedl Craft reaction

- **Preparation of 2-amino-anthraquinone**



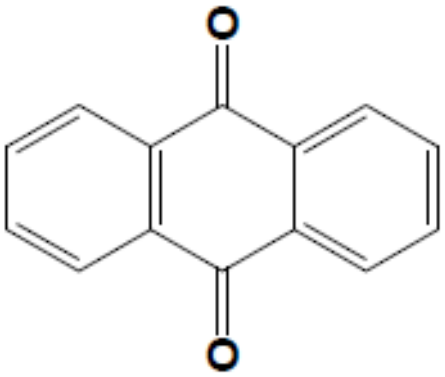
Anthraquinone-2-sulfonic acid

Alizarin



1,2-dihydroxyanthraquinone
Alizarine

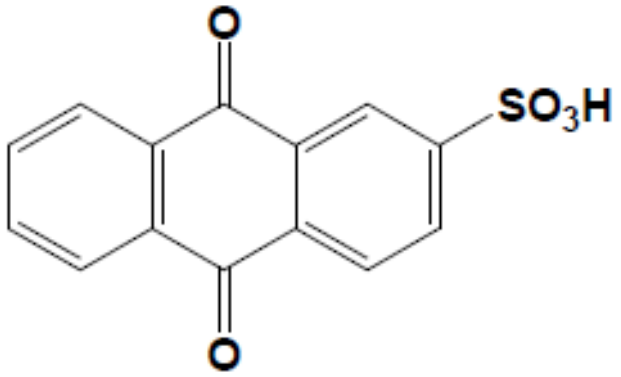
Preparation



Anthraquinone

Oleum, H_2SO_4

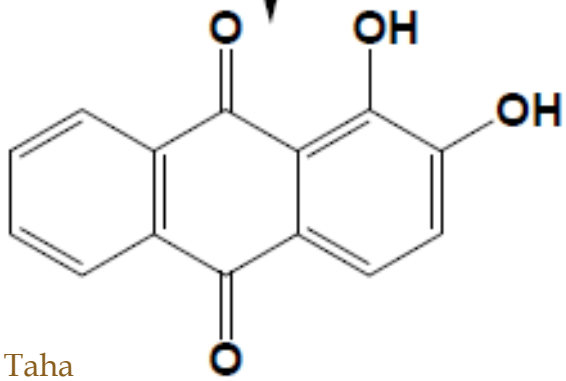
160°C



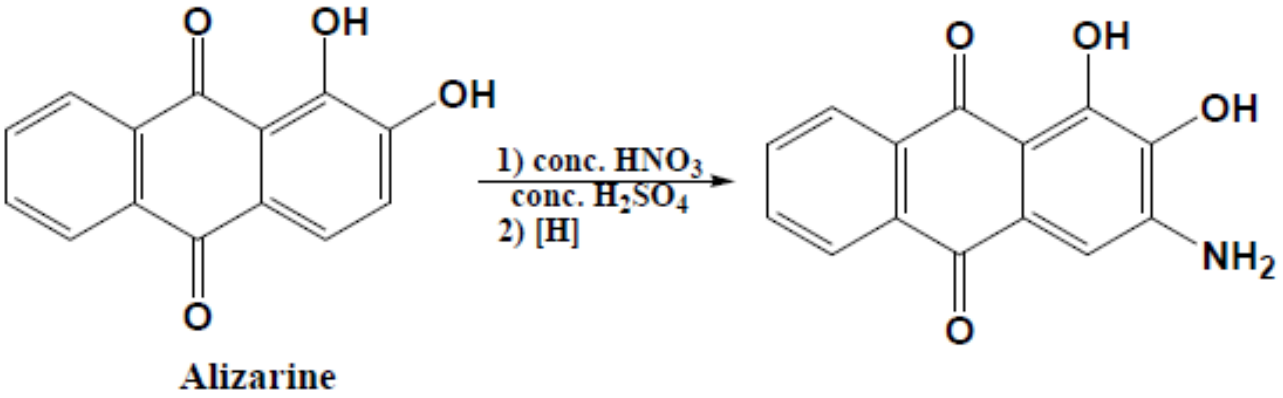
9,10- anthraquinone-2- sulfonic acid

1)NaOH, Δ

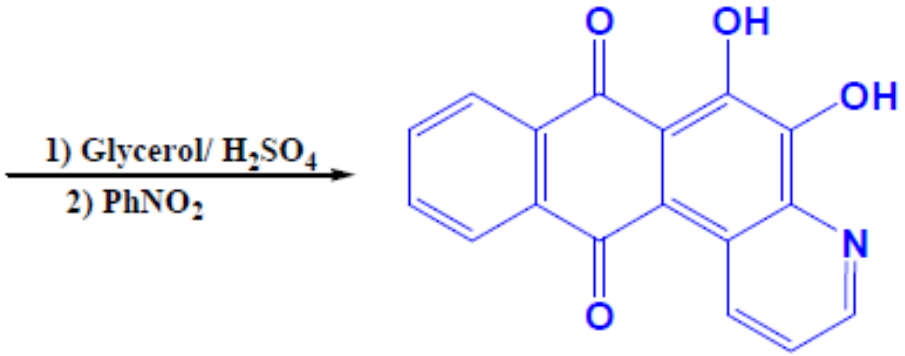
2) [O]



Preparation of Alizarine Blue



Alizarine

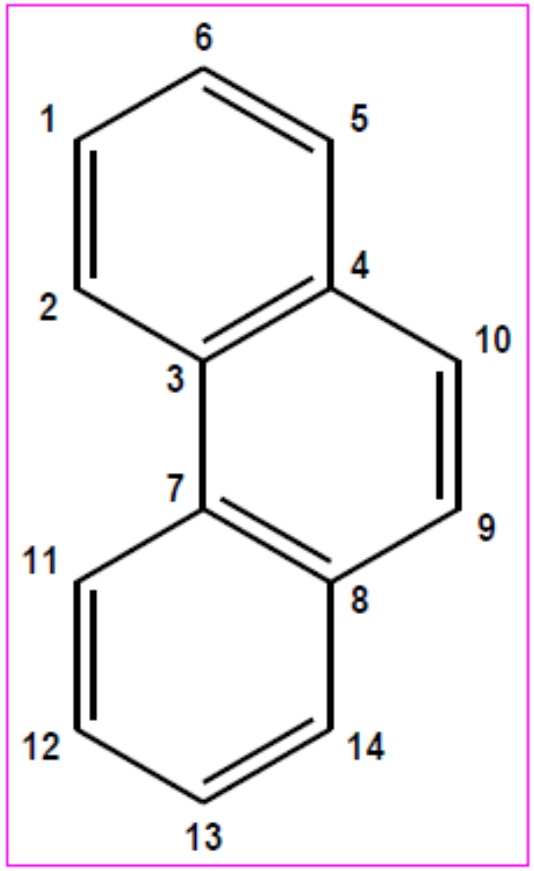


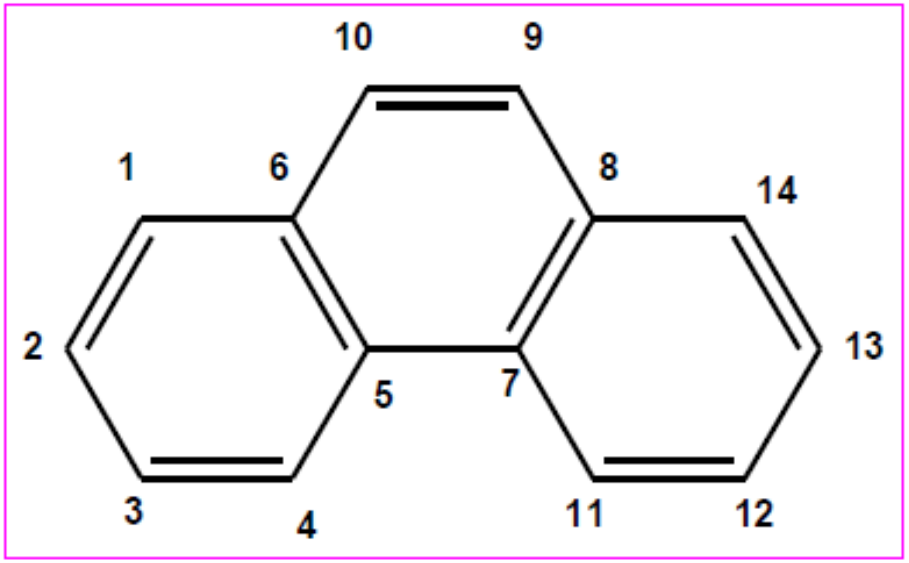
Alizarine Blue

Alizarine blue is used for dyeing wool by blue color

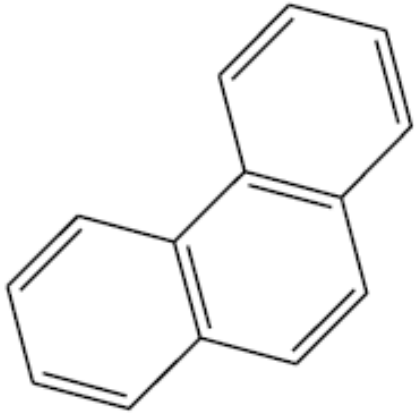
المحاضرة ٨

Phenanthrene

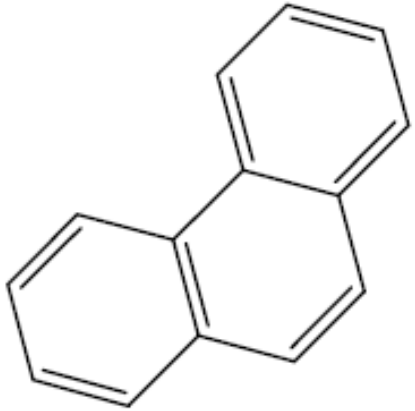


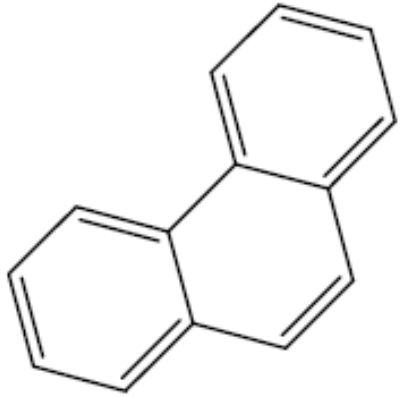


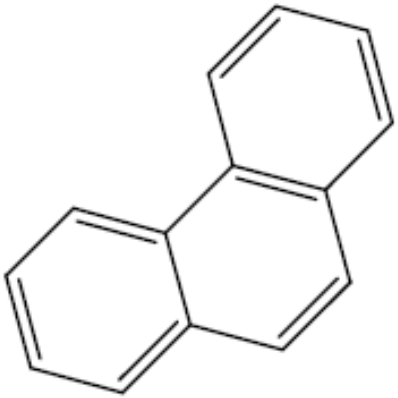
Position of double bond

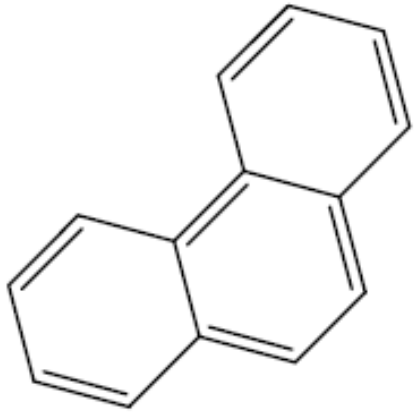


The most stable
3 benzenoid rings



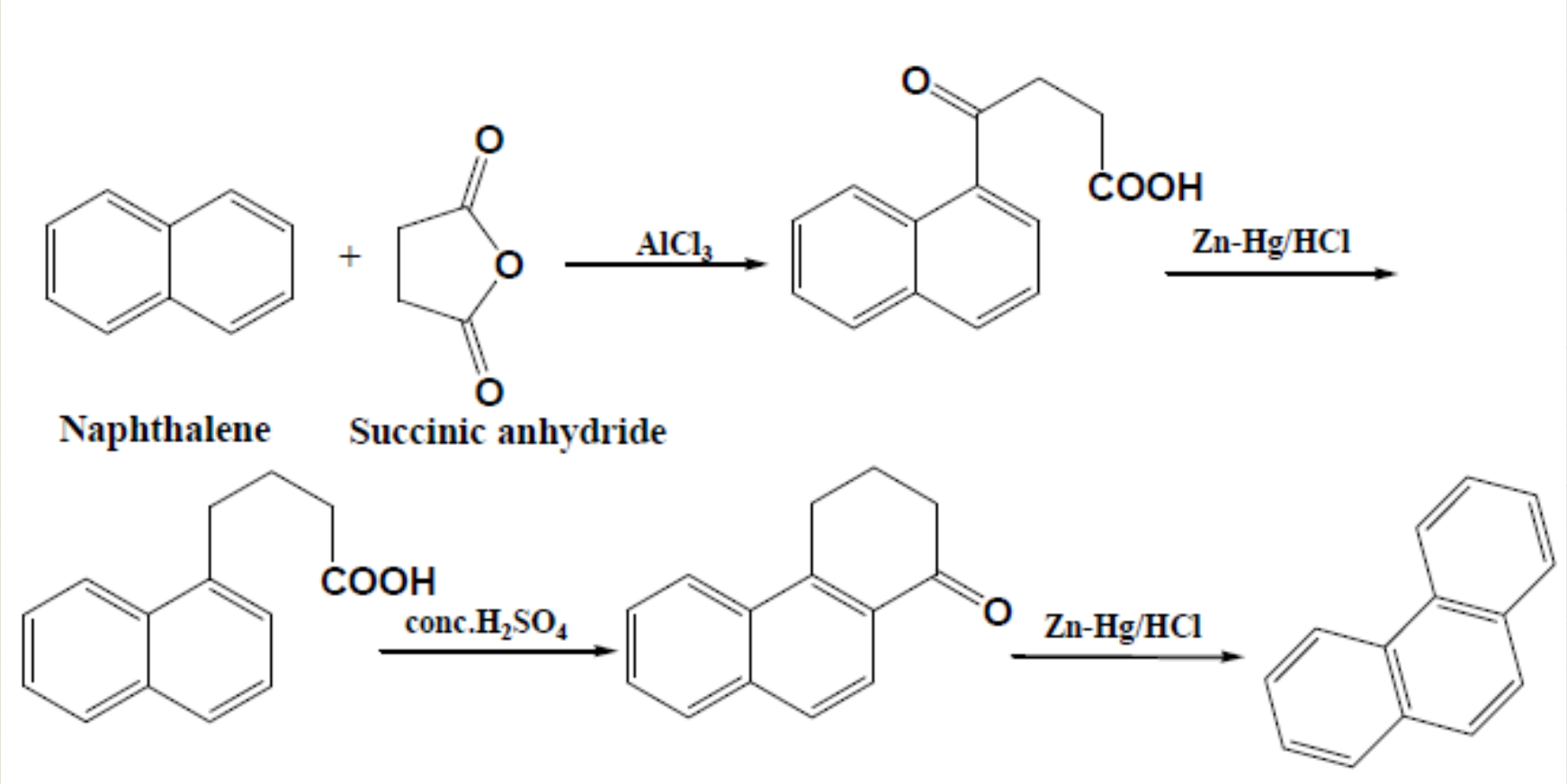






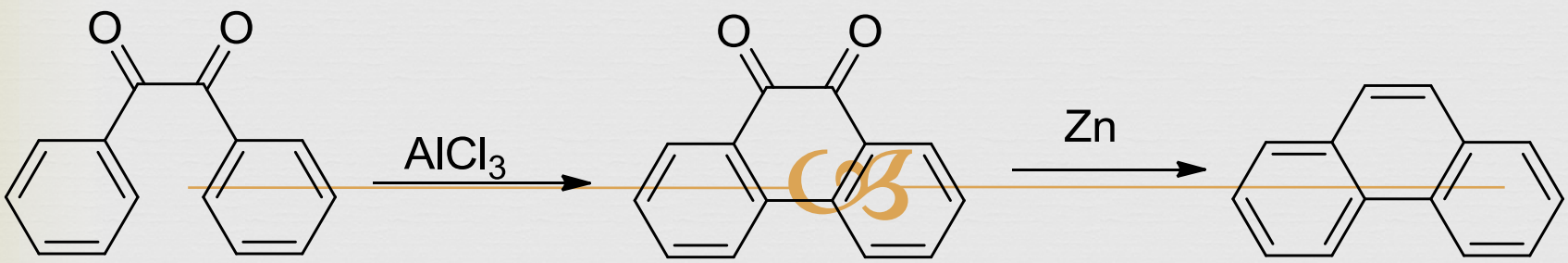
Preparation of phenanthrene

1) Howrth method

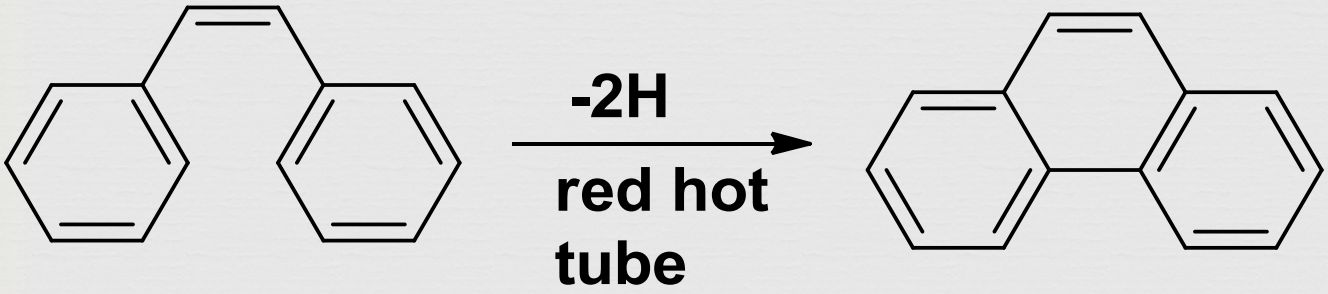


2) Posher method

3- By benzil

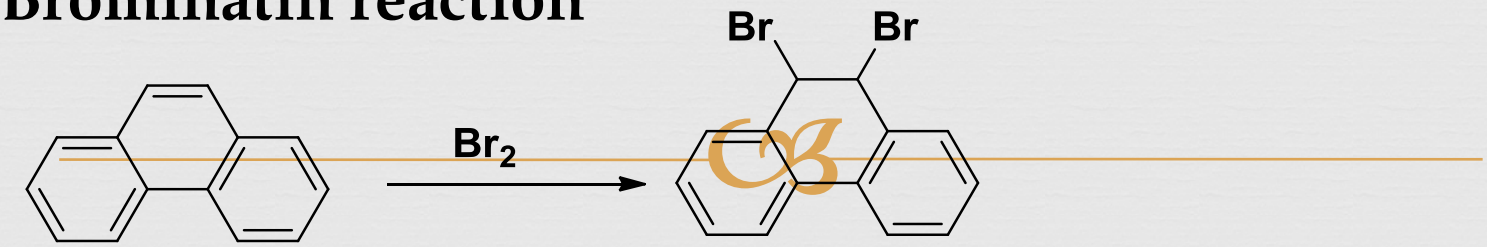


4- by stilbene

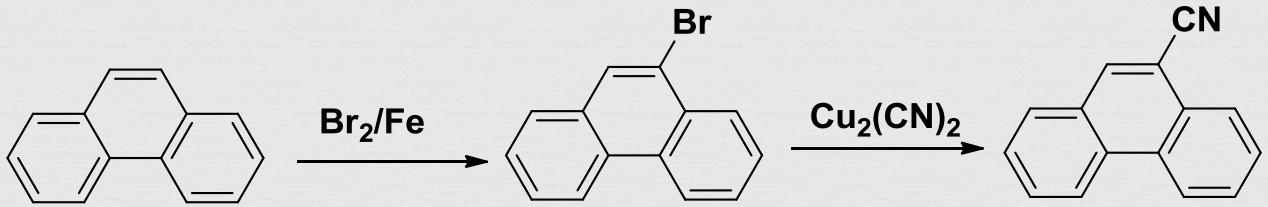


Chemical reactions:

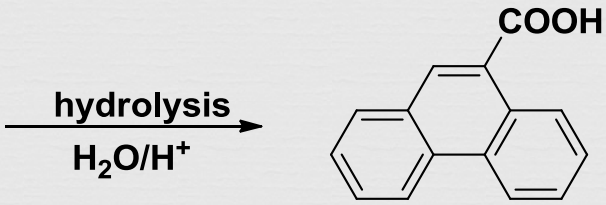
1) Brominatin reaction



9,10-phenanthracenedibromide

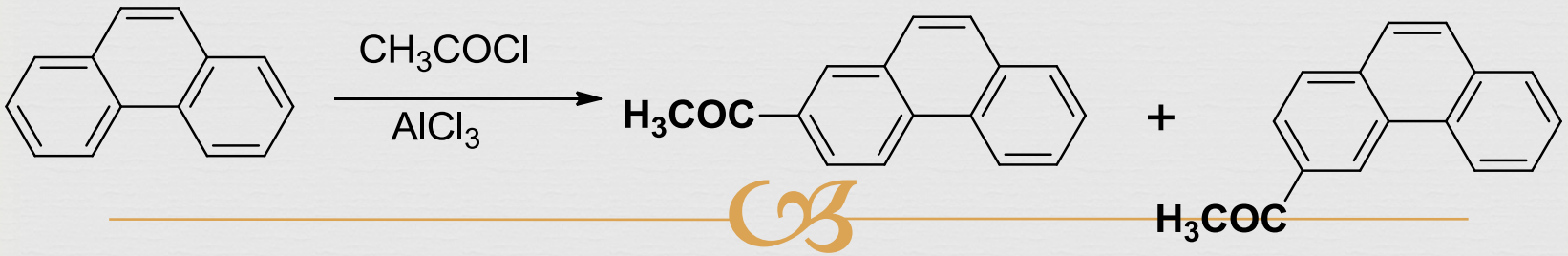


9,bromophenanthracene

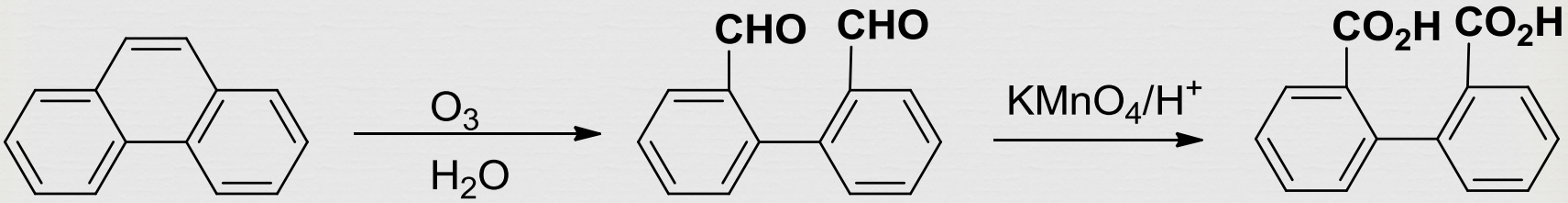


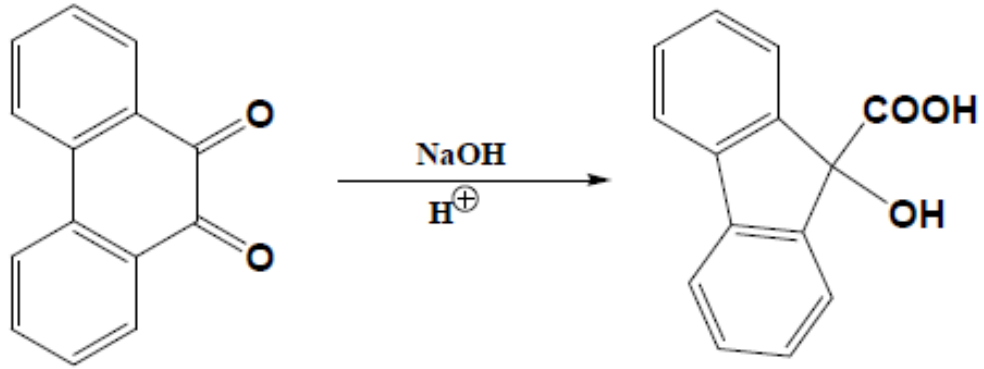
phenanthracene-9-carboxylic acid

Friedel Crafts



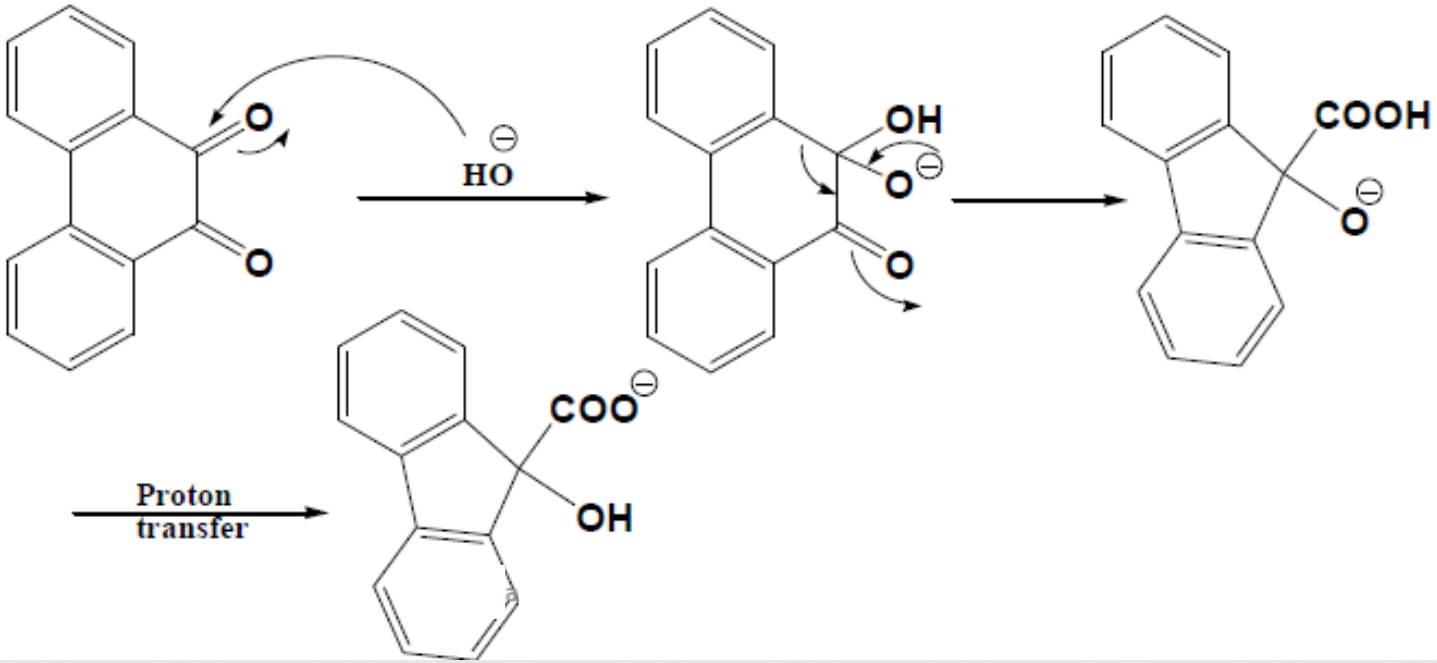
Ozone reaction

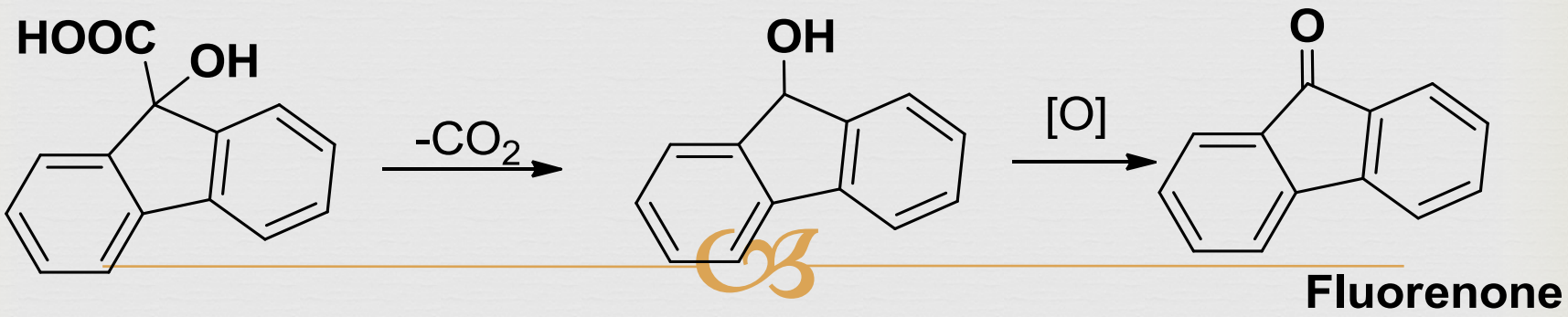




Phenanthraquinone **9-hydroxy-9*H*-flourene-9-carboxylic acid**

Mechanism

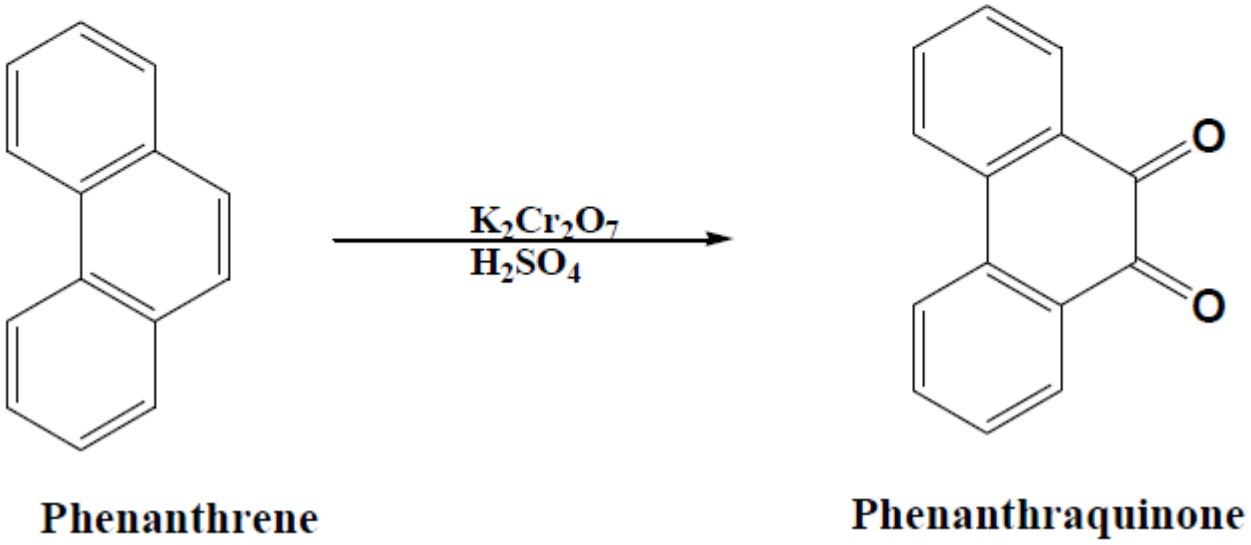




Fluorenone

Phenanthraquinone

- Preparation



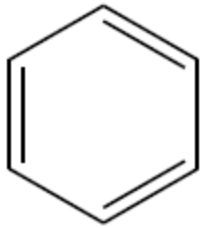
Phenanthrene **Phenanthraquinone**

Condition necessary for aromaticity

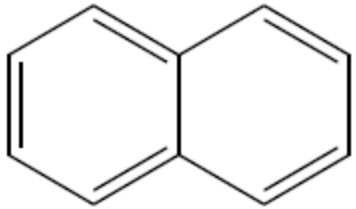
Any compound to be aromatic, it must be;

- 1. Cyclic
- 2. Planner
- 3. All atoms must be SP2
- 4. All double bonds must be conjugated
- 5. Obey Huckle rule which state that any aromatic compound must contain 4n+2 pi electrons where n 0,1,2,3,...

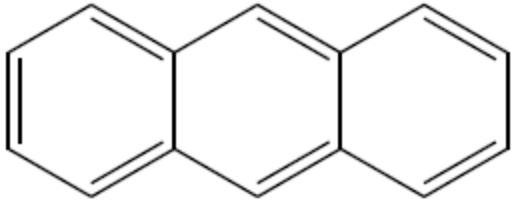
Examples



n=1
6 π electron

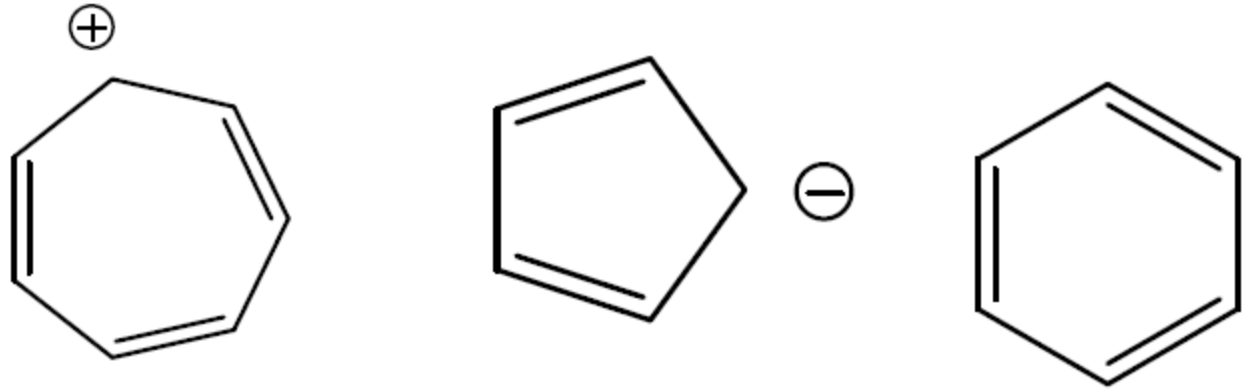


n=2
10 π electron



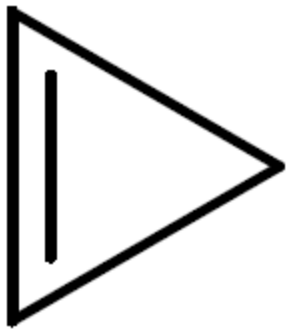
n=3
14 π electron

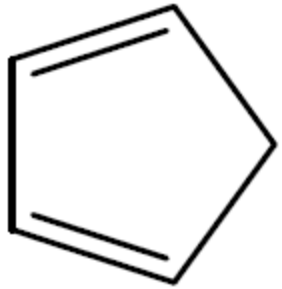
Examples of non- benzenoid aromatic cmpound



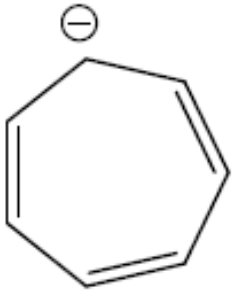
All are aromatic(cyclic, planner,1, and agree with Huckle rule: 4n+2= 6 (n=1)

Examples of non- aromatic





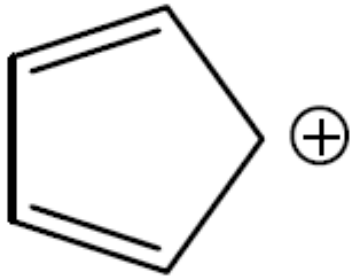
Not aromatic; both contain Sp3



Not aromatic

Does not obey Huckel rule

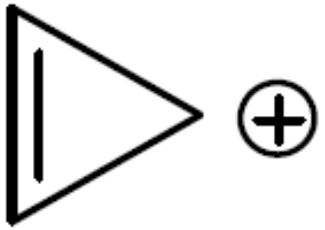
4n+2=8; n=1.5



Not aromatic

Does not obey Huckel rule

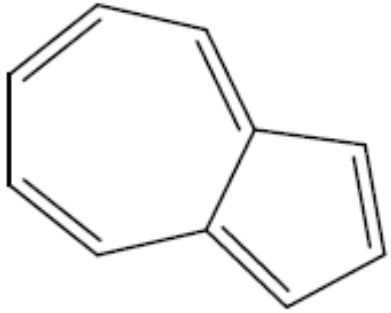
4n+2=4; n=0.5



Aromatic; cyclic, planner,

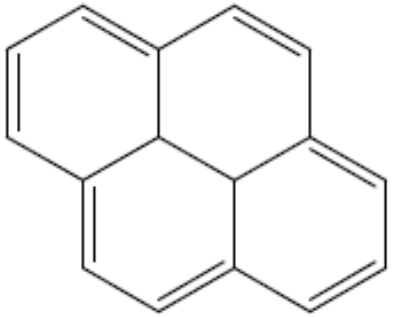
obey Huckel rule

4n+2=2; n=0



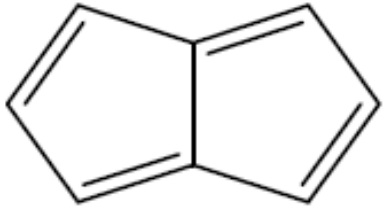
Aromatic

4n+2=10; n=2



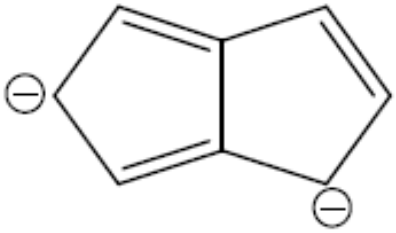
Aromatic

4n+2=14; n=3

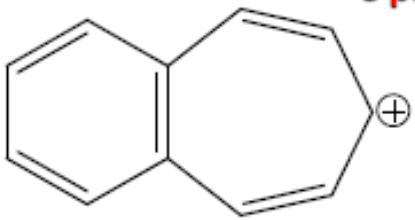


Not Aromatic

8 pi electrons



Aromatic



Aromatic