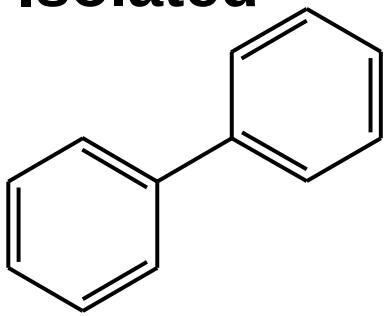
Polynuclear Aromatic Hydrocarbons

Polynuclear Hydrocarbons

Benzenoid

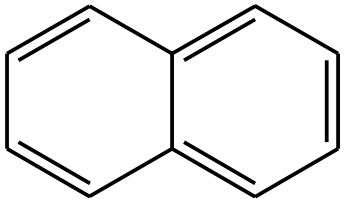
Isolated



Biphenyl

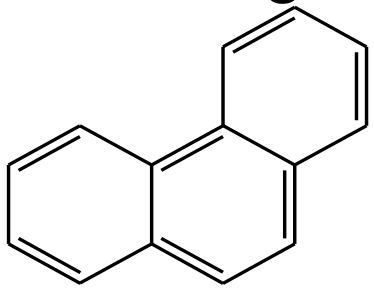
Fused rings

Linear



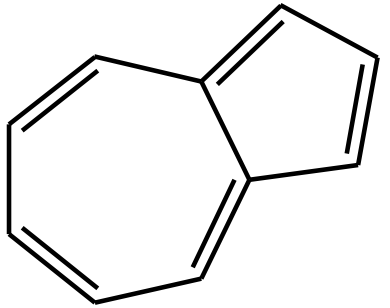
Naphthalene

Angular



Phenanthrene

Non- Benzenoid



Azulene

I. Isolated Ring Polynuclear Hydrocarbons

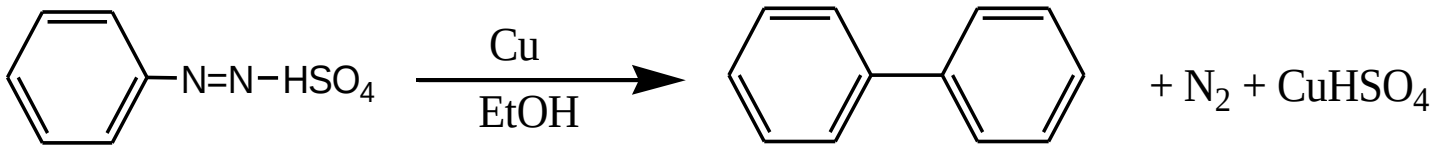
Biphenyl (diphenyl):

Preparation of Biphenyl

a) Fittig reaction

$$2Ph\text{-}Br + 2Na \xrightarrow[soln]{ether} Ph\text{-}Ph + 2NaBr$$

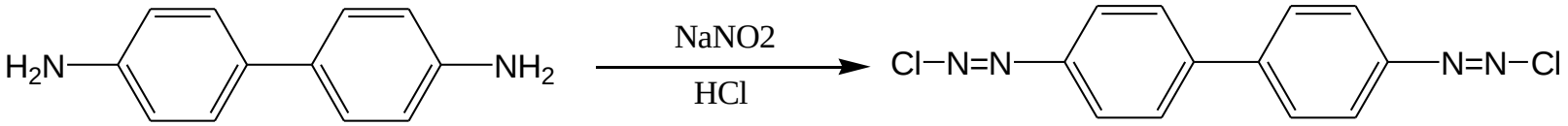
b) From benzene diazonium sulphate



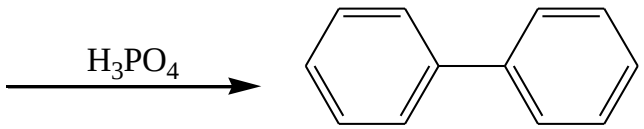
$+ N_2 + CuHSO_4$

Biphenyl

c) From benzidine

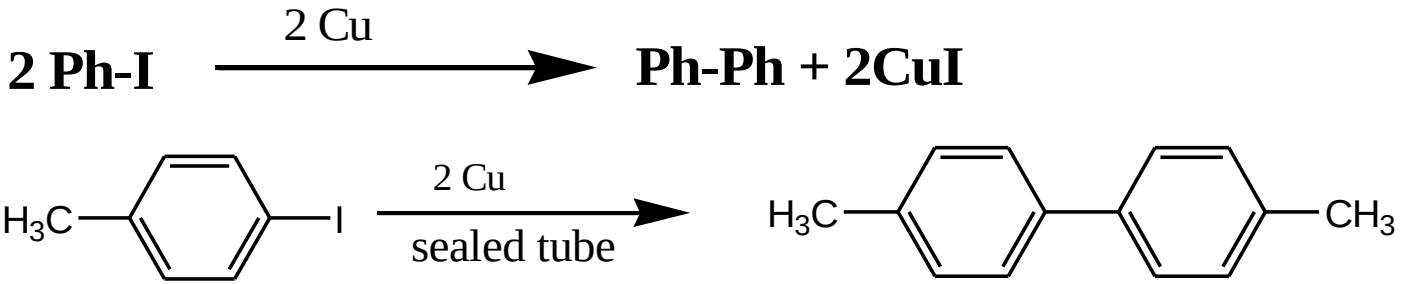


Benzidine

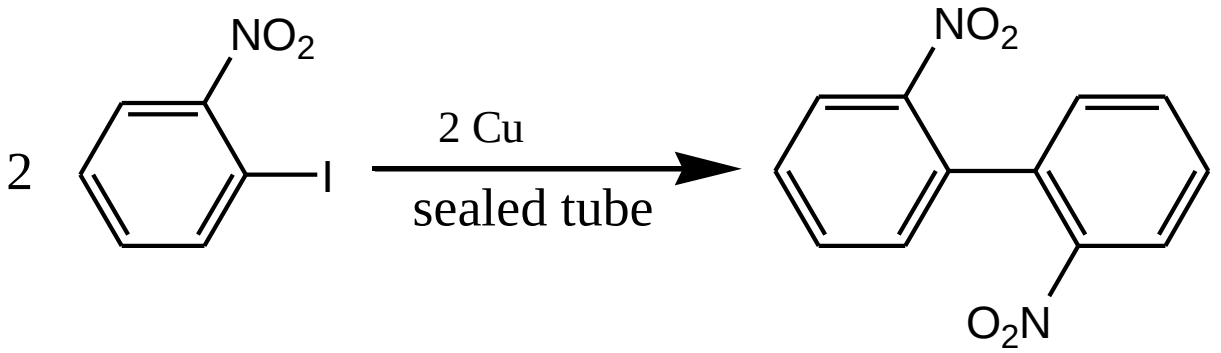


Biphenyl

d) Ulmann diaryl synthesis

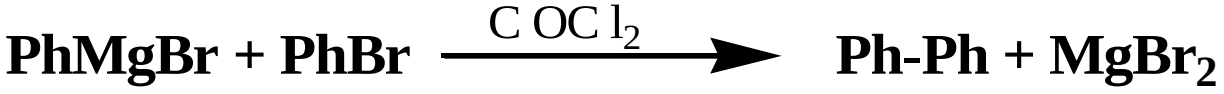


4,4'- Dimethyl-biphenyl



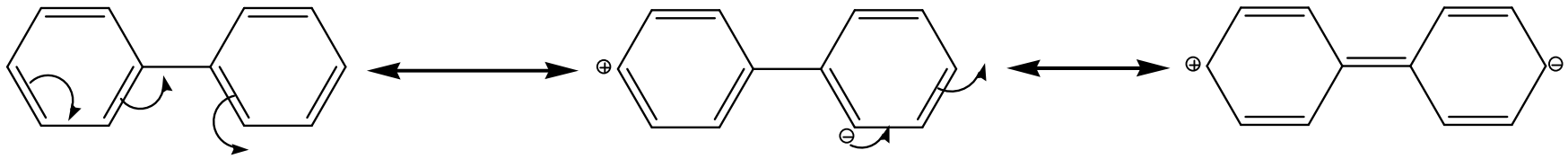
2,2'- Dinitro-biphenyl

e) By using Arylmagnesium halide



Reactions of biphenyl
Biphenyl undergoes substitution reactions,

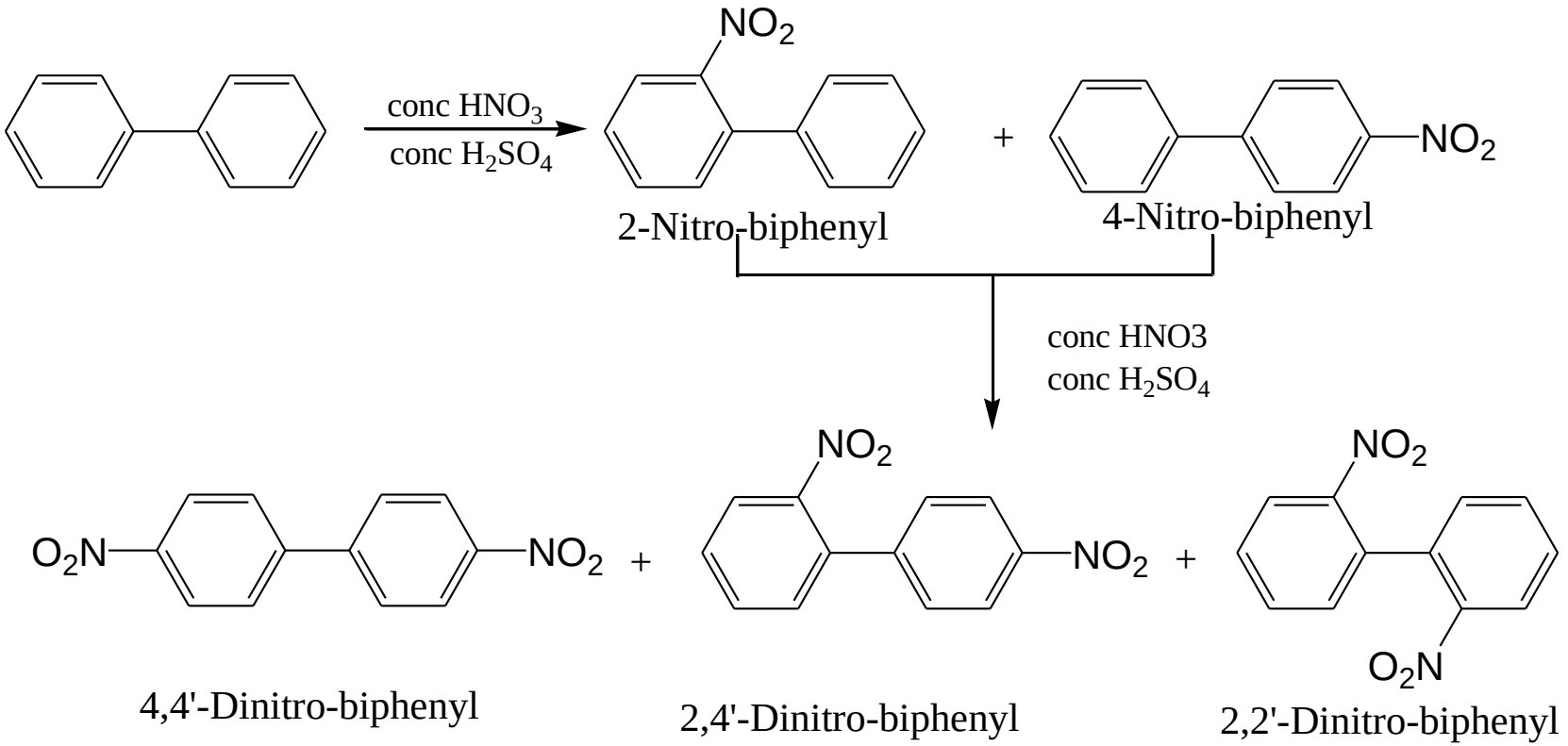
In biphenyl one ring act as electron donating group and the other act as electron withdrawing group



Resonance shows that O- and P- are the most reactive positions towards electrophilic substitution.

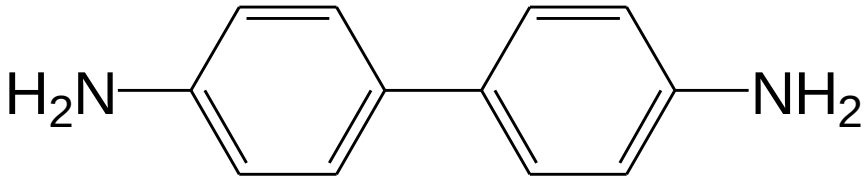
The electrophilic substitution occurs in 4- position (major) and 2- position (minor) due to steric effect of other benzene ring.

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

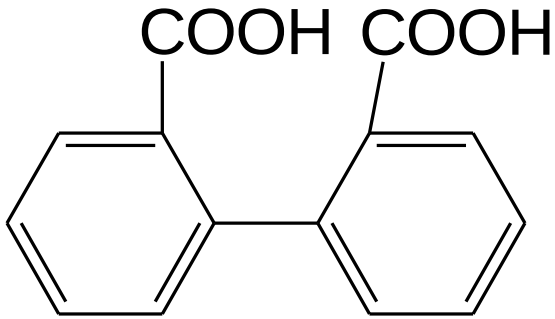


Biphenyl derivatives

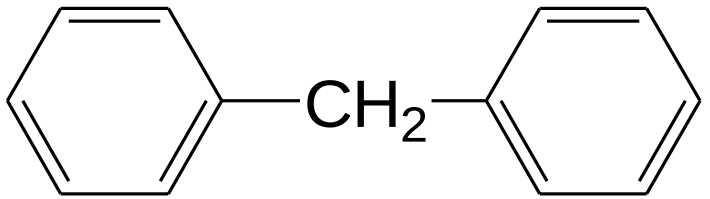
(1) Benzidine (4, 4`-diaminobiphenyl)



(2) Diphenic acid

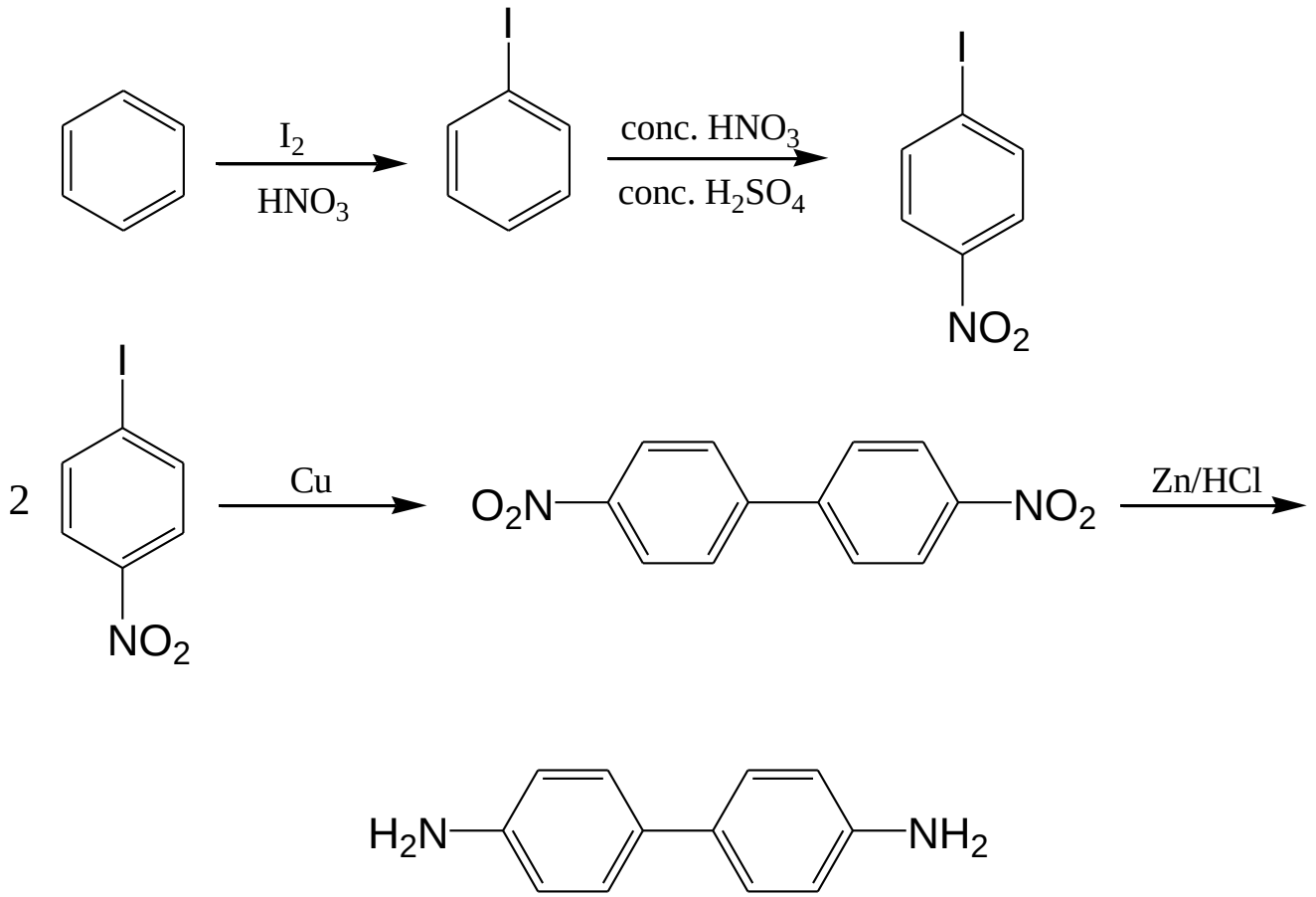


(3) Diphenyl methane

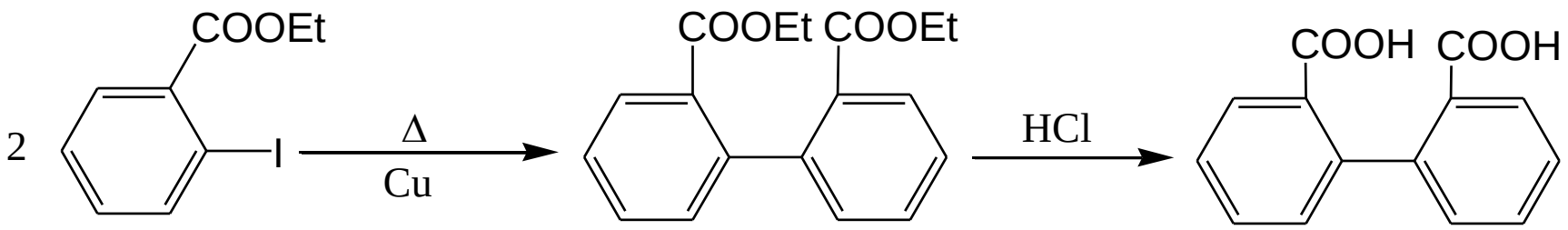


Q. Show how could you prepare benzidine from benzene?

- Answer

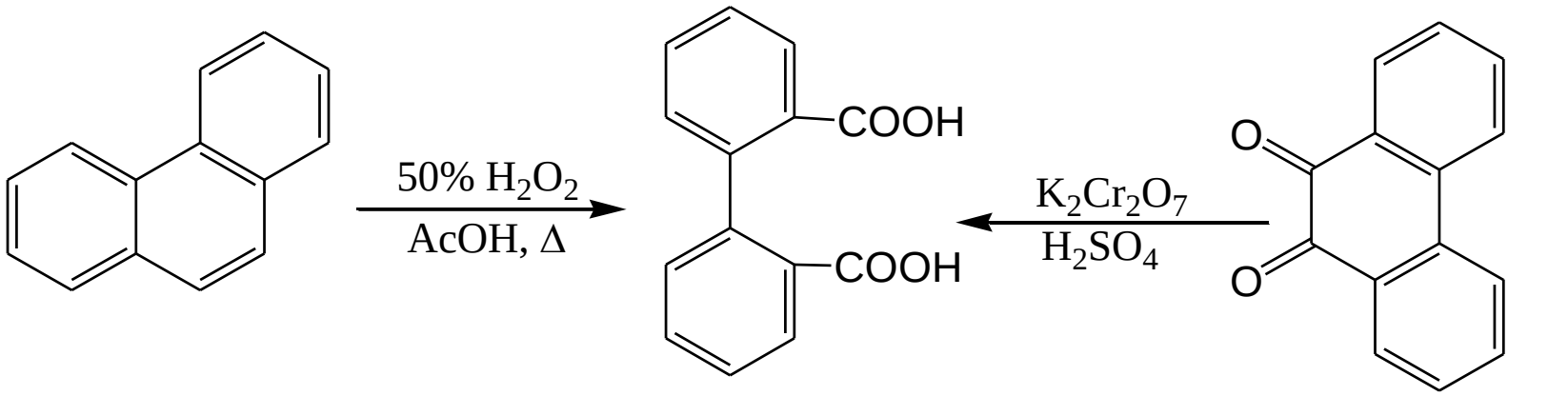


Ulmann diaryl synthesis



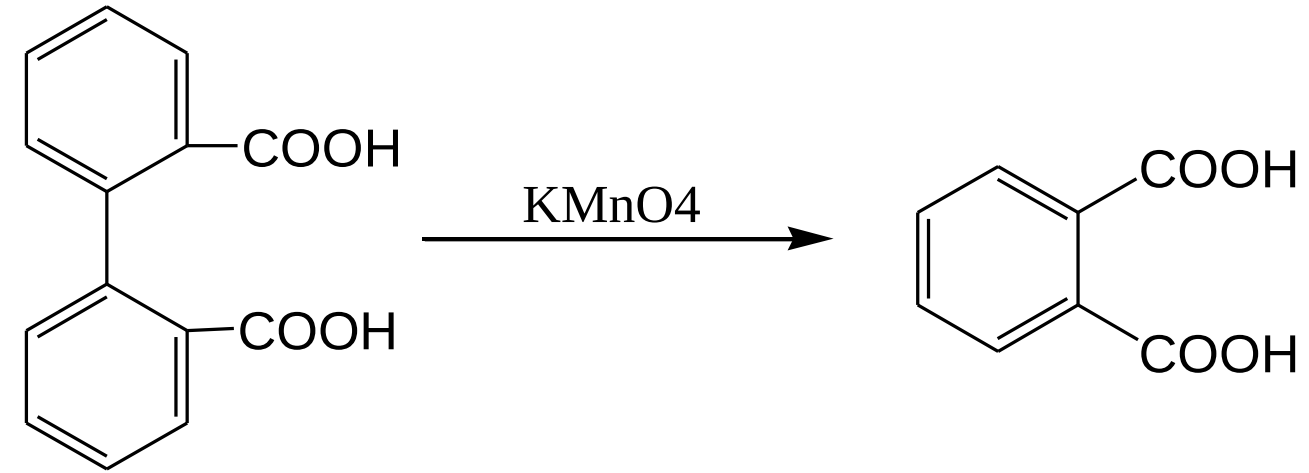
biphenyl- 2,2'- dicarboxylic acid
(Diphenic acid)

oxidation of Phenanthrene or phenanthraquinone



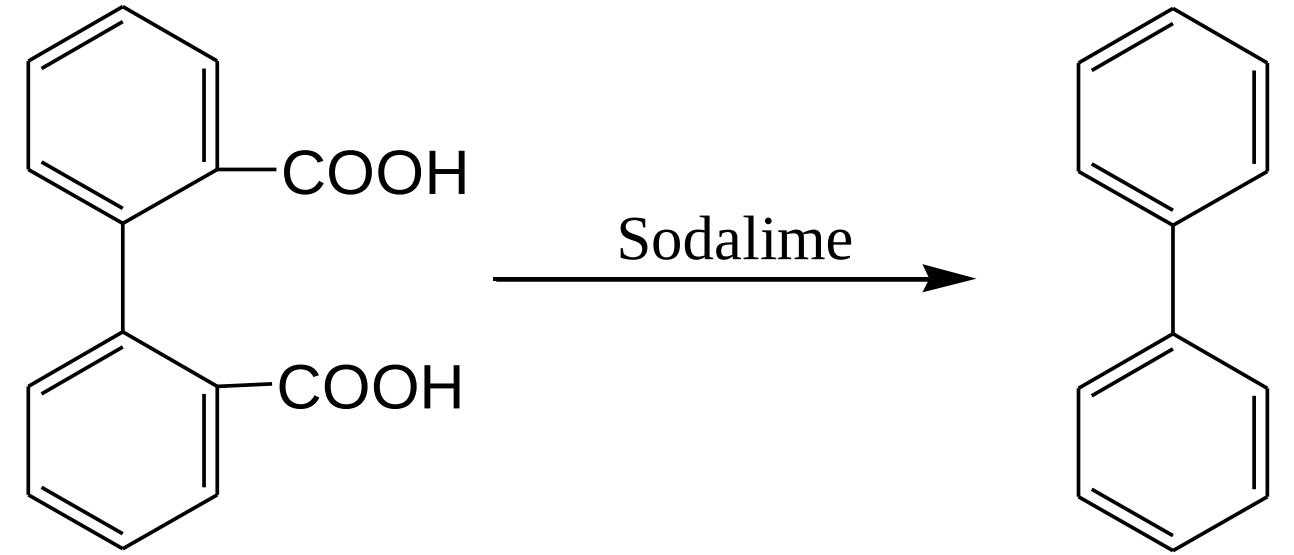
phenanthrene **Diphenic acid** **phenanthraquinone**

Oxidation of KMnO4

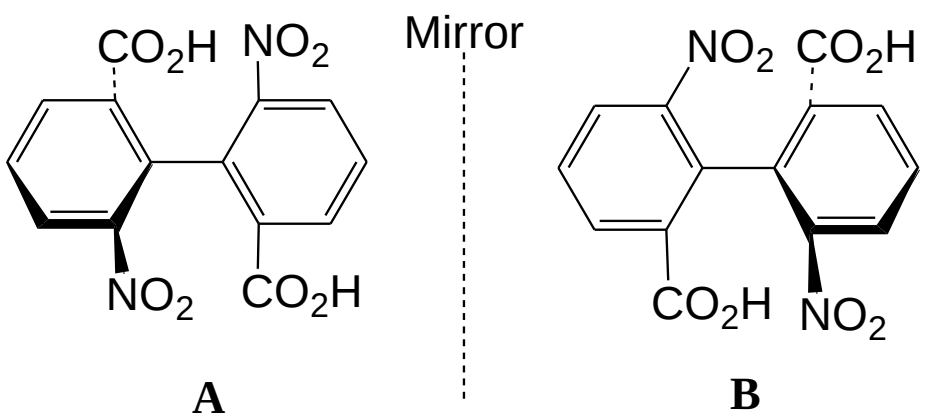


Diphenic acid **pthalic acid**

with sodalime

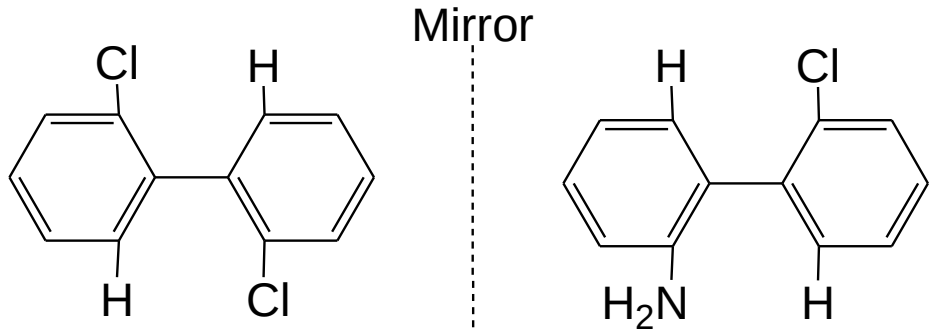


Diphenic acid **biphenyl**



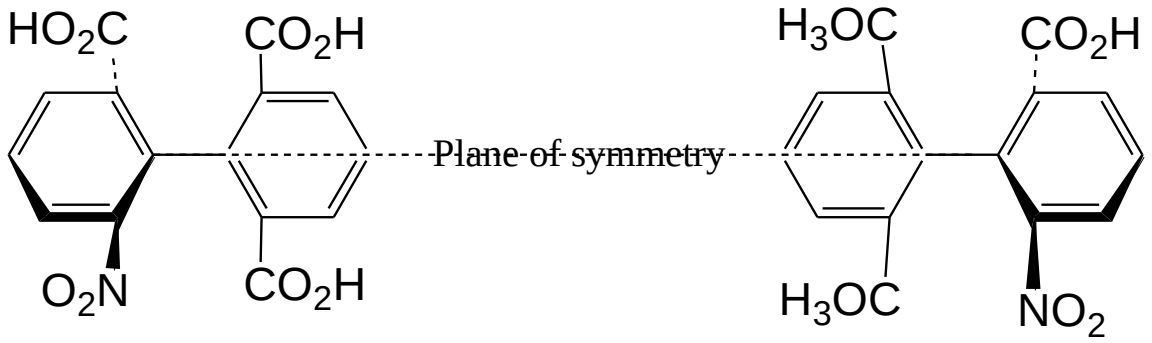
A **B**

Optically active

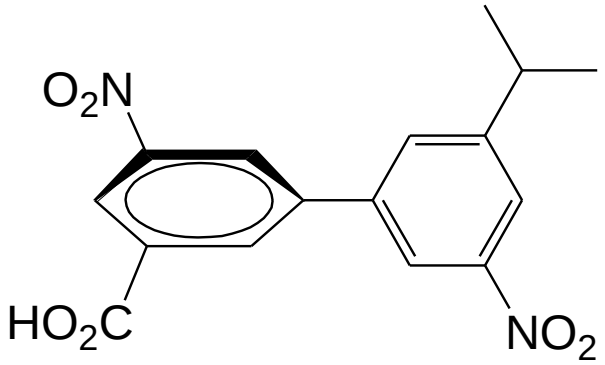


Optically active

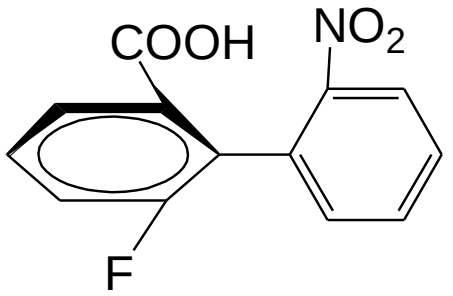
- When o- position contains ***two similar groups***, the molecule is optically inactive due to presence of plane of symmetry .. for example



Optically inactive due to presence of plane of symmetry

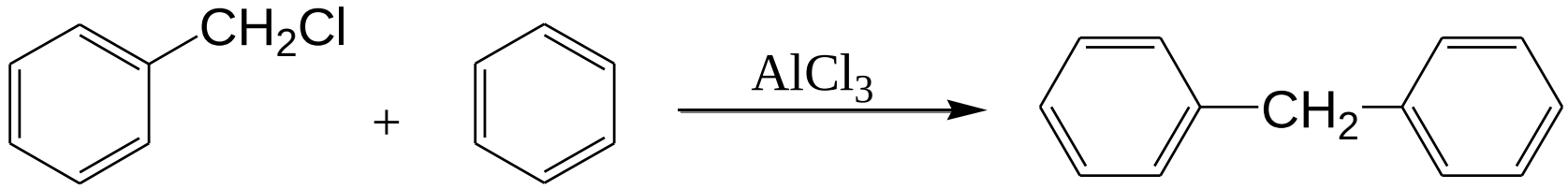


Optically active
free rotation is possible

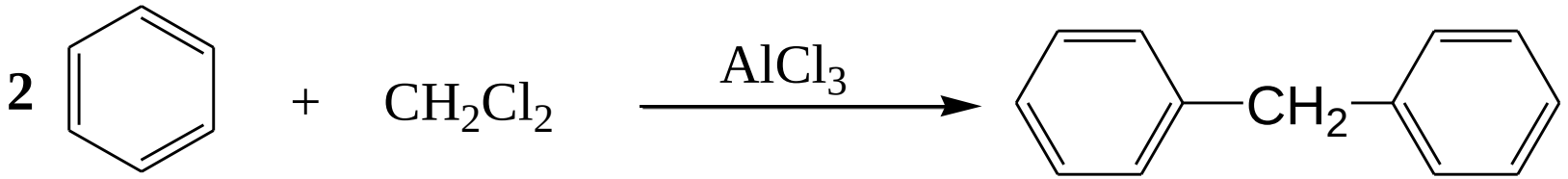


Optically active
F is a small atom so permit by free rotation

Friedel- Crafte



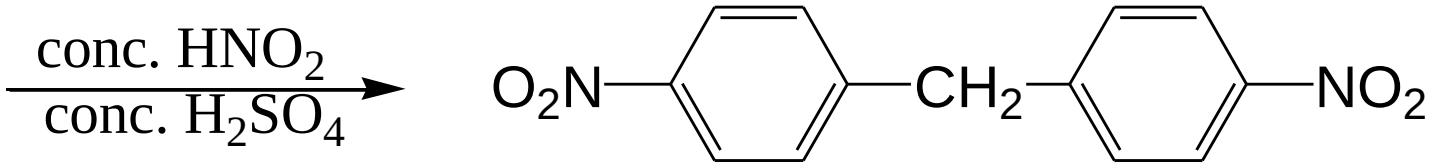
Benzyl chloride **Diphenyl methane**



Diphenyl methane

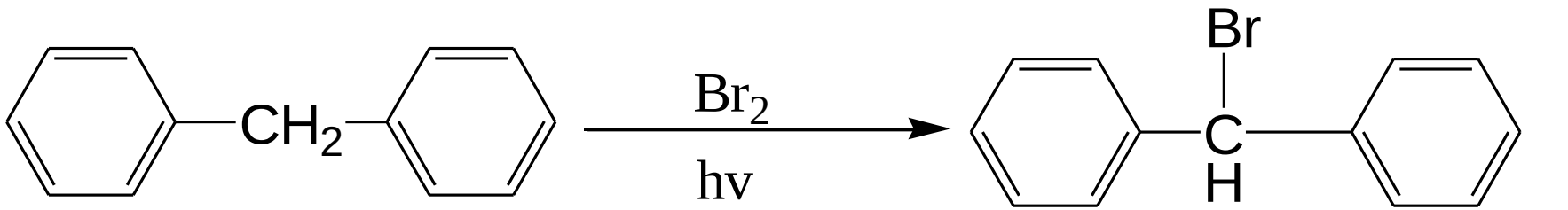
1. Nitration

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



bis(4- nitrophenyl)methane

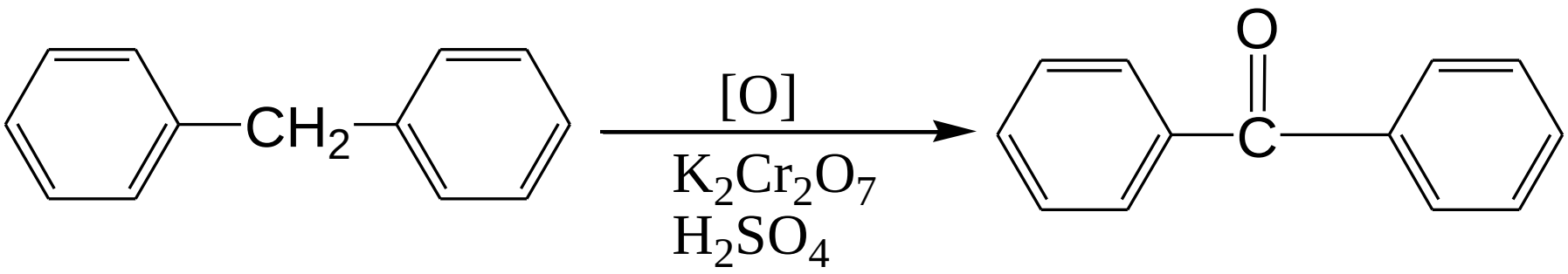
2. Halogenation



Diphenyl methane

Diphenylmethylbromide

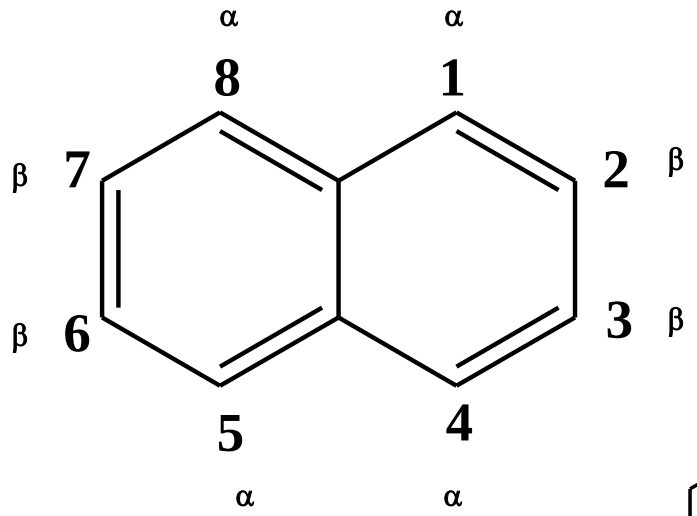
3. Oxidation

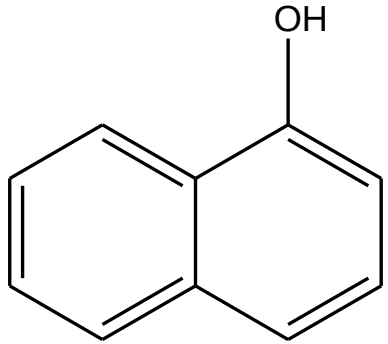


Diphenyl methane **benzophenone**

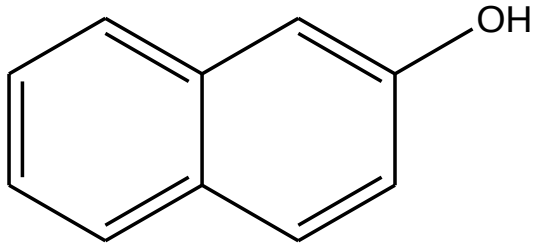
II. Fused System

a) Naphthalene

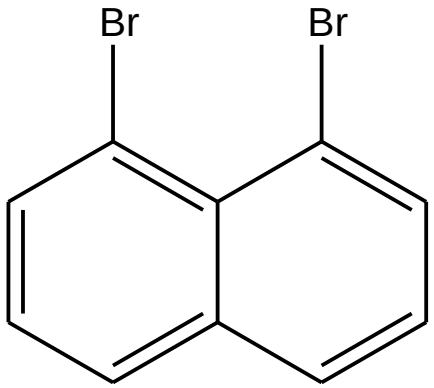




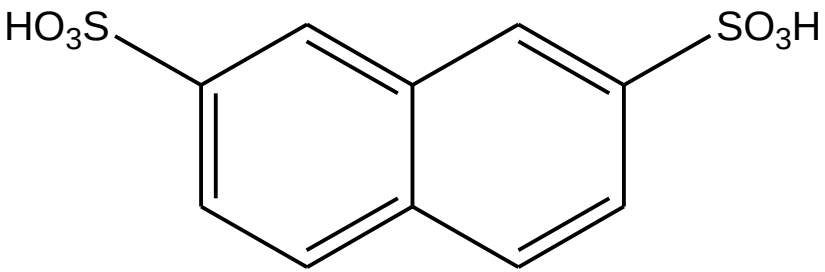
1-Naphthol or α-Naphthol



2-Naphthol or β -Naphthol



1,8- Dibromo-naphthalene

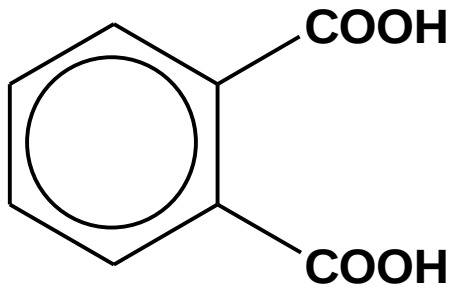


Naphthalene-2,7- disulfonic acid

Structure elucidation of naphthalene

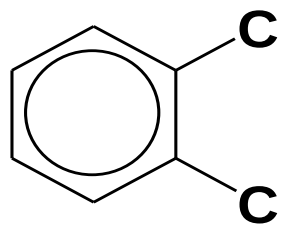
1- Molecular Formula: C_6H_8

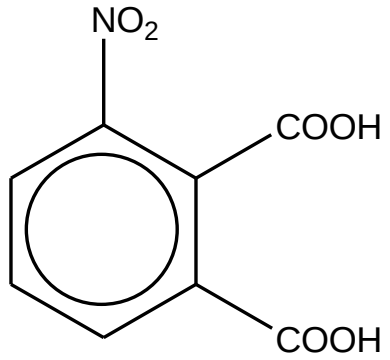
2- Naphthalene $\xrightarrow{[\,O\,]}$



Phthalic acid

So naphthalene contain the skeleton

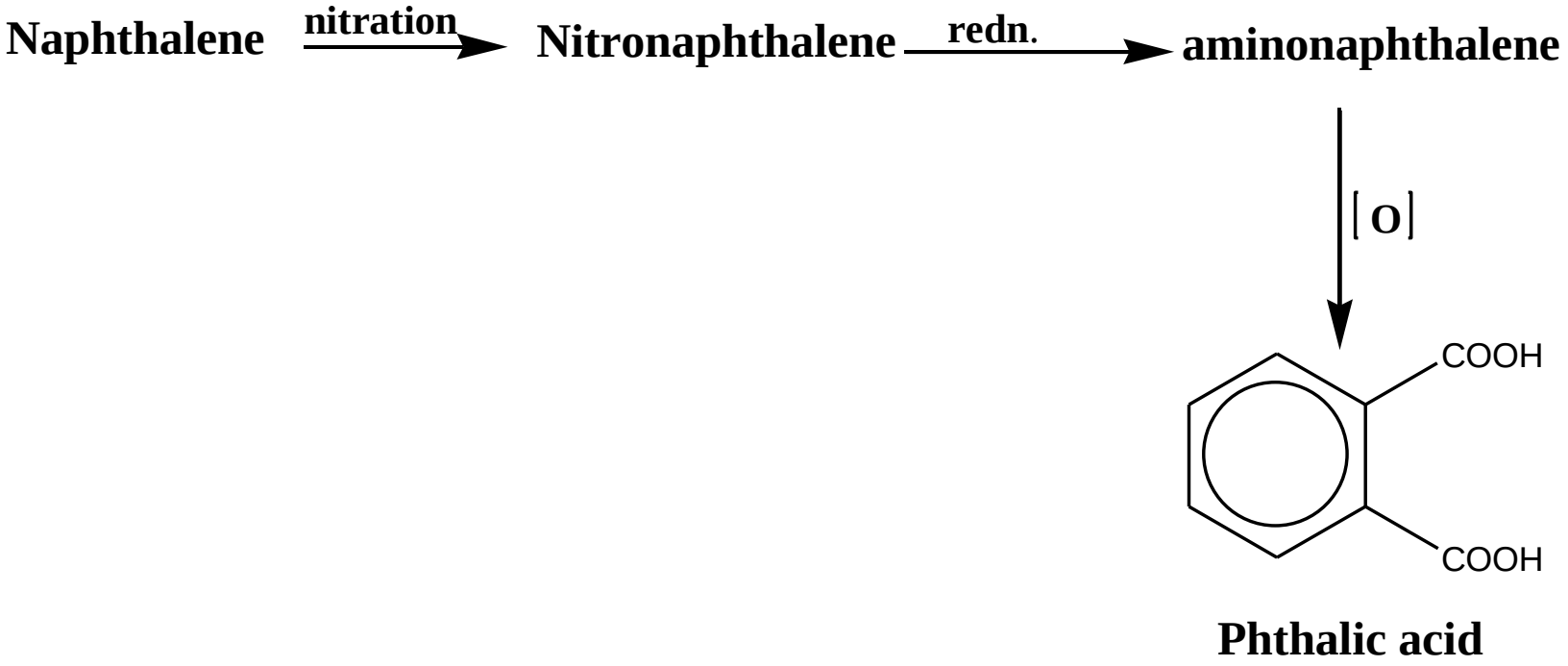


3- **Naphthalene** $\xrightarrow{\text{nitration}}$ **Nitronaphthalene** $\xrightarrow{[\,O\,]}$ 

Nitrophthalic acid

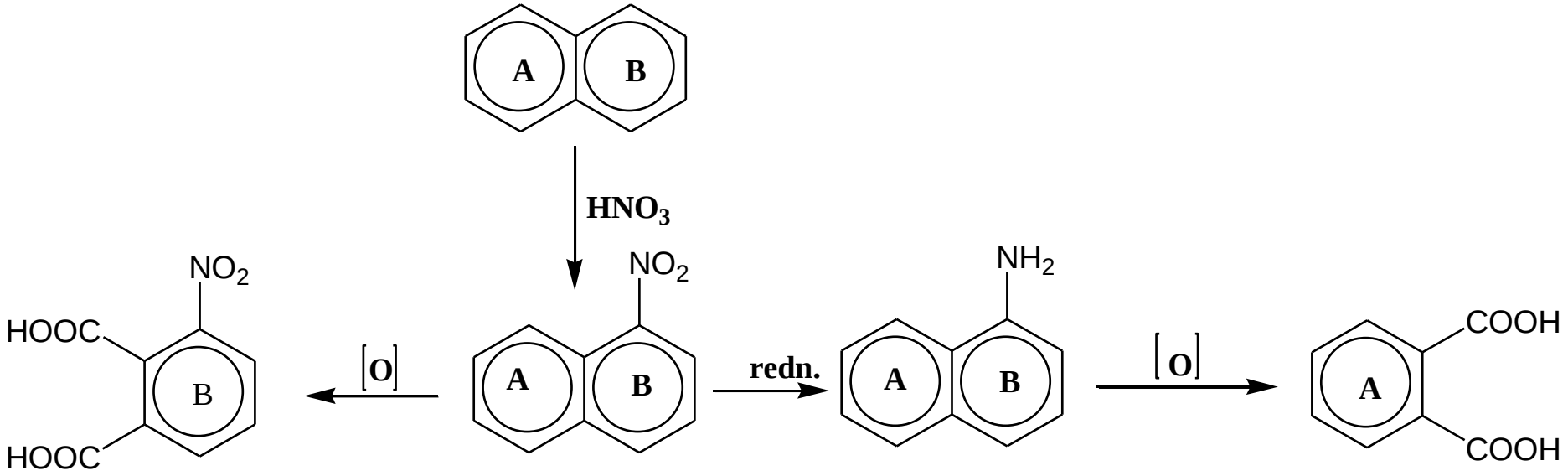
So nitro group is present in benzene ring

4-



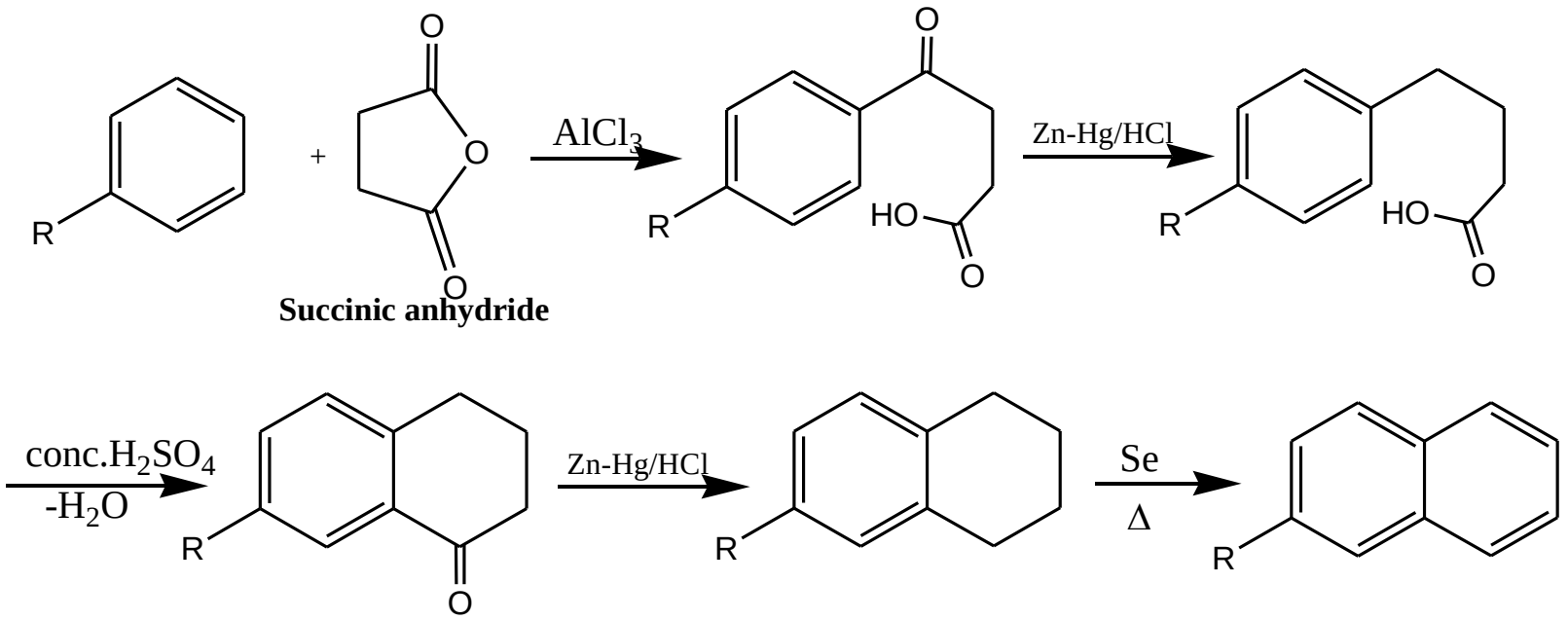
The benzene ring in phthalic acid produced by oxidation of aminonaphthalene is not the same ring is that obtained by oxidation of nitronaphthalene.

i.e. Naphthalene contains two benzene rings and we can explain this by this equation

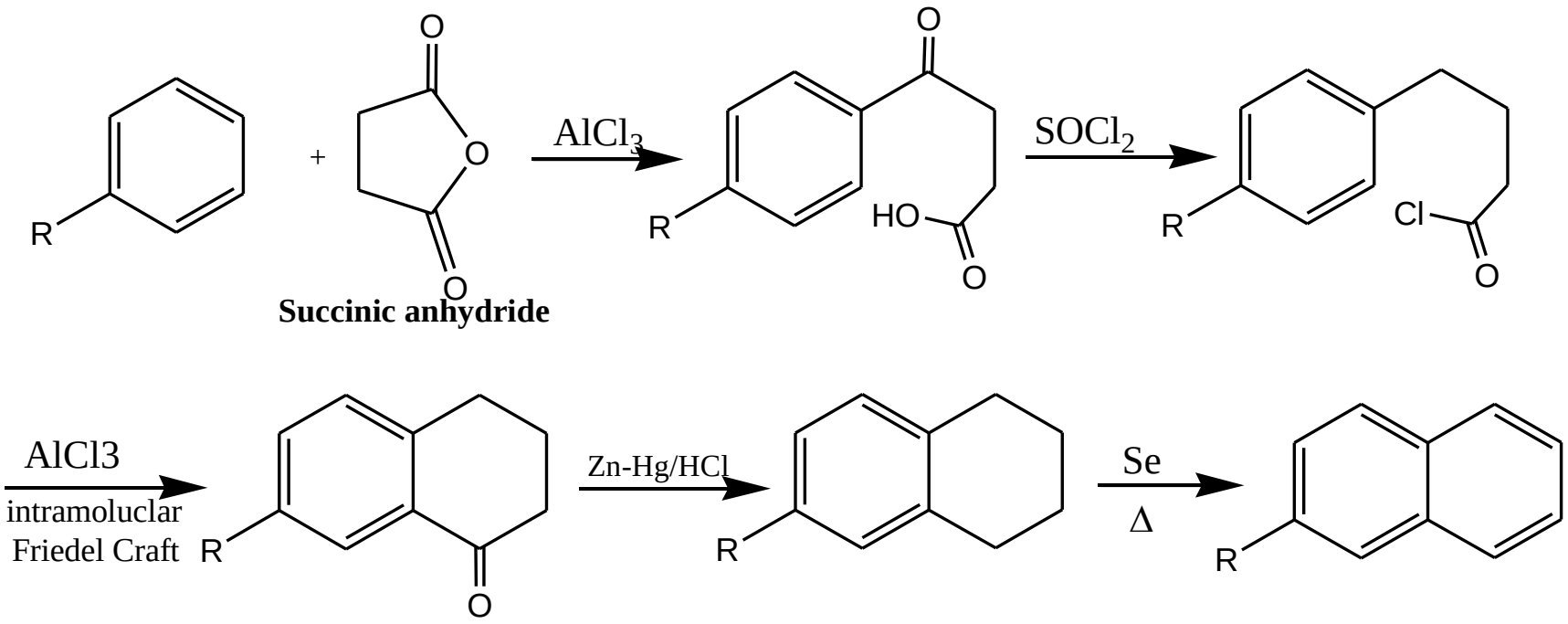


The structure of naphthalene is confirmed by method of its analysis

1- Howarth method

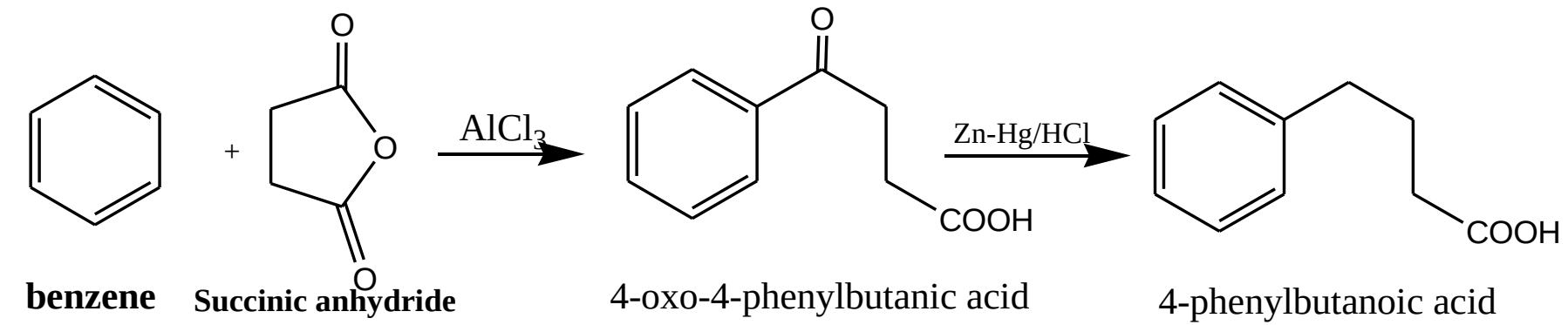


Other way of cyclization

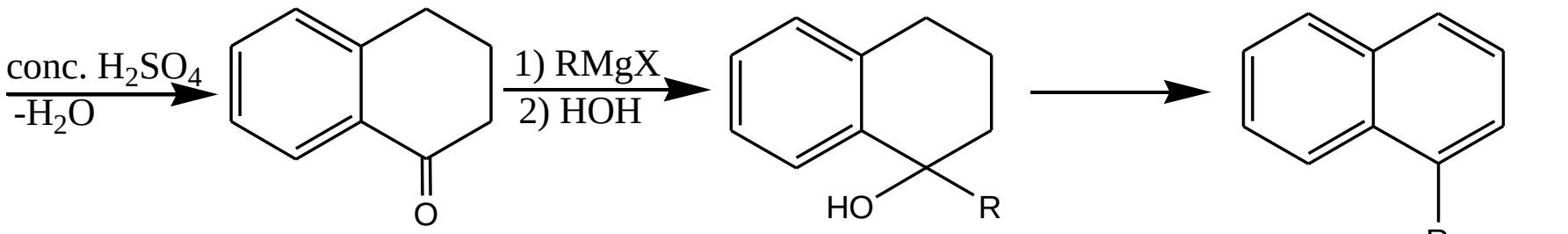


- The reaction occurs if R is o- or p- directing group such as NH_2, NHR, OH, OR, R, halogen.
- If R is m- directing group (e.g. NO_2, CN, COOH, $COCH_3$, SO_3H) no reaction occur.
- The above reaction gives β -substituted naphthalene.

Synthesis of 1-alkyl naphthalene

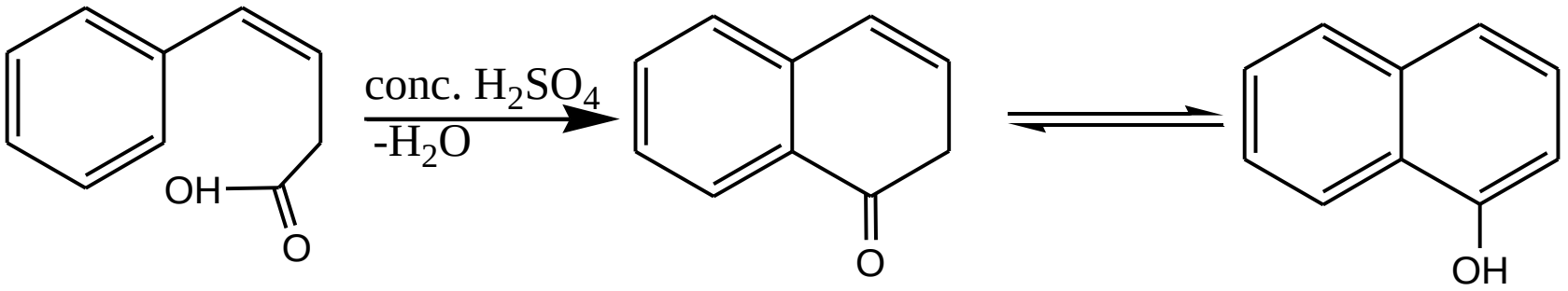


benzene **Succinic anhydride** 4-oxo-4-phenylbutanic acid 4-phenylbutanoic acid

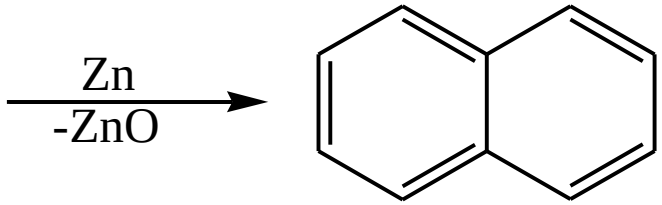


1-tetralone 1- Alkyl naphthalene

2- From β-benzylidene – propenoic acid



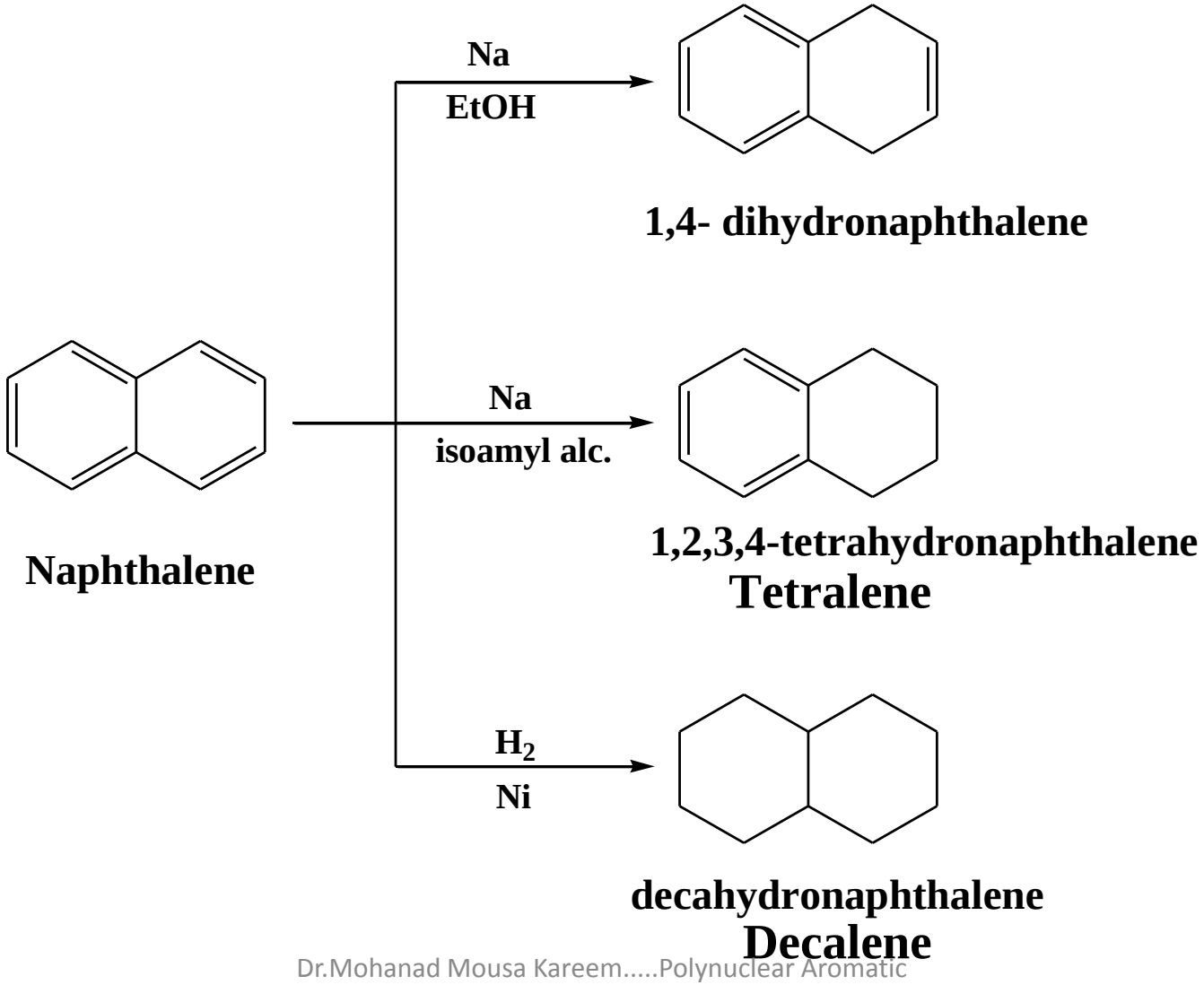
β-Benzylidene-3-propenpoic acid



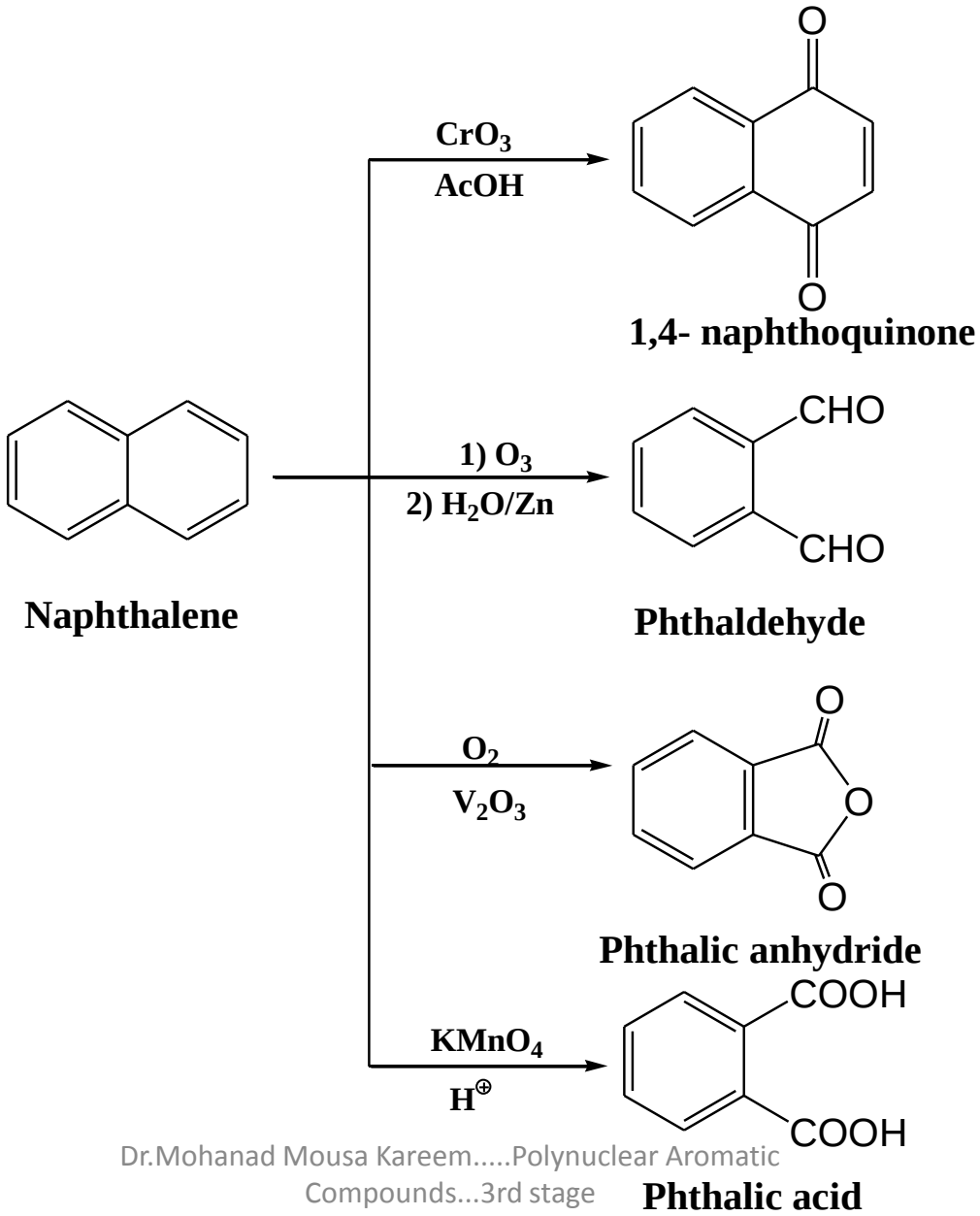
naphthalene

Chemical Reactions of naphthalene

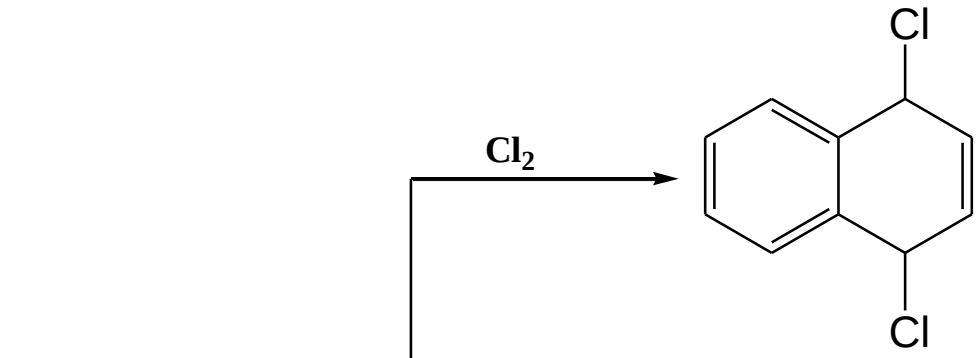
1. Reduction


Na
EtOH
1,4- dihydronaphthalene
Na
isoamyl alc.
1,2,3,4-tetrahydronaphthalene
Tetralene
Naphthalene
H2
Ni
decahydronaphthalene
Decalene

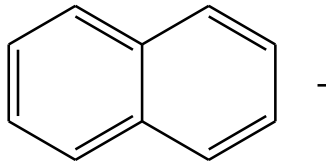
2. Oxidation


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

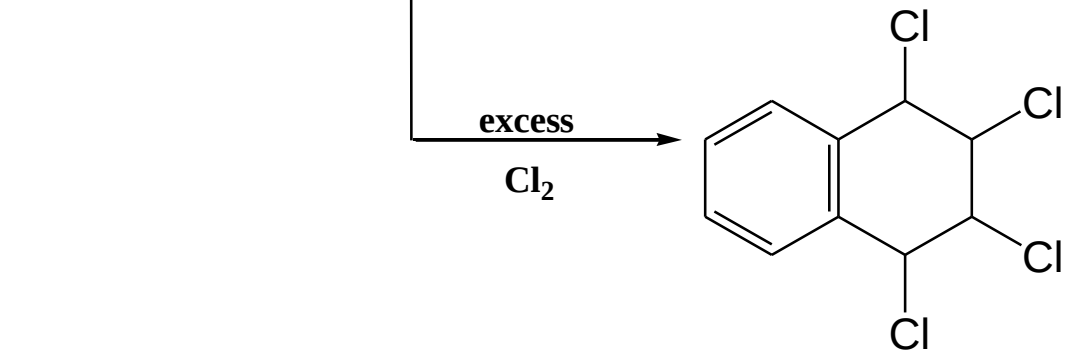
3. Addition of Cl_2



1,4- dichloro- 1,4- dihydronaphthalene



Naphthalene

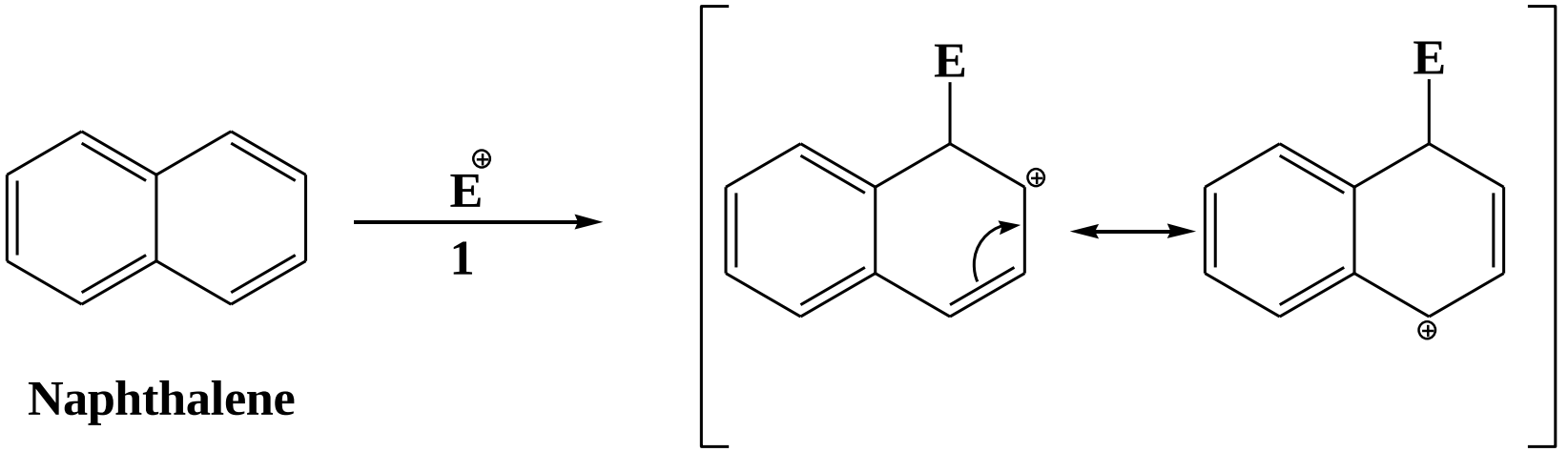


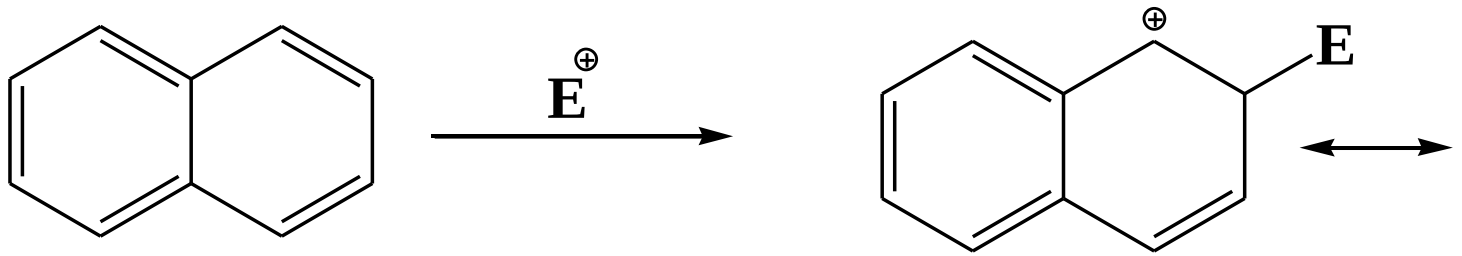
1,2,3,4- tetrachloro- 1,2,3,4-tetrahydronaphthalene

4. Electrophilic substitution reaction

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

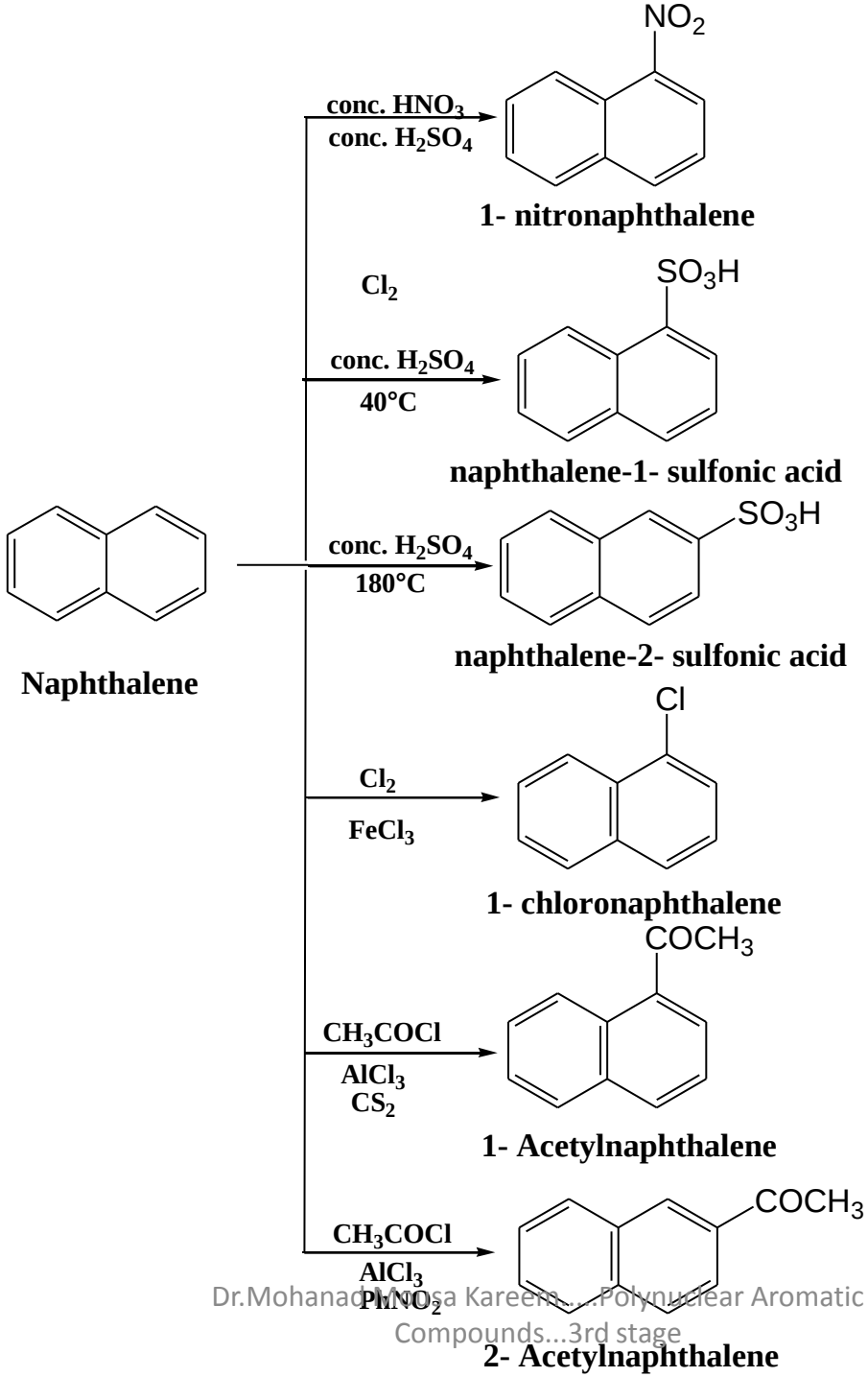
At position 1; carbocation intermediate stabilize by two resonance





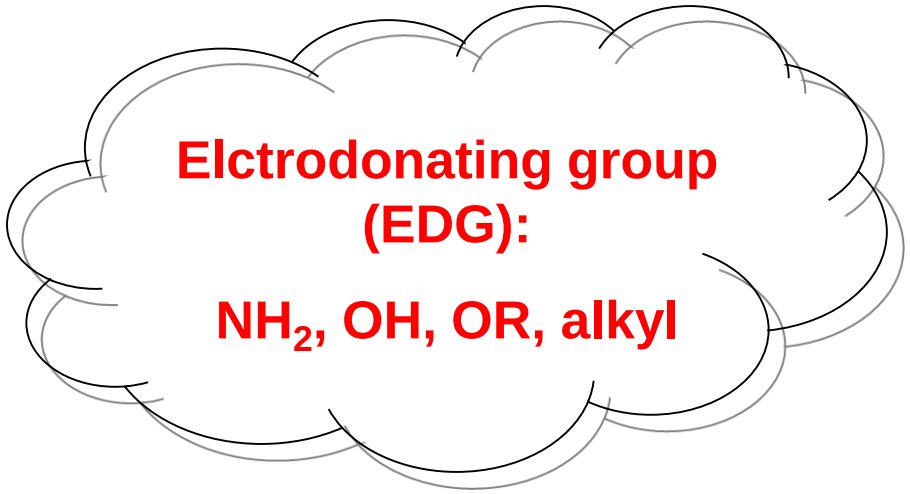
So carbocation is more stable position 1 than 2

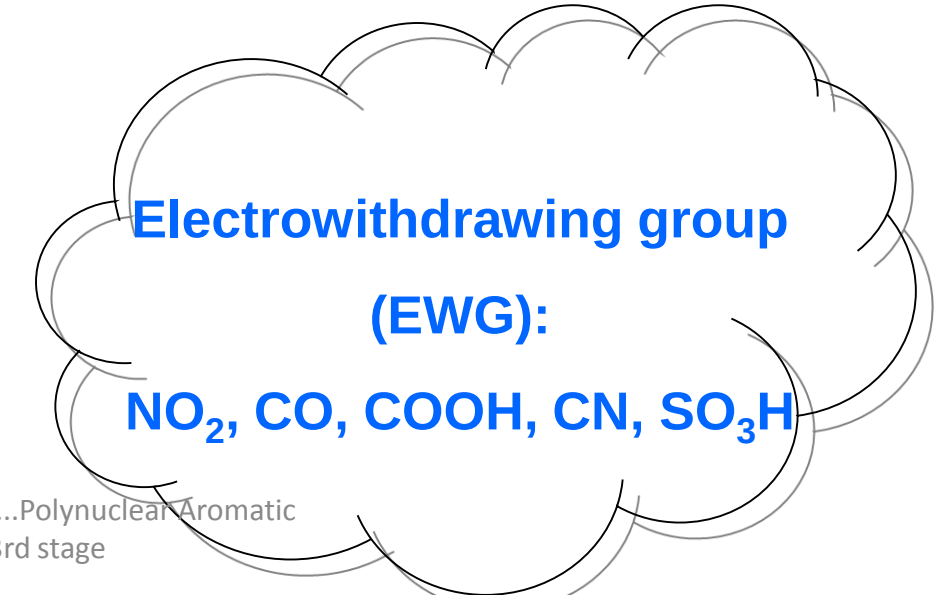
Examples of electrophilic substitution


NO2
conc. HNO3
conc. H2SO4
1- nitronaphthalene
Cl2
SO3H
conc. H2SO4
40°C
naphthalene-1- sulfonic acid
SO3H
conc. H2SO4
180°C
naphthalene-2- sulfonic acid
Naphthalene
Cl
Cl2
FeCl3
1- chloronaphthalene
COCH3
CH3COCl
AlCl3
CS2
1- Acetylnaphthalene
COCH3
CH3COCl
AlCl3
PhNO2
2- Acetylnaphthalene

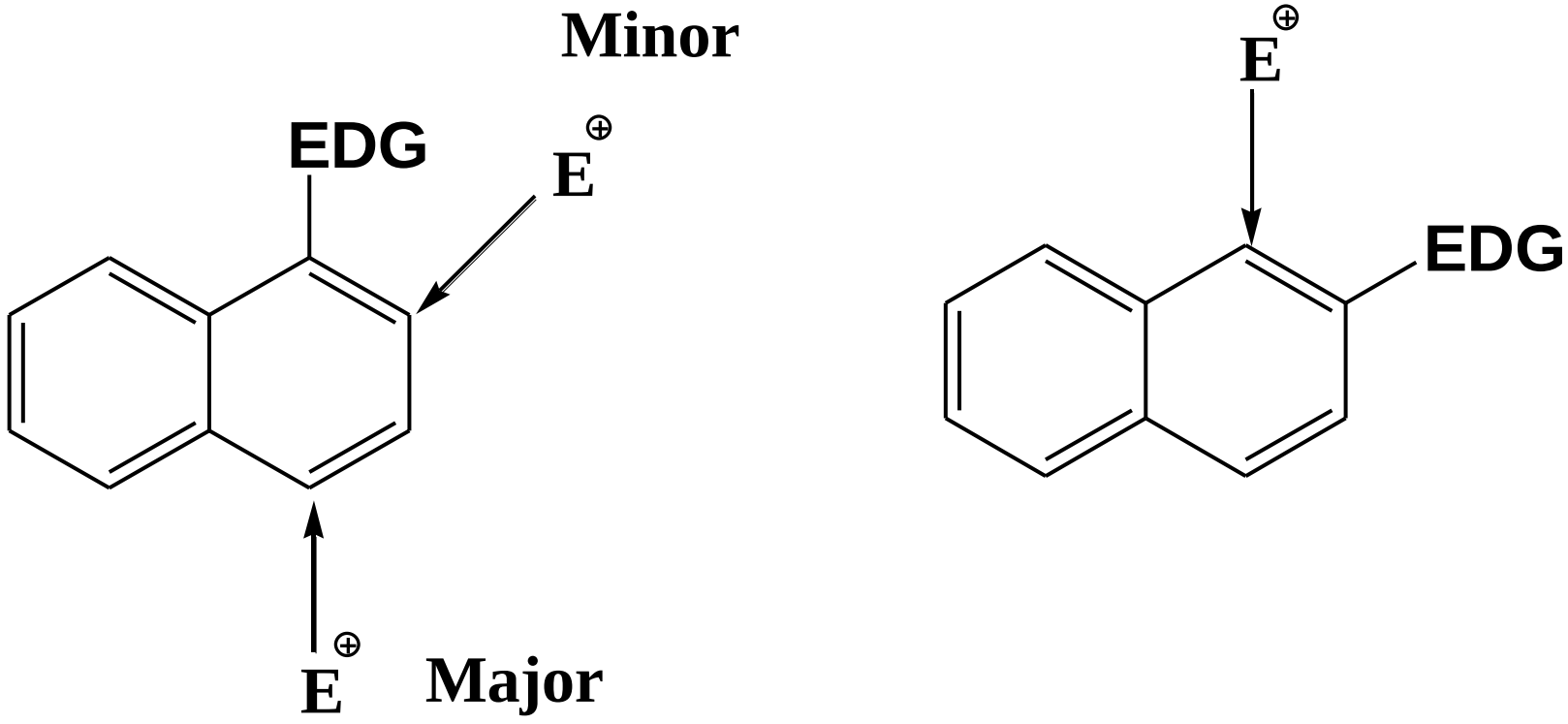
Substituted naphthalene

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

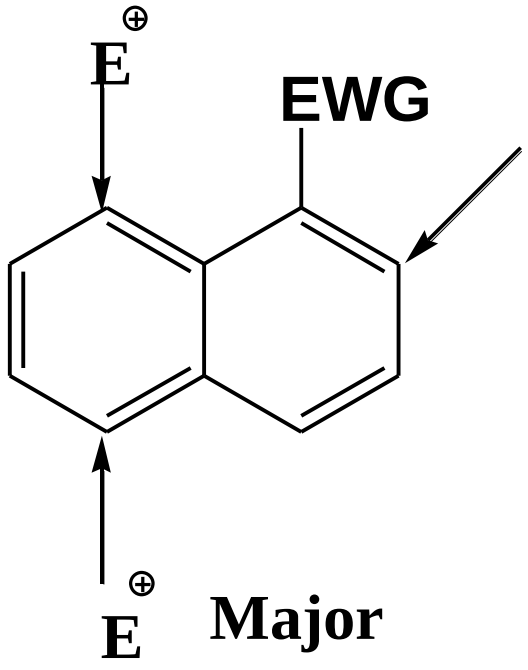




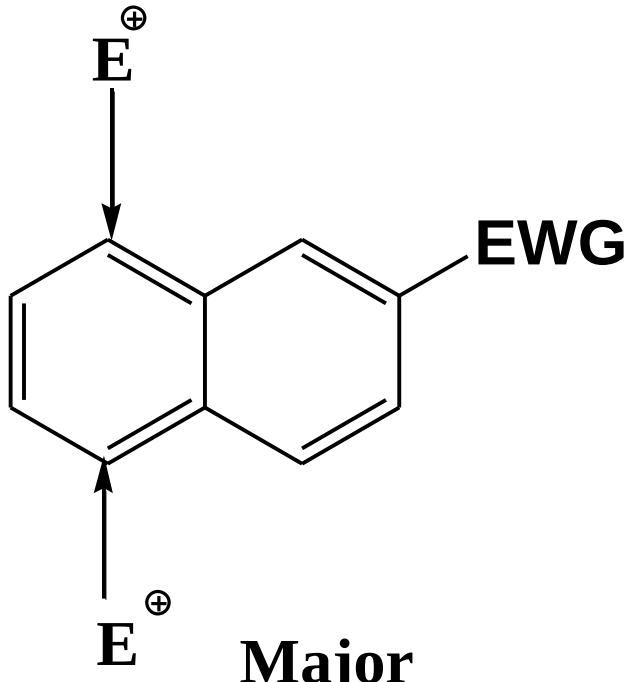
Homonuclear attack



Heteronuclear attack

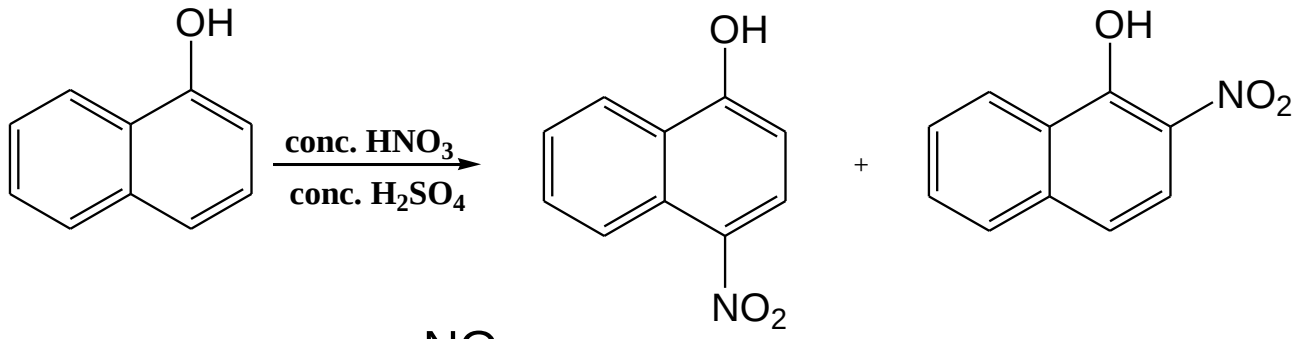


Major

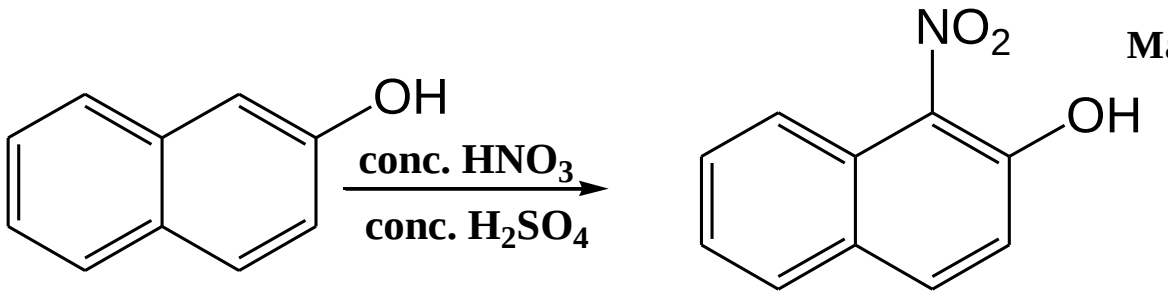


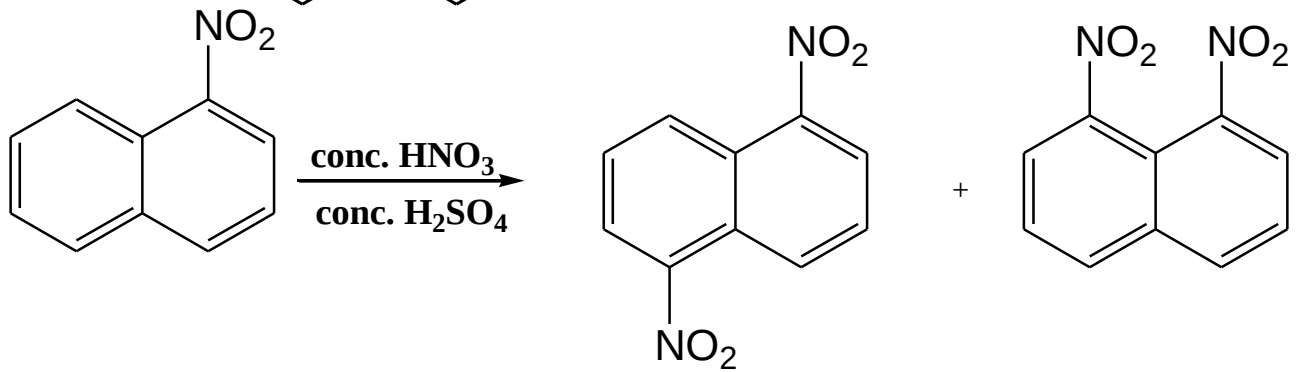
Major

Examples:

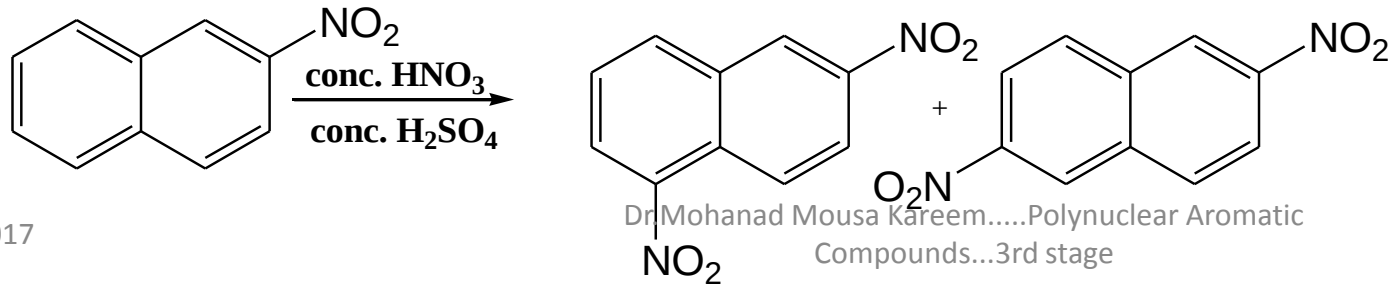


Major





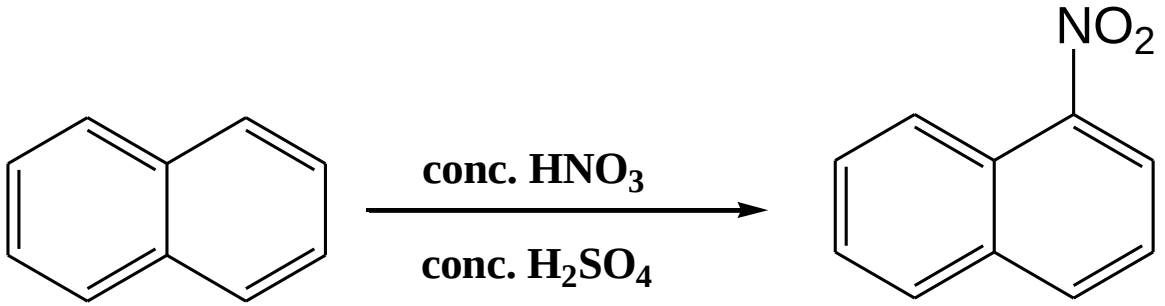
Major **Minor**



Naphthalene derivatives

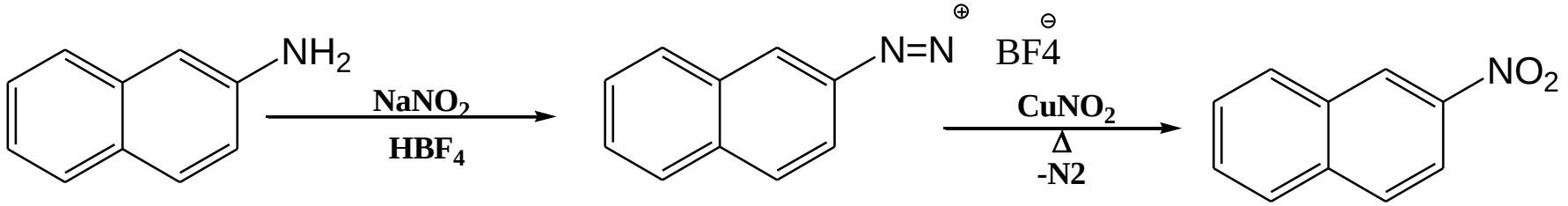
1. Nitronaphthalene

- **1. naphthalene is prepared by direct nitration**



Naphthalene **1- nitronaphthalene**

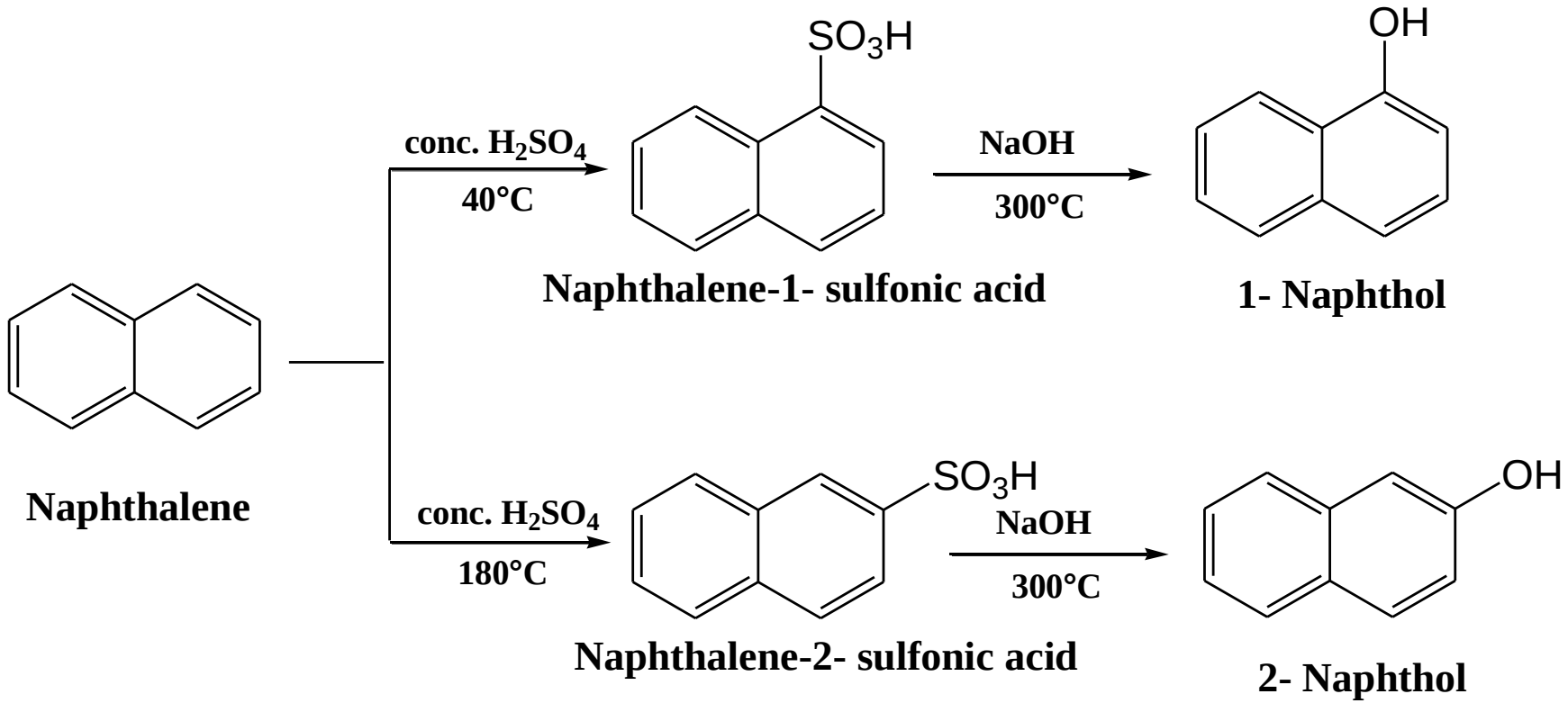
- **2. naphthalene is prepared by indirect method**



2- Aminonaphthalene

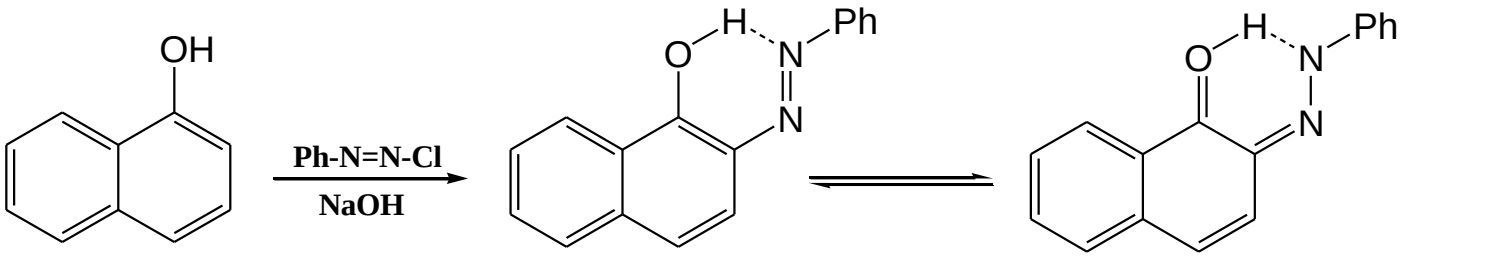
2. Naphthols

- **Preparation:**



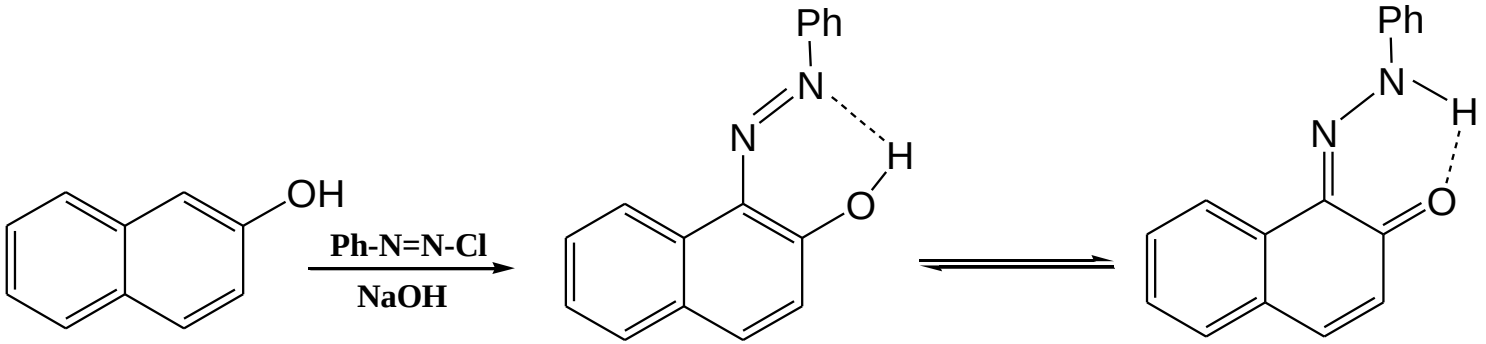
- **Properties:**

1- Reaction of α and β- naphthols with aryl diazonium salt



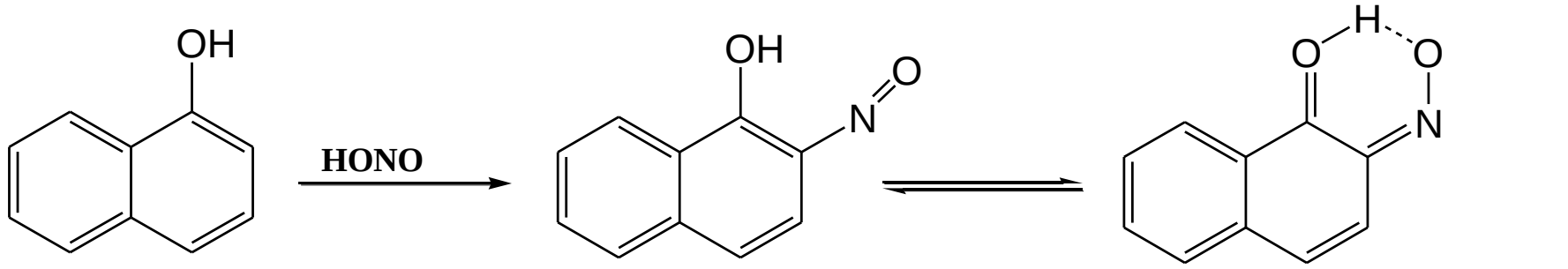
2- phenylazo-1- Naphthol *hydrazo form stable by intermol. H.B*

Azo form

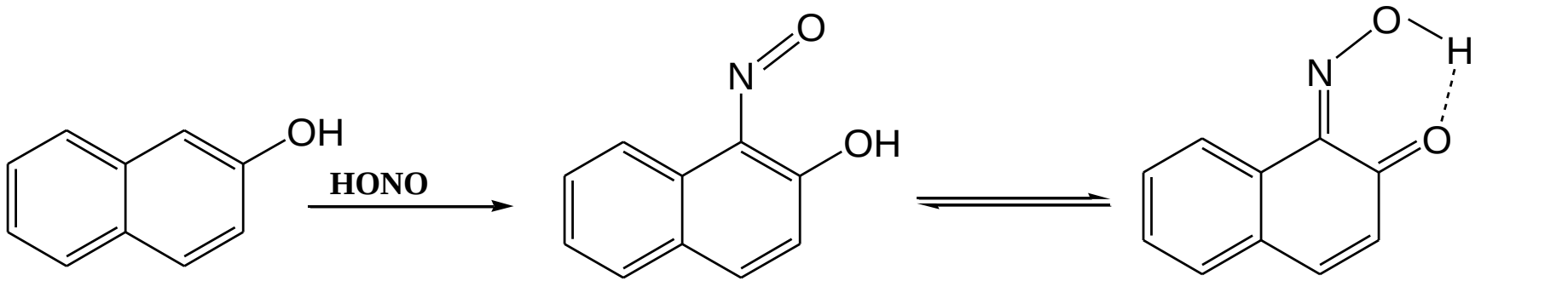


2- phenylazo-2- Naphthol

2- Reaction of α and β- naphthols with nitrous acid

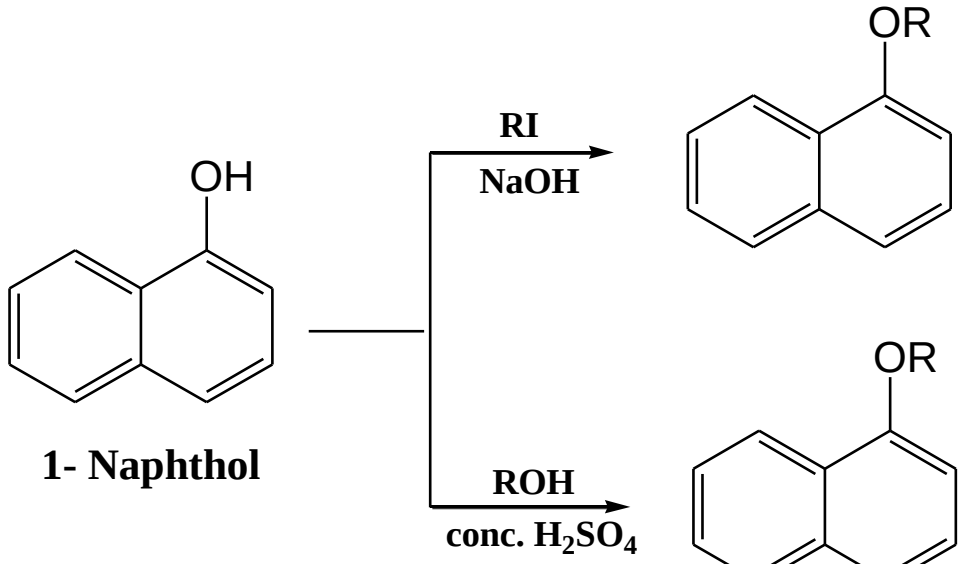


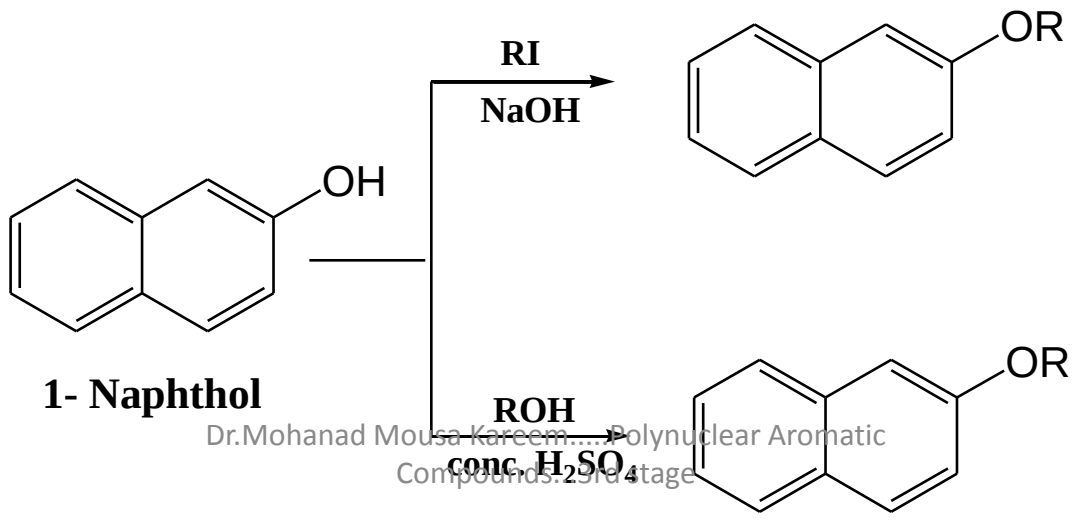
1- Naphthol **2- nitroso-1- naphthol** **[1,2]naphthoquinone-2-oxime**



2- Naphthol **2- nitroso-2- naphthol** **[1,2]naphthoquinone-1-oxime**

3- Conversion of α and β- naphthols to naphthyl ether

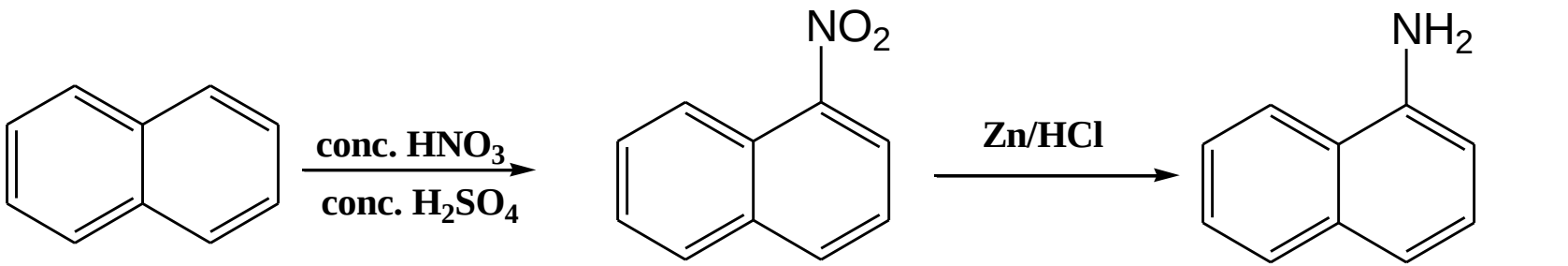




3. Naphthylamine

- **Preparation:**

1- Naphthylamine

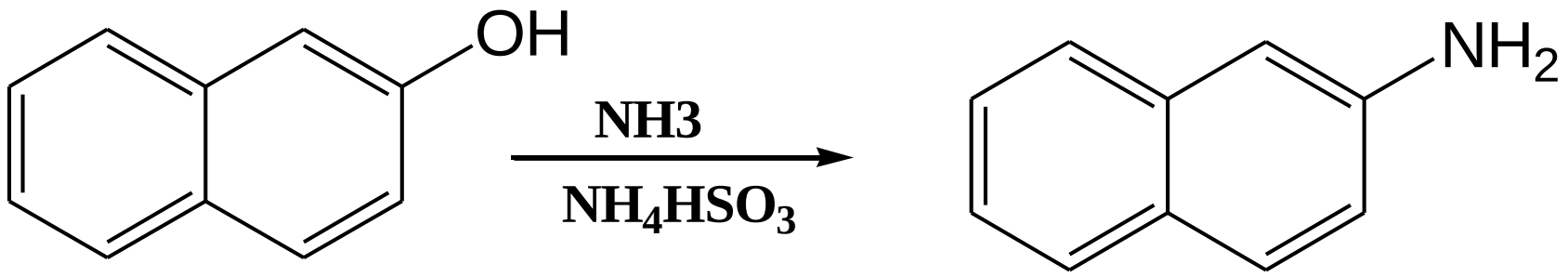


1- Nitronaphthalene **1- aminonaphthalene**

Preparation:

2- Naphthylamine

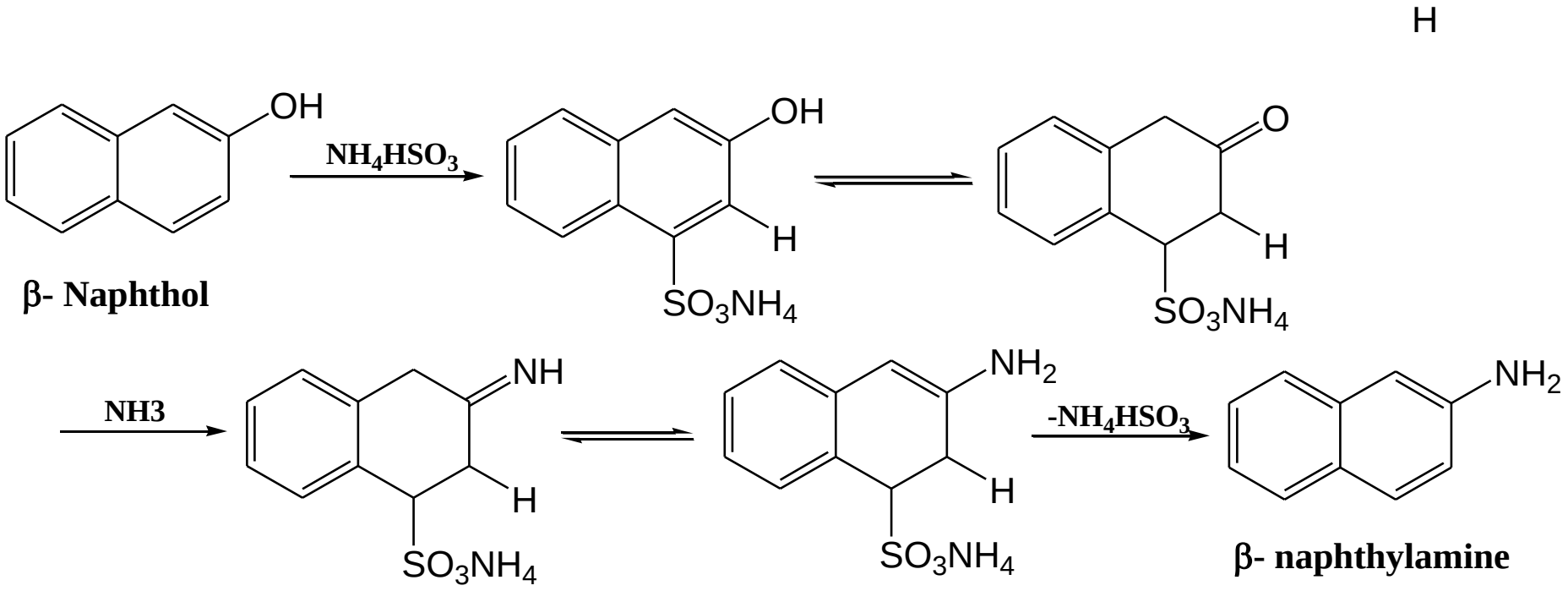
Bucherer reaction



β- Naphthol

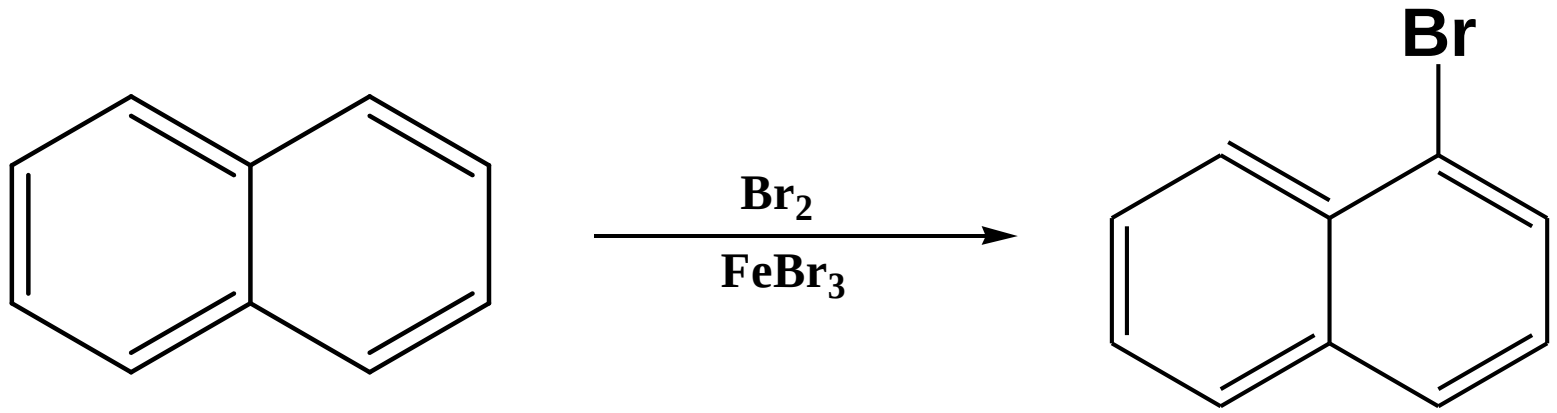
β- naphthylamine

Mechanism


H
OH
NH4HSO3
OH
H
SO3NH4
O
H
SO3NH4
β- Naphthol
NH3
NH
H
SO3NH4
NH2
H
SO3NH4
-NH4HSO3
NH2
β- naphthylamine

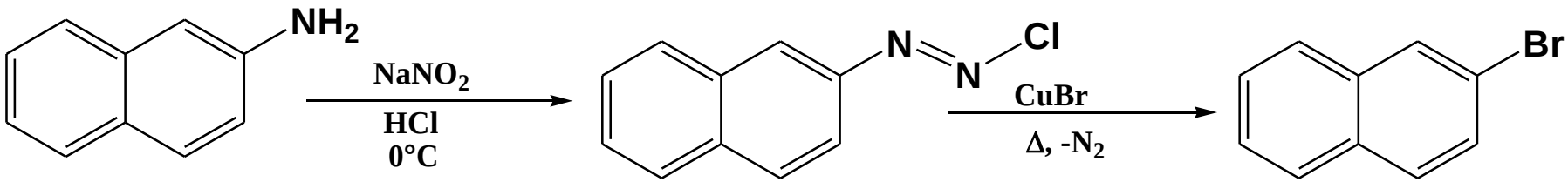
4. Halogenated naphthalene

- **A) Preparation of 1- halogented naphthalene**



1- bromonaphthalene

- **B) Preparation of 2- halogenated naphthalene via Sandemeyer**



2- Naphthylamine

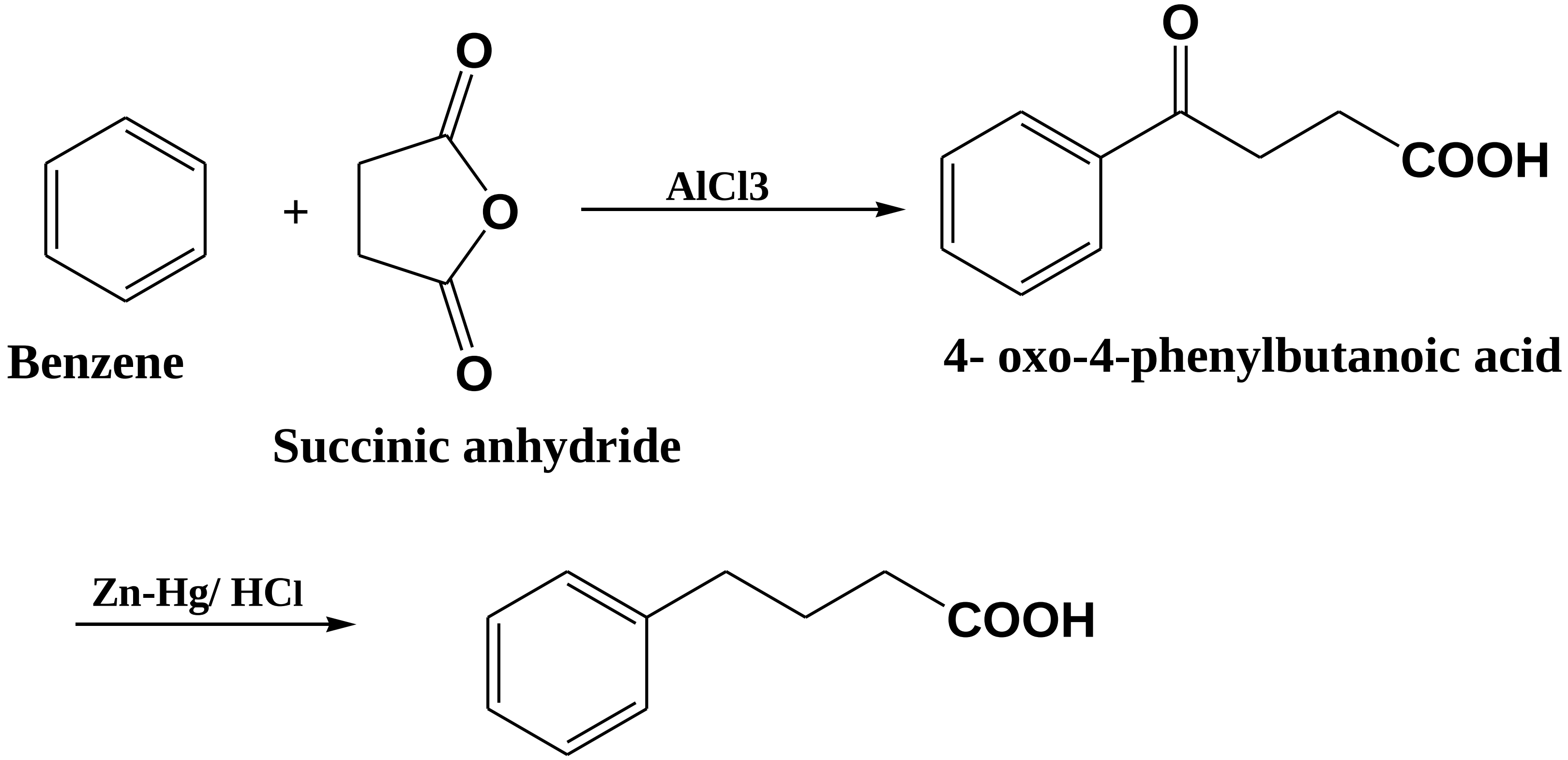
Questions:

Convert 2- naphthol to:

- A) 2- bromonaphthol
- b) Naphthalene -2- carboxylic acid
- C) 1,2- naphthaquinone-1- oxime
- D) Ethyl β–naphthyl ether

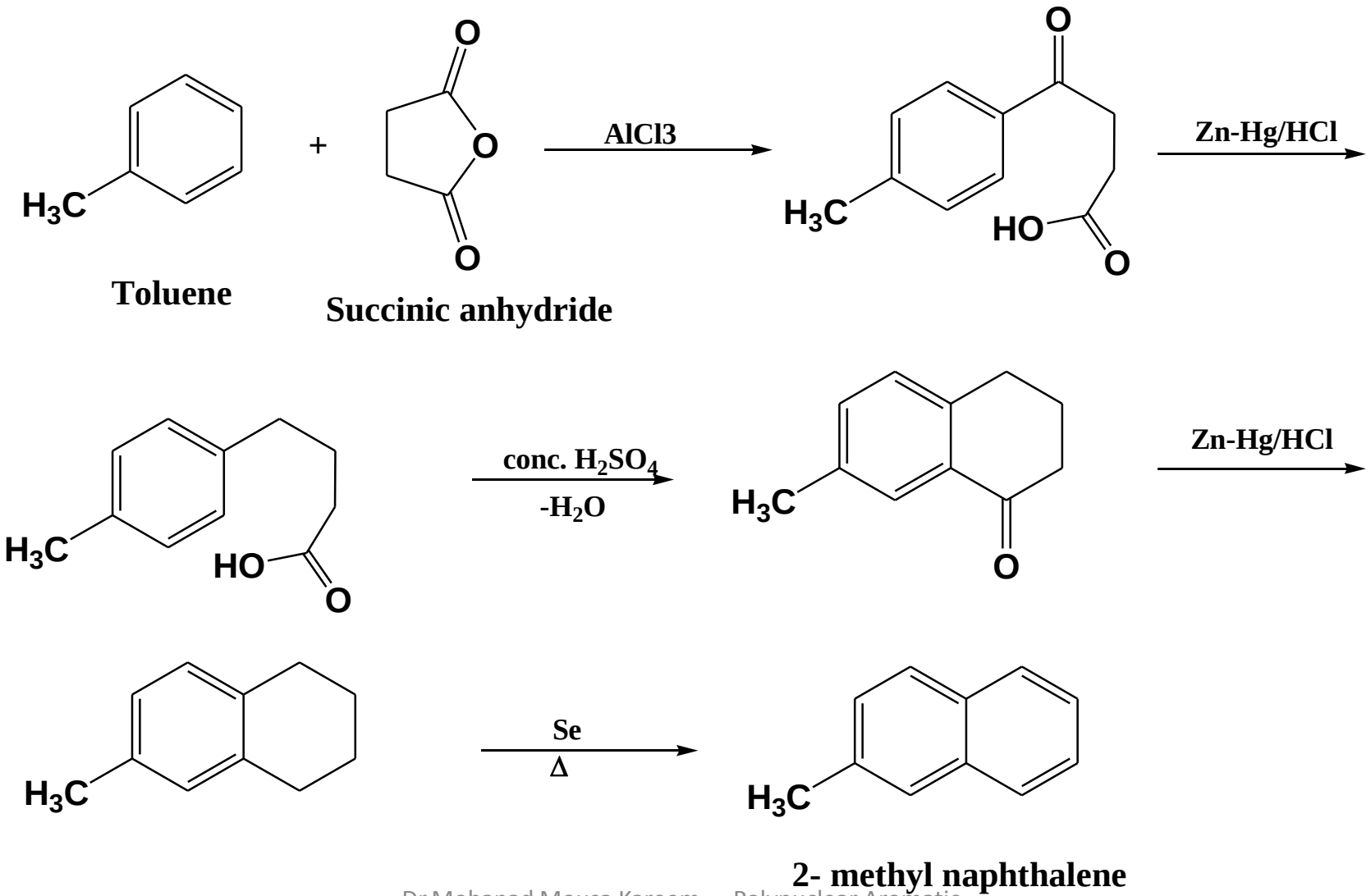
5. Alkyl naphthalene

- **Synthesis of 1- alkyl naphthalene**



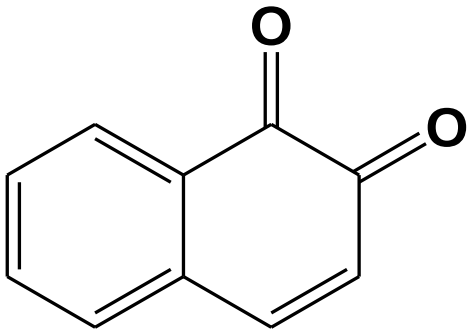
4-phenylbutanoic acid

- **Synthesis of 2- alkyl naphthalene**

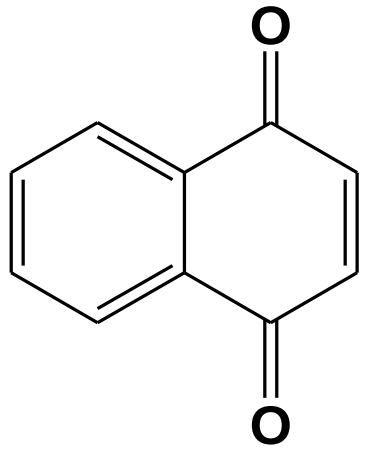


6. Naphthaquinones

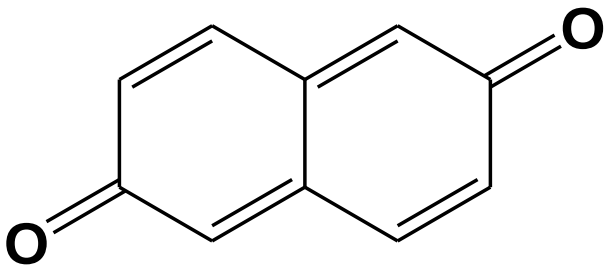
- There are six possible naphthaquinones, but only common are 1,2; 1,4; 2,6- naphthaquinones



1,2- Naphthaquinone



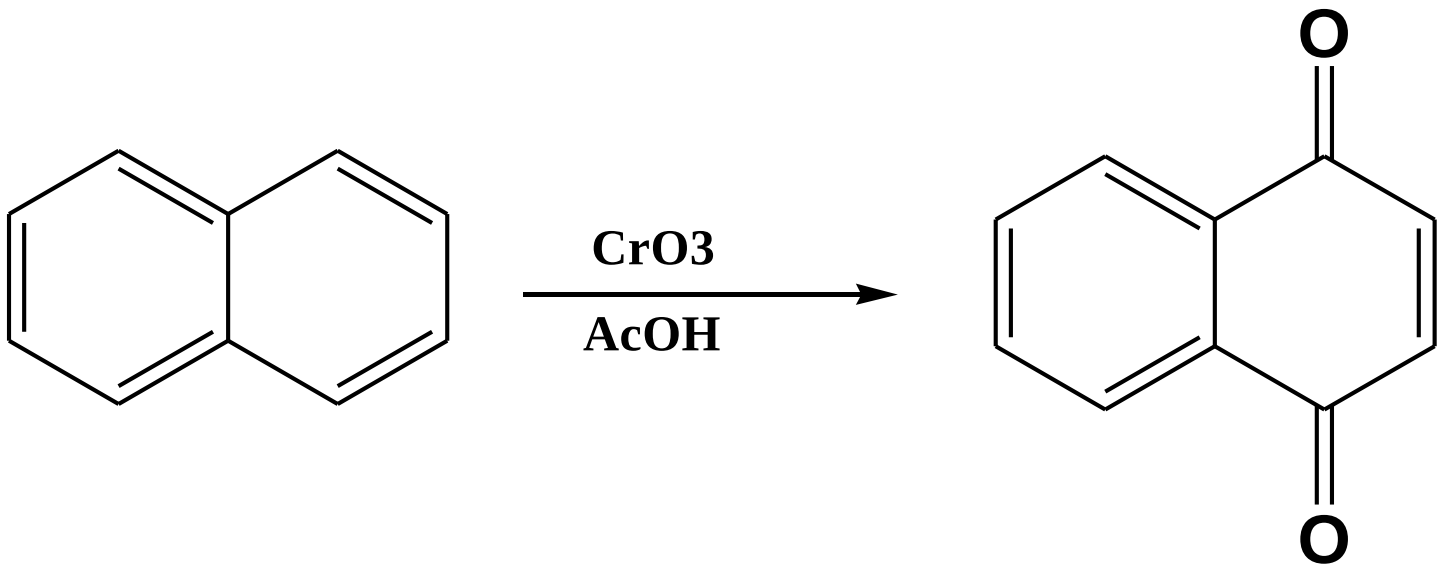
1,4- Naphthaquinone



2,6- Naphthaquinone

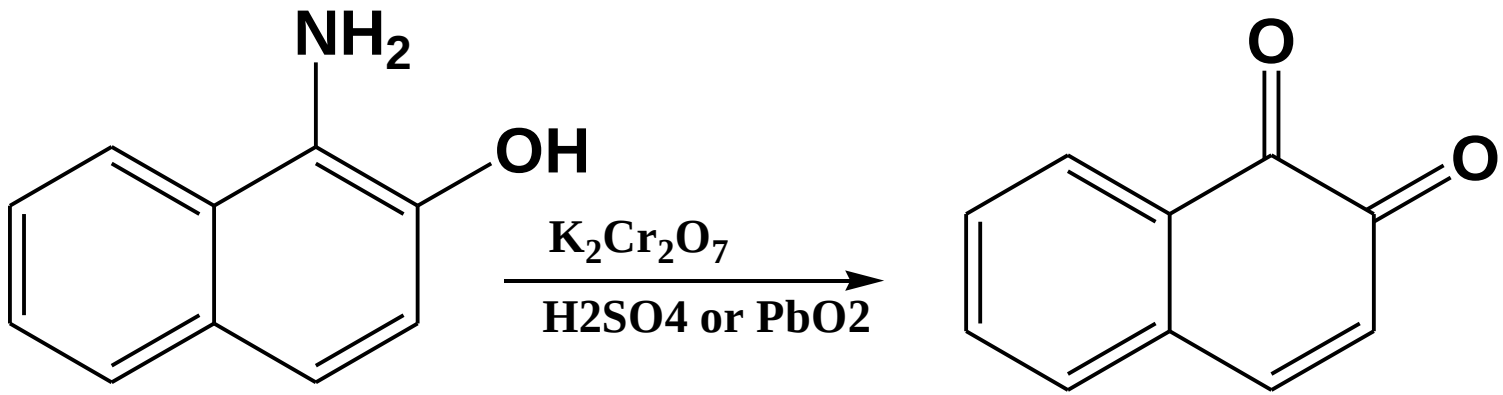
Preparation of naphthaquinones

1,4- Naphthaquinone:



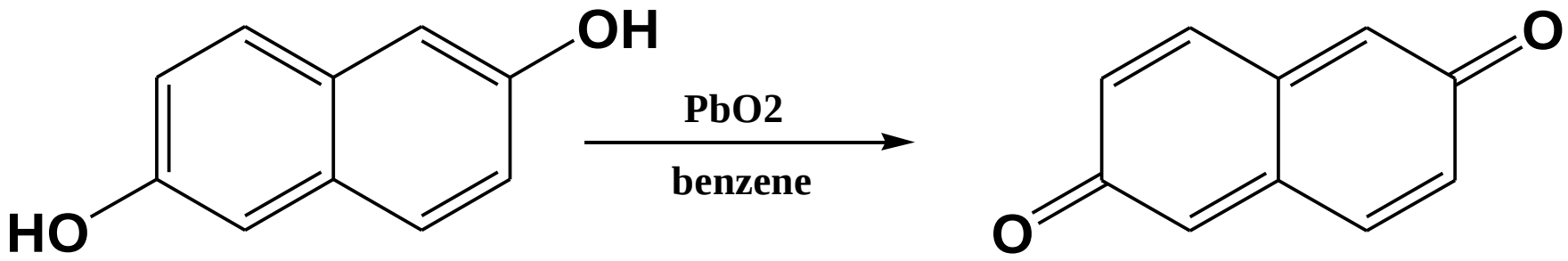
Naphthalene **1,4- Naphthaquinone**

1,2- Naphthaquinone:



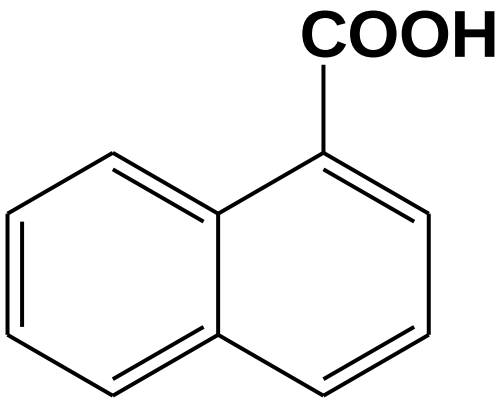
1- Amino- 2-naphthol **1,2- Naphthaquinone**

2,6- Naphthaquinone:

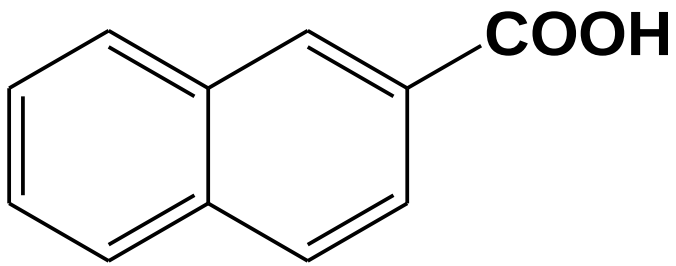


2,6- dihydroxynaphthalenel **2,6- Naphthaquinone**

7. Naphthoic acid



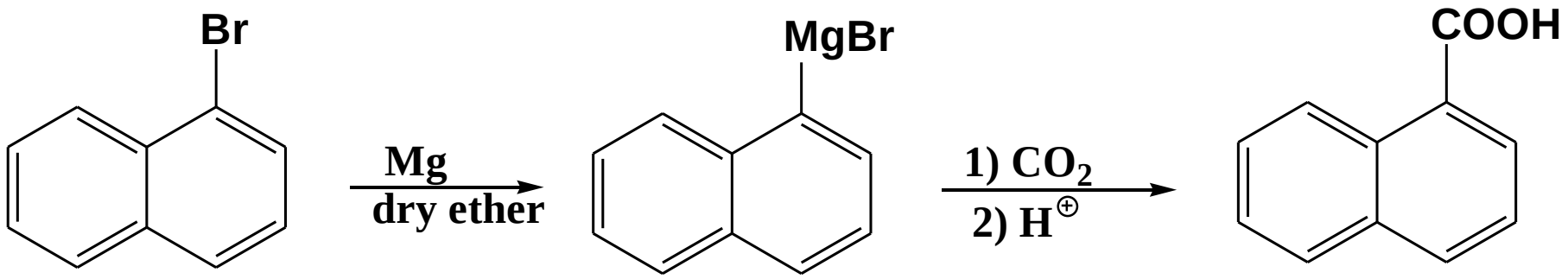
1- Naphthoic acid
or
α- Naphthoic acid



2- Naphthoic acid
or
β- Naphthoic acid

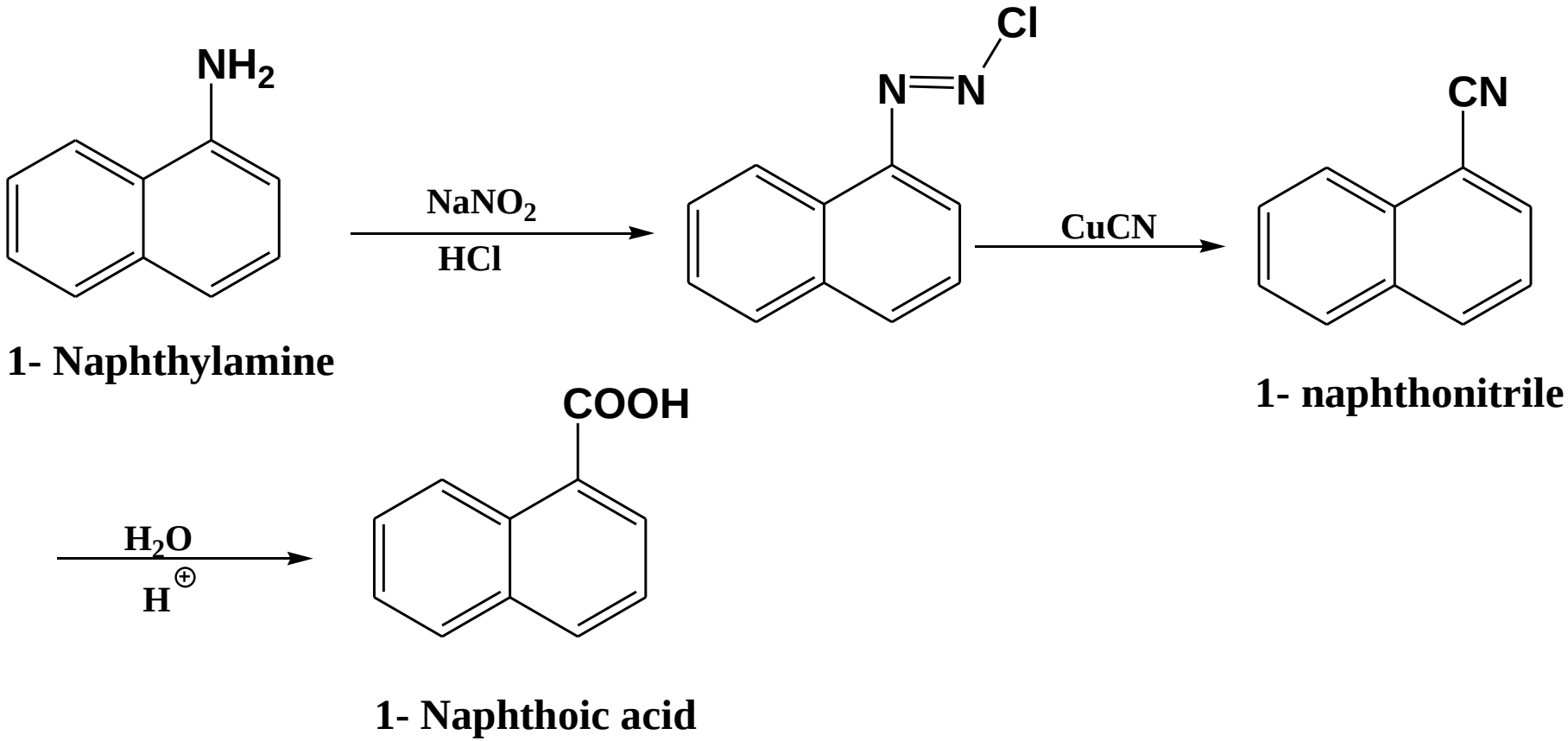
Preparation of 1-naphthoic acid

From bromonaphthalene

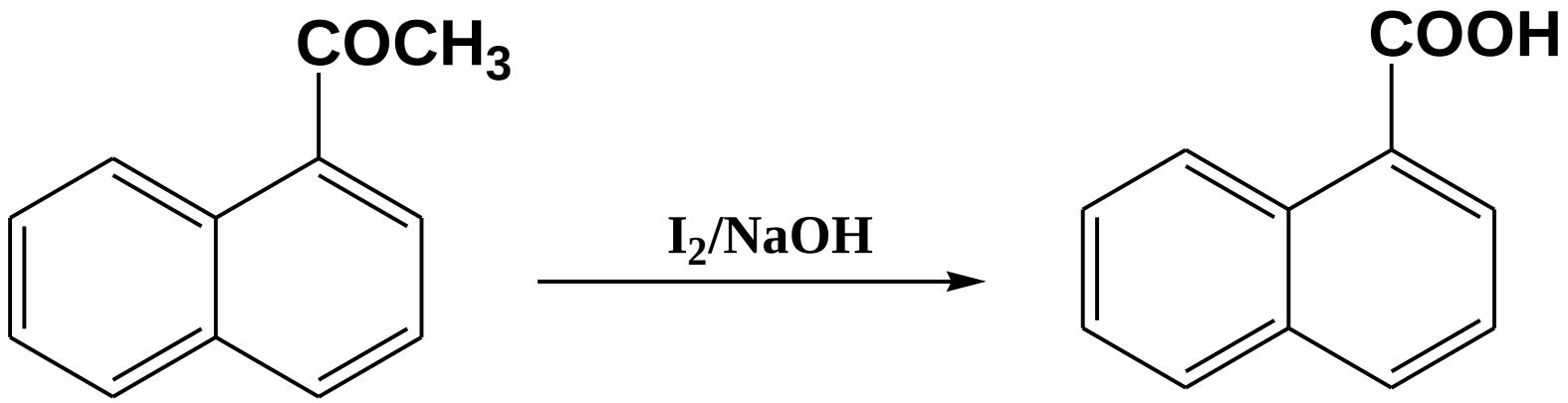


1- bromonaphthalene **1- naphthyl magnesium bromide** **1- Naphthoic acid**

From 1- naphthylamine



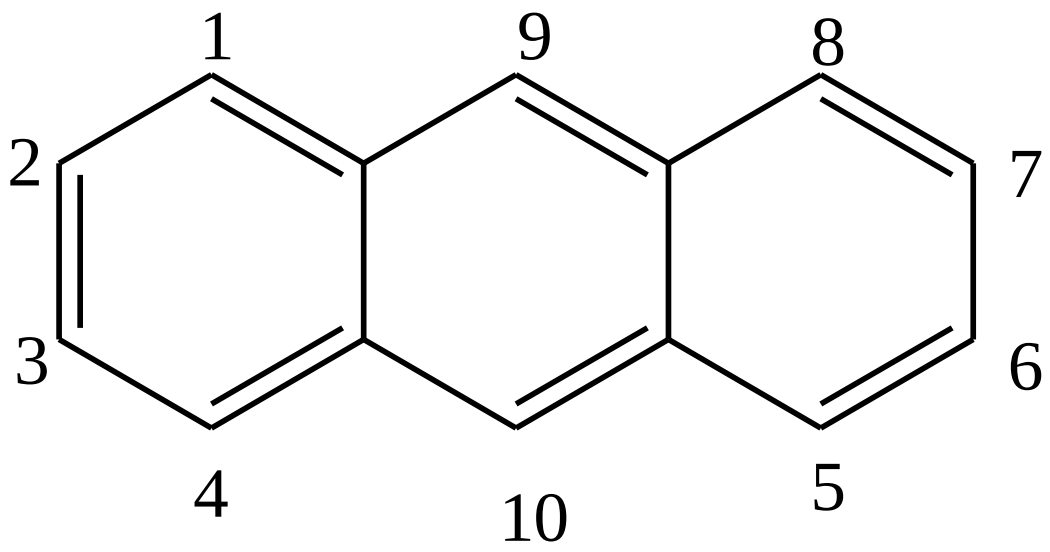
From 1- acetylacetophenone



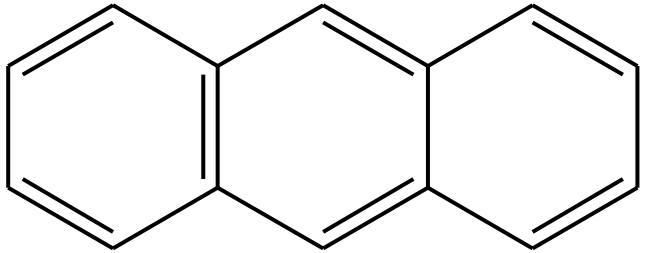
1- Acetylacetophenone **1- Naphthoic acid**

2- Naphthoic acid can be prepared by the same above methods

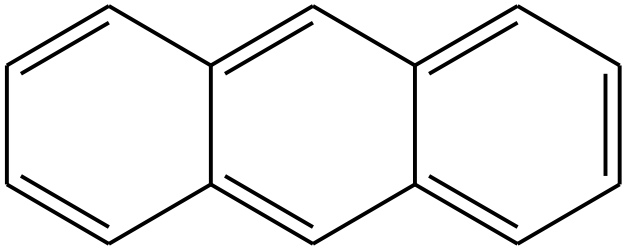
Anthracene



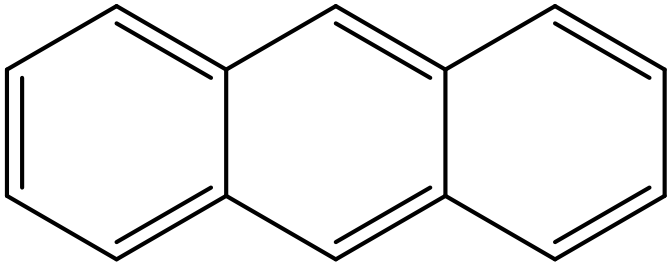
- **Anthracene has 4 isomers:**

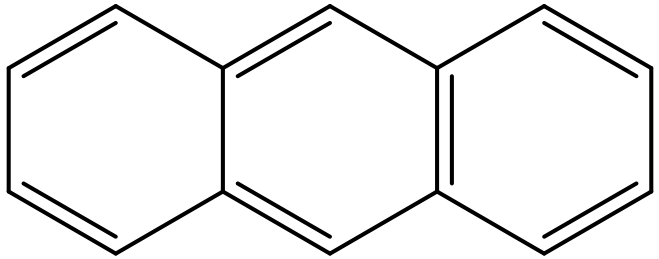


I



II

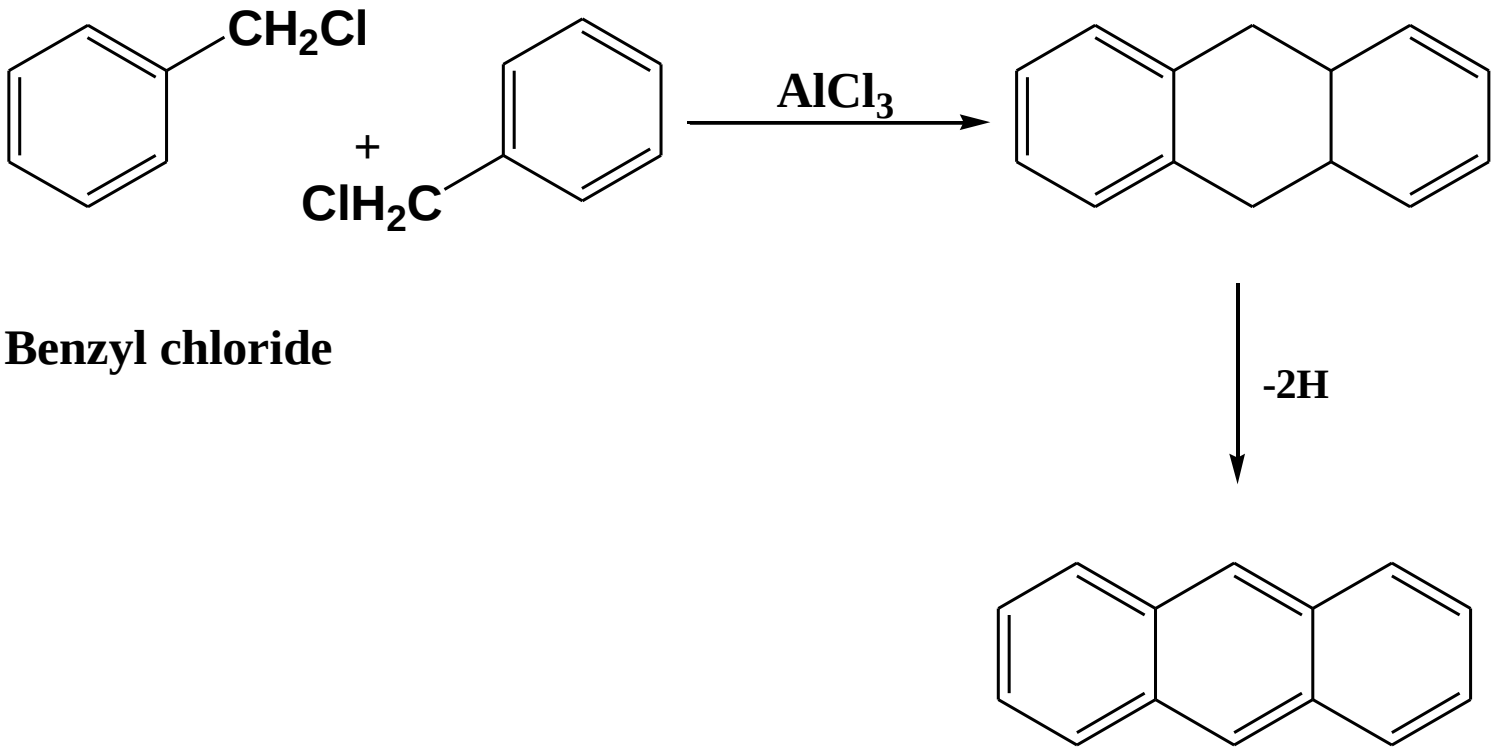




Resonance I, II are more stable, contain 2 benzene rings.

Synthesis of anthracene

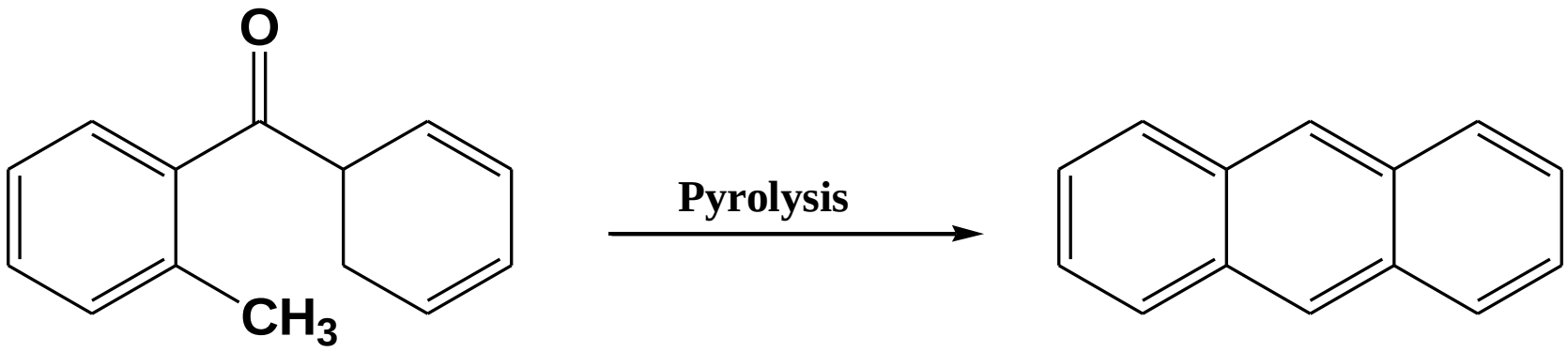
- 1. Friedl Crafts



Benzyl chloride

Anthracene

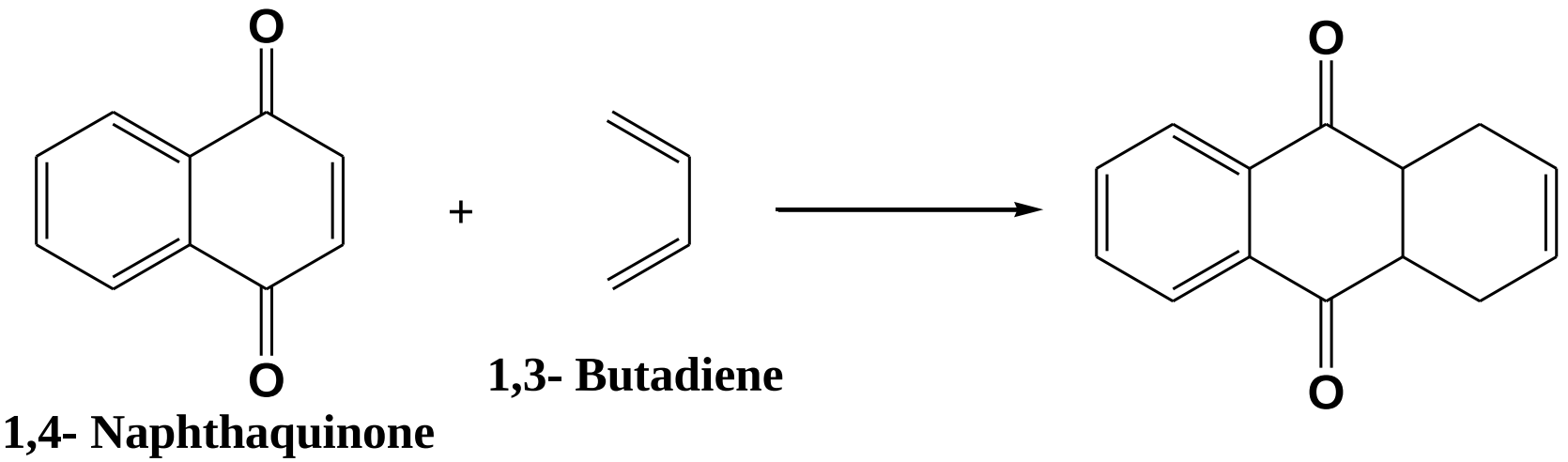
- 2. Elbe reaction



o- Methyl- benzenophenone
or o- Benzoyl- toluene

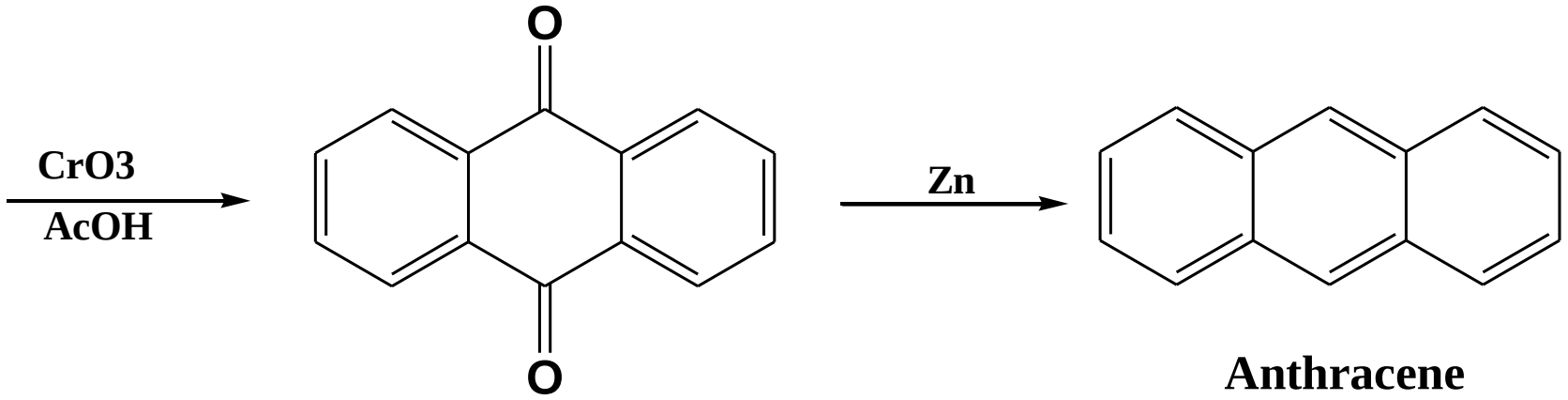
Anthracene

- 3. From 1,4- Naphthoquinone



1,4- Naphthaquinone

1,3- Butadiene

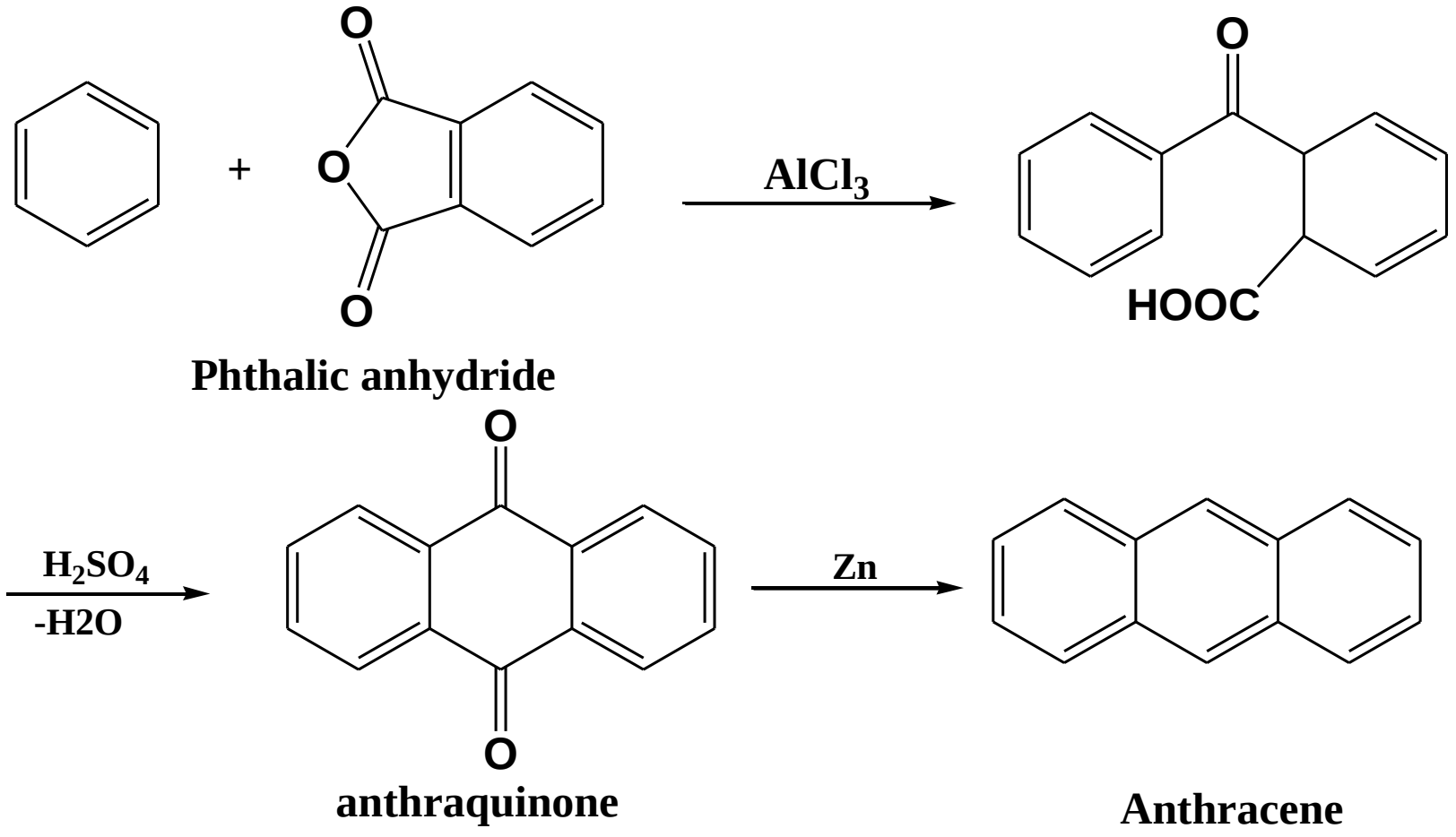


9,10- anthraquinone

Anthracene

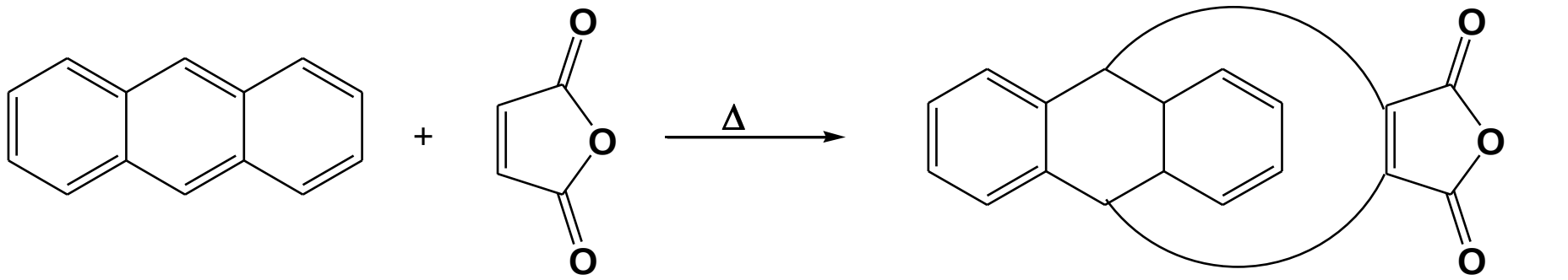
The above method shows presence of naphthalene in anthracene

- 4. From benzene and phthalic anhydride



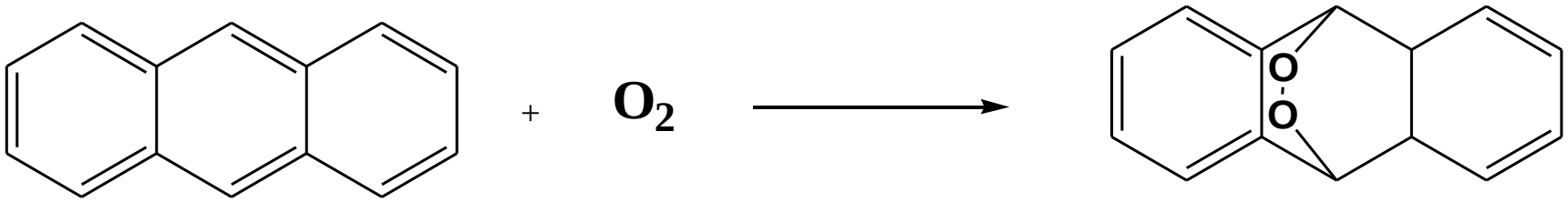
Chemical reactions

- **1) Diels Alder**



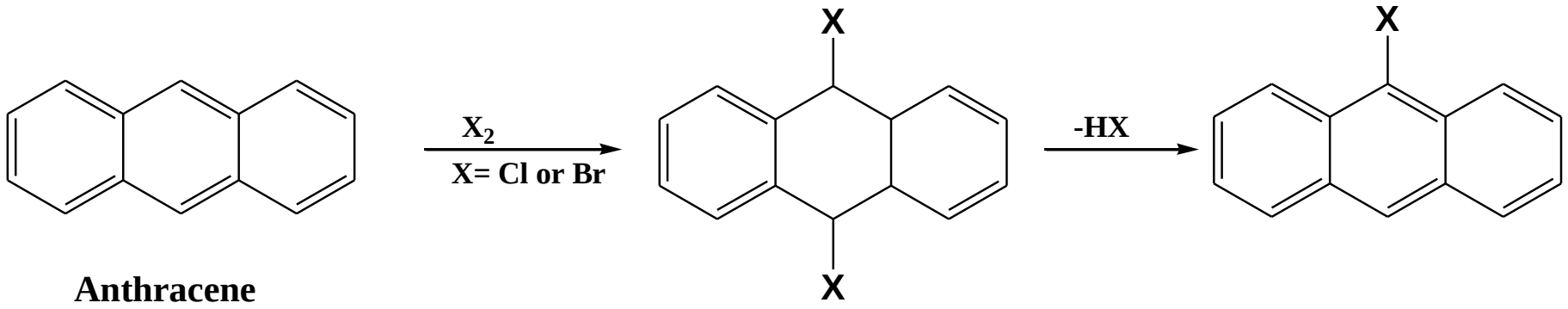
Anthracene **Maleic anhydride** **Endo- anthracene- maleic anhydride adduct**

- **2) Addition of one molecule of O_2**



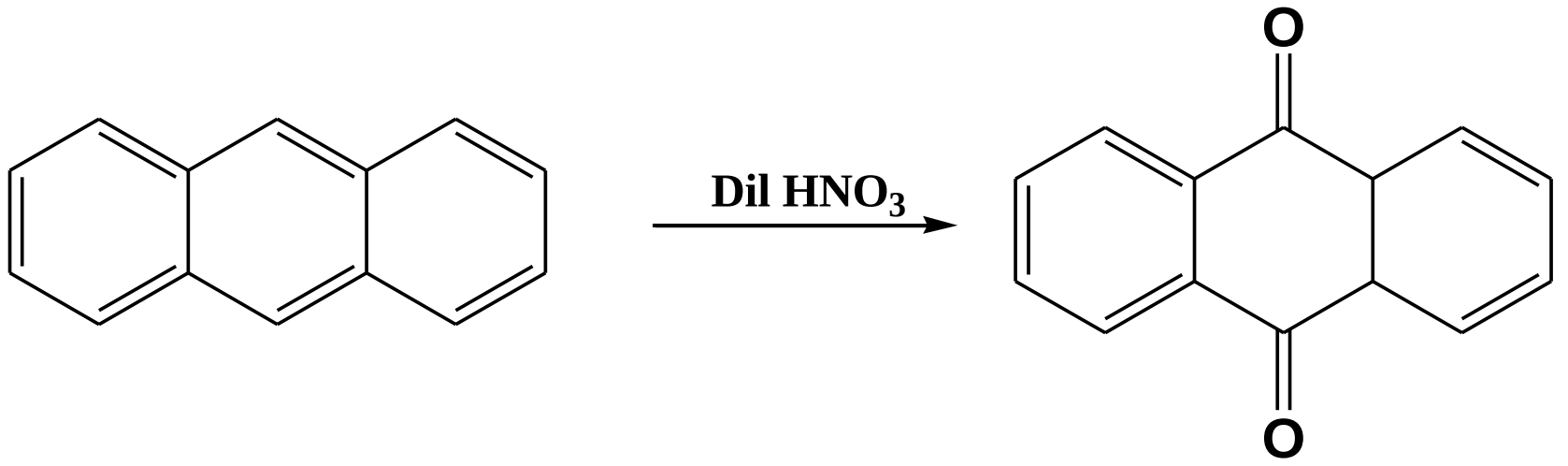
Anthracene **Anthracene epoxide**

• 3) Halogenation of anthracene



Anthracene

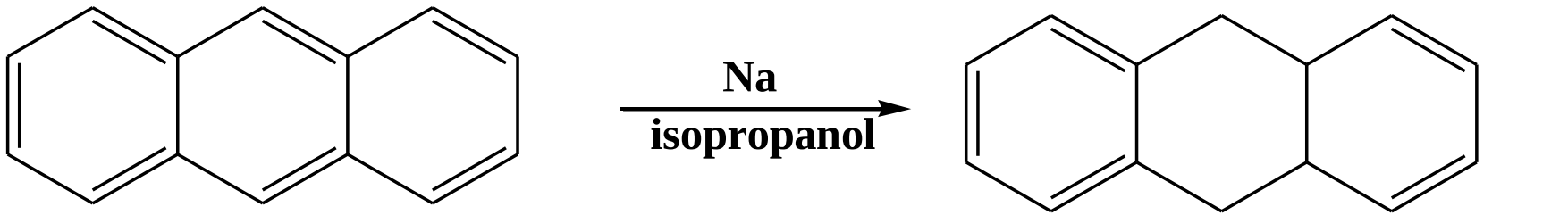
- **4) Oxidation of anthracene**



Anthracene **9, 10- Anthraquinone**

In using dil. HNO3 only to obtain 9,10- anthraquinone

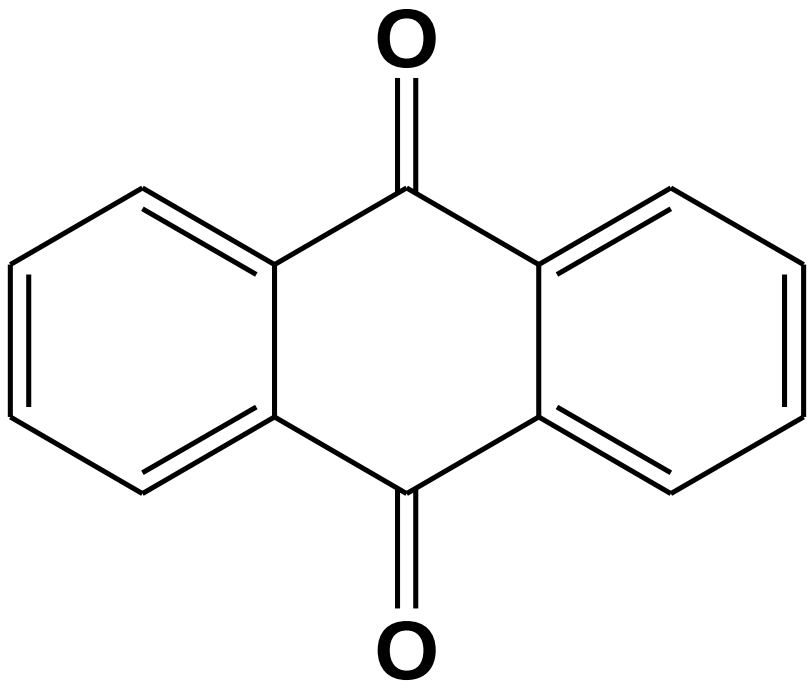
- **4) Reduction of anthracene**



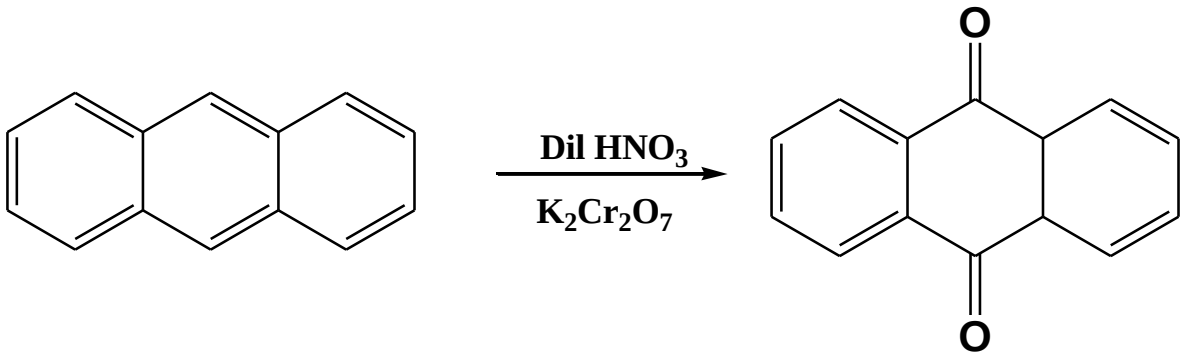
Anthracene

9, 10- Dihydroanthracene

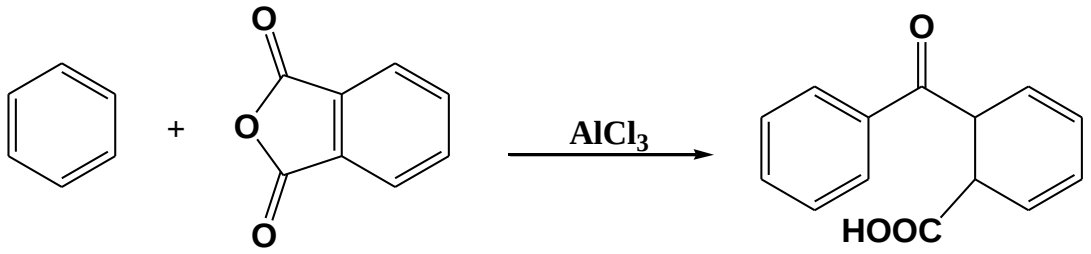
Anthraquinone



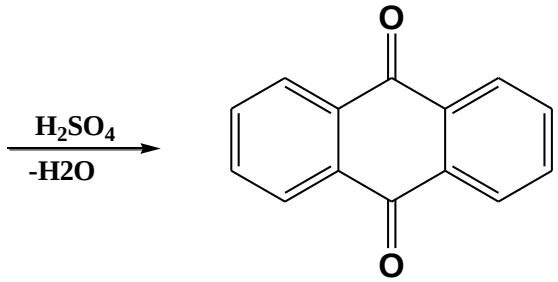
Preparation



Anthracene **9, 10- Anthraquinone**

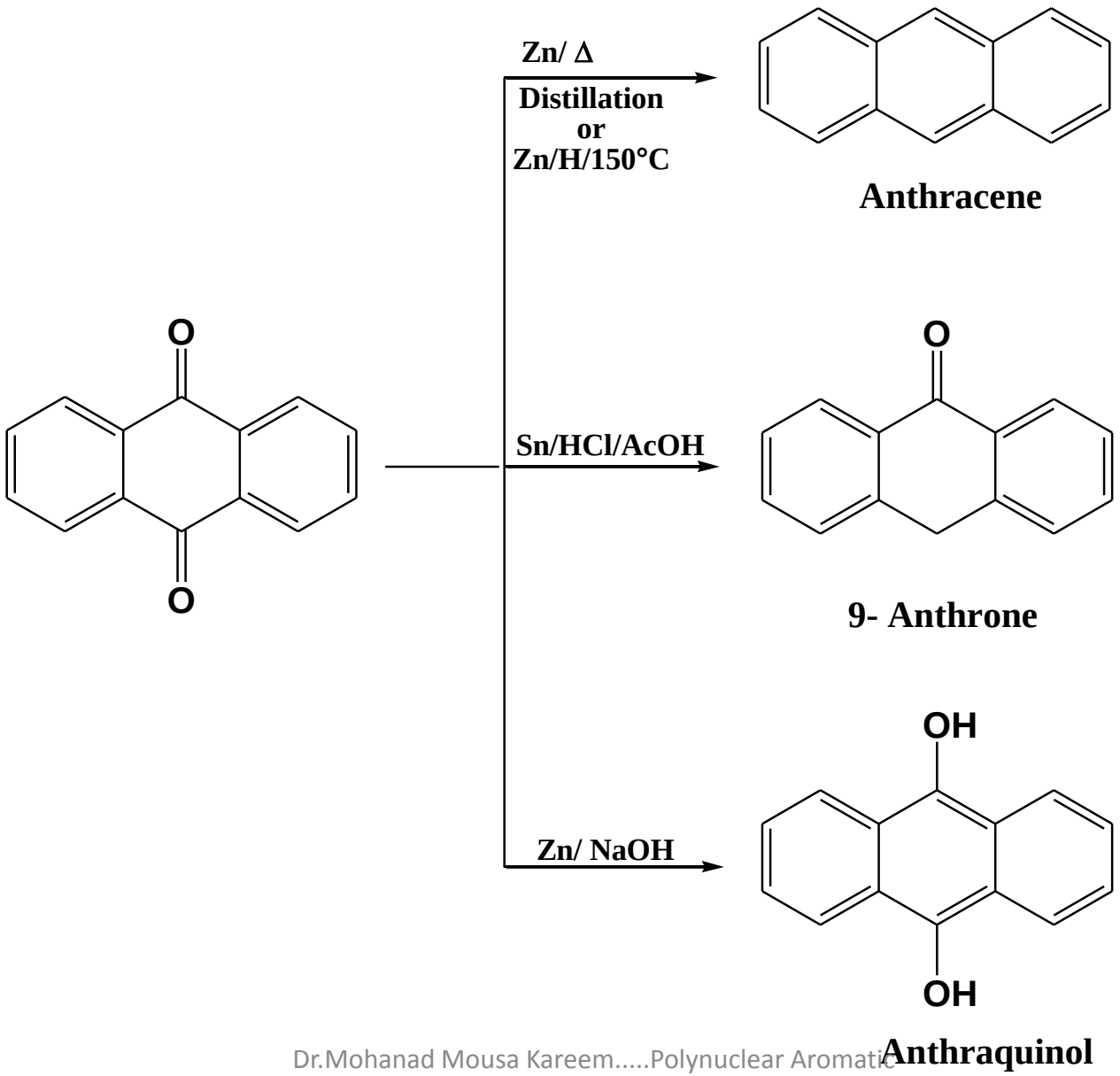


Phthalic anhydride

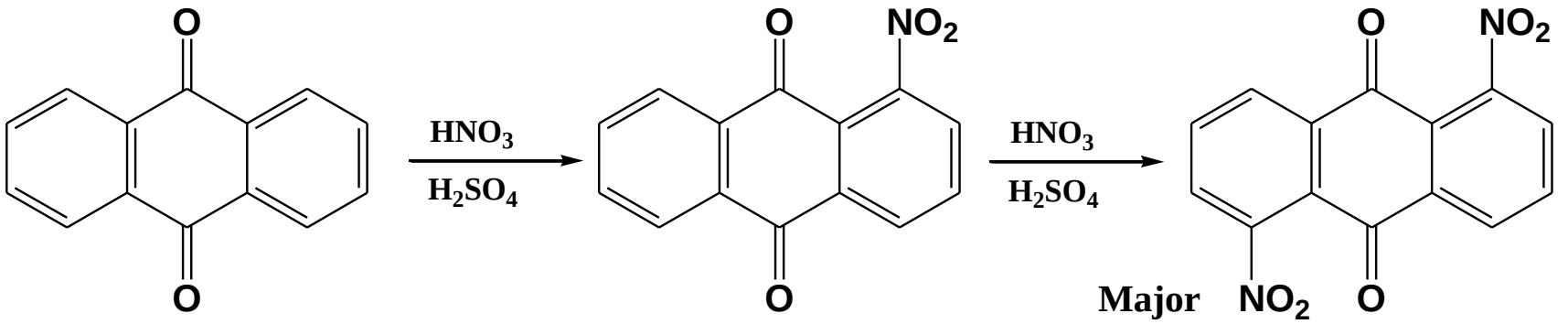


anthraquinone

Chemical Reactions


Zn/ Δ
Distillation
or
Zn/H/150°C
Anthracene
O
O
Sn/HCl/AcOH
O
9- Anthrone
Zn/ NaOH
OH
OH
Anthraquinol

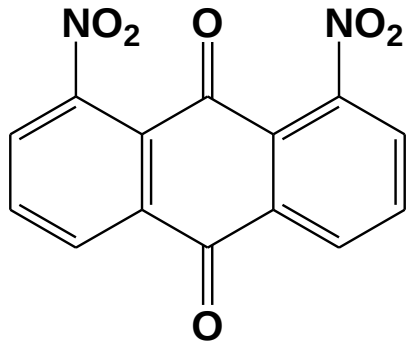
- **Nitration**



1- nitro-9,10- anthraquinone

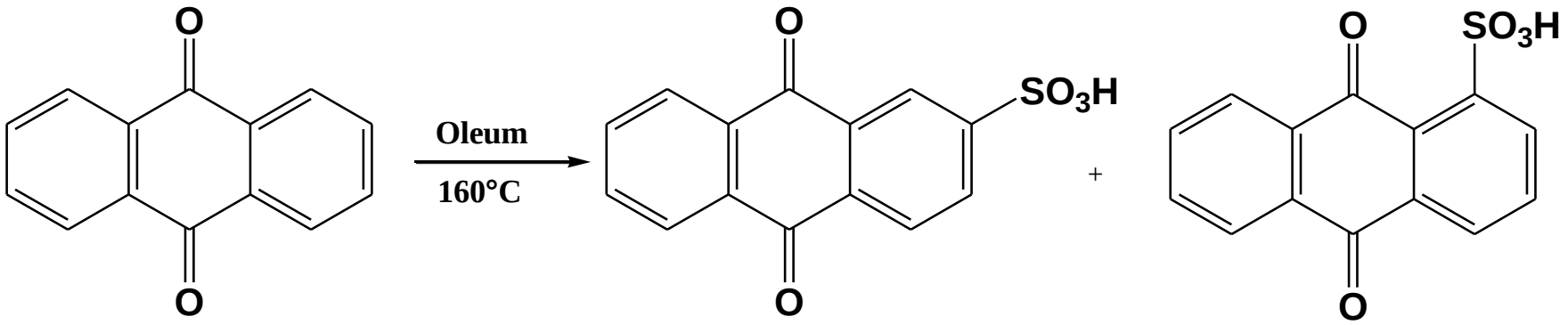
1,5- dinitroanthraquinone

+



1,8- dinitroanthraquinone

- **Sulphonation**



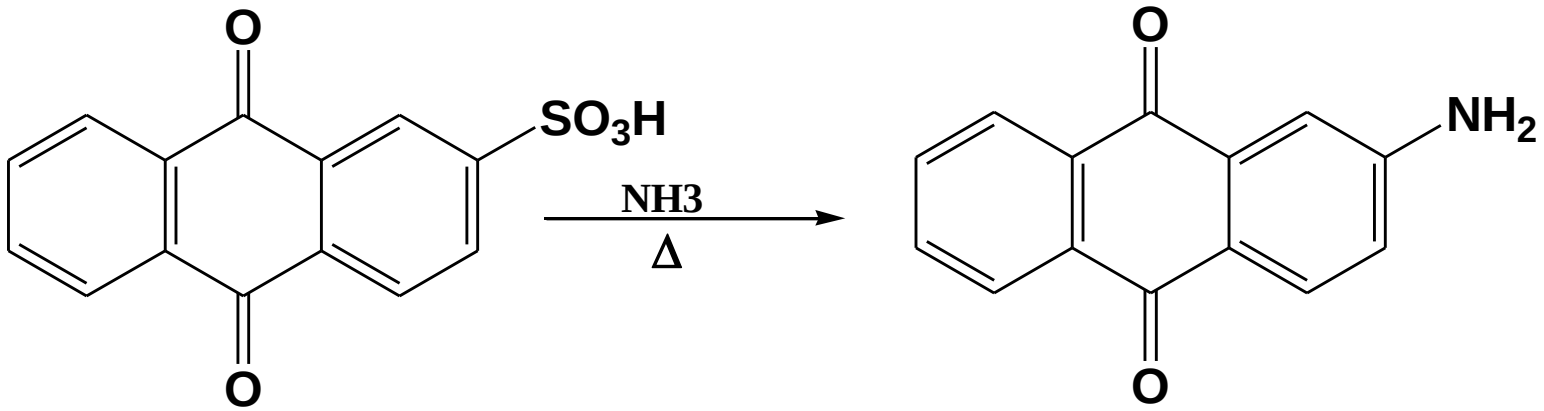
Anthraquinone-2-sulfonic acid

Major

small

Anthraquinone does not undergo Friedl Craft reaction

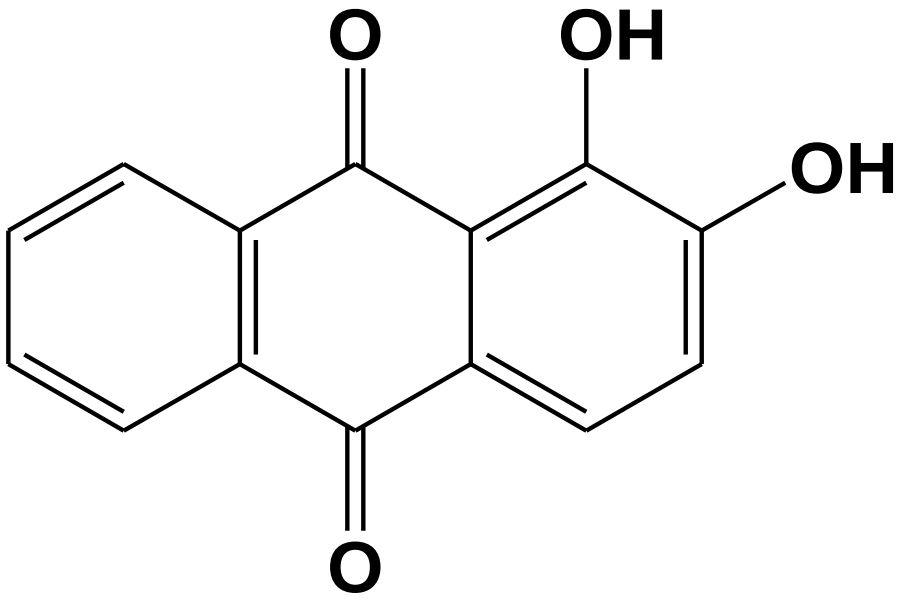
- **Preparation of 2-amino-anthraquinone**



Anthraquinone-2-sulfonic acid

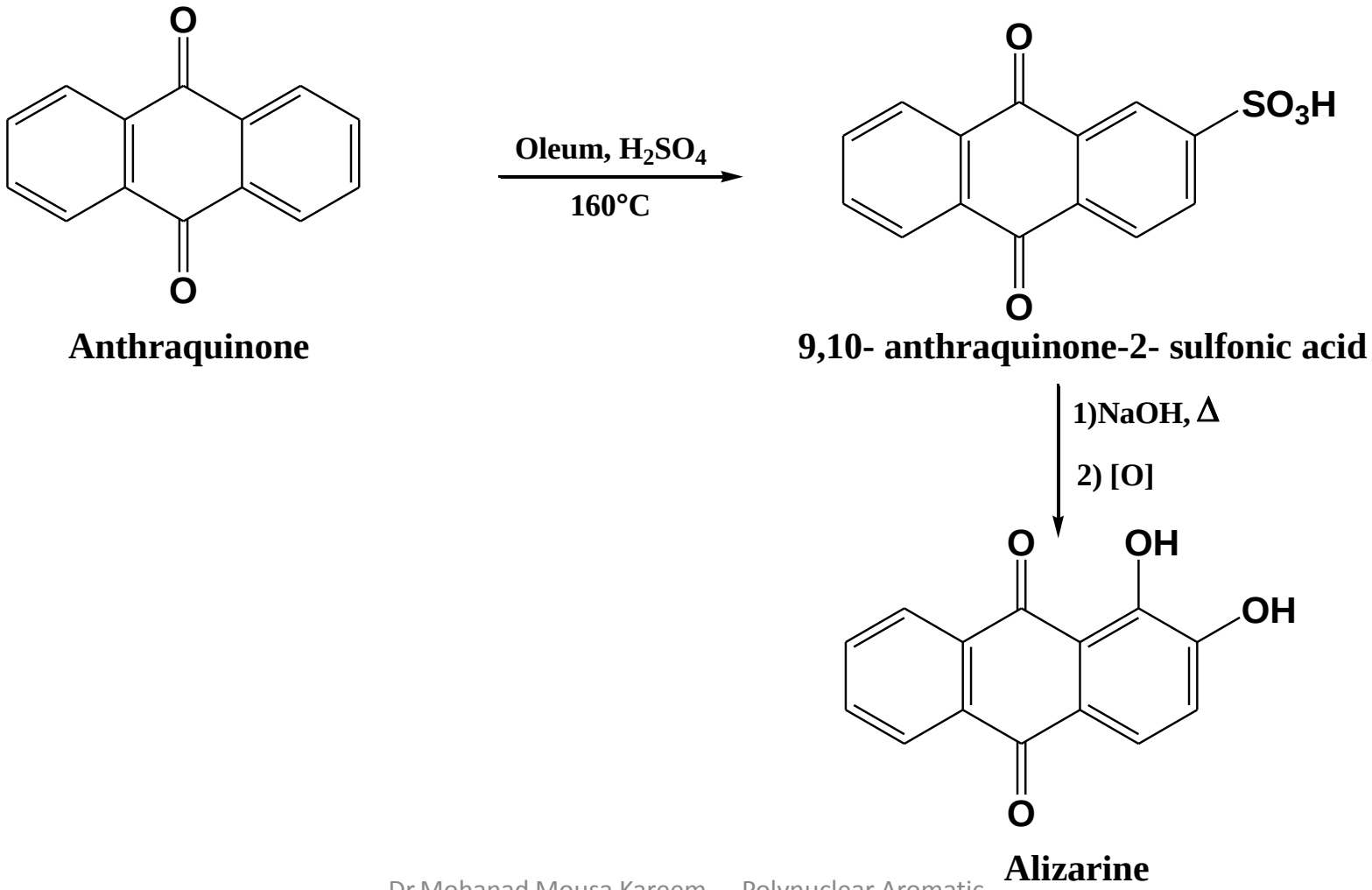
2- amino-anthraquinone

Alizarin



1,2-dihydroxyanthraquinone
Alizarine

Preparation

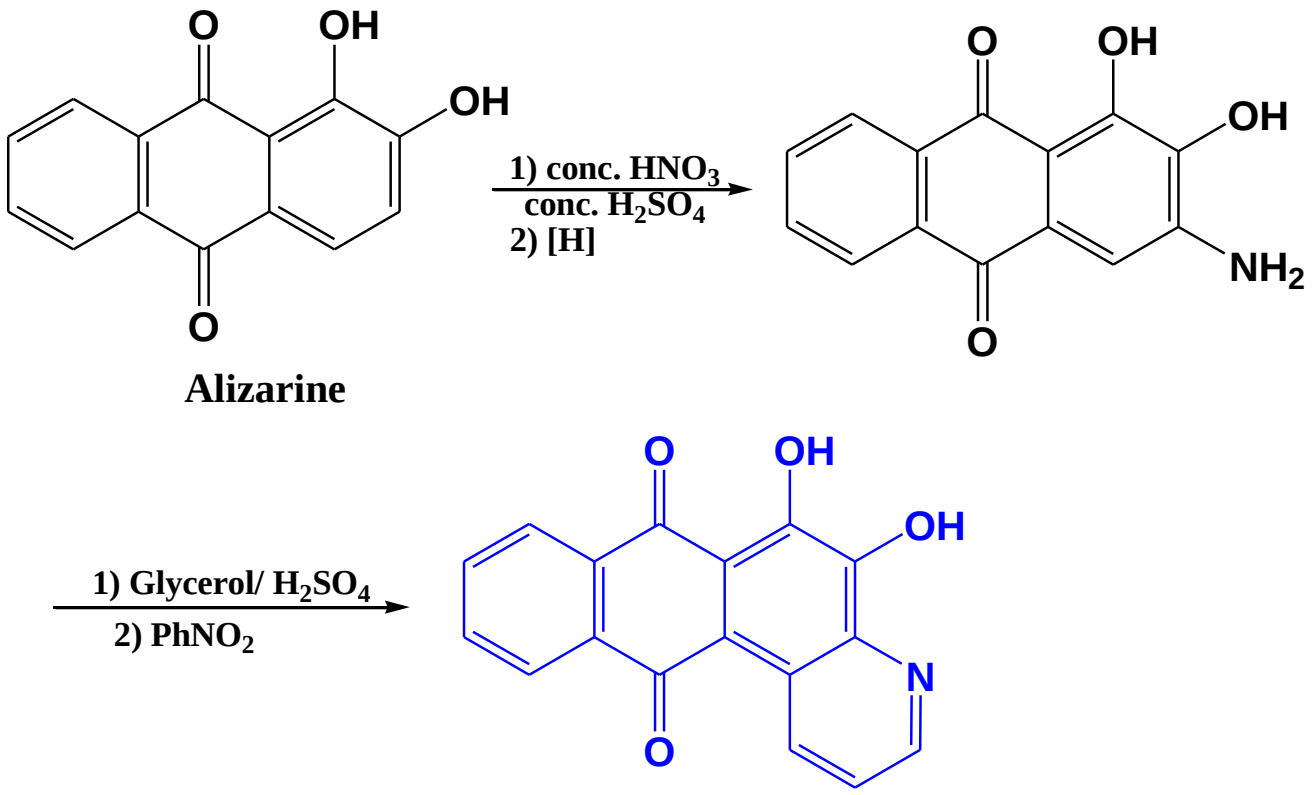


Anthraquinone

9,10- anthraquinone-2- sulfonic acid

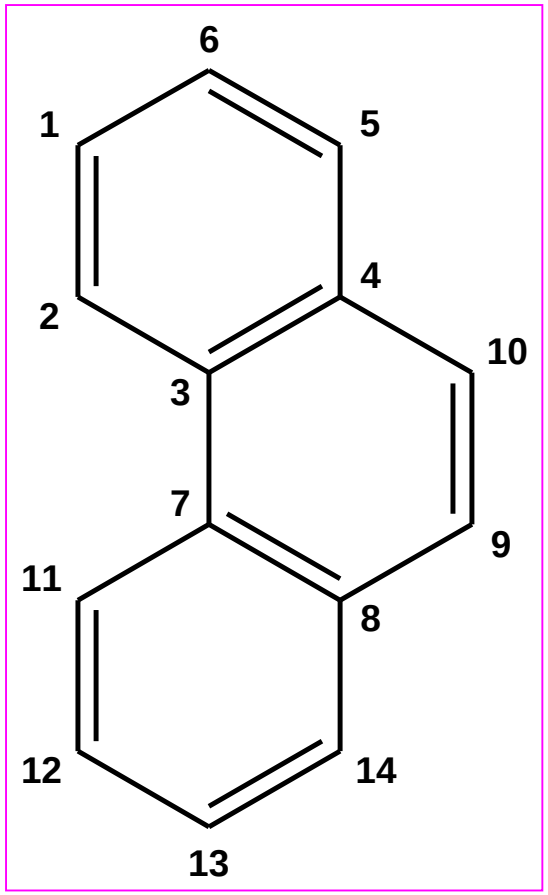
Alizarine

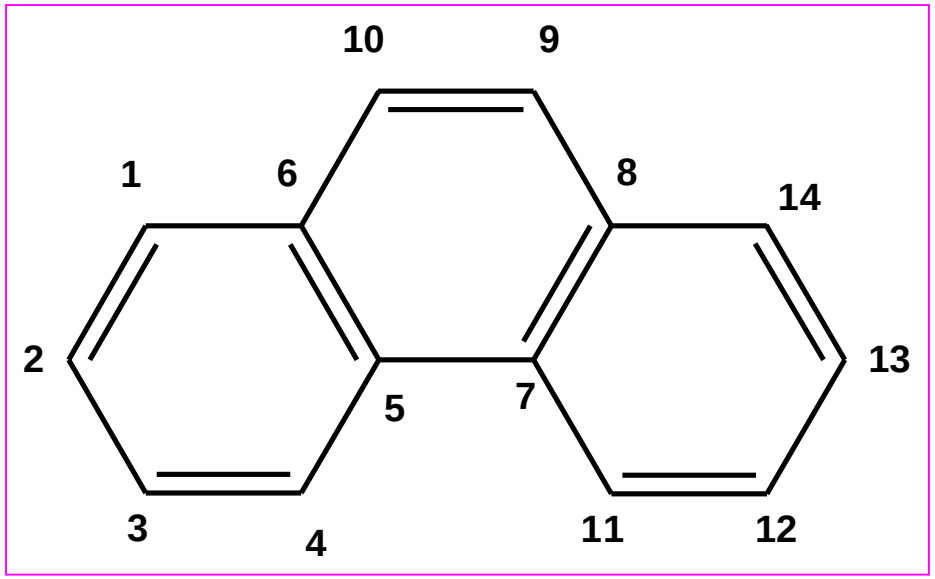
Preparation of Alizarine Blue



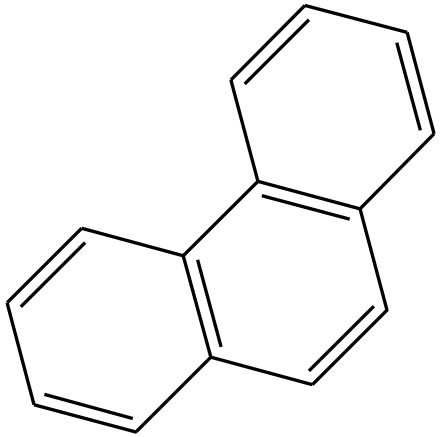
Alizarine blue is used for dyeing wool by blue color

Phenanthrene

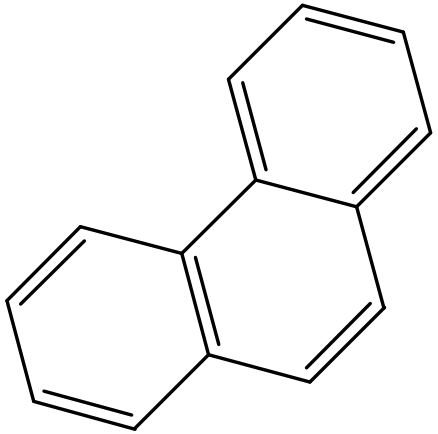


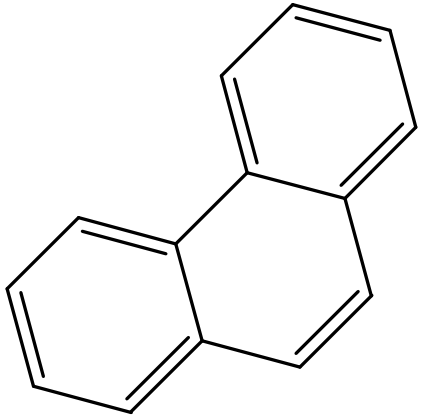


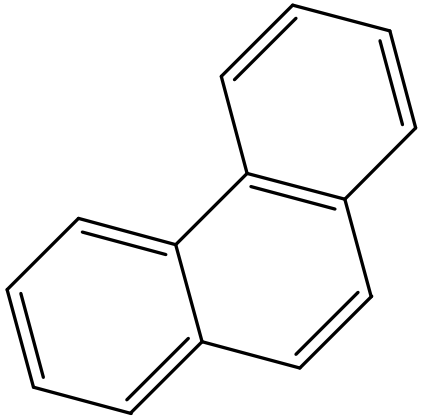
Position of double bond

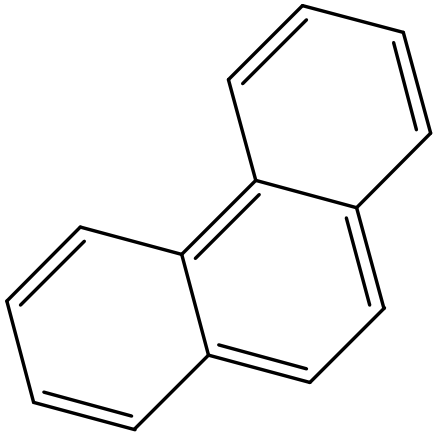


The most stable
3 benzenoid rings



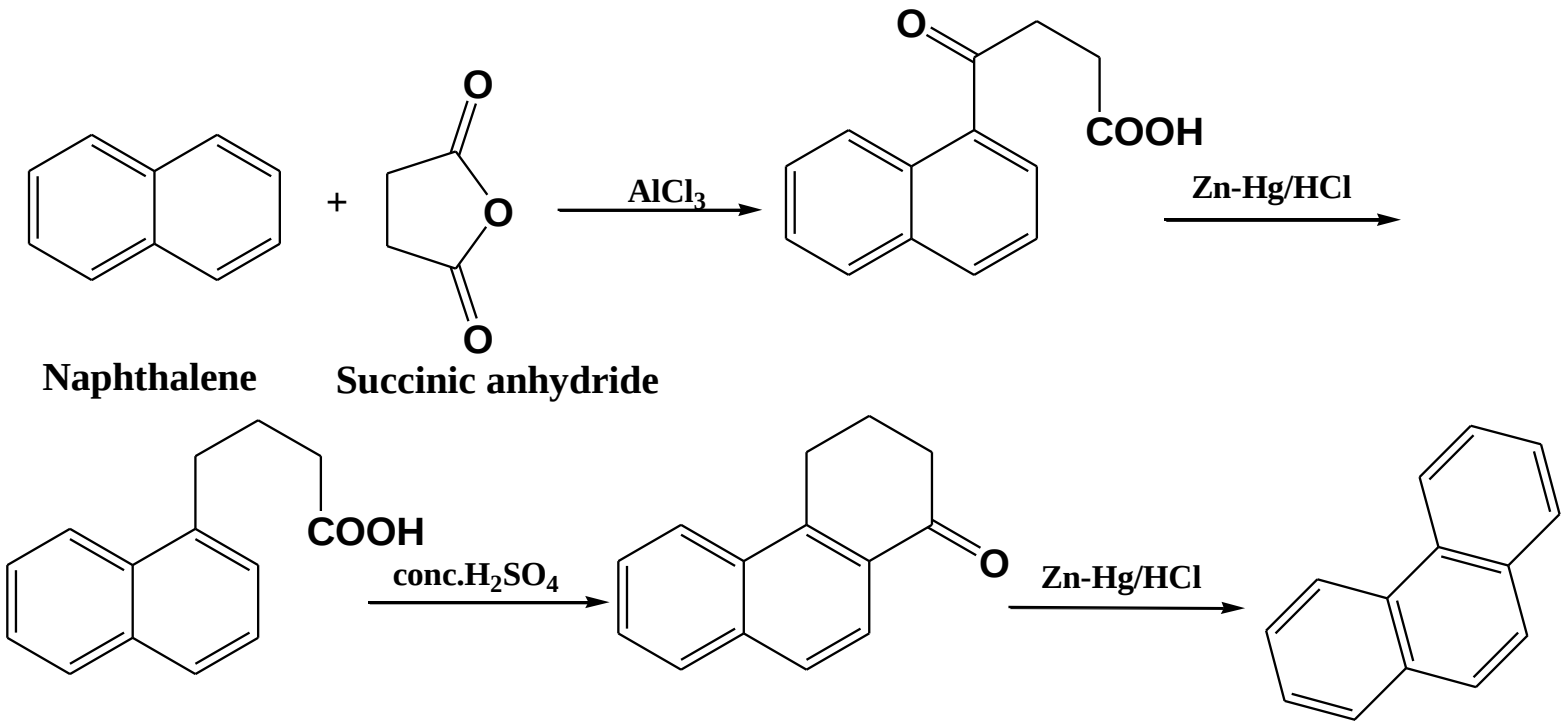




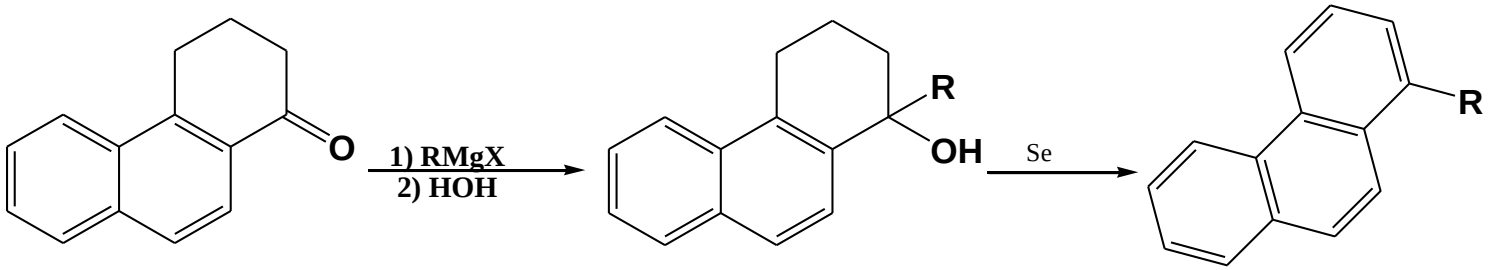


Preparation of phenanthrene

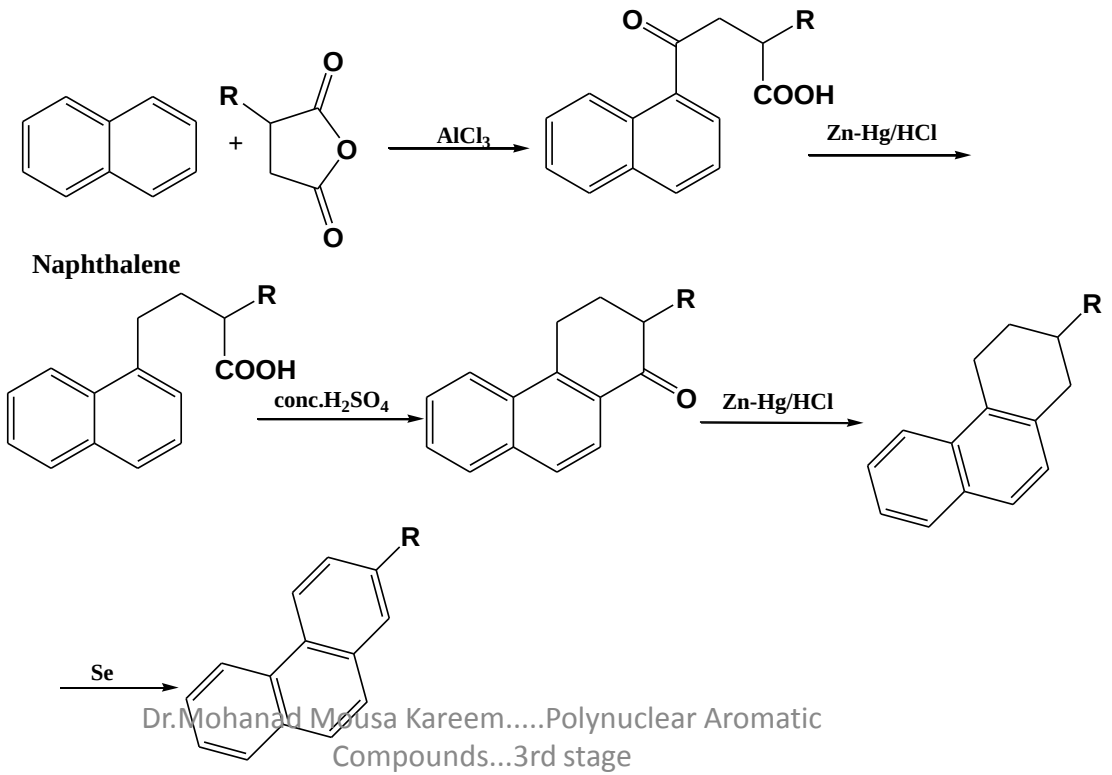
- **1) Howrth method**



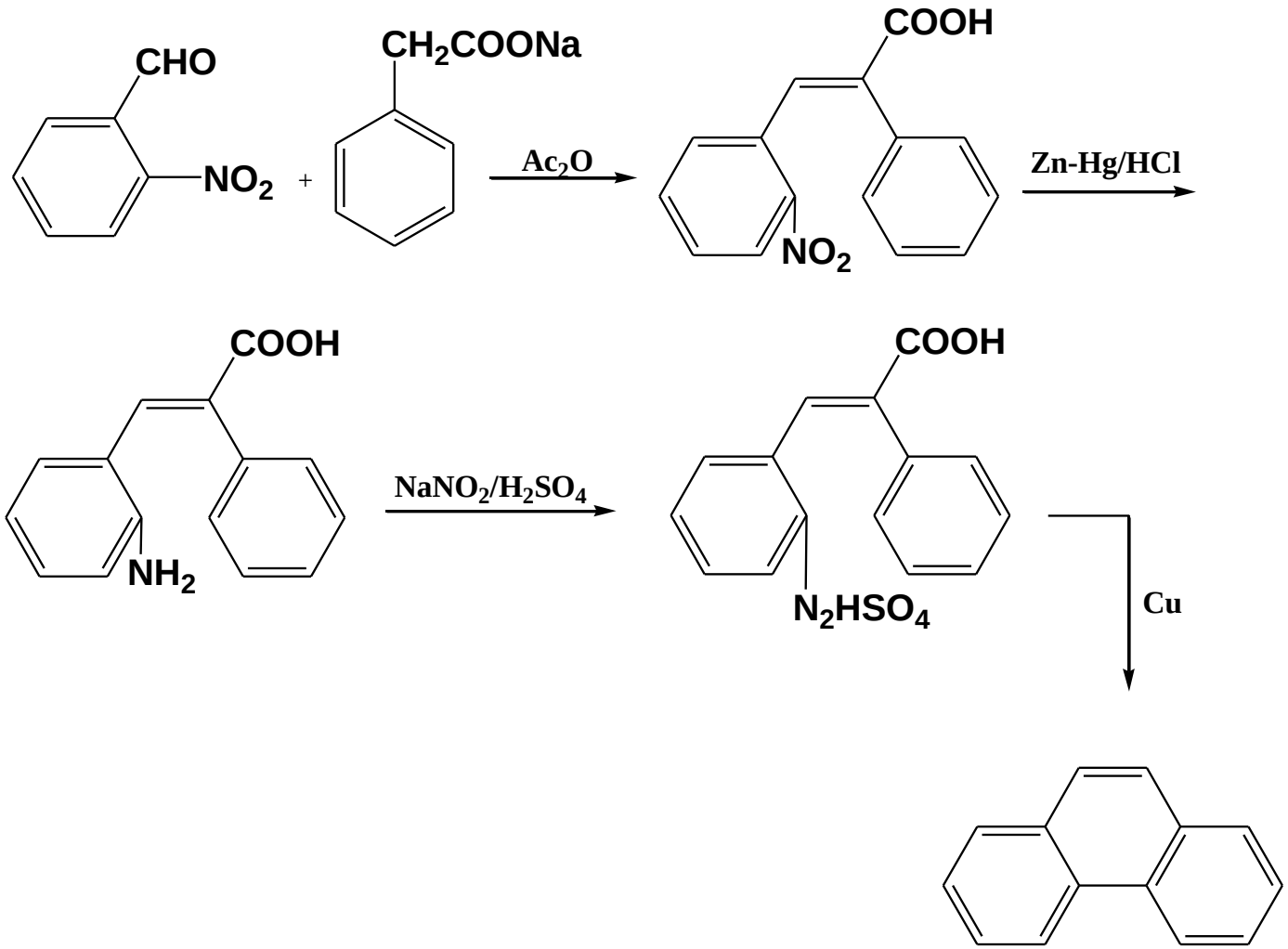
Preparation of 1- alkyl phenanthrene:



- **Preparation of 2- alkyl phenanthrene:**

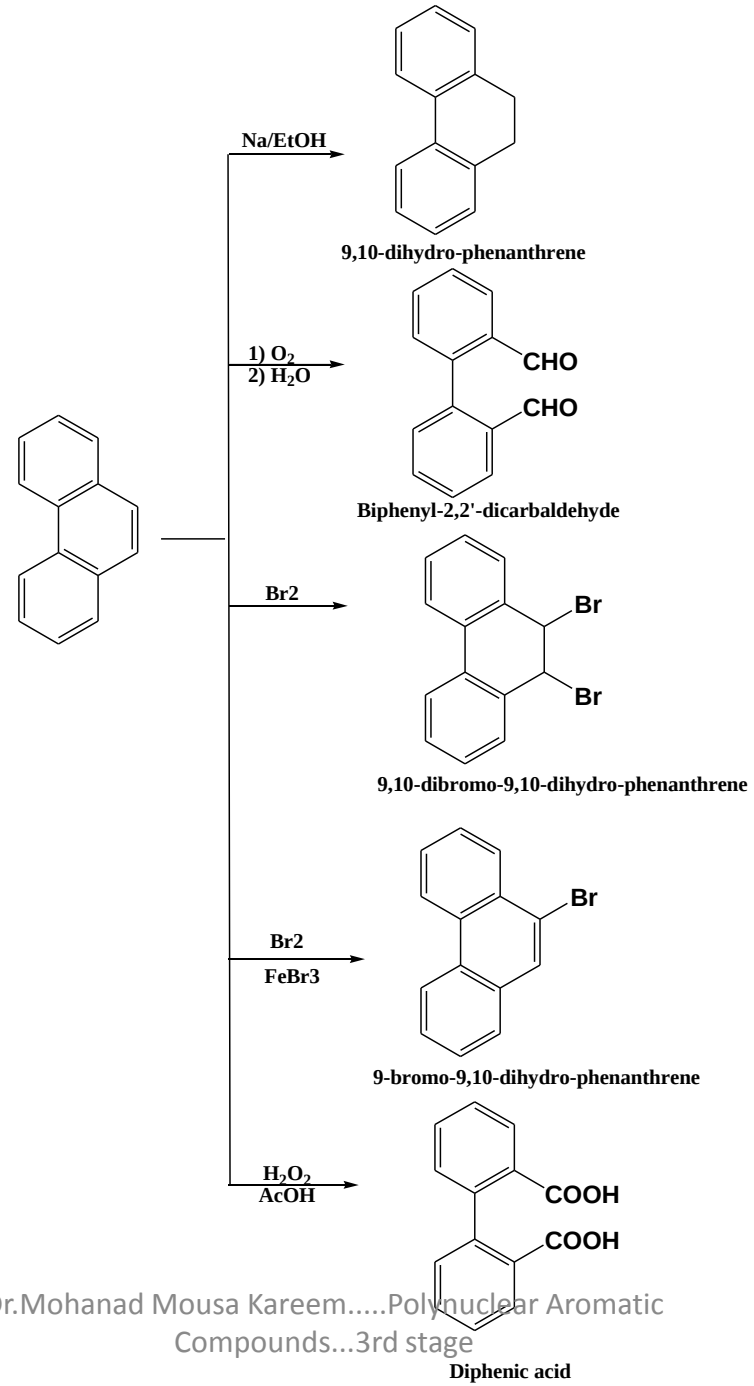


- 2) Posher synthesis

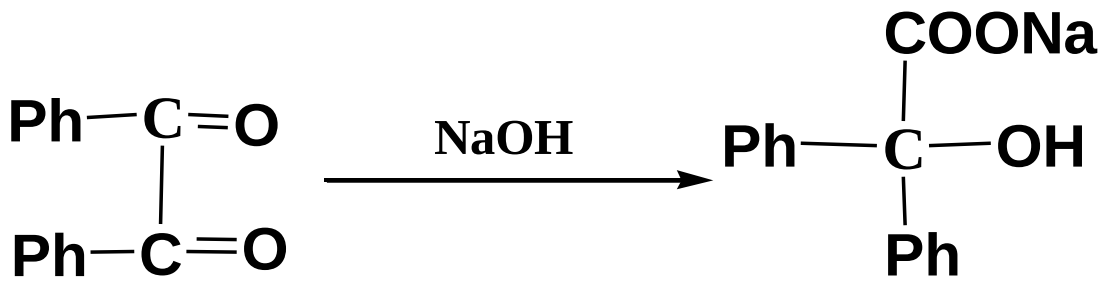


Phenanthrene

Chemical Reactions

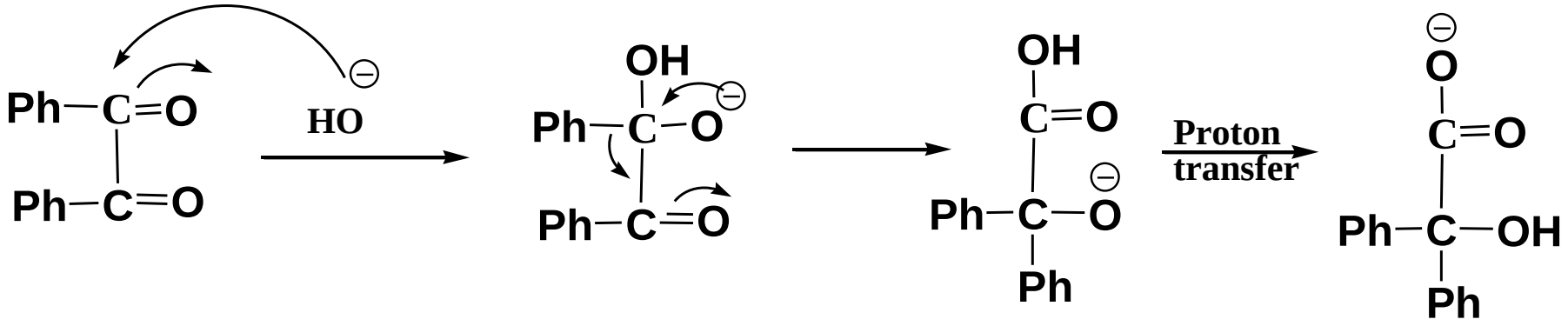

Na/EtOH
9,10-dihydro-phenanthrene
1) O_2
2) H_2O
CHO
CHO
Biphenyl-2,2'-dicarbaldehyde
Br2
Br
Br
9,10-dibromo-9,10-dihydro-phenanthrene
Br2
FeBr3
Br
9-bromo-9,10-dihydro-phenanthrene
H_2O_2
AcOH
COOH
COOH
Diphenic acid

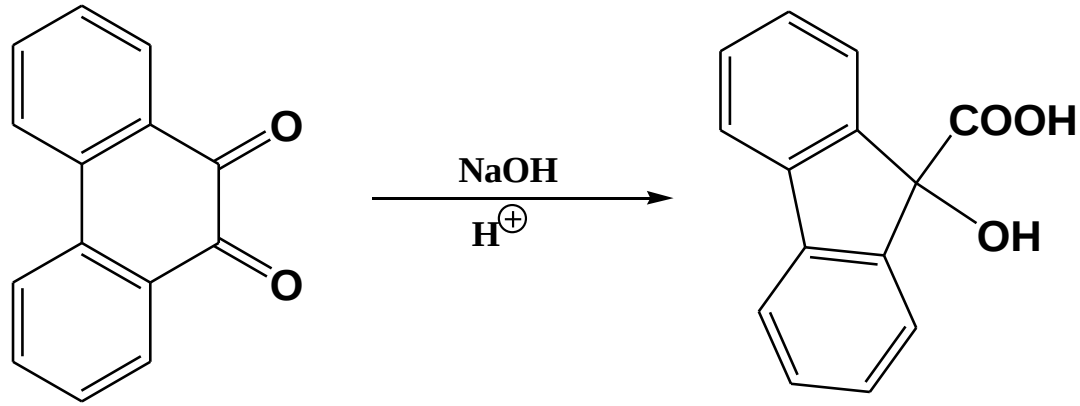
Benzil-Benzilic rearrangement



Benzil **Benzilic acid salt**

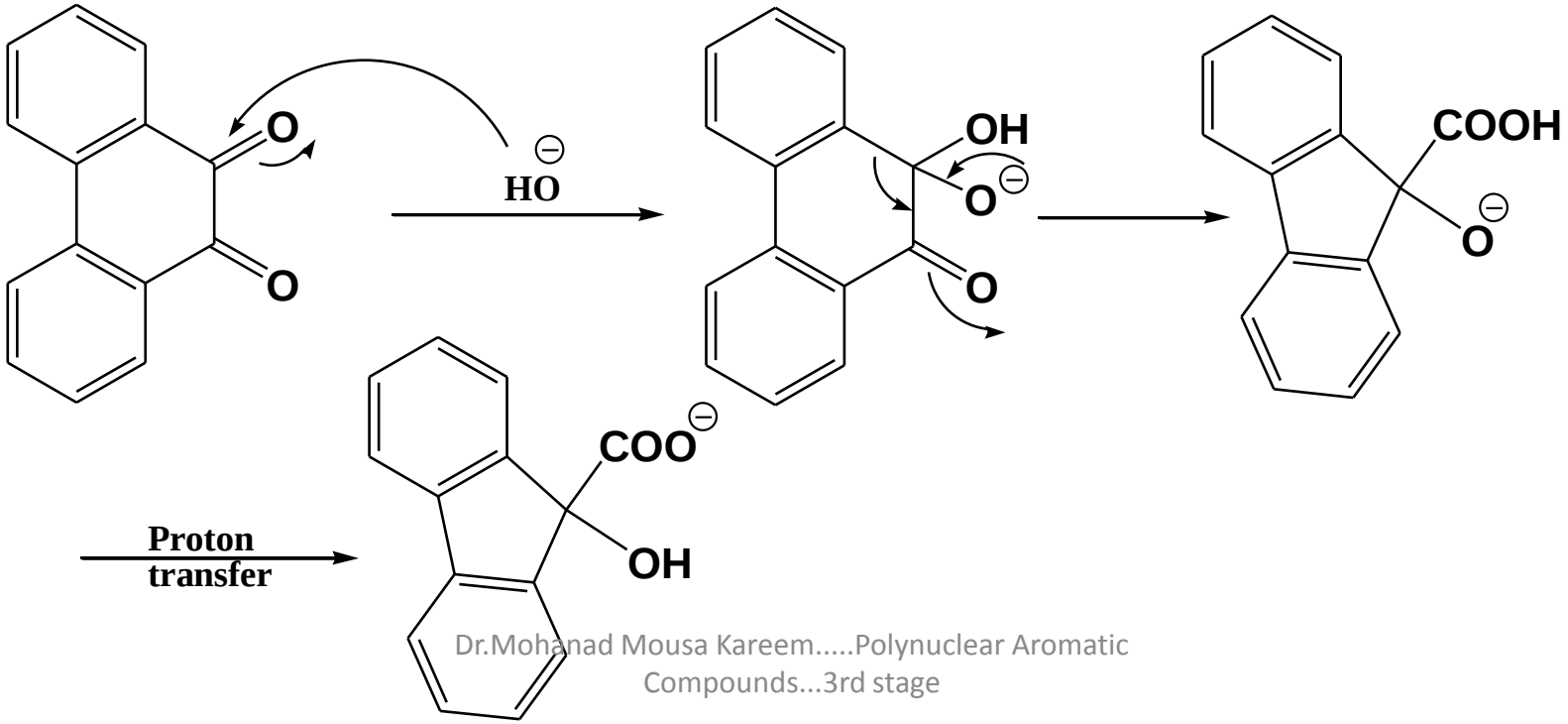
Mechanism





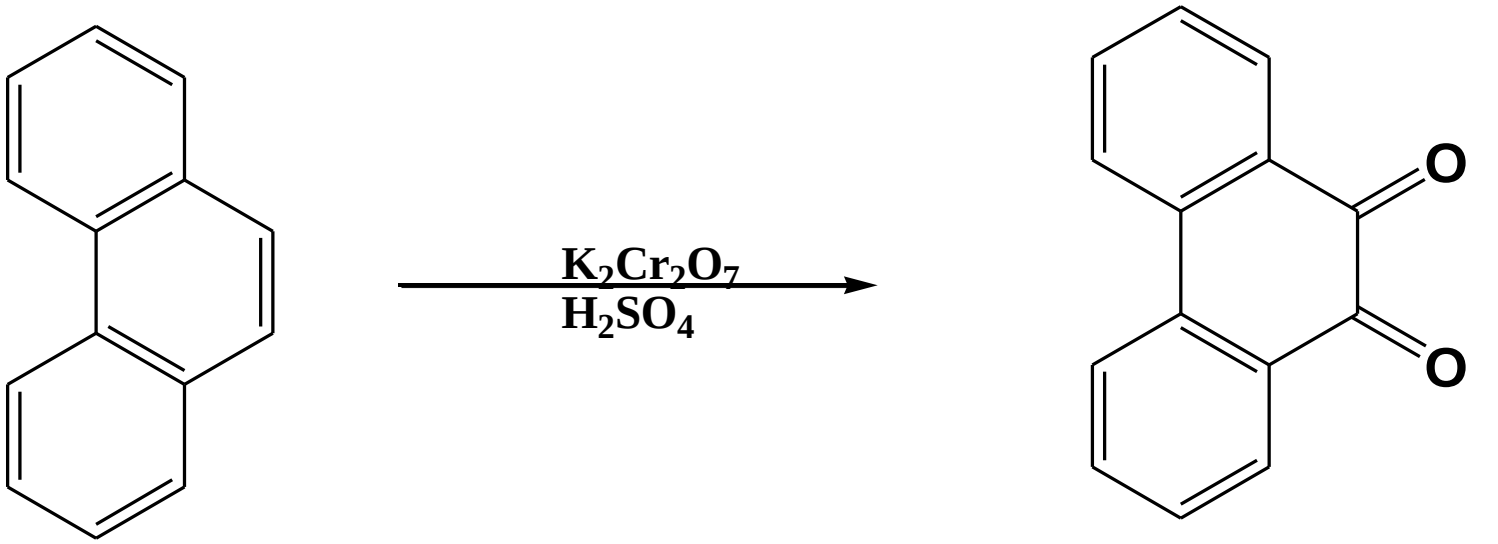
Phenanthraquinone **9-hydroxy-9*H*-flourene-9-carboxylic acid**

Mechanism



Phenanthraquinone

- Preparation



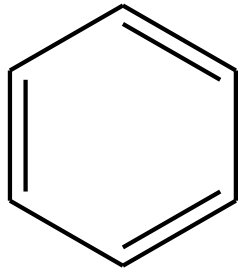
Phenanthrene **Phenanthraquinone**

Condition necessary for aromaticity

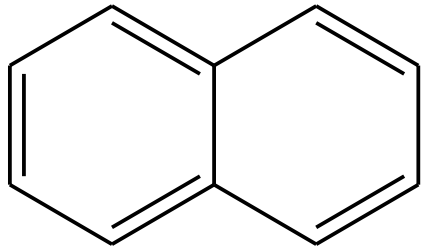
Any compound to be aromatic, it must be;

- 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,…

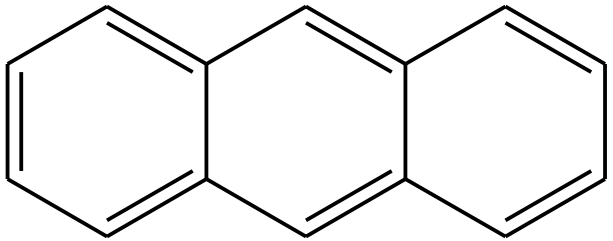
Examples



n=1
6 π electron

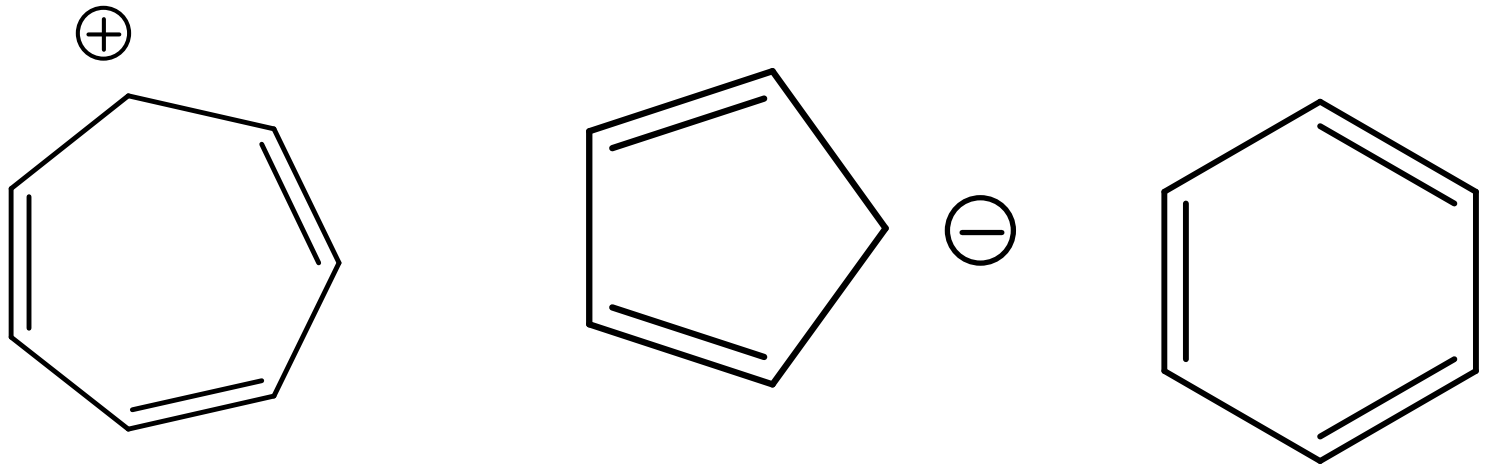


n=2
10 π electron



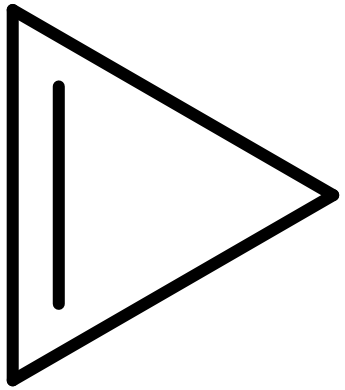
n=3
14 π electron

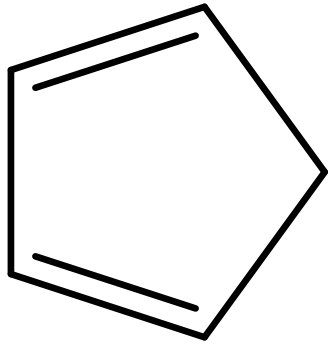
Examples of non- benzenoid aromatic cmpound



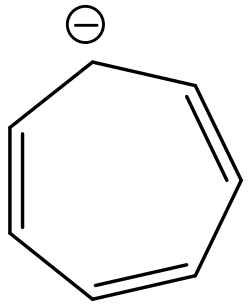
All are aromatic(cyclic, planner,1, and agree with Huckle rule: 4n+2= 6 (n=1)

Examples of non- aromatic





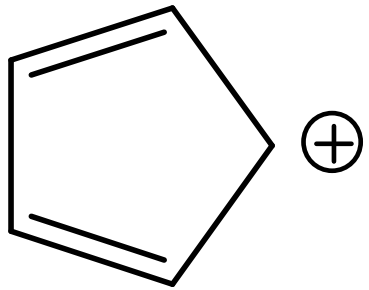
Not aromatic; both contain Sp3



Not aromatic

Does not obey Huckel rule

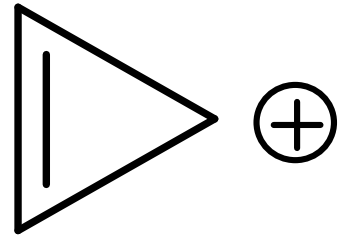
4n+2=8; n=1.5



Not aromatic

Does not obey Huckel rule

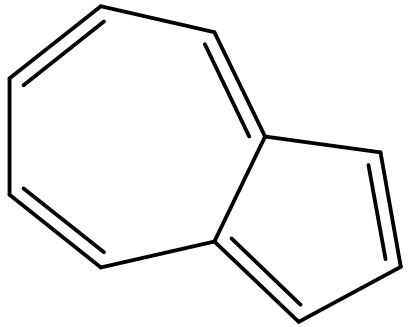
4n+2=4; n=0.5



Aromatic; cyclic, planner,

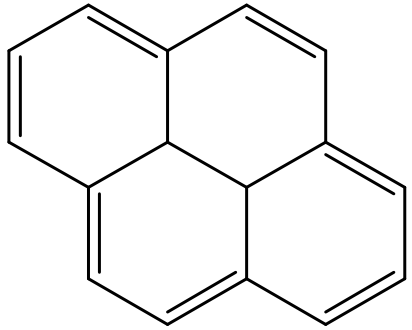
obey Huckel rule

4n+2=2; n=0



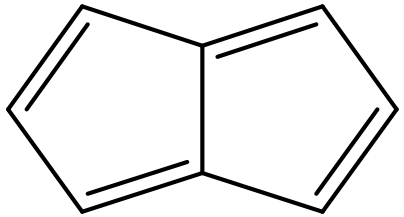
Aromatic

4n+2=10; n=2



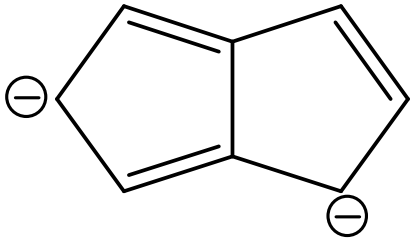
Aromatic

4n+2=14; n=3



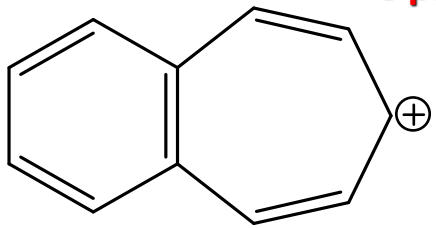
Not Aromatic

8 pi electrons



Aromatic

4n+2=10; n=2



Aromatic

4n+2=10; n=2