جامعـــة تكريـــــــــت
كلية التربية للبـــنات
قســـــم الكيميـــــاء

المرحـلة الثالثـــة

الكيميـاء العضويـة

الفصـــل العاشـــر

الهيدروكربونات الاروماتية متعددة الحلقات

POLYNUCLEAR AROMATIC HYDROCARBONS

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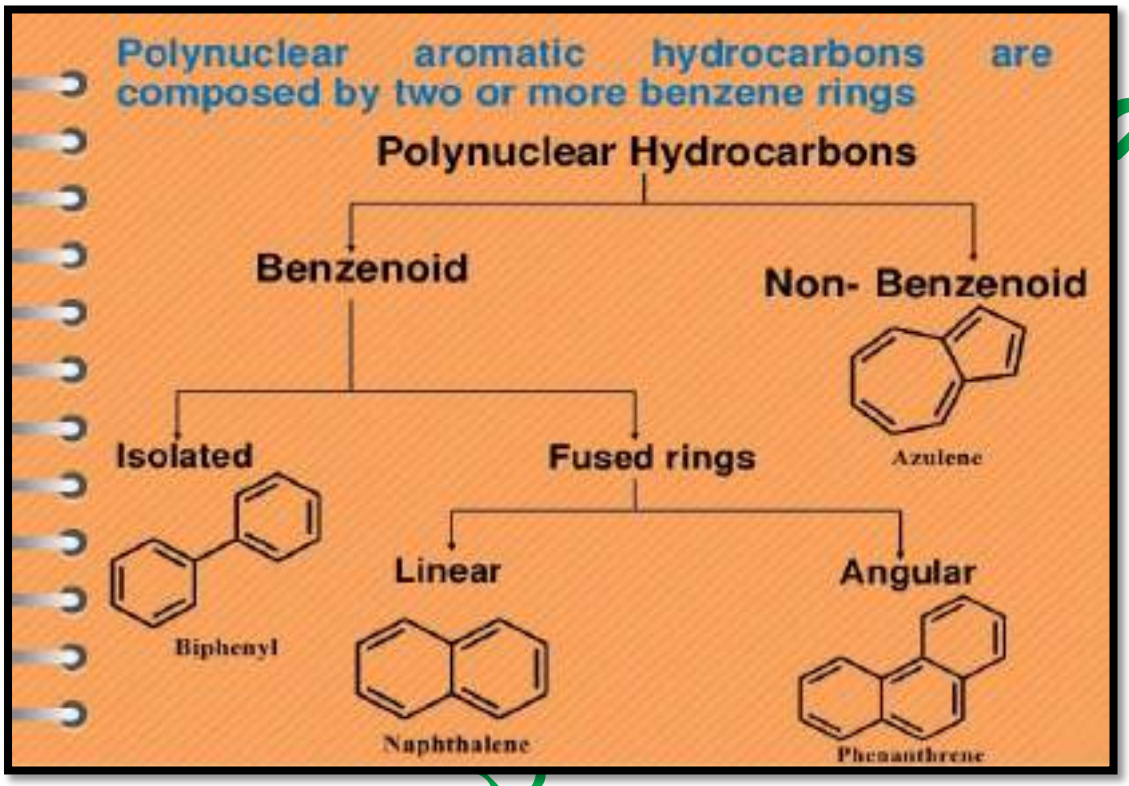
الهيدروكاربونات الاروماتية متعددة الحلقات

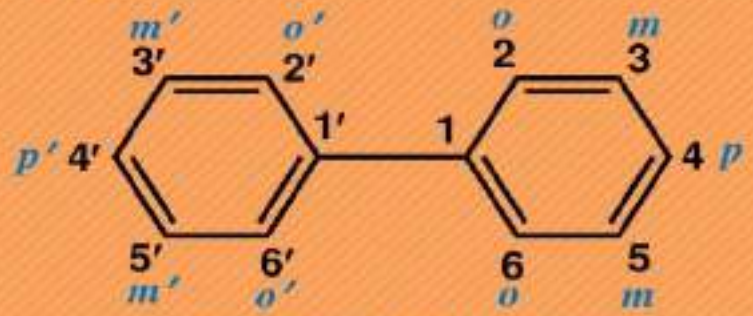
POLYNUCLEAR AROMATIC HYDROCARBONS

Polynuclear aromatic hydrocarbons are composed by two or more benzene rings



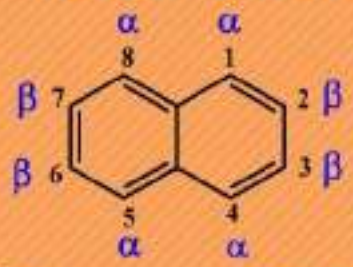
- **Benzenoid:** Similar to benzene in structure or linkage; having an aromatic ring system.
- **Fused or condensed ring system:** When two rings share a pair of carbon atoms, the rings are said to be fused rings.

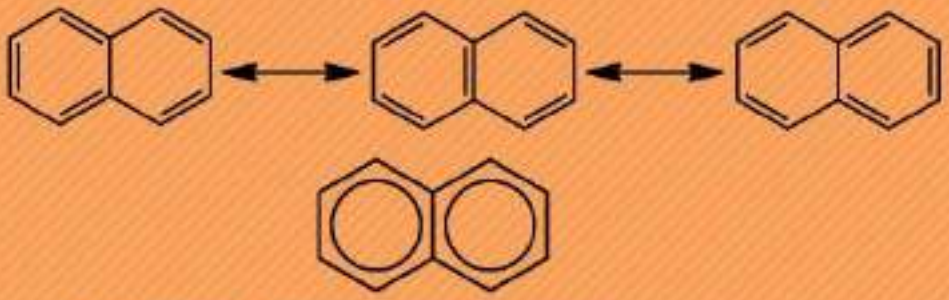
Isolated ring



Biphenyl or diphenyl

Naphthalene ($C_{10}H_8$)



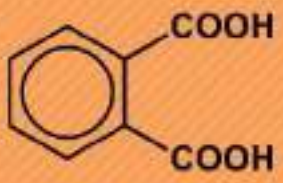


- Shows aromatic properties
- Satisfy Huckel's rule (4n+2)
  =(4*2+2)=10

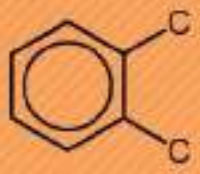
- All C=C are not same (X-ray diffraction study)
- $C_1=C_2=1.36$ Å
- $C_2=C_3=1.40$ Å
- Resonance energy of naphthalene is 61 Kcal/mol
  Benzene, 36 Kcal/mol
- 2nd aromatic ring is less stable (61-36)=25 Kcal/mol
- Naphthalene is less aromatic (more reactive) than benzene

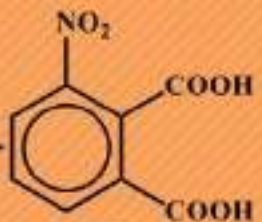
Structure elucidation of naphthalene

1. **Molecular Formula:** $C_{10}H_8$

2. **Naphthalene** $\xrightarrow{[O]}$ 

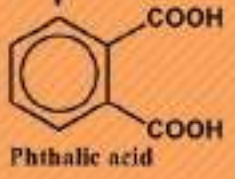
So naphthalene contains the skeleton



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

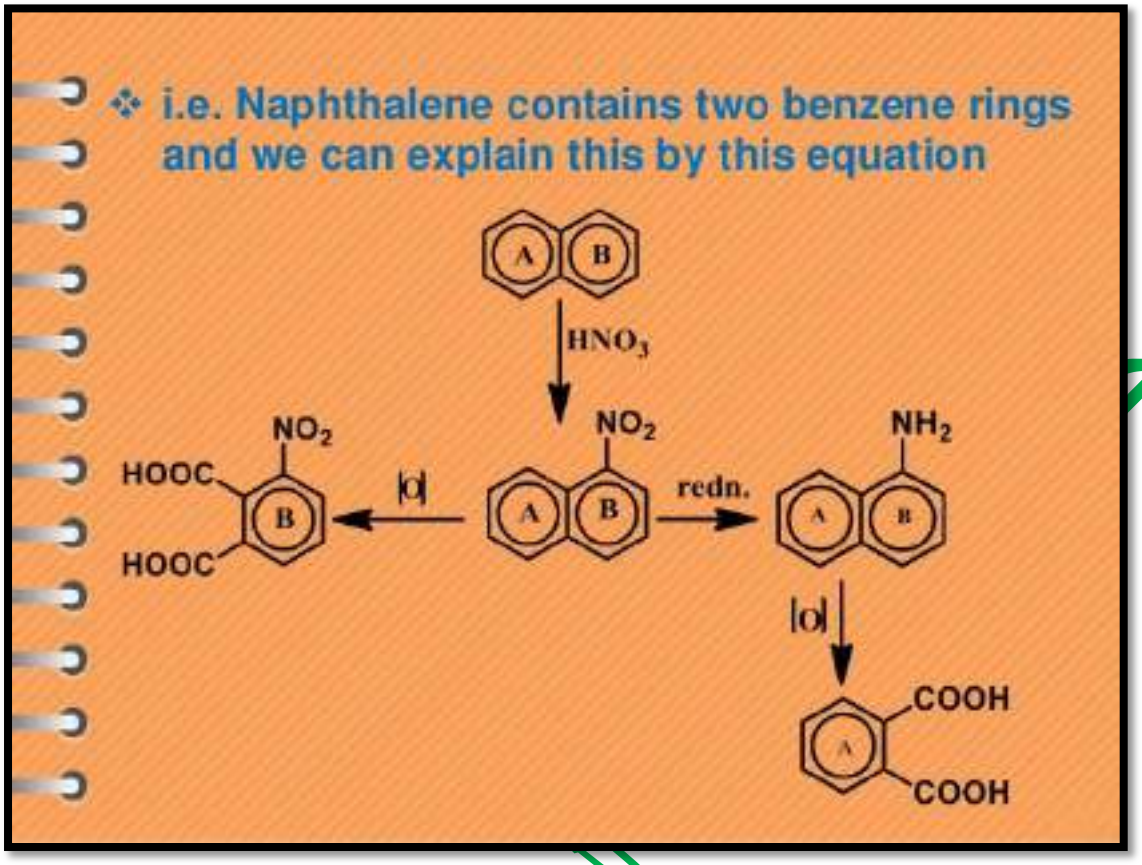
Nitrophthalic acid

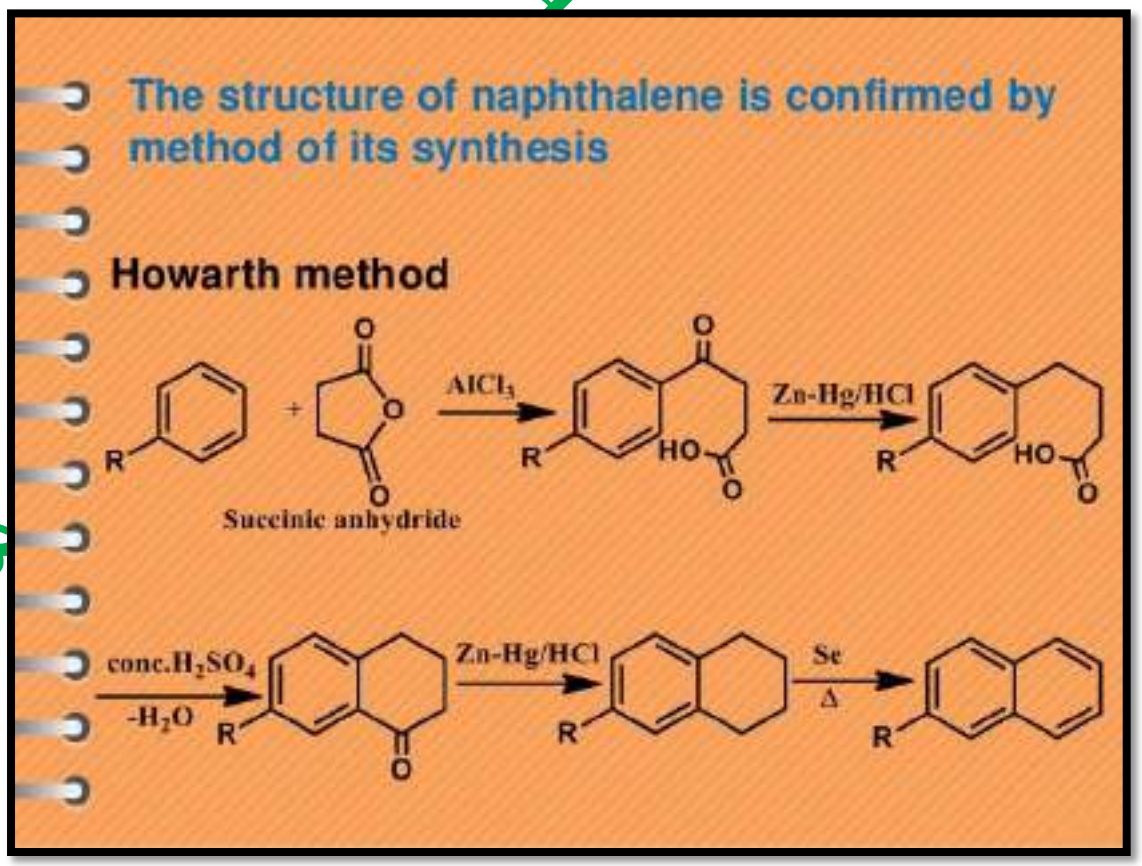
❖ So nitro group is present in benzene ring

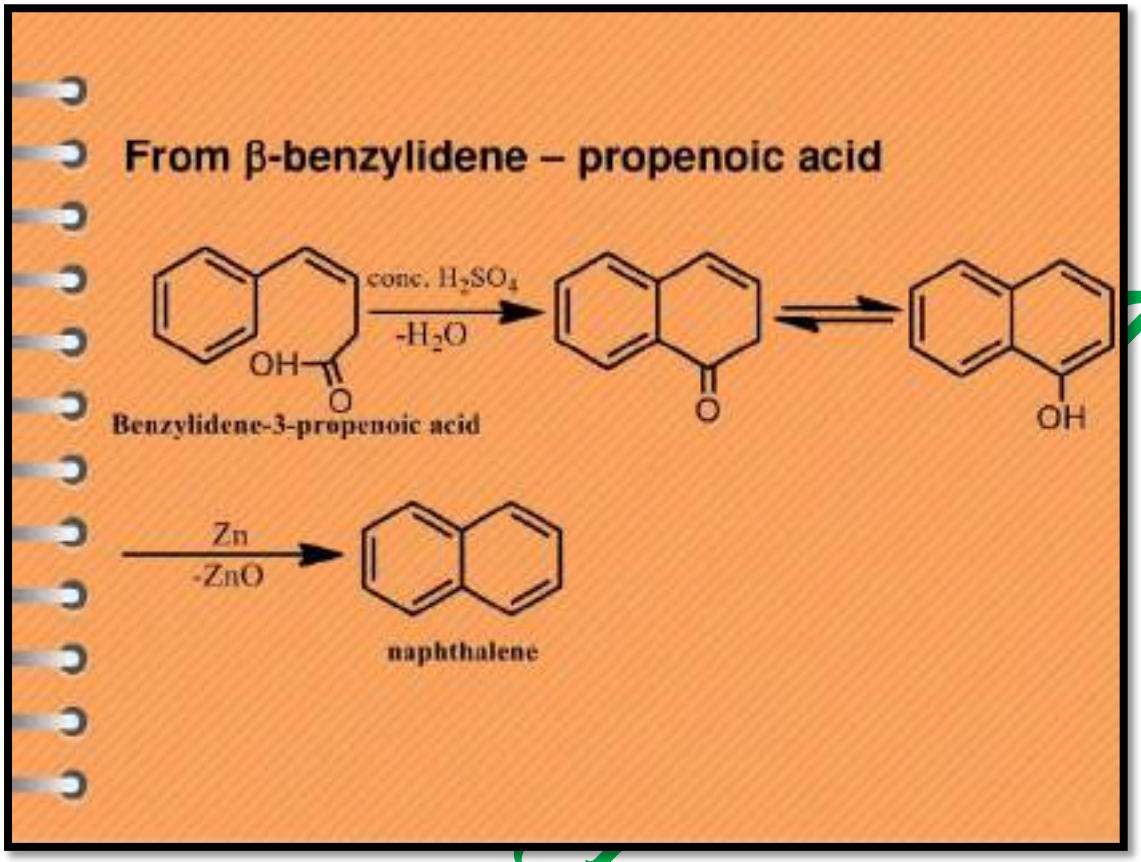
4. **Naphthalene** $\xrightarrow{\text{nitration}}$ **Nitronaphthalene** $\xrightarrow{\text{redn.}}$ **aminonaphthalene** $\xrightarrow{[O]}$ 

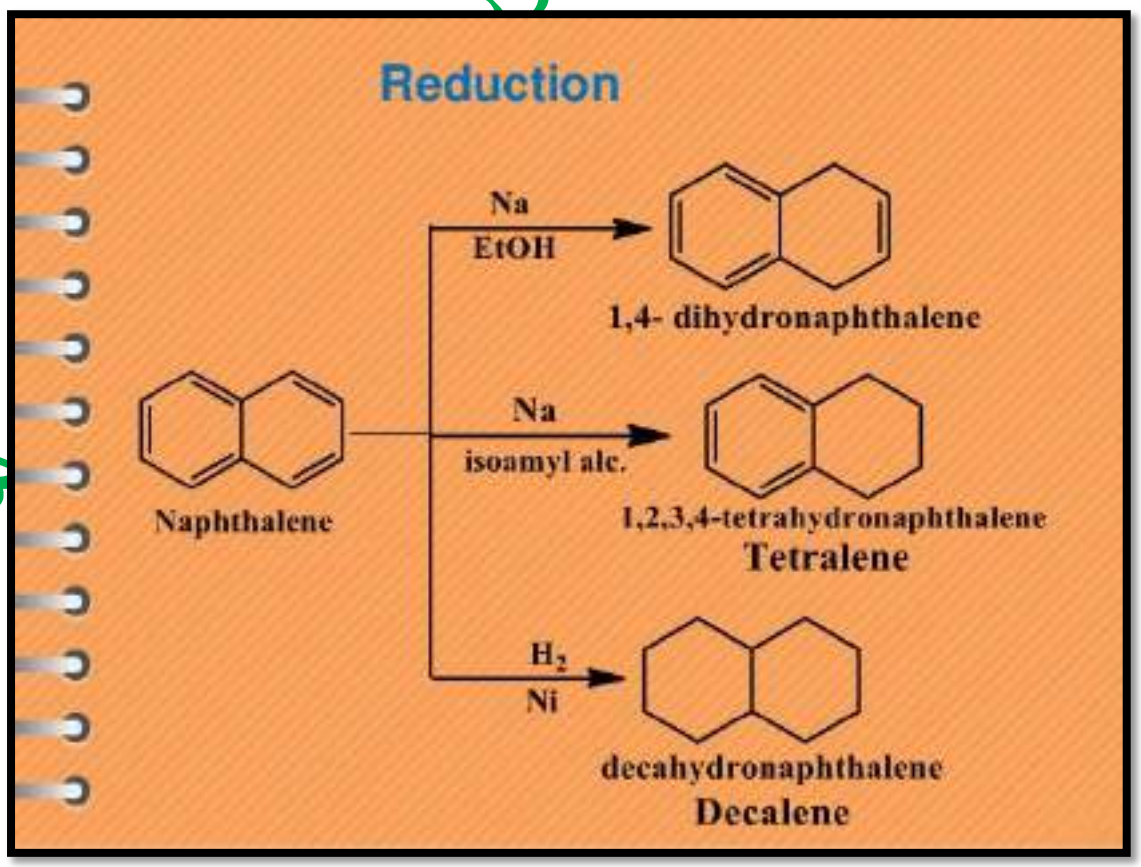
Phthalic acid

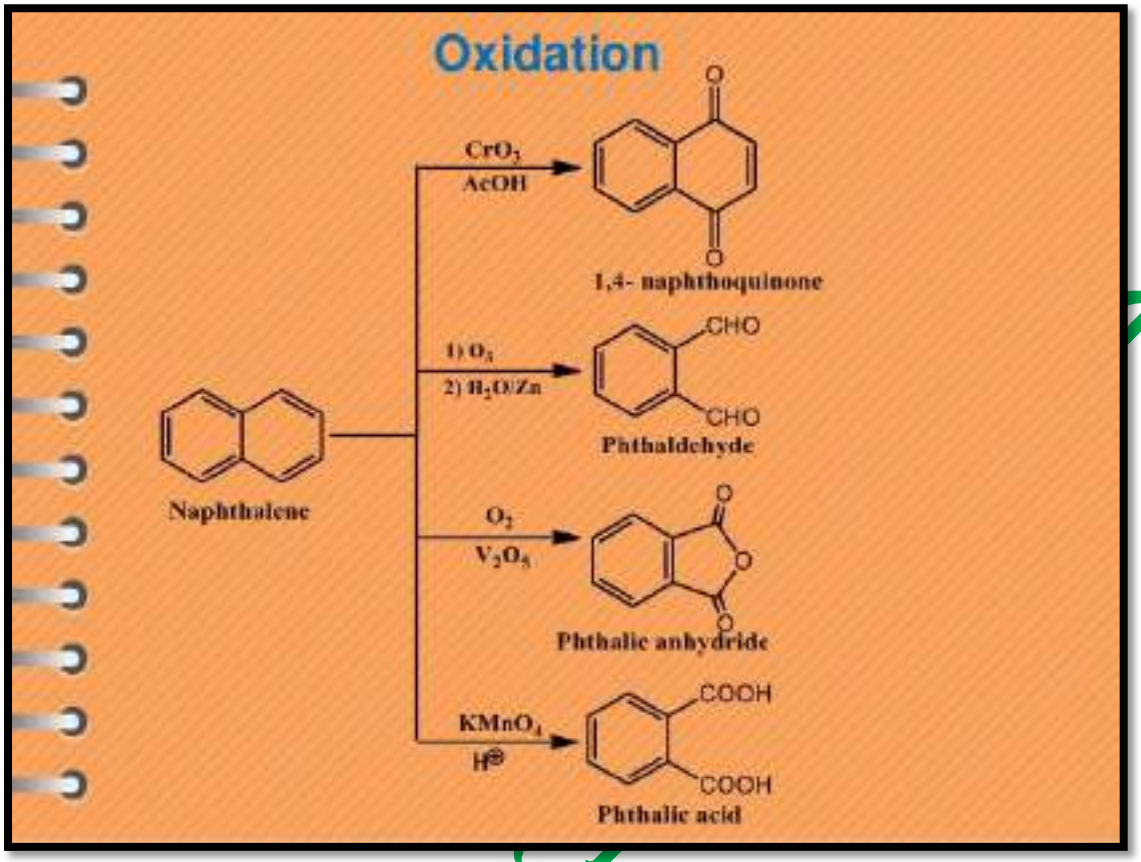
❖ The benzene ring in phthalic acid produced by oxidation of aminonaphthalene is not the same ring is that obtained by oxidation of nitronaphthalene.

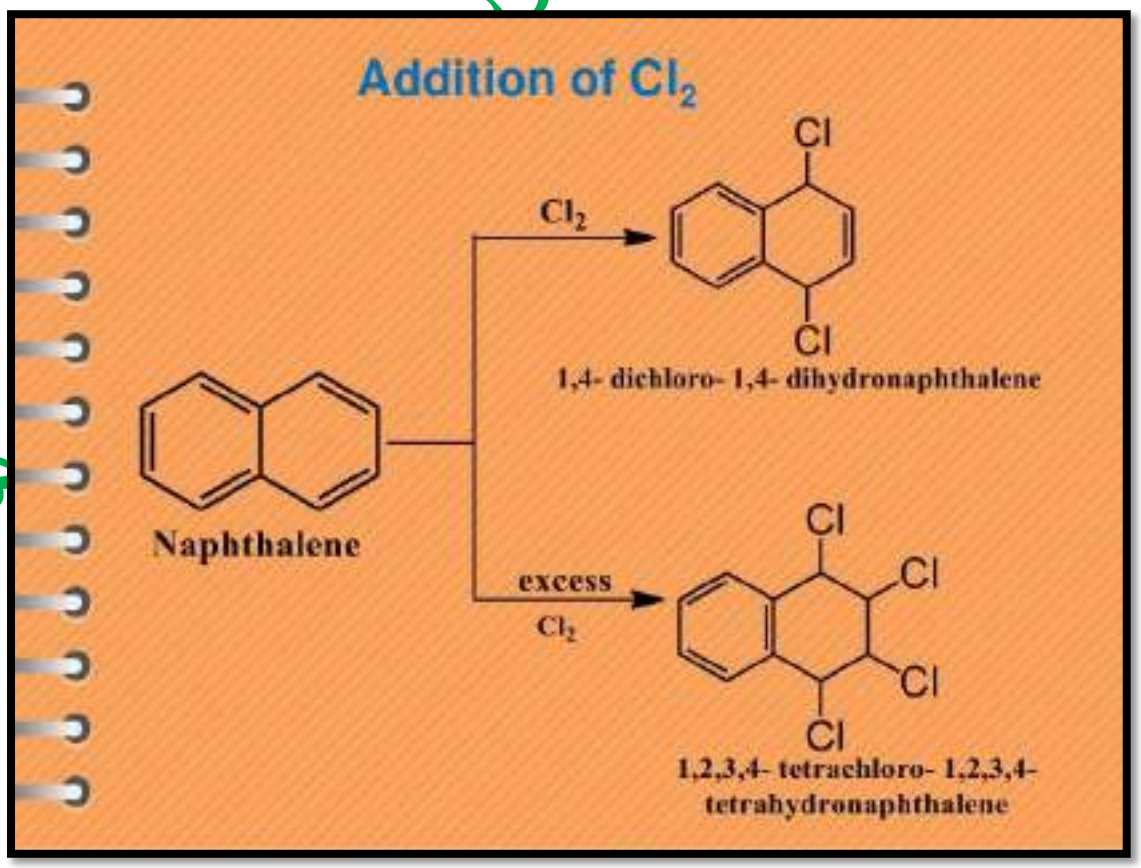

i.e. Naphthalene contains two benzene rings and we can explain this by this equation
A
B
HNO3
NO2
NO2
NH2
HOOC
HOOC
B
[O]
A
B
redn.
A
B
[O]
COOH
COOH
A

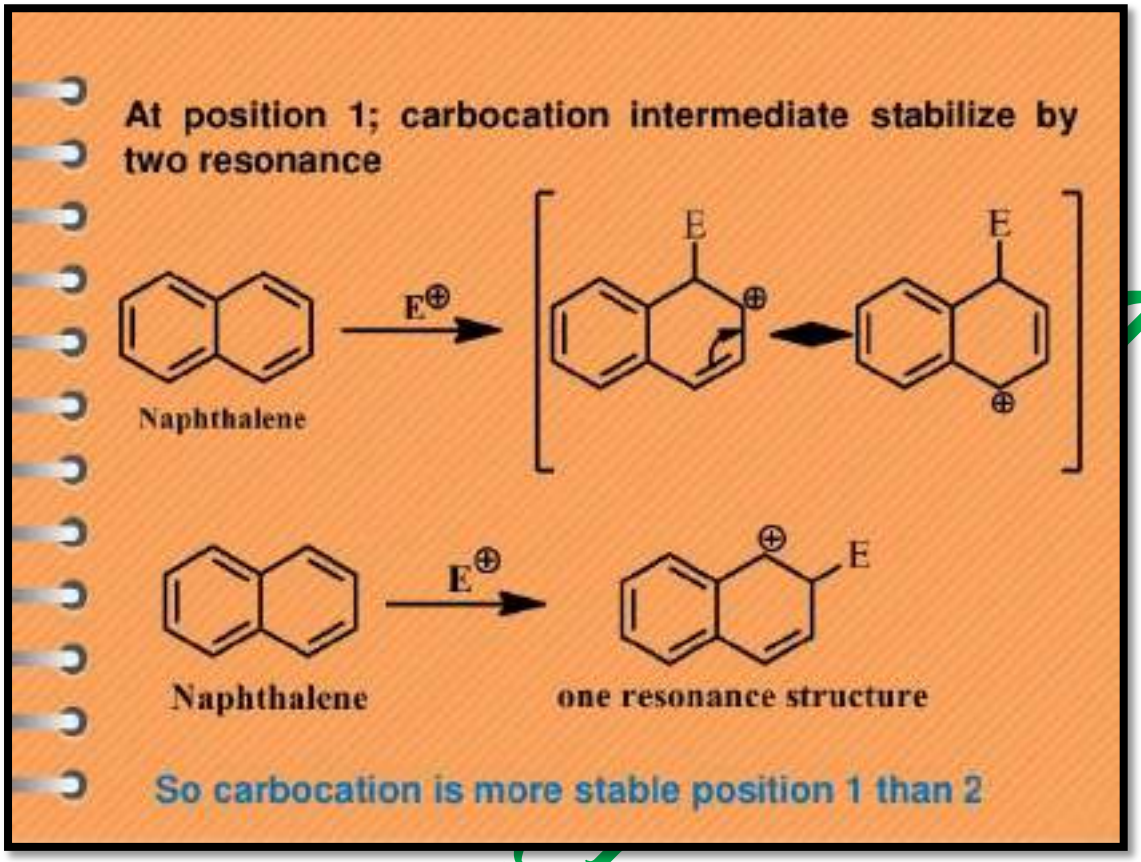

The structure of naphthalene is confirmed by method of its synthesis
Howarth method
R
O
O
O
O
Succinic anhydride
AlCl3
R
HO
O
O
Zn-Hg/HCl
R
HO
O
conc.H2SO4
-H2O
R
O
Zn-Hg/HCl
R
Se
Δ
R

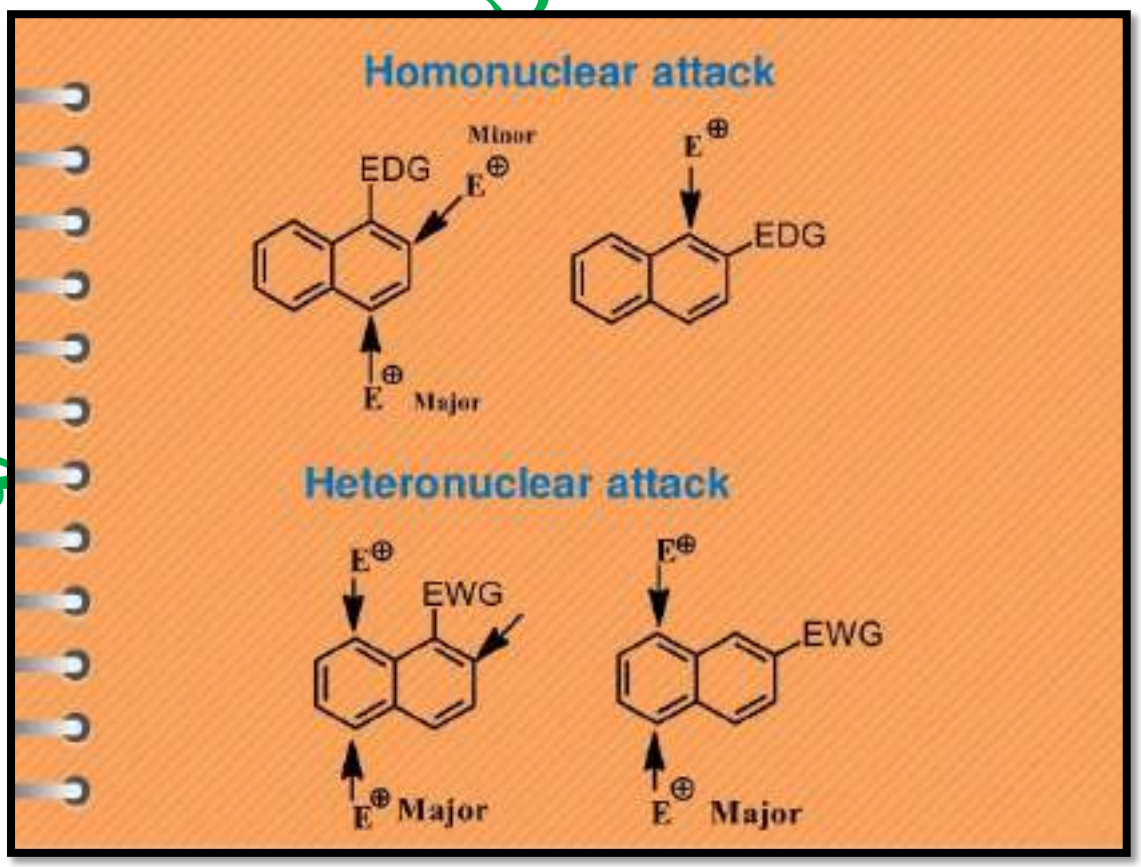

From β-benzylidene – propenoic acid
conc. H_2SO_4
$-H_2O$
OH
O
Benzylidene-3-propenoic acid
O
OH
Zn
-ZnO
naphthalene


Reduction
Na
EtOH
1,4- dihydronaphthalene
Naphthalene
Na
isoamyl alc.
1,2,3,4-tetrahydronaphthalene
Tetralene
H_2
Ni
decahydronaphthalene
Decalene


Oxidation
CrO_3
AcOH
1,4- naphthoquinone
1) O_3
2) H_2O/Zn
CHO
CHO
Phthaldehyde
Naphthalene
O_2
V_2O_5
Phthalic anhydride
$KMnO_4$
$H^{\oplus}$
COOH
COOH
Phthalic acid


Addition of Cl_2
Cl_2
Cl
Cl
1,4- dichloro- 1,4- dihydronaphthalene
Naphthalene
excess
Cl_2
Cl
Cl
Cl
Cl
1,2,3,4- tetrachloro- 1,2,3,4-
tetrahydronaphthalene


At position 1; carbocation intermediate stabilize by two resonance
E
E
E⊕
Naphthalene
E⊕
E
Naphthalene
one resonance structure
So carbocation is more stable position 1 than 2

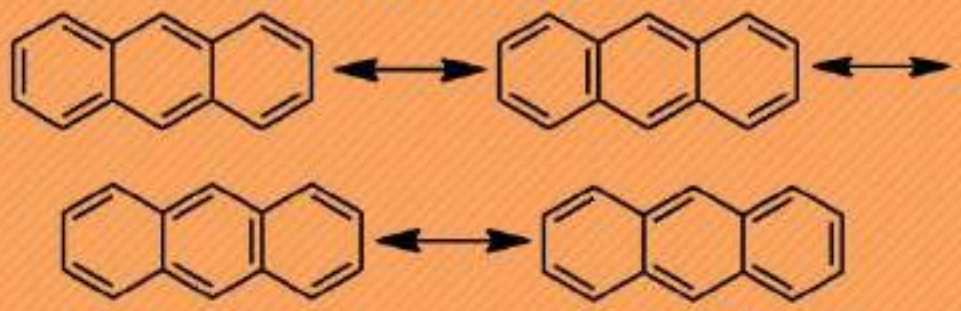

Homonuclear attack
Minor
EDG
E⊕
E⊕
EDG
E⊕
Major
Heteronuclear attack
E⊕
EWG
E⊕
EWG
E⊕
Major
E⊕
Major

Examples

Anthracene ($C_{14}H_{10}$)

- monosubstitution ($C_{14}H_9X$) = 3 isomers
- Disubstitution ($C_{14}H_8X_2$) = 15 isomers

Anthracene ($C_{14}H_{10}$)

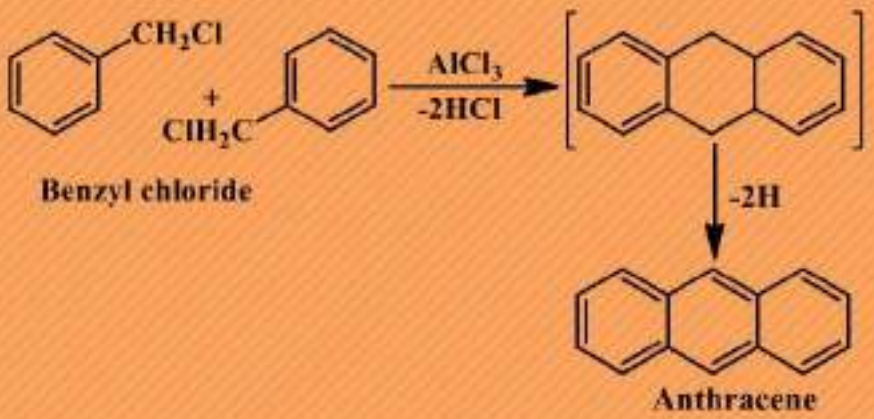


- C_1-C_2 bond to have more double bond character (shorter bond length)
- C_2-C_3 bond to have more single bond character (longer bond length)
- From X-ray diffraction study: C_1-C_2 bond = 1.37 Å
  C_2-C_3 bond = 1.42 Å
- Resonance energy 84 kcal mol^{-1}, average 28, less aromatic than benzene

Synthesis of anthracene

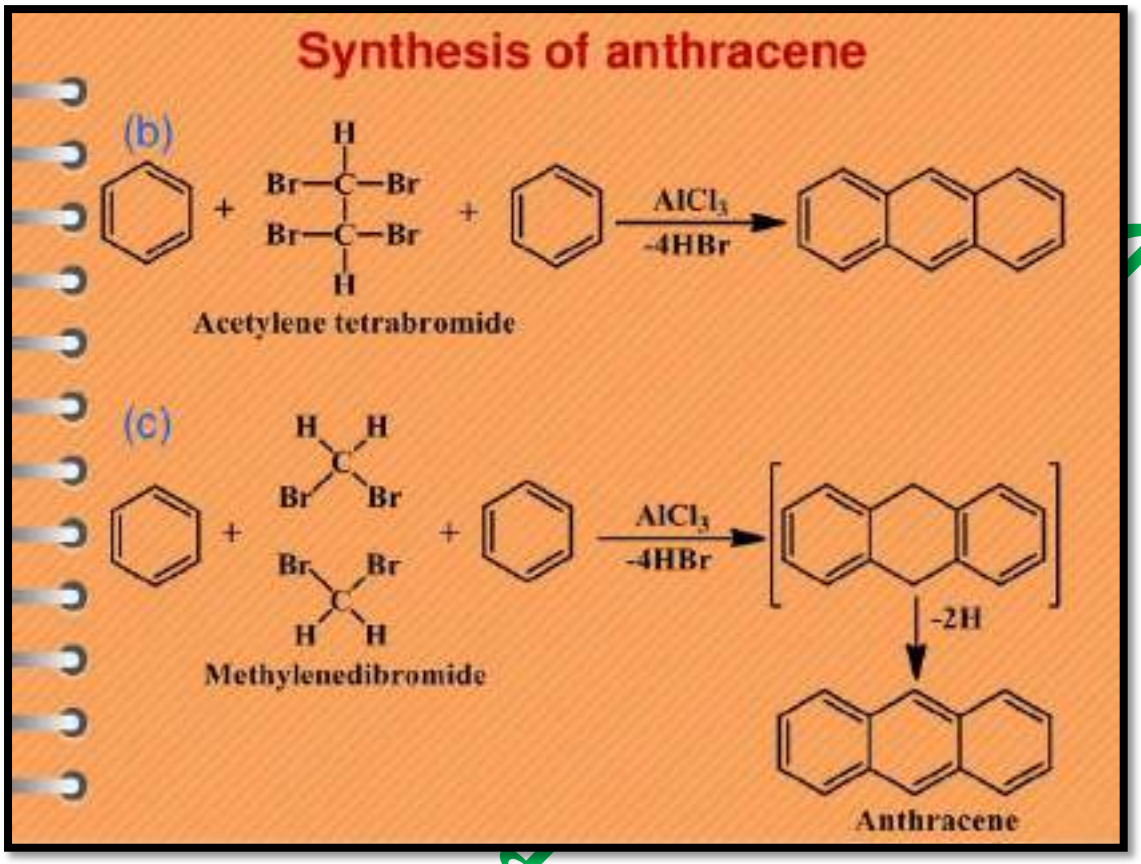
(i) By Friedel Crafts reaction

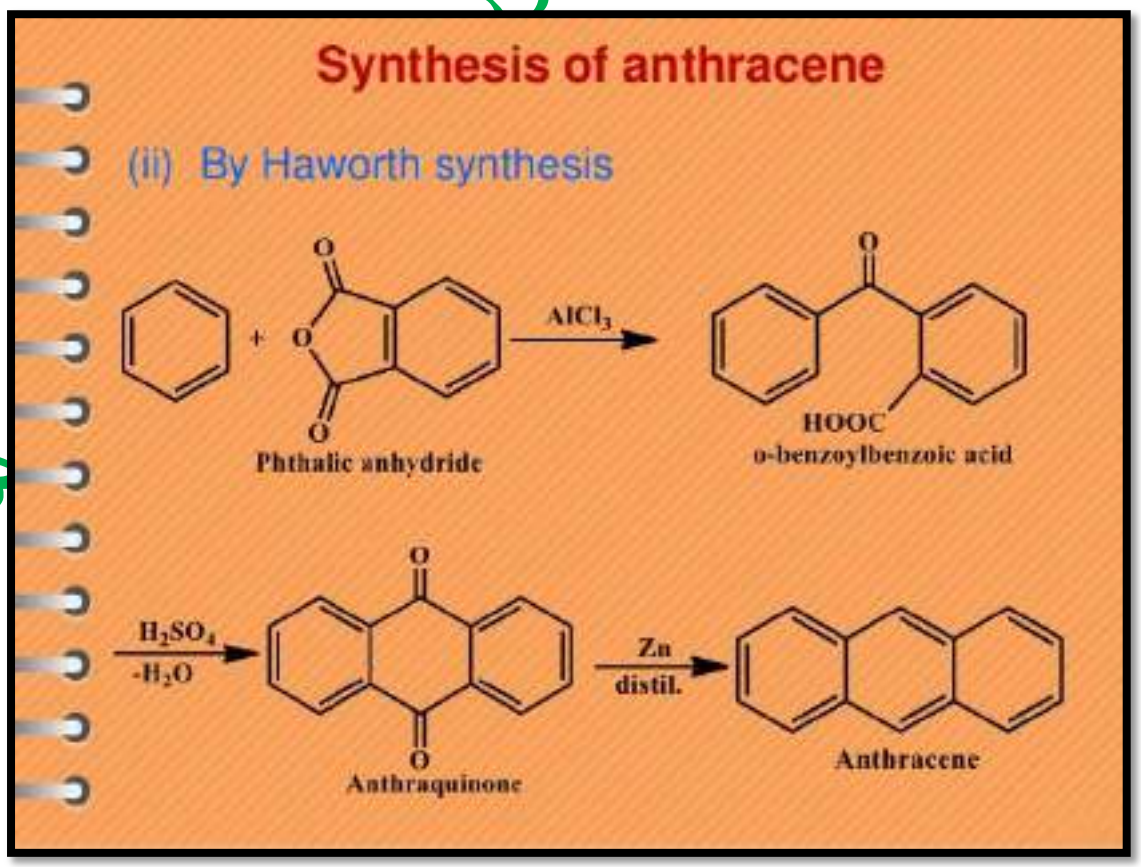
(a)

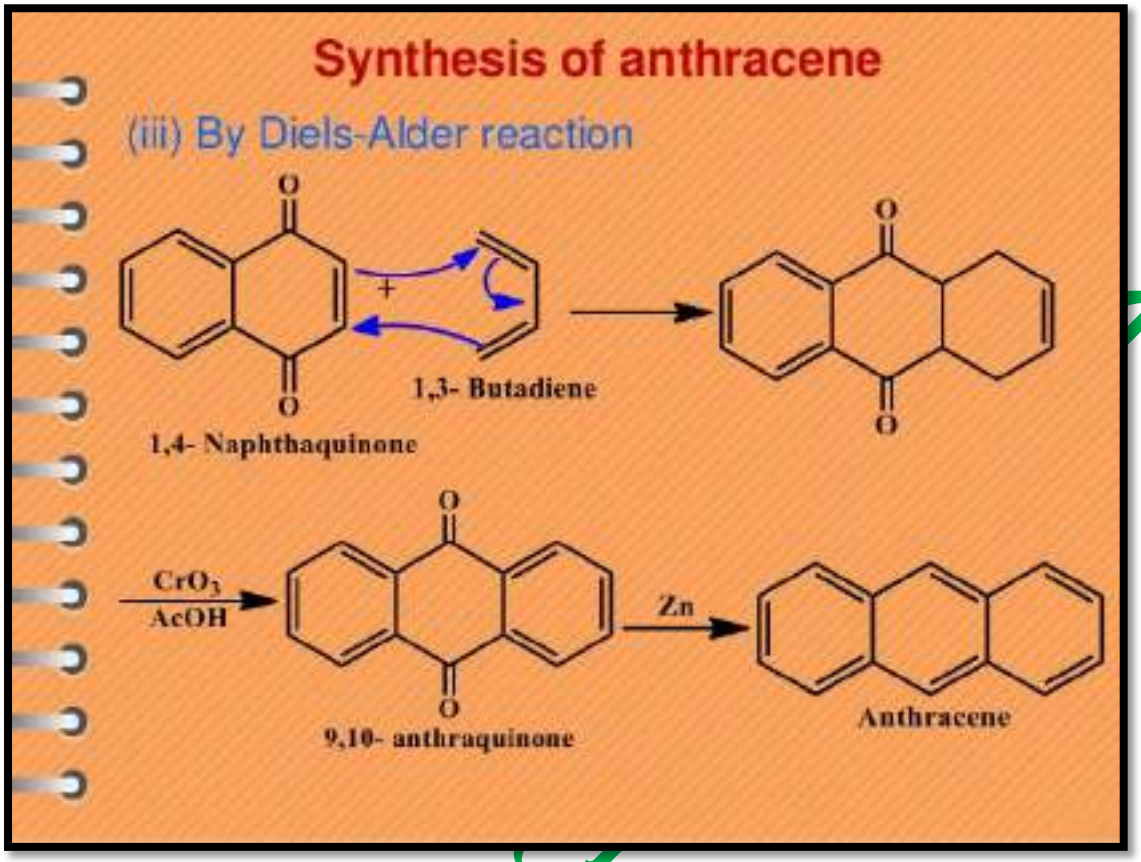


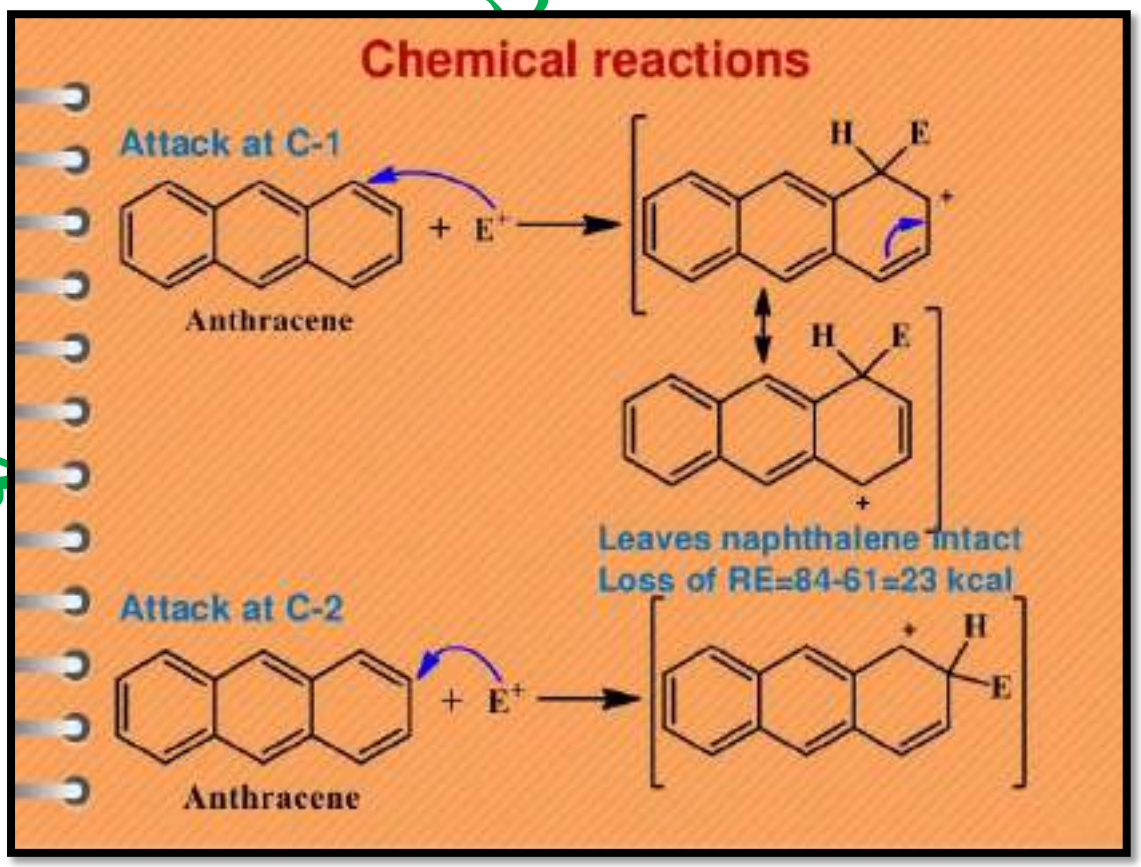
Benzyl chloride

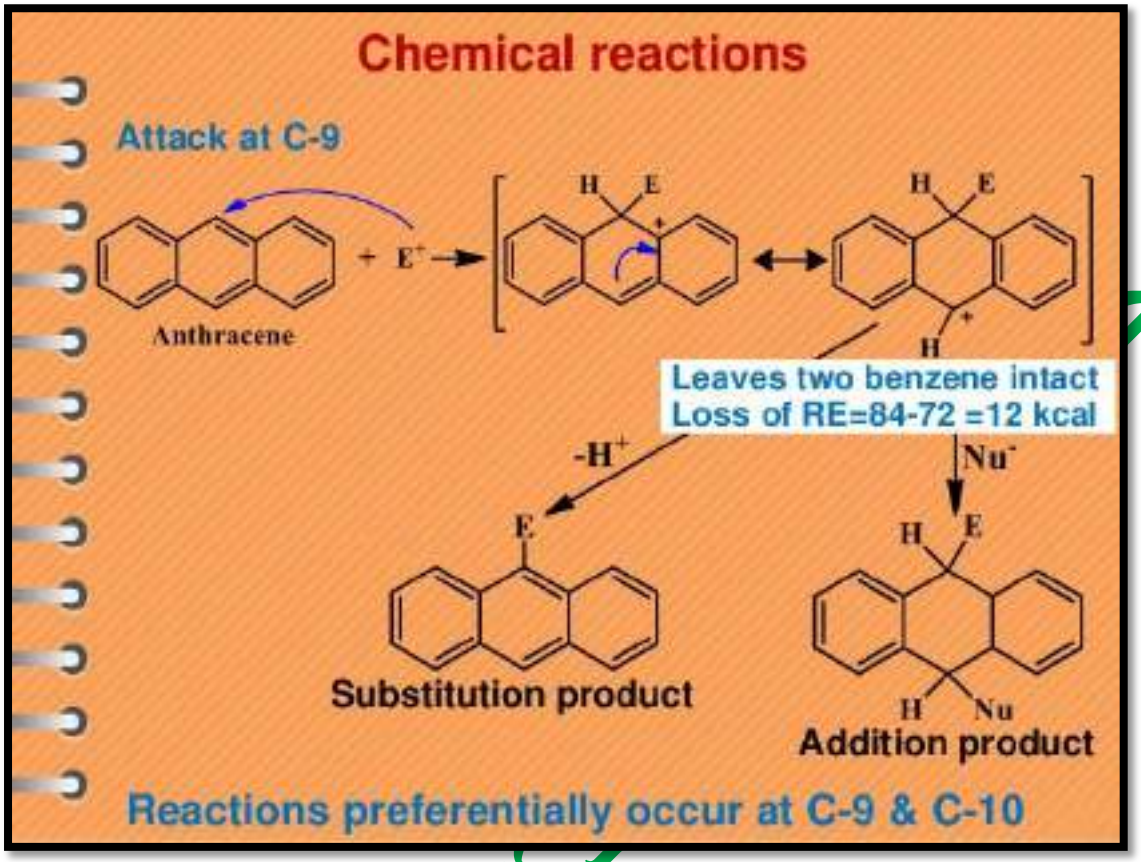
Anthracene

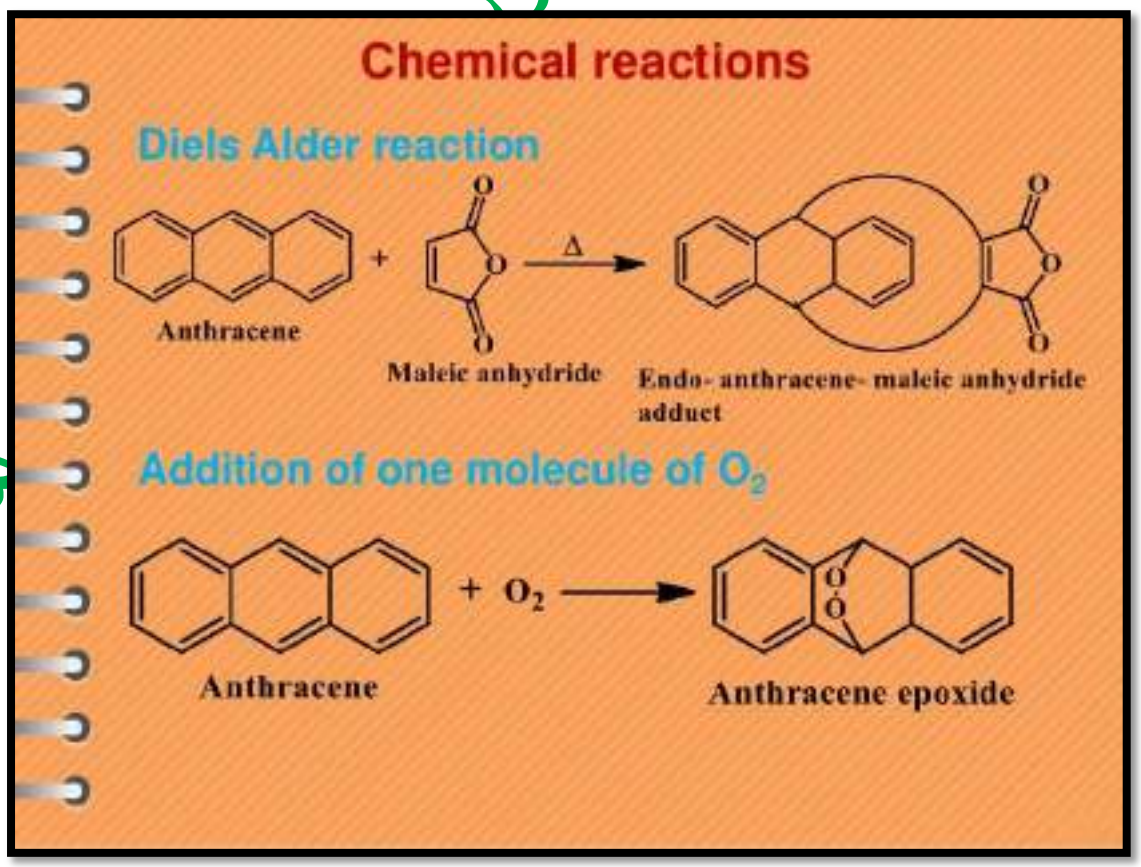

Synthesis of anthracene
(b)
Acetylene tetrabromide
AlCl3
-4HBr
(c)
Methylenedibromide
AlCl3
-4HBr
-2H
Anthracene


Synthesis of anthracene
(ii) By Haworth synthesis
Phthalic anhydride
AlCl3
HOOC
o-benzoylbenzoic acid
H2SO4
-H2O
Anthraquinone
Zn
distil.
Anthracene


Synthesis of anthracene
(iii) By Diels-Alder reaction
1,4- Naphthaquinone
1,3- Butadiene
CrO_3
AcOH
Zn
9,10- anthraquinone
Anthracene

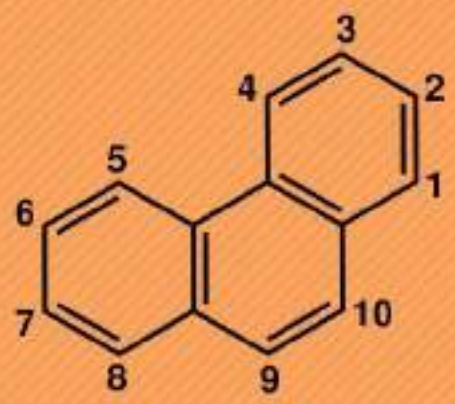

Chemical reactions
Attack at C-1
Anthracene
Leaves naphthalene intact
Loss of RE=84-61=23 kcal
Attack at C-2
Anthracene

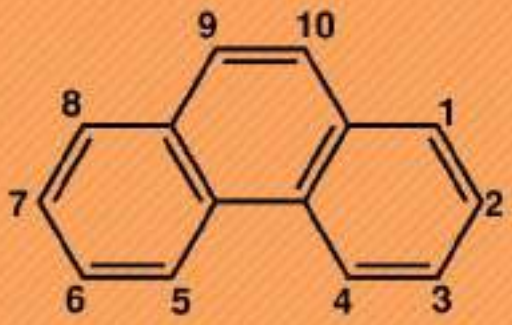

Chemical reactions
Attack at C-9
Anthracene
Leaves two benzene intact
Loss of RE=84-72 =12 kcal
Substitution product
Addition product
Reactions preferentially occur at C-9 & C-10


Chemical reactions
Diels Alder reaction
Anthracene
Maleic anhydride
Endo- anthracene- maleic anhydride adduct
Addition of one molecule of O2
Anthracene
Anthracene epoxide

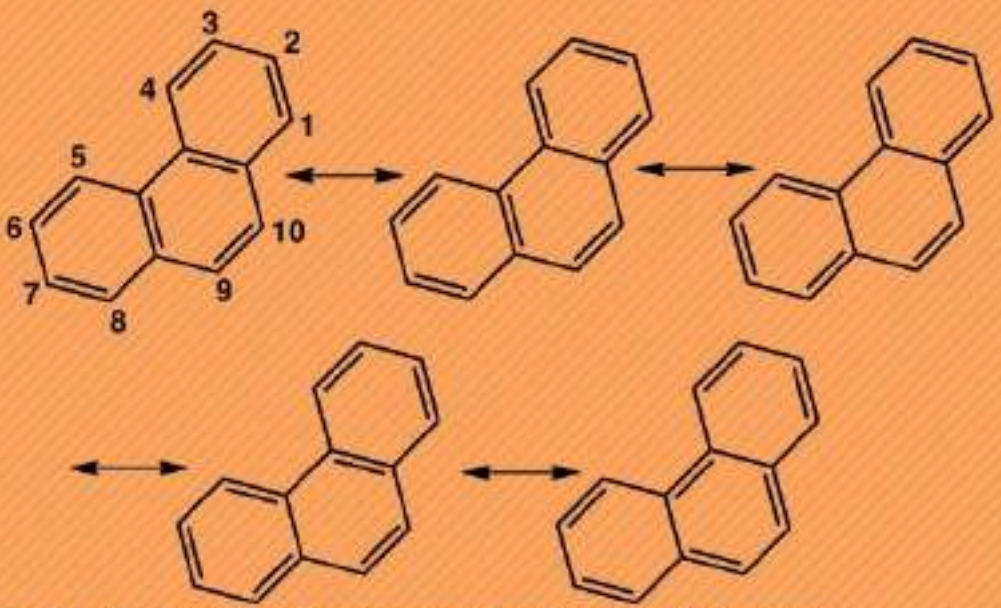
Phenanthrene $C_{14}H_{10}$

- monosubstitution ($C_{14}H_9X$) = 5 isomers
- Disubstitution ($C_{14}H_8X_2$) = 25 isomers





Position of double bond



- C_9-C_{10} bond to have more double bond character
- RE 92 kcal/mole, 92-72=20 Kcal/mole to remove the aromaticity of the middle ring

Preparation of phenanthrene

1) Howrth method