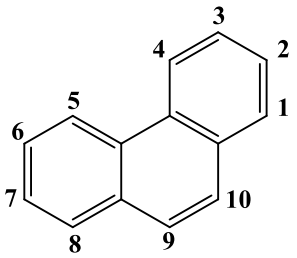
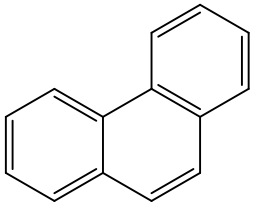
PHENANTHRENE

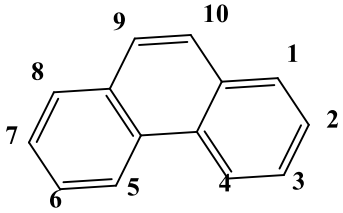
Molecular formula: $C_{14}H_{10}$



Phenanthrene structure can be presented mainly in two forms.



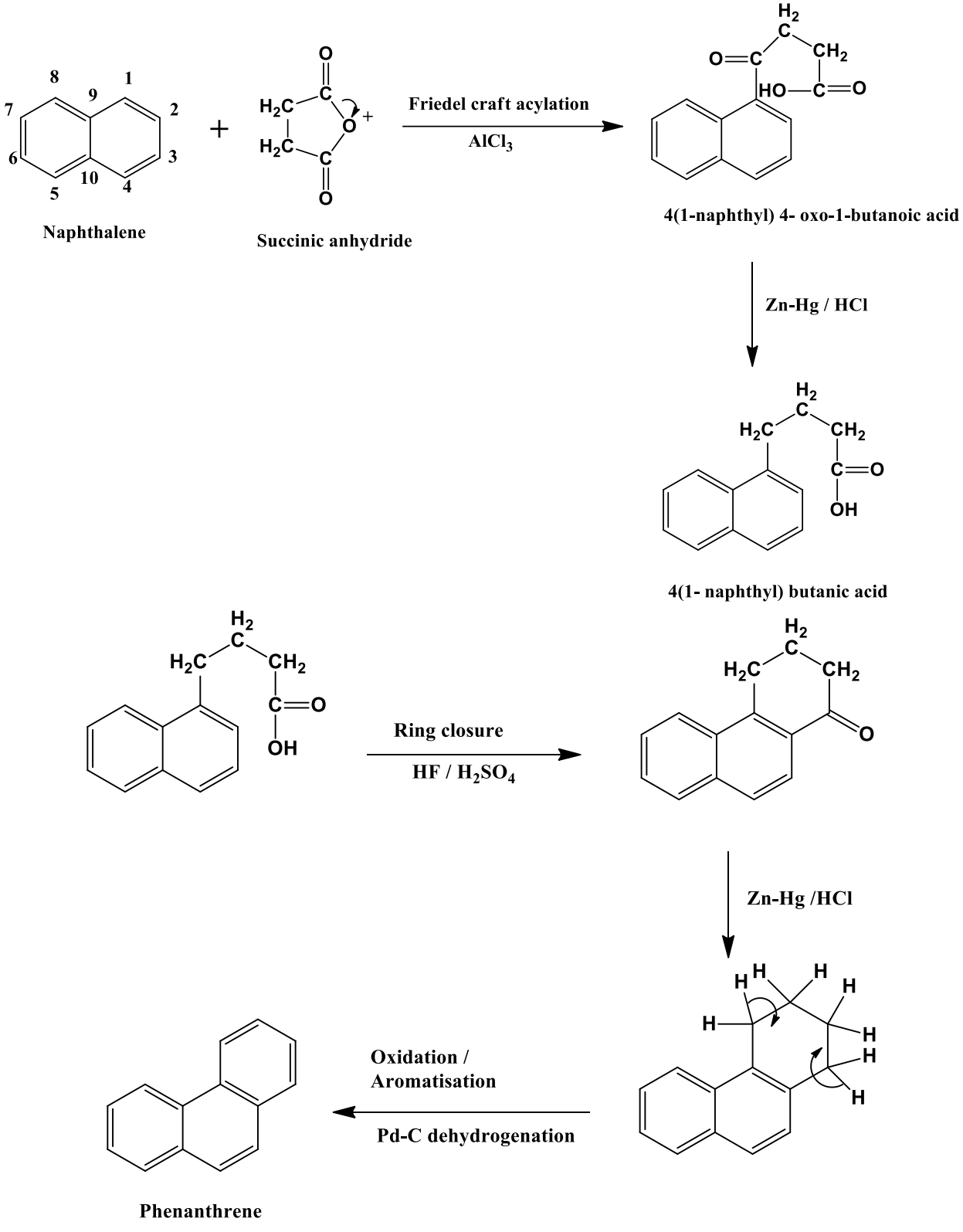
I



II

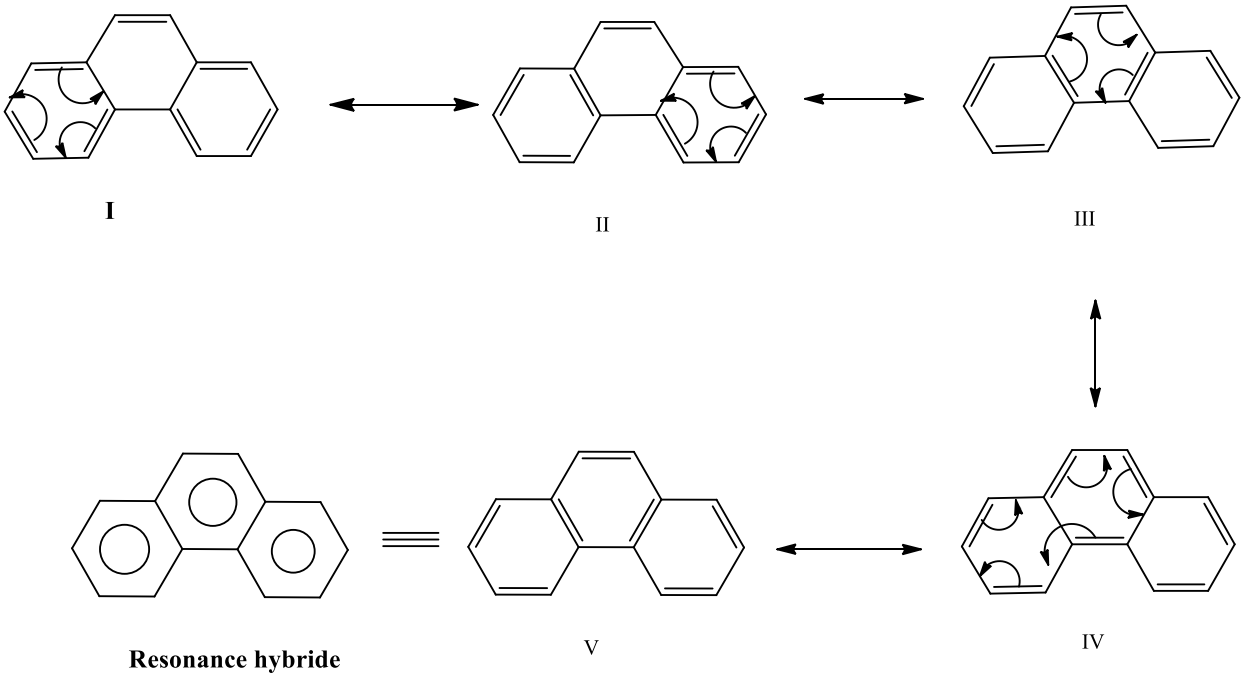
Method of Preparations

1. **Haworth synthesis**
   - **i)** Friedel craft acylation
   - **ii)** Clemmensen reduction
   - **iii)** Ring closure
   - **iv)** Aromatisation


Naphthalene
Succinic anhydride
Friedel craft acylation
AlCl3
4(1-naphthyl) 4- oxo-1-butanoic acid
Zn-Hg / HCl
4(1- naphthyl) butanic acid
Ring closure
HF / H2SO4
Zn-Hg /HCl
Oxidation /
Aromatisation
Pd-C dehydrogenation
Phenanthrene

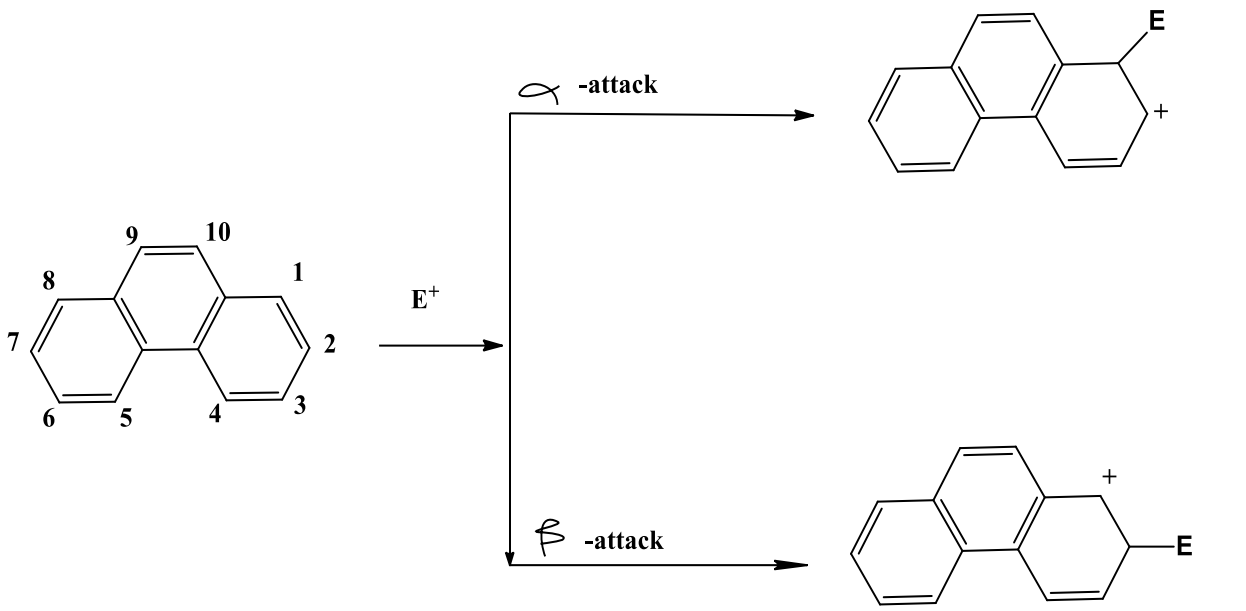
Chemical Properties

1. Phenanthrene is an aromatic compound because it follow huckel rule and has a total no. of $14\pi e^-$ (n=3).
2. **Resonating structure**



3. Electrophillic substitution reaction

- Phenanthrene is aromatic in nature and hence undergo characteristic reactions of compounds i.e., electrophillic substitution reaction.
- There are three different in this compound, where monosubstitution can take place, α, β, γ. This can be decided on the basis of loss of resonance energy in substitution of three positions.
- Electrophillic attack on α and β positions left a naphthalene ring intact.



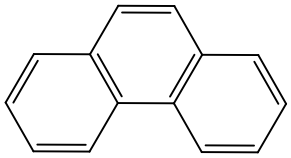
Naphthalenering intact in both cases

The resonance energy of phenanthracene = 381 KJ / mol
The resonance energy of naphthalene = 255.2 KJ / mol
So in α and β substitution , the loss in resonance energy
= Resonance energy[phenanthrene – naphthacene]
= 125.8 KJ / mol

Attack on γ position

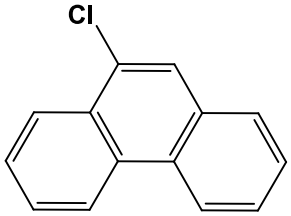
The resonance energy of 1 benzene ring is 150.6 KJ / mol
For two benzene rings = 150.6 x 2 = 301.2 KJ / mol
So during γ substitution, loss in resonance energy =Resonance energy (phenanthrene- 2 benzene rings)
= 79.8 KJ / mol
Therefore from energy point of view, electrophillic attack on γ position is favoured as compared to that of α and β position.

Eg.



Chlorination

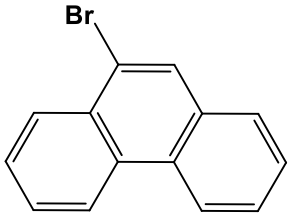
Cl_2 / △ / CCl_4



9- Chlorophenanthrene

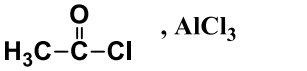
Bromination

Br_2

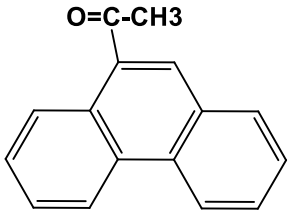


9- Bromophenanthrene

Friedel craft acylation



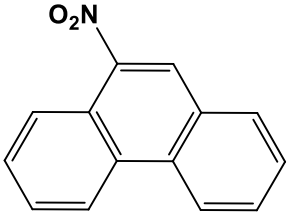
, $AlCl_3$



9- acetyl phenanthrene

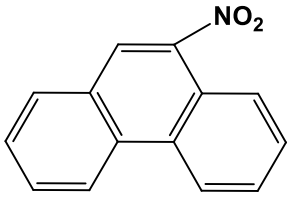
nitration

$HNO_3 + H_2SO_4$



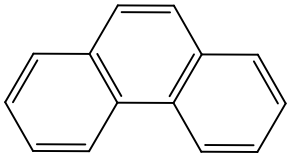
+

9- nitrophenanthrene (37%)

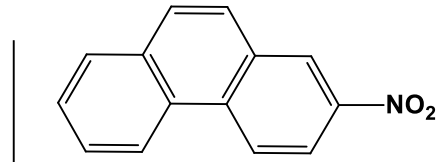


1- nitrophenanthrene (27%)

+

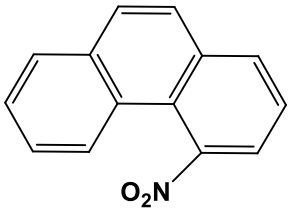


3- nitrophenanthrene (23%)



2 nitrophenanthrene (7%)

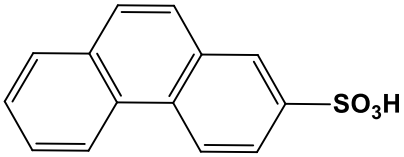
+



4 nitrophenanthrene (6%)

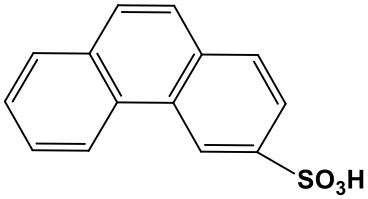
sulphonation

H_2SO_4



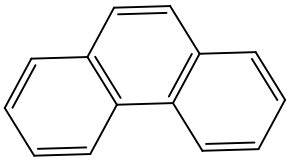
Phenanthrene 2- sulphonic acid

+



Phenanthrene 3- sulphonic acid

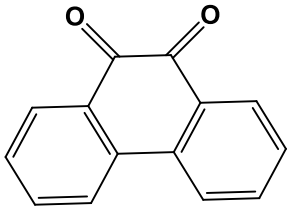
4. Oxidation



Phenanthrene

[O]

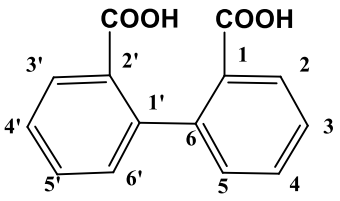
$Na_2Cr_2O_7 + CH_3COOH$
Or $CrO_3 + CH_3COOH$



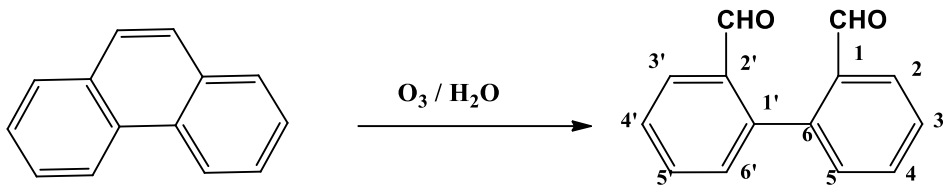
9,10 Phenanthroquinone

$Na_2Cr_2O_7$ + or
CH_3COOH

H_2O_2 / CH_3COOH

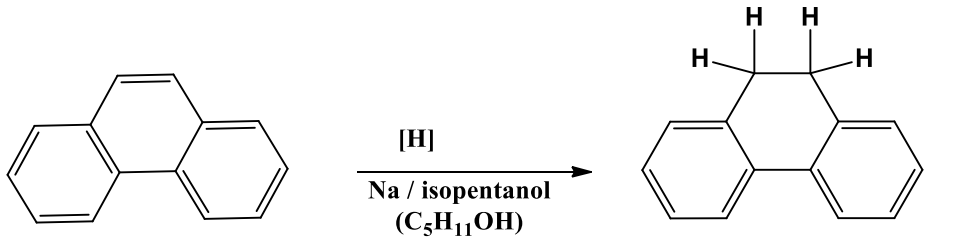


2, 2' diphenic acid



Phenanthrene **2,2' - diphenic aldehyde**

5. Reduction



Phenanthrene **9,10 dihydrophenanthrene**

Phenanthrene derivative

1. Phenanthraquinone