Polynuclear Hydrocarbons

BSc. Part III Hons.

Organic chemistry

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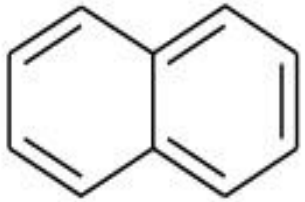
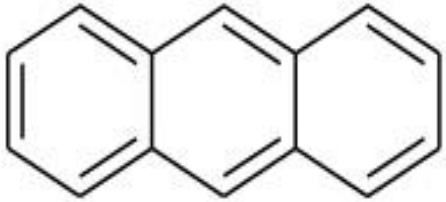
- Hydrocarbon molecule with two or more closed rings; examples are Naphthalene with two benzene rings side by side, or diphenyl with two bond connected benzene rings. Also known as polycyclic hydrocarbon.

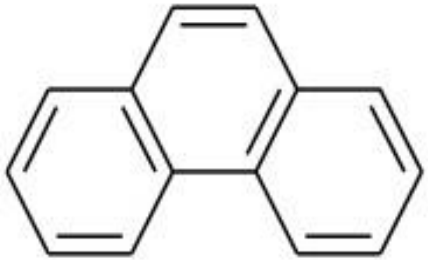
Polynuclear Aromatics



Naphthalene

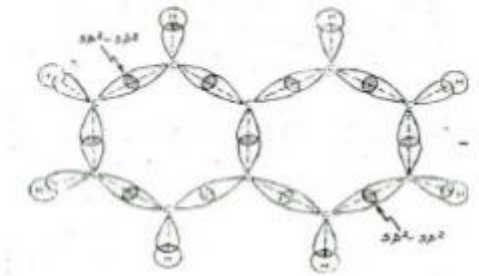


Anthracene



Phenanthrene

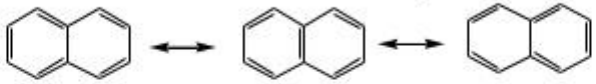
Molecular orbital structure of naphthalene



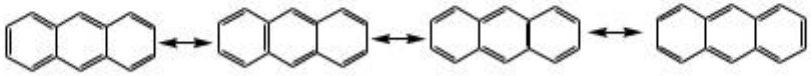
Aromatic character of naphthalene, anthracene and phenanthrene

- Resonance energy of A = 61 kcal mol^{-1}
- Resonance energy of B = 84 kcal mol^{-1}
- Resonance energy of C = 92 kcal mol^{-1}
- Resonance energy of benzene = 36 kcal mol^{-1}

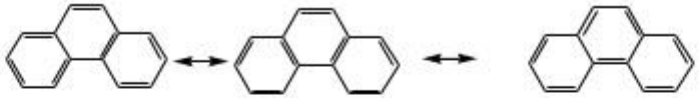
Resonance Forms of Naphthalene

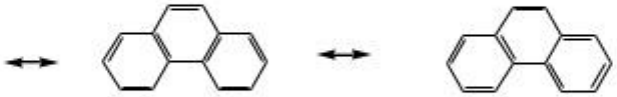


Resonance Forms of Anthracene



Resonance Forms of Phenanthrene



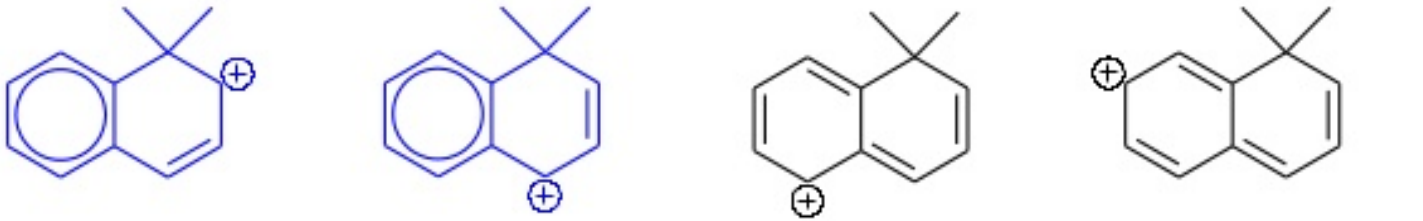


Conclusion on reactivity

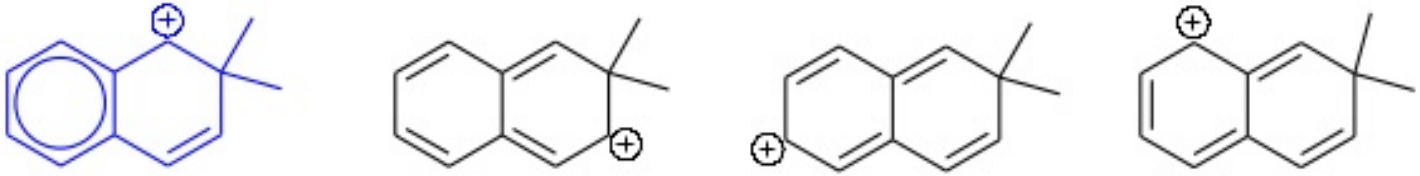
- Naphthalene undergoes electrophilic substitution at C-1 position
- Anthracene and phenanthrene are undergoes electrophilic substitution at C-9 position.

Why is EAS in naphthalene mostly to the alpha-position?

α

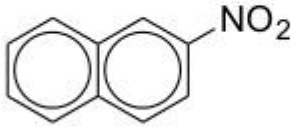


β



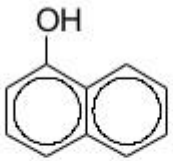
Naphthalene: nomenclature:

Mono substituted: α- 1-
β- 2-

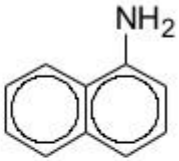


2-nitronaphthalene
β-nitronaphthalene

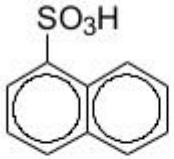
Special names:



α-naphthol



α-naphthylamine

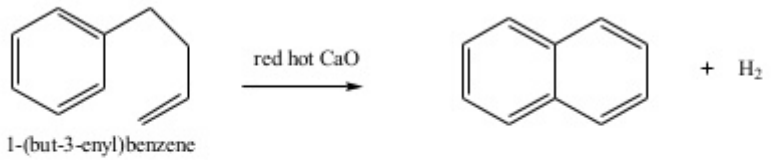


α-naphthalenesulfonic acid

also β–

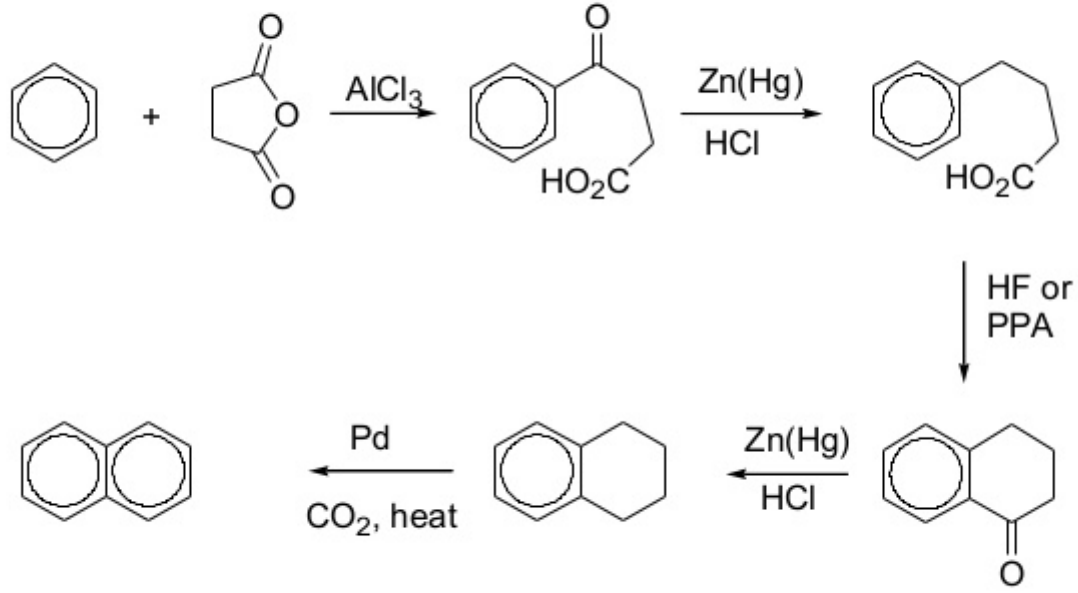
Synthesis of napthalene

1. From petroleum: extracton with copper at 680°c.
2. From 4-phenyl -1-butene: 4-phenyl -1-butene is passed over red hot calcium oxide to form napthalene



1-(but-3-enyl)benzene

4. Haworth Synthesis of naphthalene



Properties of napthalene

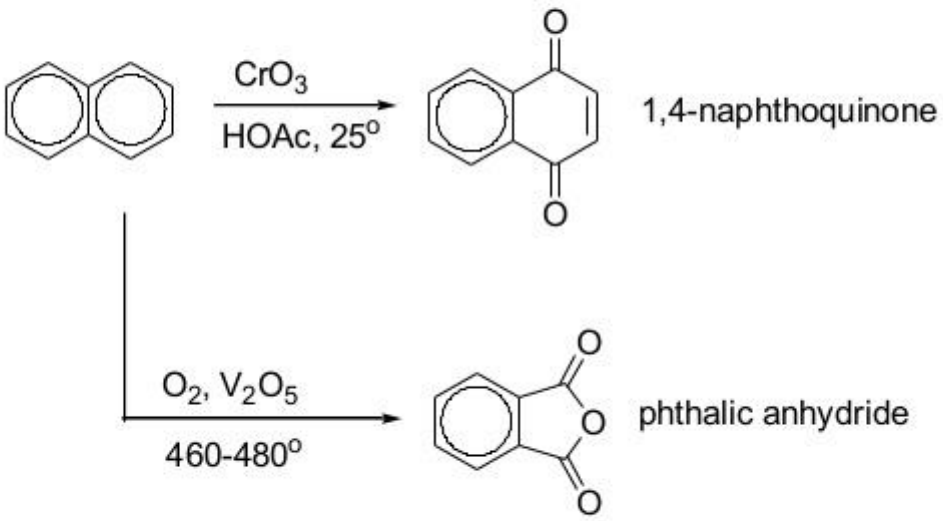
- It is colorless crystaline solid. Melts at 82°c
- It is insoluble in water
- It has mouth ball like odour

Uses of Napthalene

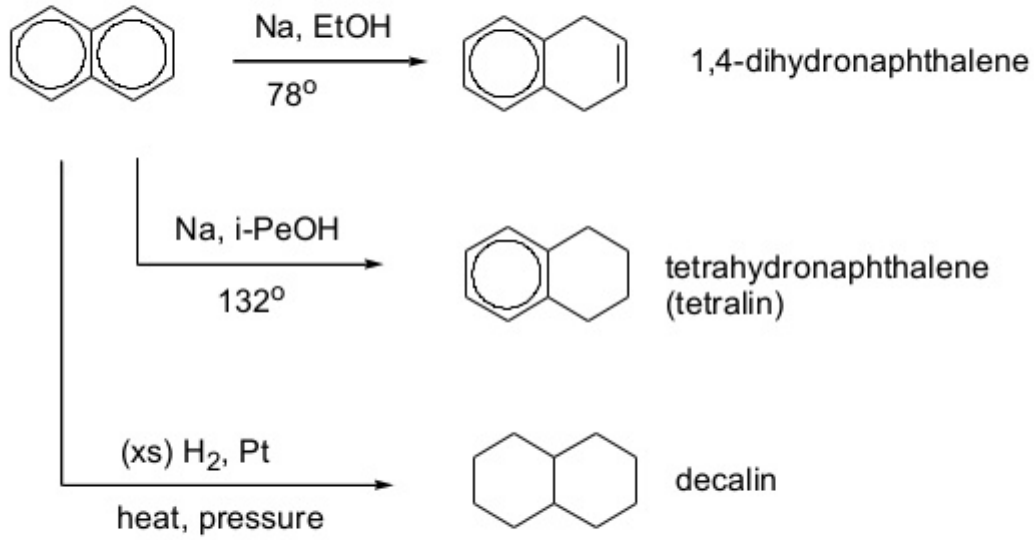
- Napthalene as moth balls has been used to protect woolen goods from moths.
- It is also used for increasing illuminating power of coal gas.
- Napthalene is used in the manufacturing of phthaleic anhydride, carbaryl for insectiside, 2-napthol, dyes, some medicinal products.
- Propranolol,-antihypertensive drugs.
- Tolnapthate-Antifungal
- Menadione-Vitamin-K
- Naphazoline- Vasoconstrictor for rhinitis and sinusitis

Naphthalene, reactions:

1) oxidation:

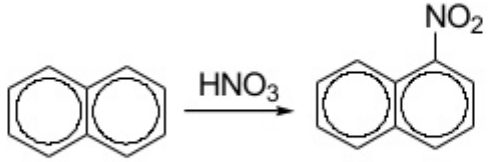


2. Reduction:

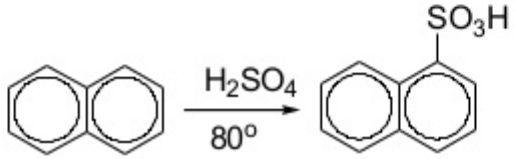

Na, EtOH
78°
1,4-dihydronaphthalene
Na, i-PeOH
132°
tetrahydronaphthalene
(tetralin)
(xs) H2, Pt
heat, pressure
decalin

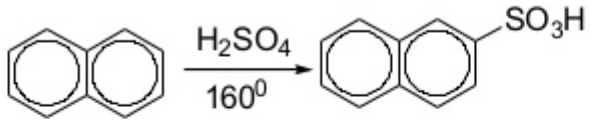
3. Electrophilic Aromatic Substitution:

a) nitration

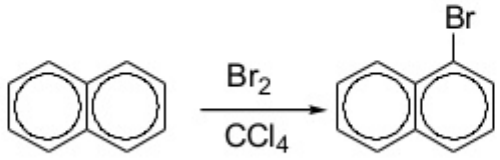


b) sulfonation





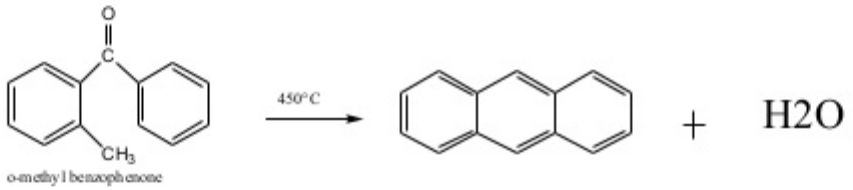
c) halogenation



nocatalyst required

1. Elbe synthesis

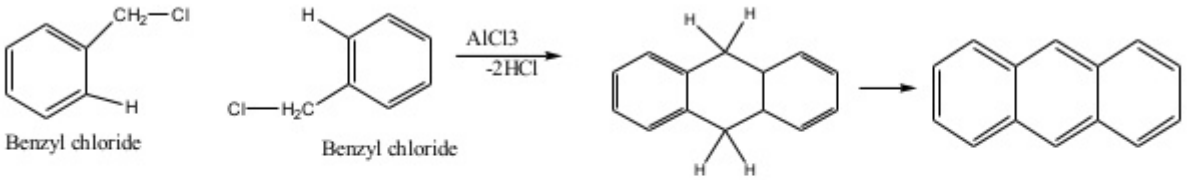
- The conversion of a diaryl ketone containing a methyl or methylene group *ortho to the carbonyl function is known as the Elbs Reaction*.
- when o-methylbenzophenone **is heated at 450°C, anthracene is formed.**



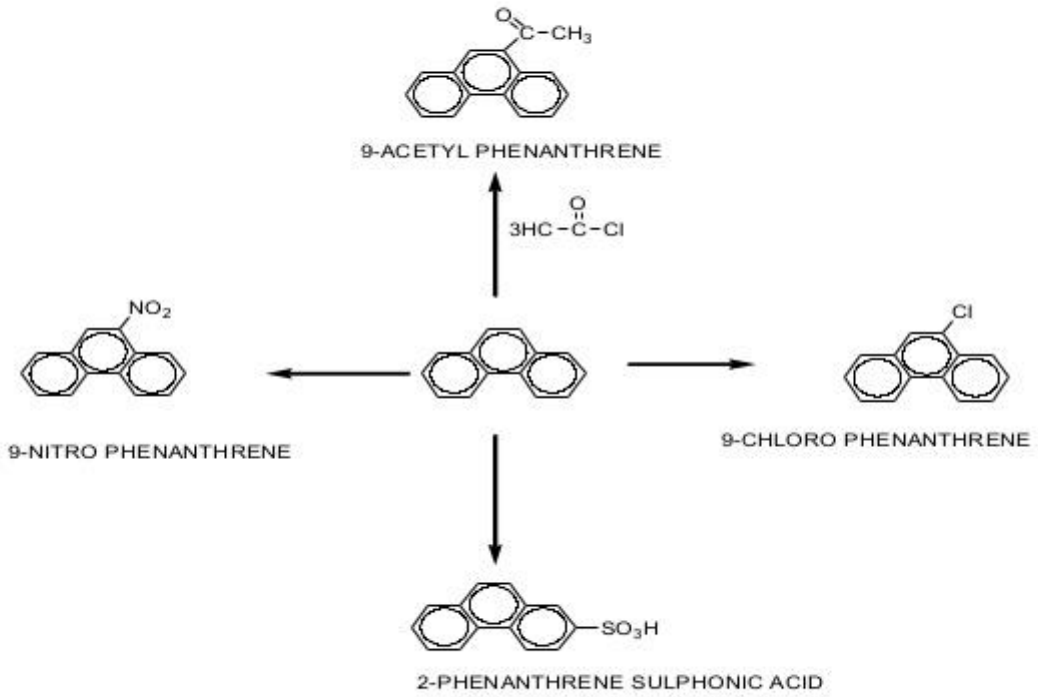
o-methylbenzophenone

2. Friedel-Crafts Reactions

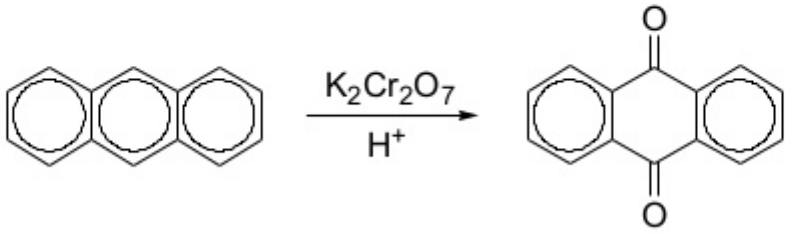
- Benzyl chloride reacts with itself to form 9,10-dihydroanthracene,which readily loses two hydrogen atoms to yield anthracene.



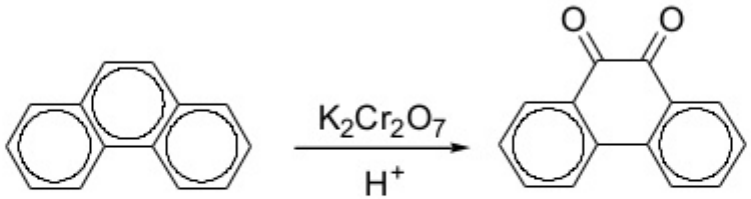
Electrophilic substitution of Phenanthrene



Oxidation:

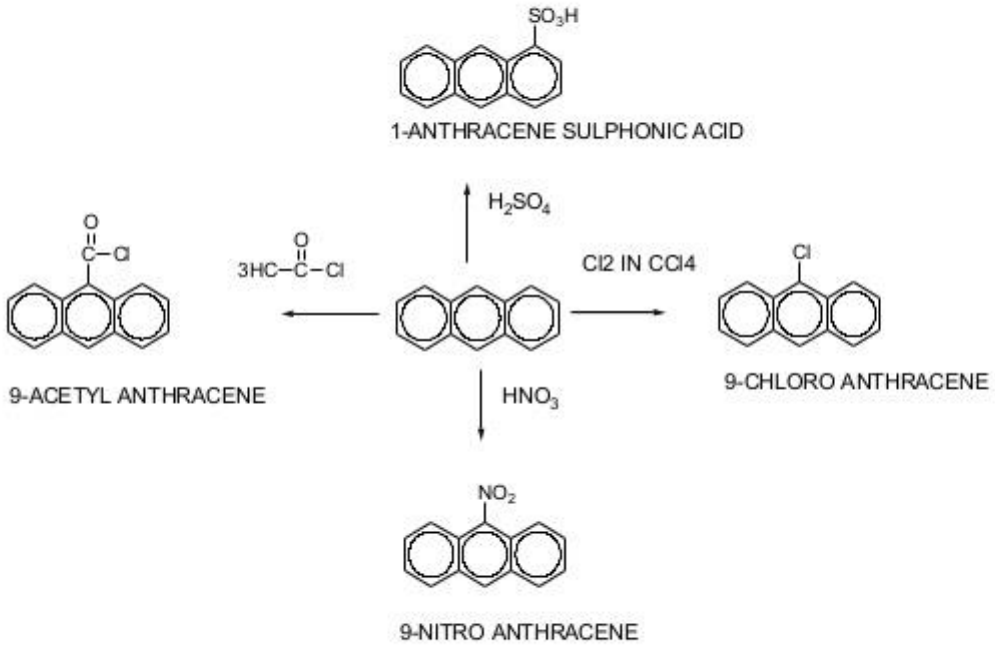


9,10-antraquinone



9,10-penanthrone

Electrophilic substitution reactio n of Anthracene



Uses of anthracene and Phenanthrene

- A. Anthracene-Synthesis of anthrquinone
- Anthraquinone is used in the manufacture of alizarin and several other dyes.
- Purgative drugs-Senna, Rhubarb, Cascara
- Dithrol-Antifungal
- B. phenanthrene is used as carcinogenic
- Steroid moiety contain phenanthrene nucleus.
- Sex hormones, Bile acids.
- Steroid used as oral contraceptive and antiinflamatory agent
- Cardiac glycosides, Morphine , codeine