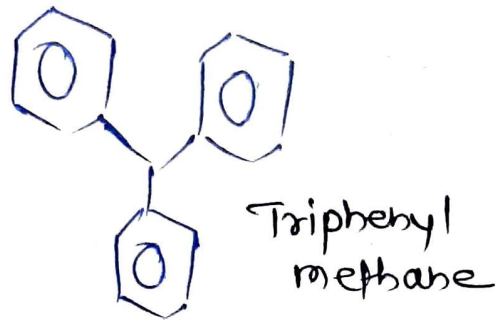
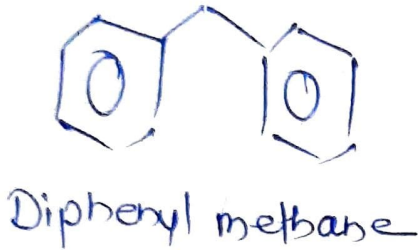
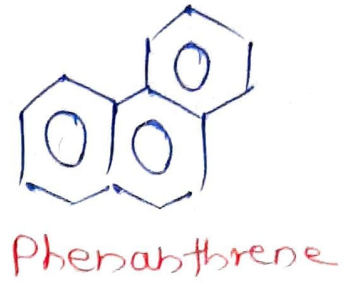
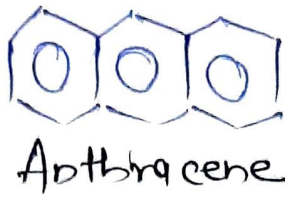


UNIT IV

POLYNUCLEAR HYDROCARBONS

→ Containing multiple aromatic ring & made up of Carbon & Hydrogen atom only



PNH

Benzenoid

Non-Benzenoid

Isolated



biphenyl

- diphenyl methane
- triphenyl methane



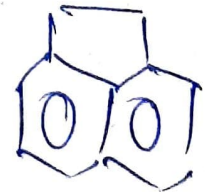
Azulene



Fluorene



Acenaphthylene

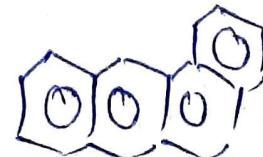
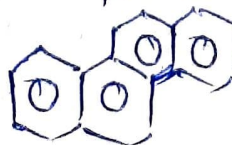


Acenaphthene

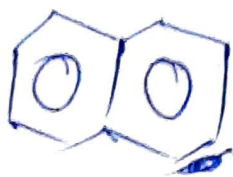
Fused Ring

→ Linear - Naphthalene, Anthracene,

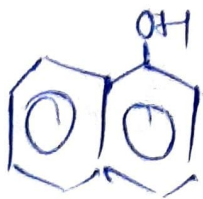
→ Angular - Phenanthrene, ~~Gay~~ Chrysene, Benz(a)anthracene



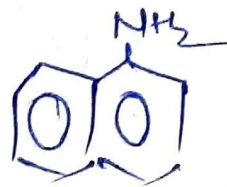
I NAPHTHALENE & ITS DERIVATIVES



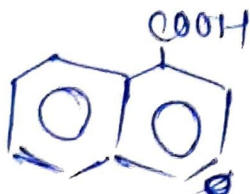
Naphthalene



Naphthol's



Naphthylamine



Naphthoic acid

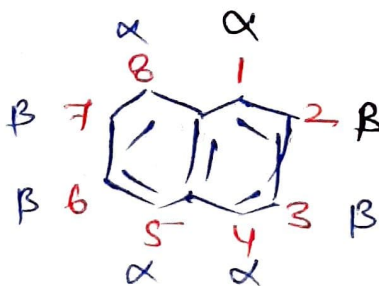
(A) Naphthalene



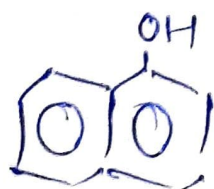
Orbital Structure



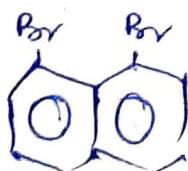
Kekule Type Structure



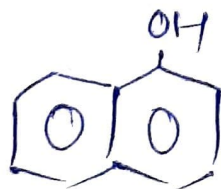
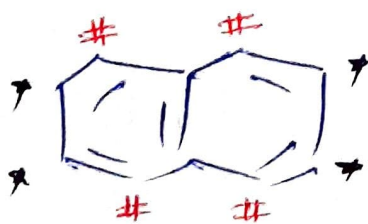
- * Mono substituted named - α , β
- * poly substituted = 1, 2, —



α -naphthol
(1-naphthol)



1,8-Dibromo
naphthalene

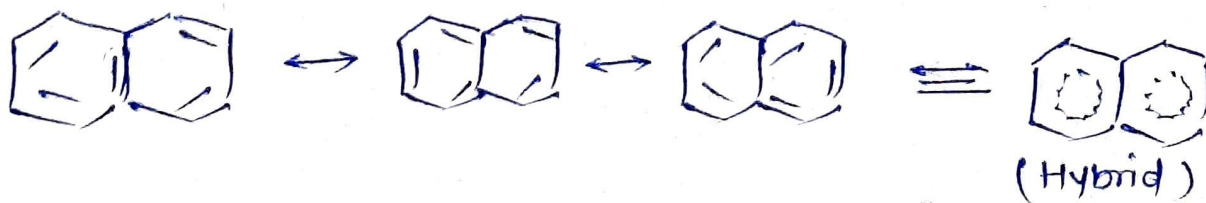


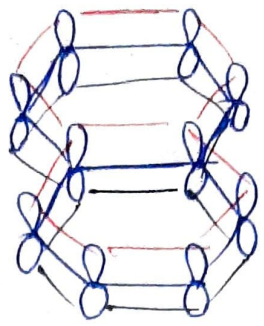
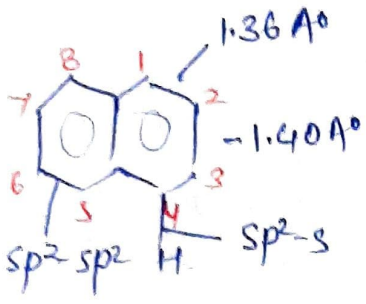
mp = 95°C



mp = 122°C

Resonance





properties :- ① Colourless solid crystal

mp: 80°C , BP: 217°C

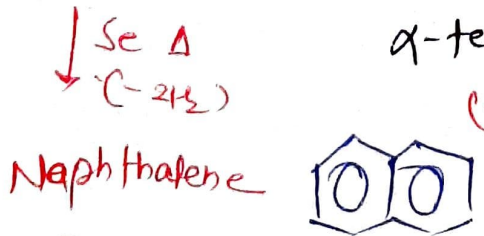
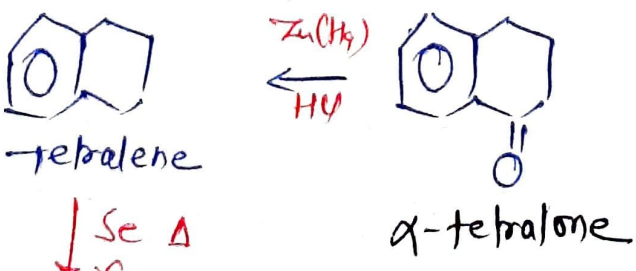
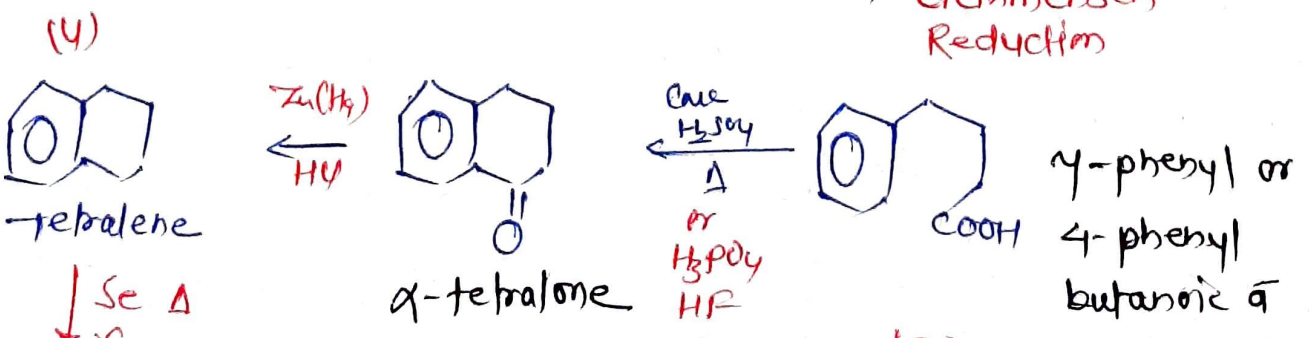
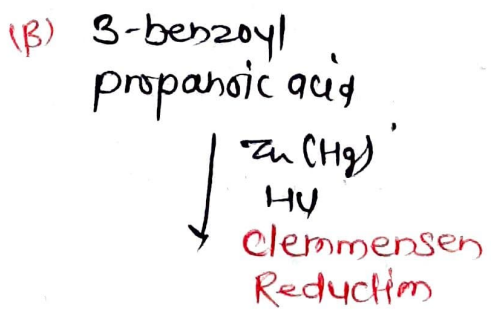
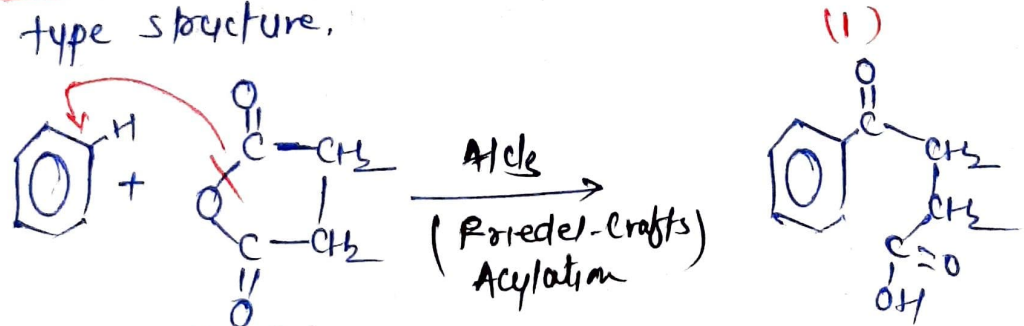
Insoluble in water & soluble in org. solvent - alcohol, benzene, ether

Synthesis of Naphthalene

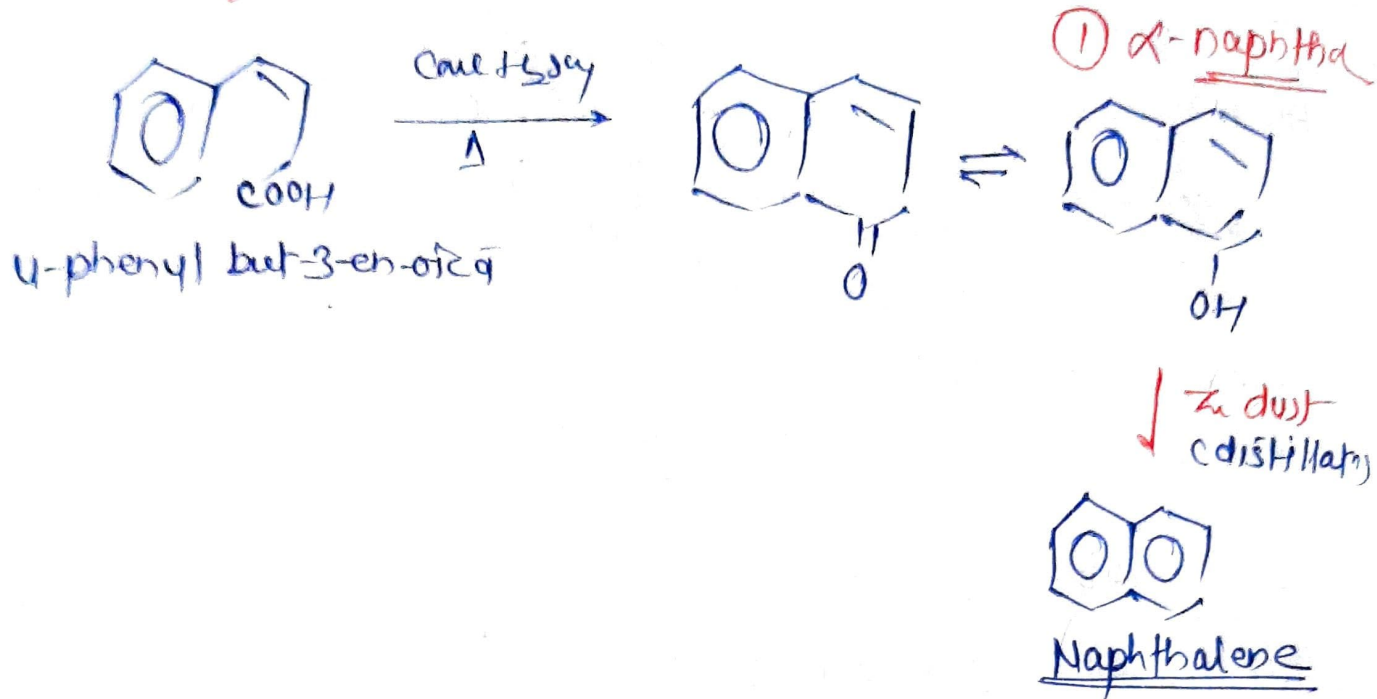
From Coal Tar = It is a major constituents of coal tar.

Middle oil fraction ($170^\circ\text{C} - 230^\circ\text{C}$) of coal tar is chilled when naphthalene crystal forms crystal.

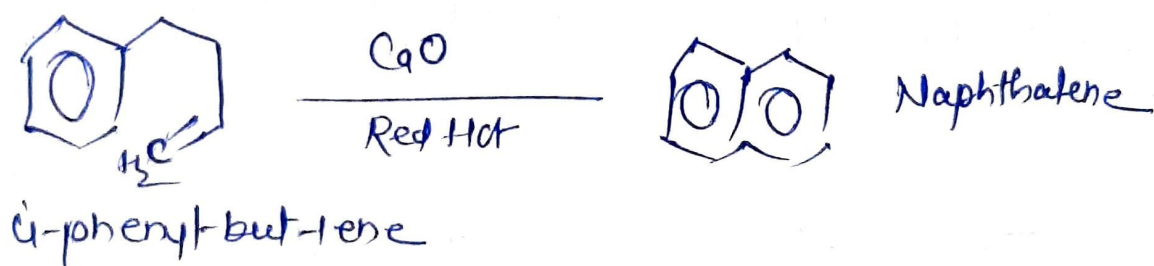
Haworth Synthesis (1932) → It provides the proof of Kekule type structure.



③ Fitting Reaction - from 4-phenyl but-3-enoic acid

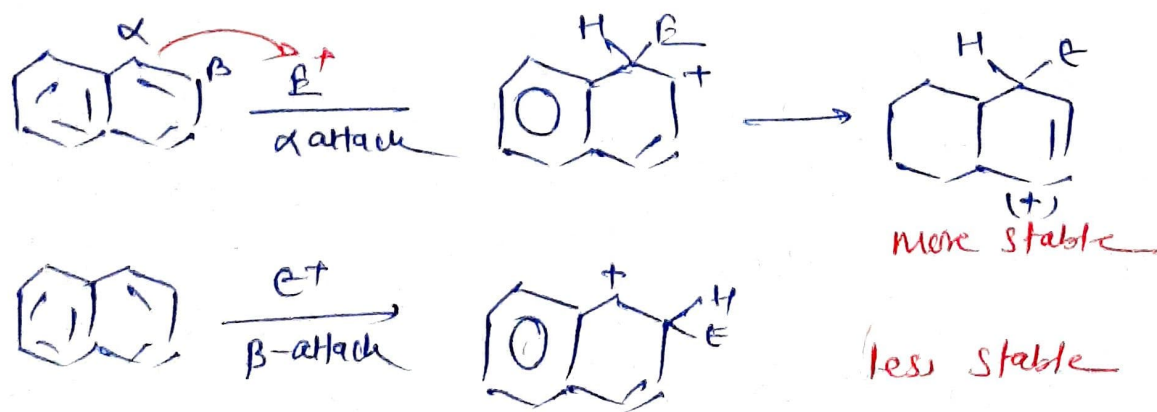


④ From 4-phenyl but-1-ene

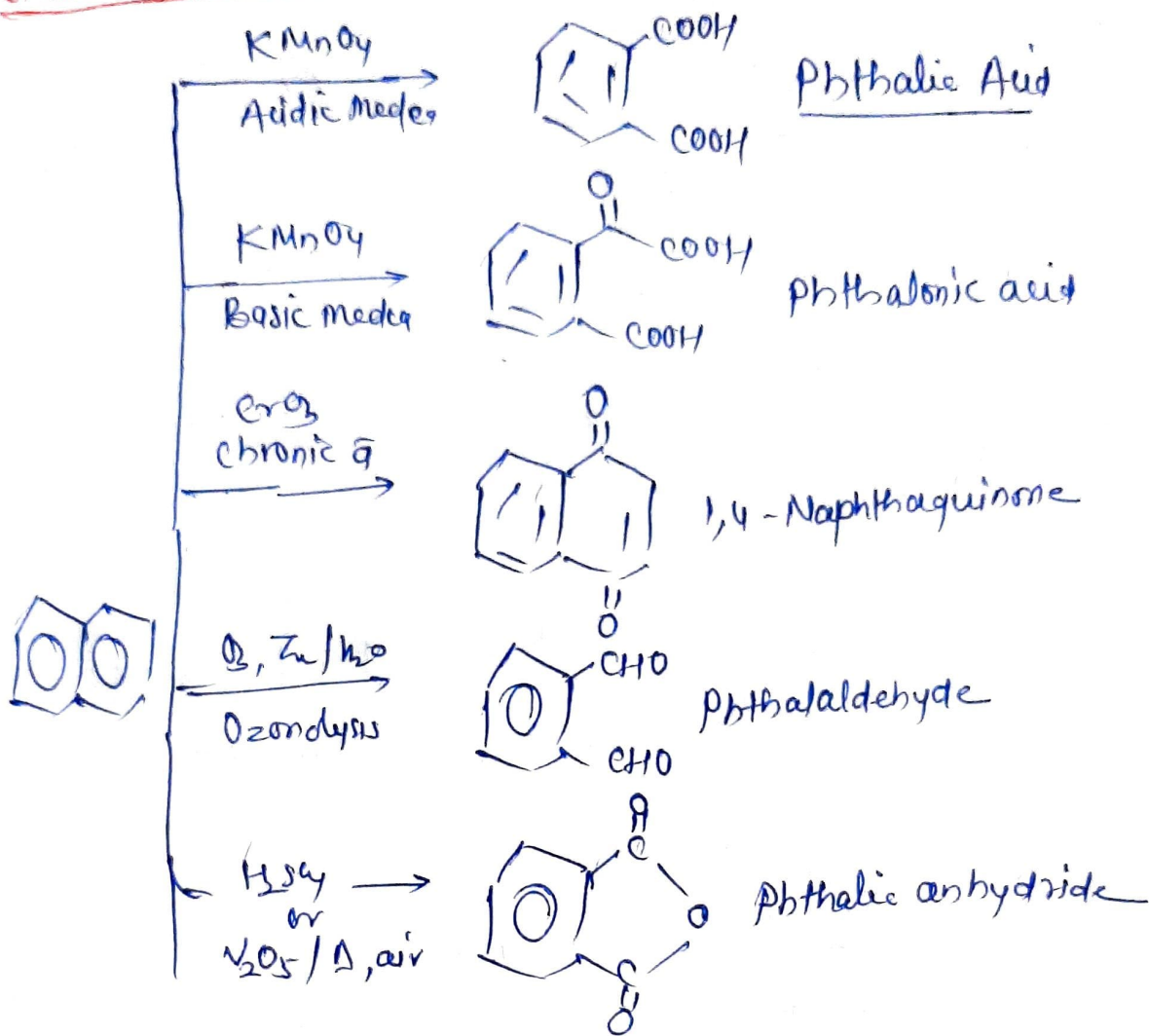


CHEMICAL REACTION - More Reactive than benzene, easily undergoes oxidⁿ, Redⁿ, Addⁿ (ESR), These reactions indicate the naphthalene is less reactive than benzene.

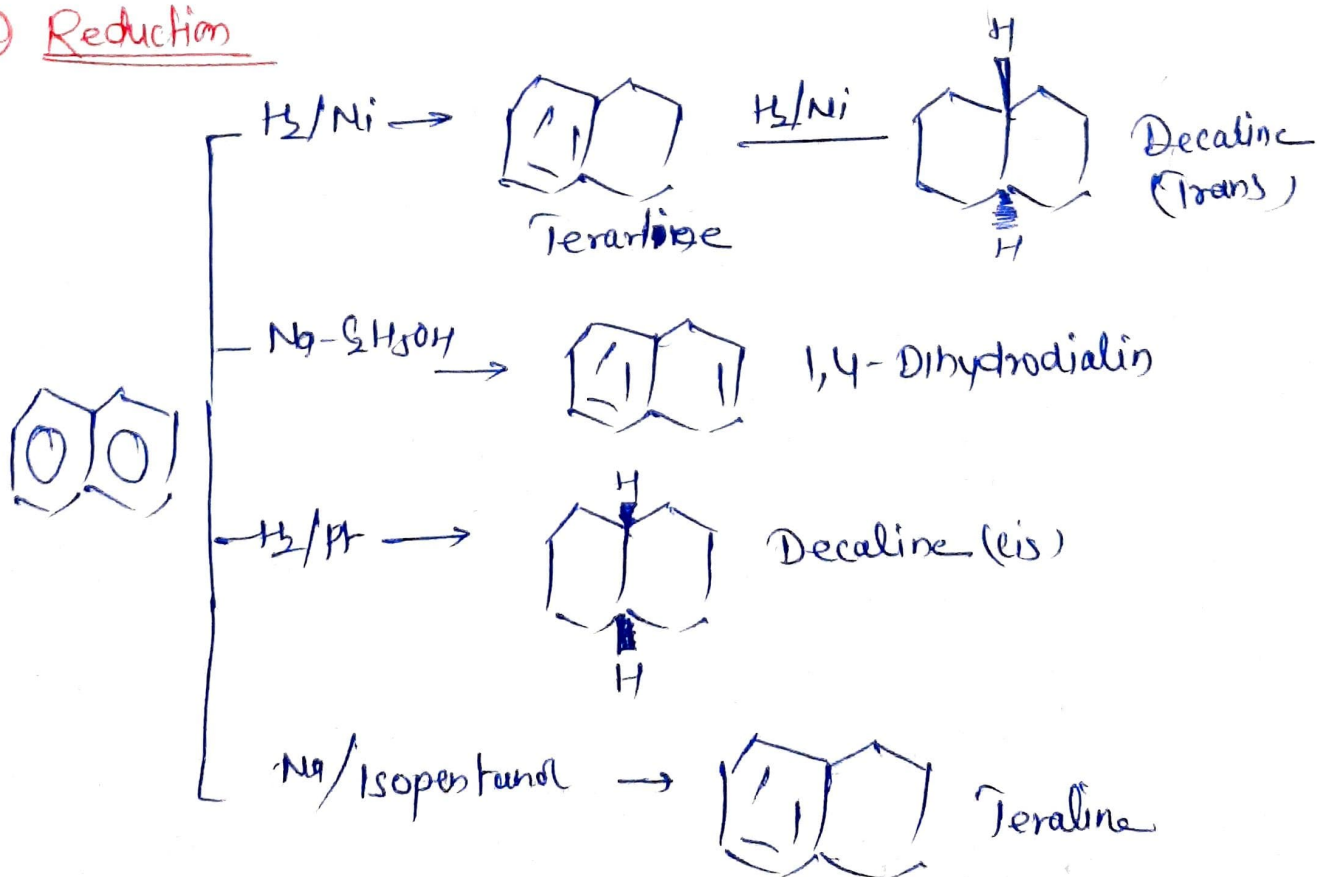
• α -product is more predominates due to stable intermediate carbonium ion



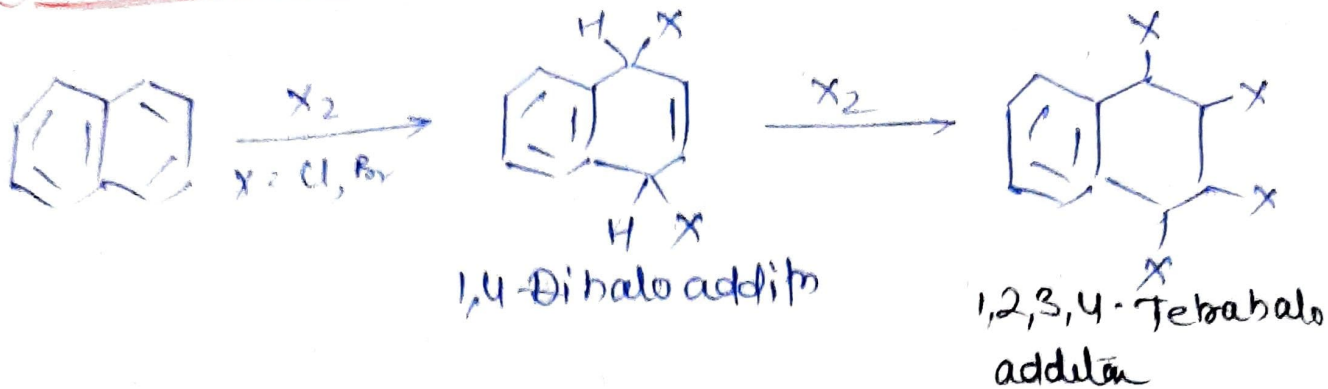
1) Oxidation Reaction



2) Reduction

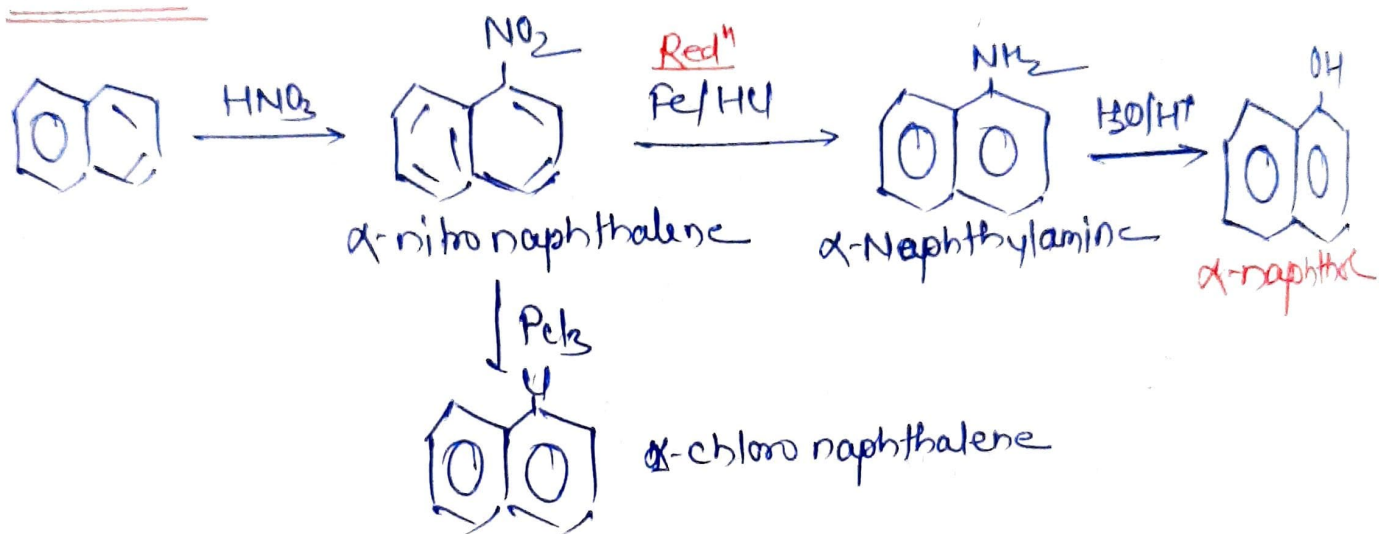


⑤ Addition Reaction

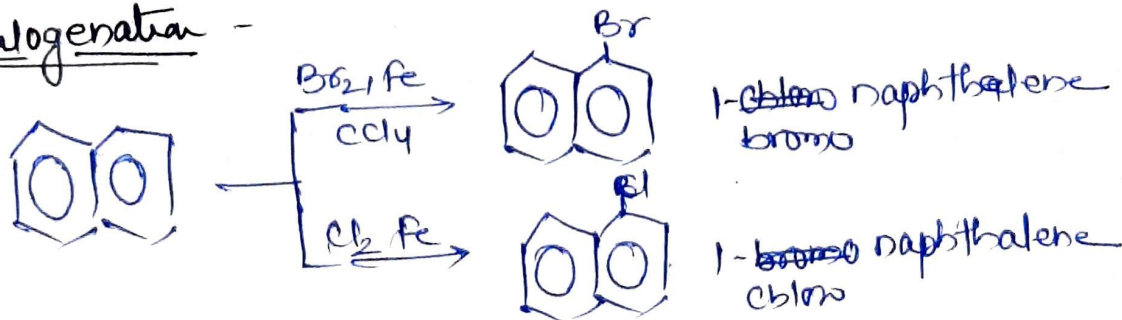


④ ESR → Preferably at C₁-position (C α).

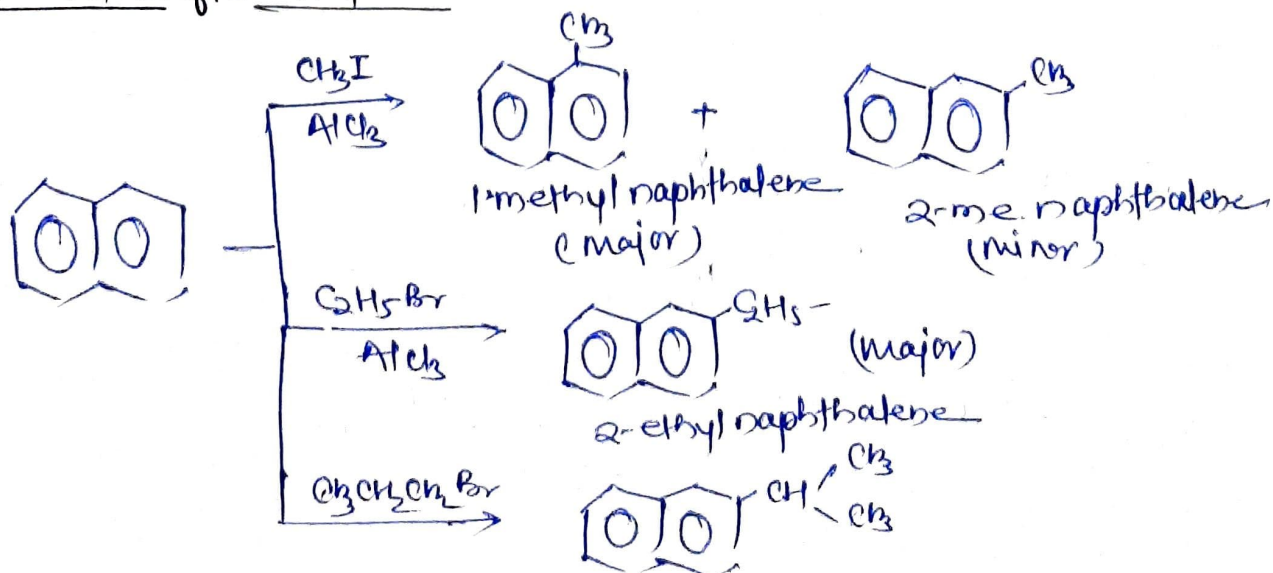
③ Nitration -



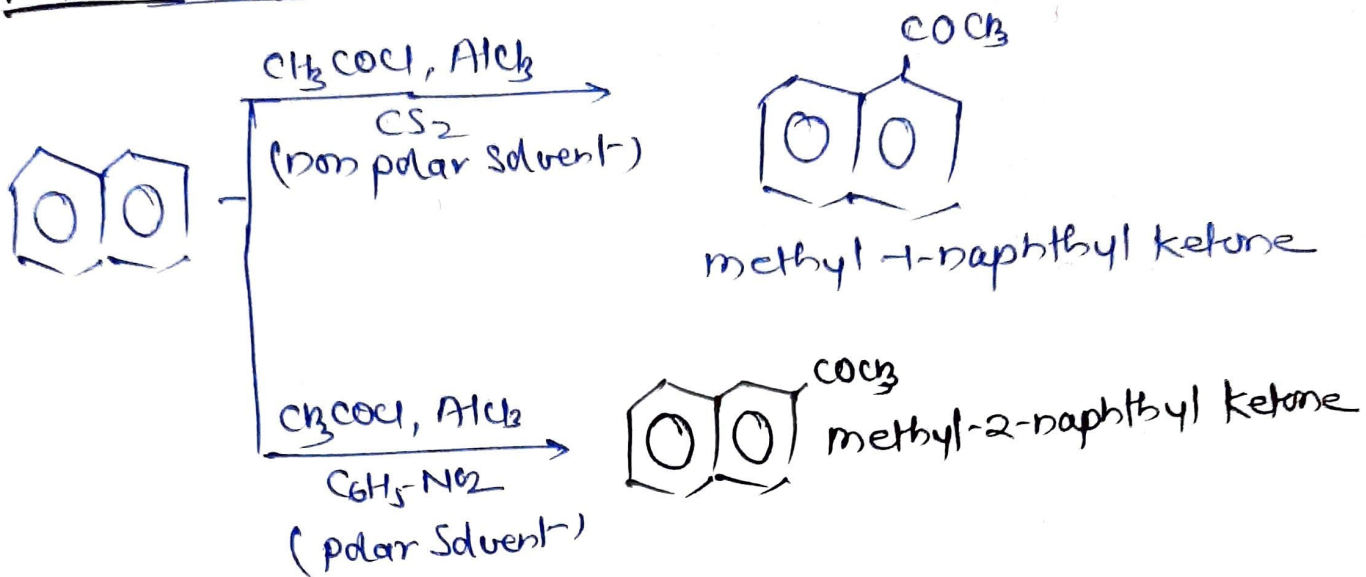
② Halogenation -



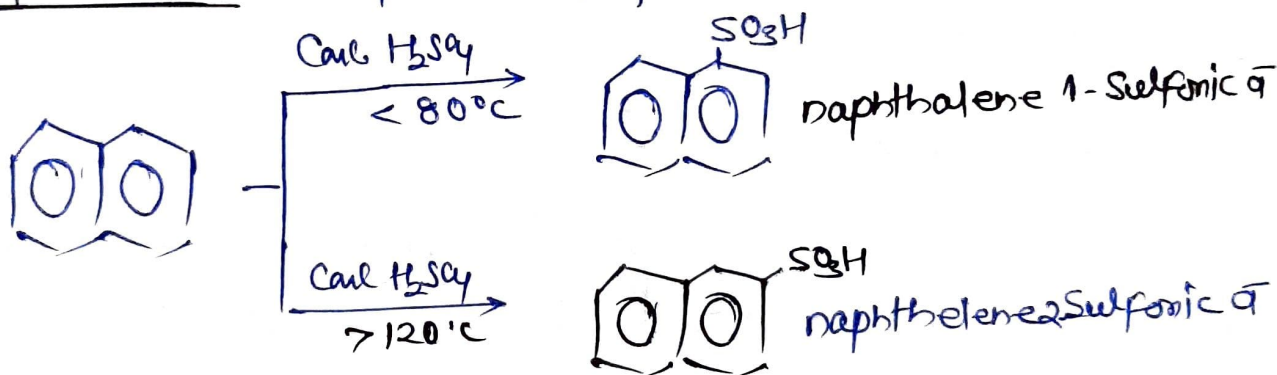
① Friedel Crafts Alkylation - at mild condⁿ (low temp)



(D) Friedel-Crafts Acylation - depends upon solvent



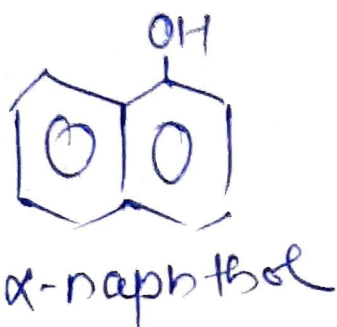
(e) Sulphonation - depends on temp.



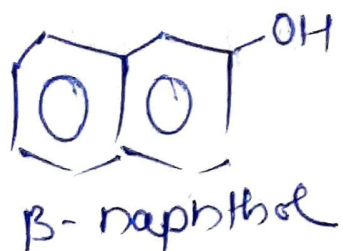
Medicinal Uses Naphthalene & its derivative are used as

- Follow -
- ① production of phthalic anhydride
 - ② Synthesis of various dyes (>900)
 - ③ Carbonyl derivatives used as insecticide
 - ④ Synthesis of various drugs e.g. - Nadolol (β -blocker)
 - ⑤ Sulfonated \rightarrow surfactant
 - ⑥ Naphthalene Sulfonic acids are used to make plasticizers, dispersant in synthetic & natural rubber etc.
 - ⑦ used as fumigants
 - ⑧ Also used in veterinary medicine in dusting powder & internally as an intestinal antiseptic & vermicides.
 - ⑨ Also act well in curing the cough, urine infections, eyes trouble & fever.

I. NAPHTHOLS



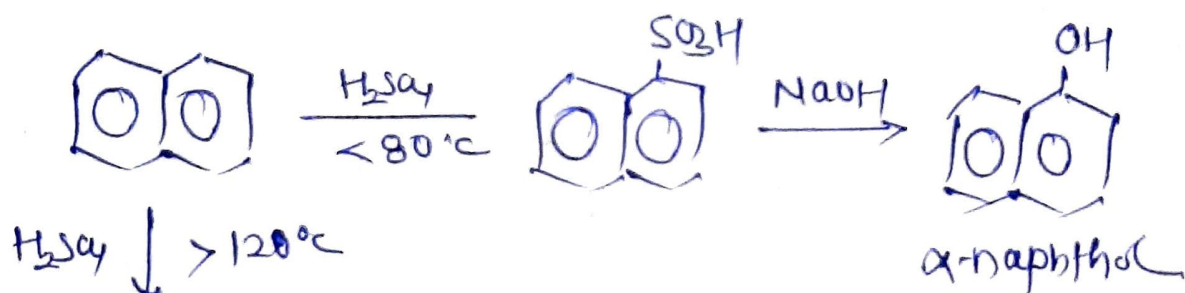
- Colourless solid
- mp - $\alpha = 123^{\circ}\text{C}$
 $\beta = 96^{\circ}\text{C}$



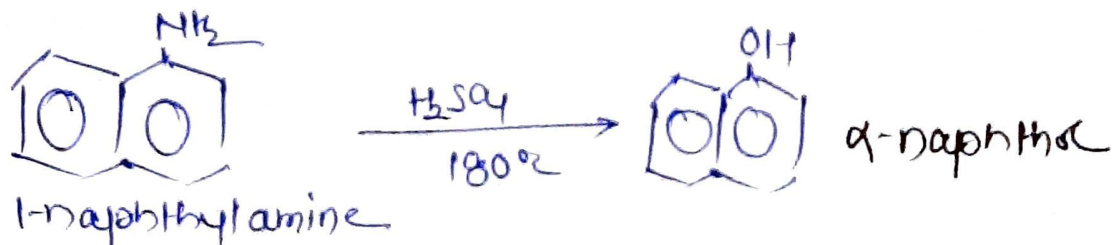
- water insoluble, soluble in benzene

Synthesis: -

① From Naphthalene Sulfonic acid

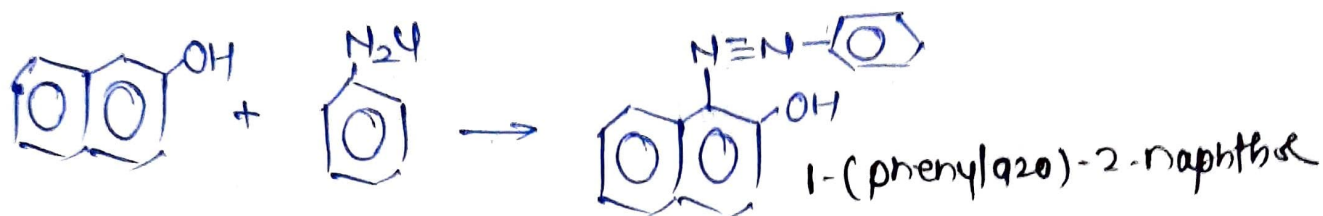
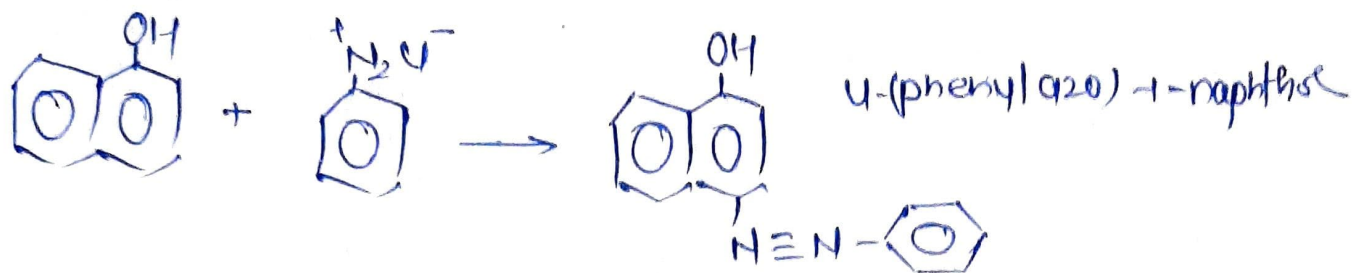


② From naphthylamine

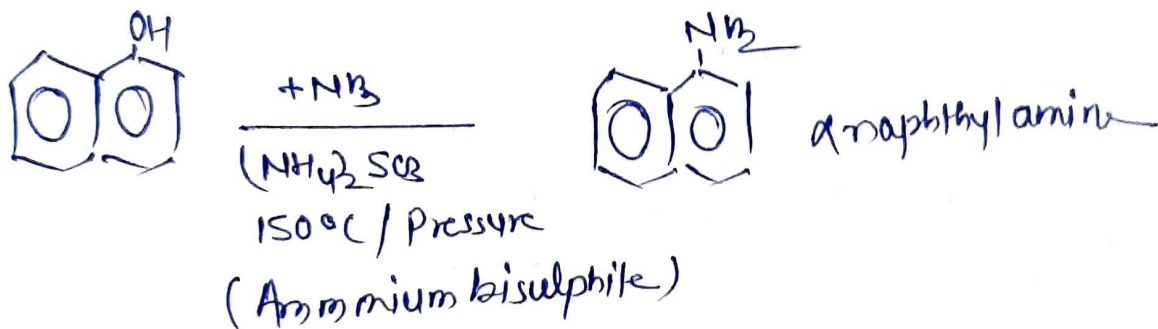


Chemical Reaction

① coupling Reaction

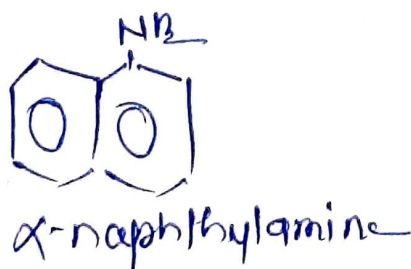


② Reacts with Ammonia (Bucherer Reaction)



Use - Insecticides, Dye industry, Perfumery

II Naphthylamine

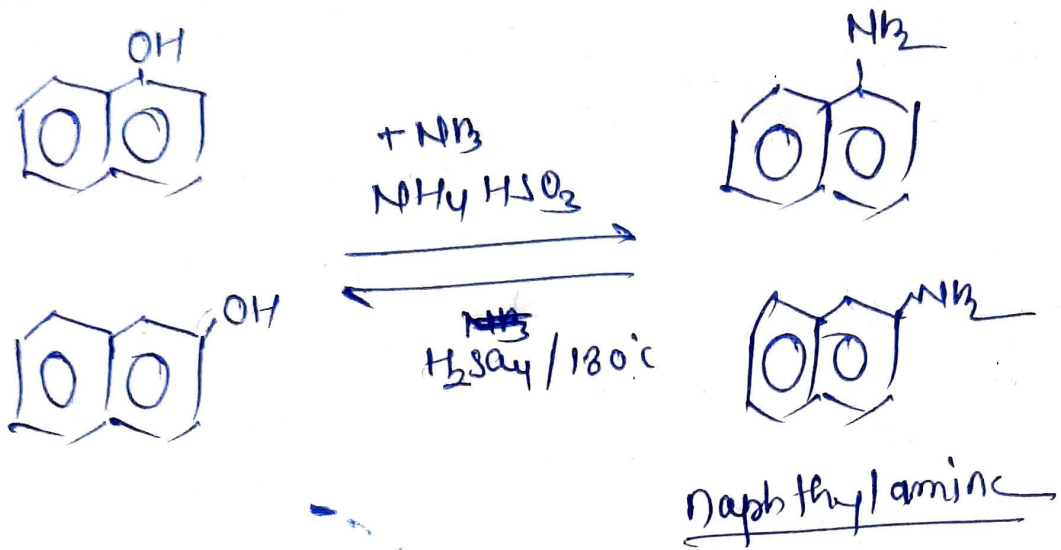


- Colourless solid
- mp(α) - 50°C , (β) 113°C
- water insoluble & soluble in alcohol, ether
- α -nap. → unpleasant odour

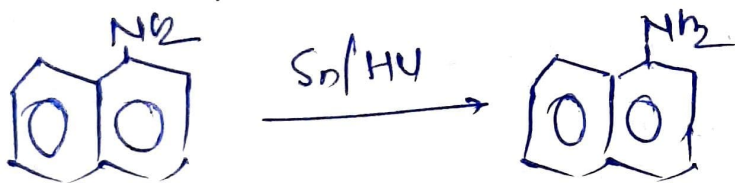


Synthesis Methods

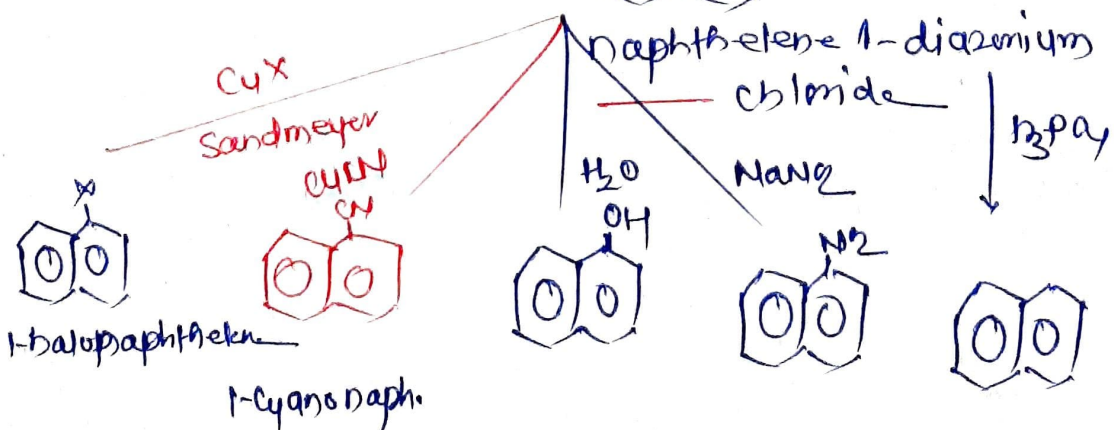
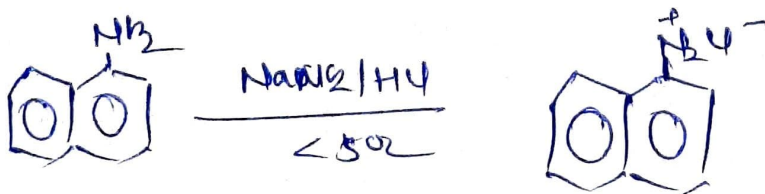
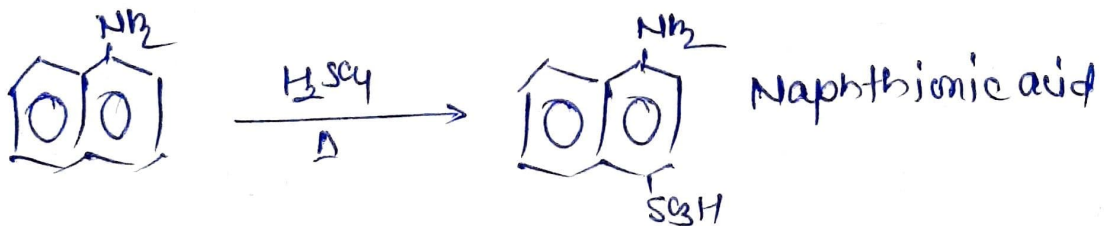
① Bucherer Reaction - from Naphthalene



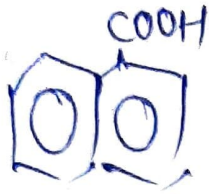
② From Nitronaphthalene



Chemical Reaction

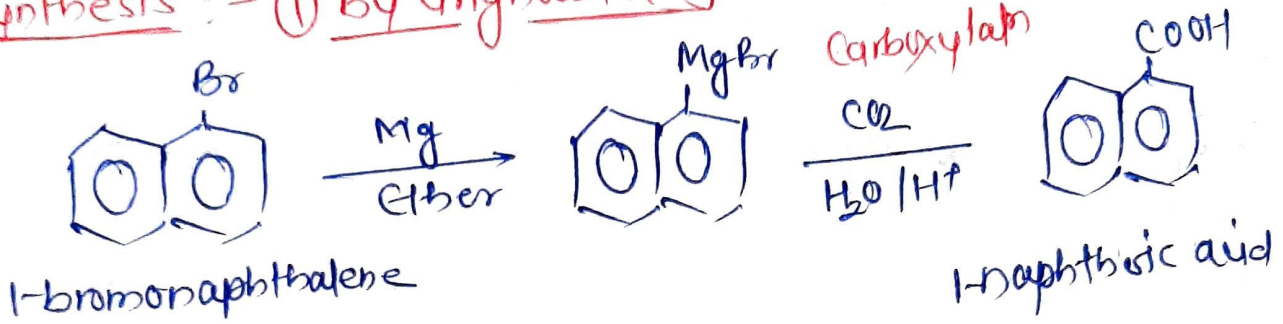


III Naphthoic Acid

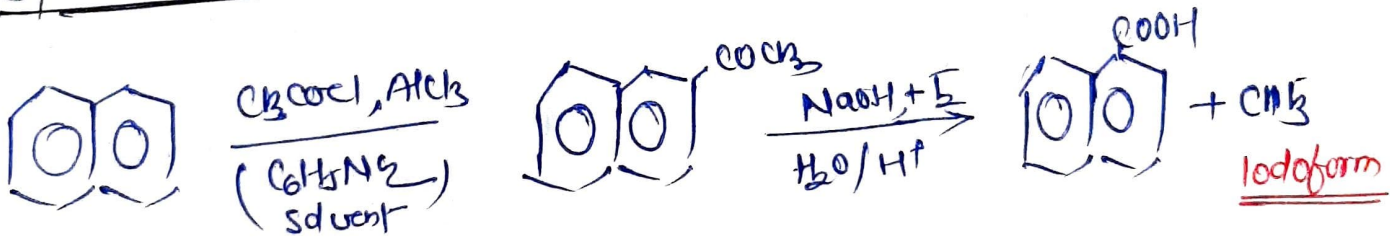


- $C_{10}H_7COOH$ ($C_{11}H_8O_2$)
- 172.18 g/mol
- white solid
- mP = 161°C BP = 300°C

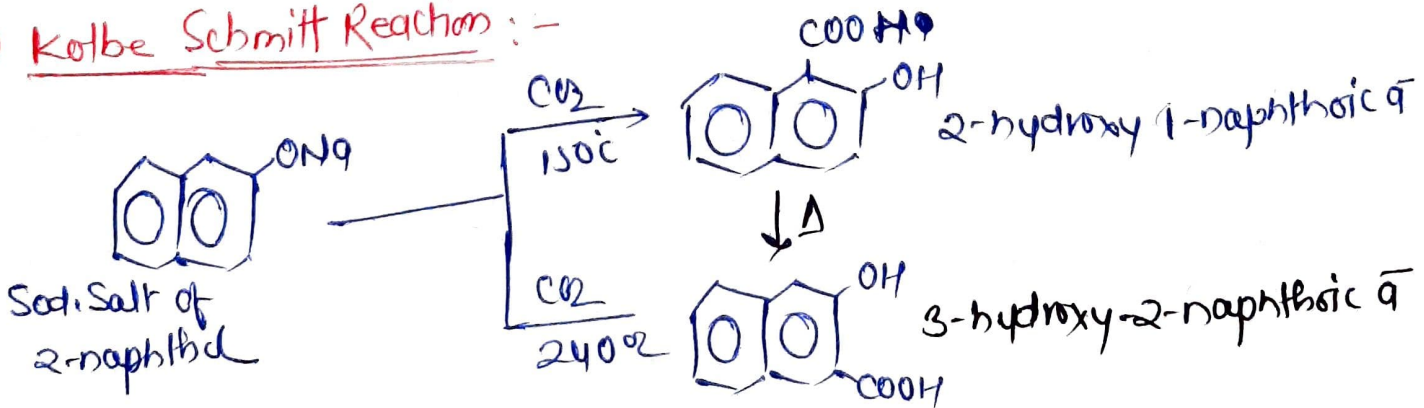
Synthesis :- ① By Grignard Reagent



② By iodoform Reaction

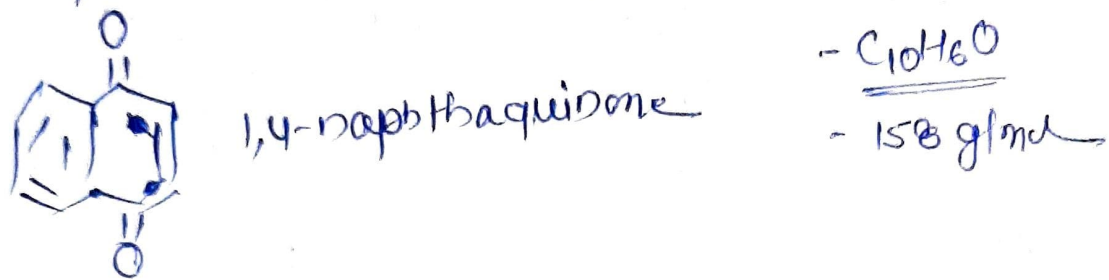
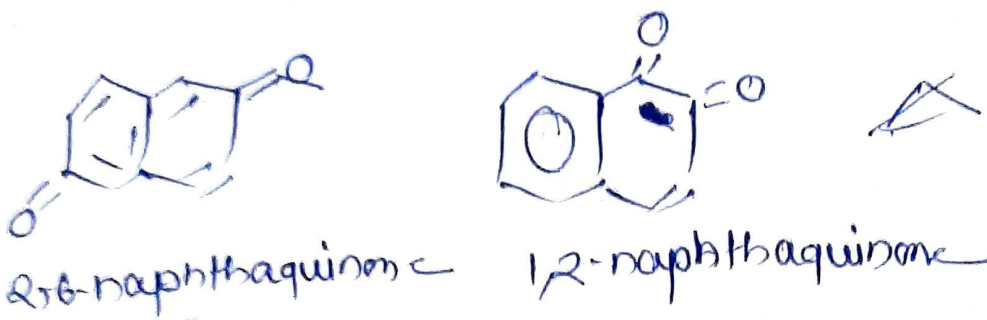


③ Kolbe Schmitt Reaction :-

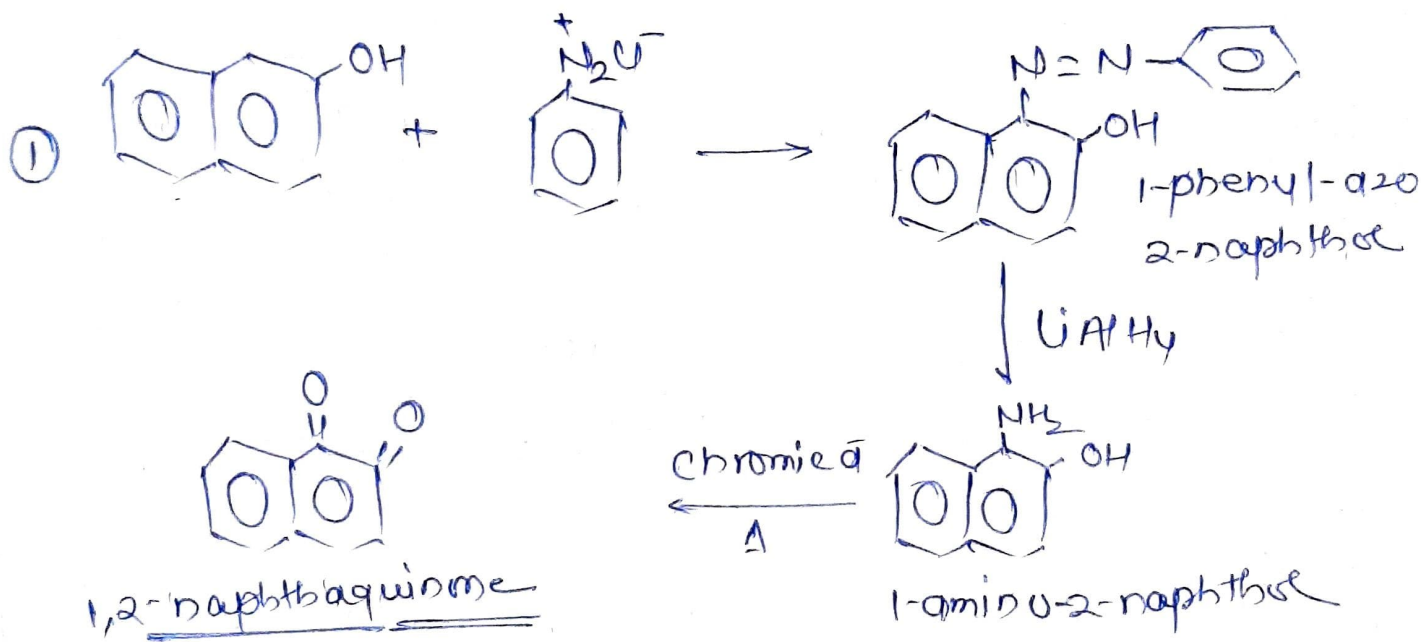


Chemical Reagent

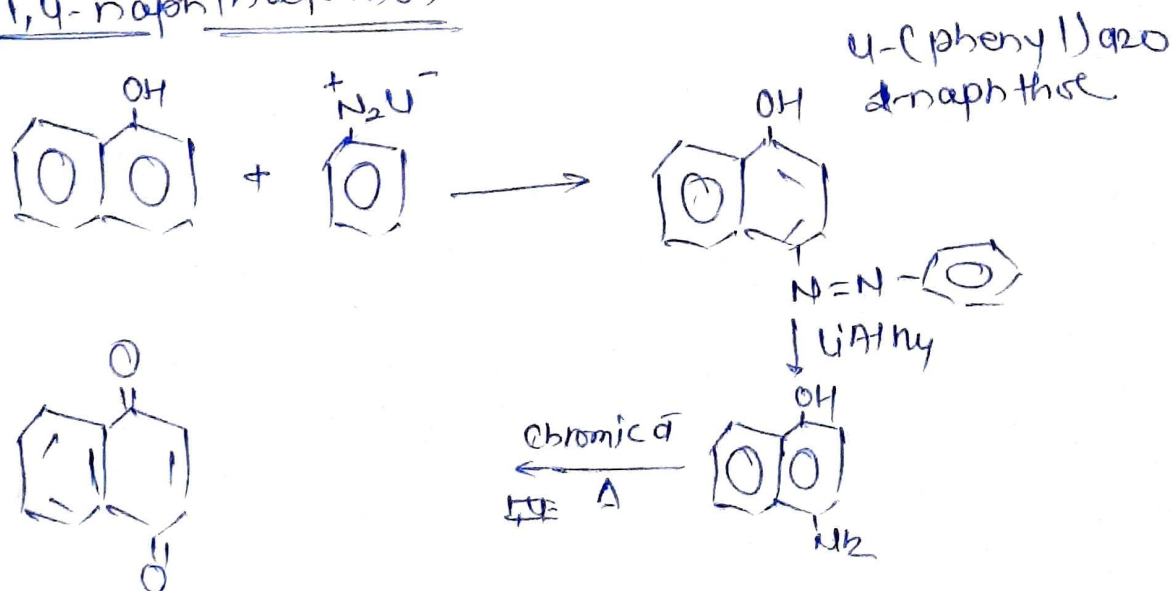
IV. Naphthaquinone



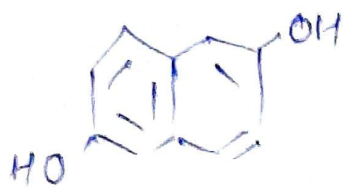
Synthesis :-



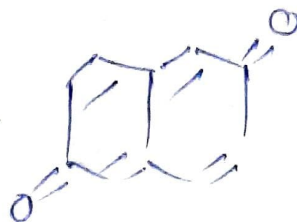
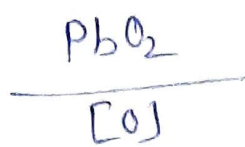
② 1,4-naphthaquinone



③ 2,6-naphthaquinone



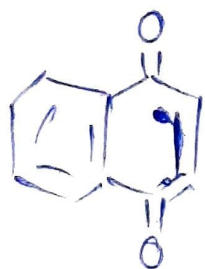
2,6-dihydroxy
naphthalene



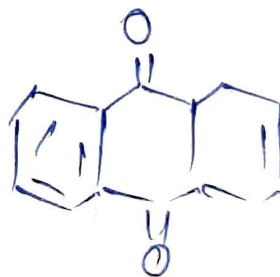
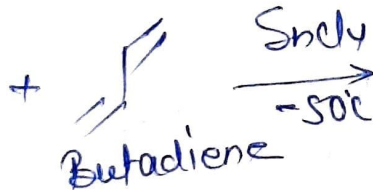
2,6-naphthaquinone

All Naphthaquinone have oxidizing properties but 2,6-naphthaquinone is strong oxidizing agent.

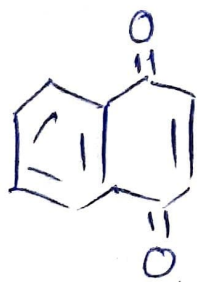
Chemical Reaction - Cycloaddition at low temp.



1,4-naphthaquinone
naphthalene-1,4-dione



Anthraquinone



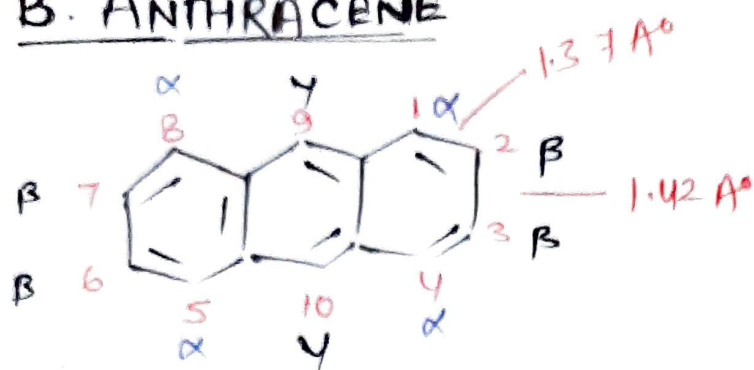
volatile yellow tridinic crystal

$\text{C}_{10}\text{H}_6\text{O}_2$

158.15 g/mol

MP = 126°C

B. ANTHRACENE

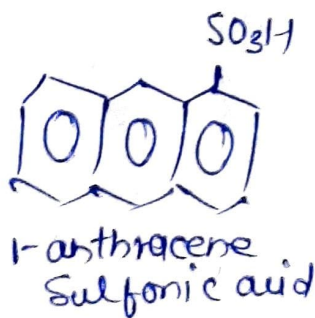


- MF = $C_{14}H_{10}$ → MP = $218^\circ C$, BP = $340^\circ C$
- MW = 178 g/mol → colourless solid
- shows blue fluorescence in UV light.
- 1% in coal tar ($300-350^\circ C$)
- Insoluble in water & soluble in alcohol & ether

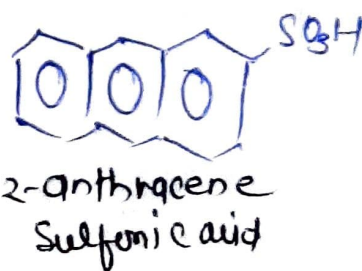
Nomenclature :-



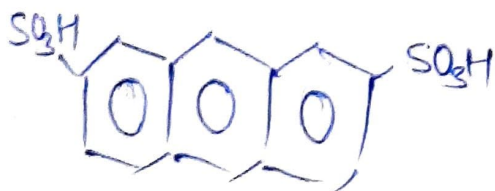
9-bromoanthracene



1-anthracene Sulfonic acid



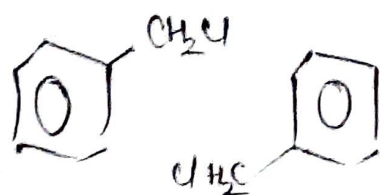
2-anthracene Sulfonic acid



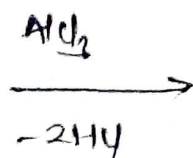
Anthracene 2,7-disulfonic acid

SYNTHESIS

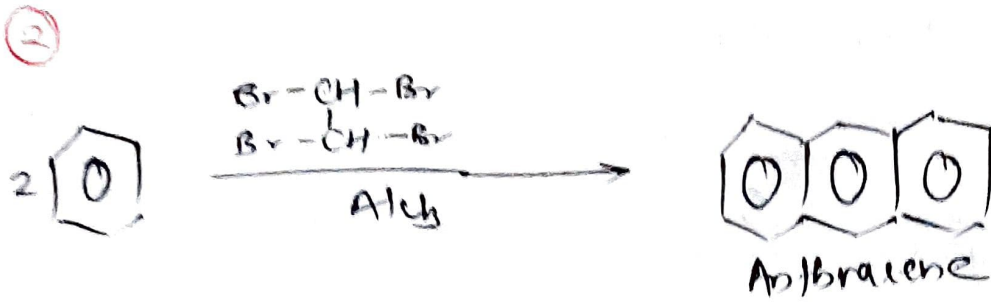
① Friedel Crafts Reaction



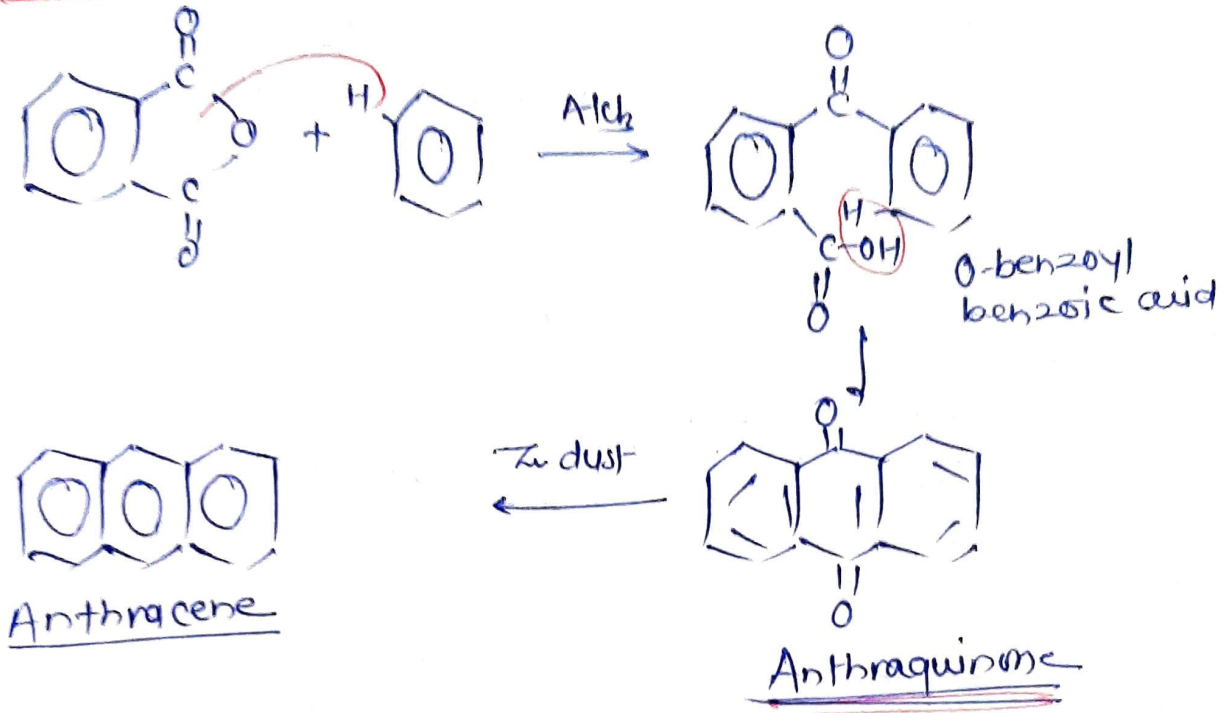
Benzyl chloride



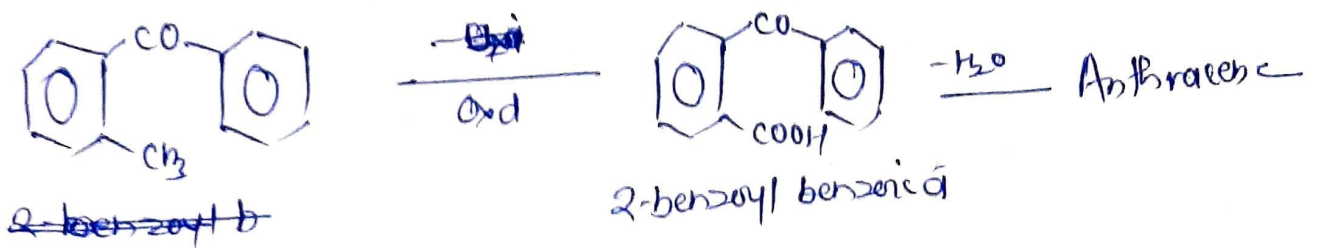
Anthracene



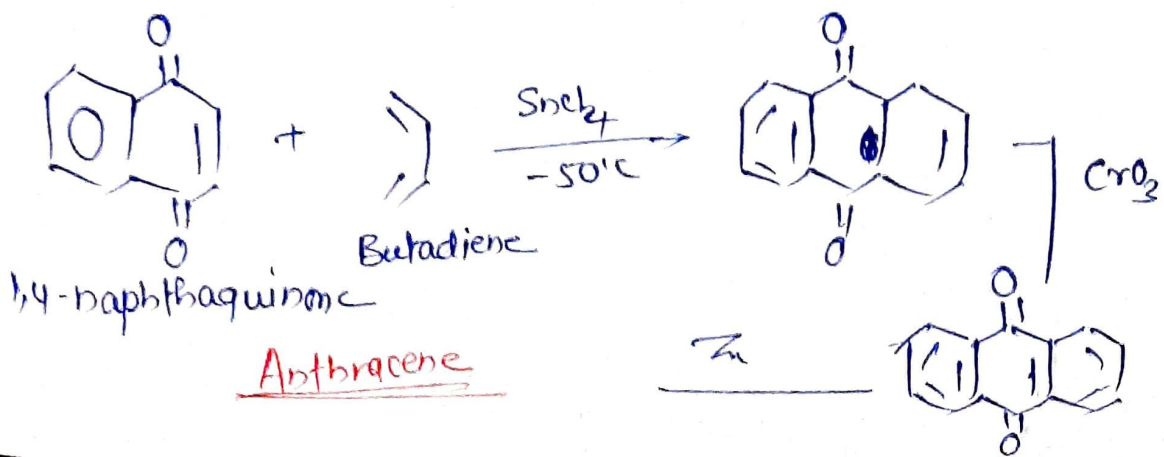
(3) Haworth Synthesis



(ii) Elbs Reaction - by pyrolysis of o-methyl benzophenone



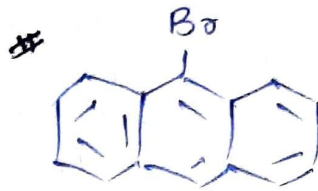
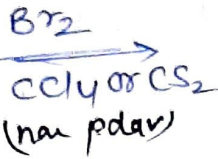
(iii) Diels-Alder Reaction



CHEMICAL REACTION

ESR

Halogenation

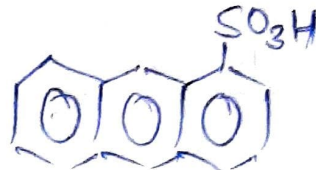


9-bromo Anthracene

Sulfonation



low temp



1-Anthracene Sulfonic acid

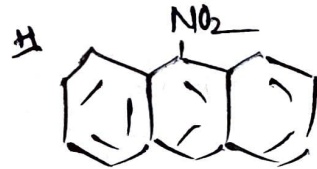
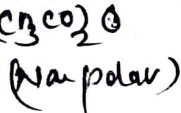
High temp



2-Anthracene Sulfonic acid

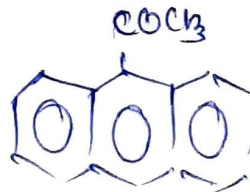


Nitric acid
Nitration

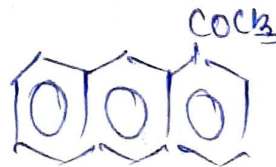
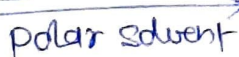


9-nitro Anthracene

(Acetylation)

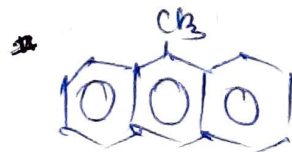
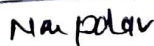


9-Acetyl Anthracene



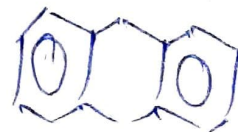
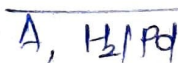
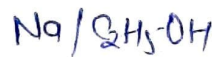
1-acetyl anthracene

Alkylation



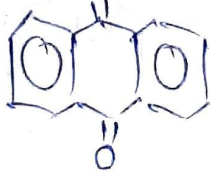
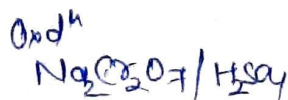
9-methyl anthracene

Reduction - Hydrogenation



9,10-dihydroanthracene

Oxidation



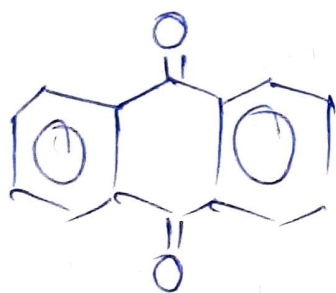
9,10-Anthraquinone

(Anthraquinone)

USES

- ① wood preservative
- ② Insecticide
- ③ Synthesis of drugs, dyes
- ④ used as Scintillator for detector of high energy photons, e^- & α -particle
- ⑤ Derivatives used as purgative (Emodin), spasmodic (Alizarines), etc, cathartics (Anthraquinone glycosides)
- ⑥ antimalarial, anti-HIV, antifungal, Antibacterial, antiviral, hepatoprotective, & diuretic etc.

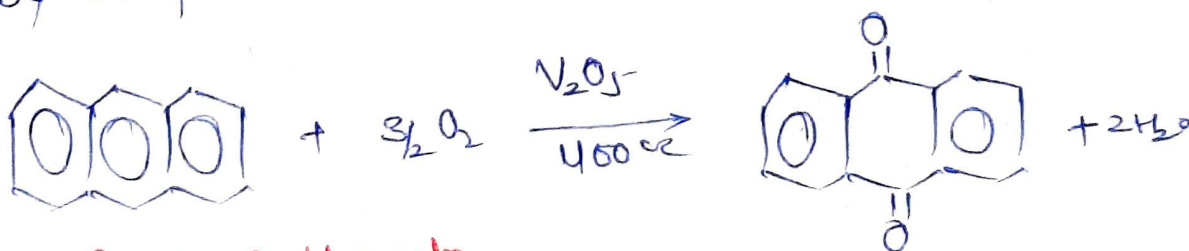
① Anthraquinone



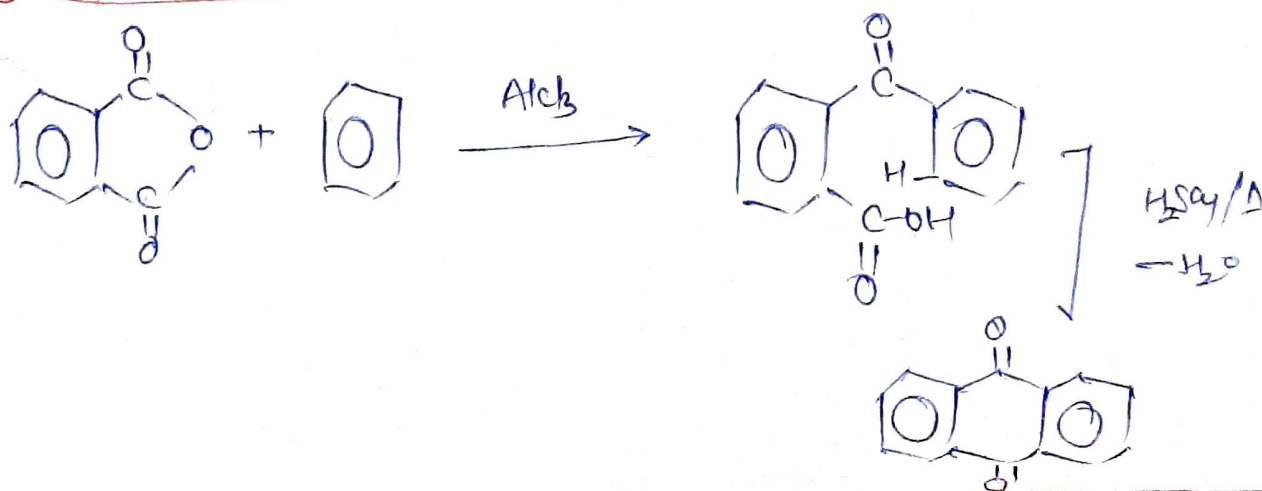
- 9,10-anthraquinone - referred as Anthraquinone
- yellow solid, needle like crystal
- mp = 286°C
- insoluble in water.
- soluble in alcohol, ether, benzene

Synthesis

- ① by Catalytic Oxidation

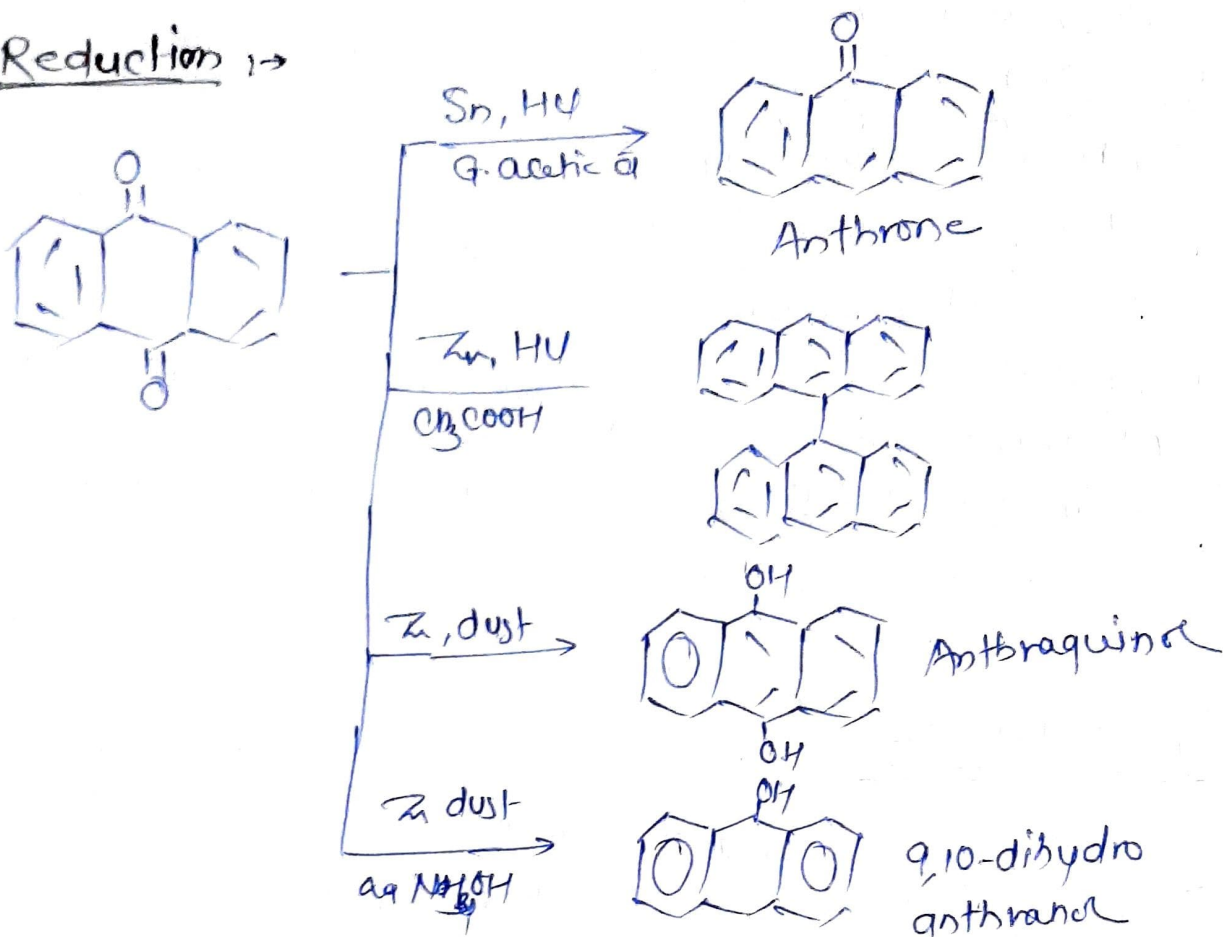


- ② by Fries-Craft reaction

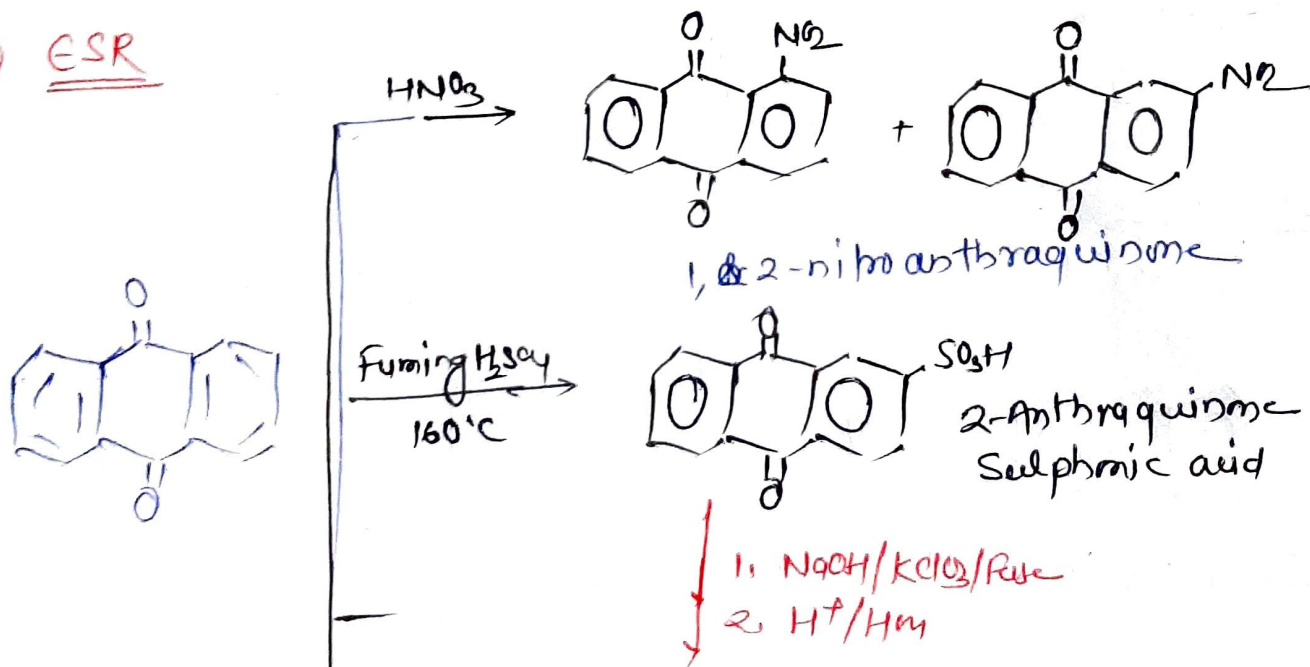


CHEMICAL REACTION

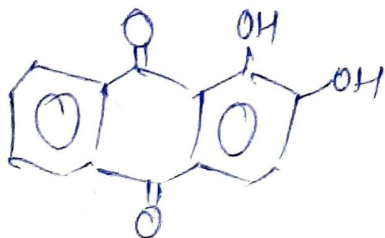
D) Reduction \rightarrow



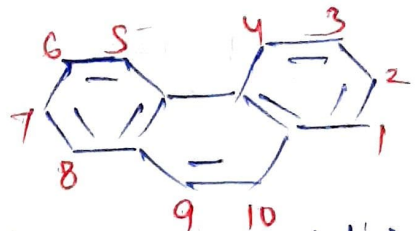
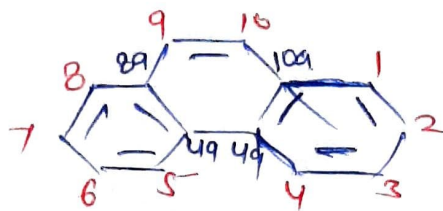
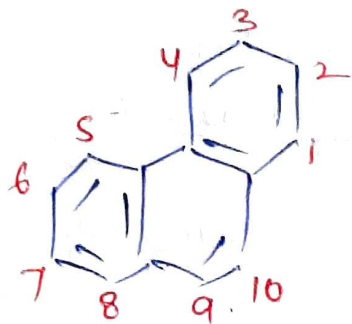
② ESR



uses - manufacturing of Alizarin (1,2-dihydroxy Anthraquinone)



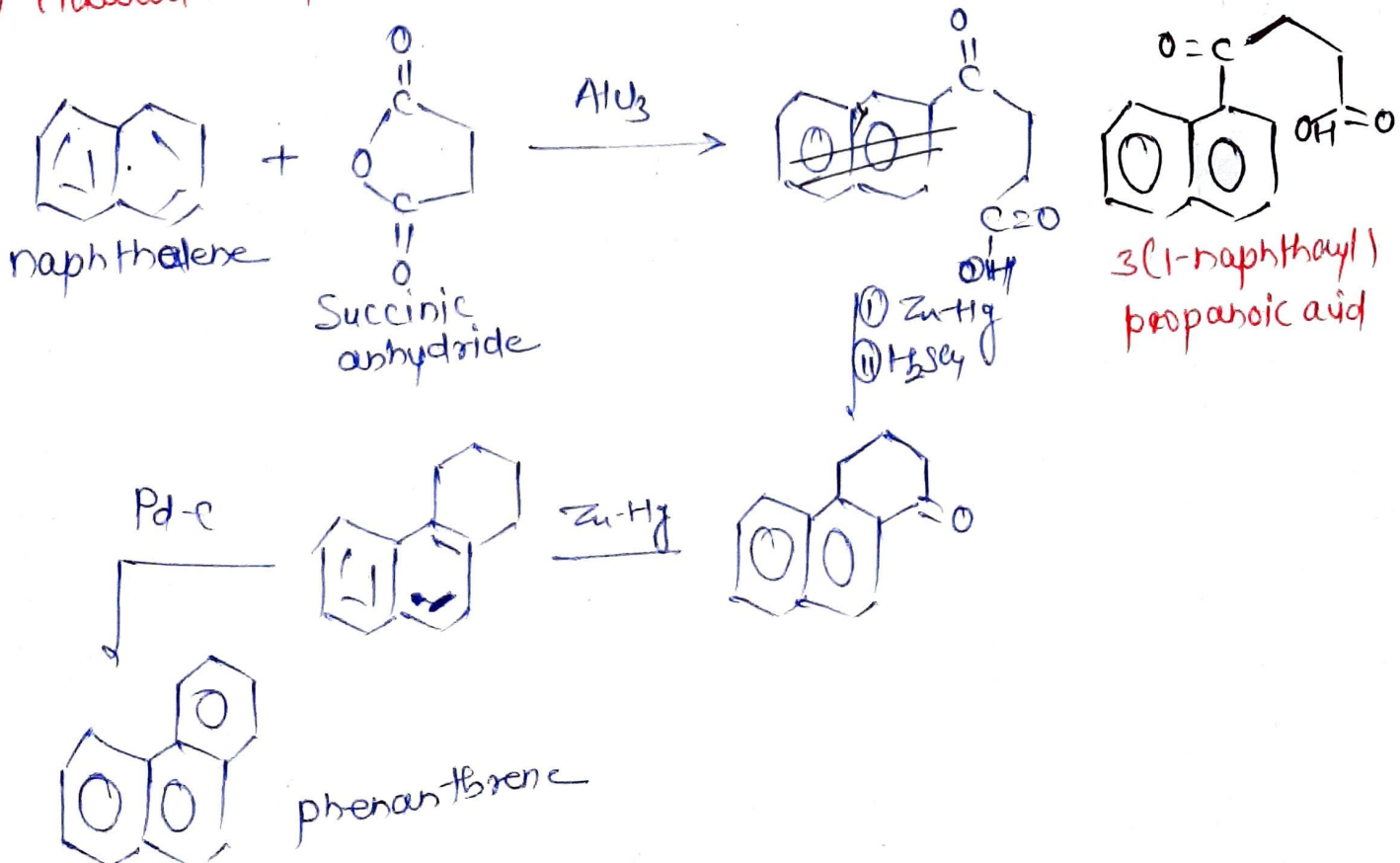
C. PHENANTHRENE



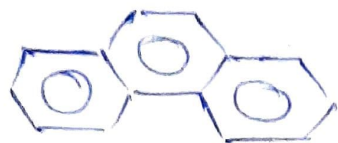
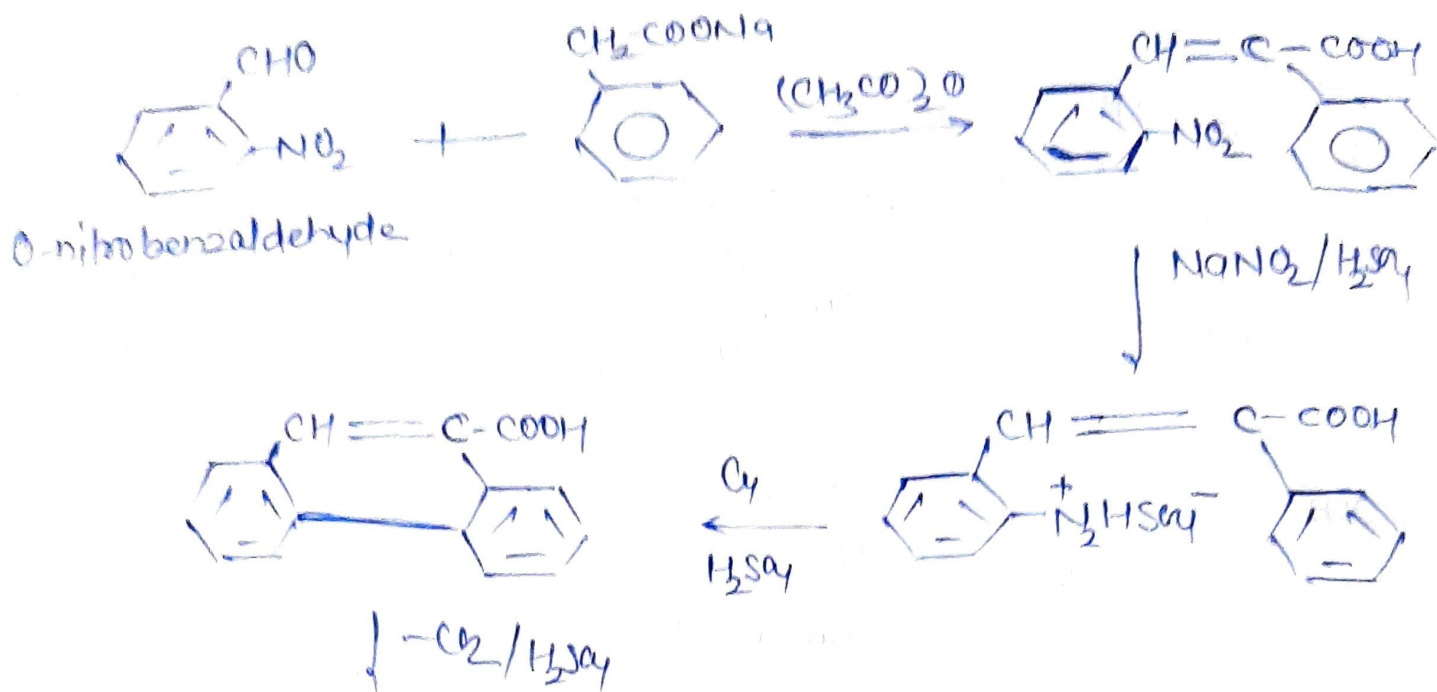
- Colourless crystalline substance obtained from coal tar
- ↳ is isomeric with anthracene
- It is a fused ring 3 polynuclear angular hydrocarbon
- very reactive in the position 9, 2, 10
- $C_{14}H_{10}$, 178.23 g/mol, $MP = 101^\circ C$, $BP = 332^\circ C$
- water insoluble, soluble in org solvent toluene, CCl_4 , ether, $CHCl_3$

Synthesis

① Haworth's Synthesis

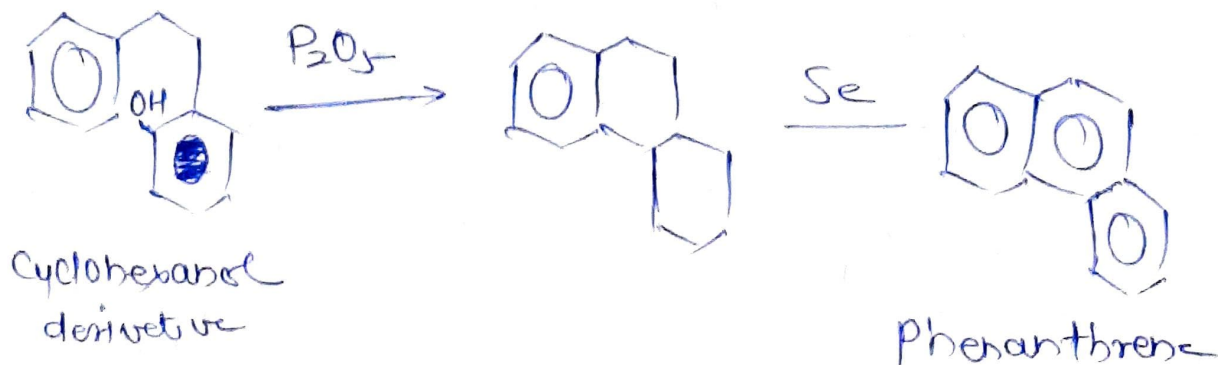


② Pechmann Synthesis

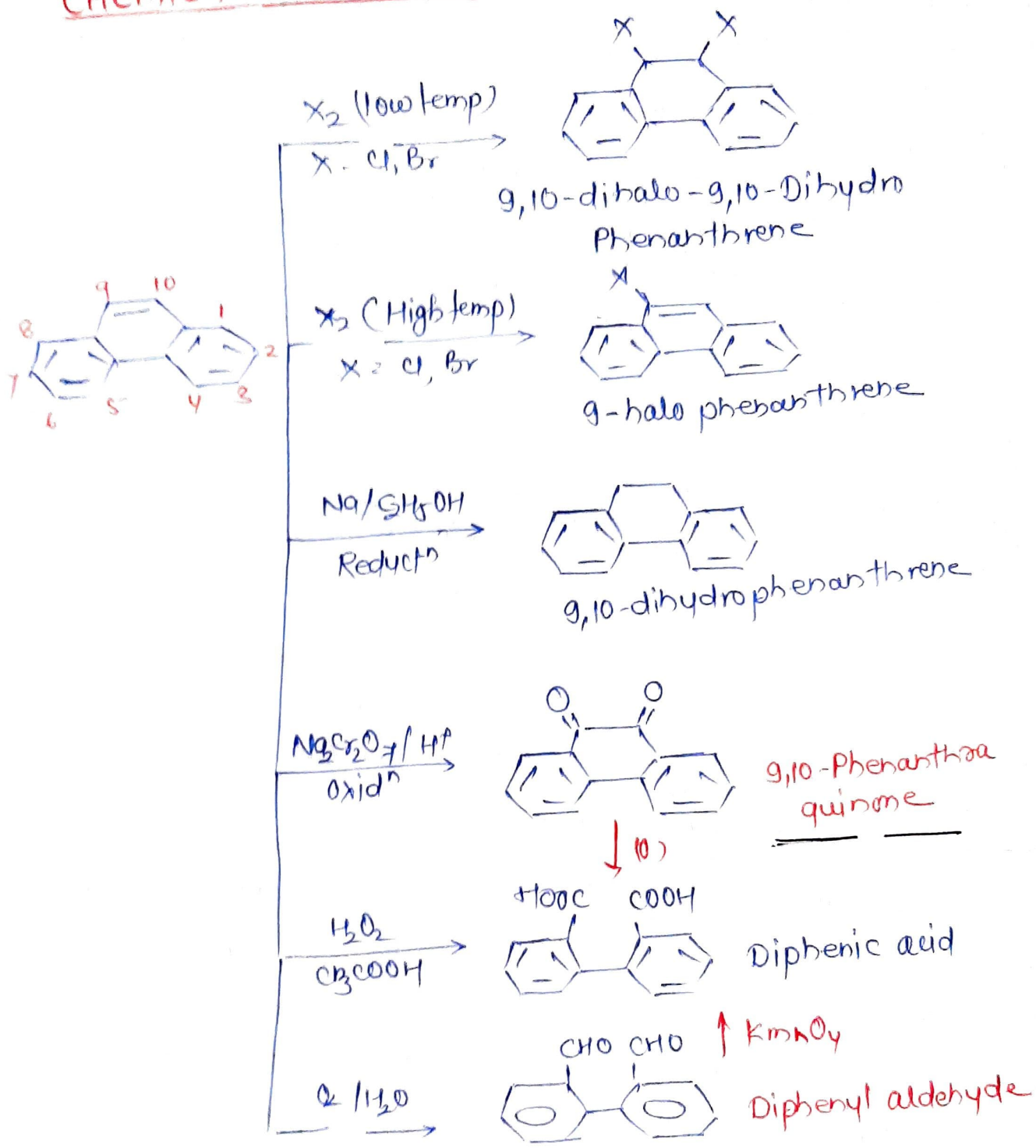


Phenanthrene

③ Bardhan - Sengupta Phenanthrene Synthesis



CHEMICAL REACTIONS

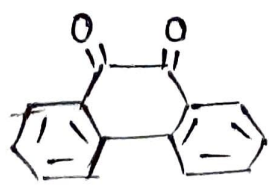


PHENANTHRAQUINONE

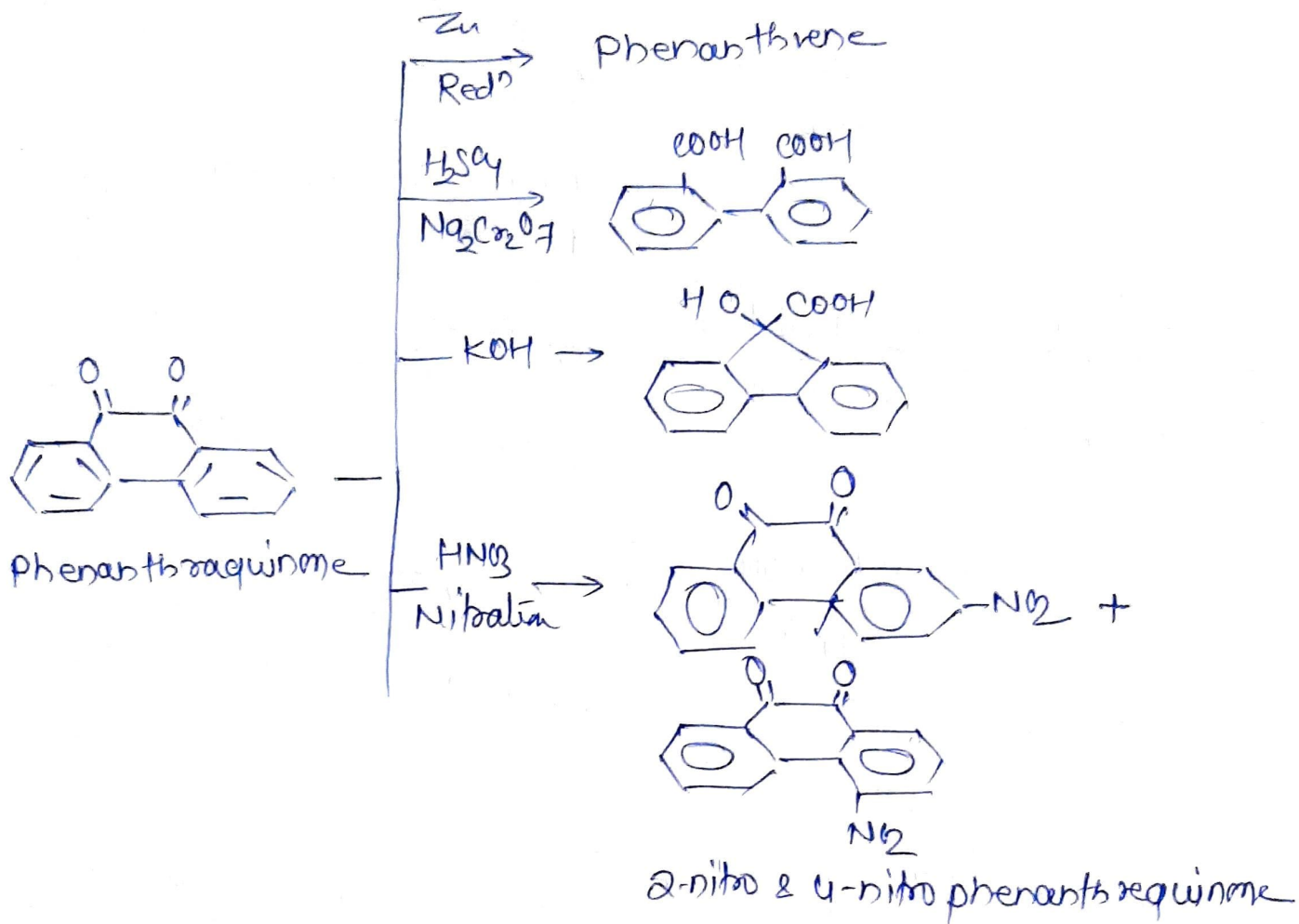
- Solid, odourless & not steam volatile.



- ① $Na_2Cr_2O_7, CH_3COOH$ or
- ② CrO_3, CH_3COOH



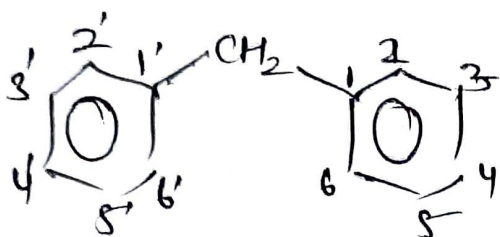
CHEMICAL REACTION



USES OF Phenanthrene & derivatives -

- ① manufacturing of pesticides & dyes, drugs, & resins
- ② 9,10-biphenyl dicarboxylic acid derivative is used to manufacturing of polyester & alkyl resin.
- ③ phenanthroquinone can be used as dyes, fungicides, & polymerization inhibitors

D. Diphenyl Methane

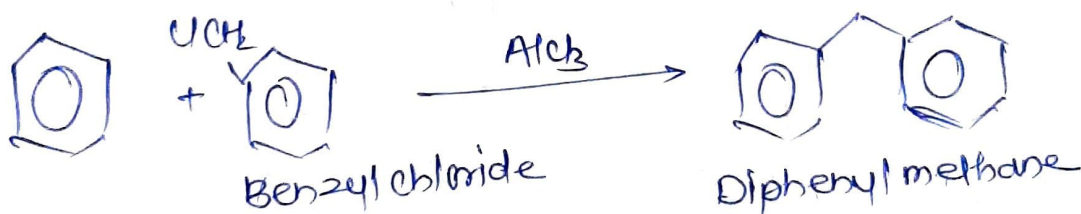


- $(C_6H_5)_2CH_2$
- $C_{12}H_{12}$
- 168.23 g/mol
- mP = 22-24°C
- BP = 264°C

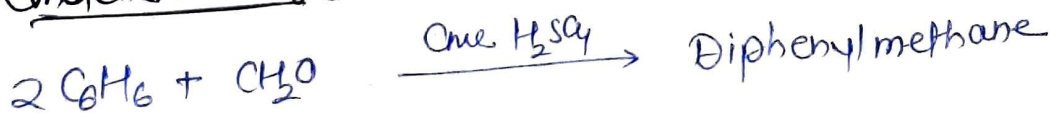
- Diphenyl methyl group is also known as "Benzhydryl"

Synthesis -

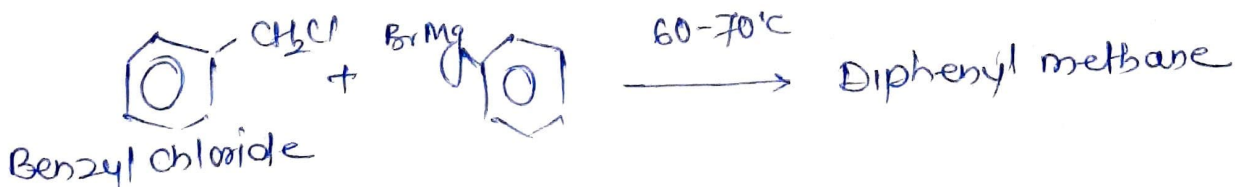
① Friedel Crafts Condensation



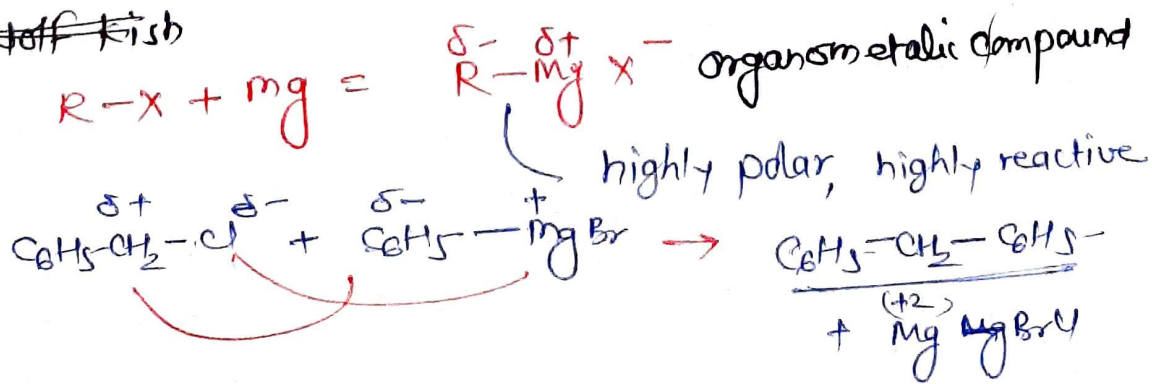
② Condensation of Formaldehyde -



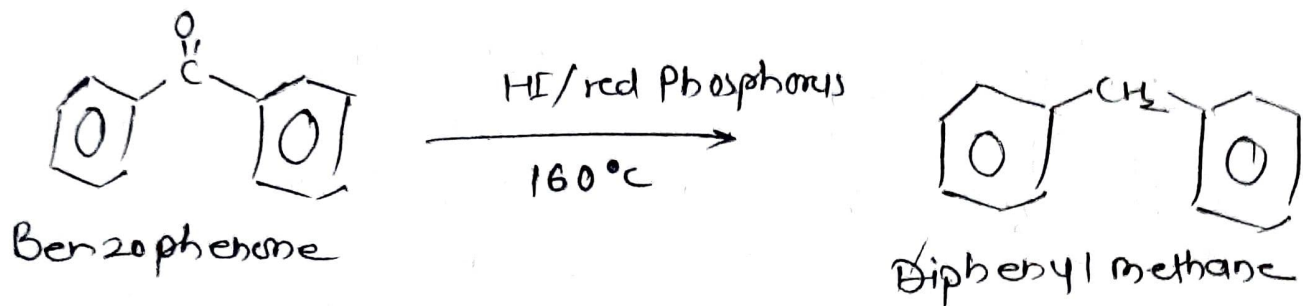
③ Form Grignard Reagent



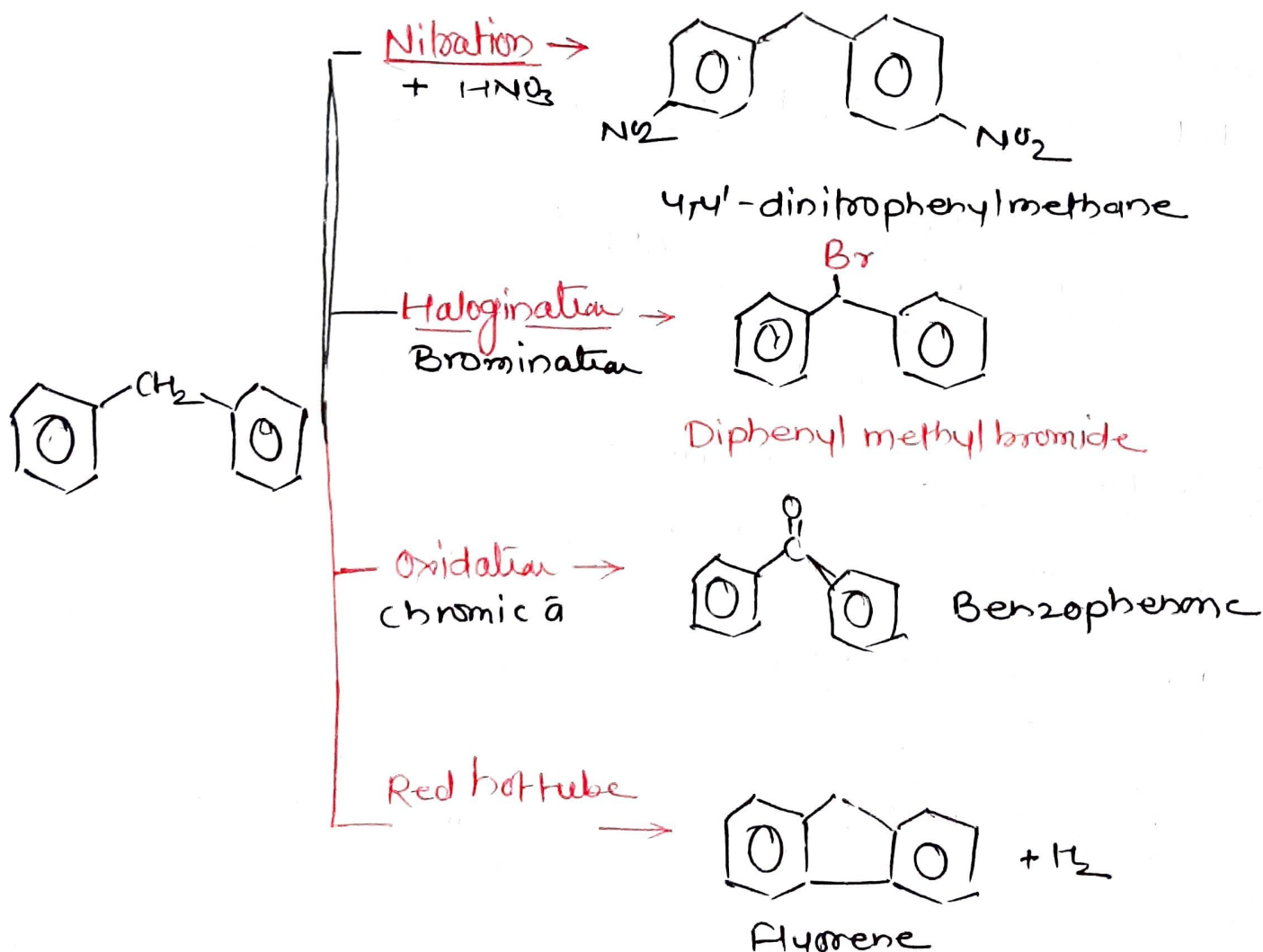
④ ~~Hoff~~ Krich



4. Wolff-Kishner Reduction

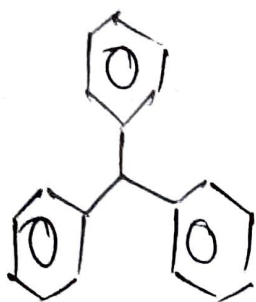


CHEMICAL REACTIONS



use - As Antispasmodic, antitumor, antihistaminic, anti anxiety

E. TRIPHENYL METHANE



Triphenylmethane

- $C_{19}H_{16}$ $(C_6H_5)_3CH$
- 244.3 g/mol
- ~~1,1,1~~
- 1,1,1-Triphenylmethane
- Colourless solid
- soluble in non polar org. solvent

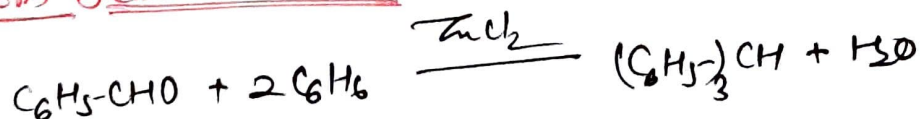
- It is the basic moiety of many synthetic dyes like malachite green, Magenta, crystal violet.

SYNTHESIS

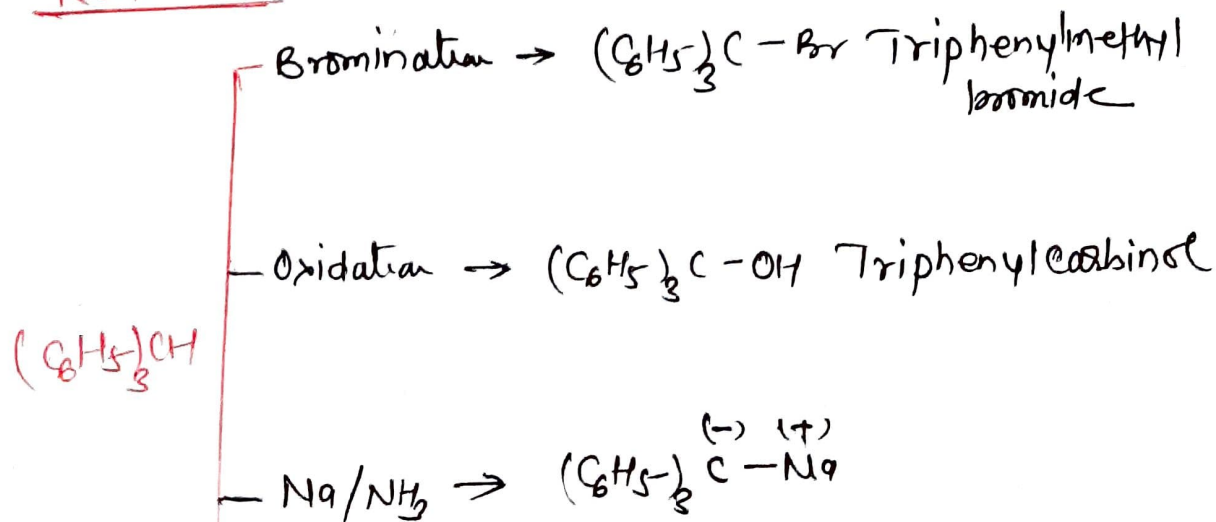
① Friedel-Crafts Reaction - Alkylation



② From Benzaldehyde



REACTION



uses - Preparation of colouring dyes called triaryl methane used as pH