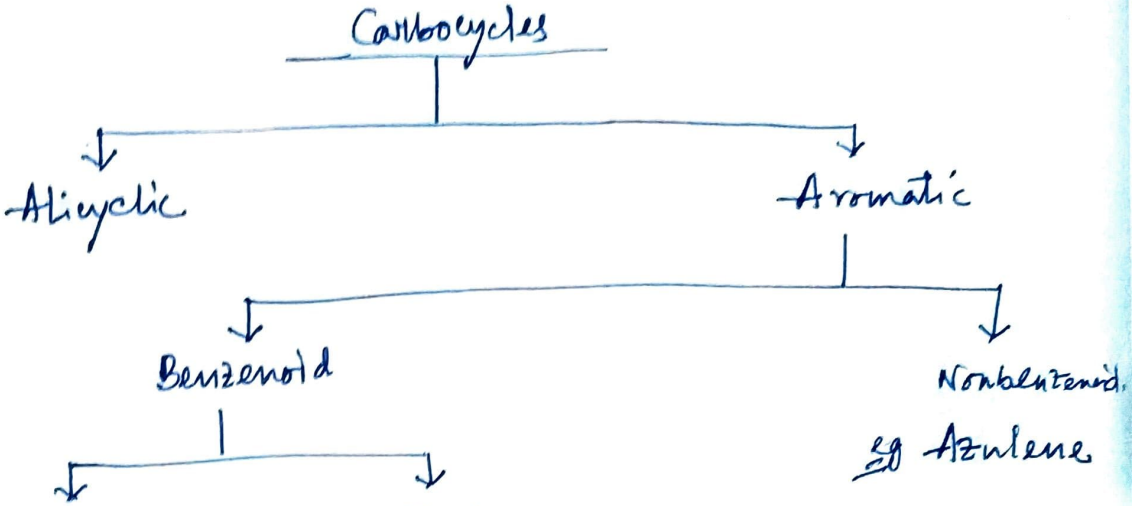
Carbocycles and Heterocycles :-

Synthetic methods include Haworth, Bardhan - Sengupta, Bogert - Cook and other useful syntheses (with mechanistic details) fixation of double bonds and Fries rule; reaction (with mechanism) of naphthalene, anthracene, phenanthrene and their derivatives.

—o—

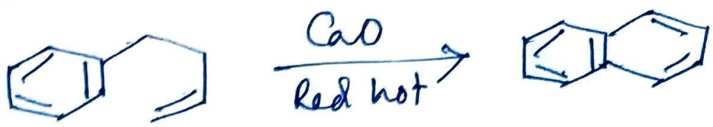
Carbocycles are cyclic hydrocarbons are categories as.

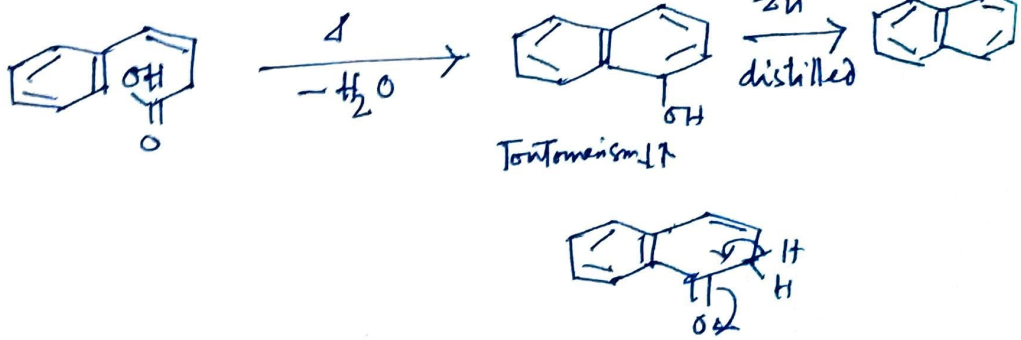


we shall focus on fused benzenoid carbocycles —

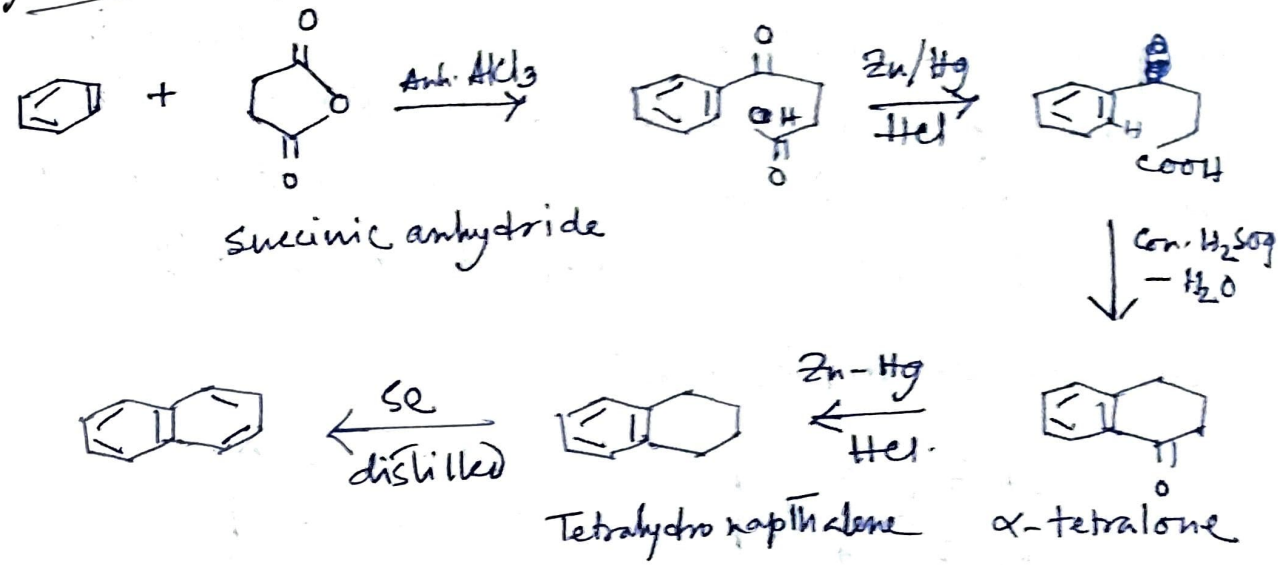
Naphthalene :- ($C_{10}H_8$)

Synthesis :-

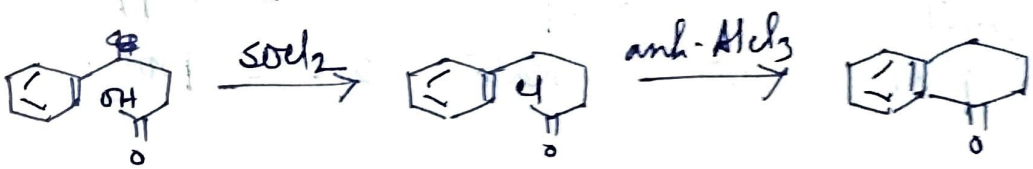
(i) 

(ii) 

(iii) Howarth Synthesis:-



The reaction may also be carried out as -

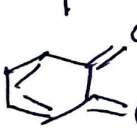


Position of Double bond:-

Naphthalene have three resonating structures -

It should be noted that - linearly fused aromatic hydrocarbon have (n+1) number of resonating structures where n is equal to number of rings.

Fries rule:- Fries compared the possible arrangement of double bonds in polynuclear compounds with benzo-quinones. Structure II & III have arrangement

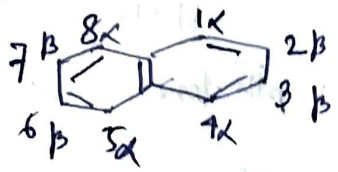


corresponds to o-benzoquinones. Since quinones are far more reactive than a purely aromatic compound. Fries believed that the stable form of a polynuclear compound did not contain this quinonoid arrangement.

Note: the most

Rule:- the most stable arrangement of a polynuclear compound is that form which has the maximum number of rings in the benzenoid condition ie three double bonds in each individual ring. ie structure -I is stabler than II or III.

Isomerism of naphthalene :-



1, 4, 5, 8 → α.
2, 3, 6, 7 → β.

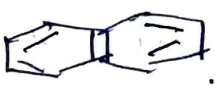
1,2 → ortho.
1,3 → meta
1,4 → para
1,5 → ana
1,6 → epi
1,7 → kata
1,8 → peri
2,6 → amphi
2,7 → pros.

Monosubstituted products $C_{10}H_7X$: Two ; 1 & 2.
Di " " $C_{10}H_6X_2$: 10
$C_{10}H_6XY$: 14
$C_{10}H_5X_3$: 14
$C_{10}H_4X_4$: 22

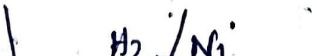
Reactions of naphthalene :-

① 

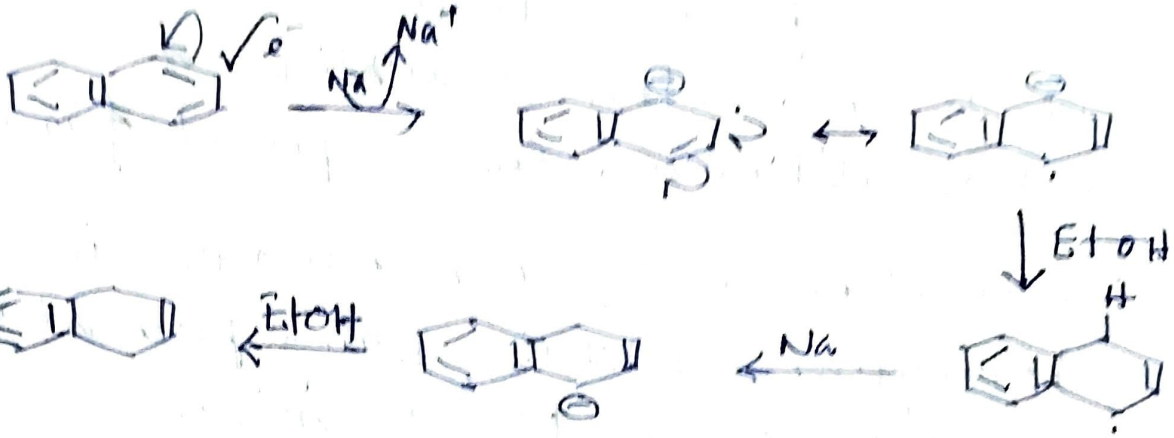
1,4-dihydronaphthalene
or
1,4-dialin.



tetralin



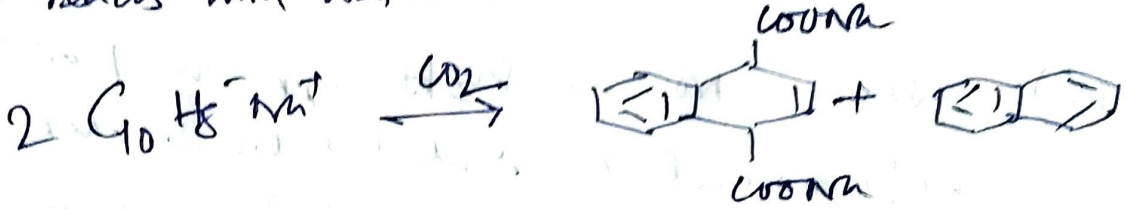
decalin



(2) Naphthalene reacts with sodium without loss of hydrogen to give a highly coloured addition compound

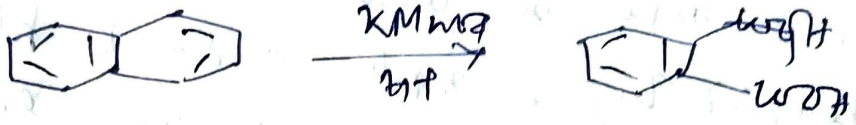
$$C_{10}H_8 + Na \longrightarrow C_{10}H_8^- Na^+$$

which reacts with water to 1,4-tetrahydro naphthalene

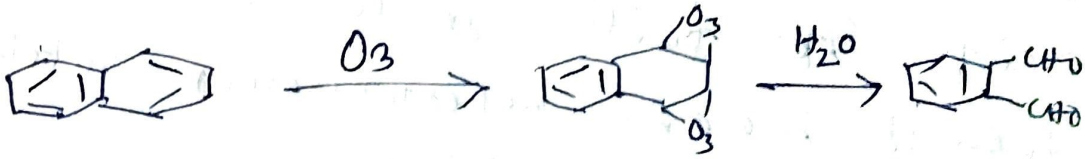


(3)

(4)



(5)



Substitution of naphthalene:—

The 1st gr. always enter the 1-position in naphthalene except two cases (i) Sulphonation at high Tempt. and (ii) Friedel-Craft- reaction.

Introduction of second substituent can give rise to homonuclear substitution or to hetero-nuclear substitution. Some empirical formulation-

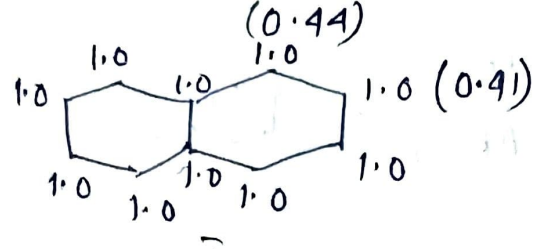
(a) When Cl, Br, OH, CH_3, NHR, $NHCOCH_3$ in 1-position homonuclear substitution taking place at 4-position in major and 2- position minor.

(b) When OH, $-CH_3$, $-NHR$, $-NHCOCH_3$ at 2-position homonuclear substitution will take place at 1- position. Only $-SO_3H$ gr. entering is an exception it enters at 6 position.

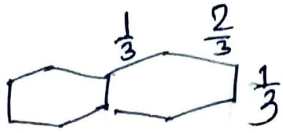
(c) When $-NO_2$, $-SO_3H$ gr in 1 or 2- position heteronuclear substitution takes place in 5 or 8 position. If Cl or NH_2 in 2- place same generic occurs.

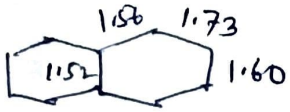
Homonuclear v. Heteronuclear substitution can be characterized by simple oxidn & phthalic acid. If further gr in benzene ring then it means heteronuclear substitution had taken place.

* Napthalene 10 π electrons equally distributed, hence, at first site, it might be expected, positions 1 & 2 would be attacked equally by usual electrophilic substitution.



I

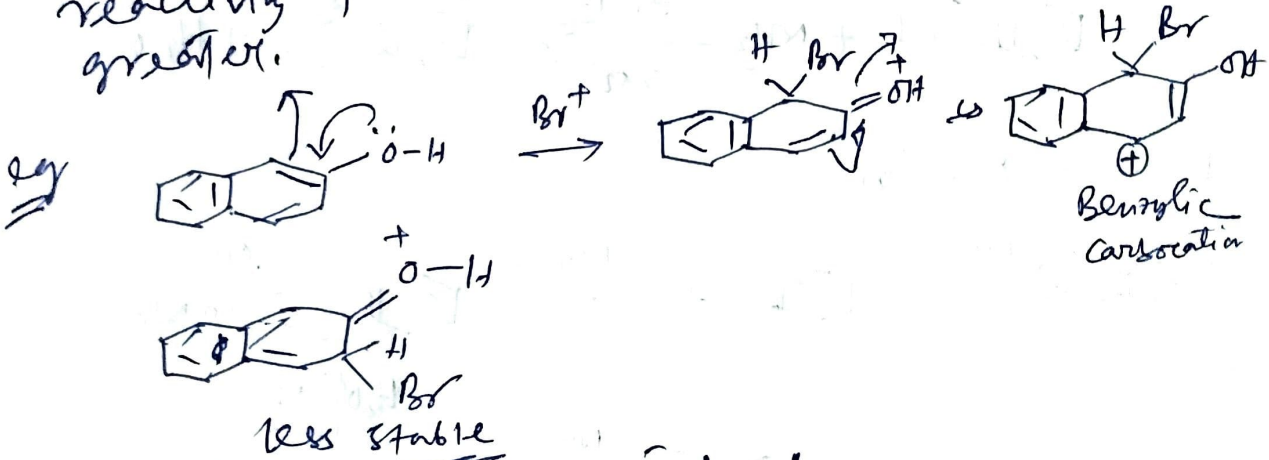




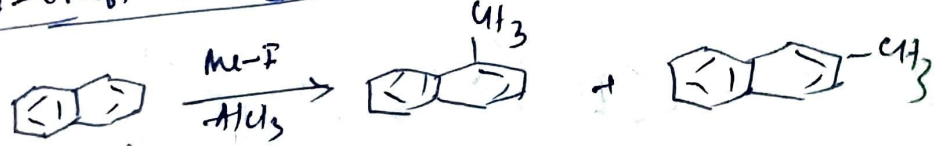
II

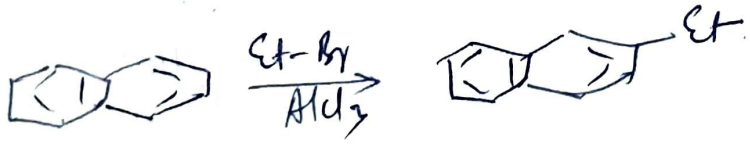
There is, however, another factor which must be considered when the charge densities are equal at various position, This is the self-polarisability of the position and the larger the magnitude of this self-polarisibility, more reactivity will that point. Here in naphthalene self-polarisibility at 1-position is greater than 2-position and hence 1-position have greater reactivity than 2.

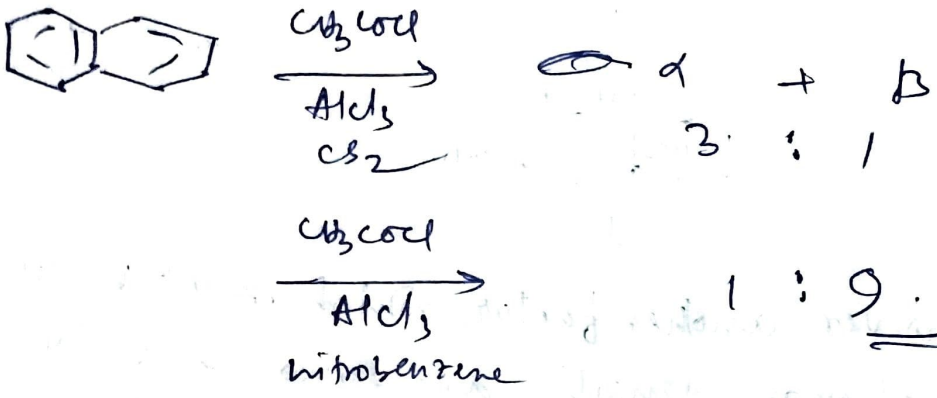
In fig II show the bond & order by calculation and III ~~bond~~ double bond character of various bond on the basis of two one can also say that the reactivity of 1 & 2 -position in naphthalene is greater.



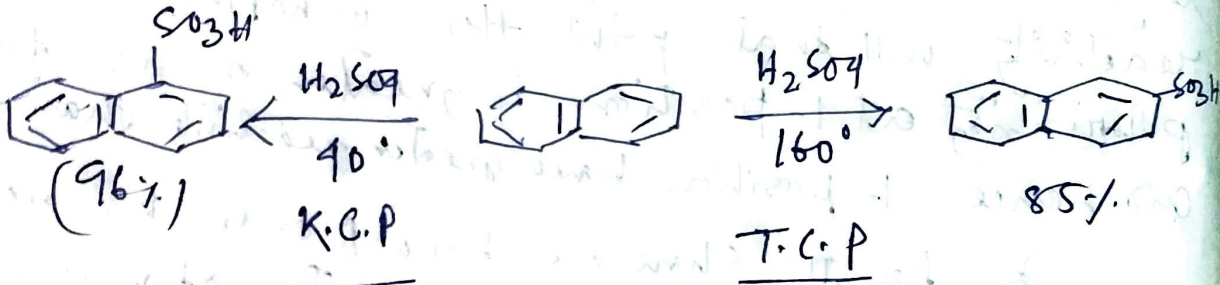
Friedel-Craft reaction of naphthalene :-



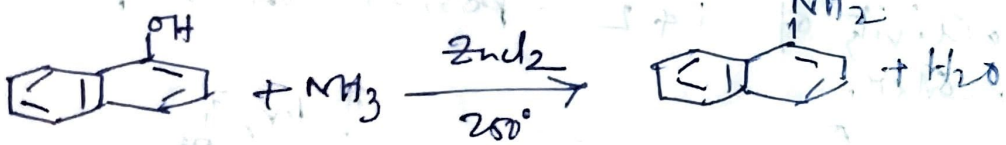




Naphthalenesulphonic acid :-



Some Reactions :-



Bucherer Reaction