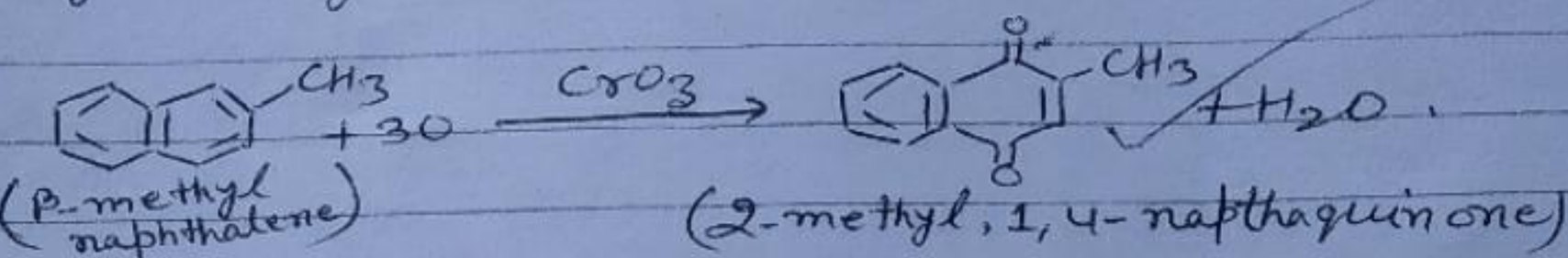
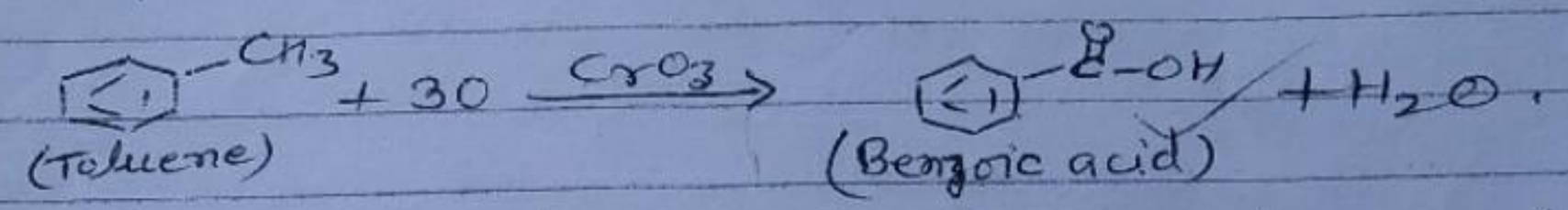
Benzene is not oxidised by these oxidising agent. A Comparative study can be observed by taking toluene and β-methyl naphthalene.



(β-methyl naphthalene) (2-methyl, 1, 4-napthaquinone)



(Toluene) (Benzoic acid)

These evidences clearly show the greater reactivity of naphthalene than benzene.

STRUCTURE

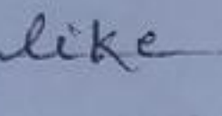
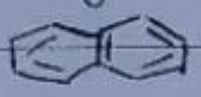
Structure of naphthalene follows from the following:-

(1) From elemental analysis, percentage composition, molecular weight determination, showed its molecular formula to be $C_{10}H_8$.

(2) From molecular formula, it appears to be a highly unsaturated compound, but the usual test of unsaturation are not given at all. i.e, it does not decolourised bromine water and alk. $KMnO_4$ solution. But it gives substitution reaction similar to those given by benzene, which is a closed chain compound. Hence, naphthalene has structural similarity to benzene.

(3) Naphthalene is oxidised by Conc. H_2SO_4 in presence of mercuric sulphate to give phthalic acid of known structure.

Thus, naphthalene contains a benzene ring with substituent in ortho-position.

④ Therefore we can tentatively represent naphthalene as— $C_6H_4\{C_4H_4\}$. which may have structure like  . But this compound would give all the tests of unsaturation. i.e, will decolourise dilute alk $KMnO_4$ solution and bromine water. Therefore this structure is discarded i.e, no such open side chain is present. If the Carbon-atoms are joint to form another benzene ring. The structure of naphthalene becomes  i.e, two benzene ring fused together and this explains why it does react with dilute $KMnO_4$ solution and bromine-water.

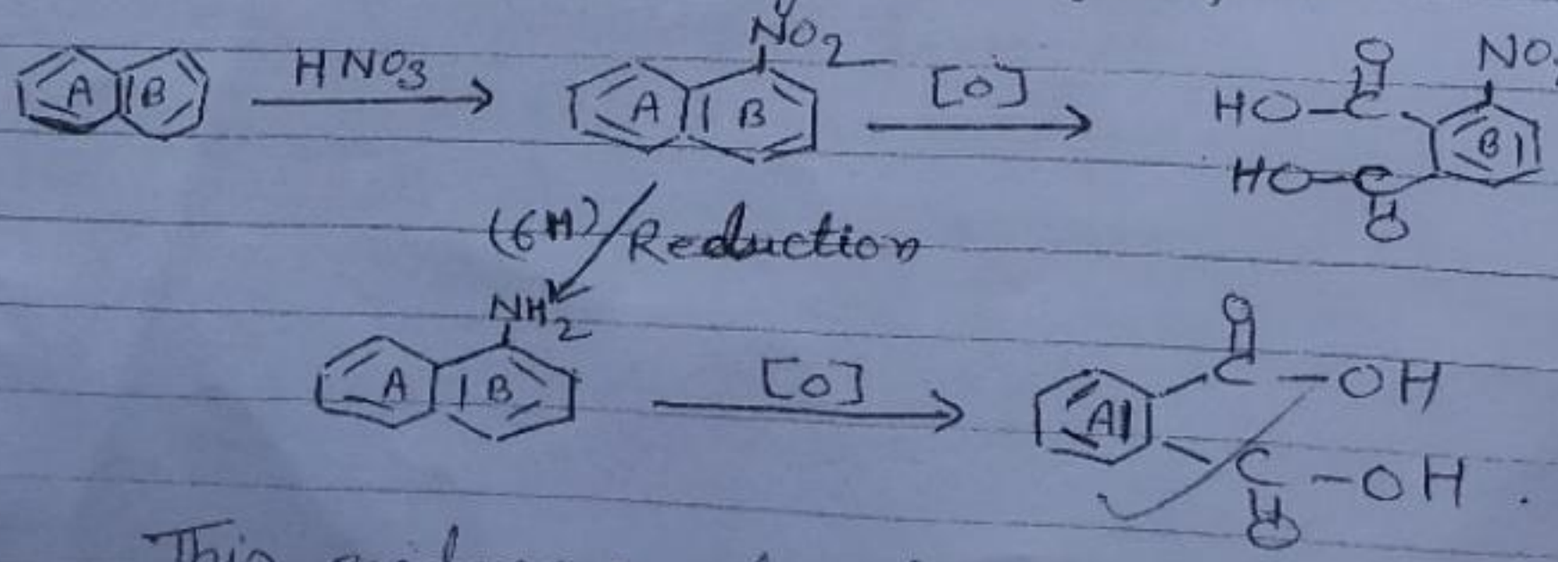
⑤ The presence of two benzene ring in naphthalene is proved by nitrating and subjecting the resulting compound to direct oxidation and next first reduction then oxidation.

$C_{10}H_8 \xrightarrow{\text{Nitration}} \underset{\text{nitro naphthalene}}{C_{10}H_7NO_2} \xrightarrow{[O]}$ Nitro phthalic acid

↓ Reduction

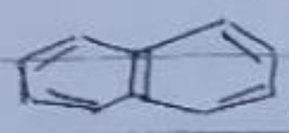
Amino phthalic acid $\xrightarrow{[O]}$ Phthalic acid.

Considering the above structure of naphthalene the reaction can be very well justified.



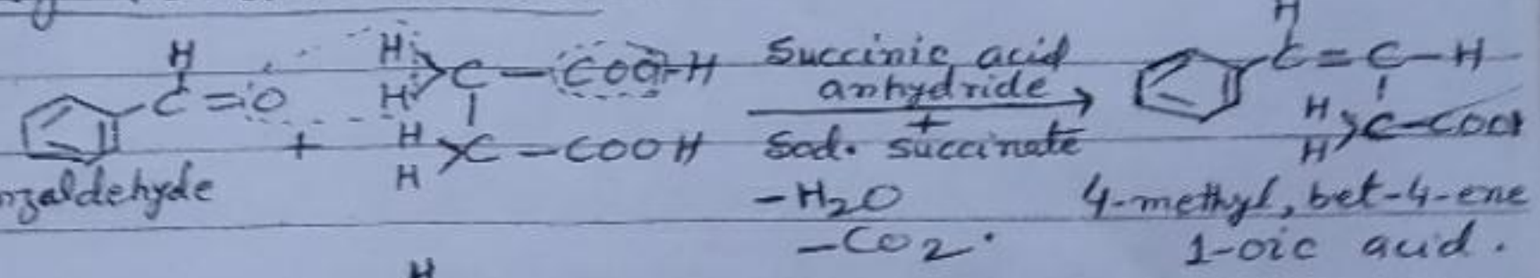
This evidences clearly proves the presence

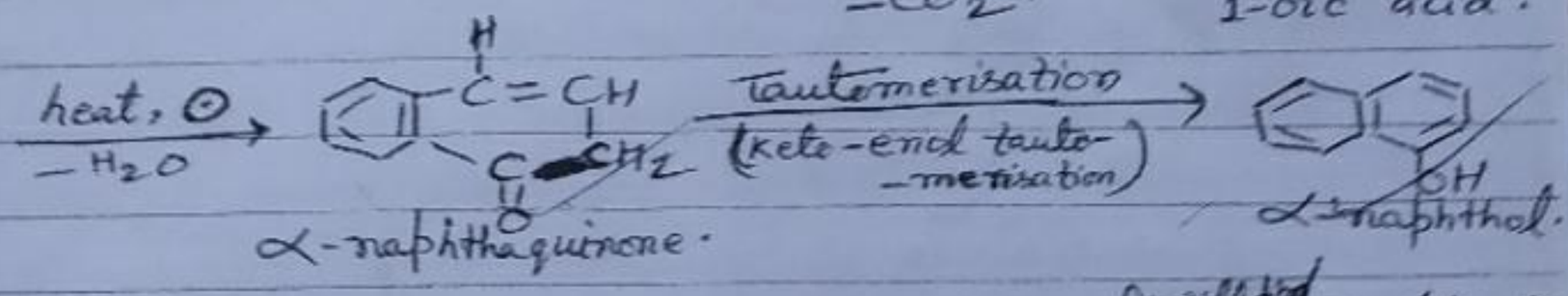
of two benzene ring in naphthalene fused together. Hence the structure of naphthalene is—



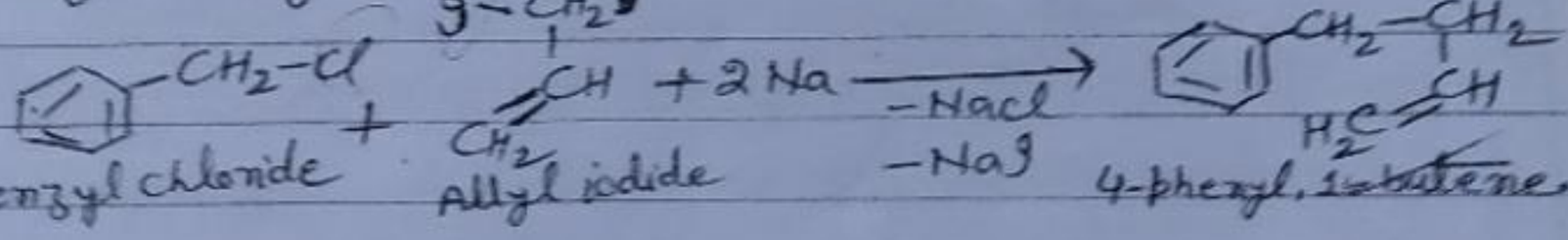
This structure is confirmed by synthesis:→

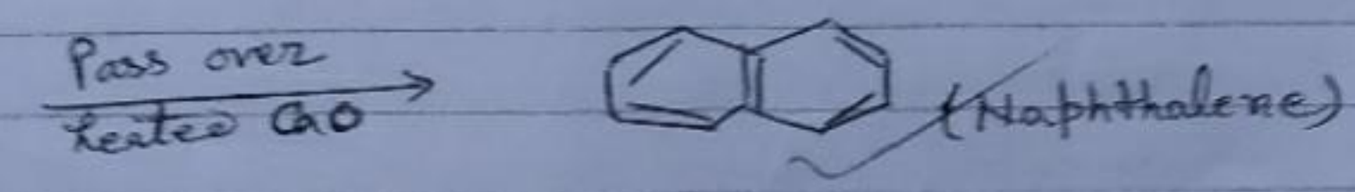
(i) By Perkin reaction:—



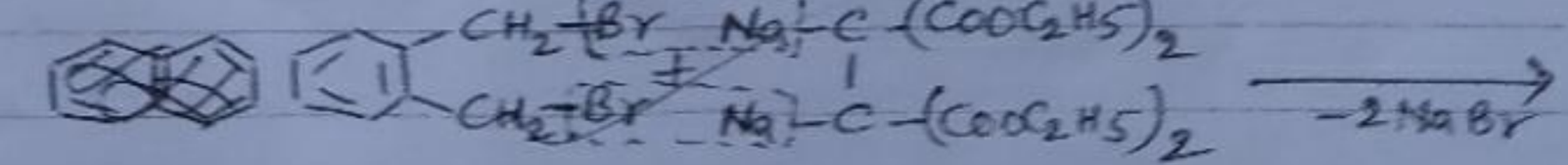


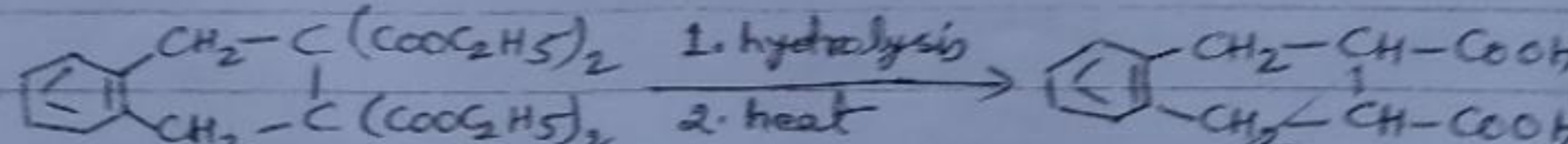
(ii) By Fittig reaction:→

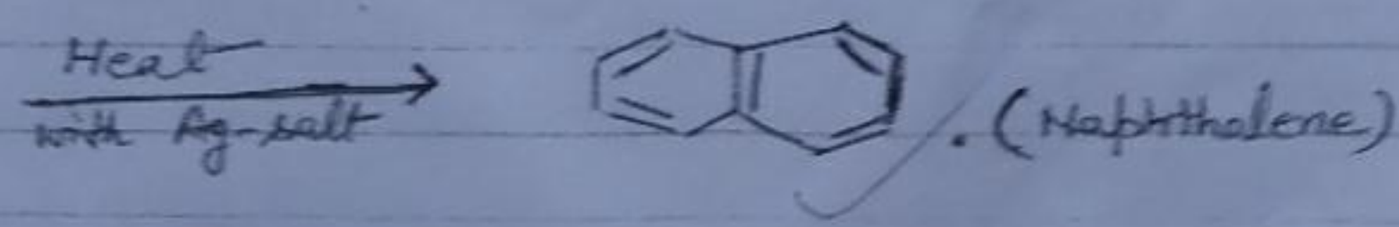




(iii) From ortho-xylene dibromide:→

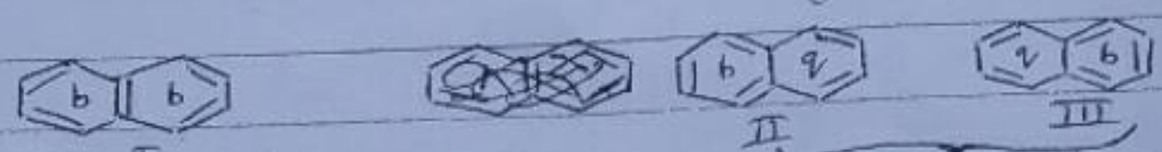






Position of double bond :→

The possible arrangement of single and double bond in naphthalene are represented by the structure — I , II and III .

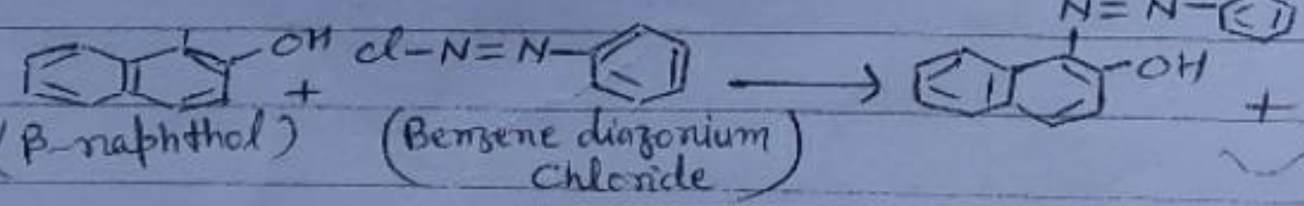


I
Symmetrical

II, III
Unsymmetrical

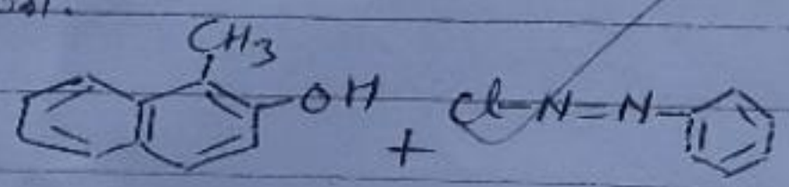
Naphthalene is actually a resonance hybrid of these structures, which is proved by X-ray electron defraction and dipole moment measurment. But II and III are ortho-quinonoidal structure. Quinones are far more reactive than a pure aromatic compound. According to 'Fries' the most stable arrangement of polynuclear hydrocarbon is that form which has maximum number of ring in benzenoid condition. Therefore, naphthalene tends to behave as a structure I, rather than II and III.

Chemical evidences (such as coupling and rearrangement) clearly show the fixation of double bond in naphthalene as shown in structure I. On reaction with benzene diazonium chloride - (α) β-naphthol couples at 1-position not at 3.

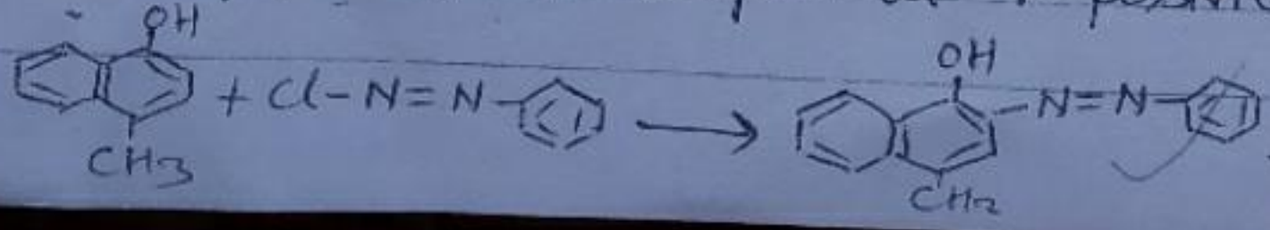


(β-naphthol) (Benzene diazonium Chloride)

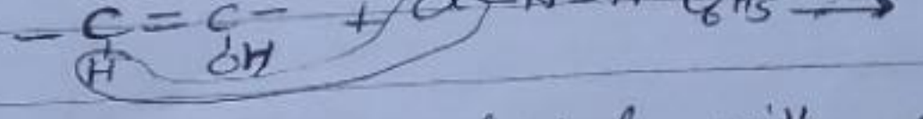
(b) 1-methyl, 2-naphthol fails to inter into coupling reaction.



(c) 4-methyl, α-naphthol couples at β-position.



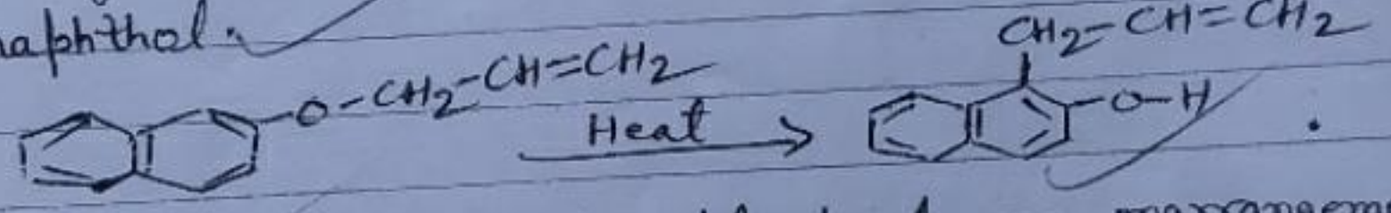
This interpretation gets further support from aliphatic enols having grouping $-CH=\underset{OH}{C}-$, which couples with $C_6H_5N_2Cl$ to give diazo compound.



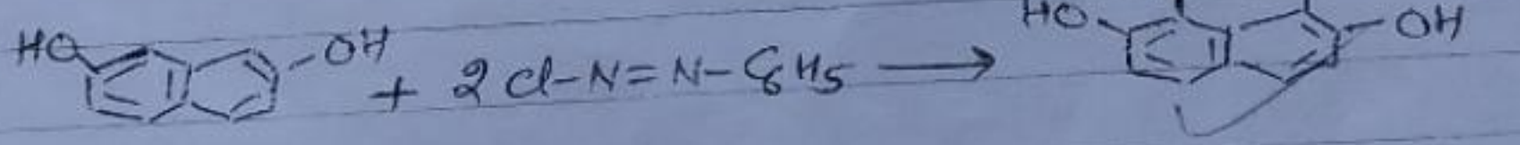
Where as alcohol with structure $-CH_2-\overset{OH}{CH}-$ donot. Therefore, diazo group can attack a position connected to a hydroxylated carbon-atom by double bond and not one by single bond.

This indicates that 1,2-carbon atoms are joint by a double bond and 2,3 by a single bond.

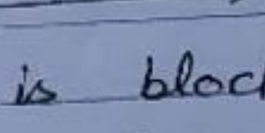
Rearrangement also favours the symmetrical structure i.e, β-naphthyl allyl ether gets rearranged itself on heating and affords 1-allyl β-naphthol.



If position 1 is blocked no rearrangement occures. The two rings of the symmetrical structure have the same bond character is proved by Coupling. 2,7-dihydroxy naphthalene with $C_6H_5N_2Cl$ in alkaline solution couples to give dye.



If 1,8-position is blocked by alkyl group no coupling occures. Hence, Structure of naphthalene is —



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Note:→ Orbital Picture of naphthalene is —