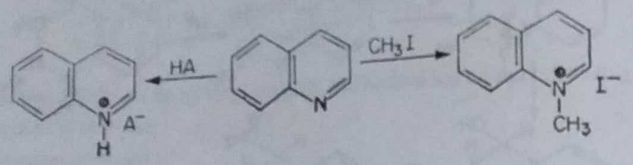
19.7.3 Structure, reactivity and orientation [See p. 812 (Sec. 17.4.4.f)]

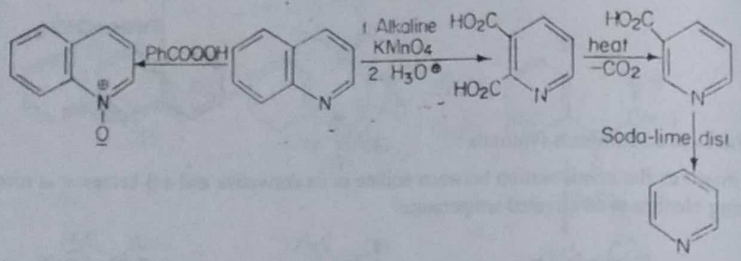
19.7.4 Chemical properties

Since quinoline is 2, 3-benzopyridine, it resembles pyridine in many of its reactions. Quinoline is also an aromatic compound containing delocalised 10 π-e's (Huckele number); again since pyridine ring of quinline is a deactivated one, it undergoes S_E as well as S_N reactions. As pyridine resembles nitrobenzene, quinoline resembles *a*-nitronaphthalene. However, quinoline is a basic compound, but it is less basic than pyridine. On this back ground let us discuss its main reactions as stated below :

(a) Basic character :

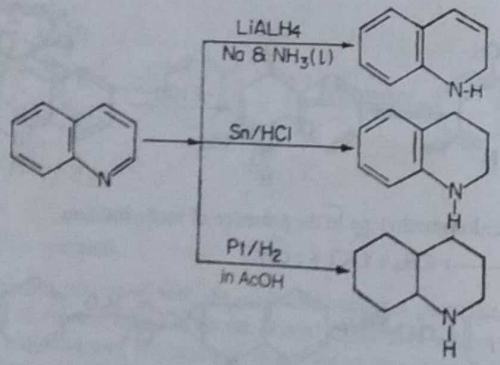


(b) Oxidation :

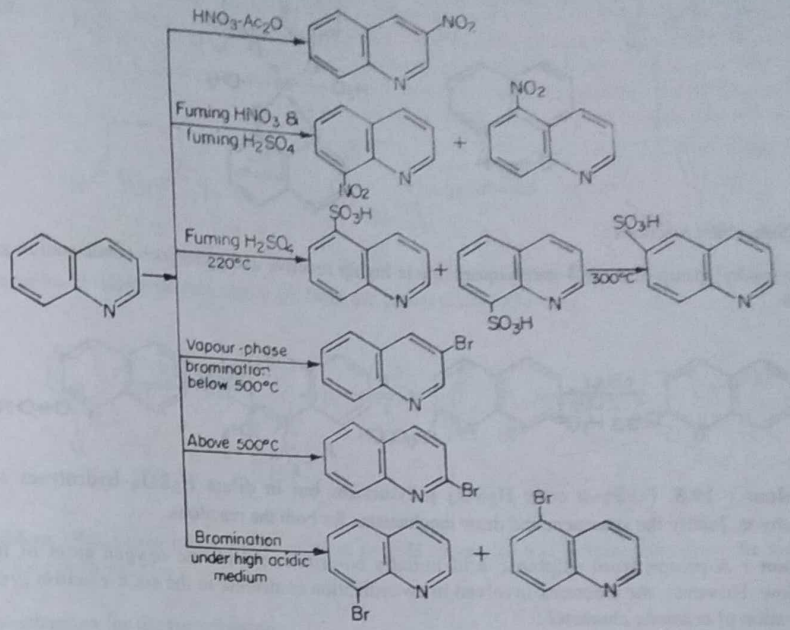


Pyridine ring in quinoline being deactivated, it is resistant to oxidation; for this reason, the benzene ring opens in this case. The sequential reactions written above show that quinoline contains a pyridine ring.

(c) Reduction :

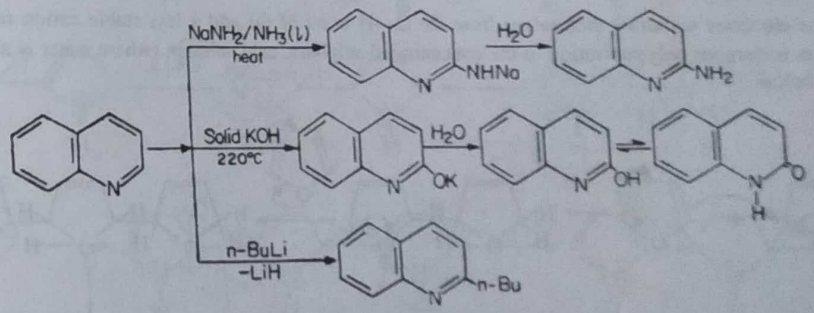


(d) Electrophilic substitution reactions :

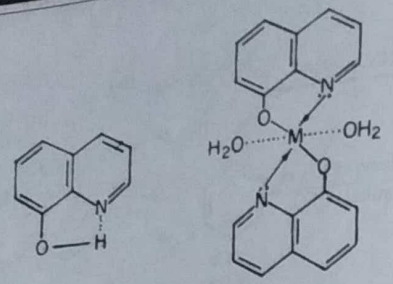


(e) Nucleophilic substitution reacitons :

Nucleophilic substitution reactions occur at 2-position if this position is blocked, the reaction occurs at 4-position.

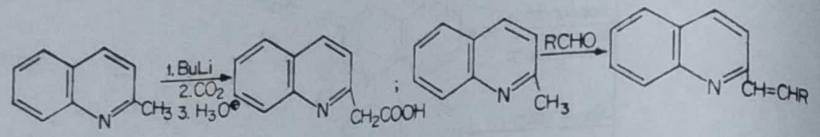


Note : 8-hydroxyquinoline is a chelated compound as shown below; it forms complex salts with magnesium, zinc, cadmium and other metals. These salts are used for gravimetric analysis.



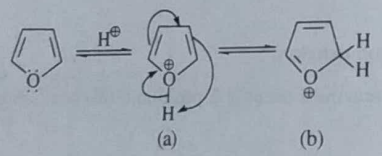
(f) Side-chain reactions :

The methyl group of 2- or 4-methylquinoline is highly reactive and undergoes condensation and other reactions.



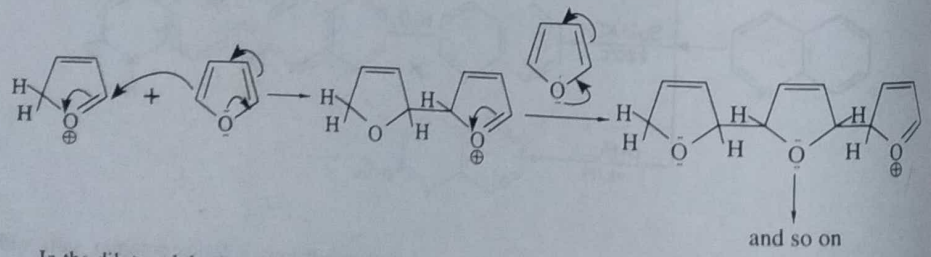
Problem : 19.5. Furan in conc H_2SO_4 polymerises but in dilute H_2SO_4 hydrolyses to form succinaldehyde. Justify the statement and draw mechanisms for both the reactions.

Solution : A proton from sulphuric acid initially co-ordinates with the oxygen atom of furan as shown below. However, the electrons involved in co-ordination contribute to the six π-electron system for the preservation of aromatic character :



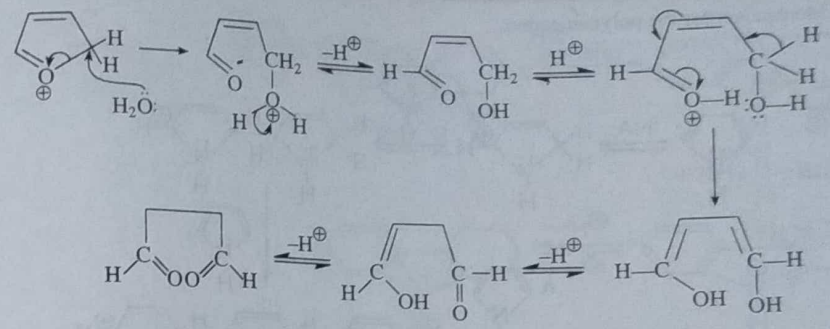
(a) (b)

The electrons withdraw themselves from the $\overset{\oplus}{O}$—H bond of (a) and a less stable cation forms (b). (b) them undergoes polymarisation in the concentrated sulphuric acid solution (where water is absent) as shown below :

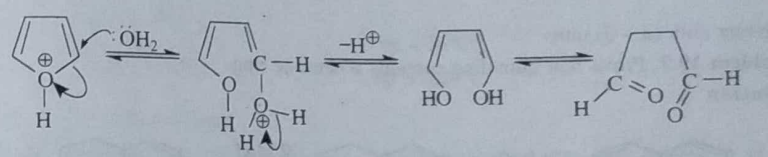


and so on

In the dilute sulphuric acid solution the unstable cation (b) is attacked by water at the methylene C and succinaidehyde is formed through several steps.



However succinaldehyde may also form from the cation (a) as follows :



Problem 19.6. In the mineral acid medium pyrrole trimerises and polymerises draw the mechanistic steps for the reactions.

a. Mechanism for the trimerisation :