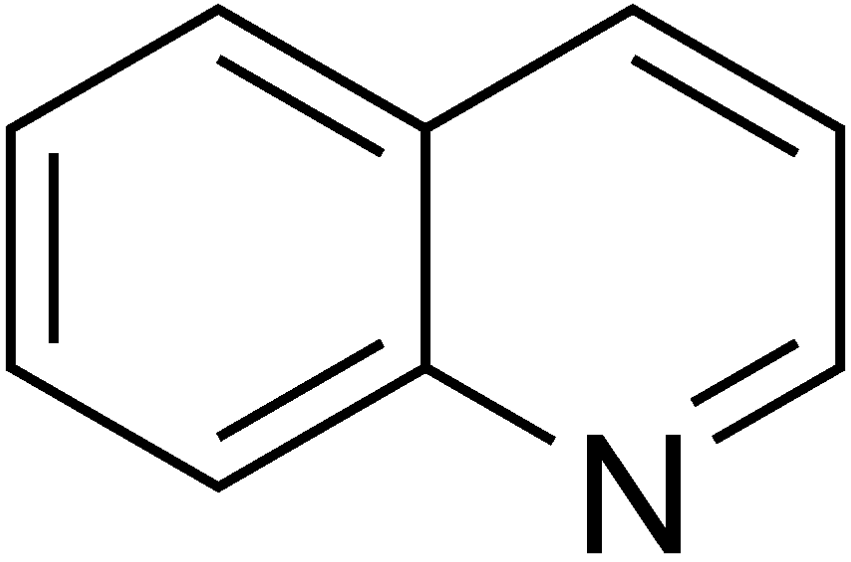
Preparation and Properties of Quinoline

Quinoline



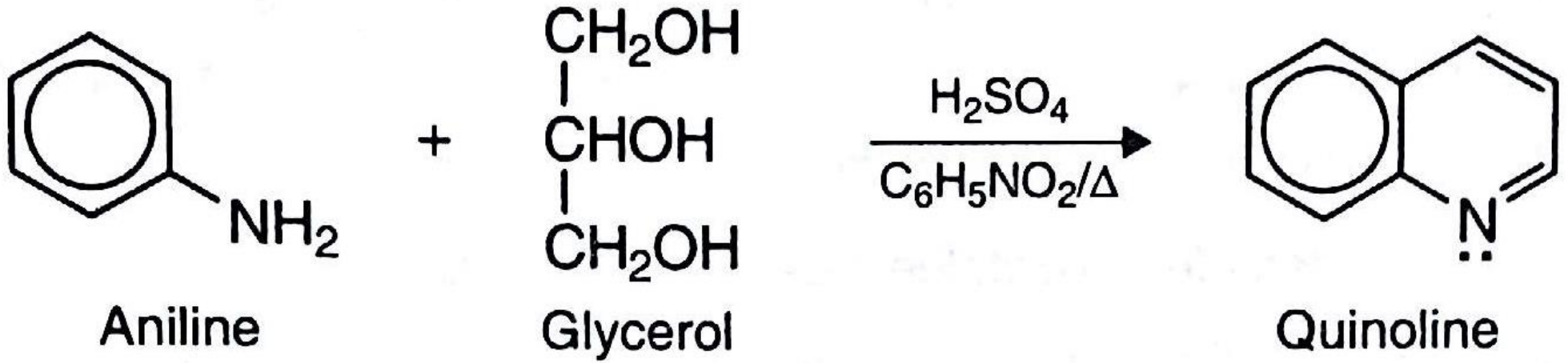
Quinoline consists of a benzene ring fused to the **Alpha and Beta** positions of a pyridine ring. It derives its name from the fact that it was first obtained by heating the famous **antimalarial alkaloid "*quinine*"**, with alkali.

Quinoline occurs in coal-tar, bone oil, and in *angostura* bark.

Preparation Methods

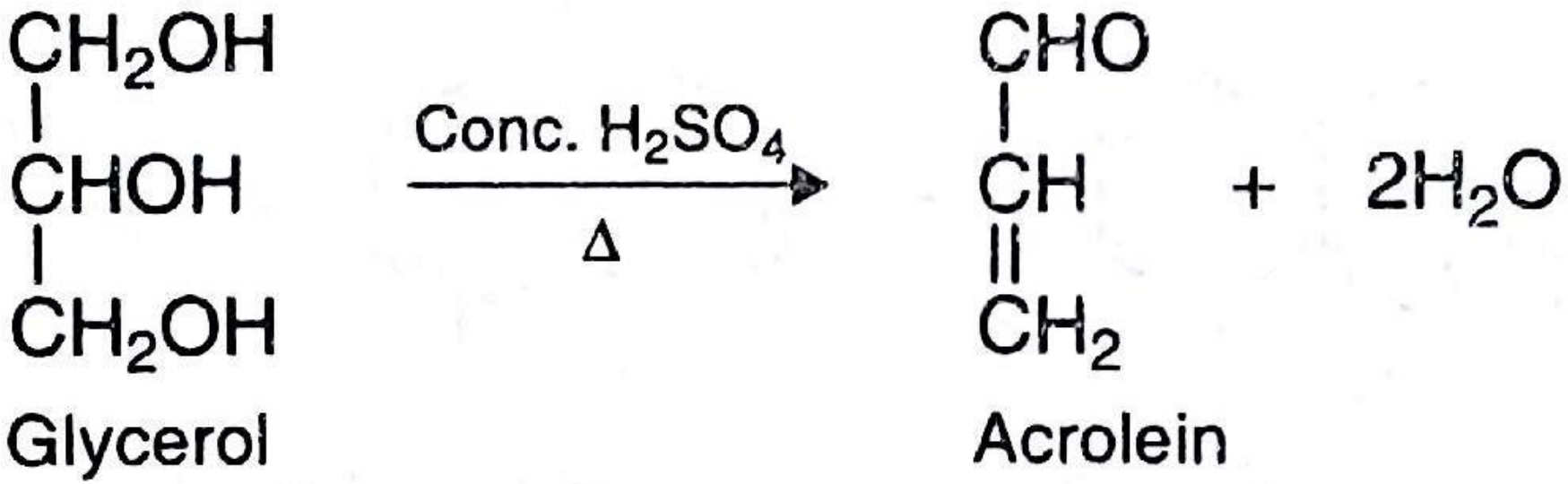
(1) By Skraup Synthesis: (Commercial method)

In this reaction, a mixture of aniline and glycerol is heated in the presence of sulphuric acid and a mild oxidizing agent, usually nitrobenzene or arsenic pentoxide. The reaction is exothermic and tends to become very violent. Ferrous sulphate or boric acid is generally added to make the reaction less violent.

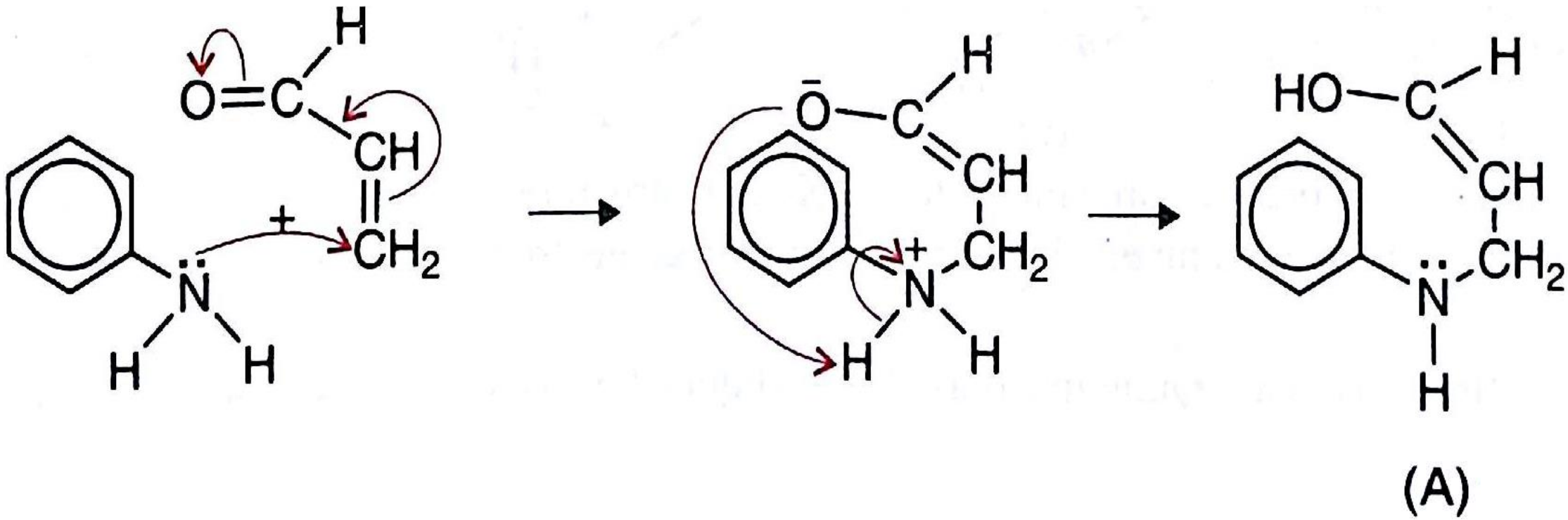


Mechanism

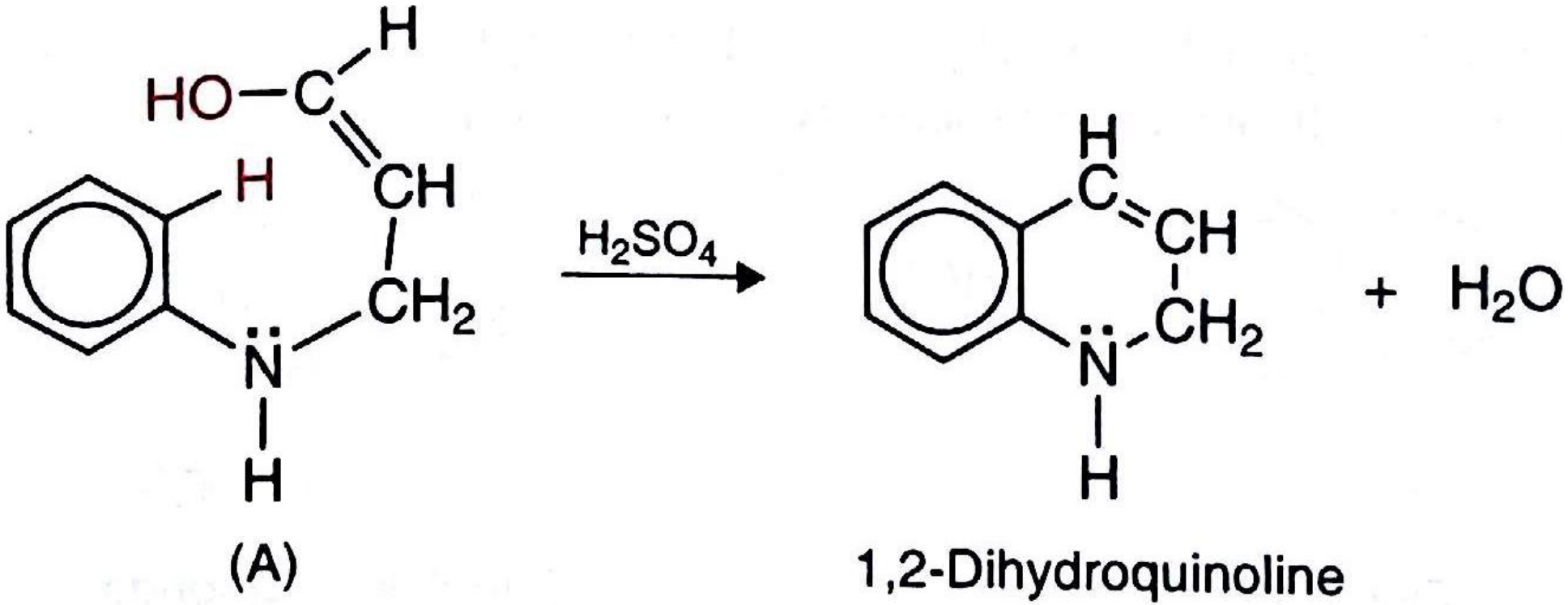
Step 1: Glycerol undergoes dehydration with sulphuric acid to give acrolein.



Step 2: Aniline adds to acrolein (1,4-addition) to give (A).



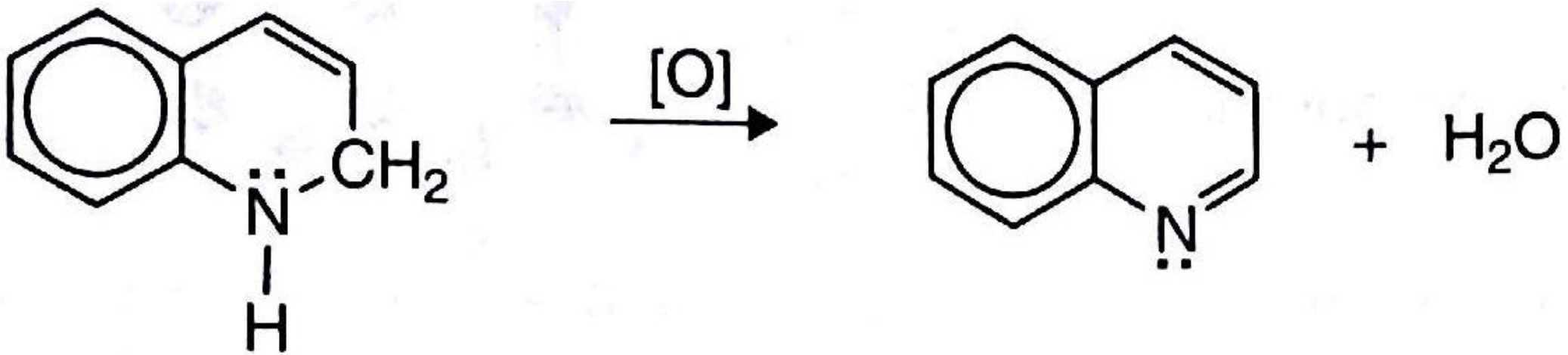
Step 3: Compound (A) Undergoes ring closure in the presence of sulphuric acid to form 1,2- dihydroquinoline.



(A)

1,2-Dihydroquinoline

Step 4: 1,2-Dihydroquinoline undergoes oxidation with nitrobenzene to finally yield quinoline. Nitrobenzene itself is reduced to aniline which is reused in step (2).

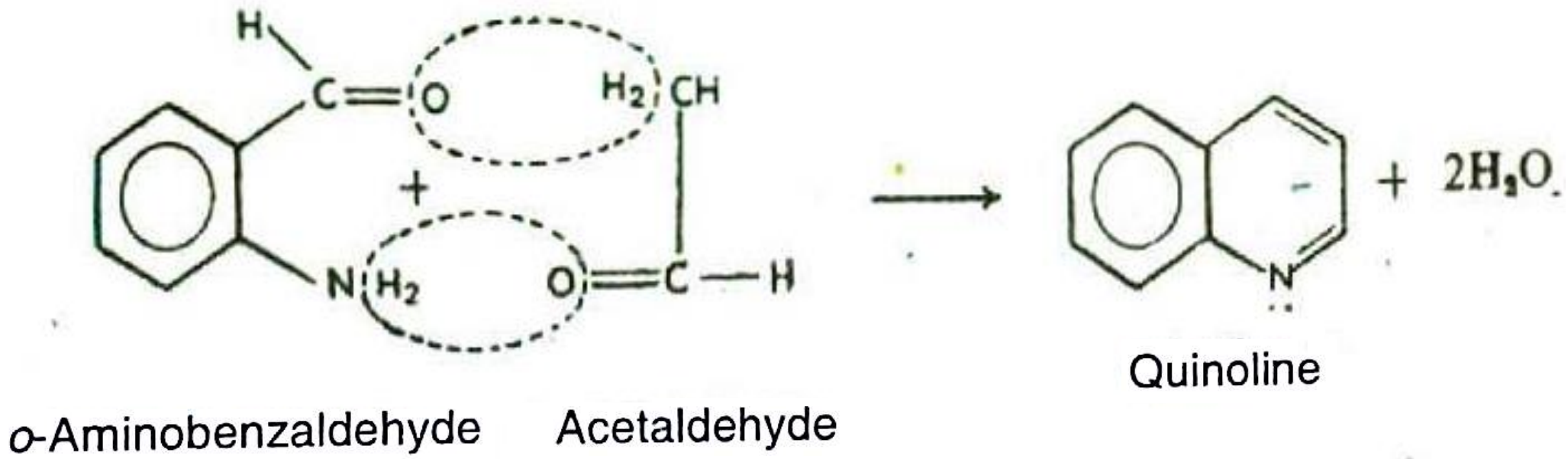


1,2-Dihydroquinoline

Quinoline

(2) By the Friedlander Synthesis:

This involves the condensation of o-aminobenzaldehyde with acetaldehyde in the presence of an alkali.



Physical properties of Quinoline

Quinoline is a colorless liquid,

Boiling Point is **237°C**

It turns yellow on standing, and has pyridine-like smell

Quinoline is miscible with most organic solvents, and dissolves in water to about **0-7 %** at room temperature

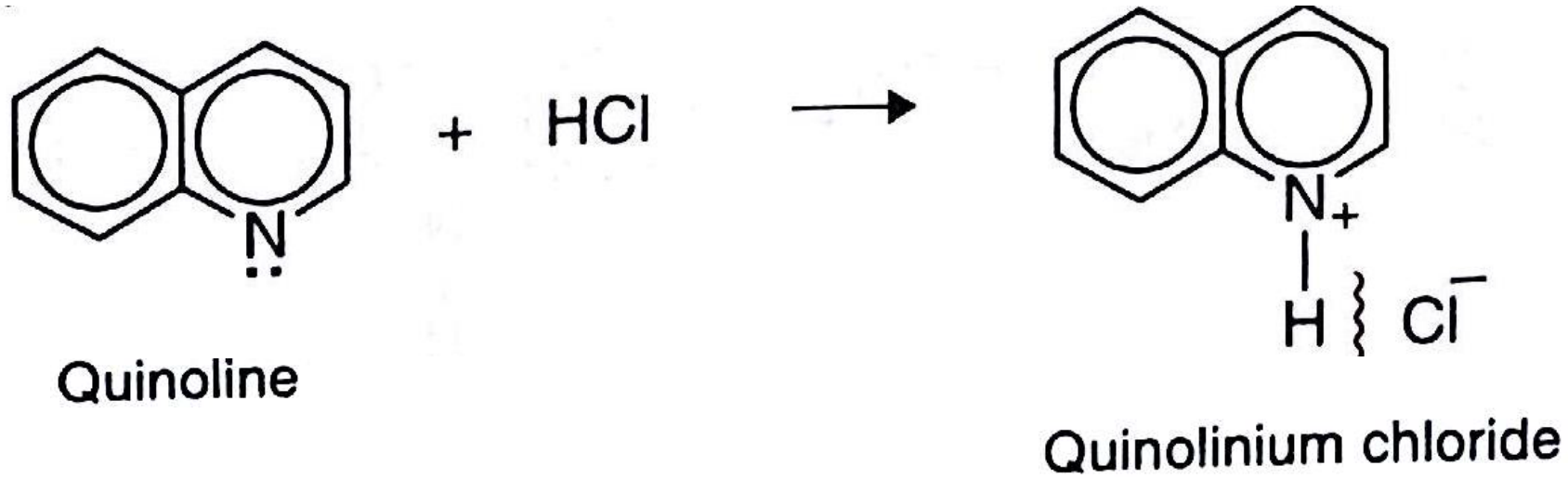
Chemical Properties

1. Basic character
2. Electrophilic Substitution Reaction (at C-5, and C-8)
3. Nucleophilic Substitutions Reaction (C-2 or at C-4 if C-2 is blocked)
4. Oxidation
5. Reduction
6. Reaction with alkyl halides

Chemical properties of Quinoline

Basic Character:

Quinoline is a slightly weaker base. It reacts with acids to yield salts which are sparingly soluble in water.



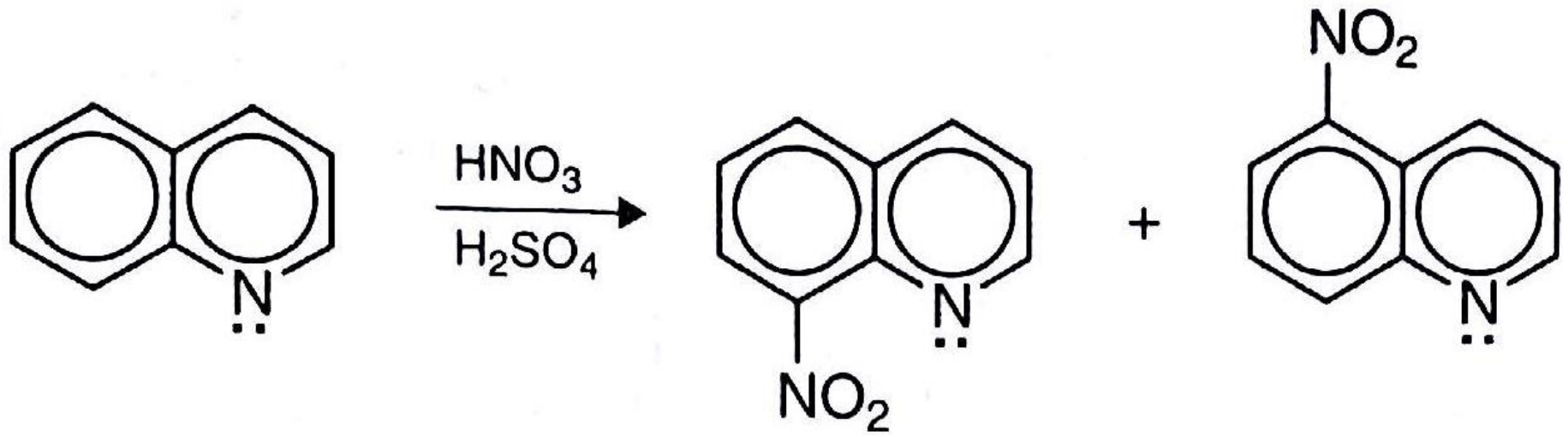
Quinoline

Quinolinium chloride

Electrophilic Substitutions

Quinoline undergoes electrophilic substitution reactions only under vigorous conditions. Substitution occurs at C-8 and C-5.

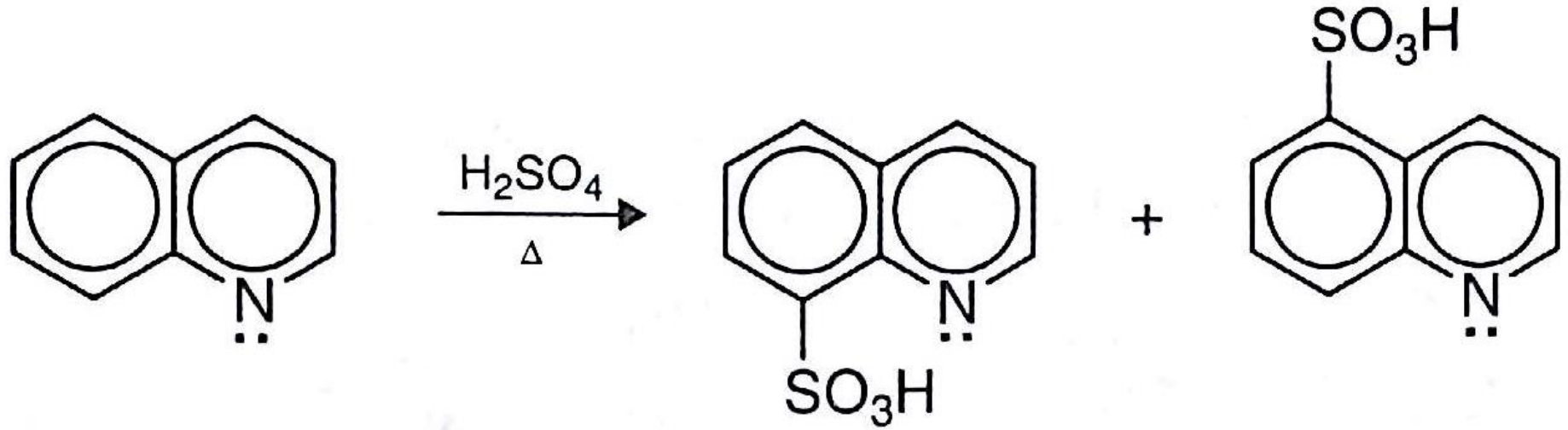
a) Nitration: Quinoline undergoes nitration with fuming nitric acid in the presence of fuming sulphuric acid to give a mixture of 8-nitroquinoline and 5-nitroquinoline.



Quinoline

8- and 5-Nitroquinoline

(b) Sulphonation: Quinoline may be sulphonated with fuming sulphuric acid at 220°C to yield a mixture of quinoline-8-sulphonic acid and quinoline-5-sulphonic acid.



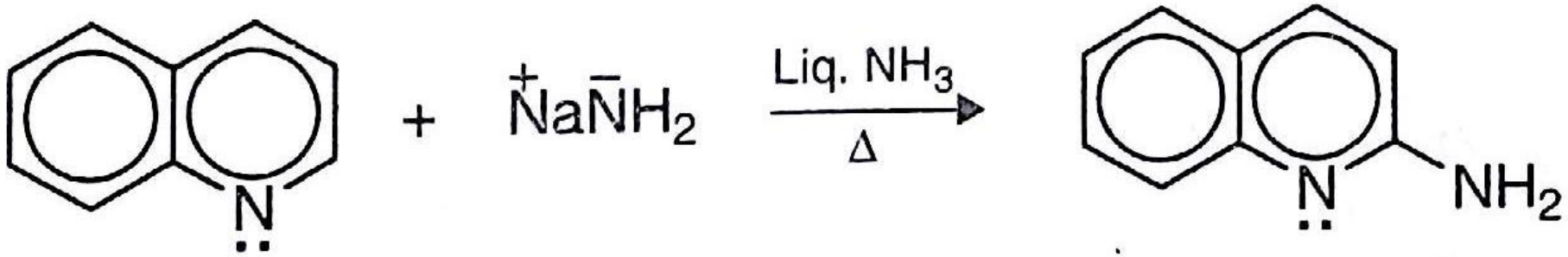
Quinoline

8- and 5-Quinolinesulfonic acid

(3) Nucleophilic Substitutions

Quinoline also undergoes nucleophilic substitution reactions. Substitution occurs at C-2 (or at C-4 if C-2 is blocked).

(a) **Reaction with Sodamide:** Quinoline reacts with sodamide in liquid ammonia at about 100°C to form 2-aminoquinoline.

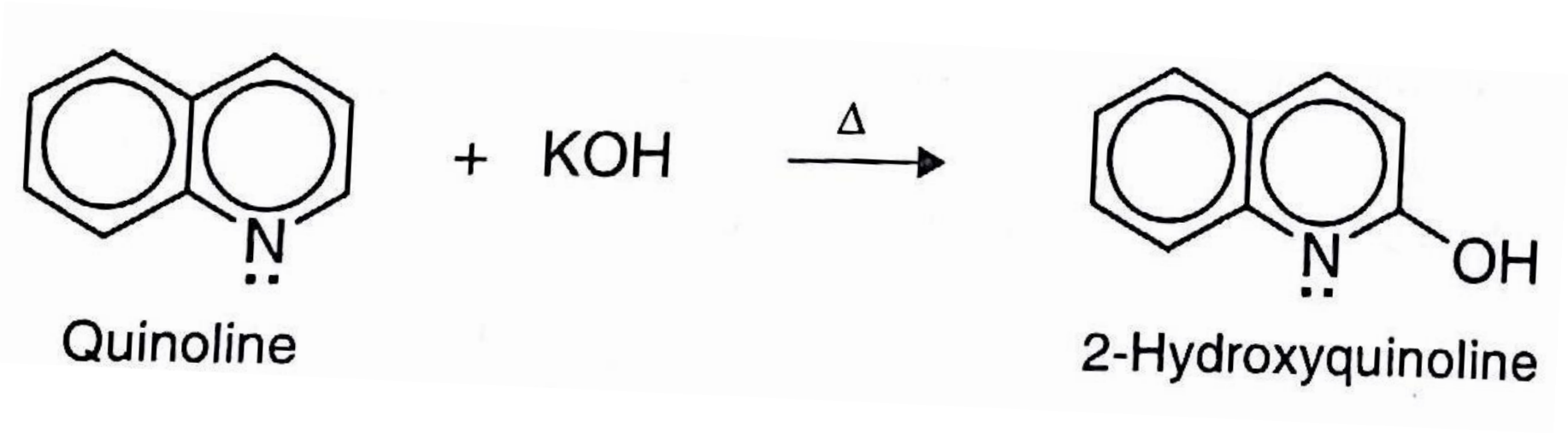


Quinoline

2-Aminoquinoline

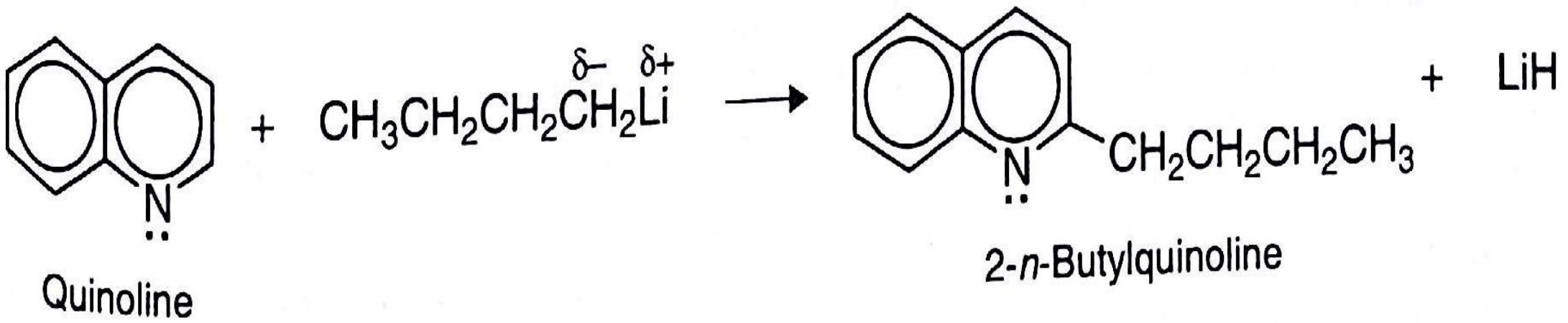
(b) Reaction with Potassium Hydroxide.

Quinoline reacts with potassium hydroxide at 220°C to give 2-hydroxyquinoline.



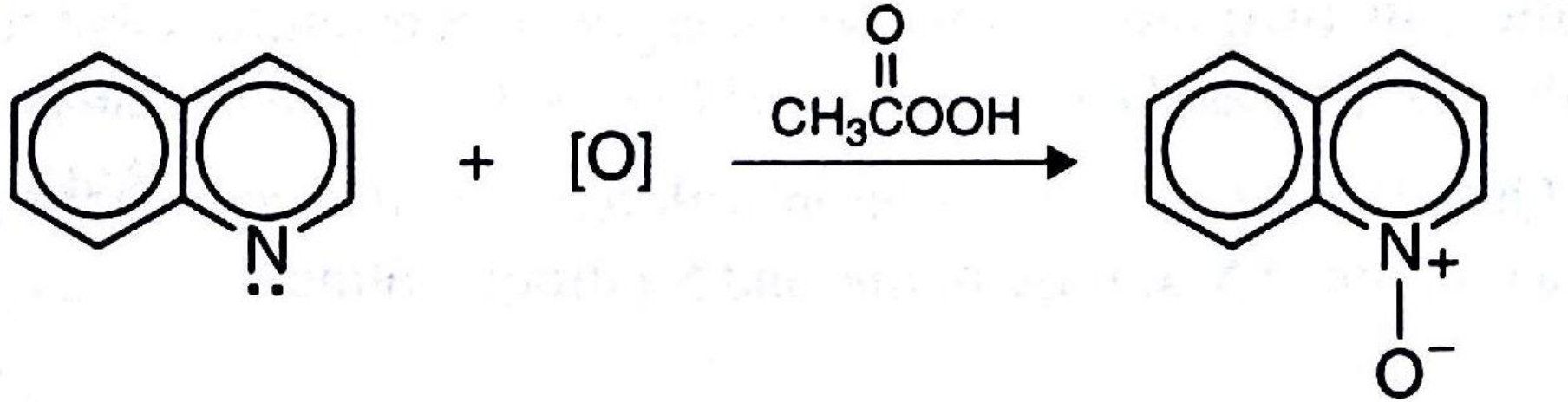
(c) Reaction with n-Butyl-lithium

Quinoline reacts with n-butyl-lithium to yield 2-n-butylquinoline.



(4) Oxidation.

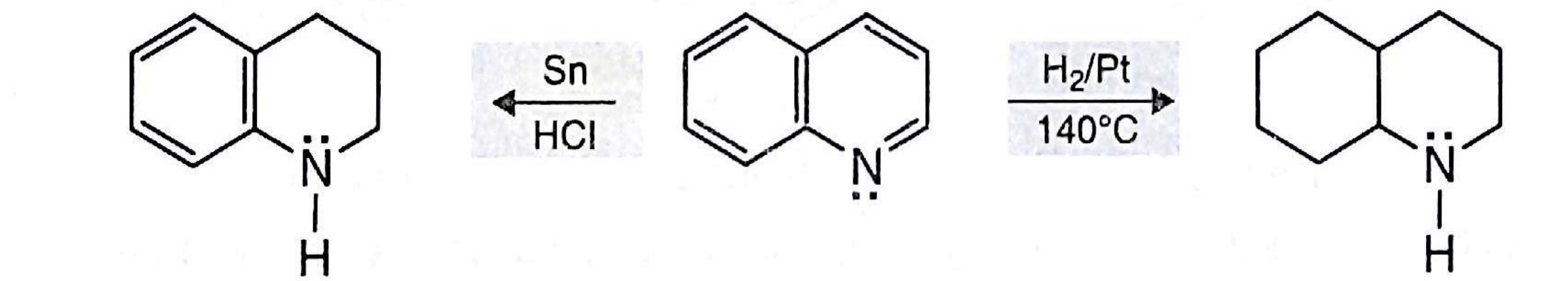
Quinoline is oxidized by peracetic acid to give quinoline-N-oxide



Quinoline

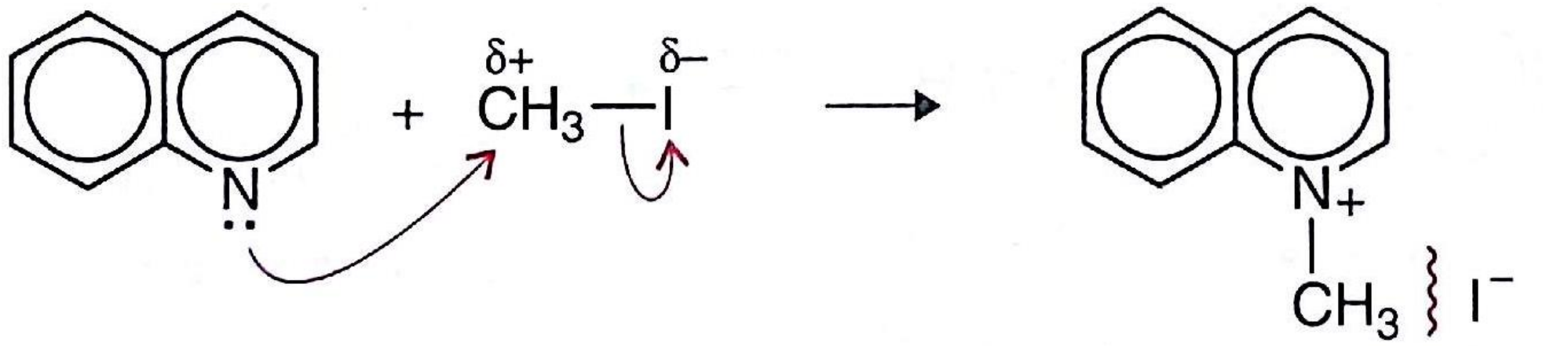
Quinoline-*N*-oxide

(5) Reduction: Mild reduction of quinoline with tin and hydrochloric acid gives 1,2,3,4-tetrahydroquinoline. Whereas, reduction with hydrogen and platinum catalyst produces decahydroquinoline.



(6) Reaction with alkyl halides:

Quinoline give *N*-alkylquinolinium halides by reacting with alkyl halides. For example, with methyl iodide it give *N*-methylquinolinium halide



Quinoline

N-Methylquinolium iodide
(1-Methylquinolium iodide)