application.

9.3.2 Classification According to Chemical Structure

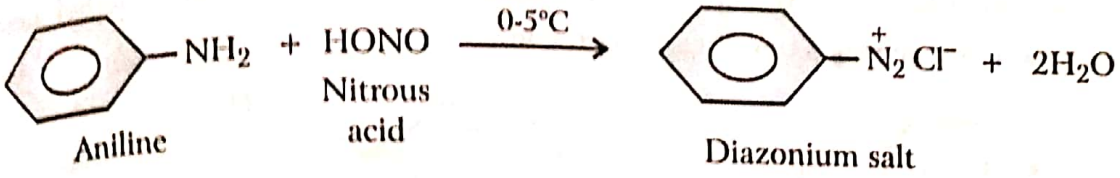
1. **Azo Dyes:** The azo dyes represent the largest and the most significant group of dyes. These are, characterized by the presence of one or more azo groups (—N ═ N —). These azo groups form bridges between two or more benzene or in general aromatic rings. In the resulting dyes an aromatic system joined to the azo group is a chromophore and the OH group or NH_2 an auxochrome.

Preparation of azo dyes involves the following two steps:

Step 1: Conversion of primary aromatic amines into diazonium compounds by treatment with sodium nitrite in excess hydrochloric acid at a low temperature. This process is known as diazotisation.

$$NaNO_2 + HCl \longrightarrow HONO + NaCl$$

Sod. nitrite — Nitrous acid

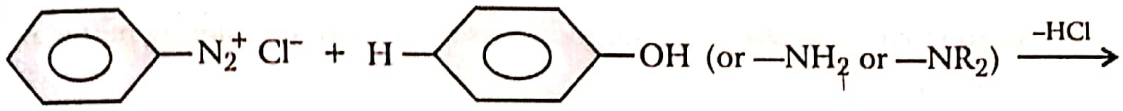


Aniline — Diazonium salt

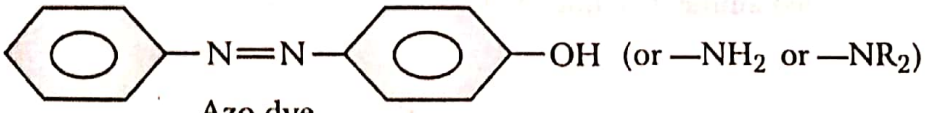
Step 2: Coupling of diazonium compounds can be achieved in two frequently observed ways

(i) Coupling with phenols, naphthols and other aromatic alcohols. Such a coupling reaction with phenols and naphthols is carried out in basic solution.

(ii) The second method is coupling with anilines and other aromatic amines. It is again important to know that unlike coupling with phenols, these coupling reactions with amines are carried in weakly acidic medium.



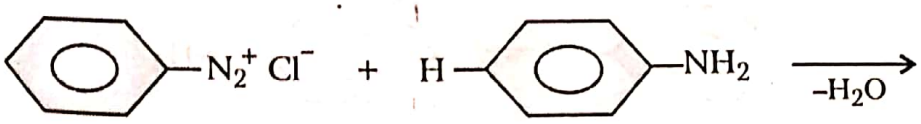
Diazonium salt — Phenol



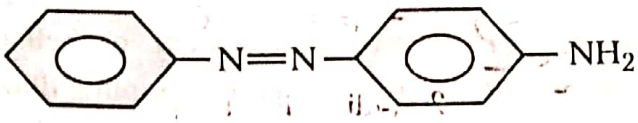
Azo dye

All these reactions are carried out at low temperatures (0–5°C). The low temperature is maintained to lessen the high reactivity of diazonium compounds.

(a) **Aniline Yellow:** It is p-aminoazobenzene. Aniline yellow is the simplest azo dye and is obtained by coupling benzene diazonium salt with aniline in acidic medium.



Benzene diazonium salt — Aniline

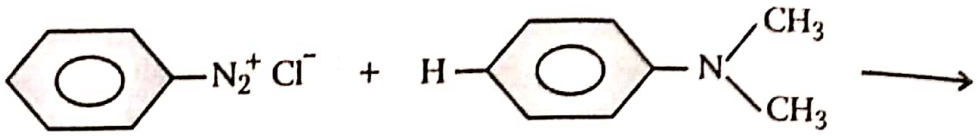


p-aminoazobenzene

(ANILINE YELLOW)

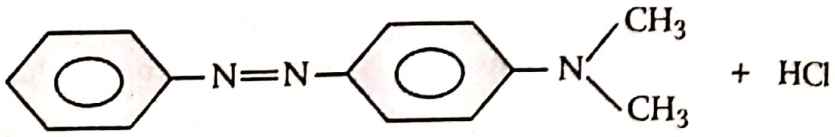
Aniline yellow is used as a dye for oils and lacquers and is also an intermediate for other dyes.

(b) **Butter Yellow:** The chemical formula is p-N,N-dimethylaminoazobenzene. It is obtained by coupling benzene diazonium chloride with N, N-dimethyl aniline, reaction medium is once again kept acidic.



Benzene diazonium salt

N,N-dimethyl aniline

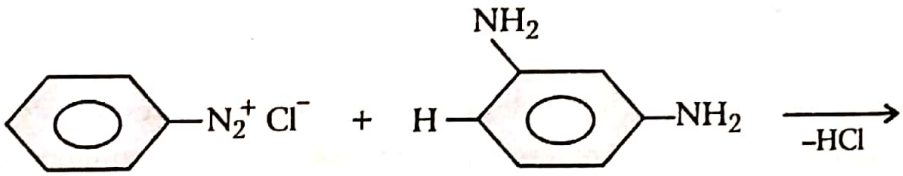


p-N, N-Dimethylaminoazobenzene

(BUTTER YELLOW)

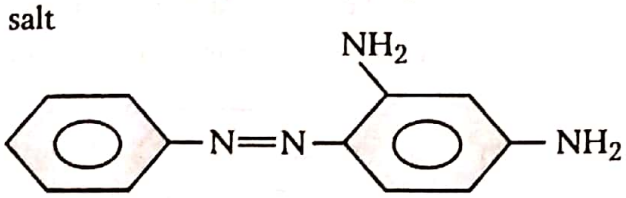
Butter yellow, as the name suggests, has been used for coloring butter, margarine and oils.

(c) **Chrysoidine:** The chemical composition is 2,4-diaminoazo -benzene. Chrysoidine is prepared by coupling benzene diazonium chloride with m-phenylenediamine in acidic medium.



Benzene diazonium salt

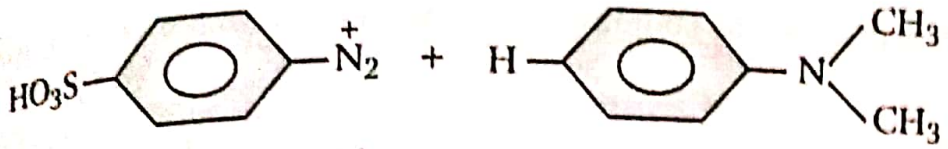
m-phenylene diamine



2, 4-diaminoazobenzene

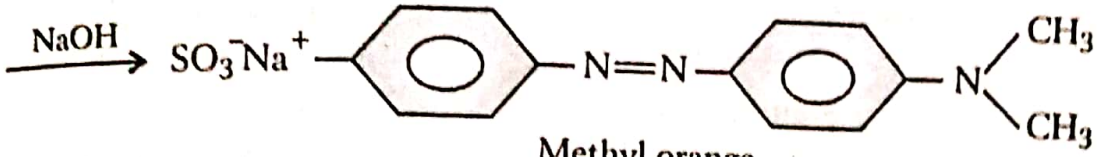
(CHRYSOIDINE)

(d) **Methyl Orange:** It is prepared by treatment of helianthine with sodium hydroxide, whereas helianthine is obtained by coupling diazotised sulfanilic acid with N, N-dimethylaniline. Methyl orange is not used for dyeing textiles because it is too reactive towards acids. It is mostly used as an indicator in acid-base titrations. As a matter of fact, it is used to detect the end point of the acid base titration reactions in the acidic range (3.1-4.4).



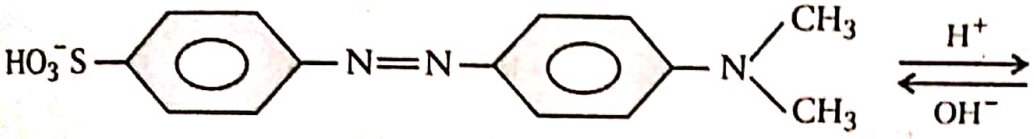
diazotized sulfanilic acid

N,N-dimethyl aniline

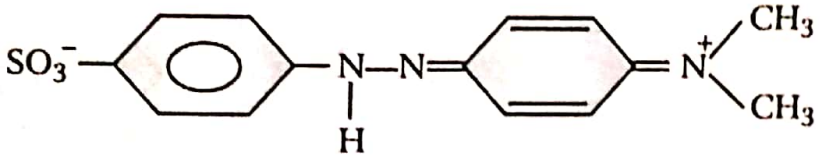


Methyl orange

It is yellow in basic solutions (above pH 4.4), while red in acidic solution (below pH 3.1). This change in the color is attributed to change in the structure of its ion.Under alkanline conditions the ion contains the azo chromophore, while under acidic conditions it contains p-quinoid chromophore.

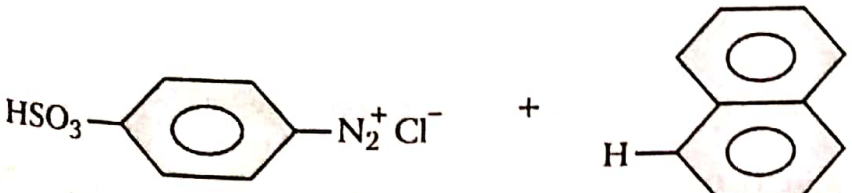


Yellow in basic solution (azo chromophore)



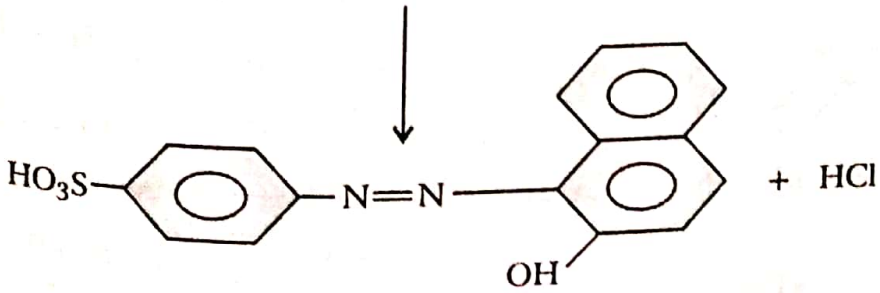
Red in acid solution (p-quinoid chromophore)

(e) **Orange II:** It is obtained by coupling diazotized sulfanilic acid with β-naphthol in basic medium.



Diazotized sulfanilic acid

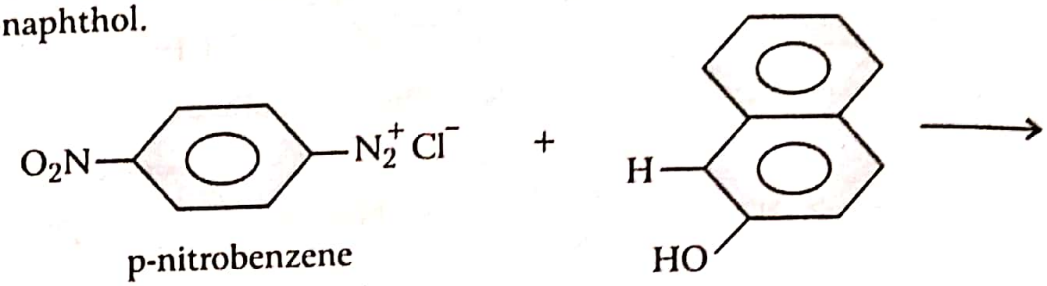
β-naphthol



Orange II

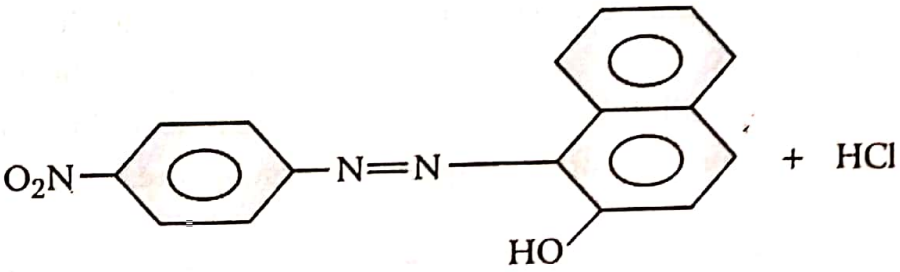
Orange II is used to dye wool, silk, nylon, paper and leather.

(f) **Para Red:** It is prepared by coupling p-nitrobenzenediazonium chloride with beta β -naphthol.



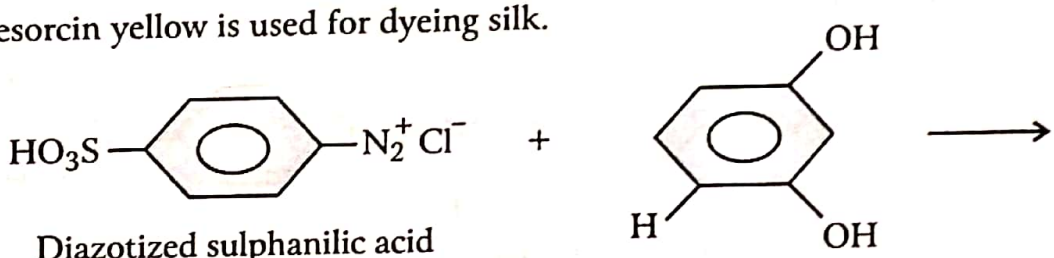
p-nitrobenzene diazonium chloride

β-naphthol



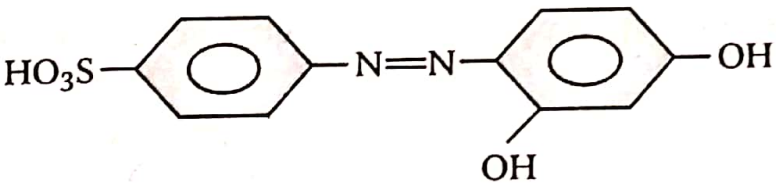
Para red

(g) **Resorcin Yellow:** It is made by coupling diazotized sulfanilic acid with resorcinol. Resorcin yellow is used for dyeing silk.



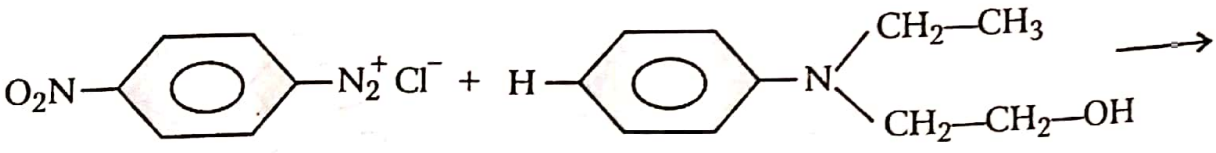
Diazotized sulphanilic acid

Resorcinol



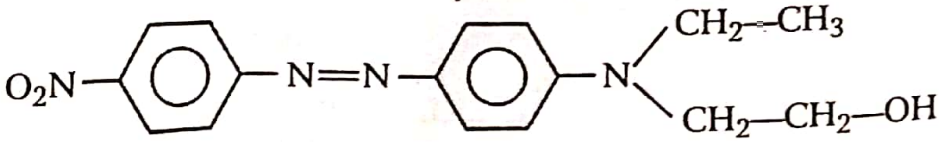
Resorcin yellow

(h) **Disperse Red 1:** Disperse red 1 is used for dyeing nylon, polyesters cellulose acetates and plastics. It is obtained by coupling p-nitrobenzenediazonium chloride with N-ethyl-N- (β-hydroxyethyl) aniline in acidic medium.



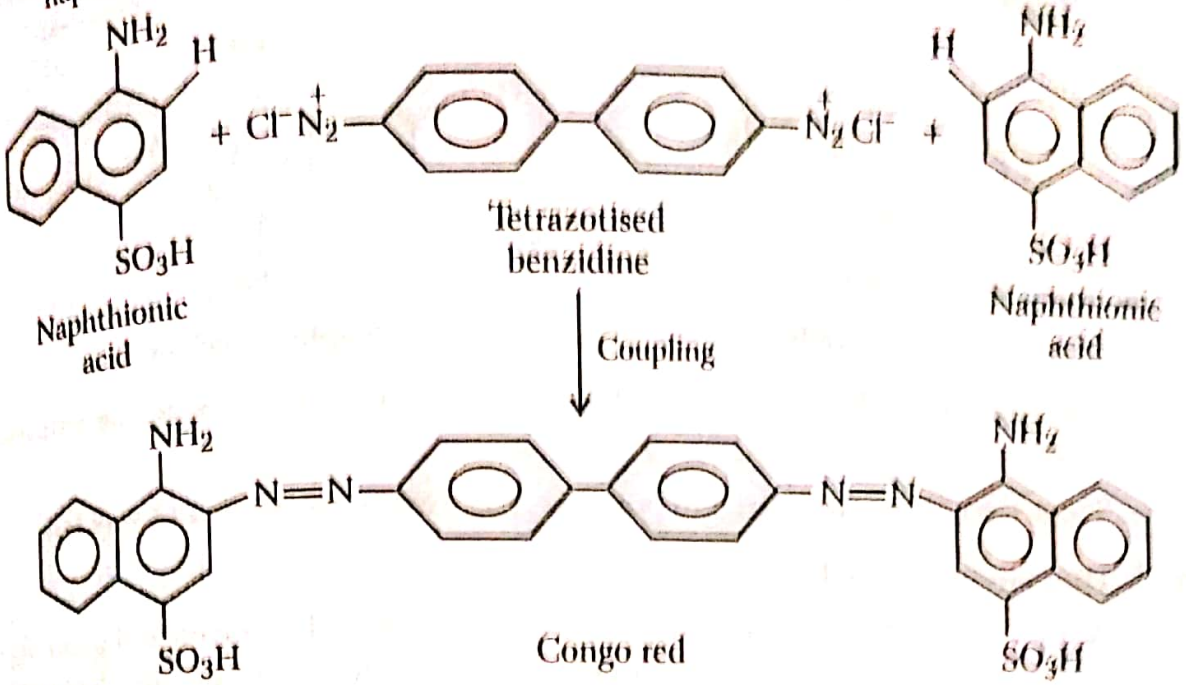
p-nitro benzene diazonium salt

N-ethyl-N-(β-hydroxy ethyl) aniline



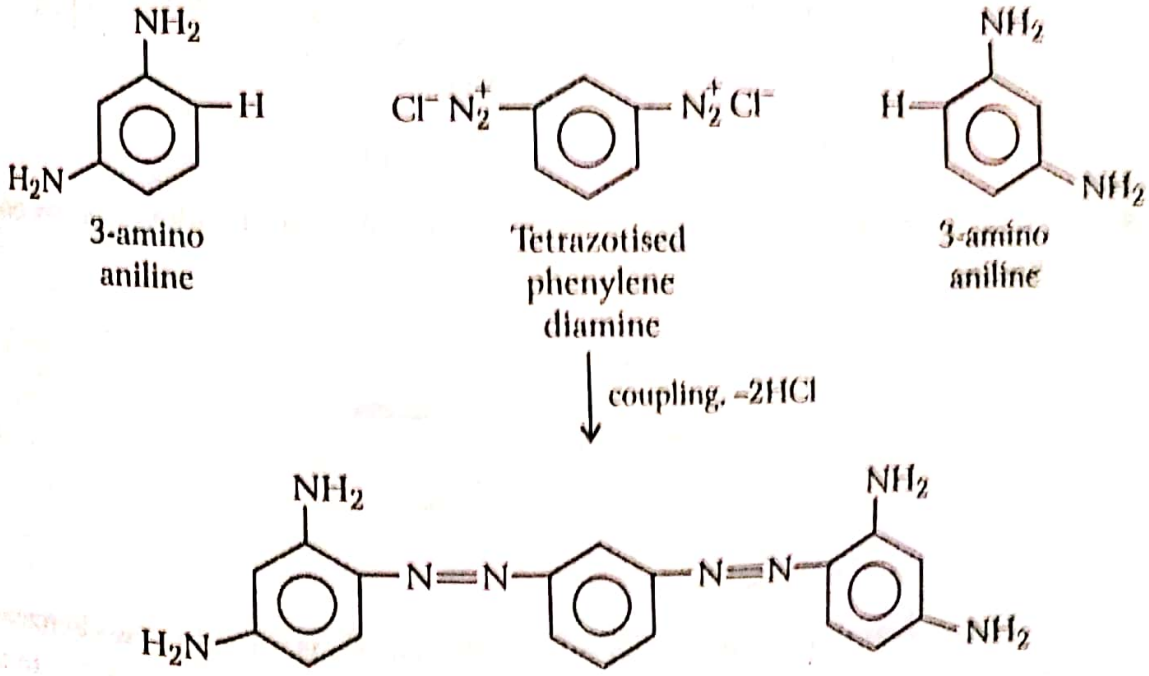
Disperse red I

(i) **Congo Red:** It is a diazo dye. It means, the dye molecule contains two azo groups. Congo red is made by coupling tetrazotised benzidine with two molecules of naphthionic acid.



Congo red is not a good dye for textiles. It is because the color change upon addition of an acid. However, it used to be an important stuff for dyeing paper in the past. Congo red is used as an indicator. It is blue in acidic solutions (below pH 3) and red in solutions above *pH* value 3.

(j) **Bismarck Brown:** It is also a diazo dye. Bismarck brown is obtained by coupling tetrazotised m-pheonylenediamine with two molecules of *m*-phenylenediamine.



Bismark brown

Bismarck brown is used for dyeing leather, wool, and cotton.