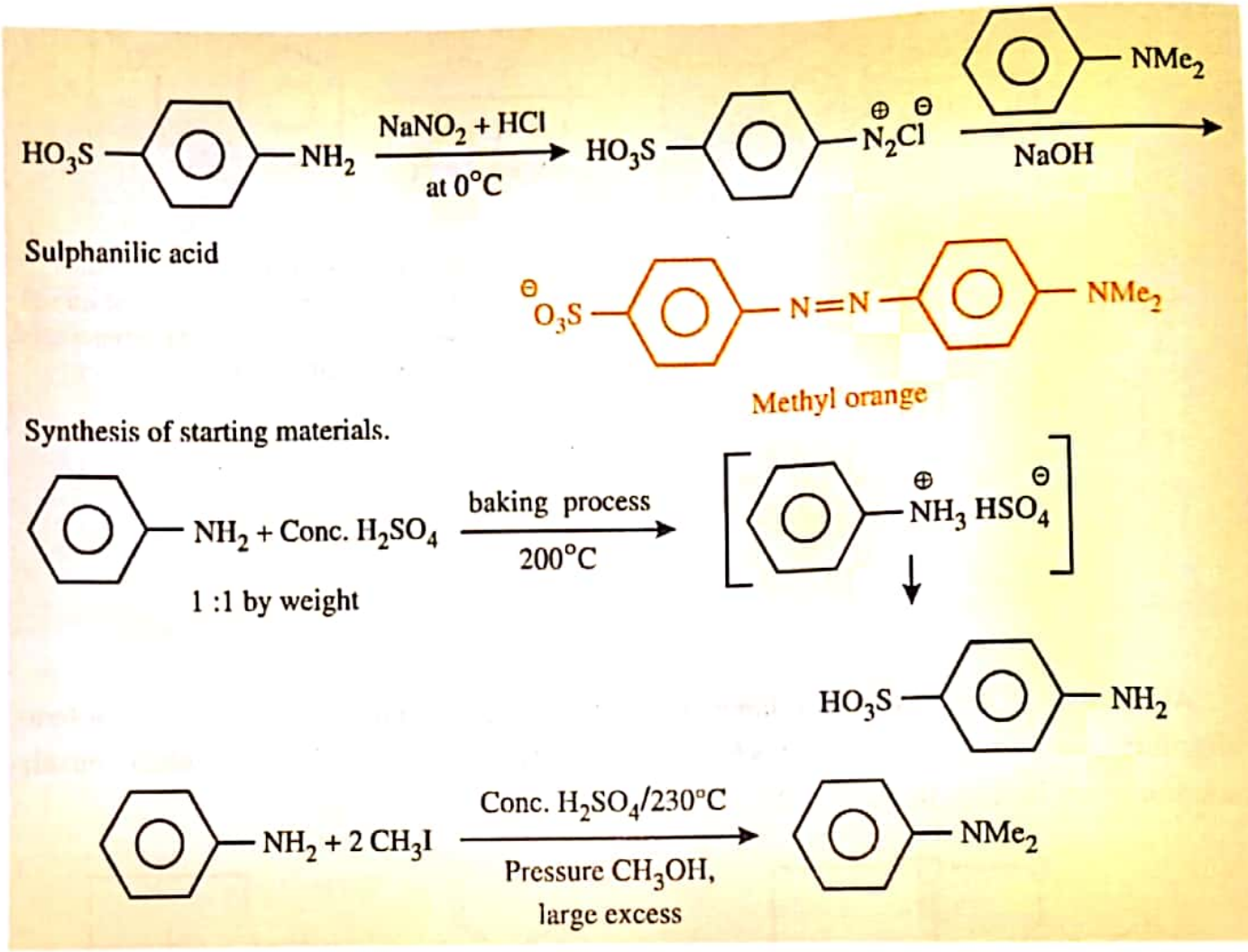
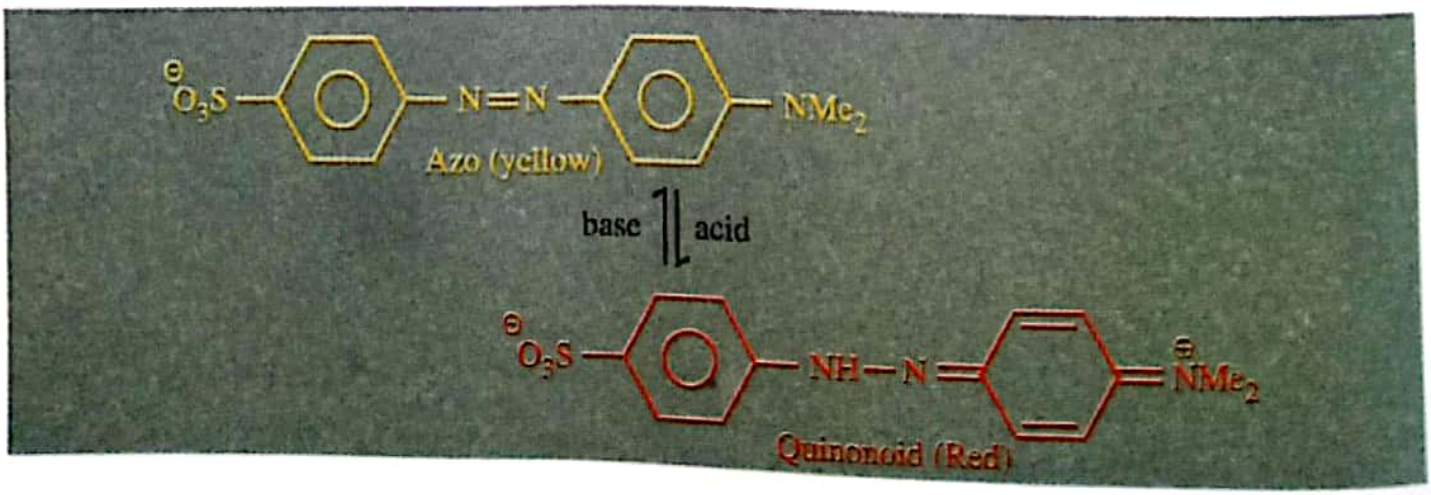
Methyl orange

Methyl orange is synthesized by coupling diazotised sulphanilic acid with N, N-dimethyl aniline.



Methyl orange imparts orange colour to wool and silk but the colour is not fast to sunlight or washing. That is why it is not used as a dye.

It is a valuable indicator for acid-base titration because it gives yellow colour in basic solution and red colour in acid solution. The change in colour is due to the change in the chromophore of the ion.



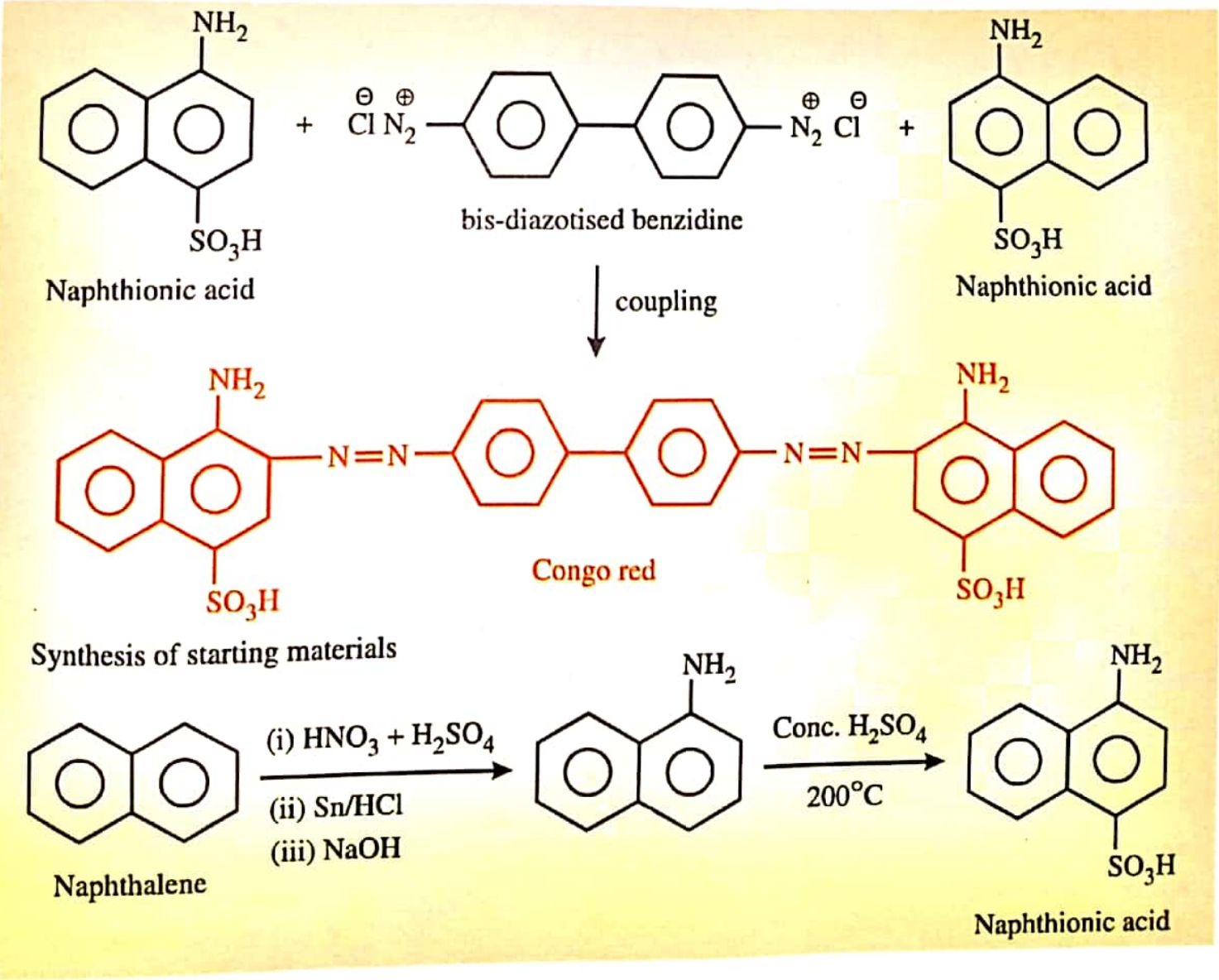
Pk_{Ind}	Change of colour		pH-range
	acid	base	
3.7	Red	Yellow	$Pk_{Ind} \pm 1$
			2.7 - 4.7

Methyl orange indicator can be used during the titration of (i) strong acid-strong base e.g. HCl versus NaOH, at the equivalence point pH = 7 and pH jumps sharply from 4 to 10, yellow to Red. (ii) Strong acid-weak base e.g. HCl versus Na_2CO_3 at the equivalence point pH < 7. Yellow to Red.

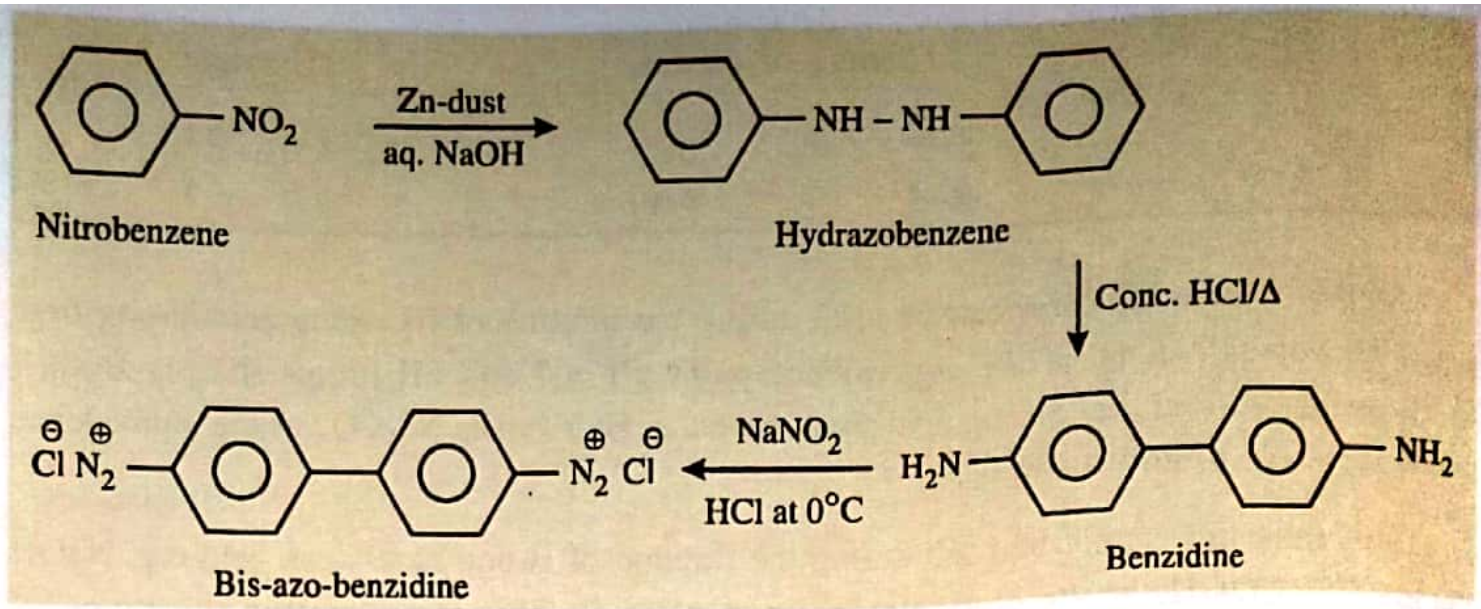
This indicator cannot be used during the titration of strong base-weak acid e.g. NaOH versus CH_3COOH, at the equivalence point pH > 7. This is not within the range of Pk_{Ind} ±1 of Methyl orange.

Congo red

Congo red is synthesized by coupling, bis-diazotised benzidine (1 mole) with Naphthionic acid (1-naphthyl-amine-4-sulphonic acid) (2 moles).

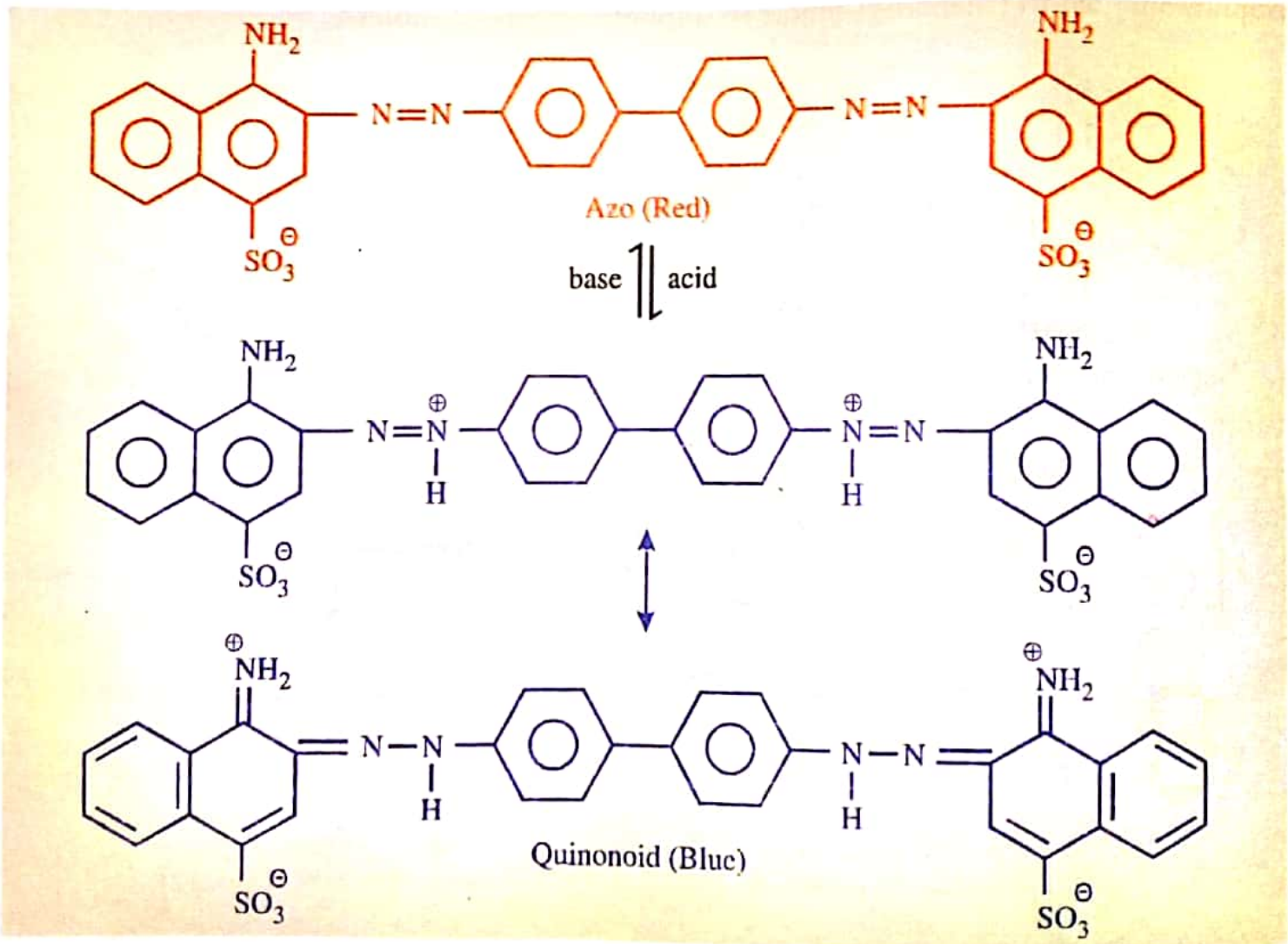


Synthesis of starting materials



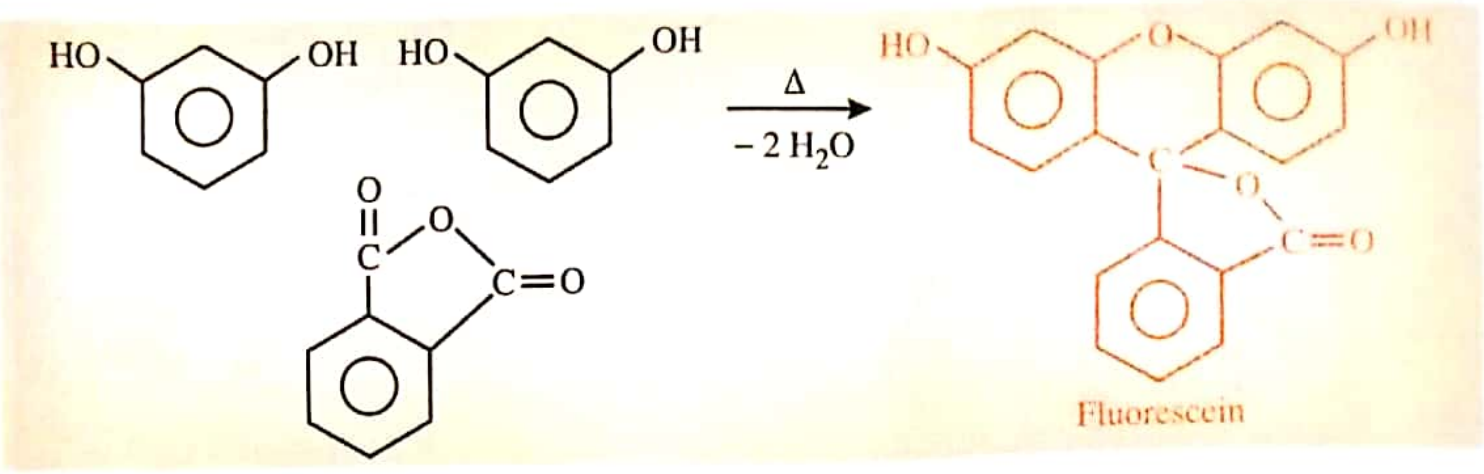
Congo red is a direct dye and its sodium salt dyes cotton a full red from aqueous solution.

Congo red is also used as an indicator being red in alkali and blue in acid solution.

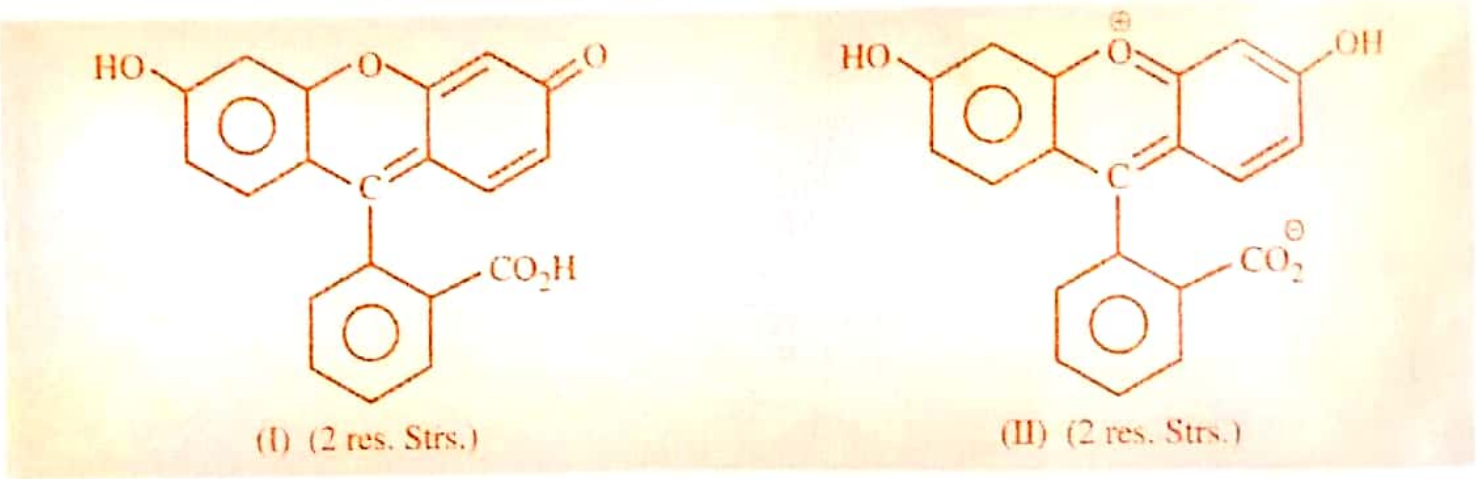


Fluorescein

Fluorescein is prepared by heating phthalic anhydride (1 mole) and resorcinol (2 moles) at 200°C or at 110-120°C with anhydrous oxalic acid.



Fluorescein is an orange solid, insoluble in water. Since Fluorescein is coloured and hence it exists in para-quinonoid (I) and ortho-quinonoid (II) forms—the latter being in the form of dipolar-ion, predominates.



It dissolves in alkali to a reddish brown solution which on dilution exhibits a strong yellowish-green fluorescence (persists up to 4×10^6 times dilution). It dyes wool and silk yellow from the acid bath.

Malachite green

Malachite green is synthesized by condensing N, N-dimethyl aniline (2 moles) with benzaldehyde (1 mole) at 100°C in the presence of conc. H_2SO_4. The leuco-base produced is oxidised with PbO_2 in a solution of acetic acid with a little hydrochloric acid, the resulting colour base (colourless) gives Malachite green with excess hydrochloric acid.

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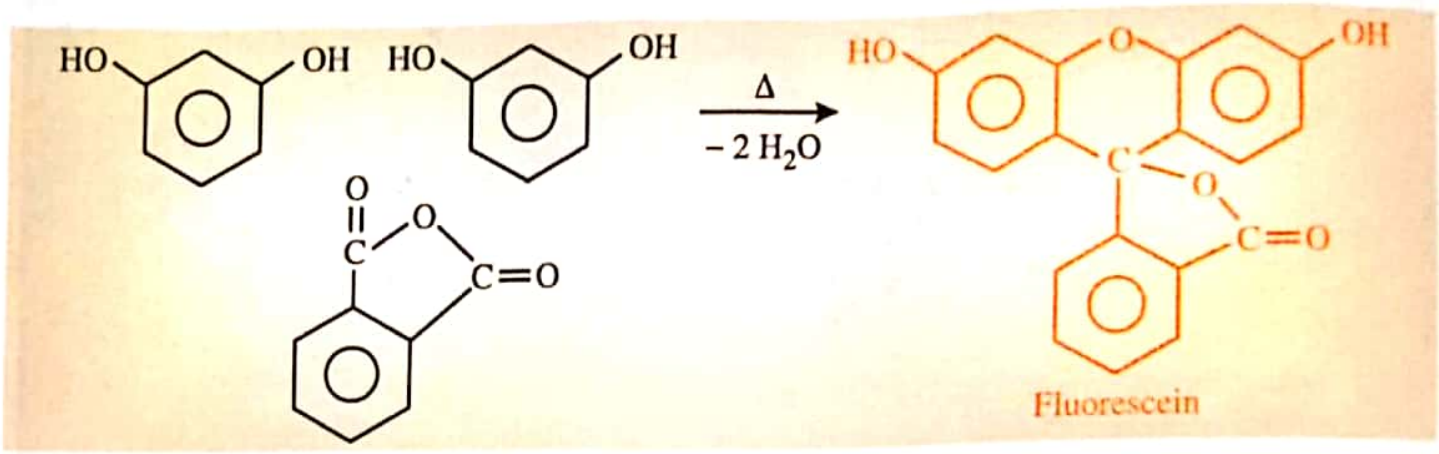

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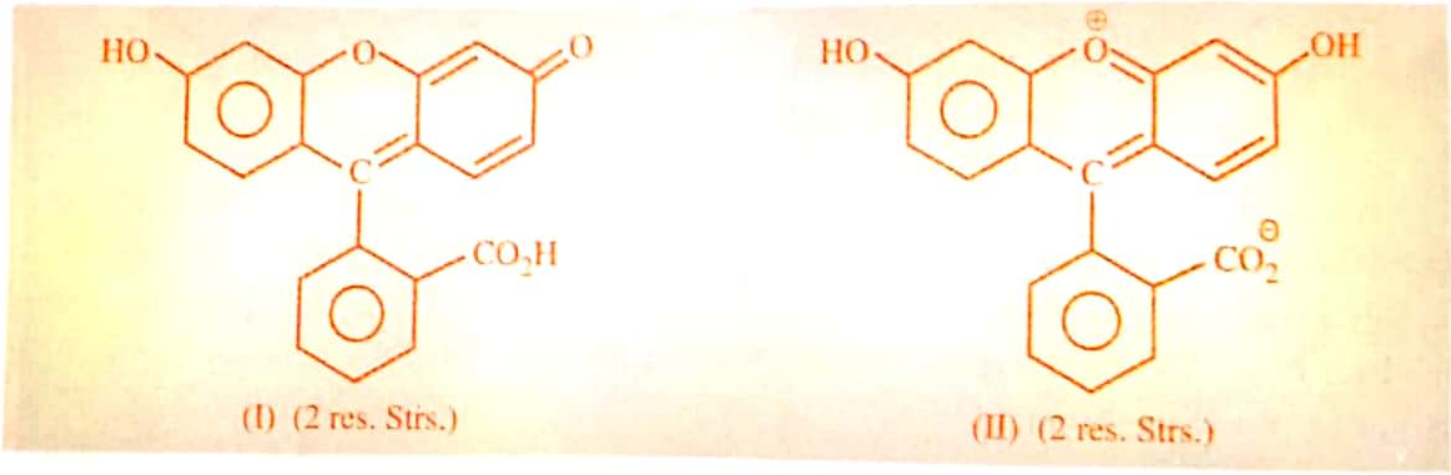

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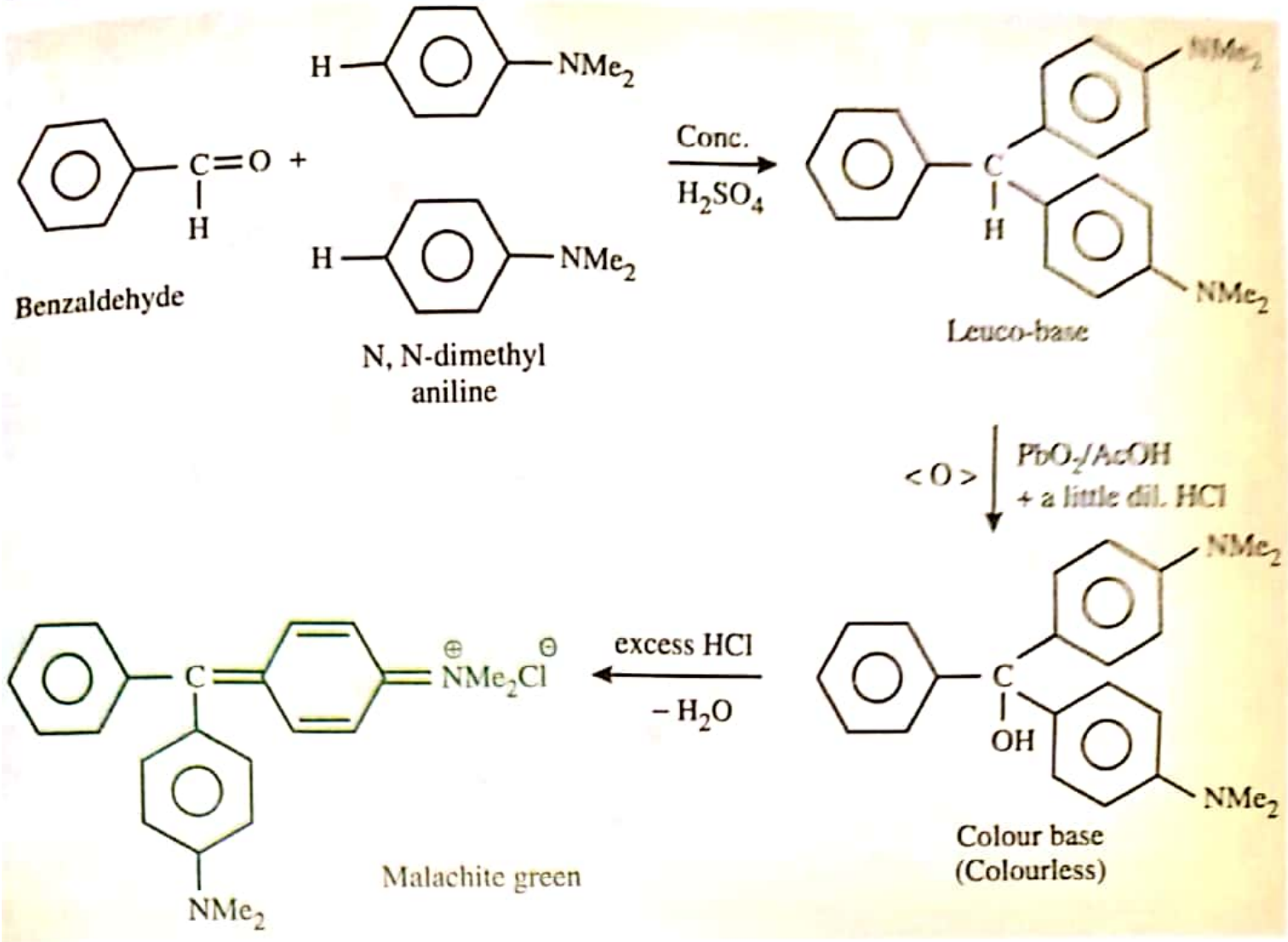
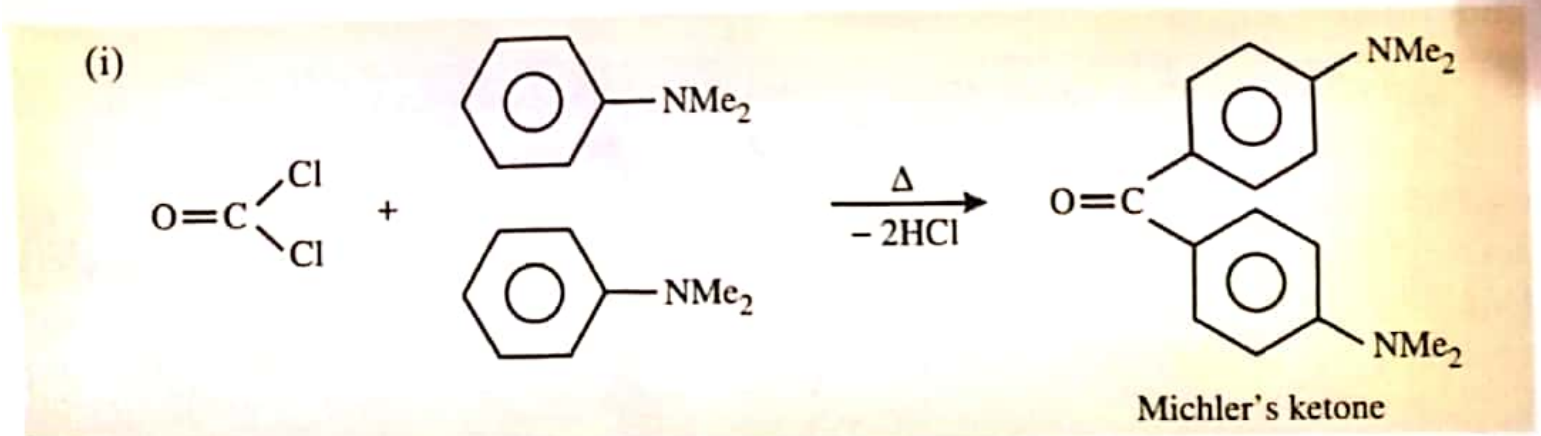


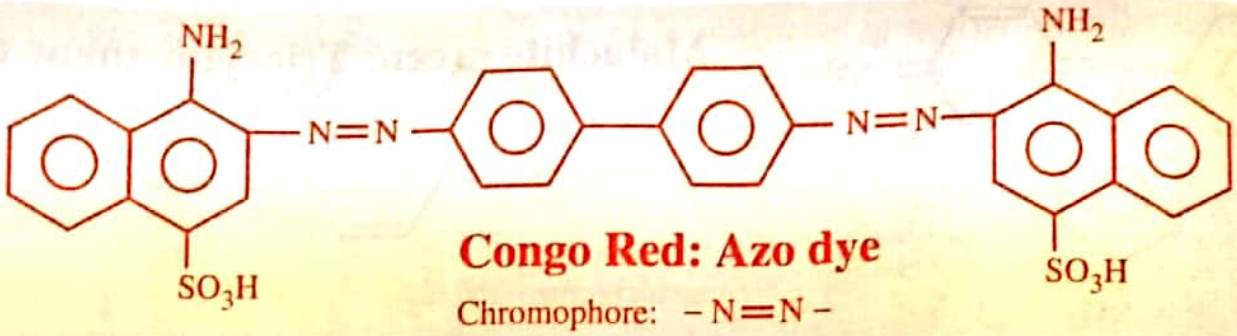
Malachite green is a deep green-blue colour. It dyes wool and silk directly and cotton mordanted with tannic acid to deep green. The colour is not too fast in light and fades rapidly in light and because of this reason it is rarely used in textiles. This dye is commonly used for colouring paper, type writer ribbons and for those articles where fastness to light is not of much importance.

It is a powerful antiseptic.

Crystal violet

Crystal violet is synthesized by heating N, N-dimethyl aniline with carbonyl chloride.





Congo Red: Azo dye

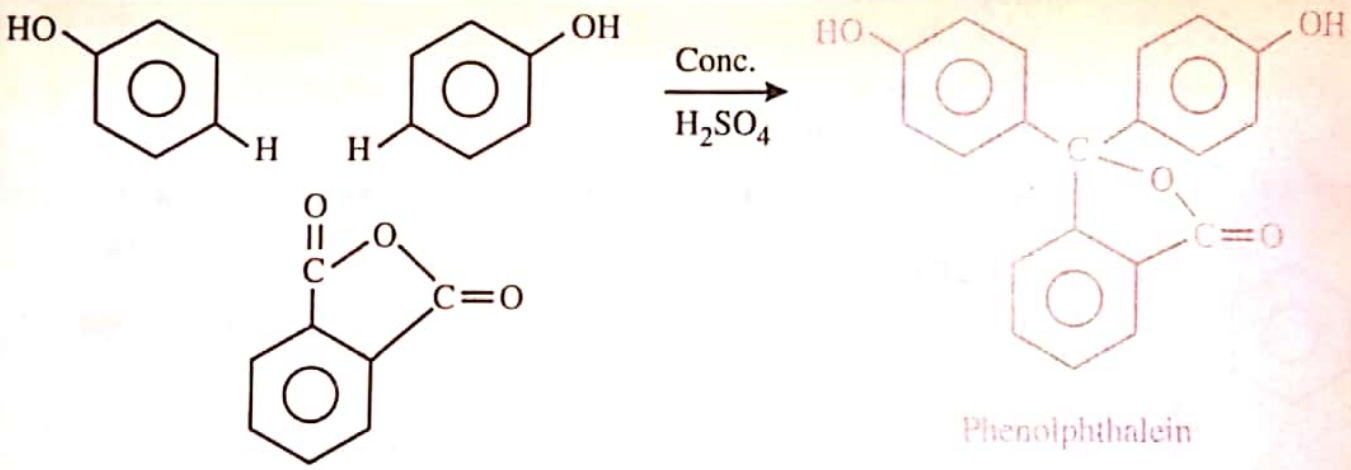
Chromophore: $-N=N-$

auxochrome: $-NH_2$, $-SO_3H$

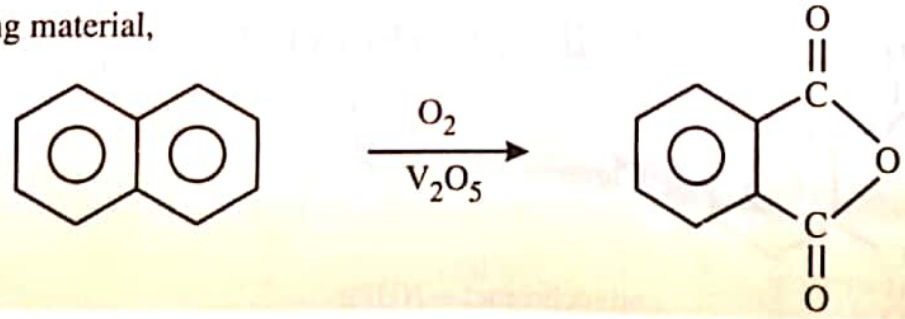
9.6 Synthesis of dyes and their uses

Phenolphthalein

Phenolphthalein is synthesized by heating phthalic anhydride (1 mole) with phenol (2 moles) in the presence of conc. H_2SO_4.



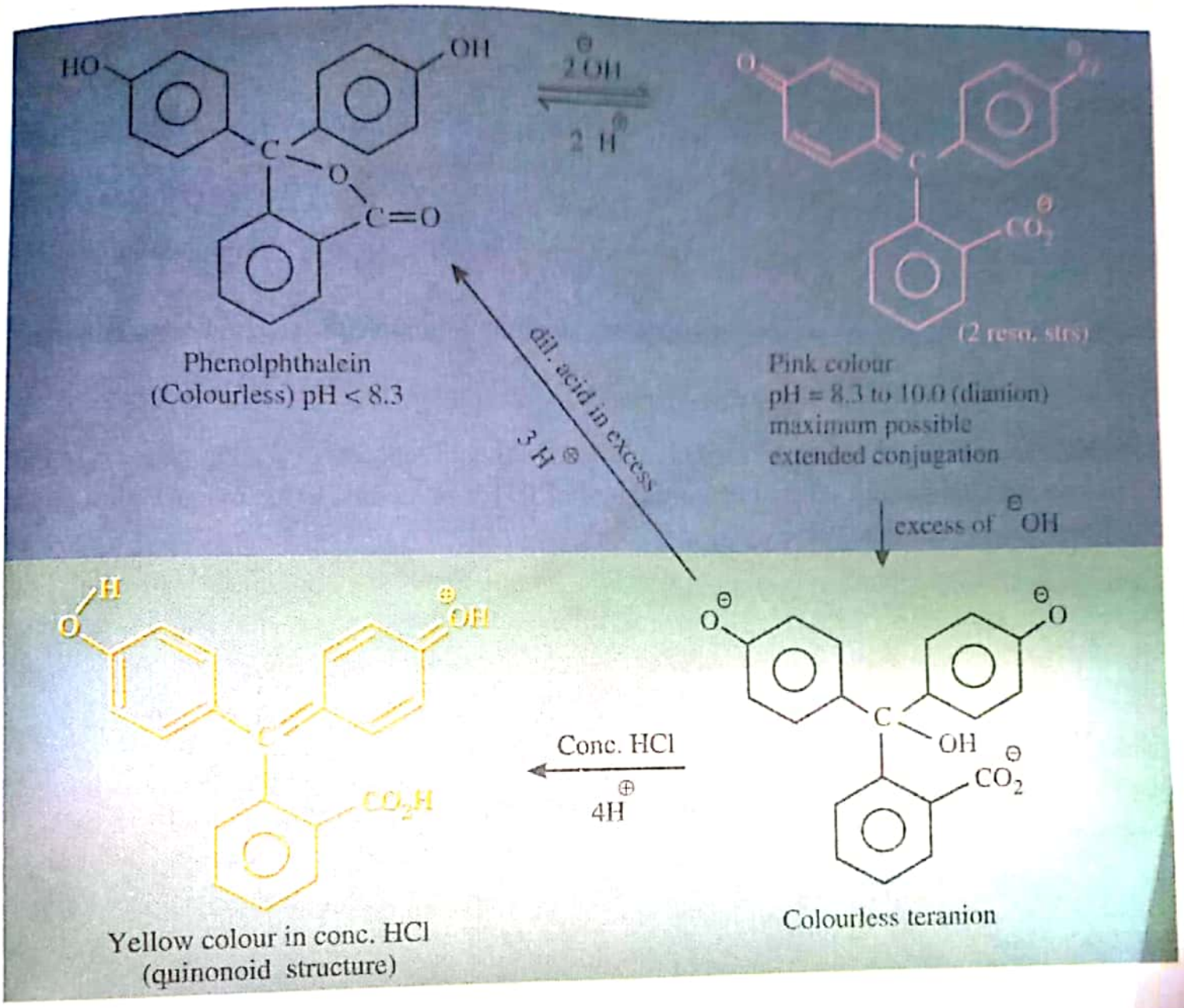
Starting material,



Phenolphthalein is a white crystalline solid, insoluble in water but soluble in alkali and in alcohol. It is used as an acid-base indicator rather than a dye.

In alkali phenolpthalein gives a red colour due to the formation of quinonoid structure (dianion). On addition of a large excess of alkali, a teranion is formed which is again benzenoid. The coloured dianion may easily revert back to colourless benzenoid form in acid. On addition

of conc. HCl, the colourless teranion miraculously, gives yellow colour while the dilute acids simply protonate the teranion. The following reactions explain the whole sequence.



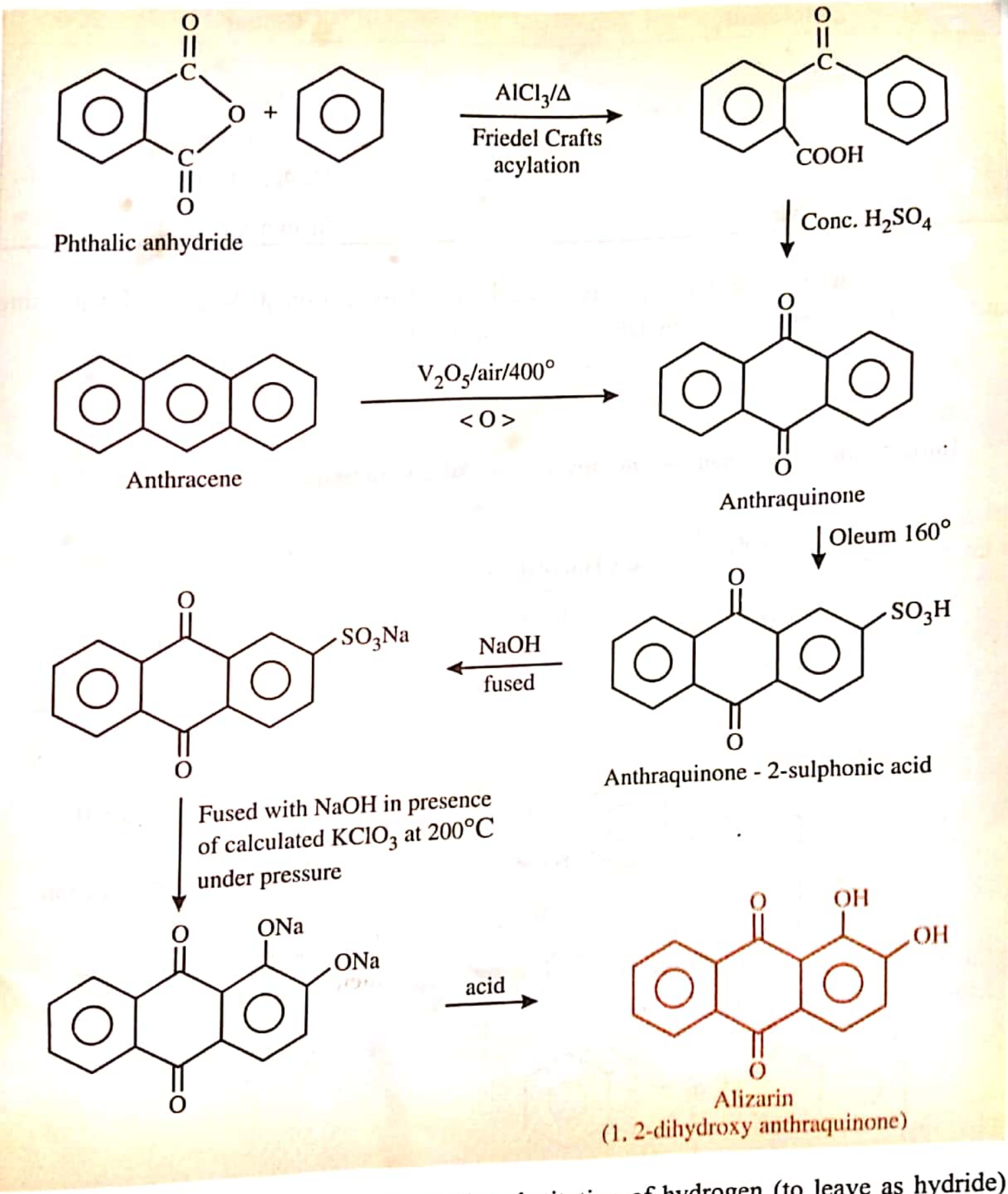
	Change of colour		
$Pk_{Ind.}$	acid	base	pH-range ($Pk_{Ind} \pm 1$)
9.6	colourless	Red	8.3-10.0

Phenolphthalein indicator can be used during the titration of (i) strong acid-strong base, at the equivalence point pH = 7, pH jumps sharply from 4.0 to 10.0, Red to colourless (ii) strong base-weak acid, at the equivalence point, pH > 7, Red to colourless.

This indicator cannot be used during the titration of strong acid-weak base e.g. H_2SO_4 versus Na_2CO_3. At the equivalence point pH < 7. This is not within the range of $Pk_{Ind} \pm 1$.

Alizarin

Alizarin can be synthesized by the following sequence of reactions.



The function of $KClO_3$ for nucleophilic substitution of hydrogen (to leave as hydride) at 1 – C by nucleophilic $^{\ominus}OH$ which is facilitated by the presence of an oxidiser $KClO_3$ (... hydride).

Alizarin is a ruby-red crystal. It is a mordant dye—the common mordants being metallic hydroxides

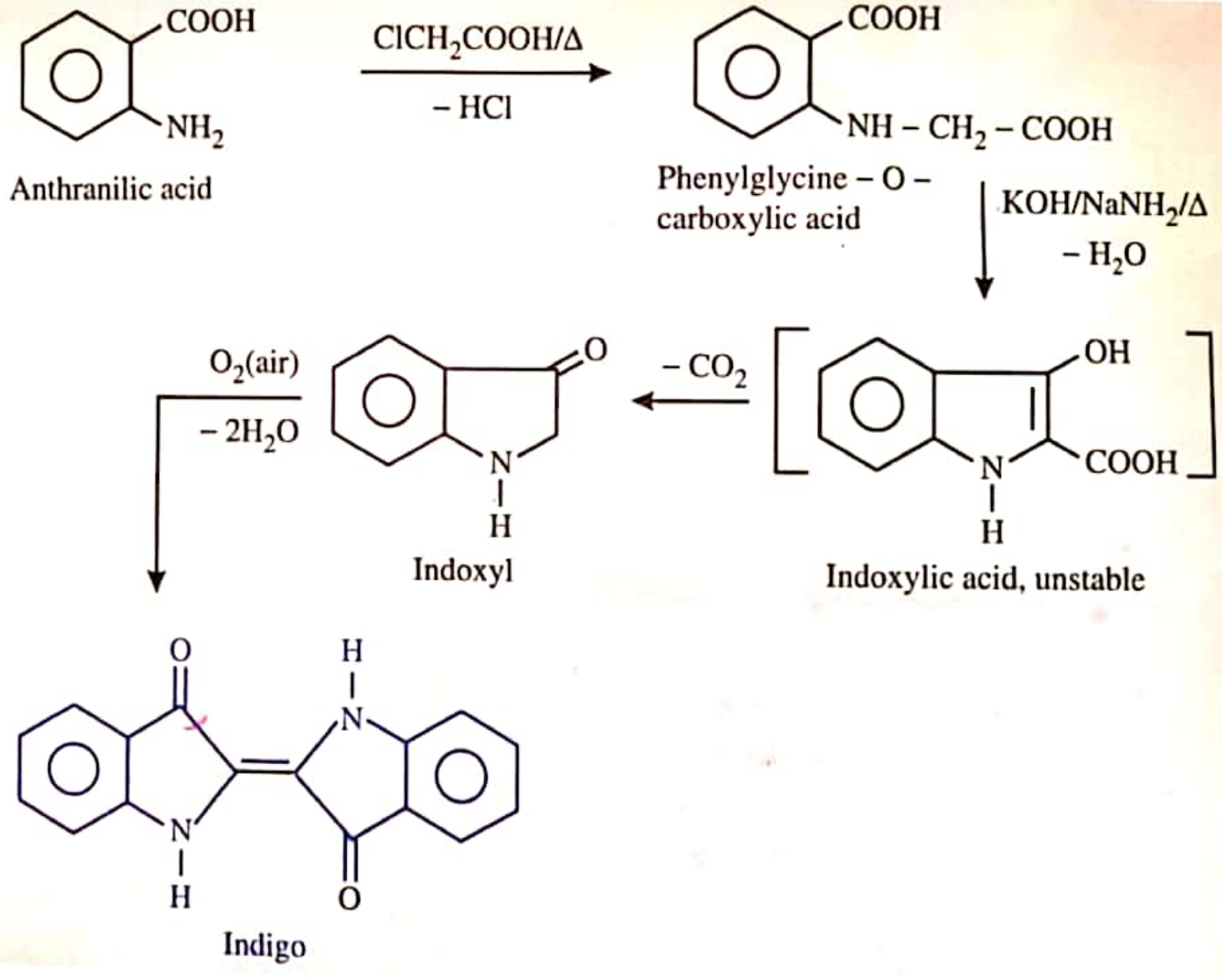
Mordants	Colour
Al^{+3}	Turkey red
Fe^{+2}	Violet
Fe^{+3}	Violet black
Cr^{+3}	Brown-violet

Aluminium and iron lakes are usually employed for cotton dyeing and for printing and aluminium and chromium lakes for wood dyeing.

Indigo

Indigo can be synthesized by any of the following sequence of reactions.

1.



Anthranilic acid

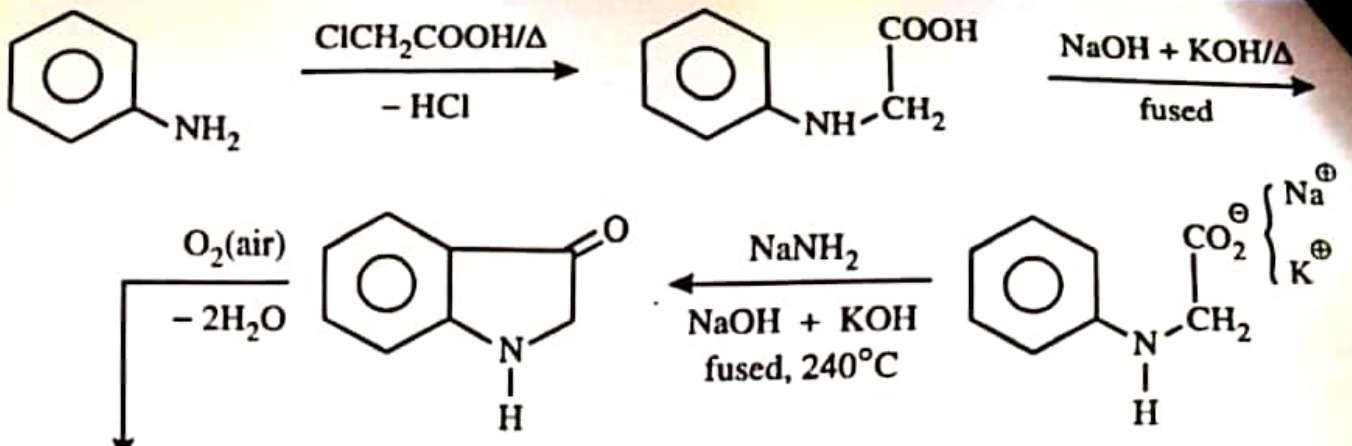
Phenylglycine – O – carboxylic acid

Indoxylic acid, unstable

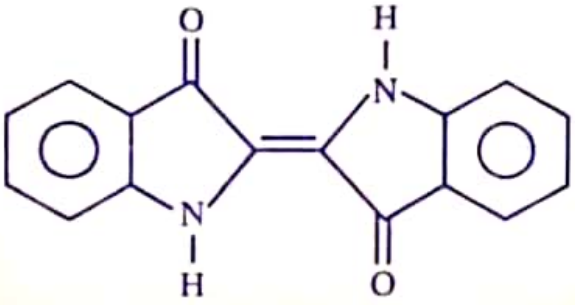
Indoxyl

Indigo

2.

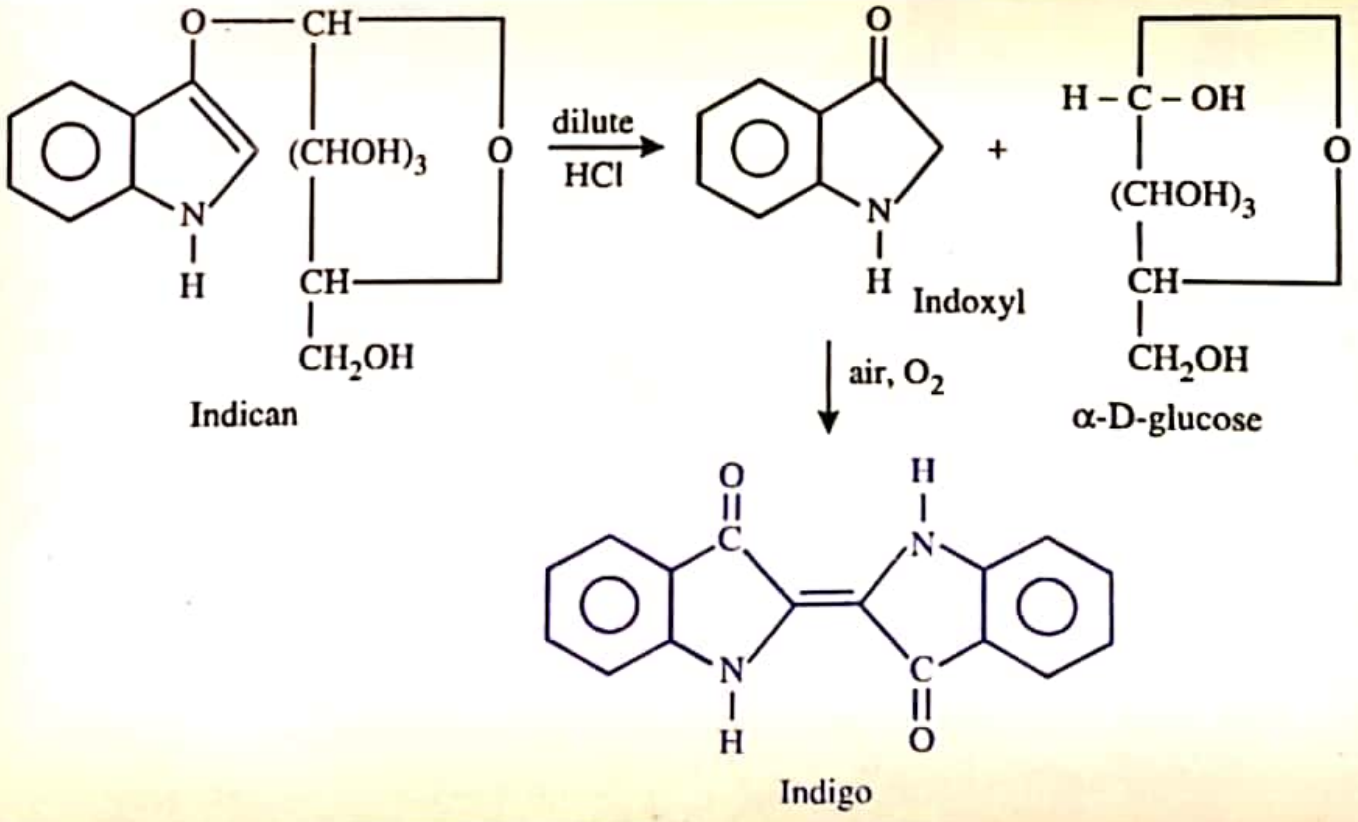


Equimolecular mixture of Na and K-salts of phenyl glycine - the mixed salts requires to lower the temperature and the yield of Indoxyl is better.



Indigo

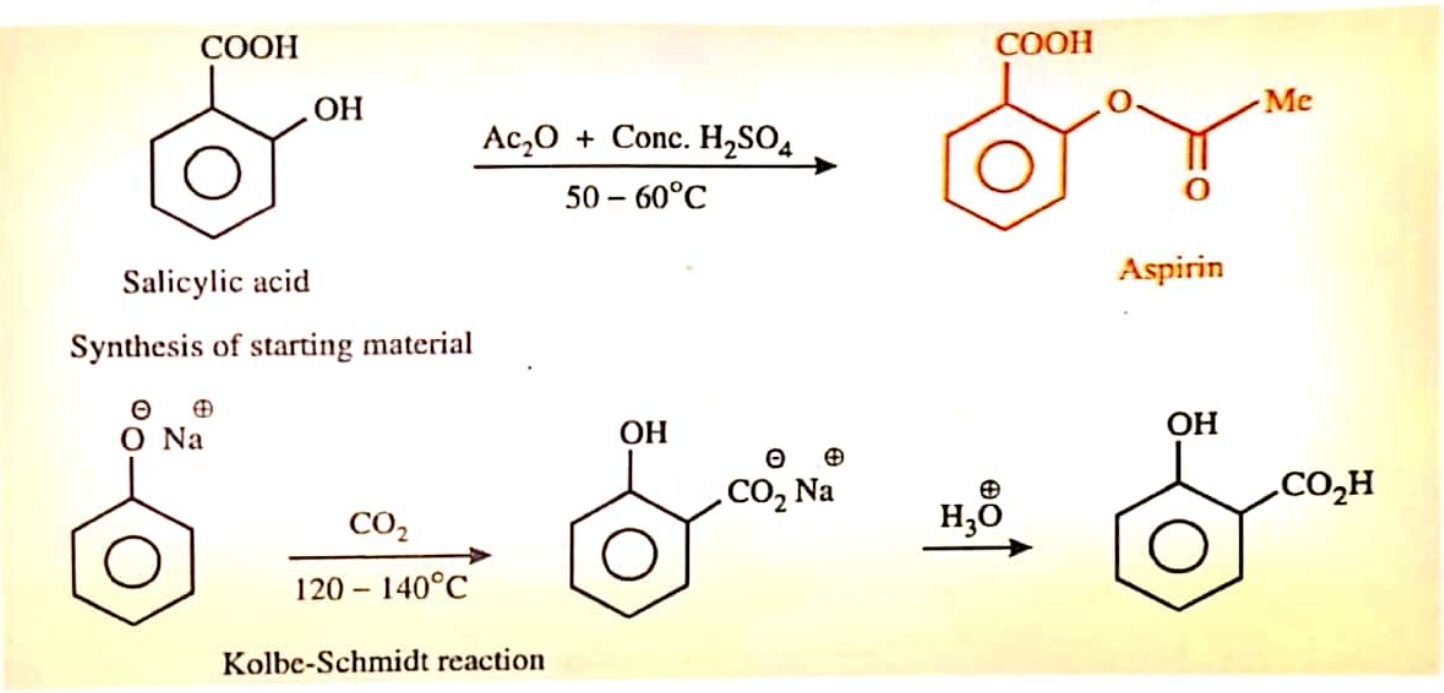
At one time it was obtained in large quantities in India from the Indigo plant (Indigofera). Indigofera plants contain Indican which on hydrolysis produces, Indoxyl which on air-oxidation gives Indigo. Indican is the glycoside of Indoxyl.



Indigo is a dark-blue amorphous powder with a copper lustre.

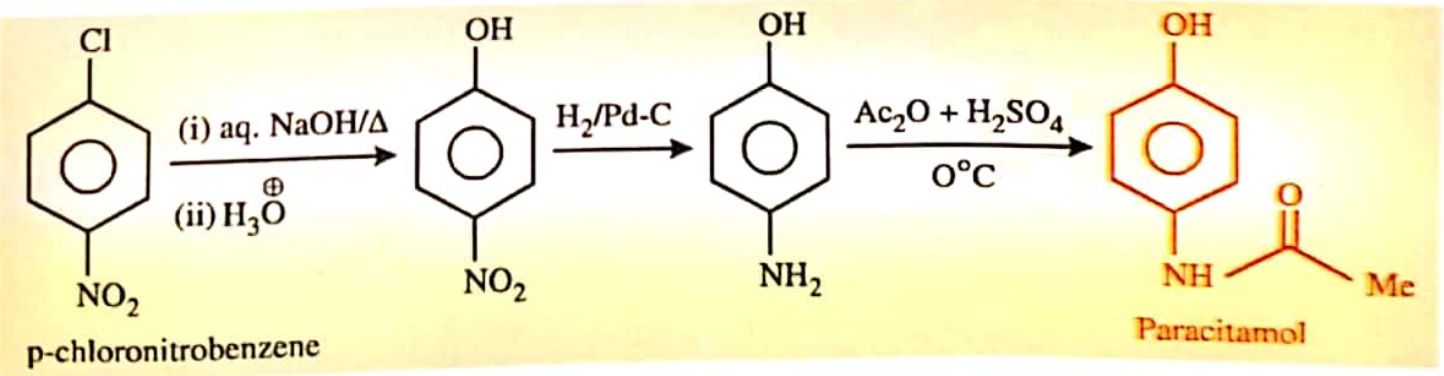
10.2 Synthesis of drugs

Aspirin



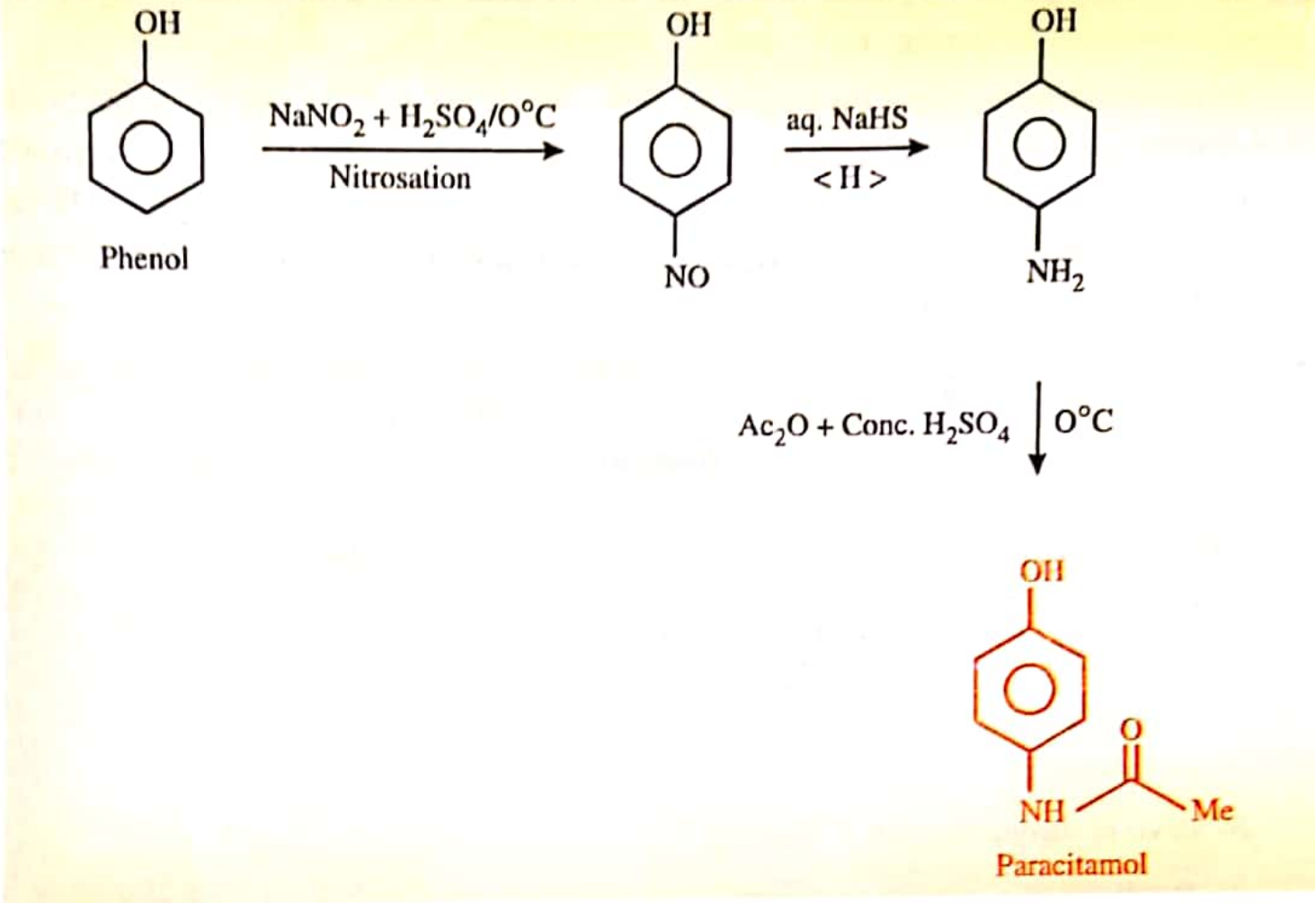
Paracitamol

Method A (starting from parachloro nitrobenzene)

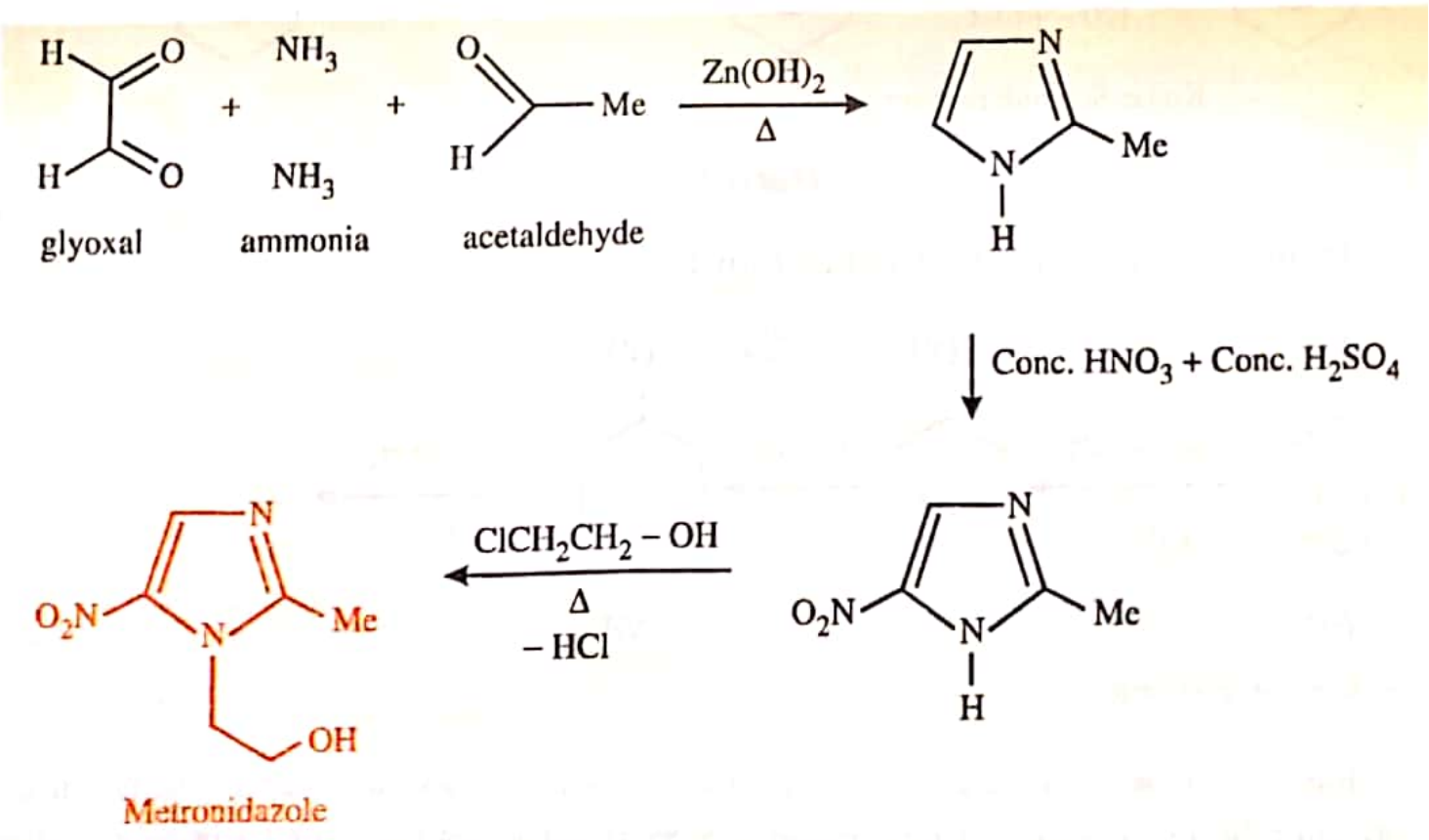


First step is activated aromatic nucleophilic substitution and last step is chemoselective acetylation of amino group. Amino group is more reactive and nucleophilic in acid medium.

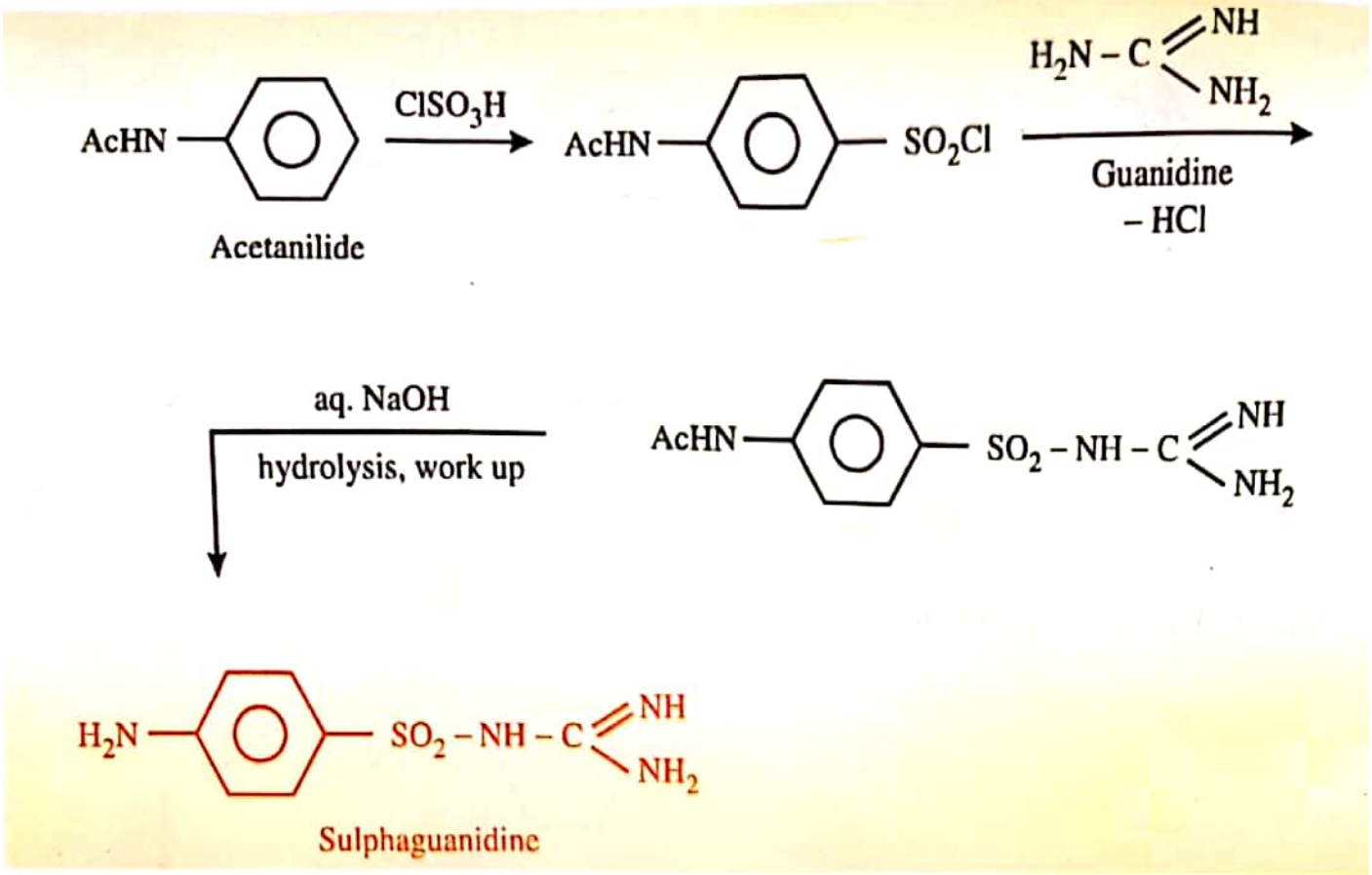
Method B (starting from phenol)



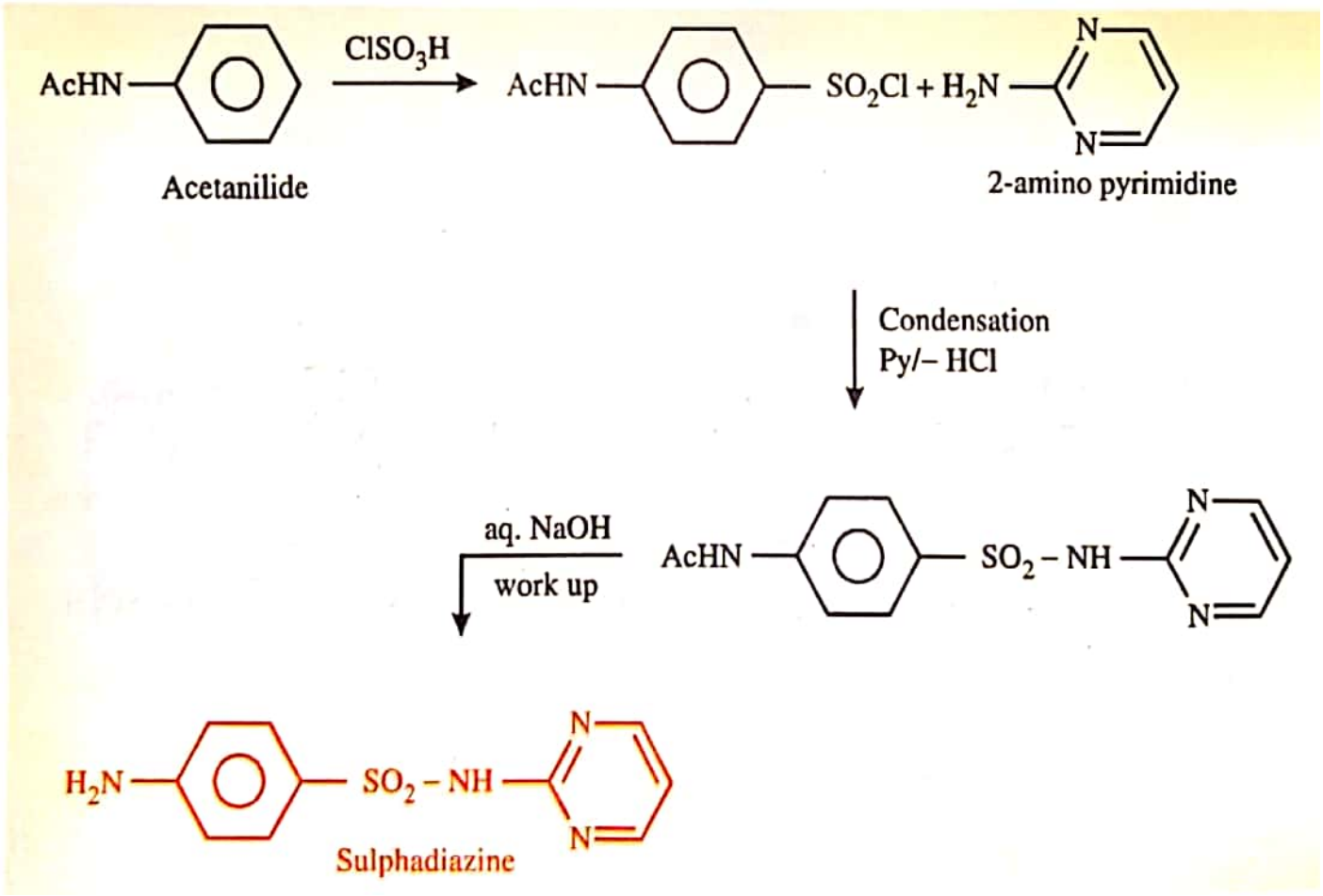
Metronidazole



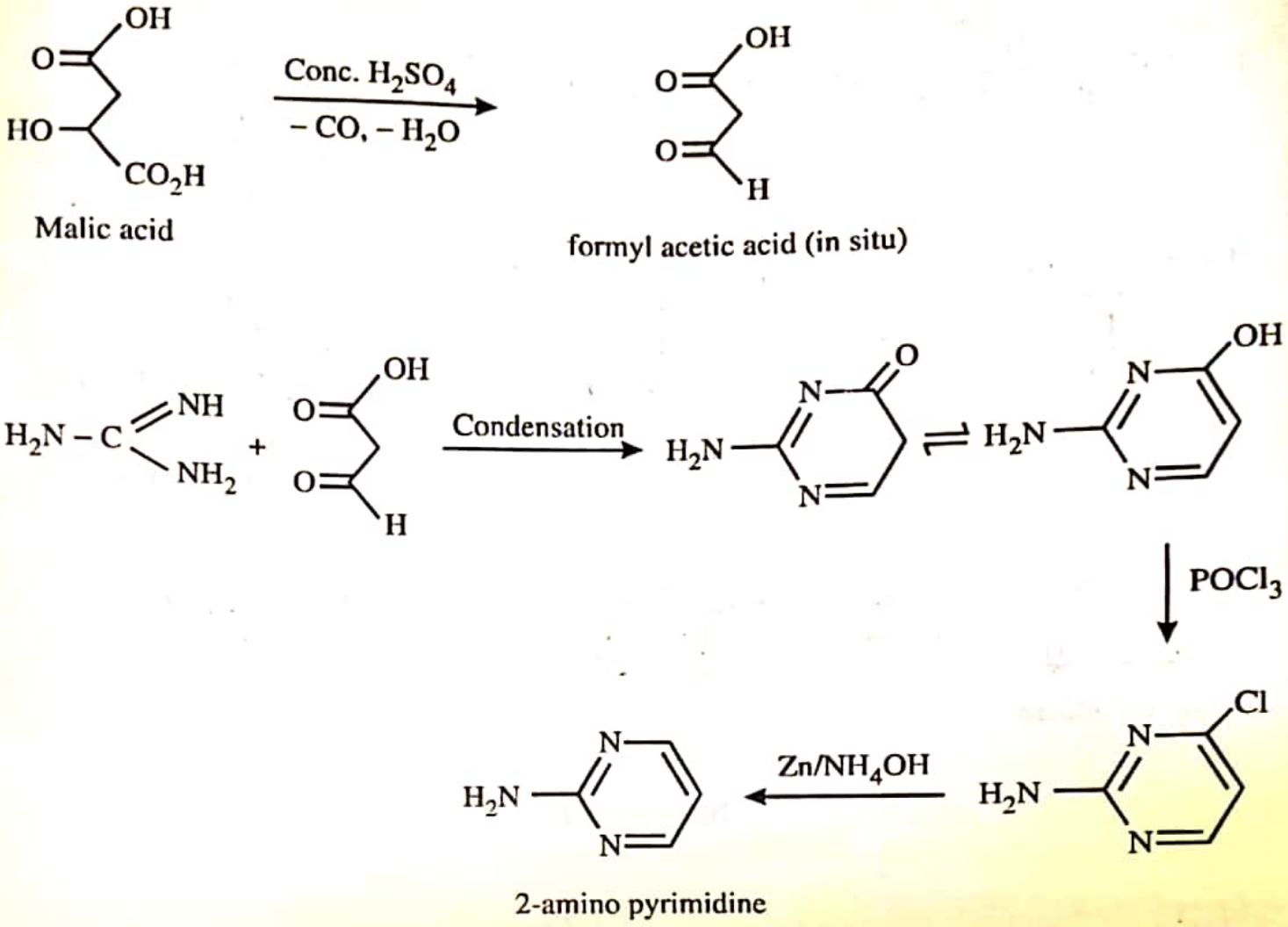
Sulphaguanidine



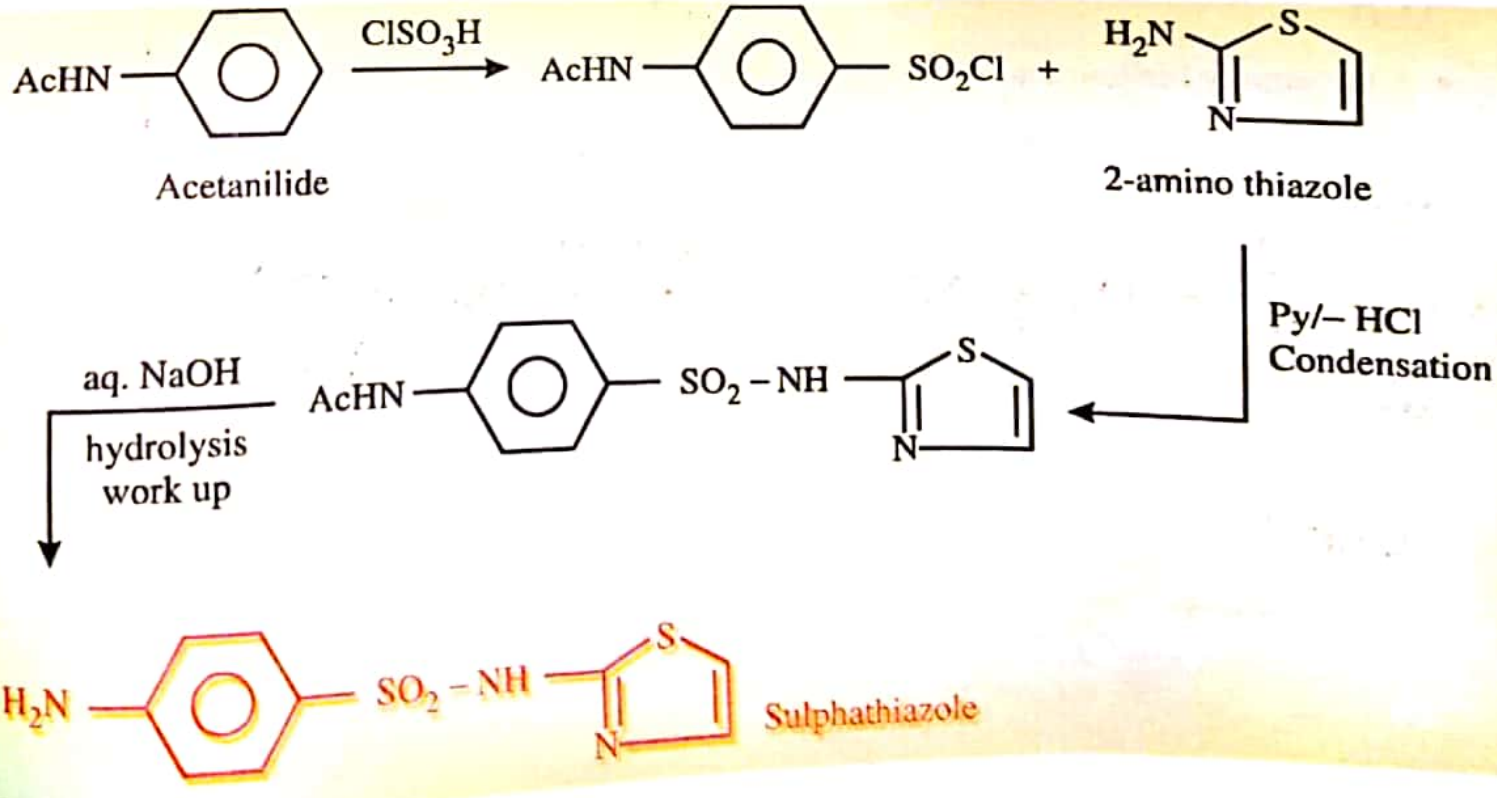
Sulphadiazine



Preparation of starting material 2-amino pyrimidine



Sulphathiazole



Adrenaline