

## NOTE

## Synthesis of Some New Phenolic Azo Schiff Bases—Part I

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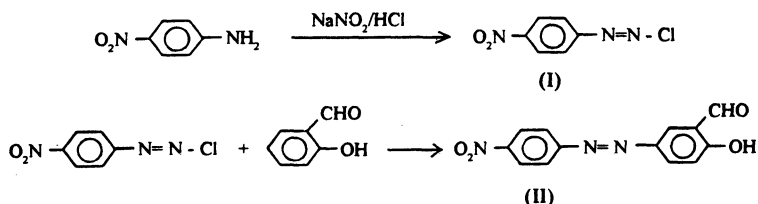
*p*-Nitroaniline on diazotisation gives *p*-nitrobenzene diazonium chloride (I) which on condensation with salicylaldehyde gives 2-hydroxy-5-(4-nitrophenylazo) benzaldehyde (II). The compound (II) on condensation with substituted aniline gives 2-hydroxy-5-(4-nitrophenyl azo) benzylidine substituted aniline, *i.e.*, substituted phenolic azo Schiff bases.

Anticancer Schiff bases have been synthesised by condensation of aniline with substituted benzaldehyde<sup>1</sup>. Benzaldehyde-2-hydroxy aniline was prepared by condensation of *o*-aminophenol with substituted benzaldehyde in ethanol in presence of 2–3 drops of concentrated H<sub>2</sub>SO<sub>4</sub>.<sup>2</sup> Benzoxazoles were prepared by cyclisation of O,N-diacetyl derivative of *o*-aminophenol at lower temperature by treating aminophenol with carboxylic acid or its derivative<sup>3</sup>. It was suggested that azomethine linkage might be responsible for biological activities of Schiff bases<sup>4</sup>. Some oxime derivatives having ethoxy group have been reported to possess antiinflammatory activities<sup>5</sup>. Some 2-oxothiazoline hydrazones from 3-methoxy,  $\Delta$ -allyloxy-benzaldehyde are endowed with anti-HIV activity<sup>6</sup>. Some new azo pyrazoles have been synthesised by Jolly *et al.*<sup>7</sup> Recently some new azo Schiff bases have been synthesised by the reaction of 5-*p*-methoxyphenylazo salicylaldehyde with primary aromatic amines<sup>8</sup>.

Literature survey indicates that 2-hydroxy-5-(*p*-nitrophenylazo) benzylidine aniline was not prepared from 2-hydroxy-5-(*p*-nitrophenylazo) benzaldehyde. Hence it was thought interesting to prepare 2-hydroxy-5-(*p*-nitrophenylazo) benzylidine substituted aniline.

Synthesis of 2-hydroxy-5-(*p*-nitrophenylazo) benzaldehyde (II)

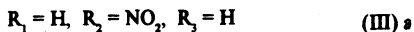
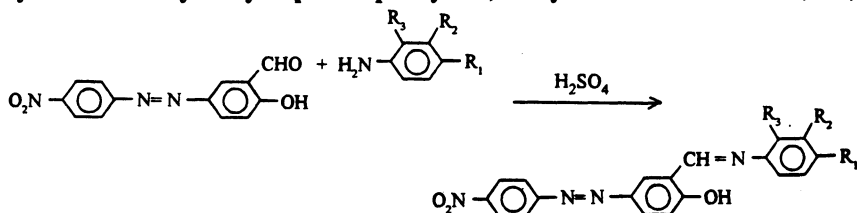
*p*-Nitroaniline (4.5 mL) was dissolved with sodium nitrite (40 g). The cold solution of salicylaldehyde (59 mL, 6 N) in aqueous sodium hydroxide (40 mL, 12 N) was added slowly with constant stirring below 5°C. The resulting crude solid was washed with water and recrystallised from benzene to get 2-hydroxy-5-(*p*-nitrophenylazo) benzaldehyde (m.p. 194°C).



Compound II: m.w. = 271, m.p. = 194°C, Colour = Yellow

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### Synthesis of 2-hydroxy-5-(*p*-nitrophenylazo)benzylidene-*m*-nitroaniline(IIIa)




Compound III: m.f.  $\text{C}_{19}\text{H}_{13}\text{N}_5\text{O}_5$ , m.w. = 391, m.p. = 260°C, Colour = Yellow

2-Hydroxy-5-(*p*-nitrophenylazo) benzaldehyde condensed with *m*-nitroaniline in ethanolic medium in presence of concentrated  $\text{H}_2\text{SO}_4$ , when compound IIIa was obtained

IR spectrum of compound IIIa (Nujol): 3700–3000 (Ar—OH stretching), 1550 (N=N stretching of azo phenyl) 1620  $\nu(\text{CH}=\text{N}$  azomethane), 1550  $\nu(\text{Ar}-\text{NO}_2$  stretching), 1600, 1500 (Ar stretching), 1300 (ArNO<sub>2</sub> stretching).

PMR (in  $\text{CDCl}_3$  TMS as internal standard): 7.2–8.6 m (11H, Ar—H); 9.1s (1H, H of CH—N); 14.2 s (1H Ar—OH)

TABLE-1  
ANALYTICAL DATA OF PHENOLIC AZO SCHIFF BASES.

S.No.	—R <sub>1</sub>	—R <sub>2</sub>	—R <sub>3</sub>	m.p. (°C)	Colour	m.w.	Yield (%)
IIIa	H	NO <sub>2</sub>	H	260	Yellow	391	55
IIIb	NO <sub>2</sub>	H	H	252	Yellow	391	50
IIIc	H	H	NO <sub>2</sub>	183	Brick red	391	56
IIId	CH <sub>3</sub>	H	H	232	Red	360	83
IIIe	H	CH <sub>3</sub>	H	190	Red	360	85
IIIf	H	H	CH <sub>3</sub>	203	Brown	360	88
IIIg	SO <sub>3</sub> H	H	H	188	Yellow	426	38
IIIh	H			222	Brown/grey	396	48
IIIi	H	H	H	215	Brown	346	60

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