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New Disperse Dyes From Substituted Pyridines. *Part-I.* Synthesis of Methyl-4, 6, Dihydroxy-2oxo-1-Phenyl-5-Arylazopyridine-3-Carboxylate and Their Derivatives

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The reaction of methyl-4, 6, dihydroxy-2oxo, 1-phenyl pyridine-3 carboxylate **(iii)** with diazotized aromatic amines **(ii)**, yielded compounds **(iv)** showing absorption bands between λ_{max} 570-590 nm, characteristic of azo dyes. An aqueous solution of **(iv)** having a non-ionic dispersing agent and a dye carrier at pH 5-6 and temperature 135°C and 75°C when applied to polyester and acetate fiber respectively furnished beautiful colours ranging from orange to yellow.

Key words: Azo dyes, Subsituted pyridines, Disperse dyes, Spectroscopic studies.

Introduction

For the last few years substituted pyridines were given due attention as a versatile reagent for the synthesis of heterocyclic compounds (Deeb *et al* 1990; Caballero *et al* 1993; Abu-Shanab *et al* 1997; Himeno *et al* 1998) having different types of biological activities (Abdul Aziz 1996; Lukevice 1996). During the past few years synthesis and dying performance of several 5-arylazo pyridine dyes have been reported and evaluated for light and wash fastness on polyester synthetic fibers (Mohareb and Sherif 1992).

In continuation of our previous work (Butt *et al* 1991) on the synthesis of subsituted pyridine and further reactions of methyl 1, 2-dihydro 4, 6 dihydroxy-2-oxo-1-phenyl pyridine-3-carboxylate **(iii)** was carried out. Compound **(iii)** on reaction with diazodized aromatic amines **(ii)**, yielded azo compounds **(iv)**. The visible absorption spectra of these compounds indicated their dye nature, as they appeared between λ_{max} 570-590 nm. When an aqueous solution of these compounds was applied to polyesters and acetate fibers, beautiful shades ranging from orange to yellow obtained.

Experimental

Melting points were taken on Gallen-Kamp melting point apparatus and are uncorrected. The IR spectra were measured in KBr on a Jasco A-30 - Spectrophotometer. Visible light spectra were determined in methanol 95% on spectromiczo Baush & Lomb. The ^{1}Hnmr was recorded in $CdCl_3$ at 500-MHz on Brucker AM-300 ASPECT 300 spectrophotometer. Mass spectrum was determined using a Finningan Varian MAT 112 photometer. Micro analysis was carried out by microanalytical laboratories PCSIR Labs., Lahore.

*Synthesis of methyl-4,6-dihydroxy-2-oxo-1-phenyl-pyridine-3-carboxylate **(iii)***. The titled compound **(iii)** was prepared according to the reported method (Butt *et al* 1991) for the synthesis of methyl-4, 6 dihydroxy-2-oxo-phenyl-5-arylazopyridine-3-carboxylate **(iv a-o)**. Compound **(iii)** 2.61 g, (0.01 mol) was dissolved in 0.5% sodium hydroxide (200 ml) and the temperature was kept at 0°C. To this was added diazonium chloride **(ii)** solution, prepared by taking 0.093 g aniline (0.01 mole) in 5N HCl (15 ml) and 5N sodium nitrite solution (2 ml) was added. Starch iodide paper was used to check the appropriate amount of sodium nitrite present in the reaction mixture. The reaction mixture was stirred for one hour. Coloured solid was separated out. It was filtered, washed with water, dried and crystallized with a mixture of chloroform: methanol (1:1). The molar ratios, yields, m.ps and solvent of crystallization of compounds **(iv a-o)** are recorded in Table 3.

*General procedure for the methylation of compounds **(iv-a)***. Compound **(iv-a)** 1.21 g (0.01 mol) was dissolved in chloroform. The temperature of solution was kept at 0°C. A freshly prepared ethereal solution of diazomethane was added to **(iv-a)**. The reaction mixture was kept overnight at 0°C. Ether was removed under vacuo. The gummy material obtained was treated with ether again and filtered. Evaporation of solvent afforded **(v-a)**, crystallized from methanol: chloroform (1:1), m.p. 260°C. elemental analysis found: C, 63.60; H, 4.40; N, 11.20; required for $C_{20}H_{17}N_3O_5$; C, 63.30; H, 4.50; N, 11.10.

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Table 1
Visible light absorption and I R spectrum of **(IV)**

S.no.	Compound **(IV)** R"	Visible light absorption in 95% MeOH λ_{max}. nm	log ε	I.R ν_{max} C=O (lact) cm^{-1}	I.R.ν_{max} C=O (ester) cm^{-1}	I.R.ν_{max} OH cm^{-1}
a	Phenyl	572	4.20	1640	1690	3400
b	*o*-Nitro phenyl	570	4.30	1645	1725	3440
c	*m*-Nitrophenyl	570	4.51	1630	1710	3480
d	*p*-Nitrophenuyl	571	4.45	1645	1700	3460
e	*o*-Methyl phenyl	570	4.22	1620	1675	3420
f	*m*-Methyl phenyl	572	4.23	1625	1695	3440
g	*p*-Methyl phenyl	575	4.20	1620	1985	3440
h	*o*-methoxy phenyl	575	4.25	1640	1690	3420
i	*m*-Methoxy phenyl	570	4.22	1620	1790	3480
j	*p*-Methoxy phenyl	572	4.35	1630	1690	3440
k	*m*-Bromo phenyl	571	4.40	1620	1680	3440
l	*p*-Bromo phenyl	570	4.20	1630	1690	3340
m	*o*-Chlorophenyl	570	4.25	1625	1680	3340
n	*m*-Chlorophenyl	572	4.25	1635	1695	3480
o	*p*-Chlorophenyl	575	4.30	1630	1690	3340

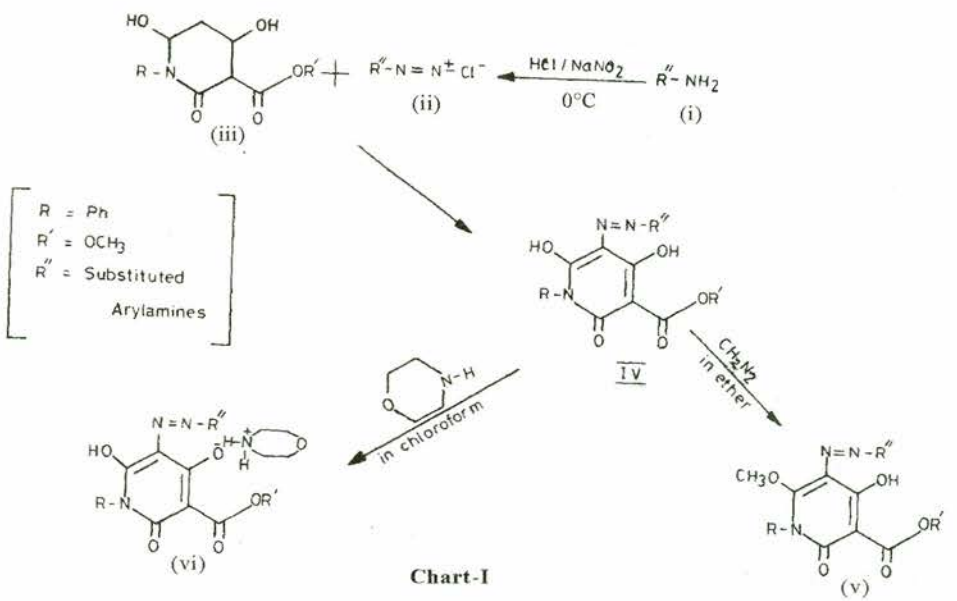

Chart-I

*Morpholinum **(iv)***. The compound **(iv)** (3.65 g; 0.01 mole) morpholine 0.83 g, 0.01 mole, chloroform (30 ml) was added. Mixture was refluxed under anhydrous condition for 30-min, on removal of solvent under vacuo, crystalline solid obtained which on further crystallization from methanol yielded **(vi)** m.p 220°C (d), elemental analysis: found: C, 61.25; N, 12.35 required for $C_{23}H_{20}N_4O_6$; C, 61.60; H, 4.46; N, 12.5.

*Method of application of disperse dyes **(iv a-o)** on polyester fibre.* 0.1% solution of **(iv a-o)** was prepared in water. 200 ml. containing 0.6 to 1 g non-ionic dispersing agent. To this 0.6-1 g dye carrier was added and pH of the solution was adjusted to 5-6 by dilute acetic acid. 10 g fabric was taken and dipped in the above solution. The temperature was raised to 130°C with agitation. The fabric now removed, rinsed with cold water and then with 1% soap solution at 95°C. Finally the fabric was washed with cold water and dried.

Results and Discussion

To synthesize pyridine based new disperse azo dyes, compound **(iii)** was taken as starting material. It was prepared

Table 2
Physical data of compounds **(iv a-o)**

S.no.	Compound **(III)** 0.01 mole in 0.5% sodium hydroxide	II-R 0.01 mole in HCl (Conc) 5 ml 0°C	Sod.nitrite (5N) 0°C	% Yield	Solvent for crystalisation	M.P. °C	Colour
a	2.61 g 200 ml^{-1}	*o*-Nitrophenyl 1.38 g	2.5 ml	75	Methanol and chloroform	275	Yellow
b	2.61 g 200 ml^{-1}	*m*-nitrophenyl 1.38 g	2.5 ml	70	MeOH:$CHCl_3$	246	Yellow
c	2.61 g 200 ml^{-1}	*p*-Nitrophenyl 1.38 g	2.5 ml	60	MeOH:$CHCl_3$	175	Yellow
d	2.61 g 200 ml^{-1}	*o*-Methylphenyl 1.16 g	2.0 ml	60	MeOH:$CHCl_3$	240	Yellow
e	2.61 g 200 ml^{-1}	*m*-Methylphenyl 1.16 g	2.0 ml	65.5	MeOH:$CHCl_3$	236	Yellow
f	2.61 g 200 ml^{-1}	*p*-Methylphenyl 1.16 g	2.0 ml	70	MeOH:$CHCl_3$	240	Yellow
g	2.61 g 200 ml^{-1}	*o*-Methoxyphenyl 1.22 g	2.5 ml	65	MeOH:$CHCl_3$	265	(Orange Yellow)
h	2.61 g 200 ml^{-1}	*m*-Methoxyphenyl 1.22 g	2.5 ml	60	MeOH:$CHCl_3$	228	Yellow
i	2.61 g 200 ml^{-1}	*p*-Methoxyphenyl 1.22 g	2.5 ml	65	MeOH:$CHCl_3$	232	(Orange Yellow)
j	2.61 g 200 ml^{-1}	*m*-Bromophenyl 1.72 g	3.0 ml	64	MeOH:$CHCl_3$	224	Yellow
k	2.61 g 200 ml^{-1}	*p*-Bromophenyl 1.72 g	3.0 ml	68	MeOH:$CHCl_3$	245	Yellow
l	2.61 g 200 ml^{-1}	*o*-Chlorophenyl 1.27 g	2.5 ml	60	MeOH:$CHCl_3$	285	Yellow
m	2.61 g 200 ml^{-1}	*m*-Chlorophenyl 1.28 g	2.5 ml	65	MeOH:$CHCl_3$	240	Yellow
n	2.61 g 200 ml^{-1}	*p*-Chlorophenyl 1.28 g	2.5 ml	75	MeOH:$CHCl_3$	212	Yellow

according to the method described before (Butt *et al* 1991). The model compound **(iv-a)** discussed here was prepared by the addition of diazotized solution of aniline to **(iii)**. Compound **(iv-a)** in its IR spectrum (KBr) showed absorption at ν_{max}=3495(OH, ν_{max} C=O 1690 and ν_{max} C=O (lactone) 1640 cm^{-1} while the visible light absorption was observed at λ_{max} 572 nm, (log ε 4.2). Its mass spectrum showed molecular ionic peak at m/z 365 corresponding to its molecular formula $C_{19}H_{15}N_3O_5$. Its base peak appeared at m/z 77, (100%) the other prominent peaks present were at m/Z 333^+ (94) 256^+ (44) 172^+ (9) 118^+ (25) 93^+ (47) and 91^+ (46). The molecular formula was further confirmed by its elemental analysis found: C, 62.20; H, 3.98; N, 11.81; required for $C_{19}H_{15}N_3O_5$: C 62.50; H, 4.10 and N, 11.50. ^{1}Hnmr, spectrum of **(iv-a)** in $CDCl_3$ showed a singlet at 58.15 Hz indicated the presence of two hydroxyl protons in nature. On addition of D_2O this peak did not undergo complete exchange. It was due to the hydrogen bonding between ester carbonyl next to hydrogen of hydroxyl group. Another singlet centred at δ 3.95 Hz was due to the three methyl protons of ester group. Two multiples centred between δ 7.18-7.29 Hz and δ 7.42-7.51 Hz accounting for the ten protons of the two phenyls present in the molecule. The visible light absorption spectra, IR spectra, physical data and elemental analysis of other similarly prepared compounds **(iv b-o)** are shown in Table 1, 2 and 3.

Now one of the hydroxyl group of **(iii)** in the neighbourhood of nitrogen under goes methylation with an ethereal solution of diazomethane. By keeping the reaction mixture over night at 0°C methoxy derivative **(v-a)** was obtained which on crystallization with a 1:1 mixture of chloroform and methanol afforded crystalline solid m.p 260°C. Its molecular formula confirmed through its elemental analysis as $C_{20}H_{17}N_3O_5$. With

Table 3
Elemental analysis of compounds **(iv a-o)**

S.no.	Molecular formula	Found			Requires		
		C	H	N	C	H	N
a	$C_{19}H_{15}N_3O_5$	62.2	3.89	11.81	62.50	4.10	11.50
b	$C_{19}H_{14}N_4O_7$	54.81	3.28	13.43	59.90	3.40	13.50
c	$C_{19}H_{14}N_4O_7$	54.69	3.25	13.40	54.90	3.40	13.50
d	$C_{19}H_{14}N_4O_7$	54.79	3.15	13.23	54.90	3.40	13.50
e	$C_{19}H_{14}N_4O_5$	63.01	4.31	11.17	63.30	4.50	11.10
f	$C_{19}H_{14}N_4O_5$	63.18	4.29	10.90	63.30	4.50	11.10
g	$C_{19}H_{14}N_4O_5$	63.24	4.27	11.00	63.30	4.50	11.10
h	$C_6H_{14}N_4O_6$	60.65	4.18	10.42	60.80	4.30	10.60
i	$C_6H_{14}N_4O_6$	60.64	4.16	10.30	60.80	4.30	10.60
j	$C_6H_{14}N_4O_6$	60.64	4.21	10.48	60.80	4.30	10.60
k	$C_{19}H_{14}N_4O_5Br$	51.22	3.10	9.40	51.40	3.20	9.50
l	$C_{19}H_{14}N_4O_5Br$	51.27	3.16	9.40	51.40	3.20	9.50
m	$C_{19}H_{14}N_4O_5Cl$	57.00	3.39	10.45	57.10	3.50	10.50
n	$C_{19}H_{14}N_4O_5Cl$	56.80	3.40	10.40	57.10	3.50	10.50
o	$C_{19}H_{14}N_4O_5Cl$	56.90	3.38	10.50	57.10	3.50	10.50

morpholine, compounds **(iv-a)** yielded morpholinum salt **(vi-a)** which could be converted back into the original compound i.e. **(iv-a)** by treating with mineral acids.

The polyester fabric was treated at 130°C with an aqueous solution of **(iv a-o)** having nonionic dispersing agent and a dye carrier at pH between 5-6, for one hour. Upon washing and drying showed various shades of orange-yellow colours. Applications of dyes will appear in a separate communication.

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