Asian Journal of Chemistry Vol. 21, No. 1 (2009), 304-312

Synthesis and Application of Bifunctional Reactive Dyes Based on 3-(4-Aminophenyl)-5-benzylidene-2-substituted phenyl-3,5-dihydro-imidazol-4-one

DEVANG N. WADIA and PRAVIN M. PATEL*
Department of Industrial Chemistry, V.P. & R.P.T.P. Science College
Vallabh Vidyanagar-388 120, India
E-mail: drpravinpatel@rediffmail.com

A series of nine novel heterocyclic based monoazo bifunctional reactive dyes were synthesized using various substituted imidazol-4-one. Heterobifunctional reactive dyes provide great opportunity for efficient dye fiber reaction due to the mixed double-anchors such as sulphatoethylsulphone and monochlorotriazinyl reactive groups, which may cover a wide range of application temperatures. Prepared heterobifunctional reactive dyes were applied to wool fibers using various parameters. The optimized exhaustion (% E) and fixation (% F) were determined. Analysis of dye solutions being adjusted to different pH conditions was carried out to verify the structure of dye moieties. The synthesized dyes were characterized using standard spectroscopic methods and then dyeing performance on wool fabric was assessed. Wash and light fastness properties of prepared dyes showed promising results.

Key Words: Imidazolone, Reactive dyes, Wool, Exhaustion, Fixation.

INTRODUCTION

The past three decades have witnessed considerable innovation in the field of azo dye chemistry based on heterocyclic systems and studies in the synthesis of such derivatives have been reported[1-5]. Most of the recent research has focused on structural variations of existing types, for example variations in substituent, especially on the side chains of the coupling components. The use of heterocyclic coupling component and diazo components in the synthesis of azo dyes is well established and the resultant dyes exhibit good tinctorial strength and brighter dyeing than those derived from aniline-based components. Heterocyclic based azo dyes are found to have excellent properties as dyes for polyester, cotton and wool textiles[6-9]. A majority of acid dyestuffs are sulphonic acid derivatives of azo dyes. They are applied from a dye-bath rendered acidic by addition of mineral acid or an organic acid. The free dye acids are difficult to isolate and are hygroscopic in nature making it difficult to pack and store them. These dyes are invariably isolated as sodium salts. Reactive dyes react chemically with amino groups within wool fibers to form a covalent bond. Theoretically, by virtue of the covalent nature of the dye-fiber bond, reactive dyeing on wool fibers can display excellent wash fastness without any recourse to an after treatment. Especially, reactive dyes containing heterobifunctional groups can provide great opportunity for efficient dye-fiber reaction due to the sulphatoethylsulphone and monochlorotriazinyl reactive systems, which may cover a wide range of application temperatures[10-12]. Many different heterocyclic diazo components have been studied, especially derivatives of thiazole, imidazole, benzimidazole owing to the marked bathochromic effect of such groups[13-15]. However, no report including the use of an amino derivative of this heterocycle in the preparation of reactive dyes is evident in the literature. In the present paper, the synthesis, characterization, application and dyeing properties of some reactive dyes derived from imidazolo-4-ones derivatives are reported.

EXPERIMENTAL

All the chemicals and solvents used are of laboratory grade and solvents were purified. Completion of the reaction was monitored by TLC (silica gel GF_{254} (E. Merck), toluene:methanol (8:2). The final dyes were purified by column chromatography using silica gel in increasing percentage of ethyl acetate in carbon tetrachloride. Infrared spectrum (KBr, cm^{-1}) were recorded on a Shimadzu-8400 FT-IR spectrometer, ^{1}H PMR spectra on a Brucker spectrometer (300 MHz) using TMS as a internal standard (chemical shift in δ, ppm)in $CDCl_3$ and DMSO-d_6 and C, H, N analysis on Perkin Elmer (USA) 2400 Series. Wool fabrics and dyeing facilities was provided by Atul Ltd. (India).

Preparation of 4-arylidene-2-phenyl-5-(4*H*)-oxazolones: 4-Arylidene-2-phenyl-5-(4*H*)-oxazolones were prepared according to the reported method[16,17].

General procedure for the preparation of 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3, 5-dihydro-imidazol-4-one (a): Equimolar amounts of 4-arylidene-2-phenyl-5-(4*H*)-oxazolone and *p*-phenylene diamine were taken in a reaction flask equipped with a reflux condenser and kept under reflux for 6 h, with dry pyridine as solvent. The content of the reaction mixture was poured in an ice-water medium to give coloured precipitates. The completion of reaction was monitored by TLC using toluene:methanol (8:2), yield 62-70 %. The product was crystallized from ethyl alcohol[17].

Preparation of 3-(4-amino-phenyl)-5-(4-methoxybenzylidene-2-phenyl-3,5-dihydro-imidazol-4-one) (a): Equimolar amount of 4-methoxy benzylidene-2-phenyl-5-(4*H*)-oxazolones and *p*-phenylene diamine were taken in a reaction flask equipped with a reflux condenser and kept under reflux for 6 h with dry pyridine as solvent. The content of the reaction mixture was poured in ice-water medium to give coloured precipitates. The completion of reaction was monitored by TLC using toluene:methanol (8:2), yield 62-70 %. The product was crystallized from ethyl alcohol[17].

IR (KBr, ν_{max}, cm^{-1}): 3300-3270 (-NH), 3100-3010 (aromatic C-H), 1600-1500 (C=C stretch), 1690 (C=O, imidazolinone ring), 1251 (C-O-C asymmetric stretch), 1026 (C-O-C symmetric stretch). ^{1}H NMR (δ, ppm): 8.04-6.60 (m, 13H, Ar-H), 6.01 (s, 1H, Ph-C=CH), 4.63 (br, 2H, $-NH_2$), 3.73 (s, 3H, $-OCH_3$)[17].

Preparation of 3-[4-(4,6-Dichloro-[1,3,5]triazin-2-ylamino)-phenyl]-5-(4-methoxy-benzylidene)-2-phenyl-3,5-dihydro-imidazol-4-one (b): A solution of cyanuric chloride (9.75 g, 0.053 mol) in acetone (40 mL) was poured into a vigorously stirred mixture of crushed ice (100 g) and water (100 mL). To this mixture a solution of 3-(4-amino phenyl)-5-(4-methoxy benzylidene)-2-phenyl-3,5-dihydro-imidazol-4-one (a), in water (100 mL, pH 6.5) was added dropwise at 0-5 ºC over 0.5 h at pH 3.5-4.5, using Na_2CO_3 solution (10 % w/v). The solution was stirred for further 1 h to complete the reaction[18].

Diazotization of 4-aminophenyl-β-sulfatoethyl sulfone (c) and coupling with 1-naphthol-8-amino-3,6-disulphonic acid [H-acid] (d): To the 25 mL of water in a beaker 2.96 g (95 % 0.01 mol) of 4-aminophenyl-β-sulfatoethyl sulfone (c) was added. While stirring the suspension was cooled down to 5 ºC using ice. To this solution 3.67 mL (3 N, 0.011 mol) of $NaNO_2$ and 5 g of ice were added. Then, 2.6 mL of conc. HCl was added to obtain a diazo component of 4-aminophenyl-β-sulfatoethyl sulfone. Completion of diazotization reaction was checked by starch iodide test. Excess HNO_2 was removed by adding a small amount of sulfamic acid.

The coupling solution was prepared by taking 3.9 g (82 %, 0.01 mol) of 1-napthol-8-amino-3,6-disulphonic acid (H-acid) in another beaker and 40 mL of water was added and the pH was adjusted between 9-10, using 10 % Na_2CO_3. The above prepared diazo solution was transferred to dropping funnel and was added dropwise to coupling solution while keeping the temperature 0-5 ºC to complete the coupling reaction[19].

Preparation of 5-(4-chloro-6-{4-[4-(4-hydroxy-benzylidene)-5-oxo-2-phenyl-4,5-dihydro-imidazol-1-yl]-phenylamino}-[1,3,5]triazin-2-ylamino)-4-hydroxy-3-[4-(2-sulfooxy-ethanesulfonyl)-phenylazo]-napthalene-2,7-disulfonic acid (e): A solution of 3-[4-(4,6-dichloro-[1,3,5]triazin-2-ylamino)-phenyl]-5-(4-methoxy benzylidene)-2-phenyl-3,5-dihydro-imidazol-4-one (b) (5 g, 0.01 mol) was prepared in 100 mL water and 10 mL of 10 % HCl in a beaker.

To this resulting solution, an aqueous solution (200 mL, pH 6.5) of compound (d) (6.1 g, strength 93 %, 0.01 mol) was added dropwise at 35 ºC over 1 h with the pH maintained between 6.0-6.5 using sodium carbonate solution (10 % w/v) and 10 % HCl. The mixture was stirred for a further 1 h to complete the reaction. The product was then used as dyes[20].

IR (KBr, ν_{max}, cm^{-1}): 3447 (OH), 3290(s) N-H, 1707(s) C=O imidazolinone ring, 1596(s) N=N, 1600-1500 (C=C *str.*), 1600-1500(s) C=C, below 900(br) C-H, 1900-1500(s) C=N, 1221 (C-O-C asymm. *str.*), 1042 (C-O-C symm. *str.*) 1138(s) S=O, 780(s) C-Cl. ^{1}H NMR (δ, ppm): 7.52-6.74 (m, 20H, Ar-H), 4.47 (m, 1H, OH), 3.77 (br, 2H, NH), 2.82-2.36 (s, 4H, CH_2O).

General procedure for dyeing

Wool blend fabric: Knitted wool, 70/30, blended fabric of 310 g/m^2, was initially treated in an aqueous solution with a liquor ratio 50:1 containing 0.5 g/L sodium carbonate and 2 g/L non-ionic at 60 ºC for 0.5 h, after which time it was thoroughly rinsed and dried at room temperature.

Dyeing procedure: Dyes were first applied to wool component (2 g samples) using 1 % owf Albegal A, 5 % of ammonium sulphate and 3 % dye. Samples were introduced into the dyebath at 50 ºC and the temperature was raised to 98-100 ºC over 40 min, then the pH of the dyebath was adjusted to 4.5 to 5.0 by diluted acetic acid and the dyeing continued at the boil for a further 1 h. After this time, the dyebath temperature was reduced to 60 ºC and then the samples were removed from the dye pots, rinsed in cold water and warm water[21] for 10 min.

Determination of exhaustion (% E) and fixation (% F): To determine dyeing characteristics, absorbance measurements of the original dyebath and the exhausted dyebath were carried out using a Shimadzu UV-2401PC UV/Visible spectrophotometer. Using a previously established absorbance/concentration relationship at the λ_{max} of the dyes, the quantity of reactive dye in solution was calculated and the extent of exhaustion (% E) achieved was determined using following equation, where D_0 and D_t are the quantities of dye initially in the bath and of residual dye in the final bath, respectively[22] (Table-1).

$$\%\ E = \frac{(D_0 - D_t)}{D_0} \times 100 \qquad (1)$$

Unfixed dye from the fabrics was extracted using 25 % aqueous pyridine solution and then measured spectrophotometrically. The extent of fixation (% F) was calculated using eqns. 2, where D_e is the amount of extracted dye.

$$\%\ F = \frac{(D_0 - D_t - D_e)}{D_0 - D_t} \times 100 \qquad (2)$$

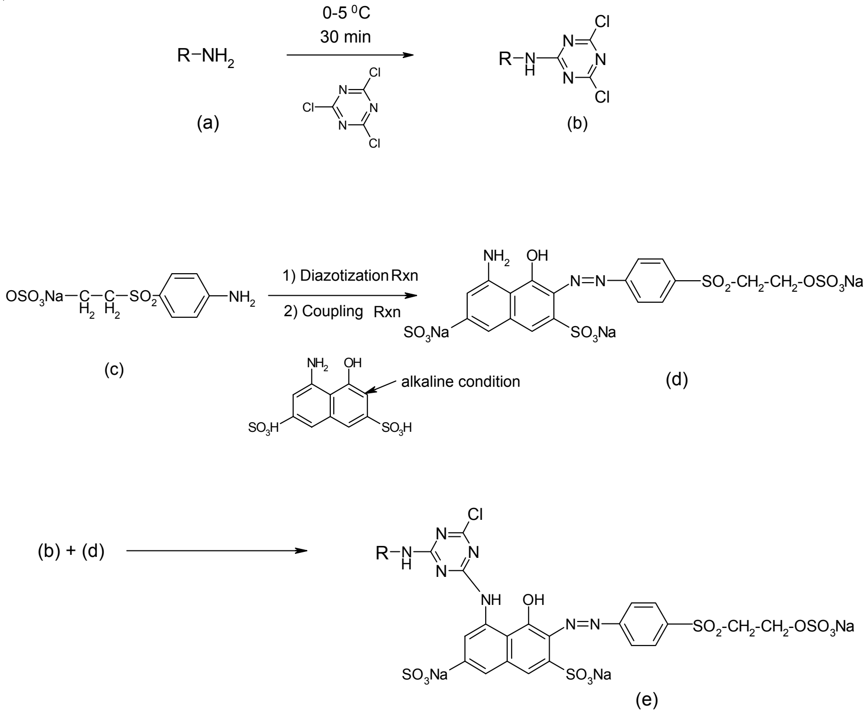
TABLE-1
CHARACTERIZATION, % EXHAUSTION AND FIXATION DATA OF DYES D1-D9

Dye	Substitution (x) / [m.w. (g/mol)]	Yield (%) / (λ_{max}, nm)	Found (calcd.) %			Exhaustion (%)	Fixation (%)
			C	H	N		
D1	4-OCH_3 (1092.51)	63 (395)	48.37 (48.19)	3.02 (3.10)	11.63 (11.70)	71.25	78.28
D2	3,4,5-OCH_3 (1152.56)	65 (397)	47.89 (47.93)	3.23 (3.12)	10.87 (10.94)	85.31	84.78
D3	4-OH (1078.48)	65 (420)	47.92 (47.87)	2.81 (2.90)	11.76 (11.58)	85.09	80.98
D4	4-Cl (1096.93)	65 (366)	47.17 (47.13)	2.73 (2.79)	11.52 (11.63)	86.56	55.22
D5	2-OH,3-CH_3 (1108.51)	62 (420)	47.58 (47.63)	3.16 (3.19)	11.29 (11.41)	65.93	76.22
D6	2-OH (1078.48)	55 (402)	47.81 (47.76)	2.91 (2.85)	11.57 (11.63)	78.12	74.68
D7	4-$N(CH_3)_2$ (1105.55)	70 (376)	48.79 (48.71)	3.30 (3.38)	12.60 (12.67)	70.93	81.24
D8	H (1062.48)	71 (393)	48.53 (48.54)	3.12 (3.18)	11.81 (11.90)	71.00	84.71
D9	4-F (1080.47)	69 (365)	47.76 (47.86)	2.93 (2.87)	11.60 (11.55)	78.43	79.66

Fastness measurements: Wool fibres dyed with a 1/1 strength of the auxiliary standard were used to test colour fastness to washing at 40 ºC. Fastness to light was measured using a Xenotest 150S apparatus (Heraus Hanau). The results are shown in Table-2.

TABLE-2
SHADES AND FASTNESS PROPERTIES OF DYES D1-D9

Dye	Colour of dyed fabrics	Light fastness	Wash fastness
D1	Light Purple	4-5	5
D2	Dark Purple	5	5
D3	Dark Purple	5	4-5
D4	Light Purple	5	4
D5	Dark Purple	4-5	5
D6	Dark Purple	5	4-5
D7	Light Purple	5	5
D8	Light Purple	5	4-5
D9	Light Purple	4-5	5



R = 3-(4-Amino phenyl)-5-benzylidene-2-substituted(x)phenyl-3,5-dihydro imidazol-4-one

Scheme

RESULTS AND DISCUSSION

Starting compound 4-arylidene-2-phenyl-5-(4*H*)-oxazolones derivatives were prepared by Erlenmeyer condensation of benzolyglycine with different aldehydes in presence of sodium acetate and acetic anhydride[16,17].

The prepared 5-oxazolone were treated with *p*-phenylene diamine in basic medium to prepared 3-(4-amino phenyl)-5-benzylidene-2-substituted phenyl-3,5-dihydro-imidazol-4-one (a). The IR spectrum of compound (a) showed the NH bands at 3300-3270 cm^{-1} and the C=O band nearly at 1690 cm^{-1}.

^1H NMR spectrum shows broad peak at 4.63 ppm was due to the protons of the $-NH_2$ group. The benzylidene proton of (Ph-C=CH) was found in downfield region at δ 6.01 ppm. In the case of $4-OCH_3$, singlet is observed at δ 3.73 ppm which corresponds to the three protons of $-OCH_3$. Compound (b) and (d) were prepared by known reported methods[18,19]. The final dye (e) was the condensation product of compounds (b) and (d)[20]. The IR spectrum of compound (e) showed the OH bands nearly at 3447 cm^{-1}, NH bands nearly at 3290 cm^{-1}, the C=O band nearly at 1707 cm^{-1}, N=N bands nearly at 1596 cm^{-1} and the C-Cl bands nearly at 780 cm^{-1}.

^{1}H NMR spectrum showed a multiplet at δ 7.527-6.754 ppm due to aromatic protons (20 H), the benzylidene proton of (Ph-C=CH) was also found in the same region but was overlapped by multiplet of aromatic protons, the spectrum showed a singlet at δ 4.475 ppm due to -OH protons (1H), a singlet was seen at δ 3.775 ppm due to -NH protons (2H), a triplet was seen at δ 2.827-2.763 ppm due to protons of $-H_2C-CH_2-O-SO_3Na$ (2H), an another triplet was seen at δ 2.486-2.367 ppm due to protons of $-H_2C-CH_2-O-SO_3Na$ (2H).

The absorption maxima of the dyes varied from 365-420 nm; which was light to dark purple shades. Comparing the λ_{max} values of dyes D2, D3, D5, D6 with those of dyes D1, D4, D7, D8, D9 a bathochromic and hyperchromic effect was observed. As expected the incorporation of an electron donating group gave rise to bathochromic effect.

Introduction of strong electron donating group provides bathochromic shades, thus most bathochromic dye prepared was dye D5 due to presence of two electron donating group. (2-OH, 3-OCH_3, 420 nm).

Introduction of electron withdrawing group provides hypsochromic effect, thus most hypsochromic dye prepared was dye D9 due to presence of electron withdrawing group (4-F, 365 nm).

Dyeing properties: In this context, the aim was to determine the level of fastness, displayed by prepared heterocyclic acid dyes on wool substrates. The dyes were applied to wool at a 2 % shade. % Exhaustion and % fixation values, λ_{max} values are shown in Table-1. The hues and data on dye fastness properties are shown in Table-2. The results showed that dyes D1-D9 had reasonably good wash and light fastness properties.

Effect of pH on exhaustion (% E), fixation (% F): The results (Figs. 1 and 2) show that exhaustion (% E) of the dyes on wool fibers increased

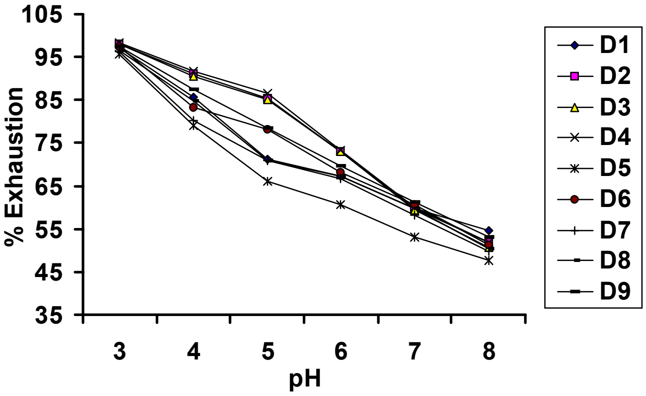


Fig. 1. Effect of application pH on exhaustion (% E)

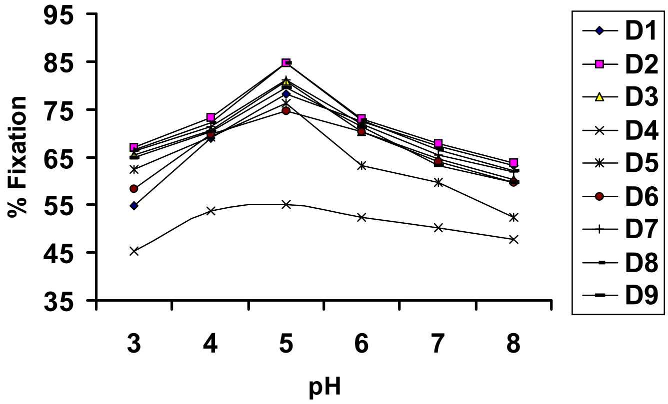


Fig. 2. Effect of application pH on fixation (% F)

with decreasing pH of application and that fixation (% F) of the dyes on wool fibers increased with increasing pH of application. Results displays that the highest total fixation efficiency was achieved at pH 5. At lower pH values, higher extent of protonation of the amino groups within wool fibers leads to high exhaustion and low fixation, because the ensuing low concentrations of nucleophilic amino groups in the substrates are unable to react with the dye. In addition, at low pH, the dye is prevalent only at low concentration in the dyebath. Hence, the majority of dye fiber interaction can be assumed to have occurred between protonated amino groups and dye.

ACKNOWLEDGEMENTS

The authors are thankful to Principal V.P & R.P.T.P Science College, Head and Industrial Chemistry Department for providing laboratory facility and to Atul Ltd.(Gujarat) for providing dyeing facilities.

REFERENCES

1. O. Annen, R. Egli, B. Henzi, H. Jakob and P. Matzinger, *Rev. Prog. Coloration*, **17**, 72 (1987).
2. K.M. Patel, V.H. Patel, M.P. Patel and R.G. Patel, *Dyes Pigments*, **55**, 53 (2002).
3. A.D. Towns, *Dyes Pigments*, **42**, 3 (1999).
4. J.H. Choi, S.H. Hong and A.D. Towns, *J. Soc. Dyers Colourists*, **115**, 32 (1999).
5. J.H. Choi, S.H. Hong, E.J. Lee and A.D. Towns, *J. Soc. Dyers Colourists*, **116**, 273 (2000).
6. E. Sternberg and D. Dolphin, in ed.: M. Matsuoka, Infrared Absorbing Dyes, New York, Plenum, Ch. 15 (1990).
7. G. Hallas and A.D. Towns, in ed.: M.F. Ansell, Rodd's Chemistry of Carbon Compounds, Amsterdam, Elsevier, Vol. 4, edn. 2, Ch. 45.
8. P.F. Gordon, in eds.: D.R. Waring and G. Hallas, The Chemistry and Application of Dyes, New York, Plenum, Ch. 8 (1990).
9. P. Gregory, *Rev. Prog. Coloration*, **24**, 1 (1994).

10. J.A. Taylor, K. Pasha and D.A.S. Phillips, *Dyes Pigments*, **51**, 145 (2001).
11. M. Matsui, U. Meyer and H. Zollinger, *J. Soc. Dyers Colour.*, **104**, 425 (1988).
12. K. Hunger, Industrial Dyes: Chemistry, Properties, Applications, Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA; pp. 113-28 (2003).
13. M.A. Weaver and L. Shuttleworth, *Dyes Pigments*, **3**, 81 (1982).
14. L.S. Efros, G.N. Kul'bitskii and M.G. Romanova, *Chem. Heterocycl. Comp.*, **6**, 205 (1970).
15. Y. Zhanga, G. Zhanga, Q. Gana and S. Wang, *Dyes Pigments*, **74**, 531 (2007).
16. A.I. Vogel, A Text Book of Practical Organic Chemistry, Longman, London, p. 909 (1971).
17. P.V. Bhatt, D.N. Wadia, P.M. Patel and R.M. Patel, *Asian J. Chem.*, **18**, 1248 (2006).
18. J. Mokhtari, D.A.S. Philips and J.A. Taylor, *Dyes Pigments*, **63**, 51 (2004).
19. K. Yusung, S.K. Young, K. Jinsoo, et.al, United States Patent Application Publication, Pub. No - US 2004/0143106 Al (2004).
20. J. Mokhtari, D.A.S. Phillips and J.A. Taylor, *Dyes Pigments*, **64**, 163 (2005).
21. E. Shishtawy, Y.A. Youssef, N.S.E. Ahmed and A.A. Mousa, *Dyes Pigments*, **72**, 57 (2007).
22. Y.A. Sona, J.P. Honga, H.T. Lima and T.K. Kim, *Dyes Pigments*, **66**, 231 (2005).

(*Received*: 13 December 2007; *Accepted*: 20 August 2008) AJC-6771