

AlCl₃-Catalyzed diazocoupling of 1-(aryl/hetaryl)-3-phenyl-1*H*-pyrazol-2-in-5-ones in aqueous medium. Synthesis of hetaryl-azopyrazolones and their application as disperse dyes

Salem A. Basaif, Mohamed A. Hassan*, Adil A. Gobouri

Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, P.O. Box 80203, Saudi Arabia

Received 20 March 2005; received in revised form 12 July 2005; accepted 23 September 2005

Available online 23 November 2005

Abstract

Organic synthesis in water is a new methodology of green chemistry. AlCl₃-catalyzed diazocoupling of 1-(aryl/hetaryl)-3-phenyl-1*H*-pyrazol-2-in-5-ones (**1**) in water with different aryl/hetaryldiazonium salts afforded the corresponding hetaryl-azopyrazolones (**2**) as colored products with high yields. These dyes were characterized by UV–vis, FT-IR and ¹H NMR spectroscopic techniques and elemental analysis. Cotton, wool, silk and polyesters fabrics were dyed and their photostability and color fastness were identified.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: AlCl₃-Catalyst; Diazocoupling in water; 1-(Aryl/hetaryl)-3-phenyl-1*H*-pyrazol-2-in-5-ones; Photostability; Color fastness

1. Introduction

5-Pyrazolones are very important class of heterocycles due to their biological and pharmacological activities [1,2] which exhibit anti-inflammatory [3], herbicidal [4], fungicidal [5], bactericidal [5], plant growth regulating [4], antipyretic [6] and protein kinase inhibiting [7] properties. Also, they are used as key starting material for the synthesis of commercial aryl/hetarylazopyrazolone dyes [8,9].

On the other hand, it is well known that the most important commercial application of pyrazolinones is their use as good fastness dyestuffs for wool, cotton, silk, leather, rubber and synthetic polyamides (Nylons). Many azopyrazolone dyes have been utilized as chromogenic reagents for the colorimetric determinations [10,11] and as indicators for complexometric titrations [12]. Also, there are some arylazopyrazolone dyes having potent antimicrobial activities [13].

In recent years water has become an intriguing reaction medium, especially for metal salt catalyzed organic reactions

[14,15]. In many cases the catalyst and/or the aqueous medium can be recovered and reused, thereby reducing the environment impact of this process [16–18].

Water as a reaction medium has particularly captured the interest of organic chemists [14,15,19,20] and reactions previously thought impossible in water are now a reality. Many Lewis acids work well in aqueous medium [21,22], and even AlCl₃, SnCl₂ and TiCl₄ which were previously used under anhydrous conditions are excellent catalysts in water [16].

One of the greatest advantages of aqueous media [23] with respect to organic solvents is the possibility to control and change the pH during the reactions. These affect the acid/base equilibria and the nature and concentration of the active species, with dramatic effects on reaction rates and product selectivity [24]. Therefore, we reported here the synthesis of many new 4-arylaazo-3-substituted-1*H*-2-pyrazolin-5-ones in water that might be used as useful azodyes.

2. Experimental

All melting points reported are uncorrected. IR spectra were recorded using Perkin Elmer's Spectrum RXIFT-IR spectrophotometer (ν in cm⁻¹). The NMR spectra were recorded

* Corresponding author. Ain Shams University, Faculty of Science, Chemistry Department, Abbasia, Cairo, Egypt. Tel.: +20 2 483 1836; fax: +20 10 164 8960.

E-mail address: mahassan77@yahoo.com (M.A. Hassan).

Table 1
Physical data of 1-(aryl/hetaryl)-3-phenyl-1*H*-pyrazol-2-in-5-ones (**1a–c**)

Compound	Molecular formula (m. wt)	M.p. (°C)	Yield	Elemental analysis: calcd. (found)		
				C	H	N
1a	C ₁₄ H ₁₁ N ₃ O (237.09)	116	88	70.86 (70.1)	4.68 (4.63)	17.72 (17.59)
1b	C ₁₅ H ₁₁ N ₂ OCl (270.06)	160	93	66.65 (66.53)	4.11 (4.08)	10.37 (10.25)
1c	C ₁₆ H ₁₄ N ₂ O ₂ (266.11)	129	90	72.15 (72.03)	5.30 (5.28)	10.52 (10.40)

on Bruker Avance DPX400 spectrometer, using pyridine-*d*₅ as a solvent and TMS as an internal standard (chemical shifts in δ values in ppm). The UV–vis spectra were recorded in ethanol using Shimadzu, Carry 50 (λ in nm). Elemental analyses were performed on Perkin Elmer 2400, series II micro-analyzer. Ethyl benzoylacetate, 2-hydrazinopyridine, 4-chlorophenylhydrazine hydrochloride and 4-methoxyphenylhydrazine hydrochloride are Aldrich products and they are used without any further purification.

*2.1. Condensation of β -ketoester with hydrazines: formation of 5-hydroxy-3-phenyl-1-(pyrid-2-yl)-1*H*-pyrazole (**1a**) and 1-(4-chloro/methoxy)-phenyl-3-phenyl-2-pyrazolin-5-ones (**1b,c**)*

A mixture of ethyl benzoylacetate (0.024 mol) and 2-hydrazino-pyridine, 4-chlorophenylhydrazine hydrochloride or 4-methoxy-phenylhydrazine hydrochloride (0.025 mol) was heated in an oil bath at 150–160 °C for 3 h then cooled and triturated with diethyl ether (20 ml). The ether was removed by filtration and the solid residue was crystallized from ethanol to give 5-hydroxy-3-phenyl-1-(pyrid-2-yl)-1*H*-pyrazole (**1a**)

and 1-(4-chloro/methoxy)-phenyl-3-phenyl-2-pyrazolin-5-ones (**1b,c**) as white crystals. The physical data are listed in Table 1.

*2.2. Diazocoupling of the pyrazolones (**1a–c**) with aromatic diazonium salt: formation of 1-aryl-4-aryldiazo-3-phenyl-2-pyrazolin-5-ones (**2–4**)*

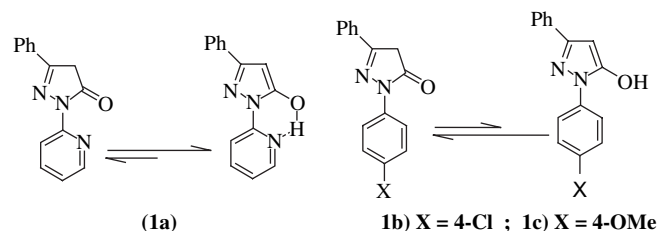
4-Aryldiazo derivatives (**2–4**) of 3-phenyl-2-pyrazolin-5-one (**1a–c**) were prepared by coupling of the respective pyrazolinone with a freshly prepared solution of the desired diazonium salt, in an ice bath, namely, 4-aminophenol hydrochloride, 4-aminobenzoic acid, 4-aminosalicylic acid, 4-amino-1-naphthalenesulphonic acid, 4-amino-*N,N*-dimethylaniline hydrochloride, 4-amino-*N,N*-diethylaniline sulphate and benzidine dihydrochloride, in water and in the presence of AlCl₃.

The desired aromatic amine (0.015 mol) was dissolved in concentrated hydrochloric acid (2 ml), diluted with water (20 ml) and cooled at 0–5 °C in an ice bath. An aqueous cold solution of sodium nitrite (0.015 mol in 20 ml water) was added to the prepared aromatic amine hydrochloride to give the desired diazonium chloride solution. The latter solution was added drop-wise with stirring for 30 min in an ice bath to a cold suspension of 1-(aryl/hetaryl)-3-phenyl-1*H*-pyrazol-2-in-5-ones

Table 2
Physical data of 1-(aryl/hetaryl)-3-phenyl-1*H*-pyrazole-4,5-dione-4-arylhydrazones (**2–4**)

Compound	Molecular formula (m. wt)	M.p. (°C) (color)	Solvent. cryst. (yield %)	Elemental analysis: calc. (found)		
				C	H	N
2a	C ₂₀ H ₁₅ N ₅ O ₂ (357.37)	254 (Red)	AcOH (83)	67.22 (67.16)	4.23 (4.18)	19.60 (19.49)
2b	C ₂₁ H ₁₅ N ₅ O ₃ (385.38)	278 (Orange)	AcOH (80)	65.45 (65.31)	3.92 (3.88)	18.17 (18.09)
2c	C ₂₁ H ₁₅ N ₅ O ₄ (401.38)	268 (Orange)	AcOH (82)	62.84 (62.71)	3.77 (3.73)	17.45 (17.28)
2d	C ₂₄ H ₁₇ N ₅ O ₄ S (471.49)	265 (Orange)	AcOH (87)	61.14 (61.02)	3.63 (3.60)	14.85 (14.67)
2e	C ₂₂ H ₂₀ N ₆ O (384.44)	186 (Deep Violet)	EtOH (92)	68.73 (68.58)	5.24 (5.19)	21.86 (21.73)
2f	C ₂₄ H ₂₄ N ₆ O (412.49)	224 (Deep Violet)	P.E. (95)	69.88 (69.72)	5.86 (5.83)	20.37 (20.22)
2g	C ₄₀ H ₂₈ N ₁₀ O ₂ (680.73)	247 (Red)	AcOH (79)	70.58 (70.41)	4.15 (4.13)	20.58 (20.42)
3a	C ₂₁ H ₁₅ N ₄ O ₂ Cl (390.83)	143 (Orange)	EtOH (87)	64.54 (64.39)	3.87 (3.83)	14.34 (14.22)
3b	C ₂₂ H ₁₅ N ₄ O ₃ Cl (418.84)	296 (Orange)	EtOH (84)	63.09 (62.93)	3.61 (3.57)	13.38 (13.21)
3c	C ₂₂ H ₁₅ N ₄ O ₄ Cl (434.84)	273 (Orange)	EtOH (85)	60.77 (60.62)	3.48 (3.46)	12.88 (12.70)
3d	C ₂₅ H ₁₇ N ₄ O ₄ ClS (504.95)	285 (Orange)	EtOH (88)	59.47 (59.28)	3.39 (3.35)	11.10 (10.98)
3e	C ₂₃ H ₂₀ N ₅ OCl (417.90)	194 (Deep Red)	P.E. (95)	66.11 (65.97)	4.82 (4.80)	16.76 (16.59)
3f	C ₂₅ H ₂₄ N ₅ OCl (445.95)	147 (Deep Violet)	P.E. (96)	67.33 (67.19)	5.42 (5.38)	15.70 (15.56)
3g	C ₂₄ H ₂₈ N ₈ O ₂ Cl ₂ (531.44)	244 (Brown)	EtOH (81)	54.24 (54.11)	5.31 (5.28)	21.08 (20.91)
4a	C ₂₂ H ₁₈ N ₄ O ₃ (386.41)	224 (Red)	AcOH (87)	68.38 (68.22)	4.70 (4.65)	14.50 (14.33)
4b	C ₂₃ H ₁₈ N ₄ O ₄ (414.42)	286 (Deep Brown)	AcOH (83)	66.66 (66.49)	4.38 (4.34)	13.52 (13.36)
4c	C ₂₃ H ₁₉ N ₄ O ₅ (431.43)	251 (Deep Orange)	AcOH (85)	64.03 (63.89)	4.44 (4.40)	12.99 (12.82)
4d	C ₂₆ H ₂₀ N ₄ O ₅ S (500.53)	266 (Deep Red)	AcOH (89)	62.39 (62.25)	4.03 (4.01)	11.19 (11.06)
4e	C ₂₄ H ₂₃ N ₅ O ₂ (413.48)	342 (Deep Violet)	EtOH (94)	69.72 (69.58)	5.61 (5.58)	16.94 (16.77)
4f	C ₂₆ H ₂₇ N ₅ O ₂ (441.53)	142 (Deep Violet)	EtOH (96)	70.73 (70.56)	6.16 (6.13)	15.86 (15.71)
4g	C ₄₄ H ₃₄ N ₈ O ₄ (738.81)	303 (Deep Red)	AcOH (73)	71.53 (71.38)	4.64 (4.62)	15.17 (15.03)

(**1a–c**, 0.01 mol) in water (50 ml) containing AlCl_3 (3.0 g). The pH of the reaction mixture was monitored between 3 and 4. After complete addition, the colored precipitated dyes were filtered, washed with water (3×25 ml) and dried. The solid products (**2–4**) are crystallized from the proper solvents. The results are listed in Table 2.



Scheme 1. 1-(Aryl/hetaryl)-3-phenyl-1H-pyrazol-2-in-5-ones (**1a–c**).

3. Result and discussion

After a long investigation using different metal salts at different pH, we found that under acidic conditions $\text{pH} \leq 4.0$, a heterogeneous reaction in aqueous medium of aromatic diazonium chlorides is coupled with 1-(aryl/hetaryl)-3-phenyl-1H-pyrazol-2-in-5-ones (**1a–c**) at 0–5 °C in the presence of aluminum chloride (AlCl_3) as catalyst to give the colored 1-(aryl/hetaryl)-3-phenyl-1H-pyrazole-4,5-dione-4-arylhydrazones (**2–4**). No

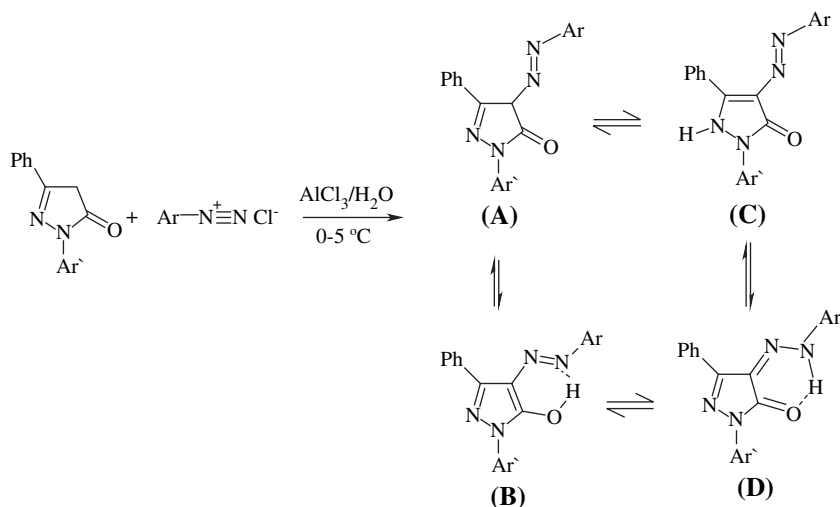
coloration or formation of azopyrazolones is observed in aqueous medium in the absence of AlCl_3 .

In continuation to our interest in pyrazolones' chemistry [25–27] and azopyrazolones [28], we have reported here the synthesis of some new intensively colored 1-(aryl/hetaryl)-3-phenyl-1H-pyrazole-4,5-dione-4-arylhydrazones (**2–4**) in water that might be used as commercial dyes.

Table 3

NMR-spectral data of 1-(aryl/hetaryl)-3-phenyl-1H-pyrazol-2-in-5-ones (**1a–c**) and 1-(aryl/hetaryl)-3-phenyl-1H-pyrazole-4,5-dione-4-arylhydrazones (**2–4**)

Dye no.	UV–vis (λ in nm)	IR spectra in KBr (ν in cm^{-1})			^1H NMR (δ in ppm)
		C=N, C=C	C=O	NH, OH	
1a	—	1610, 1585	—	3439 (enolic)	(CDCl_3): 5.97 (s, 1H, C4-H), 7.12–8.26 (m, 9H, ArH), 12.86 (b, 1H, OH).
1b	—	1588, 1569	1704	—	(CDCl_3): 3.85 (s, 2H, C4-H), 7.26–7.97 (m, 9H, ArH).
1c	—	1606, 1577	1703	—	(CDCl_3): 3.82 (s, 3H, OCH_3), 3.84 (s, 2H, C4-H), 6.96–7.87 (m, 9H, ArH).
2a	445	1596, 1554	1655	3420b, 3322	(CDCl_3 + DMSO): 7.44–8.19 (m, 13H, ArH), 10.10 (s, 1H, OH), 14.50 (b, 1H, NH).
2b	405	1582, 1544	1654	3400b, 3338	
2c	415	1600, 1545	1702	3436b, 3317	
2d	449	1579, 1546	1660	3493b	
2e	513	1575, 1542	1655	3445b	(CDCl_3): 3.04 (s, 6H, $\text{N}(\text{CH}_3)_2$), 6.77–8.63 (m, 13H, ArH), 14.49 (b, 1H, NH).
2f	530	1599, 1558	1648	3476b	(CDCl_3): 1.20 (s, 6H, $2 \times \text{CH}_3$), 3.4 (q, 4H, $2 \times \text{NCH}_2$), 6.71–8.62 (m, 13H, ArH), 14.53 (b, 1H, NH).
2g	464	1609, 1542	1665	3440b	
3a	439	1588, 1539	1632	3425b, 3368	(Pyridine- d_5 / CDCl_3): 7.0–8.6 (m, 13H, ArH), 11.90 (b, 1H, OH), 14.3 (b, 1H, NH).
3b	413	1588, 1555	1683	3440b, 3580	(Pyridine- d_5 / CDCl_3): 7.18–8.60 (m, 13H, ArH), 13.97 (b, 1H, NH), 15.8 (s, 1H, COOH).
3c	421	1597, 1549	1662	3456b, 3312	(Pyridine- d_5 / CDCl_3): 7.15–8.59 (m, 12H, ArH), 10.93 (s, 1H, OH), 13.87 (b, 1H, NH).
3d	447	1595, 1566	1661	3465b	
3e	510	1610, 1568	1660	3355b	(CDCl_3): 3.03 (s, 6H, $\text{N}(\text{CH}_3)_2$), 6.77–8.25 (m, 13H, ArH), 14.37 (b, 1H, NH).
3f	525	1601, 1554	1647	3345b	(CDCl_3): 1.21 (t, 6H, $2 \times \text{CH}_3$), 3.41 (q, 4H, $2 \times \text{NCH}_2$), 6.7–8.2 (m, 13H, ArH), 14.42 (s, 1H, NH).
3g	444	1557, 1605	1665	3325b	
4a	438	1595, 1562	1670	3423b, 3301	(Pyridine- d_5): 3.8 (s, 3H, OCH_3), 7.3–8.85 (m, 13H, ArH), 12.23 (b, 1H, OH), 13.43 (b, 1H, NH).
4b	410	1587, 1554	1690	3412b, 3336	(Pyridine- d_5): 3.85 (s, 3H, OCH_3), 7.3–8.85 (m, 13H, ArH), 13.22 (b, 1H, NH), 16.2 (s, 1H, OH).
4c	413	1610, 1548	1688	3445b, 3358	(Pyridine- d_5): 3.85 (s, 3H, OCH_3), 7.3–8.86 (m, 12H, ArH), 14.47 (b, 1H, NH), 16.93 (s, 1H, OH).
4d	446	1583, 1556	1650	3434b	
4e	489	1606, 1555	1642	3403b	(CDCl_3): 3.02 (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.85 (s, 3H, OCH_3), 6.76–8.26 (m, 13H, ArH), 14.4 (b, 1H, NH).
4f	521	1600, 1562	1673	3411b	(CDCl_3): 1.23 (s, 6H, $2 \times \text{CH}_3$), 3.4 (d, 4H, $2 \times \text{NCH}_2$), 3.87 (s, 3H, OCH_3), 6.7–8.3 (m, 13H, ArH), 14.87 (b, 1H, NH).
4g	532	1591, 1553	1654	3400b	

Scheme 2. The expected tautomers of 1-(aryl/hetaryl)-3-phenyl-1*H*-pyrazol-2-in-5-ones.

The 1-(aryl/hetaryl)-3-phenyl-1*H*-pyrazol-2-in-5-ones (**1a–c**) exist in two tautomeric forms (**I**, **II**) due to their keto–enol tautomerism. The spectral data proved that pyrazolone (**1a**) existed mainly in enol form due to intramolecular chelation by H-bond while **1b** and **1c** existed in keto form (Scheme 1).

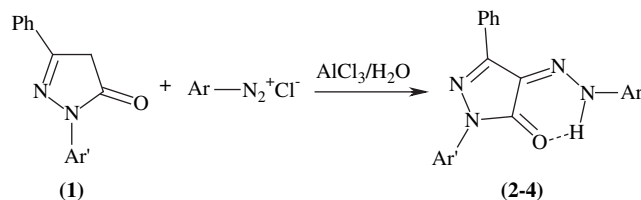
This phenomenon is confirmed by ¹H NMR and IR absorption spectra as shown in Table 3.

The approach reported here deals with the facile synthesis of some intensely colored 4-arylaazo-1-(aryl/hetaryl)-3-phenyl-2-pyrazolin-5-ones (**2–4**) that might be used as commercial dyes in aqueous medium. A cold solution of aryldiazonium chlorides of primary aromatic amines, namely, 4-aminophenol hydrochloride, 4-aminobenzoic acid, 4-aminosalicylic acid, 4-amino-1-naphthalenesulphonic acid, 4-amino-*N,N*-dimethylaniline hydrochloride, 4-amino-*N,N*-diethylaniline sulphate and benzdine dihydrochloride which were prepared by the

treatment of sodium nitrite solution with the hydrochloride solution of primary amines, are coupled at C4 of a cold solution of 1-(aryl/hetaryl)-3-phenyl-1*H*-pyrazol-2-in-5-ones (**1a–c**) in water in the presence of AlCl₃ as catalyst to give intensely colored 4-arylaazo-1-(aryl/hetaryl)-3-phenyl-2-pyrazolin-5-ones (**2–4**).

The dyes may exist in four possible tautomeric forms, namely two azo–keto forms A and C, the azo–enol form B and the hydrazone–keto form D, as shown in Scheme 2. The deprotonation of the four tautomers leads to a common anion.

Numerous investigations were carried out to establish the tautomeric structures of arylazo-5-pyrazolones both in the solid state and in solution using a variety of spectroscopic techniques. The spectral data generally lead to the conclusion that the tautomeric equilibrium of the arylazopyrazolone dyes is in favor of the hydrazone form (D) in the solid state and also in CHCl₃, DMSO and pyridine [8,29,30].



a, Ar' = pyrid-2-yl
b, Ar' = chlorophenyl,4-
c, Ar' = methoxyphenyl,4-

	Ar'	Ar		Ar'	Ar
2a	Pyrid-2-yl	C ₆ H ₄ -OH,4-	3e	chlorophenyl,4-	C ₆ H ₄ N(C ₂ H ₅) ₂ ,4-
2b	Pyrid-2-yl	C ₆ H ₄ -COOH,4-	3f	chlorophenyl,4-	C ₆ H ₄ N(C ₂ H ₅) ₂ ,4-
2c	Pyrid-2-yl	C ₆ H ₃ -OH-3,COOH,4-	3g	chlorophenyl,4-	C ₆ H ₄ -C ₆ H ₄ ,4-,4-
2d	Pyrid-2-yl	1-naphthyl-SO ₃ H,4-	4a	Methoxyphenyl,4-	C ₆ H ₄ -OH,4-
2e	Pyrid-2-yl	C ₆ H ₄ -N(CH ₃) ₂ ,4-	3b	Methoxyphenyl,4-	C ₆ H ₄ -COOH,4-
2f	Pyrid-2-yl	C ₆ H ₄ -N(C ₂ H ₅) ₂ ,4-	4c	Methoxyphenyl,4-	C ₆ H ₃ -OH-3,COOH,4-
2g	Pyrid-2-yl	C ₆ H ₄ -C ₆ H ₄ ,4-,4-	4d	Methoxyphenyl,4-	1-naphthyl-SO ₃ H,4-
3a	chlorophenyl,4-	C ₆ H ₄ -OH,4-	4e	Methoxyphenyl,4-	C ₆ H ₄ -N(CH ₃) ₂ ,4-
3b	chlorophenyl,4-	C ₆ H ₄ -COOH,4-	4f	Methoxyphenyl,4-	C ₆ H ₄ -N(C ₂ H ₅) ₂ ,4-
3c	chlorophenyl,4-	C ₆ H ₃ -OH-3,COOH,4-	4g	Methoxyphenyl,4-	C ₆ H ₄ -C ₆ H ₄ ,4-,4-
3d	chlorophenyl,4-	1-naphthyl-SO ₃ H,4-			

Scheme 3. 4-Arylaazo-1-(aryl/hetaryl)-3-phenyl-2-pyrazolin-5-ones (**2–4**).

Our spectral data listed in Table 3 proved that the 4-arylhydrazopyrazolones (D) are the existing structures of the synthesized dyes due to their stabilization by intramolecular hydrogen bonding. The color of the synthesized arylazopyrazolones (2–4) ranges from orange to deep violet crystals (Scheme 3).

The structures of arylhydrazopyrazolones (2–4) have been confirmed by elemental analysis (Table 2) and ^1H NMR, IR spectral data (Table 3).

It was observed from UV–vis absorption spectra in ethanol (Table 3) of dyes (2–4) that λ_{max} ranges from 405 to 532 nm proved that the *N*-hetaryl (pyrid-2yl) results in bathochromic shifts relative to *N*-aryl substituents when compared with analogous dyes [31]. Also, electron-donating *N,N*-dialkyl groups attached to the *p*-position of the azaryl-moiety result in bathochromic shifts relative to *p*-hydroxy group of the analogous dyes.

Wool, silk, cotton and polyester fabrics were dyed by standard direct dyeing method, that intense color ranges from Orange to Deep Violet were obtained. The percentage of fixation, photostability and wash fastness was investigated. The color fastness of the dyed fabrics was investigated using standard procedures [32].

All of the measured color fastness properties were highly acceptable for dyed wool and silk, moderately acceptable for cotton and weakly acceptable for polyester.

To study the photostability of the dyed fabrics, they were subjected to direct sunlight for five days. It was observed that the light fastness of the dyed fabrics was excellent for wool and silk, good for cotton and poor for polyester.

References

- [1] Scheibye S, El-Barbary AA, Lawesson SO, Fritz H, Rihs G. *Tetrahedron* 1982;38:3753.
- [2] Weissberger A, Wiley RH, Wiley P, editors. *The chemistry of heterocyclic compounds: pyrazolinones, pyrazolidones and derivatives*. New York: John Wiley; 1964.
- [3] Hiremath SP, Rudresh K, Saundan ARI. *Indian J Chem* 2002;41B(2):394.
- [4] Joerg S, Reinhold G, Otto S, Joachim SH, Robert S, Klaus L. *Ger Offen*; DE 3, 625, 686 (Cl C07D 231/22) [C.A. 1988; 108: 167465]; 04 February 1988.
- [5] Dhol PN, Achary TE, Nayak A. *J Indian Chem Soc* 1975;52:1196.
- [6] Souza FR, Souza VT, Ratzlaff V, Borges LP, Olivera MR, Bonacorso HG, et al. *Eur J Pharmacol* 2002;451(2):141.
- [7] Singh J, Tripathy R. *PCT Int Appl* 2001:138.
- [8] Karci F, Ertan N. *Dyes Pigments* 2002;55:99.
- [9] Ho YW. *Dyes Pigments* 2005;64:223.
- [10] Miyara H. *Bull Chem Soc Jpn* 1963;36:382; 1964;37:426; 1967;40:1875 and 2815.
- [11] Toeik. *Bull Chem Soc Jpn* 1965;38:1050.
- [12] Khalifa H, Issa RM. *Egypt J Chem* 1974;17:581.
- [13] Azarifar D, Shaebanzadeh M. *Molecules* 2002;7:885.
- [14] Li CJ, Chang TH, editors. *Organic reactions in aqueous media*. New York: Wiley; 1997.
- [15] Grieco PA, editor. *Organic synthesis in water*. London: Blackie Academic and Professional; 1998.
- [16] Fringuelli F, Pizzo F, Vaccarol L. *Tetrahedron Lett* 2001;42:1131.
- [17] Fringuelli F, Piermatti O, Pizzo F, Vaccarol L. *Curr Org Chem* 2003;7:1661.
- [18] Fringuelli F, Pizzo F, Tortoioli S, Vaccarol L. *J Org Chem* 2003; 68:8248.
- [19] Kobayashi S, Manabe K. *Acc Chem Res* 2002;35:209.
- [20] Tanaka K, Toda F. *Chem Rev* 2000;100:1025.
- [21] Fringuelli F, Taticchi A, editors. *The Diels–Alder reaction. Selected practical methods*. Chichester: Wiley; 2002.
- [22] Amantin D, Fringuelli F, Pizzo F, Vaccarol L. *J Org Chem* 2001;66:4463.
- [23] Sijbren O, Engberts JB. *Pure Appl Chem* 2000;72:1365.
- [24] Fringuelli F, Pizzo F, Tortoioli S, Vaccarol L. *Adv Synth Catal* 2002:344.
- [25] El-Shekeil A, Babaqi A, Hassan MA, Shiba S. *Heterocycles* 1988;27:2577.
- [26] Hassan MA, Döpp D. *Heterocycles* 1997;45:451.
- [27] Hassan MA, El-Kasaby M, Abou El-Regal MMK. *Phosphorus Sulfur Silicon* 1995;104:15.
- [28] Akh Khalil, Hassan MA, Mohamed MM, El-Sayed AM. *Dyes Pigments* 2005;66:241.
- [29] Ertan N. *Dyes Pigments* 2000;44:41.
- [30] Yasuda H, Midorikawa H. *J Org Chem* 1966;3:1722.
- [31] Şener I, Karci F, Kılıç E, Deligöz H. *Dyes Pigments* 2004;62:143.
- [32] *Standard methods for the determination of the colour fastness of textiles*. 3rd ed. Bradford: The Society of Dyers and Colourists; 1962.