International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.12 No.05, pp 129-133, 2019

Synthesis and Antimicrobial Activity of some Disperse Dyes derived from Pyridones

Alya M. Al-Etaibi*

***Natural Science Department, College of Health Science, Public Authority for Applied Education and Training, P.O. Box 14281, Fayha 72853, Kuwait.**

Abstract : Pyridone derivatives **4a,b** are prepared by reacting *N*-alkyl-2-cyanoacetamide **1a,b**with methyl propionylacetate. Compounds 4**a,b** are coupled with aromatic diazonium salts to produce the corresponding new azo disperse dyes **6a,b**. The antimicrobial activity of the synthesized azo disperse dyes are evaluated.
Keywords : pyridones; azo dyes; disperse dyes; antimicrobial activity.

1. Introduction

Azo dyes are the principal class of synthesized dyes. They have been extensively used in different purposes, like textile dyeing or printing and non-textile applications [1-5]. Pyridone disperse dyes are moderately recent heterocyclic intermediates for the preparation of azo dyes because azo pyridone dyes generate bright hues. Pyridone as coupling components have been shown to be significant colorants for different dyes in industrial applications. Furthermore, *N*-substituted pyridone azo disperse dyes shows good color strength and excellent light fastness [6-11]. In a continuation of our strategy aims to synthesize novel azo disperse dyes and elucidate their structures, the present study focuses on the synthesis of new azo disperse dyes derived from pyridones and evaluate their antimicrobial activities.

2. Materials and Methods

2.1. General

Melting points were recorded on a Gallenkamp apparatus. IR spectra were recorded using KBr pellets on a JASCO FTIR-6300 FT-IR spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on AvanceII 600 MHz super-conducting NMR spectrometers with proton spectra measured at 600 MHz and carbon spectra at 150 MHz, respectively. Mass spectra were measured on a high resolution GC/MS DFS-Thermo. Microanalyses were performed on Elemental-Vario Micro cube Analyzer.

DOI= http://dx.doi.org/10.20902/IJCTR.2019.120515

2. 2. General procedure for the preparation of compounds (4a,b).

A mixture of *N*-ethyl-2-cyanoacetamide or *N*-butyl-2-cyanoacetamide(10 mmol) and methyl propionylacetate (1.30 g, 10 mmol) was refluxed for six hours. The solution is diluted with water and acidified with hydrochloric acid to give white crystals of compounds **4a** [12] or **4b** [13].

2.3 General procedure for the synthesis of disperse dyes(6a,b).

A cold solution of aryldiazonium salt (10 mmol), [prepared by adding a solution of sodium nitrite (1.00 g in 10 mL H_2O) to a cold solution of aryl amine hydrochloride or aryl amine nitrate (10 mmol) with stirring as described earlier] [14]. The resulting solution of the aryldiazonium was then added to a cold solution of compound **4a,b** (10 mmol) in ethanol (20 mL) containing sodium acetate (2.00 g). The mixture was stirred at room temperature for one h and the solid product so formed was collected by filtration and recrystallized from ethanolto give compounds **6a,b.**

1,4-Diethyl-2,6-dioxo-5-(o-tolyl-hydrazono)-1,2,5,6-tetrahydro-pyridine-3-carbonitrile **(6a)**: Orange crystals (Scheme 1). Yield: 61%, M.p.: 202-204 °C, FT-IR (KBr cm^{-1}): 3439 (NH), 2224 (CN), 1669, 1631 (2CO). λ_{max} in DMF = 445 (nm). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 1.77 (t, 3H, CH_3, *J* = 7.2 Hz), 1.38 (t, 3H, CH_3, *J* = 7.2 Hz), 2.51 (s, 3H, CH_3), 3.08 (q, 2H, CH_2, *J* = 7.2 Hz), 4.07 (q, 2H, CH_2, *J* = 7.2 Hz), 7.23 (t, 1H, *J* = 7.2 Hz, *o*-tolyl-H), 7.28 (t, 1H, *J* = 7.2 Hz, *o*-tolyl-H), 7.36 (t, 1H, *J* = 7.8 Hz, *o*-tolyl-H), 7.76 (d, 1H, *J* = 8.4 Hz, *o*-tolyl-H), 15.29 (s, 1H, NH). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 13.23 (CH_3), 14.61 (CH_3), 17.28 (CH_3), 24.35 (CH_2), 35.43 (CH_2), 100.78, 114.48, 115.10, 122.44, 127.08, 127.51, 128.10, 131.63, 139.37, 160.34. 162.10, 164.26. MS (*m/z*, (%)): 310 (M^+, 100),Anal. calcd. for $C_{17}H_{18}N_4O_2$: C, 65.79; H, 5.85; N, 18.05. Found: C, 65.78; H, 6.49; N, 16.85. HRMS: m/z (EI) for $C_{17}H_{18}N_4O_2$; calcd. 310.1424; found: 310. 1424.

1-Butyl-4-ethyl-2,6-dioxo-5-(phenyl-hydrazono)-1,2,5,6-tetrahydro-pyridine-3-carbonitrile **(6b)**: Dark Yellow crystals (Scheme 1). Yield: 62%, M.p.: 168-170 °C, FT-IR (KBr cm^{-1}): 3445 (NH), 2218 (CN), 1678, 1630 (2CO). λ_{max} in DMF = 435 (nm). ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 0.97 (t, 3H, CH_3, *J* = 7.2 Hz), 1.38 (t, 3H, CH_3, *J* = 7.8 Hz), 1.42-1.41 (m, 2H, CH_2), 1.66-1.61 (m, 2H, CH_2), 3.06 (q, 2H, CH_2, *J* = 7.8 Hz), 3.97 (t, 2H, CH_2, *J* = 7.2 Hz), 7.33-7.27 (m, 1H, phenyl-H), 7.50-7.47 (m, 4H, phenyl-H), 15.09 (s, 1H, NH). ^{13}C NMR (150 MHz, $CDCl_3$, δ, ppm): 13.95 (CH_3), 14.57 (CH_3), 20.46 (CH_2), 24.34 (CH_2), 30.01 (CH_2), 40.09 (CH_2), 101.01, 114.40, 117.25, 121.87, 127.68, 130.22, 141.04, 160.47, 161.16, 164.20. MS (*m/z*, (%)): 324 (M^+, 100),Anal. calcd. for $C_{18}H_{20}N_4O_2$:C, 66.65; H, 6.21; N, 17.27. Found: C, 66.06; H, 7.01; N, 16.21. HRMS: m/z (EI) for $C_{18}H_{20}N_4O_2$; calcd. 324.1581; found: 324.1580.

2.4 Antimicrobial Activity Test

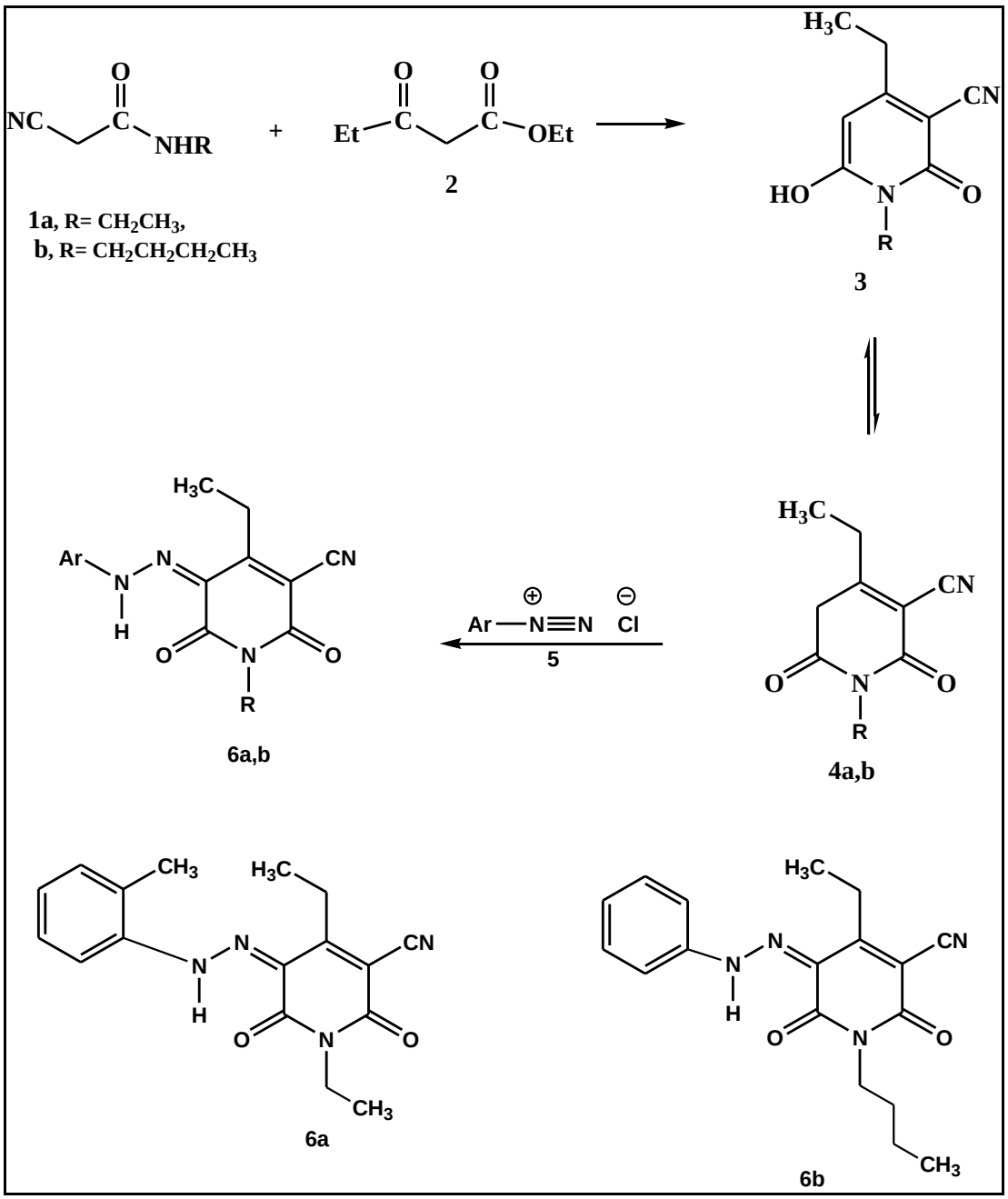
The antimicrobial activities of disperse dyes **6a,b** were tested using the agar-well diffusion technique [15] against ten different microbial cultures obtained from the Regional Center for Mycology and Biotechnology, Al-Azhar University (Cairo, Egypt). Pure cultures of *Bacillus cereus* RCMB 027 (1), *Bacillus subtilis* RCMB 015 (1) NRRL B-543, *Staphylococcus aureus* (RCMB 010010) and *Streptococcus mutants* RCMB 017 (1)ATCC 25175 (Gram positive bacterium), *Enterobacter cloacae* RCMB 001 (1)ATCC 23355, *Klebsiella pneumonia* RCMB 003 (1)ATCC 13883, *Escherichia coli* RCMB 010052ATCC 25955 and *Proteus vulgaris* RCMB 004 (1)ATCC 13315 (Gram negative bacterium), *Candida albicans* RCMB 005003 (1) ATCC 10231 and *Aspergillus flavous* (RCMB 002002) (fungi) were used in the test. An aliquot of 0.1 mL of each bacterial strain was inoculated and spread on nutrient agar (NA) while 0.1 mL of each fungi were spread on potato dextrose agar (PDA). The inoculated plates were supplied with 100 µL of each of the tested dyes with a total final concentration of 100 mg mL^{-1} . The dyes were included in 4 mm wells produced by sterile cork borer. The NA plates were incubated at 37 °C for 24 h while PDA plates were incubated at 25 °C for 24–48 h.

3. Results and Discussion

3.1. Chemistry and characterizations

Our primary strategy is to synthesize pyridone derivative **4a** and convert it into a new monoazo disperse dyes that were used in dyeing polyester fabrics by utilizing different dyeing methods [12,14]. In order to complete this strategy, novel monoazo disperse dyes arylhydrazono-1.4-diethyl-2,6-dioxo-

tetrahydropyridine-3-carbonitrile and arylhydrazono-1-butyl- 4-ethyl-2,6-dioxo-tetrahydropyridine-3-carbonitrile **6a,b** were synthesized in a simple and efficient route (Scheme 1).



Scheme 1. Synthesis of disperse dyes 6a, b.

1-Alkyl-4-ethyl-2,6-dioxo-1,2,5,6-tetrahydro-pyridine-3-carbonitrile **4a,b** were prepared via reaction of *N*-ethyl-2-cyanoacetamide **1a**or *N*-butyl-2-cyanoacetamide**1b** withmethyl propionylacetate **5**. Coupling of compounds **4a,b** with aromatic diazonium salts afforded the corresponding pyridone azo disperse dyes **6a,b** in a good yields. Structural elucidations of these disperse dyes were confirmed by mass spectroscopy, FTIR, elemental analysis, and NMR spectroscopic data.

3.2. Antimicrobial activity

The obtained results listed in Table 1 showed that the prepared disperse dyes have given adequate and promising results that can be utilized for medical and pharmaceutical objectives. Firstly, disperse dyes **6a,b** showed moderate antibacterial activities against *Streptococcus mutants*. In contrast dyes **6a,b** showed no antibacterial activities against *Bacillus cereus*, *Bacillus subtilis* and *Staphylococcus aureus* as Gram positive bacteria. Secondly, the same phenomena repeated with disperse dyes **6a,b** showed no anti-fungi activities against of *Aspergillus flavous* while disperse dye **6b** showed good anti-fungi activities against of *Candida albicans*. Thirdly, disperse dyes **6a,b** showed moderate antibacterial activities against *Enterobacter cloacaewhilst* the both dyes showed no antibacterial activities against *Klebsiella pneumonia* . Furthermore, disperse dye **6a** showed good antibacterial activities against both *Escherichia coli* and *Proteus vulgaris* whereas disperse dye **6b** showed no activities for the same microorganisms as Gram negative bacteria.

Evaluations of different dyeing methods either at temperatures in the region of 130 °C or at lower temperatures in the presence of an accelerating agent (carriers) and estimation of dyeing performance for these azo disperse dyes are under investigations.

Table 1.Antimicrobial results of the synthetic disperse dyes 6a,b.

Microorganisms	Dye numbers		Control
	6a	6b	
FUNGI			*Ketoconazole*
Candida albicans RCMB 005003 (1) ATCC 10231	NA	8	20
Aspergillus flavous (RCMB 002002)	NA	NA	16
Gram Positive Bacteria			*Gentamyin*
Bacillus cereus RCMB 027 (1)	NA	NA	25
Bacillus subtilis RCMB 015 (1) NRRL B-543	NA	NA	26
Staphylococcus aureus (RCMB 010010)	NA	NA	24
Streptococcus mutants RCMB 017 (1)ATCC 25175	12	10	20
Gram Negative Bacteria			*Gentamyin*
Enterobacter cloacae RCMB 001 (1)ATCC 23355	11	9	27
Klebsiella pneumonia RCMB 003 (1)ATCC 13883	NA	NA	21
Escherichia coli RCMB 010052ATCC 25955	8	NA	30
Proteus vulgaris RCMB 004 (1)ATCC 13315	10	NA	25

RCMB: Regional Center for Mycology and Biotechnology, NA: No activity

4. Conclusions

New disperse dyes arylhydrazono-1.4-diethyl-2,6-dioxo- tetrahydropyridine-3-carbonitrile and arylhydrazono-1-butyl- 4-ethyl-2,6-dioxo-tetrahydropyridine -3-carbonitrile **6a,b** were synthesized in a simple and efficient route with a good yields by reacting pyridones with aromatic diazonium salts. These dyes showed satisfactory antimicrobial activity against Gram positive bacteria, Gram negative bacteria and fungi.

Acknowledgments:

The RSP unit general facilities of the faculty of science, Kuwait University GFS (GS 01/01, GS 01/05, GS 01/03, and GS 03/01 and GS 02/13) are gratefully acknowledged.

Conflicts of Interest:

"The author declares no conflict of interest."

References

1. Al-Qalaf, F.; Almohammad, K.; El-Apasery, M.A.; Mahmoud, H. Synthesis of some biologically active monoazo disperse dyes derived from nicotinic acid derivatives under microwave irradiation for dyeing polyester fabrics. *Eur. J. Chem.* 2013, 4, 211-215.
2. Al-Etaibi, A.M.; El-Apasery, M.A.; Ibrahim, M.R.; Al-Awadi, N.A. A facile synthesis of new monoazo disperse dyes derived from 4-hydroxyphenylazopyrazole-5-amines: evaluation of microwave assisted dyeing behavior. *Molecules*2012, 17, 13891-13909.
3. El-Apasery, A. M.; Shakra, S.; Abbas, D.; Gaffer, H.; Allam, A.; Synthesis of some azo disperse dyes based on pyridone moiety and their application on polyester fabrics, *Egypt. J. Chem.*, 2018, 60(6). 97-102.
4. El-Apasery, M. A.; Hussein, A. M.; El-Adasy, A. A. M.; Saleh, M. O.; Kamel, M. M. Microwave Assisted Synthesis of Some Azo Disperse Dyes with Antibacterial Activities. Part 1, *Egypt. J. Chem.*, .2019, 62(5). 1253 – 1259.
5. Al-Etaibi, A. M.; Alnassar, H. S.; El-Apasery, M. A. Dyeing of Polyester with Disperse Dyes: Part 2. Synthesis and Dyeing Characteristics of Some Azo Disperse Dyes for Polyester Fabrics. *Molecules*, 2016, 21 (7), 855-861.
6. Ertan, N.; Gurkan, P. Synthesis and Properties of Some Azo Pyridone Dyes and Their Cu(II)Complexes. *Dyes Pigments* 1997, *33*, 137–147.
7. Ashkar, S.M.; El-Apasery, M.A.; Touma, M.M.; Elnagdi, M.H. Synthesis of some novel biologically active disperse dyes derived from 4-methyl-2,6-dioxo-1-propyl-1,2,5,6-tetrahydropyridine-3-carbonitrile as coupling component and their colour assessment on polyester fabrics. *Molecules*. 2012, *17*, 8822–8831.
8. Sakoma, K.J.; Bello, K.A.; Yakubu, M.K. Synthesis of Some Azo Disperse Dyes from 1-Substituted 2-Hydroxy-6-pyridone Derivatives and Their Colour Assessment on Polyester Fabric. *Open J. Appl. Sci.* 2012, *2*, 54–59.
9. Helal, M.H. Synthesis and characterisation of a new series of pyridinone azo dyes for dyeing of synthetic fibers. *Pigm. Resin Technol.* 2004, *33*, 165–171.
10. Balalaie, S.; Kowsari, E.; Hashtroudi, M.S. An Efficient Method for the Synthesis of 3-Cyano-6-hydroxy-2(1H)-pyridinones under Microwave Irradiation and Solvent-free Conditions. *Chem. Mon*. 2003, *134*, 453–456.
11. El-Bayouki, M.; Abdel Hameed, K.; Asyouni, W.M.; Mohamed, Y.A.; Aly, M.M.; Abbas, S.Y. Novel 4(3H)-quinazolinones containing biologically active thiazole, pyridinone and chromene of expected antitumor and antifungal activities. *Eur. J. Chem.* 2011, *2*, 455–462.
12. Al-Etaibi, A ; El-Apasery, M. A.; Al-Awadi, N. The effect of dispersing agent on the dyeing of polyester fabrics with disperse dyes derived from 1, 4-diethyl-2, 6-dioxo-1, 2, 5, 6-tetrahydropyridine-3-carbonitrile, *Eur. J. Chem*., 2013, 4 (3), 240-244.
13. Tallant, N. A.; Millard, C. Monoazo dyestuffs useful for colour filters and ink jet printing. 2001, Patent WO 2001021714A2.
14. Al-Etaibi, A ; El-Apasery, M. A.; Mahmoud, H.; Al-Awadi, N. Synthesis, characterization and antimicrobial activity, and applications of new azo pyridone disperse dyes on polyester fabric, *Eur. J. Chem.*, 2014, *5 (2)*, 321-327.
15. Isaacson, D.M.; Kirschbaum, J. Assays of antimicrobial substances. In Manual of Industrial Microbiology and Biotechnology; Demain, A.L., Solomon, N.A., Eds.; ASM: Washington, DC, USA, 1986, 410–435.

*****