Facile bifunctional dyeing of polyester fabrics with new antibacterial β-Oxoalkanenitriles disperse dyes.

Tarek Abou Elmaaty, Fathi El-Taweel, Eman Abd El-Aziz, Mohamed Yusif and Satoko Okubayashi.

Abstract— A series of β-Oxoalkanenitriles disperse dyes were synthesized. The structures of all dyes were established by elemental analysis and spectral studies (IR, 1H-NMR, MS). These dyes were applied to polyester fabrics as disperse dyes by using conventional dyeing method. Fabrics dyed with the dyes under study furnished generally deep and bright intense hues ranging from light yellow to orange. Fastness properties of dyed polyester samples were measured and the position of color in CIELAB coordinates (L*, a*, b*, H*, C*) was assessed. Finally, the antibacterial activity of the synthesized dyes and dyed samples was also evaluated qualitatively according to AATCC test method (147-1988).

Index Terms— β-Oxoalkanenitriles dyes, polyester fabric, Azo Disperse Dyes, antibacterial activity.

1 INTRODUCTION

Heterocycles have been put too much use in the chemistry of disperse dyes which, as has been claimed, was the first area to foster the industrial exploitation of heterocyclic amines. Numerous heterocyclic dyes are now marketing to produce a full range of dispersed dyestuffs. [1]

On the other hand, there has been increasing interest in building antibacterial properties into textiles. Consumers worldwide are looking for clothing that provides greater comfort and remains fresh and odor-free in use. In recent years, there has been increasing interest in syntheses of heterocyclic compounds that have biological and commercial importance. [2]- [6]

β-Oxoalkanenitriles are highly multifunctional reagents which undergo a wide range of condensation and cyclization reactions.[7]-[12] In spite of the enormous number of reports on the chemistry of acyl and aroylacetonitriles, very little attention has been paid to the chemistry of azoloylketonitriles. Azoloylketonitriles compounds especially those bearing antipyrine moiety plays an important role in modern organic synthesis, not only because they constitute a particularly useful class of heterocyclic compounds but also because they are of great biological interest and they can also be used as intermediates in the dyestuff industry.

In view of these findings and in continuation to our interest in this class of compounds, we report here on the synthesis and antibacterial activities of some aryl hydrazones of β-oxoalkanenitriles and their application as disperse dyes for synthetic fabrics.

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2 EXPERIMENTAL

2.1 Materials

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Polyester 100 % (7 g/m²) was used throughout the study.

2.2 Methods

2.2.1Synthesis

Preparation of aryl hydrazones 2a-g:

A cold solution of β-oxoalkanenitriles 2a-c (0.01mole) in ethanol (10 ml) was treated with a saturated sodium acetate solution (10 ml) and then with the aryl diazonium salts (prepared with the amine hydrochloride and sodium nitrite). The mixture was left in the refrigerator for overnight. The formed solid products were collected by filtration, recrystallized from the proper solvents and then identified as 2a-g.

(E)-2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-N'-(2-methoxyphenyl)-2-oxoacetohydrazonoyl cyanide 2a: Formed orange crystals from ethanol in 70 % yield, m. p. 205-207oC. IR (v/cm-1): 3435 (NH), 2216(conjugated CN), 1657(CO), 1614(C=N); 1H-NMR (DMSO-d6) (δ,ppm): 2.57 (s,3H,CH3), 3.84 (s,3H,N-CH3), 9.96- 7.49(m, 9H, aromatic protons), 14.34(s,1H,NH). .Anal. Calcd. For C21H19N5O3 (389.41): C,64.77; H, 4.92; N, 17.98. Found: C, 64. 67; H, 4.76; N, 17.62 ;(M+ = 389 m/z).

(E)-2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-2-oxo-N'-(p-tolyl) acetohydrazonoyl cyanide 2b: Formed yellow crystals from ethanol / DMF in 73 % yield, m.p.235-237oC. IR (v/cm-1): 3429 (NH), 2200(conjugated CN), 1655(CO), 1614(C=N); 1H-NMR (DMSO-d6)(δ,ppm): 2.28 (s,3H,CH3), 2.48 (s,3H,CH3), 3.19 (s,3H,N-CH3), 7.13- 7.59 (m,9H,aromatic protons), 11.99(brs.,1H,NH). Anal. Calcd. For C21H19N5O2 (373.41): C, 67.55; H, 5.13; N, 18.76. Found: C, 67.64; H, 5.26; N, 18.62 ;(M+ = 373 m/z).

(E)-2-([1,1'-biphenyl]-4-yl)-N'-(4-chlorophenyl)-2-oxoacetohydrazonoyl cyanide 2c: Formed orange crystals from ethanol in 73 % yield, m.p.215-217oC. IR (v/cm-1): 3444

(NH), 2222(conjugated CN), 1655(CO), 1614 (C=N); 1H-NMR (DMSO-d6)(δ,ppm): 7.40-8.00(m,13H,aromatic protons), 12.38(s,1H,NH). Anal. Calcd. For C21H14ClN5O (359.81): C, 70.10; H, 3.92; N, 11.68. Found: C,70.22; H,3.86; N,11.74.

(E)-2-([1,1'-biphenyl]-4-yl)-N'-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-2-oxoacetohydrazonoyl cyanide 2d: Formed yellow crystals from ethanol/ DMF in 75 % yield, m.p. 170 -172oC. IR (ν/cm-1): 3427 (NH), 2180 (conjugated CN), 1630 (CO), 1614(C=N); 1H-NMR (DMSO-d6)(δ,ppm): 2.23(s,3H,CH3), 3.23 (s,3H,N-CH3), 7.39-7.96 (m,14H,aromatic protons). Anal.Calcd. For C26H21N5O2 (435.48): C, 71.71; H, 4.86; N, 16.08. Found: C, 71.83; H, 3.86; N, 16.24 ;(M+ = 435 m/z).

(E)-N'-(2-chlorophenyl)-2-oxo-2-(p-tolyl) acetohydrazonoyl cyanide 2e: Formed yellow crystals from ethanol/ DMF in 70 % yield, m. p. 145-147oC. IR (ν/cm-1): 3441 (NH), 2222(conjugated CN), 1650 (CO), 1614(C=N); 1H-NMR (DMSO-d6)(δ,ppm): 2.42 (s,3H,CH3), 7.26-7.88 (m,8H,aromatic protons), 10.83(s,1H,NH). Anal. Calcd. For C16H12ClN3O (297.74): C, 64.54; H, 4.06; N, 14.11. Found: C, 64.73; H, 4.21; N, 14.25 ; (M+ = 297 m/z).

(E)-N'-(2-chloro-4-methylphenyl)-2-oxo-2-(p-tolyl) acetohydrazonoyl cyanide 2f: Formed yellow crystals from ethanol/ DMF in 73 % yield, m.p.165-167oC. IR (ν/cm-1): 3427 (NH), 2214 (conjugated CN), 1641(CO), 1614(C=N); 1H-NMR (DMSO-d6)(δ,ppm): 2.28(s,3H,CH3), 2.49(s,3H,CH3), 7.22-(m,7H,aromatic protons), 12.29 (s,1H,NH). Anal. Calcd. For C17H14ClN3O (311.77): C, 65.49; H, 4.53; N, 13.48. Found: C, 65.65; H, 4.21; N, 13.37; (M+ = 311 m/z).

(E)-N'-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-2-oxo-2-(p-tolyl) acetohydrazonoyl cyanide 2g: Formed orange crystals from ethanol/ DMF in 73 % yield, m.p.120-122oC. IR (ν/cm-1): 3447 (NH), 2175(CN), 1641(CO), 1614 (C=N); 1H-NMR (DMSO-d6) (δ,ppm): 2.25(s,3H,CH3), 2.49(s,3H,CH3), 3.22(s,3H,N-CH3), 7.20-7.69(m,9H,aromatic protons). Anal. Calcd. For C21H19N5O2 (373.41): C, 67.55; H, 5.13; N, 18.76. Found: C, 67.63; H, 5.21; N, 18.38 ;(M+ = 373 m/z).

2.2.2 Dyeing Procedures

Preparation of Dye Dispersion:

The required amount of the dye (2% shade) was dissolved in a solution of (2 g/dm3), an anionic dispersing agent, then the dye was precipitated in a fine dispersion ready for use in dyeing.

Dyeing of Polyester:

The dye bath (1:20 liquor ratio) containing 5 g/ dm3 carrier, 4% ammonium sulphate and acetic acid at pH= 5.5, was brought to 60oC. The polyester fabric was entered at this degree and run for 15 minutes. 2% Dye in the fine dispersion was added, temperature was raised to the boil within 45 minutes, dyeing was continued at the boil for about 1 hour, then dyed material was rinsed and soaped with 2% nonionic detergent to improve rubbing and wet fastness.

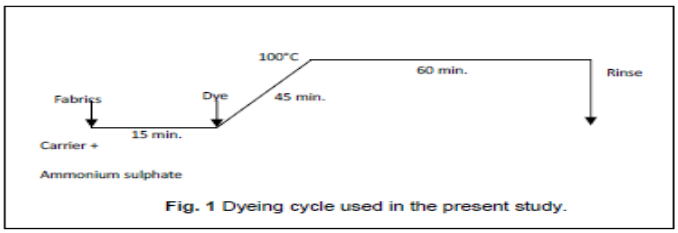


Fig. 1 Dyeing cycle used in the present study.

2.3 Measurments

All melting points are uncorrected and measured on Griffin & George MBF 010T (London) apparatus. Recorded yields correspond to the pure products. IR (KBr) spectra were recorded on a Perkin Elmer SP-880 spectrometer and 1H-NMR spectra were measured on Varian 270 MHz spectrometer with DMSO-d6 as solvent and TMS as internal standard. Chemical shifts are reported in δ units (ppm). Microanalyses were performed on a LECO CHN-932 elemental analyzer and carried out in the Microanalytical Data Unit at Cairo and Damietta Universities. Mass spectra were recorded on a MS 30(AEI) instrument at 70 eV ionization energy.

Fastness to washing, rubbing, light and sublimation was tested according to JIS L 0844, JIS L 0842: 2004 and JIS L 0849 test methods respectively.

The color parameters of the dyed polyester fabric were measured using the (Konica Minolta spectrophotometer CM-3600 d). The following CIELAB coordinates were measured, lightness (L*), chroma (C*), hue (h), the degree of redness (+ve) and greenness (- ve) (a*), and degree of yellowness (+ve) and blueness (-ve) (b*).

Antibacterial activity assessment against G+ve bacteria (S. aureus) and G−ve bacteria (E. coli) was evaluated qualitatively according to AATCC Test Method (147-1988), and expressed as zone of growth inhibition ZI (mm).

3 RESULTS AND DISCUSSION

3.1 Discussion of the synthetic strategy

β-Oxoalkanenitriles are widely used as a key intermediates for preparation of a large number of heterocycles. Heterocycles incorporating antipyrinyl moiety are well known as analgesic and antipyretic drugs [6]. Our synthetic strategy directed towards preparation of some new arylhydrazonopropanenitriles for different applications. Thus, we have found that, β-oxoalkanenitriles 1a-c coupled with aryl/heteroaryl diazonium salts to afford arylhydrazonopropanenitriles 2a-g. The structure of compounds 2a-g were established on basis of their both correct elemental analysis and spectral data. Thus, IR spectra of 2a-g showed the presence of signals at ν ≈ 3427-3444 cm-1 attributable to NH groups, ν ≈ 2175-2222 cm-1 attributable to conjugated cyano functions and ν ≈ 1630-1655cm-1 attributable to carbonyl functions .1-HNMR spectra of 2a-g exhibit in addition to aromatic protons and methyl groups, signals at δ ≈ 10.83-14-34 ppm due to NH protons. Mass spectra of 2a-g are in good agreement with the proposed structures 2a-g.

3.2 Factors affecting disperse dyeing of polyester fabrics

3.2.1 Dye concentration:

Fig.2 shows the effect of the dye concentration on the extent of dye uptake in all dyes (2a- g), expressed as the K/S value, of the dyed polyester substrates. As is evident, increasing the dye concentration from 2% to 6% brings about a noticeable increase in the K/S value, this probably due to more amount of

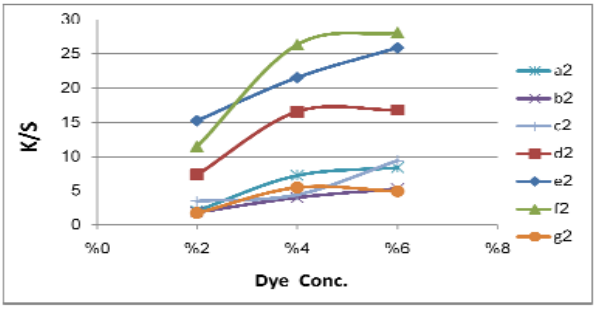


Fig.2: effect of dye concentration

3.2.2 Fastness properties:

The physical data for the dyed fabrics given in Table 1, show that the disperse dyeing displayed moderate fastness levels to light. The light fastness of each of the dyes was measured by employing the standard method for determination of color fastness of textiles. Several reports suggest that fading of azo dyes is mainly a consequence of decomposition of the –N=N– moiety either by oxidation, reduction or photolysis. The rates of these processes should be sensitive to the chemical structure of the dye, the type of substrate and treatment conditions.
Since the dyed substrate employed in this study is a polyester fabrics (i.e., non-proteinic), the fading process likely occurs by oxidation. [13]

Table 1
Fastness properties of Polyester dyed fabrics

Dye	2a	2b	2c	2d	2e	2f	2g
Fastness to dry rubbing Fastness to washing	5	5	5	5	5	5	5
Changing in color	5	5	5	5	5	5	5
Staining in color with cotton Fastness to light	5 1-2	5 2	5 2-3	5 1	5 4	5 3-4	5 1

The results obtained in table 1 also showed that dyed fabrics have excellent fastness levels to washing and rubbing fastness properties that may be due to the absence of solubilizing groups, which affects solubility, and wash ability of the dye-out of the fabrics or to the size of the dye molecule is considered relatively big. [13]

3.2.3 Antimicrobial Activities

The antimicrobial activities of the synthesized disperse dyes and the dyed polyester fabrics were screened against selected bacteria by the agar well diffusion method and their inhibition zones diameters, given in Table 2, reveal that all tested dyes showed positive antimicrobial activities against the examined +ve and G-ve bacteria.

dye	ZI of the dyestuff		ZI of the dyed PE fabrics	
	G –ve E.Coli	G+ve S.Aureus	G –ve E.Coli	G+ve S.Aureus
2a	15.5	17	8	9
2b	16	12	10	8
2c	15	19	2	5
2d	21	24.5	16.5	20
2e	11	14	12	10
2f	12	16	11	6
2g	21	24	20.5	24
2a	15.5	17	8	9

Table 2: Diameter of the zones of inhibition of the tested disperse dyes against Gram positive, Gram negative bacteria

The remarkable improvement in the antibacterial activity of the dyed samples could be discussed in terms of non specific action; i.e. multi-target, causing damage of bacterial cells or via inhibition of a specific bacterial target, i.e. inhibition of bacterial fatty acid synthesis through the blocking of lipid biosynthesis . [14]

3.2.4 Color assessment

The following CIELAB are measured, lightness (L*) chroma (C*), hueangle from 0 to 360 (h), (a*) value represents degree of redness (positive) and greenness (negative) and (b*) represents the degree of yellowness (positive) and blueness (negative).

The measured K/S given by the reflectance spectrometer is directly correlated to the dye concentration on the dye substrate.

Table 3
Color coordinates of the dyes.

Dye	1*	a*	b*	C*	H	K/S
2a	91.44	-11.26	57.83	58.91	101.02	2.1128
2b	91.9	-11.55	44.82	46.29	104.46	1.87376
2c	92.7	-15.33	52.6	54.79	106.24	3.4968
2d	80.47	13.51	78.86	80	80.28	7.34952
2e	89.47	-12.45	67.25	68.4	100.49	15.24917
2f	92.8	-18.49	62.86	65.53	106.39	11.45791
2g	87.55	0.55	59.62	95.63	89.47	1.77144

The color of the synthesized dyes on polyester fabrics was evaluated using CIELAB system in terms of L*, a* and b*. The color coordinated listed in table 3 indicate that the dye has good affinity to polyester fabric and tend to give the following

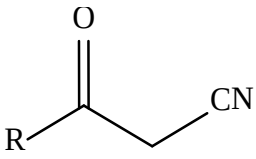
i- The dyes under study showed good affinity to polyester fabrics at the given temperature and gave generally bright and intense hues ranging from yellow to red.

ii-The color hues of the dyes on polyester fabrics are shifted to the yellowish direction on the yellow-blue axis according to the positive values of b*.

iii- The color hues of the dyes (2a, 2b, 2c, 2e, and 2f) on polyester fabric are shifted to the greenish direction on the red- green axis as indicated from the negative value of a*. While the color hue of dye (2d, 2g) on polyester fabric is shifted to the reddish direction on the red-green axis as indicated from the positive value of a*.

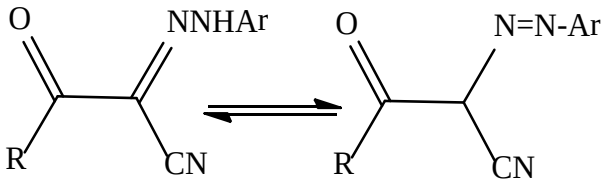
4 CONCLUSION

In summary, a series of monoazo disperse dyes based on β-Oxoalkanenitriles were synthesized. The dyes produced in this manner were then applied to polyester fabrics by using a high temperature dyeing method at 100 °C. The dyed polyester fabrics, which display yellowish to orange hues, displayed excellent washing and rubbing fastness and moderate light fastness. Finally, the biological activity of both the synthesized compounds and the dyed samples was tested against Gram positive bacteria and, Gram negative bacteria.



1 a,R = antipyrinyl
b,Ar = $C_6H_4Ph(4)$
c,Ar = $C_6H_4CH_3(4)$

$ArN_2^+Cl^-$



2 a,R = antipyrinyl ; Ar = $C_6H_4OCH_3(2)$
b,R = antipyrinyl ; Ar = $C_6H_4CH_3(4)$
c,R = $C_6H_4Ph(4)$; Ar = $C_6H_4Cl(4)$
d,R = $C_6H_4Ph(4)$; Ar = antipyrinyl
e,R = $C_6H_4CH_3(4)$; Ar = $C_6H_4Cl(2)$
f,R = $C_6H_4CH_3(4)$; Ar = $C_6H_3Cl(2).CH_3(4)$
g, d,R = $C_6H_4CH_3(4)$; Ar = antipyrinyl

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