Solvent-Free One-Pot Synthesis of Some Azo Disperse Dyes Under Microwave Irradiation: Dyeing of Polyester Fabrics

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ABSTRACT: The one-pot synthesis of some azo disperse dyes were carried by heating of aniline, sodium nitrite, potassium hydrogen sulfate with active methylene compounds under focused microwave heating in absence of the solvent. Also, by heating of diazoaminobenzene with active methylene in acetic acid solution, in the presence of few drops of hydrochloric acid, were described. Syntheses of novel heterocyclic aromatic compounds as potential intermediates for preparation of azo disperse dyes were studied. The dyeing of polyester fabrics with disperse dyes by the use of high-temperature dyeing method at 130°C and carrier dyeing method were also used. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 695–699, 2008

Key words: disperse dyes; dyeing; polyester fabrics; UV–vis spectroscopy; microwave heating

INTRODUCTION

Synthesis of azo dyes using microwave irradiation has received considerable attention in the recent years.[1,2] Thus, treating equimolar amounts of aromatic amine, sodium nitrite, potassium hydroxide, and 2-naphthol or 2-naphthylamine in the presence of few drops of water as initiator with microwave irradiation was reported to give azo product.[1] In addition, irradiation by microwave of nitroarenes in the presence of bismuth metal and potassium hydroxide could be coupled to give azo dye.[2] Since 1986, when Gedye[3] and Giguere[4] published their first articles on microwave-assisted synthesis in a household microwave oven, there has been enormous interest in this research filed. Several recent publications[5–12] had covered technical and synthetic achievements in this area published in more than thousand articles. Almost every reaction type has been conducted in domestic microwave oven in which generally shorter reaction times and better yields were observed. The utility of microwave organic reaction enhancement technology developed by Bose[13] or the dye technologies developed by Varma[14] has substantially added green value to this technology as it saves waste and energy. In a previous study,[15] the utility of an explorer microwave oven assisted synthesis of azo disperse dyes by the use of solvent was investigated. This work was undertaken with a view toward synthesis of azo disperse dyes by the use of focused microwave heat without solvent. Also, syntheses of new heterocyclic aromatic compounds as potential intermediates for the preparation of azo disperse dyes were studied. The studies also included dyeing of polyester fibers with disperse dyes by carrier and high temperature (HT) dyeing methods.

EXPERIMENTAL

Materials

Scoured and bleached polyester 100% (150 130 g/m², 70/2 denier) was obtained from El-Shourbagy, Egypt. The fabric was further treated before dyeing with a solution containing 5 g/L nonionic detergent (Hostapal CV, Clariant-Egypt) and 2 g/L sodium carbonate at a liquor ratio 50 : 1 at 60°C for 30 min, thoroughly washed in water and air dried at room temperature.

2-Cyanothioacetamide, ethyl acetoacetate, 1,3-cyclohexanedione, 5,5-dimethyl-1,3-cyclohexanedione, 1,4-naphthoquinone, and 2-bromoacetophenone were obtained from Aldrich. All other chemicals used in the study were of reagent grade.

General procedure for the synthesis of azo disperse dyes 6-9

Method A: a mixture of compounds 1–4 (0.01 mol), aniline (0.93 g, 0.01 mol), sodium nitrite (0.69 g, 0.01

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mol), and potassium hydrogen sulfate (1.36 g, 0.01 mol) were ground to fine powder into which one drop of water was added, and the mixture was placed in a dried heavy-walled Pyrex tube containing a small stir bar. The tube containing the reaction mixture was fitted with PCS cap, and then it was exposed to an automated explorer microwave irradiation at 80–90°C for 5 min at the power of 70 W. The build-up of pressure in the closed reaction vessel was carefully monitored and found to be typically in the range 20–40 psi. After the irradiation, the reaction tube was cooled with high-pressure air through an inbuilt system in the instrument until the temperature had fallen below 50°C. The crude product was poured onto water, the solid product, so formed, was collected by filtration and crystallized from ethanol.

Method B: a mixture of compounds 1–4 (0.01 mol) and diazoaminobenzene 5 (0.01 mol) and glacial acetic acid (2 mL) in the presence of hydrochloric acid (0.1 mL) were heated in an explorer microwave at 120°C for 5 min at the power of 100 W. The build-up of pressure in the closed reaction vessel was carefully monitored and found to be typically in the range 40–80 psi. After the irradiation, the reaction tube was cooled with high-pressure air through an inbuilt system in the instrument until the temperature had fallen below 50°C. The mixture was left to cool at room temperature, and then poured onto ice-water containing sodium carbonate (2 g). The solid product, so formed, was collected by filtration and recrystallized from the specified solvent.

All of the reactions under microwave irradiation were conducted in heavy-walled Pyrex tubes (capacity 10 mL) fitted with PCS cap. Microwave heating was carried out with a single mode cavity Explorer Microwave Synthesizer (CEM, NC), producing continuous irradiation and equipped with simultaneous external air-cooling system. Infra red (IR) spectra were recorded in KBr disks using a Perkin–Elmer System 2000 FTIR spectrophotometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker DPX 400, superconducting NMR spectrometer in CDCl$_3$ or DMSO as solvent and TMS as internal standard; chemical shifts are reported in units (ppm). Mass spectra were measured on MS 30 and MS 9 (AEI), 70 eV. Microanalyses were performed on a LECO CHNS-932 Elemental Analyzer.

2-Cyano-2-(phenylhydrazono)ethanethioamide (6)

Yield (75%), mp. 215°C; IR ν_{max}: 3234 and 3140 (NH$_2$), 3061 (NH), 2209 cm^{-1} (CN); λ_{max} (C$_2$H$_5$OH) = 477 nm, ^{1}H NMR (DMSO-d_6) δ_H: 7.10–7.74 (m, 5H, Arom-H), 9.34, 9.68 (s, 2H, NH$_2$); 11.57 (s, 1H, NH). ^{13}C NMR : (DMSO-d_6) δ_C: 188.94 (CS), 143.11; 130.44,

125.36, 117.50, 111.67; 123.37 (imine, aromatic and cyano carbons). MS (EI) m/z = 204 (M$^+$). Anal. Calcd. for C$_9$H$_8$N$_4$S : C, 52.93; H, 3.95; N, 27.43; S, 15.70. Found: C, 53.39; H, 4.05; N, 27.39; S, 16.04.

Ethyl 3-oxo-2-(phenylhydrazono)butanoate(7)

Yield (73%); mp. 77°C; IR ν_{max}: 3063 (NH), 1710 cm^{-1} (CO); λ_{max} (C$_2$H$_5$OH) = 434 nm, ^{1}H NMR (DMSO-d_6) δ_H: 11.57 (Br, 1H, NH), 7.44–7.06 (m, 5H, Arom-H), 4.30 (q, 2H, CH$_2$), 2.47 (s, 3H, CH$_3$), 1.27 (t, 3H, CH$_3$). ^{13}C NMR: (DMSO-d_6) δ_C: 194.60 (acetyl carbonyl carbon), 163.64 (ester carbonyl carbon), 143.47, 131.80, 130.45, 126.34, 117.17 (imine and aromatic carbons), 61.45 (CH$_2$), 26.48, 14.92 (2CH$_3$). MS (EI) m/z = 234 (M$^+$). Anal. Calcd. for C$_{12}$H$_{14}$N$_2$O$_3$: C, 61.53; H, 6.02; N, 11.96. Found: C, 61.52; H, 6.01; N, 12.11

2-(Phenylhydrazono)cyclohexane-1,3-dione (8)

Yield (85%), m.p. 144°C; IR ν_{max}: 3055 (NH), 1676 (CO), 1628 cm^{-1} (CO); λ_{max} (C$_2$H$_5$OH) = 454 nm, ^{1}H NMR (DMSO-d_6); δ_H 1.94–2.00 (m, 2H, cyclohexanyl-H); 2.50–2.67 (m, 4H, cyclohexanyl-H), 7.20–7.81 (m, 5H, Arom-H), 14.84 (s, 1H, NH). ^{13}C NMR: (DMSO-d_6) δ_C: 198.63, 194.21 (2CO), 142.50, 132.31, 130.71, 127.41, 118.34 (imine and aromatic carbons), 39.56, 39.88, 18.90 (cyclohexyl-CH$_2$). MS (EI) m/z = 216 (M$^+$). Anal. Calcd. for C$_{12}$H$_{12}$N$_2$O$_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.46; H, 5..42; N, 13.00.

5,5-Dimethyl-2-(phenylhydrazono)cyclohexane-1, 3-dione (9)

Yield (91%), m.p.149°C; IR ν_{max}: 3052 (NH), 1673 (CO), 1632 cm^{-1} (CO); λ_{max} (C$_2$H$_5$OH) = 442 nm, ^{1}H NMR (DMSO-d_6); δ_H 1.03 (s, 6H, 2CH$_3$); 2.50–2.63 (m, 4H, cyclohexanyl-H); 7.24–7.61 (m, 5H, Arom-H), 14.88 (s, 1H, NH). ^{13}C NMR: (DMSO-d_6) δ_C: 197.68, 193.53 (2CO), 142.30, 130.93, 130.54, 127.31, 117.94 (aromatic and imine carbons), 52.77 (cyclohexyl-CH$_2$), 39.71 (cyclohexyl-t-carbon), 31.14, 28.83 (2CH$_3$). MS (EI) m/z = 244 (M$^+$). Anal. Calcd. for C$_{14}$H$_{16}$N$_2$O$_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.84; H, 6.49; N, 11.67.

1-(5-Hydroxynaphtho [1,2-b]furan-3-yl)butan-1-one (14)

A mixture of 10 (1.41 g, 0.01 mol) and naphthoquinone (1.58 g, 0.01mol) were dissolved in glacial acetic acid (10 mL) and then stirred over night at room temperature. The solid formed crystals were collected by filtration and crystallized from ethanol. This compound was obtained as buff crystals in yield 1.98 g (78%); mp 228°C; ir(KBr) ν_{max} = 1668

(CO) cm^{-1}. ^{1}H NMR (DMSO-d_6); δ_H = 0.94 (t, 3H, J = 7.2 Hz, CH$_3$), 1.64 (sextet, 2H, J = 7.2 Hz, CH$_2$), 2.90 (t, 2H, J = 7.2 Hz, CH$_2$), 7.53–7.59 (m, 2H, Arom-H), 7.65 (t, 1H, J = 7.2 Hz, Arom-H), 8.17 (d, 1H, J = 8.2 Hz, Arom-H), 8.23 (d, 1H, J = 8.3 Hz, Arom-H), 9.01 (s, 1H, furyl-H); 10.26 (s, 1H, OH). MS (EI.70EV) m/z = 254 [M$^+$]; Anal. Calcd. for C$_{16}$H$_{14}$O$_3$ (254.28); C, 75.57; H, 5.54. Found C, 75.32; H, 5.45.

(5-Benzoyl-1-phenyl-1H-pyrazol-3-yl)thiophen-2-yl-methanone (17)

A mixture of compound 15 (2.58 g, 10 mmol) and 2-bromoacetophenone (1.99 g, 10 mmol) in ethanol (20 mL) in the presence of potassium carbonate (1.38 g) were refluxed for 3 h. The mixture was left to cool at room temperature, then poured onto water, the solid product, so formed, was collected by filtration and crystallized from dioxane. Compound 17 formed orange crystals; yield: 2.86 g (80%); m.p. 137°C, IR (cm^{-1}) 1640, 1660 (CO), ^{1}H NMR (DMSO-d_6): (7.31–7.34 (m, 1H, arom-H), 7.43 (s, 1H, pyrazyl-H), 7.47–7.51 (m, 3H, arom-H), 7.57–7.62 (m, 4H, arom-H), 7.73 (t, 1H, J = 7.4 Hz, arom-H), 7.95 (d, 2H, J = 8.0 Hz, arom-H), 8.13–8.14 (m, 1H, arom-H), 8.51–8.51 (m, 1H, arom-H), ^{13}C NMR (DMSO-d_6): (186.0 (CO, C9), 178.8 (CO, C5), 150.3 (C4), 142.0 (C6), 141.4 (C1), 140.2 (C16), 137.5 (C10), 137.4 (C8), 136.9 (C3), 135.4 (C15), 130.7 (C12), 130.3 (C21), 130.1 (C19), 125.8 (C13), 121.6 (C17), 118.9 (C2), 115.5 (C7), MS (EI, 70 EV) m/z = 358 [M$^+$]; NM. Anal. Calcd. for C$_{21}$H$_{14}$N$_2$O$_2$S (358.41) : C, 70.37; H, 3.93; N, 7.81 ; S, 8.94. Found: C, 70.37; H, 4.04; N, 7.99; S, 8.86.

Dyeing

High-temperature dyeing method[16]

Dyeing of polyester was carried out at a temperature of 130°C during 60 min, under pressure in an Ahiba dyeing machine at a liquor ratio 50 : 1 and pH 5.5 in the presence of dispersing agent sodium lignin sulfonate (1 : 1) ratio of dye weight with a 4% shade. After dyeing, the samples were thoroughly washed and then subjected to a surface reduction cleaning [(5 g NaOH + 6 g sodium hydrosulphite)/L]. The samples were heated in this solution for 10 min at 60°C and finally thoroughly washed and then air dried.

Carrier dyeing[17]

Slow addition of the carrier (benzyl alcohol, 1% of liquor volume dissolve) in an equal volume of methanol, to water (1 : 40 liquor ratio) containing sodium lignin sulfonate (1 : 1 ratio of dye weight) was stirred ∼ 20 min at 60°C to give the emulsion prod-

uct. The polyester fabrics was run for 15 min then the dye (4% shade) was added followed by raising the temperature of the bath to its boiling point within 20 min. Dyeing was continued at the boiling for about 2 h, and the samples were thoroughly washed and then subjected to a surface reduction cleaning. After that, the samples were thoroughly washed and then air dried.

Measurements and analyses

#### Color measurements of the dyed fabrics

The color yield of the dyed samples (4 × 4 cm) was evaluated by light reflectance technique. Reflectance measurements of the dyed fabrics were performed on a PerkinElmer (Lambda 3B) UV–vis spectrophotometer. The color strength expressed as K/S values was assessed by applying the Kubelka-Mink equation as follows:[18]

$$K/S = [(1 - R)^2/2R] - [(1 - R_o)^2/2R_o]$$

where R is the decimal fraction of the reflectance of the dyed fabric, R_o the decimal fraction of the reflectance of the undyed fabric, K the absorption coefficient, and S the scattering coefficient.

RESULTS AND DISCUSSION

Azo disperse dyes are generally synthesized in two steps, the diazotization of aromatic primary amines followed by the coupling reaction between diazonium salts and phenols, active methylenes, or aromatic amines. Here, a simple synthetic method for
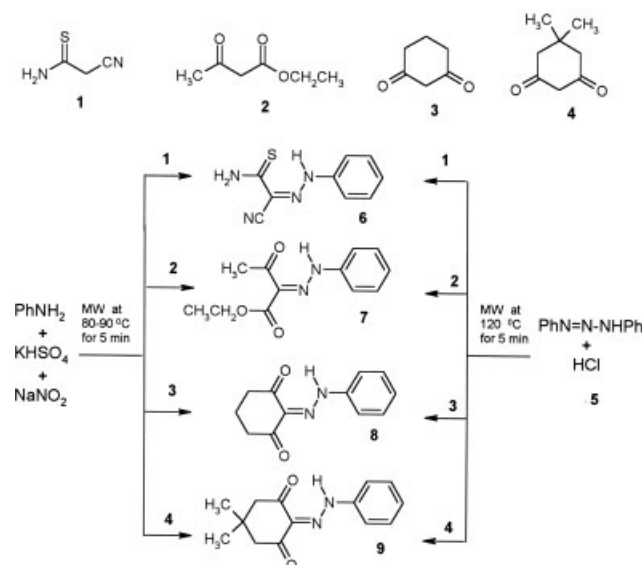
Scheme 1 Synthesis of some azo disperse dyes under microwave irradiation.

TABLE I
**Comparisons Between the Two Methods of Synthesis of Azo Disperse Dyes 6-9**

Dye no.	K/S		With solvent				Solvent-free			
	Carrier	H.T	Power (W)	Temp. (°C)	Pressure (psi)	Yield (%)	Power (W)	Temp. (°C)	Pressure (psi)	Yield (%)
6	11.52	14.17	100	120	70	75	70	80	21	79
7	11.52	12.18	100	120	82	73	70	90	31	68
8	6.84	11.84	100	120	46	85	70	80	41	82
9	6.39	11.84	100	120	50	91	70	90	27	85

azo disperse dyes was carried out in one pot in the presence or absence of solvents by inducing with microwave irradiation. Because of the easy availability of microwave ovens, microwave irradiation has been recently used to promote various types of organic reactions[19,20] including those in the absence of solvents "dry media,"[21,22] which were carried out often on solid mineral supports. The application of microwave technique to the synthesis of azo disperse dyes in the solid state without any mineral support were studied and found that the reaction occurred in a very short time with high yields. In a typical run, an equimolar mixture of aniline, sodium nitrite, potassium hydrogen sulfate with active methylene compounds 1–4 was grinded to fine powder and irradiated with microwave for 5 min at 80–90°C in an explorer microwave oven, after the addition of a drop of water followed by the thorough agitation of the mixture. The action between water and microwave activated the reactants, thus the reaction occurred rapidly. Here, water acted as an activator or initiator (cf. Scheme 1 and Table I). In contrast to the classical two-steps synthesis of azo disperse dyes, the present method has a number of advantages, such as reducing the reaction time, improving the yields and simplifying the experimental procedure since neither solvent nor cooling is necessary. More importantly, this microwave method will be more economical and less harmful in the environmental point of view, when applied to industrial synthesis of disperse dyes. When compounds 1–4 were kept at room temperature in acetic acid solutions in the presence of hydrochloric acid with equimolecular amount of diazoaminobenzene 5, no coupling occurred while rearrangement of five into *p*-aminoazobenzene was observed. However, when the reaction mixture was heated in a focused microwave at 120°C for 5 min, in glacial acetic acid and in the presence of few drops of hydrochloric acid the azo disperse dyes 6–9 were formed in good yields. The presence of reaction products was confirmed according to elemental analysis and spectral data. For example, IR of compound 6 reveals the presence of NH_2, NH, and CN group at 3234 and 3140 (NH_2), 3061 (NH), and 2209 (CN) cm^{-1}, respectively. ^1H NMR shows aromatic protons at 7.10–7.74 ppm and

NH at 11.57 ppm. In addition, ^{13}C NMR data agree with the expected one. Thus, signals at 143.11; 130.44, 125.36, and 117.50 correspond to the aromatic carbon atoms. Moreover, MS (EI) shows *m/z* at 204 (M^+) (Scheme 1).

The results presented in the tables (1) indicate that the color strength K/S values of the carrier dyed samples show a slightly decrease in comparing with HT dyeing method. The dyeing results depend on many factors, for example, temperature and time. Thus, at a temperature of 100–110°C, the dyes can already diffuse into fiber due to the increased mobility of the polyester at the start of the glass transition.[23] For polyester, as the temperature increased, the diffusion coefficient increased.[24] Santos et al.[25] have been recently reported that the main effect on the dye incorporation was the dyeing time for the modified fibers, but for the nonmodified fibers, the pressure and the temperature presented analogous main effect. The results obtained might be attributed to the fact that raising of dyeing temperature above 100°C causes significant increase of the rate of diffusion of disperse dyes into polyester fiber and higher dye uptake.[23–25]

Comparisons between the two methods of synthesis of azo disperse dyes 6–9. Naphthofuran derivates are interesting compounds because of considerable utility as intermediates in the synthesis of disperse
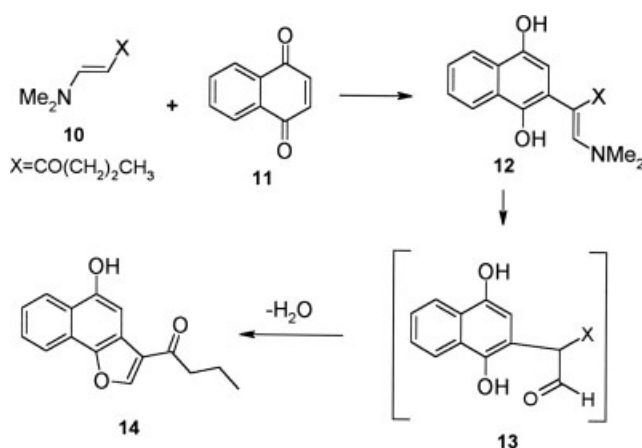
Scheme 2 Synthesis of naphthofuran derivate as an intermediate in the preparation of disperse dyes.
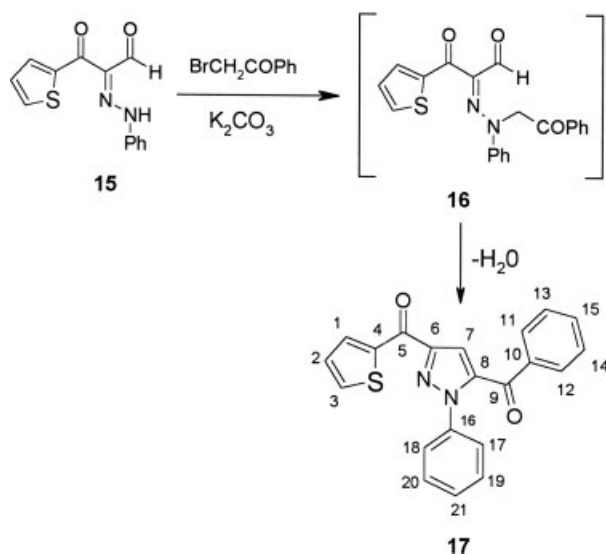
Scheme 3 A novel simple and efficient route to the synthesis of condensed thienoylpyrazole derivate as an intermediate in the preparation of disperse dyes.

dyes.[26] The enaminone 10 reacted readily with naphthoquinone 11 to yield naphthofuran 14 through the nonisolated 12 and 13. The reaction product was believed to be formed through the addition of 10 to 11 to yield 12, which hydrolyzed to 13 and then cyclized to give 14. Possible direct cyclization of product 12 seems least likely as this would then be an endo-trig cyclization to 14 (cf. Scheme 2).

A large number of arylazopyrazole disperse dyes are reported in literature,[27–30] but very few condensed pyrazole derivatives carrying an arylazo function on the pyrazole ring have been reported. In continuation of interest in the synthesis of pyrazoles as new intermediates for disperse dyes; this aticle deals with a novel simple and efficient route to the synthesis of condensed thienoylpyrazole 17. Compounds 15 reacted with phenacyl bromide to give products that may be formulated as thienoylpyrazole 17. Thus, structure of compound 17 could be established based on elemental analysis and spectral data. It is believed that thienoylpyrazole 17 is formed via intermediate 16, which could not be however, isolated (cf. Scheme 3).

CONCLUSIONS

Some azo disperse dyes have been obtained in good yields at 80–120°C for 5 min and in one step, when aniline, sodium nitrite, and potassium hydrogen sulfate were treated with active methylene compounds under microwave irradiation. The K/S values of dyeing of polyester fabrics carried out by using of HT dyeing method at 130°C were higher than those obtained during carrier dyeing method, which could descend the dyeing temperature to about 100°C. A novel simple and efficient route to the synthesis of heteroaromatic compounds as an intermediate for disperse dyes were also discussed.

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