



The microwave-assisted synthesis of 5-arylaazo-4,6-disubstituted-3-cyano-2-pyridone dyes

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ABSTRACT

A novel protocol for the rapid synthesis of pyridone colorants under controlled microwave irradiation in a dedicated reactor is described. Short reaction times, high isolated yields, and versatility for different substrates are the advantages of the reported method.

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1. Introduction

Azo compounds are the largest group of colorants in terms of number and production volume of currently marketed dyes and pigments. The importance of azo compounds as colorants is due to the simplicity of their synthesis by diazotization and azo coupling, and to the almost innumerable possibilities presented by variation on the diazo compounds and coupling components, in conjunction with their generally high molar extinction coefficient and moderate/high fastness properties [1]. An important group of yellow disperse dyes are based on pyridone derivatives as coupling components, which can easily be obtained from 3-oxobutanoates and 2-cyanoacetamides. These dyes have largely replaced yellow disperse dyes based on pyrazolones [1]. Pyridone disperse yellow dyes, such as C.I. Disperse Yellows 114, 119 and 211, are commonly used for dyeing polyester fabrics [2,3].

These and other azo dyes have traditionally been prepared from pyridone as a coupling component and various diazonium salts (Scheme 1a) [4–16]. Unreacted pyridone and low yields of the corresponding products are the main disadvantages of this method [4–16]. Alternatively, arylazo colorants containing pyridone rings can also be prepared from β -diketones and various diazonium salts,

followed by condensation with cyanoacetamide (Scheme 1b, R^1 , R^2 = Me) [17,18]. The arylazo dyes obtained in such manner do not contain unreacted pyridone material and are generally obtained in higher yields. Long reaction times, the use of a toxic and strong base for the condensation step, are the other disadvantages of this method.

This paper concerns an improved method for synthesising novel, 5-arylaazo-4,6-disubstituted-3-cyano-2-pyridone dyes from β -diketones and various diazonium salts, followed by high speed microwave-assisted condensation with cyanoacetamide.

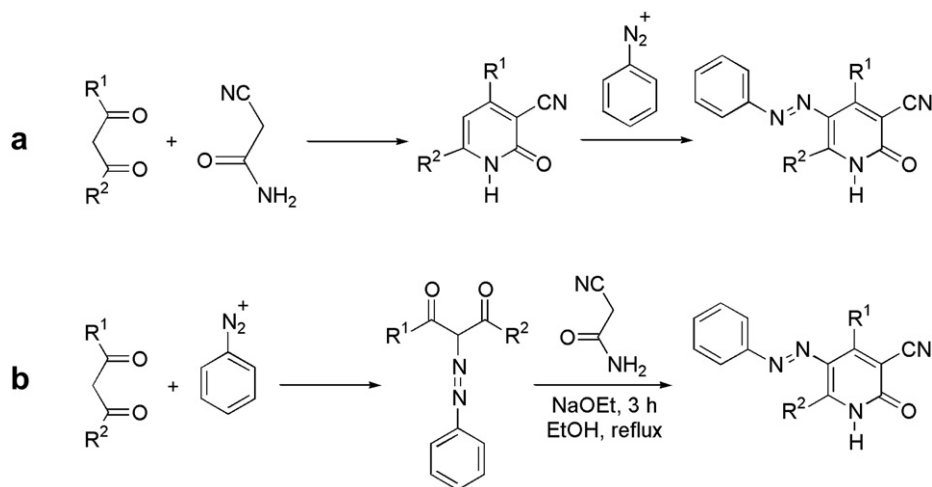
2. Experimental

2.1. General

All starting materials were obtained from Aldrich and Fluka, and were used without further purification. 1,3-Dicarbonyl compounds **2** and **4** were prepared following reported methods [17–19]. Melting points were taken on Stuart SMP3 melting point apparatus. The ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz instrument. A Biotage Initiator 2.5 EXP was used for the microwave experiments. Analytical HPLC analysis (Shimadzu LC 20) was carried out on a C 18 reversed-phase analytical column (150 $\times$ 4.6 mm, particle size 5 μm) using mobile phases A (water/acetonitrile 90:10 (v/v) + 0.1% TFA) and B (acetonitrile + 0.1% TFA)

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Scheme 1. Synthetic methods for the preparation of arylazopyridones.

at a flow rate of 0.5 mL/min. The following gradient was applied: linear increase from solution 30% B to 100% B in 9 min, hold at 100% solution B for 5 min. Low-resolution mass spectra were obtained on an Agilent 1100 LC/MS instrument using atmospheric pressure chemical ionization (APCI) in positive or negative mode. The UV–vis absorption spectra were taken in the region between 200 and 600 nm using a Shimadzu 1700 UV–vis spectrophotometer in 1.00 cm cells at 25 ± 0.1 °C in ethanol at concentration 5×10^{-5} mol dm^{-3} .

2.2. Synthesis of pyridone colorants

A mixture of the dicarbonyl compound **2** or **4** (1 mmol), cyanoacetamide (2 mmol, 168 mg) and potassium hydroxide (1.7 mmol, 95 mg) in absolute ethanol (2 mL) was irradiated for 5 min (Table 1). The resulting solid product was collected by filtration and washed with 2×5 mL of water and 5 mL of ethanol. All products were identified either by comparison with authentic samples or in the case of novel structures by $^1\text{H}/^{13}\text{C}$ NMR spectroscopy in addition to MS analysis.

2.2.1. 4,6-Dimethyl-2-oxo-5-(phenyldiazenyl)-1,2-dihydropyridine-3-carbonitrile (**1a**)

Orange powder, Mp >300 °C (Lit. Mp 278–279 °C [7]). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm) = 7.65 (d, J = 8.3 Hz, 2 H, Ar-H), 7.46 (t, J = 9 Hz, 2 H, Ar-H), 7.33 (t, J = 8 Hz, 1 H, Ar-H), 2.53 (s, 3 H, CH_3), 2.51 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ (ppm) = 170.6, 162.1, 154.0, 148.4, 132.3, 129.4, 128.6, 121.6, 120.2, 96.2, 25.3, 19.7. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ): 349 (3.96). MS (pos. APCI) m/z : 253.4 [$\text{M} + \text{H}^+$], MS (neg. APCI) m/z : 251.4 [$\text{M} - \text{H}^+$], (M = 252.3).

2.2.2. 5-((2,6-Dimethylphenyl)diazenyl)-4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (**1b**)

Orange powder, Mp >300 °C. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm) = 7.11 (brs, 3 H, Ar-H), 2.55 (s, 3 H, CH_3), 2.27 (s, 6 H, 2 CH_3). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ (ppm) = 161.7, 152.7, 147.9, 133.0, 129.7, 129.2, 126.7, 126.4, 120.3, 95.9, 25.4, 19.9, 19.7. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ): 459 (2.85), 351 (4.12). MS (pos. APCI) m/z : 281.4 [$\text{M} + \text{H}^+$], (M = 280.3).

2.2.3. 5-((2-Iodophenyl)diazenyl)-4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (**1c**)

Orange powder, Mp >300 °C. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm) = 8.06 (d, J = 8.6 Hz, 1H, Ar-H), 7.15–7.20 (m, 1 H, Ar-H), 7.45–7.51 (m, 2 H, Ar-H), 2.71 (s, 3 H, CH_3), 2.65 (s, 3 H, CH_3). ^{13}C

NMR (75 MHz, $\text{DMSO}-d_6$) δ (ppm) = 163.9, 157.2, 153.2, 152.9, 140.0, 131.6, 129.5, 117.5, 117.3, 101.8, 100.2, 21.9, 21.2. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ): 384 (4.24). MS (pos. APCI) m/z : 379.0 [$\text{M} + \text{H}^+$], (M = 378.0).

2.2.4. 5-((4-Bromophenyl)diazenyl)-4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (**1d**)

Orange powder, Mp >300 °C (Lit. Mp >300 °C [16]). ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm) = 7.64 (d, J = 9 Hz, 2 H, Ar-H), 7.58 (d, J = 9 Hz, 2 H, Ar-H), 2.55 (s, 3 H, CH_3), 2.52 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$) δ (ppm) = 170.4, 162.4, 153.0, 149.0, 132.4, 132.3, 123.4, 121.3, 119.9, 96.7, 25.1, 19.8. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ): 366 (4.26). MS (pos. APCI) m/z : 333.0 [$\text{M} + \text{H}^+$], MS (neg. APCI) m/z : 330.3 [$\text{M} - \text{H}^+$], (M = 331.2).

2.2.5. 5-((4-Bromo-2,6-dimethylphenyl)diazenyl)-4,6-dimethyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (**1e**)

Orange powder, Mp >300 °C. ^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ (ppm) = 7.30 (s, 2 H, Ar-H), 2.24 (s, 6H, 2 CH_3), 2.45 (s, 3H, CH_3),

Table 1

Optimization of different parameters in the reaction of phenylazo acetylacetone (**2a**) and cyanoacetamide (**3**).

Entry ^a	KOH (equiv.)	Amide (equiv.)	T (°C)	Time (min)	Conversion (%) ^b
1	1.7	1	80	15	13
2	1.7	1	90	15	34
3	1.7	1	100	15	42
4	1.7	1	110	15	50
5	1.7	1	120	15	47
6	1.7	1	130	15	59
7	1.7	1	140	15	46
8	1.7	1	200	15	51
9	1.7	1	130	15	65
10	1.7	1.3	130	15	70
11	1.7	1.5	130	15	79
12	1.7	1.7	130	15	96
13	1.7	2	130	15	99
14	1.7	2	130	3	92
15	1.7	2	130	5	99
16	1.7	2	130	10	99
17	1.7	2	130	15	99
18	1	2	130	5	76
19	1.5	2	130	5	95
20	1.7	2	130	5	>99

^a Reaction conditions: A mixture of the phenylazo acetylacetone (**2a**) (1 mmol), cyanoacetamide (**3**) and potassium hydroxide in absolute ethanol (2 mL) was irradiated for the appropriate time.

^b Conversion of phenylazo acetylacetone (**2a**) measured by HPLC–UV at 369 nm.

2.40 (s, 3H, CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) = 170.3, 162.1, 151.7, 148.2, 132.9, 132.5, 131.5, 120.2, 118.5, 96.2, 25.5, 19.9, 19.4. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ)]: 458 (3.19), 355 (4.22). MS (neg. APCI) m/z : 358.1 [M - H⁺], (M = 359.2).

2.2.6. 4,6-Dimethyl-5-((2-nitrophenyl)diazenyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (**1f**)

Orange powder, Mp >300 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) = 7.87 (d, *J* = 13.8 Hz, 1 H, Ar-H), 7.67–7.69 (m, 2 H, Ar-H), 7.43–7.49 (m, 1 H, Ar-H), 2.48 (s, 3 H, CH₃), 2.44 (s, 3 H, CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) = 170.5, 164.1, 149.8, 147.2, 146.1, 133.0, 128.1, 123.7, 119.5, 118.4, 97.4, 25.4, 19.8. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ)]: 385 (4.19). MS (pos. APCI) m/z : 298.1 [M + H⁺], MS (neg. APCI) m/z : 296.1 [M - H⁺], (M = 297.2).

2.2.7. 5-((2,6-Dimethylphenyl)diazenyl)-2-oxo-4,6-diphenyl-1,2-dihydropyridine-3-carbonitrile (**1g**)

Red solid, Mp 161–162 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) = 7.42–7.45 (m, 1 H, Ar-H), 7.26–7.36 (m, 8 H, Ar-H), 6.80–6.82 (m, 2 H, Ar-H), 2.48 (s, 3 H, CH₃), 1.62 (s, 6 H, 2 CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) = 170.0, 161.8, 150.4, 149.9, 142.0, 139.1, 132.6, 131.0, 129.8, 129.1, 128.7, 128.2, 127.6, 127.5, 127.4, 127.2, 119.8, 96.4, 19.1. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ)]: 367 (4.13). MS (pos. APCI) m/z : 405.2 [M + H⁺], MS (neg. APCI) m/z : 403.2 [M - H⁺], (M = 404.4).

2.2.8. 2-Oxo-4,6-diphenyl-5-(phenyldiazenyl)-1,2-dihydropyridine-3-carbonitrile (**1h**)

Yellow powder, Mp 190–192 °C (dec). ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) = 7.47–7.50 (m, 2 H, Ar-H), 7.33–7.35 (m, 6 H, Ar-H), 7.18–7.26 (m, 5 H, Ar-H), 6.89–6.92 (m, 2 H, Ar-H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) = 170.2, 161.8, 152.7, 149.0, 141.3, 138.8, 131.5, 130.5, 129.2, 129.1, 128.9, 128.0, 127.4, 121.4, 119.9, 96.7. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ)]: 370 (4.01). MS (pos. APCI) m/z : 377.5 [M + H⁺], MS (neg. APCI) m/z : 375.6 [M - H⁺], (M = 376.4).

2.2.9. 5-((4-Bromo-2,6-dimethylphenyl)diazenyl)-2-oxo-4,6-diphenyl-1,2-dihydropyridine-3-carbonitrile (**1i**)

Dark red solid, Mp 179–180 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) = 7.41–7.44 (m, 2 H, Ar-H), 7.26–7.34 (m, 8 H, Ar-H), 7.03 (s, 2 H, Ar-H), 1.58 (s, 6 H, 2 CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) = 169.9, 162.2, 150.0, 149.3, 141.9, 139.0, 133.7, 132.5, 131.4, 129.8, 128.7, 128.3, 127.6, 127.6, 127.4, 119.7, 119.6, 96.7, 18.8. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ)]: 374 (4.08). MS (neg. APCI) m/z : 482.2 [M - H⁺], (M = 483.4).

2.2.10. 6-Hydroxy-4-methyl-2-oxo-5-(phenyldiazenyl)-1,2-dihydropyridine-3-carbonitrile (**5a**)

Orange powder, Mp >300 °C (Lit. Mp 288–289 °C [8]). ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) = 13.74 (s, 1H, NH)/10.17* (s, 1H, NH), 7.54 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.40 (t, *J* = 7.5 Hz, 2 H, Ar-H), 7.17*–7.32* (m, 5 H, Ar-H), 6.91 (t, *J* = 7.2 Hz, 1 H, Ar-H), 2.51* (s, 3 H, CH₃)/2.32 (s, 3 H, CH₃) (tautomeric ratio, %: **5a**/**5a*** = 50:50). UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ)]: 430 (4.19), 353 (4.19). MS (neg. APCI) m/z : 253.2 [M - H⁺], (M = 254.2).

2.2.11. 5-((2,6-Dimethylphenyl)diazenyl)-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (**5b**)

Orange powder, Mp >300 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) = 14.23 (s, 1 H, NH), 7.02 (d, *J* = 7.5 Hz, 2 H, Ar-H), 6.85 (t, *J* = 7.5 Hz, 1H, Ar-H), 2.34 (s, 6 H, 2 CH₃), 2.23 (s, 3 H, CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) = 197.2, 165.4, 156.1, 140.2, 138.1, 129.6, 129.1, 128.8, 127.3, 123.0, 27.3, 20.0. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ)]: 412 (4.06). MS (neg. APCI) m/z : 281 [M - H⁺], (M = 282.3).

2.2.12. 5-((4-Bromo-2,6-dimethylphenyl)diazenyl)-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (**5c**)

Orange powder, Mp >300 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) = 13.96 (s, 1H, NH), 7.21 (s, 2 H, Ar-H), 2.33 (s, 6 H, 2 CH₃), 2.22 (s, 3 H, CH₃). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) = 196.9, 164.7, 163.5, 139.9, 132.0, 131.7, 131.1, 129.4, 126.6, 113.9, 27.4, 19.7. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ)]: 432 (3.62), 350 (4.08). MS (neg. APCI) m/z : 360.1 [M - H⁺], (M = 361.1).

2.2.13. 5-((4-Bromophenyl)diazenyl)-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (**5d**)

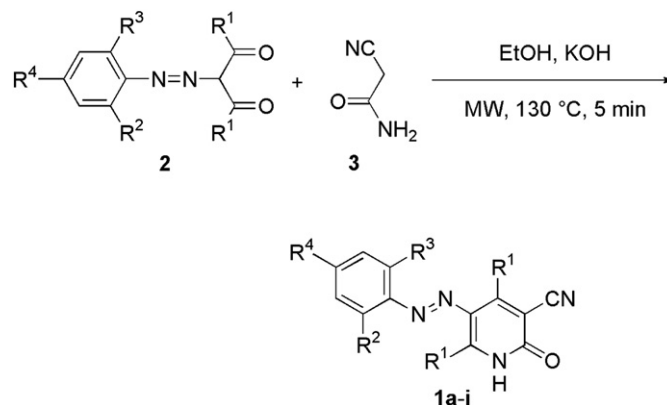
Orange powder, Mp >300 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) = 13.74 (s, 1H, NH)/10.26* (s, 1H, NH), 7.57* (d, *J* = 9 Hz, 2 H, Ar-H), 7.46* (d, *J* = 9 Hz, 2 H, Ar-H), 7.44 (d, *J* = 9 Hz, 2 H, Ar-H), 7.16 (d, *J* = 9 Hz, 2 H, Ar-H), 2.51* (s, 3 H, CH₃)/2.13 (s, 3 H, CH₃), (tautomeric ratio, %: **5d**/**5d*** = 62:38). UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ)]: 348 (3.69). MS (neg. APCI) m/z : 329.1 [M - H⁺], (M = 333.1).

2.2.14. 6-Hydroxy-2-oxo-4-phenyl-5-(phenyldiazenyl)-1,2-dihydropyridine-3-carbonitrile (**5e**)

Orange powder, Mp >300 °C. ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) = 13.96 (s, 1H, NH), 7.82 (d, *J* = 6.9 Hz, 2 H, Ar-H), 7.57 (t, *J* = 7.5 Hz, 1 H, Ar-H), 7.47 (t, *J* = 7.5 Hz, 2 H, Ar-H), 7.19–7.24 (m, 2 H, Ar-H), 6.99 (d, *J* = 7.5 Hz, 2 H, Ar-H), 6.81 (t, *J* = 7.5 Hz, 1 H, Ar-H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) = 193.4, 165.6, 144.3, 140.6, 138.6, 132.5, 129.7, 128.4, 120.7, 113.3. UV–vis (ethanol): $\lambda_{\text{max}}/\text{nm}$: [(log ϵ)]: 360 (4.24). MS (pos. APCI) m/z : 318.9 [M + H⁺], MS (neg. APCI) m/z : 315.1 [M - H⁺], (M = 316.3).

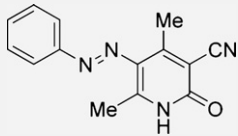
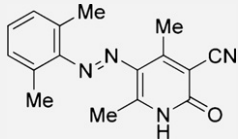
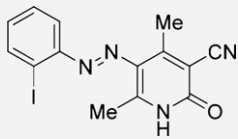
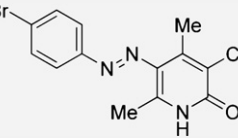
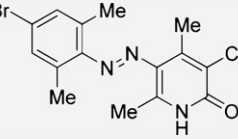
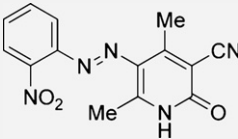
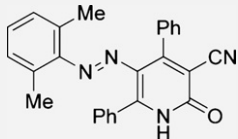
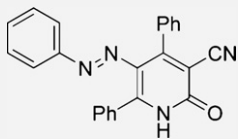
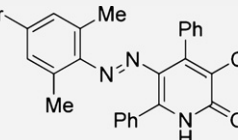
3. Results and discussion

As a starting point for our investigation, we examined the synthesis of 5-phenylazo-4,6-dimethyl-3-cyano-2-pyridone (**1a**) from phenylazo acetylacetone (**2a**) and cyanoacetamide (**3**), using KOH as the base for the reaction (Scheme 2, Table 1) in ethanol as the solvent. The use of KOH instead of the previously employed sodium ethoxide [17,18] was found to be more convenient. All studies were performed applying controlled single-mode microwave heating in sealed vessels [20,21]. Screening of reaction conditions focused on different amounts of the KOH, amide, and variations in reaction time and temperature. As can be seen in Table 1 among different temperatures a better result was obtained at 130 °C (entries 1–8). The effect of the molar excess of amide **3** was checked and it was found that in the presence of 2 equivalents of the amide an optimum result was obtained (Table 1, entries 9–13). Running the reaction for different periods of times (Table 1, entries 13–16), revealed that complete conversions were generally

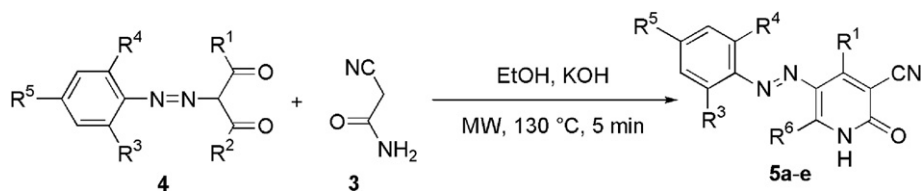


Scheme 2.

Table 2
Synthesis of pyridone colorants **1a-i** (Scheme 2).

Entry	R ¹	R ²	R ³	R ⁴	Product	Yield (%) ^a
1	Me	H	H	H		99
2	Me	Me	Me	H		100
3	Me	I	H	H		100
4	Me	H	H	Br		92
5	Me	Me	Me	Br		100
6	Me	NO ₂	H	H		100
7	Ph	Me	Me	H		83
8	Ph	H	H	H		72
9	Ph	Me	Me	Br		72

^a Isolated yield.



Scheme 3.

obtained after 5 min. Along the same lines it was established that the highest conversions were achieved employing 1.7 equivalents of KOH base (Table 1, entries 17–20). Evaluation of isolated yields for the reaction under the optimum conditions represented in Table 1, entry 20 afforded 99% of the corresponding pyridone product **1a**.

Having optimized conditions in hand that allow the preparation of pyridone **1a** within 5 min in high isolated yield (Table 1, entry 20), the synthesis of a variety of different 5-aryazo-4,6-disubstituted-3-cyano-2-pyridone dyes **1b–i** from the condensation of diketones **2** and cyanoacetamide (**3**) was investigated (Scheme 2). The results are summarized in Table 2. As can be seen, products with methyl substituents at position 4 and 6 on the pyridone ring were obtained in almost quantitative yield. An important feature of this work is the preparation of 4,6-disubstituted derivatives in high yields in a short period of time (Table 2, entries 7–9) which is not

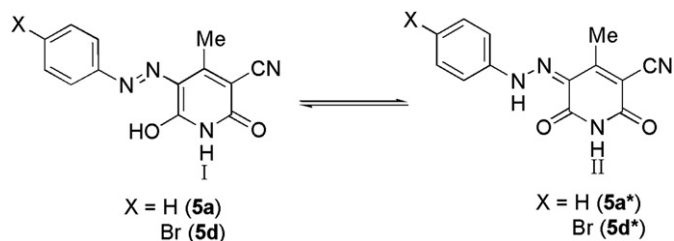
possible under conventional heating. For example, pyridone **1g** was obtained in only 50% isolated yield after 6 h reflux in ethanol. It worth noting that this is the first report of a high yielding preparation of 4,6-diphenylsubstituted pyridone dyes. The improvement in product yield and reaction time clearly shows the advantage of running reactions at higher temperature as compared to the conventional oil bath experiment at the boiling point of the solvent [20,21].

In addition to the results obtained with 1,3-diketone substrates **2** we also evaluated β -ketoesters **4** under the optimized condition (Scheme 3). The results are summarized in Table 3. The lower yields in these cases can be related to the lower reactivity of β -ketoesters **4** compared to diketones **2**. The UV–vis absorption maxima (λ_{max}) of the electronic transitions involving the free non-bonding electrons of the azo group of the synthesized pyridone dyes and the

Table 3
Synthesis of pyridone colorants.

Entry	R ¹	R ² /R ⁶	R ³	R ⁴	R ⁵	Product	Yield (%) ^a
1	Me	OEt/OH	H	H	H	 5a	47
2	Me	OEt/OH	Me	Me	H	 5b	50
3	Me	OEt/OH	Me	Me	Br	 5c	80
4	Me	OEt/OH	H	H	Br	 5d	93
5	Ph	OEt/OH	H	H	H	 5e	78

^a Isolated yield.



Scheme 4. The equilibrium between azo form (I) and hydrazone form (II) of 5-(4-substituted arylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridones [15].

molecular extinction coefficients (given as $\log \varepsilon$) in ethanol are given in [Experimental](#) section. The spectra were run in spectroquality ethanol using concentrations of $5 \times 10^{-5} \text{ mol dm}^{-3}$. The obtained data confirm that the positions of the UV–vis absorption maxima depend on the nature of the substituents of the diazo component as well as on the nature of the substituents of the pyridone component. Introduction of a substituent into the diazo component predominantly leads to a bathochromic shift of the long-wavelength absorption maximum as compared to that of the unsubstituted dyes [15,16,18]. Change of the substituents in the pyridone component leads also mainly to bathochromic shifts as compared to that of the 4,6-dimethyl substituted pyridone dyes. It should be mentioned that the arylazo pyridone dyes prepared in this work may exist in two tautomeric forms and that the tautomerism is influenced mainly by the nature of the substituents and the polarity of the solvents [16]. This tautomerisation was observed in the ^1H NMR spectra of some of the prepared derivatives **5a** and **5d** (Scheme 4) (see [Experimental](#) Section).

4. Conclusion

In conclusion a rapid and efficient method for the synthesis of an important group of azo-based dyes was introduced. Compared to the traditional method applying conventional heating, the use of controlled sealed vessel microwave heating allowed the preparation of a variety of pyridone colorants in very short reaction times and high yields.

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