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Short communication

SHORT COMMUNICATION

Synthesis of 5-(substituted phenylazo)-6-hydroxy-4-methyl-3--cyano-2-pyridones from ethyl 3-oxo-2-(substituted phenylazo)butanoates

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Abstract: A new procedure for the synthesis of known azo pyridone dyes is presented. A series of 5-(substituted arylazo)-6-hydroxy-4-methyl-3-cyano-2--pyridones were prepared from ethyl 3-oxo-2-(substituted phenylazo)butanoates and cyanoacetamide in acetone using potassium hydroxide as a catalyst by simple refluxing the reaction mixture. The structure of these dyes was confirmed by FT-IR, NMR and UV–Vis spectroscopy.

Keywords: azo compounds; cyclocondensation reaction; cyanoacetamide; pyridone.

INTRODUCTION

Azo pyridone dyes are important pyridone derivatives that have largely replaced yellow disperse dyes based on pyrazolones due to their bright hues.[1,2] Pyridone disperse yellow dyes, such as C.I. Disperse Yellows 114, 119 and 211, are used for dyeing polyester fabrics.[3,4] The conventional reaction route for the preparation of these azo dyes comprises the reaction of pyridone as a coupling component and various diazonium salts.[5–16] Alternatively, arylazo colorants containing pyridone rings can also be prepared from β-diketones and various diazonium salts followed by condensation with cyanoacetamide.[17,18] Recently, a microwave procedure for the synthesis of azo pyridone dyes using the second reaction route was reported.[19]

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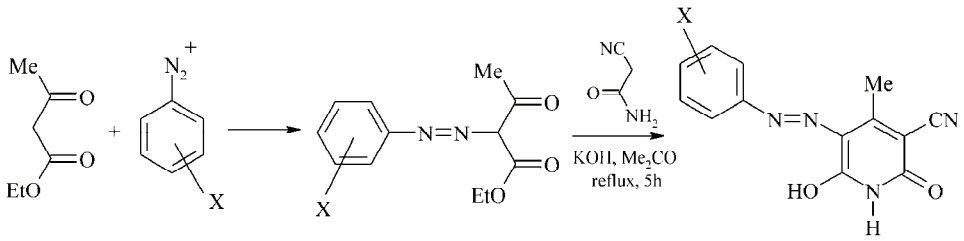
Herein, a conventional synthesis of certain 5-(substituted phenylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridones from ethyl 3-oxo-2-(substituted phenylazo)-butanoates, obtained from ethyl acetoacetate and diazonium salts, and cyanoacetamide is reported (Scheme 1).



Scheme 1. Reaction route for the synthesis of certain 5-(substituted phenylazo)-6-hydroxy-4--methyl-3-cyano-2-pyridones *via* ethyl 3-oxo-2-(substituted phenylazo)butanoates (X = H (**3**), 4-Me (**3**), 4-MeO (**3**), 4-Cl (**4**), 4-Br (**5**), 4-NO_2 (**6**), 3-Me (**7**), 3-Cl (**8**), 2-MeO (**9**), 2-Cl (**10**)).

RESULTS AND DISCUSSION

Characteristic and spectroscopic data of the prepared compounds

*1,2-Dihydro-6-hydroxy-4-methyl-2-oxo-5-(phenylazo)-3-pyridinecarbonitrile (**1**)*. Orange powder; yield: 33 %; m.p. 285–286 °C (lit. m.p. 288.1 °C,[2] 278––279 °C,[8] 278–280 °C[12]). FTIR (KBr, cm^{-1}): 3447 (NH hydrazo), 3189 (NH heterocyclic), 2231 (CN), 1688, 1667 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / / ppm): 2.51 (3H, *s*, CH_3), 7.29 (1 H, *t*, J = 7.2 Hz, Ar–H), 7.48 (2H, *t*, J = 7.5 Hz, Ar–H), 7.66 (2H, *d*, J = 7.2 Hz, Ar–H), 12.04 (1H, *s*, N–H heterocyclic), 14.55 (1H, *s*, N–H hydrazone form). UV–Vis (EtOH) (λ_{max} / nm (log ε)): 399 (4.37).

*1,2-Dihydro-6-hydroxy-4-methyl-5-[(4-methylphenyl)azo]-2-oxo-3-pyridine-carbonitrile (**2**)*. Orange powder; yield: 12 %; m.p. 277–278 °C (lit. m.p. 284.4 °C,[2] 285–286 °C,[8] 252–254 °C[12]). FTIR (KBr, cm^{-1}): 3478 (NH hydrazo), 3176 (NH heterocyclic), 2225 (CN), 1680, 1648 (C=O). ^{1}H-NMR (200 MHz, DMSO––d_6, δ / ppm): 2.50 (3H, *s*, CH_3), 3.34 (3H, *s*, $ArCH_3$), 7.29 (2H, *d*, Ar–H, J = 8.4 Hz), 7.57 (2H, *d*, Ar–H, J = 8.4 Hz), 12.00 (1H, *s*, N–H heterocyclic), 14.65 (1H, *s*, N–H hydrazone form). UV–Vis (EtOH) (λ_{max} / nm (log ε)): 433 (4.03), 399 (4.12).

*1,2-Dihydro-6-hydroxy-5-[(4-methylphenyl)azo]-4-methyl-2-oxo-3-pyridine-carbonitrile (**3**)*. Dark red powder; yield: 11 %; m.p. 270–271 °C (lit. m.p. 272––273 °C[8]). FTIR (KBr, cm^{-1}): 3435 (NH hydrazo), 3189 (NH heterocyclic), 2225 (CN), 1682, 1659 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.51 (3H, *s*, CH_3), 3.36 (3H, *s*, OCH_3), 7.40 (2H, *d*, J = 7.8 Hz, Ar–H), 7.60 (2H, *d*, J = 7.8 Hz,

Ar–H), 12.08 (1H, *s*, N–H heterocyclic), 14.36 (1H, *s*, N–H hydrazone form). UV–Vis (EtOH) (λ_{max} / nm (log ε)): 447 (3.70), 393 (3.90).

*5-[(4-Chlorophenyl)azo)-1,2-dihydro-6-hydroxy-4-methyl-2-oxo-3-pyridine-carbonitrile (**4**)*. Orange powder; yield: 61 %; m.p. 302–303 °C (lit. m.p. 301––302 °C,[8] 288–289 °C[12]). FTIR (KBr, cm^{-1}): 3438 (NH hydrazo), 3142 (NH heterocyclic), 2227 (CN), 1673, 1642 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / / ppm): 2.48 (3H, *s*, CH_3), 7.51 (2H, *d*, *J* = 9.0 Hz, Ar–H), 7.69 (2H, *d*, *J* = 9.0 Hz, Ar–H), 12.06 (1H, *s*, N–H heterocyclic), 14.16 (1H, *s*, N–H hydrazone form); UV–Vis (EtOH) (λ_{max} / nm (log ε)): 396 (4.12).

*5-[(4-Bromophenyl)azo)-1,2-dihydro-6-hydroxy-4-methyl-2-oxo-3-pyridine-carbonitrile (**5**)*. Orange powder; yield: 53 %; m.p. 308–309 °C (lit. m.p. >300 °C[19]). FTIR (KBr, cm^{-1}): 3444 (NH hydrazo), 3136 (NH heterocyclic), 2227 (CN), 1673, 1664 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.48 (3H, *s*, CH_3), 7.57 (2H, *d*, *J* = 9.0 Hz, Ar–H), 7.67 (2H, *d*, *J* = 9.0 Hz, Ar–H), 12.07 (1H, *s*, N–H heterocyclic), 14.43 (1H, *s*, N–H hydrazone form). UV–Vis (EtOH) (λ_{max} / / nm (log ε)): 396 (4.32).

1,2-Dihydro-6-hydroxy-4-methyl-5-[(4-nitrophenyl)azo]-2-oxo-3-pyridinecar-bonitrile (**6**). Dark orange powder; yield: 54 %; m.p. >320 °C (lit. m.p. 324.0 °C,[2] 326–327 °C,[8] 326–328 °C[12]). FTIR (KBr, cm^{-1}): 3431 (NH hydrazo), 3116 (NH heterocyclic), 2227 (CN), 1696, 1672 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / / ppm): 2.52 (3H, *s*, CH_3), 7.86 (2H, *d*, *J* = 9.0 Hz, Ar–H), 8.30 (2H, *d*, *J* = 9.0 Hz, Ar–H), 12.19 (1H, *s*, N–H heterocyclic), 14.35 (1H, *s*, N–H hydrazone form). UV–Vis (EtOH) (λ_{max} / nm (log ε)): 340 (4.29).

*1,2-Dihydro-6-hydroxy-4-methyl-5-[(3-methylphenyl)azo]-2-oxo-3-pyridine-carbonitrile (**7**)*. Orange powder; yield: 51 %; m.p. 257–258 °C (lit. m.p. 266––268 °C[12]). FTIR (KBr, cm^{-1}): 3454 (NH hydrazo), 3150 (NH heterocyclic), 2218 (CN), 1671, 1645 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.35 (3H, *s*, CH_3), 2.49 (3H, *s*, $ArCH_3$), 7.09 (2H, *t*, *J* = 7.2 Hz, Ar–H), 7.21–7.45 (2H, *m*, Ar–H), 12.02 (1H, *s*, N–H heterocyclic), 14.57 (1H, *s*, N–H hydrazone form). UV–Vis (EtOH) (λ_{max} / nm (log ε)): 429 (4.37), 399 (4.31).

*5-[(3-Chlorophenyl)azo)-1,2-dihydro-6-hydroxy-4-methyl-2-oxo-3-pyridine-carbonitrile (**8**)*. Orange powder; yield: 33 %; m.p. 298–300 °C (Lit. m.p. 288––290 °C[12]). FTIR (KBr, cm^{-1}): 3444 (NH hydrazo), 3155 (NH heterocyclic), 2221 (CN), 1673, 1642 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.47 (3H, *s*, CH_3), 7.27 (1H, *d*, *J* = 9.0 Hz, Ar–H), 7.45 (1H, *t*, *J* = 8.0 Hz, Ar–H), 7.57 (2H, *d*, *J* = 9.0 Hz, Ar–H), 12.07 (1H, *s*, N–H heterocyclic), 14.34 (1H, *s*, N–H hydrazone form). UV–Vis (EtOH) (λ_{max} / nm (log ε)): 399 (4.51).

*1,2-Dihydro-6-hydroxy-5-[(2-methylphenyl)azo]-4-methyl-2-oxo-3-pyridine-carbonitrile (**9**)*. Red powder; yield: 61 %; m.p. 314–315 °C (lit. m.p. 324–325 °C[8]). FTIR (KBr, cm^{-1}): 3457 (NH hydrazo), 3142 (NH heterocyclic), 2226 (CN), 1672, 1658 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.50 (3H, *s*,

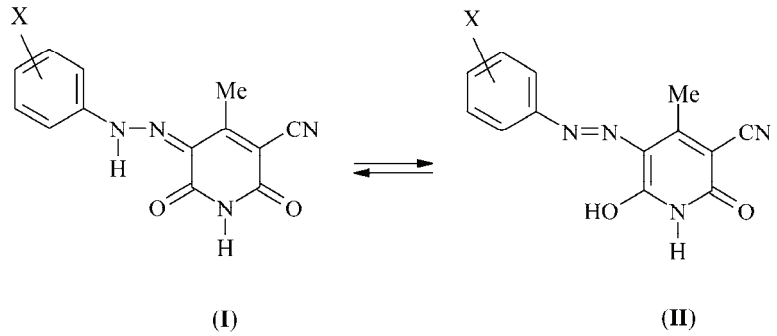
CH_3), 3.92 (3H, *s*, OCH_3), 7.00–7.33 (2H, *m*, Ar–H), 7.61 (1H, *d*, *J* = 7.2 Hz, Ar–H), 7.75 (1H, *d*, *J* = 7.4 Hz, Ar–H), 12.06 (1H, *s*, N–H heterocyclic), 14.91 (1H, *s*, N–H hydrazone form). UV–Vis (EtOH) (λ_{max} / nm (log ε)): 379 (4.23).

*5-[(2-Chlorophenyl)azo)-1,2-dihydro-6-hydroxy-4-methyl-2-oxo-3-pyridine-carbonitrile (**10**)*. Orange powder; yield: 28 %; m.p. >320 °C (lit. m.p. 347–348 °C[8]). FTIR (KBr, cm^{-1}): 3447 (NH hydrazo), 3168 (NH heterocyclic), 2223 (CN), 1675, 1660 (C=O). ^{1}H-NMR (200 MHz, DMSO-d_6, δ / ppm): 2.50 (3H, *s*, CH_3), 7.31 (1H, *t*, *J* = 8.0 Hz, Ar–H), 7.51 (1H, *t*, *J* = 7.4 Hz, Ar–H), 7.63 (1H, *d*, *J* = 8.0, Hz Ar–H), 7.90 (1H, *d*, *J* = 7.8 Hz, Ar–H), 12.22 (1H, *s*, N–H heterocyclic), 14.95 (1H, *s*, N–H hydrazone form). UV–Vis (EtOH) (λ_{max} / nm (log ε)): 423 (4.36).

In comparison to the conventional reaction route for the preparation of the studied pyridone dyes, which requests the preparation of the starting pyridone (which usually takes about 8 h),[20] and the synthesis of azo compounds (which also takes several hours),[2] the employed reaction route takes less time (about 2–3 h for the synthesis of the arylazo keto ester and 5 h for the condensation step) but gives, according to literature,[12] lower yields. Although obtained yields are lower (low to moderate), the obtained raw products were generally of high purity and the arylazo dyes obtained in such a manner do not contain unreacted pyridone material, which is present in the first reaction route.

According to the obtained results, electron-attracting substituents in phenyl group give higher yields while electron-donating substituents give lower yields, which is in accordance with the reaction mechanism of pyridone formation.[21] The unreacted intermediate can be isolated by washing the solid residue (obtained from the filtrate after isolation of the product) with hot ethanol and used again for the synthesis of the wanted azo pyridone dye by simple introduction in a new reaction mixture.

The arylazo pyridone dyes prepared in this work may exist in two tautomeric forms: the hydrazone and azo form[8,15] (Fig. 1). The infrared spectra of all syn-



(**I**) (**II**)

Fig. 1. The equilibrium between the hydrazone form (**I**) and the azo form (**II**) of 5-(substituted phenylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridones.

thesized dyes showed two intense carbonyl bands at about 1642 and 1696 cm^{-1}, which were assigned to the diketohydrazone form. The spectra exhibited a broad N–H hydrazone band in the region 3434–3457 cm^{-1} which suggests that these compounds dominantly exist in the solid state in the hydrazone tautomeric form.

The ^{1}H-NMR spectra of the dyes exhibited a signal near 14.16–14.99 ppm. This signal corresponds to the imino N–H proton resonance of the hydrazone form. The obtained results are in agreement with the data obtained by Ertan and Gurkan[12] (hydrazone form with N–H peaks in the range of 15.1–15.6 ppm) and also by Peng *et al*.[22,23] (hydrazone form with N–H peaks in the range of 14.30––16.09 ppm).

EXPERIMENTAL

Materials

All the used materials were obtained commercially, mostly from Fluka, and were used without further purification.

Equipment

The IR spectra were recorded on a Bomem FTIR Spectrophotometer, MB series, in the form of KBr pellets. The ^{1}H-NMR spectra were recorded as solutions in DMSO-d_6 using a Varian Gemini-200 instrument, with tetramethylsilane as the internal standard. The UV–Vis absorption spectra were taken using a Shimadzu 1700 UV–Vis spectrophotometer in 1.00 cm cells at 25±0.1 °C in ethanol at a concentration of 5×10^{-5} mol dm^{-3}.

Synthesis of azo pyridone dyes

To a solution of ethyl acetoacetate (0.01 mol) in 30 cm^3 of ethanol, sodium acetate (3.0 g) was added. The mixture was cooled to 0 °C and a cooled solution of arenediazonium chloride (prepared from 0.01 mol of substituted aniline in 5 cm^3 of dilute HCl (6 M) and a solution of $NaNO_2$ (0.0105 mol) in water (4.2 cm^3) was added under stirring. The stirring was continued for one hour after which the solid was collected, washed with 2×5 cm^3 of water and 2×5 cm^3 of ethanol, and dried in air.

The obtained product (0.01 mol), potassium hydroxide (0.017 mol) and cyanoacetamide (0.02 mol) were dissolved in 15 cm^3 of acetone and stirred and refluxed for 5 h. The resulting mixture was acidified using dilute HCl, and the solid product was collected by filtration and washed with 2×5 cm^3 of water and 2×5 cm^3 acetone. The obtained crystals were then recrystallized from acetone.

CONCLUSIONS

A new simple procedure for the synthesis of 5-(substituted phenylazo)-6-hydroxy-4-methyl-3-cyano-2-pyridones is presented. Synthesis from ethyl 3-oxo-2--(substituted phenylazo)butanoates in acetone gave products in low to moderate yields. These dyes exist in the hydrazone tautomeric form in the solid state and in solvent DMSO-d_6.

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ИЗВОД

СИНТЕЗА 5-(СУПСТИТУИСАНИХ ФЕНИЛАЗО)-6-ХИДРОКСИ-4-МЕТИЛ-3-ЦИЈАНО-2--ПИРИДОНА ИЗ ЕТИЛ-3-ОКСО-2-(СУПСТИТУИСАНИХ ФЕНИЛАЗО)БУТАНОАТА

ЈАСМИНА ДОСТАНИЋ[1], НАТАША ВАЛЕНТИЋ[2], ГОРДАНА УШЋУМЛИЋ[2] и ДУШАН МИЈИН[2]

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Нови поступак за синтезу познатих азо-пиридонских боја је описан у раду. Серија 5-(супституисаних фенилазо)-6-хидрокси-4-метил-3-цијано-2-пиридона је припремљена из етил-3-оксо-2-(супституисаних фенилазо)бутаноата и цијаноацетамида у ацетону коришћењем калијум-хидроксида као катализатора уз загревање.

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