Pergamon

Tetrahedron 57 (2001) 1609–1614

TETRAHEDRON

Efficient synthesis of 3-aroylcinnolines from aryl methyl ketones

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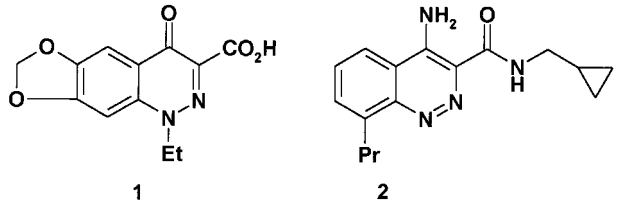
Received 20 September 2000; revised 14 November 2000; accepted 30 November 2000

Abstract—An efficient synthesis of 3-aroylcinnolines starting from the appropriate aryl methyl ketones is described. The latter were converted in two steps to the corresponding 3-oxo-3-aryl-2-arylhydrazonopropanals, which upon acid catalyzed cyclization in conc. sulfuric acid or polyphosphoric acid (PPA) led to the corresponding 3-aroylcinnolines.

1. Introduction

Significant commercial interest in the development of benzopyridazine derivatives, particularly pharmaceutical uses of pyridazines and cinnolines is shown by the large number of patents filed in this area.[1] For example cinoxacine **1**[2] is a cinnoline analogue of quinoline antibacterials used for urinary tract infection and ICI-D-7569 **2**[3] is an anxiolytic agent (Scheme 1).

In conjunction with our recent interest in the synthesis of benzopyridazines[4,5] as potential pharmaceuticals, samples of 3-aroylcinnolines with different functional substituents on the benzo moiety were required. The main synthetic route to cinnolines is the cyclization of *o*-substituted arylhydrazones[6] or diazotization of *o*-substituted anilines.[7] Both approaches cannot be readily adopted for preparing 3-acyl and/or 3-aroylcinnolines with functional substituents on the benzo moiety of the molecule. Although cyclization of functionally substituted arylhydrazones, readily obtained via coupling of diazotised aromatic amines with 1,3-bifunctionally substituted methylenes, is a very interesting approach that would enable synthesis of the required derivatives, the scope of this synthetic route has not been defined and to our knowledge the route has been adopted only a few times in the last 40 years.[8–12] Moreover, cyclization of the monophenylhydrazones of benzil and 4,6-dimethyl-1,2-cyclohexanedione in sulfuric acid was reported more than half a century ago. However, no further report for the application of this procedure to other derivatives was reported.[13]



1 2

Scheme 1.

2. Results and discussion

In the present work we describe an efficient synthesis of 3-aroylcinnolines **5** by the acid catalyzed cyclization of 3-oxo-3-aryl-2-arylhydrazonopropanals **4**. This reaction represents an easy access to 3-aroylcinnolines **5** of potential biological applications. Although the synthesis of 3-acetylcinnolines was reported a long ago,[12] its application and generality to other derivatives has not been followed up. Moreover, it constitutes a tedious, low yielding and long procedure. The present method offers an efficient, simple and general synthetic procedure for 3-acylcinnoline and its substituted derivatives, thus, complementing the few known literature procedures for the synthesis of other cinnoline derivatives.

The required 2-arylhydrazonopropanals **4a–i** were prepared as described previously via coupling diazotised aromatic amines with the enaminones **3a–g** in ethanolic sodium hydroxide solution.[14] Compounds **4** were shown based on ^{1}H NMR and ^{13}C NMR to exist as a mixture of *anti* and *syn* hydrazones with the *anti* form always prevailing as shown in Table 1. The starting enaminones **3** were readily obtained from the appropriate aryl methyl ketones.

Thus, heating the hydrazones **4a**,**b**,**d**,**e**,**h**,**i** with conc. H_2SO_4 at 100°C for 3–5 m afforded good yields of the corresponding cinnoline derivatives **5a**,**b**,**d**,**e**,**h**,**i**,**j**. However, similar treatment of the other hydrazones **4c**,**f**,**g** led to the formation of a mixture of the corresponding cinnoline together with other sulfonation products from which a pure product was

Keywords: 2-arylhydrazono-3-oxopropanal; cinnolines; aryl methyl ketones.

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0040–4020/01/$ - see front matter
PII: S0040-4020(00)01141-8

Table 1. NMR (DMSO-d_6) data for the hydrazones **4a–i** and the respective aldehydic CHO in ^{1}H NMR

Product *anti, syn* %	Molecular formula	^{1}H NMR δ		^{13}C NMR[a] δ
		anti, *syn* CHO, NH (s)	Other H's	
4a 78, 22	$C_{15}H_{12}N_2O_2$ (252.27)	10.02, 14.1 9.56, 12.3	7.18–7.89 (m, 10 H)	116.5, 117.5, 125.2, 126.8, 128.8, 129.6, 129.9, 130.2, 130.4, 130.9, 132.9, 133.0, 134.8, 137.1, 137.9, 138.7, 142.3, 143.2, 189.1, 189.6, 191.8, 193.2
4b 85, 15	$C_{15}H_{11}N_2ClO_2$ (286.5)	9.99, 14.35 9.52, 12.69	7.22–7.91 (m, 9H)	116.7, 117.7, 125.5, 126.9, 128.9, 129.7, 130.3, 130.5, 131.7, 132.8, 135.9, 136.6, 137.8, 138.0, 139.6, 142.3, 143.0, 188.9, 189.6, 190.6, 193.0
4c 78, 22	$C_{16}H_{14}N_2O_3$ (282.5)	9.96, 14.2 9.54, 11.85	7.07–7.49 (m, 9H), 3.87 (s, 3H, OCH_3)	56.35, 56.57, 114.2, 115.1, 116.2, 117.4, 124.7, 126.6, 129.7, 130.0, 130.2, 130.5, 132.6, 133.2, 133.4, 140.1, 142.4, 143.4, 163.5, 165.0, 189.3, 189.6, 189.9, 191.5
4d 79, 11	$C_{15}H_{11}N_3O_4$ (297)	10.05, 14.28 9.5, 12.5	7.05–8.39 (m, 9H)	117.9, 124.0, 127.2, 130.5, 131.9, 132.7, 142.1, 143.9, 149.9, 188.6, 190.8
4e 86, 14	$C_{13}H_{10}N_2O_3$ (242.2)	9.95, 14.31 9.51, 12.11	6.79–8.11 (m, 8H)	113.5, 114.1, 116.4, 117.8, 122.5, 123.4, 125.1, 126.9, 130.2, 130.6, 132.5, 138.3, 142.2, 143.2, 148.8, 150.3, 150.6, 152.3, 177.5, 178.4, 188.6, 189.2
4f 95, 5	$C_{13}H_{10}N_2O_2S$ (258.3)	9.99, 14.35 9.50, 12.18	7.24–8.06 (m, 8H)	116.4, 118.1, 125.0, 127.0, 128.7, 129.9, 130.2, 130.6, 132.6, 135.9, 136.7, 137.3, 138.1, 139.6, 142.2, 143.6, 181.5, 182.0, 188.9, 189.3
4g 78, 22	$C_{16}H_{14}N_2O_3$ (282.5)	9.99, 14.44 9.51, 12.78	6.98–7.87 (m, 9H), 3.75 (s, 3H, OCH_3)	56.9, 115.5, 115.7, 118.3, 119.1, 128.7, 129.3, 129.8, 130.8, 132.3, 132.7, 134.3, 135.6, 136.4, 136.8, 137.6, 138.2, 157.7, 158.7, 188.5, 189.2, 191.7, 192.6
4h 45, 55	$C_{15}H_{11}N_3O_4$ (297)	10.01, 13.9 9.63, 12.1	7.59–8.23 (m, 9H)	115.8, 117.5, 126.4, 126.5, 129.0, 130.0, 130.0, 131.1, 133.5, 134.6, 135.8, 135.9, 137.3, 143.2, 143.3, 144.6, 148.2, 149.1, 189.6, 190.2, 191.7, 193.6
4i 67, 33	$C_{15}H_{11}N_2ClO_2$ (286.5)	10.17, 14.15 9.58, 12.08	7.14–7.9 (m, 9H)	114.9, 115.7, 116.2, 117.3, 124.3, 126.1, 128.8, 129.8, 129.9, 130.9, 131.9, 132.1, 133.1, 133.3, 134.8, 134.9, 135.3, 136.5, 137.7, 140.5, 144.2, 189.2, 189.9, 191.9, 193.4

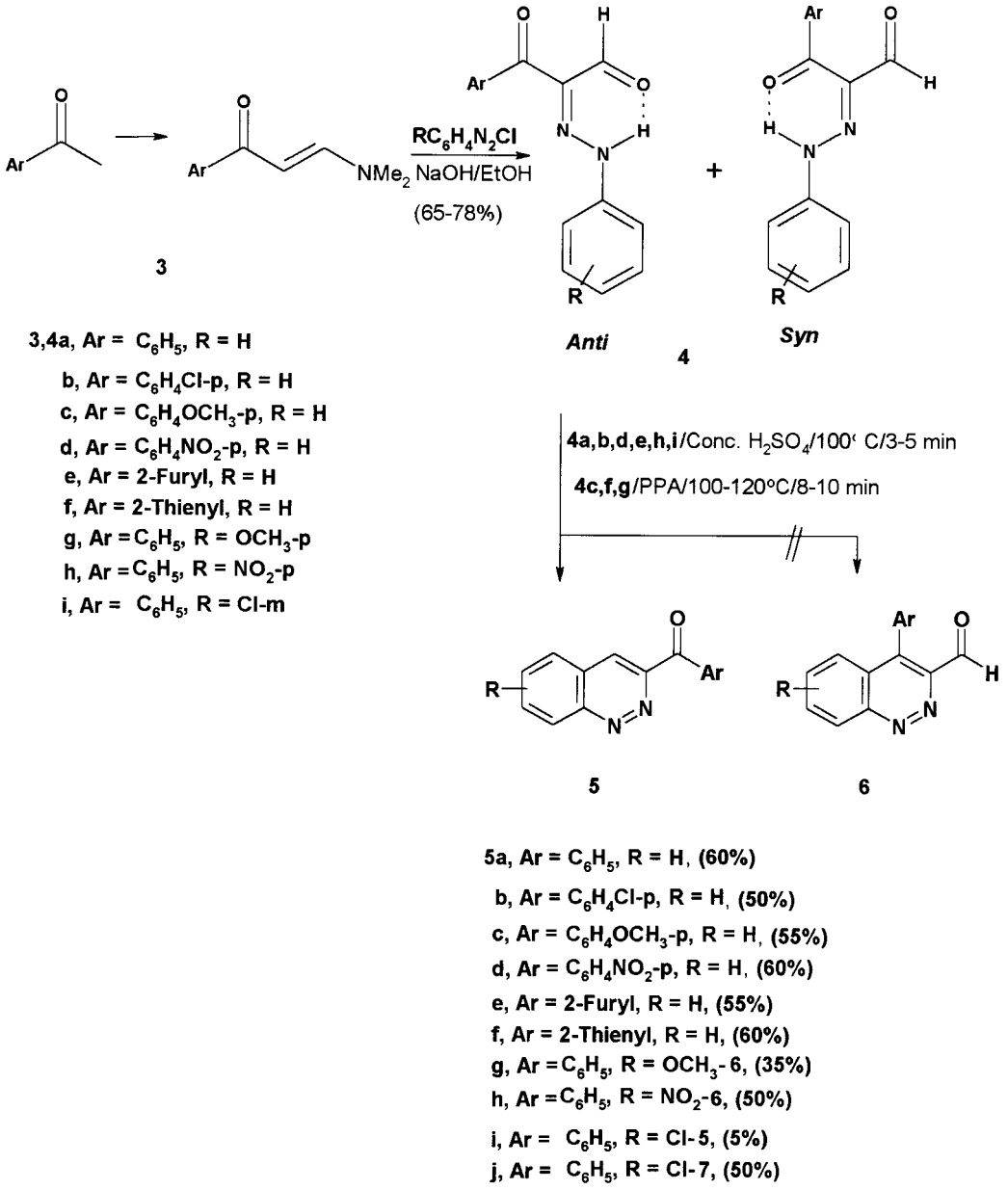
[a] Signals due to both *anti* and *syn* isomers, compound **4d** showed signals assignable for the major *anti* isomer due to solubility reason.

difficult to isolate. Replacing sulfuric acid with polyphosphoric acid overcame this problem. Thus, successful conversion of **4c**,**f**,**g** into the corresponding cinnoline derivatives **5c**,**f**,**g** was readily achieved in good yields by heating with PPA at 100–120°C for 8–10 m. Cyclization of the *m*-chlorophenylhydrazones **4i** gave as expected a mixture of the corresponding 3-benzoyl-5-chlorocinnolines **5i** and its isomeric 7-chloro derivative **5j** in about a 1:9 ratio as determined from the ^{1}H NMR spectra of the mixture obtained. From this mixture a pure sample of **5j** was obtained by fractional crystallization (Scheme 2).

The structure of the formed cinnolines was confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy. Full proton and carbon signal assignment of **5a** was made using ^{1}H NMR, NOE-difference spectra, H,H-COSY, HMQC and HMBC NMR techniques. Thus, from ^{1}H NMR, H-4 was readily assigned at δ 8.87 (s, 1H). By irradiation at H-4 from NOE-difference experiment H-5 was assigned at δ 8.3 (showed highest NOE enhancement). From these assignments and H,H-cosy, other protons were readily assigned by examining the different cross peaks. Thus, H-6, H-7, H-8 were assigned at δ 8.0 (t, 1H), 8.15 (t, 1H), 8.6 (d, 1H), respectively. The phenyl protons H-11, H-12, H-13 were assigned at δ 8.04 (d, 2H), 7.6 (t, 2H), 7.75 (t, 1H), respectively. Similarly the different cinnoline protons of other derivatives were assigned as shown in Table 2. It was found in HMBC experiment that cross peaks appear only for 3-bond H–C coupling. From decoupled ^{13}C NMR, DEPT-CH, HMQC and HMBC the

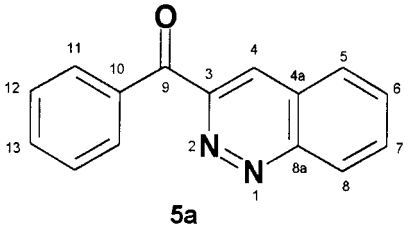
Table 2. NMR (DMSO-d_6) data for the cinnolines **5a–j**

Product	Molecular formula	^{1}H NMR δ multiplicity, J(Hz)						^{13}C NMR δ
		H-4	H-5	H-6	H-7	H-8	Other H's	
5a	$C_{15}H_{10}N_2O$ (234)	8.88 s	8.32 d, 8.0	8.01 t, 7.5	8.13 t, 8.0	8.61 d, 8.2	8.05, 7.74, 7.61 d, 7.2, t, 7.3, t, 7.5	126.2, 126.3, 129.3, 129.5, 129.8, 131.8, 133.1, 134.2, 134.3, 137.0, 151.2, 152.4, 193.6
5b	$C_{15}H_9N_2ClO$ (268.5)	8.91 s	8.34 d, 8.0	8.02 t, 7.6	8.16 t, 8.0	8.62 d, 8.5	8.13, 7.69 d, 8.5, d, 8.5	126.4, 129.4, 126.6, 129.9, 133.2, 133.7, 134.3, 135.8, 139.8, 139.2, 151.2, 152.1, 192.3
5c	$C_{16}H_{12}N_2O_2$ (264)	8.81 s	8.3 d, 8.0	8.02 t, 7.5	8.11 t, 8.0	8.61 d, 8.4	8.10, 7.14, 3.8 d, 7.0, d, 7.0, s	56.5, 114.7, 125.8, 126.4, 129.4, 129.5, 129.8, 133.0, 133.9, 134.4, 151.1, 153.1, 164.4, 191.7
5d	$C_{15}H_9N_3O_3$ (279)	9.01 s	8.37 d, 8.1	8.04 t, 8.0	8.18 t, 8.2	8.63 d, 8.7	8.42, 8.29 d, 8.8, d, 8.8	124.2, 126.3, 126.7, 129.7, 129.9, 132.9, 133.3, 134.7, 142.5, 150.6, 151.3, 151.4, 192.6
5e	$C_{13}H_8N_2O_2$ (224)	8.82 s	8.29 d, 8.6	7.97 t, 7.9	8.10 t, 8.6	8.58 d, 8.5	8.23, 8.11, 6.89 d, 1.2, d, 3.5, dd, 3.5, 1.3	113.9, 125.4, 126.0, 126.3, 129.6, 129.8, 133.1, 134.2, 150.3, 151.38, 151.42, 151.5, 178.1
5f	$C_{13}H_8N_2OS$ (240)	8.95 s	8.34 d, 8.2	8.01 t, 7.5	8.14 t, 7.22	8.62 d, 8.2	8.45, 8.23, 7.37 dd, 3.9, 1.0, dd, 4.8, 1.0 dd, 4.8, 3.9	125.7, 126.5, 129.3, 129.7, 1229.8, 133.2, 134.4, 138.4, 139.0, 140.9, 151.3, 151.5, 182.5
5g	$C_{16}H_{12}N_2O_2$ (264)	8.62 s	7.6 s	-	7.7 d, 8.6	8.51 d, 8.8	8.19, 7.73, 7.6 d, 8.0, t, 7.8, t, 7.6	
5h	$C_{15}H_9N_3O_3$ (279)	9.2 s	8.87 d, 9.3	-	8.75 dd, 9.2, 2.4	9.39 d, 2.3	8.07, 7.77, 7.63 d, 7.5, t, 7.6, t, 7.6	126.2, 126.9, 127.1, 128.1, 129.4, 131.8, 132.4, 134.6, 136.7, 149.1, 151.3, 153.4, 193.1
5i*	$C_{15}H_9N_2ClO$ (268)	8.7 s	-	8.21 d, 8.2	8.14 t, 8.3	8.65 d, 8.6	8.07, 7.74, 7.61 d, 7.8, t, 7.5, t, 7.6	
5j	$C_{15}H_9N_2ClO$ (268)	8.95 s	8.41 d, 8.2	8.05 d, 8.2	-	8.75 s	8.05, 7.74, 7.62 d, 8.3, t, 7.3 t, 7.6	125.2, 126.2, 128.5, 129.3, 131.8, 133.9, 134.4, 136.9, 138.5, 151.2, 152.7, 193.3



Scheme 2.

different carbon signals of 5a were assigned at δ 152.4 (C-3), 126.2 (C-4), 126.3 (C-4a), 129.5 (C-5), 133.0 (C-6), 134.2 (C-7), 129.8 (C-8), 151.2 (C-8a), 193.6 (C-9), 137.0 (C-10), 131.8 (C-11), 129.3 (C-12), 134.3 (C-13).



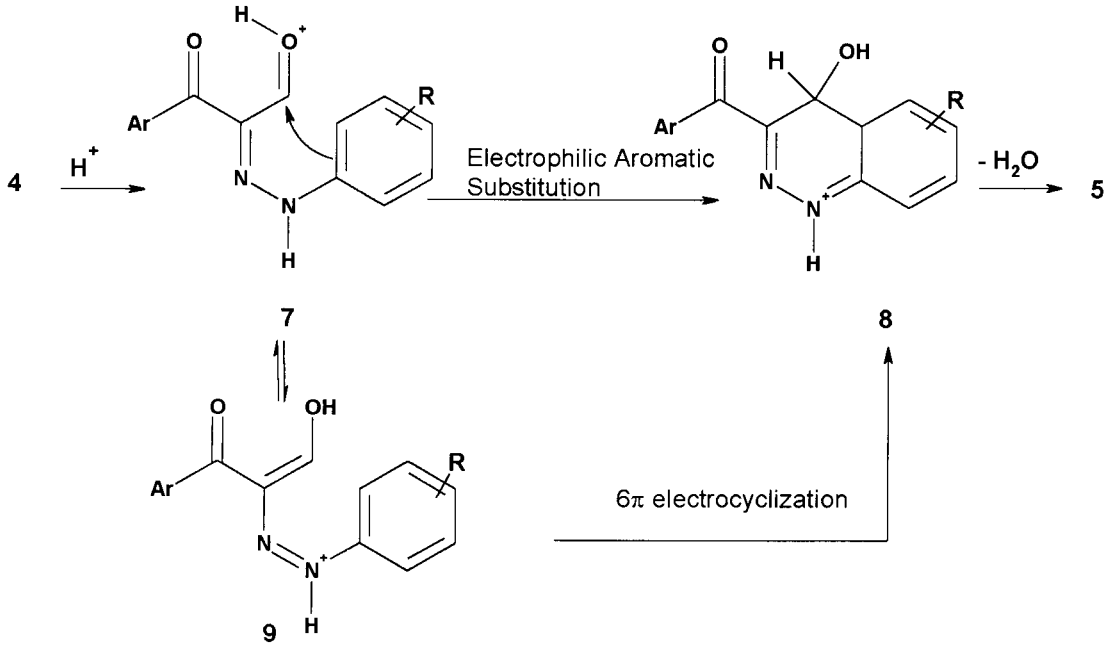
5a

2.1. Mechanism of the acid catalyzed cyclization of 2

Two mechanistic pathways may be suggested to account for the acid catalyzed conversion of **4** into **5**. Both start with protonation of **4** to **7**. The first mechanism involves a nucleophilic attack by the aromatic ring of the hydrazone moiety on the formyl carbonyl carbon (**7** to **8**), followed by elimination of water to give **5** (Scheme 3). Alternatively, one may assume initial isomerization of **7** into **9** which then undergoes 6π electrocyclization also yielding **8** via a quasi aromatic six membered transition state followed by dehydration to yield the corresponding cinnoline derivative **5**. Kinetic study of this acid catalyzed cyclization as well as gas phase pyrolytic cyclization including substituents effect proved that the second pathway is more favorable and details of this study will be the subject of another publication. Moreover, flash vacuum pyrolysis of the hydrazones **4** into the cinnolines **5** is now under investigation and will be reported soon.

3. Experimental

Melting points are uncorrected. IR: (KBr) Shimadzu IR-740



Scheme 3.

spectrometer. ^{1}H and ^{13}C NMR: Bruker Avance 400 spectrometer. Ms: Gc/Ms INCOS XL Finnigan MAT. Microanalysis: LECO CHNS-932.

3.1. 2-Arylhydrazono-3-oxopropanal 4a–i; General procedure

A cold solution of the diazonium salt (10 mmol) (prepared by adding a cold solution of sodium nitrite (0.7 g) in water (5 mL) to a solution of the appropriate arylamine (10 mmol) in conc HCl (5 mL)) was added to a cold solution of the appropriate enaminones **3** in EtOH (50 mL) containing NaOH (1.6 g). The mixture was then stirred at room temperature for 1 h, and the solid precipitated was collected and crystallized from EtOH.

3.1.1. 3-Oxo-3-phenyl-2-phenylhydrazonopropanal (4a). From aniline and **3a**. Yield 1.96 g (78%); mp 82–84°C (Lit.[14] mp 82–84°C).

3.1.2. 3-Oxo-3-(4-chlorophenyl)-2-phenylhydrazonopropanal (4b). From aniline and **3b**. Yield 2.15 g (75%); mp 135–137°C. IR: 3423, 3023, 2905, 2781, 1648, 1636 cm^{-1}. Anal. Calcd For $C_{15}H_{11}ClN_2O_2$: C, 62.82; H, 3.84; N, 9.77. Found: C, 62.79, H, 4.05, N, 9.82.

3.1.3. 3-Oxo-3-(4-methoxyphenyl)-2-phenylhydrazonopropanal (4c). From aniline and **3c**. Yield 2.03 g (72%); mp 141–143°C. IR: 3430, 3170, 2968, 2865, 2795, 1649, 1624, 1607 cm^{-1}. Anal. Calcd For $C_{16}H_{14}N_2O_3$: C, 68.08; H, 4.96; N, 9.93. Found: C, 67.84, H, 4.96, N, 9.72.

3.1.4. 3-Oxo-3-(4-nitrophenyl)-2-phenylhydrazonopropanal (4d). From aniline and **3d**. Yield 2.15 g (75%); mp 173–175°C. Anal. Calcd For $C_{15}H_{11}N_3O_4$: C, 60.61; H, 3.70; N, 14.14. Found: C, 60.36, H, 3.80, N, 13.84.

3.1.5. 3-(2-Furyl)-3-oxo-2-phenylhydrazonopropanal (4e). From aniline and **3e**. Yield 1.72 g (71%); mp 114–116°C (Lit.[14] 115–116°C).

3.1.6. 3-Oxo-2-phenylhydrazono-3-(2-thienyl)propanal (4f). From aniline and **3f**. Yield 1.9 g (74%); mp 114–115°C (Lit.[14] 113–115°C).

3.1.7. 3-Oxo-3-phenyl-2-(4-methoxyphenylhydrazono)-propanal (4g). From *p*-anisidine and **3a**. Yield 2.0 g (71%); mp 102–103°C. IR: 3435, 3084, 3009, 2968, 2855, 1645, 1631, 1607 cm^{-1}. Anal. Calcd For $C_{16}H_{14}N_2O_3$: C, 68.08; H, 4.96; N, 9.93. Found: C, 68.25, H, 5.01, N, 9.95.

3.1.8. 3-Oxo-3-phenyl-2-(4-nitrophenylhydrazono)propanal (4h). From *p*-nitroaniline and **3a**. Yield 2.16 g (73%); mp 143–145°C. IR: 3435, 3116, 3089, 2989, 1646, 1650 1596 cm^{-1}. Anal. Calcd For $C_{15}H_{11}N_3O_4$:C, 60.61; H, 3.70; N, 14.14. Found: C, 60.66, H, 3.88, N, 14.21.

3.1.9. 3-Oxo-3-phenyl-2-(3-chlorophenylhydrazono)propanal (4i). From m-chloroaniline and **3a**. Yield 1.8 g (65%); mp 141–143°C. IR: 3435, 3074, 3024, 2981, 1651, 1637, 1592 cm^{-1}. Anal. Calcd For $C_{15}H_{11}ClN_2O_2$: C, 62.82; H, 3.84; N, 9.77. Found: C, 63.09, H, 4.03, N, 9.77.

3.2. 3-Aroylcinnolines 5a–j; General procedures

(A) A mixture of the appropriate 3-oxo-2-arylhydrazonopropanal **4** (1.5 g) in conc. H_2SO_4 (20 mL) was heated at 100°C for 3–5 m. After cooling and dilution with cold water the precipitate was collected, washed with water and recrystallized from ethanol.

(B) A mixture of the appropriate 3-oxo-2-arylhydrazonopropanal **4** (1.5 g) and polyphosphoric acid (20 mL) was heated at 100–120°C for 8–10 m. After cooling and dilution with cold water the precipitate was collected, washed

with water and recrystallized from ethanol using charcoal to remove charring materials.

3.2.1. 3-Benzoylcinnoline 5a. Yellow crystals from **4a** using procedure A. Yield 0.84 g (60%); mp 138–139°C. Ms: *m/z* 234 (85, M^+), 206 (60%), 178 (40%), 129 (5%), 105 (65%), 101 (25%), 77 (100%). IR: 3055, 1661, 1615, 1599, 755, 697 cm^{-1}. Anal. Calcd For $C_{15}H_{10}N_2O$: C, 76.92; H, 4.27; N, 11.96. Found: C, 76.65, H, 4.46, N, 11.77.

3.2.2. 3-(4-Chlorobenzoyl)cinnoline 5b. Pale yellow crystals from **4b** using procedure A. Yield 0.7 g (50%); mp 152–154°C. Ms: *m/z* 268, 270 (95%, 35%, M^+), 240 (3%), 242 (1%), 212 (10%), 214 (3%), 139 (85%), 141 (30%), 129 (5%), 111 (95%), 113 (35%), 101 (25%). IR: 3054, 1661, 1615, 1589, 755, 697 cm^{-1}. Anal. Calcd For $C_{15}H_9ClN_2O$: C, 67.03; H, 3.35; N, 10.42. Found: C, 66.64, H, 3.51, N, 10.29.

3.2.3. 3-(4-Methoxybenzoyl)cinnoline 5c. Yellow crystals from **4c** using procedure B. Yield 0.77 g (55%); mp 189–191°C. Ms: *m/z* 264 (95%, M^+), 236 (25%), 208 (5%), 135 (100%), 129 (5%), 107 (20%), 101 (10%). IR: 3096, 2973, 1647, 1596, 799, 765 cm^{-1}. Anal. Calcd For $C_{16}H_{12}N_2O_2$: C, 72.71; H, 4.58; N, 10.60. Found: C, 72.42, H, 4.83, N, 10.42.

3.2.4. 3-(4-Nitrobenzoyl)cinnoline 5d. Buff powder from **4d** using procedure A. Yield 0.84 g (60%); mp 210–212°C. Ms: *m/z* 279 (100%, M^+), 251 (35%), 223 (8%), 150 (36%), 129 (6%), 101 (28%). IR: 3111, 3082, 1658, 1599, 797, 750 cm^{-1}. Anal. Calcd For $C_{15}H_9N_3O_3$: C, 64.51; H, 3.25; N, 15.05. Found: C, 64.16, H, 3.53, N, 14.67.

3.2.5. 3-(2-Furoyl)cinnoline 5e. Yellow crystals from **4e** using procedure A. Yield 0.77 g (55%); mp 181–183°C. Ms: *m/z* 224 (45%, M^+), 196 (70%), 168 (100%), 129 (10%), 101 (30%), 95 (95%), 67 (10%). IR: 3160, 3058, 1644, 1634, 1616, 1559, 766, 751 cm^{-1}. Anal. Calcd For $C_{13}H_8N_2O_2$: C, 69.64; H, 3.57; N, 12.50. Found: C, 69.37, H, 3.66, N, 12.31.

3.2.6. 3-(2-Thienoyl)cinnoline 5f. Pale yellow plates from **4f** using procedure B. Yield 0.84 g (60%); mp 140–142°C. Ms: *m/z* 240 (45%, M^+), 212 (50%), 184 (30%), 129 (5%), 111 (100%), 101 (20%), 83 (35%). IR: 3060, 1631, 1618, 793, 723 cm^{-1}. Anal. Calcd For $C_{13}H_8N_2OS$: C, 65.00; H, 3.33; N, 11.66; S, 13.33. Found: C, 64.75, H, 3.49, N, 11.62; S, 13.60.

3.2.7. 3-Benzoyl-6-methoxycinnoline 5g. Yellow crystals from **4g** using procedure B. Yield 0.49 g (35%); mp 195–197°C. Ms: *m/z* 264 (95%, M^+), 236 (25%), 208 (2%), 159 (2%), 131 (5%), 105 (100%), 77 (100%). IR: 3062, 1656, 1618, 1598, 764, 699 cm^{-1}. Anal. Calcd For $C_{16}H_{12}N_2O_2$: C, 72.71; H, 4.58; N, 10.60. Found: C, 72.49, H, 4.63, N, 10.40.

3.2.8. 3-Benzoyl-6-nitrocinnoline 5h. Yellow crystals from **4h** using procedure A. Yield 0.7 g (50%); mp 188–190°C. IR: 3065, 2924, 1641, 1625, 1595, 780, 720 cm^{-1}. Anal. Calcd For $C_{15}H_9N_3O_3$: C, 64.51; H, 3.25; N, 15.05. Found: C, 64.16, H, 3.53, N, 14.62.

3.2.9. 3-Benzoyl-7-chlorocinnoline 5j. Lemon yellow flakes from **4i** using procedure A. Yield 0.7 g (50%); mp 181–183°C. Ms: *m/z* 268, 270 (60%, 20%, M^+), 242 (15%), 240 (45%), 214 (7%), 212 (20%), 165 (1%). 163 (3%), 137 (5%), 135 (15%), 105 (70%), 77 (100%). IR: 3080, 3056, 1663, 1609, 1599, 779, 714 cm^{-1}. This compound was isolated from the reaction mixture containing also the 5-chloro-isomer **5i** by fractional crystallization. The ratio of the two isomers in the mixture as determined by ^1H NMR was 90:10 of **5j**, **5i**, respectively. Anal. Calcd For $C_{15}H_9ClN_2O$ (**5j**): C, 67.03; H, 3.35; N, 10.42. Found: C, 66.74, H, 3.53, N, 10.25.

Acknowledgements

The support of the University of Kuwait received through research grant no. SC091 and the facilities of ANALAB and SAF are gratefully acknowledged.

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