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Enaminones in Heterocyclic Synthesis: A Novel Route to Polyfunctionalized Substituted Thiophene, 2,3-Dihydro-1,3,4-Thiadiazole and Naphtho[1,2- b] Furan Derivatives

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ENAMINONES IN HETEROCYCLIC SYNTHESIS: A NOVEL ROUTE TO POLYFUNCTIONALIZED SUBSTITUTED THIOPHENE, 2,3-DIHYDRO-1,3, 4-THIADIAZOLE AND NAPHTHO[1,2-*b*] FURAN DERIVATIVES

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The enaminones 1a,b reacted with phenylisothiocyanate to afford the thioanilides 2a,b. The latter could be utilized to synthesize several new polysubstituted thiophenes 9a-f, and 1,3,4-thiadiazoles 12a-f.

Keywords: 1,3,4-thiadiazole; naphtho[1,2-*b*]benzofuran; thioanilides; thiophenes

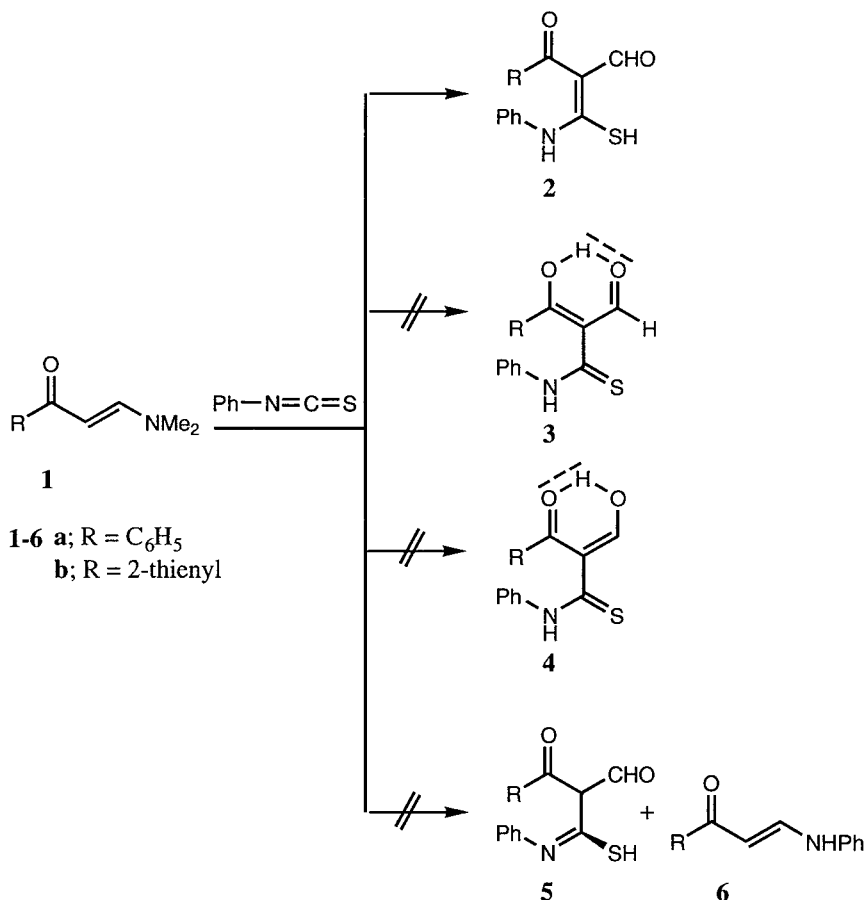
INTRODUCTION

Enaminones are readily obtainable reagents and their utility in heterocyclic synthesis has recently received a considerable interest.^{1–6} Although utility of the reactivity of the electron-deficient C-1 and C-3 in enaminones toward nucleophiles has been extensively investigated, little has been reported on reactivity of electron rich C-2 in these compounds.^{7,8} Recently, the reaction of C-2 in enaminones with some aromatic diazonium salts has been investigated in our laboratory.⁹ In continuation with this work, we report here on the reactivity of C-2 in enaminones toward some carbon electrophiles.

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DISCUSSION

It was found that the enaminones **1a,b** reacted with phenylisothiocyanate in DMF in the presence of potassium hydroxide to afford after acidification with HCl two products, the major of which were of molecular formulae corresponding to structure **2a,b** or its tautomeric forms **3a,b–5a,b** (Scheme 1). Although Regitz et al.¹⁰ have assigned hydroxymethylene structure of type **3** or **4** for diketothioamides, structure **2**



SCHEME 1

better agreed with the obtained spectral data for these compounds, thus structures **3** and **4** could be ruled out. Structure **5** was also ruled out on the basis of ¹³C NMR spectra of the isolated product which revealed the absence of any *sp*³-hybridized carbon atoms. For example, ¹³C NMR

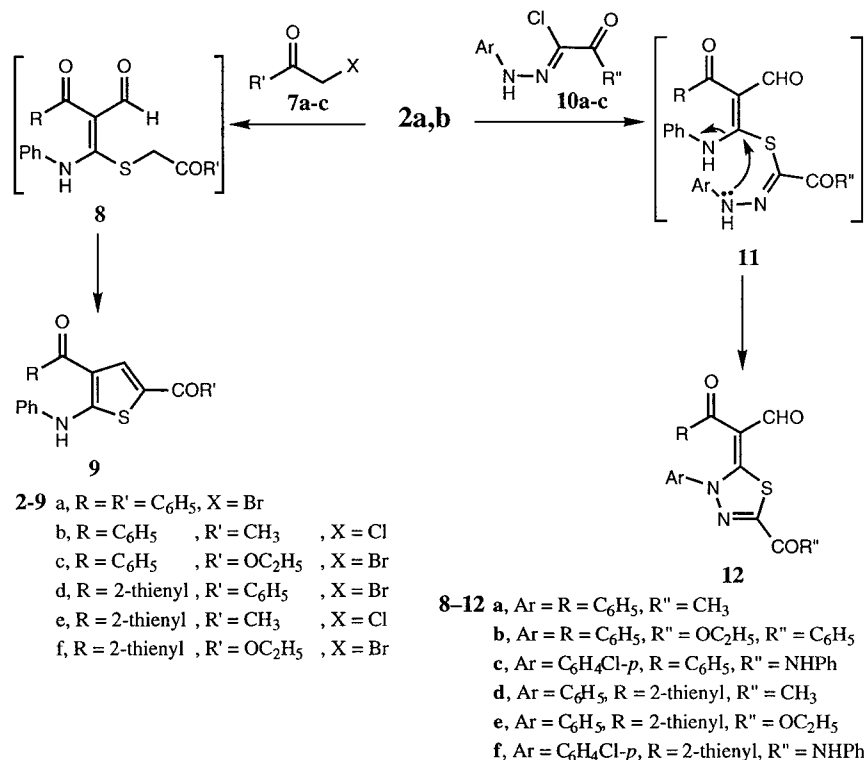
spectrum of compound **2a** revealed two low field carbonyl carbons at δ 188.91 (benzoyl C=O) and 176.5 (CHO) ppm. Moreover, ^1H NMR spectra of these products **2a,b** indicated the presence of a low field aldehydic proton in the region of δ 8.89. The existence of this proton at such value compared with that expected for aromatic aldehyde is probably due to conjugation of the double bond system in these compounds (Scheme 1).

The minor products for this reaction were assigned structure **6a,b** on the basis of the elemental analysis and spectral data of the isolated reaction products and on comparison with an authentic sample of compound **6a**.¹¹ The latter products **6a,b** were assumed to be formed via an initial conversion of a part phenyl isothiocyanate into aniline in the employed alkaline solution which, in turn, reacted with **1a,b** to afford compounds **6a,b**—though reaction of isothiocyanate with 1,3-diketones has been extensively investigated earlier.¹² To our knowledge this is the first reported reaction of an enaminone with isothiocyanate.

Compounds **2a,b** so obtained could be utilized for the synthesis of a variety of polyfunctionally substituted heteroaromatics. For example, reacting equimolar amounts of compounds **2a,b** with some α -haloketones **7a,b** and with ethyl bromoacetate (**7c**) in ethanol in the presence of a catalytic amount of triethylamine led to the formation of condensation products via hydrogen halide and water elimination. Thiophene structures **9a-f** were established for these products (Scheme 2) on the basis of the elemental analyses and spectral data of the isolated reaction products. For example, the mass spectrum of compound **9a** revealed a molecular ion peak at m/z 383 (M^+). Also, ^1H NMR spectrum of the same product indicated the involvement of the formyl group in this reaction as it revealed the thiophene H-4 as a singlet signal at δ 6.43 in addition to the aromatic protons as a multiplet at δ 6.91–7.52 and the NH signal as a singlet at δ 11.6.

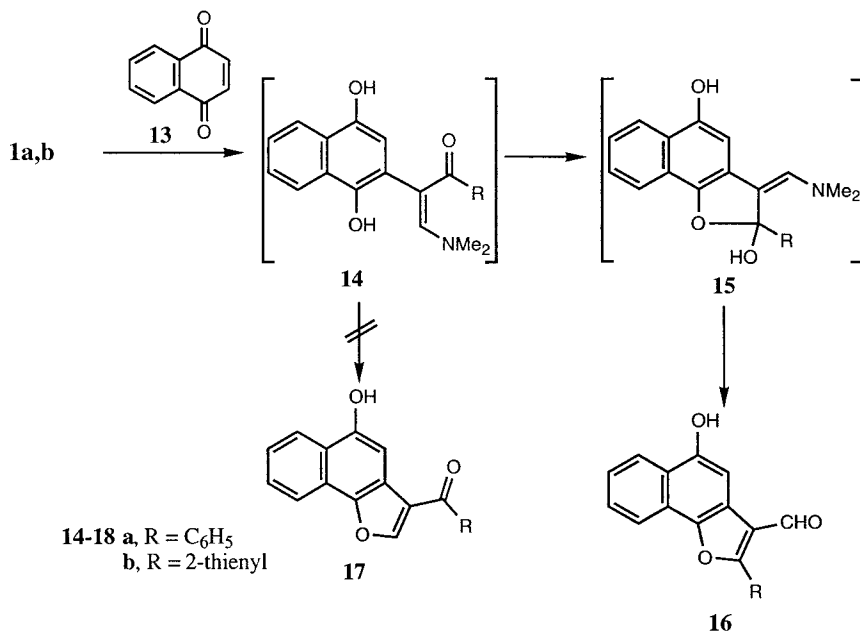
Compounds **2a,b** reacted also with some selected hydrazonyl halides **10a-c** in the presence of a catalytic amount of triethylamine to afford the 2,3-dihydro-1,3,4-thiadiazole derivatives **12a-f** (Scheme 2) on the basis of elemental analysis and spectral data of the isolated reaction products. For example, the mass spectrum of compound **12a** revealed a molecular ion peak at m/z 350 (M^+). Also, ^1H NMR spectrum of the same product revealed a singlet at 8.79 corresponding to the CHO function in addition to signals of aromatic and acetyl protons. Compounds **12a-f** are assumed to be formed via the nonisolable intermediates **11a-f** followed by an aniline molecule elimination to afford the final products **12a-f** as has been previously reported (Scheme 2).¹³

Compounds **1a,b** reacted with 1,4-naphthoquinone (**13**) in acetic acid at room temperature to afford in a quantitative yield products



SCHEME 2

of addition and dimethylamine elimination. These products were formulated the naphtho[1,2-*b*]furan carboxyaldehyde derivatives **16a,b** on the basis of elemental analysis and spectral data of the isolated reaction products. Compounds **16a,b** are suggested to be formed via an initial attack of the enaminone C-2 to the electron-deficient quinone carbon to give the nonisolable intermediate **14a,b**. The latter cyclizes to afford either the nonisolable intermediates **15a,b** which underwent hydrolysis to give the formylnaphtho[1,2-*b*]furan derivatives **16a,b** or to afford the 3-aroil-5-hydroxynaphtho[1,2-*b*]furan derivatives **17a,b** (Scheme 3). Structure **17** was ruled out on the basis of ¹H NMR spectra of the isolated reaction products which revealed the existence of aldehydic groups at δ 8.90 and the phenolic OH group at δ 10.52. The appearance of the aldehydic proton at such a higher field is probably due to ring donation by oxygen lone pair. In addition, ¹³C NMR spectrum of compound **16a** indicated the presence of the aldehydic group at δ 190.80. It was thus believed that the intermediate



SCHEME 3

adducts **14a,b** cyclized at room temperature at the aroyl carbon rather than the enaminone carbon. This preference might be attributed to thermodynamic stability of the final isolated products as a result of the presence of an external conjugation in these products. A similar sequence for such a reaction has been recently reported from our laboratory.¹⁴

In conclusion, C-2 in enaminones was reactive toward carbon electrophiles and this reactivity was useful in synthetic heterocyclic synthesis.

EXPERIMENTAL

Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a FT-IR-8201 PC spectrophotometer (Shimadzu). ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 200 MHz on a Varian Gemini spectrometer using tetramethylsilane (*TMS*) as an internal reference. Mass spectra were performed on a Shimadzu GCMS-QP1000 EX mass spectrometer at 70 eV. Elemental analyses were carried out at the Microanalytical

Data Center of Cairo University. Enaminones **1a,b**,¹⁵ phenacyl bromide (**7a**),¹⁶ and hydrazonoyl halides **10a-c**¹⁷⁻¹⁹ were prepared according to the literature.

Reaction of the Enaminones **1a,b** with Phenylisothiocyanate: Formation of **2a,b**, **6a,b**

To a stirred solution of potassium hydroxide (0.11 g, 2 mmol) in DMF (20 ml) was added either 3-*N,N*-dimethylamino-1-phenyl-2-propenone (**1a**) (0.35 g, 2 mmol) or 3-*N,N*-dimethylamino-1-(2-thienyl)-2-propenone (**2b**) (0.36 g, 2 mmol). After stirring for 2 h, phenylisothiocyanate (0.27 g, 2 mmol) was added to the resulting mixture. Stirring was continued for 6 h at room temperature, the mixture was poured onto ice-water (100 g), and acidified with dilute HCl. The solid product formed in each case was collected by filtration, washed with water and dried. Recrystallization from ethanol afforded the thioanilides **2a,b**.

2a: Yield (58%); mp 92–93°C; greyish crystals; $\nu_{\max}/\text{cm}^{-1}$ 3450 (NH), 2950 (CH), 2590 (SH), 1623, 1613 (2C=O); δ_{H} (CDCl₃) 2.62 (s, 1H, SH), 7.03–7.33 (m, 10H, 2 phenyl protons), 8.04 (s, 1H, NH), 8.80 (s, 1H, CHO); δ_{C} (CDCl₃) 188.9 (benzoyl CO), 176.5 (CHO), 142.3, 124.5 (olefinic carbons), 138.6, 136.3, 131.4, 128.7, 128.1, 122.9, 119.6 (two phenyl carbons); MS m/z (%) 283 (36) (M⁺), 105 (82), 77 (100); (Found: C, 67.7; H, 4.5; N, 5.0; S, 11.2. C₁₆H₁₃NO₂S requires C, 67.82; H, 4.62; N, 4.94; S, 11.31%).

2b: Yield (57%); mp 105–106°C; pale yellow crystals; $\nu_{\max}/\text{cm}^{-1}$ 3450 (NH), 2950 (CH), 2590 (SH), 1624, 1620 (2C=O); δ_{H} (CDCl₃) 2.60 (s, 1H, SH), 6.52–7.30 (m, 8H, Ph and 2-thienyl protons), 8.04 (s, 1H, NH), 8.82 (s, 1H, CHO); MS m/z (%) 289 (81) (M⁺), 255 (17), 77 (100); (Found: C, 58.0; H, 4.0; N, 4.6; S, 22.3. C₁₄H₁₁NO₂S₂ requires C, 58.11; H, 3.83; N, 4.84; S, 22.16%).

Upon leaving the filtrate to stand for 1 h at room temperature, another solid product was formed in each case, this was collected by filtration, washed with water, and dried. Recrystallization from ethanol afforded yellow products that were identified as the 3-phenylimino-1-phenyl-2-propenone (**6a**) and 3-phenylimino-1-(2-thienyl)-2-propenone (**6b**), respectively.

6a: Yield (25%); mp 140–142°C; lit.¹¹ mp 140–141°C, MS m/z (%) 223 (87) (M⁺), 222 (100) (M⁺-1), 146 (39), 77 (58).

6b: Yield (21%); mp 127–129°C; pale yellow crystals; $\nu_{\max}/\text{cm}^{-1}$ 3430 (NH), 1646 (C=O), 1580 (C=C); δ_{H} (CDCl₃) 6.47 (d, 1H, $J = 12.2$ olefinic-H), 6.62 (d, 1H, $J = 12.2$, olefinic-H), 7.66–7.08 (m, 8H, Ph and 2-thienyl proton), 11.76 (s, 1H, NH); MS m/z (%) 229 (81) (M⁺), 192 (18), 77 (58);

(Found: C, 68.4; H, 4.9; N, 6.0; S, 14.0. $C_{13}H_{11}NOS$ requires C, 68.10; H, 4.84; N, 6.11; S, 13.98%).

Reaction of the Aroylthioanilides **2a,b** with α -Haloketones or α -Haloesters. Formation of **9a–f**

General Procedure

To a solution of either the thioanilide **2a** (0.283 g, 1 mmol) or **2b** (0.289 g, 1 mmol) in absolute ethanol, the appropriate α -haloketones (1 mmol) viz; phenacyl bromide (**7a**), α -chloroacetone (**7b**) or ethyl bromoacetate (**7c**), and 1–2 drops of triethylamine as a catalyst were added. The reaction mixture was heated under reflux, formation of a yellowish solid, in each case, started to appear after 30–40 min. Heating was continued for 2 h; the solvent was removed under reduced pressure and the solid products were collected by filtration, washed with ethanol, and dried. Recrystallization from EtOH/DMF afforded the thiophene derivatives **9a–f**.

9a: Yield 98%, mp 265–267°C; yellow needles; $\nu_{\max}/\text{cm}^{-1}$ 3418 (NH), 3050 (CH), 1640, 1635 (C=O); δ_{H} (DMSO) 6.43 (s, 1H, thiophene H-4), 7.75–6.90 (m, 15H, aromatic protons), 11.60 (s, 1H, NH), MS m/z (%) 383 (100) (M^+), 105 (83), 77 (97); (Found: C, 75.3; H, 4.4; N, 3.7; S, 8.5. $C_{24}H_{17}NO_2S$ requires C, 75.17; H, 4.47; N, 3.65; S, 8.36%).

9b: Yield 81%, mp 205–206°C; $\nu_{\max}/\text{cm}^{-1}$ 3418 (NH), 3055 (CH aromatic), 2855 (CH-aliphatic), 1650 (C=O); δ_{H} (DMSO) 2.67 (s, 3H, CH₃), 6.45 (s, 1H, thiophene H-3), 7.50–6.88 (m, 10H, two Ph), 11.62 (s, 1H, NH); m/z (%) 321 (71) (M^+), 105 (100), 77 (63); (Found: C, 71.00; H, 4.50; N, 4.50; S, 10.00. $C_{19}H_{15}NO_2S$ requires C, 71.01; H, 4.70; N, 4.36; S, 9.98%).

9c: Yield 64%; mp 163–165°C; $\nu_{\max}/\text{cm}^{-1}$ 3417 (NH), 3047 (CH aromatic), 2947 (CH-aliphatic), 1720 (C=O ester); 1636 (C=O benzoyl); δ_{H} ($CDCl_3$) 1.13 (t, 3H, CH₃), 4.12 (q, 2H, CH₂), 6.46 (s, 1H, thiophene H-4), 7.60–6.90 (m, 10H, two Ph), 11.56 (s, 1H, NH); MS m/z (%) 351 (33) (M^+), 105 (100), 77 (66); (Found: C, 68.5; H, 4.6; N, 4.0; S, 9.0. $C_{20}H_{17}NO_3S$ requires C, 68.36; H, 4.87; N, 3.99; S, 9.12%).

9d: Yield 88%, mp 197–199°C; $\nu_{\max}/\text{cm}^{-1}$ 3420 (NH), 3050 (CH-aromatic), 2860 (CH-aliphatic), 1650 (2C=O); δ_{H} (DMSO) 6.40–6.66 (m, 4H, thiophene-H), 6.90–7.50 (m, 10H, two Ph), 11.41 (s, 1H, NH); MS m/z (%) 389 (6) (M^+), 328 (100), 180 (63), 77 (82); (Found: C, 67.7; H, 4.0; N, 3.6; S, 16.50. $C_{22}H_{15}NO_2S_2$ requires C, 67.84; H, 3.88; 3.60; S, 16.46%).

9e: Yield 76%, mp 142–144°C; $\nu_{\max}/\text{cm}^{-1}$ 3418 (NH), 3055 (CH aromatic), 2855 (CH-aliphatic), 1668 (C=O acetyl), 1620 (2-thienoyl C=O); δ_{H} ($CDCl_3$) 2.66 (s, 3H, CH₃), 7.78–6.60 (m, 9H, Ph and thienyl H), 11.48

(s, 1H, NH); MS m/z (%) 327 (100) (M^+), 105 (6), 77 (76); (Found: C, 62.4; H, 4.0; N, 4.5; S, 19.4. $C_{17}H_{13}NO_2S_2$ requires C, 62.37; H, 4.00; N, 4.28; S, 19.58%).

9f: Yield 81%, mp 165–166°C; $\nu_{\max}/\text{cm}^{-1}$ 3415 (NH), 3055 (CH aromatic), 2860 (CH-aliphatic), 1720 (C=O ester), 1620 (C=O); δ_H ($CDCl_3$) 1.14 (t, 3H, CH_3), 4.22 (q, 2H, CH_2), 7.55–6.80 (m, 9H, aromatic protons), 11.56 (s, 1H, NH), MS m/z (%) 357 (100) (M^+); (Found: C, 60.0; H, 4.1; N, 4.0; S, 18.0. $C_{18}H_{15}NO_3S_2$ requires C, 60.48; H, 4.23; N, 3.92; S, 17.94%).

Reaction of the Thioanilides 2a,b with Hydrazonyl Halides 10a–c. Formation of Compounds 12a–f

General Procedure

To a solution of either the thioanilide **2a** (0.283 g, 1 mmol) or **2b** (0.289 g, 1 mmol) in absolute ethanol (20 ml), the appropriate hydrazonyl halide **10a–c** (1 mmol) followed by triethylamine (0.3 ml) was added. The mixture was heated under reflux. Formation of colored precipitates started to take place within 5–20 min. Heating was continued for 2 h, then the reaction mixture was left to cool to room temperature. The solid products were collected by filtration, washed with ethanol, and dried. Recrystallization from EtOH/DMF afforded the corresponding 2,3-dihydro-1,3,4-thiadiazole derivatives **12a–f**.

12a: Yield 90%, mp 222–224°C; $\nu_{\max}/\text{cm}^{-1}$ 3395 (NH), 3163 (CH-aromatic), 1650 (C=O), 1597 (C=N); δ_H (DMSO) 2.42 (s, 3H, CH_3), 7.02–7.55 (m, 10H, two Ph), 8.79 (s, 1H, CHO); MS m/z (%) 350 (81) (M^+), 105 (91), 77 (100); (Found: C, 65.2; H, 4.0; N, 8.0; S, 9.3. $C_{19}H_{14}N_2O_3S$ requires C, 65.13; H, 4.03; N, 8.00; 9.15%).

12b: Yield 88%, mp 130–132°C; $\nu_{\max}/\text{cm}^{-1}$ 3040 (CH-aromatic), 2985 (CH-aliphatic), 1728 (C=O ester), 1636 (C=O), 1598 (C=N); δ_H ($CDCl_3$) 1.13 (t, 3H, CH_3), 4.12 (q, 2H, CH_2), 7.02–7.55 (m, 10H, two Ph), 8.80 (s, 1H, CHO); MS m/z (%) 380 (80) (M^+), 105 (73), 77 (100); (Found: C, 63.0; H, 4.2; N, 7.5; S, 8.5. $C_{20}H_{16}N_2O_4S$ requires C, 63.15; H, 4.24; N, 7.36; S, 8.43%).

12c: Yield 82%, mp 212–214°C; $\nu_{\max}/\text{cm}^{-1}$ 3395 (NH), 3163 (CH-aromatic), 2986 (CH-aliphatic), 1659 (C=O, CHO), 1601 (C=N); δ_H (DMSO) 6.60–7.03 (m, 14H, aromatic), 8.83 (s, 1H, CHO), 11.94 (s, 1H, NH); MS m/z (%) 461 (73) (M^+), 105 (91), 77 (100); (Found: C, 62.5; H, 3.5; Cl, 7.9; N, 9.0; S, 7.0. $C_{24}H_{16}ClN_3O_3S$ requires C, 62.41; H, 3.49; Cl, 7.68; N, 9.10; S, 6.94%).

12d: Yield 80%, mp 166–168°C; $\nu_{\max}/\text{cm}^{-1}$ 3040 (CH-aromatic), 2986 (CH-aliphatic), 1662, 1638 (C=O CHO), 1597 (C=N); δ_H (DMSO) 2.42 (s, 3H, CH_3), 6.50–7.45 (m, 8H, Ph, thienyl protons), 8.69 (s, 1H, CHO);

MS m/z (%) 356 (1.6) (M^+), 355 (6) (M^+-1), 354 (4) (M^+-21), 248 (83), 247 (93), 92 (100); (Found: C, 57.4; H, 3.4; N, 7.6; S, 18.0. $C_{17}H_{12}N_2O_3S_2$ requires C, 57.29; H, 3.39; N, 7.86; S, 17.99%).

12e: Yield 79%, mp 150–152°C; $\nu_{\max}/\text{cm}^{-1}$ 3124 (CH-aromatic), 3040 (CH-aliphatic), 1728 (C=O ester), 1674 (CHO, C=O), 1598 (C=N); δ_H (CDCl_3) 1.12 (t, 3H, CH_3), 4.24 (q, 2H, CH_2), 6.47–7.33 (m, 8H, aromatic protons), 8.90 (s, 1H, CHO); MS m/z (%) 386 (14) (M^+), 385 (56) (M^+-1), 354 (43) (M^+-2), 308 (71), 247 (6), 194 (39), 92 (66), 77 (100); (Found: C, 56.0; H, 3.7; N, 7.5; S, 16.8. $C_{18}H_{14}N_2O_4S_2$ requires C, 55.95; H, 3.65; N, 7.25; S, 16.59%).

12f: Yield 88%, mp 225–226°C; $\nu_{\max}/\text{cm}^{-1}$ 3050 (CH-aromatic), 2986 (CH-aliphatic), 1662 (C=O, CHO), 1598 (C=N); δ_H (DMSO) 6.25 (d, 1H, thiophene 3-H); 7.76–6.81 (m, 11H, aromatic protons), 11.46 (s, 1H, NH); MS m/z (%) 467 (82) (M^+), 92 (70), 77 (100); (Found: C, 56.5; H, 3.0; N, 9.0; S, 13.5; Cl, 7.5. $C_{22}H_{14}ClN_3O_3S_2$ requires C, 56.47; H, 3.02; N, 8.89; S, 13.70; Cl, 7.58%).

Reaction of the Enaminones **1a,b** with 1,4-Naphthoquinone (**13**). Formation of 2-aryl-5-hydroxynaphtho[1,2-*b*]furan-3-carboxaldehydes **16a,b**

General Procedure

To a solution of either the enaminones **1a** (1.75 g, 10 mmol) or **1b** (1.81 g, 10 mmol) in 96% acetic acid (20 ml), 1,4-naphthoquinone (**13**) (1.58 g, 10 mmol) was added. The mixture was stirred at room temperature for 24 h, then diluted with water. The solid product formed, in each case, was collected by filtration, washed with ethanol, and dried. Recrystallization from DMF afforded 2-phenyl-5-hydroxynaphtho[1,2-*b*]furan-3-carboxaldehyde (**16a**) and 5-hydroxy-2-(2-thienyl)naphtho[1,2-*b*]furan-3-carboxaldehyde (**16b**), respectively.

16a: Yield 95%, mp 275°C (dec.); $\nu_{\max}/\text{cm}^{-1}$ 3250 (OH), 1622 (CHO); δ (DMSO) 7.50–8.10 (m, 10H, aromatic H), 8.90 (s, 1H, CHO), 10.52 (s, 1H, OH); δ_c (DMSO) 121.6 (C-3), 121.8, 122.1, 124.0, 124.4, 129.3, 129.6, 130.0, 139.5 (phenyl, naphthyl carbons), 145.4 (C-5), 151.7 (C-2), 190.80 (CHO); MS m/z (%) 288 (20) (M^+), 212 (24), 211 (30), 105 (47), 77 (67); (Found: C, 79.0; H, 4.0. $C_{19}H_{12}O_3$ requires C, 79.16; H, 4.20%).

16b: yield 95%, mp 251–252°C; $\nu_{\max}/\text{cm}^{-1}$ 3250 (OH), 1632 (CHO); δ_H (insoluble in common NMR solvents); MS m/z (%) 294 (78) (M^+), 77 (100); (Found: C, 69.5; H, 3.3; S, 10.0. $C_{17}H_{10}O_3S$ requires C, 69.35; H, 3.42; S, 10.90%).

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