Studies with Enaminones: Reactivity of 1,5-Disubstituted-1,4-pentadien-3-ones Toward Electrophilic Reagents. A Novel Route to Azolylazines, Benzofuranals, Pyranones

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Several new enaminodienones prepared from substituted acetone and dimethylformamide dimethylacetal were used as precursors for synthesis of pyridines, pyranones and benzofurans.

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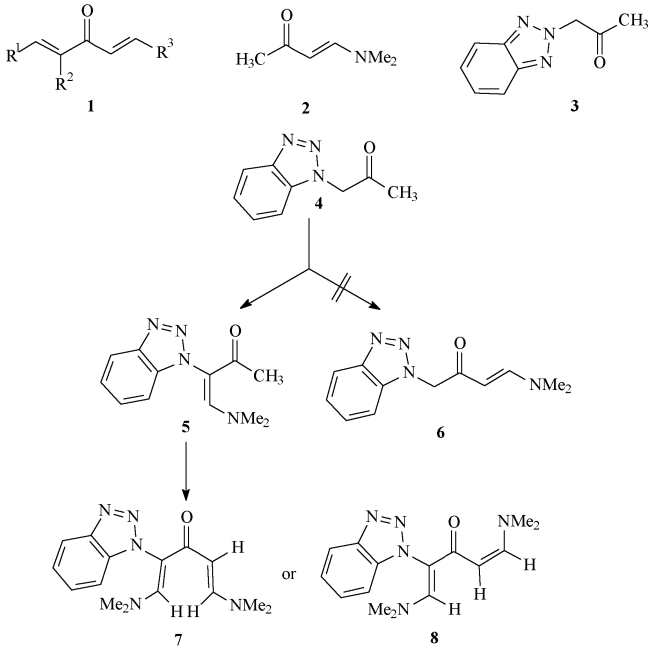
Enaminones are versatile reagents and their chemistry has recently received considerable interest [1-3]. In recent work from our laboratories we have successfully utilized enaminones as building blocks for the synthesis of a wide range of heterocycles [4-8]. In conjunction with this work we have investigated possible utility of dienones **1** for synthesis of different otherwise not readily assessable heteroaromatic compounds of potential interest, as agrochemical, pharmaceutical or dye intermediates. In the present article, we report the synthesis of several new dienones and their utility as precursor of polyfunctional heteroaromatics. It has been recently reported [9] that acetone condenses with dimethylformamide dimethylacetal to yield enaminone **2**. The Attempted condensation of **2** with another molecule of dimethylformamide dimethylacetal resulted in polymerization under reaction conditions. It is most likely that the methyl function under the reaction conditions has added to the enaminones moiety in a successive reaction. To avoid such process we decided to work with substituted acetones. Consequently, benzotriazol-1-yl-acetone was prepared *via* reacting chloroacetone with benzotriazole in basic conditions. Although this reaction has afforded, in the past, mixtures of **3** and **4** [10] modification of a procedure recently published by Katritzky *et al.*, [10-11] enabled exclusive preparation of **4**. Compound **4**, so obtained, condensed readily with dimethylformamide dimethylacetal in refluxing xylene for 10 hours. Although condensation with dimethylformamide dimethylacetal may in theory lead to a mixture of **5** and **6**, only **5** is formed in exclusively as ^{1}H NMR revealed a presence of a singlet corresponding to methyl at δ 2.53 ppm and the absence of olefinic doublet of doublet which would be observed in the ^{1}H NMR spectra of **6**. Condensing **5** further with one mole of dimethylformamide dimethylacetal in refluxing xylene afforded the dienaminone **7**. The ^{1}H NMR of this product revealed benzotriazolyl protons in addition to a singlet at δ 7.84 ppm and two doublets at δ 4.10 and 8.12 ppm for H-4 and H-5. Although the reaction of **5** with dimethylformamide dimethylacetal may also yield **8** the ^{1}H NMR indicated that only the *trans* form **7** was formed as is confirmed by coupling *J* values for olefinic doublets (Scheme 1).

Scheme 1



Condensation of 1-substituted-1-butene-3-one **9a-c** with dimethylformamide dimethylacetal, afforded the dienones **10a-c** in good yield. No trace of *Z*-form is observed, only the *E* forms **10a-c** were isolated in this reaction as indicated from the coupling values for olefinic doublets. For example **10c** showed two pairs of doublets at δ 5.26 and 7.67 ppm *J* = 12Hz and at 6.70 and 7.20 ppm *J* = 16Hz (Scheme 2).

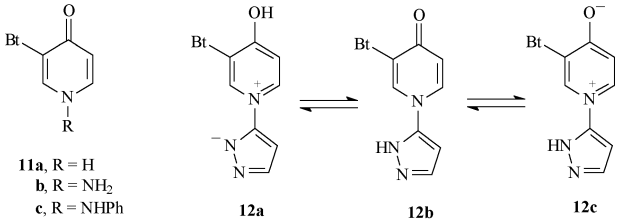
Scheme 2

9-10a, Ar = Ph
b, Ar = 4-$OCH_3C_6H_4$
c, Ar = 2-Furyl

Compounds **7** and **10** were then utilized as starting materials for synthesis of a variety of oxygen and nitrogen

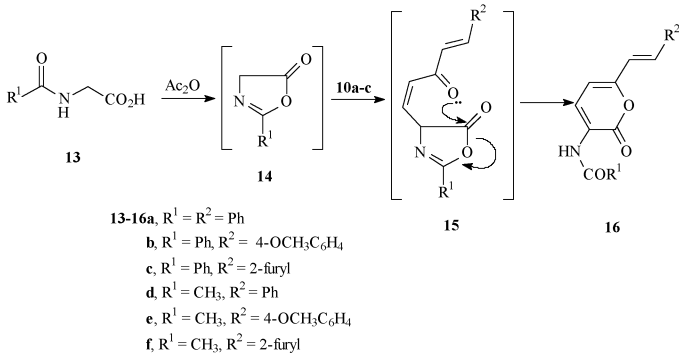
heteroaromatic. Thus reacting **7** with ammonium acetate/acetic acid resulted in the formation of benzotriazolylpyridone **11a** while reaction with hydrazines afforded the benzotriazolylpyridone **11b,c**. Reaction with aminopyrazole afforded the pyrazolyl benzotriazolylpyridone **12** that has been shown *via* ^{1}H NMR to exist as equilibrium mixture of forms **12a** and **12b** in addition to zwitterionic form **12c** as ring protons for both pyridone and pyrazole appear as multiplets (Scheme 3). Further attempts to utilize **7** as building blocks for the synthesis of heterocycles *via* reaction with active methylene reagents, resulted in the formation of a complex mixture of products. This can be readily rationalzied in terms of the existence of multiple electrophilic sites of nearly equal reactivity, consequently we shifted our investigation to **10**, in which pronounced difference in reactivity of electrophilic sites is anticipated. Compounds **10** proved to be a much better building blocks.

Scheme 3



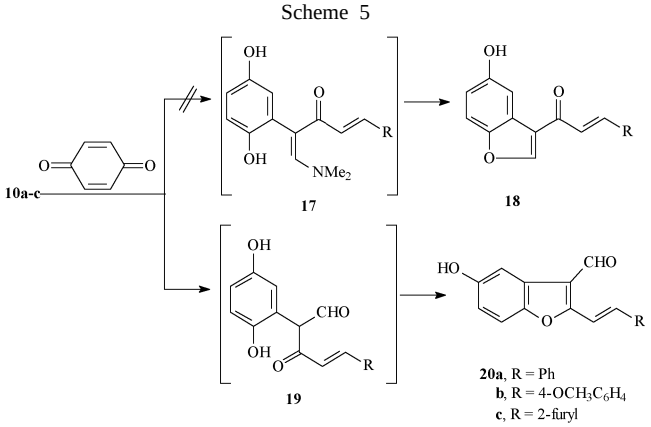
Compounds **10a-c** reacted with hippuric acid **13** in acetic anhydride to yield a product assumed to be the pyranone **16a-c** rather than the isomeric **15a-c**, based on ^{1}H NMR that revealed the existence of NH signal at approximately 9.60 ppm and absence of proton signal linked to sp^3 carbon. It is thus assumed that hipuric acid is initially cyclized into the oxazolone **14** which then adds to the enaminone moiety at C-1 yielding **15a-c** that further rearrange *via* loss of water yielding the final isolable pyranone **16a-c**. This is a new extension to the Kepe acylaminopyranone synthesis [9]. Similar reaction of **10a-c** with glycine in acetic anhydride resulted in the formation of the acetylaminopyranone **16d-f** (Scheme 4).

Scheme 4



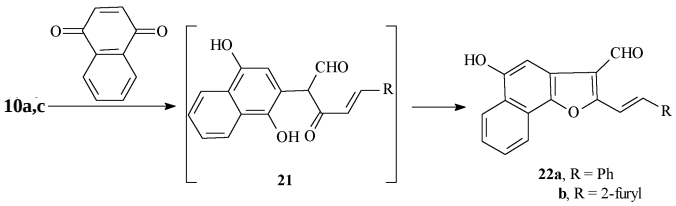
Compounds **10a-c** reacted with *p*-benzoquinone to yield a product of addition *via* dimethylamine and water elimination, this product can thus be formulated as **18** or isomeric **20**. The ^{1}H NMR, in all cases, indicated the presence of a formyl-H at δ 9.0, 9.21 and 9.17 ppm. Thus structure **20a-c** was considered most likely. It is thus believed that *p*-benzoquinone initially adds to electron rich C-2 yielding acyclic **19** which then cyclizes exclusively into **20**. Although cyclization into **18** seems to be kinetically more favored, product **20** is apparently thermodynamically more stable because of its extended conjugated double bond system (Scheme 5).

Scheme 5



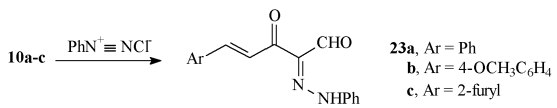
Compounds **10a,c** also reacted with naphthoquinone to yield the furonaphthofuran derivatives **22a,b** (Scheme 6).

Scheme 6



Compounds **10a-c** reacted with aromatic diazonium salts to yield the hydrazonopentenals **23a-c**. The ^{1}H NMR indicated the presence of a mixture of both *E* and *Z* forms of these pentenals in approximately equivalent ratios as ^{1}H NMR revealed two signals at δ 9.57 ppm and 10.14.ppm for a total of one proton. The low field signal is attributed to the *E* formyl-H, which is shifted by deshielding as a result of H-bonding with the carbonyl oxygen. Trials to cyclize **23a-c** into tetrahydropyridazinones failed (Scheme 7).

Scheme 7



EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded in KBr disks using a Shimadzu IR-470 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Ac-80 spectrometer with DMSO-d_6 as solvent (unless stated otherwise) and TMS as internal standard; chemical shifts are reported in δ units (ppm). Mass spectra were measured on GC/MS INCOS XL Finnigan MAT. Microanalyses were performed on LECO CHNS-932. Analytical measurements were performed in Cairo University and Kuwait University.

2-(1,2,3-Benzotriazol-1-yl)-1,5-dimethylamino-1,4-pentadiene-3-one (**7**).

A suspension of 1,2,3-benzotriazol-1-yl-acetone **4** 1.75 g (10 mmol) in xylene (30 ml) was treated with dimethylformamide dimethylacetal 2.38 g (20 mmol). The reaction mixture was refluxed for 48 hours and was allowed to cool. The solid product, so formed, was collected by filtration and crystallized from chloroform to yield: 1.54 g of **7** (60%); mp 141 °C; IR (KBr): ν 1599 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 2.48 (s, 6H, NMe_2), 2.63 (s, 6H, NMe_2), 4.10 (d, 1H, *J* 12Hz, 4-H), 7.30-7.47 (m, 4H, arom. H), 7.84 (s, 1H, 1-H), 8.12 (d, 1H, *J* 12Hz, 5-H); MS (EI, 70 EV): *m/z* 285 [M^+].

Anal. Calcd. for $C_{15}H_{19}N_5O$: C, 63.14; H, 6.71; N, 24.55. Found: C, 63.18; H, 6.53; N, 24.32.

General Procedure for the Preparation of Compounds **10a-c**.

A suspension of each of **9a-c** (10 mmol) in xylene (30 ml) was treated with dimethylformamide dimethylacetal 1.19 g (10 mmol). The reaction mixture was refluxed for 3 hours and was allowed to cool. The solid product, so formed, was collected by filtration and crystallized from ethanol.

1-Dimethylamino-5-phenyl-1,4-pentadiene-3-one (**10a**).

Compound **10a** was obtained in 87% yield (1.27 g) mp 107 °C; IR (KBr): ν 1640 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 2.72 (s, 3H, NMe), 2.83 (s, 3H, NMe), 5.38 (d, 1H, *J* 12Hz, 2-H), 7.03 (d, 1H, *J* 16Hz, 4-H), 7.32-7.43 (m, 4H; 3H arom. H, 5-H), 7.58-7.76 (m, 2H, arom. H), 7.85 (d, 1H, *J* 12Hz, 1-H); MS (EI, 70 EV): *m/z* 201 [M^+].

Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.47; H, 7.39; N, 6.74.

1-Dimethylamino-5-(4-methoxyphenyl)-1,4-pentadiene-3-one (**10b**).

Compound **10b** was obtained in 52% yield (1.20 g) mp 107 °C; IR (KBr): ν 1655 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 2.82 (s, 3H, NMe), 3.11 (s, 3H, NMe), 3.78 (s, 3H, OMe), 5.24 (d, 1H, *J* 12Hz, 2-H), 6.85 (d, 1H, *J* 16Hz, 4-H), 6.95 (d, 2H, *J* 8Hz, arom. H), 7.34 (d, 1H, *J* 16Hz, 5-H), 7.60 (d, 2H, *J* 8Hz, arom. H), 7.68 (d, 1H, *J* 12Hz, 1-H); MS (EI, 70 EV): *m/z* 231 [M^+].

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.61; H, 7.39; N, 6.07.

1-Dimethylamino-5-(2-furyl)-1,4-pentadiene-3-one (**10c**).

Compound **10c** was obtained in 80% yield (1.50 g) mp 127 °C; IR (KBr): ν 1630 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 2.83 (s, 3H, NMe), 3.11 (s, 3H, NMe), 5.26 (d, 1H, *J* 12Hz, 2-H), 6.58-6.59 (m, 1H, furyl H), 6.70 (d, 1H, *J* 16Hz, 4-H), 6.77 (d, 1H, *J* 8Hz, furyl H), 7.20 (d, 1H, *J* 16Hz, 5-H), 7.67 (d, 1H, *J* 12Hz, 1-H), 7.76 (d, 1H, *J* 8Hz, furyl H); MS (EI, 70 EV): *m/z* 191 [M^+].

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.83; H, 6.74; N, 7.45.

3-(1,2,3-Benzotriazol-1yl)-1,4-dihydropyridin-4-one (**11a**).

A mixture of **7** (2.85 g, 10 mmol), ammonium acetate (3.0g) and acetic acid (0.6 ml) was heated with stirring at 200 °C for half an hour, then left to cool and triturated with ethanol. The solid product, so formed, was collected by filtration and crystallized from ethanol to yield 1.27 g of **11a** (60%); mp 267 °C; IR (KBr): ν 3130 (NH), 1646 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 6.48-6.50 (m, 1H, arom. H), 7.43-7.54 (m, 3H, arom. H), 7.91 (d, 1H, *J* 8Hz, 5-H), 8.12 (d, 1H, *J* 8Hz, 6-H), 8.37 (s, 1H, 2-H), 12.30 (s, 1H, NH); MS (EI, 70 EV): *m/z* 212 [M^+].

Anal. Calcd. for $C_{11}H_8N_4O$: C, 62.25; H, 3.80; N, 26.40. Found: C, 61.89; H, 3.94; N, 26.37.

1-Amino-3-(1,2,3-Benzotriazol-1yl)-1,4-dihydropyridin-4-one (**11b**).

To a suspension of **7** (2.85 g, 10 mmol) in ethanol (30 ml), hydrazine hydrate (1.50 ml) was added. The reaction mixture was refluxed for 30 minutes then allowed to cool to room temperature. The solid product, so formed, was collected by filtration and crystallized from ethanol to yield **11b** 1.58 g (70%); mp 221 °C; IR (KBr): ν 3312, 3122 (NH_2), 1651 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 6.36-6.55 (m, 3H, arom. H, NH_2), 7.40-7.48 (m, 3H, arom. H), 7.80 (d, 1H, *J* 8Hz, 5-H), 8.02 (d, 1H, *J* 8Hz, 6-H), 8.26 (s, 1H, 2-H); MS (EI, 70 EV): *m/z* 227 [M^+].

Anal. Calcd. for $C_{11}H_9N_5O$: C, 58.14; H, 3.99; N, 30.82. Found: C, 58.14; H, 4.16; N, 30.83.

3-(1,2,3-Benzotriazol-1yl)-1-phenylamino-1,4-dihydropyridin-4-one (**11c**)**.**

To a suspension of **7** (2.85 g, 10 mmol) in ethanol (30 ml), phenylhydrazine hydrochloride (1.44 g, 10 mmol) was added. The reaction mixture was refluxed for 1 hour then allowed to cool at room temperature. The solid product, so formed, was collected by filtration and crystallized from ethanol to yield 2.54 g **11c** (84%); mp 198 °C; IR (KBr): = 3282 (NH), 1648 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 6.64-7.13 (m, 6H, arom. H), 7.43-7.56 (m, 3H, arom. H), 8.08-8.10 (m, 2H, arom. H), 8.26 (s, 1H, 2-H), 9.80 (s, 1H, NH); MS (EI, 70 EV): *m/z* 302 [M^+-1].

Anal. Calcd. for $C_{17}H_{13}N_5O$: C, 67.31; H, 4.32; N, 23.09. Found: C, 67.11; H, 4.13; N, 22.84.

3-(1,2,3-Benzotriazol-1yl)-1-(pyrazol-3yl)-1,4-dihydropyridin-4-one (**12**).

To a suspension of **7** (2.85 g, 10 mmol) in ethanol (30 ml), 3-aminopyrazole (0.83 g, 10 mmol) was added. The reaction mixture was refluxed for 1 hour then allowed to cool at room temperature. The solid product, so formed, was collected by filtration and crystallized from pyridine to yield 1.66 g **12** (60%); mp 309 °C; IR (KBr): ν 3126 (NH), 1652 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 6.63-6.67 (m, 2H, arom. H), 7.44-7.60 (m, 3H, arom. H), 7.89-7.92 (m, 1H, arom. H), 8.10-8.18 (m, 1H, arom. H), 8.43-8.56 (m, 1H, arom. H), 8.88-8.91 (m, 1H, arom. H), 13.40 (s, 1H, NH); MS (EI, 70 EV): *m/z* 278 [M^+].

Anal. Calcd. for $C_{14}H_{10}N_6O$: C, 60.42; H, 3.62; N, 30.20. Found: C, 60.53; H, 3.83; N, 29.92.

General Procedure for the Preparation of Compounds **16a-c**.

A solution of each of **10a-c** (10 mmol) and hippuric acid (1.79g, 10 mmol) in acetic anhydride was heated under reflux for 1 hour. The reaction mixture was concentrated *in vacuo*. The solid product obtained upon cooling was isolated by filtration and recrystallized from an ethanol/dioxane mixture.

N-{2-Oxo-6-[(*E*)-2-phenylethenyl]-2*H*-pyran-3-yl}benzamide (**16a**).

Compound **16a** was obtained in 62% yield (1.96 g); mp 212 °C; IR (KBr): ν 3343 (NH), 1706 (ring CO), 1670 cm^{-1} (amide CO); ^{1}H NMR (400 MHz, DMSO): δ 6.61 (d, 1H, *J* 8Hz, arom H), 7.01 (d, 1H, *J* 16Hz, vinyl-H), 7.25 (d, 1H, *J* 16Hz, vinyl-H), 7.34-7.41(m, 3H, arom. H), 7.54-7.56 (m, 2H, arom. H), 7.61-7.68 (m, 3H, arom. H), 7.94-7.96 (m, 2H, arom. H), 8.16 (d, 1H, *J* 8Hz, arom. H), 9.64 (s, 1H, NH); MS (EI, 70 EV): *m/z* (%) = 317 [M^+].

Anal. Calcd. for $C_{20}H_{15}NO_3$: C, 75.69; H, 4.76; N, 4.41. Found: C, 75.59; H, 4.81; N, 4.49.

N-{6-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-2-oxo-2*H*-pyran-3-yl}benzamide (**16b**).

Compound **16b** was obtained in 51% yield (1.76 g); mp 216 °C; IR (KBr): ν 3378 (NH), 1702 (ring CO), 1670 cm^{-1} (amide CO); ^{1}H NMR (400 MHz, DMSO): δ 3.79 (s, 3H, OCH_3), 6.52-6.53 (m, 1H, arom. H), 6.89-6.98 (m, 3H, arom. H, vinyl H), 7.21 (d, 1H, *J* 16Hz, vinyl-H), 7.52-7.62 (m, 5H, arom. H), 7.94 (d, 2H, *J* 8Hz, arom. H), 8.12 (d, 1H, *J* 8Hz, arom. H), 9.57 (s, 1H, NH); MS (EI, 70 EV): *m/z* 347 [M^+].

Anal. Calcd. for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03. Found: C, 72.32; H, 4.94; N, 4.11.

N-{6-[(*E*)-2-(2-Furyl)ethenyl]-2-oxo-2*H*-pyran-3-yl}benzamide (**16c**).

Compound **16c** was obtained in 73% yield (2.25 g); mp 214 °C; IR (KBr): ν 3370 (NH), 1705 (ring CO), 1676 cm^{-1} (amide CO). ^{1}H NMR (400 MHz, DMSO): δ 6.61-6.63 (m, 2H, arom. H), 6.71-6.79 (m, 2H, furyl 4-H, vinyl H), 7.09(d, 1H, *J* 16Hz, vinyl H), 7.52-7.64 (m, 3H, furyl 3-H, arom. H), 7.79-7.80 (m, 1H, furyl 5-H), 7.93-7.95 (m, 2H, arom. H), 8.11-8.13 (m, 1H, arom. H), 9.60 (s, 1H, NH); MS (EI, 70 EV): *m/z* 307 [M^+].

Anal. Calcd. for $C_{18}H_{13}NO_4$: C, 70.35; H, 4.26; N, 4.56. Found: C, 70.53; H, 4.36; N, 4.70.

General Procedure for the Preparation of Compounds **16d-f**.

A solution of each of **10a-c** (10 mmol) and glycine (0.78 g, 10 mmol) in acetic anhydride was heated under reflux for 1 hour. The reaction mixture was concentrated *in vacuo*. The solid product obtained upon cooling was isolated by filtration and recrystallized from ethanol.

N-{2-Oxo-6-[(*E*)-2-phenylethenyl]-2*H*-pyran-3-yl}acetamide (**16d**).

Compound **16d** was obtained in 90% yield (2.30 g); mp 203 °C; IR (KBr): ν 3306 (NH), 1719 (ring CO), 1676 cm^{-1} (amide CO); ^{1}H NMR (400 MHz, DMSO): δ 2.17 (s, 3H, $COCH_3$), 6.50 (d, 1H, *J* 16Hz, vinyl-H), 6.82-7.73 (m, 7H, arom. H), 8.25 (d, 1H, *J* 16Hz, vinyl-H), 9.65 (s, 1H, NH). - MS (EI, 70 EV): *m/z* 255 [M^+].

Anal. Calcd. for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.43; H, 5.16; N, 5.49.

N-{6-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-2-oxo-2*H*-pyran-3-yl}acetamide (**16e**).

Compound **16e** was obtained in 72% yield (2.05 g); mp 209 °C; IR (KBr): ν 3329 (NH), 1709 (ring CO), 1678 cm^{-1} (amide CO); ^{1}H NMR (400 MHz, DMSO): δ 2.12 (s, 3H, $COCH_3$), 3.80 (s, 3H, OCH_3), 6.45 (d, 1H, *J* 8Hz, arom. H), 6.86 (d, 1H, *J* 16Hz, vinyl-H), 6.95-6.97 (m, 2H, arom. H), 7.13 (d, 1H, *J* 16Hz, vinyl-H), 7.58-7.60 (m, 2H, arom. H), 8.15-8.17 (m, 1H, arom. H), 9.69 (s, 1H, NH); MS (EI, 70 EV): *m/z* 285 [M^+].

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.34; H, 5.28; N, 4.80.

N-{6-[(*E*)-2-(2-Furyl)ethenyl]-2-oxo-2*H*-pyran-3-yl}acetamide (**16f**).

Compound **16f** was obtained in 86.5% yield (2.12 g); mp 192 °C; IR (KBr): ν 3331 (NH), 1706 (ring CO), 1682 cm^{-1} (amide CO). ^{1}H NMR (400 MHz, DMSO): δ 2.12 (s, 3H, $COCH_3$), 6.52-6.74 (m, 4H, 2H furyl 4-H, 3-H, pyranyl H, vinyl H), 7.01(d, 1H, *J* 16Hz, vinyl H), 7.76 (s, 1H, furyl H), 8.14 (d, 1H, *J* 8Hz, pyranyl H), 9.69 (s, 1H, NH); MS (EI, 70 EV): *m/z* 245 [M^+].

Anal. Calcd. for $C_{13}H_{11}NO_4$: C, 63.67; H, 4.52; N, 5.71. Found: C, 63.35; H, 4.54; N, 5.71.

General Procedure for the Preparation of Compounds **20a-c** and **22a-b**.

To a stirred solution of each of **10a-c** (10 mmol) in acetic acid 50 ml, each of *p*-benzoquinone and naphthoquinone (10 mmol) was added. Stirring lasted over night at room temperature. The reaction mixture was evaporated *in vacuo*, and the solid product obtained was isolated by filtration and recrystallized from dioxan.

2-Phenylethylidene-5-hydroxybenzo[*b*]furan-3-al (**20a**).

Compound **20a** was obtained in 59% yield (1.50 g); mp 229 °C; IR (KBr): ν 3262 br (OH), 1650 cm^{-1} (CO); ^{1}H NMR (400 MHz, DMSO): δ 4.40 (br s, 1H, OH), 6.95-6.98 (m, 1H, arom. H), 7.45-7.47 (m, 4H, arom. H), 7.71 (d, 1H, *J* 16Hz, vinyl H), 7.79-7.84 (m, 4H, arom. H, vinyl H), 9.00 (s, 1H, CHO). MS (EI, 70 EV): *m/z* 264 [M^+].

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.40; H, 4.69.

5-Hydroxy-2-(4-methoxyphenylethylidene)benzo[*b*]furan-3-al (**20b**).

Compound **20b** was obtained in 86% yield (2.50 g); mp 223 °C; IR (KBr): ν 3264 br (OH), 1640 cm^{-1} (CO); ^{1}H NMR (400 MHz, DMSO): δ 3.82 (s, 3H, OCH_3), 6.84-6.86 (m, 1H, arom. H), 7.03 (d, 2H, *J* 8Hz, arom. H), 7.50 (d, 1H, *J* 8Hz, arom. H), 7.59-7.63 (m, 3H, arom. H, vinyl H), 7.82 (d, 2H, *J* 8Hz, arom. H), 9.21 (s, 1H, CHO), 9.47 (br s, 1H, OH); MS (EI, 70 EV): *m/z* 294 [M^+].

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.80. Found: C, 73.20; H, 4.75.

5-Hydroxy-2-(2-furylethylidene)benzo[*b*]furan-3-al (**20c**).

Compound **20c** was obtained in 82% yield (2.10 g); mp 230 °C; IR (KBr): ν 3221 br (OH), 1650 cm^{-1} (CO); ^{1}H NMR (400 MHz, DMSO): δ 6.68-6.69 (m, 1H, furyl 4-H), 6.84-6.87 (m, 1H, furyl 3-H), 7.05 (d, 1H, *J* 8Hz, arom. H), 7.38 (d, 1H, *J* 16Hz, vinyl H), 7.48-7.61 (m, 3H, arom. H, vinyl H), 7.90 (m, 1H, furyl 5-H), 9.17 (s, 1H, CHO), 9.47 (br s, 1H, OH); MS (EI, 70 EV): *m/z* 254 [M^+].

Anal. Calcd. for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96. Found: C, 70.89; H, 4.05.

5-Hydroxy-2-(phenylethylidene)naphtho[1,2-*b*]furan-3-al (**22a**).

Compound **22a** was obtained in 73% yield (2.30 g); mp 287 °C; IR (KBr): ν 3190 br (OH), 1649 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 7.46-7.90 (m, 10H, arom. H, vinyl H), 9.36-9.42 (m, 2H, arom. H), 9.42 (s, 1H, CHO), 10.32 (br s, 1H, OH); MS (EI, 70 EV): *m/z* 314 [M^+].

Anal. Calcd. for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49. Found: C, 80.24; H, 4.54.

5-Hydroxy-2-(fur-2-yl-ethylidene)naphtho[1,2-*b*]furan-3-al (**22b**).

Compound **22b** was obtained in 56% yield (1.70 g); mp 265 °C; IR (KBr): ν 3201 br (OH), 1650 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 6.71-6.72 (m, 1H, furyl 4-H), 7.08 (d, 1H, *J* 8Hz, arom. H), 7.44 (d, 1H, *J* 16Hz, vinyl H), 7.57-7.70 (m, 4H, arom. H, vinyl H, furyl 3-H), 7.93 (d, 1H, *J* 8Hz, furyl 5-H), 8.20-8.26 (m, 2H, arom. H), 9.30 (s, 1H, CHO), 10.28 (br s, 1H, OH); MS (EI, 70 EV): *m/z* 304 [M^+].

Anal. Calcd. for $C_{19}H_{12}O_4$: C, 74.99; H, 3.97. Found: C, 74.69; H, 3.91.

General Procedure for the Preparation of Compounds **23a-c**.

A cold solution of benzenediazonium salt (10 mmol) was prepared by adding a solution of sodium nitrite (1.5 g into 10 ml H_2O) to a cold solution of aniline hydrochloride with stirring. The resulting solution of the benzenediazonium salt was then added to a cold solution of each of **10a-c** (10 mmol) in ethanol (50 ml) containing sodium hydroxide.

3-Oxo-5-phenyl-2-phenylhydrazono-4-pentene-1-al (**23a**).

Compound **23a** was obtained in 80% yield (2.22 g); mp 140 °C; IR (KBr): ν 3118 (NH), 1660, 1641 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 7.47-7.52 (m, 6H, arom. H, vinyl-H), 7.73-7.75 (m, 5H, arom. H), 7.82 (d, 1H, *J* 16Hz, vinyl H), 9.69 (s, 1H, CHO), 10.39 (s, 1H, NH); MS (EI, 70 EV): *m/z* 278 [M^+].

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.36; H, 5.07; N, 10.07. Found: C, 73.18; H, 5.10; N, 9.91.

3-Oxo-5-(4-methoxyphenyl)-2-phenylhydrazono-4-pentene-1-al (**23b**).

Compound **16a** was obtained in 60% yield (1.84 g); mp 152 °C; IR (KBr): ν 3120 (NH), 1658, 1639 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 3.89 (s, 3H, OCH_3), 7.02-7.76 (m, 10H, arom. H, vinyl-H), 7.83 (d, 1H, *J* 16Hz, vinyl H), 9.65 (s, 1H, CHO), 10.16 (s, 1H, NH); MS (EI, 70 EV): *m/z* 308 [M^+].

Anal. Calcd. for $C_{18}H_{16}N_2O_3$: C, 70.11; H, 5.23; N, 9.09. Found: C, 70.02; H, 5.33; N, 8.91.

5-(2-Furyl)-3-oxo-2-phenylhydrazono-4-pentene-1-al (**23c**).

Compound **23c** was obtained in 65% yield (1.74 g); mp 129 °C; IR (KBr): ν 3115 (NH), 1652, 1639 cm^{-1} (CO); ^1H NMR (400 MHz, DMSO): δ 6.65-6.68 (m, 1H, furyl-H), 6.96- 6.97 (m, 1H, furyl-H), 7.31-7.34 (m, 1H, furyl-H), 7.51-7.78 (m, 6H, arom. H, vinyl-H), 7.78 (d, 1H, *J* 16Hz, vinyl H), 9.57 (s, 1H, CHO), 10.14 (s, 1H, NH); MS (EI, 70 EV): *m/z* 268 [M^+].

Anal. Calcd. for $C_{15}H_{12}N_2O_3$: C, 67.15; H, 4.51; N, 10.44. Found: C 66.87; H, 4.73; N, 10.40.

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