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The 3-anilinoenones **3a,b** were prepared from the corresponding 3-dimethyl-aminopropenones. The reactivity of **3a,b** towards a variety of carbon and nitrogen nucleophiles as well as naphthoquinones is reported.

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In the last few years we have been involved in a program aimed at exploring-chemistry of enaminones [1-3]. During this phase of our research a variety of 3-dimethylamino-1-substituted propen-1-ones **1a-c** were prepared in good yield *via* refluxing methylketones with dimethylformamide dimethylacetal (DMFDMA). These enaminones **1** proved to be excellent precursors for heterocycles and polyaryl benzenes [4-10] (Figure 1).

In conjunction to previous interest in developing synthesis of polyfunctionally substituted heteroaromatics, we report now on reactivity of **1** and its further utility in heterocyclic chemistry. Compounds **1a-c** reacted with aniline to yield products of addition and dimethylamine elimination. The formed anilino derivatives proved to be *cis* products **3a,b** and the *trans* form **2a,b** were completely excluded since olefinic protons appeared as a doublet with  $J = 7$  Hz. The predominance of the *cis* form is attributed to fixation through hydrogen bonding (Figure 1).

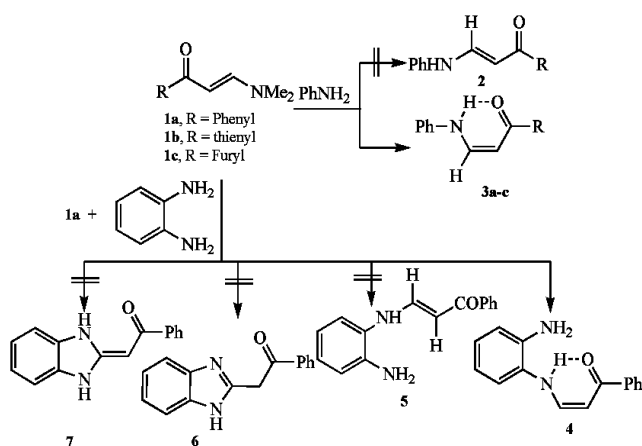


Figure 1

Compound **1a** reacted with 1,2- phenylenediamine to yield product that may be formulated as **4** or stereois-

meric **5** or cyclic products **6** or **7**. Structure **4** was established through <sup>1</sup>H NMR and <sup>13</sup>C NMR. Thus, <sup>13</sup>C NMR revealed the absence of any carbon atoms with *sp*<sup>3</sup> hybridization (Figure 1). Structures **6** and **7** were excluded based on the presence of olefinic proton doublets at  $\delta$  6.05 ppm and 7.98 ppm ( $J = 7$  Hz).

The reaction of compound **3a** with ethyl cyanoacetate or malononitrile in the presence of piperidine proved to depend on applied reaction conditions. It is believed that in acetic acid the formed condensation product **8** is cyclized into **9** and then hydrolysed to **10**. Finally, compound **10** reacts with piperidine to yield **11** (Figure 2).

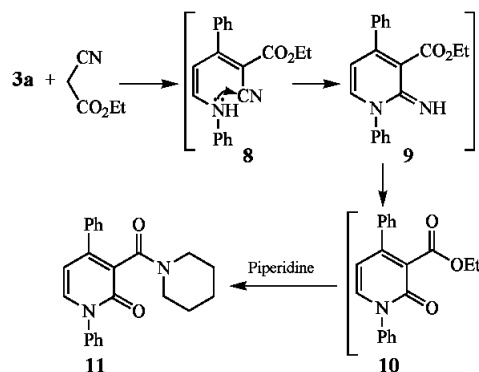


Figure 2

On the other hand, in ethanol malononitrile initially dimerizes to form **12**, which then condenses with **3a** to yield **13**. Compound **13** then loses ammonia and cyclized to **14**, which subsequently reacts with piperidine to yield final **15** (Figure 3). Under similar conditions compound **3a** failed to condense with ethyl cyanoacetate.

Spectral and analytical data supports the proposed structure **15**. Thus, in the mass spectrum of **15** a molecular ion peak is observed at  $m/z$  406. The <sup>1</sup>H NMR spectrum revealed a 10 proton multiplet at  $\delta = 1.25-3.72$

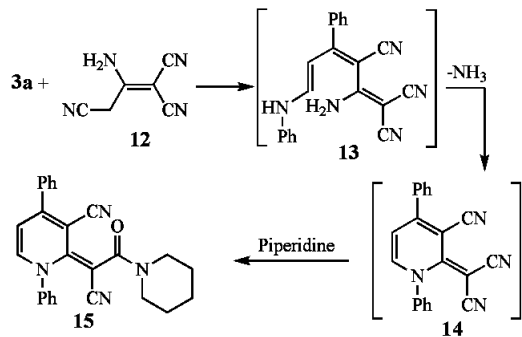


Figure 3

corresponding to the piperidenyl protons a two protons doublet at  $\delta = 6.09$  and  $7.96$  ( $J = 8\text{Hz}$ ) for the dihydro-pyridine protons and a 10 proton aromatic multiplet at  $\delta = 7.10\text{-}7.52$  ppm.

The reaction of **3a** with naphthoquinone afforded **17**. Structure **18** was excluded as 2D NMR indicated that the carbonyl carbon is not attached to any protons. It is of value to report that **1a** was also reported to afford a naphthofuran derivative but the structure has not been unambiguously established [11,12]. It is believed that **16** is an intermediate in this reaction (Figure 4).

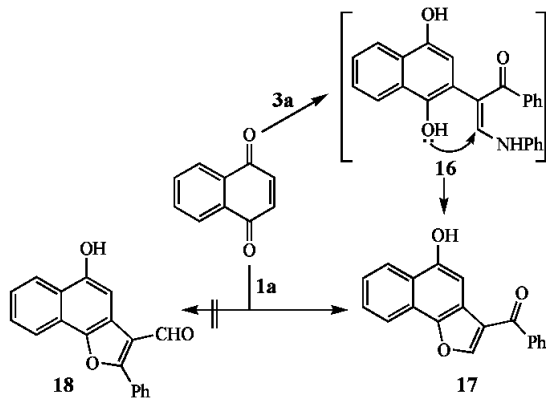


Figure 4

Structure **17** was supported by spectral data. Thus,  $^{13}\text{C}$  NMR revealed a carbonyl carbon at  $\delta = 182.4$  ppm. HMQC indicate that this carbon is not attached to any protons. On the other hand, the low field proton at  $\delta = 8.64$  ppm was found to be attached to C-2 at  $\delta = 152.4$  ppm.

The reaction of **3a** with acetylacetone in refluxing acetic acid and in presence of ammonium acetate yields product that may be formulated as pyridine derivative **20**. The same compound has been previously obtained from reaction of **1a** with acetylacetone [10,13]. It is believed that **19** is an intermediate (Figure 5). Similar to the behavior of **3a**

towards acetylacetone it reacted with cyanothioacetamide to yield **22** through intermediacy of **21** (Figure 5). Again this product proved identical with authentic specimens of 6-phenyl pyridine. Structures **20** and **22** are preferred over possible 4-phenyl pyridine structures based on  $^1\text{H}$  NMR, which revealed pyridyl hydrogen resonances as doublets with  $J = 7$  Hz. Isomeric 4-phenyl pyridine should show lower coupling ( $J = 2\text{-}3$  Hz) [10].

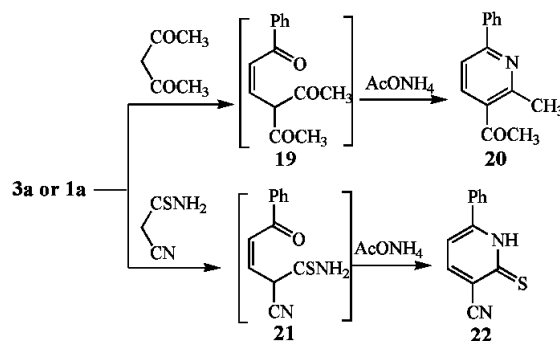


Figure 5

## EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded in KBr with a Pye Unicam SP 1100 spectrophotometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Varian EM-390-400 MHz spectrometer in deuteriochloroform or  $[\text{D}_6\text{DMSO}]$  as solvent and TMS as internal standard; chemical shifts are reported in  $\delta$  (ppm). Mass spectra were measured on MS 30 and MS 9 (AEI), 70 eV. Microanalyses were performed on LECO CHNS-932. Microwave experiments were conducted in a microwave oven DAEWOO, edition II (KOR-8667).

### General Procedure for Preparation of Compounds (1a,b).

Dimethylformamide dimethylacetal (DMFDMA) (0.01 mol) was added to methylketones (0.01 mol) in xylene (50 ml). The reaction mixture was refluxed for 6-9 h. Removal of solvent under reduced pressure yielded the crude product, which was crystallized from ethanol. Compounds (**1a,b**) were obtained as yellow crystals with physical characteristics identical with those reported in literature [1].

### General Procedure for Preparation of Compounds (3a,b).

A solution of **1a,b** (0.01 mol) in ethanol (30 ml) was treated with aniline (0.01 mol) and the reaction mixture was then refluxed for 3 h. Solvent was then evaporated in vacuum. The resulting products were triturated with  $\text{H}_2\text{O}$  and acidified with HCl. The solid products, so formed, were collected by filtration and crystallized from ethanol. Compounds (**3a,b**) were formed as yellow crystals.

### 1-Phenyl-3-(phenylamino)-2-propene-1-one (3a).

This compound was obtained in yield (1.99 g, 89%); mp  $123\text{-}125$  °C (EtOH); ir (KBr):  $\nu_{\text{max}}/\text{cm}^{-1}$  3063 (NH), 3093 (NH), 1669 (CO); ms:  $m/z = 223$  ( $\text{M}^+$ );  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$

(ppm) = 6.05 (d, 1H,  $J = 7$  Hz, olefinic-H), 7.09- 7.95 (m, 10H, arom-H). 7.97(d, 1H,  $J = 7$  Hz, olefinic-H), 12.15 (br, 1H, NH).

*Anal.* Calcd. for  $C_{15}H_{13}NO$  (223.27): C, 80.69; H, 5.86; N, 6.27%. Found C, 80.45; H, 5.93; N, 6.41.

#### 1-(3-Furyl)-3-(phenylamino)-2-propene-1-one (**3b**).

This compound was obtained in yield (1.76 g, 83%); mp 140-142 °C (EtOH); ir (KBr):  $\nu$  max/cm<sup>-1</sup>: 3110 (NH), 1654 (CO); ms:  $m/z = 213$  (M<sup>+</sup>); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  (ppm) = 5.94 (d,  $J = 7$  Hz olefinic-H), 6.52 (d,  $J = 8$  Hz, furyl H-3), 7.09-7.52 (m, 7H, arom-H and furyl H), 7.54 (d,  $J = 7$  Hz olefinic-H), 11.91 (br, 1H, NH).

*Anal.* Calcd for  $C_{13}H_{11}NO_2$  (213.23): C, 73.22; H, 5.19; N, 6.56%. Found C, 73.17; H, 5.17; N, 6.69.

#### 3-[(2-Aminophenyl)amino]-1-phenylprop-2-en-1-one (**4**).

A solution of **1a** (0.01 mol) in DMF (5 ml) was treated with 1,2-phenylenediamine (0.01 mol) and refluxed for 12 h then poured into water. The solid product, so formed, was collected by filtration and crystallized from ethanol. This compound was obtained in yield 1.95g (82%); mp 175-176 °C (EtOH); ir (KBr):  $\nu$  max/cm<sup>-1</sup>: 3218 and 3155 (2NH), 3093 (NH), 1624 (CO); ms:  $m/z = 238$  (M<sup>+</sup>); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  (ppm) = 6.05 (d,  $J = 7$  Hz, olefinic CH), 6.08-7.53 (m, 9H, arom-H), 7.98 (d,  $J = 7$  Hz, olefinic CH), 12.37 (br, 1H, NH); <sup>13</sup>C nmr (dimethyl sulfoxide-d<sub>6</sub>):  $\delta$  (ppm) = 191.31(CO), 147.71 (C-3 olefinic C), 139.66, 137.58, 131.88, 128.90, 129.83, 127.71, 125.69, 120.36, 118.15, 117.69, 94.25 (C-2 olefinic C), 147.71 (C-3 olefinic C).

*Anal.* Calcd. for  $C_{15}H_{14}N_2O$  (238.82): C, 75.60; H, 5.92; N, 11.75%. Found C, 75.35; H, 5.80; N, 11.75.

#### 1,4-Diphenyl-3(piperidylcarbonyl)hydropyridine-2-one (**11**).

A mixture of **3a** (0.1 mol), ethyl cyanoacetate (0.1 mol), glacial acetic acid (2 ml) and piperidine (0.1 mol) was heated in a microwave oven for 2 min. then triturated with ethanol. Solid product formed, was collected by filtration and crystallized from dioxane. This compound was obtained in yield (2.43 g, 68%); mp 290-292 °C; ir (KBr):  $\nu$  max/cm<sup>-1</sup>: 1654 (CO); ms:  $m/z = 358$  (M<sup>+</sup>); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  (ppm) = 1.34-4.19 (m, 10 H, piperidyl-H), 6.43 (d, 1H, pyridyl-H), 7.97 (d, 1H, pyridyl-H), 6.46-7.87 (m, 10H, arom-H).

*Anal.* Calcd for  $C_{23}H_{22}N_2O_2$  (358.44): C, 77.07; H, 6.18; N, 7.81%. Found C, 77.16; H, 6.21; N, 7.73.

#### 2-(1-Cyano-2-oxo-2-piperidylethylidene)-1,4-diphenyl-1,2-dihydro-pyridine-3-carbonitrile (**15**).

A mixture of **3a** (0.01 mol) and malononitrile in ethanol (10 ml) was refluxed for 3 h. The resulting solution was poured into water and the resulting reaction product was collected by filtration and crystallized from acetic acid. This compound was obtained in yield (2.92 g, 72%); mp 226-228 °C; ir (KBr):  $\nu$  max/cm<sup>-1</sup>: 2187 (CN), 1654 (CO); ms:  $m/z = 406$  (M<sup>+</sup>); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  (ppm) = 1.25-3.72 (m, 10 H, piperidyl-H), 6.09 (d, 1H, pyridyl-H), 7.96 (d, 1H, pyridyl-H), 7.10-7.52 (m, 10H, arom-H).

*Anal.* Calcd for  $C_{26}H_{22}N_4O$  (406.48): C, 76.82; H, 5.45; N, 13.78%. Found C, 75.72; H, 5.66; N, 13.39.

#### (5-Hydroxynaphtho[1,2-*b*]furan-3-yl)-phenylmethanone (**17**).

A mixture of (**3a**) and naphthoquinone (0.01mol) were dissolved in glacial acetic acid (10ml) then stirred over night at

room temperature. The so formed crystals were collected by filtration and crystallized from ethanol. This compound was obtained in yield (2.41g, 84%); mp 272-274 °C; ir (KBr):  $\nu$  max/cm<sup>-1</sup>: 1613 (CO); ms:  $m/z = 288$  (M<sup>+</sup>); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  (ppm) = 7.44-8.21 (m, 10H, arom-H), 8.64 (s, 1H, furyl-H), 10.24 (br, 1H, OH); <sup>13</sup>C nmr (dimethyl sulfoxide-d<sub>6</sub>):  $\delta$  (ppm) = 182.4 (CO), 152.4 (C-2), 150.6, 147.7 (C-OH), 133.4, 132.2, 129.5, 128.8, 128.1, 126.5, 125.3, 124.8, 116.3, 114.8, 105.4.

*Anal.* Calcd for  $C_{19}H_{12}O_3$  (288.30); C, 79.15; H, 4.19%. Found C, 79.12; H, 4.19.

#### 1-(2-Methyl-6-phenyl-3-pyridyl)ethan-1-one (**20**).

Equimolecular amount of (0.01 mol) of **3a** or **1a** were dissolved in acetic acid (20 ml) then treated with acetylacetone (0.01 mol), then with ammonium acetate (10 ml) then refluxed for 1.5 h. The resulting solution was poured into water then the solid products formed were collected and crystallized from ethanol. This compound was obtained in yield (1.68 g, 80%); mp 92 °C; ir (KBr):  $\nu$  max/cm<sup>-1</sup>: 1685 (CO); ms:  $m/z = 211$  (M<sup>+</sup>); <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  (ppm) = 2.65 (s, 3H, CH<sub>3</sub>CO), 2.87 (s, 3H, CH<sub>3</sub>), 7.47-7.53 (m, 6H, arom-H and, pyridyl H) 7.67 (d, 1H,  $J = 8$  Hz pyridyl H-4).

*Anal.* Calcd for  $C_{14}H_{13}NO$  (211.26); C, 79.59; H, 6.20; N, 6.63%. Found C, 79.33; H, 6.20; N, 6.68.

#### 6-Phenyl-2-thioxohydropyridine-3-carbonitrile (**22**).

A solution of **3a** or **1a** was dissolved in acetic acid then treated with 2-cyano-thioacetamide, and then with ammonium acetate (2 g) and refluxed for 1.5 h. The resulting solution was poured into water and crystallized from ethanol. This compound was obtained in yield (1.50 g, 71%); mp 245-247 °C; ir (KBr):  $\nu$  max/cm<sup>-1</sup>: 3093 (NH), 2211(CN); ms:  $m/z = 212$  (M<sup>+</sup>); <sup>1</sup>H nmr (dimethyl sulfoxide-d<sub>6</sub>):  $\delta$  (ppm) = 7.11 (d, 1H,  $J = 7$  Hz, pyridyl H-4), 7.53-7.7 (m, 5H, arom-H), 14.21 (br, 1H, NH). <sup>13</sup>C nmr (dimethyl sulfoxide-d<sub>6</sub>):  $\delta$  (ppm) = 179.54 (CS). 154.52, 145.75, 132.31, 132.05, 129.59, 129.34, 129.06, 117.98, 116.00, 112.73 (arom. carbons).

*Anal.* Calcd for  $C_{12}H_8N_2S$  (212.27); C, 67.89; H, 3.79; N, 13.19; S, 15.10 %. Found C, 67.55; H, 3.83; N, 13.32; S, 15.07.

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