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Synthesis of 6-Acylmethylphenanthridine Enaminones

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A series of 6-acylmethylphenanthridine derivatives were synthesized by reaction of aliphatic and aromatic esters with 6-methylphenanthridine in the presence of phenyllithium. Enaminone form of the obtained compounds was investigated by spectroscopic methods. The results revealed that the presence of aromatic rings on 3- and 4-position of 2-acylmethylquinolines (6-acylmethylphenanthridines) is the most important factor for the preference of the enaminone form **b**. It was found that the intramolecular hydrogen bonding is the only factor that can damage aromaticity of the phenanthridine moiety.

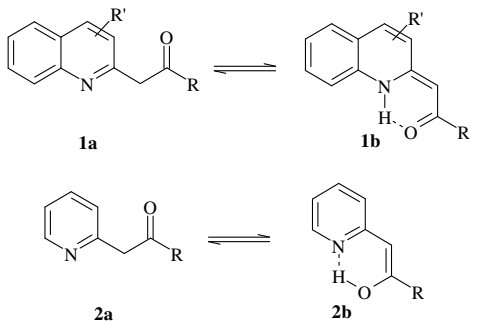
Keywords: Phenanthridine; Enaminone, 2-Ketomethylquinolines, Tautomerism, Hydrogen bonding, Aromaticity

INTRODUCTION

Substituted phenanthridines are an important class of heterocyclic compounds for the study of material sciences and medicinal chemistry and have a broad range of biological activities [1-3]. For example, 6-aryl-substituted phenanthridines have been reported as potent DNA-intercalating antitumor agents [4].

Tautomerism in 2-acylmethylquinolines and 2-acylmethylpyridines has been studied by various spectroscopic methods and ketimine-enaminone and ketimine-enolimine equilibria (Scheme 1) were reported for these compounds, respectively [5-11].

It was reported that enaminone form **1b** was the main tautomer of 2-acylmethylquinolines [9,11]. Changing the side chain substituent with a bulky aliphatic group resulted in an increase in the proportion of ketimine form **1a** [9]. When **R** is a phenyl group, it has been proven that electron-donating substituents in the para position of the phenyl group reduces the amount of the form **1b** but strong electron-withdrawing substituents cause the transformation of form **1a** to form **1b** due to strong internal hydrogen bonding [9]. Substituents R' in positions 3 and 4 also cause an increase in the ratio of form **1b**



R = Me, Et, *i*-Pr, *t*-Bu, CH_2Cl, CH_2Br, CH_2I, CF_3, COOEt, CN, Ph, 2-Py
R' = Me, Ph

Scheme 1

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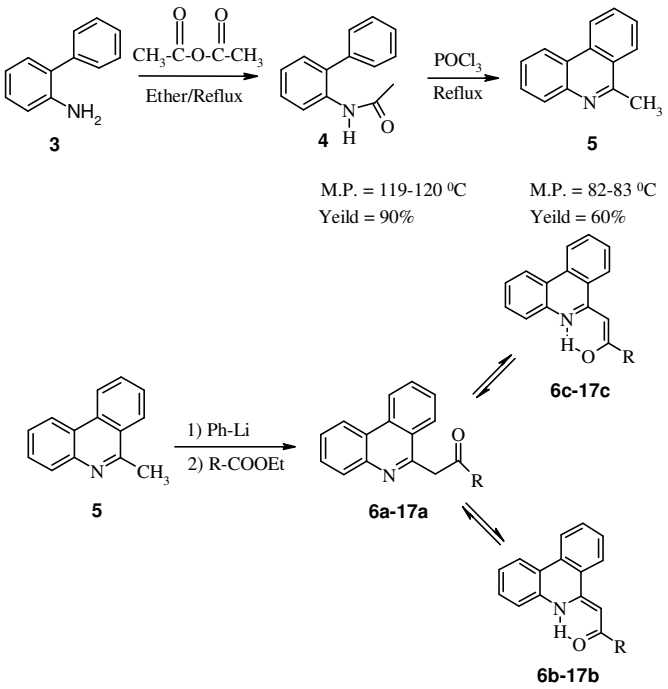

R (**Compd**) = Me (**6**), Et (**7**), *n*-Pr (**8**), *i*-Pr (**9**), *t*-Bu (**10**), Ph (**11**), *p*-Me-C_6H_4 (**12**), *p*-F-C_6H_4 (**13**), *p*-Me_2N-C_6H_4 (**14**), *p*-$(CH_2)_4N$-C_6H_4 (**15**), *p*-Cl-C_6H_4 (**16**), *p*-MeO-C_6H_4 (**17**).

Scheme 2

to form **1a** [9].

The effects of substituent, temperature and solvent on tautomeric ratio in 2-acylmethylpyridines have been studied. The ketimine **2a**-enolimine **2b** tautomerism has also been studied and it has been observed that enolimine **2b** is the predominant form in solution [10].

In order to study the effect of an additional aromatic ring at the 3,4-position of 2-acylmethylquinolines on tautomeric equilibria, a series of aliphatic and aromatic 6-acylmethyl-phenanthridine derivatives were synthesized by the routes in Scheme 2.

EXPERIMENTAL

Melting points were determined using a Mettler FP5 apparatus and are uncorrected. IR spectra were taken by a Shimadzu recording spectrometer, Model 435. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 125 MHZ NMR AC80 spectrometer with $CDCl_3$ as the solvent. Ultraviolet spectra were obtained by a Shimadzu 160 UV spectrometer and mass spectra were taken by a Micromass Platlform II mass spectrometer. *Ortho*-phenylaniline **3** was purchased from the Merck Chemical Company. *Ortho*-acetylaminobiphenyl **4** was prepared as previously described [17]. 6-Methylphenanthridine **5** was prepared by the Bischler-Napieraski method [18,19]. Compounds **6-17** were prepared by the Goldberg and Levine method [20,21]. They were purified *via* plate chromatography and crystallized from ethanol.

General Procedure for Preparation of 6-ketomethyl-Phenanthridines

6-Methylphenanthridine (10 mmol) in dry diethyl ether (20 ml) was added dropwise to a solution of phenyllithium (12 mmol) in dry diethyl ether (20 ml). After stirring under an argon atmosphere for 30 min, aliphatic or aromatic esters (10 mmol) in dry diethyl ether (20 ml) were added dropwise to the lithium derivative of 6-methylphenanthridine. The mixture was refluxed for 5-6 h. The resulting crude product was dissolved in cold water (30 ml), the organic layer was separated, dried (using $MgSO_4$) and evaporated. Pure product was obtained by thin layer chromatography using n-hexane/ethylacetate (6:1) as the eluent.

1-(5 H-phenanthridine-6-ylidene)-propan-2-one (6). Yield: 45%; M.p.: 126-128 ^{o}C; IR (KBr): 1620, 1600, 1550 cm^{-1}; MS (EI, 70 eV): *m/z (%)* = 235 (M^+, 100), 220 (M^+-Me, 70), 192 (M^+-CH_3CO, 40), 165 ($M^{+\cdot}$-$CH_3COCH{=}CH_2$, 35), 43 (CH_3CO^+, 15); UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$: 420 (40584), 396 (43404), 253 (34827); ^{1}H NMR (500 MHz $CDCl_3$): δ = 2.19 (3 H, s, C**H**$_3$), 5.98 (1H, s, C=C**H**), 7.14-8.23 (8H, m, C_{13}**H**$_8$N), 15.08 (1H, s, N**H**); ^{13}C NMR(75 MHz $CDCl_3$): δ = 29.86 (**C**H_3), 88.50 (vinyl-**C**), 118.12, 120.27, 122.82, 122.91, 123.53, 124.42, 125.40, 128.34, 130.13, 132.20, 135.19, 151.81 (aryl-**C**), 194.75 (**C**=O).

1-(5 H-phenanthridine-6-ylidene)-butane-2-one (7). Yield: 43%; M.p.: 94-96 ^{o}C; IR (KBr): 1620, 1600, 1550 cm^{-1}; MS (EI, 70 eV): *m/z (%)* = 249 (M^+, 90), 220 (M^+-Et, 100), 192 (M^+-CH_3CH_2CO, 40), 165 ($M^{+\cdot}$-$CH_3CH_2COCH{=}CH_2$, 37), 57 ($CH_3CH_2CO^+$, 12); UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$: 421 (41170), 397 (43219), 255 (37083); ^{1}H NMR(300 MHz $CDCl_3$): δ = 1.17 (3H, t, J = 7.5 Hz, C**H**$_3$), 2.45 (2H, q, J = 7.5 Hz, C**H**$_2$), 6.00

(1H, s, C=C**H**), 7.17-8.22 (8H, m, C_{13}**H**$_8$N), 15.11 (1H, s, N**H**); ^{13}C NMR(75 MHz $CDCl_3$): δ = 10.8 (**C**H_3), 35.84 (**C**H_2), 87.50 (vinyl-**C**), 118.06, 120.24, 122.81, 122.91, 123.47, 124.58, 125.39, 128.32, 130.15, 132.16, 132.54, 135.29, 151.93 (aryl-**C**), 198.72 (**C**=O).

1-(5 H-phenanthridine-6-ylidene)-pentan-2-one (8). Yield: 50%; M.p.: 87-89 °C; IR (KBr): 1618, 1600, 1552 cm^{-1}; MS (EI, 70 eV): *m/z (%)* = 263 (M^+, 16), 220 (M^+-Pr, 22), 192 (M^+-$CH_3CH_2CH_2CO$, 100), 165 ($M^{+\cdot}$-$CH_3CH_2CH_2COCH$=CH_2, 23), 71 ($CH_3CH_2CH_2CO^+$, 36); UV ($CHCl_3$): λ_{max}(ε): 421 (41291), 398 (44262), 256 (45735); ^{1}H NMR(500 MHz $CDCl_3$) δ = 1.07 (3H, t, J = 7.3 Hz, C**H**$_3$), 1.82 (2H, sextet J = 7.3 Hz, C**H**$_2$), 2.53 (2H, t, J = 7.5 Hz, C**H**$_2$), 6.12 (1H, s, C=C**H**), 7.22-8.32 (8H, m, C_{13}**H**$_8$N), 15.30 (1H, s, N**H**); ^{13}C NMR (125 MHz $CDCl_3$): δ = 14.04 (**C**H_3), 22.56 (**C**H_2), 44.55 (**C**H_2), 87.74 (vinyl-**C**), 117.60, 122.32, 122.40, 122.99, 124.88, 127.87, 128.58, 129.16, 129.62, 131.65, 132.04, 134.78, 151.39, (aryl-**C**), 197.39 (**C**=O).

3-Methyl-1-(5-H-phenanthiridine-6-ylidene)-pentan-2-one (9). Yield: 48%; M.p.: 130-132 °C; IR (KBr): 1615, 1600, 1550 cm^{-1}; MS (EI, 70 eV): *m/z (%)* = 263 (M^+, 30), 220 (M^+-i Pr, 79), 192 (M^+-Me_2CHCO, 100), 165 ($M^{+\cdot}$-$Me_2CHCOCH$=CH_2, 40), 71 (Me_2CHCO^+, 13); UV ($CHCl_3$): λ_{max}(ε): 422 (32381), 398 (35123), 254 (44320); ^{1}H NMR (500 MHz $CDCl_3$): δ = 1.30 (6H, d, J = 6.8 Hz, 2C**H**$_3$), 2.76 (1H, septet J = 6.8 Hz, C**H**), 6.16 (1H, s, C=C**H**), 7.29-8.34 (8H, m, C_{13}**H**$_8$N), 15.32 (1H, s, N**H**); ^{13}C NMR (125 MHz $CDCl_3$): δ = 20.07 (2**C**H_3), 40.12 (**C**H), 86.05 (vinyl-**C**), 117.61, 122.34, 122.45, 123.00, 124.92, 127.83, 128.42, 129.22, 129.66, 131.67, 132.48, 134.84, 151.94 (aryl-**C**), 201.63 (**C**=O).

3,3-Dimethyl-1-(5H-phenanthridine-6-ylidene)-butan-2-one (10). Yield: 55%; M.p.: 125-127 °C; IR (KBr): 1618, 1598, 1548 cm^{-1}; MS (EI, 70 eV): *m/z (%)* = 277 ($M^{+\cdot}$, 35), 220 [$M^{+\cdot}$-$(Me)_3C$, 100], 192 ($M^{+\cdot}$-[$(Me)_3C$-CO], 30), 165 ($M^{+\cdot}$-[$(Me)_3C$-CO-CH=CH_2], 15), 57 [$(Me)_3C^+$]; UV ($CHCl_3$): λ_{max}(ε): 422 (38752), 398 (41882), 253 (37228); ^{1}H NMR (500 MHz $CDCl_3$): δ = 1.36 (9H, s, 3 C**H**$_3$), 6.35 (1H, s, C=C**H**), 7.27-8.34 (8H, m, C_{13}**H**$_8$N), 15.46 (1H, s, N**H**); ^{1}H NMR (500 MHz DMSO-d_6): δ = 1.15 (9H, s, 3C**H**$_3$), 6.35 (1H, s, C=C**H**), 7.21-8.48 (8H, m, C_{13}**H**$_8$N), 15.26 (1H, s, N**H**); ^{13}C NMR (125 MHz $CDCl_3$): δ = 28.17 (3**C**H_3), 41.75 **C**$(CH_3)_3$, 83.27 (vinyl-**C**), 117.63, 119.75, 122.25, 122.36, 122.92, 124.37, 124.75, 127.74, 129.56, 131.50, 131.89, 134.78, 152.08 (aryl-**C**), 203.18 (**C**=O).

2-(5H-phenanthridine-6-ylidene)-1-phenylethanone (11). Yield: 60%; M.p.: 127-130 °C (from ethanol), Lit. [22] 130-132 °C (from ethanol); IR (KBr): 1597, 1552 cm^{-1}; MS (EI, 70 eV): *m/z (%)*: 297 ($M^{+\cdot}$, 3), 220 (M^+-C_6H_5, 2), 192 ($M^{+\cdot}$-C_6H_5CO, 15), 165 ($M^{+\cdot}$-[C_6H_5CO-CH=CH_2], 7), 105 ($C_6H_5CO^+$, 100), 77 (C_6H_5, 42); UV ($CHCl_3$): λ_{max}(ε): 441 (49509), 416 (45084), 252 (36441); ^{1}H NMR (500 MHz $CDCl_3$): δ = 6.87 (1H, s, C=C**H**), 7.30-8.41 (13H, m, C_{13}**H**$_8$N, C_6**H**$_5$), 15.93 (1H, s, N**H**); ^{13}C NMR (125 MHz $CDCl_3$): δ = 85.19 (vinyl-**C**), 117.98, 120.15, 122.36, 122.47, 123.42, 124.22, 124.98, 126.86, 127.93, 128.28, 129.72, 130.57, 131.84, 132.03, 134.53, 140.64, 152.63 (aryl-**C**), 186.83 (**C**=O).

1-(4-Methylphenyl)-2-(5H-phenanthridine-6-ylidene)-ethanone (12). Yield: 67%; M.p.: 104-106 °C; IR (KBr): 1595, 1550 cm^{-1}; MS (EI, 70 eV): *m/z (%)* = 311 ($M^{+\cdot}$, 100), 296 ($M^{+\cdot}$-Me, 15), 220 (M^+-[*p*-MeC_6H_4], 27), 192 ($M^{+\cdot}$-[*p*-MeC_6H_4CO], 18), 165 ($M^{+\cdot}$-[*p*-MeC_6H_4CO-CH=CH_2], 18), 119 (*p*-$MeC_6H_4CO^+$, 45), 91(*p*-MeC_6H_4, 20); UV ($CHCl_3$): λ_{max}(ε): 442 (52838), 417 (48080), 252 (34832); ^{1}H NMR (500 MHz $CDCl_3$): δ = 2.48 (3H, s, C**H**$_3$), 6.85 (1H, s, C=C**H**), 7.30-8.40 (12H, m, C_{13}**H**$_8$N, C_6**H**$_4$), 15.88 (1H, s, N**H**); ^{13}C NMR (125 MHz $CDCl_3$): δ = 21.40 (**C**H_3), 84.97 (vinyl-**C**), 117.86, 120.04,.122.32, 122.41, 123.25, 124.29, 124.91, 126.88, 127.86, 128.97, 129.66, 131.71, 131.96, 134.61, 137.88, 140.91, 152.41 (aryl-**C**), 186.74 (**C**=O).

1-(4-Fluorophenyl)-2-(5H-phenanthridine-6-ylidene)-ethanone (13). Yield: 60%; M.p.: 115-117 °C; IR (KBr): 1620, 1592, 1550 cm^{-1}; MS (EI, 70 eV): *m/z (%)* = 315 ($M^{+\cdot}$, 100), 220 ($M^{+\cdot}$-[*p*-FC_6H_4], 30], 192 ($M^{+\cdot}$-[*p*-FC_6H_4CO], 20), 165 ($M^{+\cdot}$-[*p*-FC_6H_4CO-CH=CH_2], 17), 123 (*p*-$FC_6H_4CO^+$, 35), 95 (*p*-FC_6H_4, 15); UV ($CHCl_3$): λ_{max}(ε): 440 (52416), 415 (47155), 252 (38241); ^{1}H NMR (500 MHz $CDCl_3$): δ = 6.81 (1H, s, C=C**H**), 7.18-8.41 (12H, m, C_{13}**H**$_8$N, C_6**H**$_4$), 15.87 (1H, s, N**H**); ^{13}C NMR (125 MHz $CDCl_3$): δ = 84.74 (vinyl-**C**), 115.06, 115.23, 117.94, 120.13, 122.36, 122.47, 123.48, 124.11, 124.93, 127.92, 128.97, 128.99, 129.73, 131.88, 134.43, 136.84, 152.65 (aryl-**C**), 185.38 (**C**=O).

1-(4-Dimethylaminophenyl)-2-(5H-phenanthridine-6-ylidene)-ethanone (14). Yield: 65%; M.p.: 198-200 °C; IR (KBr): 1600, 1550 cm^{-1}; MS (EI, 70 eV): *m/z (%)*: = 340 (M^+, 100), 148 (*p*-$Me_2NC_6H_4CO^+$, 75], 121 (*p*-$Me_2NC_6H_5$, 40); UV

($CHCl_3$): $\lambda_{max}(\varepsilon)$: 456 (55386), 430 (49130), 252 (42975); ^{1}H NMR (500 MHz $CDCl_3$): δ = 3.10 (6H, s, 2C**H**$_3$), 6.83 (1H, s, C=C**H**), 6.79-8.36 (12H, m, C_{13}**H**$_8$N, C_6**H**$_4$), 15.72 (1H, s, N**H**); ^{13}C NMR (125 MHz $CDCl_3$): δ = 40.10 [N(**C**$H_3)_2$], 84.46 (vinyl-**C**), 110.98, 117.59, 119.79, 122.32, 122.42, 122.72, 124.81, 124.84, 127.81, 128.16, 128.73, 129.63, 131.43, 131.94, 135.13, 140.91, 152.15 (aryl-**C**), 186.65 (**C**=O).

1-(4-pyrrolidine-phenyl)-2-(5H-phenanthridine-6-ylidene)-ethanone (15). Yield: 65%; M.p.: 241-243 °C; IR (KBr): 1590, 1550 cm^{-1}; MS (EI, 70 eV): *m/z (%)* = 366 (M^+, 20), 219 (M^+-[*p*-$(CH_2)_4NC_6H_4$], 5), 192 ($M^{+\cdot}$-[*p*-$(CH_2)_4NC_6H_4CO^+$], 10), 174 [*p*-$(CH_2)_4NC_6H_4CO^+$, 100], 165 ($M^{+\cdot}$-[*p*-$(CH_2)_4NC_6H_4$CO-CH=CH_2], 10), 147 [*p*-$(CH_2)_4NC_6H_5$, 72]; UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$: 459 (57153), 434 (51676), 253 (38808); ^{1}H NMR (500 MHz $CDCl_3$): δ = 2.09 (4H, t, J = 6.4 Hz, 2C**H**$_2$), 3.43 (4H, t, J = 6.4 Hz, 2C**H**$_2$), 6.77 (1H, s, C=C**H**), 6.64-8.36 (12H, m, C_{13}**H**$_8$N, C_6**H**$_4$), 15.63 (1H, s, N**H**); ^{13}C NMR (500 MHz $CDCl_3$): δ = 25.36 [N(CH_2**C**$H_2)_2$], 47.55[N(**C**$H_2CH_2)_2$], 84.00 (vinyl-**C**), 111.09, 117.59, 119.79, 122.34, 122.42, 122.72, 124.81, 124.84, 127.81, 128.16, 128.58, 129.63, 131.43, 131.94, 135.13, 140.91, 152.15 (aryl-**C**), 186.89 (**C**=O).

1-(4-Chlorophenyl)-2-(5H-phenanthridine-6-ylidene) ethanone (16). Yield: 60%; M.p.: 169-171 °C; IR (KBr): 1620, 1600, 1550 cm^{-1}; MS (EI, 70 eV): *m/z (%)* = 331 (M^+, 60), 220 (M^+-[*p*-ClC_6H_4], 38], 192 ($M^{+\cdot}$-[*p*-$ClC_6H_4CO^+$], 35), 165 ($M^{+\cdot}$-[*p*-ClC_6H_4CO-CH=CH_2], 40), 139 (*p*-$ClC_6H_4CO^+$, 85); UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$: 443 (55740), 419 (49186), 252 (41937); ^{1}H NMR (500 MHz $CDCl_3$): δ = 6.60 (1H, s, C=C**H**), 7.21-8.19 (12H, m, C_{13}**H**$_8$N, C_6**H**$_4$), 15.71 (1H, s, N**H**); ^{13}C NMR (125 MHz $CDCl_3$): δ = 84.88 (vinyl-**C**), 118.05, 120.25, 122.41, 122.51, 123.64, 124.06, 124.99, 127.99, 128.26, 128.48, 129.79, 131.97, 132.06, 134.38, 136.63, 139.00, 152.80 (aryl-**C**), 185.13 (**C**=O).

1-(4-Methoxyphenyl)-2-(5H-phenanthridine-6-ylidene) ethanone (17). Yield: 70%; M.p.: 159-160 °C; IR (KBr): 1590, 1550 cm^{-1}; MS (EI, 70 eV): *m/z (%)*: = 327 (M^+, 35), 220 (M^+-[*p*-$MeOC_6H_4$], 15], 192 ($M^{+\cdot}$-[*p*-$MeOC_6H_4CO$], 10), 165 (M^+-[*p*-$MeOC_6H_4$CO-CH=CH_2], 15), 135 (*p*-$MeOC_6H_4CO^+$, 100); UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$: 443 (57094), 418 (51633), 251 (42052); ^{1}H NMR (500 MHz $CDCl_3$): δ = 3.83 (3H, s, OC**H**$_3$), 6.62 (1H, s, C=C**H**), 6.93-8.12 (12H, m, C_{13}**H**$_8$N, C_6**H**$_4$), 15.60 (1H, s, N**H**); ^{13}C NMR (125 MHz $CDCl_3$): δ = 55.35 (O**C**H_3), 84.67 (vinyl-**C**), 113.55, 117.78, 120.00, 122.37, 122.42, 123.15, 124.37, 124.87, 127.87, 128.73, 129.66, 131.66, 131.94, 133.33, 134.71, 152.21, 161.78 (aryl-**C**), 186.15 (**C**=O).

RESULTS AND DISCUSSION

^{1}H NMR spectra of compounds **6-17** (Table 1) show the signals of the vinyl protons at 5.98-6.87 ppm without any signal of methylene protons which are expected to appear at 4-5 ppm [12,13]. The enaminone forms **6b-17b** exhibited NH resonances in the range δ = 15.08-15.93 ppm due to the strong intramolecular hydrogen bonding between the NH proton and the carbonyl oxygen. The ^{13}C NMR spectra of these compounds (Table 1) reveal signals in the range δ = 83-88 ppm for vinyl carbon and δ = 185-203 ppm for carbonyl carbon. This proves that the carbonyl group is conjugated with the aromatic system. There is no signal present in the range of 45-55 ppm for methylene protons in forms **6a-17a**.

In the IR spectra of the above compounds, the carbonyl band appears in the range of 1620-1600 cm^{-1} (Table 2) and there is no band at 1720 cm^{-1} which indicates that the carbonyl bond is conjugated with the carbon-carbon double

Table 1. ^{1}H ($CDCl_3$ 500 MHz) and ^{13}C NMR Data ($CDCl_3$ 125 MHz)

	^{1}H NMR		^{13}C NMR	
Compound	=C**H**	N**H**	=**C**H	**C**=O
6	5.98	15.08	88.50	194.75
7	6.00	15.11	87.50	198.72
8	6.12	15.30	87.74	197.39
9	6.16	15.32	86.05	201.63
10	6.35	15.46	83.27	203.18
11	6.87	15.93	85.19	186.83
12	6.85	15.88	84.97	186.74
13	6.81	15.87	84.74	185.38
14	6.83	15.72	84.46	186.65
15	6.77	15.63	84.00	186.89
16	6.60	15.71	84.88	185.13
17	6.62	15.60	84.67	186.15

Table 2. IR Bands (KBr, cm^{-1}) and UV Data ($CHCl_3$, nm)

Compound	IR			UV		
	C=O /C=C	Ar	C=C /C=O	λ_{max1}	λ_{max2}	λ_{max3}
6	1620	1600	1550	420	396	253
7	1620	1600	1550	421	397	255
8	1618	1600	1552	421	398	256
9	1615	1600	1550	422	398	254
10	1618	1598	1548	422	398	253
11	1615	1597	1552	441	416	252
12	1615	1595	1550	442	417	252
13	1620	1592	1550	440	415	252
14	1600	1590	1550	456	430	252
15	1600	1590	1550	459	434	253
16	1620	1600	1550	443	419	252
17	1600	1590	1550	443	418	251

bond. This is consistent with a previous report [13].

The UV spectra of the compounds (Table 2) show strong peaks above 300 nm which is also consistent with the conjugated system. The respective bands in the spectra of the compounds carrying alkyl groups **6-10** are blue-shifted withrespect to those carrying aromatic groups **11-17**. These data are consistent with previous reports [8,14-16].

In the ^{1}H NMR spectra of compounds **6-17,** the signals at δ = 5.98-6.87 ppm (=C**H**) and δ = 15.08-15.93 ppm (N**H**) disappeared upon addition of D_2O, which shows that both of these hydrogens are acidic and can be exchanged with deuterium according to Scheme 3.

The effect of solvent has been studied typically on compound **10** using DMSO-d_6. The position of *tert*-butyl and N**H** protons changed only about 0.2 ppm upfield and no trace of the second tautomer was observed (see Experimental section).

In conclusion, based on the spectral data, all the compounds exclusively have the enaminone form **6b-17b** both in solution and in the solid state. Therefore, the aromatic ring in 3,4-position of 2-acylmethylquinolines (6-acylmethyl-phenanthridines) seems to be the most important factor for the preference of enaminone form **b**. In this regard, various aliphatic and aromatic substituents do not have any effect on the tautomeric ratio. The intramolecular hydrogen bonding is the only factor that can damage the aromaticity of the phenanthridine moiety.

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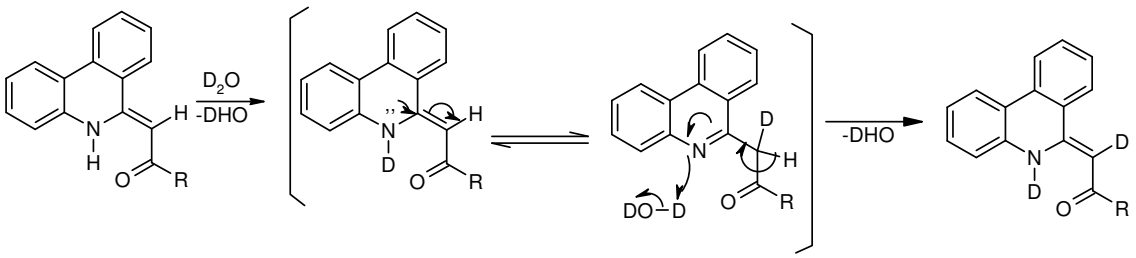

Scheme 3

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