A Study on Chemical Behaviors of Some 4-Pyrones Synthesized By One-Step Reactions towards Various Amines

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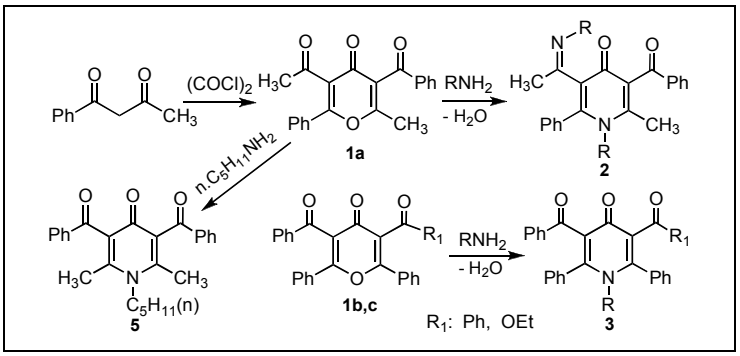

Cycloaddition of acetylbenzoyl ketene generated *in situ* as an intermediate during one-step reaction between excess benzoylacetone and oxalylchloride to C=C double bond of cyclic enol form of benzoylacetone gave 3-acetyl-5-benzoyl-6-methyl-2-phenyl-4(4*H*)-pyrone **1a**. Condensation reactions of **1a** together with 3,5-dibenzoyl-2,6-diphenyl-4(4*H*)-pyrone **1b** and 3-benzoyl-5-ethoxycarbonyl-2,6-diphenyl-4(4*H*)-pyrone **1c** with two-fold excess primary amines provided a series of 3-benzoyl-1-alkyl-5-(1-alkylimino-ethyl)-6-phenyl-2-methyl-4(1*H*)-pyridinone **2**, 3,5-dibenzoyl-1-alkyl-2,6-diphenyl-4(1*H*)-pyridinone **3a-c** and 3-benzoyl-1-alkyl-5-ethoxycarbonyl-2,6-diphenyl-4(1*H*)-pyridinone **3d,e** derivatives, respectively. In addition, while prolonged reaction of *n*-pentylamine with unsymmetrical pyrone derivative **1a** gives a symmetrical pyridinone derivative namely 3,5-dibenzoyl-2,6-dimethyl-1-pentyl-4(1*H*)-pyridinone **5**, much prolonged action *n*-pentylamine and then aqueous *n*-pentylamine on **1b** resulted in degradation of the 4-pyrone ring to give dibenzoylmethane.

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INTRODUCTION

Six-membered nitrogen heterocycles are key units in medicinal chemistry and versatile intermediates in organic synthesis [1]. 4(1*H*)-Pyridinones have shown various pharmacological effects such as antibacterial [2], antifungal [3], anti-malarial [4], cardiotonic agents [5], antihypertensive [6], anti-neoplastic [7], anti-inflammatory [8], analgesic [9], and treatment of Parkinson's disease [10]. On the other hand, the reaction of primary amines with 4(1*H*)-pyrones to form 4(1*H*)-pyridinones has been known for more than 90 years [11]. It has been utilized for the preparation of a variety of these pyridinones; despite the fact that this reaction has somewhat limited scope, being reliable only for small alkyl and aryl amines [11,12].

Recently, one step synthesis of 3,5-dibenzoyl-2,6-dipheyl-4-pyrone derivative **1b** from the reaction of dibenzoylmethane with oxalyl chloride has been reported by our group [13]. Also, we demonstrated that α-oxoketene generated *in situ* from 4-ethoxycarbonyl-5-phenyl-2,3-dihydrofuran-2,3-dione in refluxing xylene has reacted easily with dibenzoylmethane to give 3-benzoyl-5-ethoxycarbonyl-2,6-diphenyl-4-pyrone **1c** in a good yield [13]. α-Oxoketenes (acylketenes) are highly reactive molecules that usually can not be observed and isolated under ordinary reaction conditions, although several examples have been detected by low temperature ir spectroscopy technique [14], and some sterically or electronically hindered α-oxoketenes have been stabilized by preparative flash vacuum pyrolysis method in recent years [15]. A simple useful procedure of the generation of α-oxoketenes is the thermal decarbonylation of 2,3-dihydrofuran-2,3-diones at approximately 80-140°C in solution [17].

These ketenes are currently of considerable interest, not only because of mechanistic and theoretical considerations [18], but also because of their use as synthetic building blocks in organic synthesis [15, 16].

Here, we envisioned that we could generate acetyl benzoylketene as a reactive intermediate via one-step reaction of benzoylacetone with oxalylchloride similar to the formation of dibenzoyl ketene [13] and trapped it in [4+2] cycloaddition reaction with excess benzoylacetone to give the titled compound **1a**, namely 3-acetyl-5-benzoyl-2-phenyl-6-methyl-4-pyrone. In addition, we also

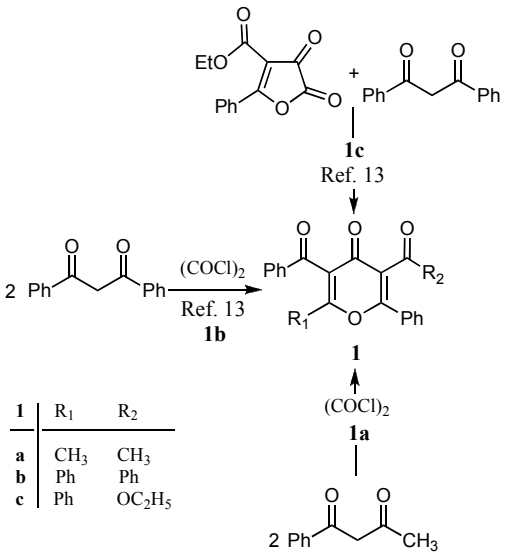
planned to investigate chemical behaviors of **1a** together with **1b** and **1c** towards a series of amine derivatives in comparison with each-other.

RESULTS AND DISCUSSION

Our attempt to synthesize some new six membered aza-heterocycles *via* reactions of **1b** and **1c** together with **1a**, which we synthesized in this work, with a series of alkyl or aryl amines, led to the formation of various heterocyclic compounds having pyridine and pyridinone ring systems (Scheme 3 and 4).

While **1b** and **1c** from 4-pyrone derivatives which were investigated in terms of their chemical behaviors towards amines were obtained according to procedure given in the literature [14], **1a** was prepared by refluxing of a mixture of benzoylacetone (2 mmole) and oxalylchloride (1 mmole) in xylene (Scheme 1).

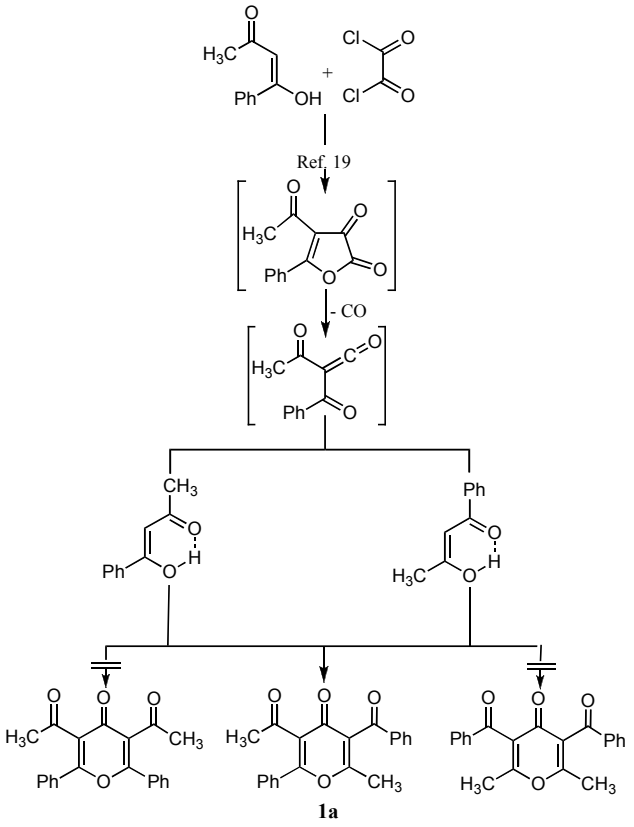
Scheme 1



1	R_1	R_2
a	CH_3	CH_3
b	Ph	Ph
c	Ph	OC_2H_5

In the preparation of **1a**, both 4-acetyl-5-phenyl-2,3-furandione [19] and acetylbenzoyl ketene used for the reaction were generated *in situ* from a mixture of benzoylacetone and oxalylchloride in boiling xylene. Thus, [4+2] cycloaddition of acetylbenzoyl ketene, generated by thermolysis of 4-acetyl-5-phenyl-2,3-furandione formed during one-step reaction, to C=C double bond of cyclic enol form of excess benzoylacetone having a strong intramolecular hydrogen bond led to the formation of a new 4-pyrone derivative **1a**, which provide a versatile synthetic method for 3,5-diacyl-4*H*-pyron-4-ones. Since both benzoylacetone and acetylbenzoyl ketene posses unsymmetrical structures, this reaction may produce three isomeric 4-pyrone derivatives. However, the result of TLC study for reaction illustrates the presence of only one product, the structure of which was identified as 3-acetyl-5-benzoyl-2-phenyl-6-methyl-4-pyrone **1a**, mainly based upon ^{13}C nmr spectroscopic data of **1a** (see experimental). This is an indication of regio-specifically proceeding of cycloaddition reaction between acetylbenzoyl ketene and benzoylacetone (Scheme 2).

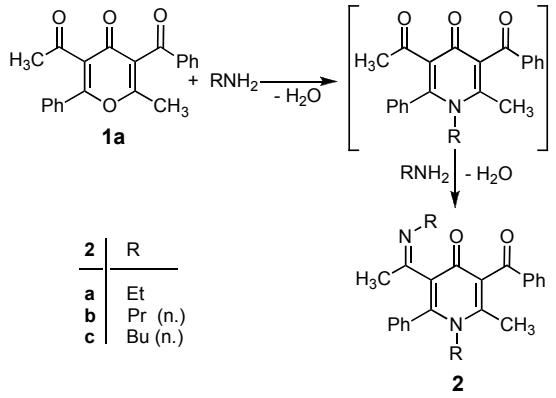
Scheme 2



So far, studies reported on reactivity of α-oxoketenes show that these reactive intermediates are capable of undergoing [4+2] cycloaddition reactions with hetero-dienophiles such as Schiff-bases, nitriles, isocyanates, carbonyls and vinyl ethers to give various oxazinone, oxazindione, dioxinone and 4-pyrone derivatives [20], respectively. Our previous [13] and present studies related to the synthesis of 4-pyrones are of importance because of showing that α-oxoketenes are also capable of undergoing Diels-Alder reactions with enol forms of some dicarbonyl compounds.

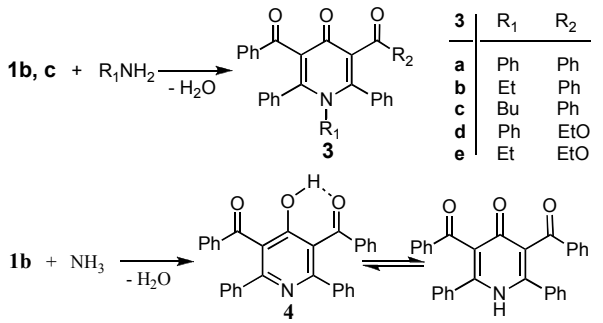
The structure of **1a** was confirmed by analytical and spectral data (see experimental). In addition, compound **1a** could be easily converted *via* its reactions with a series of primary amine derivatives in ethanol into the corresponding pyridinone derivatives **2**, structures of which were also elucidated by elemental analysis and spectroscopic data (see experimental) (Scheme 3).

Scheme 3



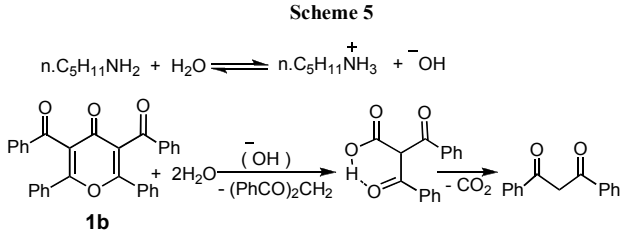
Condensation reactions of all 4-pyrone derivatives with two-fold excess primary amines were performed in butanol or ethanol at boiling temperature for a time between 20 or 40 hours. Compounds **1b** and **1c** having phenyl groups at both C-2 and C-6 positions exhibits similar behaviors towards primary amines. While the reactions between ethylamine and **1b** or **1c** proceeded smoothly affording the corresponding substituted 4-pyridinones, the reactions with amines bearing bulky groups afforded the corresponding substituted 4-pyridinones in lower yields, even with prolonged reaction times (Scheme 4).

Scheme 4



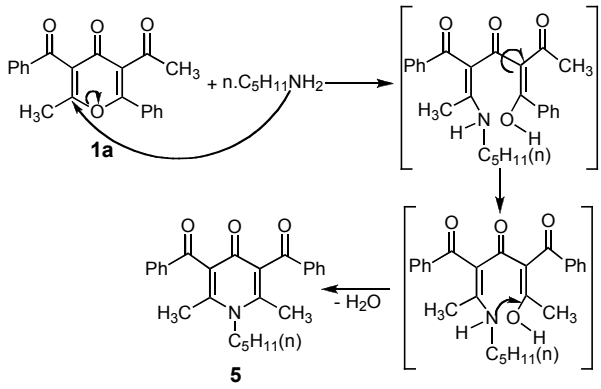
Much prolonged action of *n*-pentylamine and then aqueous *n*-pentylamine on **1b** resulted in degradation of the 4-pyrone ring, and ultimately gave dibenzoylmethane (Scheme 5).

Scheme 5



The reactions of **1a** with two-fold excess primary amines were found to be significantly different. Upon treatment with excess amines in ethanol at boiling temperature for 20 hours, the resulting acetyl-4-(1*H*)-pyridinones underwent a second condensation reactions between acetyl groups and amines to yield the corresponding alkylimino-4-(1*H*)-pyridinones (Scheme 3). In these reactions performed in polar solvents using excess amine, while benzoyl groups in 4-pyrones **1b** and **1c** did not react with primary amines, the undergoing condensation reactions of acetyl groups in **1a** with amines is interesting. In similar manner, symmetrical derivative **5** formed during the reaction of **1a** with *n*-pentylamine also did not react *via* its benzoyl group with *n*-pentylamine. This shows that the formation of alkylimino-4-(1*H*)-pyridinones is a process consisting of reactions having two steps following each-other (Scheme 3 and 6).

Scheme 6



Our experiments show that the appearance of steric hindrance depended on the size of both alkyl groups in primary amines and functionalities at C-2 and C-6 positions on pyrane ring of 4-pyrones. Indeed, while 2,6-diphenylpyrones **1b** and **1c** could not react with *n*-pentylamine, **1a** could react with the same reagent, even when it is accompanying with a rearrangement.

While reactions of other all primary amines with **1a** derived the products having unsymmetrical structures, in the case that starting materials are *n*-pentylamine and **1a**, due to this steric effect, only a pyridinone derivative with symmetrical structure could be obtained.

Consequently, in the present work, novel 4-pyridinone derivatives have been synthesized from three different pyrones. One of the 4(1*H*)-pyrones is obtained regio-specifically. The new compounds have been characterized by elemental analyses, FT-IR, ^{1}H nmr and ^{13}C nmr spectral data (see experimental).

EXPERIMENTAL

IR spectra were recorded on a Bio-Rad Win-1000 FT-IR spectrometer in KBr pellets. The ^{1}H nmr and ^{13}C nmr spectra

were recorded on a Varian (200 MHz) and Varian (50 MHz) spectrometers using $SiMe_4$ as the reference. Elemental analyses were performed on a Carlo Erba EAGER 200. Melting points were determined on an Electrothermal Gallenkamp apparatus. 3,5-dibenzoyl-2,6-diphenyl-4-pyrone **1b**, 3-benzoyl-5-ethoxycarbonyl-2,6-diphenyl-4-pyrone **1c** were synthesized according to the published procedures [13].

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. All solvents were dried by refluxing with appropriate drying agents and distilled before use. The homogeneity of the products was tested in each step by TLC (SiO_2).

3-Acetyl-5-benzoyl-2-phenyl-6-methyl-4-pyrone (1a). Benzoylacetone of (0.32 g, 2 mmole) and oxalylchloride (0.086 ml, 1 mmole) in xylene were heated for 4 hours at reflux temperature. After the solvent were removed by evaporation, the oily residue was dissolved in ether. After 10 hours, the formed crystals were collected by filtration and recrystallized from ethanol to give 0.066 g (20%) of **1a**, mp 184°C; ir (KBr): (CH, aromatic) 3050, (CH, aliphatic) 2950, C=O 1704, 1672, 1643 cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.93-7.43 (m, 10H, CH, aromatic), 2.39 (s, 3H, CH_3), 2.30 ppm (s, 3H, CH_3-C=O); ^{13}C nmr ($CDCl_3$): δ 201.47 (C=O, acetyl), 194.71 (C=O, benzoyl), 176.86 (C=O, C-4), 166.54 (C-6), 163.98 (C-2), 138.45, 136.14, 133.66, 132.75, 131.37, 131.29, 130.91, 130.85, 130.33, 128.81, 34.01 (CH_3), 20.36 ppm (CH_3-C=O). Anal. Calcd. for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.62; H, 4.85.

General Procedures for Pyridinone Derivatives (2a-c). 3-Acetyl-5-benzoyl-2-phenyl-6-methyl-4-pyrone **1a** (1 mmol) and amine derivative (2 mmol) were refluxed in ethanol for 24 hours. The solvent was evaporated under reduced pressure to give an oily residue which was treated with ether and finally crystallized from indicated solvent and solvent for each compound: **2a**, ethanol; **2b**, ethanol:water; **2c**, ethanol:water.

3-Benzoyl-1-ethyl-5-(1-ethyliminoethyl)-6-phenyl-2-methyl-4(1*H*)-pyridinone (2a). Yield 60%, mp 193°C; ir (KBr): (CH, aromatic) 3050, (CH, aliphatic) 2950, (C=O and C=N-) 1685, 1670, 1619 cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.96-7.26 (m, 10H, CH, aromatic), 4.02-3.91 (q, 2H, N-CH_2-), 3.74-3.68 (q, 2H, =N-CH_2-), 2.25 (s, 3H, CH_3), 2.22 (s, 3H, CH_3), 1.36-1.28 (t, 3H, N-CH_2-*CH_3*), 1.13-1.09 ppm (t, 3H, =N-CH_2-*CH_3*); ^{13}C nmr ($CDCl_3$): δ 198.51 (C=O, benzoyl), 175.69 (C=O, C-4), 158.29 (C, imino), 148.63 (C-6), 147.25 (C-2), 139.05, 135.48, 132.27, 131.39, 131.29, 130.93, 130.77, 130.71, 130.60, 46.15 (N-CH_2-), 45.10 (=N-CH_2-), 19.30 (CH_3), 19.25 (CH_3), 17.15 (N-CH_2-*CH_3*), 17.11 (=N-CH_2-*CH_3*). Anal. Calcd. for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25. Found: C, 77.61; H, 6.77; N, 7.24.

3-Benzoyl-1-propyl-5-(1-propyliminoethyl)-6-phenyl-2-methyl-4(1*H*)-pyridinone (2b). Yield 55%, mp 168°C; ir (KBr): (CH, aromatic) 3075, (CH, aliphatic) 2960, (C=O and C=N-) 1704, 1667, 1619 cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.98-7.26 (m, 10H, CH, aromatic), 3.92-3.85 (t, 2H, N-*CH_2*-CH_2-), 3.85-3.55 (t, 2H, =N-*CH_2*-CH_2-), 2.31 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 1.85-1.77 (m, 2H, N-CH_2-*CH_2*-), 1.65-1.50 (m, 2H, =N-CH_2-*CH_2*-), 1.07-1.00 (t, 3H, N-CH_2-CH_2-*CH_3*), 0.70-0.62 ppm (t, 3H, =N-CH_2-CH_2-*CH_3*); ^{13}C nmr ($CDCl_3$): δ 198.48 (C=O, benzoyl), 175.69 (C=O, C-4), 162.79 (C, imino), 151.98 (C-6), 148.60 (C-2), 139.06, 135.48, 132.39, 131.90, 131.42, 131.34, 130.95, 130.77, 130.68, 130.60, 51.89 (N-CH_2-), 51.50 (=N-CH_2-), 33.71 (CH_3), 33.65 (CH_3), 25.89 (N-CH_2-*CH_2*-CH_3), 25.55 (=N-CH_2-*CH_2*-CH_3), 19.48 (N-CH_2-CH_2-*CH_3*), 12.92 ppm (=N-CH_2-CH_2-*CH_3*). Anal. Calcd. for $C_{27}H_{30}N_2O_2$: C, 78.23; H, 7.29; N, 6.76. Found: C, 78.32; H, 7.28; N, 6.75.

3-Benzoyl-1-butyl-5-(1-butyliminoethyl)-6-phenyl-2-methyl-4(1*H*)-pyridinone (2c). Yield 41%, mp 193°C; ir (KBr): (CH, aromatic) 3060, (CH, aliphatic) 2975, (C=O and C=N-) 1693, 1666, 1620 cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.98-7.26 (m, 10H, CH, aromatic), 3.94-3.68 (t, 2H, N-*CH_2*-CH_2-), 3.64-3.60 (t, 2H, =N-*CH_2*-CH_2-), 2.30 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 1.81-1.65 (m, 4H, N-CH_2-*CH_2*-*CH_2*-CH_3), 1.56-1.37 (m, 4H, =N-CH_2-*CH_2*-*CH_2*-CH_3), 1.03-0.96 (t, 3H, N-CH_2-CH_2-CH_2-*CH_3*), 0.72-0.64 ppm (t, 3H, =N-CH_2-CH_2-CH_2-*CH_3*); ^{13}C nmr ($CDCl_3$): δ 198.48 (C=O, benzoyl), 175.67 (C=O, C-4), 175.49 (C, imino), 151.98 (C-6), 148.61 (C-2), 139.09, 135.71, 135.44, 132.39, 131.88, 131.40, 131.32, 131.02, 130.76, 130.58, 51.19 (N-CH_2-), 49.97 (=N-CH_2-), 34.28 (CH_3), 34.13 (CH_3), 21.89 (N-CH_2-*CH_2*-CH_2CH_3), 21.52 (=N-CH_2-*CH_2*-CH_2CH_3), 19.46 (N-CH_2-CH_2-*CH_2*-CH_3 and =N-CH_2-CH_2-*CH_2*-CH_3), 15.57 (-N-CH_2-CH_2-CH_2-*CH_3*), 15.08 ppm (=N-CH_2-CH_2-CH_2-*CH_3*). Anal. Calcd. for $C_{29}H_{34}N_2O_2$: C, 78.70; H, 7.74; N, 6.33. Found: C, 78.65; H, 7.73; N, 6.34.

General Procedures for Pyridinone Derivatives (3a-c). 3,5-dibenzoyl-2,6-diphenyl-4-pyrone **1b** (1 mmol) and amine derivative (2 mmol) were refluxed in 1-butanol for a time between 20 and 40 hours (24 h for **3a**, 20 h for **3b** and 40 h for **3c**). The solvent was evaporated under reduced pressure to give an oily residue which was treated with ether and finally crystallized from ethanol.

3,5-Dibenzoyl-1,2,6-triphenyl-4(1*H*)-pyridinone (3a). Yield 35%, mp 272°C (24 hours); ir (KBr): (CH, aromatic) 3061, (C=O) 1664, 1615 cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.91-6.91 ppm (CH, aromatic); ^{13}C nmr ($CDCl_3$): δ 196.45 (C=O, benzoyl), 175.93 (C=O), 152.29 (C-2), 140.82, 139.32, 135.13, 133.97, 133.07, 132.06, 131.88, 131.33, 130.90, 130.36, 129.73 ppm. Anal. Calcd. for $C_{37}H_{25}NO_3$: C, 83.59; H, 4.74; N, 2.63. Found: C, 83.53; H, 4.75; N, 2.63.

3,5-Dibenzoyl-1-ethyl-2,6-diphenyl-4(1*H*)-pyridinone (3b). Yield 65%, mp 257°C (20 hours); ir (KBr): (CH, aromatic) 3060, (CH, aliphatic) 2950, (C=O) 1677, 1615 cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.81-7.27 (m, 20H, CH, aromatic), 3,67-3.63 (q, 2H, CH_2), 0.92-0.85 ppm (t, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ 196.64 (C=O, benzoyl), 175.27 (C=O), 151.97 (C-2), 139.29, 135.03, 134.21, 133.63, 131.84, 131.33, 131.17, 130.57, 130.33, 47.44 (CH_2), 17.89 ppm (CH_3). Anal. Calcd. for $C_{33}H_{25}NO_3$: C, 81.97; H, 5.21; N, 2.90. Found: C, 81.88; H, 5.22; N, 2.90.

3,5-Dibenzoyl-1-*n*-butyl-2,6-diphenyl-4(1*H*)-pyridinone (3c). Yield 27%, mp 228°C (40 hours); ir (KBr): (CH, aromatic) 3050, (CH, aliphatic) 2932, (C=O) 1677, 1615 cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.82-7.26 (m, 20H, CH, aromatic), 3,56-3.48 (t, 2H, CH_2), 1.39-1.31 (m, 2H, CH_2), 0.73-0.62 (m, 2H, CH_2), 0.43-0.35 ppm (t, 3H, CH_3); ^{13}C nmr ($CDCl_3$): δ 196.62 (C=O, benzoyl), 175.27 (C=O), 152.07 (C-2), 139.35, 135.01, 134.08, 133.73, 131.81, 131.39, 131.18, 130.50, 130.30, 52.06 (CH_2), 34.44 (CH_2), 21.22 (CH_2), 14.70 ppm (CH_3). Anal. Calcd. for $C_{35}H_{29}NO_3$: C, 77.83; H, 7.10; N, 3.40. Found: C, 77.86; H, 7.09; N, 3.39.

General Procedures for Pyridinone Derivatives (3d, 3e). 3-benzoyl-5-ethoxycarbonyl-2,6-diphenyl-4-pyrone **1c** (1 mmol) and amine derivative (2 mmol) were refluxed in 1-butanol for 24 hours. The solvent was evaporated under reduced pressure to give an oily residue which was treated with ether and finally crystallized from ethanol.

3-Benzoyl-5-ethoxycarbonyl-1,2,6-triphenyl-4(1*H*)-pyridinone (3d). Yield 35%, mp 246°C (10 hours); ir (KBr): (CH, aromatic) 3061, (CH, aliphatic) 2981, (C=O) 1730, 1669, 1618 cm^{-1}; ^1H nmr ($CDCl_3$): δ 8.00-6.80 (m, 20 H, CH, aromatic), 4.07-3.96 (q, 2H, CH_2), 0.97-0.88 (t, 3H, CH_3); ^{13}C nmr

($CDCl_3$): δ 196.09 (C=O, benzoyl), 174.00 (C=O, C-4), 167.21 (C=O, ester), 152.08 (C-2), 151.86 (C-6), 140.82, 139.28, 138.41, 135.02, 134.35, 134.01, 133.95, 133.50, 132.05, 132.00, 131.50, 131.05, 131.35, 131.05, 130.49, 130.33, 130.25, 129.91, 63.25 (CH_2), 15.70 ppm (CH_3). Anal. Calcd. for $C_{33}H_{25}NO_3$: C, 81.97; H, 5.21; N, 2.90. Found: C, 81.92; H, 5.22; N, 2.90.

3-Benzoyl-1-ethyl-5-ethoxycarbonyl-2,6-diphenyl-4(1*H*)-pyridinone (3e). Yield 55%, mp 209°C (24 hours); ir (KBr): (CH, aromatic) 3064, (CH, aliphatic) 2976, (C=O) 1734, 1673, 1620 cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.75-7.23 (m, 15H, CH, aromatic), 3.97-3.87 (q, 2H, O-CH_2), 3.64-3.53 (q, 2H, N-CH_2), 1.17-1.10 (t, 3H, O-CH_2-*CH_3*), 0.92-0.81 ppm (t, 3H, N-CH_2-*CH_3*); ^{13}C nmr ($CDCl_3$): δ 196.33 (C=O, benzoyl), 173.96 (C=O, C-4), 167.29 (C=O, ester), 152.87 (C-2), 151.59 (C-6), 139.25, 135.00, 134.21, 134.09, 133.47, 132.05, 131.77, 131.29, 131.13, 130.64, 130.48, 130.27, 129.54, 63.09 (O-CH_2), 60.07 (N-CH_2), 17.75 (O-CH_2-*CH_3*), 15.70 ppm (N-CH_2-*CH_3*). Anal. Calcd. for $C_{29}H_{25}NO_3$: C, 79.98; H, 5.79; N, 3.22. Found: C, 79.95; H, 5.80; N, 3.21.

3,5-Dibenzoyl-2,6-diphenyl-4-hydroxypyridin (4). 3,5-Dibenzoyl-2,6-diphenyl-4-pyrone **1a** (0,46 g, 1 mmol) and excess ammonia were refluxed in ethanol for 72 hours. The solvent was evaporated under reduced pressure to give an oily residue which was treated with ether and finally crystallized from ethanol. Yield 35%, mp 294°C; ir (KBr): (NH) 3375, (b, OH) 3370-2500, (CH, aromatic) 3050, (C=O) 1671, 1617 cm^{-1}; ^1H nmr ($CDCl_3$): δ 11.08 (b, OH), 7.93-7.33 ppm (CH, aromatic). Anal. Calcd. for $C_{31}H_{21}NO_3$: C, 81.74; H, 4.65; N, 3.08. Found: C, 81.70; H, 4.66; N, 3.07.

The Reaction of 1b with Aqueous *n*-Pentylamine. The 4-Pyrone **1b** (0.46 g, 1 mmol) and n-pentylamine derivative (0.23 ml, 2 mmol) were refluxed in butanol for 40 hours. The solvent was evaporated under reduced pressure to give an oily residue which dissolved in aqueous ether. After evaporation of ether, the same residue was dissolved in ethanol (%96), and the solution was allowed to crystallize. After three or four months, red colored big crystals (0.34 g, 76%) consisting of dibenzoylmethane was isolated by filtration; it was identified by comparison of its mp 78°C and TLC with an authentic sample [21].

3,5-Dibenzoyl-2,6-dimethyl-1-pentyl-4(1*H*)-pyridinone (5). 3-Acetyl-5-benzoyl-2-phenyl-6-methyl-4-pyrone **1a** (0.33 g, 1 mmol) and n-pentylamine derivative (0.23 ml, 2 mmol) were refluxed in ethanol for 36 hours. The solvent was evaporated under reduced pressure to give an oily residue which was treated with ether and finally crystallized from ethanol. Yield 35%, mp 210°C; ir (KBr): (CH, aromatic) 3100, (CH, aliphatic) 2956-2928, (C=O) 1670, 1621 cm^{-1}; ^1H nmr ($CDCl_3$): δ 7.90-7.26 (m, 10H, CH, aromatic), 3.98-3.85 (t, 2H, N-CH_2-), 2.30 (s, 6H, CH_3), 1.75-1.71 (m, 2H, N-CH_2-*CH_2*-$CH_2CH_2CH_3$), 1.41-1.34 (m, 4H, N-CH_2-CH_2-*CH_2*-*CH_2*-CH_3), 0.96-0.90 ppm (t, 3H, N-CH_2-CH_2-CH_2-CH_2-*CH_3*); ^{13}C nmr ($CDCl_3$): δ 198.47 (C=O, benzoyl), 175.68 (C=O, C-4), 148.58 (C-2 and C-6), 139.09, 135.44, 132.42, 131.33, 130.58, 50.20 (N-CH_2-), 31.87 (CH_3), 30.70 (N-CH_2-*CH_2*-$CH_2CH_2CH_3$), 24.19 (N-CH_2CH_2-*CH_2*-CH_2CH_3), 19.46 (N-$CH_2CH_2CH_2$-*CH_2*-CH_3), 15.85 ppm (N-$CH_2CH_2CH_2CH_2$-*CH_3*). Anal. Calcd. for $C_{26}H_{21}NO_3$: C, 78.97; H, 5.35; N, 3.54. Found: C, 78.91; H, 5.34; N, 3.55.

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