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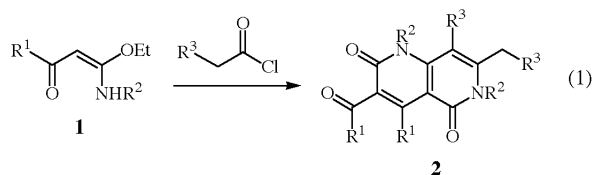
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Novel method for the synthesis of 3-acyl-1,6-dialkyl-7-methyl-1,6-naphthyridine-2,5(1*H*,6*H*)-diones (**2**) was developed. The reaction of 2-acyl-1-alkylamino-1-ethoxyethylenes (**1**) with acetyl chloride or β -keto amide **3** with acetyl chloride in the presence of *p*-toluenesulfonic acid gave **2** in moderate yield (14–59% yield).

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Introduction.

In continuing our studies [1,2] on the utilization of 2-acyl-1-alkylamino-1-ethoxyethylenes (α -oxoketene *O,N*-acetals, **1** [3,4]), prepared easily from CS₂ via β -oxo thionoesters, we are interested in the reaction of **1** with acetyl chloride as an electrophile and found that the reaction of 2-acyl-1-alkylamino-1-ethoxyethylenes (**1**) with acetyl chloride gave 1,6-naphthyridine-2,5(1*H*,6*H*)-diones (**2**). Compound **2** has scarcely been reported in the literature thus far. Herein we wish to describe the preparation of **2** in a single step.



Results and Discussion.

Heating a solution of 4-ethoxy-4-methylamino-3-buten-2-one (**1a**) in acetyl chloride for 6 hours followed by recrystallization of the chromatographically isolated product gave a white powder. Spectroscopic analyses indicated the formation of 3-acetyl-1,4,6,7-tetramethyl-1,6-naphthyridine-2,5(1*H*,6*H*)-dione (**2a**). By single crystal X-ray structure analysis of the product from the

reaction of **1e**, its structure was confirmed as 3-benzoyl-7-methyl-4-phenyl-1,6-dipropyl-1,6-naphthyridine-2,5(1*H*,6*H*)-dione (**2e**) (see Experimental section). Using dichloromethane, benzene, or dimethyl formamide (DMF) as a solvent, lowering the temperature, and/or extending the reaction time resulted in lower yields of the desired products. The representative results using various **1** with acyl chloride are listed in Table 1.

Employing 3-ethoxy-3-methylamino-1-phenyl-2-propen-1-one (**1e**) resulted in the formation of **2e** with a benzoyl substituent on the 3-position of the 1,6-naphthyridine-2,5(1*H*,6*H*)-dione framework and a phenyl substituent on the 4-position. The reaction using propionyl chloride instead of acetyl chloride gave 1,6-naphthyridine-2,5(1*H*,6*H*)-dione derivative (**2f**), which has an ethyl group on the 7-position and a methyl substituent on the 8-position. Although their yields were low, these products demonstrated that the 3- and 4-substituents of **2** came from the starting material **1** and the 7- and 8-substituents came from acyl chloride.

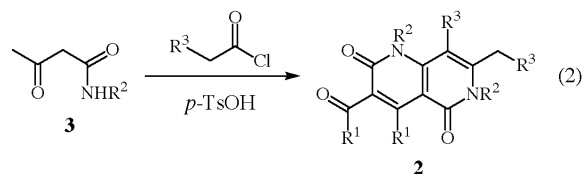
In reaction product **2**, the ethyl group of the ethoxy moiety in **1** was not incorporated. Therefore the use of 3-oxobutanamide **3** was examined (equation 2). The reaction of **3** with acetyl chloride gave **2** in low yield. On the other hand, the reaction of **3** with acetyl chloride in the presence of *p*-toluenesulfonic acid gave **2** in similar or better yields to that of the reaction of **1** with acetyl chloride (Table 1). For example, *N*-propyl-3-oxobutanamide **3b** afforded **2b** in 59% yield.

Table 1

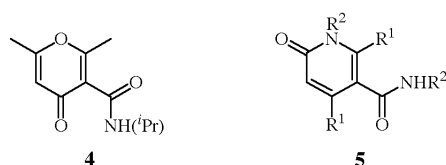
Synthesis of 3-Acyl-1,6-dialkyl-7-methyl-1,6-naphthyridine-2,5(1*H*,6*H*)-diones (**2**) from α -Oxoketene *O,N*-acetals (**1**) or β -Ketoamides (**3**)[a]

entry			R ¹	substrate R ²	R ³		product 2 Yield [b] from 1	Yield [b] from 3
1	1a	3a	CH ₃	CH ₃	H	2a	46	33
2	1b	3b	CH ₃	<i>n</i> -C ₃ H ₇	H	2b	46	59
3	1c	3c	CH ₃	<i>i</i> -C ₃ H ₇	H	2c	8 (34)	4(44)
4	1d	3d	CH ₃	CH ₂ C ₆ H ₅	H	2d	14	30
5	1e		C ₆ H ₅	<i>n</i> -C ₃ H ₇	H	2e	14	
6	1a		CH ₃	CH ₃	CH ₃	2f	15	

[a] Reaction conditions: α -oxoketene *O,N*-acetals (**1**) (4.0 mmol) in acyl chloride (10.0 mL) for 6 hours at reflux temperature or *N*-alkyl-3-oxobutanamide (**3**) (2.0 mmol) and *p*-TsOH (3.0 mmol) in acetyl chloride (10.0 mL) for 6 hours at reflux temperature. [b] Isolated yield based on **1** or **3**. Figures in parentheses show the yield of **4**.



1,6-Naphthyridine-2,5(1*H*,6*H*)-diones are rare compounds in the literature, and there are only few reports dealing with their preparation [5]. For example, 1,6-dimethyl-1,6-naphthyridine-2,5(1*H*,6*H*)-dione was synthesized by the Skraup reaction, alkylation, and then oxidation,[6] while the reaction of ethyl *N*-benzylacetimidate with diketene was demonstrated to give 1,6-naphthyridine-2,5(1*H*,6*H*)-diones in moderate yields [7]. 4-Hydroxy derivatives were also produced from (alkylamino)pyridones [8] or from ethyl β -(alkylamino)-crotonate [9]. Thus, this method for the preparation of **3** may be an alternative.



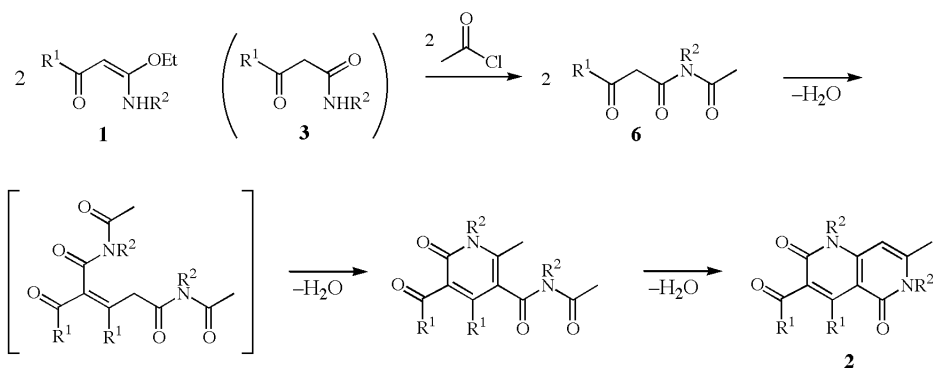
In the case of **1c**, 2,6-dimethyl-3-isopropylamino-carbonyl-4*H*-pyran-4-one (**4**) was obtained in 34% yield accompanied with **2c** in 8% yield. Spectroscopic and X-ray crystallographic analyses revealed the structure of **4**. Kato *et al.* reported that the reaction of amines with diketene gave *N*-alkyl-3-oxobutanamide, pyridone, or pyrone derivatives [10]. In this report, the alkyl substituents on the nitrogen atom affected the type of products, and the substrates with a sterically hindered substituent, such as isopropyl and cyclohexyl, converted to

Table 2 Crystallographic Data of 2e and 4		
	2e	4
chemical formula	C ₂₉ H ₃₂ N ₂ O ₄	C ₁₁ H ₁₅ NO ₃
formula weight	472.58	209.24
crystal	colorless, prismatic	colorless, prismatic
size, mm	0.5 x 0.5 x 0.2	0.2 x 0.1 x 1.0
crystal system	monoclinic	monoclinic
space group	P2 ₁ /c	P2 ₁ /c
<i>a</i> , Å	13.561(3)	9.771(4)
<i>b</i> , Å	14.460(3)	6.972(3)
<i>c</i> , Å	13.626(2)	16.626(3)
β , deg	108.08(1)	94.03(2)
<i>V</i> , Å ³	2540.2(8)	1129.7(6)
<i>Z</i>	4	4
<i>D</i> _{calc} , g/cm ³	1.236	1.230
μ (MoK α), cm ⁻¹	0.82	0.89
radiation, (Å)	Mo, 0.71069 (graphite monochromated)	
scan type	ω -2 θ	ω -2 θ
scan rate, °/min	16	16
scan width, deg	1.89 + 0.30 tan θ	1.78 + 0.30 tan θ
2 θ max, deg	55.0	55.0
no of unique data	6065	2814
no of obsd. (<i>I</i> > 3 σ (<i>I</i>))	2965	1352
<i>R</i>	0.077	0.064
<i>R</i> _w	0.069	0.055
Goodness of Fit	4.68	4.52
Max Shift/Error	0.03	0.00

pyrone derivatives.[10] Our results also agree with the tendency observed in the literature. That is, in the case of substrate **1c**, the only substrate having a sterically hindered isopropyl group, a pyrone derivative was the main product, and a pyrone was not obtained from any other substrates.

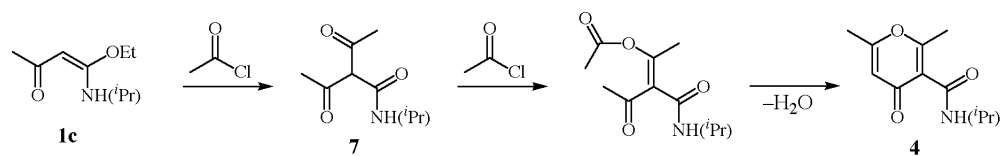
From this reaction we have found the formation of a small amount of 2-pyridone derivative **5**. This compound was considered to be formed from the reaction of **1** with acid generated acetyl chloride and commented in a separate paper.

Scheme 1



Plausible way of formation of 3-acyl-1,6-dialkyl-7-methyl-1,6-naphthyridine-2,5(1*H*,6*H*)-diones (**2**).

Scheme 2



Plausible way of formation of 3-acyl-1,6-dialkyl-7-methyl-1,6-naphthyridine-2,5(1*H*,6*H*)-diones (**2**).

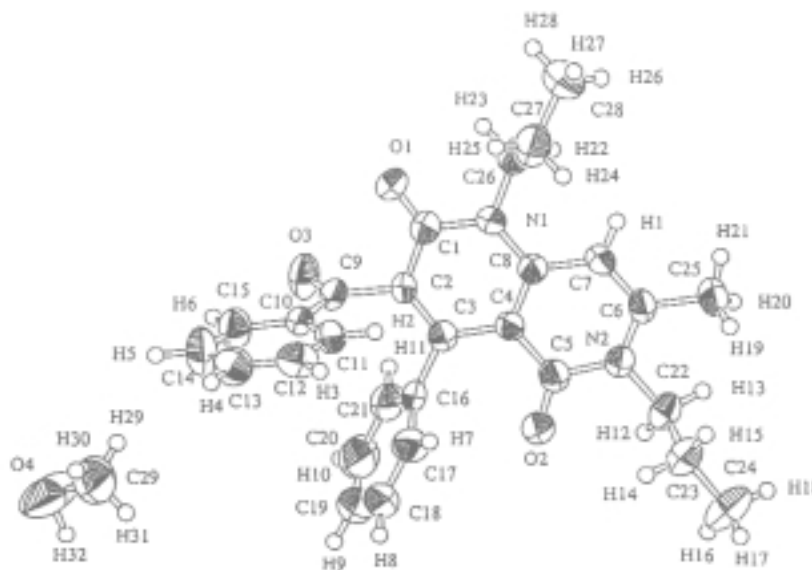


Figure 1. X-Ray structure of 3-Benzoyl-4,7-dimethyl-1,6-dipropyl-1,6-naphthyridine-2,5(1*H*,6*H*)-dione (**2e**).

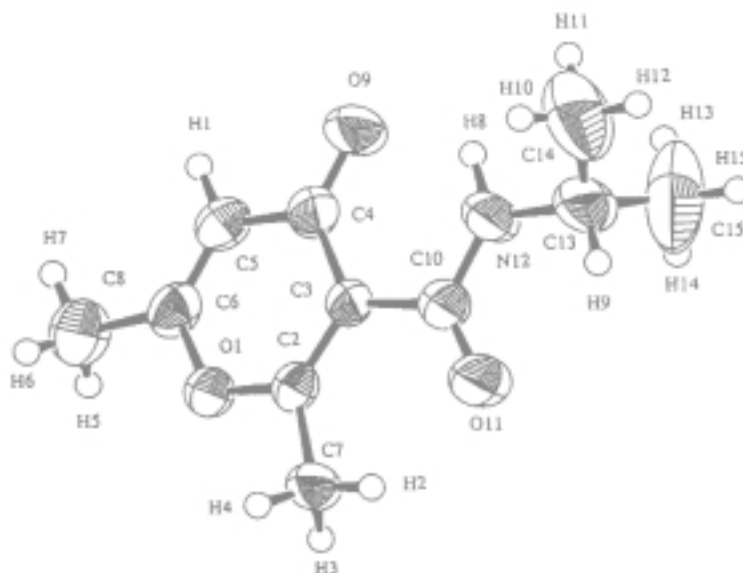


Figure 2. X-Ray structure of 2,6-dimethyl-3-isopropylcarbamoyl-4*H*-pyran-4-one (**4**).

Table 3
Selected Bond Distances and Angles for **2e**

Intramolecular Distances, Å (standard deviation)					
O(1)—C(1)	1.225(5)	O(2)—C(5)	1.222(5)	N(1)—C(1)	1.412(5)
N(1)—C(8)	1.384(5)	N(2)—C(5)	1.399(5)	N(2)—C(6)	1.363(5)
C(1)—C(2)	1.437(6)	C(2)—C(3)	1.358(5)	C(3)—C(4)	1.450(5)
C(4)—C(5)	1.453(5)	C(4)—C(8)	1.380(5)	C(6)—C(7)	1.353(5)
C(7)—C(8)	1.429(5)				
Selected Bond Angles, deg (standard deviation)					
C(1)—N(1)—C(8)	122.6(4)	C(5)—N(2)—C(6)	123.0(4)		
N(1)—C(1)—C(2)	115.0(4)	C(1)—C(2)—C(3)	123.9(4)		
C(2)—C(3)—C(4)	118.5(4)	C(3)—C(4)—C(5)	120.6(4)		
C(3)—C(4)—C(8)	119.1(4)	C(5)—C(4)—C(8)	120.3(4)		
N(2)—C(5)—C(4)	116.1(4)	N(2)—C(6)—C(7)	120.6(4)		
C(6)—C(7)—C(8)	120.1(4)	N(1)—C(8)—C(4)	120.7(4)		
N(1)—C(8)—C(7)	119.7(4)	C(4)—C(8)—C(7)	119.5(4)		

Table 4
Selected Bond Distances and Angles for **4**

Intramolecular Distances, Å (standard deviation)					
O(1)—C(2)	1.364(3)	O(1)—C(6)	1.368(4)	O(9)—C(4)	1.237(4)
C(2)—C(3)	1.350(4)	C(3)—C(4)	1.469(4)	C(4)—C(5)	1.439(4)
C(5)—C(6)	1.319(5)				
Selected Bond Angles, deg (standard deviation)					
C(2)—O(1)—C(6)	120.2(3)	O(1)—C(2)—C(3)	122.7(3)		
C(2)—C(3)—C(4)	118.5(3)	C(3)—C(4)—C(5)	115.4(3)		
C(4)—C(5)—C(6)	122.2(3)	O(1)—C(6)—C(5)	120.9(3)		

A plausible way of formation for **2** is postulated as follows. First, nucleophilic attack of **1** to acetyl chloride occurs to give a monoacetylated intermediate **6**. Self-condensation of intermediate **6** may yield the product **2** (Scheme 1). In the reaction of ethyl *N*-benzylacetimidate with diketene,[7] the condensation of two ethyl *N*-benzylacetimidates occurred first, and then the condensed product reacts with diketene. In our system, GC-MS analysis of the reaction mixture during the course of the reaction indicated that monoacetylated and diacetylated intermediates were formed, before the product was formed, while dimeric compounds of **1** were not observed by GC-MS. Furthermore the reaction of **1** with diketene did not yield any condensation product. Accordingly, we consider *N*-acylation to be the first and key step for this reaction.

Usually the nucleophilic character of an enamine is located on the β -carbon as well as on the nitrogen. In the case of **1c**, a sterically hindered isopropyl group is attached on the nitrogen atom and, therefore, acylation takes place on the β -carbon to give **7** as the major intermediate. Intermediate **7** is then acylated on oxygen of the acetyl

group, followed by an intramolecular cyclization to yield **4**. This is the reason why **1c** underwent conversion to form **4** as the major product and **2c** was formed in low yield.

Conclusions.

2-Acyl-1-alkylamino-1-ethoxyethylenes **1** act as nucleophiles. In the presence of acyl chloride, the nucleophilic nitrogen attacked acyl chloride first, followed by the self-condensation of the acylated intermediate to give 1,6-naphthyridine-2,5(1*H*,6*H*)-diones **2**. In contrast, the sterically hindered isopropyl group on nitrogen underwent reaction with the β -carbon of acyl chloride to give the pyrone derivative **4**. *N*-Alkyl-3-oxobutanamides **3** were used as alternative starting materials for the preparation of **2**.

Acknowledgment.

We thank Dr. Takayuki Yamashita for helpful discussions during the course of this work. This work was partially supported by a research fund from Kyo-eisha Chemical Co., Ltd., and by a grant to RCAST at Doshisha University from the Ministry of Education, Japan.

EXPERIMENTAL

Instrumentation.

Proton nuclear magnetic resonance (^1H NMR) spectra were measured on a JEOL JNM A-400 (400 MHz) spectrometer using tetramethylsilane as an internal standard. IR spectra were measured on a Shimadzu IR-408 spectrometer. Mass spectra (GC-MS) were recorded on a Shimadzu GP2000A instrument. Elemental analyses were performed at the Microanalytical Center of Kyoto University. X-Ray analyses were conducted on a Rigaku RASA-7R four-circle diffractometer. Melting points were measured on a Yanako Model MP and were not corrected.

All solvents were dried by standard methods [11]. Commercially available compounds were used without purification. 2-Acyl-1-alkylamino-1-ethoxyethylenes (**1**) [1] and *N*-alkyl-3-oxobutanamides (**3**) [4,12] were prepared according to literature methods.

Preparation of 1,6-Naphthyridine-2,5(1*H*,6*H*)-diones (**2**).Method A. From 4-Ethoxy-4-methylamino-3-buten-2-one (**1a**) with Acetyl Chloride.

This is a typical procedure for the reaction of 2-acyl-1-alkylamino-1-ethoxyethylenes (**1**) with acyl chloride. In a 25-mL flask equipped with a reflux condenser were introduced 4-ethoxy-4-methylamino-3-buten-2-one (**1a**, 0.57 g, 4.0 mmol) and acetyl chloride (10 mL). The mixture was stirred under reflux for 6 hours and then diluted with ethyl acetate (20 mL). Methanol was added dropwise to this mixture, which was cooled in an ice-water bath to avoid decomposition of acetyl chloride, and then the solvent was removed under reduced pressure. To the resulting mixture was added saturated aqueous sodium hydrogen carbonate (10 mL) and chloroform (30 mL) and the resulting layers were separated. The organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate = 2:3 followed by 1:3) and by recrystallization from methanol to give white solids (**2a**, 0.48 g, 1.8 mmol, 46 % yield).

Method B. From *N*-Propyl-3-oxobutanamide (**3b**) with Acetyl Chloride in the Presence of *p*-Toluenesulfonic Acid.

Typical procedure: In a 25-mL flask having a reflux condenser were added *N*-propyl-3-oxobutanamide (**3b**, 0.29 g, 2.0 mmol), acetyl chloride (10 mL), and *p*-toluenesulfonic acid hydrate (0.57 g, 3.0 mmol). The mixture was heated at reflux for 6 hours. The work-up of the mixture was the same as in the reaction of **1a** with acetyl chloride (*vide ante*). 3-Acetyl-4,7-dimethyl-1,6-dipropyl-1,6-naphthyridine-2,5(1*H*,6*H*)-dione (**2b**) was obtained as a white solid (0.38 g, 1.2 mmol, 59 %). 3-Acetyl-1,6-dibenzyl-4,7-dimethyl-1,6-naphthyridine-2,5(1*H*,6*H*)-dione (**2d**) was identified by comparison of its ^1H NMR and IR spectral data with that in literature.[7]

3-Acetyl-1,4,6,7-tetramethyl-1,6-naphthyridine-2,5(1*H*,6*H*)-dione (**2a**).

Compound **2a** has mp 239.0-240.5 °C; IR (KBr) 1595 (br), 1688; MS (*m/z*) 268; ^1H NMR (deuteriochloroform): δ 2.47 (3H, s, CH_3), 2.51 (3H, s, CH_3), 2.60 (3H, s, CH_3), 3.51 (3H, s, NCH_3), 3.58 (3H, s, NCH_3), 7.42 (1H, s, $-\text{CH}=\text{}$).

Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3$: C, 64.60; H, 6.20; N, 10.76%. Found: C, 64.67; H, 6.14; N, 10.59%.

3-Acetyl-4,7-dimethyl-1,6-dipropyl-1,6-naphthyridine-2,5(1*H*,6*H*)-dione (**2b**).

Compound **2b** has mp 136.5-136.8 °C; IR (KBr) 1615 (br), 1699; MS (*m/z*) 316; ^1H NMR (deuteriochloroform): δ 1.01 (3H, t, $J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.02 (3H, t, $J = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.66-1.77 (4H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.48 (3H, s, CH_3), 2.50 (3H, s, CH_3), 2.61 (3H, s, CH_3), 3.94 (2H, t, $J = 8.0$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 4.09 (2H, t, $J = 7.8$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 6.04 (1H, s, $-\text{CH}=\text{}$).

Anal. Calcd. for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_3$: C, 68.33; H, 7.65; N, 8.85%. Found: C, 68.39; H, 7.58; N, 8.94%.

3-Acetyl-1,6-diisopropyl-4,7-dimethyl-1,6-naphthyridine-2,5(1*H*,6*H*)-dione (**2c**).

Compound **2c** has mp 173.0-173.5 °C; IR (KBr) 1600 (br), 1698; MS (*m/z*) 316; ^1H NMR (deuteriochloroform): δ 1.59 (6H, d, $J = 7.2$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.65 (6H, d, $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 2.47 (3H, s, CH_3), 2.49 (3H, s, CH_3), 2.56 (3H, s, CH_3), 4.54 (1H, br, $\text{NCH}(\text{CH}_3)_2$), 6.18 (1H, s, $-\text{CH}=\text{}$).

Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_3$: C, 68.33; H, 7.65; N, 8.85%. Found: C, 68.04; H, 7.57; N, 8.88%.

3-Isopropylcarbamoyl-2,6-dimethyl-4*H*-pyran-4-one (**4**).

Compound **4** has mp 93.5-94.0 °C; IR (KBr) 1682, 1639 cm^{-1} ; MS (*m/z*) 209; ^1H NMR (deuteriochloroform): δ 1.23 (6H, d, $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 2.29 (3H, s, CH_3), 2.80 (3H, s, CH_3), 4.17 (1H, octet, $J = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 6.21 (1H, s, $-\text{CH}=\text{}$), 9.56 (1H, br, NH).

Anal. Calcd. for $\text{C}_{11}\text{H}_{15}\text{NO}_3$: C, 63.15; H, 7.18 ; N, 6.70%. Found: C, 63.12; H, 7.10; N, 6.67%.

3-Benzoyl-7-methyl-4-phenyl-1,6-dipropyl-1,6-naphthyridine-2,5(1*H*,6*H*)-dione (**2e**).

Compound **2e** has mp 221.5-222.0 °C; IR (KBr) 1615 (br), 1675 (shoulder); ^1H NMR (deuteriochloroform): δ 0.89 (3H, t, $J = 7.4$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.05 (3H, t, $J = 7.6$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.61 (2H, sextet, $J = 7.5$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.81 (2H, sextet, $J = 7.6$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.50 (3H, s, CH_3), 3.84 (2H, t, $J = 7.8$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 4.17 (2H, t, $J = 8.0$ Hz, $\text{NCH}_2\text{CH}_2\text{CH}_3$), 6.16 (1H, s, $-\text{CH}=\text{}$), 7.08~7.70 (10H, m, Ar).

Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{N}_2\text{O}_3 \cdot \text{CH}_3\text{OH}$: C, 73.71; H, 6.83; N, 5.93%. Found: C, 73.98; H, 6.73; N, 5.97%.

3-Acetyl-7-ethyl-4,8-dimethyl-1,6-dipropyl-1,6-naphthyridine-2,5(1*H*,6*H*)-dione (**2f**).

Compound **2f** was obtained as an oily material: IR (neat) 1620, 1692 cm^{-1} ; MS (*m/z*) 344; ^1H -NMR (deuteriochloroform): δ 0.81 (3H, t, $J = 7.4$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.98 (3H, t, $J = 7.4$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.24 (3H, t, $J = 7.4$ Hz, CH_2CH_3), 1.63-1.76 (4H, m, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.22 (3H, s, CH_3), 2.50 (3H, s, CH_3), 2.59 (3H, s, CH_3), 2.77 (2H, q, $J = 7.4$ Hz, CH_2CH_3), 4.01 (2H, t, $J = 7.8$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$), 4.10 (2H, t, $J = 7.6$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_3$).

Anal. Calcd. for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{O}_3$: C, 69.74; H, 8.19 ; N, 8.13%. Found: C, 68.44; H, 8.56; N, 7.57%.

GC-MS Analysis of the Reaction Mixture in the Reaction of 4-Ethoxy-4-propylamino-3-buten-2-one (**1b**) with Acetyl Chloride.

In a 25-mL flask equipped with a reflux condenser were introduced 4-ethoxy-4-propylamino-3-buten-2-one (**1b**, 0.69 g, 4.0 mmol) and acetyl chloride (10 mL). The mixture was stirred under reflux for 1 hour and then diluted with ethyl acetate (20 mL). Methanol was added dropwise to this mixture, which was cooled in an ice-water bath to avoid decomposition of acetyl chloride, and then the solvent was removed under reduced pressure. To the resulting mixture was added saturated aqueous sodium hydrogen carbonate (10 mL) and chloroform (30 mL) and the resulting layers were separated. The organic layer was dried over anhydrous sodium sulfate and then analyzed by GC-MS. GC-MS (initial column temperature 100 °C for 3 minutes; heating to 280 °C at 20 °C/minute; hold 6 minutes at 280 °C) (m/z) 143 (8.8 min, M⁺ for **1b** - C₂H₄), 171 (10.5 minutes, M⁺ for **1b**), 184 (13 minutes, (M - H)⁺ for **1b** - C₂H₄ + CH₃CO - H), 213 (17 minutes, M⁺ for **1b** + CH₃CO - H), and 255 (18.5 min, M⁺ for **1b** + 2CH₃CO - 2H).

Crystallographic Data Collections and Structure Determination of **2e** and **4**.

The crystals of **2e** and **4** suitable for X-ray diffraction studies were prepared by recrystallization from methanol. Relevant crystal and data statistics are summarized in Table 2. The unit cell parameter at 20 °C was determined by a least-squares fit to 2 θ values of 10 strong higher reflections. Three standard reflections were chosen and monitored every 150 reflections and showed no significant intensity decay during the data collection (less than 2.5% for **2e** and 3% for **4**). The crystal structure was solved by the direct method (Multan) and refined by the full-matrix least squares method. Measured non-equivalent reflections with $I > 3.0\sigma(I)$ were used for the structure determination. In the subsequent refinement the function $\sum \omega(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors amplitudes, respectively. The agreement indices are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum \omega(|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}$ where $\omega^{-1} = \sigma^2(F_o) = \sigma^2(F_o^2) / (4F_o^2)$. For both **2e** and **4**, the positions of all atoms except hydrogen were found

from a difference Fourier electron density map and the positions of hydrogen atoms were determined by calculation, and then refined anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms. All calculations were performed using the teXsan crystallographic software package [13]. Structure of **2e** and **4** are shown in Figure 1 and 2, respectively. Selected bond distances and angles are summarized in Table 3 for **2e** and Table 4 for **4**.

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