Photoaddition Reaction of Pyrroles and Indoles to *N*-Methyl-2-pyridone

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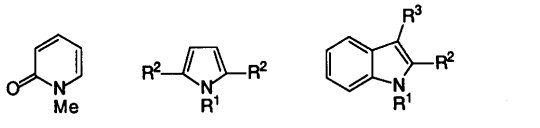
Photoaddition reactions of pyrroles (2—4) and indoles (5—8) to *N*-methyl-2-pyridone (1) have been investigated. The reaction occurred primarily by way of addition of the C_2-H bond of the pyrrole ring and the C_3-H bond of the indole ring to the pyridone nucleus, yielding 4-substituted 3,4-dihydro-1-methylpyridin-2(1*H*)-ones (9 from pyrrole; 13 and 17 from indoles) and 6-substituted 3,6-dihydro-1-methylpyridin-2(1*H*)-ones (10 from pyrrole; 14 and 18 from indoles). The presence of a methyl group(s) at the reactive site(s) of pyrrole and indole resulted in the formation of the products arising from the addition of the C_3-H bond of the pyrrole ring, and the N_1-H, C_2-H and C_6-H bonds of the indole ring. *N*-Methylpyrrole (4) and *N*-methylindole (8) did not give any detectable amount of the addition product.

Keywords photoaddition reaction; *N*-methyl-2-pyridone; indole; pyrrole; 3,4-dihydropyridin-2(1*H*)-one; 3,6-dihydropyridin-2(1*H*)-one; spin density

The single-electron transfer (SET) process in organic photochemistry has attracted much attention with the aim of discovering synthetically useful processes.[1] Recently we have shown that irradiation of *N*-alkyl-2-pyridones in the presence of *tert*-aliphatic amines gives rise to the 1,2- and 1,4-addition of an α-C–H bond in the amines to the 2-pyridone nucleus to yield 4-aminated 3,4-dihydropyridin-2(1*H*)-ones and 6-aminated 3,6-dihydropyridin-2(1*H*)-ones.[2] The application of the photoaddition reaction to an intramolecular reaction provided an effective transformation of cytisine-type lupin alkaloids to tsukushinamine-type alkaloids.[3] The photoreaction is presumed to proceed *via* an SET process from the amines to the 2-pyridone ring, followed by proton transfer and combination of the resulting radicals. It was thought that the mechanism may also be applicable to reaction of 2-pyridones and π-excessive heterocycles such as pyrrole and indole derivatives, which have oxidation potentials that are low enough to allow electron transfer to the 2-pyridone nucleus in its excited state. Indoles and pyrroles are important structural units of alkaloids or biologically active compounds. Direct introduction of an indole or a pyrrole moiety onto a 2-pyridone ring might provide a useful method for the preparation of synthetic intermediates. Here we describe the scope and the synthetic value of the photoaddition reaction of pyrroles and indoles to *N*-methyl-2-pyridone (**1**).

The photoreactions were conducted on degassed acetonitrile (CH_3CN) solutions of the π-excessive aromatic heterocycles **2**—**8** (1.2 M) and **1** (0.024 M) by external irradiation with a 400 W high-pressure mercury lamp through a Pyrex filter. Reaction products (Chart 2) were isolated by column chromatography on silica gel. Product distribution and yields are recorded in Table I. Structural assignments of the products were made by using spectroscopic data, mainly proton magnetic resonance (^{1}H-NMR) spectra. The ^{1}H-NMR assignments were established by comparison with those of the starting heterocycles and the previously reported aliphatic amine-2-pyridone photoadducts.[2,3]

Irradiation of *N*-methyl-2-pyridone (**1**) with pyrrole (**2**) gave two 1 : 1 adducts **9** and **10** in 19% and 23% isolated yields, respectively, together with the valence isomer of **1**, so-called photopyridone. The high-resolution electron impact mass (HR-EI-MS) spectra of **9** and **10** showed the M^+ ion peak at *m/z* 176.0948 and 176.0944 ($C_{10}H_{12}N_2O$),

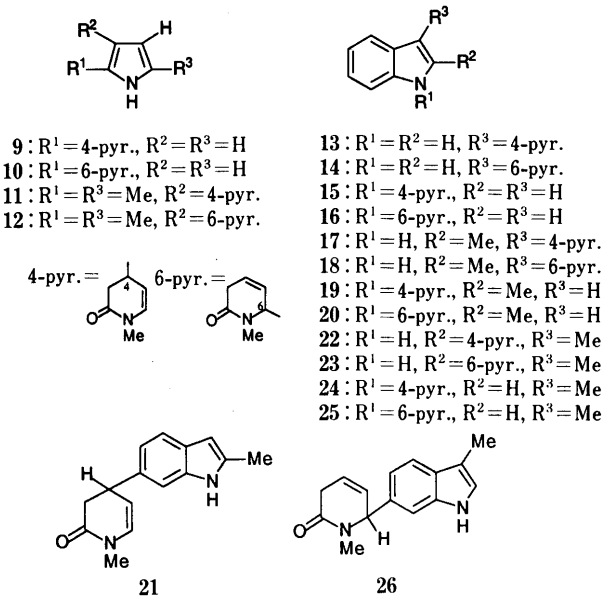


1

2 : R^1=R^2=H
3 : R^1=H, R^2=Me
4 : R^1=Me, R^2=H

5 : R^1=R^2=R^3=H
6 : R^1=H, R^2=Me, R^3=H
7 : R^1=R^2=H, R^3=Me
8 : R^1=Me, R^2=R^3=H

Chart 1



9 : R^1=4-pyr., R^2=R^3=H
10 : R^1=6-pyr., R^2=R^3=H
11 : R^1=R^3=Me, R^2=4-pyr.
12 : R^1=R^3=Me, R^2=6-pyr.

13 : R^1=R^2=H, R^3=4-pyr.
14 : R^1=R^2=H, R^3=6-pyr.
15 : R^1=4-pyr., R^2=R^3=H
16 : R^1=6-pyr., R^2=R^3=H
17 : R^1=H, R^2=Me, R^3=4-pyr.
18 : R^1=H, R^2=Me, R^3=6-pyr.
19 : R^1=4-pyr., R^2=Me, R^3=H
20 : R^1=6-pyr., R^2=Me, R^3=H
22 : R^1=H, R^2=4-pyr., R^3=Me
23 : R^1=H, R^2=6-pyr., R^3=Me
24 : R^1=4-pyr., R^2=H, R^3=Me
25 : R^1=6-pyr., R^2=H, R^3=Me

4-pyr.= 6-pyr.=

21 26

Chart 2

TABLE I. Photoaddition Products from Irradiation of **1** with Pyrroles (**2**—**3**) and Indoles (**5**—**7**)

Pyrroles or indoles	Products and yields (%)[a]				
2	**9** (19)	**10** (23)			
3	**11** (9)	**12** (19)			
5	**13** (16)	**14** (41)	**15** (12)	**16** (7)	
6	**17** (15)	**18** (56)	**19** (10)	**20** (13)	**21** (1)
7	**22** (1)	**23** (9)	**24** (6)	**25** (21)	**26** (6)

a) Isolated yields.

respectively, indicating that both **9** and **10** are 1 : 1 addition products of **1** and **2**. The infrared (IR) spectra of **9** and **10** exhibited the presence of a pyrrole N–H (3500 cm^{-1}) and a lactam carbonyl (1650, 1630 cm^{-1}, respectively). The ^{1}H-NMR spectra of **9** and **10** revealed the presence of a 2-substituted pyrrole moiety in the molecules. The remaining signals in the ^{1}H-NMR spectra of **9** and **10** were in accordance with the corresponding signals of a 4-substituted 3,4-dihydro-1-methylpyridin-2(1*H*)-one structure and a 6-substituted 3,6-dihydro-1-methylpyridin-2(1*H*)-one structure, respectively.[2] As a result, adducts **9** and **10** were assigned as 3,4-dihydro-1-methyl-4-(2′-pyrrolyl)pyridin-2(1*H*)-one and 3,6-dihydro-1-methyl-6-(2′-pyrrolyl)pyridin-2(1*H*)-one, respectively. Thus, the photoreaction of **1** with **2** gave the products which resulted from the 1,2- (**9**) and 1,4-addition (**10**) of the C_2-H bond of **2** to the 2-pyridone nucleus.

Similarly, irradiation of **1** with 2,5-dimethylpyrrole (**3**), indole (**5**), 2-methylindole (**6**), and 3-methylindole (**7**) yielded the corresponding 1 : 1 adducts **11** and **12**, **13**—**16**, **17**—**21**, and **22**—**26**, respectively, in 1—56% isolated yields (Table I).

The photoreaction of **1** and **3**, in contrast to the case of **2**, gave rise to the addition of the C_3-H of **3** to the 2-pyridone ring to yield the adducts **11** and **12** in 9% and 19% yields, respectively. However, no addition product was detected on irradiation of **1** with *N*-methylpyrrole (**4**).

Irradiation of **1** in the presence of **5** produced four adducts **13** (16%), **14** (41%), **15** (12%) and **16** (7%), arising from the 1,2- and 1,4-addition of the C_3-H and the N_1-H bond of **5** to the 2-pyridone nucleus. The similar adducts **17** (15%), **18** (56%), **19** (10%) and **20** (13%) were formed on the photoreaction of **1** with **6**. The major products **14** and **18** were both due to the 1,4-addition of the C_3-H bond of the indoles **5** and **6**. When **1** was irradiated with **7**, the N_1-H bond addition products **24** (6%) and **25** (21%) were mainly produced and the C_2-H bond addition products **22** (trace) and **23** (9%) were minor. The C_6-H addition also occurred in the photoreactions of **1** with **6** and **7** to give **21** (trace) and **26** (6%), respectively. *N*-Methylindole (**8**) also did not give any detectable amount of the addition product in the photoreaction with **1**.

The photoaddition reaction of the π-excessive nitrogen heterocycles to **1** showed some regioselectivities with regard to the position of reaction. The addition of **2** and **5** occurred exclusively on the 4 and 6 positions of **1**, in analogy with the photoreaction of the *tert*-aliphatic amine-2-pyridone system.[2] These positions are consistent with the site of the highest spin density in the ketyl radical of **1**.[4] On the other hand, the addition to **1** took place primarily on the 2 position of **2** and the 3 position of **5**. These reactive sites correspond to the carbon atoms of the highest spin density in pyrryl and indolyl radicals (Fig. 1).[5] The presence of substituents at the 2 and 5 positions of **2**, such as **3**, and of a substituent at the 3 position of **5**, such as **7**, resulted in attack by the atoms of next highest spin density of the pyrryl and indolyl radicals to the 2-pyridone ring, namely C-3 or C-4 of **3** and N-1 and C-6 of **7**. It is of interest that the addition occurred on the benzene ring (C-6) of the indole nucleus in the reaction of **1** with **6** and **7** to give **21** and **27**, respectively. In addition, the pyrrole and indole derivatives lacking the N–H group such as **4** and **8** did not give the addition

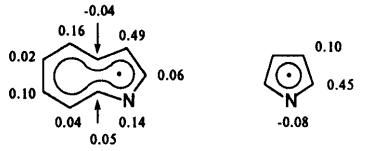


Fig. 1. Spin Densities of Pyrryl and Indolyl Radicals

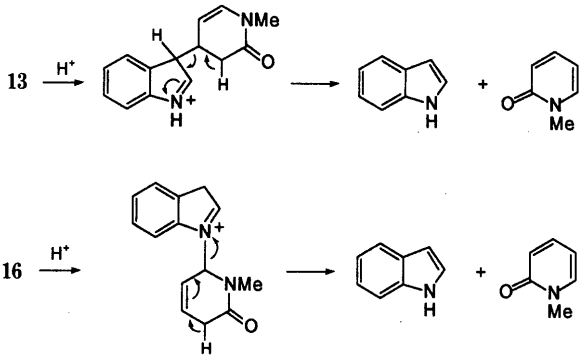


Chart 3

products, suggesting that the photoaddition reaction must involve a proton transfer process. From the above discussion, the photoreaction was presumed to proceed *via* an electron transfer from the π-excessive heterocycles to **1**, followed by proton transfer and combination of the resulting radicals.

Adducts **13**, **16** and **25** decomposed to the starting indole and **1** when they were dissolved in $CDCl_3$. These fragmentations can be explained through protonation of the indole nucleus by a trace amount of an acid in $CDCl_3$ as shown in Chart 3.

Experimental

Melting points were determined on a Yanagimoto micro melting apparatus and are uncorrected. IR spectra were recorded on a Hitachi 215 grating IR spectrometer. ^{1}H- and ^{13}C-NMR spectra were measured with a JEOL JNM-GX 400 or a JEOL JNM-GSX 270 spectrometer, and chemical shifts (δ) are given in parts per million (ppm) down field from tetramethylsilane as an internal standard. Coupling constants (*J*) are given in hertz (Hz); s, d, t, q, m and br indicate singlet, doublet, triplet, quartet, multiplet and broad, respectively. Mass spectra were taken on a JEOL D-300 instrument. Column chromatography was performed with silica gel 60 (Merck, 70—230 mesh or 230—400 mesh) using CH_2Cl_2–MeOH solvent systems. A Riko 400 W high-pressure mercury lamp was used as the irradiation source. *N*-Methyl-2-pyridone (**1**), pyrroles (**2**—**4**) and indoles (**5**—**8**) were obtained commercially and purified by distillation or recrystallization before use. CH_3CN was purified by distillation on CaH_2 after being stirred with CaH_2 for 3 d at room temperature.

General Procedure for the Photochemical Reactions A solution of **1** (40 mg, 0.37 mmol) and a π-excessive heterocycle (**2**—**8**) (18.3 mmol, 50 mol eq) in dry CH_3CN (15 ml) was flushed with N_2 for 30 min. The solution was irradiated externally for 8 h under N_2 through a Pyrex filter with a 400 W high-pressure mercury lamp. After removal of the solvent, the reaction mixture was separated by repeated column chromatography on silica gel with CH_2Cl_2–MeOH solvent systems to yield the photoaddition products.

Photoreaction of 1 with 2 Adducts **9** (12 mg) and **10** (15 mg) were obtained together with the photopyridone (10 mg) and the starting **1** (20 mg). 3,4-Dihydro-1-methyl-4-(2′-pyrrolyl)pyridin-2(1*H*)-one (**9**): colorless oil, IR (CCl_4): 3500 (pyrrolyl NH), 1650 (lactam C=O) cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 2.99 (3H, s, N_1-CH_3), 2.53 (1H, dd, *J* = 15.9, 7.4 Hz, 3-H), 2.74 (1H, dd, *J* = 15.9, 7.0 Hz, 3-H′), 3.76 (1H, m, 4-H), 5.25 (1H, dd, *J* = 7.9, 4.6 Hz, 5-H), 6.19 (1H, dd, *J* = 7.9, 1.2 Hz, 6-H), 8.90 (1H, br, N_1-H), 5.93 (2H, m, 3′-H, 4′-H), 6.62 (1H, dd, *J* = 4.3, 2.4, 5′-H). EI-MS *m/z*: 176.0948 (M^+, Calcd for $C_{10}H_{12}N_2O$: 176.0950, 100), 147 (33), 133 (66), 118 (22). 3,6-Dihydro-1-methyl-6-(2′-pyrrolyl)pyridin-2(1*H*)-one

(**10**): colorless crystals from C_6H_6, mp 154—155 °C. IR (CCl_4): 3500 (pyrrolyl NH), 1625 (lactam C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.88 (3H, s, N_1-CH_3), 3.03 (1H, dm, J=22.4 Hz, 3-H), 3.11 (1H, dm, J=22.4 Hz, 3-H'), 5.76 (1H, dm, J=10.4 Hz, 4-H), 5.81 (1H, dm, J=10.4 Hz, 5-H), 5.02 (1H, dd, J=7.6, 3.2 Hz, 6-H), 9.07 (1H, br, $N_{1'}$-H), 6.14 (2H, m, 3'-H and 4'-H), 6.78 (1H, dd, J=4.2, 2.5 Hz, 5'-H). EI-MS m/z: 176.0944 (M^+, Calcd for $C_{10}H_{12}N_2O$: 176.0950, 100), 145 (32), 133 (38), 118 (84). *Anal.* Calcd for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90. Found: C, 68.10; H, 6.82; N, 15.81.

Photoreaction of 1 with 3 Adducts **11** (8 mg) and **12** (14 mg) were obtained together with the photopyridone (12 mg) and the starting **1** (22 mg). 3,4-Dihydro-1-methyl-4-(3'-2,5-dimethylpyrrolyl)pyridin-2(1*H*)-one (**11**): colorless crystals from C_6H_6, mp 119—121 °C. IR (CCl_4): 3500 (pyrrolyl NH), 1650 (lactam C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.02 (3H, s, N_1-CH_3), 2.48 (1H, dd, J=16.5, 7.5 Hz, 3-H), 2.62 (1H, dd, J=16.5, 10.4 Hz, 3-H'), 3.56 (1H, m, 4-H), 5.11 (1H, dd, J=7.9, 3.7 Hz, 5-H), 5.95 (1H, dd, J=7.9, 2.4 Hz, 6-H), 7.44 (1H, br, $N_{1'}$-H), 2.08 (3H, s, 2'-CH_3), 5.58 (1H, d, J=2.4 Hz, 4'-H), 2.16 (3H, s, 5'-CH_3). EI-MS m/z: 204 (M^+, 100), 189 (48), 161 (35), 147 (44), 132 (21), 120 (28). *Anal.* Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.72. Found: C, 70.53; H, 7.90; N, 13.61. 3,6-Dihydro-1-methyl-6-(3'-2,5-dimethylpyrrolyl)pyridin-2(1*H*)-one (**12**): colorless crystals from C_6H_6, mp 163—164 °C. IR ($CHCl_3$): 3495 (pyrrolyl NH), 1620 (lactam C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.84 (3H, s, N_1-CH_3), 3.04 (2H, m, 3-H_2), 5.69 (2H, m, 4-H, 5-H), 4.80 (1H, m, 6-H), 7.65 (1H, br, $N_{1'}$-H), 2.18 (3H, s, 2'-CH_3), 5.30 (1H, d, J=3.1, 4'-H), 2.18 (3H, s, 5'-CH_3). EI-MS m/z: 204 (M^+, 100), 189 (40), 161 (28), 146 (78), 132 (52), 109 (50). *Anal.* Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.90; N, 13.72. Found: C, 70.71; H, 7.95; N, 13.73.

Photoreaction of 1 with 4 The column chromatographic separation of the reaction mixture gave no addition product. The starting **1** (29 mg) and the photopyridone (6 mg) were isolated.

Photoreaction of 1 with 5 Adducts **13** (13 mg), **14** (34 mg), **15** (10 mg) and **16** (6 mg) were isolated from the reaction mixture. 3,4-Dihydro-4-(3'-indolyl)-1-methylpyridin-2(1*H*)-one (**13**): colorless oil. IR (CCl_4): 3505 (indolyl NH), 1660 (lactam C=O) cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 3.02 (3H, s, N_1-CH_3), 2.67 (1H, dd, J=15.9, 7.3 Hz, 3-H), 2.81 (1H, dd, J=15.9, 7.3 Hz, 3-H'), 4.03 (1H, m, 4-H), 5.38 (1H, dd, J=8.0, 4.9 Hz, 5-H), 6.22 (1H, dd, J=8.0, 1.3 Hz, 6-H), 9.05 (1H, br, $N_{1'}$-H), 7.04 (1H, m, 2'-H), 7.58 (1H, d-like, J=8.0 Hz, 4'-H), 7.0—7.18 (2H, m, 5'-H, 6'-H), 7.39 (1H, d-like, J=7.9 Hz, 7'-H). EI-MS m/z: 226.1106 (M^+, Calcd for $C_{14}H_{14}N_2O$: 226.1107, 100), 197 (44), 183 (53), 168 (20). At 15 min after the dissolution of **13** in $CDCl_3$, the ^{1}H-NMR spectrum showed signals due to the 1:1 mixture of **1** and **5**, which were also identified by thin layer chromatography (TLC). 3,6-Dihydro-6-(3'-indolyl)-1-methylpyridin-2(1*H*)-one (**14**): colorless crystals from CH_2Cl_2, mp 209—211 °C. IR (KBr): 3500 (indolyl NH), 1610 (lactam C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.90 (3H, s, N_1-CH_3), 3.17 (2H, m, 3-H_2), 5.80 (2H, m, 4-H, 5-H), 5.25 (1H, m, 6-H), 8.29 (1H, br, $N_{1'}$-H), 7.10—7.24 (3H, m, 2'-H, 5'-H, 6'-H), 7.50 (1H, d-like, J=8.0 Hz, 4'-H), 7.39 (1H, d-like, J=8.0 Hz, 7'-H). EI-MS m/z: 226.1106 (M^+, Calcd for $C_{14}H_{14}N_2O$: 226.1107, 100), 183 (27), 168 (62), 130 (20), 109 (37). *Anal.* Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.02; H, 6.23; N, 12.34. 3,4-Dihydro-4-(1'-indolyl)-1-methylpyridin-2(1*H*)-one (**15**): colorless oil. IR (CCl_4): 1680 (lactam C=O) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.16 (3H, s, N_1-CH_3), 3.00 (2H, m, 3-H_2), 5.3—5.4 (2H, m, 4-H, 5-H), 6.34 (1H, d, J=6.6 Hz, 6-H), 7.12 (1H, d, J=3.0 Hz, 2'-H), 6.50 (1H, d, J=3.0 Hz, 3'-H), 7.62 (1H, d-like, J=7.8 Hz, 4'-H), 7.10—7.24 (2H, m, 5'-H, 6'-H), 7.34 (1H, d-like, J=8.3 Hz, 7'-H). EI-MS m/z: 226.1104 (M^+, Calcd for $C_{14}H_{14}N_2O$: 226.1107, 3), 117 (100), 110 (28), 109 (28). 3,6-Dihydro-6-(1'-indolyl)-1-methylpyridin-2(1*H*)-one (**16**): colorless oil. IR (CCl_4): 1655 (C=O) cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 2.63 (3H, s, N_1-CH_3), 3.09 (1H, dddd, J=22.7, 3.7, 3.7, 1.5 Hz, 3-H), 3.22 (1H, dddd, J=22.7, 3.2, 3.2, 2.4 Hz, 3-H'), 6.08 (1H, m, 4-H), 5.82 (1H, m, 5-H), 6.31 (1H, m, 6-H), 7.24, (1H, d, J=3.4 Hz, 2'-H), 6.56 (1H, d, J=3.4 Hz, 3'-H), 7.61 (1H, d-like, J=7.6 Hz, 4'-H), 7.08—7.22 (2H, m, 5'-H, 6'-H), 7.42 (1H, d-like, J=8.3 Hz, 7'-H). EI-MS m/z: 226.1107 (M^+, Calcd for $C_{14}H_{14}N_2O$: 226.1107, 1), 117 (100), 110 (25), 109 (28). At 15 min after the dissolution of **16** in $CDCl_3$, the ^{1}H-NMR spectrum showed signals due to the 1:1 mixture of **1** and **5**, which were also identified by TLC.

Photoreaction of 1 with 6 Adducts **17** (13 mg), **18** (37 mg), **19** (9 mg), **20** (13 mg) and **21** (trace) were isolated. 3,4-Dihydro-1-methyl-4-[3'-(2'-methylindolyl)]pyridin-2(1*H*)-one (**17**): colorless oil. IR (CCl_4): 3490 (indolyl NH), 1650 (lactam C=O) cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 3.07 (3H, s, N_1-CH_3), 2.55 (1H, dd, J=16.1, 12.7 Hz, 3-H), 2.74 (1H, ddd, J=16.1, 7.1, 1.2 Hz, 3-H'), 4.09 (1H, dddd, J=12.7, 7.1, 2.9, 2.9 Hz, 4-H), 5.22 (1H, ddd, J=7.8, 2.9, 1.2 Hz, 5-H), 6.23 (1H, dd, J=7.8, 2.9 Hz, 6-H), 8.99 (1H, br, $N_{1'}$-H), 2.34 (3H, s, 2'-CH_3), 7.50 (1H, d-like, J=7.8, 4'-H), 6.92—7.06 (2H, m, 5'-H, 6'-H), 7.27 (1H, d-like, J=8.1 Hz, 7'-H), EI-MS m/z: 240.1261 (M^+, Calcd for $C_{15}H_{16}N_2O$: 240.1264, 100), 225 (58), 197 (37), 183 (52), 168 (30). 3,6-Dihydro-1-methyl-6-[3'-(2'-methylindolyl)]-pyridin-2(1*H*)-one (**18**): colorless crystals from C_6H_6, mp 213—214°C. IR (KBr): 3500 (indolyl NH), 1600 (lactam C=O) cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 2.68 (3H, s, N_1-CH_3), 3.06 (1H, dm, J=22.4 Hz, 3-H), 3.10 (1H, dm, J=22.4 Hz, 3-H'), 5.78 (1H, dddd, J=10.3, 3.7, 3.7, 2.0 Hz, 4-H), 5.68 (1H, dddd, J=10.3, 3.7, 2.0, 2.0 Hz, 5-H), 5.29 (1H, m, 6-H), 9.18 (1H, br, $N_{1'}$-H), 2.39 (3H, s, 2'-CH_3), 7.31 (1H, d-like, J=8.1 Hz, 4'-H), 6.95—7.07 (2H, m, 5'-H,6'-H), 7.26 (1H, d-like, J=7.8 Hz, 7'-H). EI-MS m/z: 240.1261 (M^+, Calcd for $C_{15}H_{16}N_2O$: 240.1264, 100), 225 (30), 183 (21), 168 (47), 109 (22). *Anal.* Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.86; 6.75; N, 11.64. 3,4-Dihydro-1-methyl-4-[1'-(2'-methylindolyl)]pyridin-2(1*H*)-one (**19**): colorless oil. IR (CCl_4): 1660 (lactam C=O) cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 3.10 (3H, s, N_1-CH_3), 2.78 (1H, ddd, J=17.1, 8.3, 1.0 Hz, 3-H), 2.99 (1H, dd, J=17.1, 11.2 Hz, 3-H'), 5.52 (1H, dddd, J=11.2, 8.3, 2.9, 2.7 Hz, 4-H), 5.25 (1H, ddd, J=8.1, 2.9, 1.0 Hz, 5-H), 6.33 (1H, dd, J=8.1, 2.7 Hz, 6-H), 2.41 (3H, d, J=0.7 Hz, 2'-CH_3), 7.45 (2H, d-like, J=7.3 Hz, 4'-H), 6.96—7.07 (2H, m, 5'-H, 6'-H), 7.45 (1H, d, J=7.3 Hz, 7'-H). EI-MS m/z: 240.1262 (M^+, Calcd for $C_{15}H_{16}N_2O$: 240.1264, 20), 131 (96), 110 (100). 3,6-Dihydro-1-methyl-6-[1'-(2'-methylindolyl)]pyridin-2(1*H*)-one (**20**): colorless crystals from C_6H_6–*n*-C_6H_{14}, mp 153—155 °C. IR (KBr): 1640 (lactam C=O) cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 2.58 (3H, s, N_1-CH_3), 3.14 (2H, m, 3-H_2), 6.05 (1H, dddd, J=10.3, 3.7, 3.7, 1.7 Hz, 4-H), 5.73 (1H, dddd, J=10.3, 4.2, 2.0, 2.0 Hz, 5-H), 6.34 (1H, m, 6-H), 2.43 (3H, s, 2'-CH_3), 6.28 (1H, s, 3'-H), 7.47 (1H, d-like, J=7.8 Hz, 4'-H), 7.01—7.09 (2H, m, 5'-H, 6'-H), 7.22 (1H, m, 7'-H). EI-MS m/z: 240.1261 (M^+, Calcd for $C_{15}H_{16}N_2O$: 240.1264, 3), 131 (100), 110 (56). This compound could not be obtained in a sufficient amount for analysis. 3,4-Dihydro-1-methyl-4-[6'-(2'-methylindolyl)]pyridin-2(1*H*)-one (**21**): this compound was a crystalline substance but could not be obtained in a sufficient amount for analysis or measurements of the physical properties. ^{1}H-NMR (CD_3CN) δ: 3.03 (3H, s, N_1-CH_3), 2.56 (1H, dd, J=15.9, 8.3 Hz, 3-H), 2.77 (1H, dd, J=15.9, 7.1 Hz, 3-H'), 3.81 (1H, m, 4-H), 5.27 (1H, dd, J=7.8, 4.2 Hz, 5-H), 6.24 (1H, dd, J=7.8, 1.7 Hz, 6-H), 9.02 (1H, br, $N_{1'}$-H), 2.38 (3H, d, J=1.0 Hz, 2'-CH_3), 6.08 (1H, q, J=1.0 Hz, 3'-H), 7.35 (1H, d, J=8.1 Hz, 4'-H), 6.86 (1H, dd, J=8.1, 1.5 Hz, 5'-H), 7.15 (1H, broadened s, 7'-H). EI-MS m/z: 240.1264 (M^+, Calcd for $C_{15}H_{16}N_2O$: 240.1264, 100), 225 (18), 211 (19), 197 (25), 130 (22), 110 (30).

Irradiation of 1 with 7 Adducts **22** (1 mg), **23** (9 mg), **24** (5 mg), **25** (18 mg) and **26** (6 mg) were isolated together with the recovered **1** (13 mg). 3,4-Dihydro-1-methyl-4-[2'-(3'-methylindolyl)]pyridin-2(1*H*)-one (**22**): colorless oil. IR (CCl_4): 3495 (indolyl NH), 1650 (lactam C=O) cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 3.07 (3H, s, N_1-CH_3), 2.59 (1H, dd, J=16.1, 7.3 Hz, 3-H), 2.76 (1H, dd, J=16.1, 9.0 Hz, 3-H'), 4.13 (1H, dddd, J=9.0, 7.3, 4.2, 1.7 Hz, 4-H), 5.21 (1H, dd, J=7.8, 4.2 Hz, 5-H), 6.33 (1H, dd, J=7.8, 1.7 Hz, 6-H), 8.89 (1H, br, $N_{1'}$-H), 2.22 (3H, s, 3'-CH_3), 7.44 (1H, d, J=7.8 Hz, 4'-H), 6.97—7.07 (2H, m, 5'-H, 6'-H), 7.30 (1H, d, J=7.8 Hz, 7'-H). EI-MS m/z: 240.1266 (M^+, Calcd for $C_{15}H_{16}N_2O$: 240.1264, 85), 225 (30), 183 (100). 3,6-Dihydro-1-methyl-6-[2'-(3'-methylindolyl)]pyridin-2(1*H*)-one (**23**): colorless crystals from toluene, mp 183—185 °C. IR (KBr): 3490 (NH), 1620 (C=O) cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 2.74 (3H, s, N_1-CH_3), 2.97 (1H, dm, J=22.4 Hz, 3-H), 3.11 (1H, dm, J=22.4 Hz, 3-H'), 5.86 (1H, dm, J=10.4 Hz, 4-H), 5.72 (1H, dm, J=10.4 Hz, 5-H), 5.35 (1H, m, 6-H), 9.06 (1H, br, $N_{1'}$-H), 2.30 (3H, s, 3'-CH_3), 7.50 (1H, d-like, J=7.8 Hz, 4'-H), 7.02—7.14 (2H, m, 5'-H, 6'-H), 7.30 (1H, d-like, J=7.5 Hz, 7'-H). EI-MS m/z: 240.1262 (M^+, Calcd for $C_{15}H_{16}N_2O$: 240.1264, 100), 182 (90), 168 (62), 130 (28). *Anal.* Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.86; H, 6.67; N, 11.59. 3,4-Dihydro-1-methyl-4-[1'-(3'-methylindolyl)]pyridin-2(1*H*)-one (**24**): colorless oil. IR (CCl_4): 1680 (lactam C=O) cm^{-1}. ^{1}H-NMR (C_6D_6) δ: 2.61 (3H, s, N_1-CH_3), 2.48 (1H, dd, J=16.6, 7.3 Hz, 3-H), 2.62 (1H, dd, J=16.6, 4.2 Hz, 3-H'), 4.58 (1H, m, 4-H), 4.66 (1H, dd, J=7.8, 4.2 Hz, 5-H), 5.38 (1H, dd, J=7.8, 1.5 Hz, 6-H), 6.68 (1H, q, J=1.2 Hz, 2'-H), 2.23 (3H, d, J=1.2 Hz, 3'-CH_3), 7.62 (1H, d-like, J=7.8 Hz, 4'-H), 7.15—7.25 (2H, m, 5'-H, 6'-H), 7.02 (1H, d-like, J=7.5 Hz, 7'-H). EI-MS m/z: 240.1263 (M^+, Calcd for $C_{15}H_{16}N_2O$: 240.1264, 2), 131 (73), 130 (100), 110 (21), 109 (30). 3,6-Dihydro-1-methyl-6-[1'-(3'-methylindolyl)]pyridin-2(1*H*)-one (**25**): colorless oil. IR (CCl_4): 1650 (lactam C=O) cm^{-1}. ^{1}H-NMR (C_6D_6) δ: 2.48 (3H, s, N_1-CH_3), 2.78 (2H, m, 3-H_2), 5.24 (1H, dddd, J=10.0, 3.4, 3.4, 1.2 Hz, 4-H), 5.09 (1H, dddd, J=10.0, 3.6, 1.9, 1.9 Hz, 5-H), 5.34 (1H, m, 6-H), 6.48 (1H, q, J=1.2 Hz, 2'-H), 2.19 (3H, d, J=1.2 Hz, 3'-CH_3), 7.57 (1H, d-like, J=7.8 Hz, 4'-H), 7.15—7.25 (2H, m, 5'-H and 6'-H), 7.05

(1H, d-like, $J=7.5$ Hz, 7'-H). EI-MS m/z: 240.1263 (M^+, Calcd for $C_{15}H_{16}N_2O$: 240.1264, 2), 131 (90), 130 (100), 110 (28), 109 (25). At 15 min after the dissolution of **25** in $CDCl_3$, the ^{1}H-NMR spectrum showed signals due to the 1:1 mixture of **1** and **7**, which were identified by TLC. 3,6-Dihydro-1-methyl-6-[6'-(3'-methylindolyl)]pyridin-2(1*H*)-one (**26**): colorless oil. IR (CCl_4): 3500 (indolyl NH), 1620 (lactam C=O) cm^{-1}. ^{1}H-NMR (CD_3CN) δ: 2.73 (3H, s, N_1-CH_3), 2.96 (1H, dm, $J=23.0$ Hz, 3-H), 3.10 (1H, dm, $J=23.0$ Hz, 3-H'), 5.78 (1H, dm, $J=10.2$ Hz, 4-H), 5.74 (1H, dm, $J=10.2$ Hz, 5-H), 5.00 (1H, m, 6-H), 9.00 (1H, br, $N_{1'}$-H), 7.03 (1H, q, $J=1.0$ Hz, 2'-H), 2.27 (3H, d, $J=1.0$ Hz, 3'-CH_3), 7.51 (1H, d, $J=8.3$ Hz, 4'-H), 6.92 (1H, dd, $J=8.3$, 1.5 Hz, 5'-H), 7.25 (1H, d, $J=1.5$ Hz, 7'-H). EI-MS m/z: 240.1263 (M^+, Calcd for $C_{15}H_{16}N_2O$: 240.1264, 100), 182 (37), 110 (30), 109 (41).

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References and Notes

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