

**STUDIES ON NITROGEN-CONTAINING HETEROCYCLIC  
COMPOUNDS. SYNTHESIS OF BENZO[*b*][1,8]NAPHTHYRIDINE  
AND ITS OXIDATION REACTIONS WITH PEROXY ACID**

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**Abstract** - A new method for the synthesis of benzo[*b*][1,8]naphthyridine (**4**) was established through the dehydrogenation of 5,6,7,8-tetrahydro-1,9-diazaanthracene. Oxidation reactions of **4** with peroxy acid afforded seven-membered 1,4-oxazepine derivatives (**5-8**).

Nitrogen-containing heterocyclic compounds have extensive pharmaceutical applications and *m*-Amsacrin (*m*-AMSA),<sup>1</sup> an acridine derivative, has been produced as an antitumor agent. In basic research on nitrogen-containing heterocyclic compounds such as acridine, the present authors have sought new methods for the synthesis of naphthonaphthyridines such as 7,8-, 7,11-, and 11,12-diazabenz[*a*]anthracenes.<sup>2</sup> When naphtho[1,2-*b* and 2,1-*b*][1,8]naphthyridines was oxidized with peroxy acid in the usual procedure, a ring expansion was previously noted to form seven-membered 1,4-oxazepine ring.<sup>2c</sup> In the present paper, a modified method for the synthesis of benzo[*b*][1,8]naphthyridine (1,9-diazaanthracene) and the oxidation of benzo[*b*][1,8]naphthyridine are described.

### RESULTS AND DISCUSSION

Benzo[*b*][1,8]naphthyridine<sup>3</sup> was previously synthesized by the Skraup reaction of 2-aminoquinoline. However, the yield was poor, and a new method to improve this was sought. The dehydrogenation of 5,6,7,8-tetrahydro-1,9-diazaanthracene (**1**)<sup>4</sup> has not been reported to date without an 8-methyl derivative, and 8-methyl-1,9-diazaanthracene has been obtained.<sup>5</sup>

Compound (**1**) was dehydrogenated using 20 % palladium on charcoal in *p*-cymene, at 180 °C for 15 h. The desired 1,9-diazaanthracene was not obtained. Instead compounds (**2**), (47 %) and (**3**), (24 %) were produced. Compound (**2**) was considered to be 1,2,3,4-tetrahydro-1,9-diazaanthracene on the basis of its <sup>1</sup>H-NMR spectrum. Compound (**3**) was obtained by the dehydrogenation of **2** under the same conditions, suggesting **2** to be an intermediate of **3**. Compound (**3**) showed aromatic proton at 2-8 positions and

methylene and NH proton signals at  $\delta$  4.10 and at  $\delta$  7.20, respectively. The structure of **3** was therefore determined as 9,10-dihydro-1,9-diazaanthracene. Reaction conditions are summarized in Table 1.

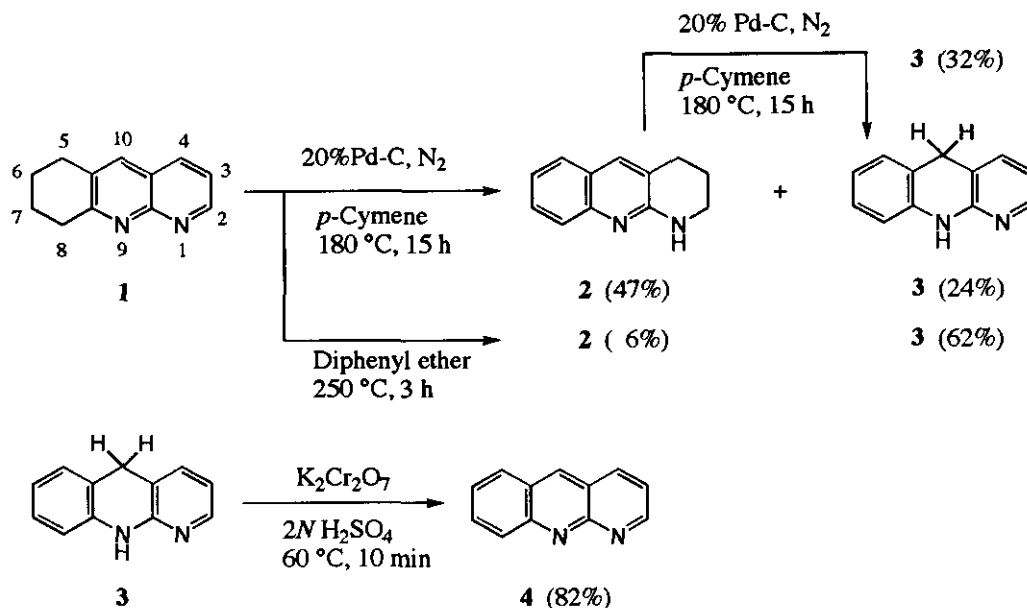
Heating at 250 °C for 3 h in diphenyl ether gave in 56% yield of **3**, which was further improved by using a larger amount of solvent, (62 %). On oxidation of **2** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), the starting material was recovered and polymerization occurred at high temperatures such as 250 °C for 1 h. Compound (**3**) was oxidized with potassium dichromate in dilute sulfuric acid to produce 1,9-diazaanthracene (**4**) in a high yield of 82 %.

Compound (**4**) was treated with *m*-chloroperbenzoic acid (*m*-CPBA) at 20 °C for 3 h to produce the expected seven-membered 1,4-oxazepine compounds (**5**, 47 %) and (**6**, 24 %). When heated at 60 °C for 3 h, the yield of **5** decreased to 21 % and that of **6** increased to 33 %. The structure of **5** was confirmed by the 2D HMBC NMR spectrum shown in Figure 1. This structure was also supported by the similarity between the NMR spectrum patterns of **5** and **6** and those of 12-acetyloxy-7,12-dihydronaphtho[1,2-*b*]pyrido[2,3-*e*][1,4]oxazepine, whose structure was previously determined by X-Ray crystallography.<sup>2c</sup>

Reactions of compound (**4**) with peracetic acid were as follows. Peracetic acid was prepared by reaction of acetic acid with 30 % hydrogen peroxide at 60 °C for 4 h. Compound (**4**) was added to the reaction mixture containing peracetic acid and reacted at 20 °C for 1 h to afford compounds (**7**) to (**10**). Compound (**7**) was found to be an 1,4-oxazepine derivative (11 %) and **8** to be an *N*-oxide (20 %). Compound (**9**) corresponded to the molecular formula C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub> on the basis of the analytical data and the MS spectrum with *m/z*: 212 (M<sup>+</sup>). <sup>1</sup>H-NMR spectrum showed a hydrogen bonded proton signal of NH---ON at  $\delta$  10.33. The proton at the 10-position vanished and signals of protons at 2, 3, and 4-positions of the pyridine ring appeared as double doublets. The structure of **9** was considered to be 1-oxy-1-azaacridone by the comparison of the proton chemical shifts with those of 1-azaacridone (**11**).<sup>6</sup> The chemical shifts of protons at positions 2, 3, and 4 ( $\delta$ : 8.72, 7.28, and 8.78) of **11** appeared in higher magnetic fields than those of **9** ( $\delta$ : 8.60, 7.19, and 8.35) due to the effect of the *N*-oxide group<sup>7</sup> in **9**. The structure of **9** was supported by the finding that oxidation of **11** with *m*-CPBA gave **9** as the sole product. (Scheme 1).

Compound (**10**) was considered to be a ring-opened compound similar to that of the product obtained from acridine<sup>8</sup> based on the <sup>1</sup>H-NMR spectrum showing signals corresponding to the CHO group at  $\delta$  9.91, NH---OC and OH---OC hydrogen bond at  $\delta$  10.50 and 10.64. To determine whether CHO or OH group of **10** was bound to the pyridine or benzene ring, the comparison of the proton NMR chemical shifts was made with the chemical shifts of 2-anilinopyridine. Structure of **10** was confirmed by the finding that when the CHO group was bound to the pyridine ring, the ring proton signals shifted to a lower field through the electron-withdrawing effect of this group and when the OH group was bound to the benzene ring, shifts to a higher magnetic field due to the electron-donating effect of the OH group were noted. Comparison of its proton NMR chemical shifts with that of 2-anilinopyridine, indicated that the CHO group was bound to the pyridine ring and the OH group was bound to the benzene ring.

## CONCLUSION



Scheme 1

Table 1. Dehydrogenation of 1 and 2 with 20% Pd-C

Compd	20% Pd-C	Solvent	Temp	Time	Product (2)	Product (3)		
(No.)	(mmol)	(g)	(mL)	(°C)	(h)	(%)	(%)	
1	10	1.0	<i>p</i> -Cymene	20	180	15	47	24
1	10	0.5	Ph-O-Ph	30	250	1	23	36
1	10	0.5	Ph-O-Ph	30	250	3	17	56
1	10	0.5	Ph-O-Ph	30	250	6	12	44
1	10	0.5	Ph-O-Ph	5	250	3	25	50
1	10	1.0	Ph-O-Ph	30	250	6	7	40
1	10	2.0	Ph-O-Ph	30	250	3	-	36
1	10	1.0	Ph-O-Ph	60	250	3	6	62
1	10	1.0	Diethylene glycol	30	250	3	7	54
2	10	1.0	<i>p</i> -Cymene	20	180	15	35	32
2	10	1.0	Diethylene glycol	30	250	3	21	43
2	1	DDQ 2 mmol	Diethylene glycol	15	250	1	polymerized	

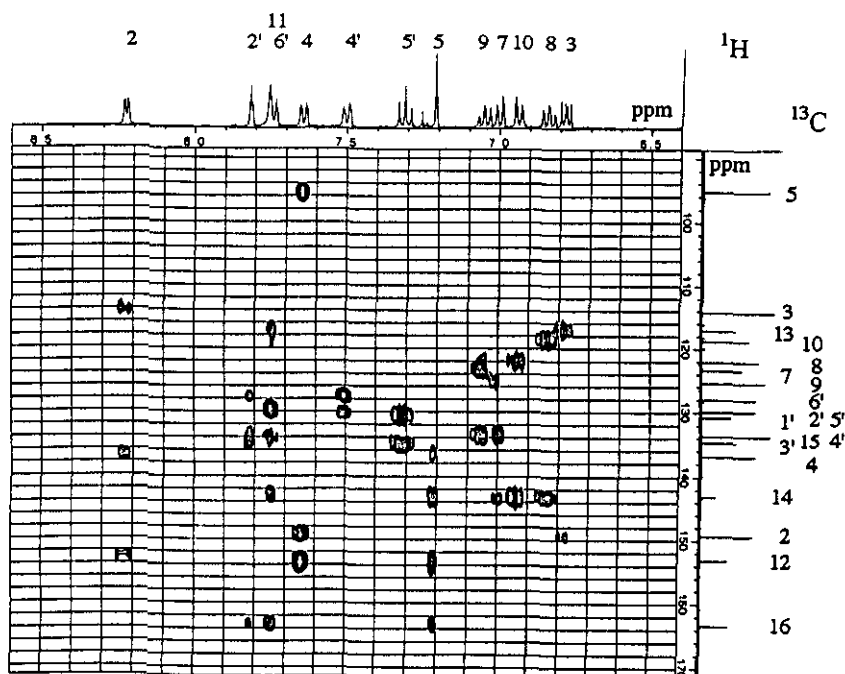
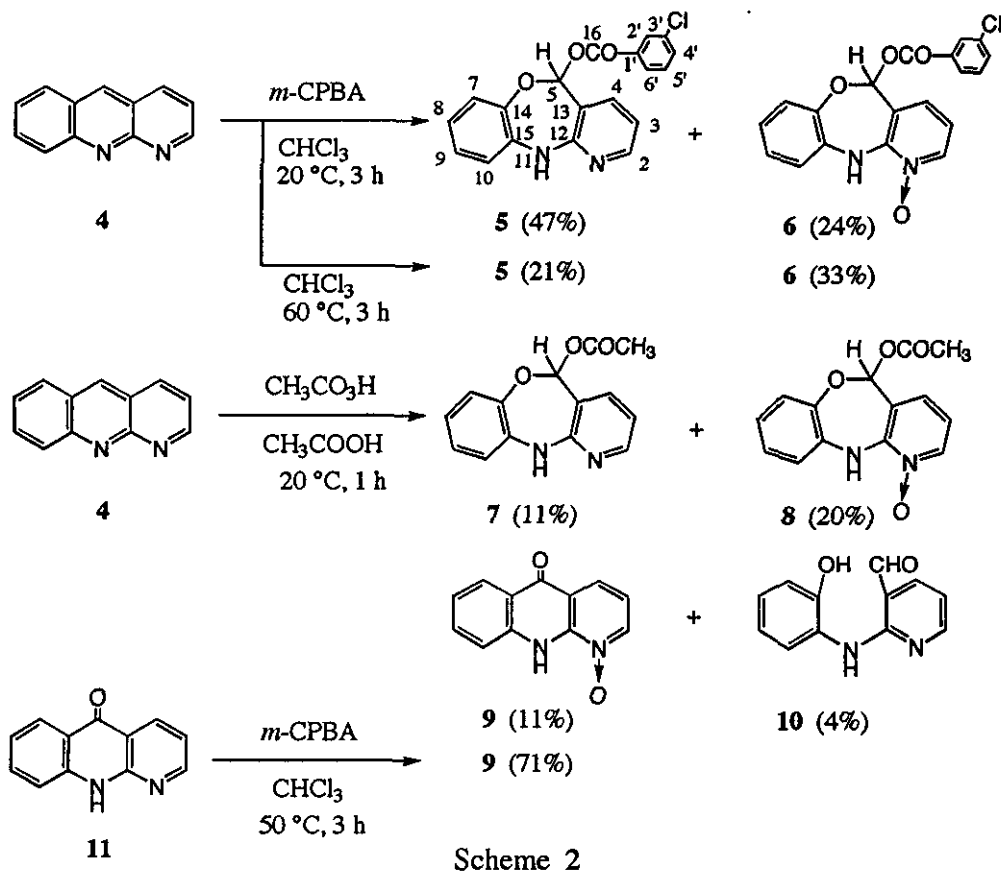


Figure 1. HMBC spectrum of compound (5) in  $\text{CDCl}_3$

Since the right hand side pyridine ring in **1** undergoes reduction more easily than the benzene ring in quinoline and benzoquinoline, isomerized **2** was obtained through the dehydrogenation and hydrogenation of **1** with Pd-C. But this type's reaction was observed only for the 5,6,7,8-tetrahydro-1,9-diazaanthracene. Ring expansion occurred during the oxidation of **4** by *m*-CPBA. Such reactions do not occur in bicyclic 1,8-naphthyridine<sup>9</sup> and tricyclic acridine.<sup>8</sup> Thus, the ring expansion may be considered characteristic of nitrogen-containing heterocycles having a benzo[*b*][1,8]naphthyridine ring. Reactions of **4** with peroxy acids gave 1,4-oxazepine in a better yield than previously noted with the naphthonaphthyridine ring.<sup>2c</sup> The productions of compound (**9**) and ring-opened compound (**10**) indicate that **4** also has acridine-like characteristics not observed in the naphthonaphthyridine ring.

## EXPERIMENTAL

<sup>1</sup>H-NMR spectra were recorded with a JEOL JNM GX-270 spectrometer with tetramethylsilane (TMS) as the internal standard. Chemical shifts are given on a  $\delta$  scale (ppm). The MS spectrum was taken with a Hitachi GC-MS M-80 spectrometer. IR and UV-VIS spectra were recorded on a JASCO IRA-I and Shimadzu UV-240 spectrophotometer, respectively.

### 9,10-Dihydro-1,9-diazaanthracene (**3**)

A mixture of **1** (0.92 g, 5 mmol) and 20% palladium on charcoal (Pd-C) (0.5 g) in diphenyl ether (or *p*-cymene) (30 mL) was heated under reflux at 250 °C (or 180 °C), with stirring for 3 h (or 15 h). Following the removal of the catalyst (Pd-C) by filtration, CHCl<sub>3</sub> (30 mL) was added to the filtrate and the mixture was then extracted with 10% HCl. The extracts were washed with CHCl<sub>3</sub>, and basified with 10% NaOH. The solution was extracted 3 times with CHCl<sub>3</sub>. The extracts were washed with water, dried over MgSO<sub>4</sub> and evaporated to dryness. The residue was chromatographed over silica gel [eluted with CHCl<sub>3</sub>-acetone (10 : 1)] to give compounds (**2**, **3**). The first elution gave 1.13 g (62%) of **3**.

**3**: pale yellow needles (cyclohexane), mp 163-165 °C; MS *m/z*: 182 (*M*<sup>+</sup>). IR (CHCl<sub>3</sub>)  $\text{cm}^{-1}$ : 3420 (NH), 1602, 1584, 1490, 1443. UV-VIS (cyclohexane)  $\lambda_{\text{max}}$  nm (log  $\epsilon$ )=287 (4.04), 384 (2.69). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 4.10 (s, 2H, H-10), 6.71 (m, 1H, H-5), 6.77 (dd, 1H, *J*=7.4, 5.0 Hz, H-3), 6.88 (m, 1H, H-6), 7.09 (m, 1H, H-8), 7.10 (m, 1H, H-7), 7.29 (br s, NH), 7.34 (dd, 1H, *J*=7.4, 1.0 Hz, H-4), 8.02 (dd, 1H, *J*=5.0, 1.0 Hz, H-2). *Anal.* Calcd for C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>: C, 79.10; H, 5.53; N, 15.37. Found: C, 79.24; H, 5.32; N, 15.20. The second elution gave 0.11g (6%) of **2**.

**2**: colorless needles (AcOEt), mp 180-182 °C; MS *m/z*: 184 (*M*<sup>+</sup>), 183 (*M*<sup>+</sup>-1). IR (CHCl<sub>3</sub>)  $\text{cm}^{-1}$ : 3425 (NH), 1628, 1500, 1444. <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 1.98 (m, 2H, H-3), 2.90 (m, 2H, H-4), 3.52 (t, 2H, *J*=5.4 Hz, H-2), 5.58 (br s, 1H, NH) 7.15 (m, 1H, H-6), 7.45 (m, 1H, H-7), 7.52 (m, 1H, H-5), 7.54 (s, 1H, H-10), 7.56 (m, 1H, H-8). *Anal.* Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>: C, 78.23; H, 6.56; N, 15.20. Found: C, 78.17; H, 5.32; N, 15.24.

### Benzo[*b*][1.8]naphthyridine (**4**)

A solution of **3** (0.91 g, 5 mmol) in 2*N*-H<sub>2</sub>SO<sub>4</sub> (30 mL) was added to a solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (1.8 g, 6.1

mmol) in water (60 mL) at 60 °C and the mixture was stirred for 10 min. The reaction mixture was made alkaline with NaOH and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> extracts were dried over MgSO<sub>4</sub> and evaporated to dryness. The residue was recrystallized from AcOEt to give 0.74g (82%) of **4** as yellow prisms, mp 197-199 °C (lit.,<sup>3</sup> mp 190-192 °C). MS *m/z*: 180 (M<sup>+</sup>). IR (KBr) cm<sup>-1</sup>: 3020, 1619, 1604, 1547, 1507, 740. UV-VIS (H<sub>2</sub>O) λ<sub>max</sub> nm (log ε)=227 (4.45), 247 (4.80), 354 (4.10). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 7.47 (dd, 1H, J=8.4, 3.7 Hz, H-3), 7.60 (m, 1H, H-6), 7.85 (m, 1H, H-7), 8.03 (m, 1H, H-5), 8.36 (dd, 1H, J=8.4, 2.0 Hz, H-4), 8.37 (m, 1H, H-8), 8.80 (s, 1H, H-10), 9.28 (dd, 1H, J=3.7, 2.0 Hz, H-2). *Anal.* Calcd for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>: C, 79.98; H, 4.47; N, 15.54. Found: C, 80.04; H, 4.53; N, 15.36.

#### Oxidation of **4** with *m*-CPBA

A solution of **4** (0.9 g, 5 mmol) and *m*-CPBA (ca. 70% purity) (2.47 g, 12 mmol) in CHCl<sub>3</sub> (50 mL) was stirred at 20 °C for 3 h. A solution of 5% Na<sub>2</sub>CO<sub>3</sub> (100 mL) was added to the reaction mixture and the whole was extracted with CHCl<sub>3</sub>. The extracts were dried over MgSO<sub>4</sub> and evaporated to dryness. The residue was chromatographed over silica gel [eluted with CHCl<sub>3</sub>] to give compounds (**5**, **6**). The first elution gave 0.82 g (47%) of **5**.

**5**: pale yellow needles (MeCN), mp 156-158 °C; MS *m/z*: 352 (M<sup>+</sup>), 323, 213, 197 (M<sup>+</sup>-OCOC<sub>6</sub>H<sub>4</sub>Cl). IR (CHCl<sub>3</sub>) cm<sup>-1</sup>: 3400 (NH), 1733 (C=O). UV-VIS (cyclohexane) λ<sub>max</sub> nm (log ε)=203 (4.66), 283 (4.15). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 6.79 (dd, 1H, J=7.4, 5.0 Hz, H-3), 6.84 (m, 1H, H-8), 6.94 (m, 1H, H-10), 7.01 (m, 1H, H-7), 7.06 (m, 1H, H-9), 7.21 (s, 1H, H-5), 7.32 (t, 1H, J=8.1 Hz, H-5'), 7.51 (m, 1H, H-4'), 7.65 (dd, 1H, J=7.4, 1.7 Hz, H-4), 7.73 (br s, 1H, NH), 7.75 (m, 1H, H-6'), 7.82 (m, 1H, H-2'), 8.23 (dd, 1H, J=5.0, 1.7 Hz, H-2); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ: 95.2 (C-5), 114.2 (C-3), 117.1 (C-13), 118.7 (C-10), 122.0 (C-8), 123.3 (C-7), 125.3 (C-9), 127.9 (C-6'), 129.8 (C-2'), 129.9 (C-5'), 130.7 (C-1'), 133.7 (C-4', 15), 134.7 (C-3'), 136.8 (C-4), 143.0 (C-14), 149.3 (C-2), 163.3 (C-16). *Anal.* Calcd for C<sub>19</sub>H<sub>13</sub>N<sub>2</sub>O<sub>3</sub>Cl: C, 65.06; H, 3.99; N, 8.12. Found: C, 64.68; H, 3.69; N, 7.94. The second elution gave 0.45 g (24%) of **6**.

**6**: pale yellow prisms (AcOEt), mp 167-168 °C; MS *m/z*: 368 (M<sup>+</sup>), 352 (M<sup>+</sup>-O), 213 (M<sup>+</sup>-OCOC<sub>6</sub>H<sub>4</sub>Cl), 197. IR (CHCl<sub>3</sub>) cm<sup>-1</sup>: 3225 (hydrogen bonding in NH---ON), 1736 (C=O). UV-VIS (cyclohexane) λ<sub>max</sub> nm (log ε)=205 (4.29), 258 (3.96), 278 (3.73). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 6.74 (dd, 1H, J=7.7, 6.7 Hz, H-3), 6.96 (m, 1H, H-9), 7.05 (m, 1H, H-8), 7.15 (m, 2H, H-7, H-10), 7.24 (s, 1H, H-5), 7.34 (t, 1H, J=8.1 Hz, H-5'), 7.35 (dd, 1H, J=7.7, 1.0 Hz, H-4), 7.54 (m, 1H, H-4'), 7.73 (m, 1H, H-6'), 7.81 (m, 1H, 2'H), 8.28 (dd, 1H, J=6.7, 1.0 Hz, H-2), 9.83 (br s, 1H, NH). *Anal.* Calcd for C<sub>19</sub>H<sub>13</sub>N<sub>2</sub>O<sub>4</sub>Cl: C, 61.87; H, 3.56; N, 7.61. Found: C, 61.87; H, 3.53; N, 7.60.

#### Oxidation of **4** with Peracetic Acid

Peracetic acid was prepared as follows: a solution of 30% H<sub>2</sub>O<sub>2</sub> (13.6 mL) in AcOH (34 mL) was stirred at 55-60 °C for 4 h, cooled to 20 °C, to which was added **4** (11.08 g, 6 mmol) and the mixture was stirred at 20 °C for 1 h. NaHSO<sub>3</sub> (ca. 12 g) was added to cause the decomposition of H<sub>2</sub>O<sub>2</sub>. The reaction mixture

was treated in the same manner as the oxidation mixture of **4** with *m*-CPBA. The first elution gave 0.05 g (4%) of **10**.

**10**: pale brown plates ( $\text{CCl}_4$ ), mp 129-131 °C; MS *m/z*: 214 ( $M^+$ ), 197 ( $M^+-\text{OH}$ ), 196 ( $M^+-\text{H}_2\text{O}$ ), 185 ( $M^+-\text{CHO}$ ), 168 (196 -CO). IR (KBr)  $\text{cm}^{-1}$ : 3445 (OH), 3400 (NH), 1645 (CHO), 1610, 1572, 1520, 1450, 760.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 6.85 (dd, 1H,  $J=7.4, 5.0$  Hz, H-3), 6.89 (m, 1H, H-4'), 7.08 (m, 2H, H-3', 6'), 7.14 (m, 1H, H-5'), 7.96 (dd, 1H,  $J=7.4, 2.0$  Hz, H-4), 8.30 (dd, 1H,  $J=5.0, 2.0$  Hz, H-2), 9.91 (s, 1H, CHO), 10.50 (br s, 1H, NH), 10.66 (s, 1H, OH). *Anal.* Calcd for  $\text{C}_{12}\text{H}_{10}\text{N}_2\text{O}_2$ : C, 67.28; H, 4.70; N, 13.08. Found: C, 67.21; H, 4.72; N, 13.01. The second elution gave 0.164 g (11%) of **7**.

**7**: pale yellow prisms (hexane), mp 124-126 °C; MS *m/z*: 256 ( $M^+$ ), 213 ( $M^+-\text{COCH}_3$ ), 197 ( $M^+-\text{OCOCH}_3$ ). IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ : 3398 (NH), 1752 (C=O). UV-VIS (cyclohexane)  $\lambda_{\text{max}}$  nm ( $\log \epsilon$ )=284 (4.32).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 2.06 (s, 3H,  $\text{OCOCH}_3$ ), 6.76 (dd, 1H,  $J=7.4, 5.0$  Hz, H-3), 6.87 (m, 1H, H-10), 6.89 (m, 1H, H-9), 6.94 (s, 1H, H-5), 7.01 (m, 1H, H-7), 7.06 (m, 1H, H-8), 7.33 (br s, 1H, NH), 7.56 (dd, 1H,  $J=7.4, 1.7$  Hz, H-4), 8.19 (dd, 1H,  $J=5.0, 1.7$  Hz, H-2). *Anal.* Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_3$ : C, 65.62; H, 4.72; N, 10.93. Found: C, 65.83; H, 4.86; N, 10.82. The third elution gave 0.33 g (20%) of **8**.

**8**: colorless needles [benzene-ligroin (1:3)], mp 142-144 °C; MS *m/z*: 272 ( $M^+$ ), 256 ( $M^+-\text{O}$ ), 229 ( $M^+-\text{COCH}_3$ ), 213 ( $M^+-\text{OCOCH}_3$ ). IR ( $\text{CHCl}_3$ )  $\text{cm}^{-1}$ : 3220 (hydrogen bonding in  $\text{NH}\cdots\text{ON}$ ), 1762 (C=O). UV-VIS (cyclohexane)  $\lambda_{\text{max}}$  nm ( $\log \epsilon$ )=210 (4.37), 261 (4.39), 304 (4.42), 349 (3.73).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 2.08 (s, 3H,  $\text{COCH}_3$ ), 6.71 (dd, 1H,  $J=6.8, 5.4$  Hz, H-3), 6.96 (s, 1H, H-5), 7.03 (m, 2H, H-8, 9), 7.12 (m, 2H, H-7, 10), 7.28 (dd, 1H,  $J=6.8, 1.0$  Hz, H-4), 8.23 (dd, 1H,  $J=5.4, 1.0$  Hz, H-2), 9.71 (br s, 1H, NH). *Anal.* Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4$ : C, 61.76; H, 4.44; N, 10.29. Found: C, 61.77; H, 4.49; N, 10.34. The fourth elution gave 0.145 g (11%) of **9**.

**9**: yellow needles (EtOH), mp > 300 °C; MS *m/z*: 212 ( $M^+$ ), 196 ( $M^+-\text{O}$ ), 168 (196 -CO). IR (KBr)  $\text{cm}^{-1}$ : 3050 (NH), 2790, 1645 (C=O), 1614, 1208 (N-O), 750.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 7.19 (dd, 1H,  $J=8.1, 6.4$  Hz, H-3), 7.42 (m, 1H, H-7), 7.53 (m, 1H, H-8), 7.79 (m, 1H, H-6), 8.35 (dd, 1H,  $J=8.1, 1.4$  Hz, H-4), 8.45 (m, 1H, H-5), 8.60 (dd, 1H,  $J=6.4, 1.4$  Hz, H-2), 10.33 (br s, 1H, NH). *Anal.* Calcd for  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_2$ : C, 67.92; H, 3.80; N, 13.20. Found: C, 67.90; H, 3.80; N, 13.01.

#### Oxidation of **11** with *m*-CPBA

A solution of **11** (0.1 g, 0.5 mmol) and *m*-CPBA (*ca.* 70% purity) (0.27 g, 1.1 mmol) in  $\text{CHCl}_3$  (100 mL) was stirred at 50 °C for 3 h. The reaction mixture was treated in the same manner as the oxidation mixture of **4** with *m*-CPBA. The elution gave 0.075 g (71%) of **9** as yellow needles (EtOH), mp > 300 °C. The product was identical to **9**, previously synthesized by the oxidation of **4** with peracetic acid, by the comparison of their IR and  $^1\text{H-NMR}$  spectra.

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