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Reaction of Spiro[4*H*-3,1-benzoxazine-4,4′-piperidin]-2(1*H*)-one Derivatives and Related Compounds with Phosphorus Oxychloride

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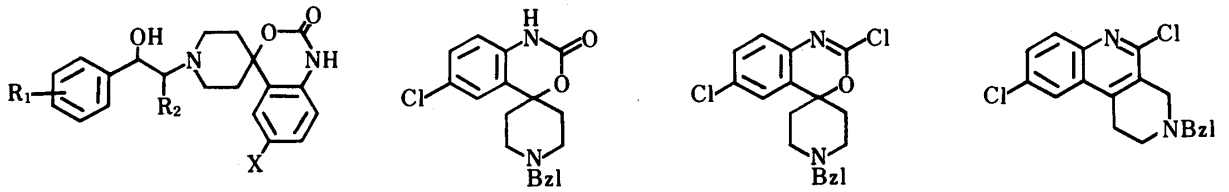
Treatment of spiro[4*H*-3,1-benzoxazine-4,4′-piperidin]-2(1*H*)-one derivatives with $POCl_3$ yielded 1,2,3,4-tetrahydro-2,9-diazaphenanthrene derivatives through a novel rearrangment. The reaction is suggested to proceed *via* the formation of an isocyanate by dehydrative cleavage of the oxazinone ring with $POCl_3$. It was also found that treatment of 4-(2-methoxycarbonylaminophenyl)-1,2,5,6-tetrahydropyridine derivatives with trichlorosilane/triethylamine gave the corresponding 10-oxo-1,2,3,4,9,10-hexahydro-2,9-diazaphenanthrene derivatives.

Keywords——spiro compound; piperidine; benzoxazine; Bischler–Napieralski reaction; phosphorus oxychloride; trichlorosilane; 2,9-diazaphenanthrene

We recently described the synthesis and the pharmacological evaluation of 1-substituted spiro[4*H*-3,1-benzoxazine-4,4′-piperidin]-2(1*H*)-one derivatives (**1**), a new class of antihypertensive agents.[1] For further modification of this series, we treated 1′-benzyl-6-chlorospiro-[4*H*-3,1-benzoxazine-4,4′-piperidin]-2(1*H*)-one (**2a**) with phosphorus oxychloride ($POCl_3$) in the hope of obtaining compound **3a**.

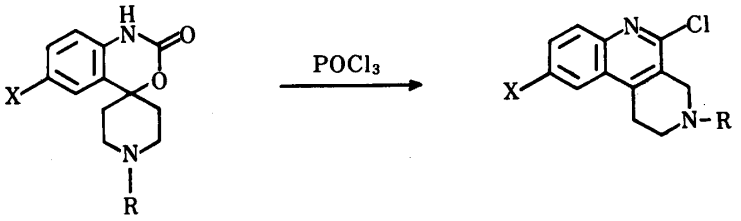


1 **2a** **3a** **4a**

Chart 1

The conversion of **2a** to **3a** was attempted firstly by stirring **2a** in $POCl_3$ at room temperature for 2 d, but no reaction took place. Accordingly, **2a** was heated under reflux for 5 h. However, the resulting product was not **3a**, but a new compound with the molecular formula $C_{19}H_{16}Cl_2N_2$ on the basis of its elemental analysis data and mass spectrum (MS) (M^+; *m/e*: 342 for ^{35}Cl). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of the compound in $CDCl_3$ indicated the presence of a 1,2,5,6-tetrahydropyridine ring (δ: 2.68—2.88, 2H, m; δ: 2.92—3.14, 2H, m; δ: 3.72, 2H, s), and a 1-chloro-3,4-disubstituted benzene ring (δ: 7.53, 1H, dd, J=8.8, 2.2 Hz; δ: 7.73, 1H, d, J=2.2 Hz; δ: 7.85, 1H, d, J=8.8 Hz). The remaining signals are those of an N-benzyl group (δ: 3.77, 2H, s; δ: 7.2—7.4, 5H, m). The infrared (IR) absorption indicates the absence of a carbonyl group. On the basis of these data, the structure of this compound was elucidated as 2-benzyl-6,10-dichloro-1,2,3,4-tetrahydro-2,9-diazaphenanthrene (**4a**). This structure was supported by the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of **4a** (Table I).

Similar reactions of **2b—e** also gave **4b—e**, respectively, but that of **2f** gave a complex

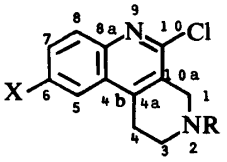


2 4

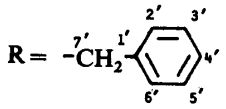
a: R=Bzl, X=Cl
b: R=Me, X=Cl
c: R=Bzl, X=H
d: R=3,4-$(CH_3O)_2C_6H_3CH_2CH_2$–, X=H
e: R=3,4-$(CH_3O)_2C_6H_3COCH_2$–, X=H
f: R=3,4-$(CH_3O)_2C_6H_3CH(OH)CH_2$–, X=H

Chart 2

TABLE I. ^{13}C-NMR Spectral Data for **4a**—**c** in $CDCl_3$



4a: X=Cl
4c: X=H



4b: X=Cl R=Me (position 11)

Position	Chemical shift (ppm)		
	4a	**4c**	**4b**
4	26.244	26.226	26.317
3	48.200	48.309	50.898
11	—	—	45.811
1	53.610	53.670	55.254
7′	62.260	62.290	—
4′	127.372	127.292	—
3′ 5′	128.420	128.358	—
2′ 6′	128.932	128.936	—
1′	137.558	137.678	—
5, 7, 8	121.841, 130.126, 130.370	122.570, 126.713, 128.784, 129.272	121.900, 130.246, 130.459
6, 10, 10a, 4a, 4b, 8a	127.129, 127.933, 132.685, 142.554, 143.967, 149.913	126.347, 128.144, 143.344, 145.629, 149.527	127.139, 127.809, 132.805, 142.126, 144.075, 149.832

mixture. Compound **4e** was reduced with $NaBH_4$ in EtOH to give **4f** in 74.6% yield (Chart 2). These results and some properties of the compounds are summarized in Table II.

The Bischler–Napieralski reaction is one of the most frequently employed methods for the synthesis of isoquinoline derivatives. As a modification of this reaction, cyclization of β-arylethylisocyanates or β-arylethylurethanes with $POCl_3$ to give the corresponding 1-hydroxy-3,4-dihydroisoquinolines or 1-chloro-3,4-dihydroisoquinolines has been reported.[2] From a consideration of these reactions, the mechanism of formation of **4a** is proposed to be as shown in Chart 3. The reaction seems to proceed by initial activation of the urethan (**2a**) to the phosphate (**5a**)[3] then to the isocyanate (**6a**) with dehydrative cleavage. The isocyanate (**6a**) may cyclize to the lactam (**7a**) or be activated to species **8a**, which cyclizes to **9a**.[3]

TABLE II

Compd. No.	Yield (%)	Method[a]	Crystn. solvent	mp (°C)	Formula	Analysis (%) Calcd (Found) C	H	N
4a	60.8	A	MeOH	147—149	$C_{19}H_{16}Cl_2N_2$	66.48	4.70	8.16
	4.8	B				(66.67	4.69	8.22)
	62.1	C						
4b	35.3	D	AcOEt	170—171	$C_{13}H_{12}Cl_2N_2$	58.45	4.53	10.49
						(58.29	4.53	10.52)
4c	66.0	A	MeOH	102—103	$C_{19}H_{17}ClN_2$	73.90	5.55	9.07
						(73.84	5.52	9.09)
4d	63.7	A	AcOEt–hexane	118—119	$C_{22}H_{23}ClN_2O_2$	69.01	6.05	7.32
						(68.84	6.08	7.26)
4e	40.4	A	DMF–EtOH	183—184	$C_{22}H_{21}ClN_2O_3$	66.58	5.33	7.06
						(66.55	5.39	7.14)
4f	60.5	E	EtOH	164—165	$C_{22}H_{23}ClN_2O_3$	66.24	5.81	7.02
						(66.21	5.73	6.94)
7a	57.3	F	DMF–EtOH	222—224	$C_{19}H_{17}ClN_2O$	70.26	5.28	8.62
						(70.16	5.34	8.74)
7b	46.2	F	MeOH	236—239	$C_{13}H_{13}ClN_2O$	62.78	5.27	11.26
						(62.55	5.23	11.12)
14	10.4	G	AcOEt	173—175	$C_{20}H_{20}ClN_3$	71.10	5.97	12.44
						(71.18	5.97	12.25)

a) See experimental.

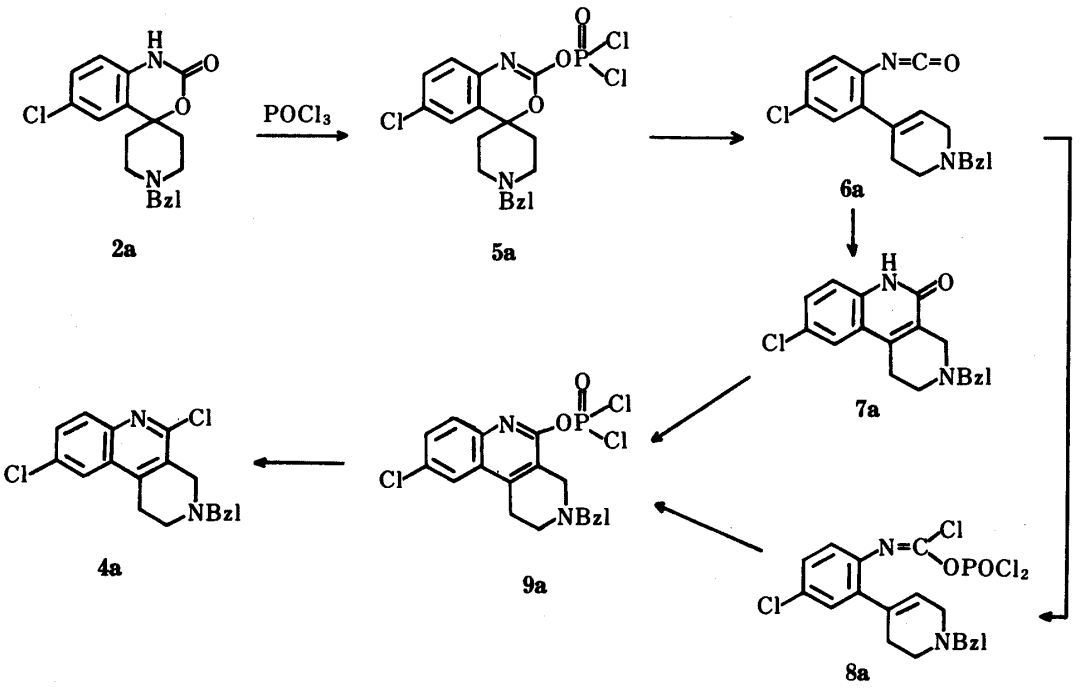


Chart 3

Compound **7a** should be activated by $POCl_3$ to species **9a**, which is converted to **4a**. In order to confirm that **2a** was converted to **4a** *via* the isocyanate (**6a**), the preparation of **6a** was necessary. Several chlorosilanes have been used to prepare isocyanates from carbamates.[4] For the preparation of the carbamate (**12a**), compound **10a**, which was previously reported by

us,[1] was chosen as the starting material. Dehydration of **10a** was attempted firstly by stirring **10a** under reflux in benzene or toluene in a Dean–Stark apparatus, in the presence of *p*-toluenesulfonic acid as a catalyst. However, this was unsuccessful and the starting materials were recovered. Finally, **10a** was stirred in conc. H_2SO_4 at room temperature for 3 h to give **11a** in 89.9% yield. The carbamate (**12a**) was obtained by treatment of **11a** with methyl chloroformate in pyridine in 60.8% yield, as shown in Chart 4. Compound **12a** thus obtained

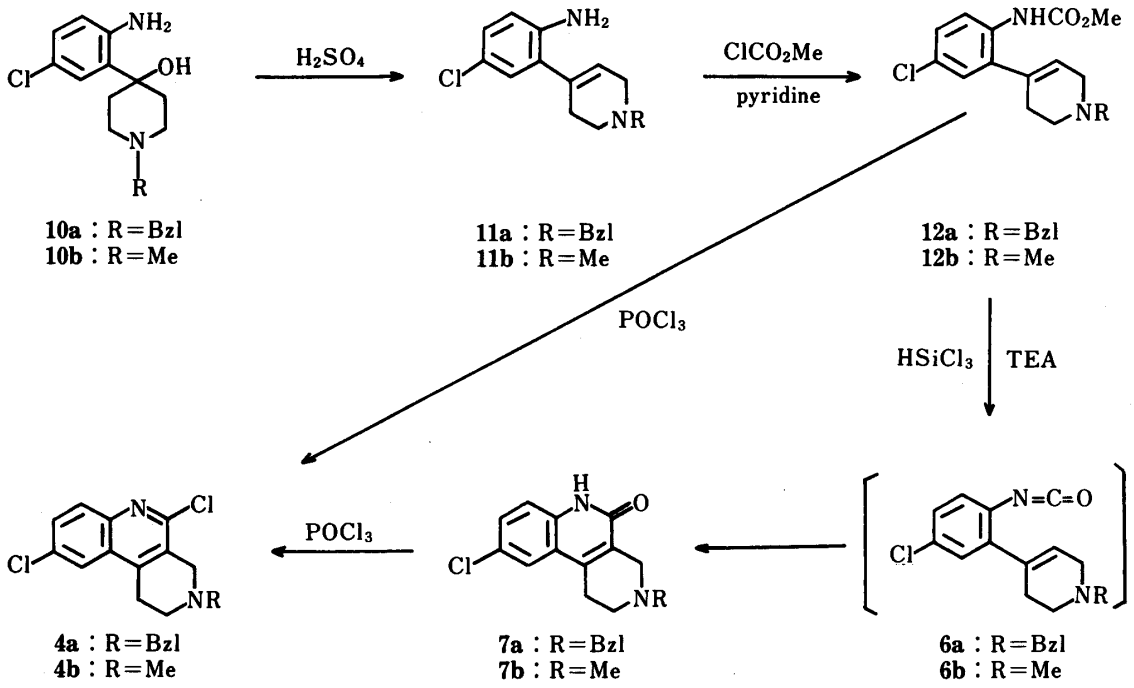
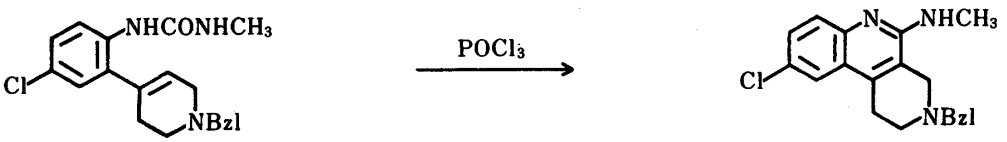


Chart 4

was heated with trichlorosilane/triethylamine (TEA) in toluene under reflux for 7 h to give a crystalline product, which absorbed in the infrared at 1650 cm^{-1}, suggesting the persistence of an amide carbonyl rather than –N=C=O. Accordingly, this product was not the isocyanate (**6a**), but a new compound which corresponded to the molecular formula $C_{19}H_{17}ClN_2O$ on the basis of its elemental analysis data and MS (M^+; *m/e*: 324). In the ^{1}H-NMR spectrum of the compound in DMSO-d_6, the singlet at δ 3.66 due to MeO protons and the multiplet at δ 5.6—5.75 due to an olefinic proton (1H) observed in **12a** had disappeared. The multiplet at δ 2.6—3.0 (4H) and singlet at δ 3.27 (2H) indicated the presence of a 3-substituted 1,2,5,6-tetrahydropyridine ring. The remaining signals are those of an N-benzyl group and a 1,2-disubstituted 4-chlorophenyl group (δ: 3.67, 2H, s; δ: 7.2—7.66, 9H, m). On the basis of these data, the structure of this compound was established to be 2-benzyl-6-chloro-10-oxo-1,2,3,4,9,10-hexahydro-2,9-diazaphenanthrene (**7a**). This compound (**7a**) was converted to **4a** by treatment with $POCl_3$ in the same manner as used for **2a**. Direct treatment of **12a** with $POCl_3$ was also tried, but **4a** was obtained in poor yield. The product (**4a**) was identical with the specimen obtained from **2a**. Similarly, **12b** gave **4b**, as shown in Chart 4. The results are summarized in Table II.

Bischler–Napieralski ring closure of urea was previously described by Schmutz *et al.*[5]: the treatment of *N*-piperidinocarboxy-2-phenylthioaniline and *N*-piperidinocarboxy-2-phenoxyaniline with $POCl_3$ gave 11-piperidinodibenzo[*b*,*f*]-1,4-thiazepine and -oxazepine, respectively. We also attempted the Bischler–Napieralski ring closure of **13**. Compound **13** was heated under reflux in $POCl_3$ for 13 h to afford the desired **14**, as shown in Chart 5.



13 14

Chart 5

Experimental

All melting points were determined on a micro melting point apparatus (Yanagimoto) and are uncorrected. IR spectra were measured on a Shimadzu IR-27G spectrometer, ^{1}H-NMR spectra on a Varian EM 390 spectrometer or a JEOL JNM-PS-100 spectrometer with tetramethylsilane as an internal standard, and ^{13}C-NMR spectra on a JEOL JNM-FX-100 spectrometer at 25.1 MHz, operating in the Fourier transform mode with tetramethylsilane as an internal standard. MS were measured on a JEOL JMS-01SG-2 spectrometer.

(A) Conversion of 2 to 4 with $POCl_3$. Typical Procedures. Synthesis of 2-Benzyl-6,10-dichloro-1,2,3,4-tetrahydro-2,9-diazaphenanthrene (4a)——A stirred suspension of 1′-benzyl-6-chlorospiro[4*H*-3,1-benzoxazine-4,4′-piperidin]-2(1*H*)-one (**2a**) (3.42 g, 10 mmol) in $POCl_3$ (50 ml) was heated under reflux for 5 h, and the reaction mixture was concentrated *in vacuo*. The residue was mixed with sat. aq. $NaHCO_3$ and extracted with AcOEt. The organic layer was concentrated to a small volume and crystals that precipitated were collected by filtration to give **4a** (2.08 g, 60.8%). Recrystallization of **4a** from MeOH afforded an analytical sample, mp 147—149 °C.

(B) Conversion of 12 to 4 with $POCl_3$. Synthesis of 2-Benzyl-6,10-dichloro-1,2,3,4-tetrahydro-2,9-diazaphenanthrene (4a)——A stirred solution of 1-benzyl-4-[2-(methoxycarbonylamino)-5-chlorophenyl]-1,2,5,6-tetrahydropyridine (**12a**) (109 mg, 0.31 mmol) in $POCl_3$ (1.5 ml) was heated under reflux for 8 h and worked up as described above to give **4a** (5.1 mg, 4.8%).

(C) Conversion of 7 to 4 with $POCl_3$. Typical Procedures. Synthesis of 2-Benzyl-6,10-dichloro-1,2,3,4-tetrahydro-2,9-diazaphenanthrene (4a)——A stirred solution of 2-benzyl-6-chloro-10-oxo-1,2,3,4,9,10-hexahydro-2,9-diazaphenanthrene (**7a**) (324.5 mg, 1 mmol) in $POCl_3$ (10 ml) was heated under reflux for 5 h and worked up as described above to give **4a** (213.0 mg, 62.1%).

(D) One-Pot Procedure for the Conversion of 12 to 4 *via* 7. Synthesis of 6,10-Dichloro-2-methyl-1,2,3,4-tetrahydro-2,9-diazaphenanthrene (4b)——A mixture of 4-(2-methoxycarbonylamino-5-chlorophenyl)-1-methyl-1,2,5,6-tetrahydropyridine (**12b**) (223 mg, 0.8 mmol), TEA (0.336 ml, 2.4 mmol), and trichlorosilane (0.24 ml, 2.4 mmol) in dry toluene (8 ml) was heated under reflux for 3 h. Then, the reaction mixture was concentrated *in vacuo* to give a crude oily residue, which was mixed with $POCl_3$ (10 ml). The solution was heated under reflux for 5 h, concentrated, and mixed with sat. aq. $NaHCO_3$ (50 ml). The mixture was extracted with AcOEt and the extract was concentrated to give a crystalline residue, which was triturated with AcOEt to afford **4b** (105.5 mg, 49.3%). Recrystallization from AcOEt gave an analytical sample, mp 170—171 °C.

(E) Reduction of 4e with $NaBH_4$ to 4f. Synthesis of 10-Chloro-2-[2-(3,4-dimethoxyphenyl)-2-hydroxyethyl]-1,2,3,4-tetrahydro-2,9-diazaphenanthrene (4f)——$NaBH_4$ (700 mg, 18.5 mmol) was added to a suspension of **4e** (700 mg, 1.77 mmol) in EtOH (50 ml) and the mixture was stirred overnight at room temperature. The precipitated crystals were collected by filtration and washed with water to give **4f** (525 mg, 74.6%). Recrystallization of **4f** from EtOH gave an analytical sample, mp 164—165 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.75—3.37 [6H, m, $>NCH_2CH_2-$ and $>NCH_2CH(OH)-$ (d, J=6 Hz at 2.82)], 3.87, 3.89, 3.92 (8H, each s, $2\times CH_3O$ and $>NCH_2C=C$), 4.88 [1H, t, J=6 Hz, $-CH(OH)-$], 6.80—7.02 (3H, m, aromatic H), 7.5—8.1 (4H, m, aromatic H).

(F) Conversion of 12 to 7 with Trichlorosilane/TEA. Typical Procedure. Synthesis of 2-Benzyl-6-chloro-10-oxo-1,2,3,4,9,10-hexahydro-2,9-diazaphenanthrene (7a)——Trichlorosilane (406.8 mg, 3 mmol) was added to a solution of 1-benzyl-4-(2-methoxycarbonylamino-5-chlorophenyl)-1,2,5,6-tetrahydropyridine (**12a**) (356.8 mg, 1 mmol) and TEA (0.42 ml, 3 mmol) in dry toluene (10 ml), and the mixture was heated under reflux for 1 h. Then, the reaction mixture was concentrated *in vacuo*. The residue was mixed with sat. aq. $NaHCO_3$ and extracted with $CHCl_3$. The extract was washed with H_2O, dried, and concentrated to give **7a** (215 mg, 66.3%) as crystals, which were recrystallized from DMF–EtOH to give an analytical sample (186 mg, 57.3%), mp 222—224 °C. IR (KBr): 1650 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 2.6—3.0 (4H, m, $>NCH_2CH_2-$), 3.27 (2H, s, $>NCH_2-C=C$, 3.67 (2H, s, $C_6H_5CH_2-$), 7.2—7.66 (9H, m, aromatic H and NH).

(G) Conversion of 13 into 14 with $POCl_3$. Synthesis of 2-Benzyl-6-chloro-10-methylamino-1,2,3,4-tetrahydro-2,9-diazaphenanthrene (14)——A solution of 1-benzyl-4-[2-(*N*-methylcarbamoylamino)-5-chlorophenyl]-1,2,5,6-tetrahydropyridine (**13**) (533.6 mg, 1.5 mmol) in $POCl_3$ (25 ml) was heated under reflux for 3 h and concentrated *in vacuo*. The residue was mixed with ice water, made basic with aq. NaOH, and extracted with $CHCl_3$. The extract was washed with sat. aq. NaCl, dried, and concentrated *in vacuo* to give an oily residue. The product was chromatographed on silica gel with AcOEt–hexane (1 : 1, v/v) to afford (**14**) (52.9 mg, 10.4%); this product was crystallized from AcOEt,

mp 173—175 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.86 (2H, t, J=6 Hz, >NCH_2CH_2–), 3.05 (2H, t, J=6 Hz, >NCH_2CH_2–), 3.10 (3H, d, J=5 Hz, $NHCH_3$), 3.38 (2H, s, >NCH_2–C=C), 3.78 (2H, s, $C_6H_5CH_2$–), 4.26 (1H, d, J=5 Hz, $NHCH_3$), 7.3—7.7 (8H, m, aromatic H).

(H) Synthesis of the Other Compounds (11a, b, 12a, b, 13). 4-(2-Amino-5-chlorophenyl)-1-benzyl-1,2,5,6-tetrahydropyridine (11a)——A solution of 4-(2-amino-5-chlorophenyl)-1-benzyl-4-hydroxypyridine (**10a**) (500 mg, 1.58 mmol) in H_2SO_4 (5 ml) was stirred for 3 h at room temperature and mixed with ice water. The mixture was made basic and extracted with ether. The ethereal extract was washed with H_2O, dried and mixed with a solution of 5.7 N HCl–AcOEt. White crystals that precipitated were collected by filtration to give **11a** (529.5 mg, 89.9%) as the 2HCl salt. Recrystallization of **11a** from MeOH–acetone afforded an analytical sample, mp 142—145 °C. *Anal.* Calcd for $C_{18}H_{19}ClN_2$: C, 58.15; H, 5.69; N, 7.54. Found: C, 58.03; H, 5.66; N, 7.50. ^{1}H-NMR (CD_3OD) δ: 2.7—3.1 (2H, m, >NCH_2CH_2–), 3.4—3.8 (2H, m, >NCH_2CH_2–), 3.90 (2H, d, J=2 Hz, >NCH_2CH=C<), 4.50 (2H, s, $C_6H_5CH_2$–), 5.8—5.95 (1H, m, –CH=C<), 7.4—7.8 (8H, m, aromatic H).

4-(2-Amino-5-chlorophenyl)-1-methyl-1,2,5,6-tetrahydropyridine (11b)——This compound was prepared from 4-(2-amino-5-chlorophenyl)-1-methyl-4-hydroxypiperidine (**10b**) in 94.1% yield as described for **11a**. Recrystallization from AcOEt–petroleum ether afforded an analytical sample, mp 75—76 °C. *Anal.* Calcd for $C_{12}H_{15}ClN$: C, 64.71; H, 6.78; N, 12.57. Found: C, 64.71; H, 6.87; N, 12.44. ^{1}H-NMR ($CDCl_3$) δ: 2.26—2.53 [5H, m, C=C–CH_2–CH_2– and N–CH_3 at 2.38 (s)], 2.56—2.75 (2H, m, C=C–CH_2–CH_2–), 3.00—3.15 (2H, m, CH_3N–CH_2–C=C), 3.76 (2H, br s, –NH_2), 5.65—5.82 (1H, m, >C=CH–), 6.5—7.05 (3H, m, aromatic H).

1-Benzyl-4-(2-methoxycarbonylamino-5-chlorophenyl)-1,2,5,6-tetrahydropyridine (12a)——Methyl chloroformate (3.1 ml, 40 mmol) was added dropwise at 0 °C to a solution of 4-(2-amino-5-chlorophenyl)-1-benzyl-1,2,5,6-tetrahydropyridine (**11a**) (2.99 g, 10 mmol) in pyridine (25 ml). The mixture was stirred for 1 h at this temperature, then allowed to warm to room temperature. The mixture was stirred for an additional 6 h, concentrated, mixed with aq. $NaHCO_3$, and extracted with AcOEt. The extract was washed with sat. aq. NaCl, dried, and concentrated to give an oily product (3.12 g, 87.6%). This product was dissolved in MeOH, the solution was mixed with 1.6 N HCl–AcOEt (20 ml), and the mixture was concentrated *in vacuo*. The residue was crystallized from MeOH to give **12a** (2.39 g, 60.8%) as the HCl salt. Recrystallization of **12a** from EtOH gave an analytical sample, mp 213—214 °C. *Anal.* Calcd for $C_{20}H_{21}ClN_2O_2 \cdot HCl$: C, 61.08; H, 5.64; N, 7.12. Found: C, 61.01; H, 5.77; N, 7.04. ^{1}H-NMR (DMSO-d_6+CD_3OD) δ: 3.2—3.85 [7H, m, >NCH_2CH_2–, CH_3O– (s, at 3.66 ppm), and –CH_2CH=C< (d, J=3 Hz at 3.75 ppm)], 4.47 (2H, s, $C_6H_5CH_2$–), 5.6—5.75 (1H, m, –CH=C<), 7.2—7.8 (8H, m, aromatic H).

4-(2-Methoxycarbonylamino-5-chlorophenyl)-1-methyl-1,2,5,6-tetrahydropyridine (12b)——4-(2-Amino-5-chlorophenyl)-1-methyl-1,2,5,6-tetrahydropyridine (**11b**) was treated with methyl chloroformate as described for **12a** to give **12b** (97.9%) as an oily product. MS *m/e*: 280 (M^+). ^{1}H-NMR ($CDCl_3$) δ: 2.25—2.5 [5H, m, $CH_3NCH_2CH_2$– and $CH_3NCH_2CH_2$– (s at 2.40)], 2.63 (2H, t, J=6 Hz, $CH_3NCH_2CH_2$–), 3.0—3.13 (2H, m, CH_3NCH_2CH=C<), 3.73 (3H, s, CH_3O), 5.6—5.8 (1H, m, –CH=C<).

1-Benzyl-4-[2-(*N*-methylcarbamoylamino)-5-chlorophenyl]-1,2,5,6-tetrahydropyridine (13)——Methyl isocyanate (1.14 g, 20 mmol) was added to a solution of 4-(2-amino-5-chlorophenyl)-1-benzyl-1,2,5,6-tetrahydropyridine (**11a**) (2.98 g, 10 mmol) in AcOEt (20 ml), and the mixture was stirred at 50 °C for 2.5 h, then concentrated. The residue was chromatographed on silica gel with AcOEt–hexane (1 : 1, v/v) to give **13** (2.68 g, 75.3%) as crystals. Recrystallization of **13** from AcOEt gave an analytical sample, mp 134—137 °C. *Anal.* Calcd for $C_{20}H_{22}ClN_3O$: C, 67.50; H, 6.23; N, 11.81. Found: C, 67.35; H, 6.34; N, 11.60. ^{1}H-NMR ($CDCl_3$) δ: 2.3—2.4 (2H, m, >NCH_2CH_2–), 2.74 (2H, t, J=6 Hz >NCH_2CH_2–), 2.79 (3H, d, J=5 Hz, $NHCH_3$), 3.05—3.15 (2H, m, >NCH_2CH=C<), 3.63 (2H, s, $C_6H_5CH_2$–), 5.54 (1H, d, J=5 Hz, $NHCH_3$), 5.65—5.7 (1H, m, –CH=C<), 6.99 (1H, d, J=2 Hz, aromatic H), 7.1—7.4 (7H, m, –NHCO–, aromatic H), 8.06 (1H, d, aromatic H).

References and Notes

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3) It is known that an O-complex such as **9a** is formed from an amide and phosphorus oxychloride. B. C. Challis and J. A. Challis, "Comprehensive Organic Chemistry," Vol. 2, ed. by I. O. Sutherland, Pergamon Press, Oxford, 1979, p. 1023. From this point of view, we may speculate that formation of an O-complex of urethane or isocyanate (**5a** or **8a**) occurs.
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