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A Novel Synthesis of 1-Acylindoxyls

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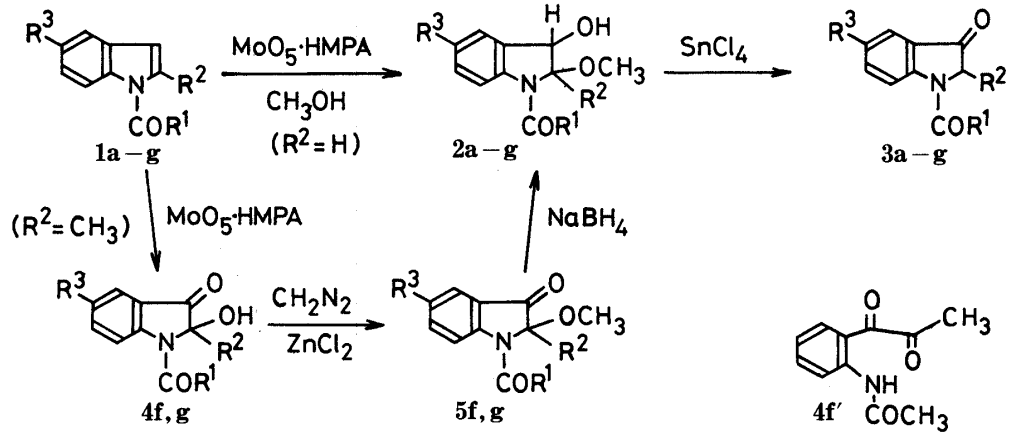
A novel and efficient synthesis of 1-acylindoxyls (**3**) from 1-acylindoles (**1**) is described. The procedure involves the demethoxylation with stannic chroride of 1-acyl-3-hydroxy-2-methoxyindoline (**2**), which were obtained by the MoO_5 oxidation of **1** in methanol. Since the MoO_5 oxidation of 2-substituted 1-acylindoles (**1f** and **1g**) gave not the corresponding indolines (**2f** and **2g**), but 2-hydroxyindoxyls (**4f** and **4g**), **2f** and **2g** were obtained by the methylation of **4f** and **4g** with diazomethane to give **5f** and **5g**, followed by the reduction of **5f** and **5g** with sodium borohydride, respectively.

Keywords——indoxyl; indole; indoline; oxidation; demethoxylation; peroxomolybdenum complex; methylation; diazomethane; reduction; sodium borohydride

1-Acylindoxyls are useful intermediates for the syntheses of biologically active compounds[1] and are prepared mainly by the cyclization of 2-carboxyphenylglycines[2] and 2-(acylamino)-α-chloroacetophenones.[3] However, little is known about the preparation of 1-acylindoxyls from 1-acylindoles. The only known examples are the oxidation of 1,3-diacylindole with lead tetraacetate[4] and the electrochemical acetoxylation of 1-acetylindole followed by elimination and hydrolysis of the acetoxylation product.[5] The former gives a low yield of 1-acetylindoxyl, and the latter gives a considerable yield of 1-acetylindoxyl, but the application of the method to other indoles has not been investigated at all. In our recent studies on the MoO_5 oxidation,[6–9] we reported an example of the preparation of 1-acetylindoxyl (**3a**) from 1-acetylindole (**1a**),[6] *i.e.*, the MoO_5 oxidation of **1a** in methanol to



a: $R^1=CH_3$, $R^2=R^3=H$; **b**: $R^1=CH_3$, $R^2=H$, $R^3=OCH_3$;
c: $R^1=CH_3$, $R^2=H$, $R^3=Br$; **d**: $R^1=C_6H_5$, $R^2=R^3=H$;
e: $R^1=OCH_3$, $R^2=R^3=H$; **f**: $R^1=R^2=CH_3$, $R^3=H$;
g: $R^1=R^2=CH_3$, $R^3=OCH_3$

Chart 1

give 1-acetyl-3-hydroxy-2-methoxyindoline (**2a**), followed by the demethoxylation of **2a**. We have now examined the generality and limitations of this preparation method. However, the MoO_5 oxidation of 2-substituted 1-acylindoles (**1**) in methanol did not give the expected 3-hydroxy-2-methoxyindolines (**2**) but 1-acyl-2-hydroxyindoxyls (**4**), and therefore we investigated the reductive dehydroxylation of **4** to 2-substituted indoxyls (**3**). The present paper describes these conversions for the preparation of 1-acylindoxyls (**3b**—**g**) from 1-acylindoles (**1b**—**g**).

Initially, we examined the application of the previously described method to several 1-acylindoles (**1b**—**e**) other than **1a**; 1-acetyl-5-methoxy- (**1b**), 1-acetyl-5-bromo- (**1c**), 1-benzoyl- (**1d**), and 1-methoxycarbonylindoles (**1e**) were treated with the peroxomolybdenum reagent, (hexamethylphosphoramido)oxodiperoxomolybdenum (VI) ($MoO_5 \cdot HMPA$), in methanol to give the corresponding indolines (**2b**—**e**). Reaction of **2b**—**e** with stannic chloride gave 1-acylindoxyls (**3b**—**e**), and the overall yields of **3b**—**e** from **1b**—**e** were 65—84%. The structures were confirmed by the spectral data (see Experimental). In the case of 1-acetyl-5-nitroindole, the MoO_5 oxidation did not occur at all. A serious limitation of this method is that the MoO_5 oxidation of 1-acetyl-2-methylindole (**1f**) in methanol did not give 1-acetyl-3-hydroxy-2-methoxy-2-methylindoline (**2f**), but 1-acetyl-2-hydroxy-2-methylindoxyl (**4f**).

Next, we attempted the conversion of **4f** to 1-acetyl-2-methylindoxyl (**3f**). Treatment of **4f** with sodium borohydride gave a complex mixture. Compound **4f** is probably in equilibrium with its acyclic tautomer **4f'**,[10] and this may account for its failure to undergo the desired reduction. This failure indicated the need for protection of the hydroxy group of **4f**. Therefore, 1-acetyl-2-methoxy-2-methylindoxyl (**5f**) was prepared in 95% yield by treatment of **4f** with an excess of diazomethane in the presence of zinc chloride. As expected, reduction of **5f** with sodium borohydride gave a 90% yield of 3-hydroxy-2-methoxyindoline (**2f**), and subsequent demethoxylation with stannic chloride gave the desired indoxyl (**3f**) in 76% yield. The overall yield of **3f** from **1f** was 41%. The structures of these compounds (**5f**, **2f**, and **3f**) were determined from the spectral data (see Experimental).

In a similar manner, 1-acetyl-5-methoxy-2-methylindoxyl (**3g**), which is an intermediate for the synthesis of indomethacin,[1a] was prepared in 56% overall yield from the indole (**1g**); the structures of **4g**, **5g**, **2g**, and **3g** were assigned on the basis of the spectral data (see Experimental).

Although several methods for the preparation of 2-unsubstituted 1-acylindoxyls (**3**) are known,[2-5] there is no efficient method for the preparation of 2-substituted indoxyl (**3**). This new method offers a simple and efficient route to either 2-unsubstituted or 2-substituted 1-acylindoxyls (**3**).

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded on a Hitachi 260-10 or 270-30 spectrophotometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were measured with a JEOL JNM-PMX 60 instrument using tetramethylsilane as an internal standard. Column chromatography was carried out on silica gel (80—100 mesh, Kanto Chemical Co., Inc.).

Materials——$MoO_5 \cdot HMPA$ was prepared by the method of Mimoun and co-workers.[11] 1-Acetyl-5-methoxy- (**1b**), 1-acetyl-5-bromo- (**1c**), and 1-acetyl-5-methoxy-2-methylindoles (**1g**) were prepared by acetylation of commercial indoles according to the procedure of Illi.[12] 1-Benzoyl- (**2d**) and 1-methoxycarbonyl-3-hydroxy-2-methoxyindolines (**2e**), and 1-acetyl-2-hydroxy-2-methylindoxyl (**4f**) were prepared by the previously described procedure.[6]

1-Acetyl-3-hydroxy-2,5-dimethoxyindoline (2b)——A solution of **1b** (1.20 g, 6.3 mmol) and $MoO_5 \cdot HMPA$ (2.49 g, 7.0 mmol) in dry CH_3OH (70 ml) was stirred at room temperature under argon for a week. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with $CHCl_3$ as an eluent to give *trans*-**2b** (0.79 g, 52%) and *cis*-**2b** (0.37 g, 25%). The stereochemistry was confirmed by comparison of the ^{1}H-NMR spectral data with those for *trans*- and *cis*-**2a**.[6]

trans-**2b**: mp 148—149 °C (from ether). *Anal.* Calcd for $C_{12}H_{15}NO_4$: C, 60.76; H, 6.37; N, 5.90. Found: C, 60.80;

H, 6.50; N, 5.90. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3412 (OH), 1665 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.95 (3H, s, $-COCH_3$), 3.33 (3H, s, $-OCH_3$), 3.2—3.45 (1H, br, OH, exchangeable with D_2O), 3.77 (3H, s, $-OCH_3$), 4.85 (1H, s, –CH–), 5.13 (1H, s, –CH–), 6.85—7.15 (2H, m, Ar-H), 7.97 (1H, d, J=8 Hz, Ar-H).

cis-**2b**: mp 158—160 °C (from ether). *Anal.* Calcd for $C_{12}H_{15}NO_4$: C, 60.76; H, 6.37; N, 5.90. Found: C, 60.75; H, 6.37, N, 5.90. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3568 (OH), 1662 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.18 (3H, s, $-COCH_3$), 2.3—2.65 (1H, br s, OH), 3.40 (3H, s, $-OCH_3$), 3.63 (3H, s, $-OCH_3$), 4.9—5.35 (2H, br s, –CH–CH–), 6.5—7.0 (2H, m, Ar-H), 7.55—8.2 (1H, br, Ar-H).

1-Acetyl-5-bromo-3-hydroxy-2-methoxyindoline (2c)——Using a procedure similar to that described above for the preparation of **2b**, **1c** (3.0 g, 12.6 mmol) was treated with MoO_5·HMPA (7.15 g, 20.1 mmol) in dry CH_3OH (200 ml). The reaction mixture was purified by column chromatography on silica gel with CH_2Cl_2–ethyl acetate (50 : 3) as an eluent to give *trans*-**2c** (1.95 g, 54%) and *cis*-**2c** (0.97 g, 27%). The stereochemistry was confirmed by comparison of the ^{1}H-NMR spectral data with that of *trans*- and *cis*-**2a**.[6]

trans-**2c**: mp 213—214 °C (from ether). *Anal.* Calcd for $C_{11}H_{12}BrNO_3$: C, 46.18; H, 4.23; N, 4.90. Found: C, 46.30; H, 4.22; N, 4.93. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH), 1671 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.03 (3H, s, $-COCH_3$), 3.33 (3H, s, $-OCH_3$), 3.2—3.5 (1H, br, OH), 4.87 (1H, s, –CH–), 5.13 (1H, s, –CH–), 7.25—7.6 (2H, m, Ar-H), 7.88 (1H, d, J=8 Hz, Ar-H).

cis-**2c**: mp 220—221 °C (from ether). *Anal.* Calcd for $C_{11}H_{12}BrNO_3$: C, 46.18; H, 4.23; N, 4.90. Found: C, 46.31; H, 4.21; N, 4.95. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3598 (OH), 1689 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.23 (3H, s, $-COCH_3$), 2.0—2.75 (1H, br, OH), 3.45 (3H, s, $-OCH_3$), 4.8—5.5 (2H, br s, –CH–CH–), 6.5—7.1 (2H, m, Ar-H), 7.6—8.1 (1H, br, Ar-H).

General Procedure for Demethoxylation of 2b—e to 1-Acylindoxyls (3b—e)——The following procedure is typical. A solution of $SnCl_4$ (1.3 mmol) in dry CH_2Cl_2 (3—5 ml) was added to a solution of **2b—e** (1 mmol) in dry CH_2Cl_2 (4—5 ml) at 0 °C. The reaction mixture was allowed to warm to room temperature, then stirred for 30 min, diluted with CH_2Cl_2 (10 ml), and washed with saturated NaCl solution. The CH_2Cl_2 layer was dried over Na_2SO_4, and concentrated *in vacuo* to give a solid, which was recrystallized from C_6H_6 (for **3b**, **c**) or ether (for **3d**, **e**) to give **3b—e**.

1-Acetyl-5-methoxyindoxyl (3b)——This was prepared from *trans*-**2b** (200 mg, 0.84 mmol) and $SnCl_4$ (290 mg, 1.1 mmol) in 94% yield (163 mg), mp 183—185 °C [lit.[3] mp 184—187 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1718, 1676 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.28 (3H, s, $-COCH_3$), 3.82 (3H, s, $-OCH_3$), 4.27 (2H, s, $-CH_2CO-$), 7.0—7.4 (2H, m, Ar-H), 8.42 (1H, d, J=8 Hz, Ar-H).

1-Acetyl-5-bromoindoxyl (3c)——This was prepared from *trans*-**2c** (285 mg, 1 mmol) and $SnCl_4$ (340 mg, 1.3 mmol) in 94% yield (238 mg), mp 196—198 °C [lit.[13] mp 187—188 °C]. *Anal.* Calcd for $C_{10}H_8BrNO_2$: C, 47.27; H, 3.17; N, 5.51. Found: C, 47.27; H, 3.09; N, 5.56. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1731, 1689 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.18 (3H, s, $-COCH_3$), 4.28 (2H, s, $-CH_2CO-$), 7.45—7.8 (2H, m, Ar-H), 8.32 (1H, d, J=9 Hz, Ar-H).

1-Benzoylindoxyl (3d)——This was prepared from *trans*-**2d** (245 mg, 1 mmol) and $SnCl_4$ (340 mg, 1.3 mmol) in 88% yield (188 mg), mp 124—125 °C. *Anal.* Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 75.70; H, 4.43; N, 5.74. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1660 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 4.28 (2H, s, $-CH_2CO-$), 7.2—7.9 (8H, m, Ar-H), 8.21 (1H, d, J=8 Hz, Ar-H).

1-Methoxycarbonylindoxyl (3e)——This was prepared from *trans*-**3e** (0.67 g, 3 mmol) and $SnCl_4$ (1.05 g, 4 mmol) in 96% yield (0.55 g), mp 268—269 °C. *Anal.* Calcd for $C_{10}H_9NO_3$: C, 62.82; H, 4.67; N, 7.33. Found: C, 63.06; H, 4.81; N, 7.23. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1705 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 3.90 (3H, s, $-OCH_3$), 4.18 (2H, s, $-CH_2CO-$), 6.95—7.8 (3H, m, Ar-H), 8.10 (1H, d, J=8 Hz, Ar-H).

1-Acetyl-2-hydroxy-5-methoxy-2-methylindoxyl (4g)——Using a procedure similar to that described above for the preparation of **2b**, **1g** (0.87 g, 4.3 mmol) was treated with MoO_5·HMPA (1.77 g, 5 mmol). The reaction mixture was chromatographed on a silica gel column. Elution with CH_2Cl_2–ethyl acetate (25 : 2) gave 1-acetyl-5-methoxy-2-methylindoxyl (**3g**) in 11% yield (0.11 g). Further elution with CH_2Cl_2–ethyl acetate (5 : 1) gave **4g** in 74% yield (0.75 g).

3g: mp 124—126 °C (from ether–*n*-hexane) [lit.[1a] mp 125 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715, 1665 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.58 (3H, d, J=7 Hz, $-CH-CH_3$), 2.35 (3H, s, $-COCH_3$), 3.82 (3H, s, $-OCH_3$), 4.27 (1H, q, J=7 Hz, $-CH-CH_3$), 7.2—7.3 (2H, m, Ar-H), 8.2—8.7 (1H, br, Ar-H).

4g: mp 182—185 °C (from C_6H_6). *Anal.* Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.39; H, 5.63; N, 5.97. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300 (OH), 1725, 1650 (C=O): ^{1}H-NMR ($CDCl_3$–DMSO-d_6) δ: 1.67 (3H, s, $-CH_3$), 2.48 (3H, s, $-COCH_3$), 3.80 (3H, s, $-OCH_3$), 5.6—6.15 (1H, br, OH, exchangeable with D_2O), 7.0—7.5 (2H, m, Ar-H), 8.40 (1H, d, J=9 Hz, Ar-H).

1-Acetyl-2-methoxy-2-methylindoxyl (5f)——A solution of $ZnCl_2$ (0.99 g, 7.2 mmol) in dry ether (10 ml) was gradually added to a solution of **4f** (0.50 g, 2.4 mmol) and diazomethane[14] (*ca.* 22 mmol) in dry ether (270 ml) at 0—5 °C. The reaction mixture was stirred at room temperature overnight. After removal of a precipitate, the filtrate was concentrated *in vacuo* to give a solid, which was recrystallized from *n*-hexane to give **5f** (0.507 g, 95%), mp 165—166 °C. *Anal.* Calcd for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.81; H, 6.07; N, 6.31. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725, 1670 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.70 (3H, s, $-CH_3$), 2.47 (3H, s, $-COCH_3$), 3.11 (3H, s, $-OCH_3$), 7.2—7.85 (3H, m, Ar-H), 8.60 (1H, d, J=8 Hz, Ar-H).

1-Acetyl-2,5-dimethoxy-2-methylindoxyl (5g)——Using a procedure similar to that described above for the preparation of **5f**, **4g** (0.52 g, 2.2 mmol) was treated with diazomethane[14] (*ca.* 40 mmol) and $ZnCl_2$ (0.9 g, 6.6 mmol) in dry ether (60 ml) and tetrahydrofuran (100 ml). The reaction mixture was purified by column chromatography on silica gel with CH_2Cl_2 to give **5g** (0.42 g, 76%), mp 126—127 °C (from ether–*n*-hexane). *Anal.* Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.57; H, 6.13; N, 5.54. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1732, 1668 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.68 (3H, s, $-CH_3$), 2.45 (3H, s, $-COCH_3$), 3.12 (3H, s, $-OCH_3$), 3.83 (3H, s, $-OCH_3$), 7.0—7.4 (2H, m, Ar-H), 8.52 (1H, d, J=8 Hz, Ar-H).

1-Acetyl-3-hydroxy-2-methoxy-2-methylindoline (2f)——Sodium borohydride (74 mg, 1.9 mmol) was gradually added to a solution of **5f** (111 mg, 0.5 mmol) in CH_3OH (3 ml) and H_2O (0.2 ml) at 0—5 °C. The reaction mixture was allowed to warm to room temperature, then stirred for 10 min, diluted with $CHCl_3$ (70 ml), and washed with H_2O. The $CHCl_3$ layer was dried over $MgSO_4$, and concentrated *in vacuo* to give **2f**[15] (101 mg, 90%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3530 (OH), 1660 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.83 (3H, s, $-CH_3$), 2.42 (3H, s, $-COCH_3$), 3.33 (3H, s, $-OCH_3$), 3.0—3.5 (1H, br, OH), 4.83 (1H, s, –CH–), 7.0—7.5 (3H, m, Ar-H), 7.84 (1H, d, J=8 Hz, Ar-H).

1-Acetyl-3-hydroxy-2,5-dimethoxy-2-methylindoline (2g)——Using a procedure similar to that described above for the preparation of **2f**, **5g** (0.24 g, 0.96 mmol) was treated with sodium borohydride (0.18 g, 4.8 mmol) in CH_3OH (65 ml) and H_2O (1.5 ml) to give **2g**[15] (0.24 g, quantitative yield). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3552 (OH), 1660 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.83 (3H, s, $-CH_3$), 2.38 (3H, s, $-COCH_3$), 2.55—2.9 (1H, br, OH), 3.32 (3H, s, $-OCH_3$), 3.77 (3H, s, $-OCH_3$), 4.85 (1H, s, –CH–), 6.65—7.05 (2H, m, Ar-H), 7.5—7.95 (1H, br, Ar-H).

1-Acetyl-2-methylindoxyl (3f)——Using a procedure similar to that described above for the preparation of **3b**, **2f** (58 mg, 0.26 mmol) was treated with $SnCl_4$ (89 mg, 0.34 mmol) in dry CH_2Cl_2 (2 ml) to give a crude product, which was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to give **3f** (38 mg, 77%), mp 101—103.5 °C (from C_6H_6) [lit.[1a] mp 104 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1675 (C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.60 (3H, d, J=7 Hz, $-CH-C\underline{H}_3$), 2.40 (3H, s, $-COCH_3$), 4.30 (1H, q, J=7 Hz, $-C\underline{H}-CH_3$), 7.1—7.85 (3H, m, Ar-H), 8.32 (1H, d, J=8 Hz, Ar-H).

1-Acetyl-5-methoxy-2-methylindoxyl (3g)——Using a procedure similar to that described above for the preparation of **3b**, **2g** (0.24 g, 0.96 mmol) was treated with $SnCl_4$ (0.27 g, 1.05 mmol) in dry CH_2Cl_2 (10 ml) to give a crude product, which was purified by column chromatography on silica gel with CH_2Cl_2–ethyl acetate (30:1) as an eluent to give **3g** (0.16 g, 77%), mp 126—127.5 °C (from ether) [lit.[1a] mp 125 °C].

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15) Compounds **2f** and **2g** were unstable to heat so that they were used in the next reaction without further purification; when **2g** was kept in $CDCl_3$ at room temperature for 15 h, it was converted to the indoxyl **3g** (checked by thin layer chromatography and continuous observation of changes in the ^{1}H-NMR spectra).