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Oxidation of Indoles with Oxodiperoxomolybdenum (VI), $MoO_5 \cdot HMPA$. Preparation of 2-Hydroxyindoxyl and Isatogen Derivatives

CHUN-SHENG CHIEN, TOSHIKATSU TAKANAMI, TOMOMI KAWASAKI, and MASANORI SAKAMOTO*

Meiji College of Pharmacy, 1–35–23, Nozawa, Setagaya-ku, Tokyo 154, Japan

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Oxidation of 1-acetylindoles **1** with (hexamethylphosphoramide)oxodiperoxomolybdenum (VI), $MoO_5 \cdot HMPA$, in dry methylene chloride gave 1-acetyl-2-hydroxyindoxyls **4**. 2-Phenylindole (**8**) was similarly treated with $MoO_5 \cdot HMPA$ to give a dimeric product **11**, while oxidation of **8** with three mol eq of $MoO_5 \cdot HMPA$ gave 2-phenylisatogen (**12**). The oxidation of other indoles, **14**, **19**, **21**, and **22**, with $MoO_5 \cdot HMPA$ in methylene chloride is also described. A possible mechanism for these oxidations is presented.

Keywords——indole; oxidation; peroxomolybdenum complex; 2-hydroxyindoxyl; isatogen; oxindole

The oxidation of indoles with peracids proceeds *via* the formation of the 2,3-epoxy intermediates, which undergo nucleophilic ring opening by peracids.[1-4] This observation prompted us to investigate the oxidation of indoles with the presumably non-nucleophilic epoxidizing agent, (hexamethylphosphoramide)oxodiperoxomolybdenum (VI), $MoO_5 \cdot HMPA$.[5] Recently we have reported[6] that the oxidation of 1-acylindoles with $MoO_5 \cdot HMPA$ in methanol affords the methanolysis products of the 2,3-epoxy intermediates. We have now found that the oxidation of 1-acylindoles **1** and 2-phenylindole (**8**) with $MoO_5 \cdot HMPA$ in inert solvents occurs non-nucleophilically to give 2-hydroxyindoxyl **4** and isatogen **12**, respectively, which could not be obtained by oxidation with peracids. In this paper we also describe the oxidation of several other indoles, **14**, **19**, **21**, and **22**, with $MoO_5 \cdot HMPA$.

Treatment of 1-acetylindole (**1a**) with $MoO_5 \cdot HMPA$ in dry methylene chloride under argon at room temperature for a week gave 1-acetyl-2-hydroxyindoxyl (**4a**) in 34% yield; the structure was assigned on the basis of the analytical and spectral data. The isomeric structure **4a'** was readily ruled out by comparison of the infrared (IR) spectrum (1730 and 1685 cm^{-1}) with that of 1-acetyl-2-methoxyindoxyl (**5**) (1730 and 1685 cm^{-1}).[6] Treatment of **1a** with $MoO_5 \cdot HMPA$ in dry acetonitrile similarly gave **4a** in 38% yield. As regards the mechanism of the oxidation, it is suggested that the 2,3-epoxide **2a** initially formed from **1a** undergoes isomerization into the indoxyl **3a** followed by further oxidation of **3a** with $MoO_5 \cdot HMPA$ to give **4a**. This is strongly supported by the following results; (i) similar treatment of **1a** with $MoO_5 \cdot HMPA$ for 5 min gave 1-acetylindoxyl (**3a**)[7] (7%) and **4a** (4%), together with recovered **1a** in 78% yield; and (ii) oxidation of **3a** with $MoO_5 \cdot HMPA$ readily took place to give **4a** in 62% yield.

For comparison, we also investigated the oxidation of **1a** with a peracid. Treatment of **1a** with *m*-chloroperbenzoic acid (*m*-CPBA) in dry methylene chloride at room temperature gave 1-acetyl-2-(*m*-chlorobezoyloxy)-3-hydroxyindoline (**6**) (34%), and small amounts of the indoxyl **3a**[7] (3%) and the oxindole **7**[7] (9%), together with recovered **1a** (11%). The formation

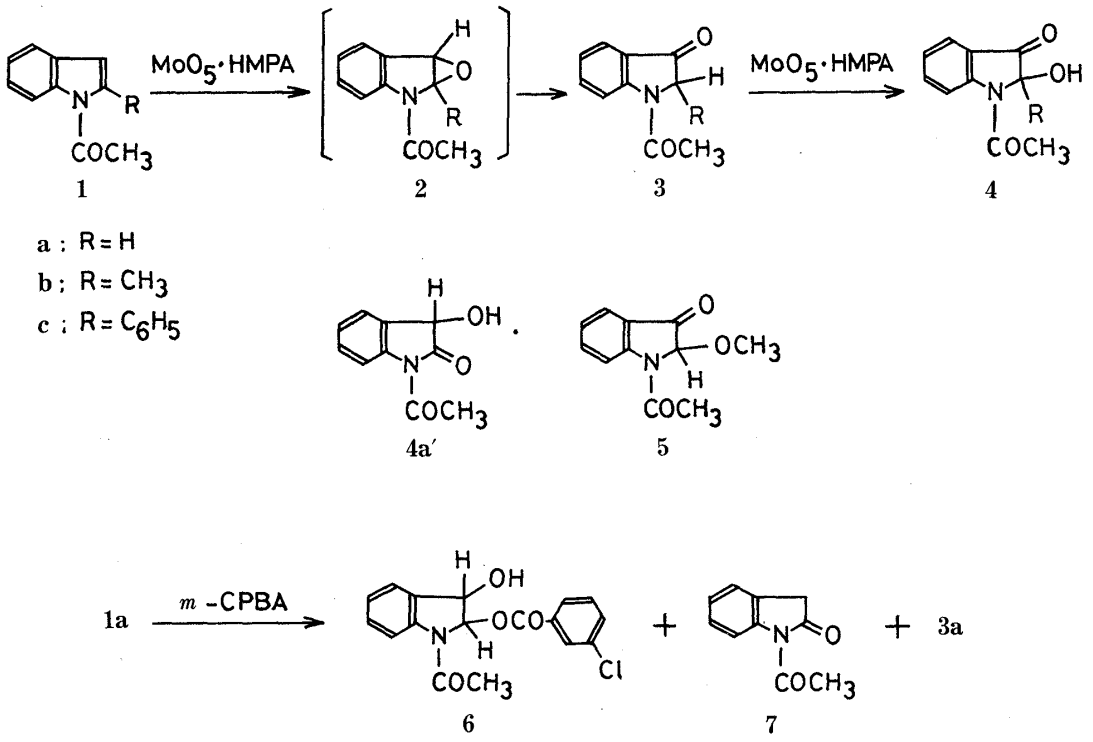

Chart 1

of **4a** was not detected by thin layer chromatography (TLC). The structure of **6** was confirmed by the spectral data and the following chemical evidence: treatment of **6** with sulfuric acid in methylene chloride gave the indoxyl **3a** in 57% yield.

Similar treatment of 1-acetyl-2-methylindole (**1b**) with $MoO_5 \cdot HMPA$ in dry methylene chloride gave 1-acetyl-2-hydroxy-2-methylindoxyl (**4b**)[6] in 55% yield, and the oxidation of 1-acetyl-2-phenylindole (**1c**) gave the 2-hydroxyindoxyl **4c**[8] and the indoxyl **3c** in 60% and 9% yields. The structure of **3c** was confirmed by the analytical and spectral data.

Oxidation of 2-phenylindole (**8**) with $MoO_5 \cdot HMPA$ in dry methylene chloride gave a dimeric product **11** in 56% yield; the structure was confirmed by comparison of the spectral data with those of an authentic sample.[3] The formation of **11** can be rationalized by assuming that the 2-hydroxyindoxyl **9**, derived from **8** by analogy with the mechanism proposed for the formation of **4**, undergoes spontaneous dehydration to form the indolone **10**[9] followed by an attack of **8** on **10** to give **11**.

On the other hand, when **8** was allowed to react with three mol eq of $MoO_5 \cdot HMPA$, 2-phenylisatogen (**12**) was obtained in 58% yield. The structure was identified by comparison of the spectral data with those of an authentic specimen.[10] The isatogen **12** was also derived from the dimeric product **11** by treatment with $MoO_5 \cdot HMPA$. The formation of **12** can be explained in terms of further oxidation of the intermediate **10** with excess $MoO_5 \cdot HMPA$. In contrast to this result, the oxidation of **8** with three mol eq of peracids proceeds *via* addition of the peracids to the intermediate **10** followed by a Baeyer–Villiger-type rearrangement of the peracidic adduct to form the 1,3-benzoxazine **13**.[3,4] The difference in these results demonstrates the non-nucleophilic character of $MoO_5 \cdot HMPA$.

Treatment of 1-acetyl-3-methylindole (**14**) with $MoO_5 \cdot HMPA$ under the same conditions as mentioned above gave a mixture of two isomeric products in 27% yield, together with 1-acetyl-3-methyloxindole (**15**) in 28% yield. The two isomeric products could be separated by fractional recrystallization from ethyl acetate to give *trans*- and *cis*-1-acetyl-2,3-

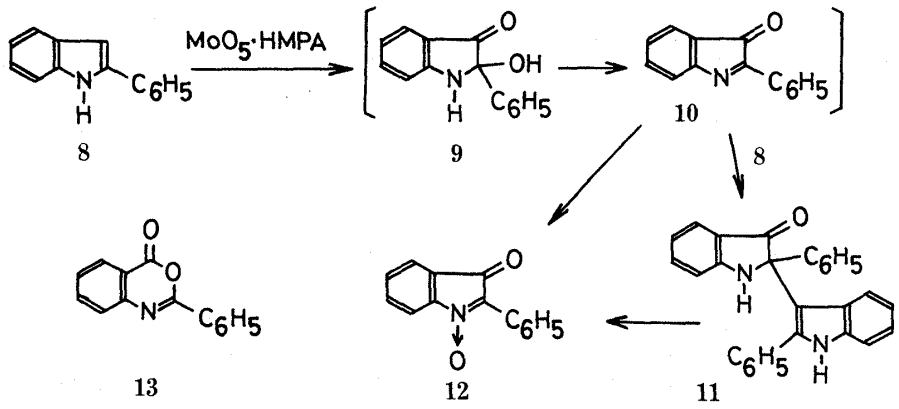

Chart 2

dihydroxy-3-methylindolines, **16** and **17**, whose structures were assigned on the basis of the spectral data and chemical evidence as follows. A solution of **16** in ethyl acetate was allowed to stand at room temperature for several hours to give a mixture of **16** and **17** (checked by TLC).[11] Treatment of **16** and **17** with acetone in the presence of ferric chloride[12] gave the acetonide **18** in 80% and 96% yields, respectively, but the reaction of the *cis*-isomer **17** proceeded slightly faster than that of the *trans*-isomer **16**.

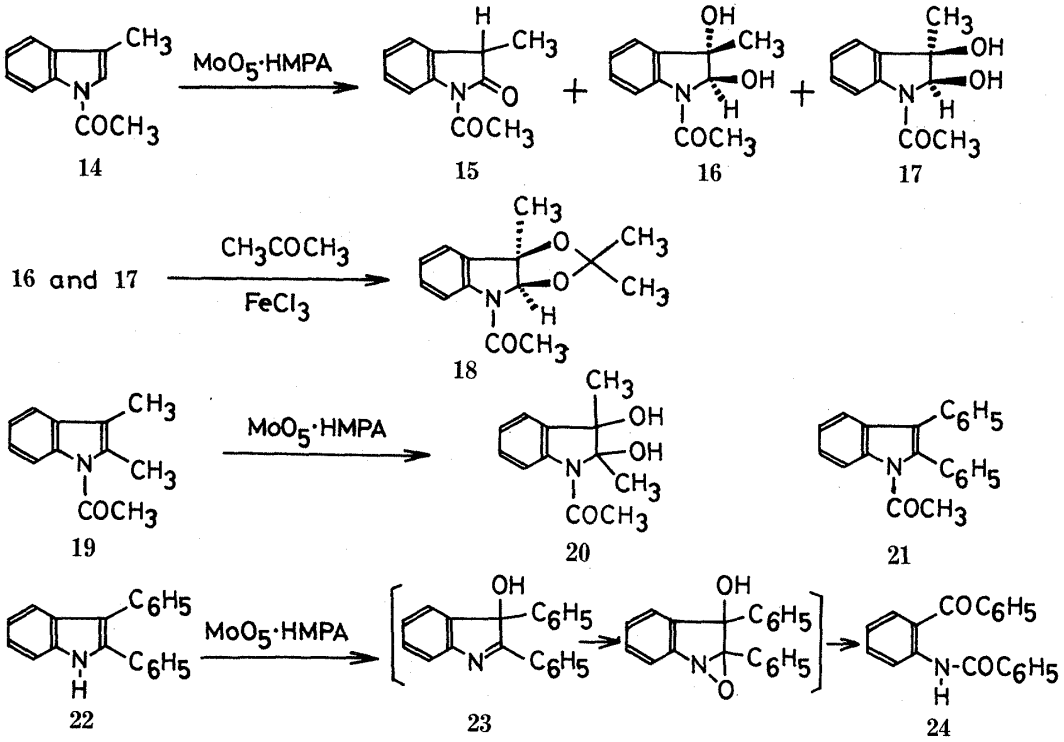

Chart 3

Similar treatment of 1-acetyl-2,3-dimethylindole (**19**) with $MoO_5 \cdot HMPA$ gave a mixture of *trans*- and *cis*-isomers of 1-acetyl-2,3-dihydroxy-2,3-dimethylindoline (**20**) in 71% yield; the structure was confirmed by comparison of the spectral data with those of an authentic sample.[13] Reaction of 1-acetyl-2,3-diphenylindole (**21**) with $MoO_5 \cdot HMPA$ did not occur under the same conditions.

Oxidation of 2,3-diphenylindole (**22**) with $MoO_5 \cdot HMPA$ gave the ketoamide **24** in 31%

yield, together with recovered **22** in 52% yield. The ketoamide **24** was also obtained from the oxidation of **22** with *m*-CPBA, which undergoes nucleophilic addition to the initially formed indolenine intermediate **23**.[2] On the other hand, since $MoO_5 \cdot HMPA$ is a non-nucleophilic oxidizing agent, the MoO_5 oxidation process may be as illustrated in Chart 3, which involves the oxidation of **23**.

Experimental

All melting points are uncorrected. IR spectra were recorded on a Hitachi 260-10 spectrophotometer. ^{1}H-Nuclear magnetic resonance (^{1}H-NMR) spectra were measured with JEOL JNM-PMX 60 using tetramethylsilane as an internal standard, and mass spectra (MS) were obtained on a JEOL D-300 spectrometer operating at 70 eV. Column chromatography was carried out on silica gel (80—100 mesh, Kanto Chemical Co., Inc.). Silica gel 60 PF_{254} (Merck) was used for preparative TLC.

Oxidation of 1-Acetylindole (1a) with $MoO_5 \cdot HMPA$——1) In CH_2Cl_2 (1 Week): A solution of **1a** (795 mg, 5 mmol) and $MoO_5 \cdot HMPA$ (1.925 g, 5.5 mmol) in dry CH_2Cl_2 (50 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 $CHCl_3$–ethyl acetate (10 : 3) as an eluent to give 1-acetyl-2-hydroxyindoxyl (**4a**) (325 mg, 34%), mp 150—152 °C (from C_6H_6). *Anal.* Calcd for $C_{10}H_9NO_3$: C, 62.82; H, 4.75; N, 7.33. Found: C, 62.96; H, 4.68; N, 7.28. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300 (OH), 1730 (C=O), 1685 (N–C=O). ^{1}H-NMR (DMSO-d_6) δ: 2.30 (3H, s, $NCOCH_3$), 5.40 (1H, d, J=7 Hz, N–C<u>H</u>–OH), 7.20 (2H, m, OH and Ar-H), 7.5—7.75 (2H, m, Ar-H), 8.25 (1H, d, J=8 Hz, Ar-H). MS *m/e*: 191 (M^+).

2) In Acetonitrile: A similar treatment of **1a** (1.590 g, 10 mmol) with $MoO_5 \cdot HMPA$ (4.010 g, 11.3 mmol) in dry acetonitrile (100 ml) gave **4a** (740 mg, 38%).

3) In CH_2Cl_2 (5 min): A similar treatment of **1a** (318 mg, 2 mmol) with $MoO_5 \cdot HMPA$ (780 mg, 2.2 mmol) in dry CH_2Cl_2 (20 ml) for 5 min gave 1-acetylindoxyl (**3a**) (26 mg, 7%) and **4a** (14 mg, 4%), together with recovered **1a** (248 mg, 78%).

3a: mp 134—136 °C (from C_6H_6) [lit.[7] mp 138 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720 (C=O), 1678 (N–C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.33 (3H, s, $NCOCH_3$), 4.28 (2H, s, N–CH_2–CO), 7.05—7.9 (3H, m, Ar-H), 8.50 (1H, br, Ar-H).

Oxidation of 1-Acetylindoxyl (3a) with $MoO_5 \cdot HMPA$——A solution of **3a** (88 mg, 0.5 mmol) and $MoO_5 \cdot HMPA$ (195 mg, 0.55 mmol) in dry CH_2Cl_2 (5 ml) was stirred at room temperature under argon for 4 d. Concentration of the mixture under reduced pressure gave a residue, which was purified by column chromatography on silica gel with $CHCl_3$–ethyl acetate (10 : 3) as an eluent to give **4a** (59 mg, 62%).

Oxidation of 1-Acetylindole (1a) with *m*-CPBA——A solution of **1a** (477 mg, 3 mmol) in dry CH_2Cl_2 (10 ml) was gradually added to a solution of *m*-CPBA (80% content, 712 mg, 3.3 mmol) in dry CH_2Cl_2 (30 ml) at 0 °C. The mixture was warmed to room temperature, stirred at the same temperature for 5 d, washed with 10% NaOH and H_2O, dried over $MgSO_4$, and concentrated under reduced pressure to give a residue. The residue was chromatographed on a silica gel column. Elution with C_6H_6 gave 1-acetyloxindole (**7**) (47 mg, 9%), together with recovered **1a** (55 mg, 11%). Elution with $CHCl_3$–ethyl acetate (10 : 3) gave **3a** (18 mg, 3%) and 1-acetyl-2-(*m*-chlorobenzoyloxy)-3-hydroxyindoline (**6**) (337 mg, 34%).

7: mp 122—123 °C (from C_6H_6) [lit.[7] mp 126 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1758 (C=O), 1708 (N–C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.63 (3H, s, $NCOCH_3$), 3.68 (2H, s, $COCH_2$), 7.05—7.4 (3H, m, Ar-H), 8.0—8.3 (1H, m, Ar-H).

6: mp 164—166 °C (from ethyl acetate). *Anal.* Calcd for $C_{17}H_{14}ClNO_4$: C, 61.54; H, 4.22; N, 4.22. Found: C, 61.44; H, 4.13; N, 4.16. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3250 (OH), 1720 (O–C=O), 1660 (N–C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.83 (1H, s, OH, exchangeable), 2.40 (3H, s, $COCH_3$), 4.42 (1H, d, J=7 Hz, –C<u>H</u>–OH), 6.07 (1H, s, –C<u>H</u>–OCOAr), 6.85—7.65 (5H, m, Ar-H), 7.7—8.3 (3H, m, Ar-H). MS *m/e*: 331 (M^+), 333 (M^++2).

Treatment of 1-Acetyl-2-(*m*-chlorobenzoyloxy)-3-hydroxyindoline (6) with H_2SO_4——Concentrated H_2SO_4 (1.0 ml) was added to a solution of **6** (331.5 mg, 1 mmol) in CH_2Cl_2 (2 ml) at 0 °C with stirring. The mixture was stirred at room temperature for 40 min, diluted with CH_2Cl_2 (17 ml), and washed with cooled H_2O. The CH_2Cl_2 layer was dried over Na_2SO_4, and concentrated *in vacuo* to give a residue. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to give 1-acetylindoxyl **3a** (100 mg, 57%).

Oxidation of 1-Acetyl-2-methylindole (1b) with $MoO_5 \cdot HMPA$——Using a procedure similar to that described above for the oxidation of **1a** with $MoO_5 \cdot HMPA$, **1b** (1.730 g, 10 mmol) was treated with $MoO_5 \cdot HMPA$ (3.905 g, 11 mmol) in dry CH_2Cl_2 (100 ml). The reaction mixture was purified by column chromatography on silica gel with CH_2Cl_2–ethyl acetate (3 : 1) as an eluent to give 1-acetyl-2-hydroxy-2-methylindoxyl (**4b**) (1.123 g, 55%), mp 133—134.5 °C (from C_6H_6), which was identical with a reported sample[6] in terms of the spectral data.

Oxidation of 1-Acetyl-2-phenylindole (1c) with $MoO_5 \cdot HMPA$——Using a procedure similar to that described above for the oxidation of **1a** with $MoO_5 \cdot HMPA$, **1c** (940 mg, 4 mmol) was treated with $MoO_5 \cdot HMPA$ (1.692 g, 4.8 mmol) in dry CH_2Cl_2 (20 ml). The reaction mixture was purified by column chromatography on silica gel with

$CHCl_3$–ethyl acetate (20:1) to give 1-acetyl-2-phenylindoxyl (**3c**) (95 mg, 9%) and 1-acetyl-2-hydroxy-2-phenylindoxyl (**4c**) (641 mg, 60%).

3c: mp 125.5—127 °C (from ethyl acetate–*n*-pentane). *Anal.* Calcd for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.57. Found: C, 76.68; H, 5.02; N, 5.59. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750 (C=O), 1680 (N–C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.05 (3H, s, $NCOCH_3$), 5.18 (1H, s, N–CH–CO), 7.0—7.9 (8H, m, Ar-H), 8.63 (1H, d, J=8 Hz, Ar-H). MS *m/e*: 251 (M^+).

4c: mp 169—170 °C (from C_6H_6) [lit.[8] mp 166—167 °C]. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3250 (OH), 1730 (C=O), 1675 (N–C=O). ^{1}H-NMR ($CDCl_3$) δ: 2.03 (3H, s, $NCOCH_3$), 5.06 (1H, br, OH, exchangeable), 6.75—8.0 (8H, m, Ar-H), 8.43 (1H, d, J=8 Hz, Ar-H). MS *m/e*: 267 (M^+).

Oxidation of 2-Phenylindole (8) with MoO_5·HMPA——1) Preparation of 2-Phenyl-2-(2-phenyl-3-indolyl)-indoxyl (**11**): Using a procedure similar to that described above for the oxidation of **1a** with MoO_5·HMPA, **8** (1.180 g, 6.1 mmol) was treated with MoO_5·HMPA (2.460 g, 6.9 mmol) in dry CH_2Cl_2 (150 ml) for 4 d. The reaction mixture was purified by column chromatography on silica gel with $CHCl_3$–ethyl acetate (9:1) as an eluent to give **11** (684 mg, 56%), mp 224—227 °C (from CH_3OH) [lit.[3] mp 220—225 °C]. *Anal.* Calcd for $C_{28}H_{20}N_2O$: C, 83.97; H, 5.03; N, 7.00. Found: C, 84.07; H, 4.79; N, 6.88. IR ν_{max}^{Nujol} cm^{-1}: 3380, 3250 (NH), 1680 (C=O). ^{1}H-NMR (DMSO-d_6) δ: 6.45—7.5 (18H, m, Ar-H), 8.37 (1H, s, NH), 11.37 (1H, s, NH). MS *m/e*: 400 (M^+).

2) Preparation of 2-Phenylisatogen (**12**): Using a procedure similar to that described above for the oxidation of **1a** with MoO_5·HMPA, **8** (193 mg, 1 mmol) was treated with MoO_5·HMPA (1.065 g, 3 mmol) in dry CH_2Cl_2 (30 ml) for 24 h. The reaction mixture was purified by column chromatography on silica gel with C_6H_6 as an eluent to give **12** (130 mg, 58%), mp 186—190 °C (from CH_3OH) [lit.[10] mp 188—189 °C]. *Anal.* Calcd for $C_{14}H_9NO_2$: C, 75.32; H, 4.06; N, 6.28. Found: C, 75.12; H, 3.78; N, 6.16. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1722 (C=O), 1705, 1390 (ArN→O). ^{1}H-NMR ($CDCl_3$) δ: 7.3—7.8 (7H, m, Ar-H), 8.45—8.8 (2H, m, Ar-H). MS *m/e*: 223 (M^+).

Oxidation of 2-Phenyl-2-(2-phenyl-3-indolyl)indoxyl (11) with MoO_5·HMPA——A solution of **11** (36 mg, 0.09 mmol) and MoO_5·HMPA (35 mg, 0.1 mmol) in dry CH_2Cl_2 (10 ml) was kept at room temperature under argon for 4 d. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with C_6H_6 as an eluent to give **12** (11 mg, 27%), together with recovered **11** (20 mg, 56%).

Oxidation of 1-Acetyl-3-methylindole (14) with MoO_5·HMPA——Using a procedure similar to that described above for the oxidation of **1a** with MoO_5·HMPA, **14** (865 mg, 5 mmol) was treated with MoO_5·HMPA (1.952 g, 5.5 mmol) in dry CH_2Cl_2 (150 ml). The reaction mixture was purified by column chromatography on silica gel with CH_2Cl_2–ethyl acetate (9:1) as an eluent to give 1-acetyl-3-methyloxindole (**15**) (273 mg, 28%) and a mixture of *trans*- and *cis*-1-acetyl-2,3-dihydroxy-3-methylindolines, **16** and **17** (279 mg, 27%), in a ratio of 1:1.

15: mp 69—72 °C (from C_2H_5OH). *Anal.* Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N. 7.40. Found: 69.85; H, 5.77; N, 7.32. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1710 (O=C–N–C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.57 (3H, d, J=8 Hz, CH_3), 2.67 (3H, s, $NCOCH_3$), 3.65 (1H, q, J=8 Hz, –C<u>H</u>–CH_3), 7.1—7.5 (3H, m, Ar-H), 8.05—8.4 (1H, m, Ar-H). MS *m/e*: 189 (M^+).

The Mixture of **16** and **17**: mp 118—122 °C (from C_6H_6). *Anal.* Calcd for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.64; H, 6.29; N, 6.70. IR ν_{max}^{Nujol} cm^{-1}: 3425, 3325 (OH), 1635 (N–C=O). ^{1}H-NMR (DMSO-d_6) δ: 1.35 (s, CH_3 of **17**), 1.48 (s, CH_3 of **16**), 2.28 (s, $NCOCH_3$ of **16** and **17**), 5.23 (br, OH and –C<u>H</u>–OH of **16** and **17**), 6.40 (br, OH of **16** and **17**), 6.95—7.5 (m, Ar-H of **16** and **17**), 7.8—8.15 (m, Ar-H of **16** and **17**). MS *m/e*: 207 (M^+).

The mixture of **16** and **17** was separated by careful fractional recrystallization from ethyl acetate. Compound **17** was less soluble than **16** in ethyl acetate.

16: mp 139—143 °C (from CH_3OH). *Anal.* Calcd for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.94; H, 6.42; N, 6.78. IR ν_{max}^{Nujol} cm^{-1}: 3200 (OH), 1635 (N–C=O). ^{1}H-NMR (DMSO-d_6) δ: 1.48 (3H, s, CH_3), 2.28 (3H, s, $NCOCH_3$), 5.27 (1H, d, J=8 Hz, –C<u>H</u>–OH), 5.30 (1H, s, OH, exchangeable), 6.45 (1H, s, OH, exchangeable), 6.95—7.45 (3H, m, Ar-H), 7.95 (1H, br d, J=8 Hz, Ar-H). MS *m/e*: 207 (M^+).

17: 124—127 °C (from acetone). IR ν_{max}^{Nujol} cm^{-1}: 3350, 3200 (OH), 1635 (N–C=O). ^{1}H-NMR (DMSO-d_6) δ: 1.35 (3H, s, CH_3), 2.28 (3H, s, $NCOCH_3$), 5.18 (1H, br d, J=7 Hz, –CH–O), 5.25 (1H, br d, OH, exchangeable), 6.25 (1H, br d, J=7 Hz, OH, exchangeable), 6.9—7.35 (3H, m, Ar-H), 7.92 (1H, br d, J=8 Hz, Ar-H).

Preparation of 1-Acetyl-2,3-isopropylenedioxy-3-methylindoline (18)——1) From **16**: A solution of **16** (6.4 mg, 0.03 mmol) and $FeCl_3$ (5 mg, 0.031 mmol) in dry acetone (2 ml) was kept at room temperature for 4 h. Then 10% K_2CO_3 (0.2 ml) was added, and the mixture was concentrated under reduced pressure to give a residue. The residue was extracted with $CHCl_3$ (30 ml), and the extract was washed with H_2O, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by preparative TLC with $CHCl_3$ as a developing solvent to give **18** (5.9 mg, 80%), mp 127—129 °C (from pet. ether). *Anal.* Calcd for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93; N, 5.66. Found: C, 67.90; H, 6.93; N, 5.40. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1670 (N–C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.03 (3H, s, CH_3), 1.48 (3H, s, CH_3), 1.68 (3H, s, CH_3), 2.38 (3H, s, $NCOCH_3$), 5.65 (1H, s, N–CH–O), 6.95—7.5 (3H, m, Ar-H), 8.07 (1H, br d, J=8 Hz, Ar-H). MS *m/e*: 247 (M^+).

2) From **17**: A similar treatment of **17** (6.4 mg, 0.03 mmol) with $FeCl_3$ (5 mg, 0.031 mmol) in dry acetone (2 ml) gave **18** (7.1 mg, 96%).

Oxidation of 1-Acetyl-2,3-dimethylindole (19) with MoO_5·HMPA——Using a procedure similar to that described above for the oxidation of **1a** with MoO_5·HMPA, **19** (561 mg, 3 mmol) was treated with MoO_5·HMPA

(1.171 g, 3.3 mmol) in dry CH_2Cl_2 (90 ml) for 24 h. The reaction mixture was purified by column chromatography on silica gel with CH_2Cl_2–ethyl acetate (5 : 1) as an eluent to give a mixture of *trans* and *cis* isomers of 1-acetyl-2,3-dihydroxy-2,3-dimethylindoline (**20**) (473 mg, 71%), mp 137—139 °C (from C_6H_6) [lit.[13] mp 130—132 °C] in a ratio of 2 : 1. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 3300 (OH), 1638 (N–C=O). ^{1}H-NMR ($CDCl_3$) δ: 1.45, 1.73 (3H, s and s, CH_3 of *cis* and *trans*), 1.55 and 1.92 (3H, s and s, CH_3 of *cis* and *trans*), 2.33 and 2.03 (3H, s and s, $NCOCH_3$ of *cis* and *trans*), 3.60 and 4.27 (2H, s and s, OH of *cis* and *trans*, exchangeable), 7.0—8.45 (4H, m, Ar-H).

Oxidation of 2,3-Diphenylindole (22) with MoO_5·HMPA——Using a procedure similar to that described above for the oxidation of **1a** with MoO_5·HMPA, **22** (1.345 g, 5 mmol) was treated with MoO_5·HMPA (1.950 g, 5.5 mmol) in dry CH_2Cl_2 (50 ml). The reaction mixture was purified by column chromatography on silica gel with CH_2Cl_2 as an eluent to give *N*-(2-benzoylphenyl)benzamide (**24**) (465 mg, 31%), together with recovered **22** (704 mg, 52%).

24: mp 83—84 °C (from C_6H_6–cyclohexane) [lit.[2] mp 88—89.5 °C]. *Anal.* Calcd for $C_{20}H_{15}NO_2$: C, 79.71; H, 5.02; N, 4.65. Found: C, 79.90; H, 4.80; N, 4.49. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3275 (NH), 1670 (C=O), 1630 (N–C=O). ^{1}H-NMR ($CDCl_3$) δ: 6.8—7.75 (12H, m, Ar-H and NH), 7.75—8.1 (2H, m, Ar-H), 8.83 (1H, d, J=8 Hz, Ar-H). MS *m/e*: 301 (M^+).

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References and Notes

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