[Chem. Pharm. Bull.]
33(5)1843—1848(1985)

Oxidation of Indoles with Oxodiperoxomolybdenum (VI), $\text{MoO}_5 \cdot \text{HMPA}$. Preparation of 2-Hydroxyindoxyl and Isatogen Derivatives

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(Received August 2, 1984)

Oxidation of 1-acetylindoles **1** with (hexamethylphosphoramide)oxodiperoxomolybdenum (VI), $\text{MoO}_5 \cdot \text{HMPA}$, in dry methylene chloride gave 1-acetyl-2-hydroxyindoxyls **4**. 2-Phenylindole (**8**) was similarly treated with $\text{MoO}_5 \cdot \text{HMPA}$ to give a dimeric product **11**, while oxidation of **8** with three mol eq of $\text{MoO}_5 \cdot \text{HMPA}$ gave 2-phenylisatogen (**12**). The oxidation of other indoles, **14**, **19**, **21**, and **22**, with $\text{MoO}_5 \cdot \text{HMPA}$ 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), $\text{MoO}_5 \cdot \text{HMPA}$.⁵ Recently we have reported⁶ that the oxidation of 1-acylindoles with $\text{MoO}_5 \cdot \text{HMPA}$ 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 $\text{MoO}_5 \cdot \text{HMPA}$ 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 $\text{MoO}_5 \cdot \text{HMPA}$.

Treatment of 1-acetylindole (**1a**) with $\text{MoO}_5 \cdot \text{HMPA}$ 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 $\text{MoO}_5 \cdot \text{HMPA}$ 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 $\text{MoO}_5 \cdot \text{HMPA}$ to give **4a**. This is strongly supported by the following results; (i) similar treatment of **1a** with $\text{MoO}_5 \cdot \text{HMPA}$ 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 $\text{MoO}_5 \cdot \text{HMPA}$ 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 MoO₅·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 MoO₅·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 MoO₅·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 MoO₅·HMPA. The formation of **12** can be explained in terms of further oxidation of the intermediate **10** with excess MoO₅·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 MoO₅·HMPA.

Treatment of 1-acetyl-3-methylindole (**14**) with MoO₅·HMPA under the same conditions as mentioned above gave a mixture of two isomeric products in 27% yield, together with 1-acetyl-3-methoxyindole (**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 chloride¹²⁾ 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 $\text{MoO}_5 \cdot \text{HMPA}$ 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 $\text{MoO}_5 \cdot \text{HMPA}$ did not occur under the same conditions.

Oxidation of 2,3-diphenylindole (**22**) with $\text{MoO}_5 \cdot \text{HMPA}$ 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 $\text{MoO}_5 \cdot \text{HMPA}$ 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. ^1H -Nuclear magnetic resonance (^1H -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 PF₂₅₄ (Merck) was used for preparative TLC.

Oxidation of 1-Acetylindole (1a) with $\text{MoO}_5 \cdot \text{HMPA}$ —1) In CH_2Cl_2 (1 Week): A solution of **1a** (795 mg, 5 mmol) and $\text{MoO}_5 \cdot \text{HMPA}$ (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 $\text{C}_{10}\text{H}_9\text{NO}_3$: C, 62.82; H, 4.75; N, 7.33. Found: C, 62.96; H, 4.68; N, 7.28. IR $\nu_{\text{max}}^{\text{CHCl}_3} \text{ cm}^{-1}$: 3300 (OH), 1730 (C=O), 1685 (N–C=O). ^1H -NMR ($\text{DMSO}-d_6$) δ : 2.30 (3H, s, NCOCH_3), 5.40 (1H, d, $J=7$ Hz, N–CH–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 $\text{MoO}_5 \cdot \text{HMPA}$ (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 $\text{MoO}_5 \cdot \text{HMPA}$ (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 $\nu_{\text{max}}^{\text{CHCl}_3} \text{ cm}^{-1}$: 1720 (C=O), 1678 (N–C=O). ^1H -NMR (CDCl_3) δ : 2.33 (3H, s, NCOCH_3), 4.28 (2H, s, N–CH₂–CO), 7.05–7.9 (3H, m, Ar-H), 8.50 (1H, br, Ar-H).

Oxidation of 1-Acetylindoxyl (3a) with $\text{MoO}_5 \cdot \text{HMPA}$ —A solution of **3a** (88 mg, 0.5 mmol) and $\text{MoO}_5 \cdot \text{HMPA}$ (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-acetylindole (**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 $\nu_{\text{max}}^{\text{CHCl}_3} \text{ cm}^{-1}$: 1758 (C=O), 1708 (N–C=O). ^1H -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 $\text{C}_{17}\text{H}_{14}\text{ClNO}_4$: C, 61.54; H, 4.22; N, 4.22. Found: C, 61.44; H, 4.13; N, 4.16. IR $\nu_{\text{max}}^{\text{CHCl}_3} \text{ cm}^{-1}$: 3250 (OH), 1720 (O–C=O), 1660 (N–C=O). ^1H -NMR (CDCl_3) δ : 1.83 (1H, s, OH, exchangeable), 2.40 (3H, s, COCH_3), 4.42 (1H, d, $J=7$ Hz, –CH–OH), 6.07 (1H, s, –CH–OCOAr), 6.85–7.65 (5H, m, Ar-H), 7.7–8.3 (3H, m, Ar-H). MS m/e : 331 (M^+), 333 ($\text{M}^+ + 2$).

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 $\text{MoO}_5 \cdot \text{HMPA}$ —Using a procedure similar to that described above for the oxidation of **1a** with $\text{MoO}_5 \cdot \text{HMPA}$, **1b** (1.730 g, 10 mmol) was treated with $\text{MoO}_5 \cdot \text{HMPA}$ (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 sample⁶⁾ in terms of the spectral data.

Oxidation of 1-Acetyl-2-phenylindole (1c) with $\text{MoO}_5 \cdot \text{HMPA}$ —Using a procedure similar to that described above for the oxidation of **1a** with $\text{MoO}_5 \cdot \text{HMPA}$, **1c** (940 mg, 4 mmol) was treated with $\text{MoO}_5 \cdot \text{HMPA}$ (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 $\text{C}_{16}\text{H}_{13}\text{NO}_2$: C, 76.47; H, 5.22; N, 5.57. Found: C, 76.68; H, 5.02; N, 5.59. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1750 (C=O), 1680 (N–C=O). $^1\text{H-NMR}$ (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 $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3250 (OH), 1730 (C=O), 1675 (N–C=O). $^1\text{H-NMR}$ (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 $\text{MoO}_5 \cdot \text{HMPA}$ —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 $\text{MoO}_5 \cdot \text{HMPA}$, **8** (1.180 g, 6.1 mmol) was treated with $\text{MoO}_5 \cdot \text{HMPA}$ (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 $\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}$: C, 83.97; H, 5.03; N, 7.00. Found: C, 84.07; H, 4.79; N, 6.88. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 3380, 3250 (NH), 1680 (C=O). $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) 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 $\text{MoO}_5 \cdot \text{HMPA}$, **8** (193 mg, 1 mmol) was treated with $\text{MoO}_5 \cdot \text{HMPA}$ (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 $\text{C}_{14}\text{H}_9\text{NO}_2$: C, 75.32; H, 4.06; N, 6.28. Found: C, 75.12; H, 3.78; N, 6.16. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1722 (C=O), 1705, 1390 (ArN→O). $^1\text{H-NMR}$ (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 $\text{MoO}_5 \cdot \text{HMPA}$ —A solution of **11** (36 mg, 0.09 mmol) and $\text{MoO}_5 \cdot \text{HMPA}$ (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 $\text{MoO}_5 \cdot \text{HMPA}$ —Using a procedure similar to that described above for the oxidation of **1a** with $\text{MoO}_5 \cdot \text{HMPA}$, **14** (865 mg, 5 mmol) was treated with $\text{MoO}_5 \cdot \text{HMPA}$ (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 $\text{C}_2\text{H}_5\text{OH}$). *Anal.* Calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_2$: C, 69.83; H, 5.86; N, 7.40. Found: 69.85; H, 5.77; N, 7.32. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1760, 1710 (O=C–N–C=O). $^1\text{H-NMR}$ (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, $-\text{CH}-\text{CH}_3$), 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 $\text{C}_{11}\text{H}_{13}\text{NO}_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.64; H, 6.29; N, 6.70. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 3425, 3325 (OH), 1635 (N–C=O). $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) 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 $-\text{CH}-\text{OH}$ 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 $\text{C}_{11}\text{H}_{13}\text{NO}_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.94; H, 6.42; N, 6.78. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 3200 (OH), 1635 (N–C=O). $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ : 1.48 (3H, s, CH_3), 2.28 (3H, s, NCOCH_3), 5.27 (1H, d, $J=8$ Hz, $-\text{CH}-\text{OH}$), 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 $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 3350, 3200 (OH), 1635 (N–C=O). $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ : 1.35 (3H, s, CH_3), 2.28 (3H, s, NCOCH_3), 5.18 (1H, br d, $J=7$ Hz, $-\text{CH}-\text{O}$), 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-isopropylendioxy-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 $\text{C}_{14}\text{H}_{17}\text{NO}_3$: C, 67.99; H, 6.93; N, 5.66. Found: C, 67.90; H, 6.93; N, 5.40. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 1670 (N–C=O). $^1\text{H-NMR}$ (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 $\text{MoO}_5 \cdot \text{HMPA}$ —Using a procedure similar to that described above for the oxidation of **1a** with $\text{MoO}_5 \cdot \text{HMPA}$, **19** (561 mg, 3 mmol) was treated with $\text{MoO}_5 \cdot \text{HMPA}$

(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 $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3420, 3300 (OH), 1638 (N–C=O). $^1\text{H-NMR}$ (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 $\text{MoO}_5 \cdot \text{HMPA}$ —Using a procedure similar to that described above for the oxidation of **1a** with $\text{MoO}_5 \cdot \text{HMPA}$, **22** (1.345 g, 5 mmol) was treated with $\text{MoO}_5 \cdot \text{HMPA}$ (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 $\text{C}_{20}\text{H}_{15}\text{NO}_2$: C, 79.71; H, 5.02; N, 4.65. Found: C, 79.90; H, 4.80; N, 4.49. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3275 (NH), 1670 (C=O), 1630 (N–C=O). $^1\text{H-NMR}$ (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^+).

Acknowledgement The authors wish to thank the staff of the Analysis Center of this college for elemental analysis (Miss K. Hibino and Miss A. Koike) and measurement of MS (Mr. K. Sato).

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