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Studies on the Syntheses of Heterocyclic Compounds. DCCLXVIII.[1] Reaction of Pyrrolo[1,2-*a*]indole Derivatives with N-Bromosuccinimide in Protic Solvents

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Treatment of the 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indoles (**1** and **7**) with N-bromosuccinimide in protic solvents such as methanol and acetic acid yielded the brominated compounds (**4** and **8**). The reaction of the pyrrolo[1,2-*a*]indole-5,8-diones (**9**—**13**) with N-bromosuccinimide in these solvents afforded the adducts (**14**—**18** and **20**—**21**). Debromination of the brominated compounds (**5b**, **15**, **16** and **20**) with tri-*n*-butyltin hydride was also described.

Keywords——pyrrolo[1,2-*a*]indoles; N-bromosuccinimide; bromination; protic solvents; debromination

Bromination of the pyrrolo[1,2-*a*]indoles such as the compound **7**[3] of the indoloquinone[4] was known as a highly efficient method for functionallization of these nuclei. Although the reactions of simply substituted indoles[5] and 1,4-benzoquinone derivatives[6] with N-bromosuccinimide (NBS) in protic solvents had been reported, the reaction of pyrrolo[1,2-*a*]indoles with NBS has not yet been fully studied. In this paper, we wish to describe the reactions of some pyrrolo[1,2-*a*]indoles with NBS in protic solvents.

In the previous paper,[7] we have mentioned the reaction of 2,3-dihydro-7-methoxy-6-methylpyrrolo[1,2-*a*]indole-9-carbonitrile (**1**) with NBS in methanol to give 8-bromo-2,3-dihydro-7-methoxy-6-methylpyrrolo[1,2-*a*]indole-9-carbonitrile (**4**) and 8-bromo-2,3-dihydro-5,7-dimethoxy-6-methylpyrrolo[1,2-*a*]indole-9-carbonitrile (**5a**). The structure of the latter one was tentatively assigned on the basis of a consideration of reaction mechanism. However, debromination of the compound **5a** revealed that the structure should be corrected to **5b**. Thus, the compound was heated with tri-*n*-butyltin hydride in benzene in the presence of azobisisobutyronitrile.[8] The methylene protons at the 3 position of the debrominated compound were observed at 4.08 ppm in the nuclear magnetic resonance (NMR) spectrum, while those protons of the starting material appeared at 4.56 ppm. Such a great difference of the chemical shift would indicate that the bromine atom was present at the 5 position. Bromination of the nitrile **1** with NBS in acetic acid furnished **4** as a sole product and no corresponding acetoxyl compound was obtained. The bromination of the aldehyde **6** with NBS in methanol gave only unidentified material. On the other hand, the treatment of the ketone **7** with one molar equivalent of NBS in methanol afforded the compound **8** which was brominated at the 9 position in good yield. The spectral data of **8** were consistent with that

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[1] Part DCCLXVII: T. Kametani and H. Nemoto, *Heterocycles*, **10**, 339 (1978).
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[3] G.R. Allen, Jr. and M.J. Weiss, *J. Org. Chem.*, **30**, 2904 (1965).
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[7] T. Kametani, K. Takahashi, Y. Kigawa, M. Ihara, and K. Fukumoto, *J. Chem. Soc. Perkin I*, **1977**, 28.
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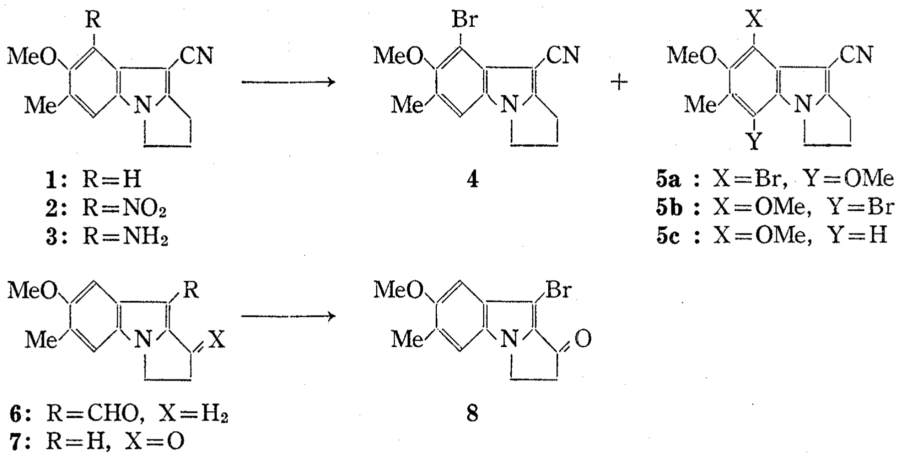
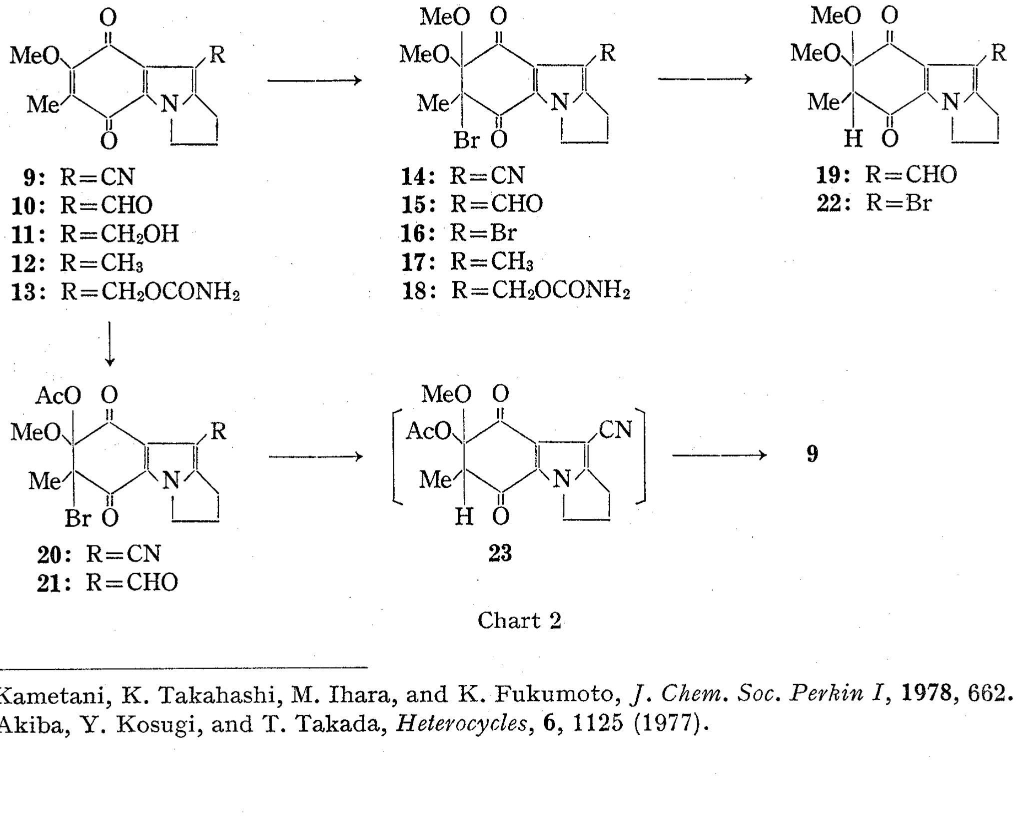
previously reported.[3] Further treatment of **8** with NBS in methanol gave an unstable, unclarified product.



1: R=H
2: R=NO_2
3: R=NH_2
4
5a : X=Br, Y=OMe
5b : X=OMe, Y=Br
5c : X=OMe, Y=H
6: R=CHO, X=H_2
7: R=H, X=O
8

Chart 1

Then, we investigated the reaction of some pyrrolo[1,2-*a*]indole-5,8-diones with NBS in protic solvents. The quinone **9** was prepared by the usual method from the nitrile **1** (nitration of **1**, followed by reduction of the nitro compound **2** and Fremy oxidation of the amine **3**). The quinone **12** was prepared from the quinone–aldehyde **10** by sodium borohydride reduction in acetic acid.[9] The reduction of the quinone part was not observed under the above condition. When the 2,3-dihydro-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (**9**) was treated with a slight excess of NBS in methanol-dichloromethane (1:1 v/v) at room temperature for 1 hr, the adduct **14** was obtained in 87% yield. The similar reactions of **10**, **12** and **13** furnished the corresponding adducts **15**, **17** and **18**, respectively. Introduction of bromine and methoxyl group to C-6 and C-7 positions was suggested by the ultraviolet (UV) spectrum (see experimental section) which is similar to that of the 2,3,6,7-tetrahydropyrrolo[1,2-*a*]-indole-5,8-dione.[10] The structures of the adducts were further supported by the debromina-



9: R=CN
10: R=CHO
11: R=CH_2OH
12: R=CH_3
13: R=CH_2OCONH_2
14: R=CN
15: R=CHO
16: R=Br
17: R=CH_3
18: R=CH_2OCONH_2
19: R=CHO
22: R=Br
20: R=CN
21: R=CHO
23

Chart 2

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9) T. Kametani, K. Takahashi, M. Ihara, and K. Fukumoto, *J. Chem. Soc. Perkin I*, **1978**, 662.
10) M. Akiba, Y. Kosugi, and T. Takada, *Heterocycles*, **6**, 1125 (1977).

tion of **15**. Namely, treatment of the adduct **15** with tri-*n*-butyltin hydride in the presence of azobisisobutyronitrile afforded the debrominated compound **19** whose methyl protons at the 6 position were observed at 1.20 ppm as doublet ($J=7$ Hz) in the NMR spectrum.

On treatment of the alcohol **11** with an excess of NBS in methanol, the dibromide **16** was obtained in 68% yield, but a reaction using an equivalent mole of NBS gave an unseparable mixture of **16** and the starting material. The dibromide **16** was also obtained by treatment of the aldehyde **10** with a large excess of NBS for a long reaction time (15 hr). The dibromide **16** was treated with tri-*n*-butyltin hydride to give the monobromide **22**.

When the reaction was carried out in acetic acid, **9** and **10** yielded the 7-acetoxybromides (**20** and **21**). Thus, treatment of the nitrile **9** with a slight excess of NBS in acetic acid–dichloromethane (1: 1 v/v) at room temperature for 15 hr gave the acetate **20** in 81% yield. The aldehyde **10** gave the acetate **21** under the similar conditions. Debromination of **20** with tri-*n*-butyltin hydride afforded no debrominated compound **23** but the starting quinone **9**.

Experimental[11]

2,3-Dihydro-7-methoxy-6-methyl-8-nitro-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (2)——To a solution of the nitrile (**1**) (226 mg) in dichloromethane (30 ml), fuming nitric acid ($d=1.50$) (0.5 ml) was added and the mixture was stirred at 0° for 30 min. The mixture was washed with water and aqueous sodium bicarbonate solution, dried over Na_2SO_4, and evaporated to leave a powder, the recrystallization of which from $CHCl_3$ gave the nitro-compound **2** (255 mg; 94%) as pale yellow needles, mp 231—232°. *Anal.* Calcd. for $C_{14}H_{13}N_3O_3$: C, 61.98; H, 4.83; N, 15.49. Found: C, 61.84; H, 4.83; N, 15.45. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2220 (CN), 1530, 1360 (NO_2). NMR ($CDCl_3$) δ: 2.42 (3H, s, 6-Me), 2.50—3.50 (4H, m, 1- and 2-H_2), 3.90 (3H, s, OMe), 4.22 (2H, t, $J=7$ Hz, 3-H_2), 7.26 (1H, s, 5-H). MS *m/e*: 271 (M^+).

2,3-Dihydro-7,8-dimethoxy-6-methyl-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (5c)——A mixture of the bromide (**5b**)[7] (67 mg), 2 drops of tri-*n*-butyltin hydride, azobisisobutyronitrile (2 mg) and benzene (5 ml) was refluxed under nitrogen atmosphere for 10 hr. After evaporation of the solvent, the residue was washed with *n*-hexane. The residual solid was recrystallized from ethanol to give **5c** (36 mg, 71%) as colorless needles, mp 172—174°. *Anal.* Calcd. for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.47; H, 6.29; N, 10.79. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2200 (CN). NMR ($CDCl_3$) δ: 2.34 (3H, s, 6-Me), 2.50—3.50 (4H, m, 1- and 2-H_2), 3.88 and 4.02 (each 3H, each s, OMe×2), 4.08 (2H, t, $J=7$ Hz, 3-H_2), 6.80 (1H, s, 5-H). MS *m/e*: 256 (M^+).

9-Bromo-2,3-dihydro-1-keto-7-methoxy-6-methyl-1*H*-pyrrolo[1,2-*a*]indole (8)——A mixture of the ketone (**7**) (215 mg), N-bromosuccinimide (180 mg), methanol (200 ml) and dichloromethane (10 ml) was stirred at room temperature for 30 min. The reaction mixture was diluted with water and extracted with dichloromethane. The organic layer was washed with aqueous sodium bicarbonate solution, dried over Na_2SO_4 and evaporated at 40°. The residual solid was recrystallized from ethanol to give **8** (238 mg; 81%) as light green needles, mp>290° (darkening from 125°), identical with the material described in the literature[3] [UV (MeOH) and NMR ($CDCl_3$)].

8-Bromo-2,3-dihydro-7-methoxy-6-methyl-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (4)——A mixture of the nitrile (**1**) (226 mg), N-bromosuccinimide (178 mg) and acetic acid (70 ml) was stirred at room temperature for 24 hr. Work-up as above followed by recrystallization from chloroform afforded **4** (250 mg; 75%) as colorless needles, mp 222—224° (lit.,[7] mp 222—224°), identical with the authentic sample[7] [IR, NMR, and thin-layer chromatography (TLC)].

2,3-Dihydro-7-methoxy-6-methyl-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (9)——(a) To a stirred mixture of the nitro compound **2** (271 mg) in 50% aqueous acetic acid (50 ml) was added iron powder (600 mg) in small portions at 80—85°. The mixture was stirred for 2 hr at this temperature. After addition of water, the mixture was extracted with dichloromethane. The extract was washed with water and aqueous sodium bicarbonate solution, dried over Na_2SO_4 and evaporated to give the amino compound **3** as a solid, which was used without purification.

To a solution of the amino compound **3** in acetone (40 ml) and 0.167 M potassium dihydrogen phosphate (20 ml), potassium nitrosodisulphonate (1.5 g) was added. The mixture was stirred for 16 hr at room temperature and then diluted with water and extracted with dichloromethane. The extract was washed with aqueous sodium chloride solution, dried over Na_2SO_4, and evaporated to leave a solid which was

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[11] All melting points are uncorrected and were measured with a Yanagimoto micro melting point apparatus (MP-S2). The infrared (IR) spectra were measured with a Hitachi 215 recording spectrophotometer, UV spectra with a Hitachi 124 spectrometer, NMR spectra with a JEOL JNM-PMX 60 spectrometer, and mass spectra with a Hitachi RMU-7 spectrometer.

chromatographed on alumina (Woelm, grade III). Elution with benzene gave an orange solid, the recrystallization of which from ethanol afforded **9** (126 mg; 49%) as orange needles, mp 256—257°. *Anal.* Calcd. for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.75; H, 4.86; N, 10.69. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 2220 (CN), 1670, 1645 (C=O). NMR ($CDCl_3$) δ: 1.96 (3H, s, 6-Me), 2.40—3.30 (4H, m, 1- and 2-H_2), 4.10 (3H, s, OMe), 4.32 (2H, t, $J=7$ Hz, 3-H_2). MS *m/e*: 256 (M^+).

(b) A mixture of the bromide **20** (40 mg), 1 drop of tri-*n*-butyltin hydride, azobisisobutyronitrile (2 mg) and benzene (2 ml) was refluxed under nitrogen atmosphere for 7 hr. After evaporation of the solvent the residual syrup was purified by silica gel thick-layer chromatography with ether to give a solid, the recrystallization of which from ethanol afforded **9** (18 mg; 70%) as orange needles, mp 256—257°, identical with the above sample of **9** (IR, NMR, and TLC).

2,3-Dihydro-7-methoxy-6,9-dimethyl-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole (12)——To a stirred solution of the aldehyde **10** (259 mg) in acetic acid (20 ml) was added sodium borohydride (100 mg) in small portions over 20 min. The resulting solution was diluted with water and extracted with dichloromethane. The organic layer was washed with water, aqueous sodium bicarbonate solution and aqueous sodium chloride solution, dried over Na_2SO_4 and evaporated to give a reddish solid, the recrystallization of which from chloroform-methanol afforded **12** (236 mg; 96%) as reddish needles, mp 188—189°. *Anal.* Calcd. for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.62; H, 6.13; N, 5.80. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1660, 1640 (C=O). NMR ($CDCl_3$) δ: 1.90 and 2.22 (each 3H, each s, 6- and 9-Me), 2.30—3.00 (4H, m, 1- and 2-H_2), 3.96 (3H, s, OMe), 4.18 (2H, t, $J=7$ Hz, 3-H_2). MS *m/e*: 245 (M^+).

6-Bromo-2,3,6,7-tetrahydro-7,7-dimethoxy-6-methyl-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (14)——A solution of the nitrile **9** (51 mg) and N-bromosuccinimide (54 mg) in methanol (20 ml) and dichloromethane (20 ml) was stirred at room temperature for 1 hr. The reaction mixture was diluted with water and the organic layer was washed with aqueous sodium bicarbonate solution, dried over Na_2SO_4, and evaporated. The residue was recrystallized from ethanol to give the bromide **14** (64 mg; 87%) as colorless needles, mp 181—182°. *Anal.* Calcd. for $C_{15}H_{15}BrN_2O_4$: C, 49.06; H, 4.12; N, 7.63. Found: C, 49.15; H, 4.28; N, 7.66. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 244 (4.38), 285 (3.82), 325 (4.14). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 2240 (CN), 1756, 1726, 1690 (C=O). NMR ($CDCl_3$) δ: 2.04 (3H, s, 6-Me), 2.50—3.50 (4H, m, 1- and 2-H_2), 3.32 and 3.84 (each 3H, each s, $2\times$OMe), 4.40 (2H, t, $J=7$ Hz, 3-H_2). MS *m/e*: 366/368 (M^+).

6-Bromo-2,3,6,7-tetrahydro-7,7-dimethoxy-6-methyl-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole-9-carboxaldehyde (15)——A solution of the aldehyde **10** (129 mg), N-bromosuccinimide (150 mg) in methanol (30 ml) and dichloromethane (35 mg) was stirred at room temperature for 20 min. Work-up as above followed by recrystallization from methanol gave **15** (110 mg; 59%) as colorless needles, mp 188—189°. *Anal.* Calcd. for $C_{15}H_{16}BrNO_5$: C, 48.66; H, 4.36; N, 3.78. Found: C, 48.29; H, 4.37; N, 3.33. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 254 (4.23), 290 (3.76), 336 (4.02). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1710, 1670 (C=O). NMR ($CDCl_3$) δ: 2.04 (3H, s, 6-Me), 2.50—3.50 (4H, m, 2- and 3-H_2), 3.34 and 3.80 (each 3H, each s, $2\times$OMe), 4.36 (2H, t, $J=7$ Hz, 3-H_2), 10.34 (1H, s, CHO). MS *m/e*: 369/371 (M^+).

6,9-Dibromo-2,3,6,7-tetrahydro-7,7-dimethoxy-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole (16)——(a) A mixture of the aldehyde **10** (518 mg), N-bromosuccinimide (1.42 g), methanol (150 ml) and dichloromethane (150 ml) was stirred at room temperature for 15 hr. Work-up as above followed by recrystallization from ethanol gave the dibromide **16** (565 mg; 67%) as colorless needles, mp 197—199°. *Anal.* Calcd. for $C_{14}H_{15}Br_2NO_4$: C, 39.93; H, 3.59; N, 3.32. Found: C, 40.11; H, 3.55; N, 2.91. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 254 (3.82), 294 (3.60), 346 (3.84). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1700 and 1775 (C=O). NMR ($CDCl_3$) δ: 2.00 (3H, s, 6-Me), 2.30—3.10 (4H, m, 1- and 2-H_2), 3.30 and 3.74 (each s, $2\times$OMe), 4.34 (2H, t, $J=7$ Hz, 3-H_2). MS *m/e*: 419 (M^+), 421 (M^++2) 423 (M^++4).

(b) A mixture of the alcohol (**11**) (26 mg), N-bromosuccinimide (36 mg) and methanol (30 ml) was stirred at room temperature for 20 min. Work-up as above followed by recrystallization from ethanol gave the compound **16** (28 mg; 68%) as colorless needles, mp 197—199°, identical with the above sample of **16** (IR, NMR, and TLC).

6-Bromo-2,3,6,7-tetrahydro-7,7-dimethoxy-6,9-dimethyl-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole (17)——A mixture of the quinone **12** (75 mg), N-bromosuccinimide (54 mg), methanol (25 ml) and dichloromethane (25 ml) was stirred at room temperature for 30 min. Work-up as above followed by recrystallization from ethanol gave the bromide **17** (96 mg; 88%) as colorless needles, mp 145—146°. *Anal.* Calcd. for $C_{15}H_{18}BrNO_4$: C, 50.57; H, 5.09; N, 3.93. Found: C, 50.76; H, 5.02; N, 3.80. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 254 (4.08), 294 (3.88), 352 (4.08). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1695, 1670 cm^{-1} (C=O). NMR ($CDCl_3$) δ: 2.02 (3H, s, 6-Me), 2.26 (3H, s, 9-Me), 2.5—3.0 (4H, m, 1- and 2-H_2), 3.30 and 3.76 (each 3H, each s, $2\times$OMe), 4.34 (2H, t, $J=7$ Hz, 3-H_2). MS *m/e*: 355/357 (M^+).

6-Bromo-9-carbamoyloxymethyl-2,3,6,7-tetrahydro-7,7-dimethoxy-6-methyl-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole (18)——A mixture of the 7-methoxymitosene (13)[3)] (60 mg), N-bromosuccinimide (36 mg), methanol (20 ml), and dichloromethane (20 ml) was stirred at room temperature for 30 min. Work-up as above followed by recrystallization from ethanol gave the bromide **18** (76 mg; 93%) as needles, mp 156—157°. *Anal.* Calcd. for $C_{16}H_{19}BrN_2O_6$: C, 46.28; H, 4.61; N, 6.75. Found: C, 46.44; H, 4.72; N, 6.76. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 250 (4.06), 290 (3.71), 342 (4.00). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3560, 3460 (NH_2), 1720, 1675 (C=O). NMR ($CDCl_3$) δ: 2.02 (3H, s, 6-Me), 2.40—3.30 (4H, m, 1- and 2-H_2), 3.32 and 3.74 (each 3H, each s, $2\times$OMe), 4.34 (2H, t,

$J=7$ Hz, 3-H_2), 5.10 (2H, br. s, NH_2, disappeared by D_2O exchange), 5.28 (2H, s, CH_2O). MS *m/e*: 414/416 (M^+).

7-Acetoxy-6-bromo-2,3,6,7-tetrahydro-7-methoxy-6-methyl-1*H*-pyrrolo[1,2-*a*]indole-9-carbonitrile (20)——A mixture of the nitrile **9** (51 mg), N-bromosuccinimide (40 mg), acetic acid (10 ml) and dichloromethane (10 ml) was stirred at room temperature for 15 hr. Work-up as above followed by recrystallization from ethanol afforded **20** (64 mg; 81%) as colorless needles, mp 178—179°. *Anal.* Calcd. for $C_{16}H_{15}BrN_2O_5$: C, 48.62; H, 3.83; N, 7.09. Found: C, 48.96; H, 3.94; N, 6.94. UV λ_{max}^{EtOH} nm (log ε): 244 (4.58), 322 (4.37). IR ${}^{CHCl_3}_{max}$ νcm^{-1}: 2220 (CN), 1705 and 1680 (C=O). NMR ($CDCl_3$) δ: 2.20 (6H, s, MeCO and 6-Me), 2.50—3.50 (4H, m, 1- and 2-H_2), 3.82 (3H, s, OMe), 4.40 (2H, t, $J=7$ Hz, 3-H_2). MS *m/e*: 394/396 (M^+).

7-Acetoxy-6-bromo-2,3,6,7-tetrahydro-7-methoxy-6-methyl-1*H*-pyrrolo[1,2-*a*]indole-9-carboxaldehyde (21)——A mixture of the aldehyde (**10**) (52 mg), N-bromosuccinimide (36 mg), acetic acid (10 ml) and dichloromethane (10 ml) was stirred at room temperature for 6 hr. Work-up as above followed by recrystallization from ethanol afforded **21** (66 mg; 83%) as colorless needles, mp 183—184°. *Anal.* Calcd. for $C_{16}H_{16}BrNO_6$: C, 48.26; H, 4.05; N, 3.52. Found: C, 48.67; H, 4.36; N, 3.53. UV λ_{max}^{EtOH} nm (log ε): 254 (4.60), 322 (4.36). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1755, 1720 and 1655 (C=O). NMR ($CDCl_3$) δ: 2.20 and 2.08 (each 3H, each s, MeCO and 6-Me), 2.50—3.50 (4H, m, 1- and 2-H_2), 3.84 (3H, s, OMe), 4.34 (2H, t, $J=7$ Hz, 3-H_2), 10.24 (1H, s, CHO). MS *m/e*: 397/399 (M^+).

2,3,6,7-Tetrahydro-7,7-dimethoxy-6-methyl-5,8-dioxo-1*H*-pyrrolo[1,2-*a*]indole-9-carboxaldehyde (19)——A mixture of the bromide (**15**) (37 mg), 1 drop of tri-*n*-butyltin hydride, azobisisobutyronitrile (2 mg) and benzene (2 ml) was refluxed under nitrogen atmosphere for 15 hr. After evaporation of the solvent, the residual syrup was purified by thick–layer chromatography on silica gel developing with ether to give a solid (15 mg; 51%). This was recrystallized from ether to give the compound **19** as colorless needles, mp 185—186°. *Anal.* Calcd. for $C_{15}H_{17}NO_5 \cdot 0.25H_2O$: C, 60.46; H, 5.88; N, 4.81. Found: C, 60.46; H, 5.91; H, 4.48. IR ${}^{CHCl_3}_{max}$ cm^{-1}: 1700, 1660 (C=O). NMR ($CDCl_3$) δ: 1.20 (3H, d, $J=7$ Hz, 6-Me), 3.18 and 3.34 (each 3H, each s, 2×OMe), 4.30 (2H, t, $J=7$ Hz, 3-H_2), 10.32 (1H, s, CHO). MS *m/e*: 291 (M^+).

9-Bromo-2,3,6,7-tetrahydro-7,7-dimethoxy-6-methyl-1*H*-pyrrolo[1,2-*a*]indole (22)——A mixture of the bromide **16** (84 mg), 5 drops of tri-*n*-butyltin hydride, azobisisobutyronitrile (2 mg) and benzene (10 ml) was refluxed under nitrogen atmosphere for 8 hr. After evaporation of the solvent, the residue was washed with *n*-hexane. The residual solid was recrystallized from ethanol to give **22** (48 mg; 71%) as colorless prisms, mp 164—166°. *Anal.* Calcd. for $C_{14}H_{16}BrNO_4 \cdot 0.25H_2O$: C, 48.41; H, 4.75; N, 4.03. Found: C, 48.41; H, 4.50; N, 3.87. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700, 1670 (C=O). NMR ($CDCl_3$) δ: 1.20 (3H, d, $J=7$ Hz, 6-Me), 2.50—3.10 (4H, m, 1- and 2-H_2), 3.18 and 3.34 (each 3H, each s, 2×OMe), 4.36 (2H, t, $J=7$ Hz, 3-H_2). MS *m/e*: 341/343 (M^+).

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