Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron 63 (2007) 4356–4359
Tetrahedron

Synthesis of 9-arylamino- and (*Z*)-9-arylimino-9*H*-pyrrolo-[1,2-*a*]indoles by reactions of 2-(pyrrol-1-yl)-benzaldehydes with aryl amines

Kazuhiro Kobayashi,* Yasutoshi Himei, Shuhei Fukamachi, Miyuki Tanmatsu, Osamu Morikawa and Hisatoshi Konishi

Department of Materials Science, Faculty of Engineering, Tottori University, 4-101 Koyama-minami, Tottori 680-8552, Japan

Received 26 January 2007; accepted 26 February 2007
Available online 12 March 2007

Dedicated to the memory of Professor Yoshihiko Ito

Abstract—Heating mixtures of 2-(pyrrol-1-yl)benzaldehydes and aryl amines under argon afforded 9-arylamino-9*H*-pyrrolo[1,2-*a*]indoles, via cyclization of the resulting 2-(pyrrol-1-yl)benzaldimine intermediates. Heating in the presence of oxygen afforded (*Z*)-9-arylimino-9*H*-pyrrolo[1,2-*a*]indoles, which were successfully hydrolyzed with hydrochloric acid to give pyrrolo[1,2-*a*]indol-9-ones.

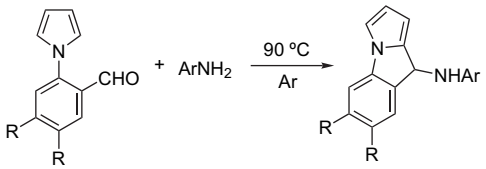
1. Introduction

As a part of our program aimed at developing new methods for the preparation of fused-heterocycles using 2-(pyrrol-1-yl)benzaldehydes as starting materials,[1] we previously described the one-pot preparation of 9-dialkylamino-9*H*-pyrrolo[1,2-*a*]indoles by reactions of 2-(pyrrol-1-yl)-benzaldehydes with secondary amine hydrochlorides in the presence of sodium iodide, chlorotrimethylsilane, and triethylamine.[1b] In this paper we wish to report that 9-arylamino- and (*Z*)-9-arylimino-9*H*-pyrrolo[1,2-*a*]indoles[2] are conveniently prepared by simply treating 2-(pyrrol-1-yl)benzaldehydes with aryl amines. To the best of our knowledge, synthesis of 9*H*-pyrrolo[1,2-*a*]indole derivatives carrying an arylamino (or arylimino) substituent at the 9-position has not been reported, though the synthesis of 9-alkylamino and 9-alkylimino derivatives have been recorded.[3] We also report that the 9-arylimino derivatives can be easily converted into the corresponding pyrrolo-[1,2-*a*]indol-9-one derivatives.[4] The 9*H*-pyrrolo[1,2-*a*]-indole skeleton has held considerable interest, because it is the basic framework of cytostatic mytomycine derivatives.[5]

2. Results and discussion

2.1. Synthesis of 9-arylamino-9*H*-pyrrolo[1,2-*a*]indoles 2

Intramolecular cyclization of 2-(pyrrol-1-yl)benzaldimines, generated from 2-(pyrrol-1-yl)benzaldehydes **1** with aryl amines, has been used in the synthesis of **2**. Thus, treatment of **1** with 2 M amounts of aryl amines at 90 °C without solvent under argon for 8 h afforded **2** in generally good yields, as shown in Scheme 1. The yields of **2b** and **2e** are somewhat lower than those of the others. This may be attributable to less reactivity of the corresponding aldimine intermediates. The quantity of aryl amines was crucial for satisfactory production of the desired products. For example, when 1 equiv of aniline was used in the reaction with **1a**, it proceeded sluggishly and was incomplete; a somewhat complicated mixture containing the starting **1a** was obtained and the yield of the desired product **2a** was considerably decreased (36%).



1a R = H
1b R = OMe

2a R = H, Ar = Ph 70%
2b R = H, Ar = *o*-Tol 61%
2c R = H, Ar = *p*-(MeO)C_6H_4 70%
2d R = H, Ar = *p*-ClC_6H_4 80%
2e R = OMe, Ar = Ph 65%

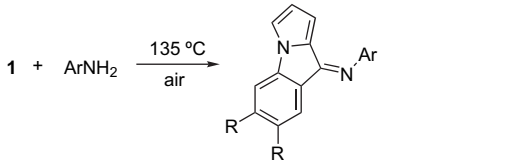
Scheme 1.

Keywords: 9-Arylamino-9*H*-pyrrolo[1,2-*a*]indole; 9-Arylimino-9*H*-pyrrolo[1,2-*a*]indole; Pyrrolo[1,2-*a*]indol-9-one; 2-(Pyrrol-1-yl)benzaldehyde; 2-(Pyrrol-1-yl)benzaldimine.
* Corresponding author. Tel./fax: +81 857 31 5263; e-mail: kkoba@chem.tottori-u.ac.jp

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.02.129

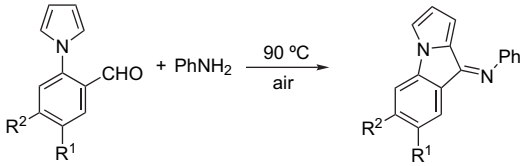
2.2. Synthesis of (*Z*)-9-arylimino-9*H*-pyrrolo[1,2-*a*]-indoles 3

The synthesis of (*Z*)-9-arylimino-9*H*-pyrrolo[1,2-*a*]indoles **3** is outlined in Scheme 2. Thus, 2-(pyrrol-1-yl)benzaldehydes **1** were treated with 2 M amounts of aryl amines at 135 °C for 4 h in the air to afford the corresponding desired products **3**. NOE experiments showed that the configuration of these iminopyrroloindoles is *Z*. For example, irradiation of the signal assignable to 3-H (δ 5.60) of **3e** resulted in an enhancement (11%) of the signal assignable to the *o*-protons of *N*-phenyl group (δ 7.06). The results shown in Scheme 2 indicate that the yields of the products **3** depend on the substituent of **1** and aryl amines. Thus, the substitution of a methoxy group on the benzene nucleus of aryl amine gave a much more satisfactory yield of the expected product **3c** but that on the benzene nucleus of **1** gave a poorer yield of the expected product **3e**, probably due to the electron donative nature of methoxy group. Preparation of the corresponding 9-imino derivative from **1a** and *p*-chloroaniline under the same conditions proved to be unsuccessful. Oxidation of **2d** to the expected imino derivatives did not occurred under these conditions, and **2d** was obtained in good yield. In contrast, we found that 2-(pyrrol-1-yl)benzaldehydes carrying a chlorine on the benzene nucleus, **1c** and **1d**, reacted with aniline at 90 °C in an argon atmosphere to give directly the corresponding 9-phenyliminopyrroloindoles **3f** and **3g**, respectively, in lower yields (about 30%). Oxidation of the corresponding 9-phenylamino derivatives to **3f** and **3g** is thought to take place rapidly only at 90 °C presumably during exposure to the contaminated oxygen. When the reactions were conducted at 90 °C in the air, the products **3f** and **3g** were obtained in fair yields, as shown in Scheme 3.



3a R = H, Ar = Ph 68%
3b R = H, Ar = *o*-Tol 58%
3c R = H, Ar = *p*-(MeO)C_6H_4 85%
3e R = OMe, Ar = Ph 33%

Scheme 2.



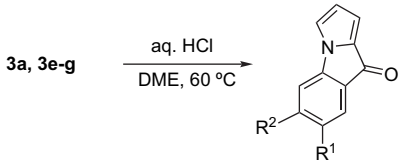
1c R^1 = Cl, R^2 = H
1d R^1 = H, R^2 = Cl

3f R^1 = Cl, R^2 = H 60%
3g R^1 = H, R^2 = Cl 56%

Scheme 3.

2.3. Synthesis of 9*H*-pyrrolo[1,2-*a*]indol-9-ones 4

The imino derivatives **3** were unchanged in concentrated hydrochloric acid–1,2-dimethoxyethane (DME) (1:5, v/v) at room temperature for a day. However, when the solutions were heated at 60 °C, hydrolysis took place cleanly to lead to the formation of the desired products **4** in good yields, as shown in Scheme 4.



4a $R^1 = R^2$ = H 64%
4e $R^1 = R^2$ = OMe 81%
4f R^1= H, R^2 = Cl 70%
4g R^1 = Cl, R^2 = H 68%

Scheme 4.

In summary, we have demonstrated convenient access to 9-arylamino- and 9-arylimino-9*H*-pyrrolo[1,2-*a*]indoles, and pyrrolo[1,2-*a*]indol-9-ones based on an intramolecular cyclization of 2-(pyrrol-1-yl)benzaldimines from 2-(pyrrol-1-yl)benzaldehydes and aryl amines. The method should be useful in heterocycle synthesis because of the ease of operations as well as the ready availability of the starting materials.

3. Experimental

3.1. General

The melting points were determined on a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncorrected. The IR spectra were recorded on a Perkin–Elmer 1600 Series FTIR spectrometer. The ^{1}H NMR spectra were determined using $SiMe_4$ as an internal reference in $CDCl_3$ with a JEOL GX270 FT NMR spectrometer operating at 270 MHz. Low-resolution mass spectra were recorded on a JEOL AUTOMASS 20 spectrometer (Center for Joint Research and Development, Tottori University). Thin-layer chromatography (TLC) was carried out using Merck Kieselgel 60 PF_{254}. All of the solvents used were dried over the appropriate drying agents and distilled under argon prior to use.

3.2. Starting materials

2-(Pyrrol-1-yl)benzaldehydes **1a**, **1b**, and **1d** were prepared by the procedure previously reported by us.[1] 4-Chloro-2-(pyrrol-1-yl)benzaldehyde (**1c**) was prepared from ethyl 2-amino-4-chlorobenzoate[6] according to the procedure for the preparation of the above compounds. Thus, this ester was allowed to react with 2,5-dimethoxytetrahydrofuran in refluxing acetic acid to give ethyl 4-chloro-2(pyrrol-1-yl)-benzoate in 68% yield; a pale yellow liquid; bp 116 °C/0.26 mmHg; IR (neat) 1720 cm^{-1}; ^{1}H NMR δ 1.13 (3H, t, *J*=7.3 Hz), 4.16 (2H, q, *J*=7.3 Hz), 6.30 (2H, dd, *J*=2.3, 2.0 Hz), 6.78 (2H, dd, *J*=2.3, 2.0 Hz), 7.35–7.4 (2H, m), 7.75 (1H, d, *J*=8.9 Hz). Calcd for $C_{13}H_{12}ClNO_2$: C, 62.53; H, 4.84; N, 5.61. Found: C, 62.41; H, 4.90; N, 5.29. This compound was reduced by $LiAlH_4$ in diethyl ether at 0 °C to give 4-chloro-2-(pyrrol-1-yl)benzyl alcohol in 95% yield; a pale yellow liquid; R_f 0.38 (1:3 AcOEt–hexane); IR (neat) 3342 cm^{-1}; ^{1}H NMR δ 1.64 (1H, br s), 4.55 (2H, s), 6.33

(2H, dd, J=2.3, 2.0 Hz), 6.85 (2H, dd, J=2.3, 2.0 Hz), 7.31 (1H, d, J=2.0 Hz), 7.36 (1H, dd, J=8.2, 2.0 Hz), 7.51 (1H, d, J=8.2 Hz). Calcd for $C_{11}H_{10}ClNO$: C, 63.62; H, 4.85; N, 6.75. Found: C, 63.33; H, 5.12; N, 6.52. This alcohol was used in the next PCC oxidation in dichloromethane at room temperature without any purification to give **1c** in 66% yield; a pale yellow liquid; bp 145 °C (oven temp)/0.20 mmHg; IR (neat) 2858, 2762, 1695 cm^{-1}; ^1H NMR δ 6.41 (2H, dd, J=2.3, 2.0 Hz), 6.92 (2H, dd, J=2.3, 2.0 Hz), 7.4–7.5 (2H, m), 7.94 (1H, d, J=8.9 Hz), 9.79 (1H, s). Calcd for $C_{11}H_8ClNO$: C, 64.25; H, 3.92; N, 6.81. Found: C, 64.15; H, 4.04; N, 6.75. Other chemicals used in this study were commercially available.

3.3. Typical procedure for the preparation of 9-arylamino-9*H*-pyrrolo[1,2-*a*]indoles 2

3.3.1. 9-Phenylamino-9*H*-pyrrolo[1,2-*a*]indole (2a). A mixture of 2-(pyrrol-1-yl)benzaldehyde (**1a**) (0.17 g, 1.0 mmol) and aniline (0.19 g, 2.0 mmol) was heated at 90 °C for 8 h under argon. After removal of excess aniline under reduced pressure, the residual solid was recrystallized from hexane–CH_2Cl_2 to give **2a** (0.17 g, 70%); a pale yellow solid; mp 100–101 °C; IR (KBr disk) 3352, 1618, 1605 cm^{-1}; ^1H NMR δ 4.00 (1H, br s), 5.71 (1H, s), 6.18 (1H, ddd, J=3.3, 2.3, 1.0 Hz), 6.30 (1H, dd, J=3.3, 2.6 Hz), 6.75–6.9 (3H, m), 7.04 (1H, dd, J=2.6, 2.3 Hz), 7.09 (1H, dd, J=7.6, 1.0 Hz), 7.2–7.3 (3H, m), 7.34 (1H, tt, J=7.6, 1.0 Hz), 7.50 (1H, d, J=7.6 Hz); MS m/z 246 (M^+, 15), 154 (100). Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.77; H, 5.83; N, 11.37.

3.3.2. 9-(2-Methylphenylamino)-9*H*-pyrrolo[1,2-*a*]indole (2b). A yellow solid; mp 127–128 °C (hexane–CH_2Cl_2); IR (KBr disk) 3377, 1620, 1603 cm^{-1}; ^1H NMR δ 2.09 (3H, s), 3.89 (1H, d, J=8.8 Hz), 5.74 (1H, d, J=8.8 Hz), 6.22 (1H, ddd, J=3.3, 2.6, 1.1 Hz), 6.31 (1H, dd, J=3.3, 3.0 Hz), 6.76 (1H, td, J=7.3, 1.1 Hz), 7.0–7.15 (4H, m), 7.15–7.3 (2H, m), 7.35 (1H, t, J=7.3 Hz), 7.53 (1H, d, J=7.3 Hz); MS m/z 260 (M^+, 18), 154 (100). Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.64; H, 6.50; N, 10.65.

3.3.3. 9-(4-Methoxyphenylamino)-9*H*-pyrrolo[1,2-*a*]indole (2c). A pale yellow solid; mp 98–99 °C (hexane–CH_2Cl_2); IR (KBr disk) 3370, 1618 cm^{-1}; ^1H NMR δ 3.70 (1H, br s), 3.78 (3H, s), 5.62 (1H, s), 6.13 (1H, ddd, J=3.3, 2.3, 1.0 Hz), 6.29 (1H, dd, J=3.3, 3.0 Hz), 6.80 (2H, d, J=8.9 Hz), 6.83 (2H, d, J=8.9 Hz), 7.0–7.15 (2H, m), 7.22 (1H, d, J=7.6 Hz), 7.33 (1H, dd, J=7.6, 7.3 Hz), 7.48 (1H, d, J=7.3 Hz); MS m/z 276 (M^+, 3.7), 275 (19), 153 (100). Calcd for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found: C, 78.03; H, 5.88; N, 10.14.

3.3.4. 9-(4-Chlorophenylamino)-9*H*-pyrrolo[1,2-*a*]indole (2d). A yellow solid; mp 111–112 °C (hexane–Et_2O); IR (KBr disk) 3354, 1620 cm^{-1}; ^1H NMR δ 4.02 (1H, d, J=8.1 Hz), 5.65 (1H, d, J=8.1 Hz), 6.15 (1H, ddd, J=3.3, 2.2, 1.1 Hz), 6.30 (1H, dd, J=3.3, 3.0 Hz), 6.74 (2H, d, J=8.8 Hz), 7.0–7.15 (2H, m), 7.18 (2H, d, J=8.8 Hz), 7.23 (1H, d, J=7.3 Hz), 7.35 (1H, t, J=7.3 Hz), 7.48 (1H, d, J=7.3 Hz); MS m/z 280 (M^+, 3.7), 278 (4.0), 154 (51), 127 (100). Calcd for $C_{17}H_{13}ClN_2$: C, 72.73; H, 4.67; N, 9.98. Found: C, 72.49; H, 4.74; N, 9.98.

3.3.5. 6,7-Dimethoxy-9-phenylamino-9*H*-pyrrolo[1,2-*a*]indole (2e). A pale yellow solid; mp 145–147 °C (hexane–CH_2Cl_2); IR (KBr disk) 3360, 1624, 1603 cm^{-1}; ^1H NMR δ 3.85 (3H, s), 3.96 (4H, s), 5.64 (1H, s), 6.14 (1H, ddd, J=3.3, 2.3, 1.0 Hz), 6.26 (1H, dd, J=3.3, 2.6 Hz), 6.75–6.9 (4H, m), 6.97 (1H, dd, J=2.6, 2.3 Hz), 7.08 (1H, s), 7.2–7.3 (2H, m); MS m/z 306 (M^+, 14), 214 (100). Calcd for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.14. Found: C, 74.59; H, 6.07; N, 9.03.

3.4. Typical procedure for the preparation of 9-arylimino-9*H*-pyrrolo[1,2-*a*]indoles 3

3.4.1. (*Z*)-9-Phenylimino-9*H*-pyrrolo[1,2-*a*]indole (3a). A mixture of 2-(pyrrol-1-yl)benzaldehyde (**1a**) (0.17 g, 1.0 mmol) and aniline (0.19 g, 2.0 mmol) was heated in the air at 135 °C for 4 h. The resulting mixture was purified by preparative TLC on silica gel (1:10 AcOEt–hexane) to give **3a** (0.17 g, 68%) as a yellow solid; mp 140–141 °C (hexane–CH_2Cl_2); IR (KBr disk) 1637, 1616 cm^{-1}; ^1H NMR δ 5.66 (1H, dd, J=3.6, 1.0 Hz), 6.10 (1H, dd, J=3.6, 2.6 Hz), 7.00 (1H, dd, J=2.6, 1.0 Hz), 7.06 (2H, dd, J=8.3, 1.3 Hz), 7.2–7.25 (3H, m), 7.35–7.5 (3H, m), 7.87 (1H, dd, J=7.6, 1.3 Hz); MS m/z 244 (M^+, 100). Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.55; H, 5.12; N, 11.20.

3.4.2. (*Z*)-9-(2-Methylphenylimino)-9*H*-pyrrolo[1,2-*a*]indole (3b). A yellow solid; mp 64–66 °C (pentane–CH_2Cl_2); IR (KBr disk) 1637, 1616 cm^{-1}; ^1H NMR δ 2.16 (3H, s), 5.51 (1H, dd, J=3.6, 1.0 Hz), 6.09 (1H, dd, J=3.6, 2.6 Hz), 6.91 (1H, dd, J=7.6, 1.3 Hz), 6.99 (1H, dd, J=2.6, 1.0 Hz), 7.09 (1H, td, J=7.6, 1.3 Hz), 7.15–7.3 (4H, m), 7.43 (1H, td, J=7.6, 1.3 Hz), 7.90 (1H, dd, J=7.6, 1.3 Hz); MS m/z 258 (M^+, 100). Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.39; H, 5.65; N, 10.65.

3.4.3. (*Z*)-9-(4-Methoxyphenylimino)-9*H*-pyrrolo[1,2-*a*]indole (3c). A orange solid; mp 143–145 °C (hexane–CH_2Cl_2); IR (KBr disk) 1636, 1618 cm^{-1}; ^1H NMR δ 3.85 (3H, s), 5.88 (1H, dd, J=3.6, 1.0 Hz), 6.13 (1H, dd, J=3.6, 2.6 Hz), 6.95 (2H, d, J=8.9 Hz), 7.00 (1H, dd, J=2.6, 1.0 Hz), 7.07 (2H, d, J=8.9 Hz), 7.15–7.25 (2H, m), 7.41 (1H, td, J=7.6, 1.3 Hz), 7.86 (1H, dd, J=7.6, 1.3 Hz); MS m/z 274 (M^+, 63), 259 (100). Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.61; H, 5.36; N, 10.07.

3.4.4. (*Z*)-6,7-Dimethoxy-9-(4-phenylimino)-9*H*-pyrrolo[1,2-*a*]indole (3e). A pale yellow solid; mp 49–50 °C (hexane–CH_2Cl_2); IR (KBr disk) 1635, 1614 cm^{-1}; ^1H NMR δ 3.95 (3H, s), 3.99 (3H, s), 5.60 (1H, dd, J=3.6, 1.0 Hz), 6.04 (1H, dd, J=3.6, 2.6 Hz), 6.75 (1H, s), 6.91 (1H, dd, J=2.6, 1.0 Hz), 7.06 (2H, dd, J=8.6, 1.3 Hz), 7.18 (1H, tt, J=7.3, 1.3 Hz), 7.35–7.45 (3H, m); MS m/z 304 (M^+, 100). Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 74.90; H, 5.24; N, 9.00.

3.4.5. (*Z*)-7-Chloro-9-(4-phenylimino)-9*H*-pyrrolo[1,2-*a*]indole (3f). The heating of a mixture of 5-chloro-2-(pyrrol-1-yl)benzaldehyde (**1c**) (0.11 g, 0.50 mmol) and aniline (93 mg, 1.0 mmol) in the air at 90 °C for 2 h gave, after purification by preparative TLC on silica gel (1:5 AcOEt–hexane), **3f** (83 mg, 60%) as a yellow solid; mp

132–133 °C (hexane–CH_2Cl_2); IR (KBr disk) 1632, 1616 cm^{-1}; ^1H NMR δ 5.73 (1H, dd, J=3.6, 1.0 Hz), 6.12 (1H, dd, J=3.6, 2.4 Hz), 6.97 (1H, dd, J=2.6, 1.0 Hz), 7.0–7.1 (3H, m), 7.11 (1H, s), 7.20 (1H, tt, J=7.3, 1.3 Hz), 7.35–7.45 (3H. m); MS m/z 278 (M^+, 100). Calcd for $C_{17}H_{11}N_2Cl$: C, 73.25; H, 3.98; N, 10.05. Found: C, 73.08; H, 4.09; N, 9.99.

3.4.6. (*Z*)-6-Chloro-9-(4-phenylimino)-9*H*-pyrrolo[1,2-*a*]-indole (3g). Heating a mixture of 4-chloro-2-(pyrrol-1-yl)benzaldehyde (**1d**) (0.41 g, 2.0 mmol) and aniline (0.37 mg, 4.0 mmol) in the air at 90 °C for 2 h gave, after purification by preparative TLC on silica gel (1:5 AcOEt–hexane), **3g** (0.31 g, 56%) as a yellow solid; mp 154–155 °C (hexane–CH_2Cl_2); IR (KBr disk) 1631, 1612 cm^{-1}; ^1H NMR δ 5.70 (1H, dd, J=3.6, 0.7 Hz), 6.13 (1H, dd, J=3.6, 2.6 Hz), 6.97 (1H, dd, J=2.6, 0.7 Hz), 7.05 (2H, dd, J=8.2, 1.3 Hz), 7.1–7.25 (3H, m), 7.41 (2H, t, J=8.2 Hz), 7.77 (1H, d, J=8.6 Hz); MS m/z 278 (M^+, 100). Calcd for $C_{17}H_{11}N_2Cl$: C, 73.25; H, 3.98; N, 10.05. Found: C, 73.36; H, 4.10; N, 9.97.

3.5. Typical procedure for the preparation of pyrrolo[1,2-*a*]indol-9-ones 4

3.5.1. Pyrrolo[1,2-*a*]indol-9-one (4a). To a stirred solution of **3a** (83 mg, 0.34 mmol) in 1,2-dimethoxyethane (DME) (5 mL) at room temperature was added 1.0 mL of concentrated hydrochloric acid. After the mixture was heated at 60 °C for 20 min, DME was evaporated and 10 mL of water was added. The crude product was extracted with CH_2Cl_2 three times (10 mL each). The combined extracts were washed with brine and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by preparative TLC on silica gel (1:5 AcOEt–hexane) to give **4a** (37 mg, 64%) as a yellow solid; mp 121–122 °C (hexane–CH_2Cl_2) (lit.,[7] 121–122 °C); IR (KBr disk) 1684 and 1620 cm^{-1}; the ^1H NMR data of this product are identical to those described in the literature.[8]

3.5.2. 6,7-Dimethoxypyrrolo[1,2-*a*]indol-9-one (4e). An orange solid; mp 166–167 °C (hexane–CH_2Cl_2); IR (KBr disk) 1686, 1616 cm^{-1}; ^1H NMR δ 3.82 (3H, s), 3.92 (3H, s), 6.16 (1H, dd, J=3.6, 2.6 Hz), 6.62 (1H, s), 6.64 (1H, dd, J=3.6, 1.0 Hz), 6.91 (1H, dd, J=2.6, 1.0 Hz), 7.19 (1H, s); MS m/z 229 (100). Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11. Found: C, 68.04; H, 5.09; N, 6.07.

3.5.3. 6-Chloropyrrolo[1,2-*a*]indol-9-one (4f). A red solid; mp 179–180 °C (hexane–CH_2Cl_2); IR (KBr disk) 1685, 1614 cm^{-1}; ^1H NMR δ 6.40 (1H, dd, J=3.6, 2.6 Hz), 6.81 (1H, dd, J=3.6, 0.7 Hz), 7.06 (1H, dd, J=2.6, 0.7 Hz), 7.05–7.15 (2H, m), 7.50 (1H, d, J=8.6 Hz); MS m/z 203 (100). Calcd for $C_{11}H_6ClNO$: C, 64.88; H, 2.97; N, 6.88. Found: C, 64.79; H, 3.25; N, 6.84.

3.5.4. 7-Chloropyrrolo[1,2-*a*]indol-9-one (4g). A yellow solid; mp 140–141 °C (hexane–CH_2Cl_2); IR (KBr disk) 1691, 1616 cm^{-1}; ^1H NMR δ 6.33 (1H, dd, J=4.0, 2.6 Hz), 6.81 (1H, dd, J=4.0, 1.0 Hz), 7.0–7.1 (2H, m), 7.40 (1H, dd, J=8.2, 2.0 Hz), 7.54 (1H, dd, J=2.6, 1.0 Hz); MS m/z 203 (100). Calcd for $C_{11}H_6ClNO$: C, 64.88; H, 2.97; N, 6.88. Found: C, 64.84; H, 3.01; N, 6.85.

References and notes

1. (a) Kobayashi, K.; Nakahashi, R.; Takanohashi, A.; Kitamura, T.; Morikawa, O.; Konishi, H. *Chem. Lett.* **2002**, 624–625; (b) Kobayashi, K.; Takanohashi, A.; Hashimoto, K.; Morikawa, O.; Konishi, H. *Tetrahedron* **2006**, *62*, 3158–3161; (c) Kobayashi, K.; Takanohashi, A.; Hashimoto, K.; Morikawa, O.; Konishi, H. *Tetrahedron* **2006**, *62*, 10379–10382.
2. For previous reports on the synthesis of 9*H*-pyrrolo[1,2-*a*]indole derivatives, see pertinent references cited in Ref. 1b. See also: (a) González-Pérez, P.; Pérez-Serrano, L.; Casarrubios, L.; Domínguez, G.; Pérez-Castells, J. *Tetrahedron Lett.* **2002**, *43*, 4765–4767; (b) Feidman, K. S.; Lyer, M. R.; Keith Hester, D., II. *Org. Lett.* **2006**, *8*, 3113–3116.
3. For the syntheses and biological activities of 9-alkylamino- and 9-alkylimino-9*H*-pyrrolo[1,2-*a*]indoles, see: (a) Rault, S.; de Sévricourt, M. C.; Godard, A. G.; Robba, M. *Tetrahedron Lett.* **1985**, *26*, 2305–2308; (b) Rault, S.; Lancelot, J. C.; Robba, M.; Quermonne, M. A.; Nammathao, B.; Louchahi-Raoul, J.; Marcy, R. *Eur. J. Med. Chem.* **1991**, *26*, 939–946.
4. For recent syntheses of pyrrolo[1,2-*a*]indol-9-ones, see: (a) Yavari, I.; Adib, M.; Sayahi, M. H. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1517–1519; (b) Campo, M. A.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 5616–5620; (c) Kashulin, I. A.; Nifant'ev, I. E. *J. Org. Chem.* **2004**, *69*, 5476–5479; The use of this class of molecules as photosensitizers has appeared: Bauer, R.; Heisler, G.; Koenigstein, C. *Spectrochim. Acta, Part A* **1994**, *50A*, 57–67.
5. Foggasy, K.; Kovács, K.; Keseru, G. N.; Tõke, L.; Faigl, F. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1039–1043 and pertinent references cited therein.
6. Keyser, G. E.; Leonard, N. J. *J. Org. Chem.* **1976**, *41*, 3529–3532.
7. Josey, A. D.; Jenner, E. L. *J. Org. Chem.* **1962**, *27*, 2466–2470.
8. Cartoon, M. E. K.; Cheeseman, G. W. H. *J. Organomet. Chem.* **1981**, *212*, 1–9.