A Convenient Synthesis of New Aminomethylenedioxypyrroloindoles *via* an Iminium Salt

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Cyclization of 2-(1-pyrrolyl)piperonylcarboxamide derivatives gave iminium perchlorates which afforded 9-(*N*-substituted-imino) and 9-(*N*-substituted amino)-6,7-methylenedioxypyrrolo[1,2-*a*]indoles.

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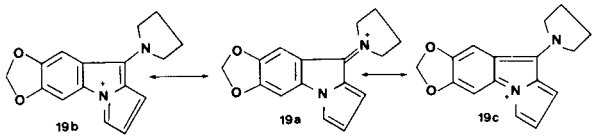
In continuation of our work on the synthesis of heterocyclic systems by cyclization of appropriate *N*-substituted pyrroles [1], we have reported the synthesis of some thienopyrrolizines and aminopyrroloindoles [2,3,4] starting from Vilsmeier salts of *N*-disubstituted carboxamide derivatives of pyrrolylthenoic acid and pyrrolylbenzoic acid. We wish to describe now the first application of this method to the preparation of new 6,7-methylenedioxypyrroloindoles, *N*-substituted-9-imino (and amino)-6,7-dioxymethylene-9*H*-pyrrolo[1,2-*a*]indoles.

Treatment of 2-(1-pyrrolyl)piperonylic acid **1** with phosphorus pentachloride in benzene provided 2-(1-pyrrolyl)-piperonylic chloride **2** which reacted with either primary amines or cyclic and aliphatic secondary amines in benzene to provide the *N*-pyrrolylpiperonylcarboxamides derivatives **3-12**. It must be pointed out that carboxamides **9-12** which are very unstable and not isolable were immediately cyclized to iminium salts.

Cyclization of the latter compounds by heating at reflux in phosphorus oxychloride afforded the iminium salts **13-22** as a mixture of hydrochlorides and phosphono dichloridates unable to be analysed. Purification of mixtures was realized by treatment with sodium bicarbonate. Then, acidification by perchloric acid led to perchlorates **13a-22a**.

The structure of these salts is clearly determined by ^{1}H-nmr spectroscopic data.

Chart 1



The α protons of the pyrrolidine ring appear as two deshielded multiplets at 4.36 and 3.36 ppm suggesting the occurrence of a restricted rotation due to the exocyclic double bond (mesomeric structure **19a**) without however excluding the two mesomeric forms **19b** and **19c** which possess a greater electronic delocalization (Chart 1).

When the stable salts **13-22** and **13a-22a** were stirred with a methanolic sodium hydroxide solution at room temperature they furnished the 6,7-methylenedioxypyrroloindolone **23**. Furthermore, the reaction of **19a** in dimethylformamide and sodium carbonate with primary amines yielded the hydrobromides of 6,7-methylenedioxy-9-(*N*-substituted imino)-9*H*-pyrrolo[1,2-*a*]indoles **24a-28a** with 30% to 50% yields. Reduction of these latter compounds using sodium borohydride in methanol gave the corresponding secondary amines **29** and **32**. On the

Chart 2

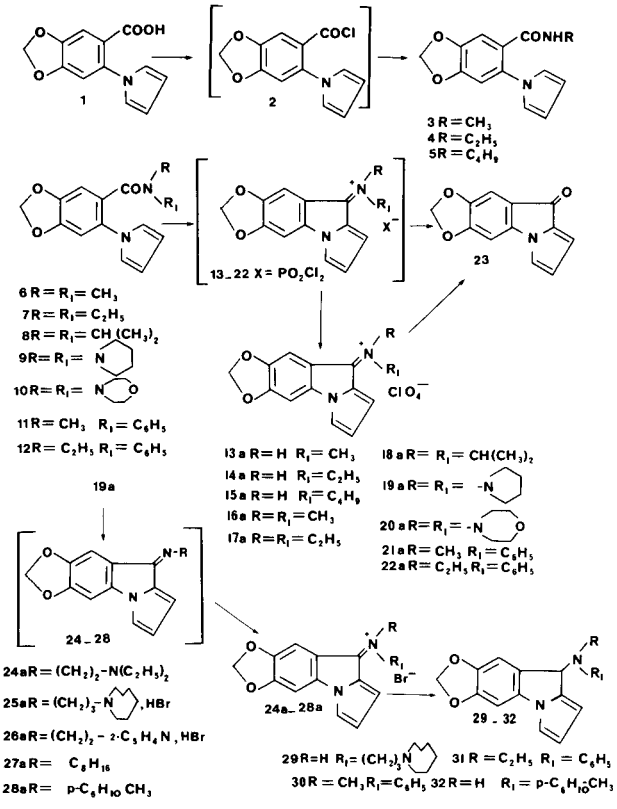


Table 1

MP, IR and ^{1}H-NMR Spectroscopic Data

Compound	mp (°C) (bp)	IR KBr ν cm^{-1}	^{1}H NMR DMSO-d_6 δ/TMS ppm
3	118	3260 (NH) 1630 (CO)	6.83 (s, 1H, H3), 7.00 (s, 1H, H6), 6.76 (t, 2H, H2'H5'), 6.06 (t, 2H, H3'H4'), 7.66 (s, 1H, NH), 2.53 (s, 3H, CH_3), 6.06 (s, 2H, CH_2)
4	124	3260 (NH) 1620 (CO)	6.86 (s, 1H, H3), 6.94 (s, 1H, H6), 6.70 (t, 2H, H2'H5'), 6.14 (t, 2H, H3'H4'), 7.70 (s, 1H, NH), 6.14 (s, 2H, CH_2), 3.06 (q, 2H, CH_2), 0.90 (t, 3H, CH_3)
5	98	3270(NH) 1630 (CO)	6.70 (s, 1H, H3), 6.80 (s, 1H, H6), 6.70 (t, 2H, H2'H5'), 6.03 (t, 2H, H3'H4'), 7.67 (s, 1H, NH), 6.03 (s, 2H, CH_2), 3.00, 1.20 (m, 6H, CH_2), 0.83 (t, 3H, CH_3)
6	160/5mm	1630 (CO)	6.70 (s, 1H, H3), 6.83 (s, 1H, H6), 6.83 (t, 2H, H2'H5'), 6.13 (t, 2H, H3'H4'), 6.13 (s, 2H, CH_2), 2.76, 2.43 (tt, 6H, CH_3)
7	88	1625 (CO)	6.86 (s, 1H, H3), 6.96 (s, 1H, H6), 6.86 (t, 2H, H2'H5'), 6.13 (t, 2H, H3'H4'), 6.13 (s, 2H, CH_2), 2.93 (m, 4H, CH_2), 0.96 (m, 6H, CH_3)
8	106	1620 (CO)	6.80 (s, 1H, H3), 6.93 (s, 1H, H6), 6.80 (t, 2H, H2'H5'), 6.13 (t, 2H, H3'H4'), 6.13 (s, 2H, CH_2), 3.43 (m, 2H, CH), 1.40, 1.26, 0.9 (m, 12H, CH_3)
13a	265	1635 (CN), 1170 1010 (ClO_4)	7.20 (s, 2H, H5H8), 7.20 (dd, 1H, H1), 6.40 (dd, 1H, H2), 7.70 (dd, 1H, H3), 6.16 (s, 2H, CH_2), 3.36 (s, 3H, CH_3)
14a	265	1650 (CN), 1160 1010 (ClO_4)	7.40 (s, 1H, H5), 7.50 (s, 1H, H8), 7.20 (dd, 1H, H1), 6.33 (dd, 1H, H2), 7.83 (dd, 1H, H3), 6.20 (s, 2H, CH_2), 3.80 (q, 2H, CH_2), 1.40 (t, 3H, CH_3)
15a	174	1655 (CN), 1150 1050 (ClO_4)	7.40 (s, 1H, H5), 7.50 (s, 1H, H8), 7.33 (dd, 1H, H1), 5.63 (dd, 1H, H2), 7.83 (dd, 1H, H3), 6.20 (s, 2H, CH_2), 3.76, 1.76, 1.46 (m, 6H, CH_2), 0.76 (t, 3H, CH_3)
16a	265	1635 (CN), 1150 1050 (ClO_4)	7.43 (s, 1H, H5), 7.60 (s, 1H, H8), 7.16 (dd, 1H, H1), 6.43 (s, 1H, H2), 7.80 (s, 1H, H3) 3.86 (s, 3H, CH_3), 3.66 (s, 3H, CH_3)
17a	265	1650 (CN), 1160 1010 (ClO_4)	7.30 (s, 2H, H5H8), 7.00 (dd, 1H, H1), 6.36 (dd, 1H, H2), 7.63 (dd, 1H,H3), 6.22 (s, 1H, CH_2), 3.73 (m, 4H, CH_2) , 136 (m, 6H, CH_3)
18a	246	1620 (CN), 1150 1050 (ClO_4)	7.40 (s, 1H, H5), 7.46 (s, 1H, H8), 7.16 (dd, 1H, H1), 6.47 (dd, 1H, H2), 7.83 (dd, 1H, H3), 6.20 (s, 2H, CH_2), 3.00 (m, 2H, CH), 1.60, 1.00 (m, 6H, CH_3)
19a	265	1645 (CN), 1160 1050 (ClO_4)	7.40 (s, 1H, H5), 7.53 (s, 1H, H8), 7.13 (dd, 1H, H1), 6.43 (dd, 1H, H2), 7.80 (dd, 1H, H3), 6.20 (s, 2H, CH_2),4.36, 3.36 (m, 4Hα, CH_2), 2.16 (m, 4Hβ, CH_2)
20a	265	1630 (CN), 1130 1050 (ClO_4)	7.36 (s, 1H, H5), 7.66 (s, 1H, H8), 7.26 (dd, 1H, H1), 6.43 (dd, 1H, H2), 7.73 (dd, 1H, H3), 6.20 (s, 2H, CH_2), 4.30 (m, 4Hα, CH_2), 4.00 (m, 4Hβ, CH_2)
21a	264	1625 (CN), 1140 1040 (ClO_4)	7.46 (s, 1H, H5), 7.70 (s, 1H, H8), 7.46 (dd, 1H, H1), 6.53 (dd, 1H, H2), 7.90 (dd, 1H, H3), 7.70 (m, 5H, C_6H_5), 3.96 (s, 3H, CH_3), 6.20 (s, 2H, CH_2)
22a	260	1610 (CN), 1140 1040 (ClO_4)	7.40 (s, 1H, H5), 7.70 (s, 1H, H8), 7.50 (dd, 1H, H1), 6.53 (dd, 1H, H2), 7.90 (dd, 1H, H3), 7.70 (m, 5H, C_6H_5), 6.23 (s, 2H, CH_2), 4.26 (q, 2H, CH_2), 1.34 (t, 3H, CH_3)
23	178	1680 (CO)	6.93 (s, 1H, H5), 7.30 (s, 1H, H8), 6.68 (dd, 1H, H1), 6.20 (dd, 1H, H2), 7.43 (dd, 1H, H3), 6.06 (s, 2H, CH_2)
24a	255	2810, 2490 (NH^+) 1640 (CN)	7.30 (s, 1H, H5), 7.36 (s, 1H, H8), 6.90 (dd, 1H, H1), 6.33 (dd, 1H, H2), 7.60 (dd, 1H, H3), 6.10 (s, 2H, CH_2), 3.73, 3.32, 2.30 (m, 10H, CH_2), 1.23 (m, 6H, CH_3)
25a	265	2800, 2500 (NH^+) 1650 (CN)	7.40 (s, 1H, H5), 7.90 (s, 1H, H8), 7.40 (dd, 1H, H1), 6.40 (dd, 1H, H2), 7.90 (dd, 1H, H3), 6.16 (s, 2H, CH_2), 3.66, 3.33 (m, 4H, CH_2), 1.83, 1.63 (m, 8H, CH_2)
26a	265	2900, 2500 (NH^+) 1650 (CN)	7.36 (s, 1H, H5), 7.73 (s, 1H, H8), 7.36 (dd, 1H, H1), 6.40 (dd, 1H, H2), 7.93 (dd, 1H, H3), 6.17 (s, 2H, CH_2), 8.83, 8.46, 8.10, 7.83 (dd, 4H, H pyridine), 4.36 (m, 4H, CH_2)
27a	265	2990, 2500 (NH^+) 1635(CN)	7.00 (s, 1H, H5), 7.46 (s, 1H, H8), 6.83 (dd, 1H, H1), 6.03 (dd, 1H, H2), 7.46 (dd, 1H, H3), 5.80 (s, 2H, CH_2), 2.10, 1.60, 1.23 (m, 15H, CH_2, CH)
28a	240	2840, 2500 (NH^+) 1630 (CN)	7.43 (s, 1H, H5), 7.80 (s, 1H, H8), 7.30 (dd, 1H, H1), 6.43 (dd, 1H, H2), 7.86 (dd, 1H, H3), 6.17 (s, 2H, CH_2), 3.30, 1.36 (m, 2H, CH), 2.00, 1.73 (m, 8H, CH_2), 0.93 (s, 3H, CH_3)
29	170/5mm	3300 (NH)	7.00 (s, 1H, H5), 7.13 (s, 1H, H8), 4.73 (s, 1H, H9), 6.00 (dd, 1H, H1), 6.10 (dd, 1H, H2), 7.13 (s, 1H, H3), 6.00 (s, 2H, CH_2), 2.40, 1.46 (m, 18H, CH_2), 2.40 (s, 1H, NH)
30	100		6.76 (s, 1H, H5), 7.26 (s, 1H, H8), 6.03 (s, 1H, H9), 6.03 (dd, 1H, H1), 6.20 (dd, 1H, H2), 7.26 (dd, 1H, H3) 6.03 (s, 2H, CH_2), 3.00 (s, 1H, CH), 2.33 (s, 3H, CH_3), 7.10 (m, 5H, C_6H_5)
31	92		6.80 (s, 1H, H5), 7.26 (s, 1H, H8), 5.93(s, 1H, H9), 6.03 (dd, 1H, H1), 6.20 (dd, 1H, H2), 7.26 (dd, 1H, H3), 6.03 (s, 2H, CH_2), 2.96 (q, 2H, CH_2), 0.96 (t, 3H, CH_3), 7.16 (m, 5H, C_6H_5),
32	40	3300 (NH)	7.23 (s, 1H, H5), 7.40 (s, 1H, H8), 4.80 (s, 1H, H9), 6.00 (dd, 1H, H1), 6.13 (dd, 1H, H2), 7.40 (dd, 1H, H3), 6.00 (s, 2H, CH_2), 1.96 (m, 2H, CH), 1.50, 1.00 (m, 8H, CH_2), 0.83 (s, 3H, CH_3)

other hand, reduction of the iminium perchlorates **21a** and **22a** with a large excess of sodium borohydride gave the 6,7-methylenedioxy-9-amino-9*H*-pyrroloindoles **30** and **31**. Further studies concerning these reactions and evaluation of antianoxic activities of all related compounds are in progress.

EXPERIMENTAL

Melting points were determined with a Kofler Heizbank apparatus and are uncorrected: IR spectra were recorded as potassium bromide Pellets on a Perkin-Elmer 257 G spectrometer and ^{1}H-nmr spectra were obtained on a Varian EM 90 spectrometer using DMSO-d_6 as a solvent. Chemical shifts are expressed in δ (ppm) downfield from tetramethylsilane as an internal reference.

General Procedure for the Preparation of *N*-Substituted and *N,N*-Disubstituted 2-(1-pyrrolyl)piperonylcarboxamides.

2-(1-Pyrrolyl)piperonyl chloride **2** (x g, x'mole) was added to a solution of 3 ml of triethylamine and an excess of primary or secondary amine in 150 ml of benzene. The mixture was stirred at room temperature for 1 hour and was acidified by adding hydrochloric acid. The organic layer was washed with water, dried over sodium sulfate and evaporated under reduced pressure. The residue could be either an oily liquid or an amorphous solid. The first one was distillated *in vacuo* and the second one was recrystallized in an appropriate solvent.

N-Methyl-2-(1-pyrrolyl)piperonylcarboxamide (**3**).

Compound **2** (3 g, 0.013 mole) was treated with 40% aqueous methylamine solution (2.52 g) to give **3**, (1.40 g, 44%) (ethyl ether).

Anal. Calcd. for $C_{13}H_{12}N_2O_3H_2O$: C, 59.53; H, 5.40; N, 10.68. Found: C, 59.22; H, 5.50; N, 10.30.

N-Ethyl-2-(1-pyrrolyl)piperonylcarboxamide (**4**).

Compound **2** (3 g, 0.013 mole) was treated with 33% aqueous ethylamine solution (4.42 g) to give **4** (1.42 g, 42%) (ethyl ether).

Anal. Calcd. for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85. Found: C, 64.95; H, 5.34; N, 10.69.

N-*n*-Butyl-2-(1-pyrrolyl)piperonylcarboxamide (**5**).

Compound **2** (3 g, 0.013 mole) was treated with *n*-butylamine (2.4 g) to give **5** (1.60 g, 43%) (ethyl ether).

Anal. Calcd. for $C_{16}H_{18}N_2O_3$: C, 67.14; H, 6.28; N, 9.78. Found: C, 67.10; H, 6.21; N, 9.68.

N,N-Dimethyl-2-(1-pyrrolyl)piperonylcarboxamide (**6**).

Compound **2** (3 g, 0.013 mole) was treated with 40% aqueous dimethylamine solution (3.65 g) to give **6**, yellow oil, bp 0.5 mm 160° (0.8 g, 24%).

Anal. Calcd. for $C_{14}H_{14}N_2O_3$: C, 65.11; H, 5.46; N, 10.85. Found: C, 65.21; H, 5.46; N, 10.94.

N,N-Diethyl-2-(1-pyrrolyl)piperonylcarboxamide (**7**).

Compound **2** (3.3 g, 0.014 mole) was treated with diethylamine (2.37 g) to give **7** (2.30 g, 53%) (ethyl ether).

Anal. Calcd. for $C_{16}H_{18}N_2O_3\cdot H_2O$: C, 63.14; H, 6.62; N, 9.21. Found: C, 63.29; H, 6.66; N, 9.45.

N,N-Diisopropyl-2-(1-pyrrolyl)piperonylcarboxamide (**8**).

Compound **2** (3 g, 0.013 mole) was treated with diisopropylamine (3.28 g, 0.032 mole) to give **8**, (1 g, 26%) (ethyl ether).

Anal. Calcd. for $C_{18}H_{22}N_2O_3$: C, 68.77; H, 7.05; N, 8.91. Found: C, 68.52; H, 6.98; N, 9.00.

General Procedure for the Preparation of 9*H*-Pyrrolo[1,2-*a*]indol-9-iminium Perchlorates.

A solution of x g of benzamide in phosphorus oxychloride was stirred and refluxed for n minutes and concentrated *in vacuo*. The residue was washed with petroleum ether and dissolved in 200 ml of water. The precipitate was removed by filtration and the mixture was adjusted first to *p*H 8 by adding sodium bicarbonate, then to *p*H 1 by adding perchloric acid. The precipitated iminium perchlorate was isolated by filtration, washed with 50 ml of water, dried and recrystallized in an appropriate solvent.

6,7-Methylenedioxy-9-(*N*-Methyliminio)-9*H*-pyrrolo[1,2-*a*]indole Perchlorate (**13a**).

Compound **3** (0.83 g, 0.003 mole) was refluxed in phosphorus oxychloride (20 ml) for 10 minutes to give **13a** (0.68 g, 61%) (acetonitrile).

Anal. Calcd. for $C_{13}H_{11}ClN_2O_6$: C, 47.80; H, 3.39; N, 8.57; Cl, 10.85. Found: C, 47.60; H, 3.40; N, 8.32; Cl, 10.50.

6,7-Methylenedioxy-9-(*N*-ethyliminio)-9*H*-pyrrolo[1,2-*a*]indole perchlorate (**14a**).

Compound **4** (0.5 g, 0.002 mole) was refluxed in phosphorus oxychloride (15 ml) for 10 minutes to give **14a**, (0.38 g, 56%) (acetone).

Anal. Calcd. for $C_{14}H_{13}ClN_2O_6$: C, 49.35; H, 3.85; N, 8.22; Cl, 10.41. Found: C, 49.05; H, 3.66; N, 7.98; Cl, 9.99.

6,7-Methylenedioxy-9-(*N*-*n*-butyliminio)-9*H*-pyrrolo[1,2-*a*]indole perchlorate (**15a**).

Compound **5** (1.30 g, 0.005 mole) was refluxed in phosphorus oxychloride (30 ml) for 10 minutes to give **15a** (0.95 g, 60%) (acetone).

Anal. Calcd. for $C_{16}H_{17}ClN_2O_6$: C, 52.11; H, 4.65; N, 7.60; Cl, 9.61. Found: C, 52.01; H, 4.47; N, 7.52; Cl, 9.39.

6,7-Methylenedioxy-9-(*N,N*-Dimethyliminio)-9*H*-pyrrolo[1,2-*a*]indole perchlorate (**16a**).

Compound **6** (0.4 g, 0.002 mole) was refluxed in phosphorus oxychloride (15 ml) for 20 minutes to give **16a** (0.21 g, 40%), (acetonitrile).

Anal. Calcd. for $C_{14}H_{13}ClN_2O_6$: C, 49.35; H, 3.85; N, 8.22; Cl, 10.41. Found: C, 49.25; H, 3.80; N, 8.32; Cl, 10.23.

6,7-Methylenedioxy-9-(*N,N*-diethyliminio)-9*H*-pyrrolo[1,2-*a*]indole perchlorate (**17a**).

Compound **7** (1 g, 0.003 mole) was refluxed in phosphorus oxychloride (30 ml) for 10 minutes to give **17a** (0.82 g, 64%) (acetonitrile).

Anal. Calcd. for $C_{16}H_{17}ClN_2O_6$: C, 52.10; H, 4.65; N, 7.60; Cl, 10.01. Found: C, 52.47; H, 4.71; N, 7.80; Cl, 9.81.

6,7-Methylenedioxy-9-(*N,N*-diisopropyliminio)-9*H*-pyrrolo[1,2-*a*]-indole perchlorate (**18a**).

Compound **8** (1 g, 0.004 mole) was refluxed in phosphorus oxychloride (30 ml) for 10 minutes to give **18a** (0.3 g, 20%)

(acetonitrile).

Anal. Calcd. for $C_{18}H_{21}ClN_2O_6$: C, 54.48; H, 5.33; N, 7.06; Cl, 8.93. Found: C, 54.28; H, 5.26; N, 7.06; Cl, 8.72.

6,7-Methylenedioxy-9-(*N*,*N*-tetramethyleneiminio)-9*H*-pyrrolo-[1,2-*a*]indole perchlorate (**19a**).

Compound **9** (2 g, 0.007 mole) was refluxed in phosphorus oxychloride (40 ml) for 10 minutes to give **19a**, (1.72 g, 67%) (acetonitrile).

Anal. Calcd. for $C_{16}H_{15}ClN_2O_6$: C, 52.40; H, 4.12; N, 7.64; Cl, 9.67. Found: C, 52.41; H, 4.11; N, 7.55; Cl, 9.58.

6,7-Methylenedioxy-9-(*N*,*N*-ethyleneoxaethyleneiminio)-9*H*-pyrrolo[1,2-*a*]indole perchlorate (**20a**).

Compound **10** (1.41 g, 0.0047 mole) was refluxed in phosphorate oxychloride (40 ml) for 10 minutes to give **20a** (1.41 g, 63%) (acetonitrile).

Anal. Calcd. for $C_{16}H_{15}ClN_2O_7$: C, 50.21; H, 3.95; N, 7.32; Cl, 9.26. Found: C, 50.12; H, 3.89; N, 7.40; Cl, 9.13.

6,7-Methylenedioxy-9-(*N*-methyl-*N*-phenyliminio)-9*H*-pyrrolo-[1,2-*a*]indole perchlorate (**21a**).

Compound **11** (1.60 g, 0.005 mole) was refluxed in phosphorus oxychloride (40 ml) for 15 minutes to give **21a**, (0.6 g, 37%) (acetonitrile).

Anal. Calcd. for $C_{19}H_{15}ClN_2O_6$: C, 56.66; H, 3.75; N, 6.95; Cl, 8.80. Found: C, 56.40; H, 3.73; N, 7.05; Cl, 8.60.

6,7-Methylenedioxy-9-(*N*-ethyl-*N*-phenyliminio)-9*H*-pyrrolo[1,2-*a*]-indole perchlorate (**22a**).

Compound **12** (1.2 g, 0.004 mole) was refluxed in phosphorus oxychloride (30 ml) for 15 minutes to give **22a** (0.5 g, 33%) (acetonitrile).

Anal. Calcd. for $C_{20}H_{17}ClN_2O_6$: C, 57.63; H, 4.11; N, 6.72; Cl, 8.51. Found: C, 57.52; H, 4.05; N, 6.88; Cl, 8.48.

6,7-Methylenedioxy-9*H*-pyrrolo[1,2-*a*]indol-9-one (**23**).

Method a.

Five g (0.012 mole) of the perchlorate of 6,7-methylenedioxy-9*H*-pyrrolo[1,2-*a*]indolylidene-9-pyrrolidinium **19a** was added to an aqueous sodium hydroxide solution (100 ml). After stirring at room temperature for 1 hour, the resulting precipitate was isolated, washed with 50 ml of water, dried and recristallized in acetonitrile, mp 178° (2.57 g, 68%); ir (potassium bromide): ν cm^{-1} 1680 (C=O).

Anal. Calcd. for $C_{12}H_7NO_3$: C, 67.51; H, 3.40; N, 6.57. Found: C, 67.55; H, 3.37; N, 6.50.

Method b.

A solution of 2 g (0.0070 mole) of methylenedioxybenzamide **9** in 70 ml of phosphorus oxychloride was stirred and refluxed for 10 minutes, then concentrated *in vacuo*. The residue was added to an aqueous sodium hydroxide solution (100 ml). The resulting precipitate was isolated, washed with 50 ml of water, dried and recrystallized from acetonitrile, mp 178° (0.9 g, 60%).

General Procedure for the Preparation of 6,7-Methylenedioxy-9*H*-pyrrolo[1,2-*a*]indol-9-iminium Hydrobromide.

Perchlorate of pyrrolidinium **19a** was added to a solution of x g of sodium carbonate and 1.5 equivalents of primary amine in 100 ml of dimethylformamide. The mixture was refluxed for 2 hours then poured into cold water and extracted with ethyl ether. The extract was washed with water, dried over sodium sulfate and concentrated *in vacuo*. The residual imine was dissolved in 20 ml of ethanol and a 40% hydrobromic acid solution in acetic acid was added. The mixture was stirred at room temperature for 30 minutes, the precipitate was collected by filtration, then recrystallized in an appropriate solvent.

6,7-Methylenedioxy-9-(3-*N*,*N*-diethylaminopropyliminio)-9*H*-pyrrolo[1,2-*a*]indole (Hydrobromide)monohydrate (**24a**).

Compound **19a** (2.5 g, 0.006 mole) and 3-*N*,*N*-diethylaminopropylamine (1.5 equivalents) gave **24**, 1.1 g (0.003 mole) which afforded hydrobromide **24a** (0.42 g, 31%) acetonitrile).

Anal. Calcd. for $C_{19}H_{26}BrN_3O_3$: C, 53.77; H, 6.17; N, 9.90; Br, 18.84. Found: C, 53.83; H, 5.97; N, 10.00; Br, 18.78.

6,7-Methylenedioxy-9-(3-*N*-hexamethyleneiminopropyliminio)-9*H*-pyrrolo[1,2-*a*]indole Bishydrobromide (**25a**).

Compound **19a** (2.5 g, 0.006 mole) and 3-*N*-hexamethyleneiminopropylamine (1.5 equivalents) gave **25** which afforded bishydrobromide **25a** (0.90 g, 44%) (acetonitrile).

Anal. Calcd. for $C_{21}H_{27}Br_2N_3O_2$: C, 49.14; H, 5.30; N, 8.19; Br, 31.14. Found: C, 48.96; H, 5.19; N, 8.11; Br, 31.11.

6,7-Methylenedioxy-9-(2-pyridyl)-ethyl-2-iminio-9*H*-pyrrolo[1,2-*a*]-indole Bishydrobromide (**26a**).

Compound **19a** (2.5 g, 0.006 mole) and 2-(2-aminoethyl)pyridine (1.5 equivalents) gave **26**, 1.1 g which afforded **26a** (0.5 g, 30%) (acetonitrile).

Anal. Calcd. for $C_{19}H_{17}Br_2N_3O_2$: C, 47.63; H, 3.58; N, 8.77; Br, 33.35. Found: C, 47.46; H, 3.45; N, 8.63; Br, 33.32.

6,7-Methylenedioxy-9-cyclooctyliminio-9*H*-pyrrolo[1,2-*a*]indole Hydrobromide (**27a**).

Compound **19a** (2.5 g, 0.006 mole) and cyclooctylamine (1.5 equivalents) gave **27**, 1.2 g which afforded **27a** (0.8 g, 53%) (acetonitrile).

Anal. Calcd. for $C_{20}H_{23}BrN_2O_2$: C, 59.56; H, 5.75; N, 6.95; Br, 19.81. Found: C, 59.26; H, 5.67; N, 6.95; Br, 20.00.

6,7-Methylenedioxy-9-(*N*-4-Methylcyclohexyliminio)-9*H*-pyrrolo-[1,2-*a*]indole Hydrobromide (**28a**).

Compound **19a** (2.5 g, 0.006 mole) and 4-methylcyclohexylamine (1.5 equivalents) gave **28**, 1 g which afforded **28a** (0.62 g, 49%) (acetonitrile).

Anal. Calcd. for $C_{19}H_{21}BrN_2O_2$: C, 58.62; H, 5.44; N, 7.20; Br, 20.62. Found: C, 58.56; H, 5.37; N, 7.16; Br, 20.62.

General Procedure for the Preparation of 6,7-Methylenedioxy-9-amino-9*H*-pyrrolo[1,2-*a*]indole.

6,7-Methylenedioxy-9*H*-pyrrolo[1,2-*a*]indoliminium perchlorate (x g) was added to a 100 ml solution of methanol containing x' equivalents of sodium borohydride. The mixture was stirred and refluxed for 1 hour and the methanol was evaporated *in vacuo*. The resulting residue was poured into cold water and extracted with ethyl ether. The extract was washed with water, dried over sodium sulfate and concentrated *in vacuo*. The precipitate was recrystallized from an appropriate solvent.

6,7-Methylenedioxy-9-(3-hexamethyleneiminiopropyl)-9*H*-pyrrolo-[1,2-*a*]indole (**29**).

Compound **25a** (0.7 g, 0.001 mole) and sodium borohydride (2

equivalents) gave **29** (0.34 g, 71%) (ethyl ether).

Anal. Calcd. for $C_{21}H_{27}N_3O_2$: C, 71.36; H, 7.70; N, 11.89. Found: C, 70.99; H, 7.70; N, 11.53.

6,7-Methylenedioxy-9*N*-methyl-*N*-phenylamino-9*H*-pyrrolo[1,2-*a*]-indole (**30**).

Compound **21a** (0.5 g, 0.001 mole) and sodium borohydride (10 equivalents) gave **30**, (0.22 g, 58%) (ethyl ether).

Anal. Calcd. for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 74.84; H, 5.26; N, 9.21.

6,7-Dioxymethylene-*N*-ethyl-*N'*-phenyl-9-amino-9*H*-pyrrolo[1,2-*a*]-indole (**31**).

Compound **22a** (0.5 g, 0.001 mole) and sodium borohydride (10 equivalents) gave **31**, (0.23 g, 60%) (ethyl ether).

Anal. Calcd. for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.40; H, 5.70; N, 8.78.

6,7-Methylenedioxy-9-*N*-(4-methylcyclohexylamino-9*H*-pyrrolo-[1,2-*a*]indole (**32**).

Compound **28a** (0.5 g, 0.001 mole) and sodium borohydride (10 equivalents) gave **32**, (0.32 g, 80%) (ethyl ether).

Anal. Calcd. for $C_{19}H_{22}N_2O_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.46; H, 6.96; N, 8.99.

REFERENCES AND NOTES

[1] J. P. Rioult, M. Cugnon de Sevricourt, S. Rault and M. Robba, *J. Heterocyclic Chem.*, **21**, 1449 (1984).

[2a] S. Rault, J. C. Lancelot, Y. Effi and M. Robba, *Heterocycles*, **20**, 477 (1983); [b] C. Wojcik-Laporte, A. M. Godard, S. Rault and M. Robba, *Heterocycles*, **23**, 1471 (1985).

[3a] D. Laduree, J. C. Lancelot and M. Robba, *Tetrahedron Letters*, **26**, 1295 (1985); [b] S. Rault, M. Cugnon de Sevricourt, A. M. Godard and M. Robba, *Tetrahedron Letters*, **26**, 2305 (1985).

[4] T. Kametani and K. Takahashi, *Heterocycles*, **9**, 293 (1979).