SYNTHESIS OF THE PARENT SYSTEMS OF DIPYRROLO[1,2-a:2',1'-c]PYRAZINE AND OF DIPYRROLO[1,2-a:2',1'-c]QUINOXALINE

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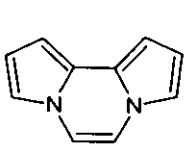
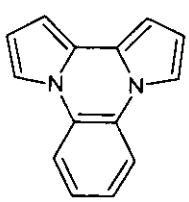
Abstract - A synthesis of the title compounds is described starting from 2,3-dimethylpyrazine and 2,3-dimethylquinoxaline, respectively. The two pyrrole rings are formed in two subsequent steps by condensation of the methyl groups of the starting azines with the carbonyl groups of the ethyl pyruvate moiety linked to the ring nitrogen atoms. Deuterium exchange reactions of dipyrrolo[1,2-a:2',1'-c]pyrazine are also reported.

Polypyrrole is amongst the most popular and attractive conductive polymers studied at present.[1] One of the disadvantages of polypyrrole is its negative oxidation potential; this causes instability of the neutral polymer to air. To modify physical and chemical properties of conductive polymers, we proposed[2] the "spacer" approach. It consists in introducing a conjugative moiety between two polymerogenic units. Within this strategy we explored the ring fusion of the two terminal pyrrolic units onto a central electron-poor heterocycle. Ring fusion of the pyrrole rings onto a central pyrazine ring seemed favourable. To do this we needed a convenient synthesis providing in gram lots the unsubstituted parent dipyrrolo[1,2-a:2',1'-c]pyrazine (**1**) and its benzo-homologue dipyrrolo[1,2-a:2',1'-c]quinoxaline (**2**). Burger and Dreier already prepared the parent heterocycle (**1**)[3] by dehydrogenative bridging of 1,2-N,N'-dipyrrolylethane: in our hands this route showed to be unsuitable for relatively large scale preparation. The dipyrroloquinoxaline system is known only in extensively substituted derivatives.[4]



(**1**)



(**2**)

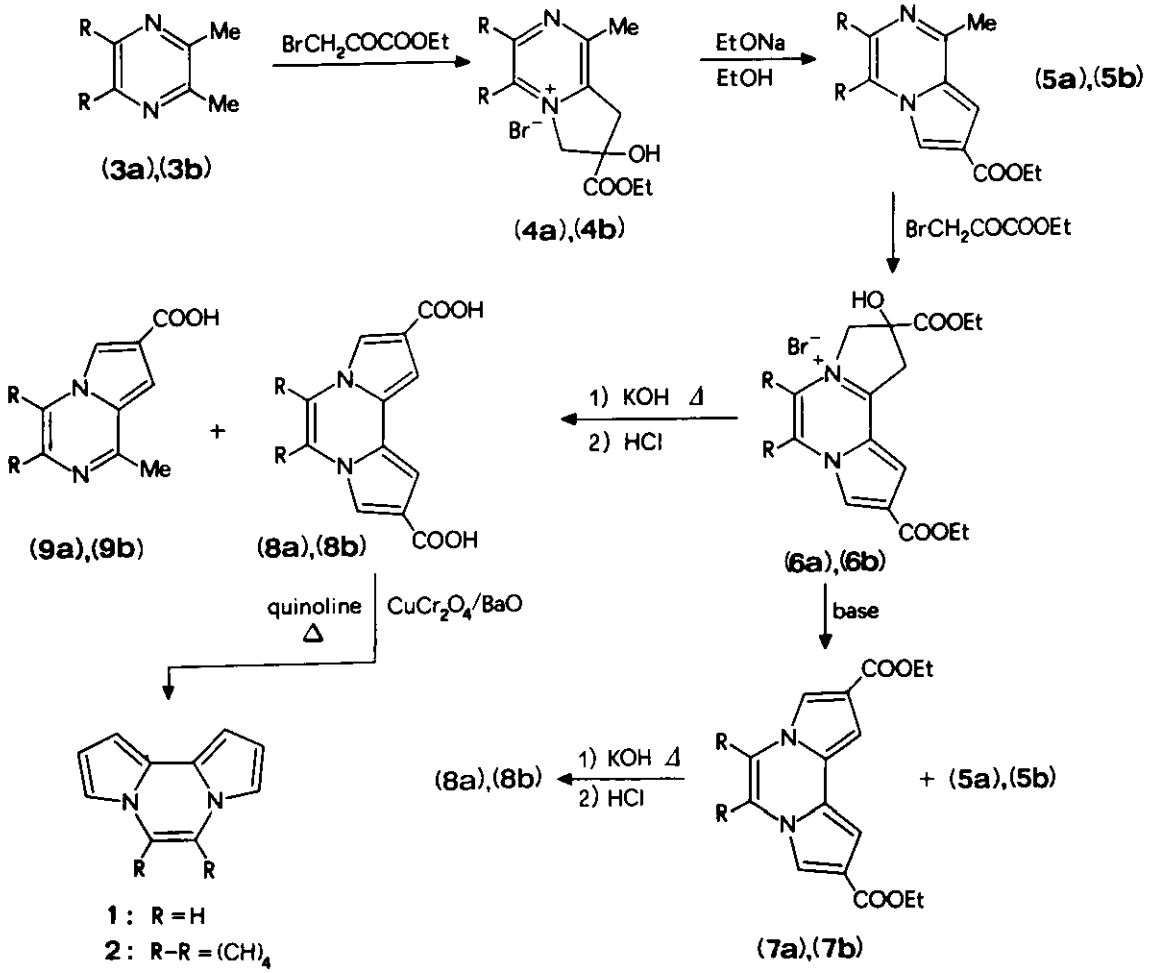
To prepare the parent compounds (**1**) and (**2**) in substantial amounts, we extended to the pyrazine and quinoxaline systems the approach of forming the five-membered ring as in the synthesis of indolizine.[5] While this work was in progress, Fraser et al.[6] described the preparation of some alkyl substituted derivatives of **1** following a similar strategy. In their paper these authors did not report the synthesis of the parent **1** and of the benzo-analogue (**2**). These compounds, besides being key monomers in our approach to conducting polymers and of potential biological interest within the indolizine alkaloids, possess inherent relevance as parent heterocyclic systems. Indeed, because of the so far difficult availability of these parent systems, relatively few data are known concerning their reactivity. Our results concern gram scale preparations of **1** and **2**; in the light of the above considerations, this offer may be relevant and convenient to the development of the chemistry of such a class of compounds.

RESULTS AND DISCUSSION

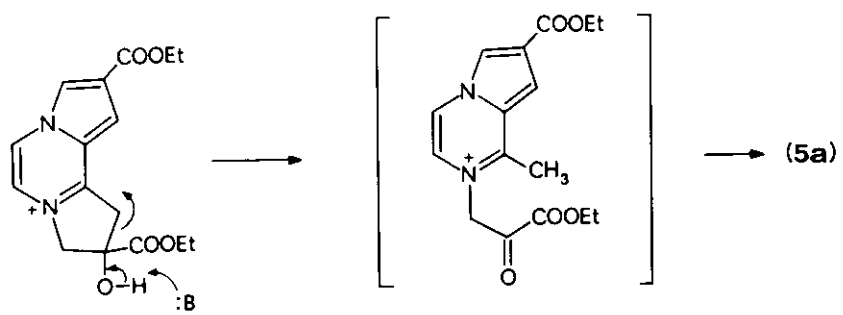
Synthesis of Dipyrrolo[1,2-a:2',1'-c]pyrazine (**1**).- Scheme 1 describes the whole synthetic approach. Reaction of ethyl bromopyruvate on 2,3-dimethylpyrazine (**3a**) in dry acetone led to the precipitation of the salt (**4a**) as a white powder. The ^{1}H nmr spectrum of **4a** in DMSO-d_6 provided evidence for the cyclic structure of the compound. In fact, it showed only one singlet methyl group, two AB systems attributable to the methylene groups of the pyrroline ring, and an exchangeable singlet due to the hydroxyl proton. Treatment of the salt (**4a**) with sodium ethoxide in ethanol gave the azaindolizine (**5a**). Further action of ethyl bromopyruvate to the compound (**5a**) in dry acetone afforded the salt (**6a**) as a precipitate insoluble in the reaction medium. The microanalytical data for this product agree with the assigned structure. However, the ^{1}H nmr spectrum in DMSO-d_6 of the product revealed to be a mixture of compound (**6a**) and of the dehydrated compound (**7a**). The solvent DMSO-d_6 used in the ^{1}H nmr recording promotes the dehydration: in fact, the amount of compound (**7a**) increased with time. The action of bases (sodium ethoxide, triethylamine, or pyridine) on the salt (**6a**) afforded the dehydrated compound (**7a**) in addition to variable amounts of the azaindolizine (**5a**). An important side reaction promoted by bases and depicted in Scheme 2 accounts for the formation of the compound (**5a**). The use of pyridine as a base reduced the occurrence of this side reaction. A two step process explains the opening of the pyrroline ring. The first is a retroaldolic reaction, while the second is likely a nucleophilic attack of the base on the azinium ion. *N*-Phenacyl- or acetonylpyrazinium derivatives undergo a similar dealkylation reaction upon treatment with bases.[7] Also in this case a nucleophilic attack of the base on the alkyl group accounts for the result but, in contrast with our case, the retroaldolic ring opening is missing.

Column chromatography allowed the isolation of the diester (**7a**); alkaline hydrolysis of the diester (**7a**) provided the diacid (**8a**) in high yields. Action of boiling alkali on the salt (**6a**) avoids the chromatographic separation of the diester (**7a**) and leads directly to the diacid (**8a**). Although this treatment did not suppress the retroaldolic reaction, the separation of the two products of the reaction, the azaindolizine carboxylic acid (**9a**) and the dipyrrolopyrazine dicarboxylic acid (**8a**) was easy thanks to the higher solubility of **9a** in water. The yields of **8a** by the direct saponification of **6a**

Scheme 1



Scheme 2



and starting from the chromatographically isolated **7a** were at all comparable. The diacid (**8a**) was decarboxylated in refluxing quinoline and in the presence of barium activated copper chromite, a catalyst commonly used[8] in decarboxylations of other pyrrole carboxylic acids.

Synthesis of Dipyrrolo[1,2-a:2',1'-c]quinoxaline (**2**).- Extension to the 2,3-dimethylquinoxaline (**3b**) of the synthetic Scheme 1 used for the preparation of the dipyrrolopyrazine (**1**) led to the obtaining of the dipyrroloquinoxaline (**2**). There are both analogies and differences in chemical behavior of the synthetic intermediates belonging to the pyrazine and quinoxaline series. Because of the lower reactivity of the quinoxaline derivatives (**3b**) and (**5b**) in comparison with the analogous pyrazine systems, we preferred to run the reaction of ethyl bromopyruvate on the pertaining bases in steps 1 and 3 in ethyl methyl ketone instead of acetone. The quinoxalinium salt (**4b**) underwent in DMSO a spontaneous dehydration to the protonated form of the ester (**5b**), at variance with the similar salt (**4a**) which instead was stable under these conditions. In the quinoxaline series the salt (**6b**) evolved in DMSO to a mixture of the diester (**7b**) and of the ring opened, protonated, and dealkylated monoester (**5b**). The monoester (**5b**) behaved as a base towards the hydrogen bromide evolved during the transformation undergone by the salt (**4b**) in DMSO; evidence for this is provided by the low-field displacement of a number of peaks of the pure monoester (**5b**) in the same solvent (see Experimental). The fact that the above low-field shifts are due to protonation effects was verified by recording the ^{1}H nmr spectrum of the monoester (**5b**) in the presence of some hydrochloric acid. Cautious treatment with aqueous alkali of the salt (**6b**) allowed the obtainment of the pure diester (**7b**). In fact, methylene chloride extracts only the diester from the mixture and leaves the alkaline salts of the carboxylic acids in the aqueous phase. The preceding data strongly suggest that the dehydration and aromatization in the quinoxaline series are easier than in the pyrazine system.

Deuterium Exchange Reactions of (**1**).- Previous investigations[6] reported on the protonation of methyl derivatives of **1** and on their deuteriation with deuteriotrifluoroacetic acid. Protonation occurred at positions 3 and 8, as evidenced by major deuteriation, with some involvement of positions 1 and 10. We approached the exchange both under acidic and basic conditions. We found that also in deuterioacetic acid as a solvent the parent (**1**) underwent deuteriation; the reaction is complete at the four pyrrolic positions 1, 3, 8, and 10. Instead, compound (**1**) can undergo an alternative deuteriation at one of the two pyrazine positions 5 or 6. Reaction of **1** with butyllithium followed by quenching with D_2O afforded the 5-deuteriodipyrrolopyrazine in high yield. ^{1}H Nmr proved the position of the deuteriation, and thus of the corresponding lithiation.

EXPERIMENTAL

Melting points are uncorrected. Dry acetone and methyl ethyl ketone were obtained leaving the pure solvent on anhydrous sodium sulphate for one day. Extracts were dried over Na_2SO_4.

6,8-Dihydro-7-ethoxycarbonyl-7-hydroxy-1-methylpyrrolo[1,2-a]pyrazinium bromide (**4a**).- A solution of 2,3-dimethylpyrazine (**3a**) (20 g, 184.9 mmol) and ethyl 3-bromopyruvate (36.06 g, 184.9 mmol) in dry acetone (230 ml) was stirred at 60 °C for 2 h and at room temperature overnight. The solid precipitate was filtered off, washed with acetone and dried to give the *compound* (**4a**) (33 g, 59%), mp 160 °C (from EtOH). ^{1}H-Nmr [300 MHz, $(CD_3)_2SO$]: ∂ 1.26 (3H, t, J = 7.1 Hz, $CH_2\underline{Me}$); 2.73 (3H, s, Me); 3.73-4.07 (2H, AB system, $\underline{J}_{AB}$=19 Hz, H-8); 4.23 (2H, q, J = 7.1 Hz, $C\underline{H}_2Me$); 5.05-5.30 (2H, AB system, $\underline{J}_{AB}$=14.8 Hz, H-6); 6.90 (1H, s, OH) and 9.09-9.25 (2H, AB system, $\underline{J}_{AB}$=3.5 Hz, H-3 and H-4). Anal. Calcd for $C_{11}H_{15}N_2O_3Br$: C, 43.6; H, 5.0; N, 9.2. Found: C, 43.7; H, 5.0; N, 9.2.

7-Ethoxycarbonyl-1-methylpyrrolo[1,2-a]pyrazine (**5a**).- A solution of sodium ethoxide [prepared from 228 mg (9.9 mmol) of sodium and 15 ml of ethanol] was dropwise added at room temperature to a stirred suspension of **4a** (3 g, 9.9 mmol) in ethanol (30 ml); stirring was maintained for 10 min. Most of the solvent was evaporated under reduced pressure and, after addition of water, the residue was extracted several times with ether. The organic phase was dried and evaporated to give the *compound* (**5a**) (1.61 g, 79.7%), mp 117 °C (from EtOH). ^{1}H-Nmr (300 MHz, $CDCl_3$): ∂ 1.39 (3H, t, J = 6.9 Hz, $CH_2\underline{Me}$); 2.68 (3H, s, Me); 4.38 (2H, q, J = 6.9 Hz, $C\underline{H}_2Me$); 7.19 (1H, s, H-8); 7.47-7.67 (2H, AB system, J_{AB} = 6.5 Hz, H-3 and H-4) and 7.87 (1H, s, H-6). Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.7; H, 6.0; N, 13.7. Found: C, 64.65; H, 6.0; N, 13.6.

1,3-Dihydro-2,9-di(ethoxycarbonyl)-2-hydroxydipyrrolo[1,2-a:2',1'-c]pyrazinium bromide (**6a**).- A solution of **5a** (12.51 g, 61.25 mmol) and ethyl 3-bromopyruvate (11.95 g, 61.25 mmol) in dry acetone (200 ml) was refluxed for 2 h. After cooling, the solid precipitate was filtered off, washed with acetone and dried to give the *compound* (**6a**) (13.62 g, 55.7%), mp 162 °C (from EtOH). ^{1}H-Nmr [300 MHz, $(CD_3)_2SO$)]: ∂ 1.30 (6H, m, $CH_2\underline{Me}$); 3.94-4.16 (2H, AB system, J_{AB} = 19 Hz, H-1); 4.24 (2H, q, J = 6.9 Hz, $C\underline{H}_2Me$ on C-9); 4.35 (2H, q, J = 6.9 Hz, $C\underline{H}_2Me$); 4.69-5.00 (2H, AB system, J_{AB} = 13.2 Hz, H-3); 6.95 (1H, br s, OH); 7.95-8.75 (2H, AB system, J_{AB} = 5.6 Hz, H-5 and H-6); 8.19 (1H, d, J = 0.9 Hz, H-8) and 8.82 (1H, d, J = 0.9 Hz, H-10). Anal. Calcd for $C_{16}H_{19}N_2O_5Br$: C, 48.1; H, 4.8; N, 7.0. Found: C, 48.2; H, 4.9; N, 7.0.

2,9-Di(ethoxycarbonyl)dipyrrolo[1,2-a:2',1'-c]pyrazine (**7a**).- *Method A.* A solution of sodium ethoxide in ethanol [prepared from 0.92 g (40.08 mmol) of sodium and 30.7 ml of ethanol] was dropwise added to a stirred suspension of the salt (**6a**) (16 g, 40.08 mmol) in ethanol (150 ml); stirring was maintained for 30 min. Most of the solvent was evaporated under reduced pressure and, after addition of water, the residue was extracted several times with methylene chloride. The dried extracts were evaporated and the residue (8.57 g) was chromatographed on silica gel with CH_2Cl_2-AcOEt (7:3, v/v) to give the *compound* (**7a**) as the first eluate (4.46 g, 37.04%), mp 137 °C (from EtOH). ^{1}H-Nmr (300 MHz, $CDCl_3$): ∂ 1.36 (6H, t, J = 7.1 Hz, $CH_2\underline{Me}$); 4.32 (4H, q, J = 7.1 Hz, $C\underline{H}_2Me$); 6.92 (2H, d, J = 1.5 Hz, H-1 and H-10); 7.06 (2H, s, H-5 and H-6) and 7.54 (2H, d, J = 1.5 Hz, H-3 and H-8). Anal. Calcd for $C_{16}H_{16}N_2O_4$: C, 64.0; H, 5.4; N, 9.3. Found: C, 63.9; H, 5.3; N, 9.25. *Compound* (**5a**) was obtained as the second eluate (1.56 g, 19%).

Method (B). A solution of the salt (**6a**) (0.239 g, 0.63 mmol) in pyridine (3 ml) was heated at 70 °C for 4 h. The reaction mixture was then poured into water, the precipitate was collected by suction and treated with aqueous hydrochloric acid (20% w/v) and methylene chloride. The organic phase was washed with water, dried, and evaporated to give the *compound* (**7a**) (0.14 g, 73%).

Dipyrrolo[1,2-a:*2',1'*-c*]pyrazine-2,9-dicarboxylic acid* (**8a**).- *Method (A)*. A solution of the salt (**6a**) (14.94 g, 37.43 mmol) and potassium hydroxide (10.5 g) in water (300 ml) was refluxed for 2 h. The resulting solution was added dropwise to aqueous hydrochloric acid (11% w/v, 63 ml) maintained at 60 °C. After cooling, the solid was collected, washed with water, and dried over $CaCl_2$, at 150 °C, under vacuum for 1 h, to give the analitically pure *compound* (**8a**) (5.97 g, 65.3%). The product decomposed without melting when heated at 300 °C. ^{1}H-Nmr [80 MHz, $(CD_3)_2SO$]: ∂ 6.90 (2H, d, J = 1.5 Hz, H-1 and H-10); 7.60 (2H, s, H-5 and H-6); 7.75 (2H, d, J = 1.5 Hz, H-3 and H-7) and 12.20 (2H, br s, OH). Anal. Calcd for $C_{12}H_8N_2O_4$: C, 59.0; H, 3.3; N, 11.5. Found: C, 59.15; H, 3.3; N, 11.4. The aqueous solution was evaporated and the residue was treated with a small quantity of methanol. Filtration of the inorganic salts and removal of the solvent afforded, as a by-product of the reaction the monoacid (**9a**), identified by its nmr spectrum. ^{1}H-Nmr [80 MHz, $(CD_3)_2SO$]: ∂ 2.9 (3H, s, Me); 7.65-8.55 (2H, AB system, J_{AB} = 5.5 Hz, H-3 and H-4); 7.95 (1H, br s, H-8) and 8.60 (1H, s, H-6).
Method (B). A solution of the diester (**7a**) (4.46 g, 14.8 mmol) and potassium hydroxide (16.8 g) in ethanol-water (7:5, v/v, 250 ml) was refluxed for 45 min. After evaporation of the ethanol, the aqueous solution was made acidic with dilute hydrochloric acid, the solid precipitate was collected, washed with water, and air dried to give the *compound* (**8a**) (3.52 g, 97%).

Dipyrrolo[1,2-a:*2',1'*-c*]pyrazine* (**1**).-The diacid (**8a**) (5.72 g, 23.42 mmol) was portionwise added to a stirred suspension of barium promoted copper chromite (9.7% BaO, Janssen Chimica, 2.13 g) in quinoline (78 ml) heated at 200 °C; the reaction mixture was then refluxed for 35 min. After cooling, methylene chloride (200 ml) was added and the catalyst was filtered off. The organic phase was washed with dilute hydrochloric acid (10%, 3x100 ml), then with water, dried, and evaporated. Flash chromatography of the residue on silica gel with methylene chloride-pentane (2:1, v/v) afforded the *compound* (**1**) (2.58 g, 70.7%), mp 78-80 °C (after sublimation at 70 °C at 0.01 mmHg) (lit.,[3] 79-80 °C). ^{1}H-Nmr (300 MHz, $CDCl_3$): ∂ 6.48 (4H, m, H-1, H-2, H-9, and H-10); 6.95 (2H, m, H-3 and H-8) and 7.03 (2H, s, H-5 and H-6). Anal. Calcd for $C_{10}H_8N_2$: C, 76.9; H, 5.2; N, 17.9. Found: C, 77.0; H, 5.2; N, 17.9.

1,3-Dihydro-2-ethoxycarbonyl-2-hydroxy-4-methylpyrrolo[1,2-a]quinoxalinium bromide (**4b**) .- A solution of 2,3-dimethylquinoxaline (**3b**) (10 g, 63.21 mmol) and ethyl 3-bromopyruvate (12.33 g, 63.21 mmol) in dry ethyl methyl ketone (80 ml) was refluxed for 3 h and stirring was maintained overnight. The precipitate was collected, washed with ethyl methyl ketone and dried to give the *compound* (**4b**) (16.15 g, 72%), mp > 230 °C (from EtOH). ^{1}H-Nmr [80 MHz, $(CD_3)_2SO$]: ∂ 1.34 (3H, t, J = 6.9 Hz, CH_2*Me*); 2.98 (3H, s, Me); 4.37 (2H, q, J = 6.9 Hz, CH_2Me); 7.71 (2H, m, H-7 and H-8); 7.91 (1H, m, H-6); 8.07 (1H, d, J = 1.2 Hz, H-3); 8.63 (1H, m, H-9) and 9.34 (1H, d, J = 1.2 Hz, H-1). Anal.

Calcd for $C_{15}H_{17}N_2O_3Br$: C, 51.0; H, 4.9; N, 7.9. Found: C, 51.1; H, 4.85; N, 8.0. As discussed in **Results** this spectrum corresponds to the protonated form of the monoester (**5b**).

2-Ethoxycarbonyl-4-methylpyrrolo[1,2-a]quinoxaline (**5b**).- A solution of sodium ethoxide in ethanol [prepared from 0.74 g (32.05 mmol) of sodium and 50 ml of ethanol] was added dropwise to a stirred suspension of **4b** (10.29 g, 29.13 mmol) in ethanol (130 ml); stirring was maintained for 3 h. Most of the solvent was removed at reduced pressure and, after addition of water, the residue was extracted several times with ether. The organic phase was dried and evaporated at reduced pressure to give the *compound* (**5b**) (7.59 g, 93%), mp 112-113 °C (from EtOH). ^{1}H-Nmr [80 MHz $(CD_3)_2SO$]: ∂ 1.31 (3H, t, J = 6.9 Hz, $CH_2\underline{Me}$); 2.66 (3H, s, Me); 4.31 (2H, q, J = 6.9 Hz, $C\underline{H}_2Me$); 7.36 (1H, d, J = 1.2 Hz, H-3); 7.54 (2H, m, H-7 and H-8); 7.83 (1H, m, H-6); 8.46 (1H, m, H-9) and 8.94 (1H, d, J = 1.2 Hz, H-1). Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.8; H, 5.6; N, 11.0. Found: C, 70.7; H, 5.5; N, 10.85.

2,11-Di(ethoxycarbonyl)dipyrrolo[1,2-a:2'1'-c]quinoxaline (**7b**).- A solution of **5b** (7.31 g, 28.75 mmol) and ethyl 3-bromopyruvate (11.21 g, 57.50 mmol) in dry ethyl methyl ketone (180 ml) was refluxed for 6 h. After cooling, the precipitate was collected, washed with ethyl methyl ketone, and dried to give the *salt* (**6b**) (6.47 g, 50%). The salt could not be obtained in analytically pure form and was used for the following reactions without any further purification. Its ^{1}H-nmr spectrum in $(CD_3)SO$ showed signals attributable to the protonated form of **4b** and of the diester (**7b**). A stirred suspension of the crude salt (**6b**) (0.5 g) in water (20 ml) was dropwise added of an aqueous solution of potassium hydroxide (0.31 g of KOH in 8 ml of water): the reaction mixture was then refluxed for 1 h. After cooling, methylene chloride (30 ml) was added, the organic phase was washed with water, dried, and evaporated. Flash chromatography of the residue on silica gel with chloroform-AcOEt (95:5, v/v) afforded the *compound* (**7b**) (0.22 g, 56.4%), mp 245-246 °C (from acetone). ^{1}H-Nmr [80 MHz, $(CD_3)_2SO$]: ∂ 1.31 (6H, t, J = 6.9 Hz, $CH_2\underline{Me}$); 4.31 (4H, q, J = 6.9 Hz, $C\underline{H}_2Me$); 7.11 (2H, d, J = 1.2 Hz, H-1 and H-12); 7.43 (2H, m, H-6 and H-7); 8.37 (2H, m, H-5 and H-8) and 8.63 (2H, d, J = 1.2 Hz, H-3 and H-10). Anal. Calcd for $C_{20}H_{18}N_2O_4$: C, 68.6; H, 5.1; N, 8.0. Found: C, 68.55; H, 5.2; N, 7.9.

Decarboxylation of the dipyrrolo[1,2-a:2',1'-c]quinoxaline-2,11-dicarboxylic acid (**8b**): *Dipyrrolo[1,2-a:2',1'-c]quinoxaline* (**2**).- A suspension of the salt (**6b**) (6.47 g, 14.38 mmol) and potassium hydroxide (4.84 g) in ethanol-water (1:1, v/v, 150 ml) was refluxed for 3 h. The resulting solution was filtered and added dropwise to dilute hydrochloric acid (11% w/v, 38 ml) maintained at 60 °C. After cooling, the precipitate was collected, washed with water, and dried under reduced pressure to give the dicarboxylic acid (**8b**) (3.6 g, 85%). ^{1}H-Nmr [90 MHz, $(CD_3)SO$]: ∂ 7.02 (2H, d, J = 1.2 Hz, H-1 and H-12); 7.49 (2H, m, H-6 and H-7); 8.32 (2H, m, H-5 and H-8) and 8.57 (2H, d, J = 1.2 Hz, H-3 and H-10). The diacid (**8b**) was used for the subsequent decarboxylation without further purification. The diacid (**8b**) (3.29g, 11.15 mmol) was rapidly added to a stirred suspension of barium promoted copper chromite (9.7% BaO, Janssen Chimica, 1 g) in quinoline (50 ml) heated at 200 °C and the

reaction mixture was refluxed for 1.5 h. After cooling, ether was added (300 ml) and the catalyst was filtered off. The organic phase was extracted with dilute hydrochloric acid (10%, 3x70 ml), washed with water, dried, and evaporated. Flash chromatography of the residue on silica gel with methylene chloride-pentane (4:1, v/v) afforded the *compound* (**2**) (1.83 g, 72%), mp 148-150 °C (after sublimation at 130 °C at 0.01 mmHg) . ^{1}H-Nmr (80 MHz, $CDCl_3$): ∂ 6.54 (4H, m, H-1, H-2, H-11, and H-12); 7.28 (2H, m, H-6 and H-7); 7.47 (2H, m, $J_{1,3}$ = 1.76 Hz, $J_{2,3}$ = 2.64 Hz, H-3 and H-10) and 7.71 (2H, m, H-5 and H-8). Anal. Calcd for $C_{14}H_{10}N_2$: C, 81.6; H, 4.85; N, 13.6. Found: C, 81.5; H, 4.8; N, 13.6.

Reaction of (**1**) *with deuterioacetic acid* (*$MeCO_2D$*).- A solution of **1** (0.5 g, 3.2 mmol) in deuterioacetic acid (5 ml) was stirred for 5 min, deuterium oxide was then added and the precipitate was collected to give the 1,3,8,10-tetradeuteriodipyrrolopyrazine. ^{1}H-Nmr (90 MHz, $CDCl_3$): ∂ 6.48 (2H, s, H-2 and H-9) and 7.03 (2H, s, H-5 and H-6).

Quenching of the anion of (**1**) *with deuterium oxide*.- A 1.4 **N** solution of butyllithium in hexane (0.67 ml) was added dropwise to a stirred solution of (**1**) (0.073 g, 0.47 mmol) under nitrogen atmosphere, at -5 °C; stirring was continued for 2 h at 0 °C. Deuterium oxide was added and the dried organic phase was evaporated to give the 5-deuterodipyrrolopyrazine (90%), M^+, 157. ^{1}H-Nmr (80 MHz, $CDCl_3$): ∂ 6.50 (4H, m, H-1, H-2, H-9 and H-10); 6.95 (2H, m, H-3 and H-8) and 7.05 (1H, s, H-6).

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