Electrochemically Induced *N*-Alkylation of Pyrroles

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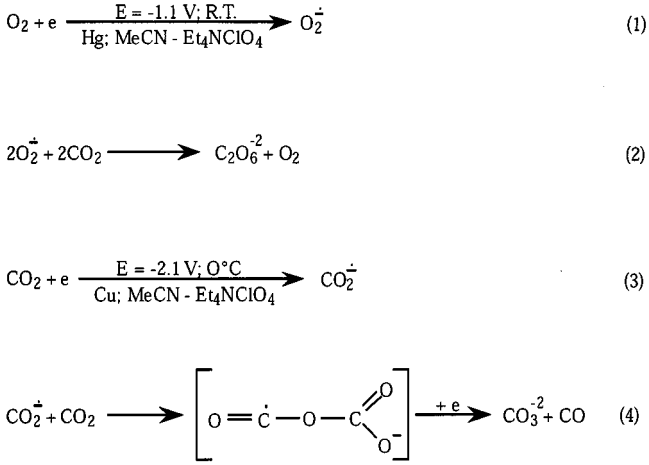
Electrochemically generated tetraethylammonium peroxydicarbonate (TEAPC) and tetraethylammonium carbonate (TEAC) react under very mild conditions with pyrroles affording, after addition of a suitable alkylating agent, the corresponding *N*-alkylated pyrroles in high yields. *C*-Alkylated pyrroles have not been isolated in any case reported.

A fair number of 1-substituted pyrroles have been identified among natural substances or their metabolites,[1] aroma compounds of foodstuffs[2] and in tobacco;[3] in addition, they have considerable importance in the pharmaceutical field as, for example, inhibitors of enzymes[4] or as anti-inflammatory,[5a] analgesic,[5a] and antirheumatic drugs.[5b]

In order to undergo *N*-substitution, the pyrrole nitrogen atom must be deprotonated. This deprotonation may occur either on a radical-cationic species formed in the presence of a suitable acceptor upon photostimulation of the pyrrole moiety[6] or by the use of deprotonating agents such as alkali metals,[7] alkali metal alkoxides,[7] or potassium hydroxide;[8] *N*-deprotonation can also be achieved under phase-transfer catalytic conditions.[9] Generally, pyrryl anions act as ambident nucleophiles and alkylation can thus take place either at the nitrogen atom or at the carbon atoms. Polar aprotic solvents, large counterions and hard electrophiles favour *N*-alkylation.[10]

Recently, we found that solutions of tetraethylammonium peroxydicarbonate [TEAPC, obtained by electrochemical reduction of dioxygen in the presence of carbon dioxide in MeCN/tetraethylammonium perchlorate (TEAP);[11a–11d] Equations 1 and 2] or tetraethylammonium carbonate (TEAC, obtained by electrochemical reduction of carbon dioxide in MeCN/TEAP;[12a,b] Equations 3 and 4) may act both as bases and as carboxylating agents. Actually, upon addition of amines, alcohols, or phenols to these solutions (followed by addition of alkyl halides), carbamates,[12][13] organic carbonates,[14][15] and ethers[14] could be isolated, respectively.

These results prompted us to study the reactivity of these solutions towards pyrroles. Since carboxylation products were not found at all, this investigation has been directed towards the study of the possibility of *N*-alkylating pyrryl anions formed by means of electrogenerated tetraethylammonium peroxydicarbonate and carbonate.



Scheme 1. Electrochemical reduction of dioxygen in the presence of carbon dioxide and electrochemical reduction of carbon dioxide

Diethyl 5-formyl-3-methylpyrrole-2,4-dicarboxylate[16] was used as a model compound to compare the reactivity of the two electrogenerated bases. The results of the reactions between the model pyrrole and TEAPC or TEAC in different ratios are reported in Figures 1 and 2. From these figures it can be seen that in the case of TEAPC one equivalent of base is sufficient to convert all the starting pyrrole into the *N*-alkylated derivative, while in the case of TEAC 2.5 equivalents are necessary.

The evaluation of the effect of different alkylating reagents and solvents on the reaction yields was performed on the system diethyl 5-formyl-3-methylpyrrole-2,4-dicarboxylate and TEAPC. The results are reported in Table 1.

It can be seen that all the alkylating reagents taken into account work well, with the only exception of 3-bromopropionitrile (Entry 7), which undergoes an elimination reaction to yield acrylonitrile.

Using benzyl or phenacyl bromide, *N*-protected pyrroles were obtained.

The reaction appears to proceed satisfactorily in all the solvents used. The only exception was THF, which reacts

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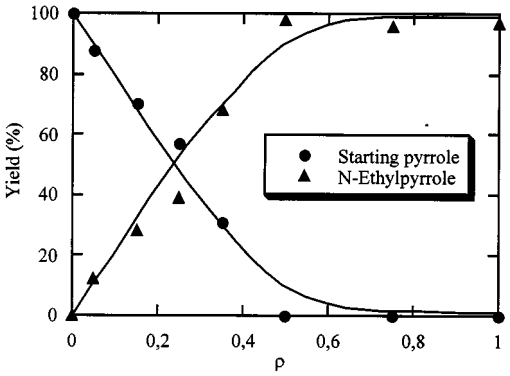


Figure 1. Reaction of diethyl 5-formyl-3-methylpyrrole-2,4-dicarboxylate with TEAPC and ethyl iodide in MeCN/TEAP; yield of *N*-ethylpyrrole vs. the molar ratio TEAPC/starting pyrrole (ρ)

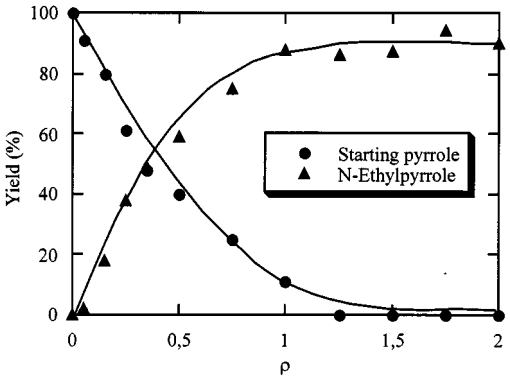


Figure 2. Reaction of diethyl 5-formyl-3-methylpyrrole-2,4-dicarboxylate with TEAC and ethyl iodide in MeCN/TEAP; yield of *N*-ethylpyrrole vs. the molar ratio TEAC/starting pyrrole (ρ)

with the electrogenerated reagent affording a number of oxidation products.

In order to ascertain the scope of this new *N*-alkylation procedure, the reaction (performed in MeCN/TEAP using EtI as alkylating reagent) was tried with the pyrrole derivatives shown in Table 2.

As can be seen, high yields of *N*-ethylpyrroles were obtained with TEAPC if the pK_a of the substrate was < 13 (the pK_a of pyrrole in Entry 5 is 13.4[17]), otherwise the starting material was recovered unchanged (except for the unsubstituted pyrrole, Entry 6, that polymerised under these reaction conditions). In no case were carboxylated pyrroles detected. It is worth noting that the pyrroles were selectively alkylated at position 1 even when *C*-alkylation was possible (Entries 8 and 9), probably due to the fact that, as stressed in the introduction, the experimental conditions strongly disfavour the latter. This regioselectivity is not, however, the major advantage of our procedure over those usually used. Indeed, apart from the excellent yields (side reactions are practically absent), the method is environmentally friendly and allows an extremely easy isolation of the product, which (and this is another bonus) in most cases shows a high degree of purity.

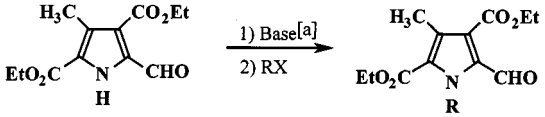
In conclusion, selective *N*-alkylation of sufficiently acidic pyrroles can be carried out under very mild and safe conditions using basic solutions easily obtained by an electrochemical methodology.

Experimental Section

Starting Materials: The following products were synthestised according to the literature: diethyl 5-formyl-3-methylpyrrole-2,4-dicarboxylate,[17] ethyl 3,5-dimethyl-4-nitropyrrole-2-carboxylate,[18] diethyl 5-chloro-3-methylpyrrole-2,4-dicarboxylate,[19] diethyl 5-bromo-3-methylpyrrole-2,4-dicarboxylate,[19] diethyl 3,5-dimethylpyrrole-2,4-dicarboxylate,[20] ethyl 3,4,5-trimethylpyrrole-2-carboxylate,[21] 2-nitropyrrole,[22] 3-nitropyrrole.[22]

General Procedure. – Preparation of the Solutions Containing TEAPC (a) or TEAC (b): (a) A solution (40.0 mL) of MeCN/TEAP (0.1 mol dm^{-3}), through which O_2 and CO_2 were simultaneously bubbling, was electrolysed (divided cell, Pt anode, I = 10 mA cm^{-2},

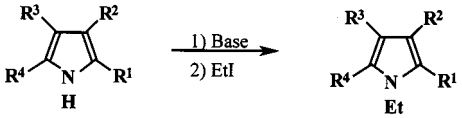
Table 1. Reaction of diethyl 5-formyl-3-methylpyrrole-2,4-dicarboxylate with peroxydicarbonate and different alkylating reagents in different solvents



Entry	Solvent/ supporting electrolyte	RX[b]	*N*-Alkylated pyrrole (yield[c])	Starting pyrrole recovered
1	MeCN/TEAP	EtI	98%	–
2	DMF/TEAP	EtI	97%	–
3	CH_2Cl_2/TBABr	EtI	94%	–
4	THF/$LiClO_4$	EtI	–	85%
5	MeCN/TEAP	MeI	91%	–
6	MeCN/TEAP	$BrCH_2Ph$	88%	–
7	MeCN/TEAP	$BrCH_2CH_2CN$	–	100%
8	MeCN/TEAP	$BrCH_2CO_2Et$	97%	–
9	MeCN/TEAP	$BrCH_2COPh$	62%	24%

[a] A molar ratio pyrrole/base of 1:1.5 was used. – [b] A five-fold excess of halide was added after 60 min. – [c] Yields refer to isolated *N*-alkylpyrrole.

Table 2. Reaction of pyrroles with TEAPC or TEAC and ethyl iodide in MeCN/TEAP



Entry	R^1, R^2, R^3, R^4	Base[a]	*N*-Alkylated pyrrole (yield[b])	Starting pyrrole recovered
1	CH_3, NO_2, CH_3, CO_2Et	TEAPC	80%	18%
2	CHO, CO_2Et, CH_3, CO_2Et	TEAPC	98%	–
3	Cl, CO_2Et, CH_3, CO_2Et	TEAPC	96%	–
4	Br, CO_2Et, CH_3, CO_2Et	TEAPC	95%	–
5	CH_3, CO_2Et, CH_3, CO_2Et	TEAPC	–	100%
6	H, H, H, H	TEAPC	–	40%
7	CH_3, CH_3, CH_3, CO_2Et	TEAPC	–	100%
8	NO_2, H, H, H	TEAPC	71%	–
9	H, NO_2, H, H	TEAPC	63%	22%
10	CH_3, NO_2, CH_3, CO_2Et	TEAC	60%	34%
11	CHO, CO_2Et, CH_3, CO_2Et	TEAC	87%	–
12	CH_3, CO_2Et, CH_3, CO_2Et	TEAC	–	71%

[a]A molar ratio pyrrole/base of 1:1.5 was used; a five-fold excess of ethyl iodide was added after 60 min. – [b] Yields refer to isolated *N*-alkylpyrrole.

room temperature) on an Hg cathode (area 12.0 cm^2) at a potential (E = −1.1 V vs. SCE) that allowed the reduction of O_2 to $O_2^{-\bullet}$. – (b) A solution (40.0 mL) of MeCN/TEAP (0.1 mol dm^{-3}) with continuous CO_2 bubbling, was electrolysed (divided cell, Pt anode, I = 15 mA cm^{-2}, 0°C) on a Cu cathode (area 9.0 cm^2) at a potential (E = −2.1 V vs. SCE) that allowed the reduction of CO_2 to $CO_2^{-\bullet}$. – After the consumption of 580 coulombs, according to the formation of 3.0 mmol of TEAPC (Equation 1 and 2) or of TEAC (Equation 3 and 4), the electrolyses were stopped and N_2 was bubbled through the solutions for 10 min.

Reaction of Pyrroles with TEAPC or TEAC: The pyrrole derivative (1.0 mmol) was added to a stirred solution of TEAPC or TEAC (1.5 mmol) in MeCN/TEAP (20 mL) at room temperature. After 1 h, a fivefold excess of alkylating reagent was added and the reaction was stirred overnight. The solvent was removed under reduced pressure and the residue extracted with diethyl ether. Purification of the products was accomplished by column chromatography. All the products were fully characterised by ^{1}H- (Bruker AC 200, 200 MHz, $CHCl_3$/$CDCl_3$ as internal reference) and ^{13}C-NMR (Bruker AC 200, 50.3 MHz, $CHCl_3$/$CDCl_3$ as internal reference) spectroscopy, MS (Fisons MD 800, EI, 70 eV), and comparison with authentic samples, whenever possible.

Isolated Products. – Diethyl 1-Ethyl-5-formyl-3-methylpyrrole-2,4-dicarboxylate: ^{1}H NMR ($CDCl_3$): δ = 10.32 (s, 1 H, C*H*O), 4.69 (q, 2 H, J = 6.94 Hz, NC$H_2$$CH_3$), 4.36 (q, 2 H, J = 7.11 Hz, 4-COOC$H_2$$CH_3$), 4.34 (q, 2 H, J = 7.10 Hz, 2-COOC$H_2$$CH_3$), 2.45 (s, 3 H, 3-C$H_3$), 1.38 (t, 3 H, J = 7.11 Hz, 4-COOCH$_2$CH_3), 1.37 (t, 3 H, J = 7.10 Hz, 2-COOCH$_2$CH_3), 1.32 (t, 3 H, J = 6.94 Hz, NCH$_2$CH_3). – ^{13}C NMR ($CDCl_3$): δ = 183.60, 163.85, 161.14, 132.70, 129.56, 126.40, 123.21, 61.04, 60.79, 42.88, 16.46, 14.21, 14.10, 12.02. – GC MS; *m*/*z* (%): 282 (9) [$M^{+\bullet}$ + 1], 281 (65) [$M^{+\bullet}$], 252 (95) [$M^{+\bullet}$ – Et], 236 (81) [$M^{+\bullet}$ – OEt], 178 (100). – $C_{14}H_{19}NO_5$ (281.3): calcd. C 59.78, H 6.81, N 4.98; found C 59.71, H 6.59, N 4.83.

Diethyl 5-Formyl-1,3-dimethylpyrrole-2,4-dicarboxylate: ^{1}H NMR ($CDCl_3$): δ = 10.34 (s, 1 H, C*H*O), 4.35 (q, 2 H, J = 7.13 Hz, 4-COOC$H_2$$CH_3$), 4.30 (q, 2 H, J = 7.11 Hz, 2-COOC$H_2$$CH_3$), 4.14 (s, 3 H, NC$H_3$), 2.46 (s, 3 H, 3-C$H_3$), 1.37 (t, 3 H, J = 7.13 Hz, 4-COOCH$_2$CH_3), 1.35 (t, 3 H, J = 7.11 Hz, 2-COOCH$_2$CH_3). – ^{13}C NMR ($CDCl_3$): δ = 184.04, 163.71, 161.20, 133.62, 129.45, 127.17, 122.67, 61.00, 60.73, 35.48, 14.17, 14.10, 11.90. – GC MS; *m*/*z* (%): 268 (8) [$M^{+\bullet}$ + 1], 267 (62) [$M^{+\bullet}$], 238 (61) [$M^{+\bullet}$ – Et], 222 (66) [$M^{+\bullet}$ – OEt], 193 (100). – $C_{13}H_{17}NO_5$ (267.3): calcd. C 58.42, H 6.41, N 5.24; found C 58.27, H 6.17, N 5.08.

Diethyl 1-Benzyl-5-formyl-3-methylpyrrole-2,4-dicarboxylate: ^{1}H NMR ($CDCl_3$): δ = 10.36 (s, 1 H, C*H*O), 7.22 (m, 3 H, *Ph*), 6.98 (m, 2 H, *Ph*), 6.07 (s, 2 H, NCH_2Ph), 4.35 (q, 2 H, J = 7.22 Hz, 4-COOC$H_2$$CH_3$), 4.26 (q, 2 H, 2-COOC$H_2$$CH_3$), 2.50 (s, 3 H, 3-C$H_3$), 1.36 (t, 3 H, J = 7.22 Hz, 4-COOCH$_2$CH_3), 1.25 (t, 3 H, J = 7.22 Hz, 2-COOCH$_2$CH_3). – ^{13}C NMR ($CDCl_3$): δ = 193.71, 163.69, 161.05, 137.69, 133.15, 129.86, 128.29, 127.02, 126.95, 126.17, 123.59, 61.00, 60.85, 49.71, 14.16, 13.93, 12.04. – GC MS; *m*/*z* (%): 343 (7) [$M^{+\bullet}$], 298 (12) [$M^{+\bullet}$ – OEt], 297 (50) [$M^{+\bullet}$ – EtOH], 91 (100) [$PhCH_2^+$]. – $C_{19}H_{21}NO_5$ (343.4): calcd. C 66.46, H 6.16, N 4.08; found C 66.29, H 6.02, N 3.91.

Diethyl 1-Ethoxycarbonylmethyl-5-formyl-3-methylpyrrole-2,4-dicarboxylate: ^{1}H NMR ($CDCl_3$): δ = 10.31 (s, 1 H, C*H*O), 5.56 (s, 2 H, NCH_2COOCH$_2$$CH_3$), 4.33 (q, 2 H, J = 7.26 Hz, 4-COOC$H_2$$CH_3$), 4.29 (q, 2 H, J = 7.30 Hz, 3-COOC$H_2$$CH_3$), 4.17 (q, 2 H, J = 7.11 Hz, NCH$_2$COOC$H_2$$CH_3$), 2.48 (s, 3 H, 3-C$H_3$), 1.33 (t, 3 H, J = 7.26 Hz, 4-COOCH$_2$CH_3), 1.32 (t, 3 H, J = 7.30 Hz, 3-COOCH$_2$CH_3), 1.27 (t, 3 H, J = 7.11 Hz, NCH$_2$COOCH$_2$CH_3). – ^{13}C NMR ($CDCl_3$): δ = 184.25, 168.26, 163.53, 161.20, 133.29, 130.38, 126.30, 123.53, 61.57, 61.20, 60.91, 48.75, 14.18, 14.02, 13.96, 12.12. – GC MS; *m*/*z* (%): 339 (1) [M^+]$^\bullet$, 310 (31) [$M^{+\bullet}$ – Et], 294 (8) [$M^{+\bullet}$ – OEt], 266 [($M^{+\bullet}$ – COOEt]), 29 (100). – $C_{16}H_{21}NO_7$ (339.3): calcd. C 56.63, H 6.24, N 4.13; found C 56.47, H 6.09, N 3.95.

Diethyl 5-Formyl-3-methyl-1-phenacylpyrrole-2,4-dicarboxylate: ^{1}H NMR ($CDCl_3$): δ = 10.34 (s, 1 H, C*H*O), 7.96 (m, 2 H, *Ph*), 7.55 (m, 3 H, *Ph*), 6.42 (s, 2 H, NCH_2Ph), 4.36 (q, 2 H, J = 7.12 Hz, 4-COOC$H_2$$CH_3$), 4.24 (q, 2 H, J = 7.11 Hz, 4-COOC$H_2$$CH_3$), 2.55 (s, 3 H, 3-C$H_3$), 1.36 (t, 3 H, J = 7.12 Hz, 4-COOCH$_2$$H_3$), 1.26 (t, 3 H, J = 7.11 Hz, 2-COOCH$_2$CH_3). – ^{13}C NMR ($CDCl_3$): δ = 192.77, 184.46, 163.67, 161.42, 134.86, 133.67, 130.56, 130.38, 128.77, 127.79, 123.66, 61.20, 60.91, 53.83, 14.24, 14.00, 12.30. –

GC MS; *m/z* (%): 371 (5) [$M^{+\bullet}$], 326 (9) [$M^{+\bullet}$ − OEt], 325 (36) [$M^{+\bullet}$ − EtOH], 105 (100) [$PhCO^+$]. − $C_{20}H_{21}NO_6$ (371.4): calcd. C 64.68, H 5.70, N 3.77; found C 64.55, H 5.57, N 3.61.

Ethyl 1-Ethyl-3,5-dimethyl-4-nitropyrrole-2-carboxylate: ^{1}H NMR ($CDCl_3$): δ = 4.27 (q, 2 H, *J* = 7.10 Hz, NCH_2CH$_3$), 4.26 (q, 2 H, *J* = 7.20 Hz, 2-COOCH_2CH$_3$), 2.54 (s, 3 H, 3-CH_3), 2.49 (s, 3 H, 5-CH_3), 1.32 (t, 3 H, *J* = 7.20 Hz, 2-COOCH$_2$CH_3), 1.26 (t, 3 H, *J* = 7.1 Hz, N−CH$_2$CH_3). − GC MS; *m/z* (%): 241 (12) [$M^{+\bullet}$ + 1], 240 (83) [$M^{+\bullet}$], 223 (100), 195 (67) [$M^{+\bullet}$ − OEt], 149 [$M^{+\bullet}$ − NO_2]. − $C_{11}H_{16}N_2O_4$ (240.3): calcd. C 54.99, H 6.71, N 11.66; found C 54.85, H 6.58, N 11.50.

Diethyl 5-Chloro-1-ethyl-3-methylpyrrole-2,4-dicarboxylate: ^{1}H NMR ($CDCl_3$): δ = 4.42 (q, 2 H, *J* = 7.22 Hz, NCH_2CH$_3$), 4.31 (q, 2 H, *J* = 7.13 Hz, 4-COOCH_2CH$_3$), 4.30 (q, 2 H, *J* = 7.09 Hz, 2-COOCH_2CH$_3$), 2.52 (s, 3 H, 3-CH_3), 1.40 (t, 3 H, *J* = 7.13 Hz, 4-COOCH$_2$CH_3), 1.38 (t, 3 H, *J* = 7.09 Hz, 2-COOCH$_2$CH_3), 1.33 (t, 3 H, *J* = 7.22 Hz, NCH$_2$CH_3). − ^{13}C NMR ($CDCl_3$): δ = 167.62, 161.12, 131.12, 60.35, 60.05, 41.60, 15.52, 14.33, 12.70. − GC MS; *m/z* (%): 290 (4) [$M^{+\bullet}$ + 3], 289 (31) [$M^{+\bullet}$ + 2], 288 (14) [$M^{+\bullet}$ + 1], 287 (100) [$M^{+\bullet}$], 244 (23) [$M^{+\bullet}$ + 2 − OEt], 242 (64) [$M^{+\bullet}$ − OEt]. − $C_{13}H_{18}ClNO_4$ (287.7): calcd. C 54.26, H 6.31, N 4.87; found C 54.11, H 6.18, N 4.71.

Diethyl 5-Bromo-1-ethyl-3-methylpyrrole-2,4-dicarboxylate: ^{1}H NMR ($CDCl_3$): δ = 4.46 (q, 2 H, *J* = 7.03 Hz, NCH_2CH$_3$), 4.32 (q, 2 H, *J* = 7.26 Hz, 4-COOCH_2CH$_3$), 4.31 (q, 2 H, *J* = 7.28 Hz, 2-COOCH_2CH$_3$), 2.52 (s, 3 H, 3-CH_3), 1.36 (t, 3 H, *J* = 7.26 Hz, 4-COOCH$_2$CH_3), 1.35 (t, 3 H, *J* = 7.28 Hz, 2-COOCH$_2$CH_3), 1.29 (t, 3 H, *J* = 7.03 Hz, NCH$_2$CH_3). − ^{13}C NMR ($CDCl_3$): δ = 163.69, 161.04, 131.79, 121.87, 114.98, 114.89, 60.33, 60.07, 43.34, 15.59, 14.26, 12.85. − GC MS; *m/z* (%): 334 (14) [$M^{+\bullet}$ + 3], 333 (97) [$M^{+\bullet}$ + 2], 332 (14) [$M^{+\bullet}$ + 1], 331 (100) [$M^{+\bullet}$], 288 (54) [$M^{+\bullet}$ + 2 − OEt], 286 (56) [$M^{+\bullet}$ − OEt]. − $C_{13}H_{18}BrNO_4$ (332.2): calcd. C 47.00, H 5.46, N 4.22; found C 46.88, H 5.34, N 4.19.

1-Ethyl-2-nitropyrrole: ^{1}H NMR ($CDCl_3$): δ = 7.18 (m, 1 H), 6.83 (m, 1 H), 6.14 (m, 1 H), 4.37 (q, 2 H, *J* = 7.09 Hz, NCH_2CH$_3$), 1.42 (t, 3 H, *J* = 7.09 Hz, NCH$_2$CH_3). − ^{13}C NMR ($CDCl_3$): δ = 128.35, 114.75, 108.56, 45.59, 16.34. − GC MS; *m/z* (%): 141 (9) [$M^{+\bullet}$ + 1], 140 (100) [$M^{+\bullet}$], 123 (50), 110 (9) [$M^{+\bullet}$ − NO], 82 (68), 29 (48). − $C_6H_8N_2O_2$ (140.1): calcd. C 51.42, H 5.75, N 19.99; found C 51.29, H 5.63, N 19.75.

1-Ethyl-3-nitropyrrole: ^{1}H NMR ($CDCl_3$): δ = 7.51 (m, 1 H, 2-*H*), 6.68 (m, 1 H, 4-*H*), 6.55 (m, 1 H, 5-*H*), 3.94 (q, 2 H, *J* = 7.32 Hz, NCH_2CH$_3$), 1.45 (t, 3 H, *J* = 7.32 Hz, NCH$_2$CH_3). − ^{13}C NMR ($CDCl_3$): δ = 121.00, 120.84, 105.58, 45.45, 15.94. − GC MS; *m/z* (%): 141 (9) [$M^{+\bullet}$ + 1], 140 (100) [$M^{+\bullet}$], 125 (11) [$M^{+\bullet}$ − CH_3], 110 (19) [$M^{+\bullet}$ − NO], 82 (41), 29 (56). − $C_6H_8N_2O_2$ (140.1): calcd. C 51.42, H 5.75, N 19.99; found C 51.27, H 5.60, N 19.77.

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[1] G. W. Gribble, *Prog. Chem. Org. Nat. Prod.* **1996**, *68*, 133−141.
[2] G. Ohloff, I. Flament, *Fortschr. Chem. Org. Naturst.* **1979**, *36*, 260−262.
[3] C. R. Enzell, I. Wahlberg, A. J. Aasen, *Fortschr. Chem. Org. Naturst.* **1977**, *34*, 62−64.
[4] M. Kato, K. Komoda, A. Namera, Y. Sakai, S. Okada, A. Yamada, K. Yokoyama, E. Migita, Y. Minobe, T. Tani, *Chem. Pharm. Bull.* **1997**, *45*, 1767−1776.
[5] [5a] *Comprehensive Medicinal Chemistry* (Eds.: P. G. Sammes, S. B. Taylor), Pergamon Press, Oxford, **1990**, vol. 6, pp. 280, 403, 613, 951, 963. − [5b] *Comprehensive Medicinal Chemistry* (Eds.: P. G. Sammes, S. B. Taylor), Pergamon Press, Oxford, **1990**, vol. 6, p. 801.
[6] P. J. Mariano, J. L. Stavinoha, in *Synthetic Organic Photochemistry* (Ed.: W. M. Horspool), Plenum Press, New York, **1984**, p. 145.
[7] R. A. Jones, G. P. Bean, in *The Chemistry of Pyrroles* (Eds.: A. T. Blomquist, H. H. Wasserman), Academic Press, London, **1977**, vol. 34, p. 173ff.
[8] H. Heaney, S. V. Ley, *J. Chem. Soc., Perkin Trans. 1* **1973**, 499−500.
[9] E. Diez-Barra, A. de la Hoz, A. Loupy, A. Sanchez-Migallon, *J. Heterocycl. Chem.* **1994**, *31*, 1715−1717.
[10] O. A. Reutov, I. P. Belestskaya, A. L. Kurts, in *Ambident Anions*, Consultants Bureau, New York, NY, **1983**, pp. 134, 235.
[11] [11a] J. L. Roberts, Jr., T. S. Calderwood, D. T. T. S. Sawyer, *J. Am. Chem. Soc*. **1984**, *106*, 4664−4670. − [11b] M. A. Casadei, S. Cesa, F. Micheletti Moracci, A. Inesi, M. Feroci, *J. Org. Chem.* **1996**, *61*, 380−383.
[12] [12a] C. Amatore, J. M. Saveant, *J. Am. Chem. Soc*. **1981**, *103*, 5021. − [12b] J. C. Gressin, D. Michelet, L. Nadjo, J. M. Savéant, *Nouv. J. Chim*. **1979**, *3*, 545. − [12c] S. Ikeda, T. Takagi, K. Ito, *Bull. Chem. Soc. Jpn*. **1987**, *60*, 2517. − [12d] M. A. Casadei, A. Inesi, F. Micheletti Moracci, L. Rossi, *Chem. Commun.* **1996**, 2575−2576.
[13] M. A. Casadei, F. Micheletti Moracci, G. Zappia, A. Inesi, L. Rossi, *J. Org. Chem.* **1997**, *62*, 6754−6759.
[14] M. A. Casadei, S. Cesa, M. Feroci, A. Inesi, L. Rossi, F. Micheletti Moracci, *Tetrahedron* **1997**, *53*, 167−176.
[15] M. A. Casadei, A. Inesi, L. Rossi, *Tetrahedron Lett.* **1997**, *38*, 3565−3568.
[16] H. Fischer, P. Ernst, *Justus Liebigs Ann. Chem.* **1926**, *447*, 139−162.
[17] A. H. Corwin, W. A. Bailey, Jr., P. Viohl, *J. Am. Chem. Soc*. **1942**, *64*, 1267.
[18] [18a] V. Cherchez, *Bull. Soc. Chim. Fr*. **1930**, *47*, 1279. − [18b] M. Taliani, Tesi di Laurea, Università "La Sapienza", Roma, **1992**.
[19] F. Giuliano, M. Penna, G. Sleiter, *Gazz. Chim. Ital*. **1986**, *116*, 589.
[20] [20a] A. Treibs, H. G. Kolm, *Justus Liebigs Ann. Chem.* **1958**, *176*, 614. − [20b] G. D'Alessandro, G. Sleiter, *J. Labelled Compd. Radiopharm*. **1980**, *17*, 813.
[21] E. Baciocchi, E. Muraglia, G. Sleiter, *J. Org. Chem*. **1992**, *57*, 2488.
[22] A. R. Cooksey, K. J. Morgan, D. P. Morrey, *Tetrahedron* **1970**, *26*, 5101.

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