Pergamon

Tetrahedron 54 (1998) 1913–1920

TETRAHEDRON

A Novel Synthesis of 3-Nitroindoles via Electrocyclization of 2,3-(Dialk-1-enyl)-4-nitropyrroles[1]

Ronald ten Have and Albert M. van Leusen*

Department of Organic and Molecular Inorganic Chemistry, Groningen University, Nijenborgh 4, NL-9747 AG Groningen, The Netherlands

Received 30 September 1997; revised 2 December 1997; accepted 4 December 1997

Abstract : 3-Nitroindoles (**10**) are prepared in good yields via a thermal 6π-electrocyclization of 2,3-(dialkenyl)-4-nitropyrroles (**4**) in nitrobenzene, a solvent which causes *in situ* aromatization of the initially formed dihydroindoles (**8**). The corresponding reaction of 2-alkenyl-3-alkadienyl-4-nitropyrroles (**5**) also leads to 3-nitroindoles (**11**), however, now together with 3-nitrotetrahydroindole derivatives (**12**). The latter compounds are formed by a tandem 6π-electrocyclization - intramolecular Diels-Alder reaction, and are the predominant (or only) products when nitrobenzene is replaced by triglyme. © 1997, Elsevier Science Ltd.

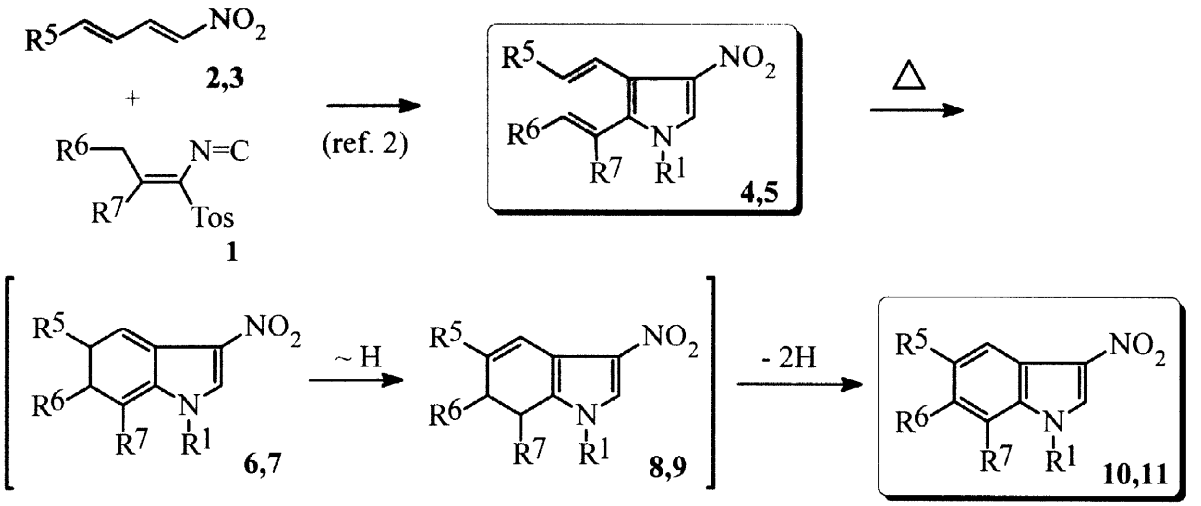
INTRODUCTION

Recently, we have described a simple method for the synthesis of 3-nitropyrroles.[2] This method offers the possibility to synthesize various substituted 3-nitropyrroles. For example, 2,3-(dialkenyl)-4-nitropyrroles[3] (**4,5**) are obtained in one operation by reaction of conjugated nitrodienes (**2**) or nitrotrienes (**3**) with 1-isocyano-1-tosyl-1-alkenes (**1**, the formal condensation products of TosMIC and ketones).[4]

We now report that 2,3-(dialkenyl)-4-nitropyrroles **4,5** are ideal precursors for the synthesis of 3-nitroindoles **10,11** (Scheme 1). At present there is no reliable, generally applicable method for the preparation of 3-nitroindoles. Although the 3-position of indoles is the prime reaction site for electrophilic substitutions, nitration may well lead to indoles with nitro groups at C-4, C-5 and/or C-6, in addition to (or instead of) C-3. The results are strongly dependent on the presence of substituents and on the acidity of the nitrating medium. Furthermore, the nitration of indoles may be complicated by oxidation and dimerization reactions.[5] The best results so far were obtained in certain *ipso* nitrations. One of the better examples of that approach is given by the preparation of 1-ethyl-3-nitro-2-phenylindole by replacement of a 3-phenylazo substituent (in 90 % yield, using 70 % HNO_3 in AcOH at rt for 50 h).[6] This approach, however, has severe limitations and, for example, does not appear to work for 2-unsubstituted indoles.[7]

0040-4020/98/$19.00
PII: S0040-4020(97)10405-7

Scheme 1 : Electrocyclization of 4-Nitropyrroles **4,5** to the Corresponding 3-Nitroindoles **10,11**



R^5 = Ph in even numbered compounds, (*E*)-PhCH=CH in odd numbered compounds
For **4** and **10**, see Table 1; for **5** and **11** Table 2

RESULTS AND DISCUSSION

The electrocyclization reaction of 2-alkenyl-1-methyl-4-nitro-3-(2-phenylethenyl)pyrroles **4** takes place in a straightforward manner. 3-Nitroindoles **10** are formed in one operation when these *N*-methylated 4-nitropyrroles **4** are heated in refluxing nitrobenzene (bp 211 °C) (Scheme 1, Table 1, entries 1-3). In analogy to previous results,[8] the reaction is assumed to proceed via the primary electrocyclization products **6** and their 1,5-hydrogen shifted isomers **8**, which are *in situ* dehydrogenated by nitrobenzene. Similar dehydrogenations by nitrobenzene are well known, for example, from the Skraup quinoline synthesis.[9]

Table 1 : 3-Nitroindoles **10** (R^5 = Ph) Prepared from Nitropyrroles **4** in Refluxing Nitrobenzene According to Scheme 1

Entry	R^1	R^6	R^7	Product	React. Time (h)	Yield (%)	Mp (°C)
1	Me	H	Me	**10a**	2½	75	173-174
2	Me	Me	Ph	**10b**	5	85	267-268
3	Me	$-(CH_2)_4-$		**10c**	2½	69	271-272
4	H	H	Me	**10d**	2	a	
5	Tos	$-(CH_2)_4-$		**10e**	1	a	

(a) Nitroindole not identified, see text

The corresponding reaction of *N*-unsubstituted nitropyrrole **4d** was not successful (Table 1, entry 4). Under the conditions of entry 1, pyrrole **4d**, resulted in a complex, tarry reaction mixture, in which according to ^{1}H NMR neither starting material **4d** nor the desired nitroindole **10d** were present. Somewhat unexpectedly, the same was found for *N*-tosyl protected nitropyrrole **4e** (entry 5).

Electrocyclization of 2-alkenyl-4-nitro-3-(4-phenyl-1,3-butadienyl)pyrroles **5** (homologs of pyrroles **4**, with an additional double bond in the C-3 substituent) in nitrobenzene did not give 5-(2-phenylethenyl)nitroindoles **11** as the only product (Scheme 1, Table 2). In addition to the 3-nitroindoles **11**, a second 3-nitroindole derivative **12** was formed frequently, occasionally even as the main product (Table 2). Evidently, compounds **12** are formed by an intramolecular Diels-Alder reaction of the primary formed electrocyclization products **7** (Scheme 2). This Diels-Alder reaction, apparently, can compete with the supposedly fast 1,5 H-shift [8] of **7** to **9**. The structure of **12a** was established unambiguously by X-ray analysis,[10] thus ruling out the alternative structure **13a**, which would have resulted from a reversed Diels-Alder cycloaddition of **7a**.

Table 2 : 3-Nitroindoles **11** (R^5 = (*E*)-PhCH=CH) and **12** Prepared from Nitropyrroles **5** in Refluxing Nitrobenzene or Triglyme According to Schemes 1 and 2

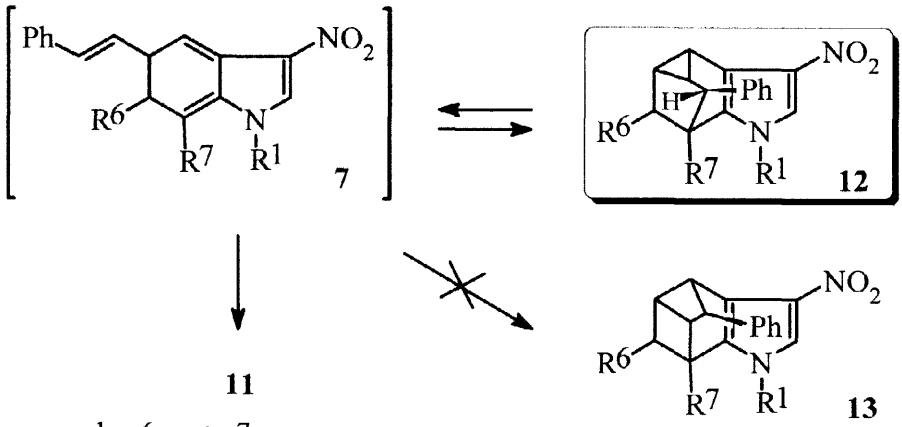
Entry	Start. Mat.	R^6	R^7	R^1	Solvent	React. Time (h)	Product	Yield (%)	
								11	**12**
1	**5a**	-$(CH_2)_4$-		Me	$PhNO_2$	3½	**a**	21	50
2	**5a**	-$(CH_2)_4$-		Me	Triglyme	2	**a**	< 1	75
3	**5b**	-$(CH_2)_4$-		H	Triglyme	2	**b**		78
4	**5c**	H	Me	Me	$PhNO_2$	2	**c**	68	12
5	**5c**	H	Me	Me	Triglyme	2	**c**	10	70
6	**5d**	H	Me	H	Triglyme	1½	**d**	46	
7	**5e**	Me	Ph	Me	$PhNO_2$	2	**e**	90	
8	**5e**	Me	Ph	Me	Triglyme	2	**e**	38[a]	

(a) Compound **11e** was identified by ^{1}H NMR in a mixture of two products.

The first electrocyclization experiments of Table 2 - with pyrrole **5a** - were carried out in refluxing nitrobenzene, following the procedure used for the reactions of Table 1. This reaction gave a mixture of two indole derivatives: 3-nitroindole **11a** (21 %) and 3-nitrotetrahydroindole derivative **12a** (50 % yield, Table 2, entry 1).[11] When the same reaction was repeated in refluxing triglyme (triethylene glycol dimethyl ether, bp 216 °C), 3-nitrotetrahydroindole **12a** was the only product (75 % yield, entry 2). Thus, nitrobenzene is likely to be involved in the formation of **11a** (entry 1), as well as the 3-nitropyrroles **10a,b,c** of Table 1. As a matter of fact **12c** is partially converted to **11c** in refluxing nitrobenzene ; the ratio **11c**:**12c** obtained after 2½ h was *ca.* 1.8 :1. The formation of **11c** in this experiment must be the result of the retro-Diels-Alder of **12c** to **7c**, followed by dehydrogenation (possibly via **9c**) by nitrobenzene (Scheme 2).

The electrocyclization of pyrrole **5b** in triglyme also gave a 3-nitrotetrahydroindole derivative, **12b**, as the only product (78 %, entry 3). This experiment shows that electrocyclization of *N*-H unprotected pyrrole is successful when carried out in triglyme, unlike the reaction of **4d** in nitrobenzene (Table 1, entry 4).[12]

Scheme 2 : Rationale of Formation of 3-Nitrotetrahydroindoles **12**

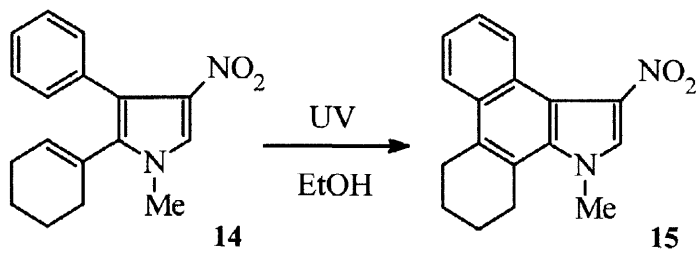


For R^1, R^6, and R^7, see Table 2

3-Nitroindoles **11c** and **11e** were the major and the sole product of entries 4 and 7 (Table 2), respectively, when the electrocyclizations were carried out in nitrobenzene. Entry 5, in triglyme, gave **12c** as the main product, as expected. The results of entries 6, and 8 are less clear cut.

Finally, the electrocyclization (and dehydrogenation) of **14**, which bears an aromatic side chain at C-3, was achieved photochemically in ethanol to give 3-nitrobenzindole **15** in 18 % yield (Scheme 3).

Scheme 3 : Photochemical Electrocyclization of Pyrrole **14** to 3-Nitroindole **15**



EXPERIMENTAL

All experiments, were carried out in a dry nitrogen atmosphere. 2,3-(Dialkenyl)-4-nitropyrroles **4,5** were prepared as published.[2] Column chromatography was performed on alumina (Brockmann 90 II/III, 0.063-0.200 mm) or silicagel (Merck, 0.040-0.063 mm). CH_2Cl_2 and Et_2O were distilled over P_2O_5 before use. Triglyme and nitrobenzene were distilled prior to use. The photoelectrocyclization was performed with a high-pressure pyrex immersion mercury UV lamp. Melting points were measured on a Mettler FP1 melting point apparatus, equipped with a Mettler FP52 microscope and are uncorrected. ^{1}H-NMR spectra were recorded on a Varian VXR-300 spectrometer (300 MHz) or on a Varian Gemini spectrometer (200 MHz).^{1}H-NMR chemical shifts were determined relative to the solvent and were converted to the TMS scale using δ ($CHCl_3$) = 7.26 and δ (DMSO) = 2.49. ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer (75.4 MHz), or on a Varian Gemini spectrometer (50.4 MHz). ^{13}C NMR chemical shifts were determined relative to the solvent and were converted to the TMS

scale using δ ($CDCl_3$) = 76.91 and δ (DMSO) = 39.7. Mass spectra were recorded on a AEI-MS-902 mass spectrometer (DI system; e.v. 70 eV; acc.v. 8 kV; multiplier 2.1 kV; I.S. temp. 120 °C). Elemental microanalyses were carried out in the Analytical Department of this laboratory.

1,7-Dimethyl-3-nitro-5-phenylindole (10a), (Typical Procedure) :

(*E*)-1-Methyl-2-(1-methylethenyl)-4-nitro-3-(2-phenylethenyl)pyrrole (**4a**, 0.54 g, 2.0 mmol) was refluxed in nitrobenzene (20 mL) for 2½ h. The solvent was removed in a bulb-to-bulb distillation unit, and the black residue was filtered through a short column of Al_2O_3 (CH_2Cl_2). The eluent was concentrated to give, after washing with pentane, **10a** as a yellow solid (0.40 g, 75 %), pure according to ^1H NMR. Crystallization from MeOH gave analytically pure **10a**, as yellow crystals: mp 173-174 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ = 2.80 (s, 3H), 4.10 (s, 3H), 7.27-7.52 (m, 4H), 7.67-7.71 (m, 2H), 7.93 (s, 1H), 8.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 19.58 (q), 38.27 (q), 116.91 (d), 122.53 (s), 122.81 (s), 126.83 (d), 127.24 (d), 127.35 (d), 128.78 (d), 131.59 (s), 133.15 (d), 134.02 (s), 137.66 (s), 140.80 (s); MS (relative intensity, %): *m/z* = 28 (7.24), 102 (3.44), 108 (3.19), 133 (4.66), 165 (4.17), 178 (4.42), 218 (4.66), 220 (6.50), 236 (6.75), 266 (M^+, 100); HRMS: *m/z* calc. for $C_{16}H_{14}N_2O_2$: 266.106, found 266.106; Anal. calc. for $C_{16}H_{14}N_2O_2$: C, 72.15; H, 5.30; N, 10.52; found C, 71.82; H, 5.17; N, 10.40.

1,6-Dimethyl-5,7-diphenyl-3-nitroindole (10b) :

Following the procedure described for **10a**, (*E,E*)-1-methyl-4-nitro-3-(2-phenylethenyl)-2-(1-phenylprop-1-enyl)pyrrole[13] (**4b**, 0.69 g, 2.0 mmol) was refluxed for 5 h. After workup, **10b** was obtained as a yellow solid (0.58 g, 85 %), pure according to ^1H NMR. Crystallization from MeOH gave analytically pure **10b**, as yellow crystals: mp 267-268 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.98 (s, 3H), 3.16 (s, 3H), 7.34-7.51 (m, 10 H), 7.92 (s, 1H), 8.21 (s, 1H); 13C NMR ($CDCl_3$, 75.4 MHz): δ = 18.29 (q), 37.67 (q), 119.39 (s), 120.65 (d), 126.79 (d), 127.16 (s), 127.84 (s), 127.97 (d), 128.03 (d), 128.37 (d), 129.47 (d), 130.30 (d), 131.14 (s), 133.08 (s), 133.19 (d), 137.47 (s), 139.46 (s), 142.23 (s); MS (relative intensity, %): *m/z* = 28 (18.38), 280 (6.80), 281 (6.60), 294 (7.12), 312 (10.15), 342 (M^+, 100); HRMS: *m/z* calc. for $C_{22}H_{18}N_2O_2$: 342.137, found 342.137; Anal. calc. for $C_{22}H_{18}N_2O_2$: C, 77.16; H, 5.30; N, 8.19; found C, 76.98; H, 5.46; N, 8.26.

1-Methyl-3-nitro-5-phenyl-6,7,8,9-tetrahydrobenz[g]indole (10c) :

Following the procedure described for **10a**, (*E*)-2-(cyclohex-1-enyl)-1-methyl-4-nitro-3-(2-phenylethenyl)pyrrole (**4c**, 0.62 g, 2.0 mmol) gave, after washing with pentane, **10c** as a yellow solid (0.43 g, 69 %), pure according to ^1H NMR. Crystallization from MeOH gave analytically pure **10c**, as yellow crystals: mp 272-273 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.68-1.95 (m, 4H), 2.65 (t, *J* = 5.8 Hz, 2H), 3.35 (t, *J* = 6.1 Hz, 2H), 4.15 (s, 3H), 7.27-7.52 (m, 5H), 7.89 (s, 1H), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 22.27 (t), 22.38 (t), 26.11 (t), 29.14 (t), 39.33 (q), 118.94 (d), 119.45 (s), 122.45 (s), 126.72 (d), 127.90 (d), 129.28 (d), 132.10 (s), 132.87 (d), 133.95 (s), 139.84 (s), 141.92 (s); MS (relative intensity, %): *m/z* = 28 (10.08), 115 (4.88), 189 (5.67), 230 (6.14), 261 (6.93), 278 (10.55), 289 (7.72), 306 (M^+, 100); HRMS: *m/z* calc. for $C_{19}H_{18}N_2O_2$: 306.137, found 306.136; Anal. calc. for $C_{19}H_{18}N_2O_2$: C, 74.49; H, 5.92; N, 9.14; found C, 74.12; H, 5.99; N, 9.10.

(*E*)-1-Methyl-3-nitro-5-(2-phenylethenyl)-6,7,8,9-tetrahydrobenz[g]indole (11a) :

(*E,E*)-2-(Cyclohex-1-enyl)-1-methyl-4-nitro-3-(4-phenylbuta-1,3-dienyl)pyrrole (**5a**, 0.40 g, 1.2 mmol) was refluxed in nitrobenzene (25 mL) for 3½ h. After cooling, the solvent was removed in a bulb-to-bulb distillation unit, and the solid residue was filtered through a short column of Al_2O_3 (CH_2Cl_2) to give a mixture of two compounds. These were separated by column chromatography on Al_2O_3. The first fraction was obtained with CH_2Cl_2/pentane (1:1) and consisted of **12a** (0.20 g, 50 %), this compound was identical by ^1H NMR with the material described below. The second fraction, eluted with CH_2Cl_2 gave **11a** as a yellow solid (84 mg, 21 %), pure according to ^1H NMR. Crystallization from EtOH (96 %) gave analytically pure **11a**, as yellow crystals: mp 241-242 °C; ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.86-1.91 (m, 4H), 2.94 (m, 2H), 3.30 (m, 2H), 4.14 (s, 3H), 7.05-7.59 (m, 7H), 7.91 (s, 1H), 8.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 22.22 (t), 22.29 (t), 26.33 (t), 27.74 (t), 39.38 (q), 115.06 (d), 119.79 (s), 122.40 (s), 126.47 (d), 126.54 (d), 127.43 (d), 127.70 (s), 128.53 (d), 130.60 (d), 132.03 (s), 132.91 (d), 134.20 (s), 134.42 (s), 137.51 (s); MS (relative intensity, %): *m/z* = 28 (19.74), 77 (6.58), 91 (6.91), 128 (11.84), 213 (7.57), 241 (6.25), 304 (10.53), 332 (M^+, 100); HRMS: *m/z* calc. for $C_{21}H_{20}N_2O_2$: 332.152, found 332.152; Anal. calc. for $C_{21}H_{20}N_2O_2$: C, 75.87; H, 6.07; N, 8.43; found C, 76.02; H, 6.01; N, 8.35.

(*E*)-1,7-Dimethyl-3-nitro-5-(2-phenylethenyl)indole (11c) :

(*E,E*)-1-Methyl -2-(1-methylethenyl)-4-nitro-3-(4-phenylbuta-1,3-dienyl)pyrrole (**5c**, 0.29 g, 1.0 mmol) was refluxed in nitrobenzene (20 mL) for 2 h. After cooling, the solvent was removed in a bulb-to-bulb distillation unit, and the solid residue was filtered through a short column of silicagel (CH_2Cl_2). After concentration, an orange solid was obtained consisting of a mixture of two compounds, which were separated by column chromatography (Al_2O_3, CH_2Cl_2). The first fraction gave **12c** (described below) as a yellow solid (35 mg, 12 %), and the second fraction gave **11c** also as a yellow solid (0.20 g, 68 %), both compounds were pure according to ^{1}H NMR. Crystallization of **11c**, from EtOH (96 %), gave analytically pure material, as yellow crystals: mp 191-192 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.79 (s, 3H), 4.12 (s, 3H), 7.20-7.57 (m, 8H), 7.96 (s, 1H), 8.28 (d, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 19.47 (q), 38.18 (q), 116.93 (d), 122.45 (s), 122.58 (s), 125.59 (d), 126.37 (d), 127.49 (d), 128.17 (s), 128.31 (d), 128.49 (d), 128.60 (d), 132.89 (d), 133.81 (s), 134.09 (s), 137.32 (s), 192.15 (s); MS (relative intensity,%): *m/z* = 115 (8.80), 129 (6.49), 202 (7.51), 203 (7.00), 228 (9.61), 243 (8.88), 244 (8.75), 245 (6.49), 257 (13.75), 292 (M^+, 100); HRMS: *m/z* calc. for $C_{18}H_{16}N_2O_2$: 292.121, found 292.121; Anal. calc. for $C_{18}H_{16}N_2O_2$: C, 73.94; H, 5.52; N, 9.59; found C, 73.51; H, 5.55; N, 9.42.

The same indole **11c** was formed when indole **12c** (50 mg, 0.17 mmol) was refluxed in nitrobenzene (10 mL) for 2½ h. After cooling, the solvent was removed in a bulb-to-bulb distillation unit. The dark solid was filtered through a short column of Al_2O_3 (CH_2Cl_2). After concentrating the eluent, the remaining oil was washed with hexane to give a yellow oil (35 mg), which consisted of a mixture of two compounds: **11c** and **12c**. The ratio 1.8 : 1 (**11c** : **12c**) was determined by ^{1}H NMR.

(*E*)-7-Methyl-3-nitro-5-(2-phenylethenyl)indole (11d)

(*E,E*)-2-(1-Methylethenyl)-4-nitro-3-(4-phenylbuta-1,3-dienyl)pyrrole (**5d**, 0.40 g, 1.43 mmol) was refluxed in triglyme (20 mL) for 1½ h. After cooling, the solvent was removed in a bulb-to-bulb distillation unit, and the solid residue was purified by crystallization from $CHCl_3$/pentane to give **11d**, as an orange solid (0.18 g, 46 %): mp > 300 °C; ^{1}H NMR (DMSO.d_6, 200 MHz): δ = 2.54 (s, 3H), 7.20-7.65 (m, 8H), 8.08 (s, 1H), 8.63 (s, 1H), 12.7 (br, 1H); ^{13}C NMR (DMSO.d_6, 50.3 MHz): δ = 16.41 (q), 115.88 (d), 120.19 (s), 122.74 (d), 123.31 (s), 126.36 (d), 127.37 (d), 127.45 (d), 128.64 (d), 128.80 (s), 128.98 (d), 130.43 (d), 133.14 (s), 134.26 (s), 137.22 (s); MS (relative intensity) : *m/z* = 28 (68.1), 77 (7.90), 101 (7.8), 109 (9.3), 115 (8.7), 122 (8.8), 176 (17.5), 189 (11.0), 217 (11.6), 230 (13.6), 243 (10.4), 248 (10.7), 278 (M^+, 100); HRMS *m/z* calc. for $C_{17}H_{14}N_2O_2$: 278.106, found 278.106.

(*E*)-1,6-Dimethyl-3-nitro-7-phenyl-5-(2-phenylethenyl)indole (11e) :

(*E,E,E*)-1-Methyl-4-nitro-3-(4-phenylbuta-1,3-dienyl)-2-(1-phenylprop-1-enyl)pyrrole (**5e**, 0.37 g, 1.0 mmol) was refluxed in nitrobenzene for 2 h. After cooling, the solvent was removed in a bulb-to-bulb distillation unit, the solid residue was washed with Et_2O to give **11e**, as a yellow solid (0.33 g, 90 %), pure according to ^{1}H NMR. Crystallization from MeOH gave analytically pure **11e**, as yellow crystals: mp 289-290 °C; ^{1}H NMR($CDCl_3$, 200 MHz): δ = 2.17 (s, 3H), 3.12 (s, 3H), 7.11-7.60 (m, 12H), 7.89 (s, 1H), 8.54 (s, 1H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 16.85 (q), 37.65 (q), 116.84 (d), 119.93 (s), 126.56 (d), 126.99 (s), 127.18 (d), 127.55 (d), 127.97 (s), 128.09 (d), 128.34 (d), 128.60 (d), 130.39 (d), 131.16 (d), 131.52 (s), 133.22 (d), 133.34 (s), 134.30 (s), 137.41 (s), 137.57 (s); MS (relative intensity, %): *m/z* = 28 (79.87), 146 (5.19), 306 (5.11), 320 (5.03), 333 (7.06), 338 (6.98), 368 (M^+, 100); HRMS: *m/z* calc. for $C_{24}H_{20}N_2O_2$: 368.152, found 368.152; Anal. calc. for $C_{24}H_{20}N_2O_2$: C, 78.23; H, 5.48; N, 7.61; found C, 77.63; H, 5.57; N, 7.55.

In another experiment, pyrrole **5e** (0.37 g, 1.0 mmol) was refluxed in triglyme (20 mL) for 2 h. After cooling, the solvent was removed in a bulb-to-bulb distillation unit, and the solid residue was filtered through a short column of Al_2O_3 (EtOAc). After concentrating the eluent, the remaining oil was crystallized twice from Et_2O to give a yellow solid (0.18 g), which consisted of a mixture of two compounds. One of these was identified as indole **11e** by ^{1}H NMR in a yield of *ca.* 38 %.

***rac*-1-Methyl-4-nitro-{(1*R*,6*S*,8*S*)-6-phenyl-5,8-(tetramethylene)tricyclo[3.2.1.0^{2,7}]oct-3-eno}[4,3-b]pyrrole[14] (12a) :**

Pyrrole **5a** (0.33 g, 1.0 mmol) was refluxed in triglyme (20 mL) for 2 h. After cooling, the solvent was removed in a bulb-to-bulb distillation unit, and the residue was filtered through a short column of Al_2O_3 (CH_2Cl_2) to give a yellow solid, which contained about 1 % of indole **11a**. One crystallization from MeOH gave **12a**, as a yellow solid (0.25 g, 75 %): mp 190-191 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.30-2.22 (m, 11H), 3.12 (t, J = 7.2 Hz, 1H), 3.19 (s, 3H), 3.55 (d, J = 2.0 Hz, 1H), 6.73-

6.78 (m, 2H), 7.00 (s, 1H), 7.07-7.28 (m, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 13.49 (d), 21.52 (t), 22.11 (d), 25.33 (t), 26.50 (t), 28.35 (t), 37.42 (q), 41.27 (d), 44.18 (d), 47.62 (s), 115.51 (s), 122.41 (d), 126.34 (d), 127.65 (d), 127.67 (d), 127.74 (d),127.92 (d), 130.75 (d), 138.58 (s); MS (relative intensity, %): *m/z* = 28 (72.54), 32 (16.73), 42 (13.15), 77 (7.09), 91 (9.32), 115 (9.96), 117 (7.73), 230 (29.63), 243 (31.35), 288 (10.47), 317 (32.25), 334 (M^+, 100); HRMS: *m/z* calc. for $C_{21}H_{22}N_2O_2$: 334.168, found 334.168; Anal. calc. for $C_{21}H_{22}N_2O_2$: C, 75.48; H, 6.64; N, 8.38; found C, 75.46; H, 6.56; N, 8.67.

***rac*-4-Nitro-{(1*R*,6*S*,8*S*)-6-phenyl-5,8-(tetramethylene)tricyclo[3.2.1.0^{2,7}]oct-3-eno}[4,3-b]pyrrole[14] (12b) :**
(*E,E*)-2-(Cyclohex-1-enyl)-4-nitro-3-(4-phenylbuta-1,3-dienyl)pyrrole (**5b**, 0.50 g, 1.6 mmol) was refluxed in triglyme (20 mL) for 2 h. After cooling, the solvent was removed in a bulb-to-bulb distillation unit, the solid residue was filtered through a short column of silicagel (CH_2Cl_2) and purified by crystallization from $CHCl_3$/pentane, to give **12b** as a yellow solid (0.38 g, 78 %), pure according to ^{1}H NMR: mp 254-255 °C; ^{1}H NMR (DMSO.d_6, 200 MHz): δ = 1.11-1.83 (m, 12H), 2.86 (t, *J* = 7.2 Hz, 1H), 3.51 (s, 1H), 6.67-6.71 (m, 2H), 7.04-7.06 (m, 3H), 7.38 (s, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ = 13.16 (d), 20.46 (t), 21.10 (d), 21.44 (d), 24.97 (t), 25.00 (t), 26.86 (t), 40.02 (d), 43.34 (d), 44.03 (s), 111.50 (s), 117.70 (d), 126.06 (d), 127.47 (d), 127.88 (d), 131.80 (s), 133.40 (s), 138.67 (s); MS (relative intensity, %): *m/z* = 28 (100), 32 (22.15), 216 (25.87), 229 (22.90), 303 (9.09), 320 (M^+, 100); HRMS: *m/z* calc. for $C_{20}H_{20}N_2O_2$: 320.152, found 320.152; Anal. Calc. for $C_{20}H_{20}N_2O_2$: C, 74.96; H, 6.30; N, 8.75; found C, 73.31; H, 6.21; N, 8.53.

***rac*-1-Methyl-4-nitro-{(1*R*,6*S*)-5-methyl-6-phenyltricyclo[3.2.1.0^{2,7}]oct-3-eno}[4,3-b]pyrrole[14] (12c) :**
Pyrrole **5c** (0.29 g, 1.0 mmol) was refluxed in triglyme (15 mL) for 2 h. Following the procedure described for **11c**, compound **12c** (0.20 g, 70 %) and compound **11c** (30 mg, 10 %) were obtained as yellow solids, both pure according to ^{1}H NMR. Crystallization from MeOH gave **12c**, as yellow crystals: mp 134-135 °C; ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.30 (d, *J* = 11.7 Hz, 1H), 1.58 (s, 3H), 1.78-1.94 (m, 3H), 2.90 (s, 1H), 3.15 (t, *J* = 7.1 Hz, 1H), 3.23 (s, 3H), 6.73-6.78 (m, 2H), 7.07-7.1 (m, 4H); ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 13.69 (d), 16.20 (d), 19.76 (d), 23.79 (q), 36.71 (q), 40. 54 (t), 43.78 (s), 51.68 (d), 114.96 (s), 122.03 (d), 126.48 (s), 127.62 (d), 127.76 (d), 129.54 (s), 132.29 (s), 138.40 (s); MS (relative intensity): *m/z* = 28 (29.80), 77 (14.97), 91 (14.24), 115 (16.57), 117 (18.02), 144 (16.57), 174 (15.41), 196 (85.17), 203 (M^+, 100), 232 (11.05), 233 (13.35), 262 (34.59), 277 (62.35), 279 (57.12), 294 (M^+, 68.90); HRMS: *m/z* calc.for $C_{18}H_{18}N_2O_2$: 294.137, found 294.137; Anal. calc. for $C_{18}H_{18}N_2O_2$: C, 73.44; H, 6.17; N, 9.52; found C, 73.40; H, 6.21; N, 9.49.

1-Methyl-3-nitro-8,9,10,11-tetrahydrodibenzo[e,g]indole (15) :
EtOH (75 mL) was added to a solution of 2-(cyclohex-1-enyl)-1-methyl-4-nitro-3-phenylpyrrole (**14**, 0.28 g, 1.0 mmol) in CH_2Cl_2 (2 mL). The stirred reaction mixture was irradiated with a high-pressure pyrex immersion mercury UV lamp at rt for 45 h. The solvent was removed and the residue was filtered through a short column of Al_2O_3 (CH_2Cl_2). After washing with pentane, a yellow solid (0.12 g) was obtained, which consisted of a mixture of starting material and indole **15** (ca. 1:1.3). Two crystallizations from EtOH (96 %) gave **15**, as yellow crystals (50 mg, 18 %), pure according to ^{1}H NMR: mp 215-216 °C; ^{1}H NMR($CDCl_3$, 300 MHz): δ = 1.89-1.98 (m, 4H), 3.16-3.18 (m, 2H), 3.27-3.29 (m, 2H), 4.16 (s, 3H), 7.54-7.58 (m, 2H), 7.96 (s, 1H), 8.02-8.04 (m, 1H), 9.25-9.27 (m, 1H); ^{13}C NMR ($CDCl_3$, 125.7 MHz): δ = 22.30 (t), 22.56 (t), 26.92 (t), 27.45 (t), 40.08 (q), 114.39 (s), 122.17 (s), 123.01 (d), 125.21 (s), 125.27 (d), 125.36 (d), 126.45 (s), 130.45 (d), 130.49 (s), 131.59 (s), 132.91 (d), 132.94 (d); MS (relative intensity, %): *m/z* = 28 (90.6), 32 (21.6), 77 (1.9), 115 (3.4), 152 (8.9), 165 (17.3), 178 (8.4), 204 (8.8), 235 (11.7), 280 (M^+, 100); HRMS: *m/z* calc. for $C_{17}H_{16}N_2O_2$: 280.121, found 280.121.

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12. It may well be that the unsuccessful electrocyclization of *N*-H unprotected **4d** is caused by the oxidative power of nitrobenzene.
13. In ref. 2 erroneously named as a 3-(4-phenylethenyl)- instead of 3-(2-phenylethenyl)-pyrrole.
14. As a result of naming the 3-nitroindole derivatives **12** tricyclo-octenopyrroles, compounds **12** become 4-nitropyrrole derivatives and the numbering of the substituents R^6 and R^7 in structure **12** (Scheme 2) no longer corresponds to the numbering used in the compounds name.