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TETRAHEDRON

2-Substituted Indazoles From Electrogenerated *Ortho*-nitrosobenzylamines.

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Abstract: An electrochemical methodology for an efficient access to *ortho*-nitrosobenzylamines has been developed. These products cyclize intramolecularly producing the desired 2-substituted indazoles in high yields. The electrochemical procedure overcomes limitations of previous chemical methods.

INTRODUCTION

The chemistry of indazole derivatives has been stimulated due to their applications in the industrial, agricultural and biological fields.[1] Different approaches to the synthesis of 2-substituted indazoles have been proposed. The reduction of secondary *ortho*-nitrobenzylamines with Sn, Zn or Fe in acidic medium,[2-4] produced 2-substituted indazoles as by-product in low yields. The direct N-alkylation[5] and N-arylation[6] of indazole yielded mixtures of 1- and 2-substituted indazole without selectivity. The reaction of *ortho*-nitrobenzylidenamines with tervalent organophosphorous reagents as deoxygenating agents, resulted in 2-aryl-indazoles with high yields, but the drastic conditions of the reaction and the limitation to using arylamines restricts this reaction.[7-9] Several studies have been carried out in order to achieve this reaction in smoother conditions, but the products were obtained with moderate yields.[10] Similar problems have been observed during the thermal decomposition of *ortho*-azidobenzylidenamines.[11,12]

The electrolysis in two steps (reduction then oxydation) at a mercury electrode of *ortho*-nitrobenzylamines, was carried out to the synthesis of the nitroso derivatives. The electrophilic character of nitroso group was used to generate the N-N bond of 2-substituted indazole. Only benzylamines bearing an electron-donating group were succesfully cyclizated. An electron-withdrawing group decreased dramatically the rate of the intramolecular cyclization and because of a large time-scale for the oxidation step, the intermolecular condensation between the hydroxylamino intermediate and the generated nitroso group produced the azoxy compounds.[13] During the last years, our laboratory has improved an electrochemical "Redox" methodology (*vide infra*), to prepare easily nitrosobenzenes in hydroalcoholic medium at room temperature, with excellent yields.[14,15] A new approach to the synthesis of 2-substituted indazoles, using as key products electrogenerated *ortho*-nitrosobenzylamines is reported in this paper.

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RESULTS AND DISCUSSION

The starting compounds *ortho*-nitrobenzylamines **1**, can be easily prepared by reduction with BH_3[16] of the amides obtained by condensation of *ortho*-nitrobenzoyl chloride and the selected primary amines.[17] When amine substituents are sensitive to BH_3, the *ortho*-nitrobenzylamines **1** can be obtained from the *ortho*-nitrobenzyl bromide and the primary amine.[18]

The electroanalytical studies performed with the amines **1a-g** in hydroalcoholic medium at a glassy carbon electrode, showed that the rate of cyclization changes with the substituent of the benzylamine. As shown by cyclic voltammetry, an electron-donating substituent increases the rate of cyclization between the benzylamine and the electrogenerated nitroso group. For a sweep rate of 200 mVs^{-1} the reduction signal of the nitroso compound is not observed (Figure 1). On the other hand, with electron-withdrawing groups the reduction signal of nitroso compound is observed even at slow sweep rate. The "quasi reversible" system observed (I_a/I_c close to 1) proves that the nitroso group reacts intramoleculary slowly with the benzylamine (Figure 2).

These results show the need to consume totally and quickly the hydroxylamine at the anode producing the nitroso derivative, in order to avoid the formation of the azoxy compounds when the cyclization is slow.[13]

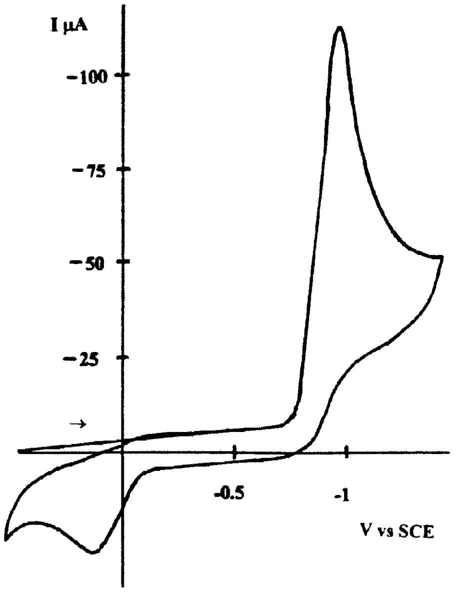


Figure 1: Cyclic voltammetry of **1f**, GC, $0.2Vs^{-1}$
80% MeOH / 20% aqueous buffer (AcOH/AcONa 2.5M)

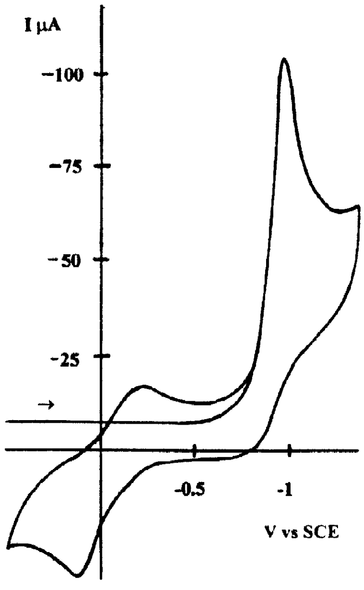
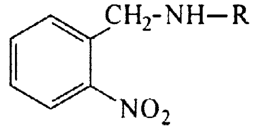


Figure 2: Cyclic voltammetry of **1g**, GC, $0.2Vs^{-1}$
80% MeOH / 20% aqueous buffer (AcOH/AcONa 2.5M)



1a: R=H
1b: R=Me
1c: R=Et
1d: R=Ph
1e: R=Ph(m-Me)
1f: R=Ph(p-OMe)
1g: R=Ph(p-CN)

This problem was solved using a "Redox" flow cell fitted with porous graphite felt electrodes of opposite polarities. Two successive electrolyses reactions were carried out in hydroalcoholic medium at room temperature: a) Reduction at 4 F/mol of nitro group **1** to the corresponding hydroxylamine **2** at the first porous electrode. b) Oxidation at 2 F/mol of the generated hydroxylamine to produce the nitroso compound **3** at the second one (Figure 3). The characteristics and principle of this cell have been previously described.[14,15]

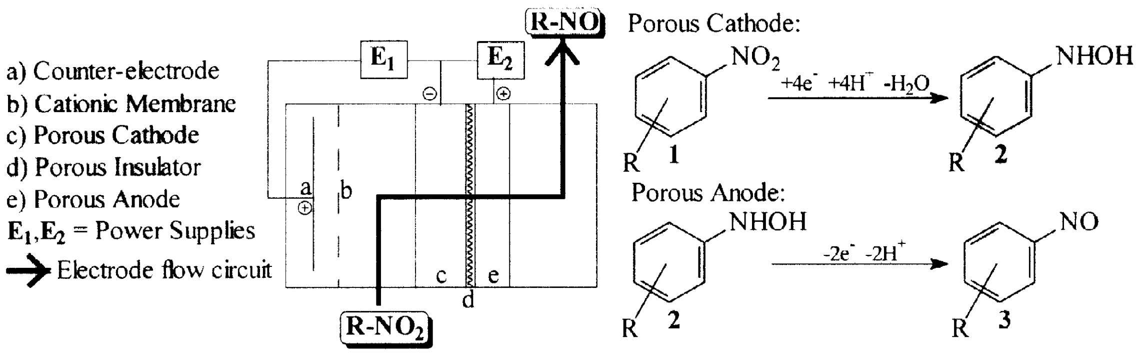
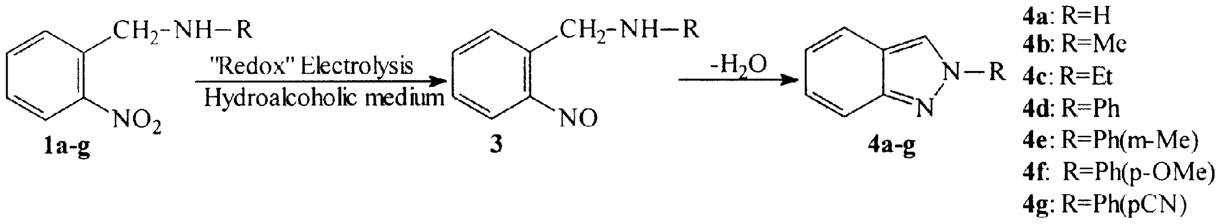


Figure 3.

After the electrolysis, the *quasi* disappearance of the reduction wave (-0.45 V to -0.55 V *vs* SCE) of nitro group **1** (> 90% by polarography) was observed. As shown in the polarographic study of the electrolyzed solution, cyclization occurred at room temperature in the reservoir of the outlet solution and it was not necessary to isolate the electrogenerated *ortho*-nitrosobenzylamines **3**. The overall reaction appears in scheme 1.



Scheme 1.

With electron-donating substituents the rate of cyclization was fast and the polarographic wave of nitroso compounds was not observed after electrolysis. With electron-withdrawing substituents, the characteristics of nitroso compounds[19] could be ascertained: two electrons reduction signal at 0 V to -0.1 V and a strong yellow color of the solution. After some hours under nitrogen, the reduction wave of nitroso group disappeared indicating the end of cyclization, to 2-substituted indazoles **4** (Figure 4).

After work up, the expected 2-substituted indazoles **4** were isolated in 70-85% yield. Some examples of the synthesis of these indazoles are given in table 1.

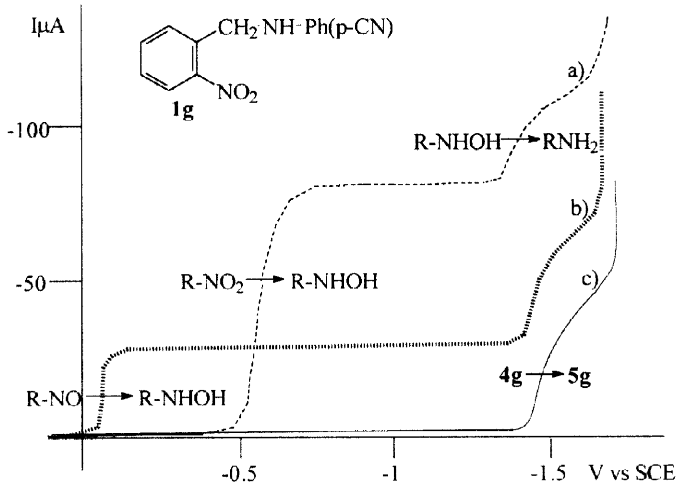


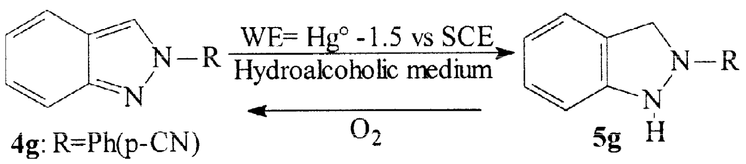
Figure 4. Electrolysis of **1g** in a "Redox" cell. Polarography of the solution: a) Solution before the electrolysis. b) Solution immediately after electrolysis. c) Electrolyzed solution after 3 h under N_2.

Table 1. Electrochemical data for **1a-g** and yields of 2-substituted indazoles **4a-g**.

Initial amine		$E_{½}$** a)	E_{pc}* a)	E_{pa}* b)	E_{pc}* b)	**Indazole, % (Isolated)**	
1a	R=H	-0.535	-0.805	+0.200	-0.185	**4a,**	70
1b	R=Me	-0.520	-0.820	+0.160	----	**4b,**	85
1c	R=Et	-0.465	-0.775	+0.250	----	**4c,**	80
1d	R=Ph	-0.485	-0.800	+0.120	- 0.200	**4d,**	71
1e	R=Ph-(m-CH3)	-0.530	-0.850	+0.135	----	**4e,**	76
1f	R=Ph-(p-OMe)	-0.495	-0.720	+0.100	----	**4f,**	72
1g	R=Ph-(p-CN)	-0.480	-0.750	+0.090	-0.200	**4g,**	70

** 80% MeOH 20% aqueous buffer (AcOH/AcONa 2.5M) Polarography, WE= Hg , c=$2x10^{-3}$M, V *vs* SCE.
* 80% MeOH 20% aqueous buffer (AcOH/AcONa 2.5M), WE= Glassy Carbon, v=$0.1Vs^{-1}$, c=$2x10^{-3}$M, V *vs* SCE. a) Reduction wave of nitro group to hydroxylamine derivative. b) Redox system hydroxylamine-nitroso.

The 2-phenyl indazole substituted with an electron-withdrawing group (**4g**), showed a reduction wave of two electrons at -1.5 V vs SCE (Figure 4. entry c). It was selectively reduced at a mercury cathode in the same hydroalcoholic medium to produce the 2-substituted indazoline **5g** with 93% yield (Scheme 2). This indazoline was air sensitive due to its low oxidation potential (-0.25 V *vs* SCE), and it was necessary to isolate it under inert atmosphere.



Scheme 2.

CONCLUSION

The efficiency of the "Redox" process to prepare aromatic nitroso compounds electrochemically in smooth conditions, from corresponding nitrocompounds without coupling avoiding the azoxy derivatives, allowed us to synthesize 2-substituted indazoles with good yields. This is a general method for the synthesis of 2-alkyl and 2-phenyl indazoles, overcoming the limitations of previous chemical preparations. The 2-phenyl-indazoles substituted with an electron-withdrawing group, can be selectively reduced at a mercury cathode to the 2-substituted indazolines with very good yields. The application of this methodology for heterocycle synthesis of six and seven members (cinnolines and benzodiazepines) is in progress.

EXPERIMENTAL

General.

Melting points were determined in a Kofler apparatus and are uncorrected. The IR spectra were recorded on a Nicolet 205 FT-IR instrument (in KBr). The NMR spectra were determined for solutions in deuterochloroform with TMS as internal reference and obtained on a Brucker DPI 200 FT spectrometer at 200 MHz (^{1}H) and 50 MHz (^{13}C). Mass spectra were obtained on a VARIAN MAT 311 high resolution mass spectrometer. Elemental analyses were obtained only for the new compounds and they were done at the « Service Central d'Analyse, Département Analyse Elémentaire CNRS» (Vernaison). Thin-layer chromatography (TLC) was performed in aluminium sheets pre-coated with silica gel (Macherey-Nagel Alugram Sil G/UV^{254}). Column chromatography was performed on silica gel (Acros 0.030-0.075mm). Reagents were purchased from Aldrich Chemical Co. and Acros Chemical Co. and they were used without previous purification.

Electrochemical instrumentation and Procedures.

Conventional electrochemical equipment was used for polarography, cyclic voltammetry and controlled potential electrolyses (EG&G Princeton Applied Research model 362-scanning potentiostat with an XY recorder). Controlled potential electrolyses were performed at a mercury pool cathode, under nitrogen atmosphere, in a cell previously described.[20] The coulometric measurements were determined with a current integrator Tacussel model IG 5 N. "Redox" electrolyses were performed at controlled current, under nitrogen atmosphere, in a flow cell previously described.[14,15] Two working electrodes (5.2 cm diameter, 12 mm thickness for cathode and 6 mm thickness for anode) were made of graphite felt (LE CARBONE LORRAINE). The cell worked with two power supplies 0-30 V/ 3 A. The current intensities were calculated from the Faraday's law; for the same current intensities in the two electrical circuits, the cathodic current is twice the anodic intensity. Electrolyses were monitored by polarography (Scan-rate : 5 mv s^{-1} ; drop-time t : 2 s).

General procedure for preparative "Redox" electrolyses. Ortho-nitrobenzylamine **1** (4-8 mmol) was dissolved in a mixture (300-1000 ml) of acetic/acetate buffer (AcOH 2.5 mol l^{-1} + AcONa 2.5 mol l^{-1}) and methanol (1:4 v:v). Nitrogen was bubbled through this solution for 30 min before electrolysis. The solution was pumped through the cell from a reservoir using a peristaltic pump. The flow rate (4.8 to 5.2 ml mn^{-1}) was measured from the outlet solution. The current intensities (I_1=I_2) were calculated from the Faraday's law according to the quantity of substrate flowing through the porous electrodes per second. The efficiency of electrolyses was controlled by polarography directly in the reservoir of the outlet solution. On complete disappearance of the nitroso reduction signal, the solution was neutralized with $NaHCO_3$ (pH=7-8) and the methanol was removed under vacuum rotary evaporation. The reaction mixture was extracted with CH_2Cl_2 (4 x 30 ml). The organic fraction was dried over $MgSO_4$ and concentrated by rotary evaporation. The crude reaction products obtained, were purified by medium pressure column chromatography.

General procedure for preparative controlled potential electrolyses. The 2-substituted indazole (4 mmol) was dissolved in a mixture (150 ml) of acetic/acetate buffer (AcOH 2.5 mol l^{-1} + AcONa 2.5 mol l^{-1}) and methanol (1:4,v:v). Nitrogen was bubbled through it for 20 min. The solution was electrolyzed under nitrogen at controlled potential (-1.5 V *vs* SCE). The electrolysis was monitored by polarography directly in the cell. After complete disappearance of the starting material the electrolysis was stopped. The hydro-organic mixture was separated from mercury with a cannula and the reduced product was separated under argon using conventional schlenck techniques; the methanol was removed under vacuum evaporation and the obtained precipitate was washed with distilled water (4 x 30 ml). The crude precipitate was dried for 1 hr under vacuum. The NMR spectrum of this crude precipitate showed more than 90% yield of indazoline.

Indazole (4a). After "Redox" electrolysis of *ortho*-nitrobenzylamine **1a** (0.88 g 5.79 mmol) in 300 ml of buffer solution and separation by column chromatography (Petroleum ether/EtOAc 85:15), the indazole **4a** was recrystallized from petroleum ether/ether and was obtained as a white crystalline product m.p. 142-145°C (lit. 147°C [21]); 0.48 g, 70%. IR (KBr): 3409, 3175, 1623, 1503, 1384, 1355, 1250, 1202, 1068, 950, 846, 743 cm^{-1}. ^1H NMR ($CDCl_3$); δ ppm J=Hz: 11.3 (s, 1H, int.-D_2O; N-H), 8.09 (d, 1H, J=0.8; H-3), 7.76 (dt, 1H, J=8.1, 1.0; H-4), 7.49 (dq, 1H, J=8.4,1.0; H-7), 7.38 (ddd, J=8.4, 6.8, 1.1; H-6), 7.16 (ddd, 1H, J=8.1, 6.7, 1.1; H-5).

2-methyl-indazole (4b). After "Redox" electrolysis of N-(*ortho*-nitrobenzyl)-methylamine **1b** (0.9 g 5.42 mmol) in 400 ml of buffer solution and purification by column chromatography (Petroleum ether/EtOAc 65:35), the indazole **4b** was recrystallized from petroleum ether/ether and was obtained as a white crystalline product m.p. 54-57°C (lit. 56°C [21]); 0.6 g, 85%. IR (KBr): 3106, 3079, 1635, 1520, 1435, 1385, 1297, 1180, 1013, 821, 755, 742 cm^{-1}. ^1H NMR ($CDCl_3$); δ ppm J=Hz: 8.07 (s, 1H; H-3), 7.87 (dq, 1H, J=8.1, 0.9; H-7), 7.78 (dt, 1H, J=7.8, 1.0; H-4), 7.26 (ddd, 1H, J=8.1, 6.2, 1.1; H-6), 6.96 (ddd, 1H, J=7.8, 6.2, 0.9; H-5), 2.75 (s, 3H; CH_3). ^{13}C NMR ($CDCl_3$); δ ppm: 148, 125.6, 123. 3, 121.8, 121.3, 119.7, 116.9, 39.9. HRMS EI *m/z* (rel. int.): M^+ 132.0688 (100), 131 (29.1), 104 (20.2), 90 (10.6), 78 (10.6), 66 (7.51), 63 (11.5), 42 (13), 39 (5.6), 28 (7.6), 18 (15.4). $C_8H_8N_2$ requires M^+ at 132.0687.

2-ethyl-indazole (4c). After "Redox" electrolysis of N-(*ortho*-nitrobenzyl)-ethylamine **1c** (1 g 5.55 mmol) in 400 ml of buffer solution and purification by column chromatography (Petroleum ether/EtOAc 70:30), the indazole **4c** was obtained as a colourless oil (lit. colourless oil [21]); 0.65 g, 80%. IR (KBr): 3098, 3010, 1639, 1515, 1394, 1158, 1142, 785, 757 cm^{-1}. ^1H NMR ($CDCl_3$); δ ppm J=Hz: 7.79 (s, 1H; H-3), 7.69 (dd, 1H, J=8.7, 0.9; H-7), 7.58 (d, 1H, J=8.4; H-4), 7.23 (ddd, 1H, J=8.7, 6.7, 1.0; H-6), 7.02 (ddd, 1H, J=8.5, 6.7, 0.7; H-5), 4.37 (q, 2H, J=7.4; CH_2), 1.53 (t, 3H, J=7.4; CH_3). ^{13}C NMR ($CDCl_3$); δ ppm: 148.5, 125.5, 121. 6, 121.5, 121.2, 119.8, 117.1, 48.2, 15.6. HRMS EI *m/z* (rel. int.): M^+ 146.0852 (43.2), 131 (1.5), 118 (100), 104 (2.6), 102 (2.6), 91 (23.6), 77 (9.4), 63 (11.3), 51 (6.23), 28 (9.6). $C_9H_{10}N_2$ requires M^+ at 146.0843.

2-phenyl-indazole (4d). After "Redox" electrolysis of N-(*ortho*-nitrobenzyl)-aniline **1d** (1.8 g 7.89 mmol) in 800 ml of buffer solution and purification by column chromatography (Petroleum ether/Acetone 93:7), the indazole **4d** was recrystallized from petroleum ether/ether and was obtained as a white crystalline product m.p. 80-82°C (lit. 82-83°C [7]); 1.08 g, 71%. IR (KBr): 3140, 3030, 1629, 1596, 1522, 1499, 1460, 1392, 1208, 1074, 1047, 781, 749, 684, 509, 438 cm^{-1}. ^1H NMR ($CDCl_3$); δ ppm J=Hz: 8.33 (d, 1H, J=0.9; H-3), 7.86 (dm, 2H, J=8.1; H-2'), 7.81 (dd, 1H, J=8.0, 1.0; H-7), 7.67 (dt, 1H, J=8.5, 1.0; H-4), 7.48 (t, 2H, J=8.1; H-3'), 7.37 (dt, 1H, J= 7.9, 1.2; H-4'), 7.32 (ddd, 1H, J=7.9, 6.3, 1.1; H-6), 7.09 (ddd, 1H, J=8.5, 6.3, 0.9; H-5). ^{13}C NMR ($CDCl_3$); δ ppm: 149.6, 140.3, 129.4, 127.7, 126.7, 122.6, 122.3, 120.7, 120.3, 117.7. HRMS EI *m/z* (rel. int.): M^+ 194.0831 (100), 193 (16.3), 168 (11.3), 167 (13.5), 165 (13.0), 140 (2.4), 139 (2.3), 129 (2.2), 118 (1.3), 115 (1.1), 97 (6.4), 91 (1.7), 77 (19.4), 66 (6.5), 63 (4.46), 51 (14.7), 18 (14.6). $C_{13}H_{10}N_2$ requires M^+ at 194.0843.

2-(*m*-methylphenyl)-indazole (4e). After "Redox" electrolysis of N-(*ortho*-nitrobenzyl)-*m*-toluidine **1e** (2 g 8.26 mmol) in 1000 ml of buffer solution and purification by column chromatography (Petroleum ether/EtOAc 97:3), **4e** was obtained as a colourless oil; 1.3 g, 76%. IR (KBr): 3050, 1634, 1612, 1592, 1519, 1494, 1384, 1055, 779, 755 cm^{-1}. ^1H NMR ($CDCl_3$); δ ppm J=Hz: 8.23 (d, 1H, J=0.7; H-3), 7.82 (dd, 1H, J=8.8, 0.7; H-7), 7.71 (s, 1H; H-2'), 7.61 (dt, 1H, J=7.6, 0.9; H-6), 7.58 (dd, 1H, J= 7.5, 0.9; H-4), 7.29 (ddd, 1H, J=8.7, 7.6, 0.9; H-6'), 7.28 (dd, 1H, J= 7.7, 7.7; H-5'), 7.15-7.01 (m, 2H; H-5 and H-4'), 2.35 (s, 3H; CH_3). ^{13}C NMR ($CDCl_3$); δ ppm: 149.2, 139.9, 139.2, 128.8, 128.1, 126.3, 122.2, 121.8, 121.09, 120.01, 119.9, 117.4, 117.3, 20.9. HRMS EI *m/z* (rel. int.): M^+ 208.0999 (100), 207 (29.3), 193 (1.5), 180 (15.1), 168 (3.9), 165 (24.2), 129 (4.5), 117 (1.2), 104 (5.8), 91 (17.9), 89 (5.7), 75 (2.4), 65 (25.5), 39 (27.7). $C_{14}H_{12}N_2$ requires M^+ at 208.1000. E.A.: $C_{14}H_{12}N_2$ requires C 80.74%, H 5.81%, N 13.45%, found C 80.59%, H 5.71%, N 13.27%.

2-(*p*-methoxyphenyl)-indazole (4f). After "Redox" electrolysis of N-(*ortho*-nitrobenzyl)-*p*-anisidine **1f** (1.82 g 6.97 mmol) in 800 ml of buffer solution and purification by column (Petroleum ether/EtOAc 90:10), the indazole **4f** was recrystallized from ether/CH_2Cl_2 and was obtained as a white crystalline product m.p. 133-135°C (lit. 130-131°C [7]); 1.12 g, 72%. IR (KBr): 3137, 3032, 2955, 2848, 1640, 1620, 1528, 1509, 1383, 1303, 1245, 1207, 1177, 1108,1047, 838, 811, 780, 755, 521 cm^{-1}. ^{1}H NMR ($CDCl_3$); δ ppm J=Hz: 8.22 (s, 1H; H-3), 7.79 (dd, 1H, J=8.7, 0.9; H-7), 7.73 (dt, 2H, J=9.1, 2.2; H-2'), 7.63 (dd, 1H, J=8.4, 1.1; H-4), 7.29 (ddd, 1H, J=8.8, 6.6, 1.1; H-6), 7.07 (ddd, 1H, J=8.4, 6.6, 0.9; H-5), 6.95 (dt, 2H, J=9.1, 2.1; H-3'), 3.78 (s, 3H;CH_3). ^{13}C NMR ($CDCl_3$); δ ppm: 160.8, 150.9, 135.1, 127.4, 123.5, 123.1, 122.99, 121.0, 121.0, 118.4, 115.24, 54.9. HRMS EI *m/z* (rel. int.): M^+ 224.0947 (100), 209 (38.6), 195 (6.6), 181 (35.9), 165 (6.9), 153 (6.9), 127 (9.69), 112 (4.79), 92 (6.79), 77 (8.72), 64 (17.5), 15 (29.1). $C_{14}H_{12}N_2O$ requires M^+ at 224.0949.

2-(*p*-benzonitrile)-indazole (4g). After "Redox" electrolysis of N-(*ortho*-nitrobenzyl)-*p*-aminobenzonitrile **1g** (2.02 g 5.9 mmol) in 800 ml of buffer solution and purification by column chromatography (Petroleum ether/EtOAc 85:15), **4g** was recrystallized from CH_2Cl_2/ether and was obtained as a yellow crystalline product m.p. 159-161°C (lit. 107°C [8]); 1.2 g, 70%. IR (KBr): 3131, 2228, 1604, 1521, 1423, 1381, 1312, 1208, 1042, 952, 839, 820, 784, 761, 547 cm^{-1}. ^{1}H NMR ($CDCl_3$); δ ppm J=Hz: 8.37 (d, 1H, J=0.9; H-3), 7.98 (dt, 2H, J=8.9, 2.2; H-2'), 7.7 (dt, 3H, J=8.9, 2.2; H-3' and H-7), 7.62 (dt, 1H, J=8.5, 1.1; H-4), 7.29 (ddd, 1H, J=8.7, 6.6, 1.1; H-6), 7.08 (ddd, 1H, J=8.5, 6.6, 0.9; H-5). ^{13}C NMR ($CDCl_3$); δ ppm: 151.6, 144.4, 134.6, 128.75, 124.1, 123.9, 121.43, 121.3, 121.1, 118.8, 118.7, 111.6. HRMS EI *m/z* (rel. int.): M^+ 219.0797 (100), 218 (7.3), 192 (12.6), 190 (10.1), 168 (4.32), 164 (3.9), 129 (2.7), 109.5 (2.7), 102 (20.6), 91 (5.9), 75 (7.7). $C_{14}H_9N_3$ requires M^+ at 219.0796. E.A.: $C_{14}H_9N_2$ requires C 76.70%, H 4.14%, N 19.17%, found C 76.05%, H 4.13%, N 19.17%.

2-(*p*-benzonitrile)-indazoline (5g). After controlled potential electrolysis of 2-(*p*-benzonitrile)-indazole **4g** (1 g 4.53 mmol) in 150 ml of buffer solution and work up of the reaction mixture, **5g** was obtained as a cream powder m.p. 118-120°C; 0.92 g, 93%. IR (KBr): 3381, 3214, 2882, 2825, 2206, 1605, 1599, 1517, 1463, 1376, 1249, 1180, 1146, 1084, 816, 784, 760, 543 cm^{-1}. ^{1}H NMR ($CDCl_3$); δ ppm J=Hz: 7.49 (dm, 2H, J=9.0; H-3'), 7.28-7.13 (m, 2H; H-4, H-6), 7.09-6.87 (m, 4H; H-7, H-5, H-2'), 5.97 (s, 1H, int-D_2O; N-H), 4.89 (s, 2H; CH_2). ^{13}C NMR ($CDCl_3$); δ ppm: 152.9, 145.2, 133.2, 128.2, 127.1, 123.2, 122.6, 120.1, 112.6, 112.2, 99.8, 55.8. HRMS EI *m/z* (rel. int.): M^+ 221.0960 (55.8), $[M-H]^+$ 220.0890 (100), 219 (28.4), 192 (3.2), 180 (1.7), 166 (2.4), 118 (3.8), 102 (9.7), 91 (8.1), 76 (5.8), 65 (2.7), 63 (3.4). $C_{14}H_{11}N_3$ requires M^+ at 221.0952 and $[M-H]^+$ at 220.0874. E.A.: $C_{14}H_{11}N_3$ requires C 76.00%, H 5.01%, N 18.99%, found C 75.18%, H 4.48%, N 18.90%.

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