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Synthesis and Electrochemical Behaviour of 2-*N*-Substituted Indazoles

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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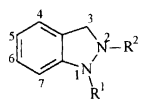
A new 2-*N*-aryl-3-methoxycarbonylindazole synthesis from the 6 F mol^{-1} reduction of appropriately substituted aryl-nitrones has been developed. The indazoles bearing an electron withdrawing group in the 2-position are electroreducible compounds at high negative potentials producing selectively the corresponding 2-*N*-substituted indazolines in aqueous alcoholic medium. The nitrile and ester groups are not reduced under the reaction conditions. Three new 2-*N*-aryl-indazolines were synthesized and characterized. A second electron withdrawing group attached at the 3-position leads to a less cathodic reduction of the 2-*N*-aryl-3-methoxycarbonylindazole. An appropriately substituted indazoline was used to generate *in situ* a new tetracyclic heterocycle.

In a previous paper we described an electrochemical approach to the synthesis of 2-substituted indazoles. We noted that 2-(4-cyanophenyl)indazole was electroreducible to the corresponding 2-(4-cyanophenyl)indazoline.[1] Owing to the low oxidation potential of 2-arylindazolines, they are air-sensitive products. We have studied more closely this new approach to the 2-substituted indazolines (Scheme 1, $R^1 = H$), in order to determine the possible applications and limitations of this reaction. These 2-substituted heterocycles are not common compounds and only 2-phenylindazoline has been described.[2,3a]

Quite a few 1,2-disubstituted indazolines (Scheme 1, R^1 and $R^2 \neq H$) can be found in the literature.[3–5] In the synthesis of the majority of these compounds, the protection of the 1- and 2-positions was done before the generation of the indazoline ring. Indazolones have been used extensively as precursors of these reduced heterocycles. After protection of the 1- and 2-positions, the carbonyl function is reduced with $LiAlH_4$ to give the 1,2-disubstituted indazoline ring.[3] The reduction of 1,2-dialkylindazolium salts with $LiAlH_4$ produced the desired 1,2-dialkylindazolines in good yields.[4] In both methods the reactive and unselective reducing agent $LiAlH_4$ is used, therefore the presence of substituents or other functions in the ring is limited in this procedure. The catalytic hydrogenation of 2-substituted indazoles produces 2-substituted 4,5,6,7-tetrahydroindazoles with no trace of 2-substituted indazoline.[5]



Scheme 1.

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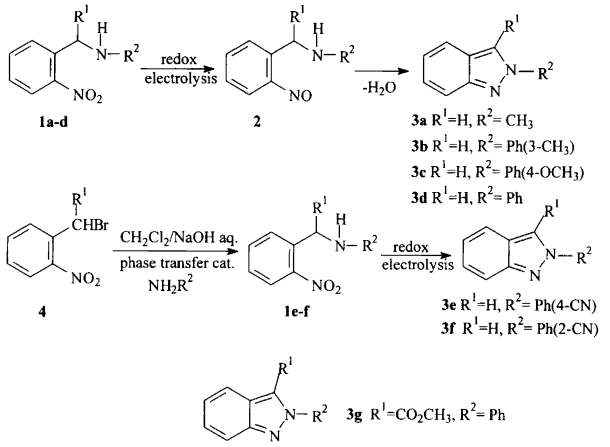
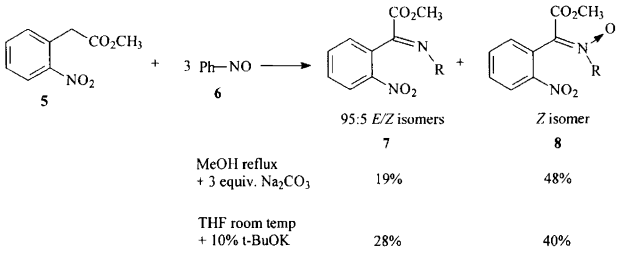
Results and discussion

Synthesis of 2-substituted-indazoles. The 2-substituted indazoles **3a–f** were synthesized from the 2-nitrobenzylamines **1** in a redox flow electrolysis cell in good yields as described previously;[1] only 3-methoxycarbonyl-2-arylindazole **3g** was synthesized by a new method.

Synthesis of 3-methoxycarbonyl-2-arylindazole **3g**. The condensation between nitrosoarenes and an activated methylene group leads to a mixture of imine and nitrone compounds (Erlich–Sachs reaction).[6a] The condensation between the 2-nitrophenylacetic acid methyl ester **5** and three equivalents of nitrosobenzene **6** in MeOH or THF produced mixtures of the imine **7** and nitrone **8** (Scheme 3). The ratio imine/nitrone is variable in this reaction, because factors such as the structure of the methylene compound, the acidity of the methylene hydrogen, the oxidizing character of the nitrosoarenes and the



Scheme 2.

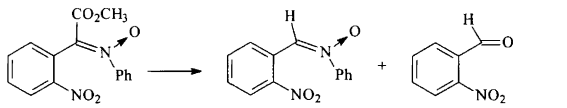


Scheme 3.

reaction conditions influence the competition between the dehydration and oxidation reactions.[6b,c]

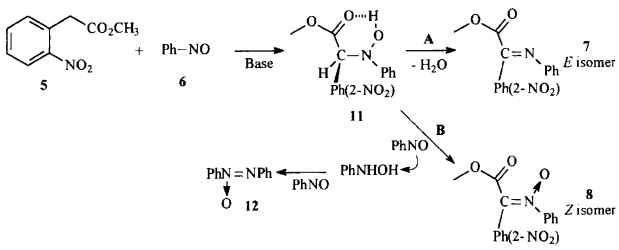
The ^{1}H NMR spectrum of the isolated imine **7** showed that a mixture of *E* and *Z* isomers was present in a 95:5 ratio. We observed two α-methoxycarbonyl group signals in the ^{1}H NMR spectrum corresponding to *E* and *Z* isomers of the imine **7** at $\delta = 3.95$ and $\delta = 3.53$, respectively. The carbon signals in the ^{13}C NMR spectrum are doubled, showing the presence of both isomers. In phenylimino compounds the nitrogen atom is of the sp^2 type and the phenyl plane is nearly perpendicular to the C=N plane.[7a,b] Owing to the anisotropic effect of the phenyl group the ^{1}H NMR shift of substituents of *E* and *Z* isomers is different (*syn* to phenyl group or *Z* isomer at high field) and their stereochemistry can be assigned.

The decarboxylation reaction of nitrone **8** produced the aldonitrone **9** in moderate yields, allowing us to determine the geometry of **8**. The decarboxylation conditions and stabilization of the electron withdrawing group $C_6H_4NO_2$-2 were used to favour an SE_1 mechanism.[8a] In this mechanism the C=N bond is not broken during the decarboxylation reaction due to the generation of a benzylic carbanion stabilized by the nitrophenyl group.[8b] The appreciable difference in the ^{1}H NMR chemical shifts of the azomethine protons of the *Z* (ca. δ 7.2–7.4) and *E* (ca. δ 8.2–8.4) aldonitrone isomers can be used to accomplish the stereochemical determination of the structure.[9] The nitrone **9** showed a chemical shift of the azomethine proton at 8.59 ppm for the *E* isomer, therefore the nitrone **8** must be the *Z* isomer. The ^{1}H NMR



MeOH–H_2O 2:1 + 1 equiv. Na_2CO_3, 2 h, reflux	28%	41%
MeOH, 2 equiv. H_2O + 1 equiv. Na_2CO_3, 18 h, reflux	40%	20%
MeOH, 2 equiv. H_2O + 1 equiv. Na_2CO_3, 18 h, room temp.	—	—

Scheme 4.



Scheme 5.

study confirmed this result because the methoxycarbonyl group of the *E* isomer of α-methoxycarbonyl-α-*N*-diphenylnitrone displays a signal at $\delta = 3.47$.[10] In our case the methoxycarbonyl group appears at $\delta = 3.65$ ppm, which is in accordance with the expected position (at low field) for the *Z* isomer, due to the same anisotropic effect of the phenylimino group observed for the imines **7**.[7]

The 2-nitrobenzaldehyde **10** is obtained as by-product. It is probably generated from the alkaline hydrolysis of the aldonitrone **9** in the reaction medium (Scheme 4).[11]

The selectivity of the condensation reaction leading to the formation of the *Z* isomer of nitrone **8** and the *E* isomer of imine **7** is an interesting result because these isomers are not generally obtained in this condensation reaction. Steric hindrance caused by the substituents in the intermediate of condensation induces the formation of isomers with the substituents in an *anti* disposition.[9,12] The stereoselectivity of the reaction probably results from an interaction between the carboxy group and the *N*-hydroxy function generated immediately after the condensation on the intermediate **11** (Scheme 5). This interaction minimizes free rotation about the C–N bond producing essentially the *E* isomer of imine **7** by pathway A according to the selective elimination of –OH group. Pathway **B** leads to the oxidation of the *N*-hydroxy function by the nitrosoarene **6** to the *Z* isomer of nitrone **8**. The azoxy-compound **12** is obtained as a by-product.

The electroanalytical study of nitrone **8** in a slightly acidic aqueous alcoholic medium showed three reduction waves during polarography and cyclic voltammetry. The first one is an irreversible prewave located at $E_{1/2} = -0.195$ V and $E_{pc} = -0.320$ V vs. SCE. The reversible system of the pair hydroxylamine-nitroso ($E_{pa} = +0.010$, $E_{pc} = -0.110$ V vs. SCE) is observed when the potential

sweep reaches −0.500 V vs. SCE, showing that in the second reduction wave ($E_{1/2}$ = −0.460 V and E_{pc} = −0.505 V vs. SCE), the reduction at 4 F mol^{-1} of the nitro group into hydroxylamino derivative occurs (Fig. 1). The electroreduction of **8** at a potential corresponding to the second cathodic wave consumed 5.8–6.3 F mol^{-1}. These results showed that, at this potential, it is possible to conduct the electroreduction of nitrone **8** with 6 F mol^{-1} to achieve the selective reduction of the nitro function into hydroxylamine and the nitrone group into imine. A third reduction wave ($E_{1/2}$ = −1.100 V and E_{pc} = −1.250 V vs. SCE) (not shown) is assigned to the reduction of the electrogenerated imine group to amine.

The results of the preparative electroreductions of nitrones **8** in aqueous alcoholic media at a mercury cathode and in a flow cell fitted with a graphite felt cathode are summarized (Table 1). Three compounds were obtained as major products: the 2-aryl-3-methoxycarbonylindazole (**3g**), the 3-methoxycarbonylbenzoisoxazole (**13**) and the 2-aryl-3-methoxycarbonylindazole 1-oxide **14** (Scheme 6).

The addition of the hydroxylamine nitrogen to the imine **15** generates the 1-hydroxyindazoline **16** which, by loss of water, produces the expected 2-aryl-3-methoxycarbonylindazole (**3g**). The carbon of the imine group in **15** bears an aryl and a carboxy group; both can stabilize the negative charge generated during the addition to the double bonds.[13,14] This stabilization could favour the nucleophilic attack of hydroxylamine group at nitrogen atom.

The low oxidation potential of *N*-hydroxy heterocycles such as **16** is known.[15] Because of the low reduction potential of the pair nitrone/imine (*vide supra*), the oxidation of **16** by the nitrone **8** produces the 2-arylindazole 1-oxide **14**. The benzoisoxazole **13** results from the *C*-addition of the hydroxylamine oxygen on the imine function of **15**. After work-up of the reaction we confirmed the presence of aniline by TLC.

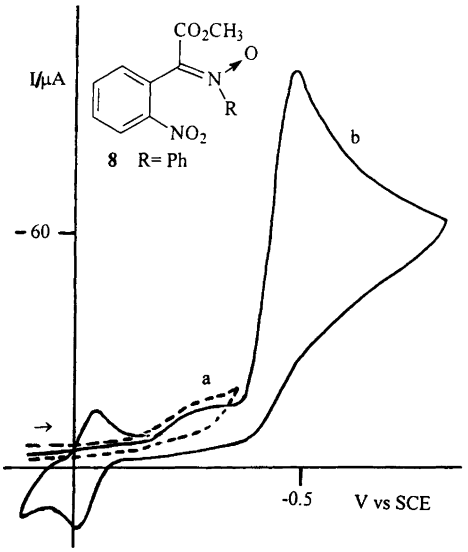


Fig. 1. Cyclic voltammogram of nitrone **8** 2 × 10^{-3} M in aqueous alcoholic medium (80% MeOH, 20% aqueous acetate buffer 2.5 M). WE = Hg^0, v = 0.1 V s^{-1}: a, sweep potential until −0.35 V; b, sweep potential until −0.85 V.

As we can see (Table 1) the yields of 2-aryl-3-methoxycarbonylindazole (**3g**) are almost the same after electrolysis at a mercury cathode or in a flow cell. Nevertheless, because of the *C* addition reaction, the possibility of nucleophilic attack of the hydroxylamino group at the ester group and the possibility of hydrolysis of the imine function complicated the reaction and the best yield for the indazole **3g** was limited (40%).

Electroanalytical study of indazoles **3**. The polarographic and voltammetric studies of indazoles **3** performed in an aqueous alcoholic medium (80% MeOH, 20% aqueous acetic buffer 2.5 M), showed that only the indazoles substituted in the 2-position with an aryl electron-withdrawing group (**3d–g**) were electroreducible compounds (Scheme 7). The electrochemical data of indazoles **3** are summarized (Table 2).

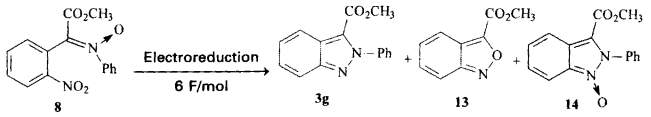
From the polarographic studies we observe that an electron-withdrawing group (CN) on the aryl substituent (**3e–f**) caused a decrease (−0.22 V) in the cathodic potential with respect to 2-phenylindazole **3d**. A second electron-withdrawing group attached to the indazole ring in the 3-position (**3g**) induces the strongest deacrease in the cathodic potential (−0.6 V) with respect to 2-phenylindazole (**3d**). These results are in accordance with easier electron transfer when the carbonyl substituent is in the 3-position since this facilitates the charge resonance, due probably to the stability of the aromatic system of the aryl substituent in the 2-position. This electron transfer is not favoured when the indazole bears an electron donating group at N-2 (even an electron-rich phenyl group **3b, c**).

The oxidation potential values of the electrogenerated indazolines **21** are very low ($E_{1/2}$ = −0.34 to −0.03) and they are air-sensitive products.

Preparative electroreduction of 2-arylindazoles **3**. The preparative electrolyses were performed at a mercury cathode in aqueous alcoholic medium (80% MeOH, 20% aqueous acetic buffer 2.5 M) or a quasi-non-aqueous medium (100% MeOH, AcOLi–AcOH 0.5 M).

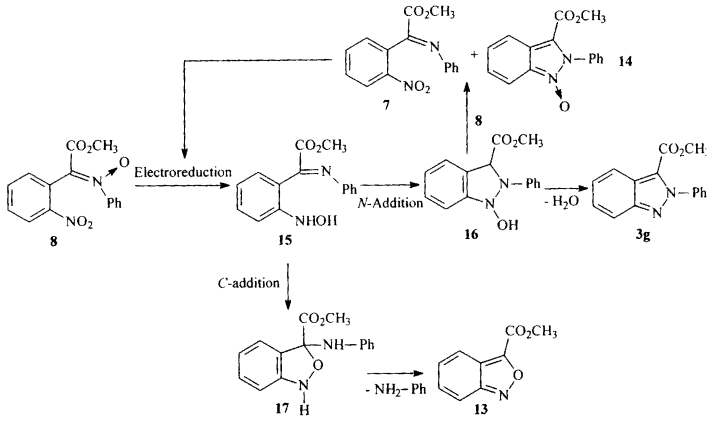
The 2-arylindazoles **3d–g** showed a reduction wave of two electrons (Fig. 2a). However, because of the proximity of the solvent discharge, the electrolyses can consume more than the theoretical quantity of electricity (2 F mol^{-1}). Compounds **3d–g** were selectively electroreduced to produce the 2-substituted indazolines **21** (Scheme 6). At the end of the electrolysis, an oxidation wave was observed for the electrogenerated indazoline (Fig. 2b). When air was bubbled through the electrolyzed solution, the anodic wave corresponding to the 2-arylindazolines **21** disappeared to regenerate the reduction wave of 2-arylindazoles **3**. Therefore, it was necessary to

Table 1.

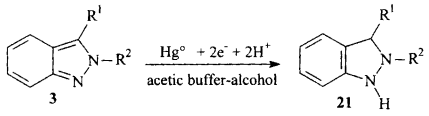


Electrolysis media	E_t/V vs. SCE	F mol^{-1}	Isolated yield (%) 3g	13	14
80% MeOH, 19% H_2O, 1% H_2SO_{4conc}	−0.35[a]	6.1	11	73	—
80% MeOH,	−0.5[a]	6.3	16	20	—
20% acetate buffer 2.5 M pH = 4.8	CCE[b]	6[c]	40	10	—
80% MeOH,	−0.7[a]	6.1	28	31	10
20% acetate buffer 2.5 M pH = 6	CCE[b]	6[c]	30	11	15
80% MeOH, 20% NH_3–NH_4NO_3 buffer	−0.8[a]	5.8	12	—	22
2.5 M pH = 9.2	CCE[b]	6[d]	13	—	25
100% MeOH	−0.8[a]	6.1	21	31	5
acetate buffer 2.5 M pH = 4.8	CCE[b]	6[e]	18	8	10

[a]Electroreduction at a mercury cathode (Controlled Potential Electrolysis). [b]Electrodreduction in a flow cell with porous graphite cathode (Controlled Current Electrolysis, CCE): 6 F mol^{-1} is the theoretical quantity of electricity used in the flow cell, flow = 5 ml s^{-1}. [c]I_{cat} = 0.157 A and c = 3.33 mM. [d]I_{cat} = 0.242 A and c = 5 mM. [e]I_{cat} = 0.536 A and c = 11 mM.



Scheme 6.



Scheme 7.

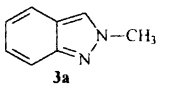
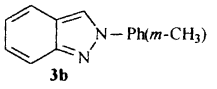
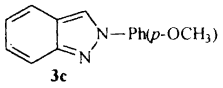
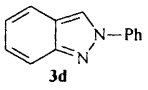
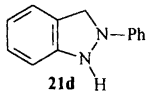
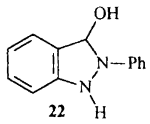
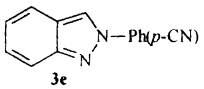
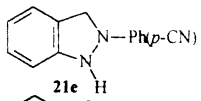
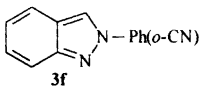
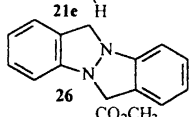
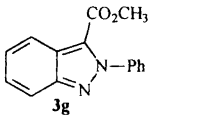
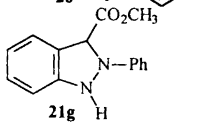
isolate the indazolines under an inert atmosphere. The products and yields are shown in Table 2.

The electroreduction of indazoles **3e** and **3g** generated the indazolines **21e** and **21g**, respectively, in very good yield (90%). These products were slowly oxidized in the solid state.

The reduction wave of indazole **3d** is near the solvent discharge. During reduction at −1.7 V vs. SCE, hydrogen was produced at electrode. After 8 F mol^{-1} the anodic wave of the generated indazoline levelled off and the electrolysis was stopped. After work-up under inert atmosphere two products were detected by ^{1}H NMR spectroscopy in the solid crude product, the expected indazoline **21d** in 65% yield, and the 2-phenyl-3-hydroxyindazoline **22** in 35% yield. When oxygen was bubbled directly into the NMR tube (solvent $CDCl_3$), the ^{1}H NMR control showed that both products regenerate the 2-phenylindazole **3d**. The indazoline **22** can be generated at the surface of the electrode by nucleophilic attack of the OH^- anion to the indazole ring. Under the electrolysis conditions the solution at the surface of the electrode must be highly basic, because of the important reduction of water. After slow recrystallization from $CHCl_3$, we obtained the pure 2-phenylindazoline (**21d**) as pale yellow crystals in 25% yield.

We have tried to trap by intramolecular cyclization the electrogenerated indazoline bearing a nitrile group attached in the *ortho*-position of the phenyl substituent. The electrolysis of indazole **3f** consumed 8 F mol^{-1} and several colours (yellow, green and blue) were

Table 2. Electrochemical data and yields of the electroreduction of indazoles **3** in 80% MeOH, 20% aqueous acetate buffer (AcOH–AcONa 2.5 M).

Indazole	$E_{1/2c}$/ V vs. SCE[a]	$E_{1/2a}$/ V vs. SCE[b]	E_{pc}/ V vs. SCE[a]	E_{pa}/ V vs. SCE[b]	E_w/ V vs. SCE	Product (isolated yield)
 **3a**	[c]	[c]	[c]	[c]	—	—
 **3b**	[c]	[c]	[c]	[c]	—	—
 **3c**	[c]	[c]	[c]	[c]	—	—
 **3d**	−1.75	−0.44	[d]	−0.35	−1.75	 **21d** 65%[e] (25%)  **22** 35%[e]
 **3e**	−1.49	−0.34	−1.53	−0.23	−1.55	 **21e** (98%)
 **3f**	−1.48	−0.03	−1.7[f]	+0.06	−1.55	 **26** (30%)
 **3g**	−1.1	−0.27	−1.43	−0.16	−1.2	 **21g** (96%)

[a]Reduction signal of indazole. [b]Oxidation signal of indazoline. [c]Non-electroactive compound. [d]Not detected. [e]Measured by ^{1}H NMR. Isolated yield in parentheses. [f]Hardly observed at $v = 0.1$ V s^{-1} but clearly observed at $v > 0.5$ V s^{-1}. Polarography: WE = Hg^0, $c = 2 \times 10^{-3}$ M. Cyclic voltammetry: WE = glassy carbon, $v = 0.1$ V s^{-1}, $c = 2 \times 10^{-3}$ M.

observed during the course of the electrolysis. The anodic wave of the electrogenerated indazoline **21f** is only partially observed and **21f** did not accumulate. After work-up a mixture of products was obtained from which the symmetrical tetracycle **26** was isolated as the major product in 30% yield. The other separated products showed a complex ^{1}H NMR spectrum and were not identified.

A mechanism for the formation of tetracycle **26** is proposed in Scheme 8. The cyclization of the electrogenerated indazoline **21f** onto the nitrile group generates an *N*-hydro-imino group **23**. These imino compounds have been shown to be unstable and easily generate polymeric compounds;[16] it is likely that this is the source of the unidentified products. The imino compound **23** can be reduced to the corresponding amine **24** under the reaction conditions.[17] Loss of ammonia generates an iminium group **25** which is reduced to the tetracycle **26**. This kind of stabilized iminium compound has been shown to have a very intense colour (e.g. crystal violet and malachite green)[18] and it is probably the reason of the strong blue colour of the electrolyte during the electrolysis. The theoretical consumption of electricity for this mechanism is 6 F mol^{-1}. The excess consumption of electricity can be attributed to hydrogen production at the high cathodic potential used (−1.5 V vs. SCE) and to secondary electrochemical reactions of polymers and by-products produced.

Conclusions

The simultaneous electroreduction involving 6 F mol^{-1} of the nitro functionality to hydroxylamine and nitrone to imine for compounds such as **8** is a new route to 2-aryl-3-methoxycarbonylindazole **3g** in moderate yields. The electrochemical reduction of 2-substituted indazoles **3** in aqueous alcoholic medium can take place only with compounds bearing an electron-withdrawing substituent, which allows a resonance stabilization. The cathodic potential decreases with the addition of a second electron-withdrawing group to the indazole ring. Owing to low oxidation potential the electrogenerated 2-substituted indazolines **21** are air-sensitive compounds. With our electrochemical methodology we can selectively reduce

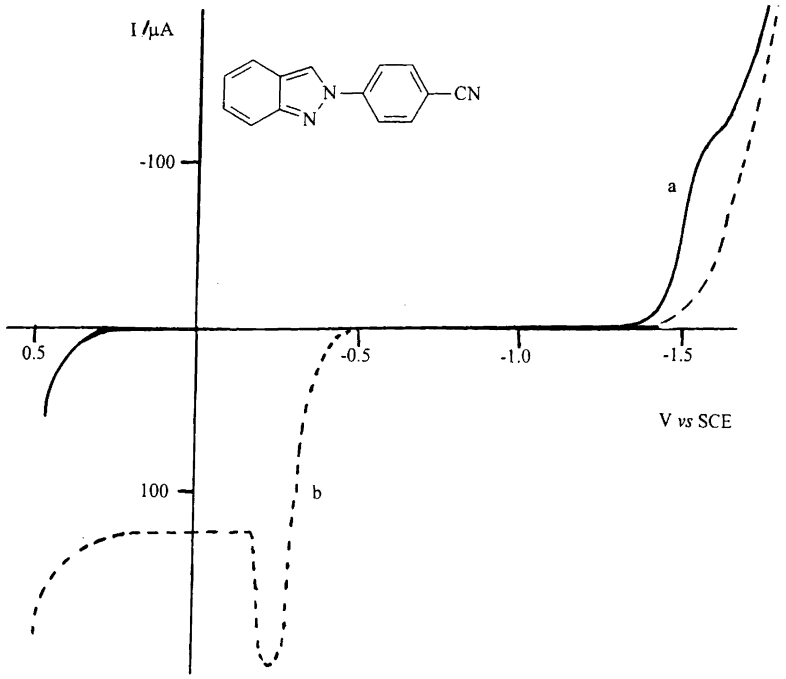
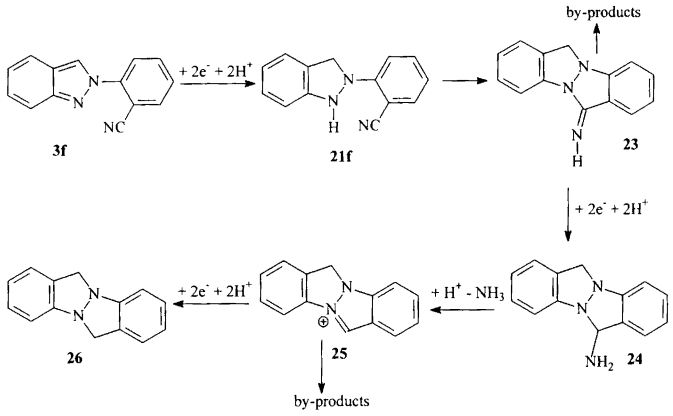


Fig. 2. Polarographic control of the electrolysis of **3e** 3.5×10^{-2} M at a Hg^0 electrode in aqueous alcoholic medium (80% MeOH, 20% aqueous acetate buffer 2.5 M): a, solution before electrolysis; b, solution immediately after 3 F mol^{-1} electroreduction at −1.55 V vs. SCE.



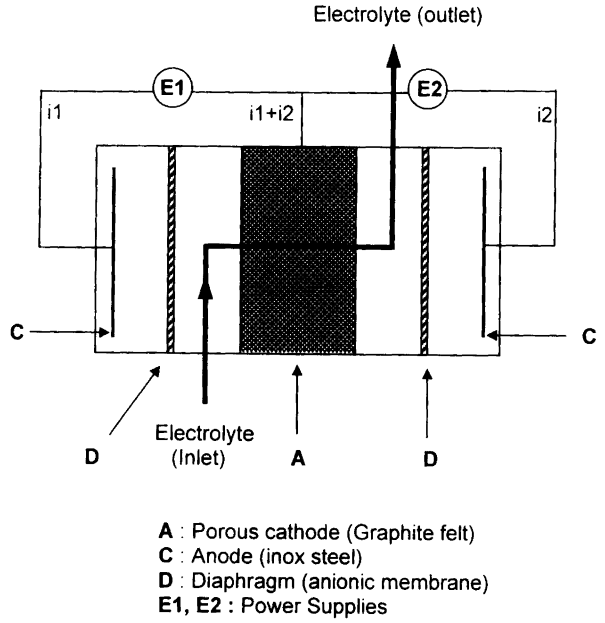
Scheme 8.

the indazole ring without affecting the nitrile and ester functions. We have shown that is possible to use the appropriately substituted indazolines **21** for generating *in situ* a tetracyclic heterocycle in a one-pot reaction.

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 deuteriochloroform with TMS as an internal reference and obtained on a Bruker DPI 200 FT spectrometer at 200 MHz (^{1}H) and 50 MHz (^{13}C). *J* values are given in Hz. 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 carried out at the *Service Central d'Analyse, Département Analyse Elémentaire CNRS* (Vernaison). Thin-layer chromatography (TLC) was performed using aluminium sheets pre-coated with silica gel (Macherey–Nagel Alugram Sil G/UV^{254}). Column chromatography was performed on silica gel (Acros 0.030–0.075 mm). Reagents were purchased from both Aldrich and Acros and were used without additional purification.

Electrochemical instrumentation and procedures. Conventional electrochemical equipment was used for polarography, cyclic voltammetry and controlled potential electrolyses (EG&G Princeton Applied Research



Scheme 9.

model 362-scanning potentiostat with an XY recorder). Controlled potential electrolyses were performed at a mercury pool cathode, under a nitrogen atmosphere, in a cell previously described.[19] The coulometric measurements were determined with a current integrator Tacussel model IG 5 N. The electrolyses in a flow cell fitted with a porous graphite cathode (Scheme 9) were performed at controlled current under a nitrogen atmosphere.[20] The solution was pumped through the cell from a reservoir using a peristaltic pump. The flow rate (4.8–5.2 ml min^{-1}) was measured from the outlet solution. The working electrode (5.2 cm diameter, 12 mm thickness for cathode) was made of graphite felt (Le Carbone Lorraine). The cell was operated with two power supplies 0–30 V/3 A. The total current intensity (I) was calculated from Faraday's law according to the quantity of substrate flowing through the porous electrodes per second and the theoretical quantity of electricity needed; for the first electrical circuit (inlet circuit) the current intensity is 2/3 of the total current intensity ($I_1 = 2/3I$) and $I_2 = 1/3I$ for the second one (outlet circuit). All the electrolyses were monitored by polarography (scan rate, 5 mV s^{-1}; drop time t, 2 s).

General procedure for preparative electrolyses of nitrone (**8**) *in the flow cell.* The nitrone (**8**) (1 g, 3.3 mmol) was dissolved in a mixture (1000 ml) of acetic acid–acetate buffer (AcOH 2.5 mol l^{-1} + AcONa 2.5 mol l^{-1}) and methanol (1:4 v:v) and nitrogen was bubbled through this solution for 30 min. The solution was electrolysed at 6 F mol^{-1} in the flow cell and the efficiency of electrolyses was controlled by polarography directly in the reservoir of the outlet solution. After electrolysis, the solution was neutralized with $NaHCO_3$ (pH = 7–8) and the methanol was removed by vacuum rotary evaporation. The reaction mixture was extracted with CH_2Cl_2 (4 × 30 ml). The organic fraction was dried over $MgSO_4$ and concentrated by vacuum 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 (1–4.5 mmol) was dissolved in a mixture (150 ml) of 20% acetic buffer (AcOH 2.5 mol l^{-1} + AcONa 2.5 mol l^{-1}) and 80% methanol, unless otherwise stated (*vide infra*). Nitrogen was bubbled through for 20 min. The solution was electrolysed under nitrogen at a controlled potential (−1.2 to −1.75 V vs. SCE). The electrolysis was monitored by polarography directly in the electrolysis cell. After complete disappearance of the starting material the electrolysis was stopped. The aqueous-organic mixture was separated from mercury with a cannula under argon pressure and the reduced product was separated under argon using conventional Schlenck techniques; the methanol was removed by vacuum evaporation and the precipitate obtained was washed with deoxygenated distilled water (4 × 30 ml). The crude precipitate was dried for 1 h under vacuum. The NMR spectrum of this crude precipitate showed a 90% yield of indazoline except for reactions starting with **3d** and **3g**.

2-Methylindazole (**3a**). After 'redox' electrolysis of *N*-(2-nitrobenzyl)methylamine **1a** (0.9 g, 5.42 mmol) in 400 ml of buffer solution and purification by column chromatography (petroleum ether–EtOAc 65:35), the indazole **3a** 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 8.07 (s, 1 H, H-3), 7.87 (dq, 1 H, J=8.1, 0.9, H-7), 7.78 (dt, 1 H, J=7.8, 1.0, H-4), 7.26 (ddd, 1 H, J=8.1, 6.2, 1.1, H-6), 6.96 (ddd, 1 H, J=7.8, 6.2, 0.9, H-5), 2.75 (s, 3 H; CH_3). ^{13}C NMR ($CDCl_3$): δ 148, 125.6, 123. 3, 121.8, 121.3, 119.7, 116.9, 39.9. HRMS EI *m/z* (rel. int.): 132.0688 (M^+, 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^+ 132.0687.

2-(3-Methylphenyl)indazole (**3b**). After 'redox' electrolysis of *N*-(2-nitrobenzyl)-3-toluidine **1b** (2 g, 8.26 mmol) in 1000 ml of buffer solution and purification by column chromatography (petroleum ether–EtOAc 97:3), **3b** 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 8.23 (d, 1 H, J=0.7, H-3), 7.82 (dd, 1 H, J=8.8, 0.7, H-7), 7.71 (s, 1 H, H-2′), 7.61 (dt, 1 H, J=7.6, 0.9, H-6), 7.58 (dd, 1 H, J=7.5, 0.9, H-4), 7.29 (ddd, 1 H, J=8.7, 7.6, 0.9, H-6′), 7.28 (dd, 1 H, J= 7.7, 7.7, H-5′), 7.15–7.01 (m, 2 H, H-5 and H-4′), 2.35 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 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.): 208.0999 (M^+, 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^+ 208.1000. Anal.: Found C 80.59; H 5.71; N 13.27. Calc. for $C_{14}H_{12}N_2$: C 80.74; H 5.81; N 13.45.

2-(4-Methoxyphenyl)indazole (**3c**). After 'redox' electrolysis of *N*-(2-nitrobenzyl)-4-anisidine **1c** (1.82 g, 6.97 mmol) in 800 ml of buffer solution and purification by column chromatography (petroleum ether–EtOAc 90:10), the indazole **3c** was recrystallized from ether–CH_2Cl_2 and was obtained as a white crystalline product m.p. 133–135 °C (lit. 130–131 °C[22]); 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}. ^1H NMR ($CDCl_3$): δ 8.22 (s, 1 H, H-3), 7.79 (dd, 1 H, J=8.7, 0.9, H-7), 7.73 (dt, 2 H, J=9.1, 2.2, H-2′), 7.63 (dd, 1 H, J=8.4, 1.1, H-4), 7.29 (ddd, 1 H, J=8.8, 6.6, 1.1, H-6), 7.07 (ddd, 1 H, J=8.4, 6.6, 0.9, H-5), 6.95 (dt, 2 H, J=9.1, 2.1, H-3′), 3.78 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 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.): 224.0947 (M^+, 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^+ 224.0949.

2-Phenylindazole (**3d**). After 'redox' electrolysis of *N*-(2-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 **3d** was recrystallized from petroleum ether–ether and was obtained as a white crystalline product m.p. 80–82 °C (lit. 82–83 °C[22]); 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 8.33 (d, 1 H, J=0.9, H-3), 7.86 (dm, 2 H, J=8.1, H-2′), 7.81 (dd, 1 H, J=8.0, 1.0, H-7), 7.67 (dt, 1 H, J=8.5, 1.0, H-4), 7.48 (t, 2 H, J=8.1, H-3′), 7.37 (dt, 1 H, J=7.9, 1.2, H-4′), 7.32 (ddd, 1 H, J=7.9, 6.3, 1.1, H-6), 7.09 (ddd, 1 H, J=8.5, 6.3, 0.9, H-5). ^{13}C NMR ($CDCl_3$): δ 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.): 194.0831 (M^+, 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^+ 194.0843.

2-Phenylindazoline (**21d**). After controlled potential electrolysis (8 F mol^{-1}) of 2-phenylindazole **3d** (0.450 g, 2.32 mmol) in 130 ml of buffer solution and work-up under an argon atmosphere, a mixture of products was obtained. The indazoline **21d** was purified by slow crystallization in $CHCl_3$. The purified product was obtained as pale yellow crystals m.p. 153–154 °C; 0.115 g, 25%. IR (KBr): 3420, 3183, 2808, 1596, 1480, 1464, 1337, 1314, 1257, 1178, 1051, 929, 856, 795, 750, 687, 523, 509 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.42–7.22 (m, 4 H), 7.17–7.01 (m, 4 H), 6.98–6.88 (m, 1 H), 5.99 (s, 1 H, exchanges with D_2O, N–H), 4.95 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$): δ 152.05, 146.6, 129.05, 127.9, 122.7, 121.1, 119.5, 115.1, 114.4, 112.1, 58.3. HRMS EI *m/z* (rel. int.): 196.0996 (M^+, 10), and $[M-H]^+$ at 195.0922 (100). $C_{13}H_{12}N_2$ requires M^+ 196.1004.

(E)-Methyl (2-nitrophenyl)(phenylimino)acetate (**7**). In a 250 ml round-bottomed flask were placed MeOH (150 ml), 2-nitrophenylacetic acid methyl esther **5** (10 g, 0.0513 mol), nitrosobenzene **6** (16.5 g, 0.154 mol) and Na_2CO_3 (16.3 g, 0.153 mol). The mixture was heated with stirring (20 h at 40 °C). The solution obtained was filtered and the methanol was removed by vacuum rotary evaporation. The crude product of reaction was purified by column chromatography (petroleum ether–AcOEt 70:30). The imine **7** was recrystallized from ether–CH_2Cl_2–petroleum ether to give a yellow crystalline product m.p. 111–113 °C; 2.1 g, 19%. IR (KBr): 3437, 3100, 2945, 2839 1721, 1647, 1525, 1342, 1222, 1025, 865, 793, 745 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.23 (ddd, 1 H, J= 8.65, 6.37, 1.2, H-3), 7.55–7.45 (m, 2 H), 7.17 (ddd, 2 H, J=7.4, 7.4, 1.8, H-3′), 7.04–6.97 (m, 2 H), 6.72 (ddd, 2 H, J=7.3, 2.3, 1.2, H-2′), 3.93 (s, 3H, CO_2CH_3). ^{13}C NMR ($CDCl_3$): δ 163.2, 157.2, 148.2, 148.0, 134.1, 130.7, 130.6, 130.3, 128.8, 125.5, 124.3, 119.9, 53.4. HRMS EI *m/z*: M^+ 284.0788. $C_{15}H_{12}N_2O_4$ requires M^+ 284.0797. Anal.: Found C 63.37; H 4.22; N 9.80; O 22.52. Calc. for $C_{15}H_{12}N_2O_4$: C 63.38; H 4.25; N 9.85; O 22.51.

(Z)-Methyl (2-nitrophenyl)(phenylimino)acetate N-*oxide* (**8**). From the previous reaction the nitrone (**8**) was isolated. After recrystallization from MeOH–ether **8** was obtained as a pale yellow crystalline product m.p. 141–143 °C; 7.35 g, 48%. IR (KBr): 3451, 3085, 3043, 2952, 1744, 1521, 1336, 1214, 1125, 773, 745, 690 425 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.27 (dd, 1 H, J=7.7, 1.2, H-3), 7.78 (ddd, 1 H, J=7.6, 7.6, 1.2, H-5), 7.65 (ddd, 1 H, J=7.7, 7.7, 1.4, H-6), 7.63 (dd, 1 H, J=7.6, 1.4, H-4), 7.5 (s, 5 H; Ph), 3.57 (s, 3 H, CO_2CH_3). ^{13}C NMR ($CDCl_3$): δ 160.9, 148.2, 147.7, 136.6, 133.9, 131.4, 130.5, 130.2, 129.1, 126.5, 125.0, 122.8, 52.8. HRMS EI *m/z*: M^+ 300.0744. $C_{15}H_{12}N_2O_5$ requires M^+ 300.0746. Anal.: Found C 59.63; H 3.97; N 9.23; O 26.95. Calc. for $C_{15}H_{12}N_2O_5$: C 60.00; H 4.03; N 9.33; O 26.64.

(E)-2-Nitrobenzaldehyde phenylimine N-*oxide* (**9**). The nitrone **8** (1 g, 3.33 mmol) was dissolved in HPLC grade MeOH (20 ml). Water (6.66 mmol, 0.120 ml) and Na_2CO_3 (0.355 mg, 3.33 mmol) were added to the solution. The heterogeneous mixture was heated with stirring (18 h). The solution was filtered and the methanol was removed by vacuum rotary evaporation. The products of reaction were extracted with CH_2Cl_2 (3 × 25 ml) and the organic phase was washed with brine twice. After treatment with $MgSO_4$ and evaporation of CH_2Cl_2, the crude product of reaction was purified by flash

chromatography (petroleum ether–AcOEt 80:20). Recrystallization from acetone–petroleum ether yielded the nitrone **9** as a yellow crystalline product m.p. 93–95 °C; 0.35 g, 40%. IR (KBr): 3135, 3105, 3075, 2852, 1603, 1570, 1521, 1340, 1201, 1098, 1068, 773, 742, 690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.38 (dd, 1 H, J=8.06, 1.4, H-3), 8.59 (s, 1 H, CH=N), 8.09 (dd, 1 H, J=8.2, 1.3, H-3), 7.82–7.75 (m, 3 H), 7.61–7.49 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 149.2, 147.5, 133.5, 130.6, 130.4, 129.4, 129.3, 128.4, 125.0, 124.5, 121.8. HRMS EI m/z: M^+ 242.0697. $C_{13}H_{10}N_2O_3$ requires M^+ 242.0691.

2-Phenyl-3-methoxycarbonylindazole (**3g**). After electrolysis (6 F mol^{-1}) in the flow cell of a solution of nitrone **8** (1.0 g, 3.33 mmol) dissolved in 1000 ml of buffer solution and work-up, purification of the crude reaction product by column chromatography (petroleum ether–AcOEt 95:5) gave the indazole **3g**. It was recrystallized from ether–petroleum ether and obtained as a cream solid m.p. 90–92 °C (lit. 169–170 °C[23]); 0.33 g, 40%. IR (KBr): 3064, 2959, 1728, 1496, 1468, 1377, 1293, 1243, 1215, 1124, 1053, 761, 742, 710 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.11 (dt, 1 H, J=8.3, 1.1, H-7), 7.86 (dt, 1 H, J=8.4, 1.1, H-4), 7.53 (s, 5 H, Ph), 7.43 (ddd, 1 H, J=8.4, 7.2, 1.1, H-5), 7.35 (ddd, 1 H, J=8.3, 7.2, 1.1, H-6), 3.92 (s, 3 H, CO_2CH_3). ^{13}C NMR ($CDCl_3$): δ 160.0, 148.4, 140.9, 129.4, 128.7, 127.1, 126.3, 125.6, 124.8, 123.9, 121.6, 118.7, 52.05. HRMS EI m/z (rel. int.): M^+ 252.0875, $C_{15}H_{12}N_2O_2$ requires M^+ 252.0898. Anal.: Found C 70.76; H 4.79; N 11.06; O 12.53. Calc. for $C_{15}H_{12}N_2O_2$ requires 71.42; H 4.79; N 11.1; O 12.68.

2-Phenyl-3-methoxycarbonylindazoline (**21g**). After controlled potential electrolysis (3 F mol^{-1}) of 2-phenyl-3-methoxycarbonylindazole **3g** (0.25 g, 1 mmol) in 130 ml of buffer solution and work-up of the reaction mixture under an argon atmosphere, the indazoline **21g** was obtained as a cream powder m.p. 94–96 °C; 0.22 g, 89%. IR (KBr): 3219, 1744, 1598, 1486, 1267, 1207, 802, 750, 687 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.35–7.19 (m, 4 H), 7.15–6.05 (m, 5 H), 6.15 (br s, 1 H, exchanges with D_2O, N–H), 5.35 (d, 1 H, J=2.3, CH), 3.83 (s, 3 H, CO_2CH_3). ^{13}C NMR ($CDCl_3$): δ 171.4, 151.7, 146.3, 129.3, 129.1, 126.7, 123.5, 123.1, 120.7, 114.6, 112.7, 71.7, 52.8. HRMS EI m/z: M^+ 254.1064. $C_{15}H_{14}N_2O_2$ requires M^+ 254.1055.

2-(4-Cyanophenyl)indazole (**3e**). After 'redox' electrolysis of 4-(2-nitrobenzyl)aminobenzonitrile **1e** (2.02 g, 5.9 mmol) in 800 ml of buffer solution and total disappearance of the nitroso group signal, the reaction was worked up. After purification of the crude product by flash chromatography (petroleum ether–EtOAc 85:15), the indazole **3e** was recrystallized from CH_2Cl_2–ether and was obtained as a yellow crystalline product m.p. 159–161 °C (lit. 107 °C[24]); 1.2 g, 70%. IR (KBr): 3131, 2228, 1604, 1521, 1423, 1381, 1312, 1208, 1042, 952, 839, 820, 784, 761, 547 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.37 (d, 1 H, J=0.9, H-3), 7.98 (dt, 2 H, J=8.9, 2.2, H-2′), 7.7 (dt, 3 H, J=8.9, 2.2, H-3′ and H-7), 7.62 (dt, 1 H, J=8.5, 1.1, H-4), 7.29 (ddd, 1 H, J=8.7, 6.6, 1.1, H-6), 7.08 (ddd, 1 H, J=8.5, 6.6, 0.9, H-5). ^{13}C NMR ($CDCl_3$): δ 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.): 219.0797 (M^+, 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^+ 219.0796. Anal.: Found C 76.05; H 4.13; N 19.17. Calc for. $C_{14}H_9N_3$: C 76.70; H 4.14; N 19.17.

2-(4-Cyanophenyl)indazoline (**21e**). After controlled potential electrolysis (3 F mol^{-1}) of 2-(4-cyanophenyl)-indazole **3e** (1 g, 4.56 mmol) in 130 ml of buffer solution with 10 ml of CH_2Cl_2, and work-up of the reaction mixture under an argon atmosphere, **21e** was obtained as a cream powder m.p. 118–120 °C; 0.90 g, 90%. IR (KBr): 3381, 3214, 2882, 2825, 2206, 1605, 1599, 1517, 1463, 1376, 1249, 1180, 1146, 1084, 816, 784, 760, 543 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.49 (dm, 2 H, J=9.0, H-3′), 7.28–7.13 (m, 2 H, H-4, H-6), 7.09–6.87 (m, 4 H, H-7, H-5, H-2′), 5.97 (s, 1 H, exchanges with D_2O, N–H), 4.89 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$): δ 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^+ 221.0952 and $[M-H]^+$ 220.0874. Anal.: Found C 75.18; H 4.48; N 18.90. Calc. for $C_{14}H_{11}N_3$: C 76.00; H 5.01; N 18.99.

2-(2-Nitrobenzylamino)benzonitrile (**1f**). In a 100 ml Erlenmeyer flask with a stopper the 2-nitrobenzyl bromide **4** (4 g, 18.5 mmol) and 2-aminobenzonitrile (2.2 g, 0.0186 mol) were dissolved in CH_2Cl_2 (50 ml). NaOH 2.5 M (30 ml) and tetrabutyammonium hydrosulfate (500 mg) were added to this solution. The heterogeneous mixture was vigorously stirred for 48 h at room temperature. The aqueous phase was separated and the organic phase was washed with brine until pH 7–8. The CH_2Cl_2 was removed by rotary vacuum evaporation. Addition of acetone–petroleum ether to the crude product of reaction promoted the crystallization of **1f**. Recrystallization in acetone–petroleum ether yielded a yellow crystalline product m.p. 155–157 °C; 2.2 g, 47%. IR (KBr): 3401, 2217, 1579, 1523, 1466, 1444, 1352, cm^{-1}. ^1H NMR (acetone-d_6): δ 8.08 (dm, 1 H, J=7.8, H-3), 7.68–7.61 (m, 2 H, H-3′, H-5), 7.52 (ddd, 1 H, J=8.5, 5.1, 1.3, H-5′), 7.44 (ddd, 1 H, J=7.7, 1.6, 0.5, H-6), 7.29 (ddd, 1 H, J=7.3, 1.6, 0.5, H-4), 6.68 (ddd, 1 H, J=7.5, 7.5, 0.9, H-4′), 6.62 (d, 1 H, J=8.2, H-6′), 6.2 (br s, 1 H, exchanges with D_2O, N–H), 4.9 (d, 1 H, J=6.2, CH_2). ^{13}C NMR (acetone-d_6): δ 150.05, 148.5, 134.6, 134.2, 133.7, 133.0, 128.9, 128.2, 125.1, 117.2, 116.9, 111.3, 96.1, 44.1.

2-(2-Cyanophenyl)indazole (**3f**). After 'redox' electrolysis of 2-(2-nitrobenzylamino)benzonitrile **1f** (4 g, 15.8 mmol) in 2600 ml of ammoniacal buffer solution (NH_4NO_3–NH_3 0.5M–50% MeOH–20% CH_2Cl_2–30% H_2O), and total disappearance of the nitroso group signal, the organic solvents were removed by vacuum rotary evaporation. The resulting precipitate was filtered and washed with water and then ether, and was recrystallized from AcOEt–petroleum ether to obtain a pale yellow crystalline product m.p. 123–125 °C (lit. 126–127 °C[25]); 3 g, 85%. IR (KBr): 2226, 1630, 1600, 1523, 1497, 1442, 1387, 1188, 1048, 950, 771, 753, 533 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.56 (d, 1 H, J=1, H-3), 7.92 (ddd, 1 H, J=8.3, 1.3, 0.5, H-3′), 7.85–7.65 (m, 4 H, H-7, H-4, H-6′, H-5′), 7.49 (ddd, 1 H, J=7.6, 7.6, 1.2, H-4′), 7.33 (ddd, 1 H, J=8.5, 6.6, 1.2, H-6), 7.11 (ddd, 1 H, J=8.5, 6.5, 0.9, H-5). ^{13}C NMR ($CDCl_3$): δ 150.1, 142.2, 134.4, 133.9, 128.4, 127.6, 125.8, 123.3, 123.0, 122.7, 120.6, 117.9, 116.5, 106.7. HRMS EI *m/z*: M^+ 219.0778, $C_{14}H_9N_3$ requires M^+ 219.0796.

6H,12H-Indazolo[1,2-a]indazole (**26**). After controlled potential electrolysis (8 F mol^{-1}) of 2-(2-cyanophenyl)-indazole (**3f**) (0.65 g, 2.96 mmol) in 150 ml of acetic acid–lithium acetate buffer solution in HPLC-grade MeOH and work-up under a normal atmosphere, we obtained the crude product of reaction. The mixture of products was purified by flash chromatography (AcOEt–petroleum ether) and the tetracycle **26** was separated. Recrystallization in ether–petroleum ether gave a white crystalline product m.p. 142–144 °C; 0.2 g, 30%. IR (KBr): 3035, 2911, 2857, 1605, 1594, 1470, 1457, 1239, 1019, 757, 723 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.2–7.05 (m, 4 H), 6.95–6.8 (m, 4 H), 4.7 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$): δ 151.8, 128.0, 127.4, 122.9, 122.6, 110.7, 56.05. HRMS EI *m/z*: M^+ 208.1028, $C_{14}H_{12}N_2$ requires M^+ 208.1004. Anal.: Found C 80.41; H 5.98; N 13.16. Calc. for $C_{14}H_{12}N_2$: C 80.74; H 5.81; N 13.45.

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