

Electrochemical-Mediated Cyclization of 2-Alkynylanilines: A Clean and Safe Synthesis of Indole Derivatives

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The electrochemical-mediated annulation of 2-alkynylanilines to the corresponding indole derivatives proceeds in good yields and under conditions that avoid the use of metal catalysts or classical organic acids and bases.

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Introduction

The synthesis of the indole ring^[1] is of particular importance in organic, pharmaceutical, and medical chemistry considering its large presence in a variety of natural substances (alkaloids) and their unique biological activities.^[2] Consequently, the development of new synthetic methods for the preparation of indole derivatives is a target of great current interest.^[3] As a response to legislative and social pressure and “green”-conscious industrial community, researchers have started to examine more ecofriendly and sustainable chemical processes^[4] that minimize the requisite reagents, solvents, cost, time, and separation processes for the desired transformation and also minimize the formation of waste. Increasing attention is now being paid to the simplification and improvement of existing procedures for their preparation in the manufacture of pharmaceutical targets. In this context, some of the main research areas involve the construction of the indole ring system from 2-ethynylaniline derivatives^[5] and the development of cheap and environmentally safe protocols.^[6] The ready availability of 2-alkynylanilines can allow the synthesis of the target indoles by using many kinds of reagents for their cyclization reaction. In particular, the most frequently used reagents are transition metals^[5] and base catalysts.^[7] In line with the demand for simplification, we developed a new strategy involving the electrogeneration of anions.^[8]

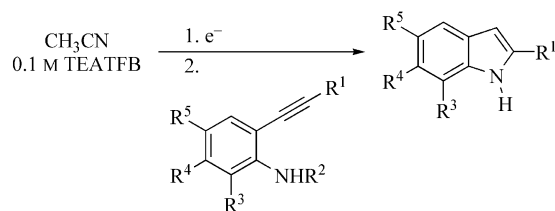
Results and Discussion

Electrochemical technology represents a valuable alternative to the classical methodologies usually employed in the synthesis of fine chemicals.^[9] The use of electrons as a “reagent” allows the formation of highly reactive intermediates with undeniable advantages in terms of green chemistry. Their generation, in fact, is usually achieved under mild reaction conditions, which avoids the use of toxic and harmful compounds like oxidative or reductive agents as well as acids, bases, and related waste byproducts. In particular, the electrochemically generated cyanomethyl anion has proved to be effective in a large number of organic reactions.^[10] In this context, particular attention was dedicated to the study of the reactivity of the electrogenerated cyanomethyl anion towards electrophilic (carbonyl compounds, Schiff bases, esters, alkyl halides, carbon dioxide, etc.) or acidic substrates (acid–base reactions). A variety of synthetic targets were conveniently obtained through the use of electrogenerated bases (EGBs). In the last few years, our research group has investigated the potentiality of the electrogenerated cyanomethyl anion, obtained by reduction of MeCN/supporting electrolyte solutions, as a base and its use in organic synthesis. Among the several applications of the methodology, we reported the synthesis of carbamates, oxazolidin-2-ones, 5-methylene-1,3-oxazolidin-2-ones, 1,3-oxazolidine-2,4-diones, and β -lactams.^[11] As part of our ongoing interest in the synthesis of indoles,^[12] we thought that cyclization of ethynylanilines induced by the electrogenerated cyanomethyl anion should represent a clear improvement in the synthesis of indoles and avoid the use of any metal catalyst or classical organic bases (Scheme 1).

Here we wish to report the scope of this new synthesis. Reaction conditions were optimized by using *N*-[2-(2-phenylethynyl)phenyl]acetamide (**1a**) as model compound. The results are reported in Table 1. We found that electrogener-

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Scheme 1. Electrochemical-mediated cyclization of 2-alkynylanilines.

ated CH_2CN^- is able to promote the formation of 2-phenyl-1*H*-indole (**2a**) in very high yields from **1a** through sequential cyclization/deprotection of the aminic functionality. The electrolyses were carried out by using the solvent-supporting electrolyte system [$\text{CH}_3\text{CN}/0.1\text{ M}$ tetraethylammonium tetrafluoroborate (TEATFB)] in a divided cell equipped with platinum electrodes under galvanostatic control ($J = 25\text{ mA cm}^{-2}$) at 0°C . 2-Alkynylaniline derivative **1** was added only at the end of the electrolysis with the aim to avoid, under the reaction conditions, reduction of substrates bearing sensitive functional groups. As reported in Table 1, both the amount of electricity supplied during the electrolysis (Q) and the reaction temperature of the following cyclization step influence the reaction yields. Product **2a** was obtained in very good yield (94%) from **1a** at 80°C by using $Q = 2.5\text{ F mol}^{-1}$ (Table 1, Entry 6). In addition, the relatively high yield of **2a** obtained by using only 1.0 F mol^{-1} of current (Table 1, Entry 3) deserves some consideration. The generation of the cyanomethyl anion is a two-electron process and it is evident that the reaction may partially follow a catalytic pathway. Deprotonation of the N–H functionality by the cyanomethyl anion is followed by intramolecular ring closure on the triple bond. The anion thus obtained may then be able to abstract a proton from the solvent, which would result in a catalytic process. Under these reaction conditions, removal of the acyl moiety by hydrolysis of the amidic functionality, catalyzed by residual water present in the reaction medium, may also be supposed.

Different solvent-supporting electrolyte systems were evaluated. The electrogenerated dimsyl anion furnished **2a** in only moderate yield (Table 1, Entry 9). Tetrabutylammonium hexafluorophosphate (Table 1, Entry 10) or the electrogenerated propionitrile anion (Table 1, Entry 11) gave **2a** in comparable yields with the above-reported optimized conditions. Although TBAHFP allows slightly higher reaction yields, the use of TEATFB was preferred because of its lower solubility in some organic solvents. Thus, workup of the reaction is simplified, and in some cases, column chromatography can be avoided.

A large-scale experiment (10.0 mmol) was also conducted on substrate **1a**. 2-Phenyl-1*H*-indole (**2a**) was isolated in very high yield (91%). No indoles, as expected, were obtained when the electrolysis was performed in an undivided cell, even if substrate **1a** was added at the beginning of the electrolysis.

To investigate the scope and limitations of the electrogenerated-cyanomethyl-anion-induced indole syntheses, we

 Table 1. Synthesis of indole **2a** by cyclization of **1a** induced by the electrogenerated cyanomethyl anion under different reaction conditions.^[a]

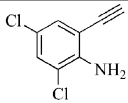
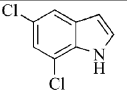
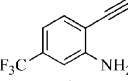
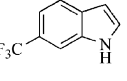
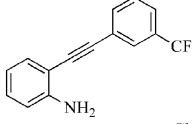
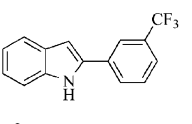
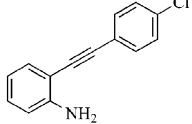
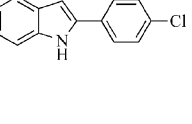
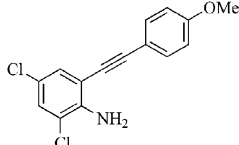
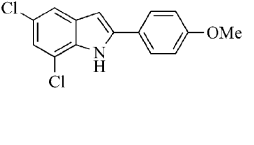
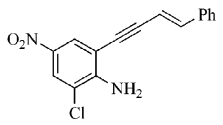
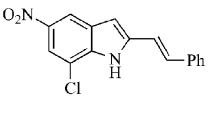
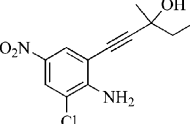
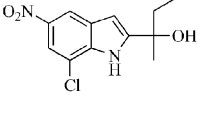
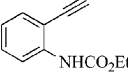
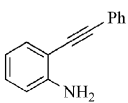
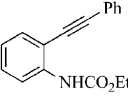
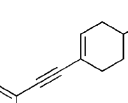
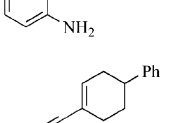
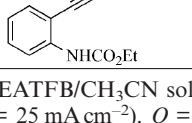
Entry	Solvent	Supporting electrolyte ^[b]	Q ^[c] [F mol ⁻¹]	T ^[d] [°C]	Time ^[d] [h]	Yield ^[e] [%]
1	MeCN	TEATFB	2.0	25	17	62 ^[f]
2	MeCN	TEATFB	2.2	25	122	67
3	MeCN	TEATFB	1.0	80	2.5	86
4	MeCN	TEATFB	1.5	80	2.5	78
5	MeCN	TEATFB	2.0	80	2.5	92
6	MeCN	TEATFB	2.5	80	1.0	94
7	MeCN	TEATFB	3.0	80	2.0	88
8	MeCN	TEATFB	3.5	80	3.0	82
9	Me ₂ SO	TEATFB	2.5	120	4.0	47 ^[g]
10	MeCN	TBAHFP	2.5	80	0.3	98
11	EtCN	TBAHFP	2.5	80	0.5	95

[a] Electrolysis of 0.1 mol L^{-1} solvent-supporting electrolyte solutions (12 mL) was carried out at 0°C in a divided cell equipped with Pt electrodes under galvanostatic control ($J = 25\text{ mA cm}^{-2}$). Compound **1a** (0.3 mmol) was added at the end of the electrolysis, and the reaction was carried out under conditions reported. [b] TEATFB = tetraethylammonium tetrafluoroborate, TBAHFP = tetrabutylammonium hexafluorophosphate. [c] Current quantity refers to the amount of **1a**. [d] Reaction times and temperatures refer to the cyclization reaction step. [e] Yields refer to isolated product. [f] Unreacted starting **1a** was recovered in 35% yield. [g] Unreacted starting **1a** was recovered in 52% yield.

next extended the process to a series of 2-alkynylanilines bearing free and/or protected amine groups. The results are reported in Table 2.

The methodology is quite general and compatible with a large variety of functional groups. The target indoles were isolated in high yields starting from substrates bearing both a terminal and an internal alkyne. The reactions were carried out according to the method described in Table 1 Entry 6 by varying the reaction time and temperature. In particular, even if the cyclization of terminal alkynes **1b** and **1c** occurred as a consequence of the activation obtained by the EWG groups (Cl and CF_3) on the aromatic rings, it distinguishes this process from other cyclization methods. Indeed, it is worth noting that 2-unsubstituted indoles were previously isolated from the corresponding 2-alkynylanilines in the presence of a twofold excess of CuI in hot DMF^[13] or a fourfold excess of *t*BuOK in refluxing *t*BuOH.^[14] The lack of formation of **2b** in the reaction of **1b** with a catalytic amount (4 mol-%) of PdCl_2 in refluxing MeCN for 7 h gives further support for the advantage of the present protocol over the previously reported methodologies.^[15] Alkynylanilines substituted at the triple bond furnish the corresponding indoles in very high yields. Although the cyclization reactions can occur at room temperature, shorter reaction times usually result by raising the temperature to 80°C (Table 2, compare Entries 7/8 and 12/13). We next examined the effect of the protecting group on

Table 2. Intramolecular cyclization of 2-alkynylanilines **1** to indoles **2** induced by the electrogenerated cyanomethyl anion.^[a]

Entry	Substrate 1	<i>T</i> [°C] ^[b]	Time [h] ^[b]	Indole	Yield [%] ^[c]
1		1b 80	0.5		2b 91
2		1c 80	5.0		2c 60
3		1d 80	3.0		2d 70
4		1e 80	2.0		2e 97
5		1f 80	18		2f 89
6		1g 80	0.5		2g 83
7		1h r.t.	20		2h 87
8		1h 80	1.0		2h 88
9		1i r.t.	3.0		3 73 ^[d]
10		1j r.t.	2.0		2j 95
11		1k 80	100		2a –
12		1l r.t.	42		2a 89
13		1l 80	0.5		2a 92
14		1m 80	20		2m –
15		1n r.t.	18		2m 78

[a] Electrolysis of 0.1 mol L⁻¹ TEATFB/CH₃CN solutions (12 mL) was carried out at 0 °C in a divided cell equipped with Pt electrodes under galvanostatic control ($J = 25 \text{ mA cm}^{-2}$). $Q = 2.5 \text{ F mol}^{-1}$ of **1** unless otherwise stated. Compound **1** (0.4 mmol) was added at the end of the electrolysis, and the reaction was carried out under the conditions reported. [b] Reaction times and temperatures refer to the following cyclization step. [c] Yields refer to isolated product. [d] Compound **1i** was present during the electrolysis.

nitrogen atom by its protection as carbamate functionality (CO_2Et); the formation of indole **2j** (95% yield) was accomplished by annulation of ethyl 2-ethynylphenylcarbamate (**1j**; Table 2, Entry 10). Furthermore, deprotection of the indolic nitrogen atom by removal of the ethoxycarbonyl group was observed. Interestingly, when added before the start of the electrolysis, **1i** underwent reduction of the $\text{C}\equiv\text{C}$ bond to give vinyl derivative **3** in 73% yield (Table 2, Entry 9). Although the electrochemical reduction of acetylene is a known procedure,^[16] the reduction of terminal alkynes under these mild conditions may offer a new synthetic opportunity. Moreover, comparison of the results obtained in the cyclization of **1n** with the lack of formation of **2m** from **1m** suggests that the $\text{p}K_{\text{a}}$ values of the N–H bond and/or the polarization of the triple bond were closely related to the efficiency of the cyclization reaction.

In no case was neutralization of the reaction mixture required during workup. Simple evaporation of the solvent and filtration through silica gel, if needed, afforded the reaction products in very good yields.

Conclusions

We developed a new application of the electrogenerated cyanomethyl anion that involves its use, as an electrogenerated base, in the synthesis of functionalized indoles from alkynylanilines. The approach proposed is very clean and safe and avoids the use of metal catalysts or classical organic acids and bases. The workup is very easy and simply requires filtration or flash chromatography of the evaporated reaction mixture without any extractive workup. Thus, this electrochemical approach represents a valuable and competitive alternative to the reported procedures.

Experimental Section

General Procedure for Electrochemical-Mediated Cyclization of Alkynylanilines: A solution (12.0 mL) of $\text{CH}_3\text{CN}/0.1\text{ M TEATFB}$ was electrolyzed under galvanostatic control (Pt cathode 1.5 cm^2 ; $J = 25\text{ mA cm}^{-2}$, $Q = 2.5\text{ F mol}^{-1}$ of **1**) at 0°C . No pre-electrolysis was required. At the end of electrolysis, 2-alkynylaniline **1** (0.4 mmol) was added to the cathode compartment, and the reaction was prolonged at the temperature and for the time reported in Table 2. The solvent was evaporated under reduced pressure. The crude mixture yielded pure indole **2** after simple filtration through silica gel. 2-Alkynylanilines **1a–c**, **1e–g**, **1i–m** and indoles **2a–c**, **2e–g**, **2j,m** are known compounds.^[5a,12e,15b,15d,17a] Compound **1d** was obtained according to ref.^[17d]; carbamate **1n** was obtained from corresponding amide **1m** by classical reaction with ethyl chloroformate in pyridine.

2-[[3-(Trifluoromethyl)phenyl]ethynyl]aniline (1d): M.p. $166\text{--}167^\circ\text{C}$. ^1H NMR (200 MHz, CDCl_3): $\delta = 7.63$ (br. s, 1 H), 7.50 (d, $J = 7.7\text{ Hz}$, 1 H), 7.39 (d, $J = 7.9\text{ Hz}$, 1 H), 7.30–7.21 (m, 2 H), 7.04–6.96 (m, 1 H), 6.57 (t, $J = 7.7\text{ Hz}$, 2 H), 4.12 (br. s, 2 H) ppm. ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 148.0$, 134.4, 132.3, 131.2, 130.3 (q, $J = 28\text{ Hz}$), 130.2, 128.9, 128.0 (q, $J = 3.7\text{ Hz}$), 124.6 (q, $J = 3.6\text{ Hz}$), 123.8 (q, $J = 272\text{ Hz}$), 117.9, 114.4, 107.1, 93.0, 87.7 ppm. MS (EI): m/z (%) = 261 (100) $[\text{M}]^+$. $\text{C}_{15}\text{H}_{10}\text{F}_3\text{N}$ (261.24): calcd. C 68.96, H 3.86; found C 69.04, H 3.84.

Ethyl 2-[(4-Phenylcyclohex-1-en-1-yl)ethynyl]phenylcarbamate (1n): M.p. $78\text{--}79^\circ\text{C}$. ^1H NMR (200 MHz, CDCl_3): $\delta = 8.19$ (d, $J = 8.3\text{ Hz}$, 1 H), 7.41–7.18 (m, 8 H), 6.95 (t, $J = 7.6\text{ Hz}$, 1 H), 6.31 (br. s, 1 H), 4.23 (q, $J = 7.0\text{ Hz}$, 2 H), 2.90–2.65 (m, 1 H), 2.60–2.26 (m, 4 H), 2.20–1.65 (m, 2 H), 1.31 (t, $J = 7.1\text{ Hz}$, 3 H) ppm. ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 153.0$, 145.9, 138.8, 138.7, 135.2, 131.4, 129.1, 128.3, 126.6, 126.1, 124.8, 122.2, 120.0, 117.4, 111.8, 97.9, 82.2, 61.1, 38.9, 33.7, 29.8, 29.3, 14.4 ppm. MS (EI): m/z (%) = 345 (100) $[\text{M}]^+$. $\text{C}_{23}\text{H}_{23}\text{NO}_2$ (345.43): calcd. C 79.97, H 6.71; found C 80.02, H 6.72.

2-(7-Chloro-5-nitro-1H-indol-2-yl)butan-2-ol (2h): Yield: 234 mg, 87%. M.p. $145\text{--}146^\circ\text{C}$. ^1H NMR (200 MHz, $[\text{D}_6]\text{acetone}$): $\delta = 10.62$ (br. s, 1 H), 8.32 (d, $J = 1.9\text{ Hz}$, 1 H), 7.86 (d, $J = 2.0\text{ Hz}$, 1 H), 6.56 (d, $J = 2.0\text{ Hz}$, 1 H), 4.36 (br. s, 1 H), 1.95–1.70 (m, 2 H), 1.50 (s, 3 H), 0.72 (t, $J = 7.4\text{ Hz}$, 3 H) ppm. ^{13}C NMR (50.3 MHz, $[\text{D}_6]\text{acetone}$): $\delta = 152.5$, 142.5, 136.9, 129.8, 116.9, 116.5, 116.4, 102.0, 72.3, 36.3, 28.4, 8.7 ppm. MS (EI): m/z (%) = 268 (100) $[\text{M}]^+$. $\text{C}_{12}\text{H}_{13}\text{ClN}_2\text{O}_3$ (268.7): calcd. C 53.64, H 4.88; found C 53.72, H 4.85.

Acknowledgments

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