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Stereoselective Electrocatalytic Oxidative Coupling of Phenylacetonitriles: Facile and Convenient Way to *trans*-α,β-Dicyanostilbenes

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Electrolysis of phenylacetonitriles in methanol in an undivided cell in the presence of sodium halides as mediators induces a stereoselective oxidative coupling process that results in the formation of *trans*-α,β-dicyanostilbenes in 60–85 % yield with 40–70 % current efficiency. The application of this efficient stereoselective electrocatalytic method to the formation of *trans*-α,β-dicyanostilbenes represents an environmentally benign synthetic strategy and is valuable from the viewpoint of large-scale processes.

Introduction

In recent years, functionally substituted α,β-dicyanostilbenes (or bisarylmaleonitriles and bisarylfumaronitiles depending on the configuration of the double bond) have played an increasing role in the synthetic approach to promising compounds in the field of materials and biomedical sciences. α,β-Dicyanostilbenes are convenient precursors for the synthesis of nonsymmetrical phthalocyanines and tetraazaporphyrines, and their metal complexes exhibit a wide range of unique properties[1] that allows their usage not only in practical industrial areas, but also in the fields of nonlinear optics and photodynamic cancer therapy.[2] Furthermore, tetraazaporphyrines are analogous to porphyrins, which play significant roles in different biological systems.[2c,2d] Functionally substituted α,β-dicyanostilbenes are valuable synthetic precursors for unusual nondoped host emitters for red organic light-emitting diodes (OLEDs) and appear as basic structural units in novel types of photoluminescent and electrochemically active soluble π-conjugated polymers.[3] The recent result shows that there is considerable binding affinity and selectivity of nonsteroidal 2,3-bisarylpropionitriles to estrogen receptors and accentuates the biomedical interest of the cyanostilbene moiety.[4]

The preparation of α,β-dicyanostilbenes from phenylacetonitrile derivatives in either Br_2- or I_2-containing alcoholic alkoxide or aqueous hydroxide by an oxidative coupling reaction has been known since the late 19th century.[5] However, the reaction has been performed somewhat differently in many cases, and the reaction yields widely varied from less than 20% to as high as 80%. Moreover, differences in the resulting stereoselectivities are observed even under the same experimental conditions.[1,3–5] This indicates that the reaction is highly sensitive to the reaction conditions and to the chemical structures of the substrates. According to the literature procedures, the essential conditions that are necessary to obtain α,β-dicyanostilbenes in a stereoselective manner with a preparative yield are the careful control of the temperature and the concentrations of the base and halogen components; the need for a free halogen constitutes a major industrial drawback as well as scale-up limitations. By considering the unique synthetic and biomedical potential of cyanostilbenes, as well as the large amount of material demanded in the optoelectronic industry, a facile and environmentally benign stereoselective approach to α,β-dicyanostilbenes, which is convenient to perform and suitable for large-scale preparations, is welcome.

The advances in electrosynthesis in the last few decades has provided organic chemists with a new and versatile synthetic device of great promise.[6] One of the most fascinating methods available in organic electrochemistry today is electrocatalytic oxidation that takes place in the presence of mediators or mediatory systems. These mediators allow the use of undivided cells and generally simplify the conduction of the electrochemical process. Among a variety of mediators, the redox system halide anion/halogen is one of the most useful for organic synthesis and large-scale processes.[7] This type of mediatory system was already successfully employed by us in a number of electrocatalytic transformations of cyano-functionalized C–H acids that contained the oxidative coupling process as an intermediate step.[8] The electrolysis in an undivided cell in the presence of an alcohol as a solvent and alkali metal halides affords the simultaneous generation of catalytic quantities of strong base (alkoxide

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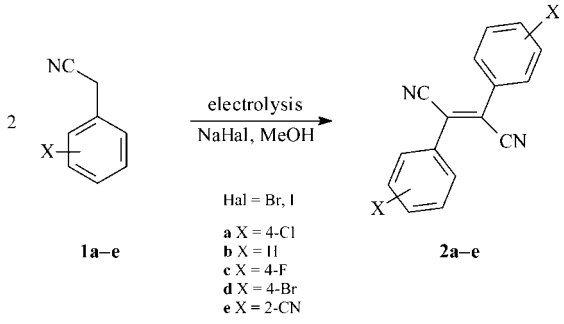
anion) at the cathode and halogen at the anode, which then go through a chemical oxidative cycle in solution that allows them to return back to the electrodes as initial halide anion and alcohol. The mild catalytic nature of the mediatory oxidative process enables low current concentrations of base and halogen along with a neutral pH of the reaction solution, which seems to be a key factor for the selective oxidative coupling of C–H acids bearing a nitrile functionality. Therefore, the application of the described electrocatalytic methodology to the base–halogen-promoted oxidative coupling process of phenylacetonitriles is highly promising as it allows the combination of the synthetic virtues of a mild catalytic oxidation protocol with the benefits and convenience of a cheap and environmentally responsible chemical reagent − electricity.

Results and Discussion

In the present study we report our results on the stereoselective electrocatalytic oxidation of phenylacetonitriles **1a**–**e** into *trans*-α,β-dicyanostilbenes **2a**–**e** in methanol in an undivided cell in the presence of sodium halides as mediators (Scheme 1, Table 1).



Scheme 1.

First, to evaluate the synthetic potential of the proposed procedure and to optimize the electrolytic conditions, the electrocatalytic oxidative coupling of (4-chlorophenyl)acetonitrile (**1a**) was studied (Table 1, Entries 1–6).

The electrolysis of (4-chlorophenyl)acetonitrile (**1a**) in methanol in an undivided cell in the presence of sodium iodide as the mediator under the constant current density of 100 mA cm^{-2} at 30 °C led to the stereoselective formation of bis(4-chlorophenyl)fumaronitrile (**2a**) in 51% yield (Table 1, Entry 1). The decrease in the temperature of electrolysis from 30 to 0 °C increased the yield of **2a** to 68% (Table 1, Entries 2 and 3). Excellent conversions (98–99%) of starting material were obtained in all experiments for a 30 to 0 °C temperature interval after passing 2.5 F mol^{-1} of electricity (Table 1, Entries 1–3). The reaction product was isolated from the reaction mixture by direct filtration after electrolysis. According to NMR spectroscopic and GC analysis, the filtrate of the reaction mixture contained oligomeric by products, which may be a result of undesired addition processes that are possible for anions of cyano-functionalized C–H acids (Table 1, Entries 1–3). An electrolysis temperature of 0 °C was found to be optimal and gave 68% yield of **2a** with 98–99% conversion (Table 1, Entry 3). Further decrease in the temperature to –30 °C suppressed the formation of undesirable oligomeric species, but the conversion of **2a** in latter cases did not exceed 70–75% (Table 1, Entries 4 and 5).

Sodium bromide is a more efficient mediator than sodium iodide for the process studied. The bromine formed at the anode during the electrolysis is a more effective oxidizer compare to iodine, and its presence promotes the chemical oxidation cycle in solution and the removal of the starting material from the undesired oligomerization reaction. Thus, electrocatalytic oxidation of (4-chlorophenyl)acetonitrile (**1a**) in methanol in an undivided cell in the presence of sodium bromide as the mediator at 0 °C leads to corresponding fumaronitrile **2a** in 85% yield (Table 1, Entry 6).

Table 1. Stereoselective indirect electrochemical oxidative coupling of phenylacetonitriles **1a**–**e**.[a]

Entry	Phenylacetonitrile	X	Mediator	Temperature [°C]	Electricity passed [F mol^{-1}]	Product yield [%][b]	Current yield [%]
1	**1a**	4-Cl	NaI	30	2.5	**2a**, 51	41
2	**1a**	4-Cl	NaI	10	2.5	**2a**, 63	51
3	**1a**	4-Cl	NaI	0	2.5	**2a**, 68	54
4[c]	**1a**	4-Cl	NaI	–10	2.5	**2a**, 55	44
5[c]	**1a**	4-Cl	NaI	–30	2.5	**2a**, 50	40
6	**1a**	4-Cl	NaBr	0	2.5	**2a**, 85	68
7[d]	**1a**	4-Cl	NaBr	0	2.5	**2a**, 81	65
8[e]	**1a**	4-Cl	NaBr	0	2.5	**2a**, 78	63
9	**1b**	H	NaI	0	2.5	**2b**, 59	47
10	**1b**	H	NaBr	0	2.5	**2b**, 61	49
11	**1c**	4-F	NaI	0	2.5	**2c**, 58	46
12	**1c**	4-F	NaBr	0	2.5	**2c**, 65	52
13	**1d**	4-Br	NaI	0	2.5	**2d**, 74	59
14	**1d**	4-Br	NaBr	0	2.5	**2d**, 86	69
15	**1e**	2-CN	NaI	0	2.8	**2e**, 53	36
16	**1e**	2-CN	NaBr	0	2.8	**2e**, 56	40

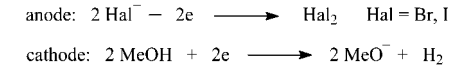
[a] Phenylacetonitrile (10 mmol), mediator (5 mmol), MeOH (20 mL), iron cathode, graphite anode, undivided cell, current density 100 mA cm^{-2}, 98–99% conversion of starting material. [b] Yields of isolated compounds based on starting **1**. [c] 70–75% conversion of starting material. [d] 2.5 mmol of mediator were used. [e] 2 mmol of mediator were used.

The effect of a varied phenylacetonitrile/mediator ratio was experimentally studied next. The electrolyses of 10 mmol of (4-chlorophenyl)acetonitrile (**1a**) in the presence of 5, 2.5 or 2 mmol of sodium bromide under the conditions indicated in Table 1 proceeded with the same conversions of starting material and led to similar reaction yields of 85–78% (Table 1, Entries 6–8). These results confirm the requirement for only a catalytic quantity of sodium halide and underscore the catalytic mediatory nature of the electrochemical process. The whole quantity of mediator could be easily isolated from the reaction mixture after electrolysis.

Under the optimal conditions (sodium halide as mediator, 0 °C reaction temperature, 2.5–2.8 F mol^{-1} electricity passed) the electrolysis of phenylacetonitriles **1a**–**e** in methanol in an undivided cell afforded corresponding bisarylfumaronitriles **2a**–**e** in 60–85% substance yields and 40–70% current yields. Products **2a**–**e** can be isolated by direct filtration of the reaction mixture after electrolysis and they do not need any further purification.

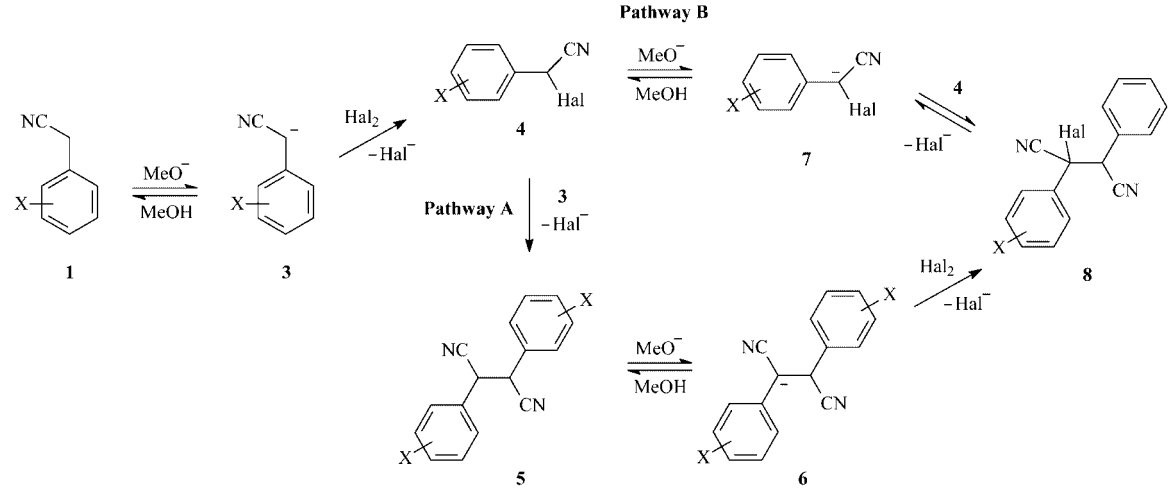
This electrocatalytic process proceeds with excellent stereoselectivity. In all experiments, only a single isomer of α,β-dicyanostilbenes was detected both in the reaction mixture and in the solid product isolated after electrolysis. The *trans* configuration of the double bond in obtained α,β-dicyanostilbenes **2a**,**b**,**d** was established by comparison of the NMR spectral characteristics (for **2b**,**d**) and melting point values (for **2a**,**b**,**d**) with the literature data.[9] We presume that the structures of α,β-dicyanostilbenes **2c**,**e** also possess a *trans* configuration of the double bond.

With the above results taken into consideration, our previous data on the mechanisms of electrochemically induced oxidative coupling of C–H acids,[8] and previous kinetic studies on the chemical dehydrodimerization reaction of phenylacetonitrile,[10] the following mechanism for the stereoselective electrocatalytic transformation of phenylacetonitriles **1a**–**e** into dicyanostilbenes **2a**–**e** is proposed. To start, the reactions that take place at each electrode during the process are shown in Scheme 2.

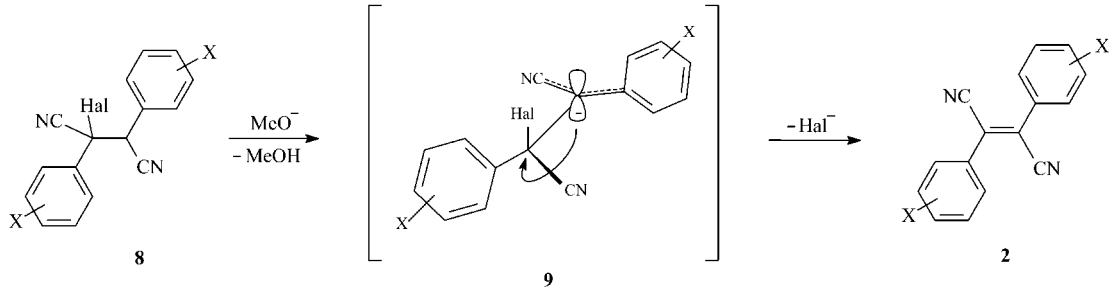


Scheme 2.

The formation of either bromine or iodine at the anode is visually observed by the corresponding colour of the solution when the electrolysis proceeds without stirring. The cathodic process leads to the formation of methoxide anions and liberation of hydrogen gas. In solution, methoxide anions can deprotonate phenylacetonitrile **1** to give rise to phenylacetonitrile anion **3** (Scheme 3). The subsequent halogenation of initially formed carbanion **3** leads to α-halobenzylcyanide **4**. Then, two pathways are possible for the following steps. α-Halobenzylcyanide **4** could be either attacked by carbanion **3** with formation of corresponding succinonitrile **5** (pathway A), or it can undergo deprotonation by methoxide anions to give rise to anion **7** (pathway B). Both pathways A and B do lead to corresponding halosuccinonitrile **8** either by halogenation of intermediate succinonitrile **5** or by the coupling of anion **7** with α-halobenzylcyanide **4**, respectively. According to kinetic studies of the chemical oxidative coupling of phenylacetonitrile, pathway A was found to be slower than pathway B because of the rate-determining halogenation step of succinonitrile anion **6**.[10] However, in the case of excess base and small quantities of halogen, pathway A could be preferable in which case the reaction mainly leads to the formation of succinonitrile **5**.[10] As for the electrocatalytic oxidation of phenylacetonitriles **1a**–**e**, we were not able to determine the presence of succinonitrile **5** either in the reaction mixture during the electrolysis (samples after 1, 1.5 and 2 F mol^{-1}) or in the solid product collected after the process (Table 1, Entries 1–4 and 6–16). The presence of 9% of succinonitrile **5a** was detected only when the electrooxidation was conducted at –30 °C after 1 F mol^{-1} passed (Table 1, Entry 5). These results indicate that both mechanistic pathways are involved in the oxidation coupling reaction, but owing to the low and equal current concentrations of base and halo-



Scheme 3.



Scheme 4.

gen in the solution during the electrocatalytic process, pathway B is faster than pathway A and formation of succinonitrile **5** is not a preferential route under the conditions studied.

The reaction of halosuccinonitrile **8** with methoxide leads to the formation of conjugated anion **9** (Scheme 4). The steric hindrance between the two phenyl groups seems to be the main reason for the subsequent stereoselective elimination of halide anion from the thermodynamically favoured conformation of **9**, which gives rise to *trans*-α,β-dicyanostilbene **2**.

The electrocatalytic oxidative conditions are a key feature of this process; superior stereoselectivity along with good yields in the coupling of phenylacetonitriles are observed. Recently, it was noted that the double bond of α,β-dicyanostilbenes is sensitive to isomerization in the presence of bases, including alkoxides.[11] It is conceivable that the base acts as a nucleophile and transforms the double bond to a rotary C–C single bond. The C–C double bond can then be restored, but with a different configuration (from *cis* to *trans* or from *trans* to *cis*), after elimination of the substituted base. In our case, the low current concentrations of the methoxide anion and halogen during the electrocatalytic process afford not only good substance yield in the oxidative chemistry of species bearing the base-sensitive nitrile group, but the base-promoted isomerization of the formed double bond is also avoided.

Conclusions

The simple electrocatalytic system presented here can produce, under neutral and mild conditions, a stereoselective and efficient transformation of phenylacetonitriles into the corresponding *trans*-α,β-dicyanostilbenes in 60–85% yield with 40–70% current efficiency. This electrocatalytic process offers a facile and convenient way to generate *trans*-α,β-dicyanostilbenes, which are valuable precursors for a variety of optoelectronic materials and biologically relevant systems. The mild catalytic nature of the developed mediatory oxidation process is the key feature that allows superior stereoselectivities and good product yields in such a reagent-sensitive reaction. The electrocatalytic procedure utilizes simple equipment and an undivided cell; it is easily carried out and is valuable from an industrial point of view due to its catalytic nature and the use of a cheap and environmentally benign chemical reagent – electricity.

Experimental Section

General Remarks: All melting points were measured with a Gallenkamp melting point apparatus and are uncorrected. GC analysis was carried out with an LKhM–80 chromatograph with a flame-ionization detector. Columns: (1) fused-silica capillary column HP–1 (5 m × 0.53 mm × 2.65 μm), (2) glass column (3 m × 3 mm) with 10% FFAP with a Chromaton N–Super (0.13–0.16 mm). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker WM-250 spectrometer at ambient temperature. Chemical shift values are relative to Me_4Si. IR spectra were registered with a SPECORD M82 spectrometer. Mass spectra (EI = 70 eV) were obtained directly with a Finningan MAT INCOS 50 spectrometer.

Typical Electrolysis Procedure: A solution of phenylacetonitrile (10 mmol) and sodium halide (5 mmol) in methanol (20 mL) was electrolyzed in an undivided cell equipped with a magnetic stirrer, a graphite anode and an iron cathode at 0 °C under a constant current density of 100 mA cm^{-2} (I = 500 mA, electrodes square 5 cm^2) until the quantity of electricity indicated in Table 1 was passed. After the electrolysis was finished, the solution was filtered to isolate the solid product, which was then rinsed with an ice-cold methanol/water solution (9:1, 2 mL), and dried under reduced pressure.

Bis(4-chlorophenyl)fumaronitrile (2a): White solid. Yield: 2.54 g (85%). M.p. 193–194 °C (ref.[12] 188 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 7.53 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, Ar), 7.79 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, Ar) ppm. ^{13}C NMR (62.53 MHz, $CDCl_3$): δ = 116.2 (2 C), 124.6 (2 C), 129.7 (4 C), 130.0 (4 C), 130.2 (2 C), 138.4 (2 C) ppm. IR (KBr): $\tilde{\nu}$ = 3092, 2224, 1592, 1492, 1404, 1256, 1092, 1012, 828, 824 cm^{-1}. MS: m/z (%) = 299 (15) [M]$^+$, 298 (71), 263 (72), 228 (100), 201 (35), 114 (27), 100 (41), 87 (24), 75 (54), 50 (42). $C_{16}H_8Cl_2N_2$ (299.16): calcd. C 64.24, H 2.70, Cl 23.70, N 9.36; found C 64.20, H 2.74, Cl 23.71, N 9.30.

Diphenylfumaronitrile (2b): White solid. Yield: 1.41 g (61%). M.p. 156–157 °C (ref.[13] 155 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 7.50–7.57 (m, 6 H, Ar), 7.80–7.86 (m, 4 H, Ar) ppm.[1b]

Bis(4-fluorophenyl)fumaronitrile (2c): White solid. Yield: 1.73 g (65%). M.p. 192 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 7.23–7.26 (m, 4 H, Ar), 7.83–7.87 (m, 4 H, Ar) ppm. ^{13}C NMR (62.53 MHz, $CDCl_3$): δ = 116.5 (d, $^2J_{C,F}$ = 22.3 Hz, 4 C), 124.1 (2 C), 127.6 (2 C), 127.8 (2 C), 130.8 (d, $^3J_{C,F}$ = 9.1 Hz, 4 C), 164.3 (d, $^1J_{C,F}$ = 253.5 Hz, 2 C) ppm. IR (KBr): $\tilde{\nu}$ = 3080, 2224, 1600, 1516, 1416, 1256, 1160, 1016, 840, 784 cm^{-1}. MS: m/z (%) = 266 (100) [M]$^+$, 265 (56), 246 (30), 239 (29), 145 (20), 119 (25), 106 (22), 94 (21),

75 (49), 50 (23). $C_{16}H_8F_2N_2$ (266.25): calcd. C 72.18, H 3.03, N 10.52; found C 72.10, H 3.09, N 10.45.

Bis(4-bromophenyl)fumaronitrile (2d): White solid. Yield: 3.33 g (86%). M.p. 216–217 °C (ref.[5f] 214 °C). ^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 7.68–7.71 (m, 8 H, Ar) ppm.[14]

Bis(2-cyanophenyl)fumaronitrile (2e): White solid. Yield: 1.57 g (56%). M.p. 239 °C. ^{1}H NMR (250.13 MHz, [D$_6$]DMSO): δ = 7.88 (t, $^3J_{1H,H}$ = 7.5 Hz, $^3J_{2H,H}$ = 7.5 Hz, 2 H, Ar), 7.98–8.12 (m, 4 H, Ar), 8.19 (d, $^3J_{H,H}$ = 7.6 Hz, 2 H, Ar) ppm. ^{13}C NMR (62.53 MHz, [D$_6$]DMSO): δ = 111.0 (2 C), 113.9 (2 C), 115.9 (2 C), 127.6 (2 C), 130.9 (2 C), 132.7 (2 C), 133.1 (2 C), 134.6 (2 C), 134.7 (2 C) ppm. IR (KBr): $\tilde{\nu}$ = 3076, 2232, 1592, 1572, 1484, 1444, 1288, 1248, 1188, 764 cm^{-1}. MS: *m*/*z* (%) = 280 (100) [M]$^+$, 279 (55), 253 (60), 226 (22), 200 (13), 126 (22), 100 (20), 87 (16), 75 (40), 50 (33). $C_{18}H_8N_4$ (280.29): calcd. C 77.13, H 2.88, N 19.99; found C 77.11, H 2.94, N 19.92.

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