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Electrocatalytic dimerization of diarylacetonitriles mediated by sodium halides

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A new electrocatalytic reaction affording tetraarylsuccinonitriles in 80–100% yields by the oxidation of diarylacetonitriles in an undivided cell with sodium halides as mediators is described.

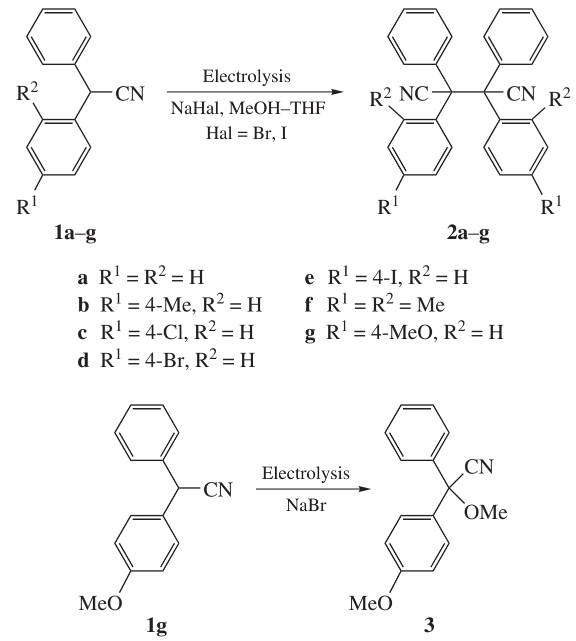
The application of redox mediators to oxidation processes in organic electrochemistry is of considerable current interest.[1–3] Mediators increase the reaction efficiency, selectivity and environmental purity with a simultaneous decrease in power consumption. The substrate oxidation occurs upon reaction with the oxidized form of mediator generated at an anode.

Halides are well-known and popular inorganic mediators,[4,5] which are widely applied to the electrocatalytic oxidation of organic compounds.[4–6] Pairs I^-/I_2 and Br^-/Br_2 with the electrochemically generated iodine and bromine as oxidants are most often used in mediated pairs.[3–5] Their advantages include accessibility and low cost, as well as the fact that the majority of the processes catalyzed by these mediators are performed in an undivided cell. For the first time, the mediated oxidation of CH acids was carried out by Okubo and Tsutsumi,[7] who accomplished electrocatalytic dimerization of malonate with potassium iodide as a mediator. This process was considerably improved by White in 1977, when the malonate dimer was obtained in 90% substance yield with sodium iodide as a mediator.[8]

Tetraphenylsuccinonitrile (TPSN) is an important organic compound in macromolecular synthesis.[9] It was used as an iniferter to prepare telechelics of *n*-butyl methacrylate and *tert*-butyl methacrylate;[10] as an initiator in the free-radical polymerization of methyl methacrylate, *n*-butyl methacrylate, *tert*-butyl methacrylate,[11] styrene[12] and vinyl monomers,[13] and as a modifier in the radiation-induced polymerization of styrene and in the production of azacycloalkane derivatives.[15]

Diarylacetonitriles (DAAs) are extensively used in the synthesis of corresponding dimers – 2,2,3,3-tetraarylsuccinonitriles (TASNs).[16–22] Chemical methods for the synthesis of TASNs are known, but they have considerable disadvantages. Thus, the autooxidation of the diphenylacetonitrile anion resulted in TPSN formation in low yields.[16] Only employment of stoichiometric and even more quantities of oxidants such as I_2,[17] $CuBr_2–H_2O_2$, $CuBr_2$–*tert*-butylhydroperoxide, $KMnO_4$ or $K_3Fe(CN)_6$ resulted in good yields of TPSN.[16] When using stoichiometric quantities of organic oxidants such as *N'*-chloro-*N*,*N*,*N''*,*N''*-tetramethylguanidine[18] and 4-methoxy-2,6-diphenylphenoxyl radical[19] and *tert*-butylperoxide (UV irradiation)[20] TPSN was obtained only in moderate yields. Multistep chemical procedures for the synthesis of TPSN were also proposed.[21,22]

Here, we report the electrocatalytic dimerization of DAAs **1a**–**g** into TASNs **2a**–**g** in an undivided cell in the presence of sodium halides as mediators (Scheme 1, Tables 1 and 2).†



a $R^1 = R^2 = H$
b R^1 = 4-Me, $R^2 = H$
c R^1 = 4-Cl, $R^2 = H$
d R^1 = 4-Br, $R^2 = H$
e R^1 = 4-I, $R^2 = H$
f $R^1 = R^2 = Me$
g R^1 = 4-MeO, $R^2 = H$

Scheme 1

First, the electrocatalytic dimerization of diphenylacetonitrile **1a** into **2a** was carefully studied (Table 1).

The quantitative yield of **2a** was obtained using NaBr as a mediator in MeOH–THF (3 : 1) as a solvent when 1.3 F mol^{-1} of electricity was passed (Table 1, entry 3). Under these optimal conditions, the other experiments were carried out (Table 2).

With NaBr as a mediator, **1a**–**f** were electrocatalytically oxidized into dimers **2a**–**f** in 80–100% yields and the only

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† *General procedure*. A solution of diarylacetonitrile **1** (5 mmol) and sodium halide (2 mmol) in methanol–THF (3:1) (10 ml) was electrolyzed in an undivided cell equipped with a magnetic stirrer, a graphite anode and an iron cathode at 20 °C under a constant current density of 100 mA cm^{-2} (I = 250 mA, electrodes square 2.5 cm^2) until the quantity of 1.3 F mol^{-1} of electricity was passed. After the electrolysis was finished, the solution was filtered to isolate solid product **2**, which was then twice rinsed with an ice-cold methanol–water solution (9:1, 5 ml), and dried under reduced pressure. Methoxy(4-methoxyphenyl)phenylacetonitrile **3** was isolated by flash chromatography on silica gel (0.060–0.200 mm) after evaporation of reaction mixture; eluent, 5% ethyl acetate in hexane.

For characteristics of products **2a**–**g** and **3**, see Online Supplementary Materials.

Table 1 Electrocatalytic dimerization of diphenylacetonitrile **1a**.[a]

Entry	Solvent	Electrolyte	Time/ min	Electricity passed/ F mol^{-1}	Yield of **2a** (%)[b]
1	MeOH	NaBr	32	1	73
2	MeOH–THF, 3:1	NaBr	32	1	80
3	MeOH–THF, 3:1	NaBr	42	1.3	100
4	MeOH–THF, 3:1	NaI	42	1.3	95

[a] **1a** (5 mmol), mediator (2 mmol), solvent (10 ml), iron cathode (2.5 cm^2) graphite anode (2.5 cm^2), current density, 100 mA cm^{-2}, 20 °C. [b] Isolated yield.

Table 2 Electrocatalytic dimerization of DAAs **1a**–**g**.[a]

Entry	Substrate	R^1	R^2	Electrolyte	Electricity passed/ F mol^{-1}	Product, yield (%)[b]
1	**1a**	H	H	NaBr	1.3	**2a**, 100
2	**1b**	Me	H	NaBr	1.3	**2b**, 95
3	**1c**	Cl	H	NaBr	1.3	**2c**, 97
4	**1d**	Br	H	NaBr	1.3	**2d**, 93
5	**1e**	I	H	NaBr	1.3	**2e**, 89
6	**1f**	Me	Me	NaBr	1.3	**2f**, 87
7	**1g**	MeO	H	NaI	1.3	**2g**, 81
8	**1g**	MeO	H	NaBr	1.3	**3**, 53[c]
9	**1g**	MeO	H	NaBr	5	**3**, 88

[a] **1a**–**g** (5 mmol), electrolyte (2 mmol), MeOH–THF, 3:1 (10 ml), iron cathode (2.5 cm^2) graphite anode (2.5 cm^2), current density, 100 mA cm^{-2}, 20 °C. [b] Isolated yield. [c] Yield based on NMR data.

electrocatalytic oxidation of **1g** under these conditions resulted in the formation of another compound, *viz*., methoxy(4-methoxyphenyl)phenylacetonitrile **3**. TASN **2g** (dimer of **1g**) was successfully obtained in 81% yield (Table 2) when sodium bromide was changed for sodium iodide as a mediator.

Taken into consideration the above results and published data on the oxidation of CH acids mediated by alkali metal halides,[7,8,23–28] the following reaction protocol (Schemes 2 and 3) for the direct one-pot dimerization of **1a**–**g** into **2a**–**g** is proposed.

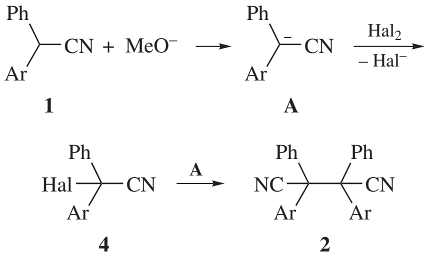
$$\text{Anode: } 2\text{Hal}^- - 2\text{e} \rightarrow \text{Hal}_2 \text{ (Hal = Br, I)}$$

$$\text{Cathode: } 2\text{MeOH} + 2\text{e} \rightarrow 2\text{MeO}^- + \text{H}_2.$$

Scheme 2

The formation of iodine or bromine at the anode is a well-known process and the corresponding colour, as well as the evolution of hydrogen at the cathode, were observed when the electrolysis was conducted without stirring the reaction mixture.

Then, the formation of DAA **1** anion **A** takes place in solution as a result of the interaction between **1** and the methoxide anion. Further halogenation of DAA and interaction of **4** with second anion **A** lead to dimer **2** (Scheme 3).



Scheme 3

Compound **1g**, having an electron-donating substituent in a phenyl ring (4-MeO group), in the presence of sodium bromide as a mediator, was oxidized directly at the anode with the formation of **1g** cation. The following methoxylation of **1g** cation afforded diaryl(methoxy)acetonitrile **3**.

Thus, the new highly efficient electrocatalytic method was found, namely, the preparation of tetraarylsuccinonitriles from diarylacetonitriles in 80–100% yields in an undivided cell in the presence of sodium halides as mediators instead of using large quantities of expensive oxidants.

The process requires the use of a commercially available mediator and inexpensive apparatus. The techniques for electrolysis and isolation of the reaction products are simple and convenient to use both under laboratory conditions and in large-scale apparatus. Therefore, this electrocatalytic method brings us a step closer to the notion of green chemistry and ideal synthesis.[28]

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2010.06.008.

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