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From 4-nitrotoluene and 4,4'-dinitrobibenzyl to *E*-4,4'dinitrostilbene: An electrochemical approach

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The dianions formed by electroreduction of *Z*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$, *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$, $O_2NC_6H_4CH_2\text{-}CH_2C_6H_4NO_2$ or $O_2NC_6H_4CMeH\text{-}CMeHC_6H_4NO_2$, as well as the anion radical arising from 4-nitrotoluene are stable, in the time scale of the cyclic voltammetry (DMF+0.10 M NBu_4BF_4). However, in the electrolysis time scale (from minutes to hours), only the dianion $O_2NC_6H_4CMeH\text{-}CMeHC_6H_4NO_2^{2-}$ remains stable, since the reduced species, *Z*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2^{2-}$, $O_2NC_6H_4CH_2\text{-}CH_2C_6H_4NO_2^{2-}$ or $O_2NC_6H_4Me^{\bullet -}$, evolve to form the *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2^{2-}$ dianion. This intermediate, is recovered as the neutral species *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$ with concomitant water reduction after the work-up with water, as demonstrated by combined electrolysis, cyclic voltammetry experiments, UV-spectroelectrochochemistry and theoretical calculations. Bulk electrolysis in optimized conditions (ACN+0.10 M NBu_4BF_4) provides 40% and 67 % isolated yield of *E*-4,4'-dinitrostilbene from 4-nitrotoluene and 4,4'-dinitrobibenzyl, respectively.

Introduction

Stilbenes have become of particular interest because of wide range of different applications ,not only in chemistry but also in life science and material science, in addition to chemistry.(1–5) Stilbene derivatives are attractive compounds because they undergo easy cis-trans isomerization that can be induced both photochemically, as well as by electrochemical reduction, the latter via an anion radical intermediate.(6–9) Thereby, although stilbene syntheses have been reported in the literature for a long time, this still remains as an area of interest, judging by the number of reports published in recent years.(10–13) In particular, nitroderivatives of stilbene are especially appealing because of its use as textile dyes (i.e.4,4'-dinitrostilbene-2,2'-disulphonic acid).(14,15) Furthermore, nitrostilbenes are reduced at less negative potentials than other stilbene derivatives,(16) thus facilitating their electrochemical *cis-trans* isomerization.

Up to now, it is known that, dinitrobibenzyls and the corresponding dinitrostilbenes are obtained by a reaction between nitrobenzylchlorides and alkoxides. For example, 4-nitrobenzylchloride yields 4,4'-dinitrostilbene ($O_2NC_6H_4CH{=}CHC_6H_4NO_2$) when reacts with an excess of sodium ethoxide in ethanol:(17)

$$p-O_2NC_6H_4CH_2Cl \xrightarrow[C_2H_5OH]{NaC_2H_5O} O_2NC_6H_4CH=CHC_6H_4NO_2$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots35-70\%$$

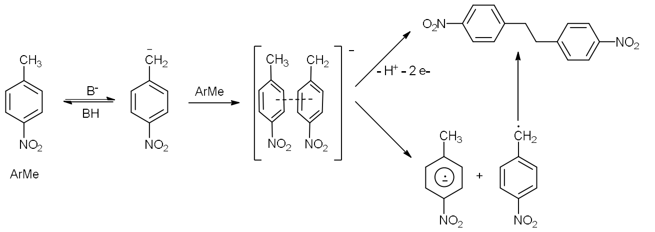
Moreover, 4,4'-dinitrobibenzyl ($O_2NC_6H_4CH_2\text{-}CH_2C_6H_4NO_2$) is also obtained by electrodimerization of corresponding nitrobenzylhalides,(18-20) via C-X heterolytic cleavage of the anion radical:

$$2p-O_2NC_6H_4CH_2X \xrightarrow{+2e^-} O_2NC_6H_4CH_2CH_2C_6H_4NO_2+2X^-$$

Depending on the reaction conditions, both 4,4'-dinitrobibenzyl and 4,4-'dinitrostilbene can be sequentially prepared by treating 4-nitrotoluene ($O_2NC_6H_4Me$) with KMeO in MeOH in the presence of air and with or without other stoichiometric oxidizing agent:(21–23)

$$O_2NC_6H_4Me \xrightarrow[65°C/10h]{KMeO/MeOH,O_2} O_2NC_6H_4CH=CHC_6H_4NO_2$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots74\%$$

Based on kinetic studies, a mechanism for conversion of nitrotoluene into dinitrobibenzyl was proposed some time ago, Scheme 1.(24,25) The reaction starts with deprotonation of nitrotoluene, followed by the formation of a charge transfer complex between the anion and the neutral molecule. This complex evolves following two different routes: (a) losing a proton and two electrons to form dinitrobibenzyl and/or (b) completing the electron transfer between the donor and the acceptor moieties to yield the nitrobenzyl radical and the nitrotoluene anion radical. The nitrobenzyl radical dimerizes to dinitrobibenzyl. Next, the nitrotoluene anion radical is oxidized back to nitrotoluene. The presence of radicals and/or anion radicals of nitrotoluene, dinitrobibenzyl and dinitrostilbene in these reaction media was evidenced by EPR and UV-visible spectroscopy.(24–26) However, the formation dinitrostilbene from dinitrobibenzyl is not described in previous work done.



Scheme 1.

Electrochemistry is a powerful tool to investigate the reaction mechanism involving electron transfer processes and, particularly, to generate anion radical intermediates in a controlled way. The electrochemical reduction of nitroaromatic compounds, A, in the absence of the other electroactive substituents, has been subject of numerous studies.(27,28) When the reduction is conducted in a protic media, depending on the pH of the medium, a wide variety of products can be

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obtained (i.e. anilines, hydroxyl amines, nitroso-compounds). However, in polar aprotic solvents, the sole reduction product of a mononitroaromatic compounds is the anion radical, $A^{\bullet-}$ (characterized in different ways), which in many cases is a persistent species in cyclic voltammetry (CV) time scale. Notice that in polar aprotic solvents and in the CV time scale, there are not chemical reactions associated to the anion radical of mononitroaromatics.

$$A \underset{E^0,k_s,\alpha}{\overset{1e^-}{\rightleftharpoons}} A^{-}$$

In the case of dinitroaromatic compounds, a two-step reduction, corresponding to the formation of anion radical, $A^{\bullet-}$, and dianion, A^{2-} are generally observed, both usually being reversible processes:(29–36)

$$A \underset{E_1^0,k_{s1},\alpha_1}{\overset{1e^-}{\rightleftharpoons}} A^{-}$$

$$A^{-} \underset{E_2^0,k_{s2},\alpha_2}{\overset{1e^-}{\rightleftharpoons}} A^{2-}$$

The easiest case is when both electron transfer reactions are fast. The appearance of the voltammogram depends upon the location of the standard potentials, E_1^0 and E_2^0 and the spacing between them, $\Delta E^0=E_2^0-E_1^0$.(37) When $\Delta E^0>100$ mV, the second electron transfer step takes place at more positive potentials than the first one, and a single two-electron transfer Nernstian wave is observed. However, if 100 mV$>\Delta E^0>-100$ mV, a single wave occurs, with an increasing voltammetric peak width, ΔE_p, compared with previous case, and a number of electrons transferred, $z<2$. The two waves become resolvable at $\Delta E^0=-125$ mV, where each wave takes on the characteristic of a one-electron Nernstian electron transfer. Note that in polar aprotic media and in CV time scale, except for the disproportionation equilibrium of the anion radical $A^{\bullet-}$ into A and A^{2-}, which is governed by ΔE^0, the two negatively charged species do not participate in any other chemical reaction.

The CV in polar aprotic solvents of nitrotoluene, dinitrobibenzyl and dinitrostilbene show reversible waves, corresponding to a fast one-electron transfer for nitrotoluene and fast two-electron transfers for the bis-arene compounds.(27–36) However, the electrochemical conversion of nitrotoluene and dinitrobibenzyl to dinitrostilbene has not been investigated up to now. Hence, the aim of this work is revisited the electrochemical behavior of cis- and trans-4,4′-dinitrostilbene (*Z*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$ and *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$), 4,4′-dinitrobibenzyl ($O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$), α,α′-dibromo-4,4′-dinitrobibenzyl ($O_2NC_6H_4CBrH$-$CBrHC_6H_4NO_2$), α,α′-dimethyl-4,4′-dinitrobibenzyl($O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2$), and 4-nitrotoluene ($O_2NC_6H_4Me$), (Chart 1), and to demonstrate that is possible to obtain *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$ by the electrochemical reduction of both $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$and $O_2NC_6H_4Me$.

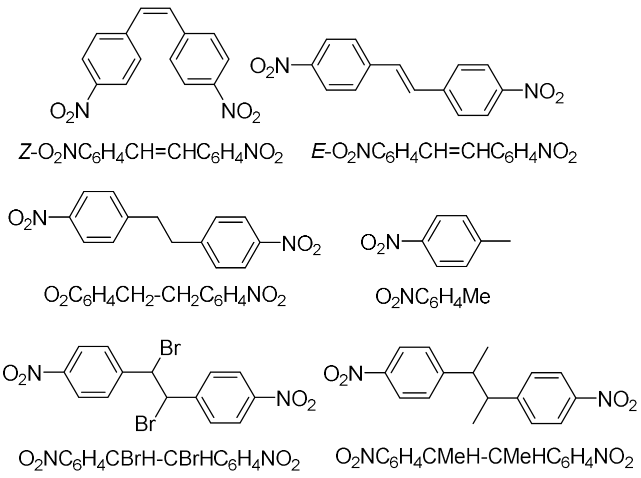


Chart 1.

Results and discussion

CV studies were performed in DMF+0.10 M Bu_4NBF_4 with a glassy carbon millimetric cathode in Ar atmosphere. Slow scan rates were used in CV experiments described in order to prevent kinetic control by the charge transfer reaction.

Figure 1 shows an overview for all investigated compounds before and after electrolysis. Before electrolysis (solid line), most of them exhibit a single reversible two-electron reduction wave, which becomes a single reversible one-electron reduction wave in the case of $O_2NC_6H_4Me$ (Table 1). These waves are concentration and sweep rate independent, corresponding to the formation of dianions ($O_2NC_6H_4CH{=}CHC_6H_4NO_2^{2-}$, $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2^{2-}$, $O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2^{2-}$) and anion-radical ($O_2NC_6H_4Me^{\bullet-}$), all of them being stable in the time range of the CV. In the case of $O_2NC_6H_4CBrH$-$CBrHC_6H_4NO_2$, two reduction waves were observed. The first corresponds to a two-electron irreversible process, while the second is a two-electron reversible one.

Table 1 include the values of voltammetric peak widths, $\Delta E_p=E_p-E_{p/2}$, standard potential, E^0, number of electrons, z, disproportionation equilibrium constant, K_{dis}, applied potential, E_{app}, and number of Faraday consumed for the compounds in DMF+0.10 M Bu_4NBF_4 at 20 ºC. Electrolyses were carried out at controlled potential, at more negative potentials than the first cathodic peak, on a graphite cathode in DMF+0.10 M Bu_4NBF_4 and under Ar atmosphere. After the passage of the desired Faradays (F), solutions were immediately analyzed by CV. The *Z*- and *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$, as well as $O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2$ show identical CV as before the electrolysis, while in the case of $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$, and $O_2NC_6H_4Me$ a new wave appears, revealing that the dianion$O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2^{2-}$ and the anion radical $O_2NC_6H_4Me^{\bullet-}$ are not stables in the time scale of the electrolysis (Figure 1, Table 1). After electrolysis, solutions were quenched with water and extracted with toluene. Composition of the toluene solutions were analyzed by GC-MS and the product distribution was established by GC.

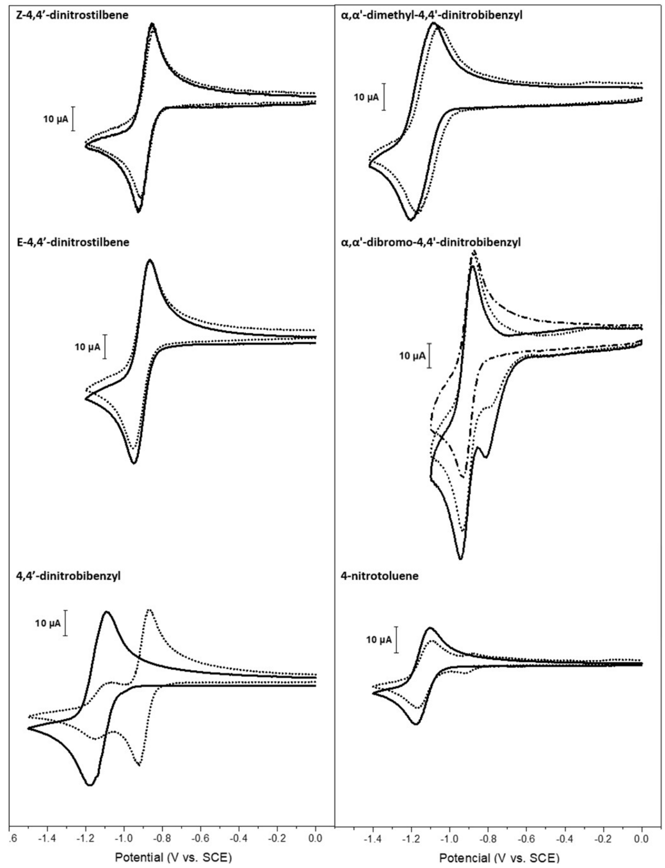


Figure 1. CV of nitroaromatic-compounds (10 mM) in DMF+0.10 M Bu_4NBF_4 at glassy carbon electrode. Scan rate, 0.50 V s^{-1}; temperature, 20 ºC; Ar atmosphere. (—) Before electrolysis; (····) After electrolysis (1F), (-·-·-·) After exhaustive electrolysis at more negative potentials than that of first cathodic peak potential

The detailed electrochemical behavior of each one of the investigated nitroderivatives is described below.

cis- and *trans*-4,4'-Dinitrostilbene (*Z*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$ and *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$).

Both compounds show a reversible reduction wave, concentration and sweep rate independent and the height of the cathodic peaks correspond to two electron transfer processes. The E^0 values are -0.89 V and -0.91 V, and the peak width, ΔE_p, are 53 mV and 48 mV, for the cis- and trans-isomer respectively:

$$O_2NC_6H_4CH=CHC_6H_4NO_2+2e^- \underset{}{\overset{E^0}{\rightleftharpoons}} O_2NC_6H_4CH=CHC_6H_4NO_2^{\;2-}$$

The two-electron transfer processes correspond to two successive one-electron transfer reductions:

$$O_2NC_6H_4CH=CHC_6H_4NO_2+e^- \overset{E_1^0}{\rightleftharpoons} O_2NC_6H_4CH=CHC_6H_4NO_2^{\;-\bullet}$$
$$O_2NC_6H_4CH=CHC_6H_4NO_2^{\;-\bullet}+e^- \overset{E_2^0}{\rightleftharpoons} O_2NC_6H_4CH=CHC_6H_4NO_2^{\;2-}$$

Since ΔE_p is 53 mV and 48 mV for the cis and trans isomers respectively, the corresponding $\Delta E^0=E_2^0-E_1^0$ are -27 mV and -15 mV.(38)In summary, the second electron transfer step occurs at slightly more negative potential than the first one, and the appearance of the wave is indistinguishable from a single two electron transfer Nernstian wave, except for the value of ΔE_p that would be 29 mV in the last case.

From ΔE^0, disproportionation equilibrium constant can be calculated:

$$2O_2NC_6H_4CH=CHC_6H_4NO_2^{\;2-} \rightleftharpoons O_2NC_6H_4CH=CHC_6H_4NO_2+O_2NC_6H_4CH=CHC_6H_4NO_2^{\;2-}$$
$$(RT/F)\ln K_{disp}=\Delta E^0=E_2^0-E_1^0$$

being K_{disp}=0.34 for *Z*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$ and 0.55 for *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$, indicating that the comproportionation of $O_2NC_6H_4CH{=}CHC_6H_4NO_2$ and $O_2NC_6H_4CH{=}CHC_6H_4NO_2^{2-}$ prevails over the disproportionation of $O_2NC_6H_4CH{=}CHC_6H_4NO_2^{\bullet-}$. This result was confirmed by UV-visible spectroelectrochemistry experiments. After electrolysis at -1.20 V during 90 s on a solution of *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$, the spectrum shows several absorption bands at 350, 604, 641 and 660 nm. The band at 350 nm is due to neutral *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$,(24–26) while the others bands are associated to *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2^{\bullet-}$ and *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2^{2-}$.(39)Therefore, in the time range corresponding to CV, *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2^{2-}$ remains stable, except for the disproportionation equilibrium.

When pale yellow solutions of *Z*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$ and *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$ were electrolyzed at -1.20 V (1.0 F), they turned dark blue. The CVs of these solutions only show the wave corresponding to *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$, Figure 1. Furthermore, when the electrolyzed solutions (2.0 F) of *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$, containing the *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2^{2-}$ dianion, were quenched with water and extracted with toluene, the *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$ was obtained with concomitant reduction of water to H_2. Furthermore, treatment in the same way the electrolyzed solutions of *Z*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$ yielded the trans- isomer exclusively, because the already reported cis- to trans- isomerization of the $O_2NC_6H_4CH{=}CHC_6H_4NO_2^{2-}$ and/or the $O_2NC_6H_4CH{=}CHC_6H_4NO_2^{\bullet-}$ species.(6–9)

$$\begin{matrix} Z-O_2NC_6H_4CH=CHC_6H_4NO_2 \\ E-O_2NC_6H_4CH=CHC_6H_4NO_2 \end{matrix} \xrightarrow[ii)H_2O]{i)-1.20V/2.0F} E-O_2NC_6H_4CH=CHC_6H_4NO_2$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 70-89\%$$

In the reaction mixture, trace amounts of 4,4'-dinitrostilbine and bis(4-nitrophenyl)ethanodione, identified by GC-MS analysis and H^1NMR, were also detected together with *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$.

4,4'-Dinitrobibenzyl, $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$

In the reduction scan, one two-electron reversible wave independent of scan rate and concentration was again obtained. The standard potential, E^0 the peak width, ΔE_p, and the number of electrons are -1.15 V, 88 mV and 1.6, respectively.

$$O_2NC_6H_4CH_2-CH_2C_6H_4NO_2+2e^- \overset{E^0}{\rightleftharpoons} O_2NC_6H_4CH_2-CH_2C_6H_4NO_2^{\;2-}$$

As in the previous case, this reaction is consistent with two successive one-electron transfer reductions

$$O_2NC_6H_4CH_2-CH_2C_6H_4NO_2 + e^- \underset{}{\overset{E_1^0}{\rightleftarrows}} O_2NC_6H_4CH_2-CH_2C_6H_4NO_2^{-\square}$$

$$O_2NC_6H_4CH_2-CH_2C_6H_4NO_2^{-\square} + e^- \overset{E_2^0}{\rightleftarrows} O_2NC_6H_4CH_2-CH_2C_6H_4NO_2^{2-}$$

The values of ΔE_p=88 mV and z=1.6 are in agreement with $\Delta E^0=E_2^0-E_1^0\cong-63$ mV that correspond to K_{disp}=0.08.(37,38) Therefore, in the time scale CV, $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2^{2-}$ remains stable, except for the disproportionation equilibrium. After a potential controlled electrolysis of $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$ at -1.20 V (1.2 F), the initial pale-yellow solution becomes dark blue. The CV of the blue solution (dotted line in Figure 1) shows a significant decrease in the peak corresponding to $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$ and the rise of the peak corresponding to the electroreduction of $O_2NC_6H_4CH$=$CHC_6H_4NO_2$. After treatment of the solution as described above, *E*-$O_2NC_6H_4CH$=$CHC_6H_4NO_2$ was obtained with 76% of yield and 15% of unreacted $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$.

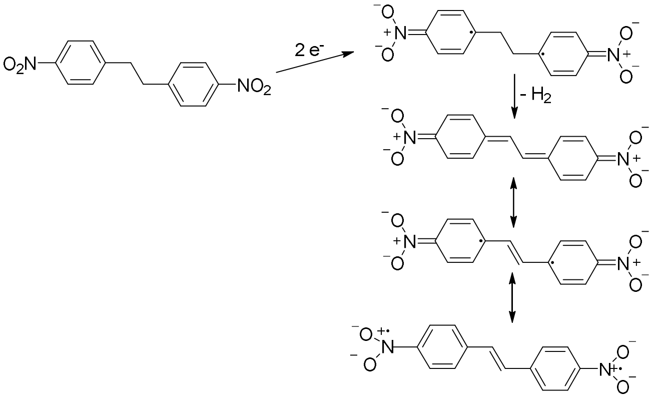
$$O_2NC_6H_4CH_2-CH_2C_6H_4NO_2 \xrightarrow[\text{ii)}H_2O]{\text{i)}-1.20\,V\,/\,1.2F} E-O_2NC_6H_4CH=CHC_6H_4NO_2$$

....76%

UV-visible spectroelectrochemical experiments corroborate the presence of $O_2NC_6H_4CH$=$CHC_6H_4NO_2^{2-}$ and $O_2NC_6H_4CH$=$CHC_6H_4NO_2^{\bullet-}$ in the electrolyzed solutions of $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$. After electrolysis of a solution of this compound at -1.20 V during 45 s, characteristic bands were observed at 604, 641 and 660 nm, corresponding to products of electrolysis of $O_2NC_6H_4CH$=$CHC_6H_4NO_2$ (see above).(39) Both $O_2NC_6H_4CH$=$CHC_6H_4NO_2^{\bullet-}$ and dianion, $O_2NC_6H_4CH$=$CHC_6H_4NO_2^{2-}$ evolve to the neutral molecule, $O_2NC_6H_4CH$=$CHC_6H_4NO_2$, in the working-up of the electrolyzed solution as described above.

The formation of the $O_2NC_6H_4CH$=$CHC_6H_4NO_2^{2-}$ from $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2^{2-}$ during the electrolysis of $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$ can be explained by loss of a hydrogen molecule arising from two acidic benzylic hydrogens from the dianion, as shown Scheme 2.

A similar process of loss of a hydrogen molecule from a nitrobenzilyc compound was reported for the anion radical of 4-nitrobenzyl cyanide anion radical that evolves to stable cyano-4-nitrobenzyl anion in a bimolecular process.(40)



Scheme 2.

Further support for the loss of H_2 was provided by DFT calculations. The $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2^{2-}$ dianion is stable being the singlet state the lowest in energy. These calculations show that the reaction from $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2^{2-}$ to *E*-$O_2NC_6H_4CH$=$CHC_6H_4NO_2^{2-}$ (both in its lowest energy singlet state) plus H_2 is almost thermoneutral. Through single bond rotation around the C-C central bonds two conformers of the reactants are obtained (Scheme 3). The anti-Ar conformer is the most stable one with the gauche-Ar form lying 9.8 kcal mol^{-1} above. By simultaneous enlargement of the two C-H distances of sp^3 carbons the approximate transition state can be located. The calculated energy barriers are quite high 50.4 kcal mol^{-1} for the anti-Ar and 95.0 kcal mol^{-1} for the gauche-Ar. The C-H distances at the transition state are ~1.7 Å (anti-) and ~1.9 Å (gauche-) where the H-H distances are ~1.8 Å in both cases. Given that the reaction coordinate procedure only provides a crude estimation to the structure of the transition state (more so in this case when the two C-H distances are artificially constrained to enlarge simultaneously) this quite high value must be considered an upper limit to the actual energy barrier of the process. The solvent effect, another factor not considered in the theoretical calculations, is also probably lowering this value. The reaction coordinates allows also the elucidation of the products after H_2 elimination. In the anti-conformer the final product is obtained in the trans- geometry whereas the gauche- structure leads to the cis-isomer. Additionally, the two reactions are almost thermoneutral, and the products are -0.4 and +0.2 kcal mol^{-1} for the anti- and gauche-, respectively.

Table 1. Voltammetric Peak Widths, $\Delta E_p=E_p-E_{p/2}$; Standard Potential, E^0; Electron's number, z; Disproportionation Equilibrium Constant, K_{dis}, Applied Potential, E_{ap}, Number of Faraday consumed (F=96500 C mol^{-1}) for the compounds in DMF+0.10 M Bu_4NBF_4 at glassy carbon electrode (CV) or graphite electrode (Electrolysis). 20 °C.

Cyclic Voltammetry

Compound	ΔE_p / mV	E^0/V*vs.* SCE	z	K_{disp}
Z-$O_2NC_6H_4CH=CHC_6H_4NO_2$	53	- 0.89	1.8	0.34
E-$O_2NC_6H_4CH=CHC_6H_4NO_2$	48	- 0.91	2.0	0.55
$O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$	88	- 1.15	1.6	0.08
$O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2$	89	- 1.15	1.6	0.06
$O_2NC_6H_4CBrH$-$CBrHC_6H_4NO_2$	77	- 0.80[b]	1.5	-
PhCBrH-CBrHPh[a]	146	- 1.55[b]	1.7	-
$O_2NC_6H_4Me$	60	- 1.18	1.0	-

			Electrolysis	
Compound	E_{ap}/V*vs.* SCE	F	conversion reactant/%[c]	*E*-$O_2NC_6H_4CH=CHC_6H_4NO_2$/%[c]
Z-$O_2NC_6H_4CH=CHC_6H_4NO_2$	-1.20	2.0	100	89[d]
E- $O_2NC_6H_4CH=CHC_6H_4NO_2$	-1.20	2.0	0	70[d,e]
$O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$	-1.20	1.2	85	76[d]
$O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2$	-1.40	[f]	0	0
$O_2NC_6H_4CBrH$-$CBrHC_6H_4NO_2$	- 0.85	[f]	100	89[d]
PhCBrH-CBrHPh[e]	-1.90	[f]	100	80[g]
$O_2NC_6H_4Me$	-1.20	1.0	37	13[d]

[a] *meso*-1,2-dibromo-1,2-diphenylethane.

[b] Value of peak potential of first wave at 0.50 V s^{-1}.

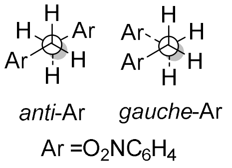
[c] By CV just after electrolysis and GC-MS analysis after treatment of electrolyzed solution.

[d] Others products are not identified.

[e] Trace amounts of 4.4'-dinitrostilibine and bis(4-nitrophenyl)ethanodione are identified by GC-MS analysis and H^1-NMR.

[f] Exhaustive

[g] Stilbene (80%) and 1-bromo,1-phenylethane (5%) are identified by GC-MS analysis after treatment of electrolyzed solution.



	anti- Ar	*gauche*-Ar
Relative energy of reactants /kcal mol^{-1}	0.0	9.8
Transition state energy[a]/kcal mol^{-1}	50.4	104.8
Energy of products/kcal mol^{-1}	-0.4 [b]	10.0 [c]

[a] for: $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2^{2-} \rightarrow O_2NC_6H_4CH=CHC_6H_4NO_2^{2-}+H_2$.

[b] *E*-$O_2NC_6H_4CH=CHC_6H_4NO_2$. [c] *Z*-$O_2NC_6H_4CH=CHC_6H_4NO_2$.

Scheme 3.

α,α'-Dimethyl-4,4'-dinitrobibenzyl, $O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2$

The presence of two methyl groups in α-position does not change the shape of the CV wave. Thus, in the reduction scan, one two-electron reversible wave, independent of scan rate and concentration, is obtained. The standard potential, E^0, the peak width, ΔE_p, and the number of electrons are -1.15 V, 89 mV and 1.6 respectively:

$$O_2NC_6H_4CMeH-CMeHC_6H_4NO_2+2e^- \xrightleftharpoons{E^0} O_2NC_6H_4CMeH-CMeHC_6H_4NO_2^{\,2-}$$

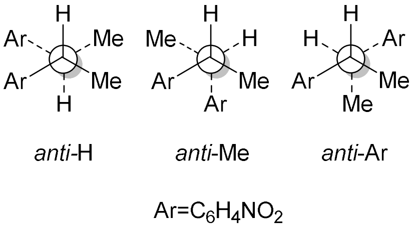
As in the previous cases of $O_2NC_6H_4CH=CHC_6H_4NO_2$ and $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$, this reaction is consistent with two successive one-electron transfer reductions:

$$O_2NC_6H_4CMeH-CMeHC_6H_4NO_2+e^- \xrightleftharpoons{E_1^0} O_2NC_6H_4CMeH-CMeHC_6H_4NO_2^{\,-\square}$$
$$O_2NC_6H_4CMeH-CMeHC_6H_4NO_2^{\,-\square}+e^- \xrightleftharpoons{E_2^0} O_2NC_6H_4CMeH-CMeHC_6H_4NO_2^{\,2-}$$

The values of ΔE_p =89 mV and z=1.6 are in agreement with $\Delta E^0=E_2^0-E_1^0 \cong -64$ mV that correspond to K_{disp}=0.06.(37,38) That is, the comproportionation of $O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2$ and $O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2^{2-}$ overcomes the disproportionation of $O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2^{\bullet-}$.

$$2O_2NC_6H_4CMeH-CMeHC_6H_4NO_2^{\,2-}$$
$$\Updownarrow$$
$$O_2NC_6H_4CMeH-CMeHC_6H_4NO_2+O_2NC_6H_4CMeH-CMeHC_6H_4NO_2^{\,2-}$$

A CV after a potential controlled exhaustive electrolysis at -1.40 V, shows that the dianion is stable. Furthermore, when the solution is quenched with water the reactant is recovered and identified by GC-MS analysis. In others words, the corresponding α,α'-dimethyl-4,4'-dinitrostilbene is not formed in the electrolysis time scale from the dianion $O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2^{2-}$, contrary to what happens with the related dianion $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2^{2-}$. This suggests that the loss of hydrogen from the dianion $O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2^{2-}$ is prevented by steric hindrance of the two methyl groups in α-position. Additionally, a theoretical study is consistent with previous electrochemical results. Calculations indicated that the $O_2NC_6H_4CMeH\text{-}CMeHC_6H_4NO_2^{2-}$ dianion is also stable, with the singlet state being the lowest in energy. (Scheme 4)



	anti-H	*anti*-Me	*anti*-Ar
Relative energy of reactants /kcal mol^{-1}	0	1.1	7.0
Transition state energy[a]/kcal mol^{-1}	--[b]	106.1	75.0

[a] ^{1}for: $O_2NC_6H_4CMeH\text{-}CMeHC_6H_4NO_2^{2-} \rightarrow O_2NC_6H_4CMe{=}CMeC_6H_4NO_2^{2-} + H_2$.

[b] The energy continuously rises as the two H-atoms are separated and the H_2 product cannot be formed.

Scheme 4.

The most stable conformation of the two central sp^3 carbon atoms has the two hydrogen atoms in anti-position so that when enlarging the two C-H bonds the formation of the H_2 molecule is unlikely. This point has been verified by performing a reaction coordinate calculation analogous to the one previously discussed for the parent 4,4'-dinitrobibenzyl dianion, $O_2NC_6H_4CH_2\text{-}CH_2C_6H_4NO_2^{2-}$, and in this case a continuous increase in energy is found as the two hydrogen atoms remain unbounded along all the calculated points. However, we have also calculated the gauche conformers (anti-Me and anti-Ar). These conformers are just 1.1 and 7.0 kcal mol^{-1} above the more stable anti-conformation, respectively, so that the two forms are predicted to be in thermal equilibrium at normal temperatures. A new reaction coordinate calculation from anti-Me and anti-Ar confirms that now the H_2 molecule can be formed at the end of the two simultaneous C-H cleavages but, surprisingly enough, the energy barriers for the process are quite high, 106.1 and 75.0 kcal mol^{-1}, respectively. A careful look at the full picture of the bond breaking reaction coordinate reveals that in the more overcrowded gauche conformations the different skeletal motions (involving both the methyl and the bulk nitrophenyl groups) that facilitate the formation of the H_2 molecule are sterically hindered and so the energy barrier is higher than the value calculated for the 4,4'-dinitrobibenzyl dianion, $O_2NC_6H_4CH_2\text{-}CH_2C_6H_4NO_2^{2-}$.

α,α'-Dibromo-4,4'-dinitrobibenzyl, $O_2NC_6H_4CBrH\text{-}CBrHC_6H_4NO_2$

At 0.50 V s^{-1}, in a reduction scan, two closely spaced two-electron waves, with the first irreversible and narrow (E_p=- 0.80 V vs. SCE, ΔE_p=77 mV) and the second reversible (E^0=-0.90 V vs. SCE), are observed. Upon raising the scan rate up to 100 V s^{-1}, the first wave remains irreversible, and no change was observed in the second one. Moreover, after the first irreversible wave, and regardless of the sweep rate used, the CV shows an anodic irreversible wave at +0.80 V vs. SCE corresponding to oxidation of bromide anion.(41–43)After an exhaustive electrolysis at -0.85 V vs. SCE in Ar atmosphere, CV of the solution only shows the second reversible wave, while the first one has disappeared. This second wave corresponds to $O_2NC_6H_4CH{=}CHC_6H_4NO_2$, as consistently demonstrated by GC-MS analysis of the solution after quenching with water and extraction with toluene. GC analysis of the previous solution show 100% conversion of the dibromo derivative, with 89% yield in *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$:

$$O_2NC_6H_4C(Br)H-C(Br)HC_6H_4NO_2 \xrightarrow[\text{ii)}H_2O]{\text{i)}-0.85\,V\,/\,\text{exhaustive}} E-O_2NC_6H_4CH=CHC_6H_4NO_2$$

....89%

In the same way, the related meso-1,2-dibromo-1,2-diphenylethane (PhCBrH-CBrHPh) (Figure 2 and Table 1) shows a similar electrochemical behaviour, independently of the scan rate used. As expected, it is more difficult to reduce (i.e. the Ep of the first wave is ca. 650 mV more negative than in the dinitrophenyl derivative), because of the lack of the electrowithdrawing NO_2 groups. In a reduction scan at 0.50 V s^{-1}, three waves are observed. The first is irreversible and wide, and corresponds to two-electron transfer (E_p=-1.55 V vs. SCE, ΔE_p=146 mV); the second is a reversible one-electron wave (E^0=-2.20 V vs. SCE) and the third, is an irreversible and narrow one-electron wave (E_p=-2.62 V vs. SCE, ΔE_p=70 mV). The latter two waves correspond to stilbene (cis- or trans-) in accordance with literature.(44–47) Moreover, after the first irreversible wave, and for all sweep rates used, the CV shows an anodic irreversible wave at +0.80 V vs SCE, corresponding to oxidation of bromide anion.(41–43) Furthermore, after exhaustive electrolysis at -1.90 V, the CV only shows the presence of the characteristic waves of the stilbene. Again, GC-MS analysis of the solution quenched with water show the presence of stilbene, as the only product (100% conversion of the reagent and 80% yield)

$$PhC(Br)H-C(Br)HPh \xrightarrow[\text{ii)}H_2O]{\text{i)}-1.90\,V\,/\,\text{exhaustive}} PhCH=CHPh$$

....80%

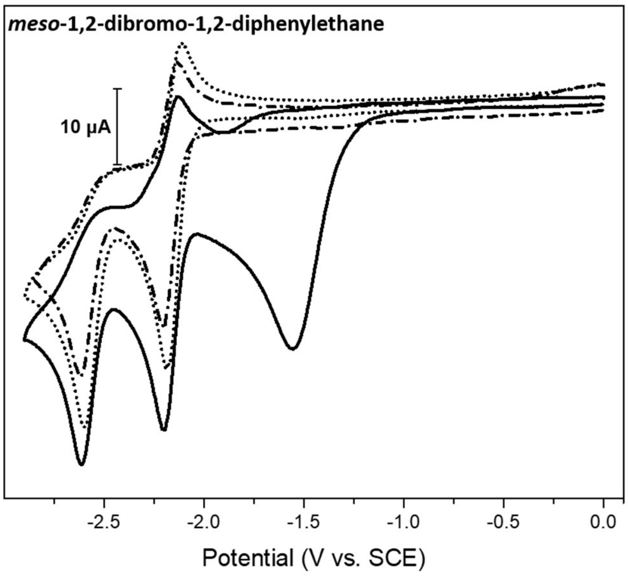
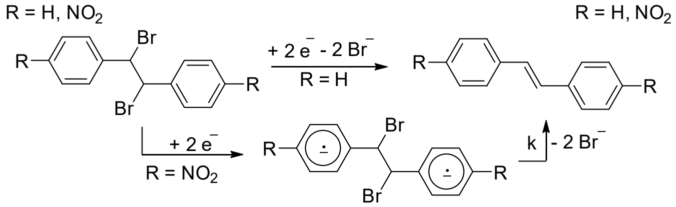


Figure 2. CV of PhCBrH-CBrHPh (6.99 mM) before (—) and after exhaustive electrolysis (····) at more negative potentials that of first cathodic peak potential) and CV of stilbene (5.97 mM) (– • –). In DMF+0.10 M Bu_4NBF_4 at glassy carbon electrode. Scan rate, 0.50 V s^{-1}; temperature, 20 ºC; Ar atmosphere.

In summary, both $O_2NC_6H_4CBrH-CBrHC_6H_4NO_2$ and related PhCBrH-CBrHPh show, after the first cathodic reduction irreversible wave, an anodic one at +0.80 V vs SCE corresponding to the oxidation of the bromide anion. Furthermore, after the first cathodic wave, those corresponding to the presence of $O_2NC_6H_4CH=CHC_6H_4NO_2$ and stilbene are observed, respectively. All these results allow us to conclude that the first reduction waves correspond to the reductive cleavage of both dibromo compounds, $O_2NC_6H_4CBrH-CBrHC_6H_4NO_2$ and PhCBrH-CBrHPh, leading to the corresponding stilbene derivatives and bromide anion. Furthermore, from the shapes of the first waves, the nitro-derivative, $O_2NC_6H_4CBrH-CBrHC_6H_4NO_2$ evolves to the stilbene derivative through a stepwise mechanism, with k > 4 10^3 s^{-1},(48) while PhCBrH-CBrHPh exhibit a concerted reductive cleavage mechanism, Scheme 5.(49,50)



Scheme 5.

Additionally, theoretical results are in good agreement with electrochemical results. It was not possible to optimize the $O_2NC_6H_4CBrH-CBrHC_6H_4NO_2^{2-}$ dianion, because it spontaneously breaks down to produce neutral 4,4'-dinitrostilbene, *E*-$O_2NC_6H_4CH=CHC_6H_4NO_2$, and two bromide anions (the alternative breaking down to Br_2 is found to be 76.13 kcal mol^{-1} higher in energy at the considered level of calculation).

4-Nitrotoluene, $O_2NC_6H_4Me$

In a reduction scan, one-electron reversible wave independent of scan rate and concentration is observed. Values of E^0, the peak width, ΔE_p, and the number of electrons are -1.18 V, 60 mV and 1.0 respectively, which are in agreement with previously reported data in the literature.(29–36) In other words, the anion radical formed in the reduction scan is stable along CV time scale.

$$O_2NC_6H_4Me + e^- \overset{E^0}{\rightleftarrows} O_2NC_6H_4Me^{-\square}$$

However, when a constant potential electrolysis at potential more negative than -1.18 V was carried out, the initial pale-yellow solution evolves to a blue dark solution. When this solution was analyzed by CV, a decrease in the wave corresponding to $O_2NC_6H_4Me$ was observed, concomitant with an increase in the wave corresponding to $O_2NC_6H_4CH=CHC_6H_4NO_2$. Moreover, only $O_2NC_6H_4Me$ and $O_2NC_6H_4CH=CHC_6H_4NO_2$ were recovered after the work-up of the electrolyzed solution. Noticeably $O_2NC_6H_4CH_2-CH_2C_6H_4NO_2$ was not detected in the reaction mixture. The combined CV and electrolysis results indicate that the chemical reactions coupled to an electron transfer process are slow. Thus, conversions and yields were consistently moderate; at -1.20 V (1F), a 13% yield of O2NC6H4CH=CHC6H4NO2, at37% conversion of $O_2NC_6H_4Me$ was achieved, and at -1.70 V (1F) these increase to 22% and 62% respectively. In both cases, the remaining material was recovered as $O_2NC_6H_4Me$:

$$O_2NC_6H_4Me \xrightarrow[\text{ii)}H_2O]{\text{i)}-1.20\,V/1.2F} E - O_2NC_6H_4CH = CHC_6H_4NO_2$$
$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 13\%$$

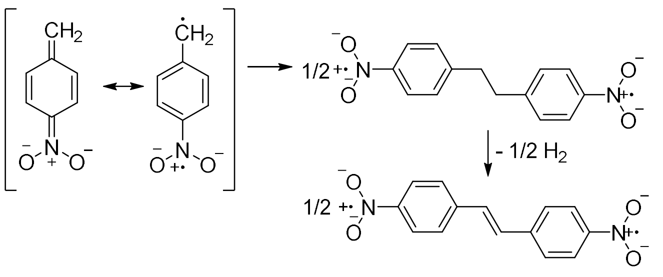
The previous results were confirmed by UV-visible spectroelectrochemistry experiments. After electrolysis at -1.20 V during 90 s of a solution of $O_2NC_6H_4Me$ (10 mM in DMF + 0.1 M Bu_4NBF_4), the spectrum shows bands at 604, 641 and 660 nm, corresponding to electrolysis products, namely of $O_2NC_6H_4CH=CHC_6H_4NO_2$, $O_2NC_6H_4CH=CHC_6H_4NO_2^{2-}$ and $O_2NC_6H_4CH=CHC_6H_4NO_2^{\bullet-}$.(39)

Several authors have shown that the reaction of $O_2NC_6H_4Me$ with an excess of potassium *tert*-butoxide renders $O_2NC_6H_4CH=CHC_6H_4NO_2$, via the nitrobenzyl anion.(21–23) A similar process was repeated here by adding 10 equivalents of PhLi and iPr_2NH in THF to a solution of $O_2NC_6H_4Me$ in DMF. This forms the nitrobenzyl anion that again evolves to $O_2NC_6H_4CH=CHC_6H_4NO_2$, as shown by CV analysis. This suggests that in the electrochemical reduction of $O_2NC_6H_4Me$, the anion radical, $O_2NC_6H_4Me^{\bullet-}$ formed evolves to the 4-nitrotoluene benzyl anion, by a H-atom transfer reaction to a neutral molecule.

$$O_2NC_6H_4CH_3^{-\square} + O_2NC_6H_4CH_3 \;\square\; O_2NC_6H_4CH_2^{-} + O_2NC_6H_4(H)CH_3^{\bullet}$$

A similar process was proposed in the evolution of 4-nitrobenzyl cyanide anion radical to the corresponding anion.(40)

Although the acidic character of $O_2NC_6H_4Me$ is well established, theoretical calculations reveal that in the anion radical $O_2NC_6H_4Me^{\bullet-}$ the process of losing a H-atom is highly endoergic by 68.1 kcal mol^{-1}. However, when the H-atom is transferred to a molecule of $O_2NC_6H_4Me$ the endoergicity dramatically decreases to 36.7 kcal mol^{-1}. As expected, the difference in the energy between the unimolecular and bimolecular reactions arises from the stabilization provided by the delocalization of the unpaired electron on the $O_2NC_6H_4(H)CH_3^{\bullet}$ radical. A value of ca. 36 kcal mol^{-1} for the bimolecular reaction is still high, but the whole process might be allowed if the effect of the surrounding media that will probably favor the reaction were taken into account. Furthermore, the process can be driven by the coupled reactions involving the products formed. Thus, the radical formed, $O_2NC_6H_4(H)CH_3^{\bullet}$, is oxidized at the working potential to $O_2NC_6H_4Me$ and H^+,(51,52) while the 4-nitrobenzylanion dimerizes to form $O_2NC_6H_4CH_2\text{-}CH_2C_6H_4NO_2^{2-}$. This, as was previously demonstrated (see above), evolves by the loss of a hydrogen molecule to $O_2NC_6H_4CH{=}CHC_6H_4NO_2^{2-}$ (Scheme 6). This dianion, $O_2NC_6H_4CH{=}CHC_6H_4NO_2^{2-}$ reacts with water producing H_2 and $O_2NC_6H_4CH{=}CHC_6H_4NO_2$ during the work-up of the solution.



Scheme 6.

Comparative CV behavior

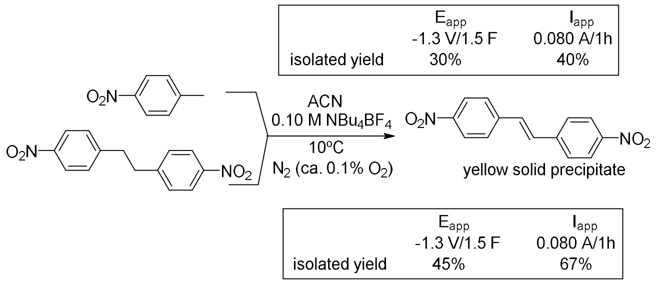
The CV of $O_2NC_6H_4Me$ and $O_2NC_6H_4CH_2\text{-}CH_2C_6H_4NO_2$, $O_2NC_6H_4CMeH\text{-}CMeHC_6H_4NO_2$and $O_2NC_6H_4CH{=}CHC_6H_4NO_2$ in DMF shows a fast two electron transfer reduction for all compounds, except for $O_2NC_6H_4Me$ that shows a one-electron transfer one. The standard potential, E^0, the peak width, ΔE_p, the number of electrons, z as well as the shape of waves are not dependent on scan rates or the concentration used. E^0 values for all compounds, except for $O_2NC_6H_4CH{=}CHC_6H_4NO_2$, differ ca. 30 mV. In the case of dinitrostilbene, because the two negative charges are more easily delocalized between the two conjugated aromatic rings the E^0 is 240 mV more positive than the rest of above mentioned compounds. When comparing the ΔE_p and z for the bielectronic processes, the expected correlation was observed to be in good agreement with the theory. Finally, the $K_{dis}<1$ of the anion radicals indicates the coexistence of the neutral molecule, the anion radical and the dianion. In summary, the four nitroaromatics show the expected reduction mechanism and the reduced species, dianion for the biaryl species or the anion radical anion for nitrotoluene are stable in the CV time scale.

However, the dianions $O_2NC_6H_4CBrH\text{-}CBrHC_6H_4NO_2^{2-}$ and their analogue without a nitro group, $PhCBrH\text{-}CBrHPh^{2-}$, are intrinsically unstable. Both evolve through fast C-Br bond breaking ($k>4x10^3$ s^{-1}) forming $O_2NC_6H_4CH{=}CHC_6H_4NO_2$, PhCH=CHPh and two bromide anions, as shown by the appearance of the waves corresponding to the reduction of $O_2NC_6H_4CH{=}CHC_6H_4NO_2$ and PhCH=CHPh and that of oxidation of the bromide anion.

Comparative electrolysis behavior

The investigated nitroderivatives show two different electrolytic behaviors. Identical I-E curves before and after electrolysis were observed for *Z*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$, *E*-$O_2NC_6H_4CH{=}CHC_6H_4NO_2$, $O_2NC_6H_4CBrH\text{-}CBrHC_6H_4NO_2$, and $O_2NC_6H_4CMeH\text{-}CMeHC_6H_4NO_2$. However, $O_2NC_6H_4CH_2\text{-}CH_2C_6H_4NO_2$ and $O_2NC_6H_4Me$ show dramatically different I-E curves before and after electrolysis. This is because, after the electron transfer, a slow chemical reaction takes place (slower in the case of 4-nitrotoluene). In both cases the chemical reaction finally evolves to *E*-4,4'-dinitrostilbene.

With the aim to improve the yields of the synthetic processes, bulk electrolysis experiments were conducted, both at constant potential or current. Best results were achieved using acetonitrile as solvent and a nitrogen flow through the solution that contains ca. 0.1% of oxygen. In these conditions, pure *E*-4,4'-dinitrostilbene precipitates from the solution as a microcrystalline yellow solid, Scheme 7. Isolated yields range from 30 to 40% from 4-nitrotoluene and from 45 to 67% in the case of 4,4'-dinitrobibenzil. In both cases experiments at constant current provides higher yields, and they are similar to those measured by GC.



Scheme 7.

Experimental

Chemicals

All reagents, ACN, DMF and NBu_4BF_4 were of the highest purity were commercial origin and used as received.

CV and Electrolysis Experiments

Voltammetry and electrolysis experiments were carried out in a jacketed five neck conical cell at 20 ºC. Three of the necks were used for the working, counter, and reference electrodes, while the other two necks were used for the argon inlet and outlet.

For cyclic voltammetry experiments a glassy carbon disk with a 1 mm diameter was used as working electrode, with the counter electrode being a 1 mm diameter Pt disk. The reference electrode is a saturated calomel electrode (SCE), separated from the working electrode compartment by a salt bridge with a ceramic frit.

The number of electrons transferred in an electron transfer step is calculated as the quotient between the function current $[I_p c^{-1} v^{-1/2}]$ of the electroactive substance and the function current, $[I_p c^{-1} v^{-1/2}]_0$ value of fluorenone (number of electrons transferred=1) in the same experimental conditions (solution and working electrode), were I_p is the peak current for reduction wave, c is the concentration of solution, and v the scan rate.

Electrolysis were performed at controlled potential (ca. 100 mV more negative than peak potential) using a carbon graphite rod as a working electrode (8.0 cm^2 of surface), a Pt rod as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. The counter electrode and the SCE were isolated from the working electrode compartment by a salt bridge, with a glass frit for the counter electrode, and a ceramic frit for the reference electrode.

After electrolysis in DMF and at constant potential were complete after the chosen quantity of coulombs was circulated or electrolysis were exhaustive (*i.e.* final current was 5% or less than the initial current), the reaction mixture was extracted, on air, with water/toluene. The organic layer was dried with Na_2SO_4 and evaporated yielding a residue that was analyzed by GC, GC-MS and H^1-NMR.

The electrolysis experiments in ACN+0.10 M NBu_4BF_4 were performed at 10 °C in N_2:O_2 (99.9:0.1) atmosphere in solutions of reagents with concentration ≥20mM in the same electrochemical cell and electrodes described. The exhaustive electrolysis realized at constant potential and current yields a yellow solid that is separated by filtration from blue solution. The solid was recrystallized in hot ethanol. Rendering pure *E*-$O_2NC_6H_4CH=CHC_6H_4NO_2$ (40% and 67%yield from 4-nitrotoluene and 4.4'dinitrobibenzyl, respectively).

DFT Calculations

The well-known B3LYP hybrid functional has been chosen with the split-valence 6-31+G(d,p) basis set that includes polarization functions on all atoms and diffuse sp functions on all atoms other than hydrogens. Geometries have been fully optimized and the transition states have been approximately located by means of a distinguished coordinate calculation that simultaneously enlarges the two C-H bonds that must be cleaved. All calculations have been carried out using the GAUSSIAN09 suite of programs.(53)

Conclusions

The anion radicals from the electroreduction of *Z*-$O_2NC_6H_4CH=CHC_6H_4NO_2$, *E*-$O_2NC_6H_4CH=CHC_6H_4NO_2$, $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$ and $O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2$undergo disproportion into the neutral and dianionic species with equilibrium constants ranging from 0.06 and 0.55. In the time scale of the CV (θ≤0.5 s), the corresponding dianions do not evolve by any chemical reaction, except for the disproportionation. Also, the anion radical 4-nitrotoluene remains stable in these conditions. However, in time scale of electrolysis (from minutes to hours), only the dianion $O_2NC_6H_4CMeH$-$CMeHC_6H_4NO_2^{2-}$ remains stable, since the reduced species, *Z*-$O_2NC_6H_4CH=CHC_6H_4NO_2^{2-}$, $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2^{2-}$ or $O_2NC_6H_4Me^{\bullet-}$, evolve totally or in part to the *E*-$O_2NC_6H_4CH=CHC_6H_4NO_2^{2-}$ dianion. This dianion, after the work-up with water, is recovered as the neutral species *E*-$O_2NC_6H_4CH=CHC_6H_4NO_2$, with concomitant water reduction.

In the case of the *Z*-$O_2NC_6H_4CH=CHC_6H_4NO_2^{2-}$ anion, the negative charge diminishes the bond order of the central C=C bond, allowing the cis- to trans- isomerization.

On the other hand, the $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2^{2-}$ dianion spontaneously releases H_2 to produce *E*-$O_2NC_6H_4CH=CHC_6H_4NO_2^{2-}$, as demonstrated by combined electrolysis CV experiments, spectroelectrochemical experiments and theoretical calculations.

Therefore, in spite of being in electroreductive conditions, the oxidized species *E*-$O_2NC_6H_4CH=CHC_6H_4NO_2$ can be obtained from $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2$. A similar situation takes place in the electroreduction of 4-nitrotoluene, but with a previous step. The corresponding anion radical, $O_2NC_6H_4Me^{\bullet-}$ is converted by intermolecular H-transfer reaction into the benzylic anion $O_2NC_6H_4CH_2^-$, which dimerizes to $O_2NC_6H_4CH_2$-$CH_2C_6H_4NO_2^{2-}$ that evolves as previously described. Again, in this case the oxidized *E*-$O_2NC_6H_4CH=CHC_6H_4NO_2$ can be obtained from 4-nitrotoluene under electroreductive conditions.

Bulk electrolysis in optimized conditions provides 40% and 67% isolated yield of *E*-4,4'-dinitrostilbene from 4-nitrotoluene and 4,4'-dinitrobibenzyl respectively.

In summary, this electrochemical study shown to be a powerful technique to elucidate the mechanism of, at first sight, puzzling reactions, and furthermore allows obtaining by electrolysis *E*-dinitrostilbene from 4-nitrotoluene or 4,4'-dinitrobibenzyl.

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References

1. Doody JJ. Production of Stilbene Azo Dyes. U.S.A.; US 3557079A 1970119, 1971. p. 3.
2. Oppliger MD. Stilbeneazo compounds, preparation thereof and use thereof. Germany; DE 3247605A1 19830707, 1983.
3. Song DH, Yoo HY, Kim JP. Synthesis of stilbene-based azo dyes and application for dichroic materials in poly(vinyl alcohol) polarizing films. Dye Pigment [Internet]. 2007;75(3):727–31. Available from: http://linkinghub.elsevier.com/retrieve/pii/S014372080600310X
4. Likhtenshtein G. Stilbenes: Applications in Chemistry, Life Sciences and Materials Scienc [Internet]. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2009. 360 p. Available from: http://doi.wiley.com/10.1002/9783527628087
5. Chen Y, Peng W, Wang S, Zhang F, Zhang G, Fan X. Supported nano-sized gold catalysts for selective reduction of 4,4'-

dinitrostilbene-2,2'-disulfonic acid using different reductants. Dye Pigment [Internet]. 2012 Nov;95(2):215–20. Available from: http://dx.doi.org/10.1016/j.dyepig.2012.03.009

6. Schulte-Frohlinde D, Blume H, Güsten H. PHOTOCHEMICAL cis-trans-ISOMERIZATION OF SUBSTITUTED STILBENES. J Phys Chem [Internet]. 1962 Dec;66(12):2486–91. Available from: http://pubs.acs.org/doi/abs/10.1021/j100818a039

7. Bard AJ, Puglisi VJ, Kenkel J V., Lomax A. Reductive coupling and isomerization of electrogenerated radical ions of cis- and trans-isomers. Faraday Discuss Chem Soc [Internet]. 1973;56:353. Available from: http://www.scopus.com/inward/record.url?eid=2-s2.0-0009649186&partnerID=tZOtx3y1

8. Yamauchi K, Takashima Y, Hashidzume A, Yamaguchi H, Harada A. Switching between Supramolecular Dimer and Nonthreaded Supramolecular Self-Assembly of Stilbene Amide-α-Cyclodextrin by Photoirradiation. J Am Chem Soc [Internet]. 2008 Apr;130(15):5024–5. Available from: http://pubs.acs.org/doi/abs/10.1021/ja7113135

9. Abdul-Rahim O, Simonov AN, Boas JF, Rüther T, Collins DJ, Perlmutter P, et al. Studies on the Nuances of the Electrochemically Induced Room Temperature Isomerization of cis -Stilbene in Acetonitrile and Ionic Liquids. J Phys Chem B [Internet]. 2014 Mar 20;118(11):3183–91. Available from: http://pubs.acs.org/doi/abs/10.1021/jp500786j

10. Wheeler OH, Pabon HNB de. Synthesis of Stilbenes. A Comparative Study. J Org Chem [Internet]. 1965;30(5):1473–7. Available from: http://dx.doi.org/10.1021/jo01016a031

11. Becker KB. Synthesis of Stilbenes. Synthesis (Stuttg) [Internet]. 1983;1983(5):341–68. Available from: http://www.thieme-connect.de/DOI/DOI?10.1055/s-1983-30334

12. Moncomble A, Floch P Le, Lledos A, Gosmini C. Cobalt-Catalyzed Vinylation of Aromatic Halides Using β-Halostyrene: Experimental and DFT Studies. J Org Chem [Internet]. 2012 Jun;77(11):5056–62. Available from: http://pubs.acs.org/doi/abs/10.1021/jo3005149

13. Shen Z-L, Knochel P. Stereoselective Preparation of Polyfunctional Alkenylindium(III) Halides and Their Cross-Coupling with Unsaturated Halides. Chem - A Eur J [Internet]. 2015 May 4;21(19):7061–5. Available from: http://doi.wiley.com/10.1002/chem.201500943

14. Sutcliffe D, Greenwood S. Manufacture of 4,4'-diaminostilbene-2,2'-disulphonic acid. United Kingdom; GB 1404853 A 19750903, 1975. p. 2.

15. Saiyed AS, Patel KN, Kamath B V., Bedekar A V. Synthesis of stilbene analogues by one-pot oxidation-Wittig and oxidation-Wittig–Heck reaction. Tetrahedron Lett [Internet]. 2012 Aug;53(35):4692–6. Available from: http://dx.doi.org/10.1016/j.tetlet.2012.06.090

16. Fry AJ. Synthetic Organic Electrochemistry. In New York: Harper & Row Publishers; 1972. p. 134–5.

17. Hanna SB, Ruehle PH. The p-nitrobenzyl system. IV. Base-induced transformations in p-nitrobenzyl chloride, bromide, iodide, tosylate, and sulfonium salts. J Org Chem [Internet]. 1975 Dec;40(26):3882–5. Available from: http://pubs.acs.org/doi/abs/10.1021/jo00914a015

18. Lawless JG, Bartak DE, Hawley MD. Electrochemical reduction of nitrobenzyl halides in acetonitrile. J Am Chem Soc [Internet]. 1969 Dec;91(25):7121–7. Available from: http://pubs.acs.org/doi/abs/10.1021/ja01053a038

19. Kirkpatrick DL, Johnson KE, Sartorelli AC. Nitrobenzyl derivatives as bioreductive alkylating agents: evidence for the reductive formation of a reactive intermediate. J Med Chem [Internet]. 1986 Oct;29(10):2048–52. Available from: http://pubs.acs.org/doi/abs/10.1021/jm00160a043

20. Andrieux CP, Le Gorande A, Saveant JM. Electron transfer and bond breaking. Examples of passage from a sequential to a concerted mechanism in the electrochemical reductive cleavage of arylmethyl halides. J Am Chem Soc [Internet]. 1992 Aug;114(17):6892–904. Available from: http://pubs.acs.org/doi/abs/10.1021/ja00043a039

21. Stansbury H, Proops W. Oxidation of p-Nitrotoluene to 4,4'-Dinitrobibenzyl and 4,4'-Dinitrostilbene. J Org Chem [Internet]. 1961 Oct;26(10):4162–4. Available from: http://pubs.acs.org/doi/abs/10.1021/jo01068a640

22. Russell GA, Moye AJ, Janzen EG, Mak S, Talaty ER. Reaction of resonance stabilized anions. XXVII. Oxidation of carbanions. 2. Oxidation of p-nitrotoluene and derivatives in basic solution. J Org Chem [Internet]. 1967 Jan;32(1):137–46. Available from: http://pubs.acs.org/doi/abs/10.1021/jo01277a035

23. Lu J-R, Wang Y-L, Feng Y, Gu L. Synthesis of 4, 4'-Dinitrodibenzyl and 4, 4'-Dinitrostilbene. Chinese J Appl Chem. 2000;17(6):653–5.

24. Russell GA, Pecoraro JM. Electron transfer processes. 20. Conversion to p,p'-dinitrostilbene and other examples of the SRN1 substitution reactions of p-nitrobenzyl derivatives. J Am Chem Soc [Internet]. 1979 Jun;101(12):3331–4. Available from: http://pubs.acs.org/doi/abs/10.1021/ja00506a032

25. Buncel E, Menon BC. Proton-transfer and electron-transfer processes in reaction of p-nitrotoluene with bases. A spectrophotometric study. J Am Chem Soc [Internet]. 1980 May;102(10):3499–507. Available from: http://pubs.acs.org/doi/abs/10.1021/ja00530a032

26. Miller JM, Pobiner H. A Spectrophotometric Study of the Reactions of p -Nitrotoluene in Basic Solution. Anal Chem [Internet]. 1964 Jan;36(1):238–9. Available from: http://pubs.acs.org/doi/abs/10.1021/ac60207a004

27. Mann CK, Barnes KK. Electrochemical Reactions in Nonaqueous Systems. In: Electrochemical Reactions in Nonaqueous Systems. New York, USA: Marcel Dekker, INC; 1970. p. 347–80.

28. Lund H, Hammerich O. Organic Electrochemistry. In: Organic Electrochemistry. 4th ed. New York, USA: Marcel Dekker, INC; 2001. p. 379–410.

29. Ammar F, Savéant JM. Thermodynamics of successive electron transfers. J Electroanal Chem Interfacial Electrochem [Internet]. 1973 Sep;47(1):115–25. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0022072873803511

30. Mohammad M. A single two electron transfer or high disproportionation: Electrochemical reduction of dinitrobibenzyl. Electrochim Acta [Internet]. 1977 Apr;22(4):487–8. Available from: http://linkinghub.elsevier.com/retrieve/pii/0013468677851050

31. Kalninsh KK, Kutsenko AD, Archegova AS. Structure, electron-accepting properties, and reactivity of nitrostilbenes. J Struct Chem [Internet]. 1998;39(4):520–31. Available from: http://link.springer.com/10.1007/BF02701382

32. Halas SM, Okyne K, Fry AJ. Anodic oxidation of stilbenes bearing electron-withdrawing ring substituents. Electrochim Acta [Internet]. 2003 Jun [cited 2014 Apr 25];48(13):1837–44. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0013468603002500

33. Kraiya C, Singh P, Todres Z V, Evans DH. Voltammetric studies of the reduction of cis- and trans-α-nitrostilbene. J Electroanal Chem [Internet]. 2004 Mar;563(2):171–80. Available from:

http://linkinghub.elsevier.com/retrieve/pii/S0022072803005412

34. Kraiya C, Singh P, Evans DH. Revisiting the heterogeneous electron-transfer kinetics of nitro compounds. J Electroanal Chem [Internet]. 2004 Mar;563(2):203–12. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0022072803005448
35. Macías-Ruvalcaba NA, Evans DH. Study of the Effects of Ion Pairing and Activity Coefficients on the Separation in Standard Potentials for Two-Step Reduction of Dinitroaromatics. J Phys Chem B [Internet]. 2005 Aug;109(30):14642–7. Available from: http://pubs.acs.org/doi/abs/10.1021/jp051641p
36. Macías-Ruvalcaba NA, Telo JP, Evans DH. Studies of the electrochemical reduction of some dinitroaromatics. J Electroanal Chem [Internet]. 2007 Feb;600(2):294–302. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0022072806005705
37. Bard AJ, Faulkner LR. Electrochemical Methods: Fundamental and Applications. In: Bard AJ, Faulkner LR, editors. Electrochemical Methods: Fundamental and Applications. 2nd ed. New York: John Wiley & Son; 2001. p. 505–9.
38. Polcyn DS, Shain I. Theory of Stationary Electrode Polarography for a Multistep Charge Transfer with Catalytic (Cyclic) Regeneration of the Reactant. Anal Chem [Internet]. 1966 Mar;38(3):376–82. Available from: http://pubs.acs.org/doi/abs/10.1021/ac60235a003
39. Álvarez-Griera L, Gallardo I, Guirado G. Estimation of nitrobenzyl radicals reduction potential using spectro-electrochemical techniques. Electrochim Acta [Internet]. 2009 Sep;54(22):5098–108. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0013468609002643
40. Bartak DE, Hawley MD. Stabilities of the anion radicals of nitrobenzyl derivatives. J Am Chem Soc [Internet]. 1972 Jan;94(2):640–2. Available from: http://pubs.acs.org/doi/abs/10.1021/ja00757a058
41. Rifi MR, Covitz FH. Introduction to Organic Electrochemistry. In: Introduction to Organic Electrochemistry. New York, USA: Marcel Dekker, INC; 1974. p. 194–219.
42. Lund T, Lund H. Indirect electrochemical reduction of some benzyl chlorides. Acta Chem Scand. 1987;41:93–102.
43. Gallardo I, Guirado G, Marquet J. Nucleophilic Aromatic Substitution of Hydrogen: A Novel Electrochemical Approach to the Cyanation of Nitroarenes. Chem Eur J [Internet]. 2001 Apr 17;7(8):1759–65. Available from: http://doi.wiley.com/10.1002/1521-3765%2820010417%297%3A8%3C1759%3A%3AAID-CHEM17590%3E3.0.CO%3B2-F
44. Gatti N, Pedersen SU, Lund H, Ernster L, Lönnberg H, Berg J-E, et al. Electrochemical Methods for Determination of Rate Constants. III. Homogeneous Electron Transfer Followed by Elimination Induced by the Substrate Anion. Acta Chem Scand [Internet]. 1988;42b(1):11–22. Available from: http://actachemscand.org/doi/10.3891/acta.chem.scand.42b-0011
45. Fawell P, Avraamides J, Hefter G. Reduction of Vicinal Dihalides. I. The Electrochemical Reduction of meso and (±)-1,2-Dibromo-1,2-diphenylethane. Aust J Chem [Internet]. 1990 Aug 1;43(8):1421. Available from: http://dx.doi.org/10.1071/CH9901421
46. Fry AJ, Porter JM, Fry PF. Electrochemical Formation and Dimerization of α - Substituted Benzyl Radicals. Steric Effects on Dimerization. J Org Chem [Internet]. 1996 Jan;61(9):3191–4. Available from: http://www.ncbi.nlm.nih.gov/pubmed/11667185
47. Bollo S, Soto-Bustamante E, Núñez-Vergara LJ, Squella JA. Electrochemical study of nitrostilbene derivatives: nitro group as a probe of the push–pull effect. J Electroanal Chem [Internet]. 2000 Sep;492(1):54–62. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0022072800002655
48. Andrieux CP, Savéant JM. Investigations of Rates and Mechanisms of Reactions. In: Bernasconi CF, editor. Investigations of Rates and Mechanisms of Reactions. 4th ed. New York: John Wiley & Sons, Inc; 1986. p. 305–90.
49. Andrieux CP, Gallardo I, Saveant JM. Outer-sphere electron-transfer reduction of alkyl halides. A source of alkyl radicals or of carbanions? Reduction of alkyl radicals. J Am Chem Soc [Internet]. 1989 Mar;111(5):1620–6. Available from: http://pubs.acs.org/doi/abs/10.1021/ja00187a014
50. Andrieux CP, Grzeszczuk M, Saveant JM. Electrochemical generation and reduction of organic free radicals. alpha-Hydroxybenzyl radicals from the reduction of benzaldehyde. J Am Chem Soc [Internet]. 1991 Nov;113(23):8811–7. Available from: http://pubs.acs.org/doi/abs/10.1021/ja00023a032
51. Andrieux CP, Pinson J. The Standard Redox Potential of the Phenyl Radical/Anion Couple. J Am Chem Soc [Internet]. 2003 Dec;125(48):14801–6. Available from: http://pubs.acs.org/doi/abs/10.1021/ja0374574
52. Gallardo I, Soler S. Electrochemically promoted arylation of iodoaromatics. J Electroanal Chem [Internet]. 2017 Aug;799(May):9–16. Available from: http://linkinghub.elsevier.com/retrieve/pii/S1572665717303946
53. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09, Revision B.01 [Internet]. Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT. Wallingford CT; 2009. Available from: citeulike-article-id:9096580