

# Nucleophilic Aromatic Substitution of Hydrogen: A Novel Electrochemical Approach to the Cyanation of Nitroarenes

Illuminada Gallardo,\* Gonzalo Guirado, and Jordi Marquet<sup>[a]</sup>

**Abstract:** The nucleophilic aromatic substitution of hydrogen through electrochemical oxidation of the intermediate  $\sigma$  complexes (Meisenheimer complexes) in simple nitroaromatic compounds is reported for the first time. The studies have been carried out with hydride and cyanide anions as the nucleophiles using cyclic voltammetry (CV) and preparative electrolysis. The cyclic voltammetry experiments allow for the detection and characterization of the  $\sigma$  complexes and led us to a proposal for the mechanism of the oxidation step. Furthermore, the power of the CV technique in the analysis of the reaction mixture throughout the whole chemical and electrochemical process is described.

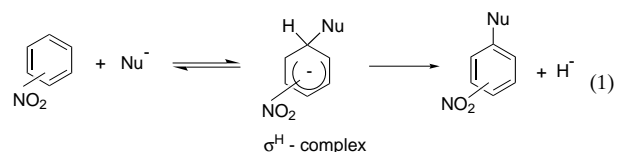
**Keywords:** cyclic voltammetry • electrochemistry • Meisenheimer complexes • nucleophilic substitution •  $\sigma$  complexes

## Introduction

The development of new environmentally favourable routes for the production of commercially relevant chemical intermediates and products is an area of considerable interest. These synthetic routes require, in most cases, the discovery of new atomically efficient chemical reactions. According to these requirements, we have focused our attention on the nucleophilic aromatic substitution in hydrogen reactions (NASH)<sup>[1, 2]</sup> as a means to generate functionalized aromatics without the need for halogenated materials or intermediates.<sup>[3]</sup> NASH reactions formally require the replacement of a hydride ion, and occur “spontaneously” consuming part of the starting material in the oxidation step, or they are promoted by the addition of external oxidants. Low yields (with few exceptions)<sup>[4]</sup> and lack of generality are the main drawbacks of these synthetic procedures.<sup>[1, 2]</sup> In addition, some of the chemical substances used as oxidants, are hazardous in their own right. In this respect, use of electrochemical techniques seem to be very attractive, but curiously enough, this approach has been almost completely neglected in the chemical literature.

Nucleophilic reagents react for example with nitroarenes. The initial step of these reaction is usually reversible addition

to the unsubstituted 1- and 4-positions to produce the  $\sigma^H$  complexes<sup>[1, 2, 5, 6]</sup>



These  $\sigma^H$  complexes may be converted into products of hydrogen-atom replacement in two ways: *vicarious* nucleophilic substitution<sup>[7-11]</sup> extensively investigated in the case of carbanionic nucleophiles and with several examples of nitrogen and oxygen nucleophiles.<sup>[12]</sup> A second strategy involves a *chemical* oxidation of a intermediate  $\sigma^H$  complex through formal displacement of H<sup>-</sup>.<sup>[1, 2, 5, 6]</sup> The rearomatization of  $\sigma^H$  adducts is difficult with mild or moderately strong chemical oxidants.<sup>[13, 14]</sup>

One variety of chemical oxidation is the electrochemical oxidation of  $\sigma^H$  adducts. In a very recent paper Terrier et al. have established,<sup>[15]</sup> by electrochemical methods, the mechanism leading to the rearomatized products for the 2-nitropropene adducts of nitrosubstituted 1,2,3-benzoxadiazoles and related 1-oxides.

<sup>1</sup>H NMR spectroscopy is the most widely used and reliable technique for investigating the structure and the reactivity of anionic  $\sigma$  complexes,<sup>[16]</sup> as well as <sup>13</sup>C and <sup>15</sup>N NMR spectroscopy, which have only recently been applied to this type of compound.<sup>[17]</sup> Stopped-flow (SF) and temperature-jump (TJ) are additional techniques that have been frequently employed.<sup>[18]</sup> Calorimetric studies,<sup>[19]</sup> radioactive exchange<sup>[20]</sup> and high-pressure stopped-flow experiments<sup>[21]</sup> have also been used to study complexation.

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Our work will show that electrochemical methods can provide additional information to the previously mentioned opening interesting possibilities in  $S_NAr$  reactions:

- Such as determining precisely the position which has been attacked by the nucleophile, the number of  $\sigma^H$  complexes formed as a result of this attack, and the amount of  $\sigma^H$  complex formed, and
- prove that the electrochemical oxidation of  $\sigma^H$  adducts leads to the rearomatized product and formal  $H^-$  substitution (from the starting nitroarene) in excellent yields.

In order to establish the mechanistic details and synthetic scope of the electrochemical method, this study has been carried out for a wide series of 1,3-dinitrobenzene derivatives and related compounds **1** to **15** (Scheme 1): 1-amino-2,4-dinitrobenzene (**1**), 1,3-dinitrobenzene (**2**), 1-methyl-2,4-dinitrobenzene (**3**), 1-methoxy-2,4-dinitrobenzene (**4**), 1-fluoro-2,4-dinitrobenzene (**5**), 1-chloro-2,4-dinitrobenzene (**6**), 1-bromo-2,4-dinitrobenzene (**7**), 3,5-dinitrobenzonitrile (**8**), 3-nitrobenzonitrile (**9**), 1,3,5-trinitrobenzene (**10**), 1-methyl-2,4,6-trinitrobenzene (**11**), 3-nitrobenzofluoride (**12**), 3,5-dinitrobenzofluoride (**13**), 2,4-dinitronaphthalene (**14**), and 2-nitrothiophene (**15**), with two nucleophiles:  $H^-$  and  $CN^-$ . The first one,  $H^-$ , has allowed us to establish the mechanism of electrochemical oxidation and subsequently the precise determination of the position which has been attacked by the nucleophile, the number of  $\sigma^H$  complexes formed as a result of this attack, and the amount of  $\sigma^H$  complex formed. The second one,  $CN^-$ , has been used to complement the study of the electrochemical oxidation of  $\sigma^H$  adducts and to establish a new environmentally friendly synthetic route for the cyanation of nitroarene systems.

## Results and Discussion

### Hydride ion as a nucleophile ( $H^-$ )

The synthesis,<sup>[22]</sup> purification, characterisation and kinetics of  $\sigma^H$  complexes **1a**<sup>-</sup> to **11a**<sup>-</sup> (Scheme 1) has been previously reported.<sup>[23]</sup>

**Electrochemical behaviour of compound 1a<sup>-</sup>:** The characteristic voltammogram ( $1.00 \text{ V s}^{-1}$ ) of **1a** in DMF is shown in Figure 1a. An irreversible two-electron oxidation wave (ca. 0.30 V) on the first anodic scan, and a reversible one-electron reduction wave (ca.  $-1.03 \text{ V}$ ) are observed. The Figure 1b shows that, on the first cathodic scan, the reversible one-electron reduction wave does not exist, while the irreversible two-electron oxidation wave appears unchanged; on the second cathodic scan the reduction wave appears (ca.  $-1.03 \text{ V}$ ). This reduction wave, at  $-1.03 \text{ V}$ , correspond to the product formed in the first anodic process.

The Figure 1c shows the cyclic voltammogram of **1**. A reduction wave is observed ( $E_p = -1.03 \text{ V}$ ) and no further oxidation wave is seen in the potential range of  $-1.2 \text{ V}$  to  $+1.5 \text{ V}$ .

Addition of authentic **1** to the solution of **1a**<sup>-</sup> cause the increase of the reduction wave. Furthermore, after exhaustive controlled potential electrolysis (2F) of a solution of **1a**<sup>-</sup> at

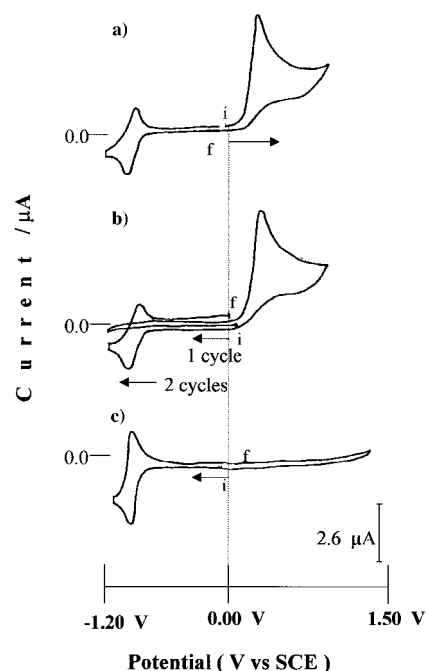


Figure 1. a) Cyclic voltammetry of **1a**<sup>-</sup> (6.0 mM) in DMF+0.1M  $n\text{Bu}_4\text{NBF}_4$  at  $10^\circ\text{C}$ . Scan rate  $1.0 \text{ V s}^{-1}$ , glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/1.00/–1.20/0.00 V. b) Cyclic voltammetry of **1a**<sup>-</sup> (6.0 mM) in DMF+0.1M  $n\text{Bu}_4\text{NBF}_4$  at  $10^\circ\text{C}$ . Scan rate  $1.0 \text{ V s}^{-1}$ , glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/–1.15/1.00/–1.15/0.00 V (two cycles). c) Cyclic voltammetry of **1a** (6.0 mM) in DMF+0.1M  $n\text{Bu}_4\text{NBF}_4$  at  $13^\circ\text{C}$ . Scan rate  $1.0 \text{ V s}^{-1}$ , glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/–1.10/1.35/0.00 V.

$+0.50 \text{ V}$ , cyclic voltammetric analysis of this solution indicated that **1** was the only final product, formed in quantitative yield. Therefore, the species arising from the oxidation of anionic  $\sigma^H$  complex **1a**<sup>-</sup> can be identified as **1**.

The voltammogram of **1a**<sup>-</sup> at  $380 \text{ V s}^{-1}$  (Figure 2) presents a reversible one-electron oxidation wave with  $E^\circ = 0.325 \text{ V}$ . That is, if there are no chemical reactions linked to electron transfer, one-electron wave is observed.

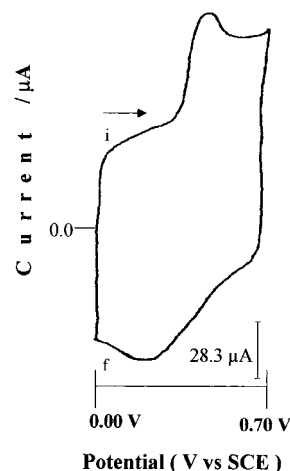
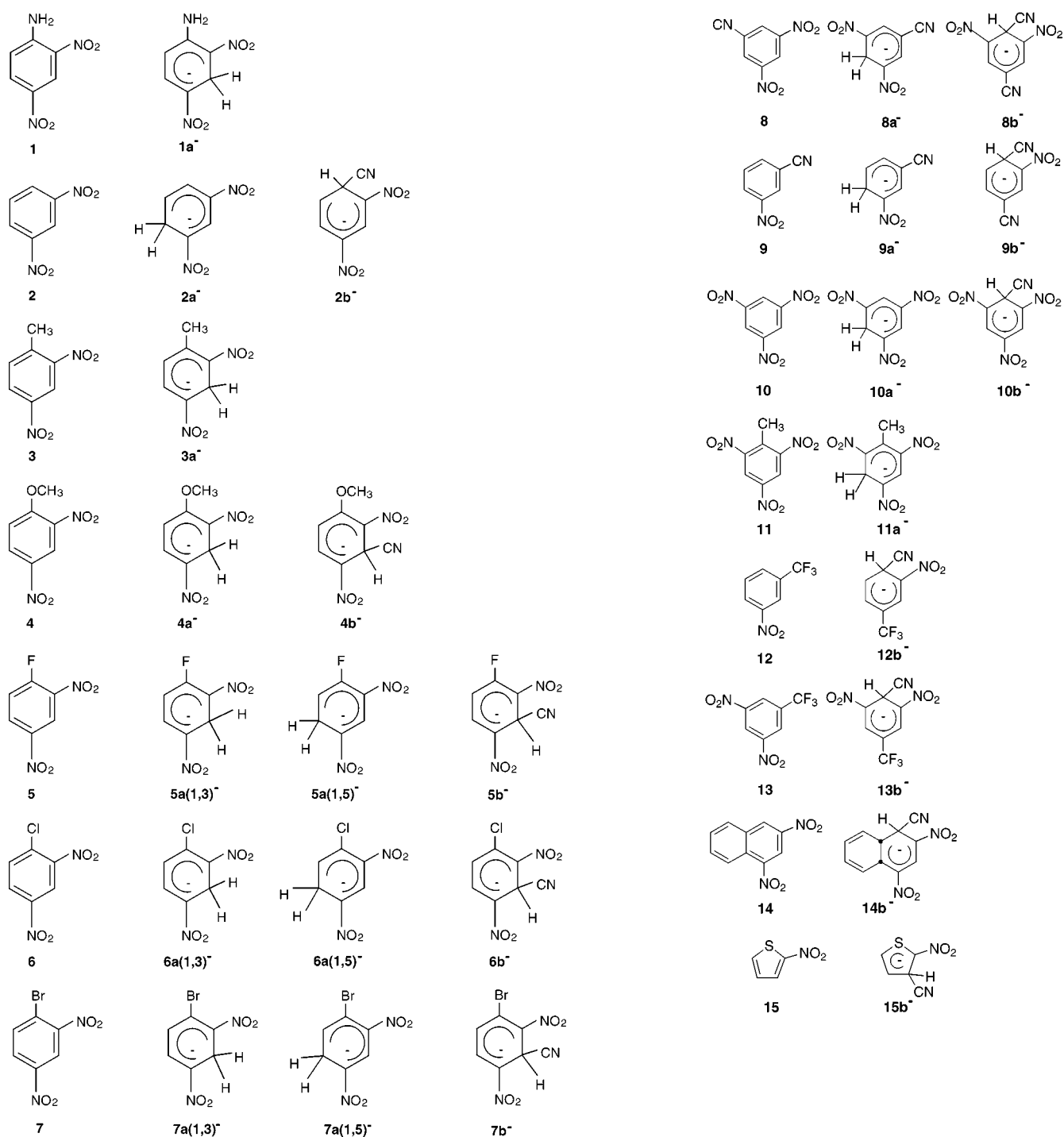
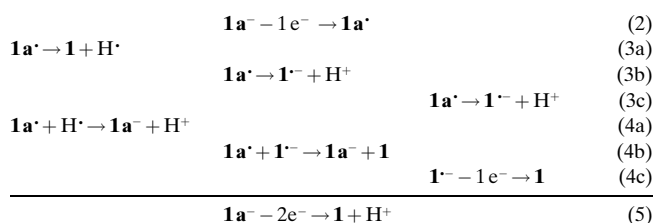


Figure 2. Cyclic voltammetry of **1a**<sup>-</sup> (6.0 mM) in DMF+0.1M  $n\text{Bu}_4\text{NBF}_4$  at  $10^\circ\text{C}$ . Scan rate  $380 \text{ V s}^{-1}$ , glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/0.70/0.00 V.



Scheme 1. Different intermediates and complexes 1–15.

**Mechanistic discussion:** Our experimental results show that after exhaustive oxidation of  $\sigma^{\text{H}}$  complex  $1\text{a}^-$ , the rearomatized substituted compound **1** is obtained as a result of formal loss of two electron and a proton. Furthermore, the voltammograms show that the oxidation of  $\sigma^{\text{H}}$  complex  $1\text{a}^-$  occurs through a three-step mechanism: a first electron transfer on the electrode, one chemical reaction and a second electron transfer in solution (DISP mechanism) or on the electrode (ECE mechanism).<sup>[24]</sup> In following Equations (2)–(5) three mechanistic hypothesis are formulated [Eqs. (2), (3a), (4a)/(2), (3b), (4b)/(2), (3b), (4c)].



In all cases, the first step [Eq. (2)] involves loss of one electron by the  $\sigma^{\text{H}}$  complex  $1\text{a}^-$  with formation of the corresponding radical,  $1\text{a}^\bullet$ . This radical undergoes first-order C–H bond

cleavage [Eqs. (3)] to give either the final rearomatized compound **1**, and hydrogen atom (as proposed by Terrier in related systems)<sup>[15]</sup> or the radical anion of the rearomatized compound **1<sup>-</sup>**, and a proton as earlier proposed by Sosonkin.<sup>[25]</sup> The final oxidation of the hydrogen atom or of the radical anion, **1<sup>-</sup>**, can be performed by the radical, **1a<sup>•</sup>** or by the electrode. In conclusion, the three mechanism are kinetically equivalent. However, in our case, for compound **1a<sup>-</sup>**, the more likely mechanism would be the mechanism described in Equations (3b)/(4b) or Equations (3b)/(4c). The C–H acidity of cyclohexadienyl radicals of **1a<sup>•</sup>** type, where the corresponding aromatic radical anion is stabilized by electron attracting groups is very significant<sup>[26]</sup> and the voltammogram of a mixture of **1a<sup>-</sup>** with 2,6-lutidine (1:0.5) shows irreversibility up to 20000 Vs<sup>-1</sup>. Furthermore, the basicity of the radical anion of dinitroaromatic compounds is very weak.<sup>[27]</sup> The reduction wave of **1** remains reversible in the presence of small amounts of added water (a one-thousand-fold excess of water is necessary for the wave to become irreversible). In spite of the relative fast cleavage of **1a<sup>•</sup>**, the present work does not give any evidence to solve the uncertainty: ECE/DISP in the last step of the mechanism.<sup>[28]</sup>

**Electrochemical behaviour of compounds 2a<sup>-</sup> to 11a<sup>-</sup>:  $\sigma^H$  Complexes 2a<sup>-</sup> to 11a<sup>-</sup>** were prepared by stoichiometric addition of tetramethylammonium borohydride to solutions of compounds **2** to **11** in DMF under inert atmosphere.

The same cyclic voltammetry experiments described for compound **1a<sup>-</sup>** were also performed with compounds **2a<sup>-</sup>** to **11a<sup>-</sup>**. The results are summarized in Table 1. From the Table 1, we see that, in these systems, the cyclic voltammetry allows for the:

1) determination of the efficiency of the hydride attack to nitroaromatic compound, **2** to **11**, in order to form the corresponding  $\sigma^H$  complexes. A 100% efficiency in  $\sigma^H$  complex formation implies that no reduction wave of nitroaromatic compound is observed, in the first cathodic

scan. If a reduction wave in the first cathodic scan appears, it would correspond to the nitroaromatic compound which has not been attacked by the hydride ion. Thus, it is possible to determine the yield of formation  $\sigma^H$  complex. This resulted in a 100% yield for the series of  $\sigma^H$  complexes.

- 2) determination of how many  $\sigma^H$  complexes are present in the mixture and their relative amounts by regarding the number and potential values of the two-electron irreversible oxidation waves. For compounds **5**, **6** and **7**, two kinds of  $\sigma^H$  complexes are identified, probably adducts 1,3 and 1,5.
- 3) conclusion that oxidation of the cyclohexadienyl anions lead to the rearomatized nitroaromatic compound, **2** to **11**, by observing only their one-electron reversible reduction wave after one anodic scan of the solution. This is confirmed by exhaustive electrolysis at potential sufficient positive of solutions of  $\sigma^H$  complexes **2a<sup>-</sup>** to **11a<sup>-</sup>**, were the only products obtained are rearomatized nitroaromatic compound, **2** to **11**, respectively.

As a summary of this part, once the mechanism of electrochemical oxidation of an authentic sample of **1a<sup>-</sup>** has been established, we have demonstrated that cyclic voltammetry is a powerful tool for studying the  $\sigma^H$  complexes formed in situ. On the other hand, the evaluation of the nucleophilic attack will probably be related with the efficiency of the nucleophilic aromatic substitution. To obtain substituted products using nucleophiles different from hydride ion is the evident extension of this work.

#### Cyanide ion (CN<sup>-</sup>) as a nucleophile

**Electrochemical behaviour of  $\sigma^H$  complex 2b<sup>-</sup>** (see Scheme 1): This adduct was prepared by careful stoichiometric addition of tetraethylammonium cyanide to a solution of **2** in DMF under inert atmosphere.

Altogether, cyclic voltammetry (Figure 3) and controlled-potential electrolysis (Table 2) experiments similar to the

Table 1. Electrolysis (2F) of **1a<sup>-</sup>–11a<sup>-</sup>** (10 mM) at oxidation peak potential (column 4) plus about 100 mV.

Nitroarene	$\sigma^H$ Complex	% $\sigma^H$ Complex	$E_{pa}$ [V] <sup>[a]</sup> $\sigma^H$ Complex	UV Spectra [nm] of the mixture	Oxidation product	Yield [%]	$E^\circ$ [V] Oxidation product <sup>[30]</sup>
<b>1</b>	<b>1a<sup>-</sup></b>	100	0.30	268, 348, 578	<b>1</b>	100	-0.95
<b>2</b>	<b>2a<sup>-</sup></b>	100	0.39	288, 354, 532, 560 594, 672, 686	<b>2</b>	100	-0.82
<b>3</b>	<b>3a<sup>-</sup></b>	100	0.25	286, 314, 352 536, 600, 698	<b>3</b>	100	-0.96
<b>4</b>	<b>4a<sup>-</sup></b>	100	0.30	264, 326, 614, 658	<b>4</b>	100	-1.00
<b>5</b>	<b>5a(1,3)<sup>-</sup></b> <b>5a(1,5)<sup>-</sup></b>	100	0.33(80%) 0.44(20%)	268, 366, 430, 550 580, 670, 684	<b>5</b>	100	-0.79
<b>6</b>	<b>6a(1,3)<sup>-</sup></b> <b>6a(1,5)<sup>-</sup></b>	100	0.32(78%) 0.44(22%)	268, 320, 360, 370 530, 576, 654, 668	<b>6</b>	100	-0.78
<b>7</b>	<b>7a(1,3)<sup>-</sup></b> <b>7a(1,5)<sup>-</sup></b>	100	0.32(70%) 0.44(30%)	268, 320, 360, 370 530, 572, 654, 668	<b>7</b>	100	-0.78
<b>8</b>	<b>8a<sup>-</sup></b>	100	0.60	268, 312, 404, 532 574, 656, 670	<b>8</b>	100	-0.62
<b>9</b>	<b>9a<sup>-</sup></b>	100	0.19	268, 350, 478, 536	<b>9</b>	100	-0.90
<b>10</b>	<b>10a<sup>-</sup></b>	100	0.77	270, 348, 478 566, 606	<b>10</b>	100	-0.58
<b>11</b>	<b>11a<sup>-</sup></b>	100	0.62	260, 486, 516, 576	<b>11</b>	100	-0.68

[a] In the case of products which form two isomeric adducts their  $E_p$  were assigned by comparison with the other products and by reported NMR data.<sup>[28, 30]</sup>

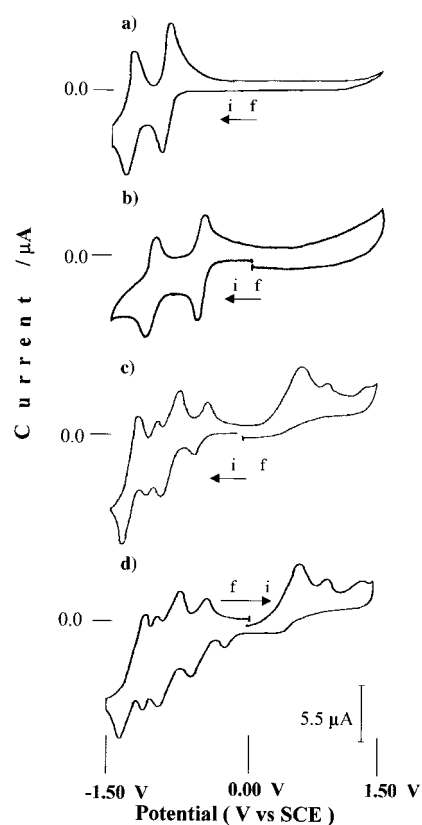
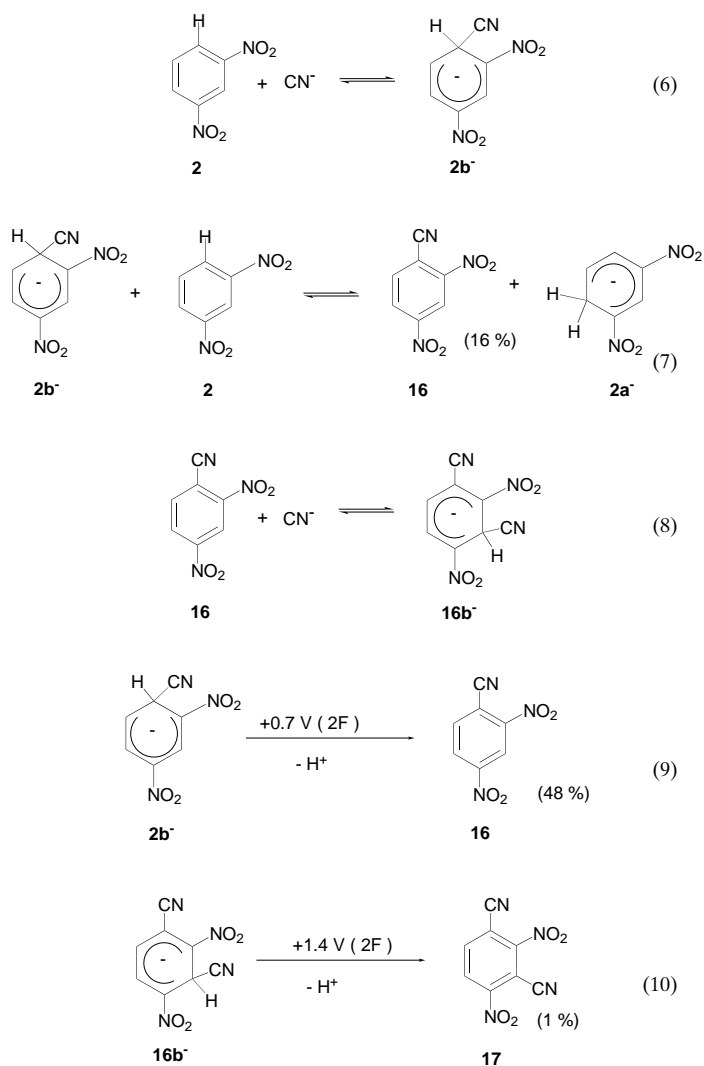


Figure 3. a) Cyclic voltammetry of **2** (6.0mM) in DMF+0.1M  $n\text{Bu}_4\text{NBF}_4$  at 13 °C. Scan rate 1.0  $\text{Vs}^{-1}$ , glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/–1.50/1.50/0.00 V. b) Cyclic voltammetry of **16** (6.0mM) in DMF+0.1M  $n\text{Bu}_4\text{NBF}_4$  at 13 °C. Scan rate 1.0  $\text{Vs}^{-1}$ , glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/–1.50/1.50/0.00 V. c) Cyclic voltammetry of the mixture between **2** (6.0mM) and tetraethylammonium cyanide (6.0mM) in DMF 1:1 under inert atmosphere +0.1M  $n\text{Bu}_4\text{NBF}_4$  at 10 °C. Scan rate 1.0  $\text{Vs}^{-1}$ , glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/–1.50/1.50/0.00 V. d) Cyclic voltammetry of the mixture between **2** (6.0mM) and tetraethylammonium cyanide (6.0mM) in DMF 1:1 under inert atmosphere +0.1M  $n\text{Bu}_4\text{NBF}_4$  at 10 °C. Scan rate 1.0  $\text{Vs}^{-1}$ , glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/1.50/–1.50/0.00 V.

ones described in the first part of the paper allow us to describe the formation of  $\sigma^{\text{H}}$  complex **2b**<sup>–</sup> and further chemical and electrochemical reactions [Eqs. (6)–(10)].

The first step [Eq. (6)] is a reversible addition of  $\text{CN}^-$  to **2** resulting in the  $\sigma^{\text{H}}$  complex **2b**<sup>–</sup> (yield 50%). This  $\sigma^{\text{H}}$  complex undergoes a *thermal* process (yield 16%). Upon reaction with **2** (in slow equilibrium process, fast enough to be established prior to cyclic voltammetry measurements but slow enough to be not displaced at slow scan rates) the rearomatized compound, 2,4-dinitrobenzonitrile (**16**)<sup>[29]</sup> is obtained [Eq. (7)]. Compound **16** gives a new  $\sigma^{\text{H}}$  complex, **16b**<sup>–</sup> with excess of  $\text{CN}^-$  [Eq. (8)].  $\sigma^{\text{H}}$  Complexes **2b**<sup>–</sup> and **16b**<sup>–</sup> undergo electrochemical oxidation at +0.70 V [Eq. (9)] and +1.40 V [Eq. (10)]. This oxidation involves formal loss of two electron and a proton and the final products are **16** (48%) and 2,4-dinitroisophthalonitrile, **17** (5%), respectively. Compounds **16** and **17** were identified by GC-MS,  $^1\text{H}$  RMN and cyclic voltammetry.

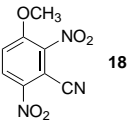
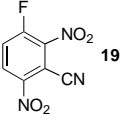
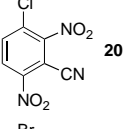
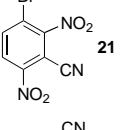
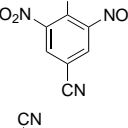
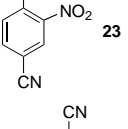
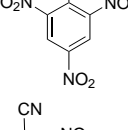
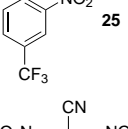
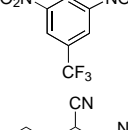
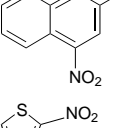
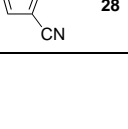


The voltammograms show the electrochemical behaviour of compound **2** (Figure 3a), compound **16** (Figure 3b) and the mixture of **2**+ $\text{CN}^-$  (Figure 3c and Figure 3d). The Figure 3c shows, starting with a reduction scan, the reduction of compound **16** (formed according to [Eq. (7)]) and the reduction of unreacted compound **2**. In an oxidation scan,  $\sigma^{\text{H}}$  complexes **2b**<sup>–</sup> and **16b**<sup>–</sup> ( $E_p = +0.59$  V and  $E_p = +0.98$  V) and the unreacted  $\text{CN}^-$  ( $E_p = +1.24$  V) are identified. A similar behaviour is obtained when the first scan is an oxidation scan (Figure 3d), the difference is the new peak reduction corresponding to compound **17** ( $E_p = -0.24$  V). Complex **17** is formed according to Equation (10).

Our results indicate that the exhaustive controlled-potential oxidation of  $\sigma^{\text{H}}$  complex formed in  $\text{S}_{\text{N}}\text{Ar}$  constitute a new route for the cyanation of nitroarenes. This study was extended to different nitroarenes (**4**–**10** and **12**–**15**) in order to establish the scope of the reaction.

**Cyanation results:**  $\sigma^{\text{H}}$  Complexes **4b**<sup>–</sup>, **5b**<sup>–</sup>, **6b**<sup>–</sup>, **7b**<sup>–</sup>, **8b**<sup>–</sup>, **9b**<sup>–</sup>, **10b**<sup>–</sup>, **12b**<sup>–</sup>, **13b**<sup>–</sup>, **14b**<sup>–</sup> and **15b**<sup>–</sup> (see Scheme 1) were prepared by careful stoichiometric addition of tetraethylammonium cyanide to solutions of the nitroarenes in DMF under inert atmosphere. Its characterisation was carried out by cyclic

Table 2. Electrolysis (2F) of **2b**<sup>-</sup>, **4b**<sup>-</sup>–**10b**<sup>-</sup>, **12b**<sup>-</sup>–**15b**<sup>-</sup> (25 mM) at oxidation peak potential (column 4) plus about 100 mV.

Nitroarene	% $\sigma$ Complexes	$\sigma^H$ Complex	$E_{pa}$ [V] $\sigma^H$ Complex	Product of NASH	Yield [%]	$r \times 100$ ( $r = \text{Ar-CN}/\sigma$ complexes)
<b>2</b>	50	<b>2b</b> <sup>-</sup>	0.59	<b>16</b>	48	96
<b>4</b>	40	<b>4b</b> <sup>-</sup>	0.61	 <b>18</b>	15	38
<b>5</b>	48	<b>5b</b> <sup>-</sup>	0.56	 <b>19</b>	8	17
<b>6</b>	57	<b>6b</b> <sup>-</sup>	0.59	 <b>20</b>	7	13
<b>7</b>	86	<b>7b</b> <sup>-</sup>	0.59	 <b>21</b>	6	7
<b>8</b>	46	<b>8b</b> <sup>-</sup>	0.92	 <b>22</b>	40	87
<b>9</b>	45	<b>9b</b> <sup>-</sup>	0.65	 <b>23</b>	45	88
<b>10</b>	65	<b>10b</b> <sup>-</sup>	1.04	 <b>24</b>	60	92
<b>12</b>	38	<b>12b</b> <sup>-</sup>	0.58	 <b>25</b>	35	92
<b>13</b>	48	<b>13b</b> <sup>-</sup>	1.03	 <b>26</b>	43	90
<b>14</b>	35	<b>14b</b> <sup>-</sup>	0.64	 <b>27</b>	35	100
<b>15</b>	35	<b>15b</b> <sup>-</sup>	0.62	 <b>28</b>	35	100

voltammetry (oxidation peak potential and intensity of the remaining nitroarene reduction wave) (columns 2, 3 and 4, Table 2). The yield of formation of  $\sigma^H$  complexes is superior to 35% in all the cases.

After exhaustive controlled potential electrolysis at oxidation peak potential plus about 100 mV, the rearomatized

substituted compound is obtained as a result of formal loss of two electron and a proton (NASH product, column 5, Table 2). The yield in  $\sigma$  complex formation (column 2, Table 2) goes from 35% to 86%. Electrochemical efficiency goes from 35% to 60% (column 6, Table 2) or from 87% to 100% (column 7, Table 2). The reaction is very clean, recovering only starting material (column 1, Table 2) apart from the reaction products (column 5, Table 2). For the compounds **4**, **5**, **6** and **7**, where a low yield in NASH is observed, the compound **16** is obtained in 30% yield.<sup>[30]</sup>

In summary, the electrochemical oxidation of  $\sigma^H$  complexes formed by addition by  $\text{CN}^-$  to nitroarenes is obtained with good yield giving rise to rearomatized compound in what formally constitutes a loss of  $\text{H}^-$ . Some advantages of this new cyanation method<sup>[31, 32]</sup> are: a) low-cost and high-availability of the reagents, b) atom economy, c) environmentally friendly (clean chemistry), d) high yields, close to 100%, over non-recovered starting material. Almost no secondary products are produced.

We are currently working in the extension of this methodology to other nucleophiles and substrates.

## Experimental Section

**Chemicals:** Compounds **1**–**9** and **12**–**15** were from Aldrich Chemical Co. Compound **10** was purchased from Supelco. Compound **11** was from Union Española de Explosivos. Tetramethylammonium borohydride was also from Aldrich. Tetrabutylammonium tetrafluoroborate (puriss

pa) and tetraethylammonium cyanide were from Fluka. Commercial products were of the highest purity available and used as received. Compound **1a**<sup>-</sup> was prepared as tetramethylammonium salt as in reference.<sup>[12]</sup> Compounds **2a**<sup>-</sup>–**11a**<sup>-</sup> were prepared in situ under nitrogen atmosphere by careful addition of one equivalent of tetramethylammonium borohydride to the corresponding nitroaromatic compound. Compounds **2b**<sup>-</sup>, **4b**<sup>-</sup>–**10b**<sup>-</sup>, **12b**<sup>-</sup>–**15b**<sup>-</sup> were prepared in situ under nitrogen

atmosphere by careful addition of one equivalent of tetraethylammonium cyanide to the corresponding nitroaromatic compound in DMF.

**General procedure for NASH in nitroarenes:** The corresponding anion (**2b<sup>-</sup>**, **4b<sup>-</sup>**–**10b<sup>-</sup>**, **12b<sup>-</sup>**–**15b<sup>-</sup>**), prepared in situ in DMF with 0.1M *n*Bu<sub>4</sub>NBF<sub>4</sub>, was oxidised electrochemically (2F) using a carbon graphite electrode. After the reaction was complete, the mixture was extracted with water/toluene. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated affording a residue that was analyzed by gas chromatography. The analysis showed the presence of the nitrocompounds: **16**, **18**–**28**. The products were analysed by GC/MS, <sup>1</sup>H NMR and cyclic voltammetry and identified by comparison of their spectroscopic behaviour with the reported in the literature in each case (**16**,<sup>[33]</sup> **18**,<sup>[34]</sup> **23**,<sup>[35]</sup> **24**,<sup>[36]</sup> **25**,<sup>[37]</sup> **26**,<sup>[38]</sup> **28**,<sup>[39]</sup> **20**<sup>[40]</sup>). Compounds **19** and **21** gave the same voltammetric behaviour as **20**.

Compound **22**: <sup>1</sup>H NMR (250 MHz, CD<sub>3</sub>CN, 25 °C, TMS): δ = 8.86 (s, 1H); MS (70 eV): *m/z* (%): 218 (13) [M]<sup>+</sup>, 188 (66), 172 (2), 168 (1), 158 (100), 128 (20), 126 (22), 102 (14), 100 (36), 99 (19), 87 (16), 75 (99), 46 (58); E° = –0.35 V.

Compound **27**:<sup>[41]</sup> <sup>1</sup>H NMR (250 MHz, CD<sub>3</sub>CN, 25 °C, TMS): δ = 8.86 (s, 1H), 8.43 (d, *J* = 7.89 Hz, 1H), 8.10 (dd, *J* = 5.26, 1.33 Hz, 1H), 8.01 (dd, *J* = 7.41, 5.26 Hz, 1H), 7.90 (dq, *J* = 7.89, 7.41, 1.33 Hz, 1H); MS (70 eV): *m/z* (%): 243 (74) [M]<sup>+</sup>, 213 (10), 167 (13), 151 (100), 150 (20), 141 (29), 140 (14), 139 (45), 138 (13), 124 (32), 102 (11), 100 (13), 99 (15), 76 (19), 74 (22), 50 (17); E° = –0.33 V.

**Instrumentation and procedures:** The electrochemical cell and measurement procedures for CV and electrolysis have been described previously.<sup>[42]</sup> All potentials are reported versus an saturated calomel electrode.

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