Electrochemical Synthesis of Alkyl Nitroaromatic Compounds

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Cyclic Voltammetry Experiments

Figure S1

a) Cyclic voltammetry of the mixture between 1,3-dinitrobenzene (20.0 mM) and BuLi (1:1) in THF/DMF mixture under inert atmosphere + 0.4M nEtN₄BF₄ at 10°C. Scan rate 1.0 Vs⁻¹, glassy carbon disk electrode (0.05 mm diameter). The scan is in the potential range: 0.00/-1.00/1.70/0.00 V (2 cycles)

b) Cyclic voltammetry of **1** (6.0 mM) in DMF + 0.1M nBu₄NBF₄ at 13°C. Scan rate 1.0 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

Figure S1b shows the electrochemical behaviour of pure 1,3-dinitrobenzene starting with a reduction scan. On the cathodic scan two reversible one-electron waves at $E_p = -0.88$ V and $E_p = -1.24$ V vs SCE, which correspond to the radical-anion and dianion of 1,3-dinitrobenzene are found. However, on the anodic scan no oxidation waves appeared, which implies that the 1,3-dinitrobenzene is not oxidable in the potential range used.

Figure S1a shows on the first cathodic scan a reversible wave at -0.88 V, which corresponds to the unreacted 1,3-dinitrobenzene (compound in blue). In this sense, the calculation of the nucleophilic attack can be easily calculated by a comparison between the initial intensity value and the final value. On the anodic scan two waves appear at 0.56 V vs. SCE. Note that the first one corresponds to a σ^H -adduct (compound in blue) and leads to the substitution product (alkyl nitroaromatic compound (compound in red)). On a second reduction scan a reduction wave appears at c.a 0.89 V (compounds in red), which corresponds to the rearomatized compound and the unreacted starting material.

After this simple voltammetric analysis, an exhaustive electrolysis at 1.50 V was performed. It is important to remark that before performing the electrolysis all the samples were analysed by means of cyclic voltammetry.