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Electroinduced Carbene Formation in the Cathodic Reduction of 1,2-Dicarbonyl Compounds via Electron-Transfer to the Solvent

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ABSTRACT

Electrochemical reduction of 9,10-phenanthrenequinone, benzil and acenaphthenequinone in 1,1,1-trichloroethane (TCE)/TBAP under constant potential conditions provides an interesting entry to new coupling products through an electron-transfer reaction in solution to the chlorinated solvent. This electroinduced reaction points out the differences in the reaction pathway followed by these 1,2-dicarbonyl compounds depending on their geometry. The intermediates nature and their behavior, both in solution and at the electrode surface, are discussed.

1. Introduction

Electron-transfer reactions in solution have attracted much attention since organic electroactive reversible acceptor systems can be employed as potential advanced materials for the design of molecular electronic devices[1] or optoelectronic switches.[2]

The electrochemical cathodic reduction of aromatic 1,2-dicarbonyl compounds is a well known process, highly dependent on both, the constant applied potential and the solvent employed. When a 1,2-quinone derivative is reduced under aprotic conditions, a reversible electrochemical behaviour is achieved, acting as an electron acceptor and evolving first to its radical anion, but further in a second reversible one-electron process, to the corresponding dianion. The preparative-scale reduction of 1,2-quinones at Pt electrode in dichloromethane as solvent, was already described to be followed by a homogeneous electron-transfer reaction to the solvent, when working at the second voltametric reduction potential of these systems. In that case, an interesting synthesis of 1,3-dioxols[3] was achieved after a current consumption of 2F/mol.

The importance of quinones as mediators for electrocatalysis of oxygen reduction is known and described.[4,5]

On the other hand, the electrogeneration of carbenes and their application in synthesis has been recently highlighted.[6] These authors reduced imidazolium salts to carbenes (NHCs) that subsequently were used as catalyst in interesting organic transformations.

The present paper describes the electrochemical comparative reduction of two 1,2-dicarbonyl systems: 9,10-phenanthrenequinone (**1a**) and benzil (**1b**) using 1,1,1-trichloroethane (TCE) as the solvent, under potentiostatic conditions. A behaviour between this of **1a** and **1b** is presented in the reduction of acenaphthenequinone (**1c**). Interesting electron-transfer reaction between the corresponding dianion and TCE allows the formation of carbene and radical intermediates that are now employed to get coupling products with the reduced carbonyl function. Interesting compounds and mechanism proposals that make evident the electron-transfer reaction to the solvent from these reversible electroactive systems, are given.

2. Experimental

The electrolyses were carried out using an Amel potentiostat Model 552 with electronic integrator Amel Model 721. Mass spectra (EI, ionizing voltage 70 eV) were determined using a THERMOFISHER ITQ-900 DIP/GC-MSn mass-selective detector. IR spectra of the compounds were recorded as dispersions in KBr or NaCl films on a Perkin-Elmer FT-IR spectrometer Spectrum 2000. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Varian Unity

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Table 1
Reduction potentials *E* (V, *vs. Ag/Ag*$^+$) of compounds **1a–c** (2.0 mM) in TCE/AN (3:1), 0.1 M Bu_4NClO_4 as SSE. Scan rate: 100 mV/s. Cathode: Hg, Anode: Pt. * reversibility at scan rate 1000 mV/s.

1	Substrate	Epc_1	Epc_2	Epa_1	Epa_2
a	9,10-PhQ	−0.62	−1.18	−0.48	–
b	Benzil	−1.27		−1.08*	
c	AcenaphtoQ	−0.82	−1.57	−0.79	–

300 (300 MHz) spectrometer with tetramethylsilane (TMS) as the internal standard. The chemical shifts are given in ppm. Melting points were measured on a Reichert Thermovar microhot stage apparatus and are uncorrected.

2.1. General Voltammetric Measurements.

Cyclic voltammetry of compounds **1a** and **1b** (2.0 mM) in 1,1,1-TCE: CH_3CN (AN) (3:1)/tetrabutylammonium perchlorate (TBAP) as SSE (solvent-supporting electrolyte system) at a mercury-drop working electrode, platinum wire as anode and Ag/AgCl (sat) as reference, showed two quasi-reversible reduction peaks for **1a** and one quasi-reversible reduction peak for **1b**, similarly to the already described voltammograms in dichloromethane as the aprotic solvent. Potential values are indicated in Table 1. The reduction potential limit of this SSE system is close to −1.7 V (*vs. Ag/Ag*$^+$).

The voltammograms (see Fig. 1) reveal the fast electron-transfer reaction to the solvent (chemical reaction in solution) that takes place once the dianion of **1** is electrogenerated. In fact, when scan rate in the reduction of **1b** is increased from 100 to 1000 mV/s the reversibility of this peak is clearly observed, as indicated in Table 1.

2.2. General Electrochemical Procedure:

The electrochemical reductions were performed under potentiostatic conditions in a concentric cell with two compartments separated by a porous (D4) glass frit diaphragm and equipped with a magnetic stirrer. A mercury pool was used as the cathode (12 cm^2), a platinum plate (4 cm^2) as the anode, and a Ag/AgCl (sat) electrode as the reference. The SSE was nominally anhydrous 1,1,1-TCE/AN (3:1) containing 0.1 M tetrabutylammonium perchlorate (TBAP).

A solution of the electroactive 1,2-dicarbonyl compound (2.0 mmol in 60 ml of SSE) was electrolyzed under argon atmosphere (the solution was deaerated by argon bubbling for 15 minutes) at a constant potential value, the corresponding to the dianion formation. Once the reduction was finished the solvent in the cathodic solution was removed under reduced pressure. The residue was extracted with ether/water and the organic phase dried over Na_2SO_4 and concentrated by evaporation. The resulting solids were chromatographed on silica gel (24 × 3 cm) column, using CH_2Cl_2/Hex (3/1), CH_2Cl_2/EtOH (50/1), or Hex/EtOH (30/1) as eluents. Spectroscopic description of the obtained compounds is given below.

*2-Methyl-phenanthro[9,10-d][1,3]-dioxole (**2a**):* (72% yield). Mp 60 °C. [Lit. [7] Mp 62 °C]. IR (KBr) ν = 3067, 2918, 1657, 1614, 1451, 1373, 1102, 750 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.90 (d, 3H, J = 4.9 Hz), 6.60(q, 1H, J = 4.9 Hz), 7.52–7.66(m, 4H), 7.91 (d, 2H, J = 7.9 Hz), 8.67(d, 2H, J = 8.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm): 20.9, 110.4, 120.1, 121.4, 123.3, 124.5, 126.8, 127.1, 137.8. MS m/z (relative intensity) EI: 236(M^+, 100), 221(M^+-15, 77), 208(6), 181(35), 163(28), 152(13).

1-(10-Hydroxy-phenanthren-9-yl)-ethanone [8] *(**3a**):* Mp 95 °C. [Lit. [9] Mp 97 °C]. IR (KBr) ν = 3435, 3063, 2924, 2846, 1700, 1597, 1452, 1084, 756 cm^{-1}. MS m/z (relative intensity) IE: 236 (M^+, 75), 221 (M^+-15, 100), 218 (M^+-18, 17), 193 (M^+- 43, 4), 165 (64). MS m/z (relative intensity) IQ: 277 (M^++41, 2), 265 (M^++29, 22), 237 (M^++1, 100).

*2-Benzoyl-3-chloro-3-methyl-2-phenyl-oxiran (**2b**):* (64% yield). Mp 86–88 °C. IR (KBr) ν = 3063, 2987, 2927, 1676, 1595, 1448, 1275, 1123, 782, 713, 675 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.85 (s, 3H), 7.20–7.60 (m, 8H), 7.92 (d, 2H, J = 6.8 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm): 26.6, 71.8, 82.9, 126.3, 127.8, 128.1, 128.5, 129.3, 131.6, 133.2, 133.7, 192.4. MS m/z (relative intensity) IE: 274 (M^++2, 4), 272 (M^+, 11), 237 (M^+- 35, 10), 232 (34), 230 (100), 195 (24), 165 (45), 152 (33), 124 (18), 126 (6), 105 (88), 77 (25), 51 (8). MS m/z (relative intensity) IQ (CH_4): 303 (M^++31, 1), 301 (M^++29, 3), 275 (M^++3, 5), 273 (M^++1, 18), 237 (M^++1- 35, 18), 105 (100), 91 (9). Anal. Calc. for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.77. Found: C, 70.11; H, 4.82.

(Z)-3-Hydroxy-1,2-diphenyl-2-buten-1-one (**3b**): Mp 85 °C [Lit. [10] Mp 84-6 °C]. IR (KBr) ν = 3362, 3061, 2921, 1682, 1574, 1411, 1316, 1033, 917, 737 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): keto form: 2.28 (s, 3H), 5.68 (s, 3H), 7.05-8.2 (m, 10H). Enol form: 2.05 (s, 3H), 7.05 - 8.20 (m, 10H), 11.0 (s.a, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ (ppm): keto + enol: 25.7, 29.4, 68.0, 114.2, 127.2, 127.6, 128.1, 128.5, 128.6, 128.7, 128.8, 129.0, 129.1, 129.3, 129.9, 130.2, 131.8, 133.5, 136.9, 183.0, 195.3. MS m/z (relative intensity) IE: 238 (M^+, 65), 237 (M^+-1, 100), 223 (M^+-15, 3), 221 (M^+-17, 7), 220 (M^+-18, 7), 196 (38), 165 (26), 105 (39), 77 (15), 51 (6).

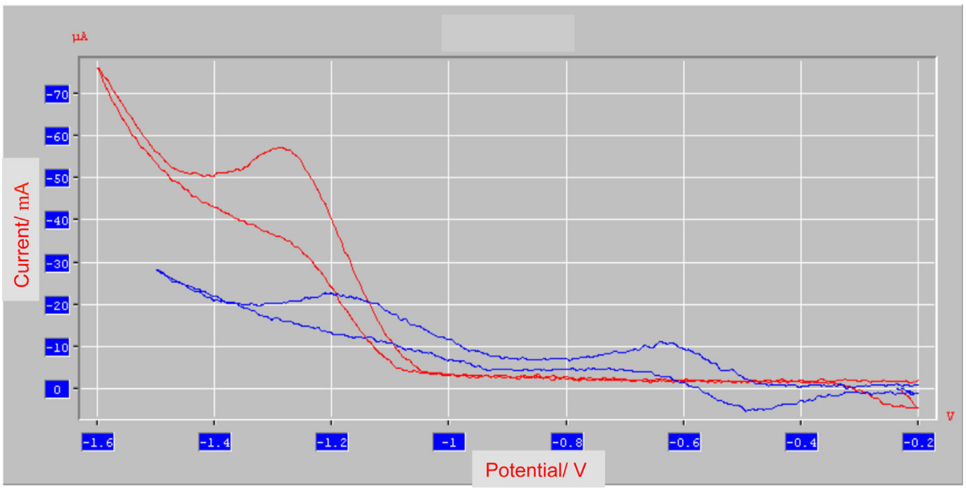

Fig. 1. Cyclic voltammetry of **1a** (blue) and **1b** (red) (2.0 mM) at Hg cathode in TCE/AN (3:1) 0.1 M TBAP scan rate: 100 mV/s.