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# Reductive electrochemical formation of 6*H*-dibenzo[*b*,*d*]pyran-6-one and 2-benzopyran-1(1*H*)-one



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# ABSTRACT

In the present Letter several carbolactones (oxidative products) are obtained under aprotic cathodic conditions in the preparative scaled electrolysis of 1,2-quinones in a divided electrochemical cell and in the presence of oxygen. When 9,10-phenanthrenequinone is reduced 6H-dibenzo[b,d]pyran-6-one and [1,1'biphenyl]-2,2'-dicarboxylic acid are obtained as major products. In the reduction of 1,2-naphthoquinone, 2-benzopyran-1(1H)-one, and 2-(2-carboxyethenyl)-benzoic acid were formed as main products. The proposed mechanism to explain the formation of these and other products, that involves an electrontransfer reaction to the oxygen in air, is now discussed.

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#### Introduction

In a previous paper<sup>1</sup> we have described the formation of benzoic acid in the cathodic reduction of benzil, performed under an argon atmosphere, with dry dichloromethane as the solvent. The mechanistic proposal of this process involved an electron-transfer reaction during the work-up (in the presence of  $O_2$ ) between the electrogenerated benzil dianion and the oxygen of the air, producing the anion radical of benzil and a superoxide anion. Subsequent coupling reaction of both, with further intramolecular nucleophylic attack to the carbonyl group, afforded a dioxetane intermediate that decomposed to benzoic acid.

Recently we have also described<sup>2</sup> that the electrochemical reduction, in acetonitrile and other aprotic solvents, of 1,2-quinones at the first reduction potential of these systems (closely to -0.5 V, vs  $Ag/Ag^+$ ) produces, in the absence of oxygen, the expected and colored anion radical after a charge consumption corresponding to a 1e-/substrate molecule process. However, the starting quinone was completely recovered, after an electron-transfer to O<sub>2</sub>, when this anion radical solution was elaborated.

This electron-transfer reaction from the anion radical of a quinone to oxygen molecules, as an indirect way to produce hydrogen

\* Corresponding author. E-mail address: fructuoso.barba@uah.es (F. Barba). peroxide, had already been described under aqueous solution by the use of glassy-carbon modified cathodes.<sup>3,4</sup>

The present communication deals with the cathodic reduction of 9,10 phenanthrenequinone (**1a**) and 1,2-naphtoquinone (**1b**) in the presence of oxygen, using nominally anhydrous acetonitrile/ LiClO<sub>4</sub> as solvent-supporting electrolyte system (SSE), to its colored anion radical. The indirect formation of superoxide anion at the cathodic solution makes possible a further coupling with the electrogenerated anion radicals to produce aromatic carbolactones **2** and carboxylic acids. Discussion and mechanism proposals to explain their formation are given.

# **Results and discussion**

#### Cathodic reduction of 9,10-phenanthrenequinone (1a)

The experimental results in the cathodic reduction of 9,10phenanthrenequinone (**1a**), in the presence of O<sub>2</sub>, and employing nominally anhydrous acetonitrile/LiClO<sub>4</sub>, were as follows: in the organic phase 30% yield of 6*H*-dibenzo[*b*,*d*]pyran-6-one (**2a**) was obtained. In the aqueous phase: [1,1'-biphenyl]-2,2'-dicarboxylic acid (**3a**, 31% yield), 2'-hydroxy-[1,1'-biphenyl]-2-carboxylic acid (**4a**, 8% yield) and 21% yield of 2-phenylbenzoic acid (**5a**) were obtained. It should be indicated that the carboxylic acids **3a**, **4a**, and **5a** were isolated after the aqueous phase was acidified and ether extracted.





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The electrolysis of this substrate at -0.5 V (vs Ag/Ag<sup>+</sup>) leads to the expected green colored anion radical. Due to the presence of oxygen in the medium, **1a** is being recovered from this anion radical at the time that superoxide anion is been formed in the catholyte solution via an electron-transfer reaction. As **1a** is again reduced in the cell at its first voltammetric peak, an indirect electrogeneration of superoxide anion is taking place. Therefore the  $O2 \cdot -$  and 9,10-phenanthrenequinone anion radical can be further coupled to give a dioxetane intermediate (**i**), as indicated in Scheme 1.

In the presence of nominally anhydrous solvent, the intermediate **i** can follow two different pathways, as indicated in Scheme 2: (a) ring cleavage to produce [1,1'-biphenyl]-2,2'-dicarboxylate (**3a**) or (b) an electrochemical Baeyer–Villiger/Dakin reaction to give an oxepine-1,2-dione, easily reduced, because it is another 1,2-dicarbonyl compound, to its anion radical intermediate. In the presence of another superoxide anion molecule, the obtained anion radical



Scheme 4.

produces a new dioxetane intermediate. The latter immediately evolves to a carbonate easily decarboxylated and lactonized to **2a** after further Li<sub>2</sub>O evolution.

The electrochemical formation of 6H-dibenzo[b,d]pyran-6-one (**2a**) starting from 9,10-phenanthrenequinone (**1a**) had never been described. Conventional Baeyer–Villiger reaction of neutral quinone with hydrogen peroxide is known to produce the corresponding anhydride.<sup>5</sup> The literature<sup>6</sup> mentioned that the photooxidation of **1a** in benzene, under oxygen, afforded [1,1'-biphenyl]-2,2'-dicarboxylic acid (**3a**) and its diaroyl peroxide, together with 1–2% yield of **2a**.

It is important to notice that direct oxygen discharge at the electrode does not take place because the applied reduction potential is only -0.5 V (vs Ag/Ag<sup>+</sup>). At this premise, when the electrolysis of **1a** was carried out in the presence of an intermittent O<sub>2</sub> bubbling, for ten times during the electrolysis, the yield of lactone **2a** was improved from 21% to 30%. However, an excess of oxygen did not increase this value anymore.

The presence of the dioxetane intermediate **i** in the mechanistic proposal, is supported by the isolation of [1,1'-biphenyl]-2,2'-dicarboxylic acid (**3a**). The formation of the monocarboxylic acid **5a** can be rationalized by the direct attack of superoxide anion to



Scheme 2.





Scheme 6.

the carbonyl group of a neutral 9,10-phenanthrenequinone molecule, as it is indicated in the Scheme 3.

In the aqueous phase of this reaction, 2'-hydroxy-[1,1'-biphe-nyl]-2-carboxylic acid (**4a**) was formed (8% yield) as indicated in Scheme 4. This hydroxylated carboxylic acid can be transformed into the lactone **2a** by reflux in the presence of catalytic amount of  $H_2SO_4$ .

## Cathodic reduction of 1,2-naphthoquinone (1b)

Electrolysis of 1,2-naphthoquinone was performed under similar experimental conditions as described for **1a**, working at the first reduction potential of this system, -0.48 V (vs Ag/Ag<sup>+</sup>) and in the presence of intermittent O<sub>2</sub> bubbling. **1b** was nevertheless added as solid portions during the electrolysis to avoid polymerization. The following products were obtained: in the organic phase, 2-benzopyran-1(1*H*)-one (isocoumarin, **2b**, 11% yield) and 1-benzopyran-2(2*H*)-one (coumarin, **2b**', 5% yield); in the aqueous phase: 2-(2-carboxyethenyl)-benzoic acid (**3b**) (46% yield), 2-(2-hydroxyethenyl)-benzoic acid (**3b**) (as 2-(formylmethyl)benzoic acid) (19% yield) and 2-vinylbenzoic acid (**5b**, 11% yield). The acids were obtained after the aqueous phase was acidified.

A wide variety of benzopyran-1-ones occur naturally, and this ring system also occurs as a structural fragment in many other natural products.<sup>7</sup>



There are numerous synthetic procedures to benzopyran-1one; however the unsubstituted benzopyran-1-one proved to be an exception.<sup>8</sup>

The pathway proposal summarized in Scheme 5 explains the formation of these products.

It should be noticed that in this case, two types of alpha-ketocarbolactones can be obtained, 2-benzopyran-1(1H)-one (**2b**) and 1-benzopyran-2(2H)-one (**2b**'). The formation of monocarboxylic acid **5b**, can be rationalized, as already explained for **5a** in Scheme 3, by attack of the superoxide anion to a carbonyl group of 1,2-naphthoquinone (**1b**). Further extrusion of CO<sub>2</sub> followed by hydrogen abstraction, and final protonation during the work-up, as summarized in Scheme 6, provides **5b**.

The isolation of 2-vinylbenzoic acid (**5b**) evidences that the evolved carbon dioxide molecule is directly joined to the aliphatic chain, instead of the joined to the aromatic ring.

It should be considered that the full yield of isocoumarine from the electrochemical cell promotes to 30%, because **4b** is the hydrolysis product of **2b** (see Scheme 7).

## **Experimental section**

#### 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  $(20 \text{ cm}^2)$  and as the anode a Pt plate  $(12 \text{ cm}^2)$ , and an Ag/AgCI (3 M) electrode as the reference. The SSE was composed by nominally anhydrous acetonitrile (%H<sub>2</sub>O  $\leq$ 0.05%) containing 0.1 M of dry lithium perchlorate (99.99%). A solution of the electroactive quinone **1** (1.0 mmol in 60 ml of SSE) was electrolyzed in the presence of oxygen (the solution was 10 times  $O_2$  bubbled for 10 s) at a constant potential of -0.5 V (vs Ag/Ag<sup>+</sup>), corresponding to the first reduction peak potential of these systems. 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<sub>2</sub>SO<sub>4</sub> and concentrated by evaporation. To isolate the carboxylic acids, the slightly alkaline aqueous phase was neutralized, ether extracted, and dried. The resulting solids were MS-analyzed and chromatographed, if needed, on silica gel (22 × 3 cm) column, using CH<sub>2</sub>Cl<sub>2</sub>/EtOH as the eluent. Some spectroscopic data of the obtained compounds are given below.

#### 6H-Dibenzo[b,d]pyran-6-one (2a)

(41 mg, 21% yield). Mp 92–93 °C. [Lit.<sup>9</sup> 92.5–94.5 °C]. MS *m/e* (relative intensity) EI: 196(M<sup>+</sup>, 100), 168(55), 139(33), 113(4).

## [1,1'-Biphenyl]-2,2'-dicarboxylic acid (3a)

(75 mg, 31% yield). Mp 224–227 °C [Lit.<sup>10</sup> 228–229 °C]. MS *m/e* (relative intensity) EI: 242(M<sup>+</sup>, 52), 225(15), 197(100), 181(12), 152(70), 139(4), 115(6). In MS partially transformed by heating into the corresponding anhydride: 224(M<sup>+</sup>, 17), 180(100), 152(44).

## 2'-Hydroxy-[1,1'-biphenyl]-2-carboxylic acid (4a)

(17 mg, 8% yield). [Lit.<sup>11</sup> mp 93 °C]. In MS is completely transformed, by heating, into the lactone **2a**.

## [1,1'-Biphenyl]-2-carboxylic acid (5a)

(42 mg, 21% yield). Mp 214–216 °C. [Lit.<sup>12</sup> 215–218 °C]. MS *m/e* (relative intensity) EI: 198(M<sup>+</sup>, 14), 197(M<sup>+</sup>–1, 100), 180(13), 153(44).

# 2-Benzopyran-1(1*H*)-one (2b)

(16 mg, 11% yield). Mp 42–44 °C. [Lit.<sup>13</sup> 45–46 °C]. MS *m/e* (relative intensity) EI: 146(M<sup>+</sup>, 38), 118(100), 90(56), 89(66), 63(30).

#### 1-Benzopyran-2(2H)-one (2b')

(7 mg, 5% yield). Mp 72–75 °C. [Lit.<sup>14</sup> 71 °C]. MS *m/e* (relative intensity) El: 146(M<sup>+</sup>, 80), 118(100), 90(41), 89(61), 63(25).

# 2-(2-Carboxyethenyl)benzoic acid (3b)

(88 mg, 46% yield). Mp 185–188 °C. [Lit.<sup>15</sup> 188–190 °C]. In MS completely transformed by heating into the corresponding anhydride:  $174(M^*, 100), 146(74), 105(80), 77(51)$ .

#### 2-(2-Hydroxyethenyl)benzoic acid (4b)

(As 2-(formylmethyl) benzoic acid): (31 mg, 19% yield). Mp 128–130 °C. [Lit.<sup>16</sup> 130–140 °C]. MS m/e (relative intensity) EI: 164(M<sup>+</sup>, 2), 163(M<sup>+</sup>–1, 16), 133(100), 119(32), 105(38), 92(38), 91(50), 89(28), 77(39), 51(28).

# 2-Vinylbenzoic acid (5b)

(16 mg, 11% yield). Mp 93–95 °C. [Lit.<sup>17</sup> 95–96 °C]. MS *m/e* (relative intensity) EI: 104(M<sup>+</sup>–44, 100), 76(51), 74(17), 50(44).

# Conclusion

Unexpected aromatic carbolactones, together with carboxylic acids, are obtained from 1,2-quinones under cathodic conditions in the presence of O<sub>2</sub>. Once again it has been demonstrated that the anion radical of these dicarbonylic compounds is a good mediator in oxygen reduction. A dioxetane dianion intermediate is involved in the proposed electrochemical Baeyer–Villiger/Dakin-type reaction to carbolactones.

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