

Electrochemical Synthesis of Bi-1,4-naphthoquinonyl Derivatives

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Electrolysis of 1,4-naphthoquinone derivatives with magnesium perchlorate as supporting electrolyte in aqueous acetic acid has led to oxidative dimerization of the quinone and is a new, convenient, and selective method of preparation of 2,2'-bi-1,4-naphthoquinonyl derivatives.

1,4-Naphthoquinone in carbon disulphide has been reported to undergo self-condensation on treatment with anhydrous aluminium chloride,¹ eight products were mentioned, including 2,2'-bi-1,4-naphthoquinonyl which was obtained in a yield of 18%. Oxidative dimerization of aminonaphthoquinones

using persulphate has also been reported and a variety of dimeric products have been obtained but it was not possible to cyclize the 3,3'-diamino-2,2'-bi-1,4-naphthoquinonyl under these conditions.² This compound can be cyclized in 50% yield by refluxing with a mixture of acetic and sulphuric acids.³

Table 1. Products formed during electrolysis of naphthoquinone derivatives at anode potentials (vs. Ag/AgCl reference electrodes).

Substrate	Product	E/V
(1)	(4)	1.2
(2)	(5)	1.4
(1), (2)	(6)	1.2
(3)	(5)	1.2

These methods have relatively poor yields and selectivities.

We report a new, convenient, and more selective synthesis of 2,2'-bi-1,4-naphthoquinonyl derivatives by electro-oxidation of some naphthoquinone derivatives. 1,4-Naphthoquinone and 2-amino-1,4-naphthoquinone (synthesized from 1,4-naphthoquinone⁴) were oxidized on a preparative scale in 50% aqueous acetic acid, in the presence of 1 mol dm⁻³ magnesium perchlorate, in a divided electrolysis cell with bright platinum electrodes. The results of direct anodic oxidation at controlled potentials and a current density ≥ 1.5 A m⁻² showed a yield of bi-1,4-naphthoquinonyl compounds of 80% with 100% current efficiency (based on an assumption of 2 F mol⁻¹ for complete conversion). In a typical experiment 100 cm³ of a 0.06 mol dm⁻³ naphthoquinone solution was electrolysed. After 12 h at average current of 7.5 mA, 0.48 g of the product was formed.

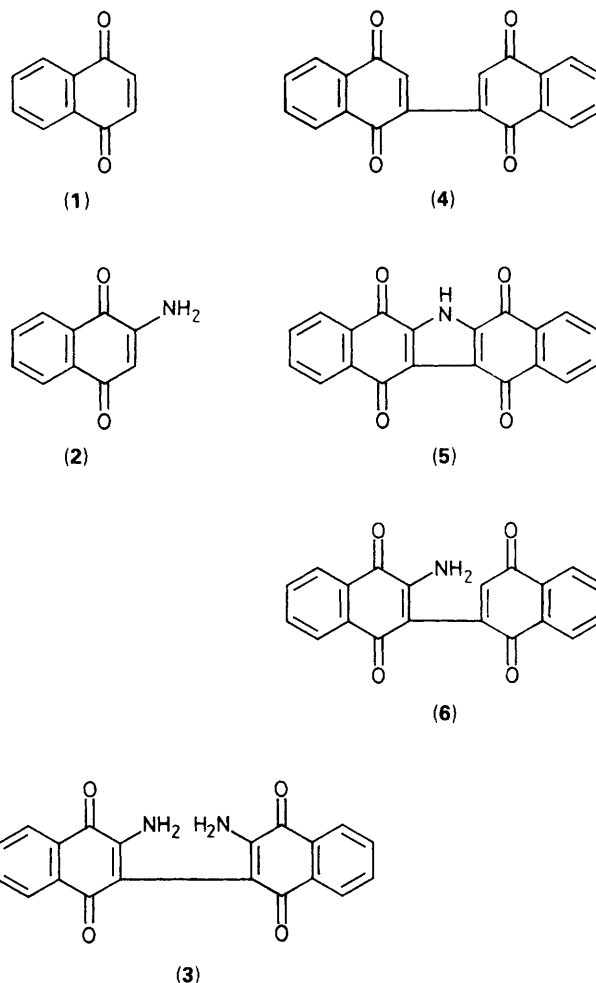
Cyclic voltammetric measurements at platinum electrodes [50% aqueous acetic acid, 1 mol dm⁻³ of Mg(ClO₄)₂, 0.02 V s⁻¹] indicated, in all cases, the reversible quinone reduction and hydroquinone oxidation peaks at potentials <0.5 V (vs. Ag/Ag⁺). The possible potentials were chosen to effect the oxidative dimerization reaction (Table 1).

The products were precipitated by neutralizing the acid with NaHCO₃, and were purified by recrystallization from glacial acetic acid. Products were identified by comparison with authentic samples, except for (6) whose identity was based only on its i.r. and mass spectra.

Electrolysis of 1,4-naphthoquinone led to oxidative dimerization and resulted in the formation of 2,2'-bi-1,4-naphthoquinonyl (4). In this case the reactions are probably catalysed by an anodic platinum oxide layer.⁶ Anodic oxidative dimerization reactions are known and have been described in terms of an EC-mechanism.⁷

The required conditions for oxidative dimerization are a nucleophilic starting material and the absence of a competing nucleophile. The effect of competing nucleophiles can be observed in the electrolysis of a mixture of 1,4-naphthoquinone and 2-amino-1,4-naphthoquinone (2). 1,4-Naphthoquinone is oxidized at a slightly lower potential than 2-amino-1,4-naphthoquinone, but the resulting 1,4-naphthoquinone radical cation is attacked readily by the stronger nucleophile, 2-amino-1,4-naphthoquinone. Co-electrolysis of 1,4-naphthoquinone and 2-amino-1,4-naphthoquinone led to the formation of 3-amino-2,2'-bi-1,4-naphthoquinonyl (6).

The 3,3'-diamino-2,2'-bi-1,4-naphthoquinonyl (4) could not be produced by anodic dimerization of 2-amino-1,4-naphthoquinones, as (4) is cyclized with the loss of ammonia to form dibenzo[*b,h*]carbazole-5,13:7,12-diquinone (5). Also, (4) is oxidized at the anode, then (5) is formed. The evolution of ammonia and the ring closure reaction are thus also electrochemically induced.



These types of asymmetrical and symmetrical coupling considerably broaden the synthetic applications of the electrochemical oxidation of naphthoquinone derivatives. The practical convenience of this method makes it an attractive alternative to the existing methods.

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