

Electrosynthesis of 3-Nitrophenothiazine. Nitration in Non-Aqueous Solutions

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Abstract: The nitration of Phenothiazine (PHEN) in acetonitrile (ACN) in the presence of excess NaNO_2 has been studied in detail. First, the electrochemical behavior of the reactants was investigated by cyclic voltammetry to determine the electrolysis conditions. Controlled-potential electrolysis was used for the electrosynthesis.

Introduction

Although the nitration of organic compounds is an area in expansion since the beginning of the century principles, its interest has not diminished. In this way, new nitration methods that outline new challenges for the interpretation of the mechanisms have appeared. The principal interest resides in that the nitrated products are fundamental source of diverse synthetic products [1-3]. The traditional nitration methods, which use aggressive mixtures of nitric and sulfuric acid, are being left, due to the high cost of the effluents treatment [4]. The electrochemical methods are an excellent way to produce the nitration intermediates [5]. Besides, it constitutes an interesting alternative procedure from the mechanistic point of view.

Experimental

An EG & PAR model 273 potentiostat-galvanostat was used for cyclic voltammetry (CV) and controlled-potential electrolysis (CPE) measurements, using a conventional three-compartment Pyrex cell, stirring with a Teflon paddle for the EPC. The working electrodes were Pt wires of area 0.235 cm^2 for CV, and Pt electrodes of larger area (ca. 16 cm^2) for CPE. The counter-electrode was a stainless steel foil of large area. All the potentials were referred to a saturated calomel electrode (SCE) and were corrected for IR drop by positive feedback techniques.

The disappearance of the reagent and the consequent apparition of the nitrated product were followed by HPLC analyses. 3-Nitrophenothiazine (3- NO_2 PHEN) was thermally synthesized as described in the literature [6].

Results and Discussion

CV studies shows that the oxidation of PHEN to proceed in two reversible one-electron steps, giving the radical cation $\text{PHEN}^{+\bullet}$ and the dication PHEN^{++} , respectively, peak I ($E_{\text{pI}} = 0.58 \text{ V}$) and peak II ($E_{\text{pII}} = 1.00 \text{ V}$). Since for the electrosynthesis we are only interested in the generation of the $\text{PHEN}^{+\bullet}$, the CV were registered until 0.8 V. The peak current I_{pI} shows a linear dependence on $v^{1/2}$ in the range of sweep rates used (i.e. 0.01 to 0.3 V s^{-1}) and E_{pI} as well as ΔE_{pI} give a constant value on v . This is the expected behavior for a fast diffusion controlled process. At the same potential, the ion NO_2^- is oxidized to NO_2 . Nevertheless, CV studies showed that the nitrated product is formed by the reaction between the FEN^{++} (formed by desproportionation of $\text{PHEN}^{+\bullet}$ and the NO_2^- ion

CPE was performed at $E = 0.5 \text{ V}$. Several samples were taken to different times of electrolysis, following by HPLC the increase of the peak of the product ($\tau = 23 \text{ min}$). A yield greater than 90% of 3- NO_2PHEN was obtained under optimized conditions. A reaction mechanism is proposed.

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References and Notes

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