



Detection of an ylide intermediate in the electrochemically-induced Stevens rearrangement of an ammonium salt by in situ UV–vis spectroelectrochemistry

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ABSTRACT

The electrochemically-induced Stevens rearrangement of 2-(benzylidimethyl)ammonium acetophenone has been investigated by in situ UV–vis spectroelectrochemistry. Voltammetric analysis and absorption spectra recorded during the potentiostatic reduction indicate that the reaction proceeds via a one-electron transfer with a Platinum cathode and generation of an ammonium ylide intermediate.

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1. Introduction

The reactivity of α -onium salts [1] is a subject of considerable interest for organic chemists both from a synthetic [2–7] and mechanistic point of view [8–11]. An important class of such reactions regards electrocyclic rearrangements (i.e. [1,2]- and [2,3]-shift) which proceed via an ylide intermediate, by means of basic treatment [12].

On the other hand, since many years, several literature reports documented an electrochemical approach to the issue which avoid the use of base reagents, the α -onium salt being directly activated on suitable electrodes [13–16].

Despite of the significant advantages of the electrosynthetic process compared to the chemical one, its usefulness is sometimes reduced because of the formation of by-products resulting from unselective C-heteroatom cleavage, especially when ammonium salts are involved [17,18]. Further mechanistic insights are therefore necessary for a better understanding of such interesting electrochemically-induced rearrangements where the formation of an ylide intermediate has been only indirectly deduced by the subsequent chemical reactivity. In particular, in a pioneering study by Iversen [19], the formation of the ammonium ylide **B** of the title compound during the electroreductive process on a Hg cathode has been postulated as a consequence of a chemical acid–base process

initiated by the enolate **A** arising from the two-electrons reductive cleavage (Scheme 1).

The in situ spectroscopic characterization of species generated by controlled-potential electrolysis could offer a valid help allowing the detection of short-life intermediates and unstable oxidation states [20–27].

Herein we report the results of a study in which the combined use of spectroelectrochemistry, quantum computations and standard chemical method, demonstrates the *direct* formation of an ylide intermediate in the electrochemically-induced Stevens rearrangement of 2-(benzylidimethyl) ammonium acetophenone (**1**) [28] via one-electron transfer process at a platinum electrode.

2. Experimental

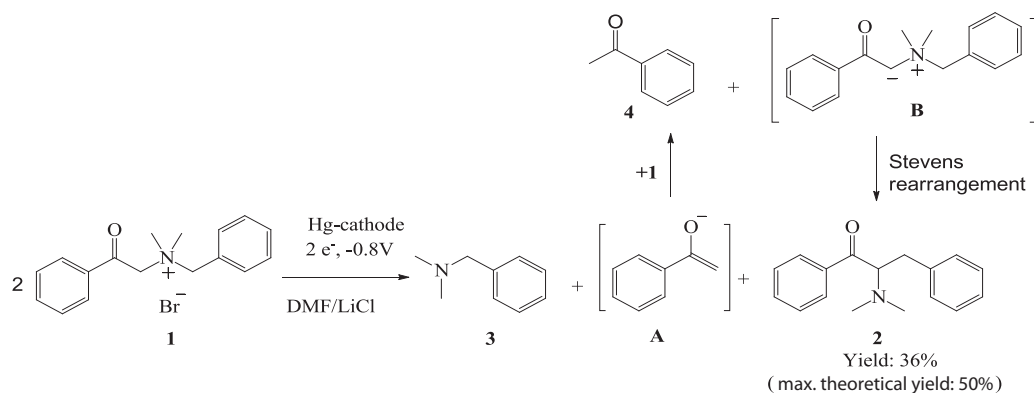
2.1. General remarks

Starting material **1** was prepared accordingly to literature [29] by using reagents and solvents as received from Aldrich or Fluka, without further purification. Thin layer chromatography (TLC) was performed using *Merck Silica Gel 60 F254* plates and visualized by fluorescence quenching at 254 nm. Column chromatographic purification of the product **2** was carried out using silica gel 60 (70–230 mesh, Merck). The NMR spectra were recorded on Bruker DRX spectrometer (400 MHz, ¹H; 100 MHz ¹³C). Spectra were referenced to residual CHCl₃ (7.26 ppm, ¹H; 77.00 ppm, ¹³C) or CD₃CN (1.94 ppm, ¹H; 118.0 and 1.4 ppm, ¹³C). All voltammetric measurements were performed with an Autolab PGSTAT302N potentiostat–galvanostat controlled by NOVA 1.8

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software version (by Metrohm-Autolab), using a positive feedback to compensate for ohmic drop. A standard three-electrode configuration was used, consisting of a Pt disk electrode as working (by Metrohm), a Pt bar as counter (by Metrohm) and a double junction Ag/AgCl (KCl 3 M) electrode (by Metrohm) in which the outer compartment is filled with LiClO₄ 0.10 M in acetonitrile.

Constant current electrolysis was performed using an Hewlett Packard DC Power Supply Mod. E3612A. Potentiostatic electrolyses for spectroelectrochemical measurements were performed using an 2051 Amel Potentiostat.

2.2. Determination of the electrons number transferred in the electrochemical process

The relationship produced during cyclic voltammetry between peak current (i_p) and scan rate ($v^{1/2}$) is described by the Randles–Sevcik equation, modified for irreversible systems [30]:

$$i_p = (2.99 \times 10^5) n(\alpha n_a)^{1/2} AD^{1/2} C v^{1/2}$$

The voltammetric experiments was performed with $C = 0.5$ mM on a Pt electrode. The diffusion coefficient $D = 2.325 \times 10^{-9}$ m²/s was determined by NMR experiments (DOSY) [31]. The derived plot of i_p vs. $v^{1/2}$ is reported below (Fig. 1).

In such a conditions, assuming $n_a = 1$ and $0.3 < \alpha < 0.7$ as reported in literature [30], it has been derived $n = 1.0 \pm 0.2$.

2.3. Procedure for electroinduced Stevens rearrangement of benzyldimethylphenacylammonium bromide 1 under galvanostatic conditions

The experiment was carried out in the cathodic compartment of a U-divided glass cell separated through a porous G-4 glass frit. Platinum spirals (apparent area 2.5 cm²) were used as anode and cathode. Catholyte was constituted by 2 mL of a solution of **1** (0.05 M) in CH₃CN. Anolyte was constituted by 2 mL of a solution of (Et)₄NClO₄ 0.1 M in CH₃CN. After 1.2 electron/molecule (**1**) were passed (current intensity 20 mA) and TLC analysis indicated the complete consumption of compound **1**, the reaction was prolonged at 50 °C for 2 h and then the catholyte was concentrated under vacuum. The crude mixture was purified on silica gel (gradient hexane:ethylacetate) yielding 2-(dimethylamino)-1,3-diphenyl-1-propanone **2** in 56% yield. Product **2** gave spectral and analytical data as reported in literature [32].

2.4. Spectroelectrochemical measurements (Fig. 4)

The experiments were performed on a single beam Varian Cary-50 spectrophotometer (scan rate 600 nm/min, resolution 1.0 nm) by using a ALS thin layer quartz glass spectroelectrochemical cell with a 0.5 mm optical path length, equipped with a Pt as counter electrode, a Pt gauze as working electrode and a double junction Ag/AgCl (KCl 3 M) electrode in which the outer compartment is filled with LiClO₄ 0.10 M in acetonitrile as reference.

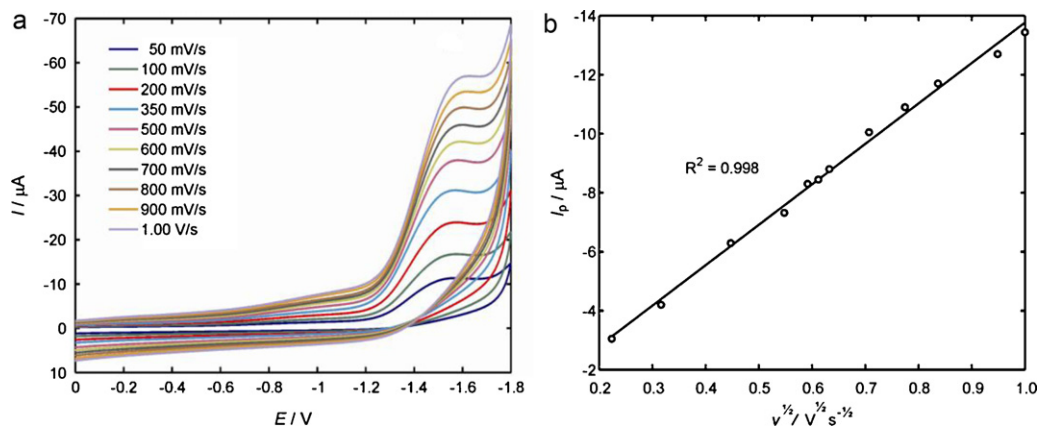


Fig. 1. (a) Cyclic voltammograms of **1** [$C = 0.5$ mM in CH₃CN 100 mM LiClO₄, Working electrode: Pt. Internal reference electrode: double junction Ag/AgCl (3 M KCl)] at different scan rates. (b) Dependence of the “normalized” peak current (i_p) on scan rate (v) observed in CV measurements.

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