Electrolytic Reduction of Azidochalcones

Electrolytic Investigations on Vinyl Azides, VI.

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Cathodic reduction of α-azidochalcones under slightly protic conditions proves to be an excellent method for a selective conversion of the azido function to an amino group without affecting other reducible parts of the molecules. The amino-propenones retain the Z-configuration about the C=C-bond of the starting material, whereas N-acetyl derivatives, obtained under mildly acetylating conditions, are partially isomerised. The low reduction potential of N,N-diacetyl-enamines of this type prevents their direct one step synthesis by electrolysis of azidochalcones under strongly acetylating conditions. The voltammetric behaviour of the azides and their reduction pathway is discussed.

(Keywords: α-Azidochalcones; Cathodic reduction; 2-Aminopropen-2-ones)

Introduction

The electrochemical investigation of α,β-unsaturated carbonyl compounds has been a continuously active area of research.

Wawzonek et al. reported two one-electron steps in polarographic reduction e.g. of benzalacetophenone in aprotic media, whereas large scale electrolysis
resulted in polymer formation due to the starting material. Many other workers lead their interest into reductive coupling of such compounds giving \( \beta,\beta' \)-carbon bonded dimers \( \text{2a-c} \), depending on experimental parameters. Preferred coupling is reported to occur in N,N-dimethylformamide (DMF)\(^3\).

The ketonic system of 2-azido-propanones, e.g. 2-azidochalcones, which should be very prone to \textit{Michael}-type reactions, has been chosen for our investigation, the results of which are presented in this paper.

Studies on azidocinnamic esters—weakly activated olefinic carbonyl groups—showed that there is no attack on carbon during cathodic reduction as reported\(^4_{a,b}\). In the ketonic system there might be the chance of effective carbon—carbon coupling. On the other hand, if in azidochalcones the olefinic skeleton is maintained, amino derivatives of chalcones may be obtained, which might find application in analytical chemistry\(^5\).

\textbf{Results and Discussion}

Acetonitrile (\( \text{AN} \)) has been chosen as aprotic solvent for electrolysis because it is easy to remove. Since the azido group is likely to be attacked by strong nucleophiles\(^6\), scavengers which react rapidly with anionic intermediates of cathodic reduction are required in the working solution. \( \text{Ac}_2\text{O} \) and proton donors like acetamide or \( \text{AcOH} \) are used for this purpose.

A typical cyclovoltammogram (CV) of azidochalcone \( \text{2a} \) in the solvent system employed is presented in Fig. 1.

\begin{center}
\includegraphics[width=\textwidth]{fig1.png}
\end{center}

Fig. 1. CV of compound \( \text{2a} \) in \( \text{AN}, 0.1 \ M \ \text{TEAB}, 200 \text{mV} \text{s}^{-1} \), on Hg; ———- \( \text{2a} \); ———- with excess of \( \text{Ac}_2\text{O} \)