TWO PAIRED ELECTROSYNTHESIS

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The highest electric current efficiency is one of the aims of the organic electrochemists. It is known that the number of electrons added at the cathode (for reduction) must simultaneously be removed at the anode (for oxidation). For instance, to obtain a product into the anodic compartment it is necessary another to be formed into the cathode. Unfortunately, in most of the processes the product in one of the compartments is undesirable. There are few examples in the literature where both compartments show a cooperative action to lead simultaneously to interesting products.¹

Herein, we describe in a first example the paired electrosynthesis of 2,6-dimethyl-4-arylpyridine-3,5-dicarbonitrile ² in acetonitrile as solvent, at platinum electrodes in a two compartment cell divided by a medium porosity glass-fritt diaphragm.

4 CH₃CN + Ar-CH₂-X
$$\xrightarrow{\text{paired electrochemical}}$$
 $\xrightarrow{\text{process, -NH}_3}$ $\xrightarrow{\text{H}_3\text{C}}$ $\xrightarrow{\text{NC}}$ $\xrightarrow{\text{NC}}$ $\xrightarrow{\text{CN}}$

Our second example on paired electrosynthesis is the formation of Cyanoacetic acid 3 by cathodic reduction of CO_2 and anodic oxidation of the tetraalkylammonium electrolyte anion; the process is conduced in acetonitrile using a divided cell with a medium porosity glass-frit diaphragm. A mechanism for this paired electrochemical reaction is proposed.

cathode:
$$CO_2 + e^- \longrightarrow CO_2^-$$

anode:
$$R_4N^+X^- \xrightarrow{-e^-} R_4N^+ + X^-$$

 $X \cdot + CH_3CN \longrightarrow HX + CH_2CN$

paired reaction:
$$CH_2CN \xrightarrow{+ CO_2} NC-CH_2-COO$$

References

- 1. Lund, H.; Baizer, M. M. Organic Electrochemistry. 3rd ed.; Lund, H., Baizer, M. M., Eds.; Marcel Dekker Inc.: N.Y. 1991; Chap.35, pp 1421-1430.
- 2. Batanero, B.; Barba, F. and Martín, A. *J. Org. Chem.* **2002**, *67*, 2369.
- 3. Batanero B., Barba F., Sánchez-Sánchez C.M. and Aldaz A. *J. Org. Chem.* **2004**, *69*, 2423.