

Functionnalization of activated C-H mediated by oxoammonium

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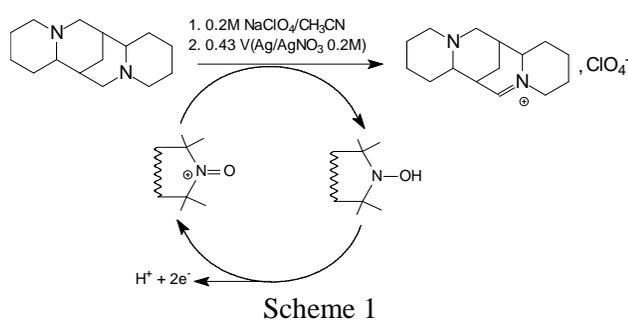
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Since the beginning of the eighties, there has been a flourish of papers describing applications of aminoxyl radicals. Particularly, the corresponding oxoammonium are well established catalysts for the oxidation of various alcohols^[1]. We recently reported a novel electrocatalytic system for the oxidation of carbohydrates to the corresponding uronic acids using Nafion-TEMPO modified graphite felt anodes^[2].

We also published an attempt to oxidize enantioselectively a *rac*-1-phenylethanol where the chiral base was found to be oxidized prior to the alcohol^[3]. In this connection we have investigated the oxidation of activated C-H by oxoammonium used in stoichiometric amount and also in catalytic amount where the oxoammonium is immobilized at the anode and electrochemically regenerated^[4].

TERTIARY AMINES

In fact (-)-Sparteine is readily oxidized at the modified anodes into the corresponding iminium (scheme 1). The oxidation wave is situated in the potential range where the oxoammonium is generated from its radical parent (Fig. 1).



In the presence of water the iminium is converted into the corresponding alcohol which is further oxidized into aphylline :

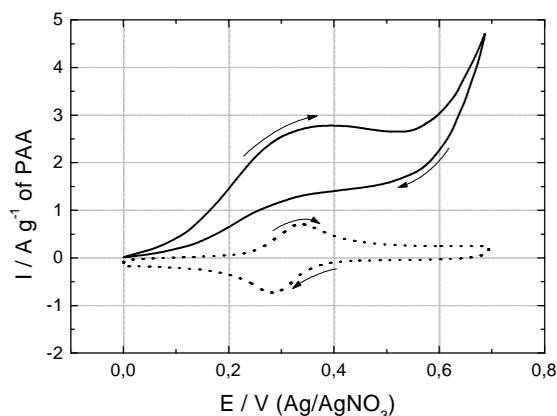
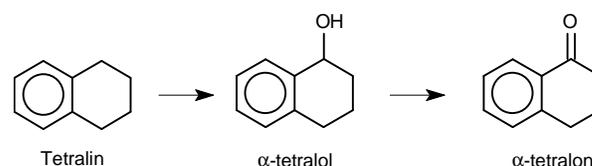


Figure 1 : Voltammograms of a Tempo-modified electrode ($1 \times 1 \times 0.5 \text{ cm}^3$) recorded in 0.2 M NaClO_4 acetonitrile solution at 10 mV s^{-1} . In the absence (···) and in the presence of sparteine (—).

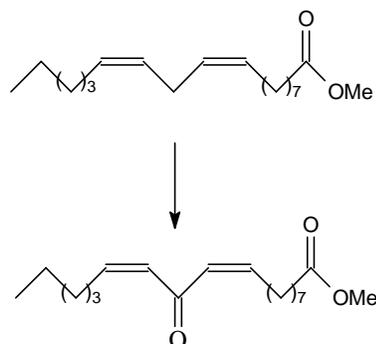
HYDROCARBONS

In the presence of an electrochemically inert base, tetralin is oxidized into α -tetralon. The primary product is the corresponding alcohol:



FATTY OLEFINES

Functionnalization of fatty olefins can be also carried out using the same modified electrodes. In acetonitrile and in the presence of water, linoleic methyl ester is oxidized in C_{10} position:



REFERENCES

- [1] A.E.J. de Nooy, A.C. Besemer and H. van Bekkum, *Synthesis*, **1996**, 1153, and references cited therein.
- [2] E.M. Belgsir and H.J. Schäfer, *Electrochem. Commun.*, **2001**, 3, 32.
- [3] E.M. Belgsir and H.J. Schäfer, *Chem. Commun.*, **1999**, 435.
- [4] Two modified graphite felt electrodes were used for preparative electrolyses at $0.4 \text{ V(Ag/AgNO}_3)$: (a) according to T. Osa, Y. Kashiwagi, K. Mukai, A. Oshawa and J. Bobbitt, *Chem.Lett.*, **1990**, 75 and (b) according ref.[3]

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