

PREPARATIVE ELECTROREDUCTION OF 5- AND 6-NITROBENZOTHIOPHENES IN ACIDIC AND BASIC HYDROMETHANOLIC SOLUTION

J. M. Chapuzet, L. Bouchard and J. Lessard

Laboratoire d'électrochimie organique
Département de chimie, Université de Sherbrooke
2500 bd. de l'Université, Sherbrooke, (Québec), J1K 2R1

Introduction

We have shown that the electroreduction of 5- and 6-nitroindoles (**1**, X=NH or NCH₃) and 5- and 6-nitrobenzofuranes (**1**, X=O), at Hg, in acidic (HX 0.15 M, pH = 0.3, X = HSO₄, Br) aqueous methanol (MeOH-H₂O 95:5, v/v) gives substituted amino derivatives **2** and the corresponding amines **3** [1-4]. The formation of substituted compounds **2** has been explained by attack of a nucleophile on diiminoquinone **4** (Y = OH and/or H) and quinonemethane imine **5** (Y = OH and/or H) resulting from dehydration of dihydroxylamines and/or hydroxylamines.

In basic medium (KOH 0.15 M, pH > 13) the main or sole product isolated was the hydrazo compound **6** resulting from the condensation between nitroso and hydroxylamine intermediates as in the classical reduction of nitroaryl compounds.

The aim of this study was to determine if the behavior of 5- and 6-nitrobenzothiophenes **1** (X=S, 5-NO₂ and 6-NO₂ respectively) was similar to that of the analogues mentioned above.

Results and discussion

The electroreductions were carried out at Hg under controlled potential conditions in MeOH-H₂O (95 : 5, v/v) acidic (HBr 0.15 M, pH = 0.3) and basic (KOH 0.15 M, pH > 13) solutions.

In acidic medium, 5-nitrobenzothiophene gave 4-substituted-5-aminobenzo-thiophenes [**2**, X=S, 5-NH₂, 4-Nu (Nu=Br and OMe)] and 6-nitrobenzothiophene gave 7-bromo-6-aminobenzo-thiophene [**2**, X=S, 6-NH₂, 7-Nu (Nu=Br)]. These results show that iminoquinonium intermediates such as **4** (X=S) and **5** (X=S) are also formed in these reductions. The reactivity and the nature of these intermediates (**4** vs **4H**⁺, **5** vs **5H**⁺) as well as the site of nucleophilic attack will be discussed in the light of theoretical calculations.

In basic medium, no dehydration of the intermediate hydroxylamines occurred since the sole product isolated was an azo derivative resulting from air oxidation of the hydrazo compound **6** (X=S, 5,5' or 6,6').

Acknowledgements

We acknowledge the financial support from the "Fonds FCAR du Québec" and from the NSERC of Canada.

References

- [1] I. Marcotte, A. Lemire and J. Lessard ; *Proceedings of the Third International Symposium on Electroorganic Synthesis*, IS-EOS ' 97, Kurashiki (in press).
- [2] I. Marcotte, M. Sc. Dissertation, Université de Sherbrooke (1999).
- [3] I. Marcotte, M. Lavoie, Y. Dory, J. M. Chapuzet, J. Lessard, *Acta Chim. Scand.*, **53** 849-856 (1999).
- [4] L. Bouchard, M. Sc. Dissertation, Université de Sherbrooke (2001).

