Tetrahedron Letters,Vol.28,No.12,pp 1275-1276,1987
Printed in Great Britain

0040-4039/87 $3.00 + .00
Pergamon Journals Ltd.

UNEXPECTED ELECTROOXIDATIONS OF AROMATIC ENOL ETHERS IN THE PRESENCE OF NON CURRENT NUCLEOPHILES.

Michel CARIOU*[1a], Jacques SIMONET[1b] and Loïc TOUPET[2b]

1) Laboratoire d'Electrochimie Organique, U.A. CNRS n° 439
2) Centre de Diffractométrie, U.A. CNRS n° 804
a) Université Catholique de l'Ouest, B.P. 808, 49005 ANGERS Cédex, France.
b) Université de Rennes I, Campus de Beaulieu, 35042 RENNES Cédex, France.

Summary : The electrooxidation of aromatic enol ethers can lead to unexpected substitution or additions by non current nucleophiles. For instance, the oxidation in the presence of lutidine leads exclusively to the corresponding N-substituted lutidinium salts whereas the use of K_2CO_3 as a base affords the anodic addition with formation of a cyclic carbonate.

Previously[1,2] was demonstrated the major influence of the nature of the base on the result of the electrooxidation of certain enamines. Therefore, it was worthwhile specifying the effect of bases such as 2,6-lutidine and K_2CO_3 on cationic intermediates of the electrooxidation of some aromatic enol ethers. The present note is devoted to the behaviour of 1,2,2-triphenyl-1-methoxy ethylene 1.

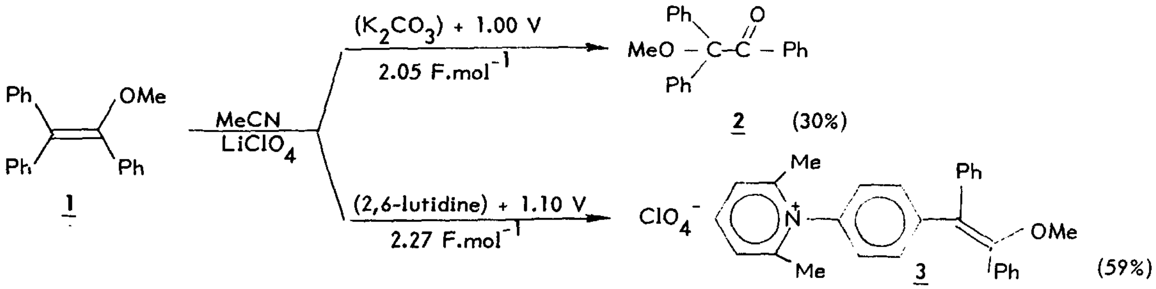
It should be recalled that most enol ethers on electrooxidation[3] in methanolic solution are known to be dimethoxylated, with or without dimerization. Moreover the electrooxidation of the enediether Ph(MeO)C=C(OMe)Ph, whose structure is close to that of 1, leads, in MeOH-KOH[4] to $Ph(MeO)_2C{-}C(OMe)_2Ph$ and $Ph{-}C(OMe)_3$, and in DMF or MeCN[5] (with or without 2,6-lutidine) to PhCO–COPh and $PhCO{-}C(OMe)_2Ph$.

On the other hand, the reaction of pyridine or pyridines not 2,6-substituted with certain cation radicals, giving pyridinium salts, is known[6] ; however other bulky pyridines, such as 2,6-lutidine, are hindered and for that reason poorly nucleophilic. They are therefore used to remove the protons formed in the anodic compartment. In methanol, the electrooxidations are carried out generally in the presence of methoxide or hydroxide ; to compare with previous results[1,2], K_2CO_3, a weak and poorly nucleophilic base, was studied.

Macroscale electrolyses. The cell and procedure were the same as those used for the electrooxidation of enamines[2] ; potentials were measured against the saturated calomel electrode.

Oxidations in acetonitrile

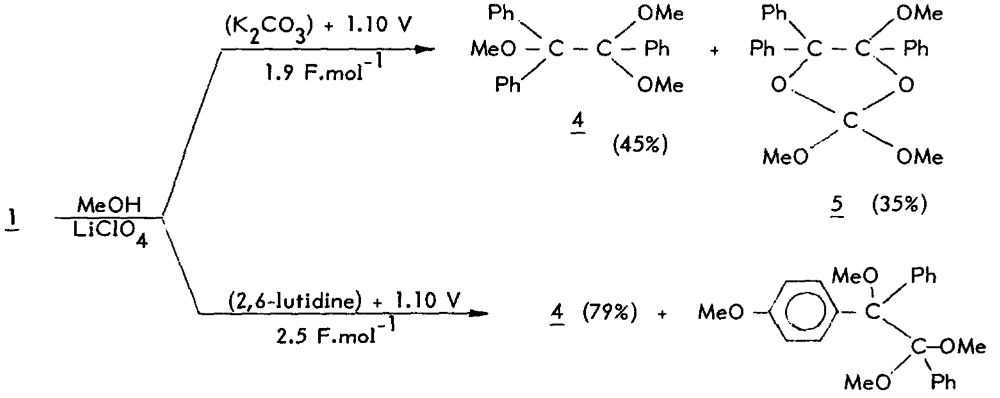
- in the presence of K_2CO_3, we have mainly obtained the α -methoxy ketone 2 (implying probably the internal migration of the methoxy group at the stage of the transient cation[5]), together with cleavage products, whereas in the presence of 2,6-lutidine, the salt 3 was formed exclusively ; the structure of 3 was demonstrated by means of X-Ray analysis :



The formation of a salt from a hindered pyridine appears to be quite general in the oxidation of 1 and was observed also with collidine, whereas in the presence of one of the most bulky bases, such as 2,6 t-butyl-4-methyl pyridine, we have obtained a similar product distribution as that formed when K_2CO_3 is used as a base. (Physical data of 3 are : m.p. 249°C (EtOH), NMR ($CDCl_3$) : ppm (TMS) 2.37 (s, 3H), 2.48 (s, 3H), 3.52 (s, 3H), 6.80-8.30 (m, 17H)).

Oxidations in methanol

- On the contrary, in the presence of K_2CO_3, the electrooxidation of 1 led to the mixture of both the expected dimethoxylated product 4 and the dioxolane derivative 5, whose structure was also determined by X-Ray analysis ; whereas in the presence of 2,6-lutidine, 1 gave principally 4 along with 20% of product 6 (here, with concomitant addition and substitution).



(Physical and spectroscopic data of 5 are : m.p. 118°C (iPr_2O), NMR ($CDCl_3$) ppm (TMS) : 3.21 (s, 3H), 3.60 (s, 6H), 6.70-7.75 (m, 15H)

These reactions are presently generalized with analogues of 1.

REFERENCES

1 - M. CARIOU and J. SIMONET, J. Chem. Soc. Chem. Commun. (1983) p. 1146-1147.
2 - M. CARIOU, R. CARLIER and J. SIMONET, Bull. Soc. Chim. Fr., (1986), p. 781-792.
3 - S. TORII, in "Electroorganic Syntheses. Methods and applications. Part I : oxidations" (Monographs in modern chemistry - Vol. 15), Kodansha-Tokyo and Verlagchemie Weinheim (1985), p. 233-235 ; K.YOSHIDA in "Electrooxidation in organic chemistry", Wiley, New York (1984), p. 196-197.
4 - R. COUTURE and B. BELLEAU, Can. J. Chem. (1972), 50, p. 3424-3425.
5 - M.A. MICHEL, P. MARTIGNY and J. SIMONET, Tetrahedron Lett. (1975), p. 3143-3146.
6 - N.L. WEINBERG in "Technique of electroorganic synthesis. Part I", Wiley, New York (1974), p. 235-533.

(Received in France 12 December 1986)