Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters 47 (2006) 8215–8216
Tetrahedron Letters

Facile electrochemical transformation of diazonium salts into carboxylic acids

M. Dolores Otero, Belen Batanero and Fructuoso Barba*

Department of Organic Chemistry, University of Alcalá, 28871, Alcalá de Henares (Madrid), Spain

Received 5 July 2006; revised 19 September 2006; accepted 22 September 2006

Abstract—The electrolyses of aryldiazonium tetrafluoroborates in dry DMF and Bu_4NHSO_4 as solvent-supporting electrolyte system, in the presence of CO_2 led to the corresponding arylcarboxylic acids in very good yields.

The electrochemical carboxylation of the aromatic ring of aryl halides is a well-known process.[1] The reaction involves the cathodic cleavage of the carbon–halogen bond to form the corresponding anion, which is added to a bubbled carbon dioxide molecule, affording the desired carboxylic acid in a good yield, particularly under pressurized cell. However the inconvenience of this reaction is the requirement of using high cathode potentials, around -2 V (vs Ag/Ag^+).

On the other hand some aromatic hydrocarbon rings such as naphthalene, phenanthrene, and acenaphthylene were converted into carboxylic acids by the reductive carboxylation on controlled potential electrolyses; however, the yields were poor.[2]

In the present letter a new procedure for the obtention of aryl carboxylic acids is described by the cathodic reduction of aryldiazonium salts in the presence of CO_2.

Few articles about the employment of diazonium salts in organic electrosynthesis have been published. Aqueous or alcoholic media have been used in the electroreductions of these salts at a mercury cathode.[3–5] Described polarography of diazonium salts showed two reduction waves. Preparative electrolysis at the first reduction value (between $+0.02$ V and -0.1 V, vs SCE) afforded arylmercury salts after a $1e^-$/substrate molecule process, involving the initial formation of radicals.[6] Preparative electrolysis at the second reduction potential value (between -0.5 V and -0.7 V, vs SCE) in a $3e^-/3H^+$ process allowed to get the corresponding phenyl-hydrazine.[7–10] The reduction of aryldiazonium salts at Cu, Fe or Ti cathodes in the presence of alkenes led to arylated products.[11] Aromatic compounds were also arylated by the electrochemical reduction of benzenediazonium tetrafluoroborates in aprotic solvents.[12]

The attachment of organic layers to conductive or semiconductive surfaces by cathodic reduction of diazonium salts has been performed.[13]

The preparation of arylcarboxylic acids from diazonium salts supposes considerable advantages related to the reduction of the C–halogen bond. Aryl anions can be obtained under low cathode potential (-1 V, vs Ag/Ag^+) by the electrochemical reduction of these substrates, allowing the presence of other substituents in the aromatic ring of the electroactive starting material. Additionally, versus the conventional methods, the final hydrolysis necessary in the Sandmeyer reaction, and the fact that it would affect other groups on the ring, is avoided. Finally, we can mention the regiospecific character of this carboxylation process.

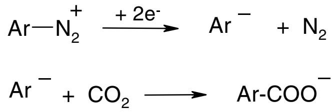
The electrolyses of aryldiazonium tetrafluoroborates in dry DMF and Bu_4NHSO_4, as the electrolyte (the cheapest tetraalkylammonium salt) in the presence of CO_2 was performed under potentiostatic -1.0 V (vs Ag/Ag^+) conditions.[14] However biphenyl was obtained as the major product (75%). Its formation can be explained due to the well-known photodediazoniation of aryldiazonium fluoroborates by dimethylformamide via a homolytic process[15] or because aryl radicals are also

---

Keywords: Aryldiazonium tetrafluoroborates; Selective cathodic carboxylation; Electrosynthesis; Carboxylic acids.

* Corresponding author. Tel.: +34 91 8854617; fax: +34 91 8854686; e-mail: fructuoso.barba@uah.es

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.09.132

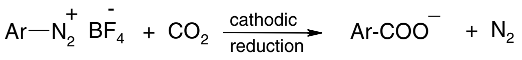


$$Ar{-}\overset{+}{N_2} \xrightarrow{+2e^-} Ar^- + N_2$$

$$Ar^- + CO_2 \longrightarrow Ar\text{-}COO^-$$

Scheme 1.

Table 1.



$$Ar{-}\overset{+}{N_2}\ \overset{-}{BF_4} + CO_2 \xrightarrow[\text{reduction}]{\text{cathodic}} Ar\text{-}COO^- + N_2$$

Ar	Yield (%)
C_6H_5	73
4-MeO–C_6H_4	90
4-Et–C_6H_4	85
2-Me–C_6H_4	91
3-Me–C_6H_4	88
4-Cl–C_6H_4	84
4-Br–C_6H_4	85
4-MeCO–C_6H_4	78
4-MeOOC–C_6H_4	77
2-MeS–C_6H_4	88

generated by the reduction of the diazonium ions at the electrode surface. The fast dimerization reaction of these aryl radicals (a second order reaction) hinders their further reduction to the corresponding anions.

Electrolysis of aryldiazonium tetrafluoroborates under low concentration conditions minimizes the dimerization process. In this case the same reduction potential value of −1.0 V (vs Ag/Ag^+) was applied, at the same time that CO_2 was bubbled into the catholyte. The solid portion addition of the electroactive salt—for 2 h—into the cathodic compartment allows the electroreduction of the C–N bond to the corresponding anion, with N_2 evolution. This anion is added in solution to a CO_2 molecule, affording the expected carboxylate, as it is indicated in Scheme 1.

This new carboxylation process provide good yields (see Table 1) independent of the electrodonating or electrowithdrawing nature of the substituents in the diazonium salt aromatic ring.

The electrolyses can also be carried out by using a power supply.[16]

Acknowledgments

This study was financed by the Spanish Ministry of Science and Education CTQ2004-05394/BQU. B.B. thanks the Spanish Ministry of Science and Technology for the '*Ramon y Cajal*' financial support.

References and notes

1. Barba, F.; Guirado, A.; Zapata, A. *Electrochim. Acta* **1982**, *27*, 1335; Matsue, T.; Kitahara, S.; Osa, T. *Denki Kagaku* **1982**, *50*, 732; Grimshaw, J. In *Rodd's Chemistry of Carbon Compounds*; Sainsbury, M., Ed.; Organic Electrochemistry; Elsevier Science, 2002; Vol. V, pp 83–84.
2. Yamamura, S. In *Rodd's Chemistry of Carbon Compounds*; Sainsbury, M., Ed.; Organic Electrochemistry; Elsevier Science, 2002; Vol. V, pp 2003–2004.
3. Bravo-Diaz, C.; Gonzalez-Romero, E. *Electroanalysis* **2003**, *15*, 303.
4. Atkinson, E. R.; Garland, C. E.; Butler, A. F. *J. Am. Chem. Soc.* **1953**, *75*, 983.
5. Elofson, R. M. *Can. J. Chem.* **1958**, *35*, 1209.
6. Kochi, J. K. *J. Am. Chem. Soc.* **1955**, *77*, 3208.
7. Rüetschi, P.; Trümpler, G. *Helv. Chim. Acta* **1953**, *36*, 1649.
8. Orange, O.; Hamet-Elfakir, C.; Caullet, C. *J. Electrochem. Soc.* **1981**, *128*, 1889.
9. Viertler, H.; Pardini, V. L.; Vargas, R. R. In *The Electrochemistry of Triple Bond—The Chemistry of Triple Bonded Functional Groups*; Patai, S., Ed.; J. Wiley and Sons: New York, 1994; Supplement C.
10. Bravo-Diaz, C.; Gonzalez-Romero, E. *Curr. Top. Electrochem.* **2003**, 9.
11. Ganushchak, N. I.; Obushak, N. D.; Kovel'chuk, E. P.; Trifonova, G. V. *Zh Obshch. Khim* **1984**, *54*, 2334.
12. Gadallah, F. F.; Elofson, R. M. *J. Org. Chem.* **1969**, *34*, 3335.
13. Pinson, J.; Podvorica, F. *Chem. Soc. Rev.* **2005**, *34*, 429.
14. The electroactive diazoniumtetrafluoroborates were prepared according to the conventional methods (In *Organic Reactions*, Krieger, R. E., Ed.; Publishing company: Huntington, NY, 1977; Vol. V, pp 198–228).
The electrochemical reductions were performed under potentiostatic conditions in a concentric cell with two compartments separated by a low porosity (D4) glass frit diaphragm and equipped with a magnetic stirrer. A mercury pool was used as the cathode, a platinum plate as the anode, and a saturated Ag/AgCl electrode as the reference. The SSE (solvent-supporting-electrolyte) was nominally anhydrous DMF containing 0.05 M tetrabutylammonium bisulfate. The electroactive substrate (3.0 mmol in 20 mL of SSE) was added during for 2 h to the cathodic compartment to be electrolyzed at a constant potential of −1.0 V (vs Ag/Ag^+). When the reaction was completed the cathodic solution was removed under reduced pressure. The residue was extracted with ether/NaOH (5%). The aqueous phase was acidified and extraction with ether was again performed. The second organic phase was dried over $MgSO_4$ and concentrated by evaporation. The resulting solid was GC chromatographed and crystallized in H_2O. The physical and spectroscopical properties of the obtained acids (available at Aldrich) were coincident with the already described in the literature (Beilstein 9,10-IV).
15. Markgraf, J. H.; Chang, R.; Cort, J. R.; Duran, J. L.; Finkelstein, M.; Gross, A. W.; Lauyne, M. H.; Moore, W. M.; Petersen, R. C.; Ross, S. D. *Tetrahedron* **1997**, *53*, 10009.
16. In order to make this reaction easy to be applied by the organic chemical community, the electrolyses were also carried out (the potentiostat is expensive and not always available) with a power supply (cheaper and affordable), with a reference electrode connected to a high resistance voltmeter, and a manual control of the potential value in −1 V (vs Ag/Ag^+). The obtained yields of carboxylic acids were almost coincident with the above mentioned by using the potentiostat.