Electrochemistry Communications 12 (2010) 973–976

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Cathodic reduction of diazonium salts in aprotic medium

Fructuoso Barba [a,*], Belen Batanero [a,*], Khalil Tissaoui [b], Noureddine Raouafi [b], Khaled Boujlel [b]

[a] Department of Organic Chemistry, University of Alcala, 28871 Alcala de Henares (Madrid), Spain
[b] Laboratoire de Chimie Analytique et d´Electrochimie, 2092 El-Manar, Tunis, Tunisia

ARTICLE INFO

Article history:
Received 14 April 2010
Received in revised form 5 May 2010
Accepted 5 May 2010
Available online 19 May 2010

Keywords:
Azobenzenes
Diazonium salts
Electrosynthesis
Diarylamine
Aryl anion
Cathodic reduction

ABSTRACT

Cathodic reduction of diazonium salts in acetonitrile led to the formation of azobenzenes, in good to moderate yields, and diarylamines as minoritary products. The reactions were carried out at the second reduction potential of the diazonium salts, involving aryl anions in the formation of the products.

1. Introduction

Azobenzenes have a wide variety of potential applications toward organic non-linear optics, optical storage media, chemosensors, and photochemical switches, due to their characteristic colour and photoresponsive properties [1–4]. Azobenzene and its derivatives which are well known for their reversible trans-cis photoisomerization, have been widely used as functional groups to prepare various photoresponsive polymers [5,6].

A new series of novel polyamidoamine dendrimers possessing azobenzene units at the core have been prepared [7].

Azobenzene is a well known photochromic molecule that shows E to Z isomerization by UV light irradiation and Z to E isomerization by visible light irradiation [8].

Classical methods for the synthesis of azobenzenes include electrophilic aromatic substitution involving aryl diazonium salts, condensation of nitrosobenzenes with anilines, and oxidative coupling of two anilines [9–12]. Buchwald-type couplings of aryl hydrazines with aryl iodides, followed by oxidation, have been employed [13]. There are publications about the preparation of azobenzenes from the crude nitroso compounds obtained by amine oxidation with oxone (a stable triple salt: 2 $KHSO_5.KHSO_4.K_2SO_4$) [14], and a new synthetic method for azobenzenes has been described starting from N-Boc aryl hydrazines via Pd-catalyzed coupling reactions with various aryl halides followed by direct oxidation with NBS/pyridine in CH_2Cl_2 [15].

Few articles have been published [16–18] concerning diazonium salts in organic electrosynthesis. However it is known that diazonium salts are easily reduced. Polarography of diazonium salts shows two reduction waves. Preparative electrolysis at the first reduction peak affords biaryl derivatives after a radical coupling [19].

Concomitant reduction of 1,2-quinones and benzene diazonium cation, at the first reduction peak of both compounds (−0.5 V, vs SCE), afforded interesting compounds such as hydroxycarboxamides, cyanomethylated or 1,2-dichloroethylated products depending on the solvent employed: DMF, CH_3CN or 1,2-dichloroethane respectively [20].

Electrolyses of different arenediazonium tetrafluorborates at their first reduction potential, in CS_2/EtOH as solvent led to the corresponding diaryl disulfides in good yield [21].

On the other hand, electrolysis of arenediazonium salts at their second reduction potential takes place through electrogenerated anions that evolve, under aqueous solution, towards the formation of phenylhydrazines [22,23], or under aprotic conditions, by bubbling CO_2 into the cathodic solution, to arylcarboxylic acids [24] in very good yield.

In the present communication the electroreduction of diazonium salts at their second reduction potential in dry acetonitrile is described

---

* Corresponding authors. Department of Organic Chemistry of the University of Alcala, Facultad de Farmacia, Campus Universitario, 28871 Alcala de Henares (Madrid), Spain. Tel.: +34 918854617/2517; fax: +34 918854686.

E-mail addresses: fructuoso.barba@uah.es (F. Barba), belen.batanero@uah.es (B. Batanero).

1388-2481/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.elecom.2010.05.004

to afford azobenzenes as main products together with small amount of diarylamines and biaryls.

2. Experimental section

The electroactive diazoniumtetrafluoroborates were prepared according to conventional methods (*Organic Reactions.* Ed Krieger, R.E. publishing company. Huntington N.Y. 1977, vol.V, pp198–228).

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. The temperature was maintained constant at 0 °C with a cryostat. A mercury pool electrode (15 cm^2) was used as the cathode, a platinum plate (5 cm^2) as the anode, and a saturated SCE electrode as the reference. The SSE (solvent-supporting-electrolyte) system was dry acetonitrile containing 0.1 M lithium perchlorate. The catholyte was 60 mL of SSE and the anolyte 20 mL of SSE. K_2CO_3 was added to the anodic compartment in order to neutralize the generated perchloric acid.

The aryldiazonium tetrafluoroborate (**1**) (1.0 mmol) was added, in small solid portions over 3 h, to the cathodic compartment, to be electrolyzed at a constant potential of −1.0 V(*vs SCE*).

Once the reaction was finished the solvent of the cathodic solution was removed under reduced pressure. The residue was extracted with ether/H_2O. The organic phase was dried over $MgSO_4$ and concentrated by evaporation. The resulting solid was purified by chromatography on silica gel 60 (35–70 mesh) in a (22 × 2.5 cm) column, using mixture $CHCl_3$/Hex (4:1) as eluent. The physical and spectroscopical properties of the obtained azobenzenes (**2**) were identical to those described in the literature. The experimental MS spectra of **2** and **3** are given:

2a: 1,2-diphenyldiazene $C_{12}H_{10}N_2$
MS (m/e, relative intensity): 182(M^+, 52), 152(30), 105(74), 77(100), 51(71).

2b: 1,2-bis(4-methoxyphenyl)diazene $C_{14}H_{14}N_2O_2$
MS (m/e, relative intensity): 242(M^+, 23), 135(66), 107(100), 92(45), 77(93), 63(38).

2c: 1,2-di-*o*-tolyldiazene $C_{14}H_{14}N_2$
MS (m/e, relative intensity): 210(M^+, 5), 167 (7), 119(5), 91 (100), 65(47).

2d: 1,2-di-*m*-tolyldiazene $C_{14}H_{14}N_2$
MS (m/e, relative intensity): 210(M^+, 20), 165(14), 119 (23), 91(100), 65(22).

2e: 1,2-bis(2,6-dimethylphenyl)diazene $C_{16}H_{18}N_2$
MS (m/e, relative intensity): 238(M^+, 4), 195(15), 105(100), 103(50), 91(9), 77(49), 51(18).

2f: 1,1′-(4,4′-(diazene-1,2-diyl)bis(4,1-phenylene))di-ethanone $C_{16}H_{14}N_2O_2$
MS (m/e, relative intensity): 266(M^+, 4), 167(33), 149(100), 119(46), 91(94), 65(15).

2g: dimethyl 4,4′-(diazene-1,2-diyl)dibenzoate $C_{16}H_{14}N_2O_4$
MS (m/e, relative intensity): 298(M^+, 6), 163(53), 135(100), 119(17), 103(34), 77(13).

2h: 1,2-bis(4-bromophenyl)diazene $C_{12}H_8Br_2N_2$
MS (m/e, relative intensity): 342(M^++4, 3) 340(M^++2, 6), 338(M^+, 3), 185(56), 183(56), 157(100), 155(100), 75(25), 50 (32).

3a: diphenylamine $C_{12}H_{11}N$
MS (m/e, relative intensity): 169 (M^+, 100), 168(80), 154(3), 141(6), 115(7), 84(6), 77(3), 51(7).

3b: bis(4-methoxyphenyl)amine $C_{14}H_{15}NO_2$
MS (m/e, relative intensity): 229 (M^+, 27), 214(100), 199(14), 171(13), 154(21), 143(34), 115(20).

3c: di-*o*-tolylamine $C_{14}H_{15}N$
MS (m/e, relative intensity): 197(M^+, 100), 180(98), 167(63), 106(34), 91(19), 77(22), 51(12).

3d: di-*m*-tolylamine $C_{14}H_{15}N$
MS (m/e, relative intensity): 197 (M^+, 100), 196(33), 182(47), 181(82), 180(47), 167(45), 115(9), 91(20), 77(13), 51(10).

3e: bis(2,6-dimethylphenyl)amine $C_{16}H_{19}N$
MS (m/e, relative intensity): 225(M^+, 55), 210(100), 195(61), 180(28), 131(26), 118(37), 91(46), 77(27), 51(14).

3f: 1,1′-(4,4′-azanediylbis(4,1-phenylene))di-ethanone $C_{16}H_{15}NO_2$
MS (m/e, relative intensity): 253(M^+, 27), 238(39), 167(100), 139 (23), 83(13), 63(7).

3g: dimethyl-4,4′-azanediyldibenzoate $C_{16}H_{15}NO_4$
MS (m/e, relative intensity): 285(M^+, 47), 254(51), 194(23), 167(100), 166(90), 140(30), 139(57), 111(18), 83(31).

3h: bis(4-bromophenyl)amine $C_{12}H_9Br_2N$
MS (m/e, relative intensity): 329(M^++4, 7), 327(M^++2, 12), 325(M^+, 7), 167(100), 139(19), 84(14), 50(8).

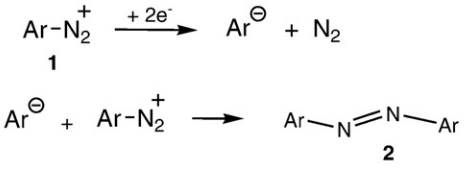
3. Results and discussion

The cathodic reduction of different diazonium salts (**1**), at the reduction potential of the second voltammetric peak of these systems (−1.0 V, *vs SCE*), has been performed in a divided cell. The formation of diarylazo compounds (**2**) as the main product is explained according to Scheme 1.

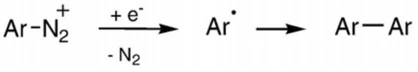
The following experimental procedure was required to get the azoderivatives:

a) the diazonium salt had to be added in small solid portions during the electrolysis to avoid a high concentration of radicals at the electrode surface, and the faster dimerization to biaryls instead of a further reduction of the radical to the desired anion (Scheme 2).
b) The temperature of the cell was maintained at 0 °C during the electrolysis, with the help of a cryostat, in order to avoid thermal decomposition of the diazonium salt.

The obtained yields in diarylazo compounds are summarized in Table 1.



Scheme 1. Formation pathway of diarylazo compounds (**2**).



Scheme 2. Formation of biaryls.

Table 1
Obtained yields of 1,2-diaryldiazenes (**2**).

Ar:	Yield of 2 (%)	M.p. (°C)
a: C_6H_5	65	67 [Lit[25]:68]
b: 4-MeO-C_6H_4	69	163 [Lit[26]:163–64]
c: 2-Me-C_6H_4	52	54 [Lit[27]:54–56]
d: 3-Me-C_6H_4	66	52 [Lit[28]:50–52]
e: 2,6-diMe-C_6H_3	72	48 [Lit[29]:46–47]
f: 4-MeCO-C_6H_4	63	193 [Lit[30]:194]
g: 4-MeOOC-C_6H_4	59	196–198 [Lit[31]:198–199]
h: 4-Br-C_6H_4	75	203 [Lit[32]:205]