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Electrocatalytic dimerisation of benzyl bromides and phenyl bromide at silver cathode in ionic liquid $BMIMBF_4$

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A simple and eco-friendly electrochemical route was developed by using silver as the cathode, magnesium as the anode and ionic liquid $BMIMBF_4$ as solvent for the electrochemical dimerisation of aromatic bromides. The electrochemical behaviour was studied at different electrodes (Ag, Cu, Ni and Ti) by cyclic voltammetry, which shows significant electrocatalytic effect of the silver electrode towards the reductive dimerisation of aromatic bromides. Biaryls were obtained in moderate to good yield (12–68%). A recycling study confirmed that the solvent can be reused multiple times without activity loss.

1. Introduction

Environmental considerations now constrain chemists to integrate the control of risks (and costs) into their procedures and the recent literature reflects various approaches aiming at eco-friendly processes. This explains the rapidly growing interest in the properties of room temperature ionic liquids (RTILs) in recent years. At first sight the ionic liquids, combining ionic conductivity and good solvating properties for organic compounds, could find a wide application in electrochemistry. In fact, such non-volatile systems, used instead of conventional organic solvent/supporting electrolyte system and maximally facilitating products isolation procedure, seem to be an ideal media for electrochemistry [1–4].

Symmetrical biaryls are important intermediates for synthesizing agrochemicals, pharmaceuticals and natural products [5–7]. Electrochemical dimerisation of aromatic bromides has been studied in ionic liquids in the last few years, however, the results are not very efficient. Barhdadi et al. [8] conducted the electrodimerisation in a mixed solvents of [octyl-mim][BF_4] ionic liquid and *N*,*N*-dimethylformamide (DMF). However, the use of an organic co-solvent can not meet the growing demand of environmental friendly technologies. The similar electrochemical reductive dimerisations were achieved in neat ionic liquid, without the need for adding extra solvent such as DMF, yet it should be catalyzed by $NiCl_2$ (bipy) or palladium nanoparticle [9,10]. For large-scale preparation most metal complexes are expensive, sensitive to oxygen and water, and toxic (especially for Ni). In addition, the presence of additive catalysts made the reaction system and the separation complicated.

In fact, if catalytic surfaces, capable of significantly lowering the reduction overpotential for RX (X = Cl, Br, I), are used as cathode materials, a simple and efficient electrochemical route may be developed without the use of homogeneous catalysts. It has been shown recently that silver has extraordinary electrocatalytic properties towards the reduction of organic halides in aprotic solvents [11–13]. Herein, we wish to report the electrochemical dimerisation of aromatic bromides at silver electrode in $BMIMBF_4$.

2. Experimental

2.1. Apparatus and reagents

Cyclic voltammograms were measured with CHI660 electrochemical analyzer (CHI, USA) in a conventional three-electrode undivided cell. Silver (Ag), copper (Cu), nickel (Ni) and titanium (Ti) electrode (d = 2 mm) was used as a working electrode, respectively. The counter electrode and the reference electrode were a Platinum wire and Silver wire, respectively. Galvanostatic electrolysis were carried out using a dc regulated power supply QJ 12001X (1A 120 V) in an undivided cell equipped by two-electrode.

^1H NMR spectra were recorded on AVANCE 500 (500 MHz) spectrometer in $CDCl_3$ with Me_4Si as an internal standard. Mass spectra were obtained on a 5973 N spectrometer connected with a HP 6890 gas chromatograph.

The room temperature ionic liquid, 1-butyl-3-methyl imidazolium tetrafluoroborate ($BMIMBF_4$), used in this study was prepared

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as prescribed in the literature [14]. Other reagents were used as received.

2.2. Preparative electrolyses

In a typical experiment, the galvanostatic electrolysis was carried out in $BMIMBF_4$ containing 0.1 M benzyl bromide in a one-compartment electrochemical cell equipped with a magnesium rod sacrificial anode and a metallic ring cathode until 1.5 F mol^{-1} of charge was passed. During electrolyses the solution was stirred and the same current density (1.1 mA cm^{-2}) was applied in all electrolysis experiments. After electrolysis, the solution was extracted with Et_2O, and the organic layers was washed with H_2O, dried over $MgSO_4$, and evaporated. All quantitative determinations were based on calibration curves. Biaryls were isolated by column chromatography with petroleum ether as eluent, biphenyl is commercially available.

Bibenzyl: GC–MS (*m/e*,%) 182 (M^+, 29), 91 (100), 77 (3), 65 (12), 28 (24); ^1H NMR (500 MHz, $CDCl_3$): δ 7.32–7.20 (10H, m, 2Ph,), 2.95 (4H, S, $2CH_2$).

4,4′-dichlorobibenzyl: GC–MS (*m/e*,%) 250 (M^+, 18), 215 (4), 125 (100), 89 (16), 75 (3); ^1H NMR (500 MHz, $CDCl_3$)*:* δ 7.27–7.05 (8H, m, 2Ph), 2.87 (4H, S, $2CH_2$).

4,4′-dimethylbibenzyl: GC–MS (m/e,%) 211 (M^+, 8), 106 (100), 78 (20), 65 (5), 51 (10); ^1H NMR (500 MHz, $CDCl_3$): δ 7.29–7.13 (8H, m, 2Ph), 2.90 (4H, S, $2CH_2$), 2.34 (6H, S, $2CH_3$).

2.3. Recycle of ionic liquid

Following electrolysis, the organic products were extracted by treating the electrolytic solution with EtO_2, and then CH_2Cl_2 was added to $BMIMBF_4$, the solvent was washed with an aqueous solution of $NaBF_4$ in order to eliminate metallic salts arising from the anodic reaction. After purification, CH_2Cl_2 was removed under reduced pressure, then $BMIMB_4$ was dried in a vacuum oven, and used again in further experiments.

3. Results and discussion

Cyclic voltammogram for the reduction of benzyl bromide was recorded at silver electrode at the scan rate of 100 mV s^{-1} in $BMIMBF_4$ under a nitrogen atmosphere (Fig. 1A). Two successive irreversible reduction peaks of unequal height, at −0.8 V (E_{p1}) and −1.2 V (E_{p2}) are associated with the reduction of $PhCH_2Br$, which represent two successive one-electron reductive cleavage of the carbon–bromine bond. The voltammetry behaviour of $PhCH_2Br$ at Ag electrode is quite similar to that observed in the organic solvents [15–16]. The reduction process involves both radical ($PhCH_2\cdot$) and carbanion ($PhCH_2^-$) intermediates. It can also be observed that the second reduction peak (E_{p2}) is 0.4 V more negative than the first reduction peak (E_{p1}), which provides a potential window save enough for the dimeric reaction between radical and radical before its reduction to the corresponding carbanion.

In order to examine the electrocatalytic properties of Ag electrode towards the reduction of $PhCH_2Br$ in $BMIMBF_4$, the voltammetry behaviours of $PhCH_2Br$ were also investigated at the most commonly used cathodes, e.g., Cu, Ni and Ti. As shown in Fig. 1B, a shoulder peak corresponding to two-electron reduction of $PhCH_2Br$ was observed at ca. −1.1 V and −1.4 V at Cu and Ni electrode, respectively. With Ti electrode, however, a single irreversible reduction peak of $PhCH_2Br$ was obtained at ca. −2.2 V, and the shape of CV curve was very similar to those pictured at glass carbon electrode in organic solvent. Since the reduction potential (E_{p1}) of $PhCH_2Br$ at Ti electrode is more negative than E_{p2} of the benzyl radical, the latter will be reduced to a carbanion as soon as it is formed [15]. The overall process is thus a two-electron reduction of $PhCH_2Br$ to $PhCH_2^-$, which is unfavorable to electrochemical dimerisation. Such a great difference of voltammetry behaviour of $PhCH_2Br$ at the four electrodes points to a significant electrocatalytic effect of the Ag electrode towards the reductive polymerization of $PhCH_2Br$ in $BMIMBF_4$.

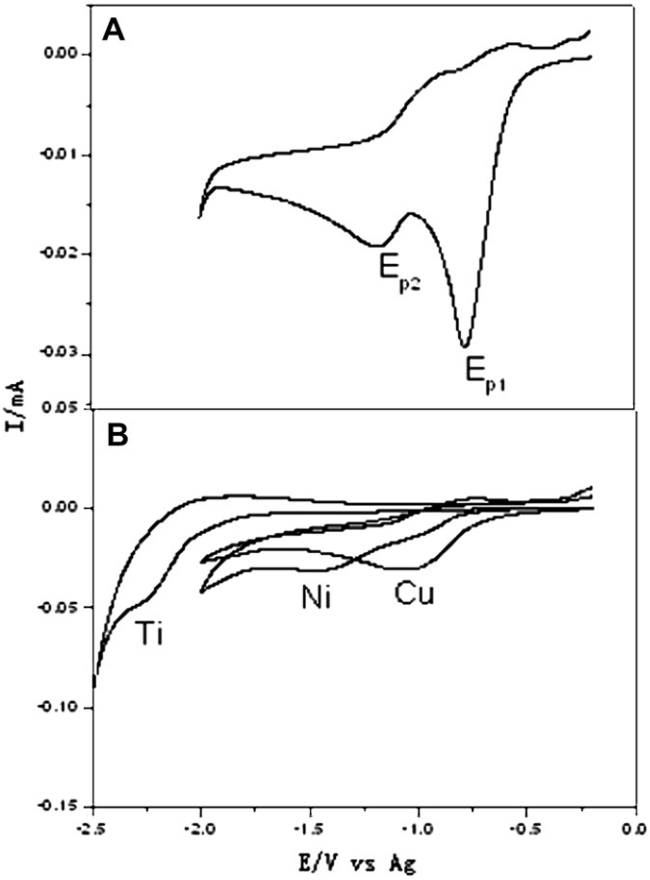

Fig. 1. Cyclic voltammograms recorded at Ag, Cu, Ni and Ti, electrode in air-free $BMIMBF_4$ containing 10 mM benzyl bromide, respectively, v = 100 mV s^{-1}, t = 20 °C.

The most relevant outcome of the above voltammetric investigation is that Ag shows a significant electrocatalytic effect towards the reduction of benzyl bromide. To confirm this, we first investigated the effect of different electrodes on the electrochemical dimerisation of benzyl bromide. Table 1 (entries 1–6) shows the results obtained with different cathodes (Ag, Cu, Ni and Ti) and anodes (Mg, Zn and Al). At the same Mg anode case, the highest

Table 1
Electrochemical dimerisation of benzyl bromide in $BMIMBF_4$[a]

Entry	Cathode/anode	Temperature (°C)	Yield (%)[b]
1	Ag/Mg	60	61
2	Cu/Mg	60	54
3	Ni/Mg	60	48
4	Ti/Mg	60	9
5	Ag/Zn	60	60
6	Ag/Al	60	57
7	Ag/Mg	20	22
8	Ag/Mg	40	47
9	Ag/Mg	50	51
10	Ag/Mg	70	62

[a] Benzyl bromide = 0.1 M, $BMIMBF_4$ = 10 mL, Current density = 1.1 mA cm^{-2}, electric charge = 1.5 F mol^{-1}.

[b] GC yield. The yield based on the starting benzyl bromide.