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Applicability of a Polymerized Ionic Liquid/Carbon Nanoparticle Composite Electrolyte to Reductive Cyclization and Dimerization Reactions

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ABSTRACT

Recently, a reusable polymerized ionic liquid/carbon nanoparticle composite electrolyte was developed and effectively applied to a variety of oxidative transformations. The efficient recovery of the composite material and its application in subsequent electroorganic conversions without sacrificing yield adds to the sustainability of the protocol. Herein, we describe our efforts to expand the operational window of the composite electrolyte to include cathodically initiated processes occurring at potentials up to −2.6 V. The results indicate that the composite electrolyte is applicable to reductive processes, but the scope of transformations appears to be limited.

1. Introduction

With the importance of "green and sustainable chemistry" continuing to be appreciated, electroorganic chemistry has gained greater attention as one of the most environmentally friendly approaches to organic synthesis [1–7]. Because it is based upon the use of electrons as reagents, electroorganic synthesis can often replace the need for conventional toxic chemical reagents. However, electrochemical transformations may require the use of large amounts of supporting electrolyte in order to ensure the movement of charge [8]. This creates a problem as one must separate it from the product(s) following an electrolysis. Unless it can be recovered and reused, unconscionable amounts of waste are generated. Such practices are no longer tolerable.

To address these issues, researchers have developed a variety of substitutes for conventional supporting electrolytes, systems intended to minimize the formation of waste. Examples include, but are not limited to the development and use of solid polymer electrolytes (SPE) [9] and solid-supported bases [10], the development of thermomorphic multiphase solutions [11], as well as a dispersion consisting of aqueous silica gel [12], and a polymeric reagent that serves as the electron carrier [13]. In addition, electrochemical microreactors and thin-layer flow cells have been developed in order to conduct electroorganic synthesis in the absence of a supporting electrolyte [14–23]. Each approach has been developed to facilitate the separation of the supporting electrolyte and isolation of the product, while minimizing the generation and disposal of waste.

In an effort to devise a general approach that bypasses the need for a traditional supporting electrolyte, we have developed and described the use of a recyclable "*polymeric ionic liquid (PIL) and Super P® carbon black composite*" as a surrogate for conventional supporting electrolytes [24]. It is formed via a three step sequence calling for (1) dissolving a known amount of the solid poly (diallyldimethylammonium triflimide), **1** (PDDA/Tf_2N), in a solvent such as acetonitrile (concentration based on repeating unit) [25], (2) adding the desired weight percent of Super P® carbon black (weight percent based upon the mass of the PIL), and (3) sonicating the resulting suspension using a low cost laboratory sonicator to afford a dispersion that has thus far remained stable and in that state for more than 2 years (Fig. 1). We attribute the stability to the existence of cation-π interactions between the Super P® carbon black and the positively charged pyrrolidinium subunits of the PIL [26].

Thus far, studies have focused upon *oxidative* processes including the oxidation of benzylic alcohols [24], the Friedel-Crafts heteroarylation of chalcone epoxides [27], and the Friedel-Crafts

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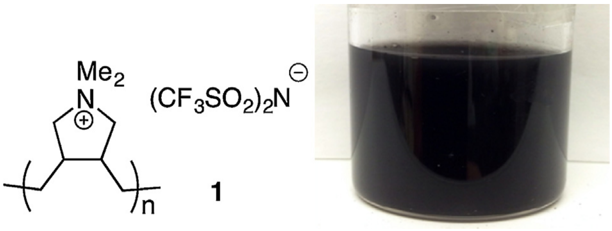

Fig. 1. Polymerized ionic liquid **1** (left) and the composite dispersion following sonication (right).

α-arylation of *N*-vinylamides [28]. In each instance, excellent yields were obtained, and the composite dispersion could be efficiently recovered and reused without the need for an additional supporting electrolyte. In addition, the ability of the composite to modify the electrode surface in-situ leads to improved electron transfer kinetics between the modified electrode and the substrate [24].

The range of potentials that is accessible to the composite dispersion extends from ca., −2.6 V to +2.6 V (in acetonitrile vs Ag/0.1 N $AgNO_3$), a range that is sufficiently large to imagine using the composite dispersion as a medium in which to conduct a host of both oxidative and reductive processes. Herein, we describe our efforts to extend the scope to include reductive transformations, turning initially to an electrohydrocyclization (EHC) that served as the key step in a total synthesis of a natural product.

2. Experimental

All reagents used were of analytical grade. The molecular weight of poly(diallyldimethylammonium) chloride was 200 000–350 000 g/mol. All solvents were distilled prior to use. Acetonitrile that was used as the solvent for electrolyses was freshly distilled from CaH_2. ^1H NMR and ^{13}C NMR spectra were recorded at the ambient probe temperature by using a Varian Unity Inova 500 MHz spectrometer (Agilent Technologies, Santa Clara, CA). Controlled potential electrolysis was carried out using a 600C Potentiostat (CH Instruments, Austin, TX). A Ag/$AgNO_3$ reference electrode (silver wire in 0.1 M *n*-Bu_4BF_4/CH_3CN solution; $c(AgNO_3) = 0.01$ M; $E_0 = -87$ mV vs ferrocene redox couple) was used and housed in a compartment that was separated from the rest of the cell using a Vycor frit [29].

2.1. Formation of the composite dispersion

The composite dispersion was prepared as reported previously [24]. Thus, a 0.5 M solution of PDDA(Tf_2N) (concentration based on repeating unit) was dissolved in dry acetonitrile (15 mL per compartment) and the desired amount (usually 1.2–10 wt % based on PIL) of Super P® carbon black (CB) was added. This suspension was then sonicated for 1.5 h to afford a stable dispersion of the composite electrolyte. The composite dispersion was directly prepared in an H-cell under an argon atmosphere. A Pt mesh anode was used as the anode. The RVC cathode had a porosity of 30 PPI. Otherwise all cathode materials used are listed in the corresponding tables.

2.2. Workup

The preferred workup calls for the dropwise addition of the catholyte into a solution of excess dichloromethane [30]. Upon addition, the composite material immediately precipitates. Filtration through a Buchner funnel separates the composite allowing it to be collected on filter paper, while the liquid contains the product. The recovered composite material was washed with dichloromethane and dried in a vacuum oven at 80 °C overnight after which it could be reused.

2.3. Dimethyl (2E,7E)-5,5-dimethylnona-2,7-dienedioate (**2**)

The known bis-unsaturated diester **2** was synthesized as described in the literature, by reduction of the corresponding glutaric acid derivative with $LiAlH_4$ followed by a Swern oxidation and subsequent Wittig olefination [31,32].

2.4. Dimethyl 2,2′-((1S,2S)-4,4-dimethylcyclopentane-1,2-diyl) diacetate (**3**)

For the synthesis of **3**, 0.122 g (0.5 mmol) of **2** and 0.134 g (1.0 mmol) of dimethyl malonate were added to the freshly prepared composite dispersion in the cathodic compartment. The resulting solution was degassed by sparging argon through the solution for 15 min. A controlled potential electrolysis was then initiated at a potential of −2.4 V (Ag/$AgNO_3$), and the progress of the reaction was monitored using TLC. After passing 74 C of charge, the current approached zero and TLC analysis showed the absence of starting material. Consequently, the electrolysis was terminated and the reaction mixture was worked up as described above. Further purification of the product was accomplished via column chromatography over silica gel (9:1 hexanes/ethyl acetate) to obtain 0.089 g (0.368 mmol, 74%) of a colorless liquid whose spectroscopic data matched those reported in literature [31].

2.5. Dimethyl (2E,8E)-deca-2,8-dienedioate (**5**)

The bis-unsaturated diester **5** was obtained by oxidative cleavage of *trans*-cyclohexane 1,2-diol with $PhI(OAc)_2$ followed by a Wittig olefination, as described in the literature [33,34].

2.6. Dimethyl 2,2′-((1S)-cyclohexane-1,2-diyl) diacetate (**6**)

For the synthesis of **6**, 0.150 g (0.66 mmol) of **5** and 0.261 g (1.98 mmol) of dimethyl malonate were added to the freshly prepared composite dispersion in the cathodic compartment. The resulting solution was degassed as described above. Thereafter, a controlled potential electrolysis was performed at a potential of −2.45 V (Ag/$AgNO_3$) and the progress of the reaction was monitored by TLC. Once the starting material had disappeared, the reaction was worked up by following the usual protocol. Purification of the product using column chromatography over silica gel did not successfully purify the product, so the yield was determined using ^1H NMR and naphthalene as an internal standard. The spectroscopic data matched those previously reported in the literature [35].