Organic Cyclisations of Propargyl and Allyl Bromoesters in Microemulsions Catalyzed by Electrogenenerated Nickel(I) Tetramethylcyclam

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Abstract

While the reductive intramolecular cyclisation of propargyl and allyl bromoesters catalysed by $[\text{Ni}(\text{tmc})]^+$ gives good yields of the desired products using N,N-dimethylformamide as the solvent, the use of this aprotic solvent presents practical, safety and environmental issues. This paper therefore reports the search for non-toxic alternatives, in particular the study of microemulsions prepared from water, hydrocarbons, surfactant and alcohol co-surfactant. It is shown that the $[\text{Ni}(\text{tmc})]^{2+}/[\text{Ni}(\text{tmc})]^+$ couple is reversible in such media and that $[\text{Ni}(\text{tmc})]^+$ reacts rapidly with propargyl and allyl bromoesters to give excellent yields of cyclic products. Indeed, these microemulsions are convenient media for such syntheses.

Keywords: Microemulsions; Cyclic voltammetry; Electrosynthesis; Electrocatalytic reduction; Intramolecular cyclisation.

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1. Introduction

The choice of the solvent is a very important factor for selective electrosynthetic processes in the laboratory or larger scale. Water remains the solvent of choice for electrolysis but severely limits the organic reactions that can be achieved. While there is an extensive literature on organic electrochemistry in aprotic solvents, such media have severe problems. They present toxicity and hazard concerns [1,2] and are seldom stable in electrolysis conditions (due both to 'pH' changes at either electrode and/or counter electrode chemistry); this, for example, led to the development of magnesium and aluminium counter electrodes, complicating the procedure [3]. Protic solvents and water/protic solvent mixtures, where applicable, are a practical solution. A more recent approach employs microemulsions [4,5] and such media have been employed for a range of organic syntheses [6] and electrosyntheses [4,5,7-11]. They are non toxic and fulfil many of the requirements for practical electrosynthesis.

We have been interested in the electrosynthesis of cyclic organic molecules mediated by square planar nickel complexes, in particular the reactions [12-16]:

1a: R = 3,4-dimethoxyphenyl

1b: R = 3,4-methylenedioxyphenyl

The previous work has been carried out in aprotic solvents. A recent paper have suggested ethanol/water [17] as an alternative. Here, we report another approach based on bicontinuous microemulsions prepared from water, hydrocarbon oils and surfactant. Such media could be ‘green’ and be appropriate media at least for laboratory synthesis. Their properties can readily be fine tuned for specific applications by adjusting their compositions [6]. All the bicontinuous microemulsions employed have previously been characterized by a variety of methods [18,19] including NMR spectroscopy, viscosity and conductivity, conductivity resulting from the presence of ionic surfactants and/or by adding inert supporting electrolyte. The microemulsions are all continuous in both oil and water.

2. Experimental Section

2.1. Reagents

Each of the following chemicals was used as received: nickel(II) bromide (Aldrich, 98%), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tetramethylcyclam, tmc, ACROS, 97%), *n*-tetradecane (ACROS, 99%), cyclohexane (Lab-Scan, 99%), 1-pentanol (ACROS, 99%), 1-butanol (ACROS, 99%), dodecane (Aldrich, 99%), cetyltrimethylammonium bromide (CTAB) (ACROS, 99%), tetradecyltrimethylammonium bromide (MTAB) (ACROS, 99%), didodecylammonium bromide (DDAB) (ACROS, 99%), sodium dodecylsulfate (SDS) (Fisher Scientific, 99%) and *n*-hexadecane (Aldrich, 99%). Deaeration procedures were carried out with zero-grade argon (Air Products).

Published procedures were employed for the preparation of [Ni(tmc)]Br₂ [20] ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)-3-propargyloxy-propanoate (**1a**) [21] ethyl 2-bromo-3-(3',4'-methylenedioxophenyl)-3-(propargyloxy)propanoate (**1b**) [21] and ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)-3-(allyloxy)propanoate (**1c**) [21].

Synthesis of 2-(3',4'-dimethoxyphenyl)-3-ethoxycarbonyl-4-methylene-tetrahydrofuran (**2a**), 2-(3',4'-dimethoxyphenyl)-3-ethoxycarbonyl-4-methyl-2,5-dihydrofuran (**3a**), 2-(3',4'-methylenedioxophenyl)-3-ethoxycarbonyl-4-methylenetetrahydrofuran (**2b**), 2-(3',4'-methylenedioxophenyl)-3-ethoxycarbonyl-4-methyl-2,5-dihydrofuran (**3b**), and 2-(3',4'-dimethoxyphenyl)-3-ethoxycarbonyl-4-methyltetrahydrofuran (**2c**) was based on the method published by McCague *et al.* [22].

Preparation of the microemulsions is straightforward and involves mixing of surfactant, hydrocarbon, water and alcohol co-surfactant in the proper proportions and stirring mechanically until clear. This may be illustrated by a specific example. 50 g of one cationic microemulsion was prepared by dissolving 8.75 g of cetyltrimethylammonium bromide in 6.25 g *n*-tetradecane and 17.5 g water then the liquid became turbid. To this 17.5 g of the co-surfactant, *n*-pentanol was added with constant stirring until the mixture became clear and stable. The anionic microemulsions were prepared similarly. The basic composition for the cationic bicontinuous microemulsions containing MTAB, CTAB, DDAB and the anionic bicontinuous microemulsions containing SDS were taken from the literature [18,19].

2.2. Cells and electrodes

Cyclic voltammograms were recorded in a three-electrode, two-compartment cell as described in earlier publications [23]. The working electrodes were fabricated from 3-mm-diameter glassy carbon rods (Tokai Electrode Manufacturing Company, Tokyo, Japan, Grade GC-20) press-fitted into Teflon shrouds to provide planar, circular working electrodes with areas of 0.07 cm². Before use, the electrodes were cleaned with an aqueous suspension of 0.05- μ m alumina (Buehler) on a Master-Tex (Buehler) polishing pad. The counter electrode was a Pt spiral in the same compartment. The experimental reference electrode was a Ag / AgCl / 3 mol dm⁻³ KCl in water, separated from the working electrode by a sinter and Luggin capillary. All solutions were deoxygenated with a fast stream of argon before each experiment. For controlled-potential electrolysis and product analysis, a divided cell with an anodic and a cathodic compartment separated by a glass sinter (as have been described in earlier publications [24]) was used. Working electrodes for controlled-potential electrolyses were disks (0.2 cm in thickness, 2.4 cm in diameter, and approximately 100 cm² in total area) sliced from reticulated vitreous carbon logs (RVC 2X1-100S, Energy Research and Generation, Oakland, CA) and graphite felt (2 cm x 2 cm x 0.5 cm) (China Yangzhou Guo Tai Fiberglass Co.,LTD) while a carbon rod was the counter electrode. Procedures for cleaning and handling of these electrodes have been described previously [25]. The catholyte and anolyte compartments were each 15 cm³ and the reference electrode was again Ag / AgCl / 3 mol dm⁻³ KCl in water mounted in a Luggin capillary. All preparative electrolyses were carried out in an

atmosphere of argon, owing to the extreme sensitivity of Ni(I) complexes to oxygen [26], and the catholyte solutions were stirred with a magnetic bar.

All potentials are quoted with respect to a Ag / AgCl / 3 M KCl in water reference electrode (-0.036 vs SCE).

2.3. Instrumentation

Cyclic voltammograms were obtained and controlled-potential electrolyses were carried out with the aid of an AUTOLAB model PGSTAT12 potentiostat–galvanostat. The data from the above experiments were acquired and stored by GPES 4.9 software, which controlled a data acquisition board installed in a personal computer.

2.4. Identification and quantitation of products

Gas chromatographic analyses were accomplished with the aid of a Chrompack, type CP 9000, instrument equipped with flame ionization detector. Products were separated with a 25 m x 0.25 mm i.d. capillary column (WCOT fused silica) with a stationary phase of poly(methylphenylsiloxane). A known quantity of an electroinactive internal standard (*n*-hexadecane) was added to a solution before each experiment to allow quantitative determination of the electrolysis products. Gas chromatographic response factors were measured experimentally with authentic samples of each product, and all product yields tabulated in this paper represent the absolute percentage of starting material incorporated into a particular product. In order to isolate the products, the reaction mixture was submitted to flash chromatography over silica gel (70-230 mesh) using ethyl acetate-hexane 1:5 as eluant.

Identities of the major products (**2** and **3**) derived from controlled-potential electrolyses were confirmed by comparison of gas chromatographic retention times as well as ¹H NMR and mass spectra for the isolated products with those of the authentic compounds [15,16].

3. Results

3.1. Cyclic voltammetry

The cyclic voltammetry of [Ni(tmc)]²⁺ in a series of microemulsions [18,19] was first investigated. Figure 1, curve A, shows a typical voltammogram for the complex at a glassy

carbon disc electrode in a MTAB/tetradecane/water/1-pentanol microemulsion. It can be seen that the voltammogram has a classical form and quantitative examination of the voltammogram confirms that the response meets the criteria for a reversible, $1e^-$ reduction [27]. Hence, it appears that $[\text{Ni}(\text{tmc})]^+$ is stable and that the $[\text{Ni}(\text{tmc})]^{2+}/[\text{Ni}(\text{tmc})]^+$ redox couple is reversible as previously found in other solvent media. Similar results were obtained for the reduction of $[\text{Ni}(\text{tmc})]^{2+}$ in the other microemulsions. Diffusion coefficients (D) and formal electrode potentials (E^o) for the $[\text{Ni}(\text{tmc})]^{2+} / [\text{Ni}(\text{tmc})]^+$ redox couple were estimated from cyclic voltammetry data using standard procedures [27]; each value reported in Table 1 is an average of at least three or more replicated experiments. Diffusion coefficients were 3 – 10 times smaller in the microemulsions than in *N,N'*-dimethylformamide (DMF/TBAB – $4.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). This is consistent with residence of this ionic complex only in the water phase of the microemulsion. Much larger D values are expected for solutes residing in the oil phase [8]. In addition, it can be observed that diffusion coefficients change by a factor of three with changing of co-surfactant from 1-pentanol to 1-butanol. In fact, these observations are in agreement with a recent study carried out by Sripriya *et al.* [28] where they report that the viscosity of bicontinuous microemulsions depend strongly on the nature of the co-surfactant; factors such as to its solubility in microemulsion phases and its chain length are important. Thus, *n*-butanol based microemulsions exhibit significantly lower viscosity as compared to that of *n*-pentanol based microemulsions; the solubility of *n*-pentanol in water (0.30 g mL^{-1}) is significantly lower than that of *n*-butanol (1.05 g mL^{-1}). UV-vis spectrum of $[\text{Ni}(\text{tmc})]\text{Br}_2$ was similar in water and in the CTAB/tetradecane/water/1-butanol microemulsion with two bands at 515 and 390 nm. The complex was insufficiently soluble in *n*-tetradecane to obtain a spectrum. These results also suggests that $[\text{Ni}(\text{tmc})]\text{Br}_2$ resides predominantly in the water phase of the microemulsion. The formal electrode potentials (Table 1), as determined by $E^o = (E_{\text{pc}} + E_{\text{pa}}) / 2$, were more negative in the microemulsions compared to DMF.

Controlled-potential electrolyses were also carried out at potentials just beyond the reduction peak for the complex and the coulometric n value was one-electron per molecule. Hence, all the data obtained indicate that the electrode reaction is:

Overall, the electrochemistry is essentially the same as in *N,N*-dimethylformamide.

As shown in Figure 1, curve B, direct reduction of a 1.7 mM solution of the bromoester, **1a**, at a glassy carbon electrode in MTAB/tetradecane/water/1-pentanol

microemulsion at a 0.10 Vs^{-1} gives a first irreversible peak at a potential approximately -1.42 V followed by a second irreversible peak at -1.71 V . Peak potentials for the first irreversible reduction of **1a** in other microemulsions were in the range -1.42 to -1.54 V . Cyclic voltammograms for 2 mM of **1b** and **1c** at a glassy carbon electrode in different microemulsions, also showed a similar behaviour. For compound **1b** in MTAB μE , the first voltammetric peak was at -1.50 V followed by a second irreversible peak at -1.69 V , whereas for compound **1c** the corresponding first peak potential is -1.45 V followed by a second irreversible peak at -1.70 V . On the basis of our previous paper [29] where we have provided a detailed analysis of the cyclic voltammograms for the direct reduction of ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)-3-(propargyloxy)propanoate (**1a**), we attribute the first peak to the irreversible two-electron reductive cleavage of the carbon-bromine bond.

After adding **1** to the microemulsion containing $[\text{Ni}(\text{tmc})]\text{Br}_2$, catalytic reduction of **1** by electrogenerated $[\text{Ni}(\text{tmc})]^+$ is evident. Figure 1, curve C, recorded for the reduction of 1 mM $[\text{Ni}(\text{tmc})]\text{Br}_2$ in the presence of 2 mM of **1a** at a glassy carbon disc in MTAB microemulsion, shows that the cathodic peak potential, associated with the formation of $[\text{Ni}(\text{tmc})]^+$, shifts to a less negative value (*e.g.* -0.88 V) which is due to the rapid reaction of $[\text{Ni}(\text{tmc})]^+$ with **1a** and the anodic wave due to oxidation of $[\text{Ni}(\text{tmc})]^+$ back to $[\text{Ni}(\text{tmc})]^{2+}$ vanishes because of the chemical consumption of $[\text{Ni}(\text{tmc})]^+$. A cathodic postwave can also be observed which arises from the formation of $[\text{Ni}(\text{tmc})]^+$ complex unable to locate a molecule of **1a** close to the electrode surface due to depletion of **1a**. For higher concentrations of **1a**, the cathodic postwave is no longer observed. When the initial concentration of **1a** is increased to 4 and 9 mM (Figure 1, curves D and E, respectively), the cathodic peak current due to the formation of $[\text{Ni}(\text{tmc})]^+$, increases significantly with each addition of **1a**. The cause of this enhancement in the cathodic peak current is that electrogenerated $[\text{Ni}(\text{tmc})]^+$ undergoes a homogeneous reaction with **1a** close to the surface of the cathode to reform $[\text{Ni}(\text{tmc})]^{2+}$ and the catalytic cycle leading back to $[\text{Ni}(\text{tmc})]^{2+}$ is rapid. Indeed, the peak ratios suggest that the catalytic cycle in the microemulsion is rapid compared to that in *N,N*-dimethylformamide. The cyclic voltammetry experiments were repeated with **1b** and **1c** and essentially similar results were obtained in each case.

Tables 2 and 3 are a compilation of data obtained from those experiments carried out for **1a**, **1b** and **1c** in several microemulsions, where it can be concluded that the rate of the catalytic reaction increases with increasing concentration of **1** for a given mediator

concentration. The large values of the ratios, I_c/I_d , reflect the rapid overall rate of the electrocatalytic reduction of **1** mediated by $[\text{Ni}(\text{tmc})]^{2+}/[\text{Ni}(\text{tmc})]^+$. In addition, the values of I_c/I_d obtained in media containing water, i.e. in microemulsions and in ethanol/water mixtures [17] are larger than those obtained in the previous investigation in organic solvents [15,16]. Thus, the polarity of the medium may play a role in the specific catalytic activity. Similar results were also obtained in the investigation of the mediated electrochemical reduction of benzyl bromide in a bicontinuous microemulsion [10] where large values of I_c/I_d were found when compared with those obtained for the same compound in DMF.

3.2. Controlled-potential electrolysis

In the present study, controlled-potential reductions of $[\text{Ni}(\text{tmc})]^{2+}$ in the presence of various concentrations of **1** were performed at ~ -1.0 V vs Ag/AgCl in a series of microemulsions at both reticulated vitreous carbon (RVC) and carbon felt cathodes (CFC). The results of those experiments are summarised in Tables 4 - 6. Each entry is an average of at least two duplicated experiments; for every electrolysis, the current was monitored as a function of the charge passed until all of the starting material was consumed and the products were separated, identified, and quantified by gas chromatography. Product yields are tabulated as the percentage of starting material incorporated into a particular product. The current-time data were used to find the number of electrons per molecule of **1** consumed during the electrolysis.

The preparative scale controlled-potential electrolysis for **1b** and **1c** at RVC took place for only a short time before the cell current decayed to background level, and only a small amount of bromoester was consumed. In a previous investigation of the catalytic reductions of those bromoesters with electrogenerated nickel(II) complexes [16] similar rapid current decay was observed at platinum electrode and this was attributed to the formation of a passivating film on the surface of the cathode. Hence, in order to overcome this problem, the catalytic reduction of **1b** and **1c** was carried out using carbon felt cathodes instead of RVC. It was observed that the controlled-potential electrolysis occurred without cathode passivation and the current-charge curve exhibits the desired linear decay.

Gas chromatographic analysis of the electrolyzed mixtures reveals the presence of two major products 2-(3',4'-dimethoxyphenyl)-3-ethoxycarbonyl-4-methylene-tetrahydrofuran (**2a**)

and 2-(3',4'-dimethoxyphenyl-3-ethoxycarbonyl-4-methyl-2,5-dihydrofuran (**3a**) for **1a** (Eq. 1), 2-(3',4'-methylenedioxyphenyl)-3-ethoxycarbonyl-4-methylenetetrahydrofuran (**2b**) and 2-(3',4'-methylenedioxyphenyl)-3-ethoxycarbonyl-4-methyl-2,5-dihydrofuran (**2c**) for **1b** (Eq. 1) and two major products—both isomers of 2-(3',4'-dimethoxyphenyl-3-ethoxycarbonyl-4-methyltetrahydrofuran (**2c**) for **1c** (Eq.2).

Although the sum of the yields of cyclic compounds **2** - **3** accounts for less than 100% of the original starting material in some experiments, we found no evidence (*e.g.*, additional gas chromatographic peaks) for any other product. For both isomers of 2-(3',4'-dimethoxyphenyl-3-ethoxycarbonyl-4-methyltetrahydrofuran (**2c**) the yields range from 43 – 55%. It is worthwhile to compare these results with those reported by Ozaki *et al.*[30] in the study of indirect electrochemical radical cyclisation of halogeno ethers using electrogenerated nickel (I) complexes as electron-transfer catalysts. They showed that various halides cyclised preferentially *via* the 5-*exo*-trig mode in good yields to the corresponding tetrahydrofuran derivatives as sole products. They also reported that the cyclised vinyl radicals are less stable than the cyclised methyl radicals. Hence, the hydrogen abstraction from hydrogen radical donor in the medium by vinyl radicals would be higher than that by methyl radical resulting in the observed higher yields of the corresponding cyclised products. These results are similar to those obtained in the present work and again suggest the key role for radical intermediates.

The product distribution and the coulometric *n* value are not sensitive to changes in the ratio of initial concentration of **1** and of [Ni(tmc)]²⁺. Microemulsions made of cationic surfactants cetyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (MTAB) and anionic surfactant sodium dodecylsulfate (SDS) showed only small differences in product distribution of **2a:3a**, **2b:3b** and in the diastereomeric (*cis*-to-*trans*) ratio of **2c**. CTAB/dodecane/H₂O/1-pentanol, SDS/cyclohexane/H₂O/1-butanol and DDAB/dodecane/H₂O microemulsions made with hydrocarbon of different carbon chain lengths (C₁₂H₂₆ and cyclohexane) gave variable yields of both **2a:3a** and **2b:3b**. The best yields in any microemulsion seemed to be achieved with tetradecane as the hydrocarbon.

4. Discussion

It has been shown that the $[\text{Ni}(\text{tmc})]^{2+}$ mediated cyclisations of propargyl and allyl bromoesters works well in the microemulsions. The overall yields of heterocyclic products from **1** were similar in microemulsions and DMF. On the other hand, the stereoselectivity does depend on the electrolysis medium. It can be seen in Tables 4 and 5 that the intramolecular cyclisation of **1a** and **1b** in the CTAB, MTAB and SDS microemulsions leads to significantly higher ratios of **2a:3a** and **2b:3b** compared to DMF. Indeed in the microemulsions the ratio of **2:3** is generally 94:6. It may also be noted that the cyclisations occur at an acceptable current density; the adverse influence of a higher viscosity is largely offset by an increase in the rate of the catalytic cycle.

It is not the purpose of this work to investigate the mechanism of the coupled chemical reaction between $[\text{Ni}(\text{tmc})]^+$ and the alkyl halides. There is, however, substantial evidence in the literature that catalytic reductions of alkyl halides by electrogenerated nickel(I) complexes occurs *via* an inner-sphere mechanism giving rise to an alkyl-nickel intermediate which further evolution may generate alkyl radicals [26,12-17,31-46]. Moreover, all the products obtained in the microemulsions are consistent with radical intermediates. The coulometric n values ($1 < n < 1.5$) would suggest that some further reduction of radical species (either the cyclic radical intermediates in the formation of the heterocyclic products or radicals derived after H abstraction from a component in the medium) does occur. Consistent with this coulometry, all the microemulsions became basic during electrolysis. It is likely that OH^- is produced in the microemulsions containing water. Moreover, it is likely that it is the hydroxide that leads to the conversion of **2a** and **2b** to **3a** and **3b** respectively, via deprotonation of the acidic proton adjacent to the carbonyl moiety. Similar observations were described in our previous work [15, 16] carried out in organic solvents. The increased ratio of the products **2: 3** may, however, indicate that the microemulsions become less basic than the aprotic solvents during the electrolyses.

In conclusion, it has been established that catalytic electroreductive intramolecular cyclisation of bromoesters **1a**, **1b** and **1c** can afford substituted tetrahydrofurans in good yields by the use of a catalytic amount of an appropriate metal complex at ambient temperature and in an environmentally friendly procedure, which makes this procedure an attractive alternative to other synthetic methods.

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Footnotes and References

- [1] G. Long, M. E. Meek, *J. Environ. Sci. Heal.*, **2001**, *C19*, 161-187.
- [2] <http://www.npi.gov.au/>
- [3] J. Chaussard, J.C. Folest, J.Y. Nédélec, J. Périchon, S. Sibille, M. Troupel, *Synthesis* **1990**, *5*, 369-387.
- [4] J.F. Rusling, D.-L. Zhou, J. Gao, in: R.D. Weaver, F. Fisher, F.R. Kalhammer, D. Mazur (Eds), *Fundamentals and Potential Applications of Electrochemical Synthesis*, Proc. Vol. 97-6, Electrochemical Society, Pennington, New York, 1997, pp. 137-149.
- [5] J.F. Rusling, D.-L. Zhou, *J. Electroanal. Chem.* **1997**, *439*, 89–96.
- [6] M. Bourrel, R.S. Schechter, *Microemulsions and Related Systems*, Marcel Dekker, New York, 1988; J.F. Rusling, in: B.E. Conway, J.O'M. Bockris (eds.), *Modern Aspects of Electrochemistry*, pp.49-104, No. 26, Plenum, New York, 1994.
- [7] J.F. Rusling, *Mediated Electro-Organic Synthesis in Microemulsions*, in J. Texter, Ed., *Reactions and Synthesis in Surfactant Systems*, Marcel Dekker, New York, 2001, pp. 323-335.
- [8] D.L. Zhou, J. Gao, J.F. Rusling, *J. Am. Chem. Soc.* **1995**, *117*, 1127–1134.
- [9] G.N. Kamau, J.F. Rusling, *Langmuir* **1992**, *8*, 1042–1044.
- [10] D.-L. Zhou, H. Carrero, J.F. Rusling, *Langmuir* **1996**, *12*, 3067–3074.
- [11] M.O. Iwunze, N. Hu, J.F. Rusling, *J. Electroanal. Chem.* **1992**, *333*, 353-361.
- [12] E. Duñach, A. P. Esteves, A. M. Freitas, M. A. Lemos, M. J. Medeiros, S. Olivero, *Pure Appl. Chem.* **2001**, *73*, 1941–1945.
- [13] E. Duñach, A. P. Esteves, M. J. Medeiros, S. Olivero, *Tetrahedron Lett.* **2004**, *45*, 7935–7937.
- [14] E. Duñach, A. P. Esteves, M. J. Medeiros, S. Olivero, *New J. Chem.* **2005**, *29*, 633–636.
- [15] A. P. Esteves, D. M. Goken, L. J. Klein, M. A. Lemos, M. J. Medeiros, D. G. Peters, *J. Org. Chem.* **2003**, *68*, 1024–1029.

- [16] A.P. Esteves, D.M. Goken, L.J. Klein, M.J. Medeiros, D.G. Peters, *Eur. J. Org. Chem.* **2005**, 4852–4859.
- [17] E. Duñach, A. P. Esteves, M. J. Medeiros, S. Olivero, *Green Chemistry* **2006**, 8, 380–385.
- [18] A. Ceglie, K.P. Das, B. Lindman, *Colloids Surf* **1987**, 28, 29–40.
- [19] (a) M.O. Iwunze, A. Sucheta, J.F. Rusling, *Anal. Chem.* **1990**, 62, 644–649; (b) J. Georges, J.W. Chen, *Colloid Polym. Sci.* **1986**, 264, 896–902; (c) J. Georges, J.W. Chen, N. Arnaud, *Colloid Polym. Sci.* **1987**, 265, 45–51; (d) R.A. Mackey, S.A. Myers, L. Bodalbhai, A. Brajter-Toth, *Anal. Chem.* **1990**, 62, 1084–1090.
- [20] B. Bosnich, M. L. Tobe, G. A. Webb, *Inorg. Chem.* **1965**, 4, 1109–1112.
- [21] S. C. Roy, S. Adhikari, *Tetrahedron* **1993**, 49, 8415–8422.
- [22] R. McCague, R. G. Pritchard, R. J. Stoodley, D. S. Williamson, *Chem. Commun.* **1998**, 2691–2692.
- [23] K. L. Vieira, D. G. Peters, *J. Electroanal. Chem.* **1985**, 196, 93–104.
- [24] C. E. Dahm, D. G. Peters, *Anal. Chem.* **1994**, 66, 3117–3123.
- [25] J. A. Cleary, M. S. Mubarak, K. L. Vieira, M. R. Anderson, D. G. Peters, *J. Electroanal. Chem.* **1986**, 198, 107–124.
- [26] J.Y. Becker, J.B. Kerr, D. Pletcher and R. Rosas, *J. Electroanal. Chem.* **1981**, 117, 87–99.
- [27] A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980.
- [28] R. Sripriya, K.M. rajá, G. Santhosh, M. Chandrasekaran, M. Noel, *Journal of Colloid and Interface Science* **2007**, doi:10.1016/j.jcis.2007.05.080
- [29] A. P. Esteves, D. M. Goken, L. J. Klein, M. J. Medeiros, D. G. Peters, *J. Electroanal. Chem.* **2003**, 560, 161–168.
- [30] S. Ozaki, H. Matsushita, H.J. Ohmori, *J. Chem. Soc., Chem. Commun.* **1992**, 1120–1122.
- [31] K. P. Healy, D. Pletcher, *J. Organometal. Chem.* **1978**, 161, 109–120.
- [32] C. Gosden, K. P. Healy, D. Pletcher, *J. Chem. Soc., Dalton Trans.* **1978**, 972–976.
- [33] C. Gosden and D. Pletcher, *J. Organometal. Chem.* **1980**, 186, 401–409.
- [34] C. Gosden, J. B. Kerr, D. Pletcher, R. Rosas, *J. Electroanal. Chem.* **1981**, 117, 101–107.
- [35] Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, 108, 713–719.
- [36] Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, 108, 719–723.
- [37] Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, 108, 5353–5354.

- [38] Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1986**, 25, 3267–3272.
- [39] Ram, M. S.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, 25, 4115–4118.
- [40] Espenson, J. H.; Ram, M. S.; Bakac, A. *J. Am. Chem. Soc.* **1987**, 109, 6892–6893.
- [41] Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, 27, 2011–2012.
- [42] Ram, M. S.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, 27, 4231–4235.
- [43] Sadler, N.; Scott, S. L.; Bakac, A.; Espenson, J. H.; Ram, M. S. *Inorg. Chem.* **1989**, 28, 3951–3954.
- [44] M. A. Halcrow, G. Christou, *Chem. Rev.* **1994**, 94, 2421–2481.
- [45] E. Duñach, A. P. Esteves, A. M. Freitas, M. J. Medeiros, S. Olivero, *Tetrahedron Lett.* **1999**, 40, 8693–8696.
- [46] A. P. Esteves, A. M. Freitas, M. J. Medeiros, D. Pletcher, *J. Electroanal. Chem.* **2001**, 499, 95–102.

CAPTION FOR FIGURE

Figure 1. Cyclic voltammograms recorded with a glassy carbon electrode (area = 0.07cm²) at 100 mV s⁻¹ in MTAB/C₁₄H₃₀/H₂O/1-pentanol (17.5/12.5/35/35): (A) 1.0 mM [Ni(tmc)]Br₂; (B) 1.7 mM **1a**; (C) 1.0 mM [Ni(tmc)]Br₂ and 2.0 mM **1a**; (D) 1.0 mM [Ni(tmc)]Br₂ and 4.0 mM **1a**; (E) 1.0 mM [Ni(tmc)]Br₂ and 9.0 mM **1a**.

Table 1. Standard redox potentials and diffusion coefficients for [Ni(tmc)]Br₂ in several microemulsions.

FLUID (wt %)	-E° / V vs Ag/AgCl	10 ⁷ D / cm ² s ⁻¹	Viscosity / cP
DDAB ^a /C ₁₂ H ₂₆ /H ₂ O (21/40/39)	1.00	1.8 ± 1.1	—
MTAB ^b /C ₁₄ H ₃₀ /H ₂ O/1-pentanol (17.5/12.5/35/35)	0.95	3.7 ± 0.4	—
CTAB ^c / C ₁₄ H ₃₀ /H ₂ O/1-pentanol (17.5/12.5/35/35)	0.95	2.9 ± 0.7	14.12 ^e
CTAB ^c / C ₁₄ H ₃₀ /H ₂ O/1-butanol (17.5/12.5/35/35)	0.95	8.8 ± 1.4	6.56 ^e
SDS ^d / C ₁₄ H ₃₀ /H ₂ O/1-pentanol (13.3/8/52/26.7)	0.95	7.2 ± 1.2	11.77 ^e
SDS ^d /Cyclohexane/H ₂ O/1-butanol (6.5/4.5/76/13)	0.95	16.0 ± 0.6	6.59 ^e

^adidodecyltrimethylammonium bromide (DDAB); ^btetradecyltrimethylammonium bromide (MTAB);

^ccetyltrimethylammonium bromide (CTAB); ^dsodium dodecylsulfate (SDS); ^eRelative viscosity (cP) of microemulsions measured at 20 ± 0.1°C [28].

Table 2. Data of the ratio I_c/I_d obtained from the cyclic voltammetry experiments of 1.0 mM Ni(II) complexes in the presence of different concentrations of **1a in several microemulsions. Potential scan rate 0.10 V/s.**

Microemulsion (wt %)	I_c/I_d^a		
	$\gamma = 2^b$	$\gamma = 4^b$	$\gamma = 9^b$
DDAB ^a /C ₁₂ H ₂₆ /H ₂ O (21/40/39)	3.3	5.9	8.8
MTAB ^b /C ₁₄ H ₃₀ /H ₂ O/1-pentanol (17.5/12.5/35/35)	4.0	9.4	14.7
CTAB ^c /C ₁₄ H ₃₀ /H ₂ O/1-pentanol (17.5/12.5/35/35)	4.2	9.5	15.3
CTAB ^c /C ₁₄ H ₃₀ /H ₂ O/1-butanol (17.5/12.5/35/35)	2.8	6.4	10.2
SDS ^d /C ₁₄ H ₃₀ /H ₂ O/1-pentanol (13.3/8/52/26.7)	2.8	5.8	8.9
SDS ^d /Cyclohexane/H ₂ O/1-butanol (6.5/4.5/76/13)	1.4	2.8	3.7

^a I_c - catalytic peak current intensity of the catalyst in the presence of substrate and I_d - peak current intensity of the catalyst in the absence of substrate; ^b $\gamma = [RBr] / [Ni(II)]$; ^c didodecyltrimethylammonium bromide (DDAB); ^d tetradecyltrimethylammonium bromide (MTAB); ^e cetyltrimethylammonium bromide (CTAB); ^f sodium dodecylsulfate (SDS).

Table 3. Data of the ratio I_c/I_d obtained from the cyclic voltammetry experiments of 1.0 mM Ni(II) complexes in the presence of different concentrations of **1b and **1c** in several microemulsions. Potential scan rate 0.10 V/s.**

Microemulsion (wt %)	I_c/I_d^a		
	$\gamma = 2^b$	$\gamma = 5^b$	$\gamma = 10^b$
RBr = Ethyl 2-bromo-3-(3',4'-methylenedioxophenyl)-3-(propargyloxy)propanoate (1b)			
MTAB ^b /C ₁₄ H ₃₀ /H ₂ O/1-pentanol (17.5/12.5/35/35)	5.1	10.2	14.1
CTAB ^d /C ₁₄ H ₃₀ /H ₂ O/1-butanol (17.5/12.5/35/35)	3.2	6.7	10.1
SDS ^e /C ₁₄ H ₃₀ /H ₂ O/1-pentanol (13.3/8/52/26.7)	2.7	6.0	8.3
RBr = Ethyl 2-bromo-3-(3',4'-dimethoxyphenyl)-3-(allyloxy)propanoate (1c)			
MTAB ^b /C ₁₄ H ₃₀ /H ₂ O/1-pentanol (17.5/12.5/35/35)	4.3	7.4	13.7
CTAB ^d /C ₁₄ H ₃₀ /H ₂ O/1-butanol (17.5/12.5/35/35)	3.0	6.6	10.1
SDS ^e /C ₁₄ H ₃₀ /H ₂ O/1-pentanol (13.3/8/52/26.7)	2.7	6.1	11.8

^a I_c - catalytic peak current intensity of the catalyst in the presence of substrate and I_d - peak current intensity of the catalyst in the absence of substrate; ^b $\gamma = [RBr] / [Ni(II)]$; ^c tetradecyltrimethylammonium bromide (MTAB); ^d cetyltrimethylammonium bromide (CTAB); ^e sodium dodecylsulfate (SDS).

Table 4. Coulometric data and product yields for catalytic reduction of 1a by [Ni(tmc)]⁺ electrogenerated at reticulated vitreous carbon cathodes in several microemulsions.

Entry	[Ni(tmc)] ²⁺ , mM	[<u>1b</u>], mM	Time, h ^[a]	η ^[b]	Products (ratio)	Yields of cyclized products (%) ^[c]
MTAB/Tetradecane/H₂O/1-Pentanol (17.5/12.5/35/35)						
1	1.0	1.8	0.5	1.2	<u>2a,3a</u> (96:4)	97
2	0.4	1.8	2.0	1.3	<u>2a,3a</u> (93:7)	96
3	0.3	2.6	4.0	1.1	<u>2a,3a</u> (94:6)	94
CTAB/Tetradecane/H₂O/1-pentanol (17.5/12.5/35/35)						
4	0.4	1.8	1.0	1.2	<u>2a,3a</u> (99:1)	100
5	0.3	2.3	4.0	1.2	<u>2a,3a</u> (89:11)	96
CTAB/Tetradecane/H₂O/1-butanol (17.5/12.5/35/35)						
6	0.4	1.8	1.0	1.2	<u>2a,3a</u> 97:3	96
7	0.3	2.3	5.0	1.2	<u>2a,3a</u> 92:8	96
CTAB/Dodecane/H₂O/1-pentanol (17.5/12.5/35/35)						
8	0.4	1.7	1.0	1.2	<u>2a,3a</u> 97:3	67
9	0.3	2.3	4.0	1.2	<u>2a,3a</u> 88:12	68
SDS/Tetradecane/H₂O/1-pentanol (13.3/8/52/26.7)						
10	0.4	1.8	1.0	1.2	<u>2a,3a</u> 99:1	99
11	0.3	2.3	4.0	1.2	<u>2a,3a</u> 99:1	92
SDS/Cyclohexane/H₂O/1-butanol (6.5/4.5/76/13)						
12	0.4	1.8	0.5	1.2	<u>2a,3a</u> (98:2)	100
13	0.3	0.3	0.5	1.2	<u>2a,3a</u> (98:2)	83
DDAB/Dodecane/H₂O (21/40/39)						
14	0.4	1.8	1.0	1.5	<u>2a,3a</u> (88:12)	33

^[a] Time of electrolysis. ^[b]Number of electrons per molecule of starting material. ^[c] % = yield expressed as the percentage of **1** incorporated into each product.

Table 5. Coulometric data and product yields for catalytic reduction of **1b by [Ni(tmc)]⁺ electrogenerated at graphite felt cathodes in several microemulsions.**

Entry	[Ni(tmc)] ²⁺ , mM	[1b], mM	Time, h ^[a]	<i>n</i> ^[b]	Products (ratio)	Yields of cyclized products (%) ^[c]
MTAB/Tetradecane/H₂O/1-Pentanol (17.5/12.5/35/35)						
1	0.4	2.0	0.5	1.2	2b,3b (83:17)	90
2	0.26	2.5	0.7	1.2	2b,3b (69:31)	83
CTAB/Tetradecane/H₂O/1-butanol (17.5/12.5/35/35)						
3	0.4	1.9	1.0	1.0	2b,3b (99:1)	99
4	0.26	2.5	2.0	1.2	2b,3b (86:14)	101
CTAB/Dodecane/H₂O/1-pentanol (17.5/12.5/35/35)						
7	0.4	1.9	1.0	1.2	2b,3b (88:12)	95
8	0.26	2.5	2.0	1.3	2b,3b (76:24)	78
SDS/Tetradecane/H₂O/1-pentanol (13.3/8/52/26.7)						
9	0.4	2.0	0.4	1.0	2b,3b (98:2)	101
10	0.27	2.7	0.4	1.2	2b,3b (97:3)	100

^[a] Time of electrolysis. ^[b]Number of electrons per molecule of starting material. ^[c] % = yield expressed as the percentage of **1** incorporated into each product.

Table 6. Coulometric data and product yields for catalytic reduction of 1c by [Ni(tmc)]⁺ electrogenerated at graphite felt cathodes in several microemulsions.

Entry	[Ni(tmc)] ²⁺ , mM	[<u>1c</u>], mM	Time, h ^[a]	<i>n</i> ^[b]	Product (d.r.) ^[c]	Yields of cyclized products (%) ^[d]
MTAB/Tetradecane/H₂O/1-Pentanol (17.5/12.5/35/35)						
1	0.39	1.9	0.5	1.3	<u>2c</u> (7:93)	55
2	0.25	2.6	0.4	1.5	<u>2c</u> (7:93)	51
CTAB/Tetradecane/H₂O/1-pentanol (17.5/12.5/35/35)						
3	0.38	1.9	0.3	1.2	<u>2c</u> (7:93)	43
4	0.26	2.5	0.5	1.2	<u>2c</u> (7:93)	54
CTAB/Dodecane/H₂O/1-pentanol (17.5/12.5/35/35)						
5	0.26	2.6	1.0	1.5	<u>2c</u> (7:93)	45
SDS/Tetradecane/H₂O/1-pentanol (13.3/8/52/26.7)						
6	0.39	1.9	0.3	1.5	<u>2c</u> (7:93)	47
7	0.26	2.5	0.5	1.3	<u>2c</u> (7:93)	52

^[a] Time of electrolysis. ^[b] Number of electrons per molecule of starting material. ^[c] diastereomeric (*cis*-to-*trans*) ratio. ^[d] % = yield expressed as the percentage of 1 incorporated into each product.

Figure 1