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LETTERS

Electroreductive cyclisation of unsaturated halides catalysed by nickel macrocyclic complexes

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Abstract

The indirect electroreduction of unsaturated aliphatic halides using Ni(II) complexes as electron-transfer mediators is achieved in *N,N'*-dimethylformamide by constant current electrolysis between a cathode and a sacrificial anode in a diaphragmless cell. Cyclic compounds are obtained in low to high yields in conditions that avoid the usual preparation using organotin reagents. © 1999 Elsevier Science Ltd. All rights reserved.

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Radical cyclisation is emerging as one of the leading methods for the construction of cyclic systems.[1] While organotin reagents have dominated synthetic procedures involving radical chemistry over the last decade,[1] problems associated with product purification, price and toxicity have stimulated interest in the development of more user- and environmentally-friendly reagents. A convenient alternative to the tin hydride method can be the indirect electroreduction of halides using nickel[2,3] complexes as the electron transfer catalysts. In order to appreciate the synthetic scope and limits of this methodology, we investigated the cyclisation reaction of (*R*)-(−)-citronellyl bromide **1** and 6-bromo-1-hexene **2** using macrocyclic Ni(II) complexes **3–6**.

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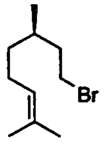

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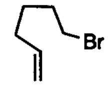

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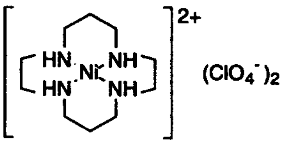

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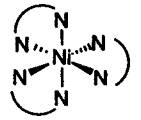
$E_e^\circ = -1.36$ V (*vs* Ag/AgCl)



NN=2,2'-bipyridyl

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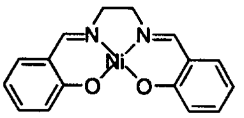
$E_e^\circ = -1.20$ V (*vs* Ag/AgCl)



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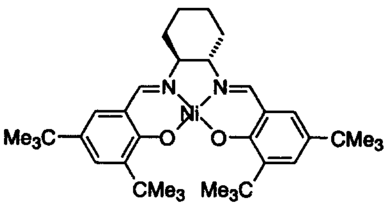
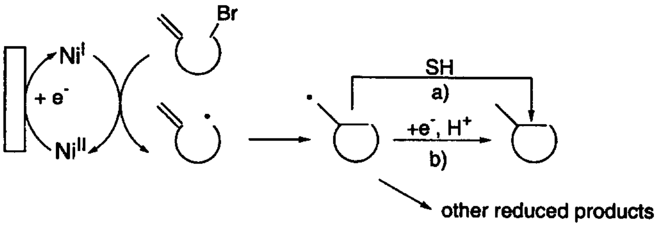
$E_e^\circ = -1.57$ V (*vs* Ag/AgCl)



6 $E_e^\circ = -1.77$ V (*vs* Ag/AgCl)

Cyclic voltammetric studies established that electrochemical reduction of Ni(II) complexes and further electron-transfer from electrogenerated Ni(I) complexes to unsaturated halides occurs[2] according to Scheme 1. None of the halides was reduced at potentials below –2.60 V.



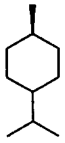
Scheme 1.

The electrolyses were carried out at constant current,[†] in DMF, in a specially designed single-compartment cell, fitted with a consumable sacrificial anode. The study was initiated by carrying out the electrolysis of **1** in DMF and in the presence of $[Ni(cyclam)](ClO_4)_2$ **3** using a sacrificial magnesium anode and a carbon fibre cathode and comparing the results when phenol was added as H-donor. In the absence of phenol the expected cyclised product, *p*-menthane (*cis* and *trans*) **7**, was obtained in 53% yield along with 2,6-dimethyl-2-octene **8** in 20% yield (Table 1, entry 1). Dimers[5] were also identified (GC and GC–MS) in 23% yield but the structures are not yet fully established. When this reaction was performed in the same experimental conditions but in the presence of phenol (2×10^{-3} mol) which has been used as an effective H-donor,[6] 2,6-dimethyl-2-octene was produced (64%) as the main product together with a minor amount of cyclised product (24%) (Table 1, entry 2). Therefore, further experiments were conducted in the absence of phenol. Under the same conditions, bromide **2** produced the cyclised product, methylcyclopentane **9**, in 46% yield (Table 1, entry 8). No reduced acyclic product was detected and only dimers (54%) were obtained as by-products.

[†] Typical electrolysis procedure: in a single-compartment cell,[4] with an Mg rod as the sacrificial anode (diameter 1 cm) and a carbon fibre cathode (apparent surface, 20 cm^2) were introduced freshly distilled DMF (50 cm^3), $n\text{-}Bu_4N^+BF_4^-$ (3×10^{-4} mol), $[Ni(cyclam)](ClO_4)_2$, (1×10^{-4} mol) and halide **1** (1×10^{-3} mol). The solution was electrolysed at room temperature, at a constant current of 60 mA until disappearance of **1** (according to GC analysis, 2–3 h). The reaction mixture was hydrolysed with 0.1 M HCl (50 cm^3), extracted with Et_2O and washed with H_2O. The dried ($MgSO_4$) organic layer was evaporated and the residue analysed by GC, GC–MS and ^1H NMR, in comparison with those of authentic samples.

Table 1
Electrochemical intramolecular cyclisation of citronellyl bromide **1** and 6-bromo-1-hexene **2** by electrogenerated Ni(I) complex in DMF containing 0.006 M tetrabutylammonium tetrafluoroborate

	Cathode	Anode	Ni^{II} L	Products (%)	
RBr = Citronellyl bromide 1				*p*-Menthane (*trans* :*cis*) 7	2,6-Dimethyl-2-octene 8
1	Carbon fibre	Magnesium	3	53 (1:0.8)	20
2	Carbon fibre	Magnesium	3	24 (1:0.7)	64
3	Carbon fibre	Zinc	3	55 (1:0.9)	24
4	Ni (foam)	Magnesium	3	13 (1:0.9)	83
5	Carbon fibre	Magnesium	4	7 (1:0.4)	21
6	Carbon fibre	Magnesium	5	27 (1:0.6)	46
7	Carbon fibre	Magnesium	6	65 (1:0.4)	13
RBr = 6-Bromo-1-hexene 2				Methylcyclopentane 9	1-hexene 10
8	Carbon fibre	Magnesium	3	46	-
9	Carbon fibre	Magnesium	5	40	38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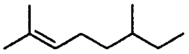
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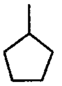
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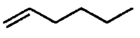
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The influence of the nature of the anode was explored next. It was observed that the change of anode from magnesium to zinc had a minor effect on product yields (Table 1, entry 3). The use of a nickel foam cathode[7] in conjunction with a magnesium anode led, for the electrolysis of **1**, to the acyclic product **8**, as the major compound, in 83% yield, with a small amount of the cyclised product **7** (13%) (Table 1, entry 4). These results show that the radical cyclisation of citronellyl bromide is strongly affected by the nature of the cathode material and a carbon fibre cathode seems to be much more effective than the nickel foam electrode. After this preliminary study, the experimental conditions were optimised and the electrolyses were all conducted in DMF, with a magnesium anode and a carbon fibre cathode.

The influence of the nature of the ligand in the reaction selectivity was also investigated. Thus, the electrolysis of **1** in the presence of $Ni(bipy)_3(BF_4)_2$ **4** afforded the cyclised product only in 7% yield together with the dehalogenation product **8** (21%) (Table 1, entry 5) and dimerisation products (64%). These results demonstrate that the $Ni(bipy)_3{}^{2+}$ system efficiently catalyses the cleavage of the halide bond but inhibits the formation of the cyclised product.[8] The electroreduction of **1** was also performed in the presence of Ni(salen) **5** as the catalytic system. Data on product yields is collected in Table 1 (entry 6) and show that the Ni(salen) catalyst also inhibits the formation of the cyclised product as $Ni(bipy)_3{}^{2+}$ system does. In accordance with the previous results and in comparison with the reaction with $[Ni(cyclam)](ClO_4)_2$ the reaction of bromide **2** with Ni(salen) produced the acyclic product in higher yield (38%) (Table 1, entry 9). However, in this case the cyclised product **9** was also formed in 40% yield (Table 1, entry 9).

An efficient electrochemical asymmetric epoxidation of olefins catalysed by a chiral Mn(III)(salen)-type complex (Jacobsen's ligand) has been reported.[9] We prepared a novel catalytic system consisting of a chiral Ni(II)(salen) complex of structure **6**. Unexpectedly, and in contrast to the related complex **5**, the chiral complex **6** revealed to be the most efficient for the catalysis of the intramolecular cyclisation reaction of **1**. Using the same experimental conditions, the cyclised product **7** was obtained in 65% yield (Table 1, entry 7). The minor products were the acyclic product **8** (13%) and dimers (10%). Most probably this more efficient cyclisation is due to the fact that the intermediate radical species might have a longer life due to the bulkiness of complex **6** in comparison with **5**. This steric protection promotes cyclisation in detriment of dimerisation or addition of hydrogen.

The isolation of *p*-menthane by the conventional tin hydride method was hampered by purification problems but other indirect methods[10] can provide the cyclised product in approximately 1:1 *trans*:*cis* ratio.

In conclusion, the nature of the ligand on nickel can strongly influence the reactivity and the selectivity of the electrochemical reaction. The above study demonstrates the preparative interest of the electroreductive catalytic cyclisation of unsaturated halides using consumable anodes and $\mathrm{Ni^{II}(L)}$ complexes. The electrochemical behaviour of model substrates such as **1** and **2** provide an example of the feasibility of exerting control and adjust the reactivity by varying the ligand environment in the catalytic system. Moreover, the electrochemical method enables the reactions to be catalytic in nickel complex and the use of mild experimental conditions operating at room temperature.

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