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Electrochemical intramolecular cyclisation of propargyl bromoethers catalysed by nickel complexes

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The electrochemical intramolecular cyclisation of propargyl 2-bromoethers **1–3** in *N*,*N*′-dimethylformamide at constant current in a diaphragmless cell has been developed using Ni^{II} complexes as electron-transfer mediators. During controlled-current electrolyses of solutions of Ni^{II} complexes in the presence of bromoethers, catalytic reduction of the latter proceeds *via* one-electron cleavage of the carbon–bromine bond to form a radical intermediate that undergoes cyclisation to afford the cyclic compounds in moderate to good yields.

Introduction

The radical methodology has emerged as one of the leading methods in synthetic organic chemistry for the construction of complex carbocyclic as well as heterocyclic compounds.[1] The versatility of this technology has aroused great interest in developing novel reagents and procedures for the generation of radicals. In addition to various synthetic methods, electrochemical radical-type cyclisations catalysed by transition metal complexes have been studied. This process is based on an EC′ mechanism:

$$Ni^{II}L + e^- \rightleftharpoons Ni^{I}L \qquad (1)$$

$$Ni^{I}L + RBr \xrightarrow{k_{cat}} Ni^{II}L + \text{products} \qquad (2)$$

in which $Ni^{II}L$, with a reduction potential less negative than the substrate (RBr), is reduced at the electrode. The reduced mediator diffuses into the solution and reduces the substrate. The catalytic reaction recycles the mediator back to the electrode according to the kinetics of the system and the relative concentration of the substrate and the mediator (called the excess factor, $\gamma = [RBr]/[Ni^{II}L]$).[2]

Several reports on the electrogenerated Ni^{I} catalysed indirect reductive radical cyclisation of various organic halides,[3] bromoacetals possessing electron-deficient olefinic moieties,[4] and 2-haloaryl ethers containing unsaturated side chains[5] have shown that the electrochemical method is an expedient alternative to the use of organometallic reagents. This nickel-mediated radical cyclisation has also been applied to the synthesis of substituted tetrahydrofurans;[6–11] the furofuran moiety is an important subunit in a wide range of biologically active natural products.[12–13] Mubarak and Peters[6] have shown that reductive intramolecular cyclisation of 6-iodo- and 6-bromo-1-phenyl-1-hexyne, catalysed by electrogenerated nickel(I) salen, leads to the production of benzylidenecyclopentane in 64–95% yield. More recently, the nickel(I) salen catalysed reduction of 6-bromo-1-hexene has been shown to entail cleavage of the carbon–bromine bond to give the 5-hexen-l-yl radical, which undergoes intramolecular cyclisation to form methylcyclopentane, as well as give dimeric species arising from coupling of both cyclic and acyclic radicals.[7] In our previous investigations of radical cyclisation reactions promoted by electrogenerated nickel(I) complexes[8–11] it was reported that electrogenerated nickel(I) complexes catalyse the intramolecular cyclisation of unsaturated halides to yield alkenyl radical type intermediates, which can react intramolecularly to give carbocyclic products.

In our previous work, we reported the electrochemical studies of intramolecular cyclisation of ethyl 2-bromo-3-(3′,4′-methylenedioxophenyl)-3-propargyloxypropanoate and ethyl 2-bromo-3-(3′,4′-dimethoxyphenyl)-3-allyloxypropanoate catalysed by the macrocyclic Ni(II) complexes **4–6**, shown in Scheme 1.[14] It was demonstrated that the electroreduction reaction of bromopropargyl and allyl esters (Scheme 2) carried out in DMF in a single-compartment cell was catalysed by the Ni(I) complexes electrogenerated from **4–6**. Only cyclisation to the five-membered ring ethers as the main products was observed, in moderate to good yields. This encouraged us to undertake further studies on analogues and derivatives of bromopropargyl esters as substrates.

Following this approach, we have investigated the use of electrogenerated nickel(I) complexes for the catalytic reduction of three propargyl bromoethers {[1-bromo-2-methoxy-2-(prop-2′-ynyloxy)ethyl]benzene (**1**), 1-[2-bromo-2-phenyl-1-(prop-2′-ynyloxy)ethyl]-4-methoxybenzene (**2**), and 2-bromo-3-(3′,4′-dimethoxyphenyl)-3-propargyloxy-propanamide (**3**)} in dimethylformamide (DMF) containing tetraalkylammonium salts. Apart from being environmentally less aggressive, this technique makes the purification of the products much easier.

Experimental

Methods and materials

Published procedures were employed for the preparation of $[Ni(tmc)]Br_2$,[15] $[Ni(cyclam)](ClO_4)_2$,[15] $[Ni(CR)]Cl_2$,[16] **1**,[17] **2**,[18] and **3**.[18] Synthesis of 2-methoxy-4-methylene-3-phenyltetrahydrofuran (**7**), 2-(4′-methoxyphenyl)-4-methylene-3-phenyltetra-

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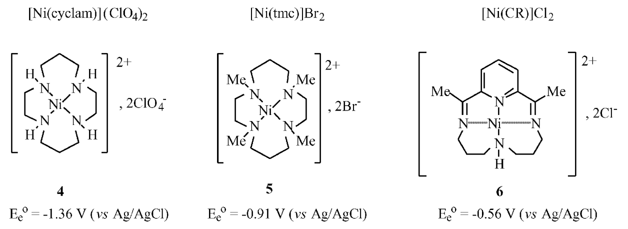


Scheme 1

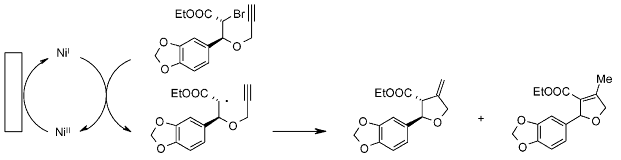
hydrofuran (**9**) and 2-(3′4′-dimethoxyphenyl)-3-carbamoyl-4-methylenetetrahydrofuran (**11**) was based on the method published by McCague *et al.*[19]

We identified the compounds by means of ^{1}H NMR spectrometry with a Varian Unity Plus 300-MHz instrument ($CDCl_3$). **7**: δ 3.41 (3H, s, OCH_3); 3.81 (1H, br s, 3-H); 4.61 (2H, app q, J 2.0 Hz, 5-H_2); 4.99 (1H, app q, J 2.0 Hz, C=CH*H*); 5.02 (1H, br s, 2-H); 5.12 (1H, app q, J 2.0 Hz, C=C*H*H); 7.20–7.40 (5H, m, C_6H_5); **9**: δ 3.64–3.70 (1H, m, 3-H); 3.78 (3H, s, OCH_3); 4.66 (1H, dq, J 13.2 and 2.4 Hz, 5-H_a); 4.72 (1H, app q, J 2.4 Hz, C=C*H*H); 4.79 (1H, d, J 9.3 Hz, 2-H); 4.84 (1H, br d, J 13.2 Hz, 5-H_b); 5.09 (1H, app q, J 2.1 Hz, C=CH*H*); 6.81 (2H, app d, J 8.5 Hz, 2′-H and 6′-H); 7.14 (2H, app d, J 8.5 Hz, 3′-H and 5′-H); 7.22–7.34 (5H, m, Ph); **11**: δ 3.38 (1H, br app dd, J 7.2 and 1.8 Hz, 3-H); 3.88 (3H, s, OCH_3); 3.89 (3H, s, OCH_3); 4.54 (1H, app dq, J 13.2 and 2.4 Hz, 5-H_a); 4.63 (1H, br app d, J 13.2 Hz, 5-H_b); 5.19 (1H, app q; J 2.4 Hz, C=CH*H*); 5.20 (1H, d, J 6.9 Hz, 2-H); 5.22 (1H, app q, J 2.4 Hz, C=C*H*H); 5.66 (1H, br s, NH); 5.73 (1H, br s, NH); 6.82–6.95 (3H, m, 2′-H, 5′-H and 6′-H).

Identities of the electrolysis products were confirmed by means of a Hewlett–Packard 5890 Series II gas chromatograph coupled to a Hewlett–Packard 5971 mass-selective detector. **7**: m/z (70 eV) 290, M^+ (0.5); 159, $[M-CH_3O]^+$ (8); 129, $[M-CH_3OCHOH]^+$ (100); 91, $[C_6H_5CH_2]^+$ (32); 77, $[M-C_6H_5]^+$ (11); **8**: m/z (70 eV) 158, M^+ (100); 129, $[M-CHO]^+$ (65); 77, $[C_6H_5]^+$ (17); **9**: m/z (70 eV) 266, M^+ (10); 129, $[M-CH_3OC_6H_4CHOH]^+$ (100); 91, $[C_6H_5CH_2]^+$ (8); 77, $[C_6H_5]^+$ (18); **10**: m/z (70 eV) 210, M^+ (100); 115, $[C_6H_5C_3H_2]^+$ (10); 89, $[C_6H_5C]^+$ (10); **11**: m/z (70 eV) 263, M^+ (73); 218, $[M-H_2NCOH]^+$ (65); 165, $[(CH_3O)_2C_6H_3CO]^+$ (100); 77, $[C_6H_5]^+$ (38).

Electrochemical cells and instrumentation

The constant-current electrolyses were carried out in a single-compartment cell (capacity 50 ml), such as described in ref. 19, with a Zn, Al or Mg rod as the sacrificial anode (diameter 1 cm) and a carbon felt cathode (apparent surface, 20 cm^2), which was formed into a cylinder around the counter electrode. Freshly distilled DMF (50 ml), n-Bu_4NBF_4 (6×10^{-3} M), $Ni^{II}L$ (2.0×10^{-3} M) and bromoether (2.0×10^{-2} M) were introduced in the cell under argon flow. The solution was stirred and electrolysed at room temperature, at a constant current of 30 mA (current density of 1.5 mA cm^{-2} and 2–5 V between the rod anode and the carbon felt cathode) until complete disappearance of the bromoether (checked by GC analysis of aliquots). Generally, 4–6 F mol^{-1} of starting material were necessary to achieve a complete conversion. The excess of electricity is accounted for mainly by the presence of a Zn anode, which can be easily oxidised and further reduced.



Scheme 2

Controlled-current electrolyses were carried out with the aid of a stabilised constant-current supply (Sodilec, EDL 36.07).

Identification and quantification of products

The DMF solvent was evaporated under vacuum, the reaction mixture was hydrolysed with 0.1 M HCl saturated with NaCl, up to pH 1–2, extracted with CH_2Cl_2 and washed with H_2O. The dried ($MgSO_4$) organic layer was evaporated and the residue analysed by GC, GC-MS and ^{1}H NMR. The crude residue was submitted to flash chromatography over silica gel (230–400 mesh) using diethyl ether–light petroleum 1 : 2 (for **7**), diethyl ether–light petroleum 1 : 3 (for **9**) and ethyl acetate–methanol 13 : 1 (for **11**) as eluants. The ^{1}H NMR spectra of different fractions collected were compared to those of authentic samples.

Results and discussion

The use of sacrificial anodes has enabled new and efficient processes in electrosynthetic reactions.[20] The cationic nickel complexes **4–6** (Scheme 1), having shown an efficient catalytic activity for the electrochemical cleavage of carbon–bromine bond of unsaturated halides,[8–11,14] were used as the catalysts in the current work. The catalytic electroreduction of propargyl bromoethers **1–3** by electrogenerated nickel(I) complexes was performed at constant current and the results are summarised in Table 1.

Cyclic voltammetric studies established that the formal electrode potential of Ni(II) complexes **4–6** occurred at −1.36, −0.91 and −0.56 V *vs.* Ag/AgCl, 3 M KCl, respectively,[9,11] with further electron transfer from the electrogenerated Ni(I) complexes to the bromoethers, according to eqns. (3)–(5) below. Cyclic voltammetric studies of solutions of bromoethers **1–3** in *N*,*N*′-dimethylformamide containing 0.1 M n-Bu_4NBF_4 at a glassy carbon electrode show two well-defined reduction peaks at potentials −1.78 and −2.84 V *vs.* Ag /AgCl for compound **1**, three well-defined reduction peaks at potentials −1.65, −2.23 and −2.49 V *vs.* Ag/AgCl for compound **2** and three well-defined reduction peaks at potentials −1.73, −2.01 and −2.25 V *vs.* Ag/AgCl for compound **3**. We attribute the first reduction peak to the irreversible reduction cleavage of the carbon–bromine bond. When voltammetric curves were reported for complexes **4–6** in the presence of bromoethers **1–3**, the reversible 1-electron reduction peak of

Table 1 Electrochemical intramolecular cyclisation[a] of propargyl ethers**1–3** catalysed by complexes **4–6**

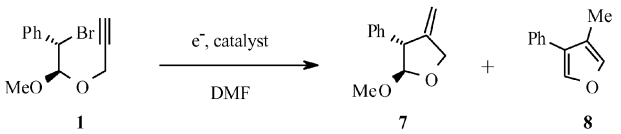
Entry	Substrate	Catalyst	Anode	Products (ratio)	% Yield of cyclised products
1	**1**	**4**	Mg	**7**, **8** (56 : 44)	63
2	**1**	**4**	Zn	**7**	48
3	**1**	**5**	Zn	**7**, **8** (64 : 36)	89
4	**1**	**6**	Zn	**7**	49
5	**1**	**5**	Al	**7**	52
6[b]	**1**	**5**	Zn	**7**, **8** (50 : 50)	100
7[c]	**1**	**5**	Zn	**7**	36
8	**2**	**5**	Al	**9**	35
9	**2**	**5**	Zn	**9**	76
10	**2**	**4**	Zn	**9**	49
11[b]	**2**	**5**	Zn	**9**	98
12	**3**	**5**	Al	**11**	13
13	**3**	**5**	Zn	**11**	83
14[b]	**3**	**5**	Zn	**11**	76

[a] Conditions: 10 mM of **1–3**; 20 mol % of **4–6**; carbon fibre cathode in DMF containing 0.006 M of Bu_4NBF_4; j = 0.15 A dm^{-2}. [b] [RBr]/[Ni(II)] = 10. [c] Cathode = Zn.

the Ni complexes became irreversible and the reduction peak increased in height.[9,11]

Experimental parameters such as the ratio of bromoethers to catalyst, the influence of the nature of the electrodes and the nature of the ligand of the catalyst were examined in order to evaluate their effect on the product distribution.

The study was initiated by carrying out the electrolysis of **1** in DMF with Mg/C couple electrodes [eqn. (3)] in the presence of [Ni(cyclam)](ClO_4)$_2$] (**4**, 20 mol %; cyclam = 1,4,8,11-tetraazacyclotetradecane). Hence, the electrolysis of **1** led to the expected cyclised product **7** as the main product in 35% yield, along with the furan derivative **8** in 28% yield (Table 1, entry 1). These results are in agreement with those reported by Olivero *et al.*[21] under the same experimental conditions where intramolecular cyclisation of propargyl 2-bromophenyl ethers led to the cyclic furan derivatives in moderate yields (31–32%). Compound **8** is probably obtained from compound **7** *via* an Ec1B mechanism where a carbanion (resulting from deprotonation and possessing a poor leaving group) is stabilised by resonance,[22] followed by a [1,3] sigmatropic rearrangement. This process affords the aromatic compound **8**, which is particularly stable.



(3)

No reaction occurred in the absence of current; in the absence of the nickel catalyst a mixture of cyclic and acyclic products was formed. The presence of the nickel complex as the catalytic system seems essential to control the selectivity of the process. Similar results were obtained in our previous investigation on the direct electrochemical reduction of a bromo propargyloxy ester at vitreous carbon cathodes in DMF;[23] the results corresponded to an anionic nature of the intermediates, also proposed in other electrochemical dehalogenation processes.[24]

The influence of the nature of the anode on the electroreduction of **1** was examined. When this reaction was performed under the same experimental conditions but in the presence of a zinc anode the cyclised compound **7** was formed as the major product in 48% yield (entry 2).

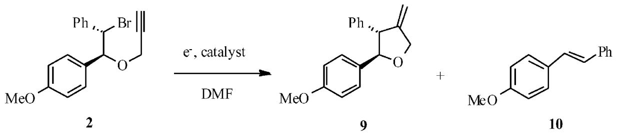
The influence of the nature of the ligand on the reaction selectivity was also investigated in reactions using a Zn/C couple of electrodes in DMF. Hence, when [Ni(tmc)]Br_2 (**5**; tmc = 1,4,8,11-tetramethylcyclam) was used as the catalyst, the electrolysis of **1** afforded the expected cyclised product **7** in 57% yield along with 32% of **8** (entry 3). The electroreduction of **1** was also performed in the presence of [Ni(CR)]Cl_2 (**6**) as the catalytic system; the electrolysis gave rise to the formation of **7** in 49% (entry 4). These results indicate that all the tested Ni(II) complexes having macrocyclic ligands efficiently catalyse the cyclisation of **1**. The process involves a selective radical-type reactivity of the reduced carbon–halogen bond of the substrate and enables the cyclisation with exclusive formation of 5-membered heterocyclic rings. Ozaki *et al.*[25] in the study of indirect electrochemical radical cyclisation of halogeno ethers using nickel(II) complexes as electron-transfer catalysts, showed that various halides cyclised preferentially *via* the 5-*exo*-trig mode to the corresponding tetrahydrofuran derivatives as sole products in good yields. These results are similar to those obtained in the present work.

The nature of the anode was also investigated in reactions using a carbon fibre cathode and in the presence of [Ni(tmc)]Br_2 as the catalytic system. It was observed that the change of the anode from zinc to aluminium had a strong effect on the product yields (entry 5).

Next, the influence of the ratio of the concentration of the bromoether and that of the catalyst was examined. No significant change was observed for the yield of the cyclised product **7** when the catalyst concentration was decreased from 20% to 10% (entry 6).

Finally, the influence of the cathode nature was also studied using a zinc anode and it was observed that the use of a zinc cathode led, for the electrolysis of **1**, to the formation of **7** in 36% yield (entry 7). These results indicated that the radical-type cyclisation of **1** could be affected by the nature of the cathode electrode. Thus, a carbon fibre cathode seemed to be more effective compared to a zinc electrode. The same phenomenon was observed in a previous investigation in our laboratory in the study of the intramolecular cyclisation of propargyl derivatives by electrogenerated nickel(I) complexes.[10]

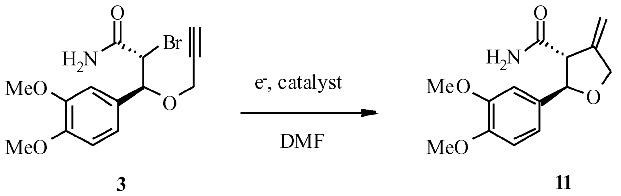
The electroreduction of propargyl bromoether **2** by the nickel(I) complex electrogenerated from **5** at a carbon fibre cathode using a sacrificial aluminium anode was also carried out [eqn. (4)].



(4)

The reaction proceeded through the cleavage of the carbon–bromine bond to afford the cyclic ether **9** in 35% yield together with the alkene **10** in 47% yield (entry 8). Compound **10** can issue from a two-electron reduction of **2** and a further elimination of the propargylic moiety. The latter process is commonly encountered as part of the so-called E1cB mechanism.[22] The influence of the nature of the anode was examined using a carbon fibre cathode and the electrolysis of **2** with a Zn anode led to the formation of **9** in 76% yield (entry 9). These results indicate that the cyclisation of **2** is strongly affected by the nature of the anode material. Using Zn/C couple electrodes with complex **4**, the electrolysis of **2** afforded cyclised **9** in 49% yield as the main product (entry 10), along with 18% of alkene **10**. These results demonstrate that the [Ni(cyclam)](ClO_4)$_2$ system catalyses the cyclisation of **2** but also the cleavage of the propargyl carbon–oxygen bond. Hence, when [Ni(tmc)]Br_2 is used as the catalyst precursor in the electrolysis of **2**, the process involves a more selective radical-type reactivity of the reduced carbon–halogen bond of the substrate, and enables a more selective formation of 5-membered heterocycles. Finally, the reaction was performed under the same experimental conditions but in the presence of 10 mol % of catalyst **5** with respect to the concentration of the bromoether **2**. The cyclised compound **9** was obtained in 98% yield as the only product of the reaction (entry 11). This result is in agreement with that presented above (entry 6) and shows that the ratio [RBr]/[Ni(II)] does not influence the reaction mechanism.

The electroreduction of **3** was also performed in the presence of **5** as the catalyst using Al/C couple of electrodes [eqn. (5)] and the cyclic compound **11** was obtained in 13% yield (entry 12).



(5)

The influence of the nature of the anode on this reaction was studied: the change from an aluminium to a zinc anode led to the formation of cyclic compound **11** in 83% yield (entry 13). Here again, the nature of the anode material strongly influenced the results, as was observed with bromoether **1** (entries 3 and 5) and bromoether **2** (entries 8 and 9). Similar results were obtained in a previous investigation in our laboratory in the study of the intramolecular cyclisation of bromo propargyl and allyl derivatives by electrogenerated nickel(I) complexes.[10,14] Interestingly, the role of the sacrificial anode was found to be important in this electroreduction, as in the present work. Moreover, it was also demonstrated that, under comparable experimental conditions, the unsaturated α-bromoesters cyclise *via* the *exo* mode to a five-membered ring to give the corresponding tetrahydrofuran derivatives as the main products. When the amount of catalyst was decreased from 20% to 10% the yield of the cyclic compound **11** was 76% (entry 14). Again, this result is in agreement with those presented above (entries 6 and 11) and shows that the change in the yield of cylised product **11** is not significant when the catalyst concentration decreases.

In summary, an effort has been done to extend the scope of the work on nickel-catalysed electrochemical reactions, by further developing the intramolecular cyclisation of bromoethers **1–3** catalysed by Ni^{II} complexes. $[Ni(cyclam)](ClO_4)_2$, $[Ni(tmc)]Br_2$ and $[Ni(CR)]Cl_2$ have been used as the catalyst precursors. The nature of the organometallic catalytic system and, particularly, of the ligand on nickel can strongly determine the reactivity, the selectivity, and the mechanism of the electrochemical reaction. The presence of Zn^{2+}, Mg^{2+} and Al^{3+} ions during the electrolyses displays an important effect in controlling the reactivity and the selectivity of the system. Thus, it seems that from the results presented in this work, the $[Ni(tmc)]Br_2$ system is the best catalyst, zinc is the best anode material and the ratio [RBr]/[Ni(II)] has no effect on the reaction mechanism.

This investigation provides an example of the feasibility of electrochemical radical-type cyclisations involving propargyl derivatives. Good yields were obtained by a careful control of the parameters mentioned above. Moreover, this method is practical since it can be conducted by the use of catalytic amounts of metal complexes such as **4–6** at ambient temperature.

Acknowledgements

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