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Electrochemical Study of Nickel(salen) and Cobalt(salen) Derivative Complexes in the Presence of Unsaturated Halides

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Abstract

The electrochemical intramolecular cyclisation of allyl 2-bromophenyl ethers in *N,N*'-dimethylformamide at constant current in a diaphragmless cell has been developed using Ni(II) and Co(II) complexes as electron-transfer mediators. Cyclic compounds are obtained in good yields under appropriate experimental conditions.

***Keywords**:* electron transfer, cyclisation, nickel, cobalt, radicals, heterocycles.

Introduction

The radical methodology has emerged as one of 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 in

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reactions involving vinyl or aryl bromides [2-4], bromoacetals [5], or α-bromoamides [6], as well as other unsaturated halides [7-10].

We have investigated the use of electrogenerated nickel(I) complex derived from **9** and cobalt(I) complex derived from **10** bearing chiral salen-type ligands for the catalytic reduction of allyl ethers **1** and **2**.

Experimental

Typical electrolysis procedure: In a single-compartment cell (capacity 50 mL), such as described in Ref. 11, with a Mg or Al rod as the sacrificial anode (diameter 1 cm) and a carbon fibre cathode (apparent surface, 20 cm^{-2}) were introduced freshly distilled DMF (50 mL), n-Bu_4NBF_4 (6×10^{-3} mol dm^{-3}), [M (salen)], (2×10^{-3} mol dm^{-3}) and allyl phenyl ether (20×10^{-3} mol dm^{-3}). The solution was stirred and electrolysed at room temperature, at a constant current of 30 mA until disappearance of allyl phenyl ether (checked by GLC analysis of aliquots). The reaction mixture was hydrolysed with 0.1M HCl saturated with NaCl, up to pH 1-2 and 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 ^1H-NMR. The crude residue was submitted to flash chromatography over silica gel (230-400 mesh) using pentane /diethyl ether (90:10) as eluant. The ^1H-NMR spectra of different fractions collected were compared, when available, to those of authentic samples. The enantiomeric excess was determined by GC.

Results and Discussion

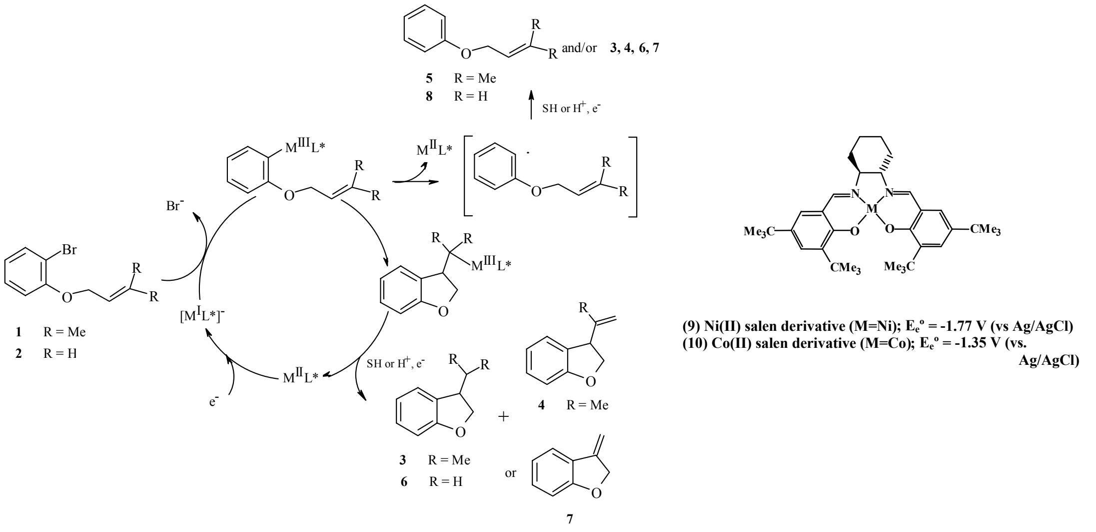
The catalytic electroreduction of allyl 2-bromophenyl ethers **1** and **2** by electrogenerated nickel(I) and cobalt(I) complexes was performed at constant current, in DMF, in a single-compartment cell fitted with a consumable sacrificial anode, under an inert gas at room temperature. The results are summarised in Table 1.

Cyclic voltammetric studies of (R,R)-(-)-N,N′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexane-diaminonickel(II) **9** and (R,R)-(-)-N,N′-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamino-cobalt(II) **10** complexes at carbon electrode in DMF containing 0.10 mol dm^{-3} show that both complexes underwent a reversible one-electron reduction at -1.77 V and -1.35 V *vs.* Ag/AgCl, 3 M KCl, respectively. On addition of allyl bromophenyl ethers, the reduction process for Ni(II) complex **9** becomes completely irreversible and the reduction peak increases in height; for the Co(II) complex **10**, the peak current of the reduction of Co(II) doesn't change although it becomes irreversible and a new reduction peak occurs at more negative potential which peak current increases as the concentration of unsaturated halide increase. The electron-transfer from the electrogenerated Ni(I) and Co(I) complexes to the allyl phenyl ethers, occurs according to Scheme 1. Halides **1** and **2** were reduced at potentials below -2.50 V.

Table 1. Electrochemical intramolecular cyclisation of alkyl ethers **1** and **2** catalysed by an electrogenerated M(I) complex (10%) in DMF containing 0.006 mol dm^{-3} tetrabutylammonium tetrafluoroborate. j = 1.5 A dm^{-2}.

Entry	Cathode	Anode	$M^{II}L$	Yeld (%)		
RBr = 3,3-dimethylallyl 2-bromophenyl ether **1**				**3**	**4**	**5**
1 [a]	Carbon fibre	Magnesium	**9**	50	10	11
2	Carbon fibre	Magnesium	**9**	46	19	12
3	Carbon fibre	Magnesium	**9**[b]	49	25	-
4	Carbon fibre	Aluminium	**9**	49	27	4
5	Carbon fibre	Magnesium	**10**	44	45	-
6	Carbon fibre	Magnesium	**10**[b]	51	38	-
7	Ni foam	Magnesium	**10**	29	16	12
RBr = allyl 2-bromophenyl ether **2**				**6**	**7**	**8**
8[a]	Carbon fibre	Magnesium	**9**	52	5	16
9	Carbon fibre	Magnesium	**9**	67	-	-
10	Platinum	Magnesium	**10**	30	6	-

[a] j = 0.3 A dm^{-2}; [b] 20 mol % of catalyst.



(9) Ni(II) salen derivative (M=Ni); E_c^{o} = -1.77 V (vs Ag/AgCl)
(10) Co(II) salen derivative (M=Co); E_c^{o} = -1.35 V (vs. Ag/AgCl)

Scheme 1

Experimental parameters such as the ratio of allyl ethers to catalyst, the influence of nature of the electrodes and of the current density were examined to evaluate the effect on the product distribution and on the enantioselectivity.

The electrolysis of **1** with a Mg/C couple of electrodes was carried out at a constant current of 60 mA in 0.3 A dm^{-2} (Table 1, entry 1) and 30 mA in 0.15 A dm^{-2} (entry 2).

In both cases, the main product was dihydrobenzofuran derivative **3,** obtained together with cyclic **4** and acyclic phenyl ether **5** as the main by-products. A very low enantiomeric excess for cyclic ether **3** was reached, up to 13%. Further experiments were conducted at a constant current of 30 mA. Next, the influence of the ratio of the concentration of the allyl bromophenyl ether and that of the catalyst was examined. An increase of the yield of **4** to 25% was found when the amount of the catalyst was increased from 10 to 20%, but the enantiomeric excess of **3** decreased to 4% (entry 3). The nature of the sacrificial electrode was also investigated. It was observed that the change of the anode from magnesium to aluminium had no effect on the product yields (entry 4), although the enantiomeric excess for **3** was reduced to zero.

In order to examine the influence of the metal nature of the catalyst, the electrolysis of **1** was carried out in the presence of cobalt(II)-salen-type complex **10** under different experimental conditions. Using a Mg/C couple of electrodes, the formation of both cyclic ethers **3** and **4** was observed in 44 and 45 % yield, respectively (entry 5). The enantiomeric excess for **3** was of 16 %. The increase of the catalyst concentration was also examined, leading to a higher yield of **3** (51 %) with 20% catalyst, though without asymmetric induction (entry 6). The influence of the cathode nature was also studied using a magnesium anode and it was observed that the use of a nickel foam cathode led, for the electrolysis of **1** to the formation of **3** and **4** in 29 and 16% yields, respectively (entry 7). These results indicated that the radical cyclisation of **1** was strongly affected by the nature of the electrodes. Thus, a carbon fibre cathode seemed to be much more effective when compared to a nickel foam electrode. The same phenomenon was observed in a previous investigation in our laboratory in the study of the intramolecular cyclisation of propargyl derivatives by nickel(I) complexes [10].

Allyl 2-bromophenyl ether **2** was reduced by nickel(I) electrogenerated complex from **9** at a carbon fibre cathode using a sacrificial magnesium anode. The reaction proceeded through the cleavage of the carbon-bromine bond to afford the cyclic phenyl ether **6** as the main product in 52%, together with exocyclic derivative **7** (5 %) and allyl phenyl ether **8** (16%) (entry 8). No asymmetric induction was observed for **6**. Using Mg/C couple electrodes with cobalt(II) complex **10**, the electrolysis of **2** afforded cyclised **6** in 67 % yield, as the main product (entry 9). The influence of the nature of the cathode was examined using Mg/Pt as the electrodes and the electrolysis of **2** led to the formation of **6** in 30 % yield (entry 10). These results indicated here again that the cyclisation of allyl 2-bromophenyl ether **2** was strongly affected by the nature of the cathode material, as already reported above for the cyclisation of **1**. Both complexes **9** and **10** did not produce any asymmetric induction in cyclic product **6**.

In conclusion, the electrochemical cyclisation of allyl phenyl ethers **1** and **2** could be conducted by the use of catalytic amounts of metal complexes such as **9** and **10** at ambient temperature and in an environmentally friendly procedure. Some modest asymmetric induction for cyclic compound **3** issued from allyl ether **1** could be observed in up to 16 % and in future work the reactivity of other alternative substrates for which we expect the improvement of the enantiomeric excess will be explored.

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