

Nickel-catalysed Electrochemical Reductive Deprotection of Allyl Ethers

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The selective deprotection of a series of functionalized alkyl and aryl allyl ethers to the parent alcohols or phenols, under non-hydrolytic conditions, is effected by the combination of electrochemistry and catalysis by Ni^{II}-bipyridine complexes.

Selective protection and deprotection of functional groups are important processes in organic synthesis.¹ Allylic ethers usually lack reactivity and, accordingly are often used as selective protecting groups for alcohols and phenols.² Their removal is usually accomplished by a two step procedure, involving strong base isomerisation of the allyl double bond by Bu^tOK in Me₂SO, followed by acidic hydrolysis of the enol ether intermediate.³ Other methods include double bond rearrangement using transition metal complexes such as Rh^I.⁴ Recently, allyl ether deprotection procedures based on the combined use of hydrides with Pd catalysis have been reported.⁵

Electrochemistry constitutes an interesting approach for mild and controlled reductive deprotection of specific, easily reducible functional groups.⁶ For other less easily reducible groups (such as allyl ethers), the combination of electrochemistry with organometallic catalysis may lead to selective transformations.⁷ In particular, we have previously described the cleavage of allyl aryl ethers by a samarium-catalysed electrochemical process.⁸

We present here an alternative method for allyl ether deprotection, through a Ni^{II}-catalysed electrochemical, one-pot procedure, as summarized in Scheme 1.

The cationic complex [Ni(bipy)₃](BF₄)₂⁹ (bipy = 2,2'-bipyridine) is a good catalyst for the electrochemical cleavage of the O-C (allyl) bond of allyl ethers, affording the parent alcohols or phenols in good yields, under mild conditions. The electrochemical method is based on the use of a single-compartment cell, fitted with a sacrificial magnesium anode.¹⁰ Reactions are carried out in DMF at constant current and at room temperature, with 10 mol% of catalyst with respect to the starting allyl ether. The electrochemical set-up is very simple and allows the deprotection on a preparative scale. The reactions at the electrodes are; at the anode, the oxidation of the magnesium rod into Mg²⁺ ions in solution, and at the cathode (carbon fibre) the reduction of the Ni^{II} into Ni⁰ complexes.

Table 1† presents the results obtained with several allyl ether derivatives. Allyl phenyl ether, or substituted aryl ethers are quantitatively cleaved to phenol, as shown in entries 1–4; ester and cyano groups in *ortho* and *para* positions are compatible with the reaction conditions. Interestingly, the aromatic chloro substituents in the allyl derivatives of entries 5 and 6 are not reduced. However, the cleavage of the allyl group in allyl-*o*-chlorophenol is followed by some reduction (protodehalogenation) of the aryl-chlorine bond (entry 7).

Allyl-*o*-bromophenol (entry 8) selectively affords phenol in a quantitative yield, through a double deallylation and protodehalogenation process. The iodo analogue (entry 9) led to phenol together with some cyclized compound. The electrochemical behaviour of these *o*-halophenyl derivatives (analogous to entries 7–9) has been reported for SmCl₃⁸ or Ni(cyclam)₂¹¹ catalysed reactions with the preferential formation of 3-methyl-dihydrobenzofuran through an electrochemical intramolecular cyclisation. In contrast with these results, the

Ni-bipy system does not favour the cyclisation process, but the C–O cleavage.

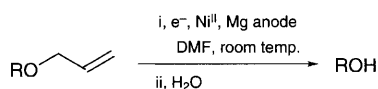
Aliphatic and benzylic allyl ethers can also be catalytically cleaved by the electrochemical system, as shown by the examples in entries 10–12.

The method is selective for allyl ethers, and homoallyl ethers or enol ethers are not cleaved under these conditions. Thus, no C–O bond cleavage occurred in the reaction of (*Z*)-(*o*-

Table 1 [Ni(bipy)₃](BF₄)₂-catalysed electrochemical cleavage of allyl ethers

Entry	Substrate	Products [yield (%)]	Total <i>O</i> -allyl cleavage (%)
1		PhOH [99]	99
2		 [86]	86
3		 [99]	99
4		 [99]	99
5		 [80] + PhOH [6]	86
6		 [96]	96
7		 [75] + PhOH [25]	98
8		PhOH [99]	99
9		 [33] + PhOH [52]	52
10		C ₉ H ₁₉ OH [77]	77 ^a
11		 [40]	40 ^a
12		 [55] + PhCH ₂ OH [43]	98
13		 [50]	—

^a The remaining product is non reacted starting material.



R = alkyl, aryl

Scheme 1

bromophenoxy)hex-3-ene (entry 13), the only product observed with this homoallyl ether arising from a protodehalogenation process on the aromatic ring. Phenyl propenyl ether did not react under the reaction conditions and could be quantitatively recovered after electrolysis.

The nature of the catalyst plays an important role in the control not only of the reaction yield, but also on the chemoselectivity, as already stated by the examples in entries 7–9.

No reaction occurred in the absence of current. Moreover, in the absence of the nickel complex and under the same electrochemical conditions as in Table 1, allyl 2-chlorophenyl ether (entry 7) led to partial isomerisation of the double bond to the corresponding enol ether (43% yield), together with some cyclisation to 3-methylbenzofuran (40%), and phenol (7%), in a non-selective process. In the non-catalysed electroreduction of allyl 4-chlorophenyl ether (entry 5), protodehalogenation and isomerisation of the double bond were observed as the main reaction pathways. This behaviour in non-catalysed reactions is in agreement with the results reported for the reduction of allyl 2-chlorophenyl ether in two-compartment cells.¹²

The fact that enol ethers are not cleaved under the Ni-catalysed electrochemical conditions is taken to indicate that this allyl ether deprotection does not proceed through a double bond isomerisation, but that it may involve the formation of π -allyl–Ni^{II} intermediate complexes. The formation of a π -allyl–Ni^{II} complex has been reported from Ni⁰ and allyl phenyl ether in a stoichiometric reaction¹³ and, under our electrochemical conditions, the cathodically electrogenerated Ni⁰–bipy species¹⁴ is likely to oxidatively add to the O–C(allyl) bond and form a π -allyl–Ni^{II} intermediate. The presence of a π -allyl intermediate is further supported by the formation of *tert*-butyl homoallyl alcohol upon addition of pivaldehyde during the electrolysis of allyl 2-chlorophenyl ether, in agreement with the nucleophilic nature of related π -allyl–Ni^{II} complexes under electrochemical conditions.¹⁵

In conclusion, the Ni(bipy)₃²⁺ catalysed electrochemical reaction offers a new method for allyl ether deprotection under simple and mild conditions, in which the operating mechanism is different from the usual deprotection procedures based on double bond isomerisation. The method enables the presence of several functional groups and avoids the use of strong acidic or basic media.

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Footnote

† *General electrolysis procedure:* Into a single-compartment cell¹⁰ fitted with a magnesium rod anode and a carbon fibre cathode, is introduced 40 cm³ of freshly distilled DMF, Bu₄NBF₄ (10^{−3} mol dm^{−3}), [Ni(bipy)₃](BF₄)₂ (0.3 mmol) and the allyl ether substrate (3 mmol). The solution is stirred and electrolysed at constant current of 60 mA (5–10 V between electrodes), up to the total consumption of the starting material (checked by GC analysis of aliquots) with 2–5 F mol^{−1} of ether. The solution is then hydrolysed with HCl (0.1 mol dm^{−3}) up to pH 1–2 and extracted with Et₂O. The organic layers were dried with MgSO₄ and then filtered and evaporated. In the case of phenol derivatives, the electrolytic solutions are directly esterified by adding K₂CO₃ and methyl iodide, stirred at 50 °C for 10 h and then extracted similarly. The products were analysed by NMR and mass spectrum, and their spectra compared to those of authentic samples.

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