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Nickel-Catalysed Electroreductive Cleavage of Propargyl Compounds

Sandra Olivero, Elisabet Duñach*

Laboratoire de Chimie Moléculaire, Associé au CNRS, Université de Nice-Sophia Antipolis, Parc Valrose, 06108 NICE Cedex 2, France

Abstract : The selective reduction of propargyl esters and aryl ethers, involving the cleavage of the propargyl-oxygen bond, affords the corresponding carboxylic acids and phenols in good yields. The reaction proceeds through electrosynthesis combined with the catalysis by Ni^{II}-bipyridine complexes, under mild conditions.
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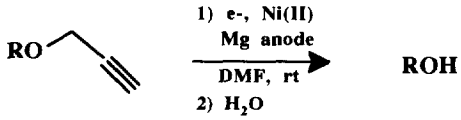
The cleavage of C(allyl)-O bonds in allyl ethers and esters has been investigated in some detail[1,2]. However, there are only a few examples dealing with the related C-O cleavage in propargylic derivatives. These methods include the use of low-valent titanium,[3] and the palladium-catalysed reductive cleavage of propargylic esters mediated by Bu_3SnH[4] or by SmI_2,[5,6]. The hydrogenolysis of propargyl esters with formic acid or formates has also been recently described[7].

We present here an alternative method of reductive cleavage of propargyl ethers and esters, by the use of a nickel-catalysed electrochemical procedure. Electrochemical reactions constitute an interesting approach for controlled functional group transformations and have been used for the removal of specific, easily reducible functional groups.[8] For other less easily reductible groups (such as propargyl ethers), the combination of electrochemistry with organometallic catalysis may increase the scope of electrochemical methods, and can lead to new and selective transformations.[9]

The Ni(II)-catalyzed electrochemical, one-pot procedure, constitutes a mild and convenient method to obtain carboxylic acids or phenol derivatives in good yields from propargyl esters or ethers, as summarized in eq. 1.



R = arylCO-, alkylCO-, aryl (1)

The electrochemical method is based on the use of a single-compartment cell, fitted with a sacrificial magnesium anode.[10] The reactions are carried out in DMF, on a preparative-scale, at constant current and at room temperature, with a consumption of 2-4 F/mol of substrate. The catalyst is the cationic complex

Fax : 33-492076142; e-mail: dunach@unice.fr

$Ni(bipy)_3^{2+}$, 2 BF_4^- [11] (bipy = 2,2'-bipyridine) used in a 10% molar ratio with respect to the substrate. The reactions at the electrodes are, at the anode, the oxidation of the magnesium rod into Mg^{2+} ions in solution, and at the cathode (carbon fiber) the reduction of the Ni(II) into Ni(0).[12] The electrogenerated Ni(0) species are responsible for the C-O cleavage reaction, by their oxidative addition into the propargyl-oxygen bond.[13] A Ni(II) exchange with magnesium ions enables the recycling of the Ni(0) catalytic species by continuous electrochemical reduction. No reaction occurred in the absence of electricity, and in the absence of the nickel catalyst the process was not selective (vide-infra).

The method has been extended to the deprotection of several propargyl derivatives as shown in Table 1. A complete C-O cleavage occurred in the case of phenyl propargyl ether (entry 1). In the case of 2-bromo and 2-iodoaryl derivatives (entries 2, 3), the propargyl group was cleaved with dehalogenation, phenol being quantitatively isolated. In the uncatalysed electrolysis of 2-bromophenyl propargyl ether a mixture of products arising from dehalogenation (15%), depropargylation (15%), triple bond isomerisation (20%) and reductive cyclisation (35%) was obtained, in a non-selective reaction.

In the presence of the Ni-bipy catalytic system and after an electrolysis of 3 F/mol, 2-chlorophenyl propargyl ether (entry 4) afforded 2-chlorophenol in 77% yield in addition to 20% phenol, thus involving the complete cleavage of the O-propargyl group, without any intramolecular cyclisation. These results indicate that the cleavage of the propargyl group occurs preferentially to the insertion of the electrogenerated Ni(0) into the C-Cl bond.

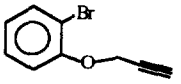
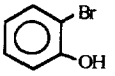
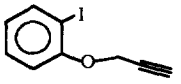
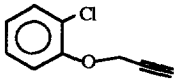
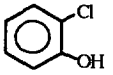
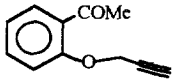
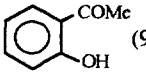
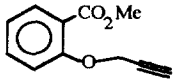
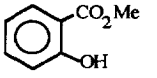
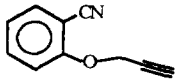
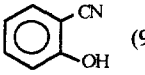
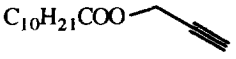
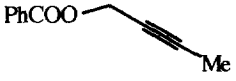
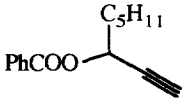
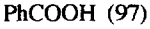
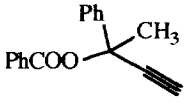
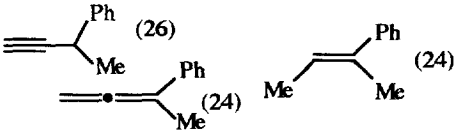
A chemoselective propargyl ether reduction was observed in the reaction of functionalysed aryl derivatives of entries 5-7. Thus, ester, cyano and most interestingly, aryl ketone functionalities were stable under the reaction conditions and were compatible with the cleavage of the oxygen-propargyl group.

We observed that allyl ethers or esters were cleaved easier than their propargyl analogs, as could be concluded by comparing the reactivity of allyl phenyl ether with that of propargyl phenyl ether. The nickel-catalysed deprotection of allyl ethers using this electrochemical procedure has been recently reported.[15]

The electrochemical reductive cleavage of propargyl esters to the parent carboxylic acids has been examined in the case of both aliphatic and aromatic esters, and the results are shown in entries 8-11. In all cases, the oxygen-carbon bond cleavage occurs in excellent yields and selectivities, the carboxylic acids being obtained quantitatively.

We also tested the cleavage of other longer chain propargyl derivatives, as shown in entries 9-11. The cleavage of an internal alkyne, such as 2-butyn-1-yl ester of entry 9 led to the expected benzoic acid quantitatively. In the case of entry 10, benzoic acid was also isolated quantitatively, together with 1-octyne. No allene, or overreduction of the produced alkyne to the corresponding alkene were observed. The electrochemical method thus allows the selective reduction of 1-octyn-3-ol to 1-octyne via the intermediate ester formation. The reduction of a tertiary alkynyl alcohol derivative was less selective, and afforded a mixture of alkyne, allene and alkene. Thus, the electrolysis of benzoic ester of entry 11, bearing a propargyl group derived from 2-phenyl-3-butyn-3-ol, led to the formation, besides the carboxylic acid, of a mixture of 3-phenyl-1-butyne, 1-methyl-1-phenyl allene and its reduced analog (*E*)-1,2-dimethyl styrene in an aprox. 1:1:1 ratio. Allene formation has been generally observed from the Pd-catalysed hydrogenolysis of propargyl esters or carbonates in the presence of formic acid.[7] The reductive cleavage of propargyl compounds to produce alkynes or allenes may have a wide synthetic application, and may be particularly useful when the process is regioselective.

Table 1. $Ni(bipy)_3(BF_4)_2$-Catalysed Reductive Electrochemical Cleavage of Propargyl Esters and Ethers.[a]

Entry	Substrate	Carboxylic acid or phenol recovered (%)
1		PhOH (99)
2		 (18)[b] + PhOH (80)
3		PhOH (99)
4		 (77)[c] + PhOH (20)
5		 (90)
6		 (98)
7		 (99)[d]
8		$C_{10}H_{21}COOH$ (98)[e]
9		PhCOOH (99)
10		PhCOOH (97) +  (55)
11		PhCOOH (95) + 

a) For the general electrolysis procedure, see note 14. b) After 3.8 F/mol. c) After 3 F/mol. d) Conversion of 70% after 2.7 F/mol. e) Conversion of 50% after 2 F/mol.

In conclusion, the Ni(bipy $)_3^{2+}$-catalysed electroreduction reaction offers a new synthetic method of propargyl cleavage, of applicability for the deprotection of propargyl esters and aryl ethers to the corresponding carboxylic acids or phenol derivatives, under simple and mild conditions. The method enables the presence of several functional groups and avoids the use of strong acidic or basic media.

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14. **General electrolysis procedure**: In a single-compartment cell[10] fitted with a magnesium rod anode and a carbon fiber cathode, are introduced 40 ml of freshly distilled DMF, n-Bu_4NBF_4 (10^{-3}M), $Ni(bipy)_3(BF_4)_2$ (0.3 mmol) and the propargyl 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 (2-4 F/mol, checked by GC analysis of aliquots). The solution is then hydrolysed with HCl, 0.1M up to pH 1-2 and extracted with Et_2O. The organic layers, dried with $MgSO_4$, are filtered and evaporated. In the case of ester derivatives, the electrolytic solutions are directly esterified by adding K_2CO_3 and methyl iodide, stirred at 50 °C for 10 hours and then extracted similarly. Alkynes and allenes of entries 10, 11 are obtained after washing the crude extract with basic aqueous solution and pentane extraction. The products are analysed by NMR, mass spectrum and their spectra compared to those of authentic samples.
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