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Electrochemical cleavage of allyl aryl ethers and allylation of carbonyl compounds: umpolung of allyl-palladium species

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Abstract

The electrochemical, Pd-catalyzed cleavage of the C–O bond of allyl aryl ethers has been examined; the method constitutes a new alternative for allyl ether deprotection. The allyl transfer from the allyl ether to the carbonyl group in 2-allyloxy benzaldehydes is reported and is an example of allyl-Pd reactivity umpolung. Pd(II) complexes, associated to several nitrogen ligands are efficient catalyst precursors for these electrochemical reactions. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: allylation; electrochemical reactions; palladium complexes; carbonyl addition.

Pd(0) complexes are well known to react with allyl halides and acetates to form π-allyl–Pd(II) complexes which present an electrophilic character.[1] Their reactivity with several nucleophiles has been extensively studied in the presence of chiral Pd complexes for the synthesis of optically active alkene derivatives.[2,3]

In the last years, the ability of Pd(0) complexes to form π-allyl–Pd(II) compounds has been combined with the use of a reducing agent for the Pd-catalyzed deprotection of allyl esters and carbonates,[4] as well as that of allyl ethers.[5]

During our studies on the electrochemical reactivity of Ni and Pd complexes with new tetraaza ligands,[6] we found that Pd complexes associated with nitrogen ligands could catalyze the cleavage of the O–C bond of 2-allyloxy-1-bromobenzene to afford 2-bromophenol under mild conditions.

In the present study, we first extended this result to the Pd-catalyzed deprotection of allyl aryl ethers using an electrochemical procedure,[7] according to Eq. 1.

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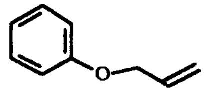
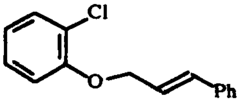
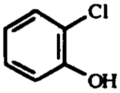
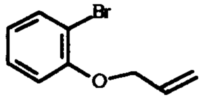
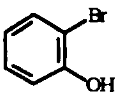
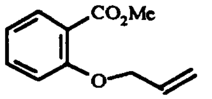
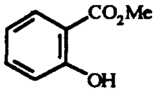
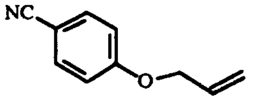
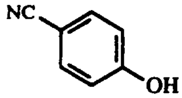
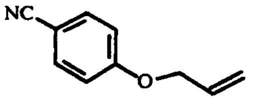
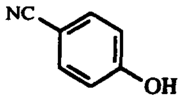
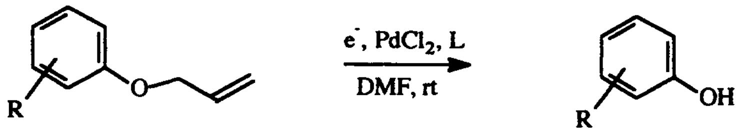
Table 1
Electrochemical cleavage of the C–O bond of allyl ethers catalyzed by Pd(II)[a]

Entry	Starting ether	Catalyst precursor (10%)	F/mol	Products	Yield of C-O cleavage
1		$PdCl_2$ + bipy (1:3)	2.5	PhOH	75%
2		" "	2.05		97%
3		" "	3.0	 + PhOH (42:58)	72%
4		" "	2.2		73%
5		" "	2.2		89%
6		$PdCl_2$ + **1a** (1:3)	2.6		99%

[a] Electroreductions were carried out with 2 mmol of allyl ether in anhydrous DMF (40 mL) at constant current intensity of 60 mA for 1.8 to 2.8 h, using tetrabutylammonium tetrafluoroborate (10^{-2} M) (Bu_4N^+,BF_4^-) as supporting electrolyte. The catalyst was introduced in a 10% molar ratio with respect to the substrate. The electrolyses were performed with Mg/stainless steel couple electrodes at 20 °C. Acidic hydrolysis and diethyl ether extraction afforded the corresponding phenol derivatives. For a better extraction of the products, in the case of entries 3, 5 and 6, the crude reaction was traeted with K_2CO_3 and MeI at 50 °C during 12 h and the corresponding ArOMe derivatives were obtained after acidic hydrolysis and diethyl ether extraction in the yields shown in the table.



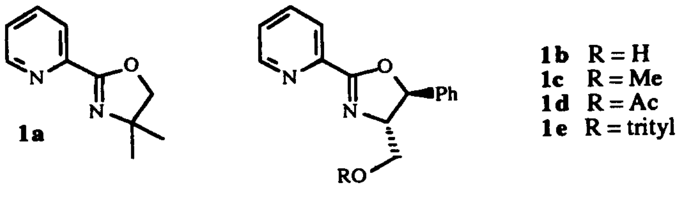
(1)

The results are presented in Table 1. The C–O cleavage reaction was carried out in DMF at room temperature, in a single compartment cell fitted with a magnesium anode and a stainless-steal cathode. The electrolyses were run under constant intensity, with a catalytic amount (10%) of $PdCl_2$ and 2,2′-bipyridine (bipy). In the electrochemical procedure, Pd(0) was formed from Pd(II); the tendency of Pd(0) complexes to form π-allyl species was enhanced by the reductive conditions, and the allyl ether cleavage occurred smoothly under very mild conditions.

Allyloxybenzene (entry 1) afforded phenol in a good yield after 2.5 F/mol electrolysis. In the case of 2-cinnamyloxy-1-chlorobenzene (entry 2) the corresponding 2-chlorophenol was obtained in excellent yield, indicating that the cleavage of the allyl group takes place without reduction of the aryl–chloride bond. The allyl moiety was protonated or dimerized by the reaction medium, as it could be shown by the presence of 3-methyl styrene and its dimers (ratio 2:3) from the electrolysis of 2-cinnamyloxy-1-chlorobenzene.

Reduction of 2-allyloxy-1-bromobenzene (entry 3) led to a mixture of phenol and 2-bromophenol in 72% yield, together with 28% of cyclized 3-methyl-dihydrobenzofuran. The presence of ester and nitrile groups was also compatible with the reaction conditions, these functional groups remaining unchanged during the allyl ether deprotection procedure (entries 4 and 5).

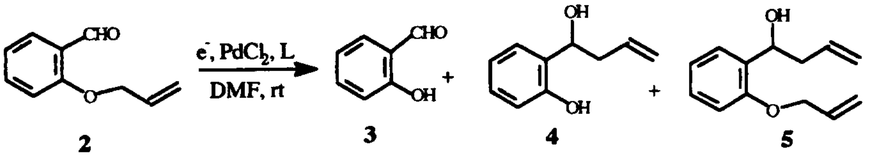
The use of pyridine-oxazoline ligand **1a** replacing bipy (Scheme 1) also led to an efficient and quantitative allyl group deprotection in the case of 4-cyano allyloxybenzene (entry 6).



Scheme 1.

In contrast to these results, the Pd-catalyzed electroreduction of 2-allyloxybenzaldehyde, **2**, afforded, after 2.05 F/mol, 55% of 2-hydroxybenzaldehyde, **3**, and 25% of 2-(1′hydroxy-3′butenyl)phenol, **4** (Eq. 2). When a formyl group was present in the *ortho* position of the aromatic allyloxy group, the C–O cleavage was followed by the partial allylation of the carbonyl moiety, to give, after hydrolysis, the corresponding homoallylic alcohol-phenol. The cleavage and the intramolecular allyl transfer reactions have already been reported in Ni-catalyzed electrochemical reactions.[8,9]

The carbonyl allylation involves a nucleophilic-type reactivity of the presumably formed π-allyl Pd intermediates, with an umpolung due to the reductive electrochemical conditions. Umpolung reactions with Pd complexes and reducing agents such as Zn have already been reported,[10] as well as electrochemical coupling reactions with Pd(II) precursors.[11]



(2)

The allylation reaction occurred with Pd complexes associated with bipy or other pyridine-oxazoline ligands, such as **1a**. Chiral pyridine-oxazoline ligands, **1b–e**, (Scheme 1) were also tested for this reaction, in order to examine the asymmetric induction into alcohol **4** (Eq. 2). The results are shown in Table 2.

The different chelating dinitrogen ligands tested were effective for the Pd-catalyzed allylation. Bis-allylated compounds, **5** (Eq. 2), were also formed, in up to 35% yield. The results indicate that the allyl transfer process is partially intra- and intermolecular. The enantiomeric excesses found for alcohols **4** were low, in the range of 1–6%.

A significant yield of products **4** and **5** (in the range of 27–64%), both issued from the umpolung of the π-allyl palladium species, has been obtained. This change of reactivity is due to the reductive electrochemical conditions.

In conclusion, the use of chelating nitrogen ligands for Pd(II) complexes enables their use as catalyst precursors for the deprotection of allyl aryl ethers and for allyl transfer reactions to carbonyl compounds under mild electrochemical conditions.

Table 2
Electrochemical Pd-catalyzed allyl transfer reaction of **2** (Eq. 2)[a]

Ligand	F/mol	Products[a]		
		% of **3**	% of **4**	% of **5**
bipy	2.05	55	25	2
1a	3.2	33	25	-
1b	2.05	20	25	35
1c	2.2	28	52	12
1d	2.05	58	30	10
1e	2.9	25	42	-

[a] Electroreductions were carried out with 2 mmol of **2**, following the same procedure as in Table 1. Distillation of DMF preceeded the acidic hydrolysis, and diethyl ether extraction afforded the corresponding products. They were analyzed by GC and NMR and compared to authentic samples.[9] Enantiomeric excesses of products **4** were measured by GC with a FS-Lipodex C column (25 m).

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