

Mild and Robust Redox-Neutral Pd/C-Catalyzed Lignol β-O-4' Bond Cleavage Through a Low-Energy-Barrier Pathway

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A Pd/C catalyzed redox neutral C–O bond cleavage of 2-aryloxy-1-arylethanols has been developed. The reactions are carried out at 80 °C, in air, using a green solvent system to yield the aryl ketones in near quantitative yields. Addition of catalytic amounts of a hydrogen source to the reaction mixture activates the catalyst to proceed through a low energy barrier pathway. Initial studies support a transfer hydrogenolysis reaction mechanism that proceeds through an initial dehydrogenation followed by an enol adsorption to Pd/C and a reductive C–O bond cleavage.

Lignin is a polyphenolic, highly cross-linked polymer that comprises up to 30% of the mass and more than 40% of the energy in wood (Figure 1).^[1] Although cellulose, hemicelluloses, and tall oil produce high-value products, lignin is currently burned to regenerate process chemicals and produce process (Figure 1), besides a few exceptions.^[4] Since the pioneering articles from the groups of Bergman^[5] and Toste^[6] on the redox-neutral depolymerization of lignin model compounds, many research groups have reported both reductive and oxidative methodologies to depolymerize lignin by means of hydrogen transfer. Bergman used a homogeneous rutheniumbased catalyst and achieved excellent yields of acetophenone derivatives by using various 2-aryloxy-



1-arylethanol model compounds and performing the reactions at 140 °C under inert conditions. (Scheme 1). However, the methodology was limited to Schlenk techniques, an expensive

catalyst, and elevated reaction temperatures.

A recyclable heterogeneous catalytic system has many advantages over homogeneous systems, especially in a largescale industrial process. Rinaldi's group has reported that Raney nickel reductively cleaves lignin, utilizing isopropyl alcohol as



Figure 1. Representative structure of native soft wood lignin with the β -O-4' ether linkage highlighted.

heat in pulp mills.^[1] Aromatic compounds are of a high value, both for fine-chemical production and as part of fuels. There is a lack of both sources of aromatic hydrocarbons other than fossil resources, and industrially applicable methods to produce such aromatic hydrocarbons from renewable feeds.^[2] Lignin is a potentially renewable source of aromatic compounds, and hence there is a need to develop efficient methods to convert lignin into high-value products.

Lignin depolymerization, by means of catalysis, is key to the efficient utilization of lignin.^[1] The β -O-4' ether bond comprises more than 50% of the monomer linkages in lignin. Also, C–O bonds are in general significantly weaker and more labile than C–C bonds.^[3] Thus, the β -O-4' ether linkage is a structural motif that is commonly targeted in lignin depolymerization

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    Supporting information for this article is available on the WWW under
http://dx.doi.org/10.1002/cssc.201500117.
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 $\begin{array}{c} \text{Ar}{-}\text{OH} \\ 3 \end{array} + \begin{array}{c} \text{O} \\ \text{Ar} \\ 2 \end{array} + \begin{array}{c} \text{O} \\ \text{Ar} \\ \text{P} \\ \text{O} \\ \text{P} \\ \text{P}$

 $\label{eq:scheme1} \begin{array}{l} \mbox{Scheme1. Redox neutral and cleavages under reductive conditions of the β-O-4'-ether linkage in 2-aryloxy-1-arylethanols to generate acetophenone. \end{array}$

mild hydrogen donor.^[7] However, this chemistry is limited to over-stoichiometric use of nickel (up to 600 wt%) and harsh reaction conditions (160–240 °C). Palladium-based catalysts have received significant attention in development of lignin depolymerization methods. Palladium on solid supports is stable to air and moisture in a wide range of pH values, which allows reactions in aqueous media and under ligand-free conditions. Generally, palladium-based lignin chemistry requires hydrogen at high pressures (above 30 bar), high temperatures (above 200 °C), or both.^[8] Processes that demand high hydrogen pressures and that operate at relatively high temperatures are in-

ChemSusChem 2015, 8, 2187 - 2192

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compatible with current pulp mills, and this renders such processes unsuitable for industrial applications.^[9] Recently, the group of Rauchfuss and our group reported the use of palladium on carbon (Pd/C) in the catalytic transfer hydrogenolysis of lignin models using mild hydrogen donors (Scheme 1).^[10] Both in Rauchfuss's and in our report, an excess of hydrogen equivalents was used in the transformation of substrate **1** to the aryl ketone **2**.

To our knowledge, there is no report of a heterogeneous catalyst operating under redox-neutral conditions to cleave the β -O-4' ether linkage. Herein, we report a comparably mild, robust, and efficient redox-neutral β -O-4' ether linkage cleavage of 2-aryloxy-1-arylethanol ethers by recyclable and commercially available Pd/C to generate aryl ketones and phenols in very high to excellent yields.

Pd/C and different additives were screened for redox-neutral cleavage of PhCH(OH)CH₂-OPh (**1 a**) to generate acetophenone (**2 a**) and phenol (**3 a**) (Table 1). Without additive and under an atmosphere of air, negligible amounts of benzylic alcohol oxi-

Table 1. Effect of additives for redox neutral cleavage of β -O-4' ethanolaryl ether bond. $\begin{array}{c} & \overset{OH}{\underset{Ph}{\overset{O}{\underset{1a}{\overset{O}{\overset{Pd}{\underset{0}{\overset{O}{\underset{0}{\overset{d}{\underset{0}{\overset{d}{\underset{0}{\overset{d}{\underset{0}{\underset{0}{\overset{d}{\underset{0}{\underset{0}{\underset{0}{\underset{0}{\underset{0}{\underset{0}{\underset{0}{\underset$				
Entry	[H]-donor	Conversion [%]	2 a [%]	4 a [%]
1 ^[b]	No	5	0	5
2 ^[a,b]	No	11	11	0
3	HCOOH	45	25	16
4	NH₄HCO₂	76	73	3
5 ^[b]	2-propanol	0	0	0
6	$NaBH_4$	100	99	0
7 ^[b]	$H_{2}^{[c]}$	100	99	0
8 ^[b,d]	$NaBH_4$	0	0	0
Yields were determined by ¹ H NMR using mesitylene as internal standard. [a] Reaction were run under argon atmosphere. [b] Reaction time is 6 h instead of 1 h, time was not optimized. [c] Amount of H ₂ was not determined (Supporting Information). [d] Without Pd/C.				

dation product **4a** and no β -O-4' ether linkage cleavage was observed (entry 1). When performing the reaction in an inert atmosphere, negligible amounts of **2a** were observed (entry 2). The addition of formic acid led to marginally better results, where the desired **2a** was generated in 25% yield (entry 3). The addition of ammonium formate led to significantly better conversion, where **2a** was generated in 73% yield (entry 4). Previous studies have shown that lower pH values accelerate the disproportionation of benzylic alcohols while higher pH values accelerate hydrogenolysis of the β -O-4' ethanolaryl ether bond.^[10c, 11] The addition of a catalytic amount of sodium borohydride led to an efficient transformation of **1a** and resulted in a quantitative yield of **2a** (entry 6).

The palladium nanoparticles on the carbon support were covered by a thin oxide layer at the beginning of the reaction.^[12] We hypothesized that the role of sodium borohydride was to remove oxygen from the reaction medium to generate

a reactive palladium surface. To prove our hypothesis, the palladium was activated by hydrogen gas, instead of NaBH₄, to remove oxides and then flushed with argon to remove the excess of hydrogen from the system. The reaction proceeded to generate products from cleaved β -O-4' ethanolaryl ethers. However, a longer reaction time was required. The addition of H⁺, Na⁺, Li⁺, K⁺ salts, or alkali did not significantly affect the outcome of the reaction (Supporting Information).^[10c,11,13] A possible explanation for the slower reaction is that the hydrogen concentration is difficult to control by hydrogen gas (vide infra).

The effect of $NaBH_4$ was investigated (Figure 2). Low reactivity was observed below 0.01 equivalents of $NaBH_4$. Between 0.01 and 0.03 equivalents of $NaBH_4$, an aerobic oxidation of the



Figure 2. Effect of NaBH₄. Products versus NaBH₄ equiv for the conversion of 1 a after 30 min.

benzylic alcohol to yield 4a was observed with cleavage of the β -O-4' ethanolaryl ether bond. A possible explanation is that the palladium is activated, but the excess of oxygen present in the reaction flask pushes the equilibrium toward dehydrogenation product 4a.^[14,12d,e] Thereby, the hydrogen adsorbed onto the palladium from the dehydrogenation of 1a is consumed by oxygen, instead of substrate 4a. The redox-neutral transfer hydrogenolysis was observed between 0.05-0.08 equivalents of NaBH₄. Under these reaction conditions, NaBH₄ efficiently removes oxygen on palladium as well as the oxygen in the reaction flask. According to the equation $NaBH_4 + (2+x)H_2O = Na$ - $BO_2 x H_2O + 4 H_2$; the amount of hydrogen liberated in the reaction (see Experimental Section) will be 0.188 mmol, and this almost equals the oxygen content in the vial. Reduction of the generated ketone was observed above 0.1 equivalents of NaBH₄. Above 0.3 equivalents of NaBH₄ the reaction was inhibited and resulted in formation of trace amounts of 1-phenylethanol (5). To study the effect of a reaction performed with excess hydrogen, a reaction was performed at 50 bar of hydrogen pressure (Scheme 2). Analysis of the products showed significant suppression of the desired cleavage reaction. The chemoselectivity had changed toward benzylic C-O bond hydrogenolysis, from which phenethoxybenzene (6) became the major product. Notably, 6 has previously been reported to be cumbersome to transform at various conditions,^[15] however at elevated temperatures C-O bond cleavage has been reporte-





Scheme 2. The effect of hydrogen excess on chemoselectivity of $\beta\text{-}0\text{-}4'$ ether linkage hydrogenolysis.

d.^[10a] Initial studies showed that NaBH₄ operated as an appropriate hydrogen model source. Sodium borohydride has many practical advantages over hydrogen gas, especially when small amounts need to be handled.^[16]

Pd/C catalyzed redox neutral cleavage of the β -O-4' ethanolaryl ether bond in lignin model compounds was investigated (Table 2). β -O-4' Ethanolaryl ethers, which mimic lignin from



cate experiments. Conversion in all cases was above 99%, neglecting amount of 4a-j was observed. [a] Reaction was run for 4 h instead of 1 h. [b] Yield of phenol, guaiacol, and syringol. [c] EtOH/H₂O was tested at redox neutral conditions. Substrates 1e and 1d' resulted in 98% and 97% yield of hydrogenolysis products respectively.

different sources, were chosen as model substrates to investigate the scope of the reaction. **1a** and **1b**, with no methoxy substitution of the aryl, model the major lignin component in the monocotyledons, such as switch grass.^[1,17] Substitution of the aryl group by a methoxy group at the R^3 and $R^{3\prime}$ positions (1 c-f) corresponds to the substitution pattern found in conifer lignin, for example in pine and spruce.^[1,17] Substitution of the aryl group by two methoxy groups at the $R^{3\prime}$ and $R^{5\prime}$ positions (1 g and h) corresponds to the substitution pattern found in lignin from the dicotyledons, for example birch and eucalyptus.^[1,17] The redox-neutral transfer hydrogenolysis of the β -O-4' ethanolaryl ethers proceeded at 80 °C to yield the corresponding acetophenones and phenols in excellent yields (92-99% yield) within 60 min (entries 1-3, 5, 7). This is to our knowledge both the mildest and fastest cleavage of β -O-4' ethanolaryl ether models ever reported, including results achieved through homogeneous catalysis. Even bulky substrates with methoxy groups at the R^{3,} and R^{5,} positions gave the corresponding aryl ketones and phenols in excellent yields under the same reaction conditions (entries 7, 8). These bulky model substrates have previously been reported to be cumbersome to transform.^[5] β -O-4' Ethanolaryl ether models having more than two methoxy groups required extended reaction times, up to 4 h (entries 4, 6, 8–10). Gratifyingly,

the redox-neutral transfer hydrogenolysis gave excellent yields also for these models. Furthermore, phenolic substrates (R^4 = OH) were transformed under the present reaction conditions to generate products **2d** and **2e** (entries 9 and 10) in excellent yields. Unprotected phenols have previously been reported to be difficult to transform.^[18] The products were easily separated, to obtain aryl ketones in excellent yields. This method allows facile separation of the catalyst from the product by decantation of the organic phase, where the Pd/C is found mainly in the water phase after the reaction. It should be noted that also phenol, guaiacol, and syringol (**3a-3c**) could be isolated in very good to excellent yields (entries 1, 5, and 7).

Pd/C is a heterogeneous catalyst on which a dimeric model compound can easily adsorb and react. To determine the compatibility of the heterogeneous catalyst with a polymeric substrate that mimics natural lignin in terms of both chemical and physical properties (e.g., solubility); the redox-neutral transfer hydrogenolysis reaction was performed on model polymer 1 d' (Scheme 3). The molecular weight of the model polymer,



Scheme 3. Redox neutral depolymerization of polymeric $\beta\text{-}0\text{-}4'$ ethanolaryl ether lignin model 1 d'.

6 kDa, corresponds to the molecular weight of native lignin. The model polymer underwent Pd/C-catalyzed β -O-4' bond cleavage reaction upon treatment at the same conditions as the dimeric models. The corresponding **2d** was isolated in a yield of 99%.

Rauchfuss et al. recently proposed a reaction mechanism for the transfer hydrogenolysis of β -O-4' ethanolaryl ethers using dioxane as hydrogen donor. The reaction was proposed to proceed through an insertion of palladium into the α -C–H bond of **1a** (Scheme 4). The C–H activated intermediate **A** trans-



Scheme 4. Reaction mechanism proposed by Rauchfuss et al. for the Pd/C catalyzed transfer hydrogenolysis of the β -O-4' ethanolaryl ether bond. Adopted from original manuscript.^[10a]



formed into intermediate **B** and tautomerized to yield product **2 a**. Experimental data, including productive reactivity of PhCH₂CH₂-OPh (**6**), PhCH(OMe)CH₂-OPh (**7**), and PhC(Me)(OH)CH₂-OPh (**8**), and lower reactivity for Ph(C=O)CH₂-OPh (**4**), supported the proposed reaction mechanism. It should be noted that these reactions proceeded at elevated temperatures (160 °C) compared to the present redox-neutral transfer hydrogenolysis (80 °C).

Previously, we proposed an alternative mechanism for the Pd/C-catalyzed transfer hydrogenolysis of β -O-4' ethanolaryl ethers by ammonium formate.^[10c] We proposed a reaction mechanism that proceeds through an initial dehydrogenation to form Ph(C=O)CH₂-OPh (**4a**) as a reactive intermediate. Under transfer hydrogenolysis conditions using formate as reducing agent, it was experimentally supported that **4a** is an intermediate in the transfer hydro-genolysis of **1a**.

We wanted to study the reac-

tion mechanism of the current

redox-neutral transfer hydroge-

nolysis of $\beta\text{-}\text{O-4'}$ ethanolaryl

ethers and determine whether

the reaction mechanism pro-

posed by Rauchfuss et al. was

operating under our conditions.

Running the reaction on models **6–8**, that cannot undergo a dehy-

drogenation of the benzylic alco-



Figure 3. Formation of 4a and 2a thought the reaction.



Scheme 5. Comparison of dimeric ketones reactivity 4k and 4a versus dimeric alcohols 1a and 1k respectively.

hol, gave no reaction using the redox neutral reaction conditions [Equations (1)–(3)]. Thereby, the transformation does not proceed through the same reac-

Ph
$$6$$
 Ph $\xrightarrow{\text{Pd/C (5 mol%)}}_{\text{EtOAc/H}_2O}$ (1)
 $O^{\text{Me}} = \frac{\text{Pd/C (5 mol%)}}{\text{Pd/C (5 mol%)}}$

$$\begin{array}{c} & & & \\ Ph & & & \\ \hline 7 & & Ph & & \\ \hline & & & \\ \hline & & & \\ \hline & & & \\ EtOAc/H_2O \\ & & 80 \ ^{\circ}C, \ 12 \ h \end{array}$$

$$Ph \underbrace{\overset{OH}{\underset{Me}{\rightarrow}} O_{Ph}}_{Me} Ph \underbrace{\overset{Pd/C (5 \text{ mol}\%)}{\underset{K}{\overset{NaBH_4 (10 \text{ mol}\%)}{\underset{K}{\rightarrow}}}}_{EtOAC/H_2O} (3)$$

tion mechanism as proposed by Rauchfuss et al.. The results from these reactions could be rationalized by that both the proton of the hydroxyl group and the α -hydride at the benzylic position are participating in C–O bond cleavage of the ether.

A plausible explanation is that the reaction proceeds through an initial dehydrogenation to generate **4a** and chemically adsorbed hydrogen. This adsorbed hydrogen is responsible for the following hydrogenolysis step. To determine if **4a** is an intermediate, the concentration of **4a** was monitored throughout the reaction (Figure 3). After a short induction period, the concentration of **4a** remains low and was observed nearly until the end of the reaction, suggesting steady-state kinetics in which $k_1 \ll k_2$.

To verify the higher reactivity of 4a versus 1a in the reaction, a cross-experiment was performed (Scheme 5). Fluoro labeling was used to introduce a reactivity difference, where the ortho-fluoro substituted species 1k reacts 2.3 times faster than 1 a (Supporting Information), and also for ease of analysis, by ¹⁹F NMR spectroscopy. Reaction of **4k** with **1a** as hydrogen donor resulted in formation of 2a in 57% conversion and 2fluorophenol (3d) in 55% conversion. The selectivity towards 4k is thereby 96% and this is much higher than what is expected (70%) based on the rate difference. Under identical conditions 4a with 1k as hydrogen donor were converted to 2a in 27% and 3d in 15%. Thereby, selectivity towards the ketone is 44% and this is again much higher than the expected (30%) from rate difference. These cross-experiments show that the dimeric ketone is more reactive than the dimeric alcohol under redox neutral reaction conditions at 80 °C.

To determine if the hydrogen in the β position participates in overall transformation, the β position was blocked using two methyl groups [substrate 1I, Equation (4)]. The reaction was performed at 80 °C and resulted in a low dehydrogenation of 1I, where no β -O-4' bond cleavage products were observed even after prolonged reaction times. However, at 160 °C full conversion of 1I to yield cleaved product 2f was observed [Equation (5)]. The experiments performed [Equations (1)–(5)



and Scheme 5] support that both the hydrogens at α and β positions of β -O-4' ethanolaryl ethers participate in the reaction performed at 80 °C.

To gain more insight into the apparent low-energy-barrier pathway in the current redox neutral reaction, the activation energy was studied. The apparent activation energy for the cleavage of **1a** under redox neutral conditions showed a low value (12 kcal mol⁻¹) (Supporting Information; 1 kcal = 4.184 kJ). The obtained apparent activation energy value is significantly lower than the corresponding calculated bond dissociation energy of the ether bond in **1a** (72.2 kcal mol⁻¹) or **4a** (61.2 kcal mol⁻¹) (Supporting Information). Therefore, further studies are needed to determine the contribution to this value from mass transfer processes and adsorption.

The following reaction mechanism is proposed for the redox neutral reaction performed at 80 °C (Scheme 6): The oxide on the palladium surface is removed by hydrogen. This is demonstrated in Figure 2, where the efficacy of the reaction is dependent on the amount of NaBH₄. The reaction starts with a reversible dehydrogenation of **1** to generate **4** and chemically adsorbed hydrogen on Pd/C. This intermediate was proven to be more reactive than the starting material (Scheme 5). The enolate form of **4** adsorbs to palladium to generate **C**.^[19] The re-



Scheme 6. Proposed reaction mechanisms for the redox neutral transfer hydrogenolysis of 1 (see Supporting Information). Metal atoms are depicted by surface for clarity.

quirements of hydrogen in the β position supports this [Equation (4)]. The basic medium may facilitate the keto-enol tautomerization and thereby also the adsorption of 4 to the palladium surface to generate C.^[13] Following a Horiuti-Polanyi-type mechanism,^[20] the atomic hydrogen may insert into either the α or β position of intermediate **C**. In route I, atomic hydrogen inserts into the β position to generate intermediate **D**. C–O bond cleavage generates intermediate E where the enol equivalent is chemically adsorbed together with the aryloxide. Intermediate E decomposes to products 2 and 3. This route gives a similar intermediate as proposed by Rauchfuss et al., however, the reaction pathway is distinctly different. In route II, atomic hydrogen inserts into the α position to give intermediate F. Palladium inserts into the C-O bond to generate G, in which a carbene and aryloxide are chemically adsorbed on palladium. Reductive elimination of aryloxide and the carbene tautomerization lead to products 2 and 3. In an environment with excess hydrogen a different chemoselectivity is observed, in which a hydrogenolysis reaction of the benzylic alcohol occurs to yield 6. At 80°C, no further reaction takes place. When the reaction temperature is increased to 160 $^\circ$ C, a C–O ether bond cleavage is reported to occur by Rauchfuss et al.^[10a] Thereby, the present methodology proceeds through a unique low energy barrier (12 kcal mol⁻¹) pathway for the lignol C–O bond cleavage via an initial dehydrogenation.

We have demonstrated the first heterogeneous lignol C-O bond cleavage under redox-neutral reaction conditions. A lowenergy-barrier pathway is operating in the reaction of β -O-4' ethanolaryl ethers. The key is to control the concentration of oxygen and hydrogen on the palladium surface. By applying catalytic amounts of hydrogen to the reaction mixture, the chemically adsorbed oxygen on the palladium surface was removed to generate an efficient catalyst. Excess hydrogen has a detrimental effect on the system, in which formation of less reactive dimeric intermediates (6) occurs. These intermediates require harsher reaction conditions for C-O bond cleavage. By applying the present redox-neutral reaction conditions, the reaction initially proceeds through a low-energy-barrier dehydrogenation to yield 2a. This intermediate was proven to be more reactive than the starting material (1 a). The mild and robust redox-neutral transfer hydrogenolysis was applied to several 2aryloxy-1-arylethanols that mimic the aryl substitution patterns in lignin from different sources. The products were isolated in very good to excellent yields in 1-4 h running the reactions at 80 °C.

Experimental Section

General procedure for β -O-4' bond transfer hydrogenolysis: To a suspension of Pd/C (50 mg, 0.023 mmol) in EtOAc (2.5 mL) and substrate (0.47 mmol), freshly prepared NaBH₄ water solution (0.5 mL, 0.092 m) was added. The suspension was stirred (600 rpm) at 80 °C (oil bath temperature) for desired time. The reaction mixture was cooled to RT and poured into a separatory funnel containing EtOAc (30 mL) and water (30 mL). The reaction vessel was rinsed with 10 mL of EtOAc. The combined organic extracts were washed with brine and dried over anhydrous Na₂SO₄, filtrated and



concentrated in vacuo to give a crude oil. The oil was purified by column chromatography.

Acknowledgements

We gratefully acknowledge the Swedish Energy Agency for financial support. We would also like to thank Professor Olle Matsson for extensive discussions on chemical kinetics.

Keywords: heterogeneous catalysis · lignin · palladium · reaction mechanisms · transfer hydrogenolysis

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Received: January 21, 2015 Revised: March 3, 2015 Published online on April 29, 2015