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Selective Ether/Ester C-O Cleavage of an Acetylated Lignin Model via Tandem Catalysis

Tracy L. Lohr, [†] Zhi Li, [†,‡] and Tobin J. Marks[*,†]

[†]*Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA.*

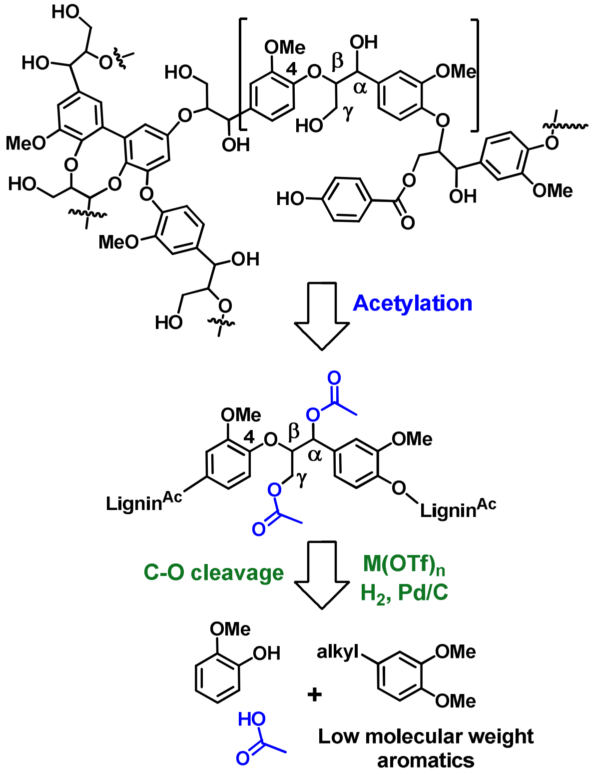
Supporting Information Placeholder

ABSTRACT: Selective ether/ester C-O bond hydrogenolysis of acetylated lignin models is achieved using a thermodynamically leveraged tandem catalytic strategy. Acetylation serves to: 1) solubilize both lignin and lignin models and 2) modify the reactivity of pendant hydroxy groups to promote more selective C-O cleavage.

KEYWORDS: Lignin, Lignin models, Tandem catalysis, Ether hydrogenolysis, Ester hydrogenolysis , biomass.

Lignin, a heterogeneous phenolic polymer which constitutes roughly 15 to 20 wt% of lignocellulosic biomass (cellulose, hemicellose, and lignin), represents one of the few renewable sources of aromatic monomers.[1] Current lignin depolymerization methodologies, including base-catalyzed,[2] acid-catalyzed,[3] metal-catalyzed,[4] ionic liquid (IL)-assisted,[5] and supercritical fluid-assisted[2b, 6] approaches, typically afford low yields (~ 10-20 % or less) of low molecular weight aromatics under relatively harsh reaction conditions (> 300 °C).[7] Recent advances include using oxidized lignin and lignin models,[8] where oxidation of the C_α alcohol facilitates depolymerizaton, with aromatic monomer yields reaching up to 52% for aspen "hardwood" lignin.[9] The most common structural lignin motifs contain a β-O-4 aryl-ether linkage,[10] a primary alcohol in the γ skeletal position, and a secondary alcohol in the α position (Scheme 1). This Laboratory has previously demonstrated an effective strategy for thermodynamically leveraged etheric and esteric C-O bond hydrogenolysis using a tandem metal triflate + supported palladium catalytic system.[11] A homogeneous $M(OTf)_n$ catalyst mediates endothermic ether or near thermoneutral ester C-O bond scission (the reverse of hydroelementation), which is coupled to exothermic Pd-catalyzed hydrogenation of the resulting C=C unsaturation, driving the overall process downhill. We next asked whether this tandem system might be applicable to cleaving the β-O-4 aryl-ether bond in lignin and lignin models. The promising results of that investigation are communicated here.

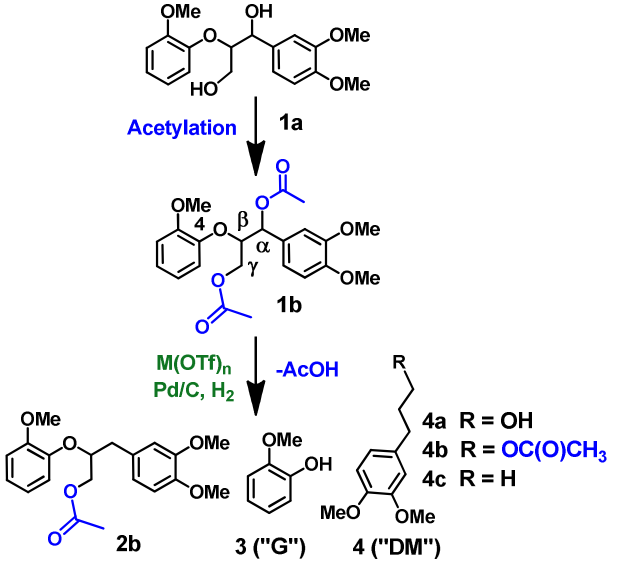
A major consideration in lignin depolymerization using the tandem metal triflate + palladium catalyst system is the reaction solvent, since strongly Lewis basic, or donor solvents depress the activity of the Lewis acid triflate catalysts,[11a-d] but usefully solubilize the lignin. The strategy employed here is lignin acetylation, rendering the substrates soluble in polar, weakly coordinating solvents without compromising triflate catalytic activity (Scheme 1). Aromatic hydrocarbon solvents are avoided to prevent their competing hydrogenation by the Pd catalyst.



Scheme 1. Strategy for cleaving guaiacyl-based lignins

Chlorinated solvents are used in this initial screen since they are polar and aprotic, and can be recycled to minimize environmental release. Experiments (Table 1) first focused on the acetylated version (**1b**) of the model dimeric substrate **1a**, which features the prevalent β-O-4 aryl-ether linkage and is a credible model for acetylated-lignin. From the accrued understanding of etheric and esteric cleavage using this tandem catalyst system,[10] it is anticipated that ester cleavage at the benzylic α position will precede other scissions since 2° esters are far more reactive than 1° esters and 2° ethers. Initial attempts to use highly Lewis acidic $Hf(OTf)_4$ at 1 bar H_2/70 °C, or at 600 psi H_2/100 °C, did not effect selective cleavage of **1b** to the constituent monomer units (Table 1). The starting dimer **1** is not recovered, and broad signals in the ^1H NMR spectrum of the waxy solid product indicate that $Hf(OTf)_4$ + Pd/C most likely induces polymerization of **1b**. Analysis of this product by GC-MS reveals only traces of styrenic intermediate **5b**, the result of secondary ester cleavage at the α position, without subsequent hydrogenation (see Scheme 2 below). Observation of **5b** by GC-MS suggests that this intermediate is formed in non-negligible amounts, and is most likely responsible for the dimer polymerization since styrenic polymerization should be facile under these reaction conditions.[12] Running the reaction at room temperature under 600 psi H_2 yielded no reaction (Table 1 entry 2) under these conditions.

Table 1. Catalytic $Hf(OTf)_4$ + $Pd/C/H_2$ mediated acetylated dimer cleavage data[a]



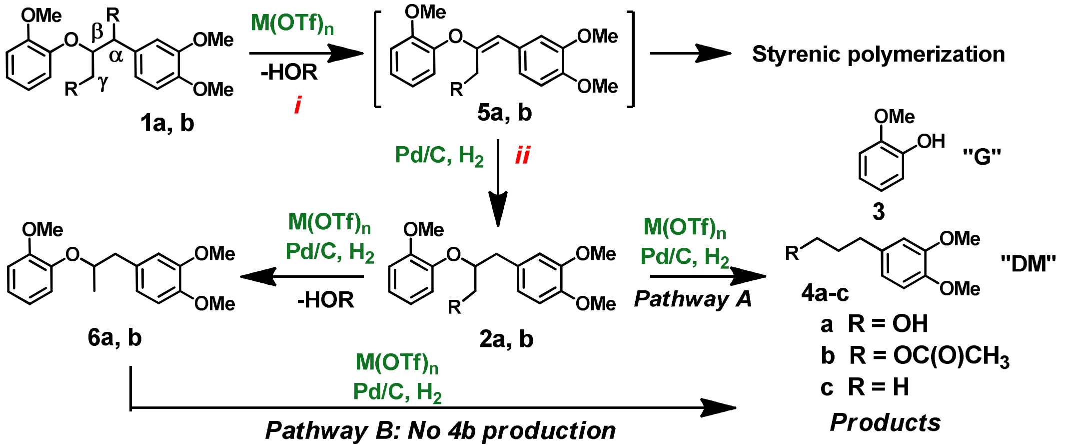
Entry	Temp °C	Yields (%)						Mass Balance %
		1b	2b	3	4a	4b	4c	G : DM
1[b]	70	-	-	-	-	-	-	0 : 0
2[c]	25	100	-	-	-	-	-	100
3[c]	100	-	-	-	-	-	-	0 : 0

[a] Reaction conditions: 1 mL of 0.1 M solution of **1b** in $CDCl_3$, 0.5 mol% $Hf(OTf)_4$, 0.2 mol% Pd/C (10 wt%) for 16 h. Upon completion, reactor cooled to 25 °C, and contents filtered to remove catalyst. Solvent removed in vacuo to yield beige oily solids. G = guaiacol unit recovered (yields of **2b** & **3** versus starting **1b**). DM = dimethoxyphenyl unit recovered (yields of **2b**, **4a**, **4b**, **4c** vs starting **1b**. "-" = none detected. [b] 1 psi H_2 [c] 600 psi H_2.

To suppress secondary polymerization by minimizing the **5b** steady-state concentration, it was hypothesized that slowing the ester C-O cleavage rate, *i*, relative to that of olefin hydrogenation, *ii* (Scheme 2) might capture **5b** before significant thermal/radical polymerization occurred. This goal was achieved by employing less Lewis acidic yet labile $La(OTf)_3$, increasing the H_2 concentration/pressure, and increasing the Pd catalyst loading relative to that of $La(OTf)_3$. Using a tandem catalyst with $La(OTf)_3$:Pd = 5:1 affords guaiacol (**3**)in 39% yield by ^1H NMR and GC-MS assay (Table 2, entry 1), with negligible dimethoxyphenyl (DM) products. Doubling both catalyst loadings (Table 2, entry 2) yields cleavage products **3** and **4a-c**, and monoactetate **2b**, however, the mass balance of recovered monomers is only 21% for guaiacol-based monomers and 13% for dimethoxyphenyl based monomers. No starting **1b** is recovered, indicating that mass loss likely results from styrenic **5b** polymerization. Increasing the Pd catalyst loading to La:Pd = 5:3 (Table 2 entries 3 and 4) increases the recovered monomer yields to 66% and 58% for guaiacol and dimethoxyphenyl based monomers, respectively. Finally, decreasing the La:Pd ratio to 1:1 results in 97% and 96%, recovery of the guaiacol and dimethoxyphenyl monomers, respectively (Table 2, entry 5), indicating an optimal catalyst ratio for reducing the steady-state **5b** concentration and suppressing secondary polymerization. Concentrating (Table 2, entry 6) the reaction solution results in slightly lower monomer unit recovery, albeit with similar conversions for β-O-4 aryl-ether cleavage (28% remaining **2b** versus 27% **2b** for entry 5). Diluting the reaction solution (Table 2, entry 7) at similar catalyst ratios yields higher dimethoxyphenyl monomer recovery (96%) but lower β-O-4 aryl-ether cleavage (52 % **2b**).

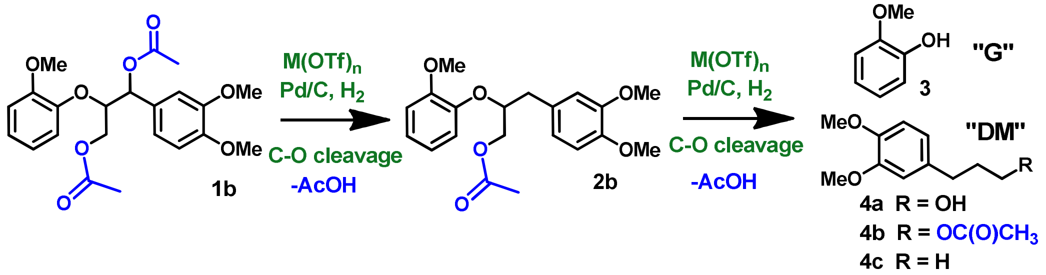
The results in entries 5-7 indicate that conducting the reaction in $Cl_2C_2H_4$ at 0.025 M substrate and 5 mol% Pd and La is optimum for **1b** hydrogenolysis. Interestingly, changing the solvent to higher boiling $Cl_4C_2H_2$ accelerates β-O-4 aryl-ether cleavage with only 14% **2b** recovered, but with lower monomer yields -- 73 and 61 % for guaiacol and dimethoxyphenyl units, respectively. Analysis of the reaction mixture by GC-MS reveals the presence of dimeric tetrachlorodienes ($Cl_4C_4H_2$), likely resulting from Pd-catalyzed $Cl_4C_2H_2$ dehydrohalogenation, followed by radical coupling of the resulting dichloroalkenes.[12] This may depress monomer yields by either "poisoning" the Pd catalyst, in turn increasing the concentration of styrenic unit **5b**, leading to increased polymerization, and/or via HCl release inducing monomer degradation and cationic styrenic polymerization.

This tandem lignin hydrogenolysis was also investigated in the room temperature ionic liquid [EMIM][OTf] (EMIM = ethylmethyl-imadizolium) as an alternative solvent to 1,2-dichloroethane.[13] Since commercially available Pd/C is not stable in in [EMIM][OTf], atomic layer deposited Pd@ALD[12d] was utilized. In this case, no monomeric cleavage products are obtained up to 185 °C, most likely



Scheme 2. Step-wise reaction profile for 1a,b C-O hydrogenolysis using a tandem $M(OTf)_n$ + Pd/C catalyst

Table 2. Acetylated dimer hydrogenolysis with a tandem $La(OTf)_3$ + Pd/C catalyst



Entry	$La(OTf)_3$	Pd/C	Temp (ºC)	H_2 (psi)	Time (h)	Yields (%)						Mass Balance %
						1b	2b	3	4a	4b	4c	G : DM
1	5%	1%	140	600	2	-	-	39	-	-	-	39 : 0
2	10%	2%	140	600	2	-	8	13	2	1	2	21 : 13
3	5%	3%	140	600	16	-	24	14	2	3	6	38 : 35
4	10%	6%	140	600	16	-	23	43	9	9	17	66 : 58
5	5%	5%	140	600	16	-	27	69	18	19	32	97 : 96
6[b]	5%	5%	140	600	16	-	28	56	6	19	11	78 : 64
7[c]	5%	5%	140	600	16	-	52	13	22	13	12	13 : 97
8[d]	5%	5%	140	600	2	-	14	59	14	34	7	73 : 61

[a]Reaction conditions: 4 mL $Cl_2C_2H_4$, 0.1 mmol **1b** ([**1b**] = 0.25 mM). Upon completion, reactor was cooled to 25 °C, and contents filtered to remove catalyst. Solvent then removed *in vacuo* to yield beige/brown oily solids. Internal CH_3NO_3 standard added. Product yields determined by ^{1}H NMR with reference to the internal standard by comparison to known component spectra. GC-MS analysis also performed on each sample as confirmation. G = guaiacol unit recovered (**2b** and **3** yields from **1b**). DM = dimethoxyphenyl unit recovered; **2b**, **4a**, **4b**, and **4c** yields from **1b**. [b]2 mL (0.50 mM). [c]6 mL (0.17 mM). [d.] 4 mL in $Cl_4C_2H_2$ (0.25 mM).

due to the reduced activity of Pd@ALD in comparison to Pd/C.[14]

In conclusion, we have successfully applied a tandem $M(OTf)_n$ + Pd/C catalytic system to the thermodynamically leveraged hydrogenolysis of acetylated model lignins. Selective cleavage is achieved via kinetic control of the two principal reaction steps, the rate of C-O scission versus that for hydrogenation. Future efforts will investigate the application of this cleavage reaction process to acetylated guaiacol-based Kraft lignins. Preliminary experiments indicate that this catalyst system also yields aromatic products from acetylated lignins.[15]

ASSOCIATED CONTENT

Experimental details, procedures, and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

* t-marks@northwestern.edu

Present Addresses

‡ (Z.L.) ShanghaiTech University, 100 Haike Road, Pudong District, Shanghai 201210, China.

Notes

The author's declare no competing financial interest.

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14. The dimer and monomer products were extracted from the ionic liquid (after dilution with water) with both toluene and dichloromethane, which both increases the amount of waste generated, but reduces the ease of ionic liquid recycling.[13] Therefore, using 1,2-dichloroethane (widely used industrially) was deemed reasonable as it is much easier to recycle, contain, and limit overall waste generation. Furthermore, 1,2-dichloroethane has very low solubility in H2O (0.84g/100g), which would enable easier cleanup of potential waste water streams.

15 La(OTf)$_3$ + Pd/C can also produce aromatic monomers from phenolic lignin, however, unlike the methoxy-substituted aromatic groups described in the present contribution, significant amounts of the phenolic aromatic groups are over-hydrogenated to cycloalkanes.

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