## Selective Hydrogenolysis of Arenols with Hydrosilanes by Nickel Catalysis

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Nickel-catalyzed hydrogenolysis of arenols has been developed through the use of hydrosilane as a reductant. Sterically demanding *N*-heterocyclic carbene (NHC) ligands are crucial for the reaction. The present protocol allows selective cleavage of Ar–O bonds of arenols over aryl and benzyl ethers.

Hydrogenolysis of Ar-O bonds in arenols and aryl ethers has gained much interest because aromatic chemicals for fuels and value-added chemicals can be obtained from renewable biomass such as lignin by such transformations.<sup>1</sup> However, these transformations are challenging because the bond dissociation energy is higher than that of other C-O bonds.<sup>2</sup> Selective hydrogenolysis of hydroxy groups over alkoxy groups in arenes is particularly difficult, although such a reaction could enable the regioselective functionalization of arenes derived from ligninbased chemical feedstocks. Selective hydrogenolysis of phenolic hydroxy groups over alkoxy groups has generally been achieved through 2-steps procedures; conversion of the hydroxy groups to activated forms such as sulfonates, esters, and ethers, followed by metal-catalyzed reductive cleavage of the resulting activated Ar-O bonds.<sup>3,4</sup> Direct reductive cleavage of phenols has been reported recently by Ir catalysis with H<sub>2</sub><sup>5</sup> and using an excess amount of LiAlH<sub>4</sub>/bases.<sup>6</sup> Although these methods reduce Ar–OH bonds exclusively over aromatic unsaturated bonds, aryl ethers are not compatible under relatively harsh reaction conditions. Herein, we report that a nickel catalyst bearing an Nheterocyclic carbene (NHC) ligand enables the hydrogenolysis of phenolic hydroxy groups with hydrosilanes as the hydrogen source. Notably, aryl and benzyl ethers are compatible under the newly developed reaction conditions.

We first examined the hydrogenolysis of the Ar-OH bond in 4-tert-butylphenol (1a) with HSi(OMe)<sub>2</sub>Me (Table 1). After screening various parameters, the reaction of 1a (0.30 mmol) with HSi(OMe)<sub>2</sub>Me (0.66 mmol) in the presence of [Ni(cod)<sub>2</sub>] (5.0 mol %) and  $Me_2N$  IPr<sup>7</sup> (5.0 mol %) in toluene at 120 °C for 24 h gave tert-butylbenzene (2a) in 88% yield, as estimated by GC analysis (Entry 1). Different ligands were then examined for the same reaction (Entries 2-8). 2a was not observed in the absence of a ligand or with PCy<sub>3</sub> as a supporting ligand for nickel (Entries 2 and 3), whereas PCy<sub>3</sub> was reported to be effective for the nickel-catalyzed hydrogenolysis of Ar-OMe bonds.<sup>4a,4b,4e</sup> Among NHC ligands, IPr and SIPr resulted in poor yields (Entries 4 and 5), although SIPr was known as the ligand of choice for the nickel-catalyzed hydrogenolysis of Ar-OAr bonds with H2.4c,4f Less electron-donating ClIPr did not afford the desired product (Entry 6), while more electron-donating <sup>Me</sup>IPr and <sup>Me</sup>IPr<sup>OMe</sup> were effective (Entries 7 and 8). The reaction using the NHC ligand generated in situ from Me2NIPr·HOTf and 'BuONa did not give 2a (Entry 9). Different hydrosilanes were also screened (Entries 10-13). Other hydrosilanes such as HSiEt<sub>3</sub> and HSi(OTMS)<sub>2</sub>Me did not afford 2a (Entries 10 and



Entry	Variation from the standard conditions	$\frac{1}{2a}/\%^a$
1	none	88
2	No <sup>Me<sub>2</sub>N</sup> IPr	<1
3	PCy <sub>3</sub> (10 mol %) instead of <sup>Me<sub>2</sub>N</sup> IPr	<1
4	IPr instead of <i>Me</i> <sub>2</sub> <i>N</i> IPr	4
5	SIPr instead of <i>Me</i> <sub>2</sub> <i>N</i> IPr	3
6	<sup>Cl</sup> IPr instead of <sup>Me<sub>2</sub>N</sup> IPr	<1
7	<sup>Me</sup> IPr instead of <sup>Me<sub>2</sub>N</sup> IPr	78
8	<sup>Me</sup> IPr <sup>OMe</sup> instead of <sup>Me<sub>2</sub>N</sup> IPr	85
9	$Me_2N$ IPr•HOTf + <sup>t</sup> BuONa (0.03 mmol) instead of $Me_2N$ IPr	<1
10	HSiEt <sub>3</sub> instead of HSi(OMe) <sub>2</sub> Me	<1
11	HSi(OTMS) <sub>2</sub> Me instead of HSi(OMe) <sub>2</sub> Me	<1
12	HSi(OEt) <sub>3</sub> instead of HSi(OMe) <sub>2</sub> Me	6
13	PMHS instead of HSi(OMe) <sub>2</sub> Me	39

<sup>a</sup>The yield was determined by GC analysis using undecane as an internal standard.

11), whereas  $HSi(OEt)_3$  and PMHS gave **2a** in low yields (Entries 12 and 13).

The reaction on a 1.0 mmol scale under the standard conditions for 24 h gave 2a in 86% by GC analysis (Table 2, Entry 1). A range of substituted phenols participated in the hydrogenolysis reaction to give the corresponding arene products **2b–2d** in modest to excellent yields (Entries 2–6). Notably, the benzylic C–O bond of silylether 1d (Entry 4) and *ortho-* and *para*-Ar–OMe bonds in 1e and 1f (Entries 5 and 6) were tolerated under the reaction conditions, allowing exclusive removal of their hydroxy groups. Both 1- and 2-naphthols were converted to naphthalene in good yields (Entries 7 and 8). Substrates containing a carbonyl functionality were not converted under these reaction conditions. In addition, the reaction of 1b in the presence of *tert*-butyl benzoate or *N*-methylacetanilide was retarded, whereas the dehydrogenative silylation of 1b was observed. The carbonyl functionalities likely inhibit the



 Table 2. Hydrogenolysis of arenols with hydrosilanes catalyzed by nickel

<sup>a</sup>Isolated yields. Values in parenthesis are yields determined by GC analysis using undecane as an internal standard. <sup>b</sup>Average of two independent reaction runs. <sup>c</sup><sup>Me</sup>IPr was used instead of <sup>Me<sub>2</sub>N</sup>IPr.

subsequent hydrogenolysis step (vide infra) in a way that is elusive at present.

A plausible reaction mechanism is depicted in Scheme 1. Although details remain yet to be clarified, we propose that the dehydrogenative silylation of arenols first proceeds by nickel



**Scheme 1.** Plausible mechanism for nickel-catalyzed hydrogenolysis of arenols with hydrosilanes.



Scheme 2. Hydrogenolysis of aryl silyl ether.

catalysis to give aryl silyl ether **3** with H<sub>2</sub> evolution, which was reported very recently<sup>8</sup> and confirmed by us using <sup>1</sup>H NMR and/ or GC-MS. Then, oxidative addition of the Ar–O bond of the aryl silyl ethers thus formed to nickel(0) gives nickel(II) intermediate **4**. Transmetalation between **4** and hydrosilanes giving **5** is followed by reductive elimination to give arene products **2** and regenerate nickel(0). On the other hand, we cannot exclude another catalytic cycle involving a silyl–Ni(I) species.<sup>4e</sup>

Since  $H_2$  is generated in the initial dehydrogenative silylation step, one can argue that the subsequent hydrogenolysis proceeds with  $H_2$  rather than with hydrosilanes.<sup>4c</sup> To verify this possibility, the reaction of **1a** with an equimolar amount of HSi(OMe)<sub>2</sub>Me was performed to confirm quantitative formation of the corresponding aryl silyl ether and liberation of  $H_2$  from an open reaction vessel by <sup>1</sup>HNMR (Scheme 2). The resulting mixture was transferred to a closed vessel, pressurized with  $H_2$ , and heated at 120 °C for 24 h to show a trace amount of **2a**, whereas treatment of the residue with the hydrosilane reagent gave **2a** in 78% yield. These experiments support the proposed mechanism in which the hydrosilane serves as a reductant in the hydrogenolysis step.

The silyl ether intermediate in the present hydrogenolysis was also confirmed by the reactions of trimethylsilyl ethers **6a** and **6b** derived from **1a** and **1b**, respectively (eq 1). The reaction conditions optimized for the hydrogenolysis of arenols also effect the reduction of **6a** and **6b**. The corresponding methyl ethers **7a** and **7b** reacted sluggishly, showing that aryl silyl ethers are more reactive than alkyl aryl ethers under the present conditions for achieving the chemoselectivity observed with **1e** and **1f** (Entries 5 and 6 of Table 1), although the rationale for the reactivity difference is yet to be elucidated.

OR <sup>2</sup>	[Ni(cod) <sub>2</sub> ] (5.0 mol%) <sup>Me<sub>2</sub>N</sup> IPr (5.0 mol%) HSi(OMe) <sub>2</sub> Me (0.36 mmol)					
R <sup>1</sup>	toluene, 120 °C, 24 h					(1)
(0.30 mmol)		R <sup>1</sup>	R <sup>2</sup>	G	C Yield (%)	
		<sup>t</sup> Bu Ph <sup>t</sup> Bu Ph	SiMe <sub>3</sub> SiMe <sub>3</sub> Me Me	(6a) (6b) (7a) (7b)	45 ( <b>2a</b> ) 96 ( <b>2b</b> ) 4 ( <b>2a</b> ) 46 ( <b>2b</b> )	

In conclusion, we have developed the nickel-catalyzed hydrogenolysis of arenols using hydrosilanes as a reducing agent. Unreactive Ar-OH bonds can be activated without conventional pre-activation through ester formation. In this transformation, hydrosilane plays two key roles; in situ activation of arenols through the formation of aryl silvl ethers and reduction of the Ar-O bond of the silvl ethers thus formed, both catalyzed by nickel/NHC. It is worth noting that aryl alkyl ethers and benzyl silyl ethers are compatible under the reaction conditions, whereas nickel catalysis has been demonstrated to effect the activation and functionalization of their C-O bonds.4c,4f,4g The present protocol can be complementary to these known nickel-catalyzed protocols to access variously substituted arenes from lignin-derived chemical feedstocks. Further studies on nickel-catalyzed direct transformations of arenols are currently underway in our laboratory.

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