

**Nickel Catalyzed Silane Reductions of  $\alpha$ ,  $\beta$  - Unsaturated Ketones and Nitriles**

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**Abstract:** Activated nickel, produced by the ultrasound-promoted reduction of nickel iodide with lithium, catalyzes the 1,4 addition of phenylsilane to  $\alpha$ ,  $\beta$ -unsaturated ketones and  $\alpha$ ,  $\beta$ -unsaturated nitriles to give, after hydrolysis, high yields of the products of 1, 2 hydrogenation. © 1998 Elsevier Science Ltd. All rights reserved.

Selective reduction of the carbon carbon double bond in conjugated systems can be achieved with a broad range of reagents.<sup>1</sup> For  $\alpha$ ,  $\beta$ -unsaturated ketones metal-based methodology such as alkali metals in liquid ammonia or amalgamated zinc in hydrochloric acid give variable yields and are often accompanied by undesirable side products.<sup>2</sup> The hydrides of sodium, aluminum, borane and the transition series offer a number of advantages over the more traditional methods of catalytic hydrogenation and metal reduction but often fail to give high selectivity.<sup>3</sup>

Metal complex catalyzed additions of  $H_2$  to  $\alpha$ ,  $\beta$ -unsaturated ketones can reduce the C=C bond selectively<sup>4</sup> by a variety of reagents including Zn-NiCl<sub>2</sub> in the presence of ultrasound,<sup>5</sup> Co<sub>2</sub>(CO)<sub>8</sub>(PR<sub>3</sub>) in the presence of phosphine ligands,<sup>6</sup> Pd/C in ethanol,<sup>7</sup> C<sub>1</sub>Rh(PPh<sub>3</sub>)<sub>3</sub> in benzene or absolute ethanol.<sup>8</sup>

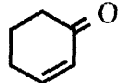
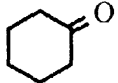
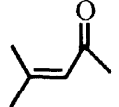
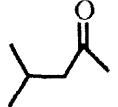
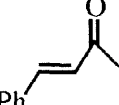
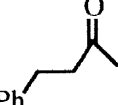
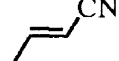
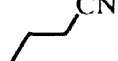
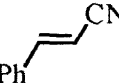
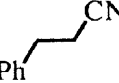
Conjugate reduction of  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds has been achieved through hydrosilylation with a number of metal complexes and hydrosilanes.<sup>9</sup> Ojima has reported that Wilkinson's catalyst will promote hydrosilylation of  $\alpha$ ,  $\beta$ -unsaturated ketones with high selectivity.<sup>10</sup> Recently, Kienan and coworkers used composite reducing systems of tin or silicon hydrides with various transition metal catalysts exhibiting superior selectivity in the conjugate reduction of Michael acceptors.<sup>11</sup>

We have demonstrated that activated nickel, produced from the ultrasonically assisted reduction of nickel iodide by lithium,<sup>12</sup> is an efficient catalyst for the hydrosilylation of olefins.<sup>13</sup> Here we report the surprisingly clean, high yield reaction of phenylsilane with  $\alpha$ ,  $\beta$ -unsaturated ketones and nitriles under mild conditions to give, after hydrolysis, the products of 1,2 hydrogenation.

In a typical experiment, activated nickel is prepared by refluxing, or sonicating in a cleaning bath, NiI<sub>2</sub> [0.044 g (0.14 mmol)] and Li [0.002 g (0.28 mmol)] in THF (3 mL) for 1.5 h. To this PPh<sub>3</sub> [0.04 g (0.15 mmol)], PhSiH<sub>3</sub><sup>14</sup> [0.88 mL (0.77 g, 7.13 mmol)] and cyclohexenone [0.68 mL (0.68 g, 7.02 mmol)] are added. Refluxing the mixture for 1 h led to complete consumption of starting materials. Hydrolysis followed by GLC analysis showed yields of >95% of cyclohexanone. Analysis of the reaction mixture prior to hydrolysis using GC-MS shows two major primary products whose m/z values and fragmentation patterns are consistent with 1-cyclohexenoxyl phenylsilane (**1**) and bis(cyclohexen-1-oxy)phenylsilane (**2**). The relative ratio of **1**:**2** is approximately 85 : 15 based on peak areas in the GC spectrum

This methodology has some noteworthy conveniences: (1) the reaction is selective for C=C reduction; (2) the primary reagents, activated nickel (commercial nickel is ineffective under these conditions) and phenylsilane, are readily available; (3) the activated nickel is fully recoverable and recyclable; (4) the reaction condition is mild and neutral; (5) the yields are high. Our results are summarized in Table 1.

Table 1. Nickel catalyzed reduction of  $\alpha$ ,  $\beta$ -unsaturated ketones and nitriles  
 $RHC=CHE$  ( $E = COR', CN$ ) +  $PhSiH_3 \rightarrow RCH_2CH_2E$  (Cat.  $Ni^*$ ,  $PPh_3$ )

Entry	Substrate	Silane	Product	Yield (%) <sup>a</sup>
1		$PhSiH_3$		95
2		$PhSiH_3$		90
3		$PhSiH_3$		95
4		$PhSiH_3$		90
5		$PhSiH_3$		95

a) GLC yields, using decane (100  $\mu$ L) as an internal standard.

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