Olefinic Reduction of α,β-Unsaturated Carbonyl Compounds Catalyzed by Activated Nickel

Soon Ok Kim,* Sora Rhee, and Seon Hwa Lee

Department of Chemistry, Sungshin Women's University, Seoul 136-742, Korea

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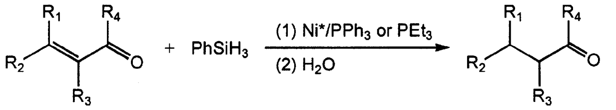
Hydrogenation of α,β-unsaturated carbonyl compounds is a widely used reaction in organic synthesis. The main problem of this reaction is to obtain an optimal regioselectivity in favor of the olefin or the carbonyl reduction. Most popular of selective reducing agents are the various metal hydrides, which, however, can limit their usefulness when high chemoselectivity is required.[1] Selective reduction of the olefinic bond of an enone system has been frequently achieved through hydrosilation.[2] The use of several transition metal catalysts for the hydrosilation was introduced[3-5] and rhodium catalysts have attracted much attention from the viewpoint of organic synthesis due to their catalytic activity, easy preparation and reduction.[4,6] It was found that, however, the rhodium catalysts method had the disadvantage of the formation of inseparable isomers, which reduced the purity of the isolated product. It has been reported that Wilkinson's catalyst may have high selectivity to promote hydrosilation of α,β-unsaturated ketones.[7] In recent years, mixed reducing systems of tin or silicon hydrides with various transition metal catalysts have been used because of their superior selectivity on the conjugate reduction.[8]

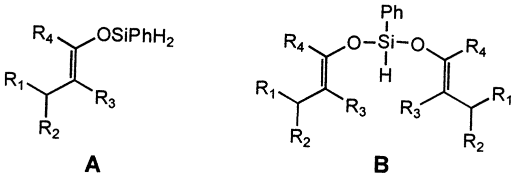
In this investigation, we demonstrate the efficiency of activated nickel (Ni*), freshly prepared from the reduction of nickel iodide by lithium, as the catalyst for the hydrosilation of olefins in an enone system and describe a scope and limitations of the proposed simple reducing system comprised of phenylsilane and activated nickel in relfuxing THF.



A typical reduction was carried out according to the following procedure: The reduction of nickel iodides (NiI_2; 28.92 mg, 0.09255 mmol) with lithium powder (Li; 1.290 mg, 0.1858 mmol) in THF (2 mL) was performed in an hour with refluxing. Triphenylphosphine (PPh_3; 26.19 mg, 0.1000 mmol), phenylsilane ($PhSiH_3$; 513.3 mg, 4.753 mmol) and 4,4-dimethyl-2-cyclohexen-1-one (580.3 mg, 4.680 mmol) were added to freshly generated nickel catalyst. Refluxing the mixture with THF for an hour led to complete consumption of starting material. The resulting silylenol ether was hydrolyzed and gas chromatography-mass spectrometric (GC-MS) examination of the product mixture showed yields of > 98% of 4,4-dimethylcyclohexanone.[9]

Two major intermediate products were detected in the reaction mixture prior to hydrolysis by GC-MS system. Their m/z values and fragmentation patterns were found to be consistent with the typical structures of A and B. In GC-MS chromatograms, the relative peak area ratio of A to B was approximately 15 : 85. These findings indicate that reaction conditions including less than one equivalent of phenylsilane toward a starting α,β-unsaturated carbonyl compound may be achievable in the present work.

The reaction conditions used are mild and neutral. Though commercial nickel is inert under these conditions, activated nickel powder is easily prepared. Phenylsilane is readily available and most of the products are formed in consistently good yield (approximately 100%). In the case of unsaturated esters, their low reactivity may stem from the unfavorable electronic effect of a carbalkoxy group. In addition of these advantages, the generality of the method (see Table 1) and the very simple and convenient experimental procedure make our reduction system superior to most other known procedure for conjugate reduction.[8,10]

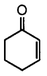
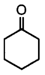
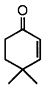
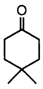
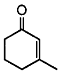
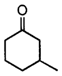
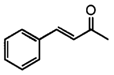
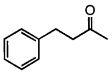
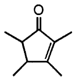
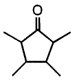
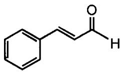
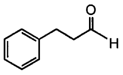
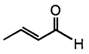
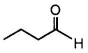
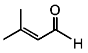
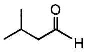
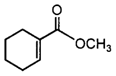
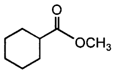
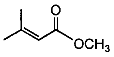
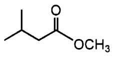


In proposed reducing system, phenylsilane is an inactive source of hydride donor. Activated nickel is thought of a transfer agent that can deliver the hydride selectively from phenylsilane to the olefinic bond of enone system, because it has been known that activated nickel readily inserts into Si-H bond and also binds specifically to alkene.[11,12] It seems likely that the donor capabilities of triphenylphosphine or triethylphosphine enhance the insertion of nickel into Si-H bond.[11] Their donor capacities were observed to be almost identical in this reaction.

The activity of nickel catalyst was highly enhanced when it was freshly generated in refluxing THF. Its activity had a significant effect on the yields of products (Table 1). That is, freshly prepared nickel led essentially to conjugate reduction with very high yields in the most α,β-unsaturated carbonyl compounds tested. On the contrary, in the reaction conditions with nickel powder exposed to air or elapsed more than 5 h from its generation, these substrates were inactive to this reaction.

In conclusion, a simple reducing system composed of phenylsilane and activated nickel in refluxing THF was found to be capable of efficient conjugate reduction of α,β-unsatur-

Table 1. Conjugate reductions of α,β-unsaturated carbonyl compounds with $PhSiH_3$/Ni*/PPh_3[a]

No.	Substrates	Products	Yield[b] (%)
1			93.1
2			98.0
3			100
4			96.9
5			81.9
6			98.6
7			100
8			100
9			6.4
10			7.7

[a] All reactions were carried out with 4.680 mmol of substrate, 0.09255 mmol of freshly prepared Ni*, 0.1000 mmol of PPh_3 and 1.0-1.5 equivalent of $PhSiH_3$ in 2 mL of refluxing THF for 1 h. [b] Yields were determined by GC-MS, using an internal standard. All products were fully identified by comparison with authentic samples. The yields of isolated products were approximately 48.9-62.3%.

ated carbonyl compounds. The process involved activated nickel-catalyzed hydrosilation, followed by hydrolysis of the intermediate silylenol ether. Activated nickel was prepared by lithium reduction of nickel iodide in refluxing THF and its activity was decreased as time goes on.

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9. Spectral data for 4,4-dimethylcyclohexanone: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.20 (s, 6H), 1.67 (t, 4H, J = 6.9 Hz), 2.35 (t, 4H, J = 6.9 Hz); IR (KBr) 2959, 2860, 1467, 1713 cm^{-1}; MS (EI) m/z (%) 126 (M$^+$, 7.11), 111 (30.1), 97 (16.0), 93 (22.0), 83 (14.1), 77 (16.0), 70 (100).
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