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Copper(I) salt mediated 1,4-reduction of α, β-unsaturated ketones using hydrosilanes

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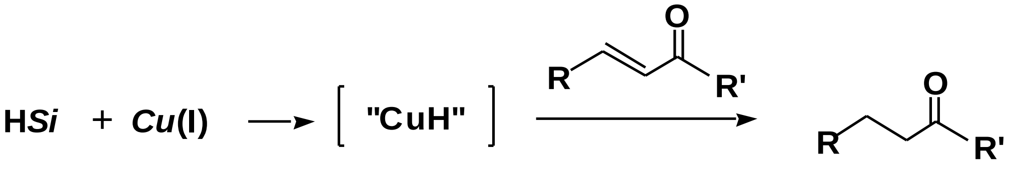
Reduction of α,β-unsaturated ketones with dimethylphenylsilane in the presence of $CuF(PPh_3)_3 \cdot 2EtOH$ is carried out to effect the reaction in a 1,4-selective manner to give the corresponding saturated ketones in excellent yields.

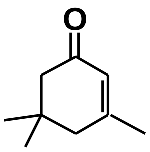
Transfer of organic groups of organosilanes to metallic species, *transmetalation*, has been our recent concern since a number of metal mediated synthetic reactions involve transmetalation as a key step.[1] The organometallic species, thus formed, undergo further transformations such as carbon-carbon or carbon-heteroatom bond formations by the reaction with several organic substrates.[2] We have disclosed that organosilicon compounds such as alkenyl-, aryl- and alkynylsilanes induce homo-coupling reactions to yield the corresponding 1,3-dienes, biaryls and 1,3-diynes, respectively, in the presence of copper(I) salt in a polar solvent.[3] The findings suggest that transmetalation of the organosilanes to copper occurs to give the organocopper species, the novel transmetalation being remarkable since an organic group on silicon is assumed to transfer onto copper without using an additional activator.[4,5] Our interest has accordingly been turned to the transmetalation of hydrosilanes to copper to generate *copper hydride* species, with which reduction of a variety of organic molecules has been reported.[6] Although the combination of a copper salt and hydrosilane has rarely been studied comparing with the reagents made of the copper salt and metal hydrides such as aluminum and tin,[7] the desired reaction, we considered, would proceed by a proper choice of the counter ion and a ligand of copper. After screening several Cu(I) species, we found that $CuF(PPh_3)_3$-$HSiPhMe_2$ system could effect 1,4-selective reduction of α,β-unsaturated ketones under mild conditions.



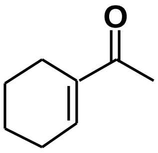
The reaction was studied using 1-phenyl-1-buten-3-one (**1a**) as a substrate and dimethylphenylsilane (**2a**) as a reducing agent in the presence of a copper(I) salt. Molar ratio of the substrate, hydrosilane, and copper salt as well as solvent, reaction temperature and period were examined. We found that the use of 2 mol amounts of **2a** and 1 mol amount of $CuF(PPh_3)_3 \cdot 2EtOH$[8] (**3**) in *N*,*N*-dimethylacetamide (DMA) was the optimum to yield 1-phenyl-2-butanone (**4a**) in a quantitative yield.[9] Results are summarized in Table 1. The yield decreased to 63% when 1 mol amount of **2a** was used. Using a catalytic amount of **3**, the reaction similarly proceeded with slight decrease in yield along with the formation of a small amount of unidentified product as well as a trace amount of 1,2-reduction product **5a**. Concerning hydrosilane, **2a** and triethylsilane (**2b**) exhibited high 1,4-selectivities to give the corresponding ketone in excellent yields, but diphenylsilane (**2c**) considerably decreased the selectivity to give **4a** and **5a** in 49% and 36% yields, respectively, in contrast with the results on rhodium-catalyzed hydrosilylation of α,β-unsaturated ketones.[10] No reaction occurred with $HSiPhCl_2$ (**2d**).

(Table 1)

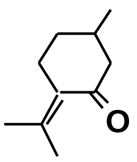
Reactions of several α,β-unsaturated ketones were carried out similarly to the optimized condition as shown in Table 1. The reactions of 2-cyclohexen-1-one (**1b**), 3-nonen-2-one (**1c**), chalcone (**1d**), and carvone (**1e**) proceeded in excellent yields with high 1,4-selectivity. However, sterically congested enones such as isophorone (**1f**), 1-acetyl-1-cyclohexene (**1g**), and pulegone (**1h**) were recovered unchanged.[11] The results also contrast to those on the reactions catalyzed by rhodium complex,[10] which undergoes the reduction of enones (**1f-h**) smoothly in a highly 1,4-selective manner. In this sense, our systems appears to be highly chemoselective. Indeed, the reaction of a 1:1 mixture of **1a** and **1f** with **2a** in the presence of **3** cleanly produced **4a** (99%) along with complete recovery of **1f** (97%).



1f



1g



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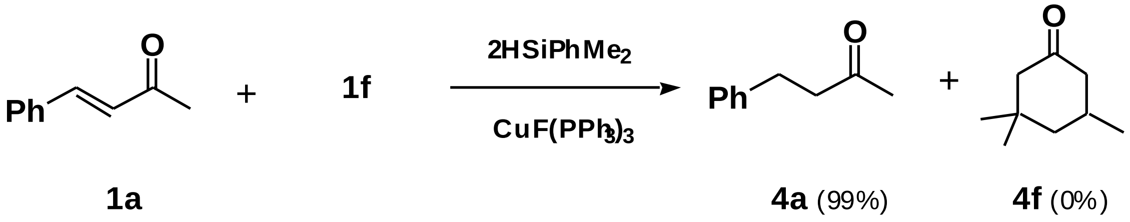
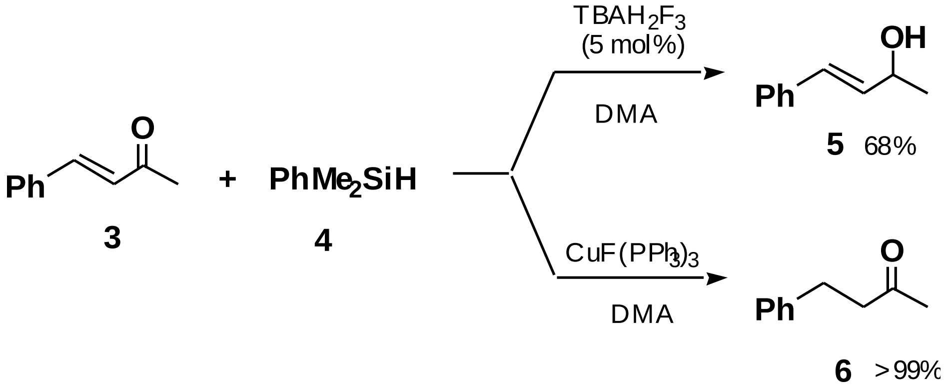


Although the mechanistic study on the transmetalation of organosilane to copper remains yet to be studied, the activation of hydrosilanes by copper fluoride **3** seems to be rather different from that by tetrabutylammonium fluoride (TBAF) or the related reagents. The reaction of **1a** and **2a** in the presence of 5 mol% of TBAHF$_2$

(tetrabutylammonium hydrogendifluoride)[12] resulted in giving predominantly 1,2-reduced product **5a** in 68% yield. Thus, 1,4- and 1,2-selective reduction of α,β-unsaturated ketones with hydrosilanes are accessible by a proper choice of copper(I) fluoride or TBAHF$_2$ in a highly selective manner, respectively.



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9 A typical experimental procedure follows: $CuF(PPh_3)_3\cdot 2EtOH$ (0.25 mmol) was dissolved in 2 mL of DMA to give a colorless clear solution, to which was added $HSiPhMe_2$ (**2**, 0.5 mmol) at 0 ˚C to give a reddish homogeneous solution. The color of the solution gradually changed to yellow after the addition of 1-phenyl-1-buten-3-one (**1a**, 0.25 mmol). The temperature of the reaction mixture was gradually raised to room temperature, and stirring was continued for 6 h to furnish **4a** in a quantitative yield after workup.

10 I. Ojima and T. Kogure, *Organometallics*, 1982, **1**, 1390. G. Z. Zheng, T. H. Chan, *ibid.*, 1995, **14**, 70.

11 The reaction of an α,β-unsaturated ester (methyl cinnamate) also resulted in no reaction. On the other hand, an α,β-unsaturated aldehyde (cinnamaldehyde) was found to effect 1,2-reduction, predominantly.

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Table 1. Copper(I) salt mediated reactions of a,b-unsaturated ketones with hydro silanes in the presence of CuF(PPh3)3 2EtOHa

substrate	hydrosilane	product (yield/%)
PhCH=CHCOMe (**1a**)	HSiPhMe2 (**2a**)	Ph(CH2)2COMe (**4a**, > 99)
1a	**2a**	**4a** (63)b
1a	**2a**	**4a** (69), PhCH=CHCH(OH)Me (**5a**, trace)c
1a	HSiEt3(**2b**)	**4a** (95)
1a	H2SiPh2(**2c**)	**4a** (49), **5a** (36) PhCH=CHCH(OH)Me
1a	HSiPhCl2(**2d**)	no reaction
(**1b**)	**2a**	(**4b**, 91)
n-C5H11CH=CHCOMe (**1c**)	**2a**	*n*-C5H11(CH2)2COMe (**4c**, 91)
PhCH=CHCOPh (**1d**)	**2a**	Ph(CH2)2COPh (**4d**, 98)
	2ad	

(**1e**) (**4e**, 85)e

a) The reactions were carried out using enone (**1**, 1.0 mmol), silane (**2**, 2.0 mmol) and CuF(PPh3)3 2EtOH (**3**, 1.0 mmol) unless specified. The yields are based on 1H NMR analyses using Cl2C=CHCl as an internal standard. b) 1 mol amount of **2a** was used. 21% of **1** was recovered. c) CuF(PPh3)3 (5 mol%) was used. d) 4 mol amout of **2a** was used.
e) Diastereomeric ratio was ca. 8:1.