JOC Notes

Asymmetric Hydrosilylation of Ketones Catalyzed by Magnetically Recoverable and Reusable Copper Ferrite Nanoparticles

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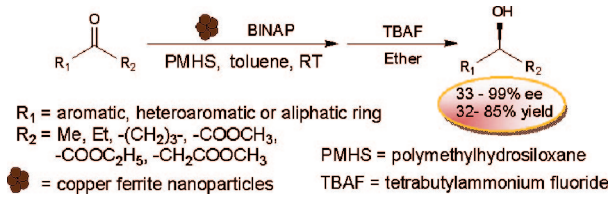

Herein we present magnetically recoverable and reusable copper ferrite nanoparticles for asymmetric hydrosilylation of several ketones. Up to 99% enantiometric excess was obtained at room temperature using polymethylhydrosiloxane as the stoichiometric reducing agent. The copper ferrite nanoparticles were magnetically separated, and the efficiency of the catalyst remains almost unaltered up to three cycles.

Intensive studies have recently been focused on the development of asymmetric catalytic systems owing to their importance in synthetic organic chemistry.[1] Catalytic asymmetric reduction of prochiral ketones leads to the formation of enantiomerically pure chiral alcohols, which are key building blocks for the manufacture of pharmaceuticals, agrochemicals, and advanced materials.[2] Asymmetric hydrogenation[3] and transfer hydrogenation[4] are the most frequently used catalytic methods for the reduction of prochiral ketones using transitional metal chiral complexes. As a result of exceedingly mild reaction conditions and operational simplicity, much effort has been directed toward the development of asymmetric hydrosilylation of carbon−carbon and carbon−heteroatom bonds using precious metals such as rhodium,[5] ruthenium,[6] and iridium.[7] Recently, asymmetric hydrosilylation of prochiral ketones using polymethylhydrosiloxane (PMHS), an inexpensive, nontoxic polymer coproduct of the silicon industry, as hydride source and easily accessible catalysts based on titanium,[8] zinc[9] and tin[10] have opened a new pathway in this area. Very recently, iron-catalyzed asymmetric hydrosilylation reactions are also reported.[11] The utility of copper for hydride delivery was studied with the Stryker reagent [CuH·PPh_3], a stoichiometric reducing agent for the reduction of enones.[12] Buchwald described a highly enantioselective 1,4-reduction of α,β-unsaturated esters and β-substituted enones using an active catalyst generated in situ from CuCl/NaO-*t*-Bu/chiral diphosphine ligands and PMHS.[13] The effectiveness of [CuH·PPh_3] for the hydrosilylation of carbonyl compounds was reported by Lipshutz.[14] Subsequent studies by the same group led to the development of highly enatioselective hydrosilylation of ketones based on CuCl/NaO-*t*-Bu/chiral diphosphine ligands.[15] Copper fluoride and copper acetate also catalyzed the asymmetric hydrosilylation reaction of prochiral ketones in presence of BINAP ligand.[16]

Industry favors the catalytic process induced by a heterogeneous catalyst over the homogeneous one in view of its ease of handling, simple workup, and regenerability. Recently, Lipshutz

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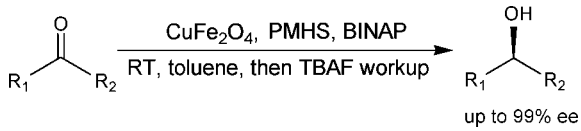
SCHEME 1. Asymmetric Hydrosilylation of Ketones Using Copper Ferrite Nanoparticles



reported copper-in-charcoal as an efficient heterogeneous catalyst for effective hydrosilylation of carbon−carbon and carbon−heteroatom bonds with excellent enantioselectivity.[17]

Magnetic nanoparticles that can be magnetized in the presence of an external magnet have been studied extensively for various biological applications such as magnetic resonance imaging, drug delivery and as biomolecular sensors.[18] Recent reports show that magnetic nanoparticles are efficient supports for catalysts and can facilitate their separation from the reaction medium after magnetization with a permanent magnetic field.[19] Recently we reported copper−aluminum hydrotalcite catalyst for asymmetric hydrosilylation of ketones.[20] As part of our ongoing research aimed at the development of reusable catalysts for various asymmetric organic transformations,[21] we herein present the results on the use of magnetically separable copper ferrite ($CuFe_2O_4$) nanoparticles for the asymmetric hydrosilylation of ketones to chiral secondary alcohols in moderate to good yields and excellent enantiomeric excess (ee) at room temperature using (*S*)-BINAP as a chiral auxiliary and PMHS as the stoichiometric reducing agent (Scheme 1).

Initially, to develop the best magnetically separable catalyst for the asymmetric hydrosilylation of ketones, Fe_3O_4 and different substituted ferrites, MFe_2O_4 ($M = Cu^{2+}$, Co^{2+} and Ni^{2+}), were synthesized by coprecipitation methods as described in the literature[22] (see Supporting Information) and screened in the presence of PMHS. Fe_3O_4 was found to be completely inactive, while $CoFe_2O_4$ and $NiFe_2O_4$ produced very little product with poor ee (Table 1, entries 2 and 3). However, $CuFe_2O_4$ produced (*S*)-phenylethanol in 85% yield with 81% ee (see Table 1). Among the different chiral ligands screened, commercially available BINAP gave excellent yields and ee's greater than that of (*R*)-(+)-2,2′-bis(diphenylphosphino)-6,6′-dimethoxy-1,1′-biphenyl (BIPHEP). The use of bidentate nitrogen-based ligands gave poor yields, and the ee decreased significantly (see Table 1). To know the effect of temperature, the reaction was conducted at 80 and −40 °C. At 80 °C, although the reaction was completed within 6 h, the ee decreased to 69%. However, the reaction was not complete even after 60 h, but the ee increased to 87% when the reaction was carried out at −40 °C (Table 1, entries 5 and 6).

The effect of different organic solvents on the asymmetric hydrosilylation of acetophenone was also examined (see Supporting Information, Table 1). A significant decrease in the rate of reaction and a small amount of product was obtained using polar solvents such as THF. Nonpolar solvents such as toluene produced (*S*)-phenylethanol in excellent yields and ee at room temperature. Next, we studied the activities of various silanes in the asymmetric hydrosilylation of acetophenone in presence of BINAP and $CuFe_2O_4$ nanoparticles (see Supporting Information, Table 1).

TABLE 1. Asymmetric Hydrosilylation of Acetophenone by Different Catalysts and Ligands at Room Temperature[a]

entry	catalyst	ligand	time (h)	yield (%)	ee (%)[b]
1	Fe_3O_4	BINAP	24		
2	$CoFe_2O_4$	BINAP	48	19	10
3	$NiFe_2O_4$	BINAP	48	24	31
4	$CuFe_2O_4$	BINAP	14	85	81
5	$CuFe_2O_4$	BINAP	6	78	69[c]
6	$CuFe_2O_4$	BINAP	60	55	87[d]
7	$CuFe_2O_4$	BIPHEP	24	67	78
8	$CuFe_2O_4$	BINAM	24	18	0
9	$CuFe_2O_4$	*e*	24	26	4
10	$CuFe_2O_4$	*f*	24	8	4
11	$CuFe_2O_4$	*g*	24	14	5
12	$CuFe_2O4$	*h*	24		

[a] Reaction conditions: substrate (1 mmol), PMHS (4 mmol), $CuFe_2O_4$ nanoparticles (10 mg, 4.3 mol % of copper), toluene (3 mL), BINAP (7 mg). [b] Absolute configurations were determined to be (*S*). [c] Reaction at 80 °C. [d] Reaction at −40 °C. [e] 1,2-Diaminocyclohexane was used. [f] 1,2-Diphenylethelene diamine was used. [g] 2,6-Bis[(4*R*)-(+)-isopropyl-2-oxazoline-2-yl] pyridine was used. [h] 2,6-Bis[(4*R*,5*R*)-4-methyl-phenyl-2-oxazolinyl] pyridine was used.

Monoaryl silanes such as phenylsilane ($PhSiH_3$) afforded excellent yields with good enantioselectivity in a short period of time (Supporting Information, Table 1, entry 4), while diaryl and dialkyl silanes furnish lower yields but the stereoselectivity remains almost unchanged (Supporting Information, Table 1, entries 5 and 7). However, with triaryl- or trialkyl silanes, only a trace amount of product was obtained (Supporting Information, Table 1, entries 6 and 8).

Eventually, the catalytic system consisting of $CuFe_2O_4$ nanoparticles (10 mg, 4.3 mol % of copper), BINAP (7 mg, 1.12 mol %) as chiral auxiliary, the cheaper and readily available siloxane, PMHS as the stoichiometric reducing agent, and toluene as solvent were chosen for the asymmetric hydrosilylation of an array of aryl alkyl ketones at room temperature. The results are listed in Table 2. Acetophenone is hydrosilylated cleanly with good ee (Table 2, entry 1). Introduction of an electron-withdrawing group at the *para*-position of acetophenone requires a shorter reaction time for the completion of the reactioin (Table 2, entries 2, 5, and 8−10). A higher ee was obtained when the *para*-position of acetophenone was substituted by bromo, chloro, and nitro groups, while fluoro and cyano groups furnished lower level of ee. Conversely, the presence of an electron-donating group such as methyl at the *para*-position (Table 2, entry 11) has little effect on enantioselectivity but requires longer reaction time for full conversion.

Another important observation is the dependence of ee on the position of the substituent group (irrespective of being electron-withdrawing or electron-donating) of the acetophenone. These values were highest when the substituent group was present at the *para*-position of the acetophenone rather than at the *meta*-position, which in turn was higher than at the *ortho*-position (Table 2, entries 2−4, 5−7, and 11−13). This demonstrates the ability of steric hindrance of *meta*- and *ortho*-substituents to modify the ee of the reaction, which is in contrast

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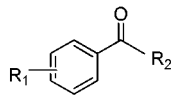
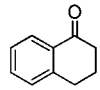
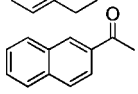
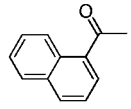
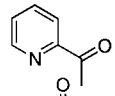
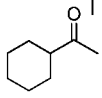
TABLE 2. Asymmetric Hydrosilylation of Prochiral Ketones Catalyzed by Copper Ferrite Nanoparticles at Room Temperature[a]

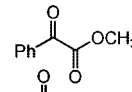
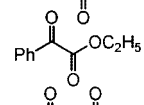
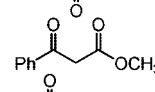
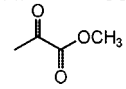
entry	substrate	time(h)	yield(%)	ee(%)[b]
				
1	R_1 = H, R_2 = Me	14	85	81
2	R_1 = 4-Br, R_2 = Me	12	78	93
3	R_1 = 3-Br, R_2 = Me	10	82	88
4	R_1 = 2-Br, R_2 = Me	10	71	51
5	R_1 = 4-Cl, R_2 = Me	12	75	86
6	R_1 = 3-Cl, R_2 = Me	8	68	77
7	R_1 = 2-Cl, R_2 = Me	10	77	59
8	R_1 = 4-F, R_2 = Me	12	72	76
9	R_1 = 4-CN, R_2 = Me	8	68	72
10	R_1 = 4-NO_2, R_2 = Me	7	73	89
11	R_1 = 4-Me, R_2 = Me	22	82	80
12	R_1 = 3-Me, R_2 = Me	30	79	74
13	R_1 = 2-Me, R_2 = Me	24	84	58
14	R_1 = 2-OMe, R_2 = Me	30	78	73
15	R_1 = H, R_2 = Et	30	76	81
16	R_1 = 4-Cl, R_2 = Et	24	82	99
17		32	66	80
18		18	76	75
19		18	71	52
20		15	62	61
21		15	32	33[c]

[a] Reaction conditions: substrate (1 mmol), PMHS (4 mmol), $CuFe_2O_4$ nanoparticles (10 mg, 4.3 mol % of copper), toluene (3 mL), BINAP (7 mg). [b] Absolute configurations were determined to be (*S*). [c] Absolute configuration was determined to be (*R*).

to the recently reported asymmetric hydrogenation of aryl ketones catalyzed by copper catalyst reported by Shimizu et al., where the obtained ee was highest in the case of *ortho*-substituted substrates.[3d]

When the methyl group of the aryl alkyl ketone is substituted with an ethyl group, the asymmetric hydrosilylation reaction still gave excellent enantioselectivity (Table 2, entries 15 and 16). Sterically demanding 2-acetonaphthone and 1-acetonaphthone (Table 2, entries 18 and 19) also afforded good yields with moderate enantioselectivity. It is significant to note that different substituents such as fluoro, bromo, chloro, cyano, and nitro (Table 2, entries 2−10) were not affected during the

TABLE 3. Reduction of Keto Esters with $CuFe_2O_4$ Nanoparticles

entry	substrate	time(h)	yield(%)	ee(%)
1		15	56	80
2		20	62	83
3		48	68	83
4		48	trace	-

[a] Reaction conditions: substrate (1 mmol), PMHS (4 mmol), $CuFe_2O_4$ nanoparticles (10 mg), toluene (3 mL), BINAP (7 mg).

TABLE 4. Recycling of the Catalytic System for the Asymmetric Hydrosilylation of Acetophenone at Room Temperature[a]

entry	catalyst recovery (%)	product yield (%)	ee (%)[b]
1		85	81
2	89	81	80
3	91	76	81

[a] Reaction conditions: substrate (1 mmol), PMHS (4 mmol), $CuFe_2O_4$ nanoparticles (10 mg), toluene (3 mL), BINAP (7 mg); reaction time is 14 h. [b] Absolute configurations were determined to be (*S*).

hydrosilylation reaction. A heteroaromatic ketone such as 2-acetylpyridine also produced the reduced product in moderate yields and ee's (Table 2, entry 20). Next, we performed the asymmetric hydrosilylation of dialkyl ketones. Cyclohexylmethyl ketone is reduced to the corresponding alcohol in 33% ee (Table 2, entry 21).

Finally, keto esters were also reduced using $CuFe_2O_4$ nanoparticles, PMHS as reducing reagent, and BINAP as chiral auxiliary at room temperature (see Table 3).

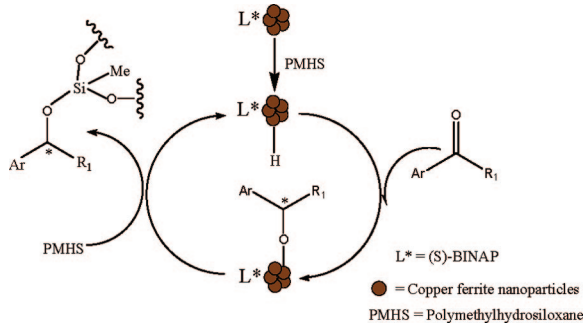
The reduction of methyl benzoyl formate produces methyl mandelate with 56% yield and 80% ee. The reduction of other α-keto esters and β-keto esters proceeded smoothly and afforded the corresponding reduced products in excellent ee. However, an aliphatic α-keto ester, methyl pyruvate, produced trace amount of the desired product under the same reaction conditions.

The feasibility of repeated use of $CuFe_2O_4$ was also examined. In Table 4, we present the results from the investigation of recycling of $CuFe_2O_4$ for three consecutive cycles of the same reaction. After each cycle, nanoparticles were magnetically concentrated, washed, air-dried, and used directly for the next cycle without further purification. No significant loss of catalytic activity was observed for $CuFe_2O_4$ in the asymmetric hydrosilylation of acetophenone.

Atomic absorption spectroscopy (AAS) was employed to determine the copper content of $CuFe_2O_4$ nanoparticles, and it was found to be 27.32%. The leaching of the metal after the first cycle was determined by AAS and was found to be negligible (0.045%). Figure 1a,b in Supporting Information shows the TEM images of the $CuFe_2O_4$ catalyst before and after use. It is observed that the synthesized nanoparticles are spherical, about 10−12 nm in size. The morphology and size of the particles do not change considerably even after three cycles. This result supports the nearly unaltered efficiency of the catalyst.

The plausible mechanism of hydrosilylation may be through the formation of copper hydride species from the reduction of

SCHEME 2. Possible Mechanism of Asymmetric Hydrosilylation Catalyzed by Copper Ferrite Nanoparticles



ligated copper ferrite nanoparticles by PMHS. At this stage we are not sure whether the active catalytic species is copper(I) or copper(II) hydride.[16b,17] The copper hydride species react with the ketone, resulting in the formation of a copper alkoxide that subsequently undergoes σ-bond metathesis with the organosilane to afford the silyl ether (Scheme 2).[13a,16b]

In conclusion, copper ferrite nanoparticles are used for the asymmetric hydrosilylation of ketones. High level of ee can be obtained by using an inexpensive and nontoxic reducing agent such as PMHS at room temperature and using commercially available BINAP as chiral auxiliary. The catalyst can be activated by the hydrosilylating reagent itself and thus obviates the need to use alkoxide bases.

Experimental Section

Representative Procedure for Asymmetric Hydrosilylation. $CuFe_2O_4$ nanoparticles (0.010 g, 4.3 mol % of copper) and (*S*)-BINAP (0.007 g, 1.12 mol %) were placed in a 25 mL round-bottom flask containing toluene (3 mL) at room temperature and stirred for 1 h. PMHS (4 mmol, 0.24 mL) was then added dropwise, and after 30 min ketone was added to the reaction mixture. After completion of the reaction (monitored by TLC), the reaction mixture was magnetically concentrated with the aid of a magnet to separate the catalyst and washed several times with ether. The reaction was quenched with water, and 10 mL of ether was added. Then TBAF (1.0 M in THF, 1.2 mL) was added, and the reaction mixture was stirred vigorously for 0.5 h. The layers were separated, and the aqueous layer was extracted with ether. The combined organic layers were dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent, hexane/ethyl acetate) to afford the desired product. (*S*)-1-Phenylethanol: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.35 (d, J = 6.79 Hz, 3H), 3.09 (br s, 1H), 4.70 (q, J = 6.04 Hz, 6.79 Hz, 1H), 7.14−7.24(m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.1, 70.0, 125.3, 127.2, 128.2, 145.7; HPLC (Daicel Chiralcel OJ-H, 5% isopropanol in hexane, flow rate 0.5 mL/min) t_R = 22.53 min (major), 25.37 min (minor); $[\alpha]^{25}_D = -39.2°$ (c 2.54, $CHCl_3$).

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Supporting Information Available: General experimental procedures and characterization data of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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