A metal-free catalytic reduction of α,β-unsaturated carbonyl compounds with phenyldimethylsilane

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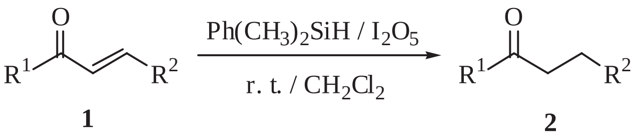
Selective reduction of α,β-unsaturated carbonyl compounds to the corresponding saturated ones by phenyldimethyl silane was promoted by a catalytic amount of I_2O_5 at ambient temperature in CH_2Cl_2.

Keywords: reduction, enones, silane, hypervalent iodine

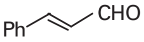
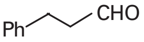
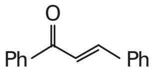
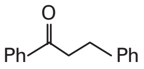
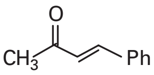
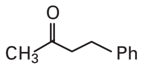
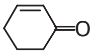
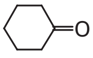
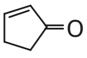
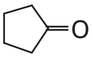
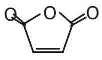
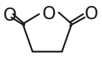
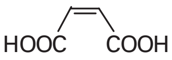
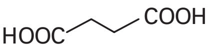
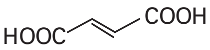
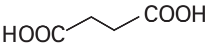
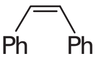
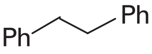
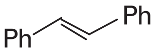
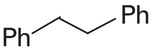
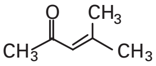
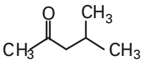
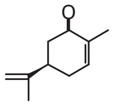
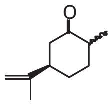
The selective reduction of α,β-unsaturated carbonyl compounds is an important functional group transformation in organic synthesis and a variety of approaches has been developed for such a transformation.[1-3] Catalytic hydrosilylation, a general protocol for reduction of unsaturated double bonds (C=C, C=O, C=N),[2] has also been used for the selective 1,4-reduction of α,β-unsaturated carbonyl compounds.[3] However, in many cases, the use of transition metal catalysts as well as the rigorously anaerobic conditions required in these reactions, have limited their use especially in industry. Obviously, it is desirable to find transition metal-free and environmentally benign catalysts. We wish to report herein a hypervalent iodine catalysed hydrosilylation reaction that selectively reduces α,β-unsaturated carbonyl compounds to the corresponding saturated ketones in high yield (Scheme 1).



Scheme 1

Hypervalent iodine reagents, such as *o*-iodoxybenzoic acid (IBX) and Dess-Martin periodinane (DMP), have been successfully used for oxidation of alcohols to the corresponding carbonyl compounds,[4] for the oxidative deoximation of oximes,[5] and for other synthetically useful transformations.[6] Iodine pentoxide (I_2O_5, IP) has rarely been employed in organic synthesis except as an alternative to IBX for the

Table 1 I_2O_5-promoted reduction of enones (1) with $Ph(CH_3)_2SiH$[a]

Entry	1		2	Time/h	Yield[b]/%
1		**2a**		2	76
2		**2b**		2	94
3		**2c**		4	79
4		**2d**		4	73
5		**2e**		4	78
6		**2f**		2	90
7		**2g**		2	83
8		**2g**		2	84
9		**2h**		2	91
10		**2h**		2	88
11		**2i**		8	48
12		**2j**		5	49[c]

[a]Reaction conditions see text.
[b]Isolated yield of pure compounds.
[c]Mixture of *2R*- and *2S*-epimers with ratio of 1:4 as determined by ^1H NMR.

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dehydrogenation of aldehydes and ketones.[7] It is of interest to find that IP activates hydrosilanes.

Results and discussion

The enone **1** was reacted with 2.2 mol % of phenyldimethylsilane and 0.2 mol % of I_2O_5 in CH_2Cl_2 solution at ambient temperature. The reaction was complete within 2–4 h giving the corresponding saturated carbonyl compound **2** in high yield. The results are listed in Table 1.

It is seen from Table 1 that cinnamaldehyde (entry 1), acyclic and cyclic α,β-unsaturated ketones (entries 2–5), maleic anhydride (entry 6), and maleic and fumaric acids (entries 7–8) were all reduced to the corresponding saturated carbonyl compounds in high to excellent yields. C*is*- and *trans*-stilbenes were also reduced to diphenylethane in excellent yields (entries 9–10). Sterically congested enones (entries 11–12) were also selectively reduced in good yields. It was reported previously that cinnamaldehyde could not be reduced by Cu(I)- and In(III)-mediated hydrosilane reduction,[3a,e] and that carvone could not be reduced by Mo (0)-mediated hydrosilane reduction.[3c] Therefore, the present approach provides a good supplement to those methods.

In conclusion, we have developed a metal-free 1,4-reduction of α,β-unsaturated carbonyl compounds by phenyldimethylsilane catalysed by I_2O_5. It was found that the reduction of the α,β-unsaturated compounds by the hydrosilane did not take place either in other solvents, such as MeOH, EtOH and THF, or in the absence of I_2O_5 despite of its poor solubility in CH_2Cl_2. The exact mechanism of this novel hydrosilane activation is still unclear and will be the subject of future research.

Experimental

Phenyldimethylsilane was from Merck. I_2O_5 and unsaturated carbonyl compounds were all purchased from commercial sources. ^{1}H NMR spectra were recorded on a Varian Mercury Plus-300 spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were recorded on a HP5988A spectrometer by direct inlet at 70 eV. Melting points were determined with a Kofler melting point apparatus and uncorrected.

In a typical experiment, I_2O_5 (0.2 mmol) was added to a CH_2Cl_2 solution (40 ml) of the enone **1** (1.0 mmol) and phenyldimethyl silane (2.2 mmol) at ambient temperature under vigorous stirring. The reaction was complete within 2–4 h as monitored by TLC. After the completion of the reaction the solid (I_2O_5) was removed by filtration and the solvent was removed from the filtrate under reduced pressure. Column chromatographic separation (silica gel, petroleum ether-acetone 20:1) gave the pure saturated carbonyl compound **2** in high yield. All the products were identified by comparing their MS and ^{1}NMR spectroscopic data and melting points (in case of solid products) with those reported in the literature and/or of authentic samples. The purity of liquid products was assessed by their ^{1}H NMR spectra (300 MHz) that did not show appreciable impurities.

3-Phenylpropionaldehyde (**2a**): EI-MS *m/z* (rel. int.): 134 (M^+, 57), 115 (6), 105 (32), 91 (100), 78 (62); δ_H (300 MHz, $CDCl_3$, TMS): 9.78 s (1H), 7.31–7.16 m (5H), 2.94 (t J = 7.2 Hz, 2H), 2.75 (t J = 7.2 Hz, 2H).

1,3-Diphenylpropan-1-one (**2b**): M.p. 67–68 °C (lit., 68–69 °C[8]); EI-MS *m/z* (rel. int.): 210 (M^+, 15), 105(100), 91 (12), 77 (68); δ_H (300 MHz, $CDCl_3$, TMS): 7.99–7.20 m (10H), 3.20 (t J = 7.5 Hz, 2H), 3.09 (t J = 7.5 Hz, 2H).

4-Phenylbutan-2-one (**2c**): EI-MS *m/z* (rel. int.): 148 (M^+, 92), 131 (60), 105 (100), 91 (78), 77 (51); δ_H (300 MHz, $CDCl_3$, TMS): 7.10–7.40 m (5H), 2.89 (t J = 6.9 Hz, 2H), 2.75 (t J = 7.2 Hz, 2H), 2.13 s (3H).

Cyclohexanone (**2d**): EI-MS *m/z* (rel. int.): 98 (M^+, 51), 83 (11), 69 (29), 55 (100), 42 (67); δ_H (300 MHz, $CDCl_3$, TMS): 2.23–2.19 m (4H), 1.78–1.74 m (4H), 1.64–1.60 m (2H).

Cyclopentanone (**2e**): EI-MS *m/z* (rel. int.): 84 (M^+, 54), 55 (100), 41 (51), 28 (64); δ_H (300 MHz, $CDCl_3$, TMS): 2.17 (t J = 6.0 Hz, 4H), 1.98 (t J = 6.0 Hz, 4H).

Dihydrofuran-2,5-dione (**2f**): M.p. 118–120 °C (lit., 120 °C[9]) EI-MS *m/z* (rel. int.): 100 (M^+, 1), 56 (100), 42 (10); δ_H (300 MHz, $CDCl_3$, TMS): 3.01 s (4H).

Succinic acid (**2g**): M.p. 188–189 °C (lit., 188 °C[9]) EI-MS *m/z* (rel. int.): 100 (M^+-18, 35), 74 (65), 55 (87), 45 (100); δ_H (300 MHz, $CDCl_3$, TMS): 1.56 s (4H).

1,2-Diphenyl ethane (**2h**): M.p. 51–52 °C (lit., 52 °C[9]) EI-MS *m/z* (rel. int.): 182 (M^+, 38), 91 (100), 77 (6); δ_H (300 MHz, $CDCl_3$, TMS): 7.15–7.29 m (10H), 2.93 d (J = 3.0 Hz, 2H), 2.90 d (J = 3.0 Hz, 2H).

4-Methylpentan-2-one (**2i**): EI-MS *m/z* (rel. int.): 100 (M^+, 4), 85 (12), 69 (6), 57 (11), 43 (100); δ_H (300 MHz, $CDCl_3$, TMS): 2.23 d (J = 6.9 Hz, 2H), 2.04 s (3H), 2.02 m (1H), 0.85 d (J = 3.0 Hz, 6H).

5-Isopropenyl-2-methylcyclohexanone (**2j**): EI-MS *m/z* (rel. int.): 152 (M^+, 19), 137 (11), 109 (25), 95 (45), 82 (30), 67 (100), 53 (36); δ_H (300 MHz, $CDCl_3$, TMS): *(2S,5S)-2-methyl-5-isopropenyl-cyclohexanone*: 4.75 s (1H), 4.73 s (1H), 2.24–2.47 m (4H), 2.14 m (1H), 1.95 m (1H), 1.74 s (3H), 1.65 m (1H), 1.37 m (1H), 1.03 d (J = 6.3 Hz, 3H); *(2R,5S)-2-methyl-5-isopropenyl-cyclohexanone*: 4.83 s (1H), 4.68 s (1H), 2.28-2.59 m (4H), 2.05 m (1H), 1.85 m (1H), 1.75 s (3H), 1.58 m (1H), 1.39 m (1H), 1.09 d (J = 6.9 Hz, 3H).

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