



# Conjugate reduction of $\alpha,\beta$ -unsaturated ketones using an $\text{Mn}^{\text{III}}$ catalyst, phenylsilane and isopropyl alcohol

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Received 7 August 2000; revised 25 September 2000; accepted 28 September 2000

## Abstract

Treatment of a variety of  $\alpha,\beta$ -unsaturated ketones with  $\text{Mn}(\text{dpm})_3$  (3 mol%)/ $\text{PhSiH}_3$  (1.3 equiv.)/isopropyl alcohol with the exclusion of air resulted in the formation of the saturated ketone. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* reduction; conjugate; manganese; phenylsilane.

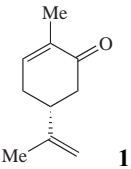
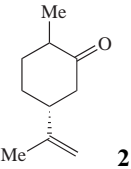
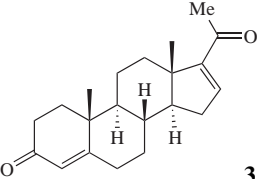
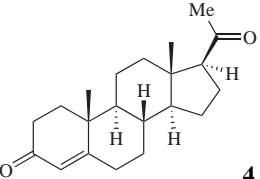
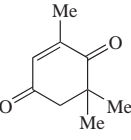
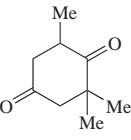
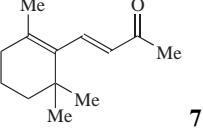
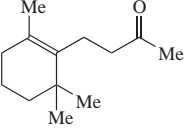
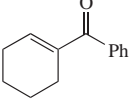
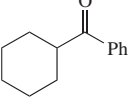
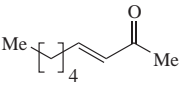
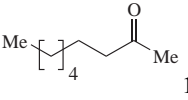
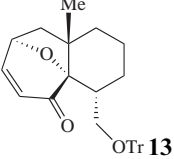
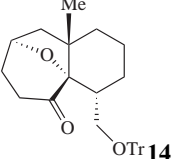
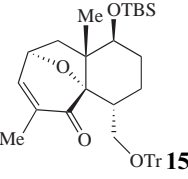
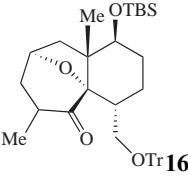
In the accompanying letter we reported the conjugate reduction of  $\alpha,\beta$ -unsaturated ketones followed by oxidation of in situ generated enolates to give  $\alpha$ -hydroxyketones using  $\text{Mn}(\text{dpm})_3(\text{cat})/\text{PhSiH}_3/\text{O}_2/i\text{-PrOH}$ .<sup>1</sup> In this letter the application of this reagent system (minus  $\text{O}_2$ ) to the conjugate reduction of  $\alpha,\beta$ -unsaturated ketones is reported.<sup>2</sup>

In a stoichiometric reaction a dark olive-green solution of  $\text{Mn}(\text{dpm})_3$  in *i*-PrOH at 23°C was treated with  $\text{PhSiH}_3$  to give a pale yellow solution, which rapidly reduced **5** to give **6**. When the same reaction was conducted with catalytic amounts of  $\text{Mn}(\text{dpm})_3$  (3 mol%) the reduction was much slower but proceeded in good yields. Table 1 lists a series of enones that were conjugatively reduced using this procedure.

Deuterium labeling experiments using  $\text{PhSiD}_3$  converted **11** (Scheme 1) into **12d** with the incorporation of one deuterium atom in the  $\beta$ -position. This demonstrates that the hydride addition is irreversible since if a putative  $\text{Mn}^{\text{III}}$  enolate **12a** could  $\beta$ -eliminate  $\text{HMn}(\text{dpm})_2$  (isotope effect) one would expect to accumulate **12b** which would be converted into the  $\beta,\beta$ -dideuterium derivative **12c**. Similarly, treatment of **5** with  $\text{Mn}(\text{dpm})_3/\text{PhSiD}_3$  gave **6** with incorporation of one deuterium atom. Attempts to increase the rate of reduction of **5** by conducting the reaction at slightly higher temperatures than 23°C did not work and also lead to small amounts of 1,2-reduction to give 4-hydroxyisophorone.<sup>3</sup> The use of alcohols other than isopropyl alcohol was not productive. For example, if methanol is substituted for isopropyl

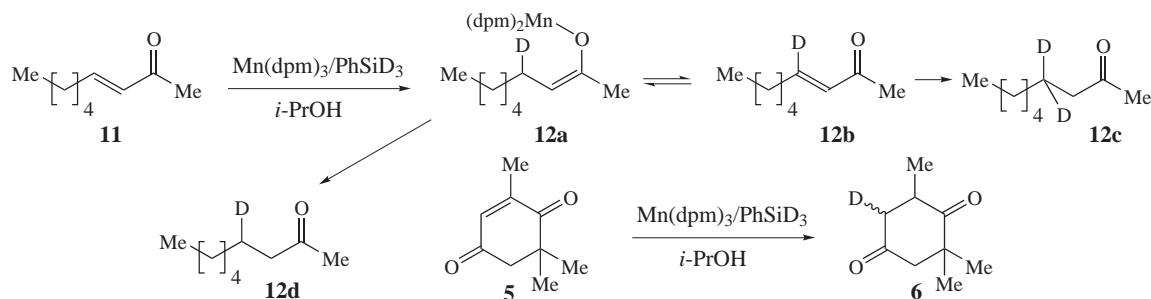
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Table 1

Entry	Substrate	Conditions	Product	Yield
1		Mn(dpm) <sub>3</sub> (3 mol%), PhSiH <sub>3</sub> (2 equiv.), <i>i</i> -PrOH (0.2 M conc of <b>1</b> )		50%
2		Mn(dpm) <sub>3</sub> (3 mol%), PhSiH <sub>3</sub> (1.3 equiv.), <i>i</i> -PrOH/DCE		99%
3		As above		99%
4		As above		25%
5		As above		50%
6		As above		74%
7		Mn(dpm) <sub>3</sub> (3 mol%), PhSiH <sub>3</sub> (1.3 equiv.), <i>i</i> -PrOH/DCM (1:4)		100%
8		As above		100%

alcohol there was rapid gas evolution (H<sub>2</sub>), no reduction of **5**, and the formation of PhSi(OMe)<sub>3</sub>.<sup>4</sup> If the proton source is *t*-BuOH the reduction proceeds very slowly, consequently *i*-PrOH is the preferred (optimal) alcohol. The use of other hydride sources was briefly

examined, and it was found that  $\text{Ph}_2\text{SiH}_2$  was very slow,  $\text{Et}_3\text{SiH}$  did not work and polymethylhydrosiloxane was also very slow and incomplete.



Scheme 1.

As expected from the results described in the accompanying paper,  $\beta,\beta$ -disubstituted  $\alpha,\beta$ -unsaturated ketones (and esters) are not conjugatively reduced using the above conditions.

## Acknowledgements

The National Institutes of Health (GM 32718), The Robert A. Welch Foundation, Merck Research Laboratories and Novartis are thanked for their support of this research.

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