



Efficient hydrosilylation of carbonyl compounds by 1,1,3,3-tetramethyldisiloxane catalyzed by Au/TiO₂

Eleni Vasilikogiannaki^a, Ioannis Titilas^a, Charis Gryparis^a, Anastasia Louka^a, Ioannis N. Lykakis^b, Manolis Stratakis^{a,*}

^a Department of Chemistry, University of Crete, Voutes, 71003 Iraklion, Greece

^b Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

ARTICLE INFO

Article history:

Received 25 January 2014

Received in revised form 25 March 2014

Accepted 27 March 2014

Available online 2 April 2014

Keywords:

Hydrosilylation

Carbonyl compounds

Gold nanoparticles

1,1,3,3-Tetramethyldisiloxane

Heterogeneous catalysis

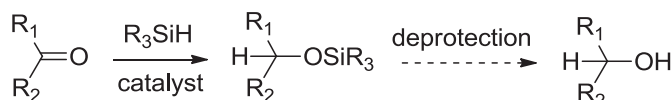
ABSTRACT

1,1,3,3-Tetramethyldisiloxane (TMDS) is a highly reactive reducing reagent in the Au/TiO₂-catalyzed hydrosilylation of carbonyl compounds relative to monohydrosilanes. The reduction of aldehydes or ketones with TMDS can be performed on many occasions at ambient conditions within short reaction times and at low loading levels of gold, whereas typical monohydrosilanes require excess heating and prolonged time for completion. The product yields are excellent, while almost stoichiometric amounts of carbonyl compounds and TMDS can be used. It is postulated that the enhanced reactivity of TMDS is attributed to the formation of a gold dihydride intermediate. This intermediate is also supported by the fact that double hydrosilylation of carbonyl compounds by TMDS is a negligible pathway.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The hydrosilylation of aldehydes or ketones (Scheme 1) is a straightforward methodology to synthesize silyl ethers of alcohols, achieving thus a double functionalization in a single process, namely, reduction of the carbonyl group and silyl protection of alcohol. The deprotection of the silyl moiety is trivial and simple, and often can take place under the reaction conditions by acid treatment, affording alcohols. This approach has practical advantages over using the classical, yet pyrophoric and moisture sensitive boron or aluminum hydrides as reducing agents. In particular, the hydrosilylation of carbonyl compounds is primarily catalyzed by a variety of metals,¹ but can be also achieved under free radical conditions.² Lewis acids (such as BF₃) can also catalyze this process³



Scheme 1. The catalytic hydrosilylation of carbonyl compounds.

through activation of the carbonyl group, yet this methodology works preferably with aromatic substrates, while silyl ethers are rapidly deprotected under the reaction conditions.

Among the existing metal-catalyzed hydrosilylation protocols, in recent years gold was proven as an active catalyst.⁴ The first example of the homogeneous gold(I)-catalyzed hydrosilylation of aldehydes was reported⁵ in 2000 using Ph₃PAuCl (3 mol %) as catalyst. The reaction requires the co-addition of 20% Bu₃P to suppress deactivation of catalyst, and operates in DMF at 70 °C. One specific example of a ketone (acetophenone) was examined in this report and shown to be completely unreactive. Later on, these studies were expanded to various Au(I)- and Au(III)-based homogeneous catalysts.^{6–9} In addition, supported gold nanoparticles have also been recognized as active heterogeneous hydrosilylation catalysts. Corma and co-workers have shown¹⁰ that Au nanoparticles supported on CeO₂ (5% mol) catalyze the hydrosilylation of some aldehydes and acetophenone in high yields (toluene, 70 °C), using a variety of hydrosilanes. The molar ratio carbonyl compound/hydrosilane in those experiments was 1:2. Following this first report, a significantly lower catalyst-loading protocol was presented by the group of Raffa¹¹ who studied the hydrosilylation of benzaldehyde and acetophenone in the presence of Au/CeO₂ (0.1–0.15 mol %, 100 °C, 18–24 h). The specific gold nanoparticles were prepared either by the metal vapor synthesis (Au_{MVS}) or by deposition-precipitation (Au_{DP}). The reaction was not chemoselective, providing apart from the anticipated silyl-protected alcohols, disilylated pinacols in

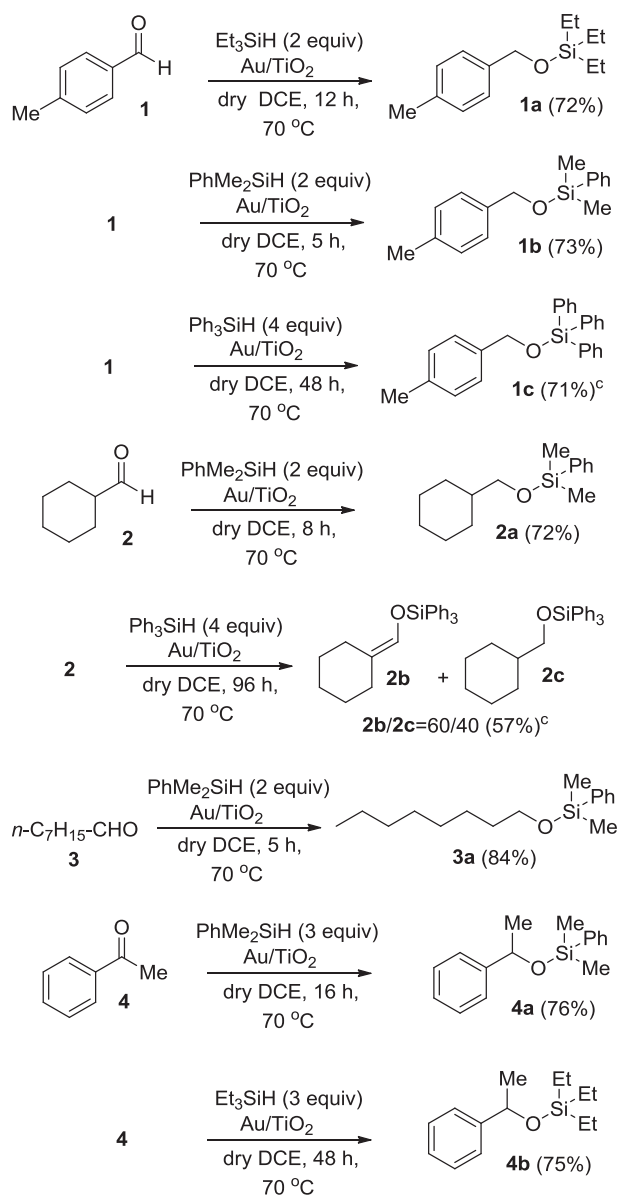
* Corresponding author. Fax: +30 2810545166; e-mail address: stratakis@chemistry.uoc.gr (M. Stratakis).

a relative ratio 40–80%. It was postulated that the hydrosilylation pathway is catalyzed by Au(I) species, whereas, Au(0) nanoparticles act as radical initiators forming silyl radicals, which undergo addition to the carbonyl group followed by dimerization of the α -silyloxy radicals. As the so far reported examples involving Au nanoparticles as catalysts focus on a limited number of substrates and there is lack of an efficient protocol in terms of low catalyst-loading, atom economy, mild conditions, and chemoselectivity, we decided to study Au/TiO₂¹² as a hydrosilylation catalyst for aldehydes and ketones. We were prompted toward this goal, as previous work from our laboratory has shown that this specific catalyst is a very efficient one and superior to other gold-based heterogeneous catalysts in the hydrosilylation of alkenes.¹³

2. Results and discussion

In our initial experiments, we tested the reaction among a series of carbonyl compounds (aldehydes and ketones) and hydrosilanes

(Et₃SiH, PhMe₂SiH) using Au/TiO₂ (0.5 mol %) as catalyst. The reaction proceeds at refluxing conditions and forms the hydrosilylation products in good yields, yet excess of hydrosilylating reagent is required (2–4 M fold depending on the bulkiness of the hydrosilane) to drive the reaction to completion within a reasonable time scale. These results are presented in Scheme 2. 1,2-Dichloroethane (DCE) is considered as the best solvent of choice, as in benzene or toluene the reaction rate is slower, while in THF although the reaction proceeds faster (~2 times compared to DCE), a gradual destruction of hydrosilane by the solvent is observed. The conversion of carbonyl compounds was 100% in all cases, yet the isolated yields of silyl ethers is not that high, apparently due to the intrinsic instability of silylated products toward deprotection under their chromatographic purification. Surprisingly, even the bulky triphenylsilane works nicely under prolonged reaction times (1.0 mol % of catalyst), yet for aldehydes only. The gold nanoparticles can be recovered at the end of the reaction and reused with little deterioration of their activity, as occurs for the vast majority of heterogeneous gold nanoparticle-catalyzed reactions. It is



a) 0.5 mol% of Au/TiO₂. b) Isolated overall yields after column chromatography.

The consumption of carbonyl compounds was 100% in all cases. c) 1.0 mol% of Au/TiO₂.

Scheme 2. Hydrosilylation of carbonyl compounds by hydrosilanes catalyzed by Au/TiO₂.^{a,b}

Download English Version:

<https://daneshyari.com/en/article/5216138>

Download Persian Version:

<https://daneshyari.com/article/5216138>

[Daneshyari.com](https://daneshyari.com)