

## Accepted Manuscript

1,3-Addition of silyl enol ethers to nitrones catalyzed by mesoporous aluminosilicate

Suguru Ito, Yoshihiro Kubota, Masatoshi Asami

PII: S0040-4039(14)01161-7

DOI: <http://dx.doi.org/10.1016/j.tetlet.2014.07.020>

Reference: TETL 44863

To appear in: *Tetrahedron Letters*

Received Date: 26 May 2014

Revised Date: 26 June 2014

Accepted Date: 4 July 2014



Please cite this article as: Ito, S., Kubota, Y., Asami, M., 1,3-Addition of silyl enol ethers to nitrones catalyzed by mesoporous aluminosilicate, *Tetrahedron Letters* (2014), doi: <http://dx.doi.org/10.1016/j.tetlet.2014.07.020>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Pergamon

TETRAHEDRON  
LETTERS

## 1,3-Addition of silyl enol ethers to nitrones catalyzed by mesoporous aluminosilicate

Suguru Ito, Yoshihiro Kubota, Masatoshi Asami\*

Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University,  
Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501, Japan

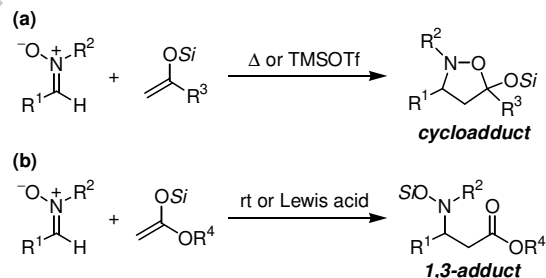
**Abstract**— Mesoporous aluminosilicate (Al-MCM-41) was found to be an effective and reusable catalyst for 1,3-addition of silyl enol ethers to nitrones. The reaction proceeded under mild reaction conditions to afford the corresponding  $\beta$ -(siloxyamino)ketones in high yields. Furthermore, a unique chemoselectivity of a nitron over an aldehyde and an acetal, which are more reactive toward silyl enol ether in the presence of Al-MCM-41 than a nitron, was observed.

© 2014 Elsevier Science. All rights reserved

**Keywords:** Al-MCM-41; Solid acid catalyst; 1,3-Addition of nitrones; Chemoselective reaction

Nitrones are generally used for 1,3-dipolar cycloaddition with dipolarophiles to afford the corresponding heterocyclic compounds because of the synthetic utility of the cycloadducts.<sup>1,2</sup> The reactions of nitrones with silyl enol ethers derived from ketones are known to give the corresponding cycloadducts under heating conditions<sup>2a</sup> or in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) (Scheme 1a).<sup>2b</sup> In contrast, the reactions of nitrones with silyl enol ethers derived from esters can afford the corresponding 1,3-adducts in the presence or absence of Lewis acids (Scheme 1b).<sup>3</sup> 1,3-Adducts of nitrones, hydroxylamine derivatives, are the precursors of amines and imines, which are synthetically useful intermediates.<sup>3,4</sup>

We have recently reported that the ordered mesoporous aluminosilicate (Al-MCM-41) could catalyze aldol reactions of silyl enol ethers with aldehydes<sup>5a</sup> and acetals<sup>5b</sup> in a heterogeneous manner. The high catalytic activity of Al-MCM-41 was attributed to their uniform pore diameter (2.7 nm) and high surface area (1120 m<sup>2</sup>/g). The catalyst was easily recovered by filtration and reusable without a significant loss of catalytic activity. Herein, we report that the Al-MCM-41 could catalyze 1,3-addition of nitrones with silyl enol ethers derived from a ketone.



**Scheme 1.** (a) 1,3-Dipolar cycloaddition of nitron with silyl enol ether, (b) 1,3-Addition of silyl enol ether to nitron.

In the first place, the reaction of *C,N*-diphenylnitron (**1a**) and 1-phenyl-1-trimethylsiloxyethene (**2a**) was examined using Al-MCM-41 (Si/Al = 26) synthesized according to a known procedure with slight modification.<sup>6,7</sup> After drying Al-MCM-41 (25 mg) at 120 °C for 1 h under vacuum, **1a** (0.5 mmol) and **2a** (0.6 mmol) in dichloromethane was added to the catalyst, and the mixture was stirred at 0 °C for 1 h. The catalyst was filtered off and washed with dichloromethane. The filtrate was then concentrated under reduced pressure to give the crude product containing the corresponding 1,3-adduct **3a** in quantitative yield (Table 1, entry 1).<sup>8</sup> The result was in sharp contrast to the reaction of **1a** with **2a** in refluxing xylene,<sup>2a</sup> where the corresponding cycloadduct was obtained. The reaction was then carried out in the presence of stoichiometric amount of Lewis acids

\* Corresponding author. Tel./fax: +81 45 339 3968; e-mail:m-asami@ynu.ac.jp.

Download English Version:

<https://daneshyari.com/en/article/5261490>

Download Persian Version:

<https://daneshyari.com/article/5261490>

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