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Morpholine Adsorbed on Silica Gel: A Novel and Mild Basic Catalyst for the Synthesis of α,β-Unsaturated Nitroalkenes

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Summary. Syntheses of α,β-unsaturated nitroalkenes have been carried out under mild condition using morpholine adsorbed on silica gel as a novel catalyst.

Keywords. *Henry* reaction; Morpholine adsorbed on silica gel; Base catalyst; α,β-Unsaturated nitroalkenes.

Introduction

Nitroalkenes are considered important because of their biological activities as insecticidal [1, 2], fungicidal [2–5], bactericidal [6, 7], rodentrepellent [8], and antitumor agents [9] as well as of other pharmacological values [6–9]. They have proved to be suitable precursors for a wide variety of target molecules. The utility of nitroalkenes in organic synthesis is largely due to their easy conversion into a variety of functionalities [10, 11]. Alternatively they are powerful dienophiles in *Diels-Alder* reactions and readily undergo addition reactions with many different nucleophiles [11]. A few nitroalkenes also occur in nature [12].

The most versatile and classical preparation of nitroalkenes involves the *Henry* condensation reaction, followed by dehydration of the resultant β-nitro alcohols [13]. For this purpose several reagents have been used [14–15]. Recently, nitroalkenes have been synthesized using Envirocat EPZG and microwaves under drastic conditions [16, 17]. The significance of nitroalkenes and the increasing importance of heterogenous catalysis in organic synthesis prompted us to investigate the *Henry* reaction in more detail.

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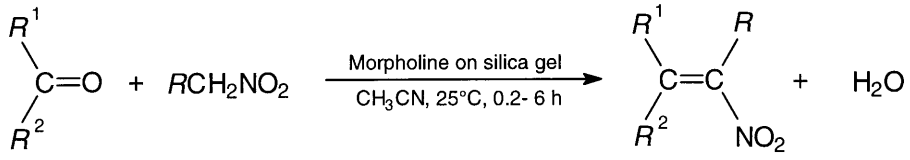
In this contribution we report on the synthesis of α,β-unsaturated nitroalkenes using morpholine supported on silica gel as an inexpensive and mild catalyst (Scheme 1).

Results and Discussion

The attempt to prepare α,β-unsaturated nitroalkenes using either morpholine or silica gel as a catalyst resulted in very poor yields, even after stirring for 12 h at room temperature. In contrast, morpholine adsorbed on silica gel acts as a mild and effective catalyst for the synthesis of various nitroolefins in good to excellent yields.



Scheme 1

The (*E*)-geometry of the newly formed double bond was readily assigned on the basis of ^{1}H NMR spectra, the vinyl proton of the (*E*)-isomer appearing at lower field than the corresponding proton of the (*Z*)-isomer because of the strong anisotropic effect of the nitro group [15]. ^{13}C NMR spectra of the products indicated that no contamination with (*Z*)-isomers occurred [14–15].

In summary, the presented method offers a mild and useful alternative to existing procedures for the chemoselective synthesis of functionalized conjugated nitroalkenes.

Exprimental

IR spectra were recorded on a Bomem MB 104 FTIR spectrometer, ^{1}H NMR spectra on a Varian 90 MHz NMR instrument (Varian FT90).

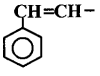
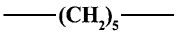
Preparation of the catalyst

A mixture of 5 g silica gel (60–120 mesh) and 1 cm^3 morpholine in 10 cm^3 acetone was stirred at room temperature for 1 h. Acetone was removed under vacuum to get a free-flowing powder of morpholine adsorbed on silica gel.

General procedure for the synthesis of α,β-unsaturated nitroalkenes

A mixture of aldehyde/ketone (5 mmol), nitromethane/nitropropane (6 mmol), and 1.5 g morpholine adsorbed on silica gel in 10 cm^3 acetonitrile was stirred at room temperature for the specified time (Table 1). After completion of the reaction the catalyst was filtered off and washed twice with 10 cm^3 ether. Removal of the solvent under reduced pressure gave a crude product which was further purified by column chromatography (silica gel 60–120 mesh, petroleum ether:ethylacetate = 4:1).

Table 1. α,β-Unsaturated nitroalkenes synthesized by *Henry*'s procedure catalyzed by morpholine adsorbed on silica gel[a]

R^1	R^2	R	Reaction time/h	Yield/%	Melting point/°C	Melting point/°C (Literature)
	H	H	0.2	78	125	124–126 [20]
	H	H	0.5	75	104	104 [20]
	H	H	6	80	112	111 [20]
	H	H	2	68	167	167–168 [19]
	H	H	2	65	168	168–169 [19]
	H	H	1.5	75	oil	–
		H	1	74	oil	–
	H	H	2.5	76	58	58–59 [19]
	H	CH_3	01	78	44	44–45 [19]
	H	CH_3	03	80	63	64–65 [19]
	H	H	0.8	80	118	120 [20]

[a] Yields refer to pure, isolated products characterized by physical constants, spectroscopic properties, and comparison with authentic samples

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