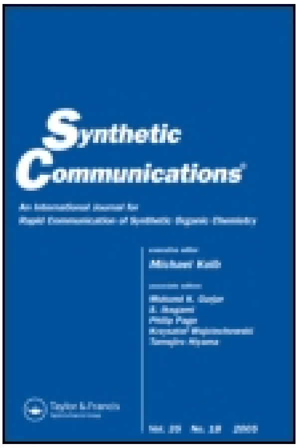

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Fe_3O_4 Nanoparticles as an Efficient and Magnetically Recoverable Catalyst for the Synthesis of α,β-Unsaturated Heterocyclic and Cyclic Ketones under Solvent-Free Conditions

Tooba Alishiri [a] , Hossein A. Oskooei [a] & Majid M. Heravi [a]
[a] Department of Chemistry , School of Sciences, Alzahra University , Tehran , Iran
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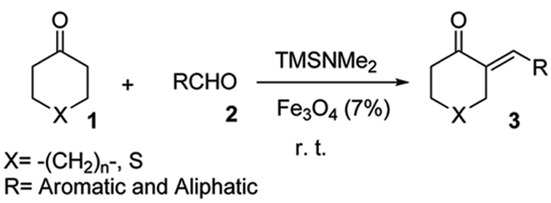
Fe_3O_4 NANOPARTICLES AS AN EFFICIENT AND MAGNETICALLY RECOVERABLE CATALYST FOR THE SYNTHESIS OF α,β-UNSATURATED HETEROCYCLIC AND CYCLIC KETONES UNDER SOLVENT-FREE CONDITIONS

Tooba Alishiri, Hossein A. Oskooei, and Majid M. Heravi
Department of Chemistry, School of Sciences, Alzahra University, Tehran, Iran

GRAPHICAL ABSTRACT



Abstract *An efficient and green procedure has been developed for the synthesis of monoarylidenes of cyclic and heterocyclic ketones. The reaction was carried out under solvent-free conditions in the presence of a catalytic amount of nanosized magnetite (Fe_3O_4). The catalyst was easily removed by using an external magnet. The structures of the products were deduced from their ^1H NMR, ^{13}C NMR, and infrared spectroscopy and mass spectrometry.*

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications® *for the following free supplemental resource(s): Full experimental and spectral details.]*

Keywords Heterogeneous catalyst; magnetic nanoparticles; magnetite (Fe_3O_4); monoarylidenes

INTRODUCTION

In recent years, Fe_3O_4 nanoparticles (magnetite nanoparticle) have attracted worldwide attention[1] because of due to their significant characteristics such as the ease of magnetical separation from the reaction mixture, which is simpler and typically more effective than filtration or centrifugation as it prevents the loss of the catalyst.[2] Various strategies have successfully demonstrated the applications of Fe_3O_4 nanoparticle–immobilized or supported catalysts in organic synthesis.[3]

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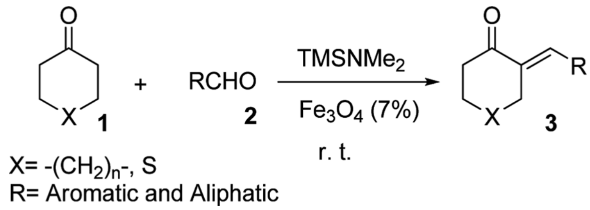
Address correspondence to Majid M. Heravi, Department of Chemistry, School of Sciences, Alzahra University, Vanak, Tehran, Iran. E-mail: mmh1331@yahoo.com



Scheme 1. General reaction for the synthesis of monoarylidene derivatives of aldehydes and enolizable ketones.

Direct use of Fe_3O_4 nanoparticles without modification as magnetically recoverable catalysts for organic transformations have been reported by many researchers. They used them in the protection of alcohols and phenols using hexamethyldisilazane;[4] three-component synthesis of α-aminonitriles from aldehydes, amines, and TMSCN;[5] synthesis of quinoxaline derivatives;[6] preparation of propargylamines;[7,8] four-component aza-Sakurai reaction;[9] selective *N*-alkylation of aromatic amines using benzylic alcohols;[10] oxidative C–C bond formation between Csp^3–H bond adjacent to nitrogen and Csp^3–H bond of nitroalkanes;[10] carbon–carbon bond formation via the Sonogashira–Hagihara reaction;[8] synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones;[12] synthesis of mono-, bis-, and tris-diindolyl methane;[13] chemoselective reduction of olefins;[14] synthesis of polysubstituted imidazoles;[15] and synthesis of benzimidazole derivatives.[16]

In continuation of our work in aldol condensation[17] and using magnetite particles,[5] in this communication we disclose the appropriate use of Fe_3O_4 in the synthesis of mono-aldol adducts.

RESULTS AND DISCUSSION

Herein, we report a facile synthesis of α,β-unsaturated compounds involving the one-pot reaction between cyclic and heterocyclic ketones and different aldehydes in the presence of TMSCN using the magnetite as a catalyst (Scheme 1).

Table 1. Fe_3O_4-catalyzed reaction of cyclopentanone, benzaldehyde, and $TMSNMe_2$

Entry	Catalyst	Solvent	Yield (%)
1	—	—	60
2	Fe_3O_4 (1%)	—	75
3	Fe_3O_4 (3%)	—	82
4	Fe_3O_4 (5%)	—	88
5	Fe_3O_4 (7%)	—	92
6	Fe_3O_4 (10%)	—	92
7	$MgBr_2OEt_2$	—	85
8	MgF_2	—	80
9	$MgClO_4$	—	75
10	$LiClO_4$	—	82
11	LiBr	—	88
12	Fe_3O_4 (7%)	H_2O	65
13	Fe_3O_4 (7%)	Hexane	88
14	Fe_3O_4 (7%)	Dichloromethane	80

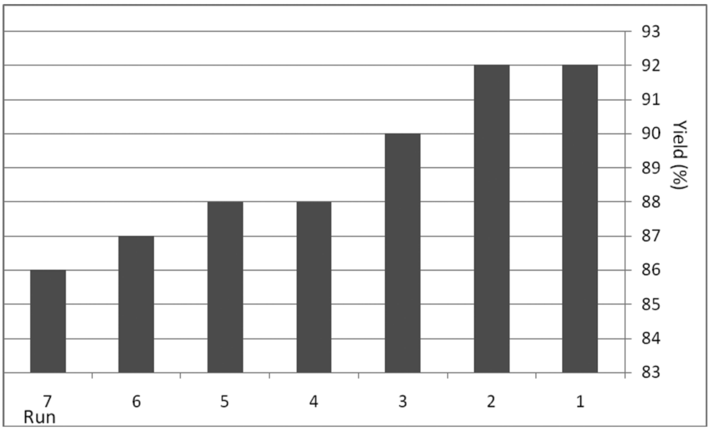


Figure 1. Efficient recovery of the catalyst.

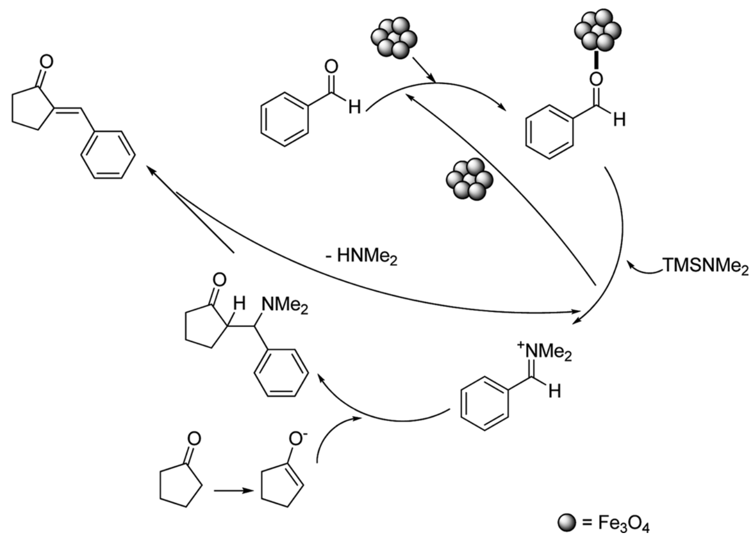
Initially we evaluated the reaction of cyclopentanone with benzaldehyde in the presence of various Lewis acides and silylated amines. The optimum results were obtained when an equimolar solvent-free mixture of two reactants came in to contact with $TMSNMe_2$ and nano-Fe_3O_4, leading to the formation of the respective products in good yields. The best result was obtained by 7 mol% of Fe_3O_4 (Table 1).

The recycling capacity of the magnetite was examined under the optimized reaction conditions. The catalyst was separated by using a bar magnet after completion of the reaction. The recovered catalyst was washed with dichloromethane and, after drying, was reused for the next cycle of the reaction. The results are shown in Fig. 1. The catalyst showed negligible loss of reactivity up to seven runs.

Based on optimized reaction conditions, a series of α,β-unsaturated compounds were synthesized, which are listed in Table 2.

Table 2. Synthesis of α,β-unsaturated heterocyclic and cyclic ketones **3**

Entry	X	R	Product	Time (h)	Yield (%)
1	-$(CH_2)_0$-	C_6H_5	A_1	4	92
2	-$(CH_2)_1$-	C_6H_5	A_2	20	95
3	-$(CH_2)_2$-	C_6H_5	A_3	20	90
4	S	C_6H_5	A_4	7	75
5	-$(CH_2)_0$-	(p-NO_2)C_6H_4	A_5	1	87
6	-$(CH_2)_1$-	(p-NO_2)C_6H_4	A_6	6	88
7	S	(p-NO_2)C_6H_4	A_7	4	72
8	S	p-FC_6H_4	A_8	4	80
9	-$(CH_2)_1$-	p-ClC_6H_4	A_9	20	80
10	S	(p-CO_2Me)C_6H_4	A_{10}	6	64
11	-$(CH_2)_1$-	(p-OMe)C_6H_4	A_{11}	22	87
12	S	(p-OMe)C_6H_4	A_{12}	9	66
13	S	2- thienyl	A_{13}	4	80
14	-$(CH_2)_1$-	2-furyl	A_{14}	14	80
15	-$(CH_2)_1$-	Me_2CHCH_2	A_{16}	16	65
16	-$(CH_2)_1$-	(p-OH)C_6H_4	A_{17}	15	85



Scheme 2. The plausible mechanism.

The suggested mechanism is schematized in Scheme 2 in accordance with the characterized products.

CONCLUSION

In summary, we reported a highly efficient method for the synthesis of α,β-unsaturated compounds in the presence of magnetic nanoparticles. Good yields, mild reaction conditions, and simplicity of removing the catalyst and recycling it for further application can be mentioned as the advantages of our protocol.

In comparison with other methods that required solvent to separate the catalyst,[17–22] in this method catalyst removed without use of any hazardous organic solvent. Magnetite is an efficient, eco-friendly and inexpensive catalyst.

EXPERIMENTAL

Melting points were measured using a capillary tube method with a Barnstead Electrothermal 9200 apparatus. Fourier transform infrared (FTIR) spectra were recorded using KBr discs on a FTIR Brucker Tensor 27 instrument. ^1H and ^{13}C NMR spectra were recorded on a Bruker AQS-Avance spectrometer at 500 and 125 MHz, using tetramethylsilane (TMS) as an internal standard. Mass spectra were documented on an Agilent Technology (HP) mass spectrometer operating at an ionization potential of 70 eV.

Preparation of Catalyst

Fe_3O_4 magnetic nanoparticles (MNPs) were synthesized by a coprecipitation method using an aqueous NaOH solution as the precipitating agent for $FeCl_3$ and $FeCl_2$.[22]

Synthesis of α,β-Unsaturated Heterocyclic and Cyclic Ketones: General Procedure

A mixture of an aldehyde (4 mmol), an amine (2 mmol), and nanosized magnetite (7 mol% with respect to aldehyde) was stirred at room temperature. An appropriate ketone (4 mmol) was then added almost immediately to the mixture. The progress of reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, magnetite was removed easily by dropping a bar magnet to the reaction vessel. The product was isolated and purified by column chromatography using hexane–ethyl acetate (30:70) as solvent system (Table 2).

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