

Silica sulfate as a recyclable and efficient catalyst for Beckmann rearrangement under microwave irradiation

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Abstract

Silica sulfate has been proved to be an efficient and recyclable catalyst for Beckmann rearrangement of a variety of oximes in acetone under microwave irradiation. This protocol has advantages of high conversion, high selectivity, short reaction time, no environmental pollution, and simple work-up procedure.

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1. Introduction

So far great efforts have been made to know and to manufacture the amides and the transformation of oximes to corresponding amides, known as the Beckmann rearrangement, is a common method, and is a topic of current interest. The conventional Beckmann rearrangement usually requires relatively high temperature and the use of strong Bronsted or Lewis acids, i.e. concentrated sulfuric acid, phosphorus pentachloride in diethyl ether, and hydrogen chloride in acetic anhydride, which lead to large amount of waste and serious corrosion problems [1,2]. On these bases, milder conditions were tried and investigation on clean, simple, and highly efficient processes became the chemists interesting undertaking.

As is known, a large number of vapor-phase Beckmann rearrangement processes such as metal ilerite [3], supported oxide [4], zeolites including MCM-41 [5], MCM-22 [6], MFI [7] and AlPO [8] have been reported, however, low selectivity and rapid decay of activity were generally resulted partially because of high temperature. Liquid-phase Beckmann rearrangement under milder conditions can afford good results

by using $\text{AlCl}_3 \cdot \text{H}_2\text{O}/\text{KI}/\text{CH}_3\text{CN}$ [9], cyanuric chloride/ CH_3CN [10], sulfamic acid [11], chloral [12], anhydrous oxalic acid [13], solid metaboric acid [14], boron trifluoride etherate [15], etc. as catalysts. Nevertheless, a relatively large amount of organic solvent such as DMF was needed, which would cause environmental problems due to volatility and toxicity. Recently, the Beckmann rearrangement in supercritical water [16] and ionic liquids [17] were reported, however, the yield in supercritical water was very low and the ionic liquid was complicated. Therefore, there still exists a need for novel and facile methods for efficient conversion of ketone and aldehyde oximes into the corresponding amides via Beckmann rearrangement.

In recent years, the use of solid supports under microwave irradiation in synthetic organic chemistry has become more popular [18] and heterogeneous reactions that are facilitated by supported reagents on various solid inorganic surfaces [19] have received attention. The advantage of these methods over conventional homogenous reactions is that they provide greater selectivity, enhanced reaction rates, cleaner products and manipulative simplicity.

In continuation of our ongoing program to develop environmentally benign methods using solid supports, we wish to report the Beckmann rearrangement using silica sulfate as catalyst under microwave irradiation.

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2. Experimental

2.1. Preparation of silica sulfate

To silica gel (10 g) in CH_2Cl_2 (50 mL), chlorosulfonic acid (5.83 g, 0.05 mol) was added dropwise over a period of 30 min under stirring at room temperature. HCl gas was evolved from reaction vessel immediately. After the addition was completed, the mixture was stirred for 30 min at room temperature. Then the solvent was evaporated off and the white solid was obtained as product, which was stored in a desiccator until use. Yield: 96%; IR (cm^{-1}): 1282 (S=O), 886, 852 (S–O).

2.2. General procedure for Beckmann rearrangement

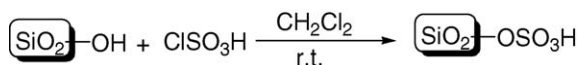
Oxime (2 mmol), silica sulfate (100 mg) and acetone (1 mL) were added into a round-bottomed flask. Then the flask was transferred into the modified microwave oven fitted with a condenser. The mixture was subjected to microwave irradiation at the power 450 W for the appropriate time as indicated in Table 2. The progress of the reaction was monitored by TLC (petroleum ether:acetone:ethyl acetate = 5:1:1). After completion of the reaction, the catalyst was filtered off. The filtrate was evaporated to remove the solvent under reduced pressure, and the residue was purified by recrystallization or chromatography to give product. All products were characterized by comparison of their melting points, IR, and ^1H NMR spectra with those of authentic samples. The Yields refer to isolated products. The selectivities were determined by GC or HPLC.

3. Results and discussion

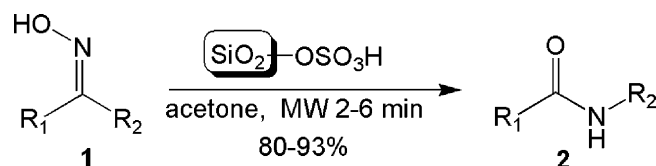
The silica sulfate was prepared by reaction of silica gel with chlorosulfonic acid in methylene chloride, and characterized by IR [1282 (S=O), 886, 852 (S–O)] (Scheme 1).

Initially, benzophenone oxime was used as a substrate to examine the feasibility of Beckmann Rearrangement using silica sulfate as catalyst. It was found that benzophenone oxime (2 mmol) mixed with 100 mg silica sulfate was the optimized ratio. After benzophenone oxime and silica sulfate in acetone were subjected to microwave irradiation for 5 min, the amide product was obtained in excellent yield (93%) by simple work-up. In order to select the appropriate microwave power, the reaction was conducted at different power level from 325 to 650 W. It was observed that 450 W of power level was to be the most promising for reaction because lower power level gave poor yield and higher power lead to destroy of substrate (Scheme 2).

The solvent effect on the Beckmann rearrangement catalyzed by silica sulfate under microwave irradiation was also investi-



Scheme 1.



$\text{R}_1, \text{R}_2 = \text{H, alkyl, aryl, heterocyclyl}$

Scheme 2.

gated. Several solvents were tested such as CCl_4 , CH_3COCH_3 , CH_3CN , CH_2Cl_2 , DMF and THF. In CH_2Cl_2 or DMF, the conversion of the substrate was proved to be good, but the selectivity to amide was quite low. In addition, the reaction hardly proceeded in CCl_4 or THF. In contrast, the reaction in CH_3COCH_3 and CH_3CN afforded amide in 99% selectivity with nearly complete conversion. Considering the environment effect, CH_3COCH_3 was proved to be the best solvent (Table 1).

To explore the generality and scope of the Beckmann rearrangement catalyzed by silica sulfate, representative ketoximes and aldoximes as substrates were examined under microwave irradiation in acetone (Table 2). Not only aromatic but also aliphatic ketoximes were smoothly rearranged under given condition. In particular, the rearrangement of most substrates was completed within 6 min. Hydroxy, methoxy, halo and nitro groups in oximes were tolerable under this condition. In the case of unsymmetrical ketoximes the reaction was selective and only one amide was produced.

Aromatic aldoximes were also converted into the corresponding primary amides in good yield under the similar conditions (entries 19–22, Table 2). It is interesting to note that sensitive furfuraldoxime was also converted into corresponding amide without any difficulty (entry 22, Table 2).

The catalyst was easily recovered and regenerated by washing with ethanol, followed by drying at room temperature for 4 h, and reused three times without significant loss of activity for the Beckmann rearrangement (entry 10, Table 2).

The Beckmann rearrangement of benzophenone oxime can be also conducted in the presence of silica sulfate under conventional reflux condition, no microwave irradiation, in CH_3CN . However, after 2 h reflux only 60% yield was provided.

Table 1
Silica sulfate catalyzed Beckmann rearrangement of benzophenone oxime in different solvents

Entry	Solvent	Conversion (%)	Selectivity (%)	
			Amide	Ketone
1	CH_3COCH_3	99	99	None
2	CH_3CN	99	99	None
3	DMF	80	25	75
4	CH_2Cl_2	70	20	80
5	THF	10	80	20
6	CCl_4	None	None	None

Table 2
Microwave-assisted Beckmann rearrangement catalyzed by silica sulfate






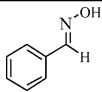
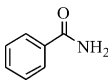
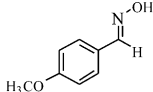
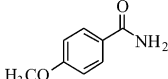
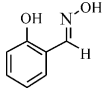
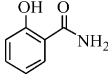
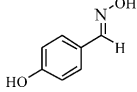
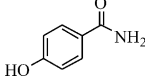
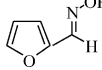
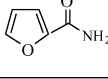
Entry	Substrate	Product ^a	Time (min)	Yield ^b (%)
1			6	85
2			6	91
3			6	90
4			5	91
5			5	91
6			3	88
7			3	86
8			4	84
9			4	88
10 ^c			3	93 (first run), 92 (second run), 89 (third run)
11			3.5	91
12			3	91
13			3.5	90
14			5	86
15			5	88
16			5	84
17			5.5	83

Table 2 (Continued)

Entry	Substrate	Product ^a	Time (min)	Yield ^b (%)
18			3.5	90
19			3	87
20			3.5	80
21			4	85
22			3	92

^a All products were characterized by comparison of their melting points, IR, and ¹H NMR spectra with those of authentic samples.

^b Yields refer to isolated products.

^c The catalyst was reused for three times without significant loss of activity.

4. Conclusion

We have developed an efficient and rapid method of Beckmann rearrangement using recoverable and reusable silica sulfate as catalyst and microwave as heating source. This protocol has advantages of high conversion, high selectivity, short reaction time, no environmental pollution, and simple work-up procedure.

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