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Short Communication

An efficient deprotection of oximes to carbonyls catalyzed by silica sulfuric acid in water under ultrasound irradiation

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ABSTRACT

Deprotection of oximes to the corresponding carbonyl compounds in silica sulfuric acid/surfactant/paraformaldehyde system can be carried out in excellent yields at 50 °C in water under ultrasound irradiation.

1. Introduction

Recovery of ketone and aldehyde from oximes is an important reaction because oxime serves as an efficient protective group for carbonyls, which are extensively used for the purification of carbonyl compounds [1]. Since many valuable reactions have been developed to prepare oximes from non-carbonyl compounds [2], the regeneration of carbonyl compounds from oximes represents a potential route for synthesis of ketones and aldehydes. Various methods have been developed for the cleavage of oximes, such as acid-catalyzed hydrolysis [3], oxidative deoximation [4], reductive deoximation [5] and deoximation of exchange of oximes with other carbonyl compounds [6]. However, some of these methods have suffered from different drawbacks such as requirements for refluxing temperature, tedious work-up, drastic conditions, long reaction times, undesired chemical yields and use of toxic reagent.

Silica sulfuric acid is an excellent candidate for sulfuric acid or chlorosulfonic acid replacement in organic reactions without any limitation such as destruction of acid sensitive functional groups, use of rather toxic solvents and expensive reagents or solvents [7]. Because of its advantages such as stable, reusable, cheap and facile, silica sulfuric acid has been used as catalyst in some organic reactions [8].

Water offers many practical and economic advantages as a reaction solvent including low cost, safe handling, and environmental compatibility. In recent years, organic reactions conducted in aqueous media have received much attention from chemists [9] because of concerns about the environment [10]. Also, most organic reactants including catalysts are insoluble in water, and the surfactants, due to their hydrophobic and hydrophilic nature, form micelles of the reactants and promote the reaction to occur in water [11]. On the other hand, a large number of organic reactions can be carried out in higher yield, shorter reaction time and milder conditions under ultrasonic irradiation than at classical conditions [12]. Recently, our laboratory reported the synthesis of oximes and methylene dioximes under ultrasound irradiation [13]. Here, we wish to report an efficient and simple procedure for deoximation to the corresponding carbonyl compounds by silica sulfuric acid/sodium dodecylsulfonate (SDS)/paraformaldehyde in water under ultrasound irradiation (Scheme 1).

2. Method

2.1. Materials and measurements

The starting materials, oximes were prepared according to the method reported in literatures [13a,13b,14]. Silica sulfuric acid was obtained according to the method reported in literature [15]. Sonication was performed in Shanghai Branson-BUG25–06 ultrasonic cleaner with a frequency of 25 kHz. The reaction flasks were immersed in every place of the cleaner in such way that the surface

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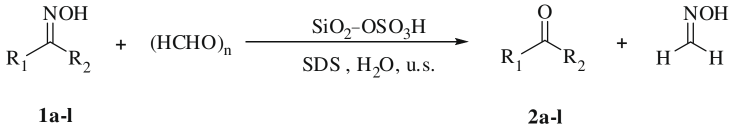


Scheme 1. Deoximation of oximes with paraformaldehyde under ultrasound.

of reactants is slightly lower than water in the cleaner, and the temperature of the water bath was controlled by the addition or removal of circulated water.

2.2. General procedure

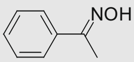
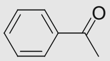
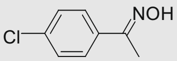
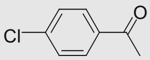
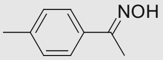
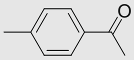
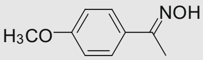
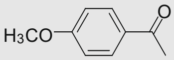
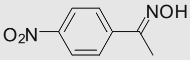
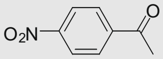
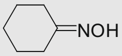
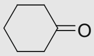
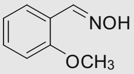
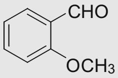
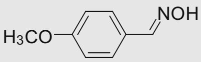
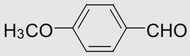
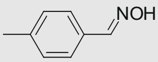
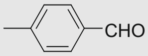
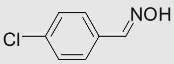
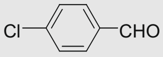
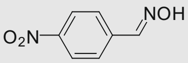
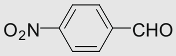
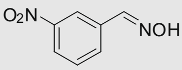
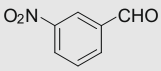
To a solution of oxime (1, 1 mmol) in water (5 mL), 0.075 g silica sulfuric acid (0.25 mmol), 0.060 g paraformaldehyde (2 mmol) and 0.015 g SDS (5 mol%) was added. The mixture was irradiated in the water bath of the ultrasonic cleaner at 50 °C for the period as indicated in Table. The progress of the reaction was monitored by thin layer chromatography. After the completion of the reaction, silica sulfuric acid was removed by filtration, and the filtrate was extracted with 15 mL ethyl acetate for three times. The combined organic layer was dried over anhydrous sodium sulfate and filtered. Ethyl acetate was evaporated under reduced pressure to give the crude product, which was separated by column chromatography on silica (200–300 mesh), eluted with petroleum ether or

Table 1
The effect of the reaction conditions on deoximation of acetophenone oxime in water under ultrasound irradiation[*].

Entry	$(HCHO)_n$ (mmol)	Catalyst (mmol)	Temp. (°C)	Time (h)	Yield (%)
1	2	0.5	30	3.5	85
2	2	0.5	40	2.5	96
3	2	0.5	50	1.5	94
4	2	0	50	4	0
5	2	0.1	50	4	78
6	2	0.2	50	2	91
7	2	0.25	50	1.5	93
8	1.5	0.25	50	2.1	93
9	2.5	0.25	50	1.5	94

[*] Substrate: acetophenone oxime, 1 mmol; H_2O, 5 mL; irradiation frequency, 25 kHz.

Table 2
Deoximation of oximes in silica sulfuric acid/surfactant/paraformaldehyde system in water at 50 °C under ultrasound irradiation.[a]

Entry	Substrate		Time (h)	Product		Isolated yield (%)
a		**1a**	1.5		**2a**	93, 95[b]
b		**1b**	3		**2b**	92
c		**1c**	1		**2c**	95
d		**1d**	2		**2d**	97
e		**1e**	2		**2e**	80
f		**1f**	1.5		**2f**	93
g		**1g**	2.5		**2g**	80
h		**1h**	2		**2h**	81, 80[b]
i		**1i**	2		**2i**	87
j		**1j**	3		**2j**	80
k		**1k**	3		**2k**	79, 75[b]
l		**1l**	3		**2l**	49

[a] Substrate: oxime, 1 mmol; $(HCHO)_n$, 2 mmol; $SiO_2–OSO_3H$, 0.25 mmol; SDS, 0.05 mmol; H_2O, 5 mL.

[b] Silica sulfuric acid was reused for the third time.

the mixture of petroleum ether and ethyl acetate (10:1). All of the products are known compounds and were identified by comparison of their physical properties (melt point and boil point) and R_f values with standard sample.

3. Results and discussion

The effect of the reaction conditions on deoximation of acetophenone oxime (**1a**) with paraformaldehyde catalyzed by silica sulfuric acid in the presence of SDS under ultrasound irradiation is summarized in Table 1.

As shown in Table 1, the reaction time was shortened from 3.5 to 1.5 h by changing the reaction temperature from 30 to 50 °C. The results showed that the reaction temperature had a significant effect, and all other reactions were carried out at 50 °C under ultrasound irradiation.

The effect of amount of silica sulfuric acid and paraformaldehyde on the reaction yields under ultrasound irradiation was also investigated. As shown in Table 1, in the absence of silica sulfuric acid, acetophenone oxime was treated for 4 h at 50 °C, no product was examined by TLC, whereas the amount of silica sulfuric acid was 0.1 mmol, acetophenone was obtained in 78% yield within the same time. By increasing the amount of silica sulfuric acid from 0.2 to 0.25 mmol, the reaction time required was shortened from 2 to 1.5 h. When decreasing the amount of paraformaldehyde from 2 to 1.5 mmol, longer reaction time was necessary to obtain the same yield. Further addition of an amount of silica sulfuric acid or paraformaldehyde had no effect on the deoximation of acetophenone oxime under ultrasound irradiation. Thus the optimum amount of silica sulfuric acid and paraformaldehyde was 0.25 and 2 mmol, respectively.

In order to verify the effect of ultrasound irradiation, we also did the experiments under silent conditions. The deoximation of **1a** and **1c** was carried out by stirring for 3 and 2.5 h at 50 °C, **2a** and **2c** were obtained in 92% and 94% yields, respectively. When under ultrasound irradiation, **2a** and **2c** were obtained in 93% and 95% yields with 1.5 and 1 h, respectively. It is apparent that deoximation of oximes can be finished in shorter time to get the same yields under ultrasound irradiation. The reason may be the phenomenon of cavitation produced by ultrasound [12].

From the results given above, the reaction conditions we chose are as follows: oxime (1 mmol), silica sulfuric acid (0.25 mmol), paraformaldehyde (2 mmol), sodium dodecylsulfonate (0.05 mmol), H_2O (5 mL). Using this reaction system, we did a series of experiments for deoximation of oximes under ultrasound irradiation. The results are summarized in Table 2.

As shown in Table 2, deoximation of some oximes were carried out in good yields with paraformaldehyde catalyzed by silica sulfuric acid in the presence of SDS under ultrasound irradiation. The different substituents in the benzene ring have some effects on the yield. When ketoximes containing electron-donating group in the benzene ring were used as substrates, ketones were obtained in good yields (Table 2, **1b**–**1d**, 92–97%), whereas ketoxime containing electron-withdrawing group gave the ketone in 80% yield (Table 2, 1e). In addition, the catalyst can be reused for the third time without significant decrease in activity (Table 2, **2a**^{b}, 2**h**^{b} and 2**k**^{b}). It is noted worthy that no Beckmann rearrangement product was obtained in present procedure.

4. Conclusion

In summary, we have found a facile and efficient method for the deprotection of oximes by silica sulfuric acid/SDS/paraformaldehyde in water under ultrasound irradiation. The present procedure avoided the use of organic solvent during the reaction, and silica sulfuric acid as catalyst can be recyclable.

Acknowledgements

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