



Ultrasound-assisted synthesis of aromatic 1,2-diketones from oximinoketones under neutral conditions in aqueous media

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ABSTRACT

We report a convenient, neutral, and facile methodology for the synthesis of aromatic 1,2-diketones from the corresponding oximinoketones in the presence of I_2 /SDS/water system under ultrasound-assisted conditions. Furthermore, a series of compounds were synthesized and characterized by melting point, IR, NMR, MS, and elemental analysis. Utilization of easy reaction conditions, very high to excellent yields, and short reaction times makes this manipulation potentially very useful.

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1. Introduction

A great deal of effort has gone into the efficient preparation of 1,2-diketones, due to their biological activity and usefulness as precursors for many useful organic transformations [1–4]. While a wide variety of methods are described in the literature for the preparation of 1,2-diketones [5–13], there are no literature examples of the synthesis of 1,2-diketones from oximinoketones. Although the oxime compounds can be deprotected to the corresponding carbonyl compounds by using a number of efficient reagents [14–20], this strategy is not free from drawbacks. Development of a better reagent in water under neutral conditions is desirable.

Organic reactions in aqueous media have attracted increasing interest currently because of environmental issues and a better understanding of biochemical processes. Water offers many practical and economic advantages as a reaction solvent, including low cost, safe handling and environmental compatibility [21,22].

The application of ultrasound in organic synthesis has been increasing because of its advantages, including a shorter reaction times, milder reaction conditions, and higher yields in comparison to classical methods [23–25]. Since in this technique the reaction is carried out normally at lower temperature relative to the usually thermal methods, the possibility of occurrence of undesired reactions is reduced, and, as a result of a cleaner reaction, the workup is easier. The generation of many cavities and a

dramatic increase in the temperature and pressure during collapse of the cavities are the most important effects of ultrasound [26,27].

Recently, a new system of I_2 /SDS/water has been used for the deprotection of oximes and imines to the corresponding carbonyl compound [28]. Herein we propose to use this system both with and without ultrasonic irradiation in the preparation of aromatic 1,2-diketones from their corresponding oximinoketones [29–31] under neutral conditions in aqueous media (Scheme 1).

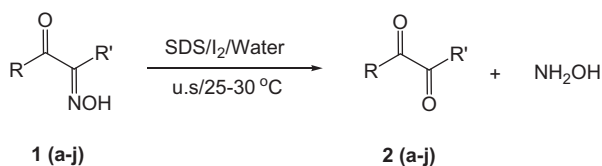
2. Experimental

2.1. General considerations

The chemicals used in this work were purchased from Merck and Aldrich chemical companies. Melting points were determined using a Mettler FP5 apparatus and are uncorrected. IR spectra were determined using KBr pellets on a Shimadzu recording spectrophotometer, Model 435. 1H and ^{13}C NMR (500 and 125 MHz) spectra were recorded on a Bruker 500 spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were taken by a Platform II from Micromass and Elemental analyses were performed using a Carlo Erba EA 1108 instrument. The ultrasonic device used was an UP 400 S instrument from Dr. Hielscher GmbH (with a frequency of 24 or 48 kHz and a nominal power of 400 W). The reaction flask was located in the ultrasonic bath, where the surface of reactants is slightly lower than the level of the water. The reaction temperature was controlled by the addition or removal of water from the ultrasonic bath.

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Scheme 1.

2.2. General procedure for the synthesis of aromatic 1,2-diketones under ultrasound irradiation

To a magnetically stirred mixture of oximinoketone (1 mmol) in H₂O (15 mL) that was exposed to ultrasonic irradiation, iodine (0.05 g, 0.2 mmol) and SDS (0.06 g, 0.2 mmol) were added at room temperature for 5 min. During the sonication, the temperature of the reaction mixture was raised to 30 °C by the addition or removal of circulating water. The progress of the reaction was followed by TLC (eluent: ethyl acetate/*n*-hexane, 4:1). The reaction went to completion after 25–35 min. The product was extracted with diethyl ether (2 × 15 mL), the organic layer was washed with brine (2 × 15 mL), dried over anhydrous Na₂SO₄, concentrated, and purified by column chromatography on neutral alumina to afford the pure product.

3. Results and discussion

We examined this reaction in the absence and presence of I₂ and sodium dodecyl sulfate (SDS). It was found that when the reaction was carried out without I₂ or SDS, no reaction occurred (Table 1, Entries 1 and 2). Therefore, both of I₂ and SDS are necessary for this reaction.

To optimize the reaction conditions, the reaction of oximinoketone **1a** and the I₂/SDS system was selected as the model reaction at 25–30 °C under ultrasound irradiation.

To find the optimum amounts of I₂/SDS, the yields of the model reaction using various amounts of I₂/SDS were obtained and compared. The results were summarized in Table 1.

From these results, it can be concluded that the optimum amounts of I₂/SDS were 0.2:0.2 mol%. The desired product was obtained in 84% yield within 35 min. (Table 1, Entry 7).

The effect of ultrasound irradiation on the reaction was also observed. As shown in Table 1, under silent conditions by using stirring for 150 min, the model reaction gave **2a** in 45% yield (Table 1, Entry 13). Under ultrasound irradiation, **2a** was obtained in 84% yield within 35 min (Table 1, Entry 7).

Table 1
Effect of reaction conditions on the reaction of oximinoketone **1a** and I₂/SDS system under ultrasound.

Entry	Molar ratio of 1a :I ₂ :SDS	Frequency (kHz)	Time (min)	Isolated yield (%)
1	1:0.0:0.1	24	60	–
2	1:0.1:0.0	24	60	–
3	1:0.1:0.1	24	40	60
4	1:0.1:0.2	24	40	63
5	1:0.1:0.3	24	40	62
6	1:0.2:0.1	24	35	78
7	1:0.2:0.2	24	35	84
8	1:0.2:0.3	24	35	82
9	1:0.3:0.1	24	35	76
10	1:0.3:0.2	24	35	79
11	1:0.3:0.3	24	35	75
12	1:0.2:0.2	48	35	82
13	1:0.2:0.2	Stirring ^a	150	45

^a Yield are related to isolated pure products.

To investigate the effect of irradiation frequency on the yields of reactions, the model reaction was sonicated at 24 and 48 kHz with electric power rating of 480 W. The yields of product were 84% and 82%, respectively (Table 1, Entries 7 and 12). This indicates that for the two frequencies of ultrasound irradiation examined, there is no difference in the reaction yield.

From the results above, the best conditions were selected as follows: oximinoketones **1 a-j** (1 mmol), iodine (0.05 g, 0.2 mmol), SDS (0.06 g, 0.2 mmol), water (15 mL), irradiation frequency 24 kHz and 25–30 °C. Under these reaction conditions, a series of experiments for the synthesis of 1,2-diketones **2 a-j** were completed with and without ultrasound respectively. The results are summarized in Table 2.

As shown in Table 2, the synthesis of 1,2-diketones **2 a-j** via the reaction of oximinoketones **1 a-j** by I₂/SDS/water system can be carried out in 80–93% yield within 30–40 min under ultrasound irradiation, while without ultrasonic irradiation the products were obtained in 30–57% yield within 120–160 min. It is apparent that ultrasonic irradiation accelerates these transformations.

To explore the scope and limitations of this reaction, we extended the procedure to alkyl and aryl groups. We found that the reaction proceeded efficiently with various aryl groups to give 1,2-diketones. However, no alkyl 1,2-diketones were obtained from reactions with alkyl groups, even under ultrasonic irradiation. Electronic effects and the nature of substituents on the aromatic ring did show effects in terms of reaction time under the reaction conditions mentioned above. When aromatic aldehydes containing electron-donating groups (such as methoxyl, or dimethylamino group) were employed, a longer reaction time was required than those of electron-withdrawing groups (such as halide groups) on aromatic rings (Table 2).

Cavitation is the origin of sonochemistry. As ultrasound passes through a liquid, the liquid can produce bubbles. These bubbles can undergo a violent collapse, which generates very high pressures and temperatures, inducing molecular fragmentation, and highly reactive species are locally produced. In addition, ultrasound is known to generate extremely fine emulsions from mixtures of immiscible liquids to enhance mass transfer from one phase into the other. One of the main consequences of these emulsions is the dramatic increase in the interfacial contact area between the reactants and an increase in the region over which any reaction between species dissolved in the different liquids can take place [26,27]. All of these can cause the reaction to take place rapidly.

Regarding the mechanism of the reaction, it is proposed that the surfactant promotes micelle formation from iodine and the oximinoketone in water, in which the electrophilic iodine activates hydration of the carbon–nitrogen double bond, possibly via an iodonium ion, that suffers attack by water to form 1,2-diketone compounds and iodine in the reaction mixture (Scheme 2).

4. Conclusion

In conclusion, we have developed a facile, neutral and efficient approach for the synthesis of aromatic 1,2-diketones from corresponding oximinoketones in water under ultrasonic irradiation. The salient features of the reaction are the following: (1) Ultrasonic irradiation accelerates these transformations in comparison with silent conditions. (2) Iodine is an efficient catalyst in the presence of SDS for the cleavage of the C=N bond. (3) In this system contamination by other products is avoided. (4) The workup procedure is simple, yields are high to excellent and the reaction times are short.

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