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Synthesis of methylene dioximes using PEG–400 as a phase transfer catalyst under microwave irradiation

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ABSTRACT

Microwave irradiation and phase transfer catalysis have been used for the synthesis of methylene dioxime. A variety of ketoximes were converted to the corresponding methylene dioximes using poly ethylene glycol (PEG-400) as a phase transfer catalyst under microwave irradiation. The method was clean, efficient and environmentally benign.

Key words: Microwave irradiation, methylene dioximes, phase transfer catalyst, PEG-400

INTRODUCTION

The phase transfer catalysis (PTC) developed at the end of 1960s and in the beginning of 1970s by Starks [1] (1971), Makosza [2] (1975), and Brandstrom [3] (1977). The PTC involves the transfer of organic molecules or ions between two liquid phases or a liquid and a solid phase. Reuben and Sjoberg (1981) [4] put forth the principle of phase transfer catalysis (PTC) that is based on the capability of certain phase-transfer agents (the PT catalysts) for the transfer of one reagent from one phase to another (immiscible) phase containing the other reagent and enhanced the rate of the reaction. Mostly the system used was both liquid phase (Water/Organic) with a catalyst as a transport shuttle having an appropriate lipophilic or hydrophilic balance to have compatibility with both phases.

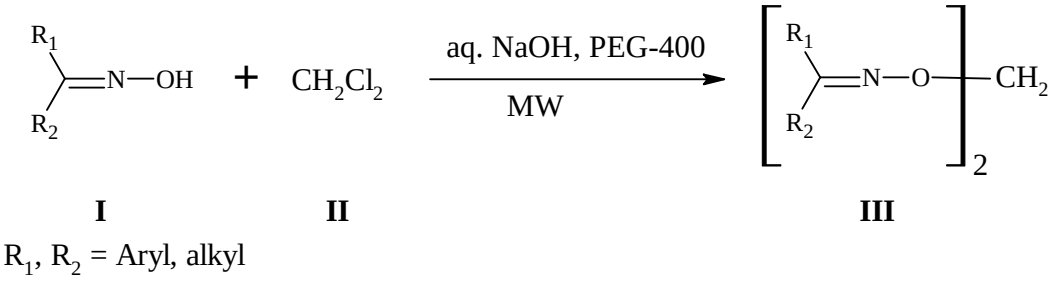
Microwave irradiation technique is the fast growing area in organic synthesis [5] since the first reports published on the microwave assisted synthesis in 1986.[6] Microwave-assisted reactions are fast, clean, economic and eco-friendly.[7] Compared to conventional methods, this technique has been accepted as a method for reducing reaction times often by orders of magnitude and for enhancing the product yield.[8] In microwave assisted organic synthesis, phase-transfer catalytic conditions (PTC) have been extensively used as a processing technique.[9] A number of phase transfer catalysis reactions were carried out under microwave irradiations.[10, 11]

The most important and commonly used PTC is polyethylene glycol (PEG) and their derivatives.[12] In commercial processes, PEG and its derivatives were widely used as PTC alternative to expensive and environmentally harmful PTCs.[12-16] In organic synthesis, PEG was considered as acyclic crown ether and are commonly used as PTC due to its thermal stability, low cost, non-toxicity and easy availability.[17] Therefore, in basic media, PEGs are good option to the onium salts. PEGs are available with various molecular weights ranging from 200 to several thousands,

PEG-200, PEG-400, PEG-600 etc. Several phase transfer reactions were carried out by using PEG as phase transfer catalyst,[18] under solvent free conditions [19] and microwave irradiations.[20]

Methylene dioximes are novel class of organic compound, used as metal capturers, anti-inflammatory and antibacterial agents.[21] In 1979, methylene dioximes were synthesized by Kirsch and Schelling [22] from the reaction between ketoximes and dichloromethane. In this reaction, dichloromethane played an important role, both as solvent and electrophile.[23] Several methods were developed for the preparation of methylene dioxime.[23,24] These methods required longer reaction time. Methylene dioxime was also synthesized under ultrasonication.[25]

In the present work we describe herein the application of microwave irradiation in the phase transfer catalysis reaction for the synthesis of methylene dioxime using PEG-400, as phase transfer catalyst. The reaction of ketoximes with dichloromethane in presence of aqueous sodium hydroxide and PEG-400 under microwave irradiation afforded methylene dioxime in high yield (Scheme 1)



I **II** **III**

R_1, R_2 = Aryl, alkyl

Scheme 1

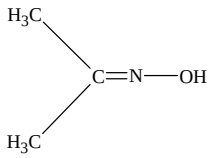
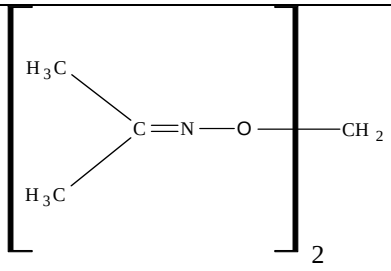
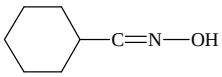
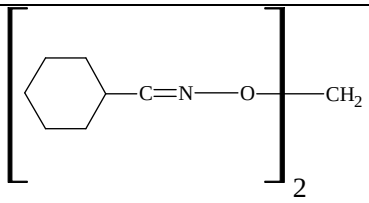
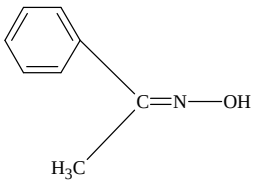
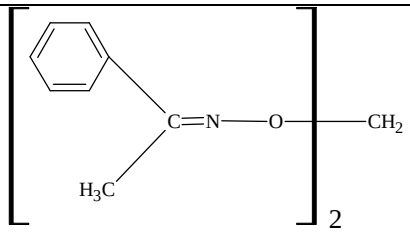
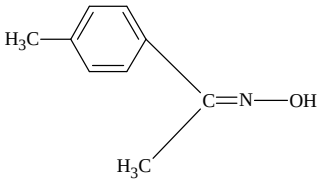
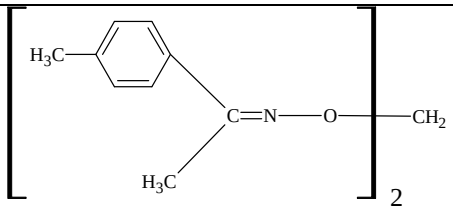
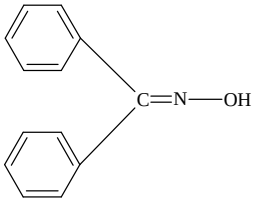
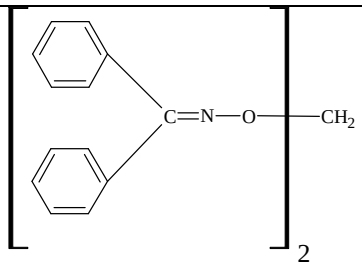
MATERIALS AND METHODS

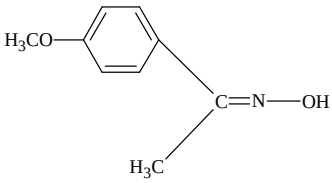
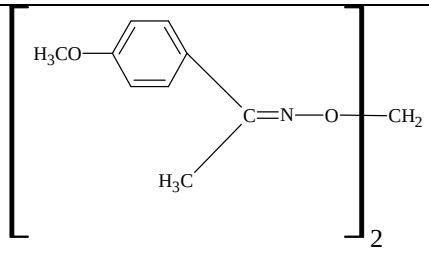
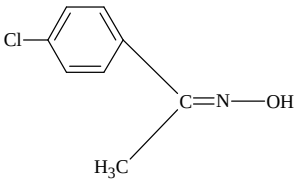
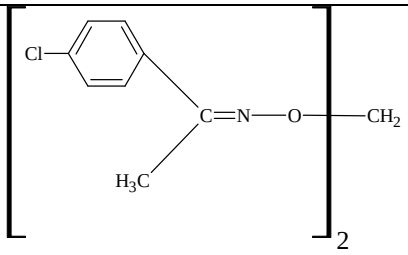
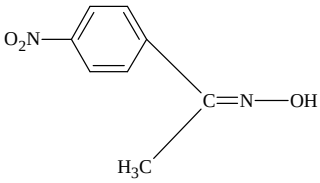
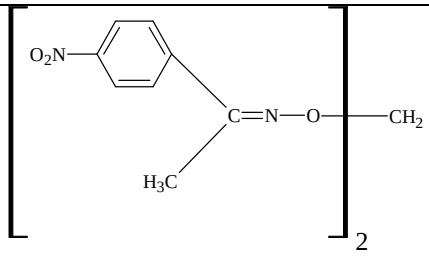
To the solution of ketoxime (3 mmol) and PEG-400 (1.13 mmol) in dichloromethane (20 mL), 50 % aqueous solution of sodium hydroxide (1 mL) was added in a 100 ml beaker at room temperature. The beaker was covered with Petri dish. Then the reaction mixture was subjected to microwave irradiation (180 W) for the time indicated in Table 1, at the interval of 10 sec. The progress of the reaction was monitored by TLC using 1:9 (V/V) ethyl acetate-petroleum ether. After completion of the reaction, the organic layer was separated and washed with water (3×20 mL), dried over anhydrous sodium sulphate and filtered. The filtrate was evaporated under reduced pressure to afford the desired products.

RESULTS AND DISCUSSION

In this method, methylene dioximes were synthesized using the phase transfer catalyst under microwave irradiation. Ketoxime (I), dichloromethane (II), PEG-400, aqueous sodium hydroxide were exposed to microwave irradiation (180 W) required 2-4 minutes to get corresponding methylene dioximes (III) in good to excellent yields (Table 1). The ketoxime with electron donating substituents (entries 4, 6) on the aromatic ring underwent faster reaction than that of electron withdrawing substituents (entries 7, 8). The advantages of this method are faster reaction, excellent yield, and use of inexpensive, non-toxic, thermally stable, environmentally benign catalyst.

Table 1 : Synthesis of methylene dioximes using PEG-400

Sr. No.	Oxime	Methylene Dioximes	Time (min.)	Yield (%)	M.P. (°C) [Lit] [22,23]
1			4	82	43 [43-44]
2			3	92	46 [47-48.5]
3			3	96	99 [99-101]
4			2	93	98 [98-99]
5			2	96	84 [85-87]

6			3	94	79 [79-82]
7			4	89	175 [176-180]
8			3	90	161 [162-164]

CONCLUSION

In conclusion, the microwave irradiation together with PEG-400 as phase transfer catalyst is effectively used for the preparation of methylene dioxime in excellent yields.

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