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# Microwave Promoted Rapid Oxidative Deoximation of Oximes under Solvent-Free Conditions

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### MICROWAVE PROMOTED RAPID OXIDATIVE DEOXIMATION OF OXIMES UNDER SOLVENT-FREE CONDITIONS

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ABSTRACT: Aldeydes and ketones are easily obtained in high yields by microwave promoted rapid oxidative deoximation of the corresponding oximes with zinc nitrate hexahydrate adsorbed on silica gel under solvent free conditions.

Regeneration of carbonyl compounds from stable and readily prepared aldoximes and ketoximes under mild reaction conditions is an important process in synthetic organic chemistry. This is because of the fact that 1) aldoximes and ketoximes are highly crystalline and very useful for isolation, identification, characterization and purification of carbonyl compounds<sup>1</sup>, 2) they can be prepared from non-carbonyl containing compounds<sup>2</sup>, where deoximation could lead to a new route for preparation of carbonyl compounds, and 3) they serve as intermediates for many reactions<sup>3</sup>. The classical method for the cleavage of oximes to aldehydes and ketones is acid hydrolysis, which is not suitable for acid

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yields with a short time of irradiation. It is noteworthy that further oxidation of the aldehydes to their carboxylic acids was not observed. Ether and phenolic groups, as well as conjugated carbon carbon double bonds, survived under these conditions. It was found that the yield of reaction in the absence of silica gel was very low. Several examples illustrating this novel and rapid procedure for the conversion of oximes to the parent carbonyl compounds are illustrated in the Table.

To show the dramatic acceleration in the rate of deprotection due to microwave irradiation, under the same experimental conditions, several oximes were heated just by conventional heating. However, only low yields of products were obtained in very long reaction times. e.g. benzaldehyde was isolated from benzaldoxime at (10-12%, 65°C, 4 min), (75%, 65°C, 8h) and (86%, 100°C, 4h).

In conclusion, the present procedure of solid phase oxidative deoximation of oximes provides a general methodology for the regeneration of carbonyl compounds from a variety of aromatic, aliphatic, polynuclear and heterocyclic oximes. The application of microwave offers a very quick and clean method for this conversion. The operational simplicity, selectivity, use of inexpensive reagents, high yields in very short reaction times, can make this procedure a useful and attractive alternative to the currently available methods.

#### **EXPERIMENTAL**

Required oximes were purchased from Fluka or were prepared in our laboratory from the corresponding carbonyl compounds according to reported

Entry	Substrate	Isolated yield <sup>(a,b)</sup> of Carbonyl Compound
1	CH=NOH	90
2	CH=NOH	89
3	О21 СН= ЮН	87
4	CH-NOH	90
5		91
6	Ме-О-СН=ЮН	92
7	CH=CH-CH=NOH	86
8	CH=NOH	87
9	Коруссияние и собрание и собрание И собрание и собрание и Собрание и собрание и соб	89
10	NOH	84
11	C(CH3)=NOH	85
12	-C(Ph)=NOH	89
13		87
14	$\bigcirc\bigcirc\bigcirc$	84

Table : Conversion of Oximes to Their Corresponding Carbonyl Compounds.

a) Yields referred to isolated yields. b) Products were characterized by comparison of their physical data, IR, NMR spectra with known samples<sup>12</sup>.

sensitive compounds<sup>4</sup>. Reductive and oxidative deoximation reactions, especially under aprotic conditions, have therefore been developed and have some advantages over the classical method.<sup>5</sup>

Many interesting reactions under dry conditions in the presence of inorganic solids such as alumina<sup>6</sup>, clay<sup>7</sup>, and silica gel<sup>8</sup> have been reported in recent years. The notable advantages for most of these reactions are operational simplicity, generality, excellent regioselectivity, absence of side reactions, and quantitative yields. In addition, in the past few years there has been a tremendous interest in microwave heating and its application in organic reactions<sup>9</sup>.

We now wish to report in this communication that zinc nitrate hexahydrate adsorbed on silica gel  $(Zn(NO_3)_2 / Silica)$  is able to perform oxidative transformation of oximes selectively and conveniently under a solvent-free conditions by microwave irradiation.

The reagent was easily prepared<sup>10</sup> by addition of silica gel to a solution of zinc nitrate in acetone. Solvent was evaporated and the white solid was dried under reduced pressure. This reagent was stable and could be stored in air at room temperature without losing its activity. Several deoximation reactions were performed, at various powers and irradiation times, in order to find the best conditions for this reaction under microwave irradiation. Oxidizing reagent to substrate ratio of 1.2:1, a reaction time of 4 minutes, and maximum power output of 200W were found to be the optimal conditions.

Our experiments show that not only ketoximes but also aldoximes underwent oxidative cleavage to the corresponding carbonyl compounds in high procedures<sup>11</sup>. Products were characterized by comparison of their physical data, IR and <sup>1</sup>HNMR spectra with known samples<sup>12</sup>. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/ UV 254 plates.

# Preparation of the Reagent and General Procedure for the Oxidative Dioximation of Oximes.

Silica gel was added to a solution of zinc nitrate hexahydrate in acetone (1.0 mmol g<sup>-1</sup> SiO<sub>2</sub>). The mixture was evaporated and the residue was finally dried in the presence of  $P_2O_5$  under vacuum at 45°C overnight. The oxime (1 mmol) was thoroughly mixed with the oxidizing agent (1.2 mmol). The resulting mixture was then taken in a Pyrex Erlenmeyer flask (25 ml) and irradiated in a commercial microwave oven (200W) for 4 minutes. The reaction mixture was then allowed to reach room temperature. The inorganic support was separated by filtration after eluting the product with acetone. The crude product obtained after evaporation of the solvent was purified by column chromatography and dried over anhydrous sodium sulfate to afford the TLC and <sup>1</sup>HNMR pure products in 84-92% isolated yields.

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