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Solid State Regeneration of Ketones from Oximes on Wet Silica Supported Sodium Periodate Using Microwaves

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Abstract: Microwave irradiation of ketoximes on wet silica supported sodium periodate under solvent-free conditions provides a fast, efficient and simple method for regeneration of ketones.
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Oximes are extensively used for purification and characterization of carbonyl compounds and in the preparation of amides *via* the Beckmann rearrangement.[1] Their synthesis from non-carbonyl compounds[2] provides an alternative pathway to aldehydes and ketones. The important role of oximes as protecting groups[3] owing to their hydrolytic stability has provided motivation for the development of newer deoximation reagents such as Raney nickel,[4a] pyridinium chlorochromate,[4b] pyridinium chlorochromate-H_2O_2,[4c] triethylammonium chlorochromate,[4d] dinitrogen tetroxide,[4e] trimethylsilyl chlorochromate,[4f] Dowex-50,[4g] dimethyl dioxirane,[4h] H_2O_2 over titanium silicalite-1,[4i] zirconium sulfophenyl phosphonate,[4j] N-haloamides,[4k] and bismuth chloride.[4l]

Recently, there has been a growing interest in the application of microwave irradiation in chemical reaction enhancement,[5-7] the salient features being improved reaction rates and formation of cleaner products. These solvent-free reactions[6,7] are especially appealing as they provide an opportunity to work with open vessels, thus avoiding the risk of high pressure development and with a possibility of carrying out the reaction on a preparative scale in addition to the associated selectivity and ease of manipulation. In continuation of our investigations on organic manipulations in solvent-free systems,[7] we now report a solid state deoximation procedure using sodium periodate ($NaIO_4$) supported on wet silica. Although $NaIO_4$ has been used extensively for oxidative purposes,[8] its use in the cleavage of ketoximes is not known, to the best of our knowledge.

Among various mineral supports examined, such as alumina, clay, silica etc., silica was found to give the best results. The irradiation of ketoximes on clay predominantly results in the formation of Beckmann rearranged products.[1b] The optimum ratio of the substrate to the reagent for deoximation is found to be 1:2 (mole/mole). The reaction remains incomplete when lower amounts of the oxidant are used or in the absence of silica support, even after prolonged exposure to microwaves (5 min). Using an alternate heating mode (oil bath) at 110° C, the reaction could be completed in 36 h. The recyclability of the silica after washing of the spent support with water and the general applicability of this rapid reaction to a variety of ketoximes under solvent-free conditions are some of the attractive features of this method. Interestingly, the procedure does not form a Schiff's base in the case of aromatic amine (entry 5). The deoximation of aldoximes under similar reaction conditions, however, results in a complex mixture of products with consumption of all the starting material.

General procedure: The reagent is prepared as described earlier by adding silica gel (40 g, 230-400 mesh, Baxter) to a stirred solution of $NaIO_4$ (10g, 46.7 mmol) in 60 mL of water.[7k] After removal of water the resulting white powder is dried in an oven at 120 °C for 12 h. The reagent (2.14 g, 2 mmol of $NaIO_4$) is wetted with water (0.6 mL) and is mixed with the neat ketoxime (1 mmol) in a small beaker. The beaker is placed in an alumina bath (heat sink) inside a Kenmore microwave oven (2450 MHz) operating at full power (900 W) for the specified time. After completion of the reaction (monitored by TLC) the product is extracted into dichloromethane (3x15 mL). Our results for the cleavage of various oxime derivatives are summarized in the **Table.**

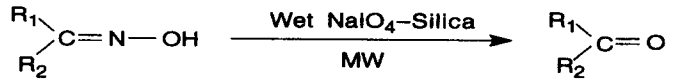

Table: Microwave-assisted deoximation using wet silica supported sodium periodate

Entry	R_1	R_2	Time (min)	Yield[a] (%)
1	C_6H_5	Me	1.5	80
2	*p*-Cl-C_6H_4	Me	1.0	75
3	*p*-OMe-C_6H_4	Me	2.0	93
4	*p*-Me-C_6H_4	Me	1.0	82
5	*p*-NH_2-C_6H_4	Me	2.5	83
6	C_6H_5	C_6H_5	1.5	89
7	$CH_3CH_2CH_2CH_2$	CH_3CH_2	0.75	68
9			1.0	78
10			1.25	86

[a]Unoptimized yields of pure isolated products that exhibited physical and spectral properties in accord with the assigned structures.

In conclusion, we have developed a solvent-free method for the facile cleavage of ketoximes using wet silica supported sodium periodate under microwave irradiation conditions.

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