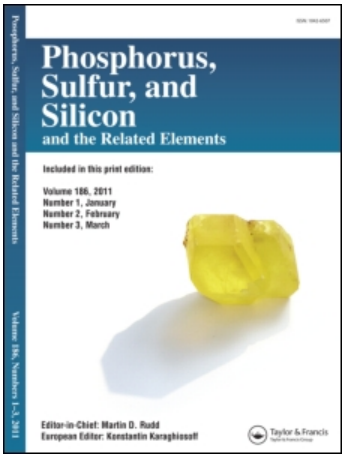

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Regeneration of Carbonyl Compounds from Oximes Using Oxone/Wet-Alumina Under Microwave Irradiation

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REGENERATION OF CARBONYL COMPOUNDS FROM OXIMES USING OXONE/WET-ALUMINA UNDER MICROWAVE IRRADIATION

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A new solventless deoximation reaction using oxone/wet-alumina, under microwave irradiation is described.

Keywords: Carbonyl compounds; deoximation reaction; ecofriendly; microwave irradiation; oxone; solventless; wet-alumina

Oximes are extensively used for purification and charactrization of carbonyl compounds.[1–3] Their synthesis from noncarbonyl compound offers an alternative route to aldehydes and ketones.[4,5] The hydrolytic stability of oximes has inspired the development of several deoximation reagents and has been of interest for several laboratories including our own.[6–9]

A reagent that is powerful in transferring oxygen, selective in its reactivity, mild toward the oxidized product, and conveniently prepared from commercially available material would be very useful. Among the known oxidizing agents with the above virtues, is potassium peroxymonosulfate ($KHSO_5$) commercially sold as oxone. Oxone is a convenient, inexpensive, and powerful oxidant used for the transformation of a wide range of functional groups[10–12] including cleavage of oximes using glacial acetic acid in the range of 1–5 h in good yields.[13]

Application of microwave irradiation is under intensive examination nowadays.[14–16] The important effects are: decreasing reaction time (up to 3 orders of magnitude) and, in some cases, cleaner reactions with

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easier workup. Organic solvents not only are expensive, but they cannot be placed in a microwave oven in open vessels (thus, avoiding the risk of high pressures and explosion). Coupling of microwave irradiation and dry media therefore is an organic chemist's delight.

We investigated the use of oxone as an oxidant for deoximation reactions under microwave irradiation and found it uncontrollable due to explosions and decomposition of materials. Reagents deposited on mineral supports have gained popularity in organic synthesis due to their selectivity and ease of manipulation.[17,18] Association of oxone with mineral supports has been pioneered by Marimoto et al.[19,20]

We mixed alumina with oxone, equal in weight, and made an intimate homogenous mixture. When neat oxime was mixed with the pure reagent and placed in a microwave oven, a sluggish deoximation was observed. However when this mixture was moistened, a rapid and efficient oxidative cleavage of oximes took place. To assess the generality of the method, a wide variety of oximes were subjected to deoximation using oxone/wet-alumina under microwave irradiation (Table I).

The usefulness of premoistened support in microwave irradiation has been noted previously.[21] In this article we wish to report that the mixture of oxone/wet-alumina can serve as an efficient, selective, mild and ecofriendly reagent for the cleavage of oximes under microwave irradiation. The best ratio of substrate/oxone was found to be 1 : 1.1.

$$R_1R_2C{=}NOH \xrightarrow[\text{microwave}]{\text{oxone/wet-alumina}} R_1R_2C{=}O$$

TABLE I Regeneration of Carbonyl Compounds[a] from Oximes[b] Using Oxone/Wet-Alumina under Microwave Irradiation

Entry	R_1	R_2	Yield(%)[c]
1	C_6H_5	H	95
2	4-$CH_3C_6H_4$	H	94
3	4-$OCH_3C_6H_4$	H	90
4	2-$NO_2C_6H_4$	H	99
5	4-$NO_2C_6H_4$	H	98
6	C_6H_5	CH_3	89
7	C_6H_5	C_6H_5	86
8	CH_3	C_3H_7	84
9	Cyclohexyl		87
10	4-$OCH_3C_6H_4$	CH_3	82

[a]All products were known and characterized by comparing their physical and spectroscopic data with those of authentic samples.

[b]Oximes are synthesized according to a known procedure.

[c]Yields refer to isolated product.

Use of excess reagent affected neither the yields nor the time of reactions. As indicated in Table I, the time of reaction is very short and yields are high to excellent. No overoxidation to carboxylic acid was observed.

In conclusion, deoximation with oxone/wet-alumina under microwave irradiation in solventless system is a rapid, manipulatively simple, inexpensive, and selective protocol and can be added to organic synthesis methodology.

EXPERIMENTAL

All compounds are known and characterized by comparision of their physical and spectroscopic data with those of authentic samples. All substrates were synthesized according to a known procedure.[22–24] Microwave irradiation were carried out in a domestic instrument at 1000 W. The reagent was prepared by grinding 5 g of alumina 60G (Type E) purchased from Merck and 5 g of oxone, which was premoistened before use.

Regeneration of Carbonyl Compounds from Oximes

General Procedure

An appropriate amount of oxime (3 mmol) and oxone/wet-alumina were mixed intimately in a pyrex beaker. To this mixture, a drop of water was added and stirred to make a homogenous mixture. The beaker was placed in a household microwave oven for 7 min for all oximes. The progress of the reaction was monitored by TLC. After completion of the reaction, $CHCl_3$ (5 ml) was added and the mixture was filtered. The solvent was evaporated to dryness to afford the corresponding carbonyl compound (Table I). (Caution: Although we did not have any accident carrying out the above reaction, the use of the microwave oven in an efficient hood is highly recommended.)

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