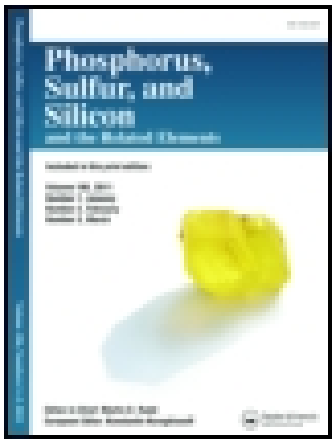

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

MICROWAVE ASSISTED OXIDATION OF BENZALDEHYDES UNDER SOLVENT-FREE CONDITION USING OXONE®/WET-ALUMINA

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Published online: 16 Aug 2010.

To cite this article: Mir M. Alavi Nikje & Mohammad A. Bigdeli (2004) MICROWAVE ASSISTED OXIDATION OF BENZALDEHYDES UNDER SOLVENT-FREE CONDITION USING OXONE®/WET-ALUMINA, Phosphorus, Sulfur, and Silicon and the Related Elements, 179:7, 1445-1448, DOI: 10.1080/10426500490463655

To link to this article: http://dx.doi.org/10.1080/10426500490463655

Phosphorus, Sulfur, and Silicon, 179:1445–1448, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490463655

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MICROWAVE ASSISTED OXIDATION OF BENZALDEHYDES UNDER SOLVENT-FREE CONDITION USING OXONE®/WET-ALUMINA

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(Received October 30, 2003; in final form November 25, 2003)

The solventless oxidation of benzaldehydes to carboxylic acids using oxone/wet-alumina under microwave irradiations is described.

Keywords: Benzaldehydes; eco-friendly; microwave irradiation; oxone/wet-alumina; solventless

The oxidation of aldehydes to carboxylic acids is an important transformation in organic synthesis and several methods have been developed to accomplish this conversion.[1] In the past, the use of oxone($2KHSO_5$, $KHSO_4$, K_2SO_4) in the presence of various solvents was developed,[2] and although all previous methods are not detrimental to the environment, organic solvents or heavy metal based oxidants are used in this transformation. Organic solvents are not only expensive but often are flammable, toxic, and environmentally hazardous. Motivated by recent interest in carring out microwave assisted reactions in solvent-free media, emphasis on green chemistry,[3] and in the continuation of our experiments for the use of oxone/wet-alumina in solventless oxidation reactions,[4] we decided to re-examine this procedure using microwave irradiations for the oxidation of benzaldehydes.

Oxone is a convenient, inexpensive, and powerful oxidant used for the transformation of a wide range of functional groups,[2] including cleavage of oximes using glacial acetic acid in the range of 1–5 h in good yields.[5]

Application of microwave irradiation currently is under intensive examination.[6] 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 work up. Organic solvents are not only expensive, but they can not be placed in microwave oven in open vessels (avoiding the risk of high pressures and explosion). Coupling of microwave irradiation and dry media therefore is organic chemists delight.

We investigated the use of oxone as an oxidant for oxidation 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.[7] Association of oxone with mineral supports has been pioneered by Marimoto et al.[8] We mixed alumina with oxone in equal weight and made and intimate a homogenous mixture. When neat benzaldehyde was mixed with the pure reagent and placed in microwave oven, a sluggish oxidation was observed. However, when this mixture was moistened, a rapid and efficient oxidation of benzaldehyde took place. To assess the generality of the method a wide variety of benzaldehydes regardless of the electron donating and electron accepting nature of the substituents on the phenyl group were subjected to oxidation using oxone/wet-alumina under microwave irradiation (Table I).

In this article, we report the mixture of oxone/wet-alumina can serve as an efficient, selective, mild, and eco-friendly reagent for the oxidation of benzaldehydes under microwave irradiation. The best ratio of substrate/oxone was found to be 1/1.1. Use of excess reagent affected neither the yields nor the time of reactions.

$$\mathrm{ArCHO} \xrightarrow[\text{Microwave Irradiations}]{\text{Oxone/wet-alumina}} \mathrm{ArCOOH}$$

TABLE I Oxidation of Benzaldehydes Using Oxone/Wet-Alumina Under Microwave Irradiation[a]

Entry	Ar	Yield (%)[b]
1	C_6H_5	98
2	4-$CH_3C_6H_4$	96
3	4-$OCH_3C_6H_4$	96
4	2-$NO_2C_6H_4$	92
5	3-$NO_2C_6H_4$	95
6	4-$NO_2C_6H_4$	91
7	3-ClC_6H_4	86
8	4-ClC_6H_4	74
9	2-OHC_6H_4	82

[a]Irradiation time 9 min for all benzaldehydes.

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

As indicated in the Table I, the time of reaction is very short and yields are high to excellent.

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

EXPERIMENTAL

All compounds are known and were characterized by comparison of their physical and spectroscopic data with those of authentic samples. All substrates were purchased from Merck company. Microwave irradiation was carried out in a domestic instrument at full power. The reagent was prepared by grinding 5 g of alumina 60G (Type E) purchased from Merck and 5 g of oxone and premoistened before use.

Oxidation of Benzaldehyde

General Procedure

An appropriate amount of benzaldehyde (3 mmol) and oxone/wet-alumina (3.3 mmol based on oxone) 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 house hold microwave oven for 9 min for all benzaldehydes. The progress of the reaction was monitored by TLC. After completion of the reaction, $CHCl_3$ (2×5 ml) was added and the mixture was filtered. The solvent was evaporated to dryness to afford the corresponding carboxylic acids (Table I).

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