

Microwave-assisted oxidation of alcohols using Magtrieve™

D. Bogdal,* M. Lukasiewicz, J. Pielichowski, A. Miciak and Sz. Bednarz

Department of Chemistry, Politechnika Krakowska, ul. Warszawska 24, 31-155 Krakow, Poland

Received 19 September 2002; revised 4 November 2002; accepted 28 November 2002

Abstract—Primary and secondary alcohols can be selectively oxidized under microwave irradiation into the corresponding aldehydes and ketones within 5–30 min using commercially available and magnetically retrievable Magtrieve™. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

The oxidation of alcohols to carbonyl compounds is a fundamental transformation in organic chemistry since carbonyl compounds are widely used as intermediates both in manufacturing and research.¹ Although the oxidation of organic compounds under non-aqueous conditions has become an effective technique for modern organic synthesis,² the methods still suffer some disadvantages including the cost of preparation, long reaction time, and tedious work-up procedures. In recent years, oxidation processes have received much attention, especially in the search for selective and environmentally friendly oxidants.^{3,4}

Microwave synthesis is a new technique for conducting chemical reactions. Acceleration of organic reactions by microwaves has been largely proven elsewhere, and in many cases, microwave techniques have become more effective than conventionally conducted reactions.⁵ Moreover, in a number of applications, reactions under microwave conditions can provide pure products in high yield.⁶

2. Results and discussion

Magtrieve™ is DuPont's trademark for the oxidant based on tetravalent chromium dioxide (CrO₂).⁷ In our research on oxidation processes, we chose Magtrieve™ as an oxidant, because it has been proven to be a useful oxidant in some reactions⁸ including the oxidation of alcohols.⁹ Magtrieve™ as an oxidant is a very well suited reagent for microwave synthesis, because as an ionic and magnetically retrievable material, it carries a benefit of efficient conversion of

electromagnetic energy into heat according to the dielectric heating mechanism. For example, the irradiation of Magtrieve™ (2.5 g) with a continuous power of microwave reactor (30%) in an open vessel (5 cm diameter) led to quick heating of the material up to 360°C within 2 min. As it was expected, the temperature recorded by means of a thermovision camera had the highest value in the center of the reaction vessel (Fig. 1). All the attempts to measure the temperature of Magtrieve™ with a thermocouple after switching off the microwave power showed much lower temperature of ca. 80–100°C which leads to an important conclusion that the only valid temperature measurement must be done during microwave experiments while the material is irradiated with a continuous power.

When toluene (15 mL), which is a weak microwave absorber, was introduced into the reaction vessel, the temperature of Magtrieve™ reached ca. 140°C within 2 min and was more uniformly distributed (Fig. 2).

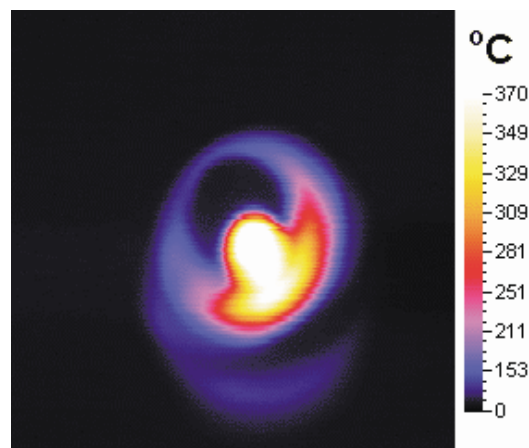


Figure 1. The temperature profile for Magtrieve™ irradiated by microwaves (2 min of irradiation).

Keywords: Magtrieve™; alcohols; oxidation; microwave irradiation.

* Corresponding author. Tel.: +(48)(12)628-25-72; fax: +(48)(12)628-20-38; e-mail: pcbogdal@cyf-kr.edu.pl

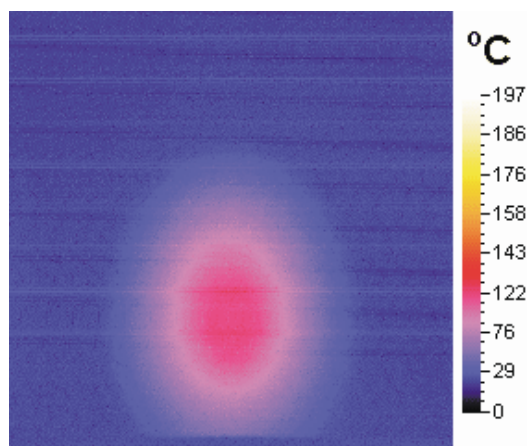


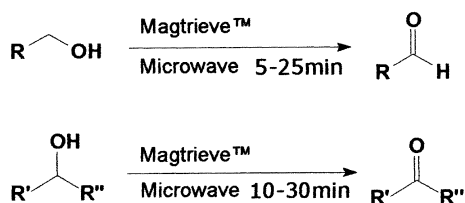
Figure 2. The temperature profile for Magtrieve™ in a toluene solution irradiated by microwaves (2 min of irradiation).

It is worth stressing that even though the temperature of the solid material was higher than the boiling point of toluene, we did not observe boiling in the reaction vessel. It leads to another important conclusion that during reactions in heterogeneous systems (solid support/organic solvent) in which microwaves have been proved to be the most effective¹⁰ the temperature of solid material can be higher than the bulk temperature of solvent and measurements of temperature with a pyrometer, thermocouple, or fiber optics thermometer does not give correct values. In such a case, the higher temperature of the solid support leads to higher conversion of reactants or/and higher reaction rates, which in turn might be a reasonable explanation for the so-called non-thermal microwave effect, i.e. an increase in reaction rates that cannot be explained by an increase in the temperature of reaction medium.¹¹ On the other hand, the application of microwave irradiation is the only simple way to maintain the temperature of the solid support higher than the bulk temperature of the reaction mixture, which implies that such a process might be more energy efficient than other conventional processes.

All the reactions were carried out under heterogeneous conditions using Magtrieve™ as an oxidant and toluene as an organic phase.

Our earlier study on microwave modification¹² of Noyori's procedure of alcohol oxidation³ showed that in the case of primary alcohols the oxidation by hydrogen peroxide is so effective that it cannot be stopped at the aldehyde stage; the equivalent carboxylic acids are the only product.

In order to solve this drawback, we attempted to apply Magtrieve™ to the oxidation of primary alcohols to aldehydes. Furthermore, we show that secondary alcohols



Scheme 1. Oxidation of alcohols using Magtrieve™.

can be oxidized to ketones under the same conditions (Scheme 1).

The experimental procedure involves a simple mixing of an alcohol with toluene in a round-bottomed flask followed by the addition of Magtrieve™ in 5:1 weight ratio for both primary and secondary alcohols.

The excess of the oxidant is required since only its surface is reduced. Then the reaction mixtures were placed inside a multimode microwave reactor (Plazmatronika, Poland) and irradiated under a reflux condenser, which allowed carrying out the process in a refluxing solvent. After the reaction, which was monitored by GC/MS analysis, the mixtures were cooled to room temperature. Then Magtrieve™ was retrieved with a magnet, and the solution was concentrated to give a crude product. The results are summarized in Table 1.

The carbonyl compounds were obtained with satisfactory yield and in a short time (Table 1). The primary alcohols were turned into the desired aldehydes without over oxidizing them to carboxylic acids. The reactivity of the secondary alcohols seems to be slightly lower, but the addition of higher amount of the oxidant did not increase the yield of desired ketones. In the case of 1-octen-3-ol, we have shown that the microwave protocol, like the conventional one, retained the alcohol/olefin chemoselectivity. For example, the oxidation of 1-octen-3-ol resulted in 1-octen-3-one; even small amounts of epoxy compounds were not detected.

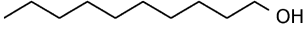
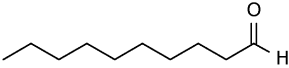

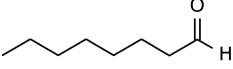
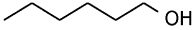
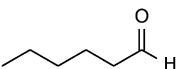
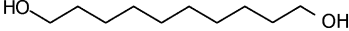
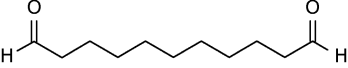
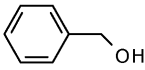
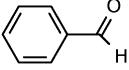
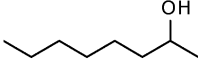
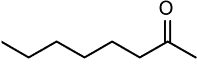
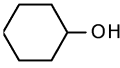
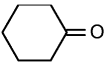
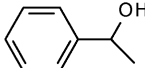
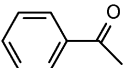
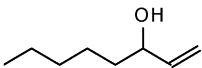
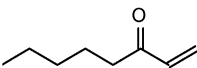
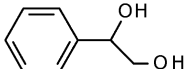
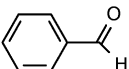
Some attempts have been made to carry out the oxidation of alcohols without a solvent or in the presence of a small amount of a solvent (toluene) under microwave irradiation. As was stated above, the reactions resulted in non-uniform heating of the reaction mixture and overheating of Magtrieve™ (up 360°C). An open flame within a reaction flask was noticed in some cases! Thus, the application of a solvent was necessary to maintain the reaction temperature and carry out safely the oxidation of alcohols in the presence of Magtrieve™ during the microwave experiment.

3. Conclusion

In conclusion, we have developed a mild, fast, and efficient method for the selective oxidation of aliphatic and benzylic alcohols to their corresponding carbonyl compounds by employing the solid and magnetically retrievable oxidant, Magtrieve™, under microwave conditions. Moreover, in comparison to the original work by Lee and Donald,⁹ the amount (excess) of the oxidant was substantially reduced under microwave conditions from 10 to 5-fold excess while the reaction yield remained at the same level.

The advantages of this protocol include a simple reaction set-up, application of commercially available reagents as well as oxidant. As was shown in the experiments with the thermovision camera, high product yields and short reaction times are the results of higher temperature of Magtrieve™ during microwave experiments in comparison with conventional processes.

Table 1. Microwave-assisted oxidation of primary and secondary alcohols using Magtrieve™ under microwave irradiation (Plazmatronika reactor)

Alcohol	Carbonyl compound	Microwave		Conventional	
		Time (min)	Yield ^a (%)	Time (min)	Yield ^a (%)
<i>Primary alcohols</i>					
		5	67	5	26
		10	77	10	41
		15	85	15	58
		20	90	20	67
				150	81
		5	45	5	18
		10	60	10	34
		15	73	15	40
		20	84	20	51
		25	99	25	–
		120	75		
		5	41	5	27
		10	52	10	36
		15	60	15	45
		120	63		
		5	67	5	23
		10	70	10	29
		15	73	15	37
		20	75 ^b	20	45
				150	57
		5	96	120	78
<i>Secondary alcohols</i>					
		10	49	10	33
		20	57	20	53
		30	73	30	69
				180	91
		30	85	120	70
		20	65	150	69
		20	98	110	80
		10	95	75	90

The power of the microwave reactor was set to 90% during first 2 min of irradiation and 70% to the end of experiment.

^a Isolated yield.

^b The amount of Magtrieve™ was doubled.

4. Experimental

4.1. General method

The reactions were carried out in a multimode microwave reactor with a continuous power regulation (PLAZMATRONIKA, Poland), which is equipped with magnetic stirrer and two inlets on the top and one side of the reactor. The inlets allowed applying an upright condenser and

introducing a fibre-optical sensor (ReFlex, Nortech) which was used to control temperature during microwave experiments.

The temperatures of Magtrieve™ during microwave experiments were recorded by means of the thermovision camera VIGO SYSTEM (V-20).

IR spectra were recorded on FT-IR BIORAD FTS-165

spectrophotometer as liquids on NaCl disks. ^1H NMR spectra were collected on Tesla 487C (80 MHz) spectrometer using TMS as an internal standard. GC/MS spectra were determined on GC/MS 5890 SERIES II HEWLETT–PACKARD gas chromatograph equipped with Ultra 2 (25 m \times 0.25 mm \times 0.25 μm) column with HEWLETT–PACKARD 5971 Series Mass Selective Detector.

4.2. Starting materials

All the chemicals were purchased from Aldrich and used as received.

All the reactions were carried out according to the oxidation procedure given for 1-octanol, which was representative of the general procedure employed for primary alcohols, and the oxidation procedure given for 2-octanol, which was representative of the general procedure employed for secondary alcohols.

4.2.1. 1-Octanal. A solution of 1-octanol (1.0 g, 7.7 mmol) in 15 mL of toluene was prepared in a 100 mL round-bottom reaction flask. Then the 5.0 g of MagtrieveTM was added, and the mixture was stirred and irradiated to reflux under an upright condenser in the microwave reactor (PLAZMATRONIKA) for the time indicated in Table 1. At the end of the exposure to microwaves, the mixture was cooled to room temperature and MagtrieveTM was completely retrieved with a magnet. Then toluene was evaporated to afford crude octanal, which was purified by Kugelrohr distillation. Yield 0.97 g (99%).

4.2.2. 2-Octanal. A solution of 2-octanol (1.0 g, 7.7 mmol) in 15 mL of toluene was prepared in a 100 mL round-bottomed flask. Then the 5.0 g of MagtrieveTM was added, and the mixture was stirred and irradiated to reflux under an upright condenser in the microwave reactor (PLAZMATRONIKA) for the time indicated in Table 1. At the end of the exposure to microwaves, the mixture was cooled to room temperature and MagtrieveTM was retrieved with a magnet. Then toluene was evaporated to afford crude 2-octanone, which was purified by Kugelrohr distillation. Yield 0.72 g (73%).

4.2.3. 1-Decanal. Yield=0.89 g (90%) liquid; bp 96–97°C/10 Torr (lit.¹³ 93–95°C/10 Torr). Spectroscopic data consistent with that found in the literature.

4.2.4. 1-Octanal. Yield=0.97 g (99%) liquid; bp 69–70°C/10 Torr (lit.¹³ 66–68°C/10 Torr). Spectroscopic data consistent with that found in the literature.

4.2.5. 1-Hexanal. Yield=0.59 g (60%) liquid; bp 122–125°C (lit.¹³ 119–124°C). Spectroscopic data consistent with that found in the literature.

4.2.6. 1,10-Decandial. Yield=0.74 g (75%) liquid; bp 132–135°C/10 Torr (lit.¹⁴ 95°C/0.5 Torr). Spectroscopic data consistent with that found in the literature.

4.2.7. Benzaldehyde. Yield=0.94 g (96%) liquid; bp 179–182°C (lit.¹³ 177–179°C). Spectroscopic data consistent with that found in the literature.

4.2.8. 2-Octanone. Yield=0.72 g (73%) liquid; bp 175–177°C (lit.¹³ 170–172°C). Spectroscopic data consistent with that found in the literature.

4.2.9. Cyclohexanone. Yield=0.83 g (85%) liquid; bp 152–154°C (lit.¹³ 154–156°C). Spectroscopic data consistent with that found in the literature.

4.2.10. Acetophenone. Yield=0.64 g (65%) solid; mp 18–20°C (lit.¹³ 19–20°C). Spectroscopic data consistent with that found in the literature.

4.2.11. 1-Octene-3-one. Yield=0.96 g (98%) liquid; bp 45–48°C/10 Torr (lit.¹³ 56–60°C/16 Torr). Spectroscopic data consistent with that found in the literature.

Acknowledgements

This work was undertaken as part of the EU sponsored D10 COST Program (Innovative Methods and Techniques for Chemical Transformations).

References

1. Trost, B. M. *Comprehensive Organic Synthesis (Oxidation)*; Pergamon: New York, 1991; Vol. 7.
2. Hudlicky, M. *Oxidations in Organic Chemistry. ACS Monographs 186*; ACS: Washington, DC, 1990.
3. (a) Sato, K.; Aoki, M.; Noyori, R. *Science* **1998**, *281*, 1646. (b) Sato, K.; Aoki, M.; Tagaki, J.; Noyori, R. *J. Am. Chem. Soc.* **1997**, *119*, 12386.
4. (a) Varma, R. S.; Saini, R. K. *Tetrahedron Lett.* **1998**, *39*, 1481. (b) Varma, R. S.; Dahiya, R. *Mol. Online* **1998**, *2*, 82. (c) Varma, R. S.; Dahiya, R. *Tetrahedron Lett.* **1998**, *39*, 1307. (d) Varma, R. S.; Saini, R. K.; Dahiya, R. *Tetrahedron Lett.* **1997**, *45*, 7823.
5. For relevant papers and reviews on microwave-assisted chemical reactions see: (a) Abramovitch, R. A. *Org. Prep. Proc. Int.* **1991**, *23*, 683. (b) Majetich, G.; Hicks, R. *J. Microwave Power Electromagn. Energy* **1995**, *30*, 27. (c) Caddick, S. *Tetrahedron* **1995**, *51*, 10403. (d) Strauss, C. R.; Trainor, R. W. *Aust. J. Chem.* **1995**, *48*, 1665. (e) Varma, R. S. *Microwave Assisted Reactions under Solvent-free Dry Conditions*. Clark, D. E.; Sutton, W. H.; Lewis, D. A.; Eds.; *American Ceramic Society, Ceramic Transactions* **1997**, *80*, 375. (f) Deshayes, S.; Liagre, M.; Loupy, A.; Luche, J. L.; Petit, A. *Tetrahedron* **1999**, *55*, 10851. (g) Varma, R. S. *Green Chem.* **1999**, 43.
6. (a) Bogdal, D.; Warzala, M. *Tetrahedron* **2000**, *56*, 8769. (b) Bogdal, D. *J. Chem. Res. (S)* **1998**, 468. (c) Bogdal, D.; Pielichowski, J.; Jaskot, K. *Org. Prep. Proc.* **1998**, *30*, 427. (d) Bogdal, D.; Pielichowski, J.; Boron, A. *Synth. Commun.* **1998**, *28*, 3029. (e) Bogdal, D.; Pielichowski, J.; Jaskot, K. *Synth. Commun.* **1997**, *27*, 1553. (f) Bogdal, D.; Pielichowski, J.; Boron, A. *Synlett* **1996**, 873.
7. Lee, R. A. US and foreign patents applied for EP-735014-A1, JP08277231-A.
8. Ko, K.; Kim, J. *Bull. Kor. Chem. Soc.* **1999**, *7*, 771.
9. Lee, R.; Donald, D. *Tetrahedron Lett.* **1997**, *22*, 3857.

10. Loupy, A.; Petit, A.; Hamelin, J.; Texier-Boullet, F.; Jacquault, P.; Mathe, D. *Synthesis* **1998**, 1213.
11. Perreux, L.; Loupy, A. *Tetrahedron* **2001**, 57, 9199.
12. Bogdal, D.; Lukasiewicz, M. *Synlett* **2000**, 143.
13. *Aldrich Handbook of Fine Chemicals and Laboratory Equipment* Ed.; Sigma-Aldrich, 2003–2004.
14. Coutrot, P.; Savignac, P. *J. Chem. Res. (M)* **1977**, 3401.