Short Communication

Microwave-assisted and solvent-free peroxidative oxidation of 1-phenylethanol with a CuII–TEMPO catalytic system

Alessandra Sabbatini a,b, Luísa M.D.R.S. Martins a,c,⁎, Kamran T. Mahmudov a,d,⁎⁎, Maximilian N. Kopylovich a, Michael G.B. Drew e, Claudio Pettinari b, Armando J.L. Pombeiro a,⁎⁎⁎

a Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal
b School of Pharmacy, University of Camerino, via S. Agostino 1, 62032 Camerino, Italy
c School of Chemistry, The University of Reading, P.O. Box 224, Whiteknights, Reading RG6 6AD, UK
d Chemical Engineering Department, ISEL, R. Conselheiro Emídio Navarro, 1959-007 Lisboa, Portugal
e School of Chemistry, Baku State University, Department of Chemistry, Z. Xalilov Str. 23, Az 1148 Baku, Azerbaijan
f Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal

⁎⁎⁎ Correspondence to: K.T. Mahmudov, Baku State University, Department of Chemistry, Z. Xalilov Str. 23, Az 1148 Baku, Azerbaijan
⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎⁎ ⁃ — see front matter. Crown Copyright © 2014 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.catcom.2014.01.024

1. Introduction

The oxidation of primary and secondary alcohols to carbonyl compounds is one of the most important reactions in synthetic organic chemistry [1,2]. Although traditional oxidation reactions can be efficient and selective, they often involve the use of harmful oxidants, such as CrO3 or KMnO4, and/or halogenated solvents, that results in the generation of large amounts of waste. To eliminate the harmful wastes, the use of more environmentally benign solvents and catalysts is of interest [7]. The sulfo group is an efficient mediator for the aerobic oxidation of alcohols [13–17], and hence it would be interesting to check its cooperative action with peroxidative oxidation of 1-phenylethanol with tert-butylhydroperoxide, leading, in the presence of TEMPO, to yields up to 85% (TON = 850) in a remarkably short reaction time (15 min, with the corresponding TOF value of 3.40 × 103 h−1) under low power (25 W) MW irradiation.

The oxidation reactions, in particular aerobic or peroxidative (with H2O2, tert-butylhydroperoxide [TBHP]), is a matter of current interest [2,3]. Moreover, it is known that microwave irradiation (MW) can provide a much more efficient synthetic method than conventional heating, so that similar yields can be obtained in a shorter time and/or the selectivity can be improved [3–6].

Another advantage is obtained via the promotion of the use of environmentally benign solvents and catalysts. Thus, the synthesis of water-soluble catalysts with pH-tunable sites is of interest for novel green catalytic processes and recycling systems [7]. The sulfo group is a good candidate to be introduced into the catalyst to fulfil these goals [8,9]. On the other hand, Schiff bases and amines are relatively cheap and environmentally tolerable ligands, which are available commercially or through simple synthetic procedures [10–12]. For example, Schiff base complexes with ON,O,O-donor sites have drawn much attention due to their interesting catalytic properties [10], while many copper compounds are inexpensive but effective catalysts for a number of oxidation reactions, in particular aerobic or peroxidative (with tert-butylhydroperoxide) oxidation of 1-phenylethanol into acetophenone (Scheme 1) [3,6,13,14].

From another perspective, the TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) radical is an efficient mediator for the aerobic oxidation of alcohols [15–17], and hence it would be interesting to check its cooperative action with a copper(II) Schiff base complex towards the peroxidative oxidation of 1-phenylethanol to acetophenone. The choice of those model reactions was justified by their importance in organic synthesis used by the chemical industry [18].

Hence, taking in mind all the above considerations, in this contribution we describe the synthesis of a new copper(II) complex with Schiff base and diethanolamine ligands and evaluate its activity in the
production of acetophenone by MW-assisted and TEMPO-mediated solvent-free peroxidative oxidation of 1-phenylethanol.

2. Experimental

2.1. General procedure for the peroxidative oxidation of 1-phenylethanol

In a typical experiment, 1-phenylethanol (5.00 mmol), TBHP (70% aqueous solution, 10.0 mmol) and catalyst precursor 1 (5 μmol, 0.1 mol% vs. substrate) were introduced to a cylindrical Pyrex tube, which was then placed in the focused microwave reactor. The system was stirred and irradiated (25 W) for 15 min at 80 °C. After the reaction, which was then placed in the focused microwave reactor. The system was allowed to cool down to room temperature. 300 μL of benzaldehyde (internal standard) and 5 mL of NCMe (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred for 10 min and then a sample (1 μL) was taken from the organic phase and analysed by GC (or GC–MS) using the internal standard method. Blank tests indicate that only traces (<0.5%) of acetophenone are generated in a Cu-free system.

3. Results and discussion

3.1. Synthesis and characterization of H2L and 1

The new Schiff base (E)-2-(((1-hydroxynaphthalen-2-yl)methylene) amino)benzenesulfonic acid (H2L) was prepared by reaction of 2-aminobenzenesulfonic acid with 1-hydroxy-2-naphthaldehyde in methanol (see Electronic Supplementary Information). Greenish-black crystals of complex [Cu(H2R)(HL)]H2O (1, Fig. 1) were obtained after reaction of Cu(NO3)2·2.5H2O with H2L in the presence of diethanolamine (H2R) in methanol. In the 1H-NMR spectrum of H2L, in DMSO-d6, CH=N and OH are observed at 9.82 and 12.00 ppm, respectively. The bands at 1627 cm⁻¹ and 1285, 1202, and 1085 cm⁻¹ in its IR spectrum are assigned to ν(C=–N) and ν(SO3), respectively. In the complex 1, these bonds shift correspondingly to 1608 cm⁻¹ and 1271, 1167, and 1071 cm⁻¹, what testifies the coordination of the N atom and the sulfonate group to the metal ion. In addition, the strong and broad ν(OH) absorptions at 3665 and 3263 cm⁻¹ are assigned to the crystallization water molecule. Elemental analysis and ESI-MS in methanol (peak at m/z 495.1 [M-H2O + H]⁺) support the proposed formulation of 1 as a monomer, which is shown by X-ray crystallography (see Electronic Supplementary Information).

3.2. Microwave-assisted catalytic peroxidative oxidation of 1-phenylethanol

Complex 1 was tested as a catalyst precursor for the oxidation of 1-phenylethanol to acetophenone using aqueous tert-butylhydroperoxide (Bu3OOH, TBHP) as oxidizing agent, under typical conditions of 80 °C, low power (25 W) microwave irradiation (MW), 15 min reaction time and in a solvent-free medium (Scheme 1). The influence of various reaction parameters such as the amounts of catalyst precursor and oxidant, type of oxidant, time, temperature and presence of additives was investigated, and the results are summarized in Table 1 and Fig. 2.

Under typical solvent- and additive-free conditions (Table 1, entry 1), 1 exhibits a high catalytic activity, leading to the production of acetophenone in 66% yield and TON (moles of product per mol of catalyst precursor) of 6.59 × 10² in the short reaction time of 15 min, with the corresponding TOF (TON per hour) value of 2.63 × 10³ h⁻¹. High selectivity towards the formation of ketone was found, and no traces of by-products were detected by GC and GC–MS analyses of the final reaction mixtures (only unreacted alcohol, apart from the ketone product).

In the present study, hydrogen peroxide (30% aqueous solution) is not such an efficient oxidant as TBHP, and 26% yield of acetophenone was achieved (entry 6, Table 1, Fig. 2). The lower yield in this case can be related to the decomposition of H₂O₂ under the used reaction conditions. On the other hand, while a 10-fold excess of the TBHP oxidant does not lead to a better conversion (entry 9, Table 1), a similar excess of hydrogen peroxide leads to a significant increase in yield as shown in Table 1 via a comparison of entries 7 and 8. Moreover, an equimolar amount of TBHP relative to substrate does not seem to be sufficient to achieve high yields (compare entries 1 and 19, Table 1) within 15 min reaction time.

The activity of 1 in the peroxidative (with tert-butylhydroperoxide) oxidation of 1-phenylethanol was also studied in the presence of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) [13–16]. The TEMPO additive provided the significant increase in yield of acetophenone (Fig. 2) from 66% to 85% under the same reaction conditions (entries 1 and 2, Table 1). A similar increase was observed when the reaction was carried out with hydrogen peroxide (instead of TBHP) in the presence of TEMPO (entries 6 and 7, Table 1 and Fig. 2).

To our knowledge, no MW-assisted TBHP (or H₂O₂)/TEMPO/Cu catalytic system has been previously reported, while several efficient aerobic TEMPO-mediated oxidations of primary and secondary alcohols
with TBHP does not seem to require the presence of protons as verdiahexane ligand \[26,27\]. In fact, the mechanism of alcohol oxidation entries 1 and 10). The presence of HNO3 also exhibited an inhibitory ef-

to the yield of acetophenone from MW-assisted proxidative oxidation of 1-phenylethanol. Moreover, carrying out the reaction in water (2 mL) does not change

effect on the acetophenone yield (Table 1, entries 1 and 11,Fig. 2), as

The previous promoting effect of basic additives \[15,16,20–26\] is not observed for the present catalytic system; in con-

The peroxidative oxidation of 1-phenylethanol is believed to pro-

in the presence of copper(II) complexes have been reported \[6,19\]. Hence, this study demonstrates the viability of using the TEMPO additive for the MW-assisted peroxidative oxidations of alcohols.

The previously recognized promoting effect of basic additives \[15,16,20–26\] is not observed for the present catalytic system; in contrast, addition of 1 M solution of Cu(NO3)2 hampers the reaction (Table 1, entries 1 and 10). The presence of HNO3 also exhibited an inhibitory effect on the acetophenone yield (Table 1, entries 1 and 11, Fig. 2), as found e.g., for the MW-assisted oxidation of 1-phenylethanol with TBHP catalysed by Cu(II) complexes bearing the 1,6-bis(2'-pyryl)-2,5-
dithiahexane ligand \[26,27\]. In fact, the mechanism of alcohol oxidation with TBHP does not seem to require the presence of protons as verified \[13,14\] in the oxidation of 1-phenylethanol with TBHP catalysed by bi-
tetra-nuclear cage-like copper(II) silesiquoxanes.

Moreover, carrying out the reaction in water (2 mL) does not change markedly the yield of acetophenone (Fig. 2), either using H2O2 or TBHP as oxidant.

The effect of the amount of catalyst precursor 1 was also studied (entries 1, 4 and 5, Table 1). It was observed that its increase from 1 μmol (0.02 mol% vs. substrate) to 5 μmol (0.1 mol%) results in an yield growth from 17% to 66%. However, if more than 10 μmol of the catalyst precursor is added, the yield remains almost unchanged, leading to the corresponding TON decrease (compare e.g. entries 4 and 5, Table 1). Blank tests in the absence of the catalyst precursor, performed under the typical reaction conditions, reveal no significant conversions (< 0.5%). It should be noted that TEMPO, by itself (i.e., in the absence of 1), leads to a low but noticeable yield (entry 3, Table 1).

The relevance of the ligands on the catalytic activity of 1 is shown by testing also the catalytic performance of Cu(NO3)2 in the same oxidation experiment and comparing the result, under the same reaction conditions, with that obtained from 1. The oxidation of 1-phenylethanol (5 mmol) at 80 °C and after 15 min, in the presence of the same molar amount of Cu(NO3)2, led to a much lower yield of acetoephene (14%) than that obtained with 1 (66%, entry 1, Table 1).

The reaction strongly depends on the temperature. Attempts to perform the oxidation of 1-phenylethanol in the presence of 1 at room temperature failed, whereas when the reaction was conducted at 50 °C, this resulted in a marked drop in the yield of acetoephene relative to that obtained at 80 °C (from 85% at 80 °C to 28% at 50 °C, entries 2 and 18, respectively, Table 1). A temperature above 80 °C does not lead to a higher ketone yield (entry 17, Table 1).

A noteworthy feature of the studied oxidations is that the MW-assisted reaction proceeds very fast even under low irradiation power (25 W). In fact, after 7 min the maximum yield has nearly reached (80%, Table 1, entry 14) with a remarkable TOF (6.65 × 103 h−1) value. This contrasts with most of the known MW-assisted organic reactions \[4,5,29,30\], which require a much higher power (typically above 200 or even 500 W).

The peroxidative oxidation of 1-phenylethanol is believed to proceed mainly via a radical mechanism which involves both carbon- and oxygen-centred radicals \[31–34\]. In the example studied here a strong inhibition effect (Fig. 2) is observed when the reaction is carried out in the presence of either a carbon-radical trap CBrCl3 (Table 1, entry 13) or an oxygen-radical trap Ph2NH (Table 1, entry 12). Thus, we can suppose that the MW-assisted oxidation of 1-phenylethanol involves free-

### Table 1

| Entry | Catalyst amount (mmol vs. substrate) | Reaction time (h) | Additive (mmol vs. substrate) | Yield (%) | TON [TOF (h−1)] |
|-------|-------------------------------------|-------------------|-------------------------------|-----------|-----------------|
| 1     | 0.1                                 | 0.25              | –                             | 65.9      | 659 (2.63 × 103) |
| 2     | 0.1                                 | 0.25              | TEMPO (2.5)                   | 85.0      | 850 (3.40 × 103) |
| 3     | 0.1                                 | 0.25              | TEMPO (2.5)                   | 8.6       | –               |
| 4     | 0.02                               | 0.25              | –                             | 16.9      | 845 (3.38 × 103) |
| 5     | 0.2                                 | 0.25              | –                             | 65.2      | 326 (1.30 × 103) |
| 6     | 0.1                                 | 0.25              | –                             | 26.2      | 262 (1.05 × 103) |
| 7     | 0.1                                 | 0.25              | TEMPO (2.5)                   | 40.6      | 406 (1.62 × 103) |
| 8     | 0.1                                 | 0.25              | TEMPO (2.5)                   | 53.8      | 538 (2.15 × 103) |
| 10    | 0.1                                 | 0.25              | K2CO3 (2.5)                   | 11.2      | 112 (448)       |
| 11    | 0.1                                 | 0.25              | H2O2 (2.5)                    | 18.3      | 183 (732)       |
| 12    | 0.1                                 | 0.25              | Ph2NH (100)                   | 4.8       | 48 (193)        |
| 13    | 0.1                                 | 0.12              | CBrCl3 (100)                  | 5.1       | 51 (205)        |
| 14    | 0.1                                 | 0.12              | TEMPO (2.5)                   | 79.8      | 798 (6.65 × 103) |
| 15    | 0.1                                 | 0.5               | –                             | 31.8      | 318 (636)       |
| 16    | 0.1                                 | –                 | –                             | 19.2      | 192 (192)       |
| 17    | 0.1                                 | 0.25              | TEMPO (2.5)                   | 83.1      | 831 (3.32 × 103) |
| 18    | 0.1                                 | 0.25              | TEMPO (2.5)                   | 27.5      | 275 (1.10 × 103) |
| 19    | 0.1                                 | 0.25              | –                             | 21.7      | 217 (868)       |

**a** Reaction conditions unless stated otherwise: 5 mmol of 1-phenylethanol, 1–10 μmol (0.02–0.2 mol% vs. substrate) of 1, 10 mmol of TBHP (2 eq., 70% in H2O), 80 °C, MW irradiation (25 W power).

**b** Moles of ketone product per 100 mol of alcohol.

**c** Turnover number = number of moles of product per mol of catalyst precursor; TOF = TON per hour (values in brackets).

**d** 10 mmol of H2O2 (30% aqueous solution) instead of TBHP.

**e** 50 mmol of H2O2 instead of TBHP.

**f** 50 mmol of TBHP.

**g** T = 90 °C.

**h** T = 50 °C.

**i** 5 mmol of TBHP.

![Fig. 2](image) **Fig. 2.** Influence of different additives (TEMPO, H2O solvent, K2CO3, HNO3, H2O2, radical traps) on the yield of acetophenone from MW-assisted oxidative oxidation of 1-phenylethanol.
4. Conclusions

In summary, a new copper(II) complex [Cu(H2R)(HL)]H2O (1) was prepared by an easy and convenient synthesis and fully characterized. It acts as an effective catalyst precursor for the mild and selective peroxyxidative oxidation of 1-phenylethanol to acetoephone in a solvent-free MW-assisted process, thus widening the scope of peroxyxidative catalytic systems suitable for MW assisted oxidative transformations of alcohols. Moreover, the use of low power MW irradiation in a solvent-free process is a significant step towards the development of green and energy saving catalytic systems in that field.

Acknowledgments

This work has been partially supported by the Foundation for Science and Technology (FCT), Portugal (PTDC/EQU-EQU/122025/2010 and PEst-CE/UI0100/2013 projects). We thank the University of Reading and the EPSRC (U.K.) for funds for the diffractometer. The authors acknowledge the Portuguese NMR Network (IST-UTL Centre) for access to the NMR facility, and IST Node of the Portuguese Network of mass-spectrometry (Dr. Conceição Oliveira) for the ESI-MS measurements.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.01.024.

Table 2

MW-assisted solvent-free oxidation of selected secondary alcohols using 1 as catalyst precursor.

| Entry | Substrate | Product | Reaction time (h) | Yieldb (%) | TON [TOF (h^-1)]c | Selectivityd (%) |
|-------|-----------|---------|------------------|------------|-------------------|-----------------|
| 1     | Cyclohexanol | Cyclohexanone | 0.25 | 28.1 | 281 (112 × 10^3) | 77.2 |
| 2     | 2-Hexanol | 2-Hexanone | 3 | 65.6 | 656 (219) | 80.0 |
| 3     | 3-Hexanol | 3-Hexanone | 0.25 | 18.4 | 184 (736) | 61.7 |
| 4     | 1-Phenylethanol | Cyclohexanone | 3 | 41.8 | 418 (139) | 49.5 |

a Reaction conditions unless stated otherwise: 5 mmol of substrate, 5 mol% (0.1 mol% vs. substrate) of 1, 10 mmol of TBHP (2 eq., 70% in H2O), 125 μmol of TEMPO, 80 °C, 15 min reaction time. MW irradiation (35 W power).
b Moles of ketone product per 100 mol of alcohol.
c Turnover number = number of moles of product per mol of catalyst precursor; TOF = TON per hour (values in brackets).
d Moles of ketone per mole of converted substrate.

References

[1] S.E. Allen, R.R. Walvoord, R. Padilla-Salinas, M.C. Kozlowski, Chem. Rev. 113 (2013) 6234–6458.
[2] Y.Y. Karabach, M.N. Kopylovich, K.T. Mahmudov, A.J.L. Pombeiro, Microwave-assisted catalytic oxidative oxidation of alcohols to carbonyl compounds, (ch.18) in: A.J.L. Pombeiro, (Ed.), Advances in Organometallic Chemistry and Catalysis: The Silver/Gold Jubilee International Conference on Organometallic Chemistry Celebratory Book, Wiley, 2014, pp. 233–245.
[3] R.R. Fernandes, J. Lasri, M.F.C. Guedes da Silva, J.A.L. da Silva, J.J.R. Frassao da Silva, A.J.L. Pombeiro, J. Mol. Catal. A Chem. 351 (2011) 100–111.
[4] Microwave Assisted Organic Synthesis, in: J.P. Tierney, P. Lidström (Eds.), Blackwell Publishing/CRC Press, Oxford, 2005.
[5] D. Dalling, C.O. Kappe, Chem. Rev. 107 (2007) 2563–2591.
[6] P.J. Figiel, M.N. Kopylovich, J. Lasri, M.F.C. Guedes da Silva, J.J.R. Frassao da Silva, A.J.L. Pombeiro, Chem. Commun. 46 (2010) 2766–2768.
[7] K.H. Saaghneshy, Chem. Rev. 109 (2009) 643–710.
[8] M.N. Kopylovich, K.T. Mahmudov, M. Haukka, P.J. Figiel, A. Mizar, J.A.L. da Silva, A.J.L. Pombeiro, Eur. J. Inorg. Chem. 27 (2011) 4175–4181.
[9] M.N. Kopylovich, Y.Y. Karabach, K.T. Mahmudov, M. Haukka, A.M. Kirillov, P.J. Figiel, A.J.L. Pombeiro, Cryst. Growth Des. 11 (2011) 4247–4252.
[10] P.A. Vágó, S. Tamhini, Coord. Chem. Rev. 248 (2004) 1717–2128.
[11] M. Sudradhar, T.R. Barman, M.G.B. Drew, E. Rentschler, J. Mol. Struct. 1037 (2013) 276–282.
[12] M. Sudradhar, T.R. Barman, J. Klänke, M.G.B. Drew, E. Rentschler, Polyhedron 53 (2013) 48–55.
[13] M.S. Dronova, A.N. Bilyachenko, A.I. Yalymov, Y.N. Kozlov, L.S. Shulpina, A.A. Korlyukov, D.E. Arkhipov, M.M. Levitsky, E.S. Shubina, G.B. Shul’pin, Dalton Trans. 43 (2014) 872–882.
[14] A.N. Bilyachenko, M.S. Dronova, A.I. Yalymov, A.A. Korlyukov, L.S. Shulpina, D.E. Arkhipov, E.S. Shubina, M.M. Levitsky, A.I. Yalymov, G.B. Shul’pin, Eur. J. Inorg. Chem. (2013) 5240–5246.
[15] P.A. Sheldon, Chem. Commun. 29 (2008) 3352–3356.
[16] K.T. Mahmudov, M.N. Kopylovich, M.F.C. Guedes da Silva, P.J. Figiel, Y.Y. Karabach, A.J.L. Pombeiro, J. Mol. Catal. A Chem. 318 (2010) 44–50.
[17] P.J. Figiel, A. Sibaoou, J.U. Ahmad, M. Nieg, M.T. Räisänen, M. Leskelä, T. Repo, Adv. Synth. Catal. 351 (2009) 2625–2632.
[18] Ullmann’s Encyclopedia of Industrial Chemistry, 6th ed. Wiley-VCH, Weinheim, 2002.
[19] M.N. Kopylovich, A. Mizar, M.F.C. Guedes da Silva, T.C.O. Mac Leod, K.T. Mahmudov, A.J.L. Pombeiro, Chem. Eur. J. 19 (2013) 588–600.
[20] G. Yang, W. Zhu, P. Zhang, X. Hua, W. Wang, J. Tian, M. Songa, Adv. Synth. Catal. 350 (2008) 542–546.
[21] L. Lin, M. Juanjuan, J. Liuyan, W. Yunyang, J. Mol. Catal. A Chem. 291 (2008) 1–4.
[22] L. Lin, M. Juanjuan, J. Liuyan, W. Yunyang, Catal. Commun. 9 (2008) 1379–1382.
[23] S. Striegel, Tetrahedron 62 (2006) 9109–9114.
[24] P. Gamez, I.W.C.E. Arends, R.A. Sheldon, J. Rejedik, Adv. Synth. Catal. 346 (2004) 805–811.
[25] P. Gamez, I.W.C.E. Arends, J. Rejedik, R.A. Sheldon, Chem. Commun. (2003) 2414–2415.
[26] J.S. Uber, Y. Vogels, D. van den Helder, I. Mutikainen, U. Turpeinen, W.T. Fu, O. Ruebea, P. Gamez, J. Rejedik, Eur. J. Inorg. Chem. (2007) 4197–4206.
[27] R.R. Fernandes, J. Lasri, M.F.C. Guedes da Silva, J.A.L. da Silva, J.J.R. Frassao da Silva, A.J.L. Pombeiro, Appl. Catal. A Gen. 402 (2011) 110–120.
[28] R.R. Fernandes, J. Lasri, A.M. Kirillov, M.F.C. Guedes da Silva, J.A.L. da Silva, J.J.R. Frassao da Silva, A.J.L. Pombeiro, Eur. J. Inorg. Chem. (2011) 3781–3790.
[29] G.C. Kappie, D. Dallingar, S. Murphy, Practical Microwave Synthesis for Organic Chemists, Wiley-VCH, Weinheim, Germany, 2008.
[30] V. Polshettiwar, R.S. Varma, Acc. Chem. Res. 41 (2008) 629–639.
[31] J.A. Howard, in: J.K. Kochi (Ed.), Free Radicals, 2, Wiley, New York, 1973, p. 3.
[32] R.E. Hulse, C.L. Clifton, Int. J. Chem. Kinet. 21 (1989) 611–619.
[33] I.N. Moiseeva, A.E. Gelkham, V.V. Minin, C.M. Larin, M.E. Bashitnov, A.A. Krasnovskii, I.I. Moiseev, Kinet. Catal. 41 (2000) 170–177.
[34] J.M. Mattalia, B. Vacher, A. Samat, M. Chanson, J. Am. Chem. Soc. 114 (1992) 4111–4115.
[35] P.J. Dyson, T.J. Geldbach, Metal Catalysed Reactions in Ionic Liquids, Springer, 2005.