



Bi₂O₃-catalyzed oxidation of aldehydes with *t*-BuOOH

Payal Malik, Debashis Chakraborty*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, Tamil Nadu, India

ARTICLE INFO

Article history:

Received 31 March 2010

Revised 21 April 2010

Accepted 24 April 2010

Available online 6 May 2010

Keywords:

Oxidation

Aldehyde

Acid

Bi₂O₃

t-BuOOH

ABSTRACT

A variety of aromatic, aliphatic and conjugated aldehydes were transformed to the corresponding carboxylic acids with 70% *t*-BuOOH solution (water) in the presence of catalytic amounts of Bi₂O₃. This method possesses a wide range of capabilities, does not involve cumbersome work-up, exhibits chemoselectivity and proceeds under mild conditions. The resulting products are obtained in good yields within reasonable time. The overall method is green.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The oxidation of aldehydes has been of contemporary interest due to diversified potentials in organic synthesis and industrial manufacturing and recognized as one of the fundamental reaction.¹ The most popular and widely used is Jones reagent for such a transformation.² However, the reaction is stoichiometric and is performed under highly acidic conditions. Substrates having acid-sensitive functionalities may not be able to tolerate such acidity. In addition, the generation of Cr-based side products may be considered as a potential environmental hazard.³ Other reagents that have been used successfully include Oxone,⁴ calcium hypochlorite⁵ and 2-hydroperoxyhexafluoro-2-propanol.⁶ Excellent catalytic methods using metals have been developed using oxidation reactions. Interesting methodologies for metal-mediated transformation of the aldehyde functionality to carboxylic acid have been reported recently.⁷ The above-mentioned reagents and methods involved have one or more limitations which include the use of superstoichiometric amounts of expensive compounds, employment of highly basic or acidic reaction conditions and high temperature. The search for catalytic processes involving environmentally benign reagents shall always remain an attractive avenue in this area. Similar catalytic transformation of the aldehydes to carboxylic acids has been reported with SeO₂.⁸ Our recent results highlight the oxidation of aldehydes to carboxylic acid using 30% H₂O₂ as the oxidant in the presence of catalytic amounts of AgNO₃.⁹ Our continued interest in studying catalytically active environmentally benign processes compelled us to investigate

the capability of Bi(III) reagents towards oxidation. It must be noted that Bi₂O₃ is reported to catalyze the oxidation of α -hydroxy ketones.¹⁰

2. Results and discussion

Initial attempts to optimize the reaction conditions for the oxidation of aldehydes to the corresponding carboxylic acids were done using 4-methoxybenzaldehyde as a suitable substrate in the presence of different solvents, oxidants and 10 mol % of Bi(III) salts (Table 1).

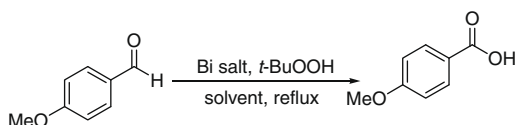
The conversion of 4-methoxybenzaldehyde to 4-methoxybenzoic acid is extremely facile in EtOAc under reflux conditions in the presence of 10 mol % Bi₂O₃ and 5 equiv 70% *t*-BuOOH (water) as the oxidant (Table 1, entry 1). Oxidation with *t*-BuOOH (water) alone in EtOAc was found to be negligible (<5%). In the presence of 5 mol % Bi₂O₃ and 5 equiv 70% *t*-BuOOH (water) as the oxidant in EtOAc, the reaction required 32 h for completion with 77% isolated yield of the product. In EtOAc, with 10 mol % Bi₂O₃ and 5 equiv 70% *t*-BuOOH (water) as the oxidant, the reaction reached to completion in much shorter time. With 5 equiv 5 M *t*-BuOOH (decane), the reaction was found complete in 2.5 h with 90% isolated yield. The reaction took much longer time for completion (20 h) when performed with 5 equiv 30% H₂O₂ in EtOAc and yielded 82% of product. Among the different solvents used for optimization (Table 1, entries 1–9), EtOAc yielded best results. The other Bi(III) salts (Table 1, entries 10–12) were found to be inferior as compared to Bi₂O₃.

Having realized the correct conditions for oxidation, we continued our quest with a variety of aromatic and aliphatic substrates (Table 2). The scope of our catalytic system is applicable for a wide range of aromatic, conjugated and aliphatic substrates. These

* Corresponding author. Tel.: +91 44 22574223; fax: +91 44 22574202.
E-mail address: dchakraborty@iitm.ac.in (D. Chakraborty).

Table 1

Optimization of the reaction conditions for the conversion of 4-methoxybenzaldehyde to 4-methoxybenzoic acid with different solvents, 5 equiv 70% *t*-BuOOH (water) and 10 mol % Bi(III) salts



Entry	Catalyst	Solvent	Time ^a (h)	Yield ^b (%)
1	Bi ₂ O ₃	EtOAc	2	97
2	Bi ₂ O ₃	MeCN	15	90
3	Bi ₂ O ₃	Toluene	20	80
4	Bi ₂ O ₃	CH ₂ Cl ₂	18	84
5	Bi ₂ O ₃	DMF	4	87
6	Bi ₂ O ₃	DMSO	5	85
7	Bi ₂ O ₃	THF	32	70
8	Bi ₂ O ₃	EtOH	17	80
9	Bi ₂ O ₃	CH ₃ NO ₂	10	82
10	BiCl ₃	EtOAc	30	71
11	BiBr ₃	EtOAc	27	80
12	Bi(NO ₃) ₃ ·5H ₂ O	EtOAc	36	79

^a Monitored using TLC until all the aldehyde was found consumed.

^b Isolated yield after column chromatography of the crude product.

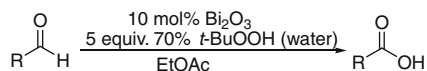
aldehydes were converted to the corresponding carboxylic acids in good isolated yields in reasonable time (Table 2). It is pertinent to mention here that mild halogenic oxidants such as hypochlorites,^{5,11} chlorites¹² and NBS¹³ are not suitable for substrates with electron-rich aromatic rings, olefinic bonds and secondary hydroxyl groups. Substitutions at different position on the phenyl ring do not hinder the reaction, although the reaction time is affected. The reaction is much faster with substrates containing electron-donating substituents in the aromatic ring (Table 2, entries 1–8 vs entries 9–13). Substitution of extremely electron-withdrawing group like –NO₂ retards the oxidation reaction considerably (Table 2, entries 11–13). Our catalytic system is mild and shows sufficient selectivity in carrying out the expected oxidation without affecting other functionalities such as phenol and amine (Table 2, entries 7 and 8). Oxidation of α , β unsaturated derivatives (Table 2, entry 15) resulted in the formation of the expected acid in very good yield.

The kinetic studies of the oxidation with 4-methoxybenzaldehyde, 4-nitrobenzaldehyde, furan-2-carboxaldehyde and butyraldehyde were explored next. High-pressure liquid chromatography (HPLC) was used to determine the various starting materials and products present as a function of time. The concentration of reactant and product for the oxidation of 4-methoxybenzaldehyde is shown in Figure 1.

The concentration of the aldehyde decreases steadily while that of the carboxylic acid increases. We have calculated the rate of such reactions. As an example let us consider the conversion of 4-methoxybenzaldehyde to 4-methoxybenzoic acid. Vant Hoff differential method was used to determine the order (*n*) and rate constant (*k*). From Figure 1, the rate of the reaction at different concentrations can be estimated by evaluating the slope of the tangent at each point on the curve corresponding to that of 4-methoxybenzaldehyde. With these data, log₁₀(rate) versus log₁₀(concentration) is plotted. The order (*n*) and rate constant (*k*) are given by the slope of the line and its intercept on the log₁₀(rate) axis. It is clear that this reaction proceeds with second-order kinetics (*n* = 2.15) and the rate constant *k* = 0.2134 L mol⁻¹ min⁻¹. For the other substrates namely 4-nitrobenzaldehyde, furan-2-carboxaldehyde and butyraldehyde, the order of the reaction *n* \approx 2 with rate constants (*k*) is 6.41 \times 10⁻³ L mol⁻¹ min⁻¹, 1.76 \times 10⁻² L mol⁻¹ min⁻¹ and 6.75 \times 10⁻² L mol⁻¹ min⁻¹, respectively (see Supplementary data for details).

Table 2

Bi₂O₃-catalyzed oxidation of aldehydes to carboxylic acids^a



Entry	Aldehyde	Acid	Time ^b (h)	Yield ^c (%)
1			2.5	90
2			2	97
3			3	93
4			6.5	90
5			4	90
6			3	92
7			3	87
8			6	89
9			2	89
10			5.2	88
11			42	84
12			40	85
13			41	82
14			10	91
15			3	90
16			8	85
17			7	90

^a Reactions performed in EtOAc with 10 mol % Bi₂O₃ and 5 equiv 70% *t*-BuOOH under reflux conditions.

^b Monitored using TLC until all the aldehyde was found consumed.

^c Isolated yield after column chromatography of the crude.

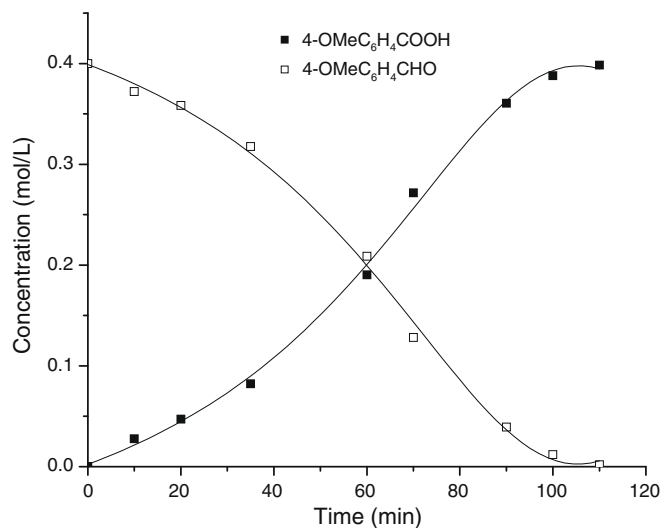


Figure 1. Concentration versus time in the oxidation of 4-methoxybenzaldehyde with 10 mol % Bi₂O₃ and 5 equiv 70% *t*-BuOOH (water) in EtOAc under reflux conditions.

3. Conclusions

In summary, we have developed a simple, efficient, chemoselective and inexpensive catalytic method for the oxidation of aldehydes to carboxylic acids with a table top reagent such as Bi₂O₃.¹⁴ It is noteworthy to mention that this method does not use ligands and other additives.

Acknowledgements

This work was supported by Department of Science and Technology and Council of Scientific and Industrial Research, New Delhi. The services from the NMR facility purchased under the FIST program, sponsored by the Department of Science and Technology, New Delhi, are gratefully acknowledged.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.04.101.

References and notes

- (a) Hollingworth, G. J. In *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Pattenden, G., Eds.; Elsevier Science: Oxford, 1995; Vol. 5, p 23; (b) Hudlicky, M. In *Oxidations in Organic Chemistry*. In ACS Monograph Series; American Chemical Society: Washington DC, 1990; Vol. 186, p 174; (c) Larock, R. C. In *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, 2nd ed.; Wiley-VCH: New York, 1999; p 1653; (d) Smith, M. B.; March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 5th ed.; Wiley-Interscience: New York, 2001; (e) Sheldon, R. A.; Van Bekkum, H. *Fine Chemicals through Heterogeneous Catalysis*; Wiley-VCH Verlag GmbH & Co.: Weinheim, 2001.
- (a) Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* **1946**, 39–45; (b) Heilbron, I.; Jones, E. R. H.; Sondheimer, F. J. *Chem. Soc.* **1949**, 604–607; (c) Bladon, P.; Fabian, J. M.; Henbest, H. B.; Koch, H. P.; Wood, G. W. *J. Chem. Soc.* **1951**, 2402–2411; (d) Curtis, R. G.; Heilbron, I.; Jones, E. R. H.; Woods, G. F. *J. Chem. Soc.* **1953**, 457–464; (e) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2548–2560; (f) Djerassi, C.; Engle, R. R.; Bowers, A. *J. Org. Chem.* **1956**, 21, 1547–1549.
- Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry*; Springer: Berlin, 1984.
- Benjamin, R. T.; Sivakumar, M.; Hollist, G. O.; Borhan, B. *Org. Lett.* **2003**, 5, 1031–1034.
- Nwaukwa, S. O.; Keehn, P. M. *Tetrahedron Lett.* **1982**, 23, 3131–3134.
- Ganem, B.; Heggs, R. P.; Biloski, A. J.; Schwartz, D. R. *Tetrahedron Lett.* **1980**, 21, 685–688.
- (a) Yamada, T.; Rhode, O.; Takai, T.; Mukaiyama, T. *Chem. Lett.* **1991**, 5–8; (b) Bhatia, B.; Punniyamurthy, T.; Iqbal, J. *J. Org. Chem.* **1993**, 58, 5518–5523; (c) Heaney, H. *Top. Curr. Chem.* **1993**, 1, 1–19; (d) Kharata, A. N.; Pendleton, P.; Badalyan, A.; Abedini, M.; Amini, M. M. *J. Mol. Catal. A: Chem.* **2001**, 175, 277–283; (e) Biella, S.; Prati, L.; Rossi, M. J. *Mol. Catal. A: Chem.* **2003**, 197, 207–212; (f) Grill, J. M.; Ogle, J. W.; Miller, S. A. *J. Org. Chem.* **2006**, 71, 9291–9296; (g) Joseph, J. K.; Jain, S. L.; Sain, J. B. *Catal. Commun.* **2007**, 8, 83–87; (h) Lim, M.; Yoon, C. M.; An, G.; Rhee, H. *Tetrahedron Lett.* **2007**, 48, 3835–3839; (i) Zhou, X. T.; Ji, H. B.; Yuan, Q. L.; Xu, J. C.; Pei, L. X.; Wang, L. F. *Chinese Chem. Lett.* **2007**, 18, 926–928; (j) Sloboda-Rozner, D.; Neimann, K.; Neumann, R. *J. Mol. Catal. A: Chem.* **2007**, 262, 109–113; (k) Mukhopadhyay, C.; Datta, A. *Catal. Commun.* **2008**, 9, 2588–2592; (l) Uyanik, M.; Ishihara, K. *Chem. Commun.* **2009**, 2086–2099.
- Młochowski, J.; Brzłaszcz, M.; Giurg, M.; Palus, J.; Wójtowicz, E. *Eur. J. Org. Chem.* **2003**, 22, 4329–4339.
- Chakraborty, D.; Gowda, R. R.; Malik, P. *Tetrahedron Lett.* **2009**, 50, 6553–6556.
- Encyclopedia of Reagents for Organic Synthesis, Vol. 1, p 538.
- (a) Stevens, R. V.; Chapman, K. T.; Stubbs, C. A.; Tam, W. W.; Albizzati, K. F. *Tetrahedron Lett.* **1982**, 23, 4647–4650; (b) Wilson, S. R.; Tofigh, S.; Misra, R. N. *J. Org. Chem.* **1982**, 47, 1360–1361.
- (a) Bal, B. S.; Childers, W. E., Jr.; Pinnick, H. W. *Tetrahedron* **1981**, 37, 2091–2096; (b) Dalcanele, E.; Montanari, F. *J. Org. Chem.* **1986**, 51, 567–569.
- (a) Ogawa, T.; Matsui, M. *J. Am. Chem. Soc.* **1976**, 98, 1629–1630; (b) Cheung, Y.-F. *Tetrahedron Lett.* **1979**, 20, 3809–3810.
- Typical experimental procedure*: To a stirred suspension of Bi₂O₃ (68 mg, 0.10 mmol) and aldehyde (1 mmol) in 2.5 mL EtOAc was added 70% *t*-BuOOH (water) (0.90 mL, 5 mmol). The reaction mixture was heated to reflux. The progress of the reaction was monitored using TLC until all aldehyde was found consumed. The crude product was treated with saturated NaHCO₃ solution. This was extracted with ethyl acetate. Finally, the aqueous layer was acidified using 2 N HCl and extracted with ethyl acetate. The organic layer was concentrated and subjected to column chromatography. The spectral data of the various carboxylic acids were found to be satisfactory in accordance with the literature (see Supplementary data for details).