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Microwave-expedited olefin epoxidation over hydrotalcites using hydrogen peroxide and acetonitrile

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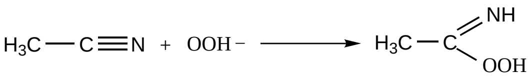
Abstract—An efficient microwave-assisted epoxidation of olefins is described over hydrotalcite catalysts in the presence of hydrogen peroxide and acetonitrile. This general and selective protocol is extremely fast and is applicable to a wide variety of substrates. Published by Elsevier Science Ltd.

Epoxidation of carbon–carbon double bonds is of immense importance in organic chemistry due to the synthetic utility of the ensuing epoxides.[1–3] Hydrogen peroxide (H_2O_2) is an ideal oxidant of choice for these oxidations since it is relatively less expensive, environmentally safe and forms innocuous water as the only by-product.[4] Epoxidation of olefins is usually conducted under strongly alkaline conditions using bases such as NaOH, Na_2CO_3 or KOH and H_2O_2 as the oxidant. However, the usage of these strong bases is highly undesirable as they result in the production of large amounts of industrial waste. Additional methods have been reported that involve reagents namely, sodium hypochlorite,[5] dioxiranes,[6] sodium perborate in the presence of a phase-transfer reagent,[7] alumina supported KF,[8] *t*-butyl hydroperoxide in the presence of a titania–silica catalyst,[9] tertiary arsine oxides and H_2O_2,[10] Ti(IV) silsesquioxane/MCM-41,[11] Ti(IV)/Sn(Ge)(IV)/MCM-41,[12] modified Ti-MCM-41,[13] Cu and Ag catalysts,[14] porphyrin-based catalysts,[15] molybdenum silicate,[16] modified natural phosphates[17] etc. One of the main drawbacks of most of these processes is the long reaction time required to achieve the desired product yield. In addition, with increased environmental awareness, close attention is being paid to the development of environmentally friendly protocols that use relatively benign oxidants such as molecular oxygen and hydrogen peroxide in combination with reusable and recyclable solid catalysts.[4]

Hydrotalcites or anionic clays are homogenous basic mixed hydroxides with a brucite-like layer structure.[18] They are shown to be highly active catalysts for epoxidation of olefins using H_2O_2 in the presence of a nitrile,[19,20] wherein H_2O_2 reacts with a basic hydroxyl function on the hydrotalcite to form a perhydroxyl anion (OOH^-), which in turn, nucleophilically attacks the nitrile to generate a peroxycarboximidic acid intermediate (**I**, Scheme 1). The subsequent oxygen transfer from the intermediate to the olefin results in the formation of epoxide and an amide. However, the reaction usually involves, in addition to the nitrile, the use of an organic solvent, which is less desired these days.

The use of microwave (MW) in enhancing chemical transformations has been gaining attention in recent years due to several advantages such as rapid reaction rates and higher yield of pure products.[21–23] This is a consequence of the selective absorption of microwave energy by polar molecules or polar transition state intermediates formed during the course of the reaction.[22a]

As part of the ongoing program on environmentally benign chemical synthesis employing alternative reaction conditions and media in our laboratory,[21] herein we report an expeditious and environmentally benign



I

Scheme 1.

Keywords: microwave-expedited synthesis; olefins; epoxidation; hydrotalcites; hydrogen peroxide.

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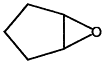
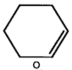
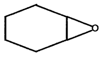
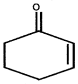
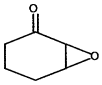
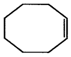
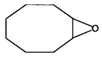
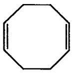
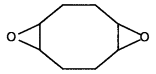
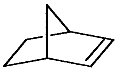
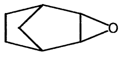
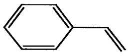
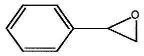
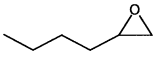
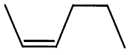
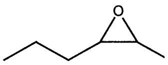
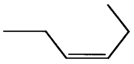
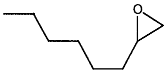
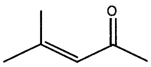
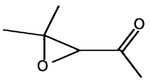
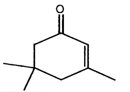
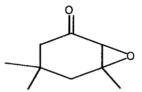
epoxidation protocol for olefins using hydrotalcite catalysts in the presence of acetonitrile (MeCN) and H_2O_2 under MW-irradiation conditions.

The results of MW-assisted olefin epoxidation over hydrotalcite catalyst are summarized in Table 1 along with the comparative reactions under conventional heating conditions using excess acetonitrile. Apparently, the selective epoxidation of a variety of olefins occurs rapidly upon MW-irradiation including substrates that are difficult to oxidize. As an example, the epoxidation of sterically hindered isophorone is difficult to accomplish.[7,8,20c] However, isophorone (entry 13) could be easily oxidized to epoxy isophorone (87% yield) using the MW-protocol. Mesityl oxide (entry 12) also formed the epoxidation product in good yield with no appreciable formation of any 1,2-dioxolane by-products. The selectivity to epoxide is extremely good with little or no formation of any Baeyer–Villiger oxidation product. The temperature of the reaction mixture immediately after MW-irradiations was found to be <60°C at 40% power level (480 W) and <70°C at 60% power level (720 W), thereby suggesting that the rate enhancement may not entirely be due to thermal effect. The intermittent heating of the samples for a short time (15 s, see experimental procedure) followed by thorough mixing for 1–2 min in a stoppered vessel ensured minimum sample loss by evaporation.

In conclusion, the olefin epoxidation occurs readily over hydrotalcite catalysts upon MW exposure of the mixture in hydrogen peroxide and acetonitrile. This is presumably due to the polar nature of the reaction intermediates (**I**, Scheme 1) that couple efficiently with microwaves and hence the dramatic rate acceleration. This approach significantly minimizes the longer reaction times required in conventional heating of olefins

Table 1. MW-assisted olefin epoxidation over hydrotalcite catalysts using H_2O_2 and acetonitrile[a]

Entry	Olefin	MW Power (W)	Time (min)	Product	Yield[b] (MW), %	Yield[b] (oil bath), %, (h)[c]
1		480	1		97	100 (5)
2		480	1		100	72 (8)
3		720	1		100	86 (4)
4		720	6		88	83 (8)
5		720	5		100	60 (5)
6		480	3		92	83 (4)
7		720	5		62	56 (8)
8		480	3		100	57 (8)
9		480	3		100	92 (8)
10		480	3		100	85 (8)
11		720	5		87	45 (24)
12		720	8		66	46 (24)
13		720	3		87	25 (24)

[a] 12.5 mmol substrate, 0.25 g hydrotalcite, 4mL acetonitrile, 50 mmol H_2O_2 (30%), [b] GC yield, [c] 12.5 mmol substrate, 0.25 g hydrotalcite, 10 mL acetonitrile, 50 mmol H_2O_2 (30%), 70 °C. All the products are known compounds and were identified by GC-MS.

with H_2O_2 and avoids the use of large excess of volatile organic solvent usually employed.

Experimental

All the olefins, $Mg(NO_3)_2·6H_2O$, $Al(NO_3)_3·9H_2O$ and NaOH were obtained from Aldrich Chemicals and used as such without any further purification. Magnesium aluminum hydroxy carbonate (hydrotalcite), $Mg_6Al_2(OH)_{16}CO_3·4H_2O$, was prepared by co-precipitation technique at a constant pH of 8 from a 0.5 M solution of $Mg(NO_3)_2·6H_2O$ and $Al(NO_3)_3·9H_2O$ in de-ionized water using a mixture of NaOH and Na_2CO_3 as the precipitants according to the procedure described elsewhere.[18,24] The solid precipitate was filtered, washed several times with de-ionized water, dried in an oven at 100°C overnight and calcined in air at 400°C for 5 h. The structure of hydrotalcite was confirmed by X-ray diffraction analysis of the dried material, which showed characteristic peaks at 2θ values of around 11.5.[18]

MW-assisted epoxidation of various olefins was conducted in liquid phase in a stoppered 125 mL conical flask using an unmodified domestic household microwave oven (Panasonic, 1200W) equipped with inverter technology, which provides a realistic control of the microwave power to the desired level. The MW oven was operated at reduced MW-power level of 40% (480 W) for low boiling olefins (<100°C) and at 60% power level (720 W) for high boiling olefins (>100°C). In all cases, the samples were subjected to MW-irradiation for a period of 15 s with 2 min mixing intervals.[25] After completion of the reaction, the mixture was extracted into diethyl ether, the organic layer was separated and analyzed by a Hewlett–Packard 6890 Gas Chromatograph using a HP-5 5% phenyl methyl siloxane capillary column (30 m×320 μm×0.25 μm) and a quadruple mass filter equipped HP 5973 mass selective detector. The product yield reported is the GC yield. The purity of the products was established by the GC–MS analysis of the samples.

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References

1. (a) Adam, W.; Saha-Moller, C. R.; Ganeshpure, P. A. *Chem. Rev.* **2001**, *101*, 3499; (b) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189.
2. (a) Sato, K.; Aoki, M.; Ogawa, M.; Hashimoto, T.; Noyori, R. *J. Org. Chem.* **1996**, *61*, 8310; (b) Venturello, C.; D'Aloisio, R. *J. Org. Chem.* **1988**, *53*, 1553.
3. (a) Coperet, C.; Adolfson, H.; Sharpless, K. B. *Chem. Commun.* **1997**, 1565; (b) de Vos, D. E.; Sels, B. F.; Reynaers, M.; Rao, Y. V. S.; Jacobs, P. *Tetrahedron Lett.* **1996**, *39*, 3221.
4. (a) Sheldon, R. A. *Green Chem.* **2000**, *1*, G1; (b) Anastas, P. T.; Bartlett, L. B.; Kirchhoff, M. M.; Williamson, T. C. *Catal. Today* **2000**, *55*, 11.
5. Foucaud, A.; Bakouetila, M. *Synthesis* **1987**, 854.
6. Yang, D.; Wong, M.-K.; Yip, Y.-C. *J. Org. Chem.* **1995**, *60*, 3887.
7. Straub, T. S. *Tetrahedron Lett.* **1995**, *36*, 663.
8. Yadav, V. K.; Kapoor, K. K. *Tetrahedron* **1996**, *52*, 3659.
9. Hutter, R.; Mallat, T.; Baiker, A. *J. Catal.* **1995**, *157*, 665.
10. van Vliet, M. C. A.; Arends, I. W. C. E.; Sheldon, R. A. *Tetrahedron Lett.* **1999**, *40*, 5239.
11. Smet, P.; Riondato, J.; Pauwels, T.; Moens, L.; Verdonck, L. *Inorg. Chem. Commun.* **2000**, *3*, 557.
12. Oldroyd, R. D.; Sankar, G.; Thomas, J. M.; Ozkaya, D. *J. Phys. Chem. B* **1998**, *102*, 1849.
13. Bhaumik, A.; Tatsumi, T. *J. Catal.* **2000**, *189*, 31.
14. Monnier, J. R.; Hartley, G. W. *J. Catal.* **2001**, *203*, 253.
15. Elemans, J. A. A. W.; Bijsterveld, E. J. A.; Rowan, A. E.; Nolte, R. J. M. *Chem. Commun.* **2000**, 2443.
16. Juwiler, D.; Blum, J.; Neumann, R. *Chem. Commun.* **1998**, 1123.
17. Fraile, J. M.; Garcia, J. I.; Mayoral, J. A.; Sebti, S.; Tahir, R. *Green Chem.* **2001**, *3*, 271.
18. Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173.
19. Yamaguchi, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **2000**, *65*, 6897.
20. (a) Fraile, J. M.; Garcia, J. I.; Marco, D.; Mayoral, J. A. *Appl. Catal. A. Gen.* **2001**, *207*, 239; (b) Fraile, J. M.; Garcia, J. I.; Mayoral, J. A. *Catal. Today* **2000**, *57*, 3; (c) Fraile, J. M.; Garcia, J. I.; Mayoral, J. A.; Figueras, F. *Tetrahedron Lett.* **1996**, *37*, 5995.
21. (a) Varma, R. S. *Tetrahedron* **2002**, *58*, 1235; (b) Varma, R. S. *Pure Appl. Chem.* **2001**, *73*, 193; (c) Varma, R. S. In *Green Chemistry*: *Challenging Perspectives*; Tundo, P.; Anastas, P. T., Eds.; Oxford University: Oxford, 2000; p. 221; (d) Varma, R. S. In *Green Chemical Syntheses and Processes*; Anastas, P. T.; Heina, L.; Williamson, T., Eds.; ACS Symposium Series, No. 767, American Chemical Society: Washington, DC, 2000, p. 292; (e) Varma, R. S. *Green Chem.* **1999**, *1*, 43.
22. (a) Perreux, L.; Loupy, A. *Tetrahedron* **2001**, *57*, 9199; (b) Lidstrom, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron* **2001**, *57*, 9225; (c) Bose, A. K.; Banik, B. K.; Lavlinskaia, N.; Jayaraman, M.; Manhas, M. S. *Chemtech* **1997**, *27*, 18.
23. Sala, G. D.; Giordano, L.; Lattanzi, A.; Proto, A.; Scettri, A. *Tetrahedron* **2000**, *56*, 3567.
24. Unnikrishnan, R.; Narayanan, S. *J. Mol. Catal. A (Chem.)* **1999**, *144*, 173.
25. In a typical reaction procedure, the catalyst (0.25 g) was mixed with the substrate (12.5 mmol), acetonitrile (4 mL) and hydrogen peroxide (50 mmol) in a 125 mL conical flask closed with a rubber stopper and subjected to MW irradiation for 15 s. The sample was then thoroughly mixed outside for 2 min and again irradiated for another 15 s. This intermittent heating–stirring cycle was repeated for the total irradiation time (see Table 1). The temperature of the bulk reaction mixture was also measured immediately after the irradiation. For comparison purposes, the experiments were also conducted in the liquid phase under conventional heating conditions in an oil bath.