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A simple and efficient protocol for epoxidation of olefins using dimethyldioxirane

Helena M. C. Ferraz,* Rozanna M. Muzzi,† Tiago de O. Vieira and Hans Viertler

Instituto de Química, Universidade de São Paulo, CEP 05508-900, São Paulo SP, Brazil

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Abstract

The reaction of a series of monoterpenic olefins and Δ^4-octalins with dimethyldioxirane led to the corresponding epoxides in excellent yields. Remarkable diastereoselectivity was observed for the Δ^4-octalins. The procedure consists simply in stirring the substrate, $NaHCO_3$ and acetone, at 0°C, with dropwise addition of an aqueous solution of oxone.

Epoxides are one of the most versatile synthetic intermediates, constituting convenient building blocks for the synthesis of many natural products.[1] Several papers[2–4] report the use of dioxiranes as a powerful and efficient reagent for epoxidation of alkenes under mild conditions. Dimethyldioxirane (DMD), either isolated or generated in situ, has been the dioxirane of choice for the conversion of olefins into epoxides.[5] The usual protocol, under biphasic conditions, involves the use of the oxone/acetone aqueous system, an appropriate buffer, benzene as solvent and a phase transfer catalyst.[6]

In this paper we report a simplified method for epoxidation of olefins with oxone. The general procedure consists simply of a dropwise addition of an aqueous solution of oxone to a stirred mixture of the substrate, $NaHCO_3$ and acetone, at 0°C. This reaction was initially performed with a series of monoterpenic olefins, furnishing the corresponding epoxides in excellent yields, although with poor diastereoselectivity (Table 1). A high chemoselectivity was observed for *cis*-carveol, which bears two differently substituted double bonds (entry 5).

During studies which recently[7] culminated in the total synthesis of the sesquiterpenic natural product Corymbolone,[8] some Δ^4-octalin derivatives were obtained as intermediates of the synthetic routes. Its reaction with DMD, under the same conditions described for the monoterpenic olefins, occurred with high diastereoselectivity, giving mainly the β-epoxides, in very good yields (Table 2).

The olefins outlined in entries 1 and 3 (Table 2) were also submitted to classical conditions of epoxidation with *m*-CPBA, leading to the α- and β-epoxides in 3:2 (95% yield) and 1:1 (92%

* Corresponding author. E-mail: hmferraz@iq.usp.br

† Present address: Universidade Federal do Mato Grosso do Sul, Campo Grande, MS, Brazil.

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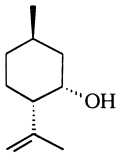
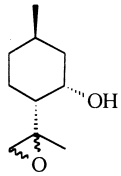
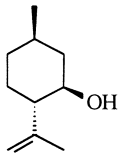
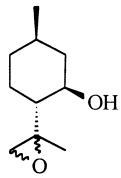
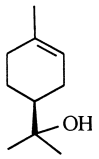
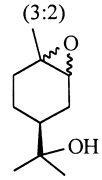
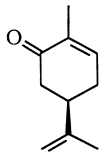
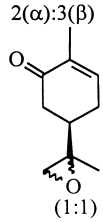
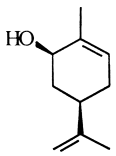
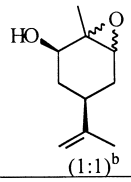
Table 1
Epoxidation of monoterpenic olefins with oxone/acetone/$NaHCO_3$, at 0°C

Entry	Substrate	Time	Product (ratio)[a]	Yield
1		3h	 (3:2)	89%
2		0,5h	 (3:2)	91%
3		4h	 2(α):3(β)	95%
4		3h	 (1:1)	96%
5		3h	 (1:1)[b]	92%

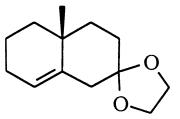
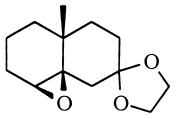
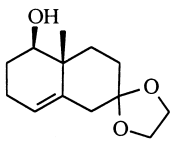
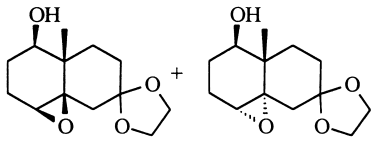
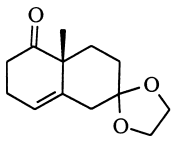
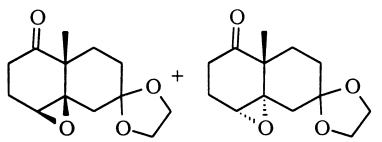
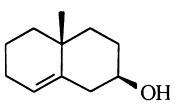
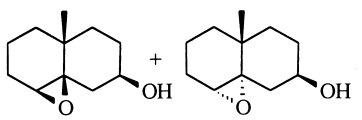
[a] *determined by* ^1H *NMR,* [b] *contamined with 5% of the diepoxide*

yield) ratio, respectively. Therefore, DMD proved to be superior to *m*-CPBA, concerning the diastereoselectivity of the epoxidation of these two substrates.

In summary, we have demonstrated a highly efficient and simple protocol for the epoxidation of Δ^4-octalin derivatives and of commercially available monoterpenic olefins[9] in excellent yields, although with variable diastereoselectivities.

Experimental. General procedure: To a stirred mixture of the olefin (2.5 mmol), $NaHCO_3$ (5.1 mmol) and acetone (5 mL), at 0°C, a solution of oxone (2.9 mmol) in water (3 mL) was added dropwise. The resulting mixture was stirred at room temperature, for the time indicated in Tables 1 and 2 and then extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$ and the solvent was evaporated. All the products were characterized on the basis of MS, ^1H NMR and ^{13}C NMR data.[10]

Table 2
Epoxidation of Δ^4-octalin derivatives with oxone/acetone/$NaHCO_3$, at 0°C

Entry	Substrate	Time	Products (ratio)[a]	Yield
1		1h		—	91%
2		12h	 (5:1)		90%
3		1,5h	 (10:3)		95%
4		1,5h	 (2:1)		87%

[a] *determined by ^1H NMR*

Acknowledgements

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