Microwave Promoted Epoxidation of α,β-Unsaturated Ketones in Aqueous Sodium Perborate†

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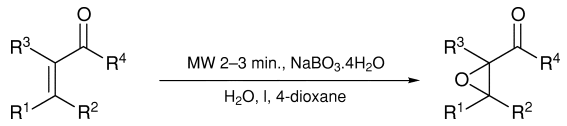
A series of α,β-unsaturated ketones has been treated with sodium perborate in water and 1,4-dioxane under microwave irradiation to produce α,β-epoxyketones in good yields.

Recently, there has been growing interest in applying microwave dielectric heating to accelerate organic reactions.[1] Oxidation reactions are less considered under microwave irradiation due to unsafe and uncontrollable experimental conditions.[2] Sodium perborate is a very cheap and widely used industrial chemical which is utilized as an oxidizing agent in organic chemistry:[3] oxidation of anilines, sulfides, ketones, hydroquinones, aromatic aldehydes, iodoarenes, aromatic nitriles, azines, sulfur heterocycles, benzylic alcohols, α-hydroxycarboxylic acids, 1,2-diketones, α-hydroxyketones, 1,2-diols, unsaturated compounds and oximes under different conditions have been reported.[4]

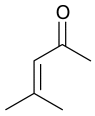
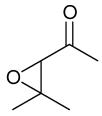
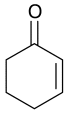
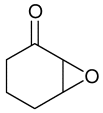
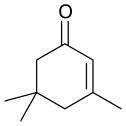
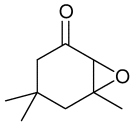
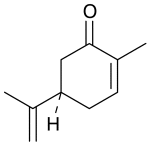
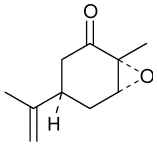
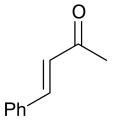
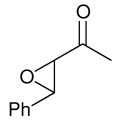
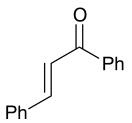
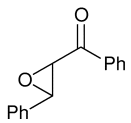
α,β-Unsaturated ketones react with sodium perborate in water and a cosolvent to produce the corresponding epoxides over a long period of time.[5] Tetrahexylammonium hydrogensulfate is used as a phase transfer catalyst for these reactions, in both biphasic solvent mixtures[6] and monophasic aqueous solutions[7] at different temperatures to enhance the rate and the yield of products. In this paper, we report epoxidation of α,β-unsaturated ketones by sodium perborate in water and a cosolvent (1,4-dioxane) under microwave irradiation for 2–3 min to produce the corresponding epoxides in good yields (Scheme 1, Table 1).



Scheme 1

As seen in Table 1, the isolated yield under microwave conditions is higher than in thermal reactions. Regiospecificity is observed for entry 4; the spectral data are identical to those of the known compound.[5] Other cosolvents such as THF, DMSO, DMF were examined along

Table 1 Epoxidation of α,β-unsaturated ketones with sodium perborate under microwave irradiation

Entry	Substrate	Product	Sodium perborate/substrate (mole ratio)	Irradiation time/min	Microwave yield[a] (%)	Thermal yield[b] (%)
1			3	2	92[c](85)[d]	88[c](55)[d]
2			3	2	100(73)	67(38)
3			3 3 4	2 3 2	51(43) 79(68) 84(75)	78(60)
4			3	3	88(82)	91(56)
5			3 3	2 3	83(79) 86(80)	100(26)
6			3	2	100(93)	–

[a]All products were characterized by IR, ^{1}H NMR and their spectroscopic data were similar to those reported. [b]From ref. 5. The time of thermal reactions were 5–26 h. [c]GC yield. [d]Isolated yield.

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with water. We observed a lower yield with those solvents than with 1,4-dioxane, under the same conditions. The optimum amount of sodium perborate is found to be 3 molar equivalents with respect to the substrate. Irradiation was carried out 3 or 4 times (each time for 15–20 s with 5 min intervals), in order to avoid increase of pressure in the closed Teflon vessel.

In conclusion, we have reduced the reaction time compared with the thermal method.[5] The isolated yields are higher than previously reported.[5–7] The reaction constitutes a safe, mild, easy to work-up and convenient method for the synthesis of α,β-epoxyketones.

Experimental

IR spectra were obtained on a Perkin-Elmer 833 spectrometer, ^{1}H NMR spectra on a Bruker 80 MHz in $CDCl_3$ using Me_4Si as internal standard. Microwave induced reactions were carried out in a Moulinex MICRO-CHEF, 900 W at 2450 MHz.

General Procedure for Epoxidation of α,β-Unsaturated Ketones.—A mixture of ketone (3 mmol) and sodium perborate (9 mmol) in water (9 mL) and 1,4-dioxane (6 mL) in a closed Teflon vessel (volume 250 mL) was irradiated for 2 min (four times, each time 30 s with 5 min intervals). After cooling, the mixture was extracted with dichloromethane (3×20 mL). The organic layer was separated and dried over magnesium sulfate. After filtration the solvent was evaporated and the residue analysed by GC and purified with a short column (eluent: light petroleum–dichloromethane, 10:1).

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