Microwave-assisted Oxidation of Alcohols by Pyridinium Chlorochromate†

J. Chem. Research (S), 1999, 118–119†

Vaishali Chakraborty and Manobjyoti Bordoloi*

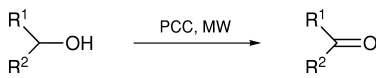
Natural Products Chemistry Division, Regional Research Laboratory, Jorhat-785006, Assam, India

An efficient and mild methodology for the oxidation of alcohols to the corresponding carbonyl functions is described using pyridinium chlorochromate under microwave irradiation.

The oxidation of the hydroxy group to a carbonyl functionality is an important transformation in organic synthesis and several methods are available to accomplish this conversion under a variety of reaction conditions.[1–4] Because of its significant role in synthetic chemistry, this reaction continues to receive attention from chemists in search of newer and selective oxidation protocols.[5] Therefore, selective methods allowing for oxidation of primary alcohols to aldehydes without over-oxidation to carboxylic acids remains challenging.

In recent years organic reactions assisted by microwave irradiation have gained special attention.[6] The chief features of the microwave reactions are the enhanced selectivity, much improved reaction rates, milder reaction conditions and formation of cleaner products. These reactions are especially appealing as they can be carried out in open vessels thus avoiding the risk of development of high pressures in addition to the associated ease of manipulation.

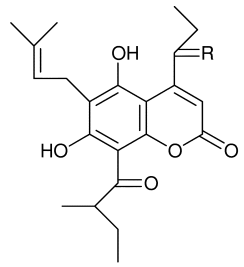
In continuation of our ongoing work on development of highly efficient oxidation protocols, we observed that the oxidation of neat alcohols (Scheme 1) with pyridinium chlorochromate (PCC) under microwave irradiation can be carried out much more quickly than using conventional techniques.



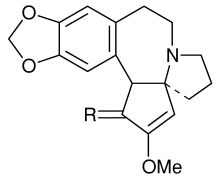
Scheme 1

In a typical reaction the alcohol in 2 ml of dry CH_2Cl_2 was treated with PCC and placed in a commercial microwave oven (operating at 2.45 GHz) and irradiated for 2 min at ambient pressure, to yield the corresponding carbonyl compound in excellent yield (Table 1). There was no evidence for the formation of any side products or that of any over-oxidation.

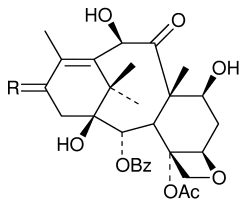
The versatility of the procedure was further demonstrated by the oxidation of some natural products such as assameine[7] **1a**, cephalotaxine **2a**, 10-deacetylbaccatin III **3a**, diosgenin **4a** and the sugar derivative 1,2:5,6-di-*O*-cyclohexylidene-α-D-glucofuranose **5a** into the corresponding ketones **1b**, **2b**, **3b**, **4b** and **5b** respectively. The reaction procedure tolerated several sensitive functional groups such as double bonds, phenolic OH, tertiary OH, oxetane and ketal functions. When a mixture of docosanol and geraniol was oxidized with PCC under microwave irradiation, docosanol was found to be unaffected with the conversion of the allylic alcohol function of geraniol into the α,β-unsaturated aldehyde. The advantages of the present method include the drastic reduction of the oxidation time, tolerance of many sensitive functional groups, mildness of the method, ease of operation and easy work up procedure. The solid remains of the reagent can be easily separated. The oxidation can also be performed under solvent-free conditions with moist PCC; the yield and other advantages remain the same.



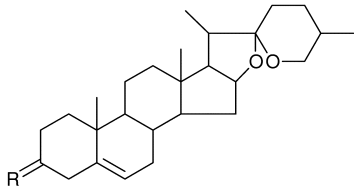
1a R = OH, H
b R = O



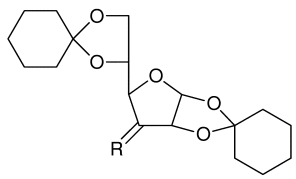
2a R = β-OH, H
b R = O



3a R =H, α-OH
b R = O



4a R =H, β-OH
b R = O



5a R = OH, H
b R = O

Experimental

General procedure.—In a typical reaction, 1 mmol of decanol was dissolved in 2 ml of CH_2Cl_2 in a 150 ml conical flask and treated with 1.5 mmol of PCC. The reaction mixture was then irradiated in the microwave oven (operating at 2.45 GHz, 200 W) for 2 min at ambient pressure. On completion of the reaction (monitored by TLC), it was quenched with 0.5 ml of methanol. The mixture was filtered through a short pad of silica gel with EtOAc and the solvent evaporated to yield decanal in 97% yield. No side products were observed to be formed. When solvent-free conditions were used, 1 mmol of decanol was mixed with moist PCC (1.5 mmol) with a pestle and mortar; the mixture was irradiated for 2 min and worked up as before to get the corresponding aldehyde with same yield. All the products were characterized by IR, NMR (^1H and ^{13}C), mass spectra and direct comparison with authentic samples.

We express our sincere thanks to the Director, Regional Research Laboratory, Jorhat for provision of facilities, Dr. N. C. Barua for constant encouragement and CSIR for financial assistance.

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Oxidation of alcohols to carbonyl compounds by PCC under microwave irradiation

Substrate	Product	Time/min	Isolated yield (%)
Decanol	Decanal	2	97
Octadecanol	Octadecanal	2	95
Hexadecanol	Hexadecanal	2	97
Docosanol	Docosanal	2	93
Geraniol	Geranial	2	97
Cholesterol	Cholest-5-en-3-one	2	94
Cyclohexanol	Cyclohexanone	2	97
Borneol	Camphor	2	90
Cephalotaxine **2a**	Cephalotaxinone **2b**	2	95
Assameine[7] **1a**	14-Oxoassameine **2b**	2	95
Diosgenin **4a**	3-Oxodiosgenin **4b**	2	90
10-Deacetylbaccatin III **3a**	13-Oxo-10-deacetylbaccatin III **3b**	2	70
1,2:5,6-Di-*O*-cyclohexylidene-α-D-glucofuranose **5a**	3-Oxo-1,2:5,6-di-*O*-cyclohexylidene-α-D-glucofuranose **5b**	10	99[a]
Docosanol + geraniol	Geranial[b]	2	92

[a]Oxidation without microwave irradiation is completed in 4 h under reflux. [b]Docosanol was recovered quantitatively.

Received, 27th May 1998; Accepted, 28th October 1998
Paper E/8/03978J

References

1 B. M. Trost, in *Comprehensive Organic Synthesis* (*Oxidation*), ed. S. V. Ley, Pergamon, New York, 1991, vol. 17, p. 260.
2 J. Einhorn, C. Einhorn, F. Ratajczak and J. L. Pierre, *J. Org. Chem*., 1996, **61**, 7452.
3 J. Muzrt, A. N'Ait Ajjou and S. Ait Mohand, *Tetrahedron Lett*., 1994, **35**, 1989.
4 R. A. Lee and D. S. Donald, *Tetrahedron Lett*., 1997, **38**, 3857.
5 I. E. Marko, P. R. Giles, M. S. Taukazaki, M. Brown and C. J. Urch, *Science*, 1996, **274**, 2044.
6 R. A. Abramovich, *Org. Prep. Proceed. Int*., 1991, **23**, 683; A. G. Whittaker and D. M. P. Mingos, *J. Microwave Power Electromagn. Energy*, 1994, **29**, 195; S. Caddick, *Tetrahedron*, 1995, **51**, 10403; for some recent reports see: H. Benhalibaba, A. Derdour, J.-P. Bazureau, F. Texier-Boullet and J. Hamelin, *Tetrahedron Lett*., 1998, **39**, 541; R. S. Varma and R. Dahiya, *Tetrahedron Lett*., 1997, **38**, 2043; R. S. Varma, R. K. Saini and H. M. Meshram, *Tetrahedron Lett*., 1997, **38**, 6265; R. S. Varma, R. K. Saini and R. Dahiya, *Tetrahedron Lett*., 1997, **38**, 7823; R. S. Varma and R. Dahiya, *Tetrahedron Lett*., 1998, **39**, 1307; R. S. Varma and R. K. Saini, *Tetrahedron Lett*., 1998, **39**, 1481, R. S. Varma, R. Dahiya and R. K. Saini, *Tetrahedron Lett*., 1997, **38**, 7029.
7 M. Bordoloi, S. Mohan, N. C. Barua, S. C. Dutta, R. K. Mathur and A. C. Ghosh, *Phytochemistry*, 1997, **44**, 939.