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Deoximation by Pyridinium Chlorochromate under Microwave Irradiation†

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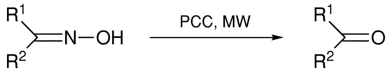
Regeneration of carbonyl functions from oximes can be accomplished by use of pyridinium chlorochromate under microwave irradiation within a short time with excellent yields.

Since oximes have been employed as ketone or aldehyde functional group equivalents in organic synthesis,[1] the conversion of oximes into their parent carbonyl compounds has received considerable attention. Oximes are useful protecting groups[2] and are extensively used for the purification and characterization of carbonyl compounds as well as in the preparation of amides.[3] Owing to the relative hydrolytic stability of oximes,[4] a wide variety of deoximation reagents have been developed such as manganese triacetate,[5a] dinitrogen tetroxide,[5b] trimethylsilyl chlorochromate,[5c] titanium silicalite,[5d] pyridinium chlorochromate,[5e] bismuth trichloride,[5f] ammonium persulfate–silica gel,[5g] sodium periodate,[5h] zirconium sulfophenyl phosphonate,[5i] *N*-halo-amides,[5j] triethylammonium chlorochromate,[5k] and Raney nickel,[5l] with certain limitations. The use of dimethyldioxirane[6a] was restricted to ketoximes whereas pyridinium chlorochromate–H_2O_2[6b] suffers from the disadvantage of over-oxidation. Deoximation using pyridinium chlorochromate[5e] suffered from the serious drawback that the reaction time was too long (12–94 h) and the yields obtained were very low.



Recently there has been a growing interest in the application of microwave irradiation in chemical reactions.[7] The salient features of the MW approach are the much improved reaction rates, formation of cleaner products and rapid reactions. We now report a facile deoximation protocol using pyridinium chlorochromate with a dramatic reduction of reaction time.

When the oxime, dissolved 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 it yielded the corresponding carbonyl compound in excellent yield (Table 1). The optimum ratio of substrate to reagent was found to be 1:1.5. It was also observed that oximes can be transformed into carbonyl compounds without using any solvent within same time span and with same yield. Based on these results, the advantages of the present method can be summarized as: (1) the reaction proceeds on the free oxime; (2) drastic reduction of reaction time; (3) reaction tolerates many sensitive functional groups and even hindered oximes (camphor oxime) undergo deoximation in excellent yield; (4) α,β-unsaturated oximes too were successfully deoximated; (5) easy work-up procedure and easy separation of the solid remains of the chromium-based oxidant. Because of its high yield, short reaction time at ambient pressure, inexpensive and reduced amount of PCC used, this method has advantages over existing ones.

Table 1 Deoximation using PCC under Microwave Irradiation

Entry	Substrate	Isolated yield (%)[a]
1	Decanal oxime	97
2	Octadecanal oxime	95
3	Hexadecanal oxime	97
4	Docosanal oxime	93
5	Geranial oxime	97
6	Cholestan-3-one oxime	94
7	Cyclohexanone oxime	97
8	Camphor oxime	90
9	16-Dehydopregnenolone-3β-acetate-20-oxime	90
10	Diosgenin 3-oxime	90
11	Acetophenone oxime	97
12	4-Chlorobenzaldehyde oxime	95
13	Benzaldehyde oxime	97
14	4-Hydroxyacetophenone oxime	96

[a] Of carbonyl compound. Reaction with only PCC gave a 47% yield after 18 h for entry 7 and a 61% yield after 15 h for entry 11.[5k]

Experimental

IR spectra were recorded on a Perkin-Elmer 237B IR spectrophotometer. NMR spectra were recorded on a Varian EM 360L (60 MHz) and Bruker Avance DPX 300 (300 MHz) instrument. Mass spectra were recorded on an INCOS 50 GC-MS instrument.

In a typical reaction, 1 mmol of benzaldehyde oxime dissolved in 2 ml of dry CH_2Cl_2 in a 150 ml conical flask was treated with 1.5 mmol of pyridinium chlorochromate and the reaction mixture was irradiated in a microwave oven (operating at 2.45 GHz, 350 W) for 2 min at ambient pressure. When the reaction was completed (TLC monitoring) 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 obtain benzaldehyde in 97% yield. There was no evidence for the formation of any side products. When solvent free conditions were used, 1 mmol of benzaldehyde oxime was mixed with moist PCC (1.5 mmol) in a pestle and mortar and then the mixture, placed in a 150 ml conical flask, was irradiated for 2 min and worked up as above to get the corresponding aldehyde with same yield. All the products were characterized by IR, NMR (^1H and ^{13}C) and mass spectra, and direct comparison with authentic compounds.

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