

Tetraethylammonium permanganate. A new selective and mild reagent for deoxygenation in solvent-free conditions[†]

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A variety of oximes are easily and efficiently cleaved in excellent yields by tetraethylammonium permanganate in a solventless system.

Keywords: tetraethylammonium permanganate, deoxygenation

Selective regeneration of protected functional groups is of great importance in multistep organic synthesis. Regeneration of carbonyl compounds from their oximes is a significant reaction and assumed added importance after the report of Barton reaction¹ in which oximes can be obtained at non-activated hydrocarbon sites. Cleavage of these oximes therefore provides an alternative pathway to aldehydes and ketones. Recently, a number of methods have been reported for the cleavage of oximes to carbonyl compounds.^{2–7} Each of these methods has its own merits and drawbacks.

In 1983, Rao and his co-workers⁸ reported triethylammonium chlorochromate as a reagent for deoxygenation with average yields of 56%. Since the chromium residues are environmentally hazardous⁹ and using its complexes has the disadvantages of potential danger (ignition or explosion) in handling and cumbersome isolation, it would be advantageous to develop oxidising methods requiring other metals

than chromium like manganese which is reported to be less toxic and less environmentally hazardous.¹⁰

Tetraethylammonium permanganate can be easily and economically prepared by addition of a saturated solution of potassium permanganate to an aqueous solution of tetraethylammonium bromide and has been used as a versatile oxidising agent.^{11–13}

Organic solvents are not only expensive but are often flammable, toxic and environmentally hazardous. Consequently, there is a scope for the development of solventless deoxygenation reactions. We have developed implementation of these reactions in a solventless system.^{14–16} Armed with these experiences in this communication we wish to report the cleavage of oximes using tetraethylammonium permanganate in solvent free conditions.

The reaction is conducted by mixing finely ground reagent and neat oxime for 5 min and leaving the mixture at room

Table 1 Oxidative cleavage of oximes^a to carbonyl compounds^b with Et₄N⁺MnO₄⁻ in a solventless system^c

Entry ^d	R ₁	R ₂	Reaction time/min	Yield/% ^d	m.p. (b.p.) °C
1	C ₆ H ₅	CH ₃	40	80	(198–200) lit. (202) ^{17b,e}
2	4-CH ₃ C ₆ H ₄	CH ₃	40	86	(224–227) lit. (224) ^{17b,e}
3	4-OCH ₃ C ₆ H ₄	CH ₃	40	83	(256–260) lit. 258 ^{17b,e}
4	4-BrC ₆ H ₄	CH ₃	35	88	48–51 lit. 51 ^{17b,e}
5	4-NO ₂ C ₆ H ₄	CH ₃	35	86	77–79 lit. 81 ^{17b,e}
6	C ₆ H ₅	H	50	96	(175–177) lit. (179) ^{17b,e}
7	4-CH ₃ C ₆ H ₄	H	50	95	(200–203) lit. (204) ^{17b,e}
8	4-OCH ₃ C ₆ H ₄	H	50	93	(245–247) lit. (248) ^{17b,e}
9	C ₆ H ₅	C ₆ H ₅	40	78	45–47 lit. 49 ^{17b,e}
10	Cyclohexyl		40	80	(153–155) lit. (156) ^{17b,e}
11	C ₃ H ₇	H	50	84	(75–79) lit. (75) ^{17b,e}
12	C ₂ H ₅	C ₂ H ₅	40	87	(98–100) lit. (102) ^{17b,e}

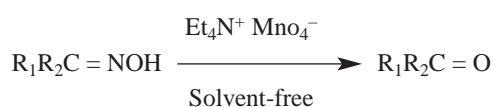
^aOximes are synthesised according to a known procedure. ¹⁷ ^bAll products were known and characterised by comparing their physical and spectroscopic data with those of authentic samples. ^cSee **Caution** in Experimental section. Precautions are particularly advised for mixing oximes 6,11,12 with the reagent see **Caution** in Experimental section. ^dYields refer to isolated product.

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[†] This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

temperature for the indicated time (Table 1).[‡] The progress of the reaction was monitored by TLC. To assess the generality of method a variety of oximes was cleaved in high yields by this method. We have investigated different substrate/reagent ratios and found that a 1:1 ratio is suitable for successful cleavage. No overoxidation to carboxylic acid was observed. The results are summarised in Scheme 1 and Table 1. Reactions with liquid oximes were exothermic and we were forced to cool the reaction using an ice bath. The presence of small amounts of water also caused destructive reactions. It is therefore our understanding that the dry medium is necessary for the selectivity of the oxidative cleavage reaction.

In summary, tetraethylammonium permanganate is a selective and efficient oxidant, which offers a new avenue for an expeditious deoximation. The inexpensive relatively non-toxic reagent and solvent free conditions are the positive features of the procedure.



R₁, R₂: Ar, Alkyl, H

Scheme 1

Experimental

All substrates were prepared according to reported procedures.¹⁷ The reagent, tetraethylammonium permanganate was synthesised following a known procedure.¹² All products are known compounds and were characterised by comparison of their physical and spectroscopic data with those of authentic samples. The compounds were identified by comparison of m.p. and b.p. data as reported in Table 1. H¹NMR structure confirmation was obtained using a 60 MHz Hitachi spectrometer and CDCl₃ as solvent. The IR spectra were obtained using a Perkin-Elmer 843 instrument and found to be comparable with those reported. The reaction was followed by TLC and IR examination *i.e.* disappearance of C=N signals (*ca* 1600 cm⁻¹) of the oximes and appearance of C=O signals of the carbonyl compounds

Caution: The procedure worked safely in our hands. However, as the reactions of the reagent with liquid and low melting point oximes (Entry 6,11,12) happened to be vigorous, we suggest that the mixing of the compounds is better done in an ice bath taking appropriate precautions. The exothermic behaviour indicates that none of the reactions should be scaled up.

Oxidative cleavage of oximes. General procedure: An appropriate oxime (3 mmol) and tetraethylammonium permanganate (3.1 mmol) were intimately mixed in a 5 ml beaker using a spatula for 5 min and the mixture was allowed to stand at room temperature for the indicated time (Table 1). The progress of the reaction was monitored by TLC using hexane:ethylacetate, 8:2. The residue was extracted with CHCl₃ (2 × 10 ml). To this extract, saturated solution of oxalic acid was added dropwise (5 ml). The residue was washed with water (2 × 10 ml). The organic layer was separated, dried, and evaporated to afford the corresponding carbonyl compound (Table 1).

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[‡] See Caution in Experimental section.