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With compliments of the Author

Development of Manganese(VI) Oxidising Agents Soluble in Organic Solvents

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The author would like to dedicate this paper to Prof. Philip J. Parsons on the occasion of his 60th birthday.

Abstract: Two manganate(VI) reagents have been prepared from permanganate salts that show excellent oxidising properties in common organic solvents.

Key words: manganite, oxidising agent, allylic alcohol, ketone, amine

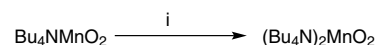
Manganese exhibits many oxidation states from +I to +VII, +II being the most stable ion. Mn(II) ions are required as a trace mineral for all living organisms as they function as a cofactor for a large number of enzymes. There are few manganese(VI) oxides in the literature that are useful to synthetic chemists. Barium¹ and potassium² variants have been extensively studied and used,³ but show their limitations due to their lack of solubility in common organic solvents. Mn(VI) oxides, just like manganese dioxide, are excellent oxidising agents and are particularly effective at oxidising primary and secondary allylic and benzylic alcohols to their corresponding aldehydes, ketones, or even carboxylic acids,⁴ and at oxidising amines,⁵ silyl ethers,⁶ and thiols.⁷

A wide range of conditions have been used including the use of microwaves,⁸ solvent-free reactions,⁹ or in conjunction with other metals or semimetals like lithium,¹⁰ copper,¹¹ arsenic,¹² tellurium,¹³ thallium,¹⁴ ruthenium (III),^{3j} and lead.¹⁵ Despite their interesting chemoselectivity, a large excess of the reagents is usually required, from 5–50 equivalents, which renders them particularly expensive on larger scale with significant waste in manganese element.

To avoid this shortfall, we synthesised two complexes that are soluble in both organic and aqueous solvents based on the corresponding ammonium salts. Because alkaline solution of potassium iodide is usually used to reduce potassium permanganate to potassium manganate,¹⁶ our initial attempts involved the use of ammonium iodides as a reducing agent for potassium permanganate, but the stability of the green complex was short-lived, with degradation to brown residues, presumably insoluble Mn(IV). Best results were obtained with trialkylammonium hydroxides and tetrabutylammonium permanganate (Bu₄N)₂MnO₄. Two reagents were synthesised using tetrabutylammonium hydroxide, tetrabutylammonium iodide, and phenyl-

trimethylammonium iodide: bistetrabutylammonium manganate (bTBAM, Scheme 1) and the mixed salt tetrabutylammonium phenyltrimethylammonium manganate. Of note those salts were found to be unstable in acidic medium, just like the other manganate oxides.¹⁷

Manganese(VI) oxides are typically green in colour, due to a combination of the relatively large molar extinction coefficient ϵ , arising from the ligand-to-metal charge transfer, and to the absorption within the visible region of the spectrum. They are usually characterised by an absorption maxima at a wavelength of 606 nm with an ϵ value of $1200 \pm 50 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.¹⁸ Permanganate, on the other hand, has an absorption maximum at a wavelength of 525 nm.



Scheme 1 Reagents and conditions: (i) Bu₄NOH, H₂O, sonication, 60 °C.

Though the salts are soluble in a variety of organic solvents, including DMSO, DMF, MeCN, acetone, THF, EtOAc, 1,4-dioxane, pyridine, CHCl₃, and CH₂Cl₂, the best solvents for the oxidation were found to be THF and acetonitrile. The compound is also moderately soluble in benzene to produce ‘green benzene’ by analogy with the well-known ‘purple benzene’ reported by Herriott and Picker.¹⁹ Table 1 exemplifies the use of bTBAM as a mild oxidising agent, with reactions occurring at room temperature. Though MnO₂ is usually successful at oxidising allylic alcohols, yields are usually lower. BaMnO₄ and K₂MnO₄ can also perform such oxidations illustrated in Table 1, but require a large excess of the oxidising agent.

In conclusion we have shown that ammonium salts of manganate oxides allow the oxidation of a variety of functional groups under mild conditions in an easy and widely applicable procedure.

Preparation of (Bu₄N)₂MnO₄ (bTBAM)

Tetrabutylammonium permanganate (1.00 g, 2.77 mmol) was added to a flask containing TBAOH solution (40 wt%, 5 mL, 7.70 mmol) and distilled H₂O (45 mL). The mixture was then placed into a sonicator bath and sonicated for 10 min at 60 °C. The mixture was subsequently poured through a sinter funnel to remove any undissolved permanganate salts. The green solution was subsequently lyophilised to give a green solid which can be kept in a desiccator under reduced pressure, or in a sealed flask under argon. ¹H NMR

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Table 1 Oxidation with 1.5 equiv of bTBAM

Entry	Substrate	Product	Time (min)	Yield (%) ^b
1			60	82
2			10	89
3			150	84
4			30	quant.
5			60	80
6			60	81
7			120	76
8			30	80 ^a

^a Conditions: 2.5 equiv of bTBAM were required.

^b Products were characterized by comparison with authentic samples, IR, TLC, mp, and NMR.

(500 MHz, CDCl₃): δ = 3.39–3.35 (16 H, m), 1.70–1.68 (16 H, m), 1.49–1.47 (16 H, m), 1.03–1.01 (24 H, m). ¹³C NMR (126 MHz, CDCl₃): δ = 59.1 (CH₂), 24.2 (CH₂), 19.7 (CH₂), 13.7 (CH₃). ESI-MS: *m/z* = 603, 242.

Preparation of [(Bu₄N)(PhMe₃N)]MnO₄

A solution of phenyltrimethylammonium iodide (1.66 g, 7.32 mmol) in MeCN (50 mL) was added to a solution of TBAI (7.02 g, 0.019 mol) in MeCN (30 mL), followed by the addition of KMnO₄ (0.514 g, 3.16 mmol) in MeCN (10 mL). The mixture was placed in a H₂O bath at 30 °C for 1 h before 1 equiv of KI was added. The mixture was then left to stir for 12 h, filtered, and the solvent was evaporated yielding dark green crystals (5.78 g, 0.011 mol).

¹H NMR (500 MHz, CDCl₃): δ = 8.02–7.97 (2 H, m), 7.63–7.61 (2 H, m), 7.55–7.53 (1 H, m), 4.01 (9 H, s), 3.40–3.34 (8 H, dt, *J* = 14.3 Hz), 1.68–1.64 (8 H, m), 1.49–1.47 (8 H, m), 1.03–1.01 (12 H, m). ¹³C NMR (125 MHz, CDCl₃): δ = 126.0 (CH), 59.2 (CH₂), 50.7 (CH₂), 24.2 (CH₂), 19.3 (CH₂), 13.4 (CH₂). ESI-MS: *m/z* = 496, 242.

General Procedure for the Oxidation of Alcohols

bTBAM (1.5 equiv) was added to a 0.01 M solution of the alcohol in THF or MeCN at r.t. and stirred for 60 min during which time the colour of the solution changed from green to brown. The suspension was then filtered over a short plug of silica, which was subsequently rinsed with Et₂O. The organic phase was washed with brine, dried

over Na₂SO₄, and concentrated under reduced pressure to give the corresponding aldehyde or ketone.

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