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CONTROLLING THE REACTIVITY OF PERMANGANATE ANION. NOVEL, STEREOSPECIFIC, DICHLORINATION OF OLEFINS

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Dedicated fondly and with deep respect to Professor K. Barry Sharpless

Abstract: *Potassium permanganate reacts with oxalyl chloride to form a chlorine-containing manganese catalyst, of yet unknown structure, that stereospecifically trans-dichlorinates olefins.*

Potassium permanganate is a powerful oxidising agent, known to react with olefins to form, under carefully-controlled conditions, *cis* vicinal diols in moderate to good yields. Usually, cleavage products and secondary compounds produced by overoxidation are also observed [1].

We recently embarked on a programme aimed at exploring and modulating the power of $KMnO_4$ in order to transform it into a much more selective and thus, synthetically useful reagent. In this letter, we report on one such successful transformation.

When a CH_2Cl_2 solution of benzyl triethyl ammonium permanganate [2], easily prepared by stirring benzyl triethyl ammonium chloride with $KMnO_4$, was treated at -40°C with two equivalents of oxalyl chloride, a vigorous gas evolution [3] took place and a brown-coloured solution formed. After stirring for 30 minutes at that temperature, (E) - 5-decene was added. A beautiful emerald-green colour developed. Working-up the reaction mixture using sodium thiosulphate produced two **clear, colourless**, organic and aqueous layers. Removal of the solvent afforded in high yields and purity, the corresponding **trans vicinal dichloride 3** (Figure 1).

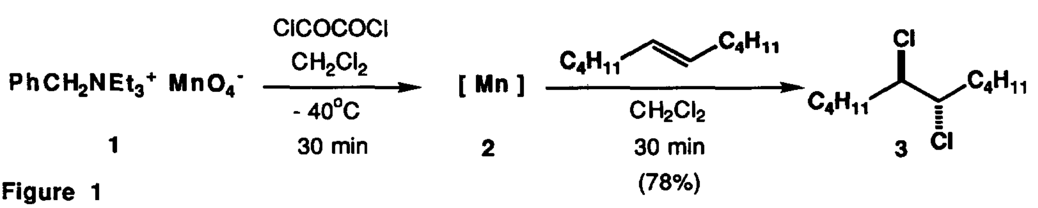
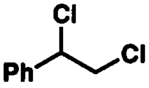
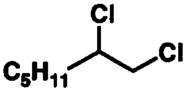
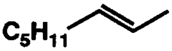
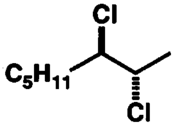
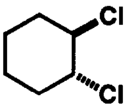
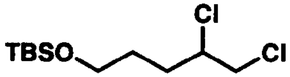
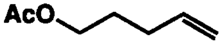
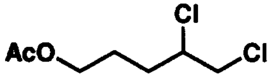
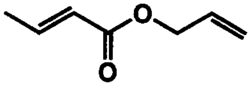
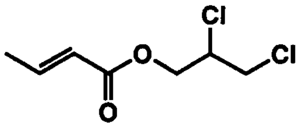


Figure 1

This surprising result appears to be general and a number of olefins were converted smoothly to the corresponding dichloride [4]. Terminal, internal and even trisubstituted olefins were found to be suitable substrates for this novel manganese reagent which tolerates such protecting groups as tert-butyldimethylsilyl and acetyl (Table 1, entries 5 and 6).

Table. Stereospecific dichlorination using manganese reagent **2**.

Entry	Substrate	Product	Yield[a]
1			98%
2			75%
3			69%
4			80%
5			87%
6			85%
7			96%

a. All yields refer to products obtained directly from the reaction mixture. These were essentially pure, as determined by GC and NMR analysis.

The reagent displays an exquisitely high chemoselectivity which is exemplified by the complete discrimination between the two electronically different double bonds of allyl crotonate (Entry 7). **Only the electron-rich double bond is dichlorinated.**

In sharp contrast with other organometallic reagents that effect *cis* dichlorination of olefins [4a-c], this manganese system affords exclusively [5] the **1,2-anti dichloride.**

Although the structure of the manganese species involved in this unique reaction has not yet been determined - mostly because of its rapid decomposition - a few comments deserve to be mentioned. The reagent is unstable at a temperature higher than -35°C. Above this temperature, a dark-green colour develops and addition of an olefin gives only a few percent of the desired dichloride. No reaction is observed if the solution of the manganese derivative is allowed to reach room temperature before addition of the olefin [6].

Another intriguing observation is the complete loss of activity if bromide ions (as tetrabutyl ammonium bromide) are added to the preformed catalyst. Any attempt to use oxalyl bromide (in order to generate the corresponding dibrominating catalyst) instead of oxalyl chloride has so far resulted only in the recovery of the starting olefin, despite the evidence of a reaction between the permanganate anion and the oxalyl bromide.

Although it is difficult at this stage to discuss a plausible reaction mechanism, it is tempting to speculate, especially in light of the high *trans* - stereoselectivity observed, that an initial *cis* - insertion into a manganese-chlorine bond takes place, leading to the manganese species **6**. Substitution of the manganese group by another chloride anion, with inversion of configuration, will then provide the observed *trans* - dichloride (Figure 2).

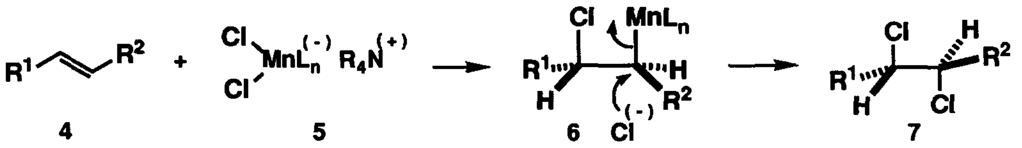


Figure 2

In conclusion, we have been able for the first time to completely modify [7] the reactivity of permanganate anion. Indeed, the formation of oxygenated products, typically observed when this reagent is treated with an olefin, has been totally suppressed and replaced by the stereospecific attachment of two chlorine atoms.

The mildness of the reaction conditions, the high yields and purity of the products obtained, coupled with the simplicity of the experimental procedure, undoubtedly makes this process a particularly appealing one for the stereospecific dichlorination of olefins.

Further work from this laboratory on the structural elucidation of this unusual reagent [8], as well as on the synthetic applications of the dichlorinated products, will be reported in due course.

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Typical Experimental Procedure

Preparation of 5, 6 - anti - dichlorodecane 3

To a CH_2Cl_2 (20 mL) solution of benzyl triethyl ammonium chloride (0.8 g, 3.8 mmol) was added solid $KMnO_4$ (0.6 g, 3.8 mmol). The purple mixture was stirred for 45 minutes, filtered through a glass-wool plug and the solid rinsed with another 10 mL of CH_2Cl_2. The purple solution was then cooled to -45°C (CH_3CN/CO_2) and oxalyl chloride (0.55 mL, 6.3 mmol) was added dropwise *via* syringe. A vigorous gas evolution took place and the colour of the solution changed to dark brown. After 30 minutes, (E)-5-decene (0.6 mL, 3.2 mmol) was added and the solution, which slowly took an emerald-green colour, was stirred for a further 30 minutes before being quenched by pouring it into a separatory funnel containing an aqueous solution of sodium thiosulphate. The colourless organic solution was separated, dried over $MgSO_4$ and the solvent removed *in vacuo* to give 0.54 g (78%) of pure 5, 6 - anti - dichlorodecane **3**.

References and Notes

1. Stewart, R. in *Oxidations in Organic Chemistry,* Part A, **1965**, 1; Wiberg, K. B. Ed.; Acad.Press (NY).
2. Lee, D. G. in *Oxidation in Organic Chemistry,* Vol 5-D, **1982**, 147; Trahanovsky, W. S. Ed; Acad. Press (NY).
3. The gas that evolved was shown to contain CO_2 by FT-IR spectroscopy. No HCl or Cl_2 was detected.
4. The formation of *cis* vicinal dichlorides by other organometallic reagents has been reported: (a) Henniger, P. W.; Dukker, L. J.; Havinga, E. *Rec. Trav. Chim. Pays-Bas,* **1966**, *85*, 1177. (b) Nugent, W. A. *Tetrahedron Let.* **1978**, 3427. (c) Donnelly, K.; Fristad, W. E.; Gellerman, B. J.; Peterson, J. R.; Selle, B. J. *Tetrahedron Lett.* **1984**, 607. For an example of *trans* dichlorination, see: Bellesia, F.; Ghelfi, F.; Pagnoni, U. M.; Pinetti, A. *J. Chem. Res. (S)* **1989**, 108.
5. The only exception we have encountered so far is *trans* - stilbene which gives a mixture of d, l and meso dichlorides (1 : 1).
6. This observation also rules out the formation and participation of chlorine as the dichlorinating agent. It is also worth noting that, under the same conditions, chlorination using molecular chlorine does not proceed to any appreciable extend.
7. For an initial modification of permanganate reactivity using acetic anhydride, see: Sharpless, K. B.; Lauer, R. F.; Repic, O.; Teranishi, A. Y.; Williams, D. R. *J. Am. Chem. Soc.* **1971**, *93*, 3303.

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