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Selective Manganese-Mediated Transformations Using the Combination: KMnO4/Me3SiCl

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Abstract: A novel manganese reagent, generated from $KMnO_4$ and Me_3SiCl, in the presence of a quaternary ammonium salt, is shown to smoothly dichlorinate alkenes, open epoxides and chemoselectively oxidise sulfides to sulfoxides. © 1997 Elsevier Science Ltd.

We disclosed recently that $KMnO_4$, in the presence of oxalyl chloride and benzyl triethylammonium chloride, reacts with a range of alkenes to afford 1,2-dichloroalkanes in good yield and high purity.[1] Unfortunately, the lack of stability of the manganese reagent coupled with its temperamental behaviour led sometimes to erratic results.[2] In this letter, we report the generation and synthetic applications of a more robust and performant manganese complex that provides a practical solution to the previously encountered problems.

Replacement of oxalyl chloride by a number of alternative promoters[3] rapidly established the unique competency of Me_3SiCl. Thus, when a CH_2Cl_2 solution of benzyltriethylammonium permanganate, easily prepared by stirring powdered $KMnO_4$ with the phase-transfer reagent, was treated at 0°C with trimethylsilyl chloride (4 eqs.), the purple solution gradually turned into a beautiful emerald-green colour. Addition of an alkene followed by stirring at room temperature and aqueous thiosulfate work-up led to the isolation of the corresponding *trans*-dichlorination product in high yield and purity (Figure 1).[4]

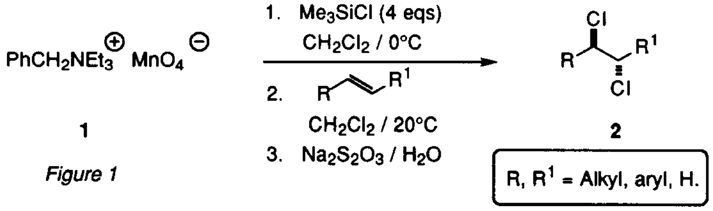


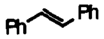
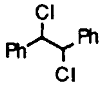
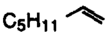
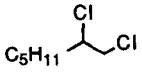
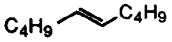
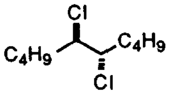
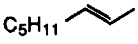
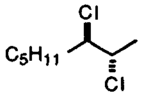
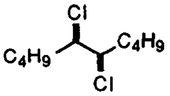
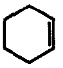
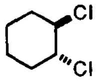
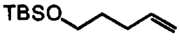
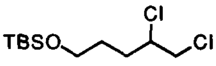
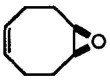
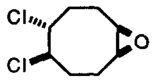
Figure 1

Some representative examples are displayed in Table 1. With the exception of the aromatic substituted olefins which give a mixture of *syn*- and *anti*-dichlorides (Table 1, Entry 1), the reaction proceeds exclusively by *anti*-dichlorination of the alkene substrates, a rather unusual process for metal-mediated dichlorinations.[5,1]

This selectivity is nicely exemplified by the halogenation of (*E*)-5-decene which gives the *anti*-dichloride (Table 1, Entry 3)) whereas the (Z)-isomer affords the corresponding *syn*-dichloride (Table 1, Entry 5). The manganese reagent also tolerates various protecting groups (For an example, see Table 1, Entry 7) and displays excellent levels of chemoselectivity. For example, chlorohydrin formation by direct epoxide opening is not observed during the chlorination of the monoepoxide of cyclo-octadiene (Table 1, Entry 8).[6]

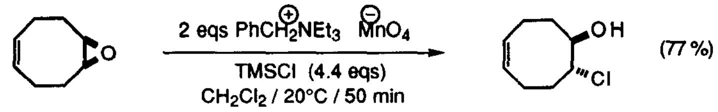
Interestingly, in the presence of an excess of TMSCl, smooth and chemoselective epoxide opening takes place, affording the corresponding *anti*-chlorohydrin **4** (Figure 2).[7]

Table 1. Dichlorination of alkenes

Entry	Substrate	Product	Yield [a]
1 [b]			95 %
2			86%
3			94%
4			84%
5			81 %
6			87%
7			82%
8 [c]			60%

(a) All Yields are for pure, isolated compounds. (b) Mixture of *Syn / anti* - isomers (1 : 1). (c) No chlorohydrin was detected in this reaction. Epoxide opening leading to bicyclic ethers was observed as a minor side-reaction (ref 6).

This observation prompted us to study the reaction of various epoxides with our manganese reagent. The results of some experiments are presented in Table 2. In the case of benzylic systems, ring opening to form the benzylic chlorides is preferred. However, in the alkyl epoxides, insertion of the chlorine atom takes place at the less sterically hindered position.



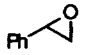
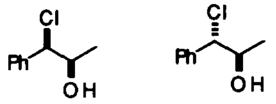
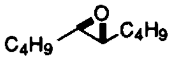
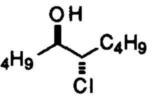
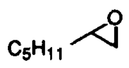
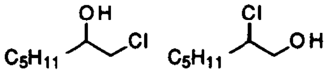
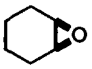
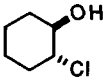
3

4

Figure 2

Finally, oxidation of sulfides was investigated using this novel manganese reagent and found to proceed smoothly, at or below room temperature, affording the desired sulfoxides in good yields (Figure 3).[8] In these cases, an excess (1.1-2 equiv.) of the manganese complex was used with inverse addition of the reagent to the sulfides. The oxidation of alkenyl sulfide **7** displays excellent chemoselectivity with only traces of olefin dichlorination being observed.

Table 2. Opening of Epoxides

Entry	Substrate	Product	Yield [(a)] (ratio)[(b)]
1			91 % (1 : 7)
2			89 % (1 : 4)[(c)]
3			97 % (-)
4			85 % (6 : 1)
5			90 % (-)

(a) All yields are for pure, isolated compounds. (b) Determined by ^{1}H NMR and ^{13}C NMR after conversion into the corresponding chloroacetates. (c) <10% of regioisomer observed in the crude product (syn: anti mixture).

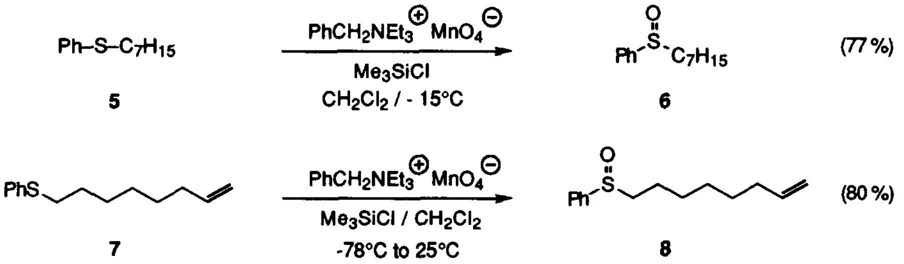


Figure 3

In summary, we have described the preparation of a novel and robust manganese complex by combining KMnO4 and TMSCl in the presence of an ammonium salt. This reagent, of yet unknown structure, was found to chemo- and stereo-selectively dichlorinate alkenes, open epoxides and oxidise sulfides to sulfoxides in high yields. Further work is now directed at determining the structure of this manganese complex,[9] understanding its mechanism of action and broadening the scope of these reactions.[10]

Acknowledgments

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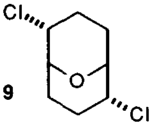
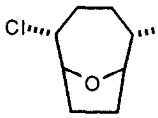
Cork, Forbairt and Ciba (ACE award to ARM) is also gratefully acknowledged. We are very grateful to Prof. A. Alexakis for numerous discussions and suggestions.

References and Notes

1. (a) Markó, I.E., Richardson, P.F. *Tetrahedron Lett.*, **1991**, *32*, 1831; (b) Richardson, P.F., Markó, I.E. *Synlett*, **1991**, 733; (c) Bellesia, F., Ghelfi, F., Pagnoni, U.M., Pinetti, A. *J. Chem. Res.(S)*, **1989**, 108; (d)Bellesia, F., Ghelfi, F., Pagnoni, U.M., Pinetti, A. *J. Chem. Res.(S)*, **1989**, 360; Bellesia, F., Ghelfi, F., Pagnoni, U.M., Pinetti, A. *J. Chem. Res.(S)*, **1990**, 188.
2. The manganese complex generated under these conditions is thermally sensitive and decomposes at temperatures above -35°C. Strict control of temperature and additives is necessary to ensure good yields.
3. Other halogen sources tested include *i.e.* $SOCl_2$, SO_2Cl_2, PCl_3, $OPCl_3$, PCl_5, CH_3COCl, $ClCOCH_2COCl$. In these cases, although some dichlorination took place, the desired dihalides were contaminated by numerous other by-products.
4. In some cases, the initial green colour of the reaction mixture discharged at the end of the reaction. A slight excess of the complex leads to a greenish solution, even after complete consumption of the alkene reagent.
5. The *anti*-stereochemistry has been established by comparison with authentic samples and by X-ray crystallographic analysis. The mixture of *syn*/*anti* isomers obtained for aromatic substituted alkenes probably originates from a competitive solvolysis of the intermediate manganese complex leading to an ion-pair which rapidly recombines with chloride ion.
6. Beside the observed dichlorides, the bicyclic ethers **9** and **10** are produced in about 30% yield by intramolecular interception of the organomanganese intermediate by the closely located epoxide.

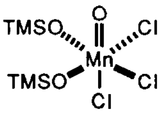
9





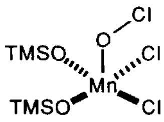
10

7. For opening of epoxides, see for example: (a) Andrews, G.C.; Crawford, T.C.; Contillo, L.G. *Tetrahedron Lett.*, **1981**, *22*, 3803; (b) Martinez, L.E.; Leighton, J.L.; Carsten, D.H.; Jacobsen, E.N. *J. Am. Chem. Soc.*, **1995**, *117*, 5897; (c) Leighton, J.L.; Jacobsen, E.N. *J. Org. Chem.*, **1996**, *61*, 389.
8. For chemoselective oxidation of sulfides into sulfoxides, see for example: (a) Reich, H.J.; Chow, F.; Peake, S.L. *Synthesis*, **1978**, 299; (b) Edwards, M.P.; Ley, S.V.; Lister, S.G.; Palmer, B.D.; Williams, D.J. *J. Org. Chem.*, **1984**, *49*, 3503; (c) Hudlicky, M. *Oxidations in Organic Chemistry*, American Chemical Society, Washington, 1995; (d) Di Furia, F.; Licini, G.; Modena, G.; Motterle, R.; Nugent, W.A. *J. Org. Chem.*, **1996**, *61*, 5175 and references cited therein.
9. Initial investigations appear to rule out $ClMnO_3$ as the active species and seem to favour either the Mn(VII) oxo derivative **11** or the hypochloride **12**. Further work is however needed to fully ascertain the stucture of the reactive complex.



11

or



12

10. To a suspension of $KMnO_4$ (444 mg; 2.81 mmol) in 17 ml CH_2Cl_2 was added $PhCH_2N(Et)_3Cl$ (640 mg; 2.81 mmol). The dark-purple solution was stirred for 45 m in at 20°C then cooled to 0°C and Me_3SiCl (1.22 g; 11.24 mmol) was added dropwise. To the emerald-green solution was added (*E*)-5-decene (394 mg; 2.81 mmol) in 3 ml CH_2Cl_2 and the solution stirred at 20°C for 40 min. The green solution was washed with aq. $Na_2S_2O_3$, dried over $MgSO_4$ and the solvent evaporated *in vacuo* giving the product (556 mg; 94%) as a clear oil.

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