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Heterogeneous Permanganate Oxidations. 5. The Preparation of Aldehydes by Oxidative Cleavage of Carbon–Carbon Double Bonds

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Under acidic or basic conditions aqueous permanganate is a vigorous, nonselective reagent that may be used to oxidize a variety of organic functional groups (e.g. double and triple bonds, primary and secondary alcohols, sulfides, sulfoxides, and aldehydes).[1] The use of various nonaqueous solvents, in which permanganate may be dissolved with the aid of phase-transfer agents, modifies the reactivity and selectivity of permanganate to the extent that it can, for example, be used to cleave carbon–carbon double bonds without the concomitant conversion of alcohols into ketones or carboxylic acids.[2] The use of solid supports[3–6] results in further modifications to the chemical properties of permanganate, the most surprising being an inversion of the selectivity observed in homogeneous solutions; adsorption on an inert support such as bentonite or copper sulfate pentahydrate produces an oxidant that is not reduced by alkenes and which can be used to convert unsaturated secondary alcohols into the corresponding unsaturated ketones without disruption of the double bonds.[7] Creation of a third phase by addition of *tert*-butyl alcohol, which is presumed to form a coating on the solid support, results in the formation of α-diketones or α-hydroxy ketones from alkenes[8] while use of permanganate with silica as a support has been reported to either cleave double bonds[9] or promote allylic oxidation.[10]

In an attempt to futher define the ways in which the chemical properties of permanganate can be attenuated by solid supports, we have investigated the use of more active supports and in this paper wish to report on a useful reaction that occurs when the solid support is moist alumina and the solvent methylene chloride. Under such conditions permanganate regains some of its "normal" reactivity and readily cleaves carbon–carbon double bonds with the products being aldehydes (as opposed to carboxylic acids which are the usual products obtained when permanganate reacts with alkenes under aqueous conditions,[1] or when the solid support is silica gel[9]). Several typical examples are summarized in Table I.

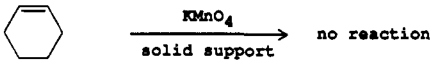
The reaction conditions are mild and easily achieved, the yields are good, the oxidant is inexpensive, and, in common with other heterogeneous permanganate oxidations, the products may be isolated by a simple filtration to remove spent oxidant adsorbed on the solid support, followed by flash evaporation of the solvent.

Table I. Products Obtained from the Oxidation of Alkenes by Permanganate Adsorbed on Moist Alumina

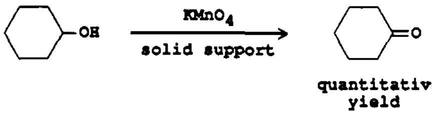
no.	reactant	reaction time (h)	product (% yield)[a]
1	cyclooctene	14	8-oxooctanal (68–73)
2	cyclododecene	14	12-oxododecanal (70–76)
3	1-pentadecene	24	tetradecanal (52–60)
4	(*E*)-Stilbene	4	benzaldehyde (71–90)
5	(*E*)-4,4′-dimethoxystilbene	1	4-methoxybenzaldehyde (90–92)
6	(*E*)-4,4′-dimethylstilbene	1	4-methylbenzaldehyde (78–90)
7	(*E*)-4,4′-dinitrostilbene	2	4-nitrobenzaldehyde (76–89)[b]
8	(*E*)-cinnamic acid	0.5	benzaldehyde (89–95)
9	(*E*)-4-nitrocinnamic acid	0.5	4-nitrobenzaldehyde (88)[c]
10	(*E*)-3-(2-thienyl)-acrylic acid	0.5	2-thiophenecarboxaldehyde (83–90)

[a] Isolated yields. Product identity was confirmed by comparison with ^1H NMR and IR spectra of authentic compounds. [b] mp 106–108 °C (lit.[14] 106 °C) [c] mp 107–108 °C (lit.[14] 106 °C)

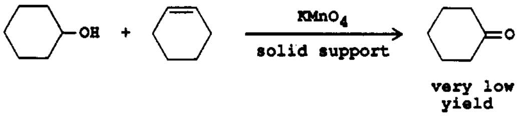
Previously reported studies have shown that the oxidation of alcohols by permanganate adsorbed on solid supports is inhibited by the presence of alkenes[11] (e.g. compare eqs 1, 2, and 3) thereby suggesting that alkenes must form complexes with permanganate even under conditions where no carbon–carbon bond cleavage is observed.



(1)



(2)



(3)

In order for bond cleavage to occur, it must be possible for the initially formed alkene/MnO_4^- complex **1** to be transformed first into a metallaoxetane (**2**) and then into a cyclic manganate(V) ester (**3**)[12] as outlined in Scheme I. The reason why such a process occurs readily with an active support such as alumina but not at all with an inert support such as bentonite may be related to the greater Lewis acidity of alumina. Conversion of **2** into **3** requires cleavage of a C–Mn bond followed by formation of an O–Mn bond. Heterolytic cleavage[13] of the C–Mn bond would be aided by a solid support that is capable of assisting the required proton transfers in a manner similar to the simplified concept presented in Scheme I.

In conclusion, it may be noted that while the function of the solid support in these reactions has only been

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[1] Stewart, R. In *Oxidation in Organic Chemistry, Part A*; Wiberg, K. B., Ed.; Academic Press: New York, 1965; Chapter 1.

[2] Lee, D. G. In *Oxidation in Organic Chemistry, Part D*; Trahanovsky, W. S., Ed.; Academic Press: New York, 1982; Chapter 2.

[3] Regen, S. L.; Koteel, C. *J. Am. Chem. Soc.* **1977**, *99*, 3827.

[4] Clark, J. H.; Cork, D. G. *J. Chem. Soc., Chem. Commun.* **1982**, 635.

[5] Quici, S.; Regen, S. L. *J. Org. Chem.* **1979**, *44*, 3436.

[6] Menger, F. M.; Lee, C. *J. Org. Chem.* **1979**, *44*, 2446.

[7] Noureldin, N. A.; Lee, D. G. *Tetrahedron Lett.* **1981**, *22*, 4889. *J. Org. Chem.* **1982**, *47*, 2790.

[8] Baskaran, S.; Das, J.; Chandrasekaran, S. *J. Org. Chem.* **1989**, *54*, 5184.

[9] Ferreira, J. T.; Cruz, W. O.; Vieira, P. C.; Yonashiro, M. *J. Org. Chem.* **1987**, *52*, 3698.

[10] Prousa, R.; Schonecker, B. *J. Prakt. Chemie* **1991**, *333*, 775.

[11] Lee, D. G.; Noureldin, N. A. *J. Am. Chem. Soc.* **1983**, *105*, 3188.

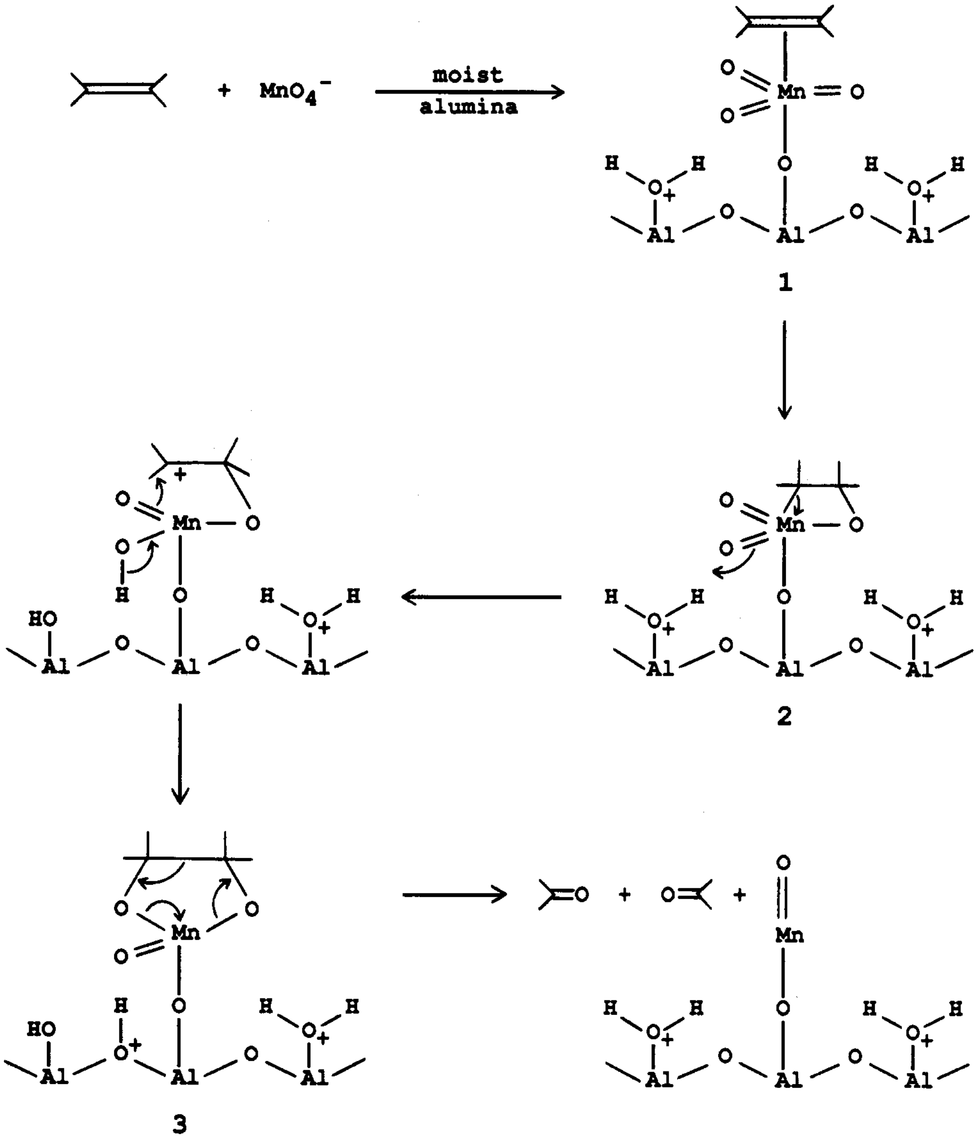
[12] Sharpless, K. B.; Teranishi, A. Y.; Backvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120. Lee, D. G.; Chen, T. *J. Org. Chem.* **1991**, *56*, 5341.

[13] Lee, D. G.; Brown, K. C.; Karaman, H. *Can. J. Chem.* **1986**, *64*, 1054.

[14] *Handbook of Chemistry and Physics*, 62nd ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, 1982; p C-126.

0022-3263/93/1958-2918$04.00/0

Scheme I Oxidation of Alkenes by Permanganate on Moist Alumina



conceptually identified, there is no doubt that its use results in a convenient reaction for the conversion of alkenes into aldehydes.

Experimental Section

In a typical procedure, finely ground $KMnO_4$ (2.2 g, 14.0 mmol), alumina (acid, Brockman Activity 1, 8.8 g), and water (2.2 mL) were ground for 5 min to give a homogeneous mixture. Stilbene (0.52 g, 2.9 mmol), dissolved in CH_2Cl_2 (100 mL), was placed in a round-bottomed flask with a magnetic stirrer and the permanganate/alumina mixture added in small portions over a 10-min period. The mixture was stirred at rt and the extent of reaction monitored by use of TLC (Whatman, 250 μm, PE SIL G/UV, diethyl ether/ethyl acetate = 5:1). After 4 h, when the reaction appeared to be complete, the mixture was filtered through a fritted glass funnel and the residue washed with portions of CH_2Cl_2 (2 × 50 mL). The solvent was then removed by flash evaporation to give a product (0.53 g, 5.0 mmol, 86%) which produced only one TLC spot and had spectral characteristics identical to those reported for benzaldehyde. Yields obtained from other alkenes are reported in Table I. As indicated in the above procedure, yields in reactions 4–7 are based on a theoretical yield of two moles of aldehyde for each mole of alkene.

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