Br^-, 85336-60-3; $Ph_2CHCHTNMe_3^+Br^-$, 85336-61-4; $PhCH_2CHTNMe_3^+Br^-$, 85336-62-5; (p-$ClC_6H_4)_2CHCH_2NMe_3^+Br^-$, 85336-63-6; $Ph_2CHCH_2NMe_3^+Br^-$, 85336-58-9; (p-$CH_3C_6H_4)_2CHCH_2NMe_3^+Br^-$, 85336-64-7; ($p$-$CH_3OC_6H_4)_2CHCH_2NMe_3^+Br^-$, 85336-65-8; ($p$-$ClC_6H_4)_2C{=}CH_2$, 2642-81-1; $(C_6H_5)_2C{=}CH_2$, 530-48-3; (p-$CH_3C_6H_4)_2C{=}CH_2$, 2919-20-2; (p-$CH_3OC_6H_4)C{=}CH_2$, 4356-69-8; $CH_3C(C_6H_5){=}CH_2$, 98-83-9; $(CH_3)_2CHC(C_6H_5){=}CH_2$, 17498-71-4; T, 10028-17-8; ^{14}C, 14762-75-5; *t*-BuLi, 594-19-4; $HNMe_2$, 124-40-3; D, 7782-39-0; (*Z*)-3-methyl-2-phenyl-1-bromo-1-butene, 85336-66-9; 3-methyl-2-phenyl-1-butene, 17498-71-4; (*E*)-3-methyl-2-phenyl-1-bromo-1-butene, 85336-67-0; (*Z*)-3-methyl-2-phenyl-1-butene-*1-d*, 85336-68-1; (*RR*,*SS*)-3-methyl-2-phenyl-1-butanol-*1-d*, 85336-69-2; *N*,*N*-dimethyl-3-methyl-2-phenyl-1-butylamine-*1-d*, 85336-70-5; (*E*)-α-methyl-β-bromostyrene, 16917-35-4; (*E*)-α-methylstyrene-β-*d*, 69912-51-2; (*E*)-2-methyl-1-bromo-1-hexene, 85336-71-6; (*Z*)-2-methyl-1-bromo-1-hexene, 85336-72-7; 2-methyl-1-hexene, 6094-02-6; (*E*)-2-methyl-1-hexene-*1-d*, 85336-73-8; (*Z*)-2-methyl-1-hexene-*1-d*, 85336-74-9; (*E*)-1-phenyl-1-(*p*-methoxyphenyl)-2-bromoethylene, 5783-23-3; 1-phenyl-1-(*p*-methoxyphenyl)ethylene, 4333-75-9; (*Z*)-1-phenyl-1-(*p*-methoxyphenyl)-2-bromoethylene, 5556-73-0; (*E*)-1-phenyl-1-(*p*-methoxyphenyl)ethylene-*2-d*, 85336-75-0; 1-hexyne-*1-d*, 7299-48-1; (*Z*)-1-hexene-*1-d*, 18963-99-0; (*E*)-1-hexene-*1-d*, 18963-98-9; 1-hexyne, 693-02-7; (*RS*,*SR*)-1-hexanol-*1,2-*d_2, 85336-76-1; (*RR*,*SS*)-1-hexanol-*1,2-*d_2, 85336-77-2; phenylacetonitrile-*1-*^{14}C, 4701-32-0; benzyl bromide, 100-39-0; sodium cyanide-^{14}C, 3396-82-5; 2-phenylethylamine-*1-*^{14}C, 85336-78-3; diphenylacetonitrile-*1-*^{14}C, 85336-79-4; 2,2-diphenylethylamine-*1-*^{14}C, 85336-80-7; 2-phenylethanol-*1-t*, 55110-72-0; 2-phenylacetyl chloride, 103-80-0; 2,2-diphenylethanol-*1-t*, 85336-81-8; diphenylacetyl chloride, 1871-76-7; 2,2-bis(*p*-chlorophenyl)ethylamine, 85336-82-9; bis(*p*-chlorophenyl)acetic acid, 83-05-6; bis(*p*-chlorophenyl)acetyl chloride, 68668-89-3; bis(*p*-chlorophenyl)acetamide, 52234-91-0; 2,2-bis(*p*-methoxyphenyl)ethylamine, 85336-83-0; *p*-anisaldehyde, 123-11-5; diethyl malonate, 105-53-3; diethyl *p*-methoxybenzalmalonate, 6768-23-6; *p*-anisyl bromide, 104-92-7; 3,3-bis(*p*-methoxyphenyl)propanoic acid, 35582-69-5; 2,2-bis(*p*-methoxyphenyl)-1-isocyanatoethane, 85336-84-1; *p*-tolualdehyde, 104-87-0.

Heterogeneous Permanganate Oxidations. 3. Mechanism of the Oxidation of Alcohols by Hydrated Copper Permanganate

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Contribution from the Department of Chemistry, The University of Regina, Regina, Saskatchewan, Canada S4S 0A2. *Received May 7, 1982*

Abstract: Secondary alcohols dissolved in methylene chloride are readily oxidized to the corresponding ketones when treated with hydrated permanganate salts under heterogeneous conditions. However, the addition of equimolar amounts of an alkene almost completely inhibits the reaction, apparently by formation of π complexes on the surface of the oxidant. When mixtures of saturated secondary and β,γ-unsaturated alcohols are treated with hydrated copper permanganate, the unsaturated alcohols are preferentially oxidized, although the converse is true when each alcohol is oxidized separately. These observations suggest that unsaturated compounds must form organometallic complexes on the reactive sites of the reagent and that oxidation of unsaturated alcohols may be initiated by complexation of the double bond followed by rearrangement within the coordination shell of manganese to give an oxygen complex that can be converted to the corresponding unsaturated ketone. The fact that γ,δ-unsaturated alcohols are not oxidized under these conditions indicates that, if the hydroxyl is not close to the point at which the π bond forms, it does not interact with the oxidant, possibly because it cannot come into the coordination shell of the manganese(VII) ion.

Introduction

The use of heterogenous reagents often increases the ease of execution and the selectivity of specific synthetic procedures.[1,2] This is particularly true for oxidation reactions where the use of solid oxidants gives products that are not contaminated with reduced oxidant and which are therefore more easily isolated and purified. For example, the use of solid permanganate salts under a solvent such as methylene chloride gives a product that is not contaminated with manganese dioxide as frequently occurs when the reaction is carried out in aqueous solutions[3,4] or in organic solvents with the aid of phase-transfer agents.[5-8]

Although chromium(VI),[9-12] iron(III),[13] periodate,[14] and hypochlorite[15] have also been used as solid oxidants, the largest number of synthetic applications have come from the use of permanganate in contact with molecular sieves,[16] silica,[16,17] alumina,[18] or hydrated metal cations such as sodium monohydrate[19] or copper(II) pentahydrate.[20-22] The hydrated cation can be introduced either by use of the appropriate permanganate salt (e.g.,

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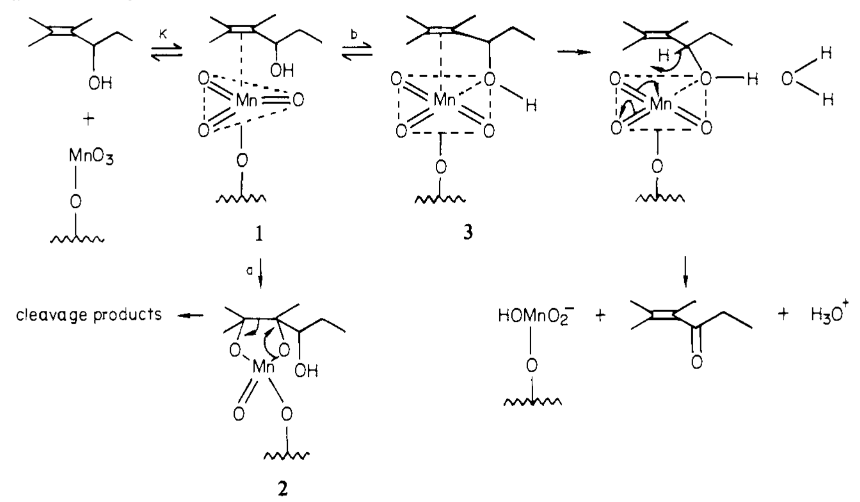
0002-7863/83/1505-3188$01.50/0

Scheme I. Possible Mechanism for the Oxidation of Unsaturated Alcohols



$NaMnO_4\cdot H_2O$[19] or $Cu(MnO_4)_2\cdot 6H_2O$[20]) or by addition of an inert salt such as $CuSO_4\cdot 5H_2O$ along with potassium permanganate.[21,22]

When used in one of these ways it is possible to rapidly convert secondary alcohols into ketones in high yields under very mild conditions.[16-22] Surprisingly, although permanganate reacts almost instantaneously with carbon–carbon double bonds in solution,[23-27] olefins are inert when treated with solid permanganates.[19,21] The procedure has consequently found application in the oxidation of unsaturated alcohols to the corresponding conjugated unsaturated ketones.[20,22] Many other organic compounds such as arenes, alkynes, amides, and oxiranes which are oxidized by permanganate in solution show little or no reactivity toward solid permanganate salts;[19] only alcohols,[4] sulfides,[3] and aldehydes[28,29] are easily oxidized both homogeneously and heterogeneously.[19,20] Hence it appears from the available data that solid permanganate exhibits a certain selectivity that is lacking when it is used homogeneously. In solution it tends to oxidize many different functional groups more or less indiscriminately;[3,4] however, when used heterogeneously it is known to be much more selective.[16-22] Interestingly, when reaction does take place it usually proceeds rapidly and gives products in nearly quantitative yields.[22]

In this paper we wish to describe the results obtained from a series of experiments that were designed to probe the mechanisms of these reactions.

Results and Discussion

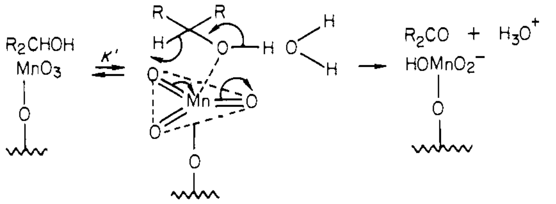
In an attempt to understand the reactions in which alcohols are oxidized by hydrated salts of permanganate under heterogeneous conditions, we have completed four series of interrelated experiments.. The experiments attempted and results obtained are as follows.

Under appropriate conditions cyclohexanol is oxidized to cyclohexanone using solid hydrated copper permanganate under methylene chloride. However, *the addition of an equimolar quantity of cyclohexene to the solution, while holding all other conditions constant, inhibits the reaction.*

$$\text{cyclohexanol} \xrightarrow[\text{methylene chloride, 25 °C, 25 min}]{Cu(MnO_4)_2\cdot 8H_2O} \text{cyclohexanone (70\%)}$$

$$\text{cyclohexanol} \xrightarrow[\text{methylene chloride, 25 °C, cyclohexene, 25 min}]{Cu(MnO_4)_2.8H_2O} \text{cyclohexanone (4\%)}$$

Scheme II. Possible Mechanism for the Oxidation of Saturated Alcohols



A similar inhibition was observed when an attempt was made to oxidize 2-decanol in the presence of 5-decene using copper sulfate pentahydrate and potassium permanganate[21,22] as the oxidant. No 2-decanone was obtained under conditions where quantitative yields were observed in the absence of alkene.[22]

These experiments seem to indicate that there are certain reactive sites on the surface of the oxidant which can bind rather firmly to carbon–carbon double bonds and thus prevent oxidation of the alcohols. Interestingly, although the alkenes must occupy the reactive sites, neither cyclohexene nor 5-decene was oxidized to any detectable extent. However, the highly substituted alkene 2,3-dimethyl-2-butene was observed to be slowly converted to acetone under these conditions.

Saturated secondary alcohols are, in general, more readily oxidized than substituted allylic alcohols;[20,21] *however, when equimolar amounts of cyclohexanol and 1-phenyl-1-buten-3-ol in a solution of methylene chloride were treated with hydrated copper permanganate, the allylic alcohol was preferentially oxidized.* Under identical conditions a quantitative yield of cyclohexanone was obtained when no unsaturated compounds were present.

$$\text{1-phenyl-1-buten-3-ol} + \text{cyclohexanol} \xrightarrow[\text{methylene chloride, 40 °C}]{Cu(MnO_4)_2\cdot 8H_2O} \text{1-phenyl-1-buten-3-one (27\%)} + \text{cleavage products (9\%)} + \text{cyclohexanone (25\%)}$$

When these results are taken together with the previous observations which indicated that carbon–carbon double bonds bind to the reactive sites on copper permanganate, it seems likely that the unsaturated alcohol is first attached to the oxidant by a π bond and subsequently oxidized.

Nonallylic unsaturated alcohols are not oxidized under conditions that lead to good yields of ketones from allylic alcohols.[20]

$$\text{1-hepten-4-ol} \xrightarrow[\text{methylene chloride, 40 °C}]{Cu(MnO_4)_2.8H_2O} \text{no reaction}$$

This result indicates that, if the hydroxyl group is not close to the point at which the π bond forms, it does not interact with the oxidant, possibly because it cannot come into the coordination shell of the manganese(VII). The previously reported failure to

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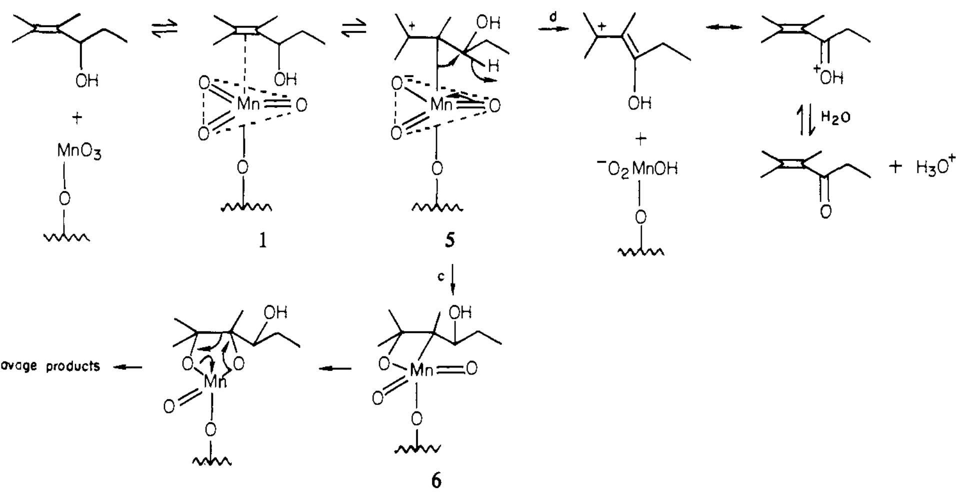
Scheme III. An Alternative Mechanism for the Oxidation of Unsaturated Alcohols



oxidize cholesterol to Δ^5-chlolestenone[20] using a heterogeneous permanganate oxidant must also be attributable to the same phenomenon.

All of these results are consistent with a mechanism for the oxidation of allylic alcohols in which the reaction is initiated by formation of a π complex to give an intermediate such as **I** in Scheme I.

Formation of similar organometallic complexes is well known for low-valent transition metals,[30] and they have also been proposed as intermediates in the oxidation of alkenes by selenium dioxide, osmium tetroxide, potassium permanganate, and chromyl chloride.[31] The involvement of similar intermediates could also account for the formation of substituted tetrahydrofurans from the oxidation of 1,5-dienes by permanganate[32-35] or ruthenium tetroxide,[36] as well as the oxidation of 5,6-dihydroxyalkenes by chromium(VI).[37]

If the oxidation of 1-phenyl-1-buten-3-ol is carried out at low temperatures, cleavage of the double bond is the predominant reaction; however, as the temperature is increased, the relative amount of noncleavage product increases dramatically and eventually predominates at reflux temperatures. The yields of products obtained at three temperatures have been summarized in Table I. Very similar results were also obtained when 1-phenyl-1-hexen-3-ol was used as the substrate; however, because of the heterogeneous nature of the reaction, reproducibility with different batches of oxidant was not high. Nevertheless, the same general trends were observed in every case.

A possible reaction mechanism consistent with these results has been outlined in Scheme I. The proposed route to cleavage products (path a) is similar to the mechanism that has been established for the corresponding homogeneous reactions.[23-27] The formation of unsaturated ketones (path b) may involve expansion of the coordination shell of manganese to give a new complex, **3**, in which both the π bond and the oxygen are ligands. Subsequent dissociation of the π bond would then give an alcohol complex which could be oxidized in the manner indicated.

In this scheme we have involved a molecule of water as a proton acceptor during the oxidative step. Although it is known that the presence of water is necessary,[21] it should be noted that there is at the present time no experimental evidence defining its exact role. Nevertheless, water must be involved in an essential step; under scrupulously dry conditions absolutely no alcohol oxidation occurs.[38]

Table I. Effect of Temperature on the Products Obtained from the Oxidation of 1-Phenyl-1-buten-3-ol by Hydrated Copper Permanganate[a]

		% yield			
temp, °C	recovered starting material, %	1-phenyl-1-buten-3-one	benzaldehyde	benzoic acid	total cleavage, %
6	84		14	3	17
26	61	26	7	5	12
34–38	41	49	6	5	11
reflux	33	59	8		8[b]

[a] The substrate (2.5 mmol in 15 mL of methylene chloride) was oxidized by 2.0 g of hydrated copper permanganate for 24 h. Yields were calculated from gas chromatograms after application of predetermined response factors. [b] At least part of the cleavage product obtained at reflux temperature was probably due to oxidation of the ketone, 1-phenyl-1-buten-3-one, which is known to be oxidatively cleaved under these conditions.[22]

Although these ideas are highly speculative, it can be mentioned that the literature contains descriptions of permanganate oxidations that must certainly involve reorganization within the coordination shell of manganese.[35] Furthermore, if this internal rearrangement has a rather high activation energy (despite the fact that it leads eventually to a more stable product), the temperature effects noted in Table I could be accounted for as being an example of kinetic and thermodynamic control in competing reaction pathways.[39,40] If it is assumed that the permangante ion remains part of the solid system, it is possible that an expansion of the coordination shell could cause a decrease in lattice energy and thus make formation of **3** a reaction with a high activation energy.

The oxidation of saturated alcohols must proceed either by an alternative mechanism such as the one suggested for the homogeneous reaction[4] or by way of complex formation as depicted in Scheme II. If the latter was to occur, the equilibrium constant for π-bond complexing (K, Scheme I) must be larger than the corresponding constant for oxygen complexation (K', Scheme II) in order for the results described above to pertain.

An alternative explanation for the temperature effects observed during the oxidation of 1-phenyl-1-buten-3-ol and 1-phenyl-1-hexen-3-ol is suggested from a theoretical study recently reported

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by Eisenstein and Hoffmann.[41] They concluded that formation of organometallic complexes between olefins and metals activated the carbon–carbon double bonds toward nucleophilic attack only if the metal moved to one end of the π system and formed a σ-like bond with one of the carbons. Such a process would leave the other carbon with a partial positive charge as depicted in Scheme III. In the case of 1-phenyl-1-buten-3-ol this positive charge would most probably develop in the benzylic position as in **5**, and the σ complex could then react in one of the two possible ways (paths c and d, Scheme III). Pathway d would have a higher activation energy because of the need to cleave a carbon–hydrogen bond in the rate-determining step. However, the product, a styryl ketone, would be expected to be quite stable. Hence this would be the product formed when the reaction was under thermodynamic control.[39,40] On the other hand, pathway c, although proceeding through a transition state of lower energy, would give rise to less stable cleavage products. The inclusion of the oxametallocyclobutene intermediate, **6**, in this pathway is based on initial proposals of Sharpless[31] and recent theoretical studies of Rappé and Goddard.[42]

Although it is impossible, on the basis of the data presently available, to distinguish between the two mechanisms outlined in Schemes I and III, we believe that they represent a starting point for a more detailed understanding of these important reactions. Regardless of the mechanistic details, however, the observed results are of potential importance to synthetic procedures. From a consideration of the temperature effects, it is clear that, as far as organic synthesis is concerned, the reaction should be carried out at higher temperatures if a good yield of α,β-unsaturated ketones is to be realized.[20,22]

Experimental Section

Materials. The alcohols and alkenes were all obtained commercially. Hydrated copper permanganate was obtained from the Carus Chemical Co. Although different batches of oxidant exhibited slightly different reactivities, as might be expected for a heterogeneous reaction, the results were usually reproducible within ±10%. Reagent grade methylene chloride (Fisher) was used as the solvent. Yields were calcd. from gas chromatograms after application of predetermined response factors. Products were identified spectrophotometrically.

Oxidation of Cyclohexanol. Hydrated copper permanganate (1.5 g, 3.4 mmol) and 5 mL of methylene chloride were stirred together for 5 min in a 25-mL round-bottomed flask. When cyclohexanol (0.25 g, 2.5 mmol) dissolved in 5 mL of methylene chloride was added, the solution began to reflux very gently. After stirring for 25 min the heterogeneous mixture was filtered through Celite, and the inorganic residue washed with 2 × 25 mL portions of methylene chloride. The combined filtrates were dried and carefully evaporated to give a product which was found to consist of 70% cyclohexanone and 30% cyclohexanol.

When the experiment was repeated under identical conditions except for the addition of cyclohexene (0.20 g, 2.5 mmol) to the initial mixture, there was no evidence of reaction when the cyclohexanol was added and the yield of cyclohexanone was reduced to 4%. The cyclohexene was also recovered quantitatively, and all but a small portion of the permanganate was found to be unreduced. A solution of cyclohexene in methylene chloride could be refluxed over the oxidant for several hours without any detectable reduction of the permanganate.

Oxidation of a Mixture of Cyclohexanol and 1-Phenyl-1-buten-3-ol. Cyclohexanol (0.25 g, 2.5 mmol) and 1-phenyl-1-buten-3-ol (0.37 g, 2.5 mmol) were dissolved in 20 mL of methylene chloride and placed in a 50-mL round-bottomed flask. Hydrated copper permanganate (1.5 g, 3.4 mmol) was added and the reaction mixture was quickly brought to reflux and held there (with stirring) for 25 min. The heat source was removed and, after a 5-min cool-down period, an additional 20 mL of methylene chloride was added. The heterogeneous mixture was filtered through Celite and, after workup as described above, 0.6 g of product was obtained. Gas chromatographic analysis indicated the following yields: 1-phenyl-1-buten-3-one, 27%; benzaldehyde, 8%; benzoic acid, 1%; 1-phenyl-1-buten-3-ol, 64%; cyclohexanone, 25%; cyclohexanol, 75%.

Oxidation of 1-Hepten-4-ol. Hydrated copper permanganate (2g, 4 mmol) was added to 1-hepten-4-ol (0.29 g, 2.5 mmol) dissolved in 15 mL of methylene chloride with stirring. The heterogeneous mixture was refluxed for 24 h and then filtered through Celite. The inorganic residue was washed thoroughly with ether, and the combined filtrates were dried and concentrated using a rotary evaporator to give 0.25 g (86%) of residue. This residue exhibited only one GLC peak and one TLC spot and gave NMR and IR spectra identical with those of the starting material. Under the same conditions, 1-phenyl-buten-3-ol was converted to the corresponding ketone in 85% yield.

Oxidation of 1-Phenyl-1-buten-3-ol. To 1-phenyl-1-buten-3-ol (0.37 g, 2.5 mmol), dissolved in 15 mL of methylene chloride, was added hydrated copper permanganate (2 g, 4 mmol) with stirring. The heterogeneous mixture was then stirred at the required temperature for 24 h and filtered through Celite. The inorganic residue was washed thoroughly with ether, and the combined filtrates were treated with dilute $HCl/NaHSO_3$, dried, and evaporated. Chromatographic analysis gave the yields reported in Table I.

Acknowledgment. The authors are grateful to the Natural Sciences and Engineering Research Council of Canada and the Carus Chemical Co. for financial assistance.

Registry No. $Cu(MnO_4)_2$, 82022-29-5; cyclohexanol, 108-93-0; 1-phenyl-1-buten-3-ol, 17488-65-2; 1-hepten-4-ol, 3521-91-3.

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