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Heterogeneous Permanganate Oxidations. 7. The Oxidation of Aliphatic Side Chains

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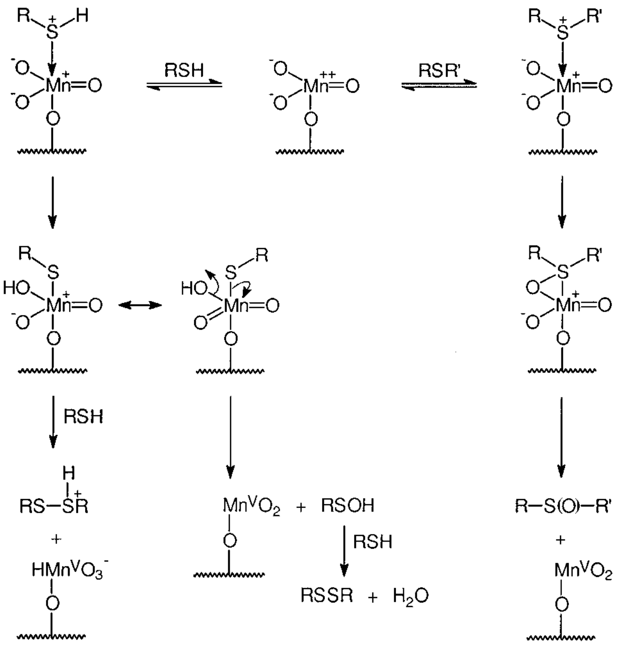
Alkylbenzene side chains are oxidized at the benzylic position when treated under heterogeneous conditions with permanganate adsorbed on a solid support. The products are alcohols if the benzylic carbon is tertiary, or ketones if it is secondary. Carbon−carbon bond cleavage, which usually occurs when these same compounds are oxidized by permanganate under homogeneous conditions, does not occur. A unique selectivity is observed for the oxidation of derivatives of indane, **1**, and tetralin, **2**, in which one of the methylenes is replaced by an oxygen. If the oxygen is in the α-position, no reaction occurs; if it is in the *β*-position, good yields of the corresponding lactone are obtained. A mechanism consistent with the observed selectivity has been proposed.

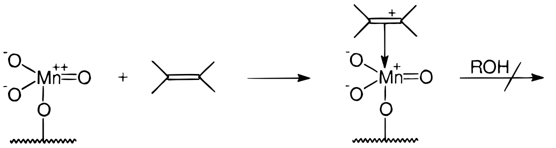
Introduction

Adsorption onto solid supports is known to cause a change in the chemical properties of many reagents.[1] One of the most striking examples of such a change in chemical reactivity that has been reported to date is with the well-known oxidant, potassium permanganate.[2] When used in solution, permanganate reacts rapidly with alkenes, converting them into diols, ketols, or cleavage products.[3] Because the reaction with alkenes is so facile in homogeneous solutions, reduction of permanganate to manganese dioxide has been used as a test for unsaturation − the so-called Baeyer test.[4] However, when permanganate is adsorbed onto an inert solid support and used as a heterogeneous oxidant, some alkenes are resistant to oxidation and may actually inhibit the rate of oxidation of other reductants.[5]

Inhibition of the oxidation of alcohols[5] and partial inhibition of the oxidation of sulfides[6] and thiols[7] by cyclohexene has been ascribed to complexation of the active sites on the surface of the heterogeneous oxidant by the alkene, as in eq 1. Inhibition is believed to be less complete with thiols and sulfides because sulfur, a much better nucleophile than oxygen,[8] can compete for active sites on the surface of the oxidant. A possible mechanism for the oxidation of these compounds is outlined in Scheme 1. As indicated in this scheme the products from the oxidation of thiols are disulfides,[7] which could be formed either by nucleophilic attack on the complexed thiol or after it had been oxidized to a sulfenic acid, RSOH.[9] Experimental information currently available does not permit distinction between these two possibilities.

Scheme 1. Possible Mechanisms for the Oxidation of Thiols and Sulfides by Permanganate Adsorbed on a Solid Support




(1)

Theoretical studies have indicated that permanganate is most accurately described as a manganese dication surrounded by four equivalent oxygens bearing a total of three negative charges.[10] Because there is no reason

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⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1997.

[1] Smith, K., Ed. *Solid Supports and Catalysts in Organic Synthesis;* Ellis Horwood and PTR Prentice Hall: New York, 1992. Laszlo, P. In *Comprehensive Organic Synthesis;* Trost, B. M., Ed., Pergamon: New York, 1991; Vol. 7, p 839.

[2] Lee, D. G. in *Encyclopedia of Reagents for Organic Synthesis;* Paquette, L. A., Ed., Wiley: New York, 1995; pp 4274−4281.

[3] Stewart, R. In *Oxidation in Organic Chemistry, Part A;* Wiberg, K. B., Ed., Academic Press: New York, 1965; pp 1−68. Lee, D. G. In *Oxidation in Organic Chemistry, Part D;* Trahanovsky, W. S., Ed., Academic Press: New York, 1982; pp 147−206.

[4] Pavia, D. L.; Lampman, G. M.; Kriz, G. S. *Introduction to Organic Laboratory Techniques;* 2nd ed., Saunders: New York, 1982; p 408. Harwood, L. M.; Moody, C. J. *Experimental Organic Chemistry;* Blackwell: London, 1989; p 246.

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

[6] Noureldin, N. A.; McConnell, W. B.; Lee, D. G. *Can. J. Chem.* **1984**, *62*, 2113.

[7] Caldwell, M. Thesis, University of Regina, 1997.

[8] Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes;* 2nd ed., VCH: Weinheim, 1991; p 236.

[9] Goto, K.; Tokitoh, N.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1124−1126. Goto, K.; Holler, M.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 1460−1461. Ishii, A.; Komiya, K.; Nakayama, J. *J. Am. Chem. Soc.* **1996**, *118*, 12836−12837.

[10] Jitsuhiro, S.; Nakai, H.; Hada, M.; Nakatsuji, H. *J. Chem. Phys.* **1994**, *101*, 1029. Buijse, M. A.; Baerends, E. J. *J. Chem. Phys.* **1990**, *93*, 4129. Ziegler, T.; Rauk, A.; Baerends, E. J. *Chem. Phys.* **1976**, *16*, 209. De Michelis, G.; Di Sipio, L. *Gazz. Chim. Ital*, **1976**, *106*, 691.

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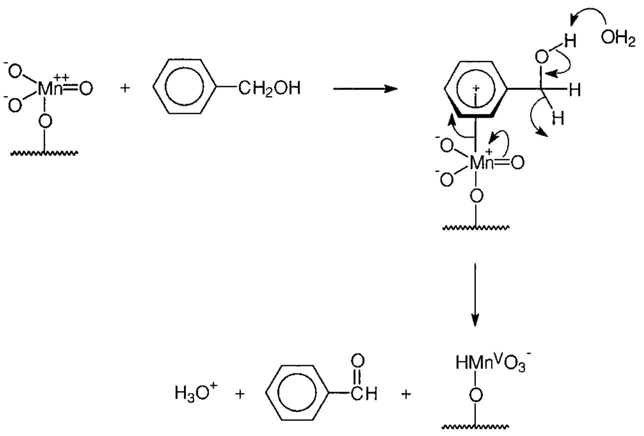
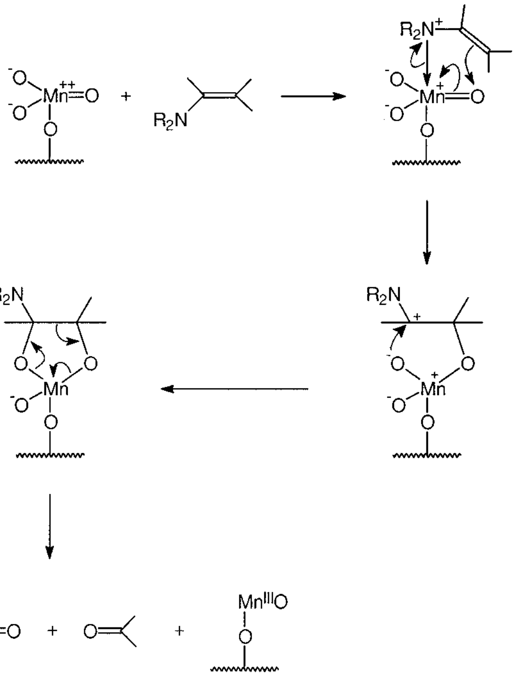
Scheme 2. Proposed Reaction Scheme for the Oxidation of Benzyl Alcohol



Scheme 3. A Possible Reaction Scheme for the Oxidative Cleavage of Enamines



to expect that adsorption on a solid support would cause a large change in the electronic structure of permanganate, it has been depicted in eq 1, and in the Schemes, as a dication surrounded by four oxygens, one of them forming an ionic bond with the solid support.

Under conditions where it has been found possible to oxidize certain alkenes by permanganate on a solid support, the products are usually epoxides,[11] diketones[12] or lactones.[13] However, it appears that cleavage of the double bond occurs only when the support is capable of entering into acid–base chemistry.[14]

Adsorption of permanganate onto solid supports such as copper(II) sulfate pentahydrate or hydrated alumina promotes oxidation of alcohols, particularly allyl and benzyl alcohols. As indicated in Scheme 2, formation of a η^6 complex with benzyl alcohol places the α-hydrogen in a position close to the manganese oxo, thus facilitating hydride transfer. Similarly, α,β-unsaturated alcohols are readily oxidized when the double bond forms a η^2 complex with the manganese.[5] However, other unsaturated alcohols in which there are one or more methylenes between the double bond and the carbon bearing the hydroxyl are not oxidized. For such compounds, the α-hydrogen is not appropriately positioned for hydride transfer to an oxo.[15]

Several studies have confirmed that it is necessary to use hydrated solid supports when alcohols are oxidized.[16] Conversely, the oxidative cleavage of enamines occurs most readily under anhydrous conditions, thus providing for the possibility of selectivity when oxidizing compounds containing both functionalities.[17] It has been suggested that the role of water during the oxidation of alcohols is to accept protons as electron transfer occurs coincidentally[5] (see Scheme 2). Oxidative cleavage of enamines, on the other hand, can occur without a proton accepting molecule, as indicated in Scheme 3, where the reaction is assumed to be initiated by bond formation between nitrogen and manganese followed by an oxidative attack on the contiguous double bond.

In this paper we wish to describe the use of permanganate adsorbed on either copper sulfate pentahydrate or alumina for the oxidation of aliphatic side chains. In solution, such oxidations result in degradation of the side chain, the usual products being benzoic acid derivatives.[18] However, under the heterogeneous conditions used for these reactions, permanganate is a milder, more selective reagent that oxidizes side chains at the benzylic position without carbon–carbon bond cleavage. Although reaction times are rather long, ketones and alcohols are obtained in good yields when the benzylic carbons are secondary or tertiary, respectively. The synthetic value of the process is explored with a wide variety of compounds and some comments concerning a possible reaction mechanism are included. A preliminary report on some of the products that may be obtained by use of this reaction has previously been published.[19]

Discussion and Results

Synthetic Usefulness. The products obtained from the oxidation of a large number of side chains using two

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[11] Hanson, J. R.; Nagaratnam, S.; Stevens, J. *J. Chem. Res. (S)* **1996**, 102. Hanson, J. R.; Hitchcock, P. B.; Liman, M. D.; Nagaratnam, S.; Manickavasager, R. *J. Chem. Res. (S)*, **1995**, 220. Parish, E. J.; Li, H.; Li, S. *Synth. Commun* **1995**, *25*, 927. Ssyamala, M. S.; Das, J.; Baskaran, S.; Chandrasekaran, S. *J. Org. Chem.* **1992**, *57*, 1928.

[12] Baskaran, S.; Das, J.; Chandrasekaran, S. *J. Org. Chem.* **1989**, *54*, 5182.

[13] Das, J.; Chandrasekaran, S. *Tetrahedron* **1994**, *50*, 11709. Baskaran, S.; Islam, I.; Vankar, P. S.; Chandrasekaran, S. *J. Chem. Soc., Chem. Commun.* **1992**, 626. Baskaran, S.; Islam, I.; Vankar, P. S.; Chandrasekaran, S. *J. Chem. Soc., Chem. Commun.* **1990**, 1670.

[14] Lee, D. G.; Chen, T.; Wang, Z. *J. Org. Chem.* **1993**, *58*, 2918. Ferreira, J. T. B.; Cruz, W. O.; Vieira, P. C.; Yonashiro, M. *J. Org. Chem.* **1987**, *52*, 3698.

[15] For example, cholesterol is resistant to oxidation under conditions where allylic alcohols are converted into the corresponding α,β-unsaturated ketones in excellent yields. Noureldin, N. A.; Lee, D. G. *J. Org. Chem.* **1982**, *47*, 2790. Noureldin, N. A.; Lee, D. G. *Tetrahedron Lett.* **1981**, *22*, 4889.

[16] Quici, S.; Regen, S. L. *J. Org. Chem.* **1979**, *44*, 3436. Lee, C.; Menger, F. M. *J. Org. Chem.* **1979**, *44*, 3446. Regen, S. L.; Koteel, C. *J. Am. Chem. Soc.* **1977**, *99*, 3837. Jefford, C. W.; Wang, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 634. Jefford, C. W.; Li, Y.; Wang, Y. *Organic Syntheses*; Overman, L. E., Ed., 1992; Vol. 71, p 207.

[17] Harris, C. E.; Chrisman, W.; Bickford, S. A.; Lee, L. Y.; Torreblanca, A. E.; Singaram, B. *Tetrahedron Lett.* **1997**, *38*, 981. Harris, C. E.; Chrisman, W.; McBride, C.; Taylor, B.; Singaram, B. Abstracts of Papers, 213th ACS National Meeting, 1997; American Chemical Society: Washington, DC; ORGN286.

[18] March, J. *Advanced Organic Chemistry;* 4th ed.; Wiley: New York, 1992; p 1183. Arndt, D. *Manganese Compounds as Oxidizing Agents in Organic Chemistry;* Open Court: La Salle, IL, 1981. Vogel, A. I. *A Textbook of Practical Organic Chemistry,* 3rd ed.; Longmans: New York, 1956; pp 520, 529, 672.

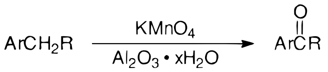
[19] Zhao, D.; Lee, D. G. *Synthesis* **1994**, 915.

Table 1. Products from the Oxidation of Side Chains

		solid supports[a]			
		copper sulfate pentahydrate		moist alumina	
reactant	product[b]	reaction time (h)	yield (%)	reaction time (h)	yield (%)
toluene	benzaldehyde			328	30
p-nitrotoluene				no reaction	
ethylbenzene	acetophenone	70	95	141	58
n-propylbenzene	ethyl phenyl ketone	70	90	169	69
n-butylbenzene	phenyl propyl ketone	72	88		
indane	1-indanone	72	78	256	70
tetralin	1-tetralone	72	95[c]		
	1,4-naphthaquinone		5[c]		
4-ethylacetophenone	1,4-diacetylbenzene	48	92		
cumene	2-phenyl−2-propanol			136	78
sec-butylbenzene	2-phenyl-2-butanol			234	79
diphenylmethane	benzophenone	72	95	282	91
fluorene	9-fluorenone	48	98	118	100
xanthene	xanthone	72	97	67	92
anthrone	anthraquinone			75	100
5-methoxyindane	5-methoxy-1-indanone	70	98	85	54
	6-methoxy-1-indanone				16
6-methoxytetralin	6-methoxy-1-tetralone	72	85[c]		
	7-methoxy-1-tetralone		5[c]		
5-nitroindane		no reaction			
phthalan	phthalide	48	95	66	91
2,3-dihydrobenzofuran		no reaction		no reaction	
isochroman	2-chromanone	72	96		
chroman		no reaction			
dihydrocoumarin		no reaction		no reaction	

[a] Isolated yields, expressed as a percentage of the hydrocarbon initially added to the oxidant unless otherwise indicated. [b] Products were identified by comparison of physical and spectroscopic properties with authentic compounds. [c] Yield determined by GLC.

different solid supports are compared in Table 1. Although the same products are produced in reasonably good yields with both solid support systems investigated, it is apparent that the reaction times are shorter when copper sulfate pentahydrate is used as the solid support. In all of these examples the products are ketones when the benzylic carbons are secondary (eq 2) and alcohols when they are tertiary (eq 3); carbon−carbon bond cleavage, as often occurs in the corresponding homogeneous permanganate oxidations,[18] is not observed.

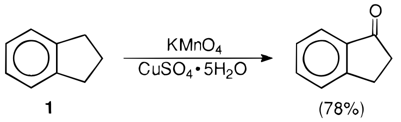


$$ArCH_2R \xrightarrow[Al_2O_3 \cdot xH_2O]{KMnO_4} Ar\overset{O}{\overset{\|}{C}}R \qquad (2)$$

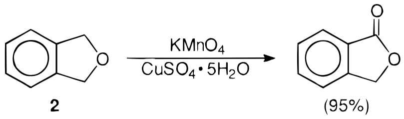
$$ArCHR_2 \xrightarrow[Al_2O_3 \cdot xH_2O]{KMnO_4} ArC(OH)R_2 \qquad (3)$$

The potential usefulness of these reactions in organic synthesis is indicated by the observation that they can be carried out under very mild conditions in neutral solutions. The yields are good, very few side products are produced, and the isolation of the products in reasonably pure form is easily achieved.

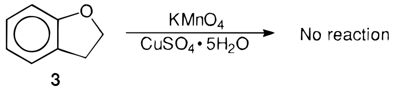
In addition, a unique selectivity is observed for the oxidation of derivatives of indane, **1**, and tetralin, **4**,[20] in which one of the methylenes is replaced by oxygen. As illustrated in eq 4−9, the *β*-oxa isomers, phthalan (**2**) and isochroman (**5**), are easily oxidized to the corresponding lactones in good yields, while the α-oxa isomers, 2,3-dihydrobenzofuran (**3**) and chroman (**6**), are resistant to oxidation. The observed selectivity does not appear to be due to electronic effects associated with the presence of an oxygen *ortho* to the benzylic position in **3** and **6** because xanthene and 5-methoxyindane, which have oxygens *ortho* and *para* to the benzylic position, are easily oxidized. In fact, a *p*-methoxy substituent appears to promote oxidation.



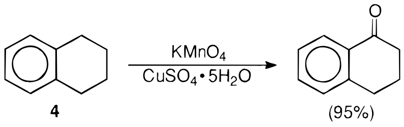
(4)



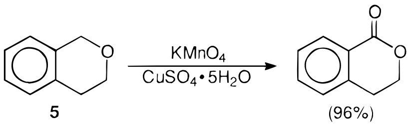
(5)



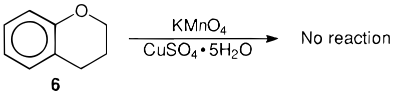
(6)



(7)



(8)



(9)

The rates of homogeneous hydrocarbon oxidations are usually controlled by the ease of C−H or C−C bond cleavage; however, heterogeneous oxidations can also be dependent on the rate of adsorption of the reactants or the rate of desorption of the products and the need for proper orientation of the adsorbed reactant.[21] Since there is no reason to expect that the cleavage of benzylic C−H

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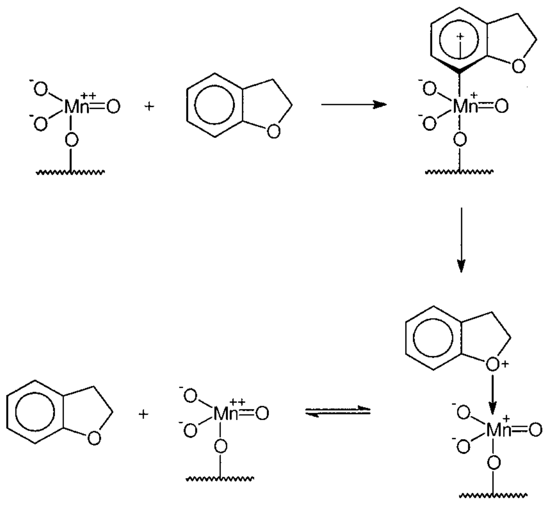
(20) Walter, W. *Handbood of Organic Chemistry;* Prentice Hall: New York, 1996; pp 624−626.

Scheme 4. Possible Reaction Scheme for the Interaction of 2,3-Dihydrobenzofuran with Permanganate Adsorbed on a Solid Support



bonds in 2,3-dihydrobenzofuran, **3**, and chroman, **6**, should be unusually difficult, it seems likely that the selectivity observed may be associated with the way in which these compounds are adsorbed onto the heterogeneous reagent.

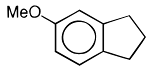
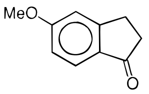
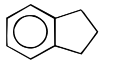
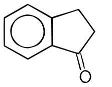
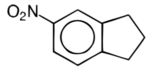
If these reactions are initiated by formation of a η^6 complex between the electron deficient manganese and the electron rich aromatic ring,[22] the presence of an oxygen adjacent to the ring may permit migration of the manganese from the aromatic ring to the oxygen, with the result that no fruitful reaction occurs as indicated in Scheme 4.

In addition, it is apparent that the reaction is very sensitive to the presence of electron-withdrawing substituents. *p*-Nitrotoluene and 5-nitroindane are not oxidized under conditions where the corresponding unsubstituted compounds are readily oxidized. The products obtained from the oxidation of 5-methoxyindane and 6-methoxytetralin indicate that the methoxy group is strongly *para*-directing. Very little of the product resulting from oxidation *meta* to the substituent is observed, especially when copper sulfate pentahydrate is used as the solid support. These observed selectivities may find empirical usefulness for specific syntheses.[23]

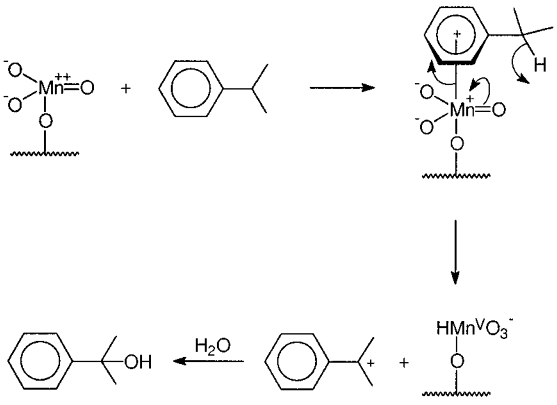
A Possible Reaction Mechanism. The main thrust of this work was directed toward the discovery of new synthetic procedures; however, the results also permit some tentative mechanistic conclusions. From the data on the oxidation of substituted indanes, summarized in Table 2, it is apparent that the rate of reaction is greatly reduced by *p*-nitro, an electron-withdrawing group, and that methoxy increases the rate and is strongly *para*-directing. This suggests that the benzylic position is electron deficient in the transition state,[24] i.e., the reaction likely takes place by hydride transfer.

In analogy with the mechanism that has been proposed for the oxidation of benzyl alcohol by permanganate under heterogeneous conditions (Scheme 2), it seems probable that the initial reaction would be between the electron-rich aromatic ring and the electron deficient manganese; i.e., electron donation from the aromatic HOMO's to the manganese LUMO. Hydride transfer could then occur, as illustrated in Scheme 5, giving a carbocation which would react with water to give an alcohol.

Table 2. Oxidation of Substituted Indanes

Indane	Time (h)	Product	Yield (%)
	70		98
	72		78
	120	No reaction	0

Scheme 5. Proposed Mechanism for the Oxidation of Cumene



The oxidation of arenes such as cumene and *s*-butylbenzene, which have only one C–H bond in the benzylic position, results in formation of tertiary alcohols that are resistant to further oxidation. However, when the alcohol is secondary, further rapid oxidation to yield the corresponding ketone would occur. Previous work has shown that such reactions are extremely facile.[5,15]

This mechanism is also consistent with an experiment which revealed that the oxidation of ethylbenzene by this reagent is prevented if cyclohexene is present in the solution. The adsorption of alkenes on transition metal surfaces is known to be largely irreversible, while benzene is a more labile adsorbate.[25] It therefore appears as if ethylbenzene cannot compete with cyclohexene for formation of an arene–manganese complex such as the one depicted in Scheme 5. It is somewhat of a mystery why cyclohexene is not itself oxidized under these conditions. Perhaps, however, the orientation of the adsorbed π-bond is such that the allylic C–H bonds are not properly directed to permit hydride transfer.

The formal oxidation state of the reduced oxidant from the reactions depicted in Schemes 1, 2, and 5, all of which

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(21) Atkins, P. *Physical Chemistry;* 5th ed.; Freeman: New York, 1994; pp 993–997.

(22) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis;* Pergamon: New York, 1982; p 68.

(23) Bartmann, W.; Trost, B. M. *Selectivity – a Goal for Synthetic Efficiency;* Verlag: Weinheim, 1984.

(24) Scudder, P. H. *Electron Flow in Organic Chemistry;* Wiley: New York, 1992; p 65.

(25) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis;* Wiley: New York, 1994; pp 62–67.

involve two-electron transfers, is +5. The cleavage reaction depicted in Scheme 3, however, involves an overall transfer of four electrons, leaving manganese with a formal oxidation state of +3. Although it is not possible to verify these oxidation states experimentally, it is obvious that a definite change in the appearance of the oxidant occurs in every case. The heterogeneous oxidant, a bright purple color initially, is a dull brown at the end of the reaction, suggesting that it may be a form of manganese dioxide, which is known to be the usual product from homogeneous permanganate oxidations under neutral conditions.[26] Since manganate(V) is known to be a very vigorous oxidant under neutral conditions,[27] it is quite likely that the products depicted in Schemes 1, 2, and 5 would be rapidly reduced by the solvent to a +4 oxidation state. Predicting the fate of the manganese(III) product produced from the cleavage reaction depicted in Scheme 3 is more difficult. It could either be reduced by the solvent to give manganese(II) or oxidized by excess oxidant to manganese dioxide.[28]

Conclusions

1. Aliphatic side chains are selectively oxidized at the benzylic position by permanganate adsorbed on solid supports (copper sulfate pentahydrate or moist alumina). The products are alcohols if the benzylic carbon is tertiary, or ketones if it is secondary; no carbon−carbon bond cleavage is observed. The reactions are carried out under mild conditions using inexpensive reagents and equipment. Although the reaction times are long, the yields are good and no side products are obtained. Furthermore, the products can be easily isolated in relatively pure form.

2. A unique selectivity is observed for the oxidation of cyclic side chains containing an oxygen as part of the ring. If the oxygen atom is in the 1-position, no oxidation occurs; if it is in the 2-position, the reaction proceeds normally to give the corresponding lactone.

3. The reaction is very sensitive to the presence of substituents on the aromatic ring. *p*-Nitro groups completely inhibit the reaction while methoxy groups promote the reaction and are strongly *para*-directing.

4. The reaction is inhibited by the presence of cyclohexene which appears to bind irreversibly to the active sites on the surface of the heterogeneous oxidant.

5. The proposed mechanism involves an initial interaction between the aromatic ring and manganese(VII) giving an η^6 complex which reacts by hydride transfer to produce a benzylic carbocation and reduced manganese. The benzylic carbocation then reacts with water to give the corresponding alcohol. If the alcohol is tertiary, it is resistant to further oxidation; if it is secondary, oxidation to a carbonyl occurs readily.

Experimental Section

Preparation of Oxidants. $KMnO_4/Al_2O_3 \cdot xH_2O$: Finely ground potassium permanganate (2.2 g, 14.0 mmol), dissolved in 5 mL of water, was added to alumina (Acid, Brockman Activity 1, 8.8 g) with stirring to give a permanganate/alumina mixture. This mixture was dried in an uncovered Petri dish overnight at room temperature before use.

$KMnO_4/CuSO_4 \cdot 5H_2O$: Equal weights of potassium permanganate and copper sulfate pentahydrate were ground together in a mortar. The resulting fine, highly colored product was then used as a heterogeneous oxidant in methylene chloride solutions.

Typical Experimental Procedures. The Oxidation of Fluorene with $KMnO_4/Al_2O_3 \cdot xH_2O$: Fluorene (0.54 g, 3.2 mmol), dissolved in 1,2-dichloroethane (120 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 room temperature (about 20 °C) and the extent of reaction monitored by use of TLC. After 118 h, analysis of the liquid phase by TLC indicated complete conversion to 9-fluorenone. The product was filtered through a fritted glass funnel and the residue washed with portions of CH_2Cl_2 (3 × 50 mL). The solvent was then removed by flash evaporation to give a product (0.59 g, 3.2 mmol, 100%) which produced only one TLC spot and melted at 82.5−85 °C (lit.[20] 85 °C). The infrared and NMR spectra were identical with those of an authentic sample of fluorenone.

Oxidation of Diphenylmethane with $KMnO_4/Al_2O_3 \cdot xH_2O$: Diphenylmethane (0.61 g, 3.6 mmol) was dissolved in 1,2-dichloroethane (120 mL) and placed in a round-bottomed flask. $KMnO_4/Al_2O_3$ reagent (11.5 g), prepared as described above, was added in small portions over a period of 15 min. The mixture was stirred at room temperature for 282 h. The spent oxidant and solid support were removed by filtration through a fritted glass funnel and the residue washed with methylene chloride (3 × 50 mL). Evaporation of the solvent gave impure product (0.62 g) which was purified by elution chromatography to yield benzophenone (0.59 g, 3.3 mmol, 91%). The melting point of the 2,4-DNP derivative was 235.5−237.5 °C (lit.[29] 239 °C). The infrared and NMR spectra were identical with those of an authentic sample.

Oxidation of Isochroman (3,4-dihydro-1*H*-2-benzopyran) with $KMnO_4/CuSO_4 \cdot 5H_2O$: Isochroman (0.188 g, 1.40 mmol), dissolved in 20 mL of dichloromethane, and oxidant (3.2 g) were placed in a 50 mL round-bottomed flask and stirred vigorously under gentle reflux. After 72 h, the product was filtered through a Celite pad and the residue washed successively with dichloromethane (3 × 20 mL) and ether (3 × 20 mL). Evaporation of the solvent gave the lactone, 2-chromanone (0.198 g, 1.35 mmol, 96%). The identity of the product was confirmed by NMR and mass spectrometry. ^1H NMR ($CDCl_3$) δ: 7.1−8.0 (m, 4H), 4.45 (t, 2H), 3.95 (t, 2H). Ms: *m*/*z* (%): 148 (M^+, 46), 118 (100), 90 (91), 62 (25), 50 (17), 39 (19).

Oxidation of 6-Methoxytetralin (6-Methoxy-1,2,3,4-tetrahydronaphthalene) with $KMnO_4/CuSO_4 \cdot 5H_2O$: 6-Methoxytetralin (0.227 g, 1.40 mmol), dissolved in 20 mL of dichloromethane, and oxidant (3.2 g) were placed in a 50 mL round-bottomed flask and stirred vigorously under gentle reflux. After 72 h, the product was filtered through a Celite pad and the residue washed successively with dichloromethane (3 × 20 mL) and ether (3 × 20 mL). Evaporation of the solvent gave an impure product (0.235 g). Analysis of this mixture by GC/MS indicated three components, 6-methoxy-1-tetralone (85%), 7-methoxy-1-tetralone (5%), and unidentified material (10%). These products were separated by elution chromatography, and the two isomers were identified by comparison of their ^1H NMR spectra with published spectra.[30]

Attempted Oxidation of Ethylbenzene with $KMnO_4/CuSO_4 \cdot 5\ H_2O$ in the Presence of Cyclohexene: The effect of cyclohexene on this reaction was assessed by running parallel experiments, one containing cyclohexene, the other

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without. In one flask, oxidant (1.6 g) was added to a solution of ethylbenzene (0.148 g, 1.44 mmol) and cyclohexene (0.164 g, 2.80 mmol) in 50 mL of dichloromethane. The solution was stirred and gently refluxed for 48 h. Analysis by GC/MS revealed no trace of the expected product, acetophenone. In a second experiment, identical with the exception that it contained no cyclohexene, analysis indicated a 58% yield of acetophenone. These results clearly indicate that the oxidation of ethylbenzene is strongly inhibited by the presence of cyclohexene.

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