Tetrahedron Letters,Vol.22,No.49,pp 4889-4890,1981 0040-4039/81/494889-02$02.00
Printed in Great Britain

SELECTIVE OXIDATION OF UNSATURATED ALCOHOLS BY POTASSIUM PERMANGANATE ADSORBED ON SOLID SUPPORTS

N. A. Noureldin and Donald G. Lee*
Department of Chemistry, University of Regina
Regina, Saskatchewan, Canada S4S 0A2

Summary: Potassium permanganate adsorbed on solid supports can be used to oxidize unsaturated secondary alcohols to the corresponding ketones without degradation of the carbon-carbon double bonds.

The adsorption of reagents onto solid supports is known to induce changes in the reactivity and selectivity of a number of important reactions including substitutions, eliminations, additions, reductions and oxidations[1]. Although in the majority of these reactions organic polymers are used for solid supports it has been observed that inorganic solids are preferable for use with permanganate[2]. Because this reagent is a strong oxidant it rapidly degrades most organic polymers[3].

Previous reports have described the use of hydrated molecular sieves, alumina and copper sulfate as solid supports for the oxidation of secondary alcohols to ketones[2]. Primary alcohols (other than benzyl alcohol) were observed to give very low yields. In our laboratories we have found that the use of potassium permanganate adsorbed on solid supports (bentonite or copper sulfate pentahydrate) not only increases the ease with which these reactions can be effected, it also induces a remarkable selectivity. Whereas permanganate in solution oxidizes unsaturated alcohols preferentially at the point of unsaturation[4], the use of solid supports supresses this reaction and allows for the formation of unsaturated ketones in high yields. This is a remarkable observation when it is recalled that the reduction of permanganate by olefins in solution is so facile that it has been used historically as a test for the presence of unsaturation[5].

Table I contains a summary of the results we have obtained for the oxidation of several representative secondary alcohols. The synthetic value of these results is apparent when it is noted that such reactions in the past have usually been achieved by the use of activated manganese dioxide[6]. The permanganate reaction does not require an activation procedure nor the use of expensive equipment or materials. In a typical procedure potassium permanganate and the solid support were first ground together in a mortar and then transferred to a 50 mL round bottomed flask. The alcohol, in 20 mL of solvent, was added and the mixture heated

Table 1. The Oxidation of Alcohols

Alcohol	Oxidant	Solvent	Time	Yield[a]
2-Decanol (3.2 mmol)	Bentonite (0.5 g) $KMnO_4$ (1 g)	CH_2Cl_2	24 h	95%
2-Decanol (2.6 mmol)	$CuSO_4 \cdot 5H_2O$ (1 g) $KMnO_4$ (1.4 g)	CH_2Cl_2	20 h	100%
1-Nonen-3-ol (3.2 mmol)	Bentonite (4.5 g) $KMnO_4$ (5.5 g)	CH_2Cl_2	60 h	82%
1-Nonen-3-ol (3.2 mmol)	$CuSO_4 \cdot 5H_2O$ (2 g) $KMnO_4$ (3 g)	CH_2Cl_2	48 h	87%
1-Octen-3-ol (3.2 mmol)	Bentonite (4.5 g) $KMnO_4$ (5.5 g)	CH_2Cl_2	60 h	92%[b]
1-Octen-3-ol (3.2 mmol)	$CuSO_4 \cdot 5H_2O$ (2 g) $KMnO_4$ (3 g)	CH_2Cl_2	48 h	89%[b]
1-Phenyl-1-buten-3-ol (2.8 mmol)	Bentonite (3.6 g) $KMnO_4$ (4.9 g)	CH_2Cl_2	20 h	91%
1-Phenyl-1-buten-3-ol (2.8 mmol)	$CuSO_4 \cdot 5H_2O$ (1.6 g) $KMnO_4$ (2.7 g)	CH_2Cl_2	20 h	90%
1-Phenyl-1-buten-3-ol (2.8 mmol)	$CuSO_4 \cdot 5H_2O$ (1.6 g) $KMnO_4$ (2.7 g)	C_6H_6	7.8 h	86%

[a] Isolated yield unless indicated otherwise.
[b] Yield estimated by glc.

under gentle reflux with good stirring for the designated time (Table 1). At the end of the reflux period the mixture was cooled to room temperature, 20 mL of ether was added and after stirring for another 10 min the solid residue was separated by filtration through Celite. This residue was washed several times with ether, after which the organic solutions were combined, dried over anhydrous magnesium sulfate and carefully evaporated to yield the product.

The following generalizations were noted: (i) Unsaturated alcohols require more oxidant and longer reflux periods than the corresponding saturated compounds. (ii) The required reflux period is, in general, shorter for copper sulfate pentahydrate as compared to bentonite. (iii) The presence of a phenyl group in conjugation with the double bond increases the ease of oxidation of the alcohols. (iv) Nonallylic unsaturated alcohols are more difficult to oxidize than the corresponding α,β-unsaturated alcohols. (v) If a large excess of oxidant and/or a long reflux period is used, cleavage of the carbon-carbon double bond may occur. For example, the oxidation of 1-phenyl-1-butene-3-ol (2.8 mmol) with 20 mmol of $KMnO_4$ and 5.1 mmol of $CuSO_4 \cdot 5H_2O$ in benzene for 22 h gave 68% ketone and 26% benzaldehyde.

REFERENCES

1. N.K. Mathur, C.K. Narang and R.E. Williams, "Polymers as Aids in Organic Chemistry", Academic Press, New York, 1980. P. Hodge and D.C. Sherrington, "Polymer Supported Reactions", Wiley, London, 1980.
2. S.L. Regen and C. Koteel, *J. Am. Chem. Soc.*, 99, 3837 (1977). S. Quici and S.L. Regen, *J. Org. Chem.*, 44, 3436 (1979). F.M. Menger and C. Lee, *J. Org. Chem.*, 44, 3446 (1979).
3. A. Reidies, private communication.
4. D.E. Ames, T.G. Goodburn, A.W. Jevans and J.F. McGhie, *J. Chem. Soc.* [*C*], 268 (1968). T. Okimoto and D. Swern, *J. Am. Oil Chem. Soc.*, 54, 867A (1977).
5. A.I. Vogel, "Elementary Practical Organic Chemistry", Longmans, Green and Co., Toronto, 1957, p. 419, 502.
6. A.J. Fatiadi, *Synthesis*, 65 (1976).

(Received in USA 12 August 1981)