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SELECTIVE OXIDATION OF ALCOHOLS BY MANGANATES

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Summary : K_2MnO_4 oxidized allylic and benzylic alcohols but did not affect saturated alcohols under phase-transfer catalysis condition, whereas a solid mixture of $BaMnO_4$, Al_2O_3, and $CuSO_4 \cdot 5H_2O$ selectively oxidized allylic, benzylic, and saturated secondary hydroxy groups to the corresponding carbonyl groups in the presence of saturated primary hydroxy groups.

Although manganate, MnO_4^{2-} has been known as an oxidizing agent for a long time,[1] its utility has been limited in organic synthesis partly because it has not shown any advantages over versatile permanganate, MnO_4^-. However, we thought that the lower oxidation potential of manganate[2] compared with permanganate might turned out to be advantageous in terms of selectivity for the oxidation of certain organic compounds. Another reason for the limited utility of the manganate is its instability in neutral and acidic aqueous solution and its insolubility in organic solvents. These problems, however, can be overcome by employing phase-transfer catalysis(PTC) or heterogeneous reactions on solid supports. In this article, we report that K_2MnO_4 under PTC condition, $BaMnO_4$-Al_2O_3-$CuSO_4 \cdot 5H_2O$, and K_2MnO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$ are efficient and selective oxidizing agents for alcohols. There has been one report that powdered $BaMnO_4$ as suspension in methylene chloride oxidized benzylic and saturated secondary alcohols to the corresponding carbonyl compounds, yet the selectivity of the reagent was not carefully examined.[3]

Oxidation under PTC condition was performed by stirring a mixture of an alcohol(1.25 mmol) and benzyltriethylammonium chloride(0.15 mmol) in benzene (5 ml) and K_2MnO_4(5.00 mmol) in 6% aqueous NaOH(10 ml) at 0°C or 25°C under nitrogen atmosphere. The products of the oxidation of allylic and benzylic alcohols varied with temperature as shown in Table 1. Thus, primary benzylic alcohols were oxidized to the corresponding carboxylic acids at 25°C, but to aldehydes at 0°C. Secondary benzylic alcohols were converted into the corresponding ketones in high yields both at 0°C and 25°C except s-phenetyl alcohol which was oxidized to benzoic acid by C-C bond cleavage at 25°C. Allylic alcohols conjugated with phenyl ring were also oxidized to benzoic acid by C-C bond cleavage both at 0°C and 25°C under PTC condition. The oxidation of primary allylic alcohols such as geraniol and crotyl alcohol provided complex mixtures of products. Saturated primary and secondary alco-

Table 1. Oxidation of Alcohols with K_2MnO_4 under PTC Conditions

Alcohol	at 25°C			at 0°C		
	Product	Time,h	Yield,%[a,b]	Product	Time,h	Yield,%[a,b]
benzyl alcohol	benzoic acid	1	(98)	benzaldehyde	0.5	60
p-methoxybenzyl alcohol	p-methoxybenzoic acid	3	(98)	p-methoxybenzaldehyde	1.5	94
benzhydrol	benzophenone	5	95	benzophenone	5	95
s-phenethyl alcohol	benzoic acid	3	(80)	acetophenone	3	93
cinnamyl alcohol	benzoic acid	1	(75)	benzoic acid	1	(65)
trans-3-hydroxy-1-phenyl-1-butene	benzoic acid	0.5	(90)	benzoic acid	0.5	(90)
4-t-butylcyclohexanol	4-t-butylcyclohexanone	12	5	4-t-butylcyclohexanone	12	5
2-octanol	no reaction	12		no reaction	12	
1-dodecanol	no reaction	12		no reaction	12	

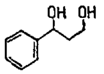
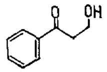
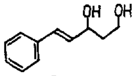
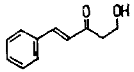
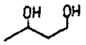
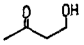
[a] The yields were determined by GC.

[b] The yields in parentheses are isolated one.

hols, however, were not oxidized under the present PTC conditions as shown in Table 1. On the other hand, olefins and sulfides remained intact under the present PTC conditions, but an α,β-unsaturated ketone, namely 4-phenyl-3-buten-2-one was oxidized to benzoic acid. The present result indicates that K_2MnO_4 under PTC condition has clearly different oxidizing ability from that of $KMnO_4$ under PTC conditions$^{4)}$ and has some selectivities toward allylic and benzylic alcohols as well.

$BaMnO_4$ and K_2MnO_4 on solid supports, on the other hand, showed excellent selectivities for the oxidation of alcohols. Like K_2FeO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$ which we reported previously as a selective oxidizing agent for alcohols,$^{5)}$ efficiencies and selectivities of $BaMnO_4$ and K_2MnO_4 were best in the combination with Woelm 200 basic chromatographic alumina$^{6)}$ and $CuSO_4 \cdot 5H_2O$. The oxidation on the solid support in the present work was performed by stirring the benzene solution(15 ml) of an alcohol(1.24 mmol) with the solid mixture$^{7)}$ of $K_2MnO_4$$^{8)}$ (1.36 g, 7.25 mmol) or $BaMnO_4$$^{9)}$ (1.60 g, 7.25 mmol), and $CuSO_4 \cdot 5H_2O$(1.36 g, or 1.60 g) at room temperature under nitrogen. After completion of the reaction, the solid reagent was removed by the filtration and evaporation of the solvent afforded the product. As shown in Table 2, $BaMnO_4$-Al_2O_3-

Table 2. Oxidation of Alcohols with $BaMnO_4$ and K_2MnO_4 on Solid Supports

Alcohol	Product	$BaMnO_4$-Al_2O_3-$CuSO_4 \cdot 5H_2O$		K_2MnO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$	
		Time,h	Yield,%[a,b]	Time,h	Yield,%[a,b]
benzyl alcohol	benzaldehyde	6	91	10	87
benzhydrol	benzophenone	2	93	6	95
_s_-phenethyl alcohol	acetophenone	6	90	10	89
cinnamyl alcohol	cinnamaldehyde	3	93	18	5
geraniol	geranial	10	91	18	10
trans-3-hydroxy-1-phenyl-1-butene	_trans_-4-phenyl-3-buten-2-one	10	80	18	5
trans-3-hydroxy-1,3-diphenyl-1-propene	_trans_-1,3-diphenyl-1-propen-3-one	2	95	18	14
5-hexen-2-ol	5-hexen-2-one	10	78	18	5
4-_t_-butylcyclohexanol	4-_t_-butylcyclohexanone	10	86	18	68
4-phenylcyclohexanol	4-phenylcyclohexanone	10	87	10	83
2-heptanol	2-heptanone	10	82	10	80
1-decanol	decanol	18	5	18	5
1-dodecanol	dodecanal	18	5	18	5
 **1**	 **2**	6	(85)	6	(80)
 **3**	 **4**	8	(80)	18	5
 **5**	 **6**	18	(65)		

[a] The yields were determined by GC.

[b] The yields in parentheses are isolated one.

$CuSO_4 \cdot 5H_2O$ efficiently oxidized benzylic, allylic, and saturated secondary alcohols to the corresponding aldehydes or ketones but the oxidation of saturated primary alcohols was very sluggish. On the other hand, K_2MnO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$ was efficient for the oxidation of benzylic alcohols and saturated secondary alcohols to the corresponding carbonyl compounds, but did not oxidize allylic alcohols and saturated primary alcohols efficiently. Furthermore, K_2MnO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$ could not oxidize a nonallylic unsaturated alcohol, namely 5-hexen-2-ol which could be oxidized by $BaMnO_4$-Al_2O_3-$CuSO_4 \cdot 5H_2O$. The selectivities of these solid reagents were further examined by applying them for the oxidation of diols, **1**, **3**, and **5**. $BaMnO_4$-Al_2O_3-$CuSO_4 \cdot 5H_2O$ oxidized benzylic, allylic, and saturated secondary hydroxy groups but did not affect saturated primary hydroxy groups in diols, **1**, **3**, and **5** to afford nicely hydroxy ketones, **2**, **4**, and **6**, respectively in reasonable yields. K_2MnO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$, on the other hand, could not efficiently oxidize **3** and gave a complex mixture of products in the oxidation of **5**. These results indicate that the manganate on solid support, especially $BaMnO_4$-Al_2O_3-$CuSO_4 \cdot 5H_2O$ is superior to $KMnO_4$ at least in terms of selectivity in the oxidation of diols containing both saturated primary and secondary hydroxy groups since $KMnO_4$ on solid supports is known to show only slight selectivities toward saturated secondary hydroxy groups over primary ones.10)

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References and Notes

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6. Al_2O_3(W-200-B, Activity Grade Super I) was purchased from ICN Pharmaceuticals, Inc. and used without further activation.
7. The solid mixture was prepared by gentle grinding a mixture of $BaMnO_4$ or K_2MnO_4, Al_2O_3, and $CuSO_4 \cdot 5H_2O$ in a mortar for 2 min.
8. K_2MnO_4 was prepared as described by R.S. Nyholm and P.R. Woolliams, *Inorg. Synth.*, **11**, 56(1968).
9. $BaMnO_4$ was purchased from Aldrich and could also be prepared according to M. Fieser "Reagents for Organic Synthesis", Vol.8, Wiley, New York, 1980, p.21. The activities of both manganates were almost same.
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