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SELECTIVE OXIDATION OF ALCOHOLS BY
K_2FeO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$

Kwan Soo Kim*, Yang Heon Song, Nam Ho Lee, and Chi Sun Hahn

Department of Chemistry
Yonsei University
Seoul 120, Korea

Summary : A solid mixture of K_2FeO_4, Al_2O_3, and $CuSO_4 \cdot 5H_2O$ efficiently oxidized allylic, benzylic, and saturated secondary alcohols to the corresponding aldehydes or ketones but did not oxidize saturated primary alcohols.

Although potassium ferrate(K_2FeO_4) is an oxidizing agent of a great potential, its utility in organic synthesis has been severely limited because of its insolubility in organic solvents. Indeed, to the best of our knowledges, there have been only three reports on the oxidation of alcohols with K_2FeO_4. In order to overcome the solubility problem, we have used K_2FeO_4 under phase-transfer catalysis condition and have recently reported that K_2FeO_4 under phase-transfer catalysis condition efficiently and selectively oxidized allylic and benzylic alcohols.1) We further explored other methods to overcome the solubility problem of K_2FeO_4.

Herein we report a solid mixture of $K_2FeO_4$2), Woelm 200 basic(W-200-B) chromatographic alumina3), and a hydrated inorganic salt such as $CuSO_4 \cdot 5H_2O$ or $Fe(NO_3)_3 \cdot H_2O$ as not only an efficient but also a remarkably selective oxidizing agent for various alcohols in organic solvents. The heterogeneous reagents often provide the manipulative convenience and selectivity of specific synthetic procedures and have been also applied to the oxidation of various alcohls. Most solid oxidants, however, have not shown selectivities for the oxidation of alcohols. Although molecular sieves impregnated with $KMnO_4$4) and a solid mixture of $KMnO_4$ and $CuSO_4 \cdot 5H_2O$5) have shown slight selectivities toward secondary alcohols, they have found to be also unfeasible for the selective oxidation of secondary alcohols in the presence of primary ones.

We examined oxidizing abilities of various solid mixtures containing K_2FeO_4 such as K_2FeO_4-Al_2O_3(W-200-B), K_2FeO_4-$SiO_2$6), K_2FeO_4-$Fe(NO_3)_3 \cdot H_2O$, K_2FeO_4-$CuSO_4 \cdot 5H_2O$, K_2FeO_4-Al_2O_3(W-200-B)-$Fe(NO_3)_3 \cdot H_2O$, and K_2FeO_4-Al_2O_3(W-200-B)-$CuSO_4 \cdot 5H_2O$. Among them, K_2FeO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$ provided the best result.7) Thus, the oxidation in the present work was performed by stirring the benzene solution(30 ml) of an alcohol(2 mmol) with the solid mixture[8)] of K_2FeO_4(1,6 g, 8 mmol), Al_2O_3(W-200-B)(0.8 g), and $CuSO_4 \cdot 5H_2O$(0.8 g) at room temperature. After completion of the reaction, the solid reagent was removed simply by the filtration and the evaporation of the solvent afforded the product.

Benzyl alcohol was readily oxidized to benzaldehyde by this solid oxidizing agent in 2 h in quantitative yield. Other benzylic alcohols were similarly transformed into the corresponding aldehydes or ketones in high yields as shown in Table. This solid oxidizing agent was also effective for the oxidation of allylic alcohols to the corresponding α,β-unsaturated aldehydes or ketones. For example, cinnamyl alcohol and trans-3-hydroxy-1-phenyl-1-butene were transformed into cinnamaldehyde and trans-4-phenyl-3-buten-2-one, respectively in almost quantitative yields. Crotyl alcohol, however, was oxidized to crotic acid and the oxidation at lower temperature with one or two equivalents of the oxidizing agent gave the same result.

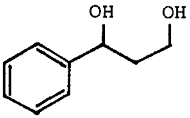
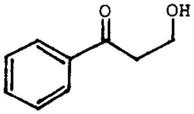
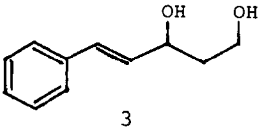
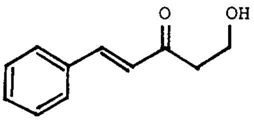
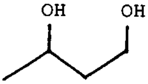
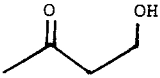
Remarkable selectivity of K_2FeO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$ was revealed in the oxidation of saturated primary and secondary alcohols. Thus, the oxidation of 4-phenylcyclohexanol completed in 12 hr to afford 4-phenylcyclohexanone in 90% yield and 2-heptanol was oxidized to 2-heptanone in 12 hr in 85% yield, whereas the oxidation of 1-decanol by the same reagent gave decanal only in 9% yield in 60 hr. Similary, other secondary alcohols were converted to the corresponding ketones in high yields but the oxidation of primary alcohols with K_2FeO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$ was very sluggish as shown in Table.

Nonallylic unsaturated secondary alcohol, namely 5-hexen-2-ol, however, was not oxidized to the corresponding ketone. In the presence of cyclohexene, saturated secondary alcohols such as 2-heptanol and 4-phenylcyclohexanol were also not oxidized. Benzyl alcohol in the presence of cyclohexene was oxidized to benzaldehyde only in 20% yield in 5 h. This result suggests that carbon-carbon double bonds bind reactive sites of K_2FeO_4.

We further examined the selectivity of K_2FeO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$ by applying this solid reagent to the oxidation of polyhydroxy compounds. Compound **1** containing both benzylic and saturated primary hydroxy groups was transformed nicely to β-hydroxyketone **2**[9)] in 95% yield. The ferrate reagent also selectively oxidized allylic hydroxy group of compound **3** without affecting saturated primary hydroxy group to afford compound **4**[10)] in 95% yield. The saturated primary and secondary hydroxy groups in the same molecule were also distinguished by this reagent. Thus, 1,3-butandiol (**5**) was cleanly oxidized to 4-hydroxy-2-butanone (**6**)[11)] in 85% yield.

There are many reagents available for the oxidation of primary or secondary alcohols to aldehydes or ketones, respectively. However, only a few of those reagents can selectively oxidize saturated primary[12)] or secondary alcohols.[13)] Unfortunately, these selective oxidizing agents do not show sufficient sectivities, are not generally applicable, or are not readily available. The efficiency, the selectivity and the ease of using K_2FeO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$ indicate that this solid oxidizing agent may prove to be a useful alternative to other reagents in the selective oxidation of polyhydroxy compounds.

Table. Oxidation of Alcohols with K_2FeO_4-Al_2O_3-$CuSO_4 \cdot 5H_2O$

Alcohol	Product	Time, h	yield %^{a,b}
benzyl alcohol	benzaldehyde	2	100
o-chlorobenzyl alcohol	*o*-chlorobenzaldehyde	7	90
benzhydrol	benzophenone	1	99
cinnamyl alcohol	cinnamaldehyde	5	98
geraniol	geranial	5	98
trans-3-hydroxy-1-phenyl-1-butene	*trans*-4-phenyl-3-buten-2-one	2	95
crotyl alcohol	crotic acid	0.5	(95)
4-*t*-butylcyclohexanol	4-*t*-butylcyclohexanone	15	75
4-phenylcyclohexanol	4-phenylcyclohexanone	15	90
2-heptanol	2-heptanone	15	85
1-decanol	decanal	60	9
1-dodecanol	dodecanal	60	15
cyclohexylmethanol	cyclohexylcarbaldehyde	60	0
5-hexen-2-ol	5-hexen-2-one	24	0
 **1**	 **2**	4	(95)
 **3**	 **4**	4	(95)
 **5**	 **6**	30	(85)

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[a] The yields were determined by GC using a column of 10% UCW-982 on Chromosorb W.
[b] The yields in parentheses are isolated ones.

References and Notes

1. K.S. Kim, Y.K. Chang, S.K. Bae, and C.S. Hahn, Synthesis, 866 (1984).
2. K_2FeO_4 was prepared as described by G.W. Thompson, L.T. Ockerman, and J.M. Schreyer, J. Amer. Chem. Soc., 73, 1379 (1951).
3. Al_2O_3(W-200-B, Activity Grade Super I) was purchased from ICN Pharmaceuticals, Inc. and used without further activation.
4. S.L. Regen and C. Koteel, J. Amer. Chem. Soc., 99, 3837 (1977).
5. F.M. Menger and C. Lee, J. Org. Chem., 44, 3446 (1979).
6. 70-230 mesh, E. Merck Kiesegel 60.
7. Although $Fe(NO_3)_3 \cdot H_2O$ was as effective as $CuSO_4 \cdot 5H_2O$, only $CuSO_4 \cdot 5H_2O$ was used for further study.
8. The solid oxidizing agent was prepared by the gentle grinding the solid mixture of K_2FeO_4 (0.16 g), Al_2O_3(0.16 g), and $CuSO_4 \cdot 5H_2O$(0.16 g) in a mortar for 2 min.
9. Compound 2 : IR(neat) 3450, 1690, 1050 cm^{-1} ; NMR($CDCl_3$) δ 2.90(s, 1H), 3.25(t, 2H), 4.10 (t, 2H), 7.30—8.30(m, 5H).
10. Compound 4 : IR(neat) 3450, 1680, 1050 cm^{-1} ; NMR($CDCl_3$) δ 2.98(t, 2H), 3.70—4.15(m, 3H), 6.70(d, 1H, J=16Hz), 7.10—7.65(m, 6H).
11. Compound 6 : IR(neat) 3510, 1720, 1050 cm^{-1} ; NMR($CDCl_3$) δ 2.20(s, 3H), 2.67(t, 2H), 3.80 (t, 2H), 4.02(s, 1H).
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