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Nickel-Catalyzed Oxidation of Allylic Alcohols with $K_2S_2O_8$

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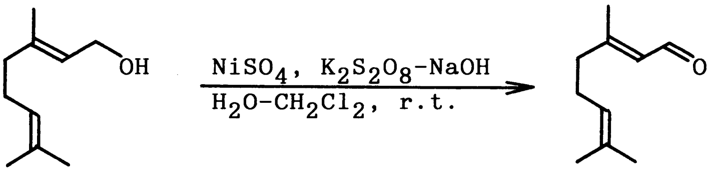
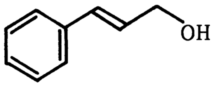
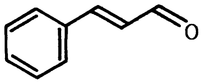
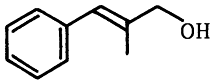
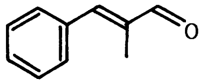
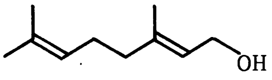
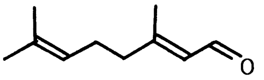
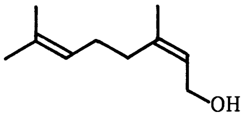
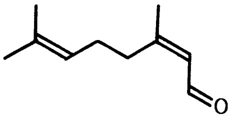
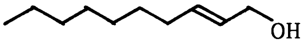
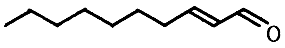
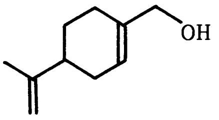
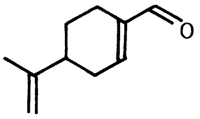
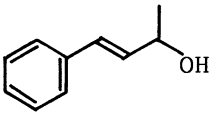
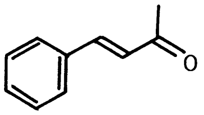
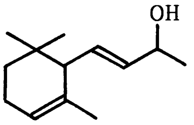
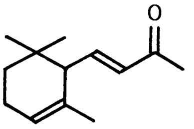
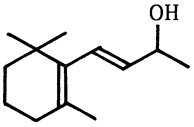
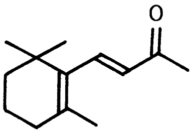
$NiSO_4$-$K_2S_2O_8$ has been found to be an efficient catalytic system for the selective oxidation of allylic alcohols to the corresponding unsaturated carbonyl compounds in excellent yields.

Selective oxidation of alcohols plays an important role in organic synthesis. Though a variety of transition metals are known to act as oxidant or catalyst in the oxidation of alcohols to carbonyl compounds, stoichiometric oxidations with a large amount of metal reagent such as active manganese dioxide are usually the method of choice especially for the oxidation of allylic alcohols to unsaturated carbonyl compounds,1) and the design of the efficient catalytic systems is of current interest.2) Here we report a new catalytic system for the oxidation of allylic alcohols to the corresponding unsaturated carbonyl compounds3,4) by nickel sulfate as a catalyst with alkaline aqueous solution of $K_2S_2O_8$ as the terminal oxidant.5)



In a typical experiment, a mixture of alcohol (5.0 mmol) in CH_2Cl_2 (10 mL), $K_2S_2O_8$ (2.0 g, 7.5 mmol) and NaOH (0.60 g, 15 mmol) in H_2O (50 mL) was stirred magnetically with aqueous 0.05 M $NiSO_4$ (2.0 mL, 0.10 mmol) at room temperature. A fine black precipitates formed immediately in the reaction mixture upon addition of $NiSO_4$. After an appropriate reaction time, the insoluble nickel compound was filtered off by passing through a short Celite column. Aldehyde or ketone was obtained from the organic layer by the usual work-up and purified by silica gel column chromatography or PTLC. Some organic acids were obtained by

Table 1. Nickel-Catalyzed Oxidation of Allylic Alcohols with $K_2S_2O_8$[a)]

Run	Alcohol	$K_2S_2O_8$/ Alcohol	Time h	Conv. %	Product	Yield[b)] %
1		1.4	6	100		82[c)]
2		1.3	24	100		92
3		1.4	24	100		91[d)]
4		1.5	24	100		94[e)]
5		1.3	24	100		78
6		1.3	24	71		87
7		1.5	24	100		96
8		1.5	24	55		95
9		2	72	56		95

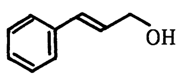
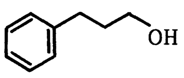
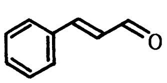
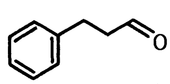
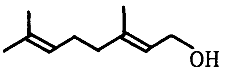
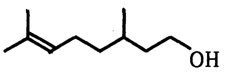
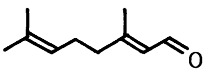
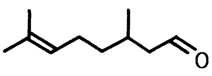
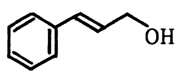
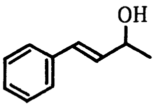
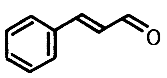
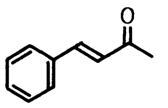
a) All reactions were carried out at room temperature by stirring the mixture of alcohol (5.0 mmol) in CH_2Cl_2 (10 mL), $K_2S_2O_8$/NaOH (molar ratio; 1:2) in H_2O (50 mL) and aqueous 0.05 M $NiSO_4$ (2.0 mL, 0.10 mmol). b) Isolated yields of unsaturated aldehydes or ketones. All the products gave satisfactory NMR and IR spectra. c) 17% of cinnamic acid was isolated from the acidified aqueous layer. d) <1% of neral was detected by GC. e) <1% of geranial was detected by GC.

the extraction of the acidified aqueous layer with CH_2Cl_2 after the decomposition of the excess oxidant with sodium bisulfite.

The results of the oxidation of allylic alcohols are listed in Table 1. Primary allylic alcohols such as geraniol and cinnamyl alcohol were oxidized to the corresponding unsaturated aldehydes in good to excellent yield. Geraniol (Run 3) was oxidized to geranial in 91% yield, and the amount of neral (the cis isomer) was below 1%. The dehydrogenation of nerol also proceeded with retention of stereochemistry, and almost no isomerization to geranial was observed (Run 4). α-Ionol and β-ionol were selectively oxidized to α-ionone and β-ionone respectively without olefin isomerization (Run 8, 9). These results show that olefinic double bonds in the substrate were inert under the reaction conditions and that this nickel-catalyzed oxidation proceeds with retention of the configuration of olefinic bond. A small amount of unsaturated carboxylic acids were produced as a by-product in the oxidation of primary allylic alcohols. The oxidation of secondary allylic alcohols gave unsaturated ketones selectively.

Saturated primary alcohols were oxidized to carboxylic acids and only a trace amount of aldehydes was detected, even when lesser amount of the oxidant was used. The oxidation of saturated alcohols was slower than that of allylic ones. For example, the oxidation of a mixture of cinnamyl alcohol and 3-phenyl-

Table 2. Selective Oxidation of Allylic Primary Alcohols[a)]

Run	Alcohol		Time/h	Product yield[b)]	
1			6	 85% (0%)	 trace (97%)
2			24	 78% (17%)	 3% (90%)
3			6	 78% (0%)	 10% (90%)

a) The alcohols (1.0 mmol each) in CH_2Cl_2 (10 mL), $NiSO_4$ (0.020 mmol) and $K_2S_2O_8$/NaOH (1.5 mmol/3.0 mmol) in H_2O (10 mL) were combined, and the mixture was stirred at room temperature. b) Determined by GC. Yields in parentheses are recovery of the starting alcohols.

1-propanol for 6 h in a competitive condition gave 85% of cinnamaldehyde and 8% of cinnamic acid, and 97% of 3-phenyl-1-propanol was recovered along with a trace amount of 3-phenyl-1-propanal and 3-phenyl-1-propionic acid. Further, it is worth noting that primary allylic alcohols were oxidized faster than secondary ones. As shown in Table 2 , the oxidation of cinnamyl alcohol in the presence of 4-phenyl-3-buten-2-ol gave 78% of cinnamaldehyde and 10% of benzalacetone with 90% recovery of the secondary alcohol.

The active species in this catalytic oxidation must be nickel peroxide, which is formed in situ from Ni(II) by the oxidant. Nickel peroxide is known as one of the stoichiometric metal reagents for the oxidation of allylic alcohols to unsaturated aldehydes or ketones.[6,7] Though the oxidation of alcohols with stoichiometric amount of nickel peroxide was performed at higher temperature, the present catalytic oxidation proceeded at room temperature, and the selectivity is higher than that of stoichiometric nickel peroxide oxidation.

The present catalytic system must provide a highly useful addition to the synthetic chemist's repertoire because the cheap and easily available catalyst and oxidant give good results with easy operation.

References

1) L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York (1967), Vol. 1, p. 636.
2) R.A. Sheldon and J.K. Kochi, "Metal-Catalyzed Oxidations of Organic Compounds," Academic Press, New York (1981).
3) Recent report on the catalytic oxidation of allylic alcohols; S. Kanemoto, S. Matsubara, K. Takai, K. Oshima, K. Utimoto, and H. Nozaki, Bull. Chem. Soc. Jpn., 61, 3607 (1988).
4) M. Matsumoto and N. Watanabe, J. Org. Chem., 49, 3435 (1984).
5) A few examples on the metal-catalyzed oxidation of alcohols with $K_2S_2O_8$ were reported, although none of these reactions is applicable for preparative purposes; G. Green, W.P. Griffith, D.M. Hollinshead, S.V. Ley, and M. Schroeder, J. Chem. Soc., Perkin Trans. 1, 1984, 681.
6) K. Nakagawa, R. Konaka, and T. Nakata, J. Org. Chem., 27, 1597 (1962).
7) M.V. George and K.S. Balachandran, Chem. Rev., 75, 491 (1975).

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