CHEMISTRY LETTERS, pp. 1481 - 1482, 1984. © The Chemical Society of Japan 1984

Zr-CATALYZED OXIDATION OF ALCOHOLS TO ALDEHYDES IN THE PRESENCE OF ^{t}BuOOH. HIGH REACTIVITY FOR PRIMARY AND ALLYLIC HYDROXYL FUNCTIONS

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$ZrO(OAc)_2$ catalyzes selective oxidation of primary alcohols to aldehydes without formation of carboxylic acids and also chemoselective oxidation of allylic alcohols to α,β-unsaturated aldehydes in the presence of ^{t}BuOOH.

Selective oxidation of hydroxyl functions (primary, secondary, allylic, etc.) plays an important role in organic synthesis. In many cases, a large amount of metal oxidizing agents is required and the design for the catalytic systems with respect to metal has been of considerable current interest.[1)] Recently we have found that the $VO(acac)_2$-^{t}BuOOH system has high oxidation activity for secondary hydroxyl functions in saturated alcohols.[2)] This remarkably high reactivity may be due to facile coordination of secondary hydroxyls to vanadium, compared to that of primary ones.[3)] Zirconium compounds contrast to above vanadium compounds are prone to forming more stable metal-alkoxides from primary alcohols. We here report that $ZrO(OAc)_2$-^{t}BuOOH system shows high oxidation reactivity for primary alcohols giving aldehydes and also high chemoselectivity for hydroxyl functions in the presence of olefinic bonds. In this $ZrO(OAc)_2$-^{t}BuOOH system, the zirconium compound acts as a catalyst for above oxidations. $ZrO(OAc)_2$ is specific as the catalyst and other zirconium compounds, e.g., $ZrCl_4$, $Zr(acac)_4$, and $ZrOCl_2$ give extremely the low catalytic activity accompanying the formation of carboxylic acids.

The oxidation of various alcohols with $ZrO(OAc)_2$ is shown in Table 1. Primary alcohols give the corresponding aldehydes within 1 h in almost quantitative yields. Benzyl alcohols are smoothly oxidized to give the corresponding aldehydes. On the other hand, secondary alcohols are not fast oxidized to the ketones. In competitive oxidation of 1-octanol and 2-octanol, an initial product ratio of octanal and 2-octanone reaches 22.4.

Oxidation of allylic alcohols using $ZrO(OAc)_2$ gives α,β-unsaturated aldehydes as main products and also in non-allylic alcohol containing an olefinic function, the yield of aldehyde reaches 71%. We expect that zirconium compounds might become a fruitful catalyst for highly selective oxidation of the hydroxyl functions in the presence of olefinic ones.4)

Table 1. Oxidation of Various Alcohols Using $ZrO(OAc)_2$ and ^tBuOOH[a)]

Alcohol	Aldehyde	Yield/%[b)]	Time/h
1-Hexanol	1-Hexanal	95	1
1-Octanol	1-Octanal	94	1
1-Dodecanol	1-Dodecanal	95	1
Benzyl alcohol	Benzaldehyde	91	1
p-Methylbenzyl alcohol	p-Methylbenzaldehyde	90	1
o-Methylbenzyl alcohol	o-Mehtylbenzaldehyde	83	1
p-Nitrobenzyl alcohol	p-Nitrobenzaldehyde	94	1
2-Octanol	2-Octanone	85	6
2-Phenylethanol	Acetophenone	70	6
Citronellol	Citronellal	74	1
2-Octen-1-ol[c)]	2-Octen-1-al	71	6

a) Alcohol 0.5 mmol, $ZrO(OAc)_2$ 0.025 mmol, ^tBuOOH 0.5 mmol, CCl_4 5 ml, reflux, N_2.
b) Yields were determined by GLPC. c) 1.5 mmol of ^tBuOOH was used.

References

1) For examples, see P. T. Lansbury, D. G. Hangauer, Jr., and J. P. Vacca, J. Am. Chem. Soc., 102, 3964 (1980); M. Matsumoto and S. Ito, J. Chem. Soc., Chem. Commun., 1981, 907; S. Kaneko, K. Oshima, S. Matsubara, K. Takai, and H. Nozaki, Tetrahedron Lett., 24, 2185 (1983). 2) K. Kaneda, Y. Kawanishi, K. Jitsukawa, and S. Teranishi, Tetrahedron Lett., 24, 5009 (1983). 3) R. K. Mittal and R. C. Mehrotra, Z. Anorg. Allg. Chem., 355, 328 (1967). 4) Concerning Zr-assisted oxidation of organic compounds, there are only two reports: T. F. Blackburn and J. Schwarz, Tetrahedron Lett., 1975, 3041; H. Yasuda, K. Nagasuna, K. Asami, and A. Nakamura, Chem. Lett., 1983, 955.

(Received June 19, 1984)