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HIGHLY SELECTIVE OXIDATION OF SECONDARY HYDROXYL FUNCTIONS USING THE VO(acac)$_2$-^{t}BuOOH SYSTEM

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Abstract: The VO(acac)$_2$-^{t}BuOOH system shows high oxidation reactivity for secondary alcohols to give ketones.

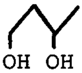
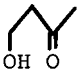
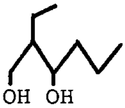
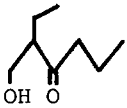
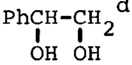
In the study of stereocontrol mechanism of allylic alcohol epoxidation, we have found that the VO(acac)$_2$-^{t}BuOOH system acts as two types of oxidizing reagents: 1) a stereoselective cis-epoxidation reagent for quasi-axial allylic alcohols and 2) an oxidative dehydrogenation reagent for quasi-equatorial alcohols.[1] This double character of the vanadium system has been interested in relation to the catalysis of both oxo- and peroxo-species.[2] In this paper, we wish to report that this vanadium-^{t}BuOOH system shows high selectivity for secondary hydroxyl functions which gives ketones, in comparison to that for primary ones.

Representative examples of alcohol oxidations are shown in Table I. Both acyclic and cyclic secondary alcohols gave the corresponding ketones in good yields. On the other hand, primary alcohols were hardly oxidized (Runs 8 and 9). In the oxidation of diols containing primary and secondary hydroxyl functions, ketoalcohols were obtained as sole products in good yields. This high selectivity for secondary hydroxyl functions was also proved by competitive oxidation of primary and secondary alcohols. Secondary alcohols were oxidized exclusively to give ketones, e.g., the product ratio of 4-dodecanone to dodecanal was more than 10^2 in the reaction of 4-dodecanol and 1-dodecanol. To best our knowledge, the VO(acac)$_2$-^{t}BuOOH system has the highest value among the reported relative oxidation rates.[3]

In addition, this vanadium system can oxidatively cleave a carbon-carbon bond of vic-diols to give the corresponding carboxylic acids (Run 13).

This high oxidation selectivity for secondary hydroxyl function may be due to facile coordination of secondary hydroxyl to a vanadium complex, compared to that for primary ones.[4] The detailed reaction mechanism for the alcohol oxidation using the VO(acac)$_2$-^{t}BuOOH system is under investigation.[5]

Table I. Oxidation of Various Alcohols Using the VO(acac)$_2$-^{t}BuOOH System[a)]

Run	Substrate	Product	Reaction time (h)	Yield[b)] (%)
1	2-Octanol	2-Octanone	6	82
2	4-Dodecanol	4-Dodecanone	6	70
3	Cyclopentanol	Cyclopentanone	6	50
4	Cyclohexanol	Cyclohexanone	6	69
5	Cyclohexanol[c)]	Cyclohexanone	24	83
6	Cyclooctanol	Cyclooctanone	4	83
7	1-Phenylethanol	Acetophenone	2	95
8	1-Dodecanol	Dodecanal	8	trace
9	Benzylalcohol	Benzaldehyde	6	20
10			24	96
11			24	92
12			24	85
13	 $\underset{OH}{PhCH}-\underset{OH}{CH_2}$[d)]	PhCOOH	24	94

a) The benzene solution (12ml) of alcohol (2mmol) and ^{t}BuOOH (6mmol) was allowed to react in the presence of VO(acac)$_2$ (0.1mmol) at 80°C under N_2.
b) Determined by GLC analysis using internal standards. c) ^{t}BuOOH (12mmol).
d) CCl_4 solvent at room temperature.

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1) T. Itoh, K. Jitsukawa, K. Kaneda, and S. Teranishi, J. Am. Chem. Soc., 1979, 101, 159. 2) R. A. Sheldon and J. K. Kochi in "Metal-Catalyzed Oxidation of Organic Compounds"; Academic Press, New York, 1981, p80. 3) H. Tomioka, K. Takai, K. Oshima, and H. Nozaki, Tetrahedron Lett., 1981, 22, 1605 and references therein. 4) R. K. Mittal and R. C. Mehrotra, Z. Anorg. Allg. Chem., 1967, 355, 328. 5) Hammett σ constant of 1-(p-substituted phenyl)ethanols gave ρ of +0.84 and also kinetic isotopic effect of k_H/k_D was 3.5 in the reaction of $PhCD(OH)CH_3$ at 3°C.

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