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Versatile Dehydrogenative Aromatization of α,β-Unsaturated Cyclohexenones with $VO(OEt)Cl_2$-Me_3SiOTf

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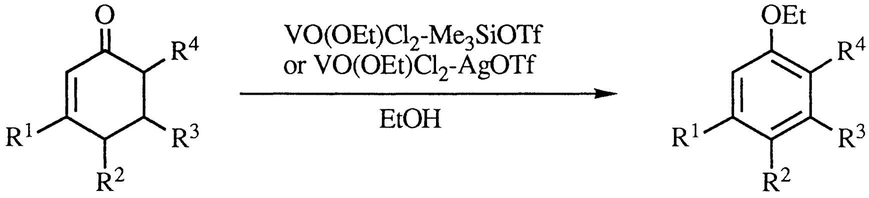
An oxovanadium compound obtained from $VO(OEt)Cl_2$ and AgOTf or Me_3SiOTf efficiently induced dehydrogenative aromatization of α,β-unsaturated cyclohexenones to give aryl ethyl ethers in good yields.

Dehydrogenative aromatization is an important oxidative transformation in organic synthesis.1) A previous paper demonstrated that $VO(OEt)Cl_2$ induces aromatization of α,β-unsaturated cyclohexenones.2) The oxidation reaction is considered to depend on the oxidative capability of Lewis acid, $VO(OEt)Cl_2$. The higher acidity is expected to increase the reactivity of oxovanadium compounds. We herein report that a combination of $VO(OEt)Cl_2$ and AgOTf or Me_3SiOTf constitutes the more reactive oxidant.

The oxovanadium compound obtained by treatment of $VO(OEt)Cl_2$ with AgOTf was found to induce dehydrogenative aromatization of 2-cyclohexen-1-one in ethanol at room temperature for 5 h giving ethyl phenyl ether [$VO(OEt)Cl_2$: AgOTf : 2-cyclohexen-1-one = 1:1:1, 75%; 2:2:1, 93%].

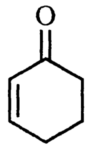
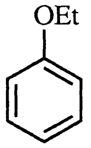
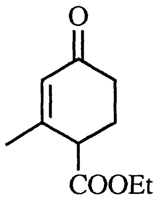
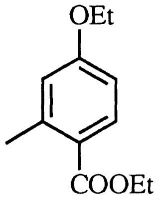
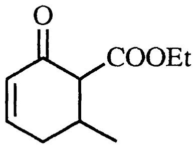
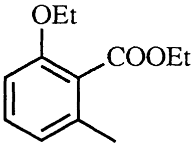
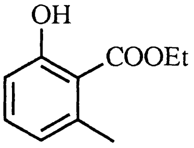


More conveniently, Me_3SiOTf was able to be used instead of AgOTf. $VO(OEt)Cl_2$ was treated with one equiv. of Me_3SiOTf in dichloromethane followed by addition of 2-cyclohexen-1-one and ethanol to produce ethyl phenyl ether (Table 1).3) It should be noted that one equiv. of the oxovanadium species was also enough for the oxidation as observed in the case of $VO(OEt)Cl_2$-AgOTf. This finding is in contrast to the reactivity of $VO(OEt)Cl_2$. More than two equiv. of $VO(OEt)Cl_2$ are required to complete the oxidative transformation in the absence of Me_3SiOTf because $VO(OEt)Cl_2$ is considered to work as a one-electron oxidant. Reaction only with $VO(OEt)Cl_2$ under similar conditions led to a complex mixture with a decrease in the yield of ethyl phenyl ether.

Ethyl phenyl ether was produced even in dichloromethane as a solvent, suggesting that the oxovanadium ethoxide participates in the introduction of ethoxy group. The formation of trimethylsilyl chloride was detected by glc in the reaction mixture of $VO(OEt)Cl_2$ and Me_3SiOTf. The oxovanadium triflate4) appears to be generated in situ via exchange of chloride with triflate, which also seems to be the case with $VO(OEt)Cl_2$ and AgOTf.

This method is extended to dehydrogenative aromatization of 2-cyclohexen-1-ones bearing ethoxycarbonyl group at 4- or 6-position to give the corresponding aryl ethyl ethers. The phenol derivative was obtained as a major product in the latter reaction possibly due to the presence of ethoxycarbonyl group at the ortho position. Two equiv. of both $VO(OEt)Cl_2$ and Me_3SiOTf were, however, used for a good conversion to ethyl 4-ethoxy-2-

Table 1. Dehydrogenative Aromatization of α,β-Unsaturated Cyclohexenones[a)]

α,β-Unsaturated Cyclohexenone	$VO(OEt)Cl_2$/ equiv.	Me_3SiOTf/ equiv.	Solvent	Product	Yield/% [b)]
	1	1	EtOH		82 (15)
	1	1	CH_2Cl_2		12 (46)
	2	–	EtOH		24 (35)
	1	1	EtOH		45 (29)
	1	2	EtOH		55 (7)
	2	2	EtOH		94 (0),76[c)]
	2	2	EtOH	 	50[c)] 34 : 66

a) Reaction conditions, 0 °C, 1 h; room temperature, 1 h. b) The yields were determined by glc based on the starting material unless otherwise stated. The numbers in parentheses represent the amount (%) of the recovered starting material. c) Isolated yield.

methylbenzoate. The yield was not raised on treatment with 1 equiv. of $VO(OEt)Cl_2$ and 2 equiv. of Me_3SiOTf.

The oxovanadium reagent obtained from $VO(OEt)Cl_2$ and AgOTf or Me_3SiOTf is powerful and versatile for oxidation. Further investigation is now in progress.

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References

1) For example, F. M. Hauser and S. A. Pogany, *Synthesis*, **1980**, 814.

2) T. Hirao, M. Mori, and Y. Ohshiro, *J. Org. Chem.*, **55**, 358 (1990).

3) A typical procedure is as follows. To a solution of $VO(OEt)Cl_2$ (1.0 mmol) in dichloromethane (1 mL) was added Me_3SiOTf (1.0 mmol) at 0 °C. After stirring at 0 °C for 1 h, 2-cyclohexen-1-one (1.0 mmol) and ethanol (1 mL) were added. The resulting mixture was stirred at 0 °C for 1 h and then at room temperature for 1 h. Ether and 5% aqueous HCl were added to the mixture, which was extracted with ether. The combined ethereal solution was washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$, and brine. TLC of the concentrated residue gave the desired ethyl phenyl ether.

4) It is reported that $VO(OTf)_3$ is insoluble in common organic solvents: S. Singh, Amita, M.S. Gill, and R. D. Verma, *J. Fluorine Chem.*, **27**, 133 (1985).

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