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Bistriphenylsilanol-Assisted Oxidation Catalyzed by Chromium(VI) Oxide of Activated Trimethylsilyl Ethers with tert-Butyl Hydroperoxide

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Bistriphenylsilanol-assisted Oxidation Catalyzed by Chromium(VI) oxide of Activated Trimethylsilyl Ethers with *tert*-Butyl Hydroperoxide

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Abstract: Secondary benzylic or allylic trimethylsilyl ethers are oxidized at room temperature to the corresponding ketones in good yields using aqueous 70% t-BuOOH and catalytic amounts of a mixture of Ph_3SiOH and CrO_3 .

During the last years, we have been interested in chromium-catalyzed oxidations in organic synthesis 1,2 and recently, we have described a new procedure using *t*-BuOOH and catalytic amounts of $(Ph_3SiO)_2CrO_2$ for the oxidation of silyl ethers.³ This procedure is particularly efficient for the oxidation of secondary benzylic or allylic trimethylsilyl ethers,⁴ but the use of this non-commercial catalyst, although easy to prepare,⁵ could limit the interest of our method. Furthermore, we have noted colour modifications of bistriphenylsilyl chromate in daylight. We are now pleased to report that fair yields can also be obtained under more convenient conditions, i.e. in using catalytic amounts of both Ph₃SiOH and CrO₃ instead of (Ph₃SiO)₂CrO₂.

The new results reported in table I have been obtained by carrying out the oxidations with commercial reagents used as received: CrO_3 (0.05 equiv.), Ph₃SiOH (0.1 equiv.) and aqueous 70 % *tert*-butyl hydroperoxide (3 equiv.).

Starting	Re	action	Ketone
material	ti	me, h	yield %
OSiMe ₃			
n-C	,H ₁₅	24	96
		24 ^a	85
OMe			
OSiMe ₃	R = Me	15	98
	R = Et	15	93
	R = Ph	24	99
	$R=(CH_2)_2CO_2M_{\Theta}$	20	96
OSiMe ₃		17	98
//////////////////////////////////////	35	41	62
ÓSiMe ₃			

^a Reaction carried out in the absence of Ph₃SiOH

The presence of triphenylsilanol as co-catalyst is essential to obtain a selective transformation. Indeed, the oxidation of 1-(*m*-methoxyphenyl)-1-trimethylsilyloxy-octane under similar conditions in the absence of Ph₃SiOH, led to a mixture of 1-(*m*-methoxyphenyl)-1-octanol (8 %) and 1-(*m*-methoxyphenyl)-1-octanone (85 %).

Since *t*-butyldimethylsilyl ethers are less prone to oxidation than trimethylsilyl ethers^{3,4} the reactivity of 1-phenyl-1-trimethylsilyloxy-4-*t*-butyldimethylsilyloxy-



Table II: Oxidation of 1-phenyl -1-trimethylsilyloxy-4-t-butyldimethylsilyloxybutane

butane towards the CrO₃/Ph₃SiOH/t-BuOOH mixture has been analyzed (Table II). As expected, these conditions led mainly to 1-phenyl -4-t-butyldimethylsilyloxy-1butanone. The presence of 1-phenyl-4-t-butyldimethylsilyloxy-1-butanol was detected but its concentration decreased with reaction time indicating that the present one pot procedure for oxidation of trimethylsilylethers probably involves deprotection as an intermediate step, followed by the *in-situ* oxidation of the corresponding alcohol.

Experimental part:

In an open round-bottom flask containing a stirred suspension of CrO_3 (0.05 equiv.) in methylene chloride (3-6 ml/mmol of substrate) was added Ph_3SiOH (0.1 equiv.) and after 2-3 mn, aqueous 70% *t*-BuOOH (3 equiv.) and then the trimethylsilyl ether. The stirred mixture was kept at room temperature in the dark

(aluminium foil) for the time indicated in the tables. After filtration on alumina and evaporation of solvents, the crude product was purified by chromatography.

<u>Caution</u>: For large scale experiments, it is necessary either to check the absence of residual peroxide before removing the solvents or preferably to carry out systematically a work-up with a reducing aqueous solution.^{3,6}

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