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Zeolite-Catalyzed Oxidation of Benzylic and Acetylenic Alcohols with t-Butyl Hydroperoxide

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Abstract : 4 Å molecular sieves catalyze the mild conversion of activated secondary alcohols into the corresponding carbonyl compounds with t-butyl hydroperoxide (TBHP). Copyright © 1996 Published by Elsevier Science Ltd

The oxidation of alcohols to carbonyl compounds represents one of the fundamental preparative reactions. Most of the available procedures are based on the employment of transition metal compounds, as reagents, for example Cr (VI). Although in the last years the achievement of many catalytic processes[1-7] has allowed to reduce the problems related to their cost and toxicity, the interest of several researchers is still devoted to the elaboration of improved methodologies for the oxidation of alcohols, characterized by efficiency, selectivity and low environmental impact.

In the course of investigations on the catalytic properties of zeolites[8], we have found that activated alcohols undergo a slow oxidation by TBHP promoted by 4 Å molecular sieves. In fact, when a benzylic (or propargylic) alcohol of type **1** (or **3**), are submitted to the action of a threefold excess of TBHP in the presence of activated zeolite in CCl_4 solution, the formation of the corresponding ketones takes usually place in satisfactory yield. (Scheme)

Scheme

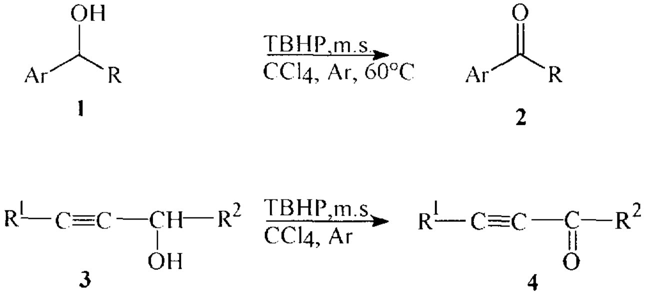

Table 1. Zeolite-Catalyzed Oxidation of Benzylic Alcohols **1**

Entry	Ar	R	Reac.Time/h	Conversion(%)	Yield (%)$^{a)}$
a	Ph	Me	120	70	55
b	Ph	Me	120	22	18$^{b)}$
c	Ph	Ph	156	100	97
d	Ph	Et	96	78	74
e	p-$NO_2C_6H_4$	Me	144	50	47
f	1-indanol		120	60	38
g	α-tetralol		120	45	35

a) All the yields are calculated on starting materials and refer to isolated chromatographically pure compounds, whose structures have been confirmed by IR and ^{1}H-NMR data.
b) In this case no zeolite was added.

Table 2. Zeolite-Catalyzed Oxidation of Propargylic Alcohols **3**

Entry	R^1	R^2	Reac. Time/h	T/°C	Yield (%)$^{a),b)}$
a	H	n-C_5H_{11}	120	60	52
b	n-C_6H_{13}	n-C_5H_{11}	120	40	66
c	Ph	n-C_5H_{11}	144	40	85
d	$CH_3CH(OH)$-	CH_3	96	60	26

a) All the yields are calculated on starting materials and refer to isolated chromatographically pure compounds, whose structures have been confirmed by IR and ^{1}H-NMR data.
b) In these cases two equivalents of TBHP were employed.

Although the oxidation proceeds very slowly the synthetic value of this procedure is confirmed by its simplicity, high degree of selectivity (as showed by the results obtained for the benzylic alcohols) and, most of all, the employment of easily available and environmental safe reagent and catalyst.
Further investigations on the mechanistic aspects are in progress.

Experimental : activated 4 Å molecular sieves (1 g) are added to a solution of alcohol (2 mmol) and TBHP (3 M iso-octane solution, 6 mmol) in CCl_4 (10 ml) in atmosphere of argon. The reaction is monitored by TLC and/or GLC. Then 0.1 N aqueous $Na_2S_2O_5$ (7.5 ml) is added and the mixture is stirred for 30'. After the usual work-up the crude product is purified by silica gel column chromatography by elution with n-pentane-diethyl ether mixtures.

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