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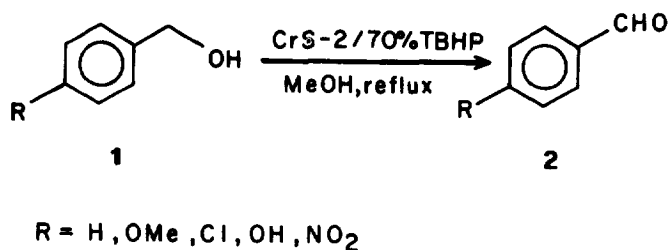
Selective Catalytic Oxidation of Benzylic Alcohols to the Corresponding Carbonyl Compounds with TBHP over CrS-2

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Abstract : Chromium containing medium pore molecular sieve (Si/Cr > 140) having MEL (CrS-2) topology selectively catalyzes the oxidation of various benzylic alcohols to the corresponding carbonyl compounds using 70% tert - butyl hydroperoxide (TBHP) as an oxidant.

The oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is a fundamental reaction in organic synthesis.¹ Such transformations are most frequently accomplished by the use of Cr (VI) - based reagents in amounts ranging from stoichiometric to large excess.² Although these procedures are usually effective, problems in the use of Cr (VI) complexes as oxidation reagents often crop up due to the lack of selectivity in oxidations, safety hazards associated with the use of large quantities of toxic chromium compounds and the need for aqueous acidic or basic conditions for reactions of chromate salts. In an attempt to circumvent these problems, attention has been focused recently on the use of catalytic amounts of soluble chromium compounds in conjunction with TBHP as the stoichiometric oxidant.³ More recently, several catalytic systems such as RuCl₂(Ph₃P)₃⁴, PdCl₂⁵, CrO₃-PTC⁶, CuCl₂-PTC⁷ and Cr-AlPO-5⁸ have been developed for the selective oxidations of benzylic alcohols to the corresponding carbonyl compounds.

Of late, transition metal - incorporated zeolites (e.g. TS-1, VS-1 etc.) have figured prominently for their remarkable catalytic properties when used with dil. H₂O₂ as oxidant.⁹ We have reported¹⁰ quite recently the synthesis and characterization of chromium silicalite-2 (CrS-2) and its unique catalytic properties in the chemoselective epoxidation of alkenes and the direct oxidation of arylamines into the nitro compounds. In this paper, we report that CrS-2 efficiently catalyzes the oxidation of a variety of benzylic alcohols into the corresponding carbonyl compounds with 70% TBHP as oxidant (Scheme 1).



SCHEME - 1

Table 1 : Oxidation of benzylic alcohols with 70% TBHP catalyzed by CrS-2

Entry	Substrate, 1	t/h	Product, 2 ^a	Yield (%) ^b
1	Benzyl alcohol	2	Benzaldehyde	20
2	4-Chlorobenzyl alcohol	3	4-Chlorobenzaldehyde	28
3	4-Hydroxybenzyl alcohol	2	4-Hydroxybenzaldehyde	30
4	4-Methoxybenzyl alcohol	2	4-Methoxybenzaldehyde	32
5	4-Nitrobenzyl alcohol	1	4-Nitrobenzaldehyde	43
6	1-Tetralol	1	1-Tetralone	41
7	4-Chloro- α -phenylbenzene -methanol	1	4-Chlorobenzophenone	41
8	4-Methoxy- α -phenylbenzene -methanol	1	4-Methoxybenzophenone	15
9	1-Phenyl-1,2 - ethanediol	2	α -Hydroxyacetophenone	35 ^c
10	Menthol	4	NR ^d	-
11	Mandelic acid	5	NR	-
12	β -Phenethyl alcohol	2	NR	-

a : Characterized by m.p., IR, ¹H and ¹³C NMR; b : Isolated after chromatographic purification; the remaining is completely starting material (selectivity = 100%); c : Though conversion was quantitative (TLC), the product decomposes slowly on purification; d : No reaction

CrS-2 (Si/Cr > 140) and VS-2 (Si/V = 80) were prepared following literature procedure.^{10,11} In a typical reaction, a mixture of 1-tetralol (1.48 g; 0.01 mol), 70% TBHP (2.6 ml; 0.02 mol) and CrS-2 (148 mg; 10% by wt) in MeOH (25 ml) was refluxed for 1h. The catalyst was filtered off and the excess TBHP decomposed by aq. Na₂SO₃. The product was purified by column chromatography to afford the pure 1-tetralone (0.59 g; 41%) and characterized.¹²

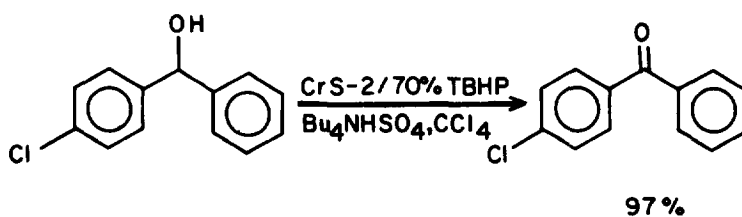
The results of CrS-2 catalyzed oxidations of benzylic alcohols with 70% TBHP at 65°C in MeOH as solvent are shown in Table 1. Evidently, CrS-2 - TBHP system oxidizes a variety of benzylic alcohols with high selectivity: primary alcohols are oxidized exclusively to aldehydes and secondary alcohols to ketones. No carboxylic acids could be detected in the reaction mixtures. Interestingly, 1-phenyl-1,2-ethanediol has been oxidized chemoselectively to α -hydroxyacetophenone in 35% yield, thereby exercising unique selectivity in oxidizing only benzylic alcohols in the presence of aliphatic alcohols. However, unactivated alcohols such as menthol, β -phenethyl alcohol, ethyl lactate and mandelic acid have failed to undergo oxidation under the reaction conditions.

Table 2 : Effect of phase transfer catalyst (PTC) on the oxidation of 4-chloro- α -phenylbenzenemethanol to 4-chlorobenzophenone with 70% TBHP catalyzed by CrS-2

Entry	Catalyst	Solvent	PTC	Yield (%) ^a
1	No catalyst	MeOH	-	0
2	CrS-2	MeOH	-	41
3	CrS-2	CCl ₄	-	70
4	CrS-2	CCl ₄	TBAHS ^b	97
5	VS-2	MeOH	TBAHS ^b	0

a : Isolated after column chromatographic purification; b : Tetrabutylammonium hydrogensulphate (catalytic).

When a catalytic amount of phase-transfer agent, e.g. tetrabutylammonium hydrogensulphate (TBAHS), is added to the reaction mixture of 4-chloro- α -phenylbenzenemethanol and CrS-2-TBHP system in carbon tetrachloride, a quantitative yield of 4-chlorobenzophenone could be obtained in 1h (Scheme 2). Such cases of CrO₃ oxidations of alcohols promoted by PTC under stoichiometric conditions are already known in the literature.¹³ Further, it is seen that vanadium silicalite (VS-2) of similar topology totally failed to catalyze the reaction. Mechanistically, the oxochromium (V) species (the redox potential¹⁴ of Cr⁵⁺/Cr⁴⁺ couple being 0.50 V) present in the zeolite framework is believed to be responsible for the conversion of alcohols to carbonyl compounds. The zeolite catalyst was recovered and reused 3 times with no loss of activity and selectivity.



S C H E M E - 2

In conclusion, we have shown that CrS-2 is an excellent recyclable, solid catalyst for the selective liquid-phase oxidation of benzylic alcohols to the corresponding carbonyl compounds using 70% TBHP as the oxidant.

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