Zirconium Hydroxide Chromate ($Zr_4(OH)_6(CrO_4)_5(H_2O)_2$): a Mild and Efficient Reagent for Oxidation of Benzylic Alcohols

M. Rahimizadeh,* H. Hassani, M. Bakavoli, and M. Gholizadeh†

*Department of Chemistry, College of Sciences, Ferdowsi University, Mashhad, Iran. *E-mail: Rahimizh@ferdowsi.um.ac.ir*
†Department of Chemistry, Sabzevar Teacher Training University, Sabzevar, Iran
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Oxidation of primary and secondary alcohols to aldehydes and ketones is one of the most important transformations in organic chemistry both at laboratory and industrial scale.[1]

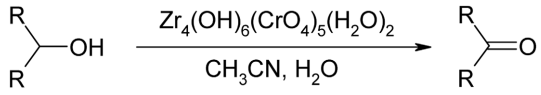
Chromate salts and other chromium (VI) oxides have been widely used as oxidizing agents for a variety of substrates[1a,2] including alcohols.[3] These oxidants are generally used in large excess,[4] but also can be used at catalytic scale in conjunction with secondary oxidants.[5] Recently several chromium(VI) reagents such as: Collins reagent (CrO_3. Py),[6] Jones reagent (CrO_3/H_2SO_4/acetone),[7] CrO_3-supported onto wet silica gel,[8] pyridinum chlorochromate (PCC),[9] Trimethyl silylchlorochromate (TMSCC),[10] Zinc chlorochromate non-hydrate (ZCCNH),[11] Zinc dichromate trihydrate,[12] 3-carboxy-pyridinum chlorochromate (CPCC)[13] and 4-(dimethylamino) pyridinum chlorochromate (DMAPCC)[14] are prepared and used in the oxidation of organic compounds.

Despite of availability of these wide classes of reagents, the need for new methods are still exists. The main requirements of these methods are simplicity, mildness of conditions, effectiveness and selectivity in degree of oxidation.

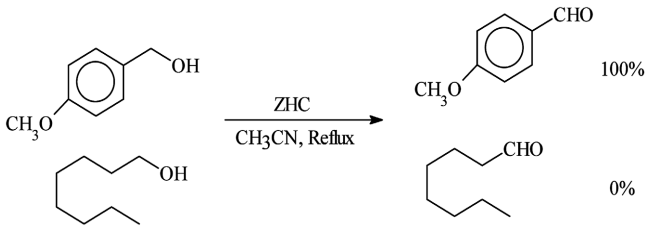
Here we wish to report zirconium hydroxide chromate[14] ($Zr_4(OH)_6(CrO_4)_5(H_2O)_2$) (ZHC) as a convenient, efficient and economical reagent for the oxidation of benzylic alcohol to the corresponding carbonyl compound in CH_3CN and H_2O (Scheme 1).

Zirconium hydroxide chromate which is a red octahedral crystalline compound was prepared from the $K_2Cr_2O_7$, $Zr(NO_3)_4$ and CrO_3.[15,16]

As shown in the Table 1, the rate of oxidation and yield of products depended on the nature of the substrate. Oxidations of benzylic alcohols with electron releasing groups (Entry 2-4) are faster than those with electron withdrawing group (Entry 5). 4-nitro-benzyl alcohol oxidizes to its corresponding aldehyde at very long time with 85% yield. Cinnamyl and allyl alcohol was converted to corresponding aldehyde in a high yield without cleavage of benzylic double bond (Entry 9, 10). Heterocyclic compounds such as pyrrol and thiophene alcohol oxidize to its corresponding aldehyde



Scheme 1



Scheme 2

(Entry 11-12). Primary and secondary aliphatic alcohols (Entry 13-15) did not oxidize under these conditions.

The reactions are relatively clean with no tar formation and no over oxidation to carboxylic acids were observed.

In order to show the chemoselectivity of the reagent for oxidation of alcohols, 4-methoxy benzyl alcohol in the presence of 1-octanol were subjected to oxidation with 2 mmol of the reagent and the only product isolated was 4-methoxy benzaldeyde (Scheme 2). These results clearly show that the presented method is potentially applicable for the chemoselective oxidation of benzylic alcohols versus saturated alcohols.

The lower acidity of this reagent in comparison with other chromates, simple preparation, stability, reactivity, easy work up procedure, chemoselectivity in oxidation and high yields make zirconium hydroxide chromate a versatile and a practical reagent for the oxidation of organic compounds.

Experimental Section

Zirconium hydroxide chromate (ZHC) (2-2.5 mmol) was added to a solution of alcohols (1 mmol) in CH_3CN or H_2O (5 mL). The resulting mixture was stirred at reflux or room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, silica gel (1 gr) was added to the mixture and the solvent was evaporated under reduced pressure. The resulting material was added on silica gel pad (3 cm thick) and washed with *n*-hexane/ethyl acetate (5 : 1, 200 mL). The filtrate was concentrated to afford the desired product in excellent yield.

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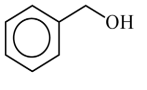
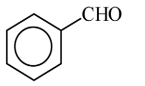
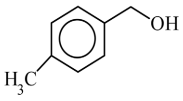
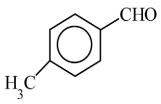
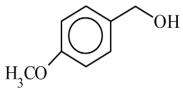
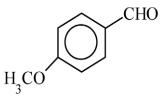
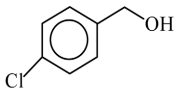
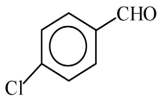
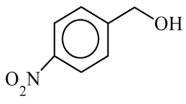
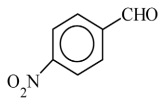
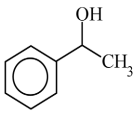
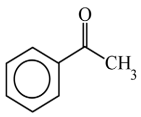
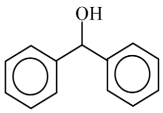
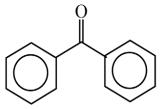
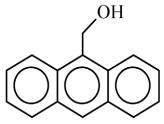
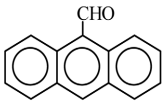
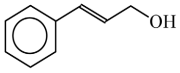
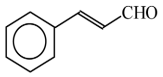
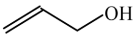
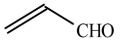
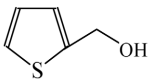
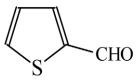
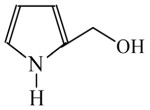
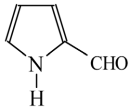
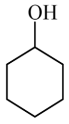
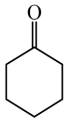
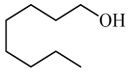
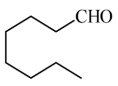
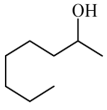
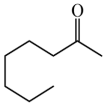
Table 1. oxidation of alcohols with ZHC

Entry	Substrate	Product	CH_3CN, Reflux		H_2O, R.T	
			Time (min)	Yield%	Time (min)	Yield%
1			30	90	30	85
2			30	93	30	88
3			20	90	30	90
4			120	90	180	85
5			12(h)	85	5(h)	85
6			30	93	30	90
7			60	92	30	85
8			40	90	50	88
9			120	85	100	85
10			180	80	120	80
11			40	90	40	88
12			50	85	40	90
13			No Reaction		No Reaction	
14			No Reaction		No Reaction	
15			No Reaction		No Reaction	

[a]Yields refer to isolated products and 2,4-dinitrophenyl-hydrazine derivative. Structures are confirmed by IR, ^{1}H-NMR, mp and bp.

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