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Regeneration of carbonyl compounds from their oximes with zirconium hydroxide chromate $[Zr_4(OH)_6(CrO_4)_5(H_2O)_2]$

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Zirconium hydroxide chromate $[Zr_4(OH)_6(CrO_4)_5(H_2O)_2]$ has been used as a stable, mild and efficient oxidising reagent to convent oximes to their corresponding carbonyl compounds in acetonitrile.

Keywords: zirconium hydroxide chromate, oxidation, oxime, carbonyl compound

Protection of aldehydes and ketones is an important transformation in the total synthesis.[1] Oximes are useful in organic chemistry as protecting groups, synthetic intermediates for producing amines[2] and nitriles[3] and also are utilised for purification and characterisation of aldehydes and ketones.[4]

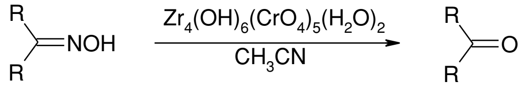
Regeneration of the carbonyl functionality from oxime, especially under mild reaction conditions, is also an important achievement from the synthetic points of view.

This transformation has been achieved by various methods which have been reviewed recently.[5] The other methods used for this purpose are: (a) hydrolytic methods which involve acidic[6] and neutral[7] conditions, (b) oxidative methods include utilisation of chromium (VI),[8] manganese,[9] thallium,[10] cerium[11] and lead,[12] (c) halogens[13] and halogenated compounds,[14] (d) reductive methods using reducing agents such as: $LiAlH_4$,[15] $Na_2S_2O_4$,[16] $Fe(CO)_5$,[17] $TiCl_4$/NaI [18] and VCl_2,[19] (e) enzymatic methods,[20] and (f) microwave irradiation techniques.[21]

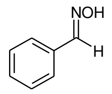
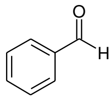
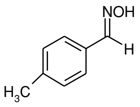
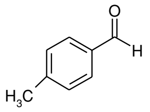
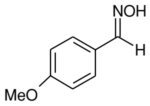
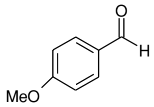
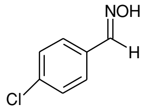
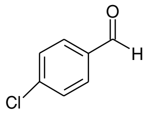
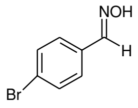
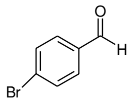
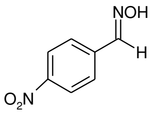
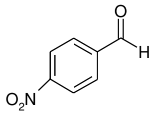
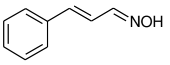
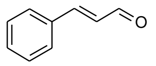
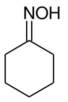
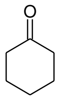
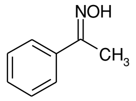
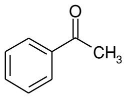
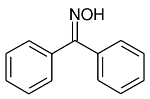
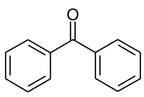
Some of these methods require drastic reaction conditions or the use of toxic and expensive compounds. We report here that zirconium hydroxide chromate[22] $[Zr_4(OH)_6(CrO_4)_5(H_2O)_2]$ as a convenient, efficient, economic oxidising agent for oxidation of oximes to corresponding aldehydes and ketones in acetonitrile. Zirconium hydroxide chromate was prepared from $K_2Cr_2O_7$, $Zr(NO_3)_4$ and CrO_3.[22] As depicted in Scheme 1, treatment of different oximes with this oxidising agent in acetonitrile at reflux temperature, afforded the corresponding carbonyl compounds in high yields.

As shown in Table 1, the rate of oxidation and yield of products depended on the nature of the substrate. Oxidations of benzaldeyde oximes with electron releasing groups (Entries 2–5) are faster than oxidation of 4-nitro benzaldeyde oxime with electron withdrawing group (Entry 6). Cinnamaldehyde oxime was converted to cinnamaldehyde in a high yield (90%) without cleavage of benzylic double bond. (Entry 7) Cyclohexanon oxime (Entry 8) did not oxidise under these conditions. Acetophenone and benzophenone oxime converted to the corresponding ketone in 20–30 min with 95% yield. (Entries 9 and 10)

We believe that this method is a novel and general strategy for deoximation of varieties of oximes to their carbonyl analogs. The rates of the reaction are fast and the yields are high. Availability, the cost of reagent, easy preparation, stability and activity of the reagent in acetonitrile and mild reaction conditions are other advantages of this reagent.



Scheme 1

Entry	Substrate	Product	Time/min	Yield[a]/%
1			30	90
2			20	92
3			20	90
4			40	85
5			40	85
6			90	85
7			40	90
8			n.r	–
9			20	95
10			30	95

[a]Yields refer to isolated products and 2,4-dinitrophenylhydrazine derivative. structures are confirmed By IR, ^1H NMR, ^{13}C NMR, m.p./b.p.

Experimental

Oxidation products were characterised by comparison with authentic samples (IR, ^1H NMR, and TLC). All yields refer to isolated products.

General procedure

Zirconium hydroxide chromate (2–3 mmol) was added to a solution of oxime (1 mmol) in acetonitrile (8 ml). The mixture was stirred

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magnetically at reflux. The progress of the reaction was followed by TLC. When the reaction was completed, silica gel (6 g) was added and the solvent was evaporated under reduced pressure. The resulting powder was applied on a silica gel pad and was washed with an appropriate amount of solvent (n-hexane–ethyl acetate, 5:1). The yield of benzaldeyde product was determined as its 2,4 dinitro phenyl hydrazone derivative.

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