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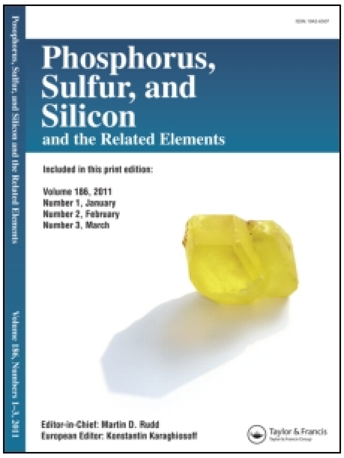

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WET ALUMINA-SUPPORTED CHROMIUM (VI) OXIDE: A MILD, EFFICIENT, AND INEXPENSIVE REAGENT FOR OXIDATIVE DEOXIMATION

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Online publication date: 16 August 2010

To cite this Article Heravi, Majid M. , Ajami, Darush , Shoar, Rahim Hekmat , Sarmad, Nooshin and Faridbod, Farnoush(2004) 'WET ALUMINA-SUPPORTED CHROMIUM (VI) OXIDE: A MILD, EFFICIENT, AND INEXPENSIVE REAGENT FOR OXIDATIVE DEOXIMATION', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 12, 2423 — 2427

To link to this Article: DOI: 10.1080/10426500490485264

URL: http://dx.doi.org/10.1080/10426500490485264

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Phosphorus, Sulfur, and Silicon, 179:2423–2427, 2004
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490485264

WET ALUMINA-SUPPORTED CHROMIUM (VI) OXIDE: A MILD, EFFICIENT, AND INEXPENSIVE REAGENT FOR OXIDATIVE DEOXIMATION

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(Received February 20, 2004; accepted April 20, 2004)

A mild, efficient, and inexpensive method for the direct conversion of oximes to carbonyl compounds upon treatment with wet alumina-supported chromium (VI) oxide is described.

Keywords: Chromium (VI) oxide; oxidative deoximation; wet alumina

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INTRODUCTION

Oximes are very useful protecting groups and are extensively used for purification and isolation of carbonyl compounds. Since oximes can be synthesized from noncarbonyl compounds,[2] their synthesis provides an alternative pathway to aldehydes and ketones. Oximes are also useful in the preparation of amides via the Beckman rearrangment.[3] Regeneration of carbonyl compounds from their oximes was even more important after the discovery of the Barton reaction, in which oximes are produced at a nonactivated hydrocarbon site.[4] Although literature enumerates quite a number of methods for the conversion of oximes into carbonyl compounds,[5] the important role of oximes as protecting groups owing to their hydrolytic stability has provided motivation for the development of newer, milder, more efficient, and less expensive reagents.

Financial support for this research from Azzahra University research council is gratefully appreciated.

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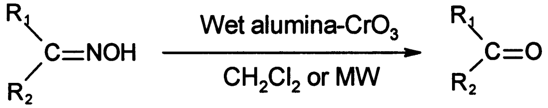
Chromium-based reagents have been used extensively in organic synthesis.[6] The concept of utilizing reagents[7] adsorbed on inert inorganic supports for organic synthesis has been reported and applied especially to chromium compounds.

In view of the current focus on using supported reagents on various solid inorganic surfaces,[8] there is merit in developing a truly heterogeneous reaction for the cleavage of oximes using mild, efficient, and inexpensive reagents. In this communication we wish to report the use of wet alumina-supported reagents chromium (VI) oxide as a mild, efficient, and inexpensive reagent for oxidative deoximation in nonaqueous condition. The reaction proceeds efficiently in high yields at refluxing temperature within a few minutes (Scheme 1).



SCHEME 1

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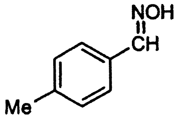
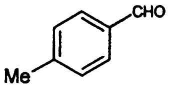
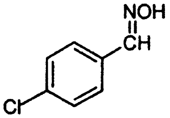
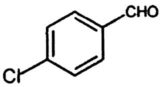
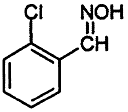
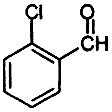
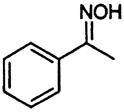
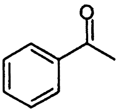
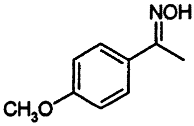
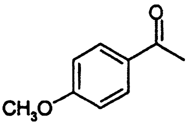
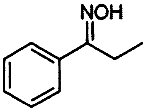
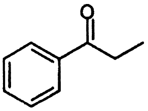
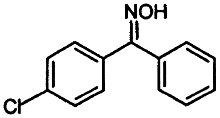
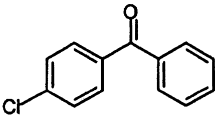
Chromium (VI) oxide was mixed with alumina and reacted with oximes in CH_2Cl_2. In the absence of alumina the reaction did not occur and, in the presence of alumina the reaction was sluggish, and considerable amounts of starting material were recovered unchanged at room temperature or even under refluxing for an extended period of time. As an example, the reaction of benzaldoxime with dry alumina-CrO_3 resulted in the formation of 35% benzaldehyde.

However, when alumina was premoistened and then mixed with chromium oxide, benzaldoxime was converted to benzaldehyde almost quantitatively in CH_2Cl_2 at room temperature.

To assess the generality of this oxidative deoximation method a variety of oximes were reacted under these conditions, and they yielded the corresponding carbonyl compounds in good-to-excellent yields (Table I). Aliphatic oximes gave low yields.

In conclusion, by comparison with presently existing methods, wet alumina-supported chromium (VI) oxide has advantages. Mild conditions, efficiency, selectivity, high yield, and being inexpensive are the main advantages of this procedure. The only draw back for this method is that in the case of none-benzylic oximes poor yields of deoximation were obtained.

TABLE I Oxidative Cleavage of Oximes with Wet Alumina-CrO_3 in CH_2Cl_2

Entry	Substrate[a]	Carbonyl compound[b]	Reaction time (min)	Yield[c] (%)
1			40	90
2			40	85
3			40	83
4			40	82
5			40	85
6			40	84
7			40	82

[a] All substrates were synthesized by known literature procedure.

[b] All products were characterized by comparison of their m.p., IR, and ^{1}HNMR spectra with those of authentic samples.

[c] Yields refer to isolated products.

EXPERIMENTAL

All oximes were prepared by standard methods.[9] Products were isolated, and their physical data were compared with those of known samples. Yields given in Table I refer to isolated products. Wet alumina was prepared by shaking neutral aluminum oxide (10 g, Aldrich-Brockmann, 150 mesh) with distilled water (2 ml). The reagent

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was prepared by mixing CrO_3 (0.8 g, 0.8 mmol) with wet alumina (2.4 g) using pestle and mortar.

General Procedure

In a flask (50 ml) a solution of 1 mmol of oxime in 20 ml of CH_2Cl_2 was prepared. Wet alumina-supported chromium oxide (0.06 g) was added, and the mixture was stirred magnetically for 40 min. The progress of reaction was monitored by thin layer chromatography (TLC) (eluent: hexane, EtOAC, 8:2). The mixture was filtered, and the solid material was washed with CH_2Cl_2. The filtrate was evaporated on a rotary evaporator, and the crude residue was directly subjected to column chromatography using the appropriate eluent. Pure carbonyl compounds were obtained in good-to-excellent yields (Table I).

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