

Communication

Tungstate Sulfuric Acid (TSA)/ KMnO_4 as a Novel Heterogeneous System for Rapid Deoximation

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Abstract: Neat chlorosulfonic acid reacts with anhydrous sodium tungstate to give tungstate sulfuric acid (TSA), a new dibasic inorganic solid acid in which two sulfuric acid molecules connect to a tungstate moiety via a covalent bond. A variety of oximes were oxidized to their parent carbonyl compounds under mild conditions with excellent yields in short times by a heterogeneous wet TSA/ KMnO_4 in dichloromethane system.

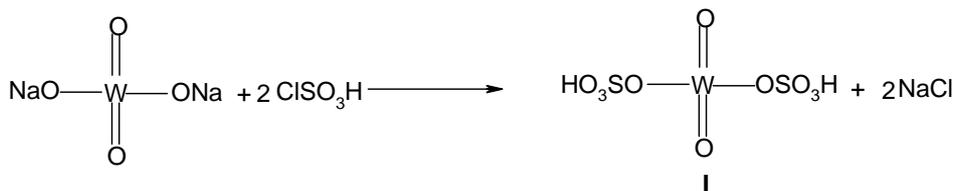
Keywords: Tungstate sulfuric acid, Oximes, Heterogeneous conditions, Solid acid

Introduction

Heterogenization of chemical systems is currently an active field of research in industrial and academic chemistry because of the resulting simplification in handling procedures and work-ups, reduction of corrosion and, from a Green Chemistry point of view, easy and clean reactions and avoidance of by-products. Considering the wide applications of acids as reagents or catalysts in organic chemistry (for producing more than 1×10^8 MT/year of products), the introduction of new inorganic solid acids can be useful in this context. Recently silica-sulfuric acid [1] and Nafion-H[®] [2] have been used for a wide variety of reactions such as production of disulfides from thiols, oxidation of 1,4-dihydropyridines [3], N-nitrosation of secondary amines [4], deprotection of acetals [5], oxidation of alcohols [6], alkylation with olefins, alkylhalides, alkyl esters, isomerization, transalkylation, acylation, nitration, ether and ester synthesis, acetal formation and rearrangement chemistry [7]. In continuation of the above and our own studies [8] on the application of inorganic solid acids, we have now found that anhydrous sodium tungstate reacts in a 1:2 mole ratio with

chlorosulfonic acid (Scheme 1) to give tungstate sulfuric acid (TSA, **I**) in a simple and clean reaction that did not require any work-up.

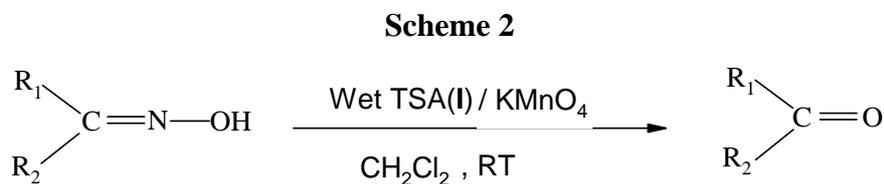
Scheme 1.



After preparation of TSA (**I**), we were interested in examining its use as a proton source in combination with KMnO_4 and water in dichloromethane as a heterogeneous system for the cleavage of oximes to regenerate the corresponding aldehydes or ketones. This is an important reaction because oximes serve as efficient carbonyl protective groups and are used extensively for the purification and characterization of such compounds. A number of methods have been reported for deoxygenation, among which we may mention chromium trioxide [9], 3-carboxypyridinium chlorochromate [10], sodium perborate [11], peroxymonosulphate ion [12], *tert*-butylhydroperoxide [13], ammonium persulphate-alumina under microwave irradiation [14] Dess-Martin periodinane [15], 1-benzyl-4-aza-1-azonia-bicyclo[2.2.2]-octane periodate [16], microwave assisted sodium periodate supported on silica [17] and KMnO_4 -dicyclohexyl-18-crown-6 [18, 19]. Classically, the recovery of the parent carbonyl compounds from oximes involves a hydrolytic cleavage which removes the hydroxylamine from equilibrium [20]. However; many of these existing methods either employ highly toxic reagents or, in the case of aldoximes, result in further oxidation of liberated aldehydes to their corresponding carboxylic acids.

Results and Discussion

In this article we wish to report a new, simple and convenient method for the effective deprotection of the oximes under mild and heterogeneous conditions using wet TSA (**I**)/ KMnO_4 in dichloromethane (Scheme 2). Different kinds of oximes were subjected to this oxidative deprotection reaction and the results are summarized in Table 1.



As evident from the results, aldoximes were generally deprotected relatively faster than ketoximes (cf. entries 1-2, 14 and 16-18). It was also interesting to note that by controlling the amounts of reagents used, it was possible to avoid further oxidation of the liberated aldehydes to the corresponding carboxylic acids (entries 1-3 and 14-18), therefore this system behaves chemoselectively towards the oxime function with controlled amounts of reagents. Oximes bearing substituents susceptible to acidic media (entries 14 and 15) did not undergo hydrolysis of these functional groups.

Table 1. Regeneration of carbonyl compounds from oximes using a heterogeneous wet TSA (I)/ KMnO₄ system in dichloromethane

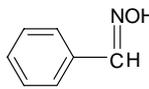
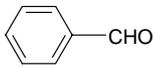
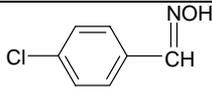
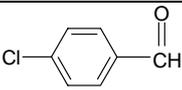
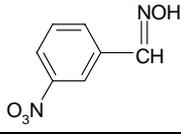
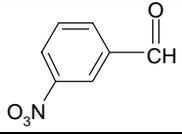
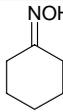
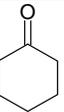
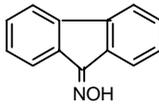
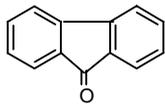
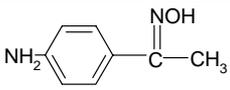
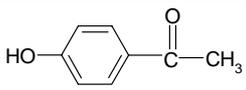
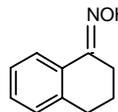
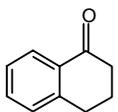
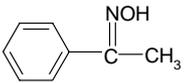
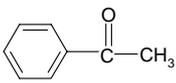
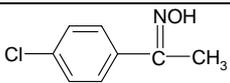
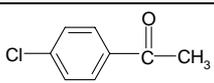
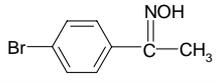
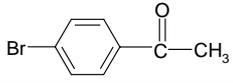
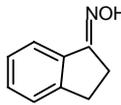
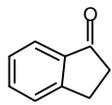
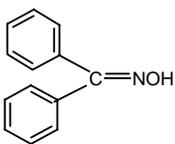
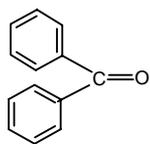
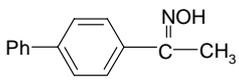
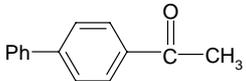
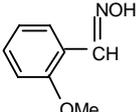
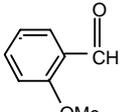
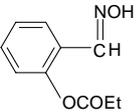
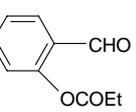
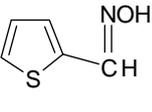
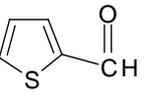
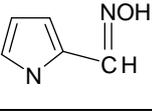
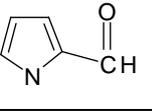
Entry	Oxime substrate	Product ^a	Time (min.)	Yield (%) ^b
1			10	91
2			5	90
3			5	92
4			12	90
5			10	93
6			10	90
7			8	92
8			10	94
9			12	90
10			8	90
11			8	94
12			15	91
13			10	92

Table 1. Cont.

14			5	90
15			12	90
16			8	92
17			10	90
18	$n\text{-C}_7\text{H}_{15}\text{-CH=NOH}$	$n\text{-C}_7\text{H}_{15}\text{-CHO}$	8	90

^a Characterized by ¹H-NMR and IR spectral analysis and comparison of TLC and physical data with authentic samples [22].

^b Yields refer to isolated and purified products.

To identify of the nature of the agent responsible for deoxygenation in our conditions, three parallel control experiments were designed using the oximes of entries 1, 3, 5 and 13: a first reaction in the presence of wet TSA, another using only wet KMnO₄ and the third one in the presence of the proposed wet TSA/KMnO₄ combination. The results showed that neither wet TSA nor wet KMnO₄ alone could accomplish the deoxygenation reactions to any great extent, even after reaction times of up to 10 h, while as the results in Table 1 show, deoxygenation was complete in 15 min. or less when the wet TSA/KMnO₄ system was used. It is well known that KMnO₄ requires an acidic medium to function as an oxidant, consequently we propose an oxidative mechanism for this reaction in which the wet TSA acts as a proton source for the KMnO₄ to oxidize the oximes.

Conclusions

In summary, we think TSA (**I**) represents a good solid acid for reactions in which protons are need as catalysts or reagents due to its efficiency, easy preparation, low cost and availability, insolubility towards all organic solvents, simplicity of handling, convenient work-up of products, clean reactions, short reaction times and high reaction yields. In this paper we have reported a convenient, efficient and practical method for the oxidative cleavage of oximes. Structural investigation of TSA (**I**) and similar solid acids and other applications of these reagents in various organic reactions are current research objectives in our laboratory.

Experimental

General

Chemicals were purchased from the Merck, Fluka and Aldrich chemical companies. Oximes were prepared from the corresponding carbonyl compounds according to the reported procedure [21]. The reactions were monitored by TLC. The products were isolated and identified by comparison of their physical and spectral data with authentic samples. IR spectra were recorded on a Jasco FT-IR 680 instrument. ¹H-NMR data were obtained on a Bruker-DPX-300 MHz Avance 2 instrument. Mass spectra were recorded on an AMD 604 spectrometer, operating in EI-mode at 70 eV and FT-mode at 0.005 V.

Preparation of tungstate sulfuric acid (TSA, **I**).

Anhydrous sodium tungstate (29.38 g, 0.1 mol) was added gradually to chlorosulfonic acid (23.304 g, 13.31 mL, 0.2 mol) contained in a 250 mL round bottomed flask placed in an ice-bath. After the completion of the addition the mixture was shaken for 1 h. A yellowish-white solid of TSA was obtained (40.2 g, 98.0 %), m.p. 285 °C (dec.); IR (KBr, cm⁻¹): 3600-2200 (OH, bs), 1240-1140 (S=O, bs), 1060 (S-O, m), 1005 (S-O, m), 880-840 (W=O, m), 450 (W-O, m).

Typical deoximation procedure: oxidation of 3-nitrobenzaldoxime (Table 1, entry 3).

To a solution of 3-nitrobenzaldoxime (0.152 g, 1 mmol) in dichloromethane (10 mL), wet TSA (**I**, 10% w/w, 1.05 g, 2 mmol) and KMnO₄ (0.316 g, 2 mmol) were added. The reaction mixture was stirred at room temperature and the transformation was determined to be finished after 5 min. by TLC (1:1 *n*-hexane-ethyl acetate). The reaction mixture was filtered and the solids washed with dichloromethane (2 × 4 mL). The filtrate was evaporated under reduced pressure and the resulting crude material was purified by flash chromatography on SiO₂ (eluent: CH₂Cl₂) to afford 3-nitrobenzaldehyde (0.139 g, 92%), m.p. = 42-43 °C (lit.[22] mp 42 °C); IR (KBr, cm⁻¹): 3050 (m), 2950 (m), 1685 (s), 1610 (m), 1570 (m), 828 (m), 760 (m); ¹H-NMR (CDCl₃): 7.9 (s, 1H), 8.0-8.4 (m, 4H) ppm; MS: m/z=151.

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Sample Availability: Available from the authors.