

Tungstate Sulfuric Acid (TSA)/NaNO₂ as a Novel Heterogeneous System for Rapid Deoximation

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Received April 14, 2005

Key Words : Tungstate sulfuric acid, Oximes, Heterogeneous conditions, Solid acid

Today, heterogenation of the chemical systems is active field in industrial and laboratorial chemistry because of simplification in handling procedures, reduction of corrosion, green chemistry point of view, avoidance of by-products, easy and clean reaction and simple work-up. Considered to wide application of acids as reagent or catalyst in organic chemistry, (for producing more than 1×10^8 mt/year of products) introduction of new inorganic solid acid can be useful in this direction. Recently silica sulfuric acid¹ 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 alcohols⁶ and alkylation with olefins, alkyhalides, alkyl esters, isomerization, transalkylation, acylation, nitration, ether and ester synthesis, acetal formation and rearrangement chemistry.⁷ In continuation of above and our studies⁸ on the application of inorganic solid acids, we found that anhydrous sodium tungstate reacts with chlorosulfonic acid (1 : 2 mole) to give tungstate sulfuric acid TSA (**I**). The reaction was performed easy, clean and without any work-up (Scheme 1).

After preparation of TSA (**I**), we were interested to examine it as proton source in combination with NaNO₂ as heterogeneous system for oxidative deprotection of oximes to related carbonyl compounds.

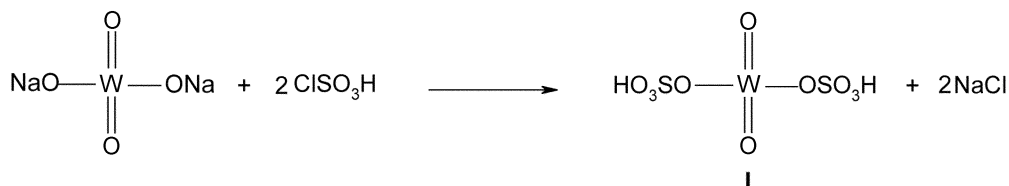
The cleavage of oximes to regenerate aldehydes and ketones is an important reaction because oximes serve as efficient protective groups for aldehydes and ketones and

extensively used for the purification and characterization of carbonyl compounds. A number of methods have been reported for deoximation. Among these are; chromium trioxide,⁹ 3-carboxy-pyridiniumchlorochromate,¹⁰ Sodium perborate,¹¹ peroxymonosulphate ion,¹² *tert*-butyl hydrogenperoxide,¹³ ammonium persulphate-alumina using microwave,¹⁴ Dess-martin periodinane,¹⁵ 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane periodate,¹⁶ microwave assisted sodium periodate supported on silica¹⁷ and KMnO₄-dicyclohexyl-18-crown-6.^{18,19}

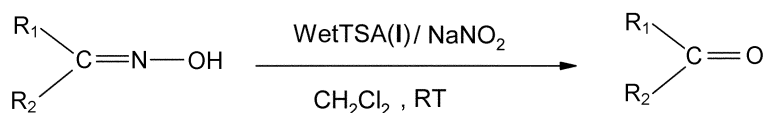
Classically, the recovery of the parent carbonyl compounds from oximes involves hydrolytic cleavage which removes the hydroxylamine from equilibrium.²⁰⁻³⁰ However; many of these existing methods either employ highly toxic reagents or give further oxidation of liberated aldehydes into their carboxylic acids.

In this article we wish to report simple and convenient method for the effective deprotection of oximes under mild and heterogeneous conditions. Different kinds of oximes were subjected to the oxidative deprotection reaction in the presence of wet (10%w/w) TSA (**I**)/NaNO₂ in dichloromethane (Scheme 2). The reactions were done under mild and heterogeneous conditions. The results are summarized in Table 1.

As evident from the results presented in Table 1 aldoximes were generally deprotected relatively sooner than ketoximes (entry 1-2, 14 and 16-18). Also it was interesting that by controlling of amount of reagents, liberated aldehydes (entry 1-3 and 14-18) *via* reaction were not further oxidized to the



Scheme 1



Scheme 2

Table 1. Regeneration of carbonyl compounds from oximes using heterogeneous Wet (10%w/w) TSA (**I**)/NaNO₂ system in dichloromethane

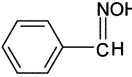
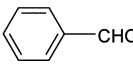
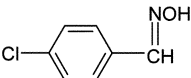
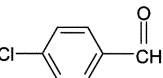
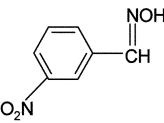
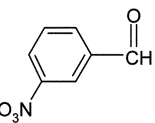
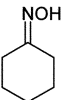
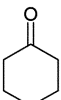
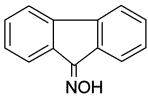
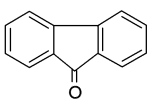
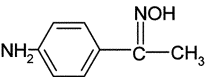
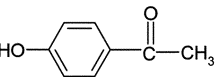
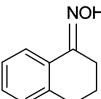
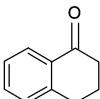
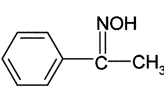
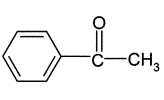
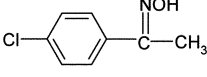
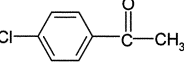
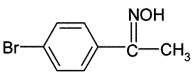
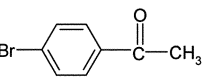
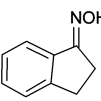
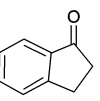
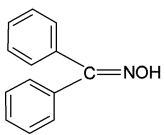
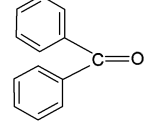
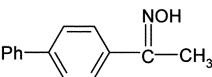
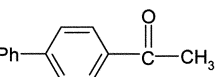
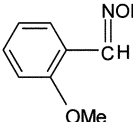
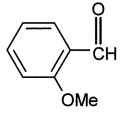
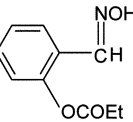
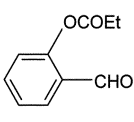
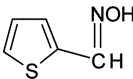
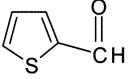
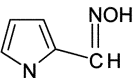
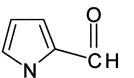
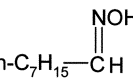
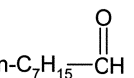
Entry	Substrate (oxime)	Product ^a	Time (min.)	Yield (%) ^b
1			7	92
2			5	93
3			8	95
4			5	94
5			10	95
6			7	90
7			8	94
8			10	97
9			5	93
10			4	92
11			8	95
12			13	93
13			10	94

Table 1. Continued

Entry	Substrate (oxime)	Product ^a	Time (min.)	Yield (%) ^b
14			5	93
15			11	92
16			5	94
17			6	93
18			9	92

^aCharacterized by ¹H NMR and IR spectral analysis and comparison (TLC) and physical data with authentic samples³¹. ^bYields refer to isolated and purified product.

corresponding carboxylic acids. Oximes bearing susceptible substituent (entry 14 and 15) to acidic media was not undergone the hydrolysis reaction. On the other hand although we suggest deprotection reaction proceeds *via in situ* generation of HNO₂ and then NO⁺ ions as oxidant species that run oxidative cleavage of oximes to regenerate of parent carbonyl compounds, these oxidant ions (NO⁺) did not attack to electron rich benzene ring (entry 14) to nitrosate it. Therefore this system behaves chemoselective only on oxime site in controlled amounts of reagents. In the case of 4-aminoacetophenon (entry 6) at first the deamination was done (*via* diazonium salt formation) and deoxygenation completed using one mole excess NaNO₂.

We suggested, TSA (**I**) play a catalytic role. To test it, recovered TSA (**I**) from the deoxygenation reaction of oximes of entries 2, 12 (washed by dichloromethane and methanol or ethanol after filtration) was used again in other reaction with NaNO₂ and related carbonyl compounds were obtained in 90% and 92% that this supported our suggestion about catalytic role of TSA (**I**).

In conclusion, we think TSA (**I**) is a good solid acid in the reaction in which proton is need as catalyst or reagent due to efficiency, easy production, insolubility to all organic solvents, simple for handling, convenient work-up of products, cheap and available, clean reactions, short times and high yields of reactions. In this paper we reported a convenient, efficient and practical method for oxidative cleavage of oximes. Structural investigation of TSA (**I**) and similar solid acids, other application of them in various organic reactions are current researches in our laboratory.

Experimental Section

General. Chemicals were purchased from Merck, Fluka, Aldrich chemical companies. Oximes were prepared from the corresponding carbonyl compounds according to the reported procedure. 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 FT-IR Jasco-instrument model. ¹H NMR data were obtained on 300 MHz Bruker model.

Preparation of tungstate sulfuric acid (I). To a 0.2 mol chlorosulfonic acid (23.304 g, 13.31 mL) in 250 mL round bottom flask equipped with ice-bath 0.1 mol (29.38 g) anhydrous sodium tungstate was added gradually. After the completion of addition the mixture was shaken for 1 h. A yellowish-white solid (TSA) of 40 g was obtained.

Typical experimental procedure for oxidation of 3-nitrobenzaldehyde. To a solution of 1 mmol (0.152 g) 3-nitrobenzaldehyde in 10 mL dichloromethane, 2 mmol (1.158 g) wet (10%w/w) TSA (I) and 2 mmol (0.069 g) NaNO₂ were added. The reaction mixture was stirred at room temperature and completed as monitored by TLC (n-hexane: ethylacetate 1 : 1) after 8 min. The reaction mixture was filtered and washed with 4 mL dichloromethane. The filtrate was evaporated under reduced pressure and the resulting crude material was purified by flash chromatography on SiO₂ (eluent: CH₂Cl₂) to afford 0.1436 g, (95%) of 3-nitrobenzaldehyde, m.p = 42-43 °C [Lit.³¹ mp 42 °C]. IR (KBr): 3050 (m), 2950 (m), 2760 (m), 1685 (s), 1610 (m), 1570 (m), 1360 (m), 828 (m), 760 (m) cm⁻¹; ¹H-NMR (CDCl₃, 300 MHz): 9.7 (s, 1H), 8.0-8.4 (m, 4H) ppm; MS: m/e = 151.

Acknowledgement. We are thankful to the Yasouj University for partial support of this work.

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