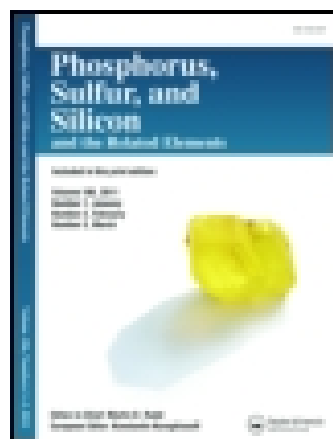


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Tandem Conversion of Protected Alcohols to Oximes

Tandem and Selective Conversion of Tetrahydropyranyl and Silyl Ethers to Oximes Catalyzed with Trichloroisocyanuric Acid

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Abstract: Direct and oxidative conversion of tetrahydropyranyl and silyl ethers to oximes is described using trichloroisocyanuric acid (TCCA) as a relatively stable and inexpensive oxidant surprisingly in a *catalytic* amount and hydroxylamine hydrochloride under solvent-free conditions. Oximes can be synthesized from these protected alcohols in the presence of some other functional groups with excellent chemoselectivity using the present tandem catalytic method.

Keywords: Tetrahydropyranyl ether, Silyl ether, Oxime, Trichloroisocyanuric acid, Tandem synthesis.

Introduction

Oximes have useful applications in organic synthesis. These stable compounds may be served as intermediates for the preparation of nitriles via dehydration,^{1,2} amides by the Beckmann rearrangement,³ nitrones,⁴ hydroximinoyl chlorides,⁵ nitrile oxides,⁵ chiral α -sulfinyl oximes,⁶ and nitro compounds.⁷ In addition, oximes have been used as selective α -activating groups⁸ and also for the protection of carbonyl groups.⁹ Some oximes treat as highly active and effective inhibitors.^{10,11} Also, oximation is a very efficient and useful way for characterization and purification of carbonyl compounds. Therefore, the attention of synthetic organic chemists is directed to a facilitation of oxime synthesis from carbonyl compounds or even other sources. Oximes are usually prepared via treatment of aldehydes or ketones with hydroxylamine hydrochloride in a basic aqueous medium with adjustment of pH. In addition, a large number of other methods have been reported for performing of this transformation.¹²⁻¹⁴ However, some methods in this area contain some disadvantages such as low yields, long reaction times, inability for the preparation of aromatic ketoximes, effluent pollution and tedious work up. Also, as far as we know the oximes synthesis directly from alcohols have been reported very less than from aldehydes or ketones especially in a catalytic manner. Two reported methods in this field are the use of a two step procedure involving substitution with $\text{PPh}_3/\text{DEAD}/O\text{-TBS-}N\text{-tosylhydroxylamine}$ in toluene-THF and subsequent treatment with CsF in acetonitrile¹⁵ and also the use of activated MnO_2 , 4 Å molecular sieves as dehydrating additive and alkoxyamines (and in certain cases, hydroxylamine itself) as their hydrochloride salts or supported on Amberlyst 15 in CH_2Cl_2 at reflux for overnight.¹⁶ However, these methods do not perform this transformation in a catalytic manner and use stoichiometric amounts of the reagents or even more for this

purpose. For example, in the latter work manganese dioxide is used in excess amounts (5-20 equiv.). Furthermore, the use of gold supported on hydroxyapatite (Au/HAP) (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) as catalyst in toluene as solvent at 90 °C under O_2 bubbling¹⁷ and also 1-methylimidazolium nitrate [Hmim][NO_3] as an acidic ionic liquid under microwave irradiation¹⁸ have also been reported for performing of this transformation. However, these methods converting alcohols directly to oximes also suffer from some other disadvantages such as long reaction times, the use of a two step procedure or reagent that is not easily available, low yields, tedious work up especially in the case of using MnO_2 , performing of this transformation in the acidic conditions and also do not provide chemoselectivity or at least, chemoselectivity of the method is ambiguous. Finally, as far as we know there is no report in the literature concerning the tandem catalytic conversion of tetrahydropyranyl and silyl ethers to oximes.

Consequently, there is a need for the development of new methods that are more convenient for the oxime synthesis especially from tetrahydropyranyl and silyl ethers. On the other hand, tandem reactions that contain multiple chemical transformations in a single-pot provide minimal work up and less waste generation in organic synthesis.¹⁹ These reactions involve the advantage that intermediates do not require isolation specially where they are unstable or difficult to handle. Also, the elimination of volatile organic solvents in organic syntheses is a most important goal in green chemistry. The solvent-free reactions²⁰ have some advantages such as formation of cleaner products, improved reaction rates, low costs, enhanced selectivity, simplicity in process and handling and prevent waste solvent generation, hazards, and toxicity.

Herein, due to importance of oximes and their synthesis especially from protected alcohols and on the other hand the importance of tandem and solvent-free reactions and also in continuation of our previous work on the tandem conversion of benzylic alcohols to oximes catalyzed with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ),²¹ we now report an ease, chemoselective and tandem conversion of primary and secondary benzylic, nonbenzylic and cyclic tetrahydropyranyl (THP) and trimethylsilyl (TMS) ethers to oximes using a catalytic amount of trichloroisocyanuric acid (TCCA) as a relatively stable and inexpensive oxidant in the presence of hydroxylamine hydrochloride under solvent-free conditions (Scheme 1).

It must be noted that the present method needs to merely a catalytic amount (instead of stoichiometric amounts) of TCCA in the presence of hydroxylamine hydrochloride for performing of this tandem transformation.

Results and Discussion

Initially, we took benzyl THP ether as an example and optimized the reaction conditions for its direct conversion to benzaldoxime using a mixture of trichloroisocyanuric acid (TCCA) and hydroxylamine hydrochloride (NH₃OHCl). The results are shown in Table 1.

As shown in this table, this reaction did not provide satisfactory results using TCCA (3 mol %) and NH₃OHCl (1.2 eq.) under solvent-free conditions even at 110°C. In this case, benzaldoxime was produced in 50% yield after 40 min (Table 1, entry 1). The yield and rate of this reaction was increased with increasing of TCCA (Table 1, entry 2). On the other hand, decreasing of temperature caused to decrease of the yield and rate of this reaction so that it was completely unsuccessful at room temperature (Table 1, entries 3, 4 and 5). Also, this reaction

was studied in refluxing CH_2Cl_2 and CH_3CN . This study showed that the operation of this reaction in these solvents under reflux condition does not provide satisfactory results compared to under solvent-free condition (Table 1, please compare entries 6 and 7 with 2). Finally, the use of TCCA/ NH_3OHCl (0.05:1.2) under solvent-free condition at 110 °C (Table 1, entry 2) was selected as the optimized reaction conditions for this transformation and applied for conversion of other tetrahydropyranyl ethers directly to their corresponding oximes. The results are shown in Table 2. In the next step, we extended the present method on the silyl ethers for their conversion directly to oximes. However, the optimized reaction temperature was determined at 100 °C in this case. The results are shown in Table 3.

As shown in these tables, primary and secondary benzylic and nonbenzylic, allylic and cyclic tetrahydropyranyl and trimethylsilyl ethers are directly converted to the corresponding oximes in moderate to generally excellent yields using a catalytic amount of TCCA (5 mol %) in the presence of hydroxylamine hydrochloride (1.2 eq.) at 110 and 100 °C respectively under solvent-free conditions. The present tandem catalytic method can also be considered as a way for characterization of the above mentioned types of THP and TMS ethers. In addition, these tables show that THP ethers are converted to oximes generally faster than TMS ethers. In addition, for obtaining deeper insight into the applicability, selectivity and limitations of this new method, the possibility of the conversion of 4-fluorobenzyl THP or TMS ether to 4-fluorobenzaldoxime was studied in the presence of some other functional groups in different binary mixtures. For this purpose, a mixture of TCCA/ NH_3OHCl (0.05:1.2) was prepared under solvent-free conditions in an oil bath at 110 or 100 °C followed by addition of 4-fluorobenzyl THP or TMS ether

respectively and other organic compound (1:1). The conversion yields obtained for these selective reactions of different binary mixtures are shown in Table 4.

As shown in this Table, it was found that aliphatic tetrahydropyranyl and trimethylsilyl ethers can be directly converted to their corresponding oximes in the presence of aromatic ones, epoxides, carboxylic esters or acids, and aldehydes with excellent chemoselectivity using the present method. In addition, benzylic tetrahydropyranyl or trimethylsilyl ethers containing electron withdrawing group at phenyl ring can be efficiently converted to oximes in the presence of benzylic THP or TMS ethers containing electron donating group with excellent chemoselectivity *via* the present method (Table 4, entry 6).

Experimental

Solvents, reagents and chemicals were obtained from Merck (Germany) and Fluka (Switzerland) Chemical Companies. Tetrahydropyranyl and trimethylsilyl ethers were prepared according to the literature.²² Products are known compounds^{21, 23} and were characterized by comparison of their physical or spectral data with authentic samples. Fourier transform-infrared (FT-IR) spectra were recorded on a Perkin-Elmer RXI spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DRX-400 spectrometer. Thin-layer chromatography (TLC) was carried out on silica-gel 254 analytical sheets obtained from Fluka.

Typical procedure for the conversion of 4-chlorobenzyl tetrahydropyranyl ether to 4-chlorobenzaldehyde oxime using NH_3OHCl catalyzed with TCCA

Hydroxylamine hydrochloride NH_3OHCl (0.083 g, 1.2 mmol) was added to a flask containing 4-chlorobenzyl tetrahydropyranyl ether (0.226 g, 1 mmol) and TCCA (0.012 g, 0.05 mmol) under solvent-free conditions in an oil bath at 110 °C. The mixture was stirred until TLC showed the completion of the reaction (60 min). Dichloromethane (5 mL) was added to the reaction mixture after cooling to room temperature. The reaction mixture was filtered and then the solvent was evaporated. The crude mixture was subjected to column chromatography on silica gel 60 (0.063-0.200 mm) using petroleum benzene-ethyl acetate (30:1) as eluent to give 4-chlorobenzaldehyde oxime (0.148 g) in 95% yield; ^1H NMR (CDCl_3 , 400 MHz): 7.44-7.46 (m, 2H), 7.59-7.61 (m, 2H), 8.15 (s, 1H), 11.39 (br, 1H) ppm; ^{13}C NMR (CDCl_3 , 100.6 MHz): 128.5, 129.2, 132.4, 134.2, 147.6 ppm.

The reaction conditions for the tandem conversion of TMS ethers to the corresponding oximes is the same as to THP ethers via the present method except the reaction temperature which is adjusted at 100 °C.

Conclusions

In conclusion, in spite of many reports in the literature about the oxidation of tetrahydropyranyl and silyl ethers to carbonyl compounds with various oxidants in stoichiometric amounts or even more, the present investigation has demonstrated that the use of a *catalytic* amount of TCCA in the presence of hydroxylamine hydrochloride under solvent-free conditions offers a simple and tandem method for the conversion of primary and secondary benzylic and nonbenzylic tetrahydropyranyl and trimethylsilyl ethers to their corresponding oximes in good to excellent yields. Oximes can be synthesized from these ethers even in the presence of some other functional groups with excellent chemoselectivity *via* the present method. Commercially

availability, relatively cheapness and easy to handle of the catalyst, easy work up, relatively low reaction times especially in the case of THP ethers, avoiding the use of any additives such as molecular sieves and applicability for the conversion of both primary and secondary these ethers can be considered as the other significant advantages of the present tandem method. In addition to synthetic importance, this one-pot oximation method can be used as a way for characterization of these ethers.

Also, it must be noted that the present method belongs to green chemistry because: 1) It contains a tandem procedure. 2) It is operated under solvent-free conditions. 3) It needs to a catalytic amount of TCCA for operation.

Acknowledgments

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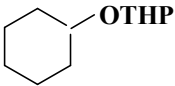
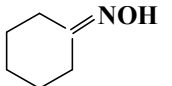
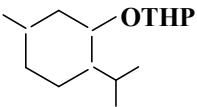
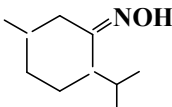
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Table 1: Conversion of benzyl THP ether to benzaldoxime using a mixture of TCCA as catalyst and NH_3OHCl in various conditions.

Entry	Solvent	Molar ratio ^a	Temp.(°C)	Time (min)	Yield (%)
1	-	1:0.03:1.2	110	40	50
2	-	1:0.05:1.2	110	30	98
3	-	1:0.05:1.2	90	150	90
4	-	1:0.05:1.2	70	420	90
5	-	1:0.05:1.2	r.t.	90	0
6	CH_2Cl_2	1:0.05:1.2	reflux	90	0
7	CH_3CN	1:0.05:1.2	reflux	90	70

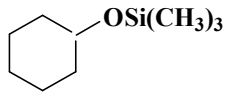
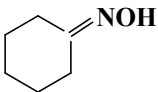
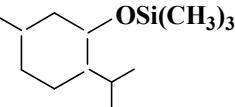
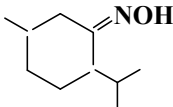
^a Molar ratio is related to THP ether:TCCA: NH_3OHCl .

Table 2: Conversion of THP ethers to oximes using a catalytic amount of TCCA (0.05 equiv.) and NH_3OHCl (1.2 equiv.) under solvent-free conditions at 110 °C.

Entry	THP Ether	Oxime	Time (min)	Yield (%) ^a
1	<i>p</i> -Cl-C ₆ H ₄ CH ₂ OTHP	<i>p</i> -Cl-C ₆ H ₄ CH=NOH	60	95
2	<i>m</i> -Cl-C ₆ H ₄ CH ₂ OTHP	<i>m</i> -Cl-C ₆ H ₄ CH=NOH	30	92
3	<i>o,p</i> -Cl ₂ -C ₆ H ₃ CH ₂ OTHP	<i>o,p</i> -Cl ₂ -C ₆ H ₃ CH=NOH	40	96
4	<i>p</i> -Br-C ₆ H ₄ CH ₂ OTHP	<i>p</i> -Br-C ₆ H ₄ CH=NOH	30	92
5	<i>p</i> -F-C ₆ H ₄ CH ₂ OTHP	<i>p</i> -F-C ₆ H ₄ CH=NOH	30	97
6	<i>p</i> -CH ₃ O-C ₆ H ₄ CH ₂ OTHP	<i>p</i> -CH ₃ O-C ₆ H ₄ CH=NOH	70	51
7	C ₆ H ₅ CH ₂ OTHP	C ₆ H ₅ CH=NOH	30	98
8	<i>p</i> - ^t Bu-C ₆ H ₄ CH ₂ OTHP	<i>p</i> - ^t Bu-C ₆ H ₄ CH=NOH	75	78
9	C ₆ H ₅ CH=CHCH ₂ OTHP	C ₆ H ₅ CH=CHCH=NOH	45	63
10	C ₆ H ₅ CH(CH ₃)OTHP	C ₆ H ₅ C(CH ₃)=NOH	120	90
11	C ₆ H ₅ CH(CH ₃)CH ₂ OTHP	C ₆ H ₅ CH(CH ₃)CH=NOH	90	97
12	CH ₃ (CH ₂) ₅ CH(CH ₃)OTHP	CH ₃ (CH ₂) ₅ C(CH ₃)=NOH	120	90
13			100	79
14			60	95

^a Isolated yields.

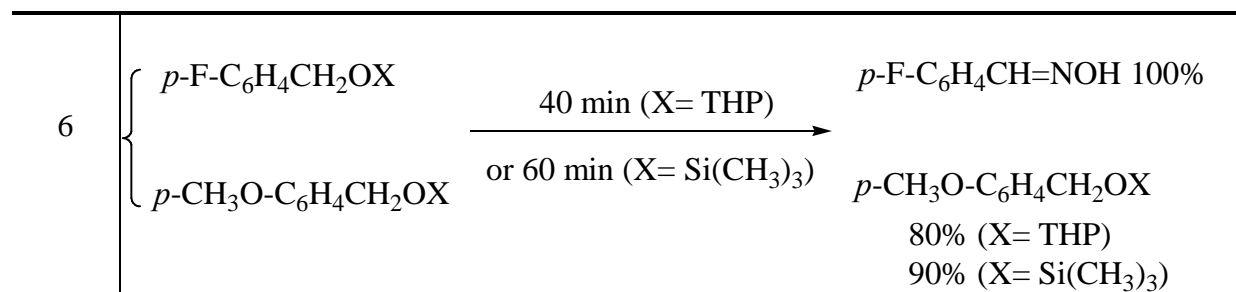
Table 3: Conversion of trimethylsilyl ethers to oximes using a catalytic amount of TCCA (0.05 equiv.) and NH_3OHCl (1.2 equiv.) under solvent-free conditions at 100 °C.

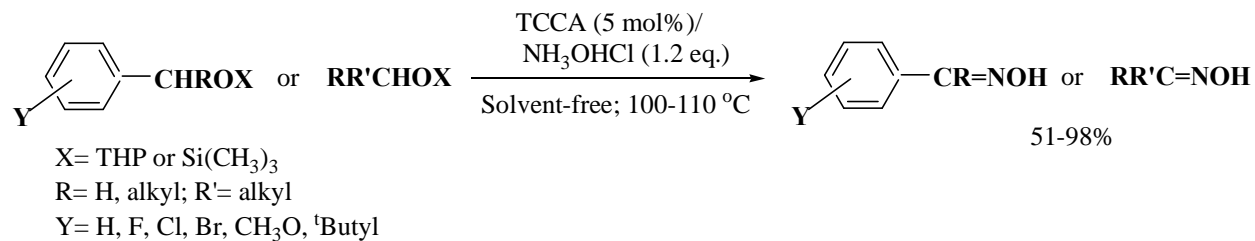
Entry	Silyl Ether	Oxime	Time (h)	Yield (%) ^a
1	$p\text{-Cl-C}_6\text{H}_4\text{CH}_2\text{OSi(CH}_3)_3$	$p\text{-Cl-C}_6\text{H}_4\text{CH=NOH}$	4.75	92
2	$m\text{-Cl-C}_6\text{H}_4\text{CH}_2\text{OSi(CH}_3)_3$	$m\text{-Cl-C}_6\text{H}_4\text{CH=NOH}$	1.5	95
3	$o,p\text{-Cl}_2\text{-C}_6\text{H}_3\text{CH}_2\text{OSi(CH}_3)_3$	$o,p\text{-Cl}_2\text{-C}_6\text{H}_3\text{CH=NOH}$	2	90
4	$p\text{-Br-C}_6\text{H}_4\text{CH}_2\text{OSi(CH}_3)_3$	$p\text{-Br-C}_6\text{H}_4\text{CH=NOH}$	1.5	96
5	$p\text{-F-C}_6\text{H}_4\text{CH}_2\text{OSi(CH}_3)_3$	$p\text{-F-C}_6\text{H}_4\text{CH=NOH}$	1	95
6	$p\text{-CH}_3\text{O-C}_6\text{H}_4\text{CH}_2\text{OSi(CH}_3)_3$	$p\text{-CH}_3\text{O-C}_6\text{H}_4\text{CH=NOH}$	4	52
7	$\text{C}_6\text{H}_5\text{CH}_2\text{OSi(CH}_3)_3$	$\text{C}_6\text{H}_5\text{CH=NOH}$	3	97
8	$p\text{-}^t\text{Bu-C}_6\text{H}_4\text{CH}_2\text{OSi(CH}_3)_3$	$p\text{-}^t\text{Bu-C}_6\text{H}_4\text{CH=NOH}$	2	95
9	$\text{C}_6\text{H}_5\text{CH=CHCH}_2\text{OSi(CH}_3)_3$	$\text{C}_6\text{H}_5\text{CH=CHCH=NOH}$	3.25	71
10	$\text{C}_6\text{H}_5\text{CH(CH}_3)\text{OSi(CH}_3)_3$	$\text{C}_6\text{H}_5\text{C(CH}_3)=\text{NOH}$	4.5	98
11	$\text{C}_6\text{H}_5\text{CH(CH}_3)\text{CH}_2\text{OSi(CH}_3)_3$	$\text{C}_6\text{H}_5\text{CH(CH}_3)\text{CH=NOH}$	1.5	90
12	$\text{CH}_3(\text{CH}_2)_5\text{CH(CH}_3)\text{OSi(CH}_3)_3$	$\text{CH}_3(\text{CH}_2)_5\text{C(CH}_3)=\text{NOH}$	2.5	80
13			4.25	90
14			3.25	73

^a Isolated yields.

Table 4: Selectivities in the conversion of THP and TMS ethers to oximes using a catalytic amount of TCCA (0.05 equiv.) and NH_3OHCl (1.2 equiv.) at 110 °C and 100 °C respectively under solvent-free conditions.

Entry	Selectivity
1	$\left\{ \begin{array}{l} p\text{-F-C}_6\text{H}_4\text{CH}_2\text{OX} \\ \text{C}_6\text{H}_5\text{OX} \end{array} \right. \xrightarrow[\text{or 60 min (X= Si(CH}_3)_3)]{30 \text{ min (X= THP)}} \left\{ \begin{array}{l} p\text{-F-C}_6\text{H}_4\text{CH=NOH} \\ \text{C}_6\text{H}_5\text{OX} \end{array} \right. \quad \begin{array}{l} 100\% \\ 100\% \end{array}$
2	$\left\{ \begin{array}{l} p\text{-F-C}_6\text{H}_4\text{CH}_2\text{OX} \\ \text{C}_6\text{H}_5\text{O}-\text{CH}_2\text{-CH}_2\text{-O} \end{array} \right. \xrightarrow{30 \text{ min (X= THP)}} \left\{ \begin{array}{l} p\text{-F-C}_6\text{H}_4\text{CH=NOH} \\ \text{C}_6\text{H}_5\text{O}-\text{CH}_2\text{-CH}_2\text{-O} \end{array} \right. \quad \begin{array}{l} 100\% \\ 100\% \end{array}$
3	$\left\{ \begin{array}{l} p\text{-F-C}_6\text{H}_4\text{CH}_2\text{OX} \\ \text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CH}_3 \end{array} \right. \xrightarrow[\text{or 120 min (X= Si(CH}_3)_3)]{30 \text{ min (X= THP)}} \left\{ \begin{array}{l} p\text{-F-C}_6\text{H}_4\text{CH=NOH} \\ \text{C}_6\text{H}_5\text{CO}_2\text{CH}_2\text{CH}_3 \end{array} \right. \quad \begin{array}{l} 100\% \\ 100\% \end{array}$
4	$\left\{ \begin{array}{l} p\text{-F-C}_6\text{H}_4\text{CH}_2\text{OX} \\ \text{C}_6\text{H}_5\text{CO}_2\text{H} \end{array} \right. \xrightarrow[\text{or 60 min (X= Si(CH}_3)_3)]{30 \text{ min (X= THP)}} \left\{ \begin{array}{l} p\text{-F-C}_6\text{H}_4\text{CH=NOH} \\ \text{C}_6\text{H}_5\text{CO}_2\text{H} \end{array} \right. \quad \begin{array}{l} 100\% \\ 100\% \end{array}$
5	$\left\{ \begin{array}{l} p\text{-F-C}_6\text{H}_4\text{CH}_2\text{OX} \\ \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO} \end{array} \right. \xrightarrow[\text{or 60 min (X= Si(CH}_3)_3)]{30 \text{ min (X= THP)}} \left\{ \begin{array}{l} p\text{-F-C}_6\text{H}_4\text{CH=NOH} \\ \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO} \end{array} \right. \quad \begin{array}{l} 100\% \\ 100\% \end{array}$





Scheme 1: Tandem conversion of primary and secondary tetrahydropyranyl and silyl ethers to oximes using a catalytic amount of TCCA in the presence of hydroxylamine hydrochloride under solvent-free conditions.