Article

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Synthesis of Oximes with $NH_2OH.HCl$/DOWEX(R)50WX4 System

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The oximation of a variety of carbonyl compounds was efficiently carried out with DOWEX(R)50WX4/ $NH_2OH{\cdot}HCl$ system. The reactions were performed in ethanol to give *Z*-aldoximation isomers of aldehydes and *E*-oximaton of acetophenone derivatives in a perfect selectively. The oximation of compounds with two carbonyl groups was carried out selectively on one carbonyl moiety. Also, the oximation of aldehydes over ketones has been accomplished successfully by this system.

Keywords: *Z*-Aldoximes; Ketoximes; *E*-Acetophenone oximes; $H_2NOH.HCl$; DOWEX(R)50WX.

INTRODUCTION

The protection of carbonyl compounds as oximes is of great interest to organic chemist, as they are readily prepared and highly stable compounds. Qximes have attracted intensive attention for several decades as an efficient method for characterization and purification of carbonyl compounds.[1] Also, they have been found application in industrial as well as medicinal areas and several studies have been shown. Oximes present properties as antimicrobial,[2a-b] antioxidant,[2c] antitumor,[2d] anti-depressive,[2e] antiviral agents and anticonvulsant.[2f] Many oximes have been investigated in the context of heavy metal complexation[2g-h] and gustative[2i] properties. They have been widely used for the preparation of a variety of nitrogen-containing compounds such as nitro compounds,[2j] isoxazolines,[2k] hydroximinoyl chlorides,[2l] nitriles,[2m] amides[2n] and nitrones.[2o-q]

Oximes were usually prepared by the reaction of carbonyl compounds and hydroxylamine hydrochloride in the presence of acids or bases such as: sulfuric acid,[3a] formic acid,[3b] pyridine,[3c] sodium acetate and sodium hydroxide.[3d-e] However, for some limitations such as: low yields, long reaction times and acid or base sensitive functionalities in aldehyde or ketone compounds, the classical methods are not suitable and many improvements methods have been carried out for the preparation of oximes such as: ammonia/oxidant/catalyst systems,[4] wet basic Al_2O_3/microwave irradiation,[5a] SiO_2/NH_2OH[5b] in the absence of any catalyst,[5c] CaO at solvent-free condition,[5d] the use of TiO_2/$SO4^{2-}$ solid superacid,[5e] ethylenediamine/oxone in water,[5f] the use of heterogeneous polyoxometalate at solvent free conditions,[5g] phase transfer catalysis,[5h] Na_2SO_4/ultrasound irradiation,[5i] $NH_2OH{\cdot}HCl$ in ionic liquids,[5j-k] titanyl acetylacetonate/NH_2OH[5l] and $NH_2OH.HCl/Bi_2O_3$.[5m] We required amounts of several aldoximes as starting materials in the synthesis project, therefore we have carried out extensive re-examination of this reaction. Herein, we thus wish to report our findings, which resulted in a simple and extremely efficient method of oximes synthesis with $NH_2OH.HCl$/DOWEX(R)50WX4 system in ethanol.

RESULTS AND DISCUSSION

Chemical methods for the synthesis of oximes usually give a mixture of the two geometrical isomers (*Z* and *E*), which have different physical properties and biological activities[6] and must be separated by chromatography or recrystallization techniques. The rate of equilibration of a mixture of *Z* and *E* isomers and the position of the equilibrium is temperature dependent.[7] Liu *et al*.[8] have reported that this inter-conversion is also solvent dependent; therefore, solvent and temperature control are critical. A few methods are available for the synthesis of *Z* and *E* isomers of aldoximes.[9a-b] In many cases, *E* isomers were obtained from the *Z* forms by the hydrochloride salt method[9c] or column chromatography.[9d] It has been shown that molecular sieve 3 Å,[9e] the silicaphosphate (P_2O_5/SiO_2)[9f] and $H_3PMo_{12}O_{40}$ under solvent-free conditions[9g] can catalyze the stereoselective oxime formation. Thus, there is considerable interest in finding more selective methods for oximes synthesis. We now report a simple and efficient method for the preparation of oximes from their corresponding carbonyl compounds and hydroxylamine hydrochloride by using of DOWEX(R)50WX4 (low price cation exchange resin, strong acid) under different conditions in ethanol.

In order to determine the most appropriate reaction

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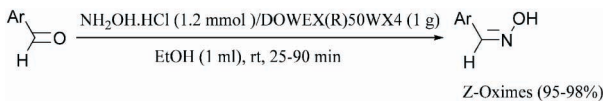
conditions for oximation a model study was carried out on the oximation of bezaldehyde. Among the tested solvents such as: C_2H_5OH, CH_3OH, DMF, CH_3CN, CH_2Cl_2, THF and solvent-free system, condensation of benzaldehyde and hydroxylamine hydrochloride was more facile and proceeded to gave highest yield in ethanol.

Interestingly, it was found that DOWEX(R)50WX4 with loading (1 g) is an efficient amounts of catalyst and $NH_2OH.HCl$ (1.2 mmol) gave exclusively benzaldoxime in 45 min with excellent yield (95%). In lower amounts of catalyst loading the conversion and isolated yields are decreased. However, oximation of benzaldehyde with hydroxylamine hydrochloride in the absence of catalyst did not occur even under extension of reaction time to one hour and benzaldehyde was completely recovered. Furthermore, the use of 1 g of catalyst is sufficient to promote the reaction and no other additives are required for this conversion. In order to evaluate the generality of the process a variety of aldehydes were ground with hydroxylamine hydrochloride in the presence of DOWEX(R)50WX4 in ethanol. In this approach, the corresponding *Z*-aldoximes were obtained in quantitative yield. The general reaction has been shown in Scheme I and the results have been reported in Table 1.

Scheme I

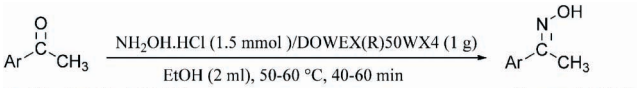


Z-Oximes (95-98%)

All reactions were performed in less than 100 minutes. As shown in the Table 1, the reaction of hydroxylamine hydrochloride with different aromatic aldehydes, in the presence of this catalyst, gave *Z*-aldoximes in excellent yields and stereoselectivity. The purity of the products was determined by ^{1}H-NMR, which showed the exclusive formation of the corresponding *Z*-aldoximes. The *Z*-stereochemistry of the products was determined from the ^{1}H-chemical shift[9a,9g] of the C(H)=N group which appeared around 8-8.5 ppm as a singlet, whereas the ^{1}H-chemical shift of the C(H)=N group for *E*-aldoximes appear in 7.30 and 7.60 ppm. In all the ^{1}H-NMR spectra ($CDCl_3$, 25 ºC), by comparison of ^{1}H-NMR of these isomers, we have observed that the C(H)=N signal in 8.10 and 8.80 have disappeared in the *Z*-aldoximes (Table 1).

The oximation of ketones was also performed well by $NH_2OH.HCl$/DOWEX(R)50WX4 system, but due to the lower reactivity of ketones relative to aldehydes, the oximation requires higher molar amounts of $NH_2OH{\cdot}HCl$ (1.5 mmol) at higher temperature (50-60 °C) (Table 2). *E*-Acetophenone oximes (table 2 , entirs 1-3) were also obtained in high to excellent yields as shown in Scheme II.

Scheme II



Ar: Ph, 4-MePh, 4-MeOPh *E*-isomer (81-98%)

The *E*-stereochemistry of acetophenone oxime derivatives was determined from the ^{1}H-chemical shift of the CH_3 group which appeared around 2.3 ppm as a singlet, whereas the ^{1}H-chemical shift of the CH_3 group for *Z*-ketoximes appeared around 2.6 ppm. In all the ^{1}H-NMR spectra ($CDCl_3$, 25 ºC), by comparison of ^{1}H-NMR of these isomers,[10a-c] we have observed that the CH_3 signal in 2.30-2.34 have disappeared in the *E*-acetophenone oxime derivatives. Benzalaceton as α,β-unsaturated ketone was also converted to the corresponding *E*-oximes[10d] with this system in high yield (Table 2, entry 4). Benzophenone and 9H-fluoren-9-one as hindered ketones (Table 2, entry 5, 6) and 4-phenylcyclohexanone as aliphatic ketone (Table 2, entry 7) were ground with hydroxylamine hydrochloride in the presence of DOWEX(R)50WX4 in ethanol and their corresponding ketoximes were obtained in quantitative yields.

It is also observed that the oximation procedure in compounds with two carbonyl functionalities (benzil) was selective and even in excess amounts of the reagents and longer reaction times proceeded only on one carbonyl group (Table 2, entry 8). In this conversion, *E*-benzilmonooxime (α-benzilmonooxime) was produced. The *E*-stereochemistry of the product was determined from the OH stretching frequency in IR spectrum which appeared around 3345 cm^{-1}, whereas it appears near 3115 cm^{-1} in the *Z*-benzilmonooxime (β-benzilmonooxime).[11]

In order to show chemoselectivity of the presented oximation system, a mixture of one equivalents of benzaldehyde and one equivalents of acetophenone was treated with ($NH_2OH.HCl$ (1.2 mmol/DOWEX(R)50WX4 (1 g)) at room temperature in ethanol (1 mL) as shown in Scheme III. The oximation of aldehyde with respect to ketone was 100%. This is general trend for the oximation of a variety of aldehydes in the presence of ketones as shown in Table

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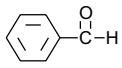
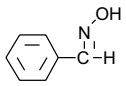
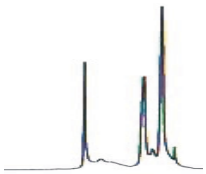
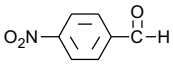
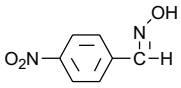
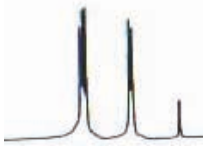
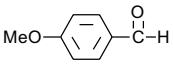
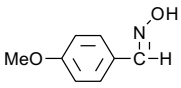
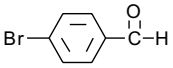
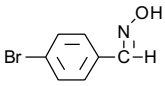
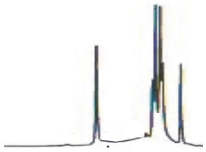
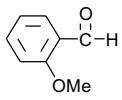
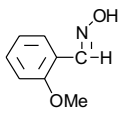
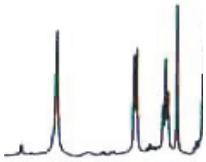
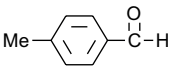
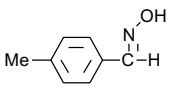
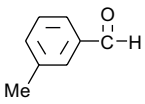
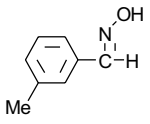
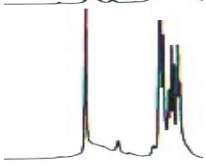
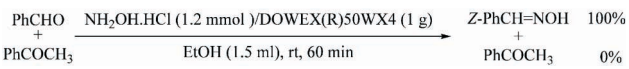
Table 1. Conversion of aldehydes (1 mmol) into *Z*-aldoximes by $NH_2OH.HCl$ (1.2 mmol)/DOWEX(R)50WX4 (1 g) system in ethanol (1 mL) at room temperature

Entry	Substrate	Product	^{1}H chemical shift of C(H)=N group (9 8 7)	Time (min)	Yield[a] (%)	Melting Point °C
1				45	95	-
2				90	97	129-131
3				40	95	43-45
4				60	96	109-110
5				25	95	87-88
6				60	98	79-81
7				60	95	-

[a] Yields refer to isolated pure products.

3; in the most cases the selectivity ratios were excellent. Therefore this methodology could be used selectively for the preparation of aldoximes of compounds that contain both aldehyde and ketone functional groups.

Scheme III



We have also checked the reusability of the catalyst using the recovered DOWEX(R)50WX4 from the reaction. It was observed that recovered catalyst could be satisfactorily used for the third run, whereas, forth run of the recovered catalyst leads to poor yield and longer reaction time as shown in Table 4. The mechanism for the influence of DOWEX(R)50WX4 is not clear, but we think that SO_3H groups on DOWEX(R)50WX4 heterogeneously protonates the carbonyl group which make it more susceptible

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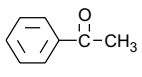
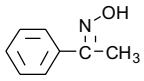
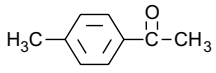
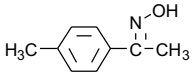
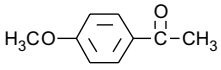
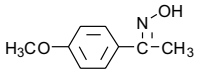
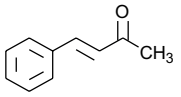
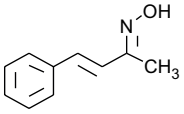
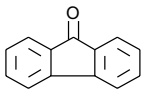
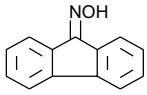
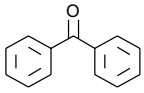
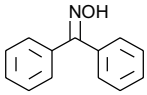
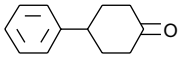
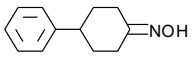
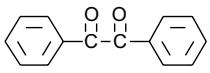
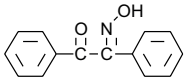
Table 2. Conversion of ketones (1 mmol) into corresponding ketoximes by $NH_2OH.HCl$ (1.5 mmol)/ DOWEX(R)50WX4 (1 g) system in ethanol (2 mL) at 50-60 °C

Entry	Substrate	Products	Time (min)	Yield[a] (%)	Melting Point °C
1			40	94	54-55
2			50	98	79-81
3[b]			60	81	77-79
4			15	95	110-112
5			60	96	194-196
6			90	98	139-141
7			15	98	104-106
8			90	96	102-103

[a] Yields refer to isolated pure products. [b] *E*-isomer and *Z*-isomer are formed 83% and 17% respectively.

Table 3. Competitive the oximation of aldehydes and ketones to the corresponding oximes with $NH_2OH.HCl$ (1.2 mmol/DOWEX(R)50WX4 (1 g)) system at room temperature in ethanol (1.5 mL)

Entry	Substrate 1	Substrate 2	Molar Ratio[a]	Time/min	Conv.1/Conv.2[b]/%
1	benzaldehyde	acetophenone	1:1	60	100:0
2	benzaldehyde	benzophenone	1:1	60	100:0
3	benzaldehyde	4-phenylcyclohexanone	1:1	60	100:0
4	benzaldehyde	9H-fluoren-9-one	1:1	60	100:0

[a] Molar Ratio as: Substrate 1/Substrate 2, [b] Conversion refer to TLC monitoring (eluent; CCl_4/Et_2O: 5/2).

for the NH_2OH attack.

CONCLUSION

In conclusion, the oximation of a variety of carbonyl compounds such as aldehydes, ketones, enones, α-diketones was carried out efficiently with DOWEX(R)50WX4/ $NH_2OH{\cdot}HCl$ system. The reactions were performed in ethanol to give *Z*-aldoximation isomers of aldehydes and *E*-oximaton of ketones in a perfect selectively. Oximation of compounds with two carbonyl groups was carried out selectively on one carbonyl moiety. The oximation of aldehydes over ketones has been accomplished successfully by this system. Also, this oximation system has the easily worked up and it can be reused for several times. There-

Table 4. Reusability of DOWEX(R)50WX4 in the preparation of banzaldoxime in the optimized conditions

Entry	Run Number	Time	Yield[a] (%)
1	1	50	95
2	2	70	91
3	3	90	83
4	4	90	35
5	5	90	10

[a] Yields refer to isolated pure products.

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fore, this new protocol for oximation of carbonyl compounds could be a useful addition to the present methodologies.

EXPERIMENTAL SECTION

General

All substrates and reagents were purchased from commercially sources with the best quality and used without further purification. DOWEX(R)50WX4 (CAS NO. 69011-20-7) was purchased from Sigma-Aldrich company. IR and ^{1}H NMR spectra were recorded on PerkinElmer FT-IR RXI and 300 MHz Bruker spectrometers, respectively. The products were characterized by their ^{1}H NMR or IR spectra and comparison with authentic samples (melting or boiling points). Organic layers were dried over anhydrous sodium sulfate. All yields referred to isolated pure products. TLC was applied for the purity determination of substrates, products and reaction monitoring over silica gel 60 F_{254} aluminum sheet.

A typical procedure for oximation of aldehydes with $NH_2OH.HCl$/DOWEX(R)50WX4 system

In a round-bottomed flask (10 mL), equipped with a magnetic stirrer a solution of benzaldehyde (0.106 g, l mmol) in ethanol (96%) (1 mL) was prepared. $NH_2OH{\cdot}HCl$ (0.084 g, 1.2 mmol) and DOWEX(R)50WX4 (1 g) was added and the reaction mixture was stirred at room temperature for 45 min. TLC monitored the progress of the reaction (eluent, CCl_4/Et_2O: 2/1). After completion of the reaction, ethanol (96%) (5 mL) was added and the reaction mixture was continued to stirring for 5 min. The mixture was dried over anhydrous Na_2SO_4. Evaporation of the solvent and a short column chromatography of the resulting crude material over silica gel (eluent; CCl_4/Et_2O: 2/1) afforded the pure *Z*-benzaldoxime (0.115 g, 95% yield, Table1, entry 1).

A typical procedure for oximation of ketones with $NH_2OH.HCl$/DOWEX(R)50WX4 system

In a round-bottomed flask (10 mL), equipped with a reflux condenser and magnetic stirrer a solution of acetophenone (0.120 g, l mmol) in ethanol (96%) (2 mL) was prepared. $NH_2OH{\cdot}HCl$ (0.105 g, 1.5 mmol) and DOWEX(R)50WX4 (1 g) was added and the reaction mixture was stirred at 50-60 °C for 40 min. TLC monitored the progress of the reaction (eluent, CCl_4/Et_2O: 5/2). After completion of the reaction, ethanol (96%) (5 mL) was added and the reaction mixture was continued to stirring for 5 min. The mixture was dried over anhydrous Na_2SO_4. Evaporation of the solvent and a short column chromatography of the resulting crude material over silica gel (eluent; CCl_4/Et_2O: 5/2) afforded the pure *E*-acetophenone oxime (0.127 g, 94% yield, Table 2, entry 1).

A typical procedure for competitive oximationn of aldehydes and ketones with $NH_2OH.HCl$/DOWEX(R)50WX4 system

In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a solution of benzaldehyde (0.106 g, l mmol) and acetophenone (0.121 g, 1 mmol) in etnanol (1.5 mL) was prepared. To this solution, $NH_2OH{\cdot}HCl$ (0.084 g, 1.2 mmol) and DOWEX(R)50WX4 (1 g) was added and the mixture was stirred at room temperature. TLC monitored the progress of reaction. After completion of the reaction (60 min), ethanol (96%) (5 mL) was added and the reaction mixture was continued to stirring for 5 min. The mixture was dried over anhydrous Na_2SO_4. After the evaporation of solvent, the resulting crude products (0.232 g) was separated by PLC over silica gel (eluent; CCl_4/Et_2O: 5/2) and afforded the pure benzaldoxime (0.117 g, 96% yield as a sole product, besides acetophenone (0.112 g, 93%) as an intact material (Table 3, entry 1).

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