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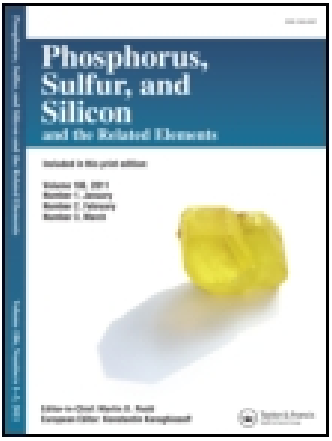

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P_2O_5/SiO_2 as an Efficient Reagent for the Preparation of Z-Aldoximes Under Solvent-Free Conditions

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P_2O_5/SiO_2 as an Efficient Reagent for the Preparation of *Z*-Aldoximes Under Solvent-Free Conditions

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A facile and efficient method for the preparation of Z*-aldoximes is improved by means of* P_2O_5/SiO_2 *reagent in solvent-free media. Advantages of this method are the use of inexpensive and selective reagent, with high yields in simple operation, and short reaction time under solvent-free conditions.*

Keywords Aldehydes; phosphorus pentoxide; protection; silica gel; *z*-aldoximes

INTRODUCTION

The oximation is a very efficient method for characterization, purification, and protection of carbonyl compounds. These compounds not only represent a convenient series of derivatives of carbonyl compounds but also may be used as intermediates for the preparation of amides by the Beckmann rearrangement,[1] nitrones,[2] hydroxyiminoyl chlorides,[3] nitrile oxide,[3] and chiral α-sulfinyl oximes.[4] The usual method for the preparation of oximes involves treatment of carbonyl compounds with hydroxylamine hydrochlorides in a basic aqueous medium with adjustment of pH. Because of improper levels of solvent or reactant being used some oximes are liquid or oil-out and the operating conditions of this method are difficult. On the other hand, chemical methods[5,6a] 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 recrystalization techniques. However, the reagents that have been used

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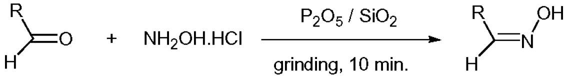
for oximation of ketones or Beckmann rearrangement also catalyze interconversion of these geometrical isomers.[7] The rate of equilibrition of a mixture of *Z* and *E* isomers and the position of the equilibrium is temperature dependent,[7a] therefore, temperature control of the experiment is critical.

Very few methods are available for the synthesis of *E* and *Z* isomer of oximes.[7d,8,9] In many cases, *E* isomers were obtained from the *Z* forms by either hydrochloride method[10] or purified by column chromatography.[5a] As a result there is always considerable interest in finding more selective methods of oximes synthesis or direct pathways.

Recently, the ability of silica gel in dry media was demonstrated using various aldehydes and ketones with hydroxylamine hydrochloride in the presence of a base[11a] or microwave irradiation,[11b] but these methods suffer from lack of stereoselectivity. Our project have been continually working on the basis of developing of new synthetic methods using P_2O_5/SiO_2 (Silicaphos) in a solid phase.[12] Having the above facts in mind, we wish to report a very simple and efficient method for selective preparation of *Z*-oximes from aldehydes using the P_2O_5/SiO_2 reagent in solid phase.

RESULTS AND DISCUSSION

In order to prepare oximes, various types of aldehydes were ground with hydroxylamine hydrochloride in the presence of P_2O_5/SiO_2 reagent in solvent-free media. In this approach, corresponding aldoximes were obtained in quantitative yield. The general reaction is illustrated according to the Scheme 1 and the results have been reported in Table I. All reactions were performed in less than 10 min.



SCHEME 1

As shown in the Table I the reaction of hydroxylamine hydrochloride with different aromatic aldehydes, including those with electron-withdrawing and donating substituents in the presence of this new catalyst, gave *Z*-aldoximes in high yield and stereoselectivity. The purity of the products was determined by ^{1}H-NMR, IR spectra, and melting point. In all ^{1}H-NMR spectra the OH group of aldoximes appeared around 8–10 as a broad singlet and in IR spectra the OH and C=N groups were observed around 3200–3500 and 1620–1660 cm^{-1}, respectively. The *Z*-stereochemistry of the products was determined from the

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TABLE I Conversion of Aldehydes into *Z*-Aldoximes in the Presence of P_2O_5/SiO_2

Entry	*Z*-aldoximes R	Yield[a,b] (%)	^{1}H chemical shift of C(H)=N group	Bp/Torr or mp (°C) Found	Reported [ref]
1	Ph	95	8.15	118	120[8]
2	2-CH_3O-C_6H_4	94	8.47	89	88–90[11b]
3	4-CH_3O-C_6H_4	90	8.1	130	132[8]
4	4-NO_2-C_6H_4	78	8.2	101	100[8]
5	4-Cl-C_6H_4	75	8.1	145	146[8]
6	4-CH_3-C_6H_4	88	8.5	70	72[8]
7	4-Me_2N-C_6H_4	80	8.1	138	138–140[11b]
8	4-HO-C_6H_4	85	8.1	90	94[8]
9	2-HO-C_6H_4	75	8.2	64	63[8]
10	4-HO-3-MeO-C_6H_3	87	8.1	116	117[13]
11	2-furyl	65	7.6	75	75–76[14]

[a] Isolated yield.

[b] All the compounds give satisfactory spectral analysis (IR and ^{1}H-NMR).

^{1}H-chemical shift[8] of the C(H)=N group which appeared around 8–8.5 as a singlet (Table I). It is very interesting that in these reactions nitriles were not formed. Only in the case of these reactions coupled with microwave irradiation, the corresponding nitriles were obtained in high yields.[12c] However, ketones such as benzophenone and acetophenone did not afford the corresponding oximes under these conditions. In order to show chemoselectivity of the presented reagent, a mixture of one equivalent of aldehyde and one equivalent of ketone was treated with two equivalents of hydroxylamine hydrochloride in the presence of P_2O_5/SiO_2 reagent at room temperature for 10 min. Only the aldehyde was selectively converted to the corresponding oxime and ketones did not react at all (Scheme 2). Therefore this methodology could be used selectively for the preparation of aldoximes of compounds that contain both aldehyde and ketone functional groups.

In conclusion, the reported procedure is an easy and novel method for the preparation of aldoximes in solvent-free medium. Also this simple and readily available reagent affords various aldoximes in a shorter reaction time (10 min), with good to excellent yields (65–95%), and high stereoselectivities (*Z*-isomers). Further studies of the new applications of P_2O_5/SiO_2 reagent in organic synthesis is in progress.

EXPERIMENTAL

All melting points recorded are uncorrected open-capillary measurements. IR spectra were recorded on a Shimadzu-IR 470

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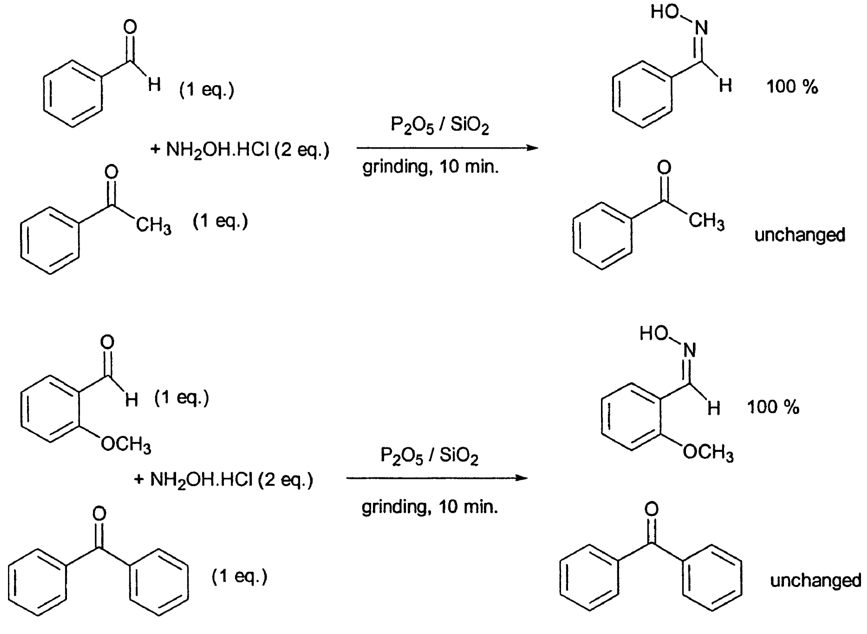

SCHEME 2

spectrophotometer. ^{1}H-NMR spectra were recorded on Bruker-80 MHz and Bruker-500 MHz instruments using tetramethylsilane as an internal standard. Silica gel 60 (230–400 mesh) was obtained from Fluka and was dried in an oven at 120°C for 2 h. The P_2O_5/SiO_2 reagent was obtained according to the earlier reported procedure.[12]

Preparation of *Z*-Aldoximes

General Procedure

In a typical reaction, a mixture of aldehyde (2 mmol), hydroxylamine hydrochloride (4 mmol) and P_2O_5/SiO_2 reagent (1 g) was ground thoroughly in a mortar for 10 minutes. Usually an immediate color change was observed. The completion of the reaction was monitored by TLC examination. After the completion of the reaction, 10 mL of 5% aqueous HCl was added to the mixture. The resulting solution was extracted with CH_2Cl_2 (2 × 10 mL). The extracts were combined and dried over $CaCl_2$. Evaporation of the solvent under vacuum gave aldoximes with high purity (based on TLC, ^{1}H-NMR, IR, and melting point).

Z-2-Methoxybenzaldoxime

m.p.: 89°C (lit. [11b], 88–90°C); IR (KBr); 3200, 1625 cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$): 8.82(bs, 1H), 8.47(s, 1H), 7.64(dd, 1H, $J_1 = 7.64$ Hz,

$J_2 = 1.5$ Hz), 7.35(dt, 1H, $J_1 = 7.70$ Hz, $J_2 = 1.5$ Hz), 6.96(t, 1H, $J = 7.48$ Hz), 6.92(d, 1H, $J = 8.35$ Hz), 3.89(s, 3H).

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