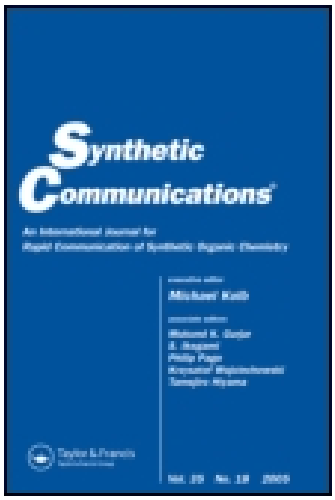

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EFFICIENT SOLVENT FREE DEOXIMATION AND DEHYDRAZONATION WITH HIO_3 IN THE PRESENCE OF WET SiO_2

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EFFICIENT SOLVENT FREE DEOXIMATION AND DEHYDRAZONATION WITH HIO_3 IN THE PRESENCE OF WET SiO_2

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ABSTRACT

This paper is a report of an efficient and convenient method for deoximation and dehydrazonation of benzylic oximes and hydrazones with HIO_3 in the presence of wet SiO_2.

Synthesis of oximes and hydrazones from carbonyl compounds, is of great interest to synthetic chemists, as they are readily prepared and highly stable compounds. Oximes and hydrazones are also extensively used for purification and characterisation of carbonyl compounds. Since oximes can be prepared from non-carbonyl compounds,[1,2] the generation of carbonyl compounds from oximes provides an alternative method for the preparation of aldehydes and ketones. Some of the methods reported for deoximation invariably require high temperature, longer reaction time,

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and the formation of over-oxidized products leading to low yields.[3–8] Little attention has been paid to the cleavage of carbon–nitrogen double bond of hydrazones and only a few reports are available dealings with the conversion of the derivatives to their corresponding carbonyl compounds.[9,10]

In this communication we introduce a simple and efficient method of deoximation and dehydrazonation of benzylic oximes and hydrazones for regeneration of aldehydes and ketones by using HIO_3 in the presence of wet SiO_2 under solvent free conditions (Table 1).

Our experiments show that benzylic oximes and hydrazones are converted to their corresponding carbonyl compounds from good to high yields. Further oxidation of aldehydes to their corresponding carboxylic acids are not observed.

In order to show the efficiency of this method we have compared some of the results with relevant ones reported in the literature[4,5,11] (Table 2).

On the basis of what we have already said, we can conclude that the present procedure of deoximation and dehydrazonation with HIO_3 in the presence of wet SiO_2 provides a very convenient and efficient method for the generation of carbonyl compounds from benzylic oximes

Table 1. Deoximation and Dehydrazonation with HIO_3 in the Presence of Wet SiO_2

Entry	Substrate	Product	Time (min)	Yield (%)
1	4-Nitrobenzaldoxime	4-Nitrobenzaldehyde	15	90
2	3-Nitrobenzaldoxime	3-Nitrobenzaldehyde	15	92
3	4-Methoxybenaldoxime	4-Methoxybenzaldehyde	10	82
4	Acetophenone oxime	Acetophenone	45	90
5	Benzophenone oxime	Benzophenone	40	87
6	Benzoin oxime	Benzoin	45	80
7	Benzaldehyde hydrazone	Benzaldehyde	10	90
8	4-Nitrobenzaldehyde hydrazone	4-Nitrobenzaldehyde	30	89
9	3-Nitrobenzaldehyde hydrazone	3-Nitrobenzaldehyde	30	85
10	4-Methoxybenzaldehyde-hydrazone	4-Methoxybenzaldehyde	5	95
11	4-Chlorobenzaldehyde-hydrazone	4-Chlorobenzaldehyde	30	82
12	Acetophenone hydrazone	Acetophenone	10	70
13	4-Methylacetophenone-hydrazone	4-Methylacetophenone	10	73

All reactions performed on a steam bath.

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Table 2. Comparison of Some of the Results Obtained by the Deoximation with HIO_3 in the Presence of Wet SiO_2[a] (1) with Some of Those Obtained by *N*-Butyltriphenylphosphonium Dichromate (2),[4] Sodium Perbromate (3)[5], and ozone (4)[11]

		(Reagent/Substrate)[a]		(h)	Yield (%)
Entry	Substrate	(1)	(2)	(3)	(4)
1	4-Nitrobenzaldoxime	(5) (0.25) (90)	(1) (0.5) (70)	(4) (12) (40)	(–) (1) (61)
2	Acetophenone oxime	(5) (0.75) (90)	–	(4) (6.5) (88)	(–) (2) (96)

[a]Wet SiO_2 : substrate (0.4 g : 1 mmol).

and hydrazones. A full research, based on this method, concerning the cleavage of carbon–nitrogen double bonds in other classes of organic compounds is under way.

EXPERIMENTAL

Chemicals were purchased from Merck, Fluka, BDH and Aldrich chemical companies. All oximes and hydrazones were prepared using standard synthetic method.[12] Products were separated and purified by different chromatography techniques, and were also identified by the comparison of their, mp, IR, NMR, bp, refractive index with those reported for the authentic samples.

General Procedure: To a mixture of HIO_3 (0.88 g, 5 mmol) and wet SiO_2 [(SiO_2/H_2O: 20% ww), 0.4 g], was added oxime or hydrazone (1 mmol). The resulting mixture was shacked on a steam bath for the definite time (Table 1). The reaction was monitored by TLC. After completion of the reaction, CH_2Cl_2 (5 ml) and sodium thiosulfate (0.5 g) were added to the mixture and the resultant mixture was filtered after 15 min. Anhydrous $MgSO_4$ was added to the filterate and filtered. Evaporation of the solvent, being followed by column chromatography on silica gel, gave the corresponding carbonyl compounds from good to high yields.

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