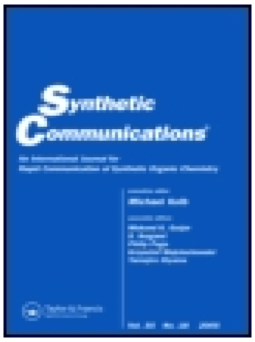

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Regeneration of Carbonyl Compounds from Oximes and Hydrazones Using Peroxymonosulfate on Silica gel under Solvent-free Conditions

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Abstract: In an environmentally benign solvent-free system, oximes and hydrazones are rapidly transformed into parent carbonyl compounds using peroxymonosulfate on silica gel under microwave irradiation in good to excellent yields.

Regeneration of carbonyl compounds from oximes and hydrazones is a very important synthetic transformation in organic synthesis because of their extensive application in the protection[1] and purification of carbonyl compounds[2] and in the preparation of amides via Beckmann rearrangement.[3] As a result, numerous methods are available for the regeneration of carbonyl compounds from such as nitrogen derivatives, but most of them suffer from drawbacks; cost, toxicity of the reagents or longer reaction periods or difficulties in isolation of

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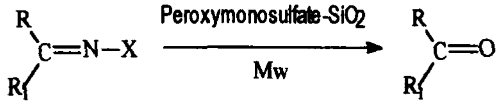
products.[4] These limitations prompted us to investigate further new convenient methodology for the deprotection of oximes and hydrazones.



X= OH, NHTs, NHPh, NMe_2

In continuation of our ongoing programme to develop environmentally benign reactions,[5] we now wish to report a facile conversion of oximes and hydrazones to their corresponding carbonyl compounds by using peroxymonosulfate 'doped' silica gel that proceeds in the solid state using microwaves.[6] Among various mineral supports examined, such as alumina, clay, silica etc., silica was found to give the best results. The role of peroxymonosulfate was confirmed by conducting a blank experiment, where the formation of carbonyl compound was not observed. Potassium peroxymonosulfate ($2KHSO_5$, $KHSO_4$, K_2SO_4), commonly called as oxone®, is an inexpensive and powerful oxidant used for the transformation of a wide range of functional groups.[7] The use of recyclable silica gel support and the general applicability of this reaction to a variety of oximes and hydrazones under solvent-free conditions are other salient feature of this protocol.

The results illustrated in Table 1 indicate that the reaction is successful for a variety of oximes and hydrazones. It is noteworthy that, unlike other oxidative hydrolytic methods, the major drawback of over-oxidation of the resulting aldehydes, is not encountered under the reaction conditions.

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Table 1. Regeneration of carbonyl compounds from oximes and hydrazones under microwave irradiation.

Entry	Substrate	Time/ min	Yield/ %[a]
1.	2,4-Dimethoxybenzaldoxime	1.5	85
2.	2,3-Dichlorobenzaldoxime	1.8	80
3.	3-Phenylpropionaldehyde oxime	2.0	82
4.	Cinnamaldehyde oxime	1.6	78[b]
5.	Acetophenone oxime	2.2	89
6.	1-Tetralone oxime	2.0	87
7.	4-*tert*-Butylcyclohexanone oxime	2.5	85
8.	Camphor oxime	2.0	74
9.	4-Nitroacetophenone tosylhydrazone	2.5	90
10.	2-Methylcyclohexanone tosylhydrazone	3.0	75[b]
11.	4-Methoxybenzaldehyde tosylhydrazone	2.8	83
12.	4-Chlorobenzaldehyde dimethylhydrazone	2.2	79
13.	Benzophenone dimethylhydrazone	1.8	92
14.	3-Phenylpropionaldehyde phenylhydrazone	2.3	89
15.	Cyclohexanone phenylhydrazone	3.0	94
16.	1-Naphthaldehyde phenylhydrazone	2.5	93

[a] Yields refer to pure isolated products, characterised by comparison of their m.p., IR, ^{1}H NMR spectra with those of authentic samples.
[b] Further increasing the reaction time gave no significant improvement in yields but rather decomposition occurred.

Interestingly, the α,β- unsaturated oximes underwent deoximation very efficiently without rearrangement of the C=C bond and the reaction is essentially chemoselective. Furthermore, functional groups such as chloro, methoxy, nitro, alkyl were also inert to this reagent and no byproduct formation was observed.

In conclusion, our present methodology offers very attractive features such as reduced reaction times, economic viability of the reagent, minimisation of side products and high yields which will have wide scope in organic synthesis.

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General Procedure: Neat oxime/hydrazone (4.0 mmol) or dissolved in dichloromethane (10 ml) is combined with silica gel (20 times w/w, 60-120 mesh) and the dry powder is mixed with peroxymonosulfate (8.0 mmol) using a vortex mixer. The reaction mixture was placed in an alumina bath inside an commercial microwave oven (operating at 2450 MHz frequency) and irradiated for a period of 1.5-3.0 min. After completion of the reaction (monitored by TLC) and the inorganic support was separated by filtration, after eluting the product with dichloromethane (4 X 10 ml). Removal of solvent and the residue on purification by column chromatography on silica gel gave the corresponding carbonyl compounds in 75-94% yield and there was no evidence for the formation of any side products.

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