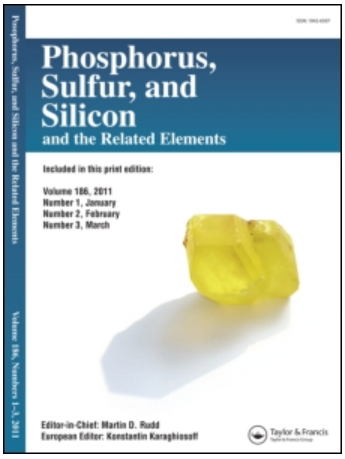

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The regeneration of carbonyl compounds from oximes were performed by using silica chromate and wet SiO_2 (w/w 50%) under microwave irradiation and solvent-free conditions with excellent yields.

Keywords Carbonyl compound; microwave irradiation; oxime; silica chromate; solvent-free

INTRODUCTION

The protection of carbonyl compounds as oximes is of great interest to organic chemists. Oximes are easily prepared and highly stable compounds that are used extensively for the purification and characterization of carbonyl compounds.[1] Since oximes can be prepared from noncarbonyl compounds, the regeneration of carbonyl compounds from oximes provides an alternative method for the preparation of aldehyde and ketones.[2–4] Oximes represent a series of derivatives for the classical identification of carbonyl compounds, as exemplified in the synthesis of erythromycin derivatives.[5] Although a number of methods for the regeneration of carbonyl compounds from oximes has been reported, such as PCC,[6] $K_5CoW_{12}O_{40}\cdot 3H_2O$,[7] $Mg(HSO_4)_2$-Wet SiO_2,[8] 2-Iodylbenzoic acid,[8] wet $NaBiO_3$-silica/MW,[10] quinolium fluorochromate,[11] $NaIO_4$-silica,[12]Dess-Martin Periodinane,[13] TiO_2,[14] Platinum (II) terpyridyl acetylide complex,[15] HIO_3,[16] polymer supported peroxodisulfate,[17] $KMnO_4/Al_2O_3$,[18] $BiCl_3$/THF/MW,[19] silica sulfuric acid/wet SiO_2,[20] silica

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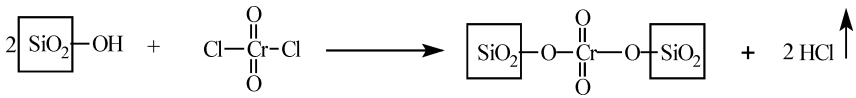
gel confined ionic liquids,[21] and N-halo compounds.[22] The discovery of new, efficient, and fast methods is a goal of organic chemists.

However, many of the conventional procedures for the regeneration of carbonyl compounds from oximes have several limitations; these reagents are often hazardous, corrosive, and expensive, along with reagents requiring long reaction times or reflux temperatures and strongly acidic media. In addition, some of the methods cited in the literature do not describe the deoximation of aldoximes or they give low yields of aldehydes or the liberated aldehydes are overoxidized.

RESULTS AND DISCUSSION

Therefore, we decided to develop a new reagent to overcome the previously discussed limitations. In continuation of our studies on the synthesis of new inorganic acidic salts and silica based resins,[23] we found that silica gel reacts with dichloro chromium oxide to give silica chromate (**I**). It is interesting to note that the reaction is easy and clean without any work-up procedure because HCl gas is evolved from the reaction vessel immediately (Scheme 1).[24]

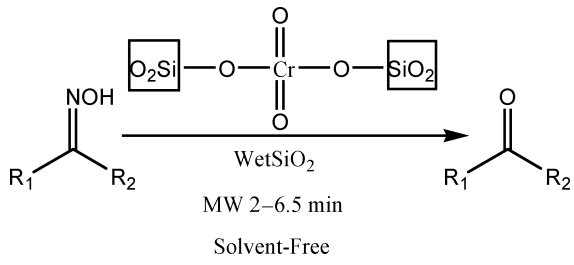


I

SCHEME 1

Recently, the growing interest in the application of microwave irradiation in chemical reaction enhancement is due to high reaction rates and the formation of cleaner products. Also solvent-free reaction conditions are especially appealing for providing an environmentally benign system.[25,26]

Therefore, we wish to report here a simple, inexpensive, mild, and chemoselective route for the effective regeneration of carbonyl compounds from oximes by using silica chromate **I** in the presence of wet SiO_2 in solvent-free conditions under microwave irradiation. Thus, various aldoximes and ketoximes were deoximated in the presence of silica chromate **I** and wet SiO_2 (50% w/w) under solvent free conditions with microwave irradiation (Scheme 2). The reaction proceeded efficiently in good yields within a few minutes; the results of these transformations are summarized in Table I.



SCHEME 2

We observed that cinnamaldehyde oximes selectively converted into the cinnamaldehyde in good yield and carbon-carbon double bonds intact and not prone to cleavage using this method (Table I, entry 9).

Also, we observed that thiophene-2-carboxaldehyde oxime and pyridine 4-carboxaldehyde oxime converted into the corresponding original aldehydes in high yields (Entry 12 and 13) without any production of the corresponding acid or N-oxide during the course of the reaction (Scheme 3).

TABLE I The Regeneration of Carbonyl Compounds From Oximes With Silica Chromate (I) and the Presence of Wet-SiO_2 Under Solvent-Free Conditions and Microwave Irradiation

Entry	Substrate	Subst./ Reagents I[a](g)	Time (Min)	Yield (%)[b,c]	M. P. (°C	Lit.[32] (°C)
1	Cyclohexanone oxime	0.5	4.5	80	159–161	162
2	Acetophenone oxime	0.5	3.5	99	245–248	250
3	Benzaldehyde oxime	0.5	4	90	234–237	237
4	4-Bromo benzaldehyde oxime	0.5	4.5	90[d]	227	228
5	Benzophenone oxime	0.5	4	95	235–237	238
6	3-Methyl acetophenone oxime	0.5	2	82	205–206	207
7	3-Nitro benzaldehyde oxime	0.7	6.5	92	290–292	292
8	4-Nitro benzaldehyde oxime	0.7	6.5	94	316–319	320
9	Cinnamaldehyde oxime	0.5	4.5	87[d]	262–264	265 dec
10	4-Methoxy benzaldehyde oxime	0.5	2	98	253–254	254
11	Camphor oxime	0.7	5	95	174–176	177
12	Thiophen 2-carboxaldehyde oxime	0.5	3	90[d]	222d	224 dec
13	Pyridine 4-carboxaldehyde oxime	0.7	5	92[e]	175–177	178–179

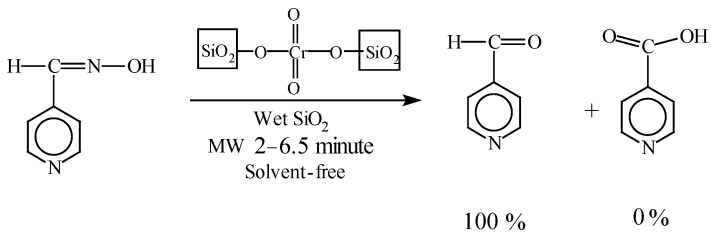
[a]Wet SiO_2: substrate (0.5 g: 1 mmol).

[b]Isolated yields.

[c]Products were characterized by m.p.s., the corresponding of 2,4-dinitrophenylhydrazone derivatives, and their IR and ^1H NMR spectra.

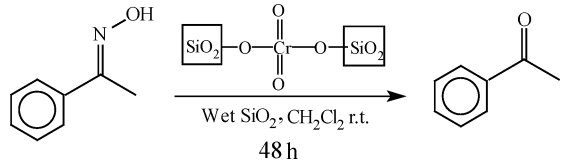
[d]m.p. of semicarbazone derivatives.

[e]m.p. of phenylhydrazone derivatives.



SCHEME 3

For showing a high reaction rate of the deoximation under microwave irradiation, as an example, acetophenone oxime was converted into acetophenone by silica chromate **I** and wet SiO_2 in CH_2Cl_2 in the absence of microwave irradiation; this reaction was completed after 48 h. However, the same reaction was completed after 3.5 min under microwave irradiation (Scheme 4).



SCHEME 4

This is the first example of a silica-chromium based oxidant with covalent linkages (silica vulcanized with CrO_2 linkages). Thus, we hoped that the silica chromate **I** would be superior to all of the previously reported chromium based oxidants[27–29] because (1) toxic chromium cations could be collected from the reaction mixture easily; (2) work-up is very simple and pure products were obtained solely by filtration and the removal of a solvent; and (3) there is no need in chelating agents such as pyridine in Pyridinium Chlorochromate (PCC). Moreover, in older procedures, the isolation of the oxidation products from reaction mixture and chelating agents such as pyridine in PCC is difficult.[30,31]

CONCLUSION

In conclusion, the cheapness and availability of the reagents, the easy and clean work-up, and high yields make this method attractive for chemists. We believe that the present methodology could be an important addition to existing methodologies.

EXPERIMENTAL

General

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. The products were characterized by m.p.s, the correspondence of 2,4-dinitrophenylhydrazone derivatives, and their IR and ^1H NMR spectra.

The Preparation of Silica Chromate[24]

A 500-mL suction flask was used. It was equipped with a constant-pressure dropping funnel containing dichloro chromium oxide (23.2 g, 0.15 mol) and a gas inlet tube for conducting HCl gas over an adsorbing solution, i.e. water. Into it were charged 100 g of silica gel. Dichloro chromium oxide was added dropwise over a period of 20 min at r.t. HCl gas evolved from the reaction vessel immediately (Scheme 1). After the addition was complete, the mixture was shaken for 90 min. A brown solid (Silica chromate) was obtained quantitatively.

The Regeneration of Acetophenone Oxime to the Acetophenone Under Solvent-Free Conditions and Microwave Irradiation as a Typical Procedure

A mixture of compound Acetophenone oxime (0.270 g, 2 mmol), silica chromate (1 g), and wet SiO_2 (50% *w/w*, 1 g) was placed inside a domestic microwave oven operating at medium power (500 w) for 3.5 min (monitored by TLC). Dichloromethane (10 mL) was added to the reaction mixture and triturated. The suspension was filtered, and the residue was washed with CH_2Cl_2 (20 mL). Anhydrous Na_2SO_4 (2 g) was added to the filtrate and filtered off after 20 min. Dichloromethane was removed. Acetophenone was obtained, and the yield was 0.118 g (99%).

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