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Microwave Promoted Regeneration of Carbonyl Compounds from Oximes using Silica Supported Chromium Trioxide

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Abstract

Silica supported chromium trioxide was found to be an efficient reagent for the oxidative cleavage of oximes to the corresponding aldehydes and ketones in "dry media", under microwave irradiation in a domestic microwave oven. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords : Oximes; cleavage reaction; microwave heating; supported reagents

Oximes are very useful for protecting carbonyl groups in organic synthesis[1] . Oximes can be prepared from carbonyl and non carbonyl compounds[2]. Deoximation of such oximes provides an alternative method for the synthesis of carbonyl compounds. Deprotection of an oxime can be achieved by oxidative cleavage, reductive cleavage or by hydrolytic cleavage depending on the structural details of the compound concerned. A number of oxidative deoximation methods have been developed which involve chromium (VI) species like trimethylammonium chlorochromate[3], chlorotrimethylsilane-(chromium),[4] pyridinium chlorochromate,[5] pyridinium chlorochromate-H_2O_2,[6] trimethylsilyl chlorochromate,[7] bis(trimethylsilyl)chromate,[8] unsupported chromium trioxide,[9] and polymer supported CrO_3 [10] as an oxidant.

Advantages such as cleaner reactions, very short reaction times, ease in work up, suppression of side and polymerized products etc. have kindled a special interest in 'dry' state microwave chemistry.[11] Silica, clay, alumina and zeolites have been used as reaction media in microwave enhanced organic synthesis. Recently, microwave assisted deoximation by silica supported ammonium persulfate, silica supported sodium periodate in dry conditions,[12,13] and silica supported bismuth trichloride in THF[14] have been reported.

We recently reported the preparation and utility of a silica supported chromium trioxide oxidant for selective oxidation of various alcohols.[15] We report here an excellent and very rapid

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deoximation by the SiO_2-CrO_3 oxidant, giving excellent yields in "dry" state MW exposure. Preparation of our reagent is straightforward.

Procedure: Dry powder obtained by evaporating dichloromethane from a well stirred mixture of acetophenone oxime (5 mmol, 0.67g), 5 ml dichloromethane and 2 g SiO_2-CrO_3 (5 mmol CrO_3 on 2 g SiO_2)[15] was irradiated in a MW oven (IFB, 750 watt output) for 45 seconds in an open beaker. After elution with dichloromethane, acetophenone was recovered in 95 % yield in pure form.

Table: Microwave promoted deoximation using silica supported chromium trioxide.

Entry	Substrate	MW Time(Sec)	Product[a]	Yield
1	Acetophenone oxime	45	Acetophenone	95
2	4-Bromoacetophenone oxime	45	4-Bromoacetophenone	94
3	4-Methylacetophenone oxime	45	4-Methylacetophenone	93
4	2,4-Dimethylacetophenone oxime	45	2,4-Dimethylacetophenone	94
5	Benzophenone oxime	45	Benzophenone	91
6	4,4-Dichlorobenzophenone oxime	45	4,4-Dichlorobenzophenone	90
7	Diisobutylketone oxime	60	Diisobutylketone	88
8	Cyclohexanone oxime	60	Cyclohexanone	87
9	2-Acetyl thiophene oxime	80	2-Acetyl thiophene	61[b]
10	2-Bromobenzaldoxime	80	2-Bromobenzaldehyde	88
11	3-Bromobenzaldoxime	80	3-Bromobenzaldehyde	82
12	4-Fluorobenzaldoxime	120	4-Fluorobenzaldehyde	85
13	4-Nitrobenzaldoxime	120	4-Nitrobenzaldehyde	57[b]
14	Cinnamaldoxime	120	Cinnamaldehyde	91
15	2-Thiophenealdoxime	60	2-Thiophenealdehyde	67[b]

a) All products are known compounds & exhibit satisfactory spectroscopic data (1H NMR & IR) & MP /BP.

b) Unreacted oxime fully recovered using column chromatography. Prolonged heating gives a mixture.

In conclusion, we report an extremely efficient method of oxidative deoximation by using silica supported chromium trioxide. Aldehydes were recovered in high yields without further oxidation to acids. Our method is simple, safe and rapid.

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