

Copper(II)-mediated regeneration of carbonyls from oximes and semicarbazones under solvent-free microwave irradiated conditions

Nilay Karchaudhuri, Aparna De and Alok Kumar Mitra*

Department of Chemistry, University of Calcutta, 92, Acharya P. C. Road, Kolkata-700 009, India

E-mail : akmitra@cucc.ernet.in Fax : 91-033-2351-9755

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Carbonyl compounds can be regenerated from the corresponding oximes and semicarbazones by a solvent-free, rapid, efficient and simple method under microwave irradiation exploiting copper(II) chloride.

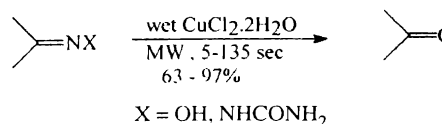
The easy preparation and high stability of oximes and semicarbazones provide the most acceptable methods of protection¹ of carbonyl compounds to the organic chemists. Oximes and semicarbazones are also extensively used for characterization and purification of carbonyls. So the methods of deprotection² of carbonyls from oximes and semicarbazones are of immense importance. Although quite a number of methods of regeneration of carbonyls are known, the search for newer, efficient and fast methods are going on.

Some of the recent methods reported for deoxygenation of carbonyls consist of dimethyl dioxirane³, *t*-butylhydroperoxide⁴, ammonium persulphate-silica⁵, manganese triacetate⁶, *N*-halo amides⁷, sodium periodate-silica⁸, Desmartin periodinane⁹, sodium bismuthate-silica¹⁰.

Moderate works on regeneration of carbonyls from the corresponding semicarbazones include pyruvic acid¹¹, sodium nitrite/glacial acetic acid¹², mercury(II) acetate, thallium(II) acetate, lead(IV) acetate¹³, clayfen¹⁴, nitrous acid¹⁵, Dowex-50¹⁶, Amberlyst 15/aq. acetone¹⁷, tetrakis-(pyridine) silver dichromate/benzene¹⁸, copper chloride/CH₃CN¹⁹, sodium bismuthate/silica²⁰, antimony trichloride²¹ etc. The method using copper chloride in CH₃CN suffers from several disadvantages involving the refluxing condition with longer reaction time (10–390 min), very poor yield for particular compound (7% for *p*-nitrobenzaldehyde) and the use of organic solvent (CH₃CN) which generates the problem of solvent-waste. So our attempt was to search for a faster, simple and solvent-free reaction condition.

Recently, the emerging trend of wide application of microwave radiation in chemical reaction enhancement²² is due to high reaction rates with the minimization of side reactions resulting cleaner products and the operational simplicity. The current approach involves the use of inorganic reagents in solvent-free condition²³ as these reactions

often involve the milder reaction, easier work-up and higher selectivity than similar reactions using organic reagents in solution. In continuation of our attempt²⁴ in this field, herein we wish to report a solid state deprotection of carbonyls from oximes and semicarbazones exploiting Cu^{II} chloride under microwave irradiation (Scheme 1).



Scheme 1

The carbonyls are regenerated in high yields (63–97%) at ambient pressure within 5–135 s (Table 1 and Table 2).

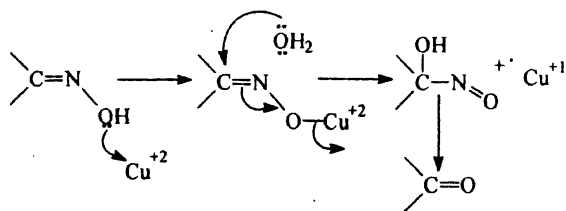
Table 1. Microwave assisted deoxygenation using cupric chloride dihydrate

Entry	Oxime of	Time s	Yield %
1	Benzaldehyde	24	92
2	Anisaldehyde	23	92
3	3-Nitrobenzaldehyde	30	74
4	4-Nitrobenzaldehyde	57	71
5	Vanillin	22	85
6	Isovanillin	74	73
7	Veratraldehyde	34	78
8	Piperonal	48	90
9	<i>O</i> -Benzylvanillin	32	84
10	<i>O</i> -Benzylisovanillin	51	79
11	Acetophenone	20	81
12	4-Methoxyacetophenone	75	74
13	4-Methylacetophenone	18	78
14	4-Nitroacetophenone	135	73
15	Benzophenone	17	91
16	Cyclohexanone	7	88
17	Isobutyl methyl ketone	48	63

Table 2. Microwave assisted regeneration of carbonyls from semicarbazones using cupric chloride dihydrate

Entry	Semicarbazone of	Time s	Yield %
1	Benzaldehyde	51	93
2	Anisaldehyde	45	92
3	3-Nitrobenzaldehyde	26	75
4	4-Nitrobenzaldehyde	30	70
5	Vanillin	12	93
6	Isovanillin	74	71
7	Veratraldehyde	19	85
8	Piperonal	50	86
9	O-Benzylvanillin	57	89
10	O-Benzylisovanillin	34	91
11	Acetophenone	7	97
12	4-Methylacetophenone	6	96
13	4-Methoxyacetophenone	10	95
14	4-Nitroacetophenone	60	88
15	2-Naphthyl methyl ketone	35	68
16	Cyclohexanone	5	92
17	7-Methoxytetralone	28	71
18	Isobutyl methyl ketone	20	70

The optimum ratio of the substrate to reagent is found to be 1 : 1 (mol/mol). The lower amount of the reagent results incomplete reaction. The dry reagent decomposes under microwave irradiation. So the reagent is moistened, as water is highly microwave active, resulting the efficient absorption of heat. By conventional heating method (oil-bath) at 110° in the presence of the reagent, the reaction was still incomplete after 22 h. The reagent has wide applicability for regeneration of both aldehydes and ketones from oximes and semicarbazones whereas many of the already reported methods cannot regenerate aldehydes from the corresponding oximes and semicarbazones. The plausible mechanism for Cu^{II} mediated regeneration of carbonyls is stated below :



Experimental

IR spectra were recorded on a Perkin-Elmer FT-IR-RXI spectrophotometer. ¹H NMR spectra were recorded on

Bruker AM 300L spectrometer operating at 300 MHz. The reactions were carried out in a domestic microwave oven (BPL, 800T/MM 261 EEP).

General procedure : A mixture of oxime/semicarbazone (1 mmol), CuCl₂·2H₂O (1 mmol) and water (0.5 ml) was taken in a 25 ml Erlenmeyer flask placed in an alumina-bath (heat-sink) inside a domestic microwave oven and irradiated for the specified time at power level of 700 W and the reaction was monitored by TLC. The product was extracted with ethyl acetate (2 × 5 ml), washed with brine (5 ml) and dried over sodium sulphate. Evaporation of the solvent afforded the product in high yield.

In conclusion, we have developed as solvent-free rapid method for the facile cleavage of carbon-nitrogen bond in oximes and semicarbazones under microwave irradiation to regenerate carbonyls.

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