

# A general approach for the microwave-assisted regeneration of carbonyl compounds from their nitrogenous derivatives

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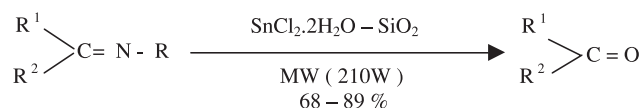
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A variety of nitrogenous derivatives of carbonyl compounds are rapidly converted into the corresponding carbonyl compounds in good yields using stannous chloride – silica gel under microwave irradiation

**Keywords:** stannous chloride, silicon dioxide, microwave, irradiation, nitrogenous compounds, carbonyl compounds

Nitrogenous derivatives serve as important synthetic intermediates as they are extensively used for the purification and characterisation of carbonyl compounds and also for the protection of carbonyl groups.<sup>1</sup> Regeneration of the parent carbonyl function is an important step in organic synthesis. Most of the methods reported<sup>2-16</sup> for the regeneration of carbonyl compounds from their nitrogenous derivatives have drawbacks under stringent conditions.

Microwave-assisted reactions are currently an increasing interest due to the novelty, and simplicity of such reactions under solvent free and eco-friendly conditions. Some non-conventional synthetic procedures have been developed<sup>17</sup> under microwave irradiation (MWI) for the generation carbonyl compounds from their oxime and semicarbazone derivatives. However, general application to a number of



nitrogenous derivatives under microwave-assisted conditions has not been reported.

These studies prompted us to develop a general synthetic protocol utilising microwave irradiation for the generation of carbonyl compounds from their nitrogenous derivatives in the presence of the catalyst  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O} - \text{SiO}_2$ , soaked with tetrahydrofuran. The semicarbazone, phenyl hydrazone, 2,4-dinitrophenylhydrazone (2,4-dnp) and oxime derivatives

**Table 1** Microwave-assisted regeneration of carbonyl compounds from nitrogenous derivatives.

Entry	Substrate	Carbonyl compounds <sup>a</sup> yields/%	M.p./b.p./°C Found (reported <sup>d</sup> )
1	<i>p</i> -Chlorobenzaldehyde semicarbazone	80 <sup>c</sup>	M.p. – 46 – 48 (47 – 50)
2	4 – Nitroacetophenone semicarbazone	84 <sup>c</sup>	M.p. – 79 – 80 (78 – 80)
3	Benzophenone semicarbazone	82 <sup>c</sup>	M.p. – 46 – 47 (46 – 48)
4	Cyclohexanone Semicarbazone	68 <sup>b</sup>	B.p. – 153 – 155 (155)
5	4 – Methoxy acetophenone Semicarbazone	86 <sup>b</sup>	B.p. – 135 – 136/15 mm (152 – 154/26 mm)
6	Acetophenone 2, 4 – dinitrophenylhydrazone	78 <sup>b</sup>	B.p. – 201 – 202 (202)
7	Benzophenone 2, 4 – dinitrophenylhydrazone	80 <sup>c</sup>	M.p. – 45 – 47 (46 – 48)
8	Cyclohexanone 2, 4 – dinitrophenylhydrazone	74 <sup>b</sup>	B.p. – 154 – 155 (155)
9	5 $\alpha$ -Cholestan-3-one 2, 4 – dinitrophenylhydrazone	88 <sup>c</sup>	M.p. – 128 – 130 (128 – 130)
10	<i>p</i> -Chloro benzaldehyde phenylhydrazone	86 <sup>c</sup>	M.p. – 47 – 49 (47 – 50)
11	Benzophenone phenylhydrazone	81 <sup>c</sup>	M.p. – 45 – 48 (46 – 48)
12	Heptanal phenylhydrazone	76 <sup>b</sup>	B.p. – 152 – 154 (153)
13	3 – Nitrobenzaldehyde oxime	85 <sup>c</sup>	M.p. – 56 – 58 (57 – 59)
14	4 – Methoxybenzaldehyde oxime	83 <sup>b</sup>	B.p. – 246 – 248 (248)
15	Acetophenone oxime	82 <sup>b</sup>	B.p. – 200 – 202 (202)
16	Heptanal oxime	84 <sup>b</sup>	B.p. – 152 – 153 (153)
17	5 $\alpha$ -Cholestan-3-one oxime	89 <sup>c</sup>	M.p. – 127 – 129 (128 – 130)

<sup>a</sup>Yield refers to parent carbonyl compounds and the reaction time was the same (8 min) for all the substrates. <sup>b</sup>Purification by distillation. <sup>c</sup>Purification by preparative column chromatography (ethyl acetate and petroleum ether) and crystallisation from ethanol. <sup>d</sup>Reported from Aldrich Chemical Catalogue.

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of aromatic aldehydes and ketones, aliphatic aldehydes and ketones, cyclic ketones and a steroidal ketone react smoothly under the reaction conditions to give the corresponding aldehydes and ketones. This rapid and environmentally safe procedure avoids the use of excess solvents and is a quite general and attractive method.

The reagent  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  alone does not regenerate the parent carbonyl compounds under microwave irradiation but the addition of  $\text{SiO}_2$  to the  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  favours the efficient selective regeneration of the corresponding carbonyl compounds of semicarbazone, phenylhydrazone, 2,4-dnp and oxime derivatives under the microwave irradiation. We speculate that silica gel acts here as an activating agent<sup>18</sup> and that the nitrogenous compounds are absorbed on the silica gel surface to facilitate the desired reactions.

In conclusion, the present microwave irradiation procedure provides a general methodology for the generation of carbonyl compounds from a variety of nitrogenous derivatives. The operational simplicity, selectivity, and cheapness, and the formation of good yields in very short times make this procedure an useful, attractive alternative to previously available methods.

### Experimental

Nitrogenous derivatives were prepared<sup>19</sup> from the carbonyl compounds. The products were characterised by m.p., b.p., spectral data and by direct comparison with the authentic samples. IR spectra were reported on a JASCO FT/IR – 5300 instrument and <sup>1</sup>H NMR spectra were recorded in deuteriochloroform on a JEAL FX – 90 instrument. The reactions were carried out in microwave oven (Kelvinator) – T 37.

#### General procedure

A mixture of the nitrogenous derivative (1 mmol), tin (II) chloride dihydrate (2 mmol) and silica gel (mesh 60–120) (200 mg) soaked with few drops of tetrahydrofuran was taken in a 50 ml. Erlenmeyer flask. The mixture was then kept inside a microwave oven and irradiated at 210W (internal temperature –60 °C) for 8 minutes. The mixture was cooled at room temperature, eluted with dichloromethane (20 ml) and then filtered. The filtrate was then washed with water and brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Evaporation of solvent furnished the crude products which, on purification by distillation and chromatography, yielded the carbonyl compounds (entries 1 – 17) in 68 – 89 % yields.

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### References

- (a) R.H. Shapiro and M.J. Heart, *J. Am. Chem. Soc.*, 1967, **89**, 5734; (b) C. B. Reese. In *Protective Groups in Organic Chemistry*, J.F.W. McOmie, Ed., Plenum Press, New York, 1973; (c) G.W. Kabalka and S.T. Summers, *J. Org. Chem.*, 1981, **46**, 1217; (d) G. Rosini and R. Ballini, *Synthesis*, 1983, 228 and references cited therein.
- E.B. Hershber, *J. Org. Chem.*, 1948, **13**, 542.
- D.H.R. Barton, D.J. Lester and S.V. Ley, *J. Chem. Soc. Chem. Commun.*, 1977, 445.
- R. Ballini and M. Petrini, *J. Chem. Soc. Perkin Trans. I*, 1988, 2563.
- P. Laszlo and E. Polla, *Synthesis*, 1985, 439.
- R.N. Butler, Morris and A.M. O'Donohue, *J. Chem. Res. (S)*, 1981, 61.
- A. McKillop, J.D. Hunt, R.D. Naylor and E.C. Taylor, *J. Am. Chem. Soc.*, 1971, **93**, 4918.
- R.H. Khan, R.K. Mathur and A.C. Ghosh, *J. Chem. Res.(S)*, 1995, 506.
- C.G. Rao, A.S. Radhkrishima and R.B. Singh, *Synthesis*, 1983, 808.
- C.H. Depuy and B.W. Ponder, *J. Am. Chem. Soc.*, 1959, **81**, 4629.
- G.A. Fleisher and E.C. Kendall, *J. Org. Chem.*, 1951, **16**, 556.
- J.E. McMurry and M. Silvestri, *J. Org. Chem.*, 1975, **40**, 1502.
- S.B. Shim, K.Kim and Y.H. Kim, *Tetrahedron Lett.*, 1987, **28**, 645.
- J.W. Bird and D.G. M. Diaper, *Can. J. Chem.*, 1969, **47**, 145.
- Y.H. Kim, H.K. Lee and H.S. Chang, *Tetrahedron Lett.*, 1987, 4285.
- N. B. Das, B. Nanda and A. Nayak, *Synthetic Commun.*, 2002, **32**, 3647.
- (a) B. Tamami and A.R. Kiasat, *Synth. Commun.*, 2000, **30**, 4129; (b) M. Ghiachi and J. Asghari, *Synth. Commun.*, 2000, **30**, 3865; (c) A.K. Mitra, A. De and N. Karchaudhuri, *Synthetic Commun.*, 2000, **30**, 1651.
- (a) A. Mc Killop and D.W. Young, *Synthesis*, 1979, 401; (b) T. Nishiguchi, N. Machida and E. Yamamoto, *Tetrahedron Lett.*, 1987, **28**, 4565.
- Vogel, A. I., *Textbook of Practical Organic Chemistry*, 5th. edn, Longman, London, 1989, 1258.