Regeneration of Ketones from Semicarbazones in the Solid State on Wet Silica Supported Sodium Bismuthate under Microwave Irradiation†

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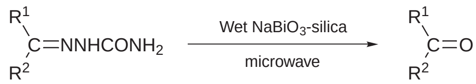
Microwave irradiation of ketosemicarbazones on wet silica supported sodium bismuthate under environmentally benign solvent-free condition provides a fast, efficient and simple method for regeneration of ketones in good yields.

Protection of carbonyl compounds as semicarbazones is of great interest to organic chemists as they are readily prepared and highly stable compounds.[1] Semicarbazones are extensively used for purification and characterisation of carbonyl compounds.[2] Although a number of methods for the regeneration of carbonyl compounds from semicarbazones have been reported, *viz.* sodium nitrite/glacial acetic acid,[3a] pyruvic acid,[3b] mercury(II) acetate, thallium(III) acetate, lead(IV) acetate,[3c] clayfen,[3d] nitrous acid,[3e] Dowex-50,[3f] tetrakis(pyridine)silver dichromate/benzene,[3g] copper chloride,[3h] 3-carboxypyridinium chlorochromate/MeCN[3i] and zirconium sulfophenyl phosphonate,[3j] the discovery of new efficient and fast methods is the goal of the organic chemists. Very recently a number of other reagents, *viz.* ammonium persulphate–Al_2O_3,[4a] bismuth trichloride,[4b] sodium periodate–SiO_2[4c] and hypervalent iodine[4d] have been successfully utilised for deprotection of semicarbazones, phenylhydrazones, hydrazones, tosylhydrazones and oximes.

Currently, the growing interest in the application of microwave irradiation in chemical reaction enhancement[5] is due to high reaction rates and formation of cleaner products. The solvent-free reaction[6] condition is especially appealing for providing an environmentally benign system. Herein we report a solid state method for regeneration of ketones from semicarbazones using sodium bismuthate supported on wet silica under microwave irradiation (Scheme 1). The reaction proceeds efficiently in good yields at ambient pressure within a few minutes (Table 1). To the best of our knowledge, this is the first report of the regeneration of ketones from semicarbazones using sodium bismuthate. Among several mineral supports examined, silica was found to give best results. The optimum molar ratio of the substrate to the reagent is found to be 1 : 2. The reaction remains incomplete when lower amounts of the reagent are used or if the reaction was performed in the absence of silica support. The dry reagent decomposes under microwave irradiation. Using conventional heating (oil bath) at 110 °C, the reaction is incomplete even after 24 h.



Scheme 1

The reagent has wide applicability for regeneration of ketones from aliphatic and aromatic ketosemicarbazones and disemicarbazones of diketones. However, semicarbazones of aldehydes under similar reaction conditions gave a complex mixture of products.

Experimental

IR spectra were run on Perkin-Elmer 782 spectrometer. ^1H NMR spectra were recorded in $CDCl_3$ solution on a Bruker AM 300L NMR spectrometer operating at 300 MHz using tetramethylsilane as the internal standard. The reactions were carried out in a domestic microwave oven (BPL-SANYO, BMO-700T, 1200 W).

General Procedure.—The reagent was prepared by adding silica gel (20 g, 230–400 mesh, SRL) to a stirred solution of $NaBiO_3$ (6.5 g, 23.2 mmol) in water (30 ml). After removal of water under reduced pressure, the dry reagent (2.28 g, 2 mmol) was moistened with water (0.5 ml) and was mixed with the neat ketosemicarbazone (1 mmol) in a 25 ml Erlenmeyer flask.[7] It was then placed in an alumina bath (heat sink) inside a domestic microwave oven operating at medium power (600 W) for a specified time (Table 1). After completion of the reaction (monitored by TLC), the product was extracted with dichloromethane (3 × 10 ml). All the products obtained were characterised by ^1H NMR spectroscopy and by comparison with IR spectra of authentic samples.

In conclusion, we have developed a solvent-free method for the facile cleavage of a variety of ketosemicarbazones in the solid state on wet silica supported sodium bismuthate.

Table 1 Microwave-assisted regeneration of ketones from semicarbazones using wet silica supported sodium bismuthate

Entry	Semicarbazone	Product	*t*/min	Yield[a] (%)
1	Isobutyl methyl ketone semicarbazone	Isobutyl methyl ketone	6	73
2	Cyclohexanone semicarbazone	Cyclohexanone	8	72
3	Acetophenone semicarbazone	Acetophenone	6	76
4	4-Methylacetophenone semicarbazone	4-Methylacetophenone	6	74
5	4-Methoxyacetophenone semicarbazone	4-Methoxyacetophenone	4	83
6	4-Nitroacetophenone semicarbazone	4-Nitroacetophenone	2	84
7	2-Hydroxyacetophenone semicarbazone	2-Hydroxyacetophenone	4	76
8	6-Methoxytetralone semicarbazone	6-Methoxytetralone	8	73
9	2-Acetylnaphthalene semicarbazone	2-Acetylnaphthalene	5	79
10	Benzil disemicarbazone	Benzil	5	85

[a] Yields refer to pure isolated products.

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7 To prevent evaporation of the low boiling products (entries 1 and 2), the reactions were carried out in an 100 ml Erlenmeyer flask fitted with a funnel as a loose top, upon which a round-bottomed flask containing ice was placed to serve as a condenser.