

Solid state regeneration of ketones from phenylhydrazones using wet silica supported sodium bismuthate under microwave irradiation

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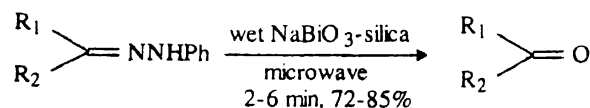
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Microwave irradiation of phenylhydrazones of ketones on wet silica supported sodium bismuthate in the solvent-free condition provides a fast, efficient and simple method for regeneration of ketones in high yields.

Protection of carbonyl compounds as phenylhydrazones¹ is of great interest to the organic chemists, as they are readily prepared and are stable compounds. Although 2,4-dinitrophenylhydrazone derivatives are used extensively for the characterization of the parent carbonyl compounds, their use as protective groups in multistep organic synthesis is, however, very much limited because of the difficulties of their deprotection². Whereas phenylhydrazones are not only extensively used for purification and characterization of carbonyl compounds, they can be deprotected rather easily. Although a number of methods for the regeneration of carbonyl compounds from phenylhydrazones are known, the discovery of newer efficient and fast methods is the goal of the organic chemists. Some of the reagents reported earlier for deprotection of phenylhydrazones are acetylacetone – HCl³, MnO₂⁴, acetone⁵, clay-ferric nitrate⁶, 3-carboxypyridinium chlorochromate⁷, ammonium persulphate⁸ and formic acid⁹. Some of these methods suffer from one or the other disadvantages like the use of excessive reagents^{3,4}, production of fair amount of byproduct⁴, long reaction time (100 h)⁵, methods applied for one example only^{5,6}, use of specialised non-commercial reagent⁷. Besides, most of the reactions are carried out in the presence of organic solvents.

Recently, the wide applicability of microwave irradiation¹⁰ in chemical reaction enhancement is due to high reaction rates with the formation of cleaner products and the operational simplicity. In recent years the use of inorganic reagents¹¹ in solvent-free condition has rapidly increased, as these reactions often involve the milder condition, easier work up and higher selectivity than similar reactions using organic reagents in solution. Herein we wish to report a solid state regeneration of ketones from phenylhydrazones using sodium bismuthate (NaBiO₃) supported on wet silica under microwave irradiation (Scheme 1). The reactions proceed efficiently in high yields (72–85%) at ambient pressure within 2–6 min (Table 1). To the best of our knowledge, this is the first report of the

regeneration of ketones from phenylhydrazones using sodium bismuthate.



Scheme 1

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

Entry	Substrate	Product	Time min	Yield* %
1	Cyclohexanone phenylhydrazone	Cyclohexanone	3	79
2	Acetophenone phenylhydrazone	Acetophenone	3	78
3	4-Methylacetophenone phenylhydrazone	4-Methylacetophenone	5	81
4	4-Methoxyacetophenone phenylhydrazone	4-Methoxyacetophenone	5	83
5	2-Hydroxyacetophenone phenylhydrazone	2-Hydroxyacetophenone	2	84
6	4-Nitroacetophenone phenylhydrazone	4-Nitroacetophenone	2	85
7	Benzophenone phenylhydrazone	Benzophenone	4	72
8	6-Methoxytetralone phenylhydrazone	6-Methoxytetralone	6	73
9	2-Acetylnaphthalene phenylhydrazone	2-Acetylnaphthalene	4	78

*Yields refer to pure isolated products.

The optimum ratio of the substrate to the reagent is found to be 1 : 2 (mol/mol). The reaction remains incomplete if lower amounts of the reagent are used or in the absence of silica support. The dry reagent decomposes under microwave irradiation, besides water absorbs the heat efficiently as it is highly microwave active. By conventional heating method (oil bath) at 110° in the presence of reagent, the reaction is still incomplete after 24 h. The reagent is applicable for

phenylhydrazones of aromatic as well as aliphatic ketones. However, the reaction with phenylhydrazones of aldehydes under similar condition results in a complex mixture of products.

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

Experimental

IR spectra were run on a Perkin-Elmer 782 spectrophotometer and ^1H NMR spectra on a Bruker AM 300L spectrometer (300 MHz). The reactions were carried out in a domestic microwave oven (BPL-SANYO, BMO-700T, 2450 MHz, 1200 W).

General procedure: The reagent was prepared by mixing silica gel (20 g, 230–400 mesh, SRL) with NaBiO_3 (6.5 g, 23.2 mmol, EM) in water (30 ml). After removal of water, the resulting powder was dried in an oven at 120° for 12 h. A typical reaction was carried out as follows. The reagent (2.28 g, 2 mmol), moistened with water (0.5 ml) was mixed with the neat phenylhydrazone (1 mmol) in a 25-ml Erlenmeyer flask¹². The flask was then placed in an alumina bath (heat sink) inside the microwave oven operating at medium power (600 W) for the specified time. After completion of the reaction (monitored by TLC), the product was extracted with dichloromethane (2×5 ml), washed with brine (5 ml) and dried over anhydrous Na_2SO_4 . Evaporation of the solvent followed by the filtration on a short silica gel column afforded the pure product. All the products were characterized by ^1H NMR spectroscopy and by comparison with IR spectra of authentic samples.

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12. To arrest the low boiling product from evaporating off (entry 1), reaction was carried out in a 100-ml Erlenmeyer flask fitted with a funnel as a loose top, upon which a round-bottomed flask containing ice was placed for serving as a condenser.