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

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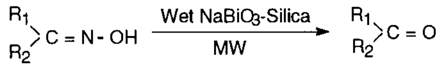
Abstract: Microwave irradiation of ketoximes on wet silica supported sodium bismuthate under environmentally friendly solvent-free condition provides a fast, efficient and simple method for regeneration of ketones in high yields.

Protection of carbonyl compounds as oximes is of great interest to organic chemists, as they are readily prepared and highly stable compounds[1]. Oximes are extensively used for purification and characterisation of carbonyl compounds and in the preparation of amides *via* Beckmann rearrangement[2]. Their syntheses from non-carbonyl compounds[3] provide an alternative route to aldehydes and ketones. Although quite a number of methods for the conversion of oximes to carbonyls are available, the discovery of newer efficient and fast methods is the goal of the organic chemists. Some of the methods reported earlier for deoximation of carbonyl compounds consist of periodic acid[4a], pyridinium chlorochromate[4b], pyridinium chlorochromate-H_2O_2[4c], triethylammonium chlorochromate[4d], Raney nickel[4e], chromic anhydride-chlorotrimethylsilane[4f], dinitrogen tetroxide[4g], Dowex-50[4h], dimethyl dioxirane[4i], t-butylhydroperoxide[4j], ammonium persulphate-silica[4k], manganese triacetate[4l], N-haloamides[4m], sodium periodate-silica[4n], Des-Martin periodinane[4o]. Some of these reagents suffer from one or the other disadvantages like long reaction time[4j], difficulties in isolation of products[4b,c], and also lacking easy availability and causing explosion under excessive heating during preparation[4o].

Recently 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 reactions[4n,6] under this condition are especially appealing for providing an environmentally benign system. Herein we wish to report a solid state deoximation procedure using sodium bismuthate ($NaBiO_3$) supported on wet silica under microwave irradiation. The reaction proceeds efficiently in high yields at ambient pressure within a few minutes (Table 1). To the best of our knowledge, this is the first report of deoximation using sodium bismuthate.

Among several mineral supports viz. alumina, silica, clay etc. examined, silica was found to give best results. The optimum ratio of the substrate to the reagent for deoximation is found to be 1:2 (mole/mole). 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. By conventional heating method (oil bath) at 110°C, the reaction was still incomplete after 24 h. The reagent has wide applicability for deoximation of aliphatic, aromatic ketoximes and dioximes of α- and β-diketones. However, the deoximation of aldoximes under similar reaction condition results in a complex mixture of products.

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, 23.35 mmol) in 30 ml of water. After removal of water, the resulting powder was dried in an oven at 120°C for 12 h. The reagent (2.3 g) was moistened with water (0.5 ml) and was mixed with the neat ketoxime (1 mmol) in a 25 ml Erlenmeyer flask[7]. The flask was then placed in an alumina bath (heat sink) inside a BPL-SANYO domestic microwave oven (2450 MHz) operating at full power (1200 w) for the specified time. After completion of the reaction (monitored by TLC) the product was extracted with dichloromethane (3x10 ml). All the compounds obtained were characterised by ^1H NMR spectroscopy and by comparison with infrared spectra of authentic samples.



$$\overset{R_1}{\underset{R_2}{>}}C=N-OH \xrightarrow[\text{MW}]{\text{Wet NaBiO}_3\text{-Silica}} \overset{R_1}{\underset{R_2}{>}}C=O$$

Table-1. **Microwave-assisted deoximation using wet silica supported sodium bismuthate**

Entry	Oxime	Product	Time (min)	Yield[a] (%)
1	Isobutyl methyl ketone oxime	Isobutyl methyl ketone	1	81
2	Cyclohexanone oxime	Cyclohexanone	5	73
3	Acetylacetone dioxime	Acetylacetone	1	72
4	Acetophenone oxime	Acetophenone	1	89
5	4-Methylacetophenone oxime	4-Methylacetophenone	1	85
6	4-Methoxyacetophenone oxime	4-Methoxyacetophenone	2.5	94
7	4-Nitroacetophenone oxime	4-Nitroacetophenone	4	82
8	2-Hydroxyacetophenone oxime	2-Hydroxyacetophenone	1	87
9	Benzophenone oxime	Benzophenone	1	90
10	Benzil dioxime	Benzil	3	88
11	6-Methoxytetralone oxime	6-Methoxytetralone	3	88
12	2-Naphthyl methyl ketone oxime	2-Naphthyl methyl ketone	1	90

[a] Yields refer to pure isolated products

In conclusion, we have developed a solvent-free method for the facile cleavage of a variety of ketoximes using wet silica supported sodium bismuthate under microwave irradiation.

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7. To arrest the low boiling products from evaporating off (entries 1,2), 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 for serving as a condenser.