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Oxidative deoximation by supported bismuth (III) nitrate mediated by DABCO under microwave irradiation.

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A mild, efficient, rapid and eco-friendly method for the direct conversion of oximes to carbonyl compounds upon treatment with bismuth(III) nitrate supported onto silica gel mediated by DABCO under microwave irradiation is described.

Keywords: oxidative deoximation, bismuth nitrate, DABCO, microwave

Oximes are very useful protecting groups and are extensively used for isolation and purification of carbonyl compounds.[1] Oximes are also useful to organic chemists as synthetic intermediates en route to amines[2] and nitriles.[3] Since oximes can be synthesised from non-carbonyl compounds,[4] their synthesis provides an alternative pathway to aldehydes and ketones. Oximes are also useful in the preparation of amides *via* the Beckman rearangment.[5] Regeneration of carbonyl compounds from their oximes is a paramount important and assumed added importance after the discovery of the Barton reaction in which oximes are produced at a non-activated hydrocarbon site.[6] The important role of oximes, owing to their hydrolytic stability, has provided motivation for the development of newer deoximation reagents.[7]

Several bismuth(III) compounds including bismuth(III) nitrate are commercially available at relatively low cost. The applications of bismuth nitrate to organic transformations have been extensively investigated.[8] Bismuth compounds are attractive candidates for use in green chemistry because bismuth is the least toxic of the heavy metals.[9] Reagents impregnated by inorganic solids, specially those that are efficient in "dry" media, have gained popularity because they display modified reactivity and selectivity.[10] During the course of our investigation, of organic manipulation in solventless system,[11] we have observed a relatively useful microwave effect.[12] The salient features of this technique are much improved reaction rate, selectivity and cleaner reaction.[13]

In continuation of our interest in using bismuth(III) nitrate on organic manipulations and deoximation reaction,[15] herein we report a solid state deoximation using silica gel-supported bismuth(III) nitrate under microwave irradiation which is accelerated by a catalytic amount of DABCO (1,4-diazatricyclo[2,2,2]octane).

As the first experiment we reacted 1:1 mole neat benzophenone oxime and bismuth(III) nitrate under microwaves irradiation. Even upon prolonged exposure to microwaves the reaction did not go to completion. However, with bismuth(III) nitrate on a mineral support the reaction completed in 1 min. Among various traditional mineral supports such as montmorllonite K-10, alumina, zeolite HZSM5, silica gel, the latter gave the best result. In case of using acetophenone oxime in the same reaction conditions the reaction remains incomplete even when using a higher amount of oxidant. DABCO / Pd has been used for highly efficient deprotection of peptides.[16] It has also used as a catalyst for the Baylis-Hellman reaction.[17] DABCO can catalyse the self and cross-condensation of α-acetylenic ketones.[18] When we added catalytic amount of DABCO to our above-mentioned deoximation protocol, the cleavage of acetophenone oximes with a molar ratio of supported bismuth(III) nitrate completed in few minutes under microwave irradiation. The optimum ratio of the substrate to the bismuth(III) nitrate is 1:1 (mole/mole) since the reaction does not go to completion with lower amounts 1: 0.5 (mole/mole), even after prolonged exposure to microwave irradiation.

To establish the generality of method various aldoximes and ketoximes were efficiently cleaved by this method in high yields and short times (Table 1). Another attractive feature of this method is the recyclability of silica gel. After washing of the support, it can be recycled for further use. Using an alternative heating mode, the reaction needed 3 hours to be completed. It is also notworthy to mention that this method is limited to aromatic oximes, cyclohexanone oxime gave poor yield.

In conclusion, the present procedure for the deoximation and regeneration of carbonyl compounds has advantages over previously reported methods and provides facile, useful, and inexpensive eco-friendly conditions.

Experimental

Yields refer to GC analysis. The products were characterised by TLC and their physical data. Bismuth(III) nitrate and DABCO were purchased and used as received. Oximes were prepared by known procedures.

Deoximation of oximes: General procedure

Bismuth(III) nitrate supported on silica gel (1mmol) and DABCO (0.1mmol) were mixed with the neat oxime (1mmol) in a small beaker. The beaker was placed inside a household microwave oven operating at 700W for the indicated time (Table1) The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was stirred in hot water and filtered off. The solid was taken up in CH_2Cl_2 (20ml). The solvent was evaporated to dryness under reduced pressure to afford the corresponding carbonyl compound. (Table 1).

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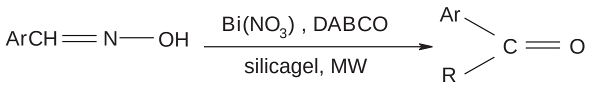
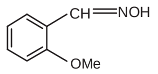
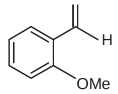
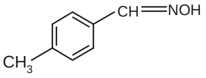
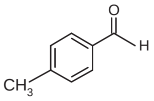
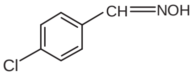
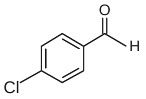
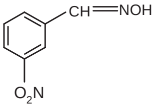
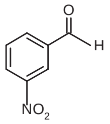
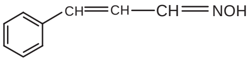
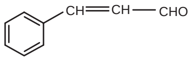
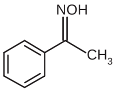
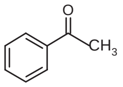
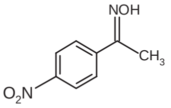
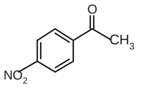
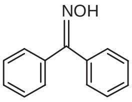
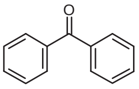


Table 1 Deoximation using, silica gel supported Bi(NO_3) mediated by DABCO, under microwave irradiation

Entry	Substrate	Reaction time/min	Product	Yeild/%
1		5		92
2		7.30		82
3		8		86
4		8		85
5		5		85
6		5		81
7		6		82
8		4		72

Yield refers to GC analysis.

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