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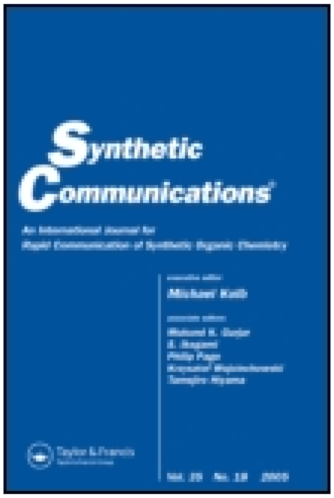

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BISMUTH NITRATE-MEDIATED DEPROTECTION OF OXIMES

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BISMUTH NITRATE-MEDIATED DEPROTECTION OF OXIMES

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ABSTRACT

Bismuth nitrate in wet silica gel was found to be an excellent reagent for the regeneration of ketones from oximes.

Oximes are widely used in synthetic chemistry in the characterization and purification of carbonyl compounds.[1] As a result, many methods are used for the regeneration of carbonyl compounds from these derivatives. Among these, acid-induced cleavage and more recently, oxidative transformation has been demonstrated as useful for this purpose. The widely used reagents for the deoximation reaction include various pyridine salts of chromium,[2] dinitrogentetroxide,[3] trimethylsilyl chloroformate,[4] Dowex-50,[5] dimethyl dioxirane,[6] zirconium sulfophenyl phosphonate.[7] To overcome the various shortcomings of these methods, recently Varma et al. have demonstrated the cleavage of semicarbazones and phenyl hydrazones with

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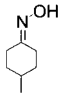
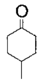
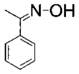
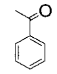
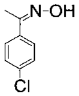
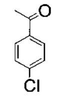
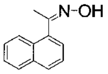
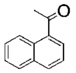
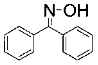
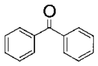
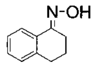
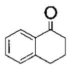
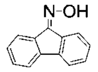
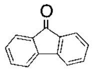
Table 1. Bismuth Nitrate-Mediated Deoximation of Ketones

Entry	Substarte	Product	Yield (%)	Time (h)	M.p./B.p. (°C) lit[a]/obs
1			97	2	169–171/168
2			89	5	202/200
3			98	9	232/231
4			87	9	302/299
5			90	5	48–49/48
6			85	1.5	113–116 (6 mm/Hg)/ 112–115 (6 mm/Hg)
7			92	10	82–85/83

[a] Available from Aldrich Chemical Company.

ammonium persulfate-clay using microwave irradiation.[8] They have also shown an oxidative cleavage of ketoximes on wet silica by sodium periodate under microwave irradiation.[9] Although, the methods reported by Varma et al. are valuable from the synthetic standpoint, extreme precautions have to be taken as these reactions were performed under microwave irradiation or ultrasonic irradiation with an oxidant. Therefore, efficient methods that can regenerate the carbonyl compounds from oximes at less stringent conditions would be useful.

We have been engaged in the use of polyaromatic compounds as anticancer agents[10] and recently have demonstrated the synthesis of dibenzofluorenone derivatives with this activity.[11] In order to do a systematic structure-activity study we require a number of pure benzylic ketones.

In continuation of our research on bismuth nitrate,[12] we now report a general method of the regeneration of ketones from their oxime derivatives in excellent yield without using any microwave irradiation or ultrasonic irradiation. We believe this is the first report of using bismuth nitrate as the reagent for the deprotection of oximes.

Several oximes were deoximated using bismuth nitrate in silica gel in the presence of a small amounts of water under reflux condition in tetrahydrofuran (THF). Aliphatic (entry 1), benzylic (entry 6), dibenzylic (entry 7) and aromatic (entry 2–5) ketoximes were deprotected in excellent yield (85–98%) by this method (Table 1).

While we demonstrated a facile aromatic nitration reaction[12] with bismuth nitrate in the presence of solid support, we did not observe any nitration of aromatic substrates under this condition during the cleavage reaction. We found a few drops of water and silica gel are essential for the success of the reaction. While THF was the optimal solvent, we can have a different solvent compositions (methanol, ethanol, acetonitrile etc). The reaction failed to produce the ketones without bismuth nitrate or silica gel.

In summary, a facile regeneration method of ketones from their respective oximes using bismuth nitrate in wet silica has been developed.[13]

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13. A representative procedure is as follows: To a suspension of oximes (1 mmol) in silica gel (1.5 g) and THF (10 mL) was added bismuth

nitrate pentahydrate (485 mg, 1 mmol) and water (2 mL). The mixture was refluxed for the specified time as indicated in the Table 1. It was then filtered to remove the silica gel, extracted with dichloromethane (25 mL), washed successively with saturated sodium bicarbonate solution, dried, evaporated and filtered through a short silica gel column to obtain the pure ketone.

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