Oxidative deprotection of trimethylsilyl ethers using bismuth nitrate supported onto montmorillonite k-10 under microwave irradiation in solventless system

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Primary and secondary trimethylsilyl ethers are converted to their carbonyl compounds efficiently using montmorillonite k-10 supported bismuth nitrate under microwave irradiation in a solventless system.

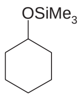
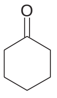
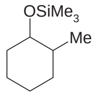
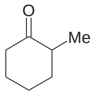
Keywords: trimethylsilyl ethers, aldehyde, bismuth nitrate, microwave

The protection of functional groups and their deprotection are important processes in synthetic chemistry of polyfunctional molecules including the total syntheses of natural products.[1-3] Large numbers of protective groups have been developed along with numerous methods for their removal. Direct oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds has attracted considerable attention in recent years[4,5] but the development of a catalytic version of these methods with low-toxic, readily available economic reagents could lead to an environmentally benign process. Bismuth compounds are environmentally friendly reagents for organic synthesis.[6] They are relatively nontoxic, readily available, inexpensive and fairly insensitive to small amount of water.[7] The biochemistry,[8] toxicology,[9] and environmental effects of bismuth compounds have been well documented and show that they are attractive candidates for use in green chemistry.

Prompted by stringent environmental protection laws in recent years there has been increasing emphasis on the use and design of eco-friendly reagents, solid state and solvent-free reactions.[10] Application of the microwave heating technique is currently under extensive examination.[11] Dry techniques have attracted much attention recently since organic solvents are expensive and hazardous and open vessels can be used for this purpose.[12] We have been engaged in bismuth based organic transformations. During this course of study we have discovered that Hantzsch, 1,4-dihydropyridine oxidation [13] and cleavage of oximes[14] can be mediated by commercially available bismuth nitrate under microwave irradiation and solvent-free conditions. As a part of an ongoing research program to develop solventless chemical transformation under microwave irradiation,[12] we report an efficient direct oxidative deprotection of trimethylsilyl ethers using clay supported bismuth nitrate under these conditions. In the present method bismuth nitrate (2mmole) was mixed thoroughly with montmorillonite k-10 (0.5 g) in a beaker using spatula. A trimethylsilyl ether was added and mixed thoroughly. This mixture was irradiated with microwaves to yield the corresponding carbonyl compound on completion of the reaction monitored by TLC (hexane: EtOAc, 8:2). The product was purified by simple filtration through a silica gel pad and evaporation of the methylene chloride eluent. A variety of trimethylsilyl ethers were converted to corresponding carbonyl compounds via this procedures and the results are shown in Table 1. It is worthwhile mentioning that in the absence of a solid support the reaction is sluggish and more seriously, molten bismuth nitrate and/ or its degradation product(s) adhered to the walls of the reaction vessel, forming an intractable mass which made the isolation of carbonyl compounds difficult and led to erratic results.

Among the solid supports such as silica gel, zeolite, alumina, montmorillonte k-10 which were examined, the latter gave the best results. Unlike other oxidative deprotection methods, the major drawback of over-oxidation of the resultant aldehydes has not been observed under the reaction conditions. In summary a facile, fast and eco-friendly solvent free direct oxidative deprotection of trimethylsilyl ethers has been developed. The significant advantage of this procedure is the mildness, speed, ease of manipulation and the absence of volatile solvent. We believe that this method will find application in modern organic synthesis.

Table 1

Entry	Substrate		Time/s	Carbonyl compound	Yield/%	m.p.(°C) or bp(°C)/ Torr	
						Found	Reported
1	$PhCH_2OSiMe_3$	**1a**	60	PhCHO	99	176–177/760	178-179/760
2	2-$ClC_6H_4CH_2OSiMe_3$	**2a**	120	2•ClC_6H_4CHO	87	212–214/760	209–215/760
3	4•$NO_2C_6H_4Ch_2OSiMe_3$	**3a**	210	4-$NO_2C_6H_4CHO$	76	105–107	150–108
4	4•$OMeC_6H_4CH_2OSiMe_3$	**4a**	180	4 $OMeC_6H_4CHO$	76	57–58	57–60
5	$PhCH=CHCH_2OSiME_3$	**5a**	120	PhCH=CHCHO	86	246/760	248/760
6	$PhCHOSiMe_3Ph$	**6a**	120	PhCOPH	80	49–51	49–51
7	$PHCHOSiMe_3COPh$	**7a**	120	PhCOCOPh	95	94–95	94–95
8		**8a**	120		90	154–155/760	155/760
9		**9a**	120		76	162/760	162–163/760
10	$MeCHOSiMe_3(CH_2)_5CH_3$	**10a**	210	$MeCO(CH_2)_5CH_3$	71	172–173/760	173/760

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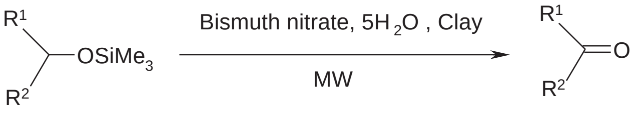

Scheme 1

Experimental

All compounds were identified by comparison of their physical data with those of authentic samples. Yields refer to isolated products.

Oxidative deprotection of benzyltrimethyl silyl ether. A typical procedure: Bismuth nitrate pentahydrate (2 mmole) was mixed with equivalent weight of montmorillonite k-10 with spatula in a beaker. Heat benzyltrimethylsilyl ether was added and mixed thoroughly with spatula to make a intimate mixture, The beaker was placed in microwave oven for 2 min. The progress of reaction was monitored by TLC. Upon completion of the reaction, CH_2Cl_2(5 ml) was added to the residue and filtered off. The filtrate was evaporated to dryness to afford benzaldehyde (yield 99%).

Selected spectroscopic data for some starting materials, **1a**: b.p. 196°C Lit.[15a] b.p. 198°C: ^{1}H NMR ($CDCl_3$); δ 0.16(s, 9H), 4.70 (s, 2H), 7.23–7.34(m. 5H); **3a**: ^{1}H NMR ($CDCl_3$); δ 0.10(s, 9H), 4.72(s, 2H), 7.19–831 (m, 4H); **5a**: b.p. 96(5 Torr) °C (Lit [15a] b.p. 100 (4 Torr) °C): **6a**: b.p. 120 (5 Torr) °C (Lit. [15a] b.p. 120(2Torr) °C): ^{1}HNMR ($CDCl_3$); δ 0.03 (s, 9H), 5.72 (s, 2H), 7.24 (M, 10): **8a**: b.p. 166°C (Lit.[15a] b.p. 168°C).

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