

SHORT
COMMUNICATIONS

Efficient Solvent-Free Deprotection of Acetals and Trimethylsilyl Ethers with Iodic Acid on Silica Gel under Microwave Irradiation*

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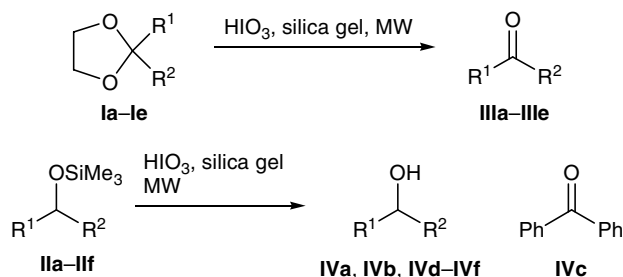
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Protection of certain functional groups and deprotection of the protected derivatives constitute important processes in the synthetic chemistry of polyfunctional molecules, including total syntheses of natural products [1]. The trimethylsilyl group is one of the most useful protecting groups for alcohols in multistep organic syntheses. Conversion into acetals is the most widely used method for protection of aldehydes and ketones; deprotection of acetals and ketals to the corresponding carbonyl compounds is an important transformation in organic synthesis [1]. Extensive studies on deprotection of these derivatives to the parent alcohols and carbonyl compounds have been carried out [2–7]. However, some of the known methods for deprotection of acetals and trimethylsilyl ethers require high temperatures and long reaction times, and they often involve toxic metal ions and solvents, which are detrimental to the environment. Therefore, there is a need for simple, less expensive, and safer procedure for deprotection of acetals and trimethylsilyl ethers.

Organic reactions promoted by microwave irradiation have recently attracted attention. The main advantage of these methods over conventional classical methods is that they ensure cleaner reactions, shorter reaction time, and easier workup [8],

In continuation of our studies on the oxidation of organic compounds [2, 9–12] we now report on the use of iodic acid HIO_3 as efficient reagent for oxidative deprotection of acetals **I** and trimethylsilyl ethers **II** to the corresponding carbonyl compounds **III** and alcohols **IV**. Initially, we added 1 mmol of substrate to 1 g of wet silica gel without HIO_3 in a mortar, and the mixture was ground with a pestle until it became

homogeneous. The mixture was then transferred to an Erlenmeyer flask and was irradiated in a microwave oven; however, no deprotection was achieved under these conditions. Then we used equimolar amounts of an acetal and HIO_3 or 0.5 equiv of the latter for trimethylsilyl ethers; the reactants were mixed with dry silica gel (1 g) in a mortar, and the mixture was transferred to an Erlenmeyer flask and was irradiated in a microwave oven. In this case, the mixture burned up, and molecular iodine deposited on the walls of the reaction flask. Therefore, we used wet silica gel and succeeded in deprotecting the substrates in good to high yields at very short times. The result of deprotection of acetals and trimethylsilyl ethers are summarized in table.



For R¹ and R², see table.

The time for the deprotection of trimethylsilyl ethers was optimized so as to avoid subsequent oxidation of the alcohol to aldehyde or ketone. However, removal of the trimethylsilyl group from diphenylmethyl trimethylsilyl ether (**IIc**) was always accompanied by formation of benzophenone (**IVc**) (according to the TLC data) despite very short reaction time; prolonged microwave irradiation resulted in the formation of benzophenone (**IVc**) as the major product.

* The text was submitted by the authors in English.

Deprotection of acetals and trimethylsilyl ethers with HIO_3 on silica gel under microwave irradiation (amounts of the reactants: substrate, 1 mmol; HIO_3 , 1 or 0.5 mmol; silica gel, 1 g; water, 1 ml; irradiation power 1000 W)

Compound no.	R ¹	R ²	Irradiation time, s	Product	Yield, ^a %
Ia		(CH ₂) ₅	40	IIIa	80
Ib	Me	Ph	20	IIIb	90
Ic	Me	4-O ₂ NC ₆ H ₄	50	IIIc	92
Id	Me	4-PhC ₆ H ₄	20	III d	95
Ie	H	4-O ₂ NC ₆ H ₄	60 ^b	IIIe	88
IIa	H	PhCH=CH	10	IVa	98
IIb	H	C ₇ H ₁₅	10	IVb	95
IIc	Ph	Ph	110	IVc	86
IId	H	Ph	10	IVd	88
IIe	H	4-MeOC ₆ H ₄	10	IVe	86
II f	Et	Ph	30	IVf	90

^a Isolated product.

^b 2 ml of water.

Thus, iodic acid is an efficient and convenient reagent for oxidative deprotection of acetals and trimethylsilyl ethers to the corresponding carbonyl compounds and alcohols. Advantages of the proposed procedure include its ready availability, low toxicity of iodic acid, solvent-free conditions, and simple workup.

General procedure for deprotection of acetals and trimethylsilyl ethers. A mixture of 1 mmol of the corresponding acetal or trimethylsilyl ether and 1 g of silica gel was ground in a mortar until it became homogeneous and was then added to a mixture of 1 (for acetals) or 0.5 mmol (for trimethylsilyl ethers) of HIO_3 and 1 ml of water in an Erlenmeyer flask. The resulting mixture was irradiated in a microwave oven at a power of 1000 W until the initial compound disappeared completely (according to the TLC data, see table). The mixture was then extracted with 25 ml of methylene chloride, the extract was filtered and evaporated, and the residue was purified by column chromatography on silica gel. The yields of the isolated carbonyl compounds and alcohols are given in table.

The products were identified by comparing their physical and spectral data with those of authentic samples. All yields refer to isolated products. The IR and NMR spectra were recorded on Perkin–Elmer 781 and Bruker DPX-500 spectrometers, respectively. The progress of reactions was monitored by TLC. Initial acetals and trimethylsilyl ethers were prepared following the procedures described in [13, 14].

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