

Note

Direct oxidative deprotection of trimethylsilyl ethers with cerium ammonium nitrate supported onto HZSM-5 zeolite under microwave irradiation in solventless system

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Received 14 March 2005; accepted (revised) 9 August 2005

Trimethylsilyl ethers are selectively and rapidly oxidized to the corresponding carbonyl compounds by cerium ammonium nitrate (CAN) supported onto HZSM-5 zeolite under microwave irradiation in solvent-free conditions.

Keywords: Deprotection, CAN, microwave irradiation, solventless system, trimethylsilyl ethers

IPC: Int.Cl.⁷ C 07 C

The protection of certain functional groups and the deprotection of the protected derivatives constitute important processes in the multistage synthetic chemistry of poly-functional molecules including the total synthesis of natural products¹. The combination of the one pot strategy with the use of eco-friendly solid acid catalyst is now the fast tool for the specific target compounds with minimum production of pollutants as well as reduction of the cost².

Heterogeneous organic reactions have proven useful to chemists in the laboratory as well as in the industrial context. Microwave heating and its application in organic synthesis is currently under intensive investigation³. The focus has lately shifted to less cumbersome solvent-free methods wherein the neat reactants, often in the presence of mineral oxides or supported catalyst undergo facile reactions to provide high yields of pure products thus eliminating or minimizing the use of organic solvents⁴.

Different salts of Ce(IV) have been employed as versatile reagents in organic synthesis⁵. In addition recently cerium(IV) as ceric ammonium nitrate has

been used for deprotection of a range of THP ethers under neutral conditions, using a little as 3 mol% in MeCN/borate buffer (pH = 8)⁶.

One of the most useful and convenient methods for protection of hydroxy groups is their transformation to trimethylsilyl ethers¹. Direct oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds has found considerable attention during recent years⁷. We were however keen to find an alternative method which could accelerate the reaction has an easy work-up and requires eco-friendly condition.

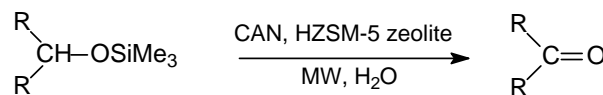
We have recently used HZSM-5 zeolite as an efficient support for the oxidation of alcohols under microwave irradiation⁸ and CAN for the solid state cleavage of semicarbazones⁹. In continuation of these studies, we report a facile and rapid direct oxidative deprotection of trimethylsilyl ethers using cerium ammonium nitrate (CAN) doped HZSM-5 zeolite under microwave irradiation in solventless system.

Among the various solid supports examined such as silica gel, montmorillonite K-10, alumina, HY zeolite and HZSM-5 zeolite, the latter proved to be superior.

The reaction is conducted by mixing 3 equivalents of zeolite supported CAN with neat ethers. The mixture was irradiated using microwave for a short time period. The corresponding carbonyl compound was obtained in high yield.

The reactions are relatively clean with no tar formation typical for many CAN mediated reactions. No overoxidation to carboxylic acids was observed (**Table I**).

It is noteworthy to mention that in the absence of zeolite, the reactions in all cases are sluggish and a considerable amount of ethers and alcohols were recovered unchanged even upon exposure to microwave irradiation for an extended period of time.



In conclusion, an environmentally benign and safe oxidant on a solid support is reported. Rapid reaction, high yield and use of inexpensive zeolite under solvent-free conditions are attractive features of this protocol.

Table I — Oxidative deprotection of trimethylsilyl ethers with HZSM-5 zeolite cerium ammonium nitrate (CAN) mixture under microwave irradiation in solventless system

Entry	Substrate	Time (min)	Product	Yield ^a (%)	m.p. or b.p. (°C)	
					Found	Lit. ¹⁰
1	C ₆ H ₅ CH ₂ OSiMe ₃	10	C ₆ H ₅ CHO	87	176-7	178
2	4-Cl-C ₆ H ₄ CH ₂ OSiMe ₃	5	4-Cl-C ₆ H ₄ CHO	91	45	47.5
3	4-NO ₂ -C ₆ H ₄ CH ₂ OSiMe ₃	5	4-NO ₂ -C ₆ H ₄ CHO	93	105-7	106
4	Ph ₂ CHOSiMe ₃	5	PhCOPh	88	49-51	48.1
5	CH ₃ (CH ₂) ₃ CH ₂ OSiMe ₃	5	CH ₃ (CH ₂) ₃ CHO	92	100	103
6	CH ₃ (CH ₂) ₅ CH ₂ OSiMe ₃	5	CH ₃ (CH ₂) ₅ CHO	92	150	152
7	CH ₃ (CH ₂) ₇ CH ₂ OSiMe ₃	8	CH ₃ (CH ₂) ₇ CHO	91	191-2	190-2
8	CH ₃ (CH ₂) ₁₄ CH ₂ OSiMe ₃	10	CH ₃ (CH ₂) ₁₄ CHO	93	33	34
9	<i>c</i> -C ₆ H ₁₁ CH ₂ OSiMe ₃	10	<i>c</i> -C ₆ H ₁₁ CHO	90	151	155.2
10	Mentol-SiMe ₃	8	(-)-Menthone	91	211	210.5

^a Yields refer to isolated product.

Experimental Section

All compounds are known and were identified by comparison with authentic samples (physical and spectroscopic data). Although we did not have any accident, for safety reasons all the experiments employing microwave ovens Panasonic 1000 W, 2450 MHz, should be performed in an efficient hood in order to avoid contact with vapours.

Preparation of CAN/wet HZSM-5 zeolite

HZSM-5 zeolite (2 g) was shaken with distilled water (4 mL). To this mixture cerium ammonium nitrate (2.18 g, 4 mmol) was added and crushed together in a mortar to form an intimate mixture.

Direct oxidative deprotection of trimethylsilyl ethers. General procedure

An appropriate silyl ether (2 mmol) was thoroughly mixed with the above catalyst (6.27 equivalent to 2 mmol CAN) using a spatula. An exothermic reaction ensues with darkening of the reagent. The progress of reaction was monitored by TLC (hexane: AcOEt; 8:2). The product was

extracted into CH₂Cl₂ (2 × 25 mL) and passed through a small bed of silica gel to afford the pure carbonyl compound (**Table I**).

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