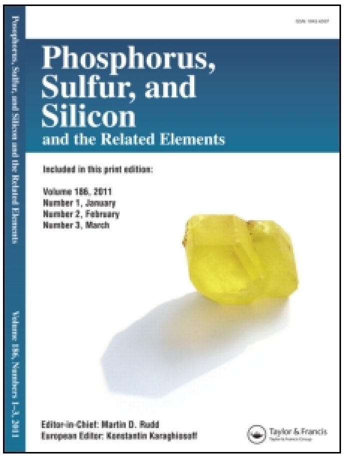

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OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL ETHERS TO CARBONYL COMPOUNDS WITH $PdCl_2(PhCN)_2$-CrO_3 AND CLAY-BIS(TRIMETHYLSILYL) CHROMATE IN SOLVENTLESS SYSTEM

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A simple and selective oxidative deprotection of trimethylsilyl ethers to carbonyl compounds is described that occurs on $PdCl_2(PhCN)_2$-CrO_3 and bis(trimethylsilyl) chromate under solvent free conditions and is expedited by microwave irradiation.

INTRODUCTION

The use of one pot reaction offers a great success in organic synthesis today. The combination of the one pot strategy with the use of eco-friendly solid acid catalysts is now the best tool for the synthesis of specific target compounds with minimum production of pollutants as well as reduction of the cost[1].

Direct oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds has found considerable attention during recent years [2,3]. We were however keen to find an alternative method which could accelerate the reaction, has an easy work up and requires eco-friendly condition.

Among the various methods which are avaible to date chromium reagent based oxidations have been very popular. However there is a serious draw-

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back against oxidants based on chromium [4]. They are corrosive and irritants for the skin and for sensitive parts of body such as eyes. Potential danger (ignition or explosion) in handling of its complexes, cumbersome isolation of products and waste disposal are other disadvantages of the utility of chromium reagents.

Organic solvents are not only expensive but are often flammable, toxic and environmentally hazardous. Microwave irradiation in organic synthesis is a useful technique nowadays [5]. Dry media using microwave heating have attracted much attention [6]. Oxidation reactions are less considered under microwave irradiation due to unsafe and uncontrollable experimental conditions [7]. Impregmentation of reagents on solid supports have circumented this problem and provide an attractive alternative in organic synthesis in view of selectivity and ease of manipulation [8].

Pd catalyzed reactions enjoy widespread application in organic synthesis[9]. Recently, deprotection of trimethylsilyl ethers by the paladium complex $PdCl_2(PhCN)_2$ under aqeous condition [10] and in solventless system [11] have been reported. We therefore reasoned that if $PdCl_2(PhCN)_2$ is used along with CrO_3 in solventless system and if one pot oxidative deprotection occurred it could offer a milder and more environmentally benign alternative to the reported methods. Indeed when a combination of CrO_3: $PdCl_2(PhCN)_2$, 20:1 was mixed with benzyl trimethylsilyl ether without solvent benzaldehyde was obtained in excellent yield. To assess the generality of this oxidative deprotection a variety of trimethylsilyl ethers were caused to react under these conditions which yields the corresponding carbonyl compound in good to excellent yields (Table I). Although the reaction does occur in dichloromethane, for the sake of environmental demand, we performed all the reactions in a solventless system. We found out that the rate of the reaction could be increased significantly if the mixture is exposed to microwave irradiation. For example benzyl trimethylsilyl ether was oxidatively deprotected at room temperature in 5 min while exposure to microwave irradiation converted that to benzaldehyde immediately. Primary silyl ethers (allylic and non allylic as well as benzylic) did not undergo overoxidation to carboxylic acids. Cinammyl trimethylsilyl ether was converted to cinammyl aldehyde showing carbon-carbon double bonds are not prone to cleavage with this method.(Table I).

TABLE I Oxidative deprotection of trimethylsilyl ethers with $PdCl_2(PhCN)_2$-CrO_3 in solventless system under microwave irradiation

Entry	*Substrate*	*Time (sec)*	*Product*	*Yield (%)*
1	$PhCH_2OSiMe_3$	10	PhCHO	99
2	5-Me-2-$NO_2C_6H_3CH_2OSiMe_3$[c]	10	5-Me-2-$NO_2C_6H_3CHO$	98
3	3-Me-$C_6H_4CH_2OSiMe_3$	10	3-MeC_6H_4CHO	98
4	$PhCH{=}CHCH_2OSiMe_3$	30	$PhCH{=}CHCHO$	92
5	Benzointrimethylsilyl ether	30	Benzil	91
6	Benzohydroltrimethylsilyl ether	10	Benzophenone	96
7	Cyclohexyltrimethylsilyl ether	120	Cyclohexanone	86
8	2-Methylcyclohexyl trimethylsilyl ether	120	2-Methylcyclohexanone	84
9	(-) Mentholtrimethylsilyl ether	90	(-) Menthone	88

RESULTS AND DISCUSSION

We have recently reported the oxidative deprotection of trimethylsilyl ethers by montmorillonite K-10 supported bis (trimethylsilyl) chromate under classical heating [12]. In continuation of manipulation of the above supported bis (trimethylsilyl) chromate [13] and in connection of our investigations on organic reactions in solventless system under microwave irradiation [14] we now report a facile oxidative deprotection of trimethylsilyl ethers to carbonyl compounds using bis (trimethylsilyl) chromate under solvent free conditiond that is accelerated by exposure to microwaves (MW). The reaction is conducted by mixing finely ground bis (trimethylsilyl) chromate supported onto montmorillonite K-10 with neat trimethylsilyl ethers. We discovered that in most cases at room temperature the reactions are completed upon simple mixing but in few cases the reactions are slow and a considerable amount of trimethylsilyl ethers and alcohols are recovered unchanged along with the desired compounds. As an example the reaction of 4-methylbenzyl trimethylsilyl ether with bis (trimethylsilyl) chromate supported onto montmorillonite K-10 at room temperature for a long period of time results in the formation of only 30% of 4-methylbenzaldehyde whereas the yield increases to 90% under microwave irradiation (Table II).

TABLE II Oxidative deprotection of trimethylsilyl ethers with bis (trimethylsilyl) chromate supported onto montmorrillonite K-10 under microwave irradiation

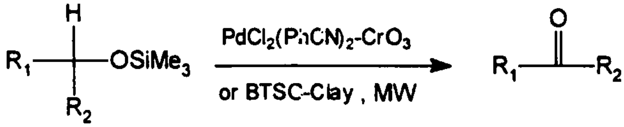
Entry	*Substrate*	*Time (sec)*	*Product*	*Yield*[a] *(%)*
1	$PhCH_2OSiMe_3$	60	PhCHO	90[b]
2	4-$MeC_6H_4CH_2OSiMe_3$[c]	120	4-MeC_6H_4CHO	85[b]
3	5-Me-2-$NO_2C_6H_3CH_2OSiMe_3$	120	5-Me-2-$NO_2C_6H_3CHO$	80[b]
4	$PhCH{=}CHCH_2OSiMe_3$	60	PhCH=CHCHO	90
5	(-) Mentholtrimethylsilyl ether	60	(-) Menthone	83
6	$C_7H_{15}CH_2OSiMe_3$	60	$C_7H_{15}CHO$	90
7	2-Ethylhexanyl trimethylsilyl ether	120	2-Ethylhexanal	88
8	Cyclohexyltrimethylsilyl ether	60	Cyclohexanone	85[b]
9	Benzohydrol trimethylsilyl ether	60	Benzophenone	88
10	2-Methylcyclohexyl trimethylsilyl ether	60	2-Methylcyclohexanone	90

a. Unoptimized yields of products that exhibited physical and spectral properties in accord with the assigned structure.

b. Yields based on the isolation of 2,4-dinoitrophenylhydrazine derivative.

c. The reaction was completed under microwave irradiation.

In conclusion the present methods provide useful alternatives to the one pot oxidative deprotection of trimethylsilyl ether. The notable advantages of these methodologies are mild and eco-friendly conditions, fast reaction and selective protocol. By development of a continuous microwave[15] reactor this methods could find applications.



EXPERIMENTAL

A National microwave (MW) oven operating at 2450 MHz (power 900W) was used for all the experiments. All products were known compounds and identified by comparison with authentic samples.

General Procedure for Oxidative Deprotection of Trimethylsilyl Ethers

Chromium trioxide (1g, 10 mmol) and $PdCl_2(PhCN)_2$ (0.191g, 0.5 mmol) were crushed together in a mortar so as to form an intimate mixture. Neat trimethylsilyl ether (10 mmol) was added to this mixture and placed in a microwave oven for the time indicated in the Table. After the reaction was complete (tlc monitoring) the crude product was treated with CH_2Cl_2 (20 mL) and filtrated through a thin pad of celite and the celite pad was washed throughly with CH_2Cl_2 (20 mL). Evaporation of the solvent gave a crude product which was further purified by column chromatography (Table I).

Oxidative Deprotection of Benzyl Trimethylsilyl Esther. A Typical Procedure

BTSC supported onto montmorillonite K-10 (0.75 g, equivalent to 1.2 mmol of chromium (VI) oxidant) was gradually added to benzyl trimethylsilyl ether (0.18g, 1 mml) in a beaker and mixed with a spatula. An exothermic reaction ensues and is completed almost immediately as confirmed by TLC (hexane : ethylacetate; 8:2). The product is extracted into methylene chloride (2×20 mL) and is passed through a small bed of alumina (1 cm) to afford pure benzaldehyde. In some cases (Entries 2, 3 and 7) brief microwave irradiation (in an unmodified household microwave oven) complete the reactions (Table II).

References

1. a) F. Tietze, U. Beifuss, *Angew. Chem., Int. Ed. Engl.*, **32**, 131 (1993).
   b) R. Grigg, V. Sridharan, *Comprehensive Organometallic Chemistry*, 2nd. E. Abel, G. Wilkinson F. G. A. Stone, Eds. Pergamon Press, New York, 1995, Vol. 12, Chapter 3,6.
   c) A. Padua, *Chem. Rev.*, 96, 233 (1996).
   d) R. Grigg, B. Putnikvic, G. Urch, *Tetrahedron Lett*, 37, 695 (1996).
   e) R. Grigg, V. Sridharan, C. Terrier, *Tetrahedron Lett.*, **37**, 4221 (1996).
   f) E. Neglish, C. Coperet, S. Ma, S. Y. Liou, F. Liu, *Chem. Rev.*, **96m**, 365 (1996).
   g) S. E. Denmark, C. B. W. Senanayake, *Tetrahedron*, **52**, 11579 (1996).
2. M. M. Heravi, D. Ajami, K. Tabar-Hydar, *J. Chem. Res.*, 620 (1998).
3. M. M. Heravi, D. Ajami, M. Ghassemzadeh, *Synthesis*, **3**, 393 (1999) and references cited therein.
4. B. G. Page, E. Nieboer, *Chromium in the Natural and Human Envitonments*, Eds. Wiley, New York, 1998, Vol. 6, pp 263–311.

5. a) S. Caddick, *Tetrahedron*, **38**, 10403 (1995).
   b) R. A. Abramovich, *Org. Prep. Proced.* Int., **23**, 623 (1991).
   c) D. M. P. Mingos, D. R. Baghu Orust, *Chem. Soc. Rev.*, **20**, 1 (1990).
6. a) A. Larry, A. Petit, M. Ramdani, C. Vanaeff, M. Maycloub, B. Labiad, D. Villemin, *Can. J. Chem.*, 71, 90 (1993).
   b) J. P. Barnier, A. Loupy, P. Pigeon, M. Ramdani, P. Jacquaqlt, *J. Chem. Soc., Perkin Trans. I*, 397 (1993).
7. R. Gedy, F. Smith, K. Westaway, H. Humera, L. Baldisera, L. R. Laberge, *Tetrahedron Lett.*, 26, 279 (1986).
8. a) A. McKillop, D.W. Yong, *Synthesis*, **38**, 2043 (1979).
   b) Balogh, P. Laszlo, *Organic Chemistry using Calys*, Springer Verlag, Berlin, 1993.
9. T. Tsuji, T. Mandai, *Synthesis*, 1, (1991) and references cied therein.
10. N. S. Wilson, B. A. Keay, *Tetrahedron Lett.*, **37**, 153 (1996).
11. M. M. Mojtahedi, M. R. Saidi, M. M. Heravi, M. Bolourtchian, *Monatsh. Chem.*, (1999) in press.
12. M. M. Heravi, D. Ajami, K. Tabar-Hydar, *J. Chem. Res.*, 620 (1998).
13. a) M. M. Heravi, D. Ajami, K. Tabar-Hydar, *Monatsh. Chem.*, **129**, 1305 (1998).
    b) M. M. Heravi, D. Ajami, *J. Chem. Res.*, 718 (1998). c) M. M. Heravi, D. Ajami, K. Tabar-Hydar, *Synth. Commun.*, **29**, 163 (1999).
14. a) M. M. Heravi, D. Ajami, M. M. Mojtahedi, M. Ghassemzadeh, *Tetrahedron Lett.*, **40**, 561 (1999).
    b) M. M. Heravi, D. Ajami, M. Ghassemzadeh, *Synth. Commun.*, **29**, 1013 (1999).
15. T. Cablewski, A. F. Faux, R. R. Strauss, *J. Org. Chem.*, **59**, 3408 (1994).