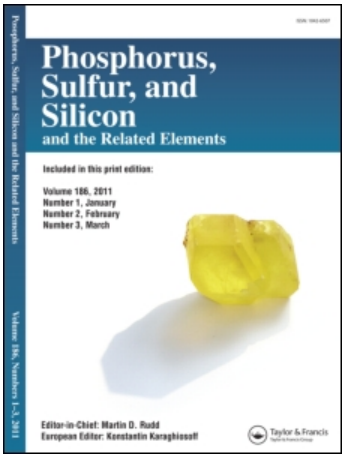

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DIRECT OXIDATIVE DEPROTECTION USING MONTMORILLONITE SUPPORTED AMMONIUM CHLOROCHROMATE UNDER CONVENTIONAL HEATING AND MICROWAVE IRRADIATION IN SOLVENTLESS SYSTEM

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DIRECT OXIDATIVE DEPROTECTION USING MONTMORILLONITE SUPPORTED AMMONIUM CHLOROCHROMATE UNDER CONVENTIONAL HEATING AND MICROWAVE IRRADIATION IN SOLVENTLESS SYSTEM

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Trimethylsilyl ethers are selectively and rapidly oxidized to the corresponding carbonyl compounds by montmorillonite k-10 supported ammonium chlorochromate under conventional heating and microwave irradition in solvent free condition.

Keywords: Ondation; Deprotection; Ammonium chlorochromate; Microwave Irradiation

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 products[1]. The trimethylsilyl group is one of the most useful protective groups for alcohols in multi-step organic synthesis and considerable efforts have been made for the development of new methods for their introduction and removal.

These methods have their own merits and drawbacks. The limitations such as aqueous reaction conditions, use of expensive reagents, long reaction times, tedious work up and low yields of products must be compensated by introduction of new method for such important functional group transformation.

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Recently we have demonstrated the use ammonium chlorochromate supported onto montmorillonite k-10 as an efficient and mild oxidzing agent under classical heating[3] and microwave irradiation[4]. Armed with these experiences now we wish to report a new and efficient method for the oxidative deprotection of trimethylsilyl ethers to their corresponding carbonyl compounds.

The reagent is easily prepared by addition of a weighed ammount of montmorillonite k-10 and ammonium chlorochromate in water and rotatory evaporating to dryness.[4] The reaction was conducted by refluxing 2.6 equivalents of a reagent and a trimethylsilyl ether in CH_2C_2 for about 3 hrs. A variety of trimethysilyl ethers were converted to their corresponding carbonyl compounds by this method (Table I).

TABLE I Oxidative deprotection of trimethylsilyl ethers with clay supported ammonium chlorochromate in CH_2Cl_2

Entry	*Substrate*	*time (h)*	*Product*	*yield%*
1	$PhCH_2OSiMe_3$	2.5	PhCHO	90
2	$4\text{-}MeC_6H_4CH_2OSiMe_3$	2.5	$4\text{-}MeC_6H_4CHO$	90
3	$2\text{-}NO_2\text{-}5\text{-}Me\text{-}C_6H_3CH_2OSiMe_3$	3	$2\text{-}NO_2\text{-}5\ MeC_6H_3CHO$	88
4	$PhCH(Me)OSiMe_3$	3	PhCOMe	85
5	$Ph_2CHOSiMe_3$	3	PhCOPh	83
6	$c\text{-}C_6H_{11}OSiMe_3$	3	Cyclohexanone	88
7	$2\text{-}MeC_6H_{10}OSiMe_3$	3	2-Methylcyclohexanone	83
8	(-)- Mentholsilyl ether	3	(-) Menthone	89
9	$PhCH{=}CHCH_2OSiMe_3$	**2.x5**	PhCH=CHCHO	65

a) yields refer to isolated products

The microwave enhanced chemical reactions[5] in general and on inorganic solid supports in particular[6], have gained popularity over the usual homogeneous and heterogeneous reactions, as they can be conducted rapidly and produce pure products in quantitative yields without the use of solvents. We wish to report here a facile oxidative deprotection of trimethylsilyl etheres using montmorillonite k-10 supported ammonium chlorochromate under solvent free conditions in a process that is accelerated by microwave irradiation.

The reaction is conducted by mixing 2.6 equivalents of clay supported ammonium chlorochromate with neat ethers. The mixture was irradiated by microwave and in a very short time, the corresponding carbonyl compound was obtained in high yield.

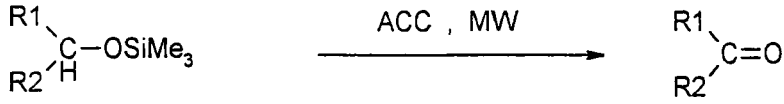
It is noteworthy to mention that in the absence of clay the reactions in all cases are sluggish and a considerable amount of ethers and alcohols were recovered unchanged in reactions in solvent at elevated temperature or exposure to microwave irradiation for an extended period of time. By use of montmorillonite k-10, however, a variety of trimethylsilyl ethers can be oxidatively deprotected in CH_2Cl_2 or solventiess system under microwave irradiation in excellent yields (**Table II**).

TABLE II Oxidative deprotection of trimethylsilyl ethers with clay supported ammonium chlorochromate using microwave irradiation in a solventiless system

Entry	*Substrate*	*time (s)*	*Product*	*yield%*
1	$PhCH_2OSiMe_3$	30	PhCHO	90
2	$4\text{-}MeC_6H_4CH_2OSiMe_3$	30	$4\text{-}MeC_6H_4CHO$	88
3	$2\text{-}NO_2\text{-}5\text{-}Me\text{-}C_6H_3CH_2OSiMe_3$	60	$2\text{-}NO_2\text{-}5\ MeC_6H_3CHO$	80
4	$PhCH(Me)OSiMe_3$	30	PhCOMe	87
5	$Ph_2CHOSiMe_3$	60	PhCOPh	82
6	$c\text{-}C_6H_{11}OSiMe_3$	120	Cyclohexanone	80
7	$2\text{-}MeC_6H_{10}OSiMe_3$	60	2-Methylcyclohexanone	82
8	(-)- Mentholsilyl ether	60	(-) Menthone	90
9	$PhCH{=}CHCH_2OSiMe_3$	60	PhCH=CHCHO	68

a) yields refer to isolated products

The reactions are relatively clean with no tar formation typical for many chromium reagents. No over-oxidation to carboxylic acids is observed. The reaction of cinnamyl ether (entry table II) gave a moderate yield of cinnamaldehyde (68%) and benzaidehyde (32%) showing the carbon - carbon double bonds are prone to cleavage by this method.



In conclusion clay supported ammonium chlorochromate is an excellent reagent for convenient oxidative deprotection of trimethylsilyl ether both under conventional heating and microwave irradiation in solvent free condition. Solvent – free microwave irradiation has an advantage over conventional heating, offering a practical and environmentally benign protocol, decreasing reaction time and in some cases giving cleaner reactions and easier work up. In addition by development of a continuous microwave reaction for organic synthesis[7], this work may have industrial application where the absence of solvent and low cost of the method may lead to environmental and cost advantages.

EXPERIMENTAL

Products were isolated and their physical data were compared with those of known samples. Trimethylsilyl ethers were synthesized according to a known procedure.[5]

Oxidative deprotection of trimethylsilyl ethers

General procedure

In a round bottomed flask (50 ml) equipped with a magnetic stirrer and a condenser a solution of trimethylsilyl ether (1.3 mmol) in CH_2Cl_2 (20 ml) was prepared. To this solution montmorillonite k-10 supported ammonium chlorochromate (1.7 g, 2.6 mmol) was added, The reaction mixture was refluxed for the specified time. The progress of the reaction was monitored by T.L.C (eluent, light petrolieum – ethyl acetate (8:2). The mixture was filtered and the solid material was washed with CH_2Cl_2 (10 ml). The filtrate was evaporated to dryness under red pressure and the resulting crude was purified on a silica gel pad. After evaporation of the solvent the pure carbonyl compound was obtained (Table I).

Oxidative deprotection of trimethylsilyl ethers under microwave irradiation

General procedure

The above reagent (1.7 g, 2.6 mmol) was added with appropriate neat trimethylsilyl ether using a beaker and mixed throughly with a spatula. The

reaction mixture in the beaker was placed inside a microwave oven and irradiated for the specified time. On completion of the reaction (TLC. hexane – ethyl acetate, 8:2) the crude product was directly charged onto a silica gel column. Elution with hexane – ethyl acetate afforded the pure carbonyl compound (Table **2**).

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