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# Microwave Assisted Deprotection of Trimethylsilyl Ethers under Solvent-Free Conditions Catalyzed by Clay or a Palladium Complex

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**Summary.** A simple method for the cleavage of trimethylsilyl ethers under microwave irradiation and solvent-free conditions in the presence of montmorillonite K-10 or a palladium complex catalyst in almost quantitative yield is reported.

**Keywords.** Trimethylsilyl ether; Deprotection; Montmorillonite; Microwave; Palladium.

**Durch Ton oder einen Palladiumkomplex katalysierte mikrowellenunterstützte Entschützung von Trimethylsilylethern unter lösungsmittelfreien Bedingungen**

**Zusammenfassung.** Eine einfache Methode zur Spaltung von Trimethylsilylethern unter Mikrowelleneinwirkung und lösungsmittelfreien Bedingungen in Gegenwart von Montmorillonit K-10 oder einem Palladiumkomplex mit nahezu quantitativen Ausbeuten wird beschrieben.

## Introduction

The transformation of alcohols and phenols to the corresponding trimethylsilyl ethers is a common way for the protecting of hydroxy groups. It has been widely used in organic synthesis to control the stereoselectivity of reactions [1]. Trimethylsilyl ethers can be deprotected conveniently by numerous methods [2–4]. While all these methods have merits, there are some limitations that can lead to lower yields in some cases. Microwave heating and its application in organic synthesis is currently under intensive investigation [5]. Although clay and alumina assisted deprotection reactions have been utilized in organic solvents, such a methodology has not been used for the deprotection of the trimethylsilyl group under microwave irradiation. The fact that clays possess Al(III) and other interlamellar cations suggests that these naturally occuring supports promote organic transformations *via* acid catalysis [6–8].

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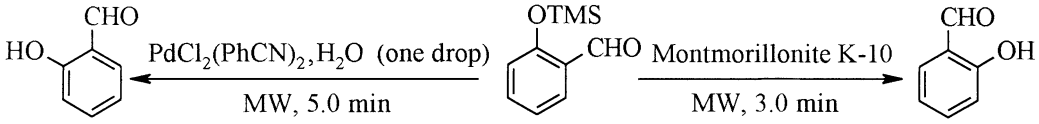
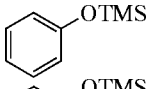
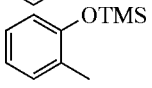
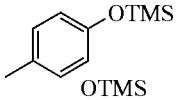
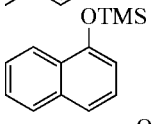
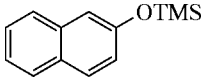
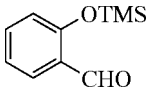
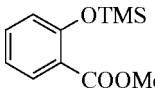
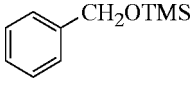
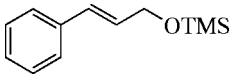
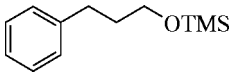
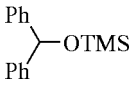
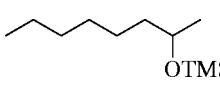
## Results and Discussion

Successful solid state reactions have been recently reported in absence of solvents for protecting alcohols and phenols with hexamethyldisilazane [9]. We now report a new, simple, and fast method for the desilylation of a variety of phenols and




**Scheme 1**

**Table 1.** Irradiation time and yields for the deprotection of phenols and alcohols catalyzed by montmorillonite K-10 or a palladium complex

| Starting material | K-10 (min) | Yield (%) | $PdCl_2(PhCN)_2$ (min) | Yield (%) |
|---|---|---|---|---|
|  | 1.0 | 100 | 3.0 | 100 |
|  | 1.0 | 100 | 3.0 | 100 |
|  | 1.0 | 98 | 3.0 | 99 |
|  | 5.0 | 100 | 5.0 | 100 |
|  | 5.0 | 98 | 5.0 | 98 |
|  | 3.0 | 99 | 5.0 | 98 |
|  | 3.0 | 100 | 5.0 | 100 |
|  | 1.0 | 99 | 3.0 | 98 |
|  | 1.0 | 98 | 3.0 | 98 |
|  | 1.0 | 100 | 5.0 | 100 |
|  | 5.0 | 97 | | |
|  | 3.0 | 88 | | |

alcohols under solvent-free conditions in almost quantitative yields using a conventional microwave oven and montmorillonite K-10 clay as solid support. The deprotection reaction of the trimethylsilyl group was also carried out with $PdCl_2(PhCN)_2$ as the catalyst under microwave irradiation. An interesting phenomenon with this complex is that the reaction works best if a drop of water is added to the reaction mixture before heating in the microwave oven. Interestingly enough, without addition of water the desilylation reaction did not occur (Scheme 1). The protected phenols and alcohols are listed in Table 1.

In conclusion, the present study shows that deprotection of the trimethylsilyl group in alcohols and phenols can successfully be performed in dry media catalyzed by commercially available montmorillonite K-10 or by $PdCl_2(PhCN)_2$ in very short time and in almost quantitative yields.

## Experimental

Activated montmorillonite K-10 clay was prepared by heating it in a commercial microwave oven (900 W) for five minutes just before use as a solid support. All compounds were identified by means of their NMR and IR spectra.

*Desilylation of phenols or alcohols in the presence of montmorillonite K-10 clay*

1 mmol of silyl ether was placed in a 5 $cm^3$ beaker, and 0.1 g of activated montmorillonite K-10 clay was added. The beaker was placed in a 50 $cm^3$ teflon container and irradiated in a microwave oven (900 W) for 1 to 5 min. The progress of the reaction was monitored by GLC. After completion of the reaction, the product was extracted with ether or $CH_2Cl_2$, filtered, and the solvent was evaporated under reduced pressure to yield the corresponding phenol or alcohol.

*Desilylation of phenols or alcohols in the presence of $PdCl_2(PhCN)_2$*

1 mmol of silyl ether was placed in a 5 $cm^3$ beaker, and 0.01 g of $PdCl_2(PhCN)_2$ (1 mol%) was added. Then one drop of water was added to the reaction mixture. The beaker was placed in a 50 $cm^3$ teflon container and irradiated in a microwave oven (900 W) for 3 to 5 min. The progress of the reaction was monitored by GLC. After completion of the reaction, the product was extracted with ether or $CH_2Cl_2$, filtered, and the solvent was evaporated under reduced pressure to yield the corresponding phenol and alcohol.

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