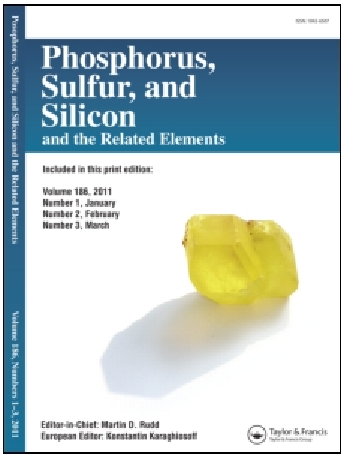

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DABCO, A REAGENT FOR DEPROTECTION OF BENZYLIC TRIMETHYLSILYL ETHERS UNDER MICROWAVE IRRADIATION IN A SOLVENTLESS SYSTEM

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DABCO, A REAGENT FOR DEPROTECTION OF BENZYLIC TRIMETHYLSILYL ETHERS UNDER MICROWAVE IRRADIATION IN A SOLVENTLESS SYSTEM

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Deprotection of trimethylsilyl ethers of benzylic alcohols to the corresponding alcohols using 1,4-diazobicyclo[2,2,2]octane (DABCO) under microwave irradiation under solvent-free conditions is reported.

Keywords: DABCO; microwave irradiation; solventless system; trimethylsilyl ethers

A trialkylsilyl group is one of the most common and widely used protecting groups.[1] This kind of protection was originally introduced to increase the volatility and stability of hydroxy groups and nowadays is applied in total and multistep syntheses in organic chemistry.[2] As a matter of fact, the silyl ether group is the gold standard for protection of hydroxy groups.[3] Although several methods have been reported for the deprotection of silyl ethers,[4] the development of mild, efficient, eco-friendly, and selective deprotections of trimethylsilyl ethers continues to be a significant aspect of organic chemical transformation.

DABCO/Pd(0) has been used for the highly efficient deprotection of peptides.[5] It has also been widely used as a catalyst for the Baylis-Hillman reaction.[6] DABCO has also been reported as a catalyst for the acceleration of benzoylation reactions.[7] DABCO has been applied to the synthesis of a zeolite as a structure-directing agent[8] and can catalyze the self- and cross-condensation of α-acetylenic ketones.[9] It has also been used to catalyze the coupling of α-keto-esters with

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acrylonitrile[10] and for the dimerization of α,β-unsaturated ketones and nitriles.[11]

There has been considerable attention to the creation and development of green and solventless methods in organic chemistry[12] dictated by stringent environmental protection laws.[13] Solvent-free reactions have been known for some time, and the environmentally friendly goal of synthesizing organic compounds without using solvents has come several steps closer in recent years.[14] Microwave irradiation in organic synthesis is a useful technique nowadays.[15] Dry media using microwave thermolysis have attracted much attention because the use of hazardous and relatively expensive organic solvents are omitted and the reaction can be conducted in open vessels.[16]

As part of our ongoing program on environmentally benign chemical transformations employing microwave irradiation in solventless systems[17] as alternative reaction conditions and media, and in continuation of our interest in deprotection of trimethylsilyl ethers,[18] we herein report an expeditious and environmentally benign deprotection of benzylic-trimethylsilyl ethers using DABCO and microwave irradiation under solvent-free conditions.

Selective removal of trimethylsilyl ethers is often implemented by either fluorine compounds[19] or aqueous acids.[20] Fluoride ions are very basic, especially under anhydrous conditions, and therefore neither fluorine compounds nor aqueous acids can be used for the deprotection of acid- and base-sensitive systems. When neat benzyltrimethylsilyl ether was mixed thoroughly with DABCO (1:1 molar ratio) and irradiated in a microwave oven, cleavage of the ether occurred in a very short time (monitored by thin layer chromatography (TLC) in excellent yield. The product was purified by silica gel chromatography. To establish the generality of the method we used various primary and secondary benzylic, aliphatic, allylic, and phenolic trimethylsilyl ethers. Surprisingly, only benzylic trimethylsilyl ethers were deprotected by DABCO under microwave irradiation in a solventless system (Table I).

A benzylic ether was deprotected selectively in the presence of a phenolic ether (Table I, entry 4). To optimize the reaction conditions, we changed the molar ratio of DABCO. The yields of reactions were found to be highly dependent on the quantity of DABCO employed. The best results were obtained with a 1:1 molar ratio of trimethylsilyl ether and DABCO. The length of irradiation also significantly affected the yields. Thus, increasing the reaction time up to 7 min produced maximum enhancement of the yield. However, the yield could not be improved further, even after prolonged irradiation. In an effort to deprotect nonbenzylic trimethylsilyl ethers, we used silica gel as a solid support. In the presence of the solid support, nonbenzylic ethers were not deprotected even after prolonged irradiation. Silica gel did not improve the yields of deprotection of benzylic silyl ethers.

In summary, the present method is an efficient, selective, and practical alternative method for the deprotection of benzylic trimethylsilyl ethers. The salient features of this methodology are the mild reaction conditions, short reaction times, high yields, selectivity, and the absence of volatile and relatively expensive solvents. We believe this procedure will find application for the deprotection of benzylic trimethylsilyl ethers in organic synthesis.

EXPERIMENTAL

Trimethylsilyl ethers were synthesized according to literature procedures.[21] DABCO was purchased and used as received. Yields refer to GC analysis. All products are known compounds and were characterized by comparison of their physical data with those of authentic samples. Although we did not have any accidents utilizing DABCO in a microwave oven, the use of a microwave oven in an efficient hood is highly recommended.

Deprotection of Benzylic Trimethylsilyl Ethers to the Corresponding Benzylic Alcohol: General Procedure

In a beaker an appropriate benzylic trimethylsilyl ether (1 mmol) and DABCO (1 mmol) were mixed thoroughly using a spatula. The beaker was placed in a microwave oven for the indicated time. The progress of reaction was monitored by TLC using petroleum ether:EtOAC (8:2) as eluent. After completion of the reaction the product was mixed with water and extracted with CH_2Cl_2. The solvent was dried and evaporated to dryness to afford the corresponding alcohols (Table I).

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