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Facile Deprotection of Trimethylsilyl Ethers With Modified Borohydride Agents; 1-Benzyl-4-AZA-1-Azoniabicyclo[2.2.2]Octane Tetrahydroborate (Baaotb)[1] Versus Tetrabutylammonium Tetrahydroborate(TBATB)

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FACILE DEPROTECTION OF TRIMETHYLSILYL ETHERS WITH MODIFIED BOROHYDRIDE AGENTS; 1-BENZYL-4-AZA-1-AZONIABICYCLO[2.2.2]OCTANE TETRAHYDROBORATE (BAAOTB)[1] VERSUS TETRABUTYLAMMONIUM TETRAHYDROBORATE(TBATB).

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Abstract: Deprotection of structurally different trimethylsilyl ethers with the modified borohydride agents BAAOTB and TBATB to their corresponding alcohols in reflexing t-BuOH is described. Both BAAOTB and TBATB are efficient reagents for this purpose. BAAOTB seems to be more selective than TBATB.

Functional group protection is almost inevitable reaction in the total synthesis of complex organic molecules. Protection of hydroxy groups has been achieved by different methods. One of the most encountered one is to protect this functionality with trimethylsilyl group. This can be achieved by the cheap and commercially available reagents; trimethylsilyl chloride (TMSCl) and hexamethyldisilazane (HMDS)[2,3].

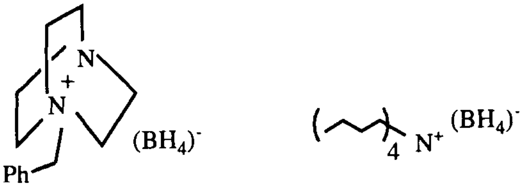
Releasing the original alcohols from their corresponding silyl ethers is important and has been proceeded by different methods e.g., 1) in common acidic aqueous media which is a slow reaction [4], 2) in aqueous hydrofluoric acid solution which is an easy process[5], and 3) in the presence of trifluoroborane[6]. These methods encounter problems such as being harmful to acid sensitive compounds and the aqueous work-up is a tedious process for the water soluble organic molecules. A recently reported deprotecting agent for trialkylsilyl ethers is methylammonium fluoride (MAF)[7] which its work-up does not need water but suffers seriously from long reaction times (1 to 7 days). Tetra-n-butylammonium fluoride[8] has been also used for the deprotections. A very recently reported reagent is the polymer supported ammonium fluoride[9] which shows higher efficiency than MAF in the deprotection reactions of trialkylsilyl ethers.

We have lately paid attention to the other alternative methods for the oxidation deprotection and deprotection of silyl ethers. Along this line we have introduced new reagents for this purpose. $AgBrO_3$ or $NaBrO_3$ in the presence of $AlCl_3$[10], $[(NO_3)_3Ce].H_2IO_6$[11,12] , and $[(NO_3)_3Ce]_2CrO_4$[13,14] are the examples of our recent achievements.

Literature search does not show any report relating to the possibility of using borohydride agents for the reductive Si-O bond cleavage in silyl ethers.

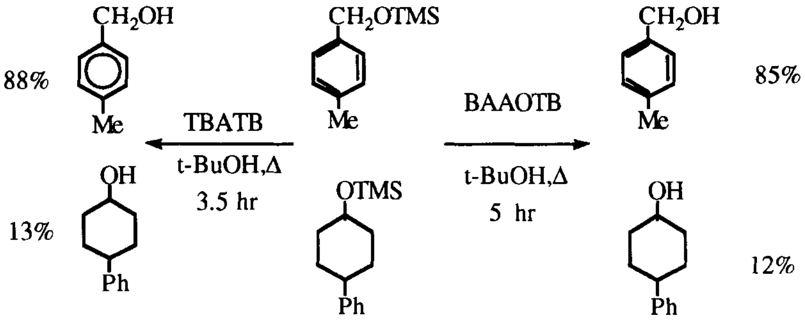
Now we report that 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane tetrahydroborate (BAAOTB)[1,15,16] and tetrabutylammonium tetrahydroborate (TBATB)[17,18] are effective reagents for the deprotection of trimethylsilyl ethers in refluxing t-BuOH (Fig. 1).

In this investigation, in a series of competetive reactions, we have compared the efficiency and the selectivity of BAAOTB versus TBATB which are presented by the reaction schemes (1-3). As it is evident, from the schemes, BAAOTB is



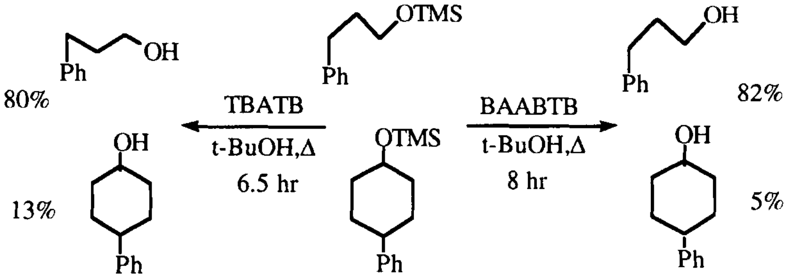
BAAOTB TBATB

Fig 1



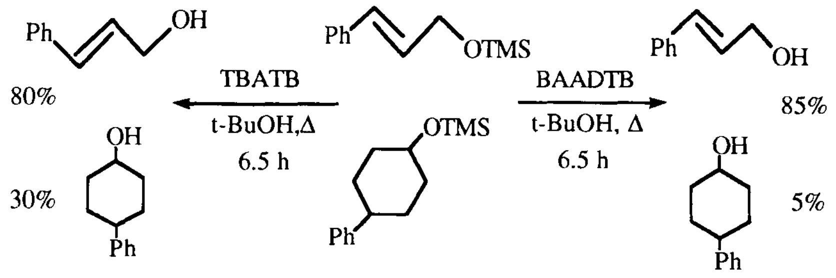
Substrates/BH_4^-(1:1:3)

Scheme 1



Substrates/BH_4^- (1:1:3)

Scheme 2



Substrates/BH_4^-(1:1:3)

Scheme 3

more selective than its analogue TBATB however, reactions are usually faster with TBATB.

The results of our investigations with BAAOTB and TBATB for Si-O bond cleavage upon the structurally different trimethylsilyl ethers are tabulated in Table.

Experimental

General : All yields refer to isolated products unless otherwise indicated. All products were characterized by comparison of their spectral and physical data with those of authentic samples. The purity determination of the substrates were accomplished by T.L.C. on silica gel polygram SIL G/UV 244 Plates or by GLC with a Schimadzu Model GC-8A instrument with a flame ionization detector and using a column of 15% carbowax 20 M/chemosorb-w acid.

General procedure for Deprotection of Trimethylsilyl Ethers to their Corresponding Alcohols with BAAOTB.

In a round-bottomed flask (25 ml) equipped with a magnetic strrier, and a condenser a sulution of the silyl ether (0.5-1 mmol) in t-BuOH (8 ml) was prepared.

The reducing agent (3-6 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 1.25-56 hr. Progress of the reaction was monitored by TLC (eluent: CCl_4/Et_2O: 5/1) or gas chromatography. After completion of reaction, the solvent was evaporated and the resulting crude material was purified on a silica gel plate (elment: CCl_4/Et_2O: 5/1) or the mixture could be extracted with ether in a continuous extraction apparatus. Evaporation of the solvent afforded the desired alcohols in 80-95% yields.

Deprotection of 4-Nitrobenzyltrimethylsilyl Ether to 4-Nitrobenzyl Alcohol with BAAOTB.

In a round-bottomed flask (25 ml) equipped with a magnetic stirrer and a condenser, a solution of 4-nitrobenzyltrimethylsilyl ether (0.21 gr, 1 mmol) in t-BuOH (8 ml) was prepared. The reducing agent (0.655 gr., 3 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 1.25 hr. The progress of the reaction was monitored by TLC (eluent: CCl_4/Et_2O: 5/1). The solvent was evaporated and the resulting crude material was purified on a silica gel plate (eluent: CCl_4/Et_2O: 5/1). Pure 4-nitrobenzyl alcohol was obtained; 0.125 gr., 90% yield; mp 93-95°C, lit[19] 92-94°C).

General Procedure for Deprotection of Trimethylsilyl Ethers to their Corresponding Alcohols with TBATB.

In a round-bottomed flasks (25 ml) equipped with a magnetic stirrer and a condenser, a solution of the silyl ether (0.5-1 mmol) in t-BuOH (8 ml) was prepared. The reducing agent (3-6 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 0.5-52 hr. Progress of the reaction was monitored by TLC (eluent: CCl_4/Et_2O: 5/1) or gas chromatography. After completion of the reaction the solvent was evaporated and the resulting crude material was

Table . Si-O Bond Cleavage of Structurally Different Trimethylsilyl Ethers with BAAOTB and TBATB.

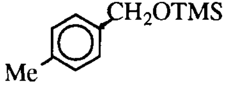
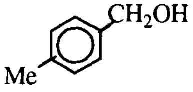
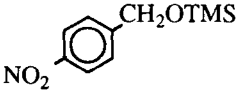
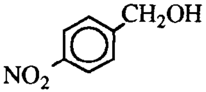
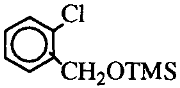
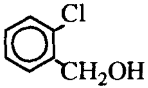
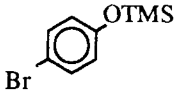
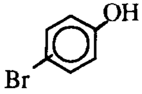
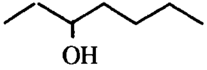
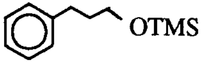
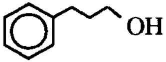
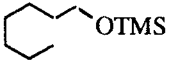
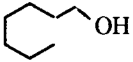
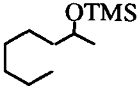
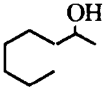
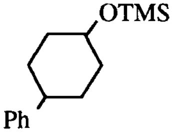
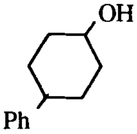
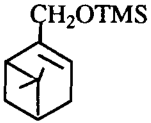
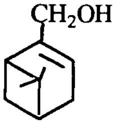
Entry	Substrate	Product	BAAOTB		TBATB	
			Rxn Time (hr)	Yield%	Rxn Time (hr)	Yield%
1			6.5	92	2.5	90
2			1.25	90	0.5	90
3			7	90	2.5	85
4			2.75	80	2	82
5			14	95	6.5	95

Table . Continued.

6			3.5	100^{GC}	4	100^{GC}
7			10	90	8	90
8			11.5	100^{GC}	9	100^{GC}
9			56	100^{GC}	52	100^{GC}
10			45	92	40	90
11			48	100^{GC}	44	100^{GC}

purified on a silica gel plate (eluent: CCl_4/Et_2O: 5/1). Pure alcohol was obtained in 82-95% yield.

Deprotection of 4-Nitrobenzyltrimethylsilyl Ether to 4-Nitrobenzyl Alcohol with TBATB. A Typical Procedure.

In a round-bottomed flask (25 ml) equipped with a magnetic stirrer and a condenser, a solution of 4-nitrobenzyltrimethylsilyl ether (0.21 gr., 1 mmol) in t-BuOH (8 ml) was prepared. The reducing agent (0.655 gr. , 3 mmol) was added. The reaction mixture was stirred magnetically under reflux condition for 0.5 hr. The progress of the reaction was monitored by TLC (eluent: CCl_4/Et_2O: 5/1). After completion of the reaction the solvent was evaporated and the resulting crude material was purified on a silica gel plate (eluent: CCl_4/Et_2:5/1). Pure 4-nitrobenzyl alcohol was obtained; 0.125 gr, 90% yield; mp 94-95°C, lit[19] 92-94°C).

Acknowledgements

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