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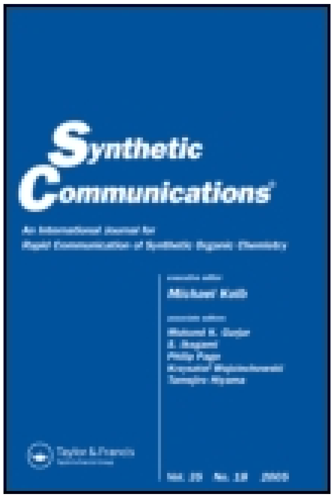

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

SELECTIVE AND EFFICIENT OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL AND TETRAHYDROPYRANYL ETHERS, ETHYLENE ACETALS AND KETALS WITH n-BUTYLTRIPHENYLPHOSPHONIUM PEROXODISULFATE $(Bu^nPPh_3)_2S_2O_8$

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Published online: 17 Aug 2006.

To cite this article: I. Mohammadpoor-Baltork, A. R. Hajipour & M. Aghajari (2002) SELECTIVE AND EFFICIENT OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL AND TETRAHYDROPYRANYL ETHERS, ETHYLENE ACETALS AND KETALS WITH n-BUTYLTRIPHENYLPHOSPHONIUM PEROXODISULFATE $(Bu^nPPh_3)_2S_2O_8$, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 32:9, 1311-1317, DOI: 10.1081/SCC-120003626

To link to this article: http://dx.doi.org/10.1081/SCC-120003626

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SYNTHETIC COMMUNICATIONS, 32(9), 1311–1317 (2002)

SELECTIVE AND EFFICIENT OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL AND TETRAHYDROPYRANYL ETHERS, ETHYLENE ACETALS AND KETALS WITH *n*-BUTYLTRIPHENYLPHOSPHONIUM PEROXODISULFATE $(Bu^{n}PPh_3)_2S_2O_8$

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ABSTRACT

n-Butyltriphenylphosphonium peroxodisulfate in refluxing acetonitrile transforms trimethylsilyl (TMS) and tetrahydropyranyl (THP) ethers, ethylene acetals and ketals to their corresponding carbonyl compounds in excellent yields. Selective oxidative deprotection of TMS and THP ethers in the presence of ethylene acetals (ketals) is of additional importance in this method.

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The protection of hydroxyl groups as their trimethylsilyl and tetrahydropyranyl ethers is an important reaction in organic chemistry.[1–7] Oxidative deprotection of the above mentioned ethers to their corresponding carbonyl compounds under mild and aprotic conditions is also of synthetic value.[8–11]

The protection of aldehydes and ketones by the formation of ethylene acetals and ketals is important in the preparation of a variety of multifunctional organic molecules.[12–14] Transformation of ethylene acetals and ketals to their parent carbonyl compounds under neutral, aprotic and non-aqueous conditions is of interest to synthetic organic chemists and several methods have been reported for this purpose.[15–17] However, some of the reported methods for the oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers, ethylene acetals and ketals show limitations such as strong protic and aqueous conditions, long reaction times, low yields of the products, tedious work-up and expensive reagents. Therefore, introduction of a milder, more selective and inexpensive reagent for the conversion of the above mentioned derivatives to their corresponding carbonyl compounds is desirable.

Recently, we have reported new methods for the oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers, ethylene acetals and ketals.[18–20] In continuation of our research in this area, we were interested to find a more efficient, more selective and inexpensive method for the oxidative deprotection of these functional groups. In this respect, we wish to report that *n*-butyltriphenylphosphonium peroxodisulfate is able to convert TMS and THP ethers, ethylene acetals and ketals to their corresponding carbonyl compounds efficiently in refluxing acetonitrile. This reagent is an inexpensive and stable oxidizing agent and has been used for the cleavage of carbon–nitrogen double bonds under non-aqueous conditions.[21]

The treatment of a variety of trimethylsilyl and tetrahydropyranyl ethers with *n*-butyltriphenylphosphonium peroxodisulfate gave the corresponding carbonyl compounds in excellent yields (Table 1). Deprotection of ethylene acetals and ketals was also investigated with this reagent and the corresponding aldehydes and ketones were obtained in excellent yields (Table 2). Interestingly, overoxidation of the products was not observed in this method. It is noteworthy that the reaction medium was almost neutral, so that some of the sensitive functionalities such as the carbon–carbon double bond remained intact (Table 1, Entries 7, 22 and Table 2, Entry 6).

In order to show the better chemoselectivity of the described method, we have also performed several competitive oxidative deprotection reactions. The experimental results show that trimethylsilyl and

Table 1. Oxidative Deprotection of TMS and THP Ethers with $(Bu^nPPh_3)_2S_2O_8$

Run	Substrate	Product	Time (min)	Yield (%)[a]
1	$PhCH_2OTMS$	PhCHO	10	98
2	$2\text{-}MeOC_6H_4CH_2OTMS$	$2\text{-}MeOC_6H_4CHO$	30	96
3	$3\text{-}MeOC_6H_4CH_2OTMS$	$3\text{-}MeOC_6H_4CHO$	10	96
4	$4\text{-}MeOC_6H_4CH_2OTMS$	$4\text{-}MeOC_6H_4CHO$	10	98
5	$4\text{-}O_2NC_6H_4CH_2OTMS$	$4\text{-}O_2NC_6H_4CHO$	30	97
6	$Ph(CH_2)_3OTMS$	$Ph(CH_2)_2CHO$	10	97
7	$PhCH{=}CHCH_2OTMS$	$PhCH{=}CHCHO$	10	98
8	PhCH(Me)OTMS	PhCOMe	20	96
9	$Ph_2CHOTMS$	Ph_2CO	20	98
10	$PhCH(OTMS)CH_2Ph$	$PhCOCH_2Ph$	25	98
11	$4\text{-}ClC_6H_4CH(Me)OTMS$	$4\text{-}ClC_6H_4COMe$	15	98
12	$4\text{-}PhC_6H_4CH(Me)OTMS$	$4\text{-}PhC_6H_4COMe$	15	99
13	α-TetralolTMS	α-Tetralone	30	97
14	$CH_3(CH_2)_6OTMS$	$CH_3(CH_2)_5CHO$	30	93
15	$CH_3(CH_2)_7OTMS$	$CH_3(CH_2)_6CHO$	30	95
16	$CH_3(CH_2)_5CH(Me)OTMS$	$CH_3(CH_2)_5COMe$	30	96
17	$PhCH_2OTHP$	PhCHO	15	95
18	$2\text{-}MeOC_6H_4CH_2OTHP$	$2\text{-}MeOC_6H_4CHO$	30	96
19	$3\text{-}MeOC_6H_4CH_2OTHP$	$3\text{-}MeOC_6H_4CHO$	15	97
20	$4\text{-}MeOC_6H_4CH_2OTHP$	$4\text{-}MeOC_6H_4CHO$	15	99
21	$4\text{-}O_2NC_6H_4CH_2OTHP$	$4\text{-}O_2NC_6H_4CHO$	15	92
22	$PhCH{=}CHCH_2OTHP$	$PhCH{=}CHCHO$	20	96
23	PhCH(Me)OTHP	PhCOMe	30	98
24	$4\text{-}ClC_6H_4CH(Me)OTHP$	$4\text{-}ClC_6H_4COMe$	20	97
25	α-TetralolTHP	α-Tetralone	20	98
26	$CH_3(CH_2)_6OTHP$	$CH_3(CH_2)_5CHO$	30	94
27	$CH_3(CH_2)_7OTHP$	$CH_3(CH_2)_6CHO$	30	96

[a] Isolated yield.

tetrahydropyranyl ethers are oxidized selectively in the presence of ethylene acetals and ketals (Table 3). These selectivities are useful achievements in organic synthesis.

We have also shown the general applicability and efficiency of the presented method in comparison with some of those reported with 3-carboxypyridinium chlorochromate (CPCC)[18] and silver bromate/aluminium chloride[10,20] (Table 4).

Even though the reaction mechanism is interesting, at the present time it is obscure to us, and we have not been able to assign any reasonable mechanism for them in our studies.

Table 2. Oxidative Deprotection of Ethylene Acetals and Ketals with $(\mathrm{Bu}^n\mathrm{PPh}_3)_2\mathrm{S}_2\mathrm{O}_8$

Run	Substrate	Product	Time (h)	Yield (%)[a]
1	Benzaldehydeethylene acetal	Benzaldehyde	1.5	97
2	2-Methoxybenzaldehydeethylene acetal	2-Methoxybenzaldehyde	2	95
3	4-Methoxybenzaldehydeethylene acetal	4-Methoxybenzaldehyde	1.5	98
4	2-Nitrobenzaldehydeethylene acetal	2-Nitrobenzaldehyde	2.5	96
5	4-Nitrobenzaldehydeethylene acetal	4-Nitrobenzaldehyde	2	98
6	Cinnamaldehydeethylene acetal	Cinnamaldehyde	1	97
7	Acetophenoneethylene ketal	Acetophenone	1.5	97
8	4-Chloroacetophenoneethylene ketal	4-Chloroacetophenone	1.5	98
9	4-Phenylacetophenoneethylene ketal	4-Phenylacetophenone	2.5	99
10	Cyclohexanoneethylene ketal	Cyclohexanone	2.5	94

[a] Isolated yield.

Table 3. Competitive Oxidative Deprotection of TMS (THP) Ethers and Ethylene Acetals (Ketals) with $(\mathrm{Bu}^n\mathrm{PPh}_3)_2\mathrm{S}_2\mathrm{O}_8$

Run	Substrate[a]	Product	Time (min)	Yield (%)[b]
1	$\mathrm{PhCH_2OTMS}$	PhCHO		98
	4-Chloroacetophenoneethylene ketal	4-Chloroacetophenone	10	0
2	$\mathrm{Ph(CH_2)_3OTMS}$	$\mathrm{Ph(CH_2)_2CHO}$		96
	4-Methoxybenzaldehydeethylene acetal	4-Methoxybenzaldehyde	10	2
3	PhCH(Me)OTMS	PhCOMe	20	95
	Benzaldehydeethylene acetal	Benzaldehyde		3
4	$4\text{-}\mathrm{O_2NC_6H_4CH_2OTHP}$	$4\text{-}\mathrm{O_2NC_6H_4CHO}$		92
	4-Methoxybenzaldehydeethylene acetal	4-Methoxybenzaldehyde	15	3
5	PhCH(Me)OTHP	PhCOMe	30	97
	Benzaldehydeethylene acetal	Benzaldehyde		2
6	$4\text{-}\mathrm{MeOC_6H_4CH_2OTHP}$	$4\text{-}\mathrm{MeOC_6H_4CHO}$		98
	4-Chloroacetophenoneethylene ketal	4-Chloroacetophenone	15	0

[a] Substrates/Oxidant (1 : 1 : 1).

[b] GLC yield.

Table 4. Comparison of Oxidative Deprotection of Some TMS and THP Ethers with $(Bu^nPPh_3)_2S_2O_8$ (I), CPCC (II)[18] and Silver Bromate/Aluminium Chloride (III)[10,20]

			Yield % (Time, min)		
Run	Substrate	Product	I	II	III
1	$PhCH_2OTMS$	PhCHO	98 (10)	97 (45)	–
2	$2\text{-}MeOC_6H_4CH_2OTMS$	$2\text{-}MeOC_6H_4CHO$	96 (30)	93 (45)	–
3	$4\text{-}O_2NC_6H_4CH_2OTMS$	$4\text{-}O_2NC_6H_4CHO$	97 (30)	–	83 (30)
4	PhCH(Me)OTMS	PhCOMe	96 (20)	93 (70)	92 (20)
5	$Ph_2CHOTMS$	Ph_2CO	98 (20)	80 (120)	98 (25)
6	$4\text{-}O_2NC_6H_4CH_2OTHP$	$4\text{-}O_2NC_6H_4CHO$	92 (15)	–	78 (150)
7	$2\text{-}MeOC_6H_4CH_2OTHP$	$2\text{-}MeOC_6H_4CHO$	96 (30)	96 (6)	90 (150)
8	$PhCH{=}CHCH_2OTHP$	$PhCH{=}CHCHO$	96 (20)	63 (10)	–

In conclusion, in this study we have introduced *n*-butyltriphenylphosphonium peroxodisulfate as a stable, inexpensive and efficient reagent for the selective oxidative deprotection of TMS and THP ethers, ethylene acetals and ketals.

EXPERIMENTAL

All of the products were characterized by comparison of their physical and spectral data with those of authentic samples. TMS and THP ethers, ethylene acetals and ketals were prepared according to described procedures.[3,4,12] Yields refer to isolated products. *n*-Butyltriphenylphosphonium peroxodisulfate was prepared as described previously.[21]

Oxidative Deprotection of TMS and THP Ethers, Ethylene Acetals, and Ketals: General Procedure

To a solution of substrate (1 mmol) in CH_3CN (15 ml), *n*-butyltriphenylphosphonium peroxodisulfate (0.826 g, 1 mmol) was added and stirred magnetically under reflux condition for the appropriate time according to Tables 1 and 2. The progress of the reaction was monitored by TLC. The reaction mixture was cooled to room temperature and filtered. The solid material was washed with CH_3CN (20 ml). The filtrates were combined and evaporated. The resulting crude material was purified on a silica gel plate with appropriate eluent. Pure carbonyl compounds were obtained in 92–99% yields (Tables 1 and 2).

ACKNOWLEDGMENT

We are thankful to the Isfahan University Research Council for partial support of this work.

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Received in Japan December 27, 2000