R. Ghorbani-Vaghei, M. Amiri, M. Chegny and H. Veis,
S. Afr. J. Chem., 2007, **60**, 58–61,
<http://journals.sabinet.co.za/sajchem/>.

Solvent-free Oxidation of Alcohols and Mild Catalytic Deprotection of Silyl Ethers with Poly(*N,N′*-dibromo-*N*-ethyl-benzene-1,3-disulphonamide) and *N,N,N′,N′*-tetrabromobenzene-1,3-disulphonamide

Ramin Ghorbani-Vaghei*, Mostafa Amiri, Mahdieh Chegny and Hojat Veisi

Department of Organic Chemistry, Faculty of Chemistry, Bu-Ali Sina University, Hamadan, Iran.

Received 14 June 2007; revised 9 July 2007; accepted 10 July 2007.

ABSTRACT

Poly(*N,N′*-dibromo-*N*-ethyl-benzene-1,3-disulphonamide) (PBBS) and *N,N,N′,N′*-tetrabromobenzene-1,3-disulphonamide (TBBDA) can be used for solvent-free oxidation of primary and secondary alcohols to the corresponding carbonyl compounds without over-oxidation, and efficient catalytic deprotection of various silyl ethers to hydroxyl groups in aprotic organic solvents under ambient conditions.

KEYWORDS

Solvent-free oxidation, alcohols, catalytic deprotection, silyl ethers, PBBS, TBBDA.

1. Introduction

The oxidation of alcohols to the corresponding aldehydes and ketones is one of the most important functional group transformations in organic synthesis. Therefore, selective oxidation of primary and secondary alcohols to aldehydes and ketones can be achieved by many reagents,[1,2] some generated *in situ*.[3]

Recently our group has exploited the application of *N,N′*-dibromo-*N,N′*-1,2-ethanediyl *bis*(*p*-toluenesulphonamide)/ dimethyl sulphide[4] for the oxidation of alcohols to aldehydes and ketones. Although the yields of aldehyde and ketone were high using this method, disadvantages included the need to use dimethyl sulphide, a volatile organic solvent, and very low temperatures.

2. Results and Discussion

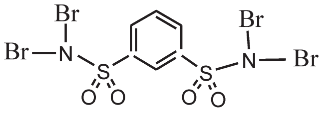
Our interest in the application of poly(*N,N′*-dibromo-*N*-ethyl-benzene-1,3-disulphonamide) (PBBS) and *N,N,N′,N′*-tetrabromobenzene-1,3-disulphonamide (TBBDA) (Scheme 1) in organic synthesis has been previously reported.[5]

Herein we report a mild and convenient method for the oxidation of alcohols using TBBDA or PBBS under solvent-free conditions (Scheme 2).

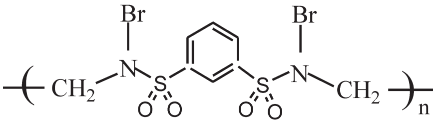
Primary and secondary alcohols were oxidized to aldehydes and ketones using PBBS or TBBDA in good to high yields under solvent-free conditions without over-oxidation to carboxylic acids (Table 1).

The advantages of PBBS and TBBDA over reported reagents for the oxidation of *p*-chlorobenzyl alcohol, *p*-methylbenzyl alcohol and benzyl alcohol are shown in Table 2. It is noteworthy that most of the previously reported reagents require heat and long times to effect reactions.

It is known that reagents containing bromine atoms which are attached to nitrogen atoms release Br^+ ions *in situ*, acting as a Lewis acid.[4,5] Therefore the following mechanism is suggested for the conversion of alcohols to aldehydes (Scheme 3).[4,6]



TBBDA



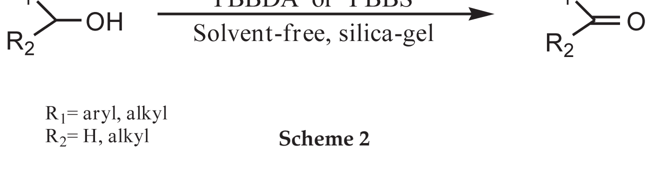
PBBS

Scheme 1

It was also found that poly(*N,N′*-dibromo-*N*-ethyl-benzene-1,3-disulphonamide) (PBBS) and *N,N,N′,N′*-tetrabromobenzene-1,3-disulphonamide (TBBDA) are efficient catalysts for the deprotection of alcoholic and phenolic silyl ethers (Scheme 4).

As shown in Table 3, treatment of a variety of trimethylsilyl ethers in the presence of dichloromethane and PBBS or TBBDA gives the corresponding alcohols and phenols in good to excellent yields. Several attempts to deprotect the silyl ethers using PBBS or TBBDA under solvent-free conditions failed.

It was observed that PBBS and TBBDA were reusable catalysts and after several runs, the catalytic activities of the reagents were almost the same as those of fresh catalysts.

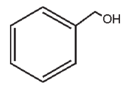
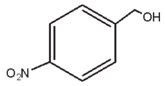
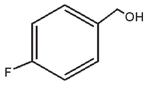
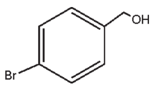
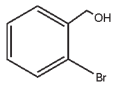
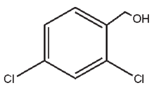
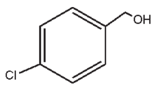
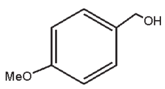
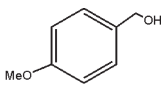
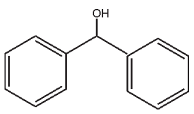
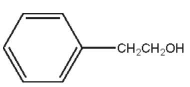
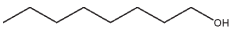


Scheme 2

---

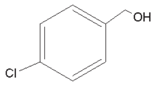
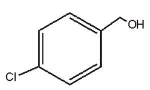
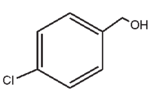
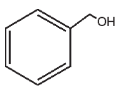
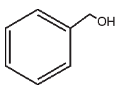
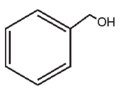
* To whom correspondence should be addressed. E-mail: rgvaghei@yahoo.com

Table 1 Solvent-free oxidation of alcohols with PBBS and TBBDA.

Entry	Substrate	PBBS		TBBDA	
		Reaction time /min	Yield[a] /%	Reaction time /min	Yield[a] /%
1		10	80	10	85
2		15	75	15	80
3		10	80	10	85
4		10	80	10	90
5		15	80	15	90
6		10	70	10	75
7		8	80	8	90
8		12	75	12	80
9		15	70	15	80
10		15	70	15	80
11		10	60	10	70
12		12	50	12	65

[a] Products were characterized from their physical properties, comparison with authentic samples and by spectroscopic methods.

Table 2 Comparison of reaction times and yields using our reagents with previously published methods.

Substrate	Reagent	Reaction time	Yield /%	Ref.
	TBBDA PBBS	8 min 8 min	90 80	–
	I_2O_5, KBr	4.5 h	70	1d
	DABCO, CH_2Cl_2, water	5 h	97	1h
	TBBDA PBBS	10 min 10 min	85 80	–
	TEMPO, CuCl, O_2, (bmim)(PF_6), 65°C	15 h	72	1j
	$(NO_3)_3CeBrO_3$, 90°C	20 min	97	6

It is noteworthy that aromatic and aliphatic silyl ethers converted to alcohols with high chemoselectivity without addition of Br^+ to aromatic groups.[5b] Furthermore, sterically-hindered silyl ethers (Table 3, entries 8 and 9) afforded good yields of their corresponding alcohols. The most remarkable advantage of this methodology is that no trace of aldehyde or acid, due to oxidation of the newly-liberated alcohol, was observed. Therefore the following mechanism can be suggested for the conversion of silyl ethers to alcohols (Scheme 5).[1i,5a,7]

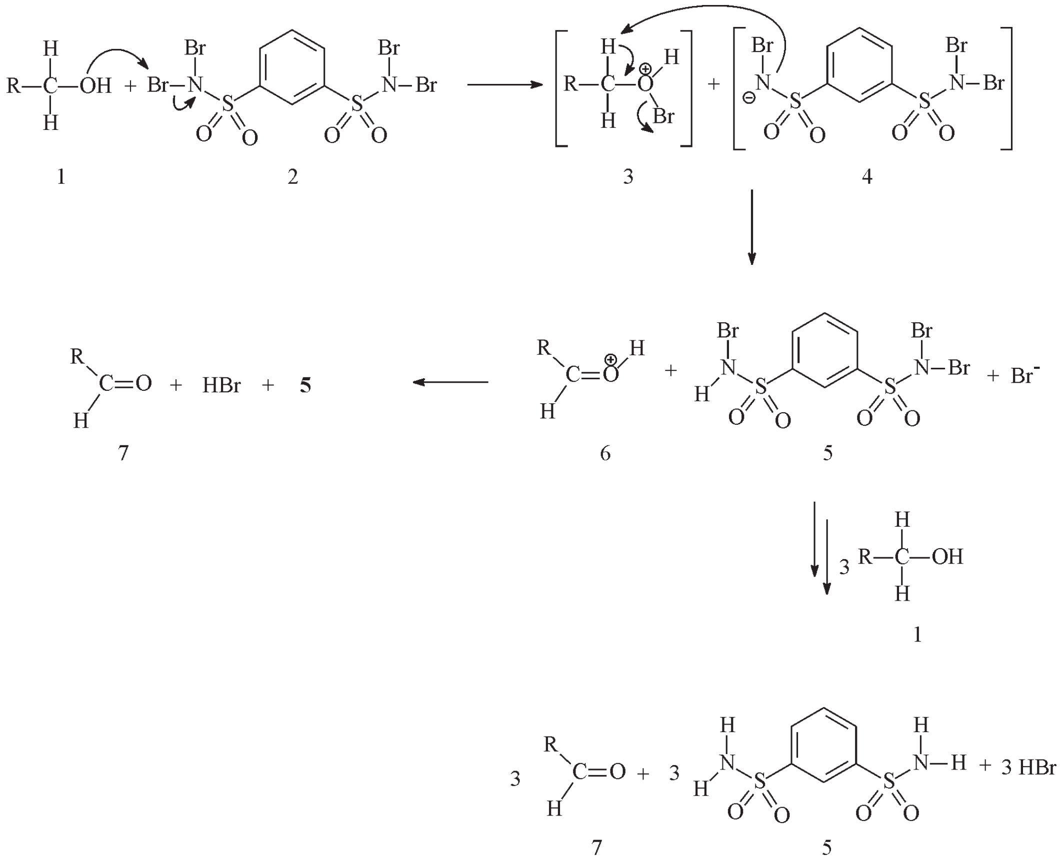
In conclusion, we have extended the application of TBBDA and PBBS for oxidation of alcohols to corresponding carbonyl compounds without over-oxidation to carboxylic acids under solvent-free conditions. These reagents are also good catalytic reagents for the deprotection of trimethylsilyl ethers to alcohols and phenols without over-oxidation of the alcohols to carbonyl and carboxylic groups.

3. Experimental

IR and NMR spectra were recorded using a Shimadzu 435-U-04 spectrophotometer (KBr pellets) and a Jeol 90 MHz FT NMR spectrometer, respectively.

3.1. General Procedure for Oxidation of Alcohols using TBBDA and PBBS under Solvent-free Conditions

Alcohol (1 mmol), PBBS (0.2 g) or TBBDA (0.2 g, 0.35 mmol) and silica gel (0.5 g) were added to a mortar and the mixture was pulverized vigorously with a pestle for the appropriate reaction time (TLC 5:1, n-hexane/acetone) at room temperature. For improved pulverization, some silica gel was added to the mortar. After completion of the reaction, CH_2Cl_2 (10 mL) was added, and the reagent was removed by filtration. Evaporation of the

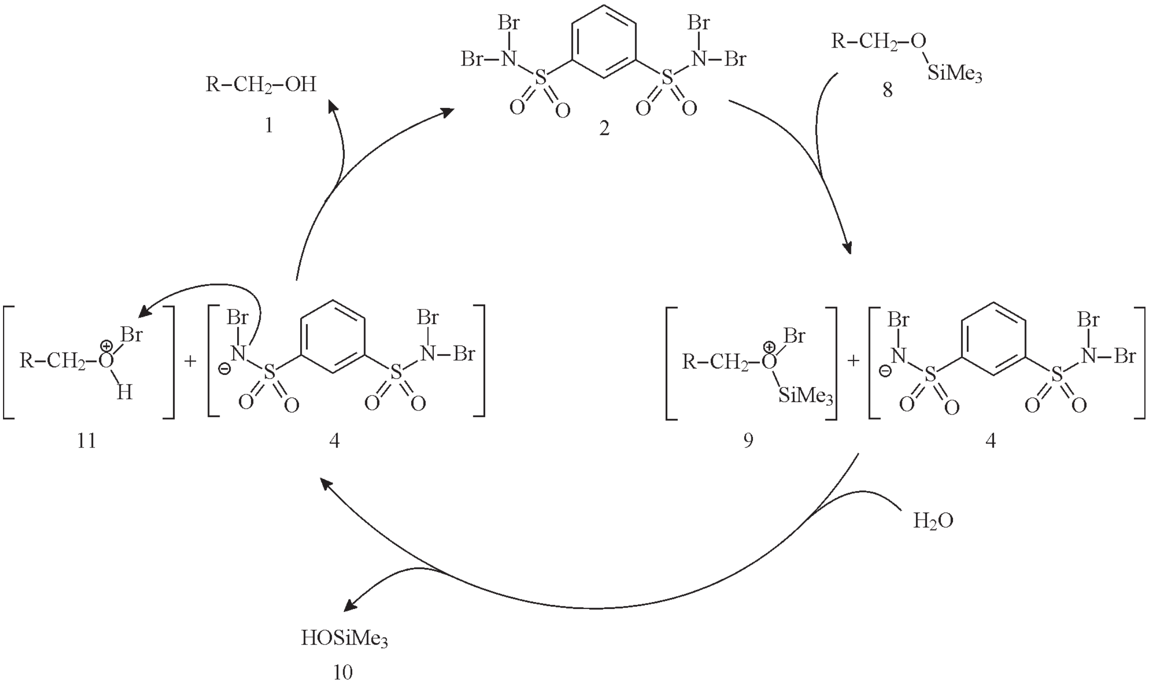


Scheme 3

$$R\text{-}OSiMe_3 \xrightarrow[CH_2Cl_2\,,\ H_2O]{\text{TBBDA or PBBS}} R\text{-}OH$$

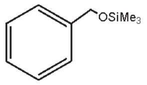
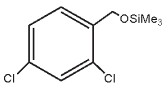
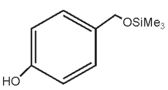
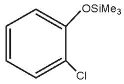
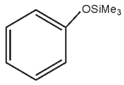
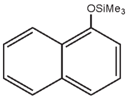
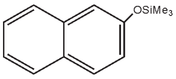
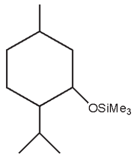
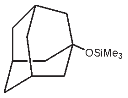
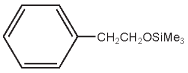
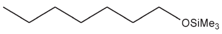
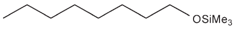
R = aryl, alkyl

Scheme 4



Scheme 5

Table 3 Catalytic deprotection of silyl ethers with PBBS and TBBDA in the presence of CH_2Cl_2.

Entry	Substrate	PBBS		TBBDA	
		Reaction time	Yield [a] /%	Reaction time	Yield [a] /%
1		60 min	83	45 min	83
2		150 min	83	100 min	85
3		40 min	80	55 min	85
4		85 min	85	80 min	80
5		24 h	90[b]	6 h	83[b]
6		24 h	85[b]	24 h	80[b]
7		24 h	87[b]	24 h	87[b]
8		270 min	87	4 h	80
9		24 h	85	24 h	85
10		145 min	85	45 min	80
11		270 min	87	140 min	80
12		275 min	80	2 h	80

[a] Products were characterized from their physical properties, comparison with authentic samples and by spectroscopic methods.

[b] Reflux conditions.

solvent under reduced pressure gave the product with good to high yields (50–90%). Further purification was achieved by column chromatography (silica-gel, n-hexane/ethyl acetate, 9:1).

3.2. General Procedure for Catalytic Deprotection of Trimethylsilyl Ethers to their Corresponding Alcohols using TBBDA and PBBS

To a mixture of trimethylsilyl ether (1 mmol), PBBS (0.02 g) or TBBDA (0.02 g, 0.04 mmol) and CH_2Cl_2 (10 mL) was added a few drops of H_2O (10 mmol). The mixture as stirred vigorously at room temperature for the specified time (Table 3). After completion of the reaction (TLC analysis), the reagents were filtered off under vacuum and washed with dichloromethane. The organic layers were separated, dried with anhydrous $MgSO_4$ and evaporation of the solvent under reduced pressure gave the alcohol. Further purification was achieved by column chromatography (silica-gel, n-hexane/ethyl acetate, 9:1).

References

1 (a) T. Sugai and A. Itoh, *Tetrahedron Lett.*, 2007, **48**, 2931–2934. (b) M. Hunsen, *Tetrahedron Lett.*, 2005, **46**, 1651–1653. (c) A. Naseem, A. Hasrat, E. Johan and J.E. Van Lier, *Tetrahedron Lett.*, 2005, **46**, 253–256. (d) L.-Q. Zhong, Y. Zaho, H. Luo, L. Chai and Q. Sheng, *Tetrahedron Lett.*, 2007, **48**, 3017–3019. (e) P. Sarmah, R. Chakrabarty, P. Phukan and K.D. Birinchi, *J. Mol. Catal. A: Chem.*, 2007, **268**, 36–44. (f) M.M. Heravi, V. Zadsirjan, Kh. Bakhtiari, H.A. Oskooie and F. F. Bamoharram, *Catal. Commun.*, 2007, 315–318. (g) M.M. Heravi, F. Derikvand, M. Ghassemzadeh and B. Neumullerc, *Tetrahedron Lett.*, 2005, **46**, 6243–6245. (h) Y. Matano, T. Suzuki, T. Shinokura and H. Imahori, *Tetrahedron Lett.*, 2007, **48**, 2885–2888. (i) G.V.M. Sharma, B. Srinivas and P.R. Krishna, *Lett. Org. Chem.*, 2005, **2**, 57–60. (j) F. Shirini, M. Esm-Hosseini and Z. Hejazi, *Synth. Commun.*, 2005, **35**, 2913–2919.

2 (a) T. Miyazawa, T. Endo, S. Shiihashi and M. Okawara, *J. Org. Chem.*, 1985, **50**, 1332–1334. (b) T. Miyazawa and T. Endo, *J. Org. Chem.*, 1985, **50**, 3930–3931.

3 (a) Z. Ma and J.M. Bobbitt, *J. Org. Chem.*, 1991, **56**, 6110–6114. (b) M.G. Banwell, V.S. Bridges, J.R. Dupuche, S.L. Richards and J.M. Walter, *J. Org. Chem.*, 1994, **59**, 6338–6343.

4 R. Ghorbani-Vaghei and A. Khazaei, *Tetrahedron Lett.*, 2003, **44**, 7525–7527.

5 (a) R. Ghorbani-Vaghei, M.A. Zolfigol, M. Chegeny and H. Veisi, *Tetrahedron Lett.*, 2006, **47**, 4505–4508. (b) R. Ghorbani-Vaghei and H. Jalili, *Synthesis,* 2005, **7**, 1099–1102. (c) R. Ghorbani-Vaghei and E. Shahbazee, *J. Braz. Chem. Soc.*, 2005, **16**, 647–649. (d) M.A. Zolfigol, R. Ghorbani-Vaghei, S. Mallakpour, G. Chehardoli, A. Ghorbani Choghamani and A.H. Yazdi, *Synthesis,* 2006, **10**, 1631–1634. (e) R. Ghorbani-Vaghei, H. Jalili, E. Shahbazee and H. Veisi, *J. Chin. Chem. Soc.*, 2006, **53**, 379–382. (f) R. Ghorbani-Vaghei, E. Shahbazee and H. Veisi, *Mendeleev Commun.*, 2005, 207–208. (g) R. Ghorbani-Vaghei, D. Azarifar and B. Maleki, *J. Chin. Chem. Soc.*, 2004, **51**, 1373–1376. (h) R. Ghorbani-Vaghei, D. Azarifar and B. Maleki, *Bull. Korean Chem. Soc.*, 2004, **25**, 953–954.

6 (a) A. Sakai, D.G. Hendrickson and W.H. Hendrickson, *Tetrahedron Lett.*, 2000, **41**, 2759–2763. (b) N. Venkatasubramanian and V. Thiagarajan, *Tetrahedron Lett.*, 1968, **9**, 1711–1714. (c) T. Shono, Y. Matsumura, J. Hayashi and M. Mizoguchi, *Tetrahedron Lett.*, 1979, **20**, 165–168. (d) M. Ueno, T. Nabana and H. Togo, *J. Org. Chem.*, 2003, **68**, 6424–6426.

7 R. Hunter, W. Hinz and P. Richards, *Tetrahedron Lett.*, 1999, **40**, 3643–3646.