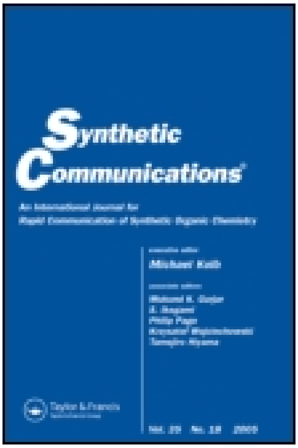


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

$(NO_3)_3CeBrO_3$: Solvent-Free Oxidation of Alcohols and Deprotection and Oxidative Deprotection of Trimethylsilyl Ethers

Farhad Shirini [a], Majid Esm-Hosseini [b] & Zoha Hejazi [a] [b]

[a] Department of Chemistry, College of Science, Guilan University, Rasht, Iran

[b] Department of Chemistry, College of Science, Urmia University, Urmia, Iran

To cite this article: Farhad Shirini, Majid Esm-Hosseini & Zoha Hejazi (2005): $(NO_3)_3CeBrO_3$: Solvent-Free Oxidation of Alcohols and Deprotection and Oxidative Deprotection of Trimethylsilyl Ethers, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 35:22, 2913-2919

To link to this article: http://dx.doi.org/10.1080/00397910500297362

Synthetic Communications®, 35: 2913–2919, 2005
Copyright © Taylor & Francis, Inc.
ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910500297362

$(NO_3)_3CeBrO_3$: Solvent-Free Oxidation of Alcohols and Deprotection and Oxidative Deprotection of Trimethylsilyl Ethers

Farhad Shirini
Department of Chemistry, College of Science, Guilan University,
Rasht, Iran

Majid Esm-Hosseini
Department of Chemistry, College of Science,
Urmia University, Urmia, Iran

Zoha Hejazi
Department of Chemistry, College of Science, Guilan University,
Rasht, Iran and Department of Chemistry, College of Science,
Urmia University, Urmia, Iran

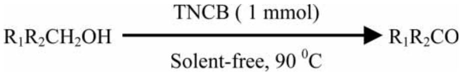
Abstract: Trinitratocerium(IV) bromate (TNCB) can be used as an efficient reagent for oxidation of alcohols and deprotection and oxidative deprotection of trimethylsilyl ethers under solvent-free conditions.

Keywords: Alcohols, deprotection, oxidation, trinitratocerium (IV) bromate, solvent-free conditions

Cerium(IV)-based reagents are among the most widely used lanthanide reagents in organic chemistry. These reagents are used for such purposes as

Received in the UK February 18, 2005

Address correspondence to Farhad Shirini, Department of Chemistry, College of Science, Guilan University, Rasht, 41335-1914, Iran. E-mail: shirini@guilan.ac.ir; fshirini@yahoo.com



Scheme 1.

oxidation,[1−4] one-electron transfer reactions,[5−7] coupling of substituted benzenes,[8] and so forth.

Recently we have reported the synthesis and application of trinitratocerium(IV) bromate in the oxidation of benzyl alcohols and acyloins in refluxing acetonitrile.[9] Although the yields of the obtained

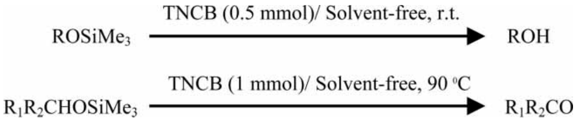
Table 1. Oxidation of alcohols using TNCB under solvent-free conditions

Entry	Substrate	Product	T(h)	Yield (%)^a
1	$PhCH_2OH$	PhCHO	0.33	95
2	$2\text{-}BrC_6H_4CH_2OH$	$2\text{-}BrC_6H_4CHO$	0.5	95
3	$2\text{-}ClC_6H_4CH_2OH$	$2\text{-}ClC_6H_4CHO$	0.42	92
4	$4\text{-}ClC_6H_4CH_2OH$	$4\text{-}ClC_6H_4CHO$	0.42	90
5	$2\text{-}MeC_6H_4CH_2OH$	$2\text{-}MeC_6H_4CHO$	0.42	95
6	$2\text{-}NO_2C_6H_4CH_2OH$	$2\text{-}NO_2C_6H_4CHO$	1	90
7	$4\text{-}NO_2C_6H_4CH_2OH$	$4\text{-}NO_2C_6H_4CHO$	3	80
8	$4\text{-}Me_3CC_6H_4CH_2OH$	$4\text{-}Me_3CC_6H_4CHO$	0.42	92
9	$PhCH(OH)CH_3$	$PhCOCH_3$	0.42	95
10	$PhCH(OH)CH_2OH$	PhCOCHO	0.8	90
11	$PhCH_2CH(OH)CH_3$	$PhCH_2COCH_3$	0.8	95
12	Cyclohexanol	Cyclohexanone	0.3	92
13	(−)-Menthol	(−)-Menthone	0.5	95
14	2-Adamantanol	2-Adamantanone	0.5	90
15	Borneol	Camphor	0.5	92
16	2-(2-Pyridyl)ethanol	2-(2-Pyridyl)ethanol	0.33	90
17	$PhCH{=}CHCH_2OH$	$PhCH{=}CHCHO$	1.5	85

^{a}Isolated yields.

Table 2. Comparison of some of the results obtained by the oxidation of alcohols with TNCB in solution (1)[9] and under solvent-free conditions (2)

		(1)			(2)		
Entry	Substrate	T(h)	Yield (%)	Oxidant/ substrate	T(h)	Yield (%)	Oxidant/ substrate
1	$PhCH_2OH$	2.5	92	4	0.33	95	1
2	$PhCH(OH)CH_3$	2.5	82	6	0.42	95	1
3	Cyclohexanol	—	—	—	0.3	92	1



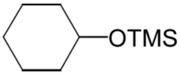
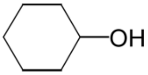
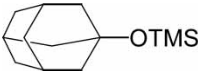
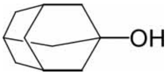
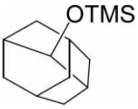
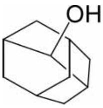
Scheme 2.

carbonyl compounds using this reagent are relatively high, the method suffers from disadvantages such as inability of the reagent to oxidize aliphatic alcohols,[10] long reaction times, and relatively high oxidant-to-substrate ratio.

In view of this and in according to our experience in solvent-free reactions,[11–13] we decided to overcome these disadvantages by conducting the previous reactions in the absence of solvent. Herein, we report that TNCB is able to oxidize the alcohols efficiently under solvent-free conditions (Scheme 1).

Different types of alcohols, including primary and secondary benzylic and aliphatic, were efficiently oxidized to their corresponding aldehydes and

Table 3. Solvent-free deprotection of trimethylsilyl ethers with TNCB

Entry	Substrate	Product	T (min)	Yield (%)[a]
1	$PhCH_2OTMS$	$PhCH_2OH$	5	95
2	$2\text{-}BrC_6H_4CH_2OTMS$	$2\text{-}BrC_6H_4CH_2OH$	2	90
3	$4\text{-}ClC_6H_4CH_2OTMS$	$4\text{-}ClC_6H_4CH_2OH$	5	92
4	$4\text{-}Me_3CC_6H_4CH_2OTMS$	$4\text{-}Me_3CC_6H_4CH_2OH$	5	80
5	$2\text{-}NO_2C_6H_4CH_2OTMS$	$2\text{-}NO_2C_6H_4CH_2OH$	1	80
6	$4\text{-}NO_2C_6H_4CH_2OTMS$	$4\text{-}NO_2C_6H_4CH_2OH$	5	85
7	$4\text{-}MeOC_6H_4CH_2OTMS$	$4\text{-}MeOC_6H_4CH_2OH$	5	95
8	$4\text{-}PhCH_2OC_6H_4CH_2OTMS$	$4\text{-}PhCH_2OC_6H_4CH_2OH$	1	90
9	$2\text{-}MeC_6H_4CH_2OTMS$	$2\text{-}MeC_6H_4CH_2OH$	1	80
10	$Ph_2CHOTMS$	Ph_2CHOH	5	92
11	PhCOCH(OTMS)Ph	PhCOCH(OH)Ph	10	75
12	$PhCH_2\ CH_2CH_2OTMS$	$PhCH_2\ CH_2CH_2OH$	1	95
13	$PhCH_2CH(OTMS)CH_3$	$PhCH_2CH(OH)CH_3$	5	92
14			1	95
15			1	92
16			1	95
17	Me_3COTMS	Me_3COH	1	82

[a] Isolated yield.

ketones in good to high yields in the absence of solvent at 90°C (Table 1). Overoxidation of the products was not observed using this method.

To show the efficiency of this method we have compared some of the results with some of those obtained by TNCB in solution (Table 2).[9]

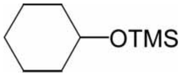
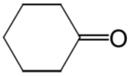
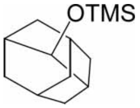
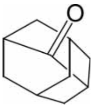
As shown in Table 2, by omitting the solvent, the reaction time and the oxidant-to-substrate ratio were reduced and the need for solvent is avoided.

Our investigations also indicated that deprotection and direct oxidative deprotection of trimethylsilyl ethers to their corresponding alcohols or carbonyl compounds have been achieved efficiently in the presence of TNCB under solvent-free conditions (Scheme 2).

The pathway of the reaction is quite dependent upon the temperature, the reaction times, and the oxidant-to-substrate ratio. Deprotection occurs at room temperature and in the presence of 0.5 molar equivalents of the reagent in few minutes (Table 3). The direct oxidative deprotection is performed using 1 molar equivalent of the reagent at 90°C with longer reaction times (Table 4).

To illustrate the efficiency of the proposed method, Table 5 compares some of the results obtained by our method with some of those reported in the literature.[14,15]

Table 4. Oxidative deprotection of trimethylsilyl ethers with TNCB under solvent-free conditions

Entry	Substrate	Product	T (h)	Yield (%)[a]
1	$PhCH_2OTMS$	$PhCHO$	0.33	97
2	$2\text{-}BrC_6H_4CH_2OTMS$	$2\text{-}BrC_6H_4CHO$	0.7	95
3	$4\text{-}ClC_6H_4CH_2OTMS$	$4\text{-}ClC_6H_4CHO$	0.33	92
4	$4\text{-}Me_3CC_6H_4CH_2OTMS$	$4\text{-}Me_3CC_6H_4CHO$	0.7	97
5	$2\text{-}NO_2C_6H_4CH_2OTMS$	$2\text{-}NO_2C_6H_4CHO$	0.5	80
6	$4\text{-}NO_2C_6H_4CH_2OTMS$	$4\text{-}NO_2C_6H_4CHO$	0.83	95
7	$4\text{-}MeOC_6H_4CH_2OTMS$	$4\text{-}MeOC_6H_4CHO$	0.83	92
8	$4\text{-}PhCH_2OC_6H_4CH_2OTMS$	$4\text{-}PhCH_2OC_6H_4CHO$	0.33	95
9	$2\text{-}MeC_6H_4CH_2OTMS$	$2\text{-}MeC_6H_4CHO$	0.33	96
10	$Ph_2CHOTMS$	Ph_2CHO	0.25	95
11	$PhCH_2\ CH_2CH_2OTMS$	$PhCH_2\ CH_2CHO$	0.5	95
12	$PhCH_2CH(OTMS)CH_3$	$PhCH_2COCH_3$	0.7	92
13			0.4	98
14			0.7	95

[a]Isolated yield.

Table 5. Comparison of some of the results obtained by the oxidative deprotection of trimethylsilyl ethers with TNCB (1), with some of those reported by $[(NO_3)_3Ce]_2CrO_4$ (2)[14] and benzyltriphenylphosphonium chlorate (3)[15]

			(1)			(2)			(3)		
Entry	Substrate	Product	Oxidant/ substrate	H	Yield (%)	Oxidant/ substrate	H	Yield (%)	Oxidant/ substrate	H	Yield (%)
1	$PhCH_2OTMS$	PhCHO	1	0.33	97	2	0.5	85	1	0.25	100
2	$Ph_2CHOTMS$	Ph_2CO	1	0.25	95	4.5	3	85	1	0.3	95
3	$Ph(CH_2)_2CH_2OTMS$	$Ph(CH_2)_2CHO$	1	0.5	95	6	5	80	1	10	85

In conclusion, in this study we have developed a mild, efficient, and excellent yielding method for oxidation of alcohols and deprotection and direct oxidative deprotection of trimethylsilyl ethers. In addition, solvent-free reaction conditions, high reaction rates, and easy and clean workup are worthy advantages of the present method.

EXPERIMENTAL

Chemicals were purchased from Fluka, Merck, and Aldrich Chemical Companies. Trimethylsilyl ethers were prepared according to the described procedures.[16–18] All products are known compounds; they are identified by comparison of their physical data and IR and NMR spectra with those of authentic samples. All yields refer to the isolated products. The purity determination of the substrates and reaction monitoring were accompanied by TLC on silica-gel polygram SILG/UV 254 plates.

Oxidation of Alcohols and Trimethylsilyl Ethers to Their Corresponding Carbonyl Compounds: General Procedure

A mixture of the substrate (1 mmol) and TNCB (1 mmol, 0.454 g) was shaken in an oil bath (90°C) for the specified time (Tables 1 and 4). The progress of the reaction was monitored by TLC. The reaction mixture was triturated with CH_2Cl_2 (5 mL) and filtered, and the solid residue was washed with CH_2Cl_2 (3 mL). Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding carbonyl compounds in good to high yields.

Deprotection of Trimethylsilyl Ethers to Their Corresponding Alcohols: General Procedure

A mixture of the substrate (1 mmol) and TNCB (0.5 mmol, 0.227 g) was shaken at room temperature for the specified time (Table 5). The progress of the reaction was monitored by TLC. The reaction mixture was triturated with CH_2Cl_2 (5 mL) and filtered, and the solid residue was washed with CH_2Cl_2 (3 mL). Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding carbonyl compounds in good to high yields.

ACKNOWLEDGMENT

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

REFERENCES

1. Shirini, F.; Azadbar, M. R. $[(NO_3)_3\,Ce]_3 \cdot H_2IO_6$: As a veratile and efficient reagent for cleavage of carbon $\rightleftharpoons$ nitrogen double bonds under heterogeneous and non-aqueous conditions. *Synth. Commun.* **2001**, *31*, 3775.
2. Al-Haq, N.; Sullivan, A. C.; Wilson, R. H. Oxidation of alcohols using cerium(IV) alkyl phosphonate modified silica. *Tetrahedron Lett.* **2003**, *44*, 769.
3. Laali, K. K.; Herbert, M.; Cushnyr, B.; Bahatt, A.; Terrano, D. Benzylic oxidation of aromatics with cerium(IV) triflate; synthetic scope and mechanistic insight. *J. Chem. Soc., Perkin Trans.* **2001**, *1*, 578.
4. Imamoto, T.; Koide, Y.; Hiayama, S. Cerium(IV) trifluoromethanesulfonate as a strong oxidizing agent. *Chem. Lett.* **1990**, 1445.
5. Iranpoor, N.; Mohammadpoor-Baltork, I.; Shirini, F. Cerric ammonium nitrate, as an efficient catalyst for mild and selective opening of epoxides in the presence of water, thiols and acetic acid. *Tetrahedron* **1991**, *47*, 9861.
6. Iranpoor, N.; Shirini, F. Tris[trinitrato Ce(IV)]paraperiodate, as an efficient heterogeneous catalyst for alcoholysis, acetolysis, and hydrolysis of epoxides. *Synth. Commun.* **1994**, *24*, 1959.
7. Iranpoor, N.; Shekarriz, M.; Shirini, F. Highly efficient, regio- and stereoselective ring opening of epoxides with $Ce(OTf)_4$. *Synth. Commun.* **1998**, *28*, 347.
8. Iranpoor, N.; Shekarriz, M. Homocoupling of substituted benzenes to symmetrical biaryls with mercury(II) in the presence of cerium(IV). *J. Chem. Res., Synop.* **1999**, 442.
9. Shirini, F.; Tajik, H.; Aliakbar, A.; Akbar, A. Oxidation of benzyl alcohols and acyloins with $(NO_3)_3CeBrO_3$. *Synth. Commun.* **2001**, *31*, 767.
10. Akbar, A. Guilan University: Iran, 2000, M.Sc. Thesis.
11. Shirini, F.; Zolfigol, M. A.; Pourhabib, A. Efficient cleavage of carbon–nitrogen double bonds under solvent-free conditions. *Synth. Commun.* **2002**, *32*, 2837.
12. Shirini, F.; Zolfigol, M. A.; Mallakpour, B.; Mohammadpoor-Baltork, I.; Mallakpour, S. E.; Hajipour, A. R. Solvent-free oxidation of thiols by $(NH_4)_2Cr_2O_7$ in the presence of $Mg(HSO_4)_2$ and wet SiO_2. *J. Chem. Res., Synop.* **2003**, *1*, 28.
13. Shirini, F.; Zolfigol, M. A.; Mohammadi, K. Silica sulfuric acid as a mild and efficient reagent for the acetylation of alcohols in solution and under solvent-free conditions. *Bull. Korean Chem. Soc.* **2004**, *25*, 325.
14. Firouzabadi, H.; Shirini, F. Bis[trinitrato cerium (IV)] chromate; $[(NO_3)_3\,Ce]_2\,CrO_4$ vs trinitrato cerium(IV) chromate dihydrate; $[(NO_3)_3Ce]\,CrO_4 \cdot 2H_2O$ in the oxidation of trimethylsilyl ethers. *Synth. Commun.* **1996**, *26*, 649.
15. Hajipour, A. R.; Mallakpour, S. E.; Mahammadpoor-Baltork, I.; Malakoutikhah, M. Benzyltriphenylphosphonium chlorate (BTPPC) as a new and mild reagent for oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers of benzylic alcohols under non-aqueous conditions. *Tetrahedron.* **2002**, *58*, 143.
16. Karimi, B.; Golshani, B. Mild and highly efficient method for the silylation of alcohols using hexamethyldisilazane catalyzed by iodine under nearly neutral reaction conditions. *J. Org. Chem.* **2000**, *65*, 7228.
17. Firouzabadi, H.; Karimi, B. Zinc chloride–catalyzed silylation of alcohols and phenols by hexamethyldisilazane. A highly chemoselective reaction. *Synth. Commun.* **1993**, *23*, 1633.
18. Shirini, F.; Zolfigol, M. A.; Mohammadi, K. A mild and efficient method for chemoselective silylation of alcohols using hexamethyldisilazane in the presence of silica chloride. *Phosphorus, Sulfur, Silicon Relat. Elem.* **2003**, *178*, 1567.