ISSN: 0974 - 7516 Volume 9 Issue 11

Organic CHEMISTRY
An Indian Journal
Full Paper

OCAIJ, 9(11), 2013 [463-468]

Oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers, acetals and ketals with *N,N'*-dibenzyl-1,4-diazoniabicyclo [2.2.2] octane peroxodisulfate under non-aqueous conditions

Mohammad Alikarami[1]*, Zahra Abbasi[2]
[1]Department of Chemistry, Ilam Branch, Islamic Azad University, Ilam, (IRAN)
[2]Department of Chemistry, Eyvan-e-Gharb Branch, Islamic Azad University, Eyvan, (IRAN)
E-mail: alikarami58@yahoo.com

ABSTRACT

An efficient and convenient conversion of trimethylsilyl (TMS) and tetrahydropyranyl (THP) ethers, acetals and ketals to the corresponding carbonyl compounds with *N,N'*-dibenzyl-1,4-diazoniabicyclo [2.2.2] octane peroxodisulfate (DBDABCOPDS) under non-aqueous conditions is described.

KEYWORDS

N,N'-dibenzyl-1,4-diazoniabicyclo [2.2.2] octane peroxodisulfate;
Trimethylsilyl ethers;
Tetrahydropyranyl ethers;
Acetals;
Ketals.

INTRODUCTION

The protection of hydroxyl groups as their trimethylsilyl and tetrahydropyranyl ethers[1-3] and aldehydes and ketones by the formation of acetals and ketals[4] is an important reaction in organic chemistry. Oxidative deprotection of the above mentioned ethers, acetal and ketals to their corresponding carbonyl compounds under mild, aprotic and non-aqueous conditions is also of synthetic value[5-8]. However, some of the reported methods for the oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers, 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.

The peroxodisulfate ion is one of the strongest oxidizing agents. The investigations[9] on application of peroxidisulfate ion in organic synthesis as an oxidant were performed in aqueous acidic or basic solution or in the presence of transition metal ions.

In recent years much attention has been given to the synthesis and application of new peroxodisulfate compounds which were used for the oxidation of organic compounds under non-aqueous conditions[10].

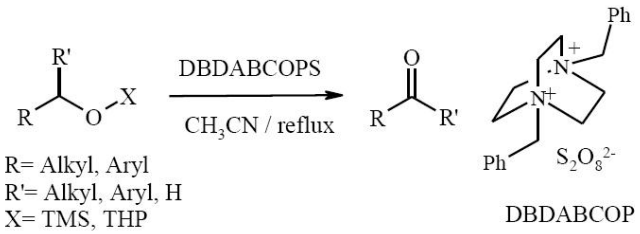
We report here a new and efficient procedure for the TMS and THP ethers, acetals and ketals to the corresponding carbonyl compounds using DBDABCOPDS under non-aqueous conditions. The results obtained with this reagent are satisfactory and proved that it is a valuable addition to the existing oxidants.

RESULT AND DISCUSSION

To find the optimum reaction conditions, we have

chosen the Ph-CH_2OTMS as a model substrate. When we have treated the Ph-CH_2OTMS with reagent in different solvents such as CH_3CN, CH_2Cl_2, $CHCl_3$, THF, n-Hexane, temperatures and mole ratio of substrate to reagent, we have found that a 1:1 mole ratio of substrate to reagent in refluxing acetonitrile gives the highest yield of the corresponding carbonyl compound. In order to show the applicability and generality of this method we have examined the reaction of TMS and THP ethers and acetal and ketals with DBDABCOPDS in refluxing acetonitrile.

The treatment of a variety of trimethylsilyl and tetrahydropyranyl ethers with DBDABCOPDS gave the corresponding carbonyl compounds in excellent yields (Scheme 1, TABLE 1).



Scheme 1

TABLE 1 : Oxidative deprotection of TMS and THP ethers with DBDABCOPDS

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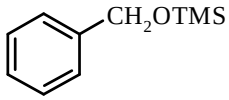
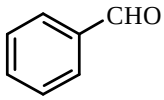
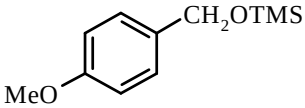
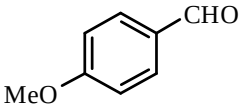
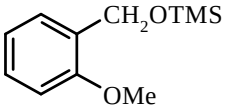
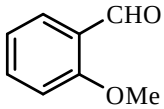
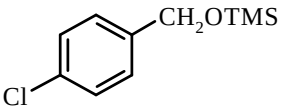
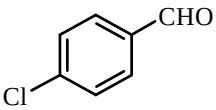
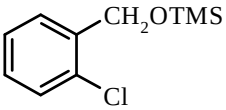
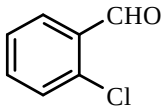
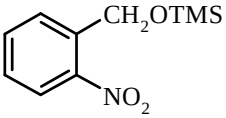
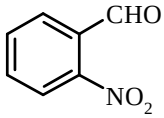
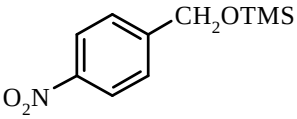
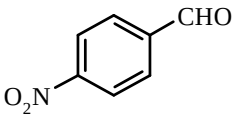
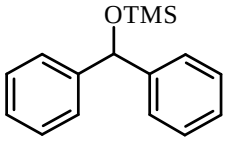
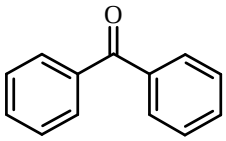
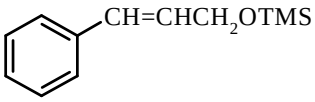
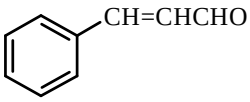
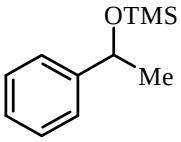
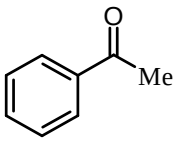
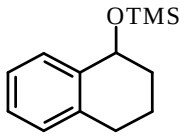
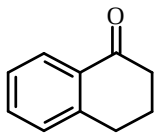
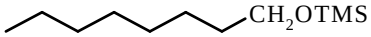
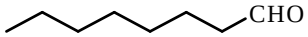
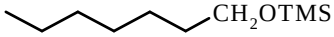
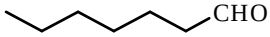
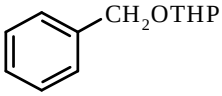
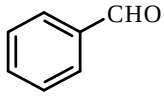
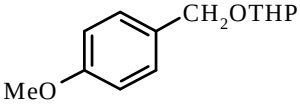
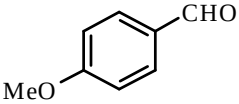
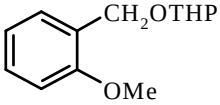
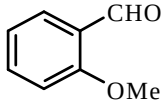
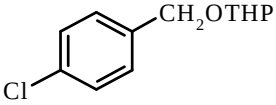
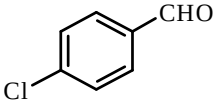
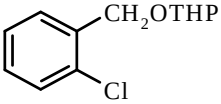
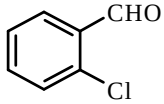
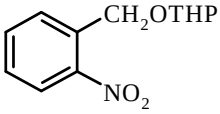
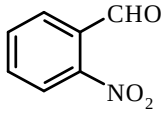
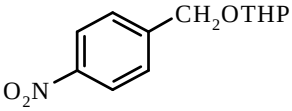
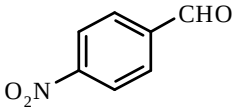
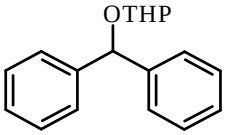
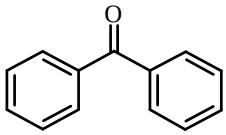
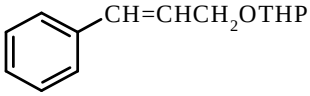
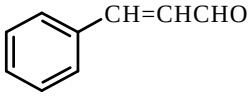
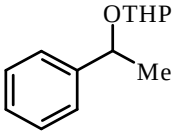
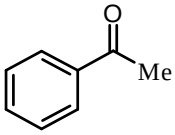
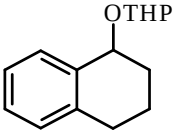
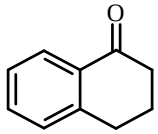
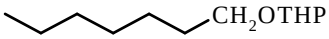
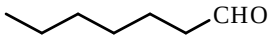
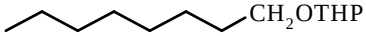
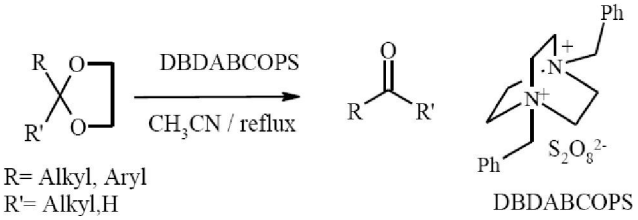
1		25		93
2		15		95
3		20		90
4		25		90
5		28		88
6		50		76
7		50		80
8		12		95
9		10		94
10		20		91

Entry	Substrate	Time(min)	product	Yield(%)[a]
11		30		97
12		50		79
13		50		83
14		25		92
15		15		93
16		20		90
17		20		90
18		25		91
19		50		76
20		50		82
21		10		95
22		15		93
23		25		94
24		30		96
25		50		84
26		50		81

[a] **Isolated yield.**

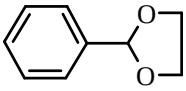
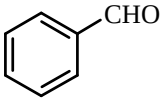
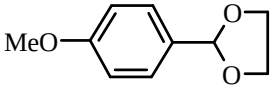
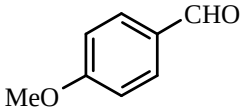
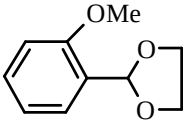
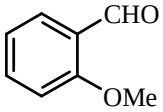
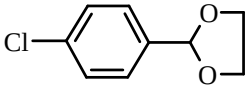
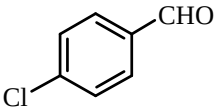
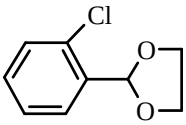
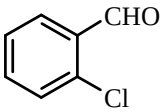
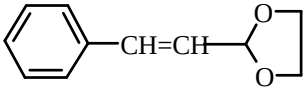
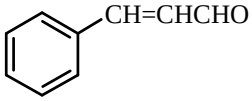
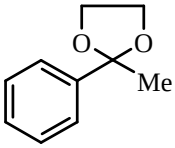
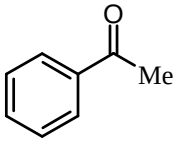
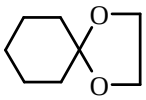
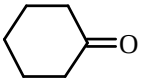
Deprotection of acetals and ketals was also investigated with this reagent and the corresponding aldehydes and ketones were obtained in excellent yields (Scheme 2, TABLE 2).

Interestingly, over oxidation 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 9, 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 tetrahydropyranyl ethers are oxidized selectively in the presence of acetals and ketals.



Scheme 2

TABLE 2 : Oxidative deprotection of ethylene acetals and ketals with DBDABCOPDS

Entry	Substrate	Time(min)	product	Yield(%)[a]
1		120		93
2		105		92
3		150		90
4		130		90
5		180		86
6		135		92
7		110		90
8		165		89

[a] **Isolated yield.**

EXPERIMENTAL

Materials were purchased from Merck and Aldrich companies. Melting points were taken on a Barnstead Electrothermal 9100 melting point apparaturs equipped with a microscope and are uncorrected. Reactions in solution were monitored by thin-layer chromatography

(TLC) of worked up reaction aliquots. Analytical TLC was performed using Merck silica gel (60 F-254) plates (0.25 mm) percolated with a fluorescent indicator. Column chromatography was carried out on silica gel 60 (70–230 mesh). NMR data were recorded on 500 MHz NMR spectrometers from Bruker. IR spectra were recorded on a Frontier FT-IR (Perkin Elmer) spectrometer using a KBr disk. All yields refer to isolated products.

Typical procedure for preparation of N,N'-dibenzy-1,4-diazoniabicyclo [2.2.2] octane peroxodisulfate

N,N'-dibenzy-1,4-diazoniabicyclo [2.2.2] octane bromide (6.44 g, 20 mmol) and potassium peroxodisulfate (6.01 g, 22.0 mmol) were dissolved in 30-35 mL of distilled water and the solution was stirred for 30 min at room temperature. The resulting white precipitate was collected and washed with cooled water and ether and dried in desiccator to afford a white solid (90%), which decomposed at >200 °C.

IR (KBr): 3050, 1486, 1260, 1050, 860, 750, 695 cm^{-1}.

^{1}H NMR (500 MHz, DMSO-d_6): δ(ppm) = 7.55-7.52 (*m*, 10H), 4.76 (s, 4H), 3.86 (s, 12H).

^{13}C NMR (125 MHz, DMSO-d_6): δ(ppm) = 137.6, 135.2, 133.7, 130.9, 71.1, 54.7.

Anal. Calcd for $C_{20}H_{26}N_2O_8S_2$: C, 54.29; H, 5.94; N, 6.33. Found: C, 53.93; H, 5.78; N, 6.43. The *N,N'*-dibenzy-1,4-diazoniabicyclo [2.2.2] octane peroxodisulfate turns out to be stable for a couple of months at room temperature, and can be stored in refrigerator permanently.

Typical procedure for oxidative deprotection of TMS and THP ethers, acetals, and ketals

To a solution of substrate (1 mmol) in CH_3CN (15 ml), *N,N'*-dibenzy-1,4-diazoniabicyclo [2.2.2] octane peroxodisulfate (0.486 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.

CONCLUSION

In conclusion, we have developed an efficient procedure for the regeneration of carbonyl compounds from TMS and THP ethers, acetals and ketals that possess significant advantages over the existing methods such as simple procedure, high yield and mild reaction conditions.

REFERENCES

[1] T.W.Greene, P.G.M.Wutz; Protective Groups in Organic Synthesis. 2nd Edition; John Wiley & Sons: New York, **(1991)**.

[2] **(a)** M.Lalonde, T.H.Chan; Synthesis, 817 **(1985)**; **(b)** H.Firouzabadi, B.Karimi; Synth.Commun., **23**, 1633 **(1993)**; **(c)** H.A.Oskooie, M.R.Abaszadeh, F.F.Zamani, M.M.Heravi; Synth.Commun., **28**, 2281 **(1998)**.

[3] **(a)** B.S.Babu, K.K.Balasubramanian; Tetrahedron Lett., **39**, 9287 **(1998)**; **(b)** K.J.Davis, U.T.Bhalerao, B.V.Rao; Synth.Commun., **29**, 1679 **(1999)**.

[4] **(a)** F.A.Meskens; J.Synthesis, 501 **(1981)**; **(b)** D.J.Kalita, R.Borah, J.C.Sarma; Tetrahedron Lett., **39**, 4573 **(1998)**; **(c)** R.Ballini, G.Bosica, B.Frullanti, R.Maggi, G.Sartori, F.Schroer; Tetrahedron Lett., **39**, 1615 **(1998)**.

[5] **(a)** R.Baker, V.B.Rao, P.D.Ravenscroft, C. J.Swain; Synthesis, 572 **(1983)**; **(b)** E.J.Parish, S.A.Kizito, R.W.Heidepriem; Synth.Commun., **23**, 223 **(1993)**.

[6] **(a)** H.Firouzabadi, I.Mohammadpoor-Baltork; Synth.Commun., **24**, 1065 **(1994)**; **(b)** H.Firouzabadi, H.Badparva, A.R.Sardarian; Iran J.Chem. & Chem.Eng., **17**, 33 **(1998)**.

[7] **(a)** E.Marcantoni, F.Nobili; J.Org.Chem., **62**, 4183 **(1997)**; **(b)** P.Saravanan, M.Chandrasekhar, R.V.Anand, V.K.Singh; Tetrahedron Lett., **39**, 3091 **(1998)**; **(c)** T.S.Li, S.H.Li; Synth.Commun., **27**, 2299 **(1997)**.

[8] **(a)** M.M.Lakouraj, M.Tajbakhsh, F.Ramzanian-Lehmali, K.Ghodrati; Monat Fur Chem., **139**, 537 **(2008)**; **(b)** M.M.Lakouraj, M.Tajbakhsh, F.Ramzanian-Lehmali; Posphorus, Sulfur, and Silicon, **183**, 1388 **(2008)**; **(c)** H.Ghasemnejad-Bosra, M.Tajbakhsh, F.Ramzanian-Lehmali, M.Shabani-Mahali, M.A.Khalilzadeh; Posphorus, Sulfur, and Silicon, **183**, 1496 **(2008)**; **(d)** R.Hosseinzadeh, M.Tajbakhsh, F.Ramzanian-Lehmali,

M.Sadatshahabi; Posphorus, Sulfur, and Silicon, **180**, 2279 **(2005)**; **(e)** M.Tajbakhsh, I.Mohamadpoor-Baltork, F.Ramzanian-Lehmali; Phosphorus, Sulfur, and Silicon, **178**, 2617 **(2003)**; **(f)** M.Tajbakhsh, I.Mohammadpoor-Baltork, F.Ramzanian-Lehmali; J.Chem.Res.(s), 185 **(2001)**.

[9] D.A.House; Kinetics and mechanism of oxidation by peroxidisulfate. Chem.Rev., **62**, 185 **(1962)**.

[10] **(a)** H.Firouzabadi, P.Salehi, I.Mohammadpoor-Baltork; Bull.Chem.Soc.Jpn., **65**, 2879 **(1992)**; **(b)** J.C.Jung, H.C.Choi, Y.H.Kim; Tetrahedron Lett., **7**, 3581 **(1993)**; **(c)** I.Mohammadpoor-Baltork, A.R.Hajipour, H.Mohammadi; Bull.Chem.Soc. Jpn., **71**, 1649 **(1998)**; **(d)** W.Minghu, Y.Guichun, C.Zuxing; Synth.Commun., **30(17)**, 3127 **(2000)**; **(e)** M.Tajbakhsh, M.M.Lakouraj, A.Fadavi; Synth.Commun., **34**, 1173 **(2004)**; **(f)** M.Norouzi, M.Tajbakhsh, H.Alinezhad, A.Geran Urimi; Journal of the Chinese Chemical Society, **55**, 508-511 **(2008)**; **(g)** M.Joshaghani, M.Bahadori, E.Rafiee, M.Bagherzadeh; Arkivoc, 260-265 **(2007)**; **(h)** W.Minghu, Y.Guichun, Ch.Zuxing; Reactive & Functional Polymers, **44**, 97–100 **(2000)**.