SHORT PAPER

J. Chem. Research (S),
2003, 348–350

Convenient transformation of thiocarbonyl to carbonyl group using benzyltriphenylphosphonium and *n*-butyltriphenylphosphonium peroxodisulfates[†]

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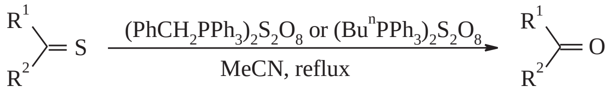
Benzyltriphenylphosphonium and *n*-butyltriphenylphosphonium peroxodisulfates are stable and easily prepared oxidising agents. These reagents are able to convert different thioamides and thioureas to their oxygen analogues in good to excellent yields. Thiono esters are also transformed to esters in high yields. Thioketones such as thiobenzophenone and thiofluorenone are converted to their ketones in high yields while, 4-nitrothiobenzophenone, 2-aminothiobenzophenone and 4-chlorothiobenzophenone remained intact in the reaction mixture.

Keywords: peroxodisulfate, thiocarbonyl, carbonyl compouns

Protection and deprotection of functional groups is a common feature in a multistep organic synthesis. Organosulfur compounds have largely demonstrated their versatility as precursors and synthons to accomplish a wide variety of reactions and functional group interconversions.[1] Deprotection of thiocarbonyls to the parent carbonyl compounds is an important process in organic synthesis. Various methods and reagents such as bromate and iodate solution,[2] dimethyl selenoxide,[3] sodium peroxide,[4] diaryl selenoxide,[5] *t*-butyl hypochlorite,[6] benzeneseleninic anhydride,[7] $NOBF_4$,[8] thiophosgene,[9] tetrabutylammonium hydrogensulfate/NaOH,[10] dimethyl sulfoxide/iodine,[11] soft NO^+ species,[12] *m*-chloroperbezoic acid,[13] trifluoroacetic anhydride,[14] manganese dioxide,[15] diaryl telluroxide,[16] clay supported ferric nitrate,[17] *N*-nitrosamines,[18] *p*-nitrobenzaldehyde/TMSOTf,[19] 2-nitrobenzenesulfonyl chloride/potassium superoxide,[20] clayfen or clayan/MW,[21] and Caro·s acid supported on silica gel[22] have been employed for this purpose. However, some of these methods have limitations such as the use of expensive or toxic reagents or they require long reaction times and or involve tedious procedures.

Recently we have introduced benzyltriphenylphosphonium and *n*-butyltriphenylphosphonium peroxodisulfates as efficient and inexpensive reagents for the oxidation of different organic compounds,[23] cleavage of carbon-nitrogen double bonds,[24] and oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers, ethylene acetals and ketals[25] under non-aqueous and aprotic conditions. We now report a convenient method for the conversion of thiocarbonyls to their corresponding carbonyl compounds using these reagents in refluxing acetonitrile (Scheme 1).

Different thioamides and thioureas reacted with benzyltriphenylphosphonium and *n*-butyltriphenylphosphonim peroxodisulfates in refluxing acetonitrile to afford the corresponding oxo compounds in good to excellent yields (entries 1–31). Thiono esters were also converted to their esters in high yields (entries 32, 33). Thioketones such as thiobenzophenone and thiofluorenone were transformed to benzophenone and fluorenone in high yields (entries 34, 38). On the other hand, 4-nitrothiobenzophenone, 4-chlorothiobenzophenone and 2-aminothiobenzophenone proved much more resistant to the deprotection conditions and were recovered unchanged from the reaction mixture (entries 35–37).



Scheme 1

The results of this study are summarised in Table 1. Both the reagents were effective in this transformation but the yields were higher in the case of benzyltriphenylphosphonium peroxodisulfate.

In summary, we have developed a new and convenient methodology for deprotection of thiocarbonyl compounds using benzyltriphenylphosphonium and *n*-butyltriphenylphosphonim peroxodisulfates as stable, inexpensive and easily prepared reagents.

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The products were identified by comparison of their physical and spectral data with those of authentic samples. Yields refer to isolated products. The thiocarbonyl compounds are either commercially available or were prepared from their corresponding carbonyl compounds according to described procedures.[26] Benzyltriphenylphosphonium and *n*-butyltriphenylphosphonim peroxodisulfates were prepared as described previously.[23,24]

General procedure: To a solution of thiocarbonyl compound (1 mmol) in MeCN (15 ml) was added $(PhCH_2PPh_3)_2S_2O_8$ or $(Bu^nPPh_3)_2S_2O_8$ (1.5-2.5 mmol) and the mixture was stirred under reflux for the appropriate time (Table 1). The progress of the reaction was monitored by TLC (eluent: CCl_4-EtOAc, 4:1). The reaction mixture was cooled to room temperature and filtered. The solid material was washed with MeCN (15 ml). The filtrate was evaporated and the resulting crude material was either recrystallised from $EtOH/H_2O$ or purified by column chromatography on silicagel to afford the pure product (Table 1) .

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

Received 17 June 2002; accepted 21 February 2003
Paper 02/1432

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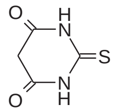
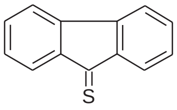
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Conversion of thiocarbonly to carbonyl group with (PhCH$_2$ PPh$_3$) S$_2$O$_8$(I) and (Bu PPh$_3$)$_2$ S$_2$O$_8$ (II)

R^1	R^2	I		II		ν_{max}/cm^{-1}	M.p. or b.p.(Lit.[28]) /°C
		Oxid./ Subs.	Yield/%[a] (t/min)	Oxid./ Subs.	Yield/%[a] (t/min)		
Me	NH$_2$	1.5	99(15)	1.5	98(15)	3340, 3168, 1680	82 (82–83[28b])
NH$_2$	NH$_2$	2	95(15)	2	90(15)	3440, 3350,1682	131–132 (132[28a,b])
NH$_2$	NHNH$_2$	2	91(25)	2	90(25)	3415, 3245, 1685	95 (96[28b])
NH$_2$	NHPh	2	90(10)	2	90(10)	3420, 3315, 1658	145–146 (147[28a,b])
PhNH	NHPh	2	90(15)	2	85(15)	3326, 1648	238–239 (238[28a])
H$_2$NC=S[b]	NH$_2$	2	82(20)	2	80(20)	3385, 3190, 1665	>320 (>320[28b])
PhN=N	NHNHPh	1.5	99(15)	1.5	98(15)	3312, 1662	154–156 (157[28b])
PhNH	Ph	1.5	80(5)	1.5	75(5)	3330, 1650	163 (163[28a,b])
PhCH$_2$NH	Ph	2	92(20)	1.5	90(20)	3312, 1638	105–106 (105–106[28b])
2-MeOC$_6$H$_4$NH	Ph	1.5	80(10)	1.5	74(10)	3424, 1650	60–61 (60[28a])
2-MeC$_6$H$_4$NH	Ph	1.5	77(10)	1.5	71(10)	3240,1648	143 (144[28a])
4-MeOC$_6$H$_4$NH	Ph	1.5	86(15)	1.5	85(15)	3324, 1645	153 (154[28a])
4-MeC$_6$H$_4$NH	Ph	1.5	90(15)	1.5	86(15)	3310, 1647	157–158 (158[28a,b])
4-BrC$_6$H$_4$NH	Ph	1.5	91(15)	1.5	82(15)	3325, 1644	202–203 (202[28b])
4-O$_2$NC$_6$H$_4$NH	Ph	1.5	84(10)	1.5	81(10)	3330, 1657	198–199 (199–200[28b])
4-MeC$_6$H$_4$	NHPh	1.5	85(15)	1.5	85(15)	3340, 1648	145 (146[28a])
4-O$_2$NC$_6$H$_4$	NHPh	1.5	86(15)	1.5	84(15)	3320, 1650	211–212 (211[28a,b])
2-MeOC$_6$H$_4$NH	4-O$_2$NC$_6$H$_4$	1.5	80(20)	1.5	81(20)	3300, 1645	146–148 (148[28c])
2-MeC$_6$H$_4$NH	4-O$_2$NC$_6$H$_4$	1.5	77(15)	1.5	75(15)	3285, 1646	153–155 (155[28c])
2-ClC$_6$H$_4$NH	4-O$_2$NC$_6$H$_4$	1.5	80(10)	1.5	80(15)	3285, 1655	159–160 (160[28c])
4-MeC$_6$H$_4$NH	2-ClC$_6$H$_4$	1.5	85(15)	1.5	81(15)	3376, 1658	130–131 (131[28a])
4-BrC$_6$H$_4$NH	Me	1.5	90(15)	1.5	88(15)	3312, 1667	168 (168[28b])
4-O$_2$NC$_6$H$_4$NH	Me	1.5	91(20)	1.5	90(20)	3405, 1680	215–216 (215–216[28b])
PhNH	3,5-(O$_2$N)$_2$C$_6$H$_3$	1.5	77(10)	1.5	75(10)	3280, 1651	232 (234[28a])
2-MeC$_6$H$_4$NH	3,5-(O$_2$N)$_2$C$_6$H$_3$	1.5	86(15)	1.5	85(15)	3320, 1644	238–240 (241–242[28c])
PhNMe	Me	2	88(45)	1.5	82(55)	1650	101–103 (101–102[28b])
PhNMe	4-O$_2$NC$_6$H$_4$	2	92(45)	2	90(45)	1646	106–107 (107[28c])
Me$_2$N	3,5-(O$_2$N)$_2$C$_6$H$_3$	2	88(45)	2	86(45)	1637	127–130 (128–130[28c])
Et$_2$N	3,5-(O$_2$N)$_2$C$_6$H$_3$	2	85(45)	2	83(45)	1638	89–90 (89–91[28c])
1-Naphthyl-NH	4-MeC$_6$H$_4$	2	73(20)	2	70(20)	3248, 1640	171–173 (173[28c])
		1.5	92(15)	1.5	90(15)	3210, 1750, 1714	247 (248[28b])
Ph	OEt	2.5	92(30)	2.5	90(30)	1720	210–212/760 (212/760[28d])
Ph	OMe	2.5	95(15)	2.5	93(15)	1725	196–197/760 (198–199/760[28d])
Ph	Ph	2.5	80(20)	2.5	75(20)	1650	49(48–29[28d])
4-O$_2$NC$_6$H$_4$	Ph	2.5	0(60)	2.5	0(60)	–	–
4-ClC$_6$H$_4$	Ph	2.5	0(60)	2.5	0(60)	–	–
2-NH$_2$C$_6$H$_4$	Ph	2.5	0(60)	2.5	0(60)	–	–
		2.5	91(15)	2.5	90(15)	1715	82–84 (82–85[28d])

[a] Isolated yields. [b] Oxamide was obtained from the reaction mixture.

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