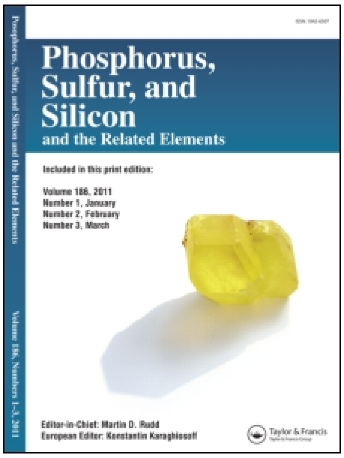


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

PHOTOCHEMICAL OXIDATIVE DEPROTECTION OF 1,3-DITHIANES TO CARBONYL COMPOUNDS WITH HYDROGEN PEROXIDE (HP)

M. H. Habibi[a]; S. Tangestaninejad[a]; I. Mohammadpoor-Baltork[a]; M. Montazerozohori[a]
[a] Isfahan University, Isfahan, Iran

To cite this Article Habibi, M. H. , Tangestaninejad, S. , Mohammadpoor-Baltork, I. and Montazerozohori, M.(2004) 'PHOTOCHEMICAL OXIDATIVE DEPROTECTION OF 1,3-DITHIANES TO CARBONYL COMPOUNDS WITH HYDROGEN PEROXIDE (HP)', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 3, 597 — 600

To link to this Article: DOI: 10.1080/10426500490422263

URL: http://dx.doi.org/10.1080/10426500490422263

Phosphorus, Sulfur, and Silicon, 179:597–600, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490422263

PHOTOCHEMICAL OXIDATIVE DEPROTECTION OF 1,3-DITHIANES TO CARBONYL COMPOUNDS WITH HYDROGEN PEROXIDE (HP)

M. H. Habibi, S. Tangestaninejad, I. Mohammadpoor-Baltork, and M. Montazerozohori
Isfahan University, Isfahan, Iran

(Received May 26, 2003; accepted September 25, 2003)

Regeneration of carbonyl compounds from their 1,3-dithianes were achieved using photochemical oxidation with (HP 30%) in relatively high yields. Thus, an efficient, economic and simple photochemical method for this deprotection has been demonstrated.

Keywords: Carbonyl compound; deprotection; dithiane; hydrogen peroxide; photochemical

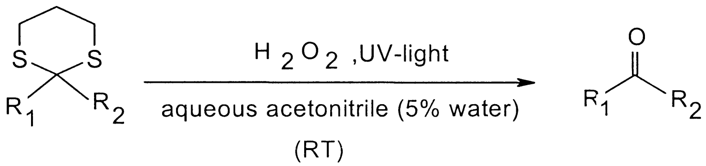
The wide use of 1,3-dithianes as protecting groups for the carbonyl functionality,[1] and as acyl equivalents,[2] has triggered the intense search for flexible deprotection strategies. Oxidative methods are important among the other methods. Some of these methods are oxidation with Cl_2,[3] Br_2,[4] I_2,[5] NCS,[6] NBS,[6] tert-BuOCl, and iron (III) phenanthroline.[7] Variants of oxidative methods that are based on one-electron transfer oxidation, however, have been introduced only recently, on one side with triarylamonium salts as mediators in an electrochemical oxidation,[8] and on the other side using photoinduced electron transfer in the presence of oxygen.[9] Recently a new method for cleavage of the 1,3-dithianes with selecfluorTM,[10] o-iodoxy benzoic acid in DMSO containing traces of water,[11] have been developed. In continuation of our previous photochemical studies [12–14] we employed hydrogen peroxide in aqueous acetonitrile (5% water) under photochemical conditions for deprotection of 1,3-dithianes.

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

Address correspondence to M. H. Habibi, Department of Chemistry, Isfahan University, Isfahan 81744, Iran.

RESULTS AND DISCUSSION

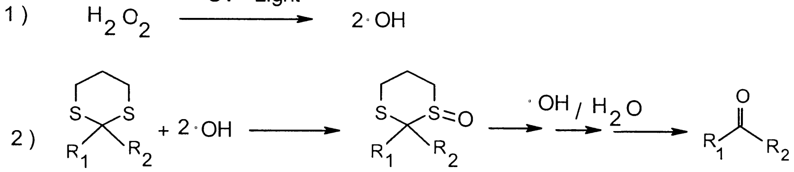
Photochemical deprotection of 1,3-dithianes was recognized by treatment of substrate with HP (30%) in acetonitrile containing 5% water for 2.5-3.5 h under irradiation at room temperature, which afforded the corresponding carbonyl compounds (Scheme 1, Table I).



SCHEME 1

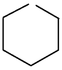
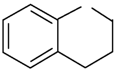
As shown in Table I, different types of dithio compounds are converted to their corresponding carbonyl compounds in acetonitrile solvent in the presence of UV light and in 75–92% yields. Under the same reaction conditions, the dithio compounds bearing nitro group on the aromatic ring were decomposed and unidentified products were produced (run 11,12).

It seems that under these conditions, hydrogen peroxide is cleaved homolytically and produces highly oxidant OH-radical that can oxidize dithio compounds, ultimately to corresponding carbonyl compounds. Therefore with regard to literature,[15,16] we propose a mechanism for this transformation which involves stepwise oxidation of dithio compounds to their disulfoxides and consequent cleavages to their parent carbonyl compounds. On the basis of this mechanism, 3–4 eq. of the reagents is required for the completion of the reaction (Scheme 2). It is noteworthy that in the absence of UV-light, deprotection did not proceed considerably even after prolonged reaction times that can be explained due to stability of these compounds.



SCHEME 2

TABLE I Photochemical Deprotection of Various 1,3-Dithianes Using HP (30%) in Acetonitrile (5% Water)

Run	R^1	R^2	Time (h)	Yield (%)[a]
1	2-$MeOC_6H_4$	H	2.5	80
2	4-BrC_6H_4	Me	2.5	92
3	Ph	Ph	3	90
4	4-ClC_6H_4	H	2.5	75
5	4-PhC_6H_4	Me	3	85
6	4-BrC_6H_4	CH_2Br	2.5	83
7	4-ClC_6H_4	Ph	3	85
8	C_6H_{13}	H	3.5	75
9			3	82
10		–	3.5	80
11	3-$O_2NC_6H_4$	H	0.5	Decompose
12	2-$O_2NC_6H_4$	H	0.5	Decompose

[a] Isolated yields.

In summary we have introduced a simple and efficient procedure for photochemical oxidative deprotection of 1,3-dithianes under neutral condition and room temperature in good to excellent yields. This reaction offers an interesting example of photochemical deprotection of dithio compounds that is useful for synthetic organic photochemistry. The advantages of this method are that it provides an economically viable and efficient photochemical methodology using a readily available reagent.

EXPERIMENTAL

General

The carbonyl derivative were prepared from corresponding carbonyl compounds and 1,3-propanedithiol according to the reported procedure.[17,18]

Conversion of 1,3-Dithianes Compounds to Their Corresponding Carbonyl Compounds; General Procedure

To a solution of 2,2-diphenyl-1,3-dithane (133 mg, 0.5 mmol) in acetonitril (20 ml) in a pyrex cell was added hydrogen peroxide (2 mmol). The reaction cell was placed in a pyrex water bath at room temperature.

The mixture was stirred magnetically and irradiated with a 400 W high-pressure Hg lamp for 3 h. After completion (as monitored by TLC), the reaction mixture concentrated by evaporation under reduced pressure and resulting crude material was purified on a silica-gel-plate (eluent: n-hexane/diethyl ether 3:1) affording the pure product (Table I) All of the products were characterized by *elemental analysis (new products)* and comparison of their spectral (IR, H-NMR), chromatographic (TLC) and physical data (melting and boiling points) with those of known samples.[19]

REFERENCES

[1] D. N. Satchell and R. S. Satchel, *Chem. Soc. Rev.*, 55 (1990).

[2] a) D. Seebach, *Synthesis*, 17 (1969); b) B.-T. Grobel and D. Seebach, *Synthesis*, 357 (1977).

[3] S. W. Lee and G. J. Dougherty, *Org. Chem.*, **5,** 81 (1940).

[4] J. C. A. Chivers and S. Smile, *J. Chem. Soc.*, 697 (1928).

[5] G. A. Russell and L. A. Ochrymowycz, *J. Org. Chem.*, **34,** 3618 (1969).

[6] E. J. Corey and B. W. Erickson, *J. Org. Chem.*, **36**(23), 3553 (1971).

[7] M. Schmittel and M. Levis, *Synlett.*, 315 (1996).

[8] M. Platen and E. Steckhan, *Chem. Ber.*, **117,** 1679 (1984).

[9] a) M. Kamata, Y. Kato, and E. Hasegawa, *Tetrahedron Lett.*, **32,** 4349 (1991); b) M. Kamata, M. Sato, and E. Hasegawa, *Tetrahedron Lett.*, **33,** 5085 (1992); c) M. Kamata, Y. Murakami, Kato, M. Tamagawa, and E. Hasegawa, *Tetrahedron*, **50,** 12821 (1994).

[10] J. Liu and C.-H. Wong, *Tetrahedron Lett.*, **43,** 4037 (2002).

[11] Y. Wu, X. Shen, J.-H. Huang, C.-J. Tang, H.-H. Liu, and Q. Hu, *Tetrahedron Lett.*, **43,** 6443–6445 (2002).

[12] M. H. Habibi and T. E. Mallouk, *J. Fluorine Chem.*, **51,** 291 (1991).

[13] M. H. Habibi and S. Farhadi, *Tetrahedron Lett.*, 2821 (1999).

[14] M. H. Habibi and S. Farhadi, *J. Chem. Research*, 776 (1998).

[15] Q. N. Porter, J. H. P. Utley, P. D. Machion, V. L Pardini, P. R. Schumacher, and H. Viertler, *J. Chem. Soc. Perkin Trans. I*, 973 (1984).

[16] M. Kamata, Y. Kato, and E. Hasegawa, *Tetrahedron Lett.*, **32,** 4349 (1991).

[17] a) H. Firouzabadi, N. Iranpoor, and B. Karimi, *Synthesis*, 58 (1999); b) D. Seebach and E .J. Corey, *J. Org. Chem.*, **40,** 231 (1975); c) B. T. Groblel and D. Seebach, *Synthesis*, 357 (1977); d) R. P. Hatch, J. Shringarpure, and S. M. Weinreb, *J. Org. Chem.*, **43,** 4172 (1978); e) J. A. Marshall and J. L. Belletire, *Tetrahedron Lett.*, 871 (1971).

[18] F. A. J. Meskens, *Synthesis*, 501 (1981).

[19] *Dictionary of Organic Compounds* (Chapman and Hall, London, 1982), 6th ed.