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Photochemical Oxidation of 1,3-Dithianes with *tert*-Butyl Hydroperoxide (TBHP)

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A variety of 1,3-dithianes deprotected to their corresponding carbonyl compounds in good to excellent yields in mild and efficient photo-oxidative method using *tert*-butyl hydroperoxide.

Key words: photochemical, oxidation, dithiane, carbonyl compound, *tert*-butyl hydroperoxide

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 electron transfer oxidation, however, have been introduced only recently, on one side with triarylammonium salts as mediators in an electrochemical oxidation [8] and on the other side using photoinduced electron transfer in the presence of oxygen [9]. Recently new oxidative methods for cleavage of the 1,3-dithiane with selecfluor^{TM} [10], *o*-iodoxy benzoic acid in DMSO containing traces of water [11] and *tert*-butyl hydroperoxide (reflux in methanol) [12] have been used in thermal conditions. The later also has been used for halogenation of arenes, alkenes, alkynes [13,14], regeneration of carbonyl compounds from their corresponding oximes, phenylhydrazones, tosylhydrazones [15] and oxidation of benzylic alcohols [16]. Despite of using of *tert*-butyl hydroperoxide for many reactions in thermal conditions and in the presence of various catalysts [16], photochemical oxidative potential of this reagent has not been considered. In continuation of previous photochemical studies [17–19] and in view of the oxidative properties of this reagent under thermal conditions, we extended the using of this reagent for oxidative deprotection of 1,3-dithianes under mild photochemical conditions at room temperature.

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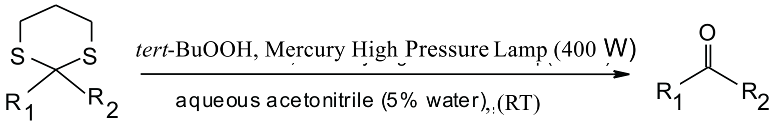
RESULTS AND DISCUSSION

Photooxidative deprotection of 1,3-dithianes was recognized by treatment of substrate with *tert*-butyl hydroperoxide (66%) in acetonitrile containing 5–10% water for 5.5–7 h depending on the nature of the compounds, under irradiation at room temperature, which afforded the corresponding carbonyl compounds (Scheme 1, Table 1).

Scheme 1



We found that acetonitrile was a better solvent than others such as alcohols and chloroform and dichloromethane in these conditions. As shown in Table 1, different types of dithio compounds are converted to their corresponding carbonyl compounds in acetonitrile solvent with irradiation of 400 W high pressure mercury lamp and in 75–93% 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). Among the 1,3-dithianes as shown in Table 1, benzaldehyde derivatives (run 1, 4, 8) have been deprotected in lower yields than others probably due to further oxidation of the corresponding aldehydes.

Similar to hydrogen peroxide, it seems that under irradiation *tert*-butyl hydroperoxide is cleaved homolytically producing HO$^\bullet$ radical, which can oxidize dithio compounds, ultimately to corresponding carbonyl compounds (Table 1).

Therefore, with regard to [12,20,9a], a mechanism for this transformation involves a stepwise oxidation of dithio compounds by HO$^\bullet$ radical under irradiation to their monosulfoxides, disulfoxides and ultimately consequent their cleavage to the parent carbonyl compounds. On the basis of this mechanism, 3–4 eq. of the reagent are required for the completion of the reaction (Scheme 2).

Scheme 2

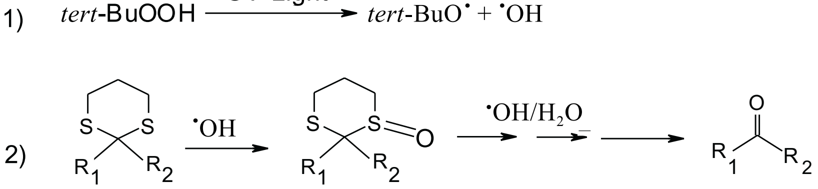
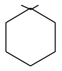
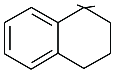


Table 1. Photochemical deprotection of various 1,3-dihianes using *tert*-butyl hydroperoxide (66%).

Run	R$_1$	R$_2$	Time/h	Yields %[a,b]
1	2-MeOC$_6$H$_4$	H	5.5	80
2	4-BrC$_6$H$_4$	Me	5.5	87
3	Ph	Ph	6	93
4	4-ClC$_6$H$_4$	H	5.5	80
5	4-PhC$_6$H$_4$	Me	7	90
6	4-BrC$_6$H$_4$	CH$_2$Br	6.5	85
7	4-ClC$_6$H$_4$	Ph	6.5	91
8	C$_6$H$_{13}$	H	7	75
9		–	6	88
10		–	7	85
11	3-O$_2$NC$_6$H$_4$	H	0.5	Decompose
12	2-O$_2$NC$_6$H$_4$	H	0.5	Decompose

[a] Refer to isolated yields. [b] The products were identified by their melting points and/or by comparison of their ^{1}H-NMR, IR and MS spectra with these ones of gemine carbonyl compounds.

It is noteworthy that in the absence of light, deprotection did not proceed considerably even after prolonged reaction time.

CONCLUSIONS

We have extended, using of *tert*-butyl hydroperoxide, the view of photochemical oxidative potential and introduced a simple, mild and efficient procedure for photochemical oxidative deprotection of 1,3-dithianes under neutral condition at room temperature in good to excellent yields. This is an interesting example of photochemical reaction of dithio compounds, that is useful for synthetic organic photochemistry. The advantages of this method is an economically viable and efficient methodology using a readily available reagents and mild reaction conditions.

EXPERIMENTAL

General. All of the products were characterized by comparison of their spectral (IR, ^{1}H-NMR), chromatographic (TLC) and physical data (melting and boiling points) with those of known samples [21]. All yields refer to isolated products. ^{1}H-NMR spectra were run on a Bruker AW 80 MHz in CDCl$_3$ relative to TMS as an internal standard. IR spectra were run on a Shimadzu IR-435 spectrophotometer. Mass spectra were recorded on AMD 604 spectrometer (EI-mode at 70 eV, FT-mode at 0.005 V). The carbonyl derivatives were prepared from corresponding carbonyl compounds and 1,3-propanedithiol according to the reported procedure [22,23,2b]. The TBHP was prepared according to [24].

General procedure for the conversion of 1,3-dithianes to their corresponding carbonyl compounds. To a solution of 2,2-diphenyl-1,3-dithiane (0.137 g, 0.5 mmol) in aqueous acetonitrile (5% water, 20 ml) placed in a photoreactor cell *tert*-butyl hydroperoxide (0.3 ml, 2 mmol) was added. The reaction cell was placed in a water bath maintained at room temperature. The mixture was stirred magnetically and irradiated with a 400 W high-pressure Hg lamp for 6 h. After completion (as monitored by TLC), the reaction mixture was concentrated *in vacuo* to a volume *ca.* 2–3 ml and resulting crude material was purified on a silica-gel-plate (eluent: n-hexane/diethyl ether, 3:1) affording the pure product (Table 1).

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