A Facile Mild Deprotection Protocol for 1,3-Dithianes and 1,3-Dithiolanes with 30% Hydrogen Peroxide and Iodine Catalyst in Aqueous Micellar System

Nemai C. Ganguly,* Sujoy Kumar Barik

Department of Chemistry, University of Kalyani, Kalyani 741235, WB, India Fax +91(33)25828282; E-mail: nemai_g@yahoo.co.in *Received 3 December 2008; revised 19 December 2008*

Abstract: A simple clean expeditious protocol for the deprotection of 1,3-dithianes and 1,3-dithiolanes has been developed using 30% aqueous hydrogen peroxide activated by iodine catalyst (5 mol%) in water in the presence of sodium dodecyl sulfate (SDS) under essentially neutral conditions. The method showed tolerance for a number of phenol protecting groups such as allyl, benzyl, TBDMS, TBDPS ethers, phenolic acetates, and benzoates as well as aminoprotecting BOC, Cbz carbamates without any detectable overoxidation.

Key words: 1,3-dithianes, 1,3-dithiolanes, iodine, 30% hydrogen peroxide, sodium dodecyl sulfate (SDS)

Protection of carbonyls and their deprotection at some appropriate stage are important transformations often encountered in synthesis of multifunctional natural and unnatural organic compounds because of their ubiquity and remarkable synthetic flexibility. Carbonyls are wellprotected as S,S-thioacetals and -ketals that are easy to prepare and stable enough under basic as well as acidic conditions.¹ 1.3-Dithianes are of special synthetic importance as they are versatile acyl anion equivalents and utilized for carbon-carbon bond formation by way of metallation.² However, damasking of these procarbonyl derivatives is not always straightforward and often requires oxidative conditions that are marred with side reactions. Traditional cleavage of these protecting groups with mercury(II) chloride ³ or hazardous and polluting heavy metal salts such as AgNO₃-NCS,^{3a} AgNO₂/AgClO₄-I₂,^{4a} $Tl(NO_3)_3$,^{4b,c} $Tl(OCOCF_3)_3$,^{4d} $Cu(NO_3)_2$,^{4e} SeO_2^{4f} (PhSeO)₂O^{4g} or toxic volatile methyl iodide⁵ adds to waste disposal problems. Of the numerous cleavage procedures currently available for these robust two-stage protecting groups,⁶ a good many rely on affinity of sulfur towards soft electrophiles generating labile sulfonium ion intermediates which are competent nucleofuges and, therefore, susceptible to hydrolytic ring opening. An alternative tactic is to oxidize 1,3-dithianes and 1,3-dithiolanes to the corresponding sulfoxides or sulfones as a prelude to hydrolytic cleavage. Utilization of hypervalent iodine reagents such as bis(trifluroacetoxy) iodobenzene (BTI),⁷ Dess-Martin periodinane (DMP),⁸ and *o*-iodoxybenzoic acid (IBX)⁹ for dethioacetalization marked a significant development in view of their low toxicity, mildness, and

SYNTHESIS 2009, No. 8, pp 1393–1399 Advanced online publication: 25.03.2009

DOI: 10.1055/s-0028-1088023; Art ID: Z26708SS

© Georg Thieme Verlag Stuttgart · New York

efficiency. Notably, oxidation reactions with IBX and DMP tolerate the presence of water to a certain level but a large amount of it is reported to be detrimental to their efficiencies.^{9d,e} In fact, deprotection of 2-methyl-2-phenyl-1,3-dithiane with DMP was very sluggish (48 h) in water.8 BTI-mediated deprotection releases stoichiometric amount of trifluoroacetic acid that causes removal of TBDPS and olefin isomerization. Cleavage protocols based on elemental iodine [I2 (1.2 equiv)-AgNO2/ AgClO₄, THF;^{4a} I₂ (3 equiv), DMSO¹⁰] have limitations of high cost and explosion-prone nature of the assisting silver salts or loss of products during workup. A recent attempt of catalytic deprotection of 2-phenyl-1,3-dithiane with iodine (20 mol%) in DMSO under neutral conditions¹¹ was disappointingly slow and low-yielding (24 h, 35 h). The peroxide-based cleaving reagents, namely, Oxone,^{12a} Oxone-KBr,^{12b} benzyltriphenylphosphonium peroxymonosulfate,¹³ 70% tert-butyl hydroperoxide,¹⁴ and 30% H₂O₂ (20 equiv)-NaI and TaCl₅ (10 mol% each)15 are also employed in stoichiometric or excess amounts. Contemporary paradigm shift towards green catalytic methods from stoichiometric ones¹⁶ motivated us to develop an environmentally compatible cost-effective catalytic dethioacetalization procedure. To this end, utilization of inexpensive commercially available 30% aqueous hydrogen peroxide as terminal oxidizer¹⁷ is quite appealing because of its nonpolluting, environmentally benign nature, and generation of water as the only byproduct of oxidation. Use of water as the reaction medium¹⁸ is also becoming increasingly important because it is noninflammable, nontoxic, safe, and its unique physical and chemical properties often boost the reactivity and selectivity of organic reactions unattainable in common organic solvents. In continuation of our interest in developing green deprotection protocols based on hydrogen peroxide and solid peroxygen compounds,¹⁹ we set out to evaluate the efficacy of 30% aqueous H₂O₂ activated with catalytic amount of iodine as a cleaving reagent in water. Electrophilic activation of hydrogen peroxide, a thermodynamically powerful but kinetically slow oxidant, with early transition metal (Ti, V, Mo, and W) compounds is well documented.²⁰ Recently, nonmetallic activation of hydrogen peroxide with water-tolerant Lewis acid iodine has been exploited for a host of synthetic purposes ranging from iodofunctionalization of activated aromatics, ketones, 1,3-diketones,²¹ alkenes,²² and pyrazoles²³ to peroxidation of carbonyl compounds.²⁴ We surmised that the thiophilicity of iodine could be utilized

for the generation of an aquo-labile sulfonium ion intermediate and this is specially attractive in the presence of aqueous hydrogen peroxide in view of facility of reoxidation of iodide ion so released to iodonium ion in a catalytic process. Herein, we reveal the scope and generality of hitherto unprecedented dethioacetalization procedure using this reagent combination in aqueous micellar environment.

1,3-Dithiane 1 derived from 3,4-methylenedioxybenzaldehyde (piperonal) was chosen as the model substrate for the optimization of deprotection conditions. Piperonal, a DOPA precursor, is a representative of oxidation-prone aromatic aldehydes that also bears a hydrolytically labile methylenedioxy moiety and therefore we felt that release of piperonal from 1,²⁵ particularly under oxidative aqueous conditions, would give a good feel of mildness of the cleaving reagent. Attempted cleavage of 1 with 30% H₂O₂ (2 molar equiv) without iodine proved abortive. In a separate experiment 1 was found to be resistant to deprotection solely with aqueous iodine (10 mol%). However, exposure of 1 to a combination of 30% H₂O₂ (0.2 mL) and iodine (10 mol%) in water for six hours at room temperature resulted in incomplete rupture and isolation of piperonal in 20% yield along with unreacted starting material. The incompleteness of cleavage was presumably due to the inadequate solubility of the substrate as well as iodine in water. At this stage we decided to explore a micellar solubilization²⁶ route to circumvent the incompatibility of an aqueous oxidizing system and the aromatic substrate. The dynamic clusters of surfactant molecules upon selfassembly into micelles can encapsulate otherwise insoluble substrates within their lipophilic cores. Micelles allow concentration of reactants within their microenvironment and can substantially alter reaction rates, pathways and product distribution compared to those in homogeneous bulk solvents. Encouraged by the recent report of promotion of iodine activation with sodium dodecyl sulfate (SDS²⁷), **1** (1 mmol) was allowed to react with 30% H₂O₂ (0.45 mL) and I_2 (5 mol%) in an aqueous solution of SDS (5 mL, 0.2 mmol). To our delight, TLC analysis indicated complete conversion of the starting material to piperonal within 30 minutes (Scheme 1). Separate exploratory experiments with other surfactants such as cetyltrimethylammonium bromide (CTAB) (cationic) and TritonX-100 (neutral) above their critical micellar concentrations (5 cmc) gave less satisfying results. Use of an excess of reagent such as 30% H₂O₂ (0.6 mL)-I₂ (10 mol%) or 30% H_2O_2 (0.2 mL)- I_2 (50 mol%) did not significantly improve the yield or reaction time. The results of optimization experiments are shown in Table 1.



Scheme 1

Entry	H ₂ O (mL)	30% H ₂ O ₂ (mL)	I ₂ (mol%)	Surfac- tant, cmc	Time (h) ^a	Yield of pip eronal (%) ^b
1	5	0.45	_	_	8	0 ^c
2	5	-	10	-	6	0 ^c
3	5	0.2	10	-	6	20
4	5	0.2	50	SDS, 5	2	75
5	5	0.60	10	SDS, 5	0.5	92
6	5	0.10	5	SDS, 5	3	70
7	5	0.45	10	SDS, 5	0.5	93
8	5	0.45	5	SDS, 5	0.5	95
9	5	0.45	5	CTAB, 5	4	60
10	5	0.45	5	Triton X100, 5	5	75

^a Reactions were carried out in 1 mmol scale of 1 at r.t.; the amounts of reagents and solvent refer to per mmol of substrate.

^b Isolated yield upon chromatography.

^c Near quantitative recovery of the dithiane **1**.

The optimized cleavage conditions $[0.45 \text{ mL } 30\% \text{ H}_2\text{O}_2, 5 \text{ mol}\% \text{ I}_2, \text{SDS} (5 \text{ cmc}) \text{ per mmol of substrate, see experimental section] proved to be generally successful for a wide array of 1,3-dithianes and 1,3-dithiolanes (Scheme 2) as presented in Table 2.$



Scheme 2



Synthesis 2009, No. 8, 1393-1399 © Thieme Stuttgart · New York

Table 2	Deprotection of 1,3-Dithianes and 1,3-Dithiolanes w	ith 30% Aqueous	H_2O_2 and I_2	Catalyst in	Water
in the Pres	resence of SDS (continued)				

Entry	Substrate	Reaction time ^a	Yield of carbonyl compound (%) ^b
2	S S	45 min	~100
3	S S	25 min	92
4	S S OH	35 min	98
5	S S OH	40 min	95
6	S OMe OH	1 h	95
7	S S NO ₂	4 h	98
8	S S S	30 min	~100
9	H ₂ N S	20 min	~100
10	Aco Me	1.5 h	97
11	S S Ph Ph	20 min	~100

Table 2 Deprotection of 1,3-Dithianes and 1,3-Dithialanes with 30% Aqueous H_2O_2 and I_2 Catalyst in Waterin the Presence of SDS (continued)

Entry	Substrate	Reaction time ^a	Yield of carbonyl compound (%) ^b
12	s S	3 h	75
13	S Me Et	20 min	92°
14	S H	1.5 h	90°
15	S H ₂ C H ₁ H ₂ C H	1 h	98
16	S Ph	1 h	92
17		1 h	~100
18	S S	1 h	94
19	S S BocHN	1.5 h	~100
20	CbzHN CbzHN	45 min	~100
21	TBDPSO	25 min	92
22	PhCH ₂ O	25 min	~100
23	S S S OTBDMS	20 min	90

Synthesis 2009, No. 8, 1393–1399 © Thieme Stuttgart · New York

Table 2	Deprotection of 1,3-Dithianes and 1,3-Dithialanes with 30% Aqueous H2O2 and I2 Catalyst in Water
in the Pres	sence of SDS (continued)

Entry	Substrate	Reaction time ^a	Yield of carbonyl compound (%) ^b
24	S S OCOPh	1 h	~100
25	S S S S S S S S S S S S S S S S S S S	1 h	90
26	s s	1.5 h	90
27	S S OH	2.5 h	95
28	S S OH	3 h	90
29	S S S S	1.5 h	95
30	SPh SPh SPh	20 min	95
31	SPh SPh OH	15 min	95
32	SPh SPh	20 min	98

 a Reaction conditions: 30% H_2O_2 (0.45 mL), I_2 (5 mol%), SDS/H_2O (5 cmc, 5 mL) per mmol of substrate, r.t.

^b Yields refer to carbonyl compounds isolated after chromatographic filtration over silica gel; all the products are known compounds, which were identified from their physical constants,²⁸ their spectral data (FTIR, ¹H NMR), and comparison with authentic samples (superimposable IR and co-TLC).

^c Yields as measured from 2,4-dinitrophenylhydrazone derivative, see experimental section.

Table 2 reveals that a aryl dithioacetal that is deactivated due to the presence of a nitro group (entry 7) underwent much slower deprotection than those activated with electron-releasing groups (entries 3-6, 9). The huge rate differential may be exploited for preferential removal of activated dithianes in the presence of nonactivated analogues. This is demonstrated by facile selective deprotection of 2-(4-hydroxyphenyl)-1,3-dithiane (entry 3) (90% yield) in an equimolar mixture with 2-(2-nitrophenyl)-1,3-dithiane (entry 7) upon treatment with 30% H₂O₂ (0.45 mL) and I₂ (5 mol%) in aqueous SDS for 25 minutes and recovery of the latter in almost quantitative yield. 1,3-Dithiolanes are also found to be more reluctant towards cleavage than 1,3-dithianes,²⁹ which are compatible with their more positive oxidation potentials than the corresponding dithianes.^{4e} An intermolecular competition experiment performed with a mixture of 1 mmol each of 2-(2-hydroxyphenyl)-1,3-dithiane (entry 4) and its 1,3dithiolane counterpart (entry 27) under optimal conditions for 35 minutes resulted in 90:10 selectivity in favor of the former. Even nonactivated dithianes (entries 12–15) were cleaved within reasonable times. To investigate the catalytic role of metal ions, particularly iron species, present in water that can possibly decrease the difference in cleavage rate between activated and nonactivated dithianes, as observed in IBX-mediated cleavage,^{9a} we carried out separate experiments of cleavage of 1,3-dithiane of cyclohexanone (entry 12) using tap water that contained fair amounts of iron salts and deionized distilled water under otherwise identical reaction conditions. Cleavage rate as well as yield of cyclohexanone remained unaffected suggesting the absence of metal ion catalysis. The reported failure of cleavage of dithioacetals with one equivalent of FeCl₃³⁰ supported our observation. However, lack of sufficient cleavage rate difference of noncyclic thioacetals (entries 30-32) and 1,3-dithianes precluded their discrimination. Gratifyingly, acid-labile cinnamaldehyde (entry 16), furan-2-aldehyde (entry 17) were smoothly released from respective dithianes without overoxidation. The hydrolysis-prone aryl acetate (entry10), benzoate (entry 24), and a number of phenol-protecting benzyl, TBDPS, TB-DMS ethers and amino-protecting BOC and Cbz carbamates were tolerated under the cleavage conditions further attesting to its mildness. Deprotections were carried out in a 1-5 mmol range without loss of efficiency in terms of yield and facility.

In conclusion, we have developed a facile deprotection method of thioacetals and thioketals using 30% aqueous H_2O_2 and 5 mol% iodine catalyst in aqueous micellar environment. Absence of overoxidation products for oxidation-prone substrates, compatibility with a large number of common functional and acid-sensitive protecting groups, manipulative simplicity, and generality combined with green features will hopefully make it a method of choice for deprotection of thioacetals and thioketals.

1,3-Propanedithiol, 1,2-ethanedithiol and benzenedithiol were purchased from Sigma-Aldrich Chemie GmbH, Germany. Iodine and SDS were obtained from Merck, Germany and SRL, India, respectively. IR spectra were recorded on a Perkin-Elmer 2400-Series II spectrometer. ¹H NMR spectra were measured on a Bruker AM-300L (300 MHz) spectrometer. Light petrol used refers to the fraction boiling at 60–80 °C.

Deprotection of 1,3-Dithianes and 1,3-Dithiolanes; 3,4-Methylenedioxybenzaldehyde (Piperonal); Typical Procedure

Finely pulverized I₂ (12.8 mg, 0.05 mmol), 2-(3,4-methylenedioxyphenyl)-1,3-dithiane (**1**; 242 mg, ~1 mmol) and finally 30% H_2O_2 (0.45 mL, 4 mmol) were added to an aqueous solution of SDS (5 mL, 57.8 mg, 0.2 mmol) and the mixture was vigorously stirred at r.t. for 30 min when its TLC examination showed complete disappearance of the starting material. The reaction was quenched by the addition of aq 5% Na₂S₂O₃ (5 mL) and the resulting mixture was extracted with EtOAc (3 × 3 mL). The combined organic extracts were washed with H₂O (2 × 2 mL) and dried (Na₂SO₄). It was concentrated and filtered through a short pad of silica gel (60–120 mesh, Spectrochem, India) using EtOAc–light petrol (1:19) as eluent to give 3,4-methylenedioxybenzaldehyde (piperonal) (144 mg, 95%); mp 37–38 °C (EtOAc–light petrol) (Lit.²⁸ mp 37 °C).

Isolation of Butanal as 2,4-Dinitrophenylhydrazone Derivative After Deprotection from its 1,3-Dithiane Derivative; Typical Procedure

To an aqueous solution of SDS (10 mL, 115 mg, 0.4 mmol) were added powdered I₂ (26 mg, 0.1 mmol), 2-butyl-1,3-dithiane (326 mg, 2 mmol) (Table 2, entry 14) and 30% H₂O₂ (0.9 mL, 8 mmol) and the mixture was stirred thoroughly at r.t. for 1.5 h. The mixture was then treated with aq 5% Na₂S₂O₃ (6 mL), extracted with Et₂O (2 × 3 mL) and dried. To the concentrated ethereal extract were added 2–3 drops of MeOH and then a methanolic solution of 2,4-dinitrophenylhydrazine (0.6 g of the reagent in 5 mL of MeOH containing 0.5 mL of concd H₂SO₄) and kept for 0.5 h. The precipitated bright yellow crystals were collected by filtration and crystal-lized from EtOAc–light petrol to give the corresponding 2,4-dinitrophenylhydrazone (456 mg); mp 119–121 °C (Lit.²⁸ mp 123 °C), which corresponds to 130 mg of butanal (90% yield).

Acknowledgment

SKB thanks University of Kalyani for financial assistance by way of a research fellowship. Facilities provided by DST-FIST Grant, Government of India are also acknowledged.

References

- (a) Green, T. W.; Wuts, P. G. M. Protective Groups in Organic Synthesis; Wiley: New York, **1999**, 3rd ed..
 (b) Kocieneski, P. J. Protecting Groups; Thieme: Stuttgart, **1994**.
- (2) Gröbel, B.-T.; Seebach, D. Synthesis 1977, 357.
- (3) (a) Corey, E. J.; Ericson, B. W. J. Org. Chem. 1971, 36, 3553. (b) Corey, E. J.; Bock, M. G. Tetrahedron Lett. 1975, 2643.
- (4) (a) Nishide, K.; Yokota, K.; Nakamura, D.; Sumiya, T.; Node, M.; Ueda, M.; Fuji, K. *Tetrahedron Lett.* **1993**, *34*, 3425. (b) Jones, P. S.; Ley, S. V.; Simkins, N. S.; Whittle, A. J. *Tetrahedron* **1986**, *42*, 6519. (c) Smith, R. A.; Hannah, D. J. *Synth. Commun.* **1979**, *9*, 301. (d) Ho, T.-L.; Wong, C. M. *Can. J. Chem.* **1972**, *50*, 3740. (e) Oksdath-Mansilla, G.; Peñéñory, A. B. *Tetrahedron Lett.* **2007**, *48*, 6150. (f) Haroutounian, S. A. *Synthesis* **1995**, 39. (g) Barton, D. H. R.; Cussons, N. J.; Ley, S. V. *J. Chem. Soc., Chem. Commun.* **1977**, 751.

- (5) Fetizon, M.; Jurion, M. J. Chem. Soc., Chem. Commun. 1972, 382.
- (6) Schelhass, M.; Waldman, H. Angew. Chem., Int. Ed. Engl. 1996, 35, 2056.
- (7) Stork, G.; Zhao, K. Tetrahedron Lett. 1989, 30, 287.
- (8) Langille, N. F.; Dakin, L. A.; Panek, J. S. *Org. Lett.* **2003**, *5*, 575.
- (9) (a) Wu, Y.; Shen, X.; Huang, J.-H.; Tang, C.-J.; Liu, H. H.; Hu, Q. *Tetrahedron Lett.* 2002, *43*, 6443. (b) Nicolaou, K. C.; Mathison, C. J. N.; Montagnon, T. *J. Am. Chem Soc.* 2004, *126*, 5192. (c) Krishnaveni, N. S.; Surendra, K.; Nageshwar, Y. V. D.; Rao, K. R. *Synthesis* 2003, 2295. (d) Corey, E. J.; Palani, A. *Tetrahedron Lett.* 1995, *36*, 7945. (e) Meyer, S. D.; Schreiber, S. L. *J. Org. Chem.* 1994, *59*, 7945.
- (10) Chattopadhyaya, J. B.; Rama Rao, A. V. *Tetrahedron Lett.* **1973**, 3735.
- (11) Iranpoor, N.; Firouzabadi, H.; Shaterian, H. R. *Tetrahedron Lett.* **2003**, *44*, 4769.
- (12) (a) Ceccherelli, P.; Curini, M.; Marcrotullio, M. C.; Epifano, F.; Rosati, O. *Synlett* **1996**, 767. (b) Desai, U. V.; Pore, D. M.; Tamhankar, B. V.; Jadhav, S. A.; Wadgaonkar, P. P. *Tetrahedron Lett.* **2006**, *47*, 8559.
- (13) Hajipour, A. R.; Mallakpour, S. E.; Bartork, I. M.; Adibi, H. Molecules 2002, 7, 674.
- (14) Wakharkar, R. D.; Mahajan, V. A.; Shinde, P. D.; Barhate, N. B. *Tetrahedron Lett.* **2002**, *43*, 6031.
- (15) Kirihara, M.; Harano, A.; Tsukiji, H.; Tajikawa, R.; Uchiyama, T.; Hatano, A. *Tetrahedron Lett.* **2005**, *46*, 6377.
- (16) *Handbook of Green Chemistry and Technology*; Clark, J. H.; Macquarrie, D., Eds.; Blackwell Science: Oxford, **2002**.
- (17) (a) Jones, C. W. Applications of Hydrogen Peroxide and Derivatives; Royal Society of Chemistry: Cambridge, 1999.
 (b) Noyori, R.; Aoki, M.; Sato, K. Chem. Commun. 2003, 1997. (c) Grigoropoulou, G.; Clark, J. H.; Elings, J. A. Green Chem. 2003, 5, 1. (d) Arends, I. W. C. E.; Sheldon, R. A. Top. Catal. 2002, 19, 133.

- (18) (a) Grieco, P. A. Organic Synthesis in Water; Thomson Science: London, 1998. (b) Li, C.-J.; Chan, T.-H. Organic Reactions in Aqueous Media; Wiley: New York, 1997.
 (c) Kobayashi, S.; Manabe, K. Acc. Chem. Res. 2002, 35, 209. (d) Manabe, K.; Limura, S.; Sun, X.-M.; Kobayashi, S. J. Am. Chem. Soc. 2002, 124, 11971; and references cited therein.
- (19) (a) Ganguly, N. C.; Sukai, A. K.; De, S.; De, P. Synth. Commun. 2001, 31, 1607. (b) Ganguly, N. C.; Datta, M. Synlett 2004, 659. (c) Ganguly, N. C.; Datta, M. J. Chem. Res., Synop. 2005, 218. (d) Ganguly, N. C.; Barik, S. Synthesis 2008, 425.
- (20) (a) Lane, B. S.; Burgess, K. *Chem. Rev.* 2003, *103*, 2457.
 (b) Ten Brink, G.-J.; Arends, I. W. C. E.; Sheldon, R. A. *Chem. Rev.* 2004, *104*, 4105.
- (21) Jereb, M.; Zupan, M.; Stavber, S. Chem. Commun. 2004, 2614.
- (22) Jereb, M.; Zupan, M.; Stavber, S. Green Chem. 2005, 7, 100.
- (23) Kim, M. M.; Ruck, R. T.; Zhao, D.; Huffman, M. A. *Tetrahedron Lett.* **2008**, *49*, 4026.
- (24) Žmitek, K.; Zupan, M.; Stavber, S.; Iskra, J. J. Org. Chem. 2007, 72, 6534.
- (25) For regeneration of piperonal from 1 under anhydrous conditions with Fe(NO₃)₃ and montmorilonite K-10 in hexane, see: Hirano, M.; Ukawa, K.; Yakabe, S.; Clark, J. H.; Morimoto, T. *Synthesis* **1997**, 858.
- (26) For a review of micellar solubilization and catalysis of organic reactions, see: (a) Tascioglu, S. *Tetrahedron* 1996, *52*, 11113; and references cited therein. (b) Myers, D. *Surfactant Science and Technology*; VCH: Weinheim, 1992. (c) Dwars, T.; Paetzold, E.; Oehme, G. *Angew. Chem. Int. Ed.* 2005, *44*, 7174.
- (27) Cerritelli, S.; Chiarini, M.; Cerichelli, G.; Capone, M.; Marsili, M. Eur. J. Org. Chem. 2004, 623.
- (28) Vogel, A. I. *A Textbook of Practical Organic Chemistry*; 3rd ed., ELBS and Longman Group Ltd.: London, **1973**.
- (29) 1,3-Dithianes, 1,3-dithiolanes and other thioacetals/ketals were prepared following literature procedures: (a) Hatch, R. P.; Shringarpure, J.; Weinreb, S. M. J. Org. Chem. 1978, 43, 4172. (b) Marshall, J. A.; Belletire, J. L. Tetrahedron Lett. 1971, 871.
- (30) Chavan, S. P.; Soni, P. B.; Kale, R. R.; Pasupathy, K. Synth. Commun. 2003, 33, 879.