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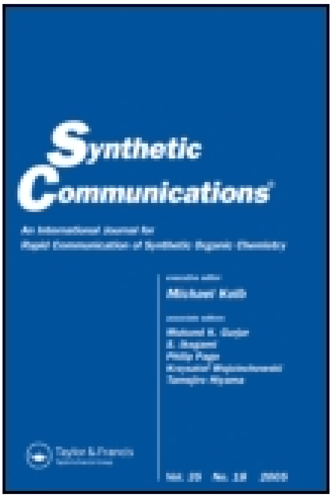

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Mild, Efficient, and Greener Dethioacetalization Protocol Using 30% Hydrogen Peroxide in Catalytic Combination with Ammonium Iodide

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Published online: 14 Jun 2011.

To cite this article: Nemai C. Ganguly & Pallab Mondal (2011) Mild, Efficient, and Greener Dethioacetalization Protocol Using 30% Hydrogen Peroxide in Catalytic Combination with Ammonium Iodide, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:16, 2374-2384, DOI: 10.1080/00397911.2010.502995

To link to this article: http://dx.doi.org/10.1080/00397911.2010.502995

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Synthetic Communications®, 41: 2374–2384, 2011
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ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.502995

MILD, EFFICIENT, AND GREENER DETHIOACETALIZATION PROTOCOL USING 30% HYDROGEN PEROXIDE IN CATALYTIC COMBINATION WITH AMMONIUM IODIDE

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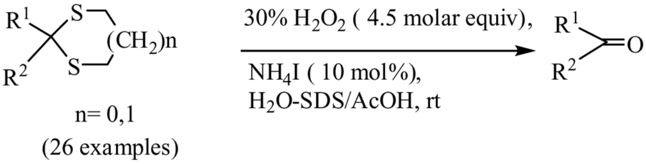
GRAPHICAL ABSTRACT



Abstract *A simple, mild, efficient, and expedient greener dethioacetalization protocol employing a catalytic amount of nontoxic ammonium iodide (10 mol%) in combination with 30% hydrogen peroxide as terminal oxidizer is revealed. The reagent accomplished facile deprotection of 1,3-dithianes and dithiolanes of activated aromatic substrates in an aqueous medium in the presence of sodium dodecylsulfate (SDS) at room temperature under virtually neutral conditions. Deactivated and sterically encumbered substrates, which are otherwise reluctant to cleave under aqueous micellar conditions, were expeditiously cleaved in good to excellent yields in acetic acid. The method is tolerant, with several acid-sensitive protecting groups, such as* tert-*butyldiphenylsilyl (TBDPS) ether, aryl acetate, NHBoc, and NHBn, and with further oxidation of oxidation-prone activated benzaldehydes and furyl aldehydes. A tentative mechanism of hypoiodous acid–mediated catalytic cleavage is proposed.*

Keywords Ammonium iodide; dethioacetalization; 1,3-dithianes; 30% hydrogen peroxide; sodium dodecylsulfate (SDS)

INTRODUCTION

The carbonyl functionality is ubiquitous in naturally occurring multifunctional as well as synthetic targets. The protection and deprotection of this synthetically flexible group at appropriate stages is often required in multistep synthetic sequences. Among the host of carbonyl protecting groups currently available, 1,3-dithianes and 1,3-dithiolanes[1] are particularly useful in view of their easy accessibility and stability under acidic as well as basic conditions. Apart from these useful features, aldehyde 1,3-dithianes are excellent acyl anion equivalents[2] that are widely utilized

Received March 12, 2010.

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for C-C bond-formation reactions. However, regeneration of the parent carbonyl compound from these procarbonyl derivatives is often not facile and requires harsh reaction conditions with attendant side reactions.

The traditional $HgCl_2$-mediated dethioacetalization method[3] or those subsequently developed utilizing heavy-metal salts such as $AgNO_2/AgClO_4$-I_2,[4] $AgNO_3$-NCS,[5] Tl^{+3} salts,[6a] SeO_2,[6b] or volatile CH_3I[7] suffer from significant limitations, primarily because of environmental concerns arising from stoichiometric or excess use of reagents and the resulting waste generation. Notwithstanding the availability of a good number of cleavage protocols, a contemporary concern for development of clean chemical processes triggered a resurgence of interest in this area.[8] Several hypervalent iodine compounds including bis(trifluoroacetoxy)-iodobenzene (BTI),[9] Dess–Martin periodinane (DMP),[10] and *o*-iodoxybenzoic acid (IBX)[11] have been employed as dethioacetalization reagents for their environmentally benign nature and mild oxidizing property. However, these methods involve stoichiometric or excess use of reagents. Replacement of existing stoichiometric methods by catalytic ones utilizing nontoxic mild reagents is one of the major goals of green chemistry. To this end, we felt that reagents that generate iodonium ion or its equivalent are attractive candidates for dethioacetalization. Iodonium ion is a competent thiophile, and we surmised that mild electrophilicity of the iodonium ion, in contrast to its chloronium and bromonium ion counterparts, combined with the sluggish and reversible nature of inherently weak C-I bond-formation reactions, would allow selective dethioacetalization in preference to ring iodination, even for activated aromatic substrates. Utilization of a catalytic amount of ammonium iodide with 30% hydrogen peroxide is hitherto unexplored for this purpose and constitutes a green approach because aqueous hydrogen peroxide is a safe, environmentally friendly terminal oxidizer that produces water as the only by-product of oxidation, thereby minimizing waste at source. Ammonium iodide is a readily available nontoxic nonmetal iodide source that can be oxidized with aqueous hydrogen peroxide without addition of catalyst or mineral acid and is inexpensive, particularly when used in catalytic amounts. Stereoselective iodoacetoxylation of protected glycals[12] and aromatic iodination[13] have been recently reported using NH_4I-H_2O_2-$Ac_2O/AcOH$ and NH_4I-H_2O_2-AcOH respectively. In our continuing efforts to develop greener synthetic protocols exploiting 30% aqueous hydrogen peroxide or its solid equivalents as terminal oxidizer,[14] we became interested in employing a catalytic amount of ammonium iodide in combination with 30% H_2O_2 for cleavage of 1,3-dithianes and allied *S,S*-acetals. Interestingly, commercial 30% H_2O_2 is fairly acidic because of the presence of acid stabilizers, and one such sample used by us exhibited a pH of 2.9. The addition of 0.1 millimolar solution of NH_4I in 5 mL of water provided a near-neutral solution of pH 7.1. Previous reports of activation of the iodonium ion in iodofunctionalization of alkenes by anionic surfactant sodium dodecylsulfate (SDS)[15] prompted us to choose an aqueous micellar route to solubilization of organic substrates for the current initiative.

RESULTS AND DISCUSSION

Initial exploratory experiments using 2-(3,4-methylenedioxyphenyl)-1,3-dithiane (**1**) as the model substrate showed that neither 30% H_2O_2 nor 20 mol% NH_4I alone was effective as a cleaving reagent under aqueous micellar conditions (Table 1).

Table 1. Optimization of cleavage conditions of 2-(3,4-methylenedioxyphenyl)-1,3-dithiane (**1**)[a] with NH_4I and 30% aqueous H_2O_2

Entry	NH_4I (mol%)	30% H_2O_2 (mL)	Solvent (mL), additive	Reaction time (min/h)	Yield[b] of carbonyl compound (%)
1	—	1	H_2O (5 mL) SDS (0.4 mmol)	8 h	No reaction
2	20	—	H_2O (5 mL) SDS (0.4 mmol)	10 h	No reaction
3	5	0.50	H_2O (5 mL) SDS (0.4 mmol)	1 h	90
4	5	1.0	H_2O (5 mL) SDS (0.4 mmol)	30 min	95
5	10	0.25	H_2O (5 mL) SDS (0.4 mmol)	1 h	85
6	10	0.50	H_2O (5 mL) SDS (0.2 mmol)	15 min	98
7	10	0.50	H_2O (5 mL) SDS (0.4 mmol)	15 min	96
8	20	0.25	H_2O (5 mL) SDS (0.2 mmol)	45 min	93
9	10	0.50	CH_3COOH (1.5 mL) H_2O (0.5 mL)	15 min	97

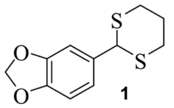
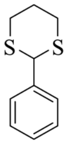
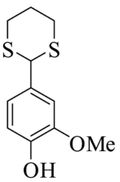
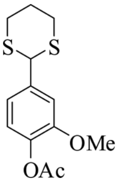
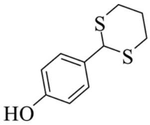
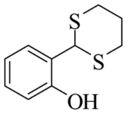
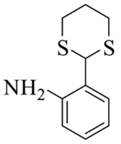
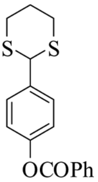
[a] Deprotections were carried out on a 1-millimolar scale at room temperature; amount of reagents/solvents refer to per mmol of substrate.

[b] Refers to isolated yield upon chromatography.

The attempted deprotection of **1** with 10 mol% of NaI or KI along with 30% H_2O_2 (0.5 mL, ~4.5 mmol) under similar conditions also proved abortive. A catalytic combination of 10 mol% of NH_4I with 30% H_2O_2 (0.5 mL, ~4.5 mmol) in water (5 mL) containing SDS (0.2 mmol) was found to be the optimized cleavage condition an released 3,4-methylenedioxybenzaldehyde (piperonal) from **1** within 15 min with a yield of 98%. Comparable efficient deprotection was also observed with identical amounts of NH_4I and 30% H_2O_2 in glacial acetic acid (1.5 mL). We preferred an aqueous medium that allowed cleavage under virtually neutral conditions without compromising expediency and efficiency. To demonstrate the utility, generality and functional group compatibility of the method, a wide assortment of *S,S*-acetals[16] was reacted under these conditions. It worked well for electron-rich aromatic aldehydes, ketones, and nonactivated dithianes (Table 2).

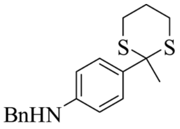
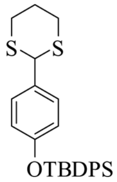
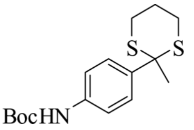
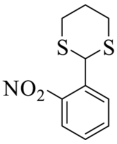
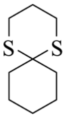
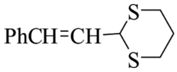
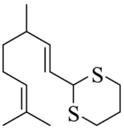
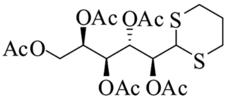
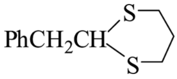
However, thioacetals derived from deactivated benzaldehydes (entries 12, 22 and 24) and sterically congested 1,3-dithiolane of camphor (entry 21) were relatively reluctant in an aqueous medium. Gratifyingly, switching over to an acetic acid medium led to faster cleavage with vast improvement in yields for these substrates. A substantial rate differential of cleavage of activated and nonactivated aromatic substrates in an aqueous medium offered scope for preferential deprotection of former in a mixture. A competition experiment performed with a mixture consisting of 1 mmol each of 1,3-dithiane, 2-nitrobenzaldehyde, and 4-hydroxy-3-methoxybenzaldehyde (vanillin) under optimized conditions for 20 min resulted in near-quantitative isolation of vanillin and unreacted dithiane of the former. Nonactivated dithianes and dithiolanes are reported to be quite reluctant to cleave under oxidative conditions.[8g] To our satisfaction, glucose pentaacetate dithiane (entry 17) as well as 1,3-dithiolane of 2-hydroxybenzaldehyde (entry 20) underwent smooth cleavage in H_2O-SDS. The tolerance of acid-sensitive phenol-protecting *tert*-butyldiphenylsilyl (TBDPS) ether, aryl acetate, NHBoc, and NHBn groups and generality of the protocol are advantageous features, adding further synthetic value to the method. Notably, bis(trifluoroacetoxy)-iodobenzene (BTI)-mediated deprotection of a 1,3-dithiane bearing a TBDPS ether group was accompanied by removal of the latter moiety and olefin

Table 2. Deprotection of *S,S*-acetals using a catalytic amount of NH_4I and 30% H_2O_2

Entry	Substrate	Reaction time[a]	Yield[b] of the carbonyl compound (%)
1	 **1**	15 min	98
2		40 min	95
3		10 min	~100
4		2 h	98
5		10 min	98
6		20 min	~100
7		30 min	97
8		1 h	80

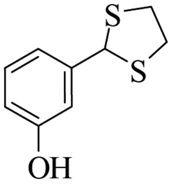
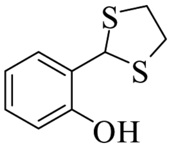
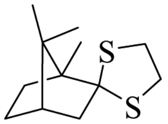
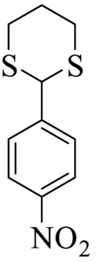
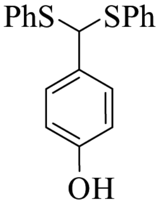
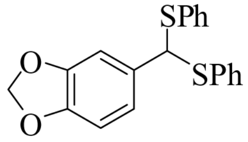
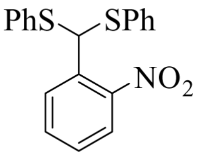
(*Continued*)

Table 2. Continued

Entry	Substrate	Reaction time[a]	Yield[b] of the carbonyl compound (%)
9		30 min	~100
10		45 min	85
11		2 h	98
12	 12	(i) 4 h (ii) 1 h	30 95[c]
13		30 min	97[d]
14		20 min	98[d]
15		1 h	~100
16		15 min	98
17		15 min	96
18		20 min	95

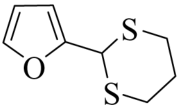
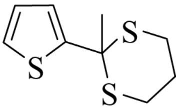
(*Continued*)

Table 2. Continued

Entry	Substrate	Reaction time[a]	Yield[b] of the carbonyl compound (%)
19		1 h	96
20		30 min	98
21		(i) 8 h (ii) 1 h	60 95[c]
22		(i) 2 h (ii) 10 min	75 98[c]
23		30 min	95
24		1.5 h	94
24		(i) 6 h (ii) 1.5 h	30 98[c]

(*Continued*)

Table 2. Continued

Entry	Substrate	Reaction time[a]	Yield[b] of the carbonyl compound (%)
25		20 min	98[d]
26		30 min	96[d]

[a] Reaction conditions: NH_4I (10 mol%), 30% H_2O_2 (0.5 mL), H_2O (5 mL), SDS (0.2 mmol) per mmol of substrate, rt.

[b] Refers to isolated yield after chromatographic purification; the carbonyl products are known compounds that showed physical and spectral features in good agreement with those reported in the literature.[18a]

[c] Reaction conditions: NH_4I (10 mol%) in H_2O (0.5 mL), CH_3COOH (1.5 mL), 30% H_2O_2 (0.5 mL) per mmol of substrate, rt.

[d] Yield was assessed from 2,4-dinitrophenylhydrazone derivative.

isomerization,[9] due to the release of potent trifluoroacetic acid as a by-product during the cleavage process. No undesired overoxidized by-product was formed even for oxidation-prone phenolic and furyl aldehydes (entries 3, 5, 6, 19, and 25). Absence of any product arising from acid-catalyzed cyclization of geranial after its release (entry 16) further attests to the mildness of the cleaving system. The current method is superior to an earlier protocol developed by us based on iodine-H_2O_2-SDS[14c] in water in terms of yield and reaction time. For example, 1,3-dithiane of piperonal and vanillin (entries 1 and 3) were deprotected in 98% and ~100% yields within 15 and 10 min respectively with the current reagent in an aqueous medium, whereas the same substrates required 0.5 and 1 h (yield 95% each) respectively with I_2-H_2O_2-SDS in water. The deprotection reaction can be tuned by appropriate selection of the reaction medium as demonstrated by removal of deactivated thioacetals, such as 1,3-dithianes of 2- and 4-nitrobenzaldehyde in acetic acid in 1 h and 10 min (95% and 98%) respectively.

Regarding the mechanistic scenario of cleavage, formation of a pale, greenish yellow solution upon addition of 30% H_2O_2 to aqueous NH_4I solution is suggestive of in situ generation of hypoiodous acid (Eq. 1, Scheme 1).

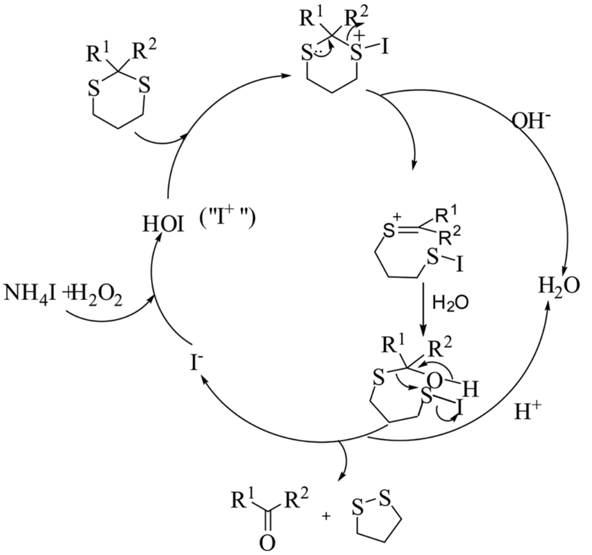
It is a stronger iodonium ion equivalent than molecular I_2 owing to its highly reactive nature. Although HOI undergoes fast pH-sensitive disproportionation into I_2 and HIO_3, particularly above pH 9 (Eq. 2),[17] it is a weak acid (pKa 10.7), and 95% of I^+ species exist in the form of HOI at pH below 9.5. It is plausible that

$$NH_4I + H_2O_2 = HOI + NH_4OH \qquad ......1$$

$$5HOI = 2I_2 + HIO_3 + 2H_2O \qquad .....2$$

$$HOI + CH_3COOH = CH_3COOI + H_2O \qquad .....3$$

Scheme 1. Generation of iodonium ion equivalent in NH_4I-H_2O_2 solution.



Scheme 2. Tentative catalytic cycle for the cleavage of 1,3-dithianes with NH_4I-H_2O_2.

HOI, usually elusive in aqueous solution, is intercepted by highly nucleophilic sulfur as soon as it is generated to form an aquo-labile sulfonium ion intermediate, paving the cleavage process. Formation of a stronger iodonium ion equivalent in the form of acetylhypoiodite in acetic acid (Eq. 3) coupled with improved solubility of the substrate accounts for better results for deactivated substrates in acetic acid. An analogous species has been suggested as intermediate in oxyiodination[13] with the same reagent. A tentative catalytic cycle for the cleavage process is delineated in Scheme 2.

CONCLUSION

We have developed a mild catalytic dethioacetalization method based on ammonium iodide catalyst and 30% H_2O_2 at room temperature, which is useful in an aqueous medium in the presence of SDS for activated aromatic substrates. Acetic acid is the preferred medium for cleavage of reluctant deactivated aromatics and sterically hindered substrates. The mildness, operational simplicity, high throughput, and generality of the protocol combined with its green features make it an attractive alternative to existing methods.

EXPERIMENTAL

Representative Procedure for the Cleavage of 2-(3,4-Methylenedioxyphenyl)-1,3-dithiane (1) with NH_4I–30% H_2O_2 in Aqueous Micellar Medium

Compound **1** (256 mg, 1.06 mmol), was added to a stirred aqueous solution of NH_4I (15.6 mg, 0.107 mmol) containing SDS (5 mL H_2O, 59 mg, ~0.2 mmol), and then 30% H_2O_2 (0.5 mL, 4.5 mmol), was added slowly as the mixture assumed a pale, greenish yellow coloration. It was thoroughly stirred for 15 min at rt when thin-layer chromatography (TLC) showed complete disappearance of the starting material. Addition of 5% sodium thiosulfate solution (5 mL) to the reaction mixture followed by extraction with EtOAc (2 × 5 mL), washing the combined organic extract with water (3 mL), drying (Na_2SO_4), and removal of solvent gave a concentrated extract. It was filtered through a short pad of silica gel (60–120 mesh, Spectrochem, India) using EtOAc–light petrol (1:10) as eluent to furnish piperonal (157 mg, 98%); mp 36–37 °C (EtOAc–light petrol) (lit.[18a] 38 °C).

Representative Procedure for the Cleavage of 2-(2-Nitrophenyl)-1,3-dithiane (12) with NH_4I–30% H_2O_2 in Glacial Acetic Acid

Glacial acetic acid (1.5 mL) and then **12** (259 mg, 1.08 mmol) were added to a stirred solution of NH_4I (15.7 mg, 0.108 mmol) in water (0.5 mL). This was followed by slow addition of 30% H_2O_2 (0.5 mL, 4.5 mmol), and the mixture was stirred for 1 h at rt (TLC monitoring). A solution of 5% sodium thiosulfate solution (5 mL) was added to quench the reaction, which was followed by extraction of the reaction mixture with EtOAc (2 × 5 mL). The combined organic extract was washed with saturated $NaHCO_3$ solution (2 × 3 mL) and water (2 × 2 mL) and then dried (Na_2SO_4). Removal of the solvent gave concentrated extract that was filtered through a short pad of silica gel (60–120 mesh, Spectrochem, India) eluting with EtOAc–light petrol (1:49) to furnish 2-nitrobenzaldehyde (154 mg, 95%); mp 42–44 °C (lit.[18a] 41–43 °C).

ACKNOWLEDGMENTS

One of the authors (P. M.) is thankful to the Council of Scientific and Industrial Research, India, for financial assistance by way of a research fellowship. We thankfully acknowledge the facilities provided by the Department of Science and Technology–Funding for Infrastructure in Science and Technology and the University Grants Commission, SAP programs, government of India, to the Department of Chemistry, University of Kalyani.

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