

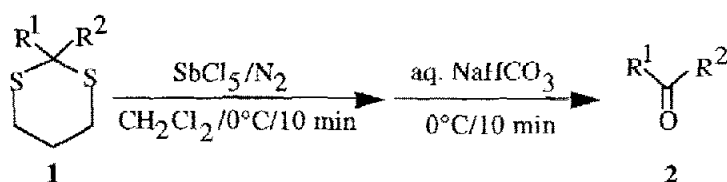
DEPROTECTION OF 1,3-DITHIANES BY ANTIMONY PENTACHLORIDE VIA SINGLE ELECTRON TRANSFER PROCESSES

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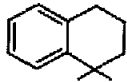
Summary: A variety of 1,3-dithianes was converted to the corresponding carbonyl compounds in good yields when those substances were treated with antimony pentachloride in methylene chloride. Single electron transfer from dithianes to antimony pentachloride was proposed as an *initiation step* of the reaction.

Activation of organic molecules through single electron transfer (SET) affords ion radical intermediates that participate in many oxidation and reduction processes.¹ Among methods to produce such species is use of proper SET oxidants and reductants. While antimony pentachloride has been favorably used for the generation of organic cation radicals,² there have been few applications of this strong SET oxidant to synthetically useful organic reactions.³ Since dedithioacetalization is recognized as an important reaction in synthetic organic chemistry,⁴ we became interested in the SET reactions of dithioacetals with antimony pentachloride.⁵ Dithioacetal cation radicals generated by a SET process are considered to undergo carbon-sulfur bond cleavage based on the accumulated data on the reactivities of organosulfur compounds.⁶ Now, we have found that antimony pentachloride mediated the deprotection of various dithioacetals to produce carbonyl compounds in good yields.



We have conducted the reactions of several 1,3-dithianes **1** with antimony pentachloride (SbCl_5) in methylene chloride (Table). In a typical experiment, to a methylene chloride solution of 1,3-dithiane **1a** was added antimony pentachloride under nitrogen at 0°C . After 10 minute stirring of this resulting mixture, the reaction was quenched by aqueous NaHCO_3 . Then, the mixture was filtered through *Celite* and the filtrate was extracted with methylene chloride. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. Addition of ether to the residue was necessary to remove the insoluble white precipitate by filtration. The filtrate was concentrated and separated by silica gel TLC to afford *p*-methylbenzophenone **2a**⁷ in almost quantitative yield. A small amount of 1,2-dithiolane-1-oxide **3**⁸ (21%) was also isolated. Under the similar conditions, dithianes **1b-1n** were deprotected to give the corresponding ketones, aldehydes, and ketoester in good to excellent yields (63-97%).

Table Deprotection of 1,3-Dithianes **1** by Antimony Pentachloride.

Substrate ^a	R ¹	R ²	SbCl ₅ /mmol	Conv./%	Carbonyl Compd. 2 / % ^b
1a	<i>p</i> -MeC ₆ H ₄	Ph	1.5	100	100
1b	<i>p</i> -ClC ₆ H ₄	Me	1.5	100	81
1c	<i>p</i> -NO ₂ C ₆ H ₄	Me	1.5	100	66
1d	<i>p</i> -MeOC ₆ H ₄	H	1.0	76	76
1d			1.2	88	86
1d			1.5	100	97
1d			1.2 ^c	92	87
1d-D	<i>p</i> -MeOC ₆ H ₄	D	1.5	100	98
1e	<i>p</i> -MeC ₆ H ₄	H	1.5	100	90
1f	PhCH ₂	PhCH ₂	1.5	100	78
1g	PhCH ₂ CH ₂	Me	1.5	100	78
1h	PhCH ₂ CH ₂	H	1.5	100	86
1i	<i>n</i> -C ₁₁ H ₂₃	H	1.5	100	81
1j			1.5	100	77
1k	-(CH ₂) ₂ CHPh(CH ₂) ₂ -		1.5	100	72
1l	PhCH=CH	Me	1.5	100	75
1m	PhCH=CH	H	1.5	100	86
1n	<i>p</i> -MeC ₆ H ₄	CO ₂ Me	1.5	71	63
1n			3.0	100	91

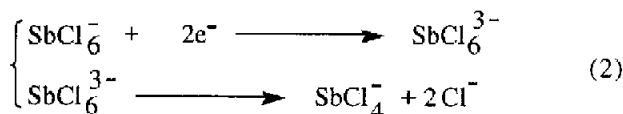
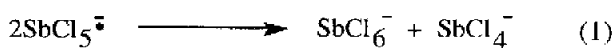
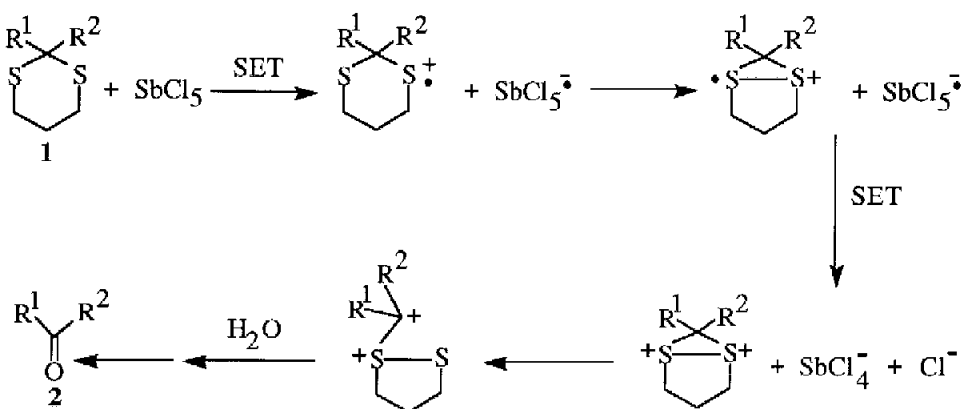
^a **1** (1.00 mmol); dry CH₂Cl₂ (10 ml); SbCl₅ (2.0 M CH₂Cl₂ solution). ^b Isolated yields. ^c Under oxygen.

In general, the yields (< 82%) of alkyl substituted ketones (**2b**, **2c**, **2f**, **2g**, **2j**, **2k**, **2l**) are relatively lower than those (> 80%) of aldehydes (**2d**, **2e**, **2h**, **2i**, **2m**). Substitution of electron withdrawing group at C₂ carbon apparently decreases the yield of carbonyl compounds (**2c** and **2n**). Isolation of deuterated benzaldehyde **2d-D** in 98% indicates that deprotonation at C₂ carbon in the involving cationic intermediates does not occur.

In addition to above, mechanistically important following observations were obtained. When **1d** (1.00 mmol) was treated with different amounts of SbCl₅ (1.0 mmol, 1.2 mmol, and 1.5 mmol), **2d** was isolated in 76%, 86%, and 97% yields, respectively. Interestingly, introduction of oxygen into the reaction solution did not affect the yield of **2d** (87%). If SET processes are involved in the reaction, addition of SET quencher should decrease the conversion of dithianes depending on the electron donating ability of the quencher. Indeed, the conversion of **1d** (36%) became lower in the presence of 1,2,4,5-tetramethoxybenzene (TMB) than that (88%) in the absence of TMB while 1,4-dimethoxybenzene (DMB) did not affect the reaction progress (conv. 83%).⁹ These results would suggest that, 1) SET is an important process of the interaction between SbCl₅ and electron donors, such as **1d** and TMB, 2) formal double electron transfer from **1d** to SbCl₅ must proceed, 3) the cation radical of **1d** does not survive long enough to be captured by molecular oxygen.

Since the detailed mechanism could not be elucidated at this moment, the reaction pathways depicted in Scheme I is tentatively proposed.¹⁰ First, SET from dithioacetals to SbCl_5 produces cation radical-anion radical pairs of those components. Subsequent SET from dithioacetal cation radicals affords dithioacetal dication, $6a$ SbCl_4^- anion, and chloride ion. While the details of sequential SET and fragmentation of SbCl_5 have not been uncovered yet, SbCl_5 anion radical is proposed to undergo disproportionation giving SbCl_6^- and SbCl_4^- anions (equation 1).² SbCl_6^- anion is considered to possess an ability of double electron transfer from electron donors to become SbCl_4^- anion and chloride ion (equation 2).² The resulting dithioacetal dication may undergo carbon-sulfur bond cleavage to afford the ring opened dication that are hydrolyzed to carbonyl compounds.¹¹

Scheme I



In summary, we have found that antimony pentachloride is quite useful for the deprotection of 1,3-dithianes to produce carbonyl compounds. We will conduct the further studies to elucidate more concrete mechanism for the reaction.¹²

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- 7) All carbonyl compounds obtained in this study were completely characterized by the direct comparison with the authentic samples.
- 8) Details of the identification of **3** have been reported in ref. 6e and 6g.
- 9) $E_p^{OX}(\mathbf{1d}) = 1.04$ V, $E_p^{OX}(\text{TMB}) = 0.77$ V, $E_p^{OX}(\text{DMB}) = 1.28$ V (vs. SCE in CH_3CN).
- 10) Notably, it was found that the use of the conventional Lewis acids, such as AlCl_3 , SbCl_3 , SnCl_4 , TiCl_4 , did not cause deprotections of **1d** and **1f** under the similar conditions (Lewis acid, 2.0 mmol; conv. of **1** = 1-4%; yields of **2** = 0%). Thus, we prefer a SET mechanism for the reaction of SbCl_5 and dithianes rather than a mechanism involving electrophilic attack of hard Lewis acid (SbCl_5) to soft Lewis base (sulfur of dithianes).
- 11) Alternatively, the dithioacetal dications react with neutral dithioacetals to afford dimer dications that are hydrolyzed to produce carbonyl compounds.^{6c}
- 12) While we think that the SET process from dithianes to SbCl_5 initiates the reaction, the following pathways would be different from those under the photosensitized conditions.^{6g} In the former case, SET oxidant generated in situ, probably SbCl_6^- anion, might exist near to initially formed dithiane cation radicals. On the other hand, in the latter case, subsequent SET from dithiane cation radicals is unlikely to occur since the steady state concentration of those cation radicals is too low to encounter the excited sensitizer.

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