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NOVEL REDUCTIVE CLEAVAGE REACTION OF THIOBENZOATES WITH SAMARIUM DIIODIDE: CONVENIENT SYNTHESIS OF DISULFIDES

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Abstract: The reductive cleavage of thiobenzoates promoted by samarium diiodide afforded various kinds of disulfides in good yields under mild and neutral conditions.

Samarium diiodide has attracted considerable interest as a powerful one-electron transfer reducing agent able to promote a wide range of reductions and coupling reactions in recent years.[1] In a recent work it has been reported that the reductive dimerization of thiocyanates mediated by SmI_2 gives disulfides via (RSCN)•-.[2] Given the recent success for C-S bond cleavage of thiocyanates by SmI_2, we reasoned that thiolesters might be cleaved into acyl anions (PhCO-) and thiyl radicals (RS•), leading to the desired transformation into disulfides and/or diketones. Disulfides are useful synthetic intermediates in a variety of chemical transformations,[3] and many synthetic methods have been developed for the preparation of disulfides.[4] The reactions of aldehydes or ketones,[5] acid chlorides,[6] esters,[7] amides[8] and acid

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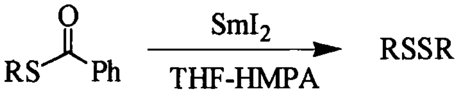
cyanides[9] with SmI_2 have been investigated. However, little attention has been concentrated on the reaction of thiolesters with SmI_2. It has been known that thiols are relatively labile under ambient atmosphere. Thus the process is highly desired in which protected thiols are directly transformed into disulfides. It has been reported that such a one-pot process is possible with alkoxystannane or nickel boride.[10] Herein we wish to report a more convenient method of the synthesis of disulfides directly from thiobenzoates promoted by samarium diiodide under mild and neutral conditions.

To the best of our knowledge, there are no literature examples for the reduction of thiolesters with SmI_2 to produce disulfides. Therefore, we decided to investigate the reduction of thiobenzoates promoted by SmI_2 in THF-HMPA system (equation 1). Thiobenzoates **1** used as thiolesters were readily prepared from the reaction of benzoyl chloride with suitable thiol.[11] When thiobenzoates **1** reacted with 2.3 equiv of SmI_2 in THF-HMPA at room temperature, the deep blue color of SmI_2 disappeared within 1-4 hours, which indicated that the reaction had been completed. A variety of thiobenzoates were converted to the corresponding disulfides by this procedure. The results are summarized in Table 1. All products obtained showed NMR, IR and mass spectral data compatible with the structure. The structures of known compounds were determined by comparison of their spectral data with those previously reported.[2,3,4]



1 **2** (1)

As shown in Table 1, reductive cleavage of aromatic thiobenzoates (entries 1-5) proceeded smoothly to give the corresponding disulfides in good yields along with a small amount of benzil, $(PhCO)_2$ as by-products, while the yields of aliphatic thiobenzoates (entries

Table 1. Reductive Cleavage of Thiobenzoates Promoted by Samarium Diiodide

Entry	Thiolester **1** R	Reaction time (hr)	Amount of SmI_2 (equiv.)	Yield(%)* Disulfide **2**	Recovered SM(%)	m.p. °C (lit.)[12]
1	Ph	1	2.3	86	0	58-59 (61)[a]
2	4-CH_3Ph	1	2.3	84	0	47-49 (46)[b]
3	4-ClPh	1	2.3	82	0	68-69 (71)[c]
4	2-BrPh	1	2.3	80	0	97 (97.5-98)[d]
5	2-Naphthyl	1	2.3	81	0	141-142 (141-143)[e]
6	$PhCH_2CH_2$	2	3.5	72**	9	oil
7	4-$ClPhCH_2$	2	3.5	70**	18	58-59 (59)[f]
8	$CH_3(CH_2)_7$	4	3.5	70**	17	oil
9	$CH_3(CH_2)_{11}$	4	3.5	71**	15	30-31 (30-31)[g]
10	$CH_3(CH_2)_{15}$	4	3.5	73**	19	49-51 (50-52)[g]
11	Cyclohexyl	4	3.5	72**	18	oil

* Isolated yield
**Yields based on the reacted thiobenzoates.

6-11) as the reactants are relatively lower than those of aromatic thiobenzoates and longer reaction times were required. Presumably this result may be attributed to the difference in stability between the radical intermediates. Because a thiophenyl radical intermediate (ArS•) from an aromatic thiobenzoate is stabilized by the neighboring aromatic ring, it has enough time to react with another radical intermediate to give disulfide. Generally the unreactivity of the thiobenzoates required a two-fold excess of SmI_2 (2.3 equiv) and in case of aliphatic thiobenzoates an additional equivalent of SmI_2 was added later but the reactions were not completed. In the reactions, the halogen atoms on the aromatic ring remained intact under the present reaction conditions. We have observed that in the absence of HMPA the reaction proceeded in lower yield (50-60%) for longer time (8-12 hrs). It is worth noting that the addition of HMPA not only accelerates the reductive cleavage of thiobenzoates, but also increases the yields of products.

Although the detailed mechanism of the reaction is not yet clear at the present stage, we assume that samarium diiodide may transfer one electron to thiobenzoates to form the radical anion (PhCOSR)•-, which was cleaved into RS• and PhCO-. The coupling of the radical RS• can give disulfides **2** and PhCO- may react with thiolesters to give benzil, $(PhCO)_2$ as by-products. In the present case we have trapped the "acyl anion" with a proton source (methanol or *t*-BuOH) which results in benzaldehyde formation. This observation could support the formation of the benzoyl anion and subsequent proton abstraction. It is speculated that disulfides can survive the present reaction conditions, since the rate of formation of disulfide is faster than that of cleavage of S-S bond in disulfide. Thus the reaction of thiobenzoate with SmI_2 was stopped at the disulfide stage. In view of the easily available starting materials, good yields, mild and neutral conditions, the present procedure could be complementary to the conventional method.

In summary, it has been found that reductive cleavage of thiobenzoates by SmI_2 results in the formation of disulfides. We think that the present procedure provides a useful method for the preparation of disulfides directly from the reduction of thiobenzoates by samarium diiodide in good yields under mild and neutral conditions. Further investigation on the extension of the reaction and the mechanistic detail is currently in progress.

EXPERIMENTAL

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. Tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl before use. ^1H NMR spectra were recorded on a FT-Bruker AF-300 (300 MHz for ^1H NMR; 75 MHz for ^{13}C NMR) using TMS as an internal standard. The solvent was $CDCl_3$ unless otherwise noted. IR spectra were obtained on a Perkin Elmer 16F PC FT-IR Shimadzu. GC-MS was recorded on a Hewlett-Packard 5890 GC. High resolution mass spectra (HRMS) were obtained on a Varian MATCH-50F instrument.

General procedure for the reaction:

A solution of phenyl thiobenzoate (250 mg, 1.17 mmol) in THF (3 mL) was added to a deep blue solution of SmI_2 (0.1M, 2.70 mmol) in THF(27 mL) and HMPA (3 mL) at room temperature under nitrogen atmosphere. The resulting mixture was stirred for one hour under these conditions. The reaction solution was quenched with dilute HCl and extracted with ether. After the usual work-up, the crude product was purified by silica gel column chromatography (hexane:ethyl acetate = 15:1) to afford diphenyl disulfide (109 mg, 86%). The product obtained is highly pure and gave mp. NMR, Mass and IR spectral data consistent with structures and in agreement with literature.[12(a)]

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