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HIGHLY EFFICIENT ONE-STEP CONVERSION OF SELENOL ESTERS INTO SYMMETRICAL DISELENIDES IN THE PRESENCE OF ELEMENTAL IODINE IN METHANOLIC SOLUTION

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A facile, efficient, and convenient procedure has been developed for the direct conversion of selenol esters into the corresponding diselenides in the presence of elemental iodine at room temperature.

Keywords Deprotection; diselenides; iodine; oxidation; selenol esters

INTRODUCTION

Organoselenium compounds have emerged as important reagents and intermediates in organic synthesis,¹ and they also have biological importance, because proteins containing selenium are essential components of certain bacterial and mammalian enzyme syntheses.² Since selenium chemistry is relatively underdeveloped, there are needs for novel synthetic strategies in selenium functionality incorporation, protection, deprotection, and conversion.

The preparation of organic selenols and diselenides has been extensively studied during the last few decades concerning synthetic application for the efficient selenylation of organic compounds.³ Among the selenium reagents, diphenyl diselenide is commonly employed for organoselenylation reactions because of its versatile reactivity (nucleophilic as well as electrophilic) depending on the reaction conditions and thus allows a myriad of transformations through α -selenocarbanions,⁴ α -selenocarbenium ions,⁵ and α -selenocarbon-centered radicals.⁶

In the recent years, a number of researchers have employed selenoacetates as efficient sources of acyl radicals.⁷ The numerous examples for the homolytic cleavage of the acyl C–Se bond to give the corresponding selenyl radicals are contrasted by the surprising paucity of examples of selenolate anions derived from selenoacyl compounds. Vinyl selenoacetates have been cleaved by sodium/HMPA in DMF to give vinyl selenolates that were oxidized with iodine to yield divinyl diselenides.⁸ Also, aryl selenoesters have been deprotected with potassium carbonate in aqueous THF to give selenolates that add

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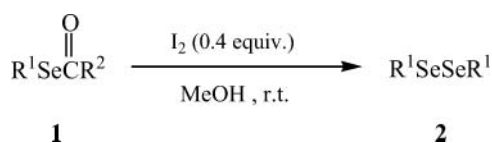
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to phenylpropionitrile and give selenocinnamitriles.⁹ Aqueous ammonia in THF¹⁰ and *n*-butylamine in ethanol¹¹ have also been used for acyl–selenium cleavage of selenoesters. In one report, UV-irradiation of a selenoester afforded a mixture of products, from which 57% of the corresponding diselenide was isolated.¹²

Elemental iodine is a mild, cheap, nontoxic, and easily available oxidizing reagent. In recent years, it has received considerable attention as an effective catalyst for various organic transformations¹³ under mild and convenient conditions to afford the corresponding products in excellent yields with high selectivity. However, there is no example of direct iodine-induced cleavage of selenol esters to afford symmetrical diselenides.

RESULTS AND DISCUSSION

In the course of our investigations on the synthesis of selenol esters from diselenides,^{14,15} we discovered a simple process for the facile cleavage of the acyl–selenium bond and subsequent oxidation promoted by elemental iodine in dry methanol at room temperature in an aerial atmosphere to afford diselenides in high to excellent yields (Scheme 1).



Scheme 1

In a model reaction, *Se*-phenyl butaneselenoate (1 mmol) was taken as a representative selenol ester. The effects of several solvents such as acetonitrile, ethanol, methanol, trichloromethane, and ethyl acetate were examined in the presence of iodine (0.4 mmol) at room temperature under ambient atmosphere, and the best result was obtained with dry methanol. Under the same reaction conditions, other experiments were also carried out with various amounts of iodine in dry methanol at room temperature (Table I); the best molar ratio of selenolester:iodine was found to be 1:0.4.

A series of selenolesters was treated with anhydrous methanol in the presence of nearly equimolar amounts of iodine (molar ratio of selenolesters:iodine = 1:0.4, as above). The results are summarized in Table II. Diselenides prepared from aryl selenolesters (Table II, entries 1–8) generally give higher yields than those produced from alkyl (benzyl)

Table I Deprotection-oxidation of *Se*-phenyl butaneselenoate with different molar ratios of iodine^a

Entry	I ₂ (mmol)	Time (h)	Yield (%) ^b
1	0.1	10.5	63
2	0.2	10	65
3	0.3	9	92
4	0.4	4.5	99
5	0.5	4.5	95

^aReaction conditions: *Se*-phenyl butaneselenoate (1 mmol), dry methanol (3 mL), room temperature.

^bYields of isolated products.

Table II Diselenides obtained by iodine-promoted cleavage of Se—CO bonds

Entry	R ¹	R ²	Diselenide	Reaction Time (h)	Yield (%) ^{a,b}
1	Ph	CH ₃	2a	2	83 ¹⁶
2	Ph	CH ₃ CH ₂	2a	5.5	87 ¹⁶
3	Ph	CH ₃ CH ₂ CH ₂	2a	4.5	99 ¹⁶
4	Ph	(CH ₃) ₃ C	2a	1	93 ¹⁶
5	Ph	Ph	2a	1	91 ¹⁶
6	4-ClC ₆ H ₄	Ph	2b	5.5	94 ¹⁷
7	4-CH ₃ C ₆ H ₄	CH ₃ CH ₂ CH ₂	2c	4.5	98 ¹⁷
8	4-CH ₃ C ₆ H ₄	CH ₃ CH ₂	2c	6	96 ¹⁷
9	PhCH ₂	CH ₃	2d	3.5	81 ^{3a}
10	PhCH ₂	CH ₃ CH ₂	2d	5	84 ^{3a}
11	PhCH ₂	CH ₃ CH ₂ CH ₂	2d	3	78 ^{3a}
12	PhCH ₂	(CH ₃) ₃ C	2d	4	85 ^{3a}
13	PhCH ₂	Ph	2d	3	88 ^{3a}

^aYields of isolated products.^bReferences for known compounds.

selenolesters (Table II, entries 9–13). It is predicted that iodine first facilitates the Se—CO bond cleavage and effects removal of the acyl group with formation of the corresponding selenols, and in the next step, it catalyzes the oxidation of the selenols to the diselenides.

CONCLUSION

In summary, we have developed a new mild, convenient, and efficient protocol for the deprotection–oxidation of selenolesters to the corresponding diselenides in the presence of iodine at room temperature.

EXPERIMENTAL

Selenolesters were prepared according to the method reported earlier.¹⁴ Yields refer to isolated products. Melting points were determined by a Büchi B-540 apparatus. IR spectra were run on an AAB FTLA 2000 instrument. The ¹H NMR (300 MHz) and ¹³C NMR (75MHz) spectra were recorded on a Bruker AQS-300 Avance NMR spectrometer. The progress of the reaction was followed by TLC using silica-gel SILG/UV 254 plates. Products were characterized by comparing their physical and spectral data with those of the authentic samples.

Typical Procedure for the Preparation of Diphenyl Diselenide

A mixture of *Se*-phenyl butaneselenoate (0.227 g, 1 mmol), I₂ (0.1 g, 0.4 mmol), and anhydrous MeOH (3 mL) was stirred in a round-bottom flask open to air at room temperature for 4.5 h. The progress of the reaction was monitored by TLC. After completion of the reaction, MeOH was removed under reduced pressure, and the residue was diluted with EtOAc (10 mL), washed with aqueous sodium thiosulfate (2 × 5 mL, 10%) and subsequently with water (2 × 5 mL). The organic layer was dried over anhydrous Na₂SO₄, followed by evaporation of the solvent to obtain the crude product, which was subjected to preparative

TLC (silica gel, eluent *n*-hexane:CH₂Cl₂ = 7:1) to afford 0.154 g (99%) of pure diphenyl diselenide as orange crystals; mp 59–60°C (lit.¹⁶ mp 58–61°C).

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