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View Article Online
DOI: 10.1039/C5RA06147D

Graphical Abstract

Synthesis of chiral N^{β}-protected amino diselenides from the corresponding amino alkyl iodides using $NaBH_2Se_3$ as a selenating reagent and their conversion to seleninic acids

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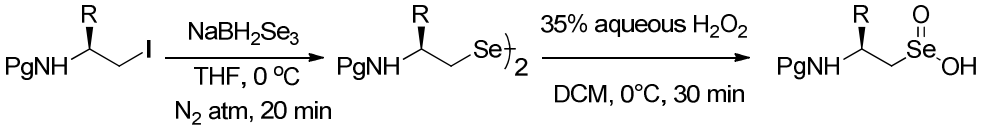
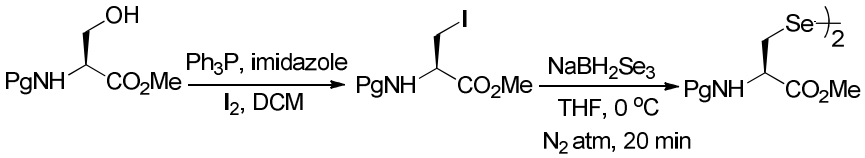


Pg = Boc, Cbz or Fmoc group; R = amino acid side chain



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A convenient approach has been presented for the synthesis of N^{β}-protected amino diselenides from the corresponding amino alkyl iodides using in situ generated $NaBH_2Se_3$ as an efficient selenating reagent. All the diselenides were obtained in good yields under very mild conditions, short duration of time and the protocol is free from racemization. The methodology has been effectively extended to the synthesis of *N*-protected L-selenocystine methyl ester. Clean oxidation of N^{β}-protected amino diselenides to the N^{β}-protected amino seleninic acids using 35% aqueous H_2O_2 has also been accomplished. The present protocol is compatible with all the common urethane protecting groups.

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ARTICLE TYPE

Synthesis of chiral N^{β}-protected amino diselenides from the corresponding amino alkyl iodides using $NaBH_2Se_3$ as a selenating reagent and their conversion to seleninic acids

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

A convenient approach has been presented for the synthesis of N^{β}-protected amino diselenides from the corresponding amino alkyl iodides using *in situ* generated $NaBH_2Se_3$ as an efficient selenating reagent. All the diselenides are obtained in good yields under very mild conditions, short duration of time and the protocol is free from racemization. The methodology has been effectively extended to the synthesis of *N*-protected L-selenocystine methyl ester. Clean oxidation of N^{β}-protected amino diselenides to the N^{β}-protected amino seleninic acids using 35% aqueous H_2O_2 has also been accomplished. The present protocol is compatible with all the common urethane protecting groups.

Introduction

Selenium is an essential trace element present in many different compounds with unequivocal functions.[1] Organoselenium compounds find applications in organic synthesis,[2] ligand chemistry[3] and in biological processes.[4] Selenium supplementation plays an important role in disease prevention like cancer, cardiovascular, neurodegenerative and Alzheimer's.[5-8] The common dietary selenium compounds are selenite, selenomethionine, methylselenocysteine and selenocysteine (SeCys). In contrast to oxygen and sulphur, the selenium based methodologies offer several unique features in organic chemistry.[9] Remarkably, diselenides have attracted much attention as intermediates in organic synthesis due to their higher stability and easier handling relative to parent selenols. Most importantly chiral diselenides have been employed as useful ligands and catalysts in various asymmetric transformations such as diethyl zinc addition to aldehydes,[10] asymmetric hydrosilylation,[11] 1,4-addition of Grignard reagents to enones,[12] stereo selective ring opening of epoxides,[13] palladium-catalyzed asymmetric allylic substitution[14] and electrophilic selenenylation of alkenes.[15] SeCys, recognized as the 21st proteinogenic amino acid, often found in enzymatic active sites, where its known function is either acting as a nucleophile, a metal ligand or a redox element. In mammals, selenium is an integral part of selenoproteins as selenocysteine.[16] The derivatives of SeCys are the convenient precursors for the synthesis of dehydroamino acids which are useful in the preparation of peptide conjugates.[17]

There are few methods reported for the synthesis of β-amino acid derived diselenides, which are employed in the synthetic organic chemistry. Braga *et al.,* reported the synthesis of β-amino diselenides from *N*-Boc-aziridines[18] as well as *N*-Boc-2-oxazolidinones[19] employing Li_2Se_2 as a selenating reagent. But these protocols are limited to the synthesis of N^{β}-Boc amino diselenides, take more time and give moderate yields. Chandrasekaran *et al.,* reported the synthesis of *N*-Ts-β-amino diselenides from aziridines using tetraethylammonium tetraselenotungstate $[(Et_4N)_2WSe_4]$ as a selenating reagent.[20] Later a variety of N^{β}-protected amino diselenides and selenocystine derivatives from sulfamidates using potassium selenocyanate (KSeCN) and benzyltriethylammonium tetrathiomolbydate $[(BnEt_3N)_2MoS_4]$ have also been reported.[21] However, longer reaction duration and use of expensive reagents which decompose on prolonged exposure to air are some of the disadvantages of these protocols. Cu(II) catalyzed synthesis of dialkyl, aryl or heteroaryl diselenides has also been known but the alkaline conditions employed in these protocols are not compatible with Fmoc chemistry.[22,23] A few other approaches have also been reported for the synthesis of dialkyl, aryl or heteroaryl diselenides from the corresponding halides.[24-27] Thus a method circumventing the use of aqueous alkali, compatible with common urethane protecting groups (Boc/Cbz/Fmoc), using easily prepared starting material is desirable for the synthesis of N^{β}-protected amino diselenides.

Seleninic acids are of synthetic importance due to their utility in the construction of seleninates, selenonates[28] and other reaction intermediates.[29,30] They have also found widespread application as catalysts in oxidation reactions.[31,32] Seleninic acid group is the most stable, among the four organic acids of selenium (selenol, selenenic, seleninic, and selenonic acids).[33] Kehler *et al.,* reported the synthesis of 3-aminopropaneseleninic acid dihydrotosylate and piperidine-4-seleninic acid dihydrotosylate from the corresponding diselenides using *p*-toluene sulfonic acid monohydrate and 35% aqueous H_2O_2.[34] Knapp *et al.,* reported the clean oxidation of selenoesters to the seleninic acids using dimethyldioxirane (DMDO) in stoichiometric amounts.[28] Oxidative cleavage of organodiselenides by aqueous Br_2,[35] aqueous H_2O_2[36] or ozone[37] has also been reported for the synthesis of seleninic acids. In continuation of our efforts in

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organoselenium chemistry[38,39] and in order to overcome the drawbacks associated with the existing protocols, we envisaged to devise a simple, mild and efficient protocol for the synthesis of N^{β}-protected amino diselenides from the corresponding alkyl iodides using *in situ* generated $NaBH_2Se_3$ as a selenating reagent. Further, the oxidation of N^{β}-protected amino diselenides to the seleninic acids using 35% aqueous H_2O_2 is delineated.

Results and discussion

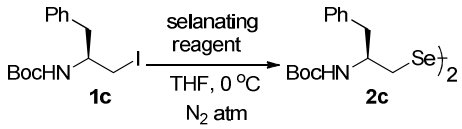
The selenating reagent for the present study was prepared by the method of Lalancette *et al.,* which involved the treatment of one mole of $NaBH_4$ with three moles of selenium in THF at 0 °C under nitrogen atmosphere (Scheme 1).[40] Hydrogen gas gets evolved immediately and within 10 minutes the conversion of black selenium powder into reddish suspension indicates the formation of sodium selenoborate ($NaBH_2Se_3$).[41,42] So far $NaBH_2Se_3$ has been employed as a reducing agent however its selenating ability has not been explored.[43]

$$NaBH_4 + 3\,Se \xrightarrow[10\ min,\ N_2\ atm]{THF,\ 0\ ^oC} NaBH_2Se_3 + H_2\uparrow$$

Scheme 1 Preparation of sodium selenoborate ($NaBH_2Se_3$)

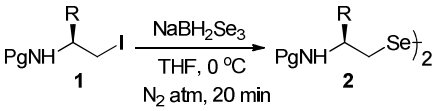
Our initial efforts were focused on the synthesis of Boc-Phe-CH_2-Se-)$_2$ (**2c**). In a typical reaction, to the freshly prepared $NaBH_2Se_3$ suspension in THF at 0 °C in a two-necked round-bottom flask under nitrogen atmosphere, a solution of Boc-Phe-CH_2-I (**1c**) in THF was added drop wise using dropping funnel at 0 °C. As monitored by TLC, the desired Boc-Phe-CH_2-Se-)$_2$ (**2c**) was formed within 20 min. After completion of the reaction, the reaction mixture was filtered through celite and washed with THF. After simple workup, Boc-Phe-CH_2-Se-)$_2$ (**2c**) was isolated by column chromatography in 95% yield (Scheme 1). The structure of Boc-Phe-CH_2-Se-)$_2$ (**2c**) was confirmed by mass spectral and NMR spectroscopic analysis [^{1}H NMR δ : 3.16-3.26 (m, 2H, -CH_2-Se-); ^{13}C NMR δ : 34.92 ppm for –CH_2-Se- carbon; ^{77}Se NMR δ 280.00 ppm]. Other selenating reagents such as Li_2Se_2,[14] $(Et_4N)_2WSe_4$[21] and Na_2Se_2[44] were found to be inefficient in affording the Boc-Phe-CH_2-Se-)$_2$ (**2c**) in good yield (Table 1). Moreover Na_2Se_2 is not compatible with Fmoc chemistry and large scale preparation of Li_2Se_2 using super hydride ($Liet_3BH$) is inconvenient due to the formation of pyrophoric byproducts. Preparation of some of these selenating reagents (Table 1, entry 2, 3) also take longer reaction duration.

Table 1 Screening of other selenating reagents for the synthesis of **2c**



Entry	Selenating reagent	Time	Yield (%)
1	Li_2Se_2	2.5 h	62
2	$(Et_4N)_2WSe_4$	70 min	68
3	Na_2Se_2	3 h	55

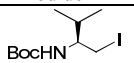
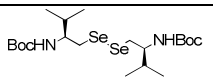
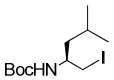
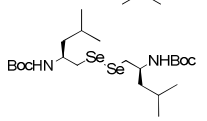
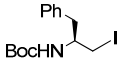
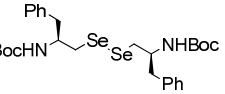
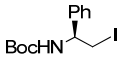
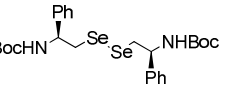
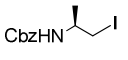
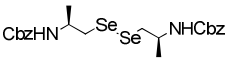
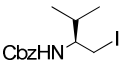
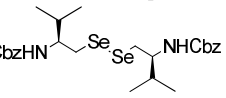
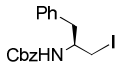
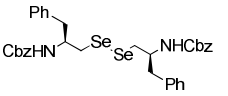
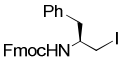
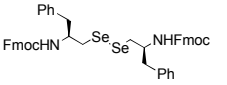
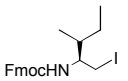
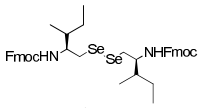
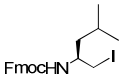
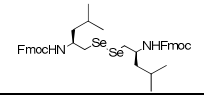
The milder condition, shorter reaction duration (20 min) and the excellent yield obtained in case of **2c** prompted us to examine the scope and generality of the present protocol for the conversion of a series of *N*-protected amino alkyl iodides **1** to the corresponding diselenides **2** (Table 2). The present methodology is an efficient one due to the following attributes: compatibility with the common urethane protecting groups like Boc/Cbz/Fmoc, starting material can be prepared easily, monoselenides and triselenides are not formed as byproducts, simple workup and purification procedure.



Pg = Boc, Cbz or Fmoc group; R = amino acid side chain

Scheme 2 Synthesis of N^{β}-protected amino diselenides **2**

Table 2 List of N^{β}-protected amino diselenides **2**

Entry	Amino alkyl iodide 1	β-Amino diselenide 2	Yield (%)
a			94
b			91
c			95
d			93
e			91
f			92
g			94
h			92
i			94
j			93

Using chiral HPLC, the racemization study of the prepared compounds Fmoc-L-Phe-CH_2-Se)$_2$- **2h** and Fmoc-D-Phe-CH_2-Se)$_2$- **2h*** was analyzed. The retention times were found to be at R_t = 15.45 min for **2h** and R_t = 17.54 min for **2h*** respectively. Intentionally prepared equimolar mixture of **2h** and **2h*** showed distinct peaks at R_t = 15.80 min and R_t = 17.38 min. This confirms that the present protocol is free from racemization.

L-Serine is the most widely used starting material for the synthesis of L-selenocysteine among the amino acids (serine, asparatic acid, glycine, cysteine) employed. The conversion of L-serine to the L-selenocysteine can be achieved directly using

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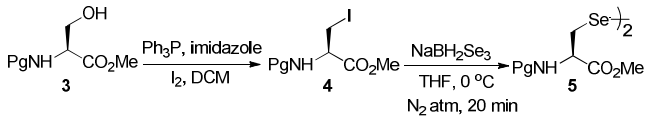
Woollin's reagent but the protocol is restricted to *N*-acetyl protection[45] and the activation through tosylates,[46] halides,[47,48,44] *β*-lactones,[49] or sulfamidates[21] using conventional selenating reagents is also known. But these protocols often suffer from several limitations, which include harsh reaction conditions, longer reaction duration, use of expensive reagents, inseparable byproducts formation, difficulty in workup, incompatibility with base sensitive groups, *etc*. A protocol which circumvents some of the drawbacks associated with reported protocols is desirable for the synthesis of L-selenocysteine from L-serine.

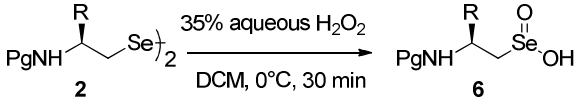
In order to demonstrate the wider scope of this reagent, we investigated $NaBH_2Se_3$ for the synthesis of *N*-protected L-selenocystine methyl ester **5** from *N*-protected L-serine methyl ester **3** through the activation to iodide **4** (Scheme 3). In brief, commercially available *N*-protected L-serine methyl ester **3** was converted to the *N*-protected L-serine iodide methyl ester **4** in excellent yield using imidazole, PPh_3 and I_2.[50] The solution of **4** in THF was then treated with *in situ* generated $NaBH_2Se_3$ to afford the *N*-protected L-selenocystine methyl ester **5** in good yield. Due to the instability and high reactivity of selenol (SeH) functional group, Secys is usually prepared as diselenide, which is reduced[51,52] *in situ* to the selenol when needed. The present methodology is more convenient than existing procedures for the synthesis of *N*-protected L-selenocystine methyl ester **5** from *N*-protected L-serine methyl ester **3**.



Pg = a) Boc (yield: 89%), b) Cbz (yield: 85%), c) Fmoc (yield: 87%)

Scheme 3 Synthesis of *N*-protected L-selenocystine methyl ester **5** from *N*-protected L-serine methyl ester **3**

Since there are no reports on the synthesis of N^{β}-protected amino seleninic acids, in the next part of the work, we concentrated on the synthesis of amino acid derived seleninic acids **6** through the oxidation of the diselenides **2** using mild H_2O_2 (35% aqueous). In a typical study, to a solution of Boc-Phe-CH_2-Se-)$_2$ (**2c**) in DCM at 0° C, 35% aqueous H_2O_2 was added drop wise under vigorous stirring till the completion of reaction (monitored by TLC, reaction mixture became yellow to colorless). After 30 min, Boc-Phe-CH_2-SeO_2H (**6c**) was formed as white precipitate, which was filtered off. A simple recrystalization from ethanol yielded Boc-Phe-CH_2-SeO_2H (**6c**) as white stable solid in 91% (Scheme 4). Other solvents such as MeCN, THF, and 1,4-dioxane were found to be inefficient in affording the desired product **6c** in good yield. The standardized reaction conditions provided all N^{β}-protected amino seleninic acids **6** in good yields (Table 3). The present protocol is more convenient for the synthesis of seleninic acids than reported synthesis from selenoesters and moreover handling of 35% aqueous H_2O_2 is easier than DMDO.[28]



Pg = Boc, Cbz or Fmoc group; R = amino acid side chain

Scheme 4 Synthesis of N^{β}-protected amino seleninic acid **6**

Table 3 List of N^{β}-protected amino seleninic acids **6**

Entry	Pg	R	Yield (%)
a	Boc	$CH(CH_3)_2$	90
b	Boc	$CH_2CH(CH_3)_2$	90
c	Boc	$CH_2C_6H_5$	91
d	Boc	C_6H_5	89
e	Cbz	CH_3	92
f	Cbz	$CH(CH_3)_2$	90
g	Cbz	$CH_2C_6H_5$	92
h	Fmoc	$CH_2C_6H_5$	90
i	Fmoc	$CHCH_3CH_2CH_3$	91

Conclusion

In conclusion, an efficient protocol for the synthesis of *N*-protected L-selenocystine methyl ester, N^{β}-protected amino diselenides employing *in situ* generated $NaBH_2Se_3$ as a selenating reagent from the corresponding amino alkyl iodides is developed. The preparation of $NaBH_2Se_3$ is simple and fast, acts as a good selenating reagent under mild conditions without any undesirable side reaction. The N^{β}-protected amino seleninic acids were also prepared by the oxidation of diselenides with 35% aqueous H_2O_2 at 0 °C. All the diselenides and seleninic acids prepared during the course of these investigations were found to be stable and were characterized by mass spectrometry, and NMR analyses.

Experimental section

General procedure for the synthesis of N^{β}-protected amino diselenides 2, 5

To a solution of sodium borohydride ($NaBH_4$, 10 mmol) in dry THF, black selenium powder (30 mmol) was added at 0 °C under N_2 atmosphere. The consumption of selenium powder in less than 10 min lead to heterogeneous reddish suspension which indicated the formation of $NaBH_2Se_3$. To the resulting $NaBH_2Se_3$ suspension, a THF solution containing N^{α}-protected amino alkyl iodide **1** or **4** (10 mmol) was added drop wise at 0 °C and the stirring was continued for another 20 min. After completion of the reaction (as monitored by TLC), the reaction mixture was filtered through celite, washed with THF and the solvent was removed under reduced pressure. The crude mass was diluted with EtOAc, washed with water (2 x 20 mL), brine (2 x 20 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue **2** or **5** was purified by column chromatography on silica gel with EtOAc/hexane (2:8).

General procedure for the synthesis of N^{β}-protected amino seleninic acids 6

To a solution of N^{β}-protected amino diselenide **2** (10 mmol) in DCM at 0 °C, 35% aqueous H_2O_2 (64 mmol) was added drop wise under vigorous stirring till the completion of reaction (monitored by TLC). The change in color from yellow to colorless indicated the complete consumption of diselenide. After 30 min, the desired product seleninic acid **6** was formed as white precipitate, which was filtered off and recrystalized using ethanol as a solvent. All seleninic acids were isolated as stable solids.

Acknowledgements

We thank the Council of Scientific and Industrial Research

View Article Online
DOI: 10.1039/C5RA06147D

(CSIR), Government of India (No. 02(0149)/13/EMR-II) for the financial assistance. Nageswara Rao Panguluri and Veladi Panduranga are thankful to CSIR for the SRF fellowship.

Notes and References

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Electronic Supplementary Information (ESI) available: [Details of mass spectrometry, ^{1}H, ^{13}C and ^{77}Se NMR spectra of synthesized compounds and chiral HPLC chromatograms are available in supplementary information].

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