SHORT PAPER

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Samarium diiodide induced reductive cleavage of the Se–Se bond in diselenides: a novel synthesis of 3-substituted-imidazolidine-2-one-1-carbonyl selenoesters[†]

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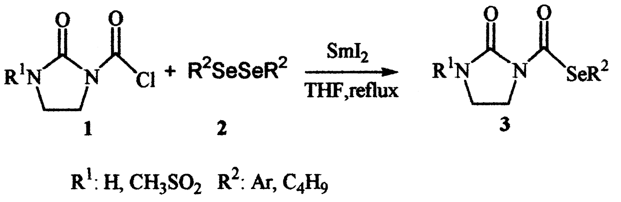
The reduction of diselenides by samarium diiodide led to samarium selenolates ($RSeSmI_2$). These species reacted with 3-substituted-1-chlorocarbonyl-imidazolidin-2-ones to give the corresponding selenoesters in good yields under mild and neutral conditions.

Keywords: samarium diiodide, diselenides, 3-substituted imidazolidine-2-one-1-carbonyl selenoesters

Organoselenium compounds have received considerable attention as useful synthetic reagents and intermediates in organic synthesis.[1] For example, selenoesters are a type of activated esters due to their weak C–Se Bond.[2] They are very useful as mild acyltransfer reagents,[3] building blocks of heterocyclic compounds including oxazoles,[4] lactones and lactams,[5] and precursors of acyl radicals.[6] While several methods for the synthesis of selenoesters have been recommended,[7] the use of selenide anions reacting with acylating agents is especially convenient and common.[8]

As a powerful and versatile electron transfer reducing and coupling agent, SmI_2 has been widely used in organic synthesis,[9] since Kagan reported a simple preparation of samarium diiodide from samarium metal and 1,2-diiodoethane.[10] For example, SmI_2 may reductively cleave Se–Se bonds to generate samarium arylselenolates[9d] which are powerful nucleophilic reagents and may react with appropriate electrophiles such as acyl halides, α,β-unsaturated esters and cyanides to produce the corresponding selenium-containing compounds.[9d,11]

Here we wish to report a convenient synthesis of 3-substituted-imidazolidine-2-one-1-carbonyl selenoesters by the reaction of 3-substituted-1-chlorocarbonyl-imidazolidin-2-ones with samarium selenolates (Scheme 1). These compounds may be difficult to synthesise by other method and we have not seen such a type of compounds reported.



Scheme 1

In our experimental work, it was found that under mild conditions, "R^2SeSmI_2" could be easily prepared from the cleavage of R^2SeSeR^2 with SmI_2 in THF, and it reacted smoothly with 3-substituted-1-chlorocarbonyl-imidazolidin-2-ones to afford a series of new selenoesters. The results are summarised in Table 1.

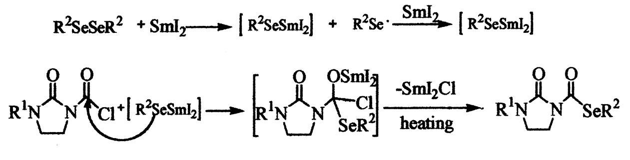
Table 1 shows that diaryl diselenides react with 3-substituted-1-chlorocarbonyl-imidazolidin-2-ones to give the desired selenoesters in good yield, and dialkyl diselenides give the corresponding selenoesters in moderate yields, because the free radical and anion of arylselenolates may be more stable than that of alkylselenolates.

Table 1 Reaction of diselenides with 3-substituted-1-chlorocarbonyl-imidazolidin-2-ones promoted by SmI_2[a]

Product	R^1	R^2	T/h	Yields/%[b]
3a	H	C_6H_5-	4	79
3b	H	$C_{10}H_7$-	3	81
3c	H	p-ClC_6H_4-	3	86
3d	H	p-$OCH_3C_6H_4$	5	80
3e	H	m-$CH_3C_6H_4$-	6	76
3f	H	C_4H_9-	8	66
3g	CH_3SO_2	C_6H_5-	4	80
3h	CH_3SO_2	$C_{10}H_7$-	3	82
3i	CH_3SO_2	C_4H_9-	8	67

[a]1 equiv. diselenide, 2 equiv. 3-substituted-1-chlorocarbonyl-imidazolidin-2-ones and 2.2 equiv. SmI_2 were used. [b]Isolated yield based on diselenide.

The possible mechanism is presented in Scheme 2.



Scheme 2

In a stepwise proces, electron transfer from SmI_2 generates "SmI_2^+" and "RSe·" radicals which combine to give the active intermediate "$RSeSmI_2$". 3-Substituted-1-chlorocarbonyl-imidazolidin-2-ones undergoes nucleophilic attack by "$RSeSmI_2$" at reflux temperature to give the corresponding products 3.

In summary, the intermolecular reductive reaction of diselenides and N-carbonyl chlorides by samarium diiodide was studied and a facile synthesis of 3-substituted-imidazolidine-2-one-1-carbonyl selenoesters has been provided for the first time.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Experimental

Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use. All reactions were carried on under a dry dinitrogen atmosphere. Melting points were uncorrected. Infrared spectra were recorded on a Bruker Vector 22 spectrometer in KBr with absorption in cm^{-1}. ^{1}H NMR spectra were recorded on a Bruker AC-80 spectrometer as DMSO solutions. *J* values are in Hz. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Mass spectra were recorded on a HP 5989B MS spectrometer. Microanalysis was carried out on a Carlo-Erba 1106 instrument.

3-substituted-1-chlorocarbonyl-imidazolidin-2-ones were prepared according to ref. 12.

General procedure: A solution of diselenide (1 mmol) in THF (1 ml) was added by syringe to a deep blue solution of SmI_2 (2.2 mmol) in THF (20 ml) at room temperature under a dry dinitrogen atmosphere. The deep blue colour of the solution soon became brown within a few minutes, and the solution was stirred for 1h. To the mixture N-carbonyl chlorides was added, then stirred at reflux temperature for a given time. The reaction mixture was quenched with dilute HC1 (0.1M) and extracted with ethyl acetate (3×0ml). The crude product was isolated in the usual way and purified by preparative thin layer chromatography using ethyl acetate and cyclohexane (1:1) as eluent.

Compound **3a**: m.p. 148–150°C; ν_{max}/cm^{-1} 3240, 3125, 2907, 1734, 1668, 1478, 1402, 1335, 1273, 1065, 1020, 978, 887, 747. δ_H 3.36 (t, *J* 10.2, 2H), 3.75–3.95 (m, 2H), 7.32–7.53 (m, 5H), 7.94 (br s, 1H). *m*/*z* (%) 270 (M$^+$, 27), 193 (9), 158 (100), 113 (52), 78 (54), 70 (89). (Found: C, 44.50; H, 3.88; N, 10.49. $C_{10}H_{10}N_2O_2Se$ requires C, 44.62; H, 3.74; N, 10.41%).

Compound **3b**: m.p. 195–197°C; ν_{max}/cm^{-1} 3239, 3130, 2910, 1739, 1677, 1475, 1406, 1335, 1077, 893, 798, 775, 750. δ_H 3.35 (t, *J* 11.5, 2H), 3.73–3.83 (m, 2H), 7.50–7.91 (m, 7H), 8.00 (br s, 1H). *m*/*z* (%) 320 (M$^+$, 11), 208 (60), 128 (100), 115 (33), 70 (13). (Found: C, 52.53; H, 3.92; N, 8.87. $C_{14}H_{12}N_2O_2Se$ requires C, 52.68; H, 3.79; N, 8.78%).

Compound **3c**: m.p. 179–180°C; ν_{max}/cm^{-1} 3225, 3132, 2906, 1738, 1673, 1473, 1405, 1340, 1280, 1087, 1012, 891, 816. δ_H 3.40 (t, *J* 8.0, 2H), 3.76–3.97 (m, 2H), 7.32–7.60 (m, 4H), 7.99 (br.s, 1H). *m*/*z* (%) 306 (C1-M$^+$, 5.1), 304 (C1-M$^+$, 12.2), 192 (67), 190 (33), 156 (18), 113 (65), 70 (100). (Found: C, 39.71; H, 2.85; N, 11.57. $C_{10}H_9ClN_2O_2Se$ requires C, 39.56; H, 2.99; N, 11.68%).

Compound **3d**: m.p. 179–181°C; ν_{max}/cm^{-1} 3250, 3133, 2974, 2909, 1722, 1685, 1590, 1494, 1401, 1331, 1248, 1177, 1072, 1020, 891, 823. δ_H 3.38 (t, *J* 8.5, 2H), 3.77–3.97 (m, 5H), 6.98 (d, *J* 8.7, 2H), 7.37 (d, *J* 8.7, 2H), 7.92 (br s, 1H). *m*/*z* (%) 300 (M$^+$, 19), 188 (63), 172 (8), 113 (18), 108 (100), 70 (45). (Found: C, 44.03; H, 4.14; N, 9.48. $C_{11}H_{12}N_2O_3Se$ requires C, 44.16; H, 4.04; N, 9.36%).

Compound **3e**: m.p. 135–137°C; ν_{max}/cm^{-1} 3261, 3137, 3049, 2981, 2906, 1736, 1674, 1478, 1402, 1283, 1069, 890, 753, 697. δ_H 2,36 (s, 3H), 3.49 (t, *J* 8.5, 2H), 3.75–3.94 (m, 2H), 7.19–7.35 (m, 4H), 7.93 (br s, 1H). *m*/*z* (%) 284 (M$^+$, 19), 172 (74), 113 (27), 91 (100), 70 (65). (Found: C, 46.80; H, 4.16; N, 9.76 $C_{11}H_{12}N_2O_2Se$ requires C, 46.65; H, 4.27; N. 9.89%).

Compound **3f**: m.p. 89–91°C; ν_{max}/cm^{-1} 3266, 3122, 2956, 2871, 1709, 1662, 1490, 1411, 1286, 1162, 1068, 898, 702. δ_H 0.88 (t, *J* 6.5, 3H), 1.20–1.58 (m, 4H), 2.73 (t, *J* 7.1, 2H), 3.36 (t, *J* 8.0, 2H), 3.76–3.98 (m, 2H), 7.77 (br s, 1H). *m*/*z* (%) 250 (M$^+$, 17), 192 (12), 138 (37), 113 (100), 70 (97), 57 (76). (Found: C, 38.45; H, 5.73; N, 11.33 $C_8H_{14}N_2O_2Se$ requires C, 38.56; H, 5.66; N, 11.24%).

Compound **3g**: m.p. 189–190°C; ν_{max}/cm^{-1} 3015, 2933, 1740, 1672, 1480, 1367, 1276, 1244, 1177, 1124, 973, 766, 749, 710, 695. δ_H 3.36 (s, 3H), 3.89–3.95 (m, 4H), 7.40–7.69 (m, 5H); *m*/*z* (%) 348 (M$^+$, 12), 191 (70), 157 (33), 127 (11), 79 (100). (Found: C, 37.94; H, 3.60; N, 8.15 $C_{11}H_{12}N_2O_4SSe$ requires C, 38.05; H, 3.48; N, 8.07%).

Compound **3h**: m.p. 183–185°C; ν_{max}/cm^{-1} 3024, 2927, 1744, 1670, 1473, 1386, 1358, 1251, 1170, 1121, 968, 797, 768, 704. δ_H 3.36 (s, 3H), 3.86–4.02 (m, 4H), 7.53–7.64 (m, 3H), 7.86–8.14 (m, 4H). *m*/*z* (%) 3.98 (M$^+$, 25), 207 (54), 191 (68), 127 (19), 115 (78), 79 (100). (Found: C, 45.20; H, 3.69; N, 7.16 $C_{15}H_{14}N_2O_4SSe$ requires C, 45.35; H, 3.55; N, 7.05%).

Compound **3i**: m.p. 153–154°C; ν_{max}/cm^{-1} 3022, 2957, 2871, 1732, 1661, 1470, 1396, 1349, 1321, 1278, 1160, 1134, 980, 772, 707, 554. δ_H 0.93 (t, *J* 6.5, 3H), 1.20–1.93 (m, 4H), 2.93 (t, *J* 7.0, 2H), 3.35 (s, 3H), 3.92–4.00 (m, 4H). *m*/*z* (%) 328 (M$^+$, 8), 191 (68), 127 (14), 113 (12), 79 (100) 57 (11). (Found: C, 33.18; H, 4.98; N, 8.91 $C_9H_{16}N_2O_4SSe$ requires C, 33.03; H, 4.93; N. 8.78%).

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