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Indium(I) iodide mediated efficient synthesis of selenoglycosides☆

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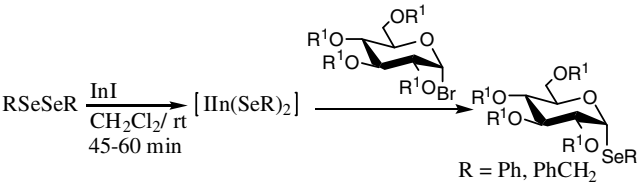
Abstract—A convenient odorless methodology has been developed for the preparation of selenoglycosides through indium(I) iodide mediated cleavage of diselenides and reaction with glycosyl bromides. The yields were excellent in all cases. Retention of the configuration at the anomeric center was observed in each case.

Selenoglycosides have been used widely in biochemical and structural investigations of glycosidases due to the fact that naturally occurring O-glycosides are not hydrolytically stable to the action of glycohydrolase enzymes.[1,2] Selenoglycosides have found many applications in the field of carbohydrate chemistry as very effective and stable glycosyl donors.[3–5] Selenoglycosides can be selectively activated in the presence of thioglycosides, which make them attractive in oligosaccharide synthesis.[6] They are also useful intermediates for the preparation of functionalized glycals, C-glycosides and glycoconjugates, etc.[5,7–9] The ongoing progress in the syntheses of complex oligosaccharides has been closely related with the development of newer glycosylation methods exploiting selenoglycosides as glycosyl donors. In general, selenoglycosides are prepared by treating halides with selenium under sodium borohydride reduction conditions[10,11] or by treating a glycosyl acetate with an arylselenol derived from the hypophosphorus acid reduction of diphenyl diselenide in the presence of $BF_3{\cdot}OEt_2$.[12–14] In both cases, there are several drawbacks including the use of obnoxious reagents and incompatibility of base-labile protecting groups under sodium borohydride reduction conditions. Therefore, there is a need to develop an odorless and convenient protocol for the preparation of selenoglycosides.

In the past, indium metal and its salts have been used in various novel rearrangements, C–C bond formations and many other useful organic transformations.[15] In a recent report, indium(I) iodide was applied successfully for the rapid preparation of unsymmetrical diorganyl selenides via cleavage of diphenyl diselenide.[16] We envisioned the use of indium(I) iodide for the cleavage of diaryl diselenides followed by reaction of the selenide anions formed in situ with a glycosyl bromide to produce selenoglycosides, avoiding the use of any malodorous reagent. In this letter, we disclose a very rapid preparation of selenoglycosides using diaryl diselenides mediated by indium(I) iodide (Scheme 1).

In a first set of experiments, indium(I) iodide (0.5 equiv) was added to a mixture of diphenyl diselenide (1.0 equiv) and acetobromo-D-glucose (2.0 equiv) in CH_2Cl_2 at room temperature. To our satisfaction, the reaction proceeded rapidly to furnish the required phenylselenoglycoside. Reducing the quantity of indium(I) iodide led to an incomplete reaction, even after 24 h. Our results with a variety of glycosyl bromides for the formation of selenoglycosides are listed in Table 1. The use of CH_3CN or $CHCl_3$ did not affect the yield of the product. A typical experimental procedure is as follows: to a solution of diphenyl diselenide (312 mg, 1.0 mmol) and per-O-acetylated glycosyl bromide (2.0 mmol) in CH_2Cl_2 (5.0 ml) was



Scheme 1.

Keywords: Carbohydrate; Cleavage reactions; Selenoglycosides; Organometallics; Indium(I) iodide.
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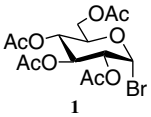
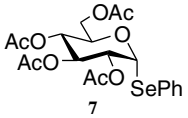
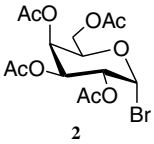
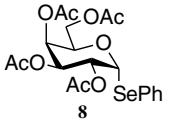
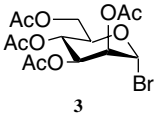
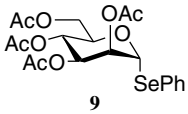
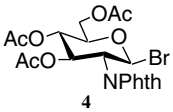
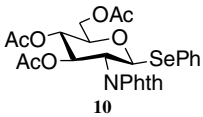
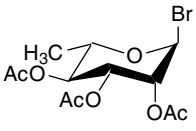
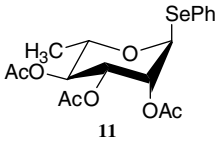
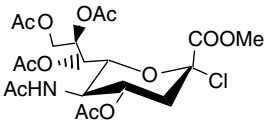
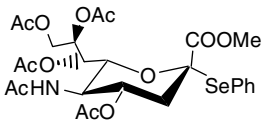
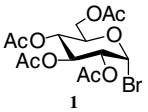
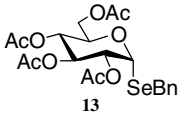
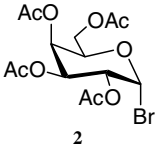
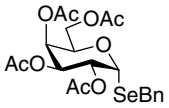
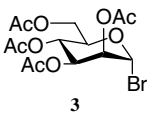
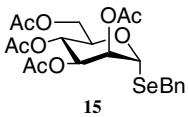
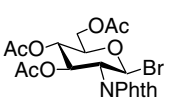
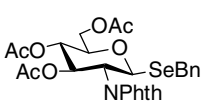
Table 1. Indium iodide mediated cleavage of diselenides and their reaction with glycosyl bromides in the formation of selenoglycosides

Entry	Dichalconides	Glycosyl halides	Products	Time (min)	Yield[a] (%)	Ref.
1	PhSeSePh	 **1**	 **7**	45	92	—
2	PhSeSePh	 **2**	 **8**	45	90	—
3	PhSeSePh	 **3**	 **9**	40	90	4
4	PhSeSePh	 **4**	 **10**	45	88	7
5	PhSeSePh	 **5**	 **11**	40	85	7
6	PhSeSePh	 **6**	 **12**	50	58[b]	17
7	BnSeSeBn	 **1**	 **13**	60	80	—
8	BnSeSeBn	 **2**	 **14**	60	85	—
9	BnSeSeBn	 **3**	 **15**	60	90	—
10	BnSeSeBn	 **4**	 **16**	60	88	—

[a] Isolated yield.
[b] Together with some glycal (~30%).

added InI (121 mg, 0.5 mmol) and the reaction mixture was stirred at room temperature for appropriate time (Table 1). After completion of the reaction (TLC; hexane–EtOAc 1:1), the reaction mixture was diluted with CH_2Cl_2 (20.0 ml). The organic layer was washed with aq $NaHCO_3$ and water successively, then dried (Na_2SO_4) and evaporated to dryness. The crude products were purified over SiO_2 using hexane–EtOAc (8:1) as eluant to furnish pure phenylselenoglycoside, as confirmed from NMR and mass spectra.[18] Known compounds gave

^{1}H NMR and ^{13}C NMR spectra that matched the data reported in the cited references. The reaction protocol is equally effective for the cleavage of dibenzyl diselenide. It is noteworthy that retention of configuration at the anomeric center was observed in every case, which may be due to the fact that the glycosylselenide formation proceeds through a free radical mechanism as in the case of samarium mediated C–C bond formation.[19] To the best of our knowledge, exclusive formation of 1,2-*cis*-selenoglycosides has not been reported earlier.

In summary, an odorless methodology has been developed for the exclusive preparation of a series of 1,2-*cis*-selenoglycosides through indium(I) iodide mediated reduction of diorganyl diselenides followed by reaction with glycosyl halides. Fast, stereoselective formation of selenoglycosides without formation of anomerized products, avoiding the use of obnoxious selenols under a neutral reaction conditions makes this protocol superior to the existing methodologies in this area.

Acknowledgements

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16. (a) Ranu, B. C.; Mandal, T.; Samanta, S. *Org. Lett.* **2003**, *5*, 1439–1441; (b) Ranu, B. C.; Mandal, T. *Synlett* **2004**, 1239–1242.
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18. Spectral data of compounds not previously reported:
Phenyl 2,3,4,6-tetra-O-acetyl-1-seleno-α-D-gluco-pyranoside (**7**): Yellow oil; $[\alpha]_D^{25}$ +28.3 (*c* 1.0, $CHCl_3$); IR (neat): 2926, 2364, 1750, 1655, 1434, 1369, 1224, 1046, 769 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.53–7.43 (m, 2H, aromatic protons), 7.23–7.15 (m, 3H, aromatic protons), 6.12 (d, $J = 5.6$ Hz, 1H, H-1), 5.25 (t, $J = 9.5$ Hz, 1H, H-3), 4.99–4.91 (m, 2H, H-2 and H-4), 4.38 (dd, $J = 12.2$ and 5.0 Hz, 1H, H-6$_a$), 4.20 (dd, $J = 12.2$ and 5.0 Hz, 1H, H-6$_b$), 3.89–3.88 (m, 1H, H-5), 2.03, 1.98, 1.96, 1.94 (4s, 12H, 4COCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.6 (2C), 170.2, 169.8, 131.9 (2C), 129.5 (2C), 129.3, 128.0, 81.2, 74.2, 71.2, 70.2, 68.5, 62.3, 21.1 (2C), 21.0 (2C), 20.9; ESI-MS: $m/z = 511$ [M+Na]. Anal. Calcd for $C_{20}H_{24}O_9Se$ (488): C, 49.29; H, 4.96. Found: C, 49.05; H, 5.12.
Phenyl 2,3,4,6-tetra-O-acetyl-1-seleno-α-D-galacto-pyranoside (**8**): Yellow oil; $[\alpha]_D^{25}$ +72.3 (*c* 1.0, $CHCl_3$); IR (neat): 2926, 1748, 1654, 1370, 1225, 1052, 771 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.56–7.52 (m, 2H, aromatic protons), 7.24–7.16 (m, 3H, aromatic protons), 5.29 (d, $J = 2.0$ Hz, 1H, H-1), 5.14 (t, $J = 9.9$ Hz, 1H, H-2), 4.90 (dd, $J = 9.8$ and 3.2 Hz, 1H, H-3), 4.80 (br s, 1H, H-4), 4.06–3.96 (m, 2H, H-6$_{ab}$), 3.85–3.79 (m, 1H, H-5), 2.01 (s, 6H, 2COCH_3), 1.98, 1.97 (2s, 6H, 2COCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.0 (2C), 169.8, 169.2, 135.5–127.8 (aromatic carbons), 81.9, 75.8, 72.1, 68.4, 67.5, 61.7, 21.1 (2C), 20.8 (2C); ESI-MS: $m/z = 511$ [M+Na]. Anal. Calcd for $C_{20}H_{24}O_9Se$ (488): C, 49.29; H, 4.96. Found: C, 49.08; H, 5.15.
Benzyl 2,3,4,6-tetra-O-acetyl-1-seleno-α-D-gluco-pyranoside (**13**): Yellow oil; $[\alpha]_D^{25}$ +74.6 (*c* 1.0, $CHCl_3$); IR (neat): 2930, 1751, 1432, 1370, 1225, 1041, 910, 759 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.33–7.25 (m, 5H, aromatic protons), 5.87 (d, $J = 5.7$ Hz, 1H, H-1), 5.28 (t, $J = 9.5$ Hz, 1H, H-3), 5.01 (t, $J = 9.5$ Hz, 1H, H-2) 4.94 (dd, $J = 9.9$ and 5.7 Hz, 1H, H-4), 4.34–4.19 (m, 2H, H-5, H-6$_a$), 3.92–3.86 (m, 1H, H-6$_b$), 3.75 (q, $J = 12$ Hz, 2H, SeCH_2Ph), 2.08, 2.02 (2s, 6H,2COCH_3) 1.99 (s, 6H, 2COCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1 (2C), 169.9, 169.6, 129.2 (2C), 129.0, 128.9 (3C), 78.8, 76.3, 71.7, 71.2, 69.8, 68.6, 26.6, 21.0 (2C), 20.9 (2C), 20.9; ESI-MS: $m/z = 525$ [M+Na]. Anal. Calcd for $C_{21}H_{26}O_9Se$ (502): C, 50.31; H, 5.23. Found: C, 50.10; H, 5.50.
Benzyl 2,3,4,6-tetra-O-acetyl-1-seleno-α-D-galacto-pyranoside (**14**): Yellow oil; $[\alpha]_D^{25}$ +92.3 (*c* 1.0, $CHCl_3$); IR (neat): 2927, 1748, 1454, 1370, 1223, 1060, 913, 766 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.33–7.22 (m, 5H, aromatic protons), 5.91 (br s, 1H, H-3), 5.44 (br s, 1H, H-1), 5.17 (br s, 2H, H-2 and H-4), 4.56–4.51 (m, 1H, H-5) 4.15–4.04 (m, 2H, H-6$_{ab}$), 3.80–3.69 (m, 2H, SeCH_2Ph), 2.14, 2.05, 2.00, 1.98 (4s, 12H, 4COCH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.1, 170.0 169.8, (2C), 128.9, 128.8 (2C), 128.6 (2C), 126.9, 78.3, 69.1, 68.3, 68.0, 67.5, 61.6, 25.7, 20.5 (2C), 20.4 (2C); ESI-MS: $m/z = 525$ [M+Na]. Anal. Calcd for $C_{21}H_{26}O_9Se$ (502): C, 50.31; H, 5.23. Found: C, 50.08; H, 5.52.
Benzyl 2,3,4,6-tetra-O-acetyl-1-seleno-α-D-manno-pyranoside (**15**): Oil; $[\alpha]_D^{25}$ +126.8 (*c* 1.0, $CHCl_3$); IR (neat): 2972, 2362, 1742, 1598, 1373, 1246, 1107, 1050, 977, 756 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.28–7.09 (m, 5H, aromatic protons), 5.35 (br s, 1H, H-2), 5.24 (br s, 1H, H-1), 5.20–5.16 (m, 2H, H-3 and H-4), 4.24–4.20 (m, 2H, H-6$_{ab}$), 3.91–3.85 (m, 1H, H-5) 3.75 (q, $J = 12.0$ Hz, 2H, SeCH_2Ph), 2.07, 2.03, 1.98, 1.90 (4s, 12H, 4COCH_3); ^{13}C

NMR (50 MHz, $CDCl_3$): δ 170.2, 169.4 (2C), 169.3, 137.6, 128.6 (2C), 128.3 (2C), 126.8, 77.3, 70.8, 70.3, 69.7, 65.8, 61.8, 27.4, 20.5, 20.4, 20.3, 20.2; ESI-MS: $m/z = 525$ [M+Na]. Anal. Calcd for $C_{21}H_{26}O_9Se$ (502): C, 50.31; H, 5.23. Found: C, 50.10; H, 5.50.

Benzyl 3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-1-seleno-β-D-glucopyranoside (**16**): Yellow oil; $[\alpha]_D^{25}$ +4.6 (*c* 1.0, $CHCl_3$); IR (neat): 2929, 1724, 1378, 1218, 1077, 767 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 7.86–7.72 (m, 4H, aromatic protons), 7.36–7.23 (m, 5H, aromatic protons), 5.79 (t, $J = 9.9$ Hz, 1H, H-3), 5.55 (d, $J = 10.8$ Hz, 1H, H-1), 5.18 (t, $J = 9.9$ Hz, 1H, H-4), 4.50 (t, $J = 10.5$ Hz, 1H, H-3), 4.30 (dd, $J = 12.3$ and 4.8 Hz, 1H, $H\text{-}6_a$), 4.12 (dd, $J = 12.3$ and 2.1 Hz, 1H, $H\text{-}6_b$) 3.95 (q, $J = 11.6$ Hz, 2H, $SeCH_2Ph$), 3.75–3.72 (m, 1H, H-5), 2.12, 2.05, 1.87 (3s, 9H, 3 $COCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ 170.7, 170.1, 169.5, 166.5 (2C), 136.9, 134.3, 132.5, 130.9, 129.8, 129.0 (2C), 128.5 (2C), 126.7, 123.7 (2C), 77.2, 75.8, 71.3, 68.8, 62.2, 54.4, 26.9, 20.8, 20.6, 20.4; ESI-MS: $m/z = 612$ [M+Na]. Anal. Calcd for $C_{27}H_{27}NO_9Se$ (589): C, 55.11; H, 4.62. Found: C, 54.90; H, 4.75.

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