Highly Efficient Route to Diselenides from the Reactions of Imines and Selenium in the Presence of Carbon Monoxide and Water

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Abstract: Reactions of selenium with imines ($RR^1C{=}NR^2$) of aldehydes and ketones in the presence of carbon monoxide, water and triethylamine lead to reductive selenation, on aerobic work-up, to afford symmetrical diselenides $(RR^1CHSe)_2$ in good to excellent yields. The proposed mechanism suggests that both *in situ* generated carbonyl selenide (SeCO) and hydrogen selenide (H_2Se) are involved in the reaction.

Keywords: carbon monoxide; diselenation; diselenides; imines; selenium

Introduction

Organoselenium chemistry has attracted considerable attention in the past decades due to its important role in the construction of bioactive compounds and applications in organic synthesis and catalysis.[1] Symmetrical diselenides (RSeSeR) are versatile synthetic reagents and potential medical agents.[2] Nucleophilic reactions of metal diselenides such as Na_2Se_2,[3] and Li_2Se_2[4] with halides or treatment of selenium with strong bases followed by reactions with halides[5] gave diselenides. Organic selenocyanates,[6] $(Et_4N)_2WSe_4$,[7] and selenoamides[8] were also successfully applied for this purpose. Both reduction of di-*t*-butyl selenoketone with $NaBH_4$[9] and reaction of benzaldehyde with bis(1,5-cyclooctanediylboryl)[10] produced RSeSeR. Oxidation of selenols with 30% hydrogen peroxide[11] and reduction of aldehydes and ketones with hydrogen selenide[12,13] in the presence of an amine afforded diselenides. Sonoda et al. used the Se/CO/H_2O system for the preparation of diselenides from a very limited number of aliphatic ketones and aldehydes,[14] or acyl chlorides[15] under rather harsh conditions, while aromatic ketones were reduced to hydrocarbons with the same method.[16]

Recently, we reported the synthesis of symmetrical diselenides from aldehydes by means of a modified Se/CO/H_2O system.[17] However, although the number of substrates was extended the modified procedure has been shown limitations such as: (1) diselenides from chloro- or dimethylamino-substituted aromatic aldehydes were only obtained in low yields (36–45%); (2) *trans*-cinnamaldehyde and 2-furaldehyde gave complex mixtures of products; and (3) no selenation reaction occurred for ketones and hydroxy-substituded aromatic aldehydes; (4) yields for some diselenides were only low to moderate. Keeping in mind that reductive selenation is very sensitive to the structural and electronic properties of the substrates, we investigated reactions of imines in the Se/CO/H_2O system. Herein, we report a highly efficient general route to symmetrical diselenides by reactions of selenium with imines of aldehydes or ketones in the presence of carbon monoxide and water.

Results and Discussion

The reaction of benzaldehyde with 1.0 equivalent of selenium in THF at 100 °C in the presence of CO (3.0 MPa), water and Et_3N for 3 h afforded, on aerobic work-up, dibenzyl diselenide (**2a**) in 84% yield (Table 1, Run 2), while the reaction of the isopropylimine of benzaldehyde, i.e., **1a**, gave **2a** in 96% yield (Table 1, Run 4). THF is a better reaction solvent than toluene for the reaction (Table 1, Runs 1–4). The results listed in Table 1 (Runs 1–4) demonstrate that the imine is more reactive than its parent aldehyde in the reductive selenation. The reductive selenation of **1a** even proceeded at room tem-

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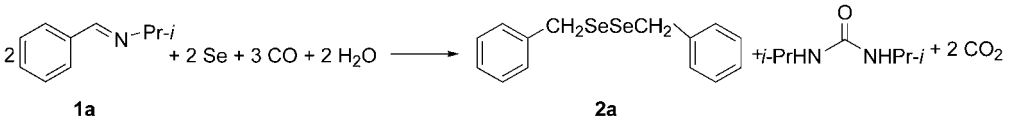
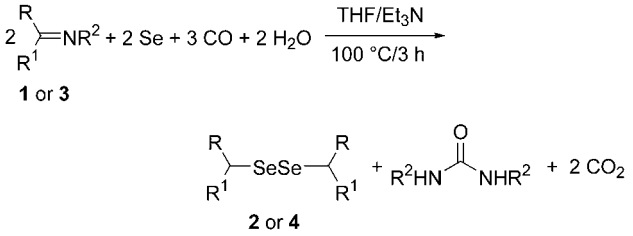
Table 1. Preparation of $(PhCH_2Se)_2$ (**2a**) from **1a**.



Run[a]	Substrate	Solvent	Temperature [°C]	Time [h]	Yield[b] [%]
1	PhCHO	toluene	100	5	43
2	PhCHO	THF	100	3	84
3	PhCH=NPr-*i* (**1a**)	toluene	100	5	84
4	**1a**	THF	100	3	96
5	**1a**	THF	80	3	92
6	**1a**	THF	rt	5	36
7[c]	**1a**	THF	100	3	92

[a] Reaction conditions: substrate, 3 mmol; Se, 3 mmol; CO, 3 MPa; Et_3N, 3 mmol; H_2O, 30 mmol; solvent, 10 mL.
[b] Yields of isolated products.
[c] No base.



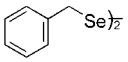
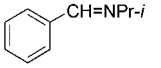
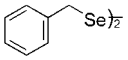
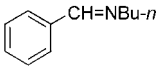
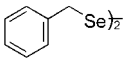
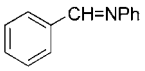
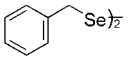
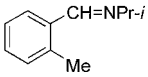
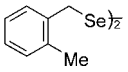
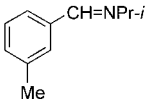
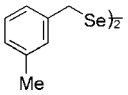
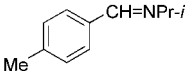
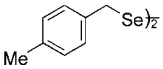
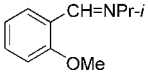
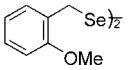
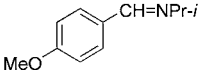
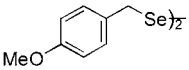
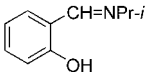
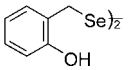
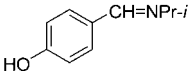
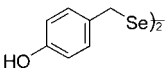
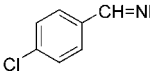
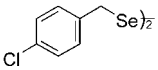
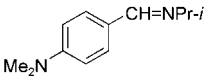
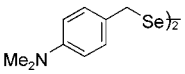
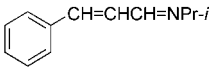
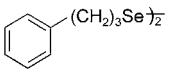
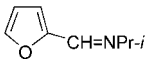
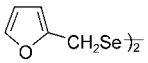
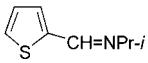
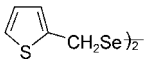
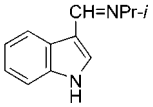
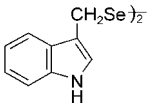
Scheme 1.

perature to give **2a** in 36% yield over a period of 5 hours (Table 1, Run 6), but **2a** could be obtained in much higher yields at elevated temperatures (80 °C, 92%; 100 °C, 96%). The presence of a base is necessary for complete conversion of the imine and a high yield of the diselenide. A base, i.e., an amine, has been suggested to stabilize the *in situ* generated SeCO species during the reaction.[12,13] Selection of the base was not critical and thus triethylamine was used in the reaction although **2a** was obtained in 92% yield without use of a base (Table 1, Run 7). A symmetrical urea, i.e., $(i\text{-PrNH})_2CO$, as the other product, could be isolated in >50% yields.

In a similar fashion, the reductive selenation of imines of aromatic aldehydes **1a**–**l** afforded diselenides **2a**–**j** in 92–99% yields (Table 2, Runs 2–13). For example, **2a** was obtained from **1a**–**c** in 95–98% yields, and bis(4-methylbenzyl) diselenide (**2d**) was isolated in 99% yield. Steric effects of the substituents only slightly affect the yields of the diselenides. Amazingly, imines of hydroxy-substituted aromatic aldehydes, i.e., **1i** and **1j**, gave the corresponding diselenides **2g** and **2h** in 92% and 96% yields, respectively (Table 1, Runs 10 and 11), while their parent aldehydes did not undergo the same type of selenation.[17] Imines of both chloro- and dimethylamino-substituted aromatic aldehydes **1k** and **1l** gave diselenides **2i** and **2j** in 93% yield, respectively, demonstrating a dramatic increase of the product yields as compared with the reported results, i.e., 36% for **2i** and 45% for **2j** from the corresponding aldehydes.[17] The isopropylimine of cinnamaldehye (**1m**) gave diselenide **2k** in 57% yield with its α,β-unsaturated carbon-carbon double bond being reduced by *in situ* generated H_2Se[18] (Table 2, Run 14). Heteroaromatic aldimines **1n**–**p** also afforded diselenides in good yields (81–85%). When the same methodology was applied to imines of aliphatic aldehydes, i.e., **1q**–**t**, good to excellent yields (89–97%) were achieved for the diselenide products (Table 2, Runs 18–21). Dibutyl diselenide was obtained in 97% yield, which is comparable with the result from the reduction of butyl selenocyanate with $LiEt_3BH$,[6a] and much higher than those by other procedures (45%[14] and 54%[17]) from aldehydes using the $Se/CO/H_2O$ system. It is worthy of note that isopropylamine was used to prepare aldimines due to its easy manipulations. *n*-Butylamine and aniline were used to prepare ketimines as described below because isopropylamine was not efficient for the stated ketimine synthesis.

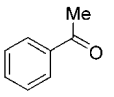
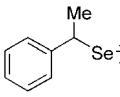
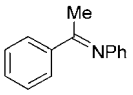
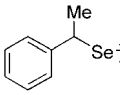
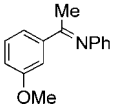
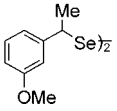
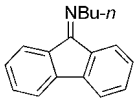
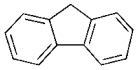
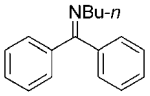
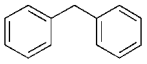
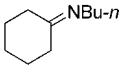
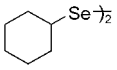
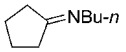
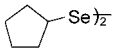
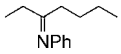
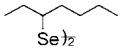
Acetophenone did not undergo selenation as aldehydes and aldimines did to form the diselenide, i.e., **4a**, and only a trace amount of ethylbenzene was detected in its reaction mixture with selenium by GC-MS analysis (Table 3, Run 1). However, the phenylimine of acetophenone (**3a**) afforded diselenide **4a** in 95% yield, and imine **3b**, i.e., the phenylimine of 3-methoxyacetophenone, gave diselenide **4b** in 91% yield (Table 3, Runs 2 and 3). Butylimines of 9-fluorenone and benzophenone, i.e., **3c** and **3d**, were reduced to hydrocarbons, i.e., 9-fluorene (91%) and diphenylmethane (79%), respectively, which is in accordance with the observation for aromatic ketones under similar conditions.[16] Imines of aliphatic cyclic and acyclic ketones, i.e., **3e**–**h**, were easily transformed into diselenides **4c**–**f** in 85–94% yields (Table 3, Runs 6–9). It is noteworthy that the present work demonstrates a much wider reaction scope and much higher

Table 2. Diselenation of aldimines **1** to diselenides **2**.

Run[a]	Aldimine		Diselenide		Yield[b] [%]
	[RCH=NR^2]	No.	[(RCH$_2$Se)$_2$]	No.	
1	PhCHO			**2a**	84
2[c]		**1a**		**2a**	98
3		**1b**		**2a**	95
4		**1c**		**2a**	98
5		**1d**		**2b**	97
6		**1e**		**2c**	97
7		**1f**		**2d**	99
8		**1g**		**2e**	94
9		**1h**		**2f**	96
10		**1i**		**2g**	92
11		**1j**		**2h**	96
12		**1k**		**2i**	93
13		**1l**		**2j**	93
14		**1m**		**2k**	57 (–)[19]
15		**1n**		**2l**	82
16		**1o**		**2m**	81
17		**1p**		**2n**	85 (–)[20]
18	*n*-PrCH=NPr-*i*	**1q**	(*n*-PrCH$_2$Se)$_2$	**2o**	97
19	*i*-BuCH=NPr-*i*	**1r**	(*i*-BuCH$_2$Se)$_2$	**2p**	89
20	*n*-C$_7$H$_{15}$CH=NPr-*i*	**1s**	(*n*-C$_7$H$_{15}$CH$_2$Se)$_2$	**2q**	90
21	*n*-C$_{11}$H$_{23}$CH=NPr-*i*	**1t**	(*n*-C$_{11}$H$_{23}$CH$_2$Se)$_2$	**2r**	93

[a] Reaction conditions: aldimine, 3 mmol; Se, 3 mmol; CO, 3 MPa, Et_3N, 3 mmol; H_2O, 30 mmol; THF, 10 mL; 100 °C; 3 h.
[b] Yield of isolated product.
[c] 2 h.

Table 3. Diselenation of ketimines **3** to diselenides **4**.

Run[a]	Ketimine [$RR^1C{=}NR^2$]	No.	Product	No.	Yield[b] [%]
1				**4a**	–
2		**3a**		**4a**	95
3		**3b**		**4b**	91
4		**3c**			91
5		**3d**			79
6		**3e**		**4c**	94
7		**3f**		**4d**	88
8		**3g**		**4e**	85
9		**3h**		**4f**	87

[a] Reaction conditions: ketimine, 3 mmol; Se, 3 mmol; CO, 3 MPa; Et_3N, 3 mmol; H_2O, 30 mmol; THF, 10 mL; 100 °C; 3 h.
[b] Isolated yield.

efficiency under much milder reaction conditions such as lower reaction temperature and/or shorter reaction time than the known procedures using Se/CO/H_2O as the reducing agent.[14,17]

Carbon monoxide/water can be used as a reducing agent in the presence of selenium.[21] Selenium can also be used as a carbonylation catalyst for the synthesis of ureas from nitroaromatics, amines or anilines.[22] A reaction mechanism is proposed for the diselenation of imines as shown in Figure 1. Selenium reacts with CO to form carbonyl selenide (SeCO) which further interacts with water, resulting in hydrogen selenide (H_2Se). Addition of H_2Se to imine gives 2-amino selenol **A** from which are formed selone **B** and an amine. The amine then undergoes selenium-catalyzed carbonylation, that is, reacting with SeCO species generated *in situ* by the reaction of CO and selenium, to afford the symmetrical urea **E** and selenium,[22] which was evidenced by the isolation of diisopropylurea. Selone **B** reacts with another equivalent of H_2Se or is nucleophilically attacked by HSe^- generated *in situ* to form diselenol **C** which is then decomposed to selenium and selenol **D**. Upon aerobic work-up **D** is oxidized to the symmetrical diselenide.

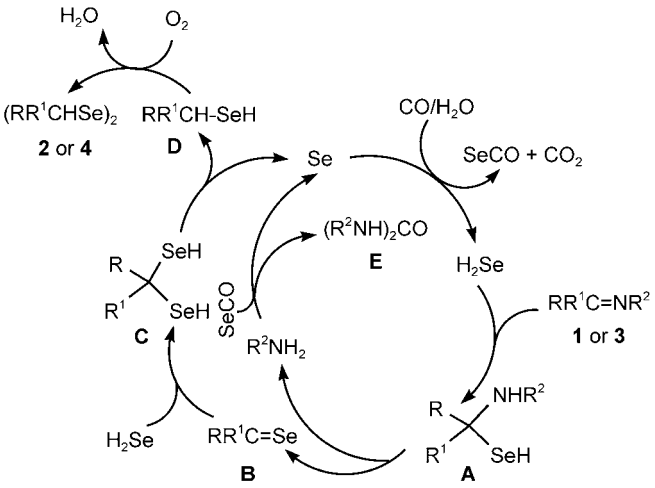


Figure 1. A proposed reaction mechanism.

Conclusions

In conclusion, a highly efficient general route has been developed to synthesize organic diselenides from imines of aldehydes and ketones. The present procedure has demonstrated an indirect and safe way to handle H_2Se. The proposed mechanism suggests that both *in situ* generated species SeCO and H_2Se are involved in the reactions.

Experimental Section

Representative Procedure for Synthesis of Diselenides 2 and 4

An imine (3 mmol), selenium (0.237 g, 3 mmol), H_2O (0.54 mL, 30 mmol), Et_3N (0.42 mL, 3 mmol), and THF (10 mL) were successively loaded into a 70-mL stainless-steel autoclave. The reactor was sealed, flushed with 1.0 MPa of carbon monoxide three times, pressurized with 3.0 MPa of carbon monoxide, and then placed in an oil bath preheated to 100 °C and stirred for 3 h. After the reaction was complete, the apparatus was cooled to ambient temperature, and the remaining carbon monoxide was evacuated. The resultant mixture was stirred in air at ambient temperature for another 2 h, and filtered through 3 cm of silica gel to remove the urea formed in the reaction. The filtrate was acidified with 2 M HCl (10 mL), diluted with 30 mL of water and then extracted with diethyl ether (3 × 40 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and all the volatiles were evaporated under reduced pressure to afford the crude product. Purification by flash column chromatography on silica gel or by recrystallization at −20 °C gave the pure products. All the products

were characterized by NMR spectroscopy and comparison with authentic samples for known compounds, and also by elemental analysis for the new compounds.

***Bis(2-hydroxybenzyl) diselenide* (2 g):** mp 92–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.17 (t), 7.12 (d), 6.91 (t), 6.84 (d) (2:2:2:2 CH, aromatic CH), 5.79 (br, 2H, 2 × OH), 3.98 (s, 4H, $SeCH_2$); $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$, 23 °C): δ = 153.72 (s, Cq, C–O), 125.42 (s, Cq, *i*-C of phenyl), 130.92, 129.15, 121.18, 116.63 (s each, 2:2:2:2 CH, aromatic CH), 27.85 (s, $SeCH_2$); anal. calcd. for $C_{14}H_{14}O_2Se_2$: C 45.18, H 3.79; found: C 44.96, H 3.67.

***Bis(4-hydroxybenzyl) diselenide* (2 h):** mp 148 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 23 °C): δ = 9.41 (s, 2H, 2 × OH), 7.05, 6.69 (d each, *J* = 7.6 and 7.8 Hz, 4:4H, aromatic CH), 3.84 (s, 4H, $SeCH_2$); $^{13}C\{^1H\}$ NMR (400 MHz, DMSO-d_6, 23 °C): δ = 156.53 (s, Cq, C–O), 130.14, 115.15 (s each, 4:4 CH, aromatic CH), 129.05 (s, Cq, *i*-C of phenyl), 31.71 (s, $SeCH_2$); anal. calcd. for $C_{14}H_{14}O_2Se_2$: C 45.18, H 3.79; found: C 44.73, H 3.77.

***Bis(3-phenylpropyl) diselenide* (2k):** ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.37, 7.28 (m each, 4:6H, aromatic CH), 2.98, 2.81 (t each, 4:4 CH, $SeCH_2$ and $PhCH_2$), 2.15 (m, 4H, 2 × CH_2); $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$, 23 °C): δ = 141.36 (s, Cq, *i*-C of phenyl), 128.59, 128.49, 126.05 (s each, 4:4:2 CH, aromatic CH), 35.49, 32.46 (s each, $SeCH_2$ and $PhCH_2$), 29.25 (s, CH_2).

***Bis(2-furfuryl) diselenide* (2 m):** ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.39 (d, *J* = 1.5 Hz, 2H, 5-H), 6.34 (t, *J* = 4.2 Hz, 2H, 4-H), 6.22 (d, *J* = 3.1 Hz, 2H, 3-H), 3.94 (s, 4H, $SeCH_2$); $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$, 23 °C): δ = 151.84 (s, Cq, C-2), 142.25 (s, CH, C-5), 110.91 (s, CH, C-3), 108.45 (s, CH, C-4), 24.13 (s, $SeCH_2$); anal. calcd. for $C_{10}H_{10}O_2Se_2$: C 37.52, H 3.15; found: C 37.62, H, 3.26.

***Bis(3-indolylmethyl) diselenide* (2o):** ^{1}H NMR (400 MHz, DMSO-d_6, 23 °C): δ = 7.56 (d), 7.34 (d), 7.20 (s), 7.08 (t), 7.02 (t) (2:2:2:2:2 CH), 4.14 (s, 4 H, $SeCH_2$); $^{13}C\{^1H\}$ NMR (400 MHz, DMSO-d_6, 23 °C): δ = 136.37 (s, Cq, C-9), 126.30 (s, Cq, C-4), 124.48, 121.36, 118.87, 118.64 (s each, 1:1:1:1 CH, aromatic CH), 111.60 (s, CH. C-2), 111.46 (s, Cq, C-3), 23.38 (s, $SeCH_2$).

***Bis(1-phenylethyl) diselenide* (4a):** mp 54–55 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.36–7.25 (m, 10H, aromatic CH), 4.03, 3.88 (q each, 1:1H, $SeCH_2$), 1.74, 1.73 (d each, 3:3H, 2 × CH_3); $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$, 23 °C): δ = 143.53 (s, Cq, *i-C* of phenyl), 128.51, 127.54, 127.42 (s each, aromatic CH), 41.39 (s, CH), 21.78 (s, CH_3); anal. calcd. for $C_{16}H_{18}Se_2$: C 52.19, H 4.93 found: C 52.13, H 4.88.

***Bis[1-(3′-methoxyphenyl)ethyl] diselenide* (4b):** ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 7.25 (m), 6.94–6.82 (m), 6.83 (s) (2:4:2 H, aromatic CH), 4.03, 3.98 (q each, 1:1H, SeCH), 3.84 (d, 6H, 2 × OCH_3), 1.76, 1.73 (d each, 6H, 2 × CH_3); $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$, 23 °C): δ = 159.59 (s, Cq, C–O), 145.07 (s, Cq, *i-C* of phenyl), 129.44 (s), 119.77 (s), 113.16 (d), 112.69 (d) (aromatic CH), 55.27 (s, OCH_3), 41.35 (s, SeCH), 21.89, 21.72 (s each, CH_3): anal. calcd. for $C_{18}H_{22}O_2Se_2$: C 50.48, H 5.18; found: C 50.70, H 5.14.

***Bis(3-heptyl) diselenide* (4f):** ^{1}H NMR (400 MHz, $CDCl_3$, 23 °C): δ = 2.87 (m, 2H, SeCH), 1.67, 1.33 (m each, 8 Ξ CH_2), 0.98, 0.91 (t each, 4 × CH_3); $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$, 23 °C): δ = 48.81 (s, SeCH), 35.22, 30.11, 28.74, 22.70 (s each, CH_2), 14.19, 12.28 (s each, CH_3).

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