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Oxidative C–Se Coupling of Formamides and Diselenides by Using Aqueous *tert*-Butyl Hydroperoxide: A Convenient Synthesis of Selenocarbamates

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An oxidative coupling reaction between formamides and diselenides under metal-free conditions is described. The C–Se bond formation occurred exclusively at the carbonyl carbon by using aqueous *tert*-butyl hydroperoxide and 4 Å molecular sieves and the coupled products, selenocarbamates, were obtained in moderate-to-good yields.

Introduction

Direct C–H functionalization of heteroatom-containing compounds by cross-dehydrogenative coupling (CDC) is one of the most efficient routes for C–C bond formation and has been used for the synthesis of versatile building blocks and biologically active natural products.[1] The advantage of using non-functionalized substrates makes this procedure more effective with wider applicability.[2] In the recent past, several efficient methods for C–H activation α to nitrogen and oxygen atoms have been developed under both transition-metal (e.g., Cu, Fe and Ru)-catalysed and metal-free conditions.[3,4] Many reports also describe the formation of C–N, C–P, C–O and C–S bonds by using CDC procedures.[5] However, C–Se bond formation by direct C–H selenylation has received very little attention and is limited to metal-catalysed reactions of electron-rich arene or indole C–H bonds with diaryl selenides.[6] Other metal-catalysed reactions of diselenides, selenols or selenohalides with substrates such as alkyl halides, alkynes, organoboranes and organosilanes have also been explored in the synthesis of organoselenides of biological and pharmaceutical importance and with applications in materials science.[7] However, the metal-catalysed reactions are generally accompanied by toxic metal impurities along with pharmaceutically important final products[8a–8c] and the mechanistic pathways are usually complicated.[8d] Thus, from the perspective of developing an efficient and greener methodology by using simple reaction conditions, a metal-free approach to direct C–Se bond formation would be an attractive strategy.

Selenocarbamates, a group of organoselenium compounds, act as precursors for α-alkylidene-β/δ-lactams exhibiting antibiotic properties.[9] The antiviral effects of compounds containing this framework have also been studied.[10] *N*-Substituted *Se*-phenylselenocarbamates are useful precursors for the generation of carbamoyl radicals and other synthetic transformations.[11] Selenocarbamates can be used as protected selenols and smoothly deprotected under alkaline conditions.[12] Traditionally, selenocarbamates have been prepared from aromatic isocyanates and haloalkanes by using LiAlHSeH as a selenating agent[12b] or from aryl halides by lithium/halogen exchange followed by selenium metal insertion and quenching with *N*,*N*-dialkylcarbamoyl chloride.[12b,12c]

Dimethylformamide is normally used as a solvent,[13] but is also considered as a source of CO, Me_2N, Me_2NCO and oxygen.[14] However, the direct C–H activation of formamides has also been reported.[15–18] In these oxidative reactions, hydrogen abstraction can occur from two different sites: the formyl C–H or the C–H α to the nitrogen atom. *tert*-Butyl hydroperoxide (TBHP)/Cu-mediated direct amidation of β-keto esters and β-dicarbonyl phenols with formamides has recently been achieved and occurs at the C–H centre of the formyl moiety.[16] The metal-free reaction of formamides with phthalimides and decarboxylative C–H acyloxylation of DMF have been reported to occur regioselectively at the C–H centre α to the nitrogen atom.[18] Xiang and co-workers reported that in the direct oxidative thiolation of DMF with diphenyl disulfide, the products corresponding to hydrogen abstraction from the formyl C–H and the C–H α to the nitrogen atom are formed in approximately equal amounts.[18a] However, by using thiophenol as a coupling partner along with $Cu(OAc)_2$/TBHP, the regioselective formation of thiocarbamate was observed.[18b] It may be noted that the reaction of simple phenol with DMF in the presence of CuCl/TBHP resulted in no product formation.[16b]

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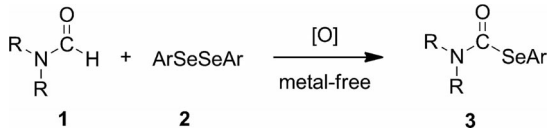
As a result of our continuing interest in developing new reactions of synthetic utility,[19] we have investigated whether an oxidative coupling reaction between formamides and diselenides can be used to form a new C–Se bond (Scheme 1). Furthermore, the regioselectivity of such a reaction would be of interest not only vis-a-vis the corresponding reactions of disulfides, but also because selenocarbamates, one of the possible products, are of considerable importance. This report describes our findings in this context.

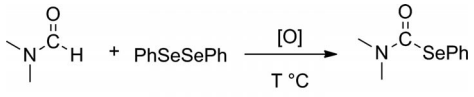


Scheme 1. Metal-free coupling of formamides and diselenides.

Results and Discussion

Our initial studies focused on the coupling of *N*,*N*-dimethylformamide (DMF, **1a**) and diphenyl diselenide (**2a**). The reaction between DMF (80 equiv., also used as a solvent) and **2a** (1 equiv.) was performed in the presence of 4 Å molecular sieves at 100 °C for 12 h under nitrogen by using 4 equiv. of aq. TBHP (70%) as oxidant. After workup and purification by column chromatography, the product **3a** was obtained in 27% yield (Table 1, entry 1) along with unreacted **2a** (45%). No other new product was detected by TLC analysis. Raising the reaction temperature to 120 °C improved the yield of **3a** to 68% (Table 1, entry 2). Low yields of **3a** were obtained upon decreasing the length of the reaction (Table 1, entries 3 and 4), but a longer reaction time did not improve the yield either (Table 1, entry 19). The reaction occurred even in the absence of molecular sieves (Table 1, entry 5), however, the positive role of molecular sieves as a weak base prompted us to use them under optimized conditions.[18a] The use of 4 equiv. of aq. TBHP gave a good yield of the product, but a lower amount of oxidant reduced the yield (Table 1, entry 13). The use of 6 M TBHP in decane also gave a moderate yield (Table 1, entry 6). In the presence of a catalyst such as CuI, CuBr or $Cu(OAc)_2$, the product **3a** was obtained in a low yield (Table 1, entries 7–10). No reaction was observed in the absence of TBHP (Table 1, entry 15), and the use of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), another oxidant, failed to afford the desired product (Table 1, entry 16), but in the presence of di-*tert*-butyl peroxide (DTBP), **3a** was obtained in 51% yield (Table 1, entry 17). Reducing the amount of DMF in the reaction (Table 1, entries 11 and 12) or increasing the amount of aq. TBHP (Table 1, entry 14) also resulted in a lower yield of the product **3a**. When the reaction was performed in air, the product yield decreased to 47% (Table 1, entry 18). Thus, the best results were obtained by using aq. TBHP (4 equiv.) and 4 Å molecular sieves at 120 °C for 12 h (Table 1, entry 2) under nitrogen.

Table 1. Optimization of reaction conditions.[a]

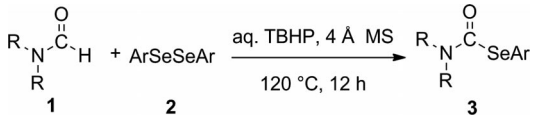


Entry	Oxidant (amount [equiv.])	Additive/catalyst	Time [h]	Temp. [°C]	Yield [%][b]
1	aq. TBHP (4)	4 Å MS	12	100	27
2	aq. TBHP (4)	4 Å MS	12	120	68
3	aq. TBHP (4)	4 Å MS	5	120	41
4	aq. TBHP (4)	4 Å MS	7	120	51
5	aq. TBHP (4)	–	12	120	60
6	TBHP (4)	4 Å MS	12	120	50
7	aq. TBHP (4)	4 Å MS/CuI	12	120	20
8	aq. TBHP (4)	4 Å MS/CuBr	12	120	27
9	aq. TBHP (4)	4 Å MS/$Cu(OAc)_2$	12	120	34
10	aq. TBHP (4)	$Cu(OAc)_2$	12	120	38
11[c]	aq. TBHP (4)	4 Å MS	12	120	37
12[d]	aq. TBHP (4)	4 Å MS	12	120	8
13	aq. TBHP (2)	4 Å MS	12	120	48
14	aq. TBHP (6)	4 Å MS	12	120	44
15	–	4 Å MS	12	120	n.r[e]
16	DDQ (4)	4 Å MS	12	120	n.r
17	DTBP (4)	4 Å MS	12	120	51
18[f]	aq. TBHP (4)	4 Å MS	12	120	47
19	aq. TBHP (4)	4 Å MS	15	120	67

[a] Reaction conditions: DMF (80 equiv.), **2a** (1 equiv.), 4 Å molecular sieves (MS) (0.15 g). [b] Isolated yield. [c] DMF (50 equiv.). [d] DMF (20 equiv.). [e] No reaction. [f] In air.

The scope of this metal-free oxidative coupling reaction was examined by using various formamides and diselenide substrates under the optimized conditions. All the form-

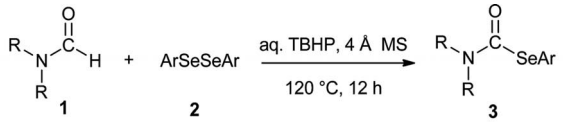
Table 2. Oxidative coupling reactions of formamides and diselenides.[a]



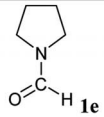
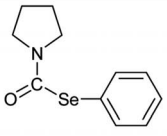
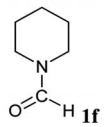
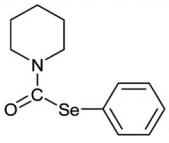
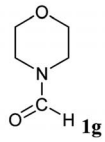
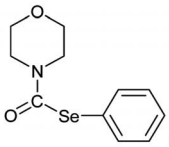
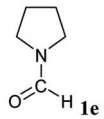
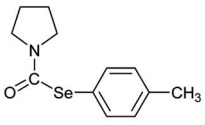
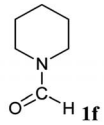
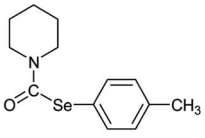
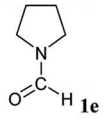
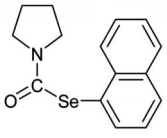
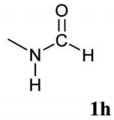
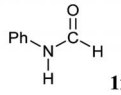
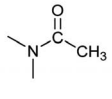
Entry	1	2	Product	Yield [%][b]
1	**1a** (R = Me)	**2a** (Ar = C_6H_5)	**3a**	68
2	**1b** (R = Et)	**2a**	**3b**	80
3	**1c** (R = Bu)	**2a**	**3c**	60
4	**1d** (R = *i*Pr)	**2a**	**3d**	70
5	**1a**	**2b** (Ar = 4-$CH_3C_6H_4$)	**3e**	68
6	**1b**	**2b**	**3f**	64
7	**1c**	**2b**	**3g**	50
8	**1d**	**2b**	**3h**	62
9	**1a**	**2c** (Ar = 4-$CH_3OC_6H_4$)	**3i**	75
10	**1b**	**2c**	**3j**	67
11	**1c**	**2c**	**3k**	62
12	**1d**	**2c**	**3l**	65
13	**1a**	**2d** (Ar = 1-naphthyl)	**3m**	67
14	**1b**	**2d**	**3n**	80
15	**1c**	**2d**	**3o**	63
16	**1a**	**2e** (Ar = 2-CH_3O-1-naphthyl)	**3p**	31
17	**1b**	**2e**	**3q**	47
18	**1a**	**2f** (Ar = $CH_2C_6H_5$)	**3r**	74
19	**1b**	**2f**	**3s**	67

[a] Reaction conditions: **1** (80 equiv.), **2** (1 equiv.), 4 Å MS (0.1 g/0.2 mmol), aq. TBHP (4 equiv.). [b] Isolated yield.

Table 3. Study of the substrate scope in the coupling reaction between formamides and deselenides.[a]



1 2 3

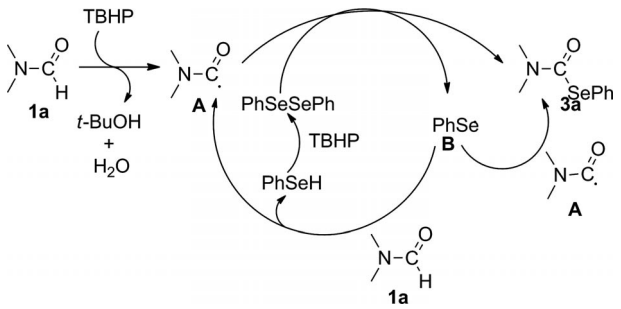
Entry	1	2	Product	Yield [%][b]
1	 1e	2a (Ar = C_6H_5)	 3t	64
2	 1f	2a	 3u	71
3	 1g	2a	 3v	58
4	 1e	2b (Ar = 4-$CH_3C_6H_5$)	 3w	57
5	 1f	2b	 3x	51
6	 1e	2d (Ar = 1-naphthyl)	 3y	70
7	 1h	2a	-	n.r.[c]
8	 1i	2a	-	n.r.
9	 1j	2a	-	n.r.

[a] Reaction conditions: **1** (80 equiv.), **2** (1 equiv.), 4 Å MS (0.1 g/0.2 mmol), aq. TBHP (4 equiv.). [b] Isolated yield. [c] No reaction.

amides, namely *N*,*N*-dimethyl-, *N*,*N*-diethyl-, *N*,*N*-dibutyl- and *N*,*N*-diisopropylformamide (**1a**–**1d**), reacted with the diaryl diselenides to give the coupled products in moderate-to-good yields (Table 2). Diselenides bearing electron-donating groups on the phenyl ring (**2b**, **2c**) smoothly afforded the corresponding coupled products **3e**–**3l** (Table 2, entries 5–12). Di-1-naphthyl diselenide (**2d**) also gave the products **3m**–**3o** in good yields (Table 2, entries 13–15). However, bis(2-methoxy-1-naphthyl) diselenide (**2e**) gave lower yields (Table 2, entries 16 and 17), which may be due to steric factors. The use of dibenzyl diselenide (**2f**) as a coupling partner also gave the products **3r** and **3s** in yields of 74 and 67%, respectively (Table 2, entries 18 and 19). In addition, no other new products were detected in these reactions.

To test the generality of this procedure, we also evaluated the reaction with cyclic formamides **1e**–**1g**. The corresponding selenocarbamates were obtained in yields of 51–71% (Table 3, entries 1–6). However, *N*-methylformamide (**1h**) and *N*-phenylformamide (**1i**) failed to give the coupled product (Table 3, entries 7 and 8). In addition, *N*,*N*-dimethylacetamide (**1j**) also failed to react (Table 3, entry 9). Therefore it can be inferred that the product corresponding to C–H abstraction α to the nitrogen atom is not formed even when formyl C–H abstraction is blocked.

It was proposed earlier that the reaction of formamide with different coupling partners such as azole, β-keto esters and thiol in the presence of oxidants like TBHP and DTBP occurs regioselectively by formyl hydrogen abstraction and proceeds through a radical pathway.[16–18] In this case also, when the radical scavenger TEMPO (4 equiv.) was added to the reaction mixture of **1a** and **2a** under the optimized reaction conditions (Table 1, entry 2), the yield of product **3a** was reduced dramatically (7%), which suggests the involvement of a radicaloid species. Therefore we have proposed a plausible mechanism for this reaction (Scheme 2). Hydrogen radical abstraction from formamide **1a** by TBHP gives intermediate **A**, which reacts with PhSeSePh to give the coupled product **3a** and selenyl radical **B**. The intermediate **B** either reacts with **1a** to give PhSeH and intermediate **A** or it directly reacts with the initially formed intermediate **A** to give the desired product. In the presence of TBHP, PhSeH is oxidized to PhSeSePh to complete the cycle.[20]



Scheme 2. Tentative mechanism for the coupling reaction between formamides and diselenides.

Conclusions

An efficient, direct metal-free coupling between formamides and diselenides has been developed that selectively affords selenocarbamates. Further studies of the scope and limitations of this green approach to the synthesis of selenium-containing compounds of biological and pharmaceutical interest are currently under investigation.

Experimental Section

General Procedure for the Coupling Reactions of 1a and 2a: Compound **1a** (2 mL, 25.6 mmol), **2a** (100 mg, 0.32 mmol), 4 Å MS (150 mg) and 70% aq. TBHP (0.2 mL, 1.28 mmol) were placed in a 10 mL flame-dried two-necked round-bottomed flask equipped with condenser and stirring bar under nitrogen. The reaction mixture was stirred at 120 °C for 12 h. The resulting reaction mixture was dissolved in ethyl acetate (20 mL) and washed with water (2× 10 mL) and brine (2× 10 mL). Evaporation of the solvent and purification of the residue by flash column chromatography over silica gel (230–400 mesh) by using ethyl acetate/hexane as eluent afforded the product **3a** (49.5 mg, 68%).

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data, and the ^{1}H, ^{13}C and ^{77}Se NMR spectra.

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[1] a) B.-J. Li, Z.-J. Shi, *Chem. Soc. Rev.* **2012**, *41*, 5588–5598; b) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215–1292; c) C. Liu, H. Zhang, W. Shi, A. Lei, *Chem. Rev.* **2011**, *111*, 1780–1824; d) W. Shi, C. Liu, A. Lei, *Chem. Soc. Rev.* **2011**, *40*, 2761–2776.

[2] a) C. J. Scheuermann, *Chem. Asian J.* **2010**, *5*, 436–451; b) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335–344; c) S.-I. Murahashi, D. Zhang, *Chem. Soc. Rev.* **2008**, *37*, 1490–1501; d) Z. Li, D. S. Bohle, C.-J. Li, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 8928–8933.

[3] a) K. M. Jones, M. Klussmann, *Synlett* **2012**, *23*, 159–162; b) E. A. Mitchell, A. Peschiulli, N. Lefevre, L. Meerpoel, B. U. W. Maes, *Chem. Eur. J.* **2012**, *18*, 10092–10142; c) K. R. Campos, *Chem. Soc. Rev.* **2007**, *36*, 1069–1084; d) M. Ghobrial, K. Harhammer, M. D. Mihovilovic, M. Schnürch, *Chem. Commun.* **2010**, *46*, 8836–8838; e) P. Liu, C.-Y. Zhou, S. Xiang, C.-M. Che, *Chem. Commun.* **2010**, *46*, 2739–2741; f) T. Zeng, G. Song, A. Moores, C.-J. Li, *Synlett* **2010**, 2002–2008; g) W. Han, A. R. Ofial, *Chem. Commun.* **2009**, 6023–6025; h) C. M. Rao Volla, P. Vogel, *Org. Lett.* **2009**, *11*, 1701–1704; i) B. Chiavarino, R. Cipollini, M. E. Crestoni, S. Fornarini, F. Lanucara, A. Lapi, *J. Am. Chem. Soc.* **2008**, *130*, 3208–3217.

[4] For recent metal-free coupling reactions, see: a) J. Dhineshkumar, M. Lamani, K. Alagiri, K. R. Prabhu, *Org. Lett.* **2013**, *15*, 1092–1095; b) B. Schweitzer-Chaput, M. Klussmann, *Eur. J. Org. Chem.* **2013**, *4*, 666–671; c) Y.-p. Zhu, M.-c. Liu, F.-c. Jia, J.-j. Yuan, Q.-h. Gao, M. Lian, A.-x. Wu, *Org. Lett.* **2012**, *14*, 3392–3395; d) R. A. Kumar, G. Saidulu, K. R. Prasad, G. S. Kumar, B. Sridhar, K. R. Reddy, *Adv. Synth. Catal.* **2012**, *354*, 2985–2991; e) Z. Wang, H. Mo, D. Cheng, W. Bao, *Org. Biomol. Chem.* **2012**, *10*, 4249–4255.

[5] a) V. P. Mehta, B. Punji, *RSC Adv.* **2013**, *3*, 11957–11986; b) R. Samanta, K. Matcha, A. P. Antonchick, *Eur. J. Org. Chem.* **2013**, 5769–5804; c) C. Zhang, C. Tang, N. Jiao, *Chem. Soc. Rev.* **2012**, *41*, 3464–3484.

[6] a) S. Zhang, P. Qian, M. Zhang, M. Hu, J. Cheng, *J. Org. Chem.* **2010**, *75*, 6732–6735; b) X.-L. Fang, R.-Y. Tang, P. Zhong, J.-H. Li, *Synthesis* **2009**, 4183–4189; c) Z. Li, J. Hong, X. Zhou, *Tetrahedron* **2011**, *67*, 3690–3697.

[7] For recent metal-catalysed C–Se coupling, see: a) I. P. Beletskaya, V. P. Ananikov, *Chem. Rev.* **2011**, *111*, 1596–1636; b) W. Lim, Y. H. Rhee, *Eur. J. Org. Chem.* **2013**, 460–464; c) S. Bhadra, A. Saha, B. C. Ranu, *J. Org. Chem.* **2010**, *75*, 4864–4867; d) L. Wang, M. Wang, K. Ren, *Adv. Synth. Catal.* **2009**, *351*, 1586–1594; e) S. N. Murthy, B. Madhav, V. P. Reddy, Y. V. D. Nageswar, *Eur. J. Org. Chem.* **2009**, 5902–5905; f) S. Patai (Ed.), *The Chemistry of Organic Selenium and Tellurium Compounds*, Wiley, New York, **1987**, vol. 2, chapters 3, 16, and 17; g) M. Soriano-Garcia, *Curr. Med. Chem.* **2004**, *11*, 1657–1669; h) F. Marini, S. Sternativo, *Synlett* **2013**, *24*, 11–19; i) M. Godoi, M. W. Paixão, A. L. Braga, *Dalton Trans.* **2011**, *40*, 11347–11355; j) D. M. Freudendahl, S. Santoro, S. A. Shahzad, C. Santi, T. Wirth, *Angew. Chem.* **2009**, *121*, 8559; *Angew. Chem. Int. Ed.* **2009**, *48*, 8409–8411.

[8] a) S. Ahuja, *Impurities Evaluation of Pharmaceuticals*, Marcel Dekker, New York, **1998**; b) F. Qiu, D. L. Norwood, *J. Liq. Chromatogr. Relat. Technol.* **2007**, *30*, 877–935; c) K. Alagiri, K. R. Prabhu, *Chem. Eur. J.* **2012**, *18*, 5160–5164; d) V. P. Ananikov, I. P. Beletskaya, *Organometallics* **2012**, *31*, 1595–1604.

[9] a) M. Toyofuku, S.-i. Fujiwara, T. Shin-ike, H. Kuniyasu, N. Kambe, *J. Am. Chem. Soc.* **2005**, *127*, 9706–9707; b) A. M. Venkatesan, Y. Gu, O. D. Santos, T. Abe, A. Aggarwal, Y. Yang, P. J. Petersen, W. J. Weiss, T. S. Mansour, M. Nukaga, A. M. Hujer, R. A. Bonomo, J. R. Knox, *J. Med. Chem.* **2004**, *47*, 6556–6568; c) C. Michaux, P. Charlier, J.-M. Frére, J. Wouter, *J. Am. Chem. Soc.* **2005**, *127*, 3262–3263; d) S. Ma, B. Wu, X. Jiang, *J. Org. Chem.* **2005**, *70*, 2588–2593.

[10] Y. N. Klimochkin, I. K. Moiseev, O. V. Abramov, G. V. Vladyko, L. V. Korobchenko, E. I. Boreko, *Khim. Farm. Zh.* **1991**, *25*, 46–49.

[11] a) J. H. Ribby, D. M. Danca, J. H. Horner, *Tetrahedron Lett.* **1998**, *39*, 8413–8416; b) A. G. M. Barrett, H. Kwon, E. M. Wallace, *J. Chem. Soc., Chem. Commun.* **1993**, 1760–1761; c) K. Kondo, M. Takarada, S. Murai, N. Sonoda, *Synthesis* **1979**, 597–598.

[12] a) S. Flemer Jr., *Molecules* **2011**, *16*, 3232–3251; b) M. Koketsu, M. Ishida, N. Takakura, H. Ishihara, *J. Org. Chem.* **2002**, *67*, 486–490; c) W. A. Reinerth, J. M. Tour, *J. Org. Chem.* **1998**, *63*, 2397–2400.

[13] S. T. Ding, N. Jiao, *Angew. Chem.* **2012**, *124*, 9360; *Angew. Chem. Int. Ed.* **2012**, *51*, 9226–9237.

[14] a) J. Kim, J. Choi, K. Shin, S. Chang, *J. Am. Chem. Soc.* **2012**, *134*, 2528–2531; b) Y. P. Zhu, Q. H. Gao, M. Lian, J. J. Yuan, M. C. Liu, Q. Zhao, Y. Yang, A. X. Wu, *Chem. Commun.* **2011**, *47*, 12700–12702; c) S. Ding, N. Jiao, *J. Am. Chem. Soc.* **2011**, *133*, 12374–12377; d) G. Zhang, X. Ren, J. Chen, M. Hu, J. Cheng, *Org. Lett.* **2011**, *13*, 5004–5007; e) J. Muzart, *Tetrahedron* **2009**, *65*, 8313–8323; f) J. S. Lee, Y. S. Jinn, J. H. Choi, *Chem. Commun.* **2001**, 956–957.

[15] a) T. Fujihara, Y. Katafuchi, T. Iwai, J. Terao, Y. Tsuji, *J. Am. Chem. Soc.* **2010**, *132*, 2094–2098; b) D. N. Sawant, Y. S. Wagh, K. D. Bhatte, B. M. Bhanage, *J. Org. Chem.* **2011**, *76*, 5489–5494; c) Y. Li, Y. Xie, R. Zhang, K. Jin, X. Wang, C. Duan, *J. Org. Chem.* **2011**, *76*, 5444–5449; d) T. He, H. Li, P. Li, L. Wang, *Chem. Commun.* **2011**, *47*, 8946–8948; e) Q. Zhao, T. Miao, X. Zhang, W. Zhou, L. Wang, *Org. Biomol. Chem.* **2013**, *11*, 1867–1873; f) S. Zhang, L. Guo, H. Wang, X. Duan, *Org. Biomol. Chem.* **2013**, *11*, 4308–4311; g) H. Wang, L. Guo, X. Duan, *Org. Biomol. Chem.* **2013**, *11*, 4573–4576.

[16] a) G. S. Kumar, C. U. Maheswari, R. A. Kumar, M. L. Kantam, K. R. Reddy, *Angew. Chem.* **2011**, *123*, 11952; *Angew. Chem. Int. Ed.* **2011**, *50*, 11748–11751; b) P. S. Kumar, G. S. Kumar, R. A. Kumar, N. V. Reddy, K. R. Reddy, *Eur. J. Org. Chem.* **2013**, 1218–1222.

[17] a) Z. Lao, W. Zhong, Q. Lou, Z. Li, X. Meng, *Org. Biomol. Chem.* **2012**, *10*, 7869–7871; b) D. Li, M. Wang, J. Liu, Q. Zhao, L. Wang, *Chem. Commun.* **2013**, *49*, 3640–3642.

[18] a) R. Tang, Y. Xie, Y. Xie, J. Xiang, J. Li, *Chem. Commun.* **2011**, *47*, 12867–12869; b) Y.-q. Yuan, S.-r. Guo, J.-n. Xiang, *Synlett* **2013**, *24*, 443–448.

[19] a) K. N. Singh, P. Singh, P. Singh, Y. Maheshwary, S. V. Kessar, A. Batra, *Synlett* **2013**, *24*, 1963–1967; b) K. N. Singh, P. Singh, A. Kaur, P. Singh, *Synlett* **2012**, *23*, 760–764.

[20] The reaction of *N*,*N*-dimethylformamide (**1a**) with PhSeH under the optimized conditions given in Table 1, entry 2 afforded the product **3a** in 36% yield, which is roughly half that observed with PhSeSePh (68%). This experiment lends support to the proposed mechanism in Scheme 2 in which intermediate formation of PhSeH is postulated. We are grateful to a referee for suggesting this experiment.

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