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A novel synthesis of organic diselenapolysulfides

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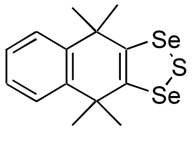
Abstract—A family of organic polychalcogenides with a common structure of $RSeS_xSeR$ (with $x = 1$, 2, 3 and $R = CH_3$, Ph, $PhCH_2$, $O_2NC_6H_4CH_2$) as well as cyclic 5,5-dimethyl-1,2-dithia-3,7-diselenacycloheptane were synthesized in good yield and high purity from the reaction of Ph_3CS_xCl with corresponding diselenides in chloroform at room temperature. Mechanistic aspects of the insertion involving the formation of an intermediate ($RSeS_xCPh_3$) are discussed. © 2003 Elsevier Science Ltd. All rights reserved.

The thermal and photochemical lability of the sulfur–chalcogen bond has resulted in a variety of interesting findings involving selenium-rich polychalcogenides. For example, compound **1** was studied for its unusual photochemical behavior,[1] while **2** has been proposed to generate trichalcogenolium species during electrochemical oxidation.[2] Interestingly, 5,5-dimethyl-dithia-3,7-diselenacycloheptane (**3b**) delivers diatomic sulfur to conjugated dienes.[3]



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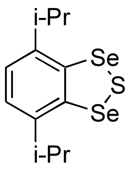

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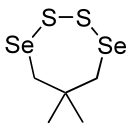

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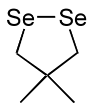
Organic polychalcogenides with a general formula $RSeS_xSeR$ ($x \geq 1$) are not easy to prepare in pure form due to their tendency to interconvert to other polychalcogenide species and are difficult to separate from unreacted starting materials and by-products.[4] There are very few effective methods to access this class of compounds. A selective preparation of aromatic diselenaheptasulfides was reported by Steudel using Cp_2TiS_5 as a template.[4] An extension of this approach to form diselenatetrasulfides with $(Cp_2TiS_2)_2$ was unsuccessful due to a low selectivity with which the target compounds formed. A direct elemental sulfur insertion into the Se–Se bond catalyzed either by iodine[5] or sodium sulfide[6a] as well as without catalysts[6b] resulted in a mixture of diselenapolysulfides. A proposed separation of the diselenapolysulfides by HPLC[4] or their selective desulfurization with mercury[5] as means to isolate the desired product does not seem to be adequate for preparative purposes. Other methods have limited scope either by the nature of the reaction applied (e.g. the decomposition of an adduct of selenenyl chloride and thiourea)[7] or by the availability of reagents as in the case of a procedure involving selenotrimethylsilanes $RSeC(Si(CH_3)_3)_3$ and sulfur chlorides.[8]

Here, we report a simple and selective sulfur insertion into the Se–Se bond in linear diselenides **4**–**7** to give the corresponding polychalcogenides **4**–**7a**–**c** with $x = 1$–3 (Eq. (1)). A cyclic diselenide **8** was also easily converted to the corresponding insertion product **3**.

$$\underset{\mathbf{4\text{-}7}}{RSeSeR} + \underset{\mathbf{9a\text{-}c}}{Ph_3CS_xCl} \longrightarrow \underset{\mathbf{4\text{-}7a\text{-}c}}{RSeS_xSeR} + \underset{\mathbf{10}}{Ph_3CCl} \qquad (1)$$



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4, R = Me; **5**, R = $PhCH_2$;
6, R = Ph; **7**, R = $p\text{-}O_2NC_6H_4CH_2$
a, x = 1; **b**, x = 2; **c**, x = 3

Previously, we reported compounds **9a**–**c** as convenient sulfur-transfer reagents delivering mono-, di- and trisulfur units into the S–S bond of di- and higher sulfides.[9] This method offers certain advantages as trityl sulfenyl **9a**, thiosulfenyl **9b** and dithiosulfenyl chloride **9c** are relatively stable, crystalline compounds readily synthesized from triphenylmethanethiol and sulfuryl chloride, sulfur dichloride and sulfur monochloride, respec-

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Keywords: diselenides; sulfur insertion; trityl sulfenyl chloride; polychalcogenides.

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tively.[10] The extension of the sulfur insertion method for diselenides **4**–**7** results in the formation of polychalcogenides **4**–**7a**–**c**.

The best results are obtained when the reactions are carried out in $CHCl_3$ at room temperature with nearly stoichiometric molar ratios of substrates. In a typical procedure, 1 mmol of a diselenide is dissolved in 5 mL of $CHCl_3$ in a round-bottom flask to which a solution of 1.05 mmol of the sulfur transfer reagent in 5 mL of $CHCl_3$ is added rapidly. After completion (5 min to 1 h), 10 mL of water was added and the reaction stirred vigorously for 1 h. The organic phase was separated, dried with anhydrous Na_2SO_4 and concentrated. The crude product was passed quickly through a silica gel plug using hexane as the eluent. Prolonged contact of the compounds with silica or Al_2O_3 causes serious decomposition. In cases, when the polarity of the product is close to that of trityl alcohol Ph_3COH (e.g. compound **7b**) triple trituration with small amounts of methanol provides satisfactory separation. The desired products were obtained in up to 90% yield and ca. 95% purity (Table 1). Crystallization from benzene provides analytical samples.

All products were characterized by ^1H and ^{13}C NMR. Additionally, their identities were confirmed by EI or FAB MS, however, compounds **5c** and **6c** did not generate a molecular peak, likely due to their low thermal stability. In all studied polychalcogenides, fragmentation results in the appearance of peaks corresponding to M-S, M-2S, M-3S, reflecting the weakness of the Se–S bonds and a readiness to lose sulfur atoms.

The structures of dibenzyl diselenatetrasulfide (**5b**) and dibenzyl diselenapentasulfide (**5c**) were established by X-ray crystallography.[11] They appear to be the first reported examples of structurally characterized organic diselenapolysulfides containing more than one sulfur atom.[12] The sulfur–sulfur bonds in both **5b** (Fig. 1) and **5c** (Fig. 2) are very similar and fall in the typical range for S–S bonds (2.02–2.06 Å). The Se–S bonds in both molecules are also alike, 2.184, 2.175 and 2.187 Å, respectively, and they closely resemble values determined for other diselenasulfides.[13] The similarity of these values is not unexpected as both molecules have the same substituents and are not strained.

Once purified, the polychalcogenides are quite stable. The oily products were unchanged in the refrigerator for months and the crystalline products are relatively stable at room temperature. Compound **5b** decomposed ca. 90% (with diselenide **5** being the main decomposition product) after one-year storage at the bench.

Decomposition in solution is significantly faster. Overnight treatment of **5b** in $CDCl_3$ gave mainly a mixture of mono- and trithiachalcogenides **5a** and **5c**, respectively (ca. 30%). The rate of decomposition and its outcome appears to be influenced by the pH of the solution. In control experiments, triethylamine and acetic acid were added to solutions of **3** in $CDCl_3$. After 3 days in the alkaline solution compound **3** completely decomposed to various products while in the acidic sample, 50% of compound **3** converted to cyclic diselenide **8**.

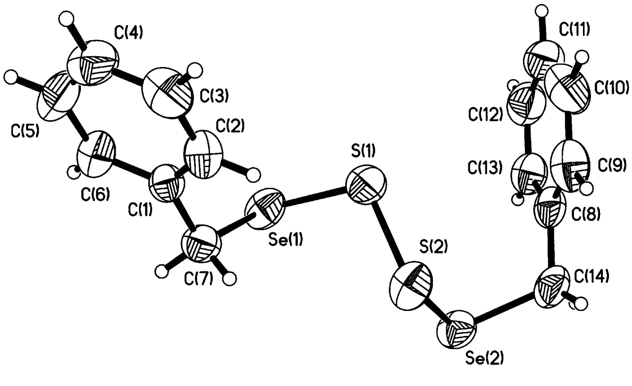


Figure 1. X-Ray structure of dibenzyl diselenatetrasulfide (**5b**). Selected bond lengths (Å) and angles (°): S(1)–S(2), 2.056(2); Se(1)–S(1), 2.184(1); Se(2)–S(2), 2.175(1); Se(1)–S(1)–S(2)–Se(2), 80.06(6).

The insertion of mono-, di- and trisulfur units into the Se–Se bond appears to be controlled mainly by electronic factors. While dimethyl and dibenzyl diselenides reacted in up to 10 min time, the diphenyl diselenides required ca. 30 min for completion. With phenyl rings electron-depleted by a nitro group, no insertion product was isolated. When the electron-withdrawing effects of the nitro group were limited by the increased distance from the diselenide bond, as in di-*p*-nitrobenzyl diselenide, the reaction proceeded smoothly.

The insertion times into the Se–Se bond in dibenzyl or diphenyl diselenides are remarkably short when compared with corresponding disulfides. For example, the insertion of a disulfur unit into the S–S bond in dibenzyl disulfide required 12 h in methylene chloride or 30 min when acetic acid was added.[9a] In this study, reaction times shorter than 15 min were observed even without adding any polar co-solvent in cases of both diselenides **5** and **7**. Due to the fast reaction rate in the case of diselenides, the slowing observed in case of

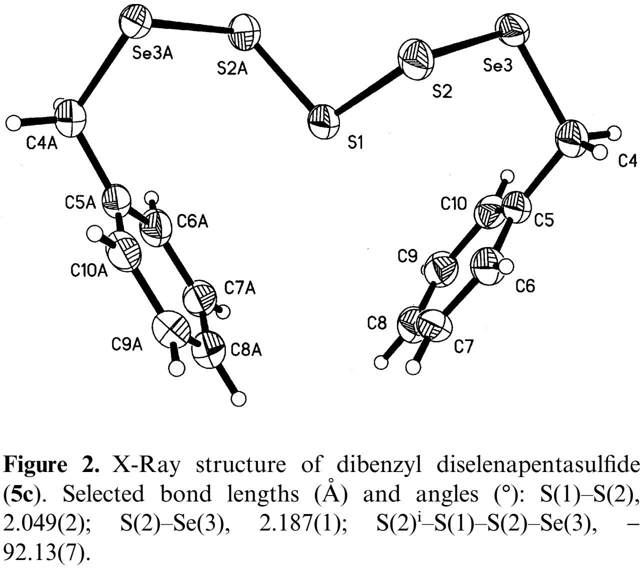
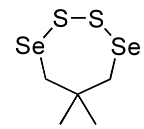


Figure 2. X-Ray structure of dibenzyl diselenapentasulfide (**5c**). Selected bond lengths (Å) and angles (°): S(1)–S(2), 2.049(2); S(2)–Se(3), 2.187(1); S(2)^i–S(1)–S(2)–Se(3), –92.13(7).

Table 1. Properties of diselenasulfides **3**–**7a**–**c**

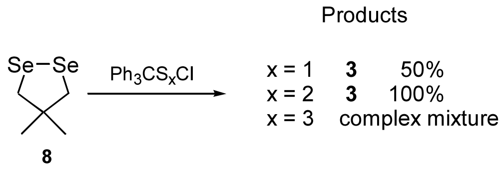
	Product	Time (min)	Yield (%)	Mp (°C)	^{1}H NMR	^{13}C NMR
3		30	100 (70)	50–51	1.08 (s, 6H); 3.52 (s, 4H)	28.54, 42.59, 49.24
4a	$(CH_3Se)_2S$	10	93	Oil	2.60	12.91
4b	$(CH_3SeS)_2$	5	98	Oil	2.71	13.85
4c	$(CH_3SeS)_2S$	5	96	Oil	1.75	14.25
5a	$(PhCH_2Se)_2S$	10	93 (75)	62–63	4.22 (s, 4H) 7.27–7.31 (m, 10H)	36.24, 127.31, 128.62, 129.28, 137.31
5b	$(PhCH_2SeS)_2$	10	96 (80)	70–71	4.40 (s, 4H) 7.20–7.34 (m, 10H)	35.49, 127.44, 128.68, 129.24, 137.30
5c	$(PhCH_2SeS)_2S$	5	94 (78)	65–66	4.43 (s, 4H) 7.26–7.36 (m, 10H)	36.66, 127.53, 128.72, 129.33, 136.98
6b	$(PhSeS)_2$	30	92	Oil	7.26–7.29 (m, 6H) 7.61–7.64 (m, 4H)	128.53, 129.19, 131.68, 132.42
6c	$(PhSeS)_2S$	30	90	Oil	7.31–7.34 (m, 6H) 7.68–7.71 (m, 4H)	128.72, 129.31, 131.43, 132.50
7b	$(O_2NC_6H_4CH_2SeS)_2$	10	(88)	95–96	4.35 (s, 4H); 7.45 (d, 4H), 8.16 (d, 4H)	33.85, 123.77, 129.85, 144.89, 146.92

Values in parentheses represent yields of solid insertion products after isolation.
Reaction times were determined by a disappearance of the yellow color from the selenenyl intermediate RSeCl.

disulfides when changing sulfur transfer reagent from $Ph_3CSSSCl$ to Ph_3CSCl was of lesser importance with only slightly modified reaction times.

Similarly, as observed with disulfides, increasing the substrate concentration positively affects the yield of products. The insertion of diselenide **5** by Ph_3CS_3Cl gave a 10% increase in the yield **5c** when the concentration of both substrates was changed from 0.1 mmol/mL to 0.2 mmol/mL.

It was discovered that hydrolysis of trityl chloride **10** formed in the reaction (Eq. (1)) increased the purity of the tetrachalcogenides. Without this additional step, all solid products (see Table 1) are isolated as oils and no crystallization could be achieved. No specific contaminant causing this problem was detected by NMR analysis in the oily products.

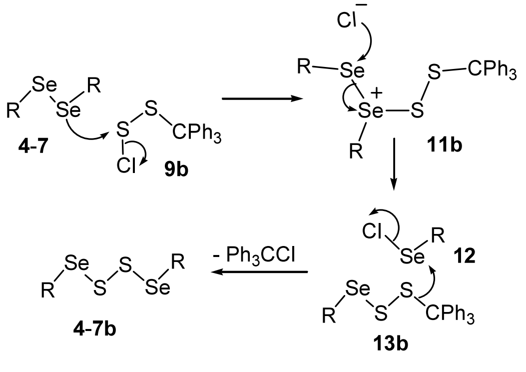


(2)

While linear diselenides reacted smoothly with all sulfur transfer reagents used in this study, cyclic diselenide **3** behaved differently. Only in the case of trityl thiosulfenyl chloride (**9b**) was the expected insertion product obtained (Eq. (2)). In the reaction with transfer reagent **9a**, no monosulfide derivative **3a** was observed (**3** formed in 50% yield). Upon addition of one more equivalent of **9a**, **3** formed in quantitative yield. In turn, the use of trityl dithiosulfenyl chloride (**9c**) failed to produce the expected trisulfide **3c** giving instead a mixture of products.

Most likely, the geometric factors make both mono- and trisulfide derivatives unfavorable and as a result, some initially formed adducts react further with more sulfur transfer reagent to give **3** or other yet unidentified compounds. No evidence for the presence of the unstable intermediates was observed by NMR. Unfortunately, we were unable to obtain X-ray quality crystals for the cyclic diselenatetrasulfide **3**. It is likely, that by determining the geometry of this molecule we might have obtained some insight about the apparent instability of diselenatri- and pentasulfides.

The reactivity of some other more functionalized diselenides was also tested. For example, according to ^{1}H NMR, the insertion of a disulfur unit into $(HOOCCH_2CH_2Se)_2$ readily occurred; however, the product decomposed upon isolation. No insertion was observed when the NH_2 group was present in a diselenide derivative.



(3)

The amine functionalities rapidly decompose the sulfur transfer reagent thus precluding any useful sulfur insertion.

The mechanism of this sulfur insertion reaction is believed to be analogous to the one proposed in the reaction of disulfides with trityl thiosulfenyl chloride (Ph_3CSSCl) and related sulfur-transfer reagents (Eq. (3)).[9] Thus, the initially formed selenonium cation **11b** would fragment to selenenyl chloride **12** and mixed selenasulfide **13b**. A recombination of **12** and **13b** would give the observed insertion products. The much higher insertion rate than we observe in the case of diselenides (as compared to disulfides) likely results from the higher nucleophilicity of selenium. However, even in the case of diselenides, the significant decrease of electron density caused by the *p*-nitro group (in *p*-$O_2NC_6H_4SeSeC_6H_4NO_2$-*p*) renders diselenides inactive towards compounds **9a**–**c**.

The insertion method described above has certain limitations (NH_2 and NO_2 groups), however, in other cases it allows an easy and selective access to many polychalcogens that are unavailable otherwise. The elucidation of the mechanism of this insertion might suggest the possibility to adapt the method to other challenging compounds.

Acknowledgements

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11. Crystal data: $C_{14}H_{14}Se_2S_2$, Mr = 404.29, crystal dimensions 0.52×0.48×0.12 mm, orthorhombic, space group *Pccn*, $a = 10.9088(4)$, $b = 33.962(1)$, $c = 8.3243(3)$ Å, $V = 3084.03(18)$ Å^3, calcd = 1.741 g/cm^3, $T = 293(2)$ K, $Z = 8$, $\lambda(\mathrm{CuK}\alpha) = 1.54178$ Å, reflections collected = 34253, independent reflections = 3031 ($R_{\mathrm{int}} = 0.0779$), final $R_1 = 0.0269$, $wR_2 = 0.072$ ($I > 2\sigma(I)$), GOF = 1.086. Crystal data: $C_{14}H_{14}Se_2S_3$, Mr = 436.352, crystal dimensions 0.28×0.27×0.16 mm, orthorhombic, space group *Pbcn*, $a = 18.859(6)$, $b = 8.493(4)$, $c = 10.136(3)$ Å, $V = 1623.5(1)$ Å^3, calcd = 1.7853 g/cm^3, $T = 293(2)$ K, $Z = 4$, $\lambda(\mathrm{CuK}\alpha) = 1.54056$ Å, reflections collected = 10854, independent reflections = 1543 ($R_{\mathrm{int}} = 0.071$), final $R_1 = 0.0347$, $wR_2 = 0.0783$ for 937 reflections ($I > 2\sigma(I)$), GOF = 0.984.
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13. For instance, the Se–S bond length in $((CH_3)_3Si)_3CSeSSeC((CH_3)_3Si))_3$ was reported to be 2.213 (see Ref. 5) and 2.202 Å in the case of *o*-$O_2NC_6H_4SeSSeC_6H_4NO_2$-*o* (see Ref. 12).