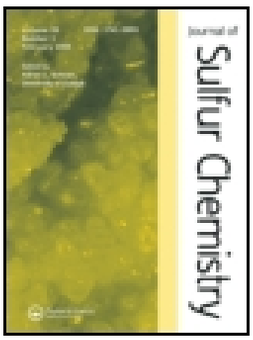

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Synthesis of hetaryl-substituted 1,2,4-trithiolanes via a three-component reaction with dihetaryl thioketones, benzyl azide, and 2,2,4,4-tetramethyl-3-thioxocyclobutanone

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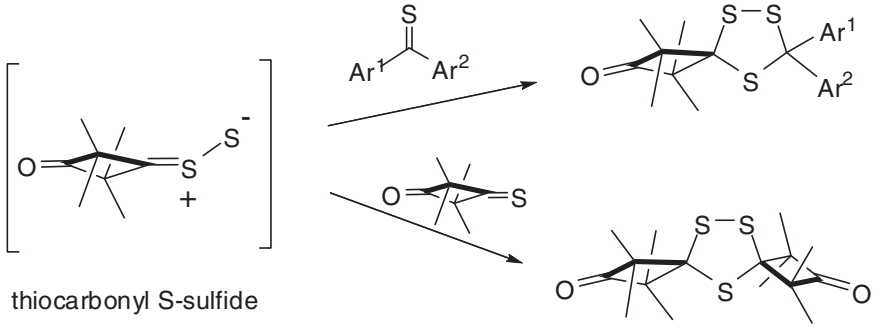
The three-component reactions with a hetaryl thioketone, 2,2,4,4-tetramethyl-3-thioxocyclobutanone, and excess benzyl azide performed at 60°C in the presence of $LiClO_4$ lead to the formation of two types of 1,2,4-trithiolanes. As the major products, the non-symmetrical dihetaryl-substituted spiro-1,2,4-trithiolanes are formed. In addition, the symmetrical dispiro-1,2,4-trithiolane is identified. These products are formed in competitive [3 + 2] cycloadditions of the in-situ-generated thiocarbonyl *S*-sulfide with the thioketones used in the reaction.



thiocarbonyl S-sulfide

Keywords: thioketones; organic azides; [3 + 2] cycloadditions; thiocarbonyl *S*-sulfides; sulfur heterocycles

1. Introduction

Among five-membered poly-sulfur heterocycles, 1,2,4-trithiolanes constitute an important class of compounds. Some of them, for example, the parent 1,2,4-trithiolane and its 3,5-dialkyl-substituted derivatives are widely spread in nature. The parent compound was isolated as the major component from Shiitaki mushrooms (*Lentinus edodes*) [1] and later on also from bitter beans (*Parkia speciosa*).[2] *Cis*- and *trans*-3,5-dimethyl-1,2,4-trithiolane are known as important components in the mixture of sulfur-heterocycles, which determine the flavor of boiled beef meat.[3,4] The corresponding diethyl derivatives were identified in the composition of

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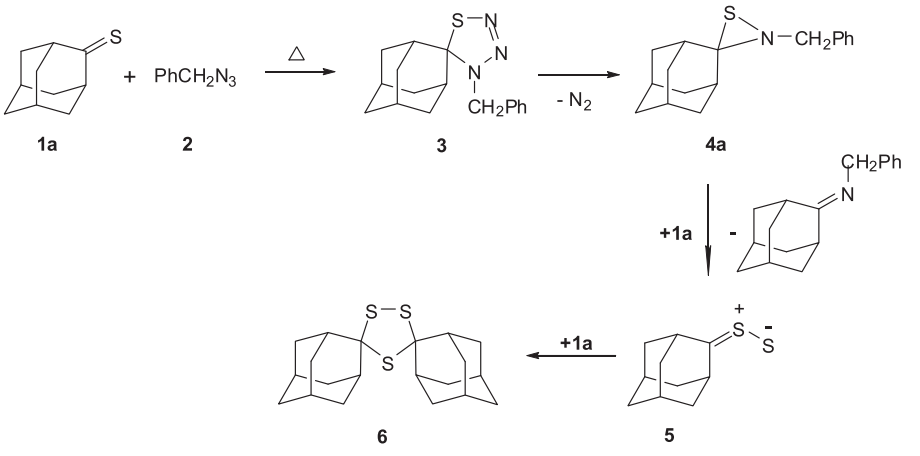


Scheme 1. Sulfur transfer reaction leading to 1,2,4-trithiolane **6**.

common onion (*Allium cepa*) essential oil.[5] Both the parent compound [1] and 3,5-dialkyl 1,2,4-trithiolanes [6] have been prepared by heterocyclization reactions starting with chloroalkanes using Na_2S as the sulfur source. An alternative approach, based on the reaction of ammonia (or a primary amine), H_2S and elemental sulfur, as well as an aliphatic oxo-compound, was developed by Asinger.[7] In recent decades, an elegant method for the preparation of tetrasubstituted 1,2,4-trithiolanes via [3 + 2] cycloadditions of thioketone *S*-sulfides (thiosulfines) [8] with thioketones was elaborated by Huisgen.[9,10] In that case, the elusive thiosulfines are generated *in situ* and immediately trapped by the C=S group of the 'superdipolarophilic' thioketone. The Huisgen method for the generation of thiosulfine comprises the transfer of the *S*-atom of a thiirane onto the C=S group.

Some time ago, we reported on a new method for the *in situ* generation of thiosulfines in the reaction of thioketones with organic azides. Thus, heating of adamantanethione (**1a**) with benzyl azide (**2**) led to dispiro-1,2,4-trithiolane **6** as the [3 + 2] cycloadduct of adamantanethione *S*-sulfide (**5**) with **1a** (Scheme 1).[11]

In this reaction, the intermediate thiaziridine **4a** is believed to act as the sulfur donor involved in the generation of the reactive 1,3-dipole **5**. On the other hand, similar reactions of thiobenzophenone (**1b**) with organic azides produce benzophenone imines and not the expected tetraphenyl-1,2,4-trithiolanes.[12] These results demonstrate the thermolability of the tetraaryl-1,2,4-trithiolanes, which therefore cannot be isolated. Finally, a three-component mixture of an aromatic thioketone, **1a** and an organic azide furnished non-symmetrical 1,2,4-trithiolanes via the [3 + 2] cycloaddition reaction, and the obtained product is stable enough to be isolated.[11] Aromatic thioketones are more reactive than cycloaliphatic analogs toward organic azides and therefore 3,3-diarylthiaziridines are the sulfur-donating intermediates. Along with **1a**, the sterically crowded 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1c**) is a good model for the synthesis of non-symmetrical 1,2,4-trithiolanes using three-component reactions.[13]

Thiocarbonyl *S*-sulfides were also postulated as reactive intermediates in a multi-step reaction between aromatic thioketone *S*-oxides and **1c** in which some non-symmetrical 1,2,4-trithiolanes were found as the final products.[14]

In a recent publication we described a convenient access to differently substituted aryl/hetaryl thioketones.[15] The presence of heteroatoms in the hetaryl ring influences the reactivity of these thioketones significantly, for example, in [3 + 2] cycloadditions with diazomethane [16] and with thiocarbonyl ylides.[17] In both cases, the cycloaddition reactions seem to occur via diradical intermediates.

The present study was aimed at testing the reactivity of selected hetaryl thioketones in three-component reactions leading to hetaryl-substituted non-symmetrical 1,2,4-trithiolanes.

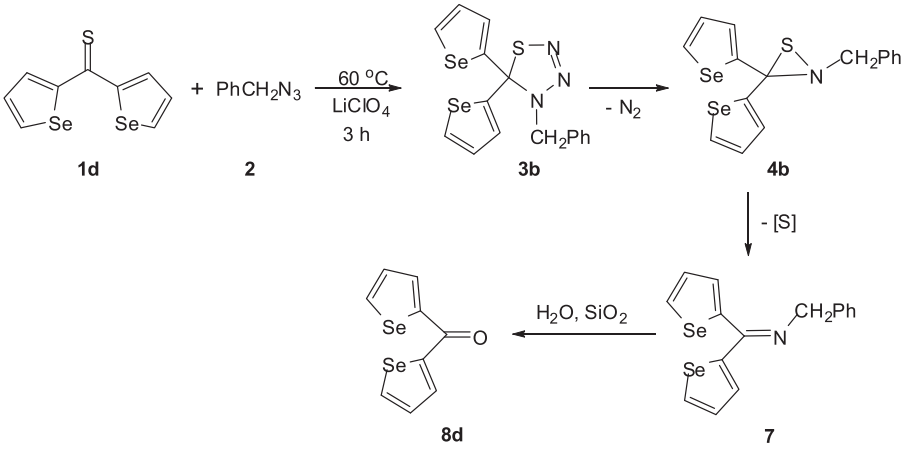
2. Results and discussion

In the test experiment, the reactivity of di(selenophen-2-yl) thioketone (**1d**) toward benzyl azide (**2**) was compared with that of thiobenzophenone (**1b**). The evolution of N_2 from the reaction mixture heated to 80°C was complete after 4 h, which indicates that **1d** is less reactive than **1b** (80°C, ca. 2.5 h) in the [3 + 2] cycloaddition with **2**. When the same reaction was performed in the presence of a catalytic amount of $LiClO_4$, the reaction temperature could be reduced to 60°C, and the conversion was complete after 3 h. The crude reaction mixture was separated chromatographically (prep. TLC) and the only product was identified as di(selenophen-2-yl) ketone (**8d**) [15] formed via hydrolysis of the corresponding *N*-benzylimine **7** (Scheme 2). It is worth of mentioning that the observed least polar fraction with R_f value ca. 0.9 was attributed to elemental sulfur S_8. This result fits well with that reported for thiobenzophenone (**1b**) [12,18] and indicates that the intermediate dihetarylthiaziridine **4b** can be expected to act as a sulfur donor.

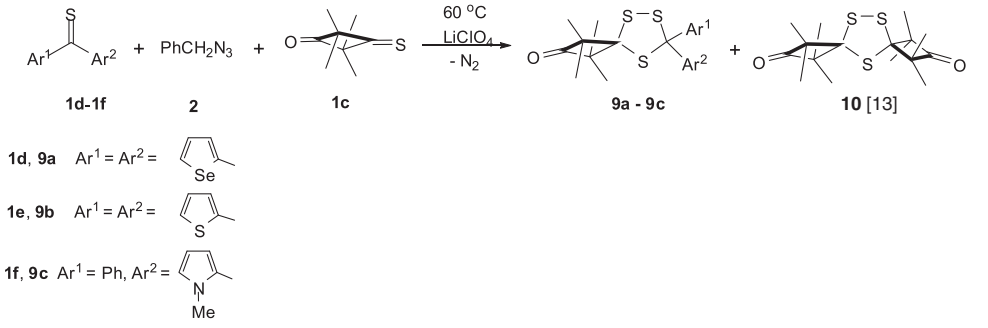
The three-component reaction with the aromatic **1d** and cycloaliphatic thioketone **1c** in excess benzyl azide (**2**) in the presence of $LiClO_4$ was performed at 60°C. In that case, the chromatographic separation of the crude mixture led to a crystalline product (less polar fraction), which in the ^{1}H-NMR spectrum showed two characteristic signals of methyl groups and three multiplets attributed to the selenophen-2-yl substituents. In the IR spectrum, the intense absorption at 1787 cm^{-1} confirms the presence of the cylobutanone unit. Finally, the structure of the spirocyclic 1,2,4-trithiolane **9a** (Scheme 3) was established by X-ray crystallography (Figure 1).

The more polar fraction isolated after chromatography was identified as a mixture of the known symmetrical dispiro-1,2,4-trithiolane **10** [13] and di(selenophen-2-yl)ketone (**8d**).[15] The analogous experiments with di(thiophen-2-yl) thioketone (**1e**) and *N*-methylpyrrol-2-yl phenyl thioketone (**1f**), respectively, yielded also the desired spiro-1,2,4-trithiolanes **9b** and **9c** side by side with **10** and the corresponding hetaryl ketones **8e**, **f** (Scheme 3).

In an extension of this study, the reaction of diferrocenyl thioketone and benzyl azide (**2**) was tested at 60°C. Only after 6 h did the evolution of N_2 cease, but the attempted separation of



Scheme 2. Two-fold extrusion reaction leading to imine **7** and its subsequent hydrolysis.



Scheme 3. Formation of symmetrical and non-symmetrical 1,2,4-trithiolanes **9** and **10** via stepwise sulfur transfer reaction.

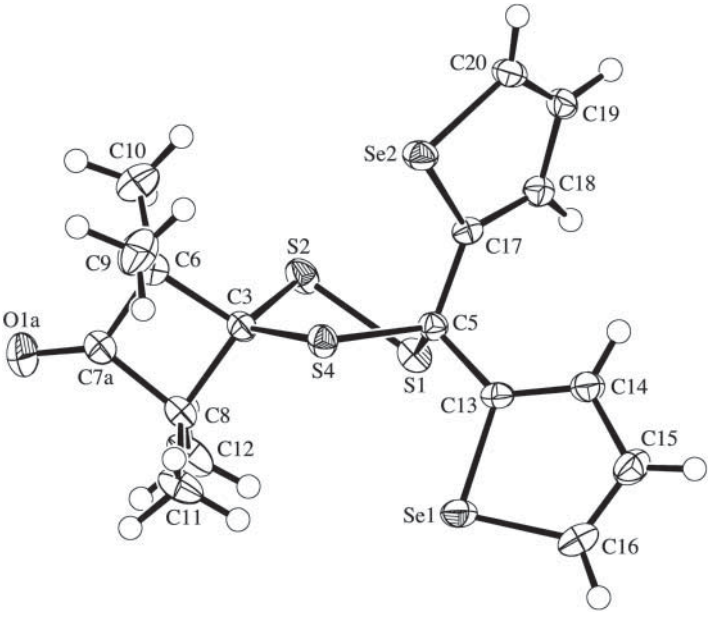


Figure 1. ORTEP plot [19] of the molecular structure of conformation A of **9a** (with 50% probability ellipsoids; arbitrary numbering of atoms).

the complex mixture was unsuccessful. Similarly, the three-component reaction with **1c** led to a complex mixture of non-identified products.

3. Conclusions

The presented study demonstrated that hetaryl thioketones are less reactive than thiobenzophenone in [3 + 2] cycloadditions with benzyl azide, and a catalytic amount of $LiClO_4$ is necessary to reduce the reaction temperature to 60°C. In the presence of the sterically crowded 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1c**), mixtures of spiro-1,2,4-trithiolanes **9** containing hetaryl substituents and dispiro-1,2,4-trithiolane **10** are formed. Both products can be separated chromatographically.

The formation of 1,2,4-trithiolanes of type **9** can occur via the [3 + 2] cycloadditions of either the thiocarbonyl *S*-sulfide of the hetaryl thioketone or the cycloaliphatic analog. On

the other hand, the formation of the dispiro-1,2,4-trithiolane **10** proves the appearance of the intermediate 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-sulfide. Aromatic thioketones are known as 'superdipolarophiles' and therefore, the first step of the reaction sequence is the [3 + 2] cycloaddition of benzyl azide (**2**) with the thioketone **1**. Additional evidence for this sequence is the absence of the products observed previously in the two-component reaction of **1c** with **2**.[20] For that reason, we propose that **1c** acts as a sulfur trapping agent and generates the corresponding thiosulfine as a key intermediate. The latter reacts in competitive [3 + 2] cycloaddition with the hetaryl thioketone as well as with **1c**.

Hetaryl-substituted 1,2,4-trithiolanes are attractive substrates for coordination chemistry and their reactions with thiophilic Pt° complexes are of special interest.[21,22]

4. Experimental Design

4.1. *General*

Melting points were determined in a capillary using a Melt-Temp. II (Aldrich) apparatus and are uncorrected. The IR spectra were recorded on an NEXUS FT-IR spectrophotometer in KBr; absorptions in cm^{-1}. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance III instrument (600 and 150 MHz, resp.) using solvent signals as reference. Chemical shifts (δ) are given in ppm and coupling constants J in Hz. All crude mixtures were separated by preparative TLC.

4.2. *Starting materials*

Dihetaryl thioketones **1d** and **1e** were obtained in a typical manner from the corresponding ketones and Lawesson's reagent in boiling toluene or benzene,[15] whereas **1f** was prepared by the treatment of *N*-methylpyrrol with thiophosgene in the presence of triethylamine.[23] 2,2,4,4-Tetramethyl-3-thioxo-cyclobutanone (**1c**) was prepared according to [24] by thionation of 2,2,4,4-tetramethylcyclobutane-1,3-dione with phosphorus pentasulfide in pyridine. Benzyl azide (**2**) was prepared from benzyl bromide and sodium azide according to a literature procedure.[25]

4.3. *Two-component reaction of di(selenophen-2-yl) thioketone (1d) and benzyl azide (2)*

A solution of 152 mg (0.5 mmol) thioketone **1d** dissolved in excess benzyl azide (**2**, 0.5 mL) was stirred magnetically and heated in an oil bath at 80°C. After 4 h evolution of nitrogen ceased and excess benzyl azide was removed in vacuo (Kugel-Rohr apparatus, 0.2 Torr, 60°C). The residual brownish oil was purified on preparative TLC plates (SiO_2, hexane/dichloromethane 1:1). The least polar fraction with R_f ca. 0.9 formed elemental sulfur, which hast not been isolated. The only fraction isolated from the plate (R_f ca. 0.5; 108 mg (75%)) was a colorless oil, which solidified at room temperature. Based on comparison of the ^{1}H NMR and IR spectra with an original sample it was identified as di(selenophen-2-yl) ketone (**8d**).[15]

4.4. *Three-component reaction with dihetaryl thioketones 1, benzyl azide (2) and 2,2,4,4-tetramethyl-3-thioxocyclobutanone (1c) – general procedure*

A mixture of the corresponding thioketone **1d–1f** (1 mmol), 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1c**, 0.5 mmol), benzyl azide (**2**, 1 mL) and a catalytic amount of $LiClO_4$ was heated in an oil bath at 60°C. After 3 h excess of azide **2** was removed under reduced pressure. The

obtained mixtures were purified by preparative TLC (SiO_2), using as the eluent a mixture of petroleum ether and ethyl acetate (97:3) for **9a** and **9b** and a mixture of dichloromethane and petroleum ether (1:1) for **9c**. Products **9**, isolated as the less polar fraction, were additionally crystallized from diethyl ether. The more polar fraction was a mixture of the known dispiro compounds **10** [13] and the corresponding hetaryl ketones **8d–8f**.[11]

1,1,3,3-Tetramethyl-7,7-di(selenophen-2-yl)-5,6,8-trithiaspiro[*3.4*]*octan-2-one* (**9a**)

Colorless crystals; yield: 217 mg (44%); m.p. 106–108°C (diethyl ether). ^{1}H NMR: 1.48, 1.51 (2*s*, 12H, 4CH_3); 7.20 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 3.8 Hz, 2CH_{arom}); 7.34 (*dd*, $J_{H,H}$ = 3.8 Hz, $J_{H,H}$ = 0.6 Hz, 2CH_{arom}); 8.00 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 0.6 Hz, 2CH_{arom}). ^{13}C NMR: 21.3, 26.4 (4CH$_3$); 67.7 (2C_q(CH$_3$)$_2$); 84.0, 89.7 (2C_qS); 129.6, 130.8, 133.7 (6CH$_{arom}$); 154.5 (2C_{arom}); 218.0 (C=O). IR (KBr): 3087*m*, 2962*m*, 1787*vs* ($\nu_{C=O}$), 1636*m*, 1458*m*, 1378*m*, 1236*m*, 1227*m*, 1171*w*, 1026*m*, 922*m*, 820*m*, 709*s*, 688*vs*. Anal. calcd for $C_{17}H_{18}OS_3Se_2$ (492.44): C 41.46, H 3.68, S 19.53; found: C 41.60, H 3.76, S 20.04.

1,1,3,3-Tetramethyl-7,7-bis(2-thienyl)-5,6,8-trithiaspiro[*3.4*]*octan-2-one* (**9b**)

Colorless crystals; yield: 200 mg (50%); m.p. 113–115°C (diethyl ether). ^{1}H NMR: 1.47, 1.52 (2*s*, 12H, 4CH_3); 6.96 (*dd*, $J_{H,H}$ = 5.2 Hz, $J_{H,H}$ = 3.7 Hz, 2CH_{arom}); 7.15 (*dd*, $J_{H,H}$ = 3.7 Hz, $J_{H,H}$ = 1.1 Hz, 2C*H*arom); 8.00 (*dd*, $J_{H,H}$ = 5.6 Hz, $J_{H,H}$ = 0.6 Hz, 2CH_{arom}). ^{13}C NMR: 21.3, 26.3 (4CH$_3$); 67.6 (2C_q(CH$_3$)$_2$); 79.7, 89.5 (2C_qS); 126.7, 126.9, 128.6 (6CH$_{arom}$); 147.5 (2C_{arom}); 218.1 (C=O). IR (KBr): 3088*m*, 2963*s*, 1789*vs* ($\nu_{C=O}$), 1640*m*, 1459*s*, 1426*s*, 1378*m*, 1363*m*, 1237*s*, 1228*s*, 1170*m*, 1042*m*, 1027*m*, 922*m*, 857*m*, 817*m*, 775*m*, 753*m*, 716*s*, 700*vs*. Anal. calcd for $C_{17}H_{18}OS_5$ (398.65): C 51.22, H 4.55, S 40.22; found: C 51.15, H 4.53, S 40.62.

1,1,3,3-Tetramethyl-7-(1-methylpyrrol-2-yl)-7-phenyl-5,6,8-trithiaspiro[*3.4*]*octan-2-one* (**9c**)

Colorless crystals; yield: 116 mg (30%); m.p. 120–122°C (diethyl ether). ^{1}H NMR: 1.43, 1.48, 1.49, 1.55 (4*s*, 12H, 4CH_3); 3.25 (*s*, 3H, CH_3N); 6.07 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 2.8 Hz, 2CH_{arom}); 6.62 (*dd*, $J_{H,H}$ = 3.6 Hz, $J_{H,H}$ = 2.2 Hz, 2CH_{arom}); 6.67 (*br. t*, $J_{H,H}$ = 2.2 Hz, 2CH_{arom}); 7.28–7.33 (*m*, 3CH_{arom}); 7.49–7.51 (*m*, 2CH_{arom}). ^{13}C NMR: 21.2, 21.5, 26.0, 26.2 (4CH$_3$); 35.8 (CH$_3$N); 66.8, 67.7 (2C_q(CH$_3$)$_2$); 81.4, 89.1 (2C_qS); 105.8, 113.9, 125.5, 127.7, 128.2, 128.4 (6 signals for 8CH$_{arom}$); 131.1, 140.5 (2C_{arom}); 218.5 (C=O). IR (KBr): 2962*s*, 2923*m*, 1783*vs* ($\nu_{C=O}$), 1593*m*, 1487*m*, 1449*s*, 1438*s*, 1377*m*, 1360*m*, 1299*s*, 1233*m*, 1167*m*, 1093*m*, 1025*m*, 882*m*, 828*m*, 776*m*, 737*m*, 718*vs*, 702*s*. Anal. calcd for $C_{20}H_{23}NOS_3$ (389.60): C 61.66, H 5.95, N 3.60, S 24.69; found: C 61.57, H 6.13, N 3.42, S 24.86.

4.5. *X-ray crystal-structure determination of 9a*

All measurements were made on an Agilent Technologies SuperNova area-detector diffractometer [26] using graphite-monochromated MoK_a radiation (λ 0.71073 Å) from a micro-focus X-ray source and an Oxford Instruments Cryojet XL cooler. Data reduction was performed with CrysAlisPro.[26] The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction using spherical harmonics [25] was applied. Equivalent reflections were merged. Data collection and refinement parameters are given below,[27] and a view of the molecule is shown in Figure 1. The structure was solved by direct methods using SHELXS-2013,[28] which revealed the positions of all non-H-atoms. The carbonyl group is disordered over two conformations. Two sets of positions were defined for the C- and O-atoms of the carbonyl group and the site occupation factor of the major conformation refined to 0.768(11). Similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered atoms, while corresponding atoms in the two conformations of

the disordered carbonyl group were restrained to have similar atomic displacement parameters. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the methyl groups). The refinement of the structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2\text{-}F_c^2)^2$. A correction for secondary extinction was not applied. Neutral atom scattering factors for non-H-atoms were taken from ref. [29] and the scattering factors for H-atoms were taken from ref. [30] Anomalous dispersion effects were included in F_c;[31] the values for f' and f" were those of ref. [32] The values of the mass attenuation coefficients are those of ref. [33] All calculations were performed using the SHELXL-2014 [34] program.

Crystal data for **9a**: $C_{17}H_{18}OS_3Se_2$, $M = 492.31$, crystallized from diethyl ether, colorless, prism, crystal dimensions 0.07 × 0.10 × 0.20 mm, triclinic, space group $P\bar{1}$, Z = 2, reflections for cell determination 12,824, 2θ range for cell determination 5–61°, $a = 6.67580(7)$ Å, $b = 8.24707(11)$ Å, $c = 18.08016(17)$ Å, $\alpha = 93.4135(9)°$, $\beta = 94.0158(8)°$, $\gamma = 106.2097(10)°$, $V = 950.243(19)$ Å^3, $T = 160(1)$ K, $D_X = 1.720$ g cm^{-3}, $\mu(\text{Mo}K_\alpha) = 4.219$ mm^{-1}, scan type ω, $2\theta_{(max)} = 60.7°$, transmission factors (min; max) = 0.714; 1.000, total reflections measured 23,628, symmetry independent reflections 5239, reflections with $I > 2\sigma(I)$ 4584, reflections used in refinement 5239, parameters refined 231, restraints 19; $R(F)$ [$I > 2\sigma(I)$ reflections] = 0.0246, $wR(F^2)$ [all data] = 0.0575 ($w = [\sigma^2(F_o^2) + (0.0232P)^2 + 0.5336P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$), goodness of fit 1.055, final Δ_{max}/σ 0.001, $\Delta\rho$ (max; min) = 0.47; –0.46 e Å^{-3}.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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