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Reactions of selenourea with benzoyl- and 2-thienoylbromoacetylenes: synthesis of 1,3-diselenetanes and 1,4-diselenafulvenes

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Abstract

A novel reaction of selenourea with benzoylbromoacetylene and 2-thienoylbromoacetylene is described. The reaction proceeds in the presence of triethylamine at −30 to 0 °C to afford new 4- and 5-membered heterocycles.

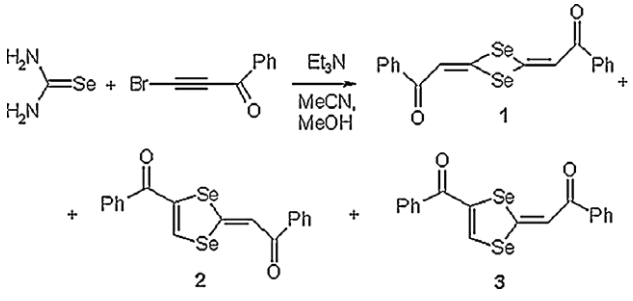
Diselenetanes and ditelluretanes are a relatively rare class of compounds. A number of 1,3-dithietanes have been synthesised,[1,2] whereas only a few representatives of the 1,3-diselenetanes and 1,3-ditelluretanes are known.[3,4]

In comparison to 1,3-diselenetanes, 1,4-diselenafulvenes are better known compounds, and have received much attention from scientists, *inter alia* as starting materials for the synthesis of tetraselenafulvalenes.[5] The latter compounds are used for the preparation of 'organic metals', ion radical salts and charge transfer complexes exhibiting conductivity.[6] Efficient methods for the preparation of 1,4-dichalcogenafulvenes have also been reported.[7]

The synthesis of chalcogen-containing heterocycles is a field of continued interest to us.[1,8–10] We have found that the reaction of elemental selenium with phenylacetylene in the system HMPA/KOH/$SnCl_2$/H_2O provided 2,6-diphenyl-1,4-diselenafulvene in 70% yield.[8] Under similar conditions the reaction of tellurium with phenylacetylene gave 2,6-diphenyl-1,4-ditellurafulvene.[8,9] We have also obtained previously unknown 1,4-ditellurin and 1,4-ditellurafulvene by the reaction of elemental tellurium with acetylene using the system HMPA/KOH/reducing agent.[9]

In the course of our systematic study of reactions of various selenium reagents with acetylenes, we have investigated a novel reaction of selenourea with benzoylbromoacetylene and 2-thienoylbromoacetylene. We found that the reaction of selenourea with benzoylbromoacetylene proceeded in the presence of triethylamine at −30 to 0 °C to afford the 4- and 5-membered heterocycle, *E*-2,4-bis(benzoylmethylene)-1,3-diselenetane (**1**) (23% yield) and *E*- and *Z*-3,5-dibenzoyl-1,4-diselenafulvene (**2** and **3**) (60% yield, $E/Z = 3/2$) (Scheme 1).[11]

Compound **1** and the mixture of *E*- and *Z*-isomer **2** and **3** were separated by column chromatography. It is also



Scheme 1.

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possible to isolate compound **1** using the differences in solubility of the products. In contrast to diselenafulvenes **2** and **3**, compound **1** exhibits low solubility in chloroform and therefore can be isolated as a solid simply by washing a sample with this solvent.

We were unable to separate the *E*- and *Z*-isomer **2** and **3** using column chromatography due to an isomerisation process. For example, when we tried to chromatograph a fraction enriched with the *Z*-isomer we were only able to isolate fractions enriched with the *E*-isomer. This indicates that the *Z*-isomer undergoes isomerisation to the more stable *E*-isomer on the column.

The structural assignment of compounds **1**, **2** and **3** was made by ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy and mass spectrometry. In the mass spectra of compounds **1**, **2** and **3**, the molecular ions ($M^{+\cdot}$ 420) were observed, but the spectra differed in their fragmentation pattern. The mass spectrum of diselenetane **1** showed a maximum peak for the phenyl group ion (77, Ph^{+}) and a peak (209) which is suggested to correspond to the selenoketene ion, $[PhC(O)C{=}C{=}Se]^{+}$. The mass spectrum of the diselenafulvenes **2** and **3** exhibited a maximum peak (105) for the fragment $[PhC(O)]^{+}$.

Compound **1** demonstrated one signal for an olefinic proton in the ^{1}H NMR spectrum and one signal for selenium in the ^{77}Se NMR spectrum indicating a symmetric heterocycle. Another symmetric 6-membered compound with the same molecular formula, that is, 2,5-dibenzoyl-1,4-diselenin, would also contain one olefinic proton signal in the ^{1}H NMR spectrum and one signal for selenium in the ^{77}Se NMR spectrum, but the observed value of the coupling constant J_{SeH} (11.2 Hz) corresponds to a vicinal position for the proton and the selenium atom and thus indicates structure **1**. The value of the geminal coupling constant $^{2}J_{SeH}$ in selenium-containing heterocycles[10] is about 50–55 Hz, and therefore product **1** was not 2,5-dibenzoyl-1,4-diselenin. The choice between the structures of the *Z*- and *E*-isomer of 1,3-diselenetane **1** was made based on the ^{77}Se spectrum, which contained only one signal. The selenium atoms are chemically equivalent in the *E*-isomer, which gives one signal in the ^{77}Se spectrum, whereas the *Z*-isomer having two chemically inequivalent selenium atoms would show two signals in the ^{77}Se spectrum.

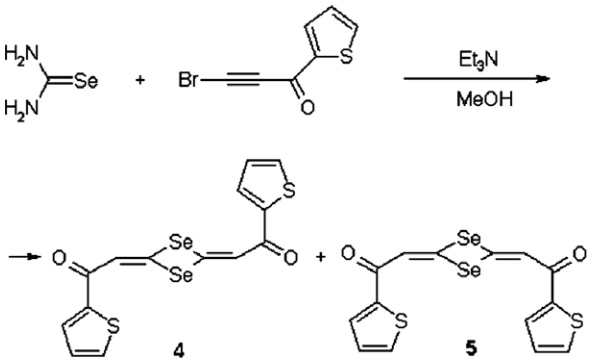
The assignment of the *E*- and *Z*-isomer, **2** and **3**, was made based on the coupling constants $^{5}J_{HH}$. The value of this coupling constant in the *E*-isomer was about 0.7 Hz, whereas in the *Z*-isomer this value was close to zero. Similar trends have been used to assign the structures of the *Z*- and *E*-isomer of 1,4-selenasilafulvenes.[10]

We did not isolate the isomer of compound **1**, *Z*-2,4-bis(benzoylmethylene)-1,3-diselenetane, from the reaction mixture, but the ^{1}H NMR and mass spectral data indicate that this compound is present in the reaction mixture in only a tiny amount. We postulate that the reaction proceeds via dimerisation of selenoketenes to give the *E*-isomer directly. This, coupled with the fact that the *E*-isomer is also more stable thermodynamically than the *Z*-isomer, leads to negligible formation of the latter isomer.

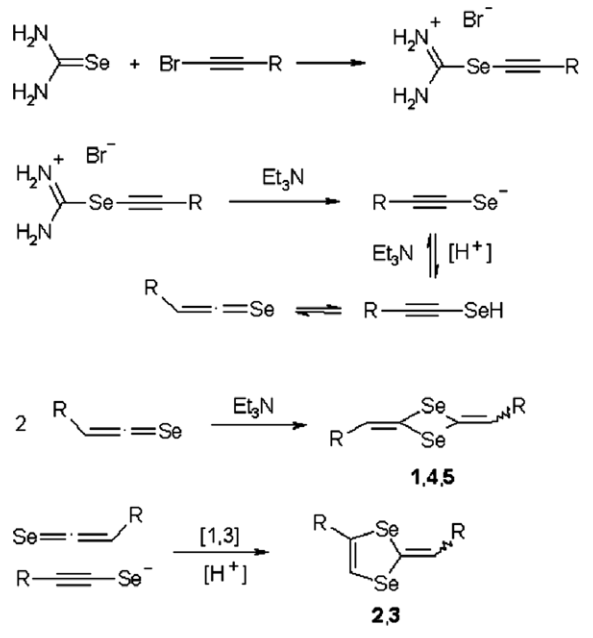
The reaction of selenourea with 2-thienoylbromoacetylene gives *E*-2,4-bis(2-thienoylmethylene)-1,3-diselenetane (**4**) (40% yield) as the major product[12] and *Z*-2,4-bis(2-thienoylmethylene)-1,3-diselenetane (**5**) (6% yield) as the minor product (Scheme 2).

The structural assignment of the *E*- and *Z*-isomer, **4** and **5**, was made by ^{1}H, ^{13}C and ^{77}Se NMR spectroscopy and mass spectrometry. In particular, the ^{77}Se spectrum of product **4** exhibits one signal indicating the *E*-isomer, which has two chemically equivalent selenium atoms. Heating the *E*-isomer **4** for 1.5 h at 120 °C in HMPA led to isomerisation[13] and formation of a mixture of the *Z*- and *E*-isomer, **4** and **5** ($Z/E = 45/55$).

According to the mass spectra, the reaction mixture contains two other compounds with the same molecular ion as selenetanes **4** and **5**. We suggest that these compounds are likely to be the *Z*- and *E*-isomer of the corresponding



Scheme 2.



Scheme 3.

1,4-diselenafulvene. The ^{1}H NMR spectra contain signals which can be attributed to the *E*- and *Z*-3,5-di(2-thienoyl)-1,4-diselenafulvene. However, the amounts of these compounds were very low and they were not isolated from the reaction mixture.

The proposed reaction path involves the formation of selenuronium salts, which generate selenoketenes and ethyneselenolates under the action of triethylamine (Scheme 3).

Selenoketenes are promising intermediates for the synthesis of selenium-containing heterocycles and some of them can be isolated at low temperature.[3] Selenoketenes are apt to both dimerisation and [1,3]-dipolar cycloaddition reaction with ethyneselenolates.[14] We suggest that selenoketene dimerisation leads to diselenetanes **1**, **4** and **5**, whereas a [1,3]-dipolar cycloaddition reaction of selenoketenes and ethyneselenolates furnishes diselenafulvenes **2** and **3**. It is noteworthy that dimerisation of thiocarbonyl compounds to 1,3-dithietanes is a known reaction which proceeds under various conditions, for example, in the presence of bases and under irradiation.[2]

Thus, we have described the novel reaction of selenourea with benzoylbromoacetylene and 2-thienoylbromoacetylene affording new 4- and 5-membered heterocycles.

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11. *Typical procedure for the preparation of diselenetane* **1** *and diselenafulvenes* **2** *and* **3**. A solution of triethylamine (0.7 ml) in absolute methanol (5 ml) was added to a solution of selenourea (0.615 g, 5 mmol) in absolute acetonitrile (10 ml) under argon at 0 °C followed by the addition of a solution of benzoylbromoacetylene (1.04 g, 5 mmol) in acetonitrile (10 ml). The reaction mixture was stirred for 2 h in an ice/water bath. The resulting yellow solid (1.32 g) was filtered off, washed with absolute methanol and dried. The solid was subjected to column chromatography (silica gel, chloroform/hexane = 1:10) to give diselenetane **1** (0.24 g, 23% yield) and diselenafulvenes **2** and **3** (0.627 g, 60% yield) as a mixture of *Z*- and *E*-isomer (*E*/*Z* = 3/2). Attempts to separate isomers **2** and **3** failed due to *Z*-*E*-isomerisation during chromatography. Diselenetane **1** was obtained as a yellow powder, mp 203–204 °C. ^{1}H NMR (400 MHz, HMPA-d_{18}): δ 8.92 (s, 2H, =CH), 8.16 (m, 4H, H_{ortho}), 7.69 (m, 2H, H_{para}), 7.55 (m, 4H, H_{meta}). ^{77}Se NMR (76.3 MHz, HMPA-d_{18}): δ 993 (J_{SeH} = 10.5 Hz). MS *m*/*z* (^{80}Se): 420 (28) $[M]^{+\cdot}$, 209 (6) $[C_6H_5C(O)C_2HSe]^+$, 105 (100) $[C_2HSe]^+$, 77 (80) $[C_6H_5]^+$, 51 (18) $[C_4H_3]^+$. Anal. Calcd for $C_{18}H_{12}O_2Se_2$: C, 51.70; H, 2.89; Se, 37.76. Found: C, 51.93; H, 3.02; Se, 38.17. The mixture of *E*- and *Z*-isomer **2** and **3** (*E*/*Z* = 3/2) was obtained as a yellow powder, mp 265–267 °C. MS, *m*/*z* (^{80}Se): 420 (20) $[M]^{+\cdot}$, 343 (5) $[M-C_6H_5]^+$, 290 (10) $[M-PhC(O)C_2H]^{+\cdot}$, 158 (9) $[C_6H_6Se]^{+\cdot}$, 133 (6) $[C(O)C_2HSe]^+$, 105 (84) $[C_2HSe]^+$, 77 (100) $[C_6H_5]^+$, 51 (23) $[C_4H_3]^+$. In the ^{1}H NMR spectrum (400 MHz, $CDCl_3$), the mixture contains signals for the *E*-isomer **2** [δ 8.53 (d, J_{HH} = 0.7 Hz, 1H, CHSe), 8.10 (d, J_{HH} = 0.7, 1H, O=CCH)] and signals for the *Z*-isomer **3** [δ 8.36 (s, 1H, CHSe), 8.02 (s, 1H, O=CCH)] along with multiplets due to the aromatic protons. In the ^{77}Se NMR spectrum (76.3 MHz, $CDCl_3$), the mixture contains signals for the *E*-isomer **2** [δ 813 ($^2J_{SeH}$ = 46.0, $^3J_{SeH}$ = 11.5, =CHSe), 694 ($^3J_{SeH}$ = 8.4, $^3J_{SeH}$ = 7.3, O=CCSe)] and signals for the *Z*-isomer **3** [δ 772 ($^3J_{SeH}$ = 10.5), 736 ($^2J_{SeH}$ = 56.4, $^3J_{SeH}$ = 10.4)].
12. *Synthesis of E-2,4-bis(2-thienoylmethylene)-1,3-diselenetane* (**4**). Triethylamine (0.7 ml) was added to a solution of selenourea (0.615 g, 5 mmol) in absolute methanol (20 ml) under argon at −30 °C followed by the addition of a solution of 2-thienoylbromoacetylene (1.07 g, 5 mmol) in absolute methanol (15 ml). The reaction mixture was stirred for 1.5 h at −30 °C. The resulting solid (0.46 g) was filtered off, washed with absolute methanol and dried. Crystallisation of the solid from 1,4-dioxane gave pure compound **4** (0.42 g, 40% yield), mp 274–275 °C (1,4-dioxane). ^{1}H NMR (400 MHz, HMPA-d_{18}): δ 8.87 (s, 2H, =CHC=O) 8.55 (m, 4H, C^3H, C^5H), 7.39 (m, 2H, C^4H). ^{13}C NMR (100.6 MHz, HMPA-d_{18}): δ 117.44 (–CH=) 128.25 (C^4), 133.28 (C^3), 136.40 (C^5), 144.76 (=C–Se), 148.87 (C^2), 181.57 (C=O). ^{77}Se NMR (76.3 MHz, HMPA-d_{18}): δ 696 ($^3J_{SeH}$ = 11.5). MS, *m*/*z*, ^{80}Se (rel. int., %): 432 (18) $[M]^{+\cdot}$, 296 (6) $[M-2\text{-}ThC(O)C2H]^{+\cdot}$, 164 (10) $[2\text{-}ThSeH]^{+\cdot}$, 133 (12) $[SeC(O)C_2H]^+$, 111 (100) $[2\text{-}ThC(O)]^+$, 83 (18) $[2\text{-}Th]^+$, 39 (26) $[C_3H_4]^+$. Anal. Calcd for $C_{14}H_8O_2S_2Se_2$: C, 39.08; H, 1.87; S, 14.90; Se, 36.70. Found: C, 39.09; H, 1.81; S, 14.86; Se, 36.18.
13. *Thermal isomerisation of the E-isomer* **4** *to the Z-isomer* **5**. A solution of the *E*-isomer **4** in HMPA-d_{18} was heated at 120 °C for 1.5 h. In the ^{1}H NMR spectrum (400 MHz, HMPA-d_{18}), the mixture contains signals for the *Z*-isomer **5**: δ 8.75 s (2H, =CHC=O), 8.56 m (4H, C^3H, C^4H), 8.36 m (2H, C^5H). According to the ^{1}H NMR data, the yields of the *Z*-isomer **5** and the *E*-isomer **4** were 45% and 55%, respectively.
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