The Isomeric Ethylene Selenodithiocarbonates

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Received October 21, 1975

Syntheses of 1-selena-3-thiolane-2-thione (**6**) and 1,3-dithiolane-2-selone (**4**) are described. Both **6** and **4** react with dimethyl acetylenedicarboxylate to give a mixture of the isomeric esters **9** and **10**. The esters are thermally interconvertible in the presence of dimethyl acetylenedicarboxylate.

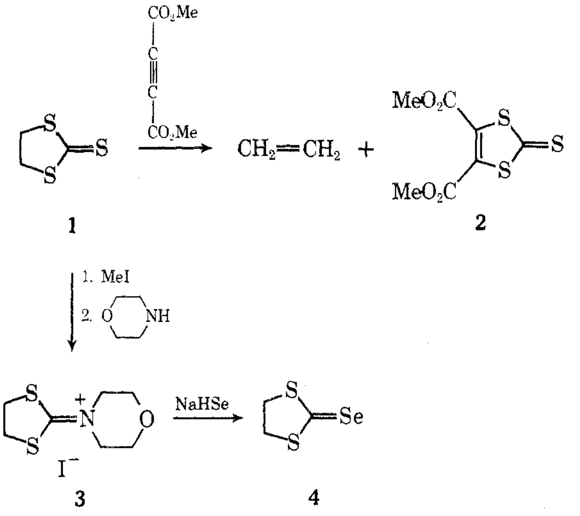
It has been known since 1965 that ethylene trithiocarbonate (**1**) reacts with dimethyl acetylenedicarboxylate to give ethylene and the isotrithione diester **2**;[1] the latter ester has acquired considerable importance recently as a readily prepared precursor of tetrathiafulvalene.[2] A 1970 study of the action of dimethyl acetylenedicarboxylate on mixed sulfur–oxygen analogues of ethylene trithiocarbonate indicated that the dithio ester function (–S–C═S) was essential for the success of the reaction.[3]

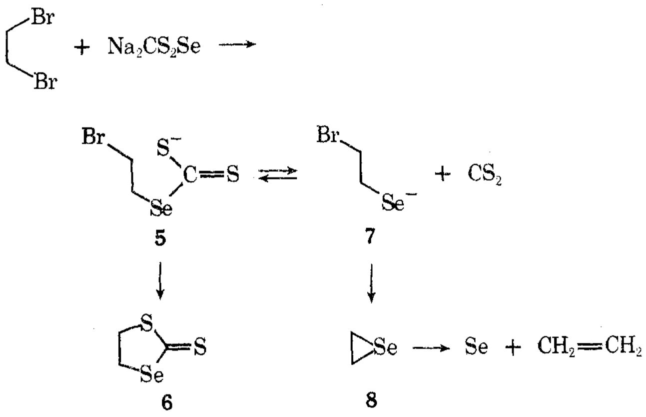
In connection with the broad problem of the synthesis of selenium analogues[4] of tetrathiafulvalene, we have studied the synthesis and dipolar addition reactions of various selenium analogues of ethylene trithiocarbonate. This paper describes the synthesis and some chemistry of the two isomeric monoselenium analogues, 1-selena-3-thiolane-2-thione (**6**) and 1,3-dithiolane-2-selone (**4**).

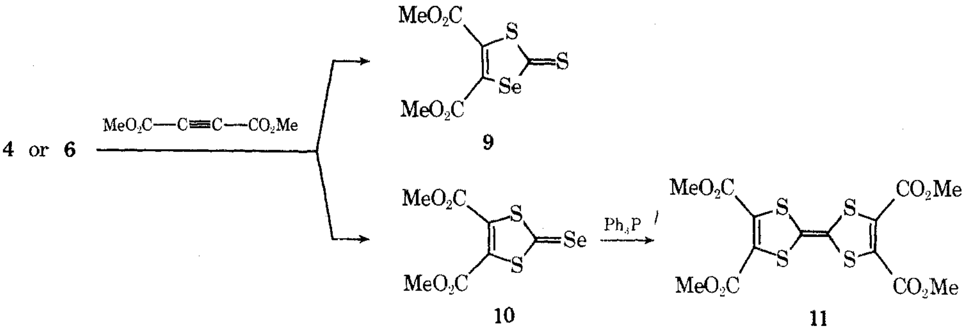
Results

Synthesis of the Isomeric Ethylene Selenodithiocarbonates. The synthesis of ethylene trithiocarbonate (**1**) from ethylene dibromide and sodium trithiocarbonate was reported more than a century ago, and affords a good yield of **1**.[5] The reaction of ethylene dibromide with the recently described selenodithiocarbonate ion[6] was expected to take place in a similar manner, the anticipated major product being the thione isomer **6** because of the superior nucleophilicity of the selenium atom of the attacking anion. The yellow thione **6**, mp 50 °C, was in fact isolated in ca. 2% yield from this reaction. The major reaction course led to the precipitation of red selenium (75%), accompanied by the vigorous evolution of ethylene. The latter process can be rationalized by assuming that the initially formed monoalkylated anion **5** is in equilibrium with carbon disulfide and the β-bromoethylselenide ion (**7**); the latter can rapidly cyclize to the extremely thermolabile[7] ethylene episelenide (**8**).

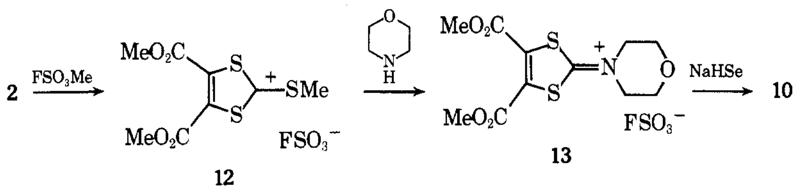
Ethylene trithiocarbonate is easily converted, via its methiodide, into the known morpholinium iodide **3**;[8] reaction of salt **3** with aqueous sodium hydrogen selenide[9] afforded (63%) the coral-red selone **4**, mp 44–45°. Solutions of **4** in nonpolar solvents were a beautiful purple in color, owing to a fairly strong selenocarbonyl absorption maximum at 570 nm.[10]







Reaction of the Ethylene Selenodithiocarbonates with Dimethyl Acetylenedicarboxylate. Selone **4** reacted with dimethyl acetylenedicarboxylate in refluxing toluene to give, in good yield, a red crystalline product, mp 85 °C. Although this material seemed to be homogeneous by all ordinary criteria, including TLC, it was found to be a mixture of the isomeric esters **9** and **10**, which could be separated partially by very slow chromatography (over 2

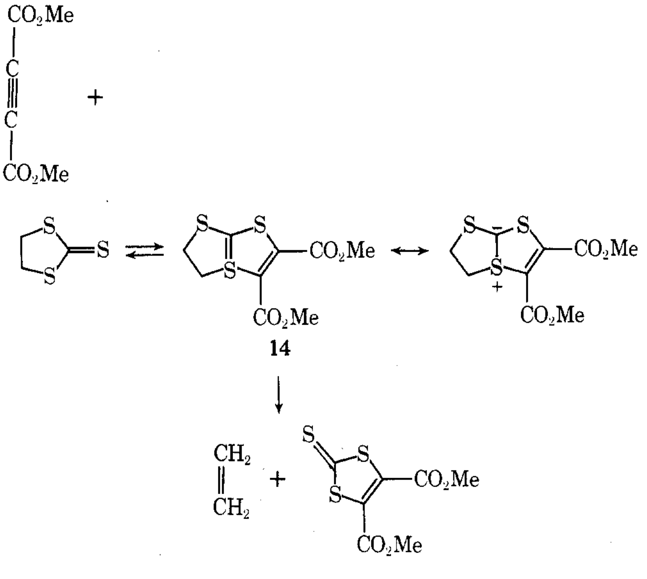


weeks) on silica. The pure components consisted of the expected yellow thione ester **9**, mp 102 °C, and the unexpected maroon selone ester **10**, mp 79 °C; the deep color of the latter was attributed to selone absorption at 540 nm. The reaction of thione **6** with dimethyl acetylenedicarboxylate afforded a similar mixture of the isomeric esters **9** and **10**.

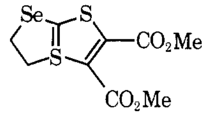
The structure **10** assigned to the maroon ester was supported by its deselenation by triphenylphosphine to give the known[11] black tetracarbomethoxytetrathiafulvalene (**11**). Further confirmation of structure **10** was obtained by an unrelated synthesis. Thus, thione ester **2** was alkylated by methyl fluorosulfonate to give the salt **12**, which reacted with morpholine to give immonium salt **13**. Reaction of **13** with sodium selenide–acetic acid gave the maroon ester **10**.

Discussion

Although the reaction of dimethyl acetylenedicarboxylate with ethylene trithiocarbonate has been recognized as a 1,3-dipolar addition,[1,12] no discrete chemical intermediate has hitherto been proposed. We suggest that the bicyclic "tetracovalent" sulfur heterocycle **14** is produced initially,[13] and that this unstable species then either reverts reversibly to the starting materials, or collapses irreversibly to give the observed products.



The analogous reaction of thione **6** to give a mixture of esters **9** and **10** is readily accommodated by this mechanism, since addition of the acetylene to either the -S-C=S or the -Se-C=S moiety of **6** is possible, giving rise to the different bicyclic intermediates **15** and **16**. On the other hand, the selone **4** would be expected to give only the thione ester **9** via intermediate **17**. The explanation of this apparent anomaly became clear when it was observed that, although esters **9** and **10** are quite stable in pure refluxing toluene, they are *interconverted* under the same conditions in the *presence of dimethyl acetylenedicarboxylate*. These facts point to the transient bicyclic tetraester **18** as the key species through which the isomers **9** and **10** equilibrate under the conditions of their formation from **4** and **6**.



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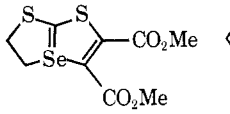

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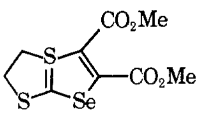

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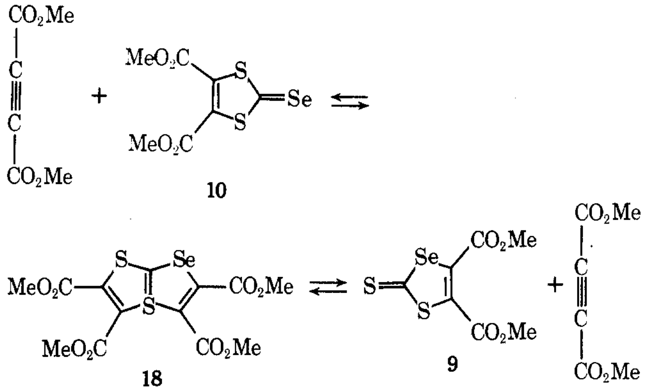

Experimental Section

Melting points are uncorrected. Chromatography was carried out using dry column silica. All organic extracts were washed to neutrality and dried over anhydrous sodium sulfate. NMR spectra ($CDCl_3$ solutions containing tetramethylsilane as internal standard), ultraviolet spectra (cyclohexane solutions), and mass spectra were determined using JEOL-JNH-PS-100, Perkin-Elmer 202 and 270B spectrometers, respectively. Molecular ions containing selenium are reported based on ^{80}Se.

1-Selena-3-thiolane-2-thione (6). To a stirred solution of selenium dioxide (1 g) in 70% aqueous dioxane (20 ml) at 0 °C under nitrogen was added sodium borohydride (0.70 g) in portions. To the resulting sodium hydrogen selenide solution was added aqueous sodium hydroxide (0.4 g in 5 ml), followed by carbon disulfide (2 ml). To the resulting reddish-violet solution was added, at 0 °C, ethylene dibromide (3 g) in dioxane (10 ml). After 1 hr, the mixture was diluted with water and benzene, and the precipitated selenium (0.6 g, 75%) filtered off. The crude product from the benzene layer was subjected to chromatography (benzene–cyclohexane, 3:2). The residue from the initial fraction crystallized from hexane to give **6** (30 mg, ~2%): mp 50 °C; mass spectrum M^+ *m/e* 184 (100%); NMR δ 3.968–4.115 (m); λ_{max} 208 nm (log ϵ 3.97), 303 (4.10), 326 (4.08), 476 (1.82). Anal. Calcd for $C_3H_4S_2Se$: 183.8919. Found: 183.8919.

1,3-Dithiolane-2-selone (4). To a stirred aqueous solution (30 ml) of sodium hydrogen selenide[9] (from 0.50 g of selenium) under nitrogen was added 40 ml of benzene followed by the morpholinium iodide **3**[8] (0.317 g) in one portion. After 0.5 h the reddish-violet benzene layer was separated and the aqueous layer extracted with more benzene (2 × 25 ml). The residue from the benzene extracts was chromatographed (benzene–cyclohexane, 1:2) to yield selone **4** (0.190 g) as the major product. Recrystallization from ether–hexane yielded pure **4** (0.115 g, 63%) as small, coral-red needles: mp 44–45°; mass spectrum M^+ *m/e* 184 (100%); NMR δ 3.870 (s); λ_{max} 217 nm (log ϵ 3.65), 298 (3.96), 355 (4.11), 570 (2.08). Anal. Calcd for $C_3H_4S_2Se$: C, 19.68; H, 2.20. Found: C, 19.92; H, 2.39.

Reaction of 4 with Dimethyl Acetylenedicarboxylate (9 + 10). A mixture of selone **4** (1.14 g) and dimethyl acetylenedicarboxylate (1.1 ml) in dry toluene (15 ml) was refluxed for 1.5 h. Evaporation of solvent, followed by crystallization of the residue from methanol, yielded a 1:1 mixture of thione ester **9** and selone ester **10** (0.695 g, mp 85 °C) as orange-red crystals. Chromatography of the residue from the mother liquor (1:1 benzene–cyclohexane) followed by crystallization yielded more of the mixture of **9** and **10** (0.405 g; total yield 61%).

Separation of 9 and 10. The foregoing mixture of **9** and **10** (0.225 g) was chromatographed very slowly in the dark using benzene–cyclohexane (1:20). Evaporation of the first few milliliters of pure yellow eluate, followed by crystallization of the residue (MeOH), afforded pure thione ester **9** (0.05 g) as yellow needles: mp 102 °C; mass spectrum M^+ *m/e* 298 (100%); NMR δ 3.90 (two barely discernible singlets); λ_{max} 250 nm (log ϵ 3.75), 305, 360, 365 (3.97). Anal. Calcd for $C_7H_6O_4S_2Se$: 297.8872. Found: 297.8854.

The intermediate band gave a mixture of **9** and **10** while the last few milliliters of red eluate upon evaporation followed by crystallization (MeOH) afforded pure selone ester **10** (0.03 g): mp 79 °C; mass spectrum M^+ *m/e* 298; NMR δ 3.909 (s); λ_{max} 210 nm (log ϵ 4.33), 290, 295 (3.17), 392 (4.30), 540 (2.51). Anal. Calcd for $C_7H_6O_4S_2Se$: 297.8872. Found: 297.8860.

Thermal Behavior of 9. A yellow solution of thione diester (5 mg) **9** in toluene (0.2 ml) was refluxed for 1.5 h in the absence of light. Work-up of the yellow solution led to recovery of **9** (3 mg), ir, melting point.

Thermal Behavior of 10. A red solution of selone diester (6 mg) **10** in toluene (0.2 ml) was refluxed for 1.5 h in the absence of light. Work-up led to recovery of **10** (3 mg), ir, melting point.

Synthesis of 10. A mixture of **2** (50 g) and methyl fluorosulfonate (25 ml) in 1:1 methylene chloride–ether (100 ml) was refluxed with stirring to yield the thiolium salt **12** (72 g, quantitative), mp 125 °C. Anal. Calcd for $C_8H_9FO_7S_4$: C, 26.37; H, 2.49. Found: C, 26.36; H, 2.66.

A stirred suspension of the above salt **12** (72 g) in dry acetonitrile (50 ml) was cooled in ice, and was treated with morpholine (18 ml) dropwise. The clear solution was stirred at room temperature for 3 h. The crude immonium salt **13** (53 g) was precipitated with ether. Recrystallization from acetone yielded pure **13** (30 g), mp 115 °C. A second crop of slightly less pure **13** (20 g) was obtained from the mother liquor of crystallization. Anal. Calcd for $C_{11}H_{14}FNO_8S_3$: C, 32.75; H, 3.50. Found: C, 32.83; H, 3.64.

To a stirred suspension of immonium salt **13** (0.20 g) in benzene (75 ml) containing acetic acid (1 ml) under nitrogen was added sodium selenide (0.50 g) followed by water (20 ml). The benzene layer turned red instantly. After stirring for 1 h, the mixture was filtered (Celite), and the benzene layer was separated. Evaporation yielded a red gum (0.130 g) which was purified by chromatography followed by crystallization, to yield pure **10** (0.05 g, ~33%), identical (melting point, ir) with the sample from the cycloaddition.

Interconversion of 9 and 10. A mixture of thione ester **9** (0.007 g) and dimethyl acetylenedicarboxylate (0.005 g) in toluene (0.05 ml) was refluxed at 110 °C for 1.5 h. Chromatography of the reaction mixture led to the isolation of a mixture of **9** and **10** (0.005 g, approximately 2:1 as estimated by uv spectroscopy) which crystallized from methanol to yield 0.003 g, **9** + **10**, mp 80–82 °C. Similarly synthetic selone ester **10** (0.04 g) and dimethyl acetylenedicarboxylate (0.02 g) in toluene (0.50 ml) led to a mixture of **9** and **10** (0.034 g, 1:1 as estimated by uv spectroscopy).

Reaction of 10 with Triphenylphosphine (11). A solution of **10** (0.02 g) and triphenylphosphine (0.02 g) in benzene (5 ml) was refluxed for 1.5 h. The solvent was removed and the residue was chromatographed (benzene–cyclohexane, 1:1). The major dark reddish-brown band was eluted separately to yield, after evaporation and crystallization (MeOH), tetraester **11**, mp 165 °C, mass spectrum M^+ *m/e* 436, identical in all respects (ir, uv, TLC, mass spectrum) with authentic **11**.[11]

Reaction of 6 with Dimethyl Acetylenedicarboxylate. A mixture of **6** (0.05 g) and dimethyl acetylenedicarboxylate (0.03 g) in toluene (0.50 ml) was refluxed for 1.5 h. After work-up a 3:1 mixture of **9** and **10** (0.034 g) was isolated.

Acknowledgment. We thank the National Science Foundation for a grant (MPS 74-03279) in support of this work, and Dr. H. D. Hartzler of Du Pont for an authentic sample of **11**.

Registry No.—**2**, 7396-41-0; **3**, 2080-54-8; **4**, 57560-02-8; **6**, 57560-03-9; **9**, 57560-04-0; **10**, 57560-05-1; **11**, 26314-39-6; **12**, 57560-07-3; **13**, 57560-09-5; selenium dioxide, 7446-08-4; carbon disulfide, 75-15-0; ethylene dibromide, 106-93-4; sodium hydrogen selenide, 12195-50-5; dimethyl acetylenedicarboxylate, 762-42-5; methyl fluorosulfonate, 421-20-5; triphenylphosphine, 603-35-0.

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