Selenium Heterocycles. XXXI (1). Reaction of Ethyl Propiolate with 5-Phenyl-2-thioxo-1,3-thiaselenole and 4-Phenyl-2-thioxo-1,3-dithiole

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Reaction of ethyl propiolate with 4-phenyl-2-thioxo-1,3-dithiole afforded 4-carbethoxy-2-thioxo-1,3-dithiole in high yield. Reaction of ethyl propiolate with 5-phenyl-2-thioxo-1,3-thiaselenole gave 4-carbethoxy-2-thioxo-1,3-thiaselenone (IX), 4-carbethoxy-2-selenoxo-1,3-dithiole (X) and 5-carbethoxy-2-thioxo-1,3-thiaselenole (XI). A possible mechanism for the formation of these compounds is given.

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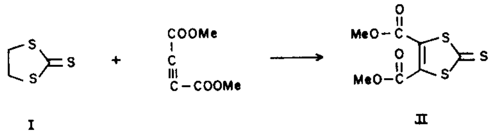
In continuation of our study on the chemistry of selenium heterocyclic compounds (2-7), we have recently reported a simple general method for the synthesis of 5-substituted 2-thioxo-1,3-thiaselenoles (8). In the present work, reaction of the latter and of the corresponding thia-analog with ethyl propiolate is reported.

It has been reported that ethylene trithiocarbonate (I) reacts with dimethyl acetylenedicarboxylate to give 4,5-dicarbomethoxy-2-thioxo-1,3-dithiole (II) in high yield (9). However, 4-phenyl-3-thioxo-1,3-dithiole was reported to be completely unreactive toward dimethyl acetylenedicarboxylate in either cold or boiling benzene. In boiling xylene a low yield (7-10%) of a 1:2 adduct of undetermined structure was isolated (10).

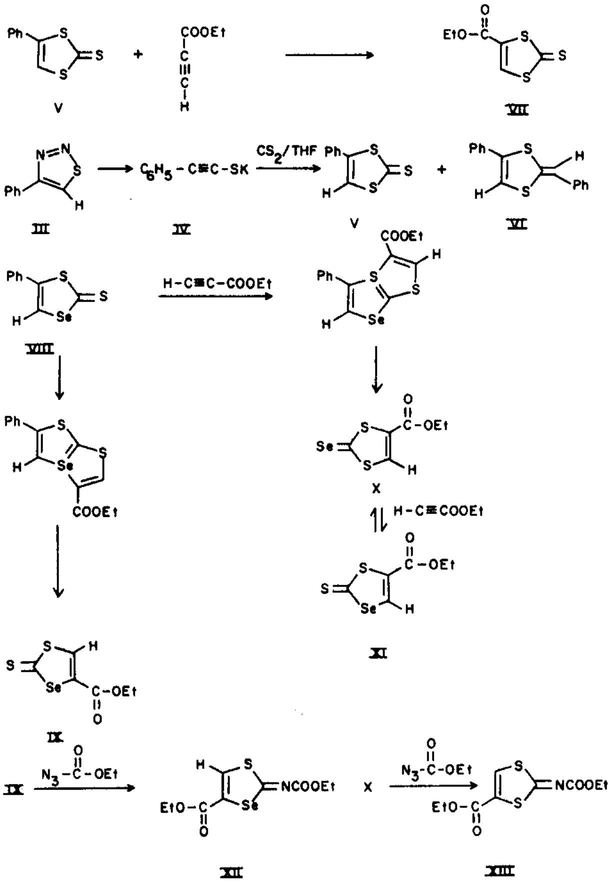


We have found that the reaction of 4-phenyl-2-thioxo-1,3-dithiole (V) with ethyl propiolate gave 4-carbethoxy-2-thioxo-1,3-dithiole (VII) (11) in high yield. Compound V was obtained through a general method for the preparation of the corresponding selenium analog reported previously (8). Decomposition of 4-phenyl-1,2,3-thiadiazole (III) with ethanolic potassium hydroxide in dioxane afforded compound IV. Addition of carbon disulfide to IV in tetrahydrofuran afforded compound V in high yield.

Reaction of 5-phenyl-3-thioxo-1,3-thiaselenole (VIII) with ethyl propiolate afforded 4-carbethoxy-2-thioxo-1,3-thiaselenole (IX) and 4-carbethoxy-2-selenoxo-1,3-dithiole (X) in a ratio of 2:1. In addition a small amount of 5-carbethoxy-2-thioxo-1,3-thiaselenole (XI) was also isolated. A possible mechanism for this reaction is shown in Scheme I.

As can be seen from this mechanism, compound XI was formed through the addition of ethyl propiolate to compound X. The structures of compounds IX, X and XI were confirmed through spectroscopic methods (ir, nmr and ms).

Scheme I



In the nmr spectra of compounds IX and X, H-5 and H-4 appears at δ 7.93 and 8.03 ppm, respectively. A similar value was observed for compound VII (11). However, as expected, in compound XI, H-4 appears at a lower field relative to compounds IX and X, namely at δ 8.68 ppm.

In addition, the structures of compounds IX and X were confirmed through reaction with ethyl azidoformate (12). Reaction of ethyl azidoformate with compounds IX and X afforded 4-carbethoxy-2-carbethoxyimino-1,3-thiaselenole (XII) and 4-carbethoxy-2-carbethoxyimino-1,3-dithiole (XIII), respectively (Scheme I).

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EXPERIMENTAL

Melting points were taken on a Kofler hot stage microscope and were uncorrected. The ir spectra were obtained on a Perkin Elmer Model 267 spectrograph. Nmr spectra were determined using a Varian T-60 spectrometer and chemical shifts (δ) are in ppm relative to internal tetramethylsilane. Mass spectra were run on a Varian MAT-311 spectrometer at 70 eV.

4-Phenyl-2-thioxo-1,3-dithiole (V).

To a stirred solution of 4-phenyl-1,2,3-thiadiazole (III, 1.62 g., 0.01 mole) in dioxane (50 ml.), a solution of potassium hydroxide (1.12 g., 0.02 mole) in ethanol (3 ml.) was added, whereupon the evolution of nitrogen ceased. The precipitate was filtered, washed with dioxane and then with dry ether. The precipitate was dissolved in tetrahydrofuran (20 ml.) and carbon disulfide (5 ml.) was added. Stirring was continued for 1 hour at room temperature. The solvent was evaporated under reduced pressure. Water (100 ml.) was added and the mixture was extracted with chloroform. The solvent was dried, filtered and evaporated. The residue was purified by tlc (silica gel, chloroform:petroleum ether; 1:1). The fast moving fraction was crystallized from ethanol to give 0.2 g. (15%) of 2,ω-diphenyl-1,4-dithiafulvene (VI), m.p. 203-204°, mixed melting point with an authentic sample (13) 203-204°. The slow moving fraction was crystallized from acetone to give 1.57 g. (75%) of V, m.p. 117-118° [lit (14) m.p. 117-118°].

Anal. Calcd. for $C_9H_6S_3$: C, 51.43; H, 2.86. Found: C, 51.62; H, 2.71.

4-Carbethoxy-2-thioxo-1,3-dithiole (VII).

A solution of compound V (630 mg., 3 mmoles) and ethyl propiolate (2 ml.) in xylene (10 ml.) was reflxued for 48 hours. The solvent was evaporated and the residue was purified by tlc (silica gel, chloroform:petroleum ether; 1:1). The product was crystallized from ether-petroleum ether to give 463 mg. (75%) of VII, m.p. 44-45° [lit. (11) m.p. 39-40°]; ir (potassium bromide): 1710 cm^{-1} (ester): nmr (deuteriochloroform): 7.92 (s, 1H, H_4), 4.35 (q, 2H, OCH_2), 1.38 ppm (t, 3H, CH_3); ms: m/e (relative intensity) 206 (M^+, 100), 178 (46), 161 (44), 133 (17), 102 (66), 90 (42), 57 (57) and 45 (27).

Anal. Calcd. for $C_6H_6O_2S_3$: C, 34.95; H, 2.91. Found: C, 35.16; H, 3.08.

Reaction of Ethyl Propiolate with 5-Phenyl-2-thioxo-1,3-thiaselenole (VIII).

A solution of cmpound VIII (1.028 g., 4 mmoles) and ethyl propiolate (2 ml.) in xylene (10 ml.) was refluxed for 10 hours. The solvent was evaporated and the residue was chromatographed (tlc, silica gel, chloroform:petroleum ether; 1:1). The fastest moving fraction was crystallized from petroleum ether to give 360 mg. (35%) of 4-carbethoxy-2-thioxo-1,3-thiaselenole (IX), m.p. 31-32°; ir (potassium bromide): 1710 cm^{-1} (ester); nmr (deuteriochloroform): 7.93 (s, 1H, H_5), 4.30 (q, 2H, OCH_2) and 1.33 ppm (t, 3H, CH_3); ms: m/e (relative intensity) 254 (M^+, 100), 252 (46), 209 (11), 130 (27), 112 (39), 105 (26), 102 (61), 101 (11), 85 (13), 76 (15), 69 (18), 58 (17) and 53 (19).

Anal. Calcd. for $C_6H_6O_2S_2Se$: C, 28.46; H, 2.37. Found: C, 28.65; H, 2.14.

The next fraction was crystallized from ether-petroleum ether to give 50 mg. (5%) of XI, m.p. 72-74°; nmr (deuteriochloroform): 8.68 (s, 1H, H_4), 4.35 (q, 2H, OCH_2) and 1.33 ppm (t, 3H, CH_3); ms: m/e (relative intensity) 254 (M^+, 100), 252 (80), 226 (24), 209 (16), 146 (41), 130 (11), 106 (42), 105 (28), 101 (42), 85 (20), 77 (14) and 53 (47).

Anal. Calcd. for $C_6H_6O_2S_2Se$: C, 28.46; H, 2.37. Found: C, 28.23; H, 2.18.

The next fraction was crystallized from ether-petroleum ether to give 155 mg. (15%) of 4-carbethoxy-2-selenoxo-1,3-dithiole (X), m.p. 61-62°; ir (potassium bromide): 1710 cm^{-1} (ester); nmr (deuteriochloroform): 8.03 (s, 1H, H_5), 4.33 (q, 2H, CH_2) and 1.32 ppm (s, 3H, CH_3); ms: m/e (relative intensity) 254 (100), 252 (40), 226 (34), 209 (26), 122 (27), 112 (16), 105 (13), 102 (24), 85 (21) and 76 (29).

Anal. Calcd. for $C_6H_6O_2S_2Se$: C, 28.46; H, 2.37. Found: C, 28.68; H, 2.58.

Reaction of 4-Carbethoxy-2-thioxo-1,3-thiaselenole (IX) with Ethyl Azidoformate.

A solution of compound IX (253 mg., 1 mmole) and 0.3 ml. of ethyl azidoformate in carbon tetrachloride (5 ml.) was refluxed overnight. The solvent was evaporated and the residue was purified by tlc (silica gel, chloroform:petroleum ether, 1:1) to give 154 mg. (50%) of 4-carbethoxy-2-carbethoxyimino-1,3-thiaselenole (XII), m.p. 93-94° (ether); ir (potassium bromide): 1730 and 1653 cm^{-1} (ester); nmr (deuteriochloroform): 8.03 (s, 1H, H_5), 4.40 (2q, 4H, OCH_2), 1.37 (2t, 6H, CH_3); ms: m/e (relative intensity) 309 (M^+, 24), 307 (11), 237 (30), 235 (14), 210 (32), 208 (16), 182 (35), 164 (17), 86 (12) and 29 (100).

Anal. Calcd. for $C_9H_{11}NO_4SSe$: C, 35.06; H, 3.57; N, 4.55. Found: C, 35.24; H, 3.38; N, 4.74.

Reaction of 4-Carbethoxy-2-selenoxo-1,3-dithiole (X) with Ethyl Azidoformate.

A solution of compound X (126.5 mg., 0.5 mmole) and 0.2 ml. of ethyl azidoformate in carbon tetrachloride (3 ml.) was refluxed overnight and worked up as above to give 65 mg. (50%) of 4-carbethoxy-2-carbethoxyimino-1,3-dithiole (XIII), m.p. 93-94° (ether-petroleum ether); ir (potassium bromide): 1730 and 1665 cm^{-1} (ester); nmr (deuteriochloroform): 7.97 (s, 1H, H_5), 4.40 (2q, 4H, OCH_2) and 1.37 (t, 6H, CH_3); ms: m/e (relative intensity) 261 (M^+, 43), 216 (34), 189 (99), 188 (20), 162 (24), 134 (27), 116 (22), 90 (22), 89 (26), 86 (29), 45 (32) and 29 (100).

Anal. Calcd. for $C_9H_{11}NO_4S_2$: C, 41.38; H, 4.21; N, 5.36. Found: C, 41.16; H, 4.00; N, 5.54.

Acknowledgment.

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