The selenonesters were somewhat unstable at room temperature, slowly depositing red selenium, and were not sufficiently stable to permit shipment for analysis. At temperatures below 0° and in solution no changes could be observed after several weeks.

Experimental Section

NMR spectra were obtained on a Varian T-60; ir and uv spectra were determined on Pye-Unicam Models SP 1200 and 8000, respectively; mass spectra were taken on a Varian Model CH5 spectrometer.

General Method for the Preparation of Selenonesters. 1,2,3-Selenadiazole (150 mg) was added to a 100-ml solution of 0.01 *N* potassium *tert*-butoxide in *tert*-butyl alcohol. After the gas evolution ceased, the resulting solution of I was added slowly through a capillary tube, over 8–9 hr, to 500 ml of alcohol, to which enough acetic acid had been added to keep the solution slightly acidic throughout the reaction. After all of I had been added the alcohol was evaporated to near dryness on a rotary film evaporator at 40° bath temperature. The solid that separated (some fulvene and salts) was centrifuged and the supernatant liquid was chromatographed on 50 g of silica gel, using 10% chloroform in petroleum ether (bp 40–60°). The selenonesters moved as yellow bands, being eluted just behind the corresponding fulvenes. The yields depended on the speed of addition of I. Nearly quantitative yields could be obtained in very dilute solution, as judged by their absorbance in the uv. Yields of isolated pure esters, however, were about 50%.

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Registry No.—I (R = Ph), 36928-61-7; I (R = *p*-MeO-Ph), 57444-37-8; I (R = *p*-Cl-Ph), 57444-38-9; I (R = *p*-O$_2$N-Ph), 57444-39-0; I (R = *β*-Naph), 57444-40-3; 4-phenyl-1,2,3-selenadiazole, 25660-64-4; 4-(*p*-methoxylphenyl)-1,2,3-selenadiazole, 27892-76-8; 4-(*p*-chlorophenyl)-1,2,3-selenadiazole, 27892-68-8; 4-(*p*-nitrophenyl)-1,2,3-selenadiazole, 27892-72-4; 4-*β*-naphthyl-1,2,3-selenadiazole, 52376-78-0; methanol, 67-56-1; ethanol, 64-17-5; isopropyl alcohol, 67-63-0.

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Organic Metals. A Novel Route to Cycloalkenotetrathiafulvalenes

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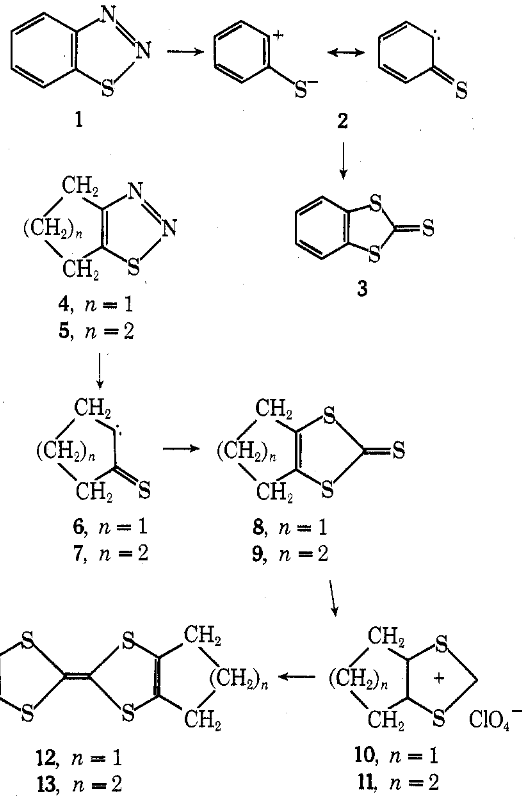
It has been known since 1961 that thermolysis of 1,2,3-benzothiadiazole (**1**) leads to the dipolar intermediate **2**, which can be efficiently intercepted by carbon disulfide to yield (84%) the benzotrithiocarbonate (**3**).[1] An attempt to carry out the analogous reaction with the parent 1,2,3-thiadiazole afforded only a 0.2% yield of vinylene trithiocarbonate.[1a] Since the poor result observed in the latter case may be attributed to the fragmentation of the thiocarbonyl carbene to sulfur and acetylene, we anticipated that cycloalkenothiocarbonyl carbenes, which could only fragment to give strained cyclic alkynes, would have a sufficient lifetime to be intercepted by carbon disulfide. This expectation has now been confirmed in the preparatively useful conversion of several cycloalkenothiadiazoles to the corresponding cycloalkenotrithiocarbonates, which in turn served as convenient precursors of the corresponding tetrathiafulvalenes.



Thus, cyclohexeno-1,2,3-thiadiazole (**5**), which is readily prepared by the thionyl chloride treatment of cyclohexanone tosylhydrazone,[2] was heated for 7 hr with carbon disulfide at 215° to give, in 42.6% yield, the trithiocarbonate **9**, identical with material prepared by the method of Fanghänel.[3] Thermolysis of cyclopenteno-1,2,3-thiadiazole (**4**) in carbon disulfide under similar conditions afforded, in 41.4% yield, the corresponding cyclopentenotrithiocarbonate (**8**), mp 105–108°. In either case, the reaction is assumed to proceed by way of a 1,3-dipolar addition of an intermediary thiocarbonyl carbene (**7** or **6**) to the thiocarbonyl group of carbon disulfide.[4]

A simple synthesis of the parent tetrathiafulvalene (TTF) consists of the peracid oxidation of vinylene trithiocarbonate to give the 1,3-dithiolium ion,[5] followed by treatment of the latter with triethylamine.[6] This procedure was readily applicable to the synthesis of the cycloalkeno TTF derivatives **12** and **13**. Thus, the cyclohexenotrithiocarbonate (**9**) was oxidized to the corresponding 1,3-dithiolium ion, isolated as the perchlorate **11**; triethylamine treatment of the latter afforded, in 73.8% overall yield from **9**, bis(cyclohexeno)tetrathiafulvalene (**13**), mp 247.6–248.2°. In a similar manner, the cyclopentenotrithiocarbonate (**8**) was converted, via the 1,3-dithiolium perchlorate **10**, into bis(cyclopenteno)tetrathiafulvalene (**12**), mp 244°, in 70% overall yield.

Charge transfer salts of **12** and **13** with the π acceptor TCNQ[7] were formed as the 1:1 TCNQ salts, **14**[8] and **15**, respectively. The four probe room temperature electrical

14, $\mathbf{12}^{\cdot +}$ $\mathrm{TCNQ}^{\cdot -}$
15, $\mathbf{13}^{\cdot +}$ $\mathrm{TCNQ}^{\cdot -}$

conductivities measured on compactions of **14** and **15** are 15 and 5×10^{-5} $(\Omega\ \mathrm{cm})^{-1}$, respectively [TTF–TCNQ: 25 $(\Omega\ \mathrm{cm})^{-1}$]. The wide difference in electrical behavior is likely associated with different crystallographic linear chain stacking of donors and acceptors in the two salts, segregated in **14** and alternating in **15**.[9]

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer and ultraviolet–visible spectra were determined on a Perkin-Elmer 202 spectrophotometer. Mass spectra were obtained on a Perkin-Elmer 270B mass spectrometer. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Cyclopenteno-1,2,3-thiadiazole (4). Improving on the precedure of Meier,[2] 176.65 g (0.7 mol) of cyclopentanone tosylhydrazone was treated cautiously at 0° with 450 ml (6.2 mol) of thionyl chloride. The dark solution was stirred at room temperature for 3 h or until gas evolution ceased. The excess thionyl chloride was removed by rotary evaporation at 60°. The resulting residue was treated with 78.55 g (1.4 mol) of potassium hydroxide in 400 ml of water, warmed gently on a steam bath for 45 min, and filtered. The solution was extracted twice with ether, the ether layers being combined, dried over $MgSO_4$, and concentrated. The resulting dark oil was distilled at 60–62° (0.05 mm) to give 30.0 g (34%) of **4** as a slightly yellow liquid [lit.[2] bp 42–46° (0.01 mm)].

Cyclohexeno-1,2,3-thiadiazole (5) was prepared as described above for the preparation of **4** using 133.19 g (0.5 mol) of cyclohexanone tosylhydrazone, 320 ml of thionyl chloride, and 56.11 g of potassium hydroxide. The dark oil was distilled at 70–71° (0.05 mm) to give 63.7 g (91%) of **5** as a colorless liquid [lit.[2] bp 51–55° (0.01 mm)].

Cyclopentenotrithiocarbonate (8). A solution of 11.0 g of **4** in 60 ml of carbon disulfide was heated to 205° for 6 h in a glass-lined stainless steel autoclave. After cooling, the excess carbon disulfide was removed by rotary evaporation. The residue was dissolved in chloroform and filtered and the chloroform solution concentrated to a dark oil. The oil was chromatographed on silica gel using hexane as eluent. The highly colored impurities (<4.5%) were discarded and the remaining yellow fractions were combined and concentrated to a yellow solid. The solid was crystallized from hexane to give 6.29 g (41.4%) of **8** as long, yellow needles: mp 105–108°; ir (KBr) 1110 and 1040 cm^{-1}; $\lambda_{\max}$ (hexane) 232 nm ($\log \epsilon$ 3.79), 268 (3.07), and 380 (4.02); mass spectrum *m/e* 174.

Anal. Calcd for $C_6H_6S_3$: C, 41.34; H, 3.47; S, 55.18. Found: C, 41.26; H, 3.56; S, 55.20.

Cyclohexenotrithiocarbonate (9). Following the above procedure for the preparation of **8**, a solution of 15 g of **5** in 60 ml of carbon disulfide was heated for 7 h at 215°. The dark oil was chromatographed using hexane–chloroform as eluent. The colorless fractions (<4%) were discarded and the remaining yellow fractions were combined and concentrated to a yellow solid. The solid was crystallized from hexane–chloroform to give 8.52 g (42.6%) of **9** as short, yellow needles: mp 81–82° (lit.[3] mp 82–83°); ir (KBr) 1055 and 899 cm^{-1}; $\lambda_{\max}$ (hexane) 234 nm ($\log \epsilon$ 3.84), 273 (3.15), and 372 (4.072); mass spectrum *m/e* 188.

Bis(cyclopenteno)tetrathiafulvalene (12). *Caution should be exercised with perchlorate salts.*[10] A solution of 0.500 g (2.87 mmol) of **8** in 20 ml of acetone was cooled to 0°. A cold solution of 2.38 g (11.72 mmol) of *m*-chloroperbenzoic acid (85%) in 20 ml of acetone was added dropwise with stirring. After 30 min, no **8** could be detected by TLC (silica gel HF, chloroform, R_f 0.86). Perchloric acid (60–62%) (3 ml) was added to the dark solution precipitating the light tan perchlorate salt **10**. Further salt precipitated on addition of 200 ml of ether and the salt was filtered, washed with ether, and dried.[10] The perchlorate salt was directly dissolved in 20 ml of acetonitrile. The solution was degassed with argon and cooled to 5°. Triethylamine, 1.0 g, was added dropwise and immediately a solid formed. After stirring for 30 min, 20 ml of water was added and the solid filtered and dried. The crude product, mp 242–245°, was sublimed at 200° (0.05 mm) to give 0.284 g (70%) of **12** as a yellow-brown solid, crystallized from acetonitrile–trichlorobenzene: mp 244°; ir (KBr) 1450, 1325, and 769 cm^{-1}; $\lambda_{\max}$ (1,2-DCE) 307 nm ($\log \epsilon$ 4.02), 327 sh (3.968), and 462 (2.248); mass spectrum *m/e* (rel intensity) 284 (M, 100), 142 (M/2, 17).

Anal. Calcd for $C_{12}H_{12}S_4$: C, 50.66; H, 4.26; S, 45.08. Found: C, 50.64; H, 4.13; S, 45.27.

Bis(cyclohexeno)tetrathiafulvalene (13). *Caution should be exercised with perchlorate salts.*[10] Following the above procedure for the preparation of **12**, 2.0 g of **9** was oxidized with 10.781 g of peracetic acid (30%) to give the hydrosulfate salt as a red oil. Treatment with 12 ml of perchloric acid (60–62%) gave the solid tan perchlorate salt **11**.[10] The perchlorate salt was directly dissolved in 30 ml of acetonitrile and treated with 1.51 g of triethylamine to give 1.49 g (90%) of **13** as a yellow solid, mp 245° dec, purified by sublimation at 190° (0.05 mm) to give **13** (82%) as a red-brown solid, crystallized from chlorobenzene: mp 247.6–248.2°; ir (KBr) 1448, 1340, and 779 cm^{-1}; $\lambda_{\max}$ (CH_3CN) 297 nm ($\log \epsilon$ 4.025), 323 sh (3.98), and 472 (2.283); mass spectrum *m/e* (rel intensity) 312 (M, 100), 156 (M/2, 9).

Anal. Calcd for $C_{14}H_{16}S_4$: C, 53.80; H, 5.16; S, 41.04. Found: C, 53.86; H, 5.15; S, 41.30.

Bis(cycloalkeno)tetrathiafulvalene–tetracyanoquinodimethane (14 and 15). Charge transfer salts **14** and **15** were formed by the known procedure[7] using rigorously purified acetonitrile under an argon atmosphere. The two solutions were mixed, heated for an additional 15 min, and allowed to cool over several hours to yield the respective salts as black needles.

For **15**: Anal. Calcd for $C_{26}H_{20}N_4S_4$: C, 60.43; H, 3.91; N, 10.85; S, 24.82. Found: C, 59.37; H, 4.09; N, 10.60; S, 24.29.

For **14**:[8] Anal. Calcd for $C_{14}H_{16}N_4S_4$: C, 58.98; H, 3.31; N, 11.47; S, 26.24. Found: C, 59.05; H, 3.35; N, 11.46; S, 26.36.

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Registry No.—**4**, 56382-73-1; **5**, 56382-72-0; **8**, 17534-29-1; **9**, 698-42-0; **12**, 57512-84-2; **13**, 35079-58-4; **14**, 57527-02-3; **15**, 57512-86-4; cyclopentanone tosylhydrazone, 17529-98-5; cyclohexanone tosylhydrazone, 4545-18-0; carbon disulfide, 75-15-0.

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Anodic Oxidation of Diphenylamine in the Presence of Methoxide Ion

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The electrochemical oxidation of diphenylamines produces the intermolecular and intramolecular coupling