of recovered benzyl bromide. At temperatures between −20 and 0° appreciable amounts of benzyl phenyl sulfide were isolated. At −40° <5% of benzyl phenyl sulfide could be detected.

[13] Posner[8c] has observed that lithium methyl(vinyl)cuprate in THF transfers the vinyl exclusively to C-3 of 2-cyclopentenone. When diethyl ether is employed instead of THF, the methyl and vinyl groups are both transferred to C-3 of 2-cyclopentenone. In our hands use of THF results in greatly diminished yields of 1,4-addition product.

[14] Yields are based on starting enone and on isolated chromatographically pure material. In general 2.0 equiv of **2** was employed and reactions were conducted at −78° (1 hr) followed by warming to −40° (2 hr).

[15] For an example of a δ-lactone fused 1,3 to the 14-membered cembrane ring system see M. B. Hossain and D. van der Helm, *Recl. Trav. Chim. Pays-Bas*, **88**, 1413 (1969).

[16] Similar selectivity has been observed in other organocopper(I) systems: (a) E. J. Corey and M. Jautelet, *Tetrahedron Lett.*, 5787 (1968); (b) E. J. Corey and I. Kuwajima, *ibid.*, 487 (1972); (c) I. Kuwajima and Y. Doi, *ibid.*, 1163 (1972).

Synthesis of α-Substituted Selenonesters

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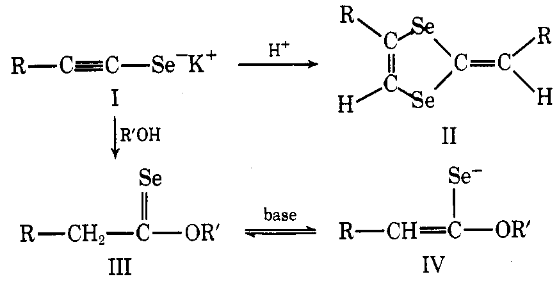
The syntheses of very few selenonesters have been reported[1]. We wish to report a new general synthesis of α-substituted selenonesters.

During our previous work we had observed that arylethynylselenolate salts (I), prepared from 4-aryl-1,2,3-selenadiazoles, dimerized to form 1,3-diselenafulvenes (II).[2] Raap[3] has reported that aryl- or alkylethynylthiolates under certain conditions react with alcohols to form thionesters. It appeared possible that in very dilute solutions the rate of the bimolecular step leading to the fulvene II should slow down and reaction of I with protic solvents should predominate.



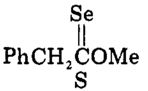
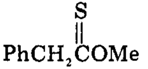
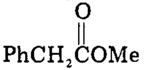
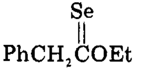
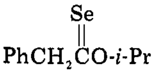
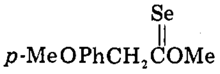
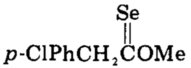
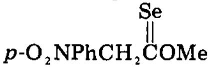
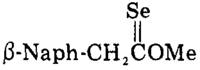
When I (R = Ph) is added to ethanol in low concentrations, besides the appearance of the characteristic absorbance at 340 nm for the fulvene a new peak at 275 nm is formed. Upon basification, this absorbance is shifted to 325 nm with an increase in absorbance. By using a technique of slow addition to a slightly acidified solution, such that the concentration of I at any time remains below 10^{-5} *M*, the formation of the fulvene is minimized; the product is essentially the 275-nm compound. Purified by column chromatography, the light yellow liquid was identified by its NMR, MS, and ir spectra as *O*-ethylphenyl selenonacetate (III).

The bathochromic shift in the uv spectrum on addition of base is attributed to the formation of the enolate ion (IV). A similar enolization of thionesters could be observed under more strongly basic conditions. Evidence for thione–enethiol equilibrium has been reported using polarographic techniques[4].

The NMR spectrum of all the selenonester derivatives formed (Table I) showed a shift of the methylene as well as the protons of the alkyl group of the ester to a lower field than the corresponding oxygen and even slightly lower than the sulfur analogues.

Besides the derivatives shown in Table I, selenonesters of acetic and propionic acids were also prepared. However, owing to their volatility, they could not be isolated in pure form and were identified only through their characteristic uv spectra.

Table I
Chemical Shifts and Ultraviolet Spectral Data of Selenoesters and Comparison with Thione and Oxygen Esters

Ester	Registry no.	NMR,[a] δ, ppm	λ_{max}, nm (ε)
 $\mathrm{PhCH_2\overset{\overset{Se}{\|}}{C}OMe}$	57444-30-1	3.95 (2 H, s), 4.13 (3 H, s), 7.2 (5 H, br s)	275 (6.7×10^3)[b]
 $\mathrm{PhCH_2\overset{\overset{S}{\|}}{C}OMe}$	5873-85-8	3.95 (2 H, s), 3.94 (3 H, s), 7.2 (5 H, br s)	240 (7.1×10^3)[b]
 $\mathrm{PhCH_2\overset{\overset{O}{\|}}{C}OMe}$	101-41-7	3.50 (3 H, s), 3.54 (2 H, s), 7.2 (5 H, br s)	214 (6.0×10^3)[b]
 $\mathrm{PhCH_2\overset{\overset{Se}{\|}}{C}OEt}$	57444-31-2	1.40 (3 H, t), 3.95 (2 H, s), 4.60 (2 H, q), 7.2 (5 H, br s)	277 (7.7×10^3)[c]
 $\mathrm{PhCH_2\overset{\overset{Se}{\|}}{C}O\text{-}\mathit{i}\text{-}Pr}$	57444-32-3	1.30 (6 H, d), 3.90 (2 H, s), 5.60 (1 H, m), 7.2 (5 H, br s)	282 (8.3×10^3)[d]
 $\mathit{p}\text{-}\mathrm{MeOPhCH_2\overset{\overset{Se}{\|}}{C}OMe}$	57444-33-4	3.89 (2 H, s), 3.95 (2 H, s), 4.18 (3 H, s), 6.75 (2 H, d), 7.20 (2 H, d)	275 (7.6×10^3)[b]
 $\mathit{p}\text{-}\mathrm{ClPhCH_2\overset{\overset{Se}{\|}}{C}OMe}$	57444-34-5	3.98 (2 H, s), 4.18 (3 H, s), 7.25 (4 H, br s)	275 (7.0×10^3)[b]
 $\mathit{p}\text{-}\mathrm{O_2NPhCH_2\overset{\overset{Se}{\|}}{C}OMe}$	57444-35-6	4.0 (2 H, s), 4.16 (3 H, s), 7.4 (2 H, d), 8.1 (2 H, d)	275 (1.68×10^4)[b]
 $\beta\text{-}\mathrm{Naph\text{-}CH_2\overset{\overset{Se}{\|}}{C}OMe}$	57444-36-7	4.20 (5 H, s), 7.6 (7 H, m)	276 (1.3×10^4)[b]

[a] In carbon tetrachloride with Me_4Si as internal reference. [b] In methanol. [c] In ethanol. [d] In 2-propanol.

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.

References and Notes

(1) R. Mayer, S. Scheithauer, and D. Kunz, *Chem. Ber.*, **99**, 1393 (1966).
(2) M. H. Ghandehari, D. Davalian, M. Yalpani, and M. H. Partovi, *J. Org. Chem.*, **39**, 3906 (1974).
(3) R. Raap, *Can. J. Chem.*, **46**, 2251 (1968).
(4) D. Kunz, S. Scheithauer, S. Bleisch, and R. Mayer, *J. Prakt. Chem.*, **312**, 426 (1970).

Organic Metals. A Novel Route to Cycloalkenotetrathiafulvalenes

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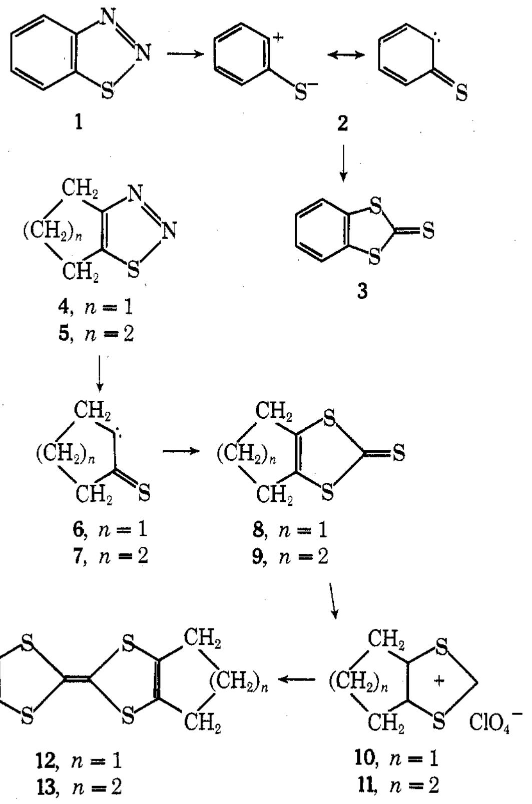
It has been known since 1961 that thermolysis of 1,2,3-benzothiadiazole (**1**) leads to the dipolar intermediate **2**, which can be efficiently intercepted by carbon disulfide to yield (84%) the benzotrithiocarbonate (**3**).[1] An attempt to carry out the analogous reaction with the parent 1,2,3-thiadiazole 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, $\mathbf{12}^{\cdot+}$ TCNQ$^{\cdot-}$
15, $\mathbf{13}^{\cdot+}$ TCNQ$^{\cdot-}$