

was stirred for 1 h, **20** (0.1 g, 0.0004 mol) in 2 mL of anhydrous THF was added dropwise, and the mixture was stirred for 1.5 h at room temperature. The reaction mixture was filtered, and the solvent was removed to give crude **9**. Purification by silica gel chromatography using hexane as the eluant gave pure **9** (30 mg, 33%): mp 81–82 °C; NMR δ 5.25 (d, 1 H, J = 12 Hz), 5.8 (d, 1 H, J = 18 Hz), 6.65–7.0 (m, 1 H), 7.1–7.9 (m, 9 H); MS, m/e (relative intensity) 228 (M^+ , 100). UV λ_{\max} (ϵ) 360 (8390), 344 (7930), 329 (5520), 295 (18400), 283 (24800), 278 (34100), 267 (37800), 253 (43400).

Anal. Calcd for $C_{18}H_{12}$: C, 94.69; H, 5.30. Found: C, 94.37; H, 5.11.

3-(2-Hydroxyethyl)fluoranthene (21). The alcohol **21** was prepared from 3-fluoranthenylic acid (2.6 g, 0.01 mol) and $LiAlH_4$ (0.36 g, 0.01 mol) under conditions similar to those described for reduction of **17**: yield 85%; mp 91–93 °C; NMR δ 1.7 (br s, 1 H, OH), 3.3 (t, 2 H, CH_2), 3.8 (t, 2 H, CH_2) 7.2–8.0 (m, 9 H); MS, m/e (relative intensity) 246 (M^+ , 6.7), 215 (100).

Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.72. Found: C, 87.51; H, 5.88.

3-(2-Chloroethyl)fluoranthene (22). A solution of $SOCl_2$ (3 mL) in 10 mL of dry benzene was added slowly to a stirred solution of alcohol **21** (0.49 g, 0.0022 mol) in 10 mL of dry benzene. After being stirred for 1 h, the mixture was then heated at reflux for 12 h. The reaction mixture was cooled, washed with H_2O , aqueous $NaHCO_3$, and H_2O , dried ($MgSO_4$), and concentrated. The resulting yellow solid was preabsorbed onto silica gel and purified by chromatography on a column of silica gel with hexane– CH_2Cl_2 (90:10) as eluant to yield 0.2 g (37%) of the chloride **22** as light yellow crystals: mp 89–90 °C; NMR δ 3.6 (d, 2 H, CH_2), 3.85 (d, 2 H, CH_2Cl), 7.2–7.5 (m, 4 H), 7.6–8.0 (m, 5 H); MS, m/e (relative intensity) 229 (M^+ – Cl, 34.4), 215 (100).

3-Vinylfluoranthene (10). A suspension of 3-(2-chloroethyl)fluoranthene (0.26 g, 0.001 mol) and KOH (200 mg) in ethanol was heated at reflux for 1 h. Conventional workup followed by chromatography on silica gel eluting with hexane– CH_2Cl_2 (90:10) afforded **10** as a yellow solid: mp 100 °C (0.15 g, 66%); NMR δ 5.45 (dd, 1 H, J = 1.2 Hz, J = 11.0 Hz), 5.8 (dd, 1 H, J = 1.2 Hz, J = 19 Hz), 7.1–7.9 (m, 9 H), 8.0 (d, 1 H); MS, m/e (relative intensity) 228 (M^+ , 100); UV λ_{\max} (ϵ) 376 (1110), 363 (1200), 335 (79701), 293 (22000), 238 (34400).

Anal. Calcd for $C_{18}H_{12}$: C, 94.69; H, 5.30. Found: C, 94.35; H, 5.54.

Mutagenicity Assays. Mutagenicity assays were performed as previously described²⁶ using *S. typhimurium* TA100 (TA 1535/pKm 1101) provided by Dr. Bruce Ames of the University of California, Berkeley, CA. Male F344 rats or Sprague–Dawley rats (250–350 g) were treated with a single ip injection of 500 mg/kg Aroclor 1254, 5 days prior to sacrifice, and the liver 9000g supernatants were prepared for use as the metabolic activation system.²⁷ Reported values are the means of triplicate assays. Standard deviations were less than 10% of the means.

Acknowledgment. We thank Dr. Tomiko Shimada and Dr. Edmond J. LaVoie for carrying out the mutagenicity assays.

Registry No. **2**, 243-17-4; (**E**)-**3**, 98677-74-8; (**Z**)-**3**, 98677-86-2; **4**, 88746-54-7; **5**, 201-06-9; **6**, 98677-75-9; **7**, 98677-76-0; **8**, 206-44-0; **9**, 98677-77-1; **10**, 98677-78-2; **11**, 77061-03-1; **12**, 88746-65-0; **13**, 883-20-5; **14**, 24471-57-6; **15**, 50781-52-7; **16**, 25177-46-2; **17**, 98677-79-3; **18**, 98677-80-6; **19**, 98677-81-7; **20**, 98677-82-8; **21**, 98677-83-9; **22**, 98677-84-0; 11H-benzo[*b*]fluoren-11-one, 3074-03-1; 11-ethyl-11-hydroxybenzo[*b*]fluorene, 98677-85-1; 9-phenanthreneacetyl chloride, 98677-87-3; 4-hydroxy-4-(2-propenyl)-4,5-dihydroacephenanthrylene, 98677-88-4; 4-hydroxy-4-(1-propenyl)-4,5-dihydroacephenanthrylene, 98677-89-5; 1-bromopropene, 590-14-7; 4-ethenyl-4-hydroxy-4,5-dihydroacephenanthrylene, 98677-90-8; 2-(bromomethyl)fluoranthene, 88746-58-1; methyltriphenylphosphonium bromide, 1779-49-3; 3-fluoranthenylic acid, 24827-02-9.

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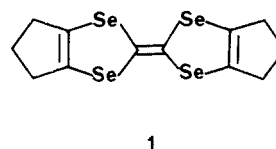
A Convenient Synthesis of Hexamethylenetetraselenafulvalene (HMTSF)

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Hexamethylenetetraselenafulvalene (HMTSF, **1**)¹ is known to form electrically conducting charge-transfer complexes with TCNQ (tetracyanoquinodimethane) (σ_{RT} = 2000 $cm^{-1} \Omega^{-1}$)² and with TNAP (tetracyanonaphthoquinodimethane) (σ_{RT} = 2900 $cm^{-1} \Omega^{-1}$)³, with the TCNQ complex remaining metallic as $T \rightarrow 0$ K.⁴ However, widespread studies of HMTSF complexes have been hindered by the lack of availability of the π -donor molecule **1**. We wish to provide a new synthetic pathway to HMTSF and report for the first time the physical properties of this interesting donor component for organic metals.



HMTSF was first synthesized from CSe_2 ⁵ via piperidinium diselenocarbamate, which was reacted with α -halocyclopentanone (**2**). The resulting selenocarbamate was then taken through two synthetic steps to yield the appropriate 2-selenoxo-1,3-diselenole (**3**) (Scheme I). Triethylphosphite-induced coupling of the resulting selone (**3**) provided HMTSF. Later,⁶ HMTSF was obtained through the same basic synthetic pathway, except that formation of the piperidinium diselenocarbamate was accomplished via consecutive H_2Se reactions with *N,N*-dimethylphosgeneiminium chloride, in the presence of piperidine.

These routes to HMTSF are not only long and inefficient but also involve the use of expensive, highly toxic, and malodorous CSe_2 or H_2Se .

In our approach to **1**, we adopted a procedure similar to those used to synthesize the sulfur and tellurium donors: DBTTF,⁷ DBTTeF,⁸ HMTTeF,⁹ and BDMT–TTTeF.¹⁰

(1) Recommended IUPAC name: 5,5',6,6'-Tetrahydro- $\Delta^{2,2'}$ -bi-4H-cyclopenta-1,3-diselenole. Current Chemical Abstracts name: 2-(5,6-Dihydro-4H-cyclopenta-1,3-diselenol-2-ylidene)-5,6-dihydro-4H-cyclopenta-1,3-diselenole.

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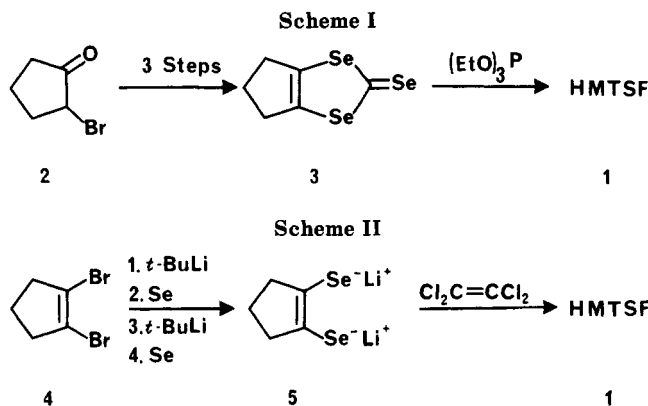
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The reaction scheme is outlined in Scheme II.

It was previously thought that tetrachloroethylene would only produce tetrachalcogenafulvalenes from organodithiols and organoditelluride dianions (similar to 5, where Se^-Li^+ is replaced by either SH or Te^-Li^+ , respectively). However, we wish to report the first synthesis of a selenium π -donor molecule utilizing the "tetrachloroethylene" route. We have found it crucial that the following conditions be adhered to in the preparation of 1: (1) 1,2-dibromocyclopentene be freshly distilled; (2) the reaction mixture be warmed to 25 °C before the addition of the second equivalent of Se to give 5; (3) tetrachloroethylene be added (after all of the selenium has reacted) at 25 °C; (4) the reaction mixture be warmed to 45 °C for a 36-h period. Utilization of these steps gave HMTSF (1) in 11% yield from 1,2-dibromocyclopentene ("carbamate" route gives HMTSF in yields 7–17% based on the bromoketone). The physical data of the product, elemental analysis, IR, NMR, mp, and mass spectrum, were identical with those of a sample of HMTSF prepared by the "carbamate" route.⁵ The molecular ion peak, in the mass spectrum, exhibited an isotopic cluster which matched a computer-simulated pattern of $\text{C}_{12}\text{H}_{12}\text{Se}_4$, and the overall fragmentation pattern was identical with a previously published spectrum of HMTSF.¹¹ It is interesting to note that when using tetrachloroethylene to produce sulfur heterofulvalenes, harsher conditions are needed (refluxing Et_3N) than are needed in the synthesis of tellurium heterofulvalenes (–78 → 25 °C). The conditions reported here for the synthesis of the selenium compound HMTSF are intermediate between the conditions required for the preparation of the sulfur and tellurium heterofulvalenes. Conditions used in the synthesis of HMTTeF do not give detectable amounts of HMTSF.⁹

Selenocenes (Figure 1) have been demonstrated to provide a stable source of organodiselenide dianions (similar to 5) by cleavage of the two diseleno bridges with LiAlH_4 .¹² However, oxidation of 5, with oxygen, did not cleanly give the expected selenocine 6, but produced products of higher oxidation states (selenoxides), as determined by mass spectroscopy.

In conclusion, HMTSF can now be made utilizing the readily accessible 1,2-dibromocyclopentene (4) in a one-pot reaction with tetrachloroethylene, without the use of expensive and highly toxic CSe_2 or H_2Se .

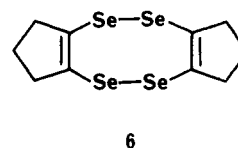


Figure 1.

Experimental Section

The melting point was determined on a Thomas-Hoover Unimelt capillary melting point apparatus and is uncorrected. Infrared spectra were obtained with a Perkin-Elmer 599B spectrophotometer. ^1H NMR spectra were taken in CDCl_3 or $\text{CDCl}_3/\text{CS}_2$ (1:1) on a Varian XL-400 spectrometer with tetramethylsilane as an internal standard. Low-resolution mass spectra were obtained on a KRATOS MS-50 mass spectrometer (at The Middle Atlantic Mass Spectrometry Laboratory, The Johns Hopkins University, School of Medicine). Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN.

1,2-Dibromocyclopentene (4).¹³ Cyclopentanone was reacted with PCl_5 , according to literature procedure,¹⁴ to give 1-chlorocyclopentene, which was brominated immediately after isolation (1-chlorocyclopentene decomposes rapidly above –30 °C) to give 1,2-dibromo-1-chlorocyclopentane (40%). The product was subsequently added to a solution of $t\text{-BuOK}$ in $t\text{-BuOH}$ (25 °C) at a very slow rate ($\sim 0.1\text{ mL min}^{-1}$) to avoid localized heating, which gives rise to excessive polymerization. The yield of 1,2-dibromocyclopentene was 67%.

Hexamethylenetetraselenafulvalene (1). To a THF solution (35 mL) of fresh distilled 1,2-dibromocyclopentene (2.26 g, 10 mmol), cooled to –78 °C, was added dropwise 11.1 mL of 1.8 M (20 mmol) fresh $t\text{-BuLi}$ in pentane, the temperature of the reaction mixture being kept below –55 °C. The resulting opaque yellow solution was allowed to stir at –78 °C for 2.5 h, and finely ground Se (0.79 g, 10 mmol) was then added via a solid addition flask to the mixture at –20 °C. The reaction mixture was stirred until all Se had reacted (ca. 0.5 h). The clear solution was cooled to –78 °C, and 11.1 mL of 1.8 M (20 mmol) $t\text{-BuLi}$ in pentane was added, while the reaction temperature was kept below –55 °C. The resulting clear yellow solution was allowed to stir at –78 °C for 2.5 h; then the reaction mixture was allowed to warm to 25 °C over a 0.5 h period. Finely ground Se (0.79 g, 10 mmol) was then added via a solid addition flask and allowed to stir until all Se had reacted (0.25 h). To the resulting opaque white solution was added 0.83 g (0.51 mL, 5 mmol) of tetrachloroethylene at 25 °C, and the mixture was then stirred at 45 °C for 36 h. After ca. 12 h, the pink product began to precipitate out. The reaction mixture was slowly cooled to –20 °C to facilitate the crystallization of HMTSF. After filtration, the pink, microcrystalline solid was washed with benzene, then with H_2O , and finally with hexane and dried to yield 270 mg (11.4%) HMTSF: mp 207–209 °C dec; IR (KBr) 2960 (w), 2940 (w), 2900 (s), 2842 (s), 1600 (w), 1440 (m), 1435 (m), 1310 (m), 1120 (m), 849 (w), 730 (w) cm^{-1} ; ^1H NMR (1:1 $\text{CDCl}_3/\text{CS}_2$) 2.6 (t, $J = 7\text{ Hz}$, 4 H), 2.3 (q, $J = 7\text{ Hz}$, 2 H), ppm; MS, m/z (relative intensity) 478 (30), 477 (11), 476 (71), 475 (25), 474 (100, M^+), 473 (44), 472 (94), 471 (45), 470 (68), 469 (33), 468 (37), 467 (17) (calcd relative intensities, 32, 12, 75, 26, 100, 44, 93, 44, 67, 32, 37, 17, respectively), 39 ($3\text{M}^+ - \text{Se}$), 330 (9, $\text{M}^+ - \text{C}_5\text{H}_6\text{Se}$), 328 (12), 326 (11), 318 (10), 317 (16), 316 (34, $\text{M}^+ - 2\text{Se}$), 315 (45), 314 (35), 313 (46), 312 (31), 311 (27), 310 (14), 309 (11), 287 (8), 249 (8), 238 (11), 237 (18), 236 (31, $\text{M}^+ - 3\text{Se}$), 235 (48), 234 (22), 233 (25), 232 (13), 231 (10), 170 (17), 169 (37), 167 (20), 155 (26), 154 (21), 153 (25), 145 (11), 142 (7), 141 (17), 128 (11), 117 (11), 90 (11), 89 (19), 78 (10), 66 (17), 65 (36, C_5H_5^+). A sample for analysis was recrystallized from chlorobenzene. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{Se}_4$: C, 30.53; H, 2.56. Found: C, 30.65; H, 2.69.

Note Added in Proof. Addition of HMPA (1:1 HMPA/THF) to the reaction mixture containing 5 enhances the reaction rate ($5 \rightarrow 1$) apparently without increasing the overall yield.

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Novel Reaction of 2-(Methylthio)-1-pyrroline with Acyl Chlorides in the Presence of Triethylamine

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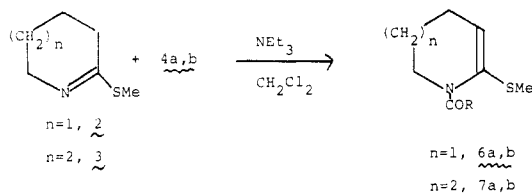
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Keiichi Aoe

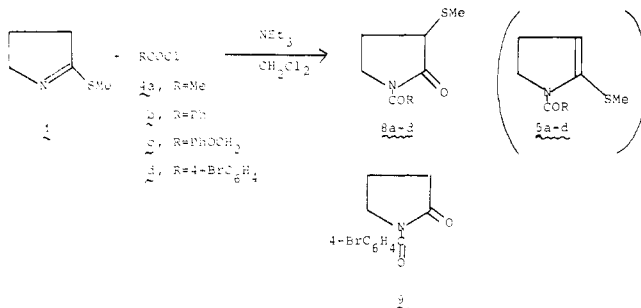
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Received January 21, 1985

In connection with our research on activated lactams,¹ we required a variety of *N*-acyl ketene *S,N*-acetals.² Bose et al.³ reported that the reaction of 2-(methylthio)-1-pyrroline (1) with phenoxyacetyl chloride (4c) in the presence of triethylamine gave *N*-phenoxyacetyl ketene *S,N*-acetal (5c). We tried the similar reaction of cyclic thioimides (1, 2, and 3) with acetyl chloride (4a) and benzoyl chloride (4b). Although *N*-acyl ketene *S,N*-acetals (6a,b and 7a,b) were obtained as expected from 2 and 3, respectively, the corresponding *N*-acyl-2-(methylthio)-2-pyrrolines (5a,b) were not isolated. The ¹H NMR spectra



of 6a,b and 7a,b showed peaks of vinyl protons at C-3 position as characteristic triplets (Table I). However, compounds 8a,b obtained from 1 have no peaks for vinyl protons in the ¹H NMR. Microanalyses data of 8a,b were consistent with the addition of one oxygen atom to the molecular formulas of the corresponding *N*-acyl ketene *S,N*-acetals (5a,b). Next, 1 was allowed to react with 4c and 4-bromobenzoyl chloride (4d) to give 8c and 8d together with the lactam 9, respectively. The spectral patterns of 8c and 8d were similar to those of 8a,b.



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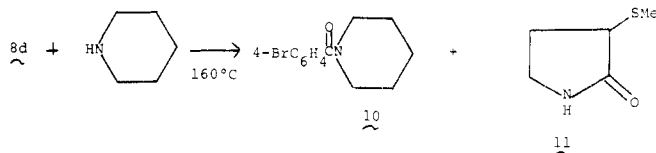
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Table I. Reaction of Cyclic Thioimides (1, 2, and 3) with Acyl Halides (4a-d)

| compd | yield, % | ¹ H NMR (C ₃ -H), δ |
|-------|-----------------|---|
| 6a | 73 | 5.50 (t, <i>J</i> = 4 Hz) |
| 6b | 83 | 5.47 (t, <i>J</i> = 4 Hz) |
| 7a | 54 | 5.70 (t, <i>J</i> = 7 Hz) |
| 7b | 73 | 5.67 (t, <i>J</i> = 6 Hz) |
| 8a | 50 | 3.47 (dd, <i>J</i> = 8 and 4 Hz) |
| 8b | 39 | 3.37 (dd, <i>J</i> = 9 and 5 Hz) |
| 8c | 48 | 3.55 (dd, <i>J</i> = 8 and 4 Hz) |
| 8d | 64 | 3.47 (dd, <i>J</i> = 8 and 4 Hz) |
| | 69 ^a | |
| | 17 ^b | |
| 9 | 2 | |
| | 0 ^a | |
| | 54 ^b | |

^a Reaction was carried out in an atmosphere of O₂. ^b Reaction was carried out with exclusion with O₂.

Since no physical and spectral data for 5c were reported by Bose, we decided to determine the structures of 8a-d. Heating of 8d with piperidine at 160 °C afforded the amide (10) and 3-(methylthio)pyrrolidin-2-one (11)⁴ in 85% and 96% yields, respectively. Formation of 11 suggested the



existence of a methylthio group at C-3 position in 8d. The structure of 8d was then determined finally by X-ray crystallography (Figure 1). In order to speculate on potential mechanisms for this unusual transformation, the following experiments were carried out. The reaction of 1 with 4d in an atmosphere of oxygen gas (O₂) resulted in a little increase of 8d (69%) and no isolation of 9. Next, the similar reaction with exclusion of O₂ was carried out (Experimental Section). ¹H NMR spectrum of a crude product before chromatography revealed a signal at δ 5.00 (t, *J* = 3 Hz) due to a vinyl proton at C₃ position, supporting the structure of 5d. After chromatography, 8d and 9 were obtained in 17% and 54% yields, respectively. These results suggested the participation of an oxygen molecule in this reaction.⁵

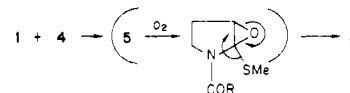
On the other hand, the reaction of 2-(methylthio)-3-methyl-1-pyrroline (12) with 4d gave only the normal product, *N*-acyl ketene *S,N*-acetal (13), in 79% yield. It was found that the novel products were formed only in the reaction using 3-unsubstituted 2-(methylthio)-1-pyrroline.

Experimental Section

¹H NMR spectra were recorded on a JEOL PMX (60 MHz) spectrometer and a Varian XL-200 (200 MHz) spectrometer in

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(5) Although insufficient experimental evidence deter us from offering a mechanism, we have a temporary explanation as shown below.



The formation of *N*-acyl ketene *S,N*-acetals 5 followed by the epoxidation with air (oxygen) and rearrangement of the methylthio group accompanied with the cleavage of the epoxide ring might afford the products (8). The existence of 5 would be supported by the reaction with exclusion of O₂. In this reaction, 5d would be hydrolyzed to give compound 9 by chromatography. It is known that cyclic alkenes were epoxidized with O₂. (van Sickle, D. E.; Mayo, F. R.; Arluck, R. M. *J. Am. Chem. Soc.* 1965, 87, 4824.) However, the precise mechanism remains unclear.