

Table I. Addition of *tert*-Butyl Hypiodite (1) to Selected Olefins in CCl₄

olefin	condition ^a	product	yield, ^b %
styrene	BF ₃	2- <i>tert</i> -butoxy-2-phenylethyl iodide	95
styrene	UV	2- <i>tert</i> -butoxy-1-phenylethyl iodide	83
(<i>E</i>)- β -methylstyrene	BF ₃	<i>erythro</i> -1- <i>tert</i> -butoxy-1-phenyl-2-iodopropane	100
(<i>Z</i>)- β -methylstyrene	BF ₃	<i>threo</i> -1- <i>tert</i> -butoxy-1-phenyl-2-iodopropane	92
(<i>E</i>)-4-octene	BF ₃	<i>erythro</i> -4- <i>tert</i> -butoxy-5-iodooctane	85
(<i>Z</i>)-4-octene	BF ₃	<i>threo</i> -4- <i>tert</i> -butoxy-5-iodooctane	c
<i>tert</i> -butylethylene	BF ₃	1- <i>tert</i> -butoxy-2-iodo-3,3-dimethylbutane	54
1-hexene	BF ₃ ^f	2- <i>tert</i> -butoxy-1-iodohexane (38%) ^d 1- <i>tert</i> -butoxy-2-iodohexane (62%) ^e	75

^a All reactions were done in CCl₄ at room temperature. ^b Yields are based on GC analyses. ^c Yield was not determined. ^d Markovnikov regioisomer (M). ^e Anti-Markovnikov (AM) regioisomer. ^f The same ratio of products was obtained in the dark with O₂ present as a radical inhibitor.

(min) at 11.2 and 11.5. (Fluoro chlorides were also observed). The GC analyses from either (*E*)- or (*Z*)- β -methylstyrene and *tert*-butyl hypochlorite were identical. The diastereomers were present in nearly equal amounts. The mass spectra were identical, indicating that they were a mixture of diastereomers, *erythro*- and *threo*-1-*tert*-butoxy-1-phenyl-2-chloropropane. The mass spectra confirmed these structures. Mass spectrum, *m/e* M - CH₂Cl 163 (19), M - C₄H₉O (chlorine isotopes) 155 (2) and 153 (7), 117 (9), 115 (9), C₆H₅CHOH 107 (100), C₆H₅CO 105 (7), C₇H₇ 91 (10), 79 (15), C₄H₉ 57 (54).

Reaction of *tert*-Butyl Hypobromite ((CH₃)₃COBr) with (*Z*)- β -Methylstyrene. *tert*-Butyl hypobromite was added to (*Z*)- β -methylstyrene under the same conditions as for 1 and *tert*-butyl hypochlorite. GC analysis (column B, programmed from 120-170 °C, 15 °C/min) showed two diastereomers with retention times (min) of 10.6 and 10.8 in a 3:1 ratio, respectively. (Fluoro bromides were also observed.) The mass spectra were identical and, on the basis of the spectra, were assigned as a mixture (diastereomers) of *erythro*- and *threo*-1-*tert*-butoxy-1-phenyl-2-bromopropane: mass spectrum, *m/e* M - C₄H₉O (bromine isotopes) 199 (8) and 197 (8), C₆H₅CH(O)C₄H₉ 163 (25), 117 (16), 115 (7), C₆H₅CHOH 107 (100), C₆H₅CO 105 (8), C₇H₇ 91 (10), 79 (14), C₄H₉ 57 (52).

Acknowledgment. Support for this work was provided by Research Corporation and the Research Associates of Point Loma Nazarene College. We thank the Southern California Regional NMR Facility at California Institute of Technology, supported by National Science Foundation, Grant No. CHE 84-40137, for the 500-MHz data.

Registry No. 1, 917-97-5; PhCH=CH₂, 100-42-5; (*E*)-PhCH=CHMe, 873-66-5; (*Z*)-PhCH=CHMe, 766-90-5; (*E*)-PrCH=CHPr, 14850-23-8; (*Z*)-PrCH=CHPr, 7642-15-1; CH₂=CHBu-*t*, 558-37-2; CH₂=CHBu, 592-41-6; PhCH(OBu-*t*)CH₂I, 13684-99-6; PhCHICH₂OBu-*t*, 111558-77-1; *erythro*-PhCH(OBu-*t*)CHIME, 111558-78-2; *threo*-PhCH(OBu-*t*)CHIME, 111558-79-3; *erythro*-PrCH(OBu-*t*)CHIPr, 111558-80-6; *threo*-PrCH(OBu-*t*)CHIPr, 111558-81-7; *t*-BuOCH₂CHIBu-*t*, 111558-82-8; BuCH(OBu-*t*)CH₂I, 111558-83-9; *t*-BuOCH₂CHIBu, 111558-84-0; *erythro*-PhCH(OBu-*t*)CHClMe, 111558-85-1; ClOBu-*t*, 507-40-4; *threo*-PhCH(OBu-*t*)CHClMe, 111558-86-2; BrOBu-*t*, 1611-82-1; *erythro*-PhCH(OBu-*t*)CHBrMe, 111558-87-3; *threo*-PhCH(OBu-*t*)CHBrMe, 111558-88-4.

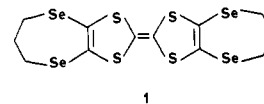
Synthesis of 4,5:4',5'-Bis(propylene-1,3-diseleno)tetrathiafulvalene

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Received March 27, 1987

Because of the unique transport properties of charge-transfer (C-T) complexes based on the π -electron-donor molecules, 4,5:4',5'-bis(alkylenedithio)tetrathiafulvalenes,¹ the properties of the partially selenium substituted donor 4,5:4',5'-bis(propylene-1,3-diseleno)tetrathiafulvalene (BPDS₂-TTF, 1)² were investigated. This molecule was



of particular interest to us since much of the current research in this area³ has focused on increasing the dimensionality of the transport in C-T salts derived from these donors. One of the simplest ways of increasing dimensionality^{4,5} is to incorporate either selenium or tellurium into the donor molecules.^{6,7} The increased overlap expected from the larger orbitals of these chalcogens is believed to increase both inter- and intramolecular overlaps, thereby enhancing conductivity in at least two directions, and thus impart greater two-dimensional character to their C-T salts. In addition, the greater steric requirements of the bulky diselenopropylene groups of 1 are expected to lead to an expansion of the unit cell and thereby favorably affect electronic properties. In this paper, I report the synthesis of BPDS₂-TTF and describe some selected physical properties of this donor.

Results and Discussion

Several chalcogen-substituted TTFs have been reported in the literature. The first reported procedure for incorporating four tellurium atoms onto the TTF skeleton involves lithiation of TTF followed by reaction with elemental tellurium to give a TTF tetratelluride anion.⁸ Attempts to cap this anion with dihaloalkanes resulted in the formation of uncharacterized solids. These results suggest that in the tellurium-substituted system only tetrakis(alkyltelluro)-TTF is isolable since insertion of methylene or ethylene groups might be difficult for steric reasons. More recently, the synthesis of the methylenediseleno-substituted TTF, BMDSe-TTF, and the ethylenediseleno-substituted TTF, BEDSe-TTF, has been reported by Lee,⁷ who used a similar procedure to that described above for tellurium insertion. These partially selenium substituted donors were prepared by blocking the

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(2) Recommended IUPAC name: 6,6',7,7'-tetrahydro- $\Delta^{2,2'}$ -bi-5H-[1,4]diselenepino[2,3-d]-1,3-dithiole. Current *Chemical Abstracts* name: 2-(6,7-dihydro-5H-[1,4]diselenepino[2,3-d]-1,3-dithiol-2-ylidene)-6,7-dihydro-5H-[1,4]diselenepino[2,3-d]-1,3-dithiole.

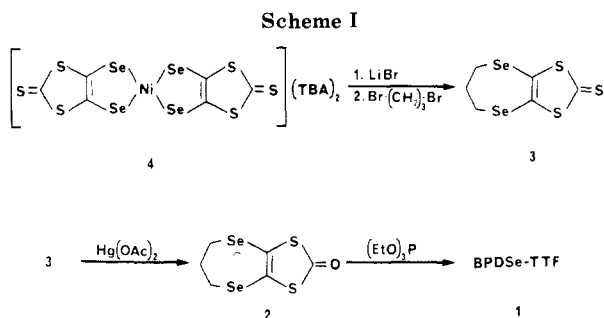
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reactive TTF tetraselenide anion with silylethoxymethyl groups. The blocking groups could then be deblocked in the presence of fluoride ions and capped with dihaloalkanes.

I report an alternative synthesis scheme for bis(alkylenediseleno)tetrathiafulvalenes (BADSe-TTF), which is exemplified through the synthesis of 1. This procedure begins with the air- and moisture-stable organometallic complex bis(tetrabutylammonium) bis(2-thioxo-1,3-dithiole-4,5-diselenolato)nickelate(II) [(TBA)₂[Ni(dsit)₂], 4,⁸ prepared by the lithiation of 1,3-dithiole-2-thione followed by reaction with selenium and complexation with nickel chloride and tetrabutylammonium bromide. The reaction scheme for 1 is outlined in Scheme I.

Refluxing an acetonitrile solution of (TBA)₂[Ni(dsit)₂] (4) with 4 equiv of lithium bromide for 1 h is believed to result in the in situ formation of 4,5-bis(lithioseleno)-1,3-dithiole-2-thione. Addition of excess alkylating agent (1,3-dibromopropane) to the reaction mixture and refluxing at 78 °C over a 20-h period resulted in the formation of 3 in 52% yields. The crude material is usually of sufficient purity to be used for subsequent reactions. When methylene dibromide or ethylene dibromide are used as the alkylating agents, 4,5-(methylenediseleno)-1,3-dithiole-2-thione⁹ and 4,5-(ethylenediseleno)-1,3-dithiole-2-thione, respectively, are obtained. It should be noted that relatively minor amounts of an uncharacterized dark solids are always obtained from the filtered reaction mixture. On the basis of their solubility characteristics, these solids appear to be polymeric.

The conventional coupling procedures¹⁰ consisting of refluxing 3 in either neat solutions or benzene solutions of triethyl phosphite failed to give significant quantities of BPDSe-TTF. These results are similar to those found by us in the synthesis of the all-sulfur analogue of 1, BPDT-TTF.^{1b} Although Mizuno et al.¹⁰ reported obtaining BPDT-TTF by the direct coupling of the thione, no significant yields of this material have been obtained in our hands. However, coupling could easily be achieved by first oxidizing 4,5-(propylenediseleno)-1,3-dithiole-2-thione (3) to 4,5-(propylenediseleno)-1,3-dithiole-2-one (2) followed by reaction of the latter material with triethyl phosphite. It should be pointed out that in all procedures discussing the synthesis of bis(alkylenedichalcogeno)-TTF from the 4,5-(alkylenedichalcogeno)-1,3-dithiole-2-thiones, coupling reactions are affected only with the 4,5-(alkylenedichalcogeno)-1,3-dithiol-2-ones.

The oxidation of 3 was carried out in a refluxing mixture of chloroform, aqueous acetic acid, and mercuric acetate.¹¹ When milder oxidation conditions were used, as reported

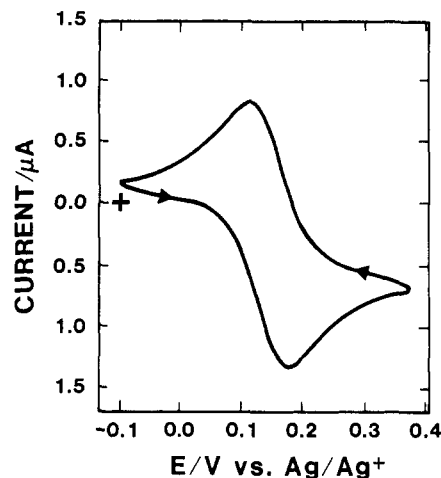


Figure 1. Cyclic voltammogram of 4.2×10^{-4} M (1) with 0.1 M TBAASeF₆ in BN, platinum bead electrode, sweep rate 100 mV s⁻¹.

for the synthesis of bis(dimethylvinylenedithio)-TTF,¹² 2 was obtained in lower yields and purity. However, reaction at reflux with 1 equiv of mercuric acetate gave crude 2 in virtually quantitative yields. Purification of this product was achieved by recrystallization from acetonitrile followed by gradient sublimation¹³ at 85 °C and 10⁻⁵ Torr. These combined procedures resulted in 75% yields of analytically pure 2. When 2 was refluxed in neat triethyl phosphite, a yellow solid formed shortly after the solution began to reflux. This solid was subsequently identified as the coupled product BPDSe-TTF, which was isolated in 46% yields. The use of the same reaction sequence and similar preparative conditions resulted in the formation of BMDSe-TTF and BEDSe-TTF.⁹

The cyclic voltammogram (CV) of 1 (Figure 1) showed one reversible BPDSe-TTF oxidation wave with peak potentials of +0.18 and +0.11 V vs a silver reference electrode. These respective waves correspond to removal of one electron to form the radical cation with application of increasing positive potentials, which is reduced back to the neutral donor molecule upon reversal of the scan direction, i.e. application of less positive potentials. A CV of the all-sulfur analogue BPDT-TTF gave peak potentials of +0.19 and +0.13 V vs a silver reference electrode. The replacement of sulfur by selenium, therefore, results in a slight lowering of the oxidation potential. The couple in the voltammogram of 1 exhibited reversible electrochemical behavior ($\Delta E_p \approx 65$ mV) and suggests a facile electron transfer between the radical cation and neutral BPDSe-TTF. When the anodic potential was increased above +0.4 V, another anodic wave was observed (not shown) with a peak potential of +0.54 V. However, this second wave, corresponding to oxidation of the radical cation to the dication, was quasi-reversible in nature. Although different electrode materials, solvents or support electrolytes could result in a reversible second oxidation wave; when other solvents and electrolytes have been used, similar results were obtained, and this electrochemical behavior is thus believed to be characteristic of the material. This observation suggests that incorporation of selenium into this donor results in an unstable dicationic species, and these donors may require special precautions during the electrochemical crystal growth.

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In summary, utilizing the organometallic reagent 4, I have been able to obtain BPDSe-TTF in an overall yield of 17%. This general procedure can also be extended to the other members of the BADSe-TTF donor series. In addition, this procedure permits the isolation of asymmetric sulfur/selenium donors not accessible by other methods. The electrochemistry of 1 indicates only reversible oxidation to the radical cation and not to the dication in this solvent system.

Experimental Section

Melting points were determined on a Mettler FP80/82 hotstage and are uncorrected. Ultraviolet-visible spectra were obtained on a Varian Cary 2300 spectrophotometer in either CH_2Cl_2 or dichlorobenzene. Infrared spectra were obtained with a Beckman IR 4260 spectrophotometer. ^1H NMR spectra were taken in CDCl_3 or $\text{CDCl}_3/\text{CS}_2$ (1:1) on a Chemmagetics Inc. spectrometer with tetramethylsilane as an internal standard. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

Electrochemistry Equipment. For cyclic voltammetry, a Princeton Applied Research Model 173 potentiostat Model 175 universal programmer were used in the standard three-electrode configuration (a platinum bead working electrode, a platinum mesh counter electrode, and $\text{Ag}/0.1\text{ M AgNO}_3$ in acetonitrile reference electrode). The electrolyte was 0.1 M tetrabutylammonium hexafluoroantimonate (TBAAsF_6 , recrystallized from water/methanol) in benzonitrile (BN), which had been freshly distilled from CaH_2 under argon.

4,5-(Propylene-1,3-diseleno)-1,3-dithiole-2-thione (3). Lithium bromide (1.8 g, 0.017 mol) was added to a warmed mixture of $(\text{TBA})_2[\text{Ni}(\text{dst})_2]^{18}$ (4) (4.0 g, 0.0036 mol) in acetonitrile (200 mL) in one portion. The solution was refluxed for 1 h. Propylene bromide (31.6 g, 0.017 mol) was added to the refluxing solution, and the resulting mixture was refluxed overnight (20 h). The warm solution was filtered, and the residue was washed with methylene chloride until nearly colorless. This filtrate was concentrated on a rotary evaporator to an oily residue. To this oil was added methanol (50 mL), and the precipitated olive-green solid was collected. After the solid was vacuum-dried, crude 3 (1.4 g, 52%) was obtained. Recrystallization from methanol gave analytically pure 3 (1.3 g, 48%) as yellow-brown needles: mp 126–127 °C; UV λ_{max} (CH_2Cl_2) 383 nm (ϵ 15 200); IR (KBr) 2910 (w), 1620 (w), 1490 (m), 1460 (m), 1410 (m), 1380 (m), 1330 (m), 1240 (m), 1210 (m), 1145 (m), 1050 (s), 1020 (m), 878 (m), 845 (m), 825 (m), 770 (m), 725 cm^{-1} ; NMR (200 MHz, CDCl_3) 2.92 (m, 4 H, SCH_2), 2.78 ppm (m, 2 H, CH_2). Anal. Calcd for $\text{C}_6\text{H}_8\text{S}_3\text{Se}_2$: C, 21.69; H, 1.82; S, 28.95; Se, 47.54. Found: C, 21.91; H, 1.98; S, 29.10; Se, 47.43.

4,5-(Propylene-1,3-diseleno)-1,3-dithiol-2-one (2). In a refluxing solvent mixture of chloroform (280 mL), glacial acetic acid (130 mL), and water (10 mL) was dissolved 3 (1.25 g, 0.0038 mol). To the refluxing solution was added mercuric acetate (1.25 g, 0.0039 mol) in one portion, and the suspension was stirred at reflux for 26 h. This mixture was filtered while still warm through a fine fritted funnel, and the filtrate was concentrated to dryness. Crude 2 (1.17 g, 98%) was obtained as a brown solid. Recrystallization from acetonitrile followed by further purification with gradient sublimation¹³ gave 2 (0.88 g, 75%) as bright yellow crystals: mp 102–103 °C; UV λ_{max} (CH_2Cl_2) 381 nm (ϵ 4630); IR (KBr) 2920 (w), 2870 (w), 1750 (m), 1670 (m), 1635 (s, br), 1570 (s), 1485 (m), 1420 (m), 1395 (m), 1245 (s), 1230 (s), 1160 (m), 1065 (m), 980 (m), 960 (m), 875 (s), 850 (s) 835 (m), 780 (m), 710 (m) cm^{-1} ; NMR (200 MHz, CDCl_3) 2.88 (m, 4 H, SCH_2), 2.75 ppm (m, 2 H, CH_2). Anal. Calcd for $\text{C}_6\text{H}_8\text{OS}_2\text{Se}_2$: C, 22.79; H, 1.91; O, 5.06; S, 20.28; Se, 49.95. Found: C, 22.78; H, 1.90; S, 20.18; Se, 49.89.

4,5,4',5'-Bis(propylene-1,3-diseleno)tetrathiafulvalene (1). A mixture of 2 (450 mg, 1.35 mmol) and triethyl phosphite (10 mL) was brought to reflux under an argon atmosphere. After 35 min of refluxing, methanol (5 mL) was added, and the solution was then placed in an ice bath. The yellow solid was collected by filtration, washed with methanol followed by ether, and then vacuum-dried to give 1 (223 mg, 55%) as a yellow powder. Multiple recrystallization from dichlorobenzene yielded 1 (186

mg, 46%) as amber needles: mp 272–277 °C; UV λ_{max} (dichlorobenzene) 340 (ϵ 16 000), 400 nm (ϵ 6000); IR (KBr) 2960 (w), 2920 (w), 2860 (w), 1495 (m), 1455 (w), 1410 (m br), 1365 (we), 1245 (s), 1220 (s), 1160 (m), 1025 (w), 969 (m), 875 (m), 840 (m), 830 (m), 765 (s) cm^{-1} ; NMR (200 MHz, $\text{CDCl}_3/\text{CS}_2$ (1:1 vol)) 2.82 (m, 8 H, SCH_2), 2.74 ppm (m, 4 H, CH_2). Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{S}_4\text{Se}_4$: C, 24.01; H, 2.17; S, 21.37; Se, 52.61. Found: C, 24.25; H, 2.16; S, 21.12; Se, 52.37.

Acknowledgment. I thank Dr. Roger A. Assink for recording the proton NMR spectra. This research was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Materials Sciences, under Contract No. DE-AC04-76DP00789.

Registry No. 1, 111351-57-6; 2, 111351-58-7; 3, 111351-59-8; 4, 107207-66-9; $\text{Br}(\text{CH}_2)_3\text{Br}$, 109-64-8.

Pauson-Khand Cycloaddition of Norbornenones and Norbornenols: Electronic Effect on Regioselectivity

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Received June 24, 1987

The Pauson-Khand cyclopentenone synthesis is gaining increased attention due in large measure to the high degree of stereo- and regiochemical control exhibited in several of its versions.¹ Many examples of such selectivity in this reaction have proved amenable to explanation on the basis of steric interactions during insertion of the alkene component into a formal carbon-cobalt bond of the initially formed alkyne- $\text{Co}_2(\text{CO})_8$ complex. Thus intermolecular cyclizations of alkynes with bicyclic alkenes commonly produce exo-fused products with the larger alkyne substituent at the 2-position of the cyclopentenone, a result of insertion of the less hindered face of the alkene π -bond into a less substituted C-Co bond in the complex. Conversely, large allylic substituents on the alkene tend to wind up "anti" to the new ketone (i.e., adjacent to C-4 of the new ring rather than to C-5), thereby avoiding a 1,3-pseudodiaxial interaction between the large substituent and a $\text{Co}(\text{CO})_3$ moiety.² Stereocontrol in intramolecular cyclizations to bicyclo[3.3.0]oct-1-en-3-one derivatives likewise may be predicted on the basis of minimizing similar 1,3-interactions that arise during the insertion step between substituents on the metal-complexed enyne precursors.³

In contrast to these situations, selectivity in reactions involving terminal alkenes seems to be less predictable, and the entire question of electronic effects on this process remains open. The latter is clouded by two effects. First, alkenes with strongly electron-withdrawing substituents do not give cyclopentenones with alkynes and $\text{Co}_2(\text{CO})_8$; CO insertion does not take place, and, instead, 1,3-dienes are formed.⁴ Second, although alkenes with donor groups

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