(Scheme I). Addition of oxygen almost certainly occurs at the unobstructed face of the anthracene ring though, in principle, addition at the other face would give a stereoisomeric endoperoxide. These surmises have not been explicitly tested, but endoperoxide formation by reaction of singlet oxygen with 9,10-disubstituted anthracenes is well documented.[13] The higher reactivity of **6** as compared to **4** and **5** is doubtless due to increased deformation of the anthracene ring in **6**. Thermal cleavage of anthracene endoperoxides generally involves loss of (excited state) molecular oxygen,[13] but thermal O–O bond homolysis to form anthraquinone has been observed.[14] In this regard, endoperoxide **6** is also a dioxa[2.2.2.8]paddlane which, even without the peroxide linkage, may be prone to fragmentation. There appear to be no detailed studies of this sort on 9,10-bridged anthracenes, although anthraquinone formation has been reported in an earlier unsuccessful approach to the smaller (n = 8 or less) [n](9,10)-anthracenophanes and presumably involves similar chemistry.[15]

In summary, the title compounds exhibit spectra consistent with anthracene ring deformation, and the most highly strained of these shows enhanced reactivity toward molecular oxygen. These results along with previous reports[6,15] suggest that [n](9,10)anthracenophanes with eight or less atoms in the bridging chain will be kinetically unstable in the presence of oxygen, and therefore synthetic approaches to these molecules will require precautions dictated by this enhanced reactivity. We are currently examining the mechanism of oxidation of **6**.

Experimental Section

General Methods. ^{1}H NMR spectra were taken on a Perkin-Elmer R-32 spectrometer at 90 MHz in $CDCl_3$ solution with Me_4Si as an internal reference. IR spectra (thin film) were recorded on a Perkin-Elmer 727B spectrophotometer, and UV spectra were recorded on a GCA-McPherson Series EU-700 spectrophotometer in $CHCl_3$ solution. Chromatographic separations were done by using 2000-μm silica gel thick-layer plates with CH_2Cl_2 as the eluent. All melting points are uncorrected. 9,10-Bis(chloromethyl)anthracene was prepared by the procedure of Miller et al.[7] 1,4-Butanedithiol (Aldrich), 1,5-pentanedithiol (Tridom), and 1,6-hexanedithiol (Aldrich) were used as supplied.

2,9-Dithia[10](9,10)anthracenophane (4). The procedure of Vögtle and Koo Tze Mew[4] was used with precautions to exclude light and oxygen (N_2 atmosphere) during the high-dilution reaction of 9,10-bis(chloromethyl)anthracene and 1,6-hexanedithiol in KOH–ethanol–benzene solution. After a ca. 15-h reflux, the solvents were removed at reduced pressure, and the residue was extracted continuously with $CHCl_3$. Evaporation of $CHCl_3$ left a yellow solid that was chromatographed, affording **4** in 79% yield. A small sample was recrystallized from acetone–H_2O: mp 182–184 °C; IR 3080, 2925, 1675, 1620, 1420 cm^{-1}; high-resolution mass spectrum, calcd for $C_{22}H_{24}S_2$ m/e 352.13195, found 352.13139 (M^+); the base peak for **4**–**6** corresponds to expected benzylic cleavage.

2,8-Dithia[9](9,10)anthracenophane (5). Compound **5** was isolated in 57% yield as above: mp 193–196 °C; IR 3080, 2940, 2850, 1665, 1620, 1420 cm^{-1}; high-resolution mass spectrum, calcd for $C_{21}H_{22}S_2$ m/e 338.11629, found 338.11665 (M^+).

2,7-Dithia[8](9,10)anthracenophane (6). Compound **6** was isolated in 40% yield as above: mp 157–162 °C; IR 3060, 2925, 1685, 1615, 1429 cm^{-1}; high-resolution mass spectrum, calcd for $C_{20}H_{20}S_2$ m/e 324.09727, found 324.09917 (M^+).

Oxidation of 6. A 30-mg sample of **6** was dissolved in 0.5 mL of $CDCl_3$, and oxygen was bubbled through the solution for 30 min. ^{1}H NMR spectra, run at intervals, showed complete loss of starting compound in 1 week. Partial evaporation of solvent and vacuum filtration afforded 5 mg of a yellow solid: mp 173–175 °C dec; IR 3430, 3080, 2940, 1660, 1440 cm^{-1}; partial ^{1}H NMR δ 2.35 (s), 2.95 (m), 3.80 (m), 8.35–9.55 (m); mass spectrum, m/e 408 (M^+), 206, 120 (base peak). Evaporation of the remaining solvent from the filtrate left an oily orange residue which was mainly anthraquinone (estimated 80%) by TLC and IR analyses.

Acknowledgment. We gratefully acknowledge support from the donors of the Petroleum Research Fund, administered by The American Chemical Society. All mass spectra were provided by the MIT Mass Spectrometry Facility, support by NIH Research Grant No. RR00317.

Registry No. **4**, 84050-69-1; **5**, 84050-70-4; **6**, 84050-71-5; 1,4-butanedithiol, 1191-08-8; 1,5-pentanedithiol, 928-98-3; 1,6-hexanedithiol, 1191-43-1; 9,10-bis(chloromethyl)anthracene, 10387-13-0; anthraquinone, 84-65-1.

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High-Yield Synthesis of Tetramethyltetraselenafulvalene[1] Avoiding the Use of Gaseous H_2Se

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Received July 29, 1982

Cation radical salts of tetramethyltetraselenafulvalene (TMTSF) exhibit metallic[3,4] and even superconducting properties[4-8] at low temperature. The preparative procedures reported so far use expensive (CSe_2, H_2Se) and highly toxic starting materials. We report a procedure starting from elemental selenium and with the further advantage that the risk of handling gaseous H_2Se is avoided.

TMTSF was first prepared from CS_2.[9-12] This procedure with some improvements[13] still gives the highest overall yield. Later TMTSF was obtained via consecutive H_2Se reactions starting from selenoureas[14] or *N*,*N*-dimethylphosgenimminium chloride.[15,17]

(1) IUPAC name: 4,4′,5,5′-tetramethyl-$\Delta^{2,2'}$-bi-1,3-diselenolylidene.
(2) H. C. Oersted Institute, Universitetsparken 5, Denmark, DK-2100.
(3) For a recent review see the Proceedings of the International Conference on Low Dimensional Solids, Boulder, 1981: *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 1–362.
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(12) Cowan, D. O.; Bloch, A. N.; Bechgaard, K. U.S. Patent 4 246 173, 1981.
(13) We find that reaction of piperidinium diselenocarbamate in previously deoxygenated DMF with halo ketones is instantaneous. After addition of water, filtration, and drying, the yields of pure esters similar to **3** are better than 90%.
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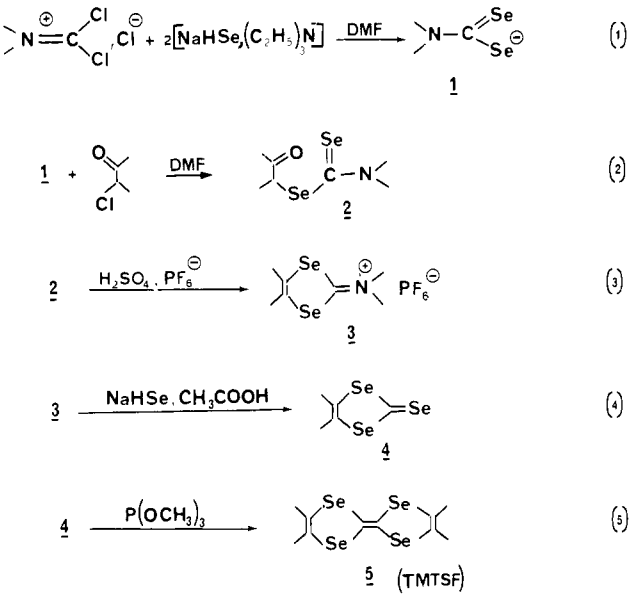
0022-3263/83/1948-0388$01.50/0

Scheme I



We have modified this latter procedure and use NaHSe in DMF–$(CH_3)_3COH$ to obtain comparable yields without handling gaseous H_2Se.

The reaction sequence is outlined in the Scheme I.

We generate NaHSe in DMF by reducing black selenium with a slight excess of $NaBH_4$. We use $(CH_3)_3COH$ as the proton donor needed to form NaHSe in an otherwise aprotic solvent.[18] $(CH_3)_3COH$ rather than primary or secondary alkohols is used to avoid side reactions of the reactive *N,N*-dimethylphosgeneimminium chloride.[19] Actually use of CH_3CH_2OH resulted in very low yields.

Also we found that NaHSe generated in C_2H_5OH[17] gave very high yields in step 3 (>92%) provided that the solution is "acidified" with 1 equiv of acetic acid.

Finally, we investigated the phosphite coupling[9,17] (step 5) which in our hands has not been very reproducible (yields ranging from 30 to 90%) and found that we reproducibly obtain yields better than 90% using Wudl's procedure[17] if the phosphite is redistilled *immediately* before use.

In conclusion, we report a modified synthesis of TMTSF from cheap and relatively nontoxic starting materials which gives a satisfactory overall yield.

Experimental Section

2-(Dimethylimino)-4,5-dimethyl-1,3-diselenolium Hexafluorophosphate (3). Powdered selenium (0.06 mol) in DMF (dried by passage through Al_2O_3, Woelm, basic, Super 1) containing 0.18 mol of $(CH_3)_3COH$ is stirred under argon,[20] and 0.06 mol $NaBH_4$ is added in small portions (~0.5 h). When the primary hydrogen evolution ceases, the stirred mixture is heated at 100 °C until colorless. Depending on the $NaBH_4$ quality, a small excess may be needed. The solution is cooled to 0 °C in ice, and 0.06 mol triethylamine is added. Solid *N,N*-dimethylphosgeneimminium chloride (0.03 mol, Fluka) is added slowly (20 min) from a side arm. The resulting solution is stirred at room temperature for 3 h and recooled in ice. 3-Chlorobutanone (0.03 mol, Fluka, redistilled) in 20 mL of DMF is added quickly. After 10 min, 50 mL water is added, the argon shield is removed, and the dark brown solution is stirred 30 min in air to oxidize eventual Se^{2-} or HSe^-. The solvents are removed on a rotary evaporator. The resulting (stinking) oil is treated with water, taken up in 200 mL of CH_2Cl_2, and washed twice with 100 mL of water. After the mixture is dried over $MgSO_4$ the solvent is removed on a rotary evaporator to yield 6–10 g of red oil, which is cyclized without further purification. The cyclization is obtained by dissolving the oil slowly (~20 min) in ice-cooled concentrated H_2SO_4. The H_2SO_4 solution is stirred for 2 h and poured into a mixture of 200 g of ice and 20 mL of 60% HPF_6 under vigorous stirring. The solid is recovered by filtration, washed with water, and dissolved in 50 mL of CH_2Cl_2 on the filter. After filtration, the solution is dried over $MgSO_4$ and filtered and the salt precipitated with ether to give, after drying, 5.5 g (44%) of **3** as a brown-yellow powder.[17] In some cases lower yields (26–35%) were obtained.

4,5-Dimethyl-1,3-diselenole-2-selone (4). Black, powdered selenium is reduced in absolute EtOH (30 mL/g of Se) with a slight excess of $NaBH_4$[18] under argon.[20] The colorless solution is cooled to −10 °C, and in quick succession 1 equiv of CH_3COOH and (solid) **3** are added. The solution is stirred under argon 2 h and allowed to warm to room temperature. The ethanol is diluted to 50% with ice–water, and the red solid is filtered, washed, with water and vacuum dried over P_2O_5. Recrystallization from toluene–heptane (1:1) gives pure **4**[10] in 92% yield after workup of the mother liquor.

Acknowledgment. This work was supported by ANVAR Grant No. 650-586.

Registry No. 1, 29891-77-8; 2, 76371-67-0; 3, 84041-23-6; 4, 53808-62-1; 5, 55259-49-9; Se, 7782-49-2; NaHSe, 12195-50-5; *N,N*-dimethylphosgeneimminium chloride, 33842-02-3; 3-chlorobutanone, 4091-39-8.

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(20) Strict exclusion of O_2 is necessary during these procedures. A convenient trap for eventual H_2Se in the effluent argon is dilute NaOH (2 M) containing 2–5% H_2O_2, thereby producing elemental selenium.

Regioselective Hydroxylation of π-Allylpalladium Complexes with the $MoO_2(acac)_2$-*t*-BuOOH Catalyst System

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Received March 15, 1982

The "templated" reaction via π-allyl–metal intermediates formed from olefins has been of interest because they provide regio- and stereoselective introduction of various functional groups at allylic position of the parent olefins.[1] For the reaction of π-allylpalladium complexes with carbanions, the mechanism of regio- and stereocontrol and its application to organic synthesis have been extensively studied.[2] However, there has been little information about selective C–O bond formation via π-allylpalldium,[3,4] e.g.:

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(2) For example, see: (a) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietshe, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416, 3426. (b) Trost, B. M.; Verhoeven, T. R. *Ibid.* **1978**, *100*, 3435.
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(4) For the catalytic acetoxylation via π-allylpalladium, Bäckvall and Nordberg have reported that in the presence of chloride ligands mainly external trans attack of the acetate anion (AcO^-) on the π-allylpalladium complex takes place; in the absence of chloride ligands both cis and trans attack can occur depending on the AcO^- concentration. See: Bäckvall, J.-E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 4959.

0022-3263/83/1948-0389$01.50/0