of **3**. After the addition of petroleum ether (40–60 °C) white crystals of **7** (40%) were obtained: mp 94–95 °C dec (from ether/petroleum ether (40–60 °C)); chemical ionization analysis, m/z 190 [(M + 1)$^+$]; IR (KBr) ν_{max} 3400–2800, 1755, 1605, 1560, 1470, 1430, 1380, 1370, 1315, 1210, 1080, 1030, 1010, 985, 940, 915, 855, 770, 685, 640 cm^{-1}; ^{1}H NMR (Me$_2$SO-d_6) δ 2.21, 2.26 (CH$_3$CO, CH$_3$CN), 13.91 (C=NOH); ^{13}C NMR (Me$_2$SO-d_6) δ 11.8 (CH$_3$CN), 19.1 (CH$_3$CO), 149.5 (C=NOH), 153.8 (CH$_3$CN), 167.0 (CH$_3$CO); ^{15}N NMR (Me$_2$SO-d_6) δ 333.0 (CH$_3$CN), 346.7, 348.5 (C=NOH, NO$_2$) [relative to external ^{15}NH$_4$NO$_3$].

Anal. Calcd for C$_5$H$_7$N$_3$O$_5$: C, 31.75; H, 3.73; N, 22.22. Found C, 31.48; H, 3.82; N, 21.93.

Similar results were obtained treating **1b** (0.100 g, 0.693 mmol) with dinitrogen tetraoxide. After ether removal **7** was isolated by preparative TLC [plates of silica gel 60 F$_{254}$, E. Merck, 2 mm; eluent, tetrahydrofuran–petroleum ether (40–60 °C) (3:7 v/v)].

2-Oximidopropanamide Oxime (Aminomethylglyoxime) (5). This compound was prepared starting from **7** following the procedure outlined by Ponzio and Ruggeri.[2] The dioxime so obtained was identical (IR, mixed mp) with a sample of **5** prepared by action of aqueous ammonia (d = 0.88) on chloromethylglyoxime.[12]

Acknowledgment. This work was partially supported by a CNR-NATO grant to R.F. at Queen Mary College in London. We are indebted to Prof. A. J. Boulton of the University of East Anglia for transporting samples **3** and **7** across Europe in open containers.

Registry No. **1a**, 108560-92-5; **1b**, 108594-43-0; **3**, 108560-93-6; **5**, 4937-85-3; **7**, 108560-94-7; dinitrogen tetraoxide, 10544-72-6.

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An Efficient Synthesis of Alkyl and Aryl Chalcogenated Derivatives of Tetrathiafulvalene

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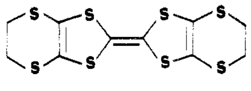
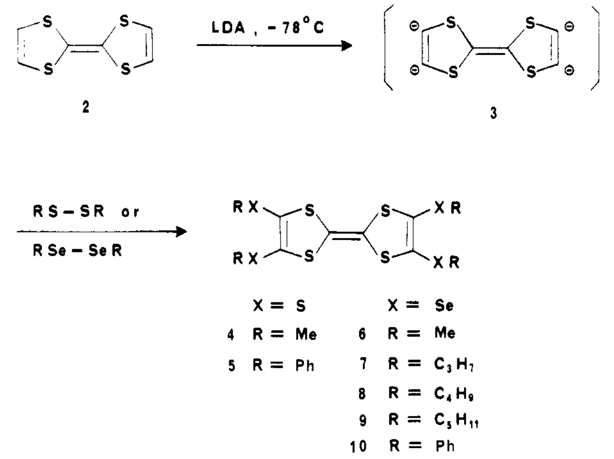
Recently, several superconducting compounds have been observed in two classes of organic synthetic metals, (TMTSF)$_2$X[1] and β-(BEDT-TTF)$_2$X,[2] where X is a monovalent anion, TMTSF and BEDT-TTH represent tetramethyltetraselenafulvalene and bis(ethylenedithio)tetrathiafulvalene (**1**), respectively. Among these materials, β-(BEDT-TTF)$_2$AuI$_2$ has the highest superconducting T_c (3.2[3] or 4.9 K[4]) at ambient pressure, and β-(BEDT-TTF)$_2$I$_3$ has the highest superconducting T_c (8 K[5]) under a pressure of 1.3 kbar. The superconductivity has been correlated to the observation of a sheetlike network of BEDT-TTF stacks linked through extensive S–S interactions, giving a two-dimensional metallic behavior.[6] The question has been raised whether the systematic modification of chalcogen atoms located at the external core of **1** from S to Se or Te will result in interesting analogues with an enhanced interstack interaction. This might in turn improve the superconducting T_c of the material. To address this issue, we have prepared a series of novel tetrachalcogenated TTF (tetrathiafulvalene) derivatives by a convenient one-pot synthesis.



1

BEDT-TTF

Scheme I



Scheme II

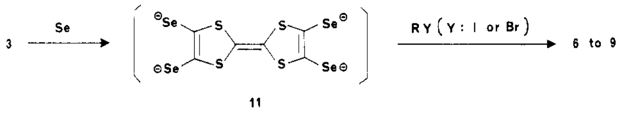


Table I. Half-Wave Potentials of TTF Derivatives Measured against SCE with 0.1 M *tert*-Butylammonium Hexafluorophosphate as Electrolyte in CH$_2$Cl$_2$

compd	$E_{1/2}{}^1$ (mV)	$E_{1/2}{}^2$ (mV)	compd	$E_{1/2}{}^1$ (mV)	$E_{1/2}{}^2$ (mV)
1	488	887	8	443	859
5	552	903	9	508	917
6	544	929	10	495	892
7	439	861			

The previous syntheses of these TTF derivatives were generally accomplished by a coupling reaction between two identical species such as, 1,3-dithiol-2-ones, 1,3-dithiole-2-thiones, 1,3-dithiole-2-selones, or other similar substrates under a variety of conditions.[7] However, these syntheses

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either require multiple steps or give low yields. Herein, we describe a facile synthesis of compounds **4** to **10** of Scheme I in good to excellent yields (64–90%) using tetraanionic TTF (**3**) as a key intermediate. As shown in Scheme I, this tetraanionic TTF was generated by the deprotonation of tetrathiafulvalene (**2**) with 4.1 equiv of LDA at −78 °C in THF according to the reported procedure.[8] Intermediate **3** was then reacted with dialkyl or diaryl disulfide or diselenide electrophiles[10] to afford a series of TTF derivatives (**4**–**10**). Compounds **6** to **9** can also be prepared via an alternative route as depicted in Scheme II. The method involved a selenium insertion reaction into the carbon–lithium bonds of **3** with a poorly crystalline selenium powder to give a tetraselenic anion of TTF (**11**). Without isolation of this tetraselenic anion **11**, it was allowed to react with various alkyl halides to furnish compounds **6** to **9**. Both methods provided smooth reactions to give excellent yields of tetrakis(alkylseleno)tetrathiafulvalenes **6**–**9**. However, several attempts to prepare sulfur analgoues of **6**–**9** failed to produce the desired products by the latter method (Scheme II), but with the former method (Scheme I) we believe that they can be synthesized in very much the same way as **4** and **5** were done. For $(PhS)_4$TTF (**5**) and $(PhSe)_4$TTF (**10**), they can only be prepared via the former method (Scheme I).

Cyclic voltammetry of these TTF derivatives (**5**–**10**) all displayed two reversible one-electron oxidation waves resembling those of BEDT-TTF (**1**) as shown in Table I. Their complexations with TCNQ (7,7,8,8-tetracyanoquinodimethane) and various counteranions by virtue of electrocrystallization technique are actively pursued and will be reported in due course.

In conclusion, we have demonstrated a general synthetic procedure[9] to prepare tetrakis(alkyl- or phenylthio)- and tetrakis(alkyl- or phenylseleno)tetrathiafulvalenes with the use of dialkyl (or diphenyl) disulfides or diselenides as electrophiles which are either commercially available or can be readily obtained via the established literature procedures.[10] A preliminary result has indicated that the same procedure can be extended to prepare tetrakis(phenyltelluro)tetrathiafulvalene.

Experimental Section

The melting points were measured on a Mettler FP 80 hot stage and are uncorrected. ^{1}H NMR spectra were recorded at 360 MHz on a Bruker spectrometer using tetramethylsilane as an internal standard. Infrared spectra were recorded with a Perkin-Elmer 283 instrument. Low-resolution mass spectra were obtained from a direct-insertion probe MS analysis under 70-eV electron-impact ionization conditions using a Finnigan 4500 spectrometer. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. Cyclic voltammetry was conducted on BAS 100 (Bioanalytical Systems, Inc.) coupled with a standard three-electrode cell from IBM. Tetrahydrofuran (THF) and dichloromethane were freshly distilled under nitrogen from sodium/benzophenone and CaH_2, respectively, prior to use.

Tetrakis(methylseleno)tetrathiafulvalene (6). Method A. To a solution of LDA, generated at 0 °C with 4.1 equiv of diisopropylamine (1.4 mL, 10 mmol) and 2.1 M *n*-BuLi in hexane (4.8 mL, 10 mmol) in anhydrous THF (150 mL), was dropwise added tetrathiafulvalene (TTF) (0.5 g, 2.45 mmol) in anhydrous THF (6 mL) at −78 °C under Ar. A yellowish suspension resulted and was stirred at −78 °C for 1 h. To the mixture was slowly added at −78 °C a selenium powder (325 mesh) (773 mg, 9.79 mmol) from an L-shaped addition tube already fitted to the reaction flask. After the addition, the mixture was continuously stirred at −78 °C for 1 h, warmed to ambient temperature, and maintained at that temperature for 1 h. During this period, selenium powder was slowly consumed to give a brownish suspension. The mixture was cooled to −10 °C and quenched with excess amounts of methyl iodide (3 mL) in THF (10 mL), which was dropwise syringed into the reaction flask. After the addition, the mixture was warmed to 25 °C, stirred for 2 h, diluted with ethyl acetate (150 mL), washed with dilute HCl solution, H_2O, and brine, and dried over $MgSO_4$. After evaporation of the solvent, the residue was filtered through silica gel and washed thoroughly with 20% ethyl acetate in hexane. Solvent was removed to afford an orange-red solid, which was recrystallized from ethyl acetate/hexane to give fine needle crystals (1.13 g, 80%): mp 88–89 °C, ^{1}H NMR ($CDCl_3$) δ 2.34 (s, CH_3); IR ν_{max} ($CHCl_3$) 2992, 2935, 1422, 1275, 910 cm^{-1}; MS (EI), *m/z* 580 (M^+, ^{80}Se). Anal. Calcd for $C_{10}H_{12}S_4Se_4$: C, 20.8; H, 2.08; S, 22.3; Se, 54.8. Found; C, 20.6; H, 2.09; S, 22.4; Se, 54.9.

Tetrakis(phenylthio)tetrathiafulvalene (5). Method B. The tetraanion of tetrathiafulvalene (**3**) (0.5 g, 2.45 mmol) was generated with LDA (10 mmol) in exactly the same fashion as that described for **6**. It was quenched with diphenyl disulfide (2.24 g, 10.3 mmol) in THF (8 mL), which was syringed into the reaction flask at a rate of 4 mL/h with a syringe drive. The resulting mixture was stirred at −78 °C for 1 h and −20 °C for 1 h and slowly warmed to room temperature overnight (15 h). A dark red solution was obtained. It was diluted with ethyl acetate (250 mL), washed thoroughly with H_2O and brine, and dried over $MgSO_4$. After evaporation of the solvent, the residue was filtered through silica gel and recrystallized twice from ethyl acetate/hexane to afford a red-orange solid (1.0 g, 64%): mp 167–169 °C; ^{1}H NMR ($CDCl_3$) δ 7.41–7.26 (m, Ar H); IR ν_{max} ($CHCl_3$) 3060, 3000, 1582, 1478, 1443, 894 cm^{-1}; MS (EI), *m/z* 636 (M^+). Anal. Calcd for $C_{30}H_{20}S_8$: C, 56.6; H, 3.14; S, 40.3. Found: C, 56.4; H, 3.15; S, 40.1.

Tetrakis(methylthio)tetrathiafulvalene (4). Method A or B. Spectroscopic and physical data for the title compound are consistent with those reported in the literature.[11]

Tetrakis(propylseleno)tetrathiafulvalene (7). Method A or B. The product was purified by Flash chromatography eluted with 5% ethyl acetate in hexane to afford a dark red oil in 85% yield for method A and 80% for method B: ^{1}H NMR ($CDCl_3$) δ 2.88 (t, 2 H, J = 7.1 Hz, $SeCH_2$), 1.79–1.73 (m, 2 H, CH_2), 1.02 (t, 3 H, J = 7.4 Hz, CH_3); IR ν_{max} ($CHCl_3$) 2968, 2935, 2878, 1458, 1380, 1282 cm^{-1}; MS (EI), *m/z* 692 (M^+, ^{80}Se).

Tetrakis(butylseleno)tetrathiafulvalene (8). Method A or B. The titled compound was obtained as a dark red oil in 84% yield for method A and 78% for method B after purification by flash chromatography eluted with 5% ether in hexane: ^{1}H NMR ($CDCl_3$) δ 2.89 (t, 2 H, J = 7.4 Hz, $SeCH_2$), 1.75–1.67 (m, 2 H, CH_2), 1.46–1.38 (m, 2 H, CH_2), 0.93 (t, 3 H, J = 7.4 Hz, CH_3); IR ν_{max} ($CHCl_3$) 2964, 2935, 2870, 1460, 1382, 1260 cm^{-1}; MS (EI); *m/z* 748 (M^+, ^{80}Se).

Tetrakis(pentylseleno)tetrathiafulvalene (9). Method A or B. After workup, the crude product was purified by flash chromatography eluted with 5% ether in hexane to furnish **9** in 90% yield for method A and 82% for method B as a dark red oil: ^{1}H NMR ($CDCl_3$) δ 2.89 (t, 2 H, J = 7.4 Hz, $SeCH_2$), 1.75–1.69 (m, 2 H, CH_2), 1.39–1.34 (m, 6 H, 3 × CH_2), 0.91 (t, 3 H, J = 7.1 Hz, CH_3); IR ν_{max} ($CHCl_3$) 2960, 2930, 2860, 1460 cm^{-1}; MS (EI), *m/z* 804 ($^+$M, ^{80}Se).

Tetrakis(phenylseleno)tetrathiafulvalene (10). Method B. After workup, the crude product was recrystallized twice from THF/hexane to give **10** in 75% yield as an orange (or brown) solid (depending on the recrystallization conditions): mp 154–156 °C, ^{1}H NMR ($CDCl_3$) δ 7.52–7.49 (m, 2 H, Ar H), 7.31–7.25 (m, 3 H, Ar H); IR ν_{max} ($CHCl_3$) 3050, 2990, 1578, 1478, 1443 cm^{-1}; MS (EI), *m/z* 828 (M^+, ^{80}Se). Anal. Calcd for $C_{30}H_{20}S_4Se_4$: C, 43.7; H, 2.43; S, 15.6; Se, 38.3. Found: C, 43.5; H, 2.42; S, 15.7; Se, 38.0.

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Registry No. **1**, 66946-48-3; **2**, 31366-25-3; **4**, 51501-77-0; **5**, 108666-51-9; **6**, 96913-57-4; **7**, 108666-52-0; **8**, 108666-53-1; **9**, 108666-54-2; **10**, 96913-58-5; MeI, 74-88-4; Se, 7782-49-2; PhSSPh, 882-33-7; MeSSMe, 624-92-0; $C_3H_7SeSeC_3H_7$, 7361-89-9; C_3H_7I, 107-08-4; $C_4H_9SeSeC_4H_9$, 20333-40-8; C_4H_9I, 542-69-8; $C_5H_{11}SeSeC_5H_{11}$, 52056-07-2; $C_5H_{11}I$, 628-17-1; PhSeSePh, 1666-13-3.

Kinetics and Mechanism of the Zn(II)-Catalyzed Hydrolysis of 2-Acetylpyridine Oxime Phenyl Sulfite[†]

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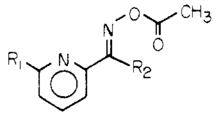
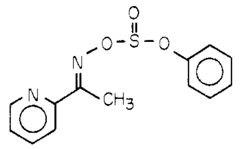
Previously, we have performed kinetic studies on the metal ion catalyzed hydrolysis of several acetyl esters of pyridine oximes **1a–d**,[1] disclosing several new catalytic features of metal ions which act as Lewis acids in organic reactions. The information obtained from such studies with small molecules makes significant contributions to the understanding of the mechanisms of not only organic and inorganic reactions but also metalloenzyme–catalyzed reactions.[2-4]



1a: $R_1 = H$, $R_2 = H$
1b: $R_1 = H$, $R_2 = CH_3$
1c: $R_1 = COOH$, $R_2 = H$
1d: $R_1 = H$, $R_2 = 2\text{-py}$

In the present study, the investigation of the catalytic effects of metal ions was extended to the hydrolysis of a sulfite ester analogue (**2**) of **1a–d**. The central sulfur atom of sulfite esters, to which three oxygen atoms are attached, contains a nonbonding electron pair and its configuration is tetrahedral.[5] Nucleophilic reactions on carboxyl esters proceed through the formation of tetrahedral intermediates.[6] On the other hand, the nucleophilic reactions on sulfite esters would occur through either a stepwise or a concerted mechanism.[5] In either mechanism of the reactions of sulfite esters, trigonal bipyramidal transition states are involved in which both the leaving group and the attacking group occupy the apical positions.[5] The differences in kinetic behavior between carboxyl and sulfite esters caused by the different structural and chemical properties of the ground states and the transition states will be discussed in this report.



2

Scheme I

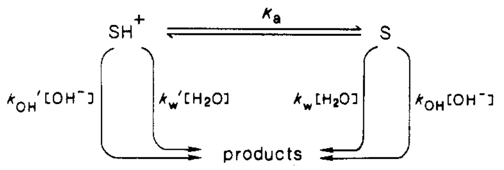


Table I. Kinetic Parameters for the Spontaneous and the Zn(II)-Catalyzed Hydrolysis of 2

reacn	parameter	value
spontaneous	k_{OH}	$2.1 \times 10^4\ M^{-1}\ s^{-1}$
	k_w'	$4.7 \times 10^{-6}\ M^{-1}\ s^{-1}$
	$k_{OH}'K_w/K_a + k_w\ [H_2O]$	$6.5 \times 10^{-5}\ s^{-1}$[a]
Zn(II)-catalyzed	k_{OH}^{M}[b]	$3.3 \times 10^8\ M^{-2}\ s^{-1}$
	k_w^{M}[c]	$1.3 \times 10^{-3}\ M^{-2}\ s^{-1}$

[a] If this value is contributed to solely by the k_w $[H_2O]$ term, k_w (the attack of water molecule at the unprotonated substrate) is $1.2 \times 10^{-6}\ M^{-1}\ s^{-1}$ being only four times smaller than k_w' (the attack of water molecule at the protonated substrate). Therefore, the contribution of k_w $[H_2O]$ to this value should be negligible, $k_{OH}'K_w/K_a$ being the major part of the observed value. This leads to the k_{OH}' value of $8.2 \times 10^6\ M^{-1}\ s^{-1}$, which is 4×10^2 times greater than the k_{OH} value. [b] Parameter k_{cat}^{OH} is much greater than $6.6 \times 10^7\ M^{-1}\ s^{-1}$ (see text). [c] Parameter k_{cat}^{w} is much greater than $2.6 \times 10^{-4}\ M^{-1}\ s^{-1}$ (see text).

Experimental Section

Materials. 2-Acetylpyridine oxime phenyl sulfite **2** was prepared by the dropwise addition of phenyl chlorosulfinate[7] (0.71 g) dissolved in 2 mL of diethyl ether to a diethyl ether solution (20 mL) containing 2-acetylpyridine oxime (0.55 g) and triethylamine (0.50 g) at 4 °C. Precipitates of the hydrochloride salt of triethylamine were removed, and the resulting solution was washed with a 0.1 N hydrochloric acid solution and then with a 5% sodium bicarbonate solution followed by water. After drying with magnesium sulfate, the solvent was removed and the resulting residue was recrystallized from chloroform–hexane, producing white crystals of **2**, mp 73 °C.

Cupric chloride and zinc chloride solutions were prepared by dissolving corresponding oxides (Aldrich, Gold Label) with hydrochloric acid.

Kinetic Measurements. Reaction rates were measured with a Beckman 5260 or a Beckman 25 UV–vis spectrophotometer at wavelengths (~280–340 nm) which afforded maximal absorbance changes during the reaction. Temperature was controlled at 25 ± 0.1 °C with a Haake E52 or a Lauda Brinkman T-2 circulator. The reactions were carried out in the presence of 0.8% (v/v) dimethyl sulfoxide at ionic strength 1.0, which was adjusted with sodium chloride. Buffers (0.005–0.04 M) used were chloroacetic acid (pH 2.5–3.5), acetic acid (pH 4–5), 2-*N*-morpholinoethanesulfonic acid (Mes) (pH 5.5–7), and 2-[1-(2-hydroxyethyl)piperazin-4-yl]ethanesulfonic acid (pH 7.5–8). pH measurements were performed with a Fisher Accumet Model 525 pH meter. The concentration of **2** employed in kinetic studies was (0.5–1) $\times 10^{-4}$ M. The pseudo-first-order rate constants were calculated from the slopes of the linear plots (correlation coef-

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[†] Dedicated to Professor Sae-Hee Chang on the occasion of his 60th birthday.

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