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Investigating the Synthesis of Unsymmetrical Tetrathiafulvalene Derivatives: Improved Yields by the Hidden Equivalent Method.

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Abstract

An improved synthesis of unsymmetrical tetrathiafulvalenes (TTFs) (**5 a-c**, **5 f-g**, **7**) is presented which results in higher yields of unsymmetrical TTFs when compared to existing methods. The synthetic method consists of pre-equilibration of thiones containing electron withdrawing groups with $P(OEt)_3$ at the minimum temperature where a reaction occurs as determined by ^{31}P NMR, followed by the slow addition of the thiones to be coupled (typically containing electron donating substituents) and a second equivalent of $P(OEt)_3$. The reaction is allowed to react for some time and a third equivalent of $P(OEt)_3$ is then added. It was also found that the purification of unsymmetrical TTF, **5a**, can be greatly simplified by selective precipitation of the symmetrical TTF tetraester (**5d**) allowing for the rapid synthesis of **5a** in multigram quantities. In addition our studies have led to some mechanistic insights of the reaction.

Introduction

Tetrathiafulvalene (TTF) (**1**) and its derivatives have received considerable attention for their ability to form organic metals and superconductors[1]. Most organic crystalline conductors have been prepared from symmetric TTF donors ($R_1=R_2$), while very few conducting salts been prepared from unsymmetrical TTF donors ($R_1 \neq R_2$) (Figure 1, **2**)[2,3].

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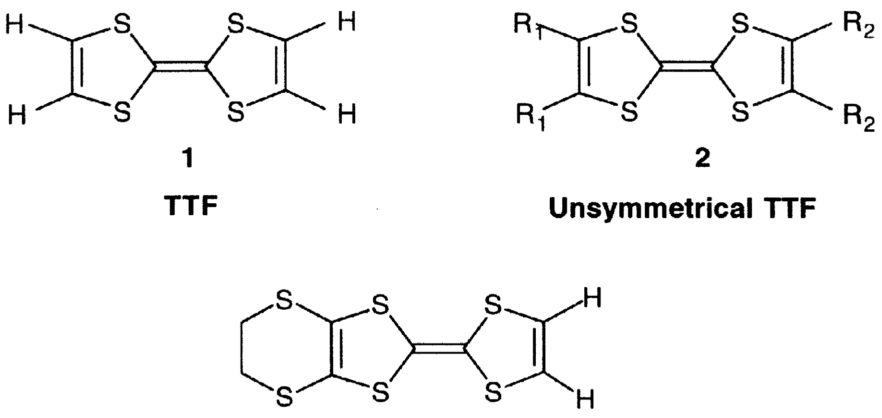
In fact, 80% of all TTF donors prepared have been symmetrical due to their ease of synthesis. If one considers the number of charge transfer salt complexes formed by symmetrical versus unsymmetrical TTFs, about 99% of all organic conductors are prepared from symmetrical TTFs.[1] The lack of research on unsymmetrical TTFs probably has origins in both theory and experiment.

Theoretically, it was believed that unsymmetrical donors would cause disorder in the crystal lattice or lead to localization of electronic wavefunctions suppressing high electrical conductivity and superconductivity.[1] However, early work by Cava, Wudl, and others indicated that unsymmetrical TTF donors could lead to organic metals and superconductors. In 1983 it was found by Fabre and Delhaes that unsymmetrical TTFs and tetraselenafulvalenes (TSFs) can form radical cation salts that exhibit metal-like conductivity.[4] Later it was reported by Kikuchi et al.[5] and by Papavassiliou[5] that unsymmetrical TTF derivatives can form organic superconductors, which led to renewed interest in these TTF donors.

Figure 1.



1
TTF

2
Unsymmetrical TTF

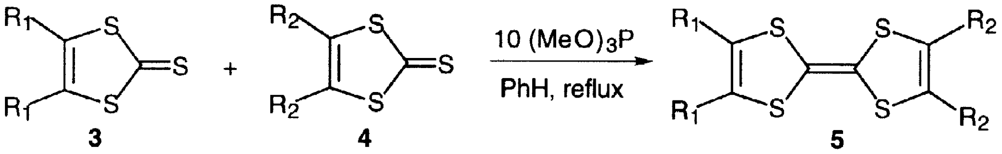
Example of an Unsymmetrical TTF

Experimentally, the synthesis and purification of unsymmetrical TTFs can be difficult. Many of the synthetic methods[3,4,7] require a number of steps and/or very difficult separation of the desired unsymmetrical TTF from the homocoupled by-products. Recent work has focused on simplifying the synthesis of unsymmetrical TTFs.[8] One of these reports describes a procedure which employs 4-thiolate mesoions of 2-(dialkylamino)-4-(alkylthio)-1,3-dithiolium salts as intermediates in the synthesis of unsymmetrical TTFs.[8a] Another method[9] has used an organotin chalcogenate as the common intermediate for synthesizing unsymmetrical organic donors. Despite these advances, most unsymmetrical TTFs are still prepared by a simple phosphine or phosphite coupling method where thiones or oxones (not shown) are coupled in one-pot (Scheme 1). Other methods have used the selective coupling of oxones to give TTF yields of ≈25%. One problem wiht this method is that the synthesis of oxones from the respective thiones and $Hg(OAc)_2$ does not always cleanly give the oxone products. Alternative routes to oxones can be quite long and arduous. Here we present a study that focuses on optimizing the reaction conditions in the straightforward phosphine or phosphite coupling method where readily available thiones are coupled (Scheme 1). This study shows how to increase the reaction yields of unsymmetrical TTFs by a procedure we call the "hidden equivalent method" (HEM). In addition, solubility differences between the products and by-products allow for the isolation of the desired TTF derivatives in multigram quantities.

Results and Discussion

The reaction we focused on was the coupling of an electron donating thione (**3a** R = SMe[10]) and an electron withdrawing thione (**4a** R = CO_2Me[11]). The homocoupled TTF by-products, **5d** and **5e**, are different enough in polarity thus allowing for easy purification and isolation of **5a**. Another advantage to using the polarity distinct thiones is that the unsymmetrical TTF produced (**5a**) provides a route into some new and interesting unsymmetrical TTFs (e.g. R_1 = SMe, R_2 = H in **5** in Scheme 1) by simply decarboxylating the methyl esters with LiBr/HMPA[12]. Furthermore, metallation of this TTF, followed by chalcogenation would lead to TTFs as precursors for the synthesis of metal-TTF based coordination complexes[13] and CdSe-TTF nanocrystallite materials.[14]

Scheme 1. Literature Preparation of Unsymmetrical TTFs



3a R_1 = SCH_3
3b R_1 = CH_3
3c R_1 = SCH_2CH_3
3d R_1 = $SC_{16}H_{33}$

4a R_2 = $COOCH_3$
4b R_2 = CF_3

5a R_1 = SCH_3; R_2 = $COOCH_3$
5b R_1 = SCH_3; R_2 = CF_3
5c R_1 = CH_3; R_2 = $COOCH_3$
5d R_1 = R_2 = $COOCH_3$
5e R_1 = R_2 = SCH_3
5f R_1 = SC_2H_5 R_2 = $COOCH_3$
5g R_1 = $SC_{16}H_{33}$ R_2 = $COOCH_3$

We began by coupling the two electronically distinct 1,3-dithiole heterocycles (**3a** and **4a**) to afford TTF framework, using the method of Papavassiliou.[7] This method calls for refluxing 1.5 mmoles of the electron withdrawing thione (e.g. **4a** or **4b**[2]), 1 mmole of the electron releasing thione (e.g. **3a**-**e**), and 10 equivalents of $(MeO)_3P$ in benzene for 4 hours. The Papavassiliou method appears to give the best yields and is the quickest, most general route to a number of unsymmetrical TTFs (Scheme 1). Using this method, we coupled the electron withdrawing thione dimethyl-2-thioxo-1,3-dithiole-4,5-dicarboxylate (**4a**) to the electron releasing thione 4,5-bis(methylthio)-1,3-dithiole-2-thione (**3a**).[7e] We found that the yields of **5a** were lower than those reported, and the products were very difficult to purify. We also found using $(EtO)_3P$ gave lower yields than $(MeO)_3P$[15]. We therefore set out to optimize this reaction.

Our first approach was to use ^{31}P NMR in order to monitor the reaction (a function of temperature) between $(EtO)_3P$ and individual thiones (**3a**, **4a**, and **4b**) in benzene. We hoped to be able to monitor the formation and/or disappearance of intermediates that have been proposed in the reaction mechanism as shown in Figure 2.

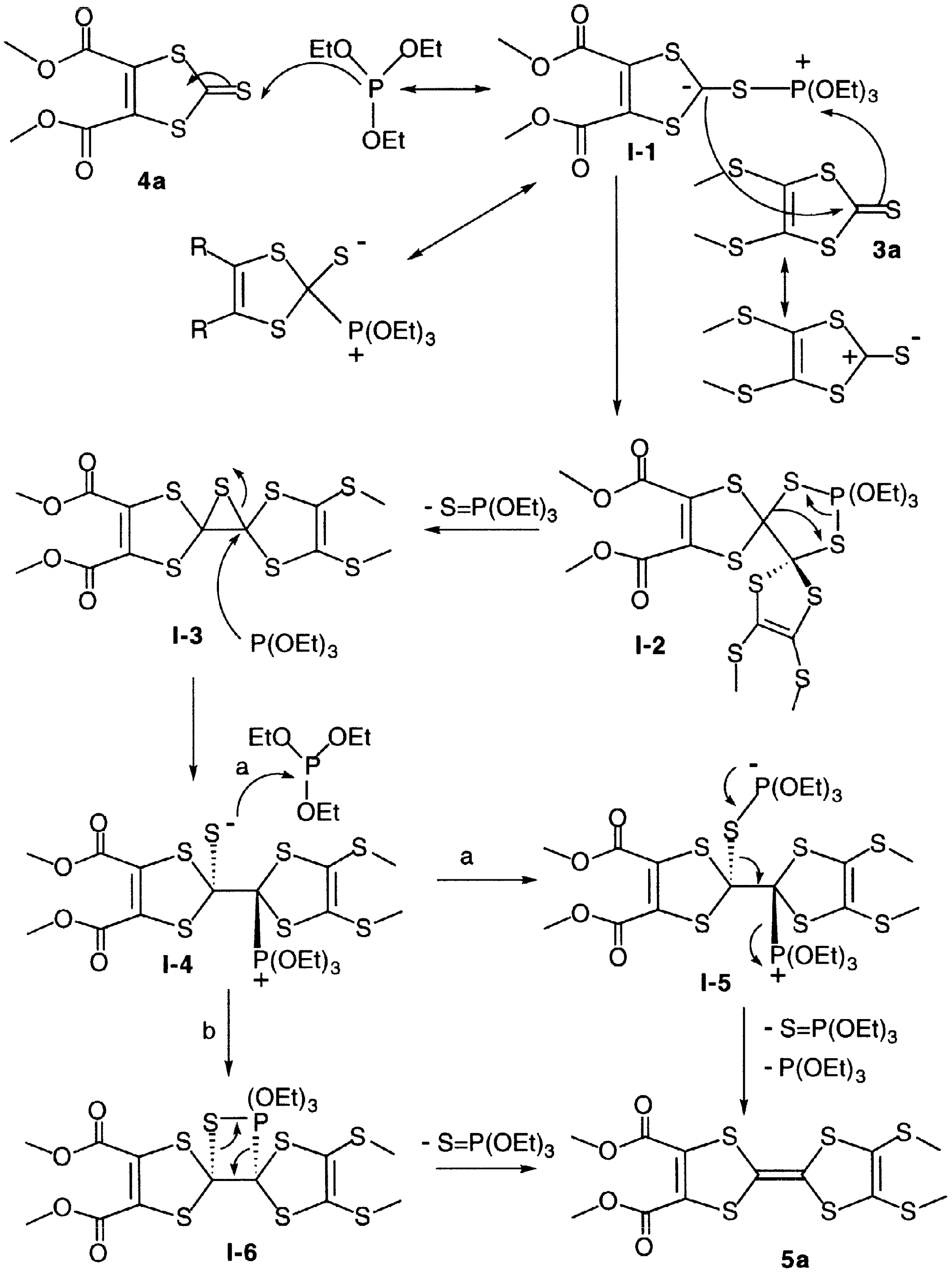
We observe the development of a peak at 10 ppm which appears in a region where an intermediate phosphonium ion such as **I-1** would occur. As spectroscopic markers, triethyl phosphite peak appeared at 140 ppm, while the phosphine sulfide by-product appears at 70 ppm. Following this resonance in the ^{31}P NMR as a function of temperature gives insight into the reactivity of individual thiones with $(EtO)_3P$. This experiment can determine which thione reacts at a faster rate with $(EtO)_3P$. The results showed that the initial reactions between the electron withdrawing thione **4a** and $(EtO)_3P$ occurred at 65°C, while the electron releasing thione **3a** failed to react with a variety of phosphorous reagents over the entire temperature range studied (up to 80°C in benzene or toluene). We also found that $(i\text{-PrO})_3P$ and **4a** also reacted at 65°C, while $(EtO)_3P$ and **4b** reacted at 0°C. In addition, similar experiments were attempted using Ph_3P as the phosphorous reagent, and the results show that the ester thione, **4a**, again reacted first relative to **3a**, but at a higher temperature (>80°C in toluene). The initial reaction temperature, as determined by ^{31}P NMR, in the case of Ph_3P and **4b** was 53°C. These results imply that trivalent valent phosphorus reagents, e.g. $(EtO)_3P$, are more reactive with thiones carrying electron withdrawing groups (i.e. **4a** and **4b**) than with thiones carrying electron releasing groups (i.e. **3a-e**). This observation is consistent with formation of an anion intermediate **I-1** (Figure 2). In addition, electronic factors appear to play a dominant role in determining the reaction rate for the initial coupling reactions. This conclusion is based on the lack of a steric effect on the reaction kinetics. We find that there is no detectable difference in the initial reaction temperatures (or kinetic differences) between the reaction of **4a** and $(EtO)_3P$ (cone angle 109°) versus **4a** and (i-PrO)$_3$P (cone angle 130°). However, therefore **4b** is found to be more reactive with trivalent phosphorous reagents than **4a**, due to the strong inductive effect of the $-CF_3$ groups on the TTF relative to -COOMe.

Based on these observations, it is concluded that the zwitterionic intermediate **I-1** is formed first--a condition necessary to initiate the coupling reaction. NMR results also show **I-1** to be present in low concentrations indicating that the first step in the reaction is most likely a reversible dissociative equilibrium. Therefore it desirable to have the electron donating thione present in the flask in order to shift the reaction equilibrium to the right.

The kinetics of the reaction were also followed by variable temperature ^{31}P NMR. The homocoupling of **4a** using $(EtO)_3P$ to give **5d** was studied in particular. Although the kinetics will be different for the formation of unsymmetrical TTFs, studying the aforementioned reaction should give us the lower limit of the reaction time needed for a complete reaction (since **4a** is more reactive to coupling). Although studies of both **4a** and **4b** were undertaken and analyzed in the same manner, only the reaction of $(EtO)_3P$ with **4a** will be presented as an illustrative model.

The reaction appears to be second order in phosphorous (Figures 3 and 4) (although it is impossible to eliminate pre-equilibrium conditions). Figure 3 shows the half-life method data, which shows (by its linearity) that the reaction is indeed second order in [phosphite]. The ordinate axis in Figure 3 is defined as the half-life of the phosphite plotted against the $[\mathrm{conc}]^{-1}$. This allows for pre-equilibrium conditions to be ruled out. The overall half-life of the reaction was also determined. Graphs from Figures 3 and 4 can be fit to the simple linear equations $y = 6.18*10^{-3} + 4.90*10^{-4}x$ with an $R^2 = 0.970$ and $y = -12.04 + 3.78x$ with an $R^2 = 0.999$, respectively. In Figure 4 the slope ($4.90*10^{-4}$) is equal to the rate constant k in Equation 1 and gives the calculated half-life ($t_{1/2} = 1/(k[A]_o)$ where $[A]_o$ is the initial phosphite concentration, of approximately 13 hours at 65°C (7 hrs. in refluxing C_6H_6). This data indicates that longer reaction times are needed to form the various key intermediates.

Figure 2. **The Proposed Mechanism for the Coupling** of Two Thiones to Yield **Unsymmetrical TTFs.**



Equation 1: Second order rate law

$[P]_t = [P]_o/(1 + kt[P]_o)$

$[P]_t$ = Concentration of phosphorous reagent at time t

$[P]_o$ = Initial concentration of phosphorous reagent

k = slope of line in Figure 4

Figure 3: The half-life method.

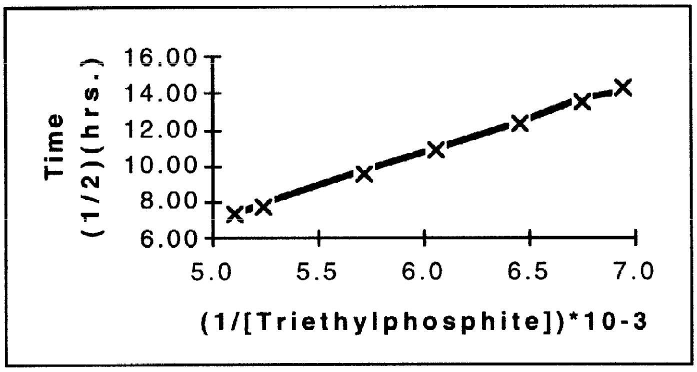
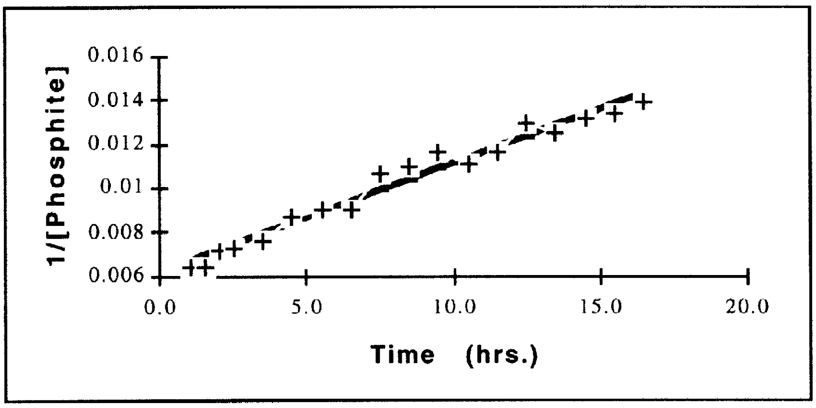


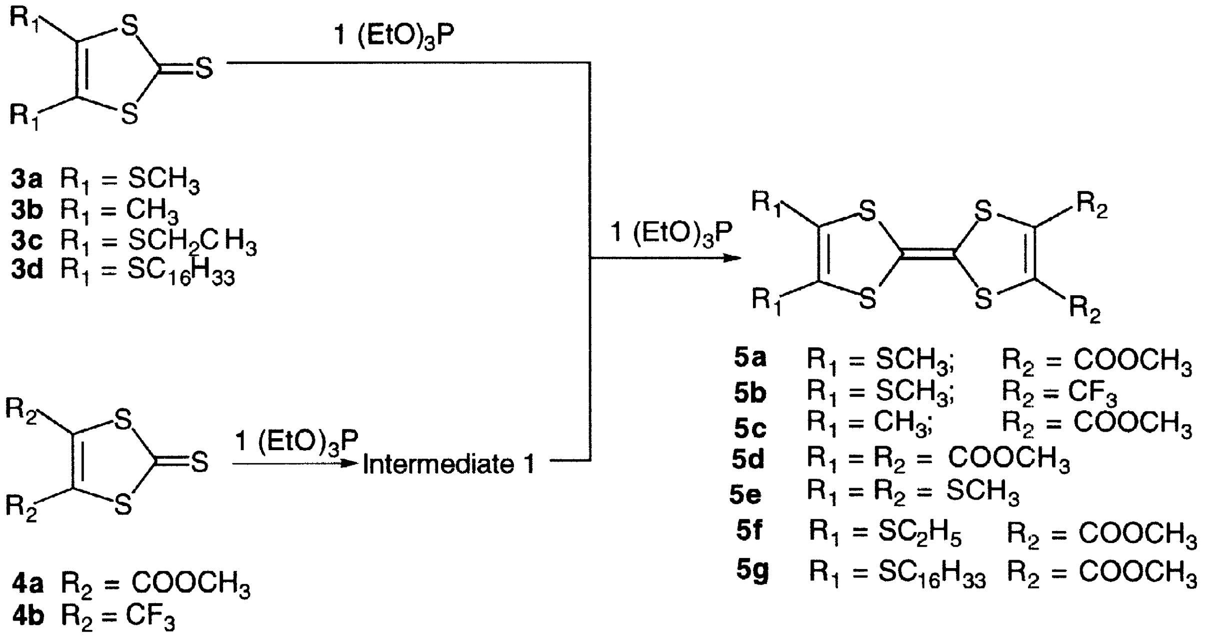
Figure 4: Plot of 1/[phosphite] vs. time.



The preceding NMR experiments provide some information that could enhance the yields of these unsymmetrical coupling reactions using the hidden equivalent method. The scheme for increasing the yields of the unsymmetrical product is shown in Scheme 2. Since the intermediate (**I-1**) is formed first, from a reaction between the thiones containing electron withdrawing groups (e.g. **4a** and **4b**) and trivalent phosphorous, we placed one equivalent of trivalent phosphorous with the electron withdrawing thione in a reaction vessel and heated this to the temperature at which we first noticed a reaction in the NMR studies. Following this the electron releasing thione and another equivalent of trivalent phosphorous (together) are added over a period of 90 min. This slow addition shifts the equilibrium from **I-2** to **I-6** (Figure 2). The reaction mixture was then heated to reflux for about 14 hours. Following this time period another equivalent of trivalent phosphorous was introduced. This "hidden equivalent" shifts the equilibrium farther to the right by pushing many of the intermediates toward completion of the reaction, as well as speeding up the overall reaction.

We initially believed the mechanism proceeds through intermediate **I-5** and not through the four membered ring phosphathiatane intermediate **I-6**. In fact, **I-5** necessitates a third equivalent of phosphorus as we added in the HEM. Support is also found in the work of Yoshida,[15] where 4,5-dicyano-1,3-dithiole-2-thione is reacted with PPh_3 in benzene to give

Scheme 2. Hidden Equivalent Method for the Preparation of Unsymmetrical TTFs



3a $R_1 = SCH_3$
3b $R_1 = CH_3$
3c $R_1 = SCH_2CH_3$
3d $R_1 = SC_{16}H_{33}$

4a $R_2 = COOCH_3$
4b $R_2 = CF_3$

5a $R_1 = SCH_3$; $R_2 = COOCH_3$
5b $R_1 = SCH_3$; $R_2 = CF_3$
5c $R_1 = CH_3$; $R_2 = COOCH_3$
5d $R_1 = R_2 = COOCH_3$
5e $R_1 = R_2 = SCH_3$
5f $R_1 = SC_2H_5$ $R_2 = COOCH_3$
5g $R_1 = SC_{16}H_{33}$ $R_2 = COOCH_3$

85% of the intermediate similar to **I-4**. However, since our kinetic data supports the second order dependence on phosphite, the betaine pathway (a) (Figure 2) can be eliminated. Indeed, we now believe pathway (b) (Figure 2) predominates, and that **I-6** is the most probable intermediate. This compound is converted to TTFs via the loss of $(EtO)_3P{=}S$ which is catalyzed by the third equivalent of phosphite, perhaps acting as a Lewis acid.

Although this method leads to increased yields of unsymmetrical tetrathiafulvalenes, purification of the products was still difficult. We found it impossible to produce large quantities of these materials in single reactions (32mmol) without running multiple silica gel columns, often consuming egregious amounts of silica gel (1.0kg/reaction). However, we have found that evaportation of the volatiles from the crude reaction of thioether thione, **3a**, and diester thione, **4a**, followed by dissolving the remaining red oily solids up in a minimum volume of CH_2Cl_2, cooling the solution to 0°C, and adding cold pentane, leads to the selective precipitation of the homo-coupled tetraester **5d**. Since this material presents the greatest difficulty in chromatographic separation, purification is greatly simplified. (As an added bonus, the tetraester **5d** may then be converted to TTF.16)) At this point the unsymmetrical product may be purified by one column using only 250 g silica gel to recover ~2-2.5 g of analytically pure product.

Table 1 presents the results of the reactions that have been optimized by the hidden equivalent method (HEM). Comparison of the HEM (Scheme 2) to the literature method (Scheme 1) shows that in the coupling of thioether thione, **3a**, and diester thione, **4a**, the yields of **5a** are nearly double. The ease of purifying **5a** by selective precipitation of the tetraester byproduct is again important, since crystallization or column chromatography are both very difficult (impossible) in large scale reactions when **5d** has not been removed. In the case where the ditrifluoro–methyl thione, **4b** is coupled with **3a** to form **5b**, the HEM is also superior to the literature method, yielding 18-24% of analytically pure unsymmetrical TTF. Using the literature method we get 10-13% crude yields and have been unable to obtain analytically pure samples by attempting to purify this material by either chromatography or by crystallization. Materials obtain by the literature method can be ultimately purified by a combination of running multiple silica gel columns, followed by one or two recrystallizations. This purification procedure leads to a TTF that is close to analytical purity. Therefore the literature reaction for the synthesis of **5a** and **5b** is much more difficult and gives lower yields relative to our new method. In both cases the analytically pure, isolated yields by our method are at least doubled.

We believe one important result is the application of the HEM to make **5c** from thiones **3b** and **4a**. We find that TTF **5c** cannot be prepared by the method shown in Scheme 1 and to our knowledge alkylated TTFs are among the most difficult to purify when derived from the phosphite coupling method. This implies that other di-alkyl thiones will not couple to form TTFs; however, we find that **5c** can be prepared by the HEM to give analytically pure sample yields of up to 4% in a straightforward way (Scheme 2). Unsymmetrical 1,2-dimethyltetrathiafulvalene and that other dialkyl TTFs can be prepared in this manner by decarboxylating molecules like **5c** with LiBr. It is important to note that although the yields are very low for this reaction, the synthesis avoids the commonly used dangerous perchlorate salts.

The results for the synthesis of **5f**, **5g**, and **7** are explained in terms of solubility. Thiones **3d** and **6** are not very soluble in benzene and therefore the HEM is comparable to the literature method, where the solvent mixture is 3:1 benzene:$(EtO)_3P$ (10 equiv. of phosphite) which readily solubilizes most, if not all thiones (Scheme 1). Therefore it appears that the HEM is quite successful when the thiones are soluble in benzene, but the results break down when the starting materials have low solubilities in the reaction medium.

The synthesis of unsymmetrical TTF **5g** is more easily accomplished using the literature method. The solubility of the thione **3d** is quite good in 10 equivalents of $(EtO)_3P$ and yields of analytically pure TTF **5g** can be obtained in a 15% yield. The HEM leads to a crude yield of 18% (95% pure) and further purification of **5g** requires more than one silica gel column.

We have also applied the HEM to the synthesis of TTFs **7** and **8** as shown below. Using the literature methods, we have found these compounds very difficult to prepare on a large scale. However, in the large scale synthesis of **7**, the HEM leads to a product that is isolated after one or two columns, while obtaining pure **7** via standard methods required

Table 1. Synthesis of Unsymmetrical TTFs.

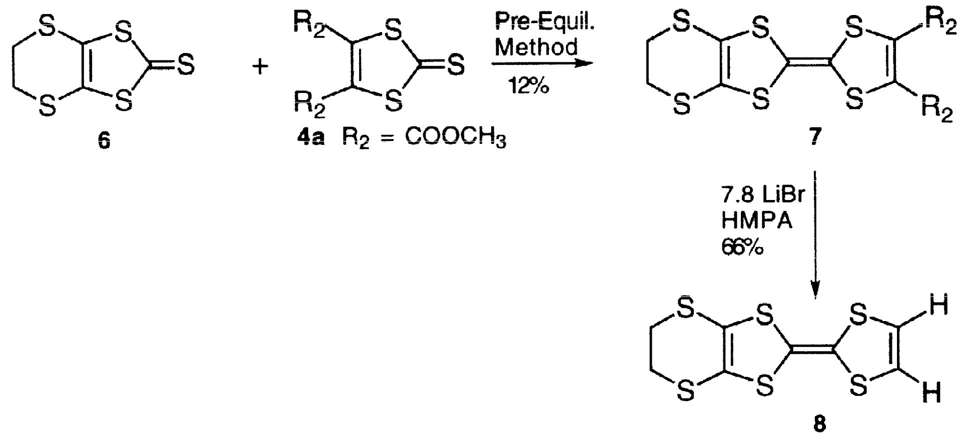
Scale	Thione	Thione	Product	Yield (mass recovered) Literature Method Scheme 1	Yield (mass recovered) Hidden Equiv. Method Scheme 2
3 mmol	**3a**	**4a**	**5a**	14% (170 mg)	24% (300 mg)
24 mmol	**3a**	**4a**	**5a**	9%[1] (0.9 g)	18%[1] (1.8 g)
32 mmol	**3a**	**4a**	**5a**	13%[1] (1.8 g)	20%[1] (2.6 g)
3 mmol	**3a**	**4b**	**5b**	-----[2]	18% (230 mg)
3 mmol	**3a**	**4b**	**5b**	-----	24%[3] (310 mg)
3 mmol	**3b**	**4a**	**5c**	0%[4]	4% (41 mg)
3 mmol	**3c**	**4a**	**5f**	16% (210 mg)	15% (200 mg)
20 mmol	**3c**	**4a**	**5f**	-----	13% (1.1 g)
3 mmol	**6**	**4a**	**7**	18% (221 mg)	12% (148 mg)
24 mmol	**6**	**4a**	**7**	------[5]	9% (886 mg)

All reaction yields are based on recovered, analytically pure product. Every sample had elemental analysis values within 0.4 % of the theoretically predicted value. [1]symmetrical tetraester (**5d**) was precipitated and filtered prior to purification of the product by chromatography [2]Yield ≈10% by NMR. Compound 90-97% pure by NMR; Anal. (calc.) for $C_{10}H_6F_6S_6$: C, 28.78 (27.77), H, 1.56 (1.40). [3]PPh_3 used instead of $P(OEt)_3$ [4]Crude yield <1% by NMR. Compound was never completely purified. [6]. Yield was 9% after 4 columns and 1 recrystallization. Yield based on a sample where the melting point and NMR was consistent with **7**.

four columns and one recrystallization. Therefore the HEM seems like a viable way to do large scale synthesis of these unsymmetrical TTFs.

In conclusion, we have synthesized the of unsymmetrical tetrathiafulvalenes (TTFs) (**5 a-c**, **5 f-g**, **7**, **8**) using an improved synthetic method we call the "hidden equivalent method" (HEM). This improved and easy method, in many cases, leads to higher reaction yields of

Scheme 3.



unsymmetrical TTFs when compared to existing approaches. In addition, it was found that the purification of unsymmetrical TTF, **5a**, can be greatly simplified by selective precipitation of the symmetrical TTF tetraester (**5d**) allowing for the rapid synthesis of **5a** in multigram quantities. Additional work here has provided additional mechanistic insights into the phosphite coupling reaction between two different thiones.

Experimental

^{1}H, ^{13}C, and ^{31}P NMR were recorded on a Bruker NR 300MHz FTNMR working at 300MHz, 75MHz, and 121MHz, respectively, with chemical shifts being given in ppm referenced to TMS, $CDCl_3$, or $(MeO)_3P$. All ^{31}P kinetic experiments were done in absolute intensity mode using fully automated sampling, transforming, and displaying with delays being set at least 5 times the value of the T_1. Samples were prepared using the tube-in-tube method with 5 mm tubes containing the reactants and C_6H_6 being placed in 10 mm tubes containing D_2O. For each ^{31}P spectrum recorded the FID was collected over 64 scans and then line broadened using a maximum value of 2. The UV-Vis data was taken in CH_3CN (dried and distilled from CaH_2) on a HP 8451A diode array spectrometer. The IR spectra were recorded on a Mattson Galaxy Series FTIR 5000 using KBr (unless otherwise noted) pellets and the electrochemistry was recorded using 0.2M $(C_4H_{10})_4NPF_6$ in CH_3CN (dried and distilled first from CaH_2 then P_2O_5) on a Pines model AFRDE4 potentiostat. Elemental analyses were done by Midwest Microlabs (Indianapolis, IN) and mass spectra were recorded at the University of Pittsburgh (Pittsburgh, PA). C_6H_6 was dried and distilled from Na/benzophenone, $(EtO)_3P$ was dried and distilled from Na metal then stored in a stoppered flask over Drierite, and PPh_3 was recrystallized from C_6H_6. All phosphorous reagents were assessed for purity before use in ^{31}P NMR studies. Reagent grade solvents were purchased from Fisher Chemical Co. and used as received. Silica Gel was J.T. Baker brand 60-200 mesh. All glassware was oven dried overnight, purged with Ar, and the reactions done under the same inert atmosphere using Schlenk techniques. Compounds **3a**[10], **3b**[16], **3c**[17], **3d,6**[19], **4b**[11], and **4a**[3b,20] were synthesized using literature procedures.

Hidden Equivalent Method:

In a typical procedure **4a** (8.0 g 32mmol), 60 mL C_6H_6, and 5.6 mL of $(EtO)_3P$ are placed in a 500 mL round bottom 3-neck flask fitted a reflux condenser, and a 125 mL addition funnel that is filled with **3a** (7.32g 32 mmol) and 5.6 mL of $(EtO)_3P$ in 120 mL of C_6H_6. The reaction is then heated to 65°C and the solution in the addition funnel is added over 90 min, while the reaction is slowly heated to reflux. Then 5.6 mL (32 mmol) of $(EtO)_3P$ is added and reaction refluxed for 18 h. The solvent is then removed is removed by rotary evaporation. The oily red-black residue is dissolved in CH_2Cl_2 (35 mL), transferred to an Erlenmeyer flask, and cooled to 0°C. Pentane (350 mL, at 0°C) is added and the resulting solid (**5d**) is filtered and is washed with 150 mL of pentane. The desired product **5a** is isolated by removing the solvent from the filtrate. Chromatography (silica) affords the desired product with analytical purity.

Tetramethyltetrathiafulavalene-4,5-dithiolate-4', 5'-dicarboxylate (5a): R_f (3:1 CH_2Cl_2:hexanes) = 0.38, Mp 91°-93°C (lit Mp[7e] 83°C); ^1H NMR($CDCl_3$) δ 2.42 (s, 3H), 3.83 (s, 3H); UV-Vis(nm) ($\varepsilon*10^3$ CH_3CN) 216 (19.8), 280 (18.0), 324 (12.8), 436 (1.98);

IR(KBr, cm^{-1}) 2950, 1730, 1710, 1595, 1520, 1310, 1280, 1090, 1020, 1000, 990; Mass Spec. (EI low res) M^+ = 412 amu; Electrochemistry (V vs. Ag wire) $\Delta E_{1/2}$ = 0.60 (rev), $\Delta E_{1/2}$ = 0.78 (rev); Anal. Calcd for $C_{12}H_{12}O_4S_6$; C, 35.10, H, 3.01. Found: C, 34.93; H, 2.93.

4,5-bis(trifluoromethyl)-4',5'-dimethyltetrathiafulavalene-4',5'-dithiolate (5b): Rf (C_6H_{14}) = 0.23; Mp 64-65° C (recrystallized from CH_3CN); ^1H NMR($CDCl_3$) δ 3.43 (s); UV-Vis (nm) (ε*10^3 CH_3CN) 220 (9.4), 308 (13.4), 322 (13.7), 424 (1.9), 440 (2.00); Mass Spec. (EI low res) M^+ = 432amu; Electrochemistry (V vs. Ag wire) $\Delta E_{1/2}$ = 0.69(rev), $\Delta E_{1/2}$ = 0.96(rev); Anal. Calcd for $C_{10}H_6F_6S_6$: C, 28.09, H, 1.35. Found: C, 27.77; H, 1.40.

4,5-dimethyl-4',5'-dimethyltetrathiafulavalene-4',5'-dicarboxylate (5c): Rf (3:1 CH_2Cl_2: C_6H_{14}) = 0.43; Mp 130°-131°C; ^1H NMR($CDCl_3$) δ 1.95 (s, 6H), 3.83 (s, 6H); UV-Vis (nm) (ε*10^3): 220 (7.7), 300 (8.0), 372 (3.4), 456 (0.8); IR(cm^{-1}) 3005, 2930, 2905, 1710,1585, 1560, 1430, 1295, 1090, 1040, 920, 780, 760, 710; Mass Spec. (EI low res) M^+ = 348 amu; Electro–chemistry (V vs. Ag wire) $\Delta E_{1/2}$ (1) = 0.48 (rev), $\Delta E_{1/2}$ (2) = 0.85 (rev); Anal. Calcd for $C_{12}H_{12}O_4S_4$: C, 41.21, H, 3.55. Found: C, 41.36; H, 3.47.

4,5-Diethyl-4',5'-dimethyltetrathiafulavalene-4,5-dithiolate-4',5'-dicarboxylate (5f): Rf (3:1 CH_2Cl_2:hexanes) = 0.49; Mp 63°-65°C; ^1H NMR ($CDCl_3$) δ 1.30 (t, 6H), 2.83 (q, 4H), 3.83 (s, 6H); UV-Vis (nm) (ε*10^3): 216 (19.8), 262 (14.9), 288 (14.5), 324 (14.6), 440 (2.0); IR (Nujol, cm^{-1}): 1750, 1720, 1600, 1450, 1390, 1250, 1020, 990; Electrochemistry (V vs. Ag wire) $\Delta E_{1/2}$ (1) = 0.63(rev), $\Delta E_{1/2}$ (2) = 0.89(rev); Mass Spec. (EI low res) M^+ = 440 amu; Anal. Calcd for $C_{14}H_{16}O_4S_6$: C 38.46, H, 3.68. Found: C, 38.16; H, 3.66.

Ethylenedithio-4',5'-dimethyltetrathiafulavalene-4',5'-dicarboxylate (7): Rf (3:1

CH_2Cl_2:C_6H_{14}) = 0.34; Mp 114°-116°C; ^{1}H NMR ($CDCl_3$) δ 3.27 (s, 4H), 3.82 (s, 6H); UV-Vis (nm) (ε*10^3): 222 (13.8), 288 (12.4 sh), 310 (17.5), 331 (13.9 sh), 432 (1.8); Electrochemistry (V vs. Ag wire) $\Delta E_{1/2}$ (1) = 0.63(rev), $\Delta E_{1/2}$ (2) = 0.93(rev); Mass Spec. (EI low res) M^+ = 410 amu; Anal.(calc.) for $C_{12}H_{10}O_4S_6$: C, 35.20 (35.11), H, 2.50 (2.45).

Decarboxylation of 5a:[12]

The unsymmetrical TTF **5a** (1.5 g, 3.64*10^{-3} mol.) is placed in a 100 mL 1-neck round bottom fitted with a condenser, 58 mL of HMPA, and a stir bar. Compound **5a** is dissolved and anhydrous LiBr (2.45 g, 28 mmol, 7.77eq.) is added. The flask is immediately placed into an oil bath that has been *preheated to 145-147°C* and the reaction is allowed to stir for 22 min., during which time the color lightens to yellow-orange. The reaction is then cooled for 5 minutes, and is then poured into 500 mL of H_2O. The orange aqueous layer is extracted with nine 300 mL aliquots of cyclohexane, one 300 mL C_6H_6 aliquot, and the organic layer is washed with 900 mL of H_2O. The organic layer is dried over anhydrous Na_2SO_4 and the volatiles are removed *in vacuo*. The crude mixture is chromatographed using 320 g of silica gel (1:1 benzene:cyclohexane). Yields vary from 7-65%.

4,5-Dimethyltetrathiafulavalene-4,5-dithiolate (5a where R_2 = H): Rf (1:1 C_6H_6:C_6H_{12}) = 0.82; Mp 55°-57°C; ^{1}H NMR($CDCl_3$) δ 2.31 (s, 6H), 6.20 (s, 2H); UV-Vis (nm) (ε*10^3 CH_3CN) 285 (13.3), 324 (12.2), 370 (2.7), 440 (1.4); IR (NaCl neat, cm^{-1}) 3030, 2950, 2905, 1550, 1495, 1425, 1310, 1260, 1090, 980, 890, 795, 775, 745, 650; Mass Spec. (EI low res) M^+ = 296 amu; Electrochemistry (V vs. Ag wire) $\Delta E_{1/2}$ (1) = 0.54 (rev), $\Delta E_{1/2}$ (2) = 0.85 (rev); Anal. Calcd for $C_8H_8S_6$: C, 32.60, H, 2.80. Found: C, 32.41, H, 2.72.

Ethylenedithiotetrathiafulavalene (8): Rf (1:1 C_6H_6:C_6H_{12}) = 0.78; mp 198°-200°C; ^{1}H NMR($CDCl_3$) δ 3.25 (s, 4H), 6.30 (s, 2H); UV-Vis (in nm) (ε*10^3) 224 (15.6), 260 (sh 9.6), 308 (17.3), 330 (sh 14.7), 370 (sh 3.5), 488 (.5); IR(cm^{-1}) 3050, 2940, 2905, 1540, 1505, 1420, 1405, 1310, 1290, 1260, 1180, 1135, 1090, 895, 790, 770, 715, 650; Electrochemistry (V vs. Ag wire) $\Delta E_{1/2}$ (1) = 0.39 (rev), $\Delta E_{1/2}$ (2) = 0.71 (rev); yields 30-66%, e.g. yield 30% gave Anal.(calc.) C, 32.45 (32.63), H, 1.97 (2.05), and yield of 41% gave Anal. Calcd for $C_8H_6S_6$: C, 32.72, H, 2.10. Found: C, 32.63; H, 2.05.

Example of Literature Method Procedure Used to Make Unsymmetrical TTFs.[7e] Thione **4a** (1.1 g, 4.5 mmol), thione **6** (0.7 g, 3 mmol), benzene (15 ml), and $(MeO)_3P$ (5ml, 45 mmol) were placed in a flask fitted with a condenser. The mixture is refluxed for 4 h, concentrated on a rotovap, and purified on silica gel (CH_2Cl_2) to give 221 mg (18%) of **7**. mp 115°-116°C; ^{1}H NMR ($CDCl_3$) δ 3.27 (s, 4H), 3.82 (s, 6H); UV-Vis (ε*10^3): 222 nm (13.8), 288 nm (12.4 sh), 310 nm (17.5), 331 nm (13.9 sh), 432 nm (1.8); Electrochemistry (V vs. Ag wire) $\Delta E_{1/2}$ (1) = 0.63(rev), $\Delta E_{1/2}$ (2) = 0.93(rev); Mass Spec. (EI low res) M^+ = 410 amu; Anal. Calcd for $C_{12}H_{10}O_4S_6$: C, 35.20, H, 2.50. Found: C, 35.11; H, 2.45.

Dimethyl-4',5'-dihexyldecyltetrathiafulavalene-4,5-dithiolate-4', 5'-dicarboxylate (5g): Rf (3:1 CH_2Cl_2:hexanes) = 0.47, Mp 64°-66°C, Anal. Calcd for $C_{42}H_{72}O_4S_4$, C, 60.35, H, 9.06. Found: C, 60.58; H, 8.65.

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