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Unexpected reaction of dimethoxycarbonyl dithiole-2-thione or tetramethoxycarbonyl TTF as dipolarophiles

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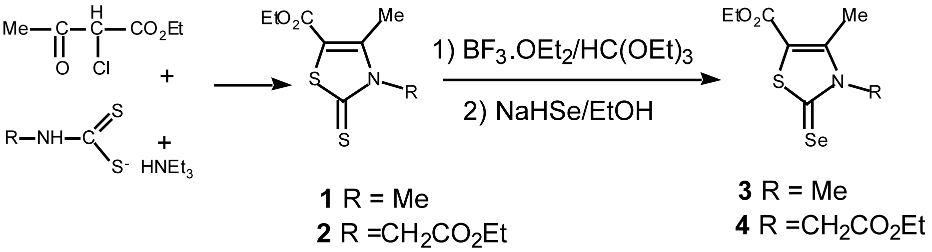
Abstract—An unexpected 1,3-dipolar cycloaddition of thiazoline-2-selone with dithiole-2-thione or tetramethoxycarbonyl–TTF in the presence of triethyl phosphite is reported. © 2002 Published by Elsevier Science Ltd.

In the field of organic materials, there is a current interest in the synthesis of electron rich olefins which will afford easily accessible cation radical species. Indeed, physical properties observed from this type of materials are due to the interactions of the radical species. Within this frame, numerous tetrathiafulvalene (TTF) derivatives have been prepared.[1] In order to either modify the redox properties of the donor core or to increase the interactions in the solid state, several unsymmetrically substituted TTF have also been synthesized using cross coupling reactions.[1] Only a few examples of their aza-analogues, dithiadiazafulvalene (DTDAF), exhibiting powerful redox behavior have been described.[2–5] Our experience in the chemistry of these donor molecules, TTF and DTDAF, prompted us to prepare mixed donor with two different heterocyclic cores: one dithiole and one thiazole rings. One possibility to form dissymmetrical donor molecules which has been extensively used in TTF chemistry consists in the cross coupling of two different dithiole-2-thiones (or -2-one or -2-selone) with trivalent phosphorus derivatives.[1] In this paper we report our attempts for the synthesis of trithiaazafulvalene (TTAF) and the unexpected 1,3-dipolar cycloaddition observed with thiazoline-2-selone in the presence of triethylphosphite and dimethoxycarbonyl dithiole-2-thione.

In order to avoid the presence of unstable unsymmetrical donor towards oxygen we chose heterocyclic rings substituted with electron withdrawing substituents. Accordingly, thiazoline-2-selone **3** and **4** were prepared by the chemical pathway described in Scheme 1. Treatment of dithiocarbamate salt with α-halogenated ketones, followed by cyclization and dehydration in the presence of sulfuric acid yields the thiazoline-2-thiones **1**, **2**.[3] As thiazoline-2-thiones are inert in the presence of trivalent phosphorus derivatives, they were converted into the selone analogues **3** and **4**. Indeed, **3** and **4**



Scheme 1.

Keywords: tetrathiafulvalene; dithiadiazafulvalene; cycloaddition; dipolarophile.

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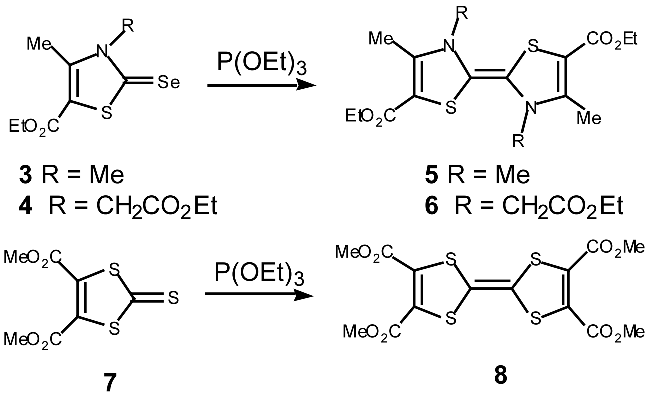


3 R = Me
4 R = CH$_2$CO$_2$Et
5 R = Me
6 R = CH$_2$CO$_2$Et
7
8

Scheme 2.

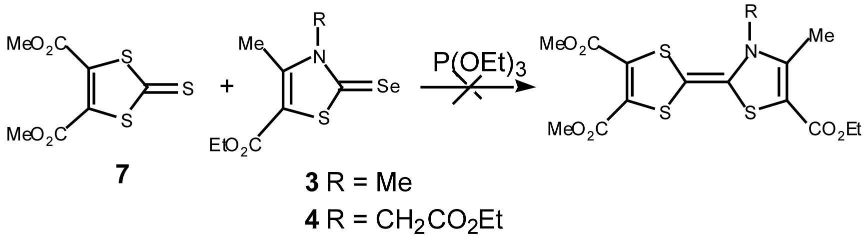
heated to reflux with triethyl phosphite yields DTDAF **5** and **6** (Scheme 2). First we evaluated the donor ability of the DTDAF formed by the intermolecular coupling of these thiazoline-2-selones. The oxidation potentials of the corresponding DTDAF were determined by cyclic voltammetry realized directly on the medium where the donors were formed. Two reversible oxidation waves are observed at Epa1 = −0.30 V and Epa2 = −0.08 V for **5** and Epa1 = −0.08 V and Epa2 = 0.39 V for **6**.

We also prepared the dimethoxycarbonyl dithiole-2-thione **7** according to the literature procedure.[6] The redox behavior of the TTF **8** obtained via the intermolecular coupling of **7** with triethylphosphite in the same experimental procedure as above was investigated by cyclic voltammetry Epa1 = 0.86 V and Epa2 = 1.25 V versus SCE.

We then mixed thiazoline-2-selone (**3** or **4**) with dithiole-2-thione **7** and heated to reflux in toluene after the addition of 5 equiv. of triethyl phosphite. We followed the evolution of the reaction by cyclic voltammetry. We did not detect a novel redox system on the cyclic voltammogram as expected for the formation of the unsymmetrical donor (Scheme 3).

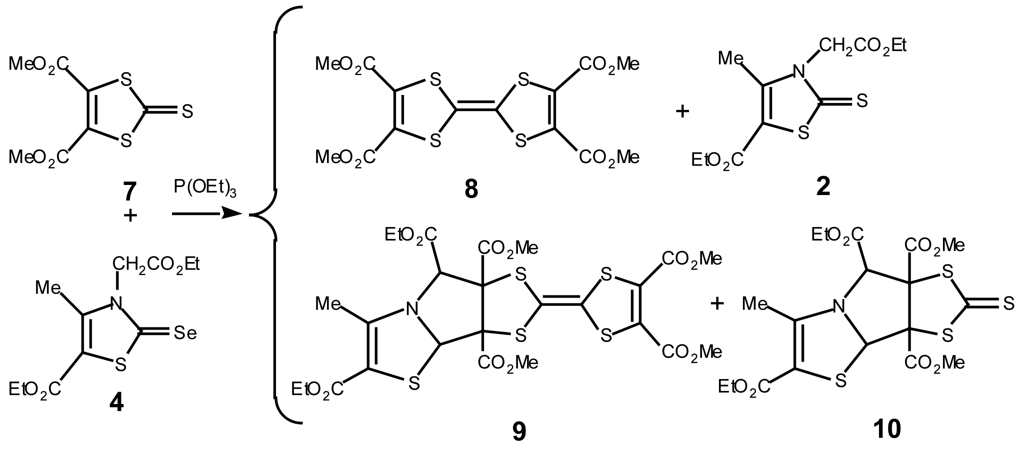
Therefore, we analyzed the medium and performed separation by column chromatography of the compounds formed for each coupling reaction. In the case of the coupling of **3** with **7** only two derivatives were obtained: the symmetrical TTF **8** together with thiazoline-2-thione **1**. Otherwise, the coupling of **4** with **7** led to TTF **8** (30%), thiazoline-2-thione **2** (25%) and a novel derivative **9**[7] (26%) and **10** (3%) (Scheme 4). The structure of **9** has been established thanks to an X-ray diffraction study and fully characterized by ^{1}H, ^{13}C NMR and elemental analysis (Fig. 1). It is probable that the formation of **9** results from the 1,3-dipolar cycloaddition of an ylide generated in situ from **4** and triethyl phosphite (Scheme 5). Indeed ylides generated from thiazolium salts are known to undergo 1,3-dipolar cycloaddition with various dipolarophiles.[8]

The dihydro TTF core is not completely coplanar. Atoms C12, C14 and C3, C4 are 0.269(3), 0.294(3) and 0.301(2), 0.743(2) Å, respectively, above the mean plane defined by the six remaining central atoms (S4/C10/S5/S1/C5/S3) (r.m.s. deviation 0.0496 Å). The two methoxycarbonyl groups attached at C3 and C4 are located *cis* with respect to the C3–C4 bond. Both pyrrolidine and thiazole rings are very distorted



7
3 R = Me
4 R = CH$_2$CO$_2$Et

Scheme 3.



7
4
8
2
9
10

Scheme 4.

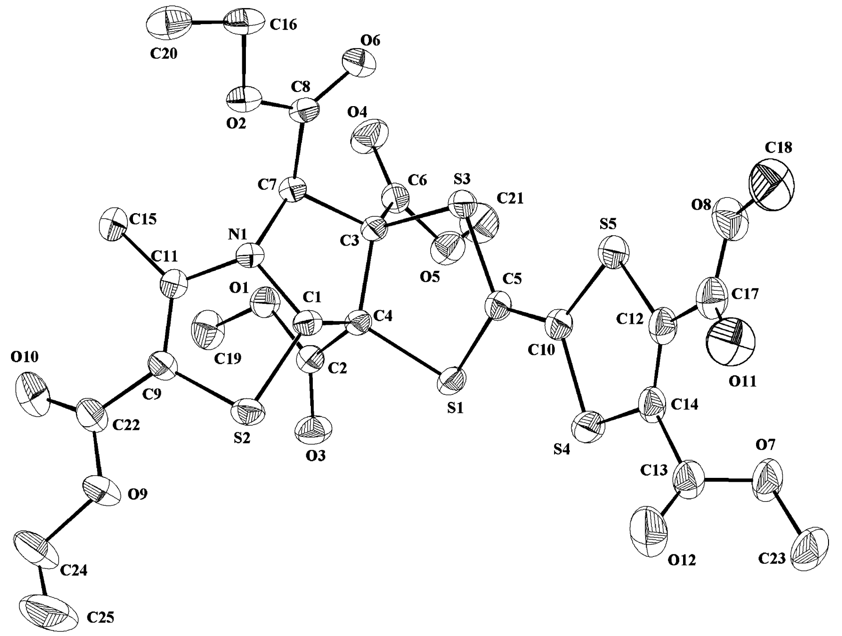
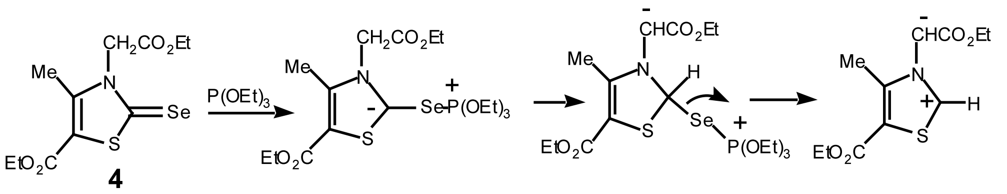


Figure 1. Molecular structure view of **9** (30% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): S1–C5 1.741(2), S1–C4 1.807(2), C5–C10 1.353(3), S4–C10 1.755(2), S4–C14 1.731 (2), C3–C4 1.559(3), C12–C14 1.339(4), C1–C4 1.563(3), C3–C7 1.564(3), N1–C1 1.467(2), N1–C7 1.477(2), N1–C11 1.392(3), C1–S2 1.790(2), C9–S2 1.770(3), C9–C11 1.360(3); S4–C10–S5 114.9(1), S1–C5–S3 117.2(1), C10–S4–C14 94.8 (1), C4–S1–C5 92.87(9), C3–S3–C5 96.77(9), S1–C4–C1 111.9(1), S3–C3–C7 113.0(1), C4–C1–S2 118.8(1), C7–N1–C11 121.2(2), C3–C7–N1 105.8(1), C4–C3–C7 103.5(1), C1–S2–C9 89.0(1), C1–N1–C11 111.0(2), S2–C1–N1 106.8(1), S2–C9–C11 112.6(2).



Scheme 5.

towards half-chair conformations owing to severe folds along the C1–C3 and N1–S2 vectors, respectively. For the first ring, the angle between the mean planes formed by C3/C7/N1/C1 and C3/C4/C1 is 138.3(1)°, while it is 153.3(1)° between the two planes formed by N1/C11/C9/S2 and N1/C1/S2 in the second ring. It results in a dihedral angle between the two square planes of 129.7(1)°.

The question arises if **9** is formed from TTF **8** generated in the reaction by the self coupling of **7** or if it is obtained by the reaction of the minor compound **10** with **7**. Preliminary test experiments show that the reaction of **8** with **4** in the presence of triethyl phosphite give the same cycloadduct **9** (20%) together with TTF **8** (69%) (Scheme 6). Those reactions demonstrate that both the dimethoxycarbonyl dithiole-2-thione **7** and the tetramethoxycarbonyl TTF **8** can act as dipolarophiles.[9] The potential of this original behavior is being further explored.

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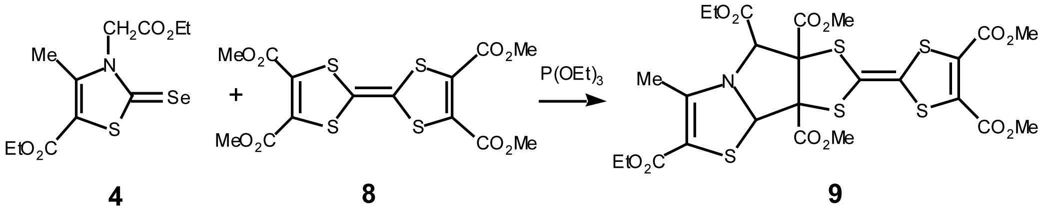

Scheme 6.

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7. Selected data for **9**: red crystals; mp 156°C (decomp.); δ_H (200 MHz; $CDCl_3$) 1.30 (t, 3H), 1.41 (t, 3H), 2.25 (s, 3H), 3.77 (s, 3H), 3.85 (s, 3H), 3.88 (s, 3H), 3.89 (s, 3H), 4.20 (q, 2H), 4.29–4.46 (ABX_3, $J_{AB}=11$ Hz, 2H), 5.55 (s, 1H), 5.64 (s, 1H); MS (EI): m/z (rel. intensity) 218 (22), 262 (100), 294 (53), 436 (34), 449 (21), 693 (18). Anal calcd for $C_{25}H_{27}NO_{12}S_5$ C, 43.28; H, 3.92; N, 2.02; S, 23.11. Found: C, 43.35; H, 3.83; N, 2.03; S, 23.37. Single-crystal diffraction measurement of crystal on a four-circle Enraf Nonius Kappa diffractometer using Mo Kα radiation ($\lambda=0.71073$ Å) and equipped with an electronic CCD detector. 15084 reflections (9240 unique, $R_{int}=0.0921$) were collected at $T=293(2)$ K with $1.55\leq\theta\leq30.09°$. Data for **9** ($C_{25}H_{27}NO_{12}S_5$, MW=693.78): Crystal in triclinic, space group $P\bar{1}$, $Z=2$, $a=10.7746(1)$, $b=11.6841(1)$, $c=13.6115(2)$ Å, $\alpha=95.8365(7)$, $\beta=101.7223(6)$, $\gamma=106.9097(5)°$, $V=1581.47(3)$ Å^3 [7805 reflections], $D_{calcd}=1.457$ mg/mm^3, $\mu=0.427$ mm^{-1}, $F(000)=720$. The structure was solved by direct methods with SIR97 and refined on F^2 using SHELXL-97. Final residuals are $wR=0.1532$ and $R_f=0.0562$ [6162 data, $I>2\sigma(I)$] with a GOF=1.054 for 389 refined parameters. Crystallographic data (excluding structure factors) for the structure reported here has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 180096.
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