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Cycloaddition of Acetylenedicarbaldehyde Monoacetal and 2,4,5-Trithioxo-1,3-dithiole: Ready Access to Novel Highly Extended and Sulfur-Rich Analogues of Tetrathiafulvalene (TTF)

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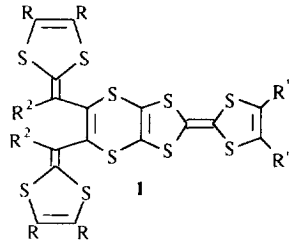
Abstract: Thiones **2**(') , **4**(') and **3**(') are readily prepared from title compounds. Bis-olefinations of **3** with Akiba's reagents **W** or **H** afford **8** which can cyclize into **9** upon acid treatment. $(i\text{-PrO})_3P$ mediated coupling of **4** with **5'** affords **7** whose formolysis in **10** and bis-olefination with **W** or **H** yields target compound **1**. The π-donor ability and stability of **8** and **1** are discussed.

The main limitations in the transport properties of the cation radical salts of the tetrathiafulvalene (TTF) series lie in their excessive monodimensional character.[1] Thus, below a given temperature, such materials suffer a breakdown of their electroconductive properties due to crystalline Peierls distortions resulting from electron-phonon coupling. For organic chemists, an exciting challenge exists in preventing the Peierls distortions by increasing the dimensionality of these salts. With this aim, structural modifications of the TTF framework have been achieved,[2] some of which have been rewarding. Hence, the substitution of S by Se, which possesses more diffuse orbitals, has led to the tetramethyltetraselenafulvalene (TMTSF) based organic superconductors.[3] Similarly, the substitution of the H atoms by sulfur rich groups in order to increase the number of S...S intra- and inter-chain contacts, such as in the mixed valence salts of bis(ethylenedithio)-TTF (BEDT-TTF), has led to the highest Tc organic superconductors of this series achieved so far.[4]

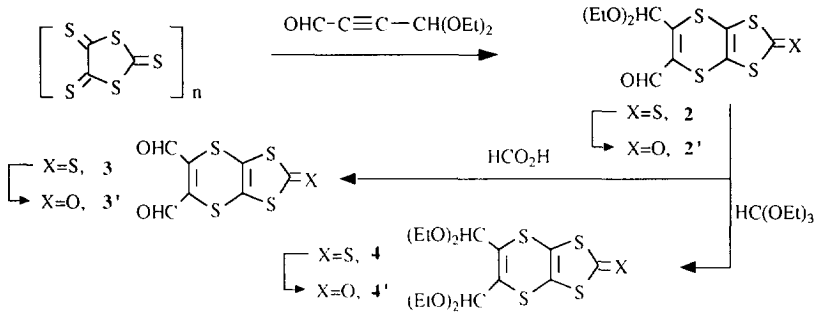
More recent development, involves the replacement of the central C=C bond of TTF by more extended conjugated spacers.[5] In this way, the contacts between the donors should be strenghthened due to the lowering of the molecular charge density on the mono- (or poly) charged species, and also to the enhancement of the π-bonding interactions. In addition, a greater space extension of the donor may result in weaker Coulombic repulsions both within and between the related polycationic states.



1

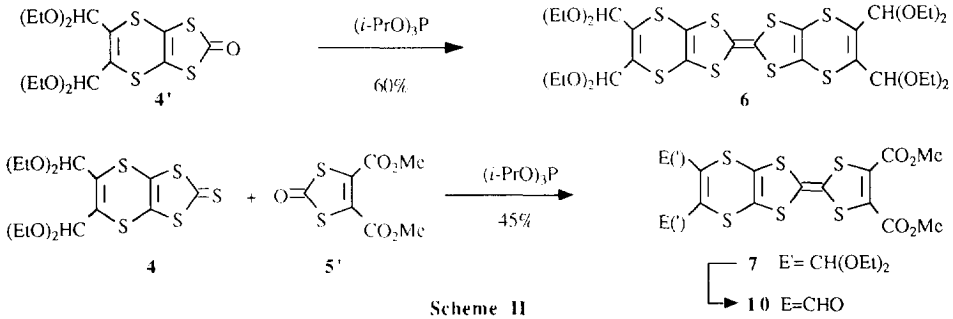
Based on these considerations, which are supported by recent results,[6] we have decided to focus on the space extended and S-rich analogues of TTF **1**. In this letter, we describe an approach to their synthesis and present some preliminary conclusions regarding their possible use as precursors for organic metals.

As outlined in Scheme I, the first step of our synthetic strategy involves the [4+2] cycloaddition of an electron-rich bis-heterodiene and an electrophilic alkyne, namely oligo(2,4,5-trithioxo-1,3-dithiole)[7] and diethoxybut-2-ynal,[8] compound **2** being isolated in 70% yield after 1 hr under reflux in benzene. Note that this 2-thioxo derivative can be readily converted (90% yield) into the corresponding 2-oxo one **2'** under standard conditions[9] ($Hg(OAc)_2$, AcOH, $CHCl_3$). Moreover, deprotection of the acetal with formic acid ($CHCl_3$, 20°C, 20 min) affords the dicarboxaldehyde **3** almost quantitatively, and a complete acetalisation of **2** in **4** can be easily carried out (90% yield) under standard conditions ($HC(OEt)_3$, EtOH, PTSA). The thioxo compounds **3** and **4** (X=S) can also be converted in **3'** and **4'** (X=O) with $Hg(OAc)_2$.



Scheme I

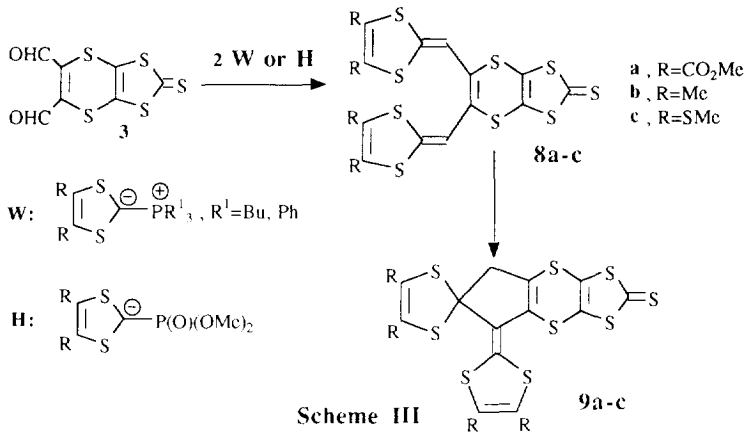
In order to build the TTF core, we have made various attempts at the self-coupling of **2**, **2'**, **3**, **4**, **4'** and cross-coupling of the latter with the 4,5-dimethoxycarbonyl-2-(thi)oxo-1,3-dithioles **5** and **5'** (Scheme II). The best results were obtained when starting from **4'** in the case of the symmetrical derivative **6**, and from **4** and **5'** in the case of the dissymmetrical derivative **7**. In both cases, the target molecules are obtained *via* the phosphite-mediated desulfurization method. A significant point regarding the synthesis is that, we have greatly improved the yields by using the sterically hindered $(i\text{-PrO})_3P$ (refluxing benzene, 2 hr) instead of the classically used trimethyl- or triethylphosphite. We ascribe this result to suppression of side reactions such as formation of Arbuzov-type product.



Scheme II

The method of introduction of both 1,4-dithiafulven-6-yl side arms of **1** was first checked by treatment of model compounds **3** with Akiba's reagents **W** or **H** bearing the adequately 4,5-disubstituted-1,3-dithiole-2-ylidene moiety[10] (BuLi, -80°C, THF on the corresponding phosphonium salts) (Scheme III), the yields of **8a-c** ranging from 80 to 95 %.

Compounds **8a-c** appear to be only moderately stable on standing in CH_2Cl_2 or $CHCl_3$ solution since they undergó a *slow* acid mediated (HCl) intramolecular cyclization[11] affording compounds **9a-c**. However, they can act as convenient π-donors for organic metals since their cyclovoltammogram (in HCl-free CH_2Cl_2) exhibits one reversible oxidation peak indicative of a good stability of their radical-cations: Pt electrode, sweeping rate $100mV.s^{-1}$, 20°C, nitrogen atmosphere, *n*-Bu_4NPF_6 0.1 $mol.l^{-1}$ in CH_2Cl_2, Epa values in V/ SCE: **8a**, 0.81; **8b**, 0.39; **8c**, 0.54.



Scheme III

Target molecules **1a** (R=R'=CO_2Me, R^2=H) and **1b** (R=Me, R'=CO_2Me, R^2=H) could be attained by a double Wittig(-Horner) olefination of the corresponding dialdehyde **10**[12] (quantitatively produced by formolysis of **7**) with **Wa** and **Hb** respectively, but they could not be isolated in the pure state, since they undergo an internal cyclization similar to that in compounds **8**. The cyclization reaction is *much faster* in this case, due to their strong π-donor ability resulting from their TTF core.[11, 6g]

Therefore, from this study, it can be concluded that target molecules **1** with R^2=H cannot behave as good precursors of conducting cation radical salts upon their oxidation because of their propensity to quickly cyclize. To act as π-donors, the internal side-reaction must be prevented, and this could be achieved by substituting the hydrogen atoms (R^2=H) of the pendent dithiafulvenyl groups with R^2=alkyl, aryl, R^2-R^2=alkylene or arylene substituents by replacing the electrophile in Scheme I with a diketonic alkyne, a quinone, or an ethylenic diketone. Corresponding experiments will be reported soon.

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12 Dialdehyde **10** quantitatively reacts with hydrazine hydrate to afford the corresponding "pyridazino TTF". This compound is very insoluble and has been characterized by PDMS and ^{1}H nmr.

(*) All new compounds gave satisfactory spectral data and/or elemental analyses; selected examples:

2 $C_{11}H_{12}S_5O_3$: Orange powder, m.p. 103°C; m.s. $M^{+\cdot}$= 352, E.I.; anal. found (theory): C 37.45 (37.50), H 3.51 (3.41), O 13.89 (13.64), S 45.43 (45.45); ^{1}H nmr, $CDCl_3$: 10.0 (s, 1H, C<u>H</u>O), 5.68 (s, 1H, C<u>H</u>(OEt)$_2$), 3.69 (m, 4H, CH$_3$C<u>H$_2$</u>O), 1.24 (t, 6H, <u>CH$_3$</u>CH$_2$O); ^{13}C nmr, $CDCl_3$: 217.7 (<u>C</u>=S), 182.3 (<u>C</u>=O), 156.5 (S-<u>C</u>-CHO), 133.7(S-<u>C</u>-CH), 128.9 (S-<u>C</u>-S-C-CHO), 127.7 (S-<u>C</u>-S-C-CH), 98.5 (<u>C</u>H(OCH$_2$CH$_3$)$_2$), 63.2 (CH(O<u>C</u>H$_2$CH$_3$)$_2$), 14.9 CH(OCH$_2$<u>C</u>H$_3$)$_2$); IR, CH_2Cl_2: 1672 C=O, 1059 C=S.

8a $C_{21}H_{14}S_9$: Black powder, mp. 239°C dec.; m.s. no ionization in FAB; anal.: C 37.17 (36.95), H 2.18 (2.05), O 18.16 (18.77), S 40.95 (42.22); ^{1}H nmr, $CDCl_3$, CS_2: 6.10 (s, 2H, C-C<u>H</u>=), 3.86 (s,3H, COO<u>Me</u>), 3.84 (s, 3H, COO<u>Me</u>).

8b $C_{17}H_{14}S_9$: Red powder, m.p. 174°C; m.s. $M^{+\cdot}$= 506, E.I.; anal.: C 40.39 (40.30), H 2.85 (2.77), S 55.1 (56.9); ^{1}H nmr, $CDCl_3$, CS_2: 6.05 (s, 2H, C-C<u>H</u>=), 1.98 (s, 6H, <u>Me</u>), 1.95 (s, 6H, <u>Me</u>).

9b $C_{17}H_{14}S_9$: Red powder; same m.s. as **8b**; ^{1}H nmr, $CDCl_3$, CS_2: 3.54 (s, 2H, C-<u>CH$_2$</u>-C), 1.95 (s, 6H, <u>Me</u>), 1.85 (s, 6H, <u>Me</u>); ^{13}C nmr, $CDCl_3$, CS_2: 213.5 (<u>C</u>=S), 136.3, 134.4, 129.4, 124.8, 122.8, 120.1, 119.5, 72.2 (S-<u>C</u>-S), 61.2 (<u>C</u>H$_2$), 14.3 (<u>C</u>H$_3$), 13.6 (<u>C</u>H$_3$).

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