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PolyAcetyl-Substituted Tetrathiafulvalenes and 1,3-dithiolic Derivatives from Hex-3-yn-2,5-dione

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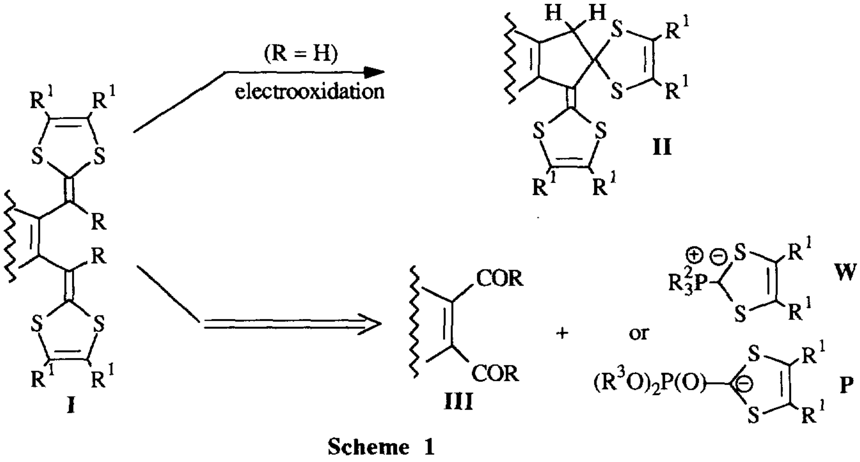
Abstract The cycloaddition of hex-3-yn-2,5-dione onto a π-CS_2 Iron complex **3** and on 3-thioxo-1,2-dithioles affords diacetylated intermediates which can be readily converted into di or tetraacetylated derivatives of the 1,3-dithiole (**5**,**6**) and tetrathiafulvalene (**2**,**8**) series, some representative electrochemical and structural features of which being also presented.

The monodimensional character of organic metals of the TTF series is responsible for the breakdown of their electroconductive properties at low temperature, because of the arising of subtle crystalline transitions (Peierls distorsion) due to electron-phonon couplings. In order to improve their transport properties at low temperature, most suitable way consists in enhancing their dimensionality.[1]

On these grounds, we have previously designed new S-rich and extended TTF derivatives substituted by two or four 1,4-dithiafulven-6-yl substituents **I** (with R = H in Scheme 1),[2-4] which effectively afforded some truly 2D cation radical salts upon electrooxidation.[3] However, despite a lot of careful electrolysis experiments, the materials harvested were most often of poor crystalline quality. An explanation for such difficulties to obtain single crystals may be found in the possible arising of a side reaction during the electrooxidative process[5] : besides their main conversion in $\mathbf{I}^{\cdot+}$, π-donors **I** may also undergo an intramolecular cyclisation (when R=H) with formation of compounds **II**, because of their two vicinal dithiafulvenyl side arms (scheme 1). Since it is well stated that the quality of the electrogenerated crystals is strongly dependent on the purity of the reagents, the possible formation of **II** may have a spoiling effect during the electrooxidation of I.

Therefore, in order to prevent such a possible side reaction which involves, in a given step, a prototropy, it was necessary to test the behavior of the derivatives **I** devoid of R = H. Since the preparation of derivatives **I**



Scheme 1

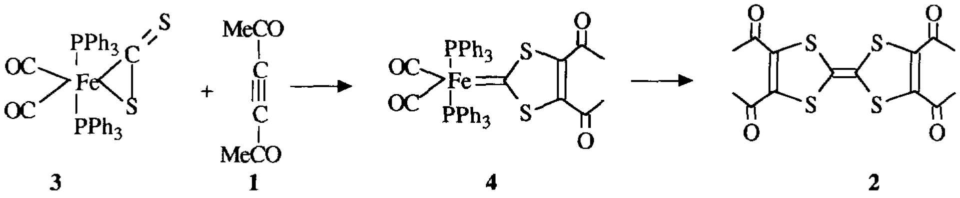
uses the poly Wittig (-Horner) olefination of polycarbonylated derivatives **III** with Akiba's reagents (i. e. the phosphorous ylids **W** or the phosphonate anions **P**), we decided to study the preparation of compounds **I** having R = Me.

We show hereafter that such polyacetylated TTF and 1,3-dithiolic derivatives can be readily reached from hex-3-yn-2,5-dione **1** and present some preliminary data related to their electrochemical and structural properties.

Synthesis §

i) Tetraacetyl TTF **2** (scheme 2)

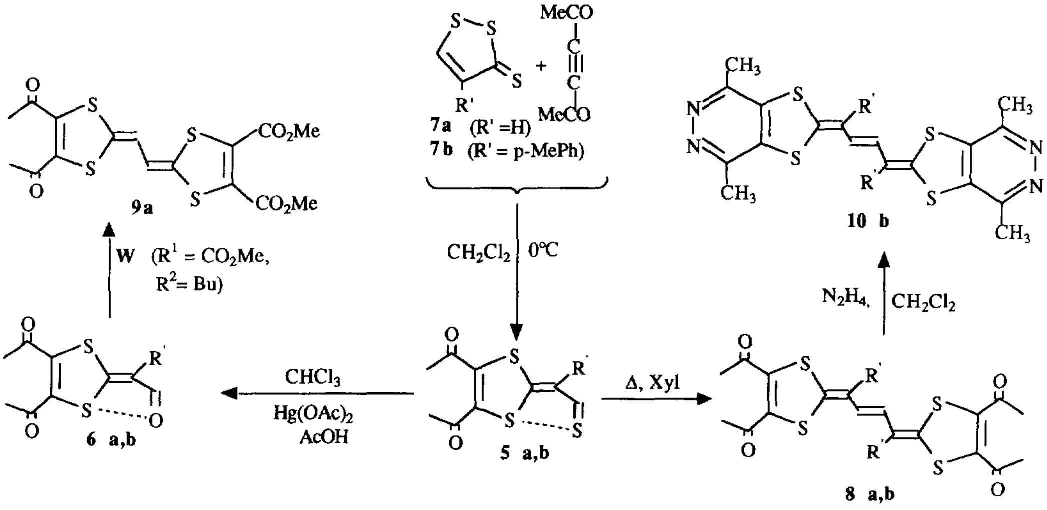
By analogy with previous works by Dixneuf *et al.*,[6] tetraacetyl TTF **2** was prepared by cycloaddition of hex-3-yn-2,5-dione **1**[7] on the η^2-CS_2 iron complex **3** in CH_2Cl_2 as solvent at 20°C, under nitrogen. After treatment of the resulting carbenic complex **4** with a stoichiometric amount of iodine, compound **2** was isolated by SiO_2 column chromatography (CH_2Cl_2 as eluent) in 20% yield.



Scheme 2

ii) Polyacetyl 1,3-dithiolic derivatives **5**, **6** and vinylogs of TTF **8** and **9** (scheme 3)

According to the well studied cycloaddition of electrophilic alkynes onto 3-thioxo-1,2-dithioles,[8] diketone **1** instantaneously reacted with **7a** or **7b** in CH_2Cl_2 at 0°C to give rise to **5a** or **5b** which, despite their thial functionality, could be isolated as stable solids.[9] Both were readily converted in the corresponding oxo



Scheme 3

derivatives **6a** and **6b** by treatment in a refluxing chloroform / acetic acid mixture, containing mercuric acetate and a little amount of water.[9a] Wittig olefination of **6a** with **W** (R^1= CO_2Me, R^2=Bu)[11] generated by deprotonation of the corresponding phosphonium tetrafluoroborate with Et_3N in CH_2Cl_2 at 20°C , afforded the vinylog of TTF **9a** in 60% yield. On the other hand, as expected, the dimerization-desulfurization of thials **5** was cleanly carried out by simple refluxing in xylene,[8,12] **8a** and **8b** being obtained in 60% yield.

iii) bis-pyridazino derivative **10b**.

Finally, the vicinal position of two acetyl groups was chemically ascertained by the production of the pyridazino heterocyclic moiety thanks to reaction with hydrazine hydrate. Thus, reaction of **8b** in CH_2Cl_2 with N_2H_4, H_2O quantively afforded the bis pyridazino derivative **10b** (scheme 3).

X-ray structure of 6b

As expected from previous structural studies on similar derivatives,[9] compounds **6** were held to exist in their δ-cis conformation thanks to strong S···O intramolecular bonding interactions. As displayed in Fig. 1, the X-ray structure[10] confirms this statement, with the occurence of a very short S(1)···O(3) distance (2.573 Å) far below the sum of the respective Van der Waals radii (3.3 Å), and larger than the single covalent S-O bond (1.75 Å).

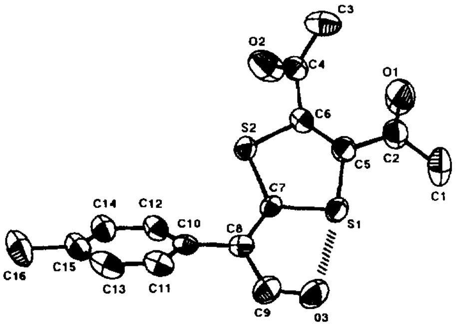


Figure 1

Electrochemical properties

They have been studied by cyclic voltammetry in a CH_2Cl_2/CH_3CN (3/1) solution [n-Bu_4]NPF_6 (0.1mol.L^{-1}), scan rate = 100 mV/s, V/SCE]. In the case of compound **2**, due to the presence of four electron withdrawing ketonic groups, the two expected 1e⁻ reversible oxidation peaks of the TTF core are located at higher potential as compared to TTF itself (Epa1 = 0.81, Epa2 = 1.14). For the corresponding vinylogs **8** and **9**, due to their larger conjugated π-system, the two 1e⁻ oxidation potentials are less positive and draw nearer (**9**) or even coalesce (**8a,b**) because of the decrease of Coulombic repulsions : **9**, Epa1 = 0.66, Epa2 = 0.88 ; **8a**, Epa1 = 0.65, Epa2 = 0.70 ; **8b**, Epa1 = Epa2 = 0.64, these results being in accordance with previous observations on related highly extended analogs of TTF.[2,13]

Conclusion

Owing to the versatility of their ketonic functionalities and their straightforward accessibility, the new compounds presented may act as powerful synthetic intermediates in TTF chemistry. In particular, their conversion to the new π-donors **I** (scheme 1) upon Wittig-Horner olefination with the P-reagents **W** or **P** will be soon reported.

§ All new compounds gave satisfactory elemental analyses and spectral data.

Selected examples :

Compound **2** : m.p = 188°C. ^1H nmr ($CDCl_3$) : 2.38(s,CH_3CO). ^{13}C nmr ($CDCl_3$) : 192.1(CO); 140.7($\underline{C}$-$COCH_3$); 111.0(C=C); 31.1(CH_3). Mass spectr. ($C_{14}H_{12}O_4S_4$): Calcd(Found) 371.962 (371.961).
I.R. (Nujol) : 1682, 1673cm^{-1}.

Compound **5a** : m.p. = 140°C. ^{1}H nmr ($CDCl_3$) : 10.80(d, 1H, C$\underline{H}$=S); 7.86(d, 1H, =C$\underline{H}$-CHS); 2.56(s, 3H, Me); 2.51(s, 3H, Me). ^{13}C nmr ($CDCl_3$) : 202.9(C=S); 192.4(C=O); 192.0(C=O); 158.7(CS(S)); 139.5(C=C); 138.0 (C=C); 120.4(=$\underline{C}$H-CHS); 30.8(Me); 30.7(Me). I.R. (nujol) : 1678 cm^{-1}(C=O). UV (CH_2Cl_2) : λ_{max} = 453.9 nm (ε = 1,4.10^4). Mass Spectr. ($C_9H_8O_2S_3$): Calcd(Found) 243.9686(243.9389). Microanalysis (Cald/Found) : C (44.24 / 44.34), H (3.30/3.24), S (39.36 / 37.94), O (13.10/13.71).

Compound **8b** : m.p. = 235°C. ^{1}H nmr ($CDCl_3$) : 7.29(AA', 4H); 7.09 (BB', 4H); 5.80(s, 2H, CH); 2.43(s, 6H, CH_3Ph); 2.30(s, 6H, CH_3); 2.23(s, 6H, CH_3). ^{13}C nmr ($CDCl_3$) : 192.4(C=O); 192.0(C=O); 139.3 ($\underline{C}$=$\underline{C}$-C(O)); 139.1(C(ar)); 139.0($\underline{C}$=$\underline{C}$-C(O)); 135.8 (C(ar)); 131.2($\underline{C}$-C_6H_4Me); 130.8 (C(ar)); 129.5(CH); 128.4 (C(ar)); 127.6(C(S)S); 30.5(CO$\underline{C}H_3$); 30.4(CO$\underline{C}H_3$); 22.1(Ph$\underline{C}H_3$). I.R. (nujol) : 1642, 1693(C=O). UV(CH_2Cl_2) : λ_{max} = 427 nm (ε = 9,5.10^4). Mass Spectr. ($C_{32}H_{28}O_4S_4$): Calcd(Found) 604.0870 (604.0853). Microanalysis (Calcd/Found) : C (63.55 / 63.73), H (4.67 / 4.75), O (10.58 / 10.40), S (21.20 / 20.28).

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10 Crystallographic data for **6b** : $C_{16}H_{14}O_3S_2$, FW=318.03, orthorhombic, space group Pbca(n°61), a=7.863(6)Å, b=36.779(8), c=10.496(5), V=3035Å^3, Z=8. The intensity data were collected on a Enraf-Nonius Mach3 diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å). The structure was solved by direct methods and the non-hydrogen atoms refined anisotropically. Final R and Rw were 0.065 and 0.070 for 2045 reflections with $I \geq 4\sigma(I)$.

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