

2-BUTYNE-1,4-DIYLIDENE-2,2'BIS (1,3-DITHIOLE) :
ACETYLENIC ANALOGS OF TETRATHIAFULVALENE

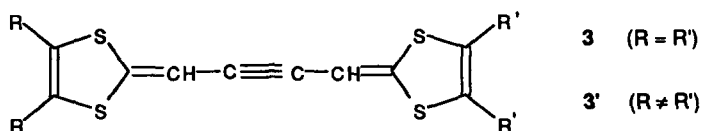
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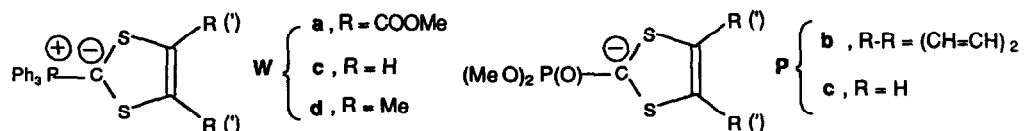
Summary: The title compounds can be prepared through Wittig or Wittig-Horner reactions between phosphoranes **W** or phosphonates anions **P** bearing the 1,3-dithiole-2-ylidene moiety and acetylenedicarbaldehyde or its acetal; the scope and limitations of this approach are presented.

Charge transfer complexes and cation-radical salts of π -donors derived from the tetrathiafulvalene (TTF) series are interesting because of their high electrical conductivity (1), so that many works are still undertaken to improve their electrical properties. With this intention, subtle chemical modifications of the TTF heterocycle (1-3) have led to organic superconductivity and have allowed little by little to raise T_c of such materials (4,5) (present record 11,6 K (6)). One of the trends recently developed involves the separation of two (or more) 1,3-dithiole moieties by extending and conjugating blocks such as ethylenic, cumulenic, aromatic and heteroaromatic π -systems, in order to decrease on-site Coulomb repulsion (1ab,3,7-12).

This Letter deals with the preparation of the unprecedented symmetrical and dissymmetrical acetylenic analogs of TTF, **3** and **3'**, for which useful properties can be expected in the fields of "organic metals" and also, for the latter, of non-linear optics (13).

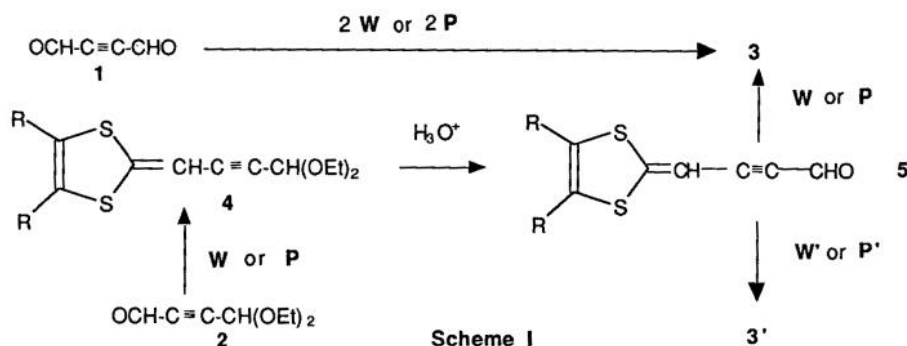


Our synthetic strategy involves Wittig or Wittig-Horner reactions between the highly reactive P-ylids **W** (14,15), or the phosphonate anions **P** (15), bearing the 1,3-dithiole-2-ylidene moiety adequately substituted,



and acetylenedicarbaldehyde **1** or its mono-diethyl-acetal **2** (16), the synthetic planning to the target molecules being depicted in Scheme I.

We show herein the scope and limitations of such a methodology whose efficiency is strongly depending on the nature of the substituents $R(\prime)$.



RESULTS AND DISCUSSION

Wittig reactions on 1 and 2 : direct access to 3 and 4 (*)

Wa-c were generated either by *quantitative* deprotonation (method α) with *n*-BuLi below -70°C in THF or, in only case of **Wa**, stabilized which two CO_2Me groups, through an *equilibrated* deprotonation (method β) with Et₃N in CH_2Cl_2 at 20°C (15). The target compounds were finally isolated either by SiO₂ column chromatography (CH_2Cl_2 + pentane) in the case of **3**, or, more readily, by selective dissolution in ether + pentane (1 : 1) in the case of **4** (decomposition on SiO₂).

The results can be summarized as follows (compound, % yield, method α or β given) : starting from **1**, **3a**, 45 %, α ; **3a**, 60 %, β ; **3c**, 23 % (or 13 % with PBu₃ instead of PPh₃), α ; **3d**, 20 %, α , and starting from **2**, **4a**, 94 %, β ; **4c**, 84 %, α ; **4d**, 90 %, α .

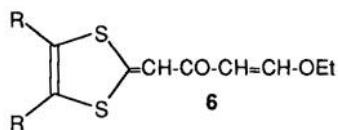
Several reasons may be invoked to explain the lower yields observed in the first series: *i*) difficulties to get truly aprotic solutions of **1**, *ii*) great propensity of **1** (and not of **2**) to undergo anionic polymerizations, here possibly promoted by **W**, and *iii*) important losses during the chromatographic isolations of **3c** and **3d** which must be separated from PPh₃ and from respectively TTF and tetramethyl-TTF (TMTTF) (having nearly similar retention times) originating either from the thermal decomposition of **Wc** and **Wd** (17), or, for the two TTFs, *via* a carbene pathway, from the base-promoted deprotonation of the starting 1,3-dithiolium cations (in slight equilibrium with the phosphonium salts (14b), particularly when R is not an electron withdrawing group).

Wittig-Horner reactions on 1 and 2 : direct access to 3 and 4 (*)

They were performed by deprotonation of the corresponding phosphonates **HPb** and the highly hygroscopic **HPc** with *n*-BuLi in THF below -70°C and further treatment with **1** (toluene soln) or **2**. Fairly satisfactory yields could only be obtained from **Pb** affording **3b** (35 %) and **4b** (60 %), whereas **2** and **Pc** afforded a mixture of the expected **4c** and an isomeric derivative (18), the amount of the latter increasing as the reaction was achieved at higher temperature.

Problems of hydrolysis of 4 into 5 (*)

Since classical hydrolysis conditions (aq. HCl or H₂SO₄ in EtOH) were unsuccessful, we applied other recommended methods. Acidolyses of **4a** and **4b** with pure formic acid (CH_2Cl_2 soln at 20°C) also failed since they afforded the unexpected **6a** (66 %) and **6b** (65 %) (as a mixture of [Z] and [E] isomers) whose structures are reminiscent of Rupe transposition products. Fortunately, the wet silicagel method (19) (SiO₂, CH_2Cl_2 , aq. oxalic acid) gave satisfactory results but only in the cases of **4a** (68 % of **5a**) and, to a less extent, of **4b** (20 % of **5b**).



Olefination of 5 into 3 or 3'(*)

Because of the above results, only **5a** was studied. After treatment with the phosphoranes **Wc** and **Wd**, the dissymmetrical acetylenic analogs of TTF were isolated in fairly good yields, 59 % for **3'ac**, and 54 % for **3'ad**, their SiO₂-chromatographic separation from the expected by-products (PPh₃ and the corresponding TTF or TMTTF) being relatively easy thanks to the differentiating polarity of their CO₂Me substituents. With **Pb** and **Wa**, compounds **3'ab** and **3a** were readily produced and isolated without any difficulty (74 and 76 % yields).

Conversion of 3a into 3c and of 3'ad into 3'cd by decarbomethoxylation (*)

In order to avoid the chromatographic separation problems related to the use of the poorly stabilized P-ylids (**Wc** or **Wd**), we studied the thermal treatment of **3a** with LiBr.H₂O in hexamethylphosphoramide (**8a**): up to 75 % yields of **3c** could be reached after the very strict conditions of the two reaction steps (i) saponification with evolution of MeBr, 45 min at 110°C, and ii) proto-decarboxylation of Li-salt, 15-17 min at 150°C) had been cautiously defined by reverse phase HPLC monitoring. Similarly, **3'ad** could be converted into **3'cd** (54 % yield).

CONCLUSION

The main limitations of our synthetic strategy lie in :

- the presence of the side products (PPh₃ and TTFs) related to non-stabilized P-ylids which makes difficult further chromatographic separations, and in the relative failures observed with **Pc**,
- the poor yields generally obtained when one starts from **1**, so that **2** might be expected as a better precursor for getting **3'**; however, the difficulties of acetal hydrolysis (**4** into **5**) often encountered strongly compromise the routes using **2**.

As it will be seen in a further paper, all that synthetic strategy can be strongly improved by starting from the cobaltcarbonyl complexes of **1** and **2** rather than from these free alkynes.

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(*) All new compounds exhibited satisfactory spectroscopic (^1H and ^{13}C nmr and ir) and analytical (elemental analyses for C, H, S and O and/or HRMS) data in accordance with the structures shown. Below are given the data related to some selected new compounds (nmr (CDCl_3) δ in $10^{-6}/\text{TMS}$, J in Hz, ir (CHCl_3) in cm^{-1}).

3a, orange coloured solid, mp 180°C ; M^+ 485.9571 calcd, 485.9573 found ; ^1H nmr 5.62 (s, 2H), 3.84(s, 6H) 3.82 (s,6H) ; ^{13}C nmr 53.4 (q, Me), 93.5 (d, =CH), 97.0 (s, C=C), 131.4 and 131.1 (SC=CS), 143.7 (SCS), 159.8 and 159.6 (q, CO_2Me) ; ir 1720 (C=O).

3c, orange coloured solid, mp 98°C ; M^+ 253.9352 calcd, 253.9356 found ; ^1H nmr 5.67 (s, 2H) and 6.31 (s, 4H).

3'ed, orange coloured solid, mp $136-138^\circ\text{C}$; M^+ 281.9665 calcd, 281.9660 found ; ^1H nmr 5.56 (d, $^5\text{J} = 2.8$, 1H, CH=), 5.66 (dd, $^5\text{J} = 2.8$ and $^5\text{J} = 1.8$, 1H, CH=), 6.30 (broad s, 2H, SCH=CHS), 1.93 (s, 6H, 2Me) ; ir 2150 (C=C).

4c, yellow liq. ; M^+ 242.0435 calcd, 242.0441 found ; ^1H nmr 5.46 (s, 2H, OCHO and CH=), 3.62 (m, 4H, 2 CH_2), 1.23 (t, 6H, 2 CH_3), 6.30 (s, 2H, SCH=CHS) ; ir 2200 (C=C).

6a, *trans* isomer, red solid, mp $115-117^\circ\text{C}$; M^+ 330.0231 calcd, 330.0225 found ; ^1H nmr 6.58 (s, 1H) 5.60 (d, $^3\text{J} = 13$, 1H), 7.63 (d, $^3\text{J} = 13$, 1H), 3.95 (q, 2H, OCH_2), 1.33 (t, 3H, CH_3), 3.90 (s, 6H, 2 CO_2Me).

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