

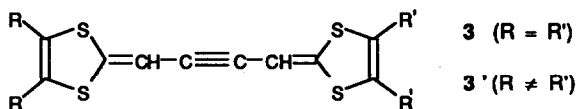
## ACETYLENIC ANALOGS OF TETRATHIAFULVALENE : ALKYNES-HEXACARBONYLDICOBALT COMPLEXES MEDIATED SYNTHESIS AND $\pi$ -DONOR PROPERTIES

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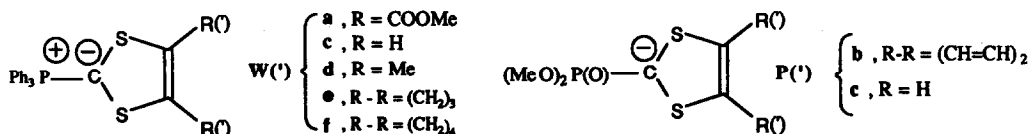
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**Summary :** The title compounds are prepared through Wittig or Wittig-Horner reactions between the dicobalthexacarbonyl complexes of acetylenedicarbonylaldehyde C1 or its acetal C2 and the phosphoranes W or the phosphonates anions P bearing the 1,3-dithiole-2-ylidene moiety, the final decomplexation being achieved with trimethylamine oxide ; their  $\pi$ -donor properties are also presented.

In the preceding paper (1), we have shown that the acetylenic analogs of tetrathiafulvalene (TTF) 3(')



could be prepared by Wittig or Wittig-Horner reactions between the P-reagents W or P bearing the 1,3-dithiole-2-ylidene moiety



and acetylenedicarbonylaldehyde 1 or its monoacetal 2 (see scheme 1 with M = nothingness).

However, severe limitations in such a methodology were found when  $\text{R} \neq \text{CO}_2\text{Me}$  and  $\text{R-R} \neq (\text{CH}=\text{CH})_2$  :

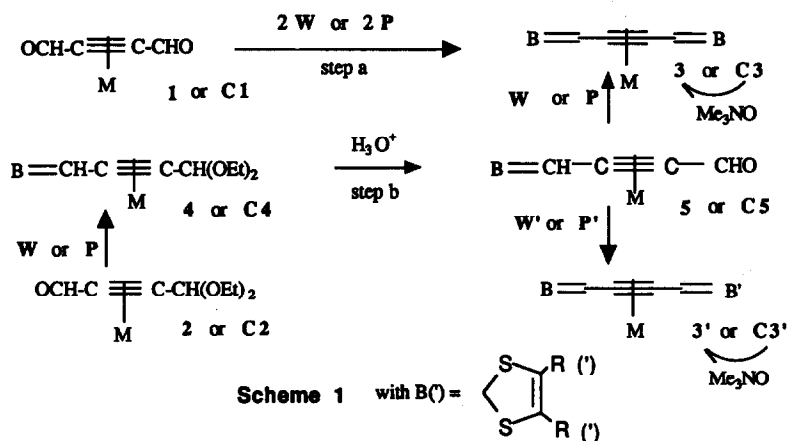
*i)* in step a, poor yields were obtained with the unstabilized P-Ylids W and 1 because of the losses encountered during the chromatographic separations of 3 from  $\text{PPh}_3$  and  $\text{R}_4\text{TTFs}$  (originating from the decomposition of W), and also from Pc and 1 because of the development of an unexpected side reaction (2),

*ii)* in step b, hydrolyses failed.

To overcome these problems, we decided to apply an organometallic modification by starting from the cobaltcarbonyl complexes C1 and C2 (3) ( $\text{M} = \text{Co}_2(\text{CO})_6$  in scheme 1) instead of the corresponding free alkynes since :

i) on  $\text{Co}_2(\text{CO})_6$  complexation, the polarity of the free alkyne was expected to be strongly reduced, making easier the chromatographic separation of  $\text{C3}'$ , compared to  $\text{3}'$ , after step a involving an unstabilized W,

ii) by avoiding the  $\alpha$ -acetylenic acetal nature of 4, thanks to the  $\text{Co}_2(\text{CO})_6$  addition to the triple bond, hydrolyses in step b were expected to proceed much more readily, in a similar way as in the case of saturated acetals.



We present here an improved synthesis of  $\text{3}'$  whose  $\pi$ -donor properties are then evaluated by cyclic voltammetry.

## RESULTS

### Syntheses (\*)

#### Wittig(-Horner) reactions on C1 (step a) and C2 : access to C3 and C4

Olefinations of C1 with  $\text{W}_{a,c-e}$  were performed as usual (THF, *n*-BuLi) but at a lower temperature ( $-90^\circ\text{C}$ ) in order to avoid ligand exchanges ( $\text{PPh}_3$  in place of CO in C1 or C2 (3a)), and as expected, the corresponding C3 could be isolated ( $\text{SiO}_2$  chrom.) without any peculiar problem (compound, % yields) : c 60%, d 64%, e 65%, and b (from Pb) 69% .

Olefinations of C2 with W or P also proceeded readily : C4c, 70% from Wc, and C4b, 76% from Pb.

Of course, C3 and C4 could also be prepared in almost quantitative yields by direct complexation of 3 and 4 with octacarbonyldicobalt in  $\text{CH}_2\text{Cl}_2$ , at  $15^\circ\text{C}$  and under nitrogen (4).

#### Hydrolyses of C4 into C5 (step b)

As expected, in sharp contrast with what happens in the case of the uncomplexed acetals 4, classical hydrolysis conditions (aq.  $\text{H}_2\text{SO}_4$ -EtOH) were strong enough to promote the required conversion of C4 : C5a 90%, b 74%, c 52%, f 45% .

### Wittig(-Horner) olefinations of C5 : access to C3'

Until now, only C5b has been checked with We-f : the expected corresponding C3'c (81%), C3'bd (90%), C3'be (89%) and C3'ef (78%) were readily isolated by SiO<sub>2</sub> chromatography.

### Oxidative decomplexation of C3(') : access to 3(')

This was expected to be delicate because of the reducing properties of the target molecules and indeed, some failures were suffered with ferric (5) and ceric (6) nitrates in EtOH. However, oxidations with trimethylamine oxide (CH<sub>2</sub>Cl<sub>2</sub> reflux) (7) afforded 3(') in fairly good yields (%) after SiO<sub>2</sub> column chromatography : 3b (59), 3c (55), 3f (58), 3'bc (65), 3'bd (68), 3'be (67) and 3'bf (60).

### Cyclic voltammetric studies of 3(')

The results show that two series of compounds can be distinguished:

- those having at least one of the two 1,3-dithiole rings substituted by the electron withdrawing substituents R = CO<sub>2</sub>Me or R-R = (CH=CH)<sub>2</sub>, in which case two poorly reversible 1e oxidation peaks are present, in agreement with the corresponding cation radical and dication generations,
- those without such substituents, in which case one observes only one non-reversible peak likely related to the formation of an unstable cation radical.

Moreover, the positions of such peaks are in good agreement with the electronic effects of the R(') substituents (table 1).

TABLE 1

Oxidation peak positions (V.SCE, MeCN, Bu<sub>4</sub>NClO<sub>4</sub> 0.1 M, 200 mV.sec<sup>-1</sup>) of 3(')

first series	3(')	3a	3b	3'ab	3'ac	3'ad	3'ae	3'af
	Epa1	.80	.67	.72	.61	.54	.54	.54
	Epa2	1.18	1.02	1.18	1.18	1.18	1.14	1.13
second series	3(')		3c	3d	3e	3f	3'cd	
	Epa1		.48	.42	.41	.42	.47	

It should be pointed out that such results are very different from those observed with the ethylenic analogs of TTF (8) whose voltammograms present only one 2e reversible peak (9).

This lack of reversibility strongly suggests that our new  $\pi$ -donors 3(') are not good candidates as precursors of highly conducting salts. Accordingly, only insulating black-green powders could be obtained when 3(') were reacted with usual acceptors (tetracyanoquinodimethane, iodine) or electro-oxidized in the presence of Bu<sub>4</sub>NClO<sub>4</sub> in various solvents.

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 9- When undertaking a comparative study on the ethylenic counterparts (8), we could decoalesce this one into two 1c reversible peaks.

(\* All new compounds exhibited satisfactory spectroscopic ( $^1\text{H}$  and  $^{13}\text{C}$  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 ( $\text{CDCl}_3$ )  $\delta$  in  $10^{-6}/\text{TMS}$ , J in Hz, ir ( $\text{CHCl}_3$ ) in  $\text{cm}^{-1}$ ).

**C3e**, black solid, m.p.  $240^\circ\text{C}$  (decomp) ;  $^1\text{H}$  nmr 6.40 (s, 2H, 2  $\text{S}_2\text{C}=\text{CH}$ ) and 2.51 (m, 6H,  $(\text{CH}_2)_3$ ) ; ir 2090, 2060 and 2020 ( $\text{C}=\text{O}$ )

**C4e**, black solid, m.p.  $91^\circ\text{C}$  (decomp) ;  $\text{M}^+$ : 567.91068 calcd, 567.9098 found ;  $^1\text{H}$  nmr 5.60 (s, 1H, OCHO), 5.65 (s, 1H,  $\text{S}_2\text{C}=\text{CH}$ ), 3.65 (m, 4H, 2  $\text{OCH}_2$ ), 1.25 (t,  $^3\text{J} = 7.0$ , 6H, 2 $\text{CH}_3$ ), 2.55 (m, 6H,  $(\text{CH}_2)_3$ ) ; ir 2020, 2050 and 2080 ( $\text{C}=\text{O}$ ).

**C5c**, black solid, m.p.  $100^\circ\text{C}$  (decomp) ;  $^1\text{H}$  nmr 6.53 (s, 3H, 3  $\text{CH}=\text{}$ ) and 10.50 (s, 1H, CHO) ; ir 2030, 2060 and 2098 ( $\text{C}=\text{O}$ ), 1650 ( $\text{CH}=\text{O}$ ).

**C5e**, black solid, m.p.  $104^\circ\text{C}$  (decomp) ;  $^1\text{H}$  nmr 6.43 (s, 1H,  $\text{S}_2\text{C}=\text{CH}$ ), 10.46 (s, 1H, CHO) and 2.53 (m, 6H, 3  $\text{CH}_2$ ) ; ir 2020, 2045 and 2080 ( $\text{C}=\text{O}$ ), 1650 ( $\text{CH}=\text{O}$ ).

**C3'bd**, black solid, m.p.  $145^\circ\text{C}$  (decomp) ; anal. calcd. C 42.73, H 1.95, S 20.74 ; found C 42.85, H 1.93, S 20.77 ;  $^1\text{H}$  nmr 6.55 and 6.68 (2s, 2H, 2  $\text{S}_2\text{C}=\text{CH}$ ), 7.30 (m, 4H,  $(\text{CH}=\text{CH})_2$ ), 1.98 and 2.03 (2s, 6H, 2Me) ; ir 2080, 2030 and 2020 ( $\text{C}=\text{O}$ ).

**3f**, yellow solid, m.p.  $216^\circ\text{C}$  (decomp.) ;  $\text{M}^+$ : calcd 362.0291, found 362.0303 ; anal. calcd. C 59.63, H 5.00, S 35.37, found C 59.61, H 4.98, S 35.30 ;  $^1\text{H}$  nmr 5.63 (s, 2H, 2  $\text{S}_2\text{C}=\text{CH}$ ), 2.26 (m, 8H, 4  $\text{CH}_2$ ) and 1.80 (m, 8H, 4  $\text{CH}_2$ ) ; ir 1540 ( $\text{C}=\text{C}$ ).

**3'bd**, yellow solid, m.p.  $102^\circ\text{C}$  ;  $\text{M}^+$ : 331.98219 calcd, 331.9821 found ; anal. calcd. C 57.79, H 3.64, found C 58.14, H 3.79 ;  $^1\text{H}$  nmr 5.57 (d,  $^5\text{J} = 2.6$ , 1H,  $\text{S}_2\text{C}=\text{CH}$ ), 5.72 (d,  $^5\text{J} = 2.6$ , 1H,  $\text{S}_2\text{C}=\text{CH}$ ), 7.18 (m, 4H,  $(\text{CH}=\text{CH})_2$ ), 1.94 (q,  $^5\text{J} = 0.8$ , 3H, Me), 1.99 (q,  $^5\text{J} = 0.8$ , 3H, Me) ;  $^{13}\text{C}$  nmr 13.52 (q,  $^1\text{J} = 129.5$ , Me), 13.63 (q,  $^1\text{J} = 129$ , Me), 95.94 (dd,  $^2\text{J} = 4.88$ ,  $^3\text{J} = 1.4$ , C=), 97.00 (dd,  $^2\text{J} = 4.6$ ,  $^3\text{J} = 0.86$ , =C), 89.50 (dd,  $^1\text{J} = 170$ ,  $^4\text{J} = 1.78$ , CH=), 93.23 (dd,  $^1\text{J} = 170$ ,  $^4\text{J} = 1.83$ , CH=), 147.74 (d,  $^2\text{J} = 2.22$ ,  $\text{S}_2\text{C}$  side diMe), 143.90 (d,  $^2\text{J} = 2.5$ ,  $\text{S}_2\text{C}=\text{}$  side benzo), 122.07 (q,  $^2\text{J} = 8.00$ , SC(Me)=), 122.55 (q,  $^2\text{J} = 8.25$ , SC(Me)=), 143.90 (d,  $^2\text{J} = 2.50$ ,  $\text{S}_2\text{C}=\text{}$  side benzo), 136.15 and 136.23 (m and m, SC=CS side benzo), 125.73 (m, benzo), 121.50 (m, benzo), 121.88 (m, benzo) and 125.75 (m, benzo) ; ir 2140 ( $\text{C}=\text{C}$ ), 1565 ( $\text{C}=\text{C}$ ).

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