Pergamon

Tetrahedron Letters 39 (1998) 8663–8666

TETRAHEDRON LETTERS

New hydroxymethyltetrathiafulvalenes and their vinylogues

Sheng-Gao Liu,[#] Michel Cariou and Alain Gorgues*[1]

Laboratoire d'Ingénierie Moléculaire et Matériaux Organiques, associé au CNRS, Université d'Angers, 2, Bd Lavoisier, F-49045 Angers, France

Received 24 June 1998; accepted 17 September 1998

Abstract: The synthesis of new π-electron donors of tetrathiafulvalene family with hydroxy functionality is described through the reduction of ester group(s) in tetrakis(methoxycarbonyl)tetrathiafulvalene **1** and its vinylogous analogue **7** by using $NaBH_4$ and LiCl in a mixed solvent of THF and CH_3OH. These new π-donors have been studied electrochemically and spectroscopically.

New functionalized tetrathiafulvalene (TTF) π-electron donors, incorporating hydroxy group(s) have attracted considerable current interest with the aim of increasing the dimensionality of organic charge transfer (CT) salts or complexes based on TTF donor molecules,[1] thereby suppressing Peierls distortions, tuning and improving the conductivity or even getting new superconducting systems, and isolating *kappa*-phase structures thanks to the formation of hydrogen bonding in the solid state.[2] In addition, the hydroxy group can serve as a reactive 'handle' enabling a variety of substituents to be attached to the system, thus resulting in new building blocks for materials.[3-5] Furthermore, diol and tetraol TTFs are key precursors for the synthesis of TTF-C_{60} dyads and C_{60}-TTF-C_{60} dumbbell triads,[6] respectively. In line with these concepts, a number of TTF derivatives containing hydroxy group(s) have been synthesized for the past few years;[3,7] however, their synthetic potential remains largely unexplored as generally they are available in only small quantities through a time-consuming and experimentally very demanding multi-step procedures. We now present here a simple and convenient synthesis of new TTFs or their vinylogues with hydroxy functionality through the reduction of ester groups in the readily synthesized tetraester-TTF **1**[8] or its vinylogous analogue **7**.

As expected, reducing the ester functions of **1** or **7** into alcohol ones was not so easy.[9] Chiang *et al.*[9a] have previously tried to reduce tetraester-TTF **1** with DIBAL/THF followed by LAH/THF in order to prepare tetraol **6**, but without great success, which resulted in both **6** and some complicated insoluble by-products. Garín *et al.*[7b] have reduced a diester-TTF into a diol by using $NaBH_4$ and $ZnCl_2$ in refluxing CH_2Cl_2 or THF. However, in our hands, the reduction of **1**, using either $NaBH_4$ or $NaBH_4$ and $ZnCl_2$ in THF and CH_3OH at 0 or 20 °C gave only trace amount of products **2-6** and, if this reduction reaction was performed at higher temperature by using large excess of $NaBH_4$, no TTF compounds were obtained due to the breakdown of the TTF framework.[10] Hence, we turned our attention to the use of a mixture of $NaBH_4$ and LiCl, which is known to greatly enhance the reducing properties of $NaBH_4$[7f] in THF and CH_3OH (4:1 v/v) at 0 or 20 °C. This methodology was previously successfully applied by Fox *et*

[1] E-mail : gorgues@univ-angers.fr

0040-4039/98/$ - see front matter
PII: S0040-4039(98)01980-7

al.[7f],using about 10% eq. of LiCl relative to $NaBH_4$, to reduce 4,5-bis(methoxycarbonyl)-2-thione-1,3-dithiole into the corresponding diol (which was then converted into **6**).When applied to **1** this reduction by $NaBH_4$/LiCl worked and additionally could be selectively oriented according to the relative amount of reagents and to temperature (Table 1). All of the products can be separated by SiO_2 column chromatography (ethyl acetate/petroleum ether 1:1 v/v).[11] It should be pointed out that although the separation of compounds **3** and **4** is difficult, their identification is quite obvious, especially by ^{13}C NMR. Compound **6** can be isolated by this straightforward method but the yield is lower than 10% in all the cases, so that the method of Fox *et al.* [7f] remains the best one for the preparation of tetraol **6**.

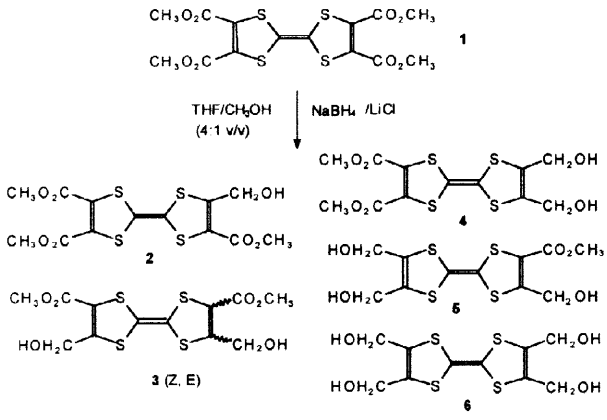
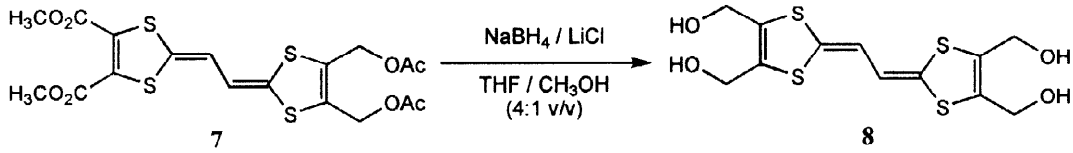


Table 1. Yields of compounds **2**, **3**, **4**, **5**, and **6** under different reaction conditions[a]

No.	**1** : $NaBH_4$: LiCl [b]	Yield / %				
		2	**3**	**4**	**5**	**6**
1[d]	1 : 4 : 1	35	20	[c]	[c]	[c]
2[d]	1 : 4 : 2	15	35	10	[c]	[c]
3[d]	1 : 4 : 3.3	[c]	36	[c]	25	[c]
4[d]	1 : 4.5 : 3.3	[c]	30	[c]	35	[c]
5[d]	1 : 4.5 : 4	[c]	25	15	40	[c]
6[e]	1 : 4 : 3.3	[c]	25	20	30	[c]

[a] other conditions are kept identical, *e.g.* reaction time 2 h; [b] molar ratio; [c] amount less than 10 %. [d] temp.: 0 °C; [e] temp.: 20 °C.

Similarly, this methodology could be successfully used for the reduction of the two different ester groups of **7** into alcohol ones, leading to the ready and first synthesis of tetraol TTF vinylogue **8**.[11] Note that compound **7** was newly prepared by us according to the methodology depicted by Yoshida *et al.*[12]; the synthesis will be published elsewhere.



In cyclic voltammetry (CV), all compounds display two reversible one-electron oxidation peaks (Table 2). Comparing the CV data of **1**-**6**, it is clear that reduction of one of the electron-withdrawing ester groups of tetraester-TTF **1** (compound **2**) lowers both the first and second oxidation potentials relative to **1**. Reduction of two ester groups (compounds **3** and **4**) has an additive effect, further lowering the values of both $E^1_{1/2}$ and $E^2_{1/2}$, a similar trend being observed upon reduction of three or all of the four ester groups (compounds **5** and **6**). This intramolecular electron-withdrawing effect of the ester group shows itself as well in the UV-Vis spectra (Figure) as a very broad low-energy absorption band at about 440 (**2**), 442 (**3**), 432 (**4**), and 432 nm (**5**), which can be assigned to an intramolecular CT from the hydroxylated TTF core to the acceptor ester group. Bryce and coworkers have already explained this kind

of intramolecular CT band in the electronic spectra in solution in the light of theoretical calculations.[13] Similarly, for compound **7**, this kind of CT band lies at about 515 nm as a very weak, broad absorption. Here also, the reduction of the ester groups of **7** into alcohol ones in **8** lowers both the first and the second oxidation potentials.

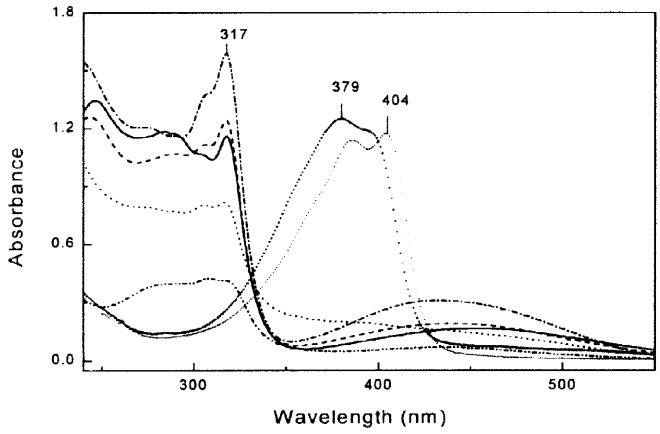


Figure . UV-Vis spectra of **1** (—), **2** (---), **3** (...), **4** (-.-), **5** (-..-), **7** (*), and **8** (+) in CH_2Cl_2 (**8** in THF). [Compound] ≈ 10^{-5} M.

Table 2. CV data[a]

Comp.	$E^1_{1/2}$	$E^2_{1/2}$	ΔE
1	0.81	1.13	0.32
2	0.63	1.00	0.37
3	0.53	0.93	0.40
4	0.51	0.90	0.39
5	0.39	0.77	0.38
6	0.28	0.63	0.35
7	0.49	0.66	0.17
8	0.19	0.35	0.16

[a] potentials in V *vs* SCE, measured in CH_3CN, 0.1 M $TBAPF_6$ at 100 mVs^{-1}, ϕ 1 mm Pt disk. [Compound] ≈ 10^{-3} M.

Comparing the UV-Vis spectra of compounds **1-5** and **7-8**, one can see two obvious differences, the first one being in shape, and the second one lying in the very large red-shift of the λ_{max} from **1-5** to **7-8**. This is in good agreement with the lower oxidation potentials of **7** (0.49 and 0.66 V) and **8** (0.19 and 0.35 V) than those of compounds **1-5**.[13]

Having clearly established the efficiency of the $NaBH_4$-LiCl system to allow the conversion $CO_2CH_3 \rightarrow CH_2OH$ in TTF series without damaging the TTF core, we will report soon the application of such a strategy to reach our C_{60}-TTF-C_{60} dumbbell systems.

References and Notes

On leave from the Organic Solids Laboratory, Chinese Academy of Sciences (Beijing) as a postdoctoral fellow of the 'Région des Pays de la Loire'.

1. Review: Bryce, M.R. *J. Mater. Chem.*, **1995**, *5*, 1481-1496.
2. Blanchard, P.; Boubekeur, K.; Sallé, M.; Duguay, G.; Jubault, M.; Gorgues, A.; Martin, J.D.; Canadell, E.; Auban-Senzier, P.; Jérome, D.; Batail, P. *Adv. Mater.*, **1992**, *4*, 579-581.
3. Marshallsay, G.J.; Bryce, M.R.; Cooke, G.; Jorgensen, T.; Becher, J.; Reynolds, C.D.; Wood, S. *Tetrahedron*, **1993**, *49*, 6849-6862.
4. Reviews: a) Bryce, M.R.; Petty, M.C. *Nature*, **1995**, *374*, 771-776 ; b) Bryce, M.R. *Chem. Soc. Rev.*, **1991**, *20*, 355-390.
5. a) Jorgensen, T.; Hansen, T.K.; Becher, J. *Chem. Soc. Rev.*, **1994**, *23*, 41-51 ; b) Hansen, T.K.; Jorgensen, T.; Stein, P.C.; Becher, J. *J. Org. Chem.*, **1992**, *57*, 6403 -6409 ; c) Hansen, T.K.; Jorgensen, T.; Jensen, F.; Thygesen, P.H.; Christiansen, K.; Hursthouse, M.B.; Harman, M.E.;

Malik, M.A.; Girmay, B.; Underhill, A.E.; Begtrup, M.; Kilburn, J.D.; Belmore, K.; Roepstorff, P.; Becher, J. *J. Org. Chem.*, **1993**, *58*, 1359-1366 ; d) Gasiorowski, R.; Jorgensen, T.; Moller, J.; Hansen, T.K.; Pietraszkiewicz, M.; Becher, J. *Adv. Mater.*, **1992**, *4*, 568-570.

6. a) Boulle, C.; Rabreau, J. M.; Hudhomme, P.; Cariou, M.; Jubault, M.; Gorgues, A.; Orduna, J.; Garín, J. *Tetrahedron Lett.* **1997**, 38, 3909-3910; b) Llacay, J.; Mas, M.; Molins, E.; Veciana, J.; Powell, D.; Rovira, C. *J. Chem. Soc., Chem. Commun.* **1997**, 659-660; c) Liu, S.G.; Hudhomme, P.; Cariou, M.; Mas, M.; Rovira, C.; Veciana, J.; Gorgues, A. to be published.
7. a) Suresh-Kumar, E.V.K.; Singh, J.D.; Singh, H.B.; Das, K.; Verghese, B. *Tetrahedron*, **1997**, *53*, 11627-11644; b) Garín, J.; Orduna, J.; Saviron, M.; Bryce, M.R.; Moore, A.J.; Morisson, V. *Tetrahedron*, **1996**, *52*, 11063-11074; c) Guillot, C.; Hudhomme, P.; Blanchard, P.; Gorgues, A.; Jubault, M.; Duguay, G. *Tetrahedron Lett.*, **1995**, *36*, 1645-1648; d) Garín, J.; Orduna, J.; Uriel, S.; Moore, A.J.; Bryce, M.R.; Wegener, S.; Yufit, D.S.; Howard, J.A.K. *Synthesis*, **1994**, 489-493; e) Moore, A.J.; Bryce, M.R.; Batsanov, A.S.; Cole , J.C.; Howard, J.A.K. *Synthesis*, **1995**, 675-682; f) Fox, M.A.; Pan, H.L. *J. Org. Chem.*, **1994**, *59*, 6519-6527; g) Blanchard, P.; Duguay, G.; Cousseau, J.; Sallé, M.; Jubault, M.; Gorgues, A.; Boubekeur, K.; Batail, P. *Synth. Met.*, **1993**, *55-57*, 2113-2117; h) Blanchard, P.; Sallé, M.; Duguay, G.; Jubault, M.; Gorgues, A. *Tetrahedron Lett.*, **1992**, *33*, 2685-2688; i) Batsanov, A.S.; Svenstrup, N.; Lau, J.; Becher, J.; Bryce, M.R.; Howard, J.A.K. *J. Chem. Soc., Chem. Commun.*, **1995**, 1201-1202; j) Jorgensen, M.; Bechgaard, K.; Bjornholm, T.; Sommer-Larsen, P.; Hansen, L.G.; Schaumburg, K. *J. Org. Chem.*, **1994**, *59*, 5877-5882.
8. a) Blanchard, P. *Thesis*, University of Nantes and Angers, **1994** ; b) Lakshmikantham, M.V.; Cava, M.P. *J. Org. Chem.*, **1980**, *45*, 2632-2636.
9. a) Hsu, S.Y.; Chiang, L.Y. *Synth. Met.*, **1988**, *27*, B651-B656; b) Sallé, M.; Gorgues, A.; Fabre, J.M.; Bechgaard, K.; Jubault, M.; Texier, F. *J. Chem. Soc., Chem. Commun.*, **1989**, 1520-1521.
10. Blanchard, P. private discussions.
11. All new compounds give satisfactory microanalysis and spectral data. Selected data for **4**: EI-MS (intensity) 380 (M^+, 100 %), 348 (M^+-CH_2OH+1, 11 %); IR (KBr, cm^{-1}) 3448 (s, br), 2926 (w), 1712 (vs), 1566 (s), 1434 (m), 1271 (vs), 1063 (m), 1036 (m), 755 (w); UV-Vis (CH_2Cl_2, λ_{max}, nm) 274, 307 (sh), 318, 432 (w, br); ^1H NMR (500 MHz, DMSO-d_6, δ in ppm) 6.19 (m, OH, *J*=5.88 Hz), 4.66 (d, CH_2, *J*=5.90 Hz), 3.72 (s, CH_3); ^{13}C NMR (DMSO-d_6, δ in ppm) 159.42, 158.76, 136.40, 115.24, 107.28, 59.90, 52.76; *Anal.* Found (*calc.*) C 37.88 (37.89), H 3.18 (3.15), O 24.52 (25.26) %. **8**: FAB$^+$-MS (intensity) 350 (M^+, 100 %); IR (KBr, cm^{-1}) 3230 (vs), 1516 (s), 1173 (s), 1011 (vs), 989 (s); UV-Vis (THF, λ_{max}, nm) 384, 404; ^1H NMR (500 MHz, DMSO-d_6, δ in ppm) 5.71 (s, 2H), 5.37 (m, 4H), 4.16 (d, 8H, *J*=5.57); ^{13}C NMR (DMSO-d_6, δ in ppm) 130.61, 129.59, 129.03, 109.81, 56.35, 56.27. *Anal.* Found (*calc.*) C 40.80 (41.14), H 4.10 (4.02), S 35.19 (36.61), O 18.83 (18.23) %.
12. Yoshida, Z.; Kawase, T.; Awaji, H.; Sugimoto, I.; Sugimoto, T.; Yoneda, S. *Tetrahedron Lett.*, **1983**, *24*, 3469-3472.
13. Batsanov, A.S.; Bryce, M.R.; Heaton, J.N.; Moore, A.J.; Skabara, P.J.; Howard, J.A.K.; Orti, E.; Viruela, P.M.; Viruela, R. *J. Mater. Chem.*, **1995**, *5*, 1689-1696.