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Direct One Pot Construction of Norbornane-fused Dihydrotetrathiafulvalenes

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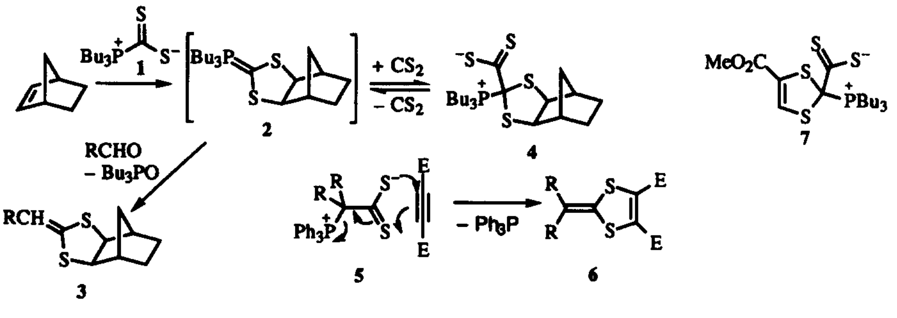
Abstract: Polycyclic dihydro-TTF structures can be constructed in a two-step one-pot procedure using cycloaddition of tributylphosphine/carbon disulfide adduct. © 1997 Elsevier Science Ltd.

Among organic conducting materials, those based on charge-transfer complexes of tetrathiafulvalene (TTF) derivatives with suitable acceptors are perhaps the most important and widely studied. Although a variety of synthetic routes to these compounds have been developed,[1] many of these involve several steps and are not amenable to construction of unsymmetrically substituted products. We describe here a convenient two-step method for formation of norbornane-fused dihydrotetrathiafulvalenes (dihydro-TTFs) from the corresponding norbornenes.

We recently reported that the crystalline adduct of tributylphosphine with carbon disulfide **1** adds to strained double bonds such as that of norbornene to give the ylide **2** which can be trapped in a Wittig reaction with aldehydes to give the 2-alkylidenedithiolanes **3**.[2] In the absence of aldehyde, **2** reacts further with carbon disulfide which is present in solution from dissociation of **1**,[3] to give a pink solid product for which the unusual zwitterionic structure **4** was proposed on the basis of analytical and spectroscopic data.[2] It was recognised that the function present is simply a special case of the trialkylphosphoniodithioacetates **5** formed from reaction of phosphonium ylides with CS_2,[4] and these were previously reported to undergo cycloaddition with acetylenic



esters to afford 2-alkylidene-1,3-dithioles **6**.[5] The formation of a TTF in low yield by direct reaction of **1** with methyl propiolate[6] also seems most likely to proceed by way of intermediate **7**, although the original authors proposed a different mechanism. When a solution of **4** in CH_2Cl_2 was stirred at room temperature with dimethyl acetylenedicarboxylate (DMAD), a slow reaction took place to give, after chromatographic purification, the desired norbornane-fused dihydro-TTF **8a** in low yield. Under the same conditions, reaction using diethyl acetylenedicarboxylate, methyl and ethyl propiolate, and methyl phenylpropiolate afforded compounds **8b-e** (Table). The spectroscopic data for these products were in agreement with expectation,[7] with the small coupling constant of 2 Hz between C1-H and C2-H indicating the *exo* configuration of the dihydro-TTF function, consistent with that previously demonstrated for the Wittig products **3**.[2]

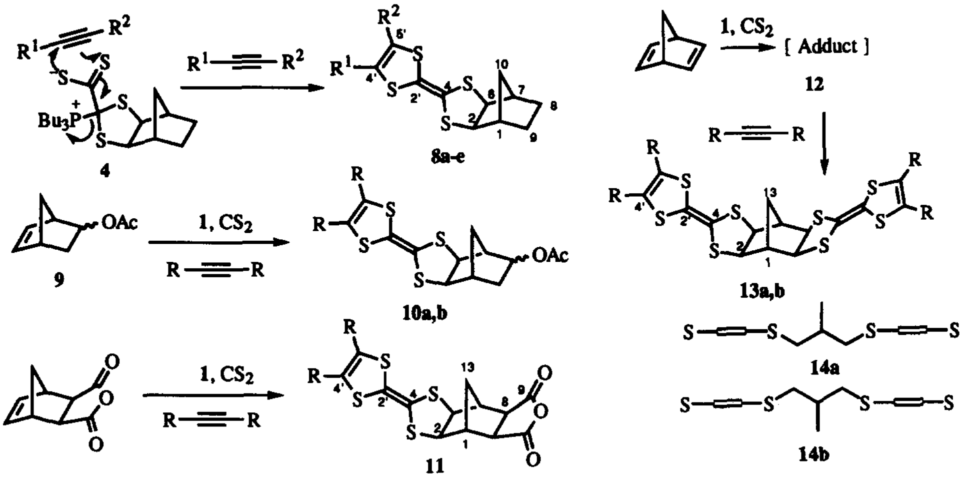


Table Formation of norbornane-fused dihydrotetrathiafulvalenes

Product	R^1	R^2	Yield (%)	mp (°C)	Product	R	Yield (%)	mp (°C)
8a	CO_2Me	CO_2Me	24	110–111	**10a**	CO_2Me	16	135–141
8b	CO_2Et	CO_2Et	23	86–87	**10b**	CO_2Et	20	(oil)
8c	CO_2Me	H	10	123–124	**11**	CO_2Me	15	272–273
8d	CO_2Et	H	17	110–112	**13a**	CO_2Me	15	284–286
8e	CO_2Me	Ph	16	48–50	**13b**	CO_2Et	23	237–239

Although 5-norbornenyl acetate **9** did not form an isolable compound analogous to **4**, treatment with two equivalents of **1**, or one equivalent of **1** and CS_2, did give a pink compound in solution detectable by TLC. When dimethyl or diethyl acetylenedicarboxylate was added, the adducts **10a,b** could be isolated. This was not the case, however, with many of the functionalised norbornenes available from Diels Alder reaction of cyclopentadiene, which were previously shown to undergo the Wittig chemistry leading to analogues of **3**.[2] The formation of the compounds analogous to **4** in these cases seems to be highly disfavoured, although the first step to afford the analogues of **2** does not present a problem. The probable reason for this was revealed by the observation that the *exo*-norbornenedicarboxylic anhydride did react readily, to afford **11**, while its more readily available *endo* isomer did not. It therefore seems likely that the formation of the compounds analogous to **4** is prevented by the presence of *endo* 5,6-substituents, probably by a combination of steric and through-space interactions. We have previously reported the effect of through-space interactions across the *endo* side of similar bicyclic systems on reactivity at a remote site.[8]

Norbornadiene also reacts readily with **1** to give a solid adduct **12** which can be trapped by Wittig reaction with an added aldehyde and, although its insolubility precluded full characterisation, it seems likely that both double bonds are functionalised in the same way as in **4**.[2] When a suspension of this material in CH_2Cl_2 was treated with dimethyl or diethyl acetylenedicarboxylate, reaction proceeded in the desired sense to directly afford the bis(dihydro-TTFs) **13a,b**. These again gave the expected analytical and spectroscopic data and further proof of the structures was obtained by a single-crystal X-ray diffraction study of **13a**.[9] Besides confirming the *exo* configuration of the dihydro-TTF functions, a side view (Figure 1) shows that the molecule bends around the four central sulfur atoms to give a structure in which all eight sulfurs and the bridgehead carbon atoms are approximately coplanar. Because of this the crystal structure was found to be disordered with respect to whether the one-carbon bridge in each molecule is up or down, as shown in forms **14a,b**.

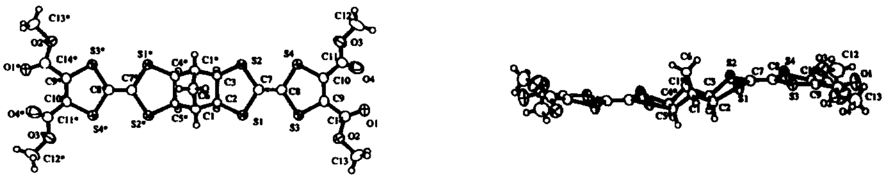


Fig. 1 Crystal structure of **13a**. Selected bond lengths (Å) and angles (°): C(2)-C(3) 1.554(10), C(2)-S(1) 1.889(7), S(1)-C(7) 1.738(4), C(7)-C(8) 1.332(5), C(8)-S(3) 1.765(4), S(3)-C(9) 1.747(4), C(9)-C(10) 1.341(5); C(3)-C(2)-S(1) 112.5(5), C(2)-S(1)-C(7) 95.1(3), S(1)-C(7)-S(2) 115.0(2), S(1)-C(7)-C(8) 122.4(3), C(7)-C(8)-S(3) 123.0(3), C(8)-S(3)-C(9) 95.3(2), S(3)-C(9)-C(10) 117.6(3), S(3)-C(9)-C(14) 116.4(3), C(10)-C(9)-C(14) 125.9(4), C(1)-C(2)-S(1) 110.6(5), C(1)-C(2)-C(3) 105.6(5), C(2)-C(1)-C(5) 111.1(5), C(2)-C(1)-C(6) 56.1(4); torsion angles C(2)-S(1)-C(7)-C(8) –147.6(4), S(1)-C(7)-C(8)-S(3) –0.2(5), C(7)-C(8)-S(3)-C(9) 171.9(4).

Dehydrogenation of **13** is expected to give bis-TTF compounds with the two functions at a fixed angle which promise interesting behaviour as donors and this is being investigated. While our work was in progress, a number of papers reported that dihydro-TTFs can also be effective donors in conducting charge-transfer complexes,[10] suggesting that the compounds obtained here may also be worth investigating in this respect.

Acknowledgement

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7. Selected spectroscopic data for **8a**, **8c**, **11** and **13a**

   8a: δ_H 1.20 (3 H, m, C8-H, C9-H and C10-H), 1.60 (2 H, m, C8-H and C9-H), 1.85 (1 H, d, *J* 10, C10-H), 2.37 (2 H, br s, C1-H, C7-H), 3.81 (6 H, s, 2 Me), 3.86 (2 H, d, *J* 2, C2-H and C6-H); δ_C 27.8 (C-8 and C-9), 32.4 (C-10), 45.1 (C-1 and C-7), 53.2 (OMe), 62.8 (C-2 and C-6), 113.3 and 119.2 (C-4 and C-2'), 131.5 (C-4' and C-5') and 160.1 (CO).

   8c: δ_H 1.20 (3 H, m, C8-H, C9-H and C10-H), 1.60 (2 H, m, C8-H and C9-H), 1.80 (1 H, d, *J* 10, C10-H), 2.35 (2 H, br s, C1-H and C7-H), 3.80 (3 H, s, Me), 3.87 (2 H, d, *J* 2, C2-H and C6-H), 7.26 (1 H, s, =CH); δ_C 27.7 (C-8 and C-9), 32.3 (C-10), 44.9 (C-1 and C-7), 52.5 (OMe), 62.6 and 62.8 (C-2 and C-6), 116.8 and 117.4 (C-4 and C-2'), 127.4 (C-5'), 131.9 (C-4') and 159.8 (CO).

   11: δ_H 1.22 (1 H, d, *J* 12, C13-H), 1.66 (1 H, d, *J* 12, C13-H), 2.72 (2 H, s, C8-H and C12-H), 3.21 (2 H, d, *J* 1, C1-H and C7-H), 3.76 (6 H, s, 2 Me) and 4.32 (2 H, d, *J* 2, C2-H and C6-H); δ_C 28.8 (C-13), 48.6 and 48.1 (C-1, C-7, C-8 and C-12), 53.9 (OMe), 60.2 (C-2 and C-6), 112.4 and 119.3 (C-4 and C-2'), 131.0 (C-4' and C-5'), 159.6 (CO_2Me) and 172.9 (C-9).

   13a: δ_H 1.86 (2 H, s, C13-H), 2.55 (2 H, s, C1-H and C7-H), 3.83 (12 H, s, 4 OMe) and 3.86 (4 H, s, C2-H, C6-H, C8-H and C12-H); δ_C 27.3 (C-13), 53.2 (OMe), 53.3 (C-1 and C-7), 60.2 (C-2, C-6, C-8 and C-12), 117.0 and 117.1 (C-4, C-10 and C-2'), 131.4 (C-4' and C-5') and 159.9 (CO).
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9. X-ray crystal data for **13a**: $C_{23}H_{20}O_8S_8$, M_r = 680.89, monoclinic, space group $P2_1/a$, a = 14.080(4), b = 6.098(3), c = 15.969(6) Å, β = 91.88(3)°, *V* = 1370.4(9) Å^3, Z = 2, r_{calcd} = 1.650 gcm^{-3}, R = 0.039, R_w = 0.036 for 1761 reflections with $I > 3\sigma(I)$ and 200 variables. Data were recorded using a Rigaku AFC7S diffractometer with Mo-Kα radiation. The structure was solved by direct methods (SIR92) and refined using full-matrix least squares methods. Hydrogen atoms were included but not refined. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number 100/420.
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