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Unusually direct synthesis of mono- and di-substituted tetrathiafulvalenes

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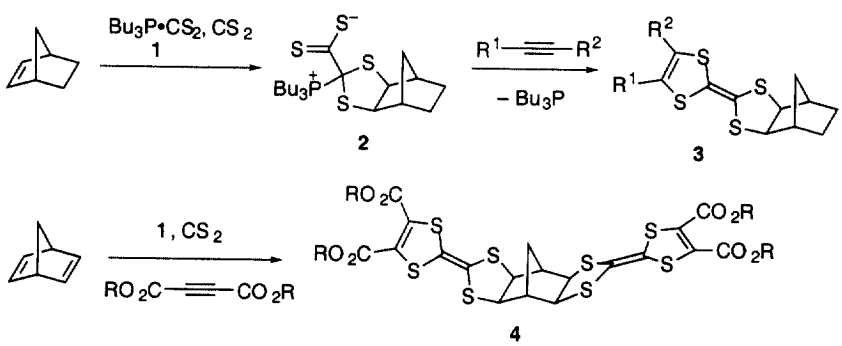
Absract

Direct reaction of norbornadiene, tributylphosphine, carbon disulfide and acetylenic diesters affords the norbornene-fused dihydrotetrathiafulvalenes **7** in addition to the bis-adducts **4** and for less reactive acetylenic dipolarophiles only **7** is isolated. Upon flash vacuum pyrolysis the compounds **7** undergo a retro Diels-Alder reaction to give substituted tetrathiafulvalenes **8**. By using the norbornadiene diester in place of norbornadiene with DMAD, **8a** can be obtained in higher overall yield. Attempted isolation of the zwitterionic structure **9** instead gave a rearrangement product with the novel 1,2,5-trithiepane stabilised ylide structure **11**.

Keywords: Thiafulvalenes, Polycyclic heterocyclic compounds, Cycloadditions, Extrusion reactions

Although substituted tetrathiafulvalenes (TTFs) are of great interest for the formation of conducting charge-transfer complexes, the routes available for their synthesis largely fall into two categories: reductive coupling of appropriate 1,3-dithiol-2-ones or -2-thiones and functionalisation of the preformed TTF nucleus [1]. The latter approach, originally reported by Green [2], has recently been improved and successfully applied in a number of cases [3-5] but despite the appearance of two convenient large scale synthetic procedures [6], TTF remains a rather expensive starting material. We describe here a novel approach which allows the *de novo* synthesis of mono- and di-substituted TTFs in only two steps from readily available starting materials, albeit in low yield.

We recently reported that the stable pink adduct **2** formed by reaction of norbornene with the adduct of tributylphosphine and carbon disulfide **1** undergoes cycloaddition with acetylenic dipolarophiles to give the norbornane-fused dihydroTTFs **3** [7]. The corresponding reaction of norbornadiene with acetylenic diesters similarly gave the bis-dihydroTTFs **4**.



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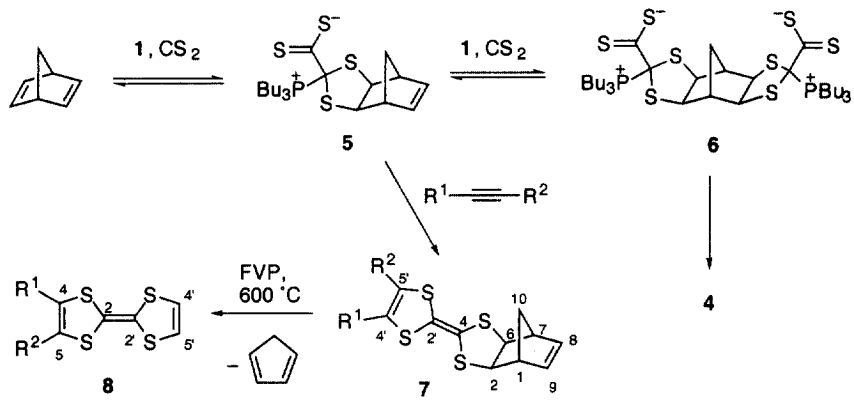
Careful examination of the product mixtures from this reaction using dimethyl and diethyl acetylenedicarboxylate has now shown that **4** is accompanied by minor products of lower R_f which have the structures **7a,b** [8]. More significantly, reaction of norbornadiene, **1** and CS_2 with less highly activated dipolarophiles such as methyl and ethyl propiolate and methyl phenylpropiolate gives no product corresponding to **4** and instead gives **7c-e** as the major isolable products, obtained in low yield after chromatography (Table). It therefore appears that both **5** and **6** are present in solution and available for reaction and that, for some reason, less reactive dipolarophiles prefer to react with **5**. The reaction products were complex mixtures which is not surprising considering the many possible modes of reaction (for example **1** may react independently with the dipolarophile [9]) but the compounds **7** were obtained in low but reproducible yield and readily isolated in pure form by simple column chromatography.



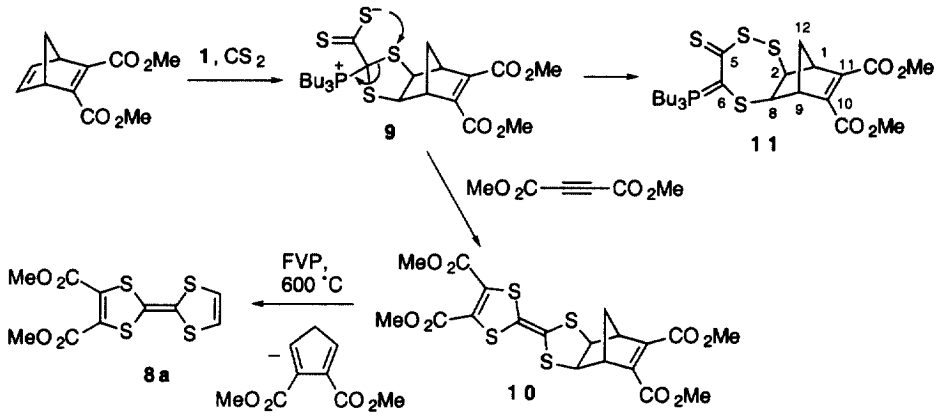
The structure of these compounds suggested that they might undergo ready retro Diels-Alder reaction and this process was seen to occur under mass spectrometric conditions [8]. When **7a-e** were subjected to flash vacuum pyrolysis (FVP) at 600 °C and 10^{-2} Torr, the reaction took the desired course: cyclopentadiene was collected in the cold trap and at the furnace exit the TTFs **8** were collected as dark red–black solids in good to excellent yield (Table). Although these products were stable for a short time, they were found to undergo

Table: Formation of cycloadducts **7** and **10** and pyrolysis to give **8**

Cyclo--adduct	R^1	R^2	Yield (%)	mp (°C)	Pyrolysis product	Yield (%)	mp (°C)	lit. mp [ref.] (°C)
7a	CO_2Me	CO_2Me	8	103–104	**8a**	98	129–131	125–127 [5]
7b	CO_2Et	CO_2Et	5	73–75	**8b**	92	60–62	63 [2]
7c	CO_2Me	H	9	137–138	**8c**	97	111–112	112–113 [10]
7d	CO_2Et	H	8	123–126	**8d**	60	76–78	80–82 [3]
7e	CO_2Me	Ph	10	90–93	**8e**	77	76–78	—
10	CO_2Me	CO_2Me	21	146–147	**8a**	73	129–131	125–127 [5]

slow [2+2] dimerisation upon storage under normal laboratory conditions, in agreement with previous reports on TTF mono- and di-esters [10,11].

In an attempt to improve the yield of the cycloaddition, particularly for the acetylenic diesters where **7a,b** were only obtained as minor products with a larger amount of **4**, we made use of the norbornadiene diester readily available from the Diels-Alder reaction of cyclopentadiene with DMAD which we have already shown to react with **1** and aldehydes on the unsubstituted double bond only [12]. By using the norbornadiene diester and DMAD under the same conditions, the adduct **10** was formed as the only isolable product in a significantly improved yield as compared to **7a** (Table) and, as expected, it also afforded **8a** upon FVP.



Finally, although there is reasonable evidence for the zwitterionic structures **2** and **6**, we have tried without success to obtain crystals of these suitable for X-ray diffraction in order to more clearly define their precise structure. Compound **9** seemed to offer a further chance to obtain this information and, when it was prepared in the absence of any dipolarophile, a yellow oily solid was obtained which had the expected molecular weight and gave correct elemental analysis results. The spectra however clearly showed that the molecule had lost its plane of symmetry and the product was in fact an isomer to which we assign the structure **11** [13]. This is supported in particular by the ^{31}P and ^{13}C NMR data [**11**: δ_P +26.0; δ_C 186.4 ($^2J_{P\text{-}C}$ 20), 83.9 ($^1J_{P\text{-}C}$ 124), *cf* **2**: δ_P +41.7; δ_C 240.1 ($^2J_{P\text{-}C}$ 8), 90.9 ($^1J_{P\text{-}C}$ 39)] which is in accord with the change from a phosphonium dithiocarboxylate to a thiocarbonyl-stabilised ylide structure. This structure can also be formed directly from **9** by the simple rearrangement process shown, thus lending some further support to the structure of **9**. The 1,2,5-trithiepane ring system present in **11** is rather uncommon although both the parent heterocycle [14] and various substituted derivatives have been described [15].

Acknowledgement

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[8] All new compounds gave satisfactory analytical and spectroscopic data. Selected spectroscopic data:
7a: δ_H 6.18 (2 H, s, 8, 9-H), 3.92 (2 H, d, *J* 2, 2, 6-H), 3.83 (6 H, s, 2 x Me), 2.95 (2 H, br s, 1, 7-H), 1.90 (1 H, d, *J* 10, 10-H *syn*) and 1.63 (1 H, d, *J* 10, 10-H *anti*); δ_C 159.9 (CO), 137.9 (=CH), 131.3 (C-4', 5'), 120.6 and 113.5 (=CS_2), 60.0 (C-2, 6), 53.1 (OMe), 50.4 (C-1, 7) and 42.4 (C-10); *m/z* 386 (M^+, 43%), and 320 (M^+–C_5H_6, 100).
7c: δ_H 7.29 (1 H, s, C=C<u>H</u>), 6.19 (2 H, d, *J* 2, 8, 9-H), 3.92 (2 H, d, *J* 2, 2, 6-H), 3.80 (3 H, s, Me), 2.96 (2 H, m, 1, 7-H), 1.96 (1 H, d, *J* 9, 10-H) and 1.63 (1 H, d, *J* 9, 10-H); δ_C 159.9 (CO), 138.04 and 137.97 (C-8, 9), 131.9 and 127.3 (C-4', 5'), 118.5 and 118.0 (=CS_2), 60.1 and 59.9 (C-2, 6), 52.6 (OMe), 50.5 (C-1, 7) and 42.5 (C-10); *m/z* 328 (M^+, 41%), 262 (M^+–C_5H_6, 100).
8a δ_H 6.35 (2 H, s) and 3.83 (6 H, s); δ_C 160.0 (CO), 132.1 (C-4, 5), 119.0 (C-4', 5'), 116.9 and 103.1 (C-2, 2') and 53.3 (OMe).
8c δ_H 7.35 (1 H, s, 5-H), 6.34 and 6.32 (2 H, AB pattern, *J* 6.5, 4', 5'-H) and 3.82 (3 H, s, Me); δ_C 168.9 (CO), 132.3 (C-5), 127.3 (C-4), 119.1 (C-4', 5'), 113.8 and 110.5 (C-2, 2') and 53.7 (Me)
10: δ_H 4.16 (2 H, d, *J* 1.5, 2, 6-H), 3.83 (6 H, s, 2 x Me), 3.80 (6 H, s, 2 x Me), 3.33 (2 H, s, 1, 7-H), 1.97 (1 H, d, *J* 10, 10-H) and 1.86 (1 H, d of quintets, *J* 10, 1.5, 10-H); δ_C 164.1 and 159.9 (CO), 144.9 (C-8, 9), 131.4 (C-4', 5'), 118.7 and 116.2 (=CS_2), 59.6 (C-2, 6), 53.6 (C-1, 7), 53.3 and 52.3 (OMe) and 41.4 (C-10); *m/z* 502 (M^+, 45%), 320 (M^+–$C_5H_4(CO_2Me)_2$, 100).

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[13] Spectroscopic data for **11**: δ_H 4.23 (1 H, dd, *J* 7, 2), 3.82 (3 H, s), 3.80 (3 H, s), 3.59 (1 H, d, *J* 7), 3.29 (1 H, d, *J* 2), 3.25 (1 H, d, *J* 1), 2.45–2.30 (6 H, m), 1.87 and 1.68 (2 H, AB pattern, *J* 10), 1.6–1.4 (12 H, m) and 0.97 (9 H, t, *J* 7); δ_C 186.4 (d, *J* 20, C-5), 164.3 and 163.9 (C=O), 144.3 and 143.1 (C-10, 11), 83.9 (d, *J* 124, C-6), 59.2 and 58.3 (C-2, 8), 52.8, 52.3, 52.2 and 51.3 (C-1, 9, OMe), 43.2 (C-12), 24.2 (d, *J* 4, Bu C-2), 24.0 (d, *J* 15, Bu C-3), 21.8 (d, *J* 53, Bu C-1) and 13.5 (Bu C-4); δ_P +26.0; *m/z* 560 (M^+, 0.2%), 530 (M^+–S, 10), 474 (2), 284 (5), 234 (50), 180 (70), 149 (36), 122 (96) and 104 (100).

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