New reactions of cyclic sulfoxides under Pummerer conditions

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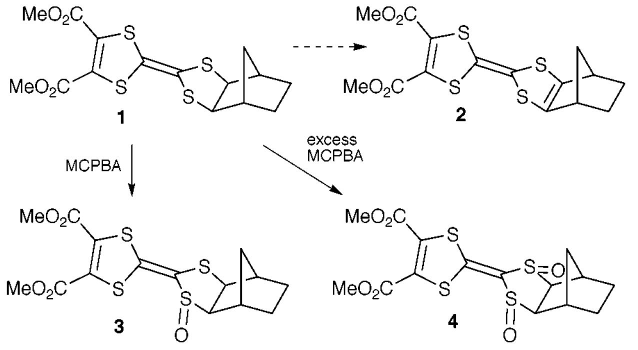
Reaction of the dihydrotetrathiafulvalene monosulfoxide 3 with TFAA results both in deoxygenation to give 1 and rearrangement to give the isomer 8, whose X-ray structure is presented; the corresponding disulfoxide 4 similarly rearranges to give 20.

We recently described the direct construction of norbornane-fused dihydrotetrathiafulvalenes such as **1** by reaction of norbornene with Bu$_3$P, CS$_2$ and acetylenic esters such as DMAD.[1] Although such dihydro-TTFs have shown some promise as potential electron donors,[2] the fully unsaturated analogues **2** would clearly be of more interest. We describe here our attempts to convert **1** into **2** which have led to the discovery both of a novel deoxygenation reaction of the sulfoxide **3** under Pummerer conditions and of its unexpected rearrangement to give the isomeric spiro compound **8**.

We decided to adopt a Pummerer approach since this has been successfully applied in the introduction of unsaturation into TTF type systems,[3] although we were aware that the rather strained nature of the expected intermediate **5** might cause some problems. Compound **1** was readily oxidised to its monosulfoxide **3** (55%) using 1 equiv. of MCPBA (Scheme 1), while use of an excess of the reagent gave the disulfoxide **4** (89%).‡ It is interesting to note that no further oxidation occurs in this system and examination of molecular models shows that introduction of oxygen on the face of the dithiolane ring *cis* to the norbornane function is sterically impossible. Both **3** and **4** were obtained as single diastereomers as shown with S=O *trans* to the norbornane function. When the sulfoxide **3** was treated with 1.1 equiv. of TFAA in CH$_2$Cl$_2$ either with or without added Hünig's base, evaporation of the reaction mixture followed by chromatography afforded two products. The first of these (38%) was readily identified as the starting dihydro-TTF **1**. Analytical and spectroscopic examination‡ of the second product (42%) revealed that it was an isomer of **3** with most of the original functionality still present, but the ^{13}C NMR signals due to the C=C double bond between the four sulfurs had been replaced by signals at δ_C 189.5 and 82.2. Its structure was finally confirmed by a single-crystal X-ray diffraction study to be the novel spiro tetrathio-orthooxalate **8** (Fig. 1).§



Scheme 1

A possible mechanism which accounts for the formation of both **1** and **8** *via* a common intermediate is shown in Scheme 2. In this the key step is participation of the dithiole ring in the initially formed salt **6** leading to a 1,2-shift of the trifluoroacetoxy group to give **7**. Although intramolecular migration of the trifluoroacetoxy group as shown seems quite likely, we cannot exclude the intermediacy of a dication, as shown, in the conversion of **6** into **7**. Attack of the trifluoroacetate at oxygen either in **6** or **7** would then give trifluoroacetyl peroxide and **1**, while the more conventional attack at CO in **7** leads to rearrangement to give **8** and regenerate the TFAA. No evidence was obtained for the formation of trifluoroacetyl peroxide but this is known to be an extremely unstable substance which rapidly decomposes to gaseous products at room temperature.[4] Although this is a completely new reaction in the dihydro-TTF system, there are a few analogous rearrangements which may all be represented as **9** going to **10** where D is an electron donor (Scheme 3). Thus, Ogura and Tsuchihashi found that treatment of the enamines **11** with Ac$_2$O gave the rearranged products **12**,[5] and the same authors later described the conversion of **13** into **14** with HCl gas in Bu^{t}OH.[6] The air oxidation of the highly reactive dithiadiazafulvalene **15** to give a low yield of a product formulated as **16**[7] also falls within the same category, as does the recently reported conversion of **17** into **18** by treatment with TFAA followed by hydrolysis.[8]

In view of these results it was of great interest to examine the behaviour of the disulfoxide **4** since the expected intermediate **19**, analogous to **7**, might rearrange with migration of either the sulfoxide sulfur to give **20** or the sulfide sulfur to give the isomer **21** containing the elusive α-keto sulfoxide functionality (Scheme 4). To the best of our knowledge no compound containing the C–C(=O)–S(=O)–C function has ever been isolated, since all attempts at generation in solution by *S*-oxidation of thioesters have resulted in rearrangement to the carboxylic–sulfenic anhydrides C–C(=O)–O–S–C which then react further.[9] In the event, treatment of **4** with 1.1 equiv. of TFAA afforded a rearranged product (42%) whose spectroscopic data‡ were more in keeping with the structure **20**, and

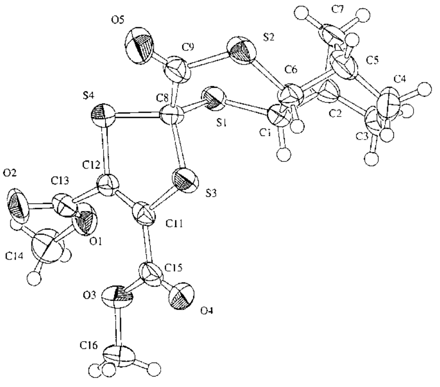


Fig. 1 X-Ray structure of the spiro compound **8**. Selected bond lengths (Å) and angles (°): S(1)–C(1) 1.816(10), S(1)–C(8) 1.834(9), S(2)–C(6) 1.821(10), S(2)–C(9) 1.76(1), C(9)–O(5) 1.21(1), C(9)–C(8) 1.51(1), C(8)–S(3) 1.828(9), C(8)–S(4) 1.825(9), S(3)–C(11) 1.761(9), S(4)–C(12) 1.756(9), C(11)–C(12) 1.31(1); C(1)–S(1)–C(8) 99.8(4), C(6)–S(2)–C(9) 108.6(5), C(8)–S(3)–C(11) 92.7(4), C(8)–S(4)–C(12) 92.4(4).

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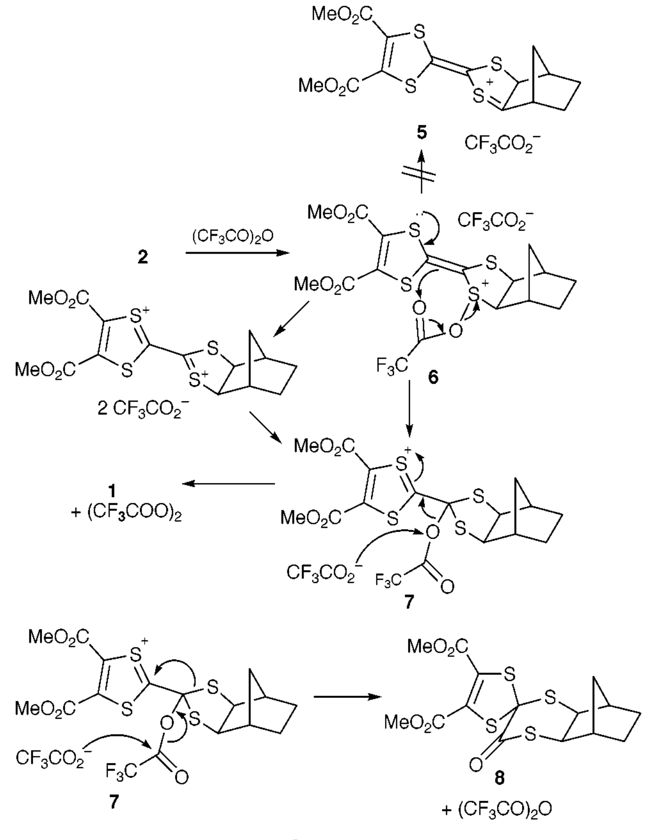
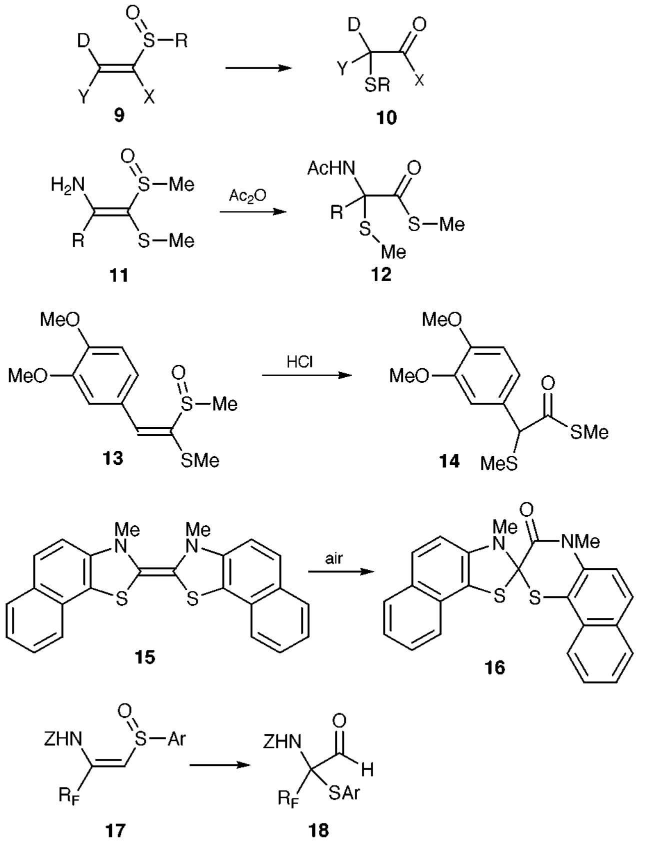


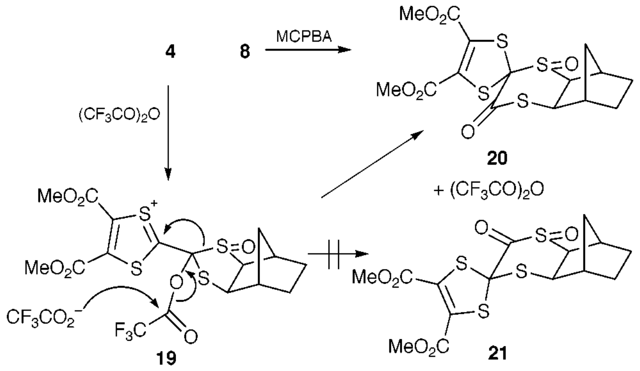
Scheme 2



Scheme 3

this was confirmed by the observation that oxidation of **8** with MCPBA gave an identical product.

Finally, in a further attempt to convert **1** into **2**, it was treated with the well established dehydrogenating agent DDQ, and to our surprise this also afforded **8** (37%). In this case we believe



Scheme 4

the mechanism to involve a series of single electron transfer steps with the oxygen in the product being provided by adventitious water, which also serves to reduce the DDQ.

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Notes and references

‡ New compounds gave satisfactory microanalytical and spectroscopic data. *Selected data* for **3**: δ_H 4.00 and 3.33 (2 H, AB pattern of d, *J* 7.2, 1.5), 3.85 (6 H, s), 2.75 (1 H, m), 2.40 (1 H, m), 1.8–1.6 (2 H, m), 1.46 (1 H, half AB pattern of m, *J* 11) and 1.4–1.2 (2 H, m); δ_C 159.6 (2 × CO_2Me), 133.1 (2 × C=C), 120.4, 112.6, 81.5 (CH–SO), 59.2 (CHS), 54.0 (2 × Me), 44.2 and 38.7 (2 × CH), 34.0, 28.7 and 27.5; *m/z* 404 (M^+, 20%), 388 (M^+–O, 10), 310 (40) and 262 (100). For **4**: δ_H 4.08 (2 H, d, *J* 2), 3.92 (6 H, s), 2.86 (2 H, m), 1.8–1.6 (2 H, m), 1.4–1.2 (3 H, m) and 0.85 (1 H, half AB pattern of m, *J* 12); δ_C 158.6 (2 × CO_2Me), 133.6 (2 × C=C), 128.3, 118.9, 83.8 (2 × CH–SO), 54.2 (2 × Me), 38.7, 36.2 and 28.0. For **8**: δ_H 3.99 (1 H, half AB pattern of d, *J* 7.3, 1.5), 3.84 and 3.83 (each 3 H, s), 3.80 (1 H, half AB pattern of d, *J* 7.3, 1.8), 2.35–2.15 (3 H, m), 1.75 (2 H, m) and 1.5–1.35 (3 H, m); δ_C 189.5 (S–CO), 160.8 and 160.2 (2 × CO_2Me), 133.8 and 125.3 (2 × C=C), 82.2 (spiro C), 54.3 (CHS), 53.4 and 53.3 (2 × Me), 48.8 (CHS), 45.9 and 40.4 (2 × CH), 34.9 (CH–CH_2–CH), 29.4 and 27.3. For **20**: δ_H 4.15 and 3.89 (2 H, AB pattern, *J* 8), 3.86 (3 H, s), 3.82 (3 H, s), 3.12 (1 H, br s), 2.40 (1 H, br s), 2.26 and 1.52 (2 H, AB pattern, *J* 11), 1.95–1.85 (2 H, m) and 1.6–1.45 (2 H, m); δ_C 185.9 (S–CO), 159.4 and 158.9 (2 × CO_2Me), 133.7 and 124.8 (2 × C=C), 91.3 (spiro C), 59.5 (CHS), 53.6 and 53.5 (2 × Me), 46.0, 43.4, 38.4, 35.5 (CH–CH_2–CH), 29.7 and 27.7.

§ *Crystal data* for **8**: $C_{15}H_{16}S_4O_5$, M = 404.53, colourless block, crystal dimensions 0.40 × 0.40 × 0.30 mm, monoclinic, space group $P2_1/a$ (#14), a = 9.321(8), b = 15.481(5), c = 12.756(7) Å, β = 105.06(5)°, V = 1777(1) Å^3, Z = 4, D_c = 1.512 Mg m^{-3}, T = 293 K, R = 0.095, R_W = 0.092 for 2278 reflections with $I > 3\sigma(I)$ and 218 variables. Data were collected on Rigaku AFC7S diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). The structure was solved by direct methods (SIR92) and refined using full-matrix least-squares methods. CCDC 182/1342. See http://www.rsc.org/suppdata/cc/1999/1673/ for crystallographic data in .cif format.

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