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Generation by Flash Vacuum Thermolysis and Cyclization of Methyl Penta-2,4-dienedithioate

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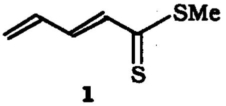
Abstract: Methyl penta-2,4-dienedithioate was generated by flash vacuum thermolysis of two precursors. It was found to be unstable and gave 6-methylthio-(2H)-thiopyran by a pericyclic cyclization.



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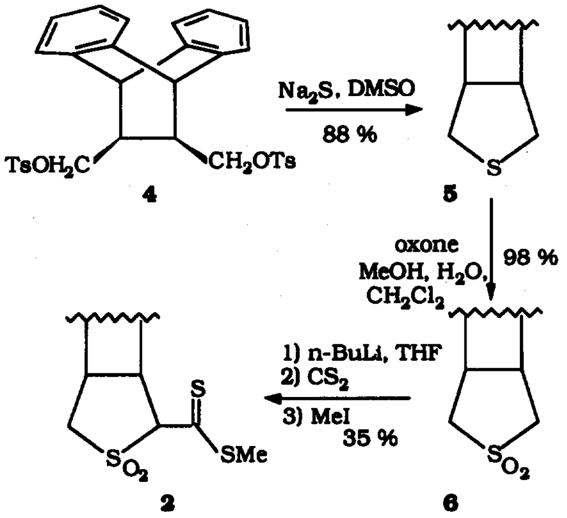
In this communication we present the formation and the cyclization of the most simple conjugated dienic dithioester, methyl penta-2,4-dienedithioate **1**, using the flash vacuum thermolysis technique (FVT)[2].

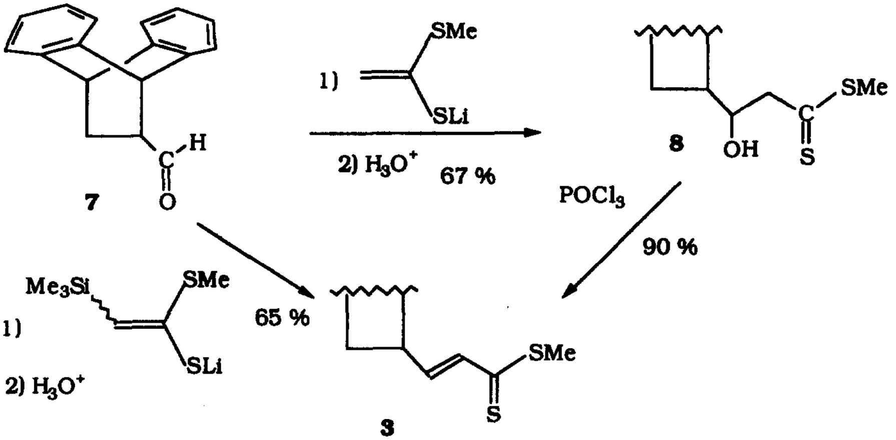
In contrast with stable saturated dithioesters[3,4], α-ethylenic dithioesters are generally reactive, easily dimerizing compounds[5]. Until now, dienic dithioesters have been only postulated as intermediates in the thermolysis of propargylic keteneditithioacetals[6], and more recently in the dehydration of β-hydroxy-γ-unsaturated dithioesters[7].



Two routes to the presumably unstable dienic dithioester 1 were developed. The first one was based on the FVT of the sulfone 2, associating a retro Diels-Alder reaction with an extrusion of sulfur dioxide, in order to generate simultaneously the whole conjugated system. This method has already proved useful for the synthesis of many other dienes[8]. The second synthesized precursor was the α-ethylenic dithioester 3. In this case, a simple retro Diels-Alder reaction[9,10] should generate the second C=C double bond.

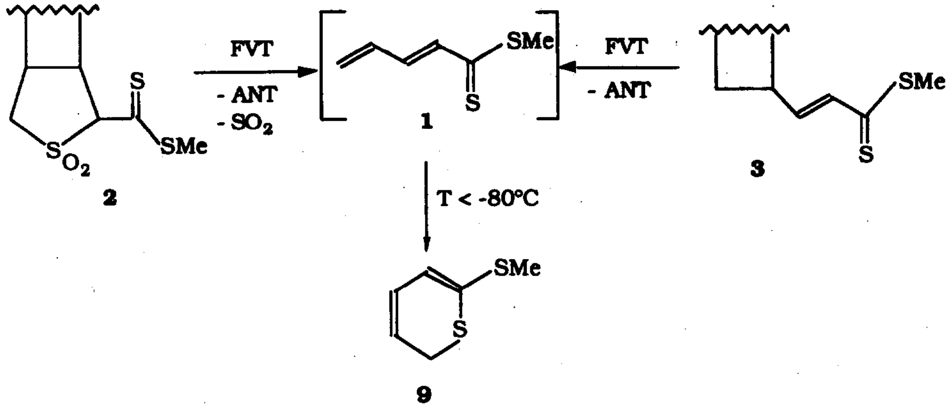
The ditosylate 4[11] was reacted with sodium sulfide in dry dimethyl sulfoxide for 15h at 100°C to give the sulfide 5 in 88% yield[12]. This sulfide was then oxidized into the sulfone 6[13] with oxone ($KHSO_5$)[14] in a mixture of water, methanol and methylene chloride (2:1:2) for 7 days (yield 98%). The sulfone 6 was deprotonated with n-butyllithium in THF from -78°C to 20°C, and reacted with carbon disulfide at room temperature. After addition of 0.5 eq. of iodomethane to the reaction mixture, the expected dithioester 2 was isolated in 35% yield from 6[15].

On the other hand, methyl dithioacetate was deprotonated with lithium diisopropylamide and the resulting lithium enethiolate[16] was reacted with the ethanoanthracenic aldehyde 7[17]. The obtained β-hydroxydithioester 8 (yield 67%)[18] was dehydrated by $POCl_3$ in pyridine[19] to give the unsaturated dithiocarboxylate 3. The same compound 3 was also synthesized in one step and 65% yield by the Peterson reaction of the aldehyde 7 with the lithium enethiolate of methyl trimethylsilyldithioacetate[20]. In spite of the bulkiness of the ethano-anthracene group, the α-ethylenic dithioester 3 is a poorly stable compound. At room temperature, it is slowly transformed into a mixture of non-identified dimers[21].



The FVT of the precursors 2 and 3 were carried out under 10^{-3} hPa at 550 and 500°C respectively. In both cases anthracene (ANT) was recovered quantitatively at the oven exit.

The ^1H NMR spectra of the volatile products trapped at -196°C were recorded at -80°C. They were clearly in agreement with the cyclic structure 9[22] rather than with the dienic structure 1. Furthermore, no thiocarbonyl carbon was observed in the ^{13}C NMR spectra.



In both cases the final product obtained was the substituted (2H)-thiopyran resulting from the *E* --> *Z* isomerisation and pericyclic cyclization of the intermediate unsaturated dithioester **1**. Previously reported MINDO/3 calculations[23] have shown that the cyclization pentadienethial → (2H)-thiopyran is favoured by 128 kJ/mol and must be much easier than the corresponding pentadienal → (2H)-pyran reaction. Our experimental results emphasize again the instability of dienic dithioesters.

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12. All new isolated products gave correct elemental analysis (C, H ± 0.4%). **5**: mp = 232°C (from CH_2Cl_2:pentane 1:1); ^1H NMR ($CDCl_3$): 2.4-2.8 (m, 6H), 3.82 (d, J = 1Hz, 2H), 6.2-7.2 (m, 8H); MS (70 eV): 264 ($M^{+\bullet}$, 12%), 178 ($ANT^{+\bullet}$, 100%).
13. **6**: mp = 273-274°C; ^1H NMR: 2.0-2.6 (m, 2H), 2.7-3.3 (m, 4H), 4.29 (d, J = 1Hz, 2H); 7.0-7.5 (m, 8H); ^{13}C NMR: 38.36, 46.92, 52.28 and 123.92-141.78 (8 aromatic C); MS: 296 ($M^{+\bullet}$,15%), 178 ($ANT^{+\bullet}$, 100%), 97 (16%), 54 (30%); IR (KBr): 1310, 1135 cm^{-1} (SO_2).
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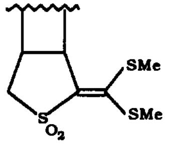
15. **2**, an orange solid, was purified by TLC (eluent: CH_2Cl_2). mp = 205-210°C; ^1H NMR: 1.9-2.8 (m, 4H), 2.75 (s, 3H), 3.4-4.5 (m, 3H), 6.8-7.5 (m, 8H); MS: 386 ($M^{+\bullet}$, 3%), 321 (4%), 178 ($ANT^{+\bullet}$, 100%), 149 (92%); IR: 1325, 1135 cm^{-1} (SO_2).
When 1 eq. of MeI was used the major product was the dithioacetal **10** and only small amounts of **2** were isolated.



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18. The aldehyde **7** was reacted with the enethiolate at -78°C for 25 min. **8** was obtained as a mixture of diastereoisomers (yield 67%). One of them was crystallized from methanol in 35% yield (mp = 148°C) and gave the following spectroscopic data: 1.0-2.2 (m, 3H), 2.50 (s, 3H), 2.9-3.4 (m, 3H), 4.30 (d, J = 2Hz, 1H), 4.80 (d, J = 1Hz, 1H), 6.8-7.4 (m, 8H); ^{13}C NMR: 19.89, 32.10, 44.41, 45.07, 56.09, 122.28-144.13 (8 aromatic C), 237.19. MS: 340 ($M^{+\bullet}$, 20%), 292 (3%), 234 (22%), 178 ($ANT^{+\bullet}$, 100%). IR: 3640 (ν_{OH}), 1462, 1163, 1148, 955, 822, 760 cm^{-1}.
19. 10 eq. of $POCl_3$ were used (90min at 0°C, then 30min at 20°C). See: Lawson, K. R.; Singleton, A.; Witham, G. H. *J. Chem. Soc. Perkin 1* **1984**, 859-864.
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21. **3** is a bright red compound which was characterized immediately after its separation by proton NMR (SMe: s, 2.45ppm) and MS (322, $M^{+\bullet}$). After a few hours the 2.45ppm singlet was considerably smaller and new singlets were observed in the 2.0-2.5 region. They were assigned to a mixture of dimers of **3**. The observation of a small peak at 644 ($M^{+\bullet}$of **3** x 2) in the mass spectrum confirmed this hypothesis. Owing to the instability of **3**, the precursor **2** is more convenient for the synthesis of **9**.
22. Oven: l = 60 cm, i.d.= 2.5 cm. The volatile products were condensed on a cold trap (liquid N_2) previously coated with CD_2Cl_2. The ^1H NMR spectrum was then recorded at -80°C. The yield was estimated to be *ca.* 50% from **2** or **3** by adding a quantitative standard in the NMR tube. The polymeric by-products were unsoluble in CD_2Cl_2. **9**: ^1H NMR: 2.41 (s, 3H), 3.25 (dd, J = 6 and 1Hz, 2H), 5.4-6.4 (m, 3H). No change occured in this spectrum upon warming the probe to room temperature, indicating that no reactive compound has been observed. ^{13}C NMR: 18.2, 27.3, 113.7, 119.5, 127.1, 140.8. MS: 144 (M+., 21%), 128 (100%) 97 (54%), 79 (45%), 71 (41%), 61 (85%).
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