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SYNTHESIS OF ENETHIOLISABLE α-OXOTHIONES BY FLASH VACUUM THERMOLYSIS

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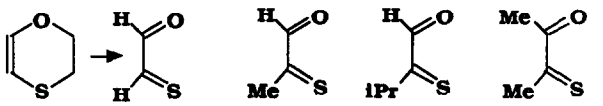
Abstract: *The retro Diels-Alder reaction of dihydrooxathiins and the retro-ene reaction of α-allylthio-carbonyl compounds were used to synthesise enethiolisable α-oxothiones.*

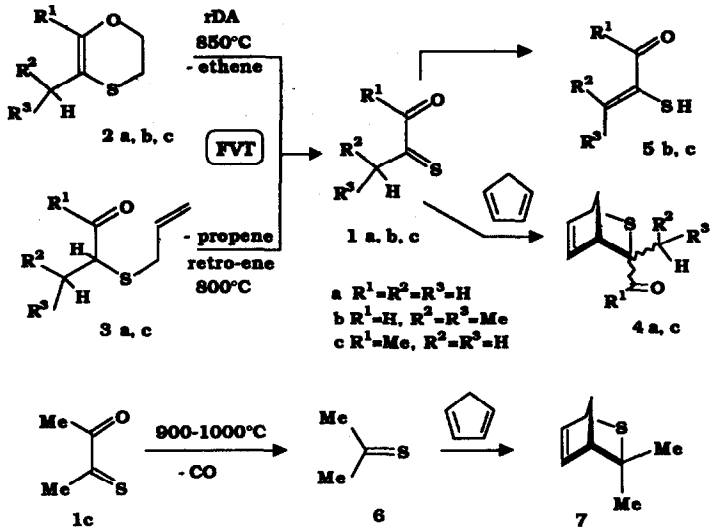


Simple enethiolisable α-oxothiones, in spite of their potentially interesting tautomerism and reactivity, remained a poorly known chemical class, limited until now to 3-thioxobutan-2-one (**1c**) which has been synthesized under flash vacuum thermolysis conditions (FVT) by retro-ene reaction of the corresponding allyl sulfide **3c**[1]. We reported recently the synthesis and photoelectron spectrum of thioxoethanal[2], obtained by FVT of the easily available 2,3-dihydro-1,4-oxathiin (retro Diels-Alder (rDA) reaction I→II) and present herein our first results concerning the preparation by this method, the thermal behaviour and the trapping with cyclopentadiene of α-oxothiones **1a-c.**

The simplest α-oxothione, compound **1a**, was obtained either by FVT at 850°C of the corresponding Diels-Alder precursor **2a**[3], or by retro-ene reaction (800°C) of the allyl sulfide **3a**[4]. Trapping of **1a** on a NaCl plate cooled at -196°C (using the coupling of the FVT oven with an optical cryostat[2]) allowed direct recording of its IR spectrum at this temperature: 2970, 2850, 2740, 1680, 1240 and 960 cm^{-1}. Upon warming to -150°C, all these bands disappeared together and a polymeric material was recovered on the plate[5]. No IR absorption was detected near 2500 cm^{-1} (ν_{SH}) demonstrating the absence of enethiolisation[6] in the case of **1a**. When gaseous cyclopentadiene was injected at the oven exit during the thermolysis, the expected adduct **4a**[7] was recovered in the trap after warming and evaporation of the excess diene (yield= 51% from **2a**).

The IR spectrum (-196°C) of the product obtained by FVT of **2b**[3] showed absorptions at 2970, 2940, 2780, 2720, 2560, 1650, 1445, 1370 and 855 cm^{-1}, all disappearing at -50°C, in agreement with the enethiol structure **5b** (as expected, the tautomerisation **1**→**5** is greatly favoured here by the presence of the two Me groups R^2 and R^3)[6]. Furthermore, if a weak band at 1265 cm^{-1}, vanishing at -150°C, could be assigned to a small amount of **1b**, no adduct **4b** was recovered after tentative trapping with cyclopentadiene.

Oxothione **1c** was obtained by FVT of the precursors **2c**[3] and, as already reported, **3c**[1], as a mixture with its enethiol **5c**, revealed by IR spectroscopy at -196°C (**1c**: 1690, 1250, 1025 cm^{-1}, disappearing at -150°C; **5c**: 3005, 2550, 1680, 1585, 1235 and 1105 cm^{-1}, disappearing at -50°C). The absence of **5c** reported in the previous work[1] could be due to the lower FVT temperature used (660°C). The presence of **1c** was confirmed by trapping with cyclopentadiene to give the adduct **4c**[7] in 38% yield, but the ^1H NMR spectrum of the FVT product of **2c** showed only the presence of the enethiol **5c**: δ ($CDCl_3$, -60°C): 2.40 (s, 3H, Me), 4.50 (d, J=2Hz, 1H, SH), 6.20 (d, 1.5Hz, 1H, =CH), 6.30 (dd, 1.5 and 2Hz, 1H, =CH).



Upon FVT of **2c** at higher temperatures (900-1000°C), loss of carbon monoxide from **1c** occured to give propanethione **6**[8], as shown by IR (1445, 1350, 1270, 1245, 1200, 1092 cm^{-1}), ^1H NMR (2.67 ppm in $CDCl_3$), and by trapping with cyclopentadiene which gave the adduct **7**[7] in 10% yield. This low yield can be due, as witnessed by IR, to a competitive evolution of **6** comprising of enethiolisation to propene-2-thiol (3000, 2545, 1620 cm^{-1})[9] and cleavage into methane and thioketene (1750 cm^{-1})[10].

REFERENCES AND NOTES

1. Giles, H.G.; Marty, R.A.; De Mayo, P. *Can. J. Chem.* **1976**, *54*, 534.
2. Bourdon, F.; Ripoll, J.L.; Vallée, Y.; Lacombe, S.; Pfister-Guillouzo, G. *J. Org. Chem.* **1990**, *55*, 2596.
3. Method of preparation of **2a-c** and description of **2c**: Parham, W.E.; Heberling, J.; Wynberg, H. *J. Am. Chem. Soc.* **1955**, *77*, 1169; description of **2a**: Dupuy, C.; Surzur, J.M. *Bull. Soc. Chim. Fr.* **1980**, II-353.
   2b: ^1H NMR ($CDCl_3$): 1.08 (d, J=7Hz, 6H), 2.30 (hept, J=7Hz, 1H), 2.94 (~t ,2H), 4.17 (~t, 2H), 6.49 (s, 1H). ^{13}C NMR ($CDCl_3$): 22.08, 25.18, 32.52, 64.85, 114.45, 133.98. MS: m/z (%), 144 ($M^{+\cdot}$,43), 129 (51), 87 (100).
4. **3a,c** were prepared according to ref[1]; **3a** : ^1H NMR ($CDCl_3$): 1.36 (d, J=7Hz, 3H), 3.0-3.5 (m, 4H), 5.0-6.2 (vinyl system), 9.31 (d, J=5, 1H). ^{13}C NMR ($CDCl_3$): 13.37, 33.42, 46.91, 118.34, 133.36, 196.65. MS: 130 ($M^{+\cdot}$, 11), 101 (32), 73 (23), 59 (44), 41 (100).
5. Due to their high reactivity, no NMR data could be obtained for **1a** and **5b**.
6. Reviews: Mayer, R. in "Sulfur in Organic and Inorganic Chemistry", Senning, A. Ed., Marcel Dekker, New York, **1972**, vol. 3, 325. Paquer, D. *Int. J. Sulf. Chem.,B* **1972**, *7*, 269.
7. **4a** was obtained as a mixture of stereoisomers (*endo/exo*: 60/40)[2]; ^1H NMR ($CDCl_3$, *endo*): 1.62 (s, 3H), 1.7-1.9 (m, 2H), 3.0-3.2 (m, 1H), 4.0-4.2 (m, 1H), 5.9-6.4 ("norbornene like" HC=CH), 8.89 (s, *endo* CHO). The *exo* isomer was characterized in particular by its Me singlet at 1.30 and CHO singlet at 9.73. IR ($CDCl_3$): 1705 cm^{-1} (C=O). MS: 154 ($M^{+\cdot}$, 20), 125 (28), 93 (12), 66 ($Cp^{+\cdot}$,73), 59 (100). **4c** was obtained as a single isomer (most probably *endo*). ^1HNMR ($CDCl_3$): 1.69 (s,3H), 1.7-1.9 (m, 2H), 2.03 (s, 3H), 3.0-3.3 (m,1H), 4.0-4.2 (m,1H), 6.0-6.4 (HC=CH).^{13}C NMR ($CDCl_3$): 27.60, 29.42, 50.05, 53.66, 54.42, 70.52, 134.79, 137.31, 209.58. MS: 168 ($M^{+\cdot}$, 27), 125 (42), 91 (17), 66 ($Cp^{+\cdot}$, 44), 59 (100). **7**: ^1H NMR ($CDCl_3$): 1.23 (s, 3H), 1.67 (s, 3H), 1.7-2.0 (m, 2H), 2.7-2.9 (m, 1H), 4.0-4.2 (m, 1H), 6.0-6.5 (HC=CH). ^{13}C NMR ($CDCl_3$): 28.50, 31.93, 50.48, 53.68, 56.43, 56.49, 132.81, 136.57. MS: 140 ($M^{+\cdot}$, 12), 75 (38), 66 ($Cp^{+\cdot}$, 70), 59 (93), 41 (100).
8. Andrieu, C.; Mollier, Y. *Spectrochim. Acta*, **1972**, *28A*, 785. Paquer, D.; Vialle, J. *Bull. Soc. Chim. Fr.* **1969**, 3595.
9. Lipscomb, R.D.; Sharkey, W.H. *J. Polymer Sc. A1* **1970**, *8*, 2187.
10. Georgiou, K.; Kroto, H.W.; Landsberg, B.M. *J. Mol. Spectro.* **1979**, *77*, 365; *J. Chem. Soc., Chem. Commun.* **1974**, 739.

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