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Thioacrolein *S*-oxide

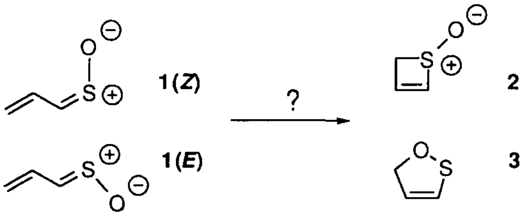
Nadia Pelloux-Léon[a], Roger Arnaud[a], Jean-Louis Ripoll[b], Pierre Beslin[b] and Yannick Vallée[a]*

[a] L.E.D.S.S., UMR CNRS,
Université Joseph Fourier, B.P. 53X, 38041 Grenoble, France
[b] LCMT, UMR CNRS, ISMRA, Université de Caen, 14050 Caen, France.

Abstract: Thioacrolein *S*-oxide was synthesized for the first time and characterized by low temperature NMR spectroscopy. Theoretical calculations about this unsaturated sulfine and two of its possible cyclic isomers were performed.

Sulfines (thiocarbonyl *S*-oxides) are generally more stable than the corresponding thioaldehydes and thioketones. For instance, methanethial polymerizes even at liquid nitrogen temperature, whereas methanethial *S*-oxide can be observed in solution at -100°C.[1,2] Another interesting example is propanethial *S*-oxide which is a natural compound produced by onions.[3] Many synthetic routes to sulfines have been developped including oxidation of thiocarbonyl compounds,[4] 1,2-elimination reactions,[5] [2 + 2] cycloreversion[6] and retro Diels-Alder reaction.[2] Flash vacuum thermolysis (FVT) has been often used.[7]

The enhanced unstability of unsaturated thiocarbonyl compounds often precludes their isolation. For instance, in contrast with simple aliphatic dithiocarboxylates, methyl propenedithioate is unstable.[8] Thioacrolein, the simplest α-unsaturated thioaldehyde has been obtained by various methods. It is a very reactive compound which dimerizes at 100K, giving dithiins.[9] We expected that its *S*-oxide would be much more stable. However, untill now, no synthesis of this α-unsaturated sulfine has been reported.[10]



In this communication, we report the first synthesis of thioacrolein S-oxide **1**, which like other sulfines can exist as *Z* and *E* stereoisomers,[4] and discuss its possible cyclization into its cyclic isomers, 2H-thiete *S*-oxide **2** and 5H-1,2-oxathiole **3**. The feasability of these cyclization processes has been investigated by means of *ab initio* molecular orbital calculations.

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* fax 00 33 76 51 43 82 ; E-mail Yannick.Vallee@ujf-grenoble.fr

All calculations were carried out using the GAUSSIAN 94 program package.[11] The stationary points of the $[C_3H_4SO]$ potential energy surface were initially located at the HF/6-31+G* level and characterized by harmonic vibrational frequencies at this level. The intrinsic reaction coordinate (IRC) utility was employed to confirm that the transition state (TS) did indeed connect to the correct minima. The HF structures were then used as starting points of optimization at the MP2(fc)/6-31+G* level. Finally, in order to gauge the effects of electron correlation, single points calculations at the QCISD(T)/6-31+G* level were run on the MP2-optimized geometries.[12]

Main results are summarized in Figure 1. The stereoisomer **1(*Z*)**, after rotation around the C-C single bond, can lead to compound **3** which is lower in energy than **1(*Z*)**. However, this rearrangement is calculated to run *via* a relatively high energy TS, which might prevent it to occur. Furthermore, this process is disfavored by entropic factors (Δ_rS = -4 cal/mol.K, $\Delta S^{\neq}$ = -4.1 cal/mol.K). The cyclic *S*-oxide **2** results from the rearrangement of stereoisomer **1(*E*)**, here also after rotation around the C-C single bond. The endothermicity of this process strongly suggest that **2** should not be observed in our experiments.

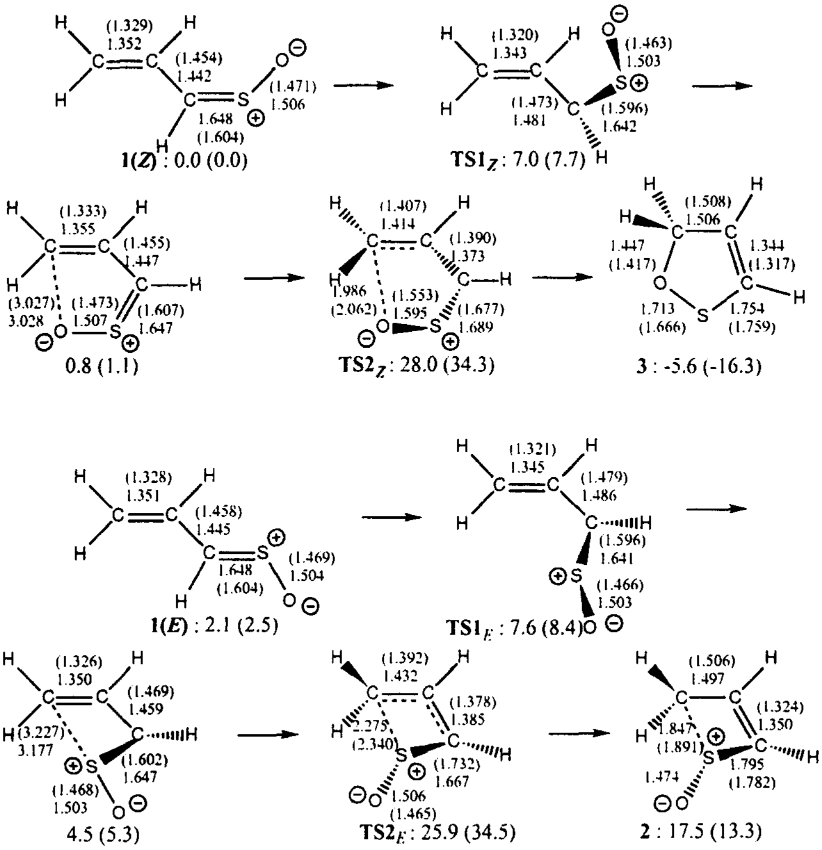
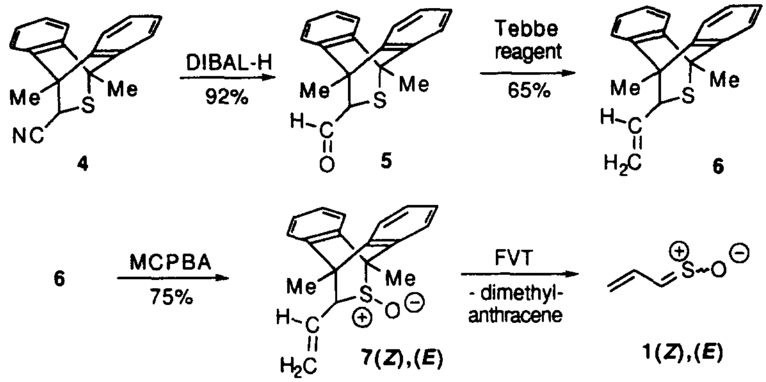


Figure 1 : Stationary points characterized on the C_3H_4SO potential surface. Relative energies are in kcal/mol ; values in brackets refer to HF/6-31+G* results. The total energy of **1(*Z*)** is equal to -588.21703 hartree at the HF level and -588.99146 hartree at the QCISD(T) one.

Our synthesis of sulfine **1** started with the 9,10-dimethylanthracene - thioformyl cyanide adduct **4** which was reduced with diisobutylaluminum hydride into aldehyde **5**.[13] Treatment of **5** by Tebbe reagent[14]



gave the vinylic compound 6.[15,16] Oxidation of sulfide 6 with MCPBA in CH_2Cl_2 gave sulfoxide 7 as a mixture of two stereoisomers (*Z*/*E* = 70/30, determined by ^1H NMR).[15] FVT[17] of 7 at 600°C quantitatively gave 9,10-dimethylanthracene which was recovered at the oven exit. The volatile products were trapped at -196°C and analysed by NMR at -60°C (solvent $CDCl_3/CFCl_3$: 4/1). The two isomeric sulfines **1**(*Z*) and **1**(*E*) were clearly observed. The major product was attributed a *Z* structure on the basis of the chemical shift of the HCSO proton[3,18] and the *Z*/*E* ratio was 78/22. Figure 2 summarized the obtained ^1H NMR data (the CH_2 protons of the *E* isomer were partially masked by those of the *Z* isomer). The ^{13}C NMR spectrum was also in agreement with the proposed structures : **1**(*Z*) : 172.4 (CSO), 125.2, 123.9 ppm ; **1**(*E*) : 181.5 (CSO), 125.5, 124.9 ppm. Furthermore, we were unable to detect any trace of the cyclic compounds **2** and **3**.[19] When the NMR sample was allowed to stand at room temperature, the signals corresponding to **1** slowly disappeared. A new product was observed by ^{13}C NMR (169.89 (CSO), 137.40, 129.00, 50.81, 25.18, 18.39 ppm) to whom was tentatively assigned the dimeric structure **8**. This product was also detected in the ^1H NMR spectrum.[20] Of special interest was the observation of a signal at 4.75 ppm which indicates structure **8** rather than its regioisomer **9**. **8** would arise from **1** by a [4π + 2π] process.[21] However, the ^1H NMR spectrum also showed the formation of other evolution products that we were unable to identify.

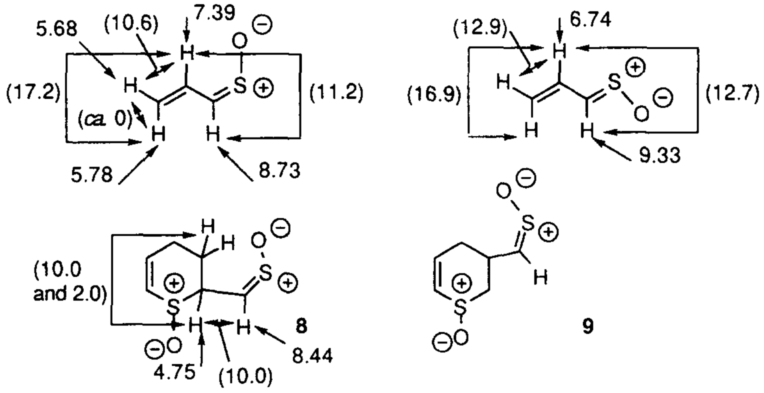


Figure 2 : δ in ppm (J in Hz)

references and notes

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12. As shown in Fig. 1, C=S and S-O bond lengths calculated at the HF and MP2 levels differ notably. HF structures seem to be in better agreement with the experimental results (for $H_2C=SO$, C=S : 1.616 Å, S-O : 1.469Å).[1] In addition, in a recent theoretical work, Ruttnik *et al.* suggested that the MP2 method would accurately reproduce the experimental structure of sulfines only if a large basis set, such as 6-311+G(2df,2p), is used. In order to test the influence of the geometries on relative energies, we have performed single point QCISD(T)/6-31+G*//HF/6-31+G* calculations of **1(*Z*)**, $\mathbf{TS2}_{\mathbf{Z}}$ and **3**. $\mathbf{TS2}_{\mathbf{Z}}$ was then found 27.2 kcal/mol higher and **3** 7.9 kcal/mol lower, than **1(*Z*)**. These results are close to those obtained with MP2 geometries. Ruttnik, P. J. A.; Burgers, P. C.; Francis, J. T.; Terlouw, J. K. *J. Phys. Chem.*, **1996**, *100*, 9694-9697.
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15. **6** : ^{13}C NMR (50MHz ; $CDCl_3$) : 17.33, 17.94, 45.55, 46.33, 59.86, 116.32, 118.53, 121.81, 123.47, 125.25, 125.47, 125.63, 126.19, 126.36, 136.73, 140.94, 144.26, 145.32, 145.59 ppm. ^1H NMR (200MHz ; $CDCl_3$) : 2.01 (s, Me), 2.25 (s, Me), 3.63 (d, J = 7.6 Hz, CH), 4.9-5.1 (m, $H_2C=CH$), 7.1-7.4 (m, ArH). **7** : IR ($CDCl_3$): 1072 cm^{-1} (ν_{SO}).^{13}C NMR (50MHz ; $CDCl_3$) **7(*Z*)** : 13.59, 16.84, 44.52, 44.76, 81.32, 120.6-142.3 (sp^2 carbons). ^1H NMR (200MHz ; $CDCl_3$), **7(*Z*)** : 1.90 (s, Me), 2.38 (s, Me), 2.78 (d, J = 8.2 Hz, CH), 4.8-5.4 (m, $H_2C=CH$), 7.2-7.5 (m, ArH) ; **7(*E*)** was characterized by a doublet at 3.49 ppm (J = 8.2 Hz).
16. We obtained a clean IR spectrum of thioacrolein[9] after a FVT (650°C)-low temperature IR coupled experiment with **6** : 1590 ($\nu_{C=C}$), 1422, 1303, 1280, 1178 (ν_{C-C}), 1065 ($\nu_{C=S}$), 990, 960, 891 cm^{-1}.
17. Oven, l = 20 cm , i.d. = 1,6 cm, p = 10^{-5} hPa. The IR spectrum of **1** was also recorded (-196°C, solid film) : 1587 ($\nu_{C=C}$), 1429, 1175 (ν_{C-C}), 1105, 1092, 980, 943, 860 cm^{-1}. The two bands at 1105 and 1092 were tentatively attributed to the $\nu_{C=S-0}$ vibration.
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19. However, the signal to noise ratio in the ^{13}C NMR spectrum was *ca.* 14/1. Thus, we cannot exclude the presence of small amounts (no more than 7%) of **3** and/or **4**.
20. Comparison of the spectrum with the one reported for the parent heterocycle 3,4-dihydro-2H-thiopyran *S*-oxide also points to structure **8** : Crumbie, R. L.; Ridley, D. D.; Steel, P. J. *Aust. J. Chem.*, **1985**, *38*, 119-132.
21. A more complete *ab initio* study of sulfines is now under investigation in Grenoble. In particular, we are studying this cycloaddition from a theoretical point of view.

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