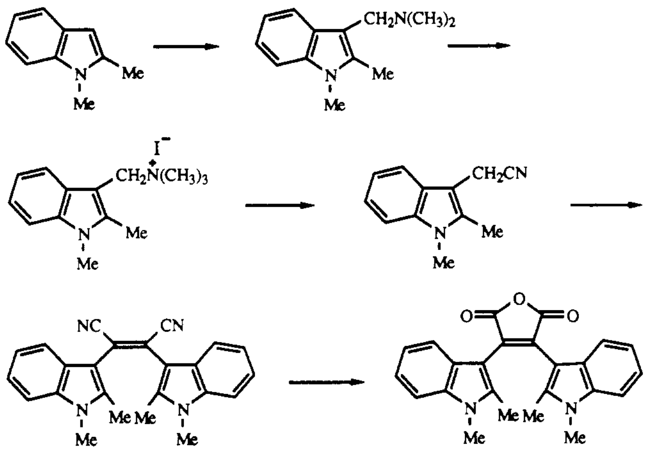
2,3-Bis(2,4,5-trimethyl-3-selenenyl)maleic Anhydride (5).[17] This was prepared from 1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-selenenyl)ethene by a similar procedure as used for 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride.[6] **5** was isolated in 35% yield by column chromatography on silica gel. The crude product was purified by recrystallization from an ether-hexane mixture: mp 230-3 °C; ^{1}H NMR (C_6D_6) δ 1.53, 1.66, 1.72, 1.84, 1.88 (×2) (18 H, ArCH_3); mass spectrum, *m/e* M$^+$ 442. Anal. Calcd for $C_{18}H_{18}O_3Se_2$: C, 49.11; H, 4.12; O, 10.90; Se, 35.87. Found: C, 49.39; H, 3.90.

1,2-Bis(1,2-dimethyl-3-indolyl)maleic anhydride was synthesized from 1,2-dimethylindole[18] as follows.



1,2-Dimethyl-3-((dimethylamino)methyl)indole.[19] A mixture of 36 mL of 25% aqueous dimethylamine and 40 mL of glacial acetic acid was cooled in an ice bath. To the solution below 5 °C were added 15 mL of 40% aqueous formaldehyde and then 1,2-dimethylindole (26.2 g, 0.18 mol). The reaction mixture was stirred gently until it became homogeneous. During the stirring the temperature rose to about 50 °C. The reaction mixture was allowed to stand at room temperature for 24 h and then poured into a 400-mL aqueous solution containing 40 g of sodium hydroxide. The oily part was collected by extraction with ether. The ether extract was washed and dried with $MgSO_4$. Removal of the solvent and distillation of the residue gave 1,2-dimethyl-3-((dimethylamino)methyl)indole in 38% yield; bp 105 °C (0.5 mmHg).

1,2-Dimethyl-3-((dimethylamino)methyl)indole Methiodide.[19] To a solution of 9.1 g of 1,2-dimethyl-3-((dimethylamino)methyl)indole in 40 mL of absolute ethanol was added in one portion 7.8 g of methyl iodide. The mixture was allowed to stand for 1 h at room temperature. Crystallization was completed by cooling, and the solid was collected and washed two times with absolute ethanol and three times with anhydrous ether. Nitrogen methiodide was isolate in 98% yield.

1,2-Dimethyl-3-(cyanomethyl)indole.[19] To a solution of 10g of sodium cyanide in 100 mL of water was added 17.2 g of the methiodide, and the mixture was refluxed for 2.5 h. Both oily and solid parts were collected by extraction with ether. The ether solution was washed three times with water, dried over $MgSO_4$, filtered, and concentrated. After the ether was removed, 1,2-dimethyl-3-(cyanomethyl)indole was isolated in 70% yield by column chromatography on silica gel. The crude product was purified by recrystallization from a ether-hexane mixture.

1,2-Dicyano-1,2-bis(1,2-dimethyl-3-indolyl)ethene (7). This was prepared from 1,2-dimethyl-3-(cyanomethyl)indole by a similar procedure as used for **3**. The coupling product was obtained as yellow crystals in 32% yield: mp 289-91 °C; ^{1}H NMR (C_6D_6) δ 1.91, 2.09 (s, 3 H × 2, Ar CH_3), 2.65, 2.69 (s, 3 H × 2, NCH_3), 6.70-7.44 (m, 4 H × 2, Ar CH_3); mass spectrum, *m/e* M$^+$ 364. HRMS *m/e* 364.16850, calcd for $C_{24}H_{20}N_4$ 364.16868.

2,3-Bis(1,2-dimethyl-3-indolyl)maleic anhydride (9).[17] This was prepared from **7** by a similar procedure as used for **5**. Yield was 57%: mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 2.04, 2.11 (s, 3 H × 2, Ar CH_3), 3.59, 3.62 (s, 3 H × 2, NCH_3), 6.91-7.36 (m, 4 H × 2, Ar H); mass spectrum, *m/e* M$^+$ 384; HRMS *m/e* 384.14564, calcd for $C_{24}H_{20}N_2O_3$ 384.14727.

Acknowledgment. This work was supported in part by Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan, and by Tokuyama Science Foundation.

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(17) Goldberg, M. A.; Ordas, E. P.; Carsch, G. *J. Am. Chem. Soc.* **1947**, *69*, 260.

(18) Fieser, L. F.; Fieser, H. *Reagents for Organic Synthesis*; John-Wiley: New York, 1967, p 336.

(19) Snyder, H. R.; Eliel, E. L. *J. Am. Chem. Soc.* **1948**, *70*, 1703.

Flash Vacuum Thermolysis of 2,3-Dihydro-1,4-oxathiin: Synthesis, Photoelectronic Spectroscopy, and Dienophilic Reactivity of Thioxoethanal[1,2]

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Thioxoethanal has been generated in the gas phase by flash vacuum thermolysis of 2,3-dihydro-1,4-oxathiin. Its characterization was performed by chemical trapping and photoelectron spectroscopy (PES). The PE HeI-HeII study led to the conclusion that thioxoethanal was obtained, with ethylene, as the only thermolysis product at 720 °C. At higher temperatures, a cleavage into methanethial and carbon monoxide was observed. The results from this PE study, as well as MNDO calculations, indicate a very weak interaction between the formyl and thioformyl moieties of the molecule through the σ C-C bond. The HOMO sulfur lone pair is only slightly stabilized by the inductive effect of the carbonyl group. These conclusions account for the observed dienophilic reactivity of thioxoethanal.

In contrast to ethanedithial (**1**) which has received much attention,[3] thioxoethanal (**2**), remains a poorly characterized compound. Ethanedithial, **1**, as well as most α-dithiones,[4] has been shown, from theoretical and experi-

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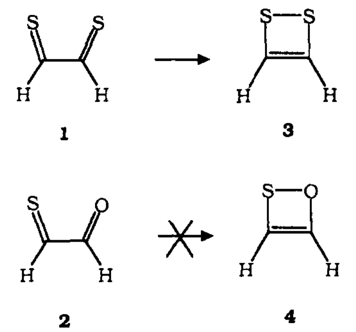
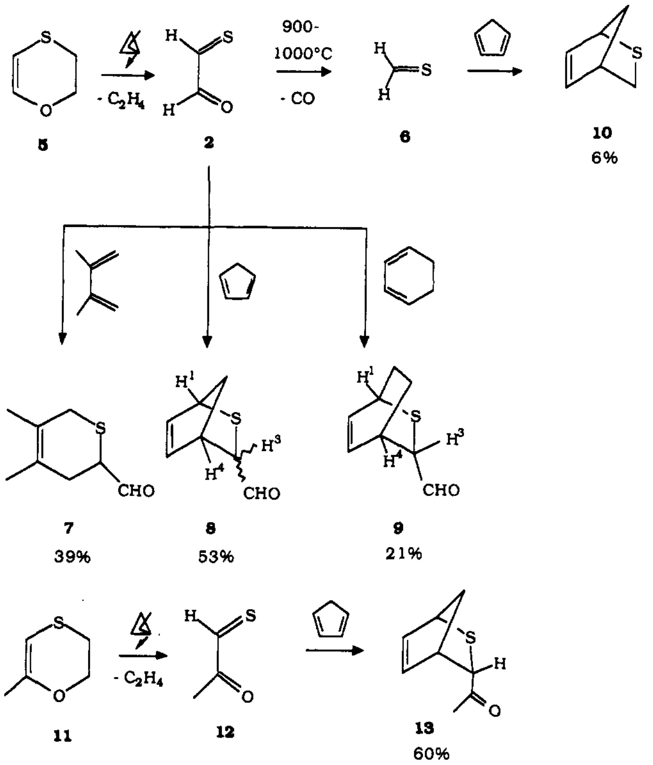
Scheme I



Scheme II



mental data, to exist in its dithiete isomeric form **3** (Scheme I). On the other hand, known α-thioxo ketones do not cyclize to oxathietes.[5] In the particular case of thioxoethanal (**2**), it has been reported, from its IR spectrum recorded in an argon matrix, that this compound should be formulated as the thial–aldehyde **2**, rather than as the oxathiete **4**.[6] The millimeter wave spectrum of **2** has been published recently.[7,8]

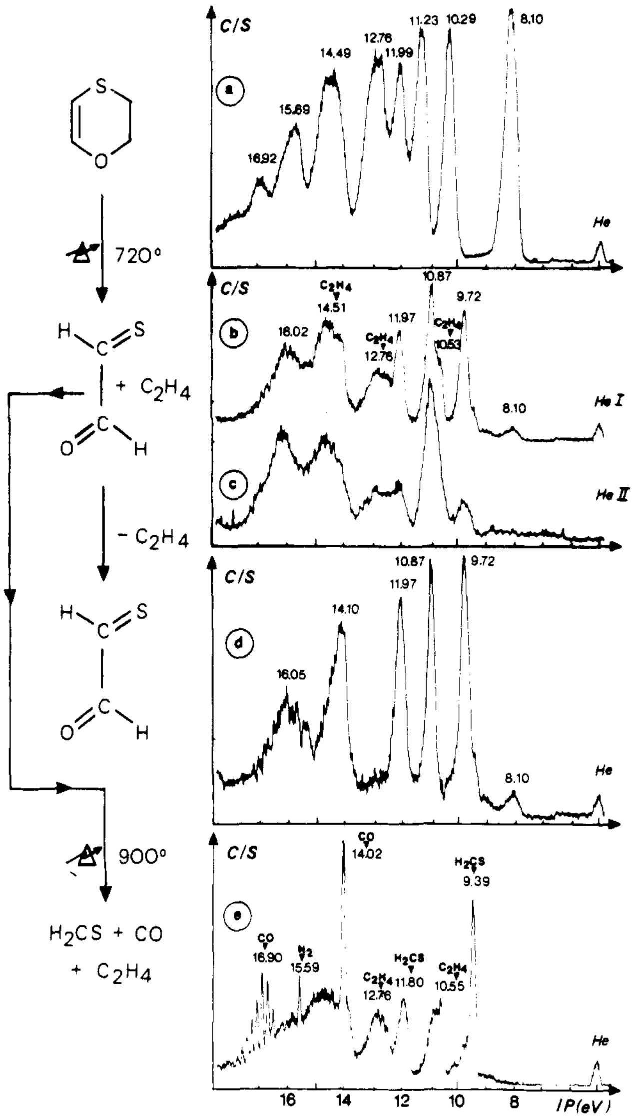


Figure 1. Photoelectron spectrum of (a) **5**; (b) the thermolysate at 720 °C; (c) the thermolysate at 720 °C under HeII ionization energy; (d) the difference between the HeI spectrum of the thermolysate and ethylene; (e) the thermolysate at 900 °C.

As part of our work concerning the synthesis by flash vacuum thermolysis (FVT) and characterization of simple thials,[9] we report herein a new gas-phase synthesis of thioxoethanal (**2**), its characterization by photoelectronic spectroscopy, and some aspects of its dienophilic reactivity.

Synthesis of Thioxoethanal. The retro-Diels–Alder reaction of simple cyclohexenes and heterocyclohexenes, when performed under FVT conditions, proved to be a reliable way toward conjugated dienic and heterodienic systems.[10,11] However, owing to the high temperatures

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(1) Retrodienic Reactions, Part 24; Part 23: see ref 11.

(2) Application of Photoelectron Spectroscopy to Molecular Properties, Part 41; Part 40: Lacombe, S.; Pellerin, B.; Guillemin, J. C.; Denis, J. M.; Pfister-Guillouzo, G. *J. Org. Chem.*, in press.

(3) Jacobsen, N.; De Mayo, P.; Weedon, A. C. *Nouv. J. Chim.* **1978**, *2*, 331. Torres, M.; Clement, A.; Strausz, O. P.; Weedon, A. C.; De Mayo, P. *Nouv. J. Chim.* **1982**, *6*, 401. Schulz, R.; Schweig, A.; Hartke, K.; Köster, J. *J. Am. Chem. Soc.* **1983**, *105*, 4519. Rodler, M.; Bauder, A. *Chem. Phys. Lett.* **1985**, *114*, 575. Jiang-qi, W.; Mohraz, M.; Heilbronner, E.; Krebs, A.; Schütz, K.; Voss, J.; Köpke, B. *Helv. Chim. Acta* **1983**, *66*, 801. Tae-Kyu, Ha; Nguyen, M. T.; Vanquickenborne, L. *Z. Naturforsch.* **1982**, *37a*, 125. Calzaferri, G.; Gleiter, R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 559. Haddon, R. C.; Wasserman, S. R.; Wudl, F.; Williams, G. R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6687. Fabian, J.; Mayer, R.; Carsky, P.; Zahradnik, R. *Z. Chem.* **1985**, *25*, 50. Goddard, J. D. *J. Mol. Struct. (Theochem)* **1987**, *149*, 39.

(4) Kusters, W.; De Mayo, P. *J. Am. Chem. Soc.* **1974**, *96*, 3502. Köpke, B.; Voss, J. *J. Chem. Res.* **1982**, (S) 314. Boar, R. B.; Hawkins, D. W.; McGhie, J. F.; Barton, D. H. R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 515.

(5) Inter alia: Giles, H. G.; Marty, R. A.; De Mayo, P. *Can. J. Chem.* **1976**, *54*, 537. Saville, B.; Steer, M. *J. Chem. Soc., Chem. Commun.* **1972**, 616. Bak, C.; Praefcke, K. *Chem. Ber.* **1979**, *112*, 2744. Köpke, B.; Voss, J. *Chem. Ber.* **1982**, *115*, 2221. Buddensiek, D.; Köpke, B.; Voss, J. *Chem. Ber.* **1987**, *120*, 575.

(6) Torres, M.; Clement, A.; Strausz, O. P. *Nouv. J. Chim.* **1983**, *7*, 269.

(7) McNaughton, D.; Bruget, D. N. *J. Mol. Spectrosc.* **1989**, *134*, 129.

(8) For theoretical calculations concerning **2**, see: Bock, C. W.; Trachtman, M.; George, P. *Chem. Phys.* **1982**, *68*, 143; *73*, 179. Vedejs, E.; Perry, D. A.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1983**, *105*, 6999.

(9) Vallée, Y.; Ripoll, J. L.; Lafon, C.; Pfister-Guillouzo, G. *Can. J. Chem.* **1987**, *65*, 290.

(10) Lasne, M. C.; Ripoll, J. L. *Synthesis* **1985**, 121.

(11) Vallée, Yo.; Ripoll, J. L.; Maume, D. *J. Anal. Appl. Pyrolysis* **1988**, *14*, 171.

required for such cycloreversions, this remained only scarcely used until now. As the FVT of 2,3-dihydro-4-hydroxythiin has been shown to give transient 3-hydroxypropenethial,[11] we anticipated that this reaction could be generalized to the synthesis of other thiocarbonyl compounds. In the case of thioxoethanal (**2**), the needed precursor was the easily available 2,3-dihydro-1,4-oxathiin (**5**)[12] (Scheme II).

At first, the heterocycle **5** was submitted to FVT–low temperature IR spectroscopy coupling experiments. After FVT at 850 °C, no more starting material could be detected in the IR spectrum of the thermolysate, recorded at −196 °C. Bands at 2860 and 1710 cm^{-1}, characteristic of an aldehyde, were observed and could be attributed to thioxoethanal (**2**), in good agreement with results presented in ref 6. However, formation of formyl groups containing polymeric material did not allow us to observe the disappearance of these bands upon warming to room temperature. On the other hand, the exclusive formation of thioxoethanal (and ethylene) in the FVT of dihydrooxathiin **5** was unambiguously established by photoelectron spectroscopy.

Photoelectron Spectroscopy. The thermolysis of 2,3-dihydro-1,4-oxathiin (**5**) was performed in a short-path system, as described elsewhere.[13] The product was slowly vaporized under 10^{-2} mbar through the oven, and the gaseous flow was dynamically analyzed by recording its PE spectrum. 2,3-Dihydro-1,4-oxathiin (**5**) began to react at 650 °C and was totally cleaved at 720 °C[14] (disappearance of starting material bands at 8.10, 10.29, and 11.23 eV; Figure 1b). A new compound, obtained besides ethylene, exhibited well-defined bands at 9.72, 10.87, 11.97, 14.10, and 16.05 eV from difference spectra between the thermolysate and ethylene (Figure 1d). When the thermolysis temperature was further raised, new bands were observed at 9.39 and 11.80 (methanethial **6**[9,15]), as well as 14.02 and 16.90 eV (carbon monoxide). At 900 °C the primary product was no longer observed in the spectrum, which only showed the bands of methanethial, carbon monoxide, and ethylene (Figure 1e).

Discussion

Given the known equilibrium shift between α-dithiones and dithietes toward the cyclic isomer,[3] in marked contrast with α-dioxo compounds, we had to determine whether the PE spectrum of the thermolysis product was concerned with thioxoethanal (**2**), or with its cyclic counterpart, the oxathiete **4**. According to our MNDO results, *trans*-thioxoethanal was found to be more stable than the oxathiete **4** by 26 kcal mol^{-1} (the gauche, trans and cis isomers of thioxoethanal were calculated to have very close energetic levels). Ab initio calculations performed, after complete geometrical optimization, on the gauche and trans forms of thioxoethanal (Monstergauss program, 3-21G* basis set) showed the trans form to be more stable than the gauche one by 3.28 kcal mol^{-1}, in agreement with previous results.[7] From these calculations, we could conclude that the orbitals energies of both trans and gauche isomers of thioxoethanal are close and would give rise to the same photoelectron spectrum.

Although experimental ionization potentials (IP's) may usually be correlated, within Koopmans' approximation, with calculated orbital eigenvalues, a strong discrepancy, due to a bad SCF description of the ground state (inaccurate basis sets), and because electron correlation effects are not considered, has always been observed between experimental and calculated IP's for molecules bearing third-row atoms involved in a double bond.[17] Moreover, extensive calculations on 1,2-dithiete **3** (and on its isomers, cis and trans ethanedithial, **1**) have concluded that the effects of electron correlation on calculated IP's at the MP2 level should be "viewed cautiously": in fact, MP2 calculations do not give more reliable evaluation of IP's than ΔSCF values neglecting electron correlation effects in the neutral and the cationic species.[18]

As the correlation of the experimental IP's with the calculated orbital eigenvalues according to Koopmans' theorem does not seem reliable, and as inclusion of electron correlation effects does not improve the results for the model compound 1,2-dithiete **3**, it did not seem worthwhile carrying out expensive ab initio calculations for the oxathiete **4** and the three isomers of thioxoethanal (**2**). Our assignment was consequently supported by comparative analysis of band intensities with photon energies (HeI 21.21 eV and HeII 40.8 eV) and by inspection of the coefficients of atomic orbitals in molecular orbitals inferred from MNDO calculations for the two compounds **2** and **4**.

For orbitals predominantly localized on sulfur, the intensity of the corresponding ionization is strongly reduced when going from HeI to HeII excitation energy.[19] This effect is stronger for pure p lone pair orbitals than for those where the sulfur lone pair interacts with another center (see for example the HeI–HeII spectra of thiirane[20] and thiophene[21]). In the present case, the HeII spectrum of the thermolysate (Figure 1c) indicates a strong decrease of the first band at 9.72 eV and a slightly smaller decrease of the third one at 11.97 eV, whereas the second band intensity is rather enhanced. From the analysis of the coefficients of atomic orbitals in molecular orbitals deduced from MNDO calculations, these observations can only be accounted for if thioxoethanal is present (and not its cyclic isomer **4**). As can be seen from the diagram (Figure 2) the HOMO of thioxoethanal is a pure p sulfur lone pair, whereas the second orbital is a nearly pure p oxygen lone pair with a slight contribution from sulfur. The third orbital is described as a pure π_{CS} double bond while the π_{CO} double bond in very weak interaction with π_{CS} is expected at deeper energetic levels. On the other hand, for the cyclic oxathiete **4**, the MNDO coefficients indicate a strong contribution from sulfur for all the first three orbitals. For this molecule, a rather slight decrease of the first three bands should be observed.

Our assignment is further supported by the correlation between the IP's of methanal, methanethial, and thioxoethanal described in Figure 3. It appears, from this diagram, that the interaction between the formyl and thio-

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[12] Parham, W. E.; Heberling, J.; Wynberg, H. *J. Am. Chem. Soc.* **1955**, *77*, 1169.

[13] Vallée, Yo.; Ripoll, J. L.; Lacombe, S.; Pfister-Guillouzo, G. *J. Chem. Res.*, in press.

[14] The different thermolysis temperatures between the IR and PES experiments may be accounted for by the differences between the operating conditions such as vacuum, sample inlet pressure, oven length, and thermocouple location.

[15] Solouki, B.; Rosmus, P.; Bock, H. *J. Am. Chem. Soc.* **1976**, *98*, 6054.

[16] B'Shary, I.; Guimon, C.; Grimaud, M.; Pfister-Guillouzo, G. *Can. J. Chem.* **1988**, *66*, 2830.

[17] Bruna, P. J.; Krumbach, V.; Peyerimhoff, S. D. *Can. J. Chem.* **1985**, *63*, 1594. Lacombe, S.; Gonbeau, D.; Cabioch, J. L.; Pellerin, B.; Denis, J. M.; Pfister-Guillouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 6964. Watts, J. D.; Rittby, M.; Bartlett, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 4155.

[18] Goddard, J. D. *J. Comput. Chem.* **1987**, *8*, 389. Von Niessen, W.; Cederbaum, L. S.; Domcke, W.; Diercksen, G. H. F. *J. Chem. Phys.* **1977**, *66*, 4893.

[19] Schulz, R.; Schweig, A.; Hartke, K.; Köster, J. *J. Am. Chem. Soc.* **1983**, *105*, 4519.

[20] Schweig, A.; Thiel, W. *Mol. Phys.* **1974**, *27*, 265.

[21] Schweig, A.; Thiel, W. *Chem. Phys. Lett.* **1973**, *21*, 541.

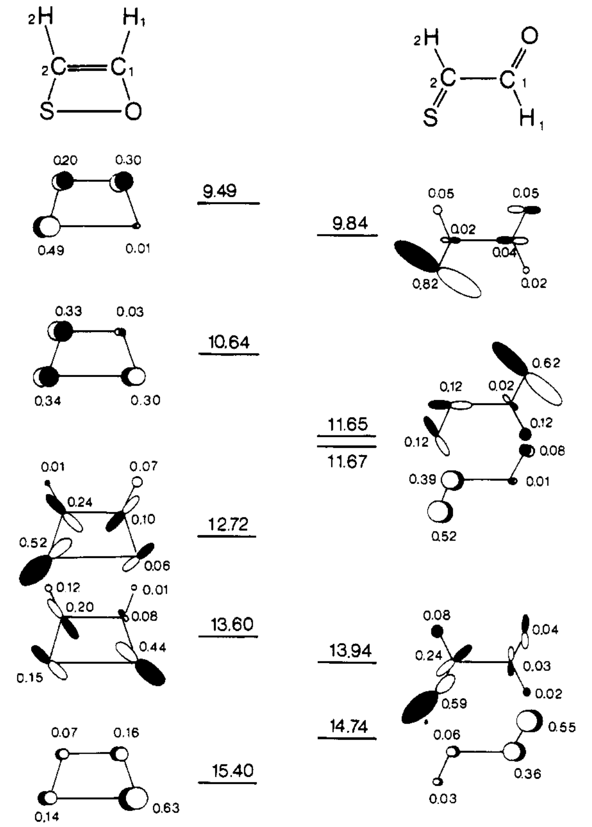

Figure 2. MNDO calculated orbital eigenvalues and squared coefficients of 4 and 2 (performed on MNDO optimized geometries: 4 (distances in Å) C^1–C^2, 1.372; C^2–S, 1.710; C^1–O, 1.382; C^1–H^1, 1.079; C^2–H^2, 1.070; (angles in degrees) C^2C^1O, 99.66; $H^1C^1C^2$, 138.86; SC^2C^1, 90.50; $H^2C^2C^1$, 136.92; SC^2C^1O, 0; $OC^1C^2H^2$, 180. 2 (distances in Å) C^1–C^2, 1.499; C^1–O, 1.221; C^1–H^1, 1.109; C^2–S, 1.544; C^2–H^2, 1.097; (angles in degrees) C^2C^1O, 123.26; $H^1C^1C^2$, 115.18; SC^2C^1, 124.74; $H^2C^2C^1$, 114.86; SC^2C^1O, 180; $OC^1C^2H^2$, 0).

formyl moieties of **2** is very weak, in agreement with the molecular orbitals description inferred from the MNDO and ab initio calculations. The first IP at 9.72 eV, attributed to the ejection of an electron from the sulfur lone pair, was observed somewhat deeper (0.34 eV) than in methanethial, owing to the inductive effect of the carbonyl group. The second band at 10.87 eV, associated with the ejection of an electron from the oxygen lone pair in very weak interaction with sulfur, was observed exactly at the same energetic level as in methanal. The third band at 11.97 eV, assigned to the ionization of the π_{CS} orbital is, as the first IP, slightly stabilized (0.21 eV) relative to methanethial. Two IP's are assigned to the fourth band, the first one attributed to the ionization of the σ_{CS} orbital, and the second to the ejection of an electron from the orbital localized on the π_{CO} double bond, weakly destabilized relative to methanal.

Briefly, the prominent feature from this diagram is the weak interaction through the σ_{CC} bond between the formyl and thioformyl moieties, in contrast with the glyoxal case. Only a slight inductive effect of the carbonyl group on the thiocarbonyl lone pair was observed. The π_{CS} double bond is somewhat stabilized relative to methanethial, and the π_{CO} double bond slightly destabilized relative to methanal. These observations point out the counterbalance between inductive and mesomeric effects.

Turning back to the results of MNDO calculations, it may be seen (Figures 2 and 3) that whereas the first and third calculated eigenvalues are in good agreement with the experimental IP's (9.84 and 11.67 for 9.72 and 11.97), this no longer holds true for the second one. The calculated eigenvalue is found 0.78 eV lower than the experimental IP, thus reflecting that the calculation method does not take the polarization effects of the oxygen lone pair properly into account.

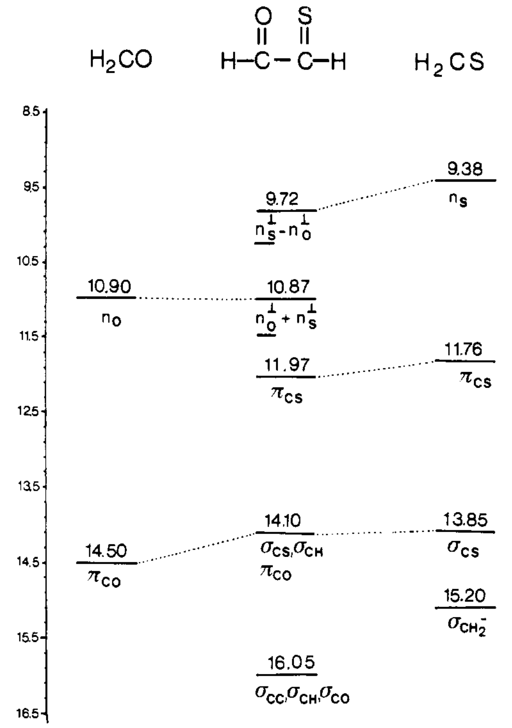

Figure 3. Correlation diagram between the experimental ionization potentials of methanal, thioxoethanal (**2**) and methanethial (**6**).

Dienophilic Reactivity. Trapping experiments with 1,3-dienes were undertaken in view to confirm the formation of thioxoethanal, **2**. According to our previous PE conclusions concerning the nature of its HOMO (pure sulfur lone pair) and its slightly stabilized energetic position relative to methanethial, thioxoethanal was expected to be a good dienophile by reference to other simple thioaldehydes.[22]

Dihydrooxathiin **5** was evaporated through the oven heated at 850 °C,[14] while an excess of gaseous diene was injected at the oven exit. Condensation of the products at −196 °C, followed by liquid chromatography, led to the expected, previously unknown, Diels–Alder adducts **7**, **8**, and **9** (Scheme II). As other thioaldehydes,[23,24] thioxoethanal **2** showed an endo selectivity when reacted with cyclic dienes. Adduct **8** was obtained, from the reaction with cyclopentadiene, as a 4/1 mixture of stereoisomers. On the ground of ^1H NMR analysis, the major isomer was attributed as endo, in agreement with[23,25] [δH^3 (8 endo) = 4.20 > δH^3 (8 exo) = 3.23; δCHO (8 endo) = 9.05 < δCHO (8 exo) = 9.90; $J_{H^3H^4}$ (8 endo) = 3 > $J_{H^3H^4}$ (8 exo) = 0]. With cyclohexadiene, practically a single isomer was observed (^1H and ^{13}C NMR, selectivity > 20/1), most likely endo (**9**, $J_{H^3H^4}$ = 3).[25]

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(22) Vedejs, E.; Eberlein, T. H.; Mazur, D. J.; McClure, C. K.; Perry; D. A.; Ruggeri, R.; Schwartz, E.; Stults, J. S.; Varie, D. L.; Wilde, R. G.; Wittenberger, S. *J. Org. Chem.* **1986**, *51*, 1556 and references therein.

(23) Vedejs, E.; Stults, J. S.; Wilde, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5452.

(24) Bladon, C. M.; Ferguson, I. E. G.; Kirby, G. W.; Lochead, A. W.; McDougall, D. C. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1541. Krafft, G. A.; Meinke, P. T. *Tetrahedron Lett.* **1985**, *26*, 1947.

(25) Gaudemer, A. In *Stereochemistry. Fundamentals and Methods*; Kagan, H. B., Ed.; Georg Thieme Publishers: Stuttgart, 1977; Vol. 1, p 44.

The cleavage of thioxoethanal (**2**) into methanethial (**6**) and carbon monoxide at higher temperature was further confirmed by trapping **6** with a 1,3-diene. FVT of 2,3-dihydro-1,4-oxathiin (**5**) at 1000 °C in the presence of cyclopentadiene gave, albeit in low yield, the expected adduct **10**[26] (Scheme II).

In the same way, the thermolysis of 6-methyl-2,3-dihydro-1,4-oxathiin (**11**) (Scheme II) led to the corresponding 1-thioxopropan-2-one, **12**, previously photochemically synthesized.[22,23] The thioaldehyde **12** was trapped by cyclopentadiene to give the endo adduct **13** in 60% yield. The exo adduct[23] was not detected.

Experimental Section

The following apparatus were used: ^{1}H NMR, Varian A 60 D and EM 360 (60 MHz). ^{13}C NMR, Bruker WP 80 SY (20.15 MHz); δ are given in ppm relative to internal $SiMe_4$ and J in hertz. IR, Perkin-Elmer 1420. MS, Nermag R10 10H. The oxathiins **5** and **11** were prepared by known methods.[12,27]

FVT of 5, IR Spectrum of Thioxoethanal, 2. Compound **5** (0.02 mL) was vaporized through a quartz oven (l = 12 cm; i.d. = 1.6 cm; 850 °C; 10^{-5} mbar) fitted on an Air Liquide optical cryostat (NaCl sample carrier and windows), and the IR spectrum of the thermolysis products (frozen film at −196 °C) was recorded in situ.

PE Spectra. The PE spectra were recorded on an Helectros 0078 photoelectron spectrometer equipped with a 127° cylindrical analyzer and monitored by a microcomputer supplemented with a digital analog converter. The spectra are calibrated on the known ionization of xenon (12.13 and 13.43 eV) and argon (15.76 and 15.93 eV). The IP's are accurate to ±0.02 eV. The thermolysis oven directly fitted on the inlet probe has been described elsewhere[13] and was designed by H. J. Lempka (Helectros Developments, Beaconsfield, U.K.); the distance between the oven exit and the ionization head does not exceed 1 cm. Compound **5** was slowly vaporized under low pressure (10^{-5} mbar in the ionization chamber) directly in the oven, and the gaseous thermolysate was continuously analyzed. The HeII spectrum was recorded in the same way except that the analyzer voltage and the sensibility were modified.

MNDO calculations were performed with the AMPAC program[28] on a Vax computer. Ab initio optimizations were performed with the Monstergauss program[29] with a 3-21G* basis set.

Diels–Alder Reactions. Representative Example: Trapping of Thioxoethanal with Cyclopentadiene. During the thermolysis of 0.1 mL (118 mg, 1.16 mmol) of the oxathiin **5** (same FVT conditions as for IR spectrum), 1 mL of freshly distilled cyclopentadiene was injected at the oven exit. The products and excess cyclopentadiene were condensed in a liquid nitrogen trap and then warmed to room temperature under N_2. Cyclopentadiene was evaporated under reduced pressure. The adduct was separated from dicyclopentadiene and polymers by passing through a short silica gel column (eluant: pentane and then pentane/CH_2Cl_2 50/50); 86 mg (0.61 mmol; yield 53%) of adduct **8** was isolated as a colorless liquid.

3-Formyl-2-thiabicyclo[2.2.1]hept-5-ene (8): endo/exo mixture (ratio 4/1); ^{1}H NMR ($CDCl_3$) δ (endo) 1.60–1.80 (m, 2 H, CH_2), 3.60–3.90 (m, 1 H, H^4), 4.20 (dd, J = 3 and 6, 1 H, H^3), 4.30 (m, 1 H, H^1), 6.05 (dd, J = 3 and 6, 1 H, HC═), 6.65 (dd, J = 3 and 6, 1 H, HC═), 9.05 (d, J = 6, 1 H, CHO); the minor exo isomer was characterized by signals at 3.23 (d, J = 5, H^3) and 9.90 (d, J = 5, CHO); ^{13}C NMR ($CDCl_3$) δ (endo) 49.01, 51.83, 53.04, 58.76, 128.53, 138.21, 199.56; δ (exo) 47.45, 47.79, 52.41, 57.73, 132.05, 138.94, 197.44; IR ($CDCl_3$) 3140, 3070, 2980, 2940, 2870, 2840, 2730, 1710, 1440, 1260, 1250, 1130, 1070 cm^{-1}; MS *m/z* 140 ($M^{\bullet+}$, 45), 111 ($M^{\bullet+}$ − CHO, 45), 79 (42), 77 (33), 66 ($C_5H_6^{\bullet+}$, 100). Anal. Calcd for C_7H_8OS: S, 22.87. Found: S, 22.65.

The following adducts have been similarly obtained by reaction of 2,3-dimethylbutadiene and cyclohexadiene, respectively.

3,6-Dihydro-4,5-dimethyl-2-formyl-2*H*-thiopyran (7): yield 39%; ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 6 H, CH_3), 2.31–2.60 (m, 2 H, CH_2), 2.70–3.00 (m, 2 H, CH_2S), 3.44 (dt, J = 1 and 5, 1 H, CH), 9.50 (d, J = 1, 1 H, CHO); ^{13}C NMR ($CDCl_3$) δ 19.71, 20.15, 27.92, 29.59, 46.72, 123.06, 125.51, 194.27; IR (NaCl) 2995, 2920, 2895, 2820, 2720, 1715, 1450, 1420, 1380, 1185, 880, 845 cm^{-1}; MS *m/z* 156 ($M^{\bullet+}$, 20), 139 (26), 124 (100), 111 (48), 105 (15), 97 (40), 85 (31), 76 (36), 60 (33), 45 (81).

3-Formyl-2-thiabicyclo[2.2.2]oct-5-ene (9): yield 21%; ^{1}H NMR ($CDCl_3$) δ 1.38–2.20 (m, 4 H, CH_2CH_2), 3.05–3.35 (m, 1 H, H^4), 3.45–3.65 (m, 1 H, H^1), 3.70 (dd, J = 3 and 4, 1 H, H^3), 6.10 (ddd, J = 1, 7 and 7.5, 1 H, HC═), 6.57 (ddd, J = 0.5, 6.5, and 7, 1 H, HC═), 9.10 (d, J = 4, 1 H, CHO); ^{13}C NMR ($CDCl_3$) δ 22.76, 29.67, 31.31, 33.70, 57.47, 129.66, 136.24, 198.08; IR (CCl_4) 3055, 2960, 2930, 2900, 2860, 2815, 2710, 1720, 1455, 1370, 1260, 1175, 905 cm^{-1}; MS *m/z* 154 ($M^{\bullet+}$, 12), 125 ($M^{\bullet+}$ − CHO, 45), 97 (100), 79 (43), 76 (26), 45 (18). Anal. Calcd for $C_8H_{10}OS$: S, 20.79. Found: S, 21.30.

The previously known adduct **10**[26] was obtained in the same way after thermolysis of **5** at 1000 °C and trapping of **6** with cyclopentadiene (yield 6%).

The thermolysis of 6-methyl-2,3-dihydro-1,4-oxathiin (**11**) at 800 °C in the presence of cyclopentadiene gave the endo adduct **13** (yield 60%, ^{1}H NMR data in agreement with that of ref 23).

Registry No. **2**, 82563-94-8; **5**, 6538-93-8; **6**, 865-36-1; **7**, 126019-26-9; *endo*-**8**, 126019-27-0; *exo*-**8**, 126019-29-2; **9**, 126019-28-1; **10**, 6841-59-4; **11**, 3643-97-8; **12**, 120512-87-0; **13**, 824-60-2; $CH_2{=}C(CH_2)C(CH_3){=}CH_2$, 513-81-5; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4.

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(26) Johnson, C. R.; Keiser, J. E.; Sharp, J. C. *J. Org. Chem.* **1969**, *34*, 860.

(27) Rooney, R. P.; Dyer, J. C.; Evans, S. A. Jr. *J. Org. Magn. Reson.* **1981**, *16*, 266.

(28) Dewar, M. J. S.; Stewart, J. J. P. *Q.C.P.E. Bull.* **1986**, *6*, 24.

(29) Monstergauss (June 1981), Petersen, N.; Powier, K.; Chemistry Department, University of Toronto, Ontario, Canada.