oxy]trimethylsilane,[9] ^{1}H NMR (C_6D_6) δ 0.14 (9 H, s), 0.88 (3 H, t), 1.65 (3 H, s), 1.87 (2 H, m), 4.75 (1 H, t).

Reactions of 2-Pentanone and 2-Pentanone-*1,1,1*-d_3 with Dialkylamide Bases. The standard procedure for preparation of the base solution involved adding 8.25–8.70 × 10^{-4} mol of amine to 7.5–8.7 × 10^{-4} mol of *n*-butyllithium in 3.0 mL of THF, at 0 °C for diisopropylamine and at −10 °C for tetramethylpiperidine. For hexamethyldisilazane the solution was prepared at room temperature and after 5 min heated to 48 °C and stirred for 15 min. It was then cooled to the temperature of the reaction and left standing for 15 min. This was necessary to ensure high yields and reproducible product ratios in the subsequent deprotonation. When HMPA was used, 3 mol/mol of base was added and the solution kept at the reaction temperature for 15–20 min prior to addition of ketone. To the base solution was added dropwise with stirring 2.5 × 10^{-4} mol of ketone in 0.2 mL of THF (see ref 8 for details of the procedure). The final solution before reaction was thus approximately 0.25 M in base, 0.75 M in HMPA (when added), and 0.08 M in ketone. See the text and Table III for the small number of cases where there were departures from these standard conditions. When the base/ketone ratio was varied (Figures 12 and 13), the base concentration was kept the same as in the standard procedure and the ketone concentration changed appropriately. The enolates were quenched after 10 min by adding 1.2 mol of trimethylsilyl chloride/mol of base. The time of quenching did not affect the results, and the quenched solutions were stable for at least 24 h. See ref 8 for details of other control experiments in a closely related system. The products were analyzed by GLC, using a J&W Scientific DB-1 (cross-linked silicone) 30-m × 0.55-mm i.d. fused silica capillary column. The column, injector, and detector temperatures were 40, 100, and 150 °C, respectively. At 60 psi of helium, 30 psi of hydrogen, and 26 psi of air, approximate retention times were 13 min for (1-pentenyl-2-oxy)-trimethylsilane, 15 min for [(*Z*)-2-pentenyl-2-oxy]trimethylsilane, and 16 min for [(*E*)-2-pentenyl-2-oxy]trimethylsilane. Peaks were cleanly separated. Toluene (retention time 6 min) was the internal standard for yield determinations. The response factor was 2.101 by weight.

Equilibration of Enolates. Solutions of LDA, LTMP, and LHMDS were prepared as above, except 8.25 × 10^{-3} mol of amine was added to 7.5 × 10^{-3} mol of butyllithium in ca. 22 mL of THF at 0 °C. When HMPA was used, 3 mol/mol of base was added. The solution was stirred at 0 °C for 20 min and 1.25 mol of ketone/mol of base (25% excess) added. Aliquots (2 mL) were taken at regular time intervals (usually 30 or 60 min) and quenched with trimethylsilyl chloride. The mixture was worked up and analyzed by GC as above. Aliquots were taken until the product ratios showed no further change.

Supplementary Material Available: Tables S1–S5 containing product ratio data used in Figures 1 and 3–7 and Tables S6 and S7 containing data on enolate equilibration used in Figures 8 and 9 (4 pages). Ordering information is given on any current masthead page.

2,5-Dithiacyclopentylideneketene and Ethenedithione, S=C=C=S, Generated by Flash Vacuum Pyrolysis

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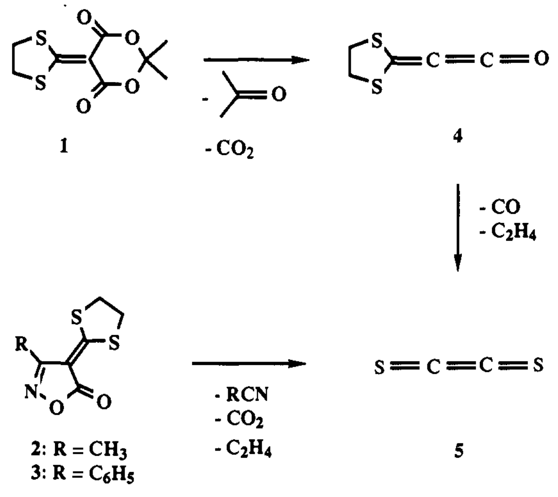
Contribution from the Department of Chemistry, The University of Queensland, Brisbane, Queensland, Australia 4072, Laboratoire de Chimie Organique Physique, Université de Reims, F-51062 Reims, France, and Laboratoire de Chimie Organique, Université de Mons Hainaut, B-7000 Mons, Belgium. *Received October 29, 1990*

Abstract: 2,5-Dithiacyclopentylideneketene (**4**) is obtained by flash vacuum pyrolysis (FVP) of the Meldrum's acid derivative **1** and characterized by MS, IR, and NMR spectroscopy. **4** is stable in solution at −50 °C. FVP of **4** as well as the isoxazolone derivatives **2** and **3** results in efficient cleavage into ethylene and ethenedithione, S=C=C=S, which is remarkably stable in the gas phase at high temperature, low pressure, and short contact times but extremely unstable in the condensed state or at higher pressures.

Introduction

Methyleneketenes ($R_2C{=}C{=}C{=}O$) are of considerable interest because of their high reactivity, which has led to the discovery of a series of remarkable molecular transformations.[2,3] In this paper we report the preparation of a relatively stable methyleneketene **4** as well as its use, surprising at first sight, in an efficient generation of ethenedithione, S=C=C=S. This molecule, like the other higher oxides and sulfides of carbon, has been the focus of much recent theoretical and experimental activity. Whereas the odd-membered compounds C_3O_2, C_3S_2, C_3OS, and C_5O_2 are relatively stable,[4] even-membered analogues have become known only very recently. Theory[5] predicts C_2O_2 and C_2S_2 to be

Scheme I



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[1] (a) University of Queensland. (b) Université de Reims. (c) Université de Mons.

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[3] (a) Wentrup, C.; Lorencak, P. *J. Am. Chem. Soc.* **1988**, *110*, 1880. (b) Lorencak, P.; Pommelet, J. C.; Chuche, J.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1986**, 369. (c) Ben Cheikh, A.; Chuche, J.; Manisse, N.; Pommelet, J. C.; Netsch, K. P.; Lorencak, P.; Wentrup, C. *J. Org. Chem.* **1991**, *56*, 970–975. (d) Baxter, G. J.; Brown, R. F. C. *Aust. J. Chem.* **1978**, *31*, 327. (e) McNab, H. *J. Org. Chem.* **1981**, *46*, 2809. (f) Pommelet, J. C.; Dhimane, H.; Chuche, J.; Celerier J.-P.; Haddad, M.; Lhommet. G. *Ibid.* **1988**, *53*, 5680. (g) Scharp, J.; Wiersum, U. E. *J. Chem. Soc., Chem. Commun.* **1983**, 629.

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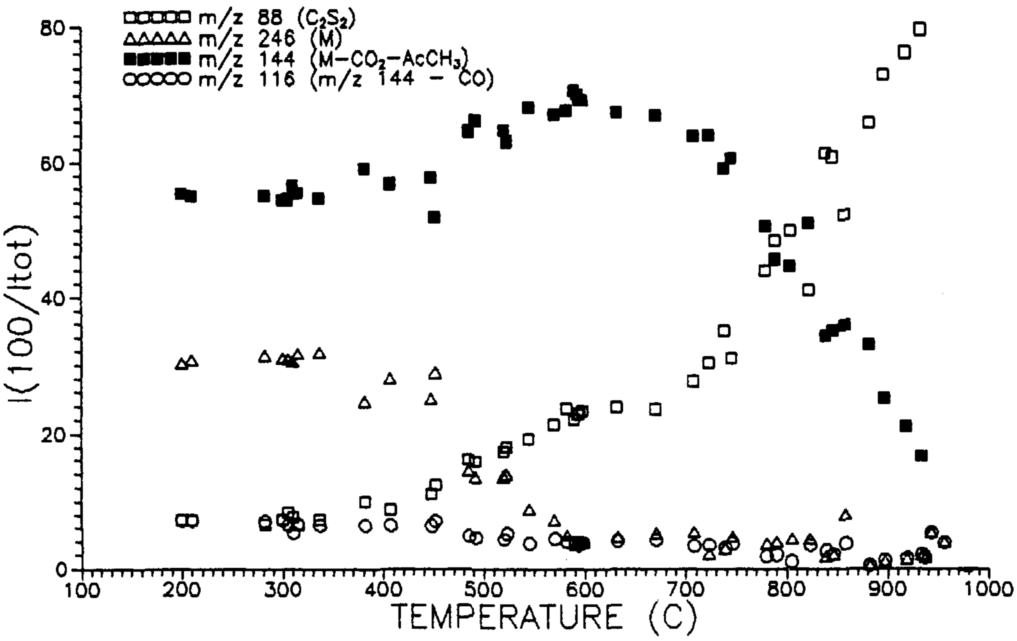


Figure 1. Temperature profiles for ions in the flash vacuum pyrolysis–mass spectrometry of **1**. Ordinates: relative intensities versus total ion current.

linear triplet ground state molecules, with $^3C_2S_2$ being an absolute minimum, about 39 kcal/mol below two isolated molecules of ^1CS. A significant barrier toward dissociation of C_2S_2 into 2CS may therefore be expected, and the synthesis of C_2S_2 should be possible under suitable conditions.[5] Indeed, Schwarz and co-workers, with use of the technique of neutralization–reionization mass spectroscopy (NRMS), have demonstrated the existence of the neutral molecules C_2S_2,[6] C_2OS,[7] C_4S_2,[8] and C_4O_2,[9] with lifetimes of at least 0.5 μs. Maier and co-workers with use of matrix isolation spectroscopy also identified[10] C_4O_2 and, very recently,[11] C_2S_2. So far, all attempts to detect C_2O_2 have been unsuccessful.[12]

It is important to verify the existence of unusual molecules with use of a variety of spectroscopic techniques as well as different methods of generation. Here, we report three thermal methods of production of C_2S_2 from the precursors **1**–**3** and establish the crucial link between NRMS and matrix isolation studies, proving that the thermally produced molecule is identical with the one detected in the mass spectrometer. We also show that C_2S_2 is quite long-lived in the gas phase at low pressure, even at very high temperatures.

Results

2,5-Dithiacyclopentylideneketene (4). The Meldrum's acid derivative **1** was subjected to flash vacuum pyrolysis (FVP) in

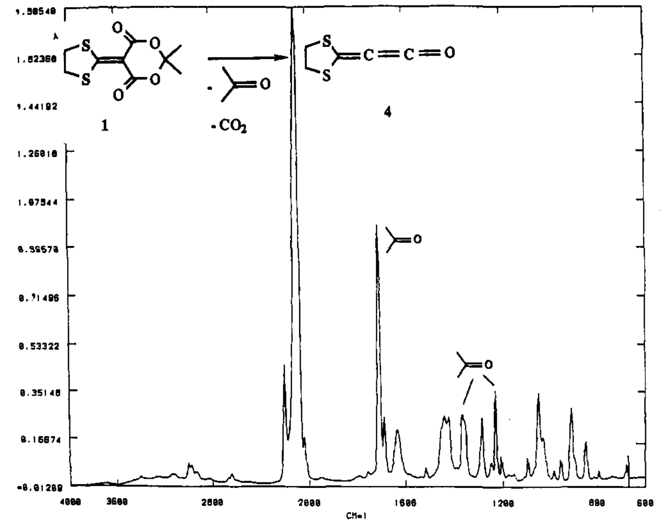
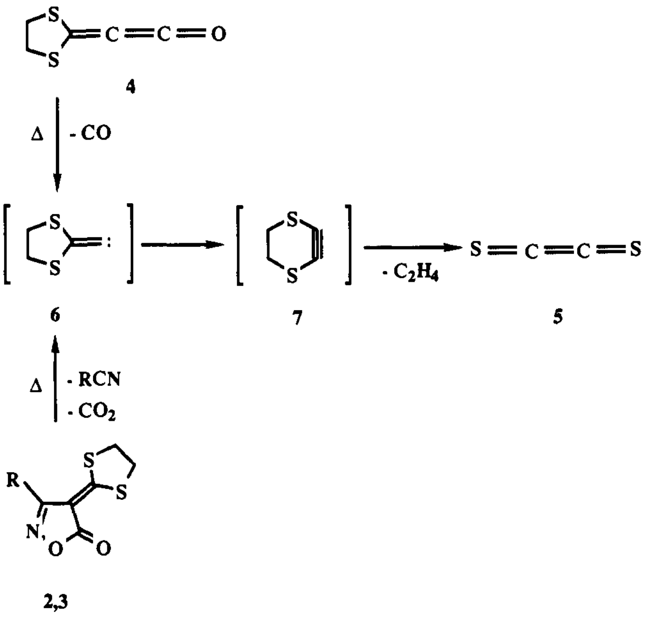


Figure 2. FTIR spectrum of **4** (77 K) produced by FVP of **1** at 675 °C.

Scheme II



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an apparatus employing a 10-cm quartz tube directly attached to the ion source of a mass spectrometer. As the pyrolysis temperature was increased, the intensity of the molecular ion of **1** decreased and had almost completely vanished at 600 °C. At the same time, the signal corresponding to **4** (*m/z* 144) increased in intensity, reaching a plateau at ca. 500–700 °C, and persisted after all the starting material (**1**) had been consumed (Figure 1). The subsequent decomposition of **4** at higher temperatures is described below.

Infrared spectroscopy confirmed the assignment of the *m/z* 144 species to methyleneketene **4**. By using a similar FVP appliance with Ar matrix isolation at 12 K, a strong ketene absorption was observed at 2078 and 2094 (shoulder) cm^{-1} together with bands due to CO_2 and acetone. The optimum temperature for formation of the ketene was 675 °C, at which temperature the starting material had been completely converted. The ketene was sufficiently stable for isolation as a neat solid at 77 K, giving the IR spectrum displayed in Figure 2. (It is often found that CO_2 condenses on the colder metal parts of the cryostat and not on the KBr disk when 77 K isolation is used; hence CO_2 does not appear in the spectrum in Figure 2. When Ar matrix isolation is used, CO_2 appears at 2340 cm^{-1}).

The use of neat rather than Ar matrix isolation is advantageous because the thermal stability of the product can be assessed more readily. The neat ketene was fairly long-lived on warmup, disappearing between −60 and −10 °C. At −50 °C its half-life was ca. 20 min.

The stability of **4** also permitted the recording of its ^1H NMR spectrum in CD_2Cl_2 solution at −45 °C, which featured a single peak at δ 3.70 ppm. The IR spectrum of this solution confirmed the continued presence of the strong ketene absorption (2080 cm^{-1}), which survived even on brief exposure to room temperature.

The ensemble of observations (IR, MS, NMR), in particular the fact that the IR-active ketene shows the same temperature profile as the *m/z* 144 species (Figure 1), identifies it as 2,5-dithiacyclopentylideneketene (**4**). The frequency of the C=C=O stretching vibration below 2100 cm^{-1} is typical of methyleneketenes.[3a,13]

Ethenedithione (C_2S_2, 5). As the ketene **4** (*m/z* 144) started disappearing at temperatures above 600 °C (Figure 1), a peak at *m/z* 88, corresponding to C_2S_2, increased strongly and at 940 °C was the most important peak (disregarding the strong signals at *m/z* 28 (CO and C_2H_4) and 44 (CO_2 and CS) (not shown)). A peak corresponding to 3,6-dithiacyclohexyne (*m/z* 116) was also present at low level; it showed no significant intensity increase with rising temperature but survived after the starting material (**1**) had been largely consumed and decreased markedly above 450 °C when the C_2S_2 signal started becoming prominent (Figure 1).

We have previously shown that 4-methyleneisoxazol-5(4*H*)-ones decompose on FVP to a nitrile, CO_2, and a vinylidene, without the intervention of a methyleneketene.[13b,c14] Therefore, the isoxazolones **2** and **3** may be expected to give the same products as obtained by decarbonylation of ketene **4**.

In the event, FVP–MS of **2** and **3** demonstrated formation of CO_2 and the corresponding nitrile as well as the *m/z* 88 ion ascribed to C_2S_2 (spectra are listed in the Experimental Section). Temperature profiles are shown in Figure 3 and demonstrate rapid increase in the intensity of the *m/z* 88 (C_2S_2) signal as pyrolysis of **2** and **3** sets in above 600 °C.[15]

The identity of the thermally produced C_2S_2 (*m/z* 88) species from **1**, **2**, and **3** was demonstrated by collision-activation mass spectrometry (CAMS). Identical CAMS were obtained in all three cases as shown in Figure 4. The fragment ions due to S^+, $CS^{\bullet+}$, C_2S^+, $S_2^{\bullet+}$, and $CS_2^{\bullet+}$ clearly identify the species as C_2S_2. Most importantly, the spectrum is also identical with the CAMS and NRMS spectra of the purely mass spectrometrically generated C_2S_2 species.[6]

By using Ar matrix isolation and infrared detection under the conditions where mass spectrometry had demonstrated the presence of C_2S_2, a new absorption was observed at 1180 cm^{-1}. In the FVP of **1**, the 1180-cm^{-1} signal kept increasing as the ketene band due to **4** decreased, and it was accompanied by bands due to C_2H_4, CO (2138 cm^{-1}), CS (1274 cm^{-1}), and CS_2 (1527 cm^{-1}) and, of course, bands due to acetone and CO_2 from the fragmentation of **1**. A typical spectrum is shown in Figure 5a. Even at a FVP temperature of 950 °C, the 1180-cm^{-1} band was still very strong; at higher temperatures it started to decrease, and more CS was formed. The same 1180-cm^{-1} species was formed on FVP of **2** and **3**. In the case of **2**, the 1180-cm^{-1} species was accompanied by signals due to acetonitrile, CO_2, and C_2H_4, and, in the case of **3**, the same spectrum was obtained except that benzonitrile had replaced acetonitrile (Figure 5b).

Comparison with the IR spectrum obtained by Maier et al.[11] by matrix photolysis of cyclic dithiocarbonates, which lend themselves much more logically to C_2S_2 formation, leaves no doubt that the same species has been generated in the two laboratories. The 1180-cm^{-1} band is in agreement with predictions[5] (1262 cm^{-1} (calcd), 1127 cm^{-1} (corr.)) for the asymmetric C=S stretch in S=C=C=S. The isotopic satellites due to ^{34}SCCS and S^{13}CCS are clearly seen at 1176 and 1163 cm^{-1}, respectively (Figure 5), with the correct relative intensities (ca. 10% and 2.5% of the main band, respectively), in conformity with a symmetrical molecule containing two sulfur and two carbon atoms. No other IR active bands are predicted for C_2S_2 above 300 cm^{-1}.[11] We cannot confirm the observation[11] of a combination band at 3083 cm^{-1}, however, and a further combination band[11] at 1725 cm^{-1} may be too weak for clear-cut assignment in our spectra. The main 1180-cm^{-1} band (1179.3 cm^{-1}[11]) is, however, identical in all cases, and the agreement is further corroborated by the UV spectrum.

The Ar matrix UV spectrum of C_2S_2 generated from **3** at 700 °C is shown in Figure 6. The band shape and wavelengths of the progression at 361–392 nm was identical for C_2S_2 produced from **1** at 900 °C and from **2** at 800 °C. The spectrum is also identical with that reported by Maier[11] and assigned to the π–π^* transition of C_2S_2. A Rydberg band[11] near 200 nm could not be confirmed.

The combination of the three spectroscopic methods (MS, IR, UV) and three different precursors (**1**–**3**) identify the observed molecule as the linear S=C=C=S (**5**). The question of spin state cannot be addressed by the present investigation, but it is quite certain that C_2S_2 has remarkable properties. It is surprisingly stable in the gas phase, even at nominal temperatures as high as 1000 °C and contact times of the order of milliseconds. This is true as long as the pressure is low (10^{-4} mbar). Under such conditions, good matrices with strong C_2S_2 peaks and little CS can be obtained (Figure 5). However, too rapid sublimation of the starting materials (**1**–**3**) suffices to generate a higher partial pressure of C_2S_2, which causes a drastic diminution of the IR (or UV) peak intensities. Furthermore, in spite of its persistence in high vacuum at high temperatures, C_2S_2 does not survive con-

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(15) In the case of **2**, there is also a less important fragment at *m/z* 141, corresponding to loss of thiirane from **2**. More interestingly, in the case of **3** an intermediate is seen at *m/z* 219, which is due to loss of CO_2 from **3**. This intermediate disappears above 750 °C, but another thermal product with *m/z* 159 continues to increase (Figure 3b). The mass of this product corresponds to Ph—N=C=C=C=S, and a corresponding peak in the Ar matrix IR spectrum at 2090 cm^{-1} may be due to this compound. The present 2090-cm^{-1} species is different from ketene **4**, and it is not formed from **2**. The decomposition of isoxazolones with expulsion of CO_2 and retention of the "nitrile" moiety is not uncommon, particularly in the case of phenylisoxazolones: Wollweber, H.-J.; Wentrup, C. *J. Org. Chem.* **1985**, *50*, 2041. Wentrup, C. *Adv. Heterocycl Chem.* **1981**, *28*, 251.

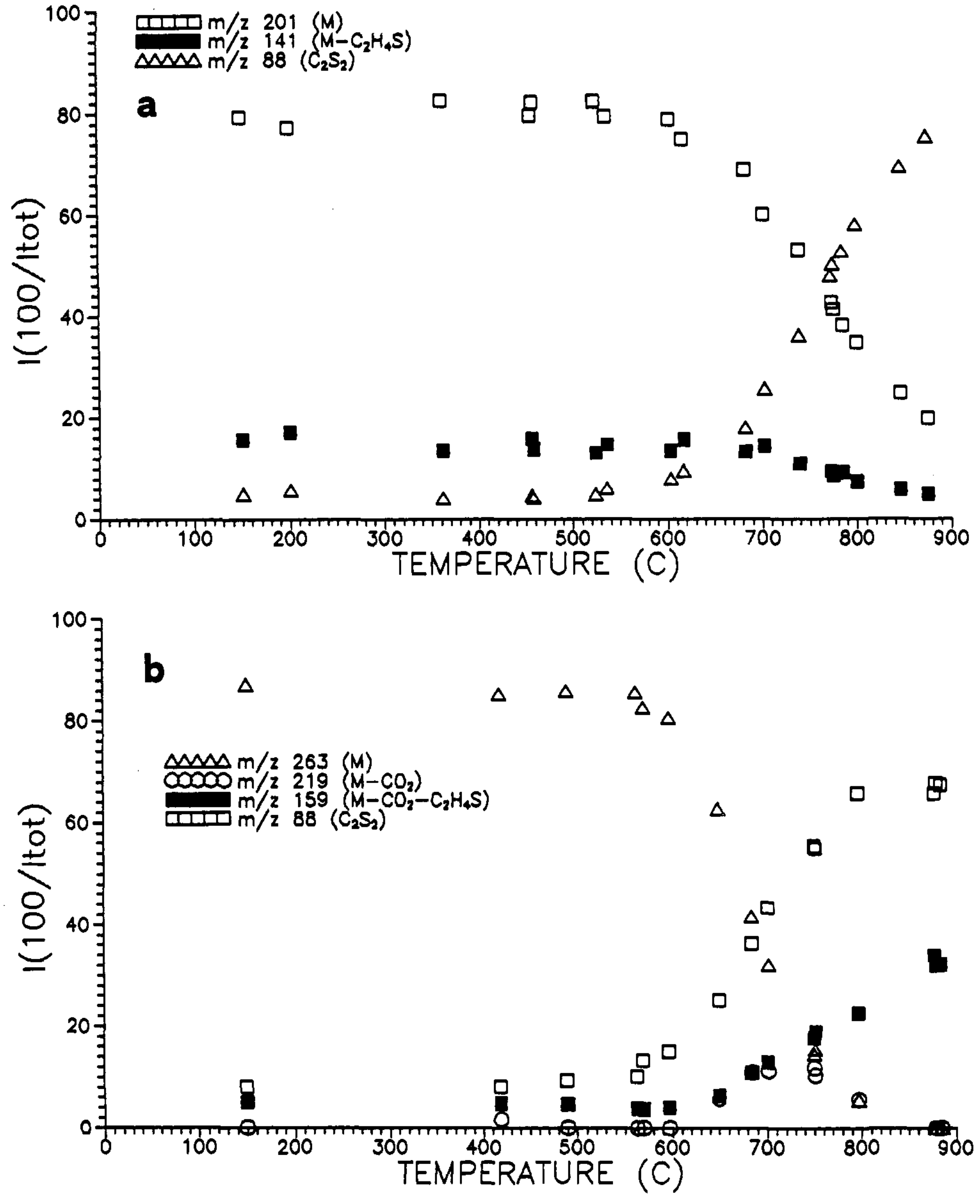

Figure 3. Temperature profiles for ions in the FVP–MS of (a) **2** and (b) **3**.

densation at 77 K. Neat condensation at 12 K without Ar gives a signal of diminished intensity at 1170 cm^{-1}, which disappears on warming to 60 K. C_2S_2 is also photochemically unstable.[11] It is completely destroyed in 9 min by broad-band UV irradiation (Ar matrix, 12 K; high-pressure Hg lamp) as observed by IR and UV spectroscopy. The IR band due to CS increases in intensity during the destruction of C_2S_2 but with a complex band structure, presumably due to the fact that CS is not formed as individual, matrix-isolated molecules but as bimolecular aggregates within the matrix cavities.

C_2S_2 is so stable at low partial pressure (ca. 10^{-4} mbar) that is survives the use of an insert of quartz rods in the pyrolysis tube, thereby increasing the surface area and collision number. There is therefore little doubt that it will also be possible to obtain high-resolution gas-phase spectra of **5**.[16]

The unusual properties—thermodynamic stability and extreme intermolecular reactivity—may well of those of a ground-state triplet molecule.[16]

Discussion and Outlook

A mechanistic rationale for the facile formation of C_2S_2 is given in Scheme II and builds on the previous observation[13c,17] that cyclohexyne, generated by FVP of cyclopentylideneketene or 4-cyclopentylideneisoxazol-5(4*H*)-ones, undergoes a formal [2 + 4]cycloreversion to ethylene and butatriene.

Thus, CO elimination from **4** and direct fragmentation of both **2** and **3** will generate the short-lived vinylidene **6**. Ring expansion generates 3,6-dithiacyclohexyne (**7**), for which there is evidence in the form of the *m/z* 116 ion in the mass spectrum.[16] Just as cyclohexyne is difficult to detect[13c] due to its fragmentation, **7** does not build up to appreciable quantities but fragments to C_2H_4 and S=C=C=S, which has been abundantly identified above.

The ease of generation of C_2S_2, in the gas phase and its longevity under the proper reaction conditions give hope that it will be possible to generate other molecules of the type X=C=C=Y by using similar techniques.[16] The molecule HN=C=C=NH and its derivatives are of particular interest to us.[18]

Conclusion

Our results build an essential bridge between the mass spectrometric and matrix-isolation techniques. The S=C=C=S molecule produced thermally in the gas phase is identical with the one generated by fragmentation of ions in the mass spectrometer and neutralized in the NRMS experiment.[6] It is also identical with the one isolated in low-temperature matrices. C_2S_2

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(16) These matters are the subject of further investigation.

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(18) Lorencak, P.; Raabe, G.; Radziszewski, J. J.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1986**, 916.

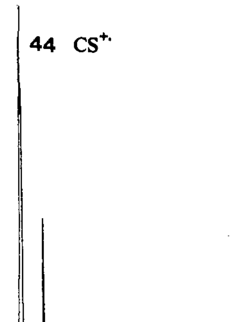

Figure 4. Collision-activation mass spectra of the m/z 88 ions (C_2S_2, **5**) produced by FVP of (a) **1** at 590 °C, (b) **2** at 778 °C, and (c) **3** at 797 °C.

is stable in the gas phase at high temperatures, low pressure, and short contact times but extremely unstable in the condensed state. It should be detectable by other rapid gas-phase spectroscopic techniques.

Experimental Section

The pyrolysis apparatus for Ar matrix and 77 K FTIR and UV spectroscopy was as previously reported[13c] and employed a 10-cm (0.8-cm i.d.) electrically heated quartz tube with a distance of 5 cm between the hot zone and the cryostat target. Ovens of similar design were directly attached to the ion sources of the mass spectrometers. IR spectra were recorded on a Perkin Elmer 1700X FTIR, UV spectra on a Cary 1 (Varian), and mass spectra on a Kratos MS25RFA on a Varian Mat 311A spectrometer.

2,2-Dimethyl-5-(2,5-dithiacyclopentylidene)-1,3-dioxane-4,6-dione (1) was prepared according to the literature method:[19] ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 6 H), 3.57 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 27.31 (q), 38.52 (t), 101.05 (s), 104.05 (s), 161.62 (s), 191.34 (s); MS (Varian Mat, 200 °C), m/z 246 (M^+, 100), 231 (6), 189 (32), 160 (6), 144 (4, 100), 116 (7, 13), 88 (C_2S_2, 12), 84 (9), 76 (1), 64 (1), 60 (83), 58 ($(CH_3)_2CO$, 1), 44 (CO_2, 7), 43 (35); MS (591 °C), m/z 246 (M^+, 5), 231 (0), 189 (1), 160 (0), 144 (4, 0), 116 (7, 5), 88 (C_2S_2, 30), 84 (12), 76 (5), 64 (5), 60 (55), 58 ($(CH_3)_2CO$, 40), 44 (CO_2, 100), 43 (99); MS (882 °C), m/z 246 (M^+, 0), 231 (0), 189 (0), 160 (0), 144 (10), 116 (0), 88 (C_2S_2, 25), 84 (10), 76 (16), 64 (10), 60 (10), 58 ($(CH_3)_2CO$, 37), 44 (CO_2, 100), 43 (96).

4-(2,5-(Dithiacyclopentylidene)-3-methylisoxazol-5(4H)-one (2). Three grams (30 mmol) of 3-methylisoxazol-5(4*H*)-one in 12 mL of DMSO was treated with 6 g (60 mmol) of triethylamine followed by 2.5 g (33 mmol) of carbon disulfide. The flask was stoppered, and the solution was stirred for 1 h and then cooled in ice until freezing of DMSO began. Dibromoethane (6.2 g, 33 mmol) was added dropwise, causing formation of a yellow precipitate, which was collected after 10 min and washed thoroughly with water. Recrystallization from acetonitrile gave 4.6 g (77%) of **2**, mp 215 °C: ^{1}N NMR (DMSO-d_6) δ 3.73 (m, 4 H), 2.39 (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 13.56, 37.25, 37.72, 105.28, 156.59, 168.64, 177.60; IR (KBr) 1717, 1550, 1522, 1176, 1065, 1000, 890, 869, 768, 572 cm^{-1}. MS (Varian Mat, 150 °C), m/z 201 (M^+, 100), 173 (20), 141 (22), 139 (22), 88 (C_2S_2, 6), 83 (21), 81 (27), 76 (CS_2, 3), 64 (S_2, 3), 60 (10), 44 (CO_2, 5), 41 (CH_3CN, 1); MS (Varian Mat, 800 °C), m/z 201 (M^+, 20), 173 (5), 141 (5), 139 (5), 88 (C_2S_2, 40), 83 (5), 81 (5), 76 (CS_2, 72), 64 (S_2, 43), 60 (5), 44 (CO_2, 100), 41

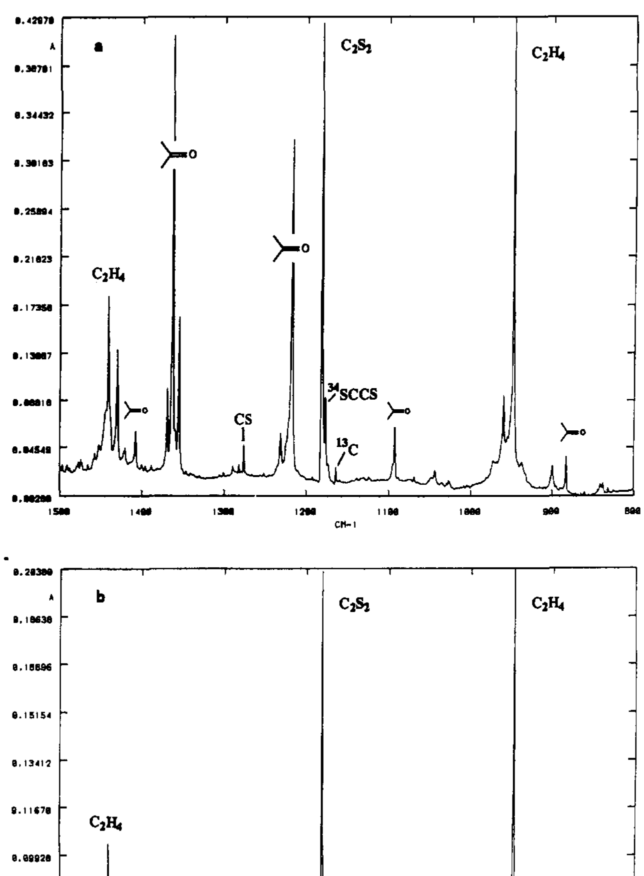

Figure 5. (a) Ar matrix FTIR spectrum (12 K) of the pyrolyzate from **1** at 900 °C (10^{-4} Torr). Bands due to acetone appear at 881, 1093, 1216, 1223, 1355, 1362, 1406, 1429, 1444, and 1722 cm^{-1} and CS_2 at 1527 cm^{-1} (absorbance 0.12). (b) Ar matrix FTIR spectrum (12 K) of the pyrolyzate from **3** at 600 °C (10^{-4} Torr). Bands at 921, 1028, 1217, 1361, 1449, and 1495 cm^{-1} are due to benzonitrile. CS_2 appears at 1527 cm^{-1} (absorbance 0.08). **2** gave a similar spectrum with CH_3CN in place of benzonitrile. Ordinates are in absorbance.

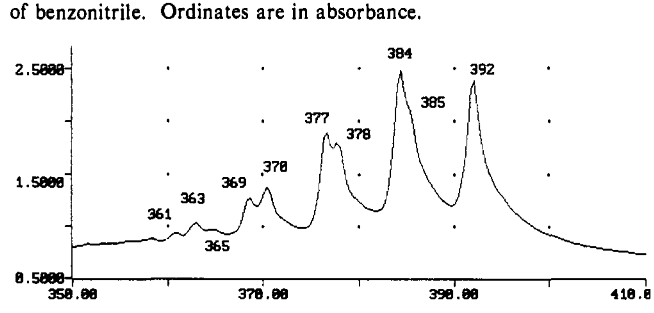

Figure 6. Ar matrix UV spectrum (12 K) of C_2S_2 (**5**) produced by FVP of **3** at 700 °C. Identical spectra were obtained from **1** at 900 °C and from **2** at 800 °C.

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(CH_3CN, 92). Anal. Calcd for $C_7H_7NO_2S_2$: C, 41.77; H, 3.51; N, 6.96. Found: C, 41.65; H, 3.44; N, 6.76.

4-(2,5-Dithiacyclopentylidene)-3-phenylisoxazol-5(4*H*)-one (3) was obtained analogously from 3-phenylisoxazol-5(4*H*)-one: yield 65%; mp 270–272 °C, ^{1}H NMR (DMSO-d_6) δ 7.53–7.49 (m, 5 H), 3.72–3.70 (m, 4 H); IR (KBr) 1722, 1527, 1385, 883 cm^{-1}. MS (Varian Mat, 150 °C), *m/z* 263 (M$^+$, 100), 235 (5), 205 (12), 167 (12), 159 (7), 145 (35), 143 (53), 103 (PhCN, 5), 92 (25), 88 (C_2S_2, 9), 77 (18), 64 (S_2, 2), 60 (10), 44 (CO_2, 5); MS (Varian Mat, 885 °C), *m/z* 263 (M$^+$, 0), 235 (0), 205 (0), 167 (0), 159 (12), 145 (0), 143 (0), 103 (PhCN, 100), 92 (0), 88 (C_2S_2, 23), 77 (32), 64 (S_2, 17), 60 (7), 44 (CO_2, 53). Anal. Calcd for $C_{12}H_9NO_2S_2$: C, 54.73; H, 3.45; N, 5.32. Found: C, 54.66; H, 3.28; N, 5.22.

2,5-Dithiacyclopentylideneketene (**4**). FVP of **1** at temperatures between 450 and 675 °C with Ar matrix isolation of the products at 12 K gave a ketene band at 2078, 2094 (shoulder) cm^{-1}, increasing in intensity with the temperature. Bands due to CO_2 (2340 cm^{-1}) and acetone were formed at the same time, and bands due to unreacted **1** decreased in intensity and had virtually disappeared at 700 °C.

FVP of **1** at 675 °C (10^{-4} mbar) with neat isolation of the product at 77 K gave rise to a very strong ketene absorption at 2080 cm^{-1} together with bands due to acetone (Figure 2) [IR (**4**, 77 K) 2080 (vs), 1625, 1420, 1293, 1054, 917, 854 cm^{-1}]. This material was stable on warming to −60 °C and disappeared on further warming to −10 °C. At −50 °C the half-life of the ketene was ca. 20 min.

In an analogous experiment, **1** was pyrolyzed at 650 °C, and the product was collected at 77 K on a cold finger. CO_2 and the majority of acetone were pumped away at −60 °C, the cold finger was recooled, and CD_2Cl_2 was distilled onto the sample. Warming to −50 °C allowed the CD_2Cl_2 solution to flow into an NMR tube [^{1}H NMR (CD_2Cl_2, −45 °C) δ 3.70 (s)]. The IR spectrum of this solution confirmed the presence of the strong C=C=O stretch at 2080 cm^{-1}, surviving brief exposure to room temperature.

The mass spectrum of **4** was obtained on both Kratos MS25RFA and Varian Mat 311 spectrometers with on-line FVP appliances. The temperature profiles of *m/z* 246 (**1**) and 144 (**4**) are shown in Figure 1. CAMS of *m/z* 144 (Variant Mat 311), *m/z* 116 (M$^+$ − CO, 75%), 88 (41), 84 (36), 60 (100).

Ethenedithione (**5**). Mass spectra of C_2S_2 (*m/z* 88) were obtained on the Kratos MS25RFA and Varian Mat 311 spectrometers with on-line FVP appliances. The temperature profile for C_2S_2 production from **1** is given in Figure 1 and from **2** and **3** in Figure 3. The CAMS of **5** (Varian Mat) produced by FVP of **1** at 590 °C, **2** at 778 °C, and **3** at 797 °C are shown in Figure 3. IR spectra (Ar, 12 K) were obtained on FVP of **1** at 700–1000 °C and of **2** and **3** at 600–1000 °C. Representative spectra are given in Figure 5: C_2S_2, 1180 cm^{-1}; ^{34}SCCS, 1176 cm (ca. 10%); S^{13}CCS, 1163 cm^{-1} (ca. 2.5%). The UV spectrum similarly obtained by FVP of **3** at 700 °C is shown in Figure 6. Identical spectra of the 350–400-nm region were obtained by FVP of **1** (900 °C) and **2** (800 °C). λ_{max} 361, 363, 369, 370, 377, 378, 384, 385 (sh), 392 nm.

The IR and UV bands ascribed to **5** disappeared on broad-band photolysis (1000 W high pressure Hg lamp) in 9 min. An increased but complex band at 1280 cm^{-1} developed during the irradiation and is ascribed to CS. Neat isolation of **5** at 12 K gave an IR band at 1170 cm^{-1}, which disappeared on warming to 60 K. The use of an insert of quartz rods in the pyrolysis tube had hardly any effet on the strength of the IR signal observed for **5** at 1180 cm^{-1} as long as the pressure was 10^{-4} mbar. Use of a higher partial pressure created by fast sublimation of **1**, **2**, or **3** or pyrolysis temperatures above 1000 °C caused increased formation of CS and CS_2 (1274 and 1527 cm^{-1}, respectively) and partial or complete disappearance of **5** (1180 cm^{-1}).

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Generation of [β-(Phenylsulfonyl)alkylidene]carbenes from Hypervalent Alkenyl- and Alkynyliodonium Tetrafluoroborates and Synthesis of 1-(Phenylsulfonyl)cyclopentenes

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Abstract: Michael-type addition of benzenesulfinic acid to alkynyl(phenyl)iodonium tetrafluoroborates in methanol gives stereoselectively (*Z*)-(β-(phenylsulfonyl)alkenyl)iodonium tetrafluoroborates in high yields. [β-(Phenylsulfonyl)alkylidene]carbenes derived from the (*Z*)-(β-(phenylsulfonyl)alkenyl)iodonium tetrafluoroborates by base treatment predominantly undergo intramolecular 1,5-carbon–hydrogen insertions to give 1-(phenylsulfonyl)cyclopentenes along with a small amount of rearranged alkynes, which is in a marked contrast with the facile 1,2-migration of β-(phenylsulfenyl) and β-(phenylsulfinyl) groups of alkylidenecarbenes. Reaction of alkynyl(phenyl)iodonium tetrafluoroborates with benzenesulfinates directly affords 1-(phenylsulfonyl)cyclopentenes via tandem Michael–carbene insertion reactions. The mechanism of 1,2-migration of [β-(phenylsulfonyl)alkylidene]carbenes is also discussed.

α-Elimination of vinyl halides[1] and vinyl triflates[2] constitutes the most general method for generation of alkylidenecarbenes.[3] Recently we reported that base treatment of vinyl(phenyl)iodonium tetrafluoroborates leads to α-elimination under mild conditions to give alkylidenecarbenes.[4] While the reactive intermediates resulting from base-induced α-elimination of vinyl halides are believed to be carbenoids,[5] the species generated from vinyl triflates and vinyliodonium salts are free carbenes. Alkylidenecarbenes are singlets with a fairly sizable singlet–triplet energy difference and electrophilic species, as are most carbenes.[3,6] They readily

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