Iminopropadienethiones, Ar-N=C=C=C=S

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Aryliminopropadienethiones 9 have been generated by flash vacuum thermolysis of isoxazolones of the type 5 and characterized by mass spectrometry and matrix isolation IR spectroscopy in conjunction with DFT calculations and chemical trapping.

Introduction

Iminopropadienones (1), a new class of compounds, have been investigated in our laboratory in recent years.^{2,3} While the simple alkyl derivatives have the character of reactive intermediates, most aryl derivative can be handled at temperatures between ca. -100 and 0 °C, but a few of these compounds are isolable at room temperature, e.g., the mesityl and neopentyl derivatives.^{3,4} This class of compounds show a rich chemistry, inter alia to produce acylketenimines 2 in stoichiometric reactions with nucleophiles (HX) and new five- to ninemembered heterocyclic rings 3 on reaction with bisnucleophiles.3,4



Our next goal was to prepare and characterize the corresponding thiones, R-N=C=C=C=S. The first results are reported in this paper.

Results and Discussion

The iminopropadienones 1 are best prepared by flash vacuum thermolysis (FVT) of Meldrum's acid derivatives of type 4 (Y = NR'_2 , SMe, or OMe).^{2,3} Since thioxo derivatives of Meldrum's acid are unknown, a different methodology had to be sought for the preparation of the iminopropadienethiones. Previous research on the ther-



mal fragmentations and rearrangements of isoxazolones⁵ made us target compounds of type **5** as possible sources of the desired iminopropadienethiones 9 by means of elimination of CO₂ and ethylene or isobutene to generate a transient nitrene 6, 1,2-phenyl group shift in the nitrene to generate the cumulene 7, a second elimination of alkene to furnish a bis-thiol 8, and elimination of H₂S to deliver the final product, 9 (Scheme 1). As detailed below, the study of the mass spectra as a function of temperature revealed that the sequence of eliminations shown in Scheme 1 is actually followed.

The required starting materials 5 were prepared by coupling of the anion of 3-phenylisoxazolone with CS₂ in

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results.

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the 4-position, followed by double alkylation of the dithiocarboxylate formed.

The FVT reactions of 5 were monitored by on-line mass spectrometry, using a thermolysis reactor fitted inside the ion source housing of a six-sector tandem mass spectrometer. Individual ions were investigated by collisional activation mass spectrometry (CAMS) and in the case of the molecular ions of 9 also neutralizationreionization mass spectrometry (NRMS).⁶ In parallel with these experiments, FVT coupled with Ar matrix isolation at 7-10 K permitted infrared spectroscopy of the products, and preparative FVT experiments allowed the isolation of the trapping product 10.

DFT calculations of structures and IR spectra of the iminopropadienethiones were performed at the B3LYP/ 6-31G** level of theory. This method has been found to give the best overall agreement with reference values from higher level calculations.7 It has also been applied successfully to a variety of ketenes in several recent publications,⁸ and specific comparisons with experimental data and with Hartree-Fock, MP2/6-31G*, G2(MP2,-SVP), or QCISD(T)/6-31G* calculations of energies, geometries, and/or spectra for ketenes have been made.9 In each of these studies the DFT method has been found to give excellent agreement with experiment and to compare well with higher level ab initio calculations. The calculations¹⁰ were carried out using the GAUSSIAN 98 suite of programs.^{11,12} The B3LYP formulation of density functional theory corresponds to Becke's three-parameter exchange functional^{12a} in combination with the Lee-Yang-Parr correctional functional.^{12b} Calculated wavenumbers were scaled by a factor 0.9613.13

FVT-MS. The mass spectra of the thermolysates were monitored over the temperature range 200 to ca. 800 °C. A selection is shown in Figure 1. The starting material 5a was stable till FVT temperatures above 300 °C, when molecular ions at m/z 235 and m/z 193 appeared,

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Figure 1. Mass spectra arising from the FVT of 5a at (a) 200 °C, (b) 600° C, (c) 720 °C.



Figure 2. (a) CAMS (O_2), and (b) NRMS (NH_3/O_2) of m/z 159from the FVT of 5a.

corresponding to the thiol 7a and the bis-thiol 8a. These were the major products at 500 °C, where only a small peak for the molecular ion of 9a, m/z 159, was detected. High temperatures, 700-800 °C, are required in order to achieve major decomposition to 9a.

The CAMS of the m/z 159 ions is shown in Figure 2a and features m/z 77 and 51 due to the phenyl cation as major fragment peaks. The second most important set

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of peaks at m/z 115 and 114 is due to loss of CS and HCS. These fragmentations are completely analogous to those of the PhNCCCO cations, thus supporting the expected structure of **9a**. The NRMS of the m/z 159 ions features a recovery signal at m/z 159, thus confirming that neutral **9a** is at least stable on the microsecond time scale of the NRMS experiment. However, the NRMS is quite different from the CAMS, featuring a strong signal at m/z 82 in particular. This corresponds to reionization of radicals NCCCS formed in the process m/z 159 $\rightarrow m/z$ 77. Thus the mass spectral investigation is completely in accord with the Ph-N=C=C=C=S structure.

The diethyl derivative **5b** behaved in a manner very similar to that of **5a**, eliminating ethylene instead of propene, and giving the same m/z 159 ion.

Further confirmation of the identity of the molecular ions of **9a** is given by the observation that the *same* m/z159 ions, i.e., with the same CAMS and NRMS, are obtained by fragmentation of the cation radical of the isoxazolopyrimidinethione **11** in the mass spectrometer (Scheme 2). We show below that neutral **9a** (minor) and PhNCCCO (major) are also produced in the FVT of **11**.

A similar set of spectra arising from the FVT of the anisyl derivative **5c** is shown in Figures S4 and S5 in the Supporting Information and support the sequence of the thermal fragmentations (Scheme 1) and the structure of p-MeO-C₆H₄NCCCS (**9c**) in a similar manner. In this case, the loss of 15 mass units from the molecular ions of **9c** is, not surprisingly, the main fragmentation in the CAMS.

Matrix Isolation. FVT of **5a** with matrix isolation of the products in Ar at 7–10 K was investigated over the temperature range 500–1100 °C. A representative series of spectra is shown in the Supporting Information. The intensity of a cumulenic species absorbing strongly at 2167 cm⁻¹ (often observed at 2163 cm⁻¹ except in high quality matrixes) increased from 600 to 900 °C and then decreased again due to extensive decomposition. Other bands assigned to the same species because they rise and fall with the same rates were observed at 2023vw, 1593m, 1493m, and 1355w cm⁻¹. Virtually all the other bands in the spectrum are accounted for; they are due to propene, water, CO₂, CS₂, benzonitrile, and unreacted starting material (Figure 3). The peaks ascribed to the cumulene are in excellent agreement with DFT calcula-



Figure 3. (Upper) Calculated (B3LYP/6-31G^{**}) IR spectrum of PhNCCCS (**9a**), and (lower) Ar matrix IR spectrum of the products of FVT of **5a** at 700 °C. The calculated data are scaled by 0.9613. C = carbon dioxide, D = carbon disulfide, H = hydrogen sulfide, N = benzonitrile, P = propene, R = starting material **5a**, S = phenyliminopropadienone **9a**, W = water, X = unassigned; the peak at 2049 cm⁻¹ is most probably due to the CN radical.

tions for PhNCCCS (**9a**) as shown in Figure 3. Full listings of the experimental and calculated wavenumbers are reported in the Supporting Information. The very weak band at 2023 cm⁻¹ is reproducible and is tentatively matched to the calculated band at 1974 cm⁻¹. Other very weak and unassigned bands are present in the vicinity of 2000 cm⁻¹. A significant peak at 2049 cm⁻¹, which continues to increase in intensity up to 1100 °C but is unstable at 50 K in matrixes without Ar, is probably due to the CN radical.¹⁴ This peak also appears in the spectrum of **9c** (see below).

The FVT of the diethyl analoue **5b** was completely analogous to that of **5a**. The same spectrum due to PhNCCCS (**9a**) was obtained, the only difference being that ethylene had replaced the propene peaks.

Analogous FVT/matrix isolation of the 3-anisylisoxazolone derivative **5c** gave rise to a species identified in like manner as *p*-MeO-C₆H₄NCCCS (**9c**) on the basis of good agreement with the DFT calculated spectrum and assignment of all other peaks to propene, water, CO₂, CS₂, H₂S, anisonitrile, and unreacted starting material, together with the peak at 2049 cm⁻¹ showing the same characteristics as reported above. The experimental and calculated spectra are shown and tabulated in the Supporting Information. The absorptions due to **9c** are

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at 2164vs, 2020vw, 1593w, 1508s, 1356w, 1295w, 1254m, 522w $\rm cm^{-1}.$

Now that the IR absorptions of PhNCCCS have been identified, it is possible to detect this compound as the minor product of FVT of the isoxazolopyrimidinethione 11. This compound is very stable thermally and undergoes FVT to give mainly phenyliminopropadienone, PhNCCCO, at 900 °C.15 A medium size peak at 2163 cm⁻¹ in the published spectrum was previously unassigned.¹⁵ Now that the IR spectrum of 9a is known, this minor product in the FVT of 11 can be identified as 9a. Not only the 2163 cm⁻¹ band, but all the other minor peaks due to **9a** are present in the spectrum. Thus, undoubtedly **11** undergoes thermal ring opening to a vinylnitrene (**12**), which rapidly undergoes the 1,2-phenyl shift to produce a transient ketenimine 13. Cycloreversion reactions of this compound yields PhNCCCO and PhNCCCS (Scheme 2). The accompanying products, HCN, HNCS, and HNCO, were also identified in the matrix IR spectrum.

Chemical Trapping. Preparative FVT experiments were conducted by condensing the thermolysis products on a liquid nitrogen cooled coldfinger. After the end of the experiments, diethylamine was injected onto the coldfinger through a septum. The coldfinger was allowed to warm to room temperature, and the thioamide **10a** (Scheme 1) was isolated by flash chromatography. The same product was obtained from **5a** and **5b**, but **5a** is easier to handle and gave the best yields. The product **10** serves as chemical proof of the structure of PhNCCCS and at the same time demonstrates the viability of performing chemical reactions with iminopropadienethiones.

Conclusion and Outlook

Isoxazolones **5** serve as preparatively viable precursors of the new class of compounds, iminopropadienethiones, R-N=C=C=C=S, whereas the isoxazolopyrimidinethiones **11** are useful for spectroscopic rather than preparative purposes. Experiments aimed at the synthesis of new iminopropadienethiones, especially those carrying electronegative substituents to increase reactivity, or sterically hindering ones to decrease reactivity, as well as further exploration of their chemical reactions are underway in our laboratories.

Experimental Section

Apparatus and procedures for FVT coupled with matrix isolation IR spectroscopy^{16,17} and for preparative FVT¹⁷ were as previously described. The 6.5 K cryostat¹⁷ was used. Ar matrixes of thermolysates were usually condensed on CsI from a dynamic vacuum of 10^{-5} to 10^{-6} mbar at 10-20 K and spectra recorded at 7 K. The pyrolysis unit built inside the ion source housing of the six-sector tandem mass spectrometer (Micromass AutoSpec 6F) was as reported.¹⁸

4-[Bis(ethylthio)methylene]-3-phenylisoxazol-5(4H)one 5b. Triethylamine (2.8 mL; 20 mmol) and then carbon disulfide (0.6 mL; 10 mmol) were added to a solution of 3-phenylisoxazol-5(4H)-one¹⁹ (1.61 g; 10 mmol) in 10 mL of DMSO (previously dried over P₂O₅ and 6A molecular sieves) at -15 °C, and the solution was stirred under N₂ at -15 °C for 0.5 h. Ethyl iodide (3.34 g; 20 mmol) was then added dropwise at $-15\ ^\circ C$ over 20 min. The solution was allowed to warm to RT, heated to 60 °C for 45 min, cooled again to RT, and poured into 100 mL of ice-water. The aqueous layer was removed by decanting, and the remaining solid was purified by flash chromatography (SiO₂/EtOAc-hexane; R_f 0.45) to yield 1.78 g (61%) of yellow crystals, mp 69-71 °C; ¹H NMR (CDCl₃) δ 1.05 (3H), 1.37 (3H), 2.68 (2H), 3.22 (2H), 7.46 (m, 5H) (the signals for the CH₃ and CH₂ groups appear broad at RT due to slow rotation of the ethyl groups but sharpen and resolve into triplets and quartets at elevated temperature); ¹³C NMR (CDCl₃) δ 13.7, 13.9, 32.2, 33.7, 107.7, 128.4, 128.5, 129.1, 130.2, 161.2, 167.3, 181.1. Anal. Calcd for $C_{14}H_{15}NO_2S_2$ C, 57.31; H, 5.15; N, 4.77. Found C, 57.08; H, 5.13; N, 4.48.

4-[Bis((1-methylethyl)thio)methylene]-3-phenylisoxazol-5(4H)-one 5a. This compound was prepared in analogy with **5b** using isopropyl iodide and purified by flash chromatography (SiO₂/CH₂Cl₂-acetone 1:1; R_f 0.8) to yield 1.76 g (58%) of yellow crystals, mp 80–81 °C; subl. 65 °C (10⁻⁴ mbar); ¹H NMR δ 1.04 (d, J = 6.3 Hz, 6 H), 1.39 (d, J = 6.3 H, 6 H), 3.39 (br m, 1 H), 4.25 (br m, 1 H), 7.45 (m, 5 H), ¹³C NMR δ 22.2, 43.3, 108.8, 128.4, 128.5, 128.9, 130.1, 161.2, 167.4, 180.1; ¹³C-DEPT δ 22.2, 43.3, 128.4, 128.5, 130.0. Anal. Calcd for C₁₆H₁₉NO₂S₂ C, 59.78; H, 5.96; N, 4.36, Found C, 59.71; H, 5.96; N, 4.18.

4-[Bis((1-methylethyl)thio)methylene]-3-(4-methoxy)phenylisoxazol-5(4*H***)-one 5c.** This compound was prepared in analogy with **5a** using 3-(*p*-methoxyphenyl)isoxazol-5(4*H*)one.²⁰ After aqueous workup as above, the yellow precipitate was recrystallized from acetonitrile to afford 2.27 g (82%) of crude product. Flash chromatography (SiO₂/CH₂Cl₂-acetone 1:1; R_f 0.8) afforded 1.53 g (56%), mp 101 °C, subl. 85 °C (10⁻⁴ mbar); ¹H NMR δ 1.02 (d, J = 5.8 Hz, 6 H), 1.35 (d, J = 4.4Hz, 6 H), 3.3h (m, 1 H), 3.81 (s, 3 H), 4.20 (m, 1 H), 6.92 (d, J= 8.8 Hz, 2 H), 7.40 (d, J = 8.8 Hz, 2 H); ¹³C NMR δ 22.9, 43.2, 55.3, 109.0, 113.8, 121.0, 129.8, 161.0, 167.4, 179.7; ¹³C-DEPT δ 22.2, 43.2, 55.3, 113.8, 129.9. Anal. Calcd for C₁₇H₂₁-NO₃S₂ C, 58.17, H, 5.98, N, 3.99. Found C, 58.28, H, 6.13, N, 3.97.

3-Diethylamino-3-phenylimino-N,N-diethylthiopropanamide 10a. Compound 5a (50 mg; 0.155 mmol) was sublimed at a temperature not exceeding 50 °C through the preparative quartz pyrolysis tube¹⁶ (700 °C/3 \times 10⁻⁶ mbar). The products were isolated on a coldfinger cooled in liquid nitrogen. After the end of the pyrolysis, diethylamine (2 mL) was injected onto the sample on the coldfinger, which was then warmed to RT. The resulting mixture was concentrated in vacuo and purified by flash chromatography (SiO₂/EtOAchexane) to yield 27 mg (57%) of 10a as a red-brown oil; ¹H NMR δ 0.85 (t, 3 H), 1.17 (t, 3 H), 1.20 (t, 6 H), 3.11 (q, 2 H), 3.48 (q, 4 H), 3.54 (s, 2 H), 3.87 (q, 2 H), 6.82 (m, 3 H), 7.15 (m, 2 Ĥ); ¹³C NMR (CDCl₃) δ 10.8, 12.7, 29.7, 40.4, 42.5, 45.9, 48.1, 120.7, 121.5, 122.9, 128.7, 153.7, 196.0. Anal. Calcd for C₁₇H₂₇N₃S C, 66.91; H, 8.85, N, 13.76. Found C, 66.64, H, 8.80; N. 13.51.

Reference Infrared Spectra (Ar matrixes, 10–20 K). Propene²¹ 3091s, 3036s, 2893s, 2941s, 2923s, 2859m, 1650s, 1453vs, 1439s, 1415m, 1373w, 1212m, 1043s, 998s, 932m, 908vs, 578s cm⁻¹. Ethylene²² 2995m, 1440s, 946s cm⁻¹. Carbon disulfide²³ 2178m, 1528 vs cm⁻¹. Carbon dioxide 2344vs, 2340vs cm⁻¹. Hydrogen sulfide (dimer)²⁴ 2567 cm⁻¹. Benzonitrile 3062w, 2241m, 2237m, 1494m, 1450m, 1288m, 1181w, 1072w, 761m cm⁻¹. *p*-Methoxybenzonitrile 2949w, 2852w, 2245m, 238m, 1615s, 1515vs, 1470m, 1306s, 1265vs, 1172m,

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Iminopropadienethiones

1045m, 835m. Hydrogen cyanide 25 3306m, 1425w, 721m cm $^{-1}$. Isothiocyanic acid 3509m, 1982s cm $^{-1}$

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(25) Pacansky, J. J. Phys. Chem. **1977**, 81, 2240. Evans, R. A.; Lorencak, P.; Ha, T.-K.; Wentrup, C. J. Am. Chem. Soc. **1991**, 113, 7261. **Supporting Information Available:** Cartesian coordinates and calculated IR spectra of **9a** and **9c** (B3LYP/6-31G**). Figures of mass spectra arising from the FVT of **5c** as a function of temperature. Figure showing the CAMS and NRMS of **9c**⁺⁺. Figure of the experimental and calculated IR spectrum of **9c**. Figures of the IR spectra arising from FVT of **5a** and **5c** as a function of temperature. Tables of experimentally observed frequencies and assignments in Ar matrix IR spectra. This material is available via the Internet at http://pubs.acs.org.

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