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Thioketenes and Iminopropadienethiones RN=C=C=C=S from Isoxazolones

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Isoxazolones **6** undergo thermal elimination of propene and isopropylthiol to produce thioketenes **7** at 500–600°C under flash vacuum thermolysis conditions. At 700–900°C further fragmentation occurs to produce iminopropadienethiones, RNCCCS **8**. In addition, 3-alkylisoxazolones **6d**–**e** rearrange to cyanothioketenes **10d**–**e**. Compounds **7**, **8**, and **10** were characterized by Ar matrix IR spectroscopy and comparison with density functional theory-calculated spectra. Thioketenes **7** reacted with amines to afford thioamides **11**. Reaction of aryliminopropadienethiones **8** with amines caused cyclization to 2-aminoquinoline-4(1*H*)-thiones **16**.

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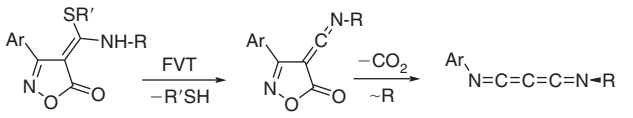
Introduction

Iminopropadienones, RN=C=C=C=O **1**, are highly reactive, theoretically interesting, and in some cases isolable compounds.[1] They can be generated from a variety of precursors, including isoxazolopyrimidinones **2**, Meldrum's acid derivatives **3**, and pyridopyrimidinones **4** and **5** by means of flash vacuum thermolysis (FVT)[1] or microwave-assisted thermolysis (Scheme 1).[2] Compounds **1** have been employed in syntheses of a variety of heterocyclic compounds, including diazepines, diazocines, mesoionic pyridopyrimidinones, and quinolones.[1–3]

The corresponding iminopropadienethiones, RN=C=C=C=S **8**, are relatively little-known compounds.[4,5] The types of precursors used to prepare the iminopropadienones RNCCCO (Scheme 1) are either unknown or, in the case of **2b**, give only modest yields of **8**.[4] 4-Substituted isoxazol-5(4*H*)-ones have proved to be excellent precursors for a variety of reactive molecules under the conditions of FVT, including acetylenes, ynamines, isocyanides, fulminates, C_2S_2, and the bis-iminopropadienes (Eqn 1).[6,7]

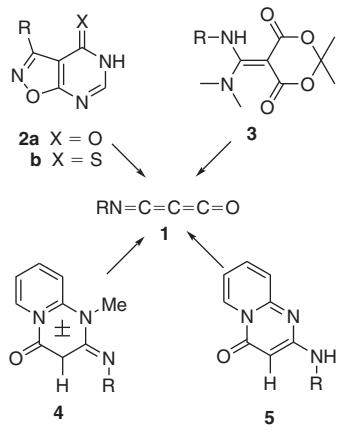


(1)

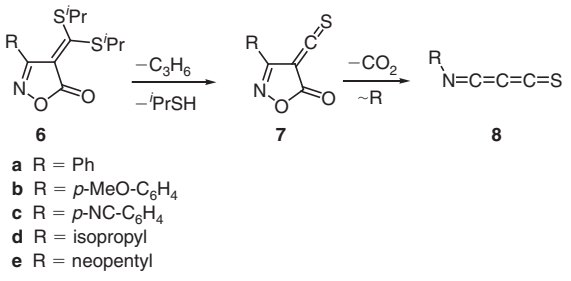
The formation of the phenyliminopropadienethiones **8a** and **8b** by FVT of isoxazolone **6a**–**b** was described previously.[4] We have now discovered that the reaction takes place in two stages, with initial formation of the thioketenes **7** (Scheme 2), which can be characterized at low temperature and trapped chemically. The results are reported herein.

Results and Discussion

The FVT of **6a** was carried out over the temperature range 300–1000°C and monitored by IR spectroscopy. The products were isolated in Ar matrices at ~10 K and investigated by IR



Scheme 1. Routes to iminopropadienones **1**.



Scheme 2. Stepwise frgmentation of 4-methylenisoxazolones.

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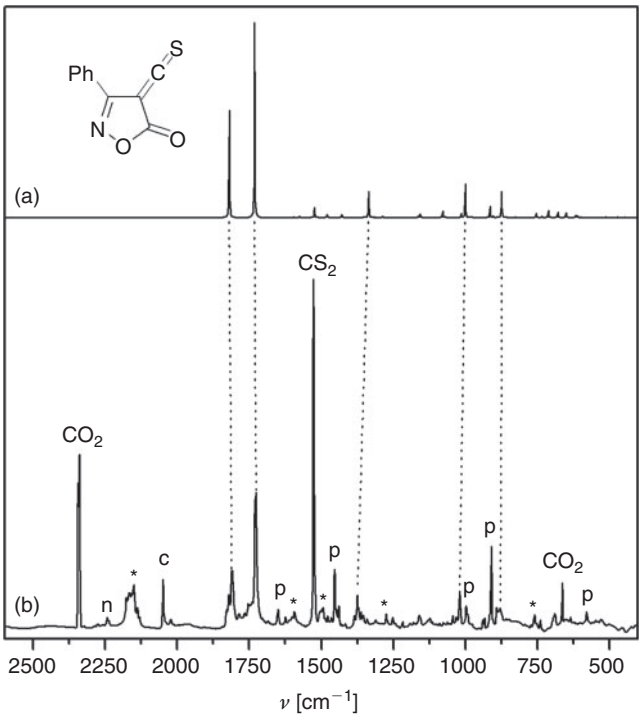


Fig. 1. (a) Calculated IR spectrum of thioketene **7a** (B3LYP/6–31G**). (b) Experimental IR spectrum of the product of FVT of **6a** at 600°C in Ar, 10 K. Bands [cm^{-1}] due to: CO_2 (2344, 663); c, OCS (2050); p, propene (1650, 1454, 1439, 997, 909, 579); CS_2 (1528); thioketene **7a** (1810, 1727, 1375, 1020, 879); *, *N*-phenyliminopropadienethione **8a** (2177, 2167, 1593, 1493, 1275, 753 cm^{-1}). Ordinate in arbitrary absorbance units.

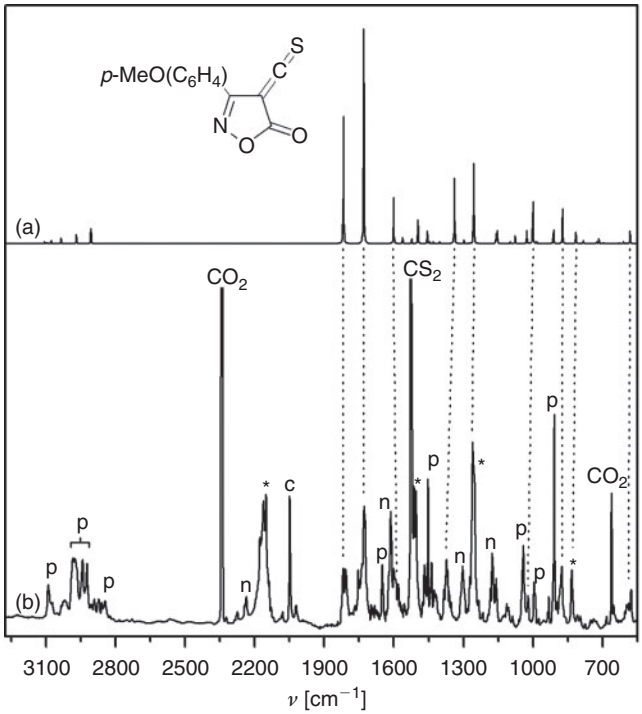
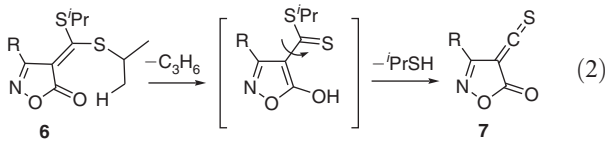


Fig. 2. Comparison of (a) calculated IR spectrum (B3LYP/6–31G**) for thioketene **7b** and (b) experimental IR spectrum of the product of FVT of **6b** at 600°C, in Ar at 10 K. Bands [cm^{-1}] due to: p, propene (3090, 2983, 2942, 2923, 2859, 1650, 1454, 1044, 997, 909, 578); c, OCS (2050); CS_2 (1528); CO_2 (2340, 663); thioketene **7b** (2891, 1819, 1729, 1593, 1469, 1374, 1261, 1115, 1022, 878, 834, 590); n, 4-methoxybenzonitrile (2238, 1612, 1305, 1177); *, *N*-(4-methoxyphenyl)iminopropadienethione **8b** (2164, 1508, 1254, 835). Ordinate in arbitrary absorbance units.

spectroscopy. Below 500°C, most of the starting material was recovered unchanged. FVT at 500–600°C led to the formation of a thioketene intermediate, to which structure **7a** is assigned (Scheme 2 and Eqn 2). This compound is characterized by its symmetric (1727 cm^{-1}) and anti-symmetric (1810 cm^{-1}) stretches in the IR spectrum, in excellent agreement with the calculated bands at 1733 and 1821 cm^{-1} (Fig. 1). Peaks due to propene (p) are clearly visible in the spectrum. Isopropylthiol was isolated in the form of its air oxidation product, diisopropyl disulfide, after workup of the products of preparative FVT experiments, but it decomposes in part to propene and hydrogen sulfide under the reaction conditions. Alternatively, **6** may eliminate two molecules of propene followed by hydrogen sulfide. A peak at 2050 cm^{-1} also seen in several other spectra is most likely due to OCS[8] rather than the CN radical, which appears in the same place.[4] Furthermore, evidence for the structure of **7** was obtained by trapping with diethylamine in preparative FVT experiments described below. A likely mechanism for formation of **7** is presented in Eqn 2. Isopropylthiol, propene, and H_2S were also detected by on-line mass spectrometry, but curiously, the thioketene **7a** was not detectable in FVT-MS studies.[4] A discord between FVT-IR and FVT-MS studies is unusual but not unprecedented. Possible reasons could be: (i) different ionization cross-sections of the various pyrolysis products; (ii) facile fragmentation of the product under electron ionisation at 70 eV; and (iii) thermal instability of the product. It is important to note that FVT-MS experiments are carried out in the high vacuum of the mass spectrometer, whereas FVT-IR is carried out in a stream of Ar, which can act as a collisional deactivator. In other words, decomposition due to chemical activation is more likely to occur in FVT-MS experiments.



(2)

The intensities of the IR bands ascribed to thioketene **7a** diminished at higher temperatures. At 700–900°C, the IR spectra were dominated by the very strong cumulenic absorption at 2167 cm^{-1} due to Ph-N=C=C=C=S **8a**.[4] Several weaker peaks due to **8a**, which were barely detectable in the 600°C spectrum (Fig. 1), increased at the same time (1593, 1493, 1355, 1275, 753, and 546 cm^{-1}). The iminopropadienethione **8a** was identified as the carrier of these signals due to the excellent agreement with the B3LYP/6–31G** calculated IR spectrum (Fig. S1, Accessory Publication).[4]

The thermolyses of the *p*-methoxyphenyl derivative **6b** were analogous to those described for **6a** above. The thioketene **7b** was obtained at 600°C (Fig. 2). Small amounts of *N*-(4-methoxyphenyl)iminopropadienethione **8b** was also formed under these conditions (Fig. 2), and this compound became the main product at 700–900°C.[4]

Similar FVT of the *p*-cyanophenyl derivative **6c** at 500–600°C gave rise to thioketene **7c** with characteristic bands at 1733 and 1817 cm^{-1} (Fig. 3). The calculated frequencies of **7c** are 1733 cm^{-1} (symmetric) and 1824 cm^{-1} (anti-symmetric)

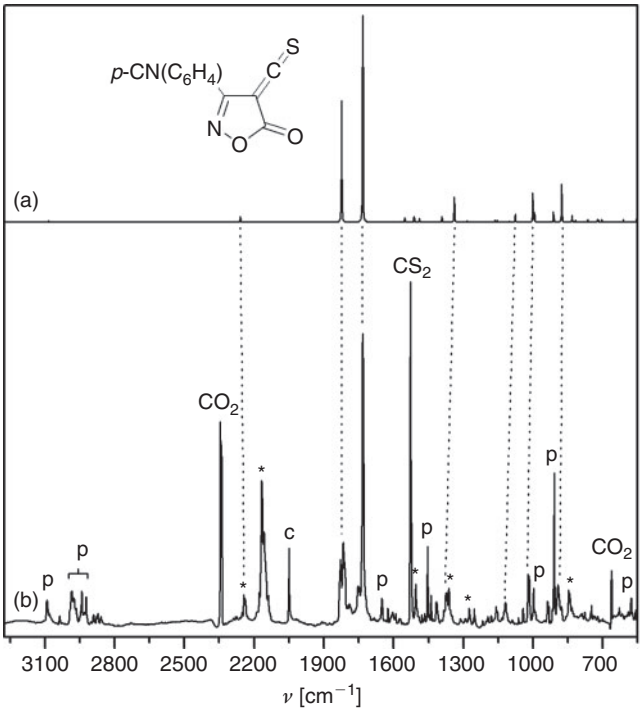


Fig. 3. Comparison of (a) calculated IR spectrum (B3LYP/6–31G**) of thioketene **7c** and (b) experimental IR spectrum of the product of FVT of **6c** at 570°C in Ar, 10 K. Bands [cm^{-1}] due to: p, propene (3091, 2984, 2941, 1651, 1453, 997, 909, 578); c, OCS (2050); CS_2 (1528); CO_2 (2344, 663); thioketene **7c** (2240, 1817, 1733, 1374, 1120, 1022, 894, 847); *, *N*-(4-cyanophenyl)iminopropadienethione **8c** (2245, 2165, 1362, 1275, 842). Ordinate in arbitrary absorbance units.

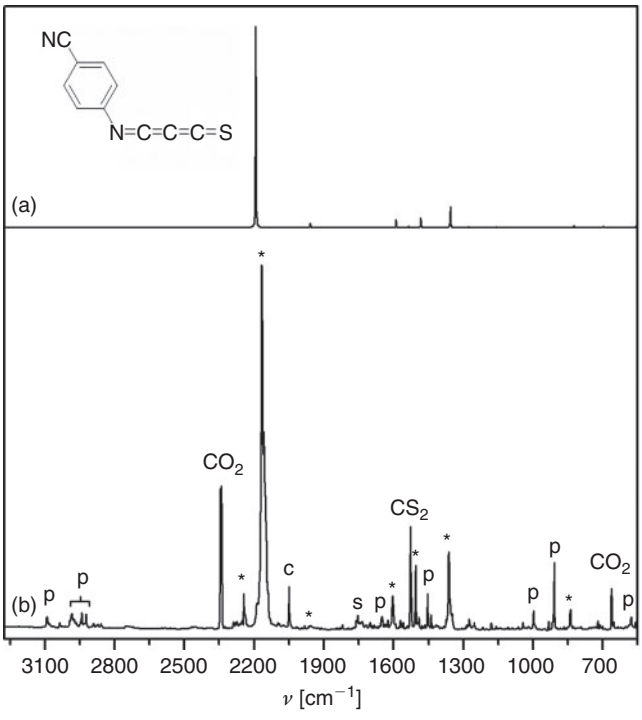


Fig. 4. IR spectrum resulting of the product of FVT of **6c** at 700°C in Ar, 10 K. Bands [cm^{-1}] due to: CO_2 (2344, 663); p, propene (3091, 2975–2923, 1650, 1453, 997, 909, 578); c, OCS (2050); CS_2 (1528); s, possibly cyano(4-cyanophenyl)thioketene **10c** (1755); *, *N*-(4-cyanophenyl)iminopropadienethione **8c** (2245, 2167, 1982, 1608, 1506, 1362, 1275, 1254, 839).

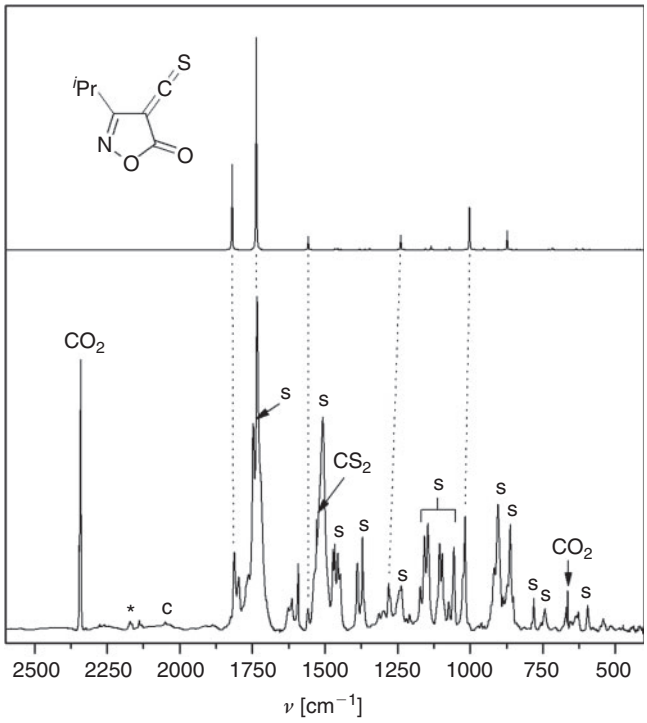
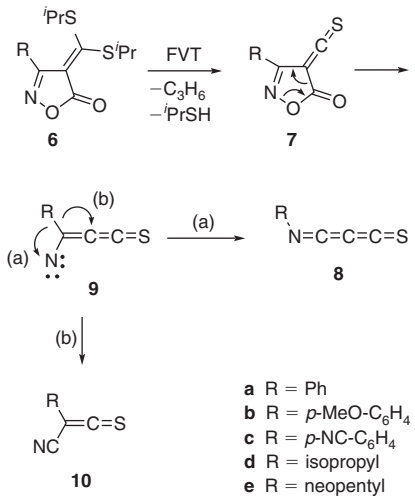


Fig. 5. Top: Calculated IR spectum of **7d**. Bottom: IR spectrum of **7d** resulting from FVT of **6d** at 500°C in Ar, 10 K. Bands [cm^{-1}] due to: CO_2 (2344, 663); CO (2138); s, starting material (1746, 1507, 1465, 1370, 1236, 1171, 1145, 1104, 1055, 916, 903, 861, 780, 742, 595); c, OCS (2050); CS_2 (1528); *, *N*-(isopropyl)iminopropadienethione **8d** (2171).



Scheme 3. Thioketenes and iminopropadienethiones from isoxazolones.

(B3LYP/6–31G**). Small amounts of imiopropadienethione **8c** were also formed under these conditions (Fig. 3).

A clean IR spectrum of **8c** was obtained by FVT of **6c** at 700°C (Fig. 4). It features a distinct and prominent band at 2167 cm^{-1} together with bands at 2245 and 1362 cm^{-1}. The corresponding calculated frequencies of **8c** are 2193, 2256, and 1357 cm^{-1}. This group of experimental bands was bleached simultaneously upon irradiation with the unfiltered UV light from a high-pressure Xe/Hg lamp while removing the infrared radiation with a water filter. A similar IR spectrum was obtained

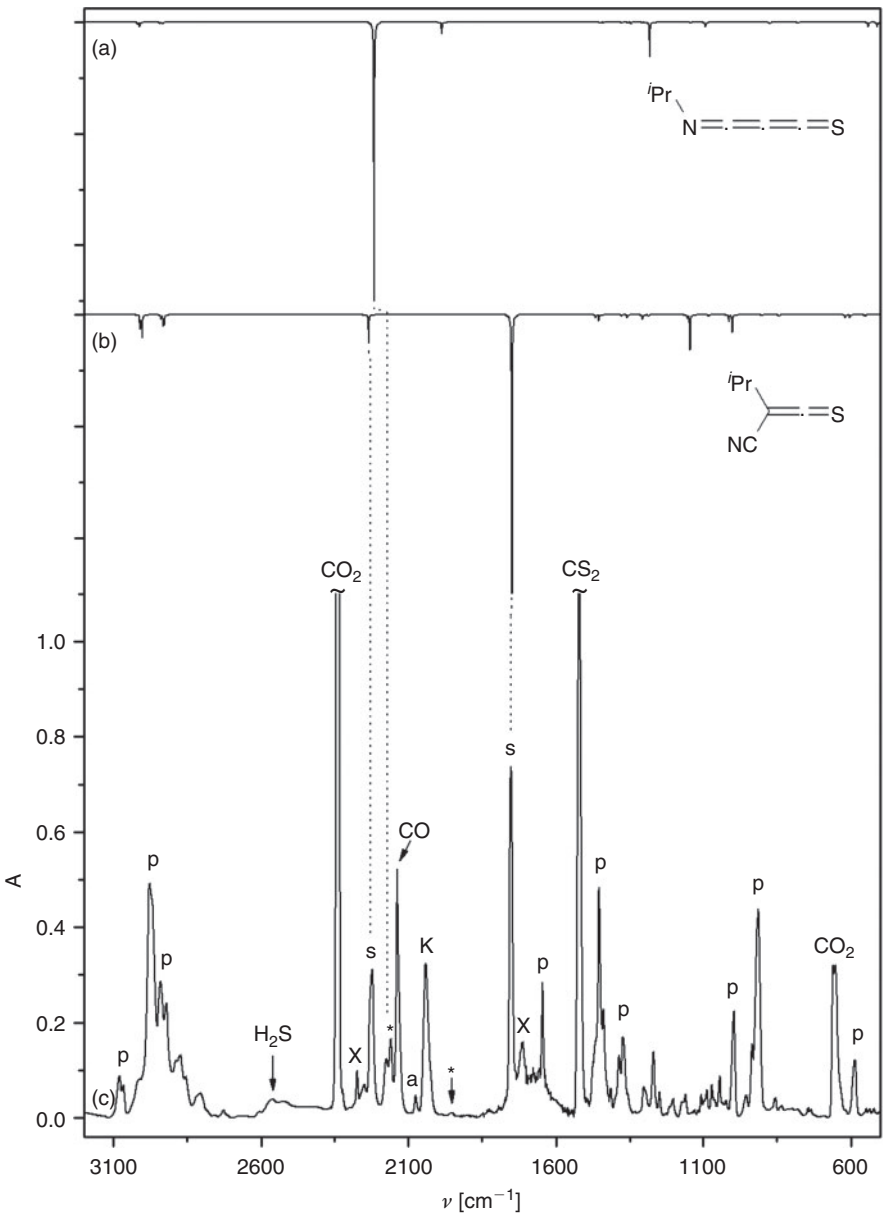


Fig. 6. (a) Calculated IR spectrum of isopropyliminopropadienone **8d**; (b) calculated IR spectrum of isopropyl(cyano) thioketene **10d** (B3LYP/6–31G**; wavenumbers scaled by a factor 0.9613); the intensities of the calculated ^{i}Pr-NCCCS **8d** are attenuated by a factor of 8 with respect to the thioketene **10d**. (c) IR spectrum of product of FVT of **6d** at 700°C isolated in Ar, 10 K. Bands [cm^{-1}] due to: p, propene (3081, 2977, 2941, 2921, 1645, 1453, 1375, 996, 913, 585); s, cyano (isopropyl)thioketene **10d** (2222, 1752); H_2S (2569); X, unassigned species (2273, 1722); K (2041) probably due to *N*-isopropylketenimine; H_2S (2561); CS_2 (1527); CO_2 (2339); CO (2138); *, *N*-isopropyliminopropadienethione **8d** (2175/2160, 1957).

in the temperature range 700–900°C. Significant decomposition occurred above 900°C, leading mainly to terephthalonitrile (2244 cm^{-1}).

FVT of **6d** at 400–600°C produced an intermediate thioketene **7d** with characteristic absorptions at 1732 and 1811 cm^{-1} (Fig. 5) in perfect agreement with the calculated bands (1732 and 1811 cm^{-1}).

In contrast to the aryl derivatives **8a**–**c**, the yields of alkyliminopropadienethiones **8d**–**e** were significantly lower, as a competing reaction leading to a new series of thioketenes **10** took overhand. This is illustrated in Scheme 3.

We assume that the initial extrusion of CO_2 from isoxazolone **7** leads to the vinylnitrene **9**.[4,6,7] Like in other vinylnitrenes,[9,10] the substituent R can migrate to N (pathway a), giving the iminopropadienethione **8**, or to C (pathway b), giving a cyanothioketene **10**. Pathway (a) has been observed in other types of arylisoxazolones,[7] but alkyl groups have been known to migrate to either C or N in vinylnitrenes.[9,10] In the case of **9d**–**e**, a preference for migration of alkyl groups to C (pathway b) leads to diminished yields of iminopropadienethiones **8d**–**e** and significant formation of cyanothioketenes **10d**–**e**. Only weak peaks possibly due to cyanothioketenes **10a**–**c** were observed in the aromatic series. It is possible that the vinylnitrenes **9** may also cyclise to azirenes, which could exist in thermal equilibrium with the nitrenes;[7,9,10] however, we have no evidence for the formation of such compounds.

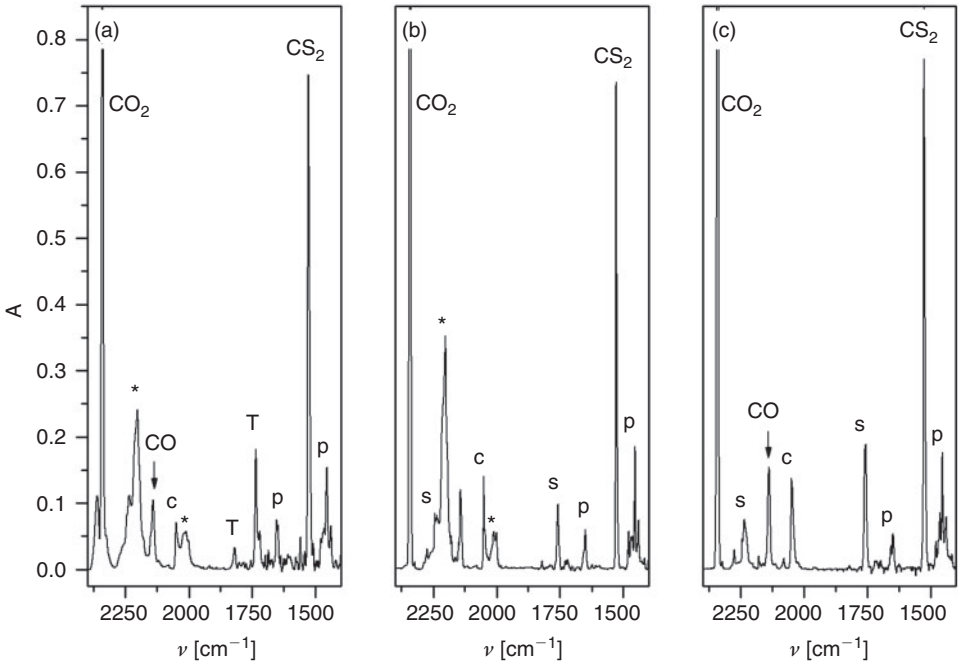


Fig. 7. IR spectra (2400–1400 cm^{-1}; Ar, 10 K) arising from the FVT of **6e** at (a) 600°C, (b) 700°C, and (c) 850°C. Bands [cm^{-1}] due to: p, propene (1650, 1453); T, thioketene **7e** (1819, 1736); s, cyano(neopentyl)thioketene **10e** (2236, 1757); c, OCS (2050); CS_2 (1528); CO_2 (2340); CO (2138); *, *N*-neopentyliminopropadienethione **8e** (2202, 2012).

FVT of **6d** at 700°C with matrix isolation in Ar at 10 K produces an IR spectrum as shown in Fig. 6. Fragmentation of the isoxazolone ring resulted in the expected formation of propene and carbon dioxide, but only weak peaks at 2175 and 2160 cm^{-1}, possibly due to *N*-isopropyliminopropadienethione **8d** were present. Similar spectra were obtained over the temperature range 600–800°C. Given the large calculated extinction coefficient of the NC_3S function (3967 km mol^{-1}), the yields of **8d** were very low. The main IR absorptions belong to carbon disulfide and a compound exhibiting typical thioketene and nitrile absorptions at 1752 and 2222 cm^{-1}, which are assigned to cyano(isopropyl)thioketene **10d** (Fig. 6). The observed frequencies agree well with the calculated IR spectrum (1750, 2236 cm^{-1}). The analogous cyano(*tert*-butyl)thioketene absorbs at 1753 cm^{-1}.[11a]

The IR spectra arising from FVT of **6e** at 600–850°C are shown in Fig. 7. Two compounds are formed initially, a thioketene assigned as **7e** absorbing at 1819 and 1736 cm^{-1}, and the neopentyliminopropadienethione **8e** absorbing at 2202 and 2012 cm^{-1} (Fig. 7a). The thioketene **7e** disappeared at 700°C, when the absorptions ascribed to **8e** reached maximum intensities (Figs 7b and 8). There is good agreement between the experimental and calculated spectra of **8e** (Fig. 8). **8e** is unstable and disappears upon warming of the solid to 120 K. At an FVT temperature of 850°C the bands labelled 's', which were already present at 700°C, correspond to the main species apart from CO_2 and CS_2 (Fig. 7c). These absorptions, at 2235 and 1756 cm^{-1}, are assigned to cyano(neopentyl)thioketene **10e** (Fig. 7c).

A summary of the main infrared absorptions of the heterocumulenes produced by FVT of isoxazolones **6a**–**e** is shown in Table S1 in the Accessory Publication. Overall, an excellent correlation was found between the observed and calculated IR absorptions at the B3LYP/6–31G** level (wavenumbners scaled by a factor 0.9613). The absorptions of **8** are roughly nine times stronger than those of **7**, which are about twice as strong as those of **10**.

Trapping with Amines

The products of FVT of isoxazolones **6** were trapped in the gas phase by mixing the pyrolysates with a stream of amine immediately at the exit of the FVT reactor but before reaching the cold finger. Alternatively, the products were trapped with amine on the cold finger; in this case, amine is deposited on the cold finger before and after the experiment, and the reaction with the pyrolysate takes place on thawing.

In this way, the thioketenes **7** produced by FVT of **6** at intermediate temperatures (500–600°C) were trapped to form the thioamides **11** (Scheme 4). Relatively low isolated yields (e.g. 42% for **11c**) are not unusual for reactive thioketenes, which tend to oligomerize readily in the condensed phase.[11] However, the neopentyl-thioketene **7e** afforded an acceptable yield of 83% of **11e**.

Trapping of the products formed by FVT of **6a** at temperatures of 700–750°C afforded the bis-addition product **17** in modest yield (18%),[4] and this was achieved only by cold trapping, i.e. by thawing of the frozen mixture of **8a** and diethylamine on the coldfinger. One reason for the poor yield of **17** is that another reaction can take place, leading to the formation of quinoline-4-thione **16a** (Scheme 4). The reaction is formulated in analogy with the corresponding cyclization of interconverting oxoketenimines and imidoylketenes to quinolones.[3] Thus, addition of amine to iminopropadienethiones **8** can take place on either the C=S or the C=N group, leading to ketenimine **12** or thioketene **13**. It is unimportant which of these is formed first, because they are expected to interconvert with low activation barriers.[12,13] The cyclization of the aryl-substituted thioketene **14** can now take place easily as a 6π

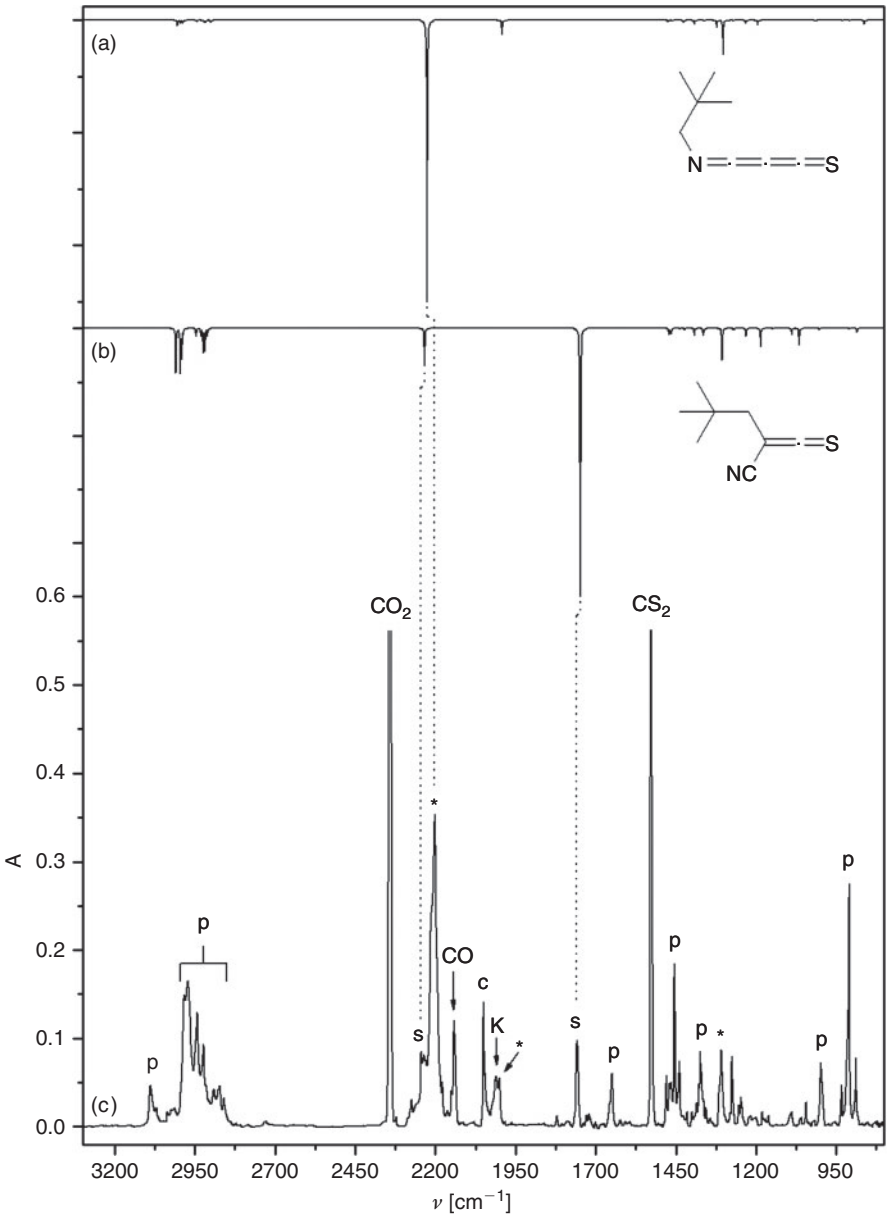


Fig. 8. (a) calculated IR spectrum of **8e**; (b) calculated IR spectrum of **10e** (B3LYP/6–31G**; wavenumbers scaled by a factor 0.9613); the intensities of neopentyl-NCCCS **8e** are attenuated by a factor of 12.5 with respect to the thioketene **10e**. (c) Experimental IR spectrum of the product of the FVT of **6e** at 700°C in Ar, 10 K. Bands [cm^{-1}] due to: CO_2 (2340); CO (2142); c, OCS (2050); s, cyano(neopentyl)thioketene **10e** (2236, 1757); CS_2 (1528); p, propene (3091, 2981, 2943, 1650, 1454, 1374, 997, 909); *, *N*-(neopentyl)iminopropadienethione **8e** (2970, 2202, 2012, 1306) (calc. 2227 cm^{-1}). Ordinate in arbitrary absorbance units.

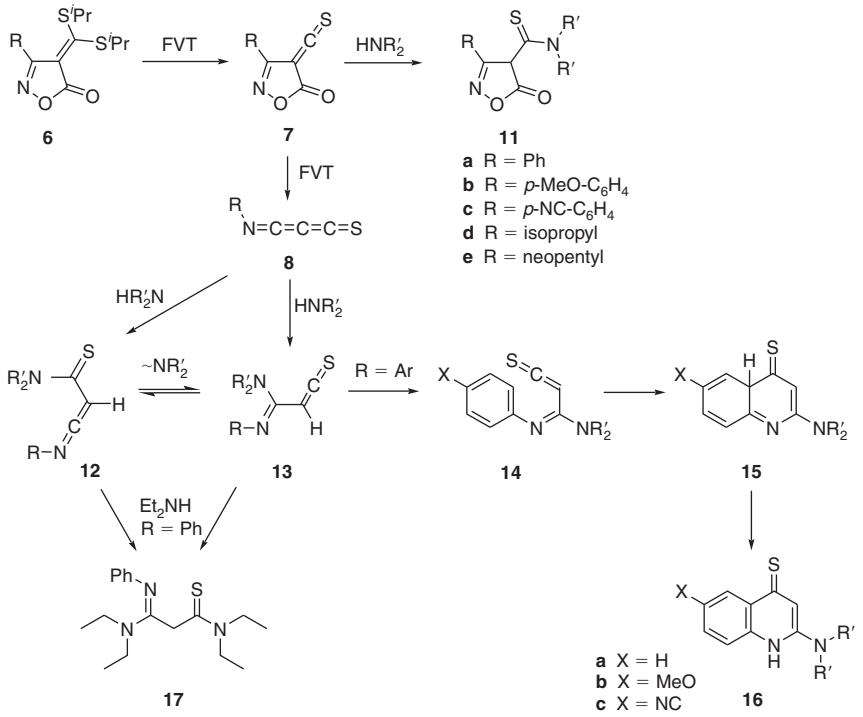
electrocyclic reaction. The resulting non-aromatic product **15** aromatizes to thioquinolone **16** in a series of H-shifts analogous to quinolone-forming cyclizations.[14]

The interconversion of the ketenimine **12** and the thioketene **13** (Schemes 4 and 5) is a very interesting reaction. As in the analogous oxoketenimine–imidoylketene rearrangement,[12] the amino groups R_2N in **12** or **13** first have to rotate into the perpendicular orientations required for optimal interaction between the amine lone pairs and the ketenimine or thioketene LUMO. These conformations, **17** and **19**, are rotational transition states (Scheme 5).

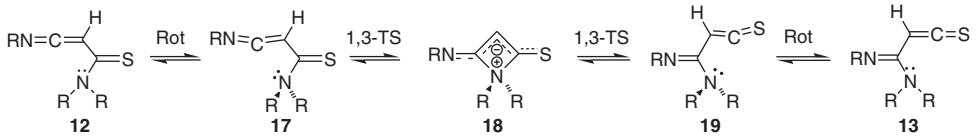
Having reached the rotational transition state, the 1,3-shifts proper take place, leading to the zwitterionic intermediate **18** via the 1,3-shift transition states. In other words, these are reactions with *sequential transition states*, characterized by a bifurcation point (valley-ridge inflection) between them.[12,15] When the rotational barrier becomes larger than the 1,3-shift barrier, there will necessarily be a 1,3-shift intermediate.[12] Details of our calculations of the energy surface will be published separately.

Conclusion

Thioketenes **7** and **10** are formed by FVT of isoxazolones **6** at medium temperatures (optimally at 500–600°C). Iminopropadienethiones RNCCCS **8a**–**c** are formed cleanly at high FVT temperatures (optimally at 700–900°C) and characterized by



Scheme 4. Chemical trapping of thioketenes **7** and iminopropadienethiones **8**.



Scheme 5. Thioxoketenimine–imidoylthioketene rearrangement.

low temperature IR spectroscopy. Trapping with amines leads to thioamides **11** or cyclization of transient imidoylthioketenes **13** to quinoline-4-thiones **16**. The nature of the thioxoketenimine–imidoylthioketene rearrangement and the potential for synthesis of little-known thioquinolones will be investigated further.

Computational Methods

The *Gaussian* 03 suite of programs[16] was used to calculate relative energies and infrared frequencies at the B3LYP/6–31G** level. Energies were corrected for zero-point vibrational energies, and all wavenumbers were scaled by a factor of 0.9613.[17] The temperature used was 298.15 K. Cartesian coordinates, absolute energies, and vibrational spectral data are provided in the Accessory Publication.

Experimental

All GC/MS data were obtained with an injector port temperature set at 200°C, with an initial oven temperature of 100°C increasing at 16°C per min until 270°C on a Zebron capillary GC column ZB-5 (30 m length). High resolution mass spectra were recorded on Kratos MS25RFA or Finnigan mass spectrometers in EI mode at 70 eV. TLC was performed on silica gel 60 and/or neutral alumina plates. Column chromatography used deactivated silica gel 60 and/or neutral alumina 90 with AR grade solvents. Microanalyses were carried out using a Carlo-Erba elemental analyser. $CDCl_3$ for NMR spectroscopy was filtered through basic alumina before use to remove any acidic impurities. Melting points are uncorrected.

Materials

Compounds **6** were prepared as described previously.[4,18]

Matrix Isolation

Matrix isolation experiments were performed using previously described apparatus.[3,19] In FVT experiments, an internal oven employed a 10 cm long, 0.7 cm i.d., electrically heated quartz tube suspended in a vacuum chamber directly flanged to the cryostat cold head, with a wall-free flight path of ~3 cm between the exit of the quartz tube and the cold target (CsI for IR spectroscopy). An alternative external oven consisted of a 20 cm (0.7 cm i.d.) quartz tube ending in a quartz flange directly flanged to the cryostat cold head; this tube was heated on a 10 cm length and had a ~5 cm unheated length connecting it to the cold head. A small amount of the precursor (5–10 mg) was co-sublimed with a stream of argon (~10 hPa min^{-1} from a 2 L reservoir) and pyrolysed through the FVT oven at the specified temperature in an operating vacuum of ~10^{-5} hPa. The resulting mixture was deposited onto the CsI optical window at 7–22 K in the course of 20 to 40 min. The IR bands were assigned by comparison with authentic samples or literature data, or, in the case of new compounds, calculated IR data. Listings of the matrix IR spectra of reference compounds are provided in the Accessory Publication.

Complete listings of the wavenumbers and intensities of all compounds identified in the matrix IR spectra derived from FVT of compounds **6a**–**e** at various temperatures (usually 500–1000°C) are presented in the Accessory Publication.

Preparative FVT

The apparatus consisted of a quartz pyrolysis tube (40 cm long, 19 mm i.d.) inserted into a tubular furnace and connected to a manifold operated at $\sim 10^{-5}$ hPa. The thermolysate was condensed on a cold finger at 77 K.

Two methods were used for trapping with amines: (a) for trapping on the cold finger at 77 K, the appropriate amine was deposited on the cold finger before the FVT reaction; further layers of amine were deposited during and after the FVT reaction. (b) For trapping in the gas phase the thermolysate was mixed with a stream of the gaseous reagent immediately at the exit of the FVT reactor but before reaching the cold finger. The mixture of thermolysate, reagent, and product was then condensed on the cold finger at 77 K. The mixture was allowed to warm to room temperature in an atmosphere of N_2.

*FVT of 4-[Bis((1-methylethyl)thio)methylene]-3-phenyl-isoxazol-5(4*H*)-one* ***6a***

The precursor **6a** (500 mg, 1.5 mmol) was thermolysed at 750°C (10^{-4} hPa) in the course of 7 h. The thermolysate was condensed on a cold finger at 77 K, and the cold finger was layered regularly with diethylamine (8 × 0.5 mL) during the course of the FVT. At the completion of the experiment, the pressure was equalised with dry nitrogen, and the liquid nitrogen trap was allowed to evaporate and warm up to RT. A red solution was collected in the receiver flask, which was magnetically stirred and kept at 0°C for 1 h. The excess amine was evaporated at 10°C (6.7 Pa), and the residue was chromatographed on basic alumina. The first fraction (*n*-hexane/diethyl ether 1:1) afforded diisopropyl disulfide (36 mg, 15%, yellow oil): GCMS: R_t 2.2 min, *m/z* 150 [$M^{+\bullet}$], 108, 43 (C_3H_6); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (d, 12H, $^3J = 6.7$ Hz, CH_3), 3.30 (septet, 2H, $^3J = 6.7$ Hz, CH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9 (CH_3), 42.7 (CH). Another fraction gave a small amount of benzonitrile (20 mg, 12%; GCMS Rt 3.1 min, *m/z* 103 [$M^{+\bullet}$]). The ethereal fraction afforded 3-(diethylamino)-*N*,*N*-diethyl-3-(phenylimino)propanethioamide **17** (84 mg, 18%, brown oil), which was purified further by Kugelrohr distillation (bp 70–80°C, 3×10^{-6} hPa) and identified by comparison with previously reported data.[4]

A polar fraction was then eluted using ethyl actetate/methanol (9:1), which consisted of 2-(diethylamino)quinoline-4(1*H*)-thione **16a** (62 mg, 17%, orange solid), mp 210–12°C; GCMS: R_t 12.7 min, *m/z* 232 [$M^{+\bullet}$]; ^{1}H NMR (200 MHz, $CDCl_3$/DMSO-d_6) δ 1.34 (t, 6H, $^3J = 7$ Hz, CH_3), 2.94 (q, 4H, $^3J = 7$ Hz, NCH_2), 5.32 (s, 1H, H-3), 7.10–7.43 (m, 2H), 7.41 (d, $^3J = 8$ Hz, H-6), 7.74 (d, 1H, $^3J = 8$ Hz, H-5), NH not observed. ^{13}C NMR (50 MHz, $CDCl_3$/DMSO-d_6) δ 11.0 (CH_3), 42.2 (NCH_2), 119.8 (C-8), 123.4 (C-3), 127.3 (C-5), 128.6 (C-6), 131.7 (C-7), 132.9 (C-4a), 143.5 (C-8a), 156.8 (C-2), 194.6 (C-4). MS (+EI) *m/z* 232 (30%) [$M^{+\bullet}$], 217 (10%), 203 (100%), 189 (15%), 160 (13%), 116 (18%), 100 (86%), 89 (16%), 72 (10%), 58 (12%). Anal. Calc. for $C_{13}H_{16}N_2S$: C 67.20, H 6.94, N 12.06. Found: C 67.36, H 6.82, N 12.02.

*FVT of 4-[Bis((1-methylethyl)thio)methylene]-3-(4-cyanophenyl)-isoxazol-5(4*H*)-one* ***6c***

The precursor **6c** (250 mg, 0.7 mmol) was gently sublimed at 80–90°C (10^{-4} hPa) and thermolysed at 550–600°C in the course of 4 h, using the diethylamine trapping procedure described above. The resulting material was dissolved in dichloromethane, adsorbed on alumina and chromatographed (eluent: ethyl acetate/methanol with the gradient increasing to 10:1) to yield 3-(4-cyanophenyl)-*N*,*N*-diethyl-5-oxo-2,5-dihydroisoxazole-4-thiocarboxamide **11c** (92 mg, 42%, yellow solid), mp 186–187°C. GCMS: R_t 13.7 min, *m/z* 257 (56%) [$M - CO_2$], 242 (10%), 214 (44%), 185 (5%), 129 (6%), 102 (8%), 57 (10%). IR (KBr) ν [cm^{-1}]: 3436(b, NH), 2253 (m, C≡N), 1642(m), 1477(m), 1269(w), 1026(s, CS), 825(m), 762(m), 628(m). ^{1}H NMR (200 MHz, $CDCl_3$/DMSO-d_6) δ 1.35 (t, 6H, $^3J = 7.3$ Hz, CH_3), 2.98 (q, 4H, $^3J = 7.3$ Hz, NCH_2), 7.63 (d, 2H, $^3J = 8.5$ Hz, H-2′), 7.74 (d, 2H, $^3J = 8.5$ Hz, H-3′), 9.40 (1H, b. s, NH). ^{13}C NMR (50 MHz, $CDCl_3$/DMSO-d_6) δ 10.4 (CH_3), 41.3 (NCH_2), 90.7 (C-4), 110.5 (C-4′), 118.0 (C≡N), 127.4 (C-2′), 130.7 (C-3′), 136.3 (C-1′), 160.0 (C-5), 170.9 (C-3), 190.7 (CS). DEPT 135 (50 MHz, $CDCl_3$/DMSO-d_6) δ 10.4 (CH_3), 41.3 (CH_2), 110.5, 127.4, 130.7, 136.3. MS (ESI) *m/z* 300 (100%) [M − H]. Anal. Calc. for $C_{15}H_{15}N_3O_2S$: C 59.78, H 5.02, N 13.94. Found: C 59.61, H 5.16, N 14.01.

*FVT of 4-[Bis-((1-methylethyl)thio)methylene]-3-(2,2-dimethyl-propyl)-4*H*-isoxazol-5-one* ***6e***

The precursor **6e** (350 mg, 1.1 mmol) was gently sublimed at 70–95°C (10^{-4} hPa) and thermolysed at 600°C in the course of 5 h in a procedure analogous to the FVT of **6c** at the same temperature (*vide supra*). Flash chromatography on alumina (eluent: first diethyl ether, then increasing gradient to ethyl acetate/methanol 10:1) afforded: *N*,*N*-diethyl-3-neopentyl-5-oxo-2,5-dihydroisoxazole-4-thiocarboxamide **11e** (250 mg, 83%), yellow oil. GCMS: R_t 9.0 min, *m/z* 226 [$M - CO_2$]. ^{1}H NMR (200 MHz, $CDCl_3$/DMSO-d_6) δ 0.88 (s, 9H, ^{t}Bu), 1.21 (t, 6H, $^3J = 7$ Hz, CH_3), 2.92 (s, 2H, CH_2), 3.96 (q, 4H, CH_2), 8.56 (b. s, 1H, NH). ^{13}C NMR (50 MHz, $CDCl_3$/DMSO-d_6) δ 11.9 (CH_3), 29.3 (CH_3), 31.3 (C), 41.6 (CH_2), 47.3 (NCH_2), 93.0 (C-4), 162.1 (C-5), 171.0 (C-3), 208.5 (C=S). DEPT-135 δ 11.9, 29.3, 41.6 (CH_2), 47.3 (CH_2). Anal. Calc. for $C_{13}H_{22}N_2O_2S$: C 57.75, H 8.20, N 10.36. Found: C 57.58, H 8.30, N 10.31.

Accessory Publication

The following data is available on the Journal's website: IR spectrum of **8a** obtained by FVT of **6a** at 900°C; listings of wavenumbers and intensities of all compounds identified in the matrix IR spectra derived from FVT of compounds **6a**–**e** at various temperatures; peak listings of reference compounds; and Cartesian coordinates, energies, and vibrational spectra of calculated molecules.

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