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Acylthioketene−Thioacylketene−Thiet-2-one Rearrangements

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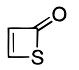
Flash vacuum thermolysis (FVT) of 6-aryl-1,3-dioxine-4-thiones **9** leads to the formation of acylthioketenes **10**, which are characterized by Ar matrix IR spectroscopy as well as on-line tandem mass spectrometry. The thioketenes **10** undergo a 1,3-shift of the aryl group to generate thioacylketenes **11**. Ketenes **11** cyclize to 3-aryl-thiet-2-ones **12**, which are also characterized by matrix IR spectroscopy and tandem mass spectrometry. The thiet-2-ones **12** undergo two kinds of reaction under the FVT conditions: (i) cheletropic CO extrusion with formation of arylthioketenes **13**, and (ii) cycloreversion to COS and arylacetylene.

Introduction

Thiet-2-ones (**1**) are usually delicate compounds, isolable as crystalline solids in the naphtho-annelated cases,[2] but oligomerizing in the benzo[2,3] and monocyclic cases[4] and being highly susceptible to nucleophilic attack at the carbonyl group with ensuing ring opening. The unstable monocyclic thiet-2-one **4** was fully characterized, including low temperature ^{13}C NMR spectroscopy, and a ^{13}C labeling experiment demonstrated that its formation by flash vacuum thermolysis (FVT) of the thiophenedione **2** proceeded via an unprecedented 1,3-shift of a phenyl group, thus interconverting the two thioacylketenes **3** and **5**. The ketenes are observable by low temperature IR spectroscopy, but the thiet-2-ones are the isolated products, being thermodynamically more stable. The ^{13}C labeling experiment demonstrated complete scrambling of the label between the two C=O carbons in **3**/**5**, but the C=S group was not (irreversibly) involved.[4] The experiments now reported explain why: acylthioketenes are of higher energy than thioacylketenes.



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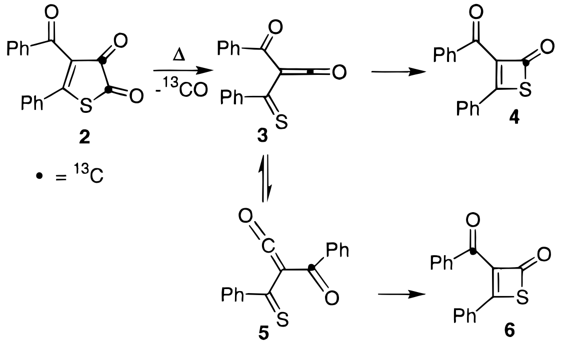
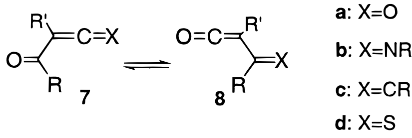


Phenyl group migration in acylketenes such as **3** have high activation barriers, necessitating flash vacuum thermolysis at ca. 700 °C.[5] Subsequently, we found that these 1,3-shifts are highly facilitated by electron-donating migrating groups, especially those possessing lone pairs that can interact favorable with the LUMOs of the ketenes (RO, RS, R_2N, Cl).[6] 1,3-Shifts of this kind have been established in acylketenes (**7a**), acylketenimines/imidoylketenes (**7b**/**8b**), and acylallenes/vinylketenes (**7c**/**8c**).[7]



Here we report our studies on the acylthioketene−thioacylketene rearrangement (**7d**/**8d**).

Results and Discussion

1. FVT-Matrix Isolation. Sublimation of the 1,3-dioxine-4-thione **9a** at 50 °C with concomitant Ar matrix isolation on a BaF_2 window at 14 K gave rise to strong IR bands due to **9a** at 1602, 1575, 1368, 1265, and 1165 cm^{-1}. FVT of **9a** at 500 °C with Ar matrix isolation of the product gave rise to acetone (1722, 1443, 1432, 1416, 1362, 1223, and 1094 cm^{-1}). A second set of bands was assigned largely to benzoylthioketene **10a** because they all disappear on thermolysis at higher temperature (750 °C), and most of these band positions agree well with the calculated IR spectrum, at the HF/6-31G*, and B3LYP/6-31G*, and B3LYP/6-311+G* levels (the calculated IR data is given in Table S1 in the Supporting Information).

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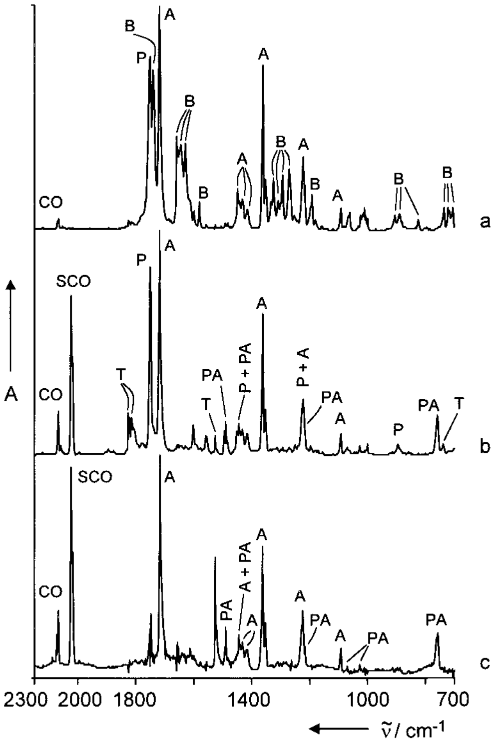
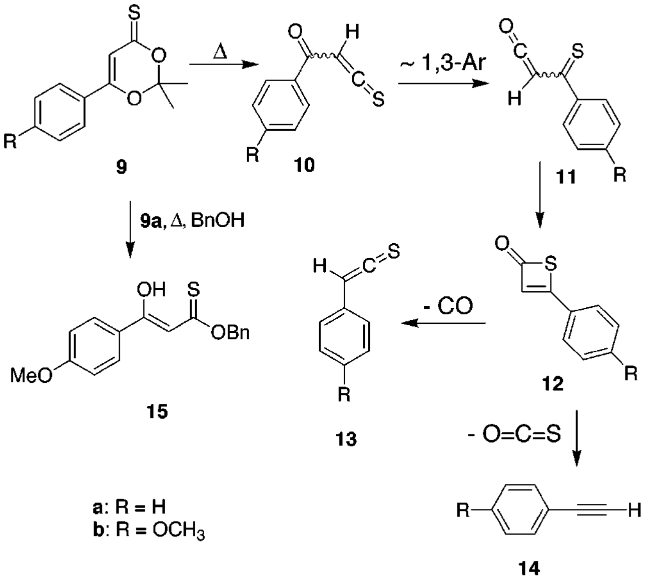


Figure 1. FVT of 1,3-dioxine-4-thione **9a**. IR spectra (Ar, 10 K) of the products formed at (a) 500 °C, (b) 750 °C, (c) 950 °C. Letters denote acetone (A), benzoylthioketene **10a** (B), phenylthioketene **12** (P), thietone **12** (T), phenylacetylene **14a** (PA). SCO appears at 2050, 2035 cm^{-1} and CO at 2139, 2148 cm^{-1}.

These bands were at 1742, 1661, 1648, 1630, 1583, 1294, 1271, 1192, 908, 892, 724, and 707 cm^{-1} (Figure 1a). Some of the bands may be due to matrix sites, and some minor ones to impurities, but there can be little doubt that the spectrum is due essentially to thioketene **10a** as a mixture of *E* and *Z* forms. At this temperature, very weak bands in the 1800 cm^{-1} range were also present; these are due to the thiet-2-one **12** which becomes more prominent at 750 °C (see below). A third major band in the 500 °C experiment at 1753 cm^{-1} is ascribed to phenylthioketene **13**. This compound has much weaker bands at 1451, 1232, and 897 cm^{-1}, and was identified by comparison with the previous IR studies[3] as well as the mass spectra reported below. At 750 °C, medium strength bands appear at 1827, 1816, and 1808 cm^{-1} (Figure 1b) in the range expected for thiet-2-ones.[2] The strongest calculated band for **12a** is at 1863 (HF/6-31G*), 1864 (B3LYP/6-31G*), or 1871 cm^{-1} (B3LYP/6-311+G*). The triad of experimental bands is ascribed to different matrix sites. New bands at 1528 (m−w) and 741 (w) cm^{-1} are also ascribed to **12a** (calculated 1573/1536/1548 and 761/726/736 cm^{-1}, at the HF/6-31G*, B3LYP/6-31G*, and B3LYP/6-311+G* levels, respectively). Also seen at 750 °C is a strong band at 2050 cm^{-1} due to OCS as well as several bands due to phenylacetylene **14a** (3340, 3328, 3315 (sites), 1490, 1217, 1071, 1026, and 759 cm^{-1}). The bands due to OCS and **14a** grow further on FVT at 950 °C, whereas those ascribed to thiet-2-one **12** disappear completely (Figure 1c).

The results are interpreted in Scheme 1. Loss of acetone from **9a** under mild FVT conditions leads to the identifiable benzoylthioketene **10a**. At slightly higher temperatures, **10a** rearranges to the thioacylketene **11a**, which undergoes electrocyclization to thiet-2-one **12a**. The ketene **11a** itself is hardly seen, except perhaps for a weak peak at 2120 cm^{-1} which is present only when the thiet-2-one is present. The thiet-2-one decomposes by cycloreversion as soon as it is formed, to give OCS and phenylacetylene **14a**. A second mode of decomposition is cheletropic extrusion of CO (2138 cm^{-1}) to furnish phenylthioketene **13a**, formally by means of a Wolff rearrangement of the putative thiobenzoylcarbene.

Scheme 1



A corresponding CO extrusion was not observed in the case of the 3-benzoyl-4-phenylthiet-2-one (**4**/**6**), which underwent quantitative cycloreversion to benzoyl(phenyl)acetylene and OCS.[4] However, competing cycloreversion *and* CO extrusion were observed in the mass spectrometric fragmentation of the molecular ion of **4**/**6**. Benzothiet-2-one undergoes high-temperature extrusion of CO to furnish thiocarbonylcyclopentadiene.[3]

The *p*-methoxyphenyl (anisyl) derivative **9b** reacted completely analogously, with the only exception that the thiet-2-one **12b** appeared already at 550 °C and reached its maximum intensity at 650 °C. This is as expected, as the electron-rich anisyl substituent should undergo the 1,3-shift more readily, giving **11b** and hence **12b** (see section 3). IR absorptions at 1754, 1734, 1644, 1632, 1606, 1261, 1227, 1170, 889, and 771 cm^{-1} can be ascribed to the acylthioketene **10b** in good agreement with B3LYP/6-31G* calculatated data (Table S2). A weak peak at 2115 cm^{-1} (650−750 °C) may be due to the ketene **11b**. Difference spectroscopy allowed the extraction of the IR spectrum of the thiet-2-one **12b**: 1825, 1821, 1499, 1216, 1174 cm^{-1}. These bands match the strongest calculated vibrations for the molecule (1863, 1488, 1264, 1165 cm^{-1} at the B3LYP/6-31G* level; Table S2). The decomposition of this material above 600 °C led to OCS, acetylene **14b**, CO, and anisylthioketene **13b** (this compound also absorbs at 1754 cm^{-1}).[3] The difference spectrum and the calculated data are given in the Supporting Information.

The number of bands observed for thioketenes **10** in both cases indicates that a mixture of the *s-Z* and *s-E* forms was present. The fact that no temperature dependence on the relative intensities was observed indicates that the two conformers are nearly isoenergetic,

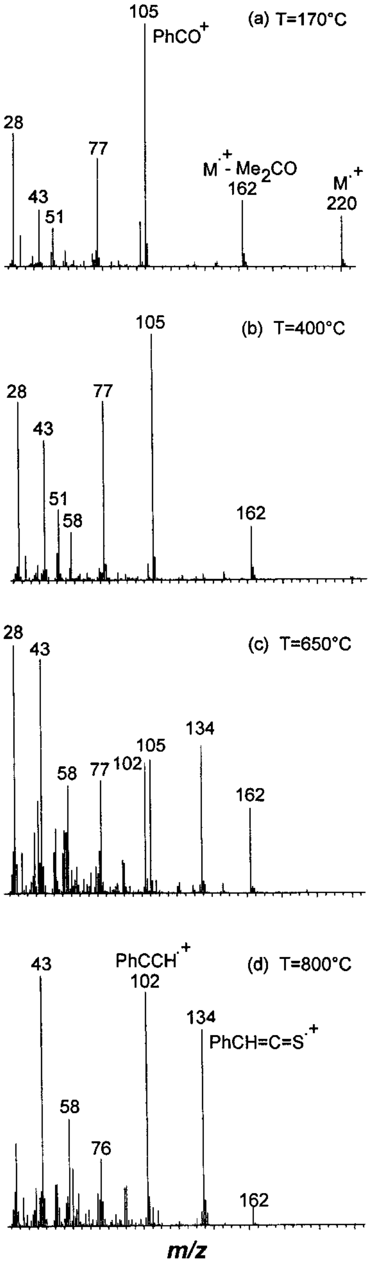


Figure 2. FVT-MS of **9a** at different temperatures.

Table 1. Calculated Relative Energies of Thioketenes, Ketenes, Thietones, and Transition States Connecting Them (kJ mol^{-1})[a,b]

species	R = H (**a**)	R = OCH$_3$ (**b**)
s-E-acylthioketene (**E10**)	11.0	10.5
s-Z-acylthioketene (**Z10**)	8.2	6.8
s-E-thioacylketene (**E11**)	0.0	0.0
s-Z-thioacylketene (**Z11**)	−5.0	−6.7
1,3-C$_6$H$_4$R shift TS (**E10** → **E11**)	148.2	130.1
thiet-2-one (**12**)	1.0	−2.6
ring closure TS (**Z11**→ **12**)	10.7	8.3

[a] B3LYP/6-311+G**//B3LYP/6-31G* + ZPVE level. [b] 4.184 kJ mol^{-1} = 1 kcal mol^{-1}.

in agreement with the results of energy calculations (Table 1).

Sato has provided evidence for the formation of transient acylthioketenes in solution upon thermolysis of dioxinethiones by means of trapping reactions.[8] Similarly, we obtained the enol *O*-benzyl thioate **15** in 80% yield

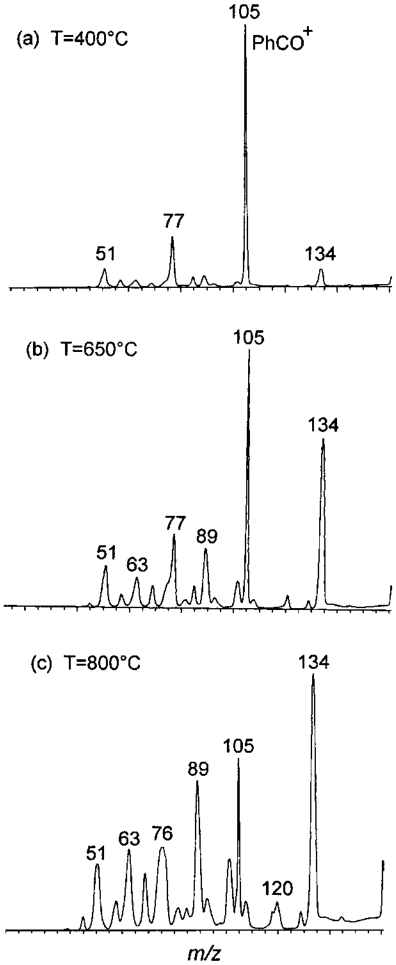


Figure 3. CAMS of *m/z* 162 at different temperatures (going from thioketene **10a** to thietone **12a**).

on thermolysis of **9b** in refluxing xylene in the presence of benzyl alcohol.

2. FVT-MS. Complete confirmation of the above results was obtained by on-line mass spectrometry studies of the thermolysis products using an FVT reactor fitted inside the ion source housing of a six-sector mass spectrometer. The mass spectra of **9a** and those resulting from FVT are shown in Figure 2 as a function of temperature. The starting material (*m/z* 220) has disappeared at 400 °C (Figure 2b). The species at *m/z* 162 is now likely to have the thioketene structure **10a**. This species undergoes simple cleavage to *m/z* 105 (PhCO$^+$) as the predominant fragmentation as seen in the collisional activation (CA) mass spectrum (CAMS) of *m/z* 162 in an MS/MS experiment (Figure 3). This is also true of the *m/z* 162 ion from Figure 2a (170 °C). As the temperature increases to 560 °C (Figure 2c), the thermal formation of PhCH=C=S (**13a**, *m/z* 134) becomes prominent, the benzoyl cation is reduced in intensity (*m/z* 105), and phenylacetylene is already becoming important (**14a**, *m/z* 102). These two fragmentation products become dominant at 800 °C, where only a little of the *m/z* 162 species is left (Figure 2d).

The changing structure of the *m/z* 162 species is illustrated in the CAMS of the mass-selected ion in Figure 3. At 650 °C, formation of a *m/z* 134 species

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Table 2. Calculated Relative Energies of Thiet-2-one 12a and Thioacylketene Z11a (kJ mol^{-1})[a,b]

level	relative energy	level	relative energy
HF/6-31G*	17.3	B3LYP/6-31G*	1.9
MP2/6-31G*	2.3	B3LYP/6-311G**	11.4
MP3/6-31G*	−5.9	B3LYP/6-311+G**	5.2
MP4SDQ/6-31G*	3.2	B3LYP/cc-pVDZ	2.7
QCISD/6-31G*	3.1	B3LYP/cc-pVTZ	1.6
QCISD(T)/6-31G*	−0.9	B3LYP/6-311+G(3df,2p)	1.6
QCISD(T)/6-311+G(3df,2p)[c]	−1.5	B3LYP/6-311+G(3df,2p) ($\epsilon = 40$)	−4.8
QCISD(T)/6-311+G(3df,2p)[c,d]	−0.7	B3LYP/6-311+G(3df,2p)[d] ($\epsilon = 40$)	−4.0

[a] Based on the B3LYP/6-31G* optimized geometry. [b] 4.184 kJ mol^{-1} = 1 kcal mol^{-1}. [c] Estimated using basis-set additivity at the MP2 level. [d] Including zero point energy correction (B3LYP/6-31G*).

competes with the simple cleavage to *m/z* 105, i.e., two different species with a mass of 162 are now present. At 800 °C the second isomer has become dominant. This isomer is identified as the thiet-2-one **12a** because of its ready extrusion of CO to give *m/z* 134 in accord with the IR observations above. The CAMS in Figure 3c is similar to that of PhCH═C═S (**13a**) itself[3] below *m/z* 100. This interpretation is also supported by the MIKE spectra: as mentioned above, the CA spectrum of the “cold” *m/z* 162 species derived from **9a** at 170 °C features essentially only *m/z* 105 (simple cleavage). The MIKE spectrum under the same conditions features a ca. 4:1 ratio of *m/z* 105 and *m/z* 134, indicating that the latter is formed in a rearrangement process.

The structures of the ions assigned as PhCH═C═S, PhCCH, and OCS (*m/z* 60) were confirmed by CAMS of the mass-selected ions and comparison with those of authentic samples and are reported in the Supporting Information.

The anisyl derivative **9b** behaved in a similar manner, and the ions were identified as described above. The essential spectra are shown in the Supporting Information. Here too, the thioketene (**10b**) is characterized by simple cleavage (*m/z* 192 → 135, prominent at 300−400 °C). As in the IR investigation, rearrangement occurred at lower temperature in this case, the thiet-2-one being dominant already at ca. 500 °C (characterized by *m/z* 192 → 164). The structures of the ions corresponding to **13b**, **14b** and OCS were confirmed by their CA mass spectra.

3. Theory. Structures and IR spectra of **10**, **11**, and **12** (**a** and **b** series) and related transition structures were calculated at the B3LYP/6-31G* level,[9] using the Gaussian 98 programs.[10] IR spectra for the **a** series were also calculated at the B3LYP/6-311+G* level. The computed IR spectral data and Cartesian coordinates are given in the Supporting Information. Improved relative energies were obtained through B3LYP/6-311+G** calculations, including B3LYP/6-31G* zero-point energy correction (scaled by 0.9804).[11] The thioacylketenes (**11**) are predicted to be more stable than acylthioketenes (**10**), by ca. 13 kJ mol^{-1} (Table 1). For both **10** and **11**, the *s-Z* conformation is the preferred conformer, but the *E*/*Z* energy differences are small.

We have shown previously that 1,3-shifts in acylketenes and related molecules are facile processes when the migrating group possesses an unshared pair of electrons capable of overlap with the vacant central carbon p orbital of the ketene LUMO.[6,7] 1,3-Alkyl migrations in contrast have very high calculated barriers and have not been observed. The observed 1,3-phenyl migration in benzoylketene[4] has a calculated barrier of 147 kJ mol^{-1} (35 kcal mol^{-1}). The rearrangement of acylthioketene **E10a** to thioacylketene **E11a** via a 1,3-phenyl shift is likewise calculated to have a barrier of 148 kJ mol^{-1} (35 kcal mol^{-1}). The migratory aptitude of a phenyl group can be rationalized in terms of the availability of the HOMO (π orbital) in the rotated phenyl group as an electron donor. **E10b** is expected to have a lower 1,3-shift barrier because of the increased electron-donating ability of the migrating group. Indeed, the calculated barrier is 130 kJ mol^{-1} (31 kcal mol^{-1}) in agreement with the experimental observation that 1,3-migration in **10b** occurred at a lower FVT temperature than for **10a**.

Thiet-2-one (**12**) and *s-Z*-thioacylketene (**Z11**) are predicted to lie very close in energy. At the B3LYP/6-311+G** + ZPVE level, **12** is slightly higher in energy, but the relative energies are rather sensitive to the basis set and the level of correlation treatment employed (Table 2). The HF treatment and moderate-sized basis sets strongly favor the open form **Z11**, but the cyclic structure is stabilized at higher levels of theory. Thus **12a** is preferred over **Z11a** by ca. 1 kJ mol^{-1} at the QCISD(T)/6-31G* level. At our best level of theory, QCISD(T)/6-311+G(3df,2p) + ZPVE, **12a** is more stable than **Z11a** by ca. 1.5 kJ mol^{-1} (Table 3). Thiet-2-ones are polar molecules (μ = 5.12 and 6.52 D for **12a** and **12b**, respectively). Thus, the thiet-2-one/acylthioketene equilibrium will be shifted toward the cyclic structure in the presence of a polar environment. In a dielectric medium of $\epsilon = 40$, **12a** is predicted to be more stable than **Z11a** by 4 kJ mol^{-1}, using Onsager's SCRF model.[12] The barrier toward ring closure (**Z11** → **12**) is of the order of 8−11 kJ mol^{-1} (2−3 kcal mol^{-1}) (Table 1). Thus, calculations agree with the experimentally observed preference for the thiet-2-ones in matrixes. As we have noted before, molecules experience polar effects even in Ar matrixes, which cannot be regarded simply as the frozen gas phase.[13]

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Conclusion

The thermal rearrangement of acylthioketenes to thioacylketenes, followed by electrocyclization of the latter to thiet-2-ones, has been demonstrated. The rearrangement is accelerated by an electron-donating substituent (OMe) on the migrating phenyl group, consistently with a donor−acceptor interaction between the migrating group and the ketene LUMO. Thioacylketenes are lower in energy than acylthioketenes, and thiet-2-ones are slightly lower in energy than the thioacylketenes.

Experimental Section

Apparatus for FVT-matrix isolation and IR spectroscopy[14] and for FVT-MS were as previously described.[15]

6-Anisyl-1,3-dioxine-4-thione (9b) was prepared by a method similar to that reported for **9a**.[8] Lawesson's reagent (2.39 g; 6 mmol) was added to a benzene solution (25 mL) of 6-anisyl-1,3-dioxine-4-one (0.92 g; 4 mmol), and the solution was refluxed for 4 h. The reaction mixture was cooled to 25 °C and filtered, and the solvent was removed in vacuo to yield a brown oil. Flash chromatography (silica gel, hexane−diethyl ether 1:1) followed by recrystallization from hexane−diethyl ether (5:1) afforded orange-yellow needles (265 mg; 37%); mp 71−73 °C; ^{1}H NMR (CDCl$_3$) 7.68 (d, 2H, $J = 9$ Hz), 6.95 (d, 2H, $J = 9$ Hz), 6.96 (s, 3H), 3.85 (s, 3H), 1.81 (s, 6H); ^{13}C NMR (CDCl$_3$) 200, 163, 156, 128, 122, 114, 106, 103, 55, 24 ppm; IR (KBr) 1588 s, 1509 s, 1257 s, 1160 s cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.49; H, 5.59.

Benzyl Anisoylthionoacetate (Enol Form) (15). A solution of **9b** (100 mg; 0.4 mmol), benzyl alcohol (41 μL; 0.4 mmol), and xylene (15 mL) was refluxed for 4 h and cooled to RT, and the solvent was removed in vacuo, affording 97 mg (80%) of the thiono ester. ^{1}H NMR (CDCl$_3$) 14.2 (s, 1H), 7.8 (d, 2H, $J = 9$ Hz), 7.4 (m, 5H), 6.9 (d, 2H, $J = 9$ Hz), 6.4 (s, 1H), 5.5 (s, 2H), 3.8 (s, 3H) ppm; ^{13}C NMR (CDCl$_3$) 207, 173, 163, 135, 131, 129, 128.4, 128.1, 126, 114, 100, 71, 55 ppm; IR (KBr) 1599 s, 1507 m, 1172 s cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_3S$: C, 67.89, H, 5.38. Found: C, 67.96; H, 5.41.

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Supporting Information Available: Difference-IR spectrum from the FVT of **9b**, showing thietone **12b** and anisoylthioketene **10b**. FVT-MS of **9b** at different temperatures. CAMS of *m/z* 192 from the FVT-MS of **9b** at various temperatures (from thioketene **10b** to thietone **12b**). CAMS of **13a**,**b**, **14a**,**b**, and OCS. Calculated IR data (Tables S1 and S2) and Cartesian coordinates (Tables S3 and S4) for all compounds **10**−**12a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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