from phosphonium salt 1 and ethyl 3-methyl-6-oxo-2-heptenoate (E/Z = 3) in identical fashion as described for 4. The ethyl 3-methyl-6-oxo-2-heptenoate was prepared by a Wittig synthesis involving 2,5-hexanedione (2 equiv) and the ylide formed from 1 equiv of triethyl phosphonoacetate (NaH, 1 equiv) in THF at 0 °C followed by purification by flash silica column chromatography: ^{1}H NMR ($CDCl_3$) E/Z isomers δ 1.3 (t, 3 H, CH_3), 2.16, 2.17 (two singlets, 6 H, 2 CH_3), 2.4 and 2.82 (2 triplets, 2 H, allylic CH_2), 2.65 (t, 2 H, CH_2 α to 6-oxo), 4.15 (q, CH_2O), 5.65 and 5.70 (2 singlets, 1 H, vinylic hydrogens, ratio 3:1 respectively); IR (neat) ν_{max} cm^{-1} 2982, 2939, 2907, 1716, 1650; MS (DCI-ammonia) m/e (relative intensity) 202 (M^+ + 18, 100), 185 (M^+ + 1, 75).

The product cyclopentene in this reaction was partially purified via flash silica gel column chromatography (10% EtOAc-90% hexane eluent) to give 380 mg of product, which proved to be 77% pure by GLC analysis (adjusted yield 45%): ^{1}H NMR ($CDCl_3$) δ 1.11 (s, 3 H, CH_3), 1.25 (t, 3 H, CH_3), 1.7 (m, 1 H, cyclopentene H_4), 1.8 (s, 3 H, propargyl CH_3), 2.0 (s, 3 H, allylic methyl), 2.1 (m, 1 H, cyclopentene H_4), 2.3 (m, 2 H, cyclopentene H_5), 2.4 (dd, 2 H, CH_2CO_2Et, J = 56 and 13 Hz), 4.1 (m, 2 H, CH_2O); ^{13}C NMR ($CDCl_3$) δ 4.5 propargyl methyl, 14.3, 16.0, 25.1, 35.5, 35.6, 44.2, 49.4, 59.9, 74.4, 90.3, 126.7, 144.59, 172.8; IR (neat) ν_{max} cm^{-1} 2962, 2912, 2210 (w), 1734 (CO); MS (EI), m/e (relative intensity) 220 (M^+, 22), 147 ($M^+ - CO_2Et$, 90), 133 (100), 117 (90), 105 (60), 91 (80); GLC (t_R) 17.9 min; MS-HREI, calcd 220.1463, found 220.1464.

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Supplementary Material Available: ^{13}C and ^{1}H NMR spectra for compounds **2-4**, and **10** and entries A, B, and D of Table I. (10 pages). Ordering information is given on any current masthead page.

Photochemical Reactions of Semicyclic Monothioimides. A Novel Photocyclization of *N*-(β,γ-Unsaturated Carbonyl) Thioamides

Masami Sakamoto,* Shoji Watanabe, Tsutomu Fujita, and Tohru Yanase

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba, 260 Japan

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The photochemistry of the nitrogen-containing thiocarbonyl compounds have received much attention from both synthetic and mechanistic viewpoints. In particular, the Paterno-Büchi reactions of thioamides[1] and thioimides[2] have been investigated for this purpose. In relation to our study on the photochemical reactions of acyclic and semicyclic monothioimides,[3] we now report on the photoreactions of *N*-(β,γ-unsaturated carbonyl) thioamides. We previously reported on the photochemistry of *N*-(α,β-unsaturated carbonyl) thioamides, which proceeded via an intramolecular [2 + 2] photocyclization to produce thietane-fused β-lactams in good yields.[3a] In contrast, we now report that the introduction of one carbon atom between the olefin and carbonyl group produced many differences in the photochemical properties.

Scheme I

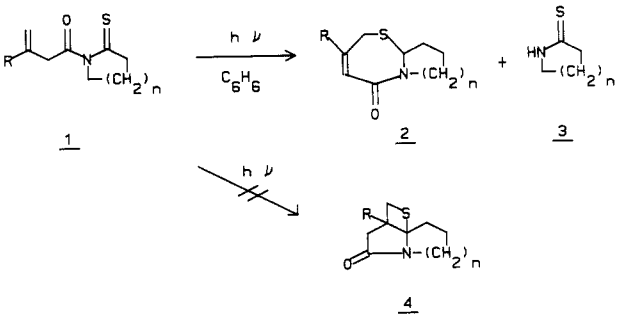

Table I. Photolysis of Monothioimides 1a-f

	n	R	yield, % 2	yield, % 3
a	1	H	24	31
b	1	Me	61	34
c	2	H	71	trace
d	2	Me	56	trace
e	3	H	38	trace
f	3	Me	46	trace

Results and Discussion

The monothioimides **1a-f** were obtained by condensation of the corresponding acids with thiolactams in the presence of DCC, whereas the monothioimides **1g,h** were synthesized from acid chlorides and thiolactams, using triethylamine as base. When *N*-(3-butenoyl)thiopyrrolidone (**1a**) was irradiated in benzene with a 1-kW high-pressure mercury lamp under nitrogen until the starting material had disappeared, 2-oxo-6-thia-1-azabicyclo[5.3.0]dec-3-ene (**2a**) was obtained in 24% yield, accompanied by thiopyrrolidone **3** (n = 1) (Scheme I). The structure of **2a** was determined on the basis of elemental analysis and spectral data. The IR spectrum ($CHCl_3$) exhibited an absorption at 1660 cm^{-1} (C=O). The ^{1}H NMR spectrum ($CDCl_3$) of the product showed new signals arising from olefinic protons at δ 6.0-6.4 (m, 2 H). The ^{13}C NMR spectrum ($CDCl_3$) exhibited three doublet signals at δ 60.5 (d), 128.9 (d), and 131.6 (d), assigned to C-7, C-3, and C-4, respectively. Furthermore, the ^{13}C NMR spectrum evidenced the disappearance of the thiocarbonyl group. The structure of thiopyrrolidone **3** was determined by comparison with an authentic sample. Photolysis of thioimides **1b-f** under the same conditions also gave the corresponding bicyclic lactams **2b-f** as shown in Table I. In these reactions, thietane **4** was not detected at all.

The formation of the bicyclic lactams **2** is reasonably explained in terms of the generation of 1,4-diradical intermediate **5** as shown in Scheme II. Presumably, the strain energy required to form thietane **4** prevents closure of diradical intermediate **5** and leads to bicyclic lactams **2** via a 1,4-hydrogen shift. We were unsuccessful in

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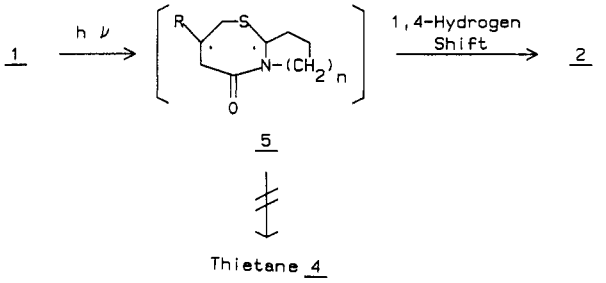
(2) (a) Machida, M.; Oda, K.; Kanaoka, Y. *Chem. Pharm. Bull.* **1985**, *33*, 3552. (b) Machida, M.; Oda, K.; Yoshida, E.; Kanaoka, Y. *J. Org. Chem.* **1985**, *50*, 1681. (c) Coyle, J. D.; Rapley, P. A.; Kamphuis, J.; Bos, H. J. T. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1957. (d) Oda, K.; Machida, M.; Aoe, K.; Nishibata, Y.; Sato, Y.; Kanaoka, Y. *Chem. Pharm. Bull.* **1986**, *34*, 1411. (e) Oda, K.; Machida, M.; Aoe, K.; Sato, Y.; Kanaoka, Y. *Ibid.* **1986**, *34*, 4414. (f) Oda, K.; Machida, M.; Kanaoka, Y. *Heterocycles* **1988**, *27*, 2417.

(3) (a) Sakamoto, M.; Aoyama, H.; Omote, Y. *J. Org. Chem.* **1984**, *49*, 396. (b) Sakamoto, M.; Aoyama, H.; Omote, Y. *Ibid.* **1984**, *49*, 1837. (c) Sakamoto, M.; Aoyama, H.; Omote, Y. *Tetrahedron Lett.* **1986**, *27*, 1335. (d) Sakamoto, M.; Watanabe, S.; Fujita, T.; Tohnishi, M.; Aoyama, H.; Omote, Y. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2203.

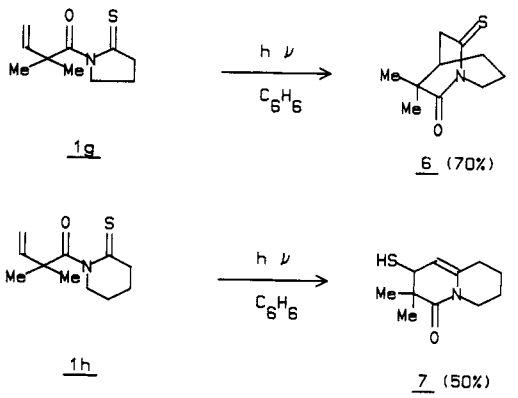
(4) Nishio, T.; Okada, N.; Kashima, C. 58th Annual Meeting of the Chemical Society of Japan, April 1989 (Kyoto). They reported that photolysis of 2-alkenyl-2-methylindan-1-thiones gave thietanes.

0022-3263/90/1955-2986$02.50/0

Scheme II



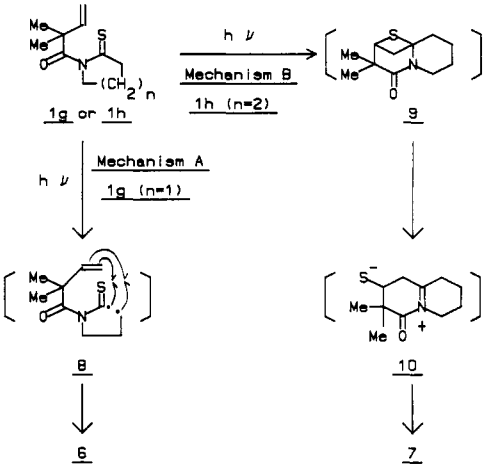
Scheme III



trapping 1,4-diradical intermediate **5** with ethyl mercaptan. Intramolecular [2 + 2] cyclizations have been reported for thioketones[4] and thioimides[1c,2b,d,c] to give thietanes. A 1,4-diradical intermediate generated by formation of a new C–S bond between the olefinic carbon and sulfur atom of the thiocarbonyl group has been proposed for these reactions. It is concluded that this photoreaction provides information concerning the intermediates in the photoreactions of thiocarbonyl groups with olefins. On the other hand, [2 + 2] photocyclization of ketones, oxetane formation, is expected to obey a "rule of five". For the photochemical reaction of thioimides **1**, formation of the seven-membered ring is preferred over the conceivable five- or six-membered diradical intermediates. The difference is explainable in terms of both the longer length of the C=S double bond compared to that of the C=O double bond and the stability of the diradical intermediate.

We attempted the photochemical reactions of **1g** and **1h**, which possess dimethyl groups between the olefin and carbonyl group, in order to prevent the 1,4-hydrogen shift in diradical intermediate **5**. When **1g** was irradiated under the same conditions as in the case of **1a–f**, bicyclic monothioimide **6** was obtained in 70% yield (Scheme III). The structure of **6** was determined on the basis of elemental analysis and spectral data. The IR spectrum ($CHCl_3$) exhibited an absorption at 1725 cm^{-1} due to the C=O bond. The ^1H NMR spectrum ($CDCl_3$) showed signals at δ 0.99 (s, 3 H), 1.32 (s, 3 H), 1.9–2.0 (m, 2 H), 2.4–2.7 (m, 2 H), 3.0–3.1 (m, 1 H), 3.2–3.3 (m, 1 H), 3.6–3.7 (m, 1 H), and 3.8–4.0 (m, 2 H). The ^{13}C NMR spectrum ($CDCl_3$) exhibited signals at δ 19.5 (q), 22.7 (t), 24.4 (q), 30.6 (t), 38.2 (t), 51.3 (s), 53.0 (d), 60.5 (t), 175.1 (s), and finally 211.6 (s), arising from the thiocarbonyl carbon. The mass spectrum exhibited the molecular ion peak m/e 197 (M^+). Photolysis of thiopiperidone derivative **1h** gave bicyclic enamide **7** in 50% yield. The IR spectrum showed absorptions at 2500 (SH) and 1660 (C=O) cm^{-1}. The ^1H NMR spectrum ($CDCl_3$) exhibited one signal for the olefinic proton at δ 4.94 (dt, J = 2 and 4 Hz, 1 H). The ^{13}C NMR spectrum ($CDCl_3$) indicated two olefinic carbons,

Scheme IV



at δ 99.2 (d) and 139.0 (s), and no thiocarbonyl carbon.

For the formation of bicyclic monothioimide **6**, a Norrish Type I reaction (α-cleavage) of the thiocarbonyl group, followed by intramolecular trapping of diradical **8** by the olefin group is postulated (mechanism A), as shown in Scheme IV. Norrish Type I photochemistry has been reported for strained thioketones,[5] dithioesters,[6] and four-membered monothioimides.[3c] The strain energy in these compounds may be an important factor in assisting C(=S)–C bond cleavage. In the case of the photolysis of **1h** (n = 2), the intermediacy of thietane **9** produced by cross-type [2 + 2] cyclization is proposed for forming bicyclic enamide **7**. The thietane ring reopens to give **7** via the zwitterionic intermediate **10** (mechanism B).

In conclusion, photolysis of *N*-(3-butenoyl)- and *N*-(3-isopentenoyl)thiolactams **1a–f** gave bicyclic lactams **2a–f** via a kind of parallel-type intramolecular cycloaddition between the sulfur atom of the thiocarbonyl group and the olefinic carbon, followed by a 1,4-hydrogen shift, and also produced thiolactams. For the formation of thiolactams **3**, a Type II cleavage reaction is postulated, in light of the fact that thioimides **1g,h**, which have no abstractable hydrogen atoms at the γ-position of the thiocarbonyl group, did not give thiolactams. However, direct cleavage of the (C=O)–N bond cannot be strictly ruled out as a minor process to produce thiolactams **3**.[3d] Irradiation of *N*-(2′,2′-dimethyl-3′-butenoyl)thiopyrrolidone (**1g**) yielded bicyclic monothioimide **6**, through α-cleavage followed by intramolecular trapping by the olefin. In the case of the photolysis of *N*-(2′,2′-dimethyl-3′-butenoyl)thiopiperidone (**1h**), the ring-opening product **7** of the thietane formed by a cross-type [2 + 2] cycloaddition reaction was obtained.

The introduction of dimethyl groups at the α-position of the carbonyl group is probably influential in the formation of monothioimides. It is concluded that the repulsion between the carbonyl and dimethyl groups makes the cross-type cyclization more favorable; however, there is no satisfactory hypothesis to explain the difference at present. This reaction not only provides a useful synthesis of some nitrogen-containing heterocycles but also yields important insights into the Paterno–Büchi reaction of thiocarbonyl compounds, since there is, to our knowledge, no previous example of 1,4-hydrogen migration in a diradical intermediate formed by addition of the sulfur atom of a thiocarbonyl group with an olefinic carbon.

(5) Muthuramu, K.; Ramamurthy, V. *J. Org. Chem.* **1980**, *45*, 4533.
(6) Muthuramu, K.; Sundari, B.; Ramamurthy, V. *Tetrahedron* **1983**, *39*, 2719.

Experimental Section

IR spectra were measured on a Jasco IRA-1 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Hitachi R-24B and JEOL-100 spectrometers using tetramethylsilane as an internal standard. The chemical shifts are in δ units (ppm) with coupling constants in hertz, and $CDCl_3$ was used as the solvent unless otherwise stated. UV spectra were measured on a Shimadzu UV-365 UV-vis-near-IR recording spectrophotometer. An Eikohsya 1000-W high-pressure mercury lamp was used as the irradiation source. Silica gel (Merk, Kieselgel 60, 230–400 mesh) was used for flash column chromatography.

Preparation of Monothioimides. Monothioimides (**1a–f**) were prepared by the reaction of N-substituted thioamide with the corresponding acid in the presence of dicyclohexylcarbodiimide (DCC). To a dry ethyl acetate (or dry THF) solution of thioamide (3.0 mmol) and carboxylic acid (3.6 mmol) was added DCC (3.6 mmol) at 0 °C, and the mixture was stirred for 24 h at room temperature. After the solvent was removed in vacuo, the resulting mixture was separated by flash column chromatography on silica gel (eluant: benzene–hexane mixture). Monothioimides (**1g,h**) were prepared by the reaction of N-substituted thioamides with 2,2-dimethyl-3-butenoyl chloride. Triethylamine (3.0 mmol) was added dropwise to a solution of thiobenzanilide (3.3 mmol) and acid chloride (3.3 mmol) in dry benzene (30 mL) at room temperature under nitrogen, and the reaction mixture was then stirred for 2 h. The precipitated triethylamine hydrochloride was removed by filtration through a Celite column, the benzene was evaporated, and the residual mixture was subjected to chromatography on silica gel (eluant: benzene–hexane). Monothioimides (**1g,h**) were isolated. All monothioimides (**1a–h**) were unstable and decomposed upon distillation; they were therefore used as soon as possible without further purification.

1-(3′-Butenoyl)pyrrolidine-2-thione (1a): IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03 (quint, J = 7 Hz, 1 H, 4-CH_2), 3.18 (t, J = 7 Hz, 2 H, 3-CH_2), 3.75 (br, 2 H, CH_2C=O), 4.13 (t, J = 7 Hz, 2 H, 5-CH_2), 5.0–5.5 (m, 2 H, C=CH_2), 5.7–6.3 (m, 1 H, HC=C).

1-(3′-Methyl-3′-butenoyl)pyrrolidine-2-thione (1b): IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.81 (s, 3 H, CH_3), 2.02 (quint, J = 7 Hz, 1 H, 4-CH_2), 3.19 (t, J = 7 Hz, 2 H, 3-CH_2), 4.00 (br, 2 H, CH_2C=O), 4.16 (t, J = 7 Hz, 2 H, 5-CH_2), 4.74 (br, 1 H, C=CH_2), 4.91 (br, 1 H, C=CH_2).

1-(3′-Butenoyl)piperidine-2-thione (1c): IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.7–2.1 (m, 4 H, 4- and 5-CH_2), 3.07 (m, 2 H, 3-CH_2), 3.75 (br, 2 H, CH_2C=O), 3.77 (m, 2 H, 6-CH_2), 5.0–5.4 (m, 2 H, C=CH_2), 5.7–6.2 (m, 1 H, HC=C).

1-(3′-Methyl-3′-butenoyl)piperidine-2-thione (1d): IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.7–2.1 (m, 4 H, 4- and 5-CH_2), 1.80 (s, 3 H, CH_3), 2.7–3.1 (m, 2 H, 3-CH_2), 3.4–4.1 (m, 4 H, 6-CH_2 and CH_2C=O), 4.75 (m, 2 H, C=CH_2), 4.90 (m, 1 H, HC=C).

1-(3′-Butenoyl)-ε-thiocaprolactam (1e): IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4–2.0 (br, 6 H, 4-, 5-, and 6-CH_2), 2.9–3.3 (br, 2 H, 3-CH_2), 3.7–3.9 (br, 4 H, 7-CH_2 and CH_2C=O), 5.0–5.4 (m, 2 H, C=CH_2), 5.7–6.2 (m, 1 H, HC=C).

1-(3′-Methyl-3′-butenoyl)-ε-thiocaprolactam (1f): IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–2.0 (br, 6 H, 4-, 5-, and 6-CH_2), 1.81 (s, 3 H, CH_3), 3.1–3.3 (br, 2 H, 3-CH_2), 3.7–4.0 (br, 4 H, 7-CH_2 and CH_2C=O), 4.8–5.1 (m, 2 H, C=CH_2).

1-(2′,2′-Dimethyl-3′-butenoyl)pyrrolidine-2-thione (1g): IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (s, 6 H, 2Me), 2.0–2.4 (m, 2 H, 4-CH_2), 2.96 (t, J = 7 Hz, 2 H, 3-CH_2), 3.97 (t, J = 7 Hz, 2 H, 5-CH_2), 5.0–5.4 (m, 2 H, C=CH_2), 5.9–6.4 (m, 1 H, HC=C).

1-(2′,2′-Dimethyl-3′-butenoyl)piperidine-2-thione (1h): IR ($CHCl_3$) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (s, 6 H, 2Me), 1.7–2.1 (m, 4 H, 4- and 5-CH_2), 2.8–3.1 (m, 2 H, 3-CH_2), 3.3–3.7 (m, 2 H, 6-CH_2), 5.0–5.4 (m, 2 H, C=CH_2), 5.9–6.5 (m, 1 H, HC=C).

General Procedure for the Photochemical Reactions of Monothioimides (1a–f). A benzene solution of the monothioimide was irradiated with a 1000-W high-pressure mercury lamp under nitrogen at room temperature until the starting material had disappeared. After evaporation of the solvent, the filtrated was subjected to chromatography on silica gel, using benzene–ethyl acetate or a benzene–hexane mixture as eluant.

2-Oxo-6-thia-1-azabicyclo[5.3.0]dec-3-ene (2a): bp 55 °C/10^{-3} mmHg; IR ($CHCl_3$) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.9–2.4 (m, 4 H, 8- and 9-CH_2), 3.0–3.8 (m, 4 H, 5- and 10-CH_2), 5.0–5.2 (m, 1 H, 7-CH_2), 6.0–6.4 (m, 2 H, 3- and 4-CH); ^{13}C NMR ($CDCl_3$) δ 23.5 (t, 9-C), 27.2 (t, 8-C), 30.9 (t, 5-C), 46.0 (t, 10-C), 60.5 (d, 7-C), 128.9 (d, 3-C), 131.6 (d, 4-C), 167.2 (s, C=O). Anal. Calcd for $C_8H_{11}NOS$: C, 56.77; H, 6.55; N, 8.27. Found: C, 56.55; H, 6.52; N, 8.06.

3-Methyl-2-oxo-6-thia-1-azabicyclo[5.3.0]dec-3-ene (2b): bp 60 °C/10^{-3} mmHg; IR ($CHCl_3$) 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.91 (s, 3 H), 1.8–2.3 (m, 4 H, 8- and 9-CH_2), 3.3–3.7 (m, 4 H, 5- and 10-CH_2), 4.9–5.1 (m, 1 H, 7-CH_2), 5.75 (br, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$) δ 22.7 (q, Me), 23.4 (t, 9-C), 30.7 (t, 8-C), 32.0 (t, 5-C), 45.8 (t, 10-C), 60.8 (d, 7-C), 123.5 (d, 3-C), 142.2 (s, 4-C), 168.0 (s, C=O). Anal. Calcd for $C_9H_{13}NOS$: C, 58.98; H, 7.14; N, 7.64. Found: C, 58.77; H, 7.13; N, 7.62.

2-Oxo-6-thia-1-azabicyclo[5.4.0]undec-3-ene (2c): bp 60 °C/10^{-3} mmHg; IR ($CHCl_3$) 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.5–2.1 (m, 6 H, 8-, 9-, and 10-CH_2), 3.0–3.3 (m, 3 H, 5- and 11-CH), 4.2–4.6 (m, 1 H, 11-CH), 5.2–5.4 (m, 1 H, 7-CH), 6.0–6.2 (m, 2 H, 3- and 4-CH); ^{13}C NMR ($CDCl_3$) δ 20.3 (t, 9-C), 24.0 (t, 10-C), 25.8 (t, 8-C), 27.1 (t, 5-C), 36.0 (t, 11-C), 58.1 (d, 7-C), 126.1 (d, 3-C), 128.2 (d, 4-C), 169.0 (s, C=O). Anal. Calcd for $C_9H_{13}NOS$: C, 58.98; H, 7.14; N, 7.64. Found: C, 58.83; H, 7.00; N, 7.65.

4-Methyl-2-oxo-6-thia-1-azabicyclo[5.4.0]undec-3-ene (2d): bp 65 °C/10^{-3} mmHg; IR ($CHCl_3$) 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.6–2.1 (m, 6 H, 8-, 9-, and 10-CH_2), 1.95 (s, 3 H, Me), 2.5–3.5 (m, 3 H, 5- and 11-CH), 4.1–4.6 (m, 1 H, 11-CH), 5.2–5.4 (m, 1 H, 7-CH), 5.7–5.9 (m, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$) δ 20.2 (t, 9-C), 22.2 (q, Me), 24.1 (t, 10-C), 27.1 (t, 8-C), 31.2 (t, 5-C), 36.2 (t, 11-C), 58.6 (d, 7-C), 122.5 (d, 3-C), 136.9 (s, 4-C), 170.7 (s, C=O). Anal. Calcd for $C_{10}H_{15}NOS$: C, 60.87; H, 7.66; N, 7.09. Found: C, 60.65; H, 7.60; N, 7.01.

2-Oxo-6-thia-1-azabicyclo[5.5.0]dodec-3-ene (2e): bp 63 °C/10^{-3} mmHg; IR ($CHCl_3$) 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.2 (m, 8 H, 8-, 9-, 10-, and 11-CH_2), 2.9–3.4 (m, 3 H, 5- and 12-CH), 4.0–4.4 (m, 1 H, 12-CH), 4.8–5.0 (m, 1 H, 7-CH), 6.0–6.2 (m, 2 H, 3- and 4-CH); ^{13}C NMR ($CDCl_3$) δ 26.1 (t), 26.5 (t), 29.2 (t), 29.5 (t), 31.1 (t), 39.8 (t, 12-C), 62.7 (d, 7-C), 127.8 (d, 3-C), 128.3 (d, 4-C), 169.3 (s, C=O). Anal. Calcd for $C_{10}H_{15}NOS$: C, 60.87; H, 7.66; N, 7.09. Found: C, 60.57; H, 7.53; N, 7.03.

4-Methyl-2-oxo-6-thia-1-azabicyclo[5.5.0]dodec-3-ene (2f): bp 65 °C/10^{-3} mmHg; IR ($CHCl_3$) 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2–2.1 (m, 8 H, 8-, 9-, 10-, and 11-CH_2), 1.95 (s, 3 H, Me), 2.5–3.6 (m, 3 H, 5- and 12-CH), 3.9–4.3 (m, 1 H, 12-CH), 4.8–5.1 (m, 1 H, 7-CH), 5.8–5.9 (m, 1 H, 3-CH); ^{13}C NMR ($CDCl_3$) δ 22.4 (q, Me), 26.4 (t), 29.3 (t), 29.6 (t), 31.4 (t), 31.5 (t), 39.9 (t, 12-C), 63.3 (d, 7-C), 122.5 (d, 3-C), 138.8 (s, 4-C), 170.1 (s, C=O). Anal. Calcd for $C_{11}H_{17}NOS$: C, 62.52; H, 8.10; N, 6.62. Found: C, 62.28; H, 7.98; N, 6.62.

6,6-Dimethyl-7-oxo-8-thioxo-1-azabicyclo[3.2.2]nonane (6): bp 68 °C/10^{-3} mmHg; IR ($CHCl_3$) 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (s, 3 H, Me), 1.32 (s, 3 H, Me), 1.9–2.0 (m, 2 H, 3-CH_2), 2.4–2.7 (m, 4-CH_2), 3.1–3.7 (m, 3 H, 5-CH and 9-CH_2), 3.8–4.0 (m, 2 H, 2-CH_2); ^{13}C NMR ($CDCl_3$) δ 19.5 (q, Me), 22.7 (t, 3-C), 24.4 (q, Me), 30.6 (t, 4-C), 38.2 (t, 9-C), 51.3 (s, 6-C), 53.0 (d, 5-C), 60.5 (t, 2-C), 175.1 (s, C=O), 211.6 (s, C=S); MS, m/e 197 (M^+). Anal. Calcd for $C_{10}H_{15}NOS$: C, 60.87; H, 7.66; N, 7.09. Found: C, 60.63; H, 7.61; N, 6.81.

4-Mercapto-3,3-dimethyl-2-oxo-1-azabicyclo[4.4.0]dec-5-ene (7): IR ($CHCl_3$) 2500 and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (s, 3 H, Me), 1.28 (s, 3 H, Me), 1.59 (d, J = 8 Hz, 1 H, SH), 1.7–1.8 (m, 2 H, 8- or 9-CH_2), 2.1–2.2 (m, 2 H, 8- or 9-CH_2), 2.6–2.7 (m, 2 H, 7-CH_2), 2.63 (dd, J = 2 and 8 Hz, 1 H, 4-CH_2), 3.4–3.7 (m, 2 H, 10-CH_2), 4.94 (dt, J = 2 and 4 Hz, 1 H, 5-CH); ^{13}C NMR ($CDCl_3$) δ 19.1 (q, Me), 20.6 (t), 21.8 (t), 23.7 (t), 25.8 (q, Me), 38.8 (t, 7-C), 43.7 (s, 3-C), 50.1 (d, 4-C), 99.2 (d, 5-C), 139.0 (s, 6-C), 178.1 (s, C=O); MS, m/e 211 (M^+).