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PHOTOCHEMISTRY OF *N*-3-BUTENYL- AND *N*-4-PENTENYL-GLUTARIMIDES: INTRAMOLECULAR THIETANE FORMATION AND THE FISSION OF THIETANE RING[1]

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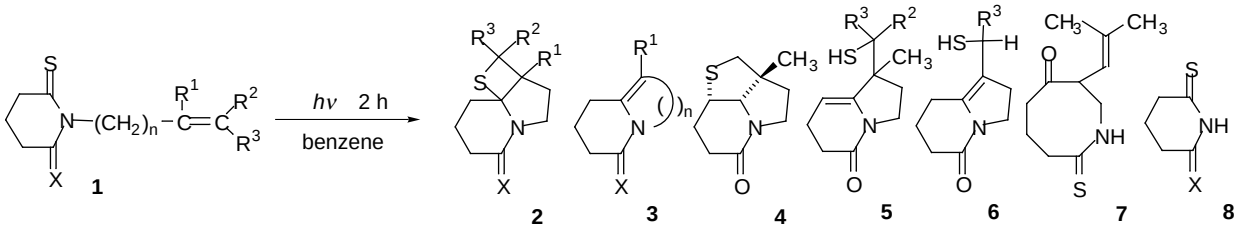
Abstract- Intramolecular photoreaction of *N*-3- or *N*-4-alkenylthio-glutarimides (two or three methylenes) gave thietanes and their fission products.

In our continuing study on the photochemistry of imides[2] and its sulfur analogues, thioimide,[3,4] we have reported that there are some distinct differences in the photochemical behaviors between the imide-carbonyls and the thioimide-carbonyls. For examples, cyclic thioimides are inert to Norrish type I and type II reactions,[5] which are representative photoreactions in the aliphatic imide system.[6] However, certain cyclic thioimides having an *N*-ω-phenylalkyl substituent underwent the Norrish type II cyclization. So the competition processes between the Norrish type II and Paterno-Büchi reaction were investigated.[7] In principle, thiosuccinimides (5-membered imide) undergo very efficiently inter- and intramolecular photocycloaddition (Paterno-Büchi-like reaction) to give thietanes.[8,9]

As an extension of this photocycloaddition, the photoreactivity of *N*-alkenyl substituted alicyclic thioimide (6-membered imide) system was investigated. Photoreactions of a series of *N*-3- or *N*-4-alkenylmono- or dithioglutarimides were carried out in benzene using a 500 W high-pressure mercury lamp through a Pyrex filter under nitrogen atmosphere at room temperature. The results are listed in Table 1. Upon irradiation of *N*-3-butenyl-, *N*-3-pentenyl-, and *N*-4-methy-3-pentenylmonothioglutarimide (**1a**, **1c**, and **1d**), the reaction mixtures complicated, and indolizine derivatives were obtained as a sole product (**6a**: 18%, **6c**: 29%, **3d**: 12%) without recovery of **1**. Irradiation of *N*-3-methyl-3-butenylmonothioglutarimide (**1b**) afforded indolizine (**5b**) in 42% yield, accompanied by tricyclic compound (**4b**) in 19% yield. In the case of *N*-3,4-dimethyl-3-pentenylmonothioglutarimide (**1e**), tricyclic thietane (**2e:** 29%) was obtained in preference to indolizine (**5e**: 2%).

Table 1. Photoreaction of **1a-l**.



1 **2** **3** **4** **5** **6** **7** **8**

Substrates						Photoproducts Yield (%)						
	X	n	R^1	R^2	R^3	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1a	O	2	H	H	H	—	—	—	—	18	—	—
1b	O	2	CH_3	H	H	—	—	19	42	—	—	—
1c	O	2	H	H	CH_3	—	—	—	—	29	—	—
1d	O	2	H	CH_3	CH_3	—	12	—	—	—	—	—
1e	O	2	CH_3	CH_3	CH_3	29	—	—	2	—	—	2
1f	S	2	H	H	H	9	39	—	—	—	—	—
1g	S	2	CH_3	H	H	—	54	—	—	—	—	—
1h	S	2	H	H	CH_3	—	35 (=**3f**)	—	—	—	—	—
1i	S	2	H	CH_3	CH_3	—	—	—	—	—	9	—
1j	S	2	CH_3	CH_3	CH_3	23	27 (=**3g**)	—	—	—	—	—
1k	S	3	H	H	H	—	42	—	—	—	—	—
1l	S	3	CH_3	H	H	—	36	—	—	—	—	—

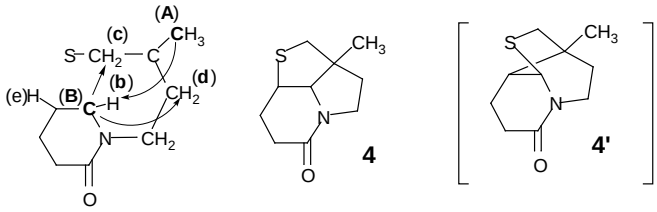
Similarly, the photoreactions of a series of dithioimides (**1f-j**) were performed. As expected, the corresponding indolizines (**3f-3h**, **3j**) were obtained in 27-54% yields, accompanied by thietanes (**2f**: 9% from **1f**, **2j**: 23% from **1j**). With **1i**, product (**7**) only was isolated in poor yield but **2i** and **3i** were not isolated even after irradiation for 10 h. When n=3 (**1k**, **1l**), photocyclization also proceeded to give quinolizine derivatives (**3k**) and (**3l**) in 42 and 36% yields, respectively.

Structures of indolizines were assigned on the basis of the spectral data and elemental analyses. For an example, MS spectrum of **6a** (1-sulfanylmethyl-2,3,6,7,8-pentahydroindolizin-5-one) showed the molecular ion peak at M^+ 183. In the IR spectrum of **6a**, the absorptions of a thiol and amide carbonyl groups appeared at 2600 and 1670 cm^{-1}, respectively. The ^{1}H-NMR spectrum of **6a** showed triplet (1.51 ppm) and doublet (3.29 ppm) with the coupling constant *J*=7.3 Hz, which indicated the presence of thiol hydrogen adjacent to a methylene. The ^{13}C-NMR spectrum showed the presence of newly formed two alkenyl carbons (134.4 and 115.9 ppm) and an amide carbonyl carbon (167.1 ppm).

Structural assignment for tricyclic thietane (**2e**: 7-aza-3,3,4-trimethyl-2-thiatricyclo[5.4.0.$0^{1,4}$]-undecan-8-one) was also made on the basis of spectral data and elemental analysis. MS spectrum

of **2e** showed the same molecular ion peak at M^+ 225 as one of **1e**, suggesting the ring closure of **1e**. The ^{1}H-NMR spectrum of **2e** showed some multiplet peaks except for the peaks due to three methyl groups (1.17, 1.43, and 1.57 ppm), but no signal due to a thiol group. The ^{13}C-NMR spectrum showed the presence of newly formed three quaternary carbons (73.7, 61.3, and 42.3 ppm) instead of the disappearance of an alkene and a thiocarbonyl carbons. The structure of tricyclic thietane was inferred to be consisting of a thietane ring, and easily confirmed on the basis of ^{1}H-NMR and ^{13}C-NMR spectra.

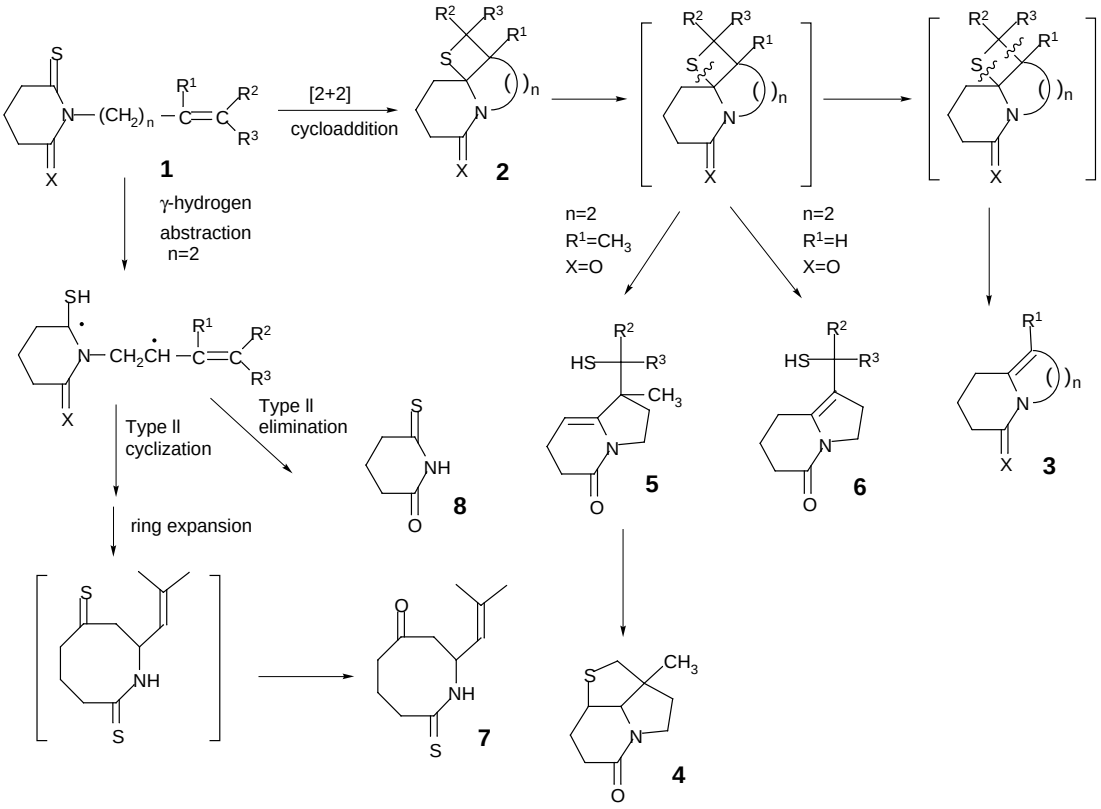
Structural assignment for tricyclic compound (**4**: 7-aza-4-methyl-2-thiatricyclo[5.3.4.0^{4,11}]-undecan-8-one) was also made on the basis of spectral data and elemental analysis. MS spectrum of **4** showed the same molecular ion peak at M^+ 197 as one of **1b**, suggesting the ring closure of **1b**. The ^{1}H-NMR spectrum of **4** showed some multiplet peaks except for the peak due to a methyl group. Further, ^{1}H-^{1}H COSY, ^{13}C-NMR, DEPT, and ^{1}H-^{13}C COSY experiments suggest the presence of the partial structure as illustrated in Scheme 1. To clarify the structure of **4**, the HMBC (^{1}H detected heteronuclear multiple bond connectivity) spectrum of **4** was measured. The cross-peaks between a methyl carbon (**A**: 21.9 ppm) and a doublet methine proton (**b**: 3.52 ppm) adjacent nitrogen atom, and between carbon (**B**: 41.9 ppm) adjacent nitrogen atom and two methylene protons (**c**, **d**) supported the structure of **4**, not **4'.** The relative stereochemistry of **4** was tentatively assigned to *cis* configuration on the basis of the coupling constant (*J*=5.6 Hz) between b and e protons, which is nearly identical with a *J* value in vicinal Karplus correlation graph. In addition, the ring configuration was assigned to be all *cis*-ring fusions on the basis of the preferred ring configuration calculated by using semi-empirical MO calculation.



Scheme1

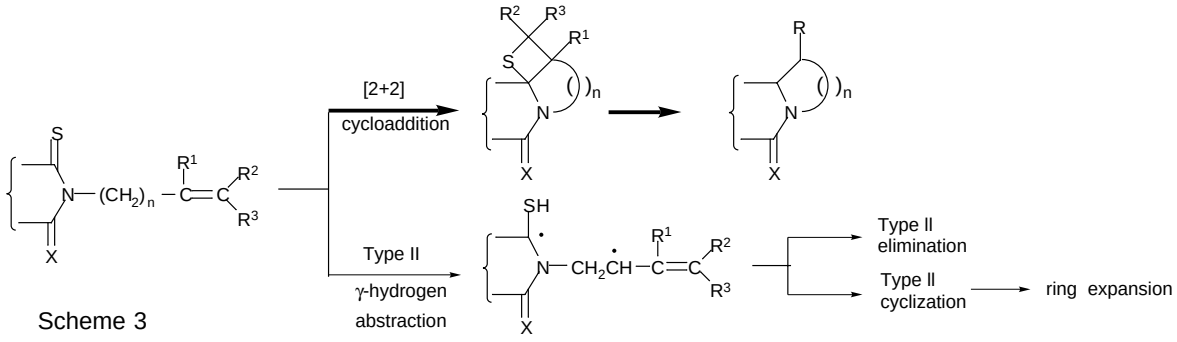
From these results, the reaction pathway for the formation of photocyclized products was outlined as shown in Scheme 2. The major reaction seems to proceed in several steps involving initial intramolecular thietane formation (**2**) between thiocarbonyl and *N*-substituted alkene, leading to fission products (**3**, **5**, and **6**). Thiols (**5**, **6**) arise from initially formed thietane followed by photochemical cleavage of the C-S bond of a thietane ring. When R^1 is methyl group, insertion reaction subsequently proceeded to give tricyclic compound (**4**), because the conformation of **5** is favorable for the intramolecular photo-insertion of thiol to alkene.[10] In fact, thiol (**5**) was easily converted to **4** by further irradiation. The other fission product is indolizine derivative (**3**). In this case, olefin metathesis due to photochemical cleavages of both C-S and C-C bonds of a thietane

ring occurred to give indolizine derivative (**3**). The formation of **7** [2-(2-methylprop-1-enyl)-8-thioxoazaperhydroocin-4-one] arises from type II hydrogen abstraction followed by ring expansion reaction by two-carbon unit derived from the side chain. Such a phenomenon was observed previously for certain succinimides.[11, 12]



Scheme 2

Consequently, in the photochemistry of alicyclic thioimide systems, not only *N*-alkenylthiosuccinimides[9] but also *N*-alkenylthioglutarimides undergo intramolecular [2+2] cycloaddition (Paterno-Büchi-like reaction) to give tricyclic thietanes in preference to type II reaction as shown in Scheme 3.



Scheme 3

Much attention has been paid to the construction of azabicycloalkane skeletons in view of the biological interest in their 5,6-[13] and 6,6-ring-fused systems.[14] Therefore, this photocycloaddition also may be added as a new entry in the syntheses of some azabicycloalkane systems.

EXPERIMENTAL

All melting points were determined on a Yamato melting point apparatus (model MP-21) and are uncorrected. IR spectra were recorded on a JASCO A-102 spectrophotometer. NMR spectra were taken on JEOL JNM LA300 and JEOL JNM EX-400 spectrometers. Chemical shifts are reported in ppm (d) relative to TMS (0.0 ppm) as an internal standard. MS spectra (MS, HRMS) were obtained on a Shimadzu GC MS 9100-MK gas chromatograph-mass spectrometer. Preparative irradiations were conducted by using a 500 W high-pressure mercury lamp (Eikosha PIH-500) through a Pyrex filter at room temperature under nitrogen atmosphere. Column chromatography was conducted using silica gel (Merck, Kieselgel 60, 70-230 mesh).

Preparation of Thioimides (1): Imides were prepared by the reported procedures.[15] Thioimides (**1**) were prepared from the corresponding imides and Lawesson's reagent according to the procedure described in ref. 5, and purified by column chromatography.

1a: Orange oil; HRMS Calcd for $C_9H_{13}NOS$: 183.0718. Found: 183.0736. **1b**: Orange oil; HRMS Calcd for $C_{10}H_{15}NOS$: 197.0874 Found: 197.0911. **1c**: Orange oil; HRMS Calcd for $C_{10}H_{15}NOS$: 197.0874 Found: 197.0878. **1d**: Orange oil; HRMS Calcd for $C_{11}H_{17}NOS$: 211.1031 Found: 211.1060. **1e**: Orange oil; HRMS Calcd for $C_{12}H_{19}NOS$: 225.1187 Found: 225.1217. **1f**: Orange oil; HRMS Calcd for $C_9H_{13}NS_2$: 199.0489. Found: 199.0455. **1g**: Orange oil; HRMS Calcd for $C_{10}H_{15}NS_2$: 213.0646. Found: 213.0619. **1h**: Orange oil; HRMS Calcd for $C_{10}H_{15}NS_2$: 213.0649. Found: 213.0655. **1i**: Orange oil; HRMS Calcd for $C_{11}H_{17}NS_2$: 227.0802. Found: 227.0798. **1j**: Orange oil; HRMS Calcd for $C_{12}H_{19}NS_2$: 241.0959. Found: 241.0952. **1k**: Orange oil; HRMS Calcd for $C_{10}H_{15}NS_2$: 213.0646. Found: 213.0620. **1l**: Orange oil; HRMS Calcd for $C_{11}H_{17}NS_2$: 227.0802. Found: 227.0776.

Irradiation of Thioimides (1) . General Procedure:

A solution of **1a** (5 mmol) in benzene (200 mL) was irradiated for 2 h with a 500 W high-pressure mercury lamp through a Pyrex filter under N_2. After removal of the solvent *in vacuo*, the residue was chromatographed over a silica gel column (hexane - ethyl acetate, 3 : 1; v/v).

7-Aza-3,3,4-trimethyl-2-thiatricyclo[5.4.0.0^{1,4}]undecan-8-one (2e): mp 82-83°C (hexane); IR (Nujol) 1670 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.17 (3H, s), 1.41 (1H, m), 1.43 (3H, s), 1.57 (3H, s), 1.93 (3H, m), 2.41 (4H, m), 3.73 (1H, m), 4.22 (1H, m); ^{13}C-NMR ($CDCl_3$) δ 17.4 (t), 20.1 (q), 28.3 (q), 31.0 (t), 31.3 (q), 33.7 (t), 34.0 (t), 42.3 (s), 43.2 (t), 61.3 (s), 73.7 (s), 168.0 (s); MS *m/z* 225 (M^+); *Anal*. Calcd for $C_{12}H_{19}NOS$: C, 63.96; H, 8.50; N, 6.22; S, 14.23. Found: C, 63.70; H, 8.45; N, 6.18; S, 14.42.

7-Aza-2-thiatricyclo[5.4.0.0^{1,4}]undecan-8-one (2f): Yellow oil ; ^{1}H-NMR ($CDCl_3$) δ 1. 61 (1H, m), 1.82 (2H, m), 2.21 (1H, m), 2.43 (1H, m), 2.54 (1H, m), 2.91 (2H, m), 3.12 (1H, m), 3.43 (2H, m), 3.92 (1H, m), 4.23 (1H, m); ^{13}C-NMR ($CDCl_3$) δ 17.4 (t), 22.2 (t), 29.5 (t), 31.3 (t), 39.9 (t), 43.8 (d), 51.2 (t), 71.4 (s), 198.5 (s); MS *m/z* 199 (M^+); HRMS Calcd for $C_{12}H_{19}NS_2$: 199.0448. Found: 199.0439.

7-Aza-3,3,4-trimethyl-2-thiatricyclo[5.4.0.0^{1,4}]undecane-8-thione (2j): Yellow oil ; ^{1}H-NMR ($CDCl_3$) δ 1.19 (3H, s), 1.46 (3H, s), 1.58 (3H, s), 1.62 (1H, m), 1.78 (2H, m), 2.01 (1H, m), 2.37 (1H, m), 2.58 (1H, m), 2.83 (1H, m), 3.01 (1H, m), 4.14 (1H, m), 4.82 (1H, m); ^{13}C-NMR ($CDCl_3$) δ 17.2 (t), 20.0 (q), 28.0 (q), 31.0 (q), 33.1 (t), 33.2 (t), 40.0 (t), 43.3 (s), 50.7 (t), 60.6 (s), 73.4 (s), 195.7 (s); MS *m/z* 241 (M^+); *Anal*. Calcd for $C_{12}H_{19}NS_2$: C, 59.70; H, 7.93; N, 5.80; S, 26.57. Found: C, 59.68; H, 7.83; N, 5.95; S, 26.72.

2,3,6,7,8-Pentahydroindolizin-5-one (3d): Yellow oil; IR (Nujol) 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.59 (2H,m), 1.88 (2H, m), 2.62 (4H, m), 3.74 (2H, m), 5.25 (1H, t, *J*=5.4 Hz); ^{13}C-NMR ($CDCl_3$) δ 19.2 (t), 23.4 (t), 26.0 (t), 40.9 (t), 52.0 (t), 112.4 (d), 139.7 (s), 168.0 (s); MS *m/z* 153 (M^+); *Anal*. Calcd for $C_8H_{11}NO$: C, 70.05; H, 8.08; N, 10.21. Found: C, 70.11; H, 8.23; N, 10.04.

2,3,6,7,8-Pentahydroindolizine-5-thione (3f): Yellow oil; ^{1}H-NMR ($CDCl_3$) δ 1.81 (2H, m), 2.58 (4H, m), 3.03 (2H, t, *J*=6.3 Hz), 4.23 (2H, t, *J*=6.3 Hz), 5.51(1H, s); ^{13}C-NMR ($CDCl_3$) δ 19.2 (t), 23.4 (t), 26.0 (t), 40.9 (t), 52.0 (t), 112.4 (d), 139.7 (s), 191.7 (s); MS *m/z* 153 (M^+); HRMS Calcd for $C_8H_{11}NS$: 153.0612. Found: 153.0589.

1-Methyl-2,3,6,7,8-pentahydroindolizine-5-thione (3g): Yellow oil; ^{1}H-NMR ($CDCl_3$) δ 1.74 (3H, s), 1.73 (2H, m), 2.49 (4H, m), 2.88 (2H, m), 4.24 (2H, m); ^{13}C-NMR ($CDCl_3$) δ 13.1 (q), 19.1 (t), 21.4 (t), 31.3 (t), 40.7 (t), 51.0 (t), 122.1 (s), 133.3 (s), 189.2 (s); MS *m/z* 167 (M^+); HRMS Calcd for $C_9H_{13}NS$: 167.0768. Found: 167.0781.

1,2,3,6,7,8-Hexahydroquinolizine-5-thione (3k): Yellow oil; ^{1}H-NMR ($CDCl_3$) δ 1.68 (2H, m), 1.89(2H, m), 2.14 (2H, m), 2.53 (2H, m), 3.07 (2H, m), 4.44 (2H, m), 5.00 (1H, t, *J*=4.0 Hz); ^{13}C-NMR ($CDCl_3$) δ 20.2 (t), 22.0 (t), 22.7 (t), 30.3 (t), 43.3 (t), 48.8(t), 109.6 (d), 135.8 (s), 198.5 (s); MS *m/z* 167 (M^+); HRMS Calcd for $C_9H_{13}NS$: 167.0768. Found: 167.0761.

9-Methyl-1,2,3,6,7,8-hexahydroquinolizine-5-thione (3l): mp 90-91.5°C (hexane-ethyl acetate); ^{1}H-NMR ($CDCl_3$) δ 1.34 (3H, s), 1.52-1.79 (6H, m), 1.92-2.50 (4H, m), 3.84 (1H, m), 4.21 (1H, m); ^{13}C-NMR ($CDCl_3$) δ 22.5 (q), 30.8 (t), 33.5 (t), 41.3 (t), 43.5 (t), 44.5 (t), 48.3 (t), 118.5 (s), 142.5 (s), 198.8 (s); MS *m/z* 181 (M^+); *Anal*. Calcd for $C_{10}H_{15}NS$: C, 66.25; H, 8.34; N, 7.73; S, 17.69. Found: C, 66.34; H, 8.29; N, 7.82; S, 17.90.

7-Aza-4-methyl-2-thiatricyclo[5.3.4.0^{4,11}]undecan-8-one (4): mp 84-85°C (hexane-ethyl acetate; ^{1}H-NMR ($CDCl_3$) δ 1.63 (3H, s), 1.78 (1H, m), 2.02 (2H, m), 2.23 (1H, m), 2.28 (1H, m), 2.72 (3H, m), 3.39 (1H, m), 3.52 (1H, d, *J*=5.6 Hz), 4.00 (2H, m); ^{13}C-NMR ($CDCl_3$) δ 21.9 (q), 23.7 (t), 27.2 (t), 34.5 (t), 41.9 (t), 43.7 (t), 44.2 (d), 55.3 (s), 74.5 (d), 169.1 (s); MS *m/z* 197 (M^+); *Anal*. Calcd

for $C_{10}H_{15}NOS$: C, 60.88; H, 7.66; N, 7.10; S, 16.25. Found: C, 60.78; H, 7.66; N, 7.05; S, 16.52.

1-Methyl-1-sulfanylmethyl-1,2,3,6,7-pentahydroindolizin-5-one (5b): Yellow oil; IR (Nujol) 2600, 1670 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.34 (3H, s), 1.51 (1H, d, *J*=7.3 Hz), 1.90 (1H, m), 1.98 (1H, m), 2.22 (2H, m), 2.31 (1H, m), 2.73 (1H, m), 3.29 (2H, d, *J*=7.3 Hz), 3.80 (2H, m), 5.35 (1H, t, *J*=5.0 Hz). ^{13}C-NMR ($CDCl_3$) δ 21.0 (q), 24.2 (t), 31.7 (t), 34.0 (t), 34.4 (t), 42.8 (t), 45.8 (s), 95.0 (d), 148.2 (s), 169.3 (s); MS *m/z* 197 (M^+); HRMS Calcd for $C_{10}H_{15}NOS$: 197.0874. Found: 197.0889.

2-Methyl-1-(1-methyl-1-sulfanylethyl)-1,2,3,6,7-pentahydroindolizin-5-one (5e): Yellow oil; IR (Nujol) 2600, 1665 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.24 (3H, s), 1.31 (3H, s), 1.42 (3H, s), 1.63 (1H, s), 2.10 (2H, m), 2.18 (2H, m), 2.43 (2H, m), 3.80 (2H, m), 5.35 (1H, t, *J*=5.0 Hz). ^{13}C-NMR ($CDCl_3$) δ 19.3 (t), 23.7 (q), 24.5 (q), 26.5 (q), 31.5 (t), 36.6 (t), 38.3 (t), 42.8 (s), 50.1 (s), 105.4 (d), 146.0 (s), 171.8 (s); MS *m/z* 225 (M^+); HRMS Calcd for $C_{12}H_{19}NOS$: 225.1187. Found: 225.1183.

1-Sulfanylethyl-2,3,6,7,8-pentahydroindolizin-5-one (6a): Yellow oil; IR (Nujol) 2600, 1670 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.51 (1H, t, *J*=7.3 Hz), 1.82 (2H, m), 2.41 (4H, m), 2.65 (2H, t, *J*=9.2 Hz), 3.29 (2H, d, *J*=7.3 Hz), 3.85 (2H, t, *J*=9.2 Hz). ^{13}C-NMR ($CDCl_3$) δ 19.6 (t), 21.3 (t), 21.9 (t), 28.0 (t), 32.2 (t), 43.5 (t), 115.9 (s), 134.4 (s), 167.1 (s); MS *m/z* 183 (M^+); HRMS Calcd for $C_9H_{13}NOS$: 183.0718. Found: 183.0710.

1-Sulfanylethyl-2,3,6,7,8-pentahydroindolizin-5-one (6c): Yellow oil; IR (Nujol) 2600, 1670 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.43 (3H, d, J=6.8 Hz), 1.73 (1H, d, *J*=4.8 Hz), 1.77 (2H, m), 2.40 (4H, m), 2.61 (1H, m), 2.70 (1H, m), 3.83 (2H, *t*, J=8.8 Hz), 4.13 (1H, m); ^{13}C-NMR ($CDCl_3$) δ 19.6 (t), 21.4 (t), 23.6 (q), 25.0 (t), 32.1 (d), 32.3 (t), 43.4 (t), 120.2 (s), 132.9 (s), 167.1 (s); MS *m/z* 183 (M^+); HRMS Calcd for $C_{10}H_{13}NO_S$: 197.0874. Found: 197.0880.

2-(2-Methylprop-1-enyl)-8-thioxazaperhydrocin-4-one (7): Yellow oil; IR (Nujol) 1710 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ1.64 (3H, s), 1.76 (3H, s), 2.01 (2H, m), 2.36 (1H, m), 2.64 (1H, m), 3.00 (2H, m), 3.58 (3H, m), 5.31 (1H, m), 9.40 (1H, br s); ^{13}C-NMR ($CDCl_3$) δ 18.5 (q), 25.3 (t), 26.0 (q), 37.9 (t), 40.8 (t), 47.8 (t), 57.0 (d), 116.3 (d), 139.2 (s), 207.9 (s), 210.7 (s); MS *m/z* 211 (M^+); Calcd for $C_{11}H_{17}NOS$: C, 65.52; H, 8.11; N, 6.63; S, 15.17. Found: C, 65.62; H, 8.08; N, 6.54; S, 15.01.

Photochemical Conversion of 5b to 4.

A solution of **5b** (50 mg) in benzene (20 ml) was irradiated for 1 h with 500 W high-pressure mercury lamp through a Pyrex filter under N_2 atmosphere at room temperature. After removal of the solvent *in vacuo*, the residue was chromatographed over a silica gel column (hexane - ethyl acetate, 3 : 1; v/v). Compound (**4**) was isolated in 84% yield (42 mg).

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