PHOTOREACTION OF 1- AND 3-ARALKYL ALICYCLIC THIOIMIDES: FACILE SYNTHESES OF VARIOUS AZABICYCLOALKANES VIA NORRISH TYPE II PROCESS[1]

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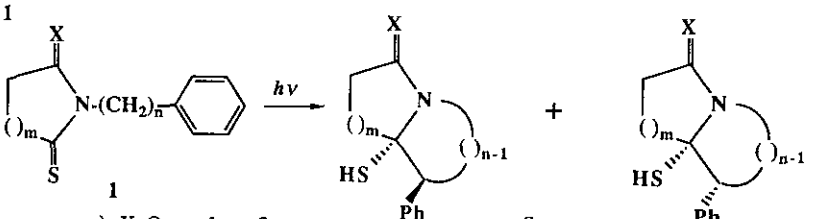
Abstract – Photolysis of the 1-(ω-aralkyl)cyclic thioimides (**1b,e,g,h**) gave a pair of stereoisomers of 1-azabicycloalkanes (2, 3) in moderate yields. Similarly, in 3-(ω-phenylalkyl)cyclic thioimides (**5a-e**), a pair of stereoisomers of 2-azabicycloalkanes (**6, 7**) were obtained.

In a previous paper, we reported that the excited thiophthalimides (aromatic thioimides) having a benzylic hydrogen at δ- and ε-positions in their 1-alkyl side chain, undergo effectively the Norrish type II reaction to give photocyclization products.[2] Similarly, thiosuccinimides (alicyclic thioimides) with a 1-(ω-phenylalkyl) substituent underwent the Norrish type II reaction to give 1-azabicycloalkane derivatives.[3] Further, our finding on the inertness of alicyclic thioimides to the Norrish type I reaction (α-cleavage)[4] had prompted us to investigate the photoreaction of 3-(ω-phenylalkyl) substituted thiosuccinimides.[5] The present report is full account of syntheses of 1- and 2-azabicycloalkanes by the photoreaction of alicyclic thioimides having a 1- or 3-aralkyl substituent.

Photolysis of a series of 1-(ω-phenylalkyl)cyclicmonothio- or dithioimides (**1a-f**) in benzene was examined with a 1 kW high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere at room temperature. The results are listed in Table I. In the cases of **1a** and **1d** (n=2), the expected photocyclized products were not isolated even upon prolonged

Scheme 1



1

a) X=O, m=1, n=2
b) X=O, m=1, n=3
c) X=O, m=1, n=4
d) X=S, m=1, n=2
e) X=S, m=1, n=3
f) X=S, m=1, n=4
g) X=S, m=2, n=3

2 **3** **4g**

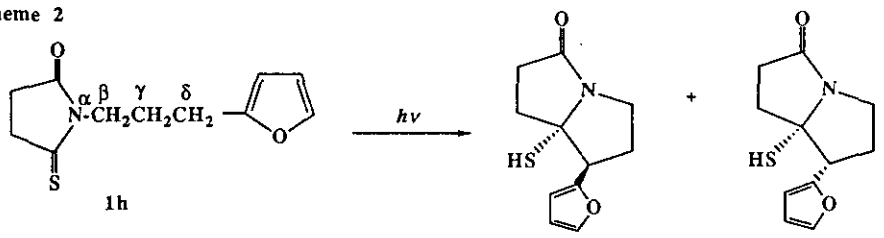
Table 1. Photoreaction of **1a-h**.

Substrate	Irradiation time (h)	Photoproduct (%) 2	3	Recovery of 1 (%)	Reaction site
1a	5			48	
1b	1	31	28		δ
1c	5			78	
1d	5			51	
1e	1	40	41		δ
1f	5			83	
1g	1	31	33		δ
1h	1	36	33		δ

irradiation, but simple mono- or dithiosuccinimide (due to the Norrish type II elimination reaction) was obtained in 18% or 13% yield, respectively. When n=3 (**1b**,**1e**), δ-hydrogen abstraction reaction proceeded effectively giving a pair of stereoisomers of 1-azabicycloalkanes, which are Norrish type II cyclization products (**2b** and **3b** from **1b**, and **2e** and **3e** from **1e**). Further, in order to investigate whether ε-hydrogen abstraction occurs or not, photolyses of thiosuccinimides *having a benzylic ε-hydrogen* (**1c**,**1f**, *n=4*) *were carried for 5 h, but it resulted in recovery of unchanged* **1c** and **1f** (78%, 83%). Similarly, in the case of glutarimide (**1g**: m=2, n=3), the δ-hydrogen abstraction reaction at the benzylic position proceeded effectively, giving the Type II products (**2g**: 31%, **3g**: 33%). On the treatment of **2g** or **3g** with a trace of hydrochloric acid, the thiol compounds were easily converted into the unsaturated compound (**4g**) in quantitative yields.

The structure of photocyclization products was assigned on the basis of elemental analyses and spectral data. For example, the mass spectrum of **2b** showed the molecular ion peak at M^+ 233 which tends to loss hydrogen sulfide (M^+-34). In the infrared spectrum, the characteristic bands for thiol group and amide carbonyl group appeared at 2500cm^{-1} and 1685cm^{-1}, respectively. The ^{13}C-nmr spectrum showed the presence of newly formed quaternary carbon substituted by thiol group [81.1 ppm(s)]. In the ^{1}H-nmr spectra, the thiol group of **3** (1.45-1.80 ppm) appeared in the upperfield region compared with those of **2** (2.60-2.75 ppm). A similar upperfield shift is observed previously for the photoproducts of *N*-(ω-phenylalkyl)monothiophthalimides.[2] This can be explained on the basis of anisotropic effects by the phenyl ring, suggesting that the configurations of thiol group and the phenyl group are *cis* for **3** and *trans* for **2**.

Scheme 2



1h **2h** **3h**

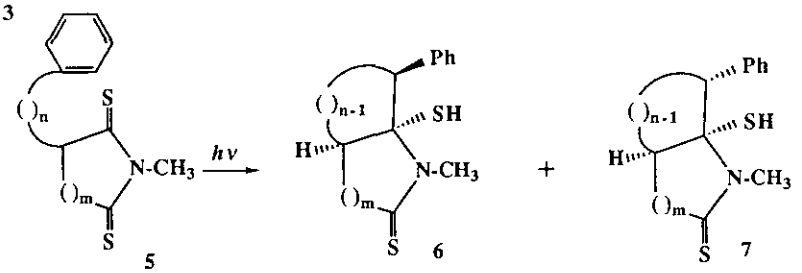
Further, taking the synthetic utility of this reaction into consideration, a furan ring which is easily transformed into other functional group was introduced instead of the phenyl ring as seen in substrate (**1h**). The photolysis of 1-(ω-furylpropyl)thiosuccinimide (**1h**) was performed under similar conditions. As expected, **1h** effectively underwent

δ-hydrogen abstraction to give a pair of stereoisomers of the Norrish type II products (**2h**, **3h**). The structure of photoproducts was determined in a similar manner as described above.

On the other hand, 3-alkylsubstituted alicyclic imides, upon irradiation, undergo the Norrish type I reaction (α-cleavage) reaction[6] in preference to the Norrish type II (cyclization) reaction, therefore, there is a limit in synthetic applicability of the substrates for the construction of the bicyclic ring system.

In order to explore the synthetic application of imide and thioimide systems, photoreaction of 3-substituted cyclic thioimides (**5**) having benzylic hydrogens was examined. The results are listed in Table II. In the cases of **5a,d** (n=2), **b,e** (n=3), **c** (n=4), a pair of stereoisomers of azabicycloalkanes (**6** and **7**) were obtained as a result of C-C bond formation between the thiocarbonyl and the benzylic carbons.

Scheme 3



5 6 7

a) m=1, n=2
b) m=1, n=3
c) m=1, n=4
d) m=2, n=2
e) m=2, n=3
f) m=2, n=4

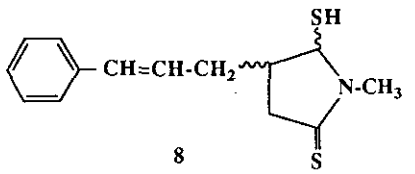


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Table 2. Photoreaction of **5a-f**.

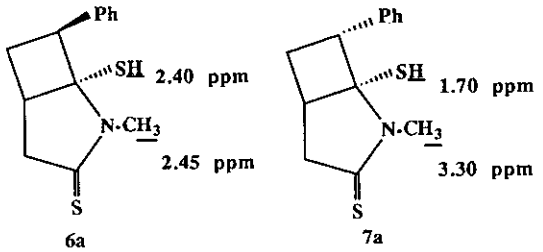
Substrate	Irradiation time (h)	Photoproduct (%) 6	7	8	Reaction site
5a	1	35	29		γ
5b	1	34	31		δ
5c	5	8*	6*		ε
5d	1	38	22	4	γ
5e	5	4*	5*		δ
5f	5				

* A mixture of two stereoisomers. Determined by ^{1}H-nmr spectroscopy. The stereochemistry of ring juncture is unknown.

The structural assignment for all of the products was based on elemental analyses and spectral data. In the ir spectra of **6** and **7**, a band at 2500 cm^{-1} indicated the presence of thiol group. The ^{1}H-nmr spectra of **6** and **7** showed some multiplet peaks except for peaks due to thiol and 1-methyl groups. The ^{13}C-nmr spectra of **6** and **7** showed the presence of newly formed quaternary carbon instead of the disappearance of one thiocarbonyl group, and one doublet at 51.3-60.5 ppm supported the presence of benzylic methine structure. The stereochemistry of **6** and **7** was determined on the basis of the ^{1}H-nmr spectra

by considering the anisotropic shielding effects of the phenyl ring, that is, a peak due to the 1-methyl group of **6a** showed upperfield shift from 3.30 to 2.45 ppm compared with that of **7a**. Thus, **6** and **7** are respectively of *trans*- and *cis*-configurations with respect to a thiol and a phenyl group.

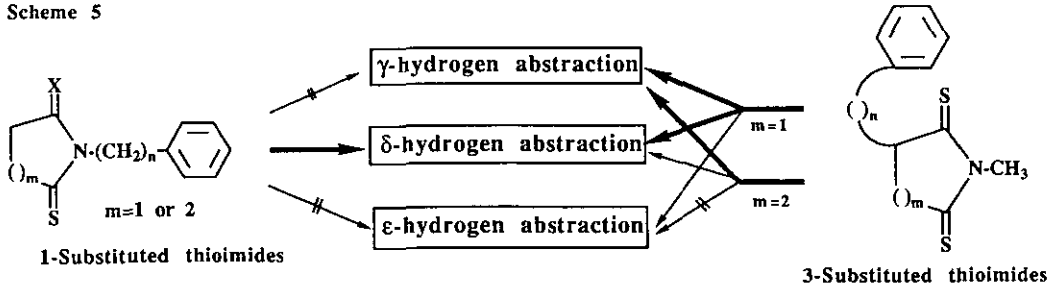
Scheme 4



In the cases of thiosuccinimides (**5a,b**, five-membered ring system), the hydrogen abstraction took place most efficiently at the benzylic position which is γ and δ to the thiocarbonyl group, respectively. But in **5c** the ability of this abstraction at the benzylic ε-position strikingly decreased and unchanged **5c** was recovered in 75% yield. Further, in the cases of thioglutarimides (six-membered ring system), only **5d** underwent effectively the γ-hydrogen abstraction reaction at the benzylic carbon, giving the type II products, while **5e** with a benzylic δ-position gave an separable mixture of **6e** and **7e** in poor yield along with recovery of unchanged **5e** (73%). When **5f** has a benzylic hydrogen available for ε-hydrogen abstraction, no cyclized products due to the Norrish type II reaction were isolated, and the substrate (**5f**) was recovered in 91% yield, even after irradiation for 5 h. In addition, the dithiosuccinimides (**5a**) and (**5b**) gave the minor products 1-methyldithiosuccinimide (from **5a**) and the reduced thiol **8** (from **5b**). This probably results initially from γ-hydrogen abstraction followed by elimination and δ-hydrogen transfer.[7]

In conclusion, in the photochemistry of thioimide systems, not only 1-substituted thioimides but also 3-substituted thioimides undergo most effectively γ and/or δ-hydrogen abstraction reaction to give various azabicycloalkanes. Interestingly ε-hydrogen abstraction is slightly observed in only 3-substituted thiosuccinimide (**5c**), but not observed in 1-substituted thioimide. Such an ability of the abstraction seems to reflect an unfavorable geometrical distance between the thiocarbonyl group and benzylic-hydrogen to be abstracted. Apparently the difference in photochemical behavior between the 3-substituted thiosuccinimides and thioglutarimides is also due to the geometrical distance of the reaction sites. In addition, it was shown that the δ-hydrogen abstraction takes place also at furfuryl position as seen in substrate (**1g**). Thus, certain 3-substituted thioimides and the thioimides having a furan in the 1-alkyl side chain may be good substrates for some synthetic photoreaction.

Scheme 5



Much attention has been paid to the construction of azabicycloalkane skeletons in view of the biological interest [8] in their 4,5-,[9] 4,6-,[10] 5,5-,[11] and 5,6- ring-fused[12] systems. This photocyclization also adds a new entry in the synthesis of some 1- and 2-azabicycloalkane systems.

EXPERIMENTAL

All mps were determined on a Yamato mp apparatus (model MP-21) and are uncorrected. Ir spectra were recorded on a JASCO-A-102 spectrophotometer. Nmr spectra were taken on a JEOL JNM FX-90Q spectrometer. Chemical shifts are reported in ppm (δ) relative to TMS (0.0 ppm) as an internal standard. The abbreviations used are as follow: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra (ms) were obtained on a JEOL JMS-QH-100 gas chromatograph-mass spectrometer. Preparative irradiations were conducted by using a 1 kW high-pressure mercury lamp (Eikosha EHB-W-1000) through a Pyrex filter at room temperature. Stirring of the reaction mixture was effected by the introduction of a stream of nitrogen at the bottom of the outer jacket. Column chromatography was conducted using silica gel (Merck, Kieselgel 60, 70-230 mesh).

Preparation of 1-substituted thioimides (1): General procedure

Imide derivatives were prepared by the reported procedure.[13] Next, thioimides (**1**) were prepared from the corresponding imide and Lawesson's reagent by the procedure described in ref. 14, and purified by column chromatography.

1a: 35 %, yellow oil, Anal. Calcd for $C_{12}H_{13}NOS$: C, 65.72; H, 5.98; N, 6.39; S, 14.62. Found: C, 65.52; H, 6.11; N, 6.19; S, 14.78.

1b: 40 %, yellow oil, Anal. Calcd for $C_{13}H_{15}NOS$: C, 66.92; H, 6.47; N, 6.00; S, 13.74. Found: C, 67.01; H, 6.66; N, 6.10; S, 13.78.

1c: 31 %, yellow oil, Anal. Calcd for $C_{14}H_{17}NOS$: C, 67.98; H, 6.93; N, 5.66; S, 12.96. Found: C, 67.78; H, 6.96; N, 5.55; S, 12.88.

1d: 33 %, yellow oil, Anal. Calcd for $C_{12}H_{13}NS_2$: C, 61.23; H, 5.57; N, 5.95; S, 27.25. Found: C, 61.42; H, 5.39; N, 6.19; S, 27.09.

1e: 39 %, yellow oil, Anal. Calcd for $C_{13}H_{15}NS_2$: C, 62.60; H, 6.06; N, 5.62; S, 25.72. Found: C, 62.55; H, 6.23; N, 5.81; S, 25.78.

1f: 37 %, yellow oil, Anal. Calcd for $C_{14}H_{17}NS_2$: C, 63.83; H, 6.50; N, 5.32; S, 24.35. Found: C, 63.98; H, 6.39; N, 5.42; S, 24.11.

1g: 36 %, yellow oil, Anal. Calcd for $C_{14}H_{17}NOS$: C, 67.98; H, 6.93; N, 5.66; S, 12.96. Found: C, 68.11; H, 6.78; N, 5.59; S, 12.89.

1h: 31 %, yellow oil, Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87; N, 6.27; S, 14.36. Found: C, 59.11; H, 5.78; N, 6.19; S, 14.59.

Preparation of 3-substituted thioimides (5): General procedure

To sodium amide (0.03 mol), prepared from 0.03 g-atom of sodium metal in 200 ml of liquid ammonia, was added 0.03 mol of appropriate imide. After 30 min, 0.033 mol of appropriate phenylalkyl bromide in 30 ml of ether was added to the stirred suspension. The reaction mixture was stirred for 1 h. The liquid ammonia was evaporated, and an equal volume of ether was added. To the resulting ethereal suspension was added a mixture of 50 ml of 6N-HCl and 100 g of crushed ice. Ethereal layer was dried over Na_2SO_4 and concentrated to give the appropriate 3-aralkyl imide, which was purified by recrystallization or distillation.

3-(2-phenylethyl)-1-methylsuccinimide: 64 %. mp 88-89 °C. Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45.

Found: C, 71.72; H, 7.14; N, 6.19.

3-(3-phenylpropyl)-1-methylsuccinimide: 69 %. mp 68-70 °C. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.55; H, 7.39; N, 5.86.

3-(4-phenylbutyl)-1-methylsuccinimide: 53 %. bp 218-224°C/2 mmHg. Anal. Calcd for $C_{15}H_{19}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 73.58; H, 7.99; N, 5.58.

3-(2-phenylethyl)-1-methylglutarimide: 59 %. bp 232-235°C/2 mmHg. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.84; H, 7.51; N, 6.18.

3-(3-phenylpropyl)-1-methylglutarimide: 57 %. bp 218-224°C/2 mmHg. Anal. Calcd for $C_{15}H_{19}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.86; H, 7.29; N, 5.97.

3-(4-phenylbutyl)-1-methylglutarimide: 67 %. bp 221-226°C/2 mmHg. Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16; N, 5.40. Found: C, 73.98; H, 7.95; N, 5.19.

Thioimides (**5**) were prepared from the corresponding imide and Lawesson's reagent by the procedure described in ref. 14 and purified by column chromatography.

5a: 31 %. mp 54-55°C. Anal. Calcd for $C_{13}H_{15}NS_2$: C, 62.60; H, 6.06; N, 5.62; S, 25.72. Found: C, 62.53; H, 6.18; N, 5.77; S, 25.53.

5b: 34 %. mp 46-47°C. Anal. Calcd for $C_{14}H_{17}NS_2$: C, 63.83; H, 6.50; N, 5.32; S, 24.35. Found: C, 63.77; H, 6.78; N, 5.27; S, 24.55.

5c: 29 %. Red oil. Anal. Calcd for $C_{15}H_{19}NS_2$: C, 64.93; H, 6.90; N, 5.05; S, 23.11. Found: C, 64.81; H, 6.78; N, 4.98; S, 23.13.

5d: 33 %. Red oil. Anal. Calcd for $C_{14}H_{17}NS_2$: C, 63.83; H, 6.50; N, 5.32; S, 24.35. Found: C, 63.96; H, 6.58; N, 5.51; S, 24.19.

5e: 39 %. Red oil. Anal. Calcd for $C_{15}H_{19}NS_2$: C, 64.93; H, 6.90; N, 5.05; S, 23.11. Found: C, 64.88; H, 7.14; N, 5.21; S, 23.33.

5f: 30 %. Red oil. Anal. Calcd for $C_{16}H_{21}NS_2$: C, 65.93; H, 7.26; N, 4.81; S, 22.00. Found: C, 65.79; H, 7.24; N, 5.07; S, 22.14.

Irradiation of 1: General procedure

A solution of **1** (5 mmol) in benzene (500 ml) was irradiated with 1 kW high-pressure mercury lamp under N_2 at room temperature. After removal of the solvent *in vacuo*, the residue was chromatographed over silica gel.

Monothiosuccinimide (from **1a**): mp 112-113°C (lit., 112-114°C).[15]

Compound **2b**: mp 71-73°C. Ir(nujol): 2500, 1685 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 2.60(1H, s, SH), 1.8-4.1(9H, m), 6.9-7.5(5H, m, ArH). ^{13}C-Nmr($CDCl_3$): δ 32.9(t), 33.5(t), 33.7(t), 39.8(t), 56.2(d), 81.1(s), 127.4(d), 127.6(dx2), 128.7(dx2), 140.5(s), 172.5(s). Ms m/z: 233(M^+), 199(M^+-H_2S). Anal. Calcd for $C_{13}H_{15}NOS$: C, 66.92; H, 6.47; N, 6.00; S, 13.74. Found: C, 66.83; H, 6.51; N, 6.18; S, 13.77.

Compound **3b**: mp 58-60°C. Ir(nujol): 2500, 1685 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 1.65(1H, s, SH), 2.2-3.7(9H, m), 7.2-7.5(5H, m, ArH). ^{13}C-Nmr($CDCl_3$): δ 30.0(t), 34.2(t), 39.3(t), 40.0(t), 56.0(d), 81.3(s), 127.8(d), 128.0(dx2), 128.5(dx2), 136.8(s), 172.6(s). Ms m/z: 233(M^+), 199(M^+-H_2S). Anal. Calcd for $C_{13}H_{15}NOS$: C, 66.92; H, 6.47; N, 6.00; S, 13.74. Found: C,

66.79; H, 6.34; N, 5.98; S, 13.61.

Dithiosuccinimide (from **1d**): mp 106-107.5°C (lit., 106-108°C).[15]

Compound **2e**: yellow oil. Ir(nujol): 2500 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 2.75(1H, s, SH), 1.6-4.3(9H, m), 6.9-7.6(5H, m, Ar H). ^{13}C-Nmr($CDCl_3$): δ 33.9(t), 43.5(t), 43.9(t), 47.8(t), 56.2(d), 86.1(s), 127.4(d), 128.6(dx2), 128.9(dx2), 142.5(s), 198.8(s). Ms m/z: 249(M^+), 215(M^+-H_2S). Anal. Calcd for $C_{13}H_{15}NS_2$: C, 62.60; H, 6.06; N, 5.62; S, 25.72. Found: C, 62.63; H, 6.12; N, 5.58; S, 25.91.

Compound **3e**: yellow oil. Ir(nujol): 2500 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 1.80(1H, s, SH), 2.4-3.8(9H, m), 7.3-7.6(5H, m, Ar H). ^{13}C-Nmr($CDCl_3$): δ 30.1(t), 41.5(t), 43.4(t), 47.4(t), 55.2(d), 86.5(s), 128.0(dx3), 128.7(dx2), 142.5(s), 198.8(s). Ms m/z: 249(M^+), 215(M^+-H_2S). Anal. Calcd for $C_{13}H_{15}NS_2$: C, 62.60; H, 6.06; N, 5.62; S, 25.72. Found: C, 62.48; H, 6.11; N, 5.41; S, 25.83.

*Compound **2g**: mp 82-84°C. Ir(nujol): 2450, 1620 cm^{-1}.* ^{1}H-Nmr($CDCl_3$): δ 2.55(1H, s, SH), 2.7-4.3(11H, m), 6.9-7.5(5H, m, ArH). ^{13}C-Nmr($CDCl_3$): δ 18.5(t), 25.3(t), 30.5(t), 33.7(t), 42.1(t), 58.2(d), 77.4(s), 127.4(d), 127.6(dx2), 128.7(dx2), 140.5(s), 168.9(s). Ms m/z: 247(M^+). Anal. Calcd for $C_{14}H_{17}NOS$: C, 67.98; H, 6.93; N, 5.66; S, 12.96. Found: C, 67.73; H, 6.81; N, 5.51; S, 12.77.

Compound **3g**: mp 104-106°C. Ir(nujol): 2450, 1620 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 1.45(1H, s, SH), 3.1-3.9(11H, m), 7.2-7.5(5H, m, ArH). ^{13}C-Nmr($CDCl_3$): δ 17.7(t), 24.6(t), 30.4(t), 32.0(t), 43.2(t), 58.3(d), 76.3(s), 127.4(d), 127.6(dx2), 128.7(dx2), 136.3(s), 168.9(s). Ms m/z: 247(M^+). Anal. Calcd for $C_{14}H_{17}NOS$: C, 67.98; H, 6.93; N, 5.66; S, 12.96. Found: C, 68.09; H, 6.93; N, 5.53; S, 13.09.

Compound **2h**: mp 128-129°C. Ir(nujol): 2500, 1680 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 2.80(1H, s, SH), 2.0-3.2(9H, m), 6.3-7.6(3H, m, Furan H). ^{13}C-Nmr($CDCl_3$): δ 31.4(t), 33.3(t), 33.9(t), 39.8(t), 49.8(d), 80.4(s), 107.3(d), 110.3(d), 142.2(d), 153.5(s), 173.2(s). Ms m/z: 223(M^+), 189(M^+-H_2S). Anal. Calcd for $C_{11}H_{13}NOS$: C, 59.17; H, 5.87; N, 6.27; S, 14.36. Found: C, 59.27; H, 5.99; N, 6.08; S, 14.29.

Compound **3h**: yellow oil. Ir(nujol): 2500, 1680 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 1.80(1H, s, SH), 2.3-3.8(9H, m), 6.2-7.4(3H, m, Furan H). ^{13}C-Nmr($CDCl_3$): δ 29.2(t), 34.1(t), 38.9(t), 39.2(t), 50.6(d), 80.5(s), 107.8(d), 110.2(d), 142.2(d), 152.1(s), 172.8(s). Ms m/z: 223(M^+), 189(M^+-H_2S). Anal. Calcd for $C_{11}H_{13}NOS$: C, 59.17; H, 5.87; N, 6.27; S, 14.36. Found: C, 59.18; H, 5.92; N, 6.27; S, 14.39.

Compound **6a**: mp 119-122°C. Ir(nujol): 2500 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 2.40(1H, s, SH), 2.0-3.5(5H, m), 2.45(3H, s, NCH_3), *3.95(1H, t, J=7 Hz, PhCH), 7.1-7.5(5H, m, ArH).* ^{13}*C-Nmr($CDCl_3$): δ 27.9(t), 32.9(q), 40.3(d), 49.0(t), 54.0(d),* 96.1(s), 127.8(dx2), 128.1(d), 129.0(dx2), 135.7(s), 202.2(s). Ms m/z: 249(M^+), 215(M^+-H_2S). Anal. Calcd for $C_{13}H_{15}NS_2$: C, 62.60; H, 6.06; N, 5.62; S, 25.72. Found: C, 62.53; H, 6.18; N, 5.77; S, 25.53.

Compound **7a**: mp 124-125°C. Ir(nujol): 2500 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 1.70(1H, s, SH), 2.1-3.5(5H, m), 3.30(3H, s, NCH_3), 3.70(1H, dd, *J*=5, 8 Hz, PhCH), 7.1-7.5(5H, m, ArH). ^{13}C-Nmr($CDCl_3$): δ 28.4(t), 30.8(q), 40.3(d), 49.6(t), 51.4(d), 83.3(s), 128.0(d), 128.4(dx2), 128.8(dx2), 138.3(s), 200.9(s). Ms m/z: 249(M^+), 215(M^+-H_2S). Anal. Calcd for $C_{13}H_{15}NS_2$: C, 62.60; H, 6.06; N, 5.62; S, 25.72. Found: C, 62.83; H, 6.25; N, 5.58; S, 25.93.

Compound **6b**: mp 131-133°C. Ir(nujol): 2500 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 1.5-3.6(8H, m), 2.30(3H, s, NCH_3), 2.50(1H, s, SH), 7.1-7.5(5H, m, ArH). ^{13}C-Nmr($CDCl_3$): δ 30.7(t), 30.9(t), 34.4(q), 49.8(t), 50.6(d), 60.5(d), 88.1(s), 128.1(d), 128.6(dx2), 128.9(dx2), 136.8(s), 201.7(s). Ms m/z: 263(M^+), 229(M^+-H_2S). Anal. Calcd for $C_{14}H_{17}NS_2$: C, 63.83; H, 6.50; N, 5.32; S, 23.35. *Found: C, 63.84; H, 6.59; N, 5.44; S, 24.40.*

Compound **7b**: mp 126-127°C. Ir(nujol): 2500 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 1.90(1H, s, SH), 2.0-3.5(8H, m), 3.20(3H, s, NCH_3), 7.1-7.5(5H, m, ArH). ^{13}C-Nmr($CDCl_3$): δ 31.8(t), 32.2(t), 33.7(q), 48.8(t), 50.5(d), 57.4(d), 89.8(s), 128.1(d),

128.4(dx2), 129.9(dx2), 138,4(s), 199.0(s). Ms m/z: 263(M^+), 229(M^+-H_2S). Anal. Calcd for $C_{14}H_{17}NS_2$: C, 63.83; H, 6.50; N, 5.32; S, 23.35. Found: C, 63.99 H, 6.38; N, 5.46; S, 24.18.

Compound **6d**: mp 135-137°C. Ir(nujol): 2500 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 1.8-3.5(7H, m), 2.10(1H, s, SH), 3.20(3H, s, NCH_3), 3.90(1H, t, *J*=8 Hz, PhC<u>H</u>), 7.2-7.5(5H, m, ArH). ^{13}C-Nmr($CDCl_3$): δ 25.1(t), 26.2(q), 37.0(t), 41.3(d), 43.6(t), 51.3(d), 73.3(s), 128.1(dx2), 128.4(dx2), 129.8(d), 137.1(s), 200.6(s). Ms m/z: 263(M^+), 229(M^+-H_2S). Anal. Calcd for $C_{14}H_{17}NS_2$: C, 63.83; H, 6.50; N, 5.32; S, 24.35. Found: C, 63.59; H, 6.55; N, 5.38; S, 24.35.

Compound **7d**: mp 131-133°C. Ir(nujol): 2500 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 1.55(1H, s, SH),1.8-3.5(7H, m), 3.40(3H, s, NCH_3), 3.80(1H, t, *J*=8 Hz, PhC<u>H</u>), 7.3-7.5(5H, m, ArH). ^{13}C-Nmr($CDCl_3$): δ 22.7(t), 27.2(q), 35.7(t), 42.5(d), 42.7(t), 52.4(d), 76.4(s), 128.0(d), 128.5(dx2), 129.(dx2), 135.7(s), 201.1(s). Ms m/z: 263(M^+), 229(M^+-H_2S). Anal. Calcd for $C_{14}H_{17}NS_2$: C, 63.83; H, 6.50; N, 5.32; S, 24.35. Found: C, 63.88; H, 6.55; N, 5.28; S, 24.51.

Compound **8**: yellow oil. Ir(nujol): 2500 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 2.20(1H, d, *J*=8 Hz, SH), 3.20(3H, s, NCH_3), 4.55(1H, dd, *J*=3, 8 Hz, HS-C<u>H</u>), 6.0-6.6(2H, m, vinyl H), 7.0-7.5(5H, m, ArH). Ms m/z: 263(M^+). Anal. Calcd for $C_{14}H_{17}NS_2$: C, 63.83; H, 6.50; N, 5.32; S, 23.34. Found: C, 63.75; H, 6.53; N, 5.48; S, 24.39.

Conversion of 2g (and 3g) into 4g

A solution of **2g** (50 mg) and one drop of conc. HCl in ethanol (5 ml) was stirred at room temperature for 30 min. After removal of the solvent, the residue was chromatographed over silica gel.

Compound **4g**: colorless oil. Ir(nujol): 1620 cm^{-1}. ^{1}H-Nmr($CDCl_3$): δ 1.80(4H,m), 2.48(2H, t, *J*=8 Hz), 2.90(2H,m), 3.95(2H, t, *J*=8 Hz), 7.1-7.6 (5H, m). ^{13}C-Nmr($CDCl_3$): δ 18.3(t), 28.0(t), 30.6(t), 34.9(t), 44.3(t), 59.8(s), 127.4(d), 127.8(dx2), 128.6(s), 128.9(dx2), 141.4(s), 168.8(s). Ms m/z: 213(M^+).

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