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Preparation of 3,3-Bis(alkylthio)-1,1-dipiperidino-2-propenylium Iodides by *S*-Alkylation of Alkyl 3,3-Dipiperidinodithioacrylates

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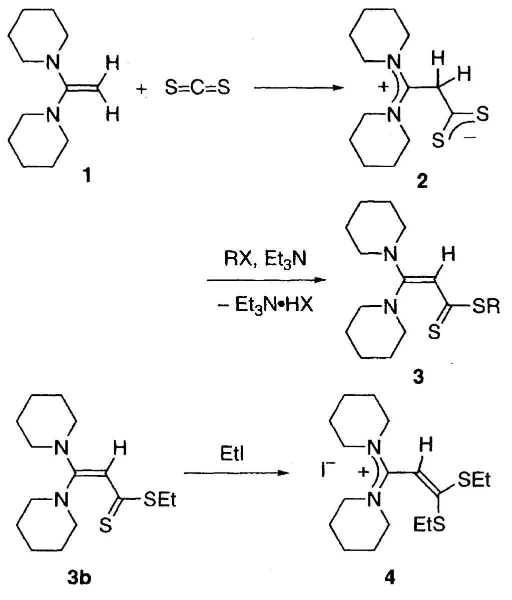
Methylation of propyl 3,3-dipiperidinodithioacrylate with iodomethane afforded a 93 : 7 mixture of (*E*)- and (*Z*)-3-methylthio-3-propylthio-1,1-dipiperidino-2-propenylium iodides nearly quantitatively, while propylation of methyl 3,3-dipiperidinodithioacrylate with 1-iodopropane produced a 6 : 94 mixture of the above isomers. Study of these iodides led to the conclusions that (a) free rotation about the C2–C3 bond is frozen for these carbenium ions, thus allowing the clearly distinguishable *E*- and *Z*-isomers to exist and (b) the alkylation takes place in such a manner that the newly formed *S*-alkyl group and the carbenium carbon atom become *cis* to each other. Such stereoselectivity was general for methylation of a series of alkyl 3,3-dipiperidinodithioacrylates and was explained by examining the preferred conformation of the starting dithioacrylates with NMR and X-ray diffraction analyses.

We have recently reported a one-pot synthesis of alkyl 3,3-dipiperidinodithioacrylates (**3**) from 1,1-dipiperidinoethene (**1**), carbon disulfide, and alkyl halides.[1] Thus, addition of carbon disulfide to the enediamine **1** affords 3,3-dipiperidinopropan-3-ylium-1-dithioate (**2**), which is alkylated in the presence of triethylamine to give **3** in good yields. During this study, we found that ethyl 3,3-dipiperidinodithioacrylate (**3b**) is further ethylated with iodoethane to give 3,3-bis(ethylthio)-1,1-dipiperidino-2-propenylium iodide (**4**) nearly quantitatively.[1] In the ^{1}H NMR spectrum, the two ethyl groups of **4** appeared as two independent A_3X_2 multiplets, indicating that the free rotation about the C_2–C_3 bond is inhibited (Scheme 1). Interestingly, the free rotation does not take place even when the NMR was determined at 100 °C. These observations lead to the conclusion that this type of the carbenium ion would be best represented as the canonical structure **5** but not the delocalized structure **7** because of small contribution of structure **6** (Chart 1). Thus, *E*- and *Z*-isomers may exist in case of the substituents on the two sulfur atoms of **5** being different. Keeping this in mind, we have investigated alkylation of a series of dithioacrylates **3** with alkyl iodides. A literature survey revealed that reactions of enamino thioketones,[2,3] enamino dithioesters,[4] and enamino thioamides[4] with alkyl halides give the corresponding *S*-alkylated iminium iodides. Furthermore, it was reported that methylation of enamino thioketones **8**, which exist as two rotameric conformers, with iodomethane afforded the *E*-isomers (*E*)-**9** predominantly (Scheme 2).[3] We report here the experimental details of the preparation of the carbenium



Scheme 1.

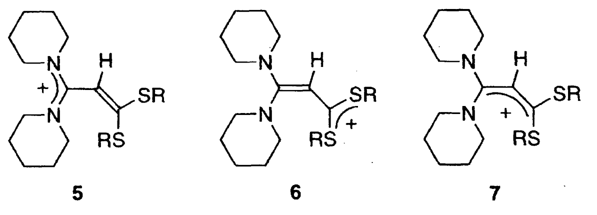
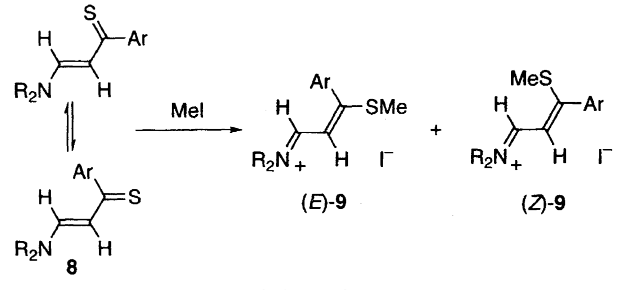


Chart 1.



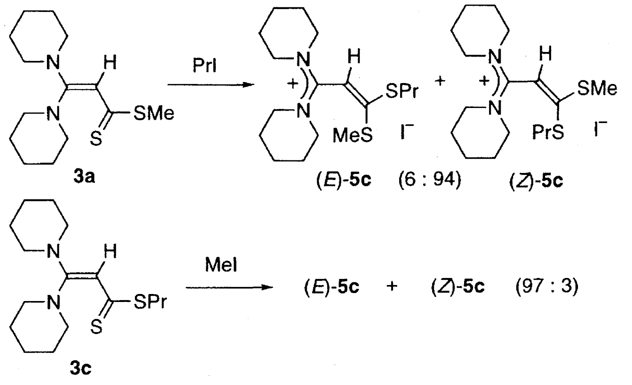
Scheme 2.

salts **5** by alkylation procedure and stereochemistry of this synthesis.

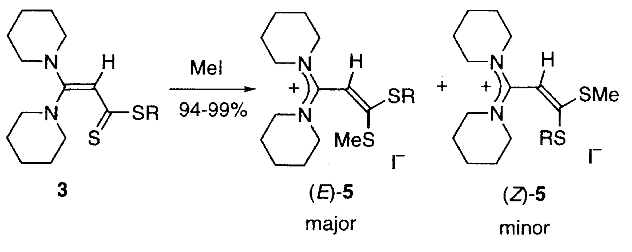
Results and Discussion

Treatment of methly 3,3-dipiperidinodithioacrylate (**3a**) with 1-iodopropane in toluene at room temperature resulted in separation of a viscous yellow oil. The oil consisted of a mixture of two isomeric carbenium salts and their ratio was determined to be 94 : 6 by the intensity ratio of *S*-methyl groups which appeared at $\delta = 2.64$ and 2.54, respectively, in ^{1}H NMR. Irradiation of the vinyl hydrogen signal of the major isomer, which appeared at $\delta = 6.40$, brought about 3% NOE at the *S*-methyl group signal, indicating that the vinyl hydrogen and the *S*-methyl group are *cis* to each other. Thus, the major isomer was assigned to the *Z*-isomer (*Z*)-**5c** and thus in turn the minor isomer to the (*E*)-**5c**. The yield of **5c** was nearly quantitative (Scheme 3). On the other hand, treatment of propyl 3,3-dipiperidinodithioacrylate (**3c**) with iodomethane gave a 97 : 3 mixture of (*E*)-**5c** and (*Z*)-**5c** nearly quantitatively as a yellow crystalline solid. Further support for the above assignment was provided by difference NOE spectra. Thus, when the vinyl hydrogen of the *Z*-isomer at $\delta = 6.40$ was irradiated, only *S*-methyl signal was observed as a distinct peak, whereas when that of the *E*-isomer at $\delta = 6.36$ was irradiated, only the α-methylene hydrogen signal of the *S*-propyl group was observed (Scheme 3).

These observations lead to the conclusion that (a) the free rotation about the C2–C3 bond is inhibited, as expected, and allows the clearly distinguishable *E*- and *Z*-isomers to exist and (b) the alkylation takes place highly stereoselectively, that is, it takes place in such a fashion that the newly formed *S*-alkyl group and the carbenium carbon become *cis* to each other. We then investigated methylation of a series of dithioacrylates **3** by iodomethane in order to establish the generality of the above results (Scheme 4). Results are summarized in Table 1. Yields are excellent (94—99%) without any exceptions. Methylation is highly stereoselective and *E*-isomers were formed preferentially with better selectivities than 95 : 5. In all these compounds, the *S*-methyl hydrogen signal of the *E*-isomers appeared at a slightly higher field than that of the corresponding *Z*-isomers. Chemical shift values of C1, C2, and C3 of the *E*-isomers concentrate in relatively narrow ranges, as shown in Chart 2.



Scheme 3.



Scheme 4.

When a solution of a 6 : 94 mixture of (*E*)-**5c** and (*Z*)-**5c** in CDCl$_3$ was allowed to stand at room temperature, the thermodynamically equilibrated ratio of 38 : 62, which did not change on further standing, was attained. On the other hand, when a solution of a 97 : 3 mixture was allowed to stand for 24 h, the ratio turned to 92 : 8. For this case, the equilibrium ratio of 38 : 62 was not reached even after 10 d because of very slow isomerization of the less hindered *E*-isomer to the more hindered *Z*-isomer. A similar slow isomerization in solution was also observed on *E*- and *Z*-mixtures of many carbenium iodides given in Table 1.

The stereoselectivity in alkylation should be explained next. Two piperidino groups of **3a** are chemically equivalent both in ^{1}H- and ^{13}C NMR spectra at room temperature, revealing that the free rotation is taking place about the C2–C3 bond on an NMR time scale. This means that the C2–C3 double bond and the thiocarbonyl group are fully conjugated, that is, the polarized structure **3a′** or **3a″** largely contributes to the ground state structure of the compound (Chart 3). The structure **3a′** should be more favorable than **3a″** because of the Coulomb attraction between the negatively charged thiolate sulfur atom and the partially positively charged nitrogen atom. The thiocarbonyl sulfur atom and the carbon atom carrying piperidino groups are placed on the *cis*-orientation for **3a′**. Thus, alkylation on this geometry would result in the preferential formation of the one isomer where the carbenium carbon and newly formed *S*-alkyl group are *cis* to each other.

In order to reveal more about the conformation of the starting dithioacrylates **3**, an X-ray diffraction analysis was

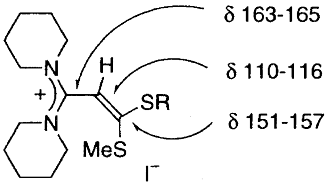


Chart 2.

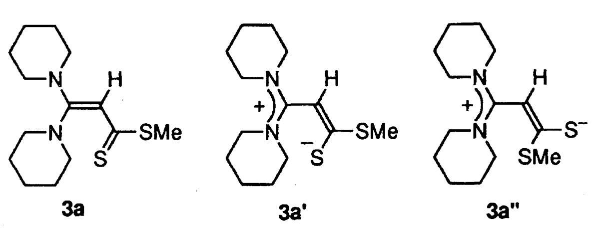


Chart 3.

Table 1. Preparation of the Carbenium Iodides **5** by *S*-Methylation of the Dithioesters **3** with Iodomethane[a)]

Run	Dithioesters (**3**)	R	Carbenium Iodides (**5**)	Yield (%)	*E* : *Z*-ratio[b)]
1	**3b**	Et	**5b**	97	95 : 5[c)]
2	**3c**	*n*-Pr	**5c**	99	97 : 3
3	**3d**	*i*-Pr	**5d**	94	96 : 4
4	**3e**	*n*-Bu	**5e**	96	97 : 3
5	**3f**	CH_2–CH=CH_2	**5f**	95	97 : 3
6	**3g**	CH_2Ph	**5g**	98	97 : 3
7	**3h**	CH_2CH_2Ph	**5h**	96	95 : 5[c)]
8	**3i**	CH_2COPh	**5i**	97	97 : 3
9	**3j**	$CH_2CO_2CH_3$	**5j**	94	97 : 3[c)]
10	**3k**	CH_2CN	**5k**	98	99 : 1

a) Unless otherwise stated, reactions were carried out using toluene as the solvent. b) *E*/*Z* ratios were determined by intensity of *S*-methyl hydrogen signals in ^{1}H NMR. c) The reactions were carried out using ether as the solvent.

performed on the methyl ester **3a**. The molecular structures of **3a** are given in Figs. 1 and 2, and the relevant bond lengths and bond angles data in Table 2. The following characteristic structural features emerge from these data. The most important fact is that the thiocarbonyl sulfur atom and the carbon atom carrrying piperidino groups are placed on a *cis*-orientation, as expected, and the distance between S1 and N1 [3.345(3) Å] is equal to the summation of the van der Waals radii (3.35 Å),[5)] indicating that weak interaction might exist between them even in the solid state. The C2–C3 bond length [1.420(4) Å] is much longer than common conjugated C–C double bonds (1.33—1.34 Å),[6)] whereas the C1–C2 bond [1.389(4) Å] is much shorter than that of the C(sp^2)–C(sp^2) single bond of compounds R_2C=C–CR=X (1.45—1.48 Å).[6)] In addition, the C1–C2 bond is shorter than the C2–C3 bond. These reveal that much double bond character is localized on the C1–C2 bond, and thus the polarized canonical structure **3a′** is the major contributor. This is also supported by the C3–N1 and C1–S1 bond length values; the former bond length [1.350(4) Å] is shorter than common C–N single bonds (1.42 Å)[6)] and the latter [1.687(3) Å] is longer than common C–S double bonds (1.67 Å).[6)] Furthermore, as shown in Fig. 2, the C1, C2, C3, and S1 atoms are placed on

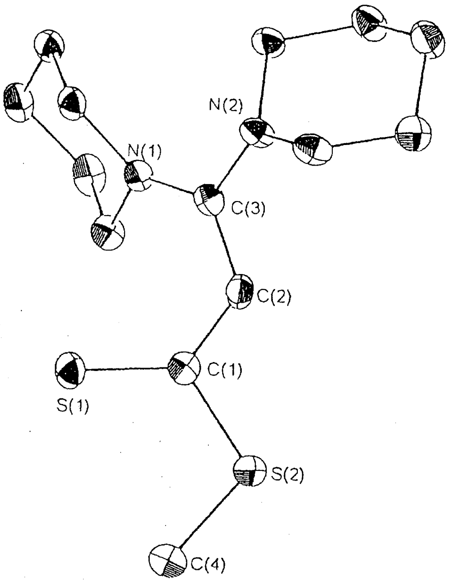


Fig. 1. Molecular structure of **3a** showing that S(1) and C(3) are placed on the same site about C(1)–C(2) bond.

Table 2. Selected Bond Lengths and Bond Angles Data of **3a**

Bond lengths	(Å)[a)]	Bond angles	(°)[a)]
C1–C2	1.389 (4)	N1–C3–N2	118.3 (3)
C2–C3	1.420 (4)	N1–C3–C2	122.8 (3)
C1–S1	1.687 (3)	N2–C3–C2	118.8 (3)
C1–S2	1.787 (3)	C1–C2–C3	126.3 (3)
C4–S2	1.797 (4)	S1–C1–C2	127.5 (3)
C3–N1	1.350 (4)	S1–C1–S2	121.4 (2)
C3–N2	1.350 (4)	C2–C1–S2	111.2 (2)
		C1–S2–C4	105.1 (2)

a) Average values of two molecules are given, which are in the range of two times of standard deviation.

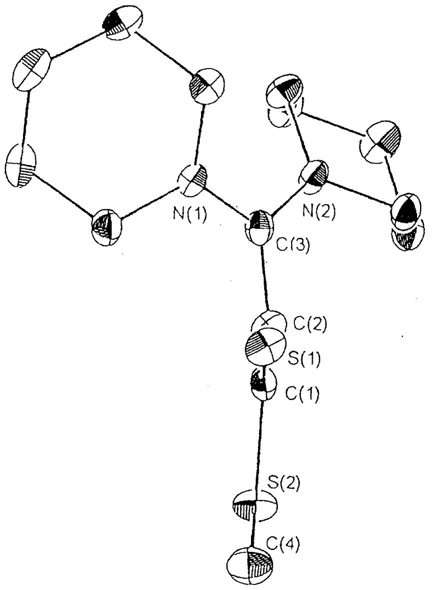


Fig. 2. Molecular structure of **3a** showing that C(1), C(2), C(3), and S(1) are placed on the same plane.

the same plane, indicating the existence of strong conjugation between these atoms. All of these structural features of **3a** would support the explanation given for the stereoselectivity in alkylation, even though the conformation in solution may not be the exactly the same as that in the crystalline state.

Experimental

Melting points are uncorrected. ^{1}H- and ^{13}C NMR spectra were determined on a JEOL EX-270 (270 MHz for ^{1}H NMR and 67.8 MHz for ^{13}C NMR) spectrometer in $\mathrm{CDCl_3}$ as the solvent and with TMS as the internal standard. Elemental analyses were performed on a Yanaco MT-3 CHN recorder, and the results obtained on the carbenium iodides **5** were all on crystalline mixtures of *E*- and *Z*-isomers, which separated out from reaction mixtures.

A Typical Procedure for the Preparation of the Carbenium Iodides 5: 3-Methylthio-3-propylthio-1,1-dipiperidino-2-propenylium Iodide (5c). A solution of 313 mg (1.0 mmol) of propyl 3,3-dipiperidinodithioacrylate (**3c**) and 75 μl (1.2 mmol) of iodomethane in 10 ml of toluene was stirred at room temperature for 24 h. The crystalline solid which separated was collected by filtration to give 450 mg (99%) of **5c** ($E:Z=97:3$); yellow needles; mp 139.0—139.5 °C. Found: C, 45.04; H, 6.84; N, 5.96%. Calcd for $\mathrm{C_{17}H_{31}IN_2S_2}$: C, 44.93; H, 6.88; N, 6.16%.

(*E*)-5c: ^{1}H NMR $\delta=1.09$ (3H, t, $J=7.3$ Hz, $\mathrm{CH_2CH_2C\underline{H}_3}$), 1.76 (2H, m, $\mathrm{CH_2C\underline{H}_2CH_3}$), 1.82 (12H, broad s, piperidine ring H at β- and γ-positions), 2.54 (3H, s, $\mathrm{SCH_3}$), 3.10 (2H, t, $J=7.3$ Hz, $\mathrm{C\underline{H}_2CH_2CH_3}$), 3.59 (8H, broad s, piperidine ring H at α-positions), 6.36 (1H, s, vinyl H); ^{13}C NMR $\delta=13.4$ (q), 15.8 (q), 21.5 (t), 23.3 (t), 25.3 (t), 36.2 (t), 52.7 (t), 110.7 (d), 156.8 (s), 164.5 (s).

(*Z*)-5c: ^{1}H NMR $\delta=1.03$ (3H, t, $J=7.3$ Hz, $\mathrm{CH_2CH_2C\underline{H}_3}$), 1.74 (2H, m, $\mathrm{CH_2C\underline{H}_2CH_3}$), 1.81 (12H, broad s, piperidine ring H at β- and γ-positions), 2.64 (3H, s, $\mathrm{SCH_3}$), 3.01 (2H, t, $J=7.3$ Hz, $\mathrm{C\underline{H}_2CH_2CH_3}$), 3.59 (8H, broad s, piperidine ring H at α-positions), 6.40 (1H, s, vinyl H).

3-Ethylthio-3-methylthio-1,1-dipiperidino-2-propenylium Iodide (5b): 97% ($E:Z=95:5$); yellow granules; mp 97.0—98.5 °C. Found: C, 43.52; H, 6.50; N, 6.37%. Calcd for $\mathrm{C_{16}H_{29}IN_2S_2}$: C, 43.63; H, 6.64; N, 6.36%.

(*E*)-5b: ^{1}H NMR $\delta=1.40$ (3H, t, $J=7.6$ Hz, $\mathrm{CH_2C\underline{H}_3}$), 1.84 (4H, broad s, piperidine ring H at γ-position), 2.05 (8H, broad s, piperidine ring H at β-positions), 2.54 (3H, s, $\mathrm{SCH_3}$), 3.11 (2H, q, $J=7.6$ Hz, $\mathrm{C\underline{H}_2CH_3}$), 3.60 (8H, broad s, piperidine ring H at α-positions), 6.28 (1H, s, vinyl H); ^{13}C NMR $\delta=13.0$ (q), 15.7 (q), 23.2 (t), 25.3 (t), 28.6 (t), 52.6 (t), 110.3 (d), 156.9 (s), 164.4 (s).

(*Z*)-5b: ^{1}H NMR $\delta=1.37$ (3H, t, $J=7.6$ Hz, $\mathrm{CH_2C\underline{H}_3}$), 1.84 (4H, broad s, piperidine ring H at γ-position), 2.05 (8H, broad s, piperidine ring H at β-positions), 2.64 (3H, s, $\mathrm{SCH_3}$), 3.06 (2H, q, $J=7.6$ Hz, $\mathrm{C\underline{H}_2CH_3}$), 3.60 (8H, broad s, piperidine ring H at α-positions), 6.30 (1H, s, vinyl H).

3-Isopropylthio-3-methylthio-1,1-dipiperidino-2-propenylium Iodide (5d): 99% ($E:Z=96:4$); yellow needles; mp 115.0—116.5 °C. Found: C, 44.85; H, 6.72; N, 5.85%. Calcd for $\mathrm{C_{17}H_{31}IN_2S_2}$: C, 44.93; H, 6.88; N, 6.16%.

(*E*)-5d: ^{1}H NMR $\delta=1.42$ (6H, d, $J=6.8$ Hz, $\mathrm{CH(C\underline{H}_3)_2}$), 1.84 (12H, broad s, piperidine ring H at β- and γ-positions), 2.52 (3H, s, $\mathrm{SCH_3}$), 3.61 (8H, broad s, piperidine ring H at α-positions), 3.74 (1H, septet, $J=6.8$ Hz, $\mathrm{C\underline{H}(CH_3)_2}$), 6.39 (1H, s, vinyl H); ^{13}C NMR $\delta=15.9$ (q), 22.7 (q), 23.2 (t), 25.3 (t), 38.5 (t), 52.6 (t), 111.9 (d), 155.8 (s), 164.2 (s).

(*Z*)-5d: ^{1}H NMR $\delta=1.36$ (6H, d, $J=6.8$ Hz, $\mathrm{CH(C\underline{H}_3)_2}$), 1.84 (12H, broad s, piperidine ring H at β- and γ-positions), 2.60 (3H, s, $\mathrm{SCH_3}$), 3.61 (8H, broad s, piperidine ring H at α-positions), 3.74 (1H, septet, $J=6.8$ Hz, $\mathrm{C\underline{H}(CH_3)_2}$), 6.40 (1H, s, vinyl H).

3-Butylthio-3-methylthio-1,1-dipiperidino-2-propenylium Iodide (5e): 96% ($E:Z=97:3$); yellow needles; mp 121.5—123.0 °C. Found: C, 46.04; H, 6.86; N, 5.77%. Calcd for $\mathrm{C_{18}H_{33}IN_2S_2}$: C, 46.15; H, 7.10; N, 5.98%.

(*E*)-5e: ^{1}H NMR $\delta=0.95$ (3H, t, $J=7.3$ Hz, $\mathrm{(CH_2)_3C\underline{H}_3}$), 1.51 (2H, m, $\mathrm{(CH_2)_2C\underline{H}_2CH_3}$), 1.72 (2H, m, $\mathrm{CH_2C\underline{H}_2CH_2CH_3}$), 1.83 (12H, broad s, piperidine ring H at β- and γ-positions), 2.54 (3H, s, $\mathrm{SCH_3}$), 3.10 (2H, t, $J=7.0$ Hz, $\mathrm{C\underline{H}_2(CH_2)_2CH_3}$), 3.60 (8H, broad s, piperidine ring H at α-positions), 6.27 (1H, s, vinyl H); ^{13}C NMR $\delta=13.6$ (q), 15.8 (q), 21.9 (t), 23.2 (t), 25.3 (t), 29.9 (t), 34.1 (t), 52.6 (t), 110.4 (d), 157.2 (s), 164.4 (s).

(*Z*)-5e: ^{1}H NMR $\delta=2.63$ (3H, s, $\mathrm{SCH_3}$), 3.02 (2H, t, $J=7.0$ Hz, $\mathrm{C\underline{H}_2CH_2CH_2CH_3}$), 6.32 (1H, s, vinyl H); the other signals overlapped with those of ***E*-5e**.

3-Allylthio-3-methylthio-1,1-dipiperidino-2-propenylium Iodide (5f): 95% ($E:Z=97:3$); yellow needles; mp 107.0—108.5 °C. Found: C, 45.33; H, 6.31; N, 6.21%. Calcd for $\mathrm{C_{17}H_{29}IN_2S_2}$: C, 45.13; H, 6.46; N, 6.19%.

(*E*)-5f: ^{1}H NMR $\delta=1.81$ (12H, broad s, piperidine ring H at β- and γ-positions), 2.55 (3H, s, $\mathrm{SCH_3}$), 3.60 (8H, broad s, piperidine ring H at α-positions), 3.79 (2H, d, $J=6.8$ Hz, $\mathrm{C\underline{H}_2CH{=}CH_2}$), 5.26 (1H, d, $J=10.3$ Hz, $\mathrm{CH_2CH{=}C\underline{H}_2}$), 5.56 (1H, d, $J=17.0$ Hz, $\mathrm{CH_2CH{=}C\underline{H}_2}$), 5.86 (1H, d/d/t, $J=17.0$, 10.3, 6.8 Hz, $\mathrm{CH_2C\underline{H}{=}CH_2}$), 6.30 (1H, s, vinyl H); ^{13}C NMR $\delta=15.8$ (q), 23.0 (t), 25.1 (t), 36.4 (t), 52.4 (t), 111.5 (d), 119.7 (t), 131.0 (d), 155.4 (d), 163.7 (s).

(*Z*)-5f: ^{1}H NMR $\delta=1.81$(12H, broad s, piperidine ring H at β- and γ-positions), 2.64 (3H, s, $\mathrm{SCH_3}$), 3.60 (8H, broad s, piperidine ring H at α-positions), 3.68 (2H, d, $J=6.8$ Hz, $\mathrm{C\underline{H}_2CH{=}CH_2}$), 5.20 (1H, d, $J=9.7$ Hz, $\mathrm{CH_2CH{=}C\underline{H}_2}$), 5.31 (1H, d, $J=16.7$ Hz, $\mathrm{CH_2CH{=}C\underline{H}_2}$), 5.87 (1H, d/d/t, $J=16.7$, 9.7, 6.8 Hz, $\mathrm{CH_2C\underline{H}{=}CH_2}$), 6.34 (1H, s, vinyl H).

3-Benzylthio-3-methylthio-1,1-dipiperidino-2-propenylium Iodide (5g): 98% ($E:Z=97:3$); yellow needles; mp 115.5—117 °C. Found: C, 50.10; H, 6.15; N, 5.58%. Calcd for $\mathrm{C_{21}H_{31}IN_2S_2}$: C, 50.19; H, 6.22; N, 5.57%.

(*E*)-5g: ^{1}H NMR $\delta=1.71$ (12H, broad s, piperidine ring H at β- and γ-positions), 2.53 (3H, s, $\mathrm{SCH_3}$), 3.43 (8H, broad s, piperidine ring H at α-positions), 4.33 (2H, s, $\mathrm{C\underline{H}_2Ph}$), 6.30 (1H, s, vinyl H), 7.26 (1H, m, Ph), 7.33 (2H, m, Ph), 7.54 (2H, m, Ph); ^{13}C NMR $\delta=15.9$ (q), 23.0 (t), 25.1 (t), 38.0 (t), 52.3 (t), 112.8 (d), 127.5 (d), 128.5 (d), 128.9 (d), 134.7 (s), 155.0 (s), 163.6 (s).

(*Z*)-5g: ^{1}H NMR $\delta=1.71$ (12H, broad s, piperidine ring H at β- and γ-positions), 2.65 (3H, s, $\mathrm{SCH_3}$), 3.43 (8H, broad s, piperidine ring H at α-positions), 4.24 (2H, s, $\mathrm{C\underline{H}_2Ph}$), 6.37 (1H, s, vinyl H), 7.26 (1H, m, Ph), 7.33 (2H, m, Ph), 7.54 (2H, m, Ph).

3-Methylthio-3-phenethylthio-1,1-dipiperidino-2-propenylium Iodide (5h): 96% ($E:Z=97:3$); light yellow powder; mp 95—97 °C. Found: C, 51.12; H, 6.41; N, 5.40%. Calcd for $\mathrm{C_{22}H_{33}IN_2S_2}$: C, 51.16; H, 6.44; N, 5.42%.

(*E*)-5h: ^{1}H NMR $\delta=1.76$ (4H, broad s, piperidine ring H at γ-position), 1.83 (8H, broad s, piperidine ring H at β-positions), 2.48 (3H, s, $\mathrm{SCH_3}$), 3.05 (2H, t, $J=7.3$ Hz, $\mathrm{C\underline{H}_2CH_2Ph}$), 3.41 (2H, t, $J=7.3$ Hz, $\mathrm{CH_2C\underline{H}_2Ph}$), 3.57 (8H, broad s, piperidine ring H at α-positions), 6.44 (1H, s, vinyl H), 7.28 (5H, m, Ph); ^{13}C NMR $\delta=15.9$ (q), 23.1 (t), 25.2 (t), 34.1 (t), 35.7 (t), 52.5 (t), 111.0 (d), 126.1 (d), 128.4 (d), 128.6 (d), 138.6 (s), 156.5 (s), 164.2 (s).

(*Z*)-5h: ^{1}H NMR $\delta=1.76$ (4H, broad s, piperidine ring H at γ-position), 1.83 (8H, broad s, piperidine ring H at β-positions), 2.66 (3H, s, $\mathrm{SCH_3}$), 2.98 (2H, t, $J=7.3$ Hz, $\mathrm{C\underline{H}_2CH_2Ph}$), 3.31 (2H, t, $J = 7.3$ Hz, $CH_2C\underline{H}_2Ph$), 3.50 (8H, broad s, piperidine ring H at α-positions), 6.40 (1H, s, vinyl H), 7.28 (5H, m, Ph).

3-Methylthio-3-phenacylthio-1,1-dipiperidino-2-propenylium Iodide (5i): 97% ($E:Z$=97 : 3); yellow powder; mp 146—148 °C. Found: C, 49.75; H, 5.83; N, 5.20%. Calcd for $C_{22}H_{31}IN_2OS_2$: C, 49.81; H, 5.89; N, 5.28%.

(*E*)-5i: ^{1}H NMR $\delta = 1.77$ (4H, broad s, piperidine ring H at γ-position), 1.82 (8H, broad s, piperidine ring H at β-positions), 2.62 (3H, s, SCH_3), 3.57 (8H, broad s, piperidine ring H at α-positions), 4.97 (2H, s, $C\underline{H}_2COPh$), 6.73 (1H, s, vinyl H), 7.53 (2H, m, Ph), 7.61 (1H, m, Ph), 8.27 (2H, m, Ph); ^{13}C NMR $\delta = 16.1$ (q), 23.3 (t), 25.3 (t), 43.8 (t), 52.7 (t), 113.2 (d), 128.8 (d), 129.2 (d), 134.1 (d), 134.7 (s), 155.5 (s), 164.3 (s), 192.9 (s).

(Z)-5i: ^{1}H NMR $\delta = 2.67$ (1H, s, SCH_3), 4.61 (2H, s, $C\underline{H}_2COPh$), 6.51 (1H, s, vinyl H); the other signals overlapped with those of (***E***)-**5i**.

3-Methoxycarbonylmethylthio-3-methylthio-1,1-dipiperidino-2-propenylium Iodide (5j): 94% ($E:Z = 97:3$); light yellow powder; mp 83.0—84.5 °C. Found: C, 43.42; H, 6.05; N, 5.54%. Calcd for $C_{18}H_{29}IN_2O_2S_2$: C, 43.55; H, 5.89; N, 5.64%.

(*E*)-5j: ^{1}H NMR $\delta = 1.84$ (4H, broad s, piperidine ring H at γ-position), 1.95 (8H, broad s, piperidine ring H at β-positions), 2.56 (3H, s, SCH_3), 3.60 (8H, broad s, piperidine ring H at α-positions), 3.78 (3H, s, $CO_2C\underline{H}_3$), 4.01 (2H, s, $C\underline{H}_2CO_2CH_3$), 6.55 (1H, s, vinyl H); ^{13}C NMR $\delta = 16.4$ (q), 23.1 (t), 25.3 (t), 35.7 (t), 52.6 (t), 52.9 (q), 114.2 (d), 154.0 (s), 163.4 (s), 168.4 (s).

(Z)-5j: ^{1}H NMR $\delta = 1.84$ (4H, broad s, piperidine ring H at γ-position), 1.95 (8H, broad s, piperidine ring H at β-position), 2.64 (3H, s, SCH_3), 3.61 (8H, broad s, piperidine ring H at α-positions), 3.77 (3H, s, $CO_2C\underline{H}_3$), 3.85 (2H, s, $C\underline{H}_2CO_2CH_3$), 6.51 (1H, s, vinyl H).

3-Cyanomethylthio-3-methylthio-1,1-dipiperidino-2-propenylium Iodide (5k): 98% ($E:Z = 99:1$); yellow powder; mp 156.5—157.5 °C. Found: C, 42.62; H, 5.79; N, 9.23%. Calcd for $C_{16}H_{26}IN_3S_2$: C, 42.57; H, 5.81; N, 9.31%.

(*E*)-5k: ^{1}H NMR $\delta = 1.78$ (4H, broad s, piperidine ring H at γ-position), 1.86 (8H, broad s, piperidine ring H at β-positions), 2.59 (3H, s, SCH_3), 3.65 (8H, broad s, piperidine ring H at α-positions), 4.39 (2H, s, $C\underline{H}_2CN$), 6.85 (1H, s, vinyl H); ^{13}C NMR $\delta = 16.6$ (q), 20.1 (t), 23.0 (t), 25.4 (t), 52.7 (t), 115.7 (s), 116.2 (s), 151.4 (s), 162.8 (s).

(Z)-5k: ^{1}H NMR $\delta = 1.78$ (4H, broad s, piperidine ring H at γ-position), 1.86 (8H, broad s, piperidine ring H at β-positions), 2.71 (3H, s, SCH_3), 3.65 (8H, broad s, piperidine ring H at α-positions), 4.16 (2H, s, $C\underline{H}_2CN$), 6.67 (1H, s, vinyl H).

X-Ray Diffraction Analysis of 3a. Crystal data : $C_{14}H_{24}N_2S_2$, $M_r = 384.48$, triclinic, $P\bar{1}$, $a = 8.240(1)$, $b = 11.363(1)$, $c = 16.308(2)$ Å, $\alpha = 74.986(7)$, $\beta = 88.877(7)$, $\gamma = 87.448(7)°$, $V = 1473.3(3)$ Å^3, $Z = 4$, $D_x = 1.733$ Mg m^{-3}, $\theta = 1 - \mu = 3.329$ nm^{-1}.

A yellow crystal with dimensions 0.1×0.07×0.06 mm was mounted on a Mac Science DIP3000 spectrometer equiped with a graphite monochrometer. The measurement was carried out at 153 K. Oscillation and nonscreen Weissenberg photographs were corrected on the imaging plates of the diffractometer by using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and the data collection was made by the Mac Denzo program system. Intensity data of 2385 unique reflections were collected in the range of $0 \leq h \leq 11$, $-15 \leq k \leq 15$, $-21 \leq l \leq 21$. Cell parameters were determined and refined by using the Mac Denzo for all observed reflections. The structure was solved by direct methods using SIR in the CRYSTAN-GM program system. The atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full matrix least squares to minimize the functions, $\Sigma(|F_o| - |F_c|)^2$, for 4143 reflections with $I > 3\sigma(I)$. The final R and R_w values were 0.044 and 0.049, respectively.

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