Synthesis and Properties of the Inner Salt, 3,3-Dipiperidino-3-propylium-1-dithioate: Adduct of 1,1-Dipiperidinoethene and Carbon Disulfide

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The nucleophilic addition of 1,1-dipiperidinoethene to carbon disulfide gives an inner salt, 3,3-dipiperidino-3-propylium-1-dithioate (**8**), in good yield. The inner salt **8** exists as an equilibrium mixture with its tautomer 3,3-dipiperidinodithioacrylic acid in the ratio of 9 : 1 in $CDCl_3$ at 22 °C. The air-oxidation of **8** leads to bis(3,3-dipiperidinothioacryloyl) disulfide. The inner salt **8**, prepared in situ, reacts with a wide variety of alkyl halides to provide a convenient synthesis of alkyl 3,3-dipiperidinodithioacrylates in one-pot.

We have been investigating the syntheses, structures, and reactivities of inner salts, 2,2-bis(dialkylamino)-2-ethylium-1-dithioate (**1**) and the related compounds.[1,2] Recently, we have also reported the unexpected formation of bis[3,3-bis(diethylamino)thioacryloyl] disulfide (**2**) by reaction of 1,1-bis(diethylamino)-2-chloroethene with carbon disulfide, where 2-chloro-3,3-bis(diethylamino)-3-propylium-1-dithioate (**3**) is a probable intermediate.[3] The intermediate **3** corresponds to a homolog of **1**. In this connection, we have now become interested in the chemistry of homologs of **1** and the related compounds, and made a literature survey about this chemistry. Reportedly, carbon disulfide adds enamines to give the initial adducts (**4**) which then isomerize to the corresponding dithioacrylic acids.[4] Application of the reaction to ketene-*S*,*N*-acetals led to the formation of the inner salts (**5**), and their isolation and reactivities were communicated briefly.[5] The inner salt (**6**) was also formed by addition of 1,1-bis(dimethylamino)ethene to carbon disulfide.[5a] Although it was reported that **6** was identified spectroscopically at low temperatures, no spectroscopic data were given in any detail. Inner salts (**7**) were also identified spectroscopically[4e] and captured chemically (Chart 1).[4e,6]

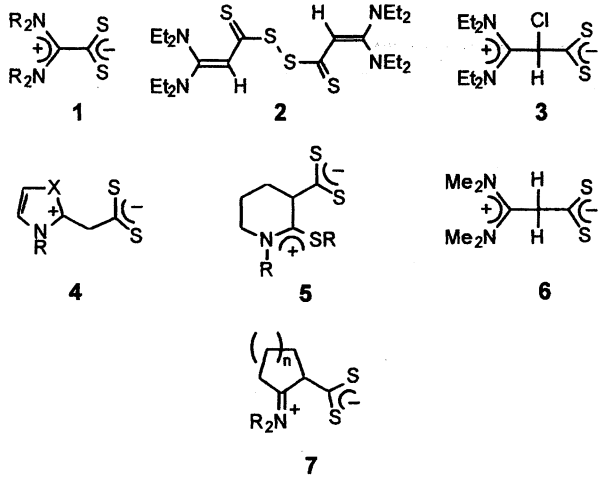


Chart 1.

We report here the preparation of 3,3-dipiperidino-3-propylium-1-dithioate (**8**) by nucleophilic addition of 1,1-dipiperidinoethene (**9**)[7] to carbon disulfide and its chemical properties. Also reported is a convenient and general synthesis of a wide variety of dithioacrylic acid esters which makes use of the reactivity of **8**.

Results and Discussion

Slow addition of the neat ethene **9** to carbon disulfide, which served as the reactant and solvent, resulted in the separation of a viscous dark-red oil. The reaction of **9** with carbon disulfide (2 molar amounts) in toluene also resulted in the separation of a dark red oil. But, in this case, the oil solidified on continuous stirring of the mixture to give an orange powder. The oil and the powder showed essentially the same ^1H and ^{13}C NMR spectra, revealing that the principal component is the expected inner salt **8**. The inner salt **8** is a reactive species, as will be described later, and could not be obtained in analytically pure form; it resisted purification by recrystallization and column chromatography. The structure of **8** is therefore elucidated by spectroscopic analyses and chemical transformations of the above orange powder (Scheme 1).

The ^1H NMR spectrum of the orange powder of **8** determined in $CDCl_3$ is shown in Fig. 1a. The two multiplets at $\delta = 1.79$ (12H) and 3.62 (8H) should be ascribed to the methylene hydrogens of piperidine rings, while the singlet at $\delta = 4.57$ (2H) is ascribed to the methylene hydrogens adjacent to the dithiocarboxylate carbon. The weak singlet at $\delta = 5.70$ may originate from the alkenic hydrogen of 3,3-dipiperidinodithioacrylic acid (**10**), the tautomer of **8**. The other signals of **10** are overlapped with the signals of **8** at

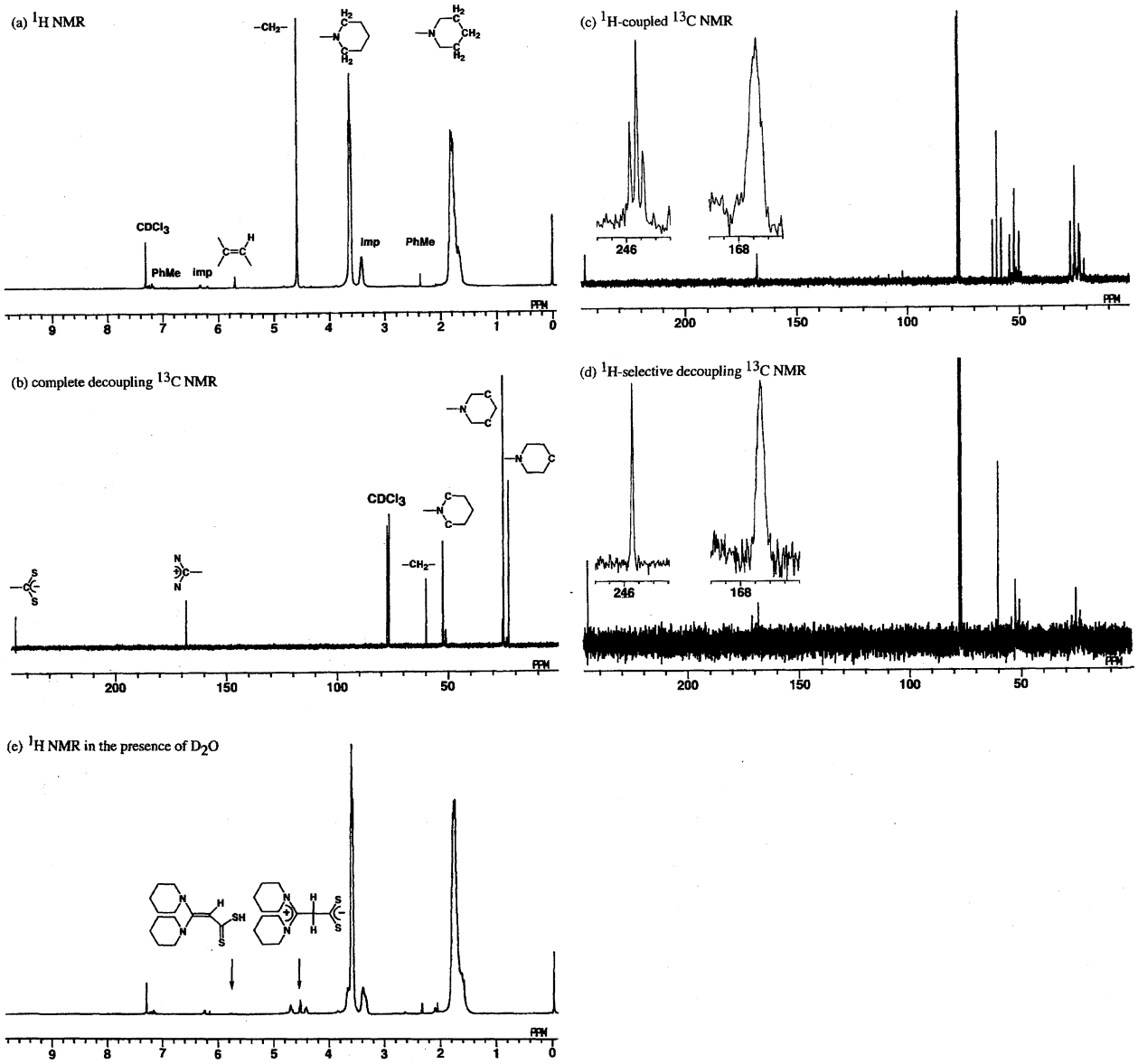
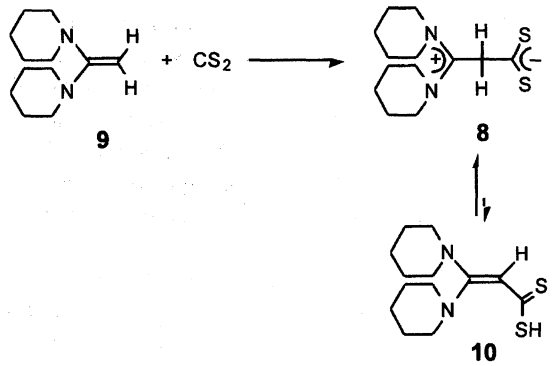


Fig. 1. NMR spectra of **8** in $CDCl_3$ (270 MHz for ^{1}H and 67.8 MHz for ^{13}C). (a) ^{1}H NMR. (b) Complete decoupling ^{13}C NMR. (c) ^{1}H-coupled ^{13}C NMR. (d) ^{1}H-selective decoupling ^{13}C NMR (irradiated at $\delta_H = 4.57$). (e) ^{1}H NMR in the presence of D_2O.



Scheme 1.

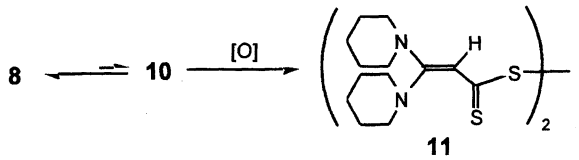
$\delta = 1.79$ and 3.62; supporting evidence for the presence of this tautomer will be given later in more detail. The other small signals seen in Fig. 1a come from impurities such as toluene (the solvent of the reaction) and by-products. The amounts of the by-products are influenced by reaction conditions for the preparation. The complete decoupling ^{13}C NMR spectrum is given in Fig. 1b, where six signals are observed in accordance with the structure of **8**. The signals due to two piperidino groups appeared as only three singlets at $\delta = 23.2$, 25.5, and 52.5, indicating that they are chemically equivalent. The signal at $\delta = 60.1$ is assigned to the methylene carbon adjacent to the dithiocarboxylate carbon by analysis of the DEPT spectrum. Two lower field signals at $\delta = 167.8$ and 245.9 are assigned to the carbenium and dithiocarboxylate carbons, respectively. Combinations of ^{1}H-coupled and ^{1}H-selective decoupling ^{13}C NMR spectra (Figs. 1c and 1d) provide further supporting evidence for the structure of **8**. In the ^{1}H-coupled ^{13}C NMR spectrum, the dithiocarboxylate carbon signal at $\delta = 245.9$ splits into a triplet ($^2J_{C-H} = 6.8$ Hz) because of the coupling with the adjacent methylene hydro-

gens, while the carbenium carbon signal at $\delta = 167.8$ splits into a broad multiplet. The latter multiplet turns to a clear triplet ($^3J_{C-H} = 3.7$ Hz) on irradiation of the α-methylene hydrogens at $\delta_H = 3.62$, which suggests that two piperidine rings are connected with the carbenium carbon. On irradiation of the methylene hydrogens at $\delta_H = 4.57$, both triplets at $\delta_C = 60.1$ ($^1J_{C-H} = 132$ Hz) and $\delta_C = 245.9$ turn to singlets, while the width of the signal at $\delta_C = 167.8$ becomes less broad because of the disappearance of the long range coupling. Thus, these NMR data are all in harmony with a bond sequence of N_2C^+ ($\delta_C = 167.8$)–CH_2 ($\delta_C = 60.1$)–CS_2^- ($\delta_C = 245.9$) and fully support the proposed structure.

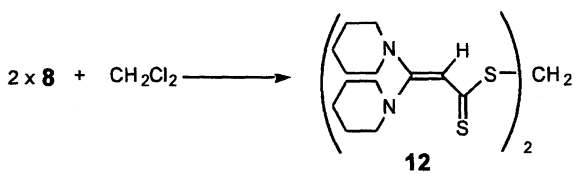
Addition of D_2O to a solution of **8** in $CDCl_3$ resulted in quick disappearance of the singlet at $\delta = 4.57$ which originates from the methylene hydrogens (Fig. 1e). The signal at $\delta = 5.70$ also disappeared. It was ascribed to the alkenic hydrogen of the dithioacrylic acid **10**, as already described. These observations reveal that the inner salt **8** and the dithiocarboxylic acid **10** are in a slow equilibrium observable on a ^{1}H NMR time scale and the methylene hydrogens of **8** are deuterated through this equilibrium. The ratio of **8** and **10** is estimated to be 9 : 1 based on the NMR signal intensities. The IR spectra, which shows a very weak absorption at 2505 cm^{-1} probably due to ν_{S-H},[8] also support the presence of the above equilibrium.

The powder of **8** melts at 92—100 °C with decomposition. It can be kept under nitrogen at room temperature at least for a month without appreciable decomposition, but is slowly oxidized in the air to give bis(3,3-dipiperidinothioacryloyl) disulfide (**11**) as the principal product (Scheme 2). More rapid oxidation takes place in solution. Thus, when the reaction of **9** and carbon disulfide was carried out in acetone and air was bubbled into the mixture, the disulfide **11** was formed in 56% yield. The disulfide **11** is also formed on attempted purification of **8** by column chromatography on basic alumina. This should be ascribed to the result of the oxidation of **8** via the dithiocarboxylic acid **10**.

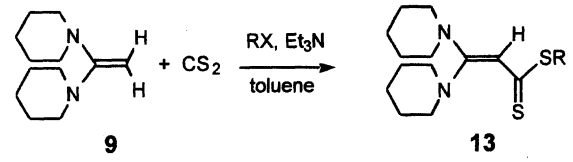
When the reaction was carried out in dichloromethane, no inner salt **8** was formed, but instead methylene bis(3,3-dipiperidinodithioacrylate) (**12**) was obtained in 43% yield along with the disulfide **11** in 5% yield. This is the result of the reaction of **8** with dichloromethane, where the latter



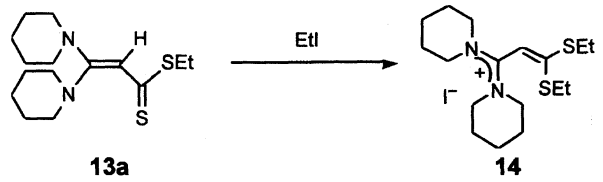
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

serves both as the solvent and the reactant (Scheme 3).

The above result implies that **8** is transformed to alkyl 3,3-dipiperidinodithioacrylates on alkylation with alkyl halides. We therefore investigated alkylation of **8** with a variety of alkyl halides. Thus, carbon disulfide (2 molar amounts) was added to a solution of **9** and triethylamine (1.5 molar amounts) in toluene. Then, ethyl bromide was added and the reaction mixture was stirred for a while. The resulting precipitate of triethylamine hydrobromide was removed by filtration and the filtrate was evaporated and the residue was purified by column chromatography to give ethyl 3,3-dipiperidinodithioacrylate (**13a**) in 74% yield. Similarly, alkylation of **8** with a variety of alkyl halides gave the corresponding alkyl dithioacrylates **13b**—**l** in moderate to excellent yields, as summarized in Table 1, (Scheme 4). This dithioester synthesis requires some comments. Among 1-haloalkanes, the most proper alkylating agents are 1-bromoalkanes (Runs 1—6). Alkylation with 1-chloroalkanes is sluggish and not practical. 1-Iodoalkanes are also not suitable reagents because they cause further alkylation of the resulting esters. Thus, the reaction of **8** with iodoethane did not give the expected ester **13a** in any amount, although triethylamine hydriodide was produced. Only the reaction carried out in the absence of triethylamine gave **13a** though in 14% yield. Similarly, the reaction with iodomethane in the absence of triethylamine gave the methyl ester **13g** in 25%

Table 1. Preparation of Alkyl 3,3-Dipiperidinodithioacrylates **13**

Run	Esters	R	X	Yield (%)
1	**13a**	Et	Br	74
2	**13b**	Pr	Br	77
3	**13c**	Bu	Br	79
4	**13d**	$CH_3(CH_2)_5$	Br	81
5	**13e**	CH_2=$CHCH_2$	Br	45
6	**13f**	$PhCH_2CH_2$	Br	80
7	**13g**	Me	I	25[a]
8	**13h**	*i*-Pr	I	37
9	**13i**	$PhCH_2$	Cl	94
10	**13j**	$PhCOCH_2$	Cl	62
11	**13k**	CH_3OCOCH_2	Cl	95
12	**13l**	$NCCH_2$	Cl	92

a) Reaction carried out in the presence of triethylamine.

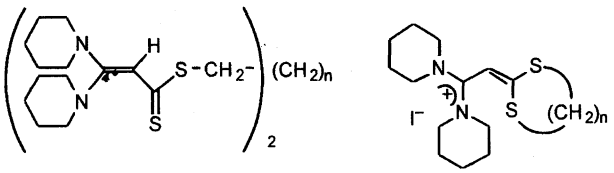


Chart 2.

yield (Run 7). A ^{1}H NMR analysis of the alkylation mixture with iodoethane in the presence of triethylamine showed the formation of the carbenium salt, 3,3-bis(ethylthio)-1,1-dipiperidino-2-propenylium iodide (**14**). A separate reaction of **13a** with iodoethane gave **14** quantitatively (Scheme 5). As to alkylation with secondary alkyl halides, 2-bromopropane is inert to **8**, while 2-iodopropane gave the isopropyl ester **13h** in 37% yield (Run 8). Cyclohexyl and *t*-butyl iodides are inert to **8** and did not give the corresponding esters even by use of excess reagents. Benzyl chloride, phenacyl chloride, methyl chloroacetate, and chloroacetonitrile, though they are alkyl halides, reacted with **8** smoothly to give the corresponding esters **13i—l** in excellent yields (Runs 9—12).

The bisester **12** was also obtained in 40% yield by carrying out the reaction in the presence of dibromomethane. On the other hand, reactions in the presence of 1,2-dibromoethane and 1,3-dibromopropane failed to give the expected **15**. This is probably because an intramolecular *S*-alkylation in the initial products, which yields **16**, is more favorable than an intermolecular alkylation. Although the formation of polar products was indicated by a tlc analysis, not much effort was exerted to isolate **16** (Chart 2).

The species that participates in the present dithioester synthesis is considered the inner salt **8**, but not the dithioacrylic acid **10**. The sulfur atom of **8** is negatively charged and therefore is much more nucleophilic than is the thiol group of the dithiocarboxylic acid **10**.

Experimental

^{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), a Brucker AC 200 (200 MHz for ^{1}H NMR and 50 MHz for ^{13}C NMR), or a Brucker AM 400 (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) spectrometer with TMS as an internal standard. Mass spectra were obtained on a Shimadzu QP-1000 spectrometer operating at 70 eV. IR spectra were obtained on a Hitachi 270-30 or 270-50 spectrophotometer and a Shimadzu FTIR-8100A spectrophotometer. Elemental analyses were performed on a Yanaco MT-3 CHN CORDER.

Reaction of 1,1-Dipiperidinoethene (9) with Carbon Disulfide in Toluene. A solution of 0.73 ml (12 mmol) of carbon disulfide in 5 ml of toluene was added dropwise to a stirred solution of 1.148 g (6 mmol) of freshly distilled **9** in 30 ml of toluene at 0 °C over a period of 0.5 h. The original colorless solution turned dark red immediately and then a dark red oil began to separate. After stirring at room temperature for 8 h, the oil solidified to give an orange solid. The solid was collected by filtration and washed with toluene and Et_2O to give 825 mg (51%) of an orange powder, mp 92—100 °C (decomp). Both ^{1}H and ^{13}C NMR spectra (see Fig. 1) revealed that the principal component of the powder is 3,3-dipiperidino-3-propylium-1-dithioate (**8**) contaminated with small amounts of unidentified products. **8**: ^{1}H NMR (270 MHz, $CDCl_3$) $\delta = 1.79$ (br. s, 12H, piperidine ring hydrogens at β- and γ-positions), 3.62 (br. s, 8H, piperidine ring hydrogens at α-positions), 4.57 (s, 2H, $S_2C\underline{CH_2}CN_2$); ^{13}C NMR (67.8 MHz, $CDCl_3$) $\delta = 23.2$ (t), 25.5 (t), 52.5 (t), 60.1 (t), 167.8 (s), 245.9 (s); ^{1}H-coupled ^{13}C NMR (67.8 MHz, $CDCl_3$, selected data) $\delta = 60.1$ (t, $^1J_{C-H} = 132$ Hz), 167.8 (br. s), 245.9 (t, $^2J_{C-H} = 6.8$ Hz); ^{1}H-selective decoupling ^{13}C NMR (67.8 MHz, $CDCl_3$, selected data) irradiated at $\delta_H = 3.62$; $\delta_C = 167.8$ (t, $^3J_{C-H} = 3.7$ Hz); irradiated at $\delta_H = 4.57$; $\delta_C = 60.1$ (s), 167.8 (t, $^2J_{C-H} = 5.8$ Hz), 245.9 (s); FT-IR (KBr) 2924, 2856, 2505 (SH), 1593, 1468, 1439, 1053, 1007 cm^{-1}.

Preparation of Bis(3,3-dipiperidinothioacryloyl Disulfide (11). A solution of 0.73 ml (12 mmol) of carbon disulfide in 5 ml of acetone was added dropwise to a stirred solution of 1.148 g (6 mmol) of freshly distilled **9** in 30 ml of acetone at 0 °C over a period of 10 min. After the mixture had been stirred at 0 °C for 0.5 h and at room temperature for 1 h, air was bubbled into the mixture, which resulted in the separation of yellow needles. After 5 h of air-bubbling, the crystals were collected by filtration to give 905 mg (56%) of analytically pure **11**: yellow needles; mp 169.5—170.0 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) $\delta = 1.66$ (br. s, 24H, piperidine ring hydrogens at β- and γ-positions), 3.39 (m, 16H, piperidine ring hydrogens at α-positions), 6.19 (s, 2H, alkenic hydrogens); ^{13}C NMR ($CDCl_3$, 67.8 MHz) $\delta = 24.1$ (t), 25.7 (t), 51.6 (t), 101.5 (d), 168.8 (s), 189.3 (s). Found: C, 57.87; H, 7.87; N, 10.26%. Calcd for $C_{26}H_{42}N_4S_4$: C, 57.95; H, 7.86; N, 10.40%.

Reaction of 1,1-Dipiperidinoethene with Carbon Disulfide in CH_2Cl_2. A solution of 8.99 g (118 mmol) of carbon disulfide in 25 ml of CH_2Cl_2 was added dropwise to a stirred solution of 5.72 g (30 mmol) of freshly distilled **9** in 100 ml of CH_2Cl_2 at 0 °C over a period of 0.5 h. After stirring at 0 °C for 0.5 h, the mixture was evaporated under reduced pressure to give an orange oil. Chromatographic separation of the oil with a column of silica gel using CH_2Cl_2–ethyl acetate (1 : 1) as the eluent gave 3.50 g (43%) of methylene bis(3,3-dipiperidinodithioacrylate) (**12**) and 387 mg (5%) of **11**. **12**: Orange granules (from acetone); mp 177.0—178.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 1.63$ (24H, t, piperidine ring hydrogens at β- and γ-positions), 3.36 (16H, s, piperidine ring hydrogens at α-positions), 5.04 (2H, s, CH_2), 5.66 (2H, s, alkenic hydrogens); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 24.12$ (t), 25.50 (t), 39.64 (t), 51.14 (t), 102.21 (d), 167.15 (s), 196.54 (s); IR (KBr) 2920, 2836, 1478, 1357, 1246, 1074 cm^{-1}; UV (CH_2Cl_2, λ_{max}/nm (ε) 398 (49400), 315 (17400), 233 (18800); MS (EI, 70 eV) *m/z* 268 (M^+). Found: C, 58.99; H, 8.13; N, 10.10%. Calcd for $C_{27}H_{44}N_4S_4$: C, 58.65; H, 8.02; N, 10.13%

A Typical Procedure for the Preparation of Esters 13. Preparation of Ethyl 3,3-Dipiperidinoacrylate (13a): A solution of 0.73 ml (12 mmol) of carbon disulfide in 5 ml of toluene was added dropwise to a solution of 1.148 g (6 mmol) of freshly distilled **9** and 1.05 ml (7.5 mmol) of triethylamine in 30 ml of toluene at 0 °C over a period of 5 min. After stirring for 5 min, 687 mg (6.3 mmol) of bromoethane in 5 ml of toluene was added dropwise at 0 °C over a period of 15 min. The mixture was stirred at 0 °C for 0.5 h and then at room temperature for 8 h. The precipitation of triethylamine hydrobromide was removed by filtration and the filtrate was evaporated under reduced pressure. Chromatographic purification of the residue with a column of silica gel using CH_2Cl_2–ethyl acetate (1 : 1) as the eluent gave 1.33 g (74%) of **13a**: yellow plates (from hexane); mp 90.5—91.0 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) $\delta = 1.30$ (3H, t, $J = 7.4$ Hz, $CH_2\underline{CH_3}$), 1.67 (12H, m, piperidine ring

hydrogens at β- and γ-positions), 3.17 (2H, t, J=7.4 Hz, $\underline{CH_2}CH_3$), 3.36 (8H, m, piperidine ring hydrogens at α-positions), 5.61 (1H, s, alkenic hydrogen); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 14.0 (q), 24.0 (t), 25.4 (t), 28.3 (t), 51.0 (t), 102.0 (d), 167.0 (s), 196.8 (s); IR (KBr) 2934, 2854, 1514, 1462, 1446, 1247 cm^{-1}. Found: C, 60.47; H, 8.80; N, 9.34%. Calcd for $C_{15}H_{26}N_2S_2$: C, 60.36; H, 8.78; N, 9.38%.

Propyl 3,3-Dipiperidinodithioacrylate (13b): Yellow plates (from hexane); mp 72.6—73.0 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.01 (3H, t, J=7.5 Hz, $CH_2CH_2\underline{CH_3}$), 1.65 (14H, m, piperidine ring hydrogens at β- and γ-positions + $CH_2\underline{CH_2}CH_3$), 3.17 (2H, t, J=7.5 Hz, $\underline{CH_2}CH_2CH_3$), 3.36 (8H, m, piperidine ring hydrogens at α-positions), 5.62 (1H, s, alkenic hydrogen); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 13.7 (q), 22.8 (t), 24.3 (t), 25.7 (t), 36.4 (t), 51.3 (t), 102.3 (d), 167.3 (s), 197.7 (s); IR (KBr) 2936, 2856, 1514, 1482, 1444, 1258 cm^{-1}. Found: C, 61.32; H, 8.90; N, 8.87%. Calcd for $C_{16}H_{28}N_2S_2$: C, 61.49; H, 9.03; N, 8.96%.

Butyl 3,3-Dipiperidinodithioacrylate (13c): Yellow plates (from hexane); mp 79.8—80.6 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 0.93 (3H, t, J = 7.3 Hz, $CH_2CH_2CH_2\underline{CH_3}$), 1.44 (4H, m, $CH_2\underline{CH_2}\underline{CH_2}CH_3$), 1.64 (12H, m, piperidine ring hydrogens at β- and γ-positions), 3.19 (2H, t, J = 7.5 Hz, $\underline{CH_2}CH_2CH_2CH_3$), 3.36 (8H, t, piperidine ring hydrogens at α-positions), 5.62 (1H, s, alkenic hydrogen); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 13.8 (q), 22.7 (t), 24.3 (t), 25.7 (t), 31.5 (t), 34.2 (t), 51.3 (t), 102.3 (d), 167.3 (s), 197.9 (s); IR (KBr) 2932, 2856, 1516, 1480, 1448, 1254 cm^{-1}. Found: C, 62.30; H, 9.07; N, 8.34%. Calcd for $C_{17}H_{30}N_2S_2$: C, 62.53; H, 9.26; N, 8.58%.

Hexyl 3,3-Dipiperidinodithioacrylate (13d): Orange oil; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 0.88 (3H, t, J = 6.8 Hz, CH_2CH_2-$CH_2CH_2CH_2\underline{CH_3}$), 1.30 (4H, m, $CH_2CH_2CH_2\underline{CH_2}\underline{CH_2}CH_3$), 1.43 (2H, m, $CH_2CH_2\underline{CH_2}CH_2CH_2CH_3$), 1.66 (14H, m, piperidine ring hydrogens at β- and γ-positions + $CH_2\underline{CH_2}CH_2CH_2CH_2CH_3$), 3.17 (2H, t, J = 7.0 Hz, $\underline{CH_2}CH_2CH_2CH_2CH_2CH_3$), 3.36 (8H, br. s, piperidine ring hydrogens at α-positions), 5.61 (1H, s, alkenic hydrogen); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 14.0 (q), 22.5 (t), 24.3 (t), 25.6 (t), 28.8 (t), 29.2 (t), 31.4 (t), 34.5 (t), 51.3 (t), 102.2 (d), 167.2 (s), 196.6 (s). Found: m/z 354.2148 (M^+). Calcd for $C_{19}H_{34}N_2S_2$: M, 354.2164.

Allyl 3,3-Dipiperidinodithioacrylate (13e): Yellow plates (from hexane); mp 111.0—112.0 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.66 (12H, br. s, piperidine ring hydrogens at β- and γ-positions), 3.36 (8H, br. s, piperidine ring hydrogens at α-positions), 3.88 (2H, d, J = 6.5 Hz, $\underline{CH_2}$–CH=CH_2), 5.06 (1H, d, J = 9.7 Hz, CH_2–CH=$\underline{CH_2}$), 5.23 (1H, d, J = 9.2 Hz, CH_2–CH=$\underline{CH_2}$), 5.62 (1H, s, alkenic hydrogen), 5.90 (1H, m, CH_2–$\underline{CH}$=CH_2); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 24.2 (t), 25.6 (t), 37.6 (t), 51.3 (t), 102.2 (d), 116.6 (t), 134.4 (d), 167.4 (s), 195.5 (s); IR (KBr) 2944, 2852, 1802, 1532, 1524, 1480, 1462, 1446, 1254 cm^{-1}. Found: C, 61.79; H, 8.43; N, 8.97%. Calcd for $C_{16}H_{26}N_2S_2$: C, 61.89; H, 8.44; N, 9.02%.

Phenethyl 3,3-Dipiperidinodithioacrylate (13f): Yellow plates (from hexane); mp 96.5—97.6 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.63 (12H, m, piperidine ring hydrogens at β- and γ-positions), 2.96 (2H, t, J=7.6 Hz, Ph$\underline{CH_2}CH_2$), 3.35 (8H, m, piperidine ring hydrogens at α-positions), 3.44 (2H, t, J=7.6 Hz, $PhCH_2\underline{CH_2}$), 5.64 (1H, s, alkenic hydrogen), 7.0—7.3 (5H, m, phenyl hydrogens); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 24.3 (t), 25.7 (t), 35.5 (t), 36.0 (t), 51.3 (t), 102.6 (d), 126.0 (d), 128.2 (d), 128.6 (d), 141.0 (s), 167.3 (s), 196.7 (s); IR (KBr) 2928, 2852, 1602, 1516, 1478, 1466, 1446, 1252 cm^{-1}. Found: C, 67.31; H, 8.10; N, 7.37%. Calcd for $C_{21}H_{30}N_2S_2$: C, 67.33; H, 8.07; H, 7.48%.

Isopropyl 3,3-Dipiperidinodithioacrylate (13h): Yellow plates (from hexane); mp 107.5—108.2 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.36 (6H, d, J = 7.3 Hz, $CH(\underline{CH_3})_2$), 1.65 (12H, br. s, piperidine ring hydrogens at β- and γ-positions), 3.36 (8H, br. s, piperidine ring hydrogens at α-positions), 3.99 (1H, sep, J = 7.3 Hz, $\underline{CH}(CH_3)_2$), 5.59 (1H, s, alkenic hydrogen); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 23.0 (q), 24.4 (t), 25.8 (t), 38.5 (d), 51.4 (t), 102.7 (d), 167.5 (s), 197.1 (s); IR (KBr) 2936, 2856, 1484, 1446, 1256 cm^{-1}. Found: C, 61.61; H, 9.08; N, 8.92%. Calcd for $C_{16}H_{28}N_2S_2$: C, 61.49; H, 9.03; N, 8.96%.

Benzyl 3,3-Dipiperidinodithioacrylate (13i): Yellow plates (from hexane); mp 108.5—109.5 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.63 (12H, br. s, piperidine ring hydrogens at β- and γ-positions), 3.33 (8H, br. s, piperidine ring hydrogens at α-positions), 4.47 (2H, s, $\underline{CH_2}Ph$), 5.58 (1H, s, alkenic hydrogen), 7.2—7.4 (5H, m, phenyl hydrogens); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 24.1 (t), 25.5 (t), 38.9 (t), 51.1 (t), 102.1 (d), 126.3 (d), 128.0 (d), 128.7 (d), 138.6 (s), 167.2 (s), 196.7 (s); IR (KBr) 2942, 2850, 1601, 1533, 1482, 1465, 1449, 1430, 1250 cm^{-1}. Found: C, 66.77; H, 7.85; N, 7.75%. Calcd for $C_{20}H_{28}N_2S_2$: C, 66.62; H, 7.83; N, 7.77%.

Phenacyl 3,3-Dipiperidinodithioacrylate (13j): Yellow plates (from cyclohexane); mp 117.5—118.0 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.63 (12H, m, piperidine ring hydrogens at β- and γ-positions), 2.96 (2H, t, CH_2), 3.35 (8H, m, piperidine ring hydrogens at α-positions), 3.44 (2H, t, CH_2), 5.64 (1H, s, alkenic hydrogen), 7.0—7.3 (5H, m, phenyl hydrogens); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 24.3 (t), 25.7 (t), 41.8 (t), 51.4 (t), 102.5 (d), 128.2 (d), 128.9 (d), 132.8 (d), 136.4 (s), 167.8 (s), 186.0 (s), 195.4 (s); IR (KBr) 2928, 2850, 1679 (C=O), 1594, 1578, 1516, 1475, 1464, 1447, 1254 cm^{-1}. Found: C, 65.03; H, 7.33; N, 6.99%. Calcd for $C_{21}H_{28}N_2OS_2$: C, 64.91; H, 7.26; N, 7.21%.

Methoxycarbonylmethyl 3,3-Dipiperidinodithioacrylate (13k): Yellow plates (from hexane); mp 90.8—91.7 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.66 (12H, br. s, piperidine ring hydrogens at β- and γ-positions), 3.37 (8H, br. s, piperidine ring hydrogens at α-positions), 3.73 (3H, s, OCH_3), 4.18 (2H, s, CH_2), 5.70 (1H, s, alkenic hydrogen); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 24.3 (t), 25.7 (t), 36.5 (q), 51.4 (t), 52.4 (t), 102.4 (d), 167.7 (s), 170.9 (s), 192.8 (s); IR (KBr) 2944, 2856, 1738 (C=O), 1522, 1484, 1446, 1284, 1266, 1186 cm^{-1}. Found: C, 56.25; H, 7.67; N, 8.06%. Calcd for $C_{16}H_{26}N_2O_2S_2$: C, 56.11; H, 7.65; N, 8.18%.

Cyanomethyl 3,3-Dipiperidinodithioacrylate (13l): Yellow plates (from hexane–CH_2Cl_2); mp 128.5—129.8 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.69 (12H, m, piperidine ring hydrogens at β- and γ-positions), 3.39 (8H, m, piperidine ring hydrogens at α-positions), 4.21 (2H, s, CH_2CN), 5.61 (1H, s, alkenyl hydrogen); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 19.3 (t), 24.1 (t), 25.6 (t), 51.4 (t), 102.6 (d), 117.7 (s), 167.6 (s), 188.2 (s); IR (KBr) 2948, 2856, 2240 (CN), 1583, 1478, 1254 cm^{-1}. Found: C, 58.17; H, 7.50; N, 13.56%. Calcd for $C_{15}H_{23}N_3S_2$: C, 58.21; H, 7.49; N, 13.58%.

Preparation of Methyl 3,3-Dipiperidinodithioacrylate (13g). A solution of 2.47 g (32.4 mmol) of carbon disulfide in 10 ml of benzene was added dropwise to a solution of 3.13 g (16.1 mmol) of freshly distilled **9** in 50 ml of benzene at room temperature over a period of 5 min. After stirring for 5 min, 1.67 g (11.8 mmol) of iodomethane was added dropwise. The mixture was stirred at room temperature for 1 h. Chromatographic purification of the mixture with column chromatography on silica gel using CH_2Cl_2/AcOEt = 1/1 as eluent gave 0.83 g (25% yield based on iodomethane) of **13g**: yellow plates (from hexane); mp 125.5—126.0 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.67 (12H, m, piperidine ring hydrogens at β- and γ-positions), 2.55 (3H, s, SCH_3), 3.37 (8H,

m, piperidine ring hydrogens at α-positions), 5.62 (1H, s, alkenic hydrogen); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 17.9 (q), 24.2 (t), 25.6 (t), 51.2 (t), 102.0 (d), 167.1 (s), 198.5 (s). Found: C, 59.38; H, 8.55; N, 9.87%. Calcd for $C_{14}H_{24}N_2S_2$: C, 59.11; H, 8.50; N, 9.85%.

Preparation of Methylene Bis (3,3-dipiperidinodithioacrylate) (12). A solution of 0.73 ml (12 mmol) of carbon disulfide in 5 ml of toluene was added dropwise to a solution of 1.148 g (6 mmol) of freshly distilled **9** and 1.05 ml (7.5 mmol) of triethylamine in 30 ml of toluene at 0 °C over a period of 5 min. After stirring for 5 min, 548 mg (3.2 mmol) of dibromomethane in 5 ml of toluene was added dropwise at 0 °C over a period of 15 min. The mixture was stirred at 0 °C for 0.5 h and then at room temperature for 8 h. The same workup as that of **13a** gave 662 mg (40%) of **12**.

Synthesis of 3,3-Bis(ethylthio)-1,1-dipiperidino-2-propenylium Iodide (14) by Ethylation of 13a. Stirring of a mixture of 298 mg (1 mmol) of **13a** and 75μl (1.2 mmol) of iodoethane in 10 ml of toluene resulted in the separation of an oil. The oil was collected by decantation, washed with pentane, and dried to give 446 mg (99%) of **14**: light yellow oil; ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 1.35 (3H, t, J = 7.3 Hz, $CH_2\underline{CH_3}$), 1.39 (3H, t, J = 7.3 Hz, $CH_2\underline{CH_3}$), 1.75 (m, 4H, piperidine ring hydrogens at γ-positions), 1.84 (m, 8H, piperidine ring hydrogens at β-positions), 3.05 (2H, q, J = 7.3 Hz, $\underline{CH_2}CH_3$), 3.14 (2H, q, J = 7.3 Hz, $\underline{CH_2}CH_3$), 3.59 (br, s, 8H, piperidine ring hydrogens at α-positions), 6.45 (s, 1H, alkenyl hydrogens); ^{13}C NMR ($CDCl_3$, 67.8 MHz) δ = 12.6 (q), 14.8 (q), 22.7 (t), 24.8 (t), 26.9 (t), 28.1 (t), 52.0 (t), 110.4 (d), 155.7 (s), 163.7 (s). Found: C, 44.89; H, 6.74; N, 5.90%. Calcd for $C_{17}H_{31}IN_2S_2$: C, 44.93; H, 6.88; N, 6.16%.

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