Reaction of Methyl Dithiocarbamates with Amines and Hydrazine. Macrocyclization via Dimethyl 2-Oxo-1,3-imidazolidinebis(carbodithioate)

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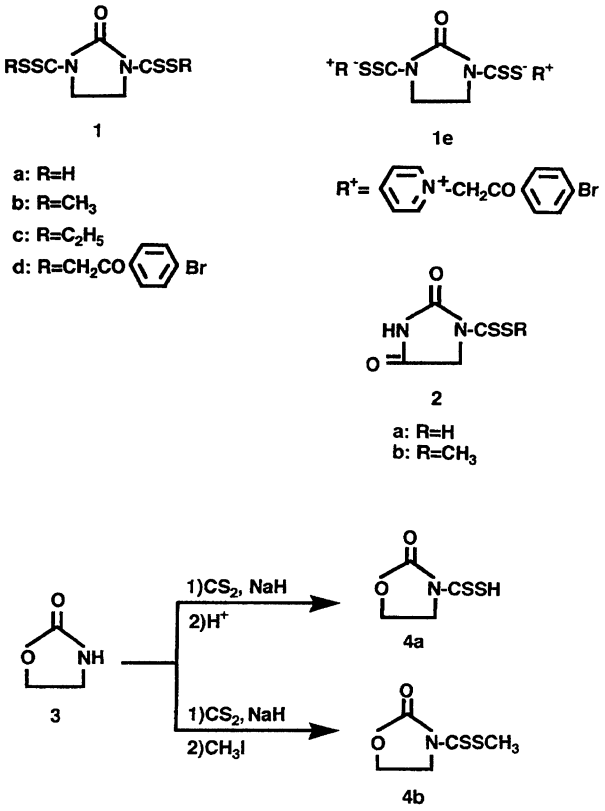
2-Oxo-1,3-imidazolidinebis(carbothioamide)s and 2,4-dioxo-1-imidazolidinecarbothioamides were prepared by the reaction of dimethyl 2-oxo-1,3-imidazolidinebis(carbodithioate) (**1b**) and methyl 2,4-dioxo-1-imidazolidinecarbodithioate (**2b**) with amines, respectively. The reaction of 2-oxazolidone with carbon disulfide gave 2-oxo-3-oxazolidinecarbodithioic acid, the methyl ester of which (**4b**) led to 2-oxo-3-oxazolidinecarbothioamides. Esters **1b**, **2b**, and **4b** reacted with hydrazine hydrate to give the corresponding thiohydrazides, from which thiosemicarbazone derivatives were obtained. Macrocyclic thioureas were synthesized by the reaction of **1b** with aliphatic diamines, polyether-containing diamines, and polyamines.

Many displacement reactions of ketene dithioacetals with nucleophiles to give various heterocyclic compounds and intermediates in organic synthesis have been reported.[1,2] The corresponding aza-analog dialkyl *N*-acylcarbonimidodithioates which were obtained from amides also react with amines to give isothiourea or guanidine derivatives.[3—9] We recently synthesized macrocyclic compounds, 9-phenylsulfonylimino-1,4-dioxa-8,10-diazacyclotridecanes, by the reaction of dimethyl *N*-phenylsulfonylcarbonimidodithioates with 1,10-diamino-4,7-dioxadecane.[10] In our continuing study of the reactions of amides with carbon disulfide, we have previously reported the synthesis of free *N*-acyl- and *N*-carbamoyldithiocarbamic acids and their esters from cyclic amides and related compounds; 2-oxo-1,3-imidazolidinebis(carbodithioic acid) (**1a**) and 2,4-dioxo-1-imidazolidinecarbodithioic acid (**2a**), and the corresponding methyl esters, dimethyl 2-oxo-1,3-imidazolidinebis(carbodithioate) (**1b**) and methyl 2,4-dioxo-1-imidazolidinecarbodithioate (**2b**) were prepared from 2-imidazolidone and hydantoin, respectively.[11]

In this paper, we wish to report the reaction of dithioate **1b** and the analogous esters with amines and hydrazine hydrate. Here, in addition to **1b** and **2b**, a new free dithiocarbamic acid, 2-oxo-3-oxazolidinecarbodithioic acid (**4a**), and its methyl ester, methyl 2-oxo-3-oxazolidinecarbodithioate (**4b**), were prepared in good yields by the reaction of 2-oxazolidone (**3**) with carbon disulfide in the presence of sodium hydride in tetrahydrofuran–dimethyl sulfoxide with cooling (Scheme 1). Acid **4a** (orange-yellow color in the crystalline state), as well as **1a** and **2a**, was exceedingly sensitive towards heavy metal ions, forming colored complexes; the characteristic reaction with nickel(II) ion produced purple-red precipitates.[11,12]

Reactions of dithioate **1b** with aliphatic primary amines (methylamine, ethylamine, isopropylamine, cyclohexylamine, benzylamine, 2-methoxyethylamine, 3-methoxypropylamine, and glycine ethyl ester) afforded dithiocarbamic acid amides, 2-oxo-1,3-imidazolidinebis(carbothioamide)s (**5a**—**h**), in moderate to good yields. Dithioates **2b** and **4b** also reacted with amines to give



Scheme 1.

thioamides, i.e., thiourea derivatives, 2,4-dioxo-1-imidazolidinecarbothioamides (**6a**—**c**), and 2-oxo-3-oxazolidinecarbothioamides (**7a**—**c**), respectively (Table 1) (Scheme 2). These reactions were almost all conducted in ethanol under reflux for 4—8 h with evolution of methanethiol. However, these three dithioates were unreactive to secondary or aromatic amines, and in most cases the starting materials were recovered.

Reactions of **1b**, **2b**, and **4b** with hydrazine hydrate led to *N*-carbothiohydrazides, i.e., thiosemicarbazide derivatives, 2-oxo-1,3-imidazolidinebis(carbothiohydrazide) (**8**), 2,4-dioxo-1-imidazolidinecarbothiohydrazide (**10**), and 2-oxo-3-oxazolidinecarbothiohydrazide (**11**), in good yields, respectively. In ad-

Table 1. Yields and Melting Points of Compounds **5**—**7**

Compd	R	Yield %	Mp θ_m/°C(Solvent)
5a	CH_3	62	236—237 (EtOH)
5b	C_2H_5	61	202 (EtOH)
5c	$CH(CH_3)_2$	73	197—199 (EtOH)
5d	Cyclohexyl	66	205—206 (EtOH)
5e	$CH_2C_6H_5$	95	174—175 (Me_2CO)
5f	$(CH_2)_2OCH_3$	57	160—161 (EtOH)
5g	$(CH_2)_3OCH_3$	85	98 (EtOH)
5h	$CH_2COOC_2H_5$	35	145—147 (EtOH)
6a	CH_3	92	262—264[a] (EtOH)
6b	$CH_2C_6H_5$	85	186[a] (EtOH)
6c	$CH_2COOC_2H_5$	41	171—172 (EtOH)
7a	CH_3	61	141—143 (EtOH)
7b	$CH_2C_6H_5$	71	132—135 (EtOH)
7c	$CH_2COOC_2H_5$	65	106[a] (EtOH)

a) Decomposition.

Table 2. Yields and Melting Points of Compounds **8**—**12**

Compd	R^1	R^2	Yield %	Mp θ_m/°C(Solvent)
8			91	225 (DMSO)
9a	CH_3	CH_3	73	178—180 (DMSO)
9b	CH_3	C_2H_5	60	154—156 (Me_2CO)
9c	H	C_6H_5	74	175—177 (THF)
9d	$-(CH_2)_5-$		81	203—204 (Py)
10			93	202[a] (EtOH–DMSO)
11			64	145—146 (EtOH–DMSO)
12a	CH_3	CH_3	76	111 (EtOH)
12b	H	C_6H_5	74	184 (EtOH)

a) Decomposition.

Table 3. Yields and Melting Points of Compounds **13**—**17**

Compd	n	Yield %	Mp θ_m/°C(Solvent)
13a	4	66	ca.188[a] (Py–EtOH)
13b	6	65	193—195[a] (Py–EtOH)
14a	2	77	229—231[a] (EtOH)
14b	4	61	190—193 (EtOH)
15		89	182—183 (EtOH)
16		56	231[a] (DMSO)
17		59	230[a] (EtOH)

a) Decomposition.

dition, thiosemicarbazone derivatives **9a**—**d** and **12a**, **b** were obtained in ca. 70% yields by the reaction of **8** or **11** with ketones (acetone, ethyl methyl ketone, and cyclohexanone) or benzaldehyde (Table 2) (Scheme 3).

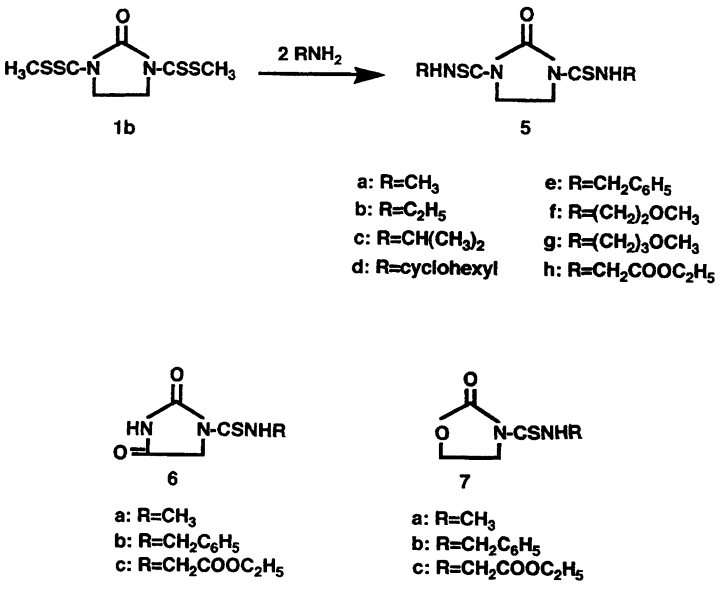
From bifunctional ester **1b** and aliphatic diamines, 11- and 13-membered macrocyclic thioureas could be synthesized; 13-oxo-2,9-dithioxo-1,3,8,10-tetraazabicyclo[8.2.1]tridecane (**13a**) and 15-oxo-2,11-dithioxo-1, 3, 10, 12- tetraazabicyclo[10.2.1]pentadecane (**13b**) were obtained using 1,4-diaminobutane and 1,6-diaminohexane in 65% yields, respectively. The reaction in ethanol under high-dilution conditions required 72 h under reflux. However, attempts to prepare a 10-membered ring compound using 1,3-diaminopropane were unsuccessful (Table 3) (Scheme 4). Also, aza-crown ethers and macrocyclic polyamines **14**—**17** were obtained by the reaction of dithioate **1b** with the corresponding polyether-containing diamines (1,10-diamino-4,7-dioxadecane, 1,12-diamino-4,9-dioxadodecane, and 1,13-diamino-4,7,10-trioxatridecane) and polyamines [*N*,*N*-bis(3-aminopropyl)methylamine and 1,4-bis(3-aminopropyl)piperazine] (Chart 1). The yields of these 14—20-membered ring compounds were similar to those of **13**. The purification of all the macrocycles, especially macrocyclic polyamines **16** and **17**, required repeated recrystallizations.

The progress and the termination of every reaction of methyl dithioate with amine could be judged by detecting the odor of methanethiol. All of the new compounds were characterized by microanalyses as well as spectral data. All mass spectra of macrocyclic compounds **13**—**17** showed molecular-ion peaks for the 1 : 1 reaction product with no further peaks above them.

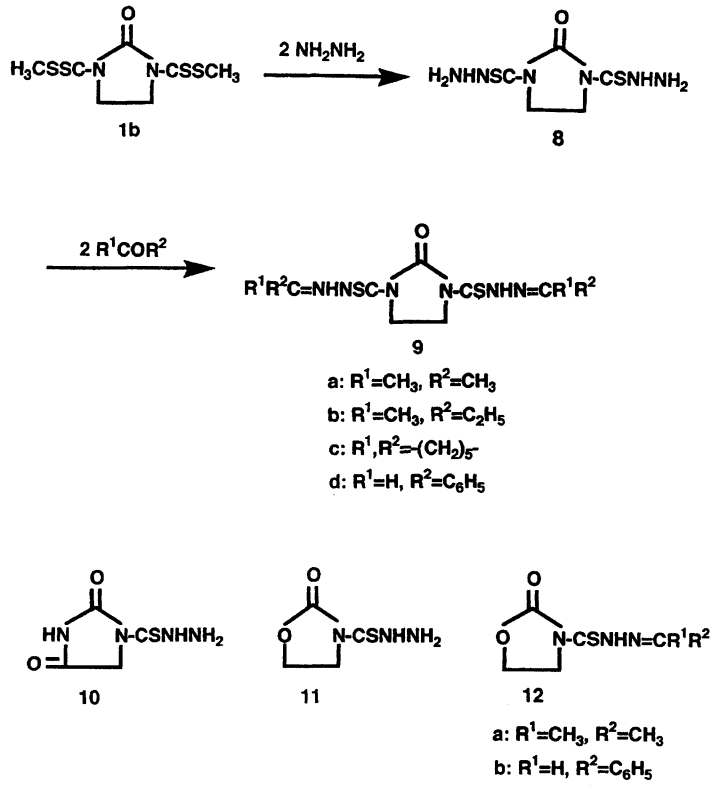
Experimental

Dimethyl 2-Oxo-1,3-imidazolidinebis(carbodithioate) (1b) was prepared by a method similar to that previously described.[11] In addition, two esters and a salt of acid **1a** were prepared.

Diethyl 2-Oxo-1,3-imidazolidinebis(carbodithio-



Scheme 2.

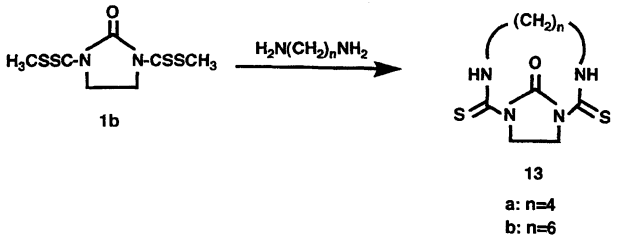


Scheme 3.

ate) (1c) was obtained from 2-imidazolidone (1 g, 0.012 mol), sodium hydride (1 g: 60% dispersion in oil; 0.025 mol), carbon disulfide (3 g, 0.039 mol), ethyl iodide (5 g, 0.032 mol), and tetrahydrofuran (20 ml) with cooling in ice: Yield 2.3 g (67%); mp 190—191 °C (EtOH); IR (KBr) 1735 cm^{-1}; UV (EtOH) λ_{max} 299 nm ($\log\varepsilon$ 3.80). Found: C, 36.86; H, 4.98; N, 9.65%. Calcd for $C_9H_{14}N_2OS_4$: 36.71; H, 4.79; N, 9.51%.

Bis(*p*-bromophenacyl) 2-Oxo-imidazolidinebis-(carbodithioate) (1d) was obtained from acid **1a** (0.6 g, 0.0025 mol),[11] 28% aqueous ammonia (9 ml), *p*-bromophenacyl bromide (1.5 g, 0.0054 mol), and ethanol (13 ml) at 70 °C: Yield 0.33 g (21%); mp 253—255 °C (DMF–Py–$CHCl_3$); IR (KBr) 1700 and 1620 cm^{-1}; UV (Dioxane) λ_{max} 249 ($\log\varepsilon$ 4.52), 258 (4.57), and 304 nm (4.77). Found: C, 39.88; H, 2.55; N, 4.43%. Calcd for $C_{21}H_{16}N_2O_3S_4Br_2$: C, 39.77; H, 2.54; N, 4.34%.

Bis[1-(*p*-bromophenacyl)pyridinium] 2-Oxo-1,3-imidazolidinebis(carbodithioate) (1e). To a solution of acid **1a** (0.2 g, 0.00084 mol) and sodium hydroxide

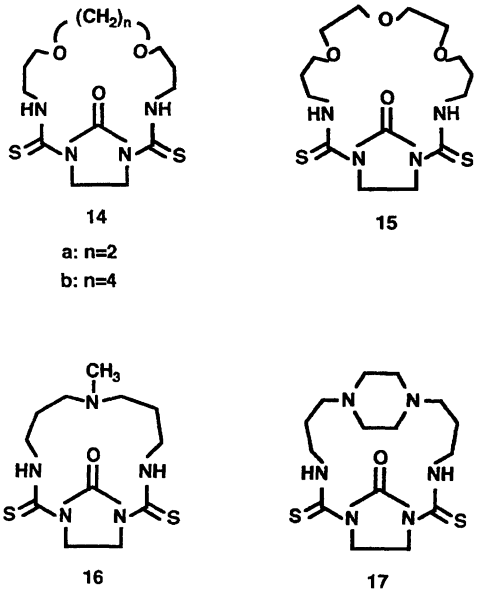


1b

13

a: n=4
b: n=6

Scheme 4.



14

a: n=2
b: n=4

15

16

17

Chart 1.

(0.08 g, 0.002 mol) in water (6 ml) was added aqueous 1-(*p*-bromophenacyl)pyridinium bromide [from *p*-bromophenacyl bromide (0.5 g, 0.0018 mol) and pyridine (2.5 ml) in water (0.5 ml)]. The mixture was stirred at room temperature for 1 h. The solid which precipitated was collected and recrystallized from pyridine–water: Yield 0.4 g (60%); mp 127—129 °C; IR (KBr) 1685 and 1620 cm^{-1}; UV (EtOH) λ_{max} 250 ($\log\varepsilon$ 4.57), 256 (4.52), and 425 nm (3.68). Found: C, 47.09; H, 3.31; N, 7.09%. Calcd for $C_{31}H_{26}N_4O_3S_4Br_2$: C, 47.31; H, 3.31; N, 7.14%.

Methyl 2,4-Dioxo-1-imidazolidinecarbodithioate (2b) was prepared by the method previously described.[11]

2-Oxo-3-oxazolidinecarbodithioic Acid (4a). A solution of 2-oxazolidone (1 g, 0.011 mol) in dimethyl sulfoxide (10 ml) and tetrahydrofuran (5 ml) was added dropwise over a period of 10 min to a mixture of sodium hydride (0.6 g: 60% dispersion in oil; 0.015 mol) and tetrahydrofuran (5 ml) with stirring at 4 °C in an ice-bath. To the white mixture was added dropwise over 10 min a solution of carbon disulfide (2 g, 0.026 mol) in tetrahydrofuran (5 ml), keeping the temperature below 6 °C. The mixture gradually changed from yellow to red, and was stirred for an additional 20 min. To decompose the excess sodium hydride, a mixture of tetrahydrofuran (7 ml) and water (5 ml), and then water (10 ml) were added dropwise to the reaction mixture at 4 °C. The whole mixture was then washed with benzene. The aqueous portion was neutralized or slightly acidified with diluted hydrochloric acid with cooling, and kept for 20 min. The yellow precipitate was collected, washed with water and then a small amount of methanol, dried, and recrystallized from acetone: Yield 1.28 g (71%); mp 116—117 °C (decomp); IR (KBr) 2490 and 1758 cm^{-1}; UV (EtOH) λ_{max} 227sh ($\log\varepsilon$ 3.61), 261 (4.11), 299sh (3.46), and 334 nm (4.03); MS *m/z* 163 (M^+). Found: C, 29.62; H, 2.91; N, 8.71%. Calcd for $C_4H_5NO_2S_2$: C, 29.44; H, 3.09; N, 8.58%.

Methyl 2-Oxo-3-oxazolidinecarbodithioate (4b). To the aqueous layer from the work-up of the reaction mixture described for **4a** was added a solution of methyl iodide (2.5 g, 0.018 mol) in methanol (5 ml). The mixture was stirred for 2 h with cooling in ice. The yellow solid which precipitated was collected, washed with water and then methanol, dried, and recrystallized from methanol: Yield 1.4 g (72%); mp 171—172 °C; IR (KBr) 1758 cm^{-1}; UV (EtOH) λ_{max} 259 ($\log\varepsilon$ 4.25) and 296 nm (4.08); MS *m/z* 177 (M^+). Found: C, 33.96; H, 3.95; N, 7.79%. Calcd for $C_5H_7NO_2S_2$: C, 33.88; H, 3.98; N, 7.90%.

2-Oxo-1,3-imidazolidinebis(carbothioamide)s (5). General Procedure. A mixture of dithioate **1b** (0.8 g, 0.003 mol), amine (0.006 mol), and ethanol (40 ml) was refluxed using a cotton wool-topped reflux condenser under a fume hood until the odor of methanethiol could no longer be detected (4—8 h). In the case of methylamine and ethylamine, 40 and 70% aqueous solutions (0.47 g, 0.006 mol, and 0.39 g, 0.006 mol) were used as amines, respectively. Glycine ethyl ester hydrochloride (0.84 g, 0.006 mol) was used as an amine together with triethylamine (0.61 g, 0.006 mol). The reaction with isopropylamine required 8 h reflux in butanol (40 ml). The solid which precipitated was collected and recrystallized.

2- Oxo- 1, 3- imidazolidinebis(*N*- methylcarbothioamide) (5a): IR (KBr) 3280 and 1700 cm^{-1}; UV (EtOH) λ_{max} 204 ($\log\varepsilon$ 3.84) and 265 nm (4.32); MS *m/z* 232 (M^+). Found: C, 36.16; H, 5.09; N, 23.83%. Calcd for $C_7H_{12}N_4OS_2$: C, 36.19; H, 5.21; N, 24.12%.

2- Oxo- 1,3- imidazolidinebis(*N*- ethylcarbothioamide) (5b): IR (KBr) 3270 and 1690 cm^{-1}; UV (EtOH) λ_{max} 204 ($\log\varepsilon$ 3.94) and 268 nm (4.46); MS *m/z* 260 (M^+). Found: C, 41.52; H, 6.19; N, 21.52%. Calcd for $C_9H_{16}N_4OS_2$: C, 41.37; H, 6.03; N, 21.19%.

2-Oxo-1,3-imidazolidinebis(*N*-isopropylcarbothioamide) (5c): IR (KBr) 3250 and 1685 cm^{-1}; MS *m/z* 288 (M^+). Found: C, 45.61; H, 6.93; N, 19.45%. Calcd for $C_{11}H_{20}N_4OS_2$: C, 45.81; H, 6.99; N, 19.42%.

2-Oxo-1,3-imidazolidinebis(*N*-cyclohexylcarbothioamide) (5d): IR (KBr) 3250 and 1682 cm^{-1}; UV (EtOH) λ_{max} 205 ($\log\varepsilon$ 3.96) and 266 nm (4.49); MS *m/z* 368 (M^+). Found: C, 55.55; H, 7.92; N, 15.46%. Calcd for $C_{17}H_{28}N_4OS_2$: C, 55.40; H, 7.66; N, 15.20%.

2- Oxo- 1,3- imidazolidinebis(*N*- benzylcarbothioamide) (5e): IR (KBr) 3275 and 1700 cm^{-1}; MS *m/z* 384 (M^+). Found: C, 59.20; H, 5.24; N, 14.50%. Calcd for $C_{19}H_{20}N_4OS_2$: C, 59.35; H, 5.24; N, 14.57%.

2- Oxo- 1, 3- imidazolidinebis[*N*- (2- methoxyethyl)carbothioamide] (5f): IR (KBr) 3250 and 1700 cm^{-1}; MS *m/z* 320 (M^+). Found: C, 40.98; H, 6.21; N, 17.63%. Calcd for $C_{11}H_{20}N_4O_3S_2$: C, 41.23; H, 6.29; N, 17.49%.

2-Oxo-1,3-imidazolidinebis[*N*-(3-methoxypropyl)carbothioamide] (5g): IR (KBr) 3270 and 1710 cm^{-1}; UV (EtOH) λ_{max} 267 nm ($\log\varepsilon$ 4.60); MS *m/z* 348 (M^+). Found: C, 44.82; H, 6.91; N, 15.99%. Calcd for

$C_{13}H_{24}N_4O_3S_2$: C, 44.81; H, 6.94; N, 16.08%.

2- Oxo- 1, 3- imidazolidinebis[*N*- (ethoxycarbonylmethyl)carbothioamide] (5h): IR (KBr) 3245, 3200, 1735, and 1707 cm^{-1}; MS *m/z* 376 (M^+). Found: C, 41.48; H, 5.40; N, 14.67%. Calcd for $C_{13}H_{20}N_4O_5S_2$: C, 41.48; H, 5.36; N, 14.88%.

2,4-Dioxo-1-imidazolidinecarbothioamides (6) and 2-Oxo-3-oxazolidinecarbothioamides (7) were prepared from dithioates **2b** and **4b** respectively using each equimolecular amine by a method similar to that described for the preparation of **5**. Compounds **7a** and **7b** were formed by stirring reaction mixtures for 24 h at room temperature.

2,4- Dioxo- 1- imidazolidine(*N*- methylcarbothioamide) (6a): IR (KBr) 3230, 1785, 1763, and 1685 cm^{-1}; MS *m/z* 173 (M^+). Found: C, 34.54; H, 4.06; N, 24.07%. Calcd for $C_5H_7N_3O_2S$: C, 34.67; H, 4.07; N, 24.26%.

2,4- Dioxo- 1- imidazolidine(*N*- benzylcarbothioamide) (6b): IR (KBr) 3200, 1775, 1760, 1730, and 1700 cm^{-1}; MS *m/z* 249 (M^+). Found: C, 52.88; H, 4.45; N, 16.61%. Calcd for $C_{11}H_{11}N_3O_2S$: C, 53.00; H, 4.45; N, 16.86%.

2,4- Dioxo- 1- imidazolidine[*N*- (ethoxycarbonylmethyl)carbothioamide] (6c): IR (KBr) 3250, 1710, and 1690 cm^{-1}; MS *m/z* 245 (M^+). Found: C, 39.05; H, 4.48; N, 17.07%. Calcd for $C_8H_{11}N_3O_4S$: C, 39.18; H, 4.52; N, 17.13%.

2- Oxo- 3- oxazolidine(*N*- methylcarbothioamide) (7a): IR (KBr) 3275 and 1730 cm^{-1}; MS *m/z* 160 (M^+). Found: C, 37.29; H, 4.92; N, 17.15%. Calcd for $C_5H_8N_2O_2S$: C, 37.49; H, 5.03; N, 17.49%.

2- Oxo- 3- oxazolidine(*N*- benzylcarbothioamide) (7b): IR (KBr) 3230 and 1730 cm^{-1}; MS *m/z* 236 (M^+). Found: C, 55.60; H, 5.10; N, 11.70%. Calcd for $C_{11}H_{12}N_2O_2S$: C, 55.91; H, 5.12; N, 11.86%.

2- Oxo- 3- oxazolidine[*N*- (ethoxycarbonylmethyl)carbothioamide] (7c): IR (KBr) 3165 and 1740 cm^{-1}; MS *m/z* 232 (M^+). Found: C, 41.31; H, 5.29; N, 11.94%. Calcd for $C_8H_{12}N_2O_4S$: C, 41.37; H, 5.21; N, 12.06%.

2- Oxo- 1, 3- imidazolidinebis(carbothiohydrazide) (8). To a suspension of **1b** (1.2 g, 0.0045 mol) in ethanol (40 ml) was added 90% hydrazine hydrate (0.6 g, 0.011 mol), and the mixture was refluxed for 3 h. The solid which precipitated was collected and recrystallized: IR (KBr) 3320, 3275, and 1700 cm^{-1}; MS *m/z* 234 (M^+). Found: C, 25.91; H, 4.30; N, 35.60%. Calcd for $C_5H_{10}N_6OS_2$: C, 25.63; H, 4.30; N, 35.87%.

2,4-Dioxo-1-imidazolidinecarbothiohydrazide (10) was prepared from a mixture of **2b** (0.48 g, 0.0025 mol), 90% hydrazine hydrate (0.15 g, 0.0027 mol), and ethanol (20 ml) which was stirred for 2 h at room temperature: IR (KBr) 3290, 3255, 3150, 1660, and 1645 cm^{-1}; MS *m/z* 174 (M^+). Found: C, 27.63; H, 3.50; N, 31.85%. Calcd for $C_4H_6N_4O_2S$: C, 27.58; H, 3.47; N, 32.17%.

2-Oxo-3-oxazolidinecarbothiohydrazide (11) was prepared by the method described for **10**: IR (KBr) 3300, 3255, 3210, 3120, and 1735 cm^{-1}; MS *m/z* 161 (M^+). Found: C, 29.79; H, 4.38; N, 26.07%. Calcd for $C_4H_7N_3O_2S$: C, 29.81; H, 4.38; N, 26.07%.

1,3-Bis(3-isopropylidenethiocarbazoyl)-2-imidazolidone (9a). A mixture of **8** (0.3 g, 0.0013 mol), acetone (0.5 g, 0.0086 mol), ethanol (40 ml), and several drops of acetic acid was refluxed for 2 h. The solid was collected, washed with ethanol, and recrystallized: IR (KBr) 3220, 3160, and 1685 cm^{-1}; UV (EtOH) λ_{max} 276 nm ($\log\varepsilon$ 3.95). Found: C, 41.90; H, 5.79; N, 26.67%. Calcd for $C_{11}H_{18}N_6OS_2$: C, 42.02; H, 5.77; N, 26.73%.

1, 3- Bis(3- *s*- butylidenethiocarbazoyl)- 2- imidazolidone (9b) was prepared from a mixture of **8** (0.5 g, 0.0021 mol) and ethyl methyl ketone (30 ml) which was refluxed for 4 h: IR (KBr) 3200, 3160, and 1680 cm^{-1}; UV (EtOH) λ_{max} 227 ($\log\varepsilon$ 5.00) and 280 nm (5.05); MS *m/z* 342 (M^+). Found: C, 45.45, H, 6.58; N, 24.46%. Calcd for $C_{13}H_{22}N_6OS_2$: C, 45.59; H, 6.47; N, 24.54%.

1, 3- Bis(3- cyclohexylidenethiocarbazoyl)- 2- imidazolidone (9c) was prepared by the method described for **9b**: IR (KBr) 3200, 3150, and 1690 cm^{-1}; UV (EtOH) λ_{max} 258sh ($\log\varepsilon$ 4.19) and 285 nm (4.29); MS *m/z* 394 (M^+). Found: C, 52.01; H, 6.81; N, 21.03%. Calcd for $C_{17}H_{26}N_6OS_2$: 51.75; H, 6.64; N, 21.30%.

1, 3- Bis(3- benzylidenethiocarbazoyl)- 2- imidazolidone (9d) was prepared by the method described for **9a**: IR (KBr) 3220, 3140, and 1690 cm^{-1}; UV (EtOH) λ_{max} 299 ($\log\varepsilon$ 4.36) and 335 nm (4.25); MS *m/z* 410 (M^+). Found: C, 55.33; H, 4.32; N, 20.67%. Calcd for $C_{19}H_{18}N_6OS_2$: C, 55.59; H, 4.42; N, 20.47%.

3- (3- Isopropylidenethiocarbazoyl)- 2- oxazolidone (12a) was prepared by the method described for **9b**: IR (KBr) 3440 and 1735 cm^{-1}; MS *m/z* 201 (M^+). Found: C, 41.66; H, 5.50; N, 20.86%. Calcd for $C_7H_{11}N_3O_2S$: C, 41.78; H, 5.51; N, 20.88%.

3- (3- Benzylidenethiocarbazoyl)- 2- oxazolidone (12b) was prepared from a mixture of **11** (0.32 g, 0.002 mol), ethanol (20 ml), and benzaldehyde (0.21 g, 0.002 mol) which was stirred for 4 h at room temperature: IR (KBr) 3150 and 1735 cm^{-1}; MS *m/z* 249 (M^+). Found: C, 53.20, H, 4.49; N, 16.67%. Calcd for $C_{11}H_{11}N_3O_2S$: C, 53.00; H, 4.45; N, 16.86%.

Macrocyclic Compounds 13—17. General Procedure. To a refluxing suspension of **1b** (0.67 g, 0.0025 mol) in ethanol (40 ml) in a 200-ml three-necked flask with a cotton wool-topped reflux condenser under a fume hood was added dropwise over 6 h a solution of diamine (0.0025 mol) in ethanol (40 ml). The reaction mixture was refluxed until the methanethiol odor could no longer be detected (1—3 d) and then transferred to a refrigerator. The solid which precipitated was collected and recrystallized.

13- Oxo- 2, 9- dithioxo- 1, 3, 8, 10- tetraazabicyclo-[8.2.1]tridecane (13a): IR (KBr) 3270 and 1680 cm^{-1}; MS *m/z* 258 (M^+). Found: C, 41.77; H, 5.64; N, 21.54%. Calcd for $C_9H_{14}N_4OS_2$: C, 41.84; H, 5.46; N, 21.69%.

15- Oxo- 2, 11- dithioxo- 1, 3, 10, 12- tetraazabicyclo-[10.2.1]pentadecane (13b): IR (KBr) 3250 and 1690 cm^{-1}; MS *m/z* 286 (M^+). Found: C, 45.98; H, 6.48; N, 19.36%. Calcd for $C_{11}H_{18}N_4OS_2$: C, 46.13; H, 6.33; N, 19.56%.

19-Oxo-2,15-dithioxo-7,10-dioxa-1,3,14,16-tetraazabicyclo[14.2.1]nonadecane (14a): IR (KBr) 3160 and 1705 cm^{-1}; MS *m/z* 346 (M^+). Found: C, 45.07; H, 6.40; N, 16.05%. Calcd for $C_{13}H_{22}N_4O_3S_2$: C, 45.07; 6.40; N, 16.17%.

21-Oxo-2,17-dithioxo-7,12-dioxa-1,3,16,18-tetraazabicyclo[16.2.1]heneicosane (14b): IR (KBr) 3250 and 1693 cm^{-1}; MS *m/z* 374 (M^+). Found: C, 48.13; H, 7.04; N, 14.89%. Calcd for $C_{15}H_{26}N_4O_3S_2$: C, 48.10; H, 7.00; N,

14.96%.

22-Oxo-2,18-dithioxo-7,10,13-trioxa-1,3,17,19-tetraazabicyclo[17.2.1]docosane (15): IR (KBr) 3220 and 1695 cm^{-1}; MS m/z 390 (M^+). Found: C, 46.07; H, 6.65; N, 14.28%. Calcd for $C_{15}H_{26}N_4O_4S_2$: C, 46.13; H, 6.71; N, 14.35%.

7-Methyl-16-oxo-2,12-dithioxo-1,3,7,11,13-pentaazabicyclo[11.2.1]hexadecane (16): IR (KBr) 3240, 3180, and 1685 cm^{-1}; MS m/z 315 (M^+). Found: C, 45.63; H, 6.59; N, 21.88%. Calcd for $C_{12}H_{21}N_5OS_2$: C, 45.69; H, 6.71; N, 22.20%.

19-Oxo-2,15-dithioxo-1,3,7,10,14,16-hexaazatricyclo[14.2.2^{7,10}.1]heneicosane (17): IR (KBr) 3265 and 1690 cm^{-1}; MS m/z 370 (M^+). Found: C, 48.07; H, 6.85; N, 22.17%. Calcd for $C_{15}H_{26}N_6OS_2$: C, 48.62; H, 7.07; N, 22.68%.

References

1) R. K. Dieter, *Tetrahedron*, **42**, 3029 (1986).
2) M. Kolb, *Synthesis*, **1990**, 171.
3) M. Sato, N. Fukada, M. Kurauchi, and T. Takeshima, *Synthesis*, **1981**, 554.
4) M. Augustin, M. Richter, and S. Salas, *J. Prakt. Chem.*, **322**, 55 (1980).
5) H. L. Wheeler and H. F. Merriam, *J. Am. Chem. Soc.*, **23**, 283 (1901).
6) M. Richter, K. Strauss, H.-D. Schadler, and M. Augustin, *J. Prakt. Chem.*, **324**, 625 (1982).
7) N. Fukada, M. Hayashi, and Y. Suzuki, *Bull. Chem. Soc. Jpn.*, **58**, 3379 (1985).
8) N. Fukada, Y. Takahashi, and M. Hayashi, *Synthesis*, **1986**, 484.
9) N. Fukada, M. Saigo, M. Mashino, K. Yanagisawa, and Y. Takeda, *J. Chem. Res., Synop.*, **1990**, 254.
10) N. Fukada, M. Takano, K. Nakai, S. Kuboike, and Y. Takeda, *Bull. Chem. Soc. Jpn.*, **66**, 148 (1993).
11) T. Takeshima, M. Ikeda, M. Yokoyama, N. Fukada, and M. Muraoka, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 692.
12) T. Takeshima, N. Fukada, E. Okabe, F. Mineshima, and M. Muraoka, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1277.