Reactivity of β-Amino Alcohols with Carbon Disulfide. Study on the Synthesis of 2-Oxazolidinethiones and 2-Thiazolidinethiones

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Optically active oxazolidinethiones and thiazolidinethiones have been used extensively by Nagao and Fujita as chiral auxiliaries.[1] These heterocycles are generally obtained by condensation of carbon disulfide with β-amino alcohols.[2-9] Surprisingly, parameters directing the formation of one or the other heterocycle have not been determined. In the formation of oxazolidinethiones **2**, the stereochemistry at the carbon bearing the oxygen was shown to be retained[9] (Scheme 1). Concerning the synthesis of thiazolidinethiones **3**, the mechanism and the stereochemistry have not been reported yet.

In our research program toward the use of β-amino alcohols for the preparation of heterocycles,[10] we investigated the reaction of carbon disulfide with β-amino alcohols. The purpose of this paper is to report on factors directing the course of the reaction and to propose a mechanism consistent with the stoichiometry and the stereochemistry of the reaction. For this study, we engaged several β-amino alcohols containing a primary, secondary, or tertiary hydroxyl group and a primary or secondary amine (Scheme 2).

This study led to the following results. Preparation of oxazolidinethiones required mild conditions, *i.e.* a stoichiometric quantity of CS_2, a low basic medium (Na_2CO_3, Et_3N), and a limited reaction time. These conditions generally allowed the access to **2** in good yields (Table 1).

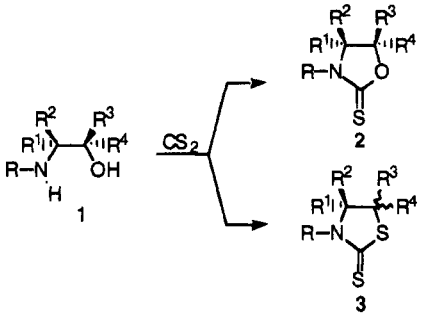
While the rates of the reaction were not influenced a lot by the nature of substituents R^1, R^2, R^3, and R^4, they were affected by the nature of the R group. Oxazolidinethiones were not obtained from secondary amines (R = CH_3) under these conditions. Oxazolidinethiones **2f** and **2g** were synthesized as described by Moreno-Mañas and Padros[9] via a two-step sequence: (i) preparation of dithiocarbamic acid **4** by treatment with CS_2 in the presence of triethylamine and (ii) cyclization in a basic medium (Scheme 3).

Preparation of thiazolidinethiones was conveniently realized under more drastic conditions *i.e.*, action of 5 equiv of CS_2 in a very alkaline medium (KOH) and a long reaction time (from 16 to 24 h) (Table 2).

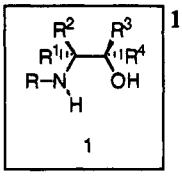
For primary and secondary alcohols, heterocycles were isolated whatever the class of the amine whereas heterocyclization did not occur with the tertiary alcohol **1e**.

All these results suggested that reaction of β-amino alcohols with an excess of CS_2 in a very alkaline medium

Scheme 1



Scheme 2



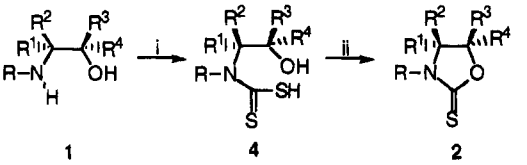
1a - $R^2 = PhCH_2$, $R = R^1 = R^3 = R^4 = H$
b - $R^1 = Ph$, $R = R^2 = R^3 = R^4 = H$
c - $R^2 = iPr$, $R = R^1 = R^3 = R^4 = H$
d - $R^2 = CH_3$, $R^3 = Ph$, $R = R^1 = R^4 = H$
e - $R^2 = PhCH_2$, $R^3 = R^4 = CH_3$, $R = R^1 = H$
f - $R = CH_3$, $R^2 = PhCH_2$, $R^1 = R^3 = R^4 = H$
g - $R = R^2 = CH_3$, $R^3 = Ph$, $R^1 = R^4 = H$

Table 1. Conversion of β-amino alcohols 1 into oxazolidinethiones 2

entry	reaction time (h)	**2** yield (%)
a	0.25	63
b	0.25	50
c	0.25	62
d	5	87
e	0.25	60
f	1	60[a]
g	1	70[a]

[a] Reaction time and yield determined from dithiocarbamic acid, obtained quantitatively from β-amino alcohol.

Scheme 3



Reagents : (i) : CS_2, Et_3N; (ii) : NaOH.

Table 2. Conversion of β-Amino Alcohols 1 into Thiazolidinethiones 3

entry	reaction time (h)	**3** yield (%)
a	16	80
b	16	77
c	16	78
d	24	43
e	16	0
f	16	61
g	16	60

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(1) (a) For a review see: Fujita, E.; Nagao, Y. *Adv. Heterocycl. Chem.* **1989**, *45*, 1. (b) Garcìa-Fernández, J. M.; Ortiz-Mellet, C.; Fuentes, J. *J. Org. Chem.* **1993**, *58*, 5192. (c) Nagao, Y.; Kumagai, T.; Nagase, Y.; Tamai, S.; Inoue, Y.; Shiro, M. *J. Org. Chem.* **1992**, *57*, 4232.
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(9) Moreno-Mañas, M.; Padros, I. *J. Heterocycl. Chem.* **1993**, *30*, 1235.
(10) Delaunay, D.; Le Corre, M. *J. Chem. Soc. Perkin Trans. 1* **1994**, 3041.

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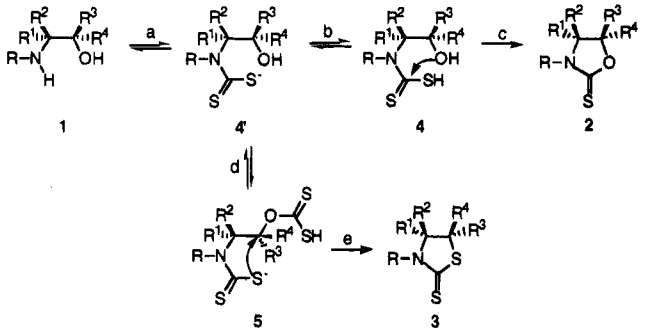
Table 3. Action of an excess of CS_2 with β-Amino Alcohol 1a

yield (%)	15 min	1.5 h	16 h
2a + 3a	80	80	80
2a/3a	80/20	20/80	0/100

Table 4. Transformation of Oxazolidinethiones 2 into Thiazolidinethiones 3

entry	**3** yield (%)	entry	**3** yield (%)
a	80	e	0
b	75	f	50
c	80	g	0
d	0		

Scheme 4



and *for a limited reaction time* should always afford a mixture of both heterocycles.

We therefore examined the crude product obtained from **1a** at different reaction times. As shown in Table 3, a mixture of both products was recovered after 15 min. Further heating increased the amount of thiazolidinethione at the expense of oxazolidinethione, leading to complete conversion after 16 h. This surprising result could be explained by a progressive conversion of oxazolidinethione into thiazolidinethione. This transformation was already envisaged by Rosen,[4] but an attempt to convert 4-methyloxazolidinethione into the corresponding thiazolidinethione was unsuccessful.

Conversion of oxazolidinethiones into thiazolidinethiones was reexamined with several oxazolidinethiones. Results, which are summarized in Table 4, show that the transformation is possible with oxazolidinethiones derived from primary alcohols. In the other cases (R^3 and/or $R^4 \neq H$), conversion of the corresponding oxazolidinethiones was not observed.

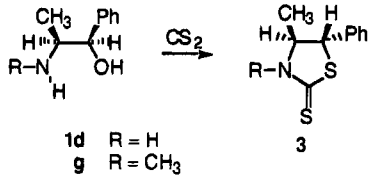
Discussion

Formation of one or the other heterocycle can be explained as follows:

Under mild conditions i.e., in a low alkaline medium and for a limited reaction time, CS_2 reacts mainly with the amino group leading to a dithiocarbamate **4'**, in equilibrium with **4** (Scheme 4). A subsequent nucleophilic attack on the thiocarbonyl group affords oxazolidinethione **2** (path c).

For this process, the steric hindrance due to the presence of a substituent on the nitrogen should alter the rate of the reaction. We effectively observed that the reaction a is slower with a secondary amine (R = CH_3) than with a primary amine (R = H). For example, after a 15 min reaction time, *N*-methylphenylalaninol **1f** is mainly recovered with a small amount of dithiocarbamic acid. However, corresponding oxazolidinethione **2f** can be obtained, as described by Moreno-Mañas and Padros,[9] by isolating the dithiocarbamic acid **4**, which is further cyclized with a strong base.

Scheme 5



The obligation to proceed through a two-step sequence with a secondary amine can be explained by the fact that reaction c should be slower than the reaction d. Thus in a very alkaline medium and in a presence of CS_2 thiocarbamate **4'** is immediately converted to intermediate **5**, preventing the formation of oxazolidinethione **2**, whereas without CS_2, this reaction is impossible.

The nature of the alcohol (primary, secondary or tertiary) does not have an important effect upon the rate of reaction c; oxazolidinethiones are always readily obtained (from primary amines).

Under more drastic conditions i.e., in a very alkaline medium, with an excess of CS_2 and for a long reaction time, intermediate **4'** can undergo an attack on the hydroxyl group leading to the intermediate **5**. This intermediate, which is not isolated, can no longer yield oxazolidinethione **2** but affords thiazolidinethione **3** via an intramolecular cyclization (path e).

Contrary to the formation of oxazolidinethiones obtained with retention of configuration,[9] the mechanism of the preparation of thiazolidinethiones should involve an inversion of the carbon bearing the oxygen. To confirm this hypothesis, the configuration of thiazolidinethione **3g**, derived from (1*R*,2*S*)-ephedrine, and thiazolidinethione **3d**, derived from (1*R**,2*S**)-norephedrine, was determined by X-ray analysis.[11] In agreement with the envisaged mechanism, **3g** and **3d** underwent an inversion of configuration (Scheme 5).

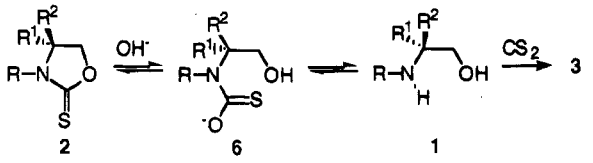
The difference in reactivity between primary, secondary, and tertiary alcohols is consistent with this mechanism. The intramolecular nucleophilic attack seems to be sensitive to steric hindrance. Indeed, this attack occurs easily when $R^3 = R^4 = H$, is more difficult when R^3 or $R^4 \neq H$, and is impossible, under the used conditions, when R^3 and $R^4 \neq H$. All these results agree with previous observations related to some β-amino alcohols.[2-8]

The oxazolidinethione/thiazolidinethione transformation, which has not been reported yet, should involve an attack on the thiocarbonyl group or on the carbon sp^3 bearing the oxygen. There is presumably formation of the unstable intermediate **6** and further decomposition with the formation of the starting β-amino alcohol (Scheme 6). This one can undergo another attack of CS_2 leading to intermediate **5** and then thiazolidinethione.

In order to prove our hypothesis, a KOH treatment, without CS_2, was applied to oxazolidinethione **2a**, result-

(11) The X-ray analysis of the compound **3d**: $S_2C_{10}H_{11}N$: M_r = 209.33, monoclinic, *C*2/*c*, a = 36.665(4), b = 5.738(2), c = 12.214(2) Å, β = 100.67(1), V = 2111.8(8) Å^{-3}, Z = 8, D_x = 1.317 mg m^{-3}, λ(Mo Kα) = 0.70926 Å, μ = 4.383 cm^{-1}, F(000) = 880, T = 294 K, final R = 0.026 for 1001 observations. The sample (0.15 × 0.15 × 0.25 mm) was studied on an automatic diffractometer CAD4 ENRAF-NONIUS with graphite monochromatized MoKα radiation. The X-ray analysis of the compound **3g**: $S_2C_{11}H_{13}N$: M_r = 520.32, monoclinic, *C*2, a = 14.98(2), b = 7.54(2), c = 13.09(3) Å, β = 127.26(12), V = 1178(5) Å^{-3}, Z = 4, D_x = 1.260 Mg m^{-3}, λ(Mo Kα) = 0.70926 Å, μ = 3.97 cm^{-1}, F(000) = 472, T = 294 K, final R = 0.044 for 837 observations. The sample (0.17 × 0.45 × 0.45 mm) was studied on an automatic diffractometer CAD4 ENRAF-NONIUS with graphite monochromatized Mo Kα radiation.

Scheme 6



ing in the formation of the expected β-amino alcohol **1a**. The mechanism of the conversion is therefore in agreement with the fact that ring opening is possible only with accessible carbon. Indeed, transformation of oxazolidinethiones occurred only with primary alcohols ($R^3 = R^4 = H$).

Consequently, thiazolidinethiones derived from primary alcohols ($R^3 = R^4 = H$) are formed via both pathways: heterocyclization (path d) and ring opening of oxazolidinethiones. Fortunately, the stereochemistry of the heterocycles is not affected because these two competitive reactions concern only primary alcohols.

In conclusion, competition between reactions leading to oxazolidinethiones **2** (path c) or thiazolidinethiones **3** (path e) can be summarized as follows: (a) by operating in a low alkaline medium, oxazolidinethione is preferentially obtained because of the difficult access to thiocarbonate. (b) by operating in a very alkaline medium with an excess of carbon disulfide both heterocycles can be produced. Nevertheless, after a long reaction time, thiazolidinethiones are generally obtained. These heterocycles can be therefore formed directly from β-amino alcohols or, in some cases, from the ring opening of oxazolidinethiones. The formation of thiazolidinethiones occurred with an inversion of configuration of the carbon bearing the oxygen.

Experimental Section

General. Melting points were determined on a Richter apparatus. Thin-layer chromatography (TLC) was carried out on Merck precoated 0.2 mm thick plates of silica gel 60 F_{254}. Column chromatography was performed on Merck silica gel 60, 70–230 mesh. Optical rotations were measured on a Perkin-Elmer 241-MC polarimeter at room temperature. ^1H NMR spectra were recorded at 300 MHz. *J* values are given in hertz. ^{13}C NMR spectra were recordered at 75.5 MHz.

General Procedure for the Preparation of 1,3-Oxazolidine-2-thiones 2. Method A: From Primary Amines (entries a–e). To a solution of β-amino alcohol (10 mmol) in 20 mL of aqueous 1 N sodium carbonate was added CS_2 (15 mmol, 0.9 mL). The reaction mixture was stirred at 100 °C (bath at 110 °C and an efficient reflux condensation) for 15 min. After cooling to room temperature, the reaction mixture was extracted with dichloromethane (2 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, and then the solvent was removed under reduced pressure to afford product **2**, which was further purified.

Method B: From Secondary Amines (entries f, g). Triethylamine (12 mmol, 1.7 mL) was added to an ice-cooled solution of β-amino alcohol (10 mmol) and carbon disulfide (12 mmol, 0.7 mL) in dichloromethane (20 mL). The mixture was refluxed overnight and washed with 1 N hydrochloric acid (3 × 10 mL). The combined organic layers were dried and evaporated to afford product **4** (100%, crude yield), which was used without further purification.

A solution of sodium hydroxide (10.2 mmol, 0.4 g) in water (1.7 mL) was added to a solution of crude compound **4** (10 mmol) in THF (3.5 mL). The mixture was refluxed for 1 h and then neutralized by addition of 1 N hydrochloric acid. Finally it was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to afford **2**, which was further purified.

(*S*)-4-Benzyl-1,3-oxazolidine-2-thione (2a): 1.2 g (63%), obtained as an oil and purified by column chromatography (ethyl acetate–cyclohexane 1:1). $[\alpha]^{22}_D$ −93.03° (*c* 1.88, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.84–2.99 (m, 2H), 4.30–4.39 (m, 2H), 4.62 (t, 1H, *J* = 7.8 Hz), 7.16–7.35 (m, 5H), 8.36 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 40.34, 57.87, 74.74, 127.44, 128.99, 129.10, 135.29, 189.34. Anal. Calcd for $C_{10}H_{11}NSO$: C, 62.14; H, 5.74; N, 7.25; S, 16.59. Found: C, 62.02; H, 5.38; N, 7.36; S, 16.63.

(*R*)-4-Phenyl-1,3-oxazolidine-2-thione (2b): 0.9 g (50%), mp 121–122°C purified by column chromatography (toluene-ethyl acetate, 9:1); $[\alpha]^{22}_D$ −79.3° (*c* 0.21, $CHCl_3$) ; ^1H NMR ($CDCl_3$) δ 4.45 (dd, 1H, *J* = 6.9, 8.8 Hz), 4.98 (t, 1H, *J* = 9.0 Hz), 5.14 (dd, 1H, *J* = 6.9, 9.2 Hz), 7.28–7.41 (m, 5H), 8.30 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 60.16, 77.62, 126.21, 129.14, 129.32, 138.04, 189.88. Anal. Calcd for C_9H_9NSO: C, 60.31; H, 5.06; N, 7.81; S, 17.89. Found: C, 60.55; H, 5.01; N, 7.95; S, 17.67.

(*S*)-4-Isopropyl-1,3-oxazolidine-2-thione (2c): 0.9 g (62%), mp 45–46 °C (ethyl acetate–cyclohexane) (lit.[8a] mp 45–46 °C (ethyl acetate–hexane)); $[\alpha]^{22}_D$ −21.60° (*c* 0.40, $CHCl_3$) (lit.[8a] −22.5, *c* 0.41, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.77 (d, 3H, *J* = 6.8 Hz), 0.82 (d, 3H, *J* = 6.7 Hz), 1.68 (m, 1H), 3.77 (dt, 1H, *J* = 6.6, 9.1 Hz), 4.23 (dd, 1H, *J* = 6.6, 9.1 Hz), 4.55 (t, 1H, *J* = 9.1 Hz), 9.00 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.90, 18.04, 32.17, 62.52, 73.53, 189.54.

***cis*-4-Methyl-5-phenyl-1,3-oxazolidine-2-thione (2d):** 1.7 g (87%), obtained by heating racemic norephedrine at 100 °C for 5 h, mp 91–92 °C (ethyl acetate–cyclohexane) (lit.[9] mp 95–97 °C (ethyl acetate–hexane)); ^1H NMR ($CDCl_3$) δ 0.86 (d, 3H, *J* = 6.6 Hz), 4.47 (dq, 1H, *J* = 6.6, 8.8 Hz), 5.96 (d, 1H, *J* = 8.8 Hz), 7.25–7.42 (m, 5H), 8.80 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.58, 56.05, 88.61, 126.23, 128.65, 128.90, 133.71, 188.73.

(*S*)-4-Benzyl-5,5-dimethyl-1,3-oxazolidine-2-thione (2e): 1.3 g (60%), mp 142–143 °C (EtOH); $[\alpha]^{22}_D$ −187.30° (*c* 0.93, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.49 (s, 3H), 1.51 (s, 3H), 2.71 (dd, 1H, *J* = 10.5, 13.5 Hz), 2.85 (dd, 1H, *J* = 4.5, 13.5 Hz), 3.88 (dd, 1H, *J* = 4.5, 10.4 Hz), 7.17–7.38 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 21.69, 27.36, 36.23, 66.33, 90.10, 127.52 128.90, 129.30, 136.00, 188.20. Anal. Calcd for $C_{12}H_{15}NSO$: C, 65.12; H, 6.83; N, 6.33; S, 14.49. Found: C, 65.37; H, 6.48; N, 6.56; S, 14.63.

(*S*)-3-Methyl-4-benzyl-1,3-oxazolidine-2-thione (2f): 1.2 g (60%), mp 84–85 °C (EtOH); $[\alpha]^{22}_D$ +76.40° (*c* 1.91, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.77 (dd, 1H, *J* = 8.4, 13.6 Hz), 3.18 (dd, 1H, *J* = 4.4, 13.6 Hz), 3.22 (s, 3H), 4.16–4.24 (m, 2H), 4.34–4.41 (m, 1H), 7.15–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 33.64, 37.95, 62.27, 70.56, 127.48, 129.03, 129.11, 134.79, 187.88. Anal. Calcd for $C_{11}H_{13}NSO$: C, 63.73; H, 6.32; N, 6.76; S, 15.47. Found: C, 63.85; H, 6.27; N, 6.53; S, 15.80.

(4*S*,5*R*)-3,4-Dimethyl-5-phenyl-1,3-oxazolidine-2-thione (2g): 1.4 g (70%), mp 120–121 °C (cyclohexane–ethyl acetate) (lit.[9] mp 123–124 °C (hexane–ethyl acetate));$[\alpha]^{22}_D$ −205.32° (*c* 1.73, CH_3OH) (lit.[9] −216, *c* 2, CH_3OH); ^1H NMR ($CDCl_3$) δ 0.85 (d, 3H, *J* = 6.7 Hz), 3.21 (s, 3H), 4.27 (dq, 1H, *J* = 6.7, 8.8 Hz), 5.79 (d, 1H, *J* = 8.8 Hz), 7.25–7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.28, 33.29, 60.73, 82.75, 126.33, 128.66, 128.87, 134.01, 187.35.

General Procedure for the Preparation of 1,3-Thiazolidine-2-thiones 3. To a solution of β-amino alcohol (10 mmol) in 50 mL of aqueous 1 N potassium hydroxide was added CS_2 (50 mmol, 3 mL). The reaction mixture was stirred at 100 °C (bath at 110 °C and an efficient reflux condensation) for 16 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane (2 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated under reduced pressure. The crude product was further purified.

(*S*)-4-Benzyl-1,3-thiazolidine-2-thione (3a): 1.7 g (80%), mp 84–85 °C (EtOH) (lit.[8c] mp 79 °C); $[\alpha]^{22}_D$ −129.17° (*c* 0.96, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.93–3.08 (m, 2H), 3.30 (dd, 1H, *J* = 6.7, 11.2 Hz), 3.56 (dd, 1H, *J* = 7.7, 11.2 Hz), 4.43–4.48 (m, 1H), 7.19–7.37 (m, 5H), 8.01 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 38.12, 39.96, 65.13, 127.43, 129.03, 129.18, 135.82, 201.05. Anal. Calcd for $C_{10}H_{11}NS_2$: C, 57.38; H, 5.30; N, 6.69. Found: C, 57.42; H, 5.06; N, 6.80.

(*R*)-4-Phenyl-1,3-thiazolidine-2-thione (3b): 1.5 g (77%), mp 124–125 °C (H_2O/EtOH) (lit.[8c] mp 125–126 °C); $[\alpha]^{22}_D$ −209.32° (*c* 0.35, $CHCl_3$) (lit.[8c] −210.0°, *c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 3.48 (dd, 1H, *J* = 8.3, 11.2 Hz), 3.84 (dd, 1H, *J* = 8.1, 11.2 Hz), 5.32 (t, 1H, *J* = 8.2 Hz), 7.34–7.45 (m, 5H), 8.10 (br s,

1H); ^{13}C NMR ($CDCl_3$) δ 41.55, 67.46, 126.28, 129.21, 129.31, 137.98, 201.57. Anal. Calcd for $C_9H_9NS_2$: C, 55.35; H, 4.64; N, 7.17. Found: C, 55.40; H, 4.68; N, 6.85.

(*S*)-4-Isopropyl-1,3-thiazolidine-2-thione (3c): 1.2 g (78%), mp 66–67 °C (Et_2O) (lit.[8b] mp 67–68 °C (CH_2Cl_2)); $[\alpha]^{22}_D$ −34.60° (*c* 0.94, $CHCl_3$) (lit.[8b] −36.81, *c* 1.16, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.00 (d, 3H, J = 7.2 Hz), 1.03 (d, 3H, J = 8.5 Hz), 2.01 (m, 1H), 3.32 (dd, 1H, J = 8.2, 11.0 Hz), 3.53 (dd, 1H, J = 8.2, 11.0 Hz), 4.11 (m, 1H), 9.05 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.18, 18.78, 31.98, 35.73, 70.20, 200.78.

***trans*-4-Methyl-5-phenyl-1,3-thiazolidine-2-thione (3d):** 0.9 g (43%), mp 75–77 °C (cyclohexane), obtained by heating racemic norephedrine at 10 0°C for 24 h with 5 N KOH ; ^1H NMR ($CDCl_3$) δ 1.37 (d, 3H, J = 6.2 Hz), 4.26–4.31 (m, 1H), 4.71 (d, 1H, J = 8.6 Hz), 7.29–7.38 (m, 5H), 9.13 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.62, 61.31, 67.64, 128.06, 128.83, 129.19, 136.73, 199.13.

(*S*)-3-Methyl-4-benzyl-1,3-thiazolidine-2-thione (3f): 1.4 g (61%), mp 74–75 °C (EtOH); $[\alpha]^{22}_D$ +115.71° (*c* 3.02, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 2.90–2.97 (m, 2H), 3.18 (dd, 1H, J = 4.6, 13.5 Hz), 3.29 (s, 3H), 3.35 (dd, 1H, J = 8.0, 11.4 Hz), 4.34–4.42 (m, 1H), 7.20–7.88 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 31.82, 35.80, 36.72, 71.37, 127.32, 129.03, 129.23, 135.76, 195.95. Anal. Calcd for $C_{11}H_{13}NS_2$: C, 59.15; H, 5.86; N, 6.27. Found: C, 59.40; H, 5.76; N, 6.39.

(4*S*,5*S*)-3,4-Dimethyl-5-phenyl-1,3-thiazolidine-2-thione (3g): 1.3 g (60%), mp 61–62 °C (H_2O/EtOH) (lit.[5] mp 64–65 °C (H_2O/EtOH)) $[\alpha]^{22}_D$ −116.24° (*c* 0.31, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.46 (d, 3H, J = 6.4 Hz), 3.27 (s, 3H), 4.16 (dq, 1H, J = 6.1, 6.4 Hz), 4.35 (d, 1H, J = 6.1 Hz), 7.34 (s, 5H); ^{13}C NMR ($CDCl_3$) δ 18.07, 34.97, 54.67, 73.26, 127.62, 128.66, 129.22, 138.65, 195.02.

General Procedure for the Transformation of 1,3-Oxazolidine-2-thiones 2 into 1,3-Thiazolidine-2-thiones 3. A mixture of oxazolidinethione **2** (10 mmol) and CS_2 (50 mmol, 3 mL) in 50 mL of aqueous 1 N potassium hydroxide was stirred at 100 °C (bath at 110 °C) for 16 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane (2 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated under reduced pressure to afford thiazolidinethiones **3**. **3a**: 80%; **3b**: 75%; **3c**: 80%; **3d**: 0%; **3e**: 0%; **3f**: 50%; **3g**: 0%.

Supporting Information Available: Copies of ^1H NMR and ^{13}C NMR spectra of **2a**, **2b**, **2e**, **2f**, **3b**, **3c**, **3d**, and **3f** (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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