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 Received May 28, 1993

Dedicated to the memory of Dr. Roland K. Robins

The preparation of a series of oxazolidine-2-thiones, both homochiral and racemic, as well as their oxidation to oxazolidin-2-ones is reported. X-Ray and pmr studies have showed that the stereochemical integrity of the starting aminoalcohol is maintained.

J. Heterocyclic Chem., **30**, 1235 (1993).

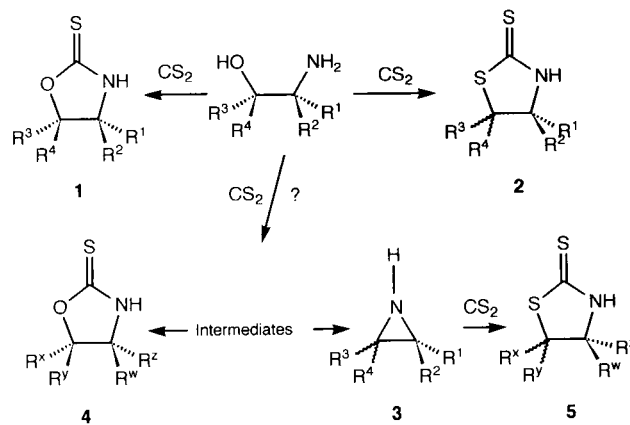
Introduction.

Homochiral oxazolidin-2-ones have found broad applications as chiral auxiliaries thanks to the contribution of Evans and coworkers [1-12]. Their preparation requires reaction of the appropriate 1,2-aminoalcohol with phosgene or one of its derivatives such as dialkyl carbonates. Diethyl carbonate has been claimed to give inconsistent results and the use of trichloromethyl chloroformate (diphosgene) has been recommended [13]. However, this reagent although less volatile than phosgene, is still quite poisonous. Another indirect method for the preparation of oxazolidin-2-ones has been reported [14] but it does not avoid the use of phosgene derivatives.

We deemed interesting to prepare oxazolidin-2-ones by methods that do not depend on phosgene, neither directly nor indirectly. We turned our attention to the preparation of oxazolidine-2-thiones and their conversion into oxazolidin-2-ones. The idea is attractive since oxazolidine-2-thiones themselves are useful chiral auxiliaries which can be prepared by condensation of 1,2-aminoalcohols with carbon disulfide [15-17]. Two papers were found on the conversion of oxazolidine-2-thiones into oxazolidin-2-ones; one came from the Evans group [6] and reports a single case. Earlier, a German group described some examples in a racemic series [18]. In both reports the reagent used was hydrogen peroxide. However, a more complete analysis suggest that the situation could be somehow more complicated. Thus, the reactions between 1,2-aminoalcohols and carbon disulfide sometimes produce thiazolidine-2-thiones, **2**, instead of oxazolidine-2-thiones, **1** [17,19-21] (see Scheme I). The factors deciding in favour of one or the other heterocycle are unknown. In the formation of thiazolidine-2-thiones, the carbon-oxygen bond of the aminoalcohol must be broken at some mechanistic step and therefore, the conservation of the stereochemistry at C5 of the heterocyclic ring is not warranted. Unfortunately all the reported examples of thiazolidine-2-thione formation involve molecules bearing a methylene group at C5 and therefore no stereochemical conclusions can be drawn.

Moreover, the reaction of aziridines, **3**, with carbon disulfide affords thiazolidine-2-thiones [22], and oxazolidin-2-ones are considered as latent aziridine equivalents [23]. If aziridines were intermediates in the reactions of 1,2-aminoalcohols with carbon disulfide to afford thiazolidine-2-thiones, even the regiochemistry of the resulting products **5** could be at stake (Scheme I). Also, formation of oxazolidine-2-thiones, **4**, from some intermediate in the pathway to **3** could produce regiochemical scrambling in **4**. In summary, we decided to study the transformations of 1,2-aminoalcohols into oxazolidine-2-thiones and into oxazolidin-2-ones paying due attention to the structural features of the obtained products.

Scheme I

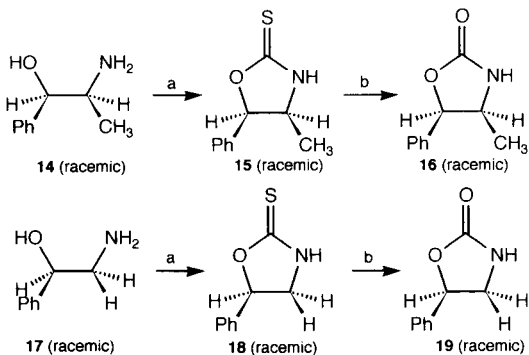
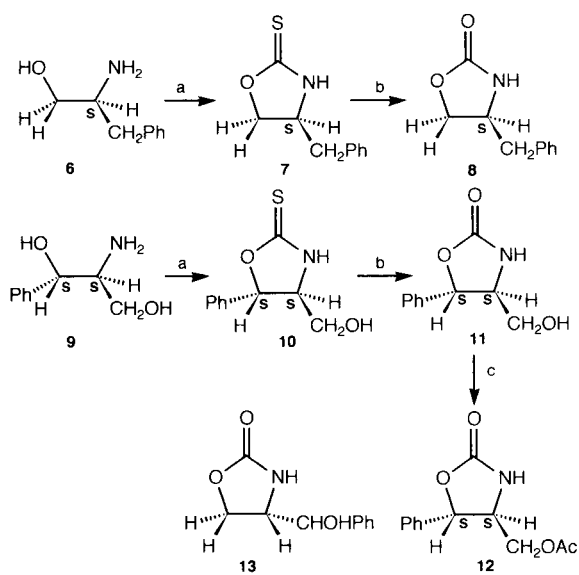


Results.

(*S*)-Alaninol, **6**, was converted into (*4S*)-4-benzyloxazolidine-2-thione, **7**, by treatment with carbon disulfide and triethylamine in dichloromethane (Scheme II). The thione **7** was not purified but converted directly into (*4S*)-4-benzyloxazolidin-2-one, **8**, by oxidation with hydrogen peroxide in alkaline medium (56% overall yield from **6**). In the same way (*1S,2S*)-2-amino-1-phenyl-1,3-propanediol, **9**, was converted sequentially into (*4S,5S*)-4-hydroxymethyl-5-phenyloxazolidine-2-thione, **10**, and (*4S,5S*)-4-hydroxy-

methyl-5-phenyloxazolidin-2-one, **11**. Two different oxazolidinones could in principle be expected from aminoalcohol **9**, *i.e.* **11** and **13**. The isolated oxazolidinone was acetylated and the pmr spectra before and after acetylation were compared. The pmr spectrum of **11** shows a doublet at δ 5.30 ($J = 5.5$ Hz, 1H) assigned to H-C5. The proton at C4 gives a multiplet at 3.75 and the methylene protons showed absorptions at δ 3.65 (dd, $J = 5.2$ and 11.3, 1H) and at δ 3.72 (dd, $J = 4.3$ and 11.3, 1H). Acetylation causes a downfield shift of about 0.5 ppm to the signals of the proton or protons (for secondary or primary alcohols respectively) linked to the functionalized carbon atom. After acetylation the signal of H-C5 appeared at δ 5.3 (d, $J = 6.1$, 1H), the same position as before acetylation, also H-C4 showed absorptions centered at δ 3.98, near the position before acetylation. However, the signals of two protons appeared clearly downfield with respect to the free alcohol; they are the methylene group signals that appeared at δ 4.16 (dd, $J = 5.5$ and 11.6, 1H) and at δ 4.35 (dd, $J = 4.3$ and 11.6, 1H). Since the signals of two protons (not one) are shifted downfield the oxazolidinone is **11**, not **13**, and its acetyl derivative is **12**.

Scheme II



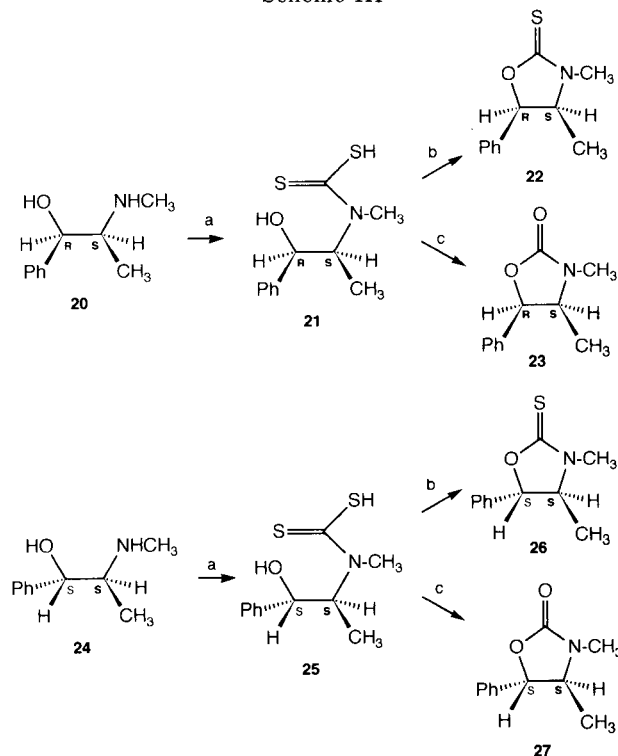
a. - $\text{CS}_2/\text{Et}_3\text{N}/\text{CH}_2\text{Cl}_2$; b. - H_2O_2 (36%)/ $\text{NaOH}/\text{H}_2\text{O}$; c. - $\text{Ac}_2\text{O}/\text{Pyrr}/\text{CH}_2\text{Cl}_2$

Racemic norephedrine, **14**, was similarly transformed into *cis*-4-methyl-5-phenyloxazolidine-2-thione, **15**, and *cis*-4-methyl-5-phenyloxazolidin-2-one, **16**. Finally, racemic 2-amino-1-phenylethanol, **17**, was converted into 5-phenyloxazolidine-2-thione, **18**, and 5-phenyloxazolidin-2-one, **19**.

In no case could thiazolidine-2-thiones and thiazolidin-2-ones be detected.

Next, we studied two preparations starting from aminoalcohols bearing a secondary amine group (Scheme III). When ephedrine, **20**, was treated with carbon disulfide and triethylamine in dichloromethane under the same experimental conditions as for aminoalcohols bearing a primary amine group, a compound was isolated which presented a strong absorption at 3401 cm^{-1} in the ir spectrum, and gave a pmr spectrum that could not be accommodated to any 5-membered cyclic structure related to **20**. Although the stability of the isolated compound did not permit to obtain good elemental analysis, it became clear from it that the ratio S:N was 2:1. However, the spectral data could not be accommodated to the possible thiazolidine-2-thione. On the basis of its chemical behaviour we tentatively assign structure **21**, bearing a dithiocarbamic acid functional group, to the isolated compound. Indeed, **21** was efficiently cyclized into (4*S*,5*R*)-3,4-dimethyl-5-phenyloxazolidine-2-thione, **22**, by treatment with sodium hydroxide in water-THF. Direct one-pot conversion of **21** into **23** was performed with hydrogen peroxide and sodium hydroxide.

Scheme III



a. - $\text{CS}_2/\text{Et}_3\text{N}/\text{CH}_2\text{Cl}_2$; b. - $\text{NaOH}/\text{H}_2\text{O}/\text{THF}$; c. - H_2O_2 (36%)/ $\text{NaOH}/\text{H}_2\text{O}/\text{THF}$

Parallel results were obtained starting from pseudoephedrine, **24**. The dithiocarbamic acid, **25**, was isolated and transformed into products **26** and **27**, diastereoisomers of **22** and **23**.

Structure **22** was confirmed by X-ray diffraction and full details will be published elsewhere. Next, we made a pmr analysis of the heterocycles to find clear correlations that could help in structural assignment.

In general in 5-membered rings the *cis* coupling constants are higher than the corresponding *trans*. Thus, in a series of six pairs of isomeric oxazolidine-2-thiones the *cis* J values are higher than the *trans* J values by a range 1.7-3.0 Hz [18]. The coupling constants between protons at C4 and C5 for our compounds are in Table 1. The values for the diastereoisomeric pairs of oxazolidine-2-thiones **22** and **26** and of oxazolidin-2-ones **23** and **27** agree well with the proposed structures. When comparing the values for **10**, **11** and **12** with those for **15** and **16** it is observed that the range for *trans* J is 5.5-6.1 whereas the range for *cis* J is 7.9-8.8. Therefore for products **7**, **8**, **18** and **19** we assign the higher values of J to the *cis* couplings and the lower values to the *trans* couplings.

Table 1. J values (Hz) between H-C4 and H-C5

| Oxazolidine-2-thiones | | Oxazolidin-2-ones | |
|-----------------------|----------------|-------------------|----------------|
| J <i>cis</i> | J <i>trans</i> | J <i>cis</i> | J <i>trans</i> |
| 7 | 7.94 | 8 | 5.49 |
| 10 | ----- | 11 | 5.49 |
| | 5.85 | 12 | 6.10 |
| 15 | 8.78 | 16 | ----- |
| 18 | 9.50 | 19 | 7.93 |
| 22 | 9.16 | 23 | 8.42 |
| 26 | ----- | 27 | 7.68 |
| | 7.93 | | |

Representative chemical shifts are in Table 2. Methyl groups at C4 that are *cis* to a phenyl group appear at δ 0.8-0.9, whereas the absorptions when both groups are mutually *trans* are in the range 1.40-1.45. Similar effects are observed for protons at C4; when the protons are *cis* to a phenyl group they show signals at δ 3.52-3.98 for products **10**, **11**, **12**, **18**, **19**, **26** and **27**, but if they are in a

Table 2. Chemical shifts of representative protons

| | Me-C4 <i>cis</i> to Ph | Me-C4 <i>trans</i> to Ph | H-C4 <i>cis</i> to Ph | H-C4 <i>trans</i> to Ph |
|-----------|---------------------------|-----------------------------|--------------------------|----------------------------|
| 10 | ----- | ----- | a | ----- |
| 11 | ----- | ----- | 3.75 | ----- |
| 12 | ----- | ----- | 3.98 | ----- |
| 15 | 0.88 | ----- | ----- | 4.44 |
| 16 | 0.78 | ----- | ----- | 4.18 |
| 18 | ----- | ----- | 3.71 | 4.13 |
| 19 | ----- | ----- | 3.55 | 4.00 |
| 22 | 0.86 | ----- | ----- | 4.25 |
| 23 | 0.76 | ----- | ----- | 4.00 |
| 26 | ----- | 1.45 | 3.81 | ----- |
| 27 | ----- | 1.39 | 3.52 | ----- |

a) Not well defined

trans situation the absorption range is 4.00-4.44 for compounds **15**, **16**, **18**, **19**, **22** and **23**. An additional observation is that protons at C4 (see Table 2) and the N-Me groups (see experimental for the last values) appear systematically at lower field for oxazolidine-2-thiones than for oxazolidin-2-ones.

The internal consistency of these spectroscopic analysis supports the proposed structures and rules out the possibilities discussed in Scheme I.

EXPERIMENTAL

(S)-4-Benzylloxazolidine-2-thione (**7**). (General Method).

Triethylamine (1.61 g, 2.20 ml, 15.8 mmoles) was added to an ice-cooled solution of (S)-alaninol (2.00 g, 13.2 mmoles) and carbon disulfide (1.20 g, 0.95 ml, 15.8 mmoles) in dichloromethane (19 ml). The mixture was refluxed overnight and partitioned with 1N hydrochloric acid (3 x 10 ml). The organic layer was dried and evaporated to afford crude **7** (2.60 g, 100%) as an oil that was used without further purification; ir (film): 3198 cm⁻¹; pmr (deuteriochloroform): δ 2.83 (dd, J = 6.4 and 13.7 Hz, 1H), 2.88 (dd, J = 7.0 and 13.7 Hz, 1H), 4.02 (m, 1H), 4.13 (dd, J = 5.8 and 8.2 Hz, 1H), 4.4 (dd, J = 7.9 and 8.2 Hz, 1H), 5.8 (broad s, 1H), 7.32 (m, 5H).

Other oxazolidine-2-thiones were prepared as for **7**.

(4S,5S)-4-Hydroxymethyl-5-phenyloxazolidine-2-thione (**10**).

Crude **10** (100%) is a yellow oil; ir (film): 3367-3206 cm⁻¹; pmr (hexadeuteriodimethyl sulfoxide): δ 3.52-4.00 (m, 3H), 5.64 (d, J = 5.8 Hz, 1H), 7.37 (m, 5H).

cis-4-Methyl-5-phenyloxazolidine-2-thione (**15**).

Crude racemic **15** (100%) was recrystallized from ethyl acetate/hexane; it had mp 95-97° (lit [15] mp of the 4*R*,5*S* enantiomer, 81-82°); ir (potassium bromide): 3220 cm⁻¹; pmr (deuteriochloroform): δ 0.88 (d, J = 6.6 Hz, 3H), 4.44 (m, 1H), 5.96 (d, J = 8.8 Hz, 1H), 7.34 (m, 5H).

5-Phenyloxazolidine-2-thione (**18**).

Crude racemic **18** was digested with diethyl ether to afford a solid, mp 135-138°; ir (potassium bromide): 3161 cm⁻¹; pmr (deuteriochloroform): δ 3.71 (dd, J = 7.7 and 10.2 Hz, 1H), 4.13 (dd, J = 9.5 and 10.2 Hz, 1H), 5.86 (apparent t, J = 8.4 Hz, 1H), 7.38 (m, 5H).

(S)-4-Benzylloxazolidin-2-one (**8**). (General Method).

Hydrogen peroxide (36%, 4.60 ml, 54.7 mmoles) was added dropwise to a mixture of crude **7** (2.60 g, 13.5 mmoles), sodium hydroxide (1.10 g, 26.9 mmoles) and water (5 ml). The mixture was stirred overnight at room temperature. Aqueous sodium hydrogen sulfite was added and the mixture was extracted with chloroform. The organic layer was dried and evaporated; the residue was recrystallized from ethyl acetate/hexane to give **8** (1.30 g, 56%), mp 88-89° (lit [24] mp 84.5-86.5°); ir (potassium bromide): 3284, 1749, 1712 cm⁻¹; pmr (deuteriochloroform): δ 2.86 (d, J = 6.7 Hz, 1H), 3.07 (m, 1H), 4.12 (dd, J = 8.5 and 5.5 Hz, 1H), 4.44 (dd, J = 8.5 and 7.9 Hz, 1H), 5.39 (broad s, 1H), 7.30 (m, 5H); cmr (deuteriochloroform): 41.2, 53.7, 69.5, 127.1, 128.9, 130.0, 135.9, 159.9; $[\alpha]_D^{25} = +5.0^\circ$ (c = 2.0, ethanol) (lit [24] $[\alpha]_D^{25} = 4.9^\circ$ (c = 1.1, ethanol)).

Other oxazolidin-2-ones were prepared as for **8**.

(4S,5S)-4-Hydroxymethyl-5-phenyloxazolidin-2-one (11)

Compound **11** (22%) had mp 101-102° (lit [25] mp 109-110°); ir (potassium bromide): 3295, 1710 cm^{-1} ; pmr (deuteriochloroform): δ 3.32 (broad s, 1H), 3.65 (dd, $J = 5.2$ and 11.3 Hz, 1H), 3.72 (dd, $J = 4.3$ and 11.3 Hz, 1H), 3.75 (m, $J = 5.5$ and 4.3 Hz, 1H), 5.30 (d, $J = 5.5$ Hz, 1H), 7.02 (broad s, 1H), 7.38 (m, 5H); cmr (deuteriochloroform): δ 61.6, 62.6, 79.0, 125.2, 128.2, 128.3, 138.6, 158.9; $[\alpha]_D = -45^\circ$ ($c = 2.0$, methanol).

(4S,5S)-4-Acetoxyethyl-5-phenyloxazolidin-2-one (12)

Pyridine (1.71 g, 1.74 ml, 21.6 mmoles) was slowly added to a solution of **11** (2.78 g, 14.4 mmoles) and acetic anhydride (2.22 g, 2.04 ml, 21.6 mmoles) in dichloromethane (10 ml). The mixture was stirred at room temperature for 48 hours, extracted sequentially with saturate aqueous sodium hydrogen carbonate, with 1*N* hydrochloric acid and with water. The organic layer was dried and evaporated to afford **12** (2.5 g, 74%), mp 143-146° (from chloroform); ir (potassium bromide): 3230, 1755, 1723 cm^{-1} ; pmr (deuteriochloroform): δ 2.11 (s, 3H), 3.98 (m, 1H), 4.16 (dd, $J = 11.6$ and 5.5 Hz, 1H), 4.35 (dd, $J = 11.6$ and 4.3 Hz, 1H), 5.28 (d, $J = 6.1$ Hz, 1H), 6.00 (broad s, 1H), 7.37 (m, 5H); cmr (deuteriochloroform): δ 20.5, 59.0, 64.3, 79.9, 125.6, 128.9, 129.0, 137.8, 158.9, 170.6; $[\alpha]_D = -50^\circ$ ($c = 1.03$ chloroform).

Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}_2$: C, 61.27; H, 5.57; N, 5.95. Found: C, 61.21; H, 5.46; N, 5.97.

cis-4-Methyl-5-phenyloxazolidin-2-one (**16**)

Racemic **16** (39%) had mp 148-149° (lit [26] mp 147-149°); ir (potassium bromide): 3262, 1743, 1726 cm^{-1} ; pmr (deuteriochloroform): δ 0.78 (d, $J = 6.1$ Hz, 3H), 4.18 (m, 1H), 5.62 (broad s, 1H), 5.67 (d, $J = 7.9$ Hz, 1H), 7.36 (m, 5H); cmr (deuteriochloroform): δ 17.4, 52.6, 81.0, 125.9, 128.4, 128.4, 134.9, 159.7.

Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{NO}_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.75; H, 6.29; N, 7.87.

5-Phenyloxazolidin-2-one (**19**)

Racemic **19** (54%) had mp 91-93° (from dichloromethane/ethyl acetate); ir (potassium bromide): 3276, 1722 cm^{-1} ; pmr (deuteriochloroform): δ 3.55 (apparent t, $J = 7.9$ Hz, 1H), 4.00 (apparent t, $J = 8.5$ Hz, 1H), 5.65 (dd, $J = 8.6$ and 7.9 Hz, 1H), 5.88 (broad s, 1H), 7.38 (m, 5H); cmr (deuteriochloroform): δ 48.2, 77.8, 125.8, 128.4, 128.8, 138.4, 160.2.

Anal. Calcd. for $\text{C}_9\text{H}_9\text{NO}_2$: C, 66.25; H, 5.56; N, 8.58. Found: C, 65.99; H, 5.78; N, 8.64.

N-(Mercaptothiocarbonyl)ephedrine (**21**)

Triethylamine (1.47 g, 2.01 ml, 14.5 mmoles) was added to an ice-cooled solution of ephedrine, **20**, (2.00 g, 12.1 mmole) and carbon disulfide (1.10 g, 0.87 ml, 14.5 mmole) in dichloromethane (20 ml). The mixture was refluxed overnight and washed with 1*N* hydrochloric acid (3 x 10 ml). The organic layer was dried and evaporated to afford product **21** (100% crude yield), mp 65-75°; ir (potassium bromide): 3402 cm^{-1} ; pmr (deuteriochloroform): δ (some signals were duplicated) 1.14 and 1.26 (d, $J = 7.0$ Hz and d, $J = 6.4$ Hz, 3H), 3.25 and 3.47 (s and s, 3H), 5.20 and 4.7 (d, $J = 2.7$ Hz and m, 1H), 5.83 and 5.0 (m, $J = 7.0$ and 3.0 Hz and m, 1H), 7.38 and 7.35 (m and m, 5H).

Anal. Calcd. for $\text{C}_{11}\text{H}_{15}\text{NOS}_2$: C, 54.74; H, 6.26; N, 5.80; S, 26.57. Found: C, 55.51; H, 6.35; N, 5.68; S, 24.87 [27].

(4S,5R)-3,4-Dimethyl-5-phenyloxazolidine-2-thione (22)

A solution of sodium hydroxide (0.17 g, 4.25 mmoles) in water (1.5 ml) was added to a solution of compound **21** (1.00 g, 4.15 mmoles) in THF (3 ml). The mixture was refluxed for 1 hour and then neutralized by addition of 1*N* hydrochloric acid. Finally it was partitioned with chloroform. The organic layer was dried and evaporated to afford **22** (0.65 g, 76%), mp 123-124° (from ethyl acetate/hexane); pmr (deuteriochloroform): δ 0.86 (d, $J = 6.7$ Hz, 3H), 3.22 (s, 3H), 4.25 (dq, $J = 9.1$ and 6.7 Hz, 1H), 5.78 (d, $J = 9.2$ Hz, 1H), 7.35 (m, 5H); cmr (deuteriochloroform): δ 14.0, 33.0, 60.4, 82.5, 126.1, 128.4, 128.6, 133.8, 187.0; ms: (m/z) 207 (M, 45), 118 (100); $[\alpha]_D = -216^\circ$ ($c = 2.0$ MeOH).

Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{NOS}$: C, 63.74; H, 6.32; N, 6.76; S, 15.47. Found: C, 63.42; H, 6.58; N, 6.79; S, 15.27.

(4S,5R)-3,4-Dimethyl-5-phenyloxazolidin-2-one (23) by Oxidation of **21**

Preparation of **22** was repeated as above with the same quantities of reagents. After the refluxing time the mixture was cooled at room temperature and a solution made of sodium hydroxide (0.33 g, 8.25 mmoles), water (2 ml) and 36% hydrogen peroxide (2.80 ml, 33.2 mmoles) was added to it. The mixture was refluxed for 48 hours. Sodium hydrogen sulfite was added and the mixture partitioned with chloroform. The organic layer was dried and evaporated to afford **23** (61%), mp 90-92° (lit [26] mp 91-92°); ir (potassium bromide): 1763 cm^{-1} ; pmr (deuteriochloroform): δ 0.76 (d, $J = 6.4$ Hz, 3H), 2.84 (s, 3H), 4.00 (dq, $J = 8.2$ and 6.4 Hz, 1H), 5.56 (d, $J = 8.2$ Hz, 1H), 7.29 (m, 5H); cmr (deuteriochloroform): δ 17.2, 28.6, 61.1, 82.3, 125.8, 128.7, 128.8, 137.5, 157.6; $[\alpha]_D = -120^\circ$ ($c = 1.18$, chloroform) (lit [26] $[\alpha]_D = -125^\circ$ ($c = 1.0$, chloroform)).

N-(Mercaptothiocarbonyl)pseudoephedrine (**25**)

This compound was prepared as for **21**. Compound **25** had mp 50-60°; ir (potassium bromide): 3400 cm^{-1} ; pmr (deuteriochloroform): δ 1.16 and 1.41 (d, $J = 6.1$ Hz and d, $J = 6.1$ Hz, 3H), 3.23 and 3.16 (s and s, 3H), 3.98 and 3.79 (m, $J = 6.1$ Hz and dq, $J = 8.2$ and 6.1 Hz, 1H), 5.43 and 5.10 (d, $J = 7.6$ Hz and d, $J = 8.2$ Hz, 1H), 7.37 (m, 5H).

Anal. Calcd. for $\text{C}_{11}\text{H}_{15}\text{NOS}_2$: C, 54.74; H, 6.26; N, 5.80; S, 26.57. Found: C, 54.88; H, 5.75; N, 5.59; S, 24.39 [27].

(4S,5S)-3,4-Dimethyl-5-phenyloxazolidine-2-thione (26)

This compound (72%) was prepared as for **22**. Thione **26** had mp 48-49° (from hexane/chloroform); pmr (deuteriochloroform): δ 1.45 (d, $J = 6.4$ Hz, 1H), 3.20 (s, 3H), 3.81 (dq, $J = 7.9$ and 6.4 Hz, 1H), 5.12 (d, $J = 7.9$ Hz, 1H), 7.35 (m, 5H); ms: (m/z) 207 (M, 40), 118 (100); $[\alpha]_D = +57.8$ ($c = 1.28$, chloroform).

Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{NOS}$: C, 63.74; H, 6.32; N, 6.77; S, 15.47. Found: C, 63.70; H, 6.37; N, 6.82; S, 15.45.

(4S,5S)-3,4-Dimethyl-5-phenyloxazolidin-2-one (27)

This compound (55%) was prepared as for **23**. Oxazolidinone **27** had bp 150°/0.1 mm Hg; ir (film): 1757 cm^{-1} ; pmr (deuteriochloroform): δ 1.35 (d, $J = 6.1$ Hz, 3H), 2.85 (s, 3H), 3.52 (m, 1H), 4.88 (d, $J = 7.9$ Hz, 1H), 7.26 (m, 5H); cmr (deuteriochloroform): δ 14.2, 28.9, 56.9, 78.2, 126.1, 128.4, 128.4, 135.2, 158.0; ms: (m/z) 191 (M, 41), 117 (15), 57 (100); $[\alpha]_D = +36.7^\circ$ ($c = 0.98$, chloroform).

Anal. Calcd. for $\text{C}_{11}\text{H}_{13}\text{NO}_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.91; H, 6.94; N, 7.15.

Acknowledgement.

Financial support from URQUIMA, S. A. is gratefully acknowledged.

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