Pergamon

Tetrahedron: *Asymmetry* 12 (2001) 711–717

TETRAHEDRON: *ASYMMETRY*

A stereochemical study of optically active thiazolidines

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Received 1 December 2000; accepted 19 February 2001

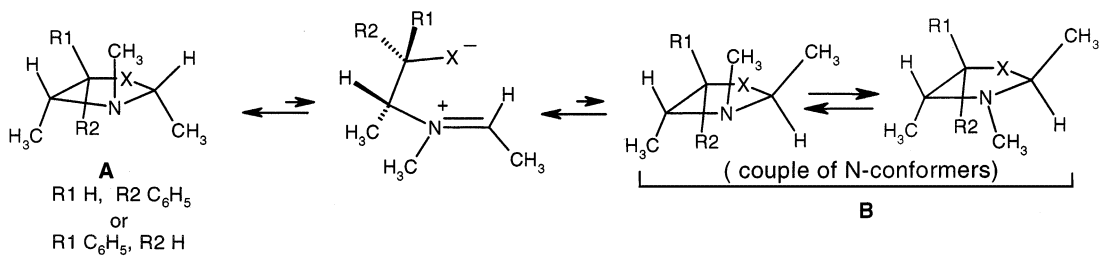
Abstract—We report a stereochemical study of a series of free *N*-H and *N*-methylated 1,3-thiazolidines bearing H or CH_3 at C-(2). These compounds were readily prepared from ephedrine and pseudoephedrines. The stereochemistry of the compounds under study was deduced using ^1H and ^{13}C NMR spectroscopy. Two isomers were found for compounds having a methyl group at C-(2) (i.e. C-(2)HCH_3); interconversion of these isomers, presumably via a non-cyclic zwitterionic intermediate, was observed.

1. Introduction

Optically active heterocycles derived from aminoalcohols[1] and aminothiols[2] are used as chiral inductors in asymmetric syntheses and, therefore, the study of their stereochemistry is of relevance. We are interested in the stereochemistry of ephedrine-derived heterocycles,[3] such as 1,3-oxazolidines and especially in the structures of their *N*-borane adducts, which we have been studying mainly by NMR spectroscopy. 1,3-Oxazolidines, bearing a substituent in the C-(2) position[3a–c] (C-(2)HR), exist as two isomers which differ in their C-(2) configuration and are in equilibrium with each other, as detailed in Scheme 1. Isomerisation may take place via a non-cyclic, short-lived, zwitterionic species. In the case of 2,3-dimethyl-1,3-oxazolidines (X = O), derived from ephedrine or pseudoephedrine, we have found that the C-(4)-methyl group determines the preferred configuration at the neighbouring nitrogen atom, with the *N*-methyl and the C-(4) methyl groups in *anti*-positions to each other. This, in turn, influences the configuration at C-(2).

In the preferred isomer (**A** in Scheme 1), the *N*-methyl group is oriented *anti* to the two *C*-methyl groups. Isomers **B** can have two conformers by inversion of the N atom. In 1,3-oxazolidines, isomers **B** are present only in very minor amounts and their structures cannot be easily studied. Furthermore, the corresponding *N*-H 1,3-oxazolidines are insufficiently stable in order to be used in conformational studies.

To further advance this work, we decided to analyse the behaviour of 1,3-thiazolidines in comparison with 1,3-oxazolidines and to revisit the stereochemistry of these heterocycles in general. The main aim was to compare *N*-methyl and *N*-H compounds (N.B. free *N*-H oxazolidines are unstable), and to investigate isomers of the type **B** (X = S).



Scheme 1. Proposed isomerisation pathway for C-(2) isomers in heteroazolidines; X = O or S atoms.

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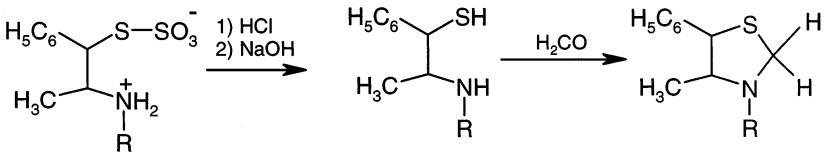
PII: S0957-4166(01)00117-3

2. Results and discussion

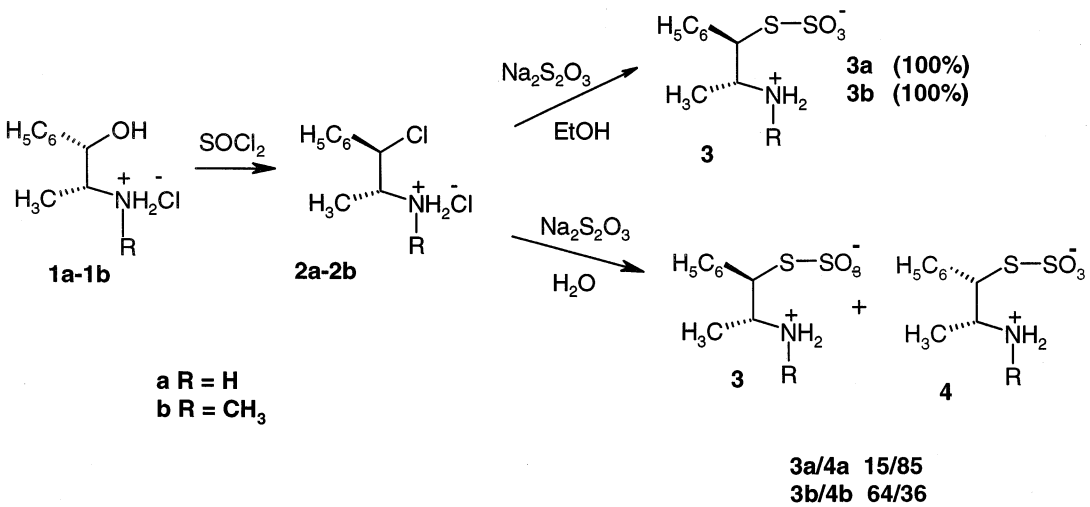
Herein, we describe the synthesis and stereochemistry of a series of 1,3-thiazolidines derived from ephedrines bearing different C-(2) substituents. In addition, we have found a stereoselective preparation of the *threo*-**3** and *erythro*-**4** isomers of the thiosulfonic deoxyephedrine derivatives. A synthetic route to 1,3-thiazolidines, starting from the respective aminothiols and formaldehyde, can be found in the literature[4] (Scheme 2). However, aminothiols oxidise readily to give the corresponding disulfides; thus, the reactions must be carried out under an inert atmosphere. Even under these conditions the yields of the disulfide products are poor.

We report here a simple method for the synthesis of 1,3-thiazolidines by the in situ reaction of thioephedrines with carbonyl compounds. The thiosulfonic amines **3a** and **3b** are available by treatment of the corresponding *threo*-isomers of the chlorodeoxyephedrine hydrochlorides **2a** and **2b** with anhydrous sodium thiosulfate in refluxing ethanol. In both reactions the configuration at C-(1) is retained completely, as was observed by NMR analyses. However, the same reaction for the chlorodeoxy-norpseudoephedrine hydrochloride **2a** in refluxing water afforded mainly *erythro*-isomers **3a** and **4a** in a 15:85 ratio, whereas the chlorodeoxy-pseudoephedrine hydrochloride **2b** gave isomers **3b** and **4b** in a 64:36 ratio (Scheme 3). Previously we reported that, in the course of the substitution reaction of chlorodeoxy-pseudoephedrines, retention of the C-(1) configuration results from double inversion via an aziridine intermediate.[3h] Presumably **4** arises from the reaction in water as the result of a competing S_N2 reaction where, because an aziridine intermediate is probably less solvated, the double inversion pathway is less favoured.

Acidic hydrolysis of the sulfonic acid group of compounds **3** and **4** in 30% aqueous HCl[3] afforded the corresponding aminothiol hydrochlorides (Table 1). In order to avoid their oxidation after neutralisation with 30% aqueous NaOH, the carbonyl compound (dissolved in $CHCl_3$) was added before the base and, under these conditions, cyclisation occurred without the formation of unwanted disulfides (Scheme 4).



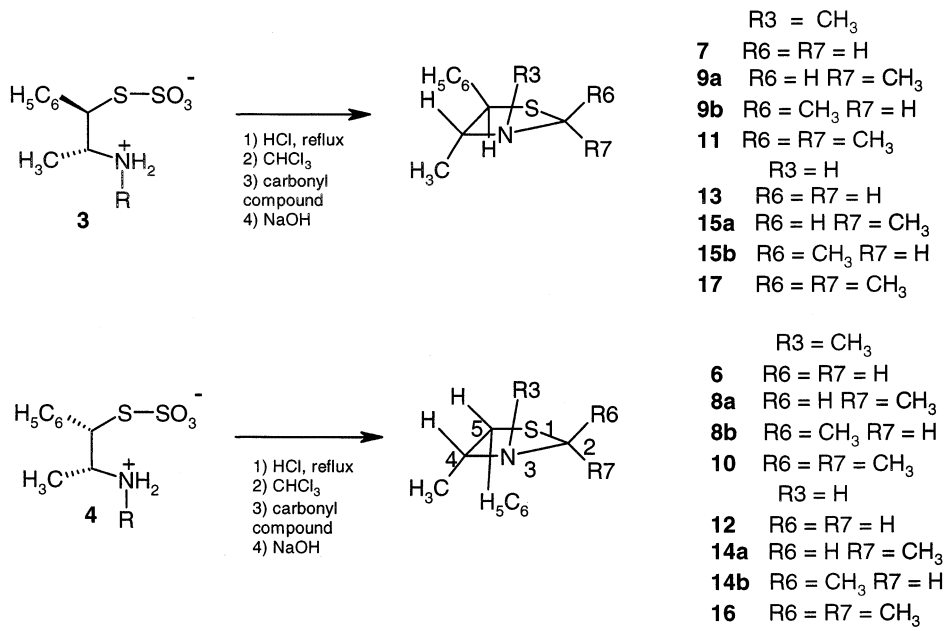
Scheme 2. Syntheses of thiazolidines.[4]



Scheme 3. Stereochemistry in the synthesis of amino thiosulfonic compounds.

Table 1. ^1H and ^{13}C NMR data of compounds **3** and **4**, δ ppm (J Hz)

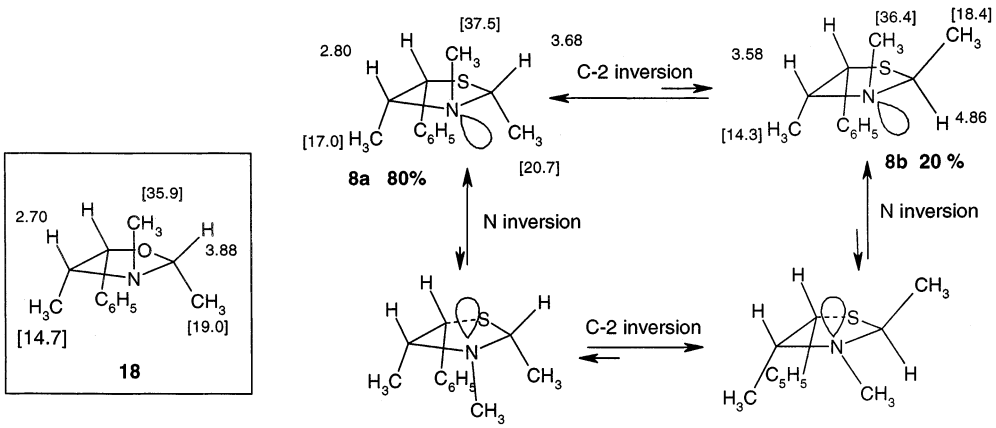
	H1 (d)	H2	CH3 (d)	N-CH_3	H-N	C_6H_5	C1	C2	C3	C4
3a	4.38 (8.6)	3.84	1.06 (6.5)		7.99	7.2–7.4	56.1	52.3	17.0	
4a	4.66 (3.3)	3.77	1.12 (6.6)		7.88	7.2–7.5	55.7	51.5	15.3	
3b	4.45 (8.8)	3.84, m	1.08, d (6.6)	2.64	8.63	7.2–7.4	59.3	54.9	14.1	31.3
4b	4.84 (3.2)	3.64, m	1.07, d (6.4)	2.68	8.41	7.2–7.4	59.5	54.3	12.8	32.0



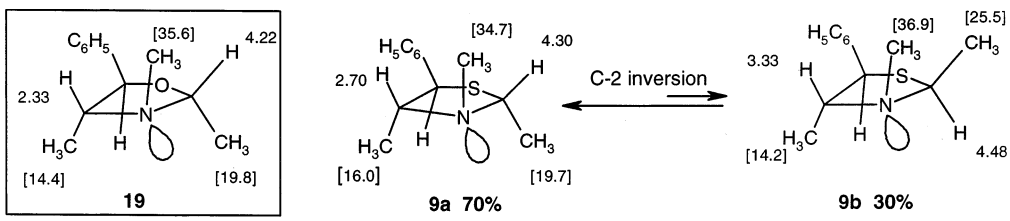
Scheme 4. Preparation of thiazolidines **7**–**17**.

The condensation of acetaldehyde with the respective aminothiols leads to two C-(2) isomers **a** and **b** in each case (compounds **8**, **9**, **14**, and **15**). Attempts to separate these isomeric mixtures by chromatography, recrystallisation and differential solubility failed and, since the ratio of both isomers remained constant in all experiments, the existence of an equilibrium is proposed, similar to that suggested previously for the analogous 1,3-oxazolidines[3a–c] (Scheme 1). Fortunately, in the case of the 1,3-thiazolidines, the second isomer **b** was present in an appreciable amount, thus allowing its solution-state structure to be elucidated (Schemes 5 and 6). In addition, the preparation of *N*-H compounds (*N*-H compounds **6**, **7**, **12**, and **13** have been previously reported by Kone and Gelbcke[4]) enabled direct comparison with the *N*-CH_3 analogues prepared in this study.

Structural assignments were based on the comparison with 1,3-oxazolidines using the steric effects exerted by



Scheme 5. Isomeric and conformational equilibrium for 2-methylthiazolidines **8a** and **8b**, with selected ^1H and [^{13}C] NMR data; analogous oxazolidine **18**[3a–c] is shown for comparison.



Scheme 6. Isomers **9a** and **9b**, and selected ^1H and [^{13}C] NMR data; analogous oxazolidine **19**[3a–c] is shown for comparison.

Table 2. ^{1}H NMR data of compounds **6–17**, δ (ppm) [J, Hz]

	H4	H5	R6	R7	CH_3	N-R	C_6H_5
6	3.17	4.72 [6.2]	3.79 [8.3]	4.45 [8.3]	0.74 [6.7]	2.47	7.15–7.50
7	2.85	4.10 [9.9]	4.15 [8.7]	4.40 [8.7]	1.24 [6.4]	2.40	7.10–7.50
8a	2.80	4.24 [6.2]	3.68	1.55 [5.8]	0.75 [6.6]	2.24	7.15–7.50
8b	3.58	4.99 [5.7]	1.52 [6.2]	4.86	0.75 [6.6]	2.40	7.15–7.50
9a	2.70	4.10 [9.4]	4.30	1.50 [5.9]	1.09 [6.9]	2.28	7.00–7.50
9b	3.33	4.16 [9.4]	1.64 [6.7]	4.48	1.08 [7.9]	2.39	7.00–7.50
10	3.32	4.19 [5.7]	1.42	1.69	0.73 [6.6]	2.21	7.00–7.50
11	3.00	4.05 [9.5]	1.54	1.54	1.01 [5.2]	2.20	7.10–7.40
12	3.37	4.49 [5.8]	4.26 [9.1]	4.53 [9.1]	0.86 [6.4]	2.10	7.20–7.50
13	3.10	3.92 [8.4]	4.37 [9.5]	4.50 [8.5]	1.23 [6.3]	2.25	7.20–7.50
14a	3.46	4.53 [5.8]	4.73	1.72 [6.2]	0.79 [6.6]	1.88	7.15–7.35
14b	3.71	4.59 [5.5]	1.54 [6.6]	4.99	0.81 [7.3]	1.88	7.15–7.40
15a	3.20	4.08 [8.9]	4.99	1.60 [6.2]	1.22 [6.4]	1.95	7.15–7.40
15b	3.40	4.10 [6.8]	1.68	4.83 [6.4]	1.20 [7.1]	1.95	7.15–7.40
16	3.84	4.60 [5.9]	1.66	1.86	0.82 [6.7]	2.12	7.15–7.35
17	3.45	4.12 [9.2]	1.78	1.70	1.19 [6.2]	2.11	7.14–7.44

methyl groups shielding the vicinal ^{13}C nuclei and the deshielding effect of the N-lone pair on vicinal ^{1}H nuclei.[3a–c]

Analysis of ^{1}H and ^{13}C NMR data for isomers **8a** and **8b** indicated that **8a** is the favoured isomer, its three methyl groups being in mutual *anti*-positions (Tables 2 and 3). This assumption is based on analogy with the corresponding 1,3-oxazolidine and the deshielding effect of the nitrogen lone pair (Scheme 5). Isomer **8b** exerts a deshielding effect on both the C-(2) and C-(4) protons, which can be attributed to a similar population of both *N*-methyl conformers. Steric effects exerted by the *N*-methyl group are reflected in the positions of the ^{13}C NMR signals of both the C-(2) and C-(4) methyl groups of **8b**. The same analysis can be applied to isomers **9a** and **9b** derived from pseudoephedrine.

The effect of the lone pair on the ^{1}H nuclear shielding of vicinal hydrogen atoms can be observed in compound **6**. In its favoured conformer, the two methyl groups are on opposite sides of the ring and one of the methyl groups is more strongly affected by the N-lone pair than the other (δ 4.45 and 3.79 ppm; Scheme 7). Comparison of **6** with the analogous *N*-H compound **12** shows that the nitrogen atom in **12** undergoes fast inversion, and that all three vicinal C–^{1}H nuclei are deshielded. On the other hand, the mutual steric shielding effects of the C-(2) and *N*-methyl groups are apparent in comparison of the ^{13}C NMR data of compounds **6** and **10**, and **10** and **16**.

Table 3. ^{13}C NMR data of compounds **6–17**, δ (ppm)

	C2	C4	C5	R6	R7	C-CH_3	N-CH_3
6	59.8	69.1	54.7			15.8	41.7
7	62.3	72.6	57.4			14.9	36.9
8a	67.4	68.5	53.5		20.7	17.0	37.5
8b	66.7	70.2	55.5	18.4		14.3	36.4
9a	68.8	73.3	57.3		19.7	16.0	34.7
9b	68.5	72.5	58.5	25.5		14.2	36.9
10	72.0	63.8	53.4	24.2	29.8	17.6	32.4
11	74.2	69.1	57.7	27.7	29.6	16.6	32.3
12	54.6	65.2	57.6			16.6	
13	54.8	69.6	62.8			17.0	
14a	65.4	64.8	59.7		21.3	16.7	
14b	64.4	62.3	60.1	25.4		16.0	
15a	65.8	69.9	65.8		21.4	17.0	
15b	64.7	66.8	64.7	25.4		17.8	
16	75.0	62.6	61.4	32.3	31.1	16.8	
17	74.9	67.5	66.5	33.8	31.8	17.1	

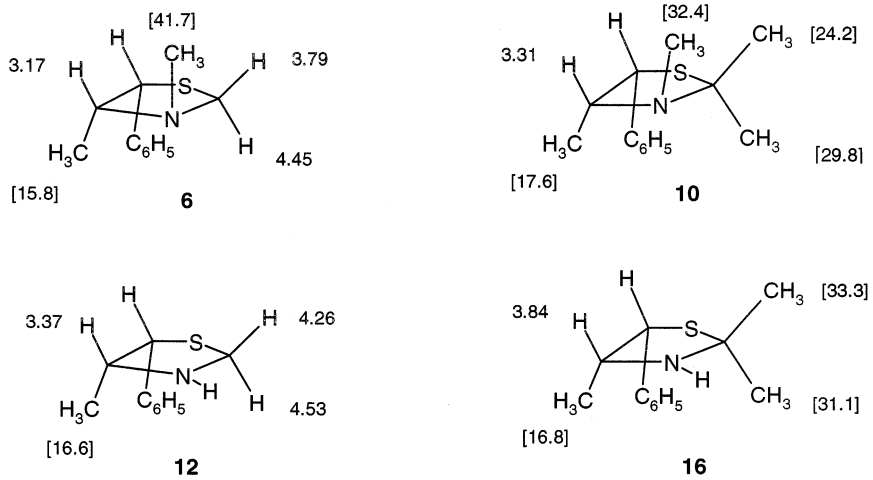
The *N*-H heterocycles **14** and **15** bearing a C-(2) methyl group (Scheme 8) have an isomeric ratio comparable to that of the *N*-methyl analogues. The signals for the C-(2) and C-(4) protons of **14a** and **15a** are shifted to higher frequencies with respect to those of **8a** and **9a**, respectively, indicating that N-lone pair inversion is rapid, and that both *N*-H conformers are present in similar concentrations.

These optically active thiazolidines **7–17** are suitable bases for the synthesis of stable *N*-BH_3 adducts, of which the synthesis and stereochemistry will be reported in due course.

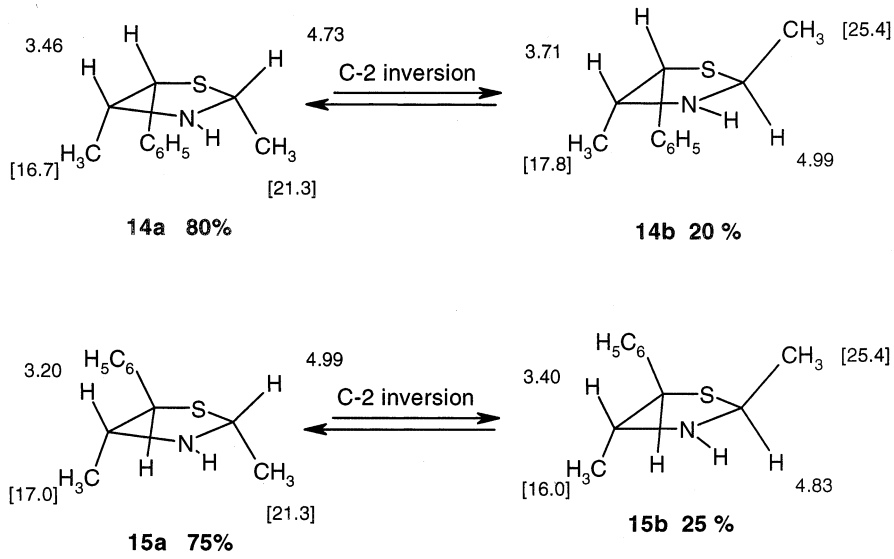
3. Conclusions

Substitution of oxygen in 1,3-oxazolidines by sulfur, to give 1,3-thiazolidines derived from ephedrines, allowed the effect of sulfur on the stereochemistry of the five-membered ring to be assessed. Structural analogies in heterocycles can be established, such as in 1,3-oxazolidines **18** and **19** versus 1,3-thiazolidines **8a** and **9a** according to the pronounced similarity of their NMR spectral data.

In contrast to 1,3-oxazolidines, 1,3-thiazolidines (with C-(2)-HR) exist as two stable isomers in a ratio that enabled the stereochemistry to be deduced from NMR data. Also, the series of *N*-H derivatives for the 1,3-thiazolidines, not available for the oxygen counterparts,



Scheme 7. Selected ^{1}H and [^{13}C] NMR data for compounds **6**, **10**, **12**, and **16**.



Scheme 8. Isomers of *N*-H thiazolidines (**14a**,**b** and **15a**,**b**), and selected ^{1}H and [^{13}C] NMR data.

made it possible to determine the effect of the *N*-substituent on the stereochemistry and conformational behaviour. The similar isomeric ratio of C-(2)-CH_3 compounds bearing *N*-H or *N*-methyl groups demonstrates that it is not the *N*-substituent that determines the formation of these isomers but the presence of oxygen or sulfur in the ring. It was also found that the more stable isomers for C-(2)-CH_3 compounds have a *cis*-arrangement of the C-(4)-CH_3 and C-(2)-CH_3 groups and an *anti*-arrangement of the *N*-CH_3 group.

4. Experimental

All reagents were of commercial quality and used without further purification. Solvents were freshly distilled before use following established procedures. Melting points were measured using a Gallenkamp apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra of 1,3-thiazolidines and thiosulfonic acids were recorded in $CDCl_3$ and DMSO-d_6, respectively, on Jeol GSX-270 and Jeol Eclipse 400 spectrometers. The EI mass spectra (20 eV) were obtained with an HP 5958 spectrometer. Compounds **2a** and **2b** were prepared as reported.[5]

4.1. (1*R*,2*R*)-Thiosulfonic deoxy-norpseudoephedrine acid 3a

To a solution of chlorodeoxy-norpseudoephedrine hydrochloride **2a** (14.6 g, 79.9 mmol) in dry ethanol (100 mL) was added sodium thiosulfate (15.15 g, 95.9 mmol) and the mixture was heated under reflux for 3 h. The reaction mixture was cooled to 0°C, and the precipitated sulfonic acid derivative was collected by filtration, washed with cold water and dried completely. A white solid was obtained (7.10 g, 63.6%);

mp 220–223°C; $[\alpha]_D = -197.92$ ($c = 19.3$ mg/10 mL, DMSO); ^{13}C NMR (DMSO-d_6) data for the phenyl group, δ (ppm): C_i 139.0, C_o 128.6, C_m 129.3, C_p 128.3.

4.2. (1*R*,2*R*)-Thiosulfonic deoxy-pseudoephedrine acid 3b

Compound **3b** was prepared from **2b** analogously to **3a**. White solid; 90% yield; mp 160°C (dec.); $[\alpha]_D = -146.3$ ($c = 15.0$ mg/10 mL, H_2O); ^{13}C NMR (DMSO-d_6) data for the phenyl group, δ (ppm): C_i 138.6, C_o 129.0, C_m 128.3, C_p 128.3.

4.3. (1*S*,2*R*)-Thiosulfonic deoxy-norephedrine acid 4a

To a solution of chlorodeoxy-norpseudoephedrine hydrochloride **2a** (7.77 g, 37.74 mmol) in water (100 mL) was added sodium thiosulfate (7.16 g, 45.3 mmol) and the reaction mixture was heated under reflux for 4 h. A slightly yellow precipitate was obtained, which was filtered off and washed with cold water (6.3 g, 67.6%); mp 219°C (dec.); $[\alpha]_D = +138.95$ ($c = 17.2$ mg/10 mL, DMSO); ^{13}C NMR (DMSO-d_6) data for the phenyl group, δ (ppm): C_i 138.7, C_o 129.2, C_m 128.8, C_p 128.2.

4.4. (1*S*,2*R*)-Thiosulfonic deoxy-ephedrine acid 4b

Compound **4b** was prepared from **2b** analogously to **4a**. A sticky solid was obtained, identified as a mixture (36:64) of the isomers **4b** and **3b**, respectively. The isomers were separated by selectively dissolving the *threo*-isomer **3b** in hot ethanol. The undissolved white solid was identified as the *erythro*-isomer **4b**; yield 30%; mp 140°C (dec.); $[\alpha]_D = +81.6$ ($c = 14.7$ mg/10 mL, DMSO); ^{13}C NMR (DMSO-d_6) data for the phenyl group, δ (ppm): C_i 139.2, C_o 129.6, C_m 129.0, C_p 128.6.

4.5. General procedure for the synthesis of 1,3-thiazolidines 6–17

The thiosulfonic compounds **3a**,**b** and **4a**,**b** were hydrolysed over 3 h at reflux with 30% aqueous HCl. The carbonyl compound (ketone or aldehyde), dissolved in $CHCl_3$, was added at rt, and the reaction mixture was stirred for 1 h (the reaction was performed at 0°C for aldehydes and at rt for ketones). $CHCl_3$ (140 mL) was added, followed by 30% aqueous NaOH, to give a pH of 8. The mixture was extracted with $CHCl_3$ and the organic extract washed with water, dried and evaporated. The crude compounds were purified by chromatography (column with silica gel 60) using $CHCl_3$ as the eluent.

4.6. (4*R*,5*S*)-2,2-Dihydro-3,4-dimethyl-5-phenyl-1,3-thiazolidine 6

Yellow liquid, 50% yield; $[\alpha]_D = -7.2$ ($c = 12.5$ mg/10 mL, $CHCl_3$); MS m/z (%): 193 (27) [M^+]; ^{13}C NMR ($CDCl_3$) data for the phenyl group, δ (ppm): C_i 139.41, C_o 129.1, C_m 128.1, C_p 127.0.

4.7. (4*R*,5*R*)-2,2-Dihydro-3,4-dimethyl-5-phenyl-1,3-thiazolidine 7

Yellow liquid, 65% yield; $[\alpha]_D = -7.4$ ($c = 17.5$ mg/10 mL, $CHCl_3$); MS m/z (%): 193 (18) [M^+]; ^{13}C NMR ($CDCl_3$) data for the phenyl group, δ (ppm): C_i 140.7, C_o 128.4, C_m 128.5, C_p 127.4.

4.8. (2*R*,4*R*,5*S*)-2-Hydro-2,3,4-trimethyl-5-phenyl-1,3-thiazolidine 8a and (2*S*,4*R*,5*S*)-2-hydro-2,3,4-trimethyl-5-phenyl-1,3-thiazolidine 8b

Yellow liquid, 80% yield. The product was a mixture (4:1) of C-(2) isomers **8a** and **8b**; MS m/z (%): 207 (10) [M^+]; ^{13}C NMR ($CDCl_3$) data for the phenyl group, δ (ppm): **8a**: C_i 142.1, C_o 129.7, C_m 127.8, C_p 127.0; **8b**: C_i 138.6, C_o 128.7, C_m 128.1, C_p 127.0.

4.9. (2*R*,4*R*,5*R*)-2-Hydro-2,3,4-trimethyl-5-phenyl-1,3-thiazolidine 9a and (2*S*,4*R*,5*R*)-2-hydro-2,3,4-trimethyl-5-phenyl-1,3-thiazolidine 9b

Brown liquid, 90% yield, which is a mixture of C-(2) isomers **9a**/**9b** in a 7:3 ratio. ^{13}C NMR ($CDCl_3$) data for the phenyl group δ (ppm), **9a**: C_i 140.5, C_o 128.6, C_m 128.5, C_p 128.5. **9b**: C_i 139.6, C_o 128.4, C_m 128.5, C_p 127.2.

4.10. (4*R*,5*S*)-2,2,3,4-Tetramethyl-5-phenyl-1,3-thiazolidine 10

The product was contaminated with the corresponding disulfide (30%), and so was only studied by NMR. ^{13}C NMR ($CDCl_3$) data for the phenyl group, δ (ppm): C_i 142.0, C_o 128.4, C_m 127.5, C_p 127.0.

4.11. (4*R*,5*R*)-2,2,3,4-Tetramethyl-5-phenyl-1,3-thiazolidine 11

Yellow liquid, 60% yield; $[\alpha]_D = +23.7$ ($c = 29.5$ mg/10 mL, $CHCl_3$); MS m/z (%): 221 (3) [M^+]; ^{13}C NMR ($CDCl_3$) data for the phenyl group, δ (ppm): C_i 140.2, C_o 128.8, C_m 128.6, C_p 127.5.

4.12. (4*R*,5*S*)-2,2,3-Trihydro-4-methyl-5-phenyl-1,3-thiazolidine 12

Yellow liquid, 81% yield; $[\alpha]_D = +55$ ($c = 13.10$ mg/10 mL, $CHCl_3$); MS m/z (%): 179 (27) [M^+]; ^{13}C NMR ($CDCl_3$) data for the phenyl group, δ (ppm): C_i 141.2, C_o 129.1, C_m 128.5, C_p 127.6.

4.13. (4*R*,5*R*)-2,2,3-Trihydro-4-methyl-5-phenyl-1,3-thiazolidine 13

Dark yellow solid, 68% yield; mp 46–50°C; $[\alpha]_D = -125.9$ ($c = 17.0$ mg/10 mL, $CHCl_3$); MS m/z (%): 179 (79) [M^+]; ^{13}C NMR ($CDCl_3$) data for the phenyl group, δ (ppm): C_i 140.7, C_o 128.6, C_m 128.1, C_p 127.3. Anal. calcd for $C_{10}H_{13}NS$: C, 66.94; H, 7.25; N, 7.81. Found: C, 66.54; H, 7.57; N, 7.30%.

4.14. (2*R*,4*R*,5*S*)-2,3-Dihydro-2,4-dimethyl-5-phenyl-1,3-thiazolidine 14a and (2*S*,4*R*,5*S*)-(−)-2,3-dihydro-2,4-dimethyl-5-phenyl-1,3-thiazolidine 14b

Greenish yellow liquid (90% yield), a mixture of C-(2) isomers **14a** and **14b** in a 3:1 ratio. MS *m*/*z* (%): 193.2 (10) [M$^+$]; ^{13}C NMR ($CDCl_3$) data of phenyl group, δ (ppm): **14a**: C_i 139.6, C_o 128.5, C_m 128.1, C_p 127.1; **14b**: C_i 141.2, C_o 128.8, C_m 128.1, C_p 127.1. Anal. calcd for $C_{11}H_{15}NS{\cdot}0.75H_2O$: C, 63.88; H, 8.04; N, 6.77. Found: C, 63.68; H, 7.54; N, 6.48%.

4.15. (2*R*,4*R*,5*R*)-2,3-Dihydro-2,4-dimethyl-5-phenyl-1,3-thiazolidine 15a and (2*S*,4*R*,5*R*)-(−)-2,3-dihydro-2,4-dimethyl-5-phenyl-1,3-thiazolidine 15b

Brown liquid (94% yield), composed of a mixture of the C-(2) isomers **15a** and **15b** in a 3:1 ratio. ^{13}C NMR ($CDCl_3$) data for the phenyl group, δ (ppm) **15a**: C_i 140.7, C_o 128.5, C_m 128.1, C_p 127.3; **15b**: C_i 140.8, C_o 128.5, C_m 128.0, C_p 127.3.

4.16. (4*R*,5*S*)-3-Hydro-2,2,4-trimethyl-5-phenyl-1,3-thiazolidine 16

Pale yellow solid, 44% yield; mp 51–54°C; $[\alpha]_D = -11.3$ ($c = 17.7$ mg/10 mL, $CHCl_3$); MS *m*/*z* (%): 207 (11) [M$^+$]; ^{13}C NMR ($CDCl_3$) data for the phenyl group, δ (ppm): C_i 140.8, C_o 128.8, C_m 128.2, C_p 127.1. Anal. calcd for $C_{12}H_{17}NS$: C, 69.56; H, 8.26; N, 6.76. Found: C, 68.43; H, 8.31; N, 6.38%.

4.17. (4*R*,5*R*)-3-Hydro-2,2,4-trimethyl-5-phenyl-1,3-thiazolidine 17

Pale yellow liquid, 43% yield; $[\alpha]_D = -146.15$ ($c = 19.5$ mg/10 mL, $CHCl_3$); MS *m*/*z* (%): 207 [M$^+$] (25); ^{13}C NMR ($CDCl_3$) data for the phenyl group, δ (ppm): C_i 139.8, C_o 128.2, C_m 128.6, C_p 127.4. Anal. calcd for $C_{12}H_{17}NS$: C, 69.56; H, 8.21; N, 6.76. Found: C, 68.75; H, 8.13; N, 6.71%.

Acknowledgements

A.C. is grateful for financial support from Conacyt Mexico (Grant No. 32190-E). The authors would like to thank Professor Bernd Wrackmeyer for the critical reading.

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