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Abstract: A simple and efficient approach to the synthesis of the new chiral hexahydropryrolo-[1’,2’,5’:3,4,5]thiazolo[3,4-c]oxazol-1-one ring system is reported. Infrared spectroscopy, quantum-chemical calculations and X-ray analysis allowed the stereochemistry assignment of (2aS,4aR,6aR)-2a,3,4,4a,6,6a-hexahydropyrrolo-[1’,2’,5’:3,4,5]thiazolo[3,4-c]oxazol-1-one.

Keywords: Hexahydro-pyrrolo[1’,2’,5’:3,4,5]thiazolo[3,4-c]oxazol-1-ones; L-Cysteine and D-Penicillamine derivatives, Matrix isolation, Infrared spectroscopy, DFT(B3LYP)/6-311++G(d,p) calculations.

INTRODUCTION

The construction of the hexahydropyrrolo[2,1-b][1,3]thiazole ring system (1) can be achieved via the Mannich condensation of L-cysteine ethyl hydrochloride with succindialdehyde and benzotriazole (Scheme 1) [1]. Compound 1 can be regarded as a masked iminium cation (2) and is reactive towards nucleophiles. In fact, 5-(1H-1,2,3-

Scheme 1.

benzotriazol-1-yl)hexahydropyrrolo[2,1-b][1,3]thiazole (1) undergoes nucleophilic substitution with a range of nucleophiles giving the 5-substituted-hexahydropyrrolo[2,1-b][1,3]thiazoles 3, in some cases with high diastereoselectivity. We anticipated that the condensation of L-cysteine with succinaldehyde would afford the iminium cation 2 (R=H), which is a potential precursor of azomethine ylide 5 via the decarboxylative approach.

It is known that cyclic α-amino acids such as 1,3-thiazolidine-4-carboxylic acids can be used for the generation of nonstabilized azomethine ylides by decarboxylative condensation with carbonyl compounds [2-10]. The involvement of an oxazolidin-5-one intermediate is strongly supported by the observation that 1,3-thiazolidine-4-carboxylic acid reacts with pivalaldehyde giving (2R,7aR)-3-tert-butyl-dihydro-thiazolo[3,4-c]oxazol-1-one selectively [11]. It has also been reported that L-cysteine reacts with paraformaldehyde to afford (R)-dihydro-thiazolo[3,4-c]oxazol-1-one in quantitatively yield [12]. The nonstabilized ylides can participate in both inter- and intramolecular 1,3-dipolar cycloaddition processes, originating a range of nitrogen heterocycles, including bridgehead heterocycles [2-10]. We set out to evaluate the viability of a route to...
azomethine ylides starting from bicyclic compounds such as the hexahydropyrrolo[2,1-b][1,3]thiazole 1 (R = H), whose 1,3-dipolar cycloaddition could lead to the synthesis of new tricyclic systems.

RESULTS AND DISCUSSION

Using the general procedure described in the literature [1] we carried out the condensation of L-cysteine with succindialdehyde (obtained in situ by treatment of 2,5-dimethoxytetrahydrofuran with 0.1 M HCl) in the presence of benzotriazole. The 5-(1H-1,2,3-benzotriazol-1-yl) hexahydropyrrolo[2,1-b][1,3]thiazole-3-carboxylic acid 6 was obtained as a diastereoisomeric mixture in 75% yield. We observed that by heating this mixture in dichloromethane a product was obtained in 61% yield together with the formation of benzotriazole. Based on the characterization data we could assign the structure of this product as being a hexahydropyrrolo[1',2',5':3,4,5]thiazolo[3,4-c]oxazol-1-one derivative 4. This result led us to study the direct condensation of L-cysteine with succindialdehyde, which afforded the same tricyclic compound 4 in 81% yield. It can be concluded that the iminium cation 7 is involved in both approaches and this intermediate undergoes an 5-endo-trig cyclization giving the new chiral tricyclic L-cysteine derivative 4 with [α]D 25 = + 30.0 (Scheme 2).

The (3R,5S,7aS) stereochemistry assignment of hexahydropyrrolo[2,1-b][1,3]thiazole 1 (R = Et) was based on NOE NMR experiments [1]. The authors observed NOE effect between H-3 and H-5 and no NOE effect was observed between H-7a with either H-3 or H-5. This led to the conclusion that H-3 and H-5 were in cis-orientation while H-3 and H-7a were in trans-orientation (see Scheme 1). The stereochemistry at C-3 and C-7a of derivates 6 and 1 should be the same and the chirality of these centers should be retained in the cyclization reaction of 6 leading to the tricyclic compound 4. However, the following discussion will demonstrate that H-3 and H-7a in compounds 6 and 1 must have cis-orientation.

Aiming to obtain data to support a proposal for compound 4 stereochemistry, quantum-chemistry calculations were carried out. The S and R configurations, at the C4 and C7 atoms have been considered as input structures of hexahydropyrrolo[1',2',5':3,4,5]thiazolo[3,4-c]oxazol-1-ones (PTO) with the R configuration preserved at the C2 atom, since PTO is obtained from an α-amino acid with R configuration (L-cysteine) while retaining chirality at this

![Scheme 2.](image_url)

**Fig. (1).** Optimized geometries of PTO stereoisomers. The numbers in parentheses denote zero-point corrected energies (in kJ mol⁻¹) relative to the most stable RSR stereoisomer.
carbon is (Fig. 1). Three minima of PTO have been located with the RSR, RSS and RRR configurations at C2, C4 and C7, respectively. Optimization of the RSS isomer resulted in breaking of the 1,3-thiazolidine ring and proton transfer to the sulfur atom. Therefore, we could conclude that this isomer is not stable in the gas-phase. The optimized structures of PTO stereoisomers are presented in Fig. (1). Different input configurations at C4 and C7 resulted in different geometries of the rings, significantly affecting the stability of the stereoisomers and leading to energies of the RSS and RRR isomers considerably higher than that of the RSR form (zero-point corrected relative energies equal to 59.2 and 69.4 kJ mol\(^{-1}\), respectively). In order to characterize in detail the reasons for such meaningful differences in the relative stabilities of the PTO stereoisomers, the energies of the pyrrolidine, 1,3-oxazolidin-5-one and 1,3-thiazolidine rings, which are the constituting building blocks of the ring-system of PTO were also calculated (Table I). These structures were built by detaching the corresponding fragment from the appropriate PTO stereoisomer and then hydrogen atoms were added in the place of the previously existing bonds with the adjacent rings. Only the lengths of the bonds associated with these hydrogen atoms were later subjected to geometry optimization. Additionally, the full geometry optimization of pyrrolidine, 1,3-oxazolidin-5-one and 1,3-thiazolidine was also performed in order to obtain the energy of the global minima of these compounds.

The energies of the three investigated five-membered rings assembled as described above were predicted by the calculations to be the lowest in the case of the RSR form, being only 12.4, 14.2 and 8.3 kJ mol\(^{-1}\) higher than those calculated for their global minima (pyrrolidine, 1,3-oxazolidin-5-one and 1,3-thiazolidine, respectively). The energy of the pyrrolidine ring was predicted to be 27.7 and 34.4 kJ mol\(^{-1}\) higher in the RSS and RRR PTO stereoisomers, respectively, when compared to that of the RSR form. This result can be directly correlated with the NH hydrogen atoms adopting the equatorial position in the two higher-energy forms. Nevertheless, it is the geometry of the 1,3-thiazolidine and of the oxazolidinone ring, respectively in RSS and RRR, which appears as the most important factor contributing to the higher energy of these forms relatively to the RSR stereoisomer. The calculated energies of these rings were higher than those predicted for the corresponding global minima by 64.0 and 63.9 kJ mol\(^{-1}\), respectively.

In its global minimum, as well as in the RSR and RSS PTO stereoisomers, the 1,3-oxazolidin-5-one ring approaches the \(1^\text{E(ax)}\) conformation (in RSR it is also close to planarity). On the other hand, the \(R\) configuration at the C4 atom in the RRR form induces considerable puckering of the 1,3-oxazolidin-5-one ring, which then adopts the \(5\text{T}_1\text{(ax)}\) conformation (C2-N3-C4-O1 and C3-C2-N3-C4 dihedral angles are equal to -48.1° and 38.8°, respectively). As the oxazolidinone ring is stabilized, partially due to delocalization of the electron density on C2 and O1, the geometry closer to planarity is favored. The puckering of the ring in the RRR stereoisomer, resulting mainly from the equatorial placement of the NH hydrogen atom, then produces the predicted significant destabilization of the molecule.

### Table 1. Energy Values [B3LYP/6-311++G(d,p)] for Stereoisomers of PTO and Separate Heterocyclic Rings Derived from PTO Stereoisomers (in kJ mol\(^{-1}\))

<table>
<thead>
<tr>
<th>Compound</th>
<th>RSR</th>
<th>RSS</th>
<th>RRR</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTO(^{a})</td>
<td>0.0</td>
<td>59.4 (59.2)</td>
<td>69.4 (69.4)</td>
</tr>
<tr>
<td>pyrrolidine(^{c})</td>
<td>12.4</td>
<td>40.1</td>
<td>46.8</td>
</tr>
<tr>
<td>1,3-oxazolidin-5-one(^{c})</td>
<td>14.2d</td>
<td>19.4</td>
<td>63.9</td>
</tr>
<tr>
<td>1,3-thiazolidine(^{c})</td>
<td>8.3d</td>
<td>64.0d</td>
<td>26.9d</td>
</tr>
</tbody>
</table>

\(^{a}\) Energies relative to the most stable stereoisomer (RSR). \(^{b}\) Zero-point corrected energy is given in parentheses; otherwise electronic energy without zero-point correction is given. \(^{c}\) Energies relative to the global minimum; structures were prepared by adding hydrogen atoms to the five-membered rings extracted from the original PTO stereoisomers’ structures; only the lengths of the bonds linking these added hydrogen atoms were subjected to subsequent optimization. \(^{d}\) First-order transition state.

Fig. (2). Comparison of the FT-IR spectra of PTO isolated in xenon (Xe) and argon (Ar) matrices with the spectra calculated for the PTO stereoisomers. The normal frequencies were scaled uniformly by 0.98. The bands due to traces of monomeric water are located in the 1630-1600 cm\(^{-1}\) range of experimental spectra. Calc. Int./km mol\(^{-1}\) denote calculated intensity.

The RSS stereoisomer is destabilized because it must adopt a geometry close to the \(2^\text{E(eq)}\) conformation of the 1,3-thiazolidine ring. Differently than for 1,3-oxazolidin-5-one, the equatorial position occupied by the NH hydrogen atom in the 1,3-thiazolidine ring is not the main reason for its destabilization, as this conformation is also adopted in
the global minimum of 1,3-oxazolidin-5-one [2Ts(eq)]. Although the geometry of the global minimum is twisted, while all others are close to the envelope conformation, the S1-C1-C2-N3 dihedral is far from planarity in all geometries, with the exception of the RSS form, where it equals 3.3°. Puckering of the S1-C1-C2-N3 plane was found to be important in the crystal structure of PTO, as well as in the crystal structure of 2,2′-Bi-1,3-thiazoline [13] (in both cases S1-C1-C2-N3 equals ca. 41-42°), stressing the importance of this factor in stabilizing the structure of the 1,3-thiazolidine ring.

It can be concluded that the co-existence in the RSR stereoisomer of PTO of close-to-minimum envelope conformations of both the pyrroline and 1,3-oxazolidin-5-one rings with the axial arrangement of the NH hydrogen atom and the conserved puckering of the S1-C1-C2-N3 plane determines the considerably higher stability of this stereoisomer when compared with the remaining isomers investigated.

In order to verify the computational predictions, the FT-IR spectra of PTO isolated in xenon (Xe) and argon (Ar) matrices were obtained, confirming the presence of the sole RSR stereoisomer (Fig. 2).

The structure of compound 4 was also determined by X-ray crystallography confirming the stereochemistry assignment (Fig. 3) [14-16]. Compound 4 crystallized in the chiral space group P2_12_1, with four symmetry related molecules in the unit cell. Each molecule has 3 chiral centers C2(R), C4(S) and C7(R) as confirmed by the Flack parameter that refined down to 0.03(6) [16]. The molecule exhibits a cup-shaped conformation with the N atom in the apical position and the five membered rings are arranged in envelope/twisted conformations. The calculated geometry for the RSR monomer and that of the monomeric unit in the crystal obtained by X-ray diffraction is similar, with the main difference noticed in the arrangement of the pyrrolidine ring. The arrangement of this ring in the crystal is approximately 4°T3, with the C5-C6-C7-N3 dihedral equal to -7.2(6)°, while in the RSR monomer it adopts the aE conformation, with the C7-N3-C4-C5 dihedral close to planarity (3.7°). As a consequence of the different arrangement of the pyrrolidine ring in the model system compared to the monomeric unit in the crystal, the dihedral angles of the pyrrolidine ring itself as well as the dihedral angles describing the spatial arrangement of the pyrrolidine ring in respect to the oxazolidinone and thiazolidine moieties (as, for example, O1-C4-C5-C6 and C5-C6-C7-S1) are also slightly different in the two datasets. In the solid state, due to the lack of conventional donors, only weak C-H...O intermolecular interactions join the molecules in chains, running along the b axis.

The selectivity of the tandem ring closure that leads to hexahydroypropolo[1′′,2′′,5′′:3,4,5]thiazololo[3,4-c]oxazol-1-one 4 can be explained considering the ring-chain tautomeric equilibria of the initial formed 1,3-thiazolidines (9) and the corresponding Schiff base 8, followed by a shift in this equilibrium towards 9a (Scheme 3). In fact, it is known that the acylation of a mixture of (2S,4R) and (2R,4R)-2-substituted-1,3-thiazolidine-4-carboxylic can lead to the selective synthesis of N-acetyl-2-substituted-1,3-thiazolidine-4-carboxylics and thiocarboxylic acids as pure stereoisomers with (2R,4R) or (2S,4R) stereochemistry depending on the reaction conditions. In fact, 2-substituted-1,3-thiazolidine-4-carboxylics can undergo selective inversion at C-2 through a mechanism involving the opening of the ring, but the protection with the acyl group prevents this epimerization and allows the isolation of pure diastereoisomers [17]. A similar chemical behavior can also explain the generation of iminium cation 10 from 1,3-thiazolidines 9. This intermediate (10) undergoes a 5-endo-trig cyclization giving selectively the tricyclic compound 4.

The reaction of D-penicillamine with succindialdehyde was also studied. The new (2αR,4αS,6αS)-6,6-dimethyl-2a,3,4,4a,6,6a-hexahydroypropolo[1′′,2′′,5′′:3,4,5]thiazololo[3,4-c]oxazol-1-one 11 was obtained as single stereoisomer in 80% yield (Scheme 4). This ring system can also be constructed via the synthesis of the corresponding 2,2-dimethyl-5-(1H-1,2,3-benzotriazol-1-yl)hexahydroypropolo[2,1-b]1,3-thiazole-3-carboxylic acid followed by its conversion into compound 11 with elimination of benzotriazole. In this case, an α-amino acid with S configuration was used leading to the chiral tricyclic compound with [α]_D _25 = -75.0.

CONCLUSION

In conclusion, we describe a one-pot synthesis of the new chiral hexahydroypropolo[1′′,2′′,5′′:3,4,5]thiazololo[3,4-c]oxazol-1-one ring system from α-amino acids (L-cysteine and D-penicillamine). The structure and vibrational spectrum of hexahydroypropolo[1′′,2′′,5′′:3,4,5]thiazololo[3,4-c]oxazol-1-one 4 were investigated in low-temperature matrices by infrared spectroscopy and by quantum-chemical calculations. The unambiguous assignment of this derivative was also based on X-ray analysis.

EXPERIMENTAL

^1H NMR spectra were recorded on a Bruker Avance 300 instrument operating at 300 MHz. ^13C spectra were recorded on a Bruker Avance 300 instrument operating at 75.5 MHz.
The solvent is deuteriochloroform except where indicated otherwise. IR spectra were recorded on a Perkin Elmer 1720X FTIR spectrometer. Mass spectra were recorded on a HP GC 6890/MSD5973 instrument under electron impact (EI) except where indicated otherwise. Optical rotations were measured on an Optical Activity AA-5 electrical polarimeter. Microanalyses were performed using an EA 1108-HNS-O Fisons instrument. Mp were recorded on a Reichert hot stage and are uncorrected. Flash column chromatography was performed with Merck 9385 silica as the stationary phase.

FT-IR spectra of the matrix-isolated PTO were recorded in the 400-4000 cm\(^{-1}\) range using a Mattson Infinity 60AR series FT-IR spectrometer, with 0.5 cm\(^{-1}\) resolution. Matrices were prepared by co-deposition, onto the cooled CsI substrate of the cryostat, of the argon or xenon isolant gas (argon, 99.9999 % and xenon, 99.995 %, obtained from Air Liquide) and the compound placed in a specially designed temperature variable mini-oven assembled inside the cryostat. The temperature of the mini-oven used to evaporate PTO was ca. 313 K. The selected temperature of the optical substrate (10 and 20 K for Ar and Xe, respectively) was obtained using an APD Cryogenics closed-cycle helium refrigeration system with a DE-202A expander. The temperature was measured directly at the sample holder by a silicon diode temperature sensor, connected to a digital controller (Scientific Instruments, Model 9650-1), with the accuracy of 0.1 K.

A solution of 2,3-dimethoxytetrahydrofuran (0.66 g, 5.1 mmol) and HCl aqueous solution (0.1 M, 20 mL) was heated to 100 °C for 45 mins, then cooled to room temperature. Dichloromethane (40 mL), benzotriazole (0.61 g, 5.1 mmol) and L-cysteine (0.6 g, 5 mmol) were successively added and stirred at room temperature for 24 h. The reaction mixture was washed with saturated Na\(_2\)CO\(_3\) solution and the aqueous phase was extracted with dichloromethane. The combined organic phase was washed with brine and dried over anhydrous Na\(_2\)SO\(_4\). After removal of the solvent the residue was washed with ethyl acetate, then with diethyl ether giving the 5-(1\(H\)-1,2,3-benzotriazol-1-yl)hexahydropyrrolo[2,1-\(b\)][1,3]thiazole-3-carboxylic acids as a diastereoisomeric mixture (65:35) in 75% yield. Mp 112.3-113.5 °C (Found: C, 53.7; H, 4.9; N, 18.7. C\(_{13}\)H\(_{14}\)N\(_4\)O\(_2\)S requires C, 53.8; H, 4.9; N, 19.3%). \(\nu\) (KBr) 1707, 1180 and 1102 cm\(^{-1}\). Major component: \(\delta\_H\) 2.18-2.45 (2H, m), 2.93-3.00 (2H, m), 3.46-3.57 (2H, m), 4.56 (1H, dd, \(J = 4.9\) and 8.1 Hz), 5.04 (1H, approx. d, \(J = 5.9\) Hz), 5.77 (1H, approx. t, \(J = 4.3\)), 7.43-7.54 (2H, m, Ar-H), 7.87-7.90 (2H, m, Ar-H); Minor component: \(\delta\_H\) 2.18-2.45 (2H, m), 2.71-2.88 (2H, m), 3.66-3.71 (2H, m), 4.41 (1H, dd, \(J = 3.2\) and 7.3 Hz), 5.23 (1H, approx. d, \(J = 5.9\)), 5.89 (1H, dd, \(J = 4.7\) and 7.4 Hz), 7.73-7.75 (2H, m, Ar-H).
8.09-8.12 (2H, m, Ar-H); m/z 172 [(M⁺-BrH), 36%], 120 (100) and 91 (25).

General Procedures for the Preparation of 2a,3,4,4a,6,6a-hexahydropyrrolo[1′,2′,5′:3,4,5]thiazolo[3,4-c]oxazol-1-ones

**Method 1**

A solution of the 5-(4H-1,2,3-benzotriazol-1-yl)hexahydropyrrolo[2,1-b][1,3]thiazole-3-carboxylic acid (3.4 mmol) in dichloromethane (20 mL) was heated at reflux for 20 h. The reaction mixture was washed with HCl aqueous (0.1 M) solution and the aqueous phase was extracted with dichloromethane. The combined organic phase was washed with brine and dried over anhydrous Na₂SO₄. After removal of the solvent the residue was purified by flash chromatography [ethyl acetate-hexane (1:1)].

**Method 2**

A solution of 2,3-dimethoxytetrahydrofuran (0.66 g, 5.1 mmol) and HCl aqueous solution (0.1 M, 20 mL) was heated to 100 °C for 45 mins, then cooled to room temperature. Dichloromethane (40 mL) and L-cysteine or D-penicillamine (5 mmol) were successively added and stirred at room temperature for 24 h. The reaction mixture was washed with saturated Na₂CO₃ solution and the aqueous phase was extracted with dichloromethane. The combined organic phase was washed with brine and dried over anhydrous Na₂SO₄. After removal of the solvent the hexahydropyrrolo[1′,2′,5′:3,4,5]thiazolo[3,4-c]oxazol-1-ones were obtained as solids.

**HPLC**

A solution of 2a,3,4,4a,6,6a-hexahydropyrrolo[1′,2′,5′:3,4,5]thiazolo[3,4-c]oxazol-1-one 4. Mp 99.3-100.2 °C (from ethyl acetate/hexane) (Found: C, 49.0; H, 5.0; N, 8.2. C₇H₆NO₃S requires C, 49.1; H, 5.3; N, 8.2%). δH (2H, m, J = 3.365 mm Hz), 2.44-2.32 (2H, m), 2.42-2.48 (2H, m), 3.45 (1H, dd, J = 5.9 and 12.2 Hz), 3.56 (1H, approx. d, J = 12.2 Hz), 4.12 (1H, approx. d, J = 5.9 Hz), 4.93 (1H, dd, J = 2.8 and 6.0 Hz), 5.55 (1H, approx. d, J = 5.0 Hz); δC 27.2, 31.4, 39.2, 67.1, 74.9, 98.4; m/z = 127 [M⁺-CO₂], 10%, 93 (100) and 65 (29). HRMS (CI⁺) m/z 172.0430 (C₁₃H₁₂NO₃S [MH⁺], requires 172.0432). [α] D² = +30 (c = 1.0, CH₂Cl₂).

**ORTEP** [14] diagram for (2a,S,4aR,6aR)-2a,3,4,4a,6,6a-hexahydropyrrolo[1′,2′,5′:3,4,5]thiazolo[3,4-c]oxazol-1-one 4: The displacement ellipsoids are drawn at the 50% probability level. Crystal data: C₂₅H₁₇NO₅S, M = 171.21, triclinic, a = 6.846(5) Å, b = 7.646(4) Å, c = 14.504(3) Å, V = 759.2(7) Å³, T=293(2) K, space group P2₁2₁2₁, Z = 4, (MoKα) = 3.365 mm⁻¹, 2203 reflections measured, of which 1144 unique (R int = 0.067), used for direct methods structure determination [15] and full matrix least-squares refinement [15]. The H atoms were placed at calculated idealized positions and refined as riding atoms. The final R (F²) was 0.056 (for I > 2σ(I)) and wR(F²) was 0.190 (for all reflections).

**COMPUTATIONAL METHODS**

The quantum chemical calculations were performed with Gaussian03 [18] using the B3LYP density functional [19,20] and the 6-311+G(d,p) basis set. The hexahydropyrrolo[1′,2′,5′:3,4,5]thiazolo[3,4-c]oxazol-1-one (PTO) structure may be considered to be built from three five-membered heterocyclic rings (pyrroline, 1,3-oxazolidin-5-one and 1,3-thiazolidine) connected by respective C-N bonds (Fig. 1). The compound has three chiral centers (C₂, C₄ and C₇ carbon atoms) allowing existence of diastereoisomers. The S and R configurations, at the C₄ and C₇ atoms has been considered as input structures of PTO with the R configuration preserved at the C₂ atom, since PTO is obtained from an α-amino acid with R configuration (L-cysteine) and the chirality at this carbon is retained. Electronic energies and vibrational frequencies were calculated for the title compound as well as for their ring constituting building blocks: pyrrolidine, 1,3-oxazolidin-5-one, and 1,3-thiazolidine.

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**REFERENCES**


