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Intermolecular Dipolar Cycloaddition Reactions of *5H,7H*-Thiazolo[3,4-*c*]oxazol-4-ium-1-olates

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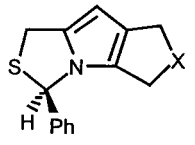
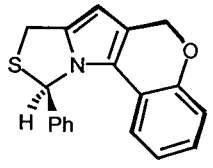
Abstract—(*5R*)-3-Methyl-5-phenyl-*5H,7H*-thiazolo[3,4-*c*]oxazol-4-ium-1-olate was generated in the presence of a range of dipolarophiles. The intermolecular 1,3-dipolar cycloaddition of this mesoionic species led to the synthesis of chiral *1H*-pyrrolo[1,2-*c*]thiazole derivatives **7a**, **7b**, **8**, **14**, **18, 19** and **20**. In the reaction with methyl and ethyl vinyl ketone, spiro compounds **9** and **15** were also obtained. The structure of compound **15** was determined by X-ray crystallography. © 2000 Published by Elsevier Science Ltd.

Introduction

We have recently described the use of *N*-acyl-2-phenyl-(*2R,4R*)-thiazolidine-4-carboxylic acids to generate *5H,7H*-thiazolo[3,4-*c*]oxazol-4-ium-1-olates with internal dipolarophiles.[1] The intramolecular 1,3-dipolar cycloaddition of these mesoionic species led to the synthesis of new chiral 3,4-dihydro-*1H*-pyrrolo[1,2-*c*]thiazole derivatives (**1** and **2**). The study was now extended to include intermolecular cycloaddition of this type of dipoles.



1a X = O
1b X = S



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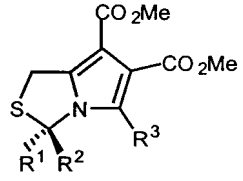

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Györgydeák et al.[2] have previously shown that chiral 3-substituted 3,4-dihydropyrrolo[1,2-*c*]thiazole-6,7-dicarboxylates (**3**) can be obtained with high enantiomeric excess from the reaction of diastereoisomerically pure 2-substituted-*N*-acetyl-1,3-thiazolidine-4-carboxylic acids with acetylenic dicarboxylates. The chirality at C-4 of the thiazolidine is lost and the chirality at C-2 (C-3 in the product) is retained.

Dipolar cycloaddition reactions of 5*H*,7*H*-thiazolo-[3,4-*c*]oxazol-4-ium-1-olate 6

In our work we observed that starting from 2-phenylthiazolidine-4-carboxylic acid (**4**) as a mixture of *2R,4R*- and *2S,4R*-diastereoisomers, chiral 3,4-dihydro-*1H*-pyrrolo[1,2-*c*]thiazole derivatives were obtained (Scheme 1). Compound **4** was heated in a solution of acetic anhydride in the presence of a dipolarophile. Under these reaction conditions the *N*-acylation occurs in situ, followed by an intermolecular dipolar cycloaddition via a mesoionic oxazolone intermediate. With dimethyl acetylenedicarboxylate compound **7a** was obtained in an overall yield of 75.5% (*R* configuration at C-3; $[\alpha]_D^{25}=+160$ and ee of 97.9%).

Compound **7a** was known in the literature and was prepared from (*2R,4R*)-2-phenyl-*N*-acetyl-1,3-thiazolidine-4-carboxylic acid.[2] According to our procedure the compound was obtained without requiring a diastereoisomerically pure compound as starting material. This result allowed us to conclude that the in situ acylation involved is a stereoselective synthesis of (*2R,4R*)-2-phenyl-*N*-acetyl-1,3-thiazolidine-4-carboxylic acid (**5**).

The intermolecular dipolar cycloaddition was also performed with the dipolarophile methyl propiolate giving exclusively the regioisomer **7b** (Scheme 1). The observed regioselectivity is consistent with that of other mesoionic

Keywords: dipolar cycloadditions; pyrrolo[1,2-*c*]thiazole; mesoionic species.
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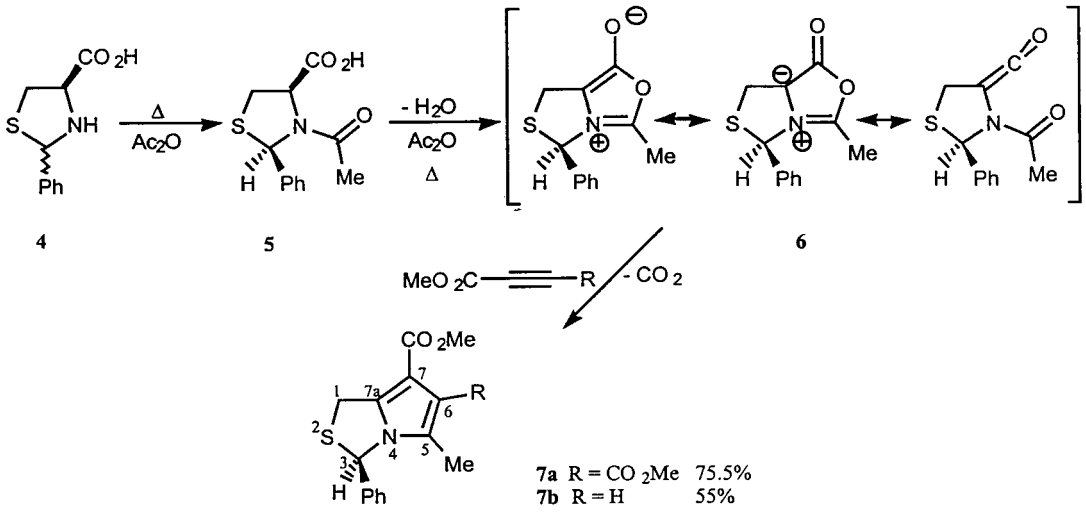
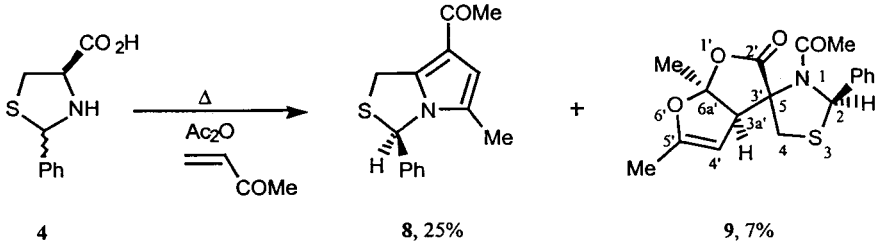


Scheme 1.



Scheme 2.

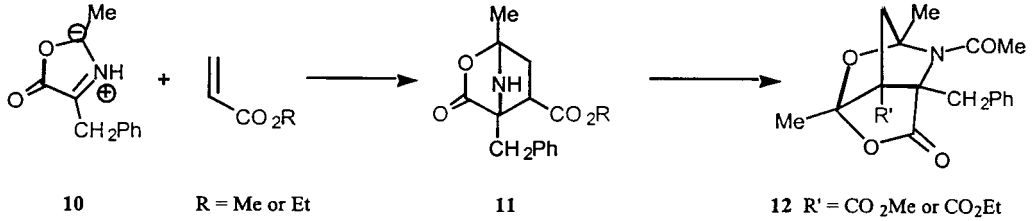
compounds of this type.[3] The product **7b** was obtained with *R* configuration at C-3 in 55% yield ($[\alpha]_D^{25}=+305$).

2-Phenylthiazolidine-4-carboxylic acid **4** was heated in acetic anhydride and methyl vinyl ketone was used as the dipolarophile (Scheme 2). In this case two products were obtained, the expected methyl (3*R*)-7-acetyl-3-phenyl-5-methyl-3,4-dihydro-*1H*-pyrrolo[1,2-*c*]thiazole **8** in 25% yield, and the spiro compound **9** in 7% yield. The structure of **9** was established by X-ray crystallography.[4]

It was observed by Texier et al.[5] that, in the cycloaddition of münchnone **10** with acrylates, the initially formed cycloadduct **11** does not lose CO_2 but instead undergoes a rearrangement giving product **12** (Scheme 3). If a similar rearrangement occurred in the reaction of mesoionic species **6** with methyl vinyl ketone, the analogous adduct would be compound **13** (Scheme 4). The observed product **9** could then be obtained by cleavage of **13** followed by a deacylation reaction whereby the acetyl group from methyl vinyl ketone would be lost.

In order to evaluate the above proposal, the reaction of **4** with ethyl vinyl ketone was performed. As expected, we obtained two products: the 3,4-dihydro-*1H*-pyrrolo[1,2-*c*]-thiazole derivative **14** in 10% yield and a spiro compound (**15**) in 8% yield (Scheme 5).

The structure of **15** was confirmed by X-ray crystallography (Fig. 1 and Table 1). The absolute structure was determined by a Flack analysis[6] that assigns the *R*,*R*,*R*,*S* configuration to the four chiral centers C2, C3′a, C5 and C6′a, respectively. The two furan rings are fused *cis*, the dihedral angle between the least-squares planes of these rings is 57.86(8)°. Both the dihydrofuran ring and the saturated furan ring deviate significantly from planarity, being slightly puckered towards C6′a- and C5-envelope conformations, respectively. The puckering parameters for the two rings as defined by Cremer et al.[7] are q_2=0.152(2) Å, ϕ_2=140.6(7)° and q_2=0.125 Å, ϕ_2=65.7°, the ϕ_2 angles for the pure envelope forms being 144 and 72°, respectively. The two Csp^3–O bonds in the furan ring system C6a′–O6′ and C6a′–O1 have practically identical values which are



Scheme 3. [5]

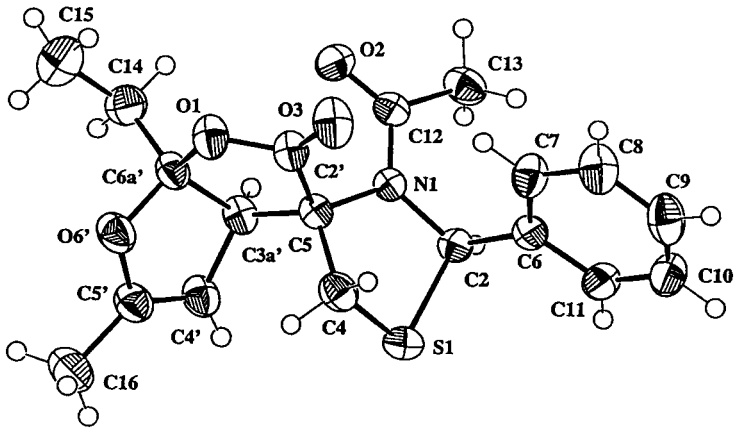


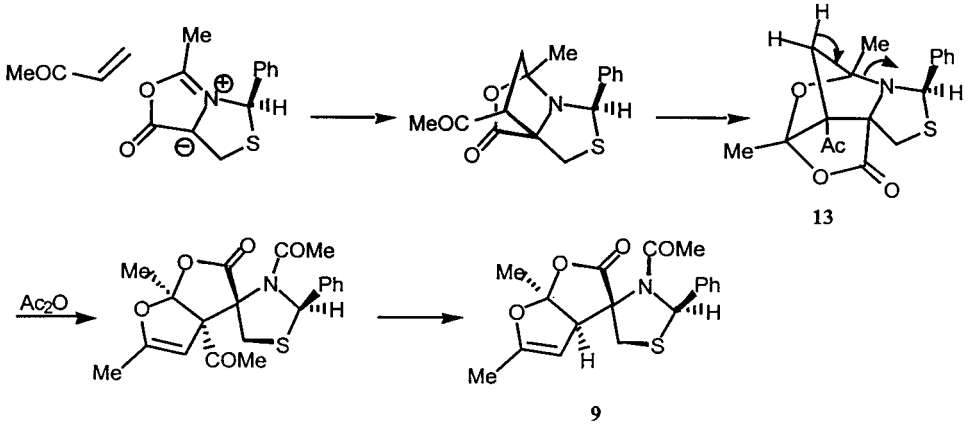
Figure 1. ORTEPII[9] plot of the molecule of compound **15**. Displacement ellipsoids are drawn at the 50% level.

Table 1. Selected bond lengths and angles (Å, °) for compound **15**

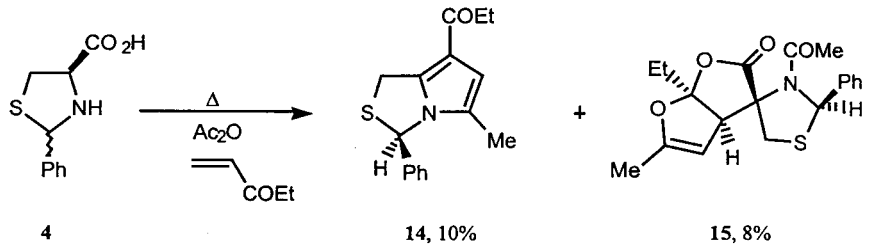
S1–C4	1.810(2)	C4′–C5′	1.313(3)	N1–C5–C4	105.26(14)
S1–C2	1.8273(17)	C4–S1–C2	89.10(8)	C2′–C5–C3a′	103.49(14)
O1–C2′	1.340(2)	C12–N1–C5	118.53(14)	O1–C2′–C5	110.91(14)
O1–C6a′	1.452(2)	C12–N1–C2	124.78(14)	C4′–C3a′–C6a′	101.17(14)
O6′–C5′	1.390(2)	C2′–O1–C6a′	111.97(14)	C5′–C4′–C3a′	110.06(17)
O6′–C6a′	1.438(2)	C5′–O6′–C6a′	106.67(14)	C4′–C5′–O6′	113.53(17)
C3a′–C4′	1.491(3)	N1–C2–S1	103.97(11)	O6′–C6a′–C3a′	106.09(15)

slightly shorter than the tabulated Csp^3–O(2) bonds in ring systems.[8] Comparing the lengths of the two C sp^2–O bonds C5′–O6′ and C2′–O1 with the tabulated value in furan [1.368 Å], there is a lengthening of the C5′–O6′ bond [1.395(3) Å] and a shortening of the C2′–O1 bond [1.351(3) Å].

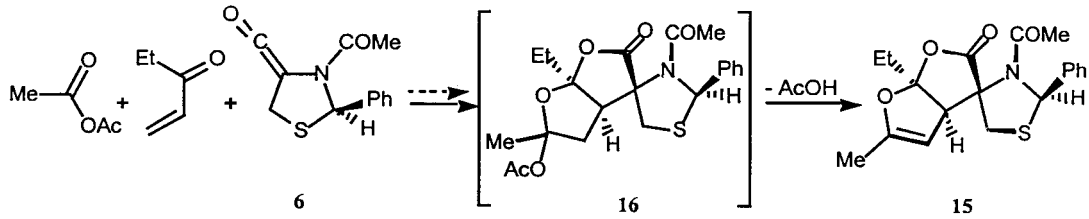
The thiazolidine ring has a twisted conformation with a local pseudo two-fold axis running through N1 and the middle of the C4–S1 bond. The two-fold asymmetry parameter[10] ΔC_2 [S1–C4] is 3.94(14)°. The puckering parameters[7] q_2 and ϕ_2 are 0.509(2) Å and 344.8(2)°. The phase angle ϕ_2 of the pure twisted conformation is 342°.



Scheme 4.



Scheme 5.



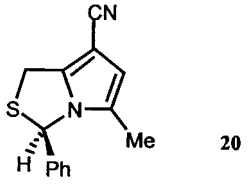
Scheme 6.

S1 and C4 are on opposite sides of the plane passing through C2, N1 and C5 at −0.500(5) and 0.370(5) Å, respectively. The values of the bond lengths S–C are in good agreement with tabulated value[8] and the bond angle C–S–C is close to the values observed in other thiazolidine compounds. The exocyclic angles around the N1 atom show some asymmetry. However, the sum of the valence angles around N1 is 359.8(3)°, indicating no significant pyramidalization of this atom. The environment of the spiro C5 atom is nearly tetrahedral, with bond angles in the range 105.23(15)–115.31(15)°. The phenyl ring has an axial position with respect to the thiazolidine ring with torsion angles −105.67(15)° [C5–N1–C2–C6] and 89.80(14)° [C4–C2–S1–C6]. The dihedral angle between the least-squares planes of the phenyl and thiazolidine rings is 81.19(7)°.

The geometry of the acetyl group is normal. It is almost coplanar with the thiazolidine group, the angle between the least-squares plane of the N1-acetyl group and that defined by N1 C2 and C5 is only 6.35(16)°. The short carboxyl C12═O2 bond is in agreement with an O atom not involved in hydrogen-bonding. In fact, cohesion of the crystal is mainly due to van der Waals interactions, with no classical hydrogen bonds present in the structure. Inspection of close contact distances shows that C7–H7···N1 [2.88(3) Å] and C15–H15C···O1 [2.893(3) Å] may correspond to weak intermolecular interactions which are probably relevant in determining the crystal packing.

These results rule out the mechanism outlined in Scheme 4, because it should lead to a product without an ethyl group. Taking into account this new observation it seems more likely that the mechanism involves the formation of the mesoionic species **6** which reacts with ethyl vinyl ketone and acetic anhydride to give the intermediate **16** which leads to the spiro compound on eliminating acetic acid (Scheme 6).

The intermolecular dipolar cycloaddition of *5H,7H*-thiazolo-[3,4-*c*]oxazol-4-ium-1-oxide with acrylonitrile was also studied (Scheme 7). A 1:1 mixture of compounds **18** and **19** was obtained in low yield. In this case the initially formed dipolar cycloadduct does not lead to the aromatization to the pyrrole ring, which requires oxidation with DDQ to give the 3,4-dihydro-*1H*-pyrrolo[1,2-*c*]thiazole derivative **20**.



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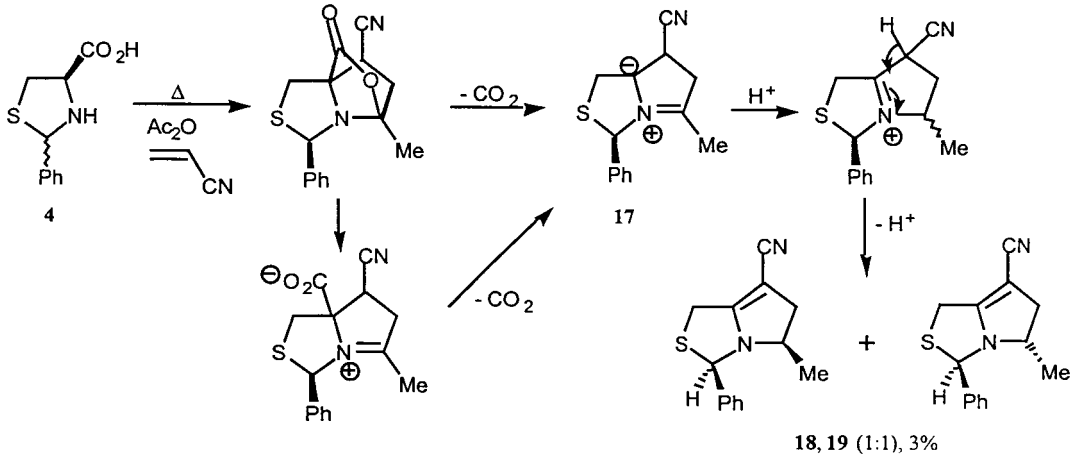
In the intermolecular dipolar cycloaddition of münchnones the primary cycloadducts are not usually isolable, because the carbon dioxide is easily eliminated, giving products with higher unsaturation with loss of information concerning the mechanism. However, Maryanoff et al. described the dipolar cycloaddition of 1,2-dicyanocyclobutene with münchones and showed that the extrusion of carbon dioxide from the primary adducts is not a concerted process, giving carboxylic acid derivatives as intermediates.[11] Thus, the elimination of carbon dioxide does not need to be a concerted process, allowing a mechanism of formation of compound **18** and **19** as described in Scheme 7. The initially formed cycloadduct can lose CO_2 either by a concerted process or by a stepwise process, giving azomethine ylide **17** which is converted into the final products.



Scheme 7.

Conclusions

The study of the intermolecular 1,3-dipolar cycloaddition of (*5R*)-3-methyl-5-phenyl-*5H*,*7H*-thiazolo[3,4-*c*]oxazol-4-ium-1-olate led to the synthesis of 1*H*-pyrrolo[1,2-*c*]thiazole derivatives as single enantiomers. The results showed that it is necessary to use strongly activated dipolarophiles in order to obtain efficient cycloadditions. From this study the synthesis of new spiro compounds was also achieved.

Experimental

General

^{1}H NMR spectra were recorded on a Brucker ACE200 spectrometer operating at 200 MHz (where indicated) or on a Brucker AMX300 instrument operating at 300 MHz. ^{13}C NMR spectra were recorded on a Brucker AMX300 instrument operating at 75.5 MHz. The solvent is deuteriochloroform. IR spectra were recorded on a Perkin–Elmer 1720X FTIR spectrometer. Mass spectra were recorded under electron impact at 70 eV on a VG Micromass 7070E instrument. Optical rotations were measured on an Optical Activity AA-5 electrical polarimeter. Mp were recorded on a Reichert hot stage and are uncorrected. Flash column chromatography was performed with Merck 9385 silica as the stationary phase. Methyl 2-phenylthiazolidine-4-carboxylate **4** was prepared as described in the literature[12] and was isolated as a mixture of the (*2R*,*4R*) and (*2S*,*4R*) diastereoisomers.

Dimethyl (3*R*)-5-methyl-3-phenyl-3,4-dihydro-*1H*-pyrrolo-[1,2-*c*]thiazole-6,7-dicarboxylate 7a. 2-Phenylthiazolidine-4-carboxylic acid **4** (1.045 g, 5 mmol), dimethylacetylene dicarboxylate (0.9 mL, 7.5 mmol) and Ac_2O (20 mL) were heated at 95–100°C for 4 h. The reaction was cooled to room temperature and was diluted with CH_2Cl_2 (50 mL). The organic phase was washed with saturated aqueous solution of $NaHCO_3$ and with water, dried (Na_2SO_4) and evaporated off. The crude product was purified by flash chromatography [hexane–ethyl acetate (3:1)] giving compound **7a** as a white solid (75.5%); mp 149–151°C (mp[2] 163–165°C) (Found; C, 61.2; H, 5.2; N, 3.9. Calcd for $C_{17}H_{17}NO_4S$ C, 61.6; H, 5.2; N, 4.6); δ_H 2.01 (3 H, s), 3.83 (3H, s), 4.31 (1H, d, J=15.0 Hz), 4.48 (1H, dd, J=15.0 and 1.5 Hz), 6.28 (1H, d, J=1.5 Hz), 7.04–7.07 (2H, m, ArH) and 7.26–7.36 (3H, m, ArH); δ_C 11.44, 30.01, 51.41, 51.58, 64.90, 106.77, 125.58, 128.99, 129.25, 130.73, 140.08, 140.51, 164.30 and 165.30; $[\alpha]_D^{25}$+160 (c=1, $CHCl_3$).

Methyl (3*R*)-5-methyl-3-phenyl-3,4-dihydro-*1H*-pyrrolo-[1,2-*c*]thiazole-7-carboxylate 7b. 2-Phenylthiazolidine-4-carboxylic acid **4** (1.045 g, 5 mmol), methyl propiolate (0.75 mL, 7.5 mmol) and Ac_2O (20 mL) were heated at 95–100°C for 4 h. The reaction was cooled to room temperature and was diluted with CH_2Cl_2 (50 mL). The organic phase was washed with saturated aqueous solution of $NaHCO_3$ and with water, dried (Na_2SO_4) and evaporated off. The crude product was purified by flash chromatography [hexane–ethyl acetate (3:1), hexane–ethyl acetate(1:1), then ethyl acetate] giving compound **7b** (55%); mp 87–89°C (from ethyl ether–hexane) (Found; C, 66.3; H, 5.7; N, 5.1; S, 11.5. $C_{15}H_{15}NO_2S$ requires C, 65.9; H, 5.5; N, 5.1; S, 11.7); δ_H 2.17 (3H, s), 3.78 (3H, s), 4.01 (1H, d, J=13.1 Hz), 4.26 (1H, d, J=13.1 Hz), 6.25 (1H, s), 6.32 (1H, s) 6.97–7.02 (2H, m, ArH) and 7.28–7.35 (3H, m, ArH); δ_C 11.80, 28.13, 50.78, 63.87, 101.60, 116.53, 125.33, 128.57, 129.06, 131.90, 133.08, 141.06 and 165.77; $[\alpha]_D^{25}$=+305 (c=1, $CHCl_3$).

(3*R*)-7-Acetyl-5-methyl-3-phenyl-3,4-dihydro-*1H*-pyrrolo-[1,2-*c*]thiazole 8 and (*R*)-spiro[(2*R*)-*N*-acetyl-2-phenyl-1,3-thiazolidine-5,3′-(3a′*R*,6a′*S*)-5′,6a′-dimethyl-3a′6a′-dihydro-*3H*-furo[2,3-*b*]furan-2-one] 9. 2-Phenylthiazolidine-4-carboxylic acid **4** (0.52 g, 2.5 mmol), methyl vinyl ketone (1 mL, 12.5 mmol) and Ac_2O (10 mL) were heated at 95–100°C for 12 h. The reaction was cooled to room temperature and was diluted with CH_2Cl_2 (25 mL). The organic phase was washed with saturated aqueous solution of $NaHCO_3$ and with water, dried (Na_2SO_4) and evaporated off. The products were isolated by flash chromatography [hexane–ethyl acetate (3:1), hexane–ethyl acetate (1:1) then ethyl acetate]: compound **8** was obtained in 25% yield and compound **9** in 7% yield.

Compound 8 was an oil: IR 2924, 1717, 1686, 1653 and 1240 cm^{-1}; δ_H 1.83 (3H, s), 2.38 (3H, s), 4.38 (1H, d, J=15.0 Hz), 4.54 (1H, dd, J=15.0 and 1.9 Hz), 6.27 (1H, d, J=1.9 Hz), 6.33 (1H, s), 7.05–7.1 (2H, m, ArH) and 7.31–7.38 (3H, m, ArH); HRMS (EI+): found 257.0874. $C_{15}H_{15}NOS$ requires 257.0874; $[\alpha]_D^{25}$=+192.3 c=0.1, $CHCl_3$).

Compound 9. Mp 202–205°C (from hexane–ethyl acetate) (Found; C, 62.62; H, 5.67; N, 4.02; S, 9.30. $C_{18}H_{19}NO_4S$ requires C, 62.59; H, 5.54; N, 4.06; S, 9.28); IR (KBr) 3020, 2940, 1788 and 1655 cm^{-1}; δ_H 1.87 (6H, m, CH_3CO and CH_3CH=), 1.90 (3H, s, CH_3), 3.09 (1H, d, J=12.1 Hz, H-4), 3.37 (1H, d, J=12.1 Hz, H-4), 3.47 (1H, m, H-3a′), 4.93 (1H, m, H-4′), 5.99 (1H, s, H-2), 7.30–7.35 (1H, m, ArH), 7.40–7.47 (2H, m, ArH) and 7.63–7.66 (2H, m, ArH); *m/z* 345 (M^+, 23%), 302 (25), 179 (48) and 148 (53).

(3*R*)-7-Propionyl-5-methyl-3-phenyl-3,4-dihydro-*1H*-pyrrolo[1,2-*c*]thiazole 14 and (*R*)-spiro[(2*R*)-*N*-acetyl-2-phenyl-1,3-thiazolidine-5,3′-(3a′*R*,6a′*S*)-5′-methyl-6a′-phenyl-3a′,6a′-dihydro-*3H*-furo[2,3-*b*]furan-2-one] 15. 2-Phenylthiazolidine-4-carboxylic acid **4** (2.09 g, 10 mmol), ethyl vinyl ketone (5.5 mL, 50 mmol) and Ac_2O (40 mL) were heated at 95–100°C for 12 h. The reaction was cooled to room temperature and was diluted with CH_2Cl_2 (25 mL). The organic phase was washed with saturated aqueous solution of $NaHCO_3$ and with water, dried (Na_2SO_4) and evaporated off. The products were isolated by flash chromatography [hexane-ethyl acetate (3:1), hexane-ethyl acetate (1:1) then ethyl acetate]: compound **14** was obtained in 10% yield and compound **15** in 8% yield.

Compound 14 was an oil: δ_H 1.19 (3H, t, J=7.2 Hz), 1.84 (3H, s), 2.75 (2H, q, J=7.2 Hz), 4.39 (1H, d, J=15.1 Hz), 4.56 (1H, d, J=15.1 Hz), 6.26 (1H, s), 6.34 (1H, s), 7.05–7.08 (2H, m, ArH), 7.30–7.36 (3H, m, ArH); HRMS (EI+):

found 271.1028. $C_{16}H_{17}NOS$ requires 271.1031; $[\alpha]_D^{25}$= +300.0 (c=0.1, $CHCl_3$).

Compound 15. Mp 189.8–191.9°C. δ_H 1.02 (3H, t, J=7.4 Hz), 1.89 (6H, m, CH_3CO and CH_3CH=), 2.24 (2H, m, CH_2CH_3), 3.10 (1H, d, J=12.1 Hz, H-4), 3.37 (1H, d, J=12.1 Hz, H-4), 3.49 (1H, m, H-3a′), 4.94 (1H, m, H-4′), 5.98 (1H, s, H-2), 7.30–7.35 (1H, m, ArH), 7.40–7.45 (2H, m, ArH) and 7.63–7.66 (2H, m, ArH); δ_C 13.6, 22.8, 29.7, 35.6, 55.8, 65.7, 74.4, 94.4, 117.1, 125.4, 128.3, 129.3, 141.5, 156.8, 168.9 and 173.2; m/z 360 (MH^+, 2%), 148 (44), 122 (100), 110 (47) and 77 (8).

(3*R*,5*S*)-7-Cyano-5-methyl-3-phenyl-3,4,5,6-tetrahydro-*1H*-pyrrolo[1,2-*c*]thiazole-7-carboxylate 18 and (3*R*,5*R*)-7-cyano-5-methyl-3-phenyl-3,4,5,6-tetrahydro-*1H*-pyrrolo-[1,2-*c*]thiazole-7-carboxylate 19. 2-Phenylthiazolidine-4-carboxylic acid **4** (6.0 g, 28.7 mmol), acrylonitrile (9.5 mL, 143.5 mmol) and Ac_2O (120 mL) were heated at 95–100°C for 16 h. The reaction was cooled to room temperature and was diluted with CH_2Cl_2 (200 mL). The organic phase was washed with saturated aqueous solution of $NaHCO_3$ and with water, dried (Na_2SO_4) and evaporated off. The crude product was purified by flash chromatography [hexane–ethyl acetate (1:1), hexane–ethyl acetate (1:2) then ethyl acetate] giving a mixture (56:44) of compounds **18** and **19** (3%). mp 96–99°C (from hexane–ethyl acetate). (Found; C, 69.03; H, 5.78; N, 11.34. $C_{14}H_{14}N_2S$ requires C, 69.39; H, 5.82; N, 11.56); IR (Nujol) 2190 and 1620 cm^{-1}; δ_H (major component) 1.14 (3H, d, J6.3 Hz), 2.67–2.77 (1H, m), 3.25–3.34 (1H, m), 3.55–3.64 (1H, m), 3.77–3.99 (2H, m), 5.57 (1H, s, C*H*Ph) and 7.26–7.47 (5H, m, ArH); δ_H (minor component) 0.84 (3H, d, J=6.3 Hz), 2.67–2.77 (1H, m), 3.14 (1H, approx. dd, J=9.6 and 14.4 Hz), 3.66–3.74 (1H, m), 3.77–3.99 (2H m), 5.14 (1H, s, C*H*Ph) and 7.26–7.47 (5H, m, ArH); m/z 242 (M^+, 60%), 165 (26), 121 (100), 105 (31) and 77 (20).

Oxidation of the mixture (**18** and **19**) with DDQ led to the formation of **(3*R*)-7-cyano-5-methyl-3-phenyl-3,4-dihydro-1*H*-pyrrolo[1,2-*c*]thiazole 20**. δ_H 1.81 (3H, s, CH_3), 4.21 (1H, d, J=14.1 Hz), 4.42 (1H, d, J=14.1 Hz), 6.20 (1H, s, C*H*Ph), 6.29 (1H, s), 7.06–7.08 (2H, m, ArH), 7.35–7.37 (3H, m, ArH).

Crystal data for $C_{19}H_{21}NO_4S$ 15. M=359.44, orthorhombic, space group $P2_12_12_1$ (# 19), a=5.944(2), b=16.251(2), c=18.664(3) Å, V=1802.8(8) Å^3, Z=4, D_c=1.324 g cm^{-3}, F_{000}=460, μ=0.20 cm^{-1}, T=296 K. Number of independent intensities 3033 from colourless prism, 0.32×0.37×0.59 mm^3. No absorption correction was applied and no significant crystal decay was detected. Structure solution by direct methods using SHELXS97.[13] R=0.0271 for 2836 reflections with $I>2\sigma$, R_w=0.0803 for 3033 reflections used in the refinement and 230 variable parameters. H-Atoms were placed at calculated positions except those of the methyl groups which were determined from a Fourier difference synthesis and refined as riding on their parent atoms. X-Ray measurements were performed on a Enraf–Nonius CAD-4 diffractometer[14] using $\omega-2\theta$ scans up to θ_{max}=25.07°. Atomic coordinates, bond lengths and angles and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre.

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References

1. Pinho e Melo, T. M. V. D.; Barbosa, D. M.; Ramos, P. J. R. S.; Rocha Gonsalves, A. M. d'A.; Gilchrist, T. L.; Beja, A. M.; Paixão, J. A.; Silva, M. R.; Alte da Veiga, L. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1219–1223.
2. Györgydeák, Z.; Szilágyi, L.; Kajtár, J.; Argay, G.; Kálmán, A. *Monatsh. Chem.* **1994**, *125*, 189–208.
3. Coppola, B. P.; Noe, M. C.; Hong, S. S.-K. *Tetrahedron Lett.* **1997**, *38*, 7159–7162.
4. Silva, M. R.; Beja, A. M.; Paixão, J. A.; Alte da Veiga, L.; Barbosa, D. M.; Soares, M. I. L.; Pinho e Melo, T. M. V. D.; Rocha Gonsalves, A. M. d'A. *Acta Crystallogr. C* **1999**, *55*, 1094–1096.
5. Texier, F.; Yebdri, O.; Laidoudi, A.; Talbi, B.; Balegroune, F.; Germain, G. *Tetrahedron Lett.* **1983**, *24*, 189–192.
6. Flack, H. D. *Acta Crystallogr. A* **1983**, *39*, 876–881.
7. Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354–1358.
8. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–19.
9. Johnson, C. K. ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA, 1976.
10. Duax, W.; Weeks, C. M.; Roher, D. C. In *Topics in Stereochemistry*, Eliel, E. L., Allinger, N., Eds.; Wiley: New York, 1976; vol. 9, pp 271–383.
11. Maryanoff, E. A.; Karash, C. B.; Turchi, I. J.; Corey, E. R.; Maryanoff, B. E. *J. Org. Chem.* **1989**, *54*, 3790–3792.
12. Gilchrist, T. L.; Rocha Gonsalves, A. M. d'A.; Pinho e Melo, T. M. V. D. *Tetrahedron* **1994**, *50*, 13709–13724.
13. Sheldrick, G. M. SHELXS97, a program for the solution crystal structures. University of Göttingen, Germany, 1997.
14. Enraf Nonius, CAD4 Software, Version 5.0, Enraf Nonius, Delft, The Netherlands, 1989.