Supporting Information

***N*-Vinyl- and *C*-Vinylpyrroles from Azafulvenium methides. Flash Vacuum Pyrolysis Route to 5-Oxo-5*H*-pyrrolizines and 1-Aza-benzo[*f*]azulenes**

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Table 1. – Selected chemical shifts (¹H NMR in CDCl₃) for 5-oxo-5*H*-pyrrolizines.

5-Oxo-5 <i>H</i> -pyrrolizines	Me at C-1	Me at C-3
5a	2.11	2.57

5b	2.22	2.70
16a	2.13	2.63
35	-----	2.68
16b	2.24	-----
16c	-----	2.71

Table 2. Sealed tube reactions using sulfolane as solvent.

Starting Compound	Reaction Conditions	Products
2a	260 °C, 2 h	3a (61%)
2c	230 °C, 3 h	3b (43%)
2e	250 °C, 1.5 h	13a (36%)
2k	260 °C, 1.5 h	13b (8%)
2d	260 °C, 1.5 h	15a (41%) and 16a (7%)
2i	260 °C, 1.5 h	15b (45%)
2b	220 °C, 1.5 h	4a (54%)
2j	220 °C, 1.5 h	4b (80%)
2l	260 °C, 1.5 h	4c (24%)

Table 3. Flash Vacuum Pyrolysis.

Starting Compound	Reaction Conditions	Products
2a	700 °C/ 8×10^{-2} mbar (2h 20 min) [200 °C]*	5a (46%)
3a	700 °C/ 4×10^{-2} mbar (2h) [150 °C]*	5a (79%)
2c	700 °C/ 6×10^{-2} mbar (2h 30 min) [150-250 °C]*	5b (44%)

3b	700 °C/ 2x10 ⁻² mbar (2h) [100-250 °C]*	5b (56%)
2e	700 °C/ 4x10 ⁻² mbar (2h) [100-250 °C]*	13a (13%) and 14 (7%)
2d	700 °C/ 6x10 ⁻² mbar (2h) [100-250 °C]*	16a (39%)
15a	700 °C/ 6x10 ⁻² mbar (1h) [100-250 °C]*	16a (72%)
2i	700 °C/ 4x10 ⁻² mbar (2.5h) [100-250 °C]*	16b (8%), 16c (13%) and 15b (3%)
15b	700 °C/ 4x10 ⁻² mbar (2h) [100-250 °C]*	16b (10%) and 16c (6%)
2b	700 °C/ 4x10 ⁻² mbar (4h) [150-250 °C]*	6a (22%)
4a	700 °C/ 4x10 ⁻² mbar (2h) [150-250 °C]*	6a (31%)
2j	700 °C/ 4x10 ⁻² mbar (5h) [100-250 °C]*	6b (2%)
2l	700 °C/ 4x10 ⁻² mbar (1.5h) [150-250 °C]*	27 (11%) and 6c (10%)
4c	700 °C/ 6x10 ⁻² mbar (1.5h) [100-250 °C]*	27 (37%) and 6c (14%)
2g	700 °C/ 4x10 ⁻² mbar (1.5h) [100-250 °C]*	35 (8%) and 34 (10%)
2f	700 °C/ 4x10 ⁻² mbar (1.5h) [100-250 °C]*	35 (24%)

* The rate of volatilisation of the starting material was controlled by the use of a Kugelrohr oven which heated the sample.

Experimental Section

General Methods. ¹H NMR spectra were recorded on an instrument operating at 300 MHz or on an instrument operating at 500 MHz. ¹³C NMR spectra were recorded on an instrument operating at 75.5 MHz or on an instrument operating at 125 MHz. The solvent is deuteriochloroform except where indicated otherwise; chemical shifts are expressed in parts per million related to internal TMS, and coupling constants (*J*) are in Hz. Mass spectra were recorded under electron impact (EI) at 70 eV in HP or where indicated, by chemical ionisation with methane (CI). Mass spectra were also recorded under ES+ where indicated.

1,3-Thiazolidine-4-carboxylic acids **7a**,^{2c} **7b**,^{2b} **7c**,³ **7d**, **7e**,³ **7f**,^{2b} **7g**,^{1,4} **7h**^{2b} were prepared by a procedure described earlier, starting from *L*-cysteine, and were isolated as a mixture of the (2*R*,4*R*) and (2*S*,4*R*)

diastereoisomers.^{2b,2c} 3-Benzoyl-1,3-thiazolidine-4-carboxylic acids **9a** and **9b** were prepared by a procedure described in the literature.^{2d} 1*H*,3*H*-Pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylates **8a**,² **8b**,² **8j**² and **8g**^{4,1} were prepared as described in the literature. The 1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2,2-dioxides **2a**,¹ **2b**¹ and **2g**^{1,4} were prepared by known synthetic procedures.

General Procedure for the Synthesis of *N*-Formyl-1,3-thiazolidines.⁵ The appropriate 2-substituted-1,3-thiazolidine-4-carboxylic acid (28.0 mmol) was added to formic acid (28.0 mL), the temperature of the reaction medium being kept below 25 °C. Acetic anhydride (19.2 mL) was added dropwise to the solution while maintaining the temperature between 10 and 18 °C. After stirring for 20 h at a temperature of the order of 20 °C, the solvent was evaporated off.

***N*-Formyl-2-methyl-1,3-thiazolidine-4-carboxylic acid 10a.** The crude product was purified by flash chromatography [hexane-ethyl acetate (1:1), then hexane-ethyl acetate (1:3)] giving **10a** as an oil (98%). IR (film) 1178, 1379, 1630, 1730 and 2933 cm⁻¹; The ¹H NMR spectrum showed the presence of two diastereoisomers: ¹H NMR 1.60 and 1.69 (3H, 2xd, *J* = 6.1 and 6.4), 3.27-3.51 (2H, m), 4.80-5.14 (1H, m), 5.20 and 5.35 (1H, 2xq, *J* = 6.1 and 6.4, *CHMe*), 8.32 and 8.38 (1H, 2xs, CHO).

***N*-Formyl-2-phenyl-1,3-thiazolidine-4-carboxylic acid 10b.** The compound was crystallised with boiling ethanol and then washed three times with ethanol and three times with diethyl ether, m.p. 177.6-179.5 °C. IR (KBr) 1200, 1371, 1639, 1743 and 2906 cm⁻¹; The ¹H NMR spectrum showed the presence of two diastereoisomers (ratio 62:38): Major component: ¹H NMR (CD₃OD) 3.38 (1H, dd, *J* = 3.7 and 12.2), 3.52 (1H, dd, *J* = 7.1 and 12.2), 4.96 (1H, dd, *J* = 3.7 and 7.1), 6.17 (1H, s, *CHPh*), 7.33-7.40 (3H, m, Ar-H), 7.70-7.72 (2H, m, Ar-H), 8.05 (1H, s, CHO). Minor component: ¹H NMR (CD₃OD) 3.41-3.48 (2H, m), 5.12 (1H, dd, *J* = 4.3 and 6.1), 6.21 (1H, s, *CHPh*), 7.22-7.30 (3H, m, Ar-H), 7.49-7.51 (2H, m, Ar-H), 8.38 (1H, s, CHO); Anal. Calcd. for C₁₁H₁₁NO₃S: C, 55.68; H, 4.67; N, 5.90; S, 13.51. Found: C, 55.66; H, 4.90; N, 5.72; S, 13.92.

General Procedure for the Synthesis of Dimethyl 3-substituted-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylates. The appropriate 2-substituted-1,3-thiazolidine-4-carboxylic acid (5 mmol), dimethyl acetylene dicarboxylate (0.9 mL, 7.5 mmol) and acetic anhydride (20 mL) were heated at 110-120 °C for 4 h. The reaction mixture was cooled to room temperature and was diluted with CH₂Cl₂

(50 mL). The organic phase was washed with a saturated aqueous solution of NaHCO_3 and with water, dried (MgSO_4) and the solvent evaporated off. The crude product was purified by flash chromatography [hexane-ethyl acetate].

Dimethyl 3-benzyl-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 8c: yield 75%, m.p. 79.8-81.5 °C (from ethyl acetate-hexane). IR (KBr) 1212, 1680 and 1717 cm^{-1} ; ^1H NMR 2.44 (3H, s), 3.17-3.20 (2H, m, CH_2Ph), 3.52 (1H, dd, $J = 1.3$ and 14.9), 3.74 (3H, s), 3.85 (3H, s), 3.91 (1H, d, $J = 14.9$), 5.48-5.52 (1H, m, CHBn), 7.00-7.03 (2H, m, Ar-H), 7.23-7.28 (3H, m, Ar-H); ^{13}C NMR 11.6 (CH_3), 29.1 (CH_2), 43.7 (CH_2Ph), 51.2, 51.4, 63.7 (CH), 106.5, 116.6, 127.4, 128.3, 129.9, 134.2, 140.5, 163.8, 165.3; HRMS (CI) m/z 346.1127 ($\text{C}_{18}\text{H}_{20}\text{NO}_4\text{S}$ [MH^+], 346.1113).

Dimethyl 3-ethyl-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 8d: yield 9%, obtained as an oil. IR (film) 1094, 1218, 1705 and 1721 cm^{-1} ; ^1H NMR 0.94 (3H, t, $J = 7.3$), 1.90-1.99 (2H, m, CH_2Me), 2.38 (3H, s), 3.79 (3H, s), 3.84 (3H, s), 4.15 (1H, d, $J = 15.0$), 4.25 (1H, dd, $J = 1.5$ and 15.0), 5.28-5.32 (1H, m, CHEt); ^{13}C NMR 8.7 (CH_3), 11.5 (CH_3), 29.3, 31.0, 51.3, 51.5, 64.6 (CH), 106.5, 116.7, 129.7, 140.1, 164.0, 165.4; MS (EI) m/z 283 (M^+ , 38%), 251 (67), 222 (100), 178 (59) and 148 (14); HRMS (CI) m/z 284.0958 ($\text{C}_{13}\text{H}_{18}\text{NO}_4\text{S}$ [MH^+], 284.0956).

Dimethyl 3-isopropyl-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 8e: yield 94%, obtained as an oil. IR (film) 1219 and 1724 cm^{-1} ; ^1H NMR 0.70 (3H, d, $J = 6.5$), 1.03 (3H, d, $J = 6.7$), 2.35-2.40 (1H, m), 2.38 (3H, s), 3.79 (3H, s), 3.84 (3H, s), 4.14 (2H, s, CH_2), 5.30 (1H, d, $J = 3.2$, $\text{CH-}i\text{-Pr}$); ^{13}C NMR 11.7 (CH_3), 13.9 (CH_3), 19.8 (CH_3), 30.1, 34.2, 51.3, 51.5, 69.9 (CH), 106.5, 117.0, 129.8, 140.6, 164.1, 165.5; HRMS (CI) m/z 298.1107 ($\text{C}_{14}\text{H}_{20}\text{NO}_4\text{S}$ [MH^+], 298.1113).

Dimethyl 3-*tert*-butyl-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 8f: yield 69%, m.p. 96.9-98.8 °C (from diethyl ether). IR (KBr) 1086, 1153, 1202, 1292, 1444, 1696 and 1725 cm^{-1} ; ^1H NMR 1.05 (9H, s), 2.40 (3H, s), 3.80 (3H, s), 3.84 (3H, s), 4.02 (1H, d, $J = 15.0$), 4.20 (1H, dd, $J = 0.9$ and 15.0), 4.96 (1H, bs, $\text{CH-}t\text{-Bu}$); ^{13}C NMR 13.9 (CH_3), 29.7 (CH_3), 30.3 (CH_2), 41.2 (C), 51.3, 51.4, 73.0 (CH), 107.2, 116.0, 132.2, 141.6, 164.1, 165.4; MS (EI) m/z 311 (M^+ , 14%), 254 (30), 222 (100) and 178 (10); HRMS (CI) m/z 311.1180 ($\text{C}_{15}\text{H}_{21}\text{NO}_4\text{S}$ [M^+], 311.1191).

Dimethyl 3-benzoyl-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 8h: yield 48%, m.p. 173.5-175.8 °C (from diethyl ether-hexane). IR (KBr) 1100, 1293, 1687, 1706 and 1729 cm^{-1} ; ^1H NMR 2.23 (3H, s), 3.81 (3H, s), 3.84 (3H, s), 4.33-4.35 (2H, m), 6.38 (1H, d, $J = 1.3$, CHCOPh), 7.52-

7.57 (2H, m, Ar-H), 7.66-7.68 (1H, m, Ar-H), 7.70-7.93 (2H, m, Ar-H); MS (EI) m/z 359 (M^+ , 8%), 254 (54), 222 (100), 207 (29) and 105 (13); Anal. Calcd. for $C_{18}H_{17}NO_5S$: C, 60.16; H, 4.77; N, 3.90; S, 8.92. Found: C, 60.24; H, 4.85; N, 3.88; S, 9.02.

General Procedure for the Synthesis of Dimethyl 3-substituted-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylates.⁶ Triethylamine (2.6 mL, 18.6 mmol) was added to a suspension of the appropriate *N*-formyl-2-substituted-1,3-thiazolidine-4-carboxylic acid (16.9 mmol) in dichloromethane (8 mL). This solution was added dropwise to a mixture of tosyl chloride (3.5 g, 18.6 mmol) in dichloromethane (8 mL) at 40 °C. Dimethyl acetylene dicarboxylate (2.3 mL, 18.9 mmol) was then added quickly followed by triethylamine (5.2 mL, 37.2 mmol). The reaction mixture was maintained refluxing for 3 h. After cooling to room temperature water was added and the organic layer was separated. The aqueous phase was extracted with dichloromethane and the organic extracts are combined, dried over magnesium sulphate and the solvent evaporated off. The crude product was purified by flash chromatography [hexane-ethyl acetate].

Dimethyl 3-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 8k: yield 42%, m.p. 62.5-64.6 °C (from diethyl ether). IR (KBr) 1063, 1138, 1160, 1200, 1300, 1687 and 1719 cm^{-1} ; 1H NMR 1.77 (3H, d, $J = 6.1$), 3.82 (3H, s), 3.83 (3H, s), 4.25 (1H, dd, $J = 0.9$ and 15.0), 4.31 (1H, dd, $J = 1.8$ and 15.0), 5.46-5.50 (1H, m, *CHMe*), 7.18 (1H, s); ^{13}C NMR 23.6, 29.8, 51.4, 51.6, 59.6 (CH), 107.6, 120.2, 120.3, 142.3, 163.7, 163.8; MS (EI) m/z 255 (M^+ , 19%), 223 (100), 208 (41), 164 (50) and 134 (18); HRMS (CI) m/z 256.0646 ($C_{11}H_{14}NO_4S$ [MH^+], 256.0644).

Dimethyl 3-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 8l: yield 75%, m.p. 122.2-122.9 °C (from diethyl ether). IR (KBr) 1067, 1284, 1710 and 1733 cm^{-1} ; 1H NMR 3.77 (3H, s), 3.86 (3H, s), 4.37 (1H, dd, $J = 0.9$ and 15.0), 4.49 (1H, dd, $J = 1.7$ and 15.0), 6.36 (1H, bs, *CHPh*), 6.90 (1H, s), 7.27-7.40 (5H, m, Ar-H); ^{13}C NMR 30.7 (CH_2), 51.4, 51.5, 66.3 (CH), 107.6, 120.5, 121.4, 127.2, 129.1, 129.7, 137.6, 142.7, 163.6, 163.7; MS (EI) m/z 317 (M^+ , 18%), 285 (100), 164 (20) and 121 (70); Anal. Calcd. for $C_{16}H_{15}NO_4S$: C, 60.56; H, 4.76; N, 4.41. Found: C, 60.51; H, 4.76; N, 4.14.

Dimethyl 3-methyl-5-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate 8i. *N*-benzoyl-2-methyl-1,3-thiazolidine-4-carboxylic acid **9a** (2.4 g; 9.6 mmol), dimethyl acetylene dicarboxylate (1.8 mL,

14.4 mmol) and acetic anhydride (38 mL) were heated at reflux for 4 h. The reaction mixture was cooled to room temperature and was diluted with CH₂Cl₂ (95 mL). The organic phase was washed with a saturated aqueous solution of NaHCO₃ and with water, dried (MgSO₄) and the solvent evaporated off. The crude product was purified by flash chromatography [ethyl acetate-hexane (1:3), ethyl acetate-hexane (1:2) then ethyl acetate-hexane (1:1)] to give the product as a white solid (57%). m.p. 120.8-122.8 °C (from diethyl ether). IR (KBr) 1110, 1161, 1196, 1228, 1442, 1485 and 1715 cm⁻¹; ¹H NMR 1.24 (3H, d, *J* = 6.2), 3.70 (3H, s), 3.82 (3H, s), 4.29 (1H, d, *J* = 15.3), 4.40 (1H, dd, *J* = 1.7 and 15.3), 5.61 (1H, dq, *J* = 1.6 and 6.2, CHMe), 7.40-7.41 (5H, m, Ar-H); ¹³C NMR 25.0 (CH₃), 29.1 (CH₂), 51.4, 51.9, 59.7 (CH), 106.5, 119.4, 128.6, 128.7, 129.2, 129.9, 130.4, 140.8, 163.8, 165.4; MS (EI) *m/z* 331 (M⁺, 86%), 299 (100), 284 (22), 272 (70), 256 (33), 240 (50), 213 (23) and 104 (13); Anal. Calcd. for C₁₇H₁₇NO₄S: C, 61.61; H, 5.17; N, 4.23; S, 9.68. Found: C, 61.56; H, 5.58; N, 4.17; S, 9.28.

General Procedure for the Synthesis of Sulfones. To a stirred ice-cold solution of the appropriate dimethyl pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate (1 mmol) in dry dichloromethane (7 mL) was added portionwise 3-chloroperoxybenzoic acid (3 eq., 3 mmol) under N₂ atmosphere. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature. After stirring at room temperature for 3 h, the reaction mixture was washed twice with 10 % (w/v) aqueous sodium bisulfite solution (2 x 20 mL) and twice with 10 % (w/v) aqueous sodium bicarbonate solution (2 x 20 mL). The organic fraction was then dried over anhydrous MgSO₄ and the solvent evaporated off. The crude product was purified by flash chromatography [hexane-ethyl acetate].

Dimethyl 3-benzyl-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2,2-dioxide 2c. This was prepared following the general procedure, except that the reaction was carried at room temperature for 4 h. The compound **2c** was obtained in 45% yield, m.p. 176.4-178.0 °C (from ethyl acetate-hexane). IR (KBr) 1170, 1386, 1700 and 1714 cm⁻¹; ¹H RMN 2.05 (3H, s), 3.22 (1H, dd, *J* = 6.3 and 14.6, CH₂Ph), 3.53 (1H, dd, *J* = 4.9 and 14.6, CH₂Ph), 3.68 (1H, d, *J* = 16.2), 3.78 (3H, s), 3.85 (3H, s), 4.51 (1H, d, *J* = 16.2), 5.09-5.13 (1H, m, CHBn), 6.97-7.01 (2H, m, Ar-H), 7.25-7.30 (3H, m, Ar-H); ¹³C RMN 11.1 (CH₃), 37.8 (CH₂), 50.7 (CH₂), 51.7, 51.8, 74.4 (CH), 112.4, 115.3, 127.2, 128.2, 129.0, 130.0, 131.9, 133.8, 163.0, 164.7; MS (EI) *m/z* 377(M⁺, 12%), 313 (79), 281 (100), 266 (27), 249 (52), 221 (35), 195 (59) and 77 (34); Anal. Calcd. for C₁₈H₁₉NO₆S: C, 57.28; H, 5.07; N, 3.71; S, 8.56. Found: C, 57.31; H,

4.94; N, 3.69; S, 8.14.

Dimethyl 3-ethyl-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2,2-dioxide 2d: yield 49%, m.p. 93.4-95.1 °C (from diethyl ether). IR (KBr) 1139, 1232, 1332, 1695 and 1727 cm⁻¹; ¹H RMN 1.01 (3H, t, *J* = 7.4), 2.13-2.24 (2H, m, CH₂Me), 3.42 (3H, s), 3.82 (3H, s), 3.87 (3H, s), 4.26 (1H, d, *J* = 16.5), 4.67 (1H, d, *J* = 16.5), 4.89 (1H, dd, *J* = 4.3 and 6.4, CH₂Et); ¹³C RMN 8.2 (CH₃), 11.5 (CH₃), 25.0 (CH₂), 51.6, 51.7, 51.8, 75.1 (CH), 112.0, 115.6, 127.1, 132.9, 163.1, 164.8; MS (EI) *m/z* 315 (M⁺, 10%), 251 (28), 236 (15), 219 (28), 204 (100) and 133 (11); HRMS (CI) *m/z* 315.0787 (C₁₃H₁₇NO₆S [M⁺], 315.0777).

Dimethyl 3-isopropyl-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2,2-dioxide 2e. This was prepared following the general procedure, except that 4 equivalents of 3-chloroperoxybenzoic acid were used and the reaction was carried at room temperature for 4 h. The compound was obtained in 41% yield, m.p. 125.8-127.6 °C (from diethyl ether). IR (film) 1139, 1333 and 1725 cm⁻¹; ¹H RMN 1.13 (3H, d, *J* = 7.0), 1.18 (3H, d, *J* = 7.1), 2.42 (3H, s), 2.43-2.53 (1H, m), 3.82 (3H, s), 3.86 (3H, s), 4.23 (1H, d, *J* = 16.4), 4.64 (1H, d, *J* = 16.4), 4.77 (1H, d, *J* = 4.3, CH-*i*-Pr); ¹³C RMN 12.0 (CH₃), 16.8 (CH₃), 17.1 (CH₃), 32.2 (CH), 51.7, 51.8, 52.1, 79.0 (CH), 112.2, 115.7, 127.5, 133.4, 163.1, 164.8; HRMS (CI) *m/z* 330.1002 (C₁₄H₂₀NO₆S [MH⁺], 330.1011).

Dimethyl 3-*tert*-butyl-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2,2-dioxide 2f. This was prepared following the general procedure, except that the reaction was carried at room temperature for 4 h. The compound was obtained in 34% yield; m.p. 166.7-168.8 °C (from ethyl acetate-hexane). IR (KBr) 1128, 1163, 1217, 1288, 1388, 1705 and 1735 cm⁻¹; ¹H NMR 1.23 (9H, s), 2.43 (3H, s), 3.83 (3H, s), 3.87 (3H, s), 4.27 (1H, d, *J* = 16.2), 4.58 (1H, d, *J* = 16.2), 4.62 (1H, s, CH-*t*-Bu); ¹³C NMR 13.6 (CH₃), 26.2 (CH₃), 37.8 (C), 51.8, 51.9, 52.2, 82.3 (CH), 113.2, 115.9, 128.4, 135.3, 162.3, 165.0; MS (EI) *m/z* 343 (M⁺, 10%), 279 (34), 264 (100), 247 (15), 232 (15), 210 (12) and 178 (12); Anal. Calcd. for C₁₅H₂₁NO₆S: C, 52.46; H, 6.16; N, 4.08; S, 9.34. Found: C, 52.61; H, 6.65; N, 4.06; S, 8.90.

Dimethyl 3-*tert*-butyl-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2-oxide: yield 8%, obtained as an oil. IR (film) 1052, 1094, 1160, 1210, 1287, 1444 and 1713 cm⁻¹; ¹H NMR 1.12 (9H, s), 2.41 (3H, s), 3.81 (3H, s), 3.86 (3H, s), 4.12 (1H, d, *J* = 17.5), 4.38 (1H, d, *J* = 17.6), 4.78 (1H, s, CH-*t*-Bu); MS (ES⁺) *m/z* 328 (MH⁺, 100%), 312 (13), 296 (64) and 279 (14).

Dimethyl 3-benzoyl-5-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2,2-dioxide 2h:

yield 48%, m.p. 149.8-160.0 °C [with decomposition] (from diethyl ether-hexane). IR (KBr) 1059, 1095, 1230, 1444 and 1692 cm^{-1} ; ^1H NMR 2.25 (3H, s), 3.83 (3H, s), 3.85 (3H, s), 4.40 (2H, s), 6.54 (1H, s, *CHCOPh*), 7.61-7.67 (2H, m, Ar-H), 7.75-7.81 (1H, m, Ar-H), 8.12-8.16 (2H, m, Ar-H); MS (EI) m/z 327 ($[\text{M}-\text{SO}_2]^+$, 48%), 295 (21), 209 (31), 105 (100) and 77 (85); Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{NO}_7\text{S}$: C, 55.24; H, 4.38; N, 3.58; S, 8.19. Found: C, 55.06; H, 4.33; N, 3.52; S, 8.43.

Dimethyl 3-methyl-5-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2,2-dioxide 2i.

This was prepared following the general procedure, except that the reaction was carried at room temperature for 4 h. The compound **2i** was obtained in 93% yield, m.p. 125.0-127.2 °C (from diethyl ether). IR (KBr) 1138, 1174, 1208, 1134 1442, 1701 and 1718 cm^{-1} ; ^1H NMR 1.34 (3H, d, $J = 6.7$), 3.71 (3H, s), 3.85 (3H, s), 4.48 (1H, d, $J = 16.7$), 4.73 (1H, d, $J = 16.7$), 5.08 (1H, q, $J = 6,7$), 7.41-7.48 (5H, m, Ar-H); ^{13}C NMR 16.8 (CH_3), 50.6, 51.9, 52.5, 71.1 (CH), 111.7, 117.9, 127.6, 128.7, 128.9, 129.4, 129.6, 133.7, 162.9, 164.8; MS (ES+) m/z 364 (MH^+ , 74%), 332 (100), 279 (35) and 268 (63); Anal. Calcd. for $\text{C}_{17}\text{H}_{17}\text{NO}_6\text{S}$: C, 56.19; H, 4.72; N, 3.85; S, 8.82. Found: C, 56.16; H, 5.00; N, 3.51; S, 8.89.

Dimethyl 3,5-diphenyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2,2-dioxide 2j: yield 47%, m.p. 195.8-196.7 °C (from diethyl ether-acetate-hexane). IR (KBr) 1134, 1339, 1715 and 1728 cm^{-1} ; ^1H NMR 3.76 (3H, s), 3.91 (3H, s), 4.49 (1H, d, $J = 16.4$), 4.84 (1H, d, $J = 16.4$), 5.91 (1H, s, *CHPh*), 6.93-6.95 (2H, m, Ar-H), 7.11-7.16 (2H, m, Ar-H), 7.21-7.30 (3H, m, Ar-H), 7.35-7.43 (3H, m, Ar-H); ^{13}C NMR 49.9 (CH_2), 52.0, 52.3, 78.3 (CH), 112.2, 117.9, 128.4, 128.5, 129.2, 129.3, 129.4, 130.5, 130.6, 134.7, 162.9, 164.9; MS (CI-) m/z 425 (M^+ , 100%) and 361 (45); Anal. Calcd. for $\text{C}_{22}\text{H}_{19}\text{NO}_6\text{S}$: C, 62.11; H, 4.50; N, 3.29. Found: C, 62.15; H, 4.75; N, 3.87.

Dimethyl 3-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2,2-dioxide 2l: yield 53%, m.p. 188.1-190.0 °C (from diethyl ether). IR (KBr) 1068, 1118, 1285, 1327, 1734 and 1743 cm^{-1} ; ^1H NMR 3.82 (3H, s), 3.90 (3H, s), 4.61 (1H, d, $J = 16.4$), 4.68 (1H, d, $J = 16.4$), 5.97 (1H, s), 7.19-7.22 (2H, m, Ar-H), 7.20 (1H, s), 7.49-7.55 (3H, m, Ar-H); ^{13}C NMR 50.9, 51.9, 52.0, 78.5 (CH), 112.4, 118.9, 124.0, 127.3, 128.5, 129.5, 129.9, 131.3, 162.8, 163.0; MS (EI) m/z 285 ($[\text{M}-\text{SO}_2]^+$, 100%), 252 (28), 222 (51), 194 (37), 167 (27) and 139 (20); Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{NO}_6\text{S}$: C, 55.01; H, 4.33; N, 4.01; S, 9.18. Found: C, 54.84; H, 4.54; N, 3.70; S, 8.91.

Dimethyl 3-phenyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2-oxide: yield 13%, m.p. 175.8-177.9 °C (from diethyl ether). IR (KBr) 1059, 1070, 1285, 1710 and 1730 cm^{-1} ; ^1H NMR 3.83 (3H,

s), 3.89 (3H, s), 4.29 (1H, d, $J = 17.0$), 4.43 (1H, d, $J = 17.0$), 6.15 (1H, s), 6.99-7.02 (2H, m, Ar-H), 7.27 (1H, s), 7.42-7.44 (3H, m, Ar-H); MS (ES+) m/z 334 (MH^+ , 100%), 302 (41) and 279 (80); Anal. Calcd. for $C_{16}H_{15}NO_5S$: C, 57.65; H, 4.54; N, 4.20. Found: C, 57.61; H, 4.68; N, 3.89.

Dimethyl 3-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate-2,2-dioxide 2k.⁷ A mixture of $Na_2WO_4 \cdot 2H_2O$ (1.3 mg, 4×10^{-3} mmol), $CH_3N[(CH_2)_7CH_3]_3Cl$ (1.6 mg, 4×10^{-3} mmol), $C_6H_5PO_3H_2$ (0.6 mg, 4×10^{-3} mmol) and aqueous 30 % H_2O_2 (1.4 mL, 12.0 mmol) was vigorously stirred at room temperature for 10 min. A solution of dimethyl 3-methyl-1*H*,3*H*-pyrrolo[1,2-*c*]thiazole-6,7-dicarboxylate **8k** (1.02 g, 4.0 mmol) in ethyl acetate (5 mL) was added dropwise and the reaction mixture was stirred at 50 °C for 94 h. The organic phase was separated, washed with saturated aqueous $Na_2S_2O_3$ and dried over $MgSO_4$. Evaporation of the solvent gave a white solid which was washed with diethyl ether giving compound **2k** in 72% yield. m.p. 150.1-152.0 °C. IR (KBr) 1137, 1209, 1236, 1339, 1687 and 1720 cm^{-1} ; 1H NMR 1.81 (3H, d, $J = 6.6$, $CHMe$), 3.85 (3H, s), 3.86 (3H, s), 4.51 (1H, d, $J = 16.5$), 4.58 (1H, d, $J = 16.5$), 4.99 (1H, q, $J = 6.6$, $CHMe$), 7.34 (1H, s); ^{13}C NMR 14.0 (CH_3), 50.9, 51.9, 51.9, 70.7 (CH), 112.4, 118.9, 122.5, 129.2, 162.9, 163.1; HRMS (CI) m/z 288.0539 ($C_{11}H_{14}NO_4S$ [MH^+], 288.0542).

^1H NMR and ^{13}C NMR spectra for selected compounds.

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MIS-2346

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User: j-14-87

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DS172-580 *seus*

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Mis 142 a

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Solvent: CDCl3

Temp: 25.0 C / 77.3 K

File: 1H_NIS-258A_CDCl3

UNIV-500 "zeus"

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X-Ray crystal data for methyl 5-isopropenyl-2-methyl-6-oxo-1,4,5,6-tetrahydro-cyclopenta[*b*]pyrrole-3-carboxylate **14.**

X-ray diffractions were collected at room temperature and refined by standard methods. The bicyclic compound **16** crystallizes in the centrosymmetric triclinic space group with the molecules joined in dimers by N-H...O hydrogen bonds. The methyl and methyl-carboxylate substituents share the Least Squares plane of the heterocyclic ring with a maximum deviation of 0.124(2) Å for C9. The other five-membered ring is slightly puckered on C5 with Cremer&Pople⁸ parameters of $Q(2) = 0.1435(19)$ Å and $f(2) = 61.1(7)^\circ$. The angle between the L.S. planes of the fused rings is $5.51(10)^\circ$. The torsion angle C3A-C4-C5-C10 is $142.39(16)^\circ$ showing that the isopropenyl substituent on C5 does not share the L.S. plane of the fused rings. Each molecule is hydrogen-bonded to its enantiomer through the H atom attached to the pyrrolic nitrogen. The bond distance N1-O3' is 2.8321(18) Å, the bond angle being 162.3° (Figure 1).

Figure 1. Thermal ellipsoid plot (50% probability level) of 6-oxo-cyclopenta[*b*]pyrrole **16**. Selected bond distances (in angstroms) and angles (in degrees): O3-C6, 1.2271(19); O1-C8, 1.204(2); O2-C8, 1.342(2); O2-C9, 1.446(2); N1-C2, 1.350(2); C2-C3, 1.408(2); C3-C3a, 1.408(2); C3A-C6a, 1.368(2); N1-C6a, 1.374(2); C3a-C4, 1.492(2); C4-C5, 1.557(2); C5-C6, 1.546(2); C6-C6A, 1.428(2); C2-N1-C6a, 108.64(13); N1-C2-C3, 108.51(14); C2-C3-C3a, 106.37(14); C6a-C3A-C3, 107.30(14); C3A-C6a-N1, 109.17(14); C6A-C3a-C4, 111.16(13); C3a-C4-C5, 103.23(12); C6-C5-C4, 105.12(13); C6a-C6-C5, 105.56(13); C3a-C6a-C6, 112.87(14).

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H7B H 0.2565 -0.2039 0.1095 0.090 Uiso 1 1 calc R . .
H7C H 0.4948 -0.2355 0.1907 0.090 Uiso 1 1 calc R . .
C8 C 0.3543(3) 0.04739(17) 0.34737(16) 0.0461(4) Uani 1 1 d . . .
C9 C 0.1989(4) 0.1698(2) 0.51925(18) 0.0605(5) Uani 1 1 d . . .
H9A H 0.0180 0.1362 0.4805 0.091 Uiso 1 1 calc R . .
H9B H 0.2096 0.2603 0.5722 0.091 Uiso 1 1 calc R . .
H9C H 0.2634 0.1141 0.5645 0.091 Uiso 1 1 calc R . .
C10 C 1.0335(4) 0.48102(17) 0.25283(17) 0.0541(5) Uani 1 1 d . . .
C11 C 1.2139(5) 0.5824(2) 0.3246(2) 0.0757(7) Uani 1 1 d . . .
H11A H 1.3298 0.5705 0.3874 0.091 Uiso 1 1 calc R . .
H11B H 1.2241 0.6651 0.3121 0.091 Uiso 1 1 calc R . .
C12 C 0.8373(6) 0.4956(3) 0.1531(3) 0.0883(8) Uani 1 1 d . . .
H12A H 0.8501 0.5883 0.1576 0.132 Uiso 1 1 calc R . .
H12B H 0.6618 0.4656 0.1601 0.132 Uiso 1 1 calc R . .
H12C H 0.8737 0.4423 0.0775 0.132 Uiso 1 1 calc R . .

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O2 0.0555(7) 0.0536(7) 0.0511(7) 0.0147(5) 0.0284(6) 0.0029(5)
N1 0.0499(7) 0.0430(7) 0.0436(7) 0.0106(6) 0.0200(6) 0.0054(5)
C2 0.0443(8) 0.0461(8) 0.0453(9) 0.0160(7) 0.0144(7) 0.0038(6)
C3 0.0428(8) 0.0460(8) 0.0453(9) 0.0163(7) 0.0171(7) 0.0045(6)
C3A 0.0423(7) 0.0439(8) 0.0443(8) 0.0141(7) 0.0178(6) 0.0074(6)
C4 0.0546(9) 0.0440(8) 0.0566(10) 0.0124(8) 0.0304(8) 0.0054(7)
C5 0.0463(8) 0.0470(9) 0.0500(9) 0.0112(7) 0.0218(7) 0.0033(7)
C6 0.0441(8) 0.0459(8) 0.0486(9) 0.0148(7) 0.0219(7) 0.0095(6)
C6A 0.0440(8) 0.0415(8) 0.0448(8) 0.0118(7) 0.0190(7) 0.0067(6)
C7 0.0726(12) 0.0476(10) 0.0588(11) 0.0124(8) 0.0235(9) -0.0026(8)
C8 0.0444(8) 0.0501(9) 0.0488(9) 0.0189(7) 0.0183(7) 0.0053(7)
C9 0.0610(10) 0.0716(12) 0.0545(10) 0.0188(9) 0.0319(9) 0.0081(9)
C10 0.0609(10) 0.0451(9) 0.0594(10) 0.0111(8) 0.0336(9) 0.0059(7)
C11 0.0859(14) 0.0534(11) 0.0830(15) 0.0065(10) 0.0435(12) -0.0080(10)
C12 0.110(2) 0.0695(14) 0.0965(19) 0.0374(14) 0.0250(16) 0.0234(14)

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_geom_special_details

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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loop_

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O2 C9 1.446(2) . ?
N1 C2 1.350(2) . ?
N1 C6A 1.374(2) . ?
N1 H1 0.8600 . ?
C2 C3 1.408(2) . ?
C2 C7 1.482(2) . ?
C3 C3A 1.408(2) . ?
C3 C8 1.460(2) . ?
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C4 C5 1.557(2) . ?
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C4 H4B 0.9700 . ?
C5 C10 1.492(2) . ?
C5 C6 1.546(2) . ?
C5 H5 0.9800 . ?
C6 C6A 1.428(2) . ?
C7 H7A 0.9600 . ?
C7 H7B 0.9600 . ?
C7 H7C 0.9600 . ?
C9 H9A 0.9600 . ?
C9 H9B 0.9600 . ?
C9 H9C 0.9600 . ?
C10 C11 1.330(3) . ?
C10 C12 1.492(3) . ?

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C11 H11A 0.9300 . ?
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 N1 C2 C7 121.05(15) . . ?
 C3 C2 C7 130.44(15) . . ?
 C2 C3 C3A 106.37(14) . . ?
 C2 C3 C8 124.10(15) . . ?
 C3A C3 C8 129.49(15) . . ?
 C6A C3A C3 107.30(14) . . ?
 C6A C3A C4 111.16(13) . . ?
 C3 C3A C4 141.53(14) . . ?
 C3A C4 C5 103.23(12) . . ?
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 C3A C4 H4B 111.1 . . ?
 C5 C4 H4B 111.1 . . ?
 H4A C4 H4B 109.1 . . ?
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 C10 C5 C4 115.02(14) . . ?
 C6 C5 C4 105.12(13) . . ?
 C10 C5 H5 106.8 . . ?
 C6 C5 H5 106.8 . . ?
 C4 C5 H5 106.8 . . ?
 O3 C6 C6A 129.93(15) . . ?
 O3 C6 C5 124.43(15) . . ?
 C6A C6 C5 105.56(13) . . ?
 C3A C6A N1 109.17(14) . . ?
 C3A C6A C6 112.87(14) . . ?
 N1 C6A C6 137.91(14) . . ?
 C2 C7 H7A 109.5 . . ?
 C2 C7 H7B 109.5 . . ?
 H7A C7 H7B 109.5 . . ?
 C2 C7 H7C 109.5 . . ?
 H7A C7 H7C 109.5 . . ?
 H7B C7 H7C 109.5 . . ?
 O1 C8 O2 123.20(15) . . ?
 O1 C8 C3 125.61(16) . . ?
 O2 C8 C3 111.19(14) . . ?
 O2 C9 H9A 109.5 . . ?
 O2 C9 H9B 109.5 . . ?
 H9A C9 H9B 109.5 . . ?
 O2 C9 H9C 109.5 . . ?
 H9A C9 H9C 109.5 . . ?
 H9B C9 H9C 109.5 . . ?
 C11 C10 C5 120.3(2) . . ?
 C11 C10 C12 122.3(2) . . ?
 C5 C10 C12 117.41(17) . . ?
 C10 C11 H11A 120.0 . . ?

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C10 C11 H11B 120.0 . . ?
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C10 C12 H12A 109.5 . . ?
C10 C12 H12B 109.5 . . ?
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C10 C12 H12C 109.5 . . ?
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N1 C2 C3 C8 -178.20(15) . . . . ?
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C8 C3 C3A C6A 177.57(17) . . . . ?
C2 C3 C3A C4 179.2(2) . . . . ?
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C3A C4 C5 C6 14.07(18) . . . . ?
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O3 C6 C6A C3A -176.84(18) . . . . ?
C5 C6 C6A C3A 6.40(19) . . . . ?
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C9 O2 C8 O1 1.6(3) . . . . ?
C9 O2 C8 C3 -178.02(14) . . . . ?
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C3A C3 C8 O1 -177.40(18) . . . . ?
C2 C3 C8 O2 179.61(15) . . . . ?
C3A C3 C8 O2 2.2(3) . . . . ?
C6 C5 C10 C11 -130.04(18) . . . . ?
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_refine_diff_density_rms               0.053

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