gas chromoatography. The retention time was 50 min when the oven was set to 145 °C, the injector to 198 °C, the detector to 225 °C, and the collector to 199 °C with a Helium flow rate of 15 mL/min. **7**: ^{1}H NMR (acetone-d_6) δ 5.08 (s, 2 H), 4.77 (s, 2 H), 2.79 (br s, 2 H), 1.29–1.76 (m, 6 H); ^{13}C NMR (acetone-d_6) δ 153.2, 100.0, 46.2, 39.6, 29.3.

2,3-Dimethylenebicyclo[2.2.2]octane (8) was synthesized by the method of Butler and Snow[14] and purified by preparative gas chromatography. The retention time was 60 min when the oven was set to 130 °C, the injector to 195 °C, the detector to 220 °C, and the collector to 200 °C. **8**: ^{1}H NMR (acetone-d_6) δ 5.23 (s, 2 H), 4.69 (s, 2 H), 2.30 (br s, 2 H), 1.66 (d, J = 7.3 Hz, 4 H), 1.53 (d, J = 8.1 H, 4 H); ^{13}C NMR (acetone-d_6) δ 150.4, 103.5, 31.1, 26.8.

2,3-Dimethylenebicyclo[2.2.3]nonane (9) was synthesized by the method of Butler and Snow[14] and purified by preparative gas chromatography. The retention time was 30 min when the oven was 128 °C, the injector 189 °C, the detector 212 °C, and the collector 182 °C. **9**: ^{1}H NMR δ 5.30 (s, 2 H), 4.69 (s, 2 H), 2.60 (br s, 2 H), 1.42–1.75 (m, 8 H); ^{13}C NMR δ 150.3, 106.6, 40.9, 36.3, 26.8, 21.9.

Isodicyclopentadiene (1) was synthesized by the method of Alder[15] and purified by the method of gas chromatography. The retention time was 10.5 min when the oven was set to 125 °C and the detector to 200 °C with a He flow rate of 63 mL/min. **1**: ^{1}H NMR (acetone-d_6) δ 5.62 (br s, 2 H), 2.91–3.18 (m, 4 H), 1.25–1.86 (m, 6 H); ^{13}C NMR (acetone-d_6) δ 156.2 (s), 114.5 (d), 46.5 (t), 45.5 (t), 39.1 (d), 29.1 (t).

4′,5′,6′,7′-Tetrahydrospirocyclopropene-1,2′-4,7-methano-2*H*-indene (2) was synthesized by the method of Paquette[16] and purified by preparative gas chromatography. The retention time was 17 min when the oven was set to 144 °C, the injector to 148 °C, and the detector to 211 °C with a He flow rate of 69 mL/min. **2**: ^{1}H NMR (acetone-d_6) δ 5.32 (br s, 2 H), 3.01 (br s, 2 H), 1.88–1.30 (m, 10 H); ^{13}C NMR (acetone-d_6) δ 152.9 (s), 122.0 (d), 46.8 (t), 40.6 (s), 39.5 (d), 29.4 (t), 11.2 (t), 10.2 (t).

General Photolysis Conditions. The diene (10–30 mg) and 1.0 mg of rose bengal were mixed with 0.6–0.7 mL of acetone-d_6 in a 5-mm NMR tube and saturated with oxygen for 25 min at −78 °C while being protected from the room lights. The solution was irradiated through a 0.5% $K_2Cr_2O_7$ filter solution (1 cm pathlength, cutoff approximately 500 nm). The progress of the reaction was monitored by low-temperature NMR at −80 °C.

4,5-Dioxatricyclo[6.2.1.0^{2,7}]undec-2(7)-ene: ^{1}H NMR (acetone-d_6; −78 °C) δ 4.85 (d, J = 16.1 Hz, 1 H), 4.66 (d, J = 15.4 Hz, 1 H), 4.49 (d, J = 15.4 Hz, 1 H), 4.25 (d, J = 16.1 Hz, 1 H), 2.83 (s, 2 H), 1.00–1.64 (m, 6 H); ^{13}C NMR (acetone-d_6; −78 °C) δ 136.84, 135.24, 69.46, 67.88, 45.45, 41.63, 41.38, 25.10, 24.83; ^{1}H NMR (acetone-d_6; 25 °C) δ 4.67 (d, J = 14.3 Hz, 2 H), 4.43 (d, J = 14.3 Hz, 2 H), 2.86 (s), 1.05–1.70 (m, 6 H); ^{13}C NMR (acetone-d_6; 25 °C) δ 137.87, 70.16, 43.16, 26.41, 47.03.

4,5-Dioxatricyclo[6.2.2.0^{2,7}]dodec-2(7)-ene was isolated by flash column chromatography: ^{1}H NMR (acetone-d_6; −78 °C) δ 4.77 (d, J = 14.6 Hz, 2 H), 4.28 (d, J = 14.6 Hz, 2 H), 2.36 (s, 2 H), 1.51 (br s, 4 H), 1.21 (br s, 4 H); ^{13}C NMR (acetone-d_6; −78 °C) δ 132.14, 68.97, 28.82, 25.25, 24.86; ^{1}H NMR ($CDCl_3$; 25 °C) δ 4.59 (s, 4 H), 2.38 (s, 2 H), 1.60 (m, 4 H), 1.33 (m, 4 H); ^{13}C NMR ($CDCl_3$; 25 °C) δ 133.13 (s), 70.58 (t, J = 144 Hz), 30.24 (d, J = 136 Hz), 26.28 (t, J = 133 Hz); IR (cm^{-1}) 2934, 2859, 2812, 1349, 1000, 960, 776; high resolution mass spectrum calculated for $C_{10}H_{14}O_2$, m/e (M^+) 166.0994, found m/e (M^+) 166.0987; mp 57–59 °C.

4,5-Dioxatricyclo[6.3.2.0^{2,7}]tridec-2(7)-ene was isolated by flash column chromatography: ^{1}H NMR (acetone-d_6; −78 °C) δ 4.82 (d, J = 16.1 Hz, 1 H), 4.70 (d, J = 16.1 Hz, 1 H), 4.28 (d, J = 16.8 Hz, 1 H), 4.22 (d, J = 16.8 Hz, 1 H), 2.23 (br s, 2 H), 2.00–1.42 (m, 10 H); ^{13}C NMR (acetone-d_6; −78 °C) δ 134.42, 134.04, 71.63, 70.65, 32.59, 32.38, 30.36, 29.79, 25.66, 23.95, 23.95; ^{1}H NMR ($CDCl_3$; 25 °C) δ 4.47 (d, J = 14.3 Hz, 2 H), 4.37 (d, J = 14.3 Hz, 2 H), 2.19 (s, 2 H), 1.50–1.90 (m, 10 H); ^{13}C NMR ($CDCl_3$; 25 °C) δ 133.13 (s), 71.30 (t, J = 143 Hz), 32.49 (d, J = 125 Hz), 29.73 (t, J = 128 Hz), 25.73 (t, J = 131 Hz), 23.12 (t, J = 124 Hz); IR (cm^{-1}) 2862, 1445, 1343, 1015; high resolution mass spectrum calculated for $C_{11}H_{16}O_2$, m/e (M^+) 180.1151, found m/e (M^+) 180.1152; mp 42–44 °C.

***syn*- and *anti*-4,5-Dioxasesquinorbornenes (3 and 4)**: ^{1}H NMR (acetone-d_6; −78 °C) δ 5.47 (s, 2 H), 5.46 (s, 2 H), 3.06 (s, 2 H), 3.03 (s, 2 H), 2.26–0.92 (m, 16 H); ^{13}C NMR (acetone-d_6; −78 °C) δ 154.4 (s), 152.7 (s), 83.1 (d, J = 168 Hz), 82.6 (d, J = 166 Hz), 59.3 (t, J = 139 Hz), 56.2 (t, J = 131 Hz), 52.3 (t, J = 140 Hz), 48.3 (t, J = 131 Hz), 42.4 (d, J = 149 Hz), 41.3 (d, J = 148 Hz), 26.2 (t, J = 135 Hz), 24.4 (t, J = 135 Hz).

***syn*- and *anti*-11-Cyclopropyl-4,5-dioxasesquinorbornenes (5 and 6)**: ^{1}H NMR (acetone-d_6; −78 °C) δ 4.93 (s, 2 H), 4.87 (s, 2 H), 3.10 (br s, 4 H), 2.14–0.60 (m, 20 H); ^{13}C NMR (acetone-d_6; −78 °C) δ 156.2 (s), 154.2 (s), 87.0 (d, J = 166 Hz), 85.8 (d, J = 166 Hz), 58.3 (s), 53.0 (t, J = 137 Hz), 48.6 (s), 48.0 (t, J = 134 Hz), 42.8 (d, J = 149 Hz), 41.9 (d, J = 149 Hz), 25.9 (t, J = 138 Hz), 25.5 (t, J = 136 Hz), 10.8 (t, J = 164 Hz), 8.24 (t, J = 152 Hz), 5.25 (t, J = 160 Hz), 3.56 (t, J = 160 Hz).

Kinetics. The rates were measured by using the Young method as described previously.[13b]

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (CHE-8418603) for the support of this research.

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Communications

Structure of FR900452, a Novel Platelet-Activating Factor Inhibitor from a *Streptomyces*

Summary: The structure of FR900452 (1) isolated from a *Streptomyces* as a potent inhibitor of platelet-activating factor has been deduced by using chemical modifications, spectroscopic measurements, and an X-ray crystal analysis of the dihydro derivative **2**.

Sir: FR900452 (1) was recently isolated from *Streptomyces phaeofaciens* No. 7739 as a potent and specific inhibitor of platelet-activating factor (PAF), an endogeneous mediator of anaphylaxis and inflammation.[1] We now report the structural elucidation of this novel natural product as **1**. The 5-(2-oxocyclopent-3-en-1-ylidene)-2-oxopiperazinyl skeleton of **1** is unique.

FR900452 was isolated as a pale-yellow powder: $C_{22}H_{25}N_3O_3S$ (HRMS: obsd, m/z 411.1567; calcd, 411.1618. Anal. Calcd for $C_{22}H_{25}N_3O_3S$: C, 64.21; H, 6.21; N, 10.21; S, 7.79. Found: C, 63.90; H, 6.31; N, 9.80; S, 7.52); $[\alpha]^{23}_D$ +97.0° (c 0.5, $CHCl_3$); UV (MeOH) 246 nm (ε 13 600), 347 (14 500); IR ($CHCl_3$) 3350, 2900, 1670, 1610, 1595 cm^{-1}. The

(1) Okamoto, M.; Yoshida, K.; Nishikawa, M.; Ando, T.; Iwami, M.; Kohsaka, M.; Aoki, H. *J. Antibiot.* **1986**, *39*, 198.

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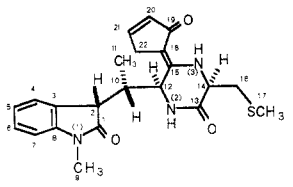
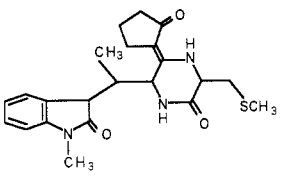


1



2

^{13}C NMR spectrum (100 MHz, $CDCl_3$) of **1** showed 13 sp_2-carbons including three carbonyls (196.7 (s), 176.2 (s), 168.5 (s)) and ten aromatic or olefinic carbons (151.0 (d), 150.1 (s), 144.4 (s), 136.3 (d), 128.4 (d), 127.5 (s), 123.2 (d), 123.1 (d), 108.4 (d), 104.9 (s)). In the sp^3-carbon region, the spectrum showed four methine (56.8 (d), 54.6 (d), 45.8 (d), 44.7 (d)), two methylene (39.3 (t), 34.6 (t)), and three methyl carbons (26.2 (q), 16.8 (q), 12.8 (q)). The ^1H NMR spectrum (400 MHz, $CDCl_3$) of **1** revealed 25 proton signals (Table I) including two exchangeable amide protons (δ 10.14, 7.10). Extensive spin decoupling and NOE experiments clarified ^1H–^1H relationships as shown in Figure 1, leading to partial structures A, B, and C, which are all consistent with the ^{13}C NMR data described above.

Partial structure B was further secured by hydrolysis of **1** with 6 N HCl (110 °C, 20 h) to give *S*-methyl-L-cysteine ($[\alpha]^{23}_D$ −12.0° (*c* 1.0, H_2O); 40% ee).[2,3] The presence of the *N*-methyl-2-oxindole unit in the partial structure A was confirmed by isolation of *N*-methyl-3-acetylidene-2-oxoindolidine (mp 78 °C)[4,5] on treatment of **1** with base (Na_2CO_3/MeOH, overnight). Catalytic hydrogenation of **1** (H_2(3 atm)/PtO_2/AcOEt) gave dihydro derivative **2**, in which two new methylene carbon signals at δ 39.3 (t) and 21.3 (t) appeared in the ^{13}C NMR spectrum ($CDCl_3$),[6] while the olefinic carbons at δ 136.3 and 151.0 in **1** disappeared. The two carbons of **1** not assigned to a partial structure (δ 150.1 and 104.9) were assigned to a tetrasubstituted olefin (partial structure D).

A reasonable connection of these partial structures was derived by the following COLOC experiment.[7] The data showed that H^a and H^i are long-range coupled to C-18 (δ 104.9) and H^m is coupled to C-15 (δ 150.1), suggesting the linkage of the partial units A, B, and C through the olefin D.[8] Long-range couplings of H^a and H^i to C-13 (δ 168.5) indicated that A and B share the C-13 carbonyl. The connection of the oxocyclopentenylidene and oxopiperazinyl moiety through C-15 and C-18 was further corroborated by the 2D INADEQUATE technique,[9] which revealed C–C couplings between C-12 (δ 54.6) and C-15, C-15 and C-18, and C-18 and C-19 (δ 196.7), respectively, thus indicating the serial linkage of these carbons. The H^a amide proton resonated in a low-field region (δ 10.14), suggesting the presence of an intramolecular hydrogen bond to the C-19 carbonyl. This was possible only when these groups were in *Z* configuration. Thus structure **1** (without stereochemistry) was proposed for FR900452.

For confirmation of the presumed structure and determination of its stereochemistry, a single-crystal X-ray analysis was undertaken using crystals of the dihydro derivative **2**: orthorhombic, space group $P2_12_12_1$; unit cell

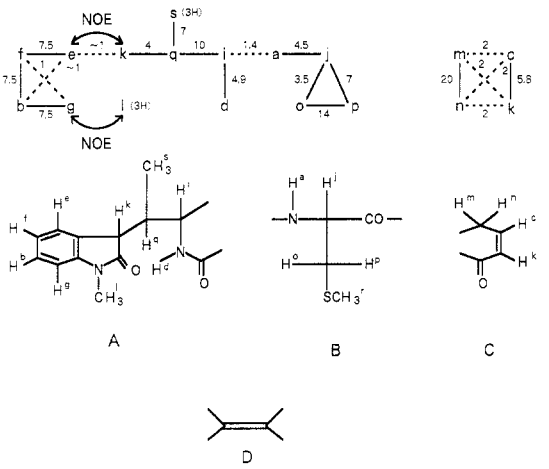


Figure 1. ^1H–^1H relationships observed in the ^1H NMR spectrum of **1** and the partial structure A, B, C, and D.

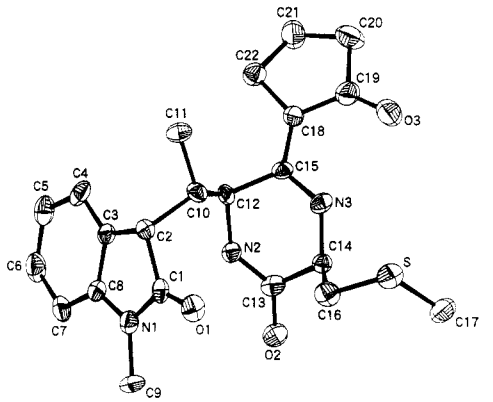


Figure 2. ORTEP drawing of FR900452 (**1**).

Table I. ^1H NMR (400 MHz, $CDCl_3$) Chemical Shifts, Multiplicities, and Coupling Constants (*J*, Hz) for FR900452 (1)

H^a	10.14, br d (4.5, exchangeable)	H^k	3.97, d (4)
H^b	7.31, dt (1, 7.5)	H^l	3.23, s (3 H)
H^c	7.22, dt (5.8, 2)	H^m	3.24, dt (20, 2)
H^d	7.10, br d (4.9, exchangeable)	H^n	3.20, dt (20, 2)
H^e	7.12, dd (7.5, 1)	H^o	3.15, dd (14, 3.5)
H^f	7.09, dt (1, 7.5)	H^p	3.08, dd (14, 7)
H^g	6.87, dd (7.5, 1)	H^q	2.99, ddq (10, 4, 7)
H^h	6.35, dt (5.8, 2)	H^r	2.29, s (3 H)
H^i	4.50, ddd (10, 4.9, 1.4)	H^s	0.70, d (7, 3 H)
H^j	4.33, ddd (7, 4.5, 3.5)		

(2) An authentic sample, prepared according to the literature, showed $[\alpha]^{23}_D$ −30.0° (*c* 1.0, H_2O): du Vigneaud, V.; Loring, H. S.; Craft, H. A. *J. Biol. Chem.* **1934**, *105*, 481.

(3) Examination of the whole HCl-treated mixture of **1** on HPLC, coupled with a chiral derivatization method using 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl isothiocyanate, also revealed that the ratio of the L and D enantiomers of *S*-methylcysteine was 7:3; column, TSK gel ODS-80T_M (TOYO SODA) (4.6 × 250 mm); eluent, 0.1% aqueous H_3PO_4–MeOH (9:1)/MeCN–MeOH (9:1), linear gradient elution from 8/2 to 6/4 within 60 min; flow rate, 1.0 mL/min; retention time, L isomer 40.2 min, D isomer 44.8 min. For the chiral derivatization method, see: Nimura, N.; Toyama, A.; Kinoshita, T. *J. Chromatogr.* **1984**, *316*, 547.

(4) Lit. mp 78 °C: Tacconi, G.; Maggi, L. D.; Righetti, P.; Desimoni, G.; Azzolina, O. *J. Chem. Soc., Perkin Trans. 2* **1976**, 150.

(5) ^{13}C NMR ($CDCl_3$): δ 167.8 (s), 143.7 (s), 136.4 (d), 128.7 (d), 128.7 (s), 123.4 (d), 122.5 (s), 122.0 (d), 108.0 (d), 26.0 (q), 15.2 (q). ^1H NMR ($CDCl_3$): δ 7.60 (1 H, d, J = 7 Hz), 7.40–7.00 (2 H, m), 7.17 (1 H, q, J = 7 Hz), 6.84 (1 H, d, J = 7 Hz), 3.24 (3 H, s), 2.29 (3 H, d, J = 7 Hz). IR ($CHCl_3$): 1700, 1660, 1610 cm^{-1}.

(6) ^{13}C NMR ($CDCl_3$): δ 206.0 (s), 176.1 (s), 168.2 (s), 151.2 (s), 144.4 (s), 128.4 (d), 127.4 (s), 123.2 (d), 123.0 (d), 108.4 (d), 105.3 (s), 56.4 (d), 54.4 (d), 46.0 (d), 44.6 (d), 39.3 (t) × 2, 28.9 (t), 26.2 (q), 21.3 (t), 16.8 (q), 12.6 (q). ^1H NMR ($CDCl_3$): δ 10.28 (1 H, br d, J = 4 Hz, exchangeable), 7.31 (1 H, br t, J = 7.5 Hz), 7.11 (1 H, br d, J = 7.5 Hz), 7.09 (1 H, dt, J = 1, 7.5 Hz), 6.95 (1 H, br d, J = 4.5 Hz, exchangeable), 6.87 (1 H, d, J = 7.5 Hz), 4.46 (1 H, ddd, J = 10, 4.5, 1 Hz), 4.26 (1 H, ddd, J = 7.5, 4, 3.5 Hz), 3.92 (1 H, d, J = 4 Hz), 3.23 (3 H, s), 3.12 (1 H, dd, J = 14, 3.5 Hz), 3.05 (1 H, dd, J = 14, 7.5 Hz), 2.94 (1 H, m), 2.64 (1 H, m), 2.53 (1 H, m), 2.4–2.3 (2 H, m), 2.25 (3 H, s), 2.0–1.8 (2 H, m), 0.85 (3 H, d, J = 7 Hz).

(7) Kessler, H.; Griesinger, C.; Zarbock, J.; Loosli, H. R. *J. Magn. Reson.* **1984**, *57*, 331.

(8) The H^a–H^i long-range coupling (J = 1.4 Hz) described above also corroborated the serial linkage of C-12, C-15, and N-3.

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a = 23.903 (3), b = 15.142 (3), and c = 5.846 (1) Å; V = 2115.9 (6) Å^3; Z = 4, D_x = 1.298 g cm^{-3}. Intensities were measured with $\omega/2\theta$ scan mode using graphite-monocromated Cu Kα radiation (λ = 1.54173 Å). Of 2093 independent reflections with $2\theta < 130°$, 1416 were judged observed ($|F_o| \geq 3\sigma(F_o)$). The structure was determined by direct methods (MULTAN 78) and successive block-diagonal least-squares and Fourier syntheses. Parameters were refined by using anisotropic temperature factors to R = 0.079 for the observed reflections.[10] A perspective drawing of the structure of **2** is given in Figure 2. The absolute stereochemistry of **2** was established to be 2*S*,10*S*,12*S*,14*R* on the basis of the isolation of *S*-methyl-L-cysteine from hydrolysis.[2]

The structure of FR900452 with absolute stereochemistry was thus established as **1**. The oxocyclopentenylidene group incorporated as a vinylogous amide in the diketopiperazine skeleton is unique and, as far as we are aware, FR900452 is the first example of this structural type. The exceptional activity of FR900452 as a PAF inhibitor is of special interest.[11]

Supplementary Material Available: Details of the X-ray crystal analysis of **2** including tables of fractional coordinates, thermal parameters, interatomic distances, and interatomic angles (5 pages). Ordering information is given on any current masthead page.

(10) Details will be reported in a forthcoming full paper.
(11) Okamoto, M.; Yoshida, K.; Nishikawa, M.; Hayashi, K.; Uchida, I.; Kohsaka, M.; Aoki, H. *Chem. Pharm. Bull.* **1986**, *34*, 3005.

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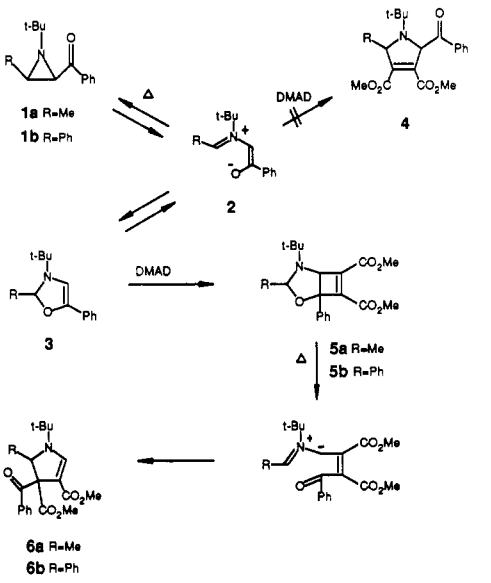
1,3-Dipoles Are Not the Only Reactive Species in 2-Acylaziridine Pyrolyses

Summary: Pyrolysis of *N-tert*-butylaziridines **1** in the presence of acetylenedicarboxylate gives adducts of structure **5**, which rearrange to **6**, rather than the expected ylide adducts **4**.

Sir: The participation of acyl-stabilized azomethine ylides in [2 + 3] dipolar cycloadditions can be utilized for the construction of five-membered rings containing nitrogen.[1,2] These ylides have been generated by using a variety of techniques including aziridine thermolysis,[1-3] oxazolium salt reduction,[4] and α-aminoester + aldehyde condensation at elevated temperatures.[5] While investigating the thermolysis of several 2-acyl aziridines, we discovered some anomalous examples which undergo a novel addition and rearrangement reaction rather than the dipolar cycloaddition.

Scheme I



Thermolysis of cis or trans aziridine **1a** in the presence of dimethyl acetylenedicarboxylate (DMAD) at 120 °C in a sealed tube gives a product which had been previously assigned as 3-pyrroline **4**.[6] Further investigation of the product by ^{1}H and ^{13}C NMR rules out structure **4** and proves the actual structure to be pyrroline **6a**.[7] A particularly distinguishing feature in the ^{13}C NMR spectrum is the highly polarized nature of the carbons which comprise the vinylogous carbamate (C-2, 149.5 ppm (d); C-3, 97.7 ppm (s)). The structure **6** explains the reported reluctance of the adduct to aromatize and readily accounts for the ^{1}H NMR and chemical degradation data described earlier.[6]

Thermolysis of aziridine **1b** at 80 °C overnight in the presence of DMAD yields the analogous pyrroline **6b** in 57% yield as a 2.6:1 mixture of diastereomers. However, when the reaction is interrupted at shorter times or run at lower temperatures, an intermediate can be obtained which is the bicyclic compound **5b** (up to 37% yield).[8,9]

(1) (a) *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience; New York, 1984. (b) Herman, H.; Huisgen, R.; Mader, H. *J. Am. Chem. Soc.* **1971**, *93*, 1779. (c) Heine, H.; Peavy, R.; *Tetrahedron Lett.* **1965**, 3123. (d) Lown, J. W. *Rec. Chem. Prog.* **1971**, *32*, 51.
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(7) **6a**: ^{1}H NMR δ 7.76–7.70 (2 H, m), 7.52–7.35 (3 H, m), 7.43 (1 H, s), 4.99 (1 H, q, J = 6.7 Hz), 3.61 (3 H, s), 3.49 (3 H, s), 1.38 (9 H, s), 1.06 (3 H, d, J = 6.7 Hz); ^{13}C NMR 193.3 (s), 172.4 (s), 164.6 (s), 149.5 (d), 137.5 (s), 132.3 (d), 128.4 (d), 127.6 (d), 97.7 (s), 70.4 (s), 62.1 (d), 55.1 (s), 52.3 (q), 50.3 (q), 30.1 (q), 18.9 (q) ppm.
(8) **5b**: ^{1}H NMR δ 7.61–7.29 (10 H, m), 5.54 (1 H, s), 4.69 (1 H, s), 3.91 (3 H, s), 3.67 (3 H, s), 0.92 (9 H, s); ^{13}C NMR 163.2 (s), 160.7 (s), 145.7 (s), 139.4 (s), 139.2 (s), 137.3 (s), 129.5 (d), 129.3 (d), 128.3 (d), 128.0 (d), 127.9 (d), 125.3 (d), 90.7 (d), 85.7 (s), 71.9 (d), 52.2 (q), 52.1 (q), 51.9 (s), 29.5 (q) ppm.

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