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.

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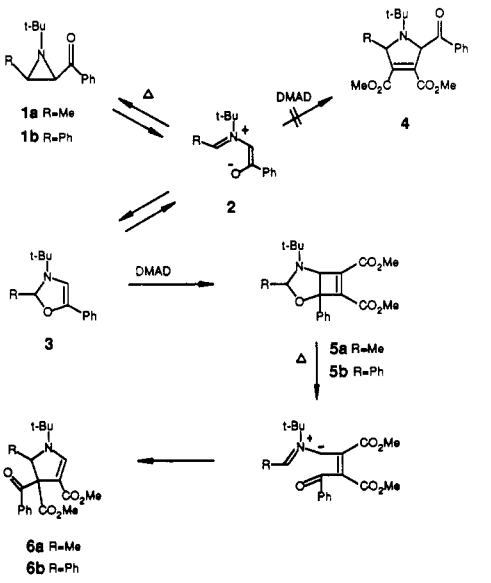
1,3-Dipoles Are Not the Only Reactive Species in 2-Acylaziridine Pyrolyses

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]

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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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Upon further heating at 80 °C, this rearranges to the previously observed **6b**.

A proposed mechanism to explain the formation of these products is outlined in Scheme I. Upon thermolysis, the aziridine opens to the ylide **2**. The ylide does not undergo a [2 + 3] cycloaddition to form pyrrolidine **4** but instead closes to the 4-oxazoline **3**. As we had observed in a recent study of oxazolium salt reduction,[4] the 4-oxazoline **3** can react with DMAD in a [2 + 2] manner to yield **5**. Under the harsh conditions employed in the thermolysis of **1a**, the intermediate **5a** rapidly rearranges via ring opening and reclosure to the pyrroline **6a**. However, in the case of aziridine **1b**, oxazoline formation occurs at a much lower temperature, and adduct **5b** can be intercepted. Further heating brings about the same isomerization to the pyrroline **6b**.

The absence of [2 + 3] cycloaddition products in this reaction is striking. An unfavorable steric interaction between the *tert*-butyl group and adjacent groups probably destabilizes planar ylide structures such as **2**. This could make electrocyclic ring closure to the relatively more flexible oxazoline rapid in comparison to the dipolar cycloaddition which is not observed. A few other examples of the aziridine/oxazoline interconversion exist[10] although this is the first case involving an *N*-alkyl group and no substitutent at the C-4 oxazoline position. The **5** → **6** conversion has not been observed previously. This process allows access to pyrrolines of a rather unusual substitution pattern, but its principal ramification is a cautionary one: there is no guarantee that 1:1 adducts obtained from reactive dipolarophiles and 2-acylaziridines will be derived from the [2 + 3] cycloaddition. The 4-oxazoline tautomer is thermally accessible as initially pointed out by Baldwin et al.,[10a] and this isomer reacts with DMAD to give **6** via a labile intermediate **5**. A preliminary reevaluation of the classical work on trapping of dipoles from *N-arylaziridines* with acetylenic dipolarophiles has revealed no anomalies in adduct structure; these experiments do indeed give [2 + 3] cycloadducts as initially reported.[1] However, the *N-alkyl* systems are not so simple. Preliminary results suggest that only those aziridines having bulky *N*-alkyl groups are likely to follow the alternative pathway described here, but the system is in delicate balance. This topic will be discussed further in a full paper.

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(9) The structure of **5b** is clear from the ^1H and ^{13}C NMR evidence. In particular, the absence of long-range coupling between the methine protons rules out structure **4** where extensive precedent requires $J_{2,5}$ = ca. 5 ± 2 Hz *regardless* of stereochemistry (see, for example, ref 3a-c). The strongest evidence for **5b** is the excellent match of ^{13}C spectra with analogous structures obtained by 2 + 2 addition of DMAD + independently generated 4-oxazolines (ref 4). Adduct **5b** lacks a bridgehead substituent compared to the earlier precedents, and the corresponding ^{13}C signal (71.9 ppm) becomes a doublet.

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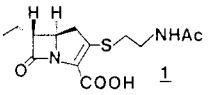
Asymmetric Synthesis of the Carbapenem Antibiotic (+)-PS-5

Summary: An asymmetric synthesis of (+)-PS-5 (**1**) has been accomplished by a route utilizing the anti-selective boron enolate–imine condensation reaction with extremely high asymmetric induction.

Sir: Recently we have found that 9-BBN enolates derived from *S*-phenyl alkanethioates react with imines smoothly, giving anti β-amino acid derivatives in a stereoselective manner.[1] One characteristic feature of this condensation reaction is that amines such as benzylamine and *p*-methoxybenzylamine can be utilized as an imine component,[2] suggesting that the use of optically active imines derived from α-methylbenzylamine and 1-(1-naphthyl)ethylamine[3] could provide optically active β-amino acid derivatives convertible to *trans*-carbapenem antibiotics. In this paper we wish to report a highly efficient asymmetric synthesis of (+)-PS-5 (**1**),[4] which is a *trans*-carbapenem antibiotic



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active against gram-positive and gram-negative bacteria including β-lactamase producing organisms. Although the elegant asymmetric syntheses of (+)-PS-5 (**1**) have been reported very recently,[5] the present synthesis is completely different from those already reported.

The imine **4** (1.2 equiv) derived from 3-(trimethylsilyl)-2-propynal and (*S*)-α-methylbenzylamine[6] was added at −40 °C to the boron enolate **3** prepared from *S*-phenyl butanethioate (**2**), 9-BBNOTf, and diisopropylethylamine (0 °C, 1 h) (Scheme I). The reaction mixture was gradually warmed to 25 °C and stirred for 20 h. After the reaction was quenched with pH 7.0 phosphate buffer and workup and short-path, silica gel chromatography, the B–N bond of the condensation products was cleaved with concentrated HCl in ether–methanol (2:1, 25 °C, 5 h) to give the β-amino acid derivative in 69% yield. These products consisted of the anti adduct **5** and the syn adducts **6** and **6′** in a ratio of 5.2:1. Exposure of the mixture **5**, **6**, and **6′** to *tert*-butylmagnesium chloride (2 equiv) in ether at 0 °C for 3 h[7] furnished the trans-β-lactam **7** in 68% yield, together with the cis-β-lactams **8** and **8′** in 3% yield.[8,9] The

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(8) The anti β-amino acid derivative was converted to the trans β-lactam in 83% yield, while the syn derivative was transformed into the cis β-lactams only in 23% yield.

(9) R_f values of the β-lactams are 0.7 for **7** and 0.5 and 0.4 for the cis β-lactams (silica gel; ether–hexane, 1:1).

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