

**Table II.** Reactions of Nucleophiles with Diol Epoxides from Benzo[c]phenanthrene and Phenanthrene<sup>a</sup>

Morpholine			
compd	solvent	$k_{\text{morph.}} \text{ M}^{-1} \text{ s}^{-1}$	
2a	10% dioxane <sup>b</sup>	$1.04 \times 10^{-3}$	
2d		$3.4 \times 10^{-3}$	
Mercaptoethanol Anion			
compd	solvent	$k_{\text{RS}^{-1}} \text{ M}^{-1} \text{ s}^{-1}$	$k_{\text{RS}^{-(1)}}/k_{\text{RS}^{-(2)}}$
1a	10% dioxane <sup>b</sup>	0.23	
2a		0.21	1.10
1d		2.28	
2d	10% dioxane <sup>b</sup>	1.49	1.53
1a		0.036	
2a		0.012	3.00
1d	50% dioxane <sup>c</sup>	1.53	
2d		0.178	8.60

<sup>a</sup> At 25 °C. <sup>b</sup> Ionic strength 0.2 M (NaClO<sub>4</sub>). <sup>c</sup> Ionic strength 0.1 M (NaClO<sub>4</sub>).

exhibit similar reactivity ( $k_{\text{H}^+}$ ) toward acid-catalyzed hydrolysis, **1a** undergoes substantially more cis hydration at acid pH (~85% as opposed to 50–60% for **1b** and **1d**).

The hydrolysis of **2a** is also subject to general acid catalysis, according to the rate law,  $k_{\text{obsd}} = k_0 + k_{\text{H}^+}a_{\text{H}^+} + k_{\text{HA}}[\text{HA}]$ . Catalytic constants,  $k_{\text{HA}}$ , measured in 10% dioxane, ionic strength 0.2 M, for phosphoric acid ( $\text{p}K_{\text{a}} = 2.1$ ),<sup>14</sup> dichloromethylphosphonate monoanion<sup>15</sup> ( $\text{p}K_{\text{a}} = 5.4$ ),<sup>14</sup> and dihydrogen phosphate monoanion ( $\text{p}K_{\text{a}} = 6.9$ )<sup>14</sup> are  $13.3$ ,  $3.2 \times 10^{-2}$ , and  $1.6 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ , respectively, corresponding to a Brønsted  $\alpha$  value of approximately 0.85 for these three acids. For **2a**, catalysis by phosphoric acid is observable in Na<sub>2</sub>HPO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub> buffers at pH 5.9–6.9, a finding similar to that of Bruice and co-workers for the 1,2- and 3,4-epoxides of 1,2,3,4-tetrahydrophenanthrene<sup>16</sup> and the diol epoxides of naphthalene.<sup>17,18</sup>

**Reactions with Nucleophiles.** Morpholine and mercaptoethanol anion react with benzo[c]phenanthrene and phenanthrene diol epoxides according to the rate laws  $k_{\text{obsd}} = k_{\text{morph}}[\text{morpholine free base}]$  or  $k_{\text{obsd}} = k_{\text{RS}^-}[\text{HOCH}_2\text{CH}_2\text{S}^-]$ . Values of  $k_{\text{morph}}$  and  $k_{\text{RS}^-}$  in 10% dioxane (Table II) are 3- to 10-fold smaller for the benzo[c]phenanthrene diol epoxides than for the corresponding phenanthrene derivatives. In 50% dioxane, where hydrogen bonding to the cis benzylic hydroxyl group may significantly stabilize the transition state for nucleophilic cleavage of some isomer-1 diol epoxides,<sup>17,20</sup> there is an even greater difference in

reactivity (43-fold) for **1a** relative to the phenanthrene derivative **1d**. The very low reactivity of **1a** relative to **1d** under conditions where hydrogen bonding is important probably results from the unfavorable conformational requirement for such hydrogen bonding in **1a** but not in **1d**.

Our results for both S<sub>N</sub>2 and solvolysis reactions indicate that the benzo[c]phenanthrene diol epoxides are the most chemically unreactive bay-region diol epoxides studied to date. Hence, their high mutagenic and tumorigenic activity is not dependent upon high chemical reactivity in simple "model" reactions and must result from more specific aspects of their reactivity, possibly involving binding phenomena with cellular macromolecules.

**Supplementary Material Available:** Details of the syntheses of **1a** and **2a** and of kinetic experiments, kinetic data for determination of general acid catalytic constants and S<sub>N</sub>2 rate constants, details of HPLC analyses of hydrolysis products, and listing of the <sup>1</sup>H NMR spectra for acetylated hydrolysis products and thioethers of **1a** and **2a** (12 pages). Ordering information is given on any current masthead page.

(20) The effect of solvent composition on the relative rates ( $k_{\text{RS}^{-(1)}}/k_{\text{RS}^{-(2)}}$ ) for isomers **1** and **2** of a given diol epoxide is consistent with a role for intramolecular hydrogen bonding in 50% dioxane. In 10% dioxane, where such hydrogen bonding should be relatively unimportant, there is no significant difference between the reactivity of diastereomers **1** and **2** in either the phenanthrene or the benzo[c]phenanthrene series ( $k_{\text{RS}^{-(1)}}/k_{\text{RS}^{-(2)}} = 1.1$ –1.5). In 50% dioxane,  $k_{\text{RS}^{-(1)}}/k_{\text{RS}^{-(2)}}$  for the phenanthrene diol epoxides is 8.6, consistent with greater stabilization, in the less aqueous solvent, of the transition state for opening of **1d**, in which intramolecular hydrogen bonding is possible, relative to **2d**. A similar value of  $k_{\text{RS}^{-(1)}}/k_{\text{RS}^{-(2)}}$  of 7.9 was observed in 50% dioxane for the diol epoxides of naphthalene.<sup>17</sup> For the benzo[c]phenanthrene derivative, **1a**, whose preferred conformation (**1a''**) has the cis benzylic hydroxyl group unfavorably located for hydrogen bonding to the epoxide,  $k_{\text{RS}^{-(1)}}$  is only three times larger than  $k_{\text{RS}^{-(2)}}$  in 50% dioxane. This is the effect that would be expected if hydrogen bonding in the transition state for reaction of **1a** cannot occur without first overcoming an unfavorable steric interaction, with the result that the net stabilization of the transition state for **1a** relative to **2a** is decreased.

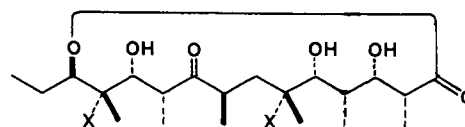
#### Acyclic Stereoselection. 14. *O*-Alkylactic Acid Esters: Reagents for the Stereoselective Construction of erythro- and threo- $\alpha$ -Methyl- $\alpha,\beta$ -dihydroxy Carbonyl Compounds<sup>1</sup>

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In their recent total synthesis of 6-deoxyerythronolide B (**1**),<sup>2</sup> Masamune and co-workers have impressively demonstrated the power of the aldol condensation for construction of the polypropionate framework characteristic of the macrolide antibiotics.<sup>3</sup>



1: X = H  
2: X = OH

For the application of such a strategy to the synthesis of eryth-

(14) These are apparent  $\text{p}K_{\text{a}}$  values determined in 10% dioxane, ionic strength 0.2 M (NaClO<sub>4</sub>), from the observed pH of buffer solutions or by titration.

(15) For preparation of the conjugate acid, see: Kinnear, A. M.; Perren, E. A. *J. Chem. Soc.* **1952**, 3437–3445. Crofts, P. C.; Kosolapoff, G. M. *J. Am. Chem. Soc.* **1953**, 75, 5738–5740.

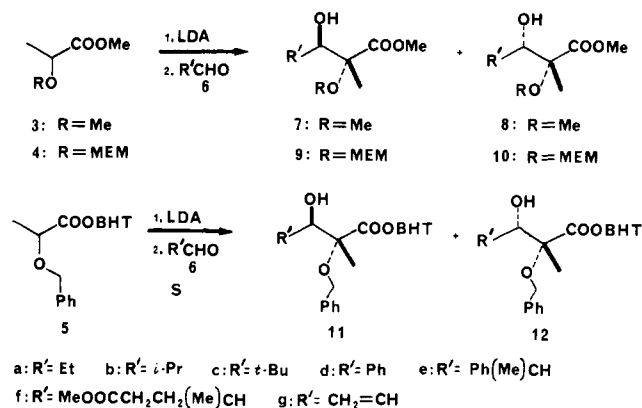
(16) Rogers, D. Z.; Bruice, T. C. *J. Am. Chem. Soc.* **1979**, 101, 4713–4719.

(17) Becker, A. R.; Janusz, J. M.; Bruice, T. C. *J. Am. Chem. Soc.* **1979**, 101, 5679–5687.

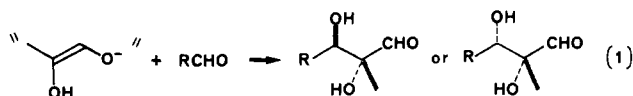
(18) The ability to observe catalysis by phosphoric acid at pH values well above its  $\text{p}K_{\text{a}}$  for the phenanthrene, naphthalene, and benzo[c]phenanthrene derivatives but not for the benzo[a]pyrene diol epoxides<sup>19</sup> may result from decreased sensitivity to catalyst acidity for the more reactive benzo[a]pyrene derivatives. An upper limit of  $800 \text{ M}^{-1} \text{ s}^{-1}$  is estimated for  $k_{\text{H}_3\text{PO}_4}$  for **2c**, based on the lack of any observable pH dependence<sup>19</sup> of the quantity,  $k_{\text{obsd}}/[\text{H}_2\text{PO}_4^-]$ , at pH 6.34–7.60 and the assumption that a 10% increase at pH 6.34 would have been detectable. This corresponds to a value of  $k_{\text{H}_3\text{PO}_4}/k_{\text{H}_2\text{PO}_4^-} \leq 1.6 \times 10^3$  for **2c**, which is smaller than the observed values of  $8.3 \times 10^3$  for **2a** and  $4.1 \times 10^4$  for 3,4-epoxy-1,2,3,4-tetrahydrophenanthrene.<sup>16</sup> Thus, for the benzo[a]pyrene diol epoxide **2c**, catalysis by the weakly acidic dihydrogen phosphate monoanion is able to swamp out any catalysis by phosphoric acid at neutral pH, where the concentration of phosphoric acid is extremely low.

(19) Whalen, D. L.; Ross, A. M.; Montemmarano, J. A.; Thakker, D. R.; Yagi, H.; Jerina, D. M. *J. Am. Chem. Soc.* **1979**, 101, 5086–5088.

Scheme I



ronolide A (2), reagents are required which are the synthetic equivalent of the lactaldehyde enolate ion (e.g., eq 1). In this



communication we report such reagents, which allow the stereoselective preparation of either the erythro or threo diastereomer of an  $\alpha$ -alkyl- $\alpha,\beta$ -dihydroxy carboxylic acid.<sup>4</sup>

Of a number of *O*-alkyllactic acid esters we have studied,<sup>5</sup> compounds 3–5 (Scheme I) have emerged as the most useful reagents. Ester 3 is prepared by the literature method.<sup>6</sup> Compound 4 is conveniently prepared by the reaction of commercially available ethyl lactate with (2-methoxyethoxy)methyl chloride,<sup>7</sup> followed by transesterification with potassium carbonate in methanol. Ester 5 is prepared by acylation of the lithium salt of 2,6-di-*tert*-butyl-4-methylphenol (BHT, "butylated hydroxytoluene") with the acid chloride of *O*-benzylsuccinic acid.<sup>8</sup>

Aldol condensations of esters 3–5 are carried out in the normal manner.<sup>3</sup> Enolates are formed with lithium diisopropylamide (LDA) in THF at  $-78^\circ\text{C}$  (30–45 min). After addition of an appropriate aldehyde at  $-78^\circ\text{C}$ , reaction is allowed to proceed for 5–45 min at this temperature and is then quenched by the addition of aqueous ammonium chloride. Best results are obtained if the condensations are carried out with solutions at least 0.5 M in enolate. Reactions are normally carried out with stoichiometric quantities of enolate and aldehyde. However, if the aldehyde is inexpensive and volatile (acrolein, propionaldehyde, isobutyraldehyde), better yields are sometimes obtained by the use of 2 equiv of aldehyde. The condensations studied with esters 3–5 are shown in Scheme I; results are summarized in Table I.

Structures were assigned to aldols 7–12 by various methods. The structures of compounds 12b and 12d were determined by single-crystal X-ray analysis.<sup>9</sup> Esters 9a and 11a were correlated with the known *erythro*-2-methyl-2,3-dihydroxypentanoic acid (Bergel's acid).<sup>10,11</sup> The structures of esters 11g and 12g were

(4) As with the simpler  $\alpha$ -alkyl- $\beta$ -hydroxy carbonyl compounds (see footnote 5, ref 3) we employ the erythro–threo convention for describing  $\alpha$ -alkyl- $\alpha,\beta$ -dihydroxy carbonyl compounds and their ethers. The same convention is used: when the backbone of the aldol is written in an extended (zig-zag) manner, if the bonds to the  $\alpha$ -alkyl group and  $\beta$ -hydroxy group both project either toward or away from the viewer, this is the erythro isomer.

(5) Other esters we have evaluated are the methyl, 2,6-dimethylphenyl, and 2,6-diisopropylphenyl esters of *O*-benzylsuccinic acid and the BHT esters of *O*-methyl- and *O*-(2-methoxyethoxy)methylsuccinic acid. Complete details will be reported in a full paper.

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(9) We thank Dr. Fred Hollander of the Berkeley Crystallography Laboratory for carrying out these structure determinations. Details will be reported in a full paper.

(10) L. D. Bergel'son, E. V. Dyatlovitskaya, M. Tichy, and V. V. Voronkova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **9**, 1612 (1962).

Table I. Reaction of Esters 3–5 with Various Aldehydes

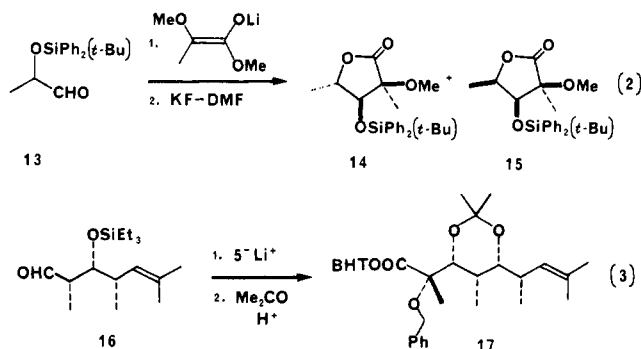
ester	aldehyde	product(s)	aldol yield, %	erythro–threo <sup>a</sup> ratio
3	6a	7a, 8a	99	70:30
3	6b	7b	98	>97:3
3	6c	7c	84	>97:3
3	6d	7d, 8d	85	75:25
3	6e	7e	99	>97:3 <sup>b</sup>
3	6f	7f	88	>97:3 <sup>c</sup>
4	6a	9a, 10a	60	82:18
4	6b	9b, 10b	83	85:15
4	6c	9c, 10c	73	88:12
4	6d	9d, 10d	95	85:15
5	6g	11g, 12g	88	25:75
5	6a	11a, 12a	57	17:83
5	6b	11b, 12b	89	<3:97
5	6d	11d, 12d	62	<3:97
5	6e	11e, 12e	40	<3:97 <sup>d</sup>

<sup>a</sup> Diastereomer ratios were determined by <sup>13</sup>C NMR spectroscopy. <sup>b</sup> Mixture of Cram's rule and anti-Cram's rule diastereomers in a ratio of 80:20. <sup>c</sup> Mixture of Cram's rule and anti-Cram's rule diastereomers in a ratio of 75:25. <sup>d</sup> The Cram's rule–anti-Cram's rule ratio is >10:1.

established by hydrogenation of these compounds to esters 11a and 12a, respectively. The remaining structures were assigned on the basis of their <sup>13</sup>C NMR spectra.<sup>12</sup>

As shown by the data in Table I, esters 3 and 4 give predominantly *erythro*-aldols. With compound 4 the erythro–threo ratios are about 6:1 with the aldehydes studied. Compound 3 gives slightly lower erythro–threo ratios with "small" aldehydes but shows very high erythro selectivity with all aliphatic aldehydes which are branched at the  $\alpha$  carbon. On the other hand, ester 5 displays excellent threo selectivity. For the small aldehydes acrolein and propionaldehyde, the threo–erythro ratios are 3:1 and 5:1, respectively. However, with benzaldehyde and  $\alpha$ -branched aliphatic aldehydes, the threo–erythro ratios are at least 97:3.

The utility of these reagents is demonstrated by eq 2 and 3.



Ester 3 reacts with (*O*-diphenyl-*tert*-butylsilyl)lactaldehyde (13) to give a crude aldol product which is treated with potassium fluoride in anhydrous dimethylformamide to effect isomerization to a 3:1 mixture of lactones 14 and 15. The major lactone, 14 (mp 82–84  $^\circ\text{C}$ ), has the relative configuration of the important carbohydrate cladinose.<sup>13</sup>

The threo–selective reagent, ester 5, reacts with aldehyde 16 to afford an 85:15 mixture of two *C*<sub>2</sub>,*C*<sub>3</sub>-*erythro*-aldols. Upon treatment with a trace of sulfuric acid in acetone solution, the major isomer is transformed into the crystalline acetone 17. The structure of compound 17 was established by single-crystal X-ray analysis.<sup>9</sup> Compound 17 has the relative stereostructure at its

(11) Actually, the identification of ester 11a was indirect. Since the hydrolysis of this ester is exceedingly slow, it was reduced with lithium aluminum hydride in refluxing THF to a diol, which was found to be identical with the diol obtained by the similar reduction of Bergel's acid.

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five chiral centers corresponding to the C<sub>2</sub>-C<sub>6</sub> portion of erythronolide A (2).

Further applications of these lactaldehyde equivalents in natural products synthesis will be reported in due course.

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**Supplementary Material Available:** ORTEP plots of compounds 12b, 12d, and 17; physical properties and methods of purification for esters 3-5 and aldols 7-12 and 17 (includes <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra and combustion analysis results) (8 pages). Ordering information is given on any current masthead page.

## Nitrone Cycloaddition. A New Approach to $\beta$ -Lactams

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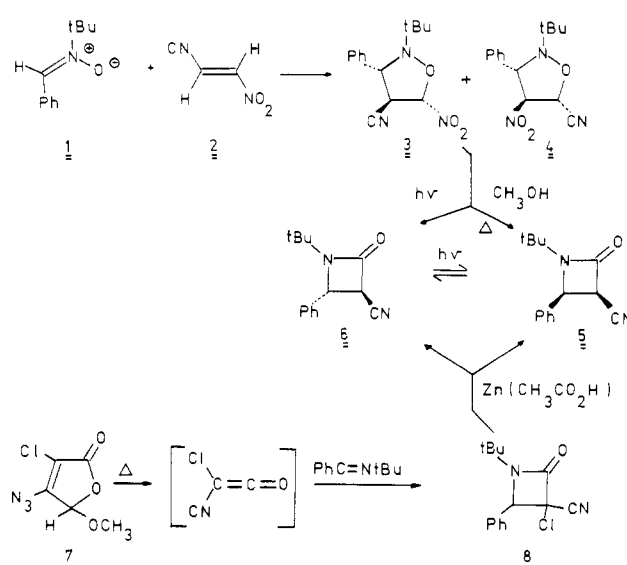
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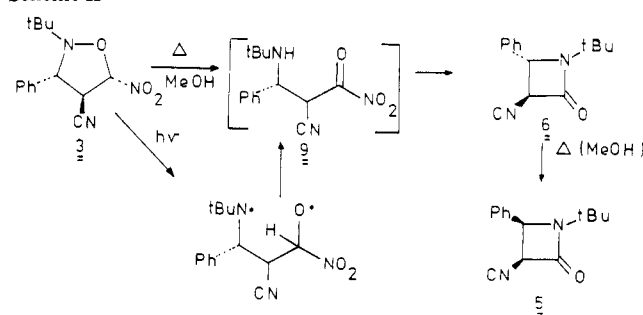
Because of their central role in the treatment of bacterial infection, the  $\beta$ -lactam antibiotics have received a great deal of attention since their discovery.<sup>2</sup> Considerable ingenuity has been demonstrated over the years in devising syntheses for the  $\beta$ -lactam system which forms the most salient feature of the penicillin and cephalosporin antibiotics.<sup>3</sup> This class of heterocycles has traditionally been prepared by the cyclization of  $\beta$ -aminopropanoic acid derivatives,<sup>4</sup> intramolecular Michael addition,<sup>5</sup> cycloaddition of heterocumulenes,<sup>6</sup> ring expansion of three-membered rings,<sup>7</sup> and ring contraction of five-membered rings.<sup>8</sup> New methods of constructing the four-membered lactam ring continue to be of interest in connection with the synthesis of analogues of the naturally occurring antibiotics.<sup>9</sup> In this report we describe a new procedure for the preparation of  $\beta$ -lactams. The key feature of the synthetic method involves 1,3-dipolar cycloaddition of a nitron to a nitro-substituted olefin followed by a subsequent reorganization of the resulting 5-nitroisoxazolidine.

The reaction of phenyl-*N*-*tert*-butylnitrone (1) with *trans*-1-cyano-2-nitroethylene (2) gave rise to a mixture of two regioisomeric isoxazolidines 3 and 4 in quantitative yield (Scheme I). The major 5-nitro-substituted regioisomer 3 (60%), mp 76-77 °C, was separated by fractional crystallization from hexane [NMR (CDCl<sub>3</sub>, 90 MHz)  $\delta$  1.00 (s, 9 H), 4.20 (dd, 1 H, *J* = 7.5 and 2.7 Hz), 4.25 (d, 1 H, *J* = 7.5 Hz), 5.65 (d, 1 H, *J* = 2.7 Hz), and 7.30 (s, 5 H); C<sup>13</sup> NMR (20 MHz, CDCl<sub>3</sub>) 26.0 (CH<sub>3</sub>), 50.2 (C<sub>4</sub>), 59.9 (*t*-Bu), 69.2 (C<sub>3</sub>), 102.5 (C<sub>5</sub>), 116.1 (CN)]. The minor 5-cyano regioisomer 4 (40%), mp 56-57 °C [NMR (CDCl<sub>3</sub>, 90

Scheme I



Scheme II



MHz)  $\delta$  1.00 (s, 9 H), 4.60 (d, 1 H, *J* = 6.0 Hz), 5.19 (dd, 1 H, *J* = 6.0 and 1.5 Hz), 5.48 (d, 1 H, *J* = 1.5 Hz), and 7.20 (m, 5 H); C<sup>13</sup> NMR (20 MHz, CDCl<sub>3</sub>) 26.1 (CH<sub>3</sub>), 59.6 (*t*-Bu), 66.7 (C<sub>2</sub>), 68.3 (C<sub>3</sub>), 98.8 (C<sub>1</sub>), and 115.8 (CN)] was isolated by medium-pressure silica gel chromatography. Heating a sample of isoxazolidine 3 in methanol gave *cis*- $\beta$ -lactam 5 in quantitative yield, mp 91-92 °C [NMR (CDCl<sub>3</sub>, 90 MHz)  $\delta$  1.15 (s, 9 H), 4.10 (d, 1 H, *J* = 6.0 Hz), 4.75 (d, 1 H, *J* = 6.0 Hz), and 7.32 (s, 5 H)].<sup>10</sup> A similar reorganization occurred when isoxazolidine 3 was subjected to ultraviolet irradiation using 2537-Å light. In this case, however, the only product isolated was *trans*- $\beta$ -lactam 6, mp 180-181 °C [NMR (CDCl<sub>3</sub>, 90 MHz)  $\delta$  1.25 (s, 9 H), 3.65 (d, 1 H, *J* = 3.0 Hz), 5.80 (d, 1 H, *J* = 3.0 Hz), and 7.40 (s, 5 H)]. Extended photolysis of either *cis*-5 or *trans*- $\beta$ -lactam 6 resulted in photoisomerization leading to a photostationary state ratio of 1:1. *trans*- $\beta$ -Lactam 6 was smoothly converted to the thermodynamically more stable *cis* isomer 5 on heating in methanol with a trace of base. The structure of the  $\beta$ -lactams (i.e., 5 and 6) were unambiguously established by comparison with independently synthesized samples. This was accomplished by heating 4-azido-3-chloro-5-methoxy-2(5*H*)-furanone (7) in the presence of *N*-benzylidene-*tert*-butylamine followed by reduction of the resulting chlorocyno-2-azetidinone 8 with zinc in acetic acid. Moore and co-workers have previously demonstrated that furanone 7 undergoes cleavage to chlorocyno ketene<sup>11</sup> which, in turn, is known to undergo [2 + 2] cycloaddition with C-N double bonds.<sup>12,13</sup>

(1) National Institutes of Health (F32-GM08052) Postdoctoral Fellow.

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