parallel-perpendicular conformation of allyl vinyl ketone complex **5**.

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Supplementary Material Available: Complete spectral characterization of complexes **2-5** and **7-9** and X-ray crystallographic data for **5** (9 pages); table of observed and calculated structure factors for **5** (8 pages). Ordering information is given on any current masthead page.

Novel Strategy for the Construction of the Oligosaccharide Fragment of Calicheamicin $\gamma_{1\alpha}^{I}$. Synthesis of the ABC Skeleton

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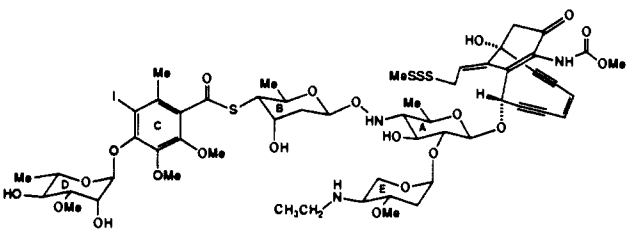
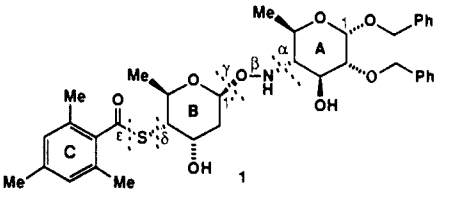
The highly unusual structures of the calicheamicins, of which calicheamicin $\gamma_{1\alpha}^{I}$ is the most prominent member,[1] coupled with their phenomenal biological activity have spurred a flurry of investigations. Whereas most of the synthetic efforts in this area have focused on biological mimics[2] and the bicyclic enediyne skeleton,[3] reports relating to the oligosaccharide fragment have been few.[4] In this communication we describe the first synthetic study that provides solutions to the stereoselective construction of the crucial bonds α-ϵ (see structure **1**) present in the calicheamicin $\gamma_{1\alpha}^{I}$ oligosaccharide, and which delivers the ABC skeleton **1** in optically active form.

On close inspection of the oligosaccharide fragment of calicheamicin $\gamma_{1\alpha}^{I}$, one identifies the following challenging synthetic features (shown in target **1**): (a) the unusual alkoxylamine bond β, linking carbohydrate units A and B via bonds α and γ; (b) the β-stereochemistry of the glycoside bond γ, which, taken in combination with the 2-deoxy nature of saccharide B, offers a unique challenge to synthetic construction; (c) the sulfur bridge, linking carbohydrate unit B with a heavily substituted aromatic system via bonds δ and ϵ; and (d) the α-stereochemistry of the N- and



Calicheamicin $\gamma_{1\alpha}^{I}$



S-bearing stereogenic centers of saccharide units A and B, respectively. Our studies provide clean and rather novel solutions to all the above challenges.

The synthetic design was based on the retrosynthetic disconnections indicated in structure **1**, which led to thiocarbonyldiimidazole ($Im_2C{=}S$) as the sulfur source, *N*-hydroxyphthalimide (HO-NPhth) as the origin of the alkoxyamino group, and precursors to rings A, B, and C as potential starting points. Scheme I outlines the synthetic strategy as designed from the above analysis, and which, in addition to solving the above-mentioned problems, avoids a potentially difficult deoxygenation step to generate the methylene group of the B ring. Thus intermediate I (Scheme I) was designed with an ester group at position 2 to assure the desired stereochemical outcome of the glycosidation reaction (I → II, β-stereochemistry) as well as a means to stereoselectively deliver the sulfur atom at position 4 via a sigmatropic rearrangement (II → III → IV). Intermediate IV was then expected to serve as a precursor to V.

Scheme II outlines the sequence leading to target **1**. Thus, following selective deprotection (DIBAL, 72%) of the diester **2**,[5] epoxidation of **3**[6] with *m*-chloroperoxybenzoic acid (MCPBA) followed by regio- and stereoselective epoxide opening by *m*-chlorobenzoic acid afforded diol **4** in 55% yield. Selective silylation (-Si^{t}BuMe$_2$, 67%) of the 3-hydroxyl group of **4** followed by exposure to Swern conditions resulted in the formation of enone **6** via an oxidation-elimination sequence (88%). 1,2-Reduction of enone **6** using $Zn(BH_4)_2$-NH_4Cl in ether[7] proceeded smoothly from the β-face and was followed by the expected, in situ, ester migration,[8] to afford the desired α-lactol **7** in good yield (ca. 8:1 α:β ratio by ^{1}H NMR). Rapid workup followed by immediate addition of HO-NPhth, Ph_3P, and diisopropyl azodicarboxylate[9] resulted in the formation of the β-glycoside **9**, presumably via intermediate **8** (53% overall yield). While the mechanism of this glycosidation is not fully understood, an S_N2 process may be occurring since the α:β ratio of the resulting glycoside **9** is dependent upon the ratio of starting lactol anomers.[10] Liberation (NH_2NH_2) of the amino group led to hydroxylamine derivative **10**, which was condensed with ketone A[5] under acidic conditions, to afford compound **11**[11] (92% overall yield from **9**). Silylation (-Si^{t}BuMe$_2$, 99%) of **11** gave **12**, which on exposure to DIBAL led to the hydroxy compound **13** (91%). Reaction of **13** with

(1) Lee, M. D.; Dunne, T. S.; Siegel, M. M.; Chang, C. C.; Morton, G. O.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3464. Lee, M. D.; Dunne, T. S.; Chang, C. C.; Ellestad, G. A.; Siegel, M. M.; Morton, G. O.; McGahren, W. J.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3466.

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(4) (a) For the synthesis of the aromatic system of calicheamicin $\gamma_{1\alpha}^{I}$, see: Nicolaou, K. C.; Ebata, T.; Styliannides, N. A.; Groneberg, R. D.; Carrol, P. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1097. (b) For the synthesis of a methyl-α-glycoside of the thio sugar, see: Van Laak, K.; Scharf, H. D. *Tetrahedron Lett.* **1989**, *30*, 4505. (c) For a synthesis of the esperamycin isopropylamino sugar, see: Golik, J.; Wong, H.; Vyas, D. M.; Doyle, T. W. *Tetrahedron Lett.* **1989**, *30*, 2497. For a synthesis of the calicheamicin $\gamma_{1\alpha}^{I}$ ethylamino sugar, see: Kahne, D.; Yang, D.; Lee, M. D. *Tetrahedron Lett.* **1990**, *31*, 21.

(5) For the synthesis of this compound, see the supplementary material.

(6) All new compounds exhibited satisfactory spectral and analytical and/or exact mass data. Yields refer to spectroscopically and chromatographically homogeneous materials.

(7) In the absence of NH_4Cl, silicon migration from O-3 to O-2 was a competing process following initial 1,2-reduction of the enone.

(8) For an example of 1,2-ester migration in a *cis*-1-*O*-acyl-2-hydroxy sugar, see: Pederson, C.; Fletcher, H. B., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 3215.

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(10) For a similar observation involving glycosyl ester formation, see: Smith, A. B., III; Hale, K. J.; Rivero, R. A. *Tetrahedron Lett.* **1986**, *27*, 5813.

(11) While a single geometrical isomer about the oxime bond was obtained, the stereochemistry has not been determined.

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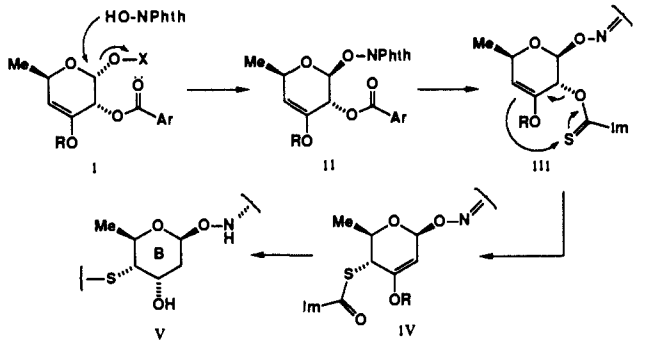
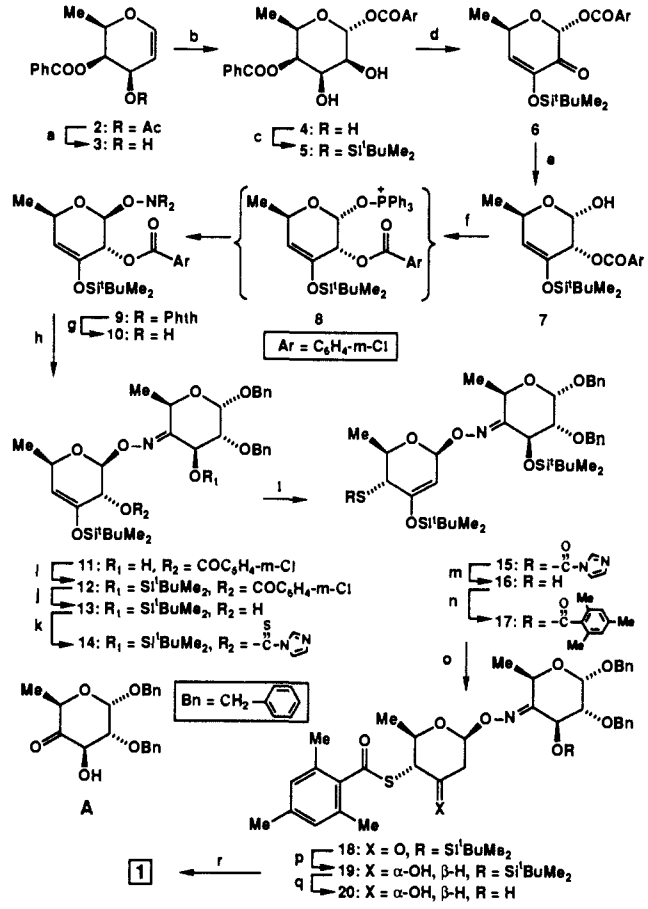
Scheme I. Synthetic Design for the Construction of the Central Ring of the Calicheamicin $\gamma_{1\alpha}^{I}$ Oligosaccharide Fragment



Scheme II. Synthesis of Compound 1[a]



[a] Reagents and conditions: (a) 1.0 equiv of DIBAL, CH_2Cl_2, -78 °C, 2.5 h, 72%, plus 15% recovered **2**; (b) 2.5 equiv of 55% MCPBA, $MgSO_4$, CH_2Cl_2, 0 °C, 0.5 h, 55%; (c) 1.5 equiv of $^tBuMe_2SiCl$, 2.0 equiv of imidazole, CH_2Cl_2, 25 °C, 30 h, 67%; (d) 1.5 equiv of $(COCl)_2$, 2.0 equiv of DMSO, 5 equiv of Et_3N, CH_2Cl_2, -78 to 25 °C, 88%; (e) 1.2 equiv of $Zn(BH_4)_2$, 0.5 equiv of NH_4Cl, ether, 0 °C, 20 min; (f) 1.1 equiv of HO-NPhth, 1.2 equiv of diisopropyl azodicarboxylate, 1.2 equiv of Ph_3P, THF, 25 °C, 0.5 h, 53% overall from **6**; (g) 1.0 equiv of N_2H_4, MeOH, 25 °C, 10 min; (h) 1.2 equiv of A, 0.1 cquiv of PPTS, PhH, 25 °C, 3 h, 92% overall from **9**; (i) 1.5 equiv of $^tBuMe_2SiOTf$, 2.5 equiv of 2,6-lutidine, -25 to 0 °C, 0.5 h, 99%; (j) 2.5 equiv of DIBAL, CH_2Cl_2, -78 °C, 1 h, 91%; (k) 1.0 equiv of thiocarbonyldiimidazole, CH_3CN, 25 °C, 20 h; (l) $PhCH_3$, 110 °C, 1 h, 85% overall from **13**; (m) 6.0 equiv of DIBAL, CH_2Cl_2, -78 °C, 2 h; (n) 2.0 equiv of 2,4,6-trimethylbenzoyl chloride, 10 equiv of Et_3N, 0.35 equiv of DMAP, CH_2Cl_2, 25 °C, 8 h, 91% overall from **15**; (o) 1.0 cquiv of TBAF, THF-H_2O-HOAc (100:25:1), 0 °C, 20 min; (p) 2.5 cquiv of K-Selectride, DME, -78 °C, 1.5 h, 74% overall from **17**; (q) 1.2 equiv of TBAF, THF, 0-25 °C, 45 min, 100%; (r) 6 equiv of $BH_3 \cdot NH_3$, 6 equiv of PPTS, 25 °C, 4 h, 85%.

thiocarbonyldiimidazole for 20 h at 25 °C gave a mixture of the thioimidazolide **14** and **15**, the latter resulting from a stereospecific [3,3]-sigmatropic rearrangement[12] of **14**. Refluxing the mixture for 1 h in toluene completed the rearrangement in 85% overall yield from **13**. Generation of the free thiol group in **15** using DIBAL resulted in the formation of **16**, which was immediately reacted with 2,4,6-trimethylbenzoyl chloride under basic conditions, to afford the desired thioester **17**. Selective desilylation was achieved with a stoichiometric amount of nBu_4NF leading to ketone **18** in good yield. As expected, stereoselective reduction of the carbonyl group of ring B with a bulky reagent (K-Selectride) led to compound **19** (74% overall yield from **17**). Desilylation of **19** led to dihydroxy compound **20** in quantitative yield. Finally, stereoselective reduction of the oxime in **20** was secured with $BH_3 \cdot NH_3$-pyridinium *p*-toluenesulfonate (PPTS), furnishing the targeted ABC system **1** in 85% yield.[13] The stereochemistry of the stereogenic centers generated in this sequence (C-4, C-1′, C-3′ and C-4′) was evident from NMR data (see supplementary material).

The described chemistry provides stereocontrolled solutions to the crucial bond constructions of the calicheamicin $\gamma_{1\alpha}^{I}$ oligosaccharide fragment and makes available the interesting subfragment **1** for DNA binding studies and other investigations in this area. Furthermore, the reported sequence is expected to facilitate the synthesis of the complete oligosaccharide fragment of these antibiotics.

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Supplementary Material Available: Schemes with reagents and conditions for the synthesis of compounds **2** and A and listing of selected R_f, $[\alpha]_D$, ^1H NMR, and mass spectrometric data for compounds A, **1**, **2**, **4**, **6**, **9**, **11**, **13**, **15**, **17**, **19**, and **20** (10 pages). Ordering information is given on any current masthead page.

(12) (a) For a rearrangement of an allylic xanthate in a carbohydrate derivative see: Ferrier, R. J.; Vethauiyasar, N. *J. Chem. Soc. D* **1970**, 1385. (b) For a rearrangement of an allylic xanthate in a 2-substituted cyclohexene derivative, see: Trost, B. M.; Hiemstra, H. *J. Am. Chem. Soc.* **1982**, *104*, 886.

(13) The precise mechanism for the axial delivery of hydride in this stereoselective process is not well understood at present.

Tellurapyrylium Dyes as Catalysts for the Conversion of Singlet Oxygen and Water to Hydrogen Peroxide

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The development of methods for light-to-chemical energy conversion is important for application to solar-energy storage schemes. While the major emphasis in such research has been water splitting for the production of hydrogen,[1-6] the photopro-

(1) For Ru(2,2′-bipyridine)$_3^{2+}$/methylviologen systems: (a) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (b) *Photogeneration of Hydrogen*; Harriman, A., West, M. A., Eds.; Academic: London, 1982. (c) *Energy Resources through Photochemistry and Catalysis*; Gratzel, M., Ed.; Academic: New York, 1983. (d) Prasad, D. R.; Khoffman, M. Z. *J. Am. Chem. Soc.* **1986**, *108*, 2568.

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