(Me₃SiSCH₂CH₂SSiMe₃;[11] TiCl₄; CH₂Cl₂; −78 °C; 0.5 h; room temperature; 2 h) followed by thermodynamically-controlled formation[12] [CSA; (CH₃)₂CO/CH₂Cl₂ (1:1), room temperature; 2 h; 60% overall from **10**] of a 1,2-acetonide from the C(5) and C(6) hydroxyls of the intermediate triol furnished **11**. Subsequent removal [NBS; (CH₃)₂CO/H₂O (9:1); 0 °C; 0.25 h; 75%] of the dithiolane-protecting group then gave keto alcohol **12**. Swern oxidation [(COCl)₂; Me₂SO; Et₃N; CH₂Cl₂; −60 °C → room temperature; 0.5 h; 90%] of the primary alcohol function present in **12** produced **13**. Introduction of the C(1)–C(2) unit was then conveniently achieved by the chemoselective, Lewis acid-mediated reaction of tri-*n*-butylcrotylstannane[13,14] with the aldehyde function of **13** (CH₃CH=CHCH₂SnBu₃; BF₃·OEt₂; CH₂Cl₂; −90 °C; 0.5 h; 82% combined) to deliver a mixture (ca. 4:1) of the desired homoallylic alcohol **14**, surprisingly contaminated with the anti adduct that was *epimeric* at C(2); both structures were confirmed by single-crystal X-ray analyses.[15] Thus, construction of the intact C(1)–C(10) intermediate **14** was achieved by an efficient process wherein the resident chirality at C(4) and C(5), which was established at the outset by a diastereoselective aldol reaction, determined the sense of emerging chirality at the four remaining stereogenic centers of this fragment.

Completion of the synthesis of the erythronolide B seco acid derivative **3** was realized by coupling the C(1)–C(10) ketone **14** with the C(11)–C(15) aldehyde **15** and subsequent unmasking of the C(1) carboxyl group by oxidative processing of the terminal olefin. Thus, chelation controlled aldol condensation of **15**[16] with the (*Z*)-enolate of **14** [LHMDS (3.0 equiv); THF, −78 °C; 3 h; 72% total (88% based on recovered **14**)] furnished a mixture (ca. 6:1) of diastereomeric syn adducts with the requisite **16** in predominance.[17] Oxidative cleavage[18] of the terminal double bond ·present in **16** [(a) O₃; MeOH; Sudan III; −95 °C; (b) Et₃N; Ac₂O; CH₂Cl₂; 0 °C → room temperature; 45 min; 61% overall] produced the methyl ester **3**.

The structure of the aldol adduct **16** was unambiguously verified by its conversion into polyol **17**. In the event, hydride reduction of **16** with Me₄NBH(OAc)₃[19] proceeded with high stereoselectivity to give the 9(*S*)-alcohol as the major product (75%), and subsequent refunctionalization of the carboxyl terminus [(a) O₃; EtOAc; Sudan III; (b) LiAlH₄] followed by removal of the hydroxyl-protecting groups (NH₂OH·HCl; KH₂PO₄; H₂O–MeOH/Δ; 4 h) gave **17**. An authentic sample of **17** was prepared from naturally derived erythronolide B (**18**)[20] by sequential hydride reduction [(a) NaBH₄; PhMe/*t*-BuOH (5:1); (b) LiAlH₄; THF]. The two samples of **17** thus independently obtained were identical by ¹³C NMR and TLC. It is noteworthy that reduction of the ketone function at C(9) of **16** gave predominantly the 9(*S*)-stereochemistry since this configuration will be required for

eventual preparation of intermediates that will be suitably constituted for macrolactonization.[4e]
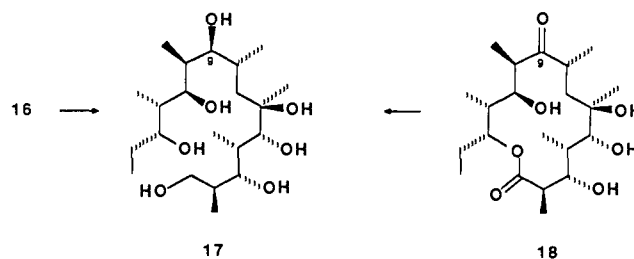
In summary, the concise synthesis of **3**, a protected derivative of the seco acid of erythronolide B, has been achieved by a convergent approach wherein the longest linear sequence employs only 14 chemical operations with the total number of steps being 18 including the transformations necessary to prepare the aldehydic partner **15** employed in the final carbon–carbon bond construction. The approach is efficient, and substantial quantities of material may be prepared so that the conversion of **3** into the natural antibiotic **1** constitutes a viable objective for future efforts.

Splitting of a Two-Electron Cyclic Voltammetric Wave into Its One-Electron Components: The (η-C₆Me₆)₂Ru²⁺/⁺/⁰ Couples†
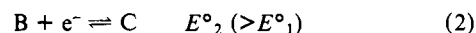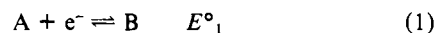
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We report results on the redox couple (η-C₆Me₆)₂Ru²⁺/⁰ which show, apparently for the first time, definitive evidence that cyclic voltammetric (CV) scan rate changes can allow visual discrimination between the two one-electron components of a two-electron electrochemical wave. Applied to the reduction of the bis-arene complex, this approach resulted in the separation of one wave into two at high scan rates and quantitative agreement between theory and experiment over a range of observation times. The results offer hope in deciphering the relative timing of charge transfer and conformational changes in multiple electron-transfer reactions.

Although there is evidence that some two-electron transfers proceed without one-electron intermediates,[1,2] it is usually thought that the reaction A + 2e⁻ ⇌ C progresses in a sequence of two discrete one-electron steps,[3] each with its own $E°$ value (eq 1 and 2).[4–6] A cyclic voltammetric wave with the characteristics of a

$$A + e^- \rightleftharpoons B \qquad E°_1 \qquad (1)$$

$$B + e^- \rightleftharpoons C \qquad E°_2 \ (>E°_1) \qquad (2)$$

(11) Evans, D. A.; Truesdale, L. K.; Nesbitt, S. L. *J. Am. Chem. Soc.* **1977,** *99*, 5009.

(12) Cf: (a) Williams, D. R.; Sit, S.-Y. *J. Am. Chem. Soc.* **1984,** *106*, 2949. (b) Tius, M. A.; Fang, A. M. *Ibid.* **1986,** *108*, 1035. (c) Meyers, A. I.; Lawson, J. P.; Walker, D. G.; Linderman, R. J. *J. Org. Chem.* **1986,** *51*, 5111. (d) El Ashry, E. S. H.; El Kilany, Y.; Singab, F. *J. Chem. Soc., Perkin Trans 1* **1988,** 133.

(13) (a) Keck, G. E.; Abbott, D. E. *Tetrahedron Lett.* **1984,** *25*, 1879, 1883. (b) Yamamoto, Y. *Aldrich. Acta* **1987,** *20*, 45.

(14) We are grateful to Prof. G. E. Keck (The University of Utah) for a generous gift of tri-*n*-butylcrotylstannane.

(15) Lynch, V. M.; Pacofsky, G. J.; Martin, S. F.; Davis, B. E. *Acta Crystallogr.* **1989,** *C45*, 973.

(16) The aldehyde **15** was prepared according to the following procedure: (1) (a) (4*S*)-4-(2-methylethyl)-3-(1-oxopropyl)-2-oxazolidinone; *n*-Bu₂BOTf; Et₃N; 0.5 h; −78 °C → 0 °C; 1 h;⁸ (b) EtCHO; −78 °C; 0.5 h; −78 → 0 °C; 1 h; 80%. (2) PhCH₂OCH₂Cl; *i*-Pr₂NEt; CH₂Cl₂; room temperature; 45 h; 91%. (3) LiAlH₄; 0 °C; 45 min; 74%. (4) (COCl)₂; Me₂SO; *N*-methylmorpholine; CH₂Cl₂; −60 °C → room temperature; 0.5 h; 88%.
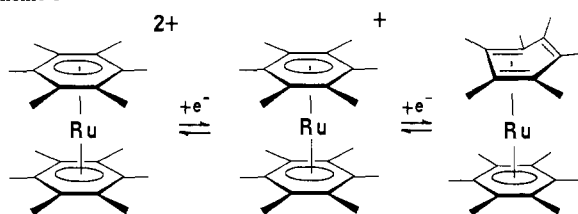
(17) The coupling constants, $J_{H(10)-H(11)}$ = 2.0 Hz and $J_{H(11)-H(12)}$ = 9.9 Hz, observed for **16** were in excellent agreement with values ($J_{H(10)-H(11)}$ = 2 Hz and $J_{H(11)-H(12)}$ = 10 Hz) reported previously. See ref 4d,j.

(18) Schreiber, S. L.; Claus, R. E.; Reagan, J. *Tetrahedron Lett.* **1982,** *23*, 3867.

(19) Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988,** *110*, 3560.

(20) We are grateful to Dr. Paul A. Lartey (Abbott Laboratories) for a generous gift of erythronolide B.

†This may be considered as Part 20 of the series Structural Consequences of Electron-Transfer Reactions. Part 19: Merkert, J.; Nielson, R. M.; Weaver, M. J.; Geiger, W. E. *J. Am. Chem. Soc.*, in press.

(1) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980; pp 84–91.

(2) Gurnee, E. F.; Magee, J. L. *J. Chem. Phys.* **1957,** *26*, 1237.

(3) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984,** *60*, 107.

(4) Bowyer, W. J.; Geiger, W. E. *J. Electroanal. Chem.* **1988,** *239*, 253.

(5) Hinkelmann, K.; Heinze, J. *Ber. Bunsenges Phys. Chem.* **1987,** *91*, 243 and references therein.

(6) Bard, A. J.; Faulkner, L. *Electrochemical Methods*; John Wiley and Sons: New York, 1980; pp 111–112.

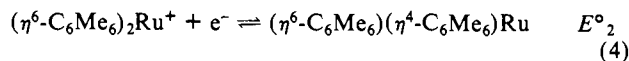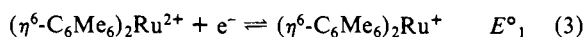**Scheme I**

net two-electron transfer is observed when $E°_2 > E°_1$, so that the intermediate B is thermodynamically unstable with respect to A and C.[6-8] If both electron transfers are kinetically unencumbered, an applied potential sufficiently negative to initiate the electron-transfer process (eq 1) will also drive the second reduction (eq 2), resulting in an overall two-electron transfer. The formal potential measured under these circumstances is the *average* of $E°_1$ and $E°_2$.[7]

There is, however, considerable interest in extracting the one-electron parameters from these reactions.[4-9] This could be accomplished, provided that the second electron transfer is slower than the first, by increasing the CV scan rate until the larger cathodic shift of the second process[10] results in splitting of the original wave into two waves.

The Ru(II) complex $(\eta^6\text{-}C_6Me_6)_2Ru^{2+}$ and its Ru(0) analogue $(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)Ru$ are both stable in CH_3CN, related by a two-electron CV wave showing only slight deviations from reversibility[7] at slow sweep rates (Figure 1). At $v < 0.05$ V/s at a Pt electrode, the cathodic branch has a width at half-height, $E_p - E_{p/2}$, of 43 mV, consistent with the difference in $E°$ values of reactions 3 and 4 being close to 0 V.

$$(\eta^6\text{-}C_6Me_6)_2Ru^{2+} + e^- \rightleftharpoons (\eta^6\text{-}C_6Me_6)_2Ru^+ \quad E°_1 \quad (3)$$

$$(\eta^6\text{-}C_6Me_6)_2Ru^+ + e^- \rightleftharpoons (\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)Ru \quad E°_2 \quad (4)$$

Marcus theory predicts that if the arene hapticity change from η^6 to η^4 occurs during the Ru(I)/Ru(0) charge transfer, the heterogeneous electron-transfer rate of the second couple should be lower than the first.[11] This is observed for the closely analogous complexes[12] $(\eta^6\text{-}C_6R_6)RhCp^{*2+}/(\eta^6\text{-}C_6R_6)RhCp^{*+}/(\eta^4\text{-}C_6R_6)$-$RhCp^*$, $Cp^* = \eta^5\text{-}C_5Me_5$, and forms the basis of the hapticity assignments in the drawing.

As the sweep rate is increased, the cathodic branch of the wave broadens and eventually a second cathodic wave separates from the first (Figure 1). At $v = 10$ V/s, two cathodic and two anodic processes are distinctly visible. The outermost cathodic and anodic features (II and IV, respectively) are coupled[13] (eq 4), as are waves I and III (eq 3). Yet higher sweep rates merely accentuate this trend. Changes in peak potentials and wave shapes with scan rate are consistent with an EE mechanism (i.e., consecutive electron transfers with simultaneous structural changes) rather than one
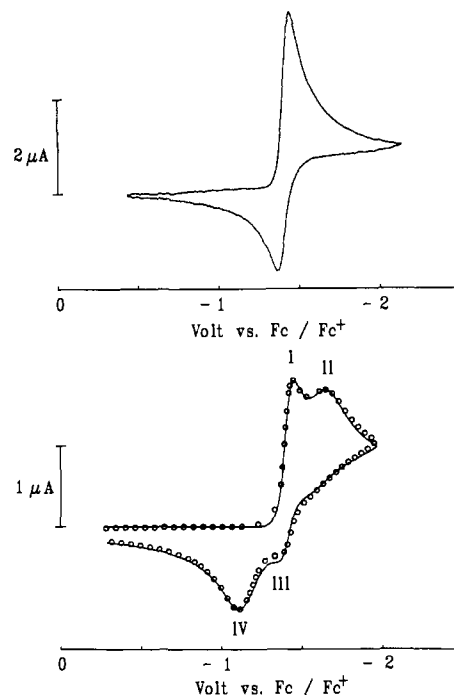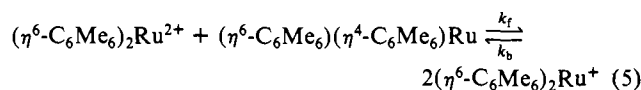
Figure 1. Cyclic voltammograms of $[(\eta^6\text{-}C_6Me_6)_2Ru][BF_4]_2$ in $CH_3CN/0.5$ M Bu_4NPF_6 at a Pt electrode, $T = 298$ K; Top: scan rate $= 0.2$ V/s, concentration $= 2.73 \times 10^{-4}$ M, area of Pt bead ca. 1 mm²; Bottom: scan rate $= 10$ V/s, concentration $= 1.31 \times 10^{-3}$ M, Pt disk ($r_0 = 238$ μm); circles = experimental values, line = values calculated by finite difference simulation [Feldberg, S. W. In *Electroanalytical Chemistry*; Bard, A. J., ed.; Marcel Dekker: New York, 1969; Vol. 3, p 199ff], with D_0 values of 7.6×10^{-6} cm²/s for the dication and 2.0×10^5 cm²/s for the neutral complex.

in which a separate geometric (hapticity) change occurs after either the first electron transfer (ECE) or the second (EEC).[14]

The rate of the homogeneous comproportionation reaction, eq 5, has a profound effect on the appearance of the waves.

$$(\eta^6\text{-}C_6Me_6)_2Ru^{2+} + (\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)Ru \underset{k_b}{\overset{k_f}{\rightleftharpoons}}$$
$$2(\eta^6\text{-}C_6Me_6)_2Ru^+ \quad (5)$$

When the rate of the comproportionation reaction is very fast, no anodic current should be observed at IV, since the Ru(0) complex would be reoxidized by the Ru(II) dication in solution rather than by the electrode. An accompanying increase in the anodic curent at III, the oxidation wave of Ru(I), would be expected. This has been confirmed by experiments at variable concentrations (10^{-4}–10^{-3} M).

Extensive digital simulations have been performed over a scan rate range of 0.5–100 V/s and a concentration range of 0.5–1.3 mM.[14] The results are consistent with the electron-transfer parameters (potentials referenced to ferrocene[0/+], which is 0.40 V positive of the SCE in this solvent/electrolyte medium): $E°_1 = -1.421$ V, $k_{s1} > 0.2$ cm/s, $\alpha_1 = 0.50$; $E°_2 = -1.403$ V, $k_{s2} = 5.6 \times 10^{-4}$ cm/s, $\alpha_2 = 0.50$; $k_b = 5.9 \times 10^4$ M^{-1} s^{-1}, $k_f = 3.0 \times 10^4$ M^{-1} s^{-1}. The $E°$ values predict an equilibrium constant for comproportionation (eq 5) of 0.5 ± 0.2. The simulations are strongly indicative of a potential-dependent α (charge-transfer) term for the second step of $d\alpha/dE = 0.22$ V^{-1}, as predicted by Marcus.[14,15]

(7) Polcyn, D. S.; Shain, I. *Anal. Chem.* **1966**, *38*, 370. The chemical reversibility of the Ru(II)/Ru(0) couple is less than complete at low scan rates, due to instability of the Ru(I) intermediate.

(8) Ryan, M. D. *J. Electrochem. Soc.* **1978**, *125*, 547.

(9) See, for example: (a) Payne, D. A.; Bard, A. J. *J. Electrochem. Soc.* **1972**, *119*, 1665. (b) Eriksrud, E. *J. Electroanal. Chem.* **1977**, *76*, 27. (c) Bond, A. M.; Grabaric, B. S.; Jones, R. D.; Rumble, N. W. *J. Electroanal. Chem.* **1979**, *100*, 625. (d) Aalstad, B.; Parker, V. D. *J. Electroanal. Chem.* **1982**, *136*, 251. (e) Galvez, J.; Park, S.-M. *J. Electroanal. Chem.* **1987**, *235*, 71. (f) Grzeszczuk, M.; Smith, D. E. *J. Electroanal. Chem.* **1984**, *162*, 189. (g) Tsaur, K.-H.; Pollard, R. *J. Electroanal. Chem.* **1985**, *183*, 91.

(10) (a) Matsuda, H.; Ayabe, Z. Z. *Elektrochem.* **1955**, *59*, 494. (b) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351. (c) Reference 6, pp 224–231.

(11) Marcus, R. A. *Ann. Rev. Phys. Chem.* **1964**, *15*, 155.

(12) (a) Bowyer, W. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5657. (b) Bowyer, W. J.; Merkert, J.; Geiger, W. E.; Rheingold, A. L. *Organometallics* **1989**, *8*, 191. (c) Merkert, J.; Neilson, R. M.; Weaver, M.; Geiger, W. E. *J. Am. Chem. Soc.*, in press. (d) Neilson, R. M.; Weaver, M. J. *Organometallics* **1989**, *8*, 1636.

(13) The oxidation of Ru(0) in peak IV actually results in Ru(II) because Ru(I) is unstable at this potential. The Ru(0)/Ru(I) oxidation is, however, the rate-limiting step at wave IV.

(14) A wave-shape analysis will be part of a forthcoming paper on this system. α is defined according to the Butler–Volmer equation. The appearance of waves II and IV cannot be ascribed to ECE- or EEC-type mechanisms, because their shifts with increasing v (– or + 92 mV/log $v =$ II and IV, respectively) are either in the wrong direction (ECE) or too larger (EEC). Agreement between theory and experiment for the relative magnitudes of peaks III and IV was markedly improved by using the different D_0 values measured for the dication and neutral complex (see figure caption).

(15) (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679. (b) Marcus, R. A. *Electrochim. Acta* **1968**, *13*, 995.

It is informative to compare the charge-transfer parameters derived from these studies with those suggested by theory to favor discrimination between the two one-electron components of a two-electron wave. Hinkelmann and Heinze predicted wave splitting for a two-electron couple with $\Delta E° = 0$ V when the second charge transfer is at least 10^2-fold slower than the first, and the homogeneous disproportionation reaction is slow.[5] The present Ru system, with $E°_2 - E°_1 = +0.02$ V and $k_{s1}/k_{s2} > 10^2$, fulfills these requirements. Presumably, a more positive $\Delta E°$ [further thermodynamic destabilization of the Ru(I) intermediate] would require a greater disparity in charge-transfer rates to see the wave splitting at these scan rates.

Claims of wave splitting for polynuclear metal complexes, interpreted in terms of EE mechanisms, have recently appeared.[16–18] However, the published voltammograms[16] appear to be more diagnostic of an EEC mechanism in which the second electron transfer gives a distinctly new compound or isomer with its own voltammetric behavior.

The present results and the appropriate theory should be helpful in evaluating the important question of the timing of geometric changes relative to electron transfer in multielectron processes, in addition to allowing access in some cases to the electron-transfer parameters of the individual steps making up an overall two-electron change. This method may be particularly appropriate in the study of interactions between weakly coupled identical metal redox sites, which have $\Delta E°$ values inherently close to 0 V.

(16) Drake, S. R.; Barley, M. H.; Johnson, B. F. G.; Lewis, J. *Organometallics* **1988,** *7,* 806 (variable temperature observation).

(17) Edwin, J.; Geiger, W. E., manuscript in preparation describing voltammetry of dimetallic complexes (variable-temperature observation).

(18) de Learie, L. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1987,** *109,* 7031.

Experimental Modeling of the Priming Mechanism of the Calicheamicin/Esperamicin Antibiotics: Actuation by the Addition of Intramolecular Nucleophiles to the Bridgehead Double Bond

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Gayle Schulte

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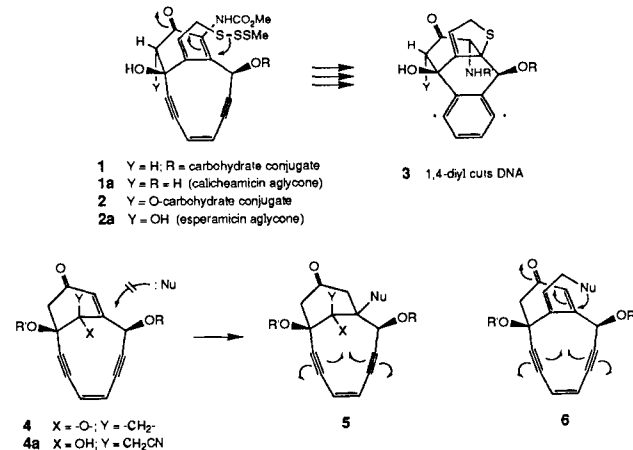*New Haven, Connecticut 06511*

A great deal of effort has been directed toward understanding the mode of action of the enediyne antibiotics, calicheamicin (**1**)[1] and esperamicin (**2**).[2] Such studies might lead to new chemotherapeutic possibilities. The goal is to obtain increasing levels

(1) (a) 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. (b) 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. (c) Zein, N.; Sinha, A. M.; McGahren, W. J.; Ellestad, G. A. *Science* **1988,** *240,* 1198. (d) Hawley, R. C.; Kiessling, L. L.; Schreiber, S. L. *Proc. Natl. Acad. Sci. U.S.A.* **1989,** *86,* 1105. (e) Zein, N.; Poncin, M.; Nilakantan, R.; Ellestad, G. A. *Science* **1989,** *244,* 697.

(2) (a) Konishi, M.; Ohkuma, H.; Saitoh, K.; Kawaguchi, H.; Golik, J.; Dubay, G.; Groenewold, G.; Krishnan, B.; Doyle, T. W. *J. Antibiot.* **1985,** *38,* 1605. (b) Golik, J.; Clardy, J.; Dubay, G.; Groenewold, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saitoh, K.; Doyle, T. W. *J. Am. Chem. Soc.* **1987,** *109,* 3461. (c) Golik, J.; Dubay, G.; Groenewold, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saitoh, K.; Doyle, T. W. *J. Am. Chem. Soc.* **1987,** *109,* 3462. (d) Long, B. H.; Golik, J.; Forenza, S.; Ward, B.; Rehfuss, R.; Dabrowiak, J. C.; Catino, J. J.; Musial, S. T.; Brookshire, K. W.; Doyle, T. W. *Proc. Natl. Acad. Sci. U.S.A.* **1989,** *86,* 2.

Scheme I

1 Y = H; R = carbohydrate conjugate
1a Y = R = H (calicheamicin aglycone)
2 Y = O-carbohydrate conjugate
2a Y = OH (esperamicin aglycone)

3 1,4-diyl cuts DNA

4 X = -O-; Y = -CH₂-
4a X = OH; Y = CH₂CN
5
6

of drug selectivity toward diseased cells without eroding the extraordinary potency of the natural products themselves. Organic synthesis is likely to play a useful role in experimentally based biomodeling, in generating analogues for evaluation, and in elaborating new conjugates for cell targeting.

A concise route to compounds of the type **4**, hitherto the most functionalized variants of the hypothetical aglycons **1a** and **2a**, has been described.[3,4] It had been expected that we could trigger cycloaromatization reactions (vide infra) via **5**. Surprisingly, no classical Michael reaction of **4** was achieved with standard nucleophiles (thiolate, cyanide, cuprate).[5,6]

While it will eventually be of interest to determine why this seemingly vulnerable bridgehead double bond has proven to be so resistant to conjugate addition,[7] our next line of attack was to study the feasibility of the intramolecular counterpart. Presumably, the in vivo priming cascade is actuated by intramolecular Michael addition of thiolate. The 1,4-diyl **3**, resulting from Bergman cycloaromatization,[8–11] is likely to be the effector species for the cutting of duplex DNA.[1c,2d,12]

The goal of our synthesis is delineated in construct **6**, wherein an intramolecular Z-disposed nucleophile (Nu) is poised to add to the hitherto resistant bridgehead olefin. In this communication we report (i) a solution to this synthetic problem, (ii) the rather facile intramolecular Michael addition of oxygen- and thiol-based nucleophiles to the double bond, and (iii) the reductive cycloaromatization reaction[8] of the resultant enediynes.

Solvolysis of the previously described compound **7**[3] under carefully determined conditions (potassium acetate, acetic acid, DMSO, 50 °C) gave acetoxyhydrin **8**,[13a] in which the enol ether functionality had been preserved. Brief reaction of **8** with dry

(3) Danishefsky, S. J.; Mantlo, N. B.; Yamashita, D. S.; Schulte, G. *J. Am. Chem. Soc.* **1988,** *110,* 6890.

(4) Syntheses of less functionalized versions of the calicheamicin/esperamicin core have been reported. See: (a) Magnus, P.; Lewis, R.; Huffman, J. C. *J. Am. Chem. Soc.* **1988,** *110,* 6921. (b) Kende, A. S.; Smith, C. A. *Tetrahedron Lett.* **1988,** *29,* 4217. (c) Tomioka, K.; Fujita, H.; Koga, K. *Tetrahedron Lett.* **1989,** *30,* 851.

(5) Mantlo, N. B.; Danishefsky, S. J. *J. Org. Chem.* **1989,** *54,* 2781.

(6) Unpublished results of N. B. Mantlo.

(7) This immunity may be accountable in terms of steric hindrance afforded by the pseudoaxial substituent of the one-carbon bridge. We do not currently discount, however, the operation of some additional or alternative influence.

(8) (a) Bergman, R. G. *Acc. Chem. Res.* **1973,** *6,* 25. (b) For earlier explorations in this area, see: Darby, N.; Kim, C. U.; Salaün, J. A.; Shelton, K. W.; Takada, S.; Masamune, S. *Chem. Commun.* **1971,** 1516.

(9) Nicolaou, K. C.; Zuccarello, G.; Ogawa, Y.; Schweiger, E. J.; Kumazawa, T. *J. Am. Chem. Soc.* **1988,** *110,* 4866.

(10) Magnus, P.; Lewis, R. T. *Tetrahedron Lett.* **1989,** *30,* 1905.

(11) For an example of reductive actuation of cycloaromatization, see ref 5.

(12) Nicolaou, K. C.; Ogawa, Y.; Zuccarello, G.; Kataoka, H. *J. Am. Chem. Soc.* **1988,** *110,* 7247.

(13) (a) The structure assigned to each new compound is consistent with its infrared and 250 MHz ¹H NMR spectra as well as parent ion identification by high resolution mass spectrometry. (b) A sample of this new compound obtained by crystallization gave C and H combustion analysis within 0.4%.