Supplementary Material Available: Details of the crystal structure determination, tables of positional parameters, calculated positional parameters of hydrogen atoms, general temperature factor expressions, bond distances, and bond angles for $[TcN_7O_2C_7H_{24}][BC_{24}H_{20}]_2$, ORTEP views of the two $[BC_{24}H_{20}]^-$ anions, details of the preparation and characterization of the complex $[TcN(en)_2(L)][B(C_6H_5)_4]_2$, and a general reaction scheme (20 pages); listing of observed and calculated structure factors for $[TcN_7O_2C_7H_{24}][BC_{24}H_{20}]_2$ (18 pages). Ordering information is given on any current masthead page.

Synthetic Studies Directed toward the Eremantholides. 2. A Novel Application of the Ramberg-Bäcklund Rearrangement to a Highly Stereoselective Synthesis of (+)-Eremantholide A

Robert K. Boeckman, Jr.,* Suk Kyoon Yoon, and Debra K. Heckendorn

Department of Chemistry, University of Rochester Rochester, New York 14627

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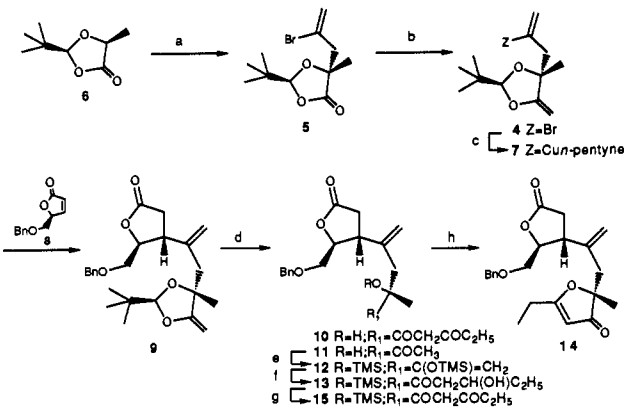
Eremantholide A (**1**) is a member of the furanoheliangolides isolated by LeQuesne and co-workers from *Eremanthus elaeagnus*.[1,2] The structure and relative stereochemistry of **1** were confirmed by X-ray crystallographic analysis of a derivative.[1] The absolute configuration of **1** (as shown) was predicated upon the biogenetic relationship of the furanoheliangolides to the germacranolides, which possess a common absolute configuration at C_7. The structure of **1** is unusual and highly strained since the molecular geometry requires that the endocyclic C_4–C_5 double bond be twisted 88° out of the plane of the 3(2*H*)-furanone ring. Eremantholide A (**1**) is also of interest because it exhibits significant levels of in vitro antitumor activity against a variety of tumor cell lines.[3,4]

The synthesis of other naturally occurring 3(2*H*)-furanones, such as jatrophone, has been reported,[5] and **1** has also been the target of several synthetic efforts, including our own preliminary studies.[6-8] Herein, we report the first stereoselective total synthesis of (+)-eremantholide A (**1**), which also confirms the assignment of its absolute configuration.

Our strategy required an α-hydroxy ketone synthon convertible into the 3(2*H*)-furanone and methodology to effect medium-ring closure and creation of the strained nine-membered-ring olefin.[7] Intact 3(2*H*)-furanone derivatives did not prove suitable; thus cyclic acetal **4** was employed, which was available from (*R*)-(−)-lactic acid via **5** (Scheme I).[9]

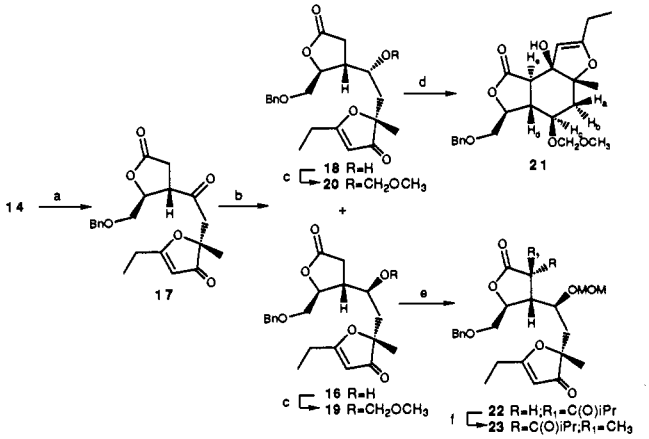
Alkylation of the (2*S*,4*S*)-(+)-lactolide **6**[9] with 2,3-dibromopropene afforded the (2*S*,4*R*)-(+)-lactolide **5** (mp 35–36 °C, >98% de) in 74% yield.[9,10] Lactolide **5** was elaborated to the desired vinyl bromide **4**, in 83% yield, by exposure to Tebbe reagent prepared in situ.[11,12] Bromide **4** was converted to the sensitive mixed cuprate reagent **7** by successive treatment with *t*-BuLi and cuprous *n*-pentyne in the presence of HMPT at −40 °C.[13,14] Addition of the optically pure butenolide **8**[15] then provided lactone (+)-**9** ($[\alpha]^{23}_D$ +5.5° (*c* 2.82, $CHCl_3$)), as a single diastereomer, in 79% yield.

Scheme I[a]



[a] Reagents: (a) LDA (1.2 equiv), THF, −78 °C, 3 h, then $H_2C{=}C(Br)CH_2Br$ (2.5 equiv), dropwise, −78 → −70 °C, 18 h; (b) Cp_2TiCl_2–$Al(CH_3)_3$ (3 equiv), THF–$PhCH_3$, 0 → 25 °C, 4 h then 25 °C, 10 h; (c) *t*-BuLi (2 equiv), Et_2O, −78 °C, ~1.5 h, then added to $Cu{\equiv}nC_3H_7$ (1 equiv), HMPT (1 equiv), Et_2O, −40 °C, 30 min followed by **8** (1 equiv), Et_2O, −40 °C, 2 h, then pH 10 NH_4Cl–NH_4OH, −40 °C → 25 °C, 1 h; (d) aqueous $(CO_2H)_2$ (saturated), HCl (1 drop), THF, 25 °C, 12 h; (e) TMSCl (5 equiv), DBU (5 equiv), CH_2Cl_2, Δ, 12 h; (f) C_2H_5CHO (1.2 equiv), then $BF_3{\cdot}Et_2O$ (1.1 equiv) (dropwise, 5 min), −78 °C, 40 min; (g) Dess–Martin periodinane (1.2 equiv), CH_2Cl_2, 20 °C, 1 h; (h) 5% HCl–THF (1:2, v/v), 25 °C, 8 h.

Scheme II[a]



[a] Reagents: (a) OsO_4 (catalytic), $NaIO_4$ (2.5 equiv), THF–H_2O, 25 °C, 12 h; (b) $NaBH_4$ (1 equiv), CH_3OH, −40 °C, 15 min; (c) $(CH_3O)_2CH_2$ (60 equiv), P_2O_5 (3 equiv), 3-Å molecular sieves, CH_2Cl_2, 25 °C, 40 min; (d) LDA (1 equiv), THF, −78 °C, 2 h; (e) LDA (2.3 equiv), THF, −78 °C, 40 min, then isobutyryl imidazolide (1.1 equiv) in THF (dropwise, 10 min), −78 °C, 1.5 h; (f) NaH (1.3 equiv), DMF, 0 °C, 40 min, then CH_3I (5 equiv), 0 °C, 3.5 h.

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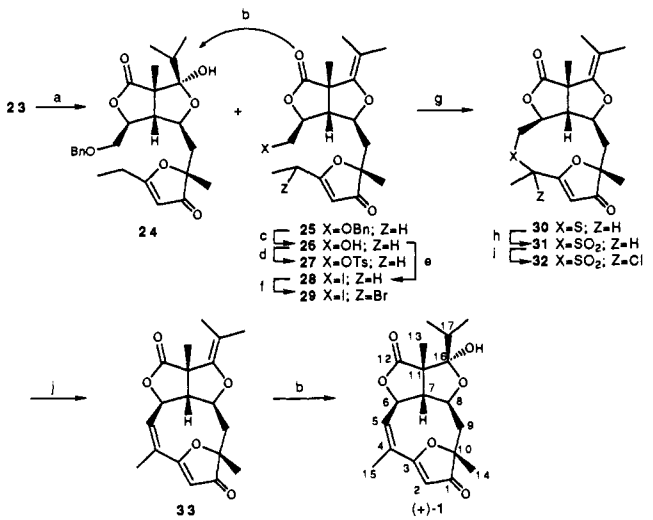
Scheme III[a]



[a] Reagents: (a) TMSBr (5 equiv), 4-Å molecular sieves, CH_2Cl_2, 0 → 25 °C, 5 h, then Amberlyst-15, 4-Å molecular sieves, 25 °C, 10 h; (b) 6 N HCl–THF (1:10, v/v), 25 °C, 3 h; (c) H_2 (1 atm), 10% Pd–C, CH_3OH, 4 h; (d) TsCl (10 equiv), Py (10 equiv), $CHCl_3$, 25 °C, 24 h; (e) MsCl (2 equiv), Et_3N (3 equiv), CH_2Cl_2, 0 °C, 3 h, then NaI (excess), acetone, Δ, 17 h; (f) LiHMDS (1.05 equiv), DME–THF, −78 °C, then addition of the anion to NBS (1 equiv), DME, −78 °C, 1.5 h; (g) TMS_2S (1 equiv), $NaOCH_3$ (2 equiv), THF (3×10^{-2} M), 0 °C, 4 h; (h) 6 N HCl–THF (1:10, v/v), 25 °C, 4 h, oxone (4 equiv), CH_3OH–H_2O, 25 °C, 6 h, then Amberlyst-15, 3-Å molecular sieves, CH_2Cl_2, 25 °C, 4 h; (i) LiHMDS (1.1 equiv), THF, −78 °C, 10 min, then C_2Cl_6 (1 equiv), 20 °C, 1 h; (j) $(C_2H_5)_3COK$ (2.2 equiv), HMPA (10 equiv), DME, 70 °C, 5 min.

Owing to our prior experience, we elaborated the 3(2*H*)-furanone first.[7,8] Since direct acylation of lactone **9** to diketone **10** proved unfeasible, an indirect sequence was employed. Mild acid hydrolysis of **9** provided hydroxy ketone **11** (99%), which was converted to disilyl enol ether **12** with TMSCl and DBU (98%).[16] Enol ether **12** underwent smooth BF_3·Et_2O-catalyzed aldol condensation with propanal, providing the expected mixture of β-hydroxy ketones **13** (80%), which were directly transformed to the 3(2*H*)-furanone lactone **14** via diketone **15** by oxidation with Dess–Martin periodinane and cyclization upon acid treatment (93%).[17] Creation of the C_8 stereocenter via chelation-controlled reduction was expected to provide the desired β alcohol **16**. Furanone **14** was converted to ketone **17** by oxidation with OsO_4(cat.)/$NaIO_4$ under standard conditions (93%). Unfortunately, highly stereocontrolled reduction of **17** to the desired β isomer did not occur. Reduction with $NaBH_4$ in CH_3OH at −78 °C (1:1.66 (α:β)) proved most efficient, since recycling proceeded smoothly, affording **16** in good overall yield (80%). Protection of **16** and **18** readily provided MOM ethers **19** and **20** (81% and 80%, respectively). The relative configuration at C_8 in **16** and **18** was established by NMR analysis of **21** obtained by treatment of **20** with LDA in THF at −78 °C.[18]

Construction of the bicyclic subunit followed as described previously (Scheme II).[7,8] The bis(enolate) derived from **19** with LDA (2.4 equiv) at −78 °C was treated with isobutyryl imidazolide, providing the required β keto lactone **22** (93%, 83% conversion).[19,20] Methylation of **22** with NaH/CH_3I afforded a single diastereomeric β keto lactone **23** (91%) as expected. Although suitable deblocking of **23** could provide either **24** or **25**, the latter was judged more compatible with subsequent transformations. Successive treatment of **23** with $TMSBr/CH_2Cl_2$ followed by Amberlyst-15/4-Å molecular sieves cleanly afforded **25** (91%).[21]

With lactone enol ether **25** in hand, we addressed creation of the strained nine-membered-ring olefin (Scheme III). Our initial efforts focused on ring closure via intramolecular alkylation of **27** and **28**, obtained by catalytic reduction of **25** over 10% Pd/C in CH_3OH (1 atm) to lactone alcohol **26** (99%) followed by standard functionalization in 57% and 89% yields, respectively. Unfortunately, attempts to cyclize **27** and **28** afforded either O-alkylation or no reaction.[8] Since heteroatom nucleophiles effected facile displacement of C_5 leaving groups, we utilized a heteroatom linker which could be excised with comcomitant ring contraction to the desired olefin. Thus, iodide **28** was treated with LiHMDS in DME followed by NBS to afford the bromo iodo lactone **29** (92%). Exposure of **29** to $TMS_2S/NaOCH_3$[22] in THF at $\sim 10^{-2}$ M at 0 °C afforded the required 10-membered-ring sulfide **30** in 45–50% yield (unoptimized).[23]

On the basis of preliminary experiments, we employed the Ramberg–Bäcklund sequence to effect the crucial ring contraction of **30** (Scheme III).[24] *This process had not been utilized for construction of medium-ring systems at the inception of our work.*[25,26] *Molecular modeling (MM2) of projected intermediates derived from* ***30*** *suggested that the low-energy conformers possessed geometries which satisfied the stereoelectronic requirements for ring contraction. Furthermore, β elimination of the C_6 oxygen appeared to be stereoelectronically disfavored (~30° dihedral angle between the proton and leaving group).* In any event, sequential treatment of sulfide **30** with 6 M HCl, oxone, and Amberlyst-15 resin afforded the sulfone enol ether **31** (99%).[27] Highly regioselective kinetic γ chlorination of **31** occurred upon exposure of **31** to NaH followed by Cl_3CCCl_3, providing a single diastereomeric chloro sulfone **32** (mp 245 °C dec), relative stereochemistry undetermined (probably α owing to steric factors), in 57% yield (unoptimized).[28]

Preliminary experiments established that dehydroeremantholide A **33** had limited stability under basic conditions. Thus, brief treatment of **32** with $(C_2H_5)_3COK$[29] in DME/HMPA at 70 °C cleanly afforded olefin **33** as a white solid (82%).[30,31] Exposure of **33** to 6 N HCl/THF at room temperature afforded crystalline synthetic (+)-eremantholide A (**1**), mp 181–182 °C, $[\alpha]^{23}_D$ 64.5° (*c* 0.07, 99% EtOH) [lit.[2] mp 182–183 °C, $[\alpha]^{23}_D$ 65° (64.5°) (*c* 0.05, 99% EtOH)], identical in all respects (IR, ^1H NMR (300 MHz), HRMS, TLC) with an authentic sample of natural (+)-eremantholide A (**1**), in 85% yield.[32,33]

Thus, the absolute configuration of (+)-eremantholide A (**1**) can now be confirmed as that originally postulated on the basis

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(30) Less hindered bases afforded **33**, which is unstable to extended exposure to strong base, along with ~20% of **31**.
(31) Naturally derived **33**, prepared from natural (+)-**1**,[33] was identical to synthetic **33** by the usual spectroscopic criteria.
(32) Synthetic (+)-**1** was identical (IR, NMR, MS, $[\alpha]_D$, and TLC in several solvents) to authentic natural (+)-**1**.[33]
(33) We thank Professor P. W. LeQuesne (Northeastern University) for a sample of natural (+)-eremantholide A (**1**).

of biogenetic considerations.[1-3] The foregoing synthetic route to (+)-1 is generally highly stereoselective and convergent, affording (+)-1 in ~21 steps from the known lactolide (+)-6.

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Highly Delocalized Cu(I)/Cu(II): A Copper–Copper Bond?

Charlie Harding,[†] Vickie McKee,[‡,§] and Jane Nelson*[,†,‡]

Chemistry Department, Open University
Milton Keynes MK7 6AA, England
School of Chemistry, Queens University
Belfast BT9 5AG, Northern Ireland
Chemistry Department, University of Canterbury
Christchurch 1, New Zealand

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The need for efficient long-distance electron transfer, for example, in the emerging field of molecular electronics,[1] has refueled interest in the electron transfer process and consequently in mixed-valence compounds.[2] The systematic study of electron transfer requires data over a wide range of internuclear separations[3] as well as from as large as possible a selection of metal cations. Thus although (d^5/d^6) second and third transition series ions such as ruthenium and osmium continue to be well-represented in the mixed-valence literature,[4] scant attention has been paid to the less well-behaved first transition series where the phenomenon not only exists but is of biological importance.[5] In particular, mixed-valence copper model systems are of interest in assisting the characterization of the half-met derivatives of coupled dicopper sites,[6] which are spectroscopically more informative than the fully oxidized or reduced states. A valuable study[7] describes the conversion of class II[8] mixed-valence dicopper molecules from EPR-localized to EPR-delocalized as a function of temperature. However, none of these models exhibits EPR delocalization at temperatures as low (77 K) as does the half-met site, and the investigators note that "it would take a remarkable binucleating ligand to obtain a mixed-valence $Cu^{II}Cu^{I}$ site where the frequency of electron exchange between copper sites remains high at very low temperatures."

By means of template condensations of tris(2-ethylamino)amine (tren) with glyoxal upon a labile group II cation template, we have[9] obtained a macrobicyclic octaaza ligand,[10] L, which although normally mononucleating can accommodate copper ions either singly or in pairs. Transmetalation of $[ML]^{2+}$ (1) with an excess of $Cu(MeCN)_4ClO_4$ yields dark brown hexagonal crystals of $Cu_2L(ClO_4)_2$ (2); when Cu(II) is used, a finely crystalline blue-green product, $[Cu_2LH]X_4$ (X = ClO_4 (3), $CF_3SO_3^-$ (4)), is obtained. Rapid titration of an aqueous solution of 3 with 5×10^{-3} M NaOH solution indicates a buffering capacity similar to that of NH_4^+ (pK_a = 9.3) and greater than that of $(C_2H_5)_3NH^+$ (pK_a = 10.6), although no inflexion point is observed in any of these titrations.

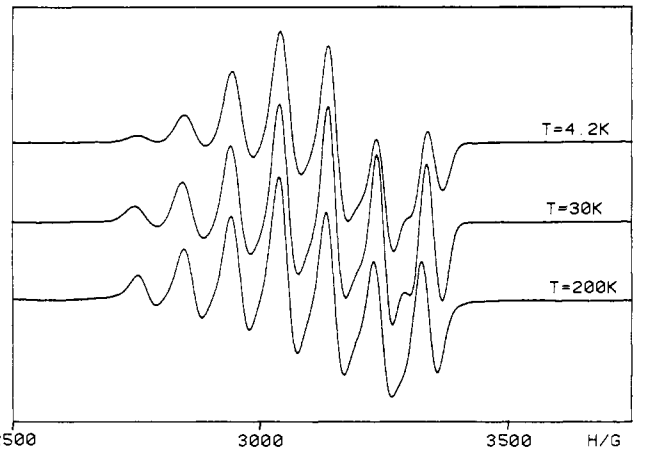

Figure 1. X-band EPR spectra of 3 as DMF glass at T = 200, 30, and 4.2 K (g = 2.137, A = 100 × 10^{-4} cm^{-1}).

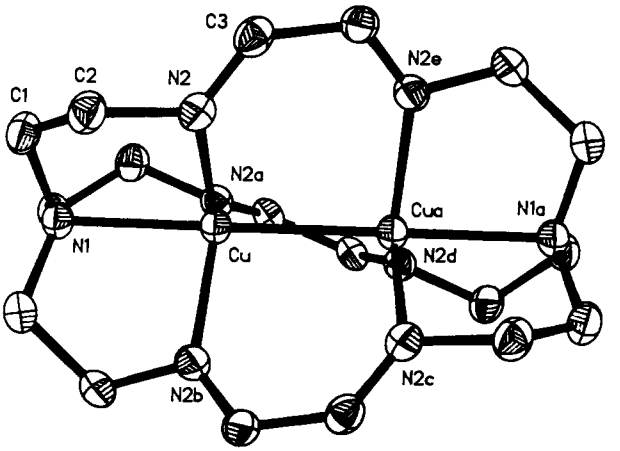

Figure 2. Structure of 2. For crystallographic data see ref 14.

It is clear that the magnetic and spectroscopic properties of 3 and 4 are not those of dicopper(II). In the temperature range 4–300 K, Curie law behavior is observed (μ = 1.9 BM per formula unit at 300 K) for 3 and 4 and both frozen and freshly made fluid dmf solution EPR spectra take the form of a near-isotropic 7-line signal retained with little change of shape (Figure 1) down to 4 K.[11] Both Nujol mull and solution electronic spectra are dominated by an intense near-infrared absorption (λ = 756 nm, ϵ = 5000 M^{-1} cm^{-1}, $\Delta\nu_{1/2}$ = 2500 cm^{-1}). The decay of the spectra exhibits several isosbestic features and obeys first-order kinetics with half-life ranging from 1–3 min in organic solvents to ~3 h in H_2O, betraying solution instability of this presumably mixed-valence species. The half-life is also pH dependent, decreasing by a factor of 50 for a pH change from 2 to 10.

X-ray crystallographic structure determination of 2 (Figure 2) shows a 2.448-Å separation of Cu^+ ions, on the lower limit of

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[†] Open University.
[‡] Queens University, Belfast.
[§] University of Canterbury.

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(11) Freezing of the DMF solution within 1 s of preparation failed to remove entirely lines that appear as shoulders on this 7-line spectrum.

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