

Figure 1. ORTEP drawing of $\text{Mo}(\text{TTP})(\text{PhC}\equiv\text{CPh})$. All atoms are represented by 50% probability thermal ellipsoids. For clarity the phenyl groups of the porphyrin were omitted. Main distances (Å) are Mo–N₁, 2.104 (3); Mo–N₂, 2.150 (3); Mo–N₃, 2.105 (3); Mo–N₄, 2.147 (3); Mo–C₉, 1.983 (4); Mo–C₁₀, 1.965 (4); C₉–C₁₀, 1.324 (5); C₁₀–C₁₀₁, 1.485 (5); C₉–C₉₁, 1.455 (5). Main angles (deg) are N₁–Mo–N₄, 85.1 (1); N₂–Mo–N₄, 145.1 (1); N₂–Mo–N₃, 85.2 (1); N₃–Mo–N₄, 84.6 (1); C₉–C₁₀–C₁₀₁, 136.4 (4); C₁₀–C₉–C₉₁, 145.4 (4).

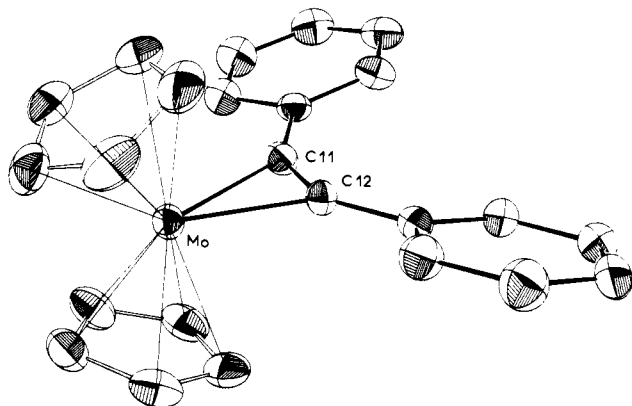


Figure 2. ORTEP drawing of $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{C}_6\text{H}_5)_2\text{C}_2$. Main distances (Å) are Mo–C₁₁, 2.143 (6); Mo–C₁₂, 2.144 (6); C₁₁–C₁₂, 1.269 (7). Average C–C distances (Å) are phenyl rings, 1.39 ± 0.01 ; Cp rings 1.42 ± 0.03 ; Mo–C₅H₅ distances range from 2.14 to 2.35.

the shape of a flattened saddle. The acetylenic carbon–carbon bond eclipses almost perfectly the opposite Mo–N₂ and Mo–N₄ bonds.⁸ Thus the Mo–N_p bonds are not equivalent: while the two staggered Mo–N_p bond distances are equal to 2.104 (3) and 2.105 (3) Å, the two eclipsed Mo–N_p bond lengths are 2.150 (3) and 2.147 (3) Å.

Evidence has been provided recently that it is possible for an acetylenic ligand to donate more than two electrons to the metal center in a mononuclear complex.^{9–12} It has also been shown that

the acetylenic carbon–carbon bond length provides a poor estimate of the number of electrons donated from acetylene to metal, a better indication being metal–carbon distances.⁹ The values found in complex **1** for these bond distances: Mo–C₉ = 1.983 (4), Mo–C₁₀ = 1.965 (4), and C₉–C₁₀ = 1.324 (5) Å suggest that the acetylenic group acts as a four-electron donor, the metal to carbon bond distances being the shortest ever found in an acetylenic complex of molybdenum.⁹ The same conclusion is reached by comparison with the structure of **2**: $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{PhC}\equiv\text{CPh})$. **2** is an 18-electron species if the acetylenic moiety donates two electrons. While the molybdenum–acetylenic bond distances are equal to 2.143 (5) and 2.144 (5) Å, the acetylenic carbon–carbon bond length is 1.27 (1) Å.

Simple molecular symmetry arguments also support the same conclusion. Complex **1** is diamagnetic and Mo(II) has formally a spin-paired $4d^4$ electronic configuration. With C_{2v} symmetry for the coordination sphere of molybdenum, the 24-atom core of the porphyrin ring being the xy plane, the metal atom located on the z axis, and the acetylenic $\text{C}\equiv\text{C}$ group parallel to x axis, most probably the $4d_{xy}$ and $4d_{xz}$ metal orbitals are doubly occupied. The empty $4d_{yz}$ orbital is thus able to accept π electron density from the acetylenic group by interaction with one bonding orbital π_{u2} in addition to that coming from π_{u1} , by interaction with d_{xz} . Furthermore the back-donation from the metal to the acetylenic moiety can be realized by interaction of the filled $4d_{xz}$ metal orbital and one π_g antibonding orbital of the acetylenic group. The geometry of **1** is thus compatible with the donation from both of the filled acetylene π_u bonding orbitals by interaction between $4d_{xz}-\pi_{u1}$ and $4d_{yz}-\pi_{u2}$, with an acetylenic ligand acting as a four-electron donor.

Acknowledgment. This work was supported in part by the C.N.R.S. (Equipe de Recherche Associée 08).

Supplementary Material Available: Complete listings of atomic coordinates and thermal parameters for **1** (Table I) and **2** (Table II) and computed and observed structure factor amplitudes for **1** (Table III) and **2** (Table IV) (40 pages). Ordering information is given on any masthead page.

(12) J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, **1980**, *102*, 3288.

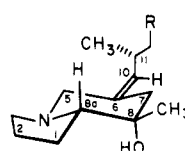
Enantiospecific Total Synthesis of Dendrobatid Toxin 251D. A Short Chiral Entry to the Cardiac-Active Pumiliotoxin A Alkaloids via Stereospecific Iminium Ion-Vinylsilane Cyclizations

Larry E. Overman* and Kenneth L. Bell

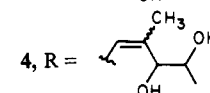
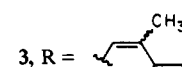
Department of Chemistry, University of California
Irvine, California 92715

Received December 1, 1980

Recently, Daly and co-workers reported¹ the crystallographic structure determination of the dendrobatid toxin 251D (**1**), which was isolated from the Ecuadoran poison-dart frog, *Dendrobates tricolor*. Analysis of mass and magnetic resonance spectra allowed



- 1, R = $\text{CH}_2\text{CH}_2\text{CH}_3$
2, R = CH_2CH_3



(7) J. L. Hoard "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, Chapter 8, p 317; W. R. Scheidt, *Acc. Chem. Res.*, **1977**, *10*, 341; D. L. Cullen, E. F. Meyer, K. M. Smith, *Inorg. Chem.*, **1977**, *16*, 1179.

(8) The same type of conformation is present in $\text{Mo}(\text{TTP})(\text{NO})_2$ and $\text{Mo}(\text{TTP})(\text{O}_2)_2$: Th. Diebold, M. Schappacher, B. Chevrier, and R. Weiss, *J. Chem. Soc., Chem. Commun.*, **1979**, 694; B. Chevrier, Th. Diebold, and R. Weiss, *Inorg. Chim. Acta*, **1976**, *19*, L57; C. Bachmann, J. Demuyne, and A. Veillard, *J. Am. Chem. Soc.*, **1978**, *100*, 2366. On the other hand the staggered conformation has been observed in $\text{Mo}(\text{CO})_2(\text{TTP})$: R. Weiss et al., unpublished result.

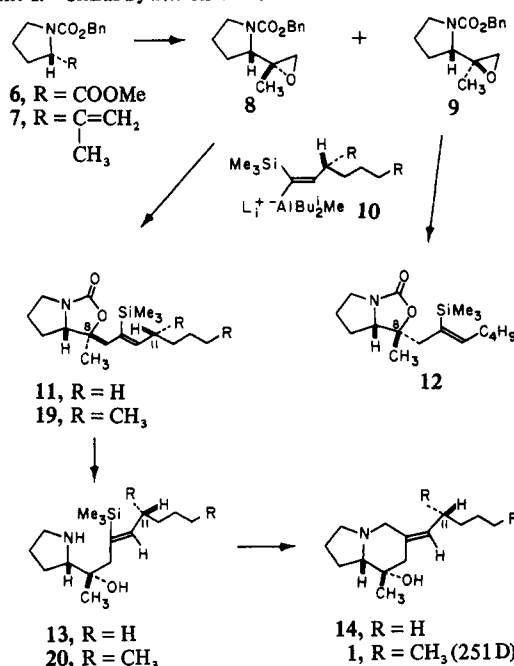
(9) W. E. Newton, J. W. McDonald, J. L. Corbin, L. Ricard and R. Weiss, *Inorg. Chem.*, **1980**, *19*, 1997.

(10) J. L. Davidson, L. Manojlovic-Muir, R. W. Muir, and A. N. Keith, *J. Chem. Soc., Chem. Commun.*, **1980**, 749.

(11) F. A. Cotton and W. T. Hall, *J. Am. Chem. Soc.*, **1979**, *101*, 5094.

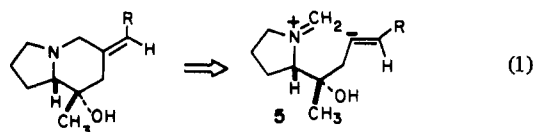
(1) Daly, J. W.; Tokuyama, T.; Fujiwara, T.; Highet, R. J.; Karle, I. L. *J. Am. Chem. Soc.* **1980**, *102*, 830.

Scheme I. Chiral Synthesis of 251D



the formulation of structures to six additional members of the pumiliotoxin A alkaloid class,^{1,2} including toxin 237A (2) and the more complex pumiliotoxins A (3) and B (4).³ These alkaloids have in common the unusual (Z)-6-alkylideneindolizidine (1-azabicyclo[4.3.0]nonane) ring system and differ only in the side chain. Herein we describe the first total synthesis of 251D. This synthesis defines a concise and enantiospecific procedure for preparing the pumiliotoxin A alkaloids from L-proline and also introduces a new, and potentially general, method for forming unsaturated azacyclic rings.

Since we felt that a vinylsilane⁴ might serve well as an equivalent for the vinyl anion functionality in hypothetical intermediate 5 (eq 1), we have pursued an approach to these alkaloids which



utilizes an iminium ion-vinylsilane cyclization to stereospecifically assemble the (Z)-6-alkylideneindolizidine ring system.⁵

Our first concern was the preparation from L-proline of chiral epoxide 8 (Scheme I). A nonstereoselective route was initially developed with the expectation that the availability of both epoxide isomers would facilitate unambiguous structural assignments. Reaction of *N*-carbobenzoyloxy-L-proline methyl ester⁶ (6) with 2.2 equiv of methylmagnesium iodide, followed by dehydration of the resultant alcohol⁸ (SOCl₂, pyridine-THF, -45 °C) gave alkene 7⁷ in 46% yield. Epoxidation of 7 with *m*-chloroperbenzoic

acid (CH₂Cl₂, 25 °C) proceeded in quantitative yield, without asymmetric induction, to give a 1:1 mixture of epoxides 8 and 9.⁷ This mixture could be conveniently separated on a large scale (Waters Prep LC500, 2 silica prepPAK columns, 92:5:3 hexane-triethylamine-ethyl acetate as eluant, 8 elutes before 9) to give the desired epoxide 8,^{7,8} [α]_D²⁵ -77.5° (c 5.1, CH₃OH), and its diastereomer 9,⁷ [α]_D²⁵ -8.0° (c 5.9, CH₃OH). Although we were unable to directly assign structures to epoxides 8 and 9 by spectroscopic means, characterization was possible after opening these hindered epoxides to incorporate the elements of the alkylidene side chain.

Introduction of the side chain was first explored in a model series which lacked the allylic methyl group at C-11.⁹ Epoxides 8 and 9 reacted¹⁰ sluggishly with silylvinyl alanate 10 (R = H, formed¹¹ by sequential treatment of 1-(trimethylsilyl)-1-hexyne with *i*-Bu₂AlH and MeLi) in refluxing ether, with the loss of benzyl alcohol, to give bicyclic carbamates 11⁷ and 12,⁷ respectively, in yields of 35–50%. NMR spectra showed that both isomers had an identical (Z)-alkene side chain, and differed only in the configuration at C-8.⁹ The rigid bicyclo[3.3.0]octane ring of carbamates 11 and 12 allowed structural assignments to be made on the basis of ¹³C NMR spectra and the expectation¹² that groups on the more sterically congested α face would be shifted upfield. Thus 11 showed absorptions for the methyl and methylene carbons attached to C-8 at 21.7 and 49.4 ppm, respectively, while these signals were observed at 26.4 and 43.8 ppm for isomer 12. Hydrolysis (20% KOH, CH₃OH-H₂O, reflux) of 11 afforded crystalline amino alcohol 13⁷ (87% yield, mp 157–158 °C). The desired assembly of the alkylideneindolizidine ring was cleanly, and stereospecifically, accomplished when 13 was treated in refluxing ethanol with paraformaldehyde (2 equiv) and *d*-10-camphorsulfonic acid (1 equiv) to give 14.^{7,13} (nor-11-methyl 237A) in 65–80% yield. The extent of silicon control of the iminium ion-olefin cyclization was extremely high, since GC/MS analysis¹⁴ of the crude cyclization product failed to detect isomers of 14.

With the general viability of the approach established, our attention turned to the preparation of the chiral 251D sidechain, which was conveniently secured as follows (eq 2). Reduction of 1-heptyn-3-one (15)¹⁵ with *B*-3-pinanyl-9-borabicyclo[3.3.1]nonane

(7) All compounds reported were homogeneous by TLC and showed ¹H NMR, ¹³C NMR, IR, and mass spectra consistent with the assigned structure; the molecular composition of all key intermediates was determined by high-resolution mass spectrometry or combustion analysis. Partial characterization data for selected intermediates are as follows.⁹ 8: ¹H NMR (250 MHz, CDCl₃) δ 3.9–4.1 (m, C₈-H), 1.34 and 1.27 (two s, CH₃). 9: ¹H NMR (250 MHz, CDCl₃) δ 3.5–3.7 (m, C₈-H), 1.18 and 1.24 (two s, CH₃). 11: IR (film) 1764 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ 6.18 (t, *J* = 8 Hz, =CH); ¹³C NMR (C₆D₆) 160.7 (s), 150.0 (d), 134.4 (s), 82.0 (s), 68.4 (d), 49.4 (t), 46.2 (t), 33.0 (t), 32.8 (t), 27.2 (t), 26.1 (t), 23.1 (t), 21.7 (q), 14.6 (q), 1.1 (q). 12: ¹H NMR (90 MHz, CDCl₃) δ 5.26 (t, *J* = 8 Hz, =CH), 3.80 (d, *J* = 14 Hz, C₈-H), 1.13 (s, C₈-CH₃); ¹³C NMR (CDCl₃) δ 131.4 (s), 128.0 (d), 71.7 (d), 68.4 (s), 54.6 (t), 52.8 (t), 48.9 (t), 32.1 (t), 27.2 (t), 24.3 (q), 23.3 (t), 22.3 (t), 21.1 (t), 13.9 (q). 20: IR (CCl₄) 3360, 1600 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 5.98 (d, *J* = 10.3 Hz, C₁₀-H), 3.56 (br t, *J* ~ 8 Hz, C₈-H), 3.4–3.1 (m, C₃-H), 1.19 (s, C₉-CH₃), 0.95 (d, *J* = 6.3 Hz, C₁₁-CH₃); ¹³C NMR (CDCl₃) 156.6, 131.3, 72.6, 68.6, 46.5, 45.8, 37.1, 36.4, 29.8, 26.5, 24.5, 23.0, 22.6, 20.7, 14.1, 1.16; mass spectrum, *m/z* (isobutane CI, relative intensity) 312 (47), 114 (25), 70 (100).

(8) This alcohol is believed to be optically pure, since the 250-MHz ¹H NMR spectrum in the presence of 0.1–0.3 equiv of tris[3-[(trifluoromethyl)hydroxymethylene]-*d*-camphorato]europium(III) showed only two singlets (conformational isomers about the amide bond) for the methyl group. A racemic sample of this alcohol showed four methyl singlets under these conditions. Similar chiral shift reagent experiments with epoxide 8 also failed to detect the presence of any enantiomer.

(9) Using the numbering system for 251D of ref 1.

(10) See: Warel, Schmitt, G.; Ahlfaenger, B. *Synthesis* 1975, 632. Negishi, E.; Baba, S.; King, A. O. *J. Chem. Soc., Chem. Commun.* 1976, 17. Malpass, D. B.; Watson, S. C.; Yeagin, G. S. *J. Org. Chem.* 1977, 42, 2712.

(11) Eisch, J. J.; Damasevitz, G. A. *J. Org. Chem.* 1976, 41, 2214. Uchida, K.; Utimoto, K.; Nozaki, H. *Ibid.* 1976, 41, 2215.

(12) See: Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 112–118.

(13) That 14 indeed has the Z stereochemistry for the 6,10 double bond is seen most clearly in the ¹³C NMR absorptions of C-5 (54.6 ppm) and C-7 (48.9) which are identical with those of 251 D¹. The successful preparation of 251D by this approach confirms this conclusion.

(14) A 10-ft column packed with 10% SP-2100 on 100/120 Supelcoport was used for this analysis.

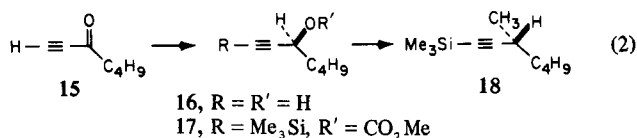
(2) Daly, J. W.; Brown, G. B.; Mensah-Dwumah, M.; Myers, C. W. *Toxicon* 1978, 16, 163.

(3) Preliminary pharmacological studies reveal powerful cardiotonic and myotonic activity for pumiliotoxin B, which is believed to involve calcium-dependent mechanisms: Maleque, M. A.; Albuquerque, E. X.; Warnick, J. E.; Daly, J. W.; Nimitkittipaisan, Y. *Fed. Proc., Fed. Am. Soc. Exp. Biol.* 1979, 38, 1399. Mensah-Dwumah, M.; Daly, J. W. *Toxicon* 1978, 16, 189.

(4) For an excellent review of electrophilic substitution reactions of organosilanes, see: Chan, T. H.; Fleming, I. *Synthesis* 1979, 761. See also: Cooke, F.; Moerck, R.; Schwindeman, J.; Magnus, P. J. *Org. Chem.* 1980, 45, 1046 and references cited therein.

(5) This approach was first described in March, 1980: Overman, L. E.; Bell, K. L. "Abstracts of Papers", 179th National Meeting of the American Chemical Society, Houston, Tx, March 1980; American Chemical Society: Washington, DC, 1980; ORGN 25.

(6) Ito, A.; Takahashi, R.; Baba, Y. *Chem. Pharm. Bull.* 1975, 23, 3081.



(prepared from 92% ee (-)- α -pinene and 9-BBN) according to the procedure of Midland¹⁶ gave (*S*)-1-heptyn-3-ol¹⁷ (**16**, 82 \pm 3% ee by 250-MHz ¹H NMR analysis of the MTPA ester¹⁷) in 60–74% yield. Conversion of **16** to silyl carbonate **17** and organocuprate coupling (CH₃MgBr, 4 equiv; CuI, 2 equiv; THF; 25 °C) according to Macdonald and Brinkmeyer¹⁸ gave silylalkyne **18**,⁷ [α]_D²⁵ -27.7° (*c* 2.0, CHCl₃), in 50% yield from **16**. We anticipated¹⁹ that propargylic coupling would occur with inversion of configuration, and our subsequent use of **18** for the synthesis of 251D rigorously establishes this stereochemical outcome.²⁰

The conversion of **18** to 251D (Scheme I) proceeded along the lines utilized to prepare **14**. Thus sequential treatment of (*R*)-silylalkyne **18** with *i*-Bu₂AlH (1 equiv), CH₃Li (1 equiv), and chiral epoxide **8** afforded carbamate **19**⁷ and its C-11 epimer in a 13:1 ratio^{21ab} (41% yield). Chromatographic separation of the minor diastereomer was difficult at this stage, and consequently this intermediate was directly hydrolyzed to give a crystalline mixture of **20**⁷ and its C-11 epimer, in 81% yield. Cyclization was best accomplished by converting amino alcohol **20** to the corresponding oxazolidine (paraformaldehyde, 1 equiv; EtOH; 80 °C), and subsequently heating this intermediate (0.1 M) in refluxing ethanol in the presence of 1 equiv of *d*-10-camphor-sulfonic acid. After chromatographic purification (silica gel, 800:20:1 CHCl₃-*i*-PrOH:NH₄OH) to remove the unwanted C-11 epimer and crystallization from hexane-ethyl acetate, pure^{21a} (+)-251D hydrochloride, mp 205–206 °C (evacuated capillary), [α]_D²⁵ + 31.4° (*c* 0.62, CH₃OH),²² was isolated in 60% yield. The ¹H NMR (250 MHz) and ¹³C NMR spectra of synthetic (+)-251D hydrochloride in CD₃OD (and the free base in CDCl₃) as well as the EI mass spectra were identical with those of the natural material¹, and synthetic (+)-251D hydrochloride was indistinguishable by capillary GLC^{21a} and TLC (in three solvent systems) with an authentic sample of 251D hydrochloride kindly furnished by Dr. John Daly.²³

The synthetic sequence reported here provides a highly convergent, concise, and *practical* route for the chemical synthesis of the pumiliotoxin A alkaloids. The enantiospecific total synthesis of 251D was achieved in 10 total steps from 1-heptyn-3-one and *N*-carbobenzyloxy-L-proline methyl ester (**6**). The overall yield was ~6% from proline ester **6**. Efforts to improve the yields of individual steps, develop a stereospecific synthesis of epoxide **8**, and prepare pumiliotoxin B by this sequence are in progress. The results of those investigations as well as other synthesis applications of iminium ion-vinylsilane cyclizations will be reported in due course.

(15) Prepared in high yield by Jones oxidation of commercially available 1-heptyn-3-ol: Joss, U.; Schaltegger, H. *Helv. Chim. Acta* **1969**, *52*, 2465.

(16) Midland, M. M.; McDowell, D. C.; Hatch, R. L.; Tramontano, A. *J. Am. Chem. Soc.* **1980**, *102*, 867.

(17) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(18) (a) Brinkmeyer, R. S.; Macdonald, T. L. *J. Chem. Soc., Chem. Commun.* **1978**, 876. (b) Macdonald, T. L.; Reagan, D. R.; Brinkmeyer, R. S. *J. Org. Chem.* **1980**, *45*, 4740.

(19) See: Whitesides, G. M.; Fischer, W. F.; San Filippo, J.; Basche, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871. Johnson, C. R.; Dutra, G. A. *Ibid.* **1973**, *95*, 7783. Fouquet, G.; Schlosser, M. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 82.

(20) Inversion of configuration in this reaction has been independently demonstrated by T. L. Macdonald et al.: Brinkmeyer, R. S.; Macdonald, T. L.; Reagan, D. R., in press; personal communication from T.L.M.

(21) (a) A 12-m, SE-30 glass capillary column (4000 plates per m) was used for this analysis. (b) The large ratio of diastereomers produced in this reaction indicates that the optical yield for the conversion of **17** to silylalkyne **18** was high.

(22) The free base is apparently levorotatory. A synthetic sample of 251D which was contaminated^{21a} with 3.6% of the C-11 epimer and 1% of the oxazolidine derived from **20** showed [α]_D²⁵ -3.1° (*c* 1.6, CHCl₃).

(23) The comparison of mp and optical rotation must await the isolation of additional natural 251D.

Acknowledgment. Financial assistance from the National Institutes of Health (HL 25854) and the Camille and Henry Dreyfus Foundation (teacher-scholar award to L.E.O.) is gratefully acknowledged. We particularly thank Dr. Barney Kane of SCM Organics for a generous sample of (-)- β -pinene, Professor T. L. Macdonald for a preprint of ref 18b, and Dr. John Daly for providing a comparison sample of 251D hydrochloride and copies of its ¹³C NMR spectra. NMR and mass spectra were determined with spectrometers purchased with the assistance of NSF instrumentation grants.

Tandem Cope-Claisen Rearrangements for the Construction of (*E,E*)-1,6-Cyclodecadienes. Effect of Ketene Acetal Substituents on $\Delta G^\ddagger_{\text{Claisen}}$ ¹

Stanley Raucher,*† John E. Burks, Jr., Ki-Jun Hwang, and Dana P. Svedberg

Department of Chemistry, University of Washington
Seattle, Washington 98195
Received December 5, 1980

The development of methods for the construction of 10-membered rings² is of paramount importance in strategies for the synthesis³ of germacrane sesquiterpenes.⁴ Although the interconversion of germacrane and elemene sesquiterpenes via Cope rearrangement has been well documented,⁵ efforts to synthesize germacrane sesquiterpenes from 1,2-divinylcyclohexanes have met with only limited success⁶ due to the reversible nature of the Cope rearrangement.⁷

For some time now, we have been intrigued with the possibility of stereospecifically and enantiospecifically⁸ preparing (*E,E*)-1,6-cyclodecadiene (**4**) via a strategy which involves shifting the unfavorable Cope equilibria between **1** or **2** and **3** with a Claisen rearrangement⁷ that irreversibly removes the 1,5-cyclodecadiene (**3**) from the Cope energy surface. An (*E,E*)-1,6-cyclodecadiene with the absolute stereochemistry shown in **4** was desired in connection with efforts directed toward the total synthesis of (+)-costunolide.

As shown in Scheme I, it should be possible to stereospecifically and enantiospecifically prepare the desired (*E,E*)-1,6-cyclo-

[†] Fellow of the Alfred P. Sloan Foundation, 1980–1982.

(1) Synthesis via Sigmatropic Rearrangements. 5. For the previous paper in this series, see: Raucher, S.; Macdonald, J. E.; Lawrence, R. F. *Tetrahedron Lett.* **1980**, 4335.

(2) (a) Marshall, J. A. *Rec. Chem. Prog.* **1969**, *30*, 3. (b) Story, P. R.; Busch, P. *Adv. Org. Chem.* **1972**, *8*, 67. (c) Brown, J. M.; Crespo, T. M.; Mander, L. N. *J. Org. Chem.* **1977**, *42*, 3984. (d) Wender, P. A.; Hubbs, J. C. *Ibid.* **1980**, *45*, 365. (e) Williams, J. R.; Callahan, J. F. *Ibid.* **1980**, *45*, 4475. (f) Reference 9.

(3) For an up-to-date list of germacrane prepared by total synthesis, see: Wender, P. A.; Lechleiter, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 6340; footnote 6.

(4) (a) Devon, T. K.; Scott, A. I. "Handbook of Naturally Occurring Compounds"; Academic Press: New York, 1972; Vol. II, pp 77–83. (b) Sörm, F. *J. Agric. Food Chem.* **1971**, *19*, 1081. (c) Fischer, N. H.; Olivier, E. J.; Fischer, H. D. *Fortschr. Chem. Org. Naturst.* **1979**, *38*, 47.

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(6) (a) Grieco, P. A.; Nishizawa, M. *J. Org. Chem.* **1977**, *42*, 1717. (b) Still, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 4186. (c) *Ibid.* **1979**, *101*, 2493.

(7) For reviews of the Cope and Claisen rearrangements, see: (a) Rhoads, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1; (b) Ziegler, F. *Acc. Chem. Res.* **1977**, *10*, 227; (c) Bennett, G. B. *Synthesis* **1977**, 589.

(8) All structures in this paper represent the single enantiomer depicted. All new compounds exhibited satisfactory infrared, proton magnetic resonance, GC, and mass spectroscopic data; yields refer to isolated, chromatographically homogeneous material. Purified on 40–60- μ m silica gel.¹⁵ GC analyses were performed on a Hewlett-Packard 5880A Level Three FID Gas Chromatograph equipped with a SP 2100 12 meter fused silica capillary column. Ratios are calculated directly from peak integrations.