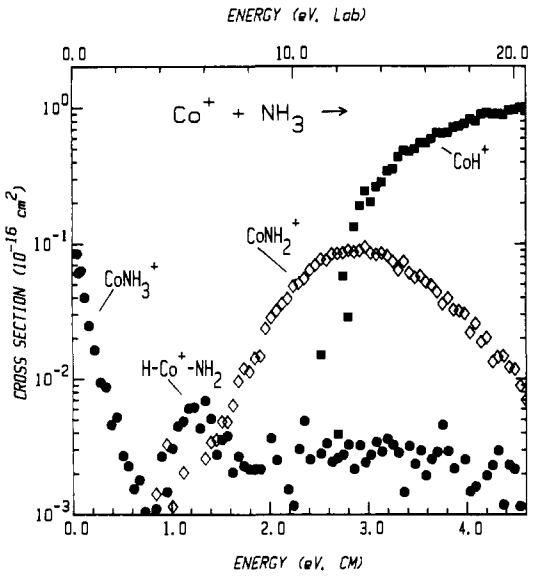


Figure 1. Variation of product cross sections for reaction of ammonia (at a pressure of 0.14 mTorr) with Co^+ (produced by surface ionization) as a function of translational energy in the center-of-mass frame (lower scale) and laboratory frame (upper scale).

in agreement with the value 65 ± 8 kcal/mol obtained from bracketing measurements.[10] Above 2.8 eV, $\sigma(CoNH_2^+)$ declines. This cannot be due to product dissociation since formation of $Co^+ + NH_2 + H$ requires 4.69 eV. An alternative explanation is that reaction 1 depletes the intermediate precursor to reaction 2. This is strongly suggested by the coincidence between the peak in $\sigma(CoNH_2^+)$ and the onset of CoH^+ formation. Similar observations have been made for the reactions of other transition-metal ions with ammonia[7,11] and methane.[12] The common intermediate is presumably $H-Co^+-NH_2$, I, the result of oxidative addition of the N-H bond to the metal center. It is well-known that Co^+ activates C-H and C-C bonds of saturated alkanes,[13,14] so the formation of I is certainly plausible.

At the lowest energies, we observe the formation of $CoNH_3^+$. The most striking aspect of $\sigma(CoNH_3^+)$ is that it contains two features. Below 0.8 eV, the cross section increases monotonically with decreasing energy, establishing that the process is a barrierless exothermic reaction. The magnitude of this feature is found to depend linearly upon pressure, establishing that the $CoNH_3^+$ formed at these energies results from stabilizing secondary collisions. Analysis of this pressure dependence by a previously outlined method[15] leads to a lifetime for $CoNH_3^+$ of ~0.2 μs at our lowest energies (~0.05 eV).

The second feature of $\sigma(CoNH_3^+)$ appears at ~0.8 eV and peaks at ~1.4 eV. The magnitude of this feature is *independent* of pressure. Thus the $CoNH_3^+$ produced at these energies must live long enough to reach the detector, ~60 μs at 1.4 eV. Since this is a very long lifetime for a five-atom molecule, we confirmed the observation by studying the reaction of $Co^+ + ND_3$. Nearly identical cross sections are obtained for all three deuterated products.

To explain these observations regarding $\sigma(CoNH_3^+)$, we assign different structures to the two features observed. The exothermic reaction must form Co^+-NH_3, the simple adduct in which the lone pair of electrons on N is donated to the cation. This exothermicity is consistent with $D°(Co^+-NH_3) = 2.5$ eV.[16] Furthermore, formation of Co^+-NH_3 is unlikely to have a barrier since the long-range part of the potential is the very attractive ion-dipole interaction. We assign the second, endothermic feature to the structure $H-Co^+-NH_2$, I. Since reaction 2 depletes this intermediate, this assignment explains why $\sigma(CoNH_3^+)$ peaks at the onset for reaction 2. This structure also allows a reasonable explanation of the long lifetime of this species, since reformation of reactants should proceed via a tight transition state needed for reductive elimination of NH_3. The lifetime of this species could be appreciable if I lies in a potential well below the ~0.8-eV barrier required for its formation. Indeed, this well is ~0.8 eV deep, assuming that $D°(HCo^+-NH_2) \approx D°(Co^+-NH_2)$.

The observation of the long-lived $HCoNH_2^+$ intermediate can probably be attributed to the balance of several factors. Compared with alkane systems, the lone-pair electrons on ammonia help stabilize the ionic intermediate. Compared with several other metal ions, Co^+ is less reactive with ammonia,[7,11,17] and in these cases, such intermediates rapidly dissociate to products. The prospect of making similar observations in other systems is of current interest in our laboratories.

Acknowledgment. This work is supported by the National Science Foundation, Grant No. 8796289.

(10) Buckner, S. W.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 4715-4716. Note that the lower limit of 61 ± 4 kcal/mol comes from an old value for $D°(Co^+-CH_3)$. A more recent determination of this bond energy is 49.1 ± 3.5 kcal/mol.[14]

(11) Clemmer, D. E.; Armentrout, P. B. *J. Phys. Chem.*, submitted for publication; work in progress.

(12) Aristov, N.; Armentrout, P. B. *J. Phys. Chem.* **1987**, *91*, 6178-6188. Sunderlin, L. S.; Armentrout, P. B. *J. Phys. Chem.* **1988**, *92*, 1209-1219; *J. Am. Chem. Soc.* **1989**, *111*, 3845-3855. Georgiadis, R.; Armentrout, P. B. *J. Phys. Chem.* **1988**, *92*, 7067-7074.

(13) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784-791.

(14) Georgiadis, R.; Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 4251-4262.

(15) Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 7509-7517.

(16) Marinelli, P. J.; Squires, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 4101-4103.

(17) Buckner, S. W.; Gord, J. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1988**, *110*, 6606-6612.

Pd-Catalyzed Synthesis of Macrocycles. A Total Synthesis of (-)-Aspochalasin B

Barry M. Trost,* Masayuki Ohmori, Steven A. Boyd, Hideki Okawara, and Steven J. Brickner

Departments of Chemistry
Stanford University, Stanford, California 94305-5080
University of Wisconsin, Madison, Wisconsin 53706
Received June 12, 1989

The extraordinary effects of the cytochalasins on mammalian cell membranes affecting transport across the membrane, cell mobility, among others, have made these important tools in cell research attractive synthetic targets.[1-4] An examination of the

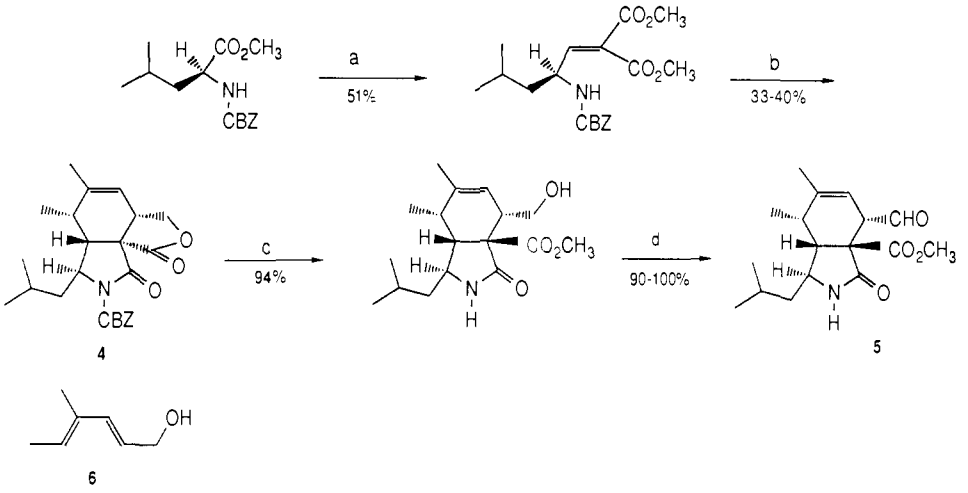
(1) Carter, S. B. *Endeavor* **1972**, *113*, 77. Binder, M.; Tamm, Ch. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 370. *Cytochalasins, Biochemical and Cell Biological Aspects*; Tanenbaum, S. W., Ed.; North Holland Publishing Co.: Amsterdam, 1978.

(2) For examples of [11]cytochalasins, see: (a) Hayakawa, S.; Matsushima, T.; Kimura, T.; Minato, H.; Kagagiri, K. *J. Antibiot.* **1968**, *21*, 523. (b) Aldridge, H. C.; Turner, W. B. *J. Chem. Soc. C* **1969**, 923. (c) Minato, H.; Katayama, T. *J. Chem. Soc. C* **1970**, 45. (d) Pendse, G. S. *Experentia* **1974**, *30*, 107. (e) Patwardhan, S. A.; Pandey, R. C.; Dev, S.; Pendse, G. S. *Phytochemistry* **1974**, *13*, 1985. (f) Cameron, A. F.; Freer, A. A.; Hesp, B.; Srawson, S. J. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1741. (g) Keller-Schierlein, W.; Kupfer, E. *Helv. Chim. Acta* **1979**, *62*, 1501. (h) Pedersen, E. J.; Larsen, P.; Boll, P. M. *Tetrahedron Lett.* **1980**, *21*, 5079. (i) Probst, A.; Tamm, C. *Helv. Chim. Acta* **1981**, *64*, 2056. (j) Cole, R. J.; Wells, J. M.; Cox, R. H.; Cutler, H. G. *J. Agric. Food Chem.* **1981**, *29*, 205. (k) Neupert-Lares, K.; Dobler, M. *Helv. Chim. Acta* **1982**, *65*, 1426. (l) Izawa, Y.; Hirose, T.; Shimizu, T.; Koyama, K.; Natori, S. *Tetrahedron* **1989**, *45*, 2323.

(3) For previous total syntheses of different cytochalasins, see: Stork, G.; Nakahara, Y.; Nakahara, Y.; Greenlee, W. J. *J. Am. Chem. Soc.* **1978**, *100*, 7775. Stork, G.; Nakamura, E. *J. Am. Chem. Soc.* **1983**, *105*, 5510. Harkin, S. A.; Jones, R. H.; Tapolczay, D. J.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 489. Thomas, E. J.; Whitehead, J. W. F. *J. Chem. Soc., Perkin Trans. 1* **1989**, 499, 507. Sauter, R.; Thomas, E. J.; Watts, J. P. *J. Chem. Soc., Perkin Trans. 1* **1989**, 519. Dyke, H.; Steel, P. G.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 525. Vedejs, E.; Rodgers, J. D.; Wittenberger, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 4822. For a synthesis of an isomer of aspochalasin C, see: Craven, A. P.; Dyke, H. J.; Thomas, E. J. *Tetrahedron* **1989**, *45*, 2417.

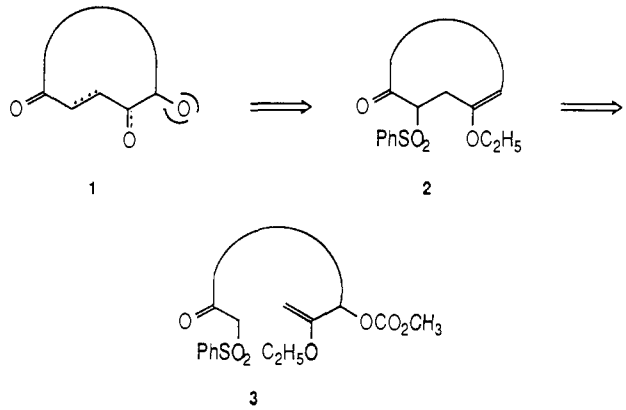
0002-7863/89/1511-8281$01.50/0

Scheme I. Synthesis of Tetrahydroisoindoline Aldehyde[a]



[a] (a) (i) DIBAL-H, $PhCH_3$, −78 °C; (ii) $CH_2(CO_2CH_3)_2$, $TiCl_4$, CCl_4, THF, 0 °C, then C_5H_5N, room temperature; (b) **6**, xylene, BHT, 130 °C; (c) (i) KOH, H_2O, CH_3OH, PhH, room temperature, then $NaHSO_4$; (ii) CH_2N_2, ether, CH_3OH; (d) $(COCl)_2$, DMSO, CH_2Cl_2, $(C_2H_5)_3N$, −78 °C.

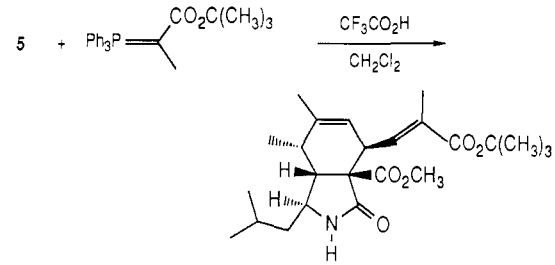
macrocyclic portion of many members of this family of compounds reveals the general oxidation pattern depicted in **1** as a common structural feature. We believe that the juxtaposition of func-



tionality present in **2** offers a very flexible strategy toward these various members. For example, protonation or hydroxylation unmasks the ketone with simultaneous introduction of a proton or a hydroxyl group. Elimination or reduction of the sulfone group provides the unsaturated or saturated derivatives. A macrocycle such as **2** should be readily available by a Pd(0)-catalyzed macrocyclization of the substrate **3**, which involves the intermediacy of a 2-alkoxy(π-allyl)palladium complex as an enolonium equivalent to initiate cyclization.[5-7] We report the realization of this scheme in the first synthesis of (−)-aspochalasin B (**13a**), an 11-membered carbocycle.[2g]

The synthesis of the key aldehyde **5**[8] is outlined in Scheme I, which evolved contemporaneously with the work of Tamm et al.[9] The excellent diastereoselectivity of the Diels–Alder reaction, which produced adduct **4** with >10:1 diastereoselectivity, is noteworthy and contrasts with an intramolecular version wherein a mixture of the two adducts representing different diastereofacial attack in which the opposite diastereomer dominates arises.

The sensitivity of the aldehyde toward epimerization was revealed by condensation with a stabilized ylide that led exclusively to the olefin from the inverted aldehyde (eq 1), even in the presence



(1)

of trifluoroacetic acid to buffer the medium (eq 1). To verify that the initial aldehyde **5** was formed without epimerization, it was reduced with sodium borohydride, which returns the original alcohol.

To obviate the problem of epimerization, and to execute the chain extension with creation of the requisite *E* olefin geometry, a Claisen rearrangement strategy evolved, as outlined in Scheme II. The utilization of 2-propenylcerium dichloride to form the methylallyl alcohol **6a**[8] proved capricious, although yields of the desired adduct **6a** were as high as 72%. We settled upon lithium dipropenylcuprate, which proved efficacious and reproducible. Almost all variations of the Claisen rearrangement failed either because of difficulties in forming the requisite vinyl ether or due to fragmentation. On the other hand, the Raucher, Chi, and Jones protocol[10] proceeded remarkably smoothly. An intimate mixture of the alcohol **6b**, ethyl β,β-diethoxyacrylate, and a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS) moistened by a small amount of chloroform undergoes condensation and rearrangement to **7**[8] even at room temperature! Chemoselective reduction of the ester **8a** to the primary alcohol with the "ate" complex formed between *n*-butyllithium and diisobutylaluminum hydride (DIBAL-H)[11] involves in situ formation of the enolate of the β-keto sulfone. Chemoselective addition of the 1-ethoxyvinyl unit to the aldehyde **8b**[8] again utilizes the corresponding cuprate reagent as the reagent of choice. It appears that the use of organocuprates for chemoselective additions to aldehydes is underappreciated and may sometimes be preferable to the more widely adopted organocerium reagents.[12] The hydrolytic insta-

(4) For some previous synthetic efforts toward cytochalasins, see: Kim, M. Y.; Starrett, J. E., Jr.; Weinreb, S. M. *J. Org. Chem.* **1981**, *46*, 5383. Harkin, S. A.; Thomas, E. J. *Tetrahedron Lett.* **1983**, *24*, 5535. Vedejs, E.; Reid, J. G. *J. Am. Chem. Soc.* **1984**, *106*, 4617 and earlier references in the series. Schmidlin, T.; Wallach, D.; Tamm, C. *Helv. Chim. Acta* **1984**, *67*, 1998 and earlier references in the series. Hensel, W. J.; Palmer, J. T.; Learn, K. S.; Fuchs, P. L. *Synth. Commun.* **1986**, *16*, 1297 and earlier references in the series. Vedejs, E.; Ahmad, S. *Tetrahedron Lett.* **1988**, *29*, 2291.

(5) Trost, B. M.; Warner, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 6112. Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1980**, *102*, 4743.

(6) Trost, B. M.; Gowland, F. W. *J. Org. Chem.* **1979**, *44*, 3448.

(7) Trost, B. M.; Brickner, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 568.

(8) Satisfactory characterization has been obtained for this compound.

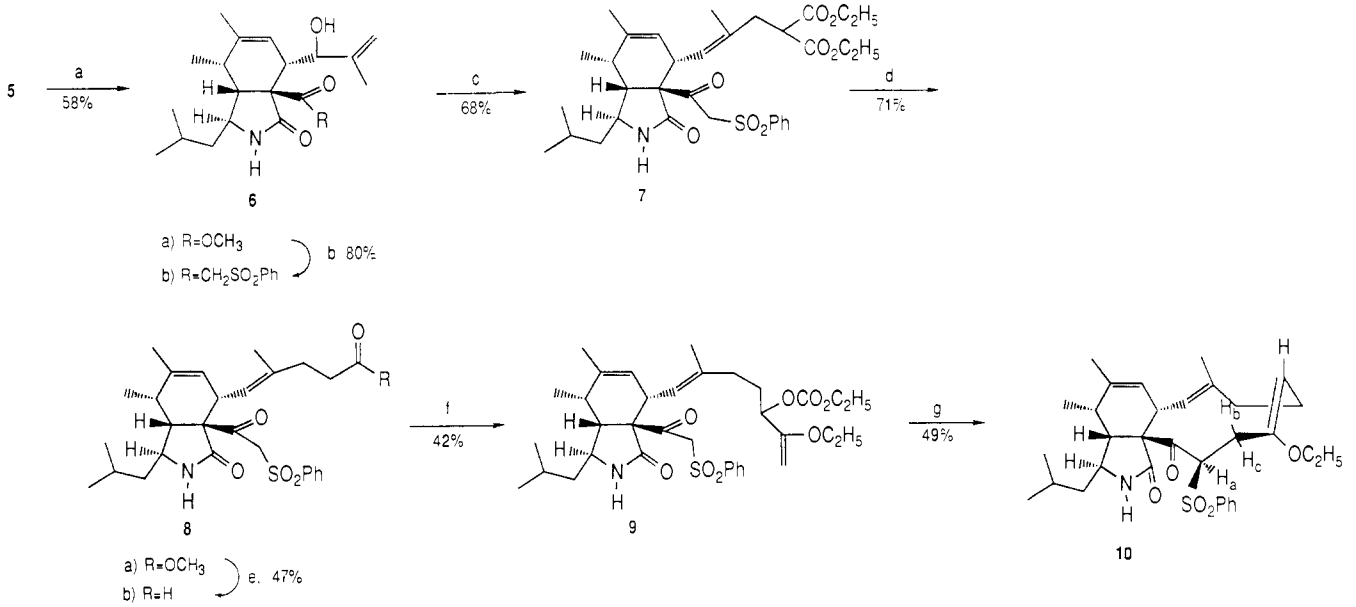
(9) Schmidlin, T.; Burckhardt, P. E.; Waespe-Sarcevic, N.; Tamm, C. *Helv. Chim. Acta* **1983**, *66*, 450.

(10) Raucher, S.; Chi, K.; Jones, D. S. *Tetrahedron Lett.* **1985**, *26*, 6261.

(11) Kovacs, G.; Galamos, G.; Juvancz, Z. *Synthesis* **1977**, 171. Trost, B. M.; Rivers, G. T.; Gold, J. M. *J. Org. Chem.* **1980**, *45*, 1835. Kim, S.; Ahn, K. H. *J. Org. Chem.* **1984**, *49*, 1717.

(12) Imamoto, T.; Kusumoto, T.; Tawarayama, Y.; Sugiura, Y.; Mita, T.; Hatanaka, Y.; Yokoyama, M. *J. Org. Chem.* **1984**, *49*, 3904.

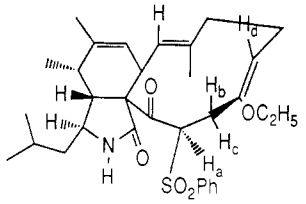
Scheme II. Creation of the Macrocycle[a]



[a] (a) $[CH_2{=}C(CH_3)]_2CuLi$, THF, −78 °C; (b) *n*-C_4H_9Li, CH_3SO_2Ph, THF, HMPA, 0 °C; (c) $(C_2H_5O)_2C{=}CHCO_2C_2H_5$, PPTS, room temperature; (d) (i) 1 N aqueous KOH, THF, room temperature, then HCl; (ii) $PhCH_3$, reflux; (iii) CH_2N_2, ether, room temperature; (e) (i) *n*-C_4H_9Li–DIBAL-H, THF, 0 °C; (ii) PCC, CH_2Cl_2, room temperature; (f) (i) $[CH_2{=}C(OC_2H_5)_2]CuLi$, THF, ether, −78 °C; (ii) $ClCO_2CH_3$, C_5H_5N, 0 °C; (g) 10% $(Ph_3P)_4Pd$, 10% dppp, THF, room temperature; reflux.

bility of the enol ether alcohol led to the immediate capping of the hydroxyl group as the desired methyl carbonate **9**.[8]

The key palladium-catalyzed cyclization, which may be performed at 0.05 M, created the 11-membered carbocycle **10**[8] as a single diastereomer! The *Z* stereochemistry of the enol ether double bond arises from the preferred formation of the *syn*-(π-allyl)palladium intermediate as previously observed for such substrates.[6,7] The stereochemistry of the sulfone simply reflects thermodynamic factors. Consideration of molecular modeling and analogy to the 8-epi analogue **11**,[13] for which we have an X-ray structure, suggest the stereochemistry and conformation depicted in **10**. In particular, the similarity of the absorptions for H_a–H_d



11

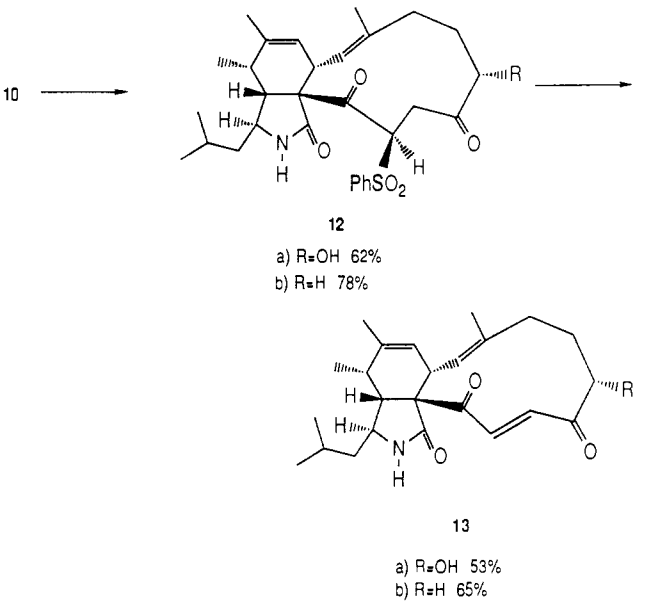
in **11**[8] (H_a, δ 5.93, dd, J = 12.2, 1.9 Hz; H_b, δ 2.84, dd, J = 14.0, 12.2 Hz; H_c, δ 2.45, dd, J = 14.0, 1.9 Hz; H_d, δ 4.32, dd, J = 10.5, 5.1 Hz) and **10** (H_a, δ 6.28, dd, J = 12.0, 2.6 Hz; H_b, δ 2.87, dd, J = 14.1, 12.1 Hz; H_c, δ 2.18, dd, J = 14.1, 2.6 Hz; H_d, δ 4.26, dd, J = 10.2, 5.4 Hz) suggests similar local conformations. The enol ether double bond isomerizes very easily to the 18,19-position in the presence of traces of a strong acid, which therefore must be scrupulously avoided.

The conformation depicted in **10** indicates that hydroxylation should occur to produce the correct epimer at C(17). In that event, treating a methylene chloride solution of the enol ether **10** with 5 equiv of peracetic acid (1.0 M in methylene chloride containing 2 equiv of acetic acid)[14] in the presence of a large excess of potassium carbonate gave the enol ether epoxide, which was directly solvolyzed to the desired α-hydroxy ketone **12a** (PPTS, water, THF, room temperature) (Scheme III). Exposing the crude β-keto sulfone to benzyltrimethylammonium fluoride (THF, methylene chloride, room temperature) gave the target compound **13a**, whose properties were identical with those of an authentic sample, including that of optical rotation[2g] ($[\alpha]^{29}_D$ −129° (*c* 0.012, $CHCl_3$)).

To demonstrate the versatility of this strategy, the enol ether **10** was simply hydrolyzed (PPTS, water, THF, reflux) and the phenylsulfonyl group eliminated with fluoride ion as before to give 17-desoxyaspochalasin. The similarity of its NMR spectrum with that of the natural product indicates that the 17-hydroxy group does not play an important conformational role.

This strategy requires only 19 steps from CBZ-leucine ester. It illustrates the utility of the transition-metal-catalyzed methodology to create 11-membered rings with a substitution pattern

Scheme III. Synthesis of 17-Desoxyaspochalasin and (−)-Aspochalasin[a]



[a] For reaction conditions, see text.

(13) Prepared from the Wittig olefination product obtained in eq 1 by conventional chain extension and a macrocyclization, the latter in direct analogy to the cyclization of **9**. The 8-epidesoxyaspochalasin B and 8-epi-aspochalasin B have been synthesized from **11**.

(14) The approximate 1 M solution of peracetic acid in methylene chloride was prepared by mixing 2.5 mL of 30% peracetic acid in acetic acid with 7 mL of methylene chloride, which forms two layers. Separation of the lower layer provides a methylene chloride solution containing approximately 1 M peracetic acid and 2 M acetic acid.

of great versatility. The presence of an electron-donating group like oxygen on the olefin substituent of the cyclization substrate **9** which destabilizes the first step of the catalytic sequence[6] does not appear to harm the macrocyclization significantly. The use of the carbonate[15] precludes the need for exogenous base. A role of the sulfone group to conformationally anchor the 11-membered ring, and ultimately control the diastereoselectivity of the hydroxylation, may be a more general one, i.e., the sulfone group serves as a stereorelay between the tetrahydroisoindolinone and the C(17) hydroxyl group. We believe that these features impart versatility to this approach for the construction of many other natural (and unnatural) macrocycles of biological interest.

Acknowledgment. We thank the National Institutes of Health, General Medical Sciences Institutes, for their generous support of our programs. S.J.B. and S.A.B. were supported in part by an NIH fellowship. We especially appreciate the generosity of Professor W. Keller-Schierlein (ETH, Zurich) for a comparison sample of (-)-aspochalasin B. Mass spectra were gratefully provided by the Mass Spectrometry Facility, University of California—San Francisco, supported by the NIH Division of Research Resources.

Supplementary Material Available: Characterization data for **4-10** and **13b**, X-ray data, ORTEP drawing, atomic coordinates, isotropic thermal parameters, and selected interatomic distances and angles for **11**, and ORTEP drawing for calculated conformation for **10** (9 pages). Ordering information is given on any current masthead page.

(15) The first use of vinyl carbonates as substrates for alkylations was performed by G. Masse in our laboratories and cited in the following: Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 7550. This area has been intensely investigated by Tsuji et al. See: Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140.

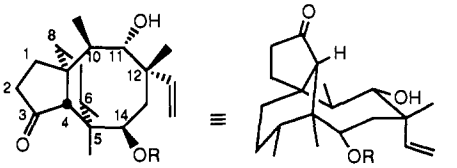
Synthetic Studies Directed toward Naturally Occurring Cyclooctanoids. 2. A Stereocontrolled Assembly of (±)-Pleuromutilin via a Remarkable Sterically Demanding Oxy-Cope Rearrangement

Robert K. Boeckman, Jr.,* Dane M. Springer, and Thomas R. Alessi

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

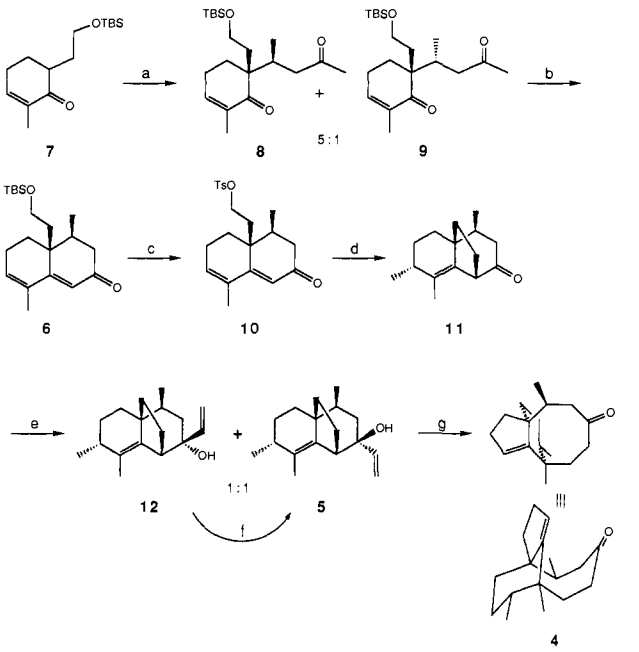
Received May 8, 1989

Pleuromutilin (**1**) represents a challenging vehicle to explore the development of methodology for the construction of eight-membered-ring systems and the direct installation of stereogenic centers in these ring systems based upon conformational analytical principles.[1-5] The complex stereostructure and chemistry of **1** (and mutilin (**2**)) and the practical utility of derivatives (e.g., tiamulin (**3**), used as an animal food additive to control dysentery in swine and poultry)[4] have stimulated other investigations, including the only successful synthetic approach to date, by Gibbons.[6,7]



1 R = $C(O)CH_2OH$
2 R = H
3 R = $C(O)CH_2S(CH_2)_2N(C_2H_5)_2$

Scheme I[a]



[a] Reagents: (a) 3-penten-2-one (1.4 equiv), LDA (1 equiv), THF, -23 °C, 2.25 h; (b) pyrrolidine (10 equiv), H^+ (catalytic), PhH, Δ, 48 h, then excess HOAc/H_2O/NaOAc (2:2:1, w/w) added, Δ, 2 h; (c) HOAc/H_2O/THF (2:1:1, v/v), 25 °C, 8 h, then *p*-TsCl (1.1 equiv), DMAP (catalytic), pyridine (8 equiv), CH_2Cl_2, 25 °C, 40 h; (d) $(CH_3)_2CuLi$ (1.05 equiv from CuBr-DMS (1.1 equiv)) and CH_3Li (2.1 equiv of 1.37 M solution in Et_2O), Et_2O, -78 °C, 1.33 h, then excess HMPA (20% v/v), 0 °C, 1 h; (e) **5** (dropwise) to CH_2=CH-MgBr (28 equiv), THF, 25 °C, 30 min; (f) PhSCl (1.4 equiv), THF, -20 °C → 25 °C, 30 min, then replace solvent with CH_3OH, $P(OEt)_3$ (3 equiv), Δ, 6 h; (g) KH (3.2 equiv), 18-crown-6 (1.5 equiv), diglyme (anhydrous), 25 °C → 110-115 °C, 1.5 h.

The two primary challenges reside in the efficient construction of the requisite substituted tricyclo[5.4.3.$0^{1,8}$]tetradecane nucleus and the stereocontrolled installation of the required eight stereogenic centers, all but one residing on the eight-membered ring. Two working hypotheses guided our selection of a strategy: (1) All the substituents (except the vinyl residue) on the eight-membered ring reside in equatorial-like environments in the most stable conformation (boat-chair (bc) from MM2 calculations). (2) The restrictions imposed on the conformations available to the eight-membered ring by the bridged bicyclic ring fusion (C_5-C_9) greatly reduce the conformational complexity of the system (only two unique low-energy conformations by MM2, bc and boat-boat (bb)). Thus, the target selected for ring-system construction was **4**, which is devoid of most of the stereogenic centers in the eight-membered ring. Construction of **4** (Scheme I) was envisioned via a key sterically demanding oxy-Cope rearrangement

(1) Isolation: Kavanaugh, F.; Hervey, A.; Robbins, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1951**, *37*, 570.
(2) Arigoni, D. *Gazz. Chim. Ital.* **1962**, *92*, 884. Arigoni, D. *Pure Appl. Chem.* **1968**, *17*, 331.
(3) Birch, A. J.; Cameron, D. W.; Holzapfel, C. W.; Rickards, R. W. *Chem. Ind.* **1963**, 374. Birch, A. J.; Holzapfel, C. W.; Rickards, R. W. *Tetrahedron* **1966**, Suppl. 8, Part II, 359.
(4) Berner, H.; Vyplel, H.; Schulz, G. *Tetrahedron* **1987**, *43*, 765. Egger, H.; Reinshagen, H. *J. Antibiot.* **1976**, *29*, 915 and 923. Laber, G.; Schutze, E. *Antimicrob. Agents Chemother.* **1975**, *7*, 517.
(5) Dobler, M.; Durr, B. G. *Cryst. Struct. Commun.* **1975**, *4*, 259.
(6) Kahn, M. *Tetrahedron Lett.* **1980**, *21*, 4547. Paquette, L. A.; Wiedeman, P. E.; Bulman-Page, P. C. *J. Org. Chem.* **1988**, *53*, 1441. Paquette, L. A.; Bulman-Page, P. C.; Pansegrau, P. D.; Wiedeman, P. E. *J. Org. Chem.* **1988**, *53*, 1450. Paquette, L. A.; Wiedeman, P. E.; Pansegrau, P. D. *J. Org. Chem.* **1988**, *53*, 1461.
(7) Gibbons, E. G. *J. Am. Chem. Soc.* **1982**, *104*, 1767.

0002-7863/89/1511-8284$01.50/0