Finally, phosphine oxide **2** was tested in a triene-forming reaction. For this purpose, alcohol **21**[30] was converted to aldehyde **24**, which served as a truncated model of **3**. α-Lithiated phosphine oxide **2** reacted with **24** (THF, −78 °C) to give an 8:1 trans–cis ratio of triene **25** (55%). Also isolated were the noneliminated adducts (35%), identified by their ability to convert to triene **25** upon resubjection to *n*-BuLi and HMPA. Model compound **25** is stable to mild acid and to storage over months, so the triene appears to confer no special instability to the molecule.[14a] In short, the successful use of phosphine oxide **2** in a model reaction and the ease with which it is made demonstrate its promise as a coupling partner for the C_{22}–C_{42} segment of rapamycin whose synthesis is described in the following paper.

Acknowledgment. We thank the National Institute of General Medical Sciences (GM-38627) for support of this project. An NSF predoctoral fellowship (to S.D.M.) and fellowship support from Takeda Chemical Industries, Ltd. (for T.M.) and Sumitomo Pharmaceuticals Co., Ltd. (for M.N.) are gratefully acknowledged. Low- and high-resolution mass spectra were obtained by Dr. Andrew Tyler, Ms. Laura Romo, and Mr. Robert J. Valentekovich at the Harvard Mass Spectrometry Facility supported by NSF (CHE-9020043) and NIH (S10-RR06716). We acknowledge the NIH BRS Shared Instrumentation Grant Program (1 S10 RR01748-01A1) and NSF (CHE88-14019) for providing NMR facilities.

Supplementary Material Available: Full experimental details (for all numbered reaction products except **21–24**), spectral and analytical data for **2** and **6–25**, and ^1H and ^{13}C spectra for **2**, **6–9**, **11–20**, and **25** (35 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(30) Romo, D.; Johnson, D. D.; Plamondon, L.; Miwa, T.; Schreiber, S. L. *J. Org. Chem.*, following communication in this issue.

Synthetic Investigations of Rapamycin. 2. Synthesis of a C_{22}–C_{42} Fragment

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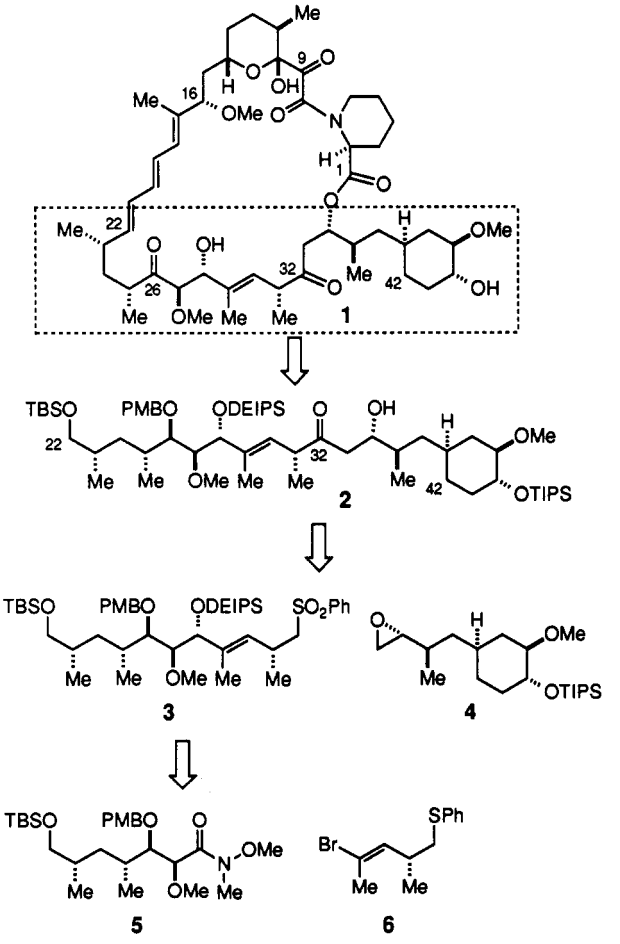
Received June 18, 1992

Summary: A concise, modular synthesis of a protected C_{22}–C_{42} segment of rapamycin is reported including as key coupling steps a vinyllithium addition to a Weinreb amide (**5** + **6** → **24**) and a nucleophilic epoxide opening with an α-lithio sulfone mediated by BF_3·OEt_2 (**4** + **27** → **28**).

In the preceding paper,[1] a synthesis of a fully protected C_{10}–C_{21} fragment of the antiproliferative agent rapamycin **1** was described. Herein, we detail a synthesis of a protected C_{22}–C_{42} fragment suitable for coupling to the previously described C_{10}–C_{21} fragment en route to a planned total synthesis of rapamycin and related molecules. The convergent synthesis of the C_{22}–C_{42} segment of rapamycin (**2**) relied on the preparation and subsequent coupling of the Weinreb amide **5**, the vinyl bromide **6**, and the epoxide **4** (Scheme I). Retrosynthetically, we envisioned obtaining the β-hydroxy ketone **2** by oxidative desulfonylation of a γ-hydroxy sulfone resulting from nucleophilic opening of the epoxide **4** by the lithiated sulfone derived from phenyl sulfone **3**. Alkylative coupling of the vinyllithium species generated from bromide **6** and the Weinreb amide **5** was expected to deliver a precursor to phenyl sulfone **3**.

Preparation of Coupling Partners 4–6. The synthesis of the Weinreb amide **5** began by DIBALH half-reduction (CH_2Cl_2, −90 °C, 2.5 h)[2] of the known ester **7** (Scheme II).[3] Direct Wittig olefination (CH_2Cl_2, rt, 18 h) of the crude aldehyde afforded the α,β-unsaturated ester **8** in 80% yield for the two steps. Reduction to the alcohol **9** (DIBALH, CH_2Cl_2, −78 → 0 °C), protection as its *tert*-butyldimethylsilyl ether (TBSCl, CH_2Cl_2, cat. DMAP, rt, 10 h), and debenzylation under dissolving metal conditions (Na^0, NH_3, −78 °C, 15 min) provided the homoallylic alcohol **10** in 93% overall yield. Hydroxyl-directed hydrogenation (CH_2Cl_2, rt, 5 h) employing 4 wt % of the rhodium catalyst described by Evans and co-workers[4] gave the desired 1,3-

Scheme I



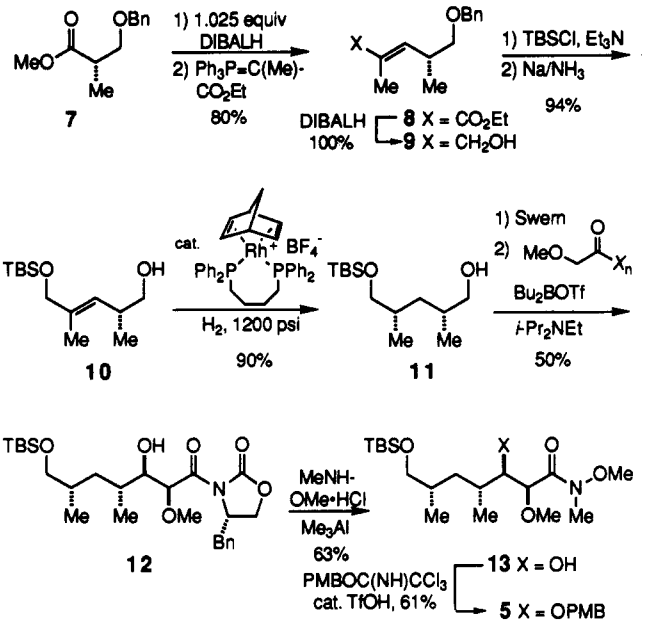
(1) Meyer, S. D.; Miwa, T.; Nakatsuka, M. Schreiber, S. L. *J. Org. Chem.*, preceding paper in this issue.

(2) For a detailed procedure of a related DIBALH half-reduction see: Keck, G. E.; Andrus, M. A.; Romer, D. R. *J. Org. Chem.* **1991**, *56*, 417.

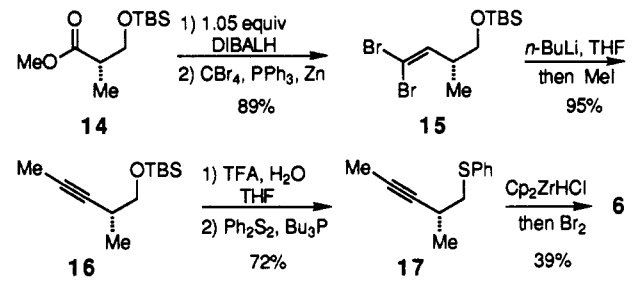
(3) (a) Roush, W. R.; Palkowitz, A. D.; Ando, K. *J. Am. Chem. Soc.* **1990**, *112*, 6348. (b) The ester **7** used in this study was prepared by benzylation of commercially available (*S*)-methyl 3-hydroxy-2-methylpropionate (Aldrich): (i) Wessel, H.-P.; Iversen, T.; Bundle, D. R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 2247. (ii) Widmer, U. *Synthesis* **1987**, 568.

0022-3263/92/1957-5060$03.00/0

Scheme II

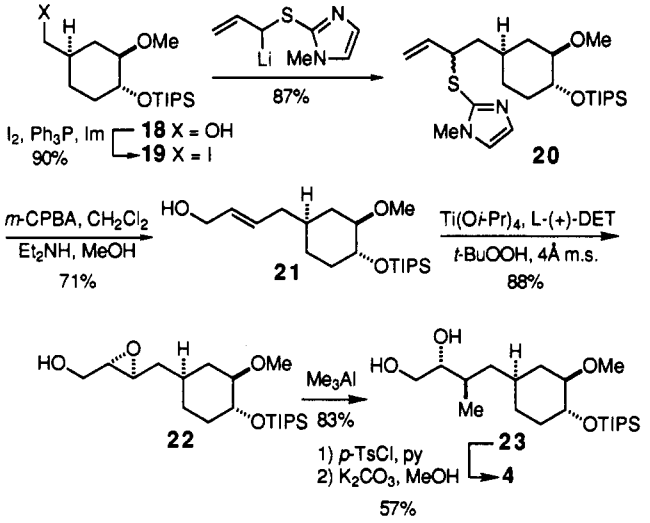


Scheme III



syn-dimethyl product **11** (90% de, vpc). Importantly, this hydrogenation was easily performed on a multigram scale (45 g) with no deterioration in yield or diastereomeric purity. Separation of the minor anti diastereomer was readily accomplished after a subsequent aldol reaction. Thus, Swern oxidation[5] of alcohol **11** and aldol condensation[6] of the crude aldehyde with the boron enolate of the (*S*)-phenylalanine-derived oxazolidone[7] (Bu_2BOTf, *i*-Pr_2EtN, toluene, −78 → 0 °C) gave the desired adduct **12** in 50% overall yield. Transamination[8] to the Weinreb amide **13** (Me_2Al·NMe(OMe), CH_2Cl_2, 0 °C → rt, 20 h) followed by protection of the secondary alcohol as the *p*-methoxybenzyl ether[9] gave the key intermediate **5** corresponding to the C_{22}–C_{28} segment of rapamycin[10] in a form suitable for alkylative coupling. The process leading to the amide **5** was readily performed on a large scale and allowed the preparation of multigram quantities of this intermediate.

Scheme IV



The vinyl bromide coupling partner **6** was prepared in six steps from the known ester **14** (Scheme III).[3a] DIBALH half-reduction[2] (CH_2Cl_2, −90 °C, 2.5 h) of ester **14** and direct dibromoolefination[11] (CH_2Cl_2, 0 °C → rt, 2 h) of the intermediate aldehyde gave the desired acetylene precursor **15** in 90% yield for the two steps. Exposure of the dibromoolefin **15** to Corey–Fuchs conditions[11] (*n*-BuLi, THF, −78 °C) and quenching of the intermediate acetylenic anion with methyl iodide (−78 °C → rt) gave the propargyl derivative **16** in 95% yield. The efficiency of the sequence leading to acetylene **16** allowed for the processing of decagram quantities of this intermediate. Deprotection (TFA) of the silyl ether of acetylene **16** and direct sulfenylation[12] (Ph_3P, Ph_2S_2, benzene, rt, 10 h) of the intermediate, volatile alcohol proceeded smoothly to give the phenyl sulfide **17**. A hydrozirconation–bromination[13] sequence (Cp_2ZrHCl, toluene, rt → 40 °C, 1 h then Br_2, −78 °C, 30 min) afforded the vinyl bromide **6** in 39% yield.[14]

Scheme IV details the preparation of the C_{33}–C_{42} fragment in six steps from the known alcohol **18**.[15] Iodination and alkylation of the alcohol with the lithiated allylic sulfide proceeded in a highly regioselective fashion to give the α-substituted allylic thioether **20** (THF, −78 °C).[16] [2,3] Sigmatropic rearrangement of the corresponding sulfoxide (*m*-CPBA, CH_2Cl_2, 0 °C → rt) and in situ cleavage of the sulfenate ester (Et_2NH, MeOH, rt) afforded trans-allylic alcohol **21** in good yield. Sharpless asymmetric epoxidation provided epoxy alcohol **22** in 88% yield and with high diastereoselectivity.[17] The C_{35} methyl group was

(4) The diastereomeric ratio obtained in this study correlates well with that previously reported for the racemic material: Evans, D. A.; Morrissey, M. M.; Dow, R. L. *Tetrahedron Lett.* **1985**, *26*, 6005.

(5) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, 165.

(6) (a) Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 2127. (b) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 3099.

(7) The oxazolidone used in this study was prepared by acylation (see ref 6b) of the (*S*)-phenylalanine-derived oxazolidone (Gage, J. R.; Evans, D. A. *Org. Synth.* **1989**, *68*, 77) with α-methoxyacetyl chloride (α-methoxyacetic acid, thionyl chloride, reflux, 1h).

(8) Levin, J. I.; Turos, E.; Weinreb, S. M. *Synth. Commun.* **1982**, *12*, 1982.

(9) Nakajima, N.; Horita, K.; Abe, R.; Yonemitsu, O. *Tetrahedron Lett.* **1988**, *29*, 4139.

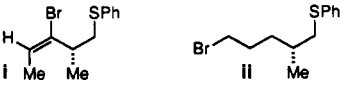
(10) An alternative synthesis of a similar C_{22}–C_{28} segment has been recently described: Hale, M. R.; Hoveyda, A. H. *J. Org. Chem.* **1992**, *57*, 1643.

(11) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.

(12) (a) Cleary, D. G. *Synth. Commun.* **1989**, 737. (b) Nagakawa, I.; Hata, T. *Tetrahedron Lett.* **1975**, 1409.

(13) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679.

(14) Compound **6** was accompanied by ~13% of a regioisomeric product **i** that was of no consequence since the corresponding vinyllithium was unreactive in the subsequent coupling step. An additional byproduct formed (~15–20%) was the primary bromide **ii**. This reaction has not been optimized on large scale; however, a small-scale run gave the desired vinyl bromide as a single regioisomer (^{1}H-NMR) in ~70% yield.

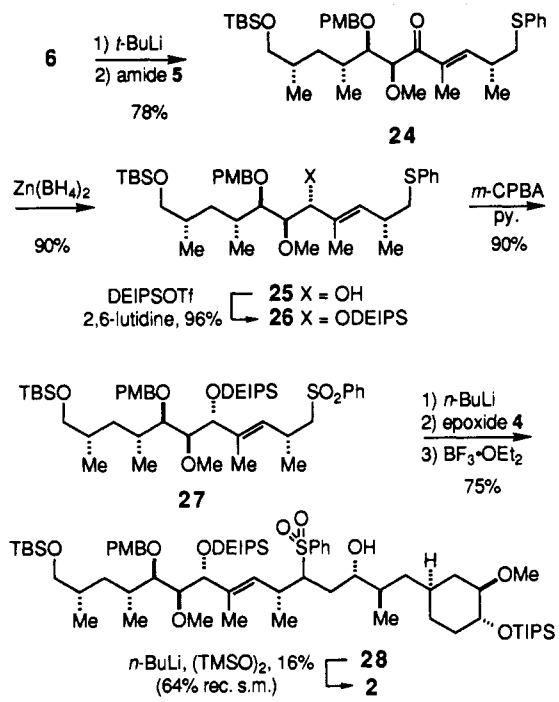


(15) Compound **18** was previously employed in a total synthesis of FK506; see: Nakatsuka, M.; Ragan, J. A.; Sammakia, T.; Smith, D. B.; Uehling, D. E.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 5583.

(16) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147.

(17) Finn, M. G.; Sharpless, K. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter, 8, p 247.

Scheme V

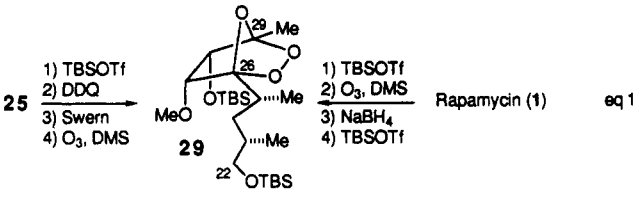


introduced by regioselective epoxide opening with trimethylaluminum (2.0 M in hexane, 0 °C) to cleanly generate the *vic*-diol **23**.[18] Conversion of **23** to the desired epoxide **4** was accomplished via standard methods in 57% yield for the two-step sequence.

Coupling of Intermediates 4–6. Having achieved efficient procedures for the preparation of coupling partners **4–6**, a protocol for their coupling was established. The vinyllithium species generated by exposure of the vinyl bromide **6** (2.0 equiv, THF, −100 °C) to *t*-BuLi (2.4 equiv) reacted smoothly with amide **5** (−78 °C, 1 h) to give enone **24** in 78% yield (Scheme V).[19] Chelation-controlled Zn(BH$_4$)$_2$ reduction (Et$_2$O, −20 °C, 1 h) occurred in a highly stereoselective fashion[20] to give the alcohol **25**, which was subsequently protected as its diethylisopropyl silyl ether **26** (DEIPSOTf, 2,6-lutidine, CH_2Cl_2, 0 °C → rt).[21] Oxidation of the sulfide **26** to the sulfone **27** proceeded smoothly by the action of *m*-CPBA (2.2 equiv, −40 °C → rt, 2 h) in the presence of excess pyridine in 78% overall yield from enone **24**.

α-Lithiation of the sulfone **27** with *n*-BuLi (−78 °C, 15 min) followed by addition of the epoxide **4** and BF$_3$·OEt$_2$ gave the desired γ-hydroxy sulfones **28** in 75% yield as a 4:1 ratio of diastereomers.[22] The diastereomers were readily separated by preparative HPLC, and the major diastereomer was isolated in 59% yield. Metalation of the major diastereomeric sulfone **28**[23] was readily achieved with *n*-BuLi; however, attempted oxidation of this and related compounds to the ketone **2** with a number of electrophilic oxygen sources (e.g., MoOPH,[24] oxaziridine,[25] *t*-BuOOMgBr[26]) has been unsuccessful with the exception of molecular oxygen[27] and bis(trimethylsilyl) peroxide.[28] Thus, metalation of the major diastereomer with *n*-BuLi (2.5 equiv, −78 °C, 15 min) followed by treatment with bis(trimethylsilyl) peroxide (−78 °C, 6 h) gave the desired β-hydroxy ketone **2** (16%, after one recycling of recovered, deprotonatable γ-hydroxy sulfone)[29] and recovered γ-hydroxy sulfones **28** as a mixture of diastereomers (64%). The oxidative desulfonylation of sulfone **28** and related systems has been quite challenging, and efforts to improve this transformation in addition to exploration of alternative strategies continue.

Confirmation of Stereochemistry. Stereochemical confirmation of the alcohol **25**, which contains five stereocenters present in rapamycin, was made by conversion to the bicyclic peroxide **29** and comparison to the same compound prepared by degradation of rapamycin as described by Goulet and Boger (eq 1).[30] Co-^{1}H- and ^{13}C-



NMR (500 MHz) indicated that the bicyclic peroxides **29** obtained by the two routes possessed the same relative configuration while comparison of optical rotations confirmed their identical absolute configuration. The C$_{31}$ stereocenter, which is lost during ozonolysis, is derived directly from (*S*)-methyl 3-hydroxy-2-methylpropionate (vide supra). The stereochemistry of the cyclohexyl epoxide **4** follows from comparison of spectral and physical data of alcohol **18** to that previously reported.[15] The remaining two stereocenters (C$_{34}$ and C$_{35}$) are derived from Sharpless epoxidation and regio- and stereospecific epoxide ring opening (vide supra).

(18) Suzuki, T.; Saimoto, H.; Tomioka, H.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 3597.

(19) Employing less than 2.0 equiv of the vinyl bromide **6** led to significant amounts of *tert*-butyl addition product and *N*-desmethoxyamide, a known product of strong, hindered bases and Weinreb amides. See: Graham, S. L.; Scholz, T. H. *Tetrahedron Lett.* **1990**, *31*, 6269. Apparently, the generated vinyllithium is competitive with *t*-BuLi for the *tert*-butyl bromide formed during the metalation. As a result, excess *t*-BuLi remains after metalation under these conditions.

(20) The diastereoselectivity of this reduction was determined to be 23:1 (α/β) after subsequent protection as the diethylisopropyl silyl ether (**26**) (500-MHz ^{1}H-NMR). (a) Nakata, T.; Tanaka, T.; Oishi, T. *Tetrahedron Lett.* **1983**, *24*, 2653. (b) For recent uses of this reagent in similar contexts and with similar outcomes, see: (i) Somers, P. K.; Wandless, T. J.; Schreiber, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 8045. (ii) Evans, D. A.; Miller, S. J.; Ennis, M. D.; Ornstein, P. L. *J. Org. Chem.* **1992**, *57*, 1067. (iii) Reference 7.

(21) Toshima, K.; Mukaiyama, S.; Kinoshita, M.; Tatsuta, K. *Tetrahedron Lett.* **1989**, *30*, 6413 (DEIPS = diethylisopropylsilyl).

(22) For previous uses of BF$_3$·OEt$_2$ in similar contexts see: (a) Yamaguchi, M.; Hirao, I. *Tetrahedron Lett.* **1983**, *24*, 391. (b) Eis, M. J.; Wrobel, J. E.; Ganem, B. *J. Am. Chem. Soc.* **1984**, *106*, 3693.

(23) The configuration at C$_{32}$ of the major and minor diastereomers of sulfone **28** has not been determined. Attempted metalation/oxidation of the minor diastereomeric γ-hydroxy sulfone under a variety of conditions has thus far been unsuccessful.

(24) (a) Little, R. D.; Myong, S. O. *Tetrahedron Lett.* **1980**, *21*, 3339. (b) Kennedy, R. M.; Biko, A.; Takemasa, T.; Okumoto, H.; Masamune, S. *Tetrahedron Lett.* **1988**, *29*, 451.

(25) Williams, D. R.; Robinson, L. A.; Amato, G. S.; Osterhout, M. H. *J. Org. Chem.* **1992**, *57*, 3740.

(26) Lawesson, S.-O.; Yang, N. C. *J. Am. Chem. Soc.* **1959**, *81*, 4230. Although some desired ketone was produced using this reagent, it was obtained as a mixture of diastereomers possibly as a result of epimerization of the sensitive allylic, α-keto center (C$_{31}$).

(27) Yamada, S.; Nakayama, K.; Takayama, H. *Tetrahedron Lett.* **1984**, *25*, 3239. Metalation and oxidation with molecular oxygen of a system related to sulfone **28** (TBS = TBDPS, DEIPS = TBS) gave the desired ketone (14%), retro-aldol-derived methyl ketone (17%), and recovered starting material as a mixture of diastereomers (67%).

(28) Hwu, J. R. *J. Org. Chem.* **1983**, *48*, 4433.

(29) That no epimerization of the labile allylic, α-keto center (C$_{31}$) had occurred during the oxidative desulfonylation was determined by inspection of the ^{1}H- and ^{13}C-NMR (500 MHz) of ketone **2**. Epimerization of this center did indeed occur in a closely related model system using *n*-BuLi and molecular oxygen as oxidant and was easily ascertained by ^{1}H NMR (500 MHz).

(30) Goulet, M.; Boger, J. *Tetrahedron Lett.* **1990**, *31*, 4845. The bicyclic peroxide **29** is formed as a single stereoisomer by both routes; however, the stereochemistry at C$_{26}$ and C$_{29}$ has not been determined (only one stereoisomer is shown). Note that the original report incorrectly depicted the exo C$_{28}$ stereochemistry.

In summary, a synthesis of a protected version of the C_{22}–C_{42} segment of rapamycin has been accomplished. The modular nature of the synthesis will facilitate the preparation of rapamycin derivatives that will be useful for mechanistic investigations. Current efforts are focused on optimization of the sulfone oxidation and coupling of the dienylphosphine oxide[1] to the fragment described herein. The outcome of these studies and the completion of the total synthesis of rapamycin will be the subject of future reports.

Acknowledgment. Financial support of this project by the National Institute of General Medical Sciences (GM-38627) is gratefully acknowledged. An American Cancer Society postdoctoral fellowship (to D.R.), a NSF predoctoral fellowship (to D.D.J.), a NATO postdoctoral fellowship (to L.P.), and support from Takeda Chemical Industries, Ltd. (to T.M.) are gratefully acknowledged. High- and low-resolution mass spectra were obtained by Dr. Andrew Tyler, Ms. Laura K. Romo, and Mr. Robert J. Valentekovich at the Harvard Mass Spectrometry Facility supported by NSF (CHE-9020043) and NIH (SIO-RR06716). We thank Dr. Mark Goulet (Merck) for spectral and physical data of the degradation products in addition to experimental details for the degradation of rapamycin. We acknowledge the NIH BRS Shared Instrumentation Grant Program (1 S10 RR01748-01A1) and NSF (CHE88-14019) for providing NMR facilities.

Supplementary Material Available: Full experimental details in addition to spectral and analytical data for all reaction products (including ^1H and ^{13}C spectra for intermediates **2**, **4**, **6**, **12**, **19**, **24–28**, and degradation product **29**) (35 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Chemically Labile Stannylene–Nitrogen Bonds. The Chemoselective and Stereoselective Synthesis of *N,N*-Bis(trimethylsilyl)enamines and *N,N*-Dialkylenamines

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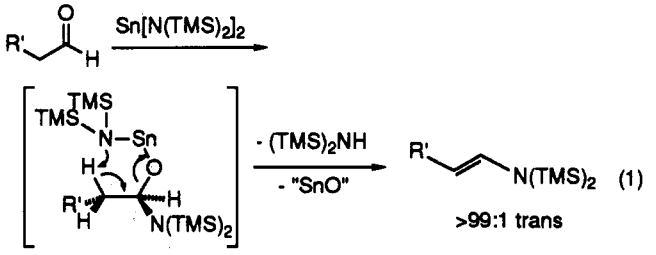
Received June 19, 1992

Summary: The chemoselective reaction of $Sn[N(TMS)_2]_2$ with primary aldehydes leads to the stereoselective synthesis of *trans-N,N*-bis(trimethylsilyl)enamines. More reactive $Sn(NR_2)_2$ (R = Et, iPr, or piperidine) can be generated in situ and then treated with aldehydes or ketones to give trans enamines.

Divalent tin compounds, otherwise known as stannylenes, have not been investigated as thoroughly as their carbon counterparts, the carbenes. In 1974, Lappert[1] and Zuckerman[2] both reported the synthesis of bis(trimethylsilyl)aminotin, $Sn[N(SiMe_3)_2]_2$, from the lithium amine salt and $SnCl_2$. Both groups reported this tin(II) amide to be a diamagnetic, thermally stable, distillable red-orange liquid which solidified to an orange-yellow solid. On the basis of a combination of cryoscopic, mass spectral, and X-ray crystallographic data, Lappert concluded that $Sn[N(TMS)_2]_2$ was monomeric in solution and dimeric in the solid state.[3]

Research in our group has focused on the development of new synthetic methods using stannylenes and germylenes. With regard to stannylenes, we have found that acetals may be selectively hydrolyzed to aldehydes *under mildly basic conditions* in the presence of tin(II) chloride.[4] Furthermore, aldehydes can be smoothly converted to β-keto esters via a tin(II) chloride promoted coupling with α-diazo compounds.[5] As an extension of these studies, we now report that tin(II) amides react with primary aldehydes to give the corresponding trans enamines stereoselectively (eq 1).[6] *This is the first example of transfer of a ligand from a tin(II) amide to an organic substrate.*[7]



(1)

Our initial experiments with tin(II) amides were conducted with $Sn[N(TMS)_2]_2$.[8] We were pleased to find that

(1) Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 895.

(2) Schaeffer, C. D.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 7160.

(3) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F., Power, P. P.; Riviere, P.; Rivere-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004.

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