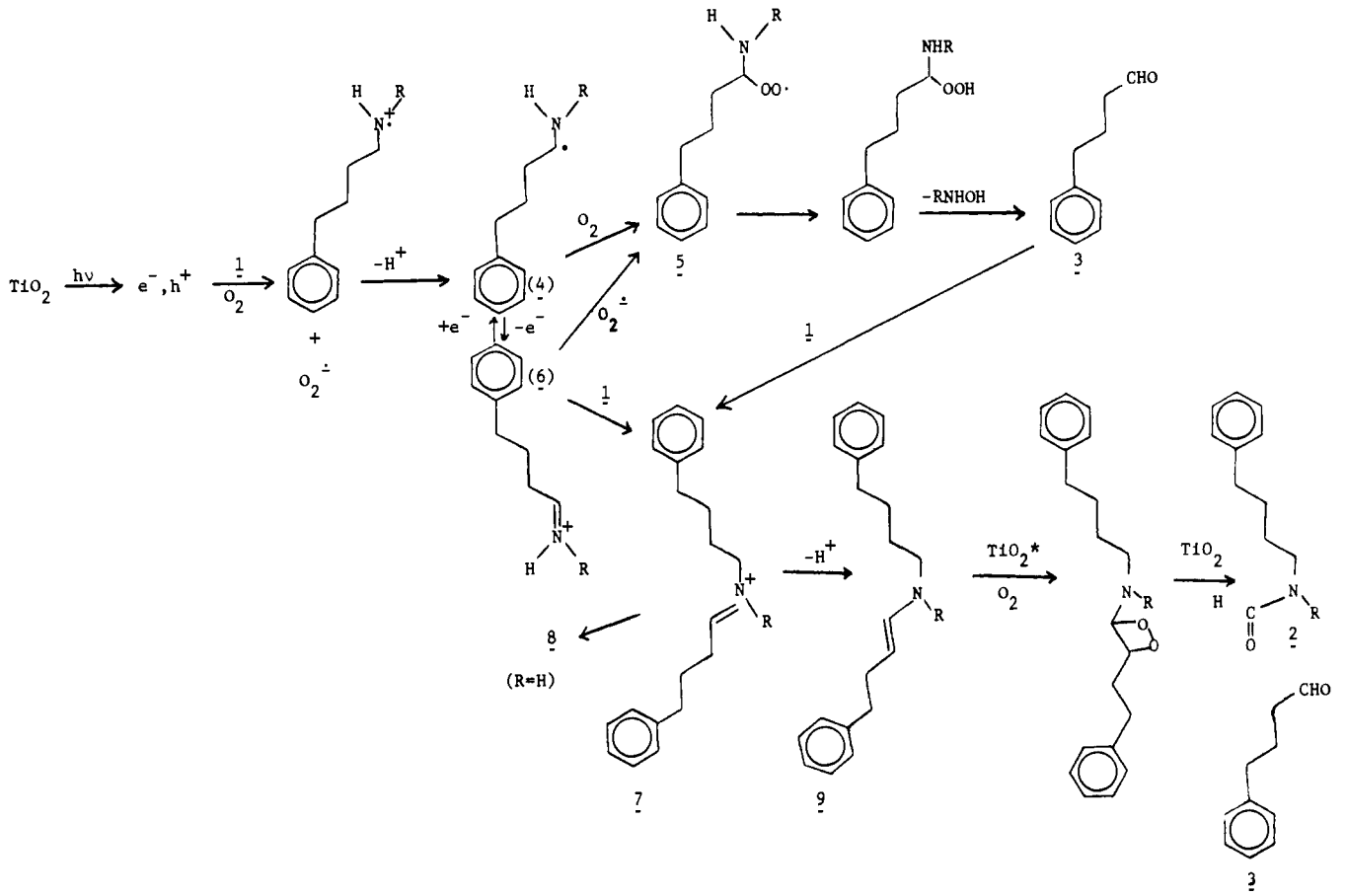
Scheme I. Proposed Mechanism for Photocatalytic Amine Oxidation



interaction of singlet oxygen with other electron-rich functional groups.[14] In fact, the concurrent operation of radical and charge-transfer mechanisms in the photooxygenation of tributylamines has already been suggested.[15]

This work is not the first description of heterogeneous photooxidation of nitrogen-containing compounds. Pichat and coworkers have previously reported, for example, that the TiO_2-photocatalyzed oxidation of gaseous ammonia gives rise to N_2 and N_2O.[16] Similarly, the photocatalyzed oxidation in aqueous suspensions of TiO_2 of toluidines to azo coupling products[17] and of amides to imides[18] have been described. The experiments reported here, however, are the first attempts at controlling the mode of photooxidation of aliphatic amines on a heterogeneous photocatalyst suspended in a nonaqueous solvent.

Although one photochemical route to the N-formylation of aliphatic amines (the photooxygenation of enamines) has been previously described,[13,19] this work represents the first demonstration that the formyl carbon can be derived from the amine itself. Hence, in addition to expanding the arsenal of redox reactions that can be accomplished on irradiated semiconductor powders, this study provides an alternate synthetic route to formylated products as well as a mechanistically important characterization of electron-transfer-induced amine oxidations. Future work will address the comparison of these semiconductor surface-mediated photocatalytic oxidations with those initiated by photexcited electron-transfer sensitizers in homogeneous solution.

Acknowledgment. This work was supported by the National Science Foundation and the Robert A. Welch Foundation. M.A.F. is grateful for support as a Alfred P. Sloan Research Fellow and as a Camille and Henry Dreyfus Teacher–Scholar.

(14) For example, see: Eriksen, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083 and other papers in this series.
(15) Davidson, R. S.; Trethewey, K. R. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 173.
(16) Mozzanega, H.; Herrmann, J. M.; Pichat, P. *J. Phys. Chem.* **1979**, *83*, 2251.
(17) Kasturirangan, H.; Ramakrishnan, V.; Kuriacose, J. C. *J. Catal.* **1981**, *69*, 216.
(18) Pavlik, J. W.; Tantayanon, S. *J. Am. Chem. Soc.* **1981**, *103*, 6755.
(19) Ando, W.; Watanabe, K. *Tokkyo Koho* **1979**, *22*, 313 (*Chem. Abstr.* **1979**, *90*, 204115j); *Ger. Offen.* 2 832 133 (*Chem. Abstr.* **1979**, *90*, 186969j).

Stereospecific Synthesis of Acyclic Unsaturated Amino Alcohols. A New Approach to *threo*- and *erythro*-Sphingosine

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The discovery of new methodology for efficient genesis of relative stereochemistry in acyclic systems has continually been of major importance in synthetic organic chemistry.[1] The recent elegant and extensive work on stereocontrol in aldol and related reactions[2] has not been matched to data by the development of methods for stereoselectively preparing nitrogen-containing acyclic molecules.[3] We now describe a conceptually new route to vicinal amino alcohols containing unsaturation that allows total control of both relative configuration and double-bond geometry.

(1) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 1.
(2) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1. Mukaiyama, T. *Org. React.* **1982**, *28*, 203.
(3) For some notable recent exceptions see: Seebach, D.; Beck, A. K.; Mukhopadhyay, T.; Thomas, E. *Helv. Chim. Acta* **1982**, *65*, 1101. Wang, Y. F.; Izawa, T.; Kobayashi, S.; Ohno, M. *J. Am. Chem. Soc.* **1982**, *104*, 6465. Parker, K. A.; O'Fee, R. *Ibid.* **1983**, *105*, 654.

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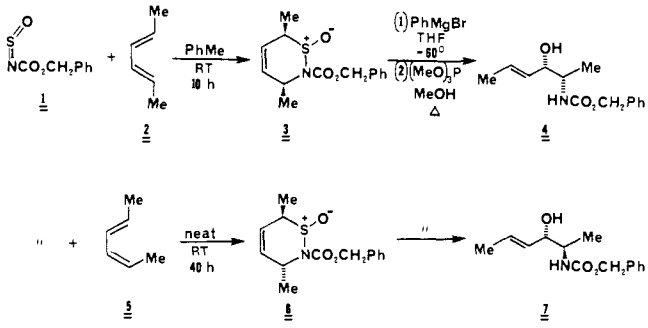
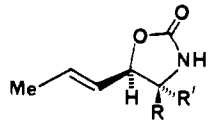
Scheme I



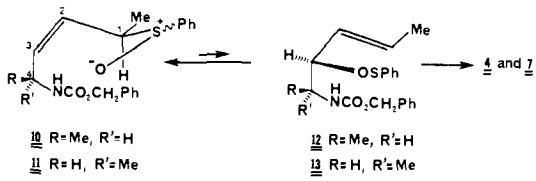
We initially tested the general approach in the simple systems outlined in Scheme I. Cycloaddition of *N*-sulfinylcarbamate **1** and (*E*,*E*)-2,4-hexadiene (**2**) at room temperature provided Diels–Alder adduct **3**[4,5] in 85% yield. Treatment of **3** with phenylmagnesium bromide gave an intermediate allylic sulfoxide,[6] which without purification was heated with trimethyl phosphite to afford the threo-*E*-unsaturated carbamate alcohol **4** as a *single* stereoisomer (85% from **3**). The configuration of **4** was established by ^{1}H NOE difference spectroscopy[7] on cyclic carbamate **8**,



8 R=H, R′=Me
9 R=Me, R′=H

prepared from the acyclic compound by treatment with sodium hydride in glyme (94%). Similarly, (*E*,*Z*)-hexadiene (**5**) was combined with **1** to afford adduct **6** (60%), although not surprisingly this cycloaddition proceded somewhat more slowly than with the *E*,*E* isomer. Treatment of **6** with phenylmagnesium bromide followed by trimethyl phosphite gave *exclusively* the *erythro-E*-carbamate **7** (85%). Once again, the stereochemistry of **7** was proven by conversion to the cyclic carbamate **9** (NaH/glyme, 88%), which showed the expected NOE enhancements.[7]

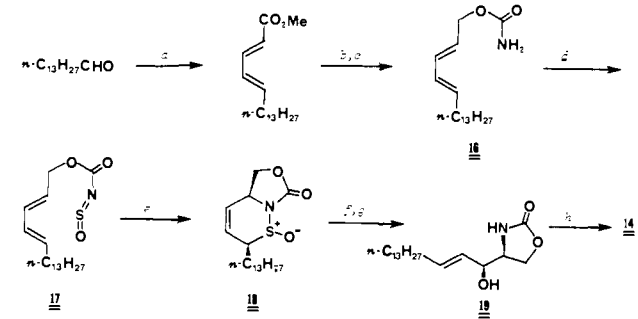
The high specificity of chirality transfer in the formation of the amino alcohol derivatives can best be explained by assuming that the allylic sulfoxides **10** and **11** formed from the Diels–Alder



10 R=Me, R′=H
11 R=H, R′=Me
12 R=Me, R′=H
13 R=H, R′=Me

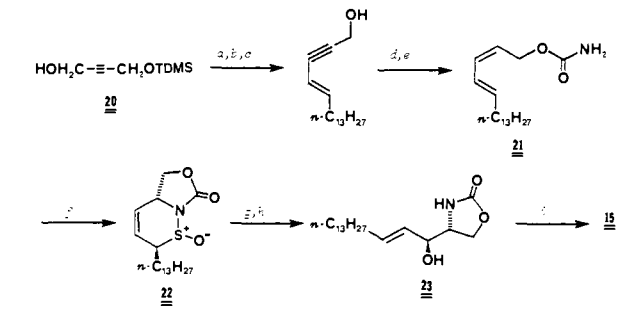
adducts upon treatment with phenyl Grignard reagent undergo [2,3] sigmatropic rearrangement to sulfenate esters **12** and **13**, respectively, via envelope-like transition states.[8,16] In both cases, the methyl group on the sulfur-bearing carbon (C-1) must occupy a pseudoequatorial position to avoid severe A^{1,3} strain with substituents on C-4. This anchor effect controls double-bond geometry

Scheme II[a]



[a] Key: (a) $(MeO)_2P(O)CH_2CH{=}CHCO_2Me$, LDA, THF, −40 °C (60%). (b) $LiAlH_4/Et_2O$, 25 °C (85%). (c) NaOCN, TFA/Et_2O (88%). (d) $SOCl_2$/py, PhMe, 0 °C (85%). (e) Room temperature, 14 h. (f) PhMgBr, −60 °C, THF. (g) $(MeO)_3P$, MeOH, 60 °C (79% from **18**). (h) $Ba(OH)_2$, dioxane/H_2O, reflux, 60 h (72%).

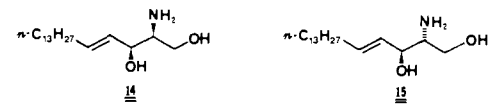
Scheme III[a]



[a] Key: (a) $BaMnO_4$, CH_2Cl_2, room temperature, 6 h. (b) n-$C_{13}H_{27}CH_2{}^+PPh_3Br^-$, n-BuLi/THF, −30 °C.[15] (c) 3.5 N HCl (58% from **20**). (d) H_2/Lindlar Catalyst, PhMe, 1 atm (80%). (e) NaOCN, TFA, Et_2O (90%). (f) $SOCl_2$/py, PhMe, room temperature, 60 h (85%). (g) PhMgBr, THF, −60 °C. (h) $(MeO)_3P$, MeOH, 60 °C, 5 h (77% from **22**). (i) $Ba(OH)_2$, glyme/H_2O, reflux, 24 h (77%).

in the rearrangement products and determines to which face of the C-2,3 double bond oxygen is transferred.

We have utilized this methodology in stereospecific synthesis of the sphingolipid bases *threo*-sphingosine (**14**) and *erythro*-



sphingosine (**15**).[9] Since we anticipated regiochemical problems in the Diels–Alder steps in these syntheses, we elected to avoid this potential difficulty by effecting intramolecular cycloadditions. To our knowledge, these are the *first* reported examples of intramolecular *N*-sulfinylimide Diels–Alder processes.[4]

Synthesis of *threo*-sphingosine is shown in Scheme II. Myristic aldehyde was transformed in three steps to (*E*,*E*)-carbamate **16**, which upon treatment with thionyl chloride/pyridine generated sulfinylcarbamate **17**. This compound cleanly cyclized at room temperature overnight to afford adduct **18**. Conversion of **18** to **19** was done exactly as in the hexadiene cases in Scheme I. Hydrolysis of the carbamate group of **19** gave racemic *threo*-sphingosine[10] completely free of the erythro isomer.

The (*E*,*Z*)-carbamate **21** needed for *erythro*-sphingosine was prepared from **20**[12] as shown in Scheme III. Intramolecular

(4) For reviews of this type of cycloaddition see: Kresze, G.; Wucherpfennig, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 49. Weinreb, S. M.; Staib, R. R. *Tetrahedron* **1982**, *38*, 3087. See also: Garigipati, R. S.; Morton, J. A.; Weinreb, S. M. *Tetrahedron Lett.* **1983**, *24*, 987.

(5) Compounds **3** and **6** are single stereoisomers at sulfur, but we have not established configuration.

(6) Thiazine *N*-oxides such as **3** and **6** have apparently not previously been opened with carbon nucleophiles. For cleavage of these systems with oxygen and sulfur nucleophiles see: Wucherpfennig, W. *Liebigs Ann. Chem.* **1971**, *761*, 16.

(7) We thank A. Freyer for conducting these experiments on a Bruker WM-360 instrument.

(8) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 563.

(9) For previous syntheses see: (a) Shapiro, D. "Chemistry of Sphingolipids"; Hermann: Paris, France, 1969. (b) Newman, H. *J. Am. Chem. Soc.* **1973**, *95*, 4098.

(10) Characterized as the triacetyl derivative, mp 68 °C (lit.[11] mp 69–71 °C for racemic **14** triacetate).

(11) Grob, C. A.; Gadient, F. *Helv. Chim. Acta* **1957**, *40*, 1145.

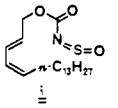
(12) Nakanishi, K.; Balogh-Nair, V.; Arnaboldi, M.; Tsujimoto, K.; Honig, B. *J. Am. Chem. Soc.* **1980**, *102*, 7947.

Diels–Alder cycloaddition of the *N*-sulfinylcarbamate derived from **21** was slow but cleanly gave the desired adduct **22**.[13] The usual two-step process served to produce carbamate alcohol **23** as a single stereoisomer. Basic hydrolysis of **23** gave racemic *erythro*-sphingosine (**15**) having solution spectra and TLC behavior identical with those of a commercial sample.[14] These sphingosine syntheses show considerably better stereocontrol than any reported to data.[9]

We are continuing to explore synthetic applications of *N*-sulfinyldienophile Diels–Alder chemistry.[4]

Acknowledgment. This research was supported by the National Science Foundation (CHE81-00132). We are extremely grateful to Professor Clayton Heathcock for a valuable discussion that led to development of the protocol discussed in this paper.

(13) Interestingly, sulfinyl carbamate i did not cyclize to **22**, probably due to difficulty in attaining the necessary *s*-cis conformation.



(14) *erythro*-D-Sphingosine was obtained from Sigma Chemical Co.

(15) No detectable amount of the *Z* isomer was produced in this Wittig reaction.

(16) **Note Added in Proof**: Recent ^{1}H NMR experiments have shown that at 50 °C *E*-allylic sulfoxide 10 rearranges rapidly to an allylic sulfoxide having a *Z* double bond (cf.: Miller, J. G.; Kurz, W.; Untch, K. G.; Stork, G. *J. Am. Chem. Soc.* **1974**, *96*, 6774). Details will be given in our full paper.

Additions and Corrections

The Mechanism of Hemiacetal Decomposition. Substituent Effects in Breakdown of Substituted Benzaldehyde Ethyl Hemiacetals [*J. Am. Chem. Soc.* **1981**, *103*, 4884]. THEODORE J. PRZYSTAS and THOMAS H. FIFE*.

Page 4889, second column, 3rd line from the bottom should read: from which ρ in the bond-breaking step can be calculated to be approximately -1.4.[32]

Ene Reaction of Singlet Oxygen: An Entropy-Controlled Process Determines the Reaction Rate [*J. Am. Chem. Soc.* **1982**, *104*, 6854–6856]. JOHN R. HURST and GARY B. SCHUSTER*.

Page 6855: The exponents of k_r in Table I should all be positive.

Page 6855: The following citations should be added to ref 10—(d) Schulte-Elte, K. H.; Rautenstrauch, V. *J. Am. Chem. Soc.* **1980**, *102*, 1738. (e) Schulte-Elte, K. H.; Muller, B.; Rautenstrauch, V. *Helv. Chim. Acta* **1978**, *61*, 2777.

Synthesis of (Trifluoromethansulfonato)pentaammineosmium(III): Osmium(III) Pentaammine Complexes [*J. Am. Chem. Soc.* **1982**, *104*, 7658]. PETER A. LAY, ROY H. MAGNUSON, J. SEN, and HENRY TAUBE*.

Page 7659, the acknowledgment should read: Support of this work by National Institutes of Health Grant No. GM13638 and National Science Foundation Grant No. CHE79-08633 is gratefully acknowledged. P.A.L. also acknowledges the support of a CSIRO postdoctoral Fellowship.

An Unprecedented Bis(carbyne) Cluster Rearrangement Involving Simultaneous Coupling and Decoupling of Carbyne Fragments: A New Homogeneous Model for C–C Bond Forming and Bond Breaking on Surfaces [*J. Am. Chem. Soc.* **1983**, *105*, 1384–1386]. NEIL T. ALLISON, JOHN R. FRITCH, K. PETER C. VOLLHARDT,* and ERIC WALBORSKY.

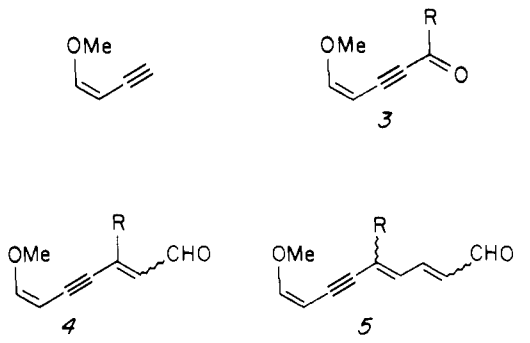
The following acknowledgment should have appeared on p 1386.

Acknowledgement. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC-03-76SF00098, and in part by NSF (CHE 82-00049). K.P.C.V. is a Camille and Henry Dreyfus Teacher–Scholar (1978–83).

Bacteriorhodopsins Containing Cyanine Dye Chromophores. Support for the External Point-Charge Model [*J. Am. Chem. Soc.* **1983**, *105*, 646–648]. F. DERGUINI, C. G. CALDWELL, M. G. MOTTO, V. BALOGH-NAIR, and K. NAKANISHI*.

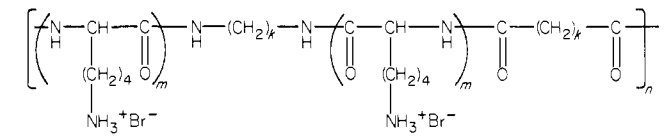
Scheme I: The stereochemistry of the 1-methoxy-1-buten-3-yne was inadvertently designated as *E*. The correct configuration of this compound and the enol ether moiety of intermediates **3–5** is *Z*. The structures for Scheme I should be as shown below. We are grateful to Dr. Heinz Gschwend of CIBA-GEIGY for bringing this to our attention.

Scheme I



New Model for the Interior of Polyelectrolyte Coatings on Electrode Surfaces. Mechanisms of Charge Transport through Protonated Poly(L-lysine) Films Containing $Fe^{III}(edta)^-$ and $Fe^{II}(edta)^{2-}$ as Counterions [*J. Am. Chem. Soc.* **1983**, *105*, 1096]. FRED C. ANSON,* JEAN-MICHEL SAVEANT, and KIYOTAKA SHIGEHARA.

The electrode coating material identified as poly-L-lysine, PLL, has been found instead to be a derivative of PLL. Authentic samples of PLL (Sigma Chemical Co.) produce coatings that are less effective at binding anions. The coating material actually employed (of which too little remains for precise characterization) is believed to be a block copolymer of polylysine with the following structure:



$k = 6$–10; $m = 20$–50; $n \sim 100$

A newly synthesized sample of such a copolymer with $k = 6$, $m = 50$, $n \sim 100$ produces coatings with properties quite similar to those reported in the published paper. This regrettable misidentification of the original coating material does not affect any of the discussion or conclusions contained in the paper.

Page 1101, Table II: The first two entries in the column headed i_k should be 0.31 and 0.53 instead of 0.031 and 0.053.