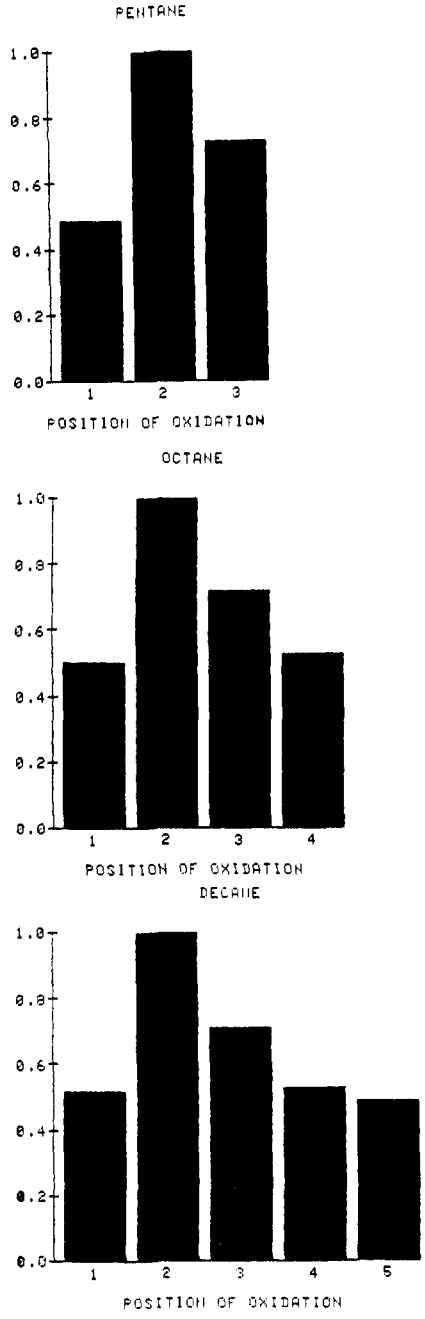

Figure 2. Regioselectivities along the chain of *n*-pentane, *n*-octane, and *n*-decane normalized for the relative number of hydrogens at each chain position (with activity at the 2-position normalized to 1.0).

oxidant by forcing such an oxidant to operate in a shape-selective environment.[13] We believe the substrate selectivity observed is a consequence of the sorption selectivity of the 5A zeolite while the ω oxidation selectivity arises from the very close fit of alkane to pore size which essentially constrains it to have an extended "linear" conformation. Thus the methyl end groups are the first to encounter (and so be oxidized by) the iron active sites in the six-ring faces of the zeolite supercages.

The overall activity of the 5A zeolite system is lower than the control, with 30% yield based on iron in this batchwise experiment. However, a recovered, calcined, and dried catalyst can be reused with the same initial activity as virgin material. We believe that a combination of organic oxidation products and the water by-product of the H_2/O_2 reaction fills the zeolite interior and eventually stops access of further hydrocarbon substrate to the active sites. It should be noted that, on the basis of the pressure drop during the course of the reaction, more than 95% of the H_2/O_2 mixture consumed gives water rather than oxidized organics.

This completely inorganic system demonstrates a remarkable similarity to the natural monoxygenase enzymes in that (1) it will take molecular oxygen at room temperature in the presence of a reducing agent and perform partial oxidation on an unactivated alkane and (2) such oxidations can be made to exhibit tremendous substrate selectivity combined with a regioselectivity reminiscent of the ω-hydroxylases. Preliminary results with other zeolite hosts (e.g., ZSM-5) have already demonstrated that if the pore system is larger, then products can be completely removed without zeolite dissolution. However, in such cases the selectivities are reduced. Finally, we note that the oxidation of aromatic substrates with identical systems is much more efficient, giving up to 30 catalytic turnovers based on iron with good substrate selectivities and regioselectivities. Full details of such studies will be reported in a future publication.

Acknowledgment. The excellent technical assistance of J. B. Jensen and J. M. Williams is appreciated as are discussions with Prof. G. D. Stucky, Dr. M. J. Nappa, and Dr. L. W. Gosser. We wish to thank K. S. Suslick for communication of his results with porphyrin systems prior to their publication.

(13) This concept has previously been demonstrated for severely hindered porphyrin systems: Nappa, M. J.; Tolman, C. A. *Inorg. Chem.* **1985**, *24*, 4711. Suslick, K.; Cook, B.; Fox, M. *J. Chem. Soc., Chem. Commun.* **1985**, 580. In micellar media: Sorokin, A. B.; Khenkin, A. M.; Marakushev, S. A.; Shilov, A. E.; Shteinman, A. A. *Dokl. Akad. Nauk SSSR* **1984**, *279*, 939.

Absolute Stereochemical Control in Allylic Oxidation via Ene Reactions of *N*-Sulfinylcarbamates

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The ene reaction of the *N*-sulfinylcarbamate of *trans*-2-phenylcyclohexanol[2,3] with simple *cis*-alkenes proceeds to form allylic sulfinamides with high levels of both absolute stereochemical as well as regiochemical control. In turn, these products can be readily converted to allylic alcohols. Overall, these two processes represent a net allylic oxidation with retention of double-bond regiochemistry that is effected with reagent-based control of absolute stereochemistry.

Over the past 15 years, Kresze[1] has studied extensively the thermal ene reactions of *N*-sulfinylcarbamates, from which it can be concluded that, in general, the regiochemical outcome can be predicted based upon a concerted transition-state model that is quite productlike. Thus, the major product from the reaction with unsymmetrical alkenes is that with the more highly substituted double bond. Our initial attempts to impose the absolute stereochemical bias[2] of chiral auxiliaries in thermal ene reactions with the *N*-sulfinylcarbamate of phenylcyclohexanol (**1**)[3,4] led to only modest levels of control. In contrast, reaction of **1** with a number of alkenes in the presence of slightly more than 1 molar equiv of tin tetrachloride[5] led to adducts with practical levels of

(1) For leading references, see: Muensterer, H.; Kresze, G.; Lamm, V.; Gieren, A. *J. Org. Chem.* **1983**, *48*, 2833. Schwobel, A.; Kresze, G. *Synthesis* **1984**, 945.

(2) High levels of asymmetric induction have also been observed in the cycloaddition of *N*-sulfinylcarbamates with dienes. See: Whitesell, J. K.; James, D.; Carpenter, J. F. *J. Chem. Soc., Chem. Commun.* **1985**, 1449.

(3) Whitesell, J. K.; Lawrence, R. M. *Chimia* **1986**, *40*, 318.

(4) Whitesell, J. K.; Chen, H.-H.; Lawrence, R. M. *J. Org. Chem.* **1985**, *50*, 4663.

(5) We have also found that levels of asymmetric induction are increased dramatically by tin tetrachloride in the ene reactions of chiral glyoxylates[6] and in the cycloaddition reactions of *N*-sulfinylcarbamates with dienes.[2]

(6) Whitesell, J. K.; Bhattacharya, A.; Buchanan, C. M.; Chen H.-H.; Deyo, D.; James, D.; Liu, C.-L.; Minton, M. A. *Tetrahedron, Symp. Print* **1986**, *42*, 2993.

(7) Bussas, R.; Muensterer, H.; Kresze, G. *J. Org. Chem.* **1983**, *48*, 2828.

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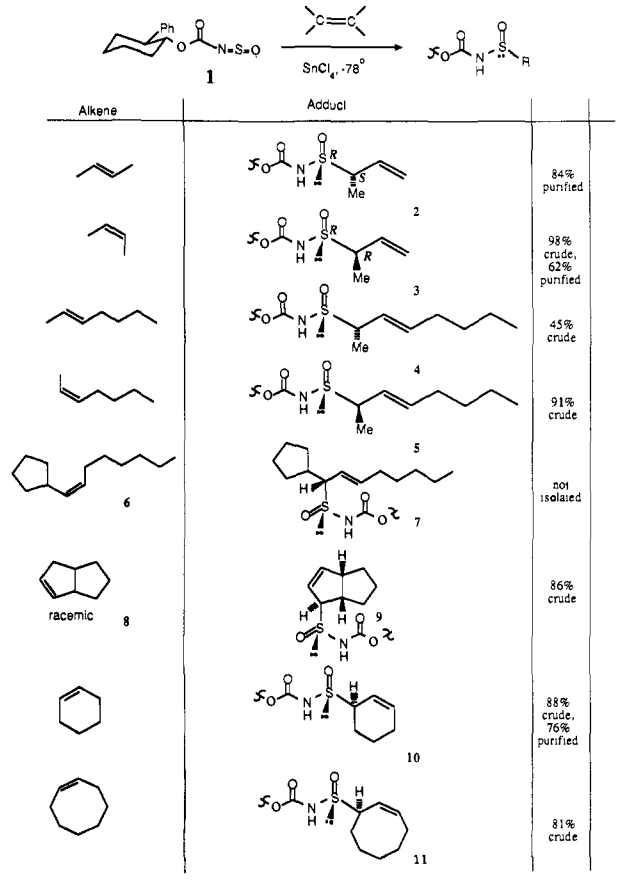
Table I

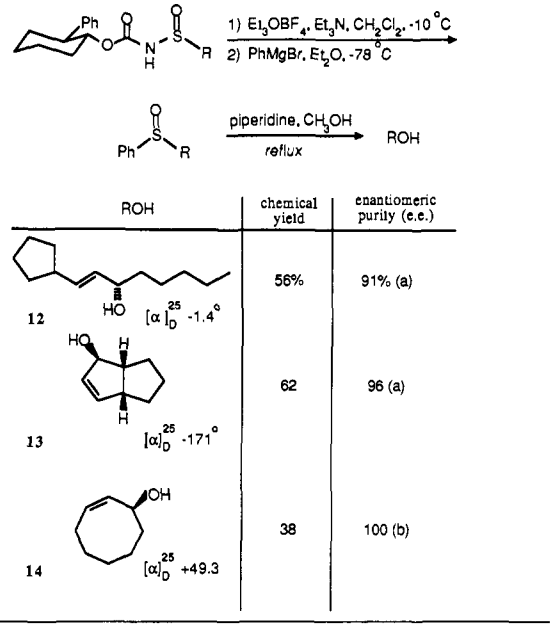


asymmetric induction both at carbon and at sulfur (Table I). Thus, the reaction of **1** with *trans*-2-butene at −78 °C for 20 min afforded the crystalline adduct **2** in 84% yield with no detectable (^{13}C NMR) contamination by other diastereomers. The absolute and relative stereochemical relationships in **2** were rigorously established by a single-crystal, X-ray analysis.[8] The reaction of **1** with *cis*-2-butene provided a different adduct (**3**). The sense of the optical rotation for **2** and **3** was the same, and since the rotation would be expected to be dominated by sulfinyl moiety,[7] we have assigned the stereochemistry for **3** the same as **2** at sulfur but opposite at carbon (see also, below).

With the unsymmetrical alkenes *cis*- and *trans*-2-octene, only the adducts resulting from carbon–carbon bond formation at C2 of the alkene were observed. While both cis and trans geometric isomers resulted from the reaction with the *trans*-alkene, only the trans isomer **5** was observed from the reaction with *cis*-2-octene. These observations are consistent with a productlike, concerted transition state where formation of the cis product from the cis starting material would involve serious steric interactions and where a high preference is expressed for the more stable double bond. Indeed, the reaction of **1** with the alkene **6** afforded the regioisomer shown (**7**), and none of the adduct with the exocyclic double bond was detected. It is important to note that we are at this point providing a model only for predictive purposes.[9]

The transition state requirements for this ene reaction imposed by the chiral auxiliary can be combined with the face selectivity of a chiral alkene such as **8** to effect a kinetic resolution of the latter.[10] Thus, reaction of **1** with **8** in a 1:3.5 molar ratio afforded

Table II



[a] Based on analysis of derived mandelic acid ester derivatives (see ref 11). [b] Based on method *a* as well as optical rotation (lit $[\alpha]_D$ 48.0, ref 12).

an 86% crude yield of two, diastereomeric adducts in a 7.3:1 ratio from which the major isomer **9** could be obtained in pure form by crystallization. The stereochemical relationships in this adduct where determined unambiguously by single-crystal, X-ray analysis[8] and are the same as would be predicted on the basis of those assumed above for the adduct from *cis*-2-butene.

On standing at room temperature, the noncrystalline adducts underwent stereorandomization, presumably either by consecutive retro ene, thermal ene reactions or by consecutive 2,3-rearrangements. Unfortunately, conditions could not be found that would intercept the intermediate species from the latter process by cleavage of the oxygen–sulfur bond to form allylic alcohols in useful yields. On the other hand, N-ethylation of the adducts (Et_3OBF_4, *i*-Pr_2NEt, CH_2Cl_2, −10 °C) followed by treatment with phenyl magnesium bromide (3 equiv, Et_2O, −78 °C) afforded allylic sulfoxides that readily underwent sequential sulfoxide–sulfenate rearrangement and cleavage (piperidine, MeOH, reflux). The transfer of the asymmetry induced in the ene reaction at the carbon bearing sulfur to that bearing oxygen in the final allylic alcohol was demonstrated in the conversion of the adducts **7**, **9**, and **11** to allylic alcohols with enantiomeric excesses of 91%, 96%, and 100%[11] (Table II).

The combination of the ene reaction of **1** followed by sulfoxide formation and rearrangement constitutes a method for allylic oxidation of simple, unactivated alkenes that has the same general features as oxidation with selenium dioxide. The high levels of stereochemical (both configurational and geometric) as well as regiochemical control observed in the reactions with unsymmetrical, 1,2-disubstituted *cis*-alkenes now provide the opportunity for the synthesis of allylic alcohols from alkenes with retention of the regioposition of the original double bond and, more importantly, with reagent-based control of absolute stereochemistry.

Acknowledgment. The research efforts that led to these results have been generously supported by the National Institutes of Health (GM-31750) and the Robert A. Welch Foundation (F-626).

Supplementary Material Available: Complete experimental details for all transformations (16 pages). Ordering information is given on any current masthead page.

(8) We are grateful to Dr. Steve Larson and Dr. Vincet Lynch (Department of Chemistry, University of Texas at Austin, Austin, TX 78712) for these structure determinations. Full details of the analyses will be reported elsewhere.

(9) We do not yet have a suitable rationalization for the role that the Lewis acid plays in increasing the level of asymmetric induction.

(10) We have previously reported on kinetic resolution in the similar ene reaction of a chiral glyoxylate with **8**. See: Whitesell, J. K.; Allen, D. A. *J. Org. Chem.* **1985**, *50*, 3025.

(11) Determined by our previously reported method. See: Whitesell, J. K.; Reynolds, D. *J. Org. Chem.* **1983**, *48*, 3548.

(12) Luche, J. L.; Damiano, J. C.; Crabbé, P. *J. Chem. Res. (S)* **1977**, 32.