this would lead to $\Delta(\Delta G^{\ddagger}_N)$ = 3.4 kcal/mol, because we already decided $\Delta(\Delta G^{\ddagger}_e)$ for **2** was about 0.5. This gives $\Delta G^{\ddagger}_N$ for **2**(Me) of 7.1–3.4 = 3.7 kcal/mol. This number is not unreasonable. Assuming proportionally of $\Delta G^{\ddagger}_N$ for chloramines and methylamines seems to work as far as it can be tested. For **3**(Me) assuming proportionality gives $\Delta G^{\ddagger}_N$ = 5.3; the number from NMR measurement is 5.5 kcal/mol. A similar estimate for **2**(Me) is $\Delta G^{\ddagger}_N[\mathbf{2}(Me)] = \Delta G^{\ddagger}_N[\mathbf{4}(Me)]\Delta G^{\ddagger}_N[\mathbf{2}(Cl)]/\Delta G^{\ddagger}_N[\mathbf{4}(Cl)]$ = 4.1 kcal/mol. Use of the $\Delta(\Delta E_p)$ values as if they were $\Delta(\Delta G^{\circ}_e)$ values does not lead to ridiculous estimates of $\Delta G^{\ddagger}_N$ values, and $\Delta(\Delta E_p)$ values seem unlikely to be much more than 0.5 kcal/mol away from the $\Delta(\Delta G^{\circ}_e)$ values. Mixing irreversible with reversible oxidation potentials in a single correlation should certainly be avoided, of course.

Nitrogen Inversion Barriers for 1(Cl) and 2(Cl). We have emphasized the assertion that the steric effects of R group size on ΔG°_e should be mirrored in $\Delta G^{\ddagger}_N$ and, hence, factored out. It should be pointed out that electronic effects of changing R groups may well also influence $\Delta G^{\ddagger}_N$. We will not indulge in a general discussion but merely point out a result we did not expect. We found **1**(Cl) to have a 0.5 kcal/mol lower barrier than **2**(Cl)[2] at −95 °C (T_c in both cases), a difference outside of what we believe our experimental error is. This difference also shows up in $\Delta(\Delta G^{\circ}_e)$, a fact of ambiguous significance. Going from 2-methyl-2-azabicyclo[2.2.2]octane [$\Delta G^{\ddagger}_N$ (−127 °C) = 6.51 (7) kcal/mol] to 1,2-dimethyl-2-azabicyclo[2.2.2]octane [$G^{\ddagger}_N$ (−127 °C) = 6.68 (8) kcal/mol] increases the barrier slightly,[5] so we had expected **2**(Cl) to have a higher barrier than **1**(Cl). We are unable to quantitatively assess the strain energy differences in either ground or transition state for replacing NCH_3 by NCl. It seems conceivable to us that the origin of the reversal C_1-methylation effect on $\Delta G^{\ddagger}_N$ in methylamines and chloramines is not steric but electronic. As we have no way of proceeding to a separation of steric and electronic effects here, we must leave the observation as an unexplained one.

Conclusions

For bicyclic R_2NX derivatives **1**–**4**, when X is Cl, N=]$_2$, or O·, so steric interactions are not increased upon electron removal, $E^{\circ\prime}$ increases in the order **1**(X) < **2**(X) < **3**(X) < **4**(X). The difference in $E^{\circ\prime}$, displayed as $\Delta(\Delta G^{\circ}_e)$ in Figure 1, increases as $\Delta G^{\ddagger}_N$ increases. These data show that 2-tetrazenes have significantly higher $\Delta G^{\ddagger}_N$ values than nitroxides. For the methylamines, E_p^{ox} changes are in the same order, and E_p^{ox} is between $\Delta(\Delta G^{\circ}_e)$ for chloramines and for 2-tetrazenes, as are the $\Delta G^{\ddagger}_N$ values of methylamines.

Quantitative consideration of the changes in $E^{\circ\prime}$ led to three conclusions. First, $\Delta G^{\ddagger}_N$ for **4**(O·) and the other nitroxides is very small, in agreement with the conclusions of Rassat and co-workers. Second, $\Delta G^{\ddagger}_N$ for **4**(N=]$_2$) is estimated to be about 5 kcal/mol. Third, the smaller $\Delta(\Delta G^{\circ}_e)$ than $\Delta(\Delta G^{\ddagger}_N)$ for **1**(Cl) and **2**(Cl) was suggested as being reasonable if **4**(Cl)$^{+\cdot}$ is significantly bent. The latter two conclusions are at present entirely unsupported by any other sort of experimental data. Both are, however, testable in principle. If the **4**(N=]$_2$) $\Delta G^{\ddagger}_N$ is really 5 kcal/mol, tetrazenes with a more restricted CNC angle will have $\Delta G^{\ddagger}_N$ in the range measurable by ^{13}C NMR. If **4**(Cl)$^{+\cdot}$ is bent, this might reasonably be expected to affect its spectral properties. Experiments designed to test both of these conclusions are in progress. If it can be established that this procedure has experimental validity, electrochemical measurements can definitely contribute to the understanding of how alkyl group structural changes affect nitrogen inversion rates in conjugated amines, where the barriers are too low to detect by dynamic NMR.

Experimental Section

2-Chloro-1,3,3-trimethyl-2-azabicyclo[2.2.2]octane [**1**(Cl)] was prepared by stirring 1.24 g of amine **9** with 21.7 mL of 5.25% hypochlorite solution (Chlorox) in 13 mL of ether at 0 °C for 1 h, extracting with ether, drying, and concentrating to give **1**(Cl) as an oil. Purification was by Kugelrohr distillation: ^1H NMR δ 1.3 (s, 3 H), 1.5 (s), 1.4–2.3 (complex); ^{13}C NMR ($CDCl_3$) δ 64.20 (C_3), 59.61 (C_1), 37.09 (C_4), 30.44 ($C_{6,7}$), 27.92 (C_3CH_3), 27.43 (C_1CH_3), 22.24 ($C_{5,8}$); ^{13}C NMR (1:1 $CD_2Cl_2CF_2Cl_2$) −127 °C δ 65.76 (C_3), 60.96 (C_1), 38.37 (C_4), 36.27 and 27.39 (C_6 and C_7), 28.83 (C_1CH_3), 28.52 (C_3CH_3), 23.48 ($C_{5,8}$); high-resolution mass spectral peak match for $C_{10}H_{18}ClN$.

9-Chloro-9-azabicyclo[3.3.1]nonane [**4**(Cl)] was prepared as previously described:[1] ^{13}C NMR ($CDCl_3$) +54 °C δ 59.96 (C_1), 28.53 (C_2), 19.93 (C_3); ^{13}C NMR ($CDCl_3$) −17 °C δ 59.69 (C_1), 33.58, 23.08 (C_2 and C_6), 20.14 and 19.51 (C_3 and C_7).

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Registry No. 1 (X = Cl), 85029-16-9; **2** (X = O·), 38058-47-8; **2** (X = Me), 85029-17-0; **3** (X = Cl), 5697-97-2; **3** (X = Me), 55100-40-8; **4** (X = Me), 491-25-8; **4** (X = Cl), 73322-95-9.

Chemistry of Oxaziridines. 4.[1] Asymmetric Epoxidation of Unfunctionalized Alkenes Using Chiral 2-Sulfonyloxaziridines: Evidence for a Planar Transition State Geometry

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Abstract: Diastereomeric 2-sulfonyloxaziridines (−)-(*S,S*)-**1** and (+)-(*R,R*)-**2** epoxidize unfunctionalized olefins **3a–g**, affording epoxides **4a–g** with better enantioselectivity than do chiral peracids or hydroperoxides. The configuration of the oxaziridine three-membered ring controls the stereochemistry of the product. The mechanism of chiral recognition is largely determined by steric factors where the orientations of the oxaziridine three-membered ring and the alkene are planar in the transition state.

The fundamental factors that control asymmetric induction remain unclear despite impressive recent achievements in the asymmetric formation of C–C and C–H bonds.[2,3] This is particularly true for the asymmetric oxidation of unfunctionalized

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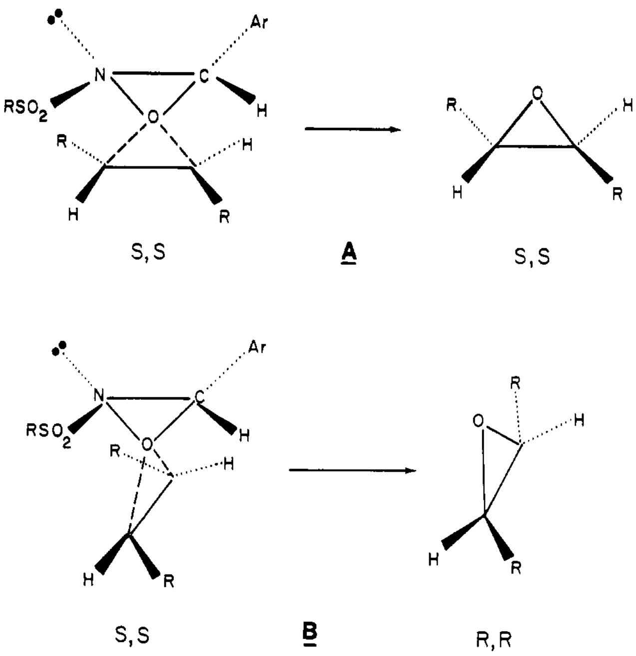
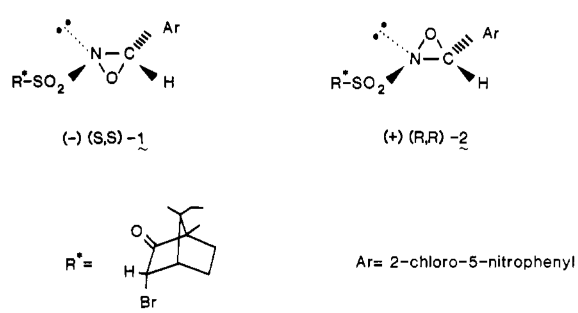


Figure 1.

substrates.[4] In these oxidations, using chiral peracids or hydroperoxides, the asymmetric bias is quite low (0–8% enantiomeric excess), with the structure of chiral oxidant and substrate having little influence on the enantioselectivity.[5-8]

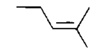
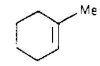
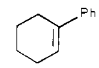
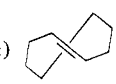
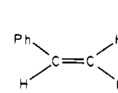
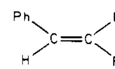
Recently, we described the synthesis of a new class of optically active oxidizing reagents, chiral 2-sulfonyloxaziridine diastereomers (−)-(*S*,*S*)-**1** and (+)-(*R*,*R*)-**2**, where *S*,*S* and *R*,*R* refer to con-



figurations of the oxaziridine three-membered rings.[1] These compounds afford 5–8 times the enantioselectivity of chiral peracids for the asymmetric oxidation of sulfides to sulfoxides.

(1) Davis, F. A.; Jenkins, R. H., Jr.; Awad, S. B.; Stringer, O. D.; Watson, W. H.; Galloy, J. *J. Am. Chem. Soc.* **1982**, *104*, 5412.
(2) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; American Chemical Society: Washington, DC, 1976.
(3) For recent reviews on asymmetric synthesis see: (a) Apsimon, J. W.; Seguin, R. P. *Tetrahedron* **1979**, *35*, 3797. (b) Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1979**, *10*, 1975. (c) Valentine, D., Jr.; Scott J. W. *Synthesis* **1978**, 329. (d) Meyers, A. I. *Acc. Chem. Res.* **1978**, *11*, 375.
(4) The efficient asymmetric epoxidation of functionalized olefins i.e., allylic alcohols, in greater than 95% enantiomeric excess has been described: Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5976. Rossiter, B. E.; Katsuki, T.; Sharpless, K. B. *Ibid.* **1981**, *103*, 464.
(5) Epoxidation of unfunctionalized olefins by chiral hydroperoxides: (a) Rebek, J., Jr.; Wolf, S.; Mossman, A. *J. Org. Chem.* **1978**, *43*, 180. (b) Rebek, J., Jr.; McCready, R. *J. Am. Chem. Soc.* **1980**, *102*, 5602.
(6) Epoxidation of olefins by chiral peracids: (a) Pirkle, W.; Rinaldi, R. *J. Org. Chem.* **1977**, *42*, 2020. (b) Montanari, F.; Moreti, I.; Torre, G. *Chem. Commun.* **1969**, *135* and references cited therein.
(7) Oxidation of achiral sulfides sulfoxides by chiral peracids: (a) Folli, U.; Iarossi, D.; Montanari, F.; Torre, G. *J. Chem. Soc. C* **1968**, 1317. (b) Mislow, K.; Green, M. M.; Laur, P.; Melillo, J. T.; Ternary, H. L., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 1958. (c) Mislow, K.; Green, M. M.; Raban, M. *Ibid.* **1965**, *87*, 2761.
(8) A chiral peroxymolybdenum(VI) complex asymmetrically epoxidizes unfunctionalized olefins with an enantiomeric excess in one case of 35% enantiomeric excess (trans-2-butene) (Kagan, H. B.; Mimoun, H.; Mark, C.; Schurig, V. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 485).

Table I. Asymmetric Epoxidation of Olefins Using Chiral 2-Sulfonyloxaziridines (−)-(*S*,*S*)-**1** and (+)-(*R*,*R*)-**2** at 60 °C in $CHCl_3$

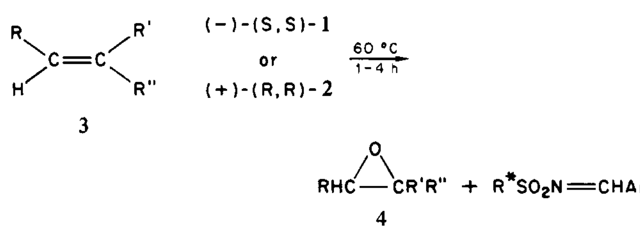
		epoxide (4a-g)		
oxaziridine[a]	olefin	% yield[b]	configuration	% ee
(−)-(*S*,*S*)-**1** (+)-(*R*,*R*)-**2**	 (3a)	35 30	(+), *S* (−), *R*	17.5[c] 17.5
(−)-(*S*,*S*)-**1** (+)-(*R*,*R*)-**2**	 (3b)	58 60	(+), 1*S*,2*R* (−), 1*R*,2*S*	12.7[d] 11.8
(+)-(*R*,*R*)-**2**	 (3c)	70	(+), 1*R*,2*R*	40.0[e]
(−)-(*S*,*S*)-**1** (+)-(*R*,*R*)-**2**	(±)  (3d)	32 37	(+), 1*S*,8*S* (−), 1*R*,8*R*	14.7[f] 13.9
(−)-(*S*,*S*)-**1** (+)-(*R*,*R*)-**2**	$PhCH{=}CH_2$ (3e)	50 57 43[h]	(−), *S* (+), *R* (+), *R*	15.8[g] 15.9 15.7
(−)-(*S*,*S*)-**1** (+)-(*R*,*R*)-**2**	 (3f)	81 80	(−), *S*,*S* (+), *R*,*R*	26.8[i] 27.7
(−)-(*S*,*S*)-**1** (+)-(*R*,*R*)-**2**	 (3g)	66 86 62[h]	(−), *S*,*S* (+), *R*,*R* (+), *R*,*R*	30.3[g] 34.9 31.5

[a] Oxaziridines were greater than 95% optically pure. [b] Isolated yields by TLC or gas chromatography. [c] Gunther, B.; Kirmze, W. *Liebigs Ann. Chem.* **1980**, 518. [d] Kazulide, T.; Masayoshi, H.; Sei, O. *Tetrahedron Lett.* **1979**, 3017. [e] Berti, G.; Macchia, B.; Macchi, F.; Monti, L. *J. Org. Chem.* **1968**, *33*, 4045. [f] See ref 11. [g] Berti, G.; Bottari, F.; Ferrarini, P. L.; Machia, B. *J. Org. Chem.* **1965**, *30*, 4091. [h] Benzene solvent. [i] Audier, H. E.; Dupin, J. F.; Jullien, J. *Bull. Soc. Chim. Fr.* **1966**, 2811.

Futhermore, the configuration of the oxaziridine three-membered ring is shown to control the stereochemistry of the product, which can be predicted by using steric arguments. The success of (−)-**1** and (+)-**2** is attributed to the fact that the active site is incorporated into a rigid three-membered ring one bond removed from the C and N chiral centers.

We now report that asymmetric epoxidations of unfunctionalized alkenes using (−)-**1** and (+)-**2** result in better optical yields than when chiral peracids or hydroperoxides are used. Furthermore, the mechanism of chiral recognition can be considered as involving a planar transition state geometry as depicted in A (Figure 1).

2-Sulfonyloxaziridines, like peracids, epoxidize alkenes in a synstereospecific manner in good to excellent yields.[9] Thus, heating 2 equiv of **3a–g** with (−)-(*S*,*S*)-**1** or (+)-(*R*,*R*)-**2** at 60



a, R = Et; R′ = R″ = Me
b, R,R′ = $-(CH_2)_4-$; R″ = Me
c, R,R′ = $-(CH_2)_4-$; R″ = Ph
d, R′ = H; R,R″ = $-(CH_2)_6-$
e, R = Ph; R′ = R″ = H
f, R = Ph; R′ = H, R″ = Me
g, R = R″ = Ph; R′ = H

°C for 1–4 h affords the corresponding optically active epoxides **4a–g** in 50–80% yield. Products were isolated by preparative TLC (silica gel) and/or gas chromatography. Optical yields were determined by the chiral shift method and by comparison of optical rotations with values reported in the literature. Agreement be-

(9) Davis, F. A.; Abdul-Malik, N. F.; Awad, S. B.; Harakal, M. E. *Tetrahedron Lett.* **1981**, *917*.
(10) Bach, R. D.; Mazur, U.; Hamama, I.; Lauderback, S. K. *Tetrahedron* **1963**, *23*, 1955.

tween the three methods was excellent. These results are summarized in Table I.

The asymmetric induction for oxygen transfer from diastereomers (−)-**1** and (+)-**2** is typically 2–5 times greater, 50 times in the case of **3c**,[11] than similar oxidations using chiral peracids[6] or hydroperoxides.[5] As observed for the asymmetric oxidation of sulfides by (−)-**1** and (+)-**2**,[1] the absolute configuration of the oxaziridine three-membered ring controls the stereochemistry of the product; i.e., (−)-(*S*,*S*)-**1** and (+)-(*R*,*R*)-**2** give epoxides of opposite stereochemistry (Table I).

A knowledge of the transition geometry is essential to developing reliable theories of asymmetric induction as well as in preparating more efficient reagents.[1-3] For epoxidations by peracids, two extreme geometries, illustrated in Figure 1 for 2-sulfonyloxaziridines, can be considered. Transition state A has planar geometry where the groups attached to the C–C bond eclipse the groups attached to the oxaziridine three-membered ring.[12] Transition state B has spiro geometry where the planes defined by the olefin and oxaziridine are oriented at right angles to one another. Molecular orbital calculations of the alkene–peracid's epoxidation mechanism have favored transition state A.[13,14]

Sharpless has proposed that the geometry of the transition state for oxygen transfer will be such that the plane defined by the peracid is oriented so that one of the nonbonded electron pairs on oxygen lies in the plane of the alkene π-bond.[14] This is closer to B than to A (Figure 1). Epoxidations by peracids and related reagents have been interpreted in terms of these ideas.[5a-b,14-16] To date, however, there is not unambiguous way of assigning the transition state geometries for alkene epoxidation.

For oxygen transfer from 2-sulfonyloxaziridines, however, it is possible to distinguish between transition states A and B using diastereomeric oxaziridines (−)-(*S*,*S*)-**1** and (+)-(*R*,*R*)-**2**. The reasonable assumption is made that the chiral recognition is largely controlled by minimizing nonbonded interactions in the transition state. Consequently, if the geometry is planar, A, attack by oxazirdine (−)-(*S*,*S*)-**1** is favored to occur on the *si*- and *si*,*si*-enantiotopic faces of the C–C double bond to give epoxides having the *S* and *S*,*S* configurations. Conversely, if the transition state is spiro, *B*, (−)-(*S*,*S*)-**1** will afford epoxides having the *R* and *R*,*R* configurations.

On the basis of Drieding models one cannot readily distniguish which transition state, *A* or *B*, is favored. However, if one chooses the planar orientation A, as predicted by molecular orbital calculations,[17] then the expected experimentally observed epoxide configuration may be correctly predicted on the basis of steric considerations. Thus (−)-(*S*,*S*)-**1** gave epoxides having the *S* and *S*,*S* configurations with alkenes **3a** and **3c–g**, while (+)-(*R*,*R*)-**2** affords epoxides with the opposite stereochemistry (Table I). The single exception is the trisubstituted alkene, 1-methylcyclohexene (**3b**). In this case the differences in steric bulk of the groups attached to the C–C double bond are minimal, and it is difficult to estimate the relative sizes of the various groups.

The increase in asymmetric induction for olefin series **3e–g** can also be explained in terms of the planar transition state A. In this series the trans groups attached to the C–C double bond are increasing in steric bulk. Thus, attack of the oxaziridine on the face of the C–C bond where these groups are eclipsed with the oxaziridine C–H and H–lone pair is increasingly favored. Note that replacement of the methyl group in **3b** by a larger phenyl group, **3c**, results in a significant increase in the asymmetric induction (11.8–39.0% enantiomeric excess).

Molecular oribtal calculations on the oxazirdine–alkene epoxidation mechanism suggests that the planar transition state geometry A is only slightly favored over their spiro geometry B.[17] The difference in energy is 3 kcal/mol (STO-3G/4-31G). The transition state is achieved by interaction of the alkene-π system with both filled and empty Walsh-type orbitals on the oxaziridine. This reaction bears a striking resemblence to the peracid epoxidations, which are believed to involve an S_N2-type displacement by the nucleophilic alkene on the O–O bond of the peracid.[12-14,18]

It was also noted from these calculations[17] that the epoxidation transition state occurs earlier along the reaction pathway for orientation A than for B, leading to reduced steric interactions. Since electronic effects appear to dictate a planar orientation with model compounds, we conclude that steric interactions will play a dominant role in deciding the topology of the transition state. We emphasize that the increased enantioselectivity exhibited by these reagents is a manifestation of the closer proximity of the oxaziridine substituents to the active site in comparison to peracids and hydroperoxides.

In summary, chiral 2-sulfonyloxaziridines give the best results to date for the asymmetric epoxidation of unfunctionalized alkenes. Significantly, these reagents have provided the first unambiguous experimental evidence that specifically addresses the geometry or orientation in the transition state for alkene epoxidation. For epoxidations using these reagents the geometry of the transition state can be considered as planar, with steric factors reponsible for the chiral recognition.

Experimental Section

Melting points were determined on the Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were measured on Varian A-60A and Jeol FX-90Q NMR spectrometers. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Solvents were purified by standard methods. Diastereomeric oxaziridines **1** and **2** were prepared as previously described[1] and were greater than 95% enantiomeric excess. Alkenes were purchased from Aldrich Chemical Co. An HP Model 5750 research chromatograph TCD detector was used in the isolations by preparative GLC.

General Procedure for Alkene Asymmetric Epoxidations. In a 10-mL round-bottom flask equipped with magnetic stirring bar and nitrogen inlet was placed 1.62 mmol of the appropriate alkene, **3a–g**, in 5 mL of chloroform or benzene. To the reaction mixture was added 400 mg (0.81 mmol) of (−)-(*S*,*S*)-2-(*d*-α-bromo-π-camphorsulfonyl)-3-(2-chloro-5-nitrophenyl)oxaziridine (**1**) or (+)-(*R*,*R*)-2-(*d*-α-bromo-π-camphorsulfonyl)-3-(2-chloro-5-nitrophenyl)oxaziridine (**2**) and the reaction mixture was heated in a thermostated oil bath with stirring for 1–4 h at 60 °C. The reaction time was predetermined by monitoring the disappearance of the oxazirdine 3-proton at 6.0 ppm by NMR. Solvent was removed under vacuum (rotator evaporator) and the residue washed with *n*-pentane (4 × 20 mL) to afford the epoxides free of the sulfonimine. Epoxides **4e–g** were isolated by preparative TLC (silica gel G), eluting with ether/*n*-pentane (1:9). The other epoxides were isolated by preparative gas chromatography as follows: **4a**, 0.25 in. × 12 ft 5% Carbowax 80/100 mesh Chromosorb, isothermal at 65 °C; **4b**, 0.25 in. × 6 ft 3% OV-17 80–100 mesh Supelcoport, isothermal at 65 °C; **4d**, 0.25 in. × 12 ft 10% FFAP on 80/100 mesh Supelcoport, isothermal at 160 °C.

1,2-Epoxy-1-phenylcyclohexane (4c). The thermal and acid sensitivity of **4c** precluded its isolation by GLC or TLC. This epoxide was obtained by heating 80 mg (0.5 mmol) of **3c** and 250 mg (0.5 mmol) of (+)-(*R*,*R*)-**2** in 5 mL of chloroform for 1 h at 60 °C. After removal of solvent the residue was washed with *n*-pentane (3 × 20 mL). Evaporation of the *n*-pentane washing afford 62 mg (70%) of pure 1,2-epoxy-1-phenylcyclohexane (**4c**).

General Procedure for Determining Optical Purities of Epoxides. Optical yields were ascertained by comparing the optical rotations of epoxides **4a–g**, obtained as describe above, with those reported in the

(11) This "butterfly" transition state was originally proposed by Bartlett, P. D. *Rec. Chem. Prog.* **1950**, *11*, 47.

(12) Bach, R. D.; Willis, C. L.; Domagala, J. M. In "Applications of Molecular Orbital Theory in Organic Chemistry"; Cismadia, I. G., Ed.; Elsevier: Amsterdam, 1977; pp 221–229. Lang, T. J.; Wolber, G. J.; Bach, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 3275.

(13) Yonezawa, T.; Kato, H.; Yamamoto, O. *Bull Chem. Soc. Jpn.* **1967**, *40*, 307. Hanzlik, R. P.; Shearer, G. O. *J. Am. Chem. Soc.* **1975**, *97*, 5231. Plesnicar, B.; Taseuki, M.; Azman, A. *Ibid.* **1978**, *100*, 743.

(14) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63.

(15) Chong, A. O.; Sharpless, K. B. *J. Org. Chem.* **1977**, *42*, 1578.

(16) Corey, E. J.; Niwa, H.; Falck, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 1586.

(17) Bach, R. D.; Wolber, G., submitted for publication.

(18) Nucleophilic attack at the oxaziridine oxygen is favored by the electron-attracting *N*-sulfonyl group. This electron-attracting group stabilizes the incipient charge in the transition state for sulfonimine ($RSO_2N{=}CHAr$) displacement and increases the size of the LUMO coefficient on oxygen. Electron-donating substituents on nitrogen will have the opposite effect, increasing the LUMO coefficient nitrogen. Attack at nitrogen in *N*-alkyloxaziridines has been reported.[19]

(19) Hata, Y.; Watanabe, M. *J. Am. Chem. Soc.* **1979**, *101*, 66.

literature (Table I). The optical yields determined in this manner were verified by a series of 90-MHz ^1H NMR spectra ($CDCl_3$) at increasing concentration of the chiral shift reagent tris[3-((heptafluoropropyl)-hydroxymethylene)-*d*-camphorato]europium(III) derivative $Eu(hfc)_3$ or tris[3-((heptafluoropropyl)hydroxymethylene)-*d*-camphorato]praseodymium(III) derivative $Pr(hfc)_3$. When the shift difference of the appropriate absorption was 6-9 Hz, the peak areas were determined by integration. Agreement between the two methods was approximately ±1.0% enantiomeric excess.

All asymmetric oxidations were carried out at least twice and the results averaged (Table I).

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Long-Range Control by Norbornane Frameworks of Cyclopentadienide Reactivity. Stereoselective Capture of Electrophiles by Tricyclo[5.2.1.$0^{2,6}$]deca-3,8-dienyl Anions[1]

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Abstract: The π-facial stereoselectivities exhibited by cyclopentadienide anions **3** and **4** in their reactions with methyl iodide, three geminally dideuterated 1,2-disubstituted ethanes, epichlorohydrin, $Cl(CH_2)_3CD_2I$, 1,4-dibromo-2-isopropylidenebutane, and deuterium oxide were determined. Analysis was achieved by a combination of ^1H and ^2H NMR spectroscopy, Diels-Alder chemistry, and $Eu(fod)_3$ shift studies. Three sets of quantum mechanical calculations were applied to these anions, only the newly developed INDO procedure proving itself uniformly consistent in predicting the observed endo stereoselectivity of **3**. Loss of stereocontrol is experienced by **3** during spirocyclopropanation, a phenomenon attributed to the probable product-like nature of such transition states and the rather unusual ground-state electronic properties of the products. A model for the influence of the added norbornene double bond in **4** is proposed which calls attention to its substantial rate-retarding effect and consequently the late timing of its transition states. Because bond energies are substantially altered at this stage, the electronic features inherent to **4** are not made apparent. Allowance is also made for ion-pairing effects that may be influential in controlling the course of deuteration at −70 °C.

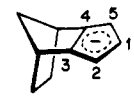
Isodicyclopentadiene (**1**) and its dehydro derivative **2** have been

1

2

the focus of considerable attention as a consequence of the π-facial stereoselecitivity which they exhibit in Diels-Alder cycloadditions.[3-5] The intricate electronic interrelationship which exists between the framework σ electrons and the 1,3-diene π network in these hydrocarbons has generated high theoretical interest in their ground-state structures,[4,5,7,8] particularly their π-bond nonequivalence. Our studies to date in this area have been focused not only on the behavior of the parent systems,[5] but also on a detailed analysis of the consequences of cyclopentadiene ring substitution.[1,9] These more recent developments have removed from serious consideration the proposal[7,10] that stereoselectivity might be governed by the stability of the isomeric adducts, as a consequence of adherence by these systems to the Bell-Evans-Polanyi principle.[11]

The complications introduced by adduct formation are seen not to be present during the capture by anions **3** and **4** of suitable



3

4

electrophilic reagents. For steric reasons, bonding was expected to be directed to the cyclopentadienide center most remote from the bicyclic units to deliver C_s-symmetric products. In these examples, the causative factors which underlie the extent of endo/exo stereoselection must clearly be electronic in nature, since the reaction site in quite distant from the methano and ethano (or etheno) bridges which distinguish the π faces. Consequently, **3**, **4**, and related carbanions offer the potential for providing

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