Diastereoselectivity in the Epoxidation of Substituted Cyclohexenes by Dimethyldioxirane[1,2]

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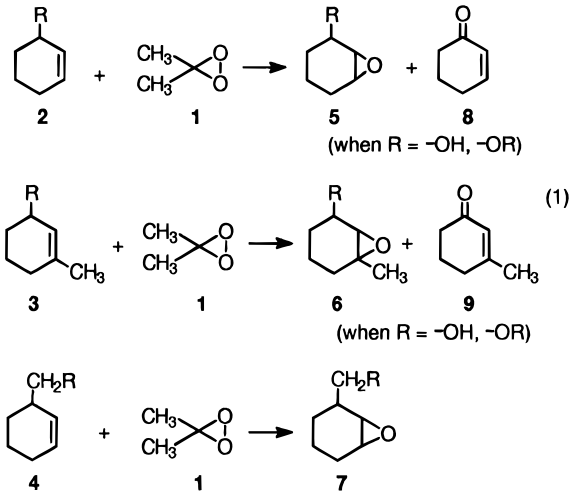
Three series of compounds based on the cyclohexene framework have been epoxidized by dimethyldioxirane. A pronounced dependence of epoxide diastereoselectivity on substituent has been observed. In addition there is a solvent influence on this stereoselectivity. The results have been explained by invoking steric, H-bonding, and dipole−dipole influences on the epoxide stereochemistry.

Introduction

The control of chemo-, regio-, and stereoselective outcomes of chemical reactions has been an ongoing goal of organic chemists.[3] This goal is currently being applied, by ourselves and others, to the reactions of dioxiranes,[4] a class of relatively new and powerful oxidants. This work gains an additional impetus when the reactions of dioxiranes and peracids are compared with respect to these various selectivities. In the work described here we have examined diastereoselectivity and, to a lesser extent, chemoselectivity in the reactions of dimethyldioxirane (**1**) with some cyclohexene derivatives. The observed diastereoselectivities are influenced by a mix of several factors including substituent size, H-bonding effects, dipole−dipole interactions, and solvent effects. A number of reports have appeared on diastereoselectivity in dioxirane reactions[5] and particularly with cyclohexene derivatives[6] and glycals.[7]

Results

We have reacted derivatives of cyclohex-2-en-1-ol (**2a**), 3-methylcyclohex-2-en-1-ol (**3a**), and the homoallylic derivative **4a** of **2a** with dimethyldioxirane **1** to give the corresponding epoxides **5**, **6**, and **7**, respectively (eq 1). In some cases the epoxides were accompanied by the enone insertion products **8** or **9**. All substrates were



oxidized first in acetone solvent. In most cases a number of mixed solvents containing acetone were also used. The results obtained in these reactions for derivatives of **2** are shown in Table 1. The products are the diastereomeric epoxides, with the enone product of a C−H insertion reaction of **1** obtained in some cases. The conversions are generally quite high. With only one exception (**2a** in acetone), when both products of epoxidation and insertion are obtained, the epoxidation product is the major product. The results indicate that epoxide diastereomer ratios are dependent both on the substituent in **2** and the solvent used. The stereochemical assignments were based on NMR chemical shifts and coupling constants and comparison with literature examples. The reaction of one substrate in this series requires an additional comment. Compound **2g** with a benzamido substituent follows the usual course and gives epoxide diastereomers, as disclosed by NMR. In this case, however, the *trans* epoxide isomer is unstable and rearranges when chromatographed to the benzoxazole derivative **10**. The *trans* arrangement of the epoxide and

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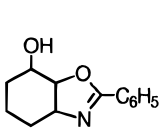
Table 1. Diastereoselectivity in Dimethyldioxirane Epoxidation of Cyclohex-2-en-1-ol Derivatives 2[a]

R in **2**		solvent system	(%)	epoxides (%)[b] trans	cis	epoxides/enone (%)	conversion(%)
OH	(**2a**)	acetone	(100)	54	46	46/54	94
		CH_2Cl_2/acetone	(75:25)	30	70	74/25	100
		CH_2Cl_2/acetone	(90:10)	22	78	84/16	89
		CH_2Cl_2/acetone	(97:3)	18	82	89/11	77
		MeOH/acetone	(90:10)	66	34	75/25	100
		$CHCl_3$/acetone	(90:10)	17	83	88/12	100
		CCl_4/acetone	(90:10)	15	85	52/48	87
		CCl_4/acetone	(95:5)	6	94	59/41	86
OCH_3	(**2b**)	acetone	(100)	85	15	78/22	100
		CCl_4/acetone	(90:10)	92	8	61/39	57
$OSi(CH_3)_3$	(**2c**)	acetone	(100)	87	13	95/5	100
		CCl_4/acetone	(90:10)	99	1	90/10	60
$OC{=}OCH_3$	(**2d**)	acetone	(100)	66	34		86
		CCl_4/acetone	(90:10)	65	35		25
$OC{=}OCH_2CH_3$	(**2e**)	acetone	(100)	66	34		82
		CH_2Cl_2/acetone	(90:10)	62	38		41
		CCl_4/acetone	(90:10)	62	38		22
COOH	(**2f**)	acetone	(100)	84	16		82
		CH_2Cl_2/acetone	(90:10)	80	20		100
		$CHCl_3$/acetone	(90:10)	87	13		54
		CCl_4/acetone	(90:10)	84	16		73
NHCOPh	(**2g**)	acetone	(100)	19	81		100
		CH_2Cl_2/acetone	(90:10)	4	96		100
		CCl_4/acetone	(90:10)	3	97		100
		MeOH/acetone	(90:10)	26	74		64
$C{=}OOCH_3$	(**2h**)	acetone	(100)	55	45		97
		CCl_4/acetone	(90:10)	68	32		56
OOH	(**2i**)	acetone	(100)	84	16		100[c]
		CH_2Cl_2/acetone	(50:50)	82	18		100[c]
CH_3	(**2j**)	acetone	(100)	48	52		100
		CH_2Cl_2/acetone	(90:10)	53	47		100
		CCl_4/acetone	(90:10)	47	53		100
CH_2CH_3	(**2k**)	acetone	(100)	55	45		100
i-Bu	(**2l**)	acetone	(100)	55	45		100
		CH_2Cl_2/acetone	(90:10)	60	40		100
		CCl_4/acetone	(90:10)	54	46		100[d]
t-Bu	(**2m**)	acetone	(100)	95	5		94
		CH_2Cl_2/acetone	(50:50)	96	4		96
CF_3	(**2n**)	acetone	(100)	90	10		70
		CH_2Cl_2/acetone	(50:50)	94	6		73
Ph	(**2o**)	acetone	(100)	82	18		100
		CCl_4/acetone	(90:10)	85	15		70
		MeOH/acetone	(50:50)	83	17		90
CN	(**2p**)	acetone	(100)	51	49		78
		CH_2Cl_2/acetone	(50:50)	57	43		74
Cl	(**2q**)	acetone	(100)	90	10		76
		CH_2Cl_2/acetone	(50:50)	93	7		74
Br	(**2r**)	acetone	(100)	92	8		58

[a] Reactions performed at rt; substrate/DMD ratio (1:1); conversion was determined by GLC analysis at 60 min. [b] The ratio of epoxide diastereoisomers was determined by GLC analysis. [c] Conversion and the ratio of the epoxides was determined by ^1H NMR after 20 h. [d] After 120 min.

benzamido groups permits a facile opening[8] of the epoxide as shown in structure **11**.



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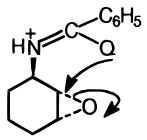

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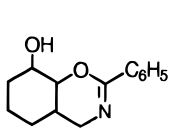

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Table 2 gives the results obtained when derivatives of **3** are oxidized by **1**. While a smaller number of substituents were used in this series the results are similar to those given by **2**. In this case, however, the epoxide is the dominant product in all cases where both epoxidation and insertion reactions are observed. Also, the presence of the 3-methyl group tends to accentuate the favoring of the *trans* epoxide when comparisons are made between substrates bearing the same substituents as in **2**. Finally, Table 3 summarizes the results obtained when derivatives of **4** are oxidized by **1**. No C−H insertion reactions are observed in this series. Again the conversions are uniformly very high. The variation in epoxide diastereomer ratio with substituent is also less pronounced in this series although there is clearly a substituent influence. Here again the substrate with the benzamido substituent **4f** gives an unstable *trans* epoxide which rearranges to the benzoxazine **12**.

(8) Roush, W. R.; Straub, J. A.; Brown, R. J. *J. Org. Chem.* **1987**, *52*, 5127.

Discussion

Substituent Effect on Epoxide Stereoselectivity. An examination of Tables 1−3 reveals that there is a strong effect of substituent on epoxide stereoisomer ratio, with the effect being greatest in compounds **3**. This is presumably due to the added steric requirements of the 3-methyl substituent. With compounds in series **2** and

Table 2. Diastereoselectivity in Dimethyldioxirane Epoxidation of 3-Methyl-2-cyclohex-2-en-1-ol Derivatives 3[a]

R in **3**		solvent system	(%)	epoxides (%)[b] trans	cis	epoxides/enone (%)	conversion (%)
OH	(**3a**)	acetone	(100)	65	31	65/35	95
		CH_2Cl_2/acetone	(80:20)	39	61	85/15	93
		CH_2Cl_2/acetone	(90:10)	35	65	89/11	96
		CH_2Cl_2/acetone	(95:5)	13	87	94/6	81
		MeOH/acetone	(90:10)	82	18	86/14	69
		Bu^{t}OH/acetone	(90:10)	73	27	88/12	85
		AcOH/acetone	(90:10)	74	26	89/11	100
		$CHCl_3$/acetone	(90:10)	17	83	93/7	91
		CCl_4/acetone	(90:10)	21	79	76/24	89
OCH_3	(**3b**)	acetone	(100)	95	5	87/13	100
		CH_2Cl_2/acetone	(80:20)	95	5	92/8	75
		CH_2Cl_2/acetone	(95:5)	95	5	91/9	92
		CCl_4/acetone	(95:5)	5	95	80/20	86
$OSi(CH_3)_3$	(**3c**)	acetone	(100)	95	5	97/3	100
		CCl_4/acetone	(90:10)	99	1	96/4	86
$OC{=}OCH_3$	(**3d**)	acetone	(100)	87	13		94
		CCl_4/acetone	(90:10)	88	12		63
CH_3	(**3e**)	acetone	(100)	73	27		100[c]
		CH_2Cl_2/acetone	(70:30)	77	23		100[c]

[a] Reactions performed at rt; substrate/DMD ratio (1:1); conversion was determined by GLC analysis at 60 min. [b] The ratio of epoxide diastereoisomers was determined by GLC analysis.

Table 3. Diastereoselectivity in Dimethyldioxirane Epoxidation of Homoallylic Cyclohexenes 4[a]

R in **4**		solvent system	(%)	epoxides (%)[b] trans	cis	conversion (%)
OH	(**4a**)	acetone	(100)	44	56	100
		CH_2Cl_2/acetone	(90:10)	30	70	100
		CH_2Cl_2/acetone	(95:5)	28	72	68
		$CHCl_3$/acetone	(90:10)	37	63	100
		CCl_4/acetone	(90:10)	33	67	92
		CCl_4/acetone	(95:5)	26	74	84
		MeOH/acetone	(90:10)	55	45	72[c]
Br	(**4b**)	acetone	(100)	38	62	100
		CH_2Cl_2/acetone	(50:50)	40	60	100
		MeOH/acetone	(50:50)	45	55	100[d]
		CCl_4/acetone	(90:10)	27	73	100[e]
$OC{=}OCH_3$	(**4c**)	acetone	(100)	40	60[f]	100
		CH_2Cl_2/acetone	(90:10)	40	60[f]	100
$C{=}OOCH_3$	(**4d**)	acetone	(100)	37	63	100[g]
		CH_2Cl_2/acetone	(90:10)	39	61	96
		CCl_4/acetone	(90:10)	29	71	91
$C{=}OOCH_2CH_3$	(**4e**)	acetone	(100)	35	65	100[g]
		CH_2Cl_2/acetone	(90:10)	38	62	87
		CCl_4/acetone	(90:10)	27	73	89
		CCl_4/acetone	(95:5)	26	74	80
		MeOH/acetone	(90:10)	41	59	84
NHC=OPh	(**4f**)	acetone	(100)	36	64	100[g]
		CCl_4/acetone	(90:10)	18	82	100
		CCl_4/acetone	(95:5)	13	87	100

[a] Reactions performed at rt; substrate/DMD ratio (1:1); conversion was determined by GLC analysis at 60 min. [b] The ratio of epoxide diastereoisomers was determined by GLC analysis. [c] After 120 min. [d] After 90 min. [e] After 300 min. [f] By ^{1}H NMR. [g] After 15 min.

3 most of the epoxide ratios appear to be determined primarily by the steric influence of the substituents. For substituents where Taft[9] steric substituent constants (E_s) are available, a plot of these constants versus log epoxide *trans*/*cis* ratios gives an excellent linear correlation. The plot in which four of these substituents are included is shown in Figure 1. This plot has an excellent correlation coefficient ($R = 0.9954$). The slope ($\delta = -0.867$) of the correlation line indicates that the steric influence is similar to that in the model system used to derive the E_s values. When an additional substituent (CH_2Br) is included, a linear plot is again obtained, but with a slightly lower correlation coefficient ($R = 0.9582$). The larger the substituent the more *trans* isomer is formed. With compounds **4** no substituent gave a predominance of *trans* isomer. Thus the homoallylic framework allows for a different interaction between substituent and attacking dioxirane. In these compounds we believe dipole−dipole interactions are important *(vide infra*).

Hydrogen Bonding Effects. There are two substituents which do not appear to follow the steric effect analysis alone. These are the hydroxyl group in compounds **2a**, **3a** and **4a** and the amide group in **2g** and **4f.** The separate influence of these substituents is particularly noticeable when the effect of solvent is examined. In all of these cases changing the solvent by increasing the amount of a second solvent leads to an increase in the amount of the *cis* epoxide. The diastereomeric epoxide distribution is, in essence, tunable depending on choice of solvent. Thus **2a** gives an epoxide *trans*/*cis* distribution in 100% acetone of 54/46, while in CCl_4/acetone (95:5) the distribution becomes 6/94 in favor of

(9) Taft, R. W. *J. Am. Chem. Soc.* **1952**, *74*, 3120.

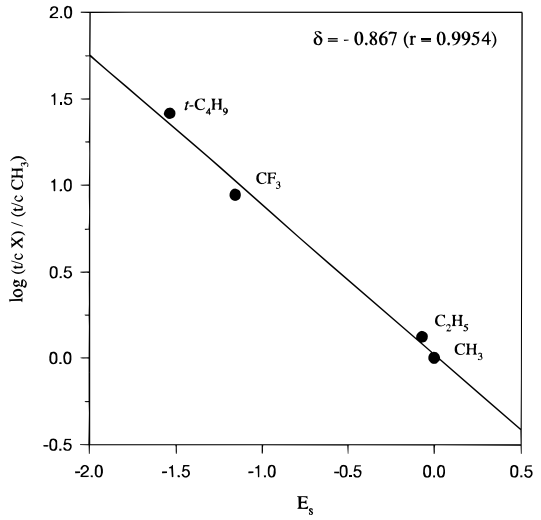
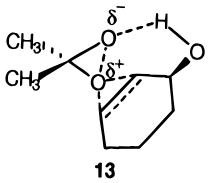


Figure 1. Plot of log epoxide *trans*/*cis* ratios versus Taft[9] steric substituent constants E_s.

the *cis* isomer. The effect is even more pronounced in the case of **3a**. Here the epoxide ratio in 100% acetone is 65/31 (*trans*/*cis*), but a solvent consisting of CCl_4/acetone (95:5) gives a ratio of 5/95 (*trans*/*cis*). A similar but diminished change is observed for **4a.** Here 100% acetone gives an epoxide ratio of 44/56 (*trans*/*cis*) as compared to a ratio of 26/74 (*trans*/*cis*) in a solvent composition of CCl_4/acetone of 95:5. Substrate **2g,** containing the NH group of an amide is also susceptible to this solvent effect. This compound gives a *trans*/*cis* epoxide ratio of 19/81 in 100% acetone, but a ratio of 3/97 in a solvent composition of 90:10, CCl_4:acetone. The corresponding compound **4f** in the homoallylic series gives a *trans*/*cis* epoxide ratio of 36/64 in acetone and a ratio of 18/82 in 90:10, CCl_4:acetone. We attribute this effect of solvent on epoxide isomer distribution, in substrates containing an OH or NH group, to the relative ease of attaining a transition state, such as **13** for **2a**, in



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which H-bonding can occur with the developing negative charge on one oxygen of the dioxirane in the activated complex. It should be noted that when the various epoxide isomer ratios are compared in acetone solvent, then the amido groups in compounds **2g** and **4f** give the highest amount of the *cis* isomer. This is presumably due to the increased acidity of the hydrogen in the amido function. This H-bonding effect should be seen as accompanying the apparent greater influence of a dipole−dipole interaction *(vide infra*). A similar transition state involving H-bonding from $-NH_3^+$ has been proposed[6d] for the epoxidation of some amino-substituted cyclohexenes.

The solvent effect is traceable largely to the ability of a second solvent to dissociate the dioxirane from its strong association with acetone. In the current work the change from 100% acetone to a solvent composition rich in CCl_4, for example, apparently leads to a dioxirane that is less solvated by acetone and consequently is more able to take advantage of intermolecular H-bonding as in **13**. On the other hand, when the diluting solvent is itself able to H-bond with the substrate, then the effect of the second solvent is diminished, or, as in the case of **2a** in MeOH: acetone (90:10), actually gives more of the *trans* isomer since such solvent H-bonding will block the *cis* approach of the dioxirane. Examination of Tables 1−3 reveals that substrates with substituents which are not capable of H-bonding give epoxide ratios which are relatively insensitive to change of solvent.

Dipole−Dipole Directing Effects. The stereoselectivity seen in the epoxides produced from substrates **4b**−**e** in the homoallylic series (Table 3) requires another explanation. In all cases the *cis* isomer is dominant. These results clearly run counter to the general steric effect argument which appears to be controlling for those compounds in series **2** and **3** not affected by H-bonding effects**.** One possible explanation is related to discussions given earlier by Curci et al.[5d] and Bovicelli and coworkers.[10] Thus formation of the *anti*-1,2;3,4-dioxide in the oxidation of naphthalene by methyl(trifluoromethyl)-dioxirane was explained[5d] by postulating an interaction between the first epoxide formed and the dipolar dioxirane, leading to an *anti* attack. On the other hand oxidation of prednisone acetate by **1** to give 80% of the 1α,2α-oxirane derivative was interpreted[10] as indicating an attractive dipole−dipole interaction between the attacking dioxirane and the carbonyl group at C_{11}. Such a stereoorienting effect leads to α attack at the neighboring 1,2 double bond. In the absence of the orienting effect of the C_{11} carbonyl group, such as in androsta-1,4-diene-3,7-dione, the major epoxidation product is the 4*β*,5*β*-epoxide.

We believe that the epoxide distributions obtained from compounds **4b**−**e** can be rationalized on the basis of similar dipole−dipole interaction arguments. In each of these compounds there is a strong dipole, a C−Br bond in **4b** and a carbonyl group in compounds **4c**−**4e.** This dipole could lead to an attractive dipole−dipole interaction with the strong dipole[11] of **1** and a resultant favoring of *cis* attack by the incoming dioxirane. The intervening methylene group in the homoallylic compounds must permit a greater influence of this type of interaction than in the compounds in series **2** where steric effects dominate in most cases. Some support for this argument comes from an examination of the epoxide ratio formed from compound **2k** with an ethyl group as substituent. This compound could be regarded as a member of the homoallylic series with methyl as substituent. The epoxide ratio obtained from **2k** is 55:45 (trans/cis). Thus when no dipole is present the steric effect is the dominant effect. The differences in the amount of the *cis* epoxide isomer obtained in compounds **4c**−**e** may reflect a difference in the proximity of the directing carbonyl group to the double bond. In compounds **4d** and **4e** the carbonyl group is closer to the double bond than it is in **4c** leading to a higher % *cis* isomer in **4d** and **4e**. The solvent effect on epoxide diastereoselectivity seen in compounds **4b**−**e** can be rationalized in a manner which parallels the explanation given for a similar effect of solvent on those compounds in series **2** and **3** that are capable of intramolecular H-bonding. In compound **4e**, for example, diluting the acetone solvent with CCl_4 leads

(10) Bovicelli, P.; Lupatelli, P.; Mincione, E. *J. Org. Chem*. **1994**, *59*, 4304.

(11) The parent dioxirane has been found to have a very strong dipole (μ = 2.5 D). Herron, J. T.; Huie, R. E. *J. Am. Chem. Soc.* **1977**, *100*, 5582.

to more *cis* epoxide, presumably because the dipole−dipole interaction is greater in this solvent combination. The effect of an H-bonding solvent in these compounds is similar to that seen in series **2** and **3** also. Thus in compounds **4b** and **4e** when the second solvent is methanol less *cis* epoxide is formed as H-bonding of the substrates with methanol reduces the opportunity for the cis-favoring dipole−dipole interaction.

Chemoselectivity. As shown in Tables 1 and 2 several of the compounds (**2a, 2b, 2c**, **3a, 3b**, and **3c**) in series **2** and **3** give enone **8** or **9**, respectively, as well as epoxide products. None of the compounds in the homoallylic series (Table 3) gave enone products. The enones are the result of a dioxirane C−H bond insertion reaction.[12] A competition between epoxidation and insertion has been studied by several other groups. Adam and coworkers[6a] have found that increasing substitution at the double bond in cyclohexenols leads to a decreasing amount of the insertion reaction. Also Marples et al.[5a] found, in the oxidation of some steroidal alcohols, that steric factors can completely block the epoxidation reaction and permit the insertion reaction to be the sole reaction. In the OH-substituted compounds **2a** and **3a** the insertion reaction is rapid as described earlier.[4] As seen in Tables 2 and 3 there is a solvent effect on the competition between epoxidation and insertion reactions. This effect is most pronounced for **2a** where the % epoxide formed varies from 89% in 97:3 (CH_2Cl_2/acetone) to 46% in 100% acetone. The solvent effect on this reaction competition is diminished in **3a** and the ethers **2b, 2c**, and **3b** and **3c.**

Comparison to Peracid Oxidations. The epoxidation of cyclohexene derivatives described here follows the original[13] observation of Henbest and Wilson that the OH group provides stereocontrol favoring the *cis* isomer in peracid epoxidations. Subsequently this same directing effect has been observed[3a] in a variety of cyclic allylic alcohols. An amide group was also found[14,15] to give this same *cis* stereoselectivity in peracid epoxidations in cyclic olefins. This observation prompted us to study the effect of an amide substituent (compounds **2g** and **4f**) in our dioxirane epoxidations. Here too we found a parallel with the peracid epoxidations with this group providing stereocontrol favoring the *cis* isomer. The stereocontrol provided by H-bonding substituents in the peracid reactions was explained by invoking the Bartlett[16] mechanism involving H-bonding between the substituent and one of the oxygens of the peracid. The functionally analagous process for the dioxirane epoxidations described here is illustrated in structure **12.** In the peracid epoxidations substituents which do not have OH or NH groups, but which contain a carbonyl group, are believed[3a,6c] to give *cis* stereoselectivity by H-bonding involving the peracid proton and the substituent carbonyl group. Obviously a similar process is not possible for the dioxirane epoxidations. Instead the involvement of dipole−dipole interactions of the type we have described for some of the compounds in series **4** apparently may provide a similar stereocontrol.

Summary. Our results indicate that epoxide diastereoselectivity in the epoxidation of cyclohexene derivatives by dimethyldioxirane is subject to a number of substrate and solvent influences. Included in the substrate influences are steric effects, H-bonding, and dipole−dipole interactions. The results suggest that these various factors could be manipulated to give desired stereocontrol in these and related epoxidations. Thus if, for example, the *cis* epoxide isomer were a synthetic target in one of the molecular frameworks used here, or in related frameworks, then the various factors affecting stereoselectivity could be chosen to maximize *cis* stereoselectivity.

Experimental Section

Instrumentation and General Methods. ^{1}H NMR spectra were recorded on a 300 MHz NMR spectrometer with tetramethylsilane (0.00 ppm) as an internal reference in $CDCl_3$ as the solvent. All NMR data are reported in ppm or δ values downfield from TMS and coupling constants, *J*, are reported in Hz. ^{13}C NMR spectra were recorded at 75 MHz in $CDCl_3$. The center peak of the solvent $CDCl_3$ at 77.00 ppm was used as an internal reference. The multiplicities of the ^{13}C NMR signals were determined by the attached proton test (APT) pulse sequence. Where necessary, COSY and HETCOR experiments were performed on a 500 MHz spectrometer (^{1}H, 500.13 MHz, and ^{13}C, 125.75 MHz). ^{19}F NMR spectra were recorded on a 500 spectrometer at 470.55 MHz and are referenced against internal $CFCl_3$ (δ 0.00 ppm). Electron impact and chemical ionization mass spectra were recorded, at 70 eV ionizing voltage, on a twin EI and CI quadrupole mass spectrometer connected to a gas chromatograph fitted with a 12 m × 0.2 mm × 0.33 μm Ultra-1 (cross-linked methyl silicone) column. UV-vis spectra were obtained on a UV-vis spectrophotometer. Infrared spectra were recorded as thin films between KBr disks or in KBr pellets on an FT-IR spectrometer. Melting points were determined on a hot-stage apparatus and are uncorrected. Gas chromatography was performed on a capillary gas chromatograph using a flame ionization detector, a fused silica DB-210 capillary column (30 m × 0.318 mm; film thickness 0.5 μm) or a fused silica DB-5 capillary column (30 m × 0.25 mm; film thickness 0.5 μm), and He as the carrier gas. The chromatograph was interfaced with an integrator. Preparative GC was performed on a preparative gas chromatograph employing a dual rhenium−tungsten filament thermal conductivity detector and using He as carrier. The columns used were a 12 ft × $^3/_8$ in. aluminum column packed with 8% SF-96 methyl silicone on chromosorb G 60/80 mesh or a 20 ft × $^3/_8$ in. aluminum column packed with a 15% SE-30 on chromosorb W 30/60 mesh or a 10 ft × $^3/_8$ in. aluminum column packed with 10% UCON-50-HB-280X on DMCS chromosorb W 45/60 mesh. Chromatographic separations on the Chromatotron were accomplished using Kieselgel 60 PF_{254} gypsum coated plates. Elemental analyses were performed by Atlantic MicroLab, Inc. (Norcross, GA) and Quantitative Technologies Inc. (Whitehouse, NJ).

Materials and Reagents. Acetone (Fisher reagent grade) was fractionally distilled over anhydrous potassium carbonate. Oxone (Du Pont), 2 $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was obtained from Aldrich and used as such. Cyclohexene (Fisher), 2-cyclohexen-1-ol, 2-cyclohexen-2-one, 3-methyl-2-cyclohexen-1-ol, phenylmagnesium bromide, ethylmagnesium bromide (all from Aldrich), 3-methylcyclohexene (Janssen Chimica), 1,3-dimethylcyclohexene, 3-methyl-2-cyclohexen-1-one (both from Wiley Organics) were of the highest purity and were used as such after verifying their purity by GLC. In a few cases, neat olefins were passed through a small column of neutral alumina (Brockman activity 1) to remove traces of oxygenated impuri-

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ties and were analyzed by GLC to verify their purity. 3-Bromocyclohexene (90% from Aldrich and Lancaster), 3-chlorocyclohexene (95% from Wiley Organics), and 3-methoxycyclohexene (90% from Alfa Morton Thiokol) were purified by fractional distillation or by bulb to bulb kugelrohr distillation. The dimethyldioxirane solution in acetone was prepared according to the literature procedure[17] and was assayed for dioxirane content using phenyl methyl sulfide, and the GLC method or concentration was determined using a calibration curve of concentration of the DMD versus UV absorbance at 335 nm.

Preparation, Purification and Characterization of the Epoxidation Substrates. The substrates were prepared according to the literautre procedures. Analytically pure samples of liquid substrates were collected by preparative GLC. The collected samples were characterized by ^{1}H and ^{13}C NMR and mass spectroscopy.

3-Methoxycyclohexene (2b). A technical grade sample was purified by fractional distillation.[18]

(2-Cyclohexen-1-yloxy)trimethylsilane (2c) was prepared by the literature procedure.[19]

3-(Acetyloxy)cyclohexene (2d) was synthesized by the standard acetylation method.[20,21]

3-(Propionyloxy)cyclohexene (2e) was prepared by reaction of 2-cyclohexen-1-ol and propionic anhydride.[22]

Cyclohex-2-ene-1-carboxylic acid (2f) was prepared by the literature procedure.[23]

3-Benzamidocyclohexene (2g) was synthesized by the literature method.[24] An analytically pure sample was isolated by recrystallization from CH_2Cl_2−hexane as a colorless crystalline solid: mp 101−103 °C; lit.[24] mp 100−101.2 °C.

2-Cyclohexene-1-carboxylic acid methyl ester (2h) was prepared by the literature procedure.[23]

3-Ethylcyclohexene (2k) was synthesized by reaction of 3-bromocyclohexene and ethylmagnesium bromide according to the literature method.[20]

3-Isobutylcyclohexene (2l) was synthesized by reaction of 3-bromocyclohexene and isobutylmagnesium bromide according to the literature method.[26]

3-*tert*-Butylcyclohexene (2m) was synthesized by reaction of 2-*tert*-butylcyclohexanone tosylhydrazone and *n*-butyllithium according to the literature method.[27]

3-(Trifluoromethyl)cyclohexene (2n) was prepared by the literature procedure.[28]

3-Phenylcyclohexene (2o) was prepared by reaction of 3-bromocyclohexene and phenylmagnesium bromide in ether according to the literature procedure.[29]

2-Cyclohexene-1-carbonitrile (2p) was prepared by the reaction of 3-bromocyclohexene with NaCN according to the literature procedure.[23]

3-Chlorocyclohexene (2q) was obtained by purification (GLC) of a technical grade sample and was collected as a colorless liquid.[30]

3-Bromocyclohexene (2r) was obtained by purification (GLC) of a technical grade sample and was collected as a colorless liquid.[31]

3-Methyl-2-cyclohexen-1-ol (3a) was prepared by $LiAlH_4$ reduction of 3-methyl-2-cyclohexen-1-one in ether.[32]

3-Methoxy-1-methylcyclohexene (3b) was synthesized by the method of Zon and Paquette.[33]

3-(Trimethylsilyloxy)-1-methylcyclohexene (3c) was prepared by following the literature procedure.[19]

3-(Acetyloxy)-1-methylcyclohexene (3d) was prepared by the standard acetylation method.[34]

2-Cyclohexene-1-methanol (4a) was prepared by the literature procedure.[35,36]

3-(Bromomethyl)cyclohexene (4b) was prepared by the literature procedure.[36]

3-[(Acetyloxy)methyl]cyclohexene (4c) was prepared by the standard procedure.[37]

2-Cyclohexene-1-acetic acid methyl ester (4d) was prepared by treating 2-cyclohexene-1-acetic acid with an excess of diazomethane[38] as a colorless liquid.[20]

2-Cyclohexene-1-acetic acid ethyl ester (4e) was prepared by the literature procedure.[39]

***N*-(2-Cyclohexen-1-ylmethyl)benzamide (4f).** To a solution of 2-cyclohexene-1-methanol mesylate[36] (0.6925 g, 3.64 mmol) in DMF (25 mL) was added sodium azide (0.5755 g, 8.85 mmol) with stirring. The reaction mixture was heated at 80 °C for 8 h. Water (100 mL) was added, and the solution was extracted with CH_2Cl_2 (50 mL). The CH_2Cl_2 layer was washed several times with water and dried with anhydrous Na_2SO_4. Evaporation of CH_2Cl_2 *in vacuo* gave an orange-yellow liquid. Bulb-to-bulb distillation (oven temp 60 °C/0.1 mmHg) of the crude sample afforded an analytically pure sample of 3-(azidomethyl)cyclohexene (0.5 g, 100%) as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 1.25−1.90 (m, 4H), 1.95−2.10 (m, 2H), 2.35 (m, 1H), 3.10−3.40 (m, 2H), 5.50−5.60 (m, 1H), 5.75−5.85 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 20.80, 25.19, 26.66, 35.75, 56.50, 127.46, 129.63; MS (EI, 70 eV) *m*/*z* 108 (M^+ − 29,1), 81(100), 79(38), 67(3), 53(13); calcd for $C_7H_{11}N_3$: 137.18.

To a solution of 3-(azidomethyl)cyclohexene (0.5 g, 3.64 mmol) in THF (25 mL) was added triphenylphosphine (0.96 g, 3.66 mmol), and the reaction mixture was stirred at 60 °C for 2 h, a solution of NaOH (2 g in 20 mL water) was added, and the reaction mixture was stirred at 60 °C for 2 h. Ether (25 mL) was added to the mixture, and it was extracted with a 20% HCl solution (50 mL). The aqueous layer was separated and extracted with ether (25 mL) and made strongly alkaline with NaOH. The solution was extracted with CH_2Cl_2 (25 mL) and anhydrous HCl gas was bubbled through the solution to afford a shiny white flaky solid which was filtered, washed with acetone, and dried *in vacuo* to give 2-cyclohexene-1-methanamine hydrochloride (0.2868 g, 54%). A part of the hydrochloride salt was neutralized with NaOH and extracted with a mixture of ether/hexane. The organic extracts were dried with anhydrous Na_2SO_4 and evaporated *in vacuo* to give a pale yellow liquid which was purified by preparative GLC to afford free 2-cyclohexene-1-methanamine as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 1.20−1.65 (m, 2H), 1.43 (br s, 2H),

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1.65−1.90 (m, 2H), 1.95−2.08 (m, 2H), 2.12 (m, 1H), 2.55−2.72 (m, 2H), 5.53−5.63 (m, 1H), 5.71−5.84 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 21.30, 25.44, 26.58, 38.92, 47.58, 128.48, 129.29; MS (EI, 70 eV): *m*/*z* 112(M + 1,1), 111(M^+,9), 94(22), 81(29), 79(100), 67(21), 53(34), 41(26); Calcd for $C_7H_{13}N$: 111.17.

To an ice-cooled solution of 2-cyclohexene-1-methanamine hydrochloride (0.2 g, 1.3546 mmol) and sodium hydroxide (0.3 g, 0.75 mmol) in water (4 mL) was added benzoyl chloride (0.2 g, 1.4727 mmol) with stirring. The reaction mixture was stirred for 2 h. A white precipitate was formed immediately. The precipitate was filtered and washed with a dilute solution of NaOH and then with water. The residue was dried *in vacuo* for 2 h. The residue was purified by radial chromatography (silica gel plate, acetone/CH_2Cl_2 (5:95) as the eluent) to afford pure **4f** as a colorless crystalline solid (0.2602 g, 90%): mp 82−84 °C; IR (KBr) 3314 (NH), 2931, 1636 (C═O), 1540, 1489, 1433, 1312, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25−1.90 (m, 4H), 1.90−2.10 (m, 2H), 2.45 (m, 1H), 3.28−3.40 (m, 1H), 3.42−3.55 (m, 1H), 5.57−5.68 (m, 1H), 5.75−5.90 (m, 1H), 6.43 (br s, 1H), 7.30−7.60 (m, 3H), 7.65−7.90 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.98, 25.20, 26.74, 35.53, 44.72, 126.73, 128.11, 128.33, 129.36, 131.12, 134.67, 167.53; MS (EI, 70 eV) *m*/*z* 216(M + 1, 0.3), 215(M^+,2), 134(19), 122(19), 105(100), 94(10), 77(30); calcd for $C_{14}H_{17}NO$: 215.28. Anal. Calcd for $C_{14}H_{17}NO$: C, 78.09; H, 7.96; N, 6.51. Found: C, 78.00; H, 7.74; N, 6.53.

General Procedure for the Epoxidation of Cyclohexene Derivatives with Dimethyldioxirane. The reactions were carried out by addition of a solution of dimethyldioxirane in acetone to a magnetically stirred solution of the substrate in acetone (or other solvent, see Tables 1−3) at room temperature (20−22 °C). An equimolar solution of dimethyldioxirane and the substrate was used. The progress of the reaction was monitored periodically by GLC and GC-MS. The ratio of epoxide diastereoisomers, as well as the product distribution, was determined by GLC analysis of the reaction mixture at 60 min unless stated otherwise. Stirring was continued until consumption of the substrate, or the reaction mixture was stirred for a longer time to attain a suitable conversion. Solvent was removed on a rotary evaporator at low temperature or where necessary, by fractional distillation. GLC analysis of the distillation fractions indicated that only minor amounts of products were contained in these fractions. The relative ratio of epoxide isomers and product distribution was determined by ^{1}H NMR analysis on the crude reaction mixture residue obtained after removal of the solvent. The ratios determined by ^{1}H NMR analysis were comparable with those determined by GLC analysis. Products in the residue were separated by preparative GLC. The collected products were reanalyzed to insure purity. The products were characterized using ^{1}H and ^{13}C NMR, infrared, and mass spectroscopy and by comparison of their spectral and chromatographic properties with those of authentic samples or with literature values.

Epoxidation of 2a by 1. The general procedure was followed to give a residue which was found to contain three major products. The products were separated by preparative GLC. One of these products was identified as ***trans*-2,3-epoxycyclohexan-1-ol (*trans*-5a)** by comparing its NMR and mass spectral data with those in the literature[19,40−42] and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.10−2.00 (m, 6H), 1.90 (br s, 1H), 3.09 (d, J = 3.72 Hz, 1H), 3.24 (m, 1H), 4.04 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 14.48, 24.07, 29.49, 53.11, 56.08, 65.80; MS (EI, 70 eV) *m*/*z* 114(M^+,0.2), 96(5), 95(4), 83(3), 71(16), 70(100), 58(40), 57(76), 41(15); calcd for $C_6H_{10}O_2$; 114.14.

The second product was identified as ***cis*-2,3-epoxycyclohexan-1-ol (*cis*-5a)** by comparing its NMR spectrum with that in the literature[40−42] and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.15−2.00 (m, 6H), 2.07 (br s, 1H), 3.35 (m, 2H), 4.01 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.13, 23.20, 29.06, 55.31, 55.47, 67.01; MS (EI, 70 eV) *m*/*z* 114(M^+, 0.3), 96(6), 95(4), 83(2), 71(13), 70(100), 58(39), 57(83), 55(13), 43(12), 41(16); calcd for $C_6H_{10}O_2$: 114.14.

The third product was identified as **2-cyclohexen-1-one (8)** by comparing its mass spectral data[43] with those in the literature and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$): δ 1.95−2.10 (m, 2H), 2.30−2.40 (m, 2H), 2.40−2.50 (m, 2H), 6.03 (dt, J = 10.0, 2.0 Hz, 1H), 7.01 (dt, J = 10.0, 4.0 Hz, 1H); MS (EI, 70 eV): *m*/*z* 97(M + 1, 2), 96(M^+, 34), 68(100), 55(5), 53(3), 42(4); Calcd for C_6H_8O: 96.13.

A minor product was also isolated from the reaction mixture and was identified as **2,3-epoxycyclohexane-1-one** by comparing its NMR[41] and mass spectral data[43] with the literature values and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$): δ 1.60−1.75 (m, 1H), 1.85−2.15 (m, 3H), 2.20−2.35 (m, 1H), 2.50−2.65 (m, 1H), 3.22 (d, J = 3.91 Hz, 1H), 3.59 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 16.97, 22.82, 36.34, 55.02, 55.85, 205.64; MS (EI, 70 eV) *m*/*z* 113(M + 1, 2), 112(M^+, 32), 83(17), 68(7), 57(20), 56(15), 55(100), 41(10); calcd for $C_6H_8O_2$: 112.13.

Epoxidation of 2b by 1. The general procedure was followed to give a residue which was found to contain three major products and a minor product. The products were separated by preparative GLC. One of the major products was identified as **3-methoxy-*trans*-1,2-epoxycyclohexane (*trans*-5b)** by comparing its properties with those in the literature[44−46] and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.10−1.30 (m, 2H), 1.35−1.55 (m, 1H), 1.65−1.90 (m, 2H), 1.95−2.10 (m, 1H), 3.11 (dd, J = 3.77, 0.71 Hz, 1H), 3.21 (m, 1H), 3.45 (s, 3H), 3.50 (dd, J = 7.94, 5.74 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.57, 24.24, 26.31, 52.92, 54.02, 56.93, 75.00; MS (EI, 70 eV) *m*/*z* 128 (M^+, 1), 127(1), 97(6), 84(9), 71(100), 67(12), 57(10), 53(8), 41(27); calcd for $C_7H_{12}O_2$: 128.17.

The second product was identified as **3-methoxy-*cis*-1,2-epoxycyclohexane (*cis*-5b)** by comparing its properties with those in the literature[44−46] and on the basis of the following data: a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 1.15−1.35 (m, 1H), 1.35−1.55 (m, 1H), 1.55−1.75 (m, 2H), 1.75−1.95 (m, 2H), 3.27 (m, 1H), 3.32 (dd, J = 4.00, 2.05 Hz, 1H), 3.46 (s, 3H), 3.628 (ddd, J = 8.90, 5.02, 2.14 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.50, 23.05, 24.49, 52.94, 53.94, 56.10, 76.60; MS (EI, 70 eV) *m*/*z* 128 (M^+, 0.1), 127(0.3), 97(12), 83(18), 71(100), 67(12), 57(10), 53(4), 41(24); calcd for $C_7H_{12}O_2$: 128.17.

The third major product was identified as **2-cyclohexen-1-one (8)** as described above. A minor product (*ca.* 1%) was identified as **2,3-epoxycyclohexan-1-one** as described above.

Epoxidation of 2c by 1. The general procedure was followed to give a residue which was found to contain three products. The products were separated by preparative GLC. One of the major products was identified as **[(*trans*-2,3-epoxycyclohexan-1-yl)oxy]trimethylsilane (*trans*-5c)** by comparing its ^{1}H NMR spectrum[19] and properties with those in the literature[47] and on the basis of the following data: a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.10−2.10 (m, 6H), 3.00 (d, J = 3.75 Hz, 1H), 3.20 (m, 1H), 3.95 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 0.10, 14.61, 24.19, 30.16, 53.20, 56.61, 66.47; MS (EI, 70 eV) *m*/*z* 186(M^+, 0.07), 171(15), 129(38), 115(7), 105(12), 89(7), 75(100), 73(66), 59(7), 45(9); calcd for $C_9H_{18}O_2Si$: 186.32.

The second product was identified as **[(*cis*-2,3-epoxycyclohexan-1-yl)oxy]trimethylsilane (*cis*-5c)** on the basis of a comparison of NMR data with the known *trans* isomer and the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9H), 1.10−1.95 (m, 6H), 3.14 (dd, J = 3.94, 1.93 Hz, 1H), 3.24 (m, 1H), 4.01 (ddd, J = 9.14, 5.90, 2.00 Hz, 1H); ^{13}C NMR

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($CDCl_3$) δ 0.45, 20.53, 22.71, 28.17, 54.74, 56.14, 69.56; MS (EI, 70 eV) *m/z* 186(M^+, 0.08), 171(10), 129(65), 115(6), 105(24), 101(12), 89(7), 79(19), 73(55), 59(11), 45(11); calcd for $C_9H_{18}O_2Si$: 186.32.

A minor product was identified as **8** as described above.

Epoxidation of 2d by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **3-(acetyloxy)-*trans*-1,2-epoxycyclohexane (*trans*-5d)** by comparing its ^1H NMR spectrum[20,48] and properties with those in the literature[40,49] and on the basis of the following data: a colorless liquid; ^1H NMR ($CDCl_3$) δ 1.20−2.15 (m, 6H), 2.09 (s, 3H), 3.07 (d, J = 3.66 Hz, 1H), 3.23 (m, 1H), 5.04 (dd, J = 7.08, 5.92 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ 14.57, 21.17, 23.75, 25.84, 52.58, 53.36, 68.07, 169.94; MS (EI, 70 eV) *m/z* 114 (M + 1 − CH_3C=O, 7), 113(M^+-CH_3C=O, 13), 112(17), 96(13), 86(10), 71(11), 70(69), 68(17), 67(16), 57(10), 55(22), 43(100), 41(10); calcd for $C_8H_{12}O_3$: 156.18.

The second product was identified as **3-(acetyloxy)-*cis*-1,2-epoxycyclohexane (*cis*-5d)** by comparing its ^1H NMR spectrum[20,48] and properties with those in the literature[40,49] and on the basis of the following data: a colorless liquid; ^1H NMR ($CDCl_3$) δ 1.20−2.00 (m, 6H), 2.11 (s, 3H), 3.30 (m, 2H), 5.13 (ddd, J = 8.93, 5.34, 1.77 Hz, 1H), ^{13}C NMR ($CDCl_3$) δ 19.45, 21.24, 22.60, 24.49, 52.84, 54.25, 70.87, 170.66; MS (EI, 70 eV) *m/z* 114 (M + 1 − CH_3C=O, 11), 113(M^+-CH_3C=O, 16), 112(27), 96(22), 86(15), 71(10), 70(97), 68(18), 67(18), 57(12), 55(16), 43(100), 41(12); calcd for $C_8H_{12}O_3$: 156.18.

Epoxidation of 2e by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **3-(propionyloxy)-*trans*-1,2-epoxycyclohexane (*trans*-5e)** on the basis of the following data: a colorless liquid, ^1H NMR ($CDCl_3$) δ 1.19 (t, J = 7.55 Hz, 3H), 1.25−2.15 (m, 6H), 2.39 (q, J = 7.55 Hz, 2H), 3.08 (d, J = 3.66 Hz, 1H), 3.25 (m, 1H), 5.08 (dd, J = 7.05, 6.90 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.17, 14.57, 23.74, 25.85, 27.73, 52.58, 53.41, 67.79, 173.36; MS (EI, 70 eV) *m/z* 126(4), 114(M + 1 − CH_3CH_2C=O, 4), 113(M^+-CH_3CH_2C=O, 7), 96(8), 70(7), 68(10), 67(9), 57(100), 55(13), 41(7); calcd for $C_9H_{14}O_3$: 170.21. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.56; H, 8.21.

The second product was identified as **3-(propionyloxy)-*cis*-1,2-epoxycyclohexane (*cis*-5e)** on the basis of a comparision of NMR data with the *trans* isomer and the following data: a colorless liquid; ^1H NMR ($CDCl_3$) δ 1.16 (t, J = 7.57 Hz, 3H), 1.20−2.00 (m, 6H), 2.39 (q, J = 7.68 Hz, 2H), 3.30 (m, 2H), 5.14 (ddd, J = 8.74, 5.31 and 1.77 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 9.19, 19.47, 22.64, 24.52, 27.73, 52.92, 54.25, 70.65, 174.13; MS (EI, 70 eV): *m/z* 126(5), 114(M + 1 − CH_3CH_2C=O, 3), 113(M^+-CH_3CH_2C=O, 6), 96(8), 70(7), 68(7), 67(8), 57(100), 55(9), 41(8); calcd for $C_9H_{14}O_3$: 170.21.

Epoxidation of 2f by 1. The general procedure was followed to give a residue which was found to contain two products. The products could not be separated by preparative GLC. A mixture of the products was analyzed by NMR. One of these products was identified as ***trans*-2,3-epoxycyclohexane-1-carboxylic acid (*trans*-5f)**[50] on the basis of the following data (from *trans:cis* mixture): ^1H NMR ($CDCl_3$) δ 1.00−2.05 (m, 6H), 2.95 (dd, J = 8.45, 6.01 Hz, 1H), 3.24 (m, 1H), 3.46 (d, J = 3.77 Hz, 1H), 9.95 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.75, 23.50, 23.75, 40.38, 52.01, 52.33, 179.02; MS (EI, 70 eV): *m/z* 142 (M^+, 0.5); calcd for $C_7H_{10}O_3$: 142.15.

The second product was identified as ***cis*-2,3-epoxycyclohexane-1-carboxylic acid (*cis*-5f)**[50] on the basis of the following data (from *trans:cis* mixture): ^1H NMR ($CDCl_3$) δ 1.00−2.05 (m, 6H), 2.90 (m, 1H), 3.24 (m, 1H), 3.49 (dd, J = 3.66, 3.17 Hz, 1H), 9.95 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.82, 21.09, 23.11, 40.70, 51.93, 52.41, 178.52; MS (EI, 70 eV): *m/z* 142 (M^+, 0.2); calcd for $C_7H_{10}O_3$: 142.15. The *trans* and *cis* epoxy carboxylic acids were converted to their esters by treating with an excess of diazomethane in ether. Separation of the esters by preparative GLC afforded *trans* and *cis* epoxy esters which had the same spectral and chromatographic properties as those of the known ***trans*-5h** and ***cis*-5h** epoxy esters isolated during the epoxidation of methyl cyclohex-2-ene carboxylate with DMD.

Epoxidation of 2g by 1. The general procedure was followed to give a colorless solid. ^1H NMR analysis of the reaction mixture indicated the presence of *cis* epoxide as the major product and *trans* epoxide as the minor product. Separation of the products was accomplished by radial chromatography of the residue on a Chromatotron (silica gel plate), using acetone/CH_2Cl_2 (5:95) as the eluent. The major product was identified as **3-benzamido-*cis*-1,2-epoxycyclohexane (*cis*-5g)** by comparing its properties with those in the literature[24] and on the basis of the following data: colorless needles (CH_2Cl_2−hexane), mp 119−121 °C, lit.[51] mp 116−117 °C; ^1H NMR ($CDCl_3$) δ 1.20−1.75 (m, 4H), 1.80−2.00 (m, 2H), 3.34 (s, 2H), 4.55−4.65 (m, 1H), 6.54 (br d, J = 7.82 Hz, 1H), 7.35−7.60 (m, 3H), 7.75−7.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.47, 23.21, 26.37, 45.67, 54.14, 54.52, 126.86, 128.35, 131.33, 134.28, 166.70; MS (EI, 70 eV): *m/z* 217(M^+, 1), 198(1), 146(15), 122(16), 105(100), 77(43), 67(2), 51(8); calcd for $C_{13}H_{15}NO_2$: 217.27.

The minor product formed during the reaction was **3-benzamido-*trans*-1,2-epoxycyclohexane (*trans*-5g)** which was identified on the basis of the following data: (from *cis:trans* mixture) ^1H NMR ($CDCl_3$) δ 2.00−2.15 (m, 1H), 3.16 (d, J = 3.66 Hz, 1H), 3.21 (m, 1H), 4.37 (m, 1H), 6.39 (br d, 1H); ^{13}C NMR ($CDCl_3$) δ 15.75, 24.05, 26.84, 45.50, 52.44, 55.00, 126.88, 128.43, 131.40, 134.31, 166.73; MS (EI, 70 eV) *m/z* 218(M + 1, 3), 217(M^+, 21), 200(12), 188(10), 174(100), 160(7), 146(85), 130(10), 117(17), 104(73), 90(14), 77(46), 57(18), 51(10); calcd for $C_{13}H_{15}NO_2$: 217.27. This mass spectrum is actually that of **7-hydroxy-2-phenyl-3a,4,5,6,7,7a-hexahydrobenzoxazole**, the thermal rearrangement product of the **3-benzamido-*trans*-1,2-epoxycyclohexane**.

The rearrangement product was also formed during chromatography and was isolated as a colorless viscous liquid and identified as **7-hydroxy-2-phenyl-3a,4,5,6,7,7a-hexahydrobenzoxazole** on the basis of the following data: a colorless liquid, solidifies very slowly on standing; IR (neat film) 3356 (OH), 2930, 2865, 1635 (C=N), 1450, 1349, 1273, 1064, 967, 911, 782, 734, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10−2.20 (m, 6H), 2.45 (br s, 1H, OH, exchangeable with D_2O), 3.74 (ddd, J = 11.45, 7.03, 4.98 Hz, 1H), 4.26−4.38 (m, 1H), 4.495 (dd, J = 8.54, 7.08 Hz, 1H), 7.35−7.55 (m, 3H), 7.85−8.10 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.50, 26.90, 29.23, 65.03, 71.43, 84.91, 127.72, 128.05, 128.20, 131.36, 131.36, 163.94; MS (EI, 70 eV) *m/z* 218(M + 1, 3), 217(M^+,21), 200(12), 188(10), 174(100), 160(7), 146(85), 130(10), 117(17), 105(70), 104(73), 90(14), 77(46), 57(18), 51(10); calcd for $C_{13}H_{15}NO_2$: 217.27. Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.75; H, 6.83, N, 6.40.

Epoxidation of 2h by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **methyl *trans*-2,3-epoxycyclohexanecarboxylate (*trans*-5h)** by comparing its NMR[50] data with those in the literature and on the basis of the following data: a colorless liquid: ^1H NMR ($CDCl_3$) δ 1.25−2.15 (m, 6H), 2.90 (dd, J = 8.98, 5.86 Hz, 1H), 3.21 (m, 1H), 3.41(d, J = 3.90 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 16.81, 23.69, 23.89, 40.61, 51.86, 51.90, 52.17, 173.73; MS (EI, 70 eV) *m/z* 156(M^+, 0.5), 141(3), 125(28), 124(16), 113(26), 100(42), 97(53), 96(83), 95(19), 87(35), 79(58), 71(100), 70(25), 69(47), 68(73), 67(49), 59(27), 58(30), 57(10), 55(57), 41(49); calcd for $C_8H_{12}O_3$: 156.18.

The second product was also isolated as a colorless liquid and was identified as **methyl *cis*-2,3-epoxycyclohexanecarboxylate (*cis*-5h)** by comparing its NMR[50] data with those in the literature and on the basis of the following data: ^1H

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NMR ($CDCl_3$) δ 1.15−2.00 (m, 6H), 2.84 (m, 1H), 3.21 (m, 1H), 3.44 (t, J = 3.5 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 18.97, 21.36, 23.21, 40.94, 51.93, 52.05, 52.26, 173.10; MS (EI, 70 eV) m/z 156(M^+, 0.2), 141(1), 125(7), 124(10), 113(24), 100(43), 97(38), 96(71), 95(18), 87(34), 79(57), 71(100), 70(22), 69(52), 68(67), 67(53), 59(30), 58(29), 57(12), 55(61), 41(57); calcd for $C_8H_{12}O_3$: 156.18.

Epoxidation of 2i by 1. The general procedure was followed to give a residue which was found to contain two products. The products could not be separated by preparative GLC. A mixture of the products was analyzed by NMR. One of these products was identified as ***trans*-2,3-epoxycyclohexan-1-yl hydroperoxide (*trans*-5i)** on the basis of the following data (from *trans:cis* mixture): ^1H NMR ($CDCl_3$) δ 1.10−2.50 (m, 6H), 3.28 (br s, 1H), 3.44 (d, J = 3.90 Hz, 1H), 4.24 (dd, J = 9.30, 5.90 Hz, 1H), 9.44 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 14.55, 24.13, 24.53, 53.24, 53.31, 78.97; MS (EI, 70 eV) m/z 130(M^+, 0.7), 112(M^+-18, 13), 97(65), 83(14), 79(86), 71(16), 70(52), 67(85), 57(100), 55(95), 53(19), 41(91); calcd for $C_6H_{10}O_3$: 130.15.

The minor product was identified as ***cis*-2,3-epoxycyclohexan-1-yl hydroperoxide (*cis*-5i)** on the basis of the following data (from *trans:cis* mixture): ^1H NMR ($CDCl_3$): δ 1.10−2.10 (m, 6H, overlapped with *trans*), 3.37 (m, 1H), 3.54 (dd, J = 4.15, 2.25 Hz, 1H), 4.39 (ddd, J = 10.56, 5.18, 2.25 Hz, 1H), 9.44 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.77, 22.89, 23.00, 52.15, 54.28, 80.11; MS (EI, 70 eV) m/z 130(M^+, 0.2), 112(M^+-18, 14), 97(80), 83(20), 79(100), 70(78), 69(59), 68(45), 67(98), 57(96), 56(13), 55(97), 53(22), 41(91); calcd for $C_6H_{10}O_3$: 130.15. The mixture of ***trans*-5i/*cis*-5i** was silylated with *N,O*-bis-(trimethylsilyl)acetamide to afford a mixture of [(*trans*/*cis*-2,3-epoxycyclohexan-1-yl)dioxy]trimethylsilane which was used for the C,H analysis. Anal. Calcd for $C_9H_{18}O_3Si$: C, 53.43; H, 8.97. Found C, 54.09; H, 8.84.

Epoxidation of 2j by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **3-methyl-*trans*-1,2-epoxycyclohexane (*trans*-5j)** by comparing its NMR properties with those in the literature[52,53] and on the basis of the following data: a colorless liquid; ^1H NMR ($CDCl_3$) δ 0.75−0.95 (m, 1H), 1.067 (d, J = 7.32 Hz, 3H), 1.25−1.50 (m, 2H), 1.50−1.80 (m, 2H), 1.90−2.10 (m, 2H), 2.83 (d, J = 3.91 Hz, 1H), 3.14 (dd, J = 3.985, 1.845 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 17.14, 19.21, 24.75, 29.05, 29.21, 52.74, 57.22; MS (EI, 70 eV) m/z 112 (M^+, 2), 111(3), 97(79), 83(31), 79(20), 71(29), 69(35), 68(100), 67(74), 57(27), 56(49), 55(67), 53(16), 43(17), 41(50); calcd for $C_7H_{12}O$: 112.17.

The second product was identified as **3-methyl-*cis*-1,2-epoxycyclohexane (*cis*-5j)** by comparing its NMR properties with those in the literature[52,53] and on the basis of the following data: a colorless liquid; ^1H NMR ($CDCl_3$) δ 1.09 (d, J = 6.89 Hz, 3H), 1.10−2.15 (m, 7H), 3.018 (dd, J = 3.535, 2.565 Hz, 1H), 3.16 (dd, J = 4.15 and 4.15 Hz, (or t, J = 4.15 Hz), 1H); ^{13}C NMR ($CDCl_3$) δ 18.52, 20.26, 23.65, 27.02, 30.09, 53.07, 57.03; MS (EI, 70 eV) m/z 112 (M^+, 2), 111(2), 97(97), 83(36), 79(25), 71(27), 69(31), 68(100), 67(73), 57(25), 56(48), 55(64), 53(18), 43(17), 41(54); calcd for $C_7H_{12}O$: 112.17.

Epoxidation of 2k by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **3-ethyl-*trans*-1,2-epoxycyclohexane (*trans*-5k)** by comparing its ^1H NMR spectral data with those in the literature[20] and on the basis of the following data: a colorless liquid; ^1H NMR ($CDCl_3$) δ 0.75−0.95 (m, 1H), 0.984 (t, J = 7.40 Hz, 3H), 1.05−2.00 (m, 7H), 2.05 (m, 1H), 2.87 (d, J = 3.90 Hz, 1H), 3.14 (dd, J = 4.04, 2.10 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.73, 17.31, 25.02, 26.92, 26.96, 36.00, 52.82, 56.32; MS (EI, 70 eV) m/z 126 (M^+, 2), 111(55), 97(69), 93(12), 83(22), 82(34), 79(22), 70(23), 69(21), 67(100), 57(17), 55(66), 43(12), 41(44); calcd for $C_8H_{14}O$: 126.20.

The second product was identified as **3-ethyl-*cis*-1,2-epoxycyclohexane (*cis*-5k)** by comparing its ^1H NMR spectral data[20] with those in the literature and on the basis of the following data: a colorless liquid; ^1H NMR ($CDCl_3$) δ 0.999 (t, J = 7.39 Hz, 3H), 1.05−2.00 (m, 7H), 2.10 (m, 1H), 3.104 (dd, J = 4.04, 2.22 Hz, 1H), 3.16 (dd, J = 4.055, 8.31 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 11.73, 20.14, 24.02, 24.93, 26.26, 36.82, 52.81, 55.54; MS (EI, 70 eV) m/z 126 (M^+, 2), 111(58), 97(70), 93(13), 83(22), 82(38), 79(24), 70(27), 69(23), 67(100), 57(19), 55(68), 43(14), 41(45); calcd for $C_8H_{14}O$: 126.20.

Epoxidation of 2l by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **3-isobutyl-*trans*-1,2-epoxycyclohexane (*trans*-5l)** on the basis of the following data: a colorless liquid; ^1H NMR ($CDCl_3$) δ 0.70−0.85 (m, 1H), 0.90 (d, J = 6.59 Hz, 3H), 0.93 (d, J = 6.59 Hz, 3H), 1.15−1.50 (m, 4H), 1.50−2.00 (m, 4H), 2.00−2.15 (m, 1H), 2.84 (d, J = 3.96 Hz, 1H), 3.13 (m or ddd, 1H); ^{13}C NMR ($CDCl_3$) δ 17.33, 22.25, 23.16, 24.98, 25.13, 27.48, 31.99, 43.45, 52.80, 56.74; MS (EI, 70 eV) m/z 154(M^+, 0.06), 139(1), 111(100), 95(28), 93(23), 79(27), 68(29), 67(52), 55(47), 41(69); calcd for $C_{10}H_{18}O$: 154.25. Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.82; H, 11.71.

The second product was identified a **3-isobutyl-*cis*-1,2-epoxycyclohexane (*cis*-5l)** on the basis of a comparision of NMR data with the *trans* isomer and the following data: a colorless liquid; ^1H NMR ($CDCl_3$) δ 0.91 (d, J = 6.24 Hz, 3H), 0.93 (d, J = 6.24 Hz, 3H), 1.00−1.30 (m, 3H), 1.30−1.60 (m, 3H), 1.60−2.00 (m, 4H), 3.05 (dd, J = 3.91, 2.69 Hz, 1H), 3.17 (dd or apt t, J = 4.15 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 20.15, 22.82, 22.94, 24.08, 24.91, 25.43, 32.59, 42.60, 53.09, 56.00; MS (EI, 70 eV) m/z 154(M^+, 0.08), 139(1), 111(100), 95(29), 93(23), 79(28), 68(29), 67(50), 55(48), 41(62); calcd for $C_{10}H_{18}O$: 154.25.

Epoxidation of 2m by 1. The general procedure was followed to give a residue which was found to contain a major and a minor product. The products were separated by preparative GLC. The major product was identified as **3-*tert*-butyl-*trans*-1,2-epoxycyclohexane (*trans*-5m)**[52] by comparing its ^1H NMR spectral data and properties with those in the literature[27] and on the basis of the following data: a colorless liquid: ^1H NMR ($CDCl_3$) δ 0.75−1.00 (m, 1H), 0.96 (s, 9H), 1.20−1.70 (m, 5H), 2.00−2.15 (m, 1H), 3.03 (d, J = 3.90 Hz, 1H), 3.14 (dd, J = 3.90, 2.00 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 17.80, 22.74, 25.08, 27.37, 32.58, 44.69, 53.13, 54.08; MS (EI, 70 eV) m/z 154(M^+, 0.5), 139(35), 121(7), 98(18), 97(100), 95(23), 83(20), 79(34), 70(21), 69(25), 57(59), 55(30), 43(17), 41(49); calcd for $C_{10}H_{18}O$:154.24.

The minor product was identified as **3-*tert*-butyl-*cis*-1,2-epoxycyclohexane (*cis*-5m)** on the basis of the following data: MS (EI, 70 eV) m/z 154(M^+, 0.5), 139(35), 121(7), 98(18), 97(100), 95(23), 83(20), 79(34), 70(21), 69(25), 57(59), 55(30), 43(17), 41(49); calcd for $C_{10}H_{18}O$:154.24. Insufficient sample was available for NMR spectral determination.

Epoxidation of 2n by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **3-(trifluoromethyl)-*trans*-1,2-epoxycyclohexane (*trans*-5n)** on the basis of the following data: a colorless liquid; ^1H NMR ($CDCl_3$) δ 1.15−1.60 (m, 3H), 1.65−1.90 (m, 2H), 2.05−2.25 (m, 1H), 2.59 (m, 1H), 3.20 (dd, J = 3.90, 0.49 Hz, 1H), 3.23 (dd, J = 3.90, 1.87 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.85, 20.41 (q, $^4J_{C-F}$ = 2.60 Hz), 23.99, 39.93 (q, $^2J_{C-F}$ = 25.90 Hz), 49.82 (q, $^3J_{C-F}$ = 4.23 Hz), 51.93, 126.76 (q, $^1J_{C-F}$ = 278.66 Hz); ^{19}F NMR ($CDCl_3$) δ −71.90 (d, J = 10.0 Hz, 3F); MS (EI, 70eV) m/z 167(M + 1, 0.5), 166(M^+, 7), 165(18), 151(93), 136(10), 125(8), 103(25), 97(100), 83(10), 77(55), 69(42), 54(55), 41(34); calcd for $C_7H_9F_3O$: 166.15. Anal. Calcd for $C_7H_9F_3O$: C, 50.61; H, 5.46. Found: C, 51.13; H, 5.59.

The second product was identified as **3-(trifluoromethyl)-*cis*-1,2-epoxycyclohexane (*cis*-5n)** on the basis of a compa-

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rision of NMR data with the *trans* isomer and the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.15−1.40 (m, 1H), 1.45−1.75 (m, 3H), 1.75−2.05 (m, 2H), 2.54 (m, 1H), 3.19 (dd, J = 4.15, 4.15 Hz, 1H), 3.30 (dd, J = 4.05, 1.87 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.14 (q, $^4J_{C-F}$ = 2.10 Hz), 19.34, 22.61, 40.83 (q, $^2J_{C-F}$ = 26.37 Hz), 49.29 (q, $^3J_{C-F}$ = 3.30 Hz), 50.55, 126.95 (q, $^1J_{C-F}$ = 279.70 Hz); ^{19}F NMR ($CDCl_3$) δ − 71.11 (d, J = 9.0 Hz, 3F); MS (EI, 70eV) m/z 167(M + 1, 0.3), 166(M$^+$, 5), 165(17), 151(88), 136(9), 125(9), 103(20), 97(100), 83(11), 77(50), 69(54), 54(47), 41(34); calcd for $C_7H_9F_3O$: 166.15.

Epoxidation of 2o by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **3-phenyl-*trans*-1,2-epoxycyclohexane (*trans*-5o)**[54] on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.18−1.70 (m, 3H), 2.05−2.25 (m, 1H), 3.14 (dd, J = 9.86, 6.00 Hz, 1H), 3.20 (d, J = 3.85 Hz, 1H), 3.31 (dd, J = 3.87, 1.72 Hz, 1H), 7.10−7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 16.88, 24.54, 29.82, 41.22, 52.72, 56.11, 126.24, 127.63, 128.39, 144.04; MS (EI, 70 eV) m/z 175(M + 1, 3), 174(M$^+$, 26), 146(16), 145(23), 131(25), 130(73), 129(50), 128(16), 117(100), 115(70), 104(37), 103(30), 91(84), 78(24), 77(35), 65(18), 51(20), 41(7); calcd for $C_{12}H_{14}O$: 174.23. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.51; H, 7.94.

The minor product was identified as **3-phenyl-*cis*-1,2-epoxycyclohexane (*cis*-5o)** on the basis of a comparision of NMR data with the *trans* isomer and the following data (from *trans:cis* mixture): a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.18−2.10 (m, 6H), 2.97 (m, 1H), 3.20 (m, 1H), 3.26 (m, 1H), 7.10−7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.57, 23.05, 27.39, 42.89, 51.99, 56.01, 124.94, 126.31, 128.27, 144.12; MS (EI, 70 eV) m/z 175(M + 1, 3), 174(M$^+$, 26), 146(16), 145(23), 131(25), 130(73), 129(50), 128(16), 117(100), 115(70), 104(37), 103(30), 91(84), 78(24), 77(35), 65(18), 51(20), 41(7); calcd for $C_{12}H_{14}O$: 174.23.

Epoxidation of 2p by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as ***trans*-2,3-epoxycyclohexane-1-carbonitrile (*trans*-5p)**[55] on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$): δ 1.30−1.70 (m, 3H), 1.70−2.10 (m, 3H), 3.14 (dd, J = 6.65, 6.00 Hz, 1H), 3.24 (m, 1H), 3.34 (d, J = 3.70 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 16.50, 22.89, 23.26, 27.01, 51.46, 51.67, 119.69; MS (EI, 70 eV) m/z 123(M$^+$, 3), 122(6), 108(20), 94(37), 80(25), 70(30), 69(29), 68(38), 67(55), 57(7), 55(28), 54(100), 42(24), 41(26); calcd for C_7H_9NO: 123.16.

The second product was also isolated as a colorless liquid and was identified as ***cis*-2,3-epoxycyclohexane-1-carbonitrile (*cis*-5p)** on the basis the following data: ^{1}H NMR ($CDCl_3$) δ 1.15−1.40 (m, 1H), 1.50−2.10 (m, 5H), 3.08 (m, 1H), 3.25 (ddd, J = 6.24, 3.71, 1.19 Hz, 1H), 3.31 (dd, J = 3.47, 3.36 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 17.84, 22.80, 23.49, 27.76, 50.50, 52.42, 119.64; MS (EI, 70 eV) m/z 123(M$^+$, 2), 122(4), 108(14), 94(28), 80(24), 70(34), 69(26), 68(35), 67(55), 57(11), 55(28), 54(100), 42(23), 41(29); calcd for C_7H_9NO: 123.16. Anal. Calcd for C_7H_9NO: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.17; H, 7.41, N, 11.48.

Epoxidation of 2q by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **3-chloro-*trans*-1,2-epoxycyclohexane (*trans*-5q)** by comparing its NMR spectral data[56,57] with those in the literature and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.20−2.15 (m, 6H), 3.15−3.40 (m, 2H), 4.37 (t, J = 5.1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.96, 23.07, 28.78, 52.75, 54.55, 55.12; MS (EI, 70 eV) m/z 132(M$^+$, 0.2), 98(6), 97(M$^+$-Cl, 94), 88(43), 79(71), 69(35), 68(28), 67(68), 57(100), 53(19), 41(55); calcd for C_6H_9ClO: 132.59.

The second product was identified as **3-chloro-*cis*-1,2-epoxycyclohexane (*cis*-5q)** by comparing its NMR spectral data[57] with those in the literature and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.20−2.10 (m, 6H), 3.35 (m, 2H), 4.29 (ddd, J= 9.53, 5.86, 1.92 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.91, 22.47, 29.62, 55.41, 56.58, 57.44; MS (EI, 70 eV) m/z 98(4), 97(M$^+$-Cl, 74), 88(22), 79(43), 69(24), 68(21), 67(49), 57(100), 53(17), 41(54); calcd for C_6H_9ClO: 132.59.

Epoxidation of 2r by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **3-bromo-*trans*-1,2-epoxycyclohexane (*trans*-5r)** by comparing its ^{1}H NMR spectral data[58,59] with those in the literature and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.25.1.95 (m, 1H), 1.80−2.20 (m, 3H), 2.50−2.80 (m, 2H), 3.27 (dd, J = 5.89, 2.93 Hz, 1H), 3.42 (dd, J = 3.74, 1.64 Hz, 1H), 4.48 (t, J = 4.77 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.77, 22.88, 28.59, 47.55, 52.92, 55.33; MS (EI, 70 eV): m/z 134(3), 132(3), 98(6), 97(M$^+$-Br, 100), 79(56), 77(10), 69(20), 67(36), 55(16), 53(12), 43(12), 41(40); calcd for C_6H_9BrO: 177.05.

The second product was identified as **3-bromo-*cis*-1,2-epoxycyclohexane (*cis*-5r)** by comparing its ^{1}H NMR spectral data[58,59] with those in the literature and on the basis of the following data: a colorless liquid, ^{1}H NMR ($CDCl_3$) δ 1.15−2.05 (m, 6H), 3.40−3.50 (m, 2H), 4.37 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 15.77, 22.80, 28.59, 55.71, 52.92, 55.33; MS (EI, 70 eV) m/z 134(2), 132(2), 98(6), 97(M$^+$-Br, 100), 79(36), 77(8), 69(12), 67(23), 55(10), 53(9), 43(9), 41(33); calcd for C_6H_9BrO: 177.05.

Epoxidation of 3a by 1. The general procedure was followed to give a residue which was found to contain three major products. The products were separated by preparative GLC. One of these products was identified as **3-methyl-*trans*-2,3-epoxycyclohexan-1-ol (*trans*-6a)** by comparing its NMR spectral data[60] spectral data with those in the literature and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.10−2.00 (m, 6H), 1.34 (s, 3H), 2.35 (br s, 1H) 2.92 (s, 1H), 3.90−4.10 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 15.78, 23.31, 29.56, 30.00, 58.90, 63.40, 66.66; MS (EI, 70 eV) m/z 128(M$^+$, 0.3), 110(2), 95(4), 84(17), 71(82), 70(100), 67(11), 60(20), 59(18), 58(16), 57(25), 55(24), 43(50); calcd for $C_7H_{12}O_2$: 128.17.

The second product was identified as **3-methyl-*cis*-2,3-epoxycyclohexan-1-ol (*cis*-6a)** by comparing its NMR spectral data[40] with those in the literature and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.20−2.10 (m, 6H), 1.35 (s, 3H), 1.50 (br s, 1H), 3.15 (d, J = 3.42 Hz, 1H), 4.01 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.01, 23.70, 28.52, 28.63, 61.40, 62.32, 66.59; MS (EI, 70 eV) m/z 128(M$^+$,1), 110(10), 95(4), 84(24), 71(80), 70(100), 67(14), 60(18), 59(17), 57(29), 55(23), 43(52); calcd for $C_7H_{12}O_2$: 128.17.

The third product was identified as **3-methyl-2-cyclohexen-1-one (9)** by comparing its NMR[40] and mass spectral data[42] with those in the literature and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.90−2.10 (m, 2H), 1.96 (s, 3H), 2.20−2.45 (m, 4H), 5.88 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 22.57, 24.46, 30.95, 36.98, 126.54, 162.51, 199.43; MS (EI, 70 eV) m/z 111(M + 1, 3), 110(M$^+$,41), 83(5), 82(100), 67(7), 54(19), 41(3); calcd for $C_7H_{10}O$: 110.15.

Epoxidation of 3b by 1. The general procedure was followed to give a residue which was found to contain two major and two minor products. The products were separated by preparative GLC. One of the major products was identified as **3-methoxy-*trans*-1,2-epoxy-1-methylcyclohexane (*trans*-6b)** on the basis of the following data: a colorless liquid; ^{1}H

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NMR ($CDCl_3$) δ 1.10−2.00 (m, 6H), 1.33 (s, 3H), 2.94 (s, 1H), 3.44 (s, 3H), 3.47 (dd, J = 8.70, 5.76 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.78, 23.31, 26.83, 29.63, 56.87, 58.57, 61.18, 75.70; MS (EI, 70 eV) m/z 142(M^+, 0.25), 95(3), 86(6), 85(100), 84(7), 74(10), 72(12), 71(49), 55(17), 43(21), 41(16); calcd for $C_8H_{14}O_2$: 142.19. Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.65; H, 9.59.

One of the minor products was identified as **3-methoxy-*cis*-1,2-epoxy-1-methylcyclohexane (*cis*-6b)** on the basis of the following data: MS (EI, 70 eV) m/z 142(M^+, 4), 110(4), 95(3), 85(5), 84(100), 83(26), 59(45), 55(19), 41(9); calcd for $C_8H_{14}O_2$: 142.19. No NMR data were obtained for the *cis* epoxide due to the very small quantity of sample.

The second major product was identified as **3-methyl-2-cyclohexen-1-one (9)** as described above.

The second minor product was also isolated and identified as **3-methyl-2,3-epoxycyclohexan-1-one** by comparing its NMR[40] and mass[42] spectral data with those in the literature and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 3H), 1.55−1.75 (m, 1H), 1.75−2.25 (m, 4H), 2.40−2.60 (m, 1H), 3.07 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.26, 22.27, 28.44, 35.71, 61.97, 62.41, 206.46; MS (EI, 70 eV) m/z 127(M + 1, 6), 126(M^+, 80), 110(24), 98(21), 97(60), 83(43), 82(60), 81(26), 71(89), 69(51), 55(100), 43(62), 42(22), 41(79); calcd for $C_7H_{10}O_2$: 126.15.

Epoxidation of 3c by 1. The general procedure was followed to give a residue which was found to contain three products. The products were separated by preparative GLC. One of these products was identified as **[(3-methyl-*trans*-2,3-epoxycyclohexan-1-yl)oxy]trimethylsilane (*trans*-6c)** on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.00−2.00 (m, 6H), 1.31 (s, 3H), 2.84 (s, 1H), 3.89 (dd, J = 8.67, 5.98 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.11, 15.96, 23.32, 29.67, 30.78, 58.83, 64.05, 67.31; MS (EI, 70 eV) m/z 186(M + 1 − CH_3, 0.09), 185(M^+-CH_3, 0.05), 171(16), 129(41), 115(6), 105(13), 101(7), 89(7), 79(11), 75(100), 73(64), 59(7), 45(10); calcd for $C_{10}H_{20}O_2Si$: 200.35. Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 59.62; H, 10.00.

The second product, a minor product, was identified as **[(3-methyl-*cis*-2,3-epoxycyclohexan-1-yl)oxy]trimethylsilane (*cis*-6c)** on the basis of a comparision of NMR data with the *trans* isomer and the following data: ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9H), 1.10−1.85 (m, 6H), 1.31 (s, 3H), 2.96 (d, J = 1.90 Hz, 1H), 4.00 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 0.45, 20.19, 24.28, 27.76, 28.04, 60.62, 63.15, 69.44; MS (EI, 70 eV) m/z 185(M^+-CH_3, 0.05), 171(9), 129(66), 115(6), 105(21), 101(12), 89(7), 79(18), 75(100), 73(55), 59(13), 45(13); calcd for $C_{10}H_{20}O_2Si$: 200.35.

The second minor product was identified as **3-methyl-2-cyclohexen-1-one (9)** as described previously.

Epoxidation of 3d by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **3-(acetyloxy)-*trans*-1,2-epoxy-1-methylcyclohexane (*trans*-6d)** on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.10−2.00 (m, 6H), 1.34 (s, 3H), 2.09 (s, 3H), 2.89 (s, 1H), 5.00 (dd, J = 7.95, 5.98 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 15.68, 21.17, 23.14, 26.20, 29.19, 58.36, 60.49, 68.78, 169.92; MS (EI, 70 eV) m/z 170(M^+, 0.1), 128(5), 127(3), 113(7), 112(52), 95(7), 84(16), 81(10), 71(19), 70(72), 67(13), 55(14), 43(100); calcd for $C_9H_{14}O_3$: 170.20. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.51; H, 8.29.

The second product was identified as **3-(acetyloxy)-*cis*-1,2-epoxy-1-methylcyclohexane (*cis*-6d)** on the basis of a comparison of NMR data with the *trans* isomer and the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.10−2.00 (m, 6H), 1.33 (s, 3H), 2.10 (s, 3H), 3.15 (d, J = 2.44 Hz, 1H), 5.11 (ddd, J = 8.36, 5.67, 2.47 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.22, 21.28, 23.94, 24.35, 28.07, 59.61, 60.37, 70.77, 170.70; MS (EI, 70 eV) m/z 170(M^+, 0.1), 128(4), 127(2), 113(4), 112(42), 95(5), 84(13), 81(8), 71(18), 70(75), 67(11), 55(12), 43(100); calcd for $C_9H_{14}O_3$: 170.20.

Epoxidation of 3e by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **1,3-dimethyl-*trans*-1,2-epoxycyclohexane (*trans*-6e)**[61] on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.70−0.90 (m, 1H), 1.05 (d, J = 7.27 Hz, 3H), 1.20−1.45 (m, 2H), 1.30 (s, 3H), 1.45−1.70 (m, 2H), 1.90 (m, 1H), 1.94 (m, 1H), 2.66 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 18.50, 19.66, 23.83, 29.75, 29.78, 30.18, 58.10, 64.76; MS (EI, 70 eV) m/z 126(M^+, 4), 111(57), 108(9), 97(35), 93(22), 83(54), 71(100), 69(35), 68(38), 67(38), 58(43), 56(30), 55(59), 43(95), 41(45); calcd for $C_8H_{14}O$: 126.19.

The second product was identified as **1,3-dimethyl-*cis*-1,2-epoxycyclohexane (*cis*-6e)**[61] on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.00−1.25 (m, 2H), 1.06 (d, J = 6.9 Hz, 3H), 1.25−1.85 (m, 4H), 1.30 (s, 3H), 1.92 (m, 1H), 2.86 (d, J = 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.09, 20.28, 24.41, 26.84, 29.07, 30.02, 58.63, 64.42; MS (EI, 70 eV) m/z 126(M^+, 5), 111(54), 108(8), 97(35), 93(20), 83(54), 71(100), 69(37), 68(39), 67(36), 58(39), 56(34), 55(64), 43(96), 41(43); calcd for $C_8H_{14}O$: 126.19.

Epoxidation of 4a by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as ***trans*-2,3-epoxycyclohexane-1-methanol (*trans*-7a)**[62] on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.80−1.10 (m, 1H), 1.20−1.80 (m, 4H), 1.88 (br s, 1H), 1.95−2.08 (m, 1H), 2.12 (m, 1H), 3.11 (d, J = 3.91 Hz, 1H), 3.19 (dd, J = 3.91, 1.95 Hz, 1H), 3.63 (dd, J = 10.70, 7.08 Hz, 1H), 3.72 (dd, J = 10.70, 5.65 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 17.11, 23.85, 24.81, 37.48, 52.76, 54.08, 65.13; MS (EI, 70 eV) m/z 128(M^+, 1), 127(11), 110(20), 98(9), 97(100), 95(25), 85(10), 84(10), 83(21), 82(22), 81(30), 80(9), 79(70), 77(20), 73(8), 71(20), 70(26), 69(35), 68(14), 67(69), 66(10), 57(50), 56(13), 55(47), 54(18), 53(19), 43(23); calcd for $C_7H_{12}O_2$: 128.17.

The second product was identified as ***cis*-2,3-epoxycyclohexane-1-methanol (*cis*-7a)** on the basis of a comparision of NMR data with the *trans* isomer and the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.10−1.65 (m, 4H), 1.75−1.85 (m, 2H), 2.06 (m, 1H), 2.22 (br s, 1H), 3.21 (ddd, J = 5.54, 3.74, 1.71 Hz, 1H), 3.25 (dd, J = 4.16, 2.49 Hz, 1H), 3.68 (dd, J = 10.35, 6.01 Hz, 1H), 3.74 (dd, J = 10.26, 7.81 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.28, 21.73, 23.85, 37.04, 52.26, 53.70, 65.23; MS (EI, 70 eV) m/z 128(M^+, 0.5), 127(9), 110(15), 98(21), 97(100), 95(21), 85(9), 84(19), 83(44), 82(20), 81(38), 80(12), 79(80), 77(22), 73(7), 71(16), 70(64), 69(39), 68(18), 67(74), 66(11), 57(45), 56(13), 55(55), 54(19), 53(20), 43(25), 42(10), 41(78); Calcd for $C_7H_{12}O_2$: 128.17.

Epoxidation of 4b by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **3-(bromomethyl)-*trans*-1,2-epoxycyclohexane (*trans*-7b)** by comparing its NMR spectral[63] data with those in the literature and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.05−1.20 (m, 1H), 1.30−1.50 (m, 2H), 1.60−1.80 (m, 2H), 2.03−2.15 (m, 1H), 2.28 (m, 1H), 3.08 (d, J = 3.72 Hz, 1H), 3.20 (dd, $J_{1,2}$ = 3.66 and $J_{2,3}$ = 2.00 Hz, 1H, 3.40 (dd, $J_{a,b}$ = 10.15 and $J_{a,3}$ = 6.41 Hz, 1H), 3.54 (dd, $J_{a,b}$ = 10.16 and $J_{b,3}$ = 5.19 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 16.88, 24.56, 26.29, 36.53, 36.85, 52.71, 55.02; MS (EI, 70 eV) m/z 191 (M^+, 0.2), 149(2), 148(3), 146(3), 112(5), 111(65), 97(23), 93(54), 91(14), 83(13), 81(16), 79(20), 77(14), 69(17), 68(8), 67(100), 57(20), 55(75), 54(10), 53(18), 43(19), 41(41); calcd for $C_7H_{11}BrO$: 191.07.

The major product was identified as **3-(bromomethyl)-*cis*-1,2-epoxycyclohexane (*cis*-7b)** on the basis of a comparison of NMR data with the known *trans* isomer and the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.10−1.35 (m, 2H), 1.40−1.60 (m, 2H), 1.75−1.95 (m, 2H), 2.23 (m, 1H), 3.24 (ddd, J = 7.63, 5.34, 1.54 Hz, 1H), 3.295 (dd, $J_{1,2}$ = 4.10 and $J_{2,3}$ =

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2.50 Hz, 1H), 3.346 (dd, $J_{a,b}$ = 9.84 and $J_{a,3}$ = 6.67 Hz, 1H), 3.54 (dd, $J_{a,b}$ = 9.84 and $J_{b,3}$ = 8.18 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.51, 23.63, 24.46, 35.35, 38.09, 53.08, 53.85; MS (EI, 70 eV) *m/z* 191(M^+, 0.07), 149(1), 148(2), 146(2), 112(4), 111(63), 97(19), 93(47), 91(10), 81(14), 79(18), 77(11), 69(15), 68(8), 67(100), 57(18), 55(72), 54(9), 53(17), 43(20), 41(48); calcd for $C_7H_{11}BrO$: 191.07.

Epoxidation of 4c by 1. The general procedure was followed to give a residue which was found to contain two products. The products could not be separated by preparative GLC. A mixture of the products was obtained by preparative GLC. One of these products was identified as **3-[(acetyloxy)-methyl]-*trans*-1,2-epoxycyclohexane (*trans*-7c)** on the basis of the following data: (from *cis:trans* mixture) ^{1}H NMR ($CDCl_3$) δ 0.85−1.05 (m, 1H), 2.08 (s, 3H), 3.01 (d, J = 3.91 Hz, 1H), 3.21 (dd, J = 3.91, 1.60 Hz, 1H) 3.95−4.20 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 16.80, 20.74, 21.60, 23.77, 34.12, 52.10, 53.35, 65.95, 170.71. The mass spectrum of the *trans*-product was identical with that of the *cis*-product.

The second product was identified as **3-[(acetyloxy)-methyl]-*cis*-1,2-epoxycyclohexane (*cis*-7c)** on the basis of the following data: (from *cis:trans* mixture) ^{1}H NMR ($CDCl_3$) δ 1.10−1.95 (m, 6H), 2.07 (s, 3H), 2.15−2.25 (m, 1H), 3.18 (m, 2H), 3.95−4.20 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.95, 20.79, 23.53, 24.49, 34.31, 52.31, 52.70, 65.95, 170.63; MS (EI, 70 eV) *m/z* 127(M^+-$CH_3C{=}O{-}O$, 5), 110(100), 95(90), 83(12), 82(67), 81(76), 67(48), 57(8), 55(21), 43(62); calcd for $C_9H_{14}O_3$: 170.21. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.51; H, 8.29.

Epoxidation of 4d by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **(*trans*-1,2-epoxycyclohexan-3-yl)methyl acetate (*trans*-7d)** by comparing its NMR spectral data[20,64] spectral data with those in the literature and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.85−1.05 (m, 1H), 1.30−1.45 (m, 2H), 1.55−1.80 (m, 3H), 2.00−2.15 (m, 1H), 2.36 (m, 1H), 2.46 (AB m, 2H), 2.94 (d, J = 3.91 Hz, 1H), 3.17 (dd, J = 3.91, 2.00 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 17.02, 24.53, 26.82, 31.43, 38.29, 51.72, 52.65, 55.48, 172.42; MS (EI, 70 eV) *m/z* 170(M^+, 1), 155(2), 139(29), 111(30), 110(28), 99(100), 97(65), 84(27), 79(23), 74(37), 67(56), 55(58), 41(37); calcd for $C_9H_{14}O_3$: 170.21.

The major product was identified as **(*cis*-1,2-epoxycyclohexan-3-yl)methyl acetate (*cis*-7d)** by comparing its NMR spectral data[20,64] with those in the literature and on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.05−1.35 (m, 2H), 1.35−1.60 (m, 2H), 1.70−1.95 (m, 2H), 2.35 (m, 1H), 2.352 (dd, J = 17.79, 6.85 Hz, 1H), 2.58 (dd, J = 17.82, 9.58 Hz, 1H), 3.16 (dd, J = 3.95, 2.15 Hz, 1H), 3.20 (dd, J = 3.94, 3.47 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 19.59, 23.60, 25.08, 31.95, 37.61, 51.62, 53.28, 55.02, 172.98; MS (EI, 70 eV) *m/z* 170(M^+, 1), 155(3), 138(16), 121(7), 111(31), 110(34), 99(100), 97(64), 84(29), 79(37), 67(59), 55(54), 41(35); calcd for $C_9H_{14}O_3$: 170.21.

Epoxidation of 4e by 1. The general procedure was followed to give a residue which was found to contain two products. The products were separated by preparative GLC. One of these products was identified as **(*trans*-1,2-epoxycyclohexan-3-yl)ethyl acetate (*trans*-7e)** on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 0.85−1.05 (m, 1H), 1.10−1.50 (m, 2H), 1.27 (t, J = 7.13 Hz, 3H), 1.60−2.00 (m, 2H), 2.00−2.15 (m, 1H), 2.36 (m, 1H), 2.42 (AB m, 2H), 2.95 (d, J = 3.91 Hz, 1H), 3.166 (dd, J = 3.91, 2.00 Hz, 1H), 4.16 (q, J = 7.13 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.33, 17.03, 24.55, 26.78, 31.46, 38.57, 52.64, 55.52, 60.50, 171.95; MS (EI, 70 eV) *m/z* 184(M^+, 21), 139(45), 113(100), 110(53), 97(68), 95(36), 81(56), 67(81), 55(77), 41(45); calcd for $C_{10}H_{16}O_3$: 184.24. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.04; H, 8.80.

The major product was identified as **(*cis*-1,2-epoxycyclohexan-3-yl)ethyl acetate (*cis*-7e)** on the basis of the following data: a colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.05−1.60 (m, 4H), 1.26 (t, J = 7.14 Hz, 3H), 1.75−1.95 (m, 2H), 2.33 (dd, J = 18.04, 6.86 Hz, 1H), 2.35 (m, 1H), 2.57 (dd, J = 18.01, 9.70 Hz, 1H), 3.16 (dd, J = 4.02, 1.98 Hz, 1H), 3.20 (dd, J = 3.94, 3.47 Hz, 1H), 4.15 (q, J = 7.14 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.33, 19.63, 23.61, 25.07, 31.98, 37.89, 53.25, 55.06, 60.39, 172.51; MS (EI, 70 eV) *m/z* 184(M^+, 1), 155(18), 138(24), 121-(16), 113(93), 110(56), 97(68), 93(43), 79(74), 67(100), 55(89), 41(56); calcd for $C_{10}H_{16}O_3$: 184.24.

Epoxidation of 4f by 1. The general procedure was followed to give a colorless solid. ^{1}H NMR analysis of the reaction mixture indicated the presence of *cis* epoxide as the major product and *trans* epoxide as the minor product. Separation of the products was accomplished by radial chromatography of the residue on a Chromatotron (silica gel plate), using acetone/CH_2Cl_2 (20:80) as the eluent. The major product was identified as **3-(benzamidomethyl)-*cis*-1,2-epoxycyclohexane (*cis*-7f)** on the basis of the following data: colorless needles (CH_2Cl_2−hexane), mp 109−111 °C; IR (KBr) 3310, 2932, 1630 (C═N), 1578, 1536, 1311, 924, 888, 848, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15−1.65 (m, 4H), 1.75−2.00 (m, 2H), 2.29 (m, 1H), 3.22 (m, 2H), 3.61 (m, 2H), 6.76 (br s, 1H), 7.35−7.55 (m, 3H), 7.70−7.90 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.55, 22.86, 23.65, 33.98, 43.51, 52.56, 54.51, 126.78, 128.43, 131.25, 134.45, 167.50; MS (EI, 70 eV) *m/z* 232 (M + 1, 0.1), 231(M^+, 1), 134(20), 105(100), 77(21); calcd for $C_{14}H_{17}NO_2$: 231.28. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.69; H, 7.41; N, 6.05. Found: C, 72.59; H, 7.40; N, 6.03.

The minor product formed during the reaction was **3-(benzamidomethyl)-*trans*-1,2-epoxycyclohexane (*trans*-7f)** which was identified on the basis of the following data: (from *cis:trans* mixture, peaks reported here are not overlapping with the major isomer) ^{1}H NMR ($CDCl_3$) δ 0.80−1.05 (m, 1H), 2.00−2.15 (m, 1H), 3.016 (d, J = 3.91 Hz, 1H), 3.16 (m, 1H), 3.35−3.47 (m, 1H), 3.55−3.67 (m, 1H), 6.79 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.00, 24.68, 25.34, 35.47, 42.75, 52.69, 53.93, 126.80, 128.33, 131.26, 134.32, 167.72; MS (EI, 70 eV) *m/z* 231(M^+, 1), 134(40), 105(100), 77(27); calcd for $C_{14}H_{17}NO_2$: 231.28. This mass spectrum is actually that of **8-hydroxy-2-phenyl-4a,5,6,7,8,8a-hexahydro-4*H*-1,3-benzoxazine**, the thermal rearrangement product of the **3-(benzamidomethyl)-*trans*-1,2-epoxycyclohexane**.

The rearrangement product was also formed during chromatography and was isolated as a colorless viscous liquid and identified as **8-hydroxy-2-phenyl-4a,5,6,7,8,8a-hexahydro-4*H*-1,3-benzoxazine** on the basis of the following data: a colorless viscous liquid, solidifies very slowly on standing; IR (neat film) 3354(OH), 2934, 2860, 1650(C═N), 1448, 1336, 1279, 1159, 1125, 1070, 1028, 1006, 991, 974, 898, 864, 839, 782, 733, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40−2.00 (m, 6H), 2.29 (m, 1H), 3.11 (br s, 1H, OH, exchangeable with D_2O), 3.42 (dd, J = 16.87, 6.57 Hz, 1H), 3.55 (dd, J = 16.85, 5.62 Hz, 1H), 3.97 (m, 1H), 4.21 (dd, J = 6.29, 4.15 Hz, 1H), 7.30−7.55 (m, 3H), 7.80−8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.95, 25.59, 28.90, 30.00, 46.40, 68.32, 77.51, 126.84, 127.93, 130.35, 133.45, 154.19; MS (EI, 70 eV) *m/z* 232(M + 1, 0.3), 231(M^+, 2), 134(46), 105(100), 77(20); calcd for $C_{14}H_{17}NO_2$: 231.28. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.69; H, 7.41; N, 6.05. Found: C, 72.53; H, 7.38; N, 6.01.

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