# Stereoselective Construction of Quaternary Centers at Ambient Temperature by the Highly Stereocontrolled Migration of Groups Containing sp-, $sp^2$-, and $sp^3$-Hybridized Carbon Atoms

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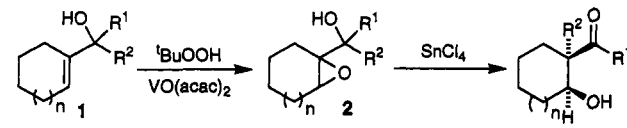
A very highly diastereoselective semipinacol rearrangement of 2,3-epoxy alcohols mediated by tin(IV) chloride at ambient temperatures is shown to be applicable to a wide variety of migrating groups including methyl, *tert*-butyl, cyclopropyl, vinyl, alkynyl, phenyl, and 2-furyl. A synthetically valuable feature is that a mixture of *syn*- and *anti*-epoxy alcohols affords only a single diastereoisomerically pure β-hydroxy ketone. Additional advantages of the reaction include the presence in the product of two adjacent stereocenters and the efficient creation of a new quaternary center, valuable features in the synthesis of a variety of natural products.

Rearrangements involving carbon-to-carbon migrations are of long-standing synthetic value and mechanistic interest. They include the Wagner–Meerwein[1] and Nametkin[2] rearrangements, the α-ketol[3] and pinacol–pinacolone rearrangements,[4–7] and semipinacol rearrangements.[8] Recently, sequential Prins cyclization–pinacol rearrangement sequences with excellent stereocontrol have been reported,[9] but control of stereochemistry during pinacol rearrangements is generally problematic.[4] A further disadvantage of both pinacol–pinacolone and most semipinacol rearrangements is the destruction of part of the unit containing two adjacent stereogenic centers.

We now report a stereoselective semipinacol rearrangement of 2,3-epoxy alchols mediated by tin(IV) chloride[10] (Scheme I). Notable features of the reaction include the presence in the product of two adjacent stereocenters, the creation of a new quaternary center, and efficient formation

**Scheme I**




of a β-hydroxy ketone (Table I). Creation of quaternary carbon centers[11] is a crucial aspect of several areas in total synthesis but is often difficult to accomplish; few general and efficient methods of constructing a quaternary center are available, and even fewer proceed with stereocontrol.[11] Of additional synthetic value is that a mixture of *syn*[12] and *anti* epoxy alcohols affords only a single diastereoisomerically pure β-hydroxy ketone. The semipinacol epoxide rearrangement, being a true rearrangement, is distinguished from pincacol "rearrangements"[13] in which dehydration occurs, as well as from rearrangements of epoxides to ketones[14] or aldehydes[15] or of epoxy ketones to diketones,[16] as has been demonstrated in related migrations induced by $TiCl_4$.[17]

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(8) Coveney, D. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 3, pp 777–732. The term "semipinacol", first used by Tiffeneau to describe a rearrangement involving migration toward the secondary carbinol center of a secondary or tertiary 1,2-diol, is now more commonly used to denote variants employing leaving groups other than OH.

(9) (a) Hopkins, M. H.; Overman, L. E.; Rishton, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 5354. (b) Hirst, G. C.; Howard, P. N.; Overman, L. E. *J. Am. Chem. Soc.* **1989**, *111*, 1514.

(10) In Lewis acid-catalyzed rearrangements of epoxides, tin(IV) chloride has been seldom used; see: Rickborn, B. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 3, pp 733–775. However, a deep-seated rearrangement involving a dyotropic shift has been reported with tin(IV) chloride: Scovell, E. G.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1978**, 529. In contrast, **3e** was not formed in appreciable quantity when a solution of epoxide **2e** in dichloromethane was saturated with HCl gas for 2 h.

(11) Martin, S. F. *Tetrahedron* **1990**, *36*, 419.

(12) Upon orienting the cycloalkenyl group and the bulkier of the other groups attached to the carbinol carbon atom to approximate coplanarity, the epoxide and hydroxyl groups then reside on the same or opposite faces, respectively referred to here as *syn* and *anti*. For a rationalization of the predominance of the *syn* isomer, see: Marson, C. M.; Benzies, D. W. M.; Hobson, A. D. *Tetrahedron* **1991**, *47*, 5491.

(13) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S. *J. Org. Chem.* **1976**, *41*, 260.

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(15) (a) Maruoka, K.; Sato, J.; Yamamoto, H. *J. Am. Chem. Soc.* **1991**, *113*, 5449. (b) Morgans, D. J.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 462.

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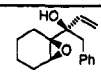
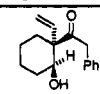
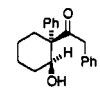
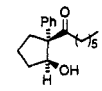
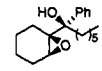
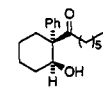
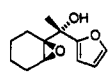
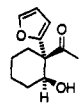
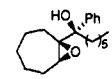
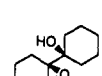
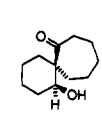
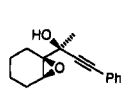
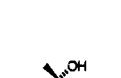
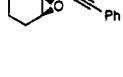
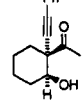
0022-3263/93/1958-5944$04.00/0 

**Table I**

| entry | epoxide[a,b] | | syn:anti[c] | product[a,d] | | yield[e] (%) | entry | epoxide[a,b] | | syn:anti[c] | product[a,d] | | yield[e] (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 |  | **2a** | |  | **3a** | 56 | 10 |  | **2i** | 100:0 |  | **3i** | 73 |
| 2 |  | **2b** | 87:13 |  | **3d** | 95 | 11 |  | **2j** | 100:0 |  | **3j** | 84 |
| 3 |  | **2c** | 85:15 |  | **3c** | 99 | 12 |  | **2k** | 100:0 |  | **3k** | 88 |
| 4 |  | **2d** | 100:0 |  | **3d** | 75 | 13 |  | **2l** | 75:25 |  | **3l** | 74 |
| 5 |  | **2e** | 0:100 |  | **3e** | 75 | 14 |  | **2m** | 62:38 |  | **3m** | 64 |
| 6 |  | **2f** | 91:9 |  | **3f** | 88 | 15 |  | **2n** | |  | **3n** | 41 |
| 7 |  | **2g** | 100:0 |  | **3g** | 43 | 16 |  | **2o** | |  | **3o** | 67 |
| 8 |  | **2g** | 0:100 |  | **3g** | 58 | 17 |  | **2p** | 80:20 |  | **3p** | 40 |
| 9 |  | **2h** | 77:23 |  | **3h** | 78 | 18 |  | **2q** | 80:20 |  | **3q** | 56 |

[a] All configurations depicted refer to racemic modifications. [b] The allylic alcohol (25 mmol) in benzene (50 mL) was stirred with aqueous $^t$BuOOH (70%, 1.3 equiv) and $VO(acac)_2$ (20 mg) at room temperature, and monitored to completion by TLC. [c] Reference 11. [d] The 2,3-epoxy alcohol (10 mmol) in dichloromethane (50 mL) was stirred at 0 °C with tin(IV) chloride (2 equiv) and monitored to completion by TLC. [e] Isolated yield.

Our particular contribution establishes the regioselective migration of a wide variety of moieties linked through a C–C bond, the migration proceeding with very high diastereoselection in every case studied. Additionally, the use of $SnCl_4$ rather than $TiCl_4$ allows the rearrangements to be conducted efficiently at 20 °C and without the need for prior protection of the hydroxylic function, for example, as an epoxy silyl ether.[17] Previous work has been largely or exclusively confined to acyclic systems. The present work shows that epoxy alcohol rearrangements can also be applied to many cyclic systems, thereby affording 1,2-difunctionalized alicycles of potential value in natural product synthesis. Epoxy silyl ether rearrangements involving 1,2-migrations of phenyl and vinyl groups in alicyclic systems using catalytic quantities of Lewis acids have been demonstrated.[18] Migrations of aryl and vinyl groups in some enantiomerically enriched 2,3-epoxy alcohols have been shown to proceed, usually with high enantiocontrol.[17,19] Although epoxy silyl ethers have been shown to undergo rearrangement to β-silyloxy aldehydes using MABR,[20] no aldehydic products were observed when $SnCl_4$ was used in the present study.

2,3-Epoxy alcohols were prepared by epoxidation of the cycloalkenyl alcohols with $^t$BuOOH and $VO(acac)_2$.[21] The allylic alcohols were prepared[22] either from the appropriate Grignard reagent and the cycloalkenyl ketone or from 1-cyclohexenyllithium[23] and the corresponding ketone. In cases where the diastereoisomeric epoxides were not readily separable, the *syn/anti* ratio[11] was determined by $^1$H NMR spectroscopy; the mixture of epoxides was then treated with $SnCl_4$.[10]

The wide variety of groups which migrate is shown in Table I. Yields reflect the relative ease of migration[4,21] of phenyl[6] and vinyl groups,[24] as compared with methyl groups.[4] The migration of an alkynyl moiety is noteworthy

(17) Maruoka, K.; Hasegawa, M.; Yamamoto, H.; Suzuki, K.; Shimazaki, M.; Tsuchihashi, G. *J. Am. Chem. Soc.* **1986**, *108*, 3827.
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(20) Maruoka, K.; Sato, J.; Yamamoto, H. *Tetrahedron* **1992**, *48*, 3749.
(21) (a) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136. (b) Sharpless, K. B.; Tanaka, S.; Yamamoto, H.; Nozaki, H.; Mioh, R. C.; Cutting, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 5254. (c) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63.
(22) Saunders, J. H. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 22.
(23) (a) For a preparation of 1-cyclohex-1-enyllithium see: Braude, E. A.; Coles, J. A. *J. Chem. Soc.* **1950**, 2014. (b) For a preparation of 1-cyclohept-1-enyllithium see: Braude, E. A.; Forbes, W. F.; Evans, E. A. *J. Chem. Soc.* **1953**, 2202.
(24) Suzuki, K.; Katayama, E.; Tsuchihashi, G. *Tetrahedron Lett.* **1984**, *25*, 1817.

(entries 7 and 8), since alkynyl groups have been found not to migrate in some pinacol rearrangements,[25] although there are exceptions.[26] A 2-furyl group has been shown[27] to migrate stereoselectively in a semipinacol rearrangement induced by $Et_3Al$, although a tertiary center was created in contrast to the quaternary carbon center formed in entry 5. Entry 6 is consistent with the migratory aptitude of the cyclopropyl moiety, which has been observed in pinacol rearrangements to be higher than that of simple alkyl groups such as methyl and 2-propyl.[28] Entry 4 reflects the preference for migration of *tert*-butyl over methyl, the partial rates for pinacol rearrangements in aqueous sulfuric acid having been determined as greater than 4000: 1.[29] Inversion at the migration terminus to give products of the relative configuration shown was confirmed by single-crystal X-ray determination of **3c**.[30]

The formation of the same diastereoisomer from either diastereoisomer of epoxy alcohol **2**, *e.g.*, entries 2, 3, 7, and 8, would appear to exclude the intermediacy of a free carbocation. Neither, however, does a simple "push-pull" mechanism[31] readily account for migration of a group of the *anti*-epoxy alcohol (*e.g.*, entry 8); if conformational mobility is restricted (for instance by coordination of both oxygen atoms to a single atom of tin), then the likely geometrical requirement of an *anti* arrangement[32] of the migrating group ($R^2$) and the epoxide oxygen cannot be met. The mechanism may be appreciably substrate-dependent, as is the pinacol–pinacolone rearrangement, for which there is no unique mechanism.[5] A possible mechanism may involve activation of the cleavage of the C–O bond of the epoxide by coordination of the epoxide oxygen atom to a Lewis acid or Brönsted acid and 1,2-migration concomitant with C–O bond cleavage in a transition state geometry resembling that of ordinary nucleophilic substitution proceeding with inversion of configuration. A colinear arrangement of the migrating group, the epoxide carbon, and the departing oxygen group would thereby be required.

The semipinacol epoxide rearrangements described herein are notable for the lack of possible competing processes, including attack by chloride and rearrangement to aldehydes or 1,2-hydride migrations to give cycloalkanones. These results show that the reaction can be effected at room temperature and in multigram quantities. Further aspects of the scope, stereochemistry, and synthetic applications of rearrangements of 2,3-epoxy alcohols are currently under investigation.

## Experimental Section

All melting points were determined with a hot-stage apparatus and are uncorrected. Chemical shifts for NMR spectra are quoted in ppm downfield from internal tetramethylsilane, and the line separations ($J$) are expressed in Hz. The following abbreviations are used to describe NMR signals: s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet; b, broad. $^{13}C$ and $^1H$ NMR spectra were obtained at operating frequencies of 68.8 and 250 MHz, respectively. Mass spectra were obtained in the chemical ionization (CI) or electron impact (EI) mode, as specified in the text. Yields are for material assessed as homogeneous by TLC and $^1H$ NMR. Thin-layer chromatography was performed on 0.2-mm aluminum-backed silica plates and visualized using ultraviolet light or developed using cerium(IV) sulfate spray. Column chromatography was performed using silica gel 60 (230–400 mesh) under gravity. Petroleum ether (40–60 fraction) and ethyl acetate were distilled prior to use. Evaporation refers to the removal of solvent under reduced pressure, unless otherwise stated.

**Formation of 2,3-Alkenols: Procedure A. 2-(1-Cyclohexenyl)propan-2-ol (1a).** A solution of 1-acetylcyclohexene (1.1 g, 8.86 mmol) in dry tetrahydrofuran (20 mL) was treated dropwise at 0 °C with a solution of methylmagnesium bromide (5.9 mL, 17.7 mmol, 3.0 M in ether). The reaction mixture was stirred at room temperature overnight and then poured into ice-cold saturated ammonium chloride solution (25 mL). The aqueous layer was separated and extracted with ether (3 × 50 mL). The combined organic extracts were washed with water (100 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography on silica using 10% ethyl acetate/petroleum ether as eluent to give **1a** as a colorless oil (0.9 g, 73%): $M^+$ 140.1203 ($C_9H_{16}O$ requires 140.120); $R_f$ = 0.59 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3340, 2915, and 1435 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 5.74 (1H, m), 3.78 (1H, s), 2.08–1.49 (8H, m) and 1.23 (6H, s); $\delta_C$ ($CDCl_3$) 143.8 (s), 118.7 (d), 72.8 (s), 28.8 (q), 25.0 (t), 24.3 (t), 23.1 (t), and 22.3 (t); $m/z$ +EI, 140 (M, 28), 139 (M − 1, 70), 125 (98), 111 (55), 97 (52), 91 (23), 79 (60), 67 (61), 59 (100), and 55 (45).

**2-(1-Cyclohexenyl)-3-buten-2-ol (1b).** Following typical procedure A (above), 1-acetylcyclohexene (4.0 g, 32.2 mmol) when treated with a solution of vinylmagnesium bromide (51.5 mL, 51.5 mmol, 3.0 M in ether) yielded a residue which was purified by column chromatography on silica using 5% ethyl acetate/petroleum ether as eluent to give **1b** as a colorless oil (1.72 g, 35%): $R_f$ = 0.36 (10% ethyl acetate/petroleum ether); $\delta_H$ ($CDCl_3$) 5.86 (1H, dd, $J$ = 19, 13 Hz), 5.71 (1H, m), 5.17 (1H, dd, $J$ = 19, 1 Hz), 5.00 (1H, dd, $J$ = 13, 1 Hz), 1.96 (4H, m), 1.51 (4H, m), and 1.32 (3H, s); $\delta_C$ ($CDCl_3$) 144.2 (d), 141.5 (s), 121.0 (d), 111.8 (t), 75.4 (s), 26.4 (q), 25.2 (t), 24.2 (t), 23.0 (t), and 22.3 (t); $m/z$ +EI 151 (M − 1, 10), 150 (17), 135 (18), 123 (80), 107 (30), 95 (50), 79 (48), 71 (32), 55 (48), and 43 (100). **1-Acetyl-2-ethenylcyclohexane** was also obtained as a colorless oil (0.52 g, 11%): $R_f$ = 0.62 (10% ethyl acetate/petroleum ether); $\delta_H$ ($CDCl_3$) 5.91 (1H, m), 5.05 (2H, m), 2.79 (1H, m), 2.58 (1H, m), 2.10 (3H, s), and 1.91-1.22 (8H, m); $\delta_C$ 141.4 (d), 138.0 (d), 115.6 (t), 114.3 (t), 56.7 (d), 53.9 (d), 43.6 (d), 41.1 (d), 31.9 (t), 31.6 (t), 29.3 (q), 28.9 (t), 28.7 (q), 25.4 (t), 25.3 (t), 24.6 (t), 23.4 (t), and 21.6 (t).

**1-(1-Cyclohexenyl)-1-phenylethanol (1c).** Following typical procedure A (above), 1-acetylcyclohexene (6.0 g, 48.3 mmol) when treated with a solution of phenylmagnesium bromide (24.2 mL, 72.5 mmol, 3.0 M in ether) gave a residue which was purified by column chromatography on silica using 10% ethyl acetate/petroleum ether as eluent to give **1c** as a colorless oil (4.6 g, 47%): $M^+$, 202.1332 ($C_{14}H_{18}O$ requires 202.1357); $R_f$ = 0.71 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3350, 2875, 1655, 1600, 1490, and 1440 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.47–7.19 (5H, m), 5.89 (1H, m), and 2.19–1.50 (11H, m); $\delta_C$ ($CDCl_3$) 146.9 (s), 142.5 (s), 127.9 (d), 126.5 (d), 125.3 (d), 121.4 (d), 76.9 (s), 28.7 (q), 25.2 (t), 24.5 (t), 22.8 (t), and 22.2 (t); $m/z$ +EI, 202 (M, 15), 187 (20), 140 (20), 129 (18), 121 (15), 105 (52), 91 (50), 77 (40), 67 (12), 55 (12), and 43 (100).

**2-(1-Cyclohexenyl)-3,3-dimethylbutan-2-ol (1d).** Following typical procedure A (above), 1-acetylcyclohexene (5.0 g, 40.3 mmol) was treated with a solution of *tert*-butyllithium (71.2 mL, 120.9 mol, 1.7 M in ether/cyclohexane) yielding a residue which was purified by column chromatography on silica using 8% ethyl acetate/petroleum ether as eluent to give **1d** as a colorless oil (1.31 g, 18%): M − 57, 125.0966 ($C_{12}H_{22}O$ − $C_4H_9$ requires 125.0966); $R_f$ = 0.62 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3450, 2960, and 1660 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 5.69 (1H, m),

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2.09 (4H, m), 1.59 (4H, m), 1.34 (1H, bs), 1.29 (3H, s), and 0.93 (9H, s); $\delta_C$ ($CDCl_3$) 142.3 (s), 123.0 (d), 78.8 (s), 38.6 (s), 27.3 (t), 26.0 (q), 25.2 (t), 23.7 (q), 23.1 (t), and 22.2 (t); *m/z* +EI, 126 (10), 125 (100), 81 (12), 67 (17), and 57 (10).

**3-(1-Cyclohexenyl)-1-phenyl-1-butyn-3-ol (1g).** Following typical procedure A (above), 1-acetylcyclohexene (3.0 g, 24.2 mmol) when treated with phenylethynyllithium [prepared from phenylacetylene (2.6 g, 25.4 mmol) and *n*-butyllithium (19.0 mL, 29.0 mmol, 1.6 M] was found to give **1g** as a colorless oil (4.66 g, 83%): $R_f$ = 0.59 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3350, 2905, 1965, 1595, 1490, and 1440 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.50–7.23 (5H, m), 6.10 1H, m), 2.23–1.49 (9H, m), and 1.65 (3H, m); $\delta_C$ ($CDCl_3$) 140.3 (s), 131.7 (d), 128.2 (d), 128.2 (d), 122.9 (s), 121.7 (d), 92.5 (s), 84.1 (s), 71.0 (s), 28.9 (q), 25.1 (t), 24.0 (t), 22.3 (t), and 22.0 (t).

**2-(1-Cyclohexenyl)-4-phenylbutan-2-ol (1h).** Following typical procedure A (above), 1-acetylcyclohexene (2.00 g, 16.1 mmol) when treated with 2-phenylethylmagnesium bromide [prepared from 1-phenyl-2-bromoethane (8.95 g, 48.4 mmol) and magnesium (1.16 g, 48.4 mmol)] yielded a residue which was purified by column chromatography on silica eluted with 15% ethyl acetate in petroleum ether to give **1h** as an oil (2.66 g, 72%): $M^+$, 230.1663 ($C_{16}H_{22}O$ requires 230.1671); $\nu_{max}$ (liquid film) 3400, 2920, 1600, and 1500 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.35–7.15 (5H, m), 5.85 (1H, m), 2.70–2.45 (2H, m), 2.15 (2H, m), 2.05 (2H, m), 1.90 (2H, m), 1.75–1.50 (4H, m and OH), and 1.40 (3H, s); $\delta_C$ ($CDCl_3$) 142.7 (s), 142.0 (s), 128.3 (d), 125.6 (d), 120.1 (d), 75.0 (s), 42.3 (t), 30.5 (t), 27.6 (q), 25.1 (t), 24.8 (t), 23.0 (t), and 22.3 (t); *m/z* +EI, 212 (18), 125 (98), 91 (100), 79 (38), and 85 (43).

**2-(1-Cyclohexenyl)-1-phenyl-3-buten-2-ol (1i).** Following typical procedure A (above), 1-(1-oxo-2-phenylethyl)cyclohexene (8.0 g, 0.040 mol) when treated with a solution of vinylmagnesium bromide (80.0 mL, 0.080 mol, 1.0 M in ether) yielded a residue which was purified by column chromatography on silica using 5% ethyl acetate/petroleum ether as eluent to give **1i** as a colorless oil (1.55 g, 17%): M − 18, 210.1444 ($C_{16}H_{20}O$ − $H_2O$ requires 210.1448); $R_f$ = 0.34 (5% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3450, 3040, 2940, 2860, 1660, 1605, 1500, and 1455 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.20 (5H, m), 6.01 (1H, dd, *J* = 17, 11 Hz), 5.68 (1H, m), 5.13 (1H, dd, *J* = 17, 1 Hz), 5.07 (1 H, dd, *J* = 11, 1 Hz), 2.97 (2H, $q_{AB}$, *J* = 16 Hz), 2.06 (4H, m), and 1.56 (4H, m); $\delta_C$ ($CDCl_3$) 142.8 (d), 140.1 (s), 136.6 (s), 130.8 (d), 127.9 (d), 126.6 (d), 122.2 (d), 112.8 (t), 77.4 (s), 45.3 (t), 25.3 (t), 25.0 (t), 23.0 (t), and 22.3 (t); *m/z* +EI, 211 (M − 17, 30), 210 (M − 18, 25), 137 (80), 119 (22), 91 (100), 79 (20), 67 (25), and 55 (42). **2-Ethenyl-1-(1-oxo-2-phenylethyl)cyclohexane** (1.90 g, 21%) was also obtained: $\delta_H$ ($CDCl_3$) 7.22 (5H, m), 5.92 (1H, m), 5.03 (2H, m), 3.70 (2H, s), 2.73 (2H, m), and 1.91–1.17 (6H, m); $\delta_C$ ($CDCl_3$) 210.8 (s), 209.8 (s), 141.4 (d), 138.4 (d), 134.4 (s), 133.9 (s), 129.7 (d), 129.6 (d), 128.5 (d), 128.1 (d), 126.8 (d), 125.3 (d), 115.6 (t), 114.6 (t), 55.0 (d), 52.1 (d), 50.1 (t), 48.5 (t), 43.8 (d), 41.4 (d), 31.9 (t), 31.3 (t), 29.2 (t), 25.4 (t), 25.3 (t), 24.4 (t), 23.9 (t), 22.9 (t), and 22.0 (t).

**1-(1-Cyclohexenyl)-1,2-diphenylethan-1-ol (1j).** Following typical procedure A (above), 1-(2-phenylacetyl)cyclohexene (5.0 g, 0.025 mol) was treated with a solution of phenylmagnesium bromide (11.7 mL, 0.035 mol, 3.0 M in ether) yielding a residue which was purified by column chromatography on silica using 10% ethyl acetate/petroleum ether as eluent to give **1j** as a colorless oil (3.75 g, 54%): $R_f$ = 0.77 (20% ethyl acetate/petroleum ether); $\delta_H$ ($CDCl_3$) 7.21 (8H, m), 6.85 (2H, m), 5.88 (1H, m), 3.31 (2H, $q_{AB}$, *J* = 15 Hz), and 2.12–1.31 (9H, m).

**1-(1-Cyclopentenyl)-1-phenylheptan-1-ol (1k).** Following typical procedure A (above), 1-(1-oxoheptyl)cyclopentene (2.7 g, 0.015 mol) when treated with a solution of phenyllithium (10.8 mL, 0.0195 mol, 1.8 M in ether/cyclohexane) yielded a residue which was purified by column chromatography on silica using 5% ethyl acetate/petroleum ether as eluent to give **1k** as a colorless oil (1.50 g, 39%): $M^+$, 226.1368 ($C_{18}H_{26}O$ requires 226.1358); $R_f$ = 0.82 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3350, 2910, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.39–7.12 (5H, m), 5.70 (1H, m), 2.39–1.52 (10H, m), 1.21 (6H, m), and 1.86 (3H, t, *J* = 8 Hz); $\delta_C$ ($CDCl_3$) 149.7 (s), 145.4 (s), 128.0 (d), 126.6 (d), 125.5 (d), 125.0 (d), 76.9 (s), 40.5 (t), 32.5 (t), 31.9 (t), 29.8 (t), 24.9 (t), 24.8 (t), 23.6 (t), 22.7 (t), and 14.1 (q); *m/z* +EI, 226 (M, 30), 211 (72), 197 (49), 183 (42), 141 (51), 129 (89), 105 (82), 91 (50), 81 (65), and 77 (100).

**1-(1-Cyclohexenyl)-1-phenylheptan-1-ol (1l).** Following typical procedure A (above), 1-(1-oxoheptyl)cyclohexene (3.0 g, 15.3 mmol) when treated with a solution of phenyllithium (15.3 mL, 27.6 mmol, 1.8 M in ether/cyclohexane) yielded a residue which was purified by column chromatography on silica using 10% ethyl acetate in petroleum ether as eluent to give **1l** as a colorless oil (2.35 g, 56%): $M^+$, 272.2133 ($C_{19}H_{28}O$ requires 272.2140); $\nu_{max}$ (liquid film) 3460, 2940, 2860, 1600, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.45–7.15 (5H, m), 6.9 (1H, m), 2.2–1.4 (11H, m), 1.4–1.0 (8H, m), and 0.9 (3H, t, *J* = 7 Hz); $\delta_C$ ($CDCl_3$) 145.9 (s), 141.7 (s), 127.9 (d), 126.5 (d), 125.7 (d), 121.4 (d), 79.0 (s), 39.2 (t), 31.8 (t), 29.8 (t), 25.3 (t), 24.8 (t), 24.8 (t), 23.5 (t), 23.0 (t), 22.7 (t), 22.4 (t), and 14.1 (q); *m/z* +EI, 272 (17), 254 (82), 201 (42), 187 (100), and 105 (33).

**1-(1-Cycloheptenyl)-1-phenylheptan-1-ol (1m).** Following typical procedure A (above), 1-(1-oxoheptyl)cycloheptene (2.0 g, 9.62 mmol) when treated with a solution of phenyllithium (9.6 mL, 17.31 mmol, 1.8 M in ether/cyclohexane) yielded a residue which was purified by column chromatography on silica using 5% ethyl acetate in petroleum ether as eluent to give **1m** as a colorless oil (1.32 g, 48%): $M^+$, 286.2294 ($C_{20}H_{30}O$ requires 286.2297); $\nu_{max}$ (liquid film) 3480, 2940, 1600, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.4–7.1 (5H, m), 6.1 (1H, t, *J* = 7 Hz), 2.2 (2H, dd, *J* = 7 and 11 Hz), 1.9 (3H, m), 1.7 (3H, m), 1.6–1.0 (13H, m), and 0.9 (3H, t, *J* = 7 Hz); $\delta_C$ ($CDCl_3$) 148.3 (s), 145.2 (s), 127.8 (d), 126.4 (d), 126.1 (d), 125.8 (d), 79.6 (s), 39.1 (t), 32.8 (t), 31.9 (t), 29.8 (t), 29.7 (t), 28.3 (t), 27.0 (t), 26.9 (t), 23.7 (t), 22.7 (t), and 14.1 (q); *m/z* +EI, 286 (10), 268 (5), 201 (100), 191 (42), and 183 (12).

**2-Phenyl-3-buten-2-ol (1p).** Following typical procedure A (above), 3-buten-2-one (2.0 g, 28.5 mmol) when treated with a solution of phenyllithium (21 mL, 37.1 mmol, 1.8 M in ether/cyclohexane) yielded a residue which was purified by column chromatography on silica using 15% ethyl acetate in petroleum ether as eluent to give **1p** as a colorless oil (0.5 g, 12%): $M^+$, 148.0889 ($C_{10}H_{12}O$ requires 148.0888); $\nu_{max}$ (liquid film) 3400, 2980, 1640, 1600, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.50–7.15 (5H, m), 6.15 (1H, dd, *J* = 10 and 16 Hz), 5.25 (1H, dd, *J* = 16 and 2 Hz), 5.10 (1H, dd, *J* = 10 and 2 Hz), 2.10 (1H, bs), and 1.65 (3H, s); $\delta_C$ ($CDCl_3$) 144.9 (s), 144.9 (d), 128.3 (d), 127.0 (d), 125.2 (d), 112.4 (t), 74.8 (s), 29.3 (q); *m/z* +CI, 148 (5), 131 (100), 121 (50), 105 (33), and 91 (45).

**3-Phenyl-4-hexen-3-ol (1q).** Following typical procedure A (above), 4-hexen-3-one (2.00 g, 20.4 mmol), when treated with a solution of phenyllithium (17 mL, 30.6 mmol, 1.8 M in ether/cyclohexane), yielded a residue which was purified by column chromatography on silica using 15% ethyl acetate in petroleum ether as eluent to give **1q** as a colorless oil (1.10 g, 31%): $M^+$, 176.1193 ($C_{12}H_{16}O$ requires 176.1201); $\nu_{max}$ (liquid film) 3460, 2980, 1600, and 1500 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.44–7.18 (5H, m), 5.82 (1H, dq, *J* = 15 and 1.5 Hz), 5.69 (1H, dq, *J* = 6 and 15 Hz), 1.88 (2H, q, *J* = 7 Hz), 1.71 (3H, dd, *J* = 6 and 1.5 Hz), and 0.81 (3H, t, *J* = 7 Hz); $\delta_C$ ($CDCl_3$) 146.1 (s), 137.5 (d), 128.0 (d), 126.6 (d), 125.6 (d), 124.1 (d), 76.8 (s), 35.1 (t), 17.8 (q), and 8.0 (q); *m/z* +EI, 176 (10), 159 (7), 147 (100), 129 (18), 105 (30), 91 (27), 77 (28), and 69 (70).

**Formation of 2,3-Alkenols: Procedure B. 1-(1-Cyclohexenyl)-1-cyclopropylethanol (1f).** Lithium (1.52 g, 23.0 mol) was beaten into thin sheets, and the sheets were cut into narrow strips and added to a 1000-mL, three-necked flask containing a broken Pasteur pipette and dry ether (200 mL). The vigorously stirred suspension was treated dropwise at room temperature with freshly distilled 1-chlorocyclohexene (9.15 g, 79.0 mol). The reaction mixture was stirred at room temperature overnight, and the resulting solution of 1-cyclohexenyllithium (31.4 mol, assuming 40% conversion) was treated dropwise at 0 °C with a solution of acetylcyclopropane (2.64 g, 31.4 mol) in dry ether (50 mL). The mixture was stirred at room temperature overnight and then poured into ice-cold ammonium chloride solution (200 mL). The layers were separated, and the aqueous layer was extracted with ether (100 mL). The combined organic extracts were dried ($Na_2SO_4$/$K_2CO_3$) and concentrated *in vacuo*. The residue was purified by column chromatography on silica using 6% ethyl acetate/petroleum ether as eluent to give **1f** as a colorless

oil (4.64 g, 89%): $M^+$, 166.1362 ($C_{11}H_{16}O$ requires 166.1358); $R_f$ = 0.45 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3400, 2915, and 1435 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 5.80 (1H, m), 2.09 (4H, m), 1.59 (4H, m), 1.28 (1H, s), 1.20 (3H, s), 0.99 (1H, m), and 0.37 (4H, m); $\delta_C$ ($CDCl_3$) 143.5 (s), 119.6 (d), 73.1 (s), 25.6 (q), 25.1 (t), 24.7 (t), 24.1 (t), 22.4 (t), 20.5 (d), 1.3 (t), and 0.9 (t); *m/z* +EI, 165 (M - 1, 40), 149 (M - 17, 55), 139 (25), and 137 (100).

**1-(1-Cyclohexenyl)-1-(2-furanyl)ethanol (1e).** Following typical procedure B (above), 2-acetylfuran (3.46 g, 31.4 mmol) gave a residue which was purified by column chromatography on silica using 10% ethyl acetate/petroleum ether as eluent to give **1e** as a colorless oil (4.56 g, 76%): $M^+$, 192.1154 ($C_{12}H_{16}O_2$ requires 192.1150); $R_f$ = 0.35 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3390, 2900, 1650, 1500, and 1445 $cm^{-1}$; $\delta_H$ [$(D_3C)_2CO$] 7.32 (1H, m), 6.24 (1H, m), 6.13 (1H, m), 5.66 (1H, m), 4.31 (1H, s), 1.95 (2H, m), 1.81 (2H, m), 1.50 (3H, s), and 1.48 (4H, m); $\delta_C$ [$(D_3C)_2CO$] 161.0 (s), 142.5 (s), 142.2 (d), 121.3 (d), 110.8 (d), 106.0 (d), 73.7 (s), 26.6 (q), 25.8 (t), 25.4 (t), 23.8 (t), and 23.2 (t); *m/z* +EI, 192 (M, 20), 177 (80), 149 (85), 111 (90), 95 (100), and 81 (38).

**1-(1-Cyclohexenyl)cyclohexan-1-ol (1n).** Following typical procedure B (above), cyclohexanone (8.91 g, 91 mmol) yielded a residue which was purified by column chromatography on silica using 5% ethyl acetate in light petroleum as eluent to give **1n** as a colorless solid (15.3 g, 94%): mp 67–68 °C (recrystallized from ethyl acetate/petroleum ether); $\nu_{max}$ (KBr disk) 3300, 2920, and 1650 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 5.75 (1H, m), 2.24–2.00 (4H, m), 1.75–1.40 (12H, m and OH), and 1.38–1.06 (H, m); $\delta_C$ ($CDCl_3$) 143.5 (s), 119.7 (d), 73.3 (s), 35.7 (t), 25.7 (t), 25.1 (t), 24.0 (t), 23.1 (t), 22.3 (t), and 22.0 (t); *m/z* +EI 180 (10), 162 (35), 137 (42), 119 (34), 109 (42), 105 (45), 91 (82), and 81 (100). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.84; H, 11.39.

**1-(1-Cyclohexenyl)cyclododecan-1-ol (1o).** Following typical procedure B (above), cyclododecanone (3.44 g, 18.9 mmol) gave **1o** as white needles (3.45 g, 69%): mp 119.5–121.5 °C (recrystallized from diisopropyl ether); $R_f$ = 0.21 (2:1 chloroform/petroleum ether); $\nu_{max}$ (KBr disk) 3350, 3050, 2940, and 2850 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 6.63–6.58 (1H, m), 3.13–3.00 (4H, m), 2.68–2.51 (8H, m), and 2.40–2.21 (19H, m); $\delta_C$ ($CDCl_3$) 142.4 (s), 120.9 (d), 76.6 (s), 32.6 (t), 26.4 (t), 26.1 (t), 25.3 (t), 23.8 (t), 23.1 (t), 22.4 (t), 22.3 (t), 22.0 (t), and 19.8 (t); *m/z* +EI, 264 (100), 246 (22), 137 (45), 122 (56), 109 (53), 81 (62), and 41 (35). Anal. Calcd for $C_{14}H_{16}O_3$: C, 81.75; H, 12.20. Found: C, 81.46; H, 12.22.

**Formation of 2,3-Epoxy Alcohols: Typical Procedure. *syn*-/*anti*-1-(1,2-Epoxycyclohexyl)-1-cyclopropylethanol (2f).** A solution of 1-(1-cyclohexenyl)-1-cyclopropylethan-1-ol (4.0 g, 24.1 mol) and vanadyl acetyl acetonate (50 mg) in benzene (100 mL) was treated dropwise at room temperature with an aqueous solution of *tert*-butyl hydroperoxide (4.34 g, 70%, 0.0337 mol). The reaction mixture was stirred at room temperature and judged complete after 16 h (monitored by TLC). The mixture was washed with saturated sodium sulfite solution (150 mL), dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by column chromatography on silica using 10% ethyl acetate/petroleum ether as eluent to give **2f** as a colorless oil (3.43 g, 78%): M - 15, 167.1076 ($C_{11}H_{18}O_2 - CH_3$ requires 167.1072); $R_f$ = 0.56 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3400 and 1445 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 3.35 (1H, m), 2.04–1.18 (8H, m), 1.09 (3H, s), 0.92 (1H, m), and 0.39 (4H, m); $\delta_C$ ($CDCl_3$) 70.3 (s), 69.8 (s), 65.5 (s), 65.4 (s), 55.6 (d), 54.7 (d), 24.8 (t), 24.6 (t), 24.4 (t), 22.1 (q), 21.5 (q), 21.1 (t), 20.8 (t), 20.7 (t), 19.3 (t), 19.3 (t), 17.1 (d), 16.9 (d), 1.0 (t), 0.2 (t), -0.3 (t), and -0.4 (t); *m/z* +EI, 181 (M - 1, 22), 167 (M - 15, 10), 165 (M - 17, 40), 147 (20), 139 (22), 128 (23), 112 (70), 98 (62), 85 (20), 69 (44), 58 (42), 55 (49), 44 (100), and 39 (60).

**2-(1,2-Epoxycyclohexanyl)propan-2-ol (2a).** Following the typical procedure (above, room temperature, 4 h), 2-(1-cyclohexenyl)propan-2-ol (3.0 g, 21.4 mol) yielded a residue which was purified by column chromatography on silica using 10% ethyl acetate/petroleum ether as eluent to give **2a** as a colorless oil (1.48 g, 44%): $R_f$ = 0.48 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3400, 2900, and 1400 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 3.40 (1H, m), 2.19 (1H, s), 2.03–1.18 (8H, m), and 1.24 (6H, s); $\delta_C$ ($CDCl_3$) 69.8 (s), 64.9 (s), 55.3 (d), 25.1 (q), 24.8 (q), 24.5 (t), 24.3 (t), 20.9 (t), and 19.1 (t); *m/z* +EI, 156 (m, 37), 141 (12), 123 (13), 109 (15), and 98 (100).

***syn*-/*anti*-2-(1,2-Epoxycyclohexyl)-3-buten-2-ol (2b).** Following the typical procedure (above, 0 °C, 2.5 h), 2-(1-cyclohexenyl)-3-buten-2-ol (1.52 g, 10 mmol) yielded a residue which was purified by column chromatography on silica using 5% ethyl acetate/petroleum ether as eluent to give **2b** as a mixture of diastereoisomers (0.86 g, 52%): $M^+$, 168.1143 ($C_{10}H_{16}O_2$ requires 168.1150); $R_f$ = 0.19 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3410, 2910, and 1635 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 5.82 (1H, dd, *J* = 18, 12 Hz), 5.27 (1H, dd, *J* = 18, 1 Hz), 5.12 (1H, dd, *J* = 12, 1 Hz), 3.31 (1H, m), 2.26 (1H, s), 1.95–1.05 (8H, m), and 1.24 (3H, s); $\delta_C$ ($CDCl_3$) 140.3 (d), 115.2 (t), 72.3 (s), 64.0 (s), 55.5 (d), 24.7 (t), 24.3 (t), 22.7 (q), 20.8 (t), and 19.2 (t); *m/z* +EI 150 ((M - 18, 18), 108 (20), 98 (90), 83 (40), 70 (45), 55 (77), and 43 (100). **2-(1,2-Epoxycyclohexyl)-3,4-epoxybutan-2-ol** was also obtained as a colorless oil, isolated as a single diastereoisomer (0.13 g, 7%): $R_f$ = 0.08 (10% ethyl acetate/petroleum ether); $\delta_H$ ($CDCl_3$) 3.31 (1H, m), 3.12 (1H, m), 2.73 (1H, m), 2.68 (1H, dd, *J* = 5, 6 Hz), 2.37 (1H, bs), 2.11–1.29 (8H, m), and 1.27 (3H, s); $\delta_C$ ($CDCl_3$) 69.5 (s), 63.1 (s), 54.7 (d), 54.1 (d), 42.6 (t), 24.6 (t), 23.9 (t), 20.6 (t), 19.8 (q), an 19.1 (t); *m/z* +EI 136 (5), 122 (8), 96 (18), 80 (20), 70 (20), 54 (24), and 42 (100); *m/z* +CI, 202 (M + 18, 40), 185 (M + 1, 30), 167 (M - 17, 100), 149 (40), 141 (20), 137 (50), 123 (56), and 107 (62).

***syn*-/*anti*-1-(1,2-Epoxycyclohexyl)-1-phenylethanol (2c).** Following the typical procedure (above, room temperature, 1.5 h), 1-(1-cyclohexenyl)-1-phenylethanol (4.6 g, 27 mmol) gave a residue which was purified by column chromatography on silica using 7% ethyl acetate/petroleum ether as eluent to give **2c** as a white solid (2.3 g, 46%): mp 40–41.5 °C (recrystallized from petroleum ether); $R_f$ = 0.30 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (KBr disk) 3460, 3100, 3070, 1605, 1500, 1455, and 1440 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.51–7.21 (5H, m), 3.71 (1H, m), 2.49 (1H, s), 2.05 (1H, m), 1.70 (2H, m), 1.65 (3H, s), and 1.45–0.90 (5H, m); $\delta_C$ ($CDCl_3$) 143.4 (s), 128.0 (d), 127.2 (d), 126.1 (d), 73.6 (s), 65.0 (s), 55.9 (d), 24.6 (t), 24.5 (t), 23.4 (q), 20.5 (t), and 18.8 (t); *m/z* +EI 218 (M, 15), 216 (12), 200 (10), 174 (25), 171 (30), 167 (15), 158 (50), 147 (50), 141 (30), and 129 (100); *m/z* +CI, 219 (M + 1, 25), 218 (M, 18), 217 (20), 201 (12), 158 (10), 121 (35), 105 (30), 98 (92), 91 (20), 83 (15), 77 (20), 70 (15), and 43 (100). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.26; H, 8.14.

***syn*-2-(1,2-Epoxycyclohexyl)-3,3-dimethylbutan-2-ol (2d).** Following the typical procedure (above, room temperature, 4 h), 2-(1-cyclohexenyl)-3,3-dimethylbutan-2-ol (1.20 g, 6.58 mmol) was found to give **2d** as a colorless oil (1.34 g, 100%): M - 17, 181.1589 ($C_{12}H_{22}O_2$ - OH requires 181.1589), M - 57, 141.0909 ($C_{12}H_{22}O_2 - C_4H_9$ requires 141.0915); $\nu_{max}$ (liquid film) 3470 and 2960 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 3.43 (1H, m), 2.32 (1H, s), 2.03 (2H, m), 1.76 (2H, m), 1.50 (2H, m), 1.34 (2H, m), 1.21 (3H, s), and 1.01 (9H, s); $\delta_C$ ($CDCl_3$) 75.3 (s), 63.6 (s), 57.8 (d), 37.2 (s), 27.3 (t), 27.0 (q), 24.2 (t), 20.6 (t), 20.2 (q), and 19.1 (t); *m/z* +EI, 141 (5), 123 (22), 98 (100), 83 (50), 70 (62), and 57 (50).

***syn*- and *anti*-1-(1,2-Epoxycyclohexyl)-1-(2-furanyl)ethanol (2e).** Following the typical procedure (above, room temperature, 30 h), 1-(1-cyclohexenyl)-1-(2-furanyl)ethan-1-ol (2.50 g, 13.0 mmol) yielded a residue which was purified by column chromatography on silica using 10% ethyl acetate/petroleum ether as eluent to give **2e** as a colorless oil (diastereomer A, 0.35 g, 13%) [$M^+$, 208.1096 ($C_{12}H_{16}O_3$ requires 208.1099); $R_f$ = 0.54 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3350, 2910, 1570, and 1490 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.38 (1H, m), 6.31 (1H, m), 6.25 (1H, m), 3.40 (1H, m), 3.03 (1H, s), 2.05 (1H, m), 1.86–1.63 (2H, m), 1.59 (3H, s), and 1.51–1.09 (5H, m); $\delta_C$ ($CDCl_3$) 157.2 (s), 142.0 (d), 109.9 (d), 106.2 (d), 70.1 (s), 64.4 (d), 54.6 (d), 24.8 (t), 24.6 (t), 21.8 (q), 20.7 (t), and 19.2 (t); *m/z* +EI, 208 (M, 4), 191 (M - 17, 62), 123 (10), 111 (95), 98 (70), 95 (48), 91 (15), 83 (35), 70 (56), 55 (43), and 43 (100)] and another colorless oil (diastereomer B, 0.13 g, 5%): $R_f$ = 0.43 (20% ethyl acetate/petroleum ether); $\delta_H$ [$(D_3C)_2CO$] 7.47 (1H, m), 6.35 (1H, m), 6.31 (1H, m), 3.52 (1H, m), 2.88 (1H, s), 2.07–1.01 (7H, m), and 1.51 (3H, s); $\delta_C$ [$(D_3C)_2CO$] 158.8 (s), 142.6 (d), 110.9 (d), 107.0 (d), 71.5 (s), 63.7 (s), 55.5 (d), 25.8 (t), 25.4 (t), 22.5 (q), 21.4 (t), and 19.8 (t). **2-Acetyl-2-(2-furanyl)cyclohexan-1-ol (3e)** was also obtained as a colorless oil (0.65 g, 24%): $M^+$, 208.1092 ($C_{12}H_{16}O_3$ requires 208.1099); $R_f$ = 0.35 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3420, 2905, 2855, 1690, 1545, and 1490 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.40 (1H, m), 6.39 (1H, m), 6.29 (1H, m), 4.47 (1H, m),

3.29 (1H, bs), 2.16 (2H, m), 2.02 (3H, s), 1.82–1.49 (4H, m), and 1.36 (2H, m); $\delta_C$ ($CDCl_3$) 210.5 (s), 153.2 (s), 142.1 (d), 110.7 (d), 108.3 (d), 70.2 (d), 57.5 (s), 29.7 (t), 27.0 (t), 25.8 (q), 21.8 (t), and 20.2 (t); *m/z* +EI, 208 (M, 28), 165 (90), 148 (100), 133 (20), 120 (28), 111 (15), 95 (21), 81 (60), and 55 (16).

***syn*- and *anti*-3-(1,2-Epoxycyclohexyl)-1-phenyl-1-butyn-3-ol (2g).** Following the typical procedure above, 3-(1-cyclohexenyl)-1-phenyl-1-butyn-3-ol (3.0 g, 13.3 mol) yielded a residue which was purified by column chromatography on silica using 10% ethyl acetate/petroleum ether as eluent to give **2g** as a colorless oil (diastereomer A, 2.08 g, 65%) [$M^+$, 242.1315 ($C_{16}H_{20}O_2$ requires 242.1307; $R_f$ = 0.50 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3375, 2890, 2195, 1595, 1480, and 1435 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.42 (2H, m), 7.28 (3H, m), 3.51 (1H, m), 2.88 (1H, s), 2.04 (4H, m), 1.82 (1H, m), 1.59 (3H, s), and 1.52–1.20 (3H, m); $\delta_C$ ($CDCl_3$) 131.8 (d), 128.3 (d), 128.2 (d), 122.6 (s), 90.4 (s), 83.9 (s), 68.3 (s), 64.5 (s), 55.2 (d), 25.5 (q), 25.1 (t), 24.6 (t), 20.7 (t), and 19.4 (t); *m/z* +EI, 242 (M, 5), 199 (20), 182 (16), 143 (100), 124 (60), 97 (72), and 42 (68)] and as a white solid (diastereomer B, 0.57 g, 18%): mp 96–98 °C (recrystallized from diisopropyl ether); $R_f$ = 0.37 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (KBr disk) 3405, 2945, 2225, 1490, and 1445 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.43 (2H, m), 7.31 (3H, m), 3.57 (1H, m), 2.57 (1H, s), 2.20 (1H, m), 2.03–1.79 (3H, m), 1.61 (3H, s), and 1.60–1.21 (4H, m); $\delta_C$ ($CDCl_3$) 131.8 (d), 128.4 (d), 128.2 (d), 122.5 (s), 89.8 (s), 84.2 (s), 69.0 (s), 64.1 (s), 56.1 (d), 25.9 (q), 24.6 (t), 24.6 (t), 20.8 (t), and 19.1 (t). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49 Found: C, 79.21; H, 7.55.

***syn*-/*anti*-2-(1,2-Epoxycyclohexyl)-4-phenylbutan-2-ol (2h).** Following the typical procedure (above, room temperature, 5 h), 2-(1-cyclohexenyl)-4-phenylbutan-2-ol (3.00 g, 13.2 mmol) was found to give **2h** as an oily solid (2.37 g, 74%), as a mixture of diastereoisomers: $\nu_{max}$ (KBr disk) 3460, 2940, 1600, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.4–7.1 (5H, m), 3.5 (1H, dd, *J* = 4 and 8 Hz), 2.9–2.5 (2H, m), 2.2–1.1 (11H, m), and 1.6 (3H, s); $\delta_C$ ($CDCl_3$) 142.6 (s), 142.5 (s), 128.5 (d), 128.4 (d), 125.8 (d), 125.8 (d), 71.7 (s), 71.5 (s), 64.8 (s), 64.1 (s), 56.1 (d), 54.1 (d), 40.6 (t), 40.4 (t), 30.0 (t), 29.8 (t), 24.8 (t), 24.7 (t), 24.4 (q), 23.6 (q), 20.8 (t), 20.8 (t), 19.2 (t), and 19.0 (t); *m/z* +CI, 247 (18), 229 (100), 211 (75), 203 (22), and 185 (22). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.89; H, 9.02.

***syn*-/*anti*-2-(1,2-Epoxycyclohexyl)-1-phenyl-3-buten-1-ol (2i).** Following the typical procedure (above, room temperature, 5 h), 2-(1-cyclohexenyl)-1-phenyl-3-buten-2-ol (1.4 g, 6.13 mmol) yielded a residue which was purified by column chromatography on silica using 5% ethyl acetate/petroleum ether as eluent to give **2i** as a colorless solid (diastereomer A, 0.11 g, 7%) mp 71–73 °C (recrystallized from diisopropyl ether); $R_f$ = 0.52 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (KBr disk) 3470, 3095, 1640, 1605, and 1500 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.25 (5H, m), 6.11 (1H, dd, *J* = 18, 13 Hz), 5.31 (1H, dd, *J* = 18, 1 Hz), 5.21 (1H, dd, *J* = 13, 1 Hz), 2.97 (2H, s), 2.79 (1H, s), 2.31 (1H, s), and 2.20-1.13 (8H, m); $\delta_C$ ($CDCl_3$) 140.5 (d), 136.5 (s), 130.8 (d), 127.8 (d), 126.5 (d), 114.7 (t), 74.8 (s), 62.9 (s), 56.1 (d), 42.3 (t), 24.8 (t), 24.4 (t), 20.5 (t), and 18.6 (t); *m/z* +EI (+ve FAB), 289 (12), 267 (22), 245 (M + 1, 60), 227 (M − 17, 100), and 209 (52). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.46; H, 8.08.] and a greasy yellow solid (diastereomer B, 0.16 g, 11%); $R_f$ = 0.44 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (KBr disk) 3480, 3405, 3080, 2950, 2870, and 1610 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.25 (5H, m), 5.95 (1H, dd, *J* = 18, 13 Hz), 5.29 (1H, dd, *J* = 18, 1 Hz), 5.20 (1H, dd, *J* = 13, 1 Hz), 3.29 (1H, m), 2.96 (2H, s), 2.20 (1H, s), and 2.10–1.19 (8H, m). **2-(1,2-Epoxycyclohexyl)-3,4-epoxy-1-phenylbutan-2-ol** was also obtained as a white solid (0.57 g, 36%): mp 55–56 °C; $R_f$ = 0.25 (10% ethyl acetate/petroleum ether); $\delta_H$ ($CDCl_3$) 7.21 (5H, m), 3.19 (1H, t, *J* = 2 Hz), 2.90 (2H, s), 2.84 (1H, s), 2.53 (2H, m), 2.31 (1H, s), and 2.20–1.10 (8H, m); $\delta_C$ ($CDCl_3$) 135.9 (s), 130.7 (d), 127.9 (d), 126.6 (d), 71.3 (s), 62.1 (s), 54.6 (d), 53.8 (d), 42.9 (t), 39.8 (t), 24.3 (t), 20.4 (t), and 18.7 (t). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.79; H, 7.70.

***syn*-1-(1,2-Epoxycyclohexyl)-1,2-diphenylethan-1-ol (2j).** Following the typical procedure (above, room temperature, 3 h), 1-(1-cyclohexenyl)-1,2-diphenylethan-1-ol (3.75 g, 13.5 mmol) yielded a residue which was purified by trituration with petroleum ether to give **2j** as a white solid (1.48 g, 37%): mp 127–128 °C (colorless prisms recrystallized from diisopropyl ether/ethyl acetate); $M^+$, 294.1625 ($C_{20}H_{22}O_2$ requires 294.1620); $R_f$ = 0.40 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (KBr disk) 3470, 3035, 2950, 1605, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.52–7.07 (10H, m), 3.47 (1H, s), 3.34 (2H, s), 2.58 (1H, s), and 2.12-0.87 (8H, m); $\delta_C$ ($CDCl_3$) 142.9 (s), 136.3 (s), 130.9 (d), 128.1 (d), 128.0 (d), 127.8 (d), 126.6 (d), 126.4 (d), 75.6 (s), 64.9 (s), 54.1 (d), 42.0 (t), 25.2 (t), 24.4 (t), 20.8 (t), and 19.0 (t); *m/z* +EI, 294 (M, 10), 203 (14), 158 (18), 105 (100), 91 (32), and 77 (22). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.63; H, 7.58.

***syn*- and *anti*-1-(1,2-epoxycyclopentyl)-1-phenylheptan-1-ol (2k).** Following the typical procedure (above, room temperature, 10 h), 1-(1-cyclopentenyl)-1-phenylheptan-1-ol (1.40 g, 5.42 mmol) yielded a residue which was purified by column chromatography on silica using 8% ethyl acetate/petroleum ether as eluent to give **2k** as a colorless oil (diastereomer A, 0.38 g, 26%) [$R_f$ = 0.30 (10% ethyl acetate/petroleum ether); $M^+$, 274.1924 ($C_{18}H_{26}O_2$ requires 274.1932); $\delta_H$ ($CDCl_3$) 7.48 (2H, m), 7.36–7.20 (3H, m), 3.60 (1H, s), 2.73 (1H, s), 2.14 (1H, m), 1.92 (3H, m), 1.69–1.20 (13H, m), and 0.88 (3H, m); $\delta_C$ ($CDCl_3$) 142.6 (s), 128.1 (d), 127.0 (d), 126.3 (d), 74.3 (s), 73.8 (s), 60.7 (d), 38.0 (t), 31.8 (t), 29.8 (t), 27.0 (t), 25.8 (t), 23.0 (t), 22.7 (t), 19.6 (t), 19.3 (t), and 14.1 (q); *m/z* +EI, 274 (M, 1), 217 (4), 161 (16), 144 (100), 129 (32), 91 (26), and 43 (52)] and a colorless oil (diastereomer B, 0.020 g, 1%); $R_f$ = 0.21 (10% ethyl acetate/petroleum ether); $\delta_H$ ($CDCl_3$) 7.32–7.11 (5H, m), 3.53 (1H, s), 2.72 (1H, s), 1.99–1.02 (16H, m), and 0.78 (3H, m); $\delta_C$ ($CDCl_3$) 144.0 (s), 128.1 (d), 126.9 (d), 125.7 (d), 75.1 (s), 73.8 (s), 62.3 (d), 37.4 (t), 31.8 (t), 29.8 (t), 27.4 (t), 26.5 (t), 23.1 (t), 22.7 (t), 19.5 (t), and 14.1 (q).

***syn*-/*anti*-1-(1,2-Epoxycyclohexyl)-1-phenylheptan-1-ol (2l).** Following the typical procedure (above, room temperature, 24 h), 1-(1-cyclohexenyl)-1-phenylheptan-1-ol (1.3 g, 4.74 mmol) was found to give **2l** as a colorless oil (1.12 g, 81%): $M^+$, 288.2095 ($C_{19}H_{28}O_2$ requires 288.2089); $\nu_{max}$ (liquid film) 3480, 2940, 2860, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.5–7.2 (5H, m), 3.5 (1H, m), 2.7 (1H, bs), and 2.3–0.7 (21H, m); $\delta_C$ ($CDCl_3$) 143.7 (s), 142.7 (s), 128.1 (d), 128.0 (d), 127.0 (d), 126.8 (d), 126.4 (d), 126.0 (d), 76.4 (s), 75.3 (s), 65.3 (s), 65.0 (s), 56.4 (d), 54.8 (d), 36.1 (t), 36.0 (t), 31.8 (t), 29.9 (t), 25.2 (t), 24.7 (t), 24.4 (t), 24.2 (t), 23.1 (t), 22.7 (t), 20.6 (t), 19.3 (t), 19.0 (t), and 14.1 (q); *m/z* +EI, 288 (10), 270 (22), 254 (37), 217 (62), and 203 (100).

***syn*-/*anti*-1-(1,2-Epoxycycloheptyl)-1-phenylheptan-1-ol (2m).** Following the typical procedure (above, room temperature, 12 h), 1-(1-cycloheptenyl)-1-phenylheptan-1-ol (1.32 g, 4.62 mmol) was found to give **2m** (0.9 g, 65%): $M^+$, 302.2229 ($C_{20}H_{30}O_2$ requires 302.2246), M − 18, 284.2136 ($C_{20}H_{28}O$ requires 284.2140); $\nu_{max}$ (liquid film) 3460, 2940, 2860, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.5–7.2 (10H, m), 3.5 (2H, m), 2.5 (1H, bs), 2.3 (1H, brs), 2.1–1.6 (8H, m), 1.6–0.9 (30H, m), and 0.85 (6H, m); $\delta_C$ ($CDCl_3$) 144.0 (s), 142.6 (s), 128.1 (d), 128.0 (d), 127.1 (d), 126.9 (d), 126.4 (d), 126.1 (d), 77.0 (s), 75.9 (s), 68.1 (s), 67.6 (s), 58.6 (d), 57.5 (d), 36.4 (t), 36.3 (t), 31.8 (t), 31.0 (t), 29.9 (t), 28.5 (t), 28.3 (t), 28.2 (t), 27.9 (t), 24.5 (t), 24.0 (t), 23.6 (t), 23.5 (t), 23.2 (t), 23.1 (t), 22.7 (t), and 14.1 (q); *m/z* +EI, 302 (12), 284 (12), 241 (33), 217 (70), and 199 (100).

**1-(1,2-Epoxycyclohexyl)cyclohexan-1-ol (2n).** Following the typical procedure (above, room temperature, 12 h), 1-(1-cyclohexenyl)cyclohexan-1-ol (2.00 g, 11.1 mmol) yielded a residue which was purified by column chromatography on silica using 15% ethyl acetate in petroleum ether as eluent to give **2n** as a colorless solid (1.87 g, 91%): mp 69–70 °C (recrystallized from petroleum ether/ethyl acetate); $\nu_{max}$ (KBr disk) 3470, 2940, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 3.4 (1H, m), and 2.1–1.0 (19H, m); $\delta_C$ ($CDCl_3$) 70.7 (s), 65.0 (s), 55.0 (d), 32.6 (t), 32.5 (t), 25.9 (t), 24.8 (t), 24.4 (t), 21.5 (t), 21.1 (t), 20.9 (t), and 19.2 (t); *m/z* +EI, 196 (22), 179 (42), 160 (22), 149 (55), 125 (60), and 111 (100). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.59; H, 10.19.

***syn*-1-(1,2-Epoxycyclohexyl)cyclododecan-1-ol (2o).** Following the typical procedure (above, reflux, 5 h), 1-(1-cyclohexenyl)cyclododecan-1-ol (2.0 g, 7.13 mmol) was found to give **2o** as white needles (1.48 g, 70%): mp 103–105 °C; $R_f$ = 0.31 (chloroform); $\nu_{max}$ (KBr disk) 3467 (br), 3015, 2936, and 2861 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 3.24–3.21 (1H, m), and 2.03–1.15 (31H, m); $\delta_C$ ($CDCl_3$) 74.7 (s), 64.6 (s), 55.9 (d), 31.5 (t), 30.4 (t), 26.6 (t), 26.5 (t), 25.9 (t), 24.6 (t), 24.55 (t), 22.5 (t), 22.4 (t), 22.2 (t), 22.0 (t),

20.5 (t), 19.8 (t), 19.7 (t), and 19.3 (t); *m/z* +EI, 280 (3), 263 (7), 183 (20), 98 (96), 55 (80), and 41 (100). Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 76.80; H, 11.53.

***syn*-/*anti*-1,2-Epoxy-3-phenylbutan-3-ol (2p).** Following the typical procedure (above, room temperature, 48 h, reflux, 1 h), 2-phenyl-3-buten-2-ol (0.50 g, 3.29 mmol) was found to give **2p** as a colorless oil (0.50 g, 71%): $M^+$, 121.0660 ($C_{10}H_{12}O_2$ requires 121.0653); $\nu_{max}$ (liquid film) 3450, 2990, 1600, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.61–7.20 (5H, m), 3.20 (1H, dd, $J$ = 3, 4 Hz), 2.88 (1H, dd, $J$ = 3, 5 Hz), 2.67 (1H, dd, $J$ = 4, 5 Hz), 2.10 (1H, brs), and 1.72 (3H, s); $\delta_C$ ($CDCl_3$) 143.6 (s), 128.4 (d), 127.4 (d), 125.0 (d), 70.7 (s), 58.7 (d), 44.4 (t), and 27.8 (q); *m/z* +EI, 147 (5), 121 (100), 104 (65), 91 (28), and 77 (26).

***syn*-/*anti*-2,3-Epoxy-4-phenylhexan-4-ol (2q).** Following the typical procedure (above, room temperature, 5 h), 3-phenyl-4-hexen-3-ol (0.70 g, 3.95 mmol) was found to give **2q** as a colorless oil (0.58 g, 76%): $M^+$, 164.0831 ($C_{10}H_{12}O_2$ requires 164.0837); $\nu_{max}$ (liquid film) 3420, 2970, 1600, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.45–7.25 (5H, m), 3.03 (2H, m), 2.20 (1H, bs), 1.97 (2H, q, $J$ = 7 Hz), 1.24 (3H, d, $J$ = 5 Hz), and 0.86 (3H, t, $J$ = 7 Hz); *m/z* +EI, 164 (8), 135 (75), 105 (100), 91 (15), 77 (22), and 57 (40).

**Semipinacol Epoxide Rearrangement of 2,3-Epoxy Alcohols: Typical Procedure. 2-Acetyl-2-(cyclopropyl)-cyclohexan-1-ol (3f).** A solution of 1-(1,2-epoxycyclohexyl)-1-cyclopropylethan-1-ol (2.0 g, 11.0 mmol) in dry dichloromethane (120 mL) was treated dropwise at 0 °C with tin(IV) chloride (2.57 mL, 5.72 g, 22.0 mol). The reaction mixture was stirred at 0 °C for 1.5 h (monitored by TLC) and then poured onto ice (150 g) and extracted with dichloromethane (2 × 100 mL). The combined organic extracts were washed with dilute hydrochloric acid (150 mL), water (150 mL), and brine (150 mL) and then dried ($MgSO_4$) and concentrated *in vacuo* to give **3f** as a colorless oil (1.75 g, 88%), as a single diastereoisomer; $M^+$, 182.1300 ($C_{11}H_{18}O_2$ requires 182.1306); $R_f$ = 0.30 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3420 and 1675 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 3.38 (1H, dd, $J$ = 12, 2 Hz), 3.31 (1H, s), 2.21 (3H, s), 1.96–1.55 (5H, m), 1.33–0.90 (4H, m), and 0.55 (4H, m); $\delta_C$ ($CDCl_3$) 216.5 (s), 76.2 (d), 53.9 (s), 32.3 (t), 28.6 (t), 27.0 (d), 24.3 (t), 22.6 (t), 17.0 (q), 1.9 (t), and 1.3 (t); *m/z* +EI, 167 (20), 164 (M − 18, 8), 149 (12), 139 (100), 121 (40), 111 (33), 97 (60), 81 (70), 69 (85), and 55 (66).

**1-Acetyl-1-methylcyclohexan-2-ol (3a).** Following the typical procedure (above, 0 °C, 30 h), 2-(1,2-epoxycyclohexanyl)-propan-2-ol (1.15 g, 7.36 mmol) yielded a residue which was purified by column chromatography on silica using 15% ethyl acetate/petroleum ether as eluent to give **3a** as a clear oil (0.64 g, 56%), as a single diastereoisomer: M − 15, 141.0908 ($C_9H_{16}O_2$ − $CH_3$ requires 141.0915; $R_f$ = 0.30 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3400, 2930, and 1685 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 3.33 (1H, bs), 2.09 (3H, s), 1.82–1.19 (8H, m) and 1.18 (3H, s); $\delta_C$ ($CDCl_3$) 217.0 (s), 75.7 (d), 52.4 (s), 33.5 (t), 31.1 (t), 25.8 (q), 23.7 (t), 22.6 (t), and 22.5 (q); *m/z* +EI 156 (M, 10), 141 (M − 15, 3), 123 (10, 109 (10), 98 (80), 95 (32), 85 (30), 81 (38), 70 (60), 59 (40), 55 (28), and 43 (100).

**2-Acetyl-2-ethenylcyclohexan-1-ol (3b).** Following the typical procedure (above, 0 °C, 1.5 h), 2-(1,2-epoxycyclohexanyl)-3-buten-2-ol (0.64 g, 3.8 mmol) was found to give **3b** as a brown oil (0.61 g, 95%), as a single diastereoisomer: $M^+$, 168.1130 ($C_{10}H_{16}O_2$ requires 168.1150); $R_f$ = 0.41 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3400, 2905, 1700, 1625, and 1445 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 5.92 (1H, dd, $J$ = 18, 12 Hz), 5.34 (1H, dd, $J$ = 12, 1 Hz), 5.21 (1H, dd, $J$ = 1 Hz), 3.82 (1H, m), 3.25 (1H, bs), 2.11 (3H, s), 1.69 (6H, m), and 1.48 (2H, m); $\delta_C$ ($CDCl_3$) 213.0 (s), 138.0 (d), 117.9 (t), 72.9 (d), 59.0 (s), 30.1 (t), 28.8 (t), 26.0 (q), 21.7 (t), and 21.5 (t); *m/z* +EI, 125 (20), 108 (30), 91 (32), 79 (72), 55 (32), 49 (40), and 43 (100).

**2-Acetyl-2-phenylcyclohexan-1-ol (3c).** Following the typical procedure (above, room temperature, 2 h), 1-(1,2-epoxycyclohexyl)-1-phenylethanol (1.0 g, 4.58 mmol) was found to give **3c** as a white solid (0.99 g, 99%), isolated as a single diastereoisomer: mp 83.5–85 °C (recrystallized from diisopropyl ether); $R_f$ = 0.28 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (solution) 3450, 3025, 2930, 2860, and 1690 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.40 (5H, m), 4.39 (1H, m), 3.24 (1H, bs), 2.26 (1H, t, $J$ = 8 Hz), 1.94 (3H, s), and 1.82–1.32 (8H, m); $\delta_C$ ($CDCl_3$) 213.0 (s), 138.8 (s), 128.8 (d), 127.6 (d), 127.2 (d), 72.7 (d), 60.3 (s), 30.0 (t), 28.2 (t), 26.1 (q), 22.0 (t), and 21.4 (t); *m/z* +EI, 218 (M, 10), 201 (M − 17, 20), 175 (15), 158 (90), 143 (20), 130 (32), 115 (25), 105 (18), 91 (60), 77 (20), and 43 (100); *m/z* +CI, 219 (M + 1, 12), 201 (M − 17, 40), 175 (18), 158 (100), 143 (20), 130 (33), 115 (30), and 105 (20). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.75; H, 8.13.

**2-Acetyl-2-*tert*-butylcyclohexan-1-ol (3d).** Following the typical procedure (above, 0 °C, 3 h), 2-(1,2-epoxycyclohexyl)-3,3-dimethylbutan-2-ol (1.10 g, 5.55 mmol) was found to give **3d** as a colorless oil (0.83 g, 75%), as a single diastereoisomer: $M^+$, 198.1624 ($C_{12}H_{22}O_2$ requires 198.1620); $R_f$ = 0.37 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3510, 2950, 2875, 1680, and 1420 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 3.52 (1H, dd, $J$ = 12, 2 Hz), 2.21 (3H, s), 1.90–0.94 (8H, m), and 1.10 (9H, s); $\delta_C$ ($CDCl_3$) 218.5 (s), 75.8 (d), 60.7 (s), 35.8 (s), 34.0 (t), 30.7 (t), 30.4 (q), 28.6 (q), 25.2 (t), and 24.0 (t); *m/z* + EI, 198 (M, 10), 123 (20), 109 (20), 81 (21), 67 (12), 57 (42) and 43 (100).

**2-Acetyl-2-(2-furanyl)cyclohexan-1-ol (3e).** Following the typical procedure above (0 °C, 1 h), 1-(1,2-epoxycyclohexyl)-1-(2-furanyl)ethan-1-ol (0.30 g, 1.44 mmol) was found to give **3e** as a colorless oil (0.225 g, 75%), as a single diastereoisomer, spectroscopically identical with the sample prepared above.

**2-Acetyl-2-(phenylethynyl)cyclohexan-1-ol (3g).** (1) Following the typical procedure above (0 °C, 1 h), *syn*-3-(1,2-epoxycyclohexanyl)-1-phenyl-1-butyn-3-ol (0.56 g, 2.31 mmol) reacted to give a residue which was purified by column chromatography on silica using 10% ethyl acetate/petroleum ether as eluent to give **3g** as white needles (0.24 g, 43%), as a single diastereoisomer: mp 63–64 °C (recrystallized from diethyl ether/petroleum ether); $M^+$ 242.1308 ($C_{16}H_{18}O_2$ requires 242.1307); $R_f$ = 0.32 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (KBr disk) 3590, 3480, 3330, 1715, 1625, 1600, and 1575 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.42 (2H, m), 7.32 (3H, m), 4.30 (1H, t, $J$ = 3 Hz), 3.31 (1H, bs), 2.41 (3H, s), and 2.09–1.44 (8H, m); $\delta_C$ ($CDCl_3$) 209.6 (s), 131.6 (d), 128.4 (d), 128.4 (d), 122.7 (s), 88.2 (s), 87.1 (s), 70.1 (d), 53.4 (s), 29.3 (t), 28.4 (t), 26.1 (q), 22.0 (t), and 19.3 (t); *m/z* +EI, 242 (M, 80), 241 (35), 191 (40), 182 (60), 181 (70), 171 (40), 165 (55), 153 (55), 144 (30), 127 (40), 115 (30), 105 (40), 91 (38), and 77 (33); *m/z* +CI, 243 (M + 1, 100), 225 (40), 182 (35), 105 (39), and 43 (22).

(2) Following the typical procedure above (0 °C, 2.5 h), *anti*-3-(1,2-epoxycyclohexanyl)-1-phenyl-1-butyn-3-ol (0.095 g, 0.392 mmol) was found to give **3g** as white needles (0.055 g, 58%), as a single diastereoisomer, spectroscopically identical with the sample prepared above.

**2-Acetyl-2-(2-phenylethyl)cyclohexan-1-ol (3h).** Following the typical procedure (above, 0 °C, 2 h), 2-(1,2-epoxycyclohexanyl)-4-phenylbutan-2-ol (0.75 g, 3.05 mmol) yielded a residue which was purified by column chromatography on silica using 25% ethyl acetate in petroleum ether as eluent to give recovered starting material (0.17 g) and **3h** as a white solid (0.46 g, 78%): mp 114–115 °C (recrystallized from diisopropyl ether); $\nu_{max}$ (KBr disk) 3450, 2990, 1600, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.33–7.13 (5H, m), 3.76 (1H, b m, (split by OH)), 3.08 (1H, br s), 2.58 (2H, m), 2.20 (3H, s), 2.10–1.78 (4H, m), 1.76–1.50 (4H, m), and 1.48–1.25 (2H, m); $\delta_C$ ($CDCl_3$) 216.0 (s), 142.0 (s), 128.5 (d), 128.3 (d), 126.0 (d), 73.5 (d), 55.9 (s), 37.5 (t), 30.9 (t), 30.7 (t), 29.7 (t), 26.4 (q), 22.5 (t), 22.2 (t); *m/z* +CI, 247 (55), 229 (100), 211 (42), 201 (55), and 185 (40). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.00; H, 9.00. Found: C, 77.87; H, 8.95.

**2-Ethenyl-2-(1-oxo-2-phenylethyl)cyclohexan-1-ol (3i).** Following the typical procedure above (0 °C, 1 h), 1-(1,2-epoxycyclohexyl)-1-(ethenyl)-2-phenylethan-1-ol (0.150 g, 0.614 mmol) was found to give **3i** as a colorless oil (0.110 g, 73%), as a single diastereoisomer: mp 64–65 °C (recrystallized from diisopropyl ether/ethyl acetate); $M^+$ 244.1457 ($C_{16}H_{20}O_2$ requires 244.1463); $R_f$ = 0.13 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (KBr disk) 3440, 1700, 1635, 1605, and 1500 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.14 (3H, m), 7.04 (2H, m), 5.90 (1H, dd, $J$ = 18, 12 Hz), 5.32 (1H, d, $J$ = 12 Hz), 5.20 (1H, d, $J$ = 18 Hz), 3.82 (1H, m), 3.78 (1H, d, $J$ = 17 Hz), 3.57 (1H, d, $J$ = 17 Hz), 3.06 (1H, bs), 2.10 (1H, m), and 1.79–1.22 (7H, m); $\delta_C$ ($CDCl_3$) 211.7 (s), 137.7 (d), 134.3 (s), 129.7 (d), 128.4 (d), 126.8 (d), 118.6 (t), 72.9 (d), 59.4 (s), 44.3 (t), 30.0 (t), 28.5 (t), 21.7 (t), and 21.4 (t); *m/z* +EI, 227 (M − 17, 5), 153 (10), 125 (20), 108 (50), 91 (100), 79 (50), 65 (20), 55 (50), 49 (42), and 41 (28); *m/z* +CI, 245 (M + 1, 40), 227 (M − 17, 51), 153 (20), 125 (22), 108 (100), 91 (88), and 49 (70). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.29; H, 8.05.

**2-(1-Oxo-2-phenylethyl)-2-phenylcyclohexan-1-ol (3j).** Following the typical procedure above (0 °C, 1 h), 1-(1,2-epoxycyclohexanyl)-1,2-diphenylethan-1-ol (0.25 g, 0.85 mmol) gave a residue which was recrystallized from diisopropyl ether to give **3j** as a white crystalline solid (0.21 g, 84%), as a single diastereoisomer: mp 54–56 °C; $M^+$, 294.1620 ($C_{20}H_{22}O_2$ requires 294.1620); $R_f$ = 0.48 (20% ethyl acetate/petroleum ether); $\nu_{max}$ (KBr disk) 3475, 3070, 3040, 1715, 1605, 1570, and 1500 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.32–7.06 (8H, m), 6.76 (2H, dd, $J$ = 9, 2 Hz), 4.24 (1H, m), 3.42 (2H, $q_{AB}$, $J$ = 19 Hz), 3.17 (1H, bs), 2.22 (2H, t, $J$ = 6 Hz), and 1.69–1.20 (6H, m); $\delta_C$ ($CDCl_3$) 211.8 (s), 138.4 (s), 134.5 (s), 130.0 (d), 129.0 (d), 128.3 (d), 128.1 (d), 127.5 (d), 126.9 (d), 72.5 (d), 60.7 (s), 44.4 (t), 29.9 (t), 27.7 (t), 22.0 (t), and 21.3 (t); $m/z$ +EI, 294 (M, 4), 276 (M – 18, 5), 203 (30), 175 (32), 158 (80), 142 (32), 129 (70), 115 (50), 107 (34), 91 (100), 79 (25), 65 (20), and 41 (14). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 81.66; H, 7.65.

**2-(1-Oxoheptyl)-2-phenylcyclopentan-1-ol (3k).** Following the typical procedure above (0 °C, 3 h), 1-(1,2-epoxycyclopentyl)-1-phenylheptan-1-ol (0.38 g, 1.385 mmol) was found to give **3k** as a colorless oil (0.45 g, 88%), as a single diastereoisomer: $M^+$, 274.1939 ($C_{18}H_{26}O_2$ requires 274.1933); $R_f$ = 0.27 (10% ethyl acetate/petroleum ether); $\nu_{max}$ (liquid film) 3420, 2920, 1885, 1595, and 1490 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.23 (5H, m), 4.41 (1H, t, $J$ = 2 Hz), 3.72 (1H, bs), 2.34–0.92 (16H, m), and 0.73 (3H, t, $J$ = 8 Hz); $\delta_C$ ($CDCl_3$) 214.5 (s), 139.1 (s), 128.9 (d), 127.4 (d), 126.7 (d), 80.4 (d), 68.5 (s), 39.6 (t), 31.4 (t), 30.8 (t), 29.2 (t), 28.6 (t), 23.6 (t), 22.4 (t), 20.7 (t), and 14.0 (q); $m/z$ +EI, 159 (10), 144 (100), 129 (12), 117 (12), 91 (20), 77 (10), and 43 (35); $m/z$ +CI, 275 (M + 1, 80), 257 (M – 17, 100), 159 (95).

**2-(1-Oxoheptyl)-2-phenylcyclohexan-1-ol (3l).** Following the typical procedure given above (20 °C, 1 h), 1-(1,2-epoxycyclohexyl)-1-phenylheptan-1-ol (0.50 g, 1.72 mmol) yielded a residue which was purified by column chromatography on silica using 15% ethyl acetate in petroleum ether as eluent to give **3l** as a colorless oil (0.37 g, 74%): $M^+$, 288.2065 ($C_{19}H_{28}O_2$ requires 288.2089); $M^+$ – 18, 270.1974 ($C_{19}H_{26}O$ requires 270.1983); $\nu_{max}$ (liquid film) 3500, 1700, 1600, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.4–7.2 (5H, m), 4.3 (1H, m), 3.3 (1H, bs), 2.3 (4H, m), 1.85–0.9 (14H, m), and 0.8 (3H, t, $J$ = 7 Hz); $\delta_C$ ($CDCl_3$) 215.2 (s), 138.8 (s), 128.8 (d), 127.7 (d), 127.1 (d), 72.7 (d), 60.1 (s), 37.6 (t), 31.4 (t), 29.8 (t), 28.5 (t), 27.6 (t), 23.7 (t), 22.4 (t), 21.9 (t), 21.3 (t), and 14.0 (q); $m/z$ +EI, 288 (10), 270 (12), 217 (21), 158 (100), 130 (22), 91 (30), and 43 (48).

**2-(1-Oxoheptyl)-2-phenylcycloheptan-1-ol (3m).** Following the typical procedure above (0 °C, 2 h), 1-(1,2-epoxycycloheptyl)-1-phenylheptan-1-ol (0.50 g, 1.7 mmol) yielded a residue which was purified by column chromatography on silica using 15% ethyl acetate in petroleum ether as eluent to give **3m** as a colorless oil (0.32 g, 64%): $\nu_{max}$ (liquid film) 3500, 1700, 1600, and 1500 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.35–7.15 (5H, m), 4.25 (1H, dd, $J$ = 11 and 1 Hz), 3.20 (1H, bs) 2.35 (1H, m), 2.15 (3H, m), 2.05–0.90 (16H, m), and 0.75 (3H, t, $J$ = 7 Hz); $\delta_C$ ($CDCl_3$) 215.3 (s), 141.3 (s), 128.6 (d), 127.6 (d), 127.0 (d), 76.5 (d), 63.4 (s), 38.6 (t), 31.9 (t), 31.5 (t), 30.2 (t), 28.7 (t), 27.6 (t), 24.1 (t), 23.1 (t), 23.0 (t), 22.4 (t), and 14.0 (q); $m/z$ +CI, 320 (25), 303 (100), 285 (38), and 172 (62).

**1-Hydroxyspiro[5.6]dodecan-7-one (3n).** Following the typical procedure above (0 °C, 24 h), 1-(1,2-epoxycyclohexyl)-cyclohexan-1-ol (1.50 g, 7.65 mmol) yielded a residue which was purified by column chromatography on silica using 15% ethyl acetate in petroleum ether as eluent to give **3n** as a colorless oil (0.62 g, 41%): $M^+$, 196.1455 ($C_{12}H_{20}O_2$ requires 195.1463); $\nu_{max}$ (liquid film) 3450, 2940, 2860, 1695, 1500, and 1450 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 3.65 (1H, t, $J$ = 7 Hz), 3.15 (1H, bs), 2.65 (1H, m), 2.45 (1H, m), 2.05 (1H, m), 1.90 (1H, m), and 1.85–1.20 (14H, m); $\delta_C$ ($CDCl_3$) 215.9 (s), 74.3 (d), 54.9 (s), 39.8 (t), 34.2 (t), 30.3 (t), 30.0 (t), 30.0 (t), 26.6 (t), 24.6 (t), 21.4 (t), and 21.3 (t); $m/z$ +EI, 196 (12), 178 (12), 149 (10), 125 (60), 111 (50), 81 (67), 67 (57), 55 (100), and 41 (73).

**1-Hydroxyspiro[5.12]octadecan-7-one (3o).** Following the typical procedure above (room temperature, 24 h), *syn*-1-(1,2-epoxycyclohexyl)cyclododecan-1-ol (0.220 g, 0.79 mmol) gave a residue which was purified by column chromatography on silica using chloroform as eluent to give **3o** as white needles (0.147 g, 67%): mp 85–86.5 °C (recrystallized from diisopropyl ether); $R_f$ = 0.27 (chloroform); $\nu_{max}$ (KBr disk) 3515, 2940, 2865, and 1690 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 3.72 (1H, dd, $J$ = 7.5, 3 Hz), 2.79 (1H, ddd, $J$ = 18.5, 10.5, 3.5 Hz), 2.31 (1H, ddd, $J$ = 18.5, 10.5, 3.5 Hz), 2.08–1.86 (2H, m), and 1.81–1.14 (27H, m); $\delta_C$ ($CDCl_3$) 218.4 (s), 73.9 (d), 55.4 (s), 37.0 (t), 35.6 (t), 30.5 (t), 28.8 (t), 26.9 (t), 26.5 (t), 26.2 (t), 25.3 (t), 24.8 (t), 24.0 (t), 23.7 (t), 22.0 (t), 21.7 (t), and 21.4 (t); $m/z$ +EI, 280 (15), 262 (9), 96 (100), 81 (58), 55 (54), and 41 (55). Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 77.04; H, 11.63.

**1-Hydroxy-2-phenylbutan-3-one (3p).** Following the typical procedure above (0 °C, 1 h), 1,2-epoxy-3-phenylbutan-3-ol (0.25 g, 1.49 mmol) yielded a residue which was purified by column chromatography on silica using 35% ethyl acetate in petroleum ether as eluent to give **3p** as a colorless oil (0.10 g, 40%): M – 43, 121.0661 ($C_8H_9O$ requires 121.0653); $\nu_{max}$ (liquid film) 3400, 2940, 1710, and 1600 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.45–7.10 (5H, m), 4.15 (1H, dd, $J$ = 12, 9 Hz), 3.90 (1H, dd, $J$ = 9, 5 Hz), 3.70 (1H, dd, $J$ = 12, 5 Hz), 2.15 (1H, bs), and 2.10 (3H, s); $\delta_C$ ($CDCl_3$) 209.3 (s), 135.5 (s), 129.2 (d), 128.5 (d), 127.9 (d), 63.9 (t), 61.6 (d), and 29.6 (q); $m/z$ +EI, 146 (34), 104 (100), 91 (32), 77 (25), and 43 (72).

**2-Hydroxy-3-phenylhexan-4-one (3q).** Following the typical procedure above (0 °C, 0.5 h), 2,3-epoxy-4-phenylhexan-4-ol (0.40 g, 2.08 mmol) yield a residue which was purified by column chromatography on silica using 15% ethyl acetate in petroleum ether as eluent to give **3q** as a colorless oil (0.23 g, 56%): M – 44, 148.0888 ($C_{10}H_{12}O$ requires 148.0881); $\nu_{max}$ (liquid film) 3420, 2980, 1710, and 1600 $cm^{-1}$; $\delta_H$ ($CDCl_3$) 7.39–7.24 (3H, m), 7.20–7.14 (2H, m), 4.40 (1H, dq, $J$ = 9, 7 Hz), 3.60 (1H, d, $J$ = 9 Hz), 3.10 (1H, brs), 2.37 (2H, qd, $J$ = 7, 1 Hz), 0.99 (3H, d, $J$ = 7 Hz), and 0.97 (3H, t, $J$ = 7 Hz); $\delta_C$ ($CDCl_3$) 212.8 (s), 136.2 (s), 129.1 (d), 128.7 (d), 127.7 (d), 69.1 (d), 66.9 (d), 35.7 (t), 20.0 (q), and 7.8 (q); $m/z$ +CI, 148 (35), 118 (100), 91 (44), 77 (12), 57 (68), and 52 (43).

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**Supplementary Material Available:** NMR spectra (45 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.