Relevance of Oxyanion Stereochemistry to Chirality Transfer in Anionic Oxy-Cope Rearrangements

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Abstract: Geometrically and optically pure (3*R*,5*E*)- and (3*R*,5*Z*)-1,5-heptadien-3-ols undergo anionic oxy-Cope rearrangement under the exclusive control of oxyanion orientation with a 58–64% preference for equatorial oxygen. Six semicyclic dienols have also been synthesized where the preferred oxyanion-driven sigmatropic rearrangement pathway is obligatorily pitted against π-facial biases offered by 4-*tert*-butylcyclohexenyl, norbornenyl, and camphenyl rings. These rearrangements therefore offer especially stringent tests of those factors that control the level and direction of chirality transfer. The data show the oxyanion to disfavor becoming involved in 1,3-diaxial relationships. Electronic factors may also contribute to the stabilization of axial oxyanion orientation. If operative, this effect cannot be large and is easily overridden. The observed preferences show that a change in relative carbinol configuration can indeed have a significant impact on the isomeric distribution obtained from the anionic oxy-Cope rearrangement.

As extensive as studies of the anionic oxy-Cope rearrangement have been,[2] little attention has been paid to the possible control of chirality transfer by the stereochemical disposition of the oxyanion substituent in the transition state.[3] The combination of a low reaction temperature,[4] a customarily favorable thermodynamic driving force,[5] and high stereoselectivity make this [3,3] sigmatropic process particularly well suited to the simultaneous elaboration of multiple stereocenters in relatively complex molecules.[6]

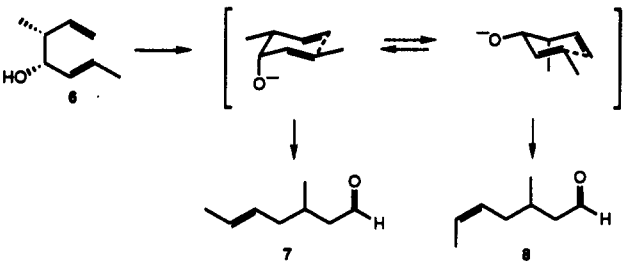
In general, the charge-accelerated oxy-Cope reaction proceeds via an early chairlike transition state,[7] although structurally-enforced passage through a boat arrangement does not arrest kinetically enhanced structural reorganization.[8] Experimental[9] and theoretical studies[10] concur that the associated transition states are usually highly dissociated, with substantial cleavage of the C3–C4 bond and little bond making at C1 and C6.

Several examples typified by **1**[11] and **2**[12] (Scheme I) have been clearly defined to occur via a chairlike transition state having a pseudoequatorial oxyanion. However, related rearrangements that proceed exclusively through chair transition structures with a pseudoaxial alkoxide substituent, e.g., **3**[13] and **4**,[14] are also known.

There exist two ways of appropriately analyzing the relative importance of oxyanion stereochemistry to the absolute stereochemical control of these reactions. In the first of these, all other steric demands on the particular system should be absent. In unsaturated alcohols constructed so that a single chiral center, the carbinol carbon, is present and structural features conducive to the independent induction of π-facial selectivity are lacking, the associated transition states will differ energetically only by virtue of oxyanion orientation. The second option is to involve systems where the added steric demands are particularly well defined. Obviously, random adoption of all possible transition-state alternatives is inimical to systematic investigation.

Two recently published studies serve to illustrate some of the factors affecting oxyanion orientation. le Noble has utilized the oxy-Cope rearrangement as a tool for assessing the electronic influence of a remote fluorine substituent in adamantane on π-facial selectivity (Scheme II).[15] The solvated oxyanion was found to compete effectively for equatorial status with the phenyl group attached to the same carbon. The authors calculate the equatorial preference for a phenyl substituent in the absence of the electronic effect imparted by the fluorine to be 73%; on this basis, we estimate the difference in energy between the two possible chairs to be only 0.63 kcal/mol. While an exceedingly large steric demand is indicated for the oxyanion, this interpretation ignores any potential electronic contribution from the phenyl substituent. Of more immediate interest would be results involving the less substituted **5**, which unfortunately proves unreactive toward KH in refluxing THF.

The contribution of Nakai and co-workers has been to examine the four stereoisomeric 4-hydroxy-3-methyl-1,5-heptadienes.[16] Their findings indicate the steric bulk associated with an oxyanion to be significant, although not as substantive as inferred by le Noble. Alcohol **6** proved to be the most revealing example, since the oxyanion and methyl group vie for equatorial orientation. The 65:35 distribution of **7** and **8** perforce necessitates that the equatorial alkoxide conformation be adopted during 35% of the isomerization events.



We report here on the behavior of **9** and **10**, two geometrically and optically pure alcohols that, because of minimal substitution, have stereochemistry set at the developing stereogenic center under the *exclusive* control of oxyanion orientation. The present effort

(1) The Ohio State University Fellow, 1986–1987, National Need Fellow (Department of Education), 1988–1989, and American Chemical Society Organic Division Fellow (Eli Lilly Co.), 1989–1990.

(2) (a) Hill, R. K. In *Asymmetric Synthesis*; Morrison, J. E., Ed.; Academic Press: Orlando, FL, 1984. (b) Hill, R. K. In *Comprehensive Organic Synthesis*; Paquette, L. A., Ed.; Pergamon Press: Oxford, 1991; Vol. 5.

(3) (a) Hauser, F. M.; Baghdanov, V. M. *Tetrahedron* **1984**, *40*, 4719. (b) Truesdale, L. K.; Swanson, D.; Sun, R. C. *Tetrahedron Lett.* **1985**, *26*, 5009.

(4) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765.

(5) Elmore, S. W.; Paquette, L. A. *Tetrahedron Lett.* **1991**, *32*, 319.

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(8) (a) Paquette, L. A.; Maleczka, R. E., Jr. *J. Org. Chem.* **1991**, *56*, 912. (b) Paquette, L. A.; Oplinger, J. A. *Tetrahedron* **1989**, *45*, 107.

(9) Gajewski, J. J.; Gee, K. R. *J. Am. Chem. Soc.* **1991**, *113*, 967.

(10) (a) Evans, D. A.; Baillargeon, D. J. *Tetrahedron Lett.* **1978**, 3315, 3319. (b) Steigerwald, M. L.; Goddard, W. W., III; Evans, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1994. (c) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877. (d) Ahlgren, G. *Tetrahedron Lett.* **1979**, 915. (e) Rozeboom, M. D.; Kiplinger, J. P.; Bartmess, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 1025. (f) Dewar, M. J. S.; Xie, C. *J. Am. Chem. Soc.* **1987**, *109*, 5893.

(11) Evans, D. A.; Nelson, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 774.

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(16) (a) Nakai, T.; Tomooka, K.; Wei, S.-Y. *Chem. Lett.* **1991**, *43*. (b) Wei, S.-Y.; Tomooka, K.; Nakai, T. *J. Org. Chem.* **1991**, *56*, 5973.

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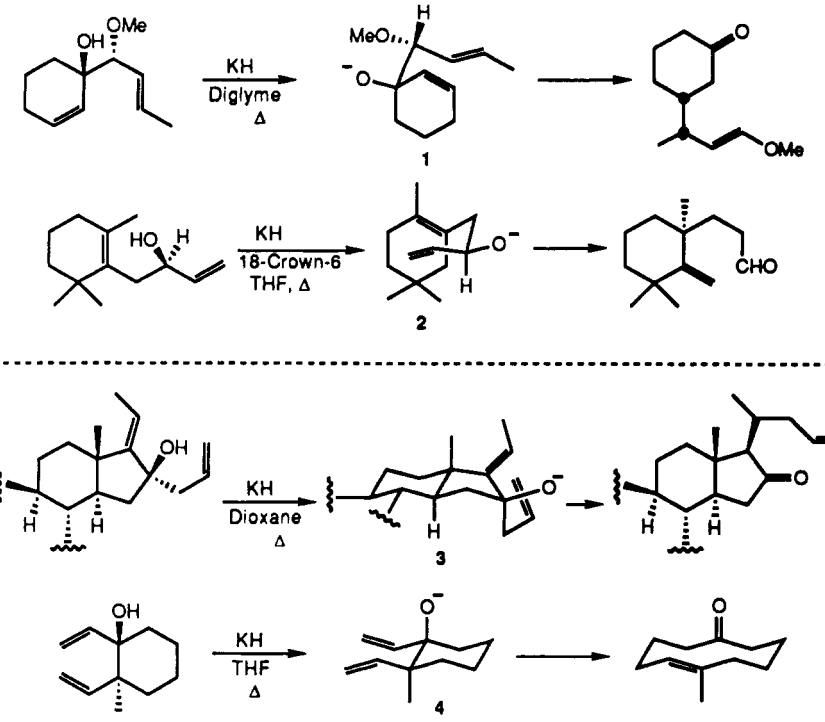
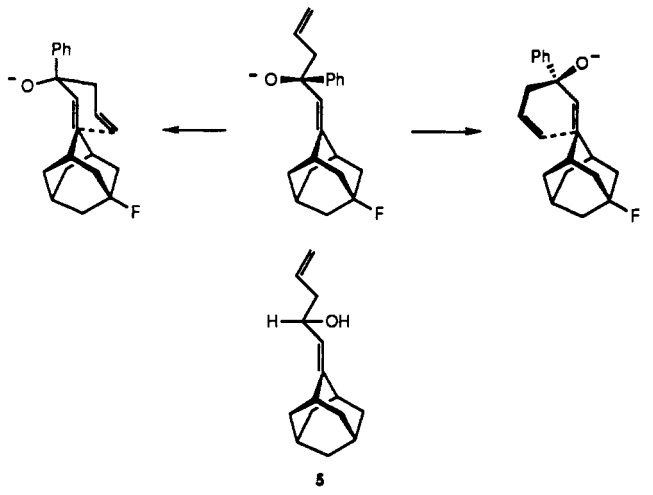
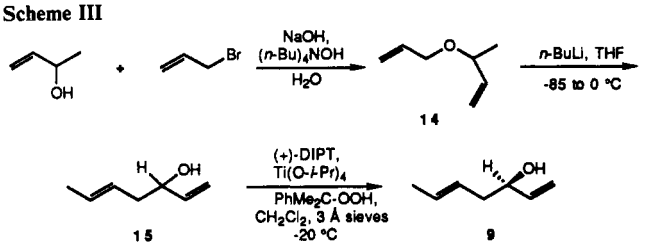
Scheme I



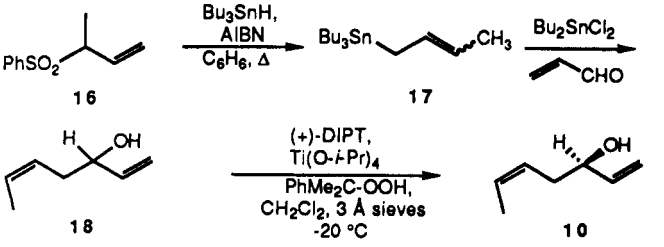
Scheme II



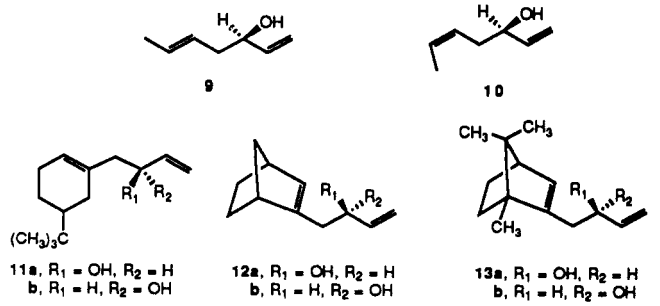
Scheme III



Scheme IV



also seeks as a complementary goal to define by means of cyclic dienols **11–13** the preferred sigmatropic pathway when oxyanion stereochemistry is obligatorily pitted against classical π-facial biases of different types.[17]



11a, R_1 = OH, R_2 = H
b, R_1 = H, R_2 = OH

12a, R_1 = OH, R_2 = H
b, R_1 = H, R_2 = OH

13a, R_1 = OH, R_2 = H
b, R_1 = H, R_2 = OH

Synthetic Considerations. Since chirality transfer is to be utilized as the rearrangement probe for **9** and **10**, it is imperative that these alcohols be both isomerically and optically pure. To this end, double-bond-forming strategies are selected that are known to lead almost exclusively to production of a single geometric isomer. Optical purity was achieved by Sharpless kinetic resolution[18] and confirmed by Mosher ester analysis.[19]

Access to **9** was realized in a straightforward sequence featuring [2,3] Wittig rearrangement[20] of the allyl ether of racemic 3-buten-2-ol (Scheme III). Capillary GC analysis indicated **15** to be 95–98% pure. The subsequent conversion to enantiomerically homogeneous (+)-**9** was best accomplished by using cumene hydroperoxide and (+)-diisopropyl L-(+)-tartrate and by carrying the oxidation to 55% completion.

Of the routes explored for the preparation of **10**, the one outlined in Scheme IV proved most efficient.[21] Following the conversion

(17) Preliminary communication: Paquette, L. A.; Maynard, G. D. *Angew. Chem.* **1991**, *103*, 1392; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1368.

(18) (a) Sharpless, K. B.; Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, S. *J. Am. Chem. Soc.* **1987**, *109*, 5765. (b) Sharpless, K. B.; Hanson, R. M. *J. Org. Chem.* **1986**, *51*, 1922. (c) Sharpless, K. B.; Carlier, P. R.; Mungall, W. S.; Schröder, G. *J. Am. Chem. Soc.* **1988**, *110*, 2978.

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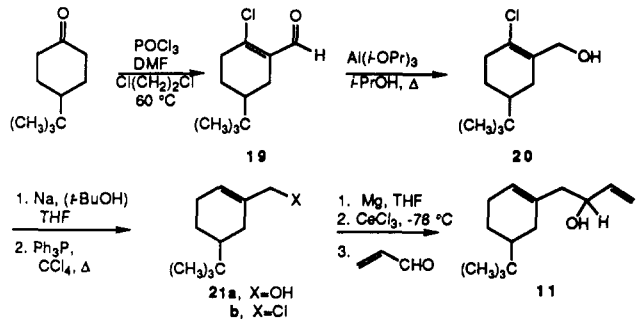
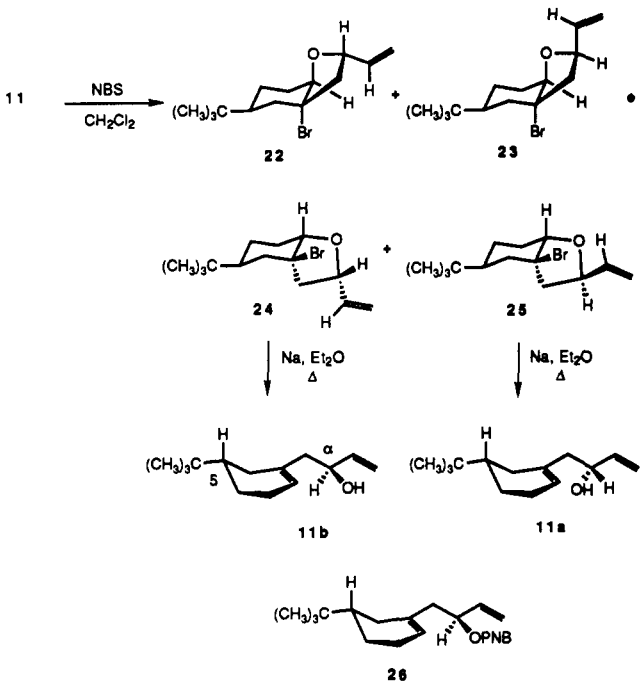
(20) (a) Nakai, T.; Mikami, K.; Taya, S.; Fujita, Y. *J. Am. Chem. Soc.* **1981**, *103*, 6492. (b) Nakai, T.; Mikami, K.; Kishi, N. *Tetrahedron* **1986**, *42*, 2911.

Scheme V



Scheme VI



of **16** to crotylstannane **17**, the isomeric mixture was treated with freshly distilled acrolein and 1.5 equiv of di-*n*-butyltin dichloride at room temperature. The resultant alcohol **18** was contaminated with less than 1% of the undesired (*E*) isomer. Enantioselective oxidation of **18** as before provided optically pure (+)-**10**.

Dienols **11a** and **11b** could be derived from β-chloro enal **19** with ensuing Meerwein–Ponndorf–Verley reduction (to minimize decomposition[22]) and dechlorination[23] (Scheme V). Chloride **21b** is then prepared, not for use in a Barbier reaction where bonding to the most substituted allylic carbon is expected,[24] but for conversion to the dichlorocerate.[25] Allylic coupling was conveniently skirted during Grignard formation by making recourse to magnesium that was activated by sonication with 0.1 equiv of anthracene.[26] Once the allylcerium reagent was in hand, condensation with acrolein led cleanly to a 1:1 mixture of **11a** and **11b**.

As expected, direct separation of this diastereomeric pair proved troublesome. The individual compounds could not be differentiated by MPLC, HPLC, or capillary GC methods, nor was silver nitrate-impregnated silica gel effective. It was reasoned that this difficulty might be overcome by rigidifying the molecules while bringing the centers of chirality into closer proximity. To this end, **11** was treated with NBS[27] as shown in Scheme VI. Both surfaces of the cyclohexene double bond proved amenable to bromonium ion formation, with the trans species being favored by ca. 4.5:1. While **22** and **23** were not chromatographically separable, **24** and **25** could be obtained in pure condition.

Independent treatment of **24** and **25** with metallic sodium in ether at reflux provided homogeneous **11b** and **11a**, respectively. The relative configuration of **11b** was established by conversion to the crystalline derivative **26** and X-ray crystallographic analysis (Figure 1). The inseparable mixture of **22** and **23** was similarly reduced to regenerate **11** for recycling purposes.

Since the Vilsmeier–Haack and Shapiro reactions[28] proceed in low yield when applied to norbornanone, the alternative protocol outlined in Scheme VII was developed for obtaining **12a** and **12b**. Dibromination of norbornene by irradiation in the presence of 1,2-dibromotetrachloroethane produced dibromide **27** with min-

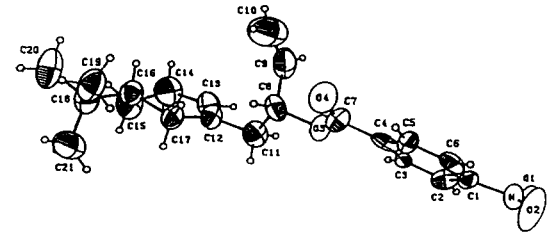


Figure 1. ORTEP drawing of **26** as determined by X-ray crystallography. The atom numbering is arbitrary.

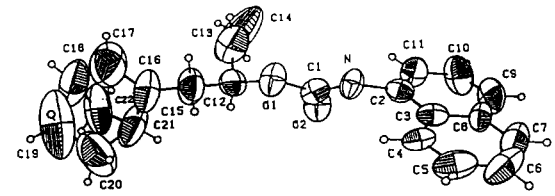
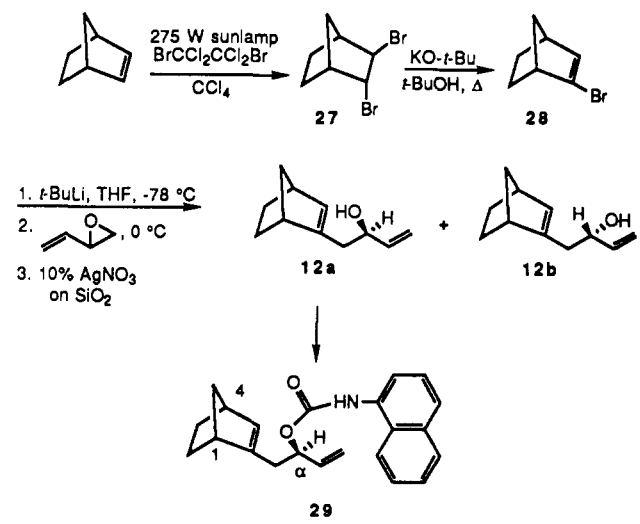


Figure 2. ORTEP drawing of **29** as determined by X-ray crystallography. The atom numbering is arbitrary.

Scheme VII



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(22) (a) Owton, W. M.; Gallagher, P. T. *Synth. Commun.* **1989**, *19*, 2731. (b) Miura, M.; Okuro, K.; Hattori, A.; Nomura, M. *J. Chem. Soc., Perkin Trans. 1* **1989**, 73.

(23) (a) Gassman, P. G.; Marshall, J. L. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 424. (b) Cream, G. E.; Serelis, A. K. *Aust. J. Chem.* **1978**, *31*, 863.

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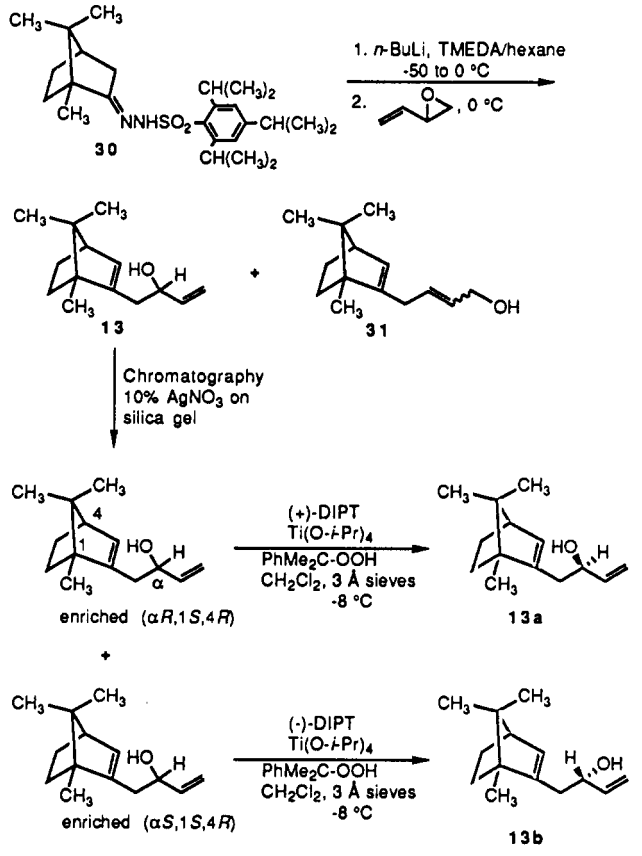
(25) Cohen, T.; Doubleday, W.; Guo, B.-S. *J. Am. Chem. Soc.* **1987**, *109*, 4710.

(26) Oppolzer, W.; Schneider, P. *Tetrahedron Lett.* **1984**, *25*, 3305.

(27) (a) Demole, E.; Enggist, P. *Helv. Chim. Acta* **1971**, *54*, 456. (b) Bartlett, P. A. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, pp 411–454.

(28) (a) Taylor, R. T.; Degenhardt, C. R.; Melega, W. P.; Paquette, L. A. *Tetrahedron Lett.* **1977**, 159. (b) Chan, T. H.; Baldassarre, A.; Massuda, D. *Synthesis* **1976**, 801. (c) Chamberlin, A. R.; Stemke, J. E.; Bond, F. T. *J. Org. Chem.* **1978**, *43*, 147. (d) Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017.

Scheme VIII

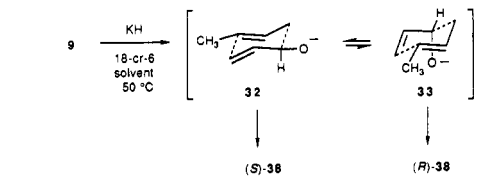


imal skeletal rearrangement.[29] Subsequent treatment of **27** with freshly prepared potassium *tert*-butoxide afforded pure **28**. Formation of the vinyllithium from **28** and condensation with butadiene monoxide[30] led to a mixture of carbinol regioisomers with the relative amount of **12** approximating 70%. In this instance, **12** could be separated into its (αR,1*R*,4*S*),(αS,1*S*,4*R*) and (αR,1*S*,4*R*),(αS,1*R*,4*S*) racemates by MPLC on a silver nitrate-impregnated silica gel column. The diastereomeric purity of each isomer was established by ^{13}C NMR spectroscopy, and the relative configurations were assigned on the basis of X-ray crystallographic analysis of α-naphthylurethane **29** (Figure 2).

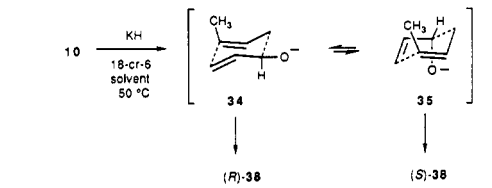
In contrast to the reported behavior of norbornanone, Shapiro methodology is recognized to be efficacious when applied to camphor, especially when the trishydrazone derivative is involved.[31] Regiospecific generation of the camphenyl anion from **30** in this fashion and its reaction with butadiene monoxide provided particularly rapid access to **13** (Scheme VIII). In this instance, the regioselectivity of electrophilic capture was lower than observed previously with norbornenyllithium. This may be an artifact of the requisite change in solvent from THF to a mixture of hexane and TMEDA. Notably, no product of addition at the 2-position of butadiene monoxide was observed. Presumably, the increase in steric hindrance relegates nucleophilic attack exclusively to the 1- and 2′-sites.

Since an enantiomerically pure starting material was employed, the resulting product mixture consisted only of the (αR,1*S*,4*R*) and (αS,1*S*,4*R*) diastereomers. These dienols could be obtained in diastereomerically enriched condition by chromatography on silver nitrate-impregnated silica gel. However, the weaker interactions of these more sterically hindered compounds with adsorbent made multiple recyclings necessary. Consequently, it proved most convenient to perform this chromatographic enrichment and then to apply the appropriate Sharpless kinetic resolution procedure to arrive at pure **13a** and **13b** (see Scheme VIII). As a bonus, the reactivity patterns exhibited by this pair of diastereomers in the final step permitted the assignment of absolute configuration to be made with confidence. Specifically, only **13a** remained after controlled epoxidation with (+)-diisopropyl tartrate as additive, and **13b** was minimally reactive toward the levorotatory diester.

Table I. Data for the Anionic Oxy-Cope Rearrangement of **9** and **10**



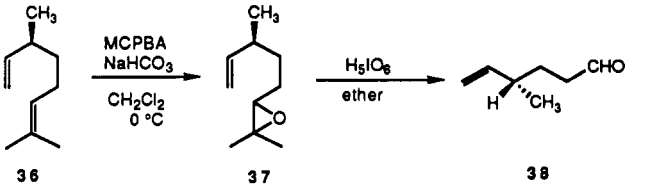
solvent	yield, %[a]	$[\alpha]_D^{25}$[b]	percent 32 based on $[\alpha]_D$	percent 32 from Mosher ester of 9
THF	69	+4.0°	64	61
DME	92	+3.7°	63	61



solvent	yield, %[a]	$[\alpha]_D^{25}$[b]	percent 34 based on $[\alpha]_D$	percent 34 from Mosher ester of 9
THF	78	-2.7°	59	57
DME	98	-2.5°	59	55
C_6H_6	83	-2.4°	58	55

[a] GC analysis values as averaged over two experiments. [b] Samples purified by preparative GC prior to measurement.

Scheme IX



Anionic Oxy-Cope Rearrangement of the Acyclic Dienols 9 and 10. Heating **9** and **10** at 50 °C with KH and 18-crown-6 in THF, DME, or benzene promoted efficient [3,3] sigmatropy, provided that quenching was ultimately effected with methanol at −78 °C. The selection of a particular solvent had only a minor effect on the product distribution and yield (Table I). Although (*R*)- and (*S*)-4-methyl-5-hexenal are known,[32] their optical rotations appear not to have been reported. Thus, pure (*S*)-**38** was prepared from (*S*)-(+)-citronellene (**36**) as shown in Scheme IX. The $[\alpha]^{25}_D$ value of +14.4° recorded for this material permitted the extent of equatorial and axial oxyanion involvement in the oxy-Cope transition states to be calculated.[33]

Independent verification of these determinations was accomplished by hydride reduction[34] of each sample of aldehyde isolated,

(29) (a) Wilt, J. W.; Chenier, P. J. *J. Org. Chem.* **1970**, *35*, 1562. (b) Paquette, L. A.; Learn, K. S.; Romine, J. L.; Lin, H.-S. *J. Am. Chem. Soc.* **1988**, *110*, 879.

(30) (a) Normant, J. F.; Cahiez, C.; Alexakis, A. *Synthesis* **1978**, 528. (b) Speckamp, W. N.; Ent. H.; Koning, H. de *Tetrahedron Lett.* **1985**, *26*, 5105. (c) Rose, C. B.; Taylor, S. K. *J. Org. Chem.* **1974**, *39*, 578.

(31) Chamberlin, A. R.; Liotta, E. L.; Bond, F. T. *Org. Synth.* **1982**, *61*, 140.

(32) (a) Ireland, R. E.; Thaisrivongs, S.; Dussault, P. H. *J. Am. Chem. Soc.* **1988**, *110*, 5768. (b) Ireland, R. E.; Anderson, R. C. Badoud, R.; Fitzsimmons B. J.; McGarvey, G. J.; Thaisrivongs, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 1988.

(33) Appropriate control experiments have shown **38** to be configurationally stable under the strongly basic conditions of the anionic oxy-Cope rearrangement.[17] Precluded by this finding is the possibility that the % ee values experimentally determined for **38** are lowered by partial racemization arising from adventitious intramolecular (or intermolecular) allylic proton abstraction by the neighboring oxido anion.

(34) Mori, K.; Masuda, S.; Suguro, T. *Tetrahedron* **1981**, *37*, 1329.

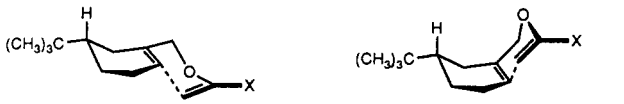
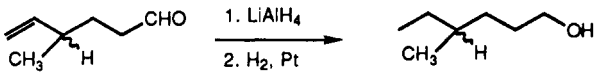


Figure 3. Ireland's Claisen rearrangement study.

catalytic hydrogenation of the resultant unsaturated alcohol in each instance, and Mosher ester analysis of **39** from the various sources. The data compilation given in Table I shows the agreement between the two forms of measurement to be very good.[35]



39

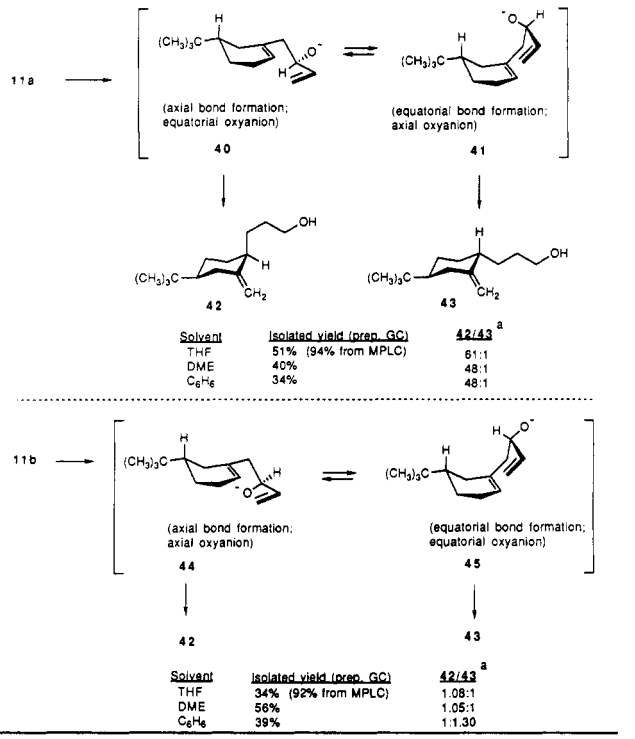
The (*E*) and (*Z*) isomers of 1,5-heptadien-3-ol both show a preference for [3,3] sigmatropic rearrangement through a chair transition state with the oxyanion in a pseudoequatorial orientation, viz., **32** and **34**. However, the extent of this preference is slight. *At least for these sterically unbiased acyclic examples, the axial oxyanion transition states 33 and 35 are virtually as energetically accessible as their equatorial counterparts.*

4-*tert*-Butylcyclohexene Case Study. Axial bond formation is recognized to be stereoelectronically preferred in cyclohexene systems.[37] Ireland's study of the Claisen rearrangement indicated in Figure 3 serves as an experimental reference point for the present study.[38] In the absence of any potential stereochemical modulation brought on by an alkoxide substituent, the ratio of axial/equatorial C–C bond formation is ≥87:13.

The anionic oxy-Cope rearrangements of **11a** and **11b** were performed in the standard fashion at 50 °C. Because the aldehydic products proved to be somewhat sensitive to decomposition, they were directly reduced with sodium borohydride prior to structural analysis and product ratio evaluation. The isolated yields were in excess of 90% when purification was effected by MPLC; isomer separation by preparative GC was expectedly less efficient (35–50%).

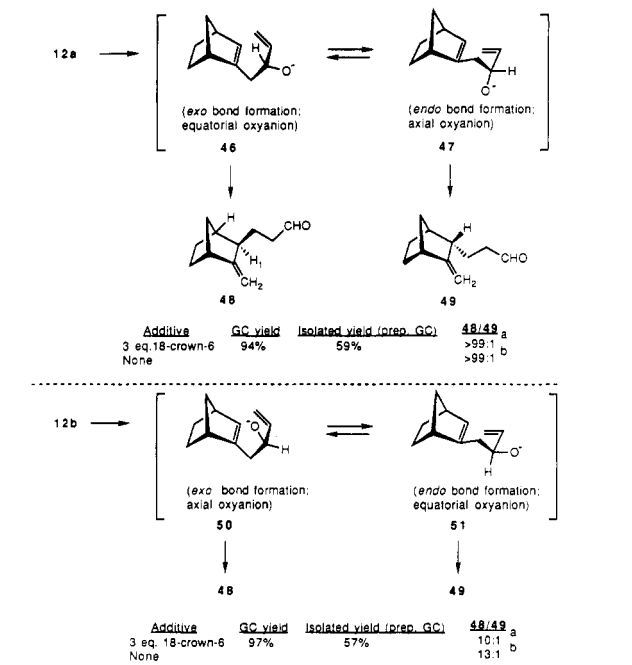
The relative configuration of the newly generated stereogenic center on the conformationally rigid *tert*-butylcyclohexene ring system was determined by means of 300-MHz ^{1}H NMR spectroscopy. The chemical shift of the tertiary allylic proton at this site is the most diagnostic probe. As previous studies have established,[38] such an equatorial proton consistently appears downfield of its axial counterpart. For **42** and **43**, this proton is seen to resonate at δ 2.24 and 1.98, respectively, in $CDCl_3$. On this basis, chirality transfer within **11a** is seen to operate at a high level, with a strong preference being exhibited for the formation

Table II. Data for the Anionic Oxy-Cope Rearrangement of **11a** and **11b**



[a] Average of two runs.

Table III. Data for the Anionic Oxy-Cope Rearrangement of **12a** and **12b**



[a] Average of two experiments. [b] Single determination.

of **42** (Table II). In contrast, both **42** and **43** result from [3,3] sigmatropy within **11b** and in approximately equal amounts.

Mechanistic Implications Derived from Involvement of a Norbornenyl Framework. Although **12a** and **12b** were subjected to the standardized anionic oxy-Cope conditions, their rearrangement rates were sufficiently accelerated that experiments could also be performed in the absence of 18-crown-6 (Table III). The major aldehydic proton in both examples, viz., **48**, was easily identified on the strength of nonexisting coupling between the allylic methine and bridgehead protons. The associated dihedral angle requires

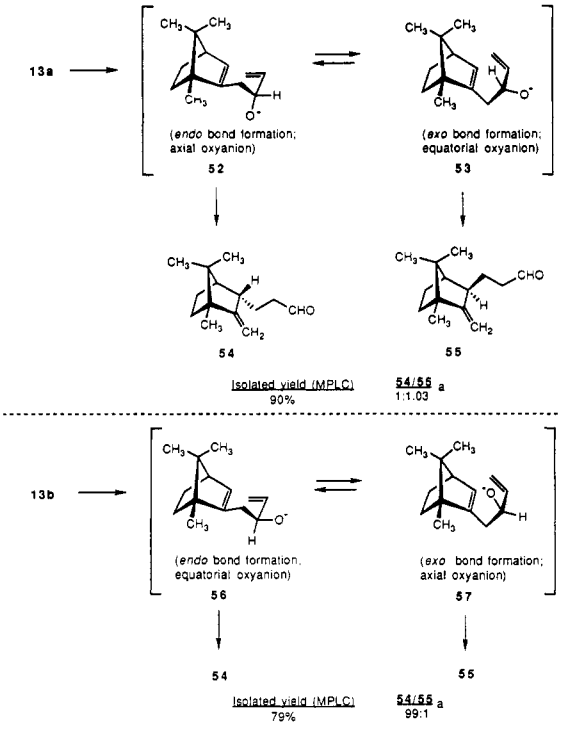
(35) The assumption that chair transition states operate exclusively during [3,3] sigmatropy has its origins in the widely disparate energies associated with the chair and boat options, at least when acyclic systems are involved.[7] No exceptions are noted,[16,36] unless steric perturbations are made overriding, nor are ambiguities expected for **9** and **10**. Nonetheless, the transition states for these dienols (Table I) hold the prospect of being completely diagnostic of rearrangement stereochemistry. Thus, **32–35** lead to pairs of (*E*)- and (*Z*)-enolate anions that differ in absolute configuration *and enolate* geometry. Should neither structural component be subject to chemical modification, knowledge of these parameters would unambiguously define the reaction trajectories. To this end, **9** was isomerized and treated with *tert*-butyldimethylsilyl chloride to give a 64:36 mixture of cis and trans TBS enol ethers, which were separately hydrogenated in a CH_2Cl_2/CH_3OH solvent system. The samples of **38** obtained from these two streams were identically enriched in the (*R*) enantiomer (20% ee). Consequently, enolate ion stereochemistry is not preserved under these circumstances, and this stereochemical assay is not seen as a useful mechanistic probe.

(36) (a) Corey, E. J.; Lee, D.-H. *J. Am. Chem. Soc.* **1991**, *113*, 4026. (b) Ireland, R. E.; Wipf, P.; Xiang, J.-N. *J. Org. Chem.* **1991**, *56*, 3572. (c) Wei, S.-Y.; Tomooka, K.; Nakai, T. Submitted for publication.

(37) The situation becomes less clear with cyclohexylidenes having an exocyclic methylene: Denmark, S. E.; Harmata, M. A.; White, K. S. *J. Am. Chem. Soc.* **1989**, *111*, 8878.

(38) Ireland, R. E.; Varney, M. D. *J. Org. Chem.* **1983**, *48*, 1829.

Table IV. Data for the Anionic Oxy-Cope Rearrangement of **13a** and **13b**



[a] Average of two experiments.

an exo orientation for the propionaldehyde substituent.[39] Minor consistent **49** could not be completely freed of its epimer. Nonetheless, the ratio of aldehydes was readily determined by capillary GC analysis.

As with the *tert*-butylcyclohexene derivatives, the product distributions that stem from **12a** and **12b** appears to be modulated by the steric demands of the oxyanion. Table III incorporates the chairlike conformers that are presumed to constitute each of the four possible transition structures. Of these, **46** clearly represents the most favorable situation since its oxyanion is equatorially oriented and sterically favored exo bond formation[40] is operating. In **50**, exo linkage of the π termini requires axial orientation of the oxyanion. The resultant steric compression is sufficiently energy demanding to allow **51** to compete, as indicated by the formation of 5–10% of endo product **49**.

Evidently, the driving force for exo bond formation is sufficiently strong that modulation by the oxyanion is not overwhelmingly pronounced. In the absence of 18-crown-6, one might anticipate tighter solvation to lead to an increased steric demand on the part of the oxyanion. This expectation was not reflected in the observed product distributions. Rather, a small *decrease* in the impact of oxyanion orientation on product distribution was noted.

Consequences of Camphenyl Steric Demands. The presence of a *syn*-methyl group in camphenyl derivatives **13a** and **13b** normally redirects electrophilic capture to the endo π-bond surface.[41] In the present context, the reversal in stereochemical bias induced by these increased steric demands was expected to influence the extent of oxyanion control in an informative way. Accordingly, the anionic oxy-Cope rearrangements of optically pure **13a** and **13b** were undertaken as before with potassium hydride in the presence of 18-crown-6 at 50 °C. The results compiled in Table IV reflect product yields following chromatographic separation. As in the experiments outlined above, the aldehyde distributions are evidently kinetically controlled, since they are essentially insensitive to the extent of total conversion of the starting materials. The basis for the assignment of endo stereochemistry to **54** emerged from ^{1}H NMR studies at 300 MHz that revealed an 11% NOE enhancement in the intensity of the *syn*-7-methyl signal upon irradiation of the allylic methine proton at C-3.

At issue in the present experiments is the relative weighting of those energetic demands associated with π-facial bonding to the camphenyl olefinic system and with the oxyanionic axial/equatorial prerogative. If the costs exerted by the bicyclic framework for exo bonding were high, the formation of **54** would prevail in either stereoisomeric series. Should the expense of axial orientation of the C–O$^-$ bond be non-negligible, rearrangement should proceed to deliver aldehyde **55** in those situations where this energetically significant preference would need to be avoided.

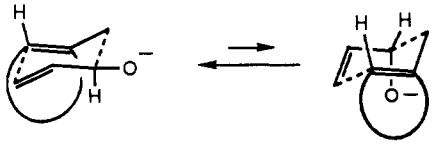
When the two effects operate cooperatively as in **56**, no departure from the efficient formation of **54** is seen. The **52**:**53** partition is of greater interest. Since **13a** is converted into essentially a 50:50 mixture of both possible stereoisomeric aldehydes, alleviation of the two opposed steric factors is met by roughly equal utilization of the two available reaction channels. In other words, the enthalpic benefit of equatorial oxyanion stereochemistry impacts in a major way on the rate-determining step.

Discussion

Unlike previous examples, dienols **9** and **10** share in common the benefit of not having π-facial selectivity enforced on either of their double bonds. In the absence of such constraints, the stereoselectivities of their anionic oxy-Cope rearrangement rest entirely on the equatorial/axial orientation of the oxyanion in the associated transition states (Table I). The extents to which (*R*)-**38** and (*S*)-**38** are formed upon isomerization of **9** and **10**, respectively, clearly show with a high degree of assurance that utilization of the axial product-forming alternatives is extensive (36–45%). These observations are striking since it has long been assumed that counterion complexation and alkoxide aggregation play an important role in making the oxyanion a somewhat bulky substituent. We also subscribe to this view (see below).

It is therefore important to ask why such steric factors do not suitably account for the results. One alternative would involve the existence of a favorable electronic contribution to the transition state when the C–O$^-$ bond is axial, thereby lowering the activation enthalpy for these specific processes.[12,42] Lee, Shin, and Kim have suggested, however, that the equatorial oxyanion bond was better able to destabilize the HOMO by donation of electron density, thus leading to improved LUMO′ overlap. The considerably higher than expected levels of axial oxyanion orientation observed presently suggest that this stereoelectronic interpretation is not correct, and more detailed considerations, perhaps of the ab initio type,[43] are in order.

In detail, the results provided by **11**–**13** (Tables II–IV) reveal that *a change in relative carbinol configuration can have a significant impact on product distribution.* As a group, these six dienols exhibit a greater propensity to fix the oxyanion equatorially than is seen with **9** and **10**. The common cause of this heightened stereoselectivity preference is the trisubstituted nature of the homoallylic double bond. As seen in the generic formulas **58** and **59**, axial orientation of the oxyanion introduces a 1,3-steric interaction not heretofore present in the acyclic examples. This



58 **59**

(39) Marchand, A. P. In *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*; Verlag Chemie International: Deerfield Beach, FL, 1982.

(40) Brown, H. C.; Kawakami, J. H.; Liu, K.-T. *J. Am. Chem. SOc.* **1970**, *92*, 5536 and references cited therein.

(41) Brown, H. C.; Kawakami, J. H.; Liu, K.-T. *J. Am. Chem. Soc.* **1973**, *95*, 2209 and references cited therein.

(42) (a) Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877. (b) Wilcox, C. F., Jr.; Carpenter, B. K. *J. Am. Chem. Soc.* **1974**, *101*, 3897.

(43) Binkley, J. S.; Poppe, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

added proximity surfaces irrespective of whether the pendant ring is *tert*-butylcyclohexenyl, norbornenyl, or camphenyl. Consequently, the isomerizations of **11a** via **41**, of **12a** via **47**, and of **13b** via **57** are strongly decelerated by the *combination* of nonbonded interactions of type **59** and untoward stereoelectronic and/or steric factors operating on the homoallyl π-bond surface indicated. Accessibility to these reaction channels is therefore very limited.

The finding that the conversion of **11b** to products is about evenly partitioned between **44** and **45** signifies that the enthalpic cost of the 1,3-diaxial interaction perpetrated in **44** is closely mirrored by the energetic disadvantages associated with equatorial C–C bonding to the cyclohexene ring. Since **13a** likewise undergoes oxy-Cope rearrangement via comparable levels of **52** and **53**, it would appear that the costs of exo sigmatropic approach to a camphenyl double bond closely parallel those associated with forming an equatorial link to C-1 of 4-*tert*-butylcyclohexene. The quite differently weighted response of **12b** (in favor of **50**) requires the enthalpic barrier to *endo*-norbornyl bond formation in **51** to be appreciably more elevated than that present in **50**. While these observations conform to expectations based upon electrophilic additions to the related bicyclic olefins,[44] the present technique provides for the first time a quantitative, clear-cut profile of the degree to which π-facial preferences are exerted by a particular ring system. We hope to exploit this technique in the course of future mechanistic undertakings associated with our interests in elucidating those factors responsible for π-face stereoselection.[45]

In conclusion, the collection of transition states depicted in Tables I–IV provides a satisfying basis for the selectivities observed with all eight probes. It is clear that the oxyanion substituent carries sufficient bulk to cause it to disfavor becoming involved in 1,3-diaxial relationships within product-determining transition states. However, this steric contribution is not overwhelmingly large, thereby allowing stereoelectronic and steric factors associated with conjoining of the π-termini to be capable of quantitative evaluation. In **9** and **10**, where ancillary facial preferences are not at issue, the oxyanion demonstrates a greater preference for axial orientation than anticipated on steric grounds alone. It is not yet clear whether stereoelectronic factors contribute to this phenomenon.

Experimental Section

Melting points are uncorrected. Optical rotations are based on concentrations of g/100 mL. ^{1}H NMR spectra were measured at 300 MHz, ^{13}C NMR spectra at 75 MHz, and ^{19}F NMR spectra at 235 MHz. Combustion analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, and exact mass measurements were determined at The Ohio State University Chemical Instrument Center. GC/MS analyses were performed with a mass selective detector GC/MS fitted with a 12 cm × 0.20 mm methyl silicone gum column and set at a flow rate of 0.2 mL/min. Capillary GC analyses were performed with a 30 m × 0.25 mm Durabond 5 column set for a flow rate of 2 mL/min at 100 °C with a split ratio of 30:1. Preparative GC separations were carried out using two columns: (A) 1.1 m × 6 mm (5% SE 30 on Chromosorb W) and (B) 2.4 m × 6 mm (5% SE 30 on Chromosorb W) with a flow rate of 12–20 mL/min. All solvents used were reagent grade and predried where appropriate. Reactions involving nonaqueous media were carried out under inert atmosphere.

Allyl 1-Methylallyl Ether (14).[20a] To 3-buten-2-ol (36.0 g, 0.500 mol) was added tetra-*n*-butylammonium hydroxide (10 mL of 0.4 M in water, 4 mmol) with ice bath cooling, followed by crushed sodium hydroxide pellets (40.0 g, 1.00 mol). With continued mechanical stirring for 30 min, allyl bromide (66.5 g, 0.550 mol) was added dropwise at 0 °C, the reaction mixture was allowed to warm to room temperature over 2.5 h and stirred at ambient temperature for 4 h, and the resultant white solid was filtered and washed with pentane (3 × 25 mL). The combined filtrates were washed with water (2 × 50 mL), dried, filtered, and distilled to give **14** (38.8 g, 69%) as a colorless liquid: bp 100–101 °C/760 Torr; IR (neat, cm^{-1}) 1640; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95–5.78 (m, 1 H), 5.76–5.60 (m, 1 H), 5.29–5.02 (series of m, 4 H), 4.04–3.75 (m, 3 H), 1.23 (d, J = 9.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.15, 135.05, 116.21, 115.56, 76.09, 68.88, 21.15.

(5*E*)-1,5-Heptadien-3-ol (15).[20] A magnetically stirred solution of **14** (10.00 g, 89.15 mmol) in THF (80 mL) under argon was cooled to −85 °C, treated dropwise with *n*-butyllithium (84.0 mL of 1.50 M in hexanes, 112 mmol), and stirred at −85 °C for 5 h. The colorless solution was allowed to warm to 0 °C over 4 h, saturated NH_4Cl solution (50 mL) was added slowly, and the mixture was diluted with ether (50 mL). The organic phase was separated, washed with water (50 mL), dried, filtered, and freed of solvent. Distillation provided 8.90 g (89%) of **15** as a colorless liquid: bp 91–93 °C/22 Torr; IR (neat, cm^{-1}) 1635; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95–5.76 (m, 1 H), 5.63–5.47 (m, 1 H), 5.47–5.33 (m, 1 H), 5.22 (d, J = 17.2 Hz, 1 H), 5.09 (d, J = 10.4 Hz, 1 H), 4.09 (dd, J = 12.3, 5.8 Hz, 1 H), 2.36–2.13 (m, 2 H), 1.96 (s, 1 H), 1.67 (d, J = 6.2 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.45, 134.03, 129.02, 126.30, 114.41, 72.00, 40.49, 17.95.

(+)-(3*R*,5*E*)-1,5-Heptadien-3-ol (9). To a flame-dried flask containing crushed, activated 3-Å molecular sieves (1.8 g) was introduced **15** (2.10 g, 18.7 mmol), *n*-decane (0.50 mL), diisopropyl L-(+)-tartrate (657 mg, 2.81 mmol), and dry CH_2Cl_2 (100 mL). The cooled (−20 °C) reaction mixture was treated with titanium tetraisopropoxide (532 mg, 1.87 mmol) and stirred for 30 min prior to the dropwise addition of cumene hydroperoxide (2.49 g of 80% which had been predried over 3-Å sieves, 13.1 mmol). Stirring was continued for 12 h at −18 °C and for another 8 h at −11 °C while the progress of reaction was monitored by capillary GC analysis. After more than 55% of the starting material had been consumed, 20 mL of a solution containing 2.2 g of citric acid and 6.6 g of ferrous sulfate was added, and the mixture was stirred at 0 °C for 1 h. The organic layer was stirred with 10 mL of 30% sodium hydroxide solution in brine (8 mL) at 0 °C for 1 h, dried, filtered, and evaporated at 0–10 °C to furnish 6.1 g of a yellow liquid which was purified by MPLC (silica gel, elution with 10% ethyl acetate/petroleum ether). There was isolated 564 mg of **9** as a colorless liquid, $[\alpha]^{25}_D$ +3.4° (c 3.41, $CHCl_3$), optically pure as judged by ^{19}F NMR analysis of the Mosher ester.

Procedure for Mosher Ester Preparation. To a magnetically stirred solution of the alcohol (0.175 mmol) in ether (2 mL) at 0 °C was added (*R*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (61.5 mg, 0.262 mmol) followed by a solution of dicyclohexylcarbodiimide (54.2 mg, 0.262 mmol) in ether (3 mL). 4-(*N*,*N*-Dimethylamino)pyridine (3.2 mg, 0.026 mmol) was introduced, and the resulting mixture was allowed to warm to ambient temperature over 1 h and stirred for an additional hour before being filtered through a tightly pressed cotton plug. The filtrate was diluted with ether (5 mL) and washed with saturated NH_4Cl solution (5 mL), water (5 mL), and brine (5 mL) prior to drying. Solvent evaporation provided a colorless semisolid. The crude product was analyzed by capillary GC and ^{19}F NMR before purification by MPLC on silica gel. Yields ranged from 95 to 100%.

2-Butenyltributylstannane (17).[21b] A magnetically stirred solution of 3-(phenylsulfonyl)-1-butene (9.20 g, 46.9 mmol), tri-*n*-butyltin hydride (31.4 g, 108 mmol), and AIBN (380 mg) in benzene (135 mL) was heated at reflux for 4.5 h under argon. The resulting cloudy solution was filtered through neutral alumina (60 mm × 120 mm) with benzene elution and concentrated under reduced pressure to give 41.1 g of colorless liquid. This liquid was distilled to provide 14.7 g (91%) of **17** (3:1 E/Z mixture) as a colorless liquid: bp 96–97 °C/0.3 Torr; IR (neat, cm^{-1}) 1633; ^{1}H NMR (80 MHz, $CDCl_3$) δ 5.85–5.03 (m, 2 H), 1.90–1.11 (series of m, 17 H), 1.10–0.77 (m, 15 H).

(5*Z*)-1,5-Heptadien-3-ol (18).[21a] A mixture of **17** (14.7 g, 42.6 mmol), freshly distilled acrolein (2.39 g, 42.6 mmol), and di-*n*-butyltin dichloride (19.4 g, 63.9 mmol) was stirred at room temperature for 24 h. The mixture was placed under reduced pressure (0.5 Torr) and warmed to 50 °C using an oil bath. A colorless liquid containing **18** (5.30 g) accumulated in an attached trap, which had been cooled to −78 °C. The crude product was distilled to provide 2.89 g (59%) of **18** as a colorless liquid: bp 96–98 °C/20 Torr; IR (neat, cm^{-1}) 3360; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96–5.84 (m, 1 H), 5.70–5.57 (m, 1 H), 5.48–5.34 (m, 1 H), 5.30–5.05 (series of m, 2 H), 4.19–4.06 (m, 1 H), 2.35–2.33 (m, 2 H), 1.66–1.66 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.48, 126.94, 125.33, 114.39, 72.30, 34.60, 12.62.

(+)-(3*R*,5*Z*)-1,5-Heptadien-3-ol (10). A sample of **18** (2.10 g, 18.7 mmol) was subjected to Sharpless kinetic resolution as described above. There was isolated 761 mg (81% based on 55% consumption) of **10** as a colorless liquid, $[\alpha]^{25}_D$ +2.0° (c 3.41, $CHCl_3$), optically pure as judged by ^{19}F NMR analysis of the Mosher ester.

5-*tert*-Butyl-2-chloro-1-cyclohexene-1-methanol (20). A cold (0–5 °C), magnetically stirred solution of DMF (16.4 g, 0.225 mol) in 1,2-dichloroethane (300 mL) was treated dropwise under argon with phos-

(44) Brown, H. C. *The Nonclassical Ion Problem*; Plenum Press: New York, 1977.

(45) (a) Paquette, L. A. In *Stereochemistry and Reactivity of Pi Systems*; Watson, W. H., Ed.; Verlag Chemie International: Deerfield Beach, FL, 1983; pp 41–73. (b) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328.

phorus oxychloride (31.5 g, 0.205 mol) at a rate such as to maintain a temperature below 10 °C. After completion of the addition, the reaction mixture was allowed to warm to ambient temperature before 4-*tert*-butylcyclohexanone (28.75 g, 0.186 mol) was introduced as a solution in 1,2-dichloroethane (100 mL). The resulting mixture was heated at 60 °C for 2 h, cooled to 5 °C, and treated with an ice-cold NaOAc solution (50 g in 100 mL of H_2O). After 10 min, the organic phase was separated, dried, filtered, and concentrated. The crude product was immediately dissolved in isopropyl alcohol (250 mL), treated with aluminum isopropoxide (38.1 g, 0.186 mol) while being stirred magnetically, and heated at 120 °C as acetone was slowly distilled through a Vigreux column over 5 h. The resulting dark-green mixture was cooled, poured into dilute HCl (100 mL of 1 N HCl and 100 g of ice), extracted with ether (200 mL), washed with a dilute NaOAc solution (10 g in 100 mL) and brine (100 mL), dried, filtered, and evaporated to leave 42.3 g of dark-brown liquid. Chromatography on silica gel (elution with 20% ether in petroleum ether) provided 20.5 g (54% overall) of **20** as a pale yellow liquid: IR (neat, cm^{-1}) 3320; ^1H NMR (300 MHz, $CDCl_3$) δ 4.25 (dd, J = 19.7, 12.2 Hz, 2 H), 2.51–2.33 (series of m, 3 H), 2.07–1.91 (m, 1 H), 1.90–1.71 (m, 2 H), 1.43–1.20 (m, 2 H), 0.89 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.40, 128.88, 63.45, 43.61, 34.96, 32.13, 29.82, 27.20, 25.10; MS m/z (M^+) calcd 202.1124, obsd 202.1121.

5-*tert*-Butylcyclohexene-1-methanol (21a). To a magnetically stirred mixture of THF (200 mL) and *tert*-butyl alcohol (10.0 g, 135 mmol) under argon were added small chunks of sodium (17.7 g, 0.770 mol). The mixture was brought to a gentle reflux before a solution of **20** (19.5 g, 96.4 mmol) in THF (50 mL) was introduced dropwise over 1 h. The mixture was refluxed for 15 h and cooled to room temperature. The solution was decanted away from the excess sodium, quenched with methanol, diluted with ether (200 mL), washed with brine (2 × 100 mL), dried, filtered, and evaporated to provide 20.2 g of a yellow liquid. Distillation gave 14.60 g (90%) of **21a** as a colorless liquid: bp 85–87 °C/1.2 Torr; IR (neat, cm^{-1}) 3320; ^1H NMR (300 MHz, $CDCl_3$) δ 5.66–5.63 (m, 1 H), 4.02–3.91 (m, 2 H), 2.21–1.62 (series of m, 6 H), 1.37–1.20 (m, 1 H), 1.18–1.02 (m, 1 H), 0.86 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.88, 122.72, 67.58, 44.21, 32.24, 27.29, 27.18, 26.30, 23.83; MS m/z (M^+) calcd 168.1514, obsd 168.1518. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.43; H, 11.96.

(5-*tert*-Butyl-1-cyclohexen-1-yl)methyl Chloride (21b). A mixture of **21a** (11.0 g, 65.4 mmol), CCl_4 (60 mL), and triphenylphosphine (22.30 g, 85.0 mmol) was stirred at reflux for 3 h. The resulting mixture was filtered and cautiously concentrated at reduced pressure to provide a colorless semisolid, which was washed with pentane (5 × 100 mL). The combined pentane extracts were evaporated carefully without heat to give 18.2 g of a pale-yellow-colored liquid, which was distilled to provide 11.1 g (91%) of **21b** as a colorless liquid: bp 65–67 °C/0.07 Torr; IR (neat, cm^{-1}) 1478, 1437, 1393; ^1H NMR (300 MHz, $CDCl_3$) δ 5.83–5.74 (m, 1 H), 4.01 (s, 2 H), 2.25–1.70 (series of m, 5 H), 1.40–1.21 (m, 1 H), 1.20–1.00 (m, 1 H), 0.90 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.67, 127.19, 50.57, 44.08, 32.24, 27.65, 27.18, 26.54, 23.37; MS m/z (M^+) calcd 186.1175, obsd 186.1190.

5-*tert*-Butyl-α-vinyl-1-cyclohexene-1-methanol (11). Magnesium (325 mesh, 841 mg, 34.6 mmol) contained in each of two flasks was flame-dried under argon, cooled to ambient temperature, and suspended in THF (25 mL). Anthracene (123 mg, 0.692 mmol) was introduced, to be followed by iodomethane (3 drops). The mixture was subjected to ultrasonic irradiation (cleansing bath) for 16 h at room temperature. The magnetically stirred green-yellow suspension was cooled to −65 °C, and chloride **21b** was added in one portion. The mixture was immediately returned to the ultrasonic bath at ambient temperature. After 30 min, the supernatant was transferred via cannula to a prestirred (2 h) suspension of anhydrous cerium(III) chloride [from 6.45 g (34.6 mmol) of heptahydrate dried at 140 °C/0.05 Torr for 4 h] under argon in THF (50 mL) at −78 °C. The mixture was stirred vigorously for 30 min before freshly dried/distilled acrolein (1.45 g, 26.0 mmol) was added rapidly dropwise. The cooling bath was removed, and the solution was allowed to warm to 0 °C before the addition of 1 N HCl (75 mL). After dilution with ether (100 mL), the organic phase was washed with water (2 × 50 mL) and brine (50 mL), dried, filtered, and evaporated under reduced pressure to provide 1.47 g of a colorless oil. Purification by MPLC (silica gel, elution with 10% ethyl acetate in petroleum ether) yielded 690 mg (38%) of a colorless oil consisting of a 1:1 mixture of racemic diastereomers **11**, which solidified on standing: mp 44–46 °C; IR (neat, cm^{-1}) 3380, 1640; ^1H NMR (300 MHz, $CDCl_3$) δ 5.95–5.82 (m, 1 H), 5.55 (s, 1 H), 5.26 (dt, J = 17.2, 1.5 Hz, 1 H), 5.10 (dt, J = 10.4, 1.5 Hz, 1 H), 4.26–4.14 (m, 1 H), 2.30–1.65 (series of m, 8 H), 1.34–1.20 (m, 1 H), 1.16–0.98 (m, 1 H), 0.88 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.77, 140.67, 134.34, 134.23, 125.20, 124.97, 114.25, 70.14, 69.81, 46.66, 45.93, 44.52, 44.39, 32.23, 32.20, 30.18, 30.10, 27.33, 27.19, 26.72, 26.60, 23.71; MS m/z (M^+) calcd 208.1827, obsd 208.1875. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.54; H, 11.54.

Bromoetherification of 11. To a magnetically stirred solution of **11** (3.20 g, 15.4 mmol) in CH_2Cl_2 (100 mL) at 0 °C under argon and shielded from light was added recrystallized *N*-bromosuccinimide (2.88 g, 16.2 mmol). The solution was allowed to reach room temperature slowly over 7 h and stirred for an additional 9 h. Evaporation of solvent followed by MPLC purification (silica gel, elution with 1% ethyl acetate in petroleum ether) gave 1.80 g of a mixture **22/23** as a yellow oil, 488 mg of colorless oily **25**, and 411 mg of **24**. The combined yield was 2.70 g (61%). Additionally, 550 mg of a yellow oil was recovered by flushing the column with a more polar solvent mixture (20% ethyl acetate in petroleum ether). This material, which appeared to be a complex mixture of bromo epoxides, was reduced with sodium metal in ether to recover **11**.

For **22**: a colorless liquid contaminated with a small amount of **23**: IR (neat, cm^{-1}) 1469, 1459, 1452, 1432, 1368, 1280; ^1H NMR (300 MHz, $CDCl_3$) δ 5.97–5.82 (m, 1 H), 5.31–5.07 (series of m, 2 H), 4.53–4.38 (m, 1 H), 4.09–4.04 (m, 1 H), 2.61–2.50 (m, 1 H), 2.40–2.32 (m, 1 H), 2.08–1.83 (series of m, 3 H), 1.60–1.16 (series of m, 4 H), 0.87 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.81, 115.41, 80.76, 76.58, 64.21, 50.18, 43.28, 38.06, 31.97, 27.43, 25.03, 20.52; MS m/z (M^+) calcd 286.0932, obsd 286.0941.

For **24**: colorless liquid; IR (neat, cm^{-1}) 1635, 1450, 1430, 1367, 1294; ^1H NMR (300 MHz, $CDCl_3$) δ 6.12–5.97 (m, 1 H), 5.38–5.10 (series of m, 2 H), 4.97–4.83 (m, 1 H), 4.61–4.54 (m, 1 H), 2.82–2.71 (m, 1 H), 2.21–1.73 (series of m, 4 H), 1.65–1.08 (series of m, 4 H), 0.88 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.83, 115.68, 83.29, 74.62, 58.35, 41.52, 39.23, 34.63, 31.99, 29.69, 27.26, 20.21; MS m/z ($M^+ - [C_4H_9]$) calcd 229.0228, obsd 229.0290.

For **25**: colorless liquid; IR (neat, cm^{-1}) 1635, 1470, 1450, 1367, 1292, 1240; ^1H NMR (300 MHz, $CDCl_3$) δ 6.10–5.95 (m, 1 H), 5.34–5.13 (m, 2 H), 4.90–4.80 (m, 1 H), 4.43–4.37 (m, 1 H), 2.53–2.25 (series of m, 2 H), 2.20–1.75 (series of m, 3 H), 1.60–1.36 (series of m, 4 H), 0.87 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.87, 115.67, 82.89, 74.03, 59.46, 41.94, 39.23, 32.86, 32.11, 29.27, 27.34, 20.21; MS m/z ($M - [C_4H_9]$) calcd 229.0228, obsd 229.0252.

Reduction of the 22/23 Mixture. To a magnetically stirred solution of **22** and **23** (1.80 g, 6.27 mmol) in dry ether (30 mL) under argon was added freshly cut and crushed sodium (433 mg, 18.8 mmol). The mixture was heated at reflux for 6 h. After complete consumption of the starting material, the mixture was cooled to 0 °C and methanol was added dropwise. The resulting solution was washed with saturated NH_4Cl solution (10 mL), water (10 mL), and brine (10 mL), and then dried, filtered, and evaporated to give 1.26 g of a yellow oil which solidified on standing. Purification by MPLC (silica gel, elution with 10% ethyl acetate in petroleum ether) gave 1.11 g (85%) of a white solid, mp 47–48.5 °C. This product was determined to contain **11b** plus a small amount of **11a** by ^{13}C NMR analysis.

Reduction of 24. To a magnetically stirred solution of **24** (411 mg, 1.43 mmol) in dry ether (10 mL) under argon was added freshly cut and crushed sodium (99 mg, 4.3 mmol). The mixture was heated at reflux for 3 h and processed in the usual manner to give 286 mg (96%) of pure **11b** as a white solid: mp 48–49 °C; IR (neat, cm^{-1}) 3380, 1642; ^1H NMR (300 MHz, $CDCl_3$) δ 5.95–5.82 (m, 1 H), 5.55 (s, 1 H), 5.26 (dt, J = 17.2, 1.5 Hz, 1 H), 5.10 (dt, J = 10.4, 1.5 Hz, 1 H), 4.26–4.14 (m, 1 H), 2.30–1.65 (series of m, 8 H), 1.34–1.20 (m, 1 H), 1.16–0.98 (m, 1 H), 0.88 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.78, 134.21, 125.15, 114.22, 69.81, 46.64, 44.37, 32.19, 30.18, 27.19, 26.71, 23.70.

Reduction of 25. To a magnetically stirred solution of **25** (488 mg, 1.70 mmol) in dry ether (10 mL) under argon was added freshly cut and crushed sodium (117 mg, 5.1 mmol). The mixture was heated at reflux for 3 h and processed as above to give 319 mg (90%) of **11a**: colorless oil; IR (neat, cm^{-1}) 3380, 1640; ^1H NMR (300 MHz, $CDCl_3$) δ 5.95–5.82 (m, 1 H), 5.55 (s, 1 H), 5.26 (dt, J = 17.2, 1.5 Hz, 1 H), 5.10 (dt, J = 10.4, 1.5 Hz, 1 H), 4.26–4.14 (m, 1 H), 2.30–1.65 (series of m, 8 H), 1.34–1.20 (m, 1 H), 1.16–0.98 (m, 1 H), 0.88 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.61, 134.30, 124.98, 114.28, 70.07, 45.89, 44.46, 32.22, 30.02, 27.16, 16.57, 23.67.

The derived *p*-nitrobenzoate (**26**) was obtained in 88% yield as colorless crystals: mp 83.5–85 °C; IR (KBr, cm^{-1}) 1708, 1600; ^1H NMR (300 MHz, $CDCl_3$) δ 8.26–8.11 (m, 4 H), 5.97–5.84 (m, 1 H), 5.72–5.60 (m, 1 H), 5.49 (s, 1 H), 5.40–5.14 (m, 2 H), 2.55–2.31 (m, 2 H), 2.04–1.82 (m, 3 H), 1.78–1.66 (m, 1 H), 1.31–1.15 (m, 1 H), 1.06–0.75 (m, 2 H), 0.85 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.84, 150.52, 136.07, 136.01, 133.09, 130.62, 125.12, 123.49, 117.02, 74.84, 44.46, 43.28, 32.20, 30.51, 27.17, 26.28, 23.55.

α-Vinyl-2-norbornene-2-ethanols 12a and 12b. A magnetically stirred solution of **28**[29b] (7.00 g, 40.4 mmol) in dry THF (125 mL) at −78 °C under argon was treated dropwise over 20 min with *tert*-butyllithium (52.3 mL of 1.7 M in pentane, 89.0 mmol). The resulting yellow solution

was stirred at −78 °C for 30 min before the internal temperature was allowed to reach 0 °C, and butadiene monoxide (2.12 g, 30.3 mmol) was introduced in rapid dropwise fashion. The reaction mixture was stirred at 20 °C for 6 h, poured into a separatory funnel containing ice/water (100 mL), and extracted with petroleum ether (150 mL). The organic phase was washed with water (2 × 100 mL) and brine (100 mL) prior to drying and concentration to leave 5.28 g of a pale yellow liquid. MPLC (silica gel, elution with 12% ethyl acetate in petroleum ether) gave 1.23 g (25%) of **12** as a colorless liquid which was susceptible to polymerization. The racemic diastereomers were separated by repeated MPLC using a column packed with 10% silver nitrate on silica gel (elution with 20% ethyl acetate in petroleum ether).

For **12a**: colorless liquid; IR (neat, cm^{-1}) 3380, 1640; ^1H NMR (300 MHz, $CDCl_3$) δ 5.97–5.80 (m, 1 H), 5.72 (s, 1 H), 5.32–5.18 (m, 1 H), 5.12–5.02 (m, 1 H), 4.29–4.14 (m, 1 H), 2.81 (d, J = 1.4 Hz, 1 H), 2.71 (s, 1 H), 2.41–2.25 (m, 2 H), 1.86 (s, 1 H), 1.70–1.51 (m, 2 H), 1.39–1.30 (m, 1 H), 1.14–0.91 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.52, 140.70, 131.26, 114.32, 70.66, 48.54, 45.61, 42.34, 38.18, 26.27, 24.49; MS m/z (M^+) calcd 164.1201, obsd 164.1197. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.29; H, 9.82.

Reaction of **12a** with α-naphthyl isocyanate provided carbamate **29** in 96% yield as a colorless solid: mp 79–80 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.95–7.82 (m, 3 H), 7.67 (d, J = 8.2 Hz, 1 H), 7.57–7.43 (m, 3 H), 6.98 (s, 1 H), 5.97–5.82 (m, 1 H), 5.70 (s, 1 H), 5.52–5.43 (m, 1 H), 5.34 (d, J = 17.2 Hz, 1 H), 5.22 (d, J = 10.5 Hz, 1 H), 2.84–2.72 (m, 2 H), 2.64–2.40 (m, 2 H), 1.70–1.56 (m, 2 H), 1.43–1.35 (m, 1 H), 1.13–0.96 (series of m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) (two carbons were not differentiated) δ 153.73, 144.43, 136.58, 134.04, 132.48, 130.96, 128.70, 125.92, 125.77, 124.95, 120.42, 116.69, 74.56, 48.46, 45.17, 42.33, 35.15, 26.39, 24.38; MS m/z (M^+) calcd 333.1728, obsd 333.1770.

For **12b**: colorless liquid; IR (neat, cm^{-1}) 3385, 1638; ^1H NMR (300 MHz, $CDCl_3$) δ 5.97–5.80 (m, 1 H), 5.72 (s, 1 H), 5.32–5.18 (m, 1 H), 5.12–5.02 (m, 1 H), 4.29–4.14 (m, 1 H), 2.82 (s, 1 H), 2.76 (s, 1 H), 2.40–2.16 (series of m, 2 H), 1.14–0.91 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 145.52, 140.64, 131.40, 114.41, 70.62, 48.59, 45.63, 42.36, 38.20, 26.29, 24.54; MS m/z (M^+) calcd 164.1201, obsd 164.1172. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.18; H, 9.91.

(αR*,1S,4R)-α-Vinyl-2-bornene-2-ethanol (13). A magnetically stirred solution of **30**[31a] (20.6 g, 47.6 mmol) and *N,N,N',N'*-tetramethylethylenediamine (100 mL) in hexane (100 mL) at −55 °C under argon was treated dropwise over 20 min with *sec*-butyllithium (100 mL of 1.30 M, 130 mmol). The resulting yellow solution was stirred at −55 °C for 2 h and allowed to warm to 0 °C as nitrogen was evolved. Butadiene monoxide (9.11 g, 130 mmol) was added rapidly dropwise, and the reaction mixture was allowed to warm to room temperature over 1.5 h and stirred overnight. The resulting pale yellow solution was cooled to 0 °C and quenched by the addition of ice. After dilution with ether (100 mL), the solution was washed with water (3 × 100 mL), saturated NH_4Cl solution (100 mL), and brine (100 mL). The organic phase was dried and concentrated to provide 12.2 g of a green-colored liquid, the column chromatography of which (silica gel, elution with 12% ethyl acetate in petroleum ether) gave 4.24 g (43%) of **13** as a colorless liquid, 1.45 g (15%) of **31** as a colorless liquid susceptible to polymerization, and 4.20 g of unidentified polar material.

For **13**: IR (neat, cm^{-1}) 3370; ^1H NMR (300 MHz, $CDCl_3$) δ 5.96–5.80 (m, 1 H), 5.80–5.66 (series of m, 1 H), 5.31–5.20 (m, 1 H), 5.14–5.04 (m, 1 H), 4.30–4.19 (m, 1 H), 2.32–2.10 (m, 3 H), 1.96–1.72 (m, 2 H), 1.59–1.16 (series of m, 2 H), 0.98–0.96 (m, 1 H), 0.98 (s, 3 H from one diastereomer), 0.97 (s, 3 H from the other diastereomer), 0.79 (s, 3 H); 0.77 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.44, 145.36, 140.66, 130.33, 129.63, 114.54, 70.22, 56.65, 56.16, 54.52, 54.22, 51.45, 51.40, 36.49, 36.21, 31.45, 31.26, 25.78, 25.66, 19.71, 19.63, 11.47; MS m/z (M^+) calcd 206.1671, obsd 206.1686.

For **31**: IR (neat, cm^{-1}) 3330; ^1H NMR (300 MHz, $CDCl_3$) δ 5.78–5.56 (m, 2 H), 5.54–5.51 (m, 1 H), 4.22–4.11 (m, 2 H), 2.84–2.60 (m, 2 H), 2.25–2.17 (m, 1 H), 1.86–1.73 (m, 1 H), 1.53–1.39 (m, 1 H), 1.35–1.18 (m, 1 H), 1.00–0.83 (m, 2 H), 0.96 (s, 3 H from one isomer), 0.95 (s, 3 H from the other isomer), 0.77 (s, 3 H), 0.75 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.65, 130.51, 130.16, 129.81, 129.34, 127.58, 63.72, 58.56, 56.33, 54.24, 51.36, 51.32, 31.45, 31.41, 30.94, 26.03, 25.95, 25.90, 19.70, 19.62, 11.41, 11.36; MS m/z (M^+) calcd 206.1671, obsd 206.1623. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.02; H, 10.69.

Kinetic Resolution To Obtain (αR,1S,4R)-α-Vinyl-2-bornene-2-ethanol (13a). Diastereomers **13a** and **13b** were partially separated by MPLC (elution with 12% ethyl acetate in petroleum ether) using a silica gel column impregnated with 10% silver nitrate. Crushed activated 3-Å molecular sieves (100 mg) were placed in a 10-mL round-bottomed flask under argon, and the apparatus was flame-dried for 20 min. After the flask had cooled, a 6:1 mixture of **13a**/**13b** was added (206 mg, 1.00 mmol) followed by CH_2Cl_2 (3 mL) and (+)-diisopropyl L-tartrate (14 mg, 0.060 mmol). The mixture was cooled to −8 °C, and titanium tetraisopropoxide (14 mg, 0.050 mmol) was added with magnetic stirring. After 30 min, predried cumene hydroperoxide (105 mg of 80%, 0.55 mmol) was introduced dropwise. The mixture was stirred at −8 °C for 12 h and quenched with 5 mL of a solution made from citric acid (22 g) and ferrous sulfate (66 g) in 200 mL of water. The mixture was stirred at 0 °C for 1 h and extracted with CH_2Cl_2 (25 mL). The organic layer was stirred with 30% sodium hydroxide in brine (5 mL) for 1 h at 0 °C before it was separated, dried, and concentrated to provide 320.4 mg of a yellow oil. MPLC on silica gel (elution with 8% ethyl acetate in petroleum ether) gave 142 mg of **13a** as a colorless liquid: $[\alpha]^{25}_D$ +4.3° (c 1.53, $CHCl_3$); IR (neat, cm^{-1}) 3370; ^1H NMR (300 MHz, $CDCl_3$) δ 5.99–5.80 (m, 1 H), 5.80–5.76 (m, 1 H), 5.31–5.20 (m, 1 H), 5.14–5.04 (m, 1 H), 4.30–4.19 (m, 1 H), 2.32–2.10 (m, 3 H), 1.96–1.72 (m, 2 H), 1.59–1.16 (series of m, 2 H), 0.98–0.96 (m, 1 H), 0.98 (s, 3 H), 0.79 (s, 3 H), 0.77 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.40, 140.65, 130.42, 114.59, 70.22, 56.70, 54.26, 51.43, 36.54, 31.49, 25.81, 19.74, 19.66, 11.48; MS m/z (M^+) calcd 206.1671, obsd 206.1623. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.80; H, 10.85.

Kinetic Resolution To Obtain (αS,1S,4R)-α-Vinyl-2-bornene-2-ethanol (13b). Analogous treatment of a 1:2 mixture of **13a** and **13b** (231 mg, 1.12 mmol), but with (−)-DIPT and an extended reaction of time of 15 h at −8 °C gave 523 mg of a yellow oil. MPLC (silica gel, elution with 8% ethyl acetate in petroleum ether) gave 93 mg of **13b** as a colorless liquid: $[\alpha]^{25}_D$ −27.6° (c 0.50, $CHCl_3$); IR (neat, cm^{-1}) 3365; ^1H NMR (300 MHz, $CDCl_3$) δ 5.96–5.80 (m, 1 H), 5.74–5.66 (m, 1 H), 5.31–5.20 (m, 1 H), 5.14–5.04 (m, 1 H), 4.30–4.19 (m, 1 H), 2.32–2.10 (m, 3 H), 1.96–1.72 (m, 2 H), 1.59–1.16 (series of m, 2 H), 0.98–0.96 (m, 1 H), 0.97 (s, 3 H), 0.79 (s, 3 H), 0.77 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.36, 140.65, 129.70, 114.60, 70.26, 56.18, 54.57, 51.49, 36.26, 31.29, 25.69, 19.73, 19.68, 11.50; MS m/z (M^+) calcd 206.1671, obsd 206.1667. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.62; H, 10.78.

(S)-4-Methyl-5-hexenal (38).[32] To a magnetically stirred mixture of *m*-chloroperoxybenzoic acid (3.74 g of 80%, 17.4 mmol) and sodium bicarbonate (2.43 g, 28.9 mmol) in dichloromethane (75 mL) at 0 °C was added (*S*)-(+)-citronellene (2.00 g, 14.5 mmol) in one portion. After 10 min, the reaction mixture was quenched by the addition of 1 N Na_2SO_3 solution (50 mL), stirred for 15 min, and treated with saturated $NaHCO_3$ solution (20 mL). The organic phase was washed with water (2 × 100 mL) prior to drying, filtration, and careful solvent evaporation. The 4.10 g of crude product was taken up in ether (80 mL), cooled to 0 °C, treated with periodic acid (3.97 g, 17.4 mmol), and stirred magnetically at room temperature for 7 h. The colorless mixture was filtered through Celite and washed with saturated $NaHCO_3$ (50 mL) and 1 N Na_2SO_3 solutions (50 mL). The two aqueous washes were extracted with ether (20 mL), and the combined ethereal solutions were dried and filtered. The ether was removed by distillation through a 20-cm Vigreux column, and the crude product was distilled bulb-to-bulb at 150 °C/15 Torr to obtain 1.14 g (70%) of **38** as a colorless liquid: $[\alpha]^{25}_D$ +14.4° (c 3.60, $CHCl_3$); IR (neat, cm^{-1}) 1712, 1640; ^1H NMR (300 MHz, $CDCl_3$) δ 9.77 (t, J = 1.6 Hz, 1 H), 5.72–5.58 (m, 1 H), 5.00 (d, J = 5.2 Hz, 1 H), 4.95 (s, 1 H), 2.46 (t, J = 1.2 Hz, 2 H), 2.25–2.08 (m, 1 H), 1.78–1.54 (m, 2 H), 1.03 (d, J = 6.7 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.50, 143.29, 113.77, 41.77, 37.42, 28.48, 20.17.

4-Methylhexanol (39).[33] To a magnetically stirred mixture of lithium aluminum hydride (170 mg, 4.48 mmol) in ether (5 mL) at 0 °C under nitrogen was added dropwise a solution of **38** (200 mg, 1.78 mmol) in ether (5 mL). The mixture was allowed to warm to room temperature over 1 h and stirred an additional 2 h before being poured slowly into a 1:1 mixture of ice and 0.1 N HCl (30 mL) with vigorous stirring. The mixture was extracted with ether (10 mL), and the organic layer was washed with brine (5 mL), dried, and concentrated to a volume of 0.8 mL. Purification of the concentrate by gas chromatography (column A at 75 °C) gave 151 mg (74%) of 4-methyl-5-hexenol as a colorless liquid: $[\alpha]^{25}_D$ +16.7° (c 2.05, $CHCl_3$); IR (neat, cm^{-1}) 3340, 1640; ^1H NMR (300 MHz, $CDCl_3$) δ 5.67–5.53 (m, 1 H), 5.00–4.90 (m, 2 H), 4.39–4.22 (m, 2 H), 2.18–2.00 (m, 1 H), 1.75–1.62 (m, 2 H), 1.36–1.24 (m, 3 H), 0.97 (d, J = 6.7 Hz, 3 H).

A solution of the above alcohol (200 mg, 1.78 mmol) in 2:1 pentane/$CHCl_3$ (9 mL) was treated with platinum oxide (2 mg), placed in a medium-pressure bottle, and magnetically stirred under 50 psi of hydrogen for 102 h. The mixture was filtered through Celite and concentrated at 10 °C on a rotary evaporator to leave 176 mg (85%) of **39** as a colorless liquid: IR (neat, cm^{-1}) 3350; ^1H NMR (80 MHz, $CDCl_3$) δ 3.63 (t, J = 6.3 Hz, 2 H), 1.72 (s, 1 H), 1.70–1.03 (series of m, 7 H), 1.00–0.86 (m, 6 H).

General Procedure for Anionic Oxy-Cope Rearrangements. To a magnetically stirred solution of alcohol (0.048 mmol) and *n*-decane (3.00

mg) in dry THF (1.5 mL) was added 18-crown-6 (38.1 mg, 0.144 mmol) followed by potassium hydride (15.4 mg, 0.384 mmol). The reaction mixture was heated at 50 °C under an inert atmosphere, and conversion to product(s) was generally complete after 3-10 h. The contents were cooled to -78 °C and quenched by dropwise addition of methanol. In the case of **11a** and **11b**, the solution was warmed to 0 °C and stirred with excess sodium borohydride for 10 min. After dilution with ether (2 mL), the solution was washed with cold NH_4Cl solution (10 mL) and water (5 mL), dried, filtered, and analyzed by capillary GC. Rotary evaporation followed by MPLC on silica gel or preparative gas chromatography (column B at 180 °C) provided pure products.

For **42**: colorless oil; IR (neat, cm^{-1}) 3340, 1640; ^1H NMR (300 MHz, $CDCl_3$) δ 4.66-4.59 (m, 2 H), 3.66 (t, J = 6.4 Hz, 2 H), 2.29-2.10 (series of m, 2 H), 1.90-1.65 (series of m, 2 H), 1.60-1.03 (series of m, 9 H); 0.82 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.36, 107.88, 63.06, 50.18, 42.63, 32.56, 32.41, 32.16, 31.07, 27.77, 27.38, 21.56; MS m/z (M^+) calcd 210.1984, obsd 210.1990. Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: 79.97; H, 12.45.

For **43**: colorless oil; IR (neat, cm^{-1}) 3350, 1642; ^1H NMR (300 MHz, $CDCl_3$) δ 4.71-4.67 (m, 1 H)), 4.57-4.53 (m, 1 H), 3.67 (t, J = 6.4 Hz, 2 H), 2.00-1.90 (m, 1 H), 1.86-1.03 (series of m, 10 H), 1.00-0.83 (m, 2 H), 0.87 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.59, 104.26, 63.43, 50.72, 42.57, 38.46, 34.41, 32.47, 30.57, 28.31, 27.49, 18.04; MS m/z (M^+) calcd 210.1984, obsd 210.1993. Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.75; H, 12.39.

For **48**: colorless liquid; IR (neat, cm^{-1}) 1721, 1650; ^1H NMR (300 MHz, $CDCl_3$) δ 9.79 (t, J = 1.8 Hz, 1 H), 4.87 (d, J = 1.2 Hz, 1 H), 4.63 (s, 1 H), 2.68 (s, 1 H), 2.50 (td, J = 8, 1.8 Hz, 2 H), 2.12 (s, 1 H), 1.95-1.82 (m, 1 H), 1.60-1.12 (series of m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.56, 159.83, 102.26, 47.87, 45.77, 42.85, 40.36, 35.76, 29.52, 28.69, 26.87; MS m/z (M^+) calcd 164.1201, obsd 164.1237. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.22; H, 9.80.

For **54**: colorless liquid; IR (neat, cm^{-1}) 1725, 1650; ^1H NMR (300 MHz, $CDCl_3$) δ 9.80 (t, J = 1.9 Hz, 1 H), 4.76-4.62 (m, 2 H), 2.58-2.45 (m, 1 H), 2.45-2.36 (m, 2 H), 2.12-1.97 (m, 1 H), 1.70-1.49 (m, 4 H), 1.45-1.08 (series of m, 2 H), 0.93 (s, 3 H), 0.89 (s, 3 H), 0.79 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.36, 163.22, 100.56, 52.25, 47.05, 46.84, 42.55, 42.33, 35.24, 23.40, 19.89, 19.13, 19.02, 12.71, MS m/z (M^+) calcd 206.1671, obsd 206.1707. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.71; H, 10.88.

For **55**: ^1H NMR (300 MHz, $CDCl_3$) δ 9.80 (t, J = 1.9 Hz, 1 H), 4.76-4.65 (m, 2 H), 2.58-2.45 (m, 2 H), 2.0-1.70 (m, 2 H), 1.70-1.49 (m, 4 H), 1.45-1.08 (series of m, 2 H), 0.92 (s, 3 H), 0.87 (s, 3 H), 0.82 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.65, 164.36, 100.42, 52.32, 49.00, 48.27, 45.93, 44.08, 34.00, 23.93, 21.37, 20.29, 19.25, 12.50.

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Registry No. 9, 136087-45-1; **10**, 136087-46-2; **11a**, 141273-11-2; **11b**, 141273-10-1; **12a**, 141273-17-8; **12b**, 141273-18-9; **13a**, 141273-20-3; **13b**, 141273-21-4; **14**, 37027-64-8; **15**, 79705-01-4; (*E*)-**17**, 35998-93-7; (*Z*)-**17**, 35998-94-8; **18**, 89634-48-0; **19**, 81292-71-9; **20**, 141273-08-7; **21a**, 62222-99-5; **21b**, 141273-09-8; **22**, 141273-12-3; **23**, 141273-13-4; **24**, 141273-14-5; **25**, 141273-15-6; **26**, 141273-16-7; **28**, 694-90-6; **29**, 141273-19-0; **30**, 63883-67-0; **31**, 141273-22-5; (*R*)-**38**, 63215-85-0; (*S*)-**38**, 93904-58-6; **42**, 141273-23-6; **43**, 141273-24-7; **48**, 37814-44-1; **49**, 141273-25-8; **54**, 136034-34-9; **55**, 136087-47-3; 3-buten-2-ol, 598-32-3; allyl bromide, 106-95-6; 3-(phenylsulfonyl)-1-butene, 54897-36-8; 4-*tert*-butylcyclohexanone, 98-53-3.

Supplementary Material Available: Experimental crystallographic details for **26** and **29**, as well as tables of final positional and thermal parameters, bond lengths, and bond angles for these derivatives (12 pages). Ordering information is given on any current masthead page.

Comparative Study of the Pyrolysis, Photoinduced Electron Transfer (PET), and Laser-Jet and 185-nm Photochemistry of Alkyl-Substituted Bicyclic Azoalkanes

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Abstract: The gas-phase pyrolysis, photoinduced electron transfer (PET), and laser-jet and 185-nm photochemistry of 2,3-diazabicyclo[2.2.1]hept-2-ene (**1a**), *syn*-7-methyl-2,3-diazabicyclo[2.2.1]hept-2-ene (*syn*-**1b**), *anti*-7-methyl-2,3-diazabicyclo[2.2.1]hept-2-ene (*anti*-**1b**), 1,4-dimethyl-2,3-diazabicyclo[2.2.1]hept-2-ene (**1c**), 7,7-dimethyl-2,3-diazabicyclo[2.2.1]-hept-2-ene (**1d**), and *syn*-7-(1-methylethyl)-2,3-diazabicyclo[2.2.1]hept-2-ene (*syn*-**1e**) were investigated and the results of their product studies compared with one another. Pyrolysis and conventional direct and benzophenone-sensitized 350-nm photolysis of the azoalkanes **1** yielded the bicyclo[2.1.0]pentanes **2** and negligible amounts of cyclopentenes **3**. PET and benzophenone-sensitized laser-jet and 185-nm photolysis of the azoalkanes **1** led to significant quantities of cyclopentene derivatives **3**, a behavior that is attributed to radical cation-type 1,3-cyclopentadiyl intermediates, which subsequently suffer hydrogen or alkyl migration. The polar character of the radical cation $D^{\bullet+}$ is clearly demonstrated by the Wagner-Meerwein rearrangement into 2,3-dimethylcyclopentene (**3'd**) in the PET and 185-nm photolysis of azoalkane **1d**. When the corresponding 1,3-cyclopentadiyl $D^{\bullet\bullet}$ was generated in the pyrolysis of 5,5-dimethylbicyclo[2.1.0]pentane (**2d**), the 3,3-dimethyl-1,4-pentadiene (**4d**) was obtained as the exclusive reaction product; instead of methyl migration, fragmentation into the 1,4-diene took place. The PET chemistry of the stereochemically labeled azoalkanes *syn*- and *anti*-**1b** revealed that the radical cations $D^{\bullet+}$ have a puckered geometry, because a stereochemical memory effect was observed for the cyclopentene products **3**. Specifically, the *pseudoaxial* substituent at the stereolabeled center migrates with preference, which speaks for a *coplanar* arrangement for the rearrangement in $D^{\bullet+}$. The common and distinct mechanistic features of the denitrogenation processes of the various thermal and photochemical activation modes will be discussed.

Unsubstituted or alkyl-substituted, saturated, cyclic azoalkanes have a weak absorption ($^1n,\pi^*$) at ca. 300-350 nm, which is separated from the $^1\pi,\pi^*$ transition by a spectral window between 250 and 300 nm.[1] Direct irradiation at 350 or 185 nm normally leads to significantly differing photoreactivity. This may be taken as evidence that Kasha's rule is being violated in these examples because of the large energy gap between S_1 and S_2. Kasha's rule[2]

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