Formation of Some Oxygen-Containing Heterocycles by Radical Cyclization: The Stereochemical Influence of Anomeric Effects

Athelstan L. J. Beckwith* and Dennis M. Page

Research School of Chemistry, and Department of Chemistry, Australian National University, Canberra, ACT 0200, Australia

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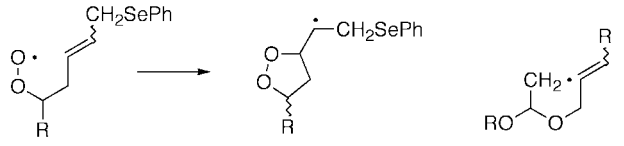
The influence of the anomeric effect on radical cyclization has been examined by determining the stereochemical outcome of the ring closure of 10 suitably substituted radicals. The stereochemistry of the products formed from the acyclic precursors **4a**−**f** indicates that for suitably constituted radicals anomeric interactions stabilize pseudoaxially substituted transition structures **14** thus affording products with stereochemistry the reverse of that normally observed.

In recent times, the use of free radical reactions for chemical synthesis has grown steadily in popularity as the processes which govern and control their outcomes have become better understood.[1] Intramolecular addition reactions of suitably constituted alkenyl radicals and related species are particularly interesting since they readily afford a variety of ring systems commonly found in many natural products.[1] The advantages offered by such reactions generally include high regioselectivity, modest to good stereoselectivity,[1−5] and high chemoselectivity.[1−5]

The highly regioselective exo-cyclization of the hex-5-enyl radical has been intensively studied. The accurate determination of its kinetics[6] has underpinned its widespread use as a mechanistic probe and as a radical clock.[7] Most monosubstituted hex-5-enyl radicals also undergo regioselective exo-cyclization while conforming to the general stereochemical guideline that 1- or 3-substituted radicals afford predominantly cis-disubstituted products, while 2- or 4-substituted radicals give mainly trans-disubstituted products.[5]

It is now generally accepted that the cyclization behavior of simple hex-5-enyl systems reflects the stereoelectronic demands of the transition structure.[2−5] The hypothesis that the strain energy engendered in attaining the optimum orbital overlap for 1,6-ring closure outweighs the steric and thermodynamic factors which would otherwise favor six-membered ring formation[2−5] has received support from theoretical analyses[8] and the modeling of transition structures by a combination of molecular orbital and molecular mechanics calculations.[8] These calculations confirm the original hypothesis that the transition structure for 1,5-exo-cyclization of hex-5-enyl radicals and related species resembles cyclohexane in its chair form.[2−5] Hence the stereoselectivity exhibited in the ring closure of monosubstituted hexenyl radicals and related species is seen to arise from the propensity of cyclizations to proceed through the more stable pseudoequatorially substituted cyclohexane-like conformation of the transition structure rather than through its less stable pseudoaxially substituted conformer.[8] Since calculations of the relative selectivities of the cyclized products tend to be overestimated when only axially substituted chairlike structures are considered, it appears that boatlike transition structures might also be involved in some reactions.[4,8]

Cyclizations of hex-5-enyl type radicals containing heteroatoms have also been studied.[1,9,10] In general such species conform to the usual guidelines.[5] For example, most 3-substituted allylperoxyl radicals undergo stereoselective cyclization to afford mainly cis-substituted 1,2-dioxolanes.[10,11] Thus **1** (R = Ph) gives **2** (R = Ph) with cis:trans = 10.[11] However, a notable exception occurs when the substituent is strongly electron withdrawing. Thus, ring closure of **1** (R = C_6F_5) affords *trans*-**2** (R = C_6F_5)[11] in preference to the expected cis product.[5]



1 **2** **3**

When these observations were first reported, no mechanistic explanation was offered for this unexpected behavior.[11] However, it occurred to us that they might

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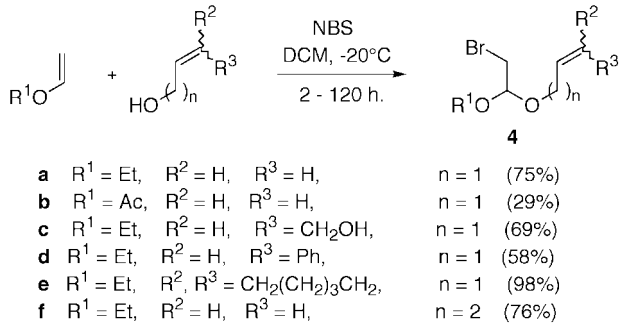
reflect the influence of the anomeric effect[12−15] on the conformation of the cyclization transition structure. Although there is some debate about the magnitude of the anomeric effect,[12−15] and indeed of the underlying cause (dipole−dipole interaction,[14,16] or *p*-*σ** MO overlap[14,17]), it is clear that 2-alkoxy- and 2-(acyloxy)tetrahydropyrans preferentially assume conformations in which the substituent occupies an axial position. By analogy, radicals of the general type **3** would be expected to undergo cyclization via axially substituted chairlike transition structures to afford cis-disubstituted products in preference to their trans isomers as predicted by the usual guidelines.[5] Preliminary experiments supported the validity of this hypothesis.[18] After our work had been commenced, two other groups independently made brief mentions of the possibility of transition state stabilization by anomeric effects in an attempt to account for some unexpected stereochemical preferences in free-radical cyclization reactions.[19] However, since a detailed study of this type of stabilization in hex-5-enyl-like ring closures had not previously been undertaken we decided to proceed with an extensive systematic survey.

Herein we describe an examination of the stereochemical outcome of the ring closure of 10 acyclic radicals suitably constituted to detect the stereochemical effect of anomeric interactions. The results, which confirm the stereoselective formation of products with stereochemistry the reverse of that predicted by the usual guidelines, are indeed consistent with the hypothesis that anomeric stabilization of suitably substituted transition structures can be sufficiently strong to outweigh the usual steric interactions of substituents.

Results

Precursors. Of the required acyclic bromo acetals, **4a**−**f** were readily prepared in modest (29%) to good yield (98%) from the appropriately substituted allyl alcohols by an established method (Scheme 1).[20,21] Cyclohexylidineethanol, required for the preparation of precursor **4e**, was obtained as previously described from cyclohexanone.[22,23] Substrate **4g** was obtained, albeit in very poor yield (3%), when an attempt was made to bromo-allyloxylate 1-hexene by Grady and Chokshi's method (Scheme 2).[24] However, treatment of allyltrimethylsilane with NBS or NBA and 3-buten-1-ol successfully afforded the required substrate **4h**, although once again in very poor yield (6%). Cleavage of 1,2-epoxyhexane[25] with diphenyl diselenide and sodium borohydride in ethanol[26] gave a hydroxyselenide (55%) which was then treated with potassium hydride and allyl bromide to give **4i** in moderate yield (35%) after preparative TLC (Scheme 2). The preparation of the mono-mercurial **4j** (52%) followed a modification of McNeely and Wright's procedure,[27] whereby 1,5-hexadiene in large excess (6−10 mol equiv) was treated with an ethanolic solution of mercury(II) acetate. Smaller quantities of diene relative to the amount of acetate tended to promote the formation of the diastereoisomers of the dimercurial **5**.

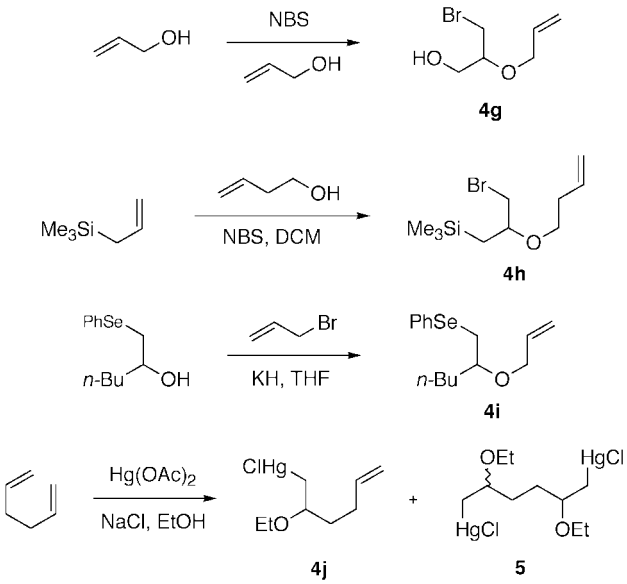
Scheme 1



4

a R^1 = Et, R^2 = H, R^3 = H, n = 1 (75%)
b R^1 = Ac, R^2 = H, R^3 = H, n = 1 (29%)
c R^1 = Et, R^2 = H, R^3 = CH_2OH, n = 1 (69%)
d R^1 = Et, R^2 = H, R^3 = Ph, n = 1 (58%)
e R^1 = Et, R^2, R^3 = $CH_2(CH_2)_3CH_2$, n = 1 (98%)
f R^1 = Et, R^2 = H, R^3 = H, n = 2 (76%)

Scheme 2



4g **4h** **4i** **4j** **5**

Ring Closures. The various precursors were cyclized by treatment with tributylstannane, or, in the case of the organomercurial **4j**, with sodium trimethoxyborohydride. The precise conditions are given in the Experimental Section and are summarized in Table 1. Usually the conditions were finally chosen after running a number of test experiments designed to assess the efficiency of the workup and analysis of the reactions mixtures, which were often complicated by the high volatility of the cyclic

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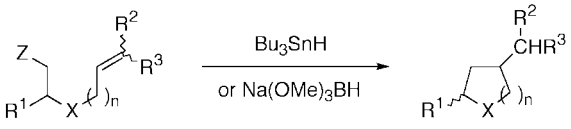
Table 1. Diastereomeric Ratios of Radical Cyclization Products

precursor	method[a]	temp (°C)	product[b]	cis/trans	yield[c] (%)
4a	A	80	**6a**	4.7	12
4a	B	40	**6a**	5.8	61
4b	B	40	**6b**[d]	3.5	48
4b	C	80	**6b**[d,e]	1.7	16
4c	A	80	**6c**	2.1	44
4c	D	ca. 20	**6c**	2.7	71
4d	A	80	**6d**	2.1	44
4d	B	40	**6a**	2.7	66
4e	A	80	**6e**	1.6	61
4f	E	80	**6f**[d,f]	0.36	50[g]
4g	B	40	**6g**	0.2	72
4h	B	40	**6h**[d]	2.2	84[g]
4i	F	80	**6i**	0.2	50
4j	G	20	**6j**[d]	1.1	—[h]

[a] A: Bu_3SnH (0.2 M), benzene, AIBN; B: Bu_3SnH (0.2 M), pentane, $Bu^tON{=}NOBu^t$; C: Bu_3SnH (syringe pump), benzene, AIBN; D: Bu_3SnH (0.2 M), benzene, AIBN, photolysis; E: Bu_3SnH (0.07 M), benzene, AIBN; F: Bu_3SnH, (0.02 M), benzene, AIBN; G: $Na(OMe)_3BH$, CH_2Cl_2. [b] Unless otherwise specified the uncyclized product was not detected. [c] Isolated. [d] Uncyclized product also formed. [e] This reaction also afforded the hydroxy compounds **8** (see text). [f] This reaction also afforded the oxepane **9** (see text). [g] Total yield of all reduced products since complete separation of cyclized and uncyclized materials was not possible. [h] Products not isolated.

Scheme 3

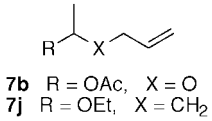


4 **6**

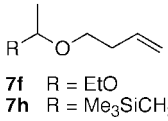
a R^1 = OEt, R^2 = H, R^3 = H, n = 1, X = O, Z = Br
b R^1 = OAc, R^2 = H, R^3 = H, n = 1, X = O, Z = Br
c R^1 = OEt, R^2 = H, R^3 = CH_2OH, n = 1, X = O, Z = Br
d R^1 = OEt, R^2 = H, R^3 = Ph, n = 1, X = O, Z = Br
e R^1 = OEt, R^2, R^3 = $CH_2(CH_2)_3CH_2$, n = 1, X = O, Z = Br
f R^1 = OEt, R^2 = H, R^3 = H, n = 2, X = O, Z = Br
g R^1 = $HOCH_2$, R^2 = H, R^3 = H, n = 1, X = O, Z = Br
h R^1 = Me_3SiCH_2, R^2 = H, R^3 = H, n = 2, X = O, Z = Br
i R^1 = $CH_3(CH_2)_3$, R^2 = H, R^3 = H, n = 1, X = O, Z = SePh
j R^1 = EtO, R^2 = H, R^3 = H, n = 1, X = CH_2, Z = HgCl

products. In general, reaction mixtures containing nonvolatile products were worked up by the DBU method[28] followed by further flash chromatography. Volatile products were purified by careful removal of solvent by distillation at ambient pressure, followed by short-path (Kugelrohr) distillation under reduced pressure to remove the material from the unwanted tributylstannane byproducts. The analysis of reaction mixtures was accomplished by NMR spectroscopy and/or gas chromatography with appropriate reference compounds. To ensure that no loss of any diastereoisomer occurred, the diastereomeric ratios of cyclized products were determined both on the crude reaction mixtures and after workup. In general, analysis of the crude mixtures indicated that the reactions had proceeded cleanly and with high efficiency. The poor yields recorded in many cases reflect the difficulty of separating the products.

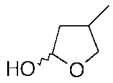
The structures and yields of the cyclic products obtained from each of the acyclic precursors are summarized in Table 1 and Scheme 3. All but two of the substrates, **4f** and **4h**, furnished a mixture of two preparatively inseparable diastereomeric cyclized products. In the cases of **4b**, **4f**, **4h**, and **4j**, the products of direct reduction, **7b**, **7f**, **7h**, and **7j**, were also detected, but only in the case of the first was it possible for the yield (9%) to be directly determined. In the case of **7f** and **7j**, isolation was impossible because of their volatility and the small amounts of material involved. An authentic sample of **7f** was obtained by reduction of **4f** with Bu_3SnH at relatively high concentration (ca. 0.2 M). The other uncyclized products were prepared as follows: **7b** by acid-catalyzed addition of acetic acid to allyl vinyl ether; **7h** by weak acid-catalyzed addition of but-3-en-1-ol to allyltrimethylsilane, and **7j** by treatment of 1-methylpent-4-en-1-ol with potassium hydride, HMPA, and ethyl iodide.



7b R = OAc, X = O
7j R = OEt, X = CH_2



7f R = EtO
7h R = Me_3SiCH_2



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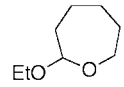

9

The reduction of **4b** at 80 °C furnished four cyclic products (each of which was five-membered), the NMR of which suggested that partial decomposition of the expected products i.e., *cis*- and *trans*-**6b**, had occurred to afford the corresponding hydroxy compounds **8**. Analysis of the crude reaction mixture by TLC indicated that the decomposition process was probably not an artifact of the workup procedure. The formation of hemiacetals **8** was eliminated by reduction of **4b** at 40 °C, but this tended to be at the expense of the formation of more **7b**. The presence of the oxepane **9** as a minor component of the product mixture obtained from the reduction of substrate **4f** was confirmed by comparison of observed data with those previously reported.[29]

The stereochemistry of both diastereomers of each of the cyclized products **6a**, **6d**, **6g**, and **6i** was rigorously determined by a combination of COSY, and 1D and 2D NOE experiments. The relative stereochemistry of the other mixtures of diastereomers was then determined by comparison of ^1H and ^{13}C NMR spectra. An exception to this procedure was the identification of *cis*- and *trans*-**6j**. In this case the coincidence of a number of chemical shifts in the ^1H NMR spectrum of the product mixture made unambiguous structural elucidation impossible, and therefore *cis*-**6j** was independently prepared from the THP ether of *cis*-3-hydroxycyclopentaneacetic acid (readily prepared from norcamphor[30,31]) as shown in Scheme 4. The identification of the diastereomers of the tetrahydropyran **6f** was accomplished by comparison of the observed NMR spectra with those reported in the literature,[32] while the diastereomers of **6h** were similarly

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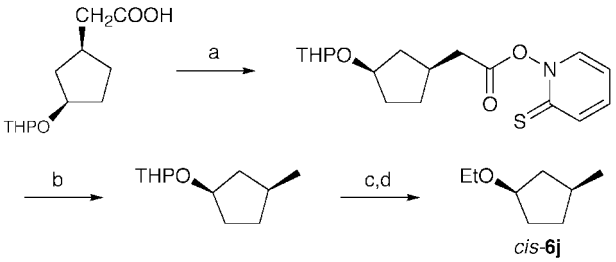
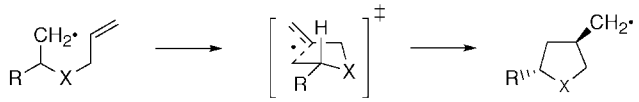
Scheme 4



Reagents: (a) *N*-Hydroxypyridine-2-thione, DCC, DMAP, benzene, reflux; (b) Bu_3SnH, AIBN, Benzene, reflux; (c) Dowex/HCl, MeOH, 45°C; (d) NaH, EtI, HMPA, Et_2O, reflux.

Scheme 5



10 **11** **12**

g R = CH_2OH, X = O
i R = $CH_3(CH_2)_3$, X = O

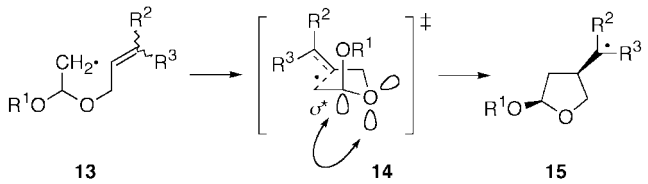
identified by comparison of the observed NMR data with those reported for the structurally similar *cis*- and *trans*-2,4-dimethyltetrahydropyrans.[33] A 1D NOE experiment conducted on *trans*-**6h** provided additional confirmation.

Discussion

The results presented in Table 1 show that with the exceptions of precursor **4j**, which shows virtually no stereoselectivity on radical cyclization, and **4f** and **4h**, which give six-membered cyclic products, the remaining ring closures fall clearly into two groups. One, comprising compounds **4g** and **4i**, behaves similarly to other substrates capable of affording 2-substituted hex-5-enyl radicals and shows a preference for radical ring closure giving trans-disubstituted cyclic products. The trans/cis ratios of 5.0 are roughly in agreement with that reported for cyclization of 2-methylhex-5-enyl radical.[2] In accord with widely accepted theory, the initially formed radicals **10g** and **10i** (Scheme 5) react preferentially through the more stable transition structures **11g** and **11i** with the substituents in the pseudoequatorial orientation to give the trans-substituted cyclic radicals **12g** and **12i**. In short, the radicals **10g** and **10i** show precisely the same behavior on cyclization as many other substituted 5-hexenyl systems containing heteroatoms in the chain.[1f]

The cyclization behavior of the other major group comprising precursors **4a**−**e** is very different in that each of these compounds undergoes stereoselective cyclization to afford mainly cis-disubstituted products in contravention to the usual guidelines.[2−5,8] The observed stereoselectivity suggests that the radicals **13a**−**e** cyclize preferentially through pseudoaxially substituted transition structures **14a**−**e** to give the cis-substituted cyclic radicals **15a**−**e** (Scheme 6). The clear implication is that for these radicals the pseudoaxially substituted chairlike transition structures are more stable than their pseudoequatorially substituted conformers. As adumbrated above, we propose that the stabilization of the axially substituted conformers reflects the anomeric interaction

Scheme 6



13 **14** **15**

a R^1 = Et, R^2 = H, R^3 = H, n = 1
b R^1 = Ac, R^2 = H, R^3 = H, n = 1
c R^1 = Et, R^2 = H, R^3 = CH_2OH, n = 1
d R^1 = Et, R^2 = H, R^3 = Ph, n = 1
e R^1 = Et, R^2, R^3 = $CH_2(CH_2)_3CH_2$, n = 1

which can occur between the two oxygen atoms as depicted in structure **14**. This anomeric interaction is not possible in the equatorially substituted conformer of **14**.

Further evidence in support of this hypothesis was obtained when **6a** with an initial diastereoisomeric ratio of cis/trans = 4.7 was treated with trifluoromethanesulfonic acid. Isomerization then occurred to give preferentially the trans diastereomer, the trans/cis ratio reaching 1.5:1. This is consistent with the steric considerations[5,8,34] which indicate the trans isomer of **6a** to be lower in energy than the cis. Clearly the observation that *trans*-**6a** is not formed preferentially by radical cyclization of **4a** (Table 1) indicates that the radical reactions proceed with kinetic control via a transition structure which is not subject to the usual steric requirements. It is also relevant that radical cyclization of **4a** in acetonitrile-d_3 gave a diastereomeric mixture of **6a** with a cis/trans ratio of 2.8 whereas the same reaction in benzene-d_6 under otherwise identical conditions gave **6a** with a cis/trans ratio of 4.2. This observation is consistent with the generalization that anomeric effects become less pronounced in more polar solvents.[12,35]

The data in Table 1 show other interesting features. For example, the cis/trans ratio for cyclization products decreases in the order **6a** > **6c** > **6d** > **6e**, i.e., it decreases in magnitude with increasing bulk of the substituent, viz., methyl < hydroxyethyl < benzyl < cyclohexyl. This is consistent with the view that the usual steric factors affecting the conformation of a substituted cyclohexane-like system[12−15,34] oppose the affects of anomeric stabilization. The results in Table 1 also show that the diastereoselectivity of cyclization increases with a decrease in reaction temperature. Hence, both the observed preference for cis-cyclization and the differences between various diastereomeric ratios must arise, at least in part, from differences in activation energies which reflect, presumably, differences in the strain energies of the transition structures.

If, as has been discussed above, the existence of a stabilizing anomeric interaction can reverse the normal diastereoselectivity for five-membered ring formation by radical cyclization, the same should be true for formation of six-membered rings. The data in Table 1 support this

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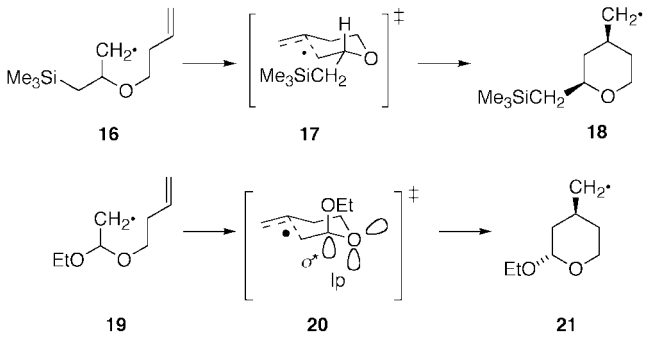
Scheme 7



hypothesis. Although experimental evidence is scanty,[36] it appears that the cyclization of substituted hept-6-enyl radicals and related species is subject to the usual thermodynamic and steric guidelines.[8a,8b] Thus, a 2-substituted heptenyl radical would be expected to afford a cis-disubstituted product via a chairlike transition structure in which both substituents are pseudoequatorial. The radical **16** (Scheme 7) derived from **4h** conforms to this hypothesis and affords mainly the cis-disubstituted radical **18** via the transition structure **17**. However, the observation that the radical **19** derived from **4f** affords mainly the trans-cyclized product suggests that the reaction affords the cyclic radical **21** via the pseudoaxially substituted transition structure **20**, which we expect to be more stable than its equatorially substituted isomer because of the anomeric interaction between the two oxygen atoms (Scheme 7). The observation that cyclization of **4f** also affords the oxepane **9** accords with previous observations that the ring closure of hept-6-enyl radicals and related species is less regioselective than that of analogous hex-5-enyl systems.[8a,37]

Although, in general, our results fully support the contention that anomeric stabilization can reverse the normal diastereoselectivity of radical cyclization, there remain two unanswered questions. First, the cyclization of the precursor **4j** is anomalous in that it shows virtually no diastereoselectivity, although as a 2-substituted hexenyl system it was expected to preferentially afford *trans*-**6j**. Perhaps, in this case the low steric bulk of the alkoxy substituent is insufficient to outweigh the overall thermodynamic factors favoring the formation of the more stable isomer *cis*-**6j**.

The second anomaly concerns the fact that cyclization of the acetoxy-substituted precursor **4b** gives a lower cis/trans ratio of products than does the ethoxy-substituted precursor **4a**. This is contrary to expectation because the acetoxy group, being more electronegative than the ethoxy,[12] should be subject to a greater anomeric effect, and hence the anomeric stabilization of transition structure **14b** should be greater than that of **14a**. Perhaps it is simply due to the higher steric demand of the acetoxy groups.[12,34] However, the formation during the cyclization of **4b** of analogous hydroxy compounds may indicate that *cis*-**6a** is more prone to decomposition than *trans*-**6b** and is thus preferentially consumed during the reaction or the workup procedure. However, definitive answers to these questions await further experimentation.

Conclusion

The observations presented above show that radicals derived from **4a**−**e** undergo 1,5-exo-cyclization to preferentially afford cis-2,4-disubstituted tetrahydrofurans. This stereochemical outcome is the reverse of that predicted from the usual steric guidelines for cyclization of substituted acyclic alkenyl radicals[2−5] and is consistent with stabilization of transition state stereochemistry by anomeric effects. Similarly the preferential formation of the trans product by 1,6-exo-cyclization of the radical generated from **4f** is contrary to expectation. However, the stereochemistry of cyclization of radicals generated from **4g**−**j** in which anomeric interactions are not possible is consistent with the usual guidelines.[2−5] These observations support the hypothesis that anomeric effects stabilize the axially substituted conformers of appropriately substituted cylization transition structures.

Experimental Section

General. NMR spectra were recorded as solutions in $CDCl_3$ (unless stated otherwise) at 25 °C on 300 or 500 MHz spectrometers with TMS or $CHCl_3$ as reference. The samples used for all NOE experiments were degassed by freeze−pump−thaw methods[38] prior to data accumulation, in Wilmad Taperlok NMR tubes. Analytical thin-layer chromatography (TLC) was conducted on glass-backed microslides coated with 0.2 mm thick Merck Silica Gel 60 GF_{254}. Preparative TLC was conducted by successive placements of small aliquots of substrate onto 20 × 20 cm glass-plates loaded with Merck Kieselgel 60 F_{254}, and the plates were then eluted. Flash chromatography[39] was conducted over Merck Kieselgel 60 (230−400 mesh) with analytical (AR) grade solvents. Gas chromatography (GC) was conducted with either a BP-1, BP-5, or a BP-10 (0.25 μm, 0.22 mm × 25 m) column.

Where necessary, solvents and reagents were purified as recommended.[38] Tributylstannane was prepared as previously described.[40] Unless stated otherwise, all reactions were conducted under an atmosphere of dry nitrogen. All radical reaction mixtures were purged with a stream of nitrogen for at least 10 min prior to commencement of the reaction. Reaction temperatures refer to the external bath temperature. All photolyses were performed at room temperature with a quartz water-jacketed, Phillips 125 W medium-pressure mercury-vapor lamp set at a distance of ca. 15 cm from the Pyrex reaction vessel. Microanalyses were performed by the Australian National University Analytical Services Unit. All yields given are for isolated products unless stated otherwise.

3-(2-Bromo-1-ethoxyethoxy)prop-1-ene (4a). Ethyl vinyl ether (3.5 mL, 36 mmol) was added dropwise to a stirred solution of NBS (5.2 g, 29 mmol) and allyl alcohol (1.9 mL, 28 mmol) in CH_2Cl_2 (20 mL) at −20 °C, and the mixture was stirred for 2 h.[20,21] The reaction mixture was then warmed to room temperature, and any precipitated material was removed by filtration through sintered glassware. Flash chromatography (30:1 hexane/diethyl ether) of the concentrated crude residue furnished the desired bromide **4a** as a colorless oil[41] (4.6 g, 75%); ^{1}H NMR ($CDCl_3$) δ 1.23 (t, 3H, J = 6.9 Hz), 3.37 (d, 2H, J = 5.43 Hz), 3.55−3.75 (m, 2H), 4.00−4.20 (m, 2H,), 4.71 (t, 1H, J = 5.43 Hz), 5.17−5.34 (m, 2H), 5.84−5.98 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 15.07, 31.57, 62.29, 67.45, 100.75,

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117.34, 133.89. Anal. Calcd for $C_7H_{13}BrO_2$: C, 40.21; H, 6.27; Br, 38.22. Found: C, 40.55; H, 6.27; Br, 38.48.

3-(2-Bromo-1-acetoxyethoxy)prop-1-ene (4b). Vinyl acetate (3.4 mL, 36 mmol) was added dropwise to a stirred solution of NBS (5.4 g, 31 mmol) and allyl alcohol (1.9 mL, 28 mmol) in CH_2Cl_2 (20 mL) at −20 °C, and the mixture was stirred for 22 h. The reaction mixture was then warmed to room temperature and stirred for a further 96 h. Workup of the reaction mixture as described for **4a** gave the bromide **4b** as a colorless oil (1.8 g, 29%); ^{1}H NMR ($CDCl_3$) δ 2.12 (s, 3H), 3.43 (dd, 1H, J = 1.83, 5.07 Hz), 3.44 (dd, 1H, J = 1.83, 5.07 Hz), 4.13 (dd, 1H, J = 5.98, 11.96 Hz), 4.24 (dd, 1H, J = 5.98, 11.96 Hz), 5.21−5.35 (m, 2H), 5.83−5.94 (m, 1H), 5.96 (t, 1H, J = 5.07 Hz); ^{13}C NMR ($CDCl_3$) δ 20.89, 31.17, 70.88, 95.05, 118.27, 132.97, 170.34. Anal. Calcd for $C_7H_{11}BrO_3$: C, 37.69; H, 4.97; Br, 35.82. Found: C, 37.63; H, 5.26; Br, 35.72.

(*Z*)-4-(2-Bromo-1-ethoxyethoxy)-2-buten-1-ol (4c). Treatment of NBS (4.7 g, 26 mmol) and (*Z*)-2-butene-1,4-diol (4.1 mL, 50 mmol) in CH_2Cl_2 (20 mL) with ethyl vinyl ether (2.4 mL, 25 mmol) as described for **4a** gave the bromide **4c** as a colorless oil (4.1 g, 69%); ^{1}H NMR ($CDCl_3$) δ 1.25 (t, 3H, J = 7.12 Hz), 1.81 (br s, 1H), 3.39 (d, 2H, J = 5.50 Hz), 3.55−3.75 (m, 2H), 4.14−4.30 (m, 4H), 4.73 (t, 1H, J = 5.5 Hz), 5.65−5.75 and 5.82−5.93 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 15.73, 32.05, 59.08, 62.59, 62.84, 101.40, 128.07, 133.21; HRMS *m*/*z* calcd for $C_6H_{10}{}^{81}BrO_2$, $[M - C_2H_5O]^+$ 194.9844, found *m*/*z* 194.9843.

(*E*)-1-Phenyl-3-(2-bromo-1-ethoxyethoxy)prop-1-ene (4d). A solution of cinnamyl alcohol (1.7 mL, 13 mmol, recrystallized), NBS (2.4 g, 13 mmol), and ethyl vinyl ether (1.6 mL, 17 mmol) in CH_2Cl_2 (20 mL) was stirred for 6 h at −20 °C and then for a further 16 h at room temperature. The usual workup gave the bromide **4d** as a colorless oil[42] (2.1 g, 58%); ^{1}H NMR ($CDCl_3$) δ 1.26 (t, 3H, J = 7.15 Hz), 3.42 (d, 2H, J = 5.5 Hz), 3.56−3.78 (m, 2H), 4.30 (qd, 2H, J = 13.35, 6.0 Hz), 4.79 (t, 1H, J = 5.5 Hz), 6.29 (dt, 1H, J = 15.9, 6.0 Hz), 6.65 (d, 1H, J = 15.9 Hz), 7.20−7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 15.13, 31.65, 62.34, 67.21, 100.75, 125.07, 126.41, 127.72, 128.47, 132.69, 136.36; HRMS *m*/*z* calcd for $C_{13}H_{17}{}^{79}BrO_2$, $[M]^{+\bullet}$ 284.0412, found *m*/*z* 284.0413. Anal. Calcd for $C_{13}H_{17}BrO_2$: C, 54.75; H, 6.01; Br, 28.02. Found: C, 54.45; H, 6.43; Br, 27.95.

1-Bromo-2-(2-cyclohexylideneethoxy)-2-ethoxyethane (4e). Treatment of NBS (470 mg, 4.2 mmol) and cyclohexylideneethanol[23] (0.5 g, 4.0 mmol) in carbon tetrachloride (20 mL) with ethyl vinyl ether (0.5 mL, 5.1 mmol) as described for **4a** gave the bromide **4e** as a colorless oil (809 mg, 98%); ^{1}H NMR ($CDCl_3$) δ 1.24 (t, J = 7.08 Hz, 3H), 1.56−1.70 (m, 6H), 2.17−2.30 (m, 4H), 3.38 (d, 2H, J = 5.55 Hz), 3.45−3.70 (m, 2H), 4.15−4.32 (dq, 2H, J = 11.63, 7.23 Hz), 4.82 (t, 1H, J = 5.52 Hz), 5.59 (t, 1H, J = 7.05 Hz); ^{13}C NMR ($CDCl_3$) δ 15.10, 26.53, 27.65, 28.22, 28.88, 31.81, 36.95, 62.06, 62.30, 100.55, 116.75, 145.61. Anal. Calcd for $C_{12}H_{21}BrO_2$: C, 52.00; H, 7.64; Br, 28.83. Found: C, 52.36; H, 7.89; Br, 28.74.

4-(2-Bromo-1-ethoxyethoxy)but-1-ene (4f). Treatment of NBS (3.0 g, 17 mmol) and 3-buten-1-ol (1.5 mL, 17 mmol) with ethyl vinyl ether (1.8 mL, 19 mmol) in CH_2Cl_2 as described above for **4a** gave the bromide **4f** as a colorless oil (2.8 g, 76%); ^{1}H NMR ($CDCl_3$) δ 1.23 (t, 3H, J = 7.14 Hz), 2.32−2.40 (qt, 2H, J = 6.71, 1.53 Hz), 3.37 (d, 2H, J = 5.56 Hz), 3.53−3.75 (m, 4H), 4.68 (t, 1H, J = 5.50 Hz), 5.03−5.15 (m, 2H), 5.76−5.92 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 15.03, 31.53, 33.99, 62.36, 65.87, 101.37, 116.59, 134.72; HRMS *m*/*z* (rel intensity) $C_6H_{10}79BrO$, $[M - EtO]^+$ 176.9915, found *m*/*z* 176.9914.

3-[2-Bromo-1-(hydroxymethyl)ethoxy]prop-1-ene (4g). An ice-chilled solution of NBS (13 g, 73 mmol) in allyl alcohol (30 mL, 0.44 mol) was treated with 1-hexene (10 g, 73 mmol), stirred for 2 h, and worked up as previously described.[24] Flash chromatography (3:1 hexane/diethyl ether) of the crude product, which contained at least five components (TLC), furnished the liquid bromo-alcohol **4g** (376 mg, 3% based on total available NBS) as the only separable compound;[43] ^{1}H NMR ($CDCl_3$) δ 1.83 (br s, 1H), 3.45 (d, 2H, J = 5.70 Hz), 3.63−3.85 (m, 3H), 4.05−4.23 (m, 2H), 5.20−5.38 (m, 2H), 5.87−6.01 (m, 1H); HRMS *m*/*z* calcd for $C_6H_{10}{}^{79}BrO$, $[M - OH]^+$ 176.9915, found *m*/*z* 176.9914. Other spectral data were consistent with those previously reported.[43]

4-[(2-Bromo-1-[(trimethylsilyl)methyl]ethoxy]but-1-ene (4h). Allyltrimethylsilane (3.8 mL, 24 mmol) was added to a light-protected solution of NBA (3.33 g, 24 mmol) and 3-butene-1-ol (2 mL, 23 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 1 h and then warmed to room temperature and stirred for a further 6 days. As the mixture still contained starting material (TLC), further portions of NBA (1.65 g, 12 mmol) and allyltrimethylsilane (1.9 mL, 12 mmol) were added. However, stirring of the reaction mixture at room temperature for a further 2 days led to no further consumption of the alcohol. The orange solution was then poured onto brine (20 mL), and the organic layer was washed with aqueous sodium thiosulfate (40 mL), dried (Na_2SO_4), and carefully evaporated under ambient pressure. Distillation of the residue under reduced pressure gave a lower boiling fraction (1.7 g, bp = 50−60 °C, 20 Torr) spectroscopically identified as 3-buten-1-ol[44] and a higher boiling fraction (612 mg, bp = 120 °C, 20 Torr), flash chromatography of which (30:1 hexane/diethyl ether) gave the bromide **4h** as a colorless oil (191 mg, 6% based on reacted 3-buten-1-ol); ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9H), 0.96 (d, 1H, J = 1.86 Hz), 0.98 (d, 1H, J = 3.70 Hz), 2.25−2.38 (m, 2H), 3.38−3.45 and 3.55−3.65 (m, 5H), 3.53−3.75 (m, 4H), 5.01−5.13 (m, 2H), 5.75−5.90 (m, 1H); ^{13}C NMR ($CDCl_3$) δ −0.89, 22.00, 34.39, 37.62, 68.54, 77.01, 116.39, 135.01; HRMS *m*/*z* calcd for $C_9H_{19}OSi$, $[M - CH_2Br]^+$ 171.1205, found *m*/*z* 171.1206. The experiment was repeated several times in order to obtain sufficient quantities of **4h** for use in subsequent reactions.

3-[2-(Phenylselenyl)-1-butylethoxy]prop-1-ene (4i). $NaBH_4$ (220 mg, 5.7 mmol) was added portionwise to a vigorously stirred solution of diphenyl diselenide (890 mg, 2.9 mmol) in ethanol (12 mL) at 0 °C as previously described.[26] After the evolution of gas had ceased, a solution of 1,2-epoxyhexane (500 mg, 5 mmol) in ethanol (2 mL) was added portionwise, and the reaction mixture was stirred at room temperature for an additional 2 h. The solvent was then removed under reduced pressure, and the residual oil was poured into water and ethyl acetate. The layers were separated, and the aqueous phase was extracted with two further portions of ethyl acetate. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Flash chromatography of the residue (10:1 hexane/diethyl ether) furnished 1-(phenylselenyl)hexan-2-ol as a pale yellow oil (718 mg, 56%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.1 Hz, 3H), 1.23−1.60 (m, 6H), 2.90 (br s, 1H), 3.15 (br s, 1H), 3.63−3.71 (m, 1H), 7.28 (m, 3H), 7.55 (m, 2H).

Potassium hydride (504 mg, 33%, 4.2 mmol) and allyl bromide (1 g, 720 μL, 8.4 mmol) were added to a chilled solution (0 °C) of 1-(phenylselenyl)hexan-2-ol (720 mg, 2.8 mmol) in dry THF (10 mL). The reaction mixture was then stirred at room temperature for 19 h, further portions of potassium hydride (1.5 equiv) and allyl bromide (3 equiv) were added, and stirring was continued for a further 25 h after which time all of the alcohol had been consumed (TLC). 2-Propanol was then cautiously added to destroy the excess of potassium hydride, and the solvent was removed under reduced pressure to give an oily residue which was worked-up in the same manner as that described above for 1-phenylselenylhexan-2-ol. However, flash chromatography failed to give a pure product which was best obtained by preparative TLC. A combination of four, 200−250 mg loadings on 200 × 200 × 2 mm plates (30:1 hexane/diethyl ether), afforded the selenide **4i** as a yellow oil (294 mg, 35%); ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.08 Hz, 3H), 1.20−1.45 (m, 4H), 1.55−1.70 (m,

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2H), 2.99 (dd, 1H, J = 12.3, 6.3 Hz), 3.11 (dd, 1H, J = 12.3, 5.3 Hz), 3.52 (quintet, 1H, J = 5.55 Hz), 3.91−4.06 (qd, 2H, J = 12.48, 5.94 Hz), 5.13 (dm, 1H, J = 10.32 Hz), 5.22 (dm, 1H, J = 15.63 Hz), 5.82−5.95 (m, 1H), 7.23 (m, 3H), 7.52 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.93, 22.60, 27.40, 32.26, 33.87, 70.31, 78.32, 116.82, 126.68, 128.22, 128.90, 132.51, 134.93. Anal. Calcd for $C_{15}H_{22}OSe$: C, 60.60; H, 7.46. Found: C, 60.65; H, 7.52.

Chloro(2-ethoxyhex-5-enyl)mercury (4j). Following the literature procedure,[27] a solution of 1,5-hexadiene (600 mg, 7.3 mmol) in ethanol (1.2 mL) was added dropwise to a vigorously stirred suspension of mercuric acetate (776 mg, 2.4 mmol) in ethanol (7 mL) at 0 °C. The mixture was then warmed to room temperature over a period of 20 min after which time a test for mercuric oxide was negative.[27] The reaction mixture was then poured into aqueous sodium chloride (10%, 10 mL) and extracted with chloroform (10 mL). The chloroform layer was washed with water (2 × 10 mL) and evaporated under reduced pressure to give a white solid mixture (937 mg) of the mercuric chloride **4j** and the two diastereomers of dichloro[μ-(2,5-diethoxy-1,6-hexanediyl)]dimercury (**5**) in a ratio of 2:1 (^{1}H NMR). The solid was then added to boiling ethanol (6 mL). Filtration of the hot suspension furnished **5** as a white powder; ^{1}H NMR ($CDCl_3$) δ 1.20 (dt, 6H, J = 6.99, 1.25 Hz), 1.40−1.78 (br m, 4H), 2.13−2.19 (dt, 2H, J = 12.30, 3.38 Hz), 2.39−2.47 (t, 1H, J = 12.12 Hz), 2.43 (superimposed dd on t, 1H, J = 10.40, 1.83 Hz), 3.38−3.50 and 3.52−3.63 (m, 4H), 3.68−3.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 15.64, 34.80, 35.55, 38.58, 38.79, 64.08, 64.20, 77.54, 77.73; IR (Polyethylene disk) 312 (Hg−Cl) cm^{-1}. Anal. Calcd for $C_{10}H_{20}Cl_2Hg_2O_2$: C, 18.64; H, 3.13, Hg, 62.26. Found: C, 18.47; H, 2.91; Hg, 62.41. Evaporation of the filtrate under reduced pressure furnished the monomercurial **4j** as a pale yellow oil (90 mg, 10%).

Repetition of the above experiment with 6 mol equiv of diene furnished the desired product **4j** (52%); ^{1}H NMR ($CDCl_3$) δ 1.19 (t, 3H, J = 7.05 Hz), 1.42−1.53 and 1.65−1.78 (m, 2H), 2.09−2.19 (m and superimposed dd, 3H, J = 12.18, 4.25 Hz), 2.42 (1H, dd, J = 12.12, 5.16 Hz), 3.40−3.52 (m, 2H), 3.68−3.78 (m, 1H), 4.96−5.06 (m, 1H), 5.72−5.87 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 15.63, 29.77, 38.08, 38.75, 64.02, 77.00, 115.01, 137.81. Anal. Calcd for $C_8H_{15}ClHgO$: C, 26.45; H, 4.16; Cl, 9.76. Found: C, 26.13; H, 4.24; Cl, 9.56.

***cis*- and *trans*-1-Ethoxy-3-methyl-cyclopentane (6j).** Potassium hydride (1.2 g, 33%, 10.8 mmol), washed with petroleum spirit (bp = 100−120 °C), was suspended in dry diethyl ether (10 mL) under nitrogen gas while being added portionwise to a vigorously stirred, chilled solution (0 °C) of a mixture of *cis*- and *trans*-3-methylcyclopentanol (830 mg, 8.3 mmol) and HMPA (800 μL, 5.4 mmol) in dry diethyl ether (10 mL). Cooling of the solution was maintained until the evolution of hydrogen gas had subsided, and freshly distilled ethyl iodide (2 mL, 24.9 mmol) was then added while the mixture was slowly warmed to room temperature. Additional portions of potassium hydride (2 × 0.5 equiv) and ethyl iodide (2 × 1.5 equiv) were added after 24 and 72 h, respectively. After 96 h, the reaction mixture was worked up as described for the preparation of substrate **4i**, and the oily residue was immediately subjected to flash chromatography. Elution with 15:1 pentane/diethyl ether gave a mixture of *cis*-**6j** and *trans*-**6j** (1.8:1) as a colorless oil (1.66 g, 60%); ^{1}H NMR ($CDCl_3$) δ 0.95−1.33 (m, 2 superimposed d, and 2 superimposed t, 15H, J = 6.65, 6.59, 7.40, 7.40 Hz), 1.55−2.00 (m, 9H), 2.05−2.17 (quintet, 2H, J = 6.7 Hz), 3.38−3.47 (q, 4H, J = 7.0 Hz), 3.83−3.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ cis-isomer: 15.47, 20.72, 32.08, 32.17, 32.57, 41.37, 64.08, 80.99; trans-isomer: 15.47, 20.53, 32.10, 32.50, 32.66, 40.95, 63.78, 80.93; HRMS m/z calcd for $C_8H_{16}O$, $[M]^{+\bullet}$ 128.1201, found m/z 128.1201. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58%. Found: C, 74.63; H, 13.00%.

***cis*-1-Ethoxy-3-methylcyclopentane (*cis*-6j).** A degassed solution of [3-(tetrahydropyranyl-2-oxy)cyclopent-1-yl]acetic acid (928 mg, 4.1 mmol), prepared as previously described,[30,31] in dry benzene (40 mL), when treated with *N*-hydroxypyridine-2-thione (654 mg, 4.9 mmol), DMAP (745 mg, 6.1 mmol), and DCC (1.26 g, 6.1 mmol) in the usual way,[45] afforded an intense yellow solution of the corresponding thiohydroxamic ester. This solution was degassed and heated at reflux while tributylstannane (3.3 mL, 12.3 mmol) and AIBN (10 mg, 61 μmol) in dry benzene (15 mL) were added over a period of 1.5 h. Refluxing of the solution was continued for 16 h after which time the reaction was complete (TLC). The excess of stannane was destroyed by the cautious addition of CCl_4 (10 mL), and the solution was refluxed for 1 h before being cooled and concentrated under reduced pressure. Flash chromatography (10:1 hexane/diethyl ether) of the crude product gave the THP-ether of 3-hydroxy-1-methylcyclopentane in low yield (200 mg, 27%). The THP ether (200 mg, 1.1 mmol) was then added to a stirred solution of acidified Dowex AG 50W−X2 resin (230 mg) in methanol (5 mL) and water (5 drops).[46] The solution was heated at 45 °C for 2 h, filtered through Celite, and poured onto a water/diethyl ether bilayer. The layers were separated, and the aqueous phase was extracted with two further portions of diethyl ether. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated to a total volume of ca. 5 mL under reduced pressure. The resultant solution of 3-hydroxy-1-methylcyclopentane was subjected directly to etherification with ethyl iodide in the manner described in the preceding experiment to give an authentic sample of *cis*-**6j** (ca. 10 mg, 7%) with the spectral features specified above.

3-(1-Acetoxyethoxy)prop-1-ene (7b). Allyl vinyl ether (1.68 g, 20 mmol) was added dropwise over ca. 5 min to a vigorously stirred solution of *p*-toluenesulfonic acid (10 mg, 0.05 mmol) and acetic acid (1.14 mL, 20 mmol) in diethyl ether (50 mL) at 5 °C. Stirring was continued at room temperature for an additional 3.5 h and the mixture was then poured onto a mixture of 1:1 brine and aqueous sodium bicarbonate (20 mL) and re-extracted. After washing of the ethereal solution for a second time in with same mixture (20 mL), the organic layer was separated, dried (Na_2SO_4), and concentrated by careful distillation under ambient pressure. Short-path (Kugelrohr) distillation under reduced pressure (bp = 70−80 °C, 22 Torr) afforded solely acetal **7b** as a colorless oil (950 mg, 33%); ^{1}H NMR ($CDCl_3$) δ 1.41 (d, 3H, J = 5.01 Hz), 2.07 (s, 3H), 3.96−4.26 (m, 2H), 5.17−5.21 (dm, 1H, J = 10.32 Hz), 5.25−5.32 (dm, 1H, J = 17.28 Hz), 5.80−5.98 (m and superimposed q, 2H, J = 3.17 Hz); ^{13}C NMR ($CDCl_3$) δ 20.65, 21.13, 69.86, 95.58, 117.39, 133.55, 170.60. Anal. Calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39. Found: C, 58.30; H, 8.57.

4-[2-[(Trimethylsilyl)methyl]ethoxy]but-1-ene (7h). 3-Buten-1-ol (1 mL, 11.5 mmol) and concentrated hydrochloric acid (ca. 5 drops) were dissolved in CH_2Cl_2 (20 mL) at 0 °C and vigorously stirred while allyltrimethylsilane (1.85 mL, 11.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise over 30 min during which time the reaction mixture was slowly warmed to room temperature. After 1.5 h, the presence of a new compound (R_f = 0.55, 15:1 hexane/diethyl ether) was detected by TLC. Further catalytic quantities of concentrated hydrochloric acid (ca. 5 drops) were added but had no effect in the hastening of the reaction, nor did addition of acetic acid (5 drops) and refluxing of the mixture for a further 5 days. The reaction was therefore poured onto saturated sodium bicarbonate solution (20 mL), and the organic layer was separated, dried (Na_2SO_4), and carefully evaporated under reduced pressure. Flash chromatography (30:1 hexane/diethyl ether) of the crude residue gave **7h** as a colorless oil (200 mg, 10%); ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9H), 0.74 (dd, 1H, J = 14.46, 7.38 Hz), 1.01 (dd, 1H, J = 14.47, 6.65 Hz), 1.17 (d, 3H, J = 6.04 Hz), 2.31 (q, 2H, J = 6.84 Hz), 3.30−3.39 (dt, 1H, J = 7.08, 7.02 Hz), 3.45−3.59 (m, 2H), 4.98−5.12 (m, 2H), 5.75−5.90 (m, 1H); ^{13}C NMR ($CDCl_3$) δ −0.83, 22.47, 25.71, 34.62, 67.24, 73.54, 115.98,

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135.52; HRMS *m*/*z* calcd for $C_9H_{19}OSi$, $[M - Me]^+$ 171.1205, found *m*/*z* 171.1206.

5-Ethoxyhex-1-ene (7j). 1-Hexen-5-ol (1.0 g, 10 mmol), prepared (65%) from 1-hexen-5-one as previously described[47] was treated with potassium hydride (1.5 g, 33%, 13 mmol) and ethyl iodide (2.4 mL, 30 mmol) as described above for **4i**. Concentration of the solution under reduced pressure afforded a yellow oil (733 mg, 57%), flash chromatography (15:1 pentane/diethyl ether) of which gave **7j** as a colorless oil (44 mg, 3%); ^{1}H NMR ($CDCl_3$) δ 1.13 (d, 3H, J = 6.11 Hz), 1.19 (t, 3H, J = 7.14 Hz), 1.40−1.55 (m, 1H), 1.55−1.68 (m, 1H), 2.03−2.22 (m, 2H), 3.33−3.44 (m, 2H), 3.49−3.60 (m, 1H), 4.95 (dm, 1H, J = 12.03 Hz), 5.02 (dm, 1H, J = 17.27 Hz), 5.74−5.89 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 15.54, 19.61, 29.75, 39.07, 63.49, 74.32, 114.28, 138.62; HRMS *m*/*z* calcd for $C_8H_{15}O$, $[M - H]^+$ 127.1123, found *m*/*z* 127.1123. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.57; H, 13.02.

General Procedures for Free Radical Cyclizations. General procedures for free-radical cyclizations are given below. In each experiment the ratios of products, including diastereoisomers, were determined by ^{1}H NMR on both the crude and isolated product mixtures. In some cases no uncyclized products were detected under the conditions employed. Where no difference within experimental error was detected, the ratio reported is that which was measured for the purified mixture. In cases where differences occurred, both sets of ratios are reported.

(A). AIBN (0.01 equiv) was added to a 0.2 M solution of the halide or selenide (0.1−7.2 mmol) in dry benzene, and the solution was degassed under a stream of dry nitrogen for 10 min. The solution was then heated at reflux, and tributylstannane (1.2 equiv) was syringed into the flask in one portion. Heating of the solution was continued until all of the starting material was consumed (TLC). The solvent was then removed either by distillation under ambient pressure or by evaporation under reduced pressure for reactions that generated mixtures containing less volatile products. If the former method was used, further purification was effected by careful, short-path (Kugelrohr) distillation under reduced pressure (ca. 15 Torr). In cases where products were of low volatility, organostannane residues were removed by a DBU workup procedure[28] followed by additional flash chromatography.

(B). This procedure is essentially the same as that specified for procedure A, except that the solvent used was pentane. Initiation was effected with bis-*tert*-butyl hyponitrite.

(C). A 0.2 M solution of the starting material (ca. 4 mmol) in dry benzene was degassed under a stream of dry nitrogen for 10 min and then heated at reflux while a solution of tributylstannane (1.2 equiv) and AIBN (0.03 equiv) in dry benzene (20 mL) was added slowly at the rate of 0.1 mL/min. All subsequent monitoring and purification steps followed procedure A.

(D). This procedure is essentially the same as A except that the reaction mixture was irradiated at room temperature with a quartz water-jacketed, 125 W medium-pressure mercury-vapor lamp.

***cis*- and *trans*-2-Ethoxy-4-methyltetrahydrofurans (6a).** **(i)** Following procedure A, a solution of **4a**[41] (1.5 g, 7.2 mmol) in dry benzene (36 mL) was treated with tributylstannane (2.3 mL, 8.6 mmol) for 2 h. Short-path (Kugelrohr) distillation of the concentrated residue furnished a colorless oil (114 mg, 12%) which comprised the two tetrahydrofurans *cis*- and *trans*-**6a**[48] in a ratio of 4.7:1. An analogous experiment in benzene-d_6 gave a ratio between *cis*- and *trans*-**6a** of 4.2:1. Repetition of the experiment with the same quantities of reagents but following procedure B afforded, after 4 h, the same products (570 mg, 61%) in a ratio of 5.8:1. ^{1}H NMR ($CDCl_3$) δ cis-isomer: 1.07 (d, 3H, J = 6.47 Hz), 1.19 (t, 3H, J = 7.10 Hz), 1.40−1.50 (m, 1H), 2.16−2.33 (m, 2H), 3.35−3.50 (m, 2H), 3.67−3.77 (m, 1H), 3.92 (t, 1H, J = 4.66 Hz), 5.11 (d, 1H, J = 3.24 Hz); trans-isomer: 1.02 (d, 3H, J = 6.76 Hz), 1.17 (t, 3H, J = 7.10 Hz), 1.50−1.62 (m, 1H), 2.02 (dd, 1H, J = 13.13, 7.56 Hz), 2.49 (sextet, 1H, J = 7.24 Hz), 3.35−3.50 (m, 2H), 3.67−3.77 (m, 1H), 4.04 (t, 1H, J = 4.66 Hz), 5.12 (d, 1H, J = 3.36 Hz); ^{13}C NMR δ cis-isomer: 15.29, 17.15, 32.94, 40.82, 63.07, 73.22, 104.66; trans-isomer: 15.23, 18.38, 31.50, 41.08, 62.60, 73.95, 104.15. Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.64; H, 11.04.

(ii) In a variation of procedure A, when a solution of bromo acetal **4a** (22 mg, 0.1 mmol) in acetonitrile-d_3 (1 mL) was treated with tributylstannane (34 μL, 0.13 mmol) and heated at reflux for 2 h, the ratio of *cis*- and *trans*-**6a** was 2.8:1.

Anomerization of *cis*- and *trans*-2-Ethoxy-4-methyltetrahydrofurans (6a). A solution of trifluoromethanesulfonic acid in ethanol (10%, 10 μL) was added to solution of a 4.7:1 mixture of *cis*- and *trans*-**6a** (20 mg, 0.15 mmol) in $CDCl_3$ (1 mL), and the mixture was kept at room temperature for 1 h with occasional agitation. ^{1}H NMR spectroscopy then indicated the ratio of *cis*- and *trans*-**6a** to be 1:1.5. Experiments in which the reaction time was 16 h or in which the mixture was heated at 40 °C for 1 h gave the same cis:trans ratio.

***cis*- and *trans*-4-Methyltetrahydrofuran-2-yl Acetates (6b).** Following procedure B, a solution of **4b** (800 mg, 3.6 mmol) in dry pentane (36 mL) was treated with tributylstannane (1.2 mL, 4.3 mmol) for 5 h. Short-path (Kugelrohr) distillation of the concentrated residue furnished a colorless oil (518 mg, 57%) which comprised *cis*- and *trans*-**6b** in a ratio of 3.5:1. In addition, a small amount of the directly reduced product **7b** was also detected, but it could not be separated from the cyclized material by flash chromatography. Integration of the appropriate signals (H_2C=C for **7b** and R^1O[R]-C*H*OR^2 for **6b**) in the ^{1}H NMR spectrum gave the ratio of **7b** to **6b** of 1:5. This gave an adjusted yield of total cyclized material (after distillation) of 250 mg (48%); ^{1}H NMR (C_6D_6) δ cis-isomer: 0.95 (d, 3H, J = 6.65 Hz), 1.50−1.57 (m, 1H), 1.84 (s, 3H), 1.94−2.04 (m, 1H), 2.06−2.16 (m, 1H), 3.59 (t, 1H, J = 8.05 Hz), 3.95 (t, 1H, J = 8.05 Hz), 6.64−6.67 (m, 1H); trans-isomer: 0.82 (d, 3H, J = 6.65 Hz), 1.36−1.46 (m, 1H), 1.86 (s, 3H), 1.94−2.04 (m, 1H), 2.28−2.42 (m, 1H), 3.35 (t, 1H, J = 7.97 Hz), 4.14 (t, 1H, J = 7.97 Hz), 6.64−6.67 (m, 1H); ^{13}C NMR ($CDCl_3$) δ cis-isomer: 17.51, 21.24, 32.14, 39.85, 75.12, 99.46, 170.5; trans-isomer: 17.11, 23.28, 30.82, 40.27, 75.43, 99.25, 176.91; HRMS: *m*/*z* calcd for $C_7H_{11}O_3$, $[M - H]^+$ 143.0708, found *m*/*z* 143.0708.

Repetition of the reaction following procedure C with heating for 24 h gave no **7b** and the ratio of *cis*- to *trans*-**6b** was 1.7:1. Partial decomposition of the cyclized products occurred to form the hemiacetals **8** (1.8:1 in favor of the trans-isomer); ^{1}H NMR (C_6D_6) δ cis-isomer: 1.04 (d, 3H, J = 6.47 Hz), 1.48−1.63 (m, 1H), 2.02−2.18 (m, 2H), 3.69 (t, 1H, J = 8.18 Hz), 3.96 (t, 1H, J = 7.88 Hz), 5.59−5.61 (m, 1H); trans-isomer: 0.89 (d, 3H, J = 6.68 Hz), 1.37−1.46 (m, 1H), 2.02−2.18 (m, 1H), 2.42−2.57 (m, 1H), 3.87 (t, 1H, J = 7.48 Hz), 4.23 (t, 1H, J = 7.63 Hz), 5.59−5.61 (m, 1H); ^{13}C NMR (C_6D_6) δ cis-isomer: 17.92, 33.73, 42.24, 73.81, 99.98. trans-isomer: 18.16, 31.92, 42.35, 74.45, 99.52.

***cis*- and *trans*-2-Ethoxy-4-(2-hydroxyethyl)tetrahydrofuran (6c).** Following procedure D, a solution of bromo acetal **4c** (1.0 g, 4.2 mmol) in dry benzene (21 mL) was treated with tributylstannane (1.4 mL, 5.0 mmol) for 3 h. The concentrated residue was then subjected to DBU workup[28] and flash chromatography (R_f = 0.18, 1:1 hexane/diethyl ether) to afford a pale yellow oil (473 mg, 71%) comprising the two tetrahydrofurans *cis*- and *trans*-**6c** in a ratio of 5.0:1. Repetition of the experiment with the same quantities of reagents, but following procedure A, afforded after 3.5 h, the same products (296 mg, 44%) in a ratio of 3.3:1; ^{1}H NMR ($CDCl_3$) δ cis-isomer: 1.20 (t, 3H, J = 7.15 Hz), 1.53 (br s, 1H), 1.53−1.59 (m, 1H), 1.73 (q, 2H, J = 6.59 Hz), 2.23−2.37 (m, 2H), 3.39−3.49 (m, 1H), 3.54 (t, 1H, J = 8.13 Hz), 3.63−3.70 (m, 2H), 3.69−3.79 (m, 1H), 3.99 (t, 1H, J = 8.13 Hz), 5.11−5.14 (m, 1H); trans-isomer: 1.18 (t, 3H, J = 7.14 Hz), 1.53 (br s, 1H), 1.60−1.69 (m, 1H), 1.73 (q, 2H, J = 6.59 Hz), 2.02−2.10 (dd, 1H, J = 12.7, 7.5 Hz), 2.48−2.58 (quintet, 1H, J = 8.00 Hz), 3.39−3.49 (m, 1H), 3.54 (t, 1H, J = 8.13 Hz), 3.63−3.70 (m, 2H), 3.69−3.79 (m, 1H), 4.08 (t, 1H, J = 8.13 Hz), 5.11−5.14

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(m, 1H); ^{13}C NMR ($CDCl_3$) δ cis-isomer: 15.13, 35.06, 35.61, 38.60, 61.52, 62.93, 71.50, 104.04; trans-isomer: 15.09, 35.84, 36.42, 39.00, 61.52, 62.49, 71.50, 103.59. HRMS *m/z* calcd for $C_8H_{15}O_3$, $[M - H]^+$ 159.1021, found *m/z* 159.1021.

***cis*- and *trans*-2-Ethoxy-4-benzyltetrahydrofurans (6d).** Following procedure A, a solution of bromo acetal **4d**[42] (710 mg, 2.5 mmol) in dry benzene (12.5 mL) was treated with tributylstannane (0.74 mL, 2.7 mmol) for 55 h. Two further aliquots of stannane (1.15 equiv and 0.73 equiv) together with small amounts of AIBN (0.01 equiv) were added at 6.5 and 30 h, respectively. The concentrated residue was worked up with DBU[28] and flash chromatography (10:1:0.5 hexane/diethyl ether/chloroform) to afford *cis*- and *trans*-**6d**[49] in a ratio of 2.1:1 as a colorless oil (512 mg, 44%); ^{1}H NMR ($CDCl_3$) δ cis-isomer: 1.23 (t, 3H, $J = 7.1$ Hz), 1.58−1.66 (ddd, 1H, $J = 13.3$, 6.6, 3.0 Hz), 2.16−2.25 (ddd, 1H, $J = 13.3$, 11.8, 5.6 Hz), 2.48 (septet, 1H, $J = 7.38$ Hz), 2.77 (dd, 2H, $J = 8.1$, 2.4 Hz), 3.38−3.50 (m, 1H), 3.61 (t, 1H, $J = 8.3$ Hz), 3.68−3.81 (m, 1H), 3.90 (t, 1H, $J = 8.4$ Hz), 5.10−5.16 (m, 1H), 7.13−7.33 (m, 5H); trans-isomer: 1.18 (t, 3H, $J = 7.1$ Hz), 1.67−1.78 (m, 1H), 1.96−2.03 (ddd, 1H, $J = 12.9$, 6.9, 1.1 Hz), 2.65−2.84 (m, 3H), 3.38−3.50 (m, 1H), 3.54−3.59 (dd, 1H, $J = 8.2$, 5.8 Hz), 3.68−3.81 (m, 1H), 3.95−4.01 (dd, 1H, $J = 8.3$, 7.0 Hz), 5.10−5.16 (m, 1H), 7.13−7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ cis-isomer: 15.23, 38.65, 39.07, 40.03, 62.98, 71.56, 104.27, 125.91, 125.99, 128.29, 128.47, 128.55, 140.69; trans-isomer: 15.05, 38.57, 38.98, 39.74, 62.60, 71.64, 103.80, 125.91, 125.99, 128.29, 128.47, 128.55, 140.50. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.42; H, 9.11.

Repetition of the experiment with **4d** (274 mg, 0.96 mmol) by a variation of procedure B afforded, after 5 days, *cis*- and *trans*-**6d** (131 mg, 66%) in a ratio of 2.7:1. In this experiment, four further aliquots of stannane (0.35 equiv) together with small amounts of AIBN (0.01 equiv) were added at 4.3, 6, 72, and 96 h, respectively.

***cis*- and *trans*-2-Ethoxy-4-cyclohexyltetrahydrofurans (6e).** Following procedure A, a solution of bromo acetal **4e** (150 mg, 0.5 mmol) in dry benzene (2.5 mL) was heated with tributylstannane (161 μL, 0.6 mmol) for 2 h. A DBU workup[28] and flash chromatography ($R_f = 0.31$, 15:1 hexane/diethyl ether) gave *cis*- and *trans*-**6e** in a ratio of 1.7:1 as a pale yellow oil (65 mg, 61%); ^{1}H NMR ($CDCl_3$) δ cis-isomer: 0.85−0.98 (m, 2H), 1.16−1.31 (m and superimposed t, 4 + 3H, $J = 7.08$ Hz), 1.44−1.70 (m, 6H), 1.80−1.95 (sextet, 1H, $J = 7.9$ Hz), 2.20−2.30 (m, 1H), 3.35−3.55 (m and t, 2H, $J = 8.06$ Hz), 3.55−3.78 (m, 1H), 3.92 (t, 1H, $J = 7.76$ Hz), 5.07−5.13 (m, 1H); trans-isomer: 0.85−0.98 (m, 2H), 1.16−1.31 (m and superimposed t, 4 + 3H, $J = 7.08$ Hz), 1.48−1.70 (m, 6H), 1.95−2.03 (dd, 1H, $J = 12.5$, 7.2 Hz), 2.15−2.30 (m, 1H), 3.35−3.55 (m and t, 2H, $J = 8.12$ Hz), 3.55−3.78 (m, 1H), 4.05 (t, 1H, $J = 8.12$ Hz), 5.07−5.13 (m, 1H); ^{13}C NMR ($CDCl_3$) δ cis-isomer: 16.00, 27.13, 38.21, 63.51, 70.65, 105.11; trans-isomer: 15.96, 27.08, 38.08, 62.92, 71.90, 104.77. The remaining signals could not be assigned to a particular isomer: 26.71, 26.77, 26.81, 32.28, 32.62, 32.79, 32.87, 41.88, 42.64, 43.74, 45.99. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.67; H, 11.50.

Reduction of 4-(2-Bromo-1-ethoxyethoxy)but-1-ene (4f). In a variation of procedure A, a solution of **4f** (980 mg, 4.4 mmol) in dry benzene (72 mL) when heated with tributylstannane (1.4 mL, 5.3 mmol) for 18 h gave a complex mixture of products (^{1}H NMR), two of which were tentatively identified as being the diastereomeric 2-ethoxy-4-methyltetrahydropyrans **6f**,[32] while the detection of olefinic resonances suggested that the uncyclized product **7f** had also been formed. The residue was then subjected to a DBU workup procedure[28] followed by repetitive flash chromatography (15:1 pentane/diethyl ether).

The first fraction, a colorless oil (112 mg), contained a 1:2 mixture of *trans*-2-ethoxy-4-methyltetrahydropyran **6f**[6] and **7f** which was identified by comparison with an authentic sample (see below); ^{1}H NMR ($CDCl_3$) δ *trans*-**6f**: 0.95 (d, 3H, $J = 6.16$ Hz), 1.29−1.50 (m, 3H), 1.35 (t, 3H, $J = 7.4$ Hz), 1.87−1.95 (dm, 1H, $J = 13.1$ Hz), 2.15−2.28 (m, 1H), 3.45−3.80 (m, 2H), 3.90−4.05 (m, 2H), 5.03 (d, 1H, $J = 4.40$ Hz). Additional spectral data were similar to those reported previously.[32]

The second fraction contained 2-ethoxyoxepane (**9**)[29] as a colorless oil (10 mg); ^{1}H NMR ($CDCl_3$) δ 1.30−1.37 (d, 3H, $J = 6.8$ Hz), 1.40−1.96 (m, 7H), 2.11−2.20 (m, 1H), 3.48−3.58 (m, 1H), 3.64−3.69 (1H, dm, $J = 12.61$ Hz, H-7a), 3.93−4.02 (t, 1H $J = 10.99$ Hz), 4.00−4.02 (m, 2H), 4.89−4.93 (dd, 1H, $J = 8.55$, 5.37 Hz); ^{13}C NMR ($CDCl_3$) δ 15.98, 23.49, 30.39, 31.55, 36.01, 61.77, 62.97, 102.22.

The third fraction contained exclusively *cis*-2-ethoxy-4-methyltetrahydropyran (*cis*-**6f**)[32] as a colorless oil (21 mg); ^{1}H NMR ($CDCl_3$) δ 0.95 (d, 3H, $J = 6.16$ Hz), 1.06−1.62 (m, 4H), 1.39 (t, 3H, $J = 6.96$ Hz), 1.88−2.00 (1H, qt, $J = 8.55$, 1.93 Hz), 3.36 (dt, 1H, $J = 11.48$, 2.99 Hz), 3.60−3.70 (m, 1H), 4.05−4.11 (ddd, 1H, $J = 11.60$, 4.33, 2.19 Hz), 4.20−4.30 (m, 1H), 4.44 (dd, 1H, $J = 8.60$, 2.32 Hz). Additional spectral data were consistent with those reported previously.[32]

4-(1-Ethoxyethoxy)but-1-ene (7f). Following procedure B a solution of **4f** (500 mg, 2.2 mmol) in dry pentane (11 mL) was treated with tributylstannane (0.71 mL, 2.6 mmol) for 5 h. A DBU workup[28] and flash chromatography (15:1 pentane/diethyl ether) gave solely **7f** as a colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, 3H, $J = 5.28$ Hz), 1.31 (d, 3H, $J = 6.80$ Hz), 2.34 (qt, 2H, $J = 6.97$, 2.09 Hz), 3.42−3.72 (m, 4H), 4.71 (q, 1H, $J = 5.58$ Hz), 5.02−5.15 (m, 2H,), 5.77−5.91 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 15.16, 19.66, 34.21, 60.63, 64.14, 99.34, 116.23, 135.21. HRMS *m/z* calcd for $C_8H_{15}O_2$, $[M - H]^+$ 143.1072, found *m/z* 143.1073.

***cis*- and *trans*-2-(Hydroxymethyl)-4-methyltetrahydrofuran (6g).** Following procedure B, a solution of **4g** (304 mg, 1.6 mmol) in dry pentane (10 mL) was treated with tributylstannane (0.52 mL, 1.9 mmol) for 5 h. A DBU workup[28] and flash chromatography ($R_f = 0.50$, diethyl ether) gave *cis* and *trans*-**4g** in a ratio of 1:5.0 as a pale yellow oil (131 mg, 72%); ^{1}H NMR ($CDCl_3$) δ cis-isomer: 1.05 (d, 3H, $J = 6.74$ Hz), 1.21−1.32 (m, 1H), 2.02−2.11 (quintet, 1H, $J = 6.80$ Hz), 2.24−2.41 (m, 1H), 3.30−3.35 (dd, 1H, $J = 8.28$, 7.12 Hz), 3.47−3.55 (dd, 1H, $J = 11.53$, 6.22 Hz), 3.66−3.71 (dd, 1H, $J = 11.50$, 3.29 Hz), 3.90−3.96 (t, 1H, $J = 8.24$ Hz), 3.96−4.10 (m, 1H); trans-isomer: 1.04 (d, 3H, $J = 6.74$ Hz), 1.53−1.61 (dd, 1H, $J = 12.47$, 6.66 Hz), 1.83−1.90 (dd, 1H, $J = 12.49$, 6.07 Hz), 2.24−2.41 (octet, 1H, $J = 6.80$ Hz), 3.31−3.36 (dd, 1H, $J = 8.28$, 7.12 Hz), 3.43−3.49 (dd, 1H, $J = 11.53$, 6.22 Hz), 3.61−3.67 (dd, 1H, $J = 11.50$, 3.29 Hz), 3.96−4.01 (dd, 1H, $J = 8.24$, 6.65 Hz), 4.08−4.17 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 17.59, 33.64, 35.34, 65.07, 75.11, 78.81; HRMS *m/z* calcd for $C_6H_{11}O_2$, $[M - H]^+$ 115.0759, found *m/z* 115.0754.

Reduction of 4-[2-Bromo-1-[(trimethylsilyl)methyl-]ethoxy]but-1-ene (4h). In a variation of procedure A, treatment of **4h** (430 mg, 1.6 mmol) with tributylstannane (0.52 mL, 1.9 mmol) in dry benzene (81 mL) for 3 h gave a complex mixture of products (^{1}H NMR). Two of these were tentatively identified as *cis*- and *trans*-**6h**, while the presence of olefinic signals suggested that **7h** had also been formed. DBU workup[28] followed by repetitive flash chromatography (30:1 pentane/diethyl ether) gave as the first fraction a mixture of *cis*-**6h** ($R_f = 0.40$) with **7h** ($R_f = 0.50$) which was identified by comparison with an authentic specimen (see above). The second fraction gave exclusively *cis*-2-[(trimethylsilyl)methyl]-4-methyltetrahydropyran (*cis*-**6h**) as a colorless oil (144 mg); ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9H), 0.74 (dd, 1H, $J = 14.56$, 7.08 Hz), 0.90 (dd, 1H, $J = 13.52$, 6.11 Hz), 0.91 (d, 3H, $J = 6.32$ Hz), 1.00−1.85 (m, 5H), 3.29−3.42 (m, 2H), 3.94 (ddd, 1H, $J = 11.26$ Hz, $J = 4.40$, 1.16 Hz); ^{13}C NMR ($CDCl_3$) δ −0.90, 22.27, 25.23, 30.45, 34.32, 43.62, 67.86, 75.68; HRMS *m/z* calcd for $C_9H_{19}OSi$, $[M - Me]^+$ 171.1205, found *m/z* 171.1206.

The third fraction gave exclusively *trans*-2-[(trimethylsilyl)-methyl]-4-methyltetrahydropyran (*trans*-**6h**) as a colorless oil (19 mg); ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9H), 0.74 (dd, 1H, $J = 14.40$, 7.30 Hz), 0.97 (dd, 1H, $J = 14.40$, 7.30 Hz), 1.03 (d, 3H, $J = 7.08$ Hz), 1.16−1.27 (m, 1H), 1.38−1.44 (dm, 1H, $J = 13.30$ Hz), 1.68−1.80 (octet, 1H, $J = 4.54$ Hz), 1.93−2.04 (m, 1H),

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3.58−3.82 (m, 3H); ^{13}C NMR ($CDCl_3$) δ −0.92, 19.00, 23.41, 24.85, 32.29, 40.37, 61.97, 70.17.

***cis*- and *trans*-2-Butyl-4-methyltetrahydrofuran (6i).** Following procedure B, **4i** (520 mg, 1.8 mmol) in dry pentane (8.7 mL) was treated with tributylstannane (0.58 mL, 2.2 mmol) for 5 h. Short-path (Kugelrohr) distillation (bp = 107 °C, 15 Torr) of the concentrated residue furnished a mixture of *cis*- and *trans*-**6i**[50] (1:5) as a colorless oil (124 mg, 50%); ^{1}H NMR ($CDCl_3$) δ cis-isomer: 0.90 (t, 3H, J = 6.7 Hz), 1.03 (d, 3H, J = 6.7 Hz), 1.07 (m, 1H), 1.21−1.72 (m, 6H), 2.08−2.17 (m, 1H), 2.22−2.36 (m, 1H), 3.30 (t, 1H, J = 7.95 Hz), 3.78 (t, 1H, J = 7.95 Hz), 3.74−3.83 (m, 1H); trans-isomer: 0.90 (t, 3H, J = 6.7 Hz), 1.01 (d, 3H, J = 6.7 Hz), 1.21−1.72 (m, 8H), 2.22−2.36 (m, 1H), 3.17 (dd, 1H, J = 8.3, 6.9 Hz), 3.80−3.87 (m, 1H), 3.90 (dd, 1H, J = 8.3, 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ cis-isomer: 13.96, 17.86, 22.68, 28.44, 35.73, 34.21, 40.82, 74.26, 80.18; trans-isomer: 13.90, 18.01, 22.68, 28.37, 35.73, 33.08, 39.53, 74.72, 78.71. Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.75. Found: C, 75.99; H, 12.58.

Reduction of Chloro(2-ethoxyhex-5-enyl)mercury (4j) with Sodium Trimethoxyborohydride. Sodium trimethoxyborohydride (200 mg, 1.55 mmol) was suspended in dry CH_2Cl_2 (15 mL), and the mixture was degassed under nitrogen for ca. 10 min. In a separate flask, the mono-mercurial **4j** (470 mg, 1.3 mmol) was dissolved in dry CH_2Cl_2 (1 mL), and the resulting solution was similarly degassed. The mercurial solution was then added via a syringe to the vigorously stirred borohydride suspension. Two additional portions of the borohydride (150 mg each, 1.2 mmol) were added at 6 and 48 h, respectively, in an attempt to hasten the consumption of the starting material. Stirring of the mixture was continued at room temperature for 3 days during which time metallic mercury formed. The mixture was then filtered through Celite, and the solvent was removed by spinning band distillation to give a mixture of *cis*-**6j**, *trans*-**6j**, and **7j** (1.1:1.0:1.3) as a pale yellow oil, the components of which were identified by comparison with authentic samples (see above). Repetition of the experiment in $CDCl_3$ confirmed that ratios above were unchanged by distillation of the crude product mixture.

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Supporting Information Available: IR and MS data for compounds **4a**−**j**, **5**, **6a**−**j**, **7b**, **7f**, **7h**, **7j**, **8**, and **9**. Copies of ^{1}H and ^{13}C NMR spectra for compounds **4c**, **4f**, **4g**, **4h**, **6b**, **6c**, **6f**, **6g**, **6h**, **7f**, **7h**, **8**, and **9** (33 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.

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