(CHN)), 3.75 (m, 1 H, C*H*(CH_2)(C=O)), 4.22 (dd, J = 5.2, 8.7 Hz, 1 H, CH_2O, syn to Ph), 4.67 (t, J = 8.8 Hz, 1 H, CH_2O, anti to Ph), 4.82 (dd, J = 2.2, 5.7 Hz, 1 H), 5.16 (dd, J = 1.6, 8.9 Hz, 1 H), 5.28 (d, J = 4.1 Hz, 1 H), C*H*(C=O)(N), *H*C=C*H*), 4.98 (dd, J = 5.1, 8.9 Hz, 1 H, CHPh), 7.2-7.5 (m, 5 H, Ph); ^{13}C NMR (75 MHz) δ 34.3, 45.8, 56.1, 57.6, 70.0, 71.3, 127.6, 128.1, 128.9, 129.0, 134.2, 139.8, 158.1, 206.4; IR (film) ν 1789 (C=O), 1747 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.39; H, 5.69; N, 5.35.

Reaction of Imine 12 with Acid Chloride 2. The reaction of acid chloride **2** (200 mg, 0.82 mmol) with cyclic imine **12** provided a complex mixture of products. The only isolable product obtained by column chromatography was 5.6% (17 mg, 0.05 mmol) of one syn diastereomer (N* and Ph syn) as a white solid: ^{1}H NMR (300 MHz) δ 1.90 (m, 2 H, CH_2), 2.07 (m, 1 H, CH_2), 2.19 (m, 1 H, CH_2), 3.01 (m, 1 H, CH_2), 3.67 (m, 1 H, CH_2), 3.96 (dd, J = 7.2, 8.8 Hz, 1 H, CH_2O, syn to Ph), 4.39 (t, J = 8.9 Hz, 1 H, CH_2O anti to Ph), 4.62 (s, 1 H, CHC=O), 4.81 (dd, J = 7.3, 9.1 Hz, 1 H, NC*H*CH_2O), 6.87 (m, 2 H, Ph), 7.0-7.5 (m, 8 H, Ph); ^{13}C NMR (75 MHz) δ 28.50, 38.02, 45.98, 59.42, 67.83, 70.66, 72.21, 126.34, 127.30, 127.64, 128.49, 128.66, 129.06, 136.86, 138.21, 157.74, 170.16 (C=O); IR ($CDCl_3$) ν 1754 (s, C=O) cm^{-1}; mass spectrum, m/e (% relative intensity) CI (NH_3) 348 (3.3, M$^+$).

Acknowledgment. Support for this research under Grant 2 ROI GM26178-12 from the National Institutes of General Medical Sciences (Public Health Service) is gratefully acknowledged.

Studies on the Intramolecular Competitive Addition of Carbon Radicals to Aldehydo and Alkenyl Groups[1]

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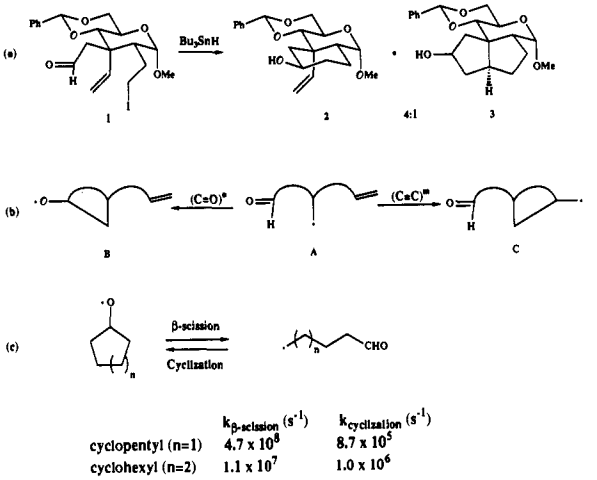
Contribution from the Paul M. Gross Chemical Laboratory, Department of Chemistry, Duke University, Durham, North Carolina 27706. *Received January 28, 1991*

Abstract: Cyclizations of ω-formylalkyl radicals can provide an efficient route to the corresponding cycloalkanols. However, if an ω-vinyl group is present, an alternative mode of cyclization exists, and there is competition between cycloalkanol and methyl cycloalkane formation (i.e. $(C=O)^n$ versus $(C=C)^m$). Cyclohexanol formation, $(C=O)^6$, usually overwhelms any alternative process, but cyclopentanol and methylcyclopentane processes ($(C=O)^5$ and $(C=C)^5$) can be competitive. The latter process involves the well-studied 5-hexenyl radical ring closure, and hence by choice of a suitable substrate, where both modes of cyclization are optional, we have obtained rate data for cyclopentanol $(C=O)^5$ formation in a direct-competition experiment. The value $k_{C=O} \geq 9.6 \times 10^5$ s^{-1} is consistent with that obtained by Beckwith and Hay. The study has also helped to define some of the requirements for optimizing the formation of cycloalkanols. Concentration of H$^\bullet$ source, usually through Bu_3SnH, must be maintained at a high level so that reduction of the cycloalkoxy radical intermediate overwhelms its decomposition by β-scission, which regenerates the acyclic precursor. However, at very high concentrations of Bu_3SnH, addition of the tin radical to the aldehydo group can also become a competitive process. The latter also occurs if radical generation is inefficient. Thus alkyl iodides that react extremely rapidly with $Bu_3Sn^\bullet$ are the preferred precursors.

Introduction

The observation, in 1986, that compound **1** reacted with tri-*n*-butyltin hydride to give compounds **2** and **3** in a 4:1 ratio suggested that intramolecular radical-aldehyde addition (A → B; $(C=O)^n$) was a viable synthetic pathway, which could compete favorably with 5-hexenyl ring closure (A → C; $(C=C)^5$) (Scheme I).[3] Although intramolecular radical-aldehyde additions had been advanced to account for rearrangements[4] and for epimerization of hydroxyl groups in various systems,[5] the observations illustrated in Scheme Ia prompted us to evaluate the competitive pathways A → B versus A → C independently,[6] and since then radical-aldehyde cyclizations have been examined as viable synthetic operations in our laboratory[7] and elsewhere.[8] Mechanistically,

Scheme I



	$k_{\beta\text{-scission}}$ (s^{-1})	$k_{\text{cyclization}}$ (s^{-1})
cyclopentyl (n=1)	4.7×10^8	8.7×10^5
cyclohexyl (n=2)	1.1×10^7	1.0×10^6

seminal observations concerning the competing pathways in Scheme Ib have been offered by Curran,[9] and kinetic data for the reversible β-scission of cyclopentoxy and cyclohexoxy radicals (Scheme Ic) have been obtained by Beckwith and Hay.[10] We

(1) This work was supported by grants from NIH (GM 37389 and GM 32569).
(2) Taken from the Ph.D. Thesis of Richard A. Walton, Duke University, Durham, NC, 1990.
(3) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986** *108*, 2117.
(4) (a) Mihailovic, M. L.; Andrejevic, V.; Jakovljevic, M.; Jeremic, D.; Stojiljkovic, A. *J. Chem. Soc., Chem. Commun.* **1970**, 854. (b) Flies, M. F.; Lalande, R.; Maillard, B. *Tetrahedron Lett.* **1976**, 439.
(5) (a) Fuller, G.; Rust, F. F. *J. Am. Chem. Soc.* **1958**, *80*, 6148. (b) Suginome, H.; Sato, N.; Masamune, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 215. (c) Robinson, C. H.; Gnoj, O.; Wayne, R.; Townley, E. R.; Kabasakalian, P.; Oliveto, E. P.; Barton, D. H. R. *J. Am. Chem. Soc.* **1961**, *83*, 1771. (d) Nickon, A.; Mahajan, J. R.; McGuire, F. J. *J. Org. Chem.* **1961**, *26*, 3617. (e) Binkley, R. W.; Koholic, D. J. *J. Carbohydr. Chem.* **1984**, *3*, 85.
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(8) Knapp, S.; Gibson, F. S.; Choe, Y. H. *Tetrahedron Lett.* **1990**, *31*, 5397.
(9) (a) Curran, D. P. *Synthesis* **1988**, 417. (b) Curran, D. P. *Synthesis* **1988**, 489.
(10) (a) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 2674. (b) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1989**, *111*, 230.

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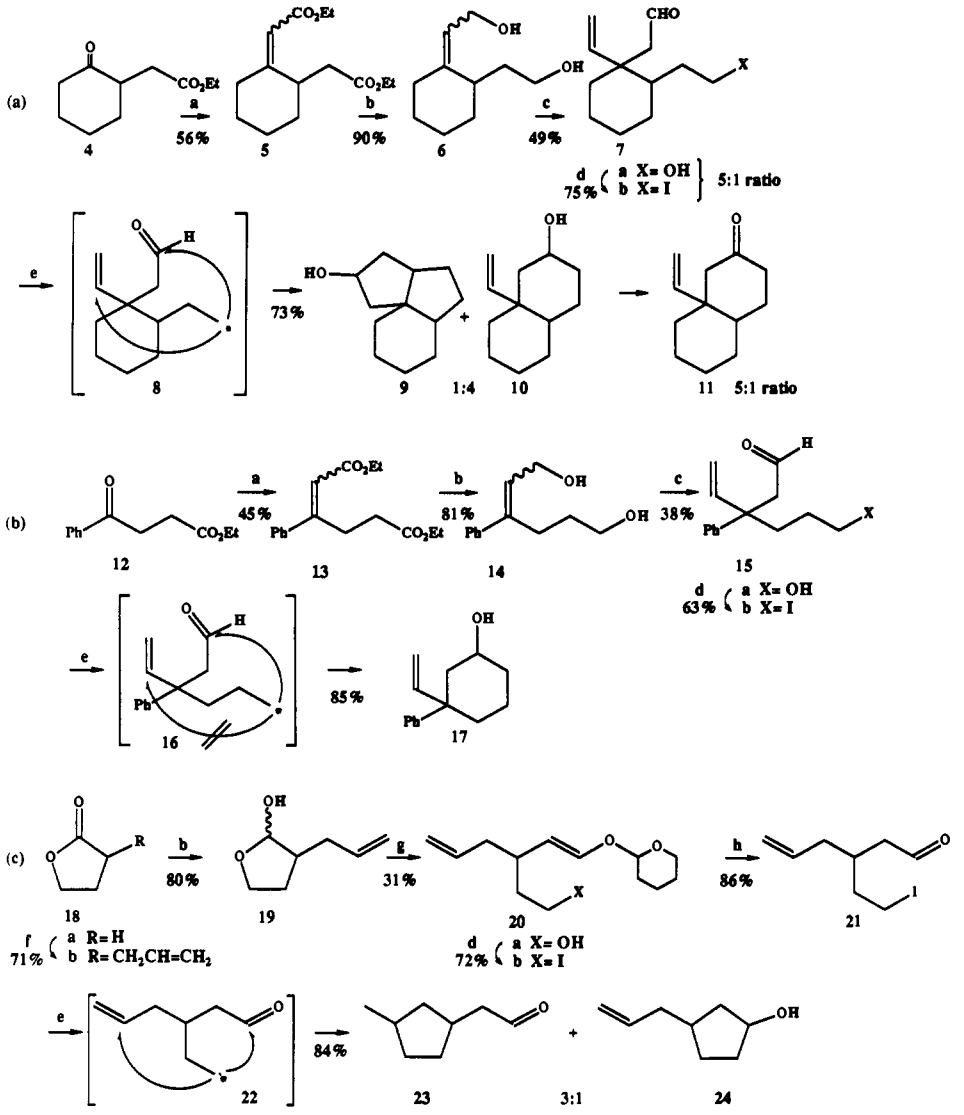
Scheme II



(a) Horner-Emmons Reaction; (b) DIBAL; (c) CH_2=CHOEt/Hg$(OCOCF_3)_2$; (d) Ph_3P/I_2; (e) Bu_3SnH; (f) LDA/allyl iodide; (g) THPOCH$_2$P$^+$Ph$_3$Cl$^-$K(NTMS)$_2$/THF; (h) $HClO_4/H_2O$

have continued our efforts to achieve a better understanding of the competing pathways in Scheme Ib, and in this paper we describe some of our results.

Synthesis of Non-Carbohydrate Models

In order to establish that the unexpected results in Scheme Ia were not due to idiosyncrasies emanating from the carbohydrate moiety, the olefinic iodo aldehydes **7b** and **15b** were devised as non-carbohydrate models. Their syntheses are outlined in Scheme IIa, b and are patterned after the preparation of **1** from the corresponding 3-keto sugar,[11] featuring a spiro-Claisen rearrangement as the key step.[12] For **7b**, cyclohexanone was processed to give **5** as a 1/1 mixture of geometric isomers. Reduction with diisobutylaluminum hydride (Dibal) led to **6**, and rearrangement gave **7a** as a 5/1 mixture of diastereomers. Iodinolysis then led to the desired product **7b**. The acyclic analogue **15b** was similarly obtained with ethyl 3-benzoylpropionate (**12**) as the starting material.

Compounds **7b** and **15b** permitted us to study the competition between cyclohexanol and methylcyclopentane formation (i.e. (C=O)^6 versus (C=C)^5), a study prompted by the results in Scheme Ia. We also decided to extend our study to include compound **21** in order to observe the competition between cyclopentanol and cyclopentane formation (i.e. (C=O)^5 versus (C=C)^5). The synthesis of compound **21**, outlined in Scheme IIc, was achieved by routine operations beginning with γ-butyrolactone.

Cyclization Studies

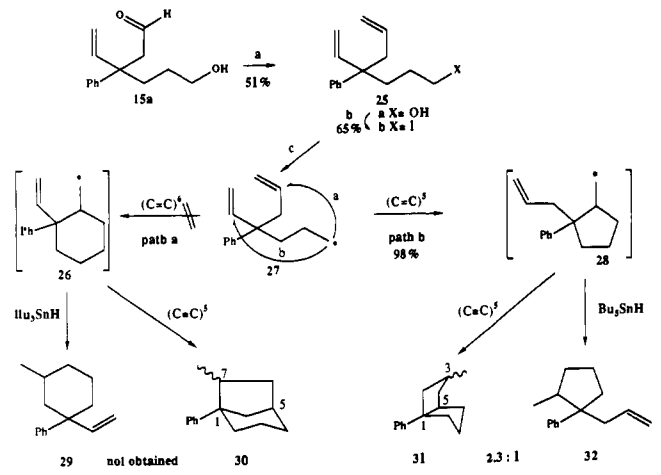
Results of radical cyclizations of the model compounds are also shown in Scheme II. Compound **7b** gave a mixture of **9** and **10** in a 1:4 ratio, identical with that found in Scheme Ia, thereby discounting any influence of the carbohydrate moiety of **1**. A significant result was the fact that oxidation of the major product, **10**, gave ketone **11** with the same ratio of diastereomers (i.e. 5:1) as the precursor **7b**, thereby revealing that (C=O)^6 cyclization had predominated irrespective of the cis or trans relationship of the radical-bearing appendage in the radical **8**.

Compound **15b** afforded **17** as the only product (85% yield), while compound **21** gave a 3/1 mixture of compounds **23** and **24**. The complete absence of a 5-hexenyl (i.e. (C=C)^5) ring closure product from substrate **15b** was remarkable, and raised the possibility that the neopentenyl location of the vinyl residue may have rendered it sterically inaccessible vis a vis the aldehydo group. To address this issue, the diene counterpart **25** was prepared and

(11) (a) Dickson, J.; Tsang, R.; Llera, J. M.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 5350. (b) Pak, H.; Dickson, J.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 5357.

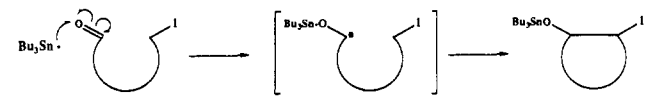
(12) (a) Wilson, S. E. *Tetrahedron Lett.* **1975**, 4651. (b) Watanabe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.* **1957**, *79*, 2628.

Scheme III



(a) $Ph_3P^+CH_2Br^-/K(NTMS)_2$; (b) Ph_3P/I_2; (c) Bu_3SnH

Scheme IV



examined (Scheme III). If steric hindrance of the neopentenyl vinyl group was indeed a factor, then ring closure of radical **27** should occur at the less hindered olefinic group (i.e. path a, $(C{=}C)^6$), comparable to the $(C{=}O)^6$ process that led to **17** to give compound **26**. The latter would then either suffer reduction to compound **29** or a serial $(C{=}C)^5$ exo ring closure leading to the bridged system **30**. Alternatively the radical **27** could undergo classical 5-hexenyl ring closure (i.e. path b, $(C{=}C)^5$) leading to **28**, which could then undergo reduction to **32** or a serial $(C{=}C)^5$ process leading to diquinnane **31**.

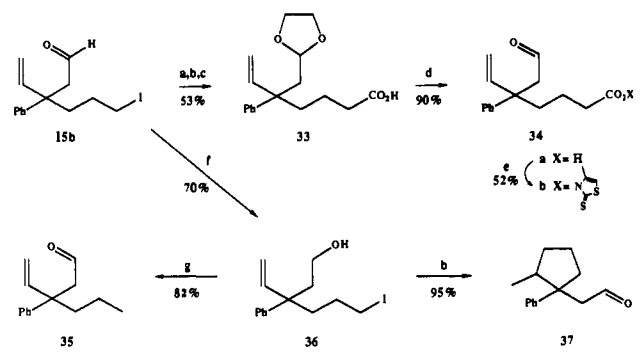
In the event, compound **30** was completely absent in the reaction of **25** with tri-*n*-butyltin hydride. Assignment of **31** as the sole bicyclic product rested upon identification of a methine proton at 2.75 ppm by NOE enhancement when the aromatic envelope was irradiated. Subsequent irradiation of this methine proton failed to cause collapse of the methyl doublet. Thus the methine proton in question must be H-5 of **31** rather than H-7 of **30**.

Further proof for the course of cyclization came from isolation of a small amount of monocyclized product, which showed resonances for allylic methylene protons at 2.28 ppm, an observation that is consistent with **32** but not **29**.

In view of the well-established stature of 5-hexenyl $(C{=}C)^5$ ring closures in radical reactions,[13] its subjugation in the reactions of **7b** and **15b** was perplexing. At the time of the initial observation[3] (Scheme Ia), we had wondered whether the process depicted in Scheme IV could be occurring, involving addition of a tin radical to the aldehydo group as the initial process.[14] Unlikely though it was in view of the affinity of tin radicals for iodide,[15] we decided to rule conclusively on this issue by generating the (presumed!!) radical **16** in an unambiguous manner.

The Barton thiohydroxamic ester procedure[16] was ideal for this purpose, and the synthesis of the required precursor **34b** was carried out in a straightforward manner as depicted in Scheme

Scheme V



(a) $HOCH_2CH_2OH$/TsOH; (b) NaCN/DMSO; (c) KOH/H_2O_2; (d) $HClO_4/H_2O$; (e) $(COCl)_2$/4-methyl-3-hydroxythiazol-2-(3H)-thione/; (f) $NaBH_4$; (g) $LiEt_3BH$/THF; (h) Bu_3SnH

V. The material was subjected to three modes of decomposition. With Bu_3SnH and AIBN as the initiator, compounds **17**, **35**, and **37** were obtained in 88%, 3%, and 5% yields, respectively. Initiation by heat or light led to **17** as the only identifiable product in 61% and 75% yields, respectively. In the absence of Bu_3SnH, the latter two experiments led to complex mixtures.

Estimation of the Rate Constant for $(C{=}C)^5$ by Competition

At the time of our initial observation[3] (Scheme Ia), insight into the radical–aldehyde ring closure process suffered from a lack of pertinent rate data. As noted above, Beckwith and Hay have now studied the 4-formylbutyl and 5-formylpentyl systems and obtained the rate data indicated in Scheme Ic.[10]

However, a different approach for obtaining rate data was open to us in view of the competitive nature of our reactions, as is conveniently summarized in Scheme Ib. Thus the product(s) from B and C should be formed in the ratio of the relevant rate con-

$$\frac{[\text{product(s) from C}]}{[\text{product(s) from B}]} = \frac{k_{(C{=}C)^m}}{k_{(C{=}O)^n}} \qquad (1)$$

stants, as stated formally in eq 1. The results in Scheme IIa,b, as well as our earlier studies, had shown that ring closures to give cyclohexanols usually overwhelm competitive procedures (i.e. $(C{=}O)^6 \gg (C{=}C)^m$). The cyclopentyl system in Scheme IIc therefore seemed more amenable to competition studies.

However, it was first necessary to examine the reversibility of the competitive processes. Extensive experiments have established that 5-hexenyl ring closure $(C{=}C)^5$ such as A → C (Scheme Ib) is not a reversible process under the normal reaction conditions.[13] We decided to address this issue for cyclohexanol and cyclopentanol formation, A → B, as shown in Scheme VI. Details of our studies in Scheme VIa,b have been published,[7,17] but in summary, the radical **41**, generated from iodide **42**, closed to give cyclohexoxy **40**, and thence cyclohexanol **38** exclusively. We then generated the cyclohexoxy radical **40** independently by treatment of the nitrate **40** with tri-*n*-butyltin hydride[17] and recovered **38** exclusively.[7] The same was true for the epimeric nitrate **43**, which afforded alcohol **45** quantitatively.[7] *These results make it clear that, under our reaction conditions, β-scission of the cyclohexoxy radical does not occur, or* **41** *and/or* **44** *would have lead to a mixture of the epimeric alcohols* **38** *and* **45**.

On the other hand, reaction of the cyclopentanol **24** with lead tetraacetate (Scheme VIc) afforded a 24% yield of **23**, thereby indicating that β-scission leading to **22** occurred rapidly.

In light of the latter finding, the proposed competition study involving **21** was complicated by the fact that β-scission of the cyclopentoxy radical **50** could give two different alkyl radicals, **22** and **47** (Scheme VII). It therefore became necessary to synthesize their reduction products, **51** and **48**, respectively, in order to have authentic materials for identification. The syntheses are shown in Scheme VIII, with details in the Experimental Section.

(13) (a) Beckwith, A. L. J.; Ingold, K. U. In *Free Radical Rearrangements*; de Mayo, P., Ed.; Academic Press: New York, 1980; pp 161–310. (b) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553.

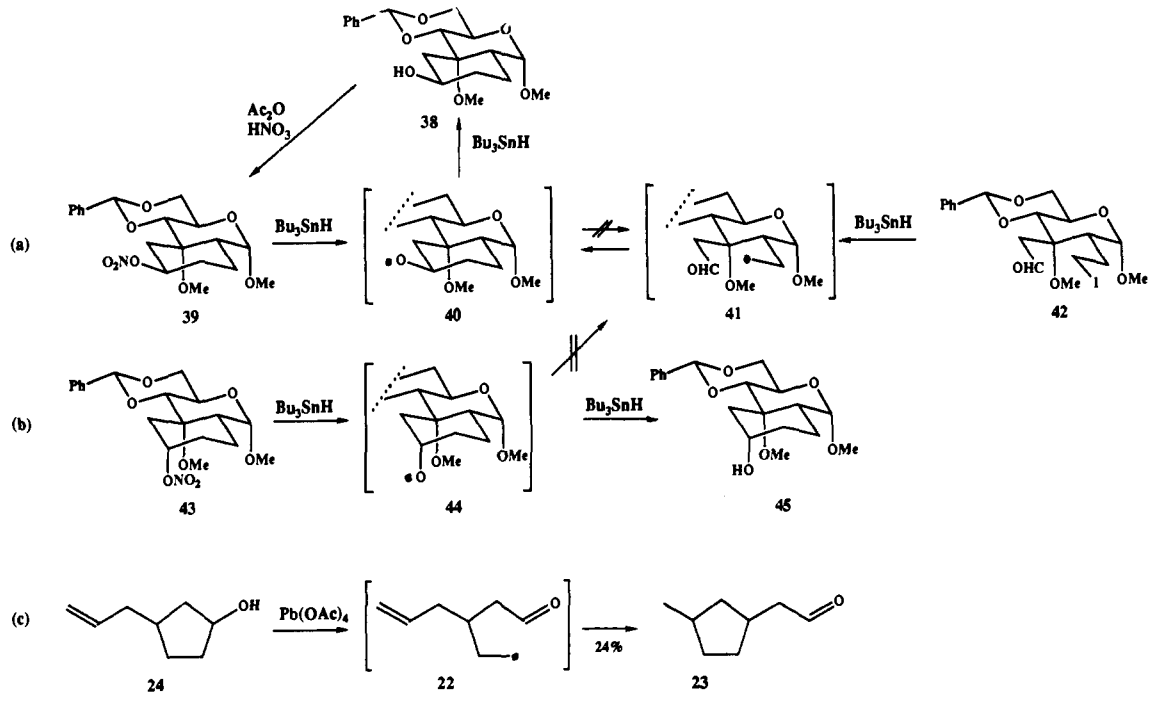
(14) (a) Sugawara, T.; Otter, B. A.; Ueda, T. *Tetrahedron Lett.* **1988**, *29*, 75. (b) Enholm, E. J.; Prasad, G. *Tetrahedron Lett.* **1989**, *30*, 4939. (c) Pereyre, M.; Quintard, J.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987; p 69.

(15) Carlson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.

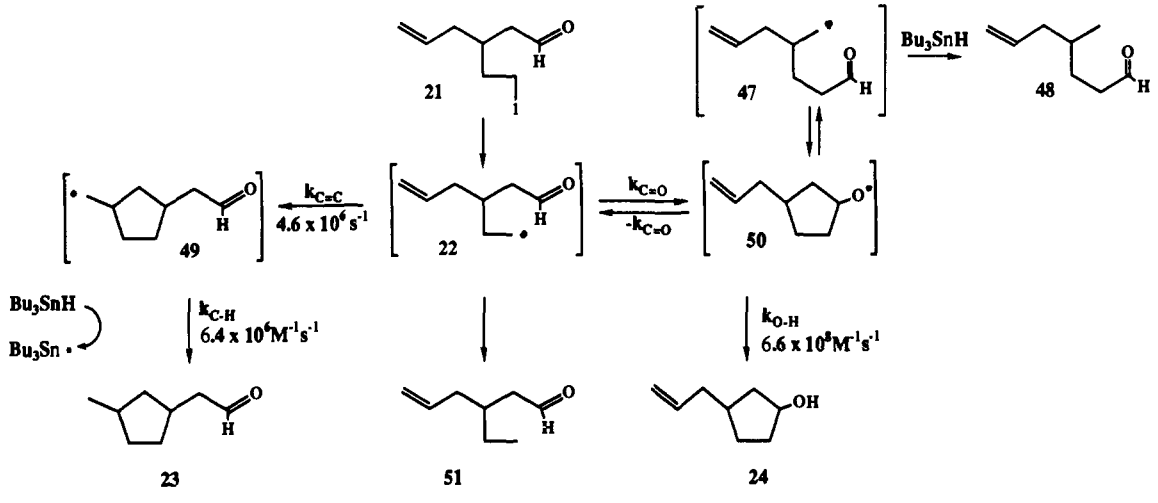
(16) (a) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron Lett.* **1985**, *41*, 3924. (b) Barton, D. H. R.; Toto, H.; Zard, S. Z. *Tetrahedron Lett.* **1985**, *41*, 5507. (c) Barton, D. H. R.; Crich, D.; Kretzschmar, G. *J. Chem. Soc., Perkin Trans. 1* **1986**, 39. (d) Barton, D. H. R.; Crich, D. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1603. (e) Barton, D. H. R.; Crich, D. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1613.

(17) Vite, G. D.; Fraser-Reid, B. *Synth. Commun.* **1988**, *18*, 1339.

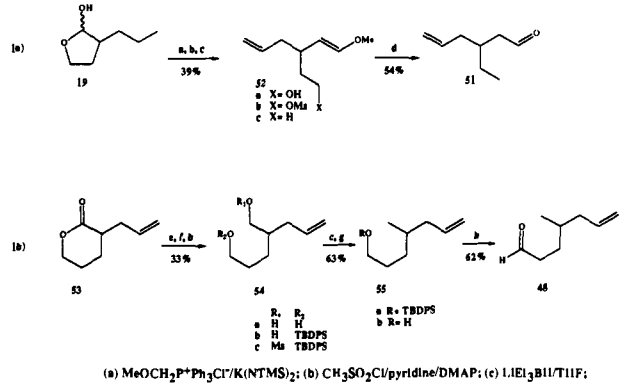
Scheme VI



Scheme VII



Scheme VIII



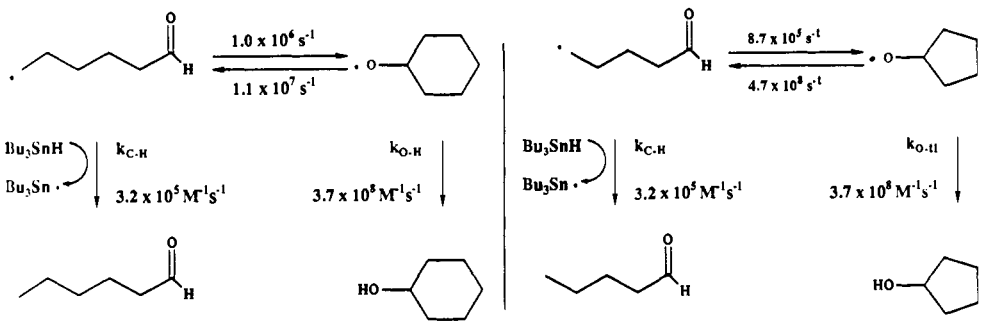
The question arose as to whether the extent of β-scission of cyclopentoxy radical was dependent on the concentration of added tri-*n*-butyltin hydride. Table Ia shows the relative amounts of **23**, **24**, and **51** formed from **21** with increasing concentrations of tri-*n*-butyltin hydride. Clearly the relative increase in formation of **24** as one proceeds down Table Ia provides evidence that reduction of the cyclopentoxy radical is highly dependent on the concentration of added tri-*n*-butyltin hydride. This is consistent

Table I. Variation in Relative Amounts of Products Formed from Treating **21** with Increasing Amounts of Bu_3SnH in Benzene at 80 °C[a]

(a)	21 (0.032 M)	Bu_3SnH	23	51	24
(i)	1	1 (0.032 M)	30	1	
(ii)	1	2 (0.064 M)	77	2.2	1
(iii)	1	2.5 (0.080 M)	13	0.6	1
(iv)	1	3 (0.096 M)	11	1.1	1
(v)	1	3.5 (0.112 M)	8.5	0.6	1
(vi)	1	4 (0.128 M)	8.3	0.4	1
(vii)	1	4.5 (0.144 M)	5.9	3.3	1
(b)	**21 (0.032 M)**	**Bu_3SnH**	**23**	**51**	**24 + 48**
(i)	1	1 (0.032 M)	30	1	
(ii)	1	2 (0.064 M)	25	1.4	1
(iii)	1	2.5 (0.080 M)	8.3	0.4	1
(iv)	1	3 (0.096 M)	6.2	0.7	1
(v)	1	3.5 (0.112 M)	6.0	0.4	1
(vi)	1	4 (0.128 M)	5.6	0.3	1
(vii)	1	4.5 (0.144 M)	4.8	2.7	1

[a] Product compositions were determined by GC/MS (see Experimental Section). Total yields were always in the range 82–85%.

Scheme IX



$$RX + Bu_3Sn\cdot \xrightarrow{25^\circ} R\cdot + Bu_3SnX$$

X = I $k = 4.3 \times 10^9\ M^{-1}s^{-1}$
X = Cl $k = 7.0 \times 10^3\ M^{-1}s^{-1}$

$$RCHO + Bu_3Ge\cdot \xrightarrow{25^\circ} RC'H\text{–}OGeBu_3$$

$k < 1 \times 10^5\ M^{-1}s^{-1}$

with the bimolecularity of the process. (The fact that comparable β-scission of the methyl radical **49** (to regenerate **22**) does not occur under the reaction conditions[13] means that the kinetics of the reductive step to give **49** → **23** is irrelevant.)

However, in view of the possibility of an alternative β-scission pathway leading to **48**, eq 1 had to be modified, as shown in eq 2, to incorporate the products from all of the competing pathways. Fom the same reason, the data in Table Ia had to be revised to that shown in Table Ib.

$$\frac{[23]}{[24] + [28]} = \frac{k_{(C=C)^5}}{k_{(C=O)^5}} \qquad (2)$$

$$\frac{4.8}{1} = \frac{4.6 \times 10^6\ s^{-1}}{k_{(C=O)^5}} \qquad (3)$$

$$k_{(C=O)^5} = 9.6 \times 10^5\ s^{-1}$$

Increasing the concentration of Bu_3SnH beyond the value in entry (vii) (Table I) led to complex mixtures giving evidence of addition of the tin radical to the aldehydo group.[14] Thus at the concentration of tri-*n*-butyltin hydride in entry (vii), the formation of **24** should be optimal, and hence the ratio of products in this entry was used to calculate the rate constant from the values[18] shown in eq 3. However although *optimal*, the concentration of **24** is not *maximal*, because the formation of **48** indicates that even at this high concentration of tri-*n*-butyltin hydride, some β-scission of the cyclopentoxy radical **50** is occurring, thereby depleting the amount of **24** formed. *As a result, the calculated rate, 9.6 × 10⁵ s⁻¹, must be regarded as a minimal value.*

This value is seen to be somewhat larger than the value of $8.7 \times 10^5\ s^{-1}$ obtained by Beckwith and Hay[10] (Scheme Ic). However, they had studied the 4-formylbutyl radical whereas our system, **22**, is a 3-alkyl analogue. In order to place this structural difference in the proper perspective, we note the difference in rate of ring closure for 5-hexenyl radicals and their 3-alkyl counterparts. From the results shown below it is seen that the rate of the latter is larger, which suggests that the rate-enhancing effect of a 3-alkyl substituent may be general.

Summary

The results in Scheme II had implied that cyclohexanol formation was more efficient than cyclopentanol formation. The above studies, coupled with the data of Beckwith and Hay for cyclization and β-scissions as shown in Scheme IX, indicate that there are two factors that contribute to this favorable result: (1) faster ring closure of the ω-formylpentyl radicals, and (2) slower β-scission of the cyclohexoxy radical. However, in spite of these favorable differences, the equilibria in Scheme IX make it clear that formation of the cycloalkanol requires the presence of a hydride donor. At the rate of the tri-*n*-butyltin hydride concentrations used, 0.05 M, the rate of hydrogen abstraction for an alkoxy radical is much gerater than the rate of β-scission, and therefore cycloalkanol formation is favored. On the contrary, the experimental conditions normally used for 5-hexenyl $(C{=}C)^5$ ring closure, which involves slow addition of the hydride donor by syringe pump, would be counterproductive when applied to $(C{=}O)^n$ cyclization reactions, for at such low concentrations of tri-*n*-butyltin hydride, competitive reactions can dominate.

In addition, an efficient method for radical generation must be employed. As also shown in Scheme IX, the cleavage of the carbon–iodine bond by the tri-*n*-butyltin radical is extremely rapid, but the cleavage of the carbon–chlorine bond is much slower. Thus use of a chloride as the radical source can result in competition from other reactions, such as the addition to the tri-*n*-butyltin radical directly to the aldehydo group[14] as depicted in Scheme IV. If the rate for the latter reaction is comparable to the known value for the closely related addition of tri-*n*-butylgermanium radical to an aldehyde[19] (Scheme IX), then the cyclizations of ω-cycloaldehydes would not be expected to proceed.

Experimental Section

General Procedures. Melting points were determined in capillary tubes and are uncorrected. ^1H NMR spectra were recorded at 300 MHz in $CDCl_3$ as solvent, and coupling constants were verified by homonuclear decoupling experiments. The progress of all reactions was monitored by thin-layer chromatography (TLC), which was performed on aluminum plates precoated with silica gel HF-254 (0.2-mm layers) containing a fluorescent indicator (Merck 5539). Detection was by UV (254 nm), followed by charring with sulfuric acid spray, or with a solution of ammonium molybdate(VI) tetrahydrate (12.5 g), and cerium sulfate hydrate (5.0 g) in 10% aqueous sulfuric acid (500 mL). Flash chromatography was performed by using Kieselgel 60 (230–400 mesh, Merck) silica gel, and petroleum ether/ethyl acetate mixtures as eluent.

Standard Procedures for Horner–Emmons Reactions. A 1 M solution of potassium *tert*-butoxide in *tert*-butyl alcohol (3.5 mL, 3 equiv) was added at 0 °C to a solution of triethyl phosphonoacetate (3.5 mM) in

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tetrahydrofuran (100 mL), and the resulting solution was stirred for 1 h. The ketone (1 mmol) in tetrahydrofuran (20 mL) was then added, and after stirring for 2 h, when TLC indicated completion, a saturated solution of ammonium chloride (10 mL) was added. The organic phase was separated and the aqueous phase extracted with ethyl acetate (3 × 20 mL), and after drying (Na_2SO_4), the solvent was removed, and the products were separated by flash chromatography (10–20% ethyl acetate/petroleum ether).

Standard Procedures for Dibal Reduction. Dibal (6 equiv) was added to a solution of the esters in toluene (50 mL) at −78 °C, and after stirring for 30 min, the excess reagent was quenched with methanol. Saturated solutions of sodium potassium tartrate (30 mL) and ammonium chloride (20 mL) were added, and the resulting two-phase system was stirred until both phases became clear (about 4 h). The organic phase was separated and the aqueous phase extracted with ethyl acetate (3 × 50 mL). The organic portions were combined and dried (Na_2SO_4), and after removal of the solvent, the products were separated by flash chromatography (10–20% ethyl acetate/petroleum ether).

Standard Procedures for the Claisen Rearrangement. A catalytic amount of mercuric trifluoroacetate was added to a solution of the allylic alcohol (1.98 mmol) in freshly distilled ethyl vinyl ether (50 mL) at room temperature, and after the reaction was complete (TLC), the solution was passed through silica gel with ethyl acetate (100 mL) containing a few drops of triethylamine. The solvent was removed and the residue was redissolved in benzonitrile (25 mL). After 2 h at reflux, the remaining vinyl ether was removed by treatment with 50 mL of an acetone/1 N hydrochloric acid mixture (10:1) under reflux for 1 h. The solution was then neutralized with sodium bicarbonate solution, and the aqueous solution was extracted with ethyl acetate. The organic phase was dried (Na_2SO_4), the solvent was removed, and the products were separated by flash chromatography (25% ethyl acetate/petroleum ether).

Standard Procedures for Iodination of Alcohols.[20] To a solution of the alcohol (1 mmol) in dry methylene chloride (50 mL) at 0 °C were added pyridine (0.31 mL, 3.84 mmol) and triphenylphosphine (301.8 mg). The solution was stirred for 30 min, after which iodine (267.9 mg) was added, and the solution was stirred overnight. A small amount of sodium bisulfite was added to react with the excess iodine, and 50 mL of a saturated solution of sodium bicarbonate was added to neutralize the solution. The organic phase was separated and the aqueous phase extracted with methylene chloride. The organic portions were combined and dried over sodium sulfate. After the solvent was removed, the products were separated by flash chromatography.

Standard Procedure for Free-Radical Reactions. A solution of tri-*n*-butyltin hydride (1.2 mM) and azodiisobutyronitrile (catalytic amount) in benzene was added by syringe to a refluxing solution of the iodides (1 mmol) in benzene (100 mL, dry, deoxygenated). After 1 h a 10% solution of ammonium hydroxide (50 mL) was added, and after stirring overnight the organic phase was separated and the aqueous phase extracted with ethyl ether. The organic phases were combined and dried (Na_2SO_4) and the products separated by flash chromatography (20% ethyl acetate/petroleum ether).

GC/MS Determination of Product Mixtures. Determination of reaction mixtures in Table I was carried out by GC/MS, on a 15 m × 0.20 μm capillary column with a 250 °C source and a 100 °C initial oven temperature. Following injection the oven temperature was increased at a rate of 20 °C/min. The peaks were identified by coinjection with purified or independently synthesized samples and comparison of their fragmentation patterns experienced under either EI or CI conditions. The peak areas used to calculate the product ratios were by use of computer software interfaced to the GC/MS. Each ratio given is the average value obtained from multiple reactions run under identical conditions.

1-(Formylmethyl)-2-(2′-iodoethyl)-1-vinylcyclohexane (7b). 2-[(Ethoxycarbonyl)methyl]cyclohexanone (**4**) (prepared from cyclohexanone by alkylation of pyrrolidine enamine[20] with ethyl bromoacetate) was converted into the iodo aldehyde **7b** as outlined in Scheme II, by using the standard procedures. The following intermediates were isolated and characterized. For **5** (56% yield), **5**(*E*): R_f 0.18 (5% ethyl acetate/petroleum ether); IR (neat) 1705, 1720, 3050 cm^{-1}; ^1H NMR δ 5.55 (s, 1 H, H-1′), 4.17–4.10 (q, 4 H, ethyl, J_{ethyl} = 6.8 Hz), 3.28–3.19 (m, 1 H, H-2), 2.77–2.65 (m, 1 H, H-6), 2.61–2.53 (dd, 1 H, H-3′, $J_{3-3'}$ = 7.8 Hz, $J_{3'-2}$ = 15.1 Hz), 2.56–2.45 (m, 1 H, H-6), 2.39–2.32 (dd, 1 H, H-3′), 1.91–1.89 (m, 1 H, H-3), 1.78–1.66 (m, 2 H, H-4), 1.63–1.52 (m 2 H, H-5), 1.42–1.32 (m, 1 H, H-3), 1.29–1.23 (t, 6 H, ethyl). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 65.93; H, 8.79. **5**(*Z*): R_f 0.11 (5% ethyl acetate/petroleum ether); IR (neat) 1705, 1725, 3050 cm^{-1}; ^1H NMR δ 5.63 (s, 1 H, H-1′), 4.45–4.35 (m, 1 H, H-2), 4.18–4.08 (q, 4 H, ethyl, J_{ethyl} = 7.1 Hz), 2.56–2.50 (d, 2 H, H-3′, $J_{3'-3'}$ = 7.5 Hz), 2.40–2.28 (m, 1 H, H-6), 2.95–2.85 (m, 1 H, H-3), 2.16–2.06 (m, 1 H, H-6), 1.80–2.74 (m, 1 H, H-3), 1.66–1.54 (m, 3 H, H-4, H-5), 1.48–1.32 (m, 1 H, H-5), 1.30–1.20 (t, 6 H, ethyl, J_{ethyl} = 7.1 Hz). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 65.99; H, 8.93. For **6** (90% yield), **6**(*Z*): R_f 0.10 (50% ethyl acetate/petroleum ether); ^1H NMR δ 5.41–5.32 (t, 1 H, H-1′, $J_{1'-2'}$ = 7.2 Hz), 4.18–4.12 (d, 2 H, H-2′, $J_{1'-2'}$ = 7.2 Hz), 3.68–3.62 (t, 2 H, H-2′, $J_{1'-2'}$ = 6.6 Hz), 2.31–2.20 (m, 1 H, H-2), 2.22–2.12 (m, 1 H, H-1), 1.78–1.35 (m, 10 H, H-3, H-4, H-5, H-6, H-1′). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.81; H, 10.60. **6**(*E*): R_f 0.16 (50% ethyl acetate/petroleum ether); ^1H NMR δ 5.62–5.52 (dt, 1 H, H-1′, $J_{1'-2'}$ = 6.7 Hz, $J_{1'-2'}$ = 8.7), 4.34–4.25 (dd, 1 H, H-2′, $J_{1'-2'}$ = 8.7 Hz), 3.96–3.88 (dd, 1 H, H-2′, $J_{1'-2'}$ = 6.7 Hz, $J_{2'-2'}$ = 11.5 Hz), 3.71–3.60 (m, 1 H, H-2′), 3.58–3.50 (m, 1 H, H-4′), 3.16–3.05 (m, 1 H, H-2), 2.80–2.50 (s, 2 H, OH) 2.23–2.10 (m, 1 H, H-6), 2.06–1.75 (m, 3 H, H-6, H-3′), 1.68–1.50 (m, 5 H, H -3, H-4, H-5), 1.38–1.22 (m, 1 H, H-4). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55: H, 10.66. Found: C, 70.44; H, 10.46. For **7a** (49% yield): R_f 0.16 (50% ethyl acetate/petroleum ether); IR (neat) 1720, 3075, 3400 cm^{-1}; ^1H NMR δ 9.76 (s, 1 H, CHO), 6.11–5.99 (dd, 1 H, H-7, $J_{7,8}$ = 10.0 Hz, $J_{7,8}$ = 15.7 Hz), 5.25–5.19 (d, 1 H, H-8, $J_{7,8}$ = 10.0 Hz), 5.12–5.06 (d, 1 H, H-8, $J_{7,8}$ = 15.7 Hz), 3.98–3.88 (dd, 1 H, H-12, $J_{11,12}$ = 12.1 Hz, $J_{12,12}$ = 12.6 Hz), 3.61–3.52 (dd, 1 H, H-12, $J_{11,12}$ = 12.1 Hz, $J_{12,12}$ = 12.6 Hz), 2.83–2.81 (s, 2 H, H-9), 1.89–1.08 (m, 11 H, H-2, H-3, H-4, H-4, H-5, H-6, H-11). Anal. Calcd for $C_{12}H_{20}O_2$: C, 70.55; H, 10.66 Found: C, 70.81; H, 10.60 For **7b** (75% yield): R_f 0.34 (15% ethyl acetate/petroleum ether); IR (neat) 1720, 3050, 3075 cm^{-1}; ^1H NMR δ 9.72–9.70 (dd, 1 H, CHO, $J_{9,10}$ = 4.2 Hz, $J_{9,10}$ = 3.7 Hz), 5.97–5.87 (dd, 1 H, H-7, $J_{7,8}$ = 17.7 Hz, $J_{7,8}$ = 11.1 Hz), 5.21–5.17 (d, 1 H, H-8, $J_{7,8}$ = 17.7 Hz), 3.29–3.21 (dt, 1 H, H-12, $J_{11,12}$ = 7.3 Hz, $J_{12,12}$ = 11.4 Hz), 3.03–2.94 (dt, 1 H, H-12, $J_{11,12}$ = 7.3 Hz, $J_{12,12}$ = 11.4 Hz), 2.53–2.45 (dd, 1 H, H-9, $J_{9,9}$ = 14.9 Hz, $J_{9,10}$ = 4.2 Hz), 2.36–2.29 (dd, 1 H, H-9, $J_{9,9}$ = 14.9 Hz, $J_{9,10}$ = 3.7 Hz), 2.01–1.76 (m, 2 H, H-11), 1.66–1.06 (m, 9 H, H-2, H-3, H-4, H-5, H-6). Anal. Calcd for $C_{12}H_{19}IO$: C, 47.07; H, 6.25. Found: C, 47.16: H, 6.20.

Tricyclo[6.4.0.0^{1,5}]dodecan-3-ol (9) and 1-Vinylbicyclo[4.4.0]decan-3-ol (10). The mixture of diastereomers, **7b** (418 mg), was subjected to the standard procedures for free-radical reactions. The alcohol **9** (41.3 mg) and the alcohol **10** (123.8 mg) were isolated as clear liquids for an overall yield of 73% (165.1 mg, 0.92 mmol). For **9**: R_f 0.18 (50% ethyl acetate/petroleum ether); ^1H NMR δ 4.32–4.22 (m, 1 H, H-3), 2.24–2.15 (m, 2 H, H-5, H-8), 1.84–0.98 (m, 17 H, H-2, H-4, H-6, H-7, H-9, H-10, H-11, H-12, OH). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.72; H, 11.04. For **10**: R_f 0.15 (50% ethyl acetate/petroleum ether); ^1H NMR δ 5.98–5.61 (dd, 1 H, H-11, $J_{11,12}$ = 11.3 Hz, $J_{11,12}$ = 17.9 Hz), 5.16–4.95 (dd, 1 H, H-12, $J_{12,12}$ = 1.4 Hz, $J_{11,12}$ = 11.3 Hz), 5.09–4.92 (dd, 1 H, H-12, $J_{12,12}$ = 1.4 Hz, $J_{11,12}$ = 17.9 Hz), 3.85–3.63 (m, 1 H, H-3), 1.98–1.88 (m, 2 H, H-2), 1.71–1.51 (m, 3 H, H-4, H-6), 1.39–1.01 (m, 11 H, H-5, H-7, H-8, H-9, H-10, OH). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.81; H, 11.10.

6-Iodo-3-phenyl-3-vinylhexanal (15b). Ethyl 3-benzoylpropionate (**12**) was converted into the title compound using the standard procedures via the intermediates shown in Scheme IIb, which were isolated and characterized as follows. For **13** (45% yield), **13**(*E*): R_f 0.33 (50% ethyl acetate/petroleum ether); IR (neat) 1715, 3050 cm^{-1}; ^1H NMR δ 7.39–7.12 (m, 5 H, Ph), 5.90 (s, 1 H, H-2), 4.15–4.08 (q, 2 H, ethyl, J_{ethyl} = 7.1 Hz), 4.02–3.94 (q, 2 H, ethyl, J_{ethyl} = 7.1 Hz), 2.80–2.74 (t, 2 H, H-4, $J_{4,5}$ = 7.2 Hz), 2.42–2.36 (t, 2 H, H-5, $J_{4,5}$ = 7.2 Hz), 2.60–1.21 (t, 3 H, ethyl, J_{ethyl} = 7.1 Hz), 1.08–1.03 (t, 3 H, ethyl, J_{ethyl} = 7.1 Hz). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55: H, 7.29. Found: C, 69.57; H, 7.30. **13**(*Z*): R_f 0.45 (50% ethyl acetate/petroleum ether); IR (neat) 1705, 1715, 3050 cm^{-1}; ^1H NMR δ 7.46–7.35 (m, 5 H, phenyl), 6.07 (s, 1 H, H-2), 4.26–4.18 (q, 2 H, ethyl, J_{ethyl} = 7.1 Hz), 4.09–4.02 (q, 2 H, ethyl, J_{ethyl} = 7.1 Hz), 3.44–3.37 (t, 2 H, H-4, $J_{4,5}$ = 7.8 Hz), 2.48–2.42 (t, 2 H, H-5, $J_{4,5}$ = 7.8 Hz), 1.34–1.29 (t, 3 H, ethyl, J_{ethyl} = 7.1 Hz), 1.23–1.18 (t, 3 H, ethyl, J_{ethyl} = 7.1 Hz). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.29. Found: C, 69.35; H, 7.36. For **14** (81% yield), **14**(*Z*): R_f 0.14 (50% ethyl acetate/petroleum ether); ^1H NMR δ 7.46–7.18 (m, 5 H, phenyl), 5.80–5.75 (t, 1 H, H-2, $J_{1,2}$ = 7.0 Hz), 4.10–4.03 (d, 2 H, H-1, $J_{1,2}$ = 7.0 Hz), 3.65–3.62 (t, 2 H, H-6, $J_{5,6}$ = 7.2 Hz), 2.48–2.45 (t, 2 H, H-4, $J_{4,5}$ = 6.5 Hz), 1.70–1.60 (tt, 2 H, H-5, $J_{5,6}$ = 7.2 Hz, $J_{4,5}$ = 6.5 Hz), 1.70–1.50 (s, 2 H, OH). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.73; H, 8.20. **14**(*E*): R_f 0.18 (50% ethyl acetate/petroleum ether); ^1H NMR δ 7.48–7.06 (m, 5 H, phenyl), 6.10–6.05 (t, 1 H, H-2, $J_{1,2}$ = 7.4 Hz), 4.37–4.35 (d, 2 H, H-1, $J_{1,2}$ = 7.4 Hz), 3.62–3.59 (t, 2 H, H-6, $J_{5,6}$ = 5.7 Hz), 2.90–2.30 (s, 2 H, OH), 2.83–2.79 (t, 2 H, H-4, $J_{4,5}$ = 6.9 Hz), 1.70–1.61 (tt, 2 H, H-5, $J_{5,36}$ = 5.7 Hz, $J_{4,5}$ = 6.9 Hz). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.73; H, 8.20. For **15a** (38% yield): R_f 0.32 (50% ethyl

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acetate/petroleum ether): IR (neat) 1720, 3050, 3100, 3400 cm^{-1}; ^1H NMR δ 9.54–9.52 (t, 1 H, H-1, $J_{1,2}$ = 2.9 Hz), 7.40–7.20 (m, 5 H, phenyl), 6.17–6.07 (dd, 1 H, H-7, $J_{7,8}$ = 10.9 Hz, $J_{7,8}$ = 17.6 Hz), 5.35–5.31 (d, 1 H, H-8, $J_{7,8}$ = 10.9 Hz), 5.21–5.15 (d, 1 H, H-6 = $J_{5,6}$ = 6.1 Hz), 2.84–2.83 (d, 2 H, H-2 $J_{1,2}$ = 2.9 Hz), 1.99–1.81 (t, 2 H, H-4, $J_{4,5}$ = 6.4 Hz), 1.50–1.35 (tt, 2 H, H-5, $J_{4,5}$ = 6.4 Hz, $J_{5,6}$ = 6.1 Hz); MS *m/e* for $C_{14}H_{18}O_2 + NH_4$ = 236 amu. For **15b** (63% yield): R_f 0.34 (15% ethyl acetate/petroleum ether); IR (neat) 1720, 3050, 3100 cm^{-1}, ^1H NMR δ 9.53–9.51 (t, 1 H, CHO, $J_{1,2}$ = 2.9 Hz), 7.39–7.21 (m, 5 H, phenyl) 6.15–6.06 (dd, 1 H, H-7, $J_{7,8}$ = 10.9 Hz, $J_{7,8}$ = 17.6 Hz), 5.36–5.32 (d, 1 H, H-8, $J_{7,8}$ = 10.9 Hz), 5.21–5.15 (d, 1 H, H-8, $J_{7,8}$ = 17.6 Hz), 3.12–3.08 (t, 2 H, H-6, $J_{5,6}$ = 6.7 Hz), 2.82–2.81 (d, 2 H, H-2, $J_{1,2}$ = 2.9 Hz), 2.04–1.94 (m, 2 H, H-4), 1.72–1.61 (m, 2 H, H-5, $J_{5,6}$ = 6.7 Hz). Anal. Calcd for $C_{14}H_{17}IO$: C, 51.24; H, 5.22. Found: C, 51.27; H, 5.15.

3-Phenyl-3-vinylcyclohexanol (17). Iodide **15b** (31.6 mg) was subjected to the standard procedure for free-radical reactions. The isomeric mixture of alcohols **17** was obtained as a clear viscous liquid (16.9 mg, 0.08 mmol, 85% yield): R_f 0.45 (50% ethyl acetate/petroleum ether); ^1H NMR δ 7.38–7.12 (m, 1 H, phenyl), 5.90–5.72 (dd, 1 H, H-7, $J_{7,8}$ = 10.6 Hz, $J_{7,8}$ = 17.4 Hz), 5.24–4.82 (d, 1 H, H-8, $J_{7,8}$ = 10.6 Hz, $J_{8,8}$ = 1.0 Hz), 5.12–4.66 (d, 1 H, H-8, $J_{7,8}$ = 17.4 Hz, $J_{8,8}$ = 1.0 Hz), 4.22–3.60 (m, 1 H, H-3), 2.70–2.21 (m, 2 H, H-2), 1.95–1.10 (m, 7 H, H-4, H-5, H-6, OH). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.88; H, 9.06.

2-Allyl-γ-butyrolactone (18b). *n*-Butyllithium (2.2 M in hexane, 31.7 mL, 69.7 mmol) was added to a solution of distilled diisopropylamine (9.79 mL, 69.7 mmol) in dry tetrahydrofuran (500 mL) at 0 °C, and then cooled to −78 °C. A solution of the lactone **18a** (5.0 g, 58.1 mmol) in tetrahydrofuran (50 mL) was added dropwise to the reaction solution, and after 30 min hexamethylphosphoramide (15.1 mL, 87.1 mmol) followed by allyl iodide (5.83 mL, 63.9 mmol) was added by way of a syringe. The reaction was allowed to stir for 2 h at −78 °C, after which the reaction was quenched by the addition of 250 mL of a saturated solution of ammonium chloride and worked up in the usual manner. Flash chromatography (20% ethyl acetae/petroleum ether) afforded **18b** as a yellow liquid (5.2 g, 71% yield): R_f 0.56 (50% ethyl acetate/petroleum ether); IR (neat) 1740, 3075 cm^{-1}; ^1H NMR δ 5.84–5.68 (m, 1 H, H-6, $J_{6,7}$ = 6.6 Hz), 5.15–5.05 (dd, 2 H, H-7, $J_{7,7}$ = 9.2 Hz, $J_{6,7}$ = 6.6 Hz), 4.36–4.12 (m, 2 H, H-4, $J_{5,6}$ = 6.8 Hz), 2.68–2.52 (m, 2 H, H-4), 2.40–2.16 (m, 1 H, H-2), 2.04–1.90 (m, 2 H, H-3). Anal. Calcd for $C_7H_{10}O_2$: C, 66.65: H, 7.99 Found: C, 66.41; H, 8.01.

Lactol of 2-Allyl-4-hydroxybutanol (19). Lactone **18b** was reduced with Dibal in 80% yield by use of the standard procedures. For **19**: R_f 0.40 (50% ethyl acetate/petroleum ether); IR (neat) 1750, 3075, 3400 cm^{-1}; ^1H NMR δ 5.89–5.69 (m, 1 H, H-6), 5.32–5.29 (t, 1 H, H-1, $J_{1,2}$ = 3.8 Hz), 5.18–5.17 (d, 1 H, H-1, $J_{1,2}$ = 3.1 Hz), 5.10–4.97 (m, 2 H, H-7), 4.11–3.75 (m, 2 H, H-4), 3.55–3.46 (s, 1 H, OH), 3.39–3.29 (s, 1 H, OH), 2.38–1.90 (m, 6 H, H-3, H-4, H-5), 1.82–1.50 (m, 1 H, H-2, $J_{1,2}$ = 3.8 Hz, $J_{1,2}$ = 3.1 Hz). Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.50; H, 9.51.

4-(2′-Iodoethyl)-6-(tetrahydropyranoxy)-1,5-hexadiene (20b). Potassium bis(trimethylsilyl)amide (0.5 M in toluene, 40.4 mL, 20.2 mmol) was added to a suspension of [(tetrahydropyranoxy)methyl)]triphenylphosphonium chloride (10.0 g, 24.2 mmol) in dry tetrahydrofuran (500 mL) at −78 °C, and after 1 h, a solution of the lactol **19** (1033.0 mg, 8.1 mmol) was added to tetrahydrofuran (15 mL). The reaction was allowed to warm to room temperature and was stirred for an additional 2 h. The reaction was quenched by the addition of 250 mL of a saturated solution of ammonium chloride and was worked up in the usual way. Flash chromatography (10% ethyl acetate/petroleum ether) afforded **20a** as mixture of alcohols (0.57 mg, 31% yield), separable into two groups of different R_f. *Less polar isomers*: R_f 0.44 (50% ethyl acetate/petroleum ether). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.13; H, 9.57. *More polar isomers*: R_f 0.35 (50% ethyl acetate/petroleum ether). Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.92; H, 9.60. Iodinolysis using the standard procedures afforded **20b**, also as a mixture of isomers of different R_f in 72% yield. *Less polar isomers*: R_f 0.64 (25% ethyl acetate/petroleum ether). Anal. Calcd for $C_{13}H_{21}IO_2$: C, 46.44; H, 6.30. Found: C, 46.55; H, 6.21. *More polar isomers*: R_f 0.53 (25% ethyl acetate/petroleum ether). Anal. Calcd for $C_{13}H_{21}IO_2$: C, 46.44: H, 6.30. Found: C, 45.99; H, 6.24.

3-(2′-Iodoethyl)-5-hexenal (21). Perchloric acid (35% solution, 0.5 mL) was added to a solution of the iodides **20b** (24.0 mg, 0.07 mmol) in ethyl ether (12 mL) at room temperature. The reaction was complete after 3 h (TLC), and the acid was then neutralized by the addition of 10 mL of a saturated solution of sodium bicarbonate. Standard workup followed by flash chromatography (10% ethyl acetate/petroleum ether) afforded aldehyde **21** as a clear liquid (15.1 mg, 86% yield). (Note: Small amounts of phosphonium products contaminated the separated product, which made it unsuitable for the intended reactions. Therefore it was necessary to reduce the aldehyde with Dibal, and reoxidize the purified alcohol with pyridinium chlorochromate): R_f 0.24 (10% ethyl acetate/petroleum ether); IR (neat) 1720, 3050 cm^{-1}; ^1H NMR δ 9.74–9.73 (t, 1 H, CHO, $J_{1,2}$ = 1.9 Hz), 5.76–5.62 (m, 1 H, H-5, $J_{5,6}$ = 1.3 Hz), 5.07–5.00 (m, 2 H, H-6, $J_{6,6}$ = 11.0 Hz, $J_{5,6}$ = 1.3 Hz), 3.18–3.14 (t, 2 H, H-8, $J_{7,8}$ = 7.4 Hz), 2.47–2.29 (m, 2 H, H-2, $J_{1,2}$ = 1.9 Hz), 2.24–1.98 (m, 3 H, H-4, H-3), 1.95–1.76 (m, 2 H, H-7, $J_{7,8}$ = 7.4 Hz). Anal. Calcd for $C_8H_{13}IO$: C, 38.12: H, 5.20. Found: C, 38.36; H, 5.42.

1-(Formylmethyl)-3-methylcyclopentane (23) and 3-Allylcyclopentanol (24). The iodo aldehyde **21** (50.2 mg, 0.20 mmol) was subjected to the standard procedure for free-radical reactions. Standard workup followed by flash chromatography (20% ethyl acetate/petroleum ether) afforded a mixture of the aldehyde **23** and alcohol **24** (20.9 mg, 84% total yield). Pure samples were obtained by GC with retention times as follows: 3-allylcyclopentanol (**24**) 2.704 min, and 1-(formylmethyl)-3-methylcyclopentane (**23**) 1.899 min. For **24**: R_f 0.46 (50% ethyl acetate/petroleum ether); IR (neat) 3060, 3300 cm^{-1}; ^1H NMR δ 5.85–5.70 (m, 1 H, H-7, $J_{7,8}$ = 10.2 Hz), 5.04–4.91 (dd, 1 H, H-8, $J_{7,8}$ = 10.2 Hz), 4.34–4.24 (m, 1 H, H-1), 2.44–2.10 (m, 1 H, H-3), 2.20–2.00 (m, 2 H, H-6), 2.05–0.80 (m, 6 H, H-2, H-4, H-5); HRMS calcd for $C_8H_{14}O + NH_4$ 144.1388, found 144.1386. For **23**: R_f 0.69 (50% ethyl acetate/petroleum ether); IR (neat) 1720 cm^{-1}; ^1H NMR δ 9.72–9.71 (t, 1 H, CHO, $J_{CHO,6}$ = 2.1 Hz), 2.45–2.36 (dd, 2 H, H-6, $J_{CHO,6}$ = 2.1 Hz, $J_{1,6}$ = 7.4 Hz), 2.40–2.22 (m, 1 H, H-1, $J_{1,6}$ = 7.4 Hz), 2.05–1.68 (m, 2 H, H-2), 1.50–1.35 (m, 1 H, H-3, $J_{3,methyl}$ = 6.6 Hz), 1.32–1.00 (m, 4 H, H-4, H-5), 0.98–0.79 (d, 3 H, methyl, $J_{methyl,3}$ = 6.6 Hz); HRMS calcd for $C_8H_{14}O + NH_4$ 144.1388, found 144.1385.

Reaction of 3-Allylcyclopentanol (24) with Lead Tetraacetate. Compound **24** (22.4 mg, 0.18 mmol) was dissolved in dry deoxygenated cyclohexane (5.0 mL). Lead tetraacetate (319.0 mg, 0.72 mmol) was then added and the solution heated to reflux for 3 h. The solution was then filtered and the solvent removed. The product mixture, separated by flash chromatography (10% ethyl acetate/petroleum ether), gave the aldehyde **23** (4.7 mg, 22% yield).

4-Phenyl-4-vinyl-6-hepten-1-ol (25a). Potassium bis(trimethylsilyl)-amide (0.5 M in tetrahydrofuran, 4.7 mL, 2.4 mmol) was added to a solution of methyltriphenylphosphonium bromide (1.7 g, 13.3 mmol) in tetrahydrofuran (100 mL) at −78 °C. After stirring for 30 min, the alcohol **15a** (103 mg, 0.47 mmol) in 5 mL of tetrahydrofuran was added, and after stirring for 1 h, the reaction was complete. The reaction was quenched by the addition of 100 mL of a saturated solution of ammonium chloride and worked up in the usual manner. Flash chromatography (25% ethyl acetate/petroleum ether) afforded diene **25a** as a viscous liquid (50.9 mg, 51% yield): R_f 0.26 (50% ethyl acetate/petroleum ether); ^1H NMR δ 7.29–7.11 (m, 5 H, phenyl), 5.93–5.83 (dd, 1 H, H-8, $J_{8,8}$ = 10.8 Hz, $J_{8,9}$ = 17.1 Hz), 5.61–5.47 (m, 1 H, H-6), 5.18–5.15 (d, 1 H, H-9, $J_{8,9}$ = 10.8 Hz), 5.09–5.02 (d, 1 H, H-9, $J_{8,9}$ = 17.1 Hz), 4.99–4.90 (m, 2 H, H-7), 3.54–3.49 (t, 2 H, H-1, $J_{1,2}$ = 6.5 Hz), 2.52–2.48 (d, 2 H, H-5, $J_{5,6}$ = 7.1 Hz), 1.82–1.64 (m, 2 H, H-3), 1.45–1.22 (m, 2 H, H-2), 1.30–1.20 (s, 1 H, OH). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.15; H, 9.47.

1-Iodo-4-phenyl-4-vinyl-6-heptene (25b). Compound **25a** (49 mg, 0.23 mmol) was subjected to iodinolysis using the standard procedure. Flash chromatography (20% ethyl acetate/petroleum ether) afforded the iodide **25b** as a clear viscous liquid (47.8 mg, 65% yield): R_f 0.55 (50% ethyl acetate/petroleum ether); ^1H NMR δ 7.30–7.10 (m, 5 H, phenyl), 5.93–5.82 (dd, 1 H, H-8), 5.60–5.45 (m, 1 H, H-6, $J_{5,6}$ = 7.1 Hz, $J_{6,7}$ = 10.1 Hz, $J_{6,7}$ = 17.6 Hz), 5.20–5.16 (d, 1 H, H-7, $J_{6,7}$ = 10.1 Hz), 5.09–5.03 (d, 1 H, H-7, $J_{6,7}$ = 17.6 Hz), 4.98–4.92 (m, 2 H, H-9), 3.08–3.02 (t, 2 H, H-5, $J_{5,6}$ = 7.1 Hz), 1.90–1.70 (m, 2 H, H-3), 1.68–1.50 (m, 2 H, H-2). Anal. Calcd for $C_{15}H_{19}I$: C, 55.23: H, 5.97. Found: C, 55.20; H, 5.93.

3-Methyl-1-phenylbicyclo[3.3.0]octane (31). Iodide **25b** (35.9 mg, 0.11 mmol) was subjected to the standard procedure for free-radical reactions. After flash chromatography (100% petroleum ether), the products were detected by thin-layer chromatography (100% petroleum ether) using a H_2SO_4–formaldehyde (36% in water) solution (10:1) as the developing agent. The material was shown by ^1H NMR to consist of two products, **31** (15.0 mg, 68% yield) and **32** (6.2 mg, 30% yield). Repeated column chromatography afforded pure samples of both isomers. For **31**: R_f 0.59 (100% petroleum ether); ^1H NMR δ 7.35–7.10 (m, 5 H, phenyl), 2.81–2.70 (m, 1 H, H-5), 2.25–2.15 (m, 1 H, H-3, $J_{3,methyl}$ = 7.1 Hz), 2.25–1.20 (m, 10 H, H-2, H-4, H-6, H-7, H-8), 1.02–0.82 (d, 3 H, H-9 (methyl), $J_{3,methyl}$ = 7.1 Hz). Anal. Calcd for $C_{15}H_{20}$: C, 94.18; H, 5.92. Found: C, 94.18; H, 5.84. For **32**: R_f 0.59 (100% petroleum ether); ^1H NMR δ 7.35–7.10 (m, 5 H, phenyl), 5.60–5.45 (m, 1 H, H-8, $J_{7,8}$ = 7.0 Hz, $J_{8,9}$ = 10.1 Hz, $J_{8,9}$ = 17.6 Hz), 5.20–5.16 (dd, 2 H, H-9, $J_{8,9}$ = 10.1 Hz, $J_{8,9}$ = 17.6 Hz), 2.81–2.70 (m, 1 H, H-5), 2.30–2.26 (d, 2 H, H-7,

$J_{7,8}$ = 7.0 Hz), 2.25–2.15 (m, 1 H, H-2, $J_{2,6}$ = 7.1 Hz), 2.25–1.20 (m, 6 H, H-3, H-4, H-5), 1.02–0.82 (d, 3 H, H-6 (methyl), $J_{2,6}$ = 7.1 Hz); HRMS calcd for $C_{15}H_{20}$ 200.1565, found 200.1568.

6-Formyl-5-phenyl-5-vinylhexanoic Acid Ethylene Acetal (33). Ethylene glycol (2 mL, excess) and a catalytic amount of *p*-toluenesulfonic acid was added to a solution of the aldehyde **15b** (1.14 g, 3.48 mmol) in dry benzene (50 mL). The solution was heated to reflux and the waer formed was continuously removed by means of a Dean–Stark apparatus. After 12 h the solution was allowed to cool to room temperature, and the acid was neutralized by the addition of 50 mL of a saturated solution of sodium bicarbonate. After standard workup, the product mixture was redissolved in dry methanol (50 mL) and treated with sodium borohydride (50 mg) to destroy any residual aldehyde, which was otherwise inseparable from the product acetal. The purified acetal (1.229 mg, 95% yield) was dissolved in dimethyl sulfoxide (10 mL) and heated with sodium cyanide (0.173 mg, 3.5 mmol) in an oil bath at 120 °C for 3 h. After cooling to room temperature, ethyl ether (20 mL), brine (20 mL), and ferrous chloride (100 mg, to react with the remaining cyanide) were added and the two-phase mixture was stirred for 2 h. Standard workup gave the nitrile as a clear viscous liquid (707.1 mg, 80% yield), a portion of which (199.3 mg, 0.78 mmol) was dissolved in 25 mL of a potassium hydroxide (30%)/hydrogen peroxide (30%) solution (6:1) and warmed to 40 °C for 1 h and then to 111 °C for 3 h, during which time ammonia was released from the solution. After cooling to room temperature, the solution was neutralized (1 N HCl) and standard workup gave the acid **33** as a white viscous liquid (155.9 mg, 69% yield): R_f 0.16 (75% ethyl acetate/petroleum ether); IR (neat) 1700, 2890, 3100, 3300 cm^{-1}; ^1H NMR δ 7.30–7.12 (m, 5 H, phenyl), 5.97–5.87 (dd, 1 H, H-8, $J_{8,9}$ = 10.9 Hz, $J_{8,9}$ = 17.6 Hz), 5.23–5.20 (dd, 1 H, H-9, $J_{8,9}$ = 10.9 Hz, $J_{9,9}$ = 0.7 Hz), 5.17–5.11 (dd, 1 H, H-9, $J_{8,9}$ = 17.6 Hz, $J_{9,9}$ = 0.7 Hz), 4.62–4.59 (t, 2 H, H-7, $J_{6,7}$ = 4.5 Hz), 3.92–3.85 (m, 2 H, ethylene acetal), 3.76–3.68 (m, 2 H, ethylene acetal), 2.32–2.25 (t, 2 H, H-2, $J_{2,3}$ = 5.6 Hz), 2.19–2.17 (t, 2 H, H-6, $J_{6,7}$ = 4.5 Hz), 2.02–1.78 (m, 2 H, H-4), 1.60–1.57 (m, 2 H, H-3, $J_{2,3}$ = 5.6 Hz). Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.15; H, 7.77.

6-Formyl-5-phenyl-5-vinylhexanoic Acid (34a). Aqueous perchloric acid (10%) was added to a solution of the acetal **33** (155.9 mg, 0.54 mmol) in ethyl ether (50 mL). After 2 h at room temperature, the acid was neutralized by the slow addition of 50 mL of a saturated solution of sodium bicarbonate. Standard workup followed by flash chromatography (25% ethyl acetate/petroleum ether) gave the aldehyde **34a** as an oil (188.9 mg, 90% yield): R_f 0.16 (75% ethyl acetate/petroleum ether); IR (neat) 1700, 3050, 3080, 3300 cm^{-1}, ^1H NMR δ 9.15–9.50 (t, 1 H, H-7, $J_{6,7}$ = 2.8 Hz), 7.38–7.20 (m, 5 H, phenyl), 6.14–6.05 (dd, 1 H, H-8, $J_{8,9}$ = 8.9 Hz, $J_{8,9}$ = 17.6 Hz), 5.34–5.30 (dd, 1 H, H-9, $J_{8,9}$ = 8.9 Hz, $J_{8,9}$ = 17.6 Hz), 2.81–2.80 (t, 2 H, H-6, $J_{6,7}$ = 2.8 Hz), 2.32–2.27 (t, 2 H, H-2, $J_{2,3}$ = 7.3 Hz), 1.98–1.80 (m, 2 H, H-4), 1.55–1.42 (m, 2 H, H-3, $J_{2,3}$ = 7.3 Hz). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.92; H, 7.17.

6-Formyl-5-phenyl-5-vinylhexanoic Acid, 2,3-Dihydro-4-methyl-2-thioxothiazol-3-yl Ester (34b). Oxalyl chloride (2.5 mL) was added to a solution of the acid **34a** (188.9 mg, 0.48 mmol) in dry benzene (15 mL) followed by dimethylformamide (2 drops). The resulting solution was stirred for 30 min at room temperature and the solvent was then removed by rotary evaporation. Dry benzene (5 mL) was added and once again removed by rotary evaporation. The residue was dissolved in 20 mL of dry ethyl ether, and pyridine (0.4 mL), 4-(dimethylamino)pyridine (catalytic amount), and 4-methyl-3-hydroxythiazole-2(3*H*)-thione were added. After 30 min the reaction was quenched by addition of 20 mL of a saturated solution of sodium bicarbonate. Standard workup followed by flash chromatography (25% ethyl acetate/petroleum ether) afforded the ester **34b** as a yellow liquid (92.3 mg, 52% yield): R_f 0.39 (50% ethyl acetate/petroleum ether); IR (neat) 1720, 1790 cm^{-1}; ^1H NMR δ 9.51–9.49 (t, 1 H, H-7, $J_{6,7}$ = 2.5 Hz), 7.37–7.18 (m, 5 H, phenyl), 6.21–6.20 (d, 1 H, heterocycle, $J_{heterocycle}$ = 1.2 Hz), 6.16–6.07 (dd, 1 H, H-8, $J_{8,9}$ = 11.0 Hz, $J_{8,9}$ = 17.6 Hz), 5.36–5.32 (d, 1 H, H-9, $J_{8,9}$ = 11.0 Hz), 5.21–5.15 (d, 1 H, H-9, $J_{8,9}$ = 17.6 Hz), 2.83–2.82 (d, 2 H, H-6, $J_{6,7}$ = 2.5 Hz), 2.72–2.55 (t, 2 H, H-2, $J_{2,3}$ = 6.9 Hz), 2.11–2.10 (d, 3 H, methyl, $J_{heterocycle}$ = 1.2 Hz), 2.10–1.95 (m, 2 H, H-4), 1.70–1.55 (m, 2 H, H-3, $J_{2,3}$ = 6.9 Hz). Anal. Calcd for $C_{19}H_{21}NO_3S_2$: C, 60.77; H, 5.64; S, 17.08; N, 3.73. Found: C, 60.70; H, 5.57; S, 17.08; N, 3.75.

3-Phenyl-3-vinylhexanal (35). Superhydride (Aldrich) (1 M solution in tetrahydrofuran, 0.28 mL, 0.28 mmol) was added to a solution of the iodide **36** (46.0 mg, 0.14 mmol) in tetrahydrofuran (12 mL). After heating for 1 h, the reaction was quenched with methanol and neutralized with a saturated solution of ammonium chloride (10 mL). After standard workup the product was separated by flash chromatography (10% ethyl acetate/petroleum ether), and the alcohol was obtained as a clear viscous liquid (23.3 mg, 82% yield). The material was dissolved in dry methylene chloride (10 mL), cooled to 0 °C, and pyridinium chlorochromate (28.4 mg, 0.13 mmol) was added. The reaction was stirred overnight at room temperature, after which the reaction was complete. Excess acid was neutralized by the addition of 10 mL of a saturated solution of sodium bicarbonate, and after standard workup the product was separated by flash chromatography (20% ethyl acetate/petroleum ether). The aldehyde **35** was obtained as a clear viscous liquid (8.3 mg, 37.4% yield): R_f 0.70 (50% ethyl acetate/petroleum ether); ^1H NMR δ 9.54–9.51 (t, 1 H, CHO, $J_{1,2}$ = 2.9 Hz), 7.40–7.18 (m, 5 H, phenyl), 6.14–6.03 (dd, 1 H, H-7, $J_{7,8}$ = 10.9 Hz, $J_{7,8}$ = 17.8 Hz), 5.30–5.28 (d, 1 H, H-8, $J_{7,8}$ = 10.9 Hz), 5.55–5.10 (d, 1 H, H-8, $J_{7,8}$ = 10.9 Hz), 2.82–2.76 (t, 2 H, H-2, $J_{1,2}$ = 2.9 Hz), 1.85–1.76 (t, 2 H, H-4, $J_{4,5}$ = 6.6 Hz), 1.24–1.06 (tt, 2 H, H-5, $J_{4,5}$ = 6.6 Hz, $J_{5,6}$ = 7.2 Hz), 0.87–0.82 (t, 3 H, H-6, $J_{5,6}$ = 7.2 Hz); HRMS (calcd for $C_{14}H_{18}O$ 220.1701, found 220.1707.

6-Iodo-3-phenyl-3-vinylhexanol (36). Sodium borohydride (35 mg, 0.92 mmol) was added to a solution of the aldehyde **15b** (150 mg, 0.46 mmol) in dry methanol (50 mL) at) °C. After stirring for 30 min at room temperature, the reaction was quenched with a small amount of wet ammonium chloride. Two-thirds of the volume of methanol was removed under reduced pressure. A saturated solution of ammonium chloride (50 mL) and ethyl ether (50 mL) were then added, and the solution was stirred for 30 min. After standard workup the product was purified by flash chromatography (20% ethyl acetate/petroleum ethers). The alcohol **36** was obtained as a clear viscous liquid (107 mg, 0.33 mmol, 70% yield): R_f 0.55 (25% ethyl acetate/petroleum ether); ^1H NMR δ 7.35–7.10 (m, 5 H, phenyl), 5.95–5.85 (dd, 1 H, H-7, $J_{7,8}$ = 10.9 Hz, $J_{7,8}$ = 17.8 Hz), 5.22–5.17 (d, 1 H, H-8, $J_{7,8}$ = 10.9 Hz), 5.14–5.07 (d, 1 H, H-8, $J_{7,8}$ = 17.8 Hz), 3.55–3.46 (t, 2 H, H-1, $J_{1,2}$ = 7.4 Hz), 3.08–3.04 (t, 2 H, H-6, $J_{5,6}$ = 6.6 Hz), 2.09–1.98 (t, 2 H, H-2, $J_{1,2}$ = 7.4 Hz), 1.88–1.79 (t, 2 H, H-4, $J_{4,5}$ = 7.6 Hz), 1.62–1.49 (m, 3 H, H-5, OH); HRMS calcd for $C_{14}H_{19}IO$ 330.0481, found 330.0483.

1-(Formylmethyl)-2-methyl-1-phenylcyclopentane (37). Compound **36** (49.3 mg, 0.15 mmol) was subjected to the standard procedure for free-radical reactions. Purification by flash chromatography (25% ethyl acetate/petroleum ether) gave a clear viscous liquid (28.7 mg, 95% yield), which was oxidized with pyridinium chlorochromate as described for **35**. Aldehyde **37** was obtained as a clear viscous liquid (20.0 mg, 71.4% yield): R_f 0.68 (50% ethyl acetate/petroleum ether); ^1H NMR δ 9.65–9.33 (t, 1 H, CHO, $J_{7,8}$ = 2.8 Hz), 7.40–7.22 (m, 5 H, phenyl), 2.90–2.39 (d, 2 H, H-7, $J_{7,8}$ = 2.8 Hz), 2.38–2.09 (m, 1 H, H-2, $J_{2,methyl}$ = 6.9 Hz), 2.10–0.95 (m, 6 H, H-3, H-4, H-5), 0.97–0.95 (d, 3 H, H-6 (methyl), $J_{2,methyl}$ = 6.9 Hz); HRMS calcd for $C_{14}H_{18}O$ 220.1701, found 220.1712.

4-Methyl-6-heptenal (48). The title compound was obtained in 62% yield by oxidation of **55b** with pyridinium chlorochromate as described above for preparation of **35**. For **48**: R_f 0.85 (50% ethyl acetate/petroleum ether); ^1H NMR δ 9.76–9.75 (t, 1 H, H-1, $J_{1,2}$ = 1.8 Hz), 5.82–5.67 (m, 1 H, H-6, $J_{6,7}$ = 7.2 Hz), 5.03–4.95 (m, 2 H, H-7, $J_{6,7}$ = 7.2 Hz, $J_{7,7}$ = 1.5 Hz), 2.45–2.35 (m, 2 H, H-2, $J_{1,2}$ = 1.8 Hz), 2.11–1.86 (m, 2 H, H-5), 1.72–1.56 (m, 1 H, H-4, $J_{4,8}$ = 6.3 Hz), 1.52–1.10 (m, 2 H, H-3), 0.89–0.86 (d, 3 H, H-8, $J_{4,8}$ = 6.3 Hz); HRMS calcd for $C_8H_{14}O$ 127.1123, found 127.1128.

3-Ethyl-5-hexenal (51). Perchloric acid (35% solution, 0.5 mL) was added to a solution of the enol ether **52c** (62.3 mg, 0.45 mmol) in ethyl ether (25 mL) at room temperature. The reaction was stirred for 3 h, after which the reaction was complete. The acid was then quenched by the addition of 25 mL of a saturated solution of sodium bicarbonate. Standard workup followed by flash chromatography (10% ethyl acetate/petroleum ether) afforded aldehyde **51** as a clear liquid (30.0 mg, 54% yield): R_f 0.38 (25% ethyl acetate/petroleum ether); IR (neat) 1700 cm^{-1}, ^1H NMR δ 9.76–9.74 (t, 1 H, CHO, $J_{1,2}$ = 2.1 Hz), 5.80–5.65 (m, 1 H, H-5, $J_{5,6}$ = 11.1 Hz), 5.05–4.95 (dd, 2 H, H-6, $J_{5,6}$ = 11.1 Hz), 2.45–2.25 (m, 2 H, H-2, $J_{1,2}$ = 2.1 Hz), 2.20–1.95 (m, 2 H, H-4), 1.98–1.20 (m, 3 H, H-3, H-7, $J_{7,8}$ = 7.1 Hz), 0.91–0.86 (t, 3 H, H-8, $J_{7,8}$ = 7.1 Hz). The material was characterized as the 2,4-dinitrophenylhydrazone, mp 120 °C. Anal. Calcd for $C_{14}H_{18}N_4O_4$: C, 54.89; H, 5.92; N, 18.29. Found: C, 54.76; H, 5.88; N, 18.36.

3-Allyl-5-methoxy-4-penten-1-ol (52a). Potassium bis(trimethylsilyl)amide (0.5 M in toluene, 143 mL, 95.5 mmol) was added to a suspension of (methoxymethyl)triphenylphosphonium chloride (46.0 g, 130 mmol) in dry tetrahydrofuran (500 mL) at −78 °C and the mixture was stirred for 1 h. A solution of the lactol **19** (2.40 g, 18.8 mM) in tetrahydrofuran (40 mL) was then added. Standard workup followed by flash chromatography (20% ethyl acetate/petroleum ether) gave the alcohols **52a** as a clear liquid (2.32 g, 79% total yield): R_f 0.40 (50% ethyl acetate/petroleum ether); ^1H NMR δ 6.32–6.28 (d, 1 H, H-5, $J_{4,5}$ = 12.6 Hz), 5.85–5.69 (m, 1 H, H-7, $J_{7,8}$ = 3.5 Hz, $J_{7,8}$ = 14.9 Hz), 5.05–4.98 (dd, 2 H, H-8, $J_{7,8}$ = 3.5 Hz, $J_{7,8}$ = 14.9 Hz), 4.55–4.46 (dd, 1 H, H-4, $J_{4,5}$ = 12.6 Hz, $J_{9,3}$ = 9.3 Hz), 3.75–3.60 (m, 2 H, H-1), 3.51 (s, 3 H, methyl), 2.20–2.01 (m, 3 H, H-6, OH), 1.79–1.67 (m, 1 H, H-3, $J_{3,4}$ = 9.3 Hz), 1.50–1.37 (m, 2 H, H-2). Anal. Calcd for $C_9H_{16}O_2$: C, 70.55;

H, 10.66. Found: C, 70.77; H, 10.47.

1-Methoxy-3-[2′-(methylsulfonoxy)ethyl]-1,5-hexadiene (52b). Pyridine (0.1 mL, 1.3 mmol) and (4-dimethylamino)pyridine (catalytic amount) were added to a solution of the alcohol **52a** (101.1 mg, 0.65 mmol) in dry methylene chloride (12 mL) at room temperature. Methanesulfonyl chloride (0.1 mL, 0.78 mmol) was then added and the resulting solution stirred for 2 h. Saturated sodium bicarbonate solution (12 mL) was then added, and workup in the usual way was followed by flash chromatography (20% ethyl acetate/petroleum ether). The methanesulfonate **52b** was obtained as a clear liquid (120.3 mg, 79% yield): R_f 0.60 (50% ethyl acetate/petroleum ether); ^{1}H NMR δ 6.33–6.29 (d, 2 H, H-1, $J_{1,2}$ = 12.7 Hz), 5.82–5.68 (m, 1 H, H-5, $J_{5,6}$ = 12.2 Hz), 5.07–5.00 (d, 2 H, H-6, $J_{5,6}$ = 12.2 Hz), 4.48–4.40 (dd, 1 H, H-2, $J_{1,2}$ = 12.7 Hz, $J_{2,3}$ = 9.2 Hz), 4.32–4.16 (m, 2 H, H-2′), 3.52 (s, 3 H, methyl), 2.99 (s, 3 H, methyl), 2.20–2.08 (m, 3 H, H-4, H-1′), 2.02–1.88 (m, 2 H, H-1′), 1.62–1.48 (m, 1 H, H-3, $J_{2,3}$ = 9.2 Hz). Anal. Calcd for $C_{10}H_{18}O_4S$: C, 53.20; H, 8.12. Found: C, 52.96; H, 8.04.

1-Methoxy-3-ethyl-1,5-hexadiene (52c). Lithium triethylborohydride (1 M in tetrahydrofuran, 0.2 mL, 0.2 mmol) was added to a solution of the methanesulfonate **52b** (35.2 mg, 0.15 mmol) in dry ethyl ether. The resulting solution was heated to reflux for 1 h. The reaction was quenched with methanol followed by the addition of 25 mL of a saturated solution of ammonium chloride. Standard workup followed by flash chromatography (10% ethyl acetate/petroleum ether) afforded the enol ether **52c** as a clear liquid (12.1 mg, 58% yield): R_f 0.63 (25% ethyl acetate/petroleum ether); ^{1}H NMR δ 6.24–6.20 (d, 1 H, H-1, $J_{1,2}$ = 12.7 Hz), 5.82–5.67 (m, 1 H, H-5, $J_{5,6}$ = 8.3 Hz), 5.00–4.92 (dd, 2 H, H-6, $J_{5,6}$ = 8.3 Hz), 4.50–4.42 (dd, 1 H, H-2, $J_{1,2}$ = 12.7 Hz, $J_{2,3}$ = 9.3 Hz) 3.48 (s, 3 H, methyl), 2.15–1.92 (m, 2 H, H-4), 1.49–1.35 (m, 1 H, H-3, $J_{2,3}$ = 9.3 Hz), 1.30–1.10 (m, 2 H, H-7, $J_{7,8}$ = 7.7 Hz), 0.84–0.80 (t, 3 H, H-8, $J_{7,8}$ = 7.7 Hz). Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.18; H, 11.67.

2-Allyl-δ-valerolactone (53). The title compound was prepared from valerolactone in 59% yield by use of the procedure described above for **18a** → **18b**. For **53**: R_f 0.52 (50% ethyl acetate/petroleum ether); IR (neat) 1740, 3050, cm^{-1}; ^{1}H NMR δ 5.84–5.70 (m, 1 H, H-6, $J_{6,7}$ = 9.3 Hz, $J_{5,6}$ = 7.5 Hz), 5.11–5.03 (m, 2 H, H-7, $J_{7,7}$ = 1.2 Hz, $J_{6,37}$ = 9.3 Hz), 4.34–4.21 (m, 2 H, H-4, $J_{3,4}$ = 5.8 Hz), 2.65–2.47 (m, 2 H, H-1, H-5, $J_{1,2}$ = 6.2 Hz), 2.32–2.22 (m, 1 H, H-5, $J_{5,6}$ = 7.5 Hz), 2.09–1.98 (m, 1 H, H-2, $J_{1,2}$ = 6.2 Hz), 1.91–1.82 (m, 2 H, H-3, $J_{3,4}$ = 5.8 Hz), 1.61–1.47 (m, 1 H, H-2). Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.82; H, 8.64.

4-(Hydroxymethyl)-6-hepten-1-ol (54a). Reduction of **53** with Dibal using the standard procedure gave **54a** in 80% yield: R_f 0.09 (50% ethyl acetate/petroleum ether); ^{1}H NMR δ 5.86–5.72 (m, 1 H, H-6, $J_{6,7}$ = 7.9 Hz, $J_{5,6}$ = 7.1 Hz), 5.08–4.99 (m, 2 H, H-7, $J_{6,7}$ = 7.9 Hz, $J_{7,7}$ = 1.1 Hz), 3.65–3.61 (t, 2 H, H-1, $J_{1,2}$ = 7.7 Hz), 3.56–3.55 (d, 2 H, H-8, $J_{4,8}$ = 4.8 Hz), 2.13–2.07 (dd, 2 H, H-5, $J_{4,5}$ = 6.6 Hz), 1.66–1.52 (m, 5 H, H-2, H-4, OH, $J_{5,6}$ = 7.1 Hz, $J_{4,8}$ = 4.8 Hz, $J_{1,2}$ = 7.7 Hz), 1.48–1.31 (m, 3 H, H-3). Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.46; H, 11.29.

2-Allyl-5-(*tert*-butyldiphenylsiloxy)-1-pentanol (54b). *tert*-Butylchlorodiphenylsilane (6.75 mL, 26.0 mmol) was added to a solution of the diol **54a** (3.4 g, 23.6 mmol) and imidazole (2.51 g, 35.4 mmol) in dry methylene chloride (250 mL) at 0 °C. The reaction was allowed to warm to room temperature and stir for an additional hour. A saturated solution of sodium bicarbonate (100 mL) was added, and standard workup followed by flash chromatography (20% ethyl acetate/petroleum ether) afforded compound **54b** as a clear liquid (3.9 g, 45% yield), whose structure was confirmed by subsequent transformations. (The other monosilylated product (9% yield) as well as the disilylated material (28.9% yield) were also formed): R_f 0.70 (50% ethyl acetate/petroleum ether); ^{1}H NMR δ 7.68–7.32 (m, 10 H, phenyl), 5.83–5.71 (m, 1 H, H-7, $J_{7,8}$ = 7.2 Hz, $J_{6,7}$ = 7.3 Hz), 5.07–4.98 (m, 2 H, H-8, $J_{7,8}$ = 7.2 Hz, $J_{8,8}$ = 2.8 Hz), 3.66–3.62 (t, 2 H, H-1, $J_{1,2}$ = 6.4 Hz), 3.53–3.50 (t, 2 H, H-5, $J_{4,5}$ = 5.8 Hz), 2.11–2.06 (dd, 2 H, H-6, $J_{2,6}$ = 6.3 Hz, $J_{6,7}$ = 7.3 Hz), 1.61–1.52 (m, 3 H, H-2, H-4, $J_{1,2}$ = 6.4 Hz, $J_{4,5}$ = 5.8 Hz, $J_{2,6}$ = 6.3 Hz), 1.39–1.24 (m, 2 H, H-3), 1.03 (s, 9 H, *tert*-butyl). Anal. Calcd for $C_{24}H_{34}O_2Si$: C, 75.34; H, 8.96. Found: C, 75.19; H, 8.76.

7-(*tert*-Butyldiphenylsiloxy)-4-(methylsulfonoxy)-1-heptene (54c). Pyridine (1.5 mL, 19.1 mmol) was added to a solution of the alcohol **54b** (3.5 g, 9.6 mmol) in dry methylene chloride (250 mL) at 0 °C. Methanesulfonyl chloride (1.48 g, 19.1 mmol) was then added to the solution along with a catalytic amount of 4-(dimethylamino)pyridine. The reaction was allowed to warm to room temperature for 1 h, and was then quenched by the addition of 100 mL of a saturated solution of sodium bicarbonate. Standard workup followed by flash chromatography (20% ethyl acetate/petroleum ether) gave the methanesulfonate **54c** as a clear liquid (4.05 g, 92% yield): R_f 0.50 (25% ethyl acetate/petroleum ether); ^{1}H NMR δ 7.76–7.33 (m, 10 H, phenyl), 5.78–5.64 (m, 1 H, H-2, $J_{2,3}$ = 6.9 Hz, $J_{1,2}$ = 10.6 Hz), 5.09–5.02 (m, 2 H, H-1, $J_{1,2}$ = 10.6 Hz, $J_{1,1}$ = 1.3 Hz), 4.10–4.06 (d, 2 H, H-8, $J_{4,8}$ = 5.4 Hz), 3.66–3.62 (t, 2 H, H-7, $J_{6,7}$ = 6.1 Hz), 2.95 (s, 3 H, methyl), 2.14–2.09 (dd, 2 H, H-3, $J_{2,3}$ = 6.9 Hz, $J_{3,4}$ = 5.7 Hz), 1.85–1.77 (m, 1 H, H-4, $J_{3,4}$ = 5.7 Hz), 1.62–1.50 (m, 2 H, H-6, $J_{6,7}$ = 6.1 Hz), 1.48–1.39 (m, 2 H, H-5). Anal. Calcd for $C_{25}H_{36}O_4SSi$: C, 65.18; H, 7.88; S, 6.96. Found: C, 65.38; H, 7.68; S, 7.19.

7-(*tert*-Butyldiphenylsiloxy)-4-methyl-1-heptene (55a). Reduction of **54c** with lithium triethylborohydride was carried out as described above (**53b** → **53c**) to give **55a** in 67% yield: R_f 0.81 (25% ethyl acetate/petroleum ether): ^{1}H NMR δ 7.55–7.28 (m, 10 H, phenyl), 5.67–5.54 (m, 1 H, H-2, $J_{1,2}$ = 5.0 Hz, $J_{2,3}$ = 7.4 Hz), 4.85–4.80 (m, 2 H, H-1, $J_{1,2}$ = 5.0 Hz, $J_{1,1}$ = 1.0 Hz), 3.54–3.49 (t, 2 H, H-7, $J_{6,7}$ = 5.8 Hz), 1.94–1.68 (m, 2 H, H-3, $J_{2,3}$ = 7.4 Hz, $J_{3,4}$ = 6.4 Hz), 1.50–1.32 (m, 1 H, H-4, $J_{3,4}$ = 6.4 Hz, $J_{4,8}$ = 6.6 Hz), 1.40–0.90 (m, 4 H, H-5, H-6, $J_{6,7}$ = 5.8 Hz), 0.90 (s, 9 H, *tert*-butyl), 0.71–0.69 (d, 3 H, H-8, $J_{4,8}$ = 6.6 Hz). Anal. Calcd for $C_{24}H_{34}OSi$: C, 78.63; H, 9.35. Found: C, 78.39; H, 9.42.

4-Methyl-6-hepten-1-ol (55b). Tetra-*n*-butylammonium fluoride (1 M in tetrahydrofuran, 0.17 mg, 0.17 mmol) was added at room temperature to a solution of **54a** (30.3 mg, 0.08 mmol) in dry ethyl ether (25 mL). The mixture was stirred for 4 h, after which the reaction was neutralized by the addition of 25 mL of a saturated solution of ammonium chloride. Standard workup followed by flash chromatography (20% ethyl acetate/petroleum ether) afforded **55b** as a clear liquid (9.6 mg, 94% yield): R_f 0.24 (25% ethyl acetate/petroleum ether); ^{1}H NMR δ 5.83–5.69 (m, 1 H, H-6, $J_{6,7}$ = 5.4 Hz), 5.01–4.49 (m, 2 H, H-7, $J_{6,7}$ = 5.4 Hz, $J_{7,7}$ = 0.9 Hz), 3.61–3.49 (t, 2 H, H-1, $J_{1,2}$ = 8.4 Hz), 2.40–2.35 (dd, 2 H, H-5, $J_{4,5}$ = 5.9 Hz, $J_{5,6}$ = 7.3 Hz), 2.09–1.83 (m, 2 H, H-5, $J_{5,6}$ = 7.3 Hz, $J_{4,5}$ = 6.9 Hz), 1.65–1.40 (m, 1 H, H-4, $J_{4,5}$ = 6.9 Hz), 1.45–1.05 (m, 4 H, H-2, H-3, $J_{1,2}$ = 8.4 Hz), 0.88–0.86 (d, 3 H, methyl (H-8), $J_{4,8}$ = 6.6 Hz). Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 75.09; H, 12.55.

Acknowledgment. We are grateful to our colleague Professor Ned A. Porter for advice and helpful discussions, and to Dr. George Dubay for expert help with the GC/MS measurements.