

Preparation and Reactions of 3-Oxa- and 4-Oxa-5-hexenyllithiums

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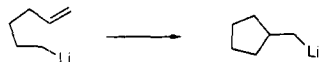
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ABSTRACT

Low-temperature lithium–iodine exchange between tert-butyllithium and the appropriate iodide has been used to generate 3-oxa-5-hexenyllithium and a variety of 4-oxa-5-hexenyllithiums. The 3-oxa system is inherently unstable and fragments via facile β -elimination to give the anion of allyl alcohol and ethylene. The 4-oxa-5-hexenyllithiums, in contrast, are stable at low temperatures but undergo novel isomerization upon warming to deliver the lithium salt of a 4-alken-1-ol in the formal equivalent of an unprecedented [1,4]-Wittig rearrangement. The rearrangement is most likely mediated by 5-exo-trig ring closure of the 4-oxa-5-hexenyllithium to a (2-tetrahydrofuranyl)methyl-lithium followed by rapid opening to the alkoxide.

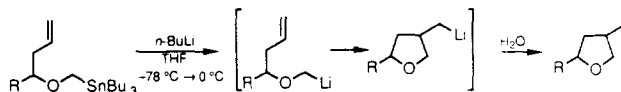
INTRODUCTION

The regiospecific cyclization of 5-hexenyllithiums provides a highly stereoselective method for the preparation of (cyclopentyl)methyl-lithiums, and this isomerization has attracted recent attention as a route to functionalized carbocyclic products [1–3].



Much less information is available on the behavior of 5-hexenyllithiums containing heteroatoms in the chain. Indeed, the only heteroatom-containing systems that have been investigated are the 2-oxa-5-hexenyllithiums. These organometal-

lics, which were prepared by Broka and co-workers from a tri-*n*-butyltin precursor via low-temperature tin–lithium exchange [4], isomerize upon warming to 0°C, as shown below, to give (3-tetrahydrofuranyl)methyl-lithiums. This facile and stereoselective 5-exo-trig cyclization provides a convenient route to substituted tetrahydrofurans.



Herein we report the generation of 3-oxa- and 4-oxa-5-hexenyllithiums [5] from the corresponding iodides by lithium–iodine exchange, and we detail the behavior of these species. As demonstrated below, the 3-oxa system is inherently unstable and fragments via facile β -elimination. The 4-oxa-5-hexenyllithiums, in contrast, are stable at low temperatures and undergo a novel isomerization upon warming to deliver the lithium salt of a 4-alken-1-ol in the formal equivalent of an unprecedented [1,4]-Wittig rearrangement [7].

RESULTS AND DISCUSSION

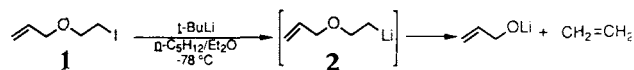
3-Oxa-5-hexenyllithiums

All attempts to prepare the parent 3-oxa-5-hexenyllithium (**2**) from 2-allyloxyethyl iodide (**1**) following our general protocol for low-temperature lithium–iodine exchange [6] led, as illustrated below, to the essentially quantitative formation of allyl alcohol and ethylene. The β -elimination was complete within minutes at -78°C, and it was, therefore, not possible to characterize the organometallic. This rather unexceptional result demonstrates that the 3-oxa-5-hexenyllithium system (and by extension other 5-hexenyllithiums capable of expulsion of a good nucleofuge at the β -position) is of no use for the preparation of substituted tetrahydro-

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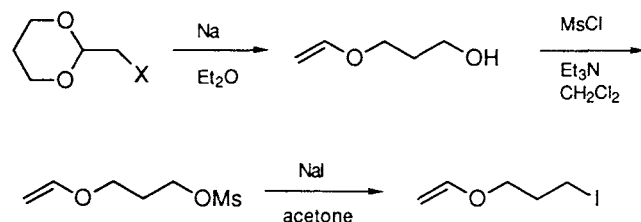
Dedicated to Professor Ernest L. Eliel on the occasion of his seventieth birthday.

furans (or other heterocycles) by 5-exo-trig isomerization [1–3].



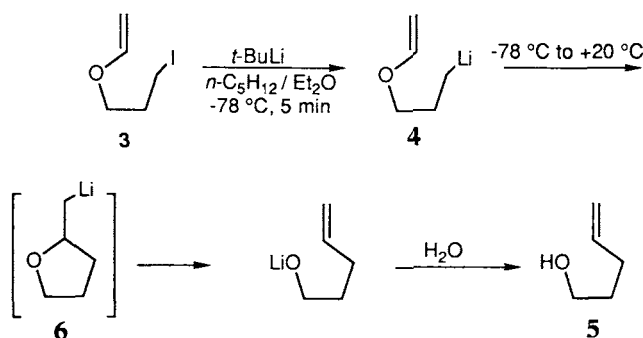
4-Oxa-5-hexenyllithiums

The title organometallics were generated from 3-iodoalkyl vinyl ethers by low-temperature lithium–iodine exchange. The iodides, in turn, were prepared for the most part, as shown below, via the mesylate from enol ether alcohols produced by the sodium-promoted fragmentation of 2-halomethyl-1,3-dioxanes. It is of some interest to note, as detailed in the Experimental section, that fragmentation of the two 4-substituted-2-halomethyl-1,3-dioxanes examined was a reasonably stereoselective process: In both cases the cleavage proceeded with preferential rupture of the less congested C(2)–O bond to give the primary enol ether alcohol as the major product of the reaction.



Treatment of an approximately 0.1 M solution of 1-ethenyloxy-3-iodopropane (**3**) in *n*-pentane–diethyl ether (3:2 by volume) at -78°C with 2.2 equivalents of *t*-BuLi served to cleanly generate the corresponding organolithium (**4**). The 4-oxa-5-hexenyllithium, which is stable in solution at low temperature, rearranges upon warming to room temperature (Scheme 1) to give the lithium salt of 4-penten-1-ol (**5**). The isomerization of **4** to the anion of **5** was effected in virtually quantitative yield by removing the cooling bath and allowing the mixture to sit at room temperature for 1 h. Addition of water to the reaction mixture delivers **5** in 93% isolated yield (Table 1). This novel rearrangement is most likely mediated, as illustrated in Scheme 1, tetrahydrofuranyl)methyl lithium (**6**) followed by rapid ring opening through β -elimination to give the alkoxide. The lifetime of **6** under the conditions used to effect the rearrangement is undoubtedly short and we have been unable to trap this cyclic species.

The isomerization of 4-oxa-5-hexenyllithiums to 4-alken-1-ols is not confined to the parent system (**4**). The results of experiments employing substituted 4-oxa-5-hexenyllithiums, summarized in Table 1, indicate that the rearrangement is a facile, clean, and high-yield process. Not surprisingly, isomerization of (2-ethenyloxymethyl)phenyl-



SCHEME 1

lithium (Table 1, entry 6) was much slower than the conversion of γ -ethenyloxy alkyl lithiums to 4-alken-1-ols (Table 1, entries 1–5). Rearrangement of the aromatic substrate (Table 1, entry 6), which presumably involves conversion of the aryllithium to a cyclic intermediate bearing a primary alkyl-lithium moiety (Scheme 1), was facilitated by the addition of 2.2 equivalents of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to the preformed aryllithium. The use of TMEDA to increase the rate of this sluggish isomerization finds ample precedent in the well-documented ability of lithiophilic Lewis base to facilitate cyclization of 5-hexenyllithiums to (cyclopentyl)methyl lithiums [3]. Another feature shared by both the cyclization of 5-hexen-

TABLE 1 Rearrangement of 4-Oxa-5-hexenyllithiums to 4-Alken-1-ols^a

Entry	Iodide	Alkenol	Yield, ^b %
1			93
2			94
3			96
5			95
6			95 ^c

^a The 4-oxa-5-hexenyllithium was generated at -78°C by addition of 2.2 equivalents of *t*-BuLi to a solution of the iodide in *n*-pentane–diethyl ether (3:2 by vol), the cooling bath was removed, and the mixture was allowed to warm to ambient temperature and stand for 1 h before the addition of an excess of water or methanol.

^b Isolated yield.

^c TMEDA (2.2 equiv.) was added following generation of the organolithium and prior to warming the mixture to facilitate cyclization of the 4-oxa-5-hexenyllithium.

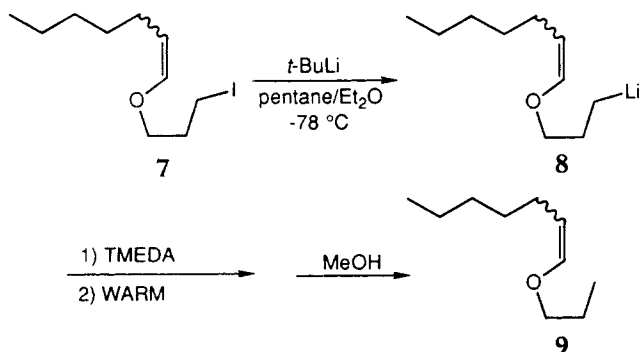
yllithiums [3] and the rearrangement of 4-oxa-5-hexenyllithiums is the reluctance of systems bearing an alkyl group at the terminal alkene carbon to undergo isomerization. Thus, for example, the 4-oxa-5-undecenyllithium (**8**), which was prepared from the corresponding iodide (**7**, *E/Z* = 90:10) as shown in Scheme 2, does not rearrange upon standing for 1 h at ambient temperature in the presence of TMEDA. Quench of such a reaction mixture gave the enol ether, 4-oxaundec-5-ene (**9**), as an approximately 90:10 mixture of *E*- and *Z*-isomers in quantitative yield. Significantly, the relative proportions of *E*- and *Z*-**8** are conserved in the isomeric composition of **9**.

The two-step transformation (Scheme 1) of 4-oxa-5-hexenyllithiums to 4-alken-1-ols (Table 1) constitutes the formal equivalent of a [1,4]-Wittig rearrangement of the γ -lithioalkyl vinyl ethers and as such is unprecedented [7]. In an effort to determine if such isomerizations could be extended to higher homologs, we prepared 5-oxa-6-heptenyllithium (**11**) from the corresponding iodide (**10**) by low-temperature lithium-iodine exchange. As illustrated in Scheme 3, **11** does indeed undergo the equivalent of a [1,5]-Wittig rearrangement when allowed to stand for 1 h at ambient temperature in the presence of TMEDA to deliver an 84% yield of 5-hexen-1-ol. This result is consistent with 6-exo-trig closure of **11** followed by rapid expulsion of the alkoxide.

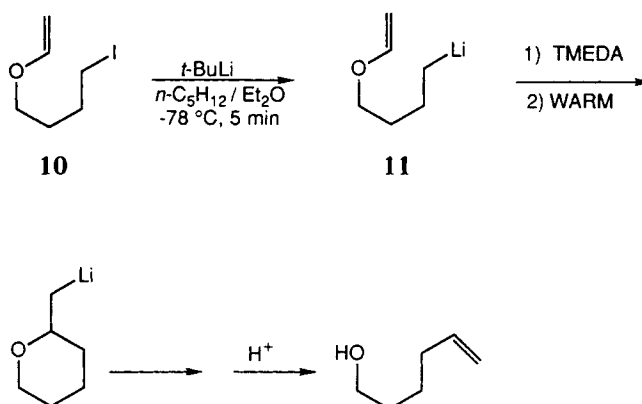
EXPERIMENTAL

General Procedures

Proton and carbon-13 magnetic resonance spectra were recorded on an IBM AF-270 NMR and shifts were referenced with respect to internal Me₄Si. A Perkin-Elmer Series 1600 FTIR instrument was used to record infrared spectra. Bulb-to-bulb distillations were carried out by using a Kugelrohr distillation apparatus, and distillation temperatures recorded using this apparatus refer to the temperature of the air bath. All boiling points are uncorrected. Analytical gas-liquid chromatography (GC) was ac-



SCHEME 2



SCHEME 3

complished using Hewlett-Packard model 5880A or 5890 chromatographs equipped with flame-ionization detectors. Preparative GC was accomplished on a Varian Aerograph A-90P instrument fitted with a 9-ft, 15% SE-30 on Chromosorb W (NAW) (80/100 mesh) column. High-resolution mass spectra were obtained on an AEI MS-902 instrument at 70 eV.

All reactions involving alkylolithiums were performed in flame-dried glassware using standard syringe/cannula techniques under an atmosphere of dry, oxygen-free argon that had been passed through a column containing an activated BASF R3-11 copper catalyst. Diethyl ether and tetrahydrofuran were freshly distilled from dark-purple solutions of sodium/benzophenone. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) was purified by distillation under nitrogen from calcium hydride. Dry, unsaturate-free *n*-pentane was obtained by repeated washings of commercial *n*-pentane with concentrated sulfuric acid until the acid layer remained clear, followed by washing with water and saturated aqueous sodium bicarbonate, drying over MgSO₄, and distillation of the purified pentane under nitrogen from lithium aluminum hydride. Methylene chloride was dried by distillation from calcium hydride. Acetone (Baker, analytical grade) was dried over calcium sulfate and distilled. Sodium iodide was dried at 100 °C (ca. 5 mm) for 8–10 h in a vacuum oven. The concentrations of solutions of *t*-butyllithium in pentane (Aldrich) were determined by titration with *sec*-butanol in xylene using 1,10-phenanthroline as indicator [8]. Flash chromatography was carried out on Merck 70-230 mesh silica gel.

Literature procedures were followed for the preparation of 2-chloromethyl-1,3-dioxane [9], *cis*-2-bromomethyl-4-methyl-1,3-dioxane [10], 2-bromomethyl-1,3-dioxepane [11], 1-ethenyloxymethyl-2-iodobenzene [12], 2-allyloxyethanol [13], *E*- and *Z*-4-oxaundec-5-en-1-ol [14], and *trans*-2-(hydroxymethyl)cyclohexanol [15]. The known 2-allyloxyethyl iodide (**1**) was prepared via the mesylate from 2-allyloxyethanol; bp 110–120 °C (760 mm):

the IR and ^1H NMR spectra of the iodide were in agreement with the literature data for this material [13].

cis- and trans-2-Bromomethyl-5-ethyl-1,3-dioxane. A solution of 12.57 g (63.8 mmol) of bromoacetaldehyde diethyl acetal, 7.60 g (73.4 mmol) of 2-hydroxymethyl-1-butanol, and a catalytic quantity of *p*-toluenesulfonic acid in 16 mL of cyclohexane was stirred at room temperature for 1 h and then distilled until the overhead temperature rose above 65°C. The residue in the flask was allowed to cool to room temperature, ca. 1 g of solid, anhydrous potassium carbonate was added, and the mixture was stirred for 1 h at room temperature. Residual solvent was removed by rotary evaporation and the residue was distilled from the potassium carbonate to give 12.2 g (91%) of the title compounds as an approximately 1:3 mixture of *cis*- and *trans*-isomers: bp 54–59°C (0.25 mm); ^1H NMR (CDCl_3) *trans*-isomer: δ 4.54 (t, J = 4.42 Hz, 1 H), 4.04 (d of d, J_{gem} = 13.28 Hz, $J_{\text{eq-ax}}$ = 4.61 Hz, 2 H), 3.92–3.85 (m, 2 H), 3.25 (d, J = 4.42 Hz, 2 H), 1.84 (m, 1 H), 1.00 (pentet, J = 7.38 Hz, 2 H), 0.79 (t, J = 7.38 Hz, 3 H); *cis*-isomer: δ 4.63 (t, J = 4.43 Hz, 1 H), 1.17 (pentet, J = 7.15 Hz, 2 H), 0.88 (t, J = 7.15 Hz, 3 H), the remaining signals were buried under the stronger signals of the *trans*-isomer; ^{13}C NMR (CDCl_3) *trans*-isomer: δ 99.35, 71.78, 35.31, 31.61, 20.75, 10.63; *cis*-isomer: δ 99.61, 69.79, 35.67, 31.77, 21.96, 11.75. An analytical sample of the isomeric mixture was prepared by preparative GC: mass spectroscopic molecular weight calcd for $\text{C}_7\text{H}_{13}\text{BrO}_2$ (M^+), 208.0099, found, 208.0096.

*trans-2-Bromoethyl-(*r*-4*a*,*t*-8*a*)-1,3-dioxadecahydronaphthalene.* The general procedure outlined above was followed. Thus, reaction of 10.1 mL (67.1 mmol) of bromoacetaldehyde diethyl acetal, 10.0 g (76.8 mmol) of *trans*-2-hydroxymethylcyclohexanol [15], 16.7 mL of cyclohexane, and a catalytic quantity of *p*-toluenesulfonic acid afforded, after distillation, 14.7 g (93%) of essentially isomerically pure title compound: bp 81–85°C (0.3 mm); ^1H NMR (CDCl_3) δ 4.75 (t, J = 4.59 Hz, 1 H), 3.94 (d of d, $J_{\text{ax-ax}}$ = 11.09 Hz, J = 4.45 Hz, 1 H), 3.40–3.24 (overlapping patterns, 4 H, i.e., 3.30 (d, J = 4.59 Hz), 3.40–3.24 (m, 2 H), 1.91–0.80 (broad m, 9 H); ^{13}C NMR (CDCl_3) δ 99.97, 81.57, 71.70, 40.68, 31.79, 31.28, 25.84, 24.88, 24.47; mass spectroscopic molecular weight calcd for $\text{C}_9\text{H}_{15}\text{BrO}_2$ (M^+), 234.0255, found, 234.0265.

Preparation of 3-Ethenyloxy-1-alkanols by Fragmentation of 2-Halomethyl-1,3-dioxanes. The procedure of Crombie and Harper [16] was followed with slight modification. Thus, an appropriately sized three-necked, round-bottomed flask fitted with a mechanical stirrer, Friedrich condenser, constant

pressure addition funnel, and rubber septa was flame dried under a stream of dry nitrogen. The flask was charged with 6 equivalents of metallic sodium (3–8 mm spheres (Aldrich) washed free from mineral spirits with dry diethyl ether) and anhydrous diethyl ether (ca. 20 mL/1 g Na). The dropping funnel was charged with the appropriate 2-halomethyl-1,3-dioxane diluted with anhydrous diethyl ether (ca. 1 mL/mmol of 2-halomethyl acetal). The haloacetal was added dropwise to the vigorously stirred suspension of sodium in ether at such a rate as to maintain gentle reflux. After complete addition the milky white suspension was stirred overnight at room temperature. Large solid chunks of sodium were removed with tweezers and the solution was carefully hydrolyzed with distilled water (ca. 5 mL/50 mmol of Na). The clear ethereal solution was separated, the aqueous layer extracted with three portions of diethyl ether, and the combined organic layers were dried over anhydrous potassium carbonate, filtered, and concentrated. The enol ether alcohols were converted to the corresponding iodides without further purification because distillation led to decomposition of these acid-sensitive materials. The following enol ether alcohols were prepared by this procedure.

3-Ethenyloxy-1-propanol. Cleavage of 9.97 g (73.0 mmol) of 2-chloromethyl-1,3-dioxane [9] with 10 g (0.43 mol) of metallic sodium afforded 7.29 g (98%) of product; ^1H NMR (CDCl_3) δ 6.46 (d of d, J_{trans} = 14.34 Hz, J_{cis} = 6.82 Hz, 1 H), 4.20 (d of d, J_{trans} = 14.34 Hz, J_{gem} = 2.05 Hz, 1 H), 4.01 (d of d, J_{cis} = 6.82 Hz, J_{gem} = 2.05 Hz, 1 H), 3.82 (t, J = 6.09 Hz, 2 H), 3.12 (broad s, 1 H), 3.74 (t, J = 6.05 Hz, 2 H), 1.90 (quintet, J = 6.10 Hz, 2 H); ^{13}C NMR (CDCl_3) δ 151.52, 86.59, 65.70, 59.60, 31.61.

3-Ethenyloxy-1-butanol and 4-Ethenyloxy-2-butanol. Cleavage of 10.0 g (51.3 mmol) of *trans*-2-bromomethyl-4-methyl-1,3-dioxane [10] with 7.0 g (0.30 mol) of metallic sodium gave 5.44 g (91%) of an isomeric mixture of products. Proton NMR revealed that the mixture was composed of ~62% 3-ethenyloxy-1-butanol and ~38% 4-ethenyloxy-2-butanol. The identity of the products was established on the basis of the spectroscopic properties given below. No attempt was made to separate the isomeric products and the mixture was used without further purification.

3-Ethenyloxy-1-butanol. ^1H NMR (CDCl_3) δ 6.19 (d of d, J_{trans} = 14.33 Hz, J_{cis} = 6.68 Hz, 1 H), 4.17 (d of d, J_{trans} = 14.33 Hz, J_{gem} = 2.00 Hz, 1 H), 3.99 (sextet, J = 6.20 Hz, 1 H), 3.89 (d of d, J_{cis} = 6.68 Hz, J_{gem} = 1.51 Hz, 1 H), 3.58 (m, 2 H, H(1)), 3.13 (broad, 1 H), 1.73–1.61 (m, 2 H), 1.13 (d, J = 6.21 Hz, 3 H); ^{13}C NMR (CDCl_3) δ 150.42, 88.31, 73.32, 58.89, 38.74, 19.69.

4-Ethenyloxy-2-butanol. ^1H NMR (CDCl_3) δ 6.34 (d of d, $J_{\text{trans}} = 14.34$ Hz, $J_{\text{cis}} = 6.82$ Hz, 1 H), 4.08 (d of d, $J_{\text{trans}} = 14.34$ Hz, $J_{\text{gem}} = 2.0$ Hz, 1 H), 3.74–3.65 (m, 4 H), 1.73–1.61 (m, 2 H), 1.10 (d, $J = 6.20$ Hz, 3 H); ^{13}C NMR (CDCl_3) δ 151.35, 86.56, 65.20, 58.89, 37.68, 23.25.

3-Ethenyloxy-2-ethyl-1-propanol. Cleavage of 5.0 g (23.9 mmol) of 5-ethyl-2-bromomethyl-1,3-dioxane with 3.3 g (0.14 mol) of metallic sodium gave 3.00 g (97%) of product: ^1H NMR (CDCl_3) δ 6.39 (d of d, $J_{\text{trans}} = 14.36$ Hz, $J_{\text{cis}} = 6.82$ Hz, 1 H), 4.12 (d of d, $J_{\text{trans}} = 14.36$ Hz, $J_{\text{gem}} = 2.00$ Hz, 1 H), 3.92 (d of d, $J_{\text{cis}} = 6.82$ Hz, $J_{\text{gem}} = 2.00$ Hz, 1 H), 3.69–3.50 (unresolved, 4 H), 2.78 (broad s, 1 H), 1.75–1.66 (m, 1 H), 1.38–1.26 (m, 2 H), 0.87 (t, $J = 7.39$ Hz, 3 H); ^{13}C NMR (CDCl_3) δ 151.68, 86.42, 68.92, 63.34, 41.90, 20.67, 11.32.

trans-[1-(2-Ethenyloxy)cyclohexyl]methanol and trans-2-(Ethenyloxymethyl)cyclohexanol. Cleavage of 10.0 g (42.5 mmol) of *trans*-2-bromomethyl-(*r*-4a,*t*-8a)-1,3-dioxadecahydronaphthalene with 5.9 g (0.26 mol) of metallic sodium afforded 6.50 g (98%) of product as a mixture of isomers. Proton NMR analysis revealed that the mixture was composed of ~65% *trans*-[1-(2-ethenyloxy)cyclohexyl]methanol and ~35% *trans*-2-(ethenyloxymethyl)cyclohexanol. The identity of the products was established on the basis of the spectroscopic data listed below. No attempt was made to separate the isomeric products and the mixture was used without further purification.

trans-[1-(2-Ethenyloxy)cyclohexyl]methanol. ^1H NMR (CDCl_3) δ 6.26 (d of d, $J_{\text{trans}} = 14.05$ Hz, $J_{\text{cis}} = 6.53$ Hz, 1 H), 4.27 (d of d, $J_{\text{trans}} = 14.05$ Hz, $J_{\text{gem}} = 1.60$ Hz, 1 H), 3.95 (d of d, $J_{\text{cis}} = 6.58$ Hz, $J_{\text{gem}} = 1.60$ Hz, 1 H), 3.64–3.49 (unresolved, 3 H), 2.50 (broad s, 1 H), 2.03–1.07 (3 unresolved broad peaks, 9 ring protons); ^{13}C NMR (CDCl_3) δ 150.43, 88.85, 81.55, 65.58, 45.04, 34.95, 31.50, 25.00, 24.30.

trans-2-(Ethenyloxymethyl)cyclohexanol. ^1H NMR (CDCl_3) δ 6.41 (d of d, $J_{\text{trans}} = 14.33$ Hz, $J_{\text{cis}} = 6.80$ Hz, 1 H), 4.15 (d of d, $J_{\text{trans}} = 14.33$ Hz, $J_{\text{gem}} = 2.06$ Hz, 1 H), 3.69 (apparent d, $J = 6.80$ Hz, 1 H), the remainder of the absorptions were obscured by the signals of the major isomer; ^{13}C NMR (CDCl_3) δ 151.52, 86.83, 73.13, 71.72, 44.22, 34.95, 31.50, 25.00, 24.43.

4-Ethenyloxy-1-butanol. Cleavage of 10.1 g (51.3 mmol) of 2-bromomethyl-1,3-dioxepane [11] with 7.2 g (0.31 mol) of metallic sodium gave 5.9 g (98%) of product: ^1H NMR (CDCl_3) δ 6.40 (d of d, $J_{\text{trans}} = 14.33$ Hz, $J_{\text{cis}} = 6.80$ Hz, 1 H), 4.12 (d of d, $J_{\text{trans}} = 14.33$ Hz, $J_{\text{gem}} = 1.97$ Hz, 1 H), 3.93 (d of d, $J_{\text{cis}} = 6.80$ Hz, $J_{\text{gem}} = 1.97$ Hz, 1 H), 3.68–3.57 (overlap-

ping patterns, 4 H, i.e., 3.66 (t, $J = 6.05$ Hz), 3.61–3.57 (m)), 2.30 (broad s, 1 H), 1.73–1.57 (m, 4 H); ^{13}C NMR (CDCl_3) δ 151.64, 86.48, 67.76, 62.24, 29.28, 25.47.

General Procedure for Preparation of 3-Iodoalkyl Vinyl Ethers. The method of Crossland and Servis [17] was followed for the preparation of the mesylate from the 3-ethenyloxy-1-alkanol. The crude mesylates were, in turn, converted into iodides by treatment with 2.2 equivalents of dry sodium iodide in anhydrous acetone (ca. 85 mL for a 25 mmol-scale reaction) containing a small quantity of anhydrous potassium carbonate (ca. 250–500 mg) to prevent hydrolysis by adventitious acid. For the most part, the nucleophilic substitutions were completed by stirring the reaction mixtures for 15 h at room temperature under an atmosphere of dry nitrogen although it was sometimes necessary to heat the reaction mixture at gentle reflux to complete the displacement. The reaction mixture was then filtered, the solids were washed with fresh acetone, and the combined filtrates and washings were washed with dilute, aqueous NaOH solution. The organic layer was dried over anhydrous potassium carbonate, filtered, and concentrated to give the iodides. Where necessary, the products were purified by chromatography.

E- and Z-1-Iodo-4-oxaundec-5-ene (7). A mixture of 3.09 g (17.9 mmol) of *E*- and *Z*-4-oxaundec-5-ene-1-ol [14] (approximately 90% *E* and 10% *Z*) was converted via the mesylate to 4.90 g (96%) of an approximately 90:10 mixture of isomeric iodides: mass spectroscopic molecular weight calcd for (the isomeric mixture) $\text{C}_{10}\text{H}_{19}\text{OI}$ (M^+) 282.0482, found, 282.0485. The mixture was used in subsequent reactions but it was possible to extract the following NMR parameters for the individual isomers from the NMR spectrum of the mixture.

E-1-Iodo-4-oxa-undec-5-ene. ^1H NMR (CDCl_3) δ 6.21 (d, $J_{\text{trans}} = 12.58$ Hz, 1 H, H(5)), 4.79 (d of t, $J_{\text{trans}} = 12.58$ Hz, $^3J = 7.32$ Hz, 1 H, H(6)), 3.70 (t, $J = 5.82$ Hz, 2 H, H(3)), 3.27 (t, $J = 6.79$ Hz, 2 H, H(1)), 2.17–2.05 (m, 2 H, H(2)), 1.91–1.86 (m, 2 H, H(7)), 1.35–1.23 (broad m, 6 H, H(8,9,10)), 0.88 (t, $J = 6.60$ Hz, 3 H, H(11)); ^{13}C NMR (CDCl_3) δ 145.70 (C(5)), 103.47 (C(6)), 64.78 (C(3)), 33.59 (C(2)), 31.58 (C(7)), 29.12 (C(8)), 24.68 (C(9)), 22.64 (C(10)), 14.07 (C(11)), 3.52 (C(1)).

Z-1-Iodo-4-oxa-undec-5-ene. ^1H NMR (CDCl_3) δ 5.92 (d, $J_{\text{cis}} = 8.07$ Hz, 1 H, H(5)), the other resonances are obscured by the strong absorptions of the *E*-isomer; ^{13}C NMR (CDCl_3) δ 144.38 (C(5)), 107.93 (C(6)), 71.11 (C(3)), 33.32 (C(2)), 14.07 (C(11)), 2.45 (C(1)), the remaining resonances are common to those of the *E*-isomer.

1-Ethenyloxy-3-iodopropane (3). 3-Ethenyloxy-1-propanol (4.60 g, 45.0 mmol) was converted via the mesylate to the title iodide. Purification by chromatography on a short column of activated alumina using pentane as the eluent gave 1.60 g (17% from alcohol) of the known [18] product; ^1H NMR (CDCl_3) δ 6.46 (d of d, $J_{\text{trans}} = 14.35$ Hz, $J_{\text{cis}} = 6.82$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 4.21 (d of d, $J_{\text{trans}} = 14.35$ Hz, $J_{\text{gem}} = 2.13$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 4.02 (d of d, $J_{\text{cis}} = 6.82$ Hz, $J_{\text{gem}} = 2.13$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 3.75 (t, $J = 5.83$ Hz, 2 H, H(1)), 3.28 (t, $J = 6.78$ Hz, 2 H, H(3)), 2.15 (pentet, $J = 5.83$ Hz, 2 H, H(2)); ^{13}C NMR (CDCl_3) δ 151.52 ($\text{OCH}=\text{CH}_2$), 86.82 ($\text{OCH}=\text{CH}_2$), 67.20 (C(1)), 32.74 (C(2)), 2.31 (C(3)).

3-Ethenyloxy-1-iodobutane. The iodide was prepared via the mesylate from 4.21 g (36.2 mmol) of a mixture of ca. 62% 3-ethenyloxy-1-butanol and ca. 38% 4-ethenyloxy-2-butanol. Column chromatography of the crude product on 500 g of a 1:1 mixture of anhydrous K_2CO_3 and silica gel (10% EtOAc/hexane) gave 3.47 g (42%) of pure title iodide: ^1H NMR (CDCl_3) δ 6.29 (d of d, $J_{\text{trans}} = 14.13$ Hz, $J_{\text{cis}} = 6.57$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 4.27 (d of d, $J_{\text{trans}} = 14.13$ Hz, $J_{\text{gem}} = 1.61$ Hz, 1 H, $\text{trans-OCH}=\text{CH}_2$), 4.04–3.92 (overlapping patterns, 2 H, i.e., 3.99 (d of d, $J_{\text{cis}} = 6.57$ Hz, $J_{\text{gem}} = 1.61$ Hz, $\text{OCH}=\text{CH}_2$), 3.80–3.71 (m, H(3)), 3.20 (m, 2 H, H(1)), 2.14–1.87 (m, 2 H, H(2)), 1.20 (d, $J = 6.20$ Hz, 3 H, H(4)); ^{13}C NMR (68 MHz, CDCl_3) δ 150.62 ($\text{OCH}=\text{CH}_2$), 88.60 ($\text{OCH}=\text{CH}_2$), 75.20 (C(3)), 40.22 (C(2)), 19.32 (C(4)), 1.79 (C(1)); mass spectroscopic molecular weight calcd for $\text{C}_6\text{H}_{11}\text{OI}$ (M^+), 225.9857, found, 225.9864.

3-Ethenyloxy-2-ethyl-1-iodopropane. The iodide was prepared via the mesylate from 3.00 g (23.0 mmol) of 3-ethenyloxy-2-ethyl-1-propanol. Column chromatography of the crude product on 500 g of a 1:1 mixture of K_2CO_3 and silica gel (10% ethyl acetate/hexane) afforded 5.40 g (98%) of pure title iodide: ^1H NMR (CDCl_3) δ 6.37 (d of d, $J_{\text{trans}} = 14.36$ Hz, $J_{\text{cis}} = 6.82$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 4.10 (d of d, $J_{\text{trans}} = 14.36$ Hz, $J_{\text{gem}} = 2.01$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 3.91 (d of d, $J_{\text{cis}} = 6.82$ Hz, $J_{\text{gem}} = 2.01$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 3.57–3.19 (unresolved, 4 H, H(1) and H(3)), 1.43–1.28 (unresolved, 3 H, H(2) and 2- CH_2CH_3), 0.84 (t, $J = 7.30$ Hz, 3 H, 2- CH_2CH_3); ^{13}C NMR (CDCl_3) δ 151.50 ($\text{OCH}=\text{CH}_2$), 86.48 ($\text{OCH}=\text{CH}_2$), 69.61 (C(3)), 40.50 (C(2)), 24.07 (2- CH_2CH_3), 11.10 (2- CH_2CH_3), 10.88 (C(1)); mass spectroscopic molecular weight calcd for $\text{C}_7\text{H}_{13}\text{OI}$ (M^+), 240.0013, found, 240.0025.

trans-1-Ethenyloxy-2(iodomethyl)cyclohexane. The iodide was prepared via the mesylate from 6.73 g (43.1 mmol) of a mixture of ca. 65% *trans*-[1-(2-ethenyloxy)cyclohexyl]methanol and ca. 35% *trans*-2-(ethenyloxymethyl)cyclohexanol. Purification of the crude product by column chromatography on

500 g of a 1 : 1 mixture of K_2CO_3 and silica gel (10% ethyl acetate/hexane) afforded 6.30 g (55% from the mixture of alcohols) of pure iodide: ^1H NMR (CDCl_3) δ 6.31 (d of d, $J_{\text{trans}} = 14.04$ Hz, $J_{\text{cis}} = 6.49$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 4.28 (d of d, $J_{\text{trans}} = 14.04$ Hz, $J_{\text{gem}} = 1.52$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 3.96 (d of d, $J_{\text{cis}} = 6.49$ Hz, $J_{\text{gem}} = 1.52$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 3.47–3.29 (m, overlapping patterns, 3 H, H(1) & $\text{CH}_2\text{-I}$), 2.07–1.18 (complex m, 9 ring protons); ^{13}C NMR (CDCl_3) δ 150.89 ($\text{OCH}=\text{CH}_2$), 88.48 ($\text{OCH}=\text{CH}_2$), 81.11 (C(1)), 43.61 (C(2)), 31.64 (C(6)), 31.22 (C(3)), 24.80 (C(5)), 24.51 (C(4)), 13.30 ($\text{CH}_2\text{-I}$); mass spectroscopic molecular weight calcd for $\text{C}_9\text{H}_{15}\text{OI}$ (M^+), 266.0168, found, 266.0179.

4-Ethenyloxy-1-iodobutane. The iodide was prepared via the mesylate from 6.2 g (53.4 mmol) of 4-ethenyloxy-1-butanol. Column chromatography of the crude product on 500 g of a 1:1 mixture of K_2CO_3 and silica gel (10% ethyl acetate/hexane) afforded 9.65 g (80%) of the known [18] title iodide: ^1H NMR (CDCl_3) δ 6.39 (d of d, $J_{\text{trans}} = 14.34$ Hz, $J_{\text{cis}} = 6.81$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 4.11 (d of d, $J_{\text{trans}} = 14.34$ Hz, $J_{\text{gem}} = 2.00$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 3.93 (d of d, $J_{\text{cis}} = 6.81$ Hz, $J_{\text{gem}} = 2.00$ Hz, 1 H, $\text{OCH}=\text{CH}_2$), 3.64 (t, $J = 6.06$ Hz, 2 H, H(4)), 3.17 (t, $J = 6.82$ Hz, 2 H, H(1)), 1.92–1.57 (m, 4 H, H(2,3)); ^{13}C NMR (68 MHz, CDCl_3) δ 151.58 ($\text{OCH}=\text{CH}_2$), 86.40 ($\text{OCH}=\text{CH}_2$), 66.48 (C(4)), 29.99 (C(3)), 29.78 (C(2)), 6.31 (C(1)).

General Procedure for the Preparation and Rearrangement of 4-Oxa-5-hexenyllithiums. An appropriately sized single-necked, round-bottomed flask, fitted with a magnetic stirring bar and a rubber septum, was flame dried under argon. The cooled flask was charged with the appropriate 3-iodoalkyl vinyl ether and enough *n*-pentane/diethyl ether (in a 3:2 ratio by volume) to give an approximately 0.1 M solution. The flask and its contents were then cooled, with stirring, to -78°C (dry-ice/acetone) and 2.2 equivalents of *t*-butyllithium in pentane (Aldrich) was added dropwise via syringe over a 5-min period. The solution was stirred for an additional 5 min at -78°C , the cooling bath was then removed, and the mixture was allowed to warm to room temperature. Upon reaching ambient temperature, the mixture was allowed to stand for 1 h without stirring. The solution was then treated with an excess of either deoxygenated methanol or deoxygenated water, washed with two portions of water, dried (anhydrous potassium carbonate), filtered, and concentrated to give the 4-alken-1-ols listed in Table 1.

The products listed in Table 1 are known compounds whose physical and spectroscopic properties were fully in accord with those reported for 4-penten-1-ol (5) [19], 5-hexen-2-ol [20], 2-ethyl-4-penten-1-ol [21], *trans*-2-allylcyclohexanol [22], 5-

hexen-1-ol [23], and (2-ethenylbenzene)methanol [24].

Treatment of 2-Allyloxyethyl Iodide (1) with t-BuLi: Formation of Allyl Alcohol and Ethylene. An approximately 0.1 M solution of 262.5 mg (1.24 mmol) of **1** in *n*-pentane–diethyl ether (3:2 by volume) was treated with 2.2 equivalents of *t*-BuLi following the procedure outlined above. The mixture was stirred at -78°C for 5 min and 1 mL of deoxygenated methanol was added to the cold solution. The only product present by gas chromatographic analysis on a 25 m \times 0.20 mm cross-linked methyl silicone column was allyl alcohol. The reaction was repeated and the effluent gas was bubbled through a cold (-78°C) pentane solution of bromine to trap the ethylene fragment and 1,2-dibromoethane was identified by GC analysis of the mixture.

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