# Synthesis of Cyclic and Acyclic Enol Ethers (Vinyl Ethers)

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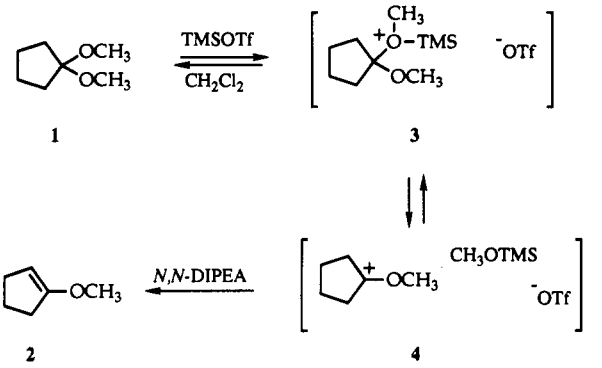
A general method has been developed for the conversion of both cyclic and acyclic acetals of cyclic ketones, acyclic ketones, and aldehydes into enol ethers through treatment of the acetal with trimethylsilyl triflate in the presence of *N,N*-diisopropylethylamine. The range of isolated yields of enol ethers from the various classes of acetals was as follows: cyclic acetals of cyclic ketones, 83–98%; acyclic acetals of ketones, 72–94%; acyclic and cyclic acetals of aldehydes, 65–90%.

Although the literature contains several methods for the preparation of enol ethers,[2-4] none of these general procedures provides all of the generally desirable qualities of giving uniformly high yields through a simple process which uses readily available reagents. We now report that treatment of acetals of enolizable ketones and aldehydes with trimethylsilyl triflate (TMSOTf) and *N,N*-diisopropylethylamine (DIPEA) yields enol ethers via a procedure which meets all of the criteria set forth above.

Noyori and others have shown that TMSOTf is a useful catalyst for the formation of acetals.[5] Our need for ready access to a wide variety of enol ethers[6] prompted us to carefully consider the mechanistic details of acetal formation through the use of TMSOTf as a catalyst. Since it was probable that an equilibrium process was involved in the Noyori approach to acetal synthesis, we reasoned that the addition of a hindered base should intercept the equilibrium process and lead to the formation of enol ethers. Our exploration of this possibility led to the development of the general method for enol ether synthesis described in this paper.[7,8]

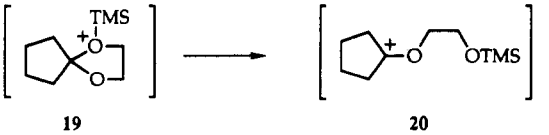
As shown in Table I, treatment of the dimethyl acetals of cyclic ketones with 1.1–1.5 equiv of TMSOTf and 1.2–1.7 equiv of DIPEA gave the appropriate cyclic methyl vinyl ethers in 72–94% distilled yields. Mechanistically, these transformations can be viewed as occurring by the stepwise process illustrated in Scheme I for the conversion

**Scheme I**




of **1** into **2**. It seems probable that the first step involves an equilibrium process in which **3** is generated. Loss of the trimethylsilyl ether of methanol would give **4**. Deprotonation of **4** by a non-nucleophilic base would then produce **2**.

Additional insight into this mechanistic speculation was provided by the study of the conversion of cyclic acetals (dioxolanes, dioxanes, and 5,5-dimethyldioxanes) of cyclic ketones into enol ethers. As shown in Table II, the various ethylene glycol acetals (dioxolanes) of ketones and propane-1,3-diol acetals (dioxanes and 5,5-dimethyldioxanes) of ketones were converted into their corresponding enol ethers in 83–98% yields upon treatment with 1.2–2.1 equiv of TMSOTf in combination with 1.3–2.3 equiv of DIPEA. As can be noted in the formation of **18** from **17**, the trimethylsilyl group was retained in the product. This is consistent with the initial formation of **19** from **17** and the sequential formation of **20** from **19**.




As shown in Table II, the formation of enol ethers from dioxolanes occurred more rapidly than from dioxanes. In addition, the 5,5-dimethylated dioxanes reacted more slowly than the unsubstituted dioxane class of acetals.

(1) University of Minnesota, Undergraduate Research Participant, 1989–1991.

(2) For leading references, see: (a) Wohl, R. A. *Synthesis* **1974**, 38. (b) Cookson, R. C.; Singh, P. *J. Chem. Soc. C* **1971**, 1477. Schank, K.; Pack, W. *Chem. Ber.* **1969**, *102*, 1892. Lindsay, D. G.; Reese, C. B. *Tetrahedron* **1965**, *21*, 1673. Meerwin, H. In Houben-Weyl, *Methoden der Organische Chemie*; Muller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1965; Vol. 6/3, p 199ff.

(3) (a) Miller, R. D.; McKean, D. R. *Tetrahedron Lett.* **1982**, *23*, 323. (b) Marsi, M.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1467. Marsi, M.; Gladysz, J. A. *Tetrahedron Lett.* **1982**, *23*, 631. Gladysz, J. A.; Williams, C.; Tam, W.; Johnson, D.; Parker, D.; Selover, J. *Inorg. Chem.* **1979**, *18*, 553. (c) Naruse, Y.; Yamamoto, H. *Tetrahedron Lett.* **1986**, *27*, 1363. (d) Katritzky, A. R.; Bayyuk, S. I.; Rachwal, S. *Synthesis* **1991**, 279.

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(5) Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron Lett.* **1981**, *37*, 3899. Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 1357. See also: Hwu, J. R.; Wetzel, J. M. *J. Org. Chem.* **1985**, *50*, 3946.

(6) Gassman, P. G.; Burns, S. J. *J. Org. Chem.* **1988**, *53*, 5576.

(7) For a preliminary report of part of this investigation, see: Gassman, P. G.; Burns, S. J. *J. Org. Chem.* **1988**, *53*, 5574.

(8) For subsequent applications and studies of our reaction, see: Sundberg, R. J.; Cherney, R. J. *J. Org. Chem.* **1990**, *55*, 6028. Rychnovsky, S.; Kim, J. *Tetrahedron Lett.* **1991**, *32*, 7219, 7223. Sundberg, R. J.; Gadamasetti, K. G. *Tetrahedron*, **1991**, *47*, 5673. Fioravanti, S.; Loreto, M. A.; Pellacani, L.; Tardella, P. A. *Tetrahedron* **1991**, *47*, 5877.

(9) Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. All boiling points are uncorrected. Proton and carbon magnetic resonance spectra were recorded on Nicolet NIC 1180E, Bruker AC-300, or Bruker AC-200 nuclear magnetic resonance spectrometers. Infrared absorption spectra were recorded on a Mattson Instruments Polaris Model fourier-transform infrared spectrophotometer as neat liquid films or dilute solutions. Mass spectra were measured on AEI-MS30 (for electron impact ionization spectra) and Finnegan 4000 (for chemical-ionization spectra) mass spectrometers.

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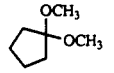
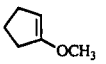
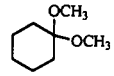
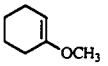
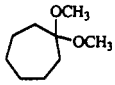
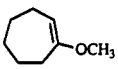
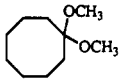
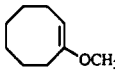
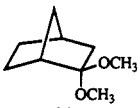
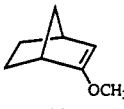
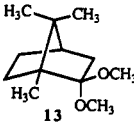
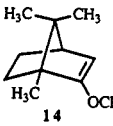
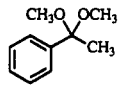
**Table I. Reaction of Ketone Dimethyl Acetals with Trimethylsilyl Triflate and *N,N*-Diisopropylethylamine**

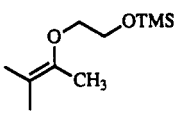
| reactant[a] | product | TMSOTf[b] (equiv) | DIPEA[c] (equiv) | temp[d] (°C) | reaction time (h) | yield[e] (%) |
|---|---|---|---|---|---|---|
|  1 |  2 | 1.1 | 1.2 | −20 → amb | 2 | 84 |
|  5 |  6 | 1.1 | 1.2 | −20 → amb | 3 | 94 |
|  7 |  8 | 1.5 | 1.6 | −20 → amb | 24 | 94 |
|  9 |  10 | 1.1 | 1.2 | −20 → amb | 4 | 91 |
|  11 |  12 | 1.1 | 1.2 | 0 → amb | 16 | 92 |
|  13 |  14 | 1.5 | 1.7 | 0 → amb | 18 | 72 |
|  15 |  16 | 1.1 | 1.3 | −23 → amb | 6 | 93 |

[a] Details regarding the preparation of the reactants may be found in the Experimental Section. [b] Trimethylsilyl trifluoromethanesulfonate. [c] *N,N*-Diisopropylethylamine. [d] The reaction mixture was cooled to the temperature indicated, the TMSOTf was added dropwise, the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature and was stirred for the time indicated. [e] Isolated (distilled) yield.

These observations, coupled with the forcing conditions required to convert **29** into **30**, indicated that steric hindrance led to considerable rate retardation. However, the rate retardation was not sufficient to stop the reaction from occurring over a reasonable amount of time.

The mechanistic considerations presented above suggest that the transfer of a proton from the cationic intermediate to the DIPEA may provide the basis for selective olefin formation. This premise was tested with a series of acetals of 2-methylcyclohexanone as shown in Table III. When **47** was treated with TMSOTf and DIPEA under the usual reaction conditions, an 89% yield of an 88:12 mixture of **48**:**49** was obtained. These results can be contrasted with those obtained through the use of other procedures[3] which gave ratios of **48**:**49** which approached the thermodynamic ratio of 63:37. Conversion of **50**, **53**, and **56** into their respective pairs of enol ethers gave isomer ratios which were at least 4:1 trisubstituted–tetrasubstituted olefin in each case.

In general, literature methods for the formation of enol ethers from acetals have been less successful with acyclic acetals than with cyclic acetals. The results of the application of our procedure to the synthesis of enol ethers from acetals of ketones are given in Table IV. As shown in Table IV, acetals of acyclic ketones gave yields of enol ethers which were very similar to those obtained from acetals of cyclic ketones. Both **63** and **66** offered the possibility of isomer formation. For **63**, a 63:37 ratio of **64**:**65** was observed with the *Z*-isomer predominating. From **66** the two possible isomers would be **67** and **68**. Only **67** was observed in 93% isolated yield. Again, it would appear that steric factors play an important role in our process and that the less hindered proton was exclusively abstracted by the hindered base.



**68**

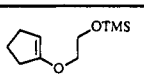
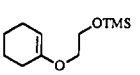
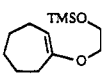
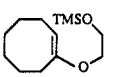
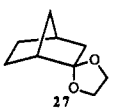
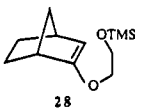
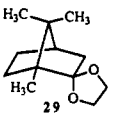
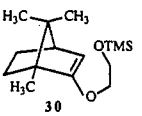
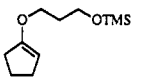
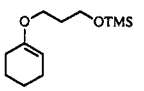
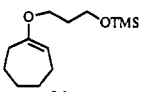
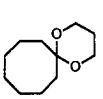
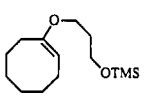
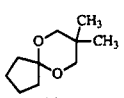
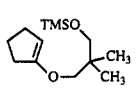
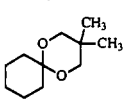
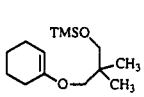
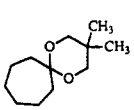
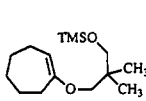
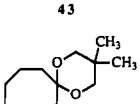
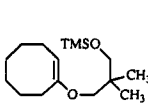
The last class of acetals to be examined was acetals of aldehydes. The enol ethers obtained from aldehyde acetals were found to be prone to facile polymerization, and as a result, yields of enol ethers were slightly lower than those obtained from acetals of ketones, as shown in Table V. For those cases in which a mixture of *E*- and *Z*-isomers could be formed, it was found that the *Z*-isomer predominated with a Z/E ratio being approximately 7:3.

In summary, a new, general process for the conversion of acetals of enolizable ketones and aldehydes into enol ethers has been developed. This process uses readily available reagents and routinely gives high yields.

## Experimental Section[9]

Dichloromethane ($CH_2Cl_2$) used in the reactions was of certified grade. DIPEA was distilled from and stored over potassium hydroxide prior to use. Reactions requiring an inert atmosphere were performed using house nitrogen as blanketing gas. 2,2-Dimethyl-1,3-dioxolane (**59**), 1,1-dimethoxy-2-phenylethane (**73**),

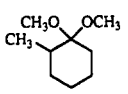
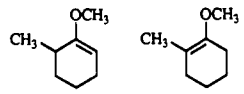
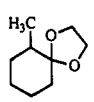
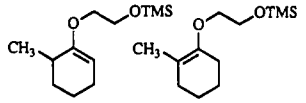
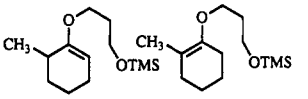
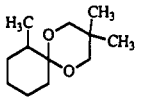
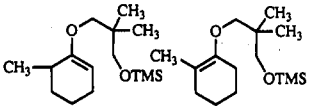
**Table II. Reaction of Cyclic Ketone Dioxolane and Dioxane Acetals with Trimethylsilyl Triflate and *N,N*-Diisopropylethylamine**

| reactant[a] | product | TMSOTf[b] (equiv) | DIPEA[c] (equiv) | temp[d] (°C) | reaction time (h) | yield[e] (%) |
|---|---|---|---|---|---|---|
|  17 |  18 | 1.2 | 1.3 | 0 → amb | 4 | 97 |
|  21 |  22 | 1.2 | 1.3 | 0 → amb | 4 | 94 |
|  23 |  24 | 1.5 | 1.6 | 0 → amb | 4 | 92 |
|  25 |  26 | 1.2 | 1.3 | 0 → amb | 4 | 98 |
|  27 |  28 | 1.2 | 1.5 | 0 → amb | 24 | 91 |
|  29 |  30 | 1.1<br>1.0 | 1.2<br>1.1 | 0 → amb;<br>reflux (40) | 5;<br>18 | 83 |
|  31 |  32 | 1.7 | 1.9 | 0 → amb | 6 | 89 |
|  33 |  34 | 1.7 | 1.9 | 0 → amb | 22 | 95 |
|  35 |  36 | 1.7 | 1.9 | 0 → amb | 6 | 93 |
|  37 |  38 | 1.7 | 1.9 | 0 → amb | 22 | 90 |
|  39 |  40 | 1.75 | 1.9 | 0 → amb | 24 | 95 |
|  41 |  42 | 1.75 | 1.9 | 0 → amb | 72 | 93 |
|  43 |  44 | 1.75 | 1.9 | 0 → amb | 45 | 93 |
|  45 |  46 | 1.75 | 1.9 | 0 → amb | 36 | 94 |

[a] Details regarding the preparation of the reactants may be found in the Experimental Section. [b] Trimethylsilyl trifluoromethanesulfonate. [c] *N,N*-Diisopropylethylamine. [d] The reaction mixture was cooled to the temperature indicated, the TMSOTf was added dropwise, the cooling bath was removed, and the reaction was allowed to warm to room temperature and was stirred for the time indicated. [e] Isolated (distilled) yield.

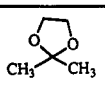
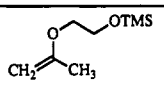
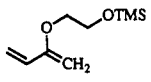
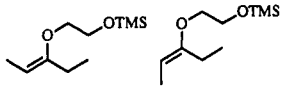
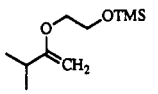
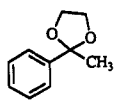
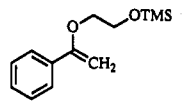
and 2-benzyl-1,3-dioxolane (**83**) were purchased from Aldrich Chemical Co. and were used without purification. With few exceptions, the acetals used in the study were previously reported compounds and were prepared via literature methods (vide infra).

**Table III. Reaction of Methyl-Substituted Cyclic Ketone Acetals with Trimethylsilyl Triflate and *N,N*-Diisopropylethylamine**

| reactant[a] | product(s) | product ratio[b] (tri:tetrasubs) | TMSOTf[c] (equiv) | DIPEA[d] (equiv) | temp[e] (°C) | reaction time (h) | yield[f] (%) |
|---|---|---|---|---|---|---|---|
|  47 |  48 49 | 88:12 | 1.1 | 1.2 | 0 → amb | 4 | 89 |
|  50 |  51 52 | 89:11 | 1.1 | 1.2 | 0 → amb | 5 | 96 |
|  53 |  54 55 | 82:18 | 1.75 | 1.9 | 0 → amb | 19 | 88 |
|  56 |  57 58 | 86:14 | 1.75 | 1.9 | 0 → amb | 16 | 90 |

[a] Details regarding the preparation of the reactants may be found in the Experimental Section. [b] Ratio of trisubstituted (major) product to tetrasubstituted (minor) product. [c] Trimethylsilyl trifluoromethanesulfonate. [d] *N,N*-Diisopropylethylamine. [e] The reaction mixture was cooled to the temperature indicated, the TMSOTf was added dropwise, the cooling bath was removed, and the reaction was allowed to warm to room temperature and was stirred for the time indicated. [f] Isolated (distilled) yield.

**Table IV. Reaction of Acyclic Ketone Dioxolane Acetals with Trimethylsilyl Triflate and *N,N*-Diisopropylethylamine**

| reactant[a] | product(s) | product ratio (*Z*:*E*) | TMSOTf[b] (equiv) | DIPEA[c] (equiv) | temp[d] (°C) | reaction time (h) | yield[e] (%) |
|---|---|---|---|---|---|---|---|
|  59 |  60 | | 1.2 | 1.3 | 0 → amb | 45 min | 90 |
|  61 |  62 | | 1.05 | 1.2 | ambient | 1 | 75 |
|  63 |  64 65 | 63:37 | 1.2 | 1.3 | 0 → amb | 2.5 | 93 |
|  66 |  67 | | 1.2 | 1.3 | 0 → amb | 1 | 93 |
|  69 |  70 | | 1.2 | 1.3 | 0 → amb | 24 | 92 |

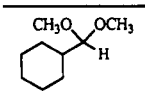
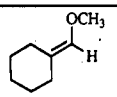
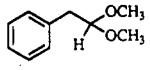
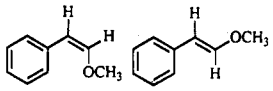
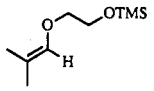
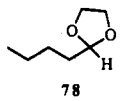
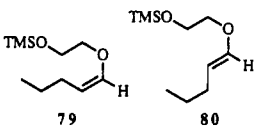
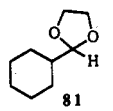
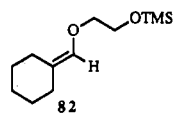
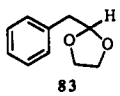
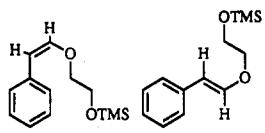
[a] Details regarding the preparation of the reactants may be found in the Experimental Section. [b] Trimethylsilyl trifluoromethanesulfonate. [c] *N,N*-Diisopropylethylamine. [d] The reaction mixture was cooled to the temperature indicated, the TMSOTf was added dropwise, the cooling bath was removed, and the reaction was allowed to warm to room temperature and was stirred for the time indicated. [e] Isolated (distilled) yield.

**Trimethylsilyl Trifluoromethanesulfonate (TMSOTf).** Trimethylsilyl triflate was prepared by the method of Emde et al.[10] and was isolated after distillation to afford 217 g (97%) of TMSOTf as a colorless, fuming liquid: bp 75–77 °C (75 mm) [lit.[10] bp 32 °C (12 mm)]; $^1$H NMR ($CDCl_3$) δ 0.49 (s); $^{13}$C NMR ($CDCl_3$) δ 118.4 (q, $J_{C-F}$ = 317 Hz), 0.3 (q).

**Preparation of Dimethyl Acetals.** In a typical procedure, the aldehyde or ketone (1.0 equiv) and trimethyl orthoformate (1.1–1.5 equiv) were dissolved in methanol (ca. 0.1 mL/mmol of ketone). The mixture was cooled, and an acid catalyst (concentrated $H_2SO_4$, *p*-toluenesulfonic acid, or Nafion resin, 1–5 mequiv) was added cautiously. The solution was refluxed with stirring until chromatographic analysis indicated that the reaction was complete (generally, several days). After cooling, the reaction mixture was neutralized with methanolic sodium methoxide. Residual methanol and trimethyl orthoformate were removed by distillation at ambient pressure; a final distillation of the crude product afforded the pure acetals used in the study. The following dimethyl acetals were prepared using this general method: 1,1-

(10) Emde, H.; Domsch, D.; Feger, H.; Frick, U.; Gotz, A.; Hergott, H.; Hofmann, K.; Kober, W.; Krageloh, K.; Oesterle, T.; Steppan, W.; West, W.; Simchen, G. *Synthesis* **1982**, 1.

**Table V. Reaction of Aldehyde Acetals with Trimethylsilyl Triflate and *N,N*-Diisopropylethylamine**

| reactant[a] | product(s) | product ratio (*Z*:*E*) | TMSOTf[b] (equiv) | DIPEA[c] (equiv) | temp[d] (°C) | reaction time (h) | yield[e] (%) |
|---|---|---|---|---|---|---|---|
|  71 |  72 | | 1.1 | 1.2 | −23; −23 → amb | 2; 1 | 87 |
|  73 |  74 75 | 70:30 | 1.1 | 2.0 | ambient | 3 min | 74 |
|  76 |  77 | | 1.1 | 1.3 | 0 | 30 min | 88 |
|  78 |  79 80 | 72:28 | 1.1 | solvent[f] | 115 | 1 | 65 |
|  81 |  82 | | 1.1 | 1.3 | 0 → amb | 45 min | 90 |
|  83 |  84 85 | 74:26 | 1.05 | 1.3 | 0 | 15 min | 72 |

[a] Details regarding the preparation of the reactants may be found in the Experimental Section. [b] Trimethylsilyl trifluoromethanesulfonate. [c] *N,N*-Diisopropylethylamine. [d] The reaction mixture was cooled to the temperature indicated, the TMSOTf was added dropwise, the cooling bath was removed, and the reaction was allowed to warm to room temperature and was stirred for the time indicated. [e] Isolated (distilled) yield. [f] Used as reaction solvent.

dimethoxycyclopentane (1);[11] 1,1-dimethoxycyclohexane (5);[12] 1,1-dimethoxycycloheptane (7);[13] 1,1-dimethoxycyclooctane (9);[14] 2,2-dimethoxybicyclo[2.2.1]heptane (11);[15] 2,2-dimethoxy-1,7,7-trimethylbicyclo[2.2.1]heptane (13);[16] 1,1-dimethoxy-1-phenylethane (15);[17] 1,1-dimethoxy-2-methylcyclohexane (47);[18] and dimethoxymethylcyclohexane (71).[19]

**Preparation of Dioxolane and Dioxane Acetals.** In a typical procedure[20] used for the preparation of these cyclic acetals, a solution of the aldehyde or ketone (1.0 equiv), the requisite diol (ethylene glycol, 1,3-propanediol, or 2,2-dimethyl-1,3-propanediol, 1.1–1.5 equiv) and *p*-toluenesulfonic acid (1–5 mequiv) was dissolved in an appropriate solvent (benzene or toluene, 0.5–2.0 mL/mmol of ketone). The mixture was then refluxed with azeotropic removal of water until the theoretical amount of water had been collected or until chromatographic analysis suggested the reaction was complete. After cooling, the reaction mixture was extracted with dilute aqueous base, washed with water, and dried. Filtration, removal of the solvent, and distillation of the crude product afforded the pure acetals used in the study. In all cases, the physical characteristics (e.g., bp) and the spectral characterization of the acetals agreed completely with the published data[21] or were consistent with the assigned structure. The following classes of acetals were prepared using this general method.

**Dioxolanes**: 1,4-dioxaspiro[4.4]nonane (17);[22] 1,4-dioxaspiro[4.5]decane (21);[23] 1,4-dioxaspiro[4.6]undecane (23);[24] 1,4-dioxaspiro[4.7]dodecane (25);[25] spiro[bicyclo[2.2.1]heptane-2,2′-[1,3]dioxolane] (27);[26] spiro[1,7,7-trimethylbicyclo[2.2.1]heptane-2,2′-[1,3]dioxolane] (29);[26] 6-methyl-1,4-dioxaspiro[4.5]decane (50);[27] 2-diethyl-1,3-dioxolane (63);[28] 2-methyl-2-(1-methylethyl)-1,3-dioxolane (66);[27] and 2-methyl-2-phenyl-1,3-dioxolane (69).[23]

The following dioxolanes were prepared with these modifications to the method described above: (a) For 2-(1-methylethyl)-1,3-dioxolane (76),[29] $CH_2Cl_2$ was used as the azeotropant, and the concentration of ethylene glycol was increased to 2.1 equiv. (b) For 2-butyl-1,3-dioxolane (78)[30] and 2-cyclohexyl-1,3-dioxolane (81),[31] the ethylene glycol concentration was increased to 2.0 equiv. (c) For 2-ethenyl-2-methyl-1,3-dioxolane (61),[32] the ethylene glycol concentration was decreased to 1.1 equiv; to minimize polymerization, hexane was used as the azeotropant,

(11) Gorman, A. A.; Gould, I. R.; Hamblett, I. *J. Am. Chem. Soc.* **1982**, *104*, 7098.
(12) Lorette, N. B.; Howard, W. L.; Brown, J. H., Jr. *J. Org. Chem.* **1959**, *24*, 1731.
(13) Zajac, W. W., Jr.; Byrne, K. J. *J. Org. Chem.* **1970**, *35*, 3375.
(14) Olah, G.; Narang, S. C.; Meidar, D.; Salem, G. F. *Synthesis* **1981**, 282.
(15) McConaghy, J. S., Jr.; Bloomfield, J. J. *J. Org. Chem.* **1968**, *33*, 3425.
(16) Traylor, T. G.; Perrin, C. L. *J. Am. Chem. Soc.* **1966**, *88*, 4934.
(17) Taylor, R. *J. Chem. Soc., Perkins Trans. 2* **1988**, 737.
(18) Huggins, M. J.; Kubler, D. G. *J. Org. Chem.* **1983**, *48*, 2813.
(19) Kropp, P. J.; Pienta, N. J. *J. Org. Chem.* **1983**, *48*, 2084.
(20) For example, see: Salmi, E. J. *Chem. Ber.* **1958**, *71*, 1805.
(21) In this section, the references given after the compound name refer to the literature procedure used to prepare the specific compound and/or the reported physical and spectral characteristics used to confirm the identify of the product.
(22) Micovic, V. M.; Stojiljkovic, A. *Tetrahedron* **1958**, *4*, 186.
(23) Sulzbacher, M.; Bergmann, E.; Pariser, E. R. *J. Am. Chem. Soc.* **1948**, *70*, 2827.
(24) Treibs, W.; Grossman, P. *Chem. Ber.* **1959**, *92*, 267.
(25) Allenger, N. L.; Juidal, S. P.; DaRooge, M. A. *J. Org. Chem.* **1962**, *27*, 4290.
(26) Zajac, W. W., Jr.; Rhu, B.; Brown, R. K. *Can. J. Chem.* **1966**, *44*, 1547.
(27) Baudin, G.; Bowdon, D.; Pietrasanta, Y.; Pucci, B. *Tetrahedron* **1978**, *34*, 3269.
(28) Thuy, V. M.; Maitte, P. *Bull. Chim. Soc. Fr.* **1975**, *11–12*, 2558.
(29) Marton, D.; Slaviero, P.; Taglianini, G. *Gazz. Chim. Ital.* **1989**, *119(6)*, 359.
(30) Chien, J.-C.; Lillya, C. P.; Xu, B. B. *J. Polymer Sci., Part A: Polym. Chem.* **1986**, *24*, 2903.
(31) Burford, C.; Cooke, F.; Roy, G.; Magnus, P. *Tetrahedron* **1983**, *39*, 867.
(32) Hahn, E. F. *J. Org. Chem.* **1973**, *38*, 2092.

and pyridinium *p*-toluenesulfonate (0.35 mol %) was used as the acidic catalyst.

**Dioxanes**: 6,10-dioxaspiro[4.5]decane (**31**);[33] 1,5-dioxaspiro-[5.5]undecane (**33**);[20] 1,5-dioxaspiro[5.6]dodecane (**35**);[34] and 7-methyl-1,5-dioxaspiro[5.5]undecane (**53**).[35]

**5,5-Dimethyldioxanes**: 3,3-dimethyl-1,5-dioxaspiro[4.5]decane (**39**);[36] 3,3-dimethyl-1,5-dioxaspiro[5.5]undecane (**41**);[36] 3,3-dimethyl-1,5-dioxaspiro[5.6]dodecane (**43**);[36] and 3,3-dimethyl-1,5-dioxaspiro[5.7]tridecane (**45**).[36]

Physical and spectral data for those acetals previously unreported in the literature are presented below.

**1,5-Dioxaspiro[5.7]tridecane (37)**: bp 91–93 °C (2 mm); $^1$H NMR ($CDCl_3$) $\delta$ 3.82 (t, $J$ = 5.7 Hz, 4 H), 1.88 (m, 4 H), 1.63 (p, $J$ = 5.7 Hz, 2 H), 1.49 (bs, 10 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 101.2 (s), 59.1 (t), 31.3 (t), 28.1 (t), 25.5 (t), 24.8 (t), 21.3 (t); IR (neat) 2900, 2845, 2695, 1465, 1380, 1245, 1140, 1105, 975, 845 cm$^{-1}$; HRMS (EI, 30 eV) for $C_{11}H_{20}O_2$ ($M^+$) calcd 184.1460, found 184.1462.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.69; H, 10.92.

**3,3,7-Trimethyl-1,5-dioxaspiro[5.5]undecane (56)**: bp 94–95 °C (8 mm); $^1$H NMR ($CDCl_3$) $\delta$ 3.72 (d, $J$ = 11.3 Hz, 1 H), 3.58 (d, $J$ = 11.3 Hz, 1 H), 3.34 (d, $J$ = 11.3 Hz, 2 H), 2.51 (bd, $J$ = 12.7 Hz, 1 H), 1.72–1.68 (m, 1 H), 1.59–1.51 (m, 3 H), 1.39–1.42 (m, 4 H), 1.11 (s, 3 H), 1.00 (d, $J$ = 6.7 Hz, 3 H), 0.75 (s, 3 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 98.9 (s), 69.7 (t), 69.5 (t), 39.4 (d), 30.8 (t), 30.0 (s), 27.4 (t), 24.7 (t), 23.1 (q), 22.7 (t), 22.4 (q), 13.9 (q); IR (neat) 2930, 2850, 1470, 1450, 1395, 1375, 1285, 1220, 1155, 1110, 1040, 960, 890, 865 cm$^{-1}$; HRMS (EI, 30 eV) for $C_{12}H_{22}O_2$ ($M^+$) calcd 198.1605, found 198.1612.

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.84; H, 11.24.

**General Procedure for the Elimination of Methanol from Dimethyl Acetals Using Trimethylsilyl Triflate (Table I). 1-Methoxycyclopent-1-ene (2).** A reaction vessel was swept with dry nitrogen and charged with 1,1-dimethoxycyclopentane (**1**, 2.65 g, 20.4 mmol, 1.0 equiv), DIPEA (3.18 g, 24.7 mmol, 1.21 equiv), and $CH_2Cl_2$[37] (40 mL, 2.0 mL/mmol of substrate). After the solution was cooled to −20 °C, TMSOTf (4.35 mL, 5.0 g, 22.4 mmol, 1.1 equiv) was added dropwise via syringe to the cold solution with stirring; the pale yellow solution was allowed to warm to, and subsequently stir at, ambient temperature for 2 h. The reaction was quenched by the addition of aqueous NaOH solution (2.1 mL of a 1.0 N solution, 0.1 equiv), stirred vigorously for approximately 1 min, diluted with ca. 100 mL of pentane, and refrigerated overnight to precipitate the trialkylammonium triflate salt. The supernatant liquid was decanted from the salt and aqueous layer, and the salt and aqueous layer was extracted with three 20-mL portions of pentane. The combined organic fractions were dried over anhydrous $Na_2CO_3$; after filtration and removal of the solvent, the crude oil was distilled. If necessary, any residual DIPEA[38] was removed by a rapid chromatographic separation on basic alumina (Brockmann Activity Grade I), eluting with pentane. The pentane was removed by distillation to afford 1.88 g (84%) of **2** as a colorless, fragrant oil. Characterization of the product gave spectral data which agreed completely with the data reported in the literature.[2a,39]

The general procedure procedure described above was followed for the majority of the dimethyl acetals using the conditions of TMSOTf and DIPEA concentrations, temperature, and time presented in Table I. The following methyl vinyl ethers were prepared using this general procedure: 1-methoxycyclohex-1-ene (**6**);[40] 1-methoxycyclohept-1-ene (**8**);[2a] 1-methoxycyclooct-1-ene (**10**);[2a] 2-methoxybicyclo[2.2.1]hept-2-ene (**12**);[15] 2-methoxy-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene (**14**);[41] and 1-methoxy-1-phenylethene (**16**).[42]

**General Procedure for the TMSOTf-Mediated Ring Opening of Cyclic Ketone Acetals (Tables II and III). 1-[2-[(Trimethylsilyl)oxy]ethoxy]cyclohexene (22).** A solution of 1,4-dioxaspiro[4.5]decane (**21**, 25.4 g, 0.179 mol, 1.0 equiv), DIPEA (30.0 g, 0.232 mol, 1.3 equiv), and dry $CH_2Cl_2$[37] (280 mL, 1.6 mL/mmol of acetal substrate) was cooled in an ice–water bath, and TMSOTf (47.7 g, 41.5 mL, 0.214 mol, 1.2 equiv) was added via syringe to the stirred solution dropwise over a period of approximately 5 min. The solution was allowed to warm to, and was subsequently stirred at, ambient temperature for 4 h. After this time, approximately 200 mL of the solvent was removed by distillation at atmospheric pressure and replaced with a roughly equal volume of pentane, added dropwise with vigorous stirring. The resulting slurry was refrigerated overnight to assist in precipitating the *N*,*N*-diisopropylethylammonium triflate salt. After the supernatant solution was removed, the residual salt was rinsed with three 100-mL portions of pentane. The solvent was removed from the combined pentane fractions by distillation at atmospheric pressure; the resulting red oil was distilled at reduced pressure to afford 36.0 g (94%) of a colorless, sweet-smelling oil: bp 73–74 °C (0.65 mm); $^1$H NMR[3b] ($CDCl_3$) $\delta$ 4.55 (bs, 1 H), 3.70 (t, $J$ = 5 Hz, 2 H), 3.65 (t, $J$ = 5 Hz, 2 H), 2.0 (m, 4 H), 1.55 (m, 4 H), 0.10 (s, 9 H); $^{13}$C NMR[3b] ($CDCl_3$, 20 MHz) $\delta$ 154.2 (s), 93.4 (d), 67.1 (t), 61.2 (t), 27.5 (t), 23.2 (t), 22.6 (t), 22.5 (t), −0.7 (q); IR (neat) 3075, 2920, 2840, 1670, 1450, 1380, 1250, 1190, 1120, 840 cm$^{-1}$.

Physical and spectral data for the compounds prepared by this procedure are listed below. In all cases, analytical samples were prepared by preparative-scale GLC (10% OV-101 on 60/80 mesh Chromosorb W-NAW, 8 ft × 0.25 in., 100–175 °C). This general procedure was used for the majority of the acetals using the conditions of TMSOTf and DIPEA concentrations, temperature, and time presented in the tables.

**1-[2-[(Trimethylsilyl)oxy]ethoxy]cyclopentene (18)**: bp 77–78 °C (4 mm); $^1$H NMR ($CDCl_3$) $\delta$ 4.40 (dt, $J_d$ = 0.3 Hz, $J_t$ = 1.7 Hz, 1 H), 3.79 (bs, 4 H), 2.5–2.0 (m, 4 H), 2.0–1.7 (m, 2 H), 0.10 (s, 9 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 159.9 (s), 93.8 (d), 70.4 (t), 61.3 (t), 31.9 (t), 29.0 (t), 21.3 (t), −0.4 (q); IR (neat) 3080, 2960, 2870, 2850, 1650, 1350, 1250, 1135, 1105, 840 cm$^{-1}$; HRMS (EI, 20 eV) for $C_{10}H_{20}O_2Si$ ($M^+$) calcd 200.1232, found 200.1234.

Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 59.93; H, 10.04.

**1-[2-[(Trimethylsilyl)oxy]ethoxy]cycloheptene (24)**: bp 80–81 °C (0.7 mm); $^1$H NMR ($CDCl_3$) $\delta$ 4.61 (t, $J$ = 6.6 Hz, 1 H), 3.68 (m, 4 H), 2.25–1.75 (m, 4 H), 1.70–1.20 (m, 6 H), 0.05 (s, 9 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 161.0 (s), 96.9 (d), 67.8 (t), 61.3 (t), 33.6 (t), 32.0 (t), 28.0 (t), 25.4 (t), 25.3 (t), −0.5 (q); IR (neat) 3060, 2910, 2840, 1662, 1250, 1230, 1170, 1105, 835 cm$^{-1}$; HRMS (EI, 30 eV) for $C_{12}H_{24}O_2Si$ ($M^+$) calcd 228.1544, found 228.1538.

Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 62.85; H, 10.51.

**1-[2-[(Trimethylsilyl)oxy]ethoxy]cyclooctene (26)**: bp 76–77 °C (0.15 mm); $^1$H NMR ($CDCl_3$) $\delta$ 4.43 (t, $J$ = 8.6 Hz, 1 H), 3.72 (dd, $J_d$ = 5 Hz, $J_d$ = 10 Hz, 4 H), 2.2–1.8 (m, 4 H), 1.6–1.3 (bs, 8 H), 0.10 (s, 9 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 157.5 (s), 95.3 (d), 67.7 (t), 61.5 (t), 31.1 (t), 29.7 (t), 28.4 (t), 26.4 (t), 26.3 (t), 25.1 (t), −0.32 (q); IR (neat) 3070, 2930, 2860, 1670, 1475, 1460, 1260, 1175, 1115, 845 cm$^{-1}$; HRMS (EI, 30 eV) for $C_{13}H_{26}O_2Si$ ($M^+$) calcd 242.1700, found 242.1693.

Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.19; H, 10.74.

**2-[2-[(Trimethylsilyl)oxy]ethoxy]bicyclo[2.2.1]hept-2-ene (28)**: bp 80–81 °C (0.4 mm); $^1$H NMR ($CDCl_3$) $\delta$ 4.49 (d, $J$ = 3.1 Hz, 1 H), 3.79 (m, 2 H), 3.74–3.58 (m, 2 H), 2.78 (s, 1 H), 2.68 (s, 1 H), 1.72–1.57 (m, 2 H), 1.47–1.44 (m, 1 H), 1.26–1.09 (m, 2 H), 1.04 (d, $J$ = 7.8 Hz, 1 H), 0.11 (s, 9 H); $^{13}$C NMR ($CDCl_3$)

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(38) This procedure was specifically used for the isolation of those methyl vinyl ethers whose boiling points were sufficiently close to that of the amine used (bp 127 °C) to prevent complete removal of the amine by simple distillation.
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δ 166.1 (s), 97.5 (d), 69.9 (t), 61.1 (t), 47.0 (t), 43.9 (d), 40.8 (d), 28.2 (t), 24.8 (t), –0.4 (q); IR (neat) 3090, 2970, 2880, 1620, 1465, 1340, 1285, 1260, 1240, 1140, 1115, 965, 845, 785 cm$^{-1}$; HRMS (CI, $NH_3$ as ionizing gas) for $C_{12}H_{22}O_2Si$ (M + H$^+$) calcd 227.1448, found 227.1467.

Anal. Calcd for $C_{12}H_{22}O_2Si$: C, 63.66; H, 9.79. Found: C, 63.50; H, 9.83.

**2-[2-[(Trimethylsilyl)oxy]ethoxy]-1,7,7-trimethylbicyclo-[2.2.1]hept-2-ene (30).** Prepared as described in the General Method with the following modification (see Table II, entry 6). After the solution was stirred at ambient temperature for 5 h, an additional aliquot (1.1 equiv) of DIPEA was added, followed by the dropwise addition of additional TMSOTf (1.0 equiv). After the addition, the flask was fitted with a reflux condenser and the solution was refluxed for an additional 18 h. After cooling, the reaction was worked up as described to afford the product: bp 86–87 °C (0.95 mm); $^1$H NMR ($CDCl_3$) δ 4.45 (d, $J$ = 3.5 Hz, 1 H), 3.82 (t, $J$ = 5.2 Hz, 2 H), 3.77–3.59 (m, 2 H), 2.21 (t, $J$ = 3.4 Hz, 1 H), 1.82 (m, 1 H), 1.48 (dt, $J_d$ = 3.2 Hz, $J_t$ = 6.2 Hz, 1 H), 1.39 (dt, $J_d$ = 3.2 Hz, $J_t$ = 8.5 Hz, 1 H), 1.03 (dt, $J_d$ = 3 Hz, $J_t$ = 9.1 Hz, 1 H), 0.92 (s, 3 H), 0.85 (s, 3 H), 0.71 (s, 3 H), 0.12 (s, 9 H); $^{13}$C NMR ($CDCl_3$) δ 165.1 (s), 96.2 (d), 69.6 (t), 61.4 (t), 55.0 (s), 53.0 (s), 49.3 (d), 31.6 (t), 27.6 (t), 19.9 (q), 19.8 (q), 10.0 (q), –0.3 (q); IR (neat) 3080, 2950, 2870, 1625, 1460, 1330, 1255, 1140, 1110, 950, 840 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{15}H_{28}O_2Si$ (M + H$^+$) calcd 269.1936, found 269.1923.

Anal. Calcd for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51. Found: C, 66.97; H, 10.55.

**1-[[3-[(Trimethylsilyl)oxy]propyl]oxy]cyclopentene (32):** bp 54–56 °C (0.2 mm); $^1$H NMR ($CDCl_3$) δ 4.40 (t, $J$ = 1.6 Hz, 1 H), 3.77 (t, $J$ = 6.2 Hz, 2 H), 3.67 (t, $J$ = 6.2 Hz, 2 H), 2.28 (m, 4 H), 1.83 (m, 4 H), 0.06 (s, 9 H); $^{13}$C NMR ($CDCl_3$) δ 159.9 (s), 93.6 (d), 65.8 (t), 59.2 (t), 32.2 (t), 32.0 (t), 29.0 (t), 21.3 (t), –0.6 (q); IR (neat) 3080, 2950, 2850, 1740, 1645, 1350, 1250, 1090, 1020, 865, 840 cm$^{-1}$; HRMS (EI, 30 eV) for $C_{11}H_{22}O_2Si$ (M$^+$) calcd 214.1389, found 214.1390.

Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.34. Found: C, 61.61; H, 10.37.

**1-[[3-[(Trimethylsilyl)oxy]propyl]oxy]cyclohexene (34):** bp 61–63 °C (0.15 mm); $^1$H NMR ($CDCl_3$) δ 4.55 (t, $J$ = 3.4 Hz, 1 H), 3.77 (t, $J$ = 6.2 Hz, 4 H), 2.02 (m, 4 H), 1.84 (p, $J$ = 6.2 Hz, 2 H), 1.63 (m, 2 H), 1.51 (m, 2 H), 0.08 (s, 9 H); $^{13}$C NMR ($CDCl_3$) δ 154.5 (s), 93.7 (d), 62.7 (t), 59.4 (t), 32.3 (t), 27.7 (t), 23.6 (t), 23.0 (t), 22.6 (t), –0.6 (q); IR (neat) 3075, 2920, 2840, 1665, 1250, 1190, 1090, 865, 835 cm$^{-1}$; HRMS (EI, 30 eV) for $C_{12}H_{24}O_2Si$ (M$^+$) calcd 228.1546, found 228.1554.

Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 63.13; H, 10.56.

**1-[[3-[(Trimethylsilyl)oxy]propyl]oxy]cycloheptene (36):** bp 82–84 °C (0.5 mm); $^1$H NMR ($CDCl_3$) δ 4.69 (t, $J$ = 6.7 Hz, 1 H), 3.68 (t, $J$ = 6.2 Hz, 2 H), 3.58 (t, $J$ = 6.2 Hz, 2 H), 2.23 (m, 2 H), 2.03 (m, 2 H), 1.84 (p, $J$ = 6.2 Hz, 2 H), 1.68 (m, 2 H), 1.50 (m, 4 H), 0.09 (s, 9 H); $^{13}$C NMR ($CDCl_3$) δ 161.3 (s), 96.9 (d), 63.1 (t), 59.4 (t), 33.9 (t), 32.3 (t), 32.2 (t), 28.3 (t), 25.7 (t), 25.5 (t), –0.5 (q); IR (neat) 3065, 2920, 2850, 1665, 1480, 1450, 1255, 1235, 1175, 1130, 1090, 840 cm$^{-1}$; HRMS (EI, 30 eV) for $C_{13}H_{26}O_2Si$ (M$^+$) calcd 242.1702, found 242.1703.

Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.29; H, 10.80.

**1-[[3-[(Trimethylsilyl)oxy]propyl]oxy]cyclooctene (38):** bp 76–78 °C (0.15 mm); $^1$H NMR ($CDCl_3$) δ 4.46 (t, $J$ = 8.3 Hz, 1 H), 3.68 (t, $J$ = 6.2 Hz, 2 H), 3.65 (t, $J$ = 6.2 Hz, 2 H), 2.20 (m, 2 H), 2.05 (m, 2 H), 1.86 (p, $J$ = 6.2 Hz, 2 H), 1.53–1.46 (m, 8 H), 0.09 (s, 9 H); $^{13}$C NMR ($CDCl_3$) δ 157.5 (s), 95.1 (d), 62.7 (t), 59.4 (t), 32.2 (t), 31.2 (t), 29.8 (t), 28.5 (t), 26.4 (t), 26.3 (t), 25.1 (t), –0.5 (q); IR (neat) 3065, 2930, 2860, 1670, 1475, 1260, 1175, 1100, 875, 845 cm$^{-1}$; HRMS (EI, 30 eV) for $C_{14}H_{28}O_2Si$ (M$^+$) calcd 256.1856, found 256.1856.

Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 65.57; H, 11.01. Found: C, 65.66; H, 11.04.

**1-[[2,2-Dimethyl-3-[(trimethylsilyl)oxy]propyl]oxy]cyclopentene (40):** bp 72–73 °C (0.25 mm); $^1$H NMR ($CDCl_3$) δ 4.39 (bs, 1 H), 3.45 (s, 2 H), 3.33 (s, 2 H), 2.33–2.28 (m, 4 H), 1.83 (m, 2 H), 0.88 (s, 6 H), 0.06 (s, 9 H); $^{13}$C NMR ($CDCl_3$) δ 160.4 (s), 93.1 (d), 74.4 (t), 68.1 (t), 36.2 (s), 31.9 (t), 29.0 (t), 21.7 (q), 21.2 (t), –0.6 (q); IR (neat) 3090, 2960, 2910, 2860, 1650, 1480, 1410, 1370, 1255, 1180, 1095, 1045, 1030, 880, 840, 750 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{13}H_{26}O_2Si$ (M + H$^+$) calcd 243.1780, found 243.1778.

Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.54; H, 10.83.

**1-[[2,2-Dimethyl-3-[(trimethylsilyl)oxy]propyl]oxy]cyclohexene (42):** bp 104–105 °C (1.3 mm); $^1$H NMR ($CDCl_3$) δ 4.57 (t, $J$ = 3.4 Hz, 1 H), 3.33 (s, 2 H), 3.32 (s, 2 H), 2.03 (bs, 4 H), 1.69–1.49 (m, 4 H), 0.88 (s, 6 H), 0.07 (s, 9 H); $^{13}$C NMR ($CDCl_3$) δ 154.8 (s), 93.3 (d), 71.4 (t), 68.3 (t), 36.1 (s), 27.8 (t), 23.6 (t), 23.0 (t), 22.9 (t), 21.7 (q), –0.6 (q); IR (neat) 3070, 2960, 2930, 2865, 2845, 1672, 1480, 1390, 1345, 1275, 1265, 1255, 1190, 1175, 1095, 880, 845, 750 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{14}H_{28}O_2Si$ (M + H$^+$) calcd 257.1936, found 257.1920.

Anal. Calcd for $C_{14}H_{28}O_2Si$: C, 65.57; H, 11.00. Found: C, 65.83; H, 11.01.

**1-[[2,2-Dimethyl-3-[(trimethylsilyl)oxy]propyl]oxy]cycloheptene (44):** bp 88–89 °C (0.35 mm); $^1$H NMR ($CDCl_3$) δ 4.66 (t, $J$ = 6.7 Hz, 1 H), 3.33 (s, 2 H), 2.32 (s, 2 H), 2.25 (m, 2 H), 2.03 (m, 2 H), 1.66 (m, 2 H), 1.54 (m, 4 H), 0.87 (s, 6 H), 0.07 (s, 9 H); $^{13}$C NMR ($CDCl_3$) δ 161.7 (s), 96.5 (d), 71.8 (t), 68.3 (t), 36.1 (s), 33.9 (t), 32.3 (t), 28.4 (t), 25.7 (t), 25.6 (t), 21.8 (q), –0.5 (q); IR (neat) 3070, 2960, 2850, 1665, 1480, 1450, 1390, 1250, 1235, 1170, 1130, 1095(s), 1050, 875, 840, 750 cm$^{-1}$; HRMS (EI, 30 eV) for $C_{15}H_{30}O_2Si$ (M$^+$) calcd 270.2013, found 270.2021.

Anal. Calcd for $C_{15}H_{30}O_2Si$: C, 66.61; H, 11.18. Found: C, 66.67; H, 11.21.

**1-[[2,2-Dimethyl-3-[(trimethylsilyl)oxy]propyl]oxy]cyclooctene (46):** bp 99–100 °C (0.35 mm); $^1$H NMR ($CDCl_3$) δ 4.43 (t, $J$ = 8.3 Hz, 1 H), 3.33 (s, 2 H), 3.29 (s, 2 H), 2.22 (m, 2 H), 2.05 (bs, 2 H), 1.46 (bm, 8 H), 0.87 (s, 6 H), 0.06 (s, 9 H); $^{13}$C NMR ($CDCl_3$) δ 158.0 (s), 94.7 (d), 71.7 (t), 68.2 (t), 36.2 (s), 31.4 (t), 29.8 (t), 28.5 (t), 26.5 (t), 26.3 (t), 25.2 (t), 21.7 (q), –0.6 (q); IR (neat) 3070, 2950, 2850, 1660, 1475, 1465, 1450, 1400, 1360, 1260, 1250, 1230, 1180, 1160, 1090 (s), 835, 740 cm$^{-1}$; HRMS (CI, $NH_3$) for $C_{16}H_{32}O_2Si$ (M + H$^+$) calcd 285.2249, found 285.2249.

Anal. Calcd for $C_{16}H_{32}O_2Si$: C, 67.55; H, 11.34. Found: C, 67.71; H, 11.36.

**1-Methoxy-6-methylcyclohex-1-ene (48) and 1-methoxy-2-methylcyclohex-1-ene (49):** bp 72–73 °C (52 mm) [lit.[43] bp 58–60 °C (22 mm)]. The isomers were separated by preparative GLC on a 10% OV-275 preparative column (8 ft × 0.25 in.) for characterization. For **48**: $^1$H NMR ($CDCl_3$) δ 4.58 (t, $J$ = 3.8 Hz, 1 H), 3.47 (s, 3 H), 2.24 (q, $J$ = 6 Hz, 1 H), 2.04 (d, $J$ = 5.6 Hz, 2 H), 1.81–1.72 (m, 1 H), 1.63–1.35 (m, 3 H), 1.07 (d, $J$ = 6.1 Hz, 3 H); $^{13}$C NMR ($CDCl_3$) δ 159.1 (s), 92.7 (d), 53.6 (q), 32.1 (d), 31.5 (t), 24.0 (t), 21.2 (t), 16.9 (q); IR (neat) 3070, 2990, 2930, 2860, 2840, 1670, 1470, 1385, 1365, 1210, 1165 (s), 1120, 1025, 790 cm$^{-1}$. For **49**: $^1$H NMR ($CDCl_3$) δ 3.47 (s, 3 H), 2.09–2.05 (m, 2 H), 1.95–1.85 (m, 2 H), 1.67–1.61 (m, 2 H), 1.58 (bs, 3 H), 1.54–1.50 (m, 2 H); $^{13}$C NMR ($CDCl_3$) δ 147.84 (s), 113.92 (s), 56.06 (q), 30.23 (t), 24.76 (t), 23.55 (t), 22.84 (t), 15.61 (q); IR (neat) 2990, 2930, 2860, 2830, 1695, 1455, 1380, 1355, 1205, 1150, 1020 cm$^{-1}$.

**1-[2-[(Trimethylsilyl)oxy]ethoxy]-6-methylcyclohex-1-ene (51) and 1-[2-[(trimethylsilyl)oxy]ethoxy]-2-methylcyclohex-1-ene (52):** bp 77–78 °C (0.8 mm). Compounds **51** and **52** were separated by preparative GLC on a 10% OV-275 column for characterization. For **51**: $^1$H NMR ($CDCl_3$) δ 4.53 (t, $J$ = 3.7 Hz, 1 H), 3.81 (t, $J$ = 5.0 Hz, 2 H), 3.72–3.59 (m, 2 H), 2.25 (bd, $J$ = 5.8 Hz, 1 H), 2.05 (bd, $J$ = 5.6 Hz, 2 H), 1.80–1.35 (m, 4 H), 1.06 (d, $J$ = 7 Hz, 3 H), 0.18 (s, 9 H); $^{13}$C NMR ($CDCl_3$) δ 158.3 (s), 93.6 (d), 67.5 (t), 61.5 (t), 32.1 (d), 31.4 (t), 24.1 (t), 20.0 (t), 19.1 (q), –0.4 (q); IR (neat) 3060, 2960, 2930, 2870, 1670, 1460, 1255, 1190, 1135, 1110, 960, 840 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{12}H_{24}O_2Si$ (M$^+$) calcd 228.1545, found 228.1542.

Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 62.93; H, 10.47.

For **52**: $^1$H NMR ($CDCl_3$) δ 3.81 (dt, $J$ = 5.8 Hz, $J$ = 4.8 Hz, 4 H), 2.07–2.02 (bm, 2 H), 1.64 (dq, $J$ = 2.2, 3.8 Hz, 2 H), 1.56 (t, $J$ = 0.8 Hz, 3 H), 1.56–1.47 (m, 4 H), 0.08 (s, 9 H); $^{13}$C NMR ($CDCl_3$) δ 147.8 (s), 114.4 (s), 70.2 (t), 62.7 (t), 30.8 (t), 26.1 (t), 24.3 (t), 23.6 (t), 16.1 (q), –0.5 (q); IR (neat) 2920, 2860, 2815, 1695, 1450, 1350, 1255, 1180, 1165, 1120, 950, 840, 750 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{12}H_{24}O_2Si$ (M$^+$) calcd 228.1545, found 228.1532.

(43) Rhoads, S. J.; Chattopadhyay, K.; Waali, E. *J. Org. Chem.* **1970**, *35*, 3352.

Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 63.16; H, 10.56.

**1-[[3-[(Trimethylsilyl)oxy]propyl]oxy]-6-methylcyclohex-1-ene (54) and 1-[[3-[(trimethylsilyl)oxy]propyl]oxy]-2-methylcyclohex-1-ene (55)**: bp 81–82 °C (0.4 mm). Compounds **54** and **55** were separated for characterization by preparative GLC on a 10% OV-275 column at 150 °C. For **54**: $^1H$ NMR ($CDCl_3$) $\delta$ 4.54 (t, $J$ = 3.8 Hz, 1 H), 3.70–3.60 (m, inc. t, $J$ = 6.2 Hz, 4 H), 2.00 (m, 2 H), 2.21 (dd, $J$ = 6.4, 6.1 Hz, 1 H), 1.85 (t, $J$ = 6.2 Hz, 2 H), 1.73–1.26 (m, 4 H), 1.04 (d, $J$ = 7 Hz, 3 H), 0.10 (s, 9 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 158.2 (s), 93.2 (d), 62.6 (t), 59.5 (t), 32.4 (t), 32.2 (d), 31.5 (t), 24.1 (t), 20.3 (t), 19.0 (q), –0.5 (q); IR ($CDCl_3$) 3060, 2950, 2925, 2870, 1660, 1460, 1440, 1340, 1260, 1250, 1220, 1170, 1070 (s,b), 1010, 960, 840 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{13}H_{26}O_2Si$ ($M^+$) calcd 242.1702, found 242.1695.

Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.72; H, 10.96.

For **55**: $^1H$ NMR ($CDCl_3$) $\delta$ 3.69 (m, inc. q, $J$ = 6.4 Hz, 4 H), 2.12 (bm, 2 H), 1.92 (bm, 2 H), 1.80 (dt, $J$ = 6.3 Hz, 2 H), 1.76–1.47 (m, 4 H), 1.58 (bs, 3 H), 0.09 (s, 9 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 146.8 (s), 114.2 (s), 64.7 (t), 59.5 (t), 33.2 (t), 30.3 (t), 25.4 (t), 23.6 (t), 22.9 (t), 15.8 (q), –0.5 (q); IR ($CDCl_3$) 2920, 2860, 1710 (w), 1690, 1440, 1375, 1350, 1260, 1250, 1155, 1075 (s,b), 1010, 960, 860, 840 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{13}H_{26}O_2Si$ ($M^+$) calcd 242.1702, found 242.1711.

Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.56; H, 10.92.

**1-[[2,2-Dimethyl-3-[(trimethylsilyl)oxy]propyl]oxy]-6-methylcyclohex-1-ene (57) and 1-[[2,2-dimethyl-3-[(trimethylsilyl)oxy]propyl]oxy]-2-methylcyclohex-1-ene (58)**: bp 88–89 °C (0.55 mm). Compounds **57** and **58** were separated for characterization by preparative GLC on a 10% OV-275 column at 150 °C. For **57**: $^1H$ NMR ($CDCl_3$) $\delta$ 4.51 (t, $J$ = 3.8 Hz, 1 H), 3.38–3.24 (m, 4 H), 2.26 (bq, $J$ = 6.5 Hz, 1 H), 2.03 (bd, $J$ = 5.8 Hz, 2 H), 1.79–1.74 (m, 1 H), 1.62–1.30 (m, 3 H), 1.05 (d, $J$ = 6.9 Hz, 3 H), 0.88 (s, 6 H), 0.06 (s, 9 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 158.4 (s), 92.8 (d), 73.6 (t), 71.4 (t), 36.3 (s), 32.4 (d), 31.6 (t), 24.2 (t), 21.7 (q), 20.6 (t), 19.0 (q), –0.6 (q); IR (neat) 3160, 2950, 2930, 2860, 1665, 1475, 1365, 1260, 1250, 1190, 1110, 1090, 875, 840 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{15}H_{30}O_2Si$ ($M^+$) calcd 270.2015, found 270.2004.

Anal. Calcd for $C_{15}H_{30}O_2Si$: C, 66.61; H, 11.18. Found: C, 66.73; H, 11.22.

For **58**: $^1H$ NMR ($CDCl_3$) $\delta$ 3.35 (s, 2 H), 3.34 (s, 2 H), 2.13–2.04 (m, 2 H), 1.94–1.87 (m, 2 H), 1.60 (bs, 3 H), 1.68–1.44 (m, 4 H), 0.890 (s, 6 H), 0.07 (s, 9 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 147.2 (s), 113.7 (s), 68.4 (t), 68.3 (t), 36.7 (s), 30.3 (t), 25.5 (t), 23.7 (t), 22.9 (t), 22.0 (q), 15.7 (q), –0.6 (q); IR (neat) 2960, 2930, 2860, 1695, 1670, 1480, 1405, 1365, 1265, 1255, 1185, 1160, 1095, 1035, 880, 840 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{15}H_{30}O_2Si$ ($M^+$) calcd 270.2015, found 270.2014.

Anal. Calcd for $C_{15}H_{30}O_2Si$: C, 66.61; H, 11.18. Found: C, 66.97; H, 11.30.

**General Procedure for the Reaction of Cyclic Acetals Derived from Acyclic Ketones with TMSOTf/DIPEA (Table IV). 2-[2-[(Trimethylsilyl)oxy]ethoxy]propene (60).** A solution of 2,2-dimethyl-1,3-dioxolane (**59**, 14.5 g, 0.142 mol, 1.0 equiv), DIPEA (23.5 g, 0.182 mol, 1.3 equiv), and dry $CH_2Cl_2$ (230 mL, 1.7 mL/mmol of acetal substrate) under nitrogen was cooled in an ice–water bath, and TMSOTf (37.9 g, 33.0 mL, 0.171 mol, 1.2 equiv) was added via syringe to the stirred solution dropwise over a period of approximately 5 min. The solution was allowed to warm to, and subsequently stirred at, ambient temperature for 45 min. Approximately 450 mL of pentane was added dropwise and with vigorous stirring to the reaction. After withdrawing the supernatant solution, the residual salt was rinsed with three 100-mL portions of pentane. The combined organic fractions were washed with 200 mL of a 10% aqueous NaOH solution and three 100-mL portions of $H_2O$ and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the resulting oil was distilled at reduced pressure to afford 22.3 g (90%) of the product as a colorless oil: bp 72 °C (24 mm); $^1H$ NMR ($CDCl_3$) $\delta$ 3.86–3.80 (bd, 4 H), 3.73–3.68 (m, 2 H), 1.89 (d, $J$ = 0.6 Hz, 3 H), 0.13 (s, 9 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 159.7 (s), 81.2 (t), 68.4 (t), 61.2 (t), 20.8 (q), –0.5 (q); IR (neat) 3122, 2992, 2875, 1659, 1597, 1380, 1281, 1251, 1093, 857 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_8H_{19}O_2Si$ ($M + H^+$) calcd 175.1154, found 175.1149.

Anal. Calcd for $C_8H_{18}O_2Si$: C, 55.12; H, 10.41. Found: C, 55.16; H, 10.43.

Physical characteristics and spectral data for the following products, prepared using the general procedure described above and the conditions given in Table IV, are presented below.

**2-[2-[(Trimethylsilyl)oxy]ethoxy]-1,3-butadiene (62)**: bp 81–82 °C (21 mm); $^1H$ NMR ($CDCl_3$) $\delta$ 6.22–5.06 (vinyl ABX, 3 H), 4.13 (bs, 1 H), 3.93–3.79 (m, 4 H), 0.14 (s, 9 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 157.5 (s), 132.5 (d), 113.5 (t), 86.4 (t), 67.8 (t), 60.4 (t), –1.2 (q); IR (neat) 3124, 3104, 3029, 2957, 2935, 1582, 1308, 1251, 1137, 1099, 843 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_9H_{19}O_2Si$ ($M + H^+$) calcd 187.1154, found 187.1160.

Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74. Found: C, 58.03; H, 9.77.

**3-[2-[(Trimethylsilyl)oxy]ethoxy]-2-pentene (*Z*- and *E*-Isomers, 64 and 65, Respectively).** Isolated as 16.1 g (93%) of a 63:37 $Z/E$ mixture of isomers: bp 48 °C (1 mm); $^1H$ NMR ($CDCl_3$) $\delta$ 4.56 (q, $J$ = 6.7 Hz, 1 H), 4.30 (q, $J$ = 6.7 Hz, 1 H), 3.81–3.61 (m, 4 H), 2.12 (m, 2 H), 1.56 (d, $J$ = 6.7 Hz, 3 H), 1.03 (m, 3 H), 0.13 (s, 9 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 158.4 (s), 156.9 (s), 103.7 (d), 90.5 (d), 70.0 (t), 68.1 (t), 62.3 (t), 61.9 (t), 25.4 (t), 23.6 (t), 12.4 (q), 12.2 (q), 11.8 (q), 10.6 (q), 0.0 (q), –0.1 (q); IR (neat) 3042, 2963, 2936, 2870, 1681, 1668, 1251, 1134, 1106, 842 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{10}H_{22}O_2Si$ ($M^+$) calcd 202.1388, found 202.1386.

Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.24; H, 10.91.

**2-[2-[(Trimethylsilyl)oxy]ethoxy]-3-methyl-1-butene (67)**: bp 74 °C (9 mm); $^1H$ NMR ($CDCl_3$) $\delta$ 3.87–3.69 (m, 6 H), 2.38–2.24 (hept, $J$ = 6.8 Hz, 1 H), 1.7 (d, $J$ = 6.9 Hz, 6 H), 0.14 (s, 9 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 169.0 (s), 78.4 (t), 68.5 (t), 61.4 (t), 33.5 (d), 21.0 (q), –0.3 (q); IR (neat) 3042, 2963, 2933, 1653, 1289, 1251, 1106, 860, 842 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{10}H_{23}O_2Si$ ($M + H^+$) calcd 203.1467, found 203.1477.

Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.34; H, 10.98.

**1-[2-[(Trimethylsilyl)oxy]ethoxy]-1-phenylethene (70)**: bp 121 °C (1.3 mm); $^1H$ NMR ($CDCl_3$) $\delta$ 7.69–7.62 (m, 2 H), 7.38–7.29 (m, 3 H), 4.68 (d, $J$ = 2.8 Hz, 1 H), 4.24 (d, $J$ = 2.8 Hz, 1 H), 0.19 (s, 9 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 160.0 (s), 136.5 (s), 128.4 (d), 128.0 (d), 125.5 (d), 82.6 (t), 69.1 (t), 61.1 (t), –0.4 (q); IR (neat) 3085, 3060, 3040, 2957, 1643, 1609, 1599, 1316, 1283, 1127, 1106, 993, 860 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{13}H_{21}O_2Si$ ($M + H^+$) calcd 237.1311, found 237.1299.

Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 65.78; H, 8.49.

**(Methoxymethylene)cyclohexane (72).** A solution of (dimethoxymethyl)cyclohexane (**71**, 7.52 g, 47.5 mmol, 1.0 equiv), DIPEA (7.39 g, 57.1 mmol, 1.2 equiv), and dry $CH_2Cl_2$ (120 mL, 2.5 mL/mmol of acetal substrate) under nitrogen was cooled to –23 °C (dry ice–$CCl_4$) bath, and TMSOTf (11.09 g, 9.65 mL, 49.9 mmol, 1.05 equiv) was added via syringe to the stirred solution dropwise over approximately 5 min. The solution was stirred at –23 °C for 2 h, and the reaction was allowed to warm to ambient temperature (ca. 1 h). Pentane (225 mL) was then added to the reaction vessel dropwise with vigorous stirring. The suspension was washed rapidly and successively with 60 mL of 0.7 M aqueous HCl, 40 mL of 0.5 M aqueous HCl, 40 mL of 5% aqueous $NaHCO_3$, and 40 mL of $H_2O$ and was dried over molecular sieves. After filtration and removal of the solvent in vacuo, the resulting oil was distilled at reduced pressure to afford 5.21 g (86%) of a colorless oil. The physical properties (bp 82 °C (46 mm)) and spectral characterization agreed with the published data.[44,45]

**1-Methoxy-2-phenylethene (*Z*- and *E*-Isomers, 74 and 75, Respectively).** To a solution of 1,1-dimethoxy-2-phenylethane (**73**, 6.16 g, 37.1 mmol, 1.0 equiv), DIPEA (9.70 g, 75.1 mmol, 2.0 equiv), and dry $CH_2Cl_2$ (115 mL, 3.0 mL/mmol of acetal substrate) under nitrogen was rapidly added TMSOTf (8.62 g, 9.65 mL, 49.9 mmol, 1.05 equiv) via syringe within 1 min. The solution

(44) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128.

(45) Rosseau, G.; LePerchec, P.; Conia, J. M. *Synthesis* **1978**, 67.

was stirred at ambient temperature for 3 min; pentane (250 mL) was added with vigorous stirring to the reaction vessel. The suspension was washed rapidly and sucessively with 50 mL of a 10% aqueous NaOH solution and three 50-mL portions of $H_2O$ and was dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the resulting oil was distilled at reduced pressure to afford 3.68 g (74%) of a colorless oil consisting of a 70:30 *Z*/*E* mixture of the isomeric vinyl ethers. The physical properties (bp [70:30 Z/E] 70–72 °C (2.1 mm)) and spectral characterization were consistent with the literature data.[46,47]

**General Procedure for the TMSOTf-Mediated Ring Opening of Cyclic Acetals of Aldehydes (Table V). 1-[2-[(Trimethylsilyl)oxy]ethoxy]-2-methyl-1-propene (77).** A solution of 2-(1-methylethyl)-1,3-dioxolane (**76**, 14.1 g, 0.121 mol, 1.0 equiv), DIPEA (20.5 g, 0.159 mol, 1.3 equiv), and dry $CH_2Cl_2$ (200 mL, 1.7 mL/mmol of acetal substrate) under nitrogen was cooled in an ice–water bath, and TMSOTf (47.7 g, 25.7 mL, 0.133 mol, 1.1 equiv) was added dropwise via syringe to the stirred solution over a period of approximately 5 min. The solution was stirred at 0 °C for 30 min. After this time, pentane (450 mL) was added dropwise to the reaction with vigorous stirring. The supernatant solution was decanted from the solid, and the residual salt was rinsed with three 50-mL portions of pentane. The combined organic fractions were washed rapidly and successively with 80 mL of a 10% aqueous NaOH solution and two 40-mL portions of $H_2O$ and were dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the resulting oil was distilled at reduced pressure to afford 20.1 g (88%) of a colorless oil: bp 79–83 °C (20 mm); $^1$H NMR ($CDCl_3$) $\delta$ 5.81 (bs, 1 H), 3.73 (s, 4 H), 1.56 (d, $J$ = 13.6 Hz, 6 H), 0.11 (s, 9 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 139.5 (d), 109.4 (s), 72.0 (t), 61.1 (t), 18.6 (q), 14.2 (q), −1.3 (q); IR (neat) 3034, 2959, 2929, 2871, 1692, 1251, 1174, 1129, 1105, 874 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_9H_{21}O_2Si$ ($M + H^+$) calcd 189.1310, found 189.1319.

Anal. Calcd for $C_9H_{20}O_2Si$: C, 57.40; H, 10.70. Found: C, 57.74; H, 10.68.

**1-[2-[(Trimethylsilyl)oxy]ethoxy]-1-pentene (*Z*- and *E*-Isomers, 79 and 80, Respectively).** A solution of 2-butyl-1,3-dioxolane (**78**, 6.44 g, 49.4 mmol, 1.0 equiv) and DIPEA (148 mL, 3 mL/mmol) under nitrogen was heated to 115 °C, and TMSOTf (12.1 g, 10.5 mL, 54.3 mmol, 1.1 equiv) was added rapidly (15 seconds) via syringe to the stirred solution. The solution was stirred for 1 min, the heating bath was removed, and the reaction was quenched by the cautious addition of 50 mL of a 10% aqueous NaOH solution. The reaction vessel was then cooled in an ice–water bath, and 150 mL of pentane was added. The supernatant solution was decanted from the solid and the residual salt was rinsed with three 50-mL portions of pentane. The combined organic fractions were washed rapidly and successively with 50 mL of a 10% aqueous NaOH solution and three 50-mL portions of $H_2O$ and were dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the resulting oil was flash distilled at reduced pressure to afford 6.45 g (65%) of a colorless oil consisting of a 72:28 *Z*/*E* mixture: bp 80–90 °C (7 mm). The isomers were separated for characterization by preparative GLC using a 6-ft column packed with 20% AP-L/2% KOH on 60–80 mesh Chrom W. For **79**: $^1$H NMR ($CDCl_3$) $\delta$ 5.95 (d, $J$ = 6.3 Hz, 1 H), 4.33 (q, $J$ = 6.3 Hz, 1 H), 3.78–3.75 (m, 4 H), 2.03 (m, 2 H), 1.35 (m, 2 H), 0.84 (t, $J$ = 7.2 Hz, 3 H), 0.13 (s, 9 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 144.0 (d), 105.7 (d), 72.1 (t), 68.8 (t), 25.0 (t), 21.9 (t), 12.7 (q), −1.5 (q); IR (neat) 3035, 2958, 2931, 2872, 1665, 1251, 1150, 1129, 1106, 843 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{10}H_{22}O_2Si$ ($M^+$) calcd 202.1389, found 202.1394.

Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.50; H, 10.98.

For **80**: $^1$H NMR ($CDCl_3$) $\delta$ 6.25 (bd, $J$ = 12.6 Hz, 1 H), 4.75 (m, 1 H), 3.80–3.71 (m, 4 H), 1.85 (m, 2 H), 1.36 (m, 2 H), 0.88 (t, $J$ = 7.3 Hz, 3 H), 0.13 (s, 9 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 145.1 (d), 103.1 (d), 69.2 (t), 60.4 (t), 28.7 (t), 22.7 (t), 12.4 (q), −1.5 (q); IR (neat) 3057, 2957, 2928, 2873, 1673, 1655, 1251, 1181, 1108, 844 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{10}H_{22}O_2Si$ ($M^+$) calcd 202.1389, found 202.1383.

Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.56; H, 10.95.

**1-[[2-[(Trimethylsilyl)oxy]ethoxy]methylene]-cyclohexane (82).** Prepared as described above for **77**; however, the reaction was allowed to warm to ambient temperature after the addition of the TMSOTf. Workup and isolation of the product afforded 18.67 g (90%) of the product as a colorless oil: bp 94–96 °C (1.6 mm); $^1$H NMR ($CDCl_3$) $\delta$ 5.79 (bs, 1 H), 3.73 (bs, 4 H), 2.17–1.49 (m, 10 H), 0.12 (s, 9 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 137.5 (d), 118.0 (s), 72.6 (t), 61.6 (t), 30.3 (t), 28.1 (t), 26.7 (t), 26.6 (t), 25.3 (t), −0.8 (q); IR (neat) 2839, 1686, 1252, 1163, 1126, 1107, 1095, 841 cm$^{-1}$; HRMS (EI, 30 eV) for $C_{12}H_{24}O_2Si$ ($M^+$) calcd 228.1544, found 228.1543.

Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 63.42; H, 10.54.

**1-[2-[(Trimethylsilyl)oxy]ethoxy]-2-phenylethene (*Z*- and *E*-Isomers, 84 and 85, Respectively).** A solution of 2-benzyl-1,3-dioxolane (**83**, 14.5 g, 88.6 mmol, 1.0 equiv), DIPEA (14.9 g, 115.3 mmol, 1.3 equiv), dry $CH_2Cl_2$ (145 mL, 2.0 mL/mmol of acetal substrate), and dry pentane (50 mL, 0.5 mL/mmol of acetal) under nitrogen was cooled in an ice–water bath, and TMSOTf (20.7 g, 18.0 mL, 93.1 mmol, 1.05 equiv) was added dropwise via syringe to the stirred solution over a period of approximately 2 min. The solution was stirred at 0 °C for 15 min; pentane (400 mL) was then added to the reaction dropwise with vigorous stirring. The supernatant solution was decanted from the solid, and the residual salt was rinsed with three 50-mL portions of pentane. The combined organic fractions were washed rapidly and successively with 50 mL of a 10% aqueous NaOH solution and three 50-mL portions of $H_2O$ and dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the resulting oil was distilled at reduced pressure to afford 14.95 g (72%) of a colorless oil comprised of a 74:26 *Z*/*E* mixture of the isomeric vinyl ethers: bp 90–97 °C (0.2 mm). The isomers were separated for characterization by preparative GLC using a 6-ft column packed with 20% AP-L/2% KOH on 60–80 mesh Chrom W. For **84**: $^1$H NMR ($CDCl_3$) $\delta$ 7.63–7.10 (m, 5 H), 6.25 (d, $J$ = 7.0 Hz, 1 H), 5.23 (d, $J$ = 7.0 Hz, 1 H), 4.01 (m, 2 H), 3.86 (m, 2 H), 0.15 (s, 9 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 147.1 (d), 136.1 (s), 128.3 (d), 128.1 (d), 125.7 (d), 105.7 (d), 74.6 (t), 61.9 (t), −0.5 (q); IR (neat) 3025, 2956, 2870, 1651, 1251, 1095, 843 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{13}H_{20}O_2Si$ ($M^+$) calcd 236.1232, found 236.1218.

Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 66.29; H, 8.56.

For **85**: $^1$H NMR ($CDCl_3$) $\delta$ 7.31–7.11 (m, 5 H), 7.04 (d, $J$ = 13.0 Hz, 1 H), 5.86 (d, $J$ = 12.9 Hz, 1 H), 3.95–3.83 (m, 4 H), 0.162 (s, 9 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 148.2 (d), 136.5 (s), 128.6 (d), 125.7 (d), 125.2 (d), 106.2 (d), 71.3 (t), 61.5 (t), −0.4 (q); IR (neat) 3059, 3025, 2957, 2872, 1654, 1640, 1252, 1167, 1104, 843 cm$^{-1}$; HRMS (CI, $CH_4$) for $C_{13}H_{20}O_2Si$ ($M^+$) calcd 236.1232, found 236.1222.

Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 66.31; H, 8.53.

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