of Si-H with the oxygen of water.[10] In addition, we find that pH 5.5 etched surfaces that have been reacted with basic (pH 9.5) solution are flat and featureless. This structure is similar to the featureless areas observed for pH 9 HF/NH_4F etched silicon and appears to be characteristic of amorphous SiO_x produced by the attack of OH^- at the Si(111):H interface. The images of the surface reacted with pH 6 aqueous solution may thus represent an intermediate state along the reaction pathway which yields an interface covered with amorphous SiO_x. In summary, these results show that it is possible to characterize at the atomic level reactions that are important to the chemical processing of semiconductor interfaces. Such information will be useful for developing new chemical procedures that produce specifically terminated interfaces.

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Tetrahydropyran Synthesis via Radical Cyclization. A Systematic Study of Substituent Effects

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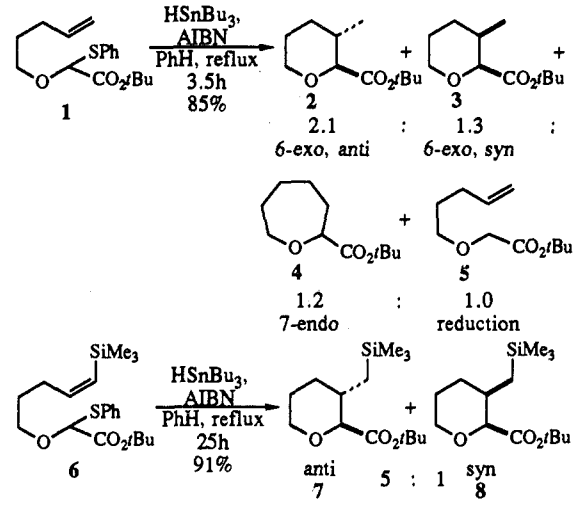
The prevalence of the hydropyran subunit in numerous polyether and ionophore natural products has stimulated the development of a variety of synthetic methods for this heterocycle.[2,3] Only syn-2,3-disubstituted hydropyrans (analogous to **3** and **8**) are available via our dioxanone-to-dihydropyran route.[2] A stereochemically complementary method for selective production of anti-2,3-disubstituted hydropyrans was sought. We report herein a systematic study of a radical cyclization[4] route to substituted tetrahydropyrans that satisfies this need, while delineating structural requirements for stereoselective closures.

Several features of prototype substrate **1** for radical cyclization offered the promise of susceptibility to the steric effects of added substituents. The carbon-centered radical arising from C-S bond homolysis would enjoy additive or synergistic, captodative stabilization[5] by geminal donor and acceptor groups, implying a relatively late transition state for cyclization. Also, the compressed C-O-C bond angle (106.8°) and shortened C-O bonds (1.41 Å) relative to the analogous all-carbon system (109.5°, 1.52 Å)[6] suggest a tight transition structure in which nonbonded interactions would be of added significance.

Scheme I



The following specific control elements were investigated: (1) the effect of the presence and stereochemistry of an alkenyl substituent on cyclization regio- and stereochemistry (e.g., **6**, **9**, and **13**); (2) the effect of a C(3) substituent on the newly formed vicinal stereocenters (e.g., **18**); (3) the effect of a *gem*-dimethyl residue in the tether on cyclization stereochemistry (e.g., **21** and **26**).

Results addressing the first of these issues are presented in Scheme I. The radical formed from the simple substrate **1**[7] upon standard treatment (see Scheme I)[4] gave rise to a mixture of four products (**2**-**5**) with little selectivity. Similar cyclization of **6** proceeded to give only the hydropyran products **7** and **8** (5:1, 91%). All anti and syn diastereomers reported here are easily distinguished by ^1H NMR; coupling constants for trans diaxial (~10 Hz) and cis (~2.5 Hz) vicinal couplings to the C(2) methines are characteristic. Relative to the cyclization of **1**, the trimethylsilyl substituent in **6** suppressed the 7-endo mode[8] of cyclization and improved the anti:syn ratio. Also, the formation of the reduction product analogous to **5** was avoided by keeping the Bu_3SnH concentration low by slow addition.[9]

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(4) Standard treatment involves the addition of the Bu_3SnH/AIBN solution over a short period of time (3.5 h) relative to the procedure described in footnote 9. For recent comprehensive reviews, see: (a) Curran, D. P. *Synthesis* **1988**, 417, 489. (b) Giese, B. *Radicals In Organic Synthesis; Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. (c) Hart, D. J. *Science* **1984**, *223*, 883. (d) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. See also: (e) Curran, D. P.; Chang, C.-T. *J. Org. Chem.* **1989**, *54*, 3140.

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(6) For recent computational and theoretical studies of radical cyclization reactions, see: (a) Laird, E. R.; Jorgensen, W. L. *J. Org. Chem.* **1990**, *55*, 9. (b) Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 959. (c) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925.

(7) Substrates **1**, **6**, **9**, **13**, **18**, **21**, and **26** were synthesized by straightforward sequences that will be detailed elsewhere. The preparation of **6** in four steps is representative: (i) *O*-Alkylation of 5-pentyn-1-ol with $BrCH_2CO_2tBu$ under phase-transfer conditions (40% aqueous NaOH, Bu_4NHSO_4, PhH, 0 → 25 °C, 90%). (ii) Acetylide silylation [2 equiv of $LiN(SiMe_3)_2$, THF, -78 → -35 → -78 °C; 2 equiv of Me_3SiCl, -78 → 0 °C; H_3O^+, 85%]. (iii) Hydroboration/protonolysis [$(c\text{-}C_6H_{11})_2BH$, THF, 0 → 25 → 0 °C; HOAc, 0 → 25 °C]. (iv) Enolate sulfenylation [$LiN(SiMe_3)_2$, THF, -78 °C; PhSSPh (inverse addition), -78 → 25 °C, 51% over two steps].

(8) For examples of direct 7-endo radical cyclizations, see: (a) Bachi, M. D.; Frolow, F.; Hoornaert, C. *J. Org. Chem.* **1983**, *48*, 1841. (b) Reference 4e. For an example of net 7-endo cyclization that probably involves 6-exo closure followed by radical rearrangement, see: (c) Crich, D.; Fortt, S. M. *Tetrahedron Lett.* **1988**, *29*, 2585.

(9) The procedure used for radical cyclization of substrate **6** is representative: To a solution of substrate **6** (371 mg, 0.976 mmol) in 50 mL of dry refluxing benzene was added dropwise a solution of Bu_3SnH (1.14 mmol) and AIBN (50 mg) in 25 mL of benzene over 25 h. The benzene was removed in vacuo, and a crude ^1H NMR spectrum was recorded. Chromatography on silica gel afforded pure diastereomers **7** (201 mg, 75.7%) and **8** (40 mg, 15.1%).

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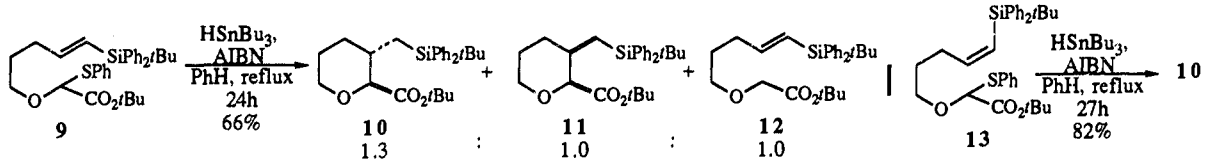
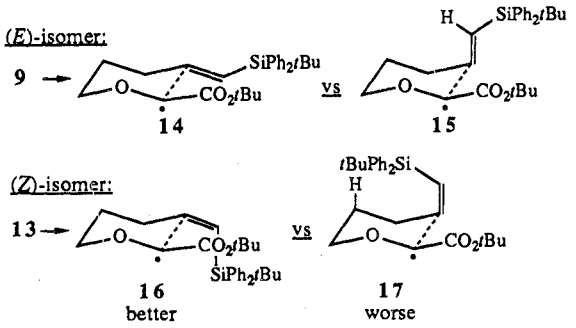
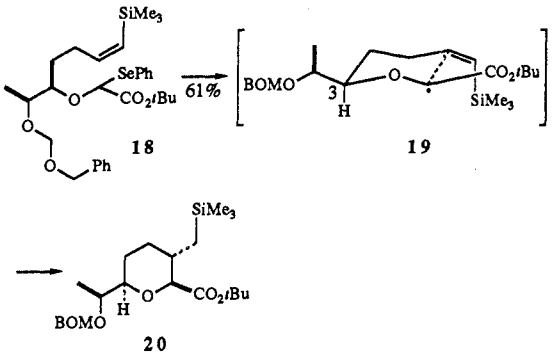
Scheme II



Scheme III



Scheme IV

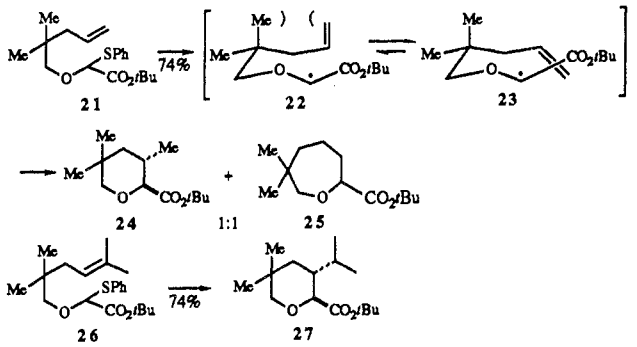


The effects of silicon substituent identity and vinylsilane geometry are illustrated in Scheme II. Cyclization of the (*E*)-(*tert*-butyldiphenyl)silyl-substituted alkene **9** proceeded unselectively, yielding **10**, **11**, and **12** in nearly equal amounts. In contrast, radical cyclization of substrate **13**, containing a (*Z*)-(*tert*-butyldiphenyl)silyl-substituted alkene, led to the anti diastereomer **10** in 82% yield; no syn diastereomer **11** was detected.

These observations can be explained by considering the cyclization conformers in Scheme III.[10] There is little to energetically differentiate **14** and **15**; thus a 1.3:1 mixture of **10** and **11** results from **9**. However, conformer **16** has a substantial advantage over **17**, thus producing only **10** from **13**. Smaller silyl substituents, as in **6**, make the conformation analogous to **17** less disfavored, leading to production of a small amount of the syn isomer **8** along with **7**.[11]

The additional effect of a substituent at C(3) on the stereochemical course of the cyclization is presented in Scheme IV. Homolytic cleavage of the carbon–selenium[12] bond in **18** resulted in a radical cyclization producing only diastereomer **20**. Equatorial

Scheme V



deployment of the tether substituent and the conformational preference for the bracketed intermediate **19** explain the transfer of stereogenicity to the newly formed asymmetric centers.[13]

The employment of a *gem*-dimethyl moiety in **21** (Scheme V) provided a steric differentiation between cyclization conformers **22** and **23**, favoring the latter.[14] Only the anti tetrahydropyran diastereomer **24** was formed, but with an equal amount of the 7-endo closure product **25**. Substitution on the alkene terminus suppressed this mode of closure, so that **26** gave the anti 6-exo product **27** as the sole tetrahydropyran diastereomer.

Acknowledgment. We gratefully acknowledge the National Institutes of Health, the Alfred P. Sloan Foundation, the National Science Foundation, and the Natural Sciences and Engineering Research Council of Canada for generous financial support.

(10) Assumption of a chair-like transition state for these cyclizations is analogous to those invoked for the all-carbon systems analyzed by Houk[6b] and by Beckwith[6c] with their respective "flexible" and "rigid reactant" MM2 models. A similar model has been invoked for rationalizing the observed stereoselectivities in radical cyclizations of (*E*)- and (*Z*)-8-bromo-6-*tert*-butyl-2-octenoates: Hanessian, S.; Dhanoa, D. S.; Beaulieu, P. L. *Can. J. Chem.* **1987**, *65*, 1859.

(11) *Z* α,β-unsaturated esters as acceptors have exhibited higher stereoselectivities than corresponding *E* isomers in radical cyclizations yielding five-membered[11a,b] and six-membered[11c] rings. Each example involves 1,3-allylic strain between the ester group and a branching γ-substituent. (a) Gaudino, J. J.; Wilcox, C. S. *Carbohydr. Res.* **1990**, *206*, 233. (b) Wilcox, C. S.; Thomasco, L. M. *J. Org. Chem.* **1985**, *50*, 546. (c) Ihara, M.; Yasui, K.; Taniguchi, N.; Fukumoto, K. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1469.

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(14) The rate-enhancing effects of substituents on the chain connecting the radical center and the acceptor are well-known. See refs 4a and 4e.

Unexpectedly Rapid Proton-Transfer Reactions of Weakly Acidic Cation Radicals

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Cation radicals[1-3] and dications[4] of aromatic compounds often exhibit superacid thermodynamic properties, yet react with bases at moderate rates. An extreme example is the dication of (*p*-methoxyphenyl)diphenylmethane, which can be observed by cyclic

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