a dynamic symmetry of $C_s \times C_3$, rendering the carbon monoxide sites equivalent but leaving the ketone sites nonequivalent. Ethyl group rotation introduces yet greater dynamic symmetry and renders the ketone sites equivalent. Thus independent probes for the tripod and for the ethyl group motion are established. Furthermore, the free arene is of a symmetry wherein the methylene protons of the ethyl groups are diastereotopic at the static limit and enantiotopic under dynamic exchange; they serve as a probe of the ethyl group motion in the free arene.

Observation of the ^{1}H NMR spectrum of **2** at room temperature reveals a singlet for the methylene protons of the ethyl group, methyl decoupled. The spectrum at -100 °C shows a clear AB pattern with $^2J_{H-H}$ = 14.5 Hz and $\delta\nu$ = 128 Hz. Coalescence occurs at -32 °C. The ^{13}C NMR spectrum of **2**-Cr shows one signal each for the ketone and carbon monoxide carbon at room temperature. At -60 °C the ketone carbon signal has split into two peaks ($\delta\nu$ = 151 Hz) of equal intensity whereas the carbon monoxide carbon signal remains a sharp singlet. At -90 °C in $CDCl_2F$[15] the carbon monoxide signal also splits into two peaks ($\delta\nu$ = 108 Hz), now of intensity 2:1. The coalescence temperatures for the ketone and carbon monoxide signals are -20 °C and -70 °C, respectively. On the basis of the above data and the Gutowsky-Holm approximation,[16] the barriers for the various processes in the cascade are as follows: free arene ethyl group = 11.3 kcal/mol; complexed arene ethyl group = 11.8 kcal/mol;[17] chromium tricarbonyl tripod = 9.5 kcal/mol (Figure 1).

The signal pattern and intensities of the ^{1}H and ^{13}C NMR spectra of **2**-Cr are consistent with the existence of only one isomer, the alternating up-down conformer, in solution at low temperature. Empirical force field calculations[18,19] on both **2** and **2**-Cr predict this same conformation to be the most stable by at least 3 kcal/mol (Figure 2).

On the basis of spectral complexities and the relative barrier heights, we conclude that the dynamics of the ethyl groups in **2** are essentially unaltered through desymmetrization to **2**-Cr.[20] However, forming the chromium tricarbonyl complex does introduce a new dynamic process, tripod rotation, and this process is gated by the motion of the ethyl groups on the arene. Thus both the steric complementarity of the arene and tripod fragments and the gated stereodynamics of the tripod motion are demonstrated rigorously in one simple system.

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Supplementary Material Available: Experimental procedures for **2** and **2**-Cr (2 pages). Ordering information is given on any current masthead page.

(14) Spectral data on **2**-Cr: mp 147-150 °C; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.19 (18 H, s), 1.26 (12 H, t, J = 7.2 Hz), 2.33 (8 H, q, J = 7.2 Hz), 2.62 (4 H, m), 2.82 (4 H, m); ^{13}C NMR ($CDCl_3$, 125.7 MHz, -60 °C) δ 14.4 (q), 19.8 (t), 19.9 (t), 20.3 (q), 22.8 (t), 23.4 (t), 25.9 (q), 26.0 (q), 36.2 (t), 43.5 (t), 43.9 (s), 105.4 (s), 108.7 (s), 115.5 (s), 117.3 (s), 214.2 (s), 215.4 (s), 234.8 (s); IR (KBr) 1945, 1935, 1870, 1855, 1845, 1835 cm^{-1}; FABMS (high resolution) found 683.1856 (calcd for $C_{31}H_{46}O_5Cr$ (M^+ + Cs) 683.1805).

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(18) Calculations using the EFF method were done with the programs MODEL and PC MODEL as distributed by Kosta Steliou (University of Montreal) and Kevin Gilbert (Serena Software), respectively.

(19) For applications and limitations of this method, see: Burkert, U.; Allinger, N. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.

(20) This is consistent with our findings on a series of **1**-Cr analogues.[10]

Chemically Etched Silicon Surfaces Viewed at the Atomic Level by Force Microscopy

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Herein we describe the first atomic force microscopy[1,2] (AFM) studies of Si(111) surfaces that directly address the atomic structure of silicon interfaces produced under a variety of etching conditions. We have shown that the atomic structure of hydrofluoric acid (HF) etched interfaces depends strongly on the pH of the etchant solution. We have also used AFM to study the reactions of atomically ordered Si(111):H interfaces with aqueous solutions and have characterized large pH-dependent changes in the interface structure. Significantly, these results suggest that AFM can be used to characterize with atomic resolution details of chemical reactions at silicon interfaces in situ.

Chemical cleaning and etching of semiconductor interfaces are essential processing steps in the production of microelectronic devices.[3-6] A case in point is HF etching of silicon which produces ultraclean and stable surfaces that can be used directly in the fabrication of high-quality devices.[6,7] Studies of HF-etched Si(111) have indicated that the stability of this interface is due to the passivation of Si dangling bonds with Si-H bonds.[8-13] Recent infrared investigations have shown that the Si(111):H interface may consist of mixtures of mono-, di-, and trihydride species, depending on the etching conditions, although only a pure monohydride termination can yield a defect-free interface.[8,9] It is important for high-quality-device fabrication to understand the microscopic structural details of these etched interfaces and to learn how the interface characteristics vary with reaction conditions; however, very few studies have characterized these interfaces on the atomic scale.[14,15]

Silicon (111 oriented, n type, 4 Ω cm) was etched with HF acid via standard procedures.[8,9,16] Several solutions were examined ranging from 48% HF to pH 9 HF/NH_4F in order to investigate how the atomic structure varies with etching conditions. Images of the surface structure were acquired in air with a commercial AFM instrument (Digital Instruments, Inc., Santa Barbara, CA) operated in the constant-force mode.[2,17] The observed surface

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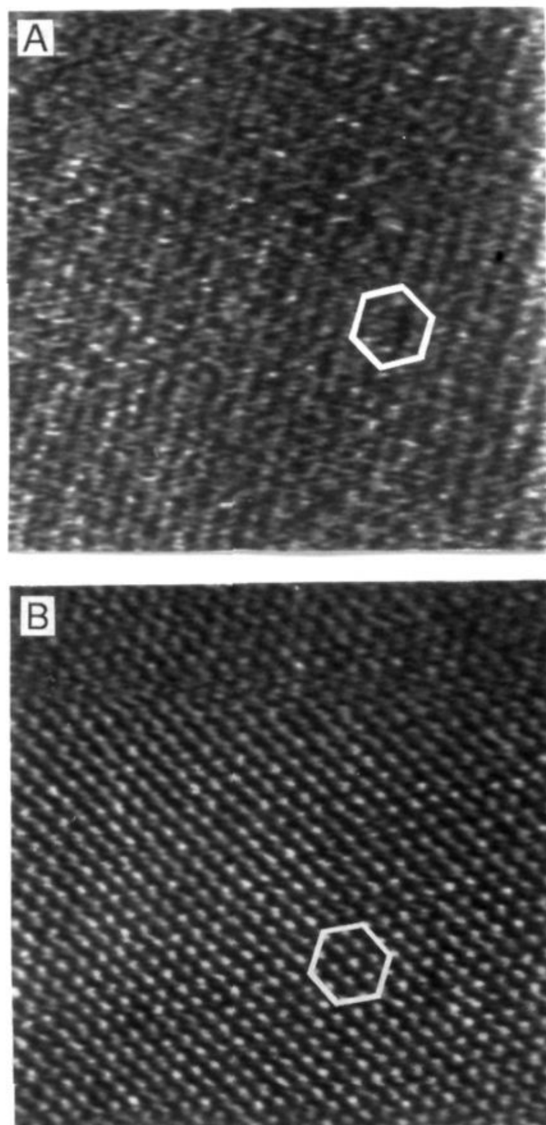

Figure 1. Unfiltered AFM images of Si(111) surfaces etched with (A) 48% HF and (B) 48% HF followed by pH 5.5 HF/NH_4F. The atomic structure is well-resolved in B but not in A. The white hexagon, which surrounds an equal area in the two images, highlights the atomic structure. The images are 170 Å on edge.

structure was stable for at least 12 h under these conditions. The images shown correspond to unfiltered data.

Gray-scale AFM images (170 × 170 Å^2) recorded on Si(111) surfaces etched with (A) 48% HF and (B) 48% HF followed by pH 5.5 HF/NH_4F are shown in Figure 1. These images are typical of the data obtained on independently etched samples for each etching condition. Although each of these images exhibit atomically flat surfaces as expected for exposed Si(111) terraces,[14] the atomic structure produced by the different etching conditions varies significantly. Images of Si(111) surfaces etched only with 48% HF exhibit areas with atomic structure, but this structure shows little order (Figure 1A). Previous studies of Si(111) surfaces etched with 48% HF indicate that the surface is terminated by mono-, di-, and trihydride species[8,9,10] and nonstoichiometric oxide, SiO_x.[10,13,18,19] The absence of well-ordered atomic structure in our images of 48% HF etched surfaces suggests that these different chemical species are distributed randomly on a ≈10 Å length scale.

In contrast, the AFM images of Si(111) surfaces subsequently etched with pH 5.5 or pH 9 HF/NH_4F solutions exhibit well-resolved atomic structure with hexagonal symmetry (Figure 1B). The atomic structure observed on Si(111) surfaces for these etching conditions is reproducible and stable for several days in air. We find that these atomically resolved regions are smaller for the pH 9 versus pH 5.5 etched surfaces and that the images of the pH 9 etched surfaces also exhibit flat, featureless areas. Recent infrared studies of these same etching conditions found that pH 5 and pH 9 HF/NH_4F solutions yield a silicon interface terminated predominantly by monohydride species, although dihydride and trihydride species were also detected on pH 5 etched surfaces.[9] Since the well-ordered hexagonal structure and monohydride species are the predominant surface features found with both etchants, we attribute the hexagonal atomic structure to monohydride-terminated Si(111).[21] In contrast to the infrared work,[8,9] our studies also show that pH 9 HF/NH_4F etched surfaces have a second type of termination that appears featureless on an atomic scale. We believe that a reasonable explanation for these featureless areas is that they correspond to amorphous SiO_x. Indeed, X-ray photoemission and electron energy loss spectroscopy studies have shown that SiO_x is present on the surface of HF-etched silicon and have indicated that hydroxide ion (present in significant concentration for the pH 9 solution) accelerates the formation of this surface oxide.[10,11,18-20] We do not expect, however, to resolve regular atomic structure for the surface oxide since it is amorphous.[15]

To investigate the validity of this explanation and the possibility of probing chemical reactions by AFM, we have carried out preliminary studies of the reactivity of the atomically ordered pH 5.5 HF/NH_4F Si(111) interfaces. A typical image of this etched Si surface following reaction with pH 6 H_2O is shown in Figure 2. Hexagonal atomic structure characteristic of the pH 5.5 and pH 9 HF/NH_4F etched surfaces is observed in images of the surfaces reacted with weakly acidic (pH 6) aqueous solutions; however, the structure is not as uniform as observed for the etched surfaces. Specifically, these images exhibit new raised features which may be due to adsorbed H_2O or localized sites of reaction

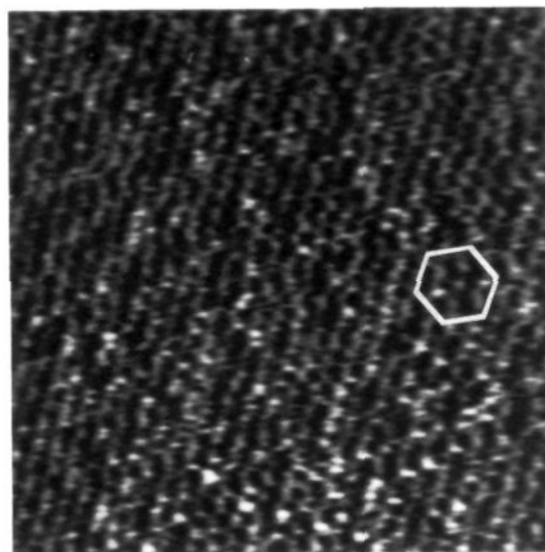

Figure 2. Gray-scale AFM images (160 × 160 Å^2) of a pH 5.5 HF/NH_4F etched Si(111) surface that has been subsequently reacted with a pH 6 aqueous solution for ca. 2 min. The atomic structure exhibits significant disorder in comparison to the unreacted surface (Figure 1B). The white hexagon highlights atomic features in this image.

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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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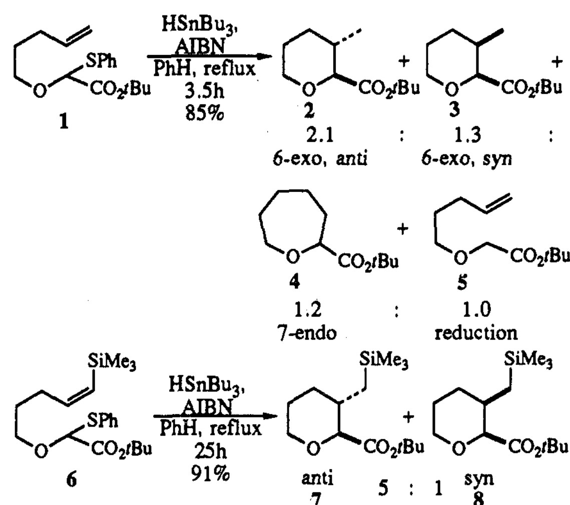
The prevalence of the hydropyran subunit in numerous polyether and ionophore natural products has stimulated the development of a variety of synthetic methods for this heterocycle.[2,3] Only syn-2,3-disubstituted hydropyrans (analogous to **3** and **8**) are available via our dioxanone-to-dihydropyran 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]

(1) (a) Recipient of a National Science Foundation Presidential Young Investigator Award (1984-1989); Research Fellow of the Alfred P. Sloan Foundation (1984-1988). (b) Recipient of a Postdoctoral Research Fellowship from the Natural Sciences and Engineering Research Council of Canada.

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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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