$$(OC)_3Mn(H)(D)(\eta^2\text{-}C_3H_5D)^-$$
1

2° CD bond oxidative addition followed by β-D or β-H migration, respectively. If the intramolecular β-migrations and their microscopic reverse rearrangements are slow compared to the fast unimolecular fragmentation of **1**, the sole product will be the *m/z* 182 ion formed by reductive elimination of HD from **1**. The results of the reaction with $(CH_3)_2CD_2$ in eq 5 with formation of about

$$(CO)_3Mn^- + (CH_3)_2CD_2 \xrightarrow{0.56} (OC)_3Mn(C_3H_5D)^- + HD \quad m/z\ 182$$
$$\xrightarrow{0.44} (OC)_3Mn(C_3H_4D_2)^- + H_2 \quad m/z\ 183 \qquad (5)$$

equal amounts of the *m/z* 182 and 183 ions clearly show that H/D scrambling in **1** is extensive, but not statistical, during the brief lifetime of the excited ion. This result means that intramolecular rearrangements of H and D between Mn and the β-carbons are fast and reversible and will not contribute significantly to the observed kinetics.

These kinetic results establish the reactivity order for oxidative addition of aliphatic CH bonds to $(OC)_3Mn^-$ as 1° < 2° < 3°, although the quantitative values given may be in error. The absence of observed oxidative addition of 3° CH bonds in the condensed phase[4] is probably due to the steric bulk of the transition-metal complex used rather than a significant difference in the intrinsic reactivities of 1°, 2°, and 3° CH bonds in the two phases.

Acknowledgment. We thank the National Science Foundation for support of this research and Professors David Macomber and Eric Maatta for helpful discussions.

Chirality Transmission via a 6-Endo Free-Radical-Mediated Cyclization Process. Regio- and Stereocontrolled Synthesis of the 22-Hydroxylated Steroid Side Chains

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Primarily through the extensive efforts of Stork,[1] Hart,[2] and Curran,[3] C–C bond formation via free-radical-mediated cyclization reactions now has a firmly established role in synthetic organic chemistry as a highly versatile and often indispensable method

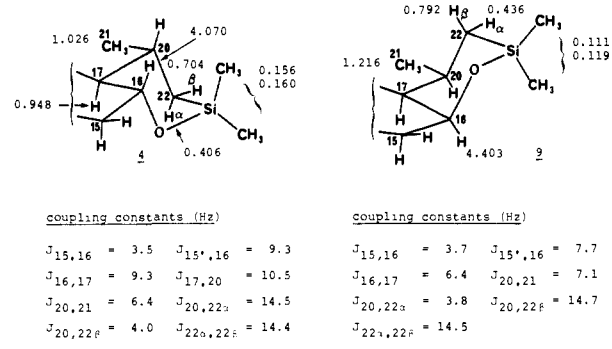
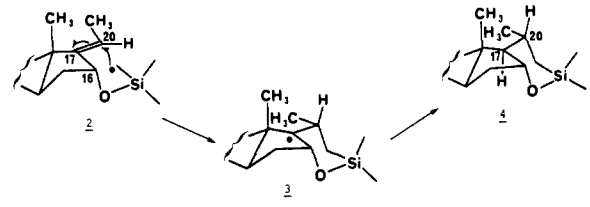


Figure 1. NMR data in $CDCl_3$ (360 MHz); chemical shifts in δ (ppm).

Scheme I



of skeleton construction.[4] The large volume of data delineating radical reactivity compiled over the past several decades un-

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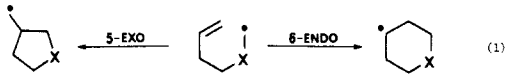
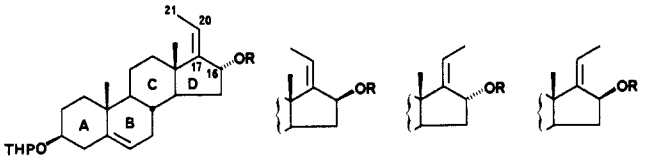
doubtedly has served to facilitate these recent remarkable developments. Among numerous guiding principles emanating from these pioneering studies,[5] the preferred 5-exo closure during cyclization of 5-hexen-1-yl radicals (**1a** in eq 1) is one of the most



1a X = CH_2
1b X = $SiMe_2$

well-documented processes in free-radical chemistry.[6] A unique exception to this general rule concerning the cyclization of carbon-centered 5-hexen-1-yl type radicals was noted in 1981 by Wilt[7] during his study dealing with the 2-sila-5-hexen-1-yl radical **1b**. The unusual inherent propensity for 6-endo cyclization of **1b** has been rationalized on stereoelectronic grounds.[7,6d,e] Furthermore, Nishiyama[4p] has recently utilized radicals generated from (bromomethyl)dimethylsilyl allyl ethers demonstrating a significant preference for 6-endo cyclization in some of these systems. In conjunction with our continuing interest in developing methods for the efficient construction of side chains of physiologically significant 22-hydroxylated steroids,[8] we had occasion to explore the synthetic potential of this highly attractive, yet underappreciated, α-silyl radical mediated cyclization reaction. In this paper we wish to describe the novel synthesis of 22-hydroxylated steroid side chains using such a reaction. The salient feature of this regio- and stereocontrolled synthesis lies in the generation of two stereocenters, C-17 and -20, in a single, radical cyclization step as a result of chirality transmission[9] from the stereodirecting 16-hydroxyl derivative (see Scheme I).

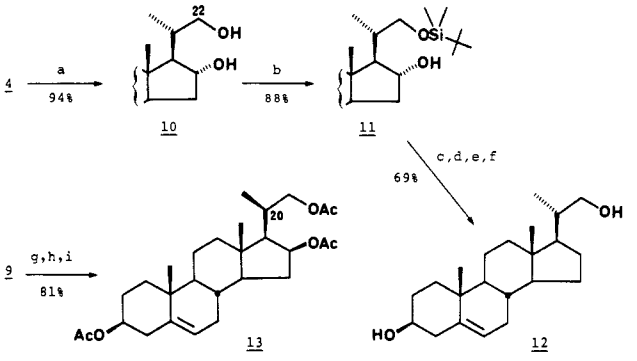
In an effort to gain insight into the regio- and stereochemical selectivity of α-silyl radical mediated cyclizations, the four conformationally rigid, stereoisomeric 16-hydroxy-17-ethylidenes **5a–8a**[10,11] were converted into their corresponding α-bromosilyl



5a R = H
5b R = $SiMe_2CH_2Br$
6a R = H
6b R = $SiMe_2CH_2Br$
7a R = H
7b R = $SiMe_2CH_2Br$
8a R = H
8b R = $SiMe_2CH_2Br$

ethers **5b–8b** with $BrCH_2SiMe_2Cl$[12]/Et_3N in CH_2Cl_2 (0° C, 0.5–1 h) in over 95% yield. The 16β-hydroxy compounds **6a** and **8a** were obtained through Mitsunobu reaction[13] (PhCOOH, Ph_3P, DEAD, room temperature, 3 h), followed by KOH hydrolysis, from their respective 16α-isomers **5a** (61%) and **7a** (56%). Treatment of **5b** with 1.5 equiv of $(n\text{-Bu})_3SnH$ at reflux in benzene in the presence of a catalytic amount of α,α'-azoisobutyronitrile (AIBN) for 10 h induced smooth cyclization of the resulting radical to give rise to **4** as the only detectable cyclized product in 70% yield together with the reduction product, the 16-(trimethylsilyl) ether of **5a** (12%). Structural assignment of **4** proved to be relatively uneventful by analysis of its 360-MHz proton NMR spectrum (see Figure 1). Thus, characteristic highly shielded chemical shifts of the C-22 methylene protons α to the silicon atom as well as large $^3J_{16,17}$, $^3J_{17,20}$, and $^3J_{20,22\alpha}$ values readily defined the structure of the newly formed heterocycle as shown. This structure was further validated by its efficient conversion into the diol **12** (Scheme II) which was identical with an authentic sample obtained by $LiAlH_4$ reduction of 3β-acetoxy-22,23-bisnor-5-cholenic acid. Similarly, the C-16β α-bromosilyl ether **6b** produced the cyclized product **9** in 65% yield, in addition to the reduction product (18%), upon treatment identical with that above. The 360-MHz proton NMR of **9** was again quite informative in elucidating its structure (Figure 1). This 20-iso structure was subsequently verified unequivocally by single-crystal X-ray analysis[14] of the triacetate **13** derived from oxidation and deprotection of **9**.

Scheme II[a]



[a] Conditions: (a) 30% H_2O_2 (excess), $KHCO_3$ (1.3 equiv)/MeOH–THF (1/1), reflux, 16 h. (b) t-$BuSiMe_2Cl$ (2.1 equiv), DMAP (catalytic), Et_3N/CH_2Cl_2, room temperature, 12 h. (c) Cl—C(=S)—OPh (2 equiv), DMAP (catalytic), pyridine/CH_2Cl_2, room temperature, 7 h. (d) $(n\text{-Bu})_3SnH$ (1.5 equiv), AIBN (catalytic)/benzene, reflux, 12 h. (e) $(n\text{-Bu})_4N^+F^-$ (4 equiv)/THF, room temperature, 5 h. (f) PPTS (catalytic)/EtOH–THF (1/1), 55 °C, 3 h. (g) See a, 90%. (h) PPTS (catalytic)/EtOH–THF (1/1), 55 °C, 1 h. (i) Ac_2O (3.5 equiv), DMAP (catalytic), Et_3N, pyridine/CH_2Cl_2, room temperature, 24 h.

In contrast, the α-bromo silyl ethers of the *Z*-allylic alcohols **7b** and **8b** did not yield cyclized products to a significant extent upon treatment with $(n\text{-Bu})_3SnH$. Namely, **7b** gave the reduction product in 60% yield, while **8b** gave a complex mixture of products in poor yield. These results appear to suggest that the C-20 methyl in the *Z*-allylic alcohol silyl ether system obstructs the trajectory of radical attack, thus impeding or obviating cyclization.

The exclusive 6-endo cyclization at C-20 observed for the radicals originating from **5b** and **6b** is clearly a manifestation of the conformational rigidity at the allylic system involved and the lower degree of alkyl substitution at C-20 vs. C-17. These structural features undoubtedly contributed to further enhance the inherent propensity for 6-endo cyclization of the α-silyl radicals. Additionally, it is noteworthy that both **5b** and **6b** yielded the 17α-H products. Apparently, the existing steroid ring system precludes formation of the alternative 17β-H products. The clear-cut stereoselective generation of two chiral centers at C-17 and -20 from both **5b** and **6b** indicates that the chirality was cleanly transmitted from the stereodirecting C-16 α-bromo silyl ether group during free-radical-mediated cyclization. This rep-

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(9) The term chirality transmission signifies that the chiral property of the inducing chiral center is preserved during a reaction. For the definition of chirality transfer, see footnote 2 in: Evans, D. A.; Chapman, K. J.; Bisaha, J. *Tetrahedron Lett.* **1984**, *25*, 4071.

(10) Koreeda, M.; Tanaka, Y. *J. Org. Chem.* **1980**, *45*, 1172.

(11) Compounds 4 and **6–11** share the same A–C ring structure as **5**. All new compounds described in this paper are crystalline solids and gave satisfactory data upon combustion and spectroscopic analyses.

(12) Purchased from Petrarch Systems, Inc., Bristol, PA. See also ref 1f and 4p.

(13) Mitsunobu, O. *Synthesis* **1981**, 1.

(14) We thank Dr. William M. Butler for performing this analysis at Department of Chemistry, The University of Michigan.

resents a rare example[15] of clean chirality induction to an sp^2 carbon which is not part of a ring, during a carbon-centered free-radical cyclization. Furthermore, the highly efficient insertion of the oxygen atom at C-22 into the C–Si bond[16] of the heterocyclic units **4** and **9** has provided a novel entry to the synthesis of the 22-hydroxylated natural and 20-iso-steroid side chains.

The results described herein have considerable implications beyond the synthesis of the steroid side chains. We believe that this type of chirality transmission approach employing the α-silyl radical-mediated cyclization should have the potential to be effectively applied in the synthesis of various acyclic molecules or their equivalents.

Acknowledgment. We are grateful for financial support from the National Institutes of Health (DK30025) and to the Michigan Cancer Institute for a fellowship to I.A.G.

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(16) (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. (b) Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2120. (c) Tamao, K.; Ishida, N. *J. Organomet. Chem.* **1984**, *269*, C37. See also ref 1f and 4p.

Photoreduction of CO_2 to CH_4 in Aqueous Solutions Using Visible Light

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Reduction of CO_2 to combustible organic products by means of solar light is of substantial interest as a means for solar energy conversion and storage.[1-3] Serious attempts have recently been directed toward the development of light-induced CO_2-fixation processes.[4-7] Reduction of CO_2 to carbon monoxide,[4] formate,[5,6] and other organic acids[7] has been reported, using homogeneous catalysts,[4,5] semiconductor particles,[6] or artificially enzyme catalyzed coupled systems.[7] Reduction of CO_2 to methane, the methanation process (eq 1), is of substantial industrial importance.[8,9] This reaction proceeds at high temperatures and pressures and is catalyzed by metal catalysts such as Ru, Mo, and Ni. Electrocatalyzed reduction of CO_2 using Ru electrodes has been reported.[10] Here we wish to report on the photocatalyzed reduction of CO_2 to methane using tris(bipyrazine)ruthenium(II), $Ru(bpz)_3^{2+}$, as sensitizer[11] and a Ru metal colloid as catalyst for the process.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (1)$$

The system is composed of an aqueous solution, pH 9.5, that includes $NaHCO_3$, 0.05 M, $Ru(bpz)_3^{2+}$, 1×10^{-4} M, triethanolamine, TEOA, 0.17 M, as electron donor, and a Ru colloid, 20 mg·L^{-1}, prepared by the citrate reduction method.[12] Illumination of this system under a gaseous atmosphere of CO_2, $\lambda > 420$ nm, results in the formation of methane. Methane analysis was performed by gas chromatography (Porapak T column) by comparison to an authentic sample as well as by mass spectrometry. The rate of CH_4 formation at time intervals of illumination[12] is displayed in Figure 1a and corresponds to a quantum yield of $\phi = 0.0025\%$. Exclusion from the system of the sensitizer, $Ru(bpz)_3^{2+}$, or the Ru colloid prevents the formation of CH_4. Similarly, exclusion of $NaHCO_3$ and CO_2 eliminates any production of methane. These results imply that all of the components are essential for the reduction of CO_2 to CH_4. The turnover number of $Ru(bpz)_3^{2+}$ is 15, implying a cyclic activity of the system.

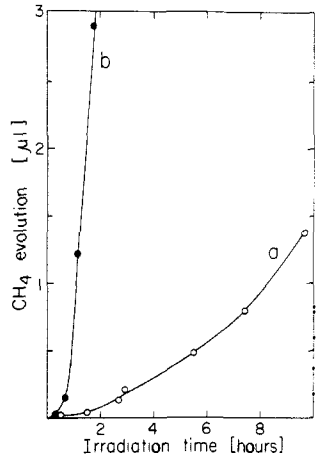

Figure 1. Rate of CH_4 formation as a function of illumination time: (a) in H_2O; (b) in water–ethanol 2:1 solution.

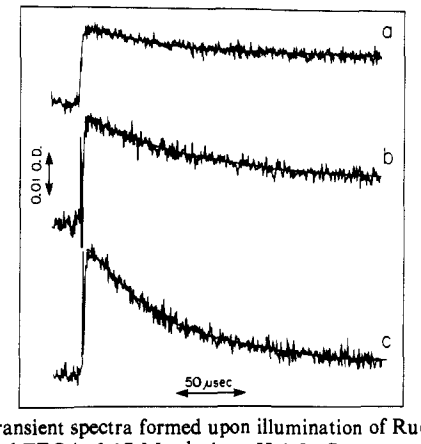

Figure 2. Transient spectra formed upon illumination of $Ru(bpz)_3^{2+}$, 2.2×10^{-5} M and TEOA, 0.17 M solution pH 9.5. Systems are flashed at $\lambda = 440$ nm and product is followed at $\lambda = 500$ nm: (a) under CO_2 or argon; (b) in the presence of Ru colloid (20 mg·L^{-1}) under argon; (c) in the presence of Ru colloid (20 mg·L^{-1}) under CO_2.

The photophysical properties of $Ru(bpz)_3^{2+}$ have been studied in detail.[11,13] It exhibits a long-lived excited state ($\tau = 1.04$ μs) that is reductively quenched by triethanolamine, TEOA (eq 2),

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \quad (2)$$

$k_q = 2 \times 10^8$ M^{-1} s^{-1}. The photoproduct, $Ru(bpz)_3^{+}$, formed by the electron-transfer process is a powerful reductant, $E°[Ru(bpz)_3^{+}/Ru(bpz)_3^{2+}] = -0.86$ V vs. SCE.

The reduction potential for half-cell reaction of CO_2 reduction to CH_4 (eq 2) at pH 7 corresponds to $E°' = -0.24$ V vs. NHE.[14] Electrochemical studies[10] have indicated that CO_2 is reduced to CH_4 at a Ru electrode at an applied potential that corresponds to -0.5 V vs. SCE. Thus, photogenerated $Ru(bpz)_3^{+}$ is thermo-

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