Trityl Cation Catalyzed Intramolecular Cyclizations of Saturated and Unsaturated γ- and δ-Alkoxysilyl Hydrides

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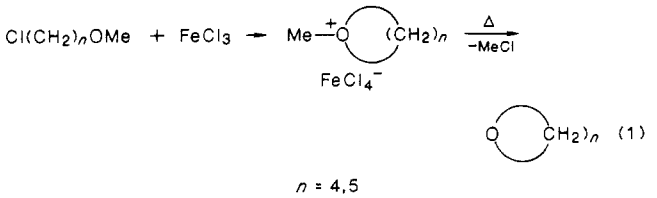
Both saturated and unsaturated γ- and δ-alkoxysilyl hydrides have been prepared as the trityl, *tert*-butyl, and benzyl ethers. These systems were used to test the possibility that silylenium ion generation by hydride abstraction (by Ph_3C^+) would result in cyclization via nucleophilic attack by ethereal oxygen on positive silicon. Indeed, the expected ethers 2,2-dimethyl-1-oxa-2-silacyclopentane (and -pentene) and 2,2-dimethyl-1-oxa-2-silacyclohexane (and -hexene) were catalytically formed from the trityl ethers in yields from 58 to 86%. The *tert*-butyl ethers gave generally higher yields of cyclization but required stoichiometric quantities of $Ph_3C^+ClO_4^-$, as did the benzyl ethers which gave the poorest yields.

Introduction

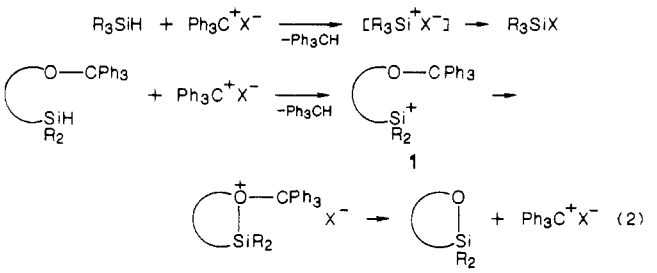
As part of a program involving both methods of generation of silylenium ions (R_3Si^+) and investigation of their potential synthetic usefulness, we have examined and report here the synthesis of cyclic silyl ethers from acyclic precursors via catalytic, in situ formation of transient silylenium ions. The basic scheme was extrapolated from Kirrmann's[1-3] syntheses of tetrahydrofuran and tetrahydropyran by cyclization of the corresponding alkyl halides upon treatment with Lewis acids, e.g., $FeCl_3$ or $SbCl_5$ (eq 1).



(1)

$n = 4,5$

Since it is now well-established[4] that the exchange reaction of trityl salts and silyl hydrides can proceed through the intermediacy of silylenium cations, it was thought that this reaction could be employed for generation of alkylsilylenium ions **1** with ethereal substitution so located as to provide intramolecular trapping and concomitantcyclization via oxygen attack on the fully charged or developing cationic silicon. It was also noted that if the trityloxy ethers were used, the reaction would be catalytic through the continuous regeneration of the trityl ion (eq 2).

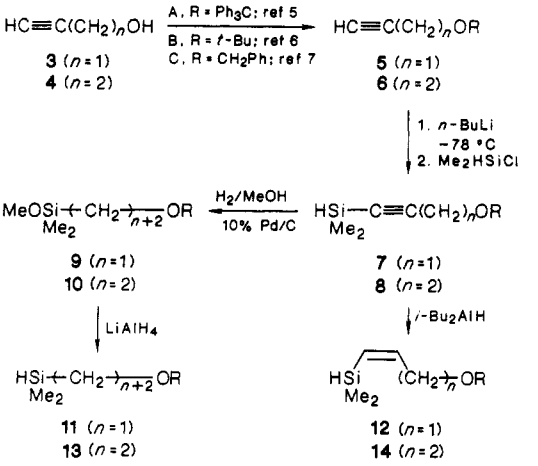


(2)

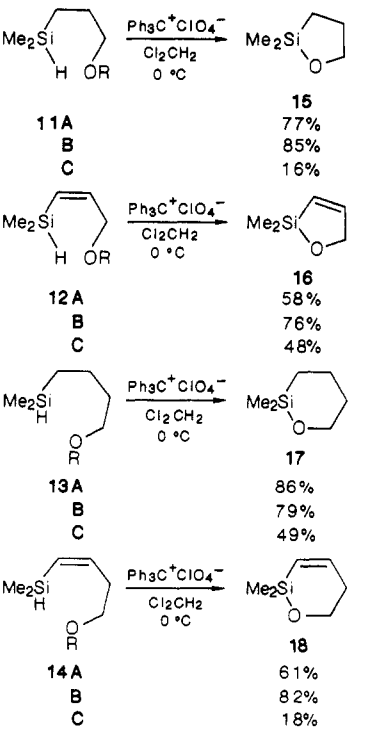
Results and Discussion

As it was of interest to develop a route to both saturated and unsaturated cyclic silyl ethers, the obvious penultimate synthetic precursors to both were the acetylenic silanes **2** which offered the advantages of synthetic ease and simple conversion to either saturated or unsaturated precursors,

Scheme I



Scheme II[a]



[a] A, R = Ph_3C; B, R = *t*-Bu; C, R = $PhCH_2$.

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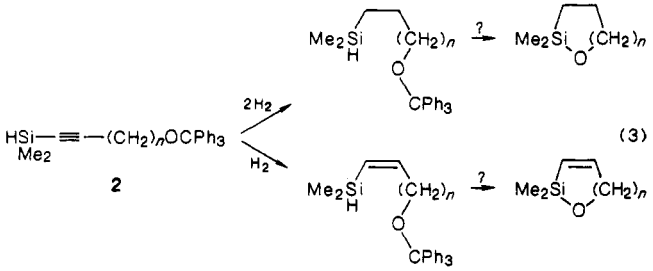
Table I

compd[a-c]	% yield	lit. ref[d]	bp, °C	^{1}H NMR, δ	^{13}C NMR, δ
5A	94	14			
5B	72	6			
5C	79	7			
6A	85		100–102 (mp)	2.0 (t, 2.6 Hz, 1 H), 2.5 (dt, 7 Hz, 2.6 Hz, 2 H), 3.2 (t, 7 Hz, 2 H), 7.4 (m, 15 H)	20.07, 62.05, 69.26, 86.22, + ArC's
6B	67		126–129	NMR spectra similar to **6A** except for R	
6C	69		101–104 (10 torr)	NMR spectra similar to **6A** except for R	
7A	93		185–190 (0.5 torr)	0.2 (d, 3.2 Hz, 6 H), 3.8 (s, 2 H), 4.1 (sep, 3.2 Hz, 1 H), 7.4 (m, 15 H)	−3.0, 53.83, 87.9, 104.2, + ArC's
7B	83		100–103 (45 torr)	NMR spectra similar to **7A** except for R	
7C	80		82–84 (0.6 torr)	NMR spectra similar to **7A** except for R	
8A	90		155–160 (0.05 torr)	0.2 (d, 3.6 Hz, 6 H), 2.4 (t, 8 Hz, 2 H), 3.1 (t, 8 Hz, 2 H), 4.0 (sep, 3.6 Hz, 1 H), 7.25 (m, 15 H)	−2.71, 21.61, 61.95, 86.75, 106.14, + ArC's
8B	87		101–104 (35 torr)	NMR spectra similar to **8A** except for R	
8C	82		106–109 (1.5 torr)	NMR spectra similar to **8A** except for R	
11A	61 (from **7A**)		145–109 (0.7 torr)	0.3 (d, 3.3 Hz, 6 H), 0.54 (m, 2 H), 1.61 (tt, 7.8 and 6.9 Hz, 2 H), 3.0 (t, 6.9 Hz, 2 H), 3.79 (m, 1 H), 7.25 (m, 15 H)	−4.39, 10.63, 25.11, 66.35, + trityl
11B	70 (from **(B)**		83–86 (5 torr)	NMR spectra similar to **11A** except for R	
11C	36 (from **7C**)		115–120 (3 torr)	NMR spectra similar to **11A** except for R	
12A	68 (from **8A**)		160–165 (0.4 torr)	0.04 (d, 3.7 Hz, 6 H), 0.53 (m, 2 H), 1.42 (m, 2 H), 1.64 (m, 2 H), 3.05 (tt, 6.4 and 2.4 Hz, 2 H), 3.84 (m, 1 H), 7.4 (m, 15 H)	−4.35, 11.05, 21.21, 33.49, 63.34, + trityl
12B	86 (from **8B**)		100–102 (1.5 torr)	NMR spectra very similar to **12A**	
12C	70 (from **8C**)		100–102 (1.5 torr)	NMR spectra very similar to **12A**	
13A	75		155–161 (0.5 torr)	0.0 (d, 3.8 hZ, 6 H), 3.72 (dd, 6.2 and 0.9 hZ, 2 H), 4.1 (sep, 3.8 Hz, 1 H), 5.63 (dt, 14.2 and 0.9 Hz, 1 H), 6.6 (dt, 14.2 and 6.2 Hz, 1 H), 7.3 (m, 15 H)	−3.32, 64.79, 126.99, 127.80, 128.85, 129.54, 144.32, 146.03
13B	88		82–85 (35 torr)	^{1}H NMR spectrum very similar to that of **13A**	−2.93, 27.69, 62.26, 73.36, 127.88, 146.99
13C	85		70–72 (0.3 torr)	^{1}H NMR spectrum very similar to that of **13A**	−3.1, 70.12, 72.4, 127.63, 127.85, 128.38, 129.77, 138.27, 145,47
14A	60		158–153 (0.5 torr)	0.13 (d, 3.8 Hz, 6 H), 2.49 (ddt, 6.9 and 6.7 and 1.6 Hz, 2 H), 3.08 (t, 6.7 Hz, 2 H), 4.21 (sep, 3.8 Hz, 1 H), 5.53 (dt, 13.9 and 1.6 Hz, 1 H), 6.35 (dt, 13.9 and 6.9 Hz, 1 H), 7.25 (m, 15 H)	−3.11, 33.99, 63.29, 86.54, 126.98, 127.77, 128.8, 144.4, 146.51
14B	73		98–101 (40 torr)	^{1}H NMR spectrum very similar to that of **14A**	−3.09, 27.61, 34.72, 61.3, 72.76, 128.05, 146.46
14C	81		96–99 (4 torr)	^{1}H NMR spectrum very similar to that of **14A**	−3.62, 33.64, 57.72, 71.43, 75.12, 127.69, 127.98, 128.33, 137.65, 145.88

[a] A, R = Ph_3C; B, R = *tert*-butyl; C, R = CH_2Ph. [b] All new compounds were characterized by ^{1}H and ^{13}C NMR, IR, mass spectra, exact mass, and satisfactory C H analyses. [c] Compounds **9** and **10** were usually carried on without purification. [d] All known compounds were characterized as in *b* except for elemental analysis.

the latter possessing the necessary cis stereochemistry for cyclization (eq 3).



The synthetic routes to the precursors for the saturated and unsaturated five- and six-membered rings are all given in Scheme I. Etherification of alcohols **3** and **4** was accomplished by the method of Hanessian[5] using *N*-(triphenylmethyl)pyridinium tetrafluoroborate. Silylation of the acetylides derived from **5** and **6** was accomplished in good yield by quenching with chlorodimethylsilane.

In addition to the trityl ethers, both the *tert*-butyl and benzyl ethers were prepared since any reasonably stable carbonium ion leaving group might be capable of sustaining the catalytic chain process. Yields for each step are presented in Table I. Catalytic hydrogenation of the triple bond also resulted in conversion of the silyl hydride to the methoxysilanes **9** and **10** which in some cases were not purified before reduction to the desired hydrides **11** and **12** with $LiAlH_4$. Partial reduction of **7** and **8** was accomplished with diisobutylaluminum hydride/*N*-methylpyrrolidine[8] to provide the cis olefins **13** and **14**. No efforts toward yield optimization were made.

Cyclizations of the four trityl ethers **11A**, **12A**, **13A**, and **14A** were conducted by adding a 0.1 molar equiv of triphenylmethyl perchlorate to a methylene chloride solution of the silyl hydride at 0 °C. The reactions were immediately complete as evidenced by GC and NMR analysis. Apparently, the *tert*-butyl and benzyl groups cannot carry the chain reaction as it was found to be necessary to use

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stoichiometric amounts of trityl perchlorate to carry the reactions of these ethers to completion. The four general cyclization reactions are given in Scheme II. Although all cyclizations were successful, the benzyl ethers were always by far the least effective.

Finally, it should be noted that while the intramolecular catalytic cyclizations originally proposed have been successful, this cannot be taken as evidence for free silylenium ions in these reactions. There is no reason to believe that nucleophilic attack by oxygen does not occur before complete loss of hydride, and we suspect that is indeed the case.

Experimental Section

Instrumentation. ^{1}H NMR were recorded on a Nicolet Model NT-300 at 300 MHz in $DCCl_3$. ^{13}C NMR spectra were obtained on the same instrument at 75.5 MHz. IR spectra (not reported but obtained for all products) were taken on an IBM 98 FTIR. GC/MS were taken on a Hewlett-Packard 5970 attached to an HP 5890 GC. Exact mass measurements were made on a Kratos MS-50 at 70 eV. Analytical GC was done on an HP 5790 GC using a 12- or 30-m RSL-150 column. All GC yields were determined with internal standards and predetermined response factors. Preparative GC was performed on a Varian Model 920 GC. Boiling and melting points are uncorrected.

Triphenylmethyl perchlorate was prepared by the method of Dauben.[9]

2,2-Dimethyl-1-oxa-2-silacyclopentane (15). Yields given in Scheme II are by GC analysis. An analytical sample was obtained by preparative GC (8 ft × $^1/_4$ in. 15% SE-30 on Chromosorb W at 90 °C) and identified by GC/MS and ^{1}H NMR comparison with literature values.[10-12]

3,3-Dimethyl-4-oxa-3-silacyclopentene (16). Yields were determined by GC analysis. An analytical sample was obtained by preparative GC (10 ft × $^1/_8$ in. 15% OV-101 column, 50–270 °C/5 °C/min) and identified by GC/MS and ^{1}H NMR comparison with an authentic sample.[13]

2,2-Dimethyl-1-oxa-2-silacyclohexane (17). Yields were determined by GC analysis. An analytical sample was obtained by preparative GC (8 ft × $^1/_4$ in. 15% SE-30 on Chromosorb W at 100 °C) and identified by GC/MS and ^{1}H NMR comparison with literature values.[10-12]

3,3-Dimethyl-4-oxa-3-silacyclohexene (18). GC determined yield. Analytical sample obtained by preparative GC (8 ft × $^1/_4$ in. 15% SE-30 Chromosorb W at 100 °C): ^{1}H NMR δ 0.17 (s, 6 H), 2.25 (tdd, 5.3, 4.0, and 2.0 Hz, 2 H), 3.95 (t, 5.3 Hz, 2 H), 5.74 (dt, 14.2 and 2.0 Hz, 1 H), 6.82 (dt, 14.2 and 4.0 Hz, 1 H); ^{13}C NMR δ −0.62, 31.12, 61.73, 127.23, 147.76; IR 2974, 2931, 1585, 1261, 1087, 1050 cm^{-1}; calcd for $C_6H_{12}OSi$ m/e 128.0658, measd m/e 128.0660. Anal. Calcd for $C_6H_{12}OSi$: C, 56.19; H, 9.43. Found: C, 56.50; H, 9.36.

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Registry No. 5A, 82816-38-4; **5B**, 16314-18-4; **5C**, 4039-82-1; **6A**, 75014-48-1; **6B**, 59574-66-2; **6C**, 22273-77-4; **7A**, 110827-10-6; **7B**, 110827-11-7; **7C**, 110827-12-8; **8A**, 110827-13-9; **8B**, 110827-14-0; **8C**, 110827-15-1; **9A**, 110827-16-2; **9B**, 110827-17-3; **9C**, 110827-18-4; **10A**, 110827-19-5; **10B**, 110827-20-8; **10C**, 110827-21-9; **11A**, 110827-22-0; **11B**, 110827-23-1; **11C**, 110827-24-2; **12A**, 110827-28-6; **12B**, 110827-29-7; **12C**, 110827-30-0; **13A**, 110827-25-3; **13B**, 110827-26-4; **13C**, 110827-27-5; **14A**, 110827-31-1; **14B**, 110827-32-2; **14C**, 110827-33-3; **15**, 3292-88-4; **16**, 110827-34-4; **17**, 5833-47-6; **18**, 110827-35-5; Me_2HSiCl, 1066-35-9; $Ph_3C^+ClO_4^-$, 3058-33-1.

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Strained Palladium(II) Complexes:[1] Synthesis and Complexation of Functionalized 8,8′-Dimethyl-2,2′-biquinolines

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The syntheses of several new 2,2′-biquinoline derivatives are described. Active metal coupling of 2-bromo-8-methylquinoline gave 8,8′-dimethyl-2,2′-biquinoline. Application of α-methyl functionalization techniques gave the derivatized 8,8′-dimethyl-2,2′-biquinolines. Formation of an N,N-coordinated Pd(II) complex with either 8,8′-bis(cyanomethyl)- or 8,8′-bis[2,2-bis(methoxycarbonyl)ethyl]-2,2′-biquinoline proved unsuccessful; however, a monometalated C,N,N complex was obtained with 8,8′-dimethyl-2,2′-biquinoline.

Introduction

Our interest in the structural features of novel strained metallacycles of the platinum metals has led us to the synthesis of diverse ligands containing varying functionalities.[2] The primary purpose has been to determine which structural features of the ligand cause those subtle changes in the binding locus so that either a metal selectivity or molecular inclusion of a neutral guest can be achieved. To this end, we herein report the expansion of our series to include a highly sterically hindered N,N-coordination site in order to determine the problems caused by molecular crowding at the binding locus.

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