7: IR (neat) ν_{CO} 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (d, 3 H, CH_3C=, J = 1.5 Hz), 1.42 (d, 3 H, CH_3CH, J = 6 Hz), 1.67 (d, 3 H, CH_3C=, J = 1.5 Hz), 1.95 (s, 3 H, $COCH_3$), 5.51 (m, 1 H, CH=), 6.05 (q, 1 H, $CHCH_3$), 7.27 (s, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 16.14, 17.65, 21.94, 22.37 (methyl carbons), 51.40 ($CHCH_3$), 119.95 (CH=), 127.23, 127.77, 128.14 (aromatic CH), 138.39, 140, 56 (quarternary carbons), 170.35 (carbonyl carbon). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.00; H, 8.57; N, 6.68.

8: IR (neat) ν_{CO} 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.73 (d, 3 H, CH_3CH), 2.23 (s, 6 H, $COCH_3$), 5.85 (q, 1 H, $CHCH_3$), 7.32 (s, 5 H, Ph); mass spectrum, (m/e) 205 (M^+), 162 [$(M-COCH_3)^+$]. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C. 70.04; H, 7.34; N, 6.46.

9: IR (neat) ν_{NH} 3250, ν_{CO} 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48 (d, 3 H, CH_3CH, J = 8 Hz), 1.92 (s, 3 H, $COCH_3$), 5.10 (m, 1 H, CH), 6.15 (br s, 1 H, NH, undergoes D_2O exchange), 7.22 (s, 5 H, Ph); mass spectrum, m/e 163 (M^+).

Reaction of 6 with Acetyl Chloride and Triethylamine. To 0.40 g (2.3 mmol) of **6** in dry benzene (50 mL) was added acetyl chloride (0.3 mL). The solution was stirred for 15 min, 0.30 g (3.0 mmol) of triethylamine was added, and the reaction mixture was stirred at room temperature for 1.5 h and then refluxed for 2 h. Workup as in procedure A above gave **7** in 82% yield.

Reaction of 10 with Acetyl Chloride and 1. Acetyl chloride (0.2 mL) was added to 0.4 g (2.0 mmol) of **10** in benzene (50 mL), and the solution was stirred for 30 min at room temperature. Addition of the zirconium hydride (0.53 g, 2.0 mmol), followed by stirring for 17 h, and the usual workup conditons gave 0.27 g (56%) of **11**/**12** in a 6:1 ratio. Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.75. Found: C, 78.62; H, 9.15; N, 5.90.

11: IR (neat) ν_{CO} 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 3 H, CH_3C=), 1.3-1.7 (m, 4 H, CH_2CH_2), 1.75-2.30 (m, 4 H, allylic hydrogens), 1.96 (s, 3 H, $COCH_3$), 4.62 (s, 2 H, CH_2Ph), 7.32 (s, 5 H, Ph); mass spectrum, m/e 243 (M^+).

12: IR (neat) ν_{CO} 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (d, 3 H, $CHCH_3$), 1.30-1.7 (m, 4 H, CH_2CH_2), 1.75-2.20 (m, 4 H, allylic hydrogens), 2.06 (s, 3 H, $COCH_3$), 4.63 (q, 2 H, CH_2Ph), 5.33 (m, 1 H, CH=), 7.32 (s, 5 H, Ph); mass spectrum, m/e 243 (M^+).

Reaction of 10 with Acetyl Chloride and Triethylamine. Reaction was effected in the manner described for **6** to give **11** and **12** in a 3:1 ratio (58% yield).

Reaction of 13 with Acetyl Chloride and 1. Reaction was effected as described for **10** to give the enamide **14** in 44% yield and **9** in 12% yield.

14: IR (neat) ν_{CO} 1645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 3 H, CH_3C=), 1.47 (m, 3 H, CH_3CH), 1.93 (s, 3 H, $COCH_3$), 0.9-2.4 (m, 8 H, saturated protons of cyclohexene ring), 5.80 (m, 1 H, $CH(CH_3)$Ph), 7.23 (s, 5 H, Ph); mass spectrum, m/e 257 (M^+), 242 [$(M - CH_3)^+$], 214 [$(M - COCH_3)^+$]. Anal. Calcd for $C_{17}H_{23}NO$: C, 79.33; H, 9.00; N, 5.44. Found: C, 79.35; H, 9.32; N, 5.38.

Reaction of 16 with 1 and Acetyl Chloride. Reaction was effected as described in procedure A of **6** to give **17** in 28% yield and **8** in 17% yield.

17: IR (neat) ν_{CO} 1642 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.52 (d, 3 H, CH_3CHPh, J = 7 Hz), 2.03 (s, 3 H, $COCH_3$), 1.20-2.33 (m, 8 H, saturated protons of cyclohexene ring), 5.48 (m, 1 H, CH=), 6.00 (q, 1 H, $CH(Ph)CH_3$), 7.35 (s, 5 H, Ph); mass spectrum, m/e 243 (M^+), 200[$(M - COCH_3)^+$]. Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.75. Found: C, 78.96; H, 9.00; N, 5.64.

Reaction of 18 with 1 and Acetyl Chloride. Reaction was effected as described in procedure A of **6** to give **19** in 34% yield and **9** in 41% yield.

19: IR (neat) ν_{CO} 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.47 (d, 3 H, CH_3CHPh, J = 8 Hz), 1.58 (m, 3 H, CH_3CH=), 2.07 s, 3 H, $COCH_3$), 5.2-5.8 (m, 2 H, olefinic protons), 6.10 (q, 1 H, $CH(Ph)CH_3$), 7.23 (s, 5 H, Ph); mass spectrum, m/e 203 (M^+). Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 77.02; H, 8.43; N, 6.54.

Reaction of 18 with 1 and Methyl Oxalyl Chloride. Reaction was effected in the same manner as described in the previous procedure (except that methyl oxalyl chloride was used instead of acetyl chloride), affording **20** in 32% yield and **21** in 27% yield.

20: IR (neat) ν_{CO} 1740, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.52 (d, 3 H, CH_3CH, J = 7 Hz), 3.78 (s, 3 H, OCH_3), 5.98 (q, 1 H, $CHCH_3$), 6.20 (br m, 1 H, NH), 7.30 (s, 5 H, Ph); mass spectrum, m/e 207 (M^+). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.31; N, 6.76. Found: C, 64.11; H, 6.38; N, 6.58.

21: IR (neat) ν_{CO} 1730, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.58 (d, 3 H, CH_3CH, J = 7 Hz), 1.82 (dd, 3 H, CH_3CH=, J_{CH_3CCH} = 2.5 J_{gem} = 7 Hz), 3.95 (s, 3 H, OCH_3), 5.1-5.7 (m, 2 H, olefinic protons), 6.30 (q, 1 H, $CHCH_3$), 7.38 (s, 5 H, Ph); mass spectrum, m/e 247 (M^+). Anal. Calcd for $C_{14}H_{17}NO_3$: C, 68.00; H, 6.93; N, 5.66. Found: C, 67.91; H, 7.16; N, 6.02.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council for support of this work.

Registry No. **1**, 37342-97-5; **6**, 18805-19-1; **7**, 76947-29-0; **8**, 76947-30-3; **9**, 6284-14-6; **10**, 31887-88-4; **11**, 76947-31-4; **12**, 76947-32-5; **13**, 76947-33-6; **14**, 76947-34-7; **16**, 6115-06-6; **17**, 76947-35-8; **18**, 56063-09-3; **19**, 76947-36-9; **20**, 76947-37-0; **21**, 76947-38-1; acetyl chloride, 75-36-5; methyl oxalyl chloride, 5781-53-3.

Silanes in Organic Synthesis. 10. Cleavage Reactions of Silylcyclopropanes with Titanium Tetrachloride and Hydrogen Chloride[1]

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Seven trimethylsilyl-substituted cyclopropanes, both mono- and bicyclic, were treated with titanium tetrachloride and anhydrous hydrogen chloride to determine the regioselectivity and stereoselectivity of electrophilic attack on their strained three-membered ring. Whereas cleavage of *exo*-6-(trimethylsilyl)bicyclo[3.1.0]hexane with $TiCl_4$ occurs predominantly at the zero bridge, the principal product obtained from treatment with HCl is the result of peripheral bond scission. In the case of *exo*-7-(trimethylsilyl)bicyclo[4.1.0]heptane, addition to an edge bond occurs regiospecifically with both reagents. Substrates **11** and **12** were examined to assess the importance of carbonium ion intervention. Structural isomerizations mediated by such intermediates were observed with both silylcyclopropanes. For 1-(trimethylsilyl)bicyclo[4.1.0]heptane and 1-(trimethylsilyl)-1-pentylcyclopropane, the altered position of the silicon substituent was seen to have a major effect on the course of ring opening. Although the present data allow some analogies to be drawn with vinylsilanes, it is clear that silylcyclopropanes have a broader range of reaction pathways available to them than do their olefinic counterparts.

Spectroscopic[2] and chemical studies[3] of vinylsilanes have played an important role in the development of our understanding of the manner in which the olefinic π cloud interacts with neighboring silicon's vacant d orbitals.[4] The

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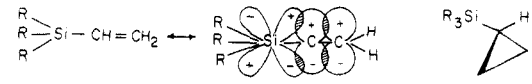
diminished reactivity of vinylsilanes toward various electrophilic reagents such as dichlorocarbene,[5] peracids,[6] iodomethylzinc iodide,[7] and singlet oxygen[1,8] has led to the postulate that C → Si π bonding as in **1** contributes substantially to their ground-state character.



1 **2**

Interestingly, no comparable analysis appears to have been made of the electronic character of silylcyclopropanes (**2**).[9] Of the two models proposed for bonding within cyclopropane rings,[10,11] that advanced by Walsh nicely explains the unusual conjugating properties of the three-membered cycle[12] and is presently favored by theoreticians.[13] Because recent reports of the behavior of **2** toward several electrophilic reagents have shown this substance to be somewhat unpredictable in product formation (see below), we felt that a systematc examination of the chemical properties of silylcyclopropanes was in order. Herein we report on their interesting reactivity toward titanium tetrachloride and hydrogen chloride under anhydrous conditions.

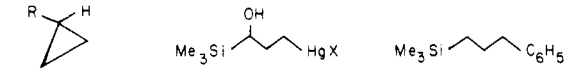
Background. Silylcyclopropanes are presently available through Simmons–Smith cyclopropanation of vinylsilanes,[14] addition of (trimethylsilyl)diazomethane to olefins,[15] condensation of cyclopropyllithium with trimethylsilyl chloride,[16] ring opening of trimethylsilyl-substituted bicyclobutanes,[15c] and (trimethylsilyl)methylenesulfurane addition to α,β-unsaturated ketones.[17] Despite the wide structural variations potentially attainable by these synthetic techniques, only the unsubstituted system **2** had so far been subjected to the action of electrophiles. When treated with such reagents as iodine monochloride,[18] acyl chlorides and $AlCl_3$,[19] and trimethylsilyl chlorosulfonate,[20] (trimethylsilyl)cyclopropane was found to experience replacement of the silyl subsitutent to give **3a–c**, respectively. With 48% hydrobromic acid or 92% sulfuric acid, cyclopropane is produced,[14c] presumably by a related pathway. In contrast, mercury salts in aqueous solution act very slowly on **2** (R = CH_3) to give the *ring-opened* products **4**.[21] With aluminum chloride in benzene, the same substrate is converted to **5** in 18% yield.[14c] A remarkable feature of the latter two reactions is their contrasting regioselectivity. Whereas **5** results from cleavage in that direction which transiently positions the positive charge as remotely as possible from the trimethylsilyl group, **4** emanates from a process which generates carbocation character α to silicon, generally a strongly destabilizing state of affairs. The electronic consequences of this phenomenon are reflected in the relative rates of attack (substantially retarded relative to other substituted cyclopropanes) of HgX_2 on **2**.[21]

When **2** is treated with elemental bromine (CCl_4, reflux 4 days) or Br_2–$AlBr_3$ (CCl_4, 2 h), mixtures of bromides **6–8** are obtained.[18] It is possible that **8** arises from initial replacement of Me_3Si by Br followed by brominative ring cleavage. The production of **6** is thought to be dependent

Table I. Comparison of the Seyferth (A) and Olofson (B) Silylcyclopropanation Procedures

olefin	method	yield, %[a]
cyclohexene	A	22.4
	B	31.3
cyclopentene	A	20.7
	B	32.2
norbornene	A	28.9
	B	33.5

[a] Yields are recorded for distilled product.



3a, R = I
b, R = COR'
c, R = SO_3SiMe_3

4 **5**

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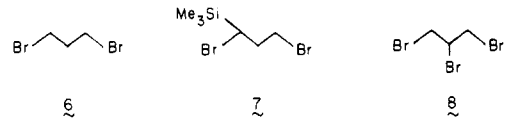
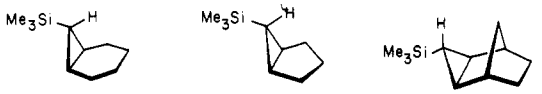


6 7 8

on the liberation of hydrogen bromide, subsequent protodesilylation, and ultimate cyclopropane ring scission.

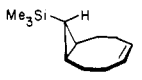
Since no information was available concerning the effect which alkyl substituents might exert on the various mechanistic options, we set out to incorporate such features into the silylcyclopropanes which are reported on here.

Substrate Selection and Synthesis. Previously, Seyferth and co-workers had shown that cuprous chloride catalyzed decomposition of (trimethylsilyl)diazomethane in cyclohexene at 0 °C yields a product mixture in which *anti*-7-(trimethylsilyl)norcarane (**9**) predominates.[15a,b]



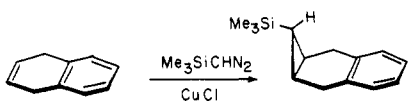
9 10 11

More recently, Olofson demonstrated that treatment of an excess of cyclohexane with a hexane solution of lithium 2,2,6,6-tetramethylpiperidide and (chloromethyl)trimethylsilane also gave **9**.[15f] While both procedures proceed best with the exclusion of oxygen and moisture, the Seyferth method makes use of (trimethylsilyl)diazomethane, itself the end product of a multistep synthesis,[15b,e,22,23] while the Olofson technique utilizes (chloromethyl)trimethylsilane, a commercially available substance. Nonetheless, direct comparison of the two methods was made by allowing a fivefold molar excess of each of three olefins to react with the two carbene precursors. As Table I indicates, the Olofson procedure consistently gave higher yields of the desired silylcyclopropanes **9**–**11**. Furthermore, whereas the Seyferth method provided products contaminated with *cis*- and *trans*-1,2-bis(trimethylsilyl)ethylenes, only trace amounts of these products were noted when (chloromethyl)trimethylsilane was utilized. Consequently, the Olofson procedure was employed in the synthesis of **12**.



12

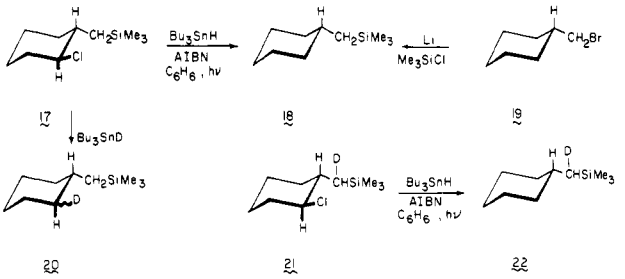
However, a limitation of the latter olefin silylcyclopropanation was made apparent in the case of 1,4-dihydronaphthalene (**13**) which was prepared by the sodium–ethanol reduction of naphthalene[24] and stringently purified by the Sand–Genssler technique.[25] When treated with (chloromethyl)trimethylsilane and lithium 2,2,6,6-tetramethylpiperidide, **13** yielded not the expected adduct **14** but a mixture of several allylic C–H insertion products



13 14

whose characterization was not pursued. The direct formation of **14** was, in contrast, achieved uneventfully by means of the Seyferth method.

Scheme I



In the case of **15** and **16**, the Simmons–Smith reaction was applied to the corresponding vinylsilanes which in turn were readily obtained from the ketones.[26]

15 16

The choice of **11** and **12** was predicated on the knowledge that norbornyl and 4-cyclooctenyl cations are highly responsive to structural isomerization. Therefore, the extent to which cationic character develops as these particular silylcyclopropanes are attacked by $TiCl_4$ and HCl should be appropriately reflected in the resultant products.

It can be seen that **9**–**12** and **14** are 2,3-disubstituted silylcyclopropanes. With **15** and **16** in hand, prototypical 1,2-disubstituted and 1-alkyl derivatives also were available.

Behavior toward Titanium Tetrachloride. Although the advantageous Lewis acid properties of titanium tetrachloride are now widely recognized,[27] this reagent has not been previously utilized to effect cyclopropane ring cleavage. Treatment of **9** with 1.2 equiv of titanium tetrachloride in dichloromethane at −78 °C for 5 h followed by a water quench afforded a single product in 84% isolated yield. The upfield portion of its ^1H NMR spectrum in $CDCl_3$ shows a singlet of area 9 at δ 0.06 due to the trimethylsilyl group and the AB portion of an ABX system centered at δ 0.40 attributable to a methylene group also bonded to the silicon atom. Downfield, there was seen a sextet centered at δ 3.59 produced by a coupling of 9.5 Hz to two protons plus coupling to a third with a constant of 4.0 Hz. This chemical shift and splitting pattern correspond uniquely to an axial proton which finds itself geminal to chlorine and vicinal to one equatorial and two axial hydrogens[28,29] and define the product to be **17**. Additional structural confirmation was derived by reductive dehalogenation to **18** (Scheme I) which proved identical with an authentic sample prepared from **19**.

When the ring-cleavage reaction mixture was quenched with deuterium oxide, the deuterated product **21** was obtained. The site of isotopic substitution was easily recognized by ^1H NMR spectroscopy (δ 0.41 peak altered to a doublet of triplets) and by reductive dechlorination to **22**. The latter silane was easily differentiated from **20**.

Upon comparable exposure of **10** to titanium tetrachloride (H_2O quench), the isomeric chlorosilanes **23a** and

(22) (a) Lappert, M. F.; Lorberth, J. *J. Chem. Soc., Chem. Commun.* **1967**, 836. (b) Schollkpf, U.; Scholz, H.-U. *Synthesis* **1976**, 271.

(23) A two-step procedure beginning with (chloromethyl)trimethylsilane has recently been devised: Barton, T. J.; Hoekman, S. K. *Synth. Ract. Inorg. Met.-Org. Chem.* **1979**, *9*, 297.

(24) Cook, E. S.; Hill, A. J. *J. Am. Chem. Soc.* **1940**, *62*, 1995.

(25) Sand, J.; Genssler, O. *Chem. Ber.* **1903**, *36*, 3699.

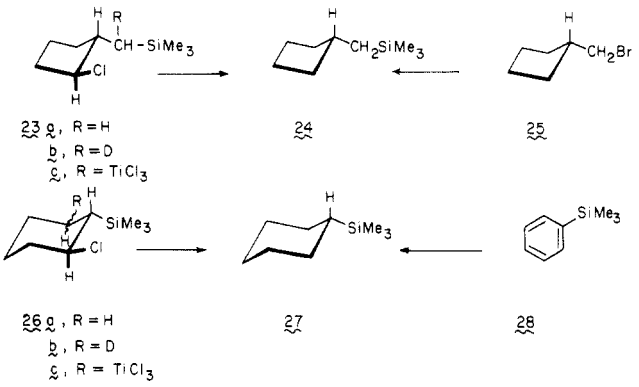
(26) (a) Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017. (b) Taylor, R. T.; Degengardt, C. R.; Melega, W. P.; Paquette, L. A. *Tetrahedron Lett.* **1977**, 159.

(27) Mukaiyama, T. *Agnew. Chem., Int. Ed. Engl.* **1977**, *16*, 817.

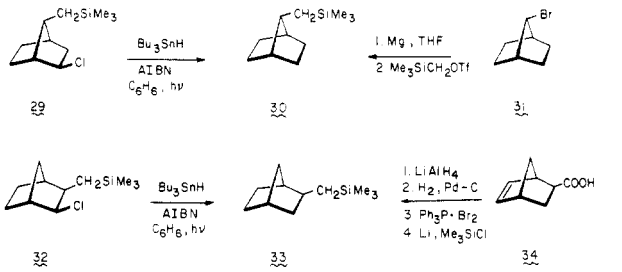
(28) Bovey, F. A. "Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1969, p 132.

(29) Jensen, F. R.; Patterson, D. B.; Dinizo, S. E. *Tetrahedron Lett.* **1974**, 1315.

Scheme II



Scheme III

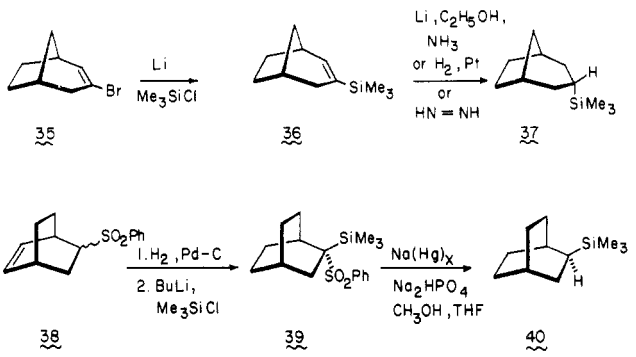


26a were formed in 85% yield (ratio 14:86). These compounds were readily separated by vapor-phase chromatography. The trans stereochemical assignment to **23a** is based upon the appearance of a downfield sextet at δ 3.8. In the case of **26a**, the ^{1}H NMR spectrum displays a similar, although less sharply defined,[30] signal at δ 3.89. Reductive dechlorination of **23a** and **26a** (Scheme II) gave pure 1-[(trimethylsilyl)methyl]cyclopentane (**24**) and (trimethylsilyl)cyclohexane (**27**), respectively.

With deuterium oxide as the quenching agent, the deuterated products **23b** and **26b** were isolated. Because the signal of the residual C_6 proton in **26b** falls under the envelope generated by the three cyclohexyl methylene groups, no information could be obtained on the stereodisposition of the isotopic label.

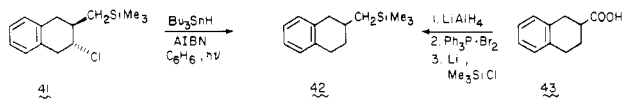
Titanochlorination[31] of **11** under the same conditions yielded a mixture of two chlorinated silanes which defied VPC separation. Additionally, because of the essentially identical chemical shifts of their trimethylsilyl singlets, reliable integration was not possible at this stage. However, reductive dechlorination of the mixture enabled us to deduce that the product ratio was 66:34. Furthermore, ^{13}C NMR analysis of the resultant silanes revealed the major product to be symmetrical and the minor unsymmetrical. The structures of these reduction products were conclusively established through independent synthesis of **30** and **33** as shown in Scheme III and by direct spectral comparisons. With this information in hand, it was possible on the basis of ^{1}H NMR spectral analysis and mechanistic rationale to deduce that **29** and **32** were the major and minor products, respectively.

Scheme IV

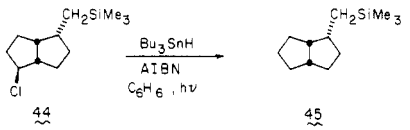


Two other possible product candidates were also synthesized as indicated in Scheme IV. Careful VPC studies indicated that neither **37** nor **40** was present in detectable amounts in the dechlorinated product mixture.

Although the behavior of **14** generally paralleled that of the parent bicyclo[4.1.0]heptane **9**, the resultant chlorosilane in this instance (**41**) was found to be contaminated with variable minor amounts of its nonchlorinated counterpart **42**. The appearance of this byproduct remains unexplained but may be linked to the fact that somewhat higher temperatures (−22 °C) were necessary to achieve ring cleavage in this case. To authenticate the structural assignment, **41** was reduced to **42** and this silane was synthesized independently from the commercially available carboxylic acid **43**.



Following reaction of **12** with 1.2 equiv of $TiCl_4$ at −78 °C for 5 h, there was isolated in 86% yield a single stereochemically homogeneous product. Its ^{1}H NMR spectrum (in $CDCl_3$) consists inter alia of a downfield singlet of area 1 at δ 4.01 in addition to an upfield doublet (J = 11 Hz, 2 H) and singlet (9 H) at δ 0.59 and 0.02, respectively. That the compound was a bicyclo[3.3.0]octane derivative was demonstrated by tri-*n*-butyltin hydride reduction to **45**, a saturated compound possessing a



CH_2SiMe_3 substituent. Consideration of bond orientations in a molecular model of **12** indicates that the (trimethylsilyl)methyl substituent is certain to adopt an endo orientation during transannular cyclization, a conclusion that is additionally supported by precedent.[32] The pseudoequatorial nature of the chlorine in **44** is suggested by the negligible spin–spin interaction of the geminal (pseudoaxial) proton with its immediate neighbors.

The response of both **15** and **16** to the action of titanium tetrachloride in dichloromethane solution at various temperatures was much less well-defined. On no occasion was the formation of chlorinated silanes observed. These silylcyclopropanes were recovered intact from reactions conducted in the region of −70 °C. At higher temperatures, some detrimethylsilylation was apparent in the midst of

(30) The calculated (Ouellette, R. J.; Baron, D.; Stolfo, J.; Rosenblum, A.; Weber, P. *Tetrahedron* **1972**, *28*, 2163) conformational parameters for axial and equatorial Me_3Si substituents show the equatorial to be favored by 3.41 kcal/mol. An experimental ^{13}C NMR study has confirmed the pronounced bias (K >100) for the equatorial isomer (Ouellette, R. J.; Vinson, E., unpublished results). The A values for Me_3Sn (1.06) and Me_3Pb (0.67) are less because of the increased length of the carbon–metal bond (Kitching, W.; Doddrell, D.; Grutzner, J. B. *J. Organomet. Chem.* **1976**, *17*, C5).

(31) The term "titanochlorination" refers to that process which involves cleavage of a cyclopropane ring with placement of a titanium and a chlorine atom in a 1,3-relationship on the new alicyclic framework.

(32) Cope, A. C.; Lee, H.-H.; Petree, H. E. *J. Am. Chem. Soc.* **1958**, *80*, 2849. Crandall, J. K.; Chang, L.-H. *J. Org. Chem.* **1967**, *32*, 532. Sheng, M. N. *Synthesis* **1972**, 194. Whitesell, J. K.; White, P. D. *Ibid.* **1975**, 602. McIntosh, J. M. *Can. J. Chem.* **1972**, *50*, 2152. Posner, G. H.; Rogers, D. Z. *J. Am. Chem. Soc.* **1977**, *99*, 8208.

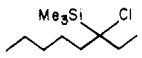
rather extensive decomposition. This behavior contrasts with that encountered with hydrogen chloride as described below.

Hydrogen Chloride Promoted Ring Scission. In the mechanistic considerations which follow, we have assumed that titanium tetrachloride is the electrophilic reagent responsible for the observed silylcyclopropane ring cleavages. Since the workup of these reactions does generate hydrochloric acid via hydrolysis of the residual $TiCl_4$ as well as the organotitanium species, it was necessary to conduct appropriate control experiments involving this reagent. When dichloromethane solutions of the highly reactive **9** were treated with aqueous hydrochloric acid under conditions which duplicated our conventional workup procedure for the $TiCl_4$ reactions, unreacted silylcyclopropane was recovered essentially quantitatively. No trace of **17** or any other chlorinated product was seen. Consequently, it is clear that the observed cleavage reactions do not occur during the processing of the reaction mixtures.

On the other hand, the (trimethylsilyl)cyclopropanes described herein do undergo facile ring opening upon treatment with *anhydrous* hydrogen chloride in dichloromethane at −78 °C. Furthermore, the strikingly different product distributions which materialize in certain cases denote somewhat divergent electrophilic demands for $TiCl_4$ and HCl. Whereas **9** gave rise uniquely to **17** as before, **10** underwent only peripheral bond cleavage to give **23a** (54% isolated), and **11** was transformed into a 92:8 mixture of **29** and **32**.

The previously recalcitrant systems **15** and **16** were found to respond cleanly to anhydrous HCl. Thus, **15** was converted to a 29:71 mixture of **17** and **46** (undefined

46

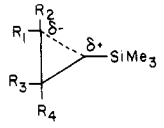


47

stereochemistry), while **16** underwent smooth ring opening to deliver the single product **47**. The structures of the last two compounds were deduced on the basis of their ^1H and ^{13}C NMR spectra (see Experimental Section).

Discussion

Silylcyclopropane Polarization and the $TiCl_4$/HCl Dichotomy. The three-membered ring of a silylcyclopropane can be written in three polarized forms (**48**–**50**).



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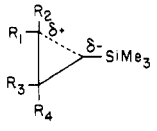

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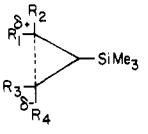
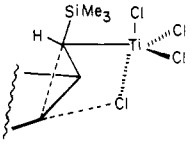


50

Appropriate overlap of the cyclopropane Walsh orbitals with the vacant d orbitals of silicon will result in the development of a negative charge α to this substituent and a positive charge on the adjacent carbon in the gound state as depicted in **49**. This particular electronic character will be enhanced by the placement of alkyl groups at R_1 and R_2. On the other hand, if $R_1 = R_2 = H$, it becomes less clear whether **49** or its electrically switched counterpart **48** will gain importance during a transition state for ring cleavage. The thermodynamic difference between a primary carbocation and a silyl-substituted secondary cation has not been elucidated. Steric factors are also known to be capable of determining ultimate product composition. Polarized state **50** can be expected to become significant when the "back bond" is more highly strained than normal, e.g., when in a bicyclo[2.1.0]pentane framework. When bond scission in this mode is sufficiently developed that the C–Si bond and the adjoining vacant p orbital can be stereoelectronically aligned, added stabilization can develop. However, this is not expected to be realized at the time that cleavage is initiated.

When dealing with the subject of electrophilic attack on cyclopropanes, one must ever be conscious of the ease with which edge-protonated three-membered rings can materialize, irrespective of whether a proton,[33a-c] acylium ion,[33d] or other positively charge species is involved. The present expectation was that this phenomenon would be most likely observed during the HCl-promoted reactions and evidence to this effect is presented below.[34]

Little is known about the mechanism by which $TiCl_4$ enters into electrophilic reactions, except perhaps in the case of the low-temperature polymerization of olefins[35] developed by Ziegler[36] and Natta where the Cossee mechanism[37] has been subjected to detailed theoretical scrutiny.[38] Perhaps much in the same manner as isonitriles insert into Ti–Cl bonds,[39] the titanium atom may become distorted toward a trigonal bypyramid as attack on the cyclopropane ring begins. The corner-titanated cyclopropanes may therefore resemble **51** and **52**, although no information is presently available concerning the question of retention or inversion of configuration at the carbon which is under siege.



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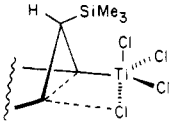


52

The formation of a titanium–carbon bond during titanochlorination has been established by D_2O quench of several reaction mixtures. The facile deuteronolysis of the C–Ti linkage[40] introduces a deuterium atom without evidence of isotopic scrambling.

Regioselectivity of Silylcyclopropane Cleavage by $TiCl_4$ and HCl. Attack of titanium tetrachloride on the bicyclo[3.1.0]hexane derivative **10** is not regiospecific. Thus, cleavage of a peripheral cyclopropyl C–C bond with formation of **23c** accounts for only 14% of the titanochlorinated product mixture. Major product **26c** (86%) results from rupture of the zero bridge bond. The parent bicyclo[3.1.0]hexane (**53**) has been reported to show a preference for fission of a three-membered ring C–C bond external to the larger ring when treated with *p*-toluene-

(33) (a) Baird, R. L; Aboderin, A. A. *J. Am. Chem. Soc.* **1964**, *86*, 252. (b) Aboderin, A. A.; Baird, R. L. *Ibid.* **1964**, *86*, 2300. (c) Collins, C. J. *Chem. Rev.* **1969**, *69*, 543. (d) Hart, H.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1966**, *88*, 5030; **1968**, *90*, 5189.

(34) For discussions relatin to the acid-catalyzed ring openings of silyl epoxides, see: Hudrlik, P. F.; Misra, R. N.; Withers, G. P.; Hudrlik, A. M.; Rona, R. J.; Arcoleo, J. P. *Tetrahedron Lett.* **1976**, 1453; Hudrlik, P. F.; Arcoleo, J. P.; Schwartz, R. H.; Misra, R. N.; Rona, R. J. *Ibid.* **1977**, 591; Hudrilik, P. F.; Hudrlik, A. M.; Rona, R. J.; Misra, R. N.; Withers, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 1993.

(35) Bestian, H.; Clauss, K. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 704.

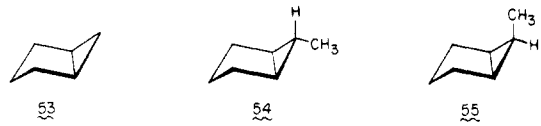
(36) Ziegler, K.; Holzkamp, E.; Breil, H.; Martin, H. *Angew. Chem.* **1955**, *67*, 541.

(37) Cossee, P. *J. Catal.* **1964**, *3*, 80. Cossee, P. "The Stereochemistry of Macromolecules"; Ketley, A. D., Ed.; Marcel Dekker: New York, 1967, Vol. I, Chapter 3, p 145.

(38) Armstrong, D. R.; Perkins, P. G.; Stewart, J. J. P. *J. Chem. Soc., Dalton Trans.* **1972**, 1972; Cassoux, P.; Crasnier, F.; Labarre, J.-F. *J. Organomet. Chem.* **1979**, *165*, 303.

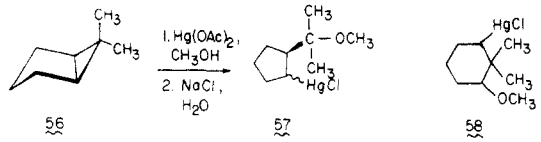
(39) Crociani, B.; Nicolini, M.; Richards, R. L. *J. Organomet. Chem.* **1975**, *101*, Cl.

(40) Eisch, J. J.; Manfre, R. J.; Komar, D. A. *J. Organomet. Chem.* **1978**, *159*, C13.



53 54 55

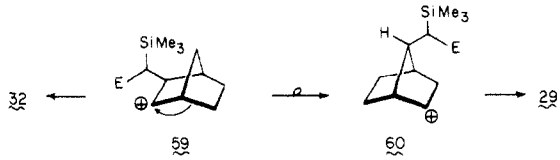
sulfonic acid in acetic acid (68–75%)[41,42] and diborane (92–95%).[43] Three known exceptions are thallium triacetate (46.5%),[44] mercuric acetate (37%),[45] and bromine (7%)[46] which show instead a greater propensity to add to the internal, more subsituted cyclopropane bond. Acid-catalyzed acetolysis of the epimeric 6-methylbicyclo[3.1.0]hexane **54**[47] and **55**[48] has indicated that alkyl substitution of the one-carbon bridge leads to an increase in internal bond cleavage. In the case of **55**, nearly equal amounts of methylcyclopentylcarbinyl acetate and *cis*-2-methylcyclohexyl acetate are produced. These findings contrast with the response of the 7,7-dimethyl derivative **56** to oxymercuration where **57** (83% trans, 17% cis) is the only cleavage product.[29] No indication was found for the presence of **58**.



56 57 58

On this basis, the behavior of **10** toward $TiCl_4$ can be viewed to extend an apparent trend. However, the clean conversion of **10** to **23a** by exclusive peripheral bond cleavage in the presence of anhydrous HCl is remarkably regiospecific *in the opposite direction* (compare **56**). This end result may be a consequence of the operation of a mechanism where greater carbocation character develops and where the electronic demands of silicon become correspondingly more apparent.

While both reagents cleave a peripheral bond of the bicyclo[4.1.0]heptane **9** and the *exo*-tricyclo[3.2.1.$0^{2,4}$]octane **11**, the differing product distributions arising from the latter silylcyclopropanes show that skeletal rearrangement is much more prevalent in the HCl reaction. Possibly the positive charge in **59** (E = $TiCl_4^-$) is more

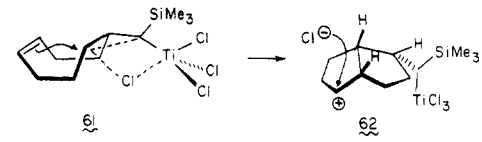


32 59 60 29

tightly coordinated than it is when E = H (compare **10**); at the very least, a driving force to position the (trimethylsilyl)methyl substituent at C-7 is made apparent under both circumstances (66% and 92%, respectively).

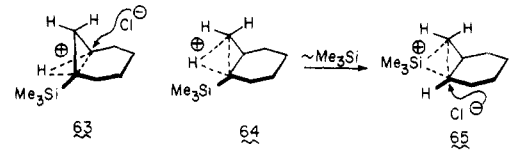
Since complete transannular reaction was witnessed upon reaction of **12** with $TiCl_4$, the double bond in **61** must rank as a more efficient neighboring group than a norbornane σ bond.

The preceding data disclose that one of the two cyclopropane bonds which flank the silicon substituent experiences preferential electrophilic attack when additional



61 62

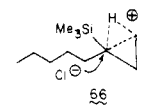
ring strain effects are absent. While the conversion of **15** to **46** (71%) can be similarly rationalized in terms of **63**,



63 64 65

the production of **17** (29%) requires that initial edge protonation as in **64** be followed by a 1,2-shift of the trimethylsilyl group to give the silicon-bridged species **65**.

The behavior of **16** is informative since evidence is provided that nucleophilic attack on an edge-protonated intermediate such as **66** can occur at the silicon-substituted carbon center if the other option involves an incipient primary carbocation.



66

Stereoselectivity Considerations. The stereochemistry of nucleophilic attack by chloride ion in the case of **9**, **10**, and **14** is net inversion. These results conform to the mechanistic postulate of the intermediacy of corner-titanated or corner-protonated cyclopropanes. For **11**, retention of configuration is seen, but this is due to the invervention of a norbornyl cation intermediate. The lone silyl chloride produced from **12** does not arise from synchronous chloride addition to **61**, for this pathway necessarily positions the halogen endo on the bicyclo[3.3.0]octane framework. The observed exo stereochemistry seemingly implicates bicyclic carbonium ion **62**, bonding to which from above the fold is known to be kinetically (and thermodynamically) favored.[49]

Electrophilic attack on cyclopropanes is known to proceed with both retention and inversion of configuration at carbon, and the energy difference for the two processes is thought to be small.[50] In the present work, it has not been possible to gain information on this aspect of the ring-cleavage process.

Summary

Titanochlorination–hydrolysis of trimethylsilyl-substituted cyclopropanes proceeds smoothly at low temperatures to deliver silyl chlorides in good to excellent yields. Anhydrous hydrogen chloride leads to analogous results, although rather divergent product distributions frequently materialize. Consequently, the pair of processes represent useful reactions for the stereospecific synthesis of otherwise difficultly accessible organosilicon compounds. The effect of the trimethylsilyl group is to promote electrophilic attack at one of the flanking cyclopropane C–C bonds. Carbonium ion rearrangements can ensue if the structural features of the substrate molecule are conducive to such bonding changes. An analogy may be drawn between silylcyclopropanes and vinylsilanes in the sense that the electrophile becomes bonded to the silyl-substituted carbon atom in both situations, except where ring strain factors become too large.

(41) LaLonde, R. T.; Forney, L. S. *J. Am. Chem. Soc.* **1963**, *85*, 3767. LaLonde, R. T.; Ding, J. *J. Org. Chem.* **1972**, *37*, 2555.
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(45) Salomon, R. G.; Gleim, R. D. *J. Org. Chem.* **1976**, *41*, 1529.
(46) Lambert, J. B.; Black, R. D. H.; Shaw, J. H.; Papay, J. J. *J. Org. Chem.* **1970**, *35*, 3214.
(47) LaLonde, R. T.; Tobias, M. A. *J. Am. Chem. Soc.* **1964**, *86*, 4068.
(48) LaLonde, R. T.; Debboli, A. D., Jr. *J. Org. Chem.* **1970**, *35*, 2657.
(49) Paquette, L. A. *Fortschr. Chem. Forsch.* **1979**, *79*, 43.
(50) DePuy, C. H. *Fortschr. Chem. Forsch.* **1973**, *40*, 73.

Experimental Section

Proton magnetic resonance spectra were recorded with Varian EM-390 and Bruker HX-90 spectrometers. Apparent splittings are given in all cases. ^{13}C NMR spectra were measured on a Bruker HP-90 instrument. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory. Preparative VPC work was done on a Varian-Aerograph A90-P3 instrument equipped with a thermal-conductivity detector.

***exo*-7-(Trimethylsilyl)bicyclo[4.1.0]heptane (9). (A) Seyferth Method.** A solution of (trimethylsilyl)diazomethane (2.86 g, 20.0 mmol) in dry, olefin-free pentane (10 mL) was added under nitrogen to a chilled (0 °C) solution of distilled cyclohexene (8.215 g, 100 mmol) in pentane (10 mL) containing 1.98 g (20.0 mmol) of cuprous chloride. The reaction mixture was stirred at 0 °C for 3 h while nitrogen was steadily evolved and then filtered through Celite. The solvent was evaporated, and the residue was distilled to give 754 mg (22.4%) of impure **9**, bp 80–85 °C (20 mm). Final purification was achieved by preparative VPC on column E (95 °C);[51] ^1H NMR ($CDCl_3$) δ 1.85–0.48 (series of m, 10 H), -0.16 (s, 9 H), -0.82 (t, J = 7 Hz, 1H); mass spectrum, calcd m/e 168.1334, obsd 168.1337.

(B) Olofson Method. A solution of cyclohexene (8.215 g, 100 mmol) in hexane (10 mL) was added to a solution containing 20.0 mmol of lithium 2,2,6,6-tetramethylpiperidide (prepared from 12.50 mL of 1.6 N n-butyllithium in hexane and 2.83 g of the amine) under a nitrogen atmosphere. Following the addition of 2.454 g (20.0 mmol) of (chloromethyl)trimethylsilane in 10 mL of hexane, the reaction mixture was heated at 85 °C for 24 h, cooled, and washed with saturated aqueous citric acid solution (50 mL) and brine (15 mL). The dried organic phase was evaporated to give 2.28 g of a yellow liquid. Distillation of this material afforded 1.046 g (31.3%) of **9**, bp 85–88 °C (26 mm).

***exo*-6-(Trimethylsilyl)bicyclo[3.1.0]hexane (10).** Reaction of 2.286 g (20.0 mmol) of (trimethylsilyl)diazomethane with 6.81 g (100 mmol) of cyclopentene in the predescribed manner yielded 640 mg (20.7%) of **10**, bp 84–88 °C (75 mm). Final purification was achieved by preparative VPC on column E (68 °C):[51] ^1H NMR ($CDCl_3$) δ 2.00–0.93 (series of m, 8 H), 0.00 (s, 9 H), -0.54 (t, J = 7 Hz, 1 H); mass spectrum, calcd m/e 154.1178, obsd 154.1181.

Reaction of cyclopentene (6.81 g, 100 mmol) with 2.454 g (20.0 mmol) of (chloromethyl)trimethylsilane and 20 mmol of lithium 2,2,6,6-tetramethylpiperidide as described above afforded 996 mg (32.2%) of **10**, bp 89–91 °C (78 mm).

***exo*-3-(Trimethylsilyl)tricyclo[3.2.1.0^{2,4}]octane (11).** When 9.42 g (100 mmol) of norbornene was treated with 2.286 g (20.0 mmol) of (trimethylsilyl)diazomethane as before there was isolated 1.041 g (28.9%) of **11**, bp 85–90 °C (10 mm). Final purification was again achieved on column E (100 °C);[51] ^1H NMR ($CDCl_3$) δ 2.22 (br s, 2 H), 1.54–0.98 (m, 6 H), 0.66–0.20 (m, 2 H), -0.03 (s, 9 H), -0.34 (t, J = 4.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 36.36, 29.84, 27.19, 19.10, -0.54, -2.00 ppm; mass spectrum, calcd m/e 180.1334, obsd 180.1338.

Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.06; H, 11.15.

From 9.42 g (100 mmol) of norbornene, 2.454 g (20.0 mmol) of (chloromethyl)trimethylsilane, and 20.0 mmol of lithium 2,2,6,6-tetramethylpiperidide there was obtained 1.207 g (33.5%) of **11**, bp 85–90 °C (12 mm).

***exo*-9-(Trimethylsilyl)bicyclo[6.1.0]non-4-ene (12).** Addition of a solution of 98% 1,5-cyclooctadiene (11.04 g, 100 mmol) in 10 mL of hexane to (chloromethyl)trimethylsilane (2.455 g, 20.0 mmol) and lithium 2,2,6,6-tetramethylpiperidide (20 mmol) in hexane as described above gave 1.027 g (26.4%) of **12**, bp 90–95 °C (5–6 mm). Final purification was achieved on column E (102 °C):[51] ^1H NMR ($CDCl_3$) δ 5.75–5.51 (t, J = 4.5 Hz, 2 H), 2.50–0.45 (series of m, 10 H), 0.01 (s, 9 H), -0.80 (t, J = 7 Hz, 1 H); mass spectrum, calcd m/e 194.1491, obsd 194.1494.

***exo*-7-(Trimethylsilyl)-3,4-benzobicyclo[4.1.0]heptane (14).** Reaction of 2.28 g (20 mmol) of (trimethylsilyl)diazomethane with 13.02 g (100 mmol) of **13** and 1.98 g of cuprous chloride in pentane in the predescribed manner (24 h) afforded 11.05 g of recovered **13** [bp 60–64 °C (1.25 mm)] and 1.86 g of **14**: 1.65 g of 88% purity (38%); bp 100–102 °C (1.25 mm). Pure **14** was obtained by preparative VPC on column B (132 °C):[51] ^1H NMR ($CDCl_3$) δ 7.28–6.97 (m, 4 H), 3.20 (d, J = 16 Hz, 2 H), 2.95 (d, J = 16 Hz, 2 H), 1.25–0.17 (m, 2 H), -0.06 (s, 9 H), -0.41 to -0.56 (m, 1 H); mass spectrum, calcd m/e 216.1334, obsd 216.1340.

Anal. Calcd for $C_{14}H_{20}Si$: C, 77.70; H, 9.32. Found: C, 77.70; H, 9.26.

1-(Trimethylsilyl)bicyclo[4.1.0]heptane (15). With magnetic stirring, diiodomethane (13.5 g, 50 mmol) was added via syringe and under nitrogen to 100 mL of 1 M ethereal ethylzinc iodide (100 mmol). This mixture was heated at gentle reflux for 1 h, at which point 1.54 g (10.0 mmol) of 1-(trimethylsilyl)cyclohexene[28] was slowly introduced. Heating was continued for an additional 4 days, during which time some of the solvent was seen to have evaporated. The cooled reaction mixure was washed with 10% hydrochloric acid (10 mL), water (10 mL), saturated sodium thiosulfate solution (3 × 10 mL), and brine (10 mL) prior to drying. The filtrate was concentrated by removal of solvent through a 5-cm Vigreux column at atmospheric pressure. The remaining solvent was removed by rotary evaporation, and the product was distilled to give 570 mg (34%) of **15**, bp 55–57 °C (25 mm). Final purification was achieved by preparative VPC on column D (102 °C):[51] ^1H NMR ($CDCl_3$) δ 1.81–1.05 (m, 8 H), 0.92–0.08 (m, 3 H), -0.08 (s, 9 H); mass spectrum, calcd m/e 168.1334, obsd 168.1337.

Anal. Calcd for $C_{10}H_{20}Si$: C, 71.34; H, 11.97. Found: C, 71.42; H, 11.93.

1-(Trimethylsilyl)-1-pentylcyclopropane (16). Treatment of 2-(trimethylsilyl)-1-heptene (2.56 g, 15.0 mmol)[28] with 20.1 g (75 mmol) of diiodomethane and 150 mL of 1 M ethereal ethylzinc iodide at the reflux temperature for 3 days as described above, followed by the usual workup and distillation, gave 1.73 g (63%) of **16**, bp 76–79 °C (27 mm). Final purification was achieved on column E (72 °C):[51] ^1H NMR ($CDCl_3$) δ 1.60–0.80 (series of m, 11 H), 0.40–0.15 (m, 3 H), 0.02 (s, 9 H); mass spectrum, calcd m/e 184.1647, obsd 184.1652.

Anal. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12. Found: C, 71.70; H, 13.06.

***trans*-1-[(Trimethylsilyl)methyl]-2-chlorocyclohexane (17).** A cold (−78 °C) magnetically stirred solution of **9** (0.100 g, 0.59 mmol) in dry dichloromethane (5 mL) was treated dropwise via syringe with 81.3 μL (140 mg, 7.40 mmol) of titanium tetrachloride. The reaction mixture was stirred at this temperature for 5 h, 1 mL of water was added, the cooling bath was removed, and stirring was maintained for an additional 15 min. The layers were separated, and the organic phase was dried, filtered, and evaporated to give 102 mg (84%) of **17**. An analytical sample was prepared by preparative VPC on column E (122 °C):[51] ^1H NMR ($CDCl_3$) δ 3.59 (sextet, J = 9.5, 9.5, 4.0 Hz, 1 H), 2.31–1.10 (series of m, 9 H), 0.48 (d, J = 10 Hz, 1 H), 0.32 (d, J = 10 Hz, 1 H), 0.06 (s, 9 H); mass spectrum, calcd m/e 189.0866, obsd 189.0871.

Anal. Calcd for $C_{10}H_{21}ClSi$: C, 58.64; H, 10.34. Found: C, 58.72; H, 10.48.

[(Trimethylsilyl)methyl]cyclohexane (18). (A) By Reductive Dechlorination of 17. A rapidly stirred, nitrogen-blanketed solution of VPC-purified **17** (75 mg, 0.37 mmol), tri-n-butyltin hydride (117 μL, 129 mg, 0.44 mmol), and azobis(isobutyronitrile) (10 mg, 0.06 mmol) in 4 mL of anhydrous benzene was irradiated with a 150-W floodlamp for 120 h. The major portion of solvent was removed by distillation at atmospheric pressure, the residue was taken up in 5 mL of ether, and the ethereal solution was stirred over 5 mL of 10% aqueous potassium fluoride for 48 h. The organic phase was dried and evaporated to leave 343 mg of a clear yellow liquid. VPC purification on column B (100 °C)[51] gave 29 mg (46%) of **18**: ^1H NMR ($CDCl_3$) δ 1.75–0.85 (series of m, 11 H), 0.49 (d, J = 6.5 Hz, 2 H), 0.013 (s, 9 H); ^{13}C NMR ($CDCl_3$) 36.95, 34.47, 26.65, 26.36, 25.83, -0.53 ppm; mass spectrum, calcd m/e 170.1491, obsd 170.1496.[52]

(B) From Cyclohexanemethanol. A solution of commerical

(51) The following VPC columns were employed: A, 1 ft × 0.25 in., 5% SE-30 on Chromosorb G; B, 3 ft × 0.25 in., 8% SE-30 on Chromosorb P; C, 6 ft × 0.25 in., 5% SE-30 on Chromosorb G; D, 12 ft × 0.25 in., 5% SE-30 on Chromosorb G; E, 12 ft × 025 in., 20% Carbowax on Chromosorb W; F, 12 ft × 0.25 in., 10% squalene on Chromosorb G.

(52) Saam, J.; Speier, J. *J. Am. Chem. Soc.* **1961**, *83*, 1351.

(Aldrich) cyclohexanemethanol (2.00 g, 17.5 mmol) in 2 mL of acetonitrile was added to a suspension of triphenylphosphine dibromide in the same solvent [from 4.60 g (17.5 mmol) of triphenylphosphine and 2.80 g (17.5 mmol) of bromine]. The reaction mixture was stirred at room temperature for 1 h, the solvent was distilled through a 10-cm Vigreux column, and the remaining volatiles were removed in vacuo (bath temperature 140 °C, 1 mm, condenser cooled to −78 °C). Redistillation of the condensate through a short-path column afforded 2.19 g (70.7%) of (bromomethyl)cyclohexane: bp 85–87 °C (17 mm); ^{1}H NMR ($CDCl_3$) δ 2.21 (d, J = 8 Hz, 2 H), 2.05–0.47 (m, 11 H); mass spectrum calcd m/e 176.0201, obsd 176.0206.[53]

A solution of this bromide (1.00 g, 5.65 mmol) and chlorotrimethylsilane (856 mg, 7.88 mmol) in dry diethyl ether (15 mL) was heated at the reflux temperature with 79 mg (11.4 mmol) of lithium powder for 70 h. The cooled reaction mixture was treated with saturated ammonium chloride solution and filtered. The ethereal phase was dried and concentrated. Distillation of the residue gave 470 mg (49%) of **18**, bp 81–83 °C (15 mm), identical in all respects with the above sample.

***trans*-1-[(Trimethylsilyl)methyl]-2-chlorocyclohexane-α-*d* (21).** Treatment of a dichloromethane solution of **9** (100 mg, 0.60 mmol) with 81.5 μL (141 mg, 7.42 mmol) of titanium tetrachloride as described previously, followed by a deuterium oxide quench and the usual workup, yielded 103 mg (80%) of **21**. Final purification was achieved on column E (122 °C):[51] ^{1}H NMR ($CDCl_3$) δ 3.59 (sextet, J = 9.5, 9.5, 4.0 Hz, 1 H), 2.31–1.10 (series of m, 9 H), 0.41 (dt, J = 9, 1 Hz, 1 H), 0.06 (s, 9 H); ^{13}C NMR ($CDCl_3$) 69.33, 42.72, 37.19, 34.37, 26.22, 25.39, (22.24, 21.36, 20.49), -0.63 ppm; mass spectrum, no parent ion, peaks observed at m/e 190 ($M^+ - CH_3$) and 170 ($M^+ - Cl$) with metastable $M^+ - Me_3SCl$ at m/e 46.

1-[(Trimethylsilyl)methyl]cyclohexane-α-*d* (22). Irradiation of a benzene solution containing 66 mg (0.32 mmol) of **21**, 101 μL (111 mg, 0.38 mmol) of tri-*n*-butyltin hydride, and 10 mg (0.061 mmol) of AIBN for 168 h afforded after workup 426 mg of a clear yellow liquid. Preparative VPC purification on column D (107 °C)[51] gave 20 mg (36.5%) of **22**: ^{1}H NMR ($CDCl_3$) δ 1.71–0.93 (series of m, 11 H), 0.48 (br d, J = 6.5 Hz, 1 H), 0.00 (s, 9 H); ^{13}C NMR ($CDCl_3$) 36.99, 34.37, 26.65, 26.36, 25.82 (t), -0.53 ppm; mass spectrum, calcd m/e 171.1553, obsd 171.1558.

1-[(Trimethylsilyl)methyl]cyclohexane-6-*d* (20). Irradiation of a benzene solution of **17** (75 mg, 0.37 mmol), 117 μL (129 mg, 0.44 mmol) of tri-*n*-butyltin deuteride, and 10 mg (0.061 mmol) of AIBN for 120 h gave after the usual workup 263 mg of a yellowish liquid. VPC purification on column B (100 °C)[51] yielded 36 mg (57%) of **20**: ^{1}H NMR ($CDCl_3$) δ 1.63–0.93 (series of m, 10 H), 0.48 (d, J = 6.5 Hz, 2 H), 0.00 (s, 9 H); ^{13}C NMR ($CDCl_3$) 36.95, 35.54 (t), 34.37, 26.65, 26.31, 25.78, -0.53 ppm; mass spectrum, calcd m/e 171.1553, obsd 171.1558.

Titanium Tetrachloride Promoted Ring Opening of 10. A magnetically stirred solution of **10** (731 mg, 4.74 mmol) in 5 mL of dry dichloromethane cooled to −78 °C was treated under nitrogen with 618 μL (1.07 g, 5.62 mmol) of titanium tetrachloride. After 5 h, 1 mL of water was added, and the reaction mixture was processed as before. There was obtained 763 mg (84.7%) of a 14:86 mixture of **23a** and **26a**. The pure isomers were obtained by preparative VPC on column E (102 °C).[51]

For **23a**: ^{1}H NMR ($CDCl_3$) δ 3.86 (sextet, J = 9.5, 9.5, 4.0 Hz, 1 H), 2.18–0.65 (series of m, 9 H), −0.01 (s, 9 H); ^{13}C NMR ($CDCl_3$) 68.89, 46.27, 25.30, 31.95, 21.90, 21.36, −0.92 ppm; mass spectrum, calcd ($M^+ - CH_3$) m/e 175.0710, obsd 175.0714.

Anal. Calcd for $C_9H_{19}ClSi$: C, 56.66; 10.04. Found: C, 56.99; H, 10.14.

For **26a**: ^{1}H NMR ($CDCl_3$) δ 3.99 (sextet, J = 9.5, 9.5, 4.0 Hz, 1 H), 2.24–0.68 (series of M, 9 H), -0.01 (s, 9 H); ^{13}C NMR ($CDCl_3$) 62.00, 38.45, 37.82, 28.55, 27.14, 25.73, -3.59 ppm; mass spectrum, calcd ($M^+ - CH_3$) m/e 175.0710, obsd 175.0714.

Anal. Calcd for $C_9H_{19}ClSi$: C, 56.66; H, 10.04. Found: C, 56.96; H, 10.15.

[(Trimethylsilyl)methyl]cyclopentane (24). (A) Reductive Dechlorination of 23a. A nitrogen-blanketed magnetically stirred solution of VPC-purified **23a** (61 mg, 10.32 mmol), tri-*n*-butyltin hydride (102 μL, 112 mg, 0.39 mmol), and AIBN (10 mg, 0.061 mmol) in 10 mL of anhydrous benzene was irradiated with a 150-W floodlamp for 120 h. A workup in the predescribed manner afforded 121 mg of a clear yellow liquid. Purification on column B (102 °C) gave 19 mg (38%) of **24**: ^{1}H NMR ($CDCl_3$) δ 1.73–1.03 (series of m, 9 H), 0.63 (d, J = 6.5 Hz, 2 H), -0.01 (s, 9 H); ^{13}C NMR ($CDCl_3$) 36.61, 36.27, 25.10, 23.89, -0.78 ppm; mass spectrum, calcd m/e 156.1334, obsd 156.1338.

(B) From (Bromomethyl)cyclopentane (25). Solutions of **25** (1.00 g, 6.13 mmol)[53] in 2 mL of dry ether and of chlorotrimethylsilane (942 mg, 8.67 mmol) in 2.5 mL of the same solvent were added successively to a rapidly stirred suspension of lithium powder (86 mg, 12.4 mmol) in 10 mL of dry ether. The reaction mixture was stirred at the reflux temperature for 24 h and processed as described earlier. Distillation of the residue gave 420 mg (44%) of **24** [bp 75–76°C (20 mm)] identical in all respects with the sample prepared above.

[(Trimethylsilyl)methyl]cyclohexane (27). (A) Reductive Dechlorination of 26a. Irradiation of a benzene solution of **26a** (161 mg, 0.84 mmol), tri-*n*-butylin hydride (298 mg, 1.02 mmol), and AIBN (10 mg) for 120 h yielded on workup 429 mg of a clear yellow oil. Preparative VPC purification on column B (102 °C)[51] furnished 68 mg (51%) of **27**: ^{1}H NMR ($CDCl_3$) δ 1.76–0.55 (series of m, 11 H), −0.05 (s, 9 H); ^{13}C NMR ($CDCl_3$) 28.21, 27.48, 26.36, −3.54 ppm; mass spectrum, calcd m/e 156.1334, obsd 156.1332.[54]

(B) Catalytic Hydrogenation of 28. A solution of **28** (2.50 g, 16.6 mmol)[54] in cyclohexane (50 mL) containing 0.5 g of 5% rhodium on carbon was hydrogenated in a Paar apparatus at 55 °C and 55 psi of H_2. After 4 h, the reaction mixture was filtered through Celite, and the colorless filtrate was distilled through a 10-cm Vigreux column to leave a clear, colorless residue. Distillation of this material gave 2.18 g (84%) of **27** [bp 68–70 °C (2.5 mm)] identical in all respects with the material obtained above.

$TiCl_4$-Promoted Opening of 10 with Deuterium Oxide Quench. Treatment of 201 mg (1.30 mmol) of **10** with 293 mg (1.55 mmol) of titanium tetrachloride as described previously, followed by quenching with deuterium oxide and the customary workup, delivered 180 mg of a mixture of **23b** and **26b**. These were separated on column E (102 °C).[51]

For **23b**: ^{1}H NMR ($CDCl_3$) δ 3.72–3.58 (m, 1 H), 2.22–0.92 (series of m, 7 H), 0.42–0.26 (m, 1 H), 0.00 (s, 9 H); mass spectrum, calcd m/e 176.0773, obsd 176.0777.

For **26b**: ^{1}H NMR ($CDCl_3$) δ 3.69 (m, 1 H), 2.09–0.37 (series of m, 8 H), 0.04 (s, 9 H); mass spectrum, calcd m/e 176.0773, obsd 176.0777.

$TiCl_4$-Promoted Ring Opening of 11. Treatment of a dichloromethane solution of **11** (871 mg, 4.88 mmol) and titanium tetrachloride (1.09 g, 5.74 mmol) as described previously followed by quenching with water and the usual workup yielded 770 mg (73.5%) of a mixture of **29** and **32**. Because these isomers proved inseparable, they were further purified as a mixture on column E (130 °C):[51] ^{1}H NMR ($CDCl_3$) δ 3.96–3.83 (m, 1 H), 2.32–0.66 (series of m, 9 H), 0.60–0.42 (overlapping d, 2 H), 0.05 and 0.04 (overlapping s, 9 H); mass spectrum, calcd m/e 201.0866, obsd 201.0872.

Anal. Calcd for $C_{11}H_{21}ClSi$: C, 60.93; H, 9.76. Found: C, 60.77; H, 9.94.

7-[(Trimethylsilyl)methyl]bicyclo[2.2.1]heptane (30) and *exo*-2-[(Trimethylsilyl)methyl]bicyclo[2.2.1]heptane (33). Irradiation of a benzene solution of the **29/32** mixture (149 mg, 0.69 mmol), tri-*n*-butyltin hydride (239 mg, 0.82 mmol), and AIBN (10 mg) as described earlier afforded 823 mg of a clear yellow liquid. VPC purification on column D (136 °C)[51] gave 83 mg (67%) of a 66:34 (by ^{1}H NMR) mixture of **30** and **33** which also proved inseparable: ^{1}H NMR ($CDCl_3$) δ 1.83–1.13 (m, 11 H), 0.52 (d, J = 7 Hz, 2 H), 0.038 (major), 0.015 (2 s, 9 H); ^{13}C NMR ($CDCl_3$) 45.56, 41.19, 30.32, 27.14, 14.88, -0.92 ppm (major); 44.83, 41.61, 38.18, 37.12, 34.93, 30.10, 28.69, 26.02, -0.70 ppm (minor); mass spectrum calcd m/e 182.1491, obsd 182.1495.

7-[(Trimethylsilyl)methyl]bicyclo[2.2.1]heptane (30). A solution of **31** (200 mg, 1.14 mmol)[55] in 2 mL of anhydrous tet-

(53) Royals, E. E.; Neal, A. H. *J. Org. Chem.* **1956**, *21*, 1448.

(54) Kanazashi, M.; Takakusa, M. *Bull. Chem. Soc. Jpn.* **1954**, *27*, 441.

(55) Marchand, A. P.; Weimar, W. R., Jr. *Chem. Ind. (London)* **1969**, 200.

rahydrofuran was added dropwise under nitrogen to a rapidly stirred refluxing suspension of sublimed magnesium (29 mg, 1.15 mmol) in the same solvent (2 mL). The reaction mixture was heated at the reflux temeprature for 2 h (iodine initiation). At this point, freshly prepared (trimethylsilyl)methyl triflate (270 mg, 1.14 mmol)[56] dissolved in 2 mL of tetrahydrofuran was added dropwise, and refluxing was continued for a further 19 h. The cooled reaction mixture was treated with saturated ammonium chloride solution, and the organic phase was dried and evaporated. The resulting yellow liquid (536 mg) was purified on column B (118 °C),[51] and 32 mg (15%) of **30** was isolated: ^{1}H NMR ($CDCl_3$) δ 1.81–1.04 (m, 11 H), 0.52 (d, J = 7 Hz, 2 H), 0.021 (s, 9 H); ^{13}C NMR ($CDCl_3$) 45.54, 41.17, 30.29, 27.09, 14.86, -0.97 ppm; mass spectrum, calcd m/e 182.1491, obsd 182.1485.

***exo*-2-[(Trimethylsilyl)methyl]bicyclo[2.2.1]heptane (33).** *exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid[57] was reduced to the alcohol with lithium aluminum hydride in 86% yield according to earlier directives.[58] Catalytic hydrogenation on 5% palladium on charcoal gave *exo*-bicyclo[2.2.1]heptane-2-methanol[58] in 94% yield. A solution of this alcohol (2.00 g, 15.8 mmol) in 3 mL of acetonitrile was added to a suspension of triphenylphosphine dibromide [from 4.16 g (15.9 mmol) of triphenylphosphine and 2.54 g (15.9 mmol) of bromine]. The reaction mixture was stirred at room temperature for 1 h and processed as described earlier. Distillation of the crude product furnished 2.53 g (85%) of *exo*-2-(bromomethyl)bicyclo[2.2.1]heptane: bp 93–94 °C (10 mm); ^{1}H NMR ($CDCl_3$) δ 3.12 (d, J = 3 Hz, 1 H), 3.08 (d, J = 1 Hz, 1 H), 2.36–2.09 (br m, 2 H), 2.05–0.90 (series of m, 9 H); mass spectrum, calcd m/e 188.0201, obsd 188.0207.

A solution of the bromide (1.00 g, 5.29 mmol) and chlorotrimethylsilane (0.80 g, 7.4 mmol) in diethyl ether (15 mL) was heated at the reflux temperature with lithium powder (74 mg, 10.7 mmol) for 95 h. The usual workup procedure and distillation afforded 510 mg of a 39:61 mixture of the bromide and **33**, bp 83–84 °C (10 mm). A 100-mg sample of this mixture was heated at reflux with 83 mg (0.55 mmol) of diazabicycloundecene in 4 mL of anhydrous tetrahydrofuran for 48 h. Conventional workup led to the isolation of 126 mg of yellow oil. VPC purification on column B (100 °C)[51] furnished 26 mg (42%) of **33**: ^{1}H NMR ($CDCl_3$) δ 2.18–0.99 (series of m, 11 H), 0.52 (d, J = 8 Hz, 2 H), 0.00 (s, 9 H); ^{13}C NMR ($CDCl_3$) 44.82, 41.61, 38.26, 37.12, 34.93, 30.08, 28.68, 26.01, -0.69 ppm; mass spectrum, calcd m/e 182.1491, obsd 182.1485.

3-(Trimethylsilyl)bicyclo[3.2.1]oct-2-ene (36). To a stirred suspension of lithium powder (297 mg, 42.8 mmol) in anhydrous ether (50 mL) were added under nitrogen via syringe 4.00 g (21.4 mmol) of 3-bromobicyclo[3.2.1]oct-2-ene[59] and 3.80 mL (29.9 mmol) of chlorotrimethylsilane. The reaction mixture was heated at the reflux temperature for 80 h, cooled, treated with saturated ammonium chloride solution, and filtered. The filtrate was dried and concentrated. Distillation of the residue provided 3.25 g (84%) of **36**: bp 87–90 °C (10 mm); ^{1}H NMR ($CDCl_3$) δ 6.17 (d with further coupling, J = 7 Hz, 1 H), 2.31–1.49 (series of m, 10 H), –0.01 (s, 9 H); mass spectrum, calcd m/e 180.1334, obsd 184.1338.

***endo*-3-(Trimethylsilyl)bicyclo[3.2.1]octane (37). (A) Lithium–Liquid Ammonia Reduction.** A 250-mL, three-necked flask was charged with 1.00 g (5.54 mmol) of **36**, 5 mL of absolute ethanol, and 100 mL of liquid ammonia. Lithium powder was added portionwise until the blue color was not longer discharged (650 mg, 94 mmol). The refluxing reaction mixture was stirred for 2 h, the solvent was allowed to evaporate, and the residue was taken up in saturated ammonium chloride solution (50 mL) and ether (20 mL). The layers were separated, the aqueous layer was extracted with ether (2 × 20 mL), and the combined organic layers were washed with 10% hydrochloric acid (20 mL), water (20 mL), and brine (20 mL) prior to being dried. Solvent evaporation left 650 mg of a clear yellow oil. Preparative VPC purification on column B (102 °C)[51] indicated this material to be composed of bicyclo[3.2.1]oct-2-ene (11%), recovered **36** (50%), and the desired **37** (39%): ^{1}H NMR ($CDCl_3$) δ 2.09–0.83 (series of m, 13 H), -0.09 (s, 9 H); ^{13}C NMR ($CDCl_3$) 33.38, 32.45, 30.71, 13.74, –3.37 ppm; mass spectrum, calcd m/e 182.1491, obsd 182.1495.

(B) Catalytic Hydrogenation of 36. A solution of **36** (100 mg, 0.56 mmol) in 5 mL of dry ethyl acetate was hydrogenated at 1500 psi of H_2 in the presence of 10 mg of platinum oxide for 120 h. The reaction mixture was filtered and evaporated to give a yellow liquid which was purified by preparative VPC on column D (102 °C).[51] There was obtained 5.3 mg (5%) of **37** identical in all respects with the above sample.

(C) Diimide Reduction of 36. A solution of **36** (100 mg, 0.56 mmol) and hydrazine hydrate (97%, 1.83 g, 55.4 mmol) in 4 mL of methanol was rapidly stirred at –10 °C while 30% hydrogen peroxide (6.29 g, 55.4 mmol) was added dropwise during 70 min. The reaction mixture was allowed to warm to room temperature and extracted with ether (2 × 5 mL). The combined organic layers were washed with water (2 × 5 mL), dried, and evaporated to leave 94 mg of a pale yellow liquid which proved to be a 46:54 mixture of **36** and **37**. Preparative VPC separation on column B (105 °C)[51] gave the pure saturated silane which was identical with the samples obtained earlier.

2-(Phenylsulfonyl)-2-(trimethylsilyl)bicyclo[2.2.2]octane (39). A solution of **38** (3.35 g, 13.5 mmol)[60] in 50 mL of dry ethyl acetate was hydrogenated at atmospheric pressure in the presence of 10% palladium on carbon (100 mg) for 40 min. The customary workup furnished 3.37 g of a colorless oil, chromatography of which on silica gel (150 g, elution with ethyl acetate–hexane, 1:1) led to the separation of phenyl ethyl sulfone (271 mg) from 2-(phenylsulfonyl)bicyclo[2.2.2]octane (2.95 g, 87.3%), an oily substance: ^{1}H NMR ($CDCl_3$) δ 7.95–7.70 (m, 2 H), 7.65–7.42 (m, 3 H), 3.40–2.95 (br t, 1 H), 2.40–1.20 (series of m, 12 H).

A solution of this sulfone (2.95 g, 11.8 mmol) in tetrahydrofuran containing 10% hexamethylphosphoramide (40 mL) was treated under nitrogen at –63 °C with 7.95 mL of 1.56 M *n*-butyllithium in hexane (12.4 mmol) via syringe. After the mixture was stirred for 15 min, 1.65 mL (13.0 mmol) of freshly distilled chlorotrimethylsilane was slowly added via syringe, and the reaction mixture was stirred at room temperature for 1 h before being treated with 10 mL of saturated ammonium chloride solution and 50 mL of ether. After filtration, the filtrate was washed with water (3 × 10 mL) and brine (10 mL), dried, and evaporated to give 3.66 g of yellowish crystals. Recrystallization of this material from chloroform–ether furnished 2.47 g (65%) of **39** as fine white needles: mp 146–147 °C; ^{1}H NMR ($CDCl_3$) δ 8.01–7.90 (m, 2 H), 7.59–7.26 (m, 3 H), 2.09–1.25 (series of m, 12 H), 0.25 (s, 9 H); mass spectrum calcd m/e 322.1423, obsd 322.1429.

Anal. Calcd for $C_{17}H_{26}O_2SSi$: C, 63.31; H, 8.13. Found: C, 63.19; H, 8.09.

2-(Trimethylsilyl)bicyclo[2.2.2]octane (40). To a magnetically stirred suspension of **39** (323 mg, 1.00 mmol) and disodium hydrogen phosphate (570 mg, 4.0 mmol) in 10 mL of dry methanol cooled in an ice bath was added under nitrogen 1.50 g of 6% sodium amalgam. The reaction mixture was stirred at 0 °C for 5 h and at room temperature for 2 h. An additional 570 mg of phosphate and 1.50 g of amalgam were added and, after 5 h, the contents of the flask were poured into 50 mL of water. This mixture was extracted with ether (3 × 20 mL), and the combined organic layers were washed with water (2 × 10 mL) and brine (10 mL) before being dried. Solvent evaporation left 205 mg of a clear yellow liquid. VPC purification gave 58 mg (32%) of **40**: ^{1}H NMR ($CDCl_3$) δ 1.72–1.39 (br m, 13 H), –0.10 (s, 9 H); ^{13}C NMR ($CDCl_3$) 29.81, 27.77, 26.07, 25.59, 25.20, 24.86, 24.52, –2.33 ppm; mass spectrum, calcd m/e 182.1491, obsd 182.1495.

Anal. Calcd for $C_{11}H_{22}Si$: C, 72.44; H, 12.16. Found: C, 72.65; H, 12.30.

***trans*-2-[(Trimethylsilyl)methyl]-3-chloro-1,2,3,4-tetrahydronaphthalene (41).** Treatment of **14** (200 mg, 0.82 mmol) in dichloromethane (4 mL) under nitrogen with 109 μL (187 mg, 0.99 mmol) of titanium tetrachloride at –22 °C for 5 h, followed

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by a water quench and the usual workup, gave 191 mg of clear yellowish liquid. VPC purification on column A (130 °C)[51] afforded 29.5 mg of a mixture of **14** and **42** and 62.5 mg (31%) of **41**: ^{1}H NMR ($CDCl_3$) δ 7.10 (br s, 4 H), 4.20–3.80 (sextet, 1 H), 3.30–3.04 (m, 2 H), 2.57–1.71 (m, 3 H), 1.24–0.87 (m, 2 H), 0.15 (s, 9 H); ^{13}C NMR ($CDCl_3$) 134.67, 133.56, 128.90, 128.61, 126.37, 126.08, 64.19, 37.97, 37.92, 35.44, 21.21, –0.63 ppm.

Anal. Calcd for $C_{14}H_{21}ClSi$: C, 66.50; H, 8.37. Found: C, 66.53; H, 8.43.

2-[(Trimethylsilyl)methyl]-1,2,3,4-tetrahydronaphthalene (42). (A) Reductive Dechlorination of 41. Irradiation of a benzene solution of **41** (136 mg, 0.54 mmol), tri-*n*-butylin hydride (185 mg, 0.64 mmol), and AIBN (10 mg) for 120 h followed by the usual workup and preparative VPC purification (column A, 132 °C)[51] yielded 80 mg (68%) of **42**: ^{1}H NMR ($CDCl_3$) δ 7.10 (s, 4 H), 2.91–2.40 (m, 4 H), 1.89–1.57 (m, 3 H), 0.692 (d, J = 7 Hz, 2 H), 0.08 (s, 9 H); ^{13}C NMR ($CDCl_3$) 137.10, 136.67, 129.14, 128.85, 125.50, 39.62, 32.96, 31.02, 29.27, 24.76, –0.53 ppm; mass spectrum, calcd m/e 218.1491, obsd 218.1495.

Anal. Calcd for $C_{14}H_{22}Si$: C, 76.99; H, 10.15. Found: C, 76.91; H, 10.10.

(B) From 1,2,3,4-Tetrahydronaphthalene-2-carboxylic Acid (43). A 5.00-g (27.8 mmol) sample of the commercially available (Aldrich) **43** was reduced with lithium aluminum hydride to the primary alcohol by a modification of the Newman and Mangham procedure.[61] A solution of this alcohol (2.00 g, 12.3 mmol) in 3 mL of acetonitrile was allowed to react with an equimolar quantity of triphenylphosphine dibromide as described earlier. Workup followed by distillation affforded 1.91 g (69%) of 2-(bromomethyl)-1,2,3,4-tetrahydronaphthalene: bp 103–104 °C (0.55 mm); ^{1}H NMR ($CDCl_3$) δ 7.97 (s, 4 H), 3.35 (d, J = 6 Hz, 2 H), 2.96–2.45 (m, 4 H), 2.3–1.1 (series of m, 3 H); mass spectrum, calcd m/e 224.0201, obsd 224.0208.

A solution of the bromide (1.00 g, 4.44 mmol) and chlorotrimethylsilane (685 mg, 6.3 mmol) in ether (15 mL) was heated at reflux with 62 mg (8.9 mmol) of lithium powder for 48 h and processed in the predescribed manner. Distillation afforded 465 mg of a mixture of the bromide and **42** (ratio 42:58 by ^{1}H NMR), bp 91–92 °C (0.8 mm).

A solution of this mixture (100 mg) and diazabicycloundecene (71 mg, 0.47 mmol) in anhydrous tetrahydrofuran (4 mL) was heated at the reflux temperature for 48 h, cooled, diluted with ether (10 mL), and worked up as described earlier. The resulting liquid was purified by preparative VPC on column B (150 °C).[51] There was obtained 5.1 mg of 2-methyl-3,4-dihydronaphthalene and 17.4 mg (30%) of **42** which was fully identical with the sample isolated above.

***endo*-2-[(Trimethylsilyl)methyl]-*exo*-6-chlorobicyclo[3.3.0]octane (44).** Reaction of **12** (583 mg, 0.30 mmol) with titanium tetrachloride (697 mg, 0.36 mmol) in dichloromethane solution in the conventional manner (5 h, –78 °C) gave 599 mg (86%) of **44** which was purified on column E (130 °C):[51] ^{1}H NMR ($CDCl_3$) δ 4.01 (s, 1 H), 2.34–0.99 (series of m, 11 H), 0.49 (d, J = 7 Hz, 2 H), 0.02 (s, 9 H); ^{13}C NMR ($CDCl_3$) 72.24, 43.40, 38.98, 32.48, 27.09, 25.97, 23.16, 21.51, –0.68 ppm; mass spectrum, calcd m/e 194.1491, obsd 194.1494.

Anal. Calcd for $C_{12}H_{23}ClSi$: C, 62.43; H, 10.04. Found: C, 62.47; H, 10.02.

***endo*-2-[(Trimethylsilyl)methyl]bicyclco[3.3.0]octane (45).** Irradiation of a benzene solution of **44** (112 mg, 0.48 mmol), tri-*n*-butyltin hydride (70 mg, 0.58 mmol), and AIBN (10 mg) for 120 h in the usual manner furnished 50 mg (52.5%) of **45** after isolation from column B (130 °C):[51] ^{1}H NMR ($CDCl_3$) δ 2.10–1.28 (series of m, 13 H), 0.42 (d, J = 7 Hz, 2 H), 0.00 (s, 9 H); ^{13}C NMR ($CDCl_3$) 42.82, 40.34, 38.11, 34.42, 32.62, 29.42, 28.69, 23.89, 23.64, –0.58 ppm; mass spectrum, calcd m/e 196.1647, obsd 196.1643.

Cleavage of 9 with Hydrogen Chloride. A slow stream of anhydrous hydrogen chloride was bubbled through a cold (–78 °C) rapidly stirred solution of **9** (100 mg, 0.58 mmol) in 4 mL of dry dichloromethane for 1 h. The reaction mixture was allowed to warm to room temperature, washed with water and sodium bicarbonate solution, dried, and evaporated. VPC purification of the residue on column B (100 °C)[51] gave 54 mg (45%) of **17**.

Cleavage of 10 with Hydrogen Chloride. Treatment of **10** (100 mg, 0.65 mmol) in an entirely analogous manner furnished 111 mg of clear colorless liquid. VPC purification on column B (100 °C)[51] yielded 67 mg (54%) of **23a**.

Cleavage of 11 with Hydrogen Chloride. Reduction of **11** (129 mg, 0.71 mmol) with anhydrous hydrogen chloride as previously described afforded a mixture of **29** and **32**. VPC purification on column B (125 °C)[51] gave 66 mg (42%) of purified mixture. This mixture was treated directly with tri-*n*-butyltin hydride in the predescribed manner. VPC purification of the resultant oil gave 38 mg (48%) of a 92:8 mixture of **30** and **33** (^{1}H NMR analysis).

Cleavage of 15 with Anhydrous Hydrogen Chloride. Treatment of **15** (100 mg, 0.60 mmol) in analogous fashion gave 108 mg of a mixture of **17** and **46** (29:71). These isomers were separated by preparative VPC on column B (108 °C).[51] There was isolated 23 mg (18%) of **17** and 54 mg (44%) of **46**: ^{1}H NMR ($CDCl_3$) δ 4.2–3.8 (m, 1 H), 2.5–0.35 (series of m, 11 H), 0.11 (s, 9 H); ^{13}C NMR ($CDCl_3$) 65.01 (d), 40.64 (t), 39.47 (t), 28.50 (t), 28.30 (t), 24.03 (d, t), 23.55 (t), –3.45 (q) ppm; mass spectrum, calcd m/e ($M^+ - CH_3$) 18.0866, obsd 189.0863.

Cleavage of 16 with Anhydrous Hydrogen Chloride. Treatment of **16** (100 mg, 0.54 mmol) with anhydrous HCl as described previously furnished a clear colorless oil (74 mg) which was purified by preparative VPC on column B (105 °C).[51] There was obtained 47 mg (39%) of pure **47**: ^{1}H NMR ($CDCl_3$) δ 2.10–1.82 (m, 16 H), 0.23 (s, 9 H); ^{13}C NMR ($CDCl_3$) 68.49, 38.33, 32.44, 31.23, 24.55, 14.05, 9.32, –2.15 ppm; mass spectrum, calcd ($M^+ - CH_3$) m/e 205.1183, obsd 205.1179.

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