Acetylated mercurial from **3b** was treated with a twofold excess of NaCl in water in analogy with the preparation of **10a** above. It was characterized by the near identity of its NMR spectrum with that of **10a:** ^{1}H NMR δ ($CHCl_3$ as internal standard) 1.50–2.27 (5 H, C-2, 4, 6), 2.12 (s, 6 H, OAc), 2.60 (q, 1 H, J = 4.5 Hz, C-5), 5.06 (quintet, 2 H, J = 3.7 Hz, C-1, 3).

3-Bromocyclohexyl Acetate (12). A solution of 3-bromomercuricyclohexyl acetate (**9,** 1.0 g, 2.38 mmol) in anhydrous pyridine (4 ml) was treated dropwise with a solution of bromine (0.64 g, 4 mmol) in pyridine (2 ml) at −40 °C. After the resulting mixture was stirred for 10 min, it was allowed to warm to 25 °C and then stirred for 1.5 h. Pyridine was removed by rotary evaporation and the oily solid residue was taken up in ether (50 ml). The solution was washed with saturated aqueous $NaHCO_3$ and then with saturated aqueous $CuSO_4$, dried ($MgSO_4$), and concentrated by rotary evaporation. The NMR spectrum of this crude material indicated almost pure **12.** A pure sample was obtained by preparative GLC (column 2): 100 MHz ^{1}H NMR δ 1.0–2.4 (8 H, C-2, 4, 5, 6), 2.03 (s, 3 H, OAc), 3.95 (tt, 1 H, J = 4, 14 Hz, C-3), 4.66 (tt, 1 H, J = 4, 11 Hz, C-1); mass spectrum (70 eV) m/e (rel intensity) 43 (92), 61 (11), 81 (100), 162 (7), 221 (63), 223 (58).

***cis*-5-Chloro-*cis*-1,3-cyclohexyl Diacetate (13c).** A solution of chlorine (1.5 ml of 1.75 M) in CCl_4 was added dropwise to a solution of *cis*-5-chloromercuri-*cis*-1,3-cyclohexyl diacetate (**10b,** 385 mg, 0.89 mmol) in pyridine (8 ml) at −40 °C under nitrogen. The resulting mixture was stirred at −40 °C for 1 h, then allowed to warm to room temperature and stirred for an additional 1 h. Solvents were removed by rotary evaporation and the residue was taken up in ether (50 ml). The solution was washed with saturated aqueous $NaHCO_3$ and then with saturated aqueous $CuSO_4$, dried ($MgSO_4$), filtered, and concentrated by rotary evaporation to give **13c** (121 mg, 58%): ^{1}H NMR δ 1.45 (d, 2 H, J = 11.5 Hz, C-4, 6), 1.85 (d, 2 H, J = 11.5 Hz, C-4, 6), 2.05 (s, 6 H, OAc), 2.1–2.8 (m, 2 H, C-2), 3.84 (tt, 1 H, J = 4, 12 Hz, C-5), 4.75 (tt, 2 H, J = 4.3, 12 Hz, C-1, 3); mass spectrum (70 eV) m/e (rel intensity) 43 (100), 79 (40), 96 (49), 97 (23), 114 (13), 138 (13), 139 (21), 174 (17), 234 (12), 236 (4).

Bromination of *cis*-5-Bromomercuri-*cis*-1,3-cyclohexyl Diacetate (10a). A solution of bromine (0.64 g, 4 mmol) in pyridine (2 ml) was added to a solution of **10a** (1.5 g, 3.14 mmol) in pyridine (6 ml) at −40 °C under an atmosphere of dry nitrogen. After completion of the addition the solution was warmed to room temperature and stirred for 2.5 h. Pyridine and other volatiles were removed in vacuo (4 mm) and the oily residue was taken up in ether (100 ml). The solution was washed with saturated aqueous $NaHCO_3$ and then saturated aqueous $CuSO_4$, dried ($MgSO_4$), filtered, and concentrated by rotary evaporation. This material was passed through a column of 80–200 mesh silica gel (10 g) with chloroform as eluting solvent. Removal of solvent by rotary evaporation gave a mixture of isomeric 5-bromo-*cis*-1,3-cyclohexyl diacetates (68%): ^{1}H NMR δ 1.3–2.8 (6 H, C-2, 4, 6), 2.00 (s, 6 H, OAc), 3.93 (tt, 0.5 H, J = 4, 12 Hz, C-5 in *cis*-5-bromo), 4.4–5.0 (1.5 H, C-1, 3 in *cis*-5-bromo and C-5 in *trans*-5-bromo), 5.24 (tt, 1 H, J = 4.5, 7.5 Hz, C-1, 3 in *trans*-5-bromo); mass spectrum (70 eV) m/e (rel intensity) 41 (28), 43 (100), 61 (36), 67 (23), 69 (31), 79 (58), 83 (39), 176 (31), 178 (29), 218 (30), 220 (31), 279 (25), 281 (25).

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Registry No.—**3a,** 285-58-5; **3b,** 694-43-9; **3c,** 40213-64-7; **3d,** 58268-46-5; **3f,** 694-44-0; **4b,** 832-09-7; **4c,** 26688-53-9; **5a,** 40991-94-4; **5b,** 58268-47-6; **5c,** 58311-28-7; **6,** 25494-20-6; **7,** 58268-48-7; **8,** 58268-49-8; **9c,** 58268-50-1; **10a,** 58268-51-2; **10b,** 58268-52-3; **12c,** 58268-53-4; **13c,** 58268-54-5; **14c,** 58268-55-6; **14t,** 58268-56-7; acetic anhydride, 108-24-7; *cis*-1,3-cyclohexanediol, 823-18-7; *trans*-1,3-cyclohexanediol, 5515-64-0; mercuric acetate, 1600-27-7; cyclohexyl acetate, 622-45-7.

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Stereochemistry of Reactions of Silacyclobutanes

B. Gary McKinnie, Norman S. Bhacca, Frank K. Cartledge,* and Jack Fayssoux

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

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Preparations and separations of geometric isomers and structural assignments based on NMR spectra are described for a number of 1-substituted 1,2-dimethylsilacyclobutanes. The stereochemical course for a number of reactions of these derivatives has been determined. There is a decided bias toward retention in the strained ring system even for reactions that are inversions in unstrained organosilanes; nevertheless, inversion can be observed to occur. Mechanistic possibilities are discussed, and an unusual temperature dependence of stereochemical outcome for Br_2 cleavage of an aryl–silicon bond is described.

In recent years considerable attention has been devoted to stereochemical studies of reactions at nonmetal atoms incorporated in strained cyclic systems. Such studies have been particularly important in development of a comprehensive rationalization of the relations between stereochemistry and mechanism in substitution reactions at four-coordinate phosphorus,[1] and recently unusual stereochemical outcomes for reactions at carbon atoms in small rings

Table I. Stereochemistry of Reactions of 1,2-Dimethyl-1-silacyclobutanes

Rxn no.	Compd[a]	Z:E ratio[b]	Reagent	Product	Z:E ratio	Predominant stereochemistry
1	R_3SiCl (1)	40:60	$LiAlH_4$	SiH (2)	59:41	Retention
	R_3SiCl (1)	22:78	$LiAlH_4$	SiH (2)	80:20	
2	R_3SiCl (1)	30:70	ZnF_2	SiF (3)	30:70	
	R_3SiCl (1)	50:50	ZnF_2	SiF (3)	30:70	Nonstereospecific
3	R_3SiF (3)	30:70	$LiAlH_4$	SiH (2)	68:32	Retention
4	R_3SiOMe (4)	30:70	$LiAlH_4$	SiH (2)	75:25	Retention
5	R_3SiCl (1)	15:85	*p*-$MeOC_6H_4MgBr$	SiC_6H_4OMe-*p* (5)	15:85	Retention
	R_3SiCl (1)	50:50	*p*-$MeOC_6H_4MgBr$	SiC_6H_4OMe-*p* (5)	50:50	
6	R_3SiCl (1)	50:50	*p*-MeC_6H_4MgBr	SiC_6H_4Me-*p* (6)	50:50	
7	$R_3SiC_6H_4OMe$-*p* (5)	50:50	HF	R_3SiF (3)	30:70	Nonstereospecific
8	R_3SiH (2)	95:5	CCl_4–Bz_2O_2	SiCl (1)	6:94	Retention
	R_3SiH	2:98	CCl_4–Bz_2O_2	SiCl (1)	95:5	
9	R_3SiH (2)	80:20	CBr_3H–Bz_2O_2	SiBr (7)	30:70	Retention
	R_3SiH (2)	2:98	CBr_3H–Bz_2O_2	SiBr (7)	90:10	

[a] R_3Si equals 1,2-dimethyl-1-silacyclobutane. [b] Isomeric ratios for R_3SiH were determined by GLC, all others from relative intensities of the Si-Me absorptions in the NMR spectra.

have been both predicted[2] and observed.[3] We now wish to report the results of a number of transformations taking place at Si atoms in the strained silacyclobutane system.

Dubac and Mazerolles have reported the stereochemistry of a number of reactions of 2-methyl- and 3-methyl-1-silacyclobutanes, all reactions that were stereospecific being proposed to occur with retention of configuration.[4] However, similar reactions in nonstrained systems also occur with retention.[5a,b] The only stereochemical study in a strained cyclic system of a reaction that occurs with inversion in nonstrained systems is the reduction of 1-chloro-1-α-naphthyl-1-silaacenaphthene.[6] Sommer and co-workers observed retention of configuration in its reduction with $LiAlH_4$ and postulated that the stereochemical crossover is associated with angle strain at Si. In a preliminary communication we have reported a similar result in the silacyclobutane ring system.[7]

Results

A convenient route for synthesis of 1-substituted 1,2-dimethyl-1-silacyclobutanes is through the chloro derivative (1). The preparation of 1 from (3-chlorobutyl)dichloromethylsilane was reported by Dubac and Mazerolles to lead to a 36:64 mixture of the *E* and *Z* isomers, respectively.[1a] We reported that a 60:40 mixture of (*E*)-1 and (*Z*)-1 was obtained.[7] The activity of the magnesium (ours being activated by the method of Damrauer[8]) may account for this difference. Further study of the reaction revealed that an 85:15 mixture of (*E*)-1 and (*Z*)-1 was actually formed which underwent isomerization on distillation at atmospheric pressure (probably owing to traces of ether at high temperature[9]) leading to the 60:40 mixture. Indeed, attempted separation of an 85:15 mixture of 1 by spinning-band distillation led to an approximately 50:50 mixture of the two isomers. The isomerization on distillation accounts for the various ratios of isomers used through this work and for the apparent enrichment of a mixture in (*E*)-1 previously reported by this group.[7]

Table I gives the results of the stereochemistry of eight reactions of 1-substituted 1,2-dimethyl-1-silacyclobutanes. The observation of predominant retention of configuration in the reduction of the chloro and fluoro derivatives (reactions 1 and 3) is contrary to the "normal" stereochemistry of inversion in these reactions; however, there has been a recent report of retention in a fluorosilacyclohexane with fused aromatic rings,[5c] and racemization has also been reported to occur in reduction of 2-fluoro-2-α-naphthyl-2-sila-1,2,3,4-tetrahydronaphthalene.[5b] Although only one isomeric ratio of the fluoro derivative 3 was available for reduction, it is apparent that the reaction is stereospecific since the equilibrium ratio of 2 is known to be a 46:54 mixture of the *Z* and *E* isomers, respectively, from isomerization of both isomers in DMF containing KCN.[10] If the reaction were nonstereospecific the equilibrium ratio of 2 would be a likely result, although any ratio is possible if epimerization of starting materials or intermediates is possible. In the latter event, the reaction is unlikely to appear to be stereospecific. By similar reasoning the reduction of the methoxy derivative 4 (reaction 4) is presumed to be stereospecific.

Table II. Stereochemistry of Bromination of 1-*p*-Anisyl-1,2-dimethyl-1-silacyclobutane

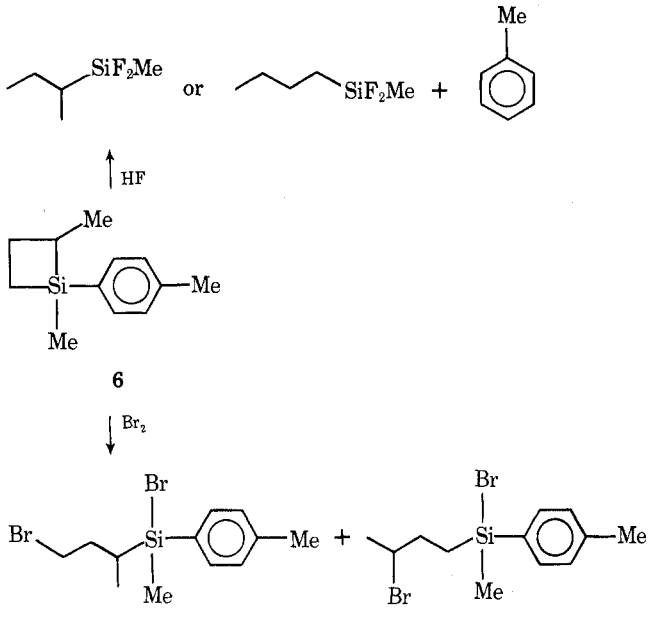
(*E*)-5:(*Z*)-5 ratio	Solvent	Temp, °C	Product ratio (*E*)-7:(*Z*)-7
50:50	CCl_4	−23	50:50
85:15	CCl_4	−23	45:55
50:50	Hexane–ether	−98	30:70
85:15	Hexane–ether	−98	20:80
50:50	CCl_4	~25	70:30
85:15	CCl_4	~25	74:26

The retention of configuration observed in the displacement of chloride ion with *p*-anisylmagnesium bromide (reaction 5) is contrary to the stereochemistry normally observed in the reaction of Grignard reagents with chlorosilanes.[12] However, aryl Grignards often fail to react with the sterically hindered chlorosilanes used in stereochemical studies[12] and thus little is known of these reactions. One chlorosilane has been shown to give predominant (56%) retention of configuration when treated with phenylmagnesium bromide.[13]

The reaction of 1 with zinc fluoride (reaction 2) (represented in Table I as being nonstereospecific) may have occurred stereospecifically, the product then undergoing isomerization induced by halide ion. Evidence for the product ratio representing an equilibrium mixture was formation of the same ratio in both preparations (reactions 2 and 7) and by the failure to observe a change in the ratio when 3 was dissolved in neat methanol. Methanol has previously been shown to give racemization of chiral fluorosilanes.[14]

The desilylation of 5 with anhydrous HF (reaction 7) represents the first reported cleavage of an aryl group from a silacyclobutane in competition with the ring opening normally observed with strong nucleophilic and electrophilic reagents.[15] Ring-opened products were the only ones observed in reaction of 1-*p*-tolyl-1,2-dimethyl-1-silacyclobutane (6) with both HF and bromine (Scheme I). Some ring

Scheme I



opening was also observed in the reaction of the anisyl derivative, **5**, with HF. However the only product obtained in reaction of **5** with bromine was 1-bromo-1,2-dimethyl-1-silacyclobutane (**7**). The results of stereochemical studies of this reaction are shown in Table II. Under the reaction conditions neither **5** nor **7** are isomerized at appreciable rates. The equilibrium mixture of (*Z*)-**7** and (*E*)-**7** at room temperature is 44:56 as demonstrated by isomerization with hexamethylphosphoric triamide.[16] Although inversion of configuration is probably the "normal" stereochemistry of desilylations with bromine,[17] racemization has been observed.[18]

Structural Assignments. The structures of the hydride derivatives (*Z*)-**2** and (*E*)-**2** were assigned from ^1H and ^{13}C chemical shifts. In many substituted cycloalkanes substituents exert an influence on the chemical shifts of protons on an adjacent carbon that is stereospecific and greater when the substituent and proton are cis to one another than when they are trans.[19] Methyl groups generally show the effect of shielding cis protons on adjacent carbons,[20] and in the *E* isomer of **2**, shielding of the proton on Si by the cis C_2-Me gives rise to a resonance at substantially higher field (δ 4.42) than the Si-H of the *Z* isomer (δ 4.75). Also the Si-Me and C_2-Me protons appear at higher field (slightly but consistently) in the *Z* isomer where they are cis to one another. The proton on C_2 could not be resolved from the other ring protons so that no useful coupling constant data are available nor could a nuclear Overhauser effect be determined. The stereochemical assignments were confirmed by ^{13}C chemical shifts for which a reasonably close analogy to the present system exists in a study of methyl-substituted phosphetanes.[21] Steric interaction between the methyl groups of the *Z* isomer of **2** gives rise to resonances at higher field for both the Si-Me (δ −7.0) and the C_2-Me (δ 15.6) relative to the Si-Me (δ −2.3) and C_2-Me (δ 17.3) of the *E* isomer. This high-field shift is also observed for the C_2 resonance of the *Z* isomer.

By reasoning similar to that applied to the hydrides, the structures of all other derivatives were assigned from the ^1H chemical shifts of the Si-Me. In each case, the *E* isomer, where the Si-Me is cis to the C_2-Me, gives rise to a resonance at higher field than the *Z* isomer (Table III). The structures of the fluoride derivatives were confirmed by ^{19}F NMR. The Si-F of the *Z* isomer of **3** where it is cis to the C_2-Me appears at a higher field than the Si-F of the *E* isomer. In both aryl derivatives, **5** and **6**, the C_2-Me of the *Z* isomer where it is cis to the aryl group appears at substantially higher field than the C_2-Me of the *E* isomer. Such diamagnetic anisotropic shifts are well known[19,22] and have previously been observed in phenyl-substituted cyclic silanes.[14c] The structures of the chloride and bromide derivatives were confirmed by stereospecific synthesis from the hydride isomers (reactions 8 and 9). Since these reactions proceed through a silyl radical intermediate,[23] they can be presumed to occur with retention of configuration.

Only in the case of the methoxide isomers are the structural assignments questionable. In the isomer of **4** assigned the *Z* structure from the chemical shifts of the Si-Me groups, the SiOMe which is presumably cis to the C_2-Me gave rise to a resonance at lower field than the SiOMe of the *E* isomer. The structural assignments of **4** made here are the same as those proposed by Dubac and Mazerolles[4a,4c] and are consistent with chemical evidence. The reduction of **4** undoubtedly occurs with retention of configuration since similar reactions of other alkoxysilanes occur with retention.[5]

Table III. NMR Spectra of Derivatives of 1,2-Dimethyl-1-silacyclobutane[a]

Compd	Si-Me	C_2-Me	Si-H	Si-F[b]	SiOMe
SiCl *E*	0.59	1.12			
SiCl *Z*	0.65	1.15			
SiH *Z*	0.28	1.05	4.75		
SiH *E*	0.32	1.11	4.42		
SiF *E*	0.25	1.05		137.6	
SiF *Z*	0.32	1.05		154.7	
SiOMe *E*	0.10				3.40
SiOMe *Z*	0.15				3.48
SiBr *E*	0.67				
SiBr *Z*	0.73				
SiC_6H_4OMe *E*	0.55	1.18			
SiC_6H_4OMe *Z*	0.57	1.03			
SiC_6H_4Me *E*	0.50	1.14			
SiC_6H_4Me *Z*	0.52	0.98			

[a] Complete spectra, solvents, and reference compounds are given in the Experimental Section. [b] ^{19}F NMR.

Discussion

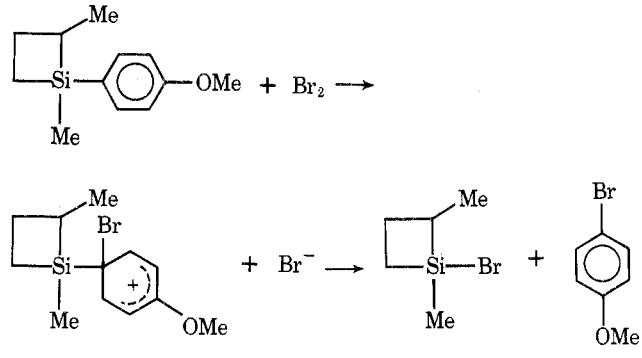
A simple rationalization of the stereochemistry of reactions 1 and 3–5 is possible. "Normal" (SN2-Si)[5a,24] attack on the back side of Si (relative to the leaving group) occurs with the same stereochemical constraints which are normal for SN2 attack on carbon, namely, the entering and leaving groups are apical and the other substituents equatorial. Attack on one of the other three faces of the approximate tetrahedron about silicon (flank attack)[25] leads preferentially to retention of configuration. Flank attack can be induced by coordination of the leaving group to some portion of the entering group (SNi-Si)[5a,26] or, as in the angle strain cases, by the inability of the substituents about Si to occupy their normal equatorial positions in the SN2-Si transition state because of prohibitive increases in angle strain.

An attractive rationalization of the bias toward retention in the silacyclobutane reactions would be formation of a pentacoordinate intermediate by axial entry of the nucleophile. Conversion of the first intermediate to other pentacoordinate intermediates can occur by turnstile rotation or Berry pseudorotation.[1] A single turnstile rotation (TR) followed by loss of the leaving group would result in retention of configuration. The same mechanism was postulated for the recently observed retention reaction of a cyclobutane[3] and has been applied numerous times in phosphorus chemistry.[1] Furthermore, by analogy to arguments applied for

phosphetanes,[27] the strained silacyclobutane ring might be expected to favor formation of extracoordinate intermediates and would be expected to span an axial and an equatorial position in a trigonal bipyramid.

That this stereochemical rationalization is not a complete description of what can occur in small rings is abundantly clear from previous observations of inversions or nonstereoselectivity occurring in four-membered P[28a] and S[28b] rings as well as the present observation of temperature-dependent stereochemical outcome in the bromination of the anisyl derivatives (**5**) in which inversion is occurring at low temperature. The latter reaction presumably proceeds through a σ complex[29] (Scheme II); however, the

Scheme II



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actual situation cannot be so simple as Scheme II implies since the reaction in nonpolar solvents is second order in Br_2.[30] The occurrence of inversion could be explained on the basis of five-coordinate intermediates using an argument similar to that advanced by Emsley[28] and assigning a high equatoriophilicity to the benzenonium ion group in intermediate **15**. This explanation would allow the four-membered ring to retain its preferred axial–equatorial placement in a trigonal bipyramid. A second scheme allowing inversion would be equatorial entry–equatorial departure (perhaps synchronously, perhaps through an intermediate) retaining the ring bonds axial–equatorial. The possibility of equatorial attack must be taken seriously for Si, and also for other nonmetals, following the work of Corriu.[31] A third possibility for inversion would be apical placement of both entering and leaving groups, forcing the ring bonds to be diequatorial. In the five-coordinate hexafluoroacetone adducts of 1-substituted phosphetanes, free energies of activation have been measured for a pseudorotation which places the four-membered ring bonds diequatorial.[32] The activation free energy varies with the substituent but is in the range of 10–20 kcal/mol. If these figures can be considered to approximately represent the free-energy difference between trigonal bipyramids which have four-membered ring bonds axial–equatorial and those where the bonds are diequatorial, then the latter can certainly be generally considered unfavorable, but nevertheless energetically accessible.

We cannot at present distinguish among these possibilities, nor do any of them afford a ready explanation of the temperature dependence of the stereochemical results. Competing mechanistic pathways which show different temperature dependencies in their rates, combined with normal temperature dependence of the compositions of equilibrium mixtures, can certainly lead to a very complex overall picture. The results are suggestive of a need for temperature-dependency studies in other stereochemical investigations.

Experimental Section

Unless otherwise stated, all reactions were run in three-neck round-bottom flasks equipped with a magnetic stirrer, reflux condenser, addition funnel, and thermometer. All glassware was flame dried and flushed with nitrogen prior to conducting the experiment under an atmosphere of nitrogen. All distillations were through a 7-cm Vigreux column unless stated otherwise. Commercial anhydrous ether was used as supplied. Methanol was dried over 3 Å molecular sieves; carbon tetrachloride over 4 Å molecular sieves. Nuclear magnetic resonance (NMR) spectra were obtained routinely on a Varian A-60A, Varian HA-100, or Varian CFT-20. Infrared (ir) spectra were recorded using a Perkin-Elmer Model 137. A Perkin-Elmer Model 900 equipped with a flame ionization detector was used for routine gas–liquid partition chromatography (GLC). Preparative GLC was carried out using a Perkin-Elmer Model F-21. GLC–mass spectra were obtained on a Perkin-Elmer 990 GLC interfaced through a Biemann-Watson separator to a Hitachi Perkin-Elmer RMS-4 mass spectrometer. Mass spectra were taken at 70 eV and are reported as *m/e* (rel abundance).

Dichloro(3-chlorobutyl)methylsilane[33] and 1-methoxy-1,2-dimethyl-1-silacyclobutane[4a,4c] (**4**) were prepared as previously reported.

1-Chloro-1,2-dimethyl-1-silacyclobutane (1). In a 1-l. three-neck flask equipped as usual was placed 21.9 g (0.900 g-atom) of 40-mesh magnesium powder and 600 ml of ether. 1,2-Dibromoethane (3 ml) was added and the mixture refluxed for 15 min. To this activated magnesium was added dropwise 61.7 g (0.300 mol) of (3-chlorobutyl)dichloromethylsilane in 40 ml of ether over an 8-h period with refluxing. Refluxing was continued for 3 days and stirring at room temperature for 5 days.

The reaction mixture was filtered under nitrogen and the residue washed twice with ether. The solvent was removed by rapid distillation and the remaining liquid distilled to give 25.5 g (63% yield) of **1**: bp 61–65 °C (92–93 mm) [lit.[4a] bp 62–64 °C (110 mm)]; NMR (100 MHz) ($CDCl_3$, internal $CHCl_3$) δ 0.59 (s) and 0.65 (s) (total, 3 H), 1.12 (d) and 1.15 (d) (total, 3 H), 1.0–2.0 (m, 4 H), and 2.45 (m, 1 H). Relative intensities of 85:15 were observed for the singlets at δ 0.59 and 0.65, respectively. MS *m/e* 134 (13), 119 (6), 108 (35), 106 (100), 92 (86), 78 (63), 63 (47), and metastables at 66.3, 64.7, and 57.3.

If the solvent was removed by slow distillation and the product distilled at 760 mm (bp 121–123 °C) a 75% yield was obtained of a 60:40 mixture of (*E*)-**1** and (*Z*)-**1**, respectively.

Keeping the reaction vessel in a cold bath at 4–6 °C during addition of the silane and for 4 days, plus 7 days at 8–10 °C failed to increase the isomeric ratio above 85:15.

Attempted spinning band distillation of **1** at 760 mm resulted in isomerization to a 47:53 mixture of the two isomers. Spinning band distillation at 150 mm (bp 81–82 °C) failed to separate the isomers.

1,2-Dimethyl-1-silacyclobutane (2) (Reaction 1). In a 250-ml three-neck flask equipped as usual was placed 125 ml of ether and 2.30 g (0.242 g-atom of H) of crushed lithium aluminum hydride. To this stirred mixture was added 23.1 g (0.172 mol) of a 60:40 mixture of (*E*)-**1** and (*Z*)-**1**, respectively, in 30 ml of ether at a rate sufficient to maintain refluxing. Refluxing was continued 0.5 h after addition was complete.

After filtering, the reaction mixture was added to 150 ml of ice water containing 30 g of ammonium chloride. The ether layer was washed once with 1 M aqueous ammonium chloride and twice with water, and dried over magnesium sulfate. Distillation gave 10.1 g (59% yield) of **2**, bp 84–87 °C [lit.[4b] bp 85–87 °C (748 mm)].

Analysis by GLC using a 16 ft × 0.125 in. column of 15% Apiezon L on 60–80 mesh Chromosorb W at 85 °C showed an impurity, 10%, retention time of 4.2 min, and the two isomers, (*E*)-**2** and (*Z*)-**2**, retention times of 4.7 and 5.3 min, 37 and 53% respectively (*Z*:*E* ratio of 59:41). Similarly reduction of a 78:22 mixture of (*E*)-**1** and (*Z*)-**1** gave an 80:20 mixture of (*Z*)-**2** and (*E*)-**2** as determined by GLC analysis of the reaction mixture.

The isomers were separated by preparative GLC on a 64 × 0.75 in. column of 10% Apiezon L on 60–80 mesh Chromosorb W operating at a temperature of 85 °C with a nitrogen flow rate of 270 ml/min. The *E* and *Z* isomers had retention times of 6.4 and 7.2 min, respectively. Attempted spinning band distillation of **2** resulted in polymerization. NMR (100 MHz) ($CDCl_3$, internal Me_4Si) **2a:** δ 0.28 (d, J = 4 Hz, 3 H), 1.05 (d, 3 H), 0.76–1.95 (m, 4 H), 2.45 (m, 1 H), and 4.75 (m, 1 H). **2b:** δ 0.32 (d, J = 4 Hz, 3 H), 1.11 (d, 3 H), 0.58–1.87 (m, 4 H), 2.40 (m, 1 H), and 4.42 (m, 1 H). ^{13}C NMR ($CHCl_3$) **2a:** δ −7.0 (Si-Me), 9.0 (C_4), 15.6 (C_2-Me), 20.4 (C_2), and 29.6 (C_3). **2b:** δ −2.3 (Si-Me), 9.0 (C_4), 17.3 (C_2-Me), 23.1

(C_2), and 28.4 (C_3). Ir (film) 2900 s, 2100 s, 1450 m, 1400 w, 1250 s, 1180 w, 1130 m, 1060 m, 970 m, 920 s, 890 s, 855 s, and 730 cm^{-1} s; mass spectrum *m/e* 100 (10), 85 (14), 72 (100), 58 (45), 43 (45), and a metastable at 51.8.

1,2-Dimethyl-1-fluoro-1-silacyclobutane (3) (Reaction 2). In a 50-ml one-neck flask were placed 15.33 g (114 mmol) of a 70:30 mixture of (*E*)-**1** and (*Z*)-**1**, respectively, and 9.0 g (87 mmol) of anhydrous zinc fluoride. The flask was equipped with a magnetic stirrer and set for distillation. Distillation gave a fraction, bp 85–112 °C, which was combined with 9.0 g (87 mmol) of fresh zinc fluoride and redistilled, the fraction bp 80–85 °C being collected. Redistillation of this fraction from 1.0 g of fresh zinc fluoride gave 9.21 g (68% yield) of **3**: bp 83–84 °C; NMR (CCl_4, internal benzene) δ 0.25 (d, J = 8 Hz) and 0.32 (d, J = 8 Hz) (total of 3 H), 1.05 (m, 3 H), and 0.83–2.25 (m, 5 H); estimated relative intensities were 70:30 for doublets at δ 0.25 and 0.32, respectively. ^{19}F NMR ($CFCl_3$, solvent as reference) δ 137.6 (m) and 154.7 (m) (relative intensities of 75:25, respectively); MS *m/e* 118 (7), 103 (6), 90 (94), 77 (77), 76 (100), 63 (50), 62 (92), 47 (83), and metastables at 42.8 and 50.2. Anal. Calcd for $C_5H_{11}FSi$: C, 50.79; H, 9.38; Si, 23.78. Found: C, 50.59; H, 9.40; Si, 23.60.

A similar preparation using a 50:50 mixture of (*E*)-**1** and (*Z*)-**1** gave a 70:30 mixture of (*E*)-**3** and (*Z*)-**3** as determined by NMR.

Reduction of 1,2-Dimethyl-1-fluoro-1-silacyclobutane (Reaction 3). In an 8-ml vial equipped with a magnetic stirrer were placed 45.6 mg (4.94 mg-atoms of H) of $LiAlH_4$ and 5 ml of ether. After equipping with a septum 0.50 g (4.2 mmol) of a 70:30 mixture of (*E*)-**3** and (*Z*)-**3** was added via syringe and the mixture stirred for 15 min. GLC–mass spectrometry analysis showed that (*Z*)-**3** and (*E*)-**3** were formed in a 68:32 ratio.

Reduction of 1,2-Dimethyl-1-methoxy-1-silacyclobutane (Reaction 4). In an 8-ml vial were placed 6.5 mg (0.73 mg-atoms of H) of $LiAlH_4$ and 2.0 ml of ether. Through a septum 52 mg (0.40 mmol) of a 70:30 mixture of (*E*)- and (*Z*)-1,2-dimethyl-1-methoxy-1-silacyclobutane was added via syringe and the mixture stirred for 0.5 h. GLC–mass spectrometry analysis showed that (*Z*)-**2** and (*E*)-**2** were formed in a 75:25 ratio.

1,2-Dimethyl-1-(*p*-anisyl)-1-silacyclobutane (5) (Reaction 5). To a solution of 26.9 g (0.200 mol) of a 50:50 mixture of (*E*)-**1** and (*Z*)-**1** in 100 ml of ether was added with stirring the top layer of a solution of *p*-anisylmagnesium bromide obtained from 39.0 g (0.208 mol) of *p*-bromoanisole and 7.0 g (0.287 g-atom) of magnesium turnings in 350 ml of ether. The lower layer was then added dropwise and the mixture stirred for 2 h under reflux.

The reaction mixture was hydrolyzed in 300 ml of ice water containing 20 g of ammonium chloride. The ether layer was washed once with water and dried over magnesium sulfate. After the solvent was removed, the remaining liquid was distilled, the fraction bp 80–86 °C (0.5 mm) was collected and redistilled to give 26.7 g (65% yield) of a 50:50 mixture of (*E*)-**5** and (*Z*)-**5**, bp 72–76 °C (0.3 mm). NMR (CH_2Cl_2, solvent as reference) (100 MHz) δ 0.55 (s) and 0.57 (s) (total 3 H) (ca. 50:50), 1.03 (d, J = 7 Hz) and 1.18 (d, J = 7 Hz) (total 3 H), 0.94–2.00 (m, 4 H), 2.55 (m, 1 H), 3.82 (s), and 3.83 (s) (total 3 H), 6.99 (m, 2 H), and 7.59 (m, 2 H); ir (film) 2900 s, 1600 s, 1480 s, 1270 s, 1240 s, 1180 m, 1130 w, 1110 s, 1040 m, 965 w, 915 w, 870 w, 850 m, and 780 cm^{-1} m; mass spectrum *m/e* 206 (14), 191 (2), 178 (32), 164 (100), 151 (61), 135 (37), 134 (38), 121 (22), 119 (19), and metastable at 109.5. Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79; Si, 13.61. Found: C, 69.91; H, 8.90; Si, 13.74.

Similarly, reaction of 4-methoxyphenylmagnesium bromide with an 85:15 mixture of (*E*)-**1** and (*Z*)-**1**, respectively, gave an 75% yield an 85:15 mixture of (*E*)-**5** and (*Z*)-**5**, respectively.

1,2-Dimethyl-1-(*p*-tolyl)-1-silacyclobutane (6) (Reaction 6). To 30.0 g (0.223 mol) of a 50:50 mixture of (*E*)-**1** and (*Z*)-**1** in 100 ml of ether was added dropwise a solution of *p*-tolylmagnesium bromide prepared from 42.0 g (0.245 mol) of 4-bromotoluene and 8.0 g (0.33 g-atom) of magnesium turnings in 400 ml of ether. After stirring under reflux for 1 h the mixture was hydrolyzed by addition to 35 g of ammonium chloride in 500 ml of ice water. The ether layer was washed once with water and dried over magnesium sulfate. After the solvent was removed, the remaining liquid was distilled to yield 29.0 g (68% yield) of a 50:50 mixture of (*E*)-**6** and (*Z*)-**6**, bp 73–75 °C (1.0 mm): NMR (CH_2Cl_2, solvent as reference) δ 0.50 (s) and 0.52 (s) (total 3 H) (ca. 50:50), 0.98 (d, J = 7 Hz) and 1.14 (d, J = 7 Hz) (total 3 H), 0.95–1.93 (m, 4 H), 2.37 (broad s, 3 H), 2.31–2.61 (m, 1 H) 7.24 (m, 2 H), and 7.56 (m, 2 H); ir (film) 2900 s, 1600 m, 1450 m, 1400 w, 1250 s, 1180 w, 1130 m, 1110 s, 970 m, 920 w, 870 m, 850 s, and 780 cm^{-1} s; mass spectrum *m/e* 190 (16), 175 (1), 162 (45), 148 (100), 135 (67), 134 (45), 133 (73), 131 (22), 119 (59), 105 (20), 93 (20), and metastables at 138.1 and 110.8. Anal. Calcd for $C_{12}H_{18}Si$: C, 75.71; H, 9.53; Si, 14.76. Found: C, 75.52; H, 9.43; Si, 15.00.

Reaction of 5 with HF (Reaction 7). In a dry polyethylene test tube equipped with a polyethylene stopper was placed 5.8 g of a 50:50 mixture of (*E*)-**5** and (*Z*)-**5**. Anhydrous HF was bubbled through the neat compound for 2 h followed by nitrogen for 1 h. Distillation gave a fraction, 0.91 g, bp 78–83 °C, the NMR spectrum of which showed chemical shifts characteristic of (*E*)-**3** and (*Z*)-**3** (ca. 70:30, respectively) and approximately an equal amount of the product obtained from reaction of **6** with HF.

Stereospecific Preparations of 1-Chloro-1,2-dimethyl-1-silacyclobutane from 1,2-Dimethyl-1-silacyclobutane (Reaction 8). In a 25-ml one-neck flask equipped with a condenser were placed 2.16 g (21.6 mmol) of 95% isomerically pure (*Z*)-**2**, 17 ml (175 mmol) of dry carbon tetrachloride, and 0.05 g of benzoyl peroxide. The mixture was held at 80 °C for 1 h, an additional 0.05 g of benzoyl peroxide added, and the mixture heated at 80 °C for 1 h longer. Analysis of the reaction mixture by NMR showed a 94:6 ratio of (*E*)-**1** and (*Z*)-**1**. Distillation gave 1.63 g (56% yield) of 94% isomerically pure (*E*)-**1**, bp 59–61 °C (89–90 mm).

Similarly, reaction of 0.178 g of 98% (*E*)-**2**, 1.0 ml of carbon tetrachloride, and 0.02 g of benzoyl peroxide in an NMR tube at 80 °C for 1 h gave >95% pure (*Z*)-**2**, as determined by NMR analysis of the reaction mixture.

Stereospecific Preparation of 7 from 2 (Reaction 9). In a dry NMR tube were placed 0.02 g of benzoyl peroxide, 1.0 ml (2.89 g, 11.4 mmol) of CBr_3H, and 78 mg (0.78 mmol) of an 80:20 mixture of (*Z*)-**2** and (*E*)-**2**. The mixture was then held at 80 °C for 0.5 h. Analysis by NMR revealed that (*E*)-**7** and (*Z*)-**7** were formed in a 70:30 ratio, respectively.

Similarly, a 2:98 ratio of (*Z*)-**2** and (*E*)-**2** gave respectively (*E*)-**7** and (*Z*)-**7** in a 10:90 ratio.

Reaction of 6 with HF. In a dry polyethylene test tube equipped with a polyethylene stopper was placed via syringe 1.7 g of **6**. Anhydrous HF was bubbled through **6** for 3 h by use of a stainless steel needle. After standing overnight nitrogen was bubbled through the solution for 1 h. The reaction mixture was analyzed directly: NMR (CCl_4, external Me_4Si) δ 0.28 (t), 0.60–1.80 (m), 2.31 (s), and 7.10 (s), the latter two chemical shifts characteristic of toluene; MS parent mass 138. The product probably was *sec*-butyl- and/or *n*-butyldifluoromethylsilane.

A similar reaction was stopped before all starting material was consumed. NMR analysis showed that no **3** was present.

Reaction of 6 with Bromine. To 4.40 g (23.2 mmol) of **6** in 10 ml of CCl_4 held in an ice bath was added 3.7 g (23.2 mmol) of bromine in 10 ml of CCl_4. After addition was completed the solvent was removed by distillation under reduced pressure and the product distilled to give 4.5 g (55% yield) of a clear liquid tentatively identified as a 2:1 mixture of bromo(3-bromobutyl)methyl(*p*-tolyl)silane and bromo(3-bromo-1-methylpropyl)methyl(*p*-tolyl)silane: bp 105–135 °C (0.9 mm); NMR (CCl_4, internal Me_4Si) δ 0.76 (s), 0.87–2.10 (m), 1.66 (d), 2.33 (s), 3.38 (m), 4.20 (m), 7.12 (d), and 7.46 (d).

1-Bromo-1,2-dimethyl-1-silacyclobutane (7). In a one-neck 100-ml flask equipped with a magnetic stirrer and addition funnel were placed 10.4 g (50.5 mmol) of a 50:50 mixture of (*E*)-**5** and (*Z*)-**5** and 20 ml of carbon tetrachloride. Bromine (8.10 g, 50.5 mmol) in 15 ml of carbon tetrachloride was added dropwise with stirring while keeping the flask in a dry ice–acetone bath at −50 to −55 °C. Distillation gave 7.50 g (83% yield) of a 50:50 mixture of (*E*)-**7** and (*Z*)-**7**: bp 70–71 °C (68 mm); NMR (CCl_4, internal benzene) δ 0.67 (s) and 0.73 (s) (total 3 H) (50:50), 1.06 (d, 3 H), and 0.97–2.78 (m, 5 H); mass spectrum *m/e* 180 (15), 178 (16), 165 (6), 163 (6), 152 (100), 150 (100), 138 (89), 136 (89), 124 (66), 122 (66), 109 (56), 107 (55), 99 (8), 90 (68), 76 (66), and 62 (57). Anal. Calcd for $C_5H_{11}BrSi$: C, 33.52; H, 6.19; Si, 15.69. Found: C, 33.64; H, 6.25; Si, 15.55.

Similarly, reaction of an 85:15 mixture of (*E*)-**5** and (*Z*)-**5** led to a 64% yield of a 45:55 mixture of (*E*)-**7** and (*Z*)-**7**, respectively.

Reaction of 5 with Bromine at −98 °C. In a 100-ml three-neck flask equipped with a mechanical stirrer, addition funnel, and thermometer were placed 5.48 g (26.6 mmol) of an 85:15 mixture of (*E*)-**5** and (*Z*)-**5** and 50 ml of ether. The flask was placed in a methanol–liquid nitrogen slurry (−98 °C) and 4.25 g (26.6 mmol) of bromine in 10 ml of dry hexane was added dropwise over a 1-h period. The mixture was stirred for 2 h as it warmed slowly to −78 °C. Analysis by NMR showed only a trace of starting material present and that (*E*)-**7** and (*Z*)-**7** were formed in ca. a 20:80 ratio respectively.

Similarly, reaction of a 50:50 mixture of (*E*)-**5** and (*Z*)-**5** gave a

30:70 ratio of (*E*)-**7** and (*Z*)-**7**.

Reaction of 5 with Bromine at Room Temperature. In a dry NMR tube was placed via syringe 0.50 ml of a 2.0 M solution of **5** in CCl_4 (*E*/*Z* ratio of 85:15). To this solution was added via syringe 0.50 ml of a 2.0 M solution of Br_2 in CCl_4. The Br_2 color disappeared immediately. Analysis of the reaction mixture by NMR immediately after reaction showed that a 74:26 ratio of (*E*)-**7** and (*Z*)-**7**, respectively, were formed and all starting material was consumed.

Similarly, a 50:50 mixture of (*E*)-**5** and (*Z*)-**5** gave a 70:30 ratio of (*E*)-**7** and (*Z*)-**7**, respectively.

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Registry No.—(*E*)-**1**, 52516-83-3; (*Z*)-**1**, 52516-84-4; (*E*)-**2**, 40726-02-1; (*Z*)-**2**, 40726-01-0; (*E*)-**3**, 53477-23-9; (*Z*)-**3**, 53477-24-0; (*E*)-**4**, 35741-84-5; (*Z*)-**4**, 35741-83-4; (*E*)-**5**, 58241-19-3; (*Z*)-**5**, 58241-20-6; (*E*)-**6**, 58241-21-7; (*Z*)-**6**, 58241-22-8; (*E*)-**7**, 58241-23-9; (*Z*)-**7**, 58241-24-0; 1,2-dibromoethane, 106-93-4; (3-chlorobutyl)dichloromethylsilane, 18145-84-1; *p*-bromoanisole, 104-92-7; 4-bromotoluene, 106-38-7; HF, 7664-39-3; carbon tetrachloride, 56-23-5; CBr_3H, 75-25-2; bromine, 7726-95-6; bromo(3-bromobutyl)methyl(*p*-tolyl)silane, 58241-25-1; bromo(3-bromo-1-methylpropyl)methyl(*p*-tolyl)silane, 58241-26-2.

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Stereospecific Synthesis of 6,*c*-10-Dimethyl(*r*-5-*C*¹)spiro[4.5]dec-6-en-2-one and Its Conversion into (±)-α-Vetispirene[1]

Drury Caine,* Anibal A. Boucugnani, Sam T. Chao, J. Byron Dawson, and Paul F. Ingwalson

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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A stereospecific synthesis of the spiro enone **6** and its conversion into (±)-α-vetispirene is described. The photochemical rearrangement of the methoxy dienone **7** was employed as a key step to establish the spiro[4.5]decane ring system.

Interest in the synthesis of spirovetivane sesquiterpenes has been aroused since Marshall and co-workers reported that β-vetivone is a member of this group rather than a hydroazulene derivative as originally reported.[2] Recently, total syntheses of (±)-β-vetivone (**1**),[2c,3a-e] (−)-β-vetivone,[3f] (±)-hinesol (**2a**),[3e,4a] (±)-agarospirol (**2b**),[5] (−)-agarospirol,[3f] (±)-β-vetispirene (**3**),[3e,4b,6] and (±)-α-vetispirene (**4**)[3e,4b] have been reported.[7] In addition, relay syntheses of anhydro-β-rotunol (**5**)[8] from β-rotunol[9] and from nootkatone[10] have appeared. Several general approaches to the spiro[4.5]decane ring skeleton of these compounds also have been published.[11]

An attractive approach to various spirovetivane sesquiterpenes appeared to involve the synthesis of the spiro[4.5]dec-6-en-2-one **6** having the carbonyl group in the five-