A Convenient Synthetic Route to Methylated Silacyclohexanes

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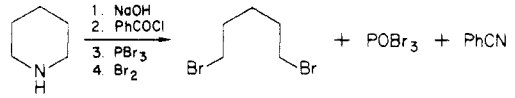
The von Braun degradation of substituted piperidines is a general and economical route to a variety of substituted primary and secondary α,ω-dibromopentanes. Grignard ring closure procedures have been carried out with seven different dibromopentanes in moderate to good yields. Ring closures with $MeClSiCl_2$ lead to product mixtures which are appreciably enriched in one isomer, affording a convenient entry into a variety of derivatives which can be used for stereochemical studies. Assignment of structures based on ^1H NMR and mass spectral fragmentation patterns is discussed.

We and others have been interested in using substituted silacycloalkanes in studies of reaction pathways at Si, conformational preferences, and interrelationships between structure and reactivity. We wish to report herein convenient synthetic procedures for a variety of methyl-substituted silacyclohexanes and some spectral properties of this class of compounds.

Preparations of silacycloalkanes are most commonly accomplished by Grignard ring closure procedures, although a number of other routes, most notably intramolecular hydrosilation, have been used.[1] For silacyclohexanes, 1,5-dihaloalkanes are reasonable precursors, and we have prepared a number of these compounds using the von Braun degradation. The procedure has been known for many years but has been seldom employed as a route to α,ω-dibromoalkanes, perhaps because it appears on the surface to be a more involved synthetic route than cyclic ether ring openings or conversion of various α,ω-difunctional compounds to dihalides. For 1,5-dibromoalkanes, the degradation is particularly useful because variously substituted piperidines are readily available and ordinarily cheap compared to substituted tetrahydropyrans. Consequently, the method is attractive even though yields are usually lower than in ether ring openings.

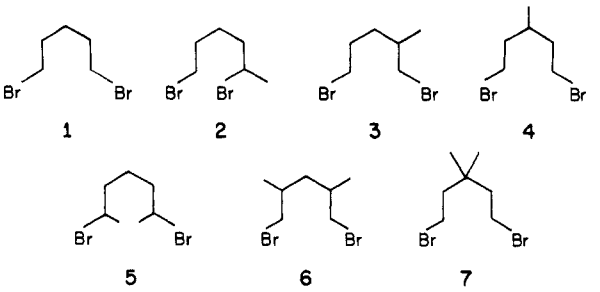
The von Braun degradation is illustrated below. The benzamide can be made in essentially quantitative yield.



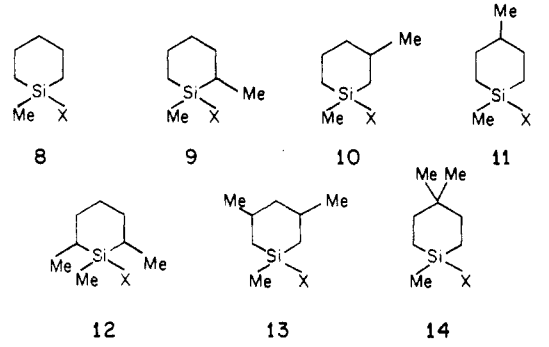
Even with the somewhat crowded 2,6-lutidine we were able to isolate 83% of the *N*-benzoyl-2,6-lutidine. We have ordinarily carried out the procedure in two stages, isolating the *N*-benzoylpiperidine. The second stage of the procedure presumably involves nucleophilic attack at the 2-position of the piperidine ring,[2] and we were concerned about the facility with which that step would proceed when the position was methyl-substituted. Yields were slightly lower with 2-methylpiperidine and 2,6-lutidine, but the route remains an attractive one. The degradation step involves a vigorous exothermic reaction as Br_2 is added, and cooling is required, but we had no difficulty in carrying out the process on a 100-g scale. Yields in the degradation step are shown in Table I. Since spectroscopic data is not in the literature for a number of these dibromides, this information is included in Table I for compounds **1–7**.

Ring Closure Reactions

The ring closure reactions of the dibromoalkanes with dichlorosilanes and Mg were carried out using standard



procedures at relatively high dilution. Yields varied from 32% to 69%, always being lowest for the isomers which have Me groups in the 2-position of the ring. The yields are in general a bit lower than in the formation of silacyclopentanes, many of which we have reported earlier,[3] presumably due to less favorable entropic factors for closure of the larger ring. Both THF and ether were used as solvents, and yields were ordinarily several percentage points higher in ether. Sonication had little effect on the yields. Table II contains information on the formation of compounds **8–14**.



a, X = Me; b, X = H; c, X = Cl; d, X = Ph

The ring closures using $RSiCl_3$ and the dibromides always resulted in formation of a minor product which had Br attached to Si as well as the expected Si–Cl, presumably due to Cl^-/Br^- exchange at Si.[4] In those cases it was particularly difficult to remove all traces of bromosilane in order to get an analytically pure chlorosilane.

In all cases the ring closures to produce chlorosilacyclohexanes gave appreciably more of the isomer which can have both C–Me and Si–Me equatorial. In **9c**, **10c**, and **11c** the cis/trans ratio was 30/70, 70/30, and 32/68, respectively. The corresponding ring closure with an α,ω-dibromide to produce 1-chloro-1,2-dimethylsilacyclopentane gives isomer distributions near 50/50,[3]

(1) Barton, T. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1982; Vol. II, pp 261–274.
(2) See: Phillips, B. A.; Fodor, G.; Gal, J.; Letourneau, F.; Ryan, J. J. *Tetrahedron* **1973**, *29*, 3309–3327 and references therein.
(3) Cartledge, F. K.; Wolcott, J. M.; Dubac, J.; Mazerolles, P.; Joly, M. *J. Organomet. Chem.* **1978**, *154*, 187–201.
(4) This long-known phenonmenon in Grignard preparations of Si–Cl compounds (Eaborn, C. *Organosilicon Compounds*; Butterworths: London, 1960; pp 176–7) is often ignored.

0022-3263/86/1951-2206$01.50/0

Table I. α,ω-Dibromides Prepared by the von Braun Degradation

compd	% yield[a]	bp (mmHg)	^{1}H NMR[b]	mass spectrum[c]	analysis, found[d]
1	63	111–112 (15)[e]	1.3–2.4 (m, 6 H), 3.3–3.6 (m, 4 H)	232 (5.5), 230 (11), 228 (5.8), 151 (71), 149 (70), 69 (100), 41 (40)	
2	58	119–120 (15)	1.72 (d, J = 6.6, 3 H), 1.33–2.37 (m, 6 H), 3.33–3.63 (t, J = 6.6, 2 H), 4.0–4.33 (m, 1 H)	246 (8.2), 244 (16), 242 (9.5), 165 (21), 163 (23), 83 (100), 55 (44)	C, 29.42; H, 4.97
3	61	113–114 (15)[f]	1.04 (d, J = 6.6, 3 H), 1.24–2.11 (m, 5 H), 3.18–3.63 (m, 4 H)	246 (0.3), 244 (1.0), 242 (0.4), 165 (22), 163 (27), 83 (100), 69 (18), 55 (21)	C, 29.68; H, 5.04
4	61	120–121 (18)	0.94 (d, J = 6.0, 3 H), 1.50–2.22 (m, 5 H), 3.25–3.68 (m, 4 H)	246 (0.6), 244 (1.5), 242 (0.8), 165 (10), 163 (12), 83 (100), 69 (9), 55 (59)	C, 29.66; H, 5.05
5	33	110–111 (10)[g]	1.74 (d, J = 6.8, 6 H), 1.30–2.51 (m, 6 H), 3.99–4.34 (m, 2 H)	260 (0.4), 258 (0.8), 256 (0.4), 179 (58), 177 (63), 98 (11), 97 (100), 67 (12), 55 (25)	C, 32.65; H, 5.51
6	44	73–75 (2)[h]	1.06 (d, J = 6.7, 6 H), 1.04–2.14 (m, 4 H), 3.17–3.60 (d, J = 5.8, 4 H)	260 (0.1), 258 (0.3), 256 (0.1), 98 (6), 97 (100)	C, 32.60; H, 5.56
7	[i]	116–117 (8)[j]	0.92 (s, 6 H), 1.8–2.5 (m, 4 H), 3.35–3.85 (m, 4 H)	260 (1.2), 258 (2.4), 256 (1.0), 179 (5), 177 (5), 98 (70), 97 (100), 67 (5), 55 (19)	C, 32.63; H, 5.56

[a] Yield in the ring opening step. [b] In $CDCl_3$ at 200 MHz relative to internal Me_4Si. [c] m/z (relative intensity). [d] Calcd for $C_6H_{12}Br_2$: C, 29.51; H, 4.92. Calcd for $C_7H_{14}Br_2$: C, 32.56; H, 5.43. [e] Lit. 108–110 (20) (ref 15). [f] Lit. 98–99 (11) (ref 16). [g] Lit. 121–123 (25) (ref 17). [h] Lit. 72–73 (2) (ref 18); also 72 (12) (ref 14). [i] Prepared by a different route (see Experimental Section). [j] Lit. 98–99 (3) (ref 19).

Table II. Silacyclohexanes Prepared in This Work

compd	% yield[a]	*cis*/*trans*[b]	bp (mmHg)	analysis[c]
9a	43		64–5 (40)[d]	142.1177; 142.1166
10a	50		62–3 (40)	142.1177; 142.1169
11a	55		65–6 (40)	142.1177; 142.1161
12a	32	50/50	97–8 (70)	C, 69.23; H 12.82; C, 69.15; H, 12.73
13a	40	50/50	80–1 (65)	C, 69.23; H, 12.82; C, 69.23; H, 12.71
14a	48		91–2 (90)	C, 69.23, H, 12.82; C, 69.08; H, 12.67
9b	43	55/45	62–3 (65)	128.1021; 128.0992 and 128.0993
10b	53	50/50	55–6 (71)	128.1021; 128.0986 and 128.0993
11b	60	52/48	57–8 (71)	128.1021; 128.0992 and 128.0993
9c	44	30/70	92–3 (50)	162.0631; 162.0629 and 162.0626
10c	60	70/30	94–5 (50)	C, 51.69; H, 9.23; C, 51.60; H, 9.35
11c	60	32/68	94–5 (55)	C, 51.69; H, 9.23; C, 51.51; H, 9.26
9d	50	58/42	126–7 (5)	C, 76.47; H, 9.80; C, 76.42; H, 9.90
10d	64	42/58	128–9 (6)	C, 76.47; H, 9.80; C, 76.43; H, 9.89
11d	60	58/42	100–1 (1)	C, 76.47; H, 9.80; C, 76.62; H, 10.01

[a] Yield in the Mg ring closure using the appropriate α,ω-dibromide and $XMeSiCl_2$. [b] Ratio observed in the ring closure using GC analysis. [c] Calcd followed by found for C, H analysis or precise mass of molecular ion. [d] Lit. 65 (40) (ref 20).

while the closure of (3-chlorobutyl)dichloromethylsilane with Mg gives 1-chloro-1,2-dimethylsilacyclobutane with an appreciable preference for the *cis*-isomer.[5] In the silacyclohexane series, the SiMeH and SiMePh derivatives are formed in ratios near 50/50. It is fortunate that the SiMeCl derivatives are available as mixtures enriched in one isomer, since it has been shown earlier[6] and will be reported in detail by us in subsequent publications, that the SiCl compounds can be converted by stereospecific routes to a variety of derivatives which are enriched in one isomer.

Spectral Properties

We and others have reported outstanding success in reproducing experimental structures and conformational energy differences in organosilicon compounds using molecular mechanics.[7] Calculations on the present series of compounds along with conformational information available through ^{13}C and 400-MHz ^{1}H NMR studies will be reported in detail later. ^{1}H NMR data obtained at 200 MHz is included here. The Si–Me resonances are of course easily identifiable, as are Si–H resonances. The ring methyl groups generally appear as doublets rising out of the multiplet for the remaining ring protons. Stereochemical assignments have been made based on the assumptions that we can predict which isomer will have a predominantly equatorial methyl group[7,8] and that equatorial Me groups on silicon appear upfield from axial methyls. The assignments agree with those of Murakami and Sakurai[6] in the *cis*- and *trans*-4-*tert*-butyl-1-methylsilacyclohexanes and in many methylcyclohexane derivatives.[9] In the spectra of mixtures of *cis*- and *trans*-**9b**, -**10b**, and -**11b** double irradiation was used to identify the Si–H signal which corresponded to the proton coupled to the methyl group. In each case the upfield (predominantly equatorial) Me is coupled to the upfield (predominantly axial) H on Si. Axial Si–H upfield from equatorial Si–H is also in agreement with the assignments of Murakami and Sakurai,[6] as well as of Carleer and Anteunis in 3,5-dimethylsilacyclohexane.[8] In methylcyclohexanes vicinal exocyclic H_3CCH couplings are larger when the ring proton is axial.[9,10] In our systems the vicinal H_3CSiH couplings are virtually the same in the two isomers; hence that criterion does not appear to be a reasonable one on which to base structural assignments.

The mass spectral fragmentation patterns are very typical for cyclic silanes, indeed for silanes in general. The fact that the present set of derivatives has methyl groups in so many different positions, however, allows us to reach some conclusions about the fragmentation pathways. The molecular ions are present in low abundances, with the exception of cases in which there are one or more Me

(5) McKinnie, B. G.; Bhacca, N. S.; Cartledge, F. K.; Fayssoux, J. *J. Org. Chem.* **1976**, *41*, 1534–9.
(6) Sakurai, H.; Murakami, M. *J. Am. Chem. Soc.* **1972**, *94*, 5080–2; Sakurai, H.; Murakami, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3185–9.
(7) See, for instance: Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982; pp 202–5; Frierson, M. R. Ph.D. Dissertation, University of Georgia, 1984; Cartledge, F. K. *J. Organomet. Chem.* **1982**, *225*, 131–9 and references therein.
(8) Carleer, R.; Anteunis, M. J. O. *Org. Magn. Reson.* **1979**, *12*, 673–8.
(9) Daneels, M.; Anteunis, M. *Org. Magn. Reson.* **1974**, *6*, 617–21 and references therein.
(10) Anteunis, M. *Bull. Soc. Chim. Belg.* **1971**, *80*, 3.

Table III. Spectral Properties of Silacyclohexanes Prepared in This Work

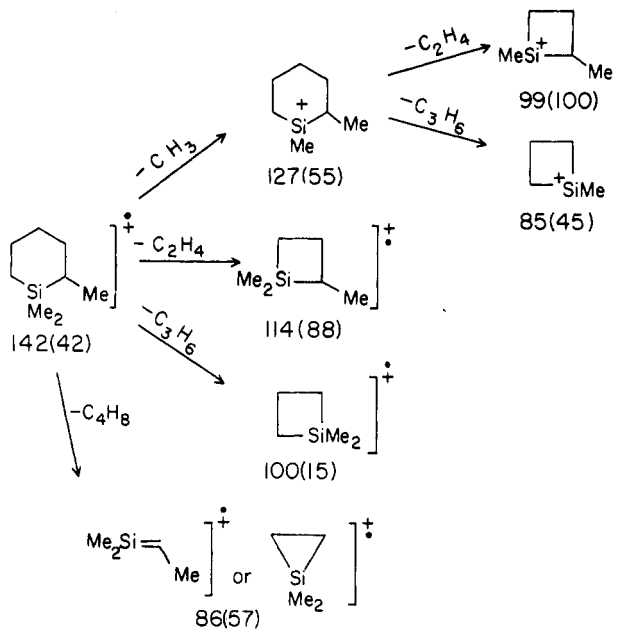
compd	^{1}H NMR[a]	mass spectrum[b]
8a	0.01 (s, 6 H); 0.45–0.49 (m, 4 H); 1.40–2.00 (m, 6 H)	128 (26), 113 (100), 86 (11), 85 (85), 72 (12), 59 (21)
9a	0.01 (s, 3 H, eq SiMe); 0.06 (s, 3 H, ax SiMe); 0.25–0.90 (m, 3 H); 0.96 (d, J = 7.08, 3 H); 1.03–2.15 (m, 6 H)	142 (42), 129 (13), 127 (55), 115 (12), 114 (88), 100 (15), 99 (100), 97 (14), 87 (38), 86 (57), 85 (45), 73 (34), 72 (28), 71 (11), 58 (19), 43 (12)
10a	−0.02 (s, 3 H, eq SiMe); 0.01 (s, 3 H, ax SiMe); 0.10–0.48 (m, 4 H); 0.94 (d, J = 6.37, 3 H); 0.96–2.2 (m, 5 H)	142 (3), 127 (50), 100 (18), 99 (100), 97 (10), 86 (13), 85 (69), 73 (19), 72 (53), 71 (18), 59 (58), 55 (11), 45 (10), 43 (28), 41 (12)
11a	−0.03 (s, 3 H, eq SiMe); 0.01 (s, 3 H, ax SiMe); 0.25–0.81 (m, 4 H); 0.86 (d, J = 6.17, 3 H); 0.94–2.15 (m, 5 H)	142 (3), 128 (10), 127 (96), 114 (45), 100 (10), 99 (100), 97 (12), 86 (22), 85 (41), 73 (13), 72 (36), 71 (11), 59 (25)
12a	0.05 (s, 3 H, eq SiMe in cis); 0.06 (s, 6 H, SiMe in trans); 0.08 (s, 3 H, ax SiMe in cis); 0.88 (d, J = 7.39, 6 H, CMe); 0.97 (d, J = 7.14, 6 H, CMe); 0.12–0.85 (m, 4 H); 1.00–2.20 (m, 12 H)	cis: 156 (53), 141 (23), 115 (12), 114 (61), 113 (36), 101 (20), 100 (65), 99 (64), 97 (12), 87 (18), 86 (83), 85 (100), 81 (23), 73 (39), 72 (18), 59 (39), 58 (12), trans: 156 (45), 141 (17), 115 (12), 114 (64), 113 (36), 101 (19), 100 (61), 99 (66), 97 (14), 91 (11), 87 (21), 86 (93), 85 (100), 81 (26), 73 (48), 72 (24), 71 (18), 59 (65), 58 (24), 55 (11), 43 (13)
13a	0.03 (s, 3 H, eq SiMe in cis); 0.05 (s, 6 H, SiMe in trans); 0.08 (s, 3 H, ax SiMe in cis); 0.10–0.85 (m, 8 H); 0.89 (d, J = 6.50, 6 H, CMe); 0.93 (d, J = 6.81, 6 H, CMe); 0.98–2.10 (m, 8 H)	cis: 156 (18), 141 (28), 128 (32), 114 (18), 102 (10), 101 (75), 99 (13), 87 (10), 73 (49), 59 (100), *trans*: 156 (20), 141 (19), 128 (20), 114 (16), 102 (10), 99 (14), 73 (61), 59 (100).
14a	0.01 (s, 6 H, SiMe); 0.46–0.64 (m, 4 H); 0.85 (s, 6 H, CMe); 1.30–1.52 (m, 4 H)	156 (13), 141 (28), 129 (10), 128 (65), 114 (17), 113 (50), 100 (75), 99 (33), 87 (14), 86 (17), 85 (47), 73 (60), 72 (61), 71 (15), 59 (100), 58 (43), 55 (27), 53 (11)
8b	0.09 (d, J = 3.74, 3 H); 0.41–1.13 (m, 4 H); 1.17–2.15 (m, 6 H); 3.85 (m, 1 H)	114 (43), 113 (27), 99 (17), 97 (21), 87 (13), 86 (100), 85 (34), 73 (9), 72 (24), 71 (48), 59 (16), 58 (43), 43 (14)
9b	0.08 (d, J = 3.65, 3 H, trans SiMe); 0.15 (d, J = 3.71, 3 H, cis SiMe); 0.94 (d, J = 7.24, 3 H); 1.09 (d, J = 6.96, 3 H); 0.21–1.12 (m, 6 H); 1.17–2.24 (m, 12 H); 3.79 (m, 1 H, trans SiH); 3.98 (m, 1 H, cis SiH)	cis: 128 (65), 127 (6), 113 (33), 101 (10), 100 (100), 99 (27), 97 (11), 86 (23), 85 (65), 73 (36), 72 (74), 71 (23), 59 (19), 58 (21), trans: 128 (44), 127 (2), 113 (31), 101 (12), 100 (100), 99 (21), 97 (10), 86 (21), 85 (58), 73 (28), 72 (83), 71 (23), 59 (15), 58 (14)
10b	0.06 (d, J = 3.57, 3 H, cis SiMe); 0.11 (d, J = 3.59, 3 H, trans SiMe); 0.13–0.92 (m, 8 H); 0.96 (d, J = 6.44, 6 H); 1.02–2.24 (m, 10 H); 3.80 (m, 1 H, cis SiH); 3.99 (m, 1 H, trans SiH)	cis: 128 (13), 127 (6), 114 (13), 113 (100), 100 (10), 86 (24), 85 (72), 72 (12), 71 (12), 59 (15), 58 (18) trans: 128 (18), 127 (3), 114 (10), 113 (100), 100 (16), 86 (31), 85 (63), 72 (12), 71 (12), 59 (13), 58 (22)
11b	0.06 (d, J = 3.49, 3 H, trans SiMe); 0.10 (d, J = 3.51, 3 H, cis SiMe); 0.25–0.80 (m, 8 H); 0.86 (d, J = 6.20 6 H); 0.90–2.15 (m, 10 H); 3.77 (m, 1 H, trans SiH); 3.84 (m, 1 H, cis SiH)	cis: 128 (16), 127 (8), 126 (36), 100 (62), 99 (11), 85 (52), 73 (16), 72 (100), 71 (19), 59 (14), 58 (20) trans: 128 (25), 127 (7), 100 (58), 99 (13), 86 (10), 85 (44), 73 (13), 72 (100), 71 (19), 59 (15), 58 (16)
8c	0.42 (s, 3 H); 0.50–1.16 (m, 4 H); 1.20–2.2 (m, 6 H)	150 (13), 148 (27), 135 (27), 133 (45), 122 (30), 121 (10), 120 (89), 107 (40), 106 (24), 105 (100), 97 (79), 94 (38), 93 (22), 92 (92), 81 (25), 80 (12), 79 (64), 78 (23), 65 (27), 63 (54)
9c	0.39 (s, 3 H, trans SiMe); 0.43 (s, 3 H, cis SiMe); 0.45–0.91 (m, 6 H); 0.95 (d, J = 6.25, 3 H); 1.02 (d, J = 7.02, 3 H); 1.10–2.35 (m, 12 H)	cis: 164 (11), 162 (34), 147 (19), 136 (20), 134 (56), 133 (10), 121 (18), 120 (12), 119 (49), 111 (13), 109 (17), 108 (34), 107 (52), 106 (100), 105 (49), 97 (21), 95 (22), 94 (20), 93 (53), 92 (41), 81 (32), 80 (20), 79 (78), 78 (35), 67 (10), 65 (15), 63 (28). trans: 164 (11), 162 (31), 147 (18), 136 (23), 134 (67), 133 (13), 121 (23), 120 (10), 119 (55), 111 (14), 109 (10), 108 (35), 107 (47), 106 (100), 105 (45), 97 (23), 95 (29), 94 (18), 93 (63), 92 (35), 81 (30), 80 (17), 79 (72), 78 (35), 65 (10), 63 (24)
10c	0.41(s, 3 H, cis SiMe); 0.44 (s, 3 H, trans SiMe); 0.45–2.20 (m, 18 H); 0.98 (d, J = 6.52, 3 H); 1.02 (d, J = 6.38, 3 H)	cis: 164 (3), 162 (7), 149 (34), 148 (10), 147 (100), 122 (10), 121 (40), 120 (31), 119 (72), 111 (27), 107 (10), 105 (26), 95 (10), 94 (26), 93 (23), 92 (66), 81 (15), 79 (45), 78 (13), 65 (17), 63 (38), trans: 164 (4), 162 (14), 149 (35), 148 (10), 147 (100), 122 (22), 121 (57), 120 (56), 119 (96), 111 (28), 107 (14), 105 (35), 95 (13), 94 (35), 93 (34), 92 (98), 81 (20), 80 (10), 79 (58), 78 (16), 65 (23), 63 (50)
11c	0.41 (s, 3 H, trans SiMe); 0.44 (s, 3 H, cis SiMe); 0.20–0.80 (m, 8 H); 0.91 (d, J = 6.22, 6 H); 0.92–2.20 (m, 10 H)	cis: 164 (11), 162 (26), 148 (18), 147 (18), 136 (32), 134 (90), 121 (15), 119 (46), 108 (32), 107 (32), 106 (100), 105 (31), 95 (23), 94 (26), 93 (61), 92 (51), 81 (17), 79 (46), 78 (22), 63 (22), trans: 164 (10), 162 (32), 147 (18), 136 (32), 134 (92), 121 (16), 119 (47), 108 (33), 107 (26), 106 (100), 105 (26), 95 (26), 94 (35), 93 (63), 92 (46), 81 (17), 79 (46), 78 (22), 63 (22)
8d	0.25 (s, 3 H); 0.50–1.10 (m, 4 H); 1.20–2.10 (m, 6 H); 7.23–7.60 (m, 5 H)	190 (11), 175 (65), 147 (44), 134 (10), 122 (11), 121 (71), 119 (16), 113 (12), 112 (100), 107 (15), 105 (54), 97 (53)
9d	0.22 (s, 3 H, trans SiMe); 0.32 (s, 3 H, cis SiMe); 0.40–2.24 (m, 18 H); 0.83 (d, J = 6.58, 6 H); 7.23–7.65 (m, 10 H)	cis: 204 (11), 190 (10), 189 (51), 162 (12), 161 (70), 159 (12), 148 (11), 147 (65), 145 (12), 135 (18), 134 (40), 133 (10), 127 (17), 126 (97), 122 (14), 121 (100), 120 (14), 119 (37), 111 (49), 107 (18), 106 (13), 105 (93), 98 (13), 95 (11), 93 (18), 91 (12), 79 (13), 55 (13), 53 (16), 43 (25), trans: 204 (0.2), 189 (21), 161 (41), 147 (33), 134 (20), 127 (12), 126 (100), 121 (49), 119 (19), 111 (21), 107 (10), 105 (42)
10d	0.18 (s, 3 H, cis SiMe); 0.30 (s, 3 H, trans SiMe); 0.31–0.90 (m, 8 H); 0.97 (d, J = 6.78, 3 H); 1.00 (d, J = 6.61, 3 H); 1.10–2.50 (m, 10 H); 7.23–7.65 (m, 10 H)	cis: 204 (1), 189 (21), 161 (37), 147 (36), 134 (22), 127 (15), 126 (100), 121 (60), 120 (10), 119 (22), 111 (28), 107 (12), 105 (59), 98 (10), 93 (12), trans: 204 (11), 190 (11), 189 (56), 162 (10), 161 (73), 159 (11), 147 (58), 145 (14), 135 (16), 134 (36), 127 (12), 126 (96), 122 (12), 121 (99), 120 (15), 119 (41), 111 (37), 107 (20), 106 (14), 105 (100), 98 (10), 93 (21), 91 (14), 79 (14), 67 (12), 53 (16), 43 (19)

Table III (Continued)

compd	^{1}H NMR[a]	mass spectrum[b]
11d	0.18 (s, 3 H, trans SiMe); 0.29 (s, 3 H, cis SiMe); 0.30–0.80 (m, 8 H); 0.84 (d, J = 6.3, 3 H); 0.91 (d, J = 6.1, 3 H); 0.95–2.20 (m, 10 H); 7.23–7.65 (m, 10 H)	cis: 204 (6), 189 (12), 161 (46), 147 (19), 134 (16), 127 (14), 126 (100), 121 (58), 120 (13), 119 (19), 111 (37), 107 (12), 105 (44), 98 (14), trans: 204 (2), 189 (18), 161 (40), 147 (22), 134 (17), 127 (14), 126 (100), 121 (64), 120 (14), 119 (20), 111 (43), 107 (14), 105 (53), 98 (13), 93 (11), 79 (10), 53 (11), 43 (12)

[a] In $CDCl_3$ with Me_4Si as internal standard. In cases where 2 isomers are present, the integration is reported on a 50/50 mixture. Cis and trans refer to the relationship between SiMe and the ring Me in **8**–**11** and the relationship between the ring Me's in **12** and **13**. [b] Mass spectra are reported as m/z (relative abundance). With a few exceptions referred to in the text, only peaks with a relative abundance ≥10% are reported.

Scheme I



groups on C2. Then the molecular ion is more prominent (≥42%). Fragmentation patterns, as with methylsilanes in general, are dominated by peaks containing Si and which arise by loss of Me radicals (and also H atoms in the cases of SiH derivatives) or olefins. For instance, Scheme I below accounts for all the prominent fragments from **9a**. Assuming that the masses 114 and 100 are the molecular ions of the silacyclobutanes, then the fragments expected[11-13] from those species should be observed and are. The M – 43 peak is generally prominent, and is the base peak in the spectrum of all the $SiMe_2$ series having one C–Me. It is written in Scheme I as arising via loss of CH_3 then C_2H_4, since it is much more prominent than would be expected if it arose via the 1,1,2-trimethylsilacyclobutane molecular ion.[12]

However, the situation is not so simple as Scheme I implies. If the olefins being eliminated were being formed in all cases by cleavage of a single Si–C and C–C bond, then loss of C_3H_6 should not be prominent in **14a** (but it is). Indeed, loss of C_2H_4 is a prominent peak in the spectrum of **13a**, which has no contiguous CH_2 groups. Clearly, either what is being eliminated is not $CH_2{=}CH_2$, or some deep seated rearrangement has taken place prior to fragmentation. Indeed, ring expansion reactions of silacycloalkane molecular ions involving C–Me groups have been proposed by Gusel'nikov and co-workers on the basis of deuterium labeling studies.[12]

Loss of a Me radical from $M^+\cdot$ leads to a prominent peak in all the spectra, but is only occasionally the base peak. There is no obvious pattern of ring Me placement that makes $(M - CH_3)^+$ more abundant. Among the hydrides, only the parent (**8b**) shows $(M - H)^+$ as a significant peak; however, $(M - H - C_2H_4)^+$, M – 29, is prominent in all of the hydrides, but in none of the $SiMe_2$ derivatives. Loss of CH_2 from $M^+\cdot$ is occasionally seen.

The M – 41 peak, seen as a metastable transition by Chernyak[11] in the spectrum of **8b**, and leading to m/e = 73, is not at all prominent generally in the derivatives here. However, m/e = 73, presumably Me_3Si^+, is generally prominent, particularly when there is a C-Me in the ring, again indicating the possibility for substantial rearrangement.

While it is not obvious thus far that ring Me placement can be readily diagnosed from the mass spectral fragmentation patterns (except with respect to the presence or absence of SiH), there are nevertheless obvious differences among the isomers, and indeed some differences between cis/trans isomers.

Experimental Section

Infrared spectra were recorded on either a Perkin-Elmer IR-137 or IR-621 grating spectrometer as neat liquid films or in CCl_4 for the solid *N*-benzoylpiperidines. ^{1}H NMR spectra were recorded on a Bruker WP-200 FT spectrometer with a probe temperature of 297 K. The spectra were recorded in $CDCl_3$ solution, and chemicals shifts are reported relative to tetramethylsilane as the internal standard. Mass spectra were obtained on a Hewlett Packard 5985 GC/MS operating at 70 eV using a 30 m × 0.25 mmi.d. 0.2-μm film OV-1-B.P. fused silica capillary column. The precise mass measurements were obtained in a Kratos MS 80 RFA high-resolution mass spectrometer operating at 70 eV using a Heliflex 13628, RSL-150 capillary column (30 m × 0.25 mm). Spectroscopic data and physical constants are reported in Tables I–III.

Piperidine and its derivatives were distilled from sodium or potassium hydroxide pellets before use. The dichlorosilane derivatives were used as purchased without further purification. The reaction for preparation of the dibromo compounds should be carried out in an efficient hood.

The preparation of **10b** from 3-methylpiperidine is described in detail. The other preparations were essentially identical, with the exceptions noted below. With piperidine and its monomethyl derivatives, the *N*-benzoyl compound is a liquid and separates from the aqueous solution used for its preparation as an oily liquid. The dimethylpiperidines yield a solid *N*-benzoyl compound which is conveniently extracted from the aqueous solution into toluene. The solid *N*-benzoylpiperidines are then dissolved in CCl_4 (ca. 50 g piperidine derivative in 150 mL) before carrying out the PBr_3/Br_2 ring opening. The Grignard ring closure reactions were all carried out by essentially the same procedure, except that

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reaction mixtures containing chlorosilane products were filtered under N_2 and then distilled rather than being subjected to a hydrolysis step. The dibromide **7** was not prepared from the corresponding piperidine, but by the method of Anteunis starting from 3,3-dimethylglutaric acid.[14]

Preparation of *N*-Benzoyl-3-methylpiperidine. Sodium hydroxide pellets (52.5 g, 1.3 mol) and 400 mL of distilled water were placed in a three-necked round-bottomed flask equipped with mechanical stirrer, nitrogen inlet system, and an addition funnel. The solution was maintained at room temperature throughout the subsequent exothermic reaction by using an ice cold water bath. 3-Methylpiperidine (99.2 g, 1.0 mol) was poured into the sodium hydroxide solution and stirring commenced. From an addition funnel benzoyl chloride (140 g, 1.0 mol) was added slowly (ca. 2 h) to the solution. The reaction mixture became yellow in color and at the end of the addition was transferred to a separatory funnel and the top, yellow oily, layer was collected. Water was removed by simple distillation, and the product was collected by reduced pressure distillation, giving a colorless heavy oily liquid (190 g, 94%), bp 203-205 °C/(10 mm).

Preparation of 1,5-Dibromo-2-methylpentane. *N*-Benzoyl-3-methylpiperidine (42.6 g, 0.21 mol) was placed in a three-necked round-bottomed flask equipped with a magnetic stirrer, thermometer, addition funnel, and nitrogen inlet system, and phosphorus tribromide (56.8 g, 0.21 mol) was added from an addition funnel over ca. 2 h. An ice-water bath was used to maintain the reaction temperature between 24 and 34 °C. Liquid bromine (10.4 mL, 0.21 mol) was placed in another addition funnel and added slowly to the reaction mixture over 4 h. The reaction mixture became a very thick dark brown oily liquid. It was heated very gently for 2 h to remove fumes of Br_2 and then distilled at 112-130 °C/5 mm to collect a mixture of oxyphosphorus tribromide, phenyl cyanide, and the dibromide product. A black residue remained in the flask. The distillate was slowly poured into an Erlenmeyer flask which contained 250 g of crushed ice to decompose the oxyphosphorus tribromide. The resulting liquid was extracted with 2 × 200 mL of ligroine and the combined ligroine layers were extracted very carefully with 10 × 15 mL of concentrated sulfuric acid in order to convert phenyl cyanide to benzoic acid. The ligroine layer was neutralized by washing with 2 × 100 mL of dilute sodium hydroxide solution, then washed with 2 × 100 mL of distilled water, and finally dried over anhydrous calcium chloride. The ligroine was removed by simple distillation, and the product, 1,5-dibromo-2-methylpentane, was collected by reduced pressure fractional distillation to give a colorless liquid (31.5 g, 61.5%), bp 113-114 °C (15 mmHg).

Preparation of 1,3-Dimethyl-1-silacyclohexane. Magnesium turnings (2.3 g, 0.1 mol) and 100 mL of anhydrous ether were placed in a three-necked round-bottomed flask equipped with a mechanical stirrer, addition funnel, reflux condenser, and nitrogen inlet system. The Mg was activated with 1.0 mL of 1,2-dibromoethane for 2 h. 1,5-Dibromo-2-methylpentane (10.0 g, 0.04 mol) and 250 mL of anhydrous ether were placed in an addition funnel and added slowly to the activated Mg. After finishing the addition, the reaction mixture was refluxed for 8 h, and then cooled to room temperature. Methyldichlorosilane (4.6 mL, 0.04 mol) in 100 mL of anhydrous ether was added at a very slow rate to the di-Grignard solution, followed by reflux of the reaction mixture for 14 h. After cooling, saturated ammonium chloride was added while cooling externally with ice water. After two layers had clearly formed, an additional 50 mL of distilled water was added. The ether layer was collected, washed with 2 × 100 mL of distilled water, and dried over anhydrous magnesium sulfate. The ether was removed by fractional distillation and the product distilled under reduced pressure through a short path distillation head to give a 50:50 mixture of two isomers (2.8 g, 53%), bp 55-56 °C (71 mmHg) as a colorless liquid.

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Utilization of a 1-Cyclobutenylphosphine Oxide as a 2-Phosphinyl-1,3-butadiene Synthon. Synthesis of Functionalized 1-Phosphinylcyclohexenes

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The Diels-Alder reactions of 2-(diphenylphosphinyl)-1,3-butadiene, generated in situ from (1-cyclobutenyl)diphenylphosphine oxide, with various unsymmetrical dienophiles such as ethyl acrylate, benzalacetone, benzalacetophenone, crotonaldehyde, ethyl methacrylate, and 1,3-butadiene gave functionalized (1-cyclohexenyl)diphenylphosphine oxides in 28-86% yields. The effect of boron trifluoride etherate and aluminum trichloride on the regiochemistry was examined. The 1-cyclobutenylphosphine oxide and a 1-cyclobutenylphosphonium salt have also been demonstrated to be good dienophiles in the Diels-Alder reactions with cyclopentadiene.

Although development of various kinds of functionalized dienes and their synthetic applications to the Diels-Alder reaction have been well-studied,[1] those of dienes having the phosphorus residues have, to our knowledge, been reported to a small degree.[2,3] On the other hand, functionalized 1-cyclohexenylphosphorus compounds are expected to be versatile reagents for introduction of cyclohexane structural units into complex organic molecules, but their syntheses have not been reported until our recent study[3] and the related studies.[4-6] Recently we reported a general synthesis[7] and some synthetic applications[3,8,9] of

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