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NMR Spectra of Organogermanium Compounds. VI.[1] NMR Spectra and Molecular Mechanics Calculations of 3-Methyl- and 3,3-Dimethylgermacyclohexanes

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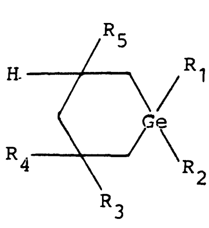
Several 3-methyl- or 3,3-dimethylgermacyclohexanes were prepared and their ^{13}C and ^{73}Ge NMR spectra were determined. Steric energies for all of stereoisomers of some of these germacyclohexanes were calculated by MM2 program. The effect of axial 3-methyl group of germacyclohexanes upon its C-5 is much the same with the corresponding effect in cyclohexanes, and is much smaller than the effect caused by axial methyl on germanium upon C-3,5. A large upfield shift is recorded for germanium nuclei when there is an axial methyl on C-3 of germacyclohexanes.

In the previous communication[2] we have reported the ^{13}C NMR spectra and molecular mechanics calculations of a variety of germacyclohexanes, i.e., germacyclohexane (**1G**) and such methyl-substituted germacyclohexanes as 1-methyl- (**2G**), 3-methyl- (**3G**), 1,1-dimethyl- (**4G**), 1,3-dimethyl- (**5G**) 1,4-dimethyl- (**6G**), and 1,1,3-trimethyl- (**9G**) germacyclohexanes. It revealed that (i) the ring is flattened around the germanium and that (ii) a methyl group on germanium has a slight preference to axial conformation to the equatorial, which is in line with the results for the corresponding silacyclohexanes.[3]

	R_1	R_2	R_3	R_4	R_5
1G	H	H	H	H	H
2G	Me	H	H	H	H
3G	H	H	Me	H	H
4G	Me	Me	H	H	H
5G	Me	H	Me	H	H
6G	Me	H	H	Me	H
7G	H	H	Me	Me	H
8G	H	H	Me	H	Me
9G	Me	Me	Me	H	H
10G	Me	H	Me	Me	H
11G	Me	Me	Me	Me	H



Furthermore, both ^{13}C and ^{73}Ge NMR data indicate that **2G** is a ca. 60:40 mixture of axial and equatorial conformers. Attempts to observe directly the two conformers by freezing the inversion on NMR timescale, however, failed because of the very low barrier for inversion. Instead, we prepared a mixture of *trans*-**6G** and *cis*-**6G** where the methyl group on germanium remains equatorial and axial, respectively. This pair of compounds is interesting as a model to estimate the magnitude of γ-gauche effect by an axial methyl group on germanium in germacyclohexanes. The chemical shift difference (1.30 ppm; the cis isomer gives the signal in a higher field) observed for C-3,5 resonances for the two compounds[4] is much smaller as compared with the corresponding difference for equatorial and axial methylcyclohexane (**2C**; 5.40 ppm).[5]

Qualitatively this is not unexpected in view of the prolonged distance between the axial methyl group on germanium and axial hydrogens on C-3,5. γ-gauche effect is also clear for the ^{13}C resonances of methyl carbon itself. Thus, the methyl groups on germanium of *trans*-**6G** and *cis*-**6G** resonate at −5.77 and −7.83 ppm, respectively.[4]

In the germacyclohexane derivatives with an axial methyl group on C-3 the axial methyl group and the germanium nuclei are in the γ-gauche relation. Hence it is expected that NMR data of such compounds will show us whether the germanium shift is also susceptible to γ-effect, and that, if ever it exists, whether the direction of this effect is upfield (as in the case of ^{13}C shifts) or not.

Study on the γ-effect in the system where a heteroatom is involved in the four-atom unit has been the target of continuing interests.[6,7] No attempt has, however, been done to observe γ-effect associated with germanium nuclei. Germanium should be very suitable for the probe of γ-effect since it does not have the lone-pair electrons which will bring in some new effect to obscure the analysis.

For this purpose we prepared 3,3-dimethyl- (**7G**), 3,5-dimethyl- (**8G**), 1,1,3-trimethyl- (**9G**), 1,3,3-trimethyl- (**10G**), and 1,1,3,3- tetramethyl-(**11G**) germacyclohexanes and determined their NMR spectra. The molecular mechanics calculation of these compounds were also carried out.

Results and Discussion

^{73}Ge Chemical Shifts. ^{73}Ge and ^{13}C NMR spectra of these germacyclohexanes were determined and the results together with the data of relevant compounds, such as **1G**, **2G**, **3G**, **4G**, *cis*-**5G**, *trans*-**5G**, and **9G**, which are necessary for comparison, were included in the Table 1.

In our previous communication,[2] we have shown that ^{73}Ge chemical shift (δ value) of germacyclohexanes without any methyl group on germanium is ca. −130 ppm, that with an axial methyl is ca. −70 ppm, that with an equatorial methyl is ca. −60 ppm and that

Table 1. ^{73}Ge[a] and ^{13}C[b] Chemical Shifts of Germacyclohexanes (**1**—**11**)

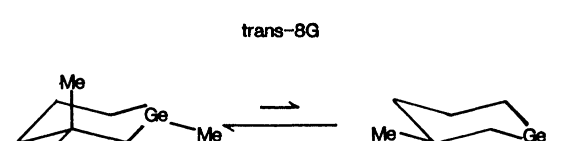
Number of compound	Position of Me	Ge-1	C-2	C-3	C-4	C-5	C-6	Me-1	Me-3
1G	None	−130.3	9.32	26.78	29.89	26.78	9.32		
2G	1	−65.3	12.10	25.58	29.61	25.58	12.10	−7.01	
3G	3	−131.2	17.55	33.18	37.90	25.71	8.10		27.09
4G	1,1	−11.3	15.33	25.90	30.50	25.90	15.33	−3.74	
cis-**5G**	1,3	−60.6	21.75	31.97	38.43	26.12	11.95	−5.28	27.60
trans-**5G**	1,3	−70.9	20.66	31.97	38.26	24.61	11.00	−7.58	27.29
7G	3,3	−142.1	23.17	32.60	42.67	22.04	8.22		32.23
trans-**8G**	3,5	−145.0	15.62	26.95	43.37	26.95	15.62		23.91
9G	1,1,3	−12.2	24.94	32.44	38.54	24.01	13.94	−4.75 −2.45	27.59
10G	1,3,3	−70.6	26.48	32.46	42.42	21.33	11.31		30.07 34.15
11G	1,1,3,3	−18.7	29.80	33.61	43.24	21.26	14.54	−0.80	30.98

a) In ppm relative to external $GeMe_4$ (δ=0). b) In ppm relative to internal $SiMe_4$ (δ=0).

with two methyl groups is ca. −15 ppm.[4]

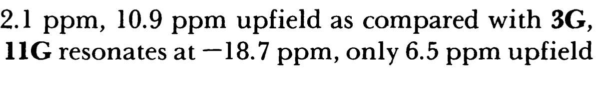
The sample of **8G** is in fact a mixture of trans and cis isomers. The ^{13}C NMR spectrum gave two sets of signals corresponding to two isomers, the ratio of which is ca. 6 : 1. The signal due to C-2 of the major stereoisomer is in the highest field among ring carbon signals, and is in higher field than that of the minor isomer. Thus, the major compenent of **8G** is the trans isomer since the ax,ax conformer of *cis*-**8G** has much higher energy than the eq,eq isomer where there is no axial methyl group.

The ^{73}Ge chemical shift of the major component, i.e., *trans*-**8G**, is −145.0 ppm, about 15 ppm upfield as compared with that of **3G**. This upfield shift is to our knowledge the first example of γ-gauche shift associated with ^{73}Ge resonances.



cis-8G

trans-8G



10G

As compared with a very large upfield shift of ^{73}Ge caused by axial methyl group on C-3 of *trans*-**8G**, the effect caused by geminal 3,3-dimethyl group upon ^{73}Ge is somewhat smaller. Thus, **7G** resonates at −142.1 ppm, 10.9 ppm upfield as compared with **3G**, and **11G** resonates at −18.7 ppm, only 6.5 ppm upfield as compared with **9G**. As described later, this difference is likely due to the difference in the dihedral angle associated with the germanium atom. Thus, the upfield shift is smaller for compounds in which the ring is more flattened around the germanium. At any rate the existence of γ-effect upon ^{73}Ge chemical shifts in germacyclohexanes is now well-established.

It is worthwhile to mention that ^{73}Ge chemical shift of **10G** clearly indicates the predominance of equatorial conformation of methyl group on germanium. Otherwise, the ^{73}Ge nucleus should resonate at ca. −80 ppm. This in turn indicates that 1,3-diaxial dimethyl interaction is operative between *Ge*-methyl and *C*-methyl groups.

^{13}C Chemical Shifts. The ^{13}C chemical shifts of compounds **1G**—**6G** and **9G** were previously reported.[4] The assignments of ^{13}C signals of **7G**, **8G**, **10G**, and **11G** were carried out based on the conventional strategy. Where appropriate, SFORD (single-frequency off-resonance decoupling) and INEPT (insensitive nuclei enhancement by polarisation transfer) spectra were recorded for facilitating the assignments. The assignments based on the multiplicity and chemical shifts consideration are consistent with the additivity relations which have been established for the germacyclohexanes.[2,4]

The effect on the ^{13}C chemical shifts of germacyclohexanes caused by an axial methyl group on C-3 can be estimated by two ways. One way is the chemical shift difference between **7G** and **3G**, or between **11G** and **9G**. This difference can be compared with the case of carbon analog, i.e., the chemical shift difference between 1,1-dimethylcyclohexane (**4C**) and methylcyclohexane (**2C**). The differences estimated from the ^{13}C chemical shifts of these compounds are tabulated in Table 2.

The other way is the chemical shift difference between **8G** and **3G**, which can be compared with the corresponding difference in methylcyclohexanes, i.e., that between *trans*-1,3-dimethylcyclohexane (*trans*-**5C**) and **2C**. The results are also included in Table 2.

Table 2. Effects of an Axial Methyl Group at C-3 upon ^{13}C Chemical Shifts[a)]

A pair of compd. compared	C-2 β	C-3 α	C-4 β	C-5 γ	C-6 δ	Me-3	
7G−**3G**	5.62	−1.05	4.77	−3.67	0.12	5.14	
11G−**9G**	4.86	1.17	4.70	−3.25	0.60	5.50	
4C−**2C**	4.05	−2.95	4.05	−3.95	0.30	6.10	
(*trans*-**8G**)−**3G**[b)]	7.52		1.24	5.47	−6.23	−2.07	−3.18
(*trans*-**5C**)−**2C**[b)]	7.50		−0.50	5.65	−5.80	−1.90	−2.25

a) In ppm. b) In *trans*-**8G** and *trans*-**5C** the carbon with axial methyl group is numbered as C-3 for the sake of comparison.

Table 3. MM2 Component Steric Energies[a)] of Cyclohexanes and Germacyclohexanes (in kcal mol^{-1}; 1 cal=4.181 J)

Compound	Position of Me	Conformation	E_s	E_c	E_b	E_{sb}	E_t	$E_{1,4}$	E_{other}
4C	1,1		9.27	0.77	1.06	0.16	3.04	0.77	−1.55
trans-**5C**	1,3	eq,ax	9.02	0.59	1.08	0.18	3.08	5.85	−1.76
cis-**5C**	1,3	eq,eq	7.21	0.55	0.57	0.13	2.13	5.72	−1.90
		ax,ax	12.55	0.61	7.52	0.26	4.58	6.28	−1.71
4G	1,1		3.53	0.41	1.81	0.15	1.40	2.35	−2.59
trans-**5G**	1,3	eq,ax	6.63	0.60	2.63	0.23	1.85	3.30	−1.97
		ax,eq	5.05	0.58	1.91	0.16	1.38	3.39	−2.36
cis-**5G**	1,3	eq,eq	5.28	0.59	1.89	0.16	1.33	3.41	−2.11
		ax,ax	7.37	0.58	2.94	0.24	2.49	3.24	−2.11
7G	3,3		7.39	1.00	2.71	0.22	1.81	3.85	−2.22
trans-**8G**	3,5	eq,ax	8.01	0.77	2.74	0.25	1.82	4.36	−1.93
cis-**8G**	3,5	eq,eq	6.62	0.76	2.00	0.18	1.30	4.46	−2.07
		ax,ax	11.16	0.78	4.70	0.36	2.73	4.50	−1.91
10G	1,3,3	eq	7.39	1.00	2.71	0.22	1.81	3.85	−2.22
		ax	8.28	1.00	3.04	0.23	2.50	3.78	−2.27
11G	1,1,3,3		7.33	1.05	3.13	0.21	2.52	3.38	−2.97

a) For definition of each component steric energies, see text.

The effects of an axial methyl group at C-3 upon other carbon shifts of germacyclohexanes are, roughly speaking, similar with these for cyclohexanes. There are, however, some difference between the substituent parameters for cyclohexanes and germacyclohexanes. Thus, in geminal dimethyl compounds, germacyclohexanes exhibit a smaller β-effect, but its γ-effect is somewhat larger. α-Effects are scattering, and it is hard to draw any definite conclusion.

In *trans*-3,5-dimethyl series, the methyl substituent parameters are much the same for cyclohexanes and germacyclohexanes.

Molecular Mechanics Calculations. In Table 3, MM2[8)] steric energies of germacyclohexanes **4G**, **5G**, **7G**, **8G**, **10G**, and **11G** are listed together with relevant cyclohexanes **4C** and **5C**. For **5C**, **5G**, and **8G**, all stereoisomers associated with the orientation of methyl group are taken into consideration.

In MM2 calculations, total steric energies (E_s) are the sum of component energies, i.e., compression energy (E_c), bending energy (E_b), strech-bend energy (E_{sb}), tortional energy (E_t), and van der Waals energy which is subdivided into the energy associated with 1,4-interaction ($E_{1,4}$) and that with other interactions (E_{other}).

Two conclusions were drawn from the previous results.[2)] It has been shown that the axial and equatorial methyl group on germanium contributes to the steric energy to much the same extent. Though the change of C-5 chemical shifts caused by an axial methyl group at C-3 of germacyclohexanes is not so much different from the corresponding value of cyclohexanes, the difference in steric energy is large. Thus, the increment of steric energies caused by geminal dimethyl groups as estimated from the difference between **7G** (7.39 kcal mol^{-1}) and **1G** (5.72 kcal mol^{-1}[2)]) (i.e., 1.67 kcal mol^{-1} difference) is much smaller than that between **4C** (9.27 kcal mol^{-1}) and **1C** (6.55 kcal mol^{-1}) (i.e. 2.72 kcal mol^{-1} difference).

Next, we attempted to compare the magnitude of 1,3-diaxial dimethyl interaction under different steric environment from the difference of steric energies among 1,3 (or 3,5)-diequatorial conformer, 1,3 (or 3,5)-equatorial, axial conformer and 1,3 (or 3,5)-diaxial conformer of the identical geometrical isomers.

Thus, for **5C**, the steric energy difference between eq,eq isomer and eq,ax isomer is +1.81 kcal mol^{-1}, while that between eq,ax isomer and ax,ax isomer is +5.32 kcal mol^{-1}. When the ring is a germacyclohexane but two methyl groups are at C-3 and C-5 as is the case with **8G**, the corresponding differences are +1.39 and +3.15 kcal mol^{-1}, respectively. This is in line with the results of the comparison given above.

When one of the methyl groups is at germanium, as is the case with **5G**,[4] the difference between 1-eq,3-eq and 1-ax,3-eq isomers is −0.23 kcal mol^{-1}, in line with the preference of axial conformation for this type of methyl group. The difference between 1-eq,3-eq and 1-eq,3-ax conformers is +1.35 kcal mol^{-1}, which is essentially identical with the value for **5C** and **8G**. The difference between 1-eq,3-eq and 1-ax,3-ax isomers of **5G** is only +2.09 kcal mol^{-1} in a sharp contrast with two previous cases, where the differences are +5.34 (*cis*-**5C**) and +4.54 kcal mol^{-1} (*cis*-**8G**), respectively. Thus, the 1,3-diaxial dimethyl interaction is smaller in germacyclohexane as compared with that in cyclohexane, and this is particularly so when one of the methyl is at germanium.

It is interesting to examine how the molecular mechanics calculations predict the structural change upon introduction of methyl groups on germanium and C-3. In Table 4, the predicted structures by MM2 for all the compounds discussed are summerized. Of all possible stereoisomers, high energy conformers are not taken into consideration.

It is clear from a glance of Table 4 that all the parameters, the bond lengths (r), the bond angles (θ), and the dihedral angles (ω) are not largely changed by the number and position of methyl groups introduced. It is slightly different from the case of methylcyclohexanes where a small change in bond length is invoked upon introduction of methyl groups.[2] A more relaxed structure of germacyclohexane as compared with cyclohexane is responsible for this phenomenon.

In one particular case where there exists a 1,3-diaxial dimethyl interaction with the buttress effect as is with **11G**, the change in dihedral angle caused by methyl groups is substantial. Thus, for germacyclohexanes without any 1,3-diaxial dimethyl interaction, the dihedral angle $\omega_{1,2}$ is in the range of 47°—49°. When there is a 1,3-diaxial dimethyl interaction present, the angle changes to 43°—44°, a substantial change. The ring is now further flattened around the germanium atom. This is also reflected in the dihedral angle $\omega_{2,3}$ which is nearly 50° for **11G**. A similar change is invoked when there is geminal 3,3-dimethyl group is present. The angle $\omega_{2,3}$ reduced to 54°.

That this change is associated with 1,3-diaxial di-

Table 4. Structures[a)] of Methylgermacyclohexanes Optimized by Molecular Mechanics Calculations

Compound	$r_{1,2}$ / nm	$r_{2,3}$ / nm	$r_{3,4}$ / nm	$r_{4,5}$ / nm	$r_{5,6}$ / nm	$r_{6,1}$ / nm	θ_1 / °	θ_2 / °	θ_3 / °
1G	0.1947	0.1530	0.1543	0.1543	0.1538	0.1947	101.6	109.9	113.5
3Geq	0.1947	0.1542	0.1546	0.1543	0.1537	0.1946	101.6	110.4	112.6
5Geq,eq	0.1947	0.1542	0.1547	0.1543	0.1537	0.1945	101.8	110.2	112.7
5Geq,ax	0.1947	0.1542	0.1547	0.1543	0.1537	0.1946	101.8	111.2	112.8
5Gax,eq	0.1947	0.1542	0.1547	0.1543	0.1537	0.1946	101.7	110.5	112.6
7G	0.1948	0.1548	0.1553	0.1543	0.1544	0.1945	101.7	112.3	111.8
8Geq,eq	0.1946	0.1541	0.1547	0.1547	0.1541	0.1946	101.6	110.2	112.7
8Geq,ax	0.1946	0.1541	0.1547	0.1547	0.1541	0.1946	101.6	110.4	112.3
9Geq	0.1946	0.1542	0.1547	0.1544	0.1538	0.1945	101.9	110.3	112.6
9Gax	0.1949	0.1542	0.1547	0.1544	0.1538	0.1945	102.3	112.7	113.2
10Geq	0.1947	0.1548	0.1553	0.1543	0.1537	0.1944	101.9	112.2	111.8
10Gax	0.1950	0.1548	0.1552	0.1537	0.1537	0.1945	102.3	113.9	112.1
11G	0.1949	0.1548	0.1533	0.1545	0.1537	0.1944	102.4	113.8	112.1

Compound	θ_4 / °	θ_5 / °	θ_6 / °	$\omega_{1,2}$ / °	$\omega_{2,3}$ / °	$\omega_{3,4}$ / °	$\omega_{4,5}$ / °	$\omega_{5,6}$ / °	$\omega_{6,1}$ / °
1G	114.6	113.5	109.9	47.8	58.2	66.4	66.4	58.2	47.8
3Geq	115.1	113.5	109.6	48.0	57.7	66.0	66.9	58.3	47.7
5Geq,eq	115.1	113.5	109.6	48.0	57.7	66.1	66.8	58.2	47.8
5Geq,ax	116.5	113.5	109.8	47.3	55.5	63.7	65.6	57.7	47.7
5Gax,eq	115.1	113.5	109.7	47.8	57.6	66.0	66.8	58.1	47.5
7G	117.3	113.6	109.7	47.2	54.3	62.6	65.3	57.9	47.7
8Geq,eq	115.6	112.7	110.2	48.1	57.8	66.3	66.3	57.8	48.1
8Geq,ax	117.0	112.9	111.1	48.0	57.4	65.2	64.0	55.6	47.2
9Geq	115.0	113.4	109.6	47.6	57.6	66.4	67.3	58.3	47.5
9Gax	116.3	113.2	109.9	43.4	52.0	62.9	67.6	58.7	45.9
10Geq	117.4	113.6	109.6	47.1	54.2	62.7	66.0	57.8	47.5
10Gax	117.4	113.4	109.7	43.1	50.5	61.5	67.7	58.5	45.6
11G	117.2	113.2	109.7	43.2	50.7	61.8	67.9	58.6	45.7

a) The definition of the structural parameters is as follows: $r_{1,2}$ is the distance between Ge-1 and C-2 in nm, θ_1 is the bond angle C-6–Ge-1–C-2 in degrees and $\omega_{1,2}$ is the tortion angle in degrees defined by the C-6–Ge-1–C-2–C-3 moiety. The other parameters are defined analogously.

methyl group is evident since a similar change is invoked in $\omega_{5,6}$ and $\omega_{6,1}$ where there is a 1,5-diaxial dimethyl interaction.

Thus, an introduction of several methyl groups in germacyclohexane is calculated to cause no significant change in the bond length and bond angle of the ring. A substantial change in the dihedral angle is predicted instead. We are continuing efforts to demonstrate experimentally these characteristics of germacyclohexanes.

Experimental

Preparation of Germacyclohexanes. The necessary precursor for 3,3-dimethylgermacyclohexanes, 1,5-dibromo-2,2-dimethylpentane does not seem to have previously been described. This arises from the fact that the treatment of 2,2-dimethyl-1,5-pentanediol with the standard brominating reagents such as hydrogen bromide or phosphorus tribromide causes a migration of *β*-methyl group (a Wagner-Meerwein rearrangement) to result in the formation of unexpected compound. Hence we treated the diol with dibromotriphenylphosphorane[9] to end up with the desired dibromopentane.

The dibromopentane was converted to the bis-Grignard reagent, which was caused to react with tetrachlorogermane to give 1,1-dichlorogermacyclohexanes. Treatment of dichlorogermacyclohexanes with lithium aluminum hydride(LAH) afforded 1,1-dihydrogermacyclohexanes (**7G** and **8G**). 1,1-Dichlorogermacyclohexanes were treated with methylmagnesium bromide to give the 1,1-dimethylgermacyclohexanes (**9G** and **11G**). Treatment of bis-Grignard reagent with dichloromethylgermane gave **10G**. The details of these procedures were described in our previous communication.[2] 1,5-dibromo-2,2-dimethylpentane. 2,2-Dimethylglutaric acid was esterified with ethanol under an acidic condition, and the ester was reduced to 2,2-dimethyl-1,3-pentanediol by means of LAH in a conventional manner.

The diol (10.0 g; 0.075 mol) and triphenylphosphine (43.8 g; 0.167 mol) were dissolved in dry *N*,*N*-dimethylformamide (DMF; 80 ml), to which bromine (27.5 g; 0.169 mol) was added dropwise under the atmosphere of argon and ice-cooling. During the addition the temperature was kept at 10—20 °C. Stirring was further continued for another 20 h at 25 °C. The forerun of the distillation under the reduced pressure (fraction of bp 63—66 °C/30 mmHg (1 mmHg≈133.322 Pa)) was discarded and the second fraction (bp 60—68 °C/4 mmHg) was collected, and this was poured into the ice-water. The heavy oil was extracted with dichloromethane, which was washed with water, dried over anhydrous calcium carbonate, and the solvent evaporated. The residue was reduced in vacuo to afford yellow oil of 2,2-dimethyl-1,5-dibromopentane (10.32 g; 53% overall), bp 125—127 °C/29 mmHg. ^{1}H NMR (90.0 MHz; $CDCl_3$) δ=1.03 (6H, s), 3.26 (2H, s), 3.38 (2H, t. J=7 Hz).

Found: C, 32.48; H, 5.50%. Calcd for $C_7H_{14}Br_2$: C, 32.59, H, 5.47%.

3,5-Dimethylpiperidine (Tokyo Kasei Co.) and benzoyl chloride were caused to react in aqueous NaOH to give 1-benzoyl-3,5-dimethylpiperidine (91%), mp 95 °C. IR (KBr) 1615 (C=O).

Found: C, 77.44; H, 8.79; N, 6.40%. Calcd for $C_{14}H_{19}NO$: C, 77.37; H, 8.81; N, 6.44%.

The benzoyl derivative was treated with PBr_3/Br_2 to afford 1,5-dibromo-2,4-dimethylpentane, bp 105—107 °C/1.5 mmHg.

Preparation of germacyclohexanes has been carried out based on the procedure described in the previous report.[2] Thus, the reaction between the bis-Grignard reagent of 1,5-dibromo-2,2-dimethylpentane and tetrachlorogermane afforded 1,1-dichloro-3,3-dimethylgermacyclohexane which, without isolation, was converted to **7G** by means of LAH, or to **11G** by the reaction with methylmagnesium bromide. Treatment of the same dibromide with dichloromethylgermane afforded **10G**.

The reaction between the bis-Grignard reagent of 1,5-dibromo-2,4-dimethylpentane and tetrachlorogermane afforded 1,1-dichloro-3,5-dimethylgermacyclohexane which, without isolation, was converted to **8G** by means of LAH. The physical properties of these germacyclohexanes are summerized in Table 5.

Measurements of Spectra. Infrared spectra were obtained with a JASCO A102 grating infrared spectrophotometer as a liquid film.

The ^{1}H NMR spectra were recorded with a Varian EM-390 spectrometer as $CDCl_3$ solution containing a small amount of tetramethylsilane (TMS) as the internal standard.

The ^{13}C NMR spectra of germacyclohexanes were recorded as solutions of $CDCl_3$ or C_6D_6 on a JEOL FX-90Q spec-

Table 5. Physical Properties of Germacyclohexanes (**7G**—**11G**)

Compound (formula)	Yield[a)] %	Bp θ_m °C/mmHg	IR(Ge-H) ν_H(neat)	^{1}H NMR δ_H(90MHz; $CDCl_3$)	MS m/z[b)]
7G ($C_7H_{14}Ge$)	14	88—90/22	2040	1.00 (6H, s, 3,3-diMe) 3.60 (2H, m, 1-H)	
8G ($C_7H_{14}Ge$)	8	97—100/17	2045	1.00 (6H, d, J=7 Hz, 3,5-Me) 3.63 (2H, m, 1-H)	
9G ($C_8H_{16}Ge$)	7	85—87/26	—	0.13 (6H, s, 1,1-diMe) 0.93 (3H. d, J=7 Hz, 3-Me)	
10G ($C_6H_{16}Ge$)	6	90—93/13	2050	0.21 (3H, d, J=3 Hz, 1-Me) 0.98 (6H, s, 3,3-diMe) 3.88 (1H, m, 1-H)	160.1 (M^+), 145.2 (M^+-15) 132.2 (M^+-28)
11G ($C_9H_{18}Ge$)	12	98—100/18	—	0.15 (6H, s, 1,1-diMe) 0.95 (6H, s, 3,3-diMe)	160.1 (M^+), 132.2 (M^+-28)

a) Yield based on the immediate precursor. b) Of the peaks due to various isotomers, only the one due to ^{74}Ge is given.

trometer at 22.50 MHz in 10 mm tube at 30°C. The condition of measurements are the standard ones.

The ^{73}Ge NMR spectra of germacyclohexanes were recorded as solutions in $CDCl_3$ (1 : 1 v/v) on a JEOL FX-90Q spectrometer equipped with an NM-IT 10LF low-frequency insert, operating at 3.10 MHz, in a 10 mm tube at 30 °C. Typical measurement conditions were as follows: pulse width, 150 μs (90°); spectral width, 2000 Hz: number of scans, 5000; pulse delay, 100 ms; data points, 4096. The ^{13}C NMR spectra were determined for the same solutions on the same instrument at 22.50 MHz. Typical measurement conditions were as follows: pulse width. 13 μs (40°): spectral width, 2000 Hz: number of scans, 500; pulse delay, 1 s; data points, 4096.

GC/MS spectra were obtained on a Hewlett-Packard 5995A instrument controlled by a Hewlett-Packard 9825 desktop computer system with a 25 m (ϕ 0.2 mm) cross-linked methyl silicone column.

Molecular Mechanics Calculations. The program used was Allinger's MM2. Since in MM2 the parameters for germanium are not available, we installed the parameters reported by Ouellette[10)] in MM2. Since the parameters were prepared for the older force field of Allinger[11)] (before MM1) based on the experimental values of methylgermane and dimethylgermane, there is some doubt as for the consistency between parameters for germanium and for other atoms. This point has been discussed in the previous communication[2)] where it has been shown that the use of the combination of MM2 and germanium parameters of Ouellette[10)] is acceptable, and this combination is used throughout this investigation.

For the sake of comparison, calculations were also carried out for the corresponding cyclohexanes, and the results were also included in Table 2.

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