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NMR SPECTRA OF ORGANOGERMANIUM COMPOUNDS. 7.[1]
NMR SPECTRA AND MNDO CALCULATIONS OF PHENYLGERMACYCLOHEXANES.

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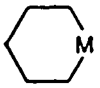
Abstract - ^{13}C nmr spectra of a variety of 1-phenylgermacyclohexanes indicates that the conformational energy of a phenyl group on germanium is essentially zero (0 - 0.1 kcal/mol), in a sharp contrast with that in phenylcyclohexanes. The results are consistent with the heats of formation of phenylgermacyclohexanes calculated by the MNDO method.

In the previous communication[2] we estimated the conformational energy of a methyl group in 1-methylgermacyclohexane(2G) by means of a combination of ^{13}C and ^{73}Ge nmr spectroscopy. Thus, a careful comparison of ^{13}C chemical shifts of trans- and cis-1,3-dimethylgermacyclohexane(3G)[2] and 1,4-dimethylgermacyclohexane(4G)[3] indicated that the methyl group on carbon remains equatorial while the methyl group on germanium could be equatorial(for cis-3G and trans-4G) or axial(for trans-3G or cis-4G). The chemical shifts of C-4 and Me-4 of trans-4G and cis-4G are essentially identical to indicate the germacyclohexane ring is fixed by Me-4. The chemical shift of Me-1 of trans-4G is 32.7 ppm and that of cis-4G is 30.2 ppm. The former may be assumed essentially identical with the chemical shift of Me-1 in 2G in the equatorial conformation(2GQ), while the latter with that in the axial conformation(2GX). If the effect of Me-4 upon chemical shifts of Me-1 is corrected for, the observed chemical shift of Me-1(33.1 ppm) of 2G is the weight-average of the chemical shifts of Me-1 of axial-4G(4GX) and equatorial-4G(4GQ). Based on this simple additivity relation, the conformational energy of a methyl in germacyclohexanes is estimated to be 0 - -0.2 kcal/mol.[2]

This conclusion was further supported by the molecular mechanics calculations of steric energies of 2GQ and 2GX where MM2 force field[4] and parameters of germanium proposed by Ouellette[5] was employed. The steric energy difference was estimated to be 0.22 kcal/mol in preference to the axial isomer.[2] This interesting phenomenon was in fact predicted by Ouellette[6] for 1-methylsilacyclohexane(2S). He did not, however, attempt any experimental verification of his prediction. Hence, to the best of our knowledge, this is the first experimental demonstration of this very unusual effect, i.e., the preference of axial conformation.

As a natural and essential extension of this investigation, we attempted to estimate the steric energy of a phenyl group in 1-phenylgermcyclohexane (5G) since it is well established that in phenylcyclohexane(5C) the phenyl group is considerably larger than a methyl group. Thus, Allinger et al.[7] estimated the conformational energy is 2.0 kcal/mol based on the dipole moment measurement of 4-(p-chlorophenyl)cyclohexanone. Garbish and Patterson[8] estimated the energy to be 3.61 kcal/mol based on the ^{1}H nmr spectra of cis-4-t-butyl-1-phenylcyclohexane. Allinger and Tribble[9] estimated that the conformational energy of a phenyl group in 5C is 3.66 kcal/mol. Eliel and Manoharan[10] showed from the low temperature ^{13}C nmr spectra of cis-4-methyl-1-phenylcyclohexane(8C) that the conformational energy of a phenyl group is 2.87 kcal/mol. All these values are in sharp contrast with that of a methyl group in cyclohexane (1.78 kcal/mol).[11] It is of interest to estimate the conformational energy of a phenyl group on germanium in germacyclohexanes.

Another interesting aspect arises in the conformation of 5C. Allinger and Tribble[9] pointed out that rotational isomerism about the Ge--C(ipso) bond is involved in 5C. Thus, of the equatorial isomer of 5C, the parallel isomer(5CQ)



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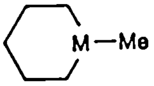

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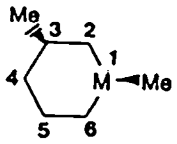

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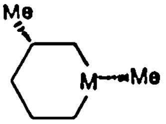

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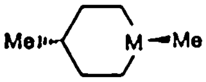

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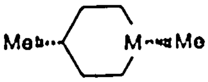

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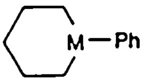

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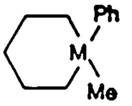

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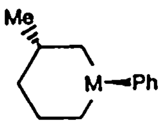

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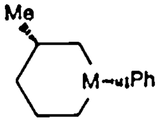

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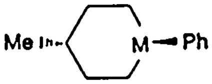
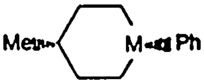


trans-8



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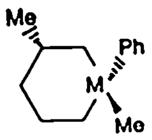
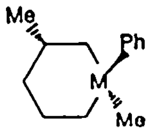


trans-9



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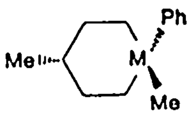
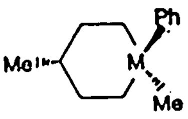
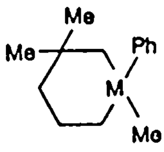


trans-10



cis-10



11

C : M=C

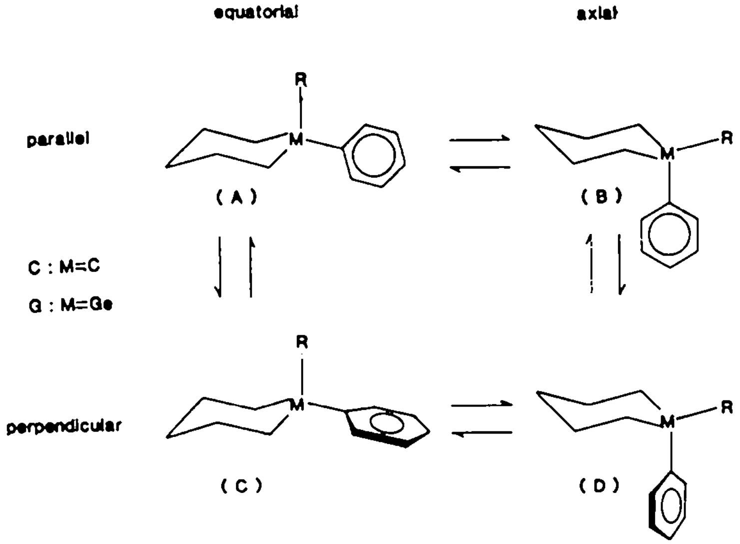
S : M=Si

G : M=Ge

in which the C-1--H-1 bond is parallel to the aromatic ring is substantially more stable (by 3.92 kcal/mol) than the perpendicular conformer(5CQ') where the C-1--H-1 bond is perpendicular to the aromatic ring. Interestingly enough, for the axial isomer of 5C, the perpendicular isomer(5CX') is more stable than the parallel conformer(5CX) by 1.56 kcal/mol. This is due to the strong interaction between ortho hydrogens of the axial phenyl group and the syn-axial hydrogens of cyclohexane in the perpendicular conformer(Fig. 1).

This rotational preference does not, however, hold for 1-methyl-1-phenylcyclohexane(6C) in the sense that the conformational energy of a phenyl group is not additive. Thus, Shapiro et al.[12] reported that in 3-phenyl-3,5,5-trimethylcyclohexanone the phenyl group remains axial and Anteunis et al.[13] reported much the same phenomenon for 4-methyl-4-phenyl-1,1-dimethoxycyclohexane. Eliel and Manoharan[10] showed by ^{13}C nmr spectra that in 6C the conformer with equatorial methyl-axial phenyl group (6CQX) predominates over the conformer with axial methyl-equatorial phenyl group (6CXQ) (The ratio is ca 3:1) which is contrary to the simple prediction based on the conformational energy of individual groups.

Allinger and Tribble[9] argued that this comes about because the most stable conformation of the axial phenyl group is not perturbed by the introduction of a geminal methyl substituent, whereas considerable perturbation occurs upon introduction of geminal methyl into equatorial phenylcyclohexane whose phenyl group is most stable in the perpendicular conformation(Fig 1).



	A	B	C	D
5 (R = H)	Q	X	Q'	X'
6 (R = Me)	XQ	QX	XQ'	QX'

Fig. 1 Conformation of phenylcyclohexanes and phenylgermacyclohexanes

It is expected that the longer Ge--C bond length will affect the conformational preference of the phenyl group, and the difference in the rotational preference.

The most straightforward procedure to assess the conformational energy of phenyl group in 5G or to decide the conformational preference between a phenyl and a methyl group in 6G is to freeze the ring reversal of these compounds on the nmr timescale, and determine the ratio of equatorial/axial conformers. This is, however, impossible because of the apparently very low barrier for ring reversal of germacyclohexane(1G) which cannot be frozen within the temperature which the cooling device attached to any nmr spectrometer can realize.[2] An alternative, and an equally potential method is introduction of an alkyl at C-3 or C-4 to freeze the ring reversal effectively. This method was successfully applied to the conformational analysis of 2G[2] and employed by many previous investigators.[14] It must be remembered that this will hold only when the conformational energy of the alkyl group is larger than that of a phenyl group on germanium. A t-butyl group will certainly satisfy this requirement. In view of much reduced conformational energy of a methyl group on germanium, however, a methyl group which is much easy to introduce may be sufficient. With this in mind, we prepared 5G and 6G. Furthermore, we prepared 1-phenyl-3-methylgermacyclohexane(7G), 1-phenyl-4-methylgermacyclohexane(8G) 1,3-dimethyl-1-phenylgermacyclo-hexane(9G) and 1,4-dimethyl-1-germacyclohexane(10G) all as a mixture of trans- and cis- geometrical isomers. 1-Phenyl-1,3,3-trimethylgermacyclohexane11G) was also prepared to compare with the results obtained by Shapiro et al.[12] and Anteunis.[13] Details of the preparation and their physical properties are given in the Experimental section.

DISCUSSION

1-PHENYLGERMACYCLOHEXANES

^{13}C NMR SPECTRA---The ^{13}C nmr spectra of phenylgermacyclohexanes 5G-11G were determined. The chemical shifts are in Table 1.

It is clear from the data in Table 1 that Me-3 and Me-4 of both trans- and cis- isomers of 7G and 8G are equatorial because the chemical shifts of Me-3 and Me-4 are essentially identical. For trans- and cis-8G, C-4 chemical shifts are also identical. The situation was identical with 4G.[2,3] For 7G, the C-3

Table 1. ^{73}Ge^{a} and ^{13}C^{b} chemical shifts of germacyclohexanes.^{c}

Compound	Ge-1	C-2	C-3	C-4	C-5	C-6	Me (position)	C-ipso	C-o
1G	-131.2	9.32	26.78	29.80	26.78	9.32			
2G	-65.3	12.10	25.58	29.61	25.58	12.10	-7.01(1)		
trans-3G	-70.9	20.66	31.97	38.26	24.61	11.00	-7.58(1) 27.29(3)		
cis-3G	-60.3	21.75	31.97	38.43	26.12	11.95	-5.28(1) 27.60(3)		
trans-4G	-61.5	11.76	34.81	35.27	34.81	11.76	-5.77(1) 23.70(4)		
cis-4G	-73.4	10.84	33.51	35.19	33.51	10.84	-7.83(1) 23.70(4)		
5G	-69.4	11.96	26.13	30.12	26.13	11.96		138.00	134.27
6G	-25.6	14.26	26.00	30.42	26.00	14.26	-4.68(1)	140.90	133.58
trans-7G		20.80	31.90	37.92	24.66	10.36	27.17(3)	141.59	134.57
cis-7G		19.81	33.37	38.27	25.87	11.34	27.61(3)	d	134.35
trans-8G	-74.9^{e}	11.09	34.63	35.23	34.63	11.09	23.49(4)	d	134.40
cis-8G	-74.9^{e}	10.19	33.63	35.02	33.63	10.19	23.32(4)	141.46	134.27
trans-9G		22.79	32.46	38.40	25.18	12.91	-6.15(1) 27.65(3)	d	133.45
cis-9G		22.88	32.59	38.57	25.18	13.00	-2.51(1) 27.78(3)	141,20	133.45
trans-10G		13.08	34.06	35.54	34.06	13.08	-3.20(1) 23.57(4)	140.89	133.40
cis-10G		12.82	34.06	35.36	34.06	12.82	-6.32(1) 23.31(4)	141.20	133.40
11G		20.76	32.34	42.56	27.96	12.44	-2.17(1) 31.55, 33.33(3)	141.97	133.35

a In ppm relative to external Ge(CH_3)$_4$. b In ppm relative to internal TMS.
c The assignments m-C and p-C signals (ca. 127-128 ppm) were not attempted.
d The chemical shifts are possibly identical with that of geometric isomers.
e The signal was not resolved into two peaks.

chemical shift of the trans isomer is somewhat at higher field than the corresponding carbon nucleus of the cis isomer. This is certainly due to the axial phenyl group of the former. The γ effect of phenyl is close to 1.5 ppm. This modest value seems reasonable in view of the large (3 to 5 ppm) upfield shift for the axial phenyl group in cyclohexane.[10]

This in turn suggests that the conformational energy of a phenyl group in 6G is substantially smaller than that of a methyl group in 2C. As a result, the phenyl group remains axial in trans-7G or cis-8G. If this assumption is correct, the chemical shifts of a carbon nucleus in 5G should be the weight-average of relevant carbon nuclei in trans- and cis-8G if the substituent effect of 4-Me is corrected for. This correction can be estimated from the chemical shifts of 4-methylgermacyclohexane.[3]

The calculation indicates that 5G exists as ca. 1:1 (from the chemical shifts of C-2,6) or ca. 2:3 mixture (from the chemical shifts of C-3,5) of axial and equatorial conformers. It corresponds to a nearly zero conformational energy (0 - 0.1 kcal/mol) of a phenyl group in germacyclohexane. This is surprising in view of the much larger conformational energy of a phenyl group over that of a methyl group in cyclohexanes.

^{73}Ge NMR SPECTRA---We also attempted to measure the ^{73}Ge nmr spectra of 5G--11G. An excessive broadening was obsered, however, in some of these compounds to prevent the observation of signals. Since tetraphenylgermane does give a detectable signal,[15] it seems that the distortion of the electric field gradient induced by a phenyl group is substantial. In Table 1 the ^{73}Ge chemical shifts in ppm relative to the external tetramethylgermane are also included as far as available.

In the conformational analysis of 1-methylgermacyclohexanes,[2,3] ^{73}Ge chemical shifts of 1G, 2G and 4G supported the conclusion drawn from ^{13}C nmr spectra and molecular mechanics calculations. Only one rather broad signal was observed for 8G (the half-width ca. 90 Hz or 30 ppm) to indicate that the chemical shift difference of the trans- and cis- isomers could not be resolved. For other germacyclohexanes 7G, 9G-11G, broadening was found too excessive to observe the signals.

MNDO CALCULATIONS---In the conformational analysis of 2G, the agreement between the conclusion drawn from nmr data and the MM2 calculation is a good complementary justification. In the case of 5G, however, this is impossible because of the lack of parameters to be used in MM2 or any other force field calculations for compounds with germanium bonded to sp^2 hybridized carbon atom.

An obvious alternative approach will be ab initio calculations to estimate the energies of the organogermanium compounds. Ab initio calculations for such compounds as 5G or 6G would be prohibitive in computation time even if the simplest basis set will be used.

Recently Dewar et al.[16] published the parameters for germanium applicable to MNDO[17] calculations. It occurred to us that the heat of formation calculated by means of MNDO might give some insight into the relative stability of stereoisomers involved. As far as the heats of formation are concerned, the parameters are reported to give fairly reasonable results in comparison with the experimental values. The comparison was, however, limited to simple compounds such as tetramethylgermane or tetrachlorogermane. We attempted to extend the comparison to more relevant compounds.

Table 2. Steric energies and the heats of formation of cyclohexanes and germacyclohexanes(kcal/mol).

Compound	Steric energy	Heat of formation	Compound	Steric energy	Heat of formation
2CQ	6.89[a]	-36.19	2GQ	4.83[a]	-31.33
2CX	8.69[a]	-35.16	2GX	4.61[a]	-31.29
5CQ	0.00[b]		5GQ		-2.85
5CQ'	3.92[b]		5GQ'		-2.40
5CX	5.22[b]		5GX		-2.79
5CX'	3.66[b]		5GX'		-1.88
6CXQ	2.06[c]		6GXQ		-13.29
6CXQ'	0.90[c]		6GXQ'		-13.70
6CQX	6.43[c]		6GQX		-12.70
6CQX'	0.00[c]		6GQX'		-13.24

a Data taken from ref. 2.
b Relative to the most stable of the four. Data taken from ref. 9.
c Relative to the most stable of the four. Data taken from ref. 9.

The heats of formation by MNDO together with some steric energy by molecular mechanics calculations for some cyclohexanes and germacyclohexanes are in Table 2. The MNDO heats of formation of equatorial-2C(2CQ) and axial-2C(2CX) are -36.19 and -35.16 kcal/mol, respectively. The difference, 2CX - 2CQ, is 1.03 kcal/mol, which is smaller than the established conformational energy of a methyl group in cyclohexane. This discrepancy certainly arises from the characteristic tendency of MNDO to underestimate the dihedral angle of butane moiety in cyclohexane. Thus, the dihedral angle of 1C as estimated by MNDO is 46.3° in sharp contrast to the experimental value of 54.9°.[10] This overestimation of the ring flattening will necessarily underestimate the repulsion between the axial methyl and H-3,5 of 2CX to make the difference of heat of formation of two conformers smaller than it should be.

The heats of formation of 2GQ(equatorial methyl) and 2GX(axial methyl) are -31.33 and -31.29 kcal/mol, respectively. Thus the difference is negligibly small, in good agreement with the results obtained by nmr measurements and force field calculations. In this case, the ring is in fact flattened, and hence the much smaller dihedral angle calculated by MNDO for 1G(29.2° in contrast to 42.8° estimated by MM2) will not influence the energy to any serious extent. Thus, we concluded that the difference in MNDO heat of formation between two conformers can be a good measure of the conformational energy.

The calculated heats of formation for 2CQ, 2CX, 2GQ, 2GX, and equatorial- and axial- 5G are listed in Table 2. For the equatorial isomer of 5G, the parallel conformer 5GQ is slightly more favorable than the perpendicular one(5GQ') while for the axial isomer the perpendicular conformer(5GX') is considerably unstable, which is the reverse of the case with 5CX'. This is due to the effect of the longer Ge--C bond which reduces the steric interaction between H-2 and H-ortho. The heats of formation of the two stabler conformers, 5GQ and 5GX, are effectively identical (the difference is 0.06 kcal/mol) which is in line with the result obtained from the nmr data.

1-METHYL-1-PHENYLGERMACYCLOHEXANES

^{13}C NMR SPECRA---In 6C the phenyl group is axial (and perpendicular) regardless of its much larger conformational energy in 5C because of the reduced steric interaction between the parallel phenyl and the geminal methyl groups of 6C.

It was of interest to see if much the same is true for the phenyl group in 6G. For this purpose, ^{13}C nmr chemical shifts of 9G and 10G as well as 6G were determined. The data are included in Table 1. Their comparison is very revealing. Thus, for 9G, the chemical shifts of C-3 and Me-3, and for 10G, the chemical shifts of C-4 and Me-4, are essentially identical for trans- and cis-isomers to indicate that Me-3 and Me-4 remains equatorial. The chemical shifts of Me-1 reflect its stereochemistry and hence are more revealing. In trans-9G and cis-10G where the methyl group on germanium is axial, the chemical shifts are at a higher field than those of cis-9G and trans-10G where the equatorial methyl resonates at a lower field. The difference amounts to 3.5-3.0 ppm, which allow us to estimate the population of conformers of 6G, i.e., the axial methyl-equatorial phenyl isomer(6GXQ) and equatorial methyl-axial phenyl isomer(6GQX). From the Me-1 chemical shifts of 6G and 9G it is estimated that the ratio 6GQX:6GXQ is ca. 2:3 while from those of 6G and 10G the ratio is ca. 1:1. Both indicate that steric requirements of a phenyl and a methyl group in 6G are essentially identical.

The ^{13}C chemical shifts of other carbon nuclei are not very much sensitive to the steric environment, and it is impossible to estimate the conformational population of 6G from these data. Yet, the characteristic chemical shifts of Me-1 is sufficient to prove the nearly identical steric requirement of a methyl and a phenyl group on germanium.

The ^{13}C chemical shifts of 11G are of interest in that this is the germanium analogue of the 11C system to which the non-additivity of conformational energy of geminally substituted species was detected for the first time. The two distinct signals for Me-3 indicate that 11G is conformationally fixed. The chemical shift of Me-1(-2.17 ppm) is in the region of equatorial methyl. Hence in this case, the phenyl is axial. This is not unexpected since the syn-axial interaction between a methyl and a phenyl group is smaller than that between two methyl groups.

MNDO CALCULATIONS---The MNDO heats of formation (Table 2) seem to support the above conclusion. The stable conformation is 6GXQ'(axial methyl and perpendicular phenyl) and 6GQX' (equatorial methyl and perpendicular phenyl). The difference is less than 0.5 kcal/mol, again to indicate a very similar conformational requirement for the two groups.

It must be added that the difference in energy between the conformations with parallel and perpendicular phenyl group is rather small (ca. 0.5 kcal/mol), in contrast with the case of 6C which is again due to the longer Ge--C bond which reduces the interaction between the parallel phenyl and geminal methyl groups.

CONCLUSION

In conclusion we have found that in the germacyclohexane ring the conformational energy of a phenyl group bonded to germanium is negligibly small (0 - 0.1 kcal/mol). Consequently, in 6G the two conformers exist in nearly identical amounts. Furthermore, there is no preference for a parallel or perpendicular phenyl group in 5G as is the case with 5C. This is another example of the effect of the longer Ge--C bond on the conformation of substituted germacyclohexanes.

ACKNOWLEDGEMENT

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EXPERIMENTAL

PREPARATION OF PHENYLGERMACYCLOHEXANES---Preparation of phenylgermacyclohexanes 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-dibromopentane and tetrachlorogermane afforded 1,1-dichlorogermacyclohexane in a 40% yield. To the dichloride (17 mmol) in diethyl ether (10 ml) there was added phenylmagnesium bromide prepared from bromobenzene (86 mmol) and magnesium (86 mmol). The mixture was refluxed for two hours, and then decomposed with ice-cold aqueous hydrochloric acid (2 M). The ether extract was dried over anhydrous calcium chloride, the solvent was removed and the residue was distilled in vacuo to give 1,1-diphenylgermacyclohexane (2.23 g; 43 %); b.p. 154-157 °C/3 torr.[18]

Bromine (7.5 mmol) was added to diphenylgermacyclohexane (7.5 mmol) in ethylene bromide(40 ml) under refluxing. After refluxing for 30 min., the solvent was removed and the residue was distilled in vacuo to give 1-bromo-1-phenylgermacyclohexane (1.94 g; 84 %). b.p. 116-118 °C/2 torr.

To lithium aluminum hydride (6.4 mmol) in diethyl ether (50 ml) was added a solution of bromophenylgermacyclohexane (6.4 mmol) in diethyl ether (5 ml). The resulting mixture was refluxed for 2h. The mixture was decomposed with ice-water and extracted with diethyl ether. The usual workup afforded 1-phenylgermacyclohexane(5G) (0.98 g; 69 %),b.p. 128-130 °C/14 torr.

Dibromomethylphenylgermane $C_6H_5(CH_3)GeBr_2$ was prepared by the method of Brook et al.[19] b.p. 139-140 °C/15 torr, $\delta_H(CDCl_3)$ 1.63 (3H, s). To a refluxing solution of dibromomethylphenylgermane (26 mmol) in diethyl ether (120 ml), was added a solution of bis-Grignard reagent prepared from 1,5-dibromopentane (26 mmol) and magnesium (89 mmol). The mixture was further refluxed for another 3 hr. The mixture was decomposed with ice-cold hydrochloric acid (2 M), and extracted with diethyl ether. The ether extract was washed with water, dried over anhydrous calcium chloride and distilled in vacuo to afford 1-methyl-1-phenylgermacyclohexane (6G) (2.71 g;44%), b.p. 95-97 °C/2 torr.

The preparation of methylphenylgermacyclohexanes 7G-11G was carried out in a similar manner starting from 2-, 3-methyl- and 2,2-dimethyl-1,5-dibromopentane, respectively. Compounds 7G-10G were obtained as a mixture of trans- and cis-isomers. Selected physical properties of these phenylgermacyclohexanes are listed in Table 3.

Table 3 Physical properties of germacyclohexanes(5G-11G)

Compounds (Formula)	yield[a] (%)	b.p. (C°/ torr)	δ_H(90MHz;$CDCl_3$)
5G ($C_{11}H_{16}Ge$)	69	128/14	4.36(1H, m, H-1)
6G ($C_{12}H_{18}Ge$)	44	96/2	0.40(3H, s, Me-1)δδδ
7G ($C_{12}H_{18}Ge$)	53	113/11	0.99(3H, d, J=6.0, Me-3) 4.41(1H, m, H-1)
8G ($C_{12}H_{18}Ge$)	73	118/6	0.86(3H, d, J=6.0Hz, Me-3) 4.33(1H, m, 1-H)
9G ($C_{13}H_{20}Ge$)	32	107/28	0.32(3H, s, Me-1); 0.42(3H, s, Me-1) 0.96(3H, d, J=6.7Hz, Me-3); 0.98(3H, d, J=6.7Hz, Me-3)
10G ($C_{12}H_{20}Ge$)	39	104/3	0.32(3H, s, Me-1); 0.40(3H, s, Me-1) 0.84(3H, d, J=6.0Hz, Me-4); 0.90(3H, d, J=6.0Hz, Me-4)
11G ($C_{13}H_{22}Ge$)	17	135/3	0.38(3H, s, Me-1); 0.88(3H, s, Me-3(ax)); 1.00(3H, s, Me-3(eq))

a Yield based on the immediate precursor.

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

The ^{13}C nmr spectra were measured as solutions in $CDCl_3$ (1:1 v/v) on a JEOL FX-90Q spectrometer at 22.50MHz. Typical measurement conditions were as follows: pulse width, 13 s(40°); spectral width, 2000 Hz; number of scans, 500; pulse delay, 1 s; data points, 4096.

The ^{73}Ge nmr spectra were recorded for the same solution on the same instrument equipped with an NM-IT 10LF low-frequency insert, operating at 3.10MHz, in a 10mm tube at 30°C. Typical measurement conditions were as follows: pulse width, 150 s (90°); spectral width, 2000 Hz; number of scans, 5000; pulse delay, 100 ms; data points, 4096.

MNDO CALCULATIONS---The one in the AMPAC^{20} package was used as the computation program. For the input geometry of phenylgermacyclohexanes, we assumed the optimized(by MM2) structure of 1G^{2} to which phenyl and methyl groups with standard bond lengths and bond angles incorporated. The computation was carried out by means of Micro VAX II with Ultrix-32 ver. 2.0-1 and VAX FORTRAN.

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