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Restricted Rotation Involving the Tetrahedral Carbon. VII. Rotation About the Carbon-Group IV Single Bond[1]

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9-*t*-Butyl-, 9-trimethylsilyl-, 9-trimethylgermyl-, and 9-trimethylstannyl-1,2,3,4-tetrachloro-9,10-dihydro-9,10-ethenoanthracenes were prepared by the addition of tetrachlorobenzyne to 1-$(CH_3)_3M$-substituted naphthalene. The carbon compound showed very high barrier to rotation, whereas the coalescence phenomenon of three methyl signals was observed for silicon, germanium, and tin compounds. The barrier ($\Delta G^{\ne}$) to rotation at 298 K was obtained as 19.1 ± 0.5, 17.2 ± 1.2, and 11.7 ± 0.4 kcal/mol for Si, Ge, and Sn compounds, respectively. The decrease in the barrier on increasing the atomic size was attributed to the release of repulsive interaction to a greater extent, since the longer bond length should result in the larger displacement of the methyl group even though the bond angle deformation is the same.

It was revealed, in one of the recent papers from this laboratory, that the barrier to rotation about a C–C single bond in some Diels-Alder adducts derived from 9-substituted anthracenes was extremely high.[2] These results allured the present authors to examine the outcome by the change of one of the sp^3 hybridized carbon to an atom of other fourth group elements.

One of the points of interest is to see the effect of

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[1] Preceding paper: M. Nakamura, M. Ōki, and H. Nakanishi, *Tetrahedron,* submitted.

[2] M. Ōki and G. Yamamoto, *Chem. Lett.* **1972**, 45.

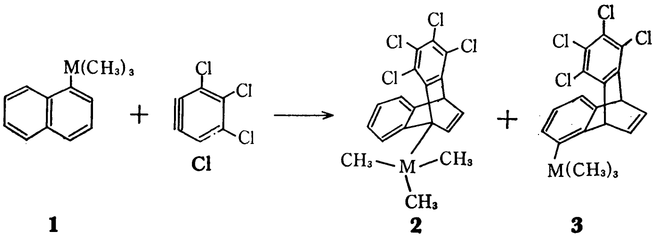
the change in bond length. As to the conformational energies of cyclohexane derivatives, it is known that chlorine, bromine, and iodine show rather similar values[3] in spite of the fact that the van der Waals radius of iodine is much greater than that of chlorine. The phenomenon has been attributed to the bond length. Namely, although the iodine atom is bulkier than chlorine, the interaction of the atom in question with the 3-hydrogen in the axial conformation is counterbalanced because the distance between hydrogen and iodine is greater.

Molecular models of 9-trimethylsilyltriptycene and its analogs indicate that the increase in bond length leads to the increased interference with the benzo bridges, because the longer C–M bond places the methyl group more closely to the substituent of the benzo group. This is just the contrary to the expectation from the analogy of the cyclohexane derivatives. This increasing interference may result in the increase in the barrier to rotation. Therefore it becomes interesting to see the effect of changing the *t*-butyl group to trimethylsilyl, trimethylgermyl, and then to trimethylstannyl.

This paper deals with the rotational barrier in 9-$(CH_3)_3$M-substituted 1,2,3,4-tetrachloro-9,10-dihydro-9,10-ethenoanthracenes, where M is C, Si, Ge, or Sn. Although the selection of the compounds was made according to the ease of syntheses, the distinct effect of the change of the central atom was observed.

Experimental

Syntheses. The syntheses of the compounds were performed by treating 1-$(CH_3)_3$M-substituted naphthalene (**1**) with tetrachlorobenzyne.[4] 1-*t*-Butylnaphthalene,[5] 1-trimethylsilylnaphthalene,[6] and 1-trimethylstannylnaphthalene[7] were known compounds and were prepared by following the procedures of literatures. The reaction of the benzyne gave both 1,4-adduct (**2**) and 5,8-adduct (**3**). The desired adduct (**2**) was separated by chromatography.



1 **2** **3**

a:M=C
b:M=Si
c:M=Ge
d:M=Sn

1-Trimethylgermylnaphthalene (1c). A solution of 1-naphthylmagnesium bromide, prepared from 10.3 g (0.05 mol) of 1-bromonaphthalene and 1.2 g (0.05 mol) of magnesium in 100 ml of ether, was added to 0.07 mol (15.0 g) of tetrachlorogermane in 50 ml of ether at −10 °C over a period of 1 hr. The mixture was set aside for 2 hr at room temperature and then heated under reflux for 0.5 hr. Methylmagnesium iodide prepared from 42.5 g (0.3 mol) of methyl iodide, 7.2 g (0.3 mol) of magnesium and 200 ml of ether was added to the above solution with vigorous stirring and the whole was refluxed for 2 hr. The mixture was cooled and treated with water. The organic layer was dried over sodium sulfate and evaporated to give a yellow oil. This crude product was directly used for the next reaction.

*1,2,3,4-Tetrachloro-9-*t*-butyl-9,10-dihydro-9,10-ethenoanthracene (2a).* A solution of butyllithium, prepared from 4.6 g (0.05 mol) of butyl bromide, 0.7 g (0.1 mol) of lithium, and 100 ml of ether, was added to a suspension of 14.2 g (0.05 mol) of hexachlorobenzene in 600 ml of ether at −30 °C over a period of 1 hr. To this mixture, a solution of 9.2 g (0.05 mol) of 1-*t*-butylnaphthalene in 50 ml of ether was added. The whole was set aside at room temperature for 1 hr, heated under reflux for 1 hr, cooled and treated with water. The organic layer was separated, washed with water, dried over sodium sulfate, and evaporated. The residue was taken up in hexane and chromatographed on alumina. Elution of the mixture with hexane gave a mixture of 1,4-adduct (**2a**) and 5,8-adduct (**3a**) in 1:2 ratio. NMR data of **3a** in $CDCl_3$ (δ from internal TMS): 1.53 (9H, s), 5.56 (1H, t, J=3.6 Hz), 6.30 (1H, t, J=3.6 Hz), 6.85—7.40 (5H, m). The NMR data for **2a** are given in Table 1.

The mixture of **2a** and **3a** was dissolved in hexane and rechromatographed on silica gel impregnated with silver nitrate. Elution with hexane gave pure **2a**, mp 162—164 °C, as a first eluate in *ca.* 5% yield based upon the starting 1-*t*-butylnaphthalene. Found: C, 60.23; H, 4.07; Cl, 35.73%. Calcd for $C_{20}H_{16}Cl_4$: C, 60.36; H, 4.06; Cl, 35.58%.

1,2,3,4-Tetrachloro-9-trimethylsilyl-9,10-dihydro-9,10-ethenoanthracene (2b), mp 157—159 °C, was similarly obtained as a mixture with the 5,8-adduct (**3b**) [NMR, $CDCl_3$, δ from TMS: 0.45 (9H, s), 5.62 (1H, q, J=4.6 and 3.0 Hz), 5.90 (1H, q, J=4.6 and 3.0 Hz), 6.95—7.43 (5H, m)] in 1:2 ratio and purified by SiO_2–$AgNO_3$ chromatography. The yield of pure **2b** was *ca.* 5%. Found: C, 55.53; H, 3.98; Cl, 34.08%. Calcd for $C_{19}H_{16}Cl_4Si$: C, 55.25; H, 3.94; Cl, 34.25%.

1,2,3,4-Tetrachloro-9-trimethylgermyl-9,10-dihydro-9,10-ethenoanthracene (2c), mp >315 °C, was similarly obtained as a mixture with **3c** (1:1.5 ratio). Pure **2c** was isolated in *ca.* 5% yield. Found: C, 49.95; H, 3.37; Cl, 31.17%. Calcd for $C_{19}H_{16}Cl_4Ge$: C, 49.74; H, 3.55; Cl, 30.89%. Only the NMR data of the 5,8-adduct (**3c**) were recorded ($CDCl_3$, δ from TMS): 0.57 (9H, s), 5.59—5.90 (2H, m), 6.97—7.41 (5H, m).

1,2,3,4-Tetrachloro-9-trimethylstannyl-9,10-dihydro-9,10-ethenoanthracene (2d), mp 165—166.5 °C, was obtained in *ca.* 5% yield. Found: C, 45.40; H, 2.98; Cl, 28.07%. Calcd for $C_{19}H_{16}Cl_4Sn$: C, 45.21; H, 2.98; Cl, 28.09%. NMR data of the 5,8-adduct (**3d**) were as follows ($CDCl_3$, δ from TMS): 0.51 (9H, s), 5.58 (2H, m), 5.70—7.50 (5H, m).

Spectral Measurement and Calculation. The NMR spectra were recorded on a Hitachi R-20B spectrometer operating at 60 MHz. The samples were dissolved in an appropriate solvent to make up *ca.* 10% solution. The temperature was read by the difference in chemical shifts of methanol protons in the lower temperature region and by that of ethylene glycol in the higher temperature region. T_2 was measured from the line-width of an appropriate additive in the sample

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[3] J. A. Hirsch, "Table of Conformational Energies-1967," in "Topics in Stereochemistry," N. L. Allinger and E. L. Eliel Ed., Interscience Publishers, New York (1967), vol. 1, p. 199.

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Table 1. The NMR data of compound **2** in deuteriochloroform at 34 °C (δ ppm)

2a	1.53 (3H, s)	1.77 (3H, s)	2.13 (3H, s)	5.71 (1H, q, J=6.0 and 2.0 Hz)	6.90—7.90 (6H, m)
2b	0.32 (3H, s)	0.67 (3H, s)	1.10 (3H, s)	5.67 (1H, q, J=6.0 and 1.2 Hz)	6.75—7.50 (6H, m)
2c	0.34 (3H, s)	0.67 (3H, s)	1.05 (3H, s)	5.66 (1H, q, J=6.0 and 1.6 Hz)	6.71—7.55 (6H, m)
2d		0.48 (9H, s)		5.58 (1H, q, J=6.0 and 1.2 Hz)	6.60—7.30 (6H, m)

solution: for mainly technical reasons, *t*-butylbenzene, tetrachloroethane, and dichloromethane were used for **2b**, **2c**, and **2d**, respectively.

Theoretical spectra were obtained by the use of EXNMR program.[1] The couplings of protons with ^{117}Sn and ^{119}Sn were neglected in the line-shape analysis because of the low natural abundance of the respective species. The agreement between the observed and the calculated spectra was excellent.

Results and Discussion

The NMR data of the adducts **2** in deuteriochloroform at 34 °C are summarized in Table 1. It is immediately noticed that the carbon, silicon, and germanium compounds show three kinds of methyl peaks, whereas the tin compound gives only one signal for the trimethylstannyl group. The rotation about the C_9–M bond must be slow on the NMR time scale for the compounds whose M is C, Si, or Ge, because, if the rotation in question is frozen, the three methyl groups must be in the different magnetic environment from each other (see **4**). The appearance of only one signal for the trimethylstannyl group in **2d** may be attributed to either a fortuitous coincidence of the chemical shifts of three methyl groups under the conditions or the fast exchange of the methyls on the NMR time scale. The latter was found to be the case because lowering the temperature caused the broadening of the signals and finally resulted in the appearance of three kinds of methyl signals. The chemical shifts at −58.5 °C from the internal TMS in CS_2 were 0.14, 0.51, and 0.85 ppm.

Temperature was raised to find the coalescence temperature and to observe the line shapes of compounds **2a**, **2b**, and **2c**. Spectra of **2b** and **2c** were temperature dependent and coalescence of the three signals was observed. However, the spectrum of **2a** was stout and did not show temperature dependence up to 200 °C. Even the broadening of the signal could not be observed.

From these results and the chemical shifts of the three methyl groups, the barrier to rotation about C_{Bu}–C_9 bond of **2a** is estimated to be at least 25 kcal/mol. The rate constants of rotation of other compounds were obtained by computer simulation of the curves. The activation energies were calculated by plotting the rate constants against the reciprocals of temperature. The $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$ were obtained by putting these data to Eyring's equation. The results are shown in Table 2.

Although the use of the same solvent is desirable for the discussion, it was impossible to use a common solvent for the series of compounds. Hexachlorobutadiene is suitable for measurement at high temperatures but is too viscous to obtain a good spectra at *ca.* 50 °C. Likewise, tetrachloroethylene is good at *ca.* 50 °C but is not suitable for measurement at high and at very low temperatures. Fortunately, however, it is known that the solvent change does not affect the activation parameters of internal rotation to a great extent in the case of biphenyl derivatives.[8] This conclusion may reasonably be transferred to the present situation, since the internal rotation is the common subject in both cases. We believe the following discussion is valid, since only the nonpolar solvents are used in the present work and no strong solute-solvent interaction is anticipated.

Descending the fourth group element from carbon to the elements of the lower period gives monotonous decrease in $\Delta G^{\neq}$'s and $\Delta H^{\neq}$'s. This is rather unexpected from the results of examination of the molecular models, as mentioned before, and demands further consideration. Recently, Oullette and his co-workers carried out the force field calculation of various butane analogs $CH_3CH_2MH_2CH_3$ containing silicon, germanium, or tin.[9] The conclusion from that calculation is that the *gauche* conformation is strikingly stable over the *trans* conformation and the barrier to rotation is mainly controlled by the stability of the ground state where nonbonding H–H attractive interaction contributes strongly to the total energy. Thus in this series, the potential of the transition state of rotation is almost the same irrespective to the kind of element M (except carbon) and the increasing size of M decreases the

Table 2. Activation parameters for rotation (at 25 °C)

	T_c (°C)	$E_a$kcal/mol	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ eu	$\Delta G^{\neq}$ kcal/mol	solvent
2a	>200				>25	hexachlorobutadiene
2b	112	20.7±0.5	20.1±0.5	0.6±1.8	19.9±0.5	hexachlorobutadiene
2c	64	15.3±0.7	14.7±0.7	−8.4±2.1	17.2±1.2	tetrachloroethylene
2d	−40	13.2±0.4	12.6±0.4	2.2±0.5	11.7±0.4	carbon disulfide

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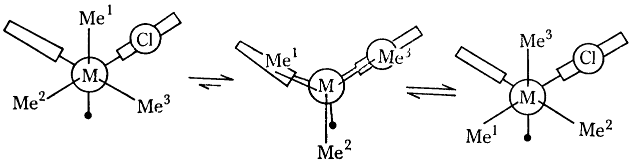
[8] B. M. Grayhill and J. E. Leffler, *J. Phys. Chem.*, **63**, 1461 (1959): I. O. Sutherland and M. V. J. Ramsey, *Tetrahedron*, **21**, 3401 (1965): M. Ōki and H. Iwamura, *ibid.*, **24**, 2377 (1968): M. Ōki, H. Iwamura, and T. Nishida, This Bulletin, **41**, 656 (1968).

[9] a) R. J. Oullette, *J. Amer. Chem. Soc.*, **94**, 7674 (1972): b) R. J. Oullette, D. Baron, J. Stolfo, A. Rosenblumn, and P. Weber, *Tetrahedron*, **28**, 2163 (1972).

barrier to rotation.

The phenomena in the Diels-Alder adducts dealt with here might have been explained in a similar manner, if the steric conditions of the butane analogs were applicable to the compounds in question. However, although the compound **2** is the ethane type molecule, the situations are quite different from those of $CH_3CH_2MH_2CH_3$. In the latter compound, it is known that the distance between the two methyl groups is larger than the sum of two van der Waals radii of the methyl. The attractive term is important even at the eclipsed conformation. On the other hand, the steric situation of compound **2** is overcrowded. Inspection of the model of the ground state (**4** and **4′**) indicates that the distance between chlorine at 1-position and a closest methyl group from that atom is within the sum of the van der Waals radii of the two substituents. Therefore, although the molecule will deform to some extent to minimize the van der Waals repulsion, the steric conditions are thought to be severe at the transition state (**5**). It seems, then, natural to seek the reason for the phenomenon in repulsive forces rather than the attractive.



4 **5** **4′**

Since the molecular model shows severe overlap of the groups at the transition state **5**, the bond length will be stretched and the bond angle distorted to help to decrease the energy of the transition state. The energy of stretching a bond and that of deforming a bond angle may be discussed in terms of force constants obtained from the infrared study. Thus the force constants of respective moieties are collected in Table 3 from the literature.[10]

Table 3. Force constants for bond stretching and angle deformation

	C	Si	Ge	Sn
Bond Stretching constant (C–M) mdyn/A	4.50	2.97	2.70	2.12
Angle bending constant (C–M–C) mdyn/rad	0.799	0.570	0.490	0.320

Although it may seem that the smaller force constants for stretching the C–M bond should play some part in lessening the barrier to rotation when M is the large atom, the molecular model is not in conformity with this idea. When M becomes large, both the C_9–M and C_{CH_3}–M bonds become longer and, as a consequence, the overlap of the chlorine and the methyl group at the transition state becomes worse. Therefore, relief of steric strain at the transition state by stretching the bond should be small in its extent, if any.

Another way of relieving the steric interference at the transition state is to deform the bond angles concerned with the $(CH_3)_3M$ group, because the other part of the molecule is very rigid. The force constants of angle bending also decreases as M becomes large. Therefore, the ease of angle deformation increases as we descend the periodic table from carbon to tin. The important point here seems to be that even the deformation of the same degree results in the different degree of release of the steric strain. When the C–M bond is longer, the actual placement of the methyl group can become more apart from the groups which contribute mainly to the strain at the transition state, even though the angle deformation is the same. Thus we believe that the longer bond distance is the main cause for decreasing the barrier to rotation, when M is the large atom, and the smaller force constants for the C–M–C angle deformation is an additional factor which helps to decrease the barrier height.

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[10] Reference 9a and literatures cited therein.