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CHEMISTRY OF ORGANOSILICON COMPOUNDS

CX. AN ELECTRON SPIN RESONANCE STUDY ON THE SILYL- AND GERMYL-SUBSTITUTED METHYL RADICALS. HYPERFINE COUPLING CONSTANTS OF β-M-H (M = Si, Ge) PROTONS

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Summary

ESR spectra of five metal-substituted methyl radicals of the type $HR^1R^2M\text{-}\dot{C}R^3R^4$ are recorded and analyzed. The magnitudes of a(β-SiH) were in a range of 14-15G, while a(β-GeH) of $\cdot CH_2GeMe_2H$ was 10.20G. These coupling constants were markedly temperature dependent, suggesting that the most stable conformation of these radicals at low temperature is one in which the β-M-H bond eclipses the p orbital on the metal radical site.

Introduction

Although hindered rotation of free radicals has been studied rather extensively by means of electron spin resonance (ESR), these studies have been limited to those on relatively stable radicals until the method of generation of free radicals in solution by coutinuous photolysis was advanced [1].

The ESR method is based on the evaluation of angular dependence of hyperfine splitting constants due to the β-hydrogen of an appropriate radical. From measurements of temperature dependence of these splittings and line broadening, important information concerning conformations and the rotational barriers of the radical are obtained.

Recently, rather unstable and reactive free radicals were found to be generated readily in high concentrations by continuous photolysis of a di-tert-butyl peroxide (DTBP) solution of a substrate [2,3]. Thi has facilitated ESR studies on various types of radicals. Fessenden [4] and Kochi and Krusic [5,6] reported the ESR spectral parameters of substituted ethyl radicals and discussed the conformations and the rotational barriers about C_α-C_β bonds of these radicals. More recentl hindered rotation about the Si-Si bond of a disilanyl radical has been examined in detail by means of ESR spectroscopy by Sakurai, Kira, and Sato [7]. On the other hand, internal rotation around the C_α-Si_β bond has been studied in various kinds of silylmethyl radicals derived from hexamethyldisiloxane, hexamethyldisilane, and halomethyldimethylchlorosilane by examination of the temperature dependent hyperfine splitting constants of the corresponding radicals in the ESR spectra [8,9].

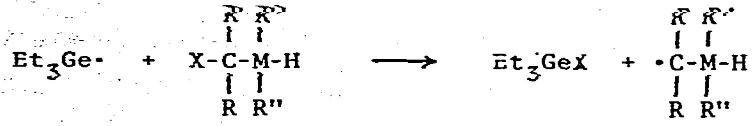
In this paper ESR spectral parameters of the dimethylgermylmethyl radical and of several kinds of silylmethyl radicals are described and the conformations around C_α-Ge_β and C_α-Si_β bonds are discussed on the basis of the temperature dependence of the corresponding hyperfine coupling constants of β-protons. These radicals generally are not easy to produce and hence no ESR study has been reported to date.

Results and Discussion

Hydrogermylmethyl and hydrosilylmethyl radicals have been generated in high concentrations by the abstraction of halogen from the corresponding halomethylgermane and halomethylsilane with the triethylgermyl radical, which is formed by abstraction of hydrogen from triethylgermane by photochemically generated t-butoxy radicals.

$$(CH_3)_3CO\text{-}OC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (1)$$

$$Et_3GeH + (CH_3)_3CO\cdot \longrightarrow Et_3Ge\cdot + (CH_3)_3COH \qquad (2)$$



$$Et_3Ge\cdot + X\text{-}\overset{R}{\underset{R}{C}}\text{-}\overset{R'}{\underset{R''}{M}}\text{-}H \longrightarrow Et_3GeX + \cdot\overset{R}{\underset{R}{C}}\text{-}\overset{R'}{\underset{R''}{M}}\text{-}H \qquad (3)$$

X = Cl, Br

R = H, Me; R', R'' = Me, Ph

M = Si, Ge

1 R=H, R'=R''=Me, M=Ge

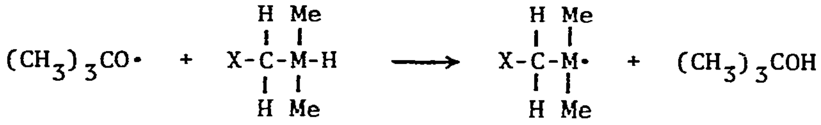
2 R=H, R'=R''=Me, M=Si

3 R=H, R'=Me, R''=Ph, M=Si

4 R=H, R'=R''=Ph, M=Si

5 R=R'=R''=Me, M=Si

In the absence of triethylgermane, photolysis of halomethylhydrogermane and halomethylhydrosilane in di-*tert*-butyl peroxide (DTBP) gave the corresponding halomethylgermyl and halomethylsilyl radicals, respectively, as identified by means of ESR spectroscopy.



$$(CH_3)_3CO\cdot + X\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{Me}{\underset{Me}{M}}\text{-}H \longrightarrow X\text{-}\overset{H}{\underset{H}{C}}\text{-}\overset{Me}{\underset{Me}{M}}\cdot + (CH_3)_3COH \qquad (4)$$

(X = Cl, M = Si, Ge)

Thus abstraction with a germyl radical offers a very convenient route to generate alkyl radicals in high concentration even for substrates having active functional groups such as Si-H and Ge-H. Hudson and Jackson reported the first generation of an alkyl radical for ESR study by abstracting a halogen atom from an alkyl halide with a silyl radical [10,11]. The present method is based on the fact that abstraction of halogen by the germyl radical proceeds with higher reactivity than by the silyl radical and with higher selectivity than with the stannyl radical. In fact, the ESR spectrum of the dimethylgermylmethyl radical could not be obtained by the abstraction of chlorine from chloromethyldimethylgermane with the tri-n-butylstannyl radical or the trimethylsi radical.

The ESR spectra of dimethylgermylmethyl radical, $HMe_2GeCH_2\cdot$ (**1**), dimethylsilylmethyl radical, $HMe_2SiCH_2\cdot$ (**2**), methylphenylsilylmethyl radical, $HMePhSiCH_2\cdot$ (**3**), diphenylsilylmethyl radical, $HPh_2SiCH_2\cdot$ (**4**) and 2-dimethylsilyl-2-propyl radical, $HMe_2SiMe_2C\cdot$ (**5**), were thus obtained as shown in Figures 1,2,3,4, and 5. These ESR signals are analysed as a doublet of triplets for the radicals, (**1**), (**2**), (**3**), an (**4**), respectively, and a doublet of septets for the radical (**5**). These doublets are assignable to the splitting due to the Ge-H (**1**) an the Si-H (**2**-**5**) protons, respectively. The hyperfine coupling constan of these radicals are given in Table 1. In contrast to the splitting

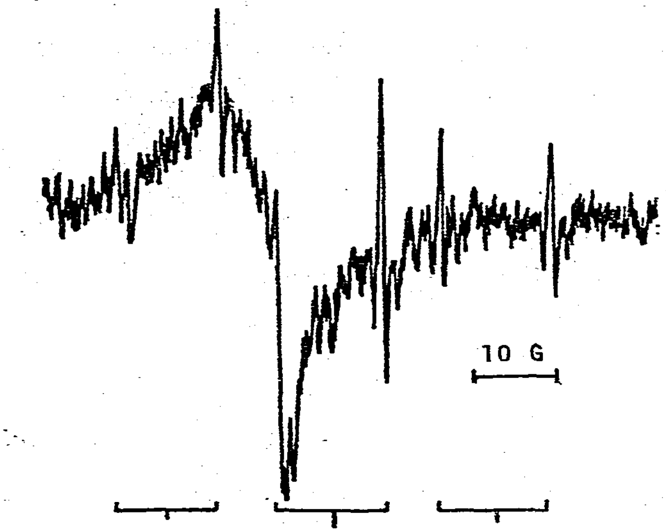


Fig. 1. ESR spectrum of the dimethylgermylmethyl radical.

due to α-hydrogen, β-hydrogen coupling constants of these radicals are found to show a marked temperature dependence. Thus, the hyperfine coupling constants due to the β-SiH group become larger at lower temperature as shown in Table 2. The temperature dependence of the

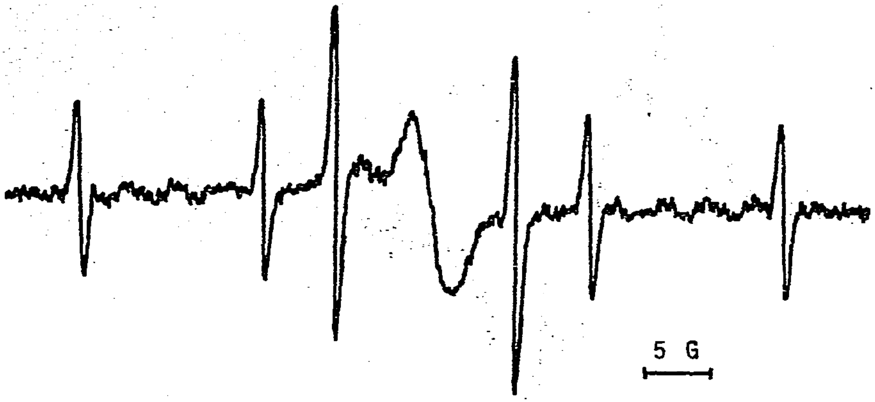


Fig. 2. ESR spectrum of the dimethylsilylmethyl radical.

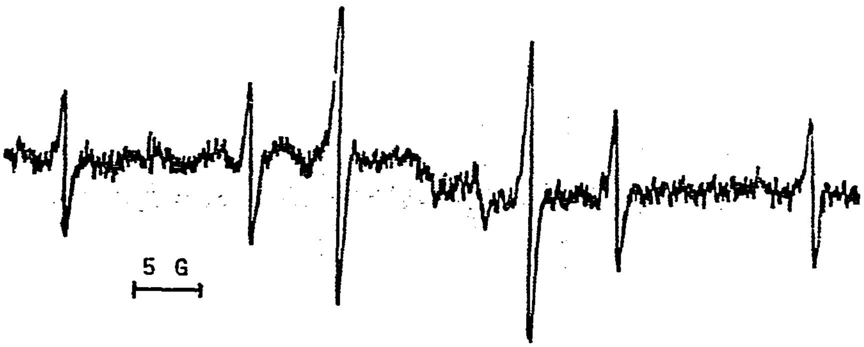


Fig. 3. ESR spectrum of the methylphenylsilylmethyl raidcal.

hyperfine coupling constants of the α- and β-protons of radicals, (2), (3), and (5) are also shown graphically in Figures 6, 7, and 8. The ESR spectra of the radicals (1) and (4) were contaminated with those due to other unidentified radicals and are not sufficiently resolved to examine the temperature dependence of the hyperfine coupling constants.

The isotropic hyperfine coupling constant of the β-hydrogen in an alkyl radical depends strongly on the angle θ between the principal axis of the p orbital containing the unpaired electron and the C-H

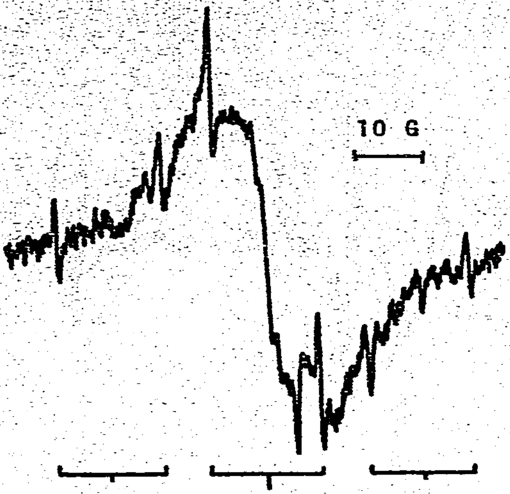


Fig. 4. ESR spectrum of the diphenylsilylmethyl radical.

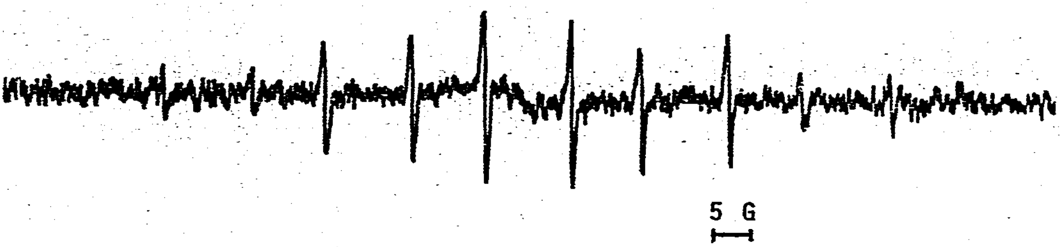
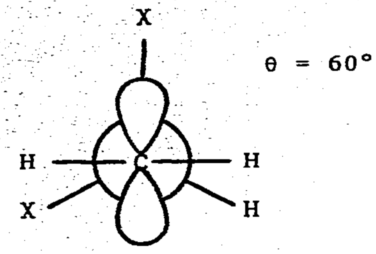


Fig. 5. ESR spectrum of the 2-dimethylsilyl-2-propyl radical.

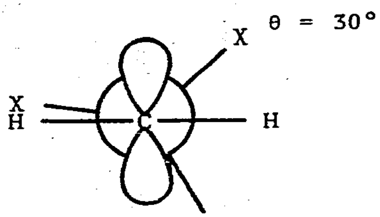
bond on the β-carbon atom, and can be represented by the empirical relationship (5), where A and B are constants.

$$a_{\beta H} = A + B\cos^2\theta \qquad (5)$$

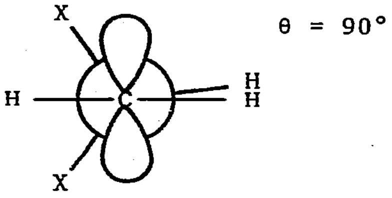
From considerations of the symmetry of substituted ethyl radicals such as $\cdot CH_2CH_2X$ and $\cdot CH_2CHX_2$, they may be considered to exist as equilibri mixtures of limited conformations, a, b, c, and d.



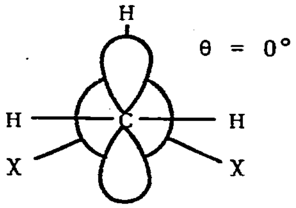
a



b



c



d

By using equation (5), the a(β-H) values can be calculated for these conformations: a(β-H) = A + 1/4 B (a), A + 3/4 B (b), A (c),

TABLE 1. HYPERFINE COUPLING CONSTANTS OF SUBSTITUTED METHYL RADICALS

Radical	Temp./°C	h.f.c.c/G a(α-H)	 a(β-H)
$\cdot CH_2CMe_2H$*	-120	22.0	35.1
$\cdot CMe_2CMe_2H$*	-140		9.4, 22.9
$\cdot CH_2SiMe_2H$	-120	20.50	15.24
$\cdot CH_2SiMePhH$	-140	21.15	15.07_5
$\cdot CH_2SiPh_2H$	-80	21.05	14.65
$\cdot CMe_2SiMe_2H$	-140		14.25, 22.90
$\cdot CH_2GeMe_2H$	-40	21.10	10.20

*Krusic and Kochi (1971)

TABLE 2. TEMPERATURE DEPENDENCE OF HYPERFINE COUPLING CONSTANTS OF $HMe_2SiCH_2\cdot$, $HMePhSiCH_2\cdot$, AND $HMe_2SiCMe_2\cdot$

Temp./°C	h.f.c.c./G					
	$HMe_2SiCH_2\cdot$ (2)		$HMePhSiCH_2\cdot$ (3)		$HMe_2SiCMe_2\cdot$ (5)	
	a(α-H)	a(β-SiH)	a(α-H)	a(β-SiH)	a(α-H)	a(β-SiH)
40					22.96	11.43
20	20.01	13.78			22.81	11.56
0	20.09	14.11			22.80	11.75
-20	20.19	14.21	21.05	13.75	22.98	12.09
-40	20.45	14.33	20.50	13.75	22.93	12.13
-60	20.27	14.54	21.03	14.24	22.93	12.38
-80	20.38	14.69	21.13	14.25	22.93	12.63
-100	20.45	14.95	21.15	14.51	22.88	13.15
-120	20.50	15.24	21.08	14.99	22.84	13.60
-140			21.15	15.08	22.90	14.25

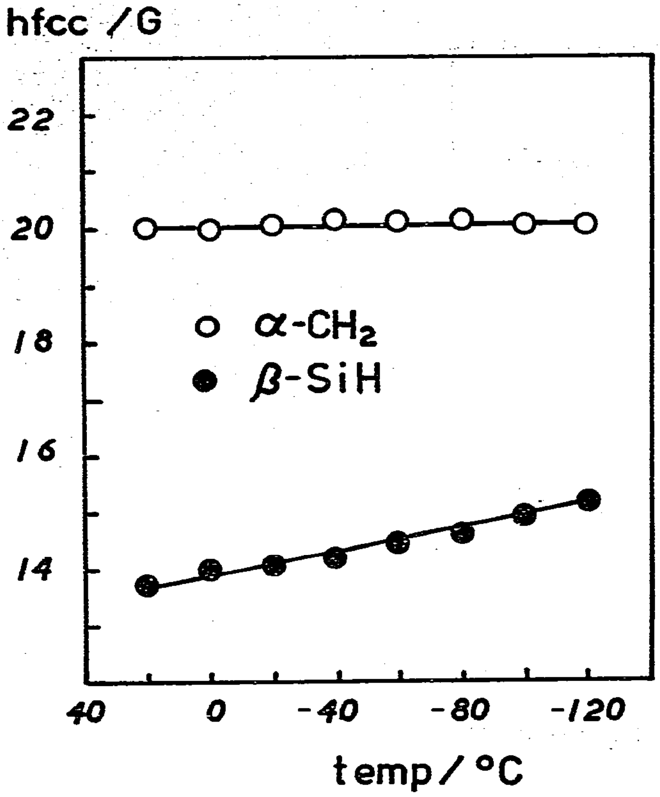


Fig. 6. Temperature dependence of h.f.c.c of $HMe_2SiCH_2\cdot$ (2)

and A + B (d). As rotation approaches the free rotation limit, a(β-H) approaches the value A + 1/2 B. Therefore, for radicals with preferred conformations (b) and (d) in the equilibrium, a(β-H) is expected to decrease with increasing temperature, whereas for radicals with equilibrium conformations (a) and (c), the corresponding value is expected to increase.

A similar angular dependence of a(β-H) should hold for silylmethyl radicals, although the values of A and B in eq. 5 are different from those in the case of ethyl radicals. From the behavior of a(β-H) on temperature change as shown in Figures 6, 7 and 8, conformations b and d with the β-silicon-hydrogen bond nearly eclipsed with the p orbital on the radical center appear to favored. For radicals (1) and (4), intensities of the ESR spectra are not sufficient to examine the tem-

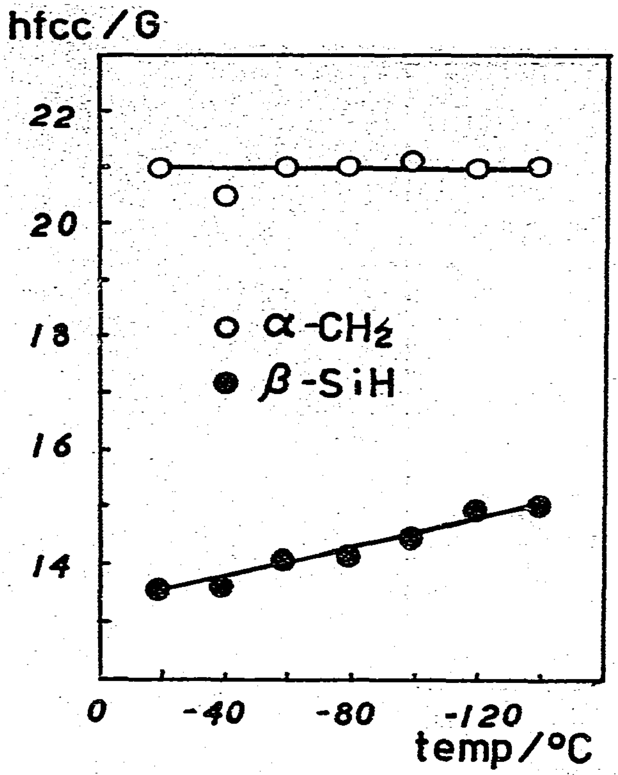
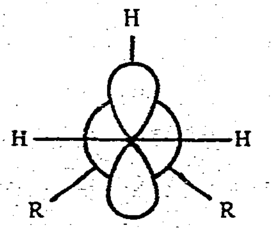


Fig. 7. Temperature dependence of h.f.c.c of HMePhSiCH$_2$· (3)

perature dependence of a(β-H), but the magnitude of a(β-H) of radicals (1) and (4) are similar to those of radicals (2), (3), and (5). Therefore, from comparison of a(β-H) values, radicals (1) and (4) should adopt the similar preferred conformation to those of (2) and (3) as shown in I.



I

The magnitude of a(β-CH$_3$) (22.9 G) for the radical (5) is quite close

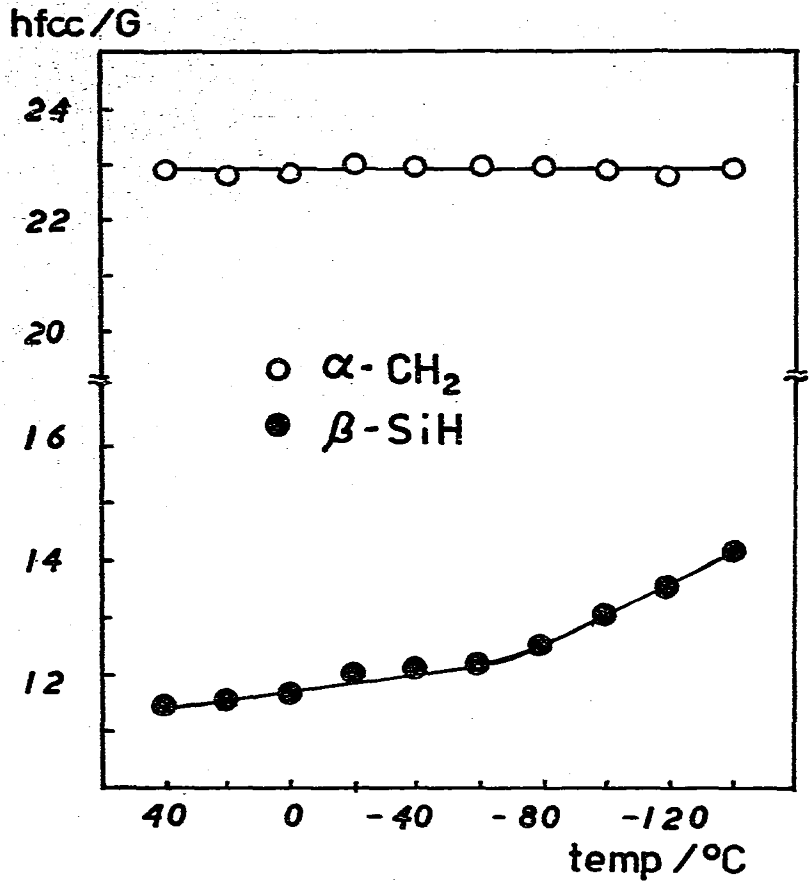
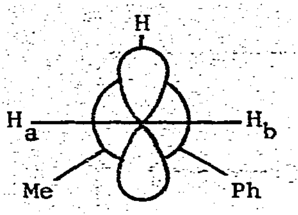


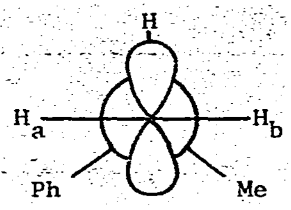
Fig. 8. Temperature dependence of h.f.c.c of $HMe_2SiCMe_2\cdot$ (5)

to that of the tert-butyl radical (22.72 G), and this value should correspond to the high-temperture limit of a(β-H) value in the tertiary radical.

Incidentally, alkyl radicals are known to be planar from many aspects of ESR studies [12,13]. The absence of any selective line broadening and the lack of splitting by γ-protons in the spectra of (1), (2), (4), and (5) are also consistent with the symmetric equilibrium conformations. For radical (3), a selective line broadening effect may occur due to equilibration between II and III.



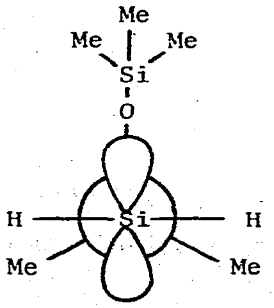
II



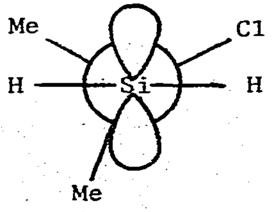
III

However, such an effect could not be analyzed sufficiently because other signals appeared and masked the original signal at higher temperature. The γ-proton coupling constant of freely rotating γ-methyl groups is 0.43 G in the trimethylsilylmethyl radical [14].

It is interesting to compare the present findings with those reported for other radicals such as trimethylsiloxydimethylsilylmethyl radical; $\cdot CH_2SiMe_2OSiMe_3$ [8] and dimethylchlorosilylmethyl radical; $\cdot CH_2SiMe_2Cl$ [9]. From the trend of temperature dependence of the a(γ-H) and a(β-Cl), the equilibrium conformations for these radicals have been assigned to IV and V, respectively. The equilibrium conformation of the pentamethyldisilanylmethyl radical; $\cdot CH_2SiMe_2SiMe_3$ [8] is not clear.

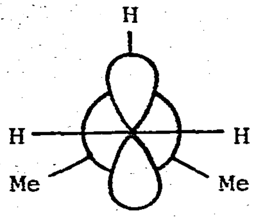


IV

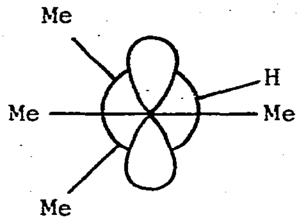


V

Similarly, from the temperature dependence of a(β-H) in the 2,3-dimethyl-2-propyl radical; $(CH_3)_2\dot{C}C(CH_3)_2H$ and the isobutyl radical, $H_2\dot{C}C(CH_3)_2H$, the equilibrium conformations are assigned to VI and VII, respectively.



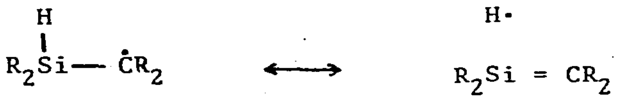
VI



VII

The values of a (β-SiH) and a(β-GeH) for silyl- and germyl-substituted methyl radicals are small in comparison with that of a(β-CH) for the isobutyl radical. These smaller values of a(β-H) might be ascribed to smaller resonance integrals both between silicon and carbon and between germanium and carbon.

Equilibrium conformations in alkyl radicals are governed by a fine balance between steric repulsion and hyperconjugation effects. In the radicals, (1) through (5), preferred conformations in which the β-metal-hydrogen bond tends to eclipse with the p orbital on the radical center are sterically unfavorable. However, the existence of such conformations as preferred ones can be partly attributed to the reason that both the Si-C (1.94 A) and the Ge-C bonds (2.00 A) are much longer than the C-C bond (1.54 A). Nonbonded interactions between α- and β-substituents in substituted methyl radicals such as the radicals (1), (2), (3), (4), and (5) are not serious and this allows these radicals to take such an eclipsed conformation. However, this factor alone is not sufficient to explain the favored eclipsed conformation. Since both (p-p) [15] and (p-d) [16] homoconjugations suggested for hetero atom-substituted ethyl radicals are not operative in these radicals, the equilibrium conformation may be stabilized by hyperconjugation betweenthe β-metal-hydrogen bond and p-orbital on carbon radical center [17].



$$R_2\overset{\overset{\textstyle H}{|}}{Si}-\dot{C}R_2 \longleftrightarrow \overset{H\cdot}{R_2Si = CR_2}$$

Experimental

ESR measurements

A mixture of di-*tert*-butyl peroxide (DTBP), triethylgermane and halomethyl compound was diluted with cyclopropane in an approximately 1:1:2:4 (v/v) ratio to give a solution. All samples were thoroughly degassed by freeze-pump-thaw cycles. The solution was placed in a cavity of a Varian E-12 ESR spectrometer and irradiated with a 500W superhigh-pressure mercury arc lamp.

Materials

DTBP was obtained commercially as reagent grade and redistilled at reduced pressure prior to use. (Chloromethyl)dimethylchlorosilane, b.p. 115°C (lit., 115°C [18]), (chloromethyl)methyldichlorosilane, b.p. 121°C (lit., 121°C [19]), (chloromethyl)trichlorosilane, b.p. 150° (lit., 152°C/734mmHg [20]) and (chloromethyldimethyl)chlorogermane, b.p. 74-8°C/110mmHg (lit., 148°C [21]) were prepared by photochlorination of the corresponding organometallic compounds. Isopropyldimethylchlorosilane was prepared from dimethyldichlorosilane and isopropylmagnesium chloride, b.p. 114°C (lit., 109.8-110°C/738mmHg [22]).

(Chloromethyl)phenylmethylchlorosilane b.p. 130°C/32mmHg (lit., 125-136°C/16mmHg [23]) and (chloromethyl)diphenylchlorosilane, b.p. 100°C/6mmHg (lit., 110-118°C/12mmHg [24]) were prepared by the reaction of the chlorosilanes and the corresponding Grignard reagent in 48 and 49% yield, respectively.

(Chloromethyl)dimethylsilane, b.p. 78°C (lit., 81°C [25]), (chloromethyl)phenylmethylsilane, b.p. 110°C/30mmHg (lit., 99-100°C/14 mmHg [24]), and (chloromethyl)diphenylsilane, b.p. 143°C/4 mmHg (lit., 175-180°C [24]) were prepared by the $LiAlH_4$ reduction of the corresponding chlorosilanes in 75, 77, and 49% yield, respectively.

Preparation of 2,3-dimethyl-2-chloro-3-bromo-2-silabutane, $ClMe_2SiCMe_2Br$

In a 50 ml two-necked flask, 5.0g (0.053 mol) of isopropyldimethychlorosilane was placed and heated to about 60°C. Then, bromine (5.8 g, 36 mmol) was added. After the addition of bromine was completed, the mixture was stirred for 12 hr. The extent of the reaction was monitored by GLC (Apiezon L 30%) of small samples from the reaction mixture. Removal of bromine by evaporation gave 3.0 g of the crude product, which was used without further purification.

Preparation of 2,3-dimethyl-3-bromo-2-silabutane, HMe_2SiCMe_2Br

Reduction of 3.0 g of crude 2,3-dimethyl-2-chloro-3-bromo-2-silabutane with 2.0 g (0.05 mol) of lithium aluminium hydride at 0°C in ether stirring for 1 hr gave 0.8 g (4.4 mmol, total yield 12.2%) of 2,3-dimethyl-3-bromo-2-silabutane, bp. 70°C/110 mmHg; n^{20}1.4479; IR (neat, cm^{-1}) 2050 (νSiH), 1240 (SiMe); NMR (δ in CCl_4) 0.18 (6H, d, J=3.4 Hz), 1.71 (6H, s), 3.88 (1H, sept., J=3.4 Hz). Anal. Calcd. for $C_{15}H_{13}BrSi$: C, 33.15; H, 7.23%. Found: C, 33.40; H, 7.29%.

Preparation of chloromethyldimethylgermane

Reduction of 5.0 g (0.027 mol) of chloromethyldimethylchlorogermane by stirring with 1.0 g (0.026 mol) of lithium aluminium hydride in ether solution at 0°C for 1 hr gave 1.2 g of crude product, bp. 80-90°C (lit., [25] 93.5-95°C). The sample for ESR measurement was purified by means of preparative GLC (30% Apiezon L 5m).

References

1 a) D. H. Geske, Progr. Phys. Org. Chem., 4 (1967) 125;
b) A. Hudson and G. R. Luckhurst, Chem. Rev., 69 (1961) 191;
c) P. D. Sullivan and J. R. Bolton, Advan. Mag. Resonance, 4 (1970) 39.

2 P. J. Krusic and J. K. Kochi, J. Am. Chem. Soc., 90 (1970) 7155.

3 A. Hudson and H. A. Hussain, Mol. Phys., 16 (1969) 199.
4 R. W. Fessenden, J. Chem. Phys., 61 (1971) 1570.
5 P. J. Krusic and J. K. Kochi, J. Am. Chem. Soc., 93 (1971) 840.
6 P. J. Krusic, P. Meakin, and J. P. Jesson, J. Phys. Chem., 75 (1971) 3438.
7 H. Sakurai, M. Kira, and M. Sato, Chem. Lett., (1973) 831.
8 P. J. Krusic and J. K. Kochi, J. Am. Chem. Soc., 91 (1969) 6161.
9 J. Cooper, A. Hudson, and R. A. Jackson, Tetrahedron Lett., (1974 1323.
10 A. Hudson and R. A. Jackson, Chem. Commun., (1969) 1323.
11 A. Hudson and J. W. Lewis, Mol. Phys., 19 (1970) 241.
12 R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 39 (1963) 2147
13 R. W. Fessenden, J. Phys. Chem., 71 (1967) 74.
14 A. Hudson and H. A. Hussain, J. Chem. Soc., (B) (1969) 793.
15 a) T. Kawamura, D. J. Edge, and J. K. Kochi, J. Am. Chem. Soc., 94 (1972) 648;
b) M. C. R. Symons, Chem. Phys. Lett., 19 (1973) 61.
16 a) T. Kawamura and J. K. Kochi, J. Am. Chem. Soc., 94 (1972) 648;
b) T. Kawamura, P. Meakin, and J. K. Kochi, ibid., 94 (1972) 8065.
17 I. N. Jung and P. R. Jones, J. Organomet. Chem., 101 (1975) 35.
18 J. R. Elliott, J. Am. Chem. Soc., 67 (1945) 1810.
19 V. A. Ponomarenko, Izvest. Akad. Nauk. S. S. S. R., Otdel. Khim. Nauk, (1957) 199; Chem. Abstr., 51 (1957) 11272.
20 F. C. Whitmore, J. Am. Chem. Soc., 65 (1946) 455.
21 L. H. Sommer, D. L. Bailey, J. R. Gould, and F. C. Whitmore, J. Am. Chem. Soc., 76 (1954) 801.
22 L. M. Dennis and W. I. Patnode, J. Am. Chem. Soc., 52 (1930) 2779.
23 Z. V. Belyakova and S. A. Golubtsov, Ah. Obshch. Kim., 31 (1961) 3178.
24 H. Schmidbaur and S. Waldmann, Chem. Ber., 97 (1964) 3381.
25 H. D. Kaesz and F. G. A. Stone, J. Chem. Soc., (1957) 1433.