0.3 kcal/mol for a monosilylamine (calculated value,[26] 0.7 kcal/mol). In general, the quantitative reliability of such estimates is limited by the approximate nature of the inversion barrier correlations, which reveal frequent deviations from linearity of several kilocalories per mole.

Reversal points are indicated in Figure 10 by the intersection of any two correlation lines. In addition to the previously identified reversal points, reversal behavior is revealed in correlations between arsines and sulfonium ions (E_{rev} = 17.1 kcal/mol) and between silyl anions and sulfonium ions (E_{rev} = 24.9 kcal/mol).[18,30]

Figure 10 also indicates ranges of planarity and pyramidality. For example, in the case of amines, the figure may be divided by the dashed line into the two regions labeled "pyramidal nitrogen" and "planar nitrogen." That portion of each correlation line which extends into the latter region corresponds to barriers for systems whose nitrogen analogs are planar.[31] More generally, a similar division of the figure into planar and pyramidal regions may be envisioned for each inversion center, the corresponding dashed line originating from the point at which the correlation line for that particular center intersects the abscissa (E_{inv} = 0).

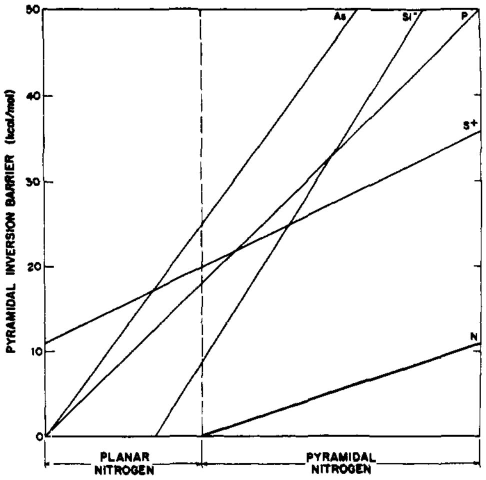


Figure 10.

The order in which the correlation lines intersect the abscissa is indicative of the order in which the respective inversion centers achieve planarity upon progression through a given series of substituents. We designate this order as the order of increasing *threshold pyramidal stability* (N < Si^- < P ~ As < S^+) of the inversion centers. In the absence of reversal points, this sequence would follow the order of relative sensitivities. However, assuming the actuality of the indicated reversal points,[18] sulfonium ions are predicted to possess the greatest threshold pyramidal stability although they exhibit the lowest sensitivity of the second- and third- row inversion centers.

---

[30] The phosphorus and arsenic correlation lines represent a special case in which a reversal point occurs at the abscissa (E_{inv} = 0).

[31] The energy values associated with the intersections of the correlation lines with the dashed line (Figure 10) correspond to the previously discussed intercepts (Table I) in correlations of the various inversion centers (ordinate) relative to amines (abscissa).

Electron Spin Resonance Study of the Conformational Stabilization of Allyl Radicals by Silicon, Germanium, Tin, and Sulfur Substituents. Barriers to Hindered Internal Rotation by Line-Shape Analysis

Takashi Kawamura,[1a] Paul Meakin,[1b] and Jay K. Kochi*[1a]

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401, and The Central Research Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898.
Received April 5, 1972

Abstract: The esr spectra of a series of allyl radicals with β substituents consisting of heteroatoms such as Si, Ge, Sn, or S show a temperature-dependent variation of the hyperfine splitting constants and a pronounced selective line broadening due to hindered internal rotation about the C_3-C_4 bond. The rates of hindered internal rotation in these radicals are derived by a comparison of the experimental line shapes with those calculated using the density matrix equation of motion. These radicals exhibit a barrier to hindered internal rotation which increases with atomic number. The source of the stabilization of the radicals by (a) hyperconjugation between the π system and the carbon-metal bond and (b) p-d homoconjugation between the π system and the metal d orbitals is analyzed qualitatively, and it is concluded that both mechanisms are important.

The enhanced reactivity of allylsilanes to free-radical addition has been attributed to the stabilization of the intermediate organometallic radicals, and the electronic interactions involved have been discussed in terms of hyperconjugation (π-σ conjugation).[2] In

---

[1] (a) Contribution No. 2093, Chemistry Department, Indiana University. (b) Contribution No. 1936, Central Research Department, E. I. du Pont de Nemours & Co.

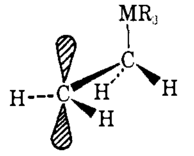
[2] (a) H. Sakurai, A. Hosomi, and M. Kumada, *J. Org. Chem.*, 34, 1764 (1969); (b) A. W. P. Jarvie and R. J. Rowley, *J. Chem. Soc. B*, 2439 (1971); (c) A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, **93**, 7330 (1971).

Table I. Proton Hfcc of Substituted Allyl Radicals, $\dot{C}H_2CH{=}CHCH_2MR_n$

MR_n	Temp, °C	$\langle g\rangle^a$	Hfcc's, G^b $a_{1\alpha}$	$a_{1\beta}$	a_2	$a_{3\beta}$	$a_4{}^c$	$a_{4'}{}^c$	$a_{\bar{4}}{}^c$	a_5
H^d	−140	2.00263	14.78	13.83	3.85	13.83			16.43	
CH_2CH_3	−130	2.00263	14.70	13.63	3.78	13.63			12.84	0.4^e
$Si(CH_3)_3$	−173	2.00266	14.28	13.38	3.68	13.38	5.82	16.26	11.04	
$Ge(CH_3)_3$	−162	2.00257	14.04	13.13	3.58	13.13	5.84	15.13	10.49	
$Sn(n\text{-}Bu)_3$	−148	2.00225	13.41	12.59	3.41	12.59	6.67	14.35	10.51	
$OC(CH_3)_3{}^f$	−151	2.00263	14.85	13.77	3.83	13.77			17.24	
$SCH_3{}^f$	−172	2.00248	14.76	13.76	3.74	13.29	1.56	15.77	8.67	

[a] Experimental error ±0.00003. Corrected to second order with respect to hyperfine interactions. [b] Experimental error ±0.04 G. [c] When the two protons bonded to C_4 are not equivalent, a_4 and $a_{4'}$ show the observed hfcc's and $a_{\bar{4}}$ shows the average of a_4 and $a_{4'}$. When the two C_4 protons are equivalent, the observed hfcc of C_4 protons is listed under $a_{\bar{4}}$. [d] Reference 7. [e] Two methylene protons in the CH_2CH_3 substituent. [f] Reference 5.

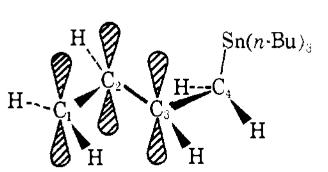
preceding papers,[3,4] radicals of the type $(CH_3)_3M\text{-}CH\dot{C}_2H_2$ (where M = C, Si, Ge, and Sn) were studied by electron spin resonance (esr). An analysis of the β-proton hyperfine splitting indicated that these radicals exist in a preferred conformational orientation in which the metal substituent occupies an eclipsed position relative to the half-filled carbon p orbital and optimally located to interact with it.[4] The absence of line width alternations in the spectra with temperature variation



is also consistent with this symmetric conformation.[5] On the basis of the *g* factor for these radicals,[3] we concluded that the odd electron is delocalized onto the carbon–metal bond hyperconjugatively as well as onto d orbitals of the metal atom (p–d) homoconjugatively to approximately the same extent ($\sim 10\%$).

The allylic adduct resulting from the addition of trialkylstannyl radical to butadiene also exists in a

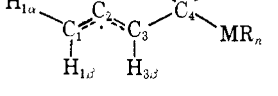
preferred conformation in which the tin nucleus lies over the π orbitals.[6] However, unlike the β protons in substituted ethyl radicals, the two protons on carbon-4 in this allylic radical are magnetically inequivalent at the lowest temperatures. Thus, hindered ro-



tation about the C_3–C_4 bond leads to selective line broadening in the esr spectra taken at higher temperatures. In this paper we analyze the rate of this process by fitting the experimental line shape with that calculated using the density matrix equation of motion. The barrier to rotation is obtained from temperature-dependence studies and compared with those derived for analogous radicals containing Ge, Si, C, S, and O.

Results

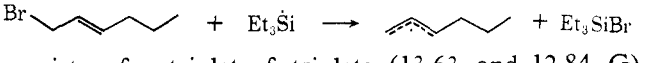
The radicals shown below were generated in solutions containing cyclopropane or mixtures of cyclopropane and ethane to allow for studies at low tem-



MR_n = $-CH_2CH_3$ (**1**)
$-Si(CH_3)_3$ (**2**)
$-Ge(CH_3)_3$ (**3**)
$-Sn(n\text{-}C_4H_9)_3$ (**4**)
$-OC(CH_3)_3$ (**5**)
$-SCH_3$ (**6**)

peratures. The esr results are presented in the following order group by group according to the behavior of their spectra.

The *trans*-Hex-2-en-1-yl Radical, 1. Upon photolysis of the mixture of di-*tert*-butyl peroxide (DTBP), triethylsilane, and *trans*-1-bromohex-2-ene, the radical **1** is formed by metathesis of the alkenyl bromide and the triethylsilyl radical. Its esr spectrum at −130°



consists of a triplet of triplets (13.63 and 12.84 G) further split into two doublets (14.70 and 3.78 G) and a small triplet (0.4 G) with a *g* factor of 2.00263. The central lines of the 12.84 G triplet are broadened. As the temperature is raised, the central lines of the 12.84-G triplet are sharpened and the peak height ratio of the triplet attains the binomial ratio of 1:2:1. These changes are accompanied by an increase of the hyperfine coupling constant (hfcc) of only this triplet (for example, at −54° the hfcc of this triplet is 13.26 G), whereas the other hfcc's and the *g* factor stay constant within the experimental error. All the hfcc's listed in Table I are assigned on the basis of a comparison with those of substituted allyl radicals.[5–7] The temperature dependence of the hfcc of the two protons attached to carbon-4 is shown in Figure 1.

Radical Adducts of Group IVB Metals to Butadiene, 2, 3, and 4. Radicals of **2**, **3**, and **4** are formed when mixtures of the corresponding trialkylmetal hydrides, butadiene, and DTBP are photolyzed. At lower temperatures the spectra of these radicals show four sets of doublets due to $H_{1\alpha}$, H_2, H_4, and $H_{4'}$ split further into

---

(3) T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972).
(4) P. J. Krusic and J. K. Kochi, *ibid.*, **91**, 6161 (1969).
(5) P. J. Krusic and J. K. Kochi, *ibid.*, **93**, 846 (1971).
(6) T. Kawamura and J. K. Kochi, *J. Organometal. Chem.*, **30**, C8 (1971).
(7) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).

$$R_3MH + (CH_3)_3C\dot{O} \longrightarrow R_3\dot{M} + (CH_3)_3COH$$

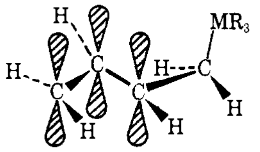
a 1:2:1 triplet due to $H_{1\beta}$ and $H_{3\beta}$, the hfcc's of which are accidentally equivalent. The esr spectrum of the germanium adduct is shown in Figure 2 as an example. The values and assignments of the observed hfcc's and g factors of these radicals are tabulated in Table I. As the temperature is raised, the "inner" two lines of the doublet of doublets corresponding to the splitting by H_4 and $H_{4'}$ become broad and then are broadened out more. When the temperature is raised further, the resonances due to H_4 and $H_{4'}$ coalesce into a triplet with a broad central line and are finally resolved into a 1:2:1 triplet at the highest temperatures. The hfcc's of $H_{1\alpha}$, $H_{1\beta}$, H_2, and $H_{3\beta}$ for these radicals stay almost constant (within ±0.1 G) as the temperature is changed, whereas the hfcc of H_4[8] increases as the temperature is raised as shown in Figure 1. The g factors do not show detectable variations with temperature changes.

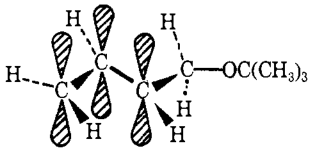
Methylthiyl Radical Adduct to Butadiene, 6. The spectrum of the sulfur radical **6** is observed during photolysis of the mixture of methanethiol, DTBP, and butadiene, as well as during the photolysis of dimethyl disulfide in butadiene.[5] The spectrum shows the same kind of behavior upon changing the temperature as those of radicals **2**, **3**, and **4**. However, the coupling constants for $H_{1\beta}$ and $H_{3\beta}$ of this radical are inequivalent. Table I and Figure 1 give the observed proton hfcc's and the temperature dependence of the hfcc of H_4, respectively.

***tert*-Butoxy Radical Adduct to Butadiene, 5.** Photolysis of the mixture of DTBP and butadiene affords the spectrum of the oxygen radical **5**.[5] The spectrum of this radical showed no line-width alternation at any of the temperatures examined (−150 ∼ −50°) and always consisted of two sets of 1:2:1 triplets due to equivalent coupling constants for $H_{1\beta}$ and $H_{3\beta}$ and two H_4 protons split further into two sets of doublets by $H_{1\alpha}$ and H_2. The observed proton hfcc's and their assignments are summarized in Table I. The temperature dependence of the hfcc of H_4 is shown in Figure 1.

Discussion

Stable Conformations of the Radicals. As shown in Figure 1, values of the hfcc for H_4 in radicals **1**, **2**, **3**, **4**, and **6** decrease as the temperature is lowered. This trend together with the magnitude of $a_{\bar{4}}$ shows[5,9] that all these radicals have as their most stable conformation one in which the carbon–metal bonds are essentially eclipsed with the π orbital on carbon-3 (which contains the odd electron). On the other hand, the magnitude and the negative temperature dependence of $a_{\bar{4}}$ of the oxygen radical **5** imply that the preferred conformation for this radical has the *tert*-butoxy substituent in the nodal plane of the π orbital.[5,9] This symmetric conformation is also consistent with the absence of selective line broadening in the spectrum.





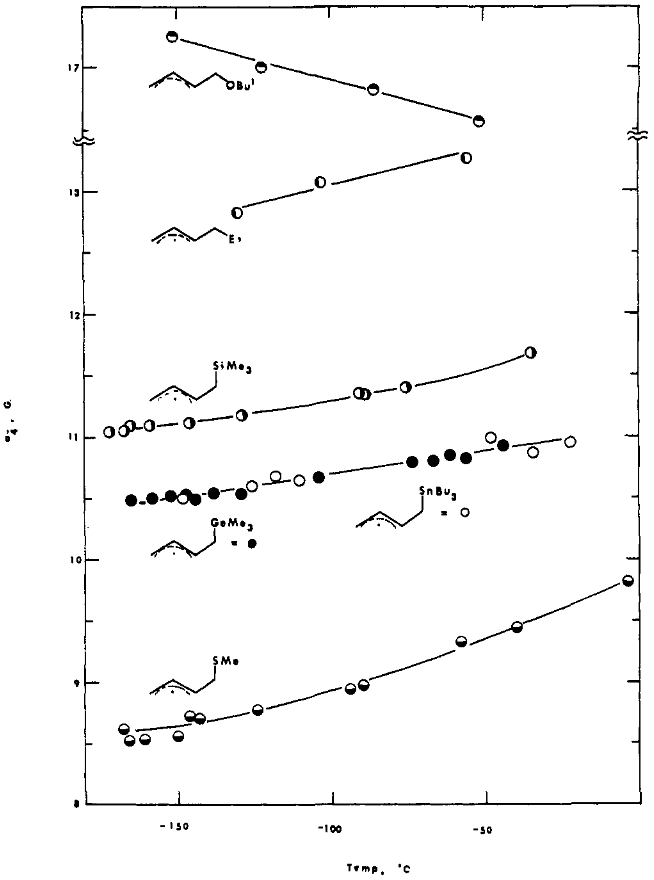


Figure 1. Temperature dependence of $a_{\bar{4}}$, the hyperfine splitting for the protons located on carbon-4 in the radicals $R_nMCH_2CH{=}CH\dot{C}H_2$: (◐) $MR_n = CH_2CH_3$, (◑) $MR_n = Si(CH_3)_3$, (●) $MR_n = Ge(CH_3)_3$, (○) $MR_n = Sn(n\text{-}Bu)_3$, (◒) $MR_n = OC(CH_3)_3$, and (◓) $MR_n = SCH_3$.

The preferred conformations of radicals **2**, **3**, **4**, and **6** can be deduced more precisely from the values of the hfcc's of the two protons attached to carbon-4 at lowest temperatures. The angles θ and θ' which decribe the dihedral angles between the pair of C_4–H bonds and the odd electron orbital at carbon-3 can be obtained from the general expression[6,10]

$$\theta = \cos^{-1}(a_\beta Q/a_\alpha B)^{1/2}, \text{ where } |B/Q| = 2.401 \quad (1)$$

by invoking a simple $\cos^2\theta$ dependence of the β-proton coupling

$$a_\beta = B\rho\cos^2\theta \quad (2)$$

and the McConnell relation for the α-proton coupling.

$$a_\alpha = Q\rho \quad (3)$$

---

[8] When the splitting due to two protons bonded to C_4 is a doublet of doublets, $a_{\bar{4}}$ is taken as the average of a_4 and $a_{4'}$.

[9] J. K. Kochi and P. J. Krusic, *Chem. Soc. Spec. Publ.*, **No. 24**, 147 (1971).

[10] T. Kawamura, M. Ushio, T. Fujimoto, and T. Yonezawa, *J. Amer. Chem. Soc.*, **93**, 908 (1971).

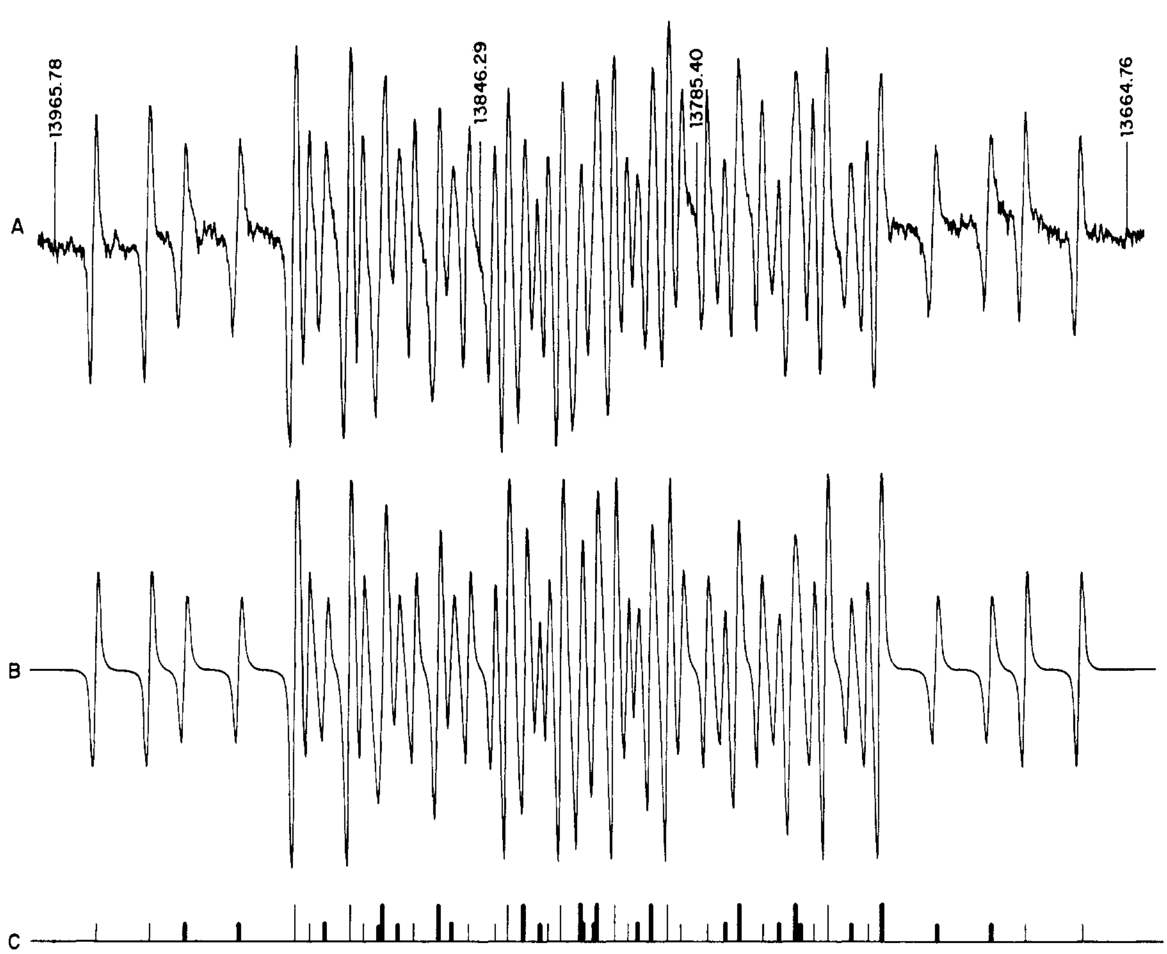


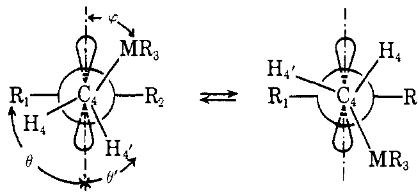
Figure 2. The esr spectrum (A) of $(CH_3)_3GeCH_2CH{=}CH\dot{C}H_2$ at −158°. The simulated spectrum (B) was constructed from the parameters in Table I. The heavy bars in the stick spectrum (C) show the "inner" lines of the doublet of doublets due to H_4 and $H_{4'}$ which are selectively broadened as the temperature is raised until they finally collapse into a 1:2:1 triplet. The proton nmr field markers are in kHz.

The values of θ and θ' together with dihedral angle φ (between the carbon–metal bond and the odd electron orbital on carbon-3) can be evaluated in this manner and are summarized in Table II. In these calculations, φ is obtained from θ and θ' by assuming that the C_3–C_4–M plane bisects the H_4–C_4–$H_{4'}$ angle.

Table II. Dihedral Angles in the Stable Conformations and the Arrhenius Parameters for the Hindered Rotation of $\dot{C}H_2CH{=}CHCH_2MR_n$

MR_n	θ, deg	θ', deg	φ, deg	ΔE, kcal/mol	Log A
CH_2CH_3				2.0 ± 1[a]	12.5–13.5[a]
$Si(CH_3)_3$	65	45	10	3.1	12.6
$Ge(CH_3)_3$	65	47	9	4.0	13.4
$Sn(n\text{-}Bu)_3$	63	47	8	4.8	13.0
$OC(CH_3)_3$	~30	~30	~90[b]	<0[c]	
SCH_3	77	46	15	3.3	12.7

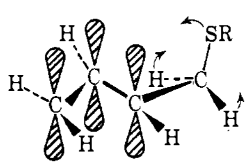
[a] Roughly estimated values. See text. [b] Results from the temperature dependence of $a_{\bar{4}}$ of radical **5**. [c] The conformation with $\varphi \simeq 0°$ is less stable than that with $\varphi \simeq 90°$. Values of θ, θ', and φ are estimated to be reliable to ±5°.



7 8

$R_1 = H;\ R_2 = CH_2{:}CH$
or $R_2 = H;\ R_1 = CH_2{:}CH$

Although the value of φ obtained for radical **6** is larger than that of the group IVB metal-substituted radicals **2**, **3**, and **4**, the value of $a_{\bar{4}}$ of the sulfur-substituted radical is significantly smaller than that of the other radicals. The latter by itself implies that the stable conformation of radical **6** has a smaller value of φ than other radicals. This inconsistency suggests that the simple $\cos^2 \theta$ rule given in eq 2 does not hold for the sulfur-substituted radical. To avoid this dilemma we suggest that carbon-4 is distorted from a tetrahedral configuration which results in a more or less asymmetric bridged structure as its most stable conformation.[5,9,11] However, it should be pointed out that the value of the hfcc for the proton bonded



---

(11) P. D. Readio and P. S. Skell, *J. Org. Chem.*, 31, 759 (1966).

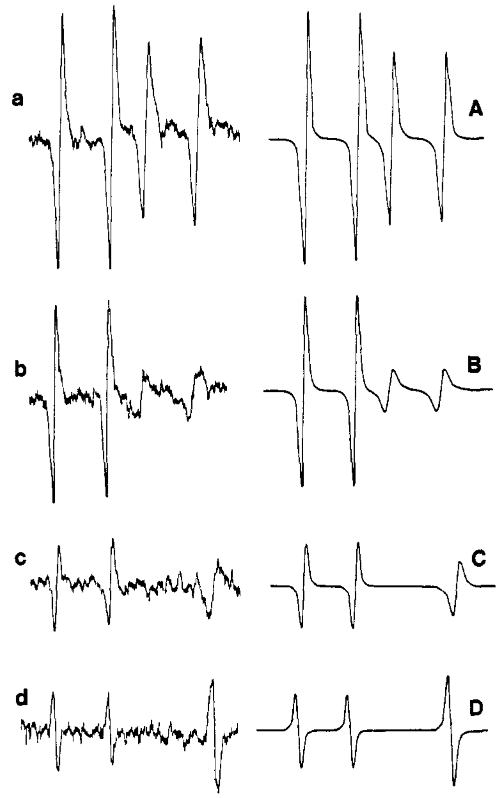


Figure 3. The temperature dependence of the outer three or four lines of the high-field wing of the esr spectrum of $(CH_3)_3GeCH_2CH{=}CH\dot{C}H_2$ at (a) −158, (b) −138, (c) −67, and (d) −44°. The portion of the simulated spectra on the right was obtained with parameters $a_2 = 3.58$ G, $a_4 = 5.84$ G, and $a_{4'} = 15.13$ G. The invariant lines are assumed to be Gaussians (with $\Delta H_{msl} = 0.30$ G) of Lorentzians ($T_2 = 5.4 \times 10^{-7}$ sec). The exchange rates of H_4 and $H_{4'}$ are (A) $\approx 1 \times 10^6$ sec^{-1}, (B) 5×10^6 sec^{-1}, (C) 1×10^9 sec^{-1}, and (D) 4×10^9 sec^{-1}.

to carbon-3 ($a_{3\beta}$) of the sulfur-substituted radical falls in the range of values of $a_{3\beta}$ of other "normal" allyl radicals and indicates that the bridging interaction is probably not large enough to result in a distortion of the planar configuration around carbon-3.

Hindered Rotation About the C_3–C_4 Bond. The temperature-dependent behavior of the hyperfine splitting pattern and the line-width alternation in the esr spectra of radicals **2**, **3**, **4**, and **6** show that the rates of the hindered rotation around the C_3–C_4 bond (which can be expressed as the exchange between conformations **7** and **8**) have the same order of magnitude as the difference between hfcc of two protons on carbon-4 expressed in frequency units, [*i.e.*, $(a_4 - a_{4'}) \times 3 \times 10^6$ sec^{-1}] at the temperatures examined in this study. The exchange rates are calculated by a comparison of the experimental spectra with the simulated spectra, which are obtained by first calculating the line shapes in the usual fashion (see below) using the Lorentzian line shape implied by the simple phenomenological density matrix equation of motion and then numerically convoluting the calculated spectrum with a Gaussian.[12]

High-field wings of spectra of the germanium radical **3** (Figure 2) at various temperatures and the corresponding simulated spectra are shown in Figure 3 as an example. The exchange rates for radicals **2**, **3**, **4**, and **6** are plotted against the reciprocal of the temperature in Figure 4, and the Arrhenius parameters obtained in this manner are listed in Table II.

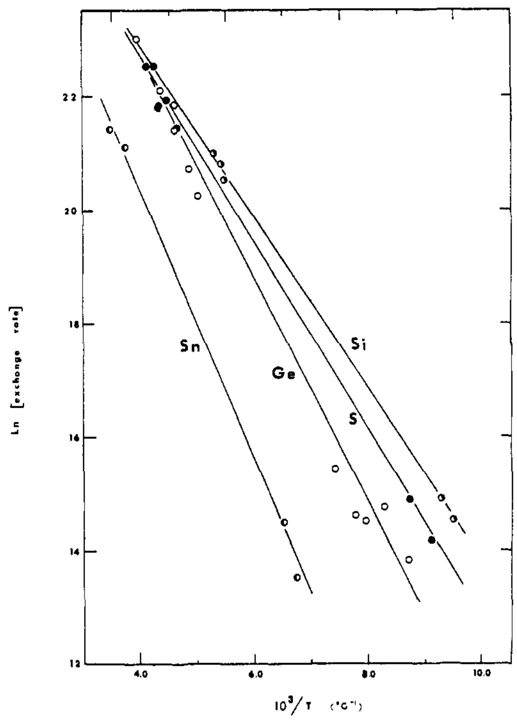


Figure 4. Arrhenius plots for the rates of the hindered rotation of $R_nMCH_2CH{=}CH\dot{C}H_2$: (◑) $MR_n = Si(CH_3)_3$, (○) $MR_n = Ge(CH_3)_3$, (◐) $MR_n = Sn(n\text{-}Bu)_3$, and (●) $MR_n = SCH_3$.

Because of the relatively poor quality of the spectra of the hydrocarbon radical **1**, we could not obtain the spectrum at the low-temperature limit or perform the complete analysis of line-width alternations of this radical. However, the rate of the hindered internal rotation of radical **1** at −106 and −130° was obtained as 6×10^{10} and 2×10^9 sec^{-1}, respectively, from the analysis of the selective line broadening of the central lines of the triplet due to the two H_4 protons by the method employed in a preceding study[6] with the assumed values of $a_4 = 5.8$ G and $a_{4'} = 21.9$ G[13] extrapolated from data of radicals **2**, **3**, and **4**. The energy barrier for the hindered internal rotation of **1** can be obtained as 2 ± 1 kcal/mol from these values and the assumed value for the frequency factor of $10^{13\pm0.5}$.

Origin of the Barriers to Hindered Internal Rotation. In this section we wish to discuss the possible origins of the relatively high barriers to hindered rotation about the C_3–C_4 bond in the radicals **2**, **3**, and **4** in which group IVB metals are present in the β position to the allylic center. Previously[3] we examined interactions between the odd electron and the group IVB metal in a series of β-substituted ethyl radicals $R_3MCH_2\dot{C}H_2$. An analysis of the g factors showed that the odd electron is hyperconjugatively delocalized to the carbon–metal bond as well as homoconjugatively to metal d orbitals to approximately the same extent. The allyl and ethyl systems are comparable since the g factors of the former group correlate well with those of ethyl

---

[12] The low- and high-temperature limit spectra and the lines not affected by the exchange process at intermediate temperatures could best be fit by a Gaussian of Lorentzians. The Gaussian component possibly arose from unresolved long range proton couplings.

[13] These values correspond to $\theta = 80°$, $\theta' = 50°$, and $\varphi = 15°$.

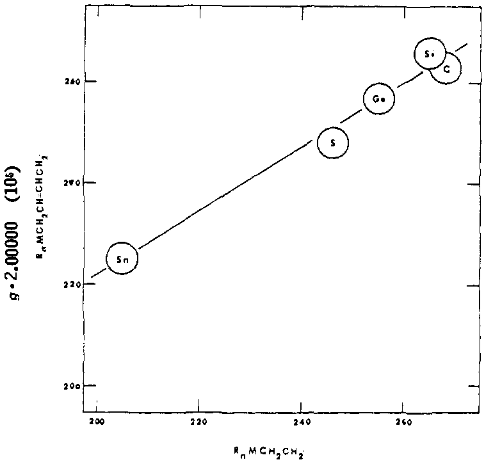


Figure 5. The correlation of the g factors of $R_nMCH_2\dot{C}H_2$ and $R_nMCH_2CH{=}CH\dot{C}H_2$.

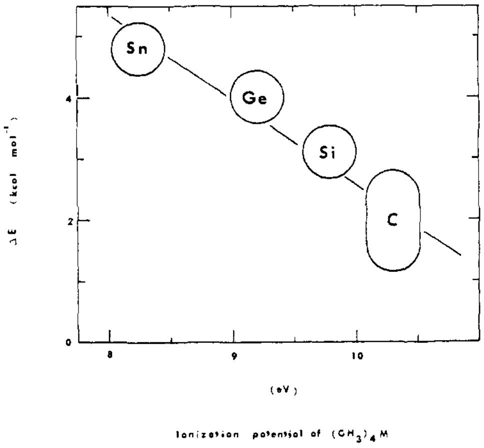


Figure 6. The barriers to hindered internal rotation ΔE in $R_3MCH_2CH{=}CH\dot{C}H_2$ in relation to the ionization potential of $(CH_3)_4M$.

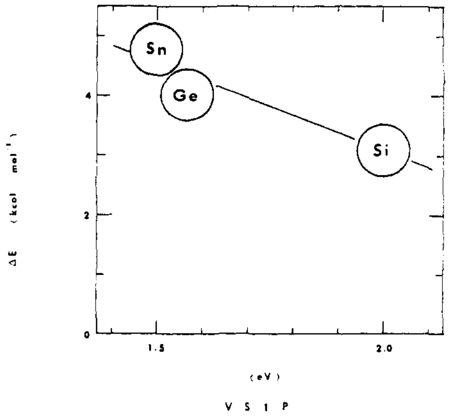


Figure 7. The barrier to hindered internal rotation ΔE in $R_3MCH_2CH{=}CH\dot{C}H_2$ and the valence state ionization potential of d orbitals on the metal (VSIP).

radicals as shown in Figure 5. The slope of 0.6 for the correlation implies that the interactions between the odd electron orbital and the heteroatom of the allyl species are similar to those involved in correspondingly substituted ethyl radicals, except the magnitude of delocalizations in the former is about one-half the odd electron delocalizations involved in the latter radicals. Such a conclusion is consistent with that expected for an extensively delocalized allyl radical in comparison with an alkyl radical.

The *hyperconjugative contribution* to the stabilization of a radical $\dot{C}H_2CH{=}CHCH_2MR_3$ involving the carbon–metal σ bond and the π system is formulated as[14,15]

$$\sum_i \frac{(2 - \nu_i)(H_{i\sigma})^2}{\epsilon_i - \epsilon_\sigma} \tag{4}$$

where i stands for the π orbitals, ϵ_σ represents the energy level of the occupied σ orbital of the carbon–metal bond, $H_{i\sigma}$ expresses the matrix element of the interaction Hamiltonian between the ith π orbital and the σ orbital, and ν_i is the number of electrons occupying the ith π orbital. The value of $(H_{i\sigma})^2$ becomes maximum when φ = 0° and is zero at φ = 90°. The magnitude of $(H_{i\sigma})^2$ for the radical $\dot{C}H_2CH{=}CHCH_2MR_3$ at the stable conformation is invariant from metal to metal as long as φ remains constant [which is true for the group IVB metal-substituted radicals (see Table II)] because $H_{i\sigma}$ arises from the overlap between the π atomic orbital on carbon-3 and the sp^3 hybrid orbital of carbon-4 which is directed toward the metal M. Thus, the hyperconjugative stabilization of these radicals at their stable conformations depends only on the value of ϵ_σ.

Hobrock and Kisner[16] studied the ionization potential, I_p, of a series of tetramethyl derivatives of Si, Ge, and Sn [$(CH_3)_4M$] and showed that the highest occupied molecular orbital of $(CH_3)_4M$ is a carbon–metal bonding orbital. If the energy barrier ΔE measured for the hindered internal rotation about the C_3–C_4 bond arises from the hyperconjugative stabilization of the radicals, then we would expect ΔE to correlate with I_p since hyperconjugation would be lost at the unstable conformation (*i.e.*, $\varphi \simeq 90°$). The trend shown in Figure 6 is indeed consistent with a hyperconjugative interaction between the π system and the carbon–metal σ bond leading to stabilization of the conformation at $\varphi \simeq 0°$.

A (p–d) *homoconjugative contribution* to the stabilization of these radicals may be considered as a delocalization of π electrons onto metal d orbitals and can be expressed as

$$\sum_i \frac{\nu_i(H_{id})^2}{\epsilon_d - \epsilon_i} \tag{5}$$

where all the notations have a significance similar to those in eq 4. In this mechanism, however, values of ϵ_d as well as those of H_{id} vary from metal to metal. Figure 7 shows the relation between the energy barrier of the hindered internal rotation ΔE and valence state ionization potentials[17] (VSIP) of valence-shell d orbitals

---

[14] *Cf.* M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962, Chapter 2.

[15] The hyperconjugative electron release from the π system to the σ antibonding orbital of the C–M bond is not taken into account.[3] *Cf.* W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829, 7476 (1970).

[16] B. G. Hobrock and R. W. Kisner, *J. Phys. Chem.*, **65**, 2186 (1961); **66**, 155 (1962).

[17] The valence state ionization potentials of the d orbitals are estimated from the simple average of all the possible term values of the configuration $(ns)^2(np)^1(nd)^1$ as suggested by Ballhausen.[18] The

of the group IVB metals. The slope of this correlation, however, is opposite to that expected from an energy barrier originating from p–d homoconjugation as given in eq 5. However, differences between d orbital ionization potentials of group IVB metals are small and the change in the stabilization by p–d homoconjugation from metal to metal may not originate from the dependence of ϵ_d on the metal but from difference in the magnitude of $(H_{id})^2$. Values of H_{id} can be estimated[18] as $Ks_{id}(H_{ii} + H_{dd})$ or $K's_{id}\sqrt{H_{ii} \cdot H_{dd}}$, where s_{id} is the overlap integral between the d orbital and *i*th π orbital. In the series of the group IVB metal-substituted radicals, H_{ii} and H_{dd} $[H_{dd} \cong \epsilon_d]$ as well as the shapes of the π molecular orbitals remain almost constant. Thus, the sum of the squares of the overlap integrals between the π atomic orbital on carbon-3 and the metal d orbitals, $(S_{\mathrm{pd}})^2$, reflects the behavior of $(H_{id})^2$. To examine the angular and the metal dependences of $(H_{id})^2$, values of $(S_{\mathrm{pd}})^2$ were calculated from Jaffe's tables[20] by assuming that the orbital exponents of the d orbitals are equal to those of valence-shell s and p orbitals.[21] The calculated values of $(S_{\mathrm{pd}})^2$ for radical **2** at the conformations $\varphi = 0°$ and $\varphi = 90°$ as well as the radical **4** at the conformation $\varphi = 90°$ are 0.015, 0.0072, and 0.0098, respectively. These results show that the magnitude of the stabilization of radical **2** by p–d homoconjugation decreases to one-half its value when the conformation changes from $\varphi = 0°$ to $\varphi = 90°$.[22] We assume that the magnitude of the stabilization of radical **4** also decreases to half when φ increases from 0 to 90°. Values of the energy barrier of the hindered internal rotation were plotted against $(S_{\mathrm{pd}})^2$ calculated at the conformation $\varphi = 90°$ in order to determine whether ΔE arises from the angular dependence of the contribution from p–d homoconjugation. The plot does extrapolate roughly to $\Delta E \simeq 2$ kcal mol^{-1} at $(S_{\mathrm{pd}})^2 = 0$, which corresponds to the value of ΔE estimated for radical **1**. Thus, the possibility that the energy barriers, ΔE, of the radicals originate from an angular dependence of the stabilization due to p–d homoconjugation cannot be excluded.

Group VIB Substituted Radicals. The stable conformation of the oxygen substituted radical, **5**, has the oxygen atom in the nodal plane of the π orbitals, whereas the sulfur–carbon bond of radical **6** is nearly eclipsed with the π orbital at its stable conformation. Furthermore, the nearly eclipsed conformation is 3.3 kcal/mol more stable than the conformation at $\varphi \simeq 90°$. This is a large energy difference when it is compared with the difference in energies between radicals **1** and **2** present in the same rows of the periodic table. Hyperconjugation between the π system and the carbon–sulfur bond, p–d homoconjugation, and p–n homoconjugation are possible interactions in radical **6**. The p–n interaction between the nonbonding electrons and the odd electron orbital was shown to be important in the β-chloroethyl radical.[23] At this juncture, however, we are unable to evaluate the importance of such an interaction in the sulfur adduct.

Conclusions

We conclude from this analysis that the energy barrier for hindered internal rotation in radicals **2**, **3**, and **4** can arise from either (a) hyperconjugation between the π system and the carbon–metal bond or (b) p–d homoconjugation between the π system and the metal d orbitals. If (a) is the mechanism for stabilization, the difference between ΔE of the group IVB substituted radicals and that of the hydrocarbon analog **1** directly measures the hyperconjugative stabilization gained on substitution by the metal. If the stabilization is due to (b), twice the difference between ΔE of the metal-substituted radical and that of **1** reflects p–d homoconjugative stabilization. It is most likely, however, that both factors are important in the stabilization of these radicals. For example, evaluation of the energy terms in eq 4 and 5 for the stable conformation ($\varphi = 0$) of the silicon-substituted radical **2** indicates that hyperconjugation is of the same order of magnitude as p–d homoconjugation (see Experimental Section).

Experimental Section

Esr Measurement. The esr spectrometer and the photolysis equipment were described earlier.[23b] To determine the *g* factor, the X-band microwave frequency was measured with a Hewlett-Packard 5248L frequency counter equipped with 5255A frequency converter. The magnetic field strength was measured with a Harvey-Wells nmr precision gaussmeter G-502. The magnetic field difference between the esr sample position and the point of the nmr probe was repeatedly calibrated daily by measuring the field difference with the perylene cation radical as a standard. The *g* factor of perylene cation in concentrated sulfuric acid is reported as 2.002583 (before the second-order corrections).[24] With this method, *g* factors could be determined within an experimental error of ±0.00003.

The esr sample was cooled by a stream of cold nitrogen gas and the temperature was measured by a copper–constantan thermocouple at the point just before the gas enters the cavity. The temperature difference between the sample during photolysis and the nitrogen gas was calibrated by measuring the temperature of *n*-pentane, liquid cyclopropane, or liquid ethane in a sample tube irradiated with the uv lamp and the temperature of the flowing gas. The correction due to the heating by radiation ranged from 2 to 13° depending on the temperature of the flowing stream of cold nitrogen gas. The probable maximum error in the determination of the temperature of the sample is ±5°.

Materials. DTBP was obtained from Shell Chemical Co., washed with acidic aqueous solution of potassium iodate and then water, dried over anhydrous magnesium sulfate, and distilled at reduced pressure. *trans*-1-Bromohex-2-ene was prepared from *trans*-hex-2-en-1-ol (Aldrich) and phosphorus tribromide.[25] Trimethylgermanium hydride was prepared by $NaBH_4$ reduction of trimethylgermanium bromide (Alfa Inorganics Co.).[26] Tri-*n*-butyltin hydride was obtained from tri-*n*-butyltin oxide and methyl hydrogen polysiloxane.[27] All other chemicals were obtained commercially: butadiene (Matheson), triethylsilane (Columbia), cyclo-

---

obtained values are Si, 2.0 eV; Ge, 1.6 eV; and Sn, 1.5 eV. Levison and Perkins[19] have calculated the valence state ionization potential of 3d orbital of Si as 2.04 eV and indicate that the present estimate is acceptable.

(18) C. T. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1964.

(19) K. A. Levison and P. G. Perkins, *Theor. Chim. Acta*, 14, 206 (1969).

(20) (a) H. H. Jaffe and G. O. Deak, *J. Chem. Phys.*, 21, 196 (1953); H. H. Jaffe, *ibid.*, 21, 258 (1953). (b) Convenient tables to calculate the other p–d overlap integrals were not available to us.

(21) *Cf.* the s–p–d approximation by D. P. Santry and G. A. Segal, *J. Chem. Phys.*, 47, 158 (1967).

(22) Traylor, *et al.*,[15] have concluded, however, from their studies for carbonium ions that the large electronics effects due to heteroatoms in the β position are removed if they are located in the nodal plane of the p orbital at C_α.

(23) (a) T. Kawamura, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 1752 (1972); (b) D. J. Edge and J. K. Kochi, *ibid.*, **94**, 6485 (1972).

(24) B. G. Segal, M. Kaplan, and G. K. Fraenkel, *J. Chem. Phys.*, 43, 4191 (1965).

(25) E. Truscheit and K. Eiter, *Justus Liebigs Ann. Chem.*, **658**, 65 (1962).

(26) J. E. Griffiths, *Inorg. Chem.*, 2, 375 (1963).

(27) K. Itoi and S. Kumano, *Kogyo Kagaku Zasshi*, 70, 82 (1967).

propane (Matheson), ethane (Matheson), trimethylsilane (Columbia), and methanethiol (Eastman).

Esr Line-Shape Calculations. Esr line shapes in the presence of exchange were calculated using the phenomenological density matrix equation of motion of Kaplan[28] and Alexander.[29] In those cases where the spectra are first order, considerable simplification is possible and the density matrix method reduces to the equations given by Sack.[30] Since the esr spectra in this study are very nearly first order (as is usually the case for organic free radicals), this approximation was used in the present analysis. Details concerning the esr line-shape calculations are given elsewhere.[31,32]

The spectra at the low- and high-temperature limits and the lines not affected by the exchange process at intermediate temperature could be fitted best by a Gaussian of Lorentzians. The Gaussian component is assumed to arise mainly from unresolved long-range proton couplings (the binomial coefficients of n approach a Gaussian function for large n). These long-range couplings should be invariant to the exchange process so that the esr line shapes in the presence of exchange can be obtained by first calculating the line shapes in the usual fashion using the Lorentzian line shape implied by the simple phenomenological density matrix equations of motion and then numerically convoluting the calculated spectrum with a Gaussian.

The exchange rates were obtained by a visual comparison of the observed and calculated spectra. The line shapes in the absence of exchange were first obtained by visually fitting one of the lines invariant to the exchange process. The exchange rate was then varied until a good fit at the exchanging lines was also obtained. In most cases the complete spectrum was not fitted; instead, several of the lines near the wings of the spectrum were used.

Calculated Stabilization of Radical 2. The energy by which the silicon-substituted radical, **2**, is stabilized due to hyperconjugation and p–d homoconjugation can be calculated with the aid of eq 4 and 5, respectively. The interaction between the odd electron orbital (the highest occupied orbital or the lowest half-occupied orbital) and the carbon–silicon bonding orbital or the silicon d orbitals is taken into account. To estimate the values of $H_{i\sigma}$ and H_{id}, the following equations were used

$$H_{i\sigma} = \frac{K}{2}S_{i\sigma}(H_{ii} + H_{\sigma\sigma})$$

$$H_{id} = \frac{K}{2}S_{id}(H_{ii} + H_{dd}) \qquad (6)$$

$$K = 1 \sim 2$$

where H_{ii}, $H_{\sigma\sigma}$, and H_{dd} are evaluated as the negative value of ionization potentials of the allyl radical (−8.15 eV),[33] that of $(CH_3)_4Si$ (−9.8 eV),[16] and the (negative) valence state ionization potential of the 3d orbital (−2.0 eV),[17] respectively. The overlap integral between the odd electron orbital ($\sqrt{1/2}\pi_1 - \sqrt{1/2}\pi_3$; π_1 and π_3 are the π atomic orbitals on C_1 and C_3) and the carbon–silicon bonding orbital ($\sqrt{1/2}\,\chi_4 + \sqrt{1/2}\chi_{Si}$; χ_4 and χ_{Si} are the sp^3 orbitals forming the carbon–silicon bond) is calculated to be 0.080 at the conformation of $\varphi = 10°$. The overlap integral between the odd electron orbital and the d orbitals is calculated as mentioned in the text. The odd electron orbital energy ϵ_i in eq 4 was equated to the negative value of the electron affinity of the allyl radical (−1.82 eV)[34] and ϵ_i in eq 5 to the negative value of the ionization potential of the allyl radical (−8.15 eV). Values of ϵ_σ and ϵ_d were evaluated as $H_{\sigma\sigma}$ and H_{dd}. The values obtained for the hyperconjugative and homoconjugative stabilizations of radical **2** at the eclipsed conformation are 1.5 ∼ 7 and 0.6 ∼ 3 kcal/mol (that is, the contribution to ΔE from the angular dependence of the p–d homoconjugation is 0.3 ∼ 1.5 kcal/mol), respectively. These calculated values are acceptable when compared with the observed energy barrier to the hindered internal rotation in Table II. Although the calculation of p–d homoconjugation is less reliable, the stabilization due to hyperconjugation and p–d homoconjugation would have the same order of magnitude.

Acknowledgment. T. K. wishes to thank the National Science Foundation for generous financial support of this research.

---

[28] J. I. Kaplan, *J. Chem. Phys.*, **28**, 278 (1958); **29**, 462 (1958).

[29] S. Alexander, *ibid.*, **37**, 967, 974 (1962); **38**, 1787 (1963); **40**, 2741 (1964).

[30] R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

[31] P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971).

[32] P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *J. Amer. Chem. Soc.*, **93**, 4701 (1971).

[33] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. J. Herron, and K. Draxl, *Nat. Bur. Stand.* (*U. S.*), *Circ.*, **No. 26**, (1969).

[34] J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, **36**, 21 (1962)

Conformational Analysis. XXVI. Conformational Equilibria in 5,5-Disubstituted 1,3-Dioxanes[1]

Ernest L. Eliel*[2a] and Rudyard M. Enanoza[2b]

Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received March 3, 1972*

Abstract: Thirteen pairs of diastereoisomers of 5,5-disubstituted 2-isopropyl-1,3-dioxanes were equilibrated by means of boron trifluoride or polystyrenesulfonic acid ("Amberlyst-15"). The geminal substituents were methyl–ethyl, methyl–isopropyl, methyl–cyclohexyl, methyl-*tert*-butyl, ethyl–isopropyl, methyl–phenyl, ethyl–phenyl, methyl–hydroxyl, methyl–methoxyl, methyl–nitro, methyl–hydroxymethyl, methyl–methoxymethyl, and methyl–carbomethoxyl. In most cases, conformational free energies for geminal substituents were found not to be additive. Potential reasons are discussed.

A large number of conformational energies (Scheme I, R = H) for monosubstituted cyclohexanes have been determined since 1955.[3] In contrast, little is known about geminally disubstituted cyclohexanes and, in particular, whether the conformational energies for geminal substituents may be considered to b

---

[1] Paper XXV: R. J. Abraham, H. D. Banks, E. L. Eliel, O. Hofer, and M. K. Kaloustian, *J. Amer. Chem. Soc.*, **94**, 1913 (1972).

[2] (a) Address correspondence to Department of Chemistry, University of North Carolina, Chapel Hill, N. C. 27514. (b) From the Ph.D. dissertation of R. M. Enanoza, University of Notre Dame, Notre Dame, Ind., 1970.

[3] *Cf.* E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley-Interscience, New York, N. Y 1965; J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).