

## An ESR study of the conformation of the transient germanium-centred tris-(2-phenyl-2-methylpropyl)germyl radical

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### Abstract

ESR data are given for the tris-(2-phenyl-2-methylpropyl)germyl (trineophylgermyl) radical. At  $T > 60^\circ\text{C}$ , the spectrum shows a septet due to the interaction of the unpaired electron with the six methylene protons, indicating their equivalence on the ESR time scale. As the temperature is lowered to  $-120^\circ\text{C}$  an alternating linewidth effect is observed, indicating the inequivalence of the two protons of the methylene groups. This inequivalence shows that the radical has a pyramidal structure which is rigid on the ESR time scale at low temperatures. The exchange of the methylene protons between the two inequivalent positions is caused by hindered rotation around the C–Ge bonds. The preferred conformation of the radical has been determined and compared with those of similar tin-centred radicals. From the line broadening, an activation energy of  $5.4 \pm 0.8$  kcal/mol for this exchange, and a lifetime of the conformation of  $3.6 \pm 0.3 \cdot 10^{-10}$  s at  $23^\circ\text{C}$  have been determined.

### Introduction

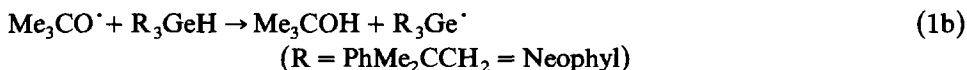
Reactions of chiral tin and germanium hydrides involving free radicals lead to optically active products [1,2], indicating a pyramidal conformation for stannyl and germyl radicals  $\text{R}_3\text{Sn}^\cdot$  and  $\text{R}_3\text{Ge}^\cdot$ , and this has been confirmed by many workers using the ESR spectra of solids [3]. In solution, the non-planar structure of a tin-centred radical was first demonstrated in the case of the trineophylstannyl radical ( $\text{R} = \text{PhMe}_2\text{CCH}_2$ ) which at room temperature shows a septet caused by interaction of the unpaired electron with the six methylene protons. At temperatures below  $40^\circ\text{C}$  an alternating linewidth effect is observed in the septet, indicating the inequivalence of the two methylene protons in each neophyl group having been explained in terms of the non-planar structure of the radical combined with hindered rotation around the Sn–C bonds [4]. This agrees with the observation that

the stannyl radicals  $R_3Sn^\cdot$  in which R is the bulky group  $Ph_2MeCCH_2$  or  $Ph_3CCH_2$  show inequivalent methylene protons (two groups of three equivalent protons) at low temperatures and six equivalent protons at high temperatures [5]. The first germanium-centred radical observed in solution was  $Me_3Ge^\cdot$  [6]. The small value of the hyperfine splitting in  $Me_3Ge^\cdot$ , 0.55 mT, which compares with 2.27 mT for  $Me_3C^\cdot$ ; is presumably partly due to the non-planarity of the radical [6]. Furthermore, the methylene protons of  $(Me_3CCH_2)_2MeGe^\cdot$  and  $(Me_3SiCH_2)_2MeGe^\cdot$  are inequivalent, indicating a pyramidal structure [7]. In contrast, in the trineopentylstannyl ( $R = Me_3CCH_2$ ) [5] and the trineopentylgermyl radical [7] there is free rotation around the Sn-C and Ge-C bonds.

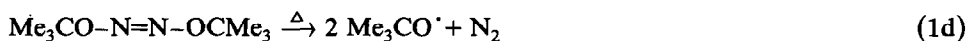
In seeking to confirm these conclusions and to obtain more information of the lifetime of the conformation adopted by the radical, we judged that a quantitative interpretation of alternating linewidth effects would be helpful. This is difficult in the case of the trineophylstannyl radical, since the ESR linewidth is about equal to the proton splitting constant. However, the ESR linewidths for germanium-centred radicals are about half and the splitting constants about twice as large as those for stannyl radicals [8,9]; thus this study was focussed on the ESR spectra of the trineophylgermyl radical [10].

## Results

The radical was generated by hydrogen abstraction from the corresponding germanium hydride by the following reaction sequence at  $-120^\circ C < T < +140^\circ C$ :



The radical was also observed when the  $Me_3CO^\cdot$  was generated thermally ( $80^\circ C$ ):



The radical was not detected when the dimer was heated to  $190^\circ C$  in the cavity of the spectrometer [10]:



ESR spectra recorded at various temperatures for trineophylgermanium hydride/di-t-butyl peroxide (1/2) mixtures are shown in Fig. 1, and the corresponding data in Table 1.

At  $+140^\circ C$ , the spectrum shows a septet due to the interaction of the unpaired electron with the six methylene protons, which are obviously equivalent. When the temperature is lowered below  $35^\circ C$ , there is a selective line broadening; the second, fourth and sixth lines are broadened, indicating inequivalence of the two methylene protons in each neophyl group and a rapid exchange of the two protons between equivalent positions. At  $-20^\circ C$ , these three lines can no longer be detected, and this is the case down to  $-80^\circ C$ . From the temperature dependence of the linewidth

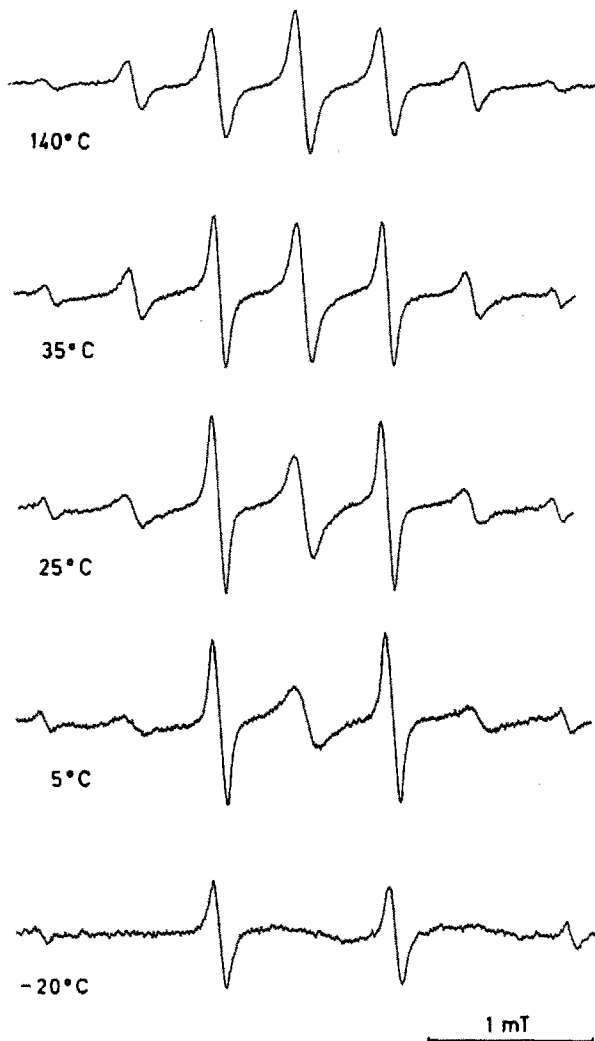


Fig. 1. ESR spectra of the trineophylgermyl radical in trineophylgermanium hydride/di-t-butyl peroxide (1/2) mixtures.

difference of the first and the fourth lines, we have determined the activation energy for the exchange to be  $5.4 \pm 0.8$  kcal/mol. From the line broadening at  $23^\circ\text{C}$ , the lifetime of the preferred conformation is calculated to be  $3.6 \pm 0.3 \cdot 10^{-10}$  s if fast exchange and Lorentzian line shapes are assumed [11].

Figure 2 shows the temperature dependence of the proton splitting constant. For the low temperature spectra the values of half of the distance between the first, third, fifth and seventh line were determined. The values of the splitting constant thus obtained show a distinct decrease with increasing temperature from 0.565 mT at  $-60^\circ\text{C}$  to 0.510 mT at  $+140^\circ\text{C}$ .

In order to obtain spectra at still lower temperatures, n-pentane was used as a solvent. Even at  $-120^\circ\text{C}$ , the spectrum shows four lines for trineophylgermanium

Table 1  
ESR data of the trineophylgermyl and related radicals

Radical	$T$ ( $^{\circ}\text{C}$ )	$g$ value	$a_{\text{H}}^{\text{CH}_2}$ (mT)	Reference	Remarks
$(\text{PhMe}_2\text{CCH}_2)_3\text{Ge}^{\cdot}$	+140	2.0096	0.510	this work	free rotation
	-60	2.0096	0.565	this work	hindered rot.
$(\text{Me}_3\text{CCH}_2)_3\text{Ge}^{\cdot}$	-120	2.0107	0.545	7	free rotation
$\text{Me}_3\text{Ge}^{\cdot}$	-70	2.0104	0.55	6	free rotation
$(\text{Me}_3\text{CCH}_2)_3\text{Sn}^{\cdot}$	-70	2.0170	0.34	5	free rotation
$(\text{PhMe}_2\text{CCH}_2)_3\text{Sn}^{\cdot}$	+25	2.0150	0.31	4	free rotation
	-20	2.0150		4	hindered rot.
$(\text{Ph}_2\text{MeCCH}_2)_3\text{Sn}^{\cdot}$	+90	2.0145	0.30	5	free rotation
	-20	2.0145	0.12;	5	fixed conforma-
$(\text{Ph}_3\text{CCH}_2)_3\text{Sn}^{\cdot}$			0.80		tion ( $\omega = 60^{\circ}$ , 120)
	+120	2.0145	0.33	5	free rotation
	+25	2.0145	0.08;	5	fixed conforma-
			0.60		tion ( $\omega = 90^{\circ}$ , 210)
$\text{Me}_3\text{Sn}^{\cdot}$	-80	2.0163	0.31	9	free rotation

hydride/di-*t*-butyl peroxide/*n*-pentane (1/1/10) mixtures, as can be seen from Fig. 1 at  $-20^{\circ}\text{C}$  ( $a_{\text{H}}$  0.56 mT). The lines are somewhat broader, perhaps indicating an additional unresolved splitting.

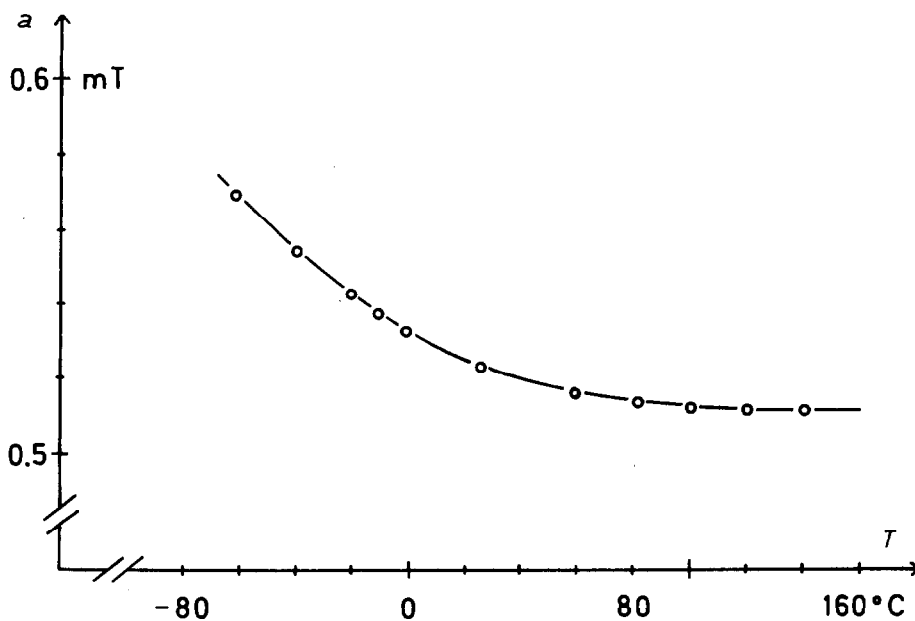


Fig. 2. Temperature dependence of the methylene proton splitting in the trineophylgermyl radical in trineophylgermanium hydride/di-*t*-butyl peroxide (1/2) mixtures.

## Discussion

The inequivalence of the methylene protons in the trineophylgermyl radical can be understood if the non-planarity of the radical is taken into account and the radical is assumed to adopt an asymmetric conformation (see Fig. 3a). Since the slow exchange limit could not be observed, a fixed conformation cannot be assigned without further assumptions; Fig. 3a has to be interpreted in such a way that the two protons have positions below and above the pyramid formed by the three C–Ge bonds. This type of interpretation has also been offered for the ESR spectrum of the trineophylstannyl radical [4] (see Table 1). Symmetric conformations, such as that in Fig. 3b, can be excluded; conformations of that kind are present in the tribenzylgermyl radical [12], which thus has equivalent methylene protons and does not show any line broadening effects.

The exchange of the two methylene protons indicated by the alternating line-width effect might be caused by hindered rotation around the C–Ge bonds or by inversion of the germanium atom through the plane defined by the three carbon atoms next to the germanium. A distinction between these two possibilities cannot be made from the ESR spectra of the trineophylgermyl radical alone, but the latter possibility is unlikely in view of Ingold's recent report of an activation energy of 7 kcal/mol for inversion in the case of the chiral 1-naphthylphenylmethylgermyl radical, which is a little higher than our value of 5.4 kcal/mol and a rate constant of  $9.6 \cdot 10^8 \text{ s}^{-1}$  at  $80^\circ\text{C}$  [13] which is somewhat lower than our value of  $2.8 \cdot 10^9 \text{ s}^{-1}$  at  $23^\circ\text{C}$  corresponding to a value of  $1.2 \cdot 10^{10} \text{ s}^{-1}$  at  $80^\circ\text{C}$ . Furthermore, the splitting constant is similar to that of  $(\text{Me}_3\text{CCH}_2)_3\text{Ge}^\cdot$  as well as to those of different tri-*n*-alkylgermyl radicals ( $0.5 \text{ mT} < a_{\text{H}} < 0.6 \text{ mT}$ ) with free rotation (Table 1 [8]). Thus, and by comparison with the ESR spectra of similar stannyl radicals (Table 1) we conclude that the selective line broadenings are caused by hindered rotation, with the implication that the pyramidal structure is fixed on the ESR time scale. All the four tin-centred radicals  $\text{R}_3\text{Sn}^\cdot$  [ $\text{R} = \text{Ph}_m\text{Me}_n\text{CCH}_2$  ( $m + n = 3$ ;  $m, n = 0-3$ )] show septets caused by interaction with six equivalent protons at high temperatures, with the coupling constants in the small range 0.30–0.34 mT. These

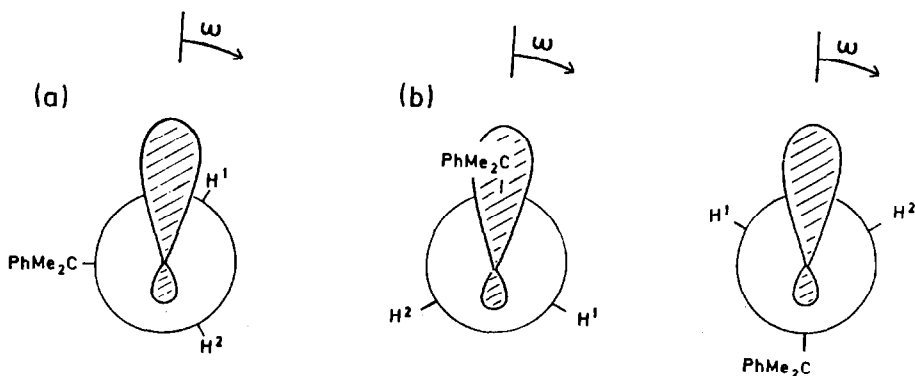


Fig. 3. Asymmetric (a) and symmetric (b) conformations of the trineophylgermyl radical; only a single neophyl group is shown for the sake of clarity.  $\omega$  defines the angle of rotation of the methylene groups (see text).

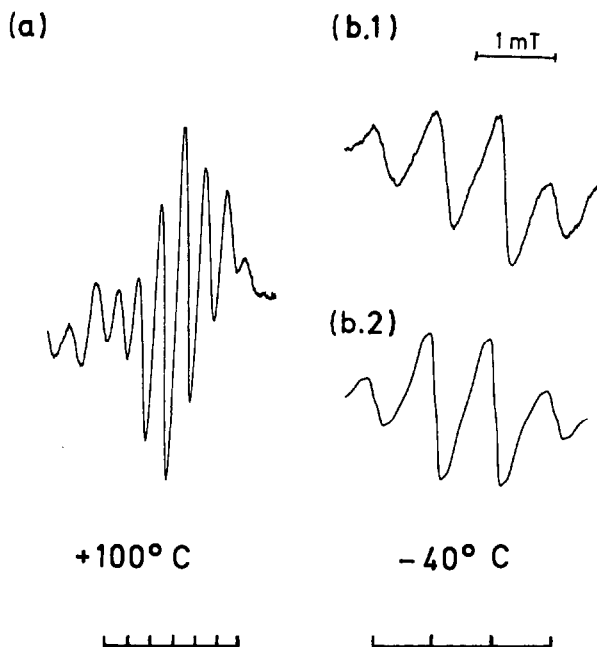


Fig. 4. ESR spectra of  $(\text{Ph}_2\text{MeCCH}_2)_3\text{Sn}^\cdot$  at (a)  $T$   $100^\circ\text{C}$  and (b.1)  $T$   $-40^\circ\text{C}$ . The low field lines are due to the presence of an impurity. The spectrum given in (b.2) is calculated with  $a_{\text{H}}(1)$  0.12 mT,  $a_{\text{H}}(2)$  0.80 mT ( $\Delta H$  0.15 mT).

values are identical with those observed for simple trialkyltin radicals such as trimethylstannyl and tri-*n*-butylstannyl [9], which correspond to the free rotation situation. At low temperatures,  $(\text{Me}_3\text{CCH}_2)_3\text{Sn}^\cdot$  ( $m = 0$ ) also shows equivalent protons, and the others selective line broadening ( $m = 1$ ) and fixed conformations ( $m = 2, 3$ ). Figure 4 shows ESR spectra of the last but one ( $m = 2$ ) at  $T$   $+100^\circ\text{C}$  (septet) and  $T$   $-40^\circ\text{C}$  (quartet of unresolved quartets). From these spectra it is concluded that the equivalence of the methylene protons at high temperatures is undoubtedly caused by free rotation; the spectrum would show a septet at high temperatures with a coupling constant of 0.46 mT, which is half the sum of the low temperature values of 0.12 mT and 0.80 mT, if the equivalence of the protons were caused by inversion at the radical center, whereas the observed value was only 0.30 mT.

The preferred conformation of the trineophylgermyl radical is now discussed. The precise relationship between the  $\beta$ -proton splittings in germyl radicals and the angle  $\omega$  between the axis of the semioccupied radical orbital and the C-H bond (see Fig. 3) is not known. A significant difference between the coupling constants for  $0^\circ < \omega < 90^\circ$  on the one hand and  $180^\circ > \omega > 90^\circ$  on the other hand has been revealed by INDO calculations on the non-planar carbon-centred radical 2-methyl-1,3-dioxolan-2-yl ([14], see Table 2), and the results are used below to analyse the methylene proton splittings in the trineophylgermyl radical, a procedure which has been used for determining the conformations of the stannyl radicals given in Table 1 [5,15\*]. The calculations indicated a free rotation value of 1.331 mT for the

\* Reference number with asterisk indicates a note in the list of references.

Table 2

Results of INDO calculations of the  $\beta$ -proton splittings in the 2-methyl-1,3-dioxolan-2-yl radical (I) and germyl radicals (II) for different values of  $\omega^a$

$\omega$ ( $^\circ$ )	$a_{\beta,I}$ (mT)	$a_{\beta,II} = a_{\beta,I} \cdot \frac{0.54}{1.331}$ (mT)
0	1.89	0.77
30/330	1.33	0.54
60/300	0.32	0.13
80/280	0.01	0.01
90/270	0.05	0.02
100/260	0.24	0.10
120/240	1.04	0.42
140/220	2.14	0.87
150/210	2.63	1.07
160/200	3.01	1.21
180	3.34	1.35

<sup>a</sup>  $\omega$  defines the angle of rotation of the  $\beta$  protons (see Fig. 3 and text).

carbon-centred radical. Couplings based on a free rotation value of 0.54 mT for germyl radicals [8] are given in the second row of Table 2. If a fixed conformation is assumed the relation  $1/2 (a(H^1) + a(H^2)) = 0.54$  mT must be fulfilled which is the case for  $\omega = 90^\circ$  ( $H^1$ ),  $210^\circ$  ( $H^2$ ) and  $\omega = 150^\circ$  ( $H^1$ ),  $270^\circ$  ( $H^2$ ) (see Fig. 5a,d). An exchange between the two conformations leads to the observed linewidth effects.

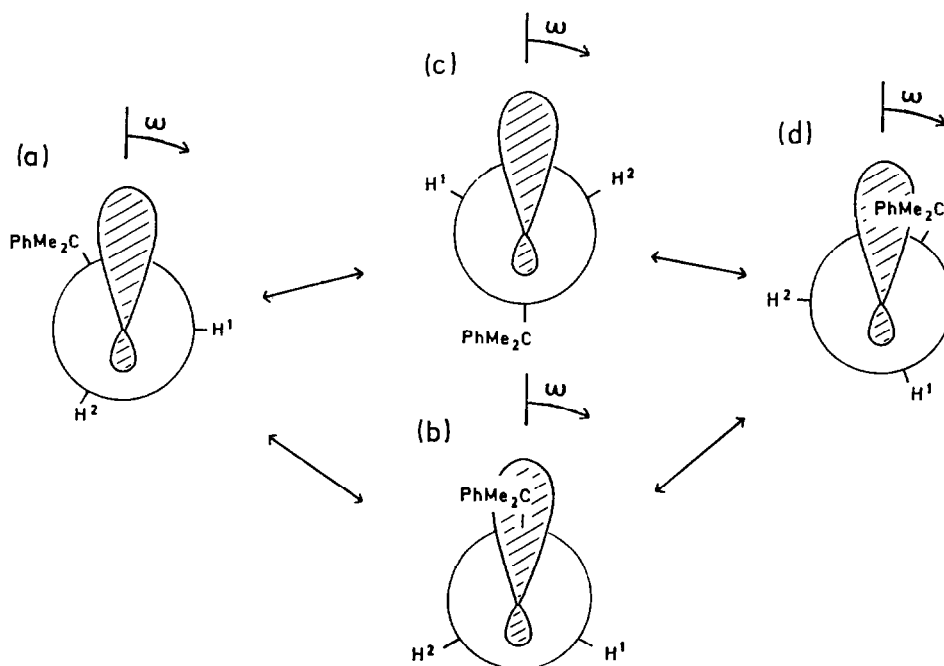


Fig. 5. Preferred conformations (a,d) and possible intermediate states (b,c) of the trineophylgermyl radical.

The two possible intermediate states between the preferred conformations are shown in Fig. 5b,c. Conformation 5b with  $\omega(\text{H}^1) = 120^\circ$  and  $\omega(\text{H}^2) = 240^\circ$  should show an averaged splitting constant  $1/2(a(\text{H}^1) + a(\text{H}^2))$  of 0.42 mT, conformation 5c with  $\omega(\text{H}^1) = 300^\circ$  and  $\omega(\text{H}^2) = 60^\circ$  of 0.13 mT. It appears that conformations like 5b and 5c become more populated with increasing temperature which explains the decrease of the splitting constant (see Fig. 2).

### Experimental

The ESR spectra were recorded and analysed as previously described [9]. Di-*t*-butyl peroxide and *n*-pentane were purified by standard methods and distilled before use. Trineophylgermane and hexaneophyldigermane were prepared as previously described [10].

### Acknowledgement

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