

mass spectrum showed the parent ion at  $m/e$  280; exact mass, 280.199867 (calcd, 280.199837).

*Anal.* Calcd for  $C_{19}H_{23}BO$ : C, 81.44; H, 8.99; B, 3.86. Found: C, 81.70; H, 9.23; B, 3.97.

**Hydroxybis(4-methoxy-2,6-dimethylphenyl)borane.** Magnesium turnings (1.00 g, 41.5 mmol) and 70 ml of dry tetrahydrofuran were placed in a three-necked flask equipped with a dropping funnel, mechanical stirrer, condenser, and nitrogen inlet. After heating this mixture at reflux for 5 min, a solution of 4-methoxy-2,6-dimethylbromobenzene (9.0 g, 41.5 mmol) in 50 ml of tetrahydrofuran was added dropwise. The solution was heated to reflux during the addition period (ca. 1 hr) and for 30 min after addition was complete. The resulting brown solution was cooled to  $-10^\circ$ , and a solution of boron trifluoride etherate (2.8 ml, 22.0 mmol) in 30 ml of anhydrous ether was added dropwise over a period of 15 min. When addition was complete, the pale yellow solution was refluxed for 15 min and then poured onto crushed ice containing 5% HCl. The organic material was extracted with ether and dried ( $MgSO_4$ ), and the solvent was distilled at reduced pressure. The resulting white solid was recrystallized from carbon tetrachloride to yield 4.0 g (65%) of the desired product, mp  $121-123^\circ$ . The  $^1H$ -nmr spectrum showed absorptions at  $\delta_{CS_2}^{TMS}$  2.13 (12 H, s,  $CH_3$ ), 3.63 (6 H, s,  $OCH_3$ ), 5.97 (1 H, s, OH), and 6.33 (4 H, s, aromatic H). The mass spectrum featured the parent ion at  $m/e$  298; exact mass, 298.174221 (calcd, 298.174016).

*Anal.* Calcd for  $C_{18}H_{23}BO_3$ : C, 72.50; H, 7.77; B, 3.63. Found: C, 72.33; H, 7.53; B, 3.90.

**Bis(4-methoxy-2,6-dimethylphenyl)methoxyborane**, mp  $76-77^\circ$ , was prepared from hydroxybis(4-methoxy-2,6-dimethylphenyl)borane and methanol in 89% yield in a manner similar to that described for the preparation of **2**. The  $^1H$ -nmr spectrum featured absorptions at  $\delta_{CS_2}^{TMS}$  2.14 (12 H, s,  $CH_3$ ), 3.63 (3 H, s,  $BOCH_3$ ), 3.66 (6 H, s,  $ArOCH_3$ ), and 6.50 (4 H, s, aromatic H). Mass spectral analysis showed the parent ion at  $m/e$  312; exact mass, 312.189560 (calcd, 312.189666).

*Anal.* Calcd for  $C_{19}H_{23}BO_3$ : C, 73.09; H, 8.07; B, 3.46; mol wt, 312. Found: C, 73.12; H, 8.14; B, 3.73; mol wt (osmometry), 310.

**Ethylidimesitylborane.** A solution of ethylmagnesium bromide (14.0 mmol) in ethyl ether was added dropwise to an ether solution of fluorodimesitylborane<sup>21</sup> (2.1 g, 7.8 mmol), with stirring. After refluxing for 10 min, the reaction mixture was poured onto crushed

ice, and the organic layer was separated and dried ( $MgSO_4$ ). The solvent was removed by distillation at reduced pressure. The crude product was recrystallized from methanol to yield 1.93 g (88%) of white needles, mp  $77-78^\circ$ . The  $^1H$ -nmr spectrum showed absorptions at  $\delta_{CS_2}^{TMS}$  1.00 (3 H, m,  $CH_2CH_3$ ), 1.77 (2 H, m,  $CH_2CH_3$ ), 2.13 (12 H, s,  $CH_3$ ), 2.18 (6 H, s,  $CH_3$ ), and 6.63 (4 H, s, aromatic H). The mass spectrum featured the parent ion at  $m/e$  278; exact mass, 278.220756 (calcd, 278.220573).

*Anal.* Calcd for  $C_{20}H_{27}B$ : C, 86.33; H, 9.78; B, 3.89; mol wt, 278. Found: C, 86.23; H, 9.79; B, 4.06; mol wt (osmometry), 277.

**Isopropylidimesitylborane**, mp  $92-93^\circ$ , was prepared in 70% yield by a procedure analogous to that described for ethylidimesitylborane. The  $^1H$ -nmr spectrum featured resonances at  $\delta_{CS_2}^{TMS}$  1.05 (6 H, d,  $J_{HH} = 7.1$  Hz,  $CH(CH_3)_2$ ), 2.12 (12 H, s,  $CH_3$ ), ca. 2.15 (1 H, m,  $CH(CH_3)_2$ ), 2.19 (6 H, s,  $CH_3$ ), and 6.65 (4 H, s, aromatic H). The mass spectrum showed the parent ion at  $m/e$  292.

*Anal.* Calcd for  $C_{21}H_{29}B$ : C, 86.30; H, 10.00; B, 3.70. Found: C, 86.14; H, 9.90; B, 3.74.

**Dnmr Measurements.**  $^1H$ -nmr spectra were recorded on a Varian A-60A spectrometer equipped with a variable-temperature accessory. Temperature measurements were based on the chemical-shift separation of the protons of a methanol sample, and utilized the temperature-shift correlation of Van Geet.<sup>38</sup> Temperatures are believed to be accurate to  $\pm 2^\circ$ , although within a given series of measurements smaller differences (ca.  $\pm 0.5^\circ$ ) are considered significant. Saturation of nmr signals was avoided. Dnmr samples were ca. 25% v/v solutions with ca. 5% v/v TMS. Samples were sealed under vacuum in precision thin-wall nmr tubes. The line-shape analyses<sup>17</sup> were performed on an IBM 360/91 computer equipped with a Calcomp plotting accessory.

The line-shape analyses were carried out as described previously.<sup>3</sup> The frequency assignments for the *o*-methyl groups of **2** are ambiguous, since several distinct assignments all give identical calculated spectra which match the experimental spectra. One arbitrary set of static parameters which produced a satisfactory fit to the experimental spectra was:  $a = 2.40$ ,  $b = 1.82$ ,  $c = d = 2.12$ ,  $e = 2.23$ , and  $f = 2.19$  ppm, for the combination of the [2,3]-flip plus the [1,2]- and [1,3]-flips (see Figure 4 for significance of letters).

(38) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970); **40**, 2227 (1968).

## Conformations and Rotation Barriers in Allylcarbinyl Radicals by Electron Spin Resonance

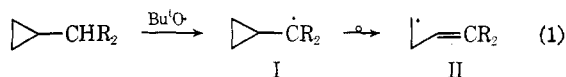
Kuang S. Chen, David J. Edge, and Jay K. Kochi\*

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. Received June 13, 1973

**Abstract:** Allylcarbinyl and 1,1,3-trimethylallylcarbinyl radicals are derived from methylcyclopropane and 1,1,2,2-tetramethylcyclopropane, respectively, by hydrogen abstraction followed by rearrangement of the corresponding cyclopropylcarbinyl intermediate. The isomeric tetramethylcyclopropyl radicals can be generated independently and shown not to be intermediates, and they do not undergo ring opening to allyl radicals. The conformations of allylcarbinyl radicals are deduced from their esr spectra. The pronounced selective line broadening observed in the spectrum of the 1,1,3-trimethylallylcarbinyl radical is attributed to hindered rotation about the  $C_\beta-C_\gamma$  bond and analysis of the line shape using the relaxation matrix theory affords a barrier of 3.5 kcal mol<sup>-1</sup>. Rotation barriers in alkyl radicals are discussed in the light of methods used to extract information from esr data.

Electron spin resonance studies of alkyl radicals derived from a variety of alkylcyclopropanes were reported previously in preliminary form.<sup>1</sup> It was shown that cyclopropylcarbinyl radicals I are readily formed from the hydrocarbons by hydrogen atom abstraction with *tert*-butoxy radicals generated photo-

chemically from di-*tert*-butyl peroxide. These radicals undergo spontaneous rearrangement at temperatures higher than about  $-100^\circ$  to afford allylcarbinyl radicals II according to eq 1. Thus, temperature is an important factor in the observation of the esr spectrum



(1) (a) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, **91**, 1877 (1969); (b) *ibid.*, **91**, 1879 (1969).

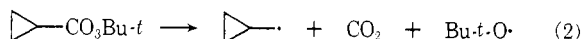
of the isomeric radicals I or II. The metastable cyclopropylcarbinyl radicals could generally be observed only at temperatures lower than  $-140^{\circ}$ . Abstraction of a hydrogen atom attached to a cyclopropane ring is energetically unfavored, and the esr spectra of the isomeric cyclopropyl radicals are not usually observed.<sup>2</sup> 1,1,2,2-Tetramethylcyclopropane appeared to be the exception, since the low-temperature spectrum taken at  $-126^{\circ}$  was attributed<sup>1b</sup> to species III derived by ring opening of the tetramethylcyclopropyl radical IV. The esr spectrum of the trimethylallylcarbinyl radical V was obtained at higher temperatures ( $-54^{\circ}$ ) as expected.

Since the results obtained from tetramethylcyclopropane are unusual, we decided to substantiate the identity of the radicals by generating them unequivocally by a more direct method using the acyl peroxide. We report in this study the esr spectrum of 2,2,3,3-tetramethylcyclopropyl radical IV, and show that it does not rearrange under these conditions. The previous esr assignments, therefore, have been reconsidered. We find that the low-temperature spectrum assigned to species III is, in fact, due to an unusual and severe temperature dependence of the line-width effect in the spectrum of V. The pronounced selective line broadening in the spectrum of V allowed us to examine the conformation of allylcarbinyl radicals and obtain the barrier-to-hindered internal rotation by line-shape analysis.

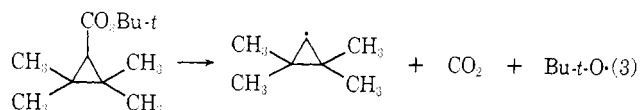
## Results and Discussion

### Cyclopropyl Radicals from the Photolysis of Peresters.

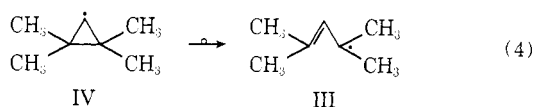
The photolysis of *tert*-butyl peresters in solution constitutes a widely applicable method for generating a specific alkyl radical for an esr investigation.<sup>3</sup> The cyclopropyl radical is produced by photolysis of *tert*-butylperoxy cyclopropanecarboxylate.



The photolysis of the *tert*-butyl perester of 2,2,3,3-tetramethylcyclopropanecarboxylic acid in cyclopropane solutions between  $-48$  and  $-108^{\circ}$  affords the intense and well-resolved esr spectrum shown in Figure 1, which is clearly associated with the 2,2,3,3-tetramethylcyclopropyl radical. The hyperfine splitting



and *g* factor at various temperatures are listed in Table I for the tetramethylcyclopropyl radical as well as the parent cyclopropyl radical. No spectrum of any other species was observed under these conditions, and there is clearly no evidence for ring opening of the 2,2,3,3-tetramethylcyclopropyl radical.



(2) The esr spectrum of the cyclopropyl radical can be produced from cyclopropane as the solvent, provided di-*tert*-butyl peroxide is carefully purified to remove traces of *tert*-butyl hydroperoxide.

(3) (a) R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 5175 (1970); (b) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, No. 24, 147 (1970).

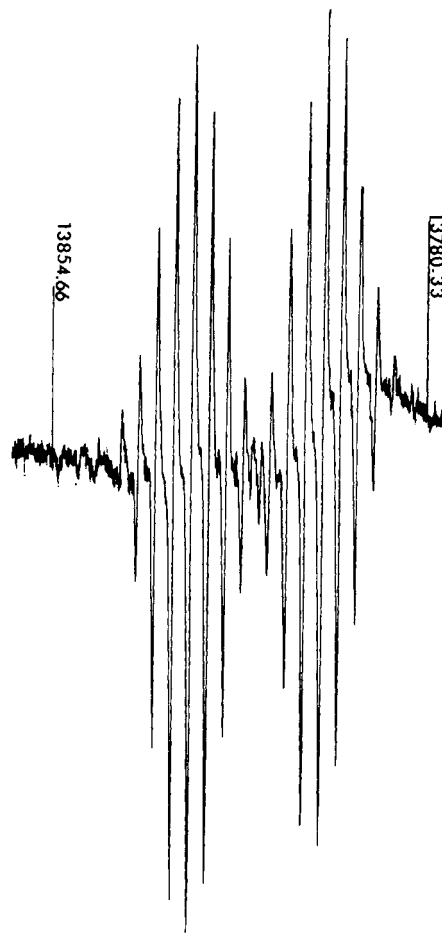


Figure 1. Esr spectrum of the 2,2,3,3-tetramethylcyclopropyl radical generated from the photolysis of the *tert*-butyl perester of 2,2,3,3-tetramethylcyclopropanecarboxylic acid at  $-84^{\circ}$ . Proton nmr field markers are in kHz.

Table I. Esr Parameters for Cyclopropyl Radicals<sup>a</sup>

Radical	Temp, $^{\circ}\text{C}$	Hyperfine splitting, G		<i>g</i>
		<i>a</i> <sub><math>\alpha</math>-H</sub>	<i>a</i> <sub><math>\beta</math>-X</sub>	
2,2,3,3-Tetramethylcyclopropyl	-48	6.31	0.79 <sup>b</sup>	2.00271
	-66	6.28	0.78 <sup>b</sup>	2.00270
	-87	6.20	0.78 <sup>b</sup>	2.00271
	-108	6.15	0.78 <sup>b</sup>	2.00271
Cyclopropyl	-94	6.66	23.54 <sup>c</sup>	2.00276
	-106	6.70	23.56 <sup>c</sup>	2.00278
	-122	6.63	23.49 <sup>c</sup>	2.00275

<sup>a</sup> In cyclopropane solutions. <sup>b</sup>  $\beta$ -CH<sub>3</sub> tridecet. <sup>c</sup>  $\beta$ -H quintet.

Recent chemical studies also indicate that cyclopropyl radicals do not isomerize rapidly to allyl radicals unless they are substituted with stabilizing groups.<sup>4</sup> These results are supported by *ab initio* calculations which suggest a high activation energy for the cyclopropyl-allyl transformation (in excess of 60 kcal mol<sup>-1</sup>).<sup>5</sup>

### Hydrogen Abstraction from Methylcyclopropanes.

(4) (a) K. Watanabe, J. Yamauchi, It. Ohya-Nishiguchi, Y. Deguchi, and H. Takaki, *Bull. Chem. Soc. Jap.*, **45**, 371 (1971); (b) H. M. Walborsky and J. C. Chen, *J. Amer. Chem. Soc.*, **92**, 7573 (1970); J. C. Chen, *Tetrahedron Lett.*, 3669 (1971); (c) J. Jacobus and D. Pensak, *J. Chem. Soc., Chem. Commun.*, 400 (1969); D. B. Ledlie, R. L. Thorne, and G. Weiss, *J. Org. Chem.*, **36**, 2186 (1971); (d) S. Sustmann, C. Ruchardt, A. Bieberbach, and G. Boche, *Tetrahedron Lett.*, 4759, 4765 (1972).

(5) L. Farnell and W. G. Richards, *J. Chem. Soc., Chem. Commun.*, 334 (1973). This estimate is undoubtedly a maximum value.

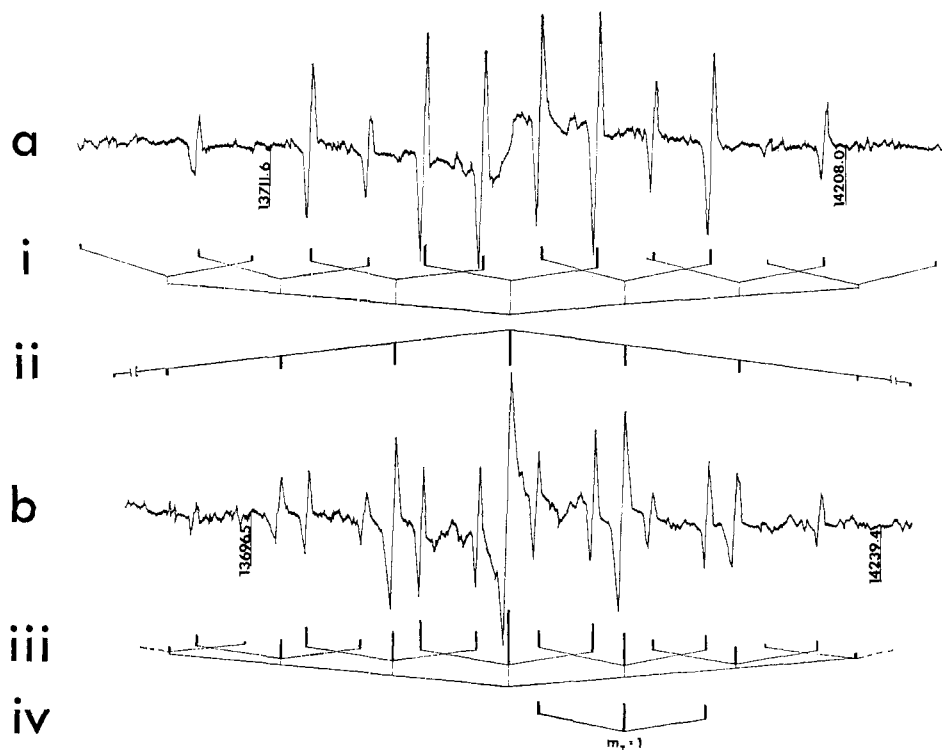


Figure 2. ESR spectra of the 1,1,3-trimethylallylcarbinyl radical obtained from 1,1,2,2-tetramethylcyclopropane and *tert*-butoxy radical at (a)  $-126^\circ$  and (b)  $-54^\circ$ . See text for assignments in stick spectra i-iv.

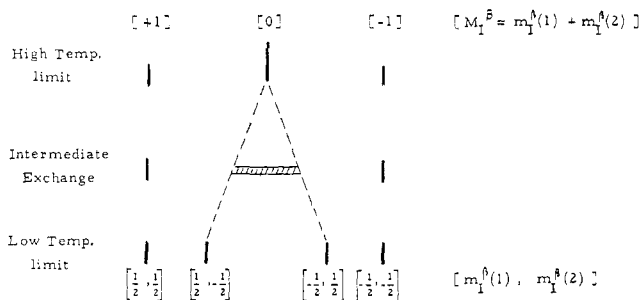
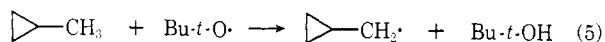
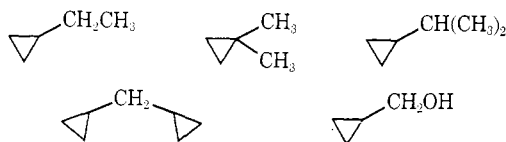


Figure 3. Modulation diagram for the out-of-phase selective line broadening in the  $\beta$  triplet; hatched area indicates broadening.

An alternative method of generating alkyl radicals for esr studies depends on the selective removal of a hydrogen atom from a hydrocarbon with photochemically produced *tert*-butoxy radicals.<sup>3b</sup> Treatment of methylcyclopropane at  $-140^\circ$  under these conditions afforded the spectrum of the cyclopropylcarbinyl radical, which has been confirmed by also generating it from the acyl peroxide.<sup>1</sup>



Other substituted cyclopropanes shown below afforded analogous radicals when treated under the same conditions.<sup>3b</sup>



On the other hand, 1,1,2,2-tetramethylcyclopropane at  $-126^\circ$  gave the well-resolved esr spectrum shown in Fig-

ure 2a. The hyperfine splittings in the spectrum could be readily (and were previously<sup>1b</sup>) interpreted as consisting of a 23.10 G septet of 34.94 G doublets as shown in the accompanying stick diagram (i). The spectrum shown in Figure 2b is obtained at higher temperature ( $-54^\circ$ ), and was assigned to the superposition of the spectrum in Figure 2a onto a new spectrum illustrated in stick diagram (ii), consisting of a nonet (*i.e.*, nine lines with  $a_H = 23.02$  G) in which the two "wing" lines are unobserved.

There is an alternative interpretation, however, in which the spectrum in Figure 2b consists of a 23.1 G septet split further into 17.47 G (*i.e.*,  $34.94/2$ ) triplets as illustrated by (iii) in Figure 2. The low-temperature spectrum in Figure 2a would then be related to the spectrum in Figure 2b by having the center line (*i.e.*,  $M_1^\beta = 0$ ) of the triplet broadened beyond detection, so that the spectrum would indeed appear to consist of a septet of doublets (with twice the triplet splitting) originally described by (i) in Figure 2.

A modulation diagram shown schematically in Figure 3 would account for such a selective broadening of the lines in the spectrum.<sup>6</sup>

In order to examine this possibility, we carefully studied the spectrum over the range of temperatures listed in Figure 4. Only a selected portion [see (iv), Figure 2] of the spectrum corresponding to the  $M_1 = 1$  manifold of the septet splitting is shown in Figure 4. Other lines have been deliberately obliterated in order to emphasize the selective broadening of the lines in the triplet and to allow a direct comparison with the modulation diagram in Figure 3. These results clearly sup-

(6) For a lucid discussion of the alternating line-width effect in esr spectra, see P. D. Sullivan and J. R. Bolton, *Advan. Magn. Resonance*, **4**, 39 (1970); A. Hudson and G. R. Luckhurst, *Chem. Rev.*, **69**, 191 (1969).

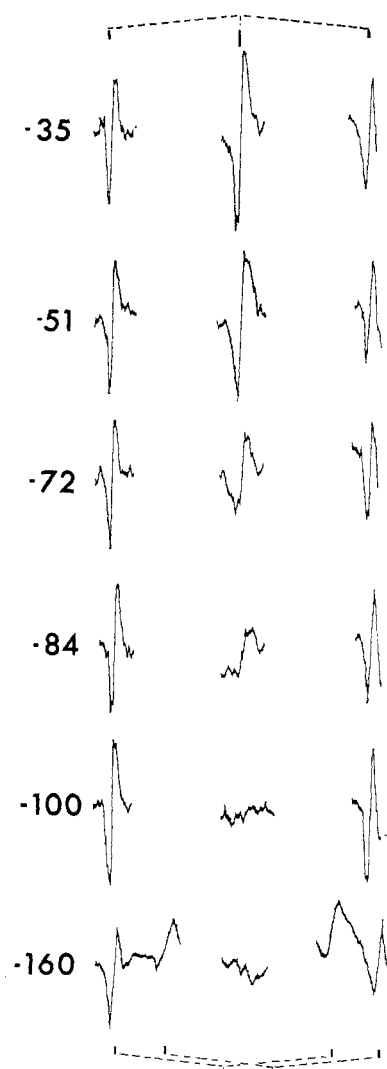
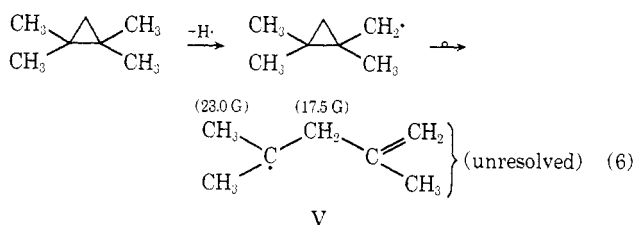


Figure 4. Temperature-dependent line-width variation of the  $M_1 = 1$  multiplet in the septet splitting, showing selective out-of-phase broadening of the  $\beta$ -proton triplet and the (partial) low-temperature limit.

port the alternative assignment involving the participation of an alternating line-width effect in the spectrum.

We conclude, therefore, that the spectra shown in Figures 2a and 2b are associated with the same species, viz., the 1,1,3-trimethylallylcarbinyl radical V, derived by the homoallylic rearrangement of the 2,3,3-trimethylcyclopropylcarbinyl radical shown in eq 6. For



further confirmation, radical V was generated independently from 4-bromo-2,4-dimethyl-1-pentene and silyl radicals by a technique also widely employed for the esr studies.<sup>7</sup> The spectrum obtained by the latter

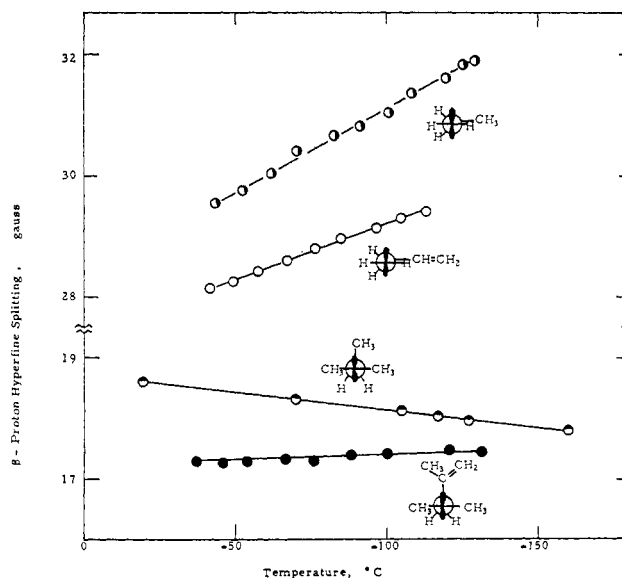
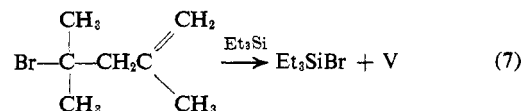


Figure 5. Temperature dependences of the  $\beta$ -proton splittings in (●) *n*-propyl, (○) allylcarbinyl, (◐) *tert*-amyl, and (●) 1,1,3-trimethylallylcarbinyl radicals.



method was the same as that derived from 1,1,2,2-tetramethylcyclopropane and showed the same pronounced alternating line-width effect on temperature variation.

Thus, the esr data for alkyl radicals derived from tetramethylcyclopropane are consistent with those generated from other methylcyclopropanes.<sup>1</sup> Moreover, these conclusions are in complete accord with chemical studies, showing hydrogen abstraction from a methyl group by *tert*-butoxy radical to be competitively favored over that from the cyclopropyl ring in these analogs.

Finally, no evidence could be found in the esr spectra (down to  $-160^\circ$ ) for reclosing the ring in the trimethylallylcarbinyl radical V to regenerate the 2,3,3-trimethylcyclopropylcarbinyl radical shown in eq 6. In this regard, the irreversibility<sup>8</sup> is similar to that previously observed<sup>1</sup> with allylcarbinyl and cyclopropylcarbinyl radicals in eq 1 ( $\text{R} = \text{H}$ ). Furthermore, our inability to observe the esr spectrum of the parent 2,3,3-trimethylcyclopropylcarbinyl radical from tetramethylcyclopropane, even at  $-160^\circ$ , is doubtlessly related to its facile rearrangement to V.

**Conformational Studies of the 1,1,3-Trimethylallylcarbinyl Radical V.** The septet splitting due to the pair of  $\alpha$ -methyl groups in V remains essentially unchanged between  $-35$  and  $-160^\circ$ . The magnitude of the triplet splitting due to the two  $\beta$ -methylene protons is also relatively invariant as shown in Figure 5. Even when the protons become inequivalent at the lowest temperature studied, the average value of the hyperfine splittings remains remarkably unchanged as shown by a comparison of the spectra at  $-160$  and  $-35^\circ$  in Figure 4.

(7) A. Hudson and R. A. Jackson, *J. Chem. Soc., Chem. Commun.*, 1327 (1969).

(8) Cf. L. K. Montgomery, J. W. Matt, and J. R. Webster, *J. Amer. Chem. Soc.*, **89**, 923, 934 (1967).

Table II. ESR Parameters for Alkyl- and Allylcarbinyl Radicals<sup>a</sup>

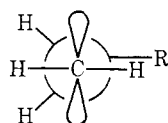
Radical	Temp, °C	$\langle g \rangle$	—Hyperfine splitting, G—		$\rho_\alpha$
			$a_\alpha$	$a_{\beta\text{-CH}_2}$	
$(\text{CH}_3)_3\dot{\text{C}}\text{CH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	-120	2.00275	22.97 <sup>c</sup>	17.52	0.78 <sup>b</sup>
$(\text{CH}_3)_3\dot{\text{C}}\text{CH}_2\text{CH}_3$	-117	2.00278	22.80 <sup>c</sup>	17.94	0.78 <sup>b</sup>
$\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}=\text{CH}_2$	-113	2.00280	22.25 <sup>d</sup>	29.42 <sup>e</sup>	
$\dot{\text{C}}\text{H}_2\text{CH}_2\text{CH}_3$	-108	2.00287	22.13 <sup>d</sup>	31.17 <sup>f</sup>	

<sup>a</sup> In cyclopropane solutions. <sup>b</sup> Obtained from the Fessenden-Fischer relationship: R. H. Fessenden and R. W. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); H. Fischer, *Z. Naturforsch., Part A*, **20**, 428 (1965). <sup>c</sup>  $\alpha\text{-CH}_3$ . <sup>d</sup>  $\alpha\text{-H}$ . <sup>e</sup>  $a_{\gamma\text{-H}} = 0.62$  G, one  $a_{\delta\text{-H}} = 0.35$  G. <sup>f</sup>  $a_{\gamma\text{-H}} = 0.27$  G.

The magnitude of the  $\beta$ -proton splitting in alkyl radicals is described by eq 8,<sup>9</sup> where  $A$  and  $B$  are con-

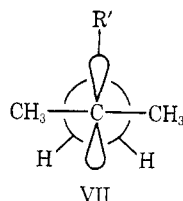
$$a_{\beta\text{-H}} = A + B \cos^2 \theta \quad (8)$$

stants and  $\theta$  is the dihedral angle between the  $\text{C}_\beta\text{-H}_\beta$  bond and the axis of the half-filled p orbital at  $\text{C}_\alpha$ . A previous analysis<sup>10,11</sup> of the temperature dependences of  $a_{\beta\text{-H}}$  for the *n*-propyl, *n*-butyl, and allylcarbinyl radicals indicated that the stable conformation for these radicals is given by



VI,  $\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2, \text{CH}_2=\text{CH}-$

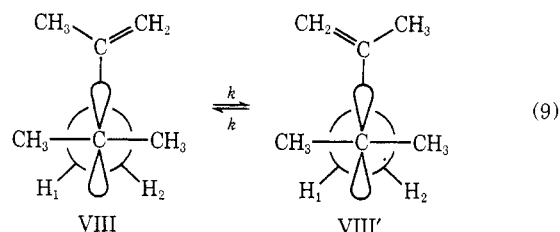
Replacement of both  $\alpha$  protons in the *n*-propyl radical by methyl groups alters the stable conformation to VII.<sup>11,12</sup> The symmetric structure for the *tert*-amyl



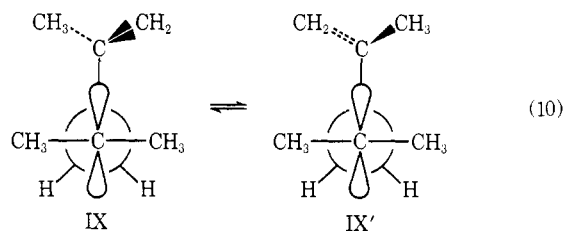
radical ( $\text{R}' = \text{CH}_3$ ) is further supported by the absence of selective line broadening in the spectrum at various temperatures.

The magnitude of the  $\beta$ -proton splitting in the 1,1,3-trimethylallylcarbinyl radical together with its invariance with temperature are similar to those of the *tert*-amyl radical as shown in Figure 5 and Table II. We conclude that the radical V also exists in the stable conformation VII [ $\text{R}' = -\text{C}(\text{CH}_3)=\text{CH}_2$ ] about the  $\text{C}_\alpha\text{-C}_\beta$  bond.

**Hindered Internal Rotation in the 1,1,3-Trimethylallylcarbinyl Radical.** Since the conformation about the  $\text{C}_\alpha\text{-C}_\beta$  bond is more or less locked in the symmetric conformation VIII, we attribute the selective line broadening of the  $\beta$  triplets in the spectrum of 1,1,3-trimethylallylcarbinyl radical to hindered internal rotation about the  $\text{C}_\beta\text{-C}_\gamma$  bond. Exchange between the



two equivalent conformers VIII and VIII' accounts for the observed out-of-phase modulation of the  $\beta$ -proton coupling constants; *i.e.*, the pairwise exchange of  $\text{H}_\beta(1)$  and  $\text{H}_\beta(2)$  is between inequivalent positions.<sup>6</sup> This selective line-width alteration contrasts with the in-phase broadening (of the outer lines of the triplet) expected for exchange between conformations IX and IX', in which the two  $\beta$  protons remain equivalent during the exchange between conformations IX and IX'. Conformation VIII should also be favored over IX on steric grounds.



Since the line broadenings above  $-100^\circ$  are in the fast exchange limit, we can apply Freed and Fraenkel's relaxation matrix theory<sup>13</sup> to the rate process, with the assumptions that the signal heights are inversely proportional to the squares of the total line widths and the line shapes are Lorentzian. The first-order rate constant is given by

$$k = 2.54 \times 10^6 \frac{(a_1 - a_2)^2}{(\Delta H)_u} \frac{1}{\sqrt{I_u/I_b} - 1} \text{ sec}^{-1} \quad (11)$$

where  $a_1$  and  $a_2$  are the hyperfine splittings in gauss for the two inequivalent  $\beta$  protons,  $(\Delta H)_u$  is the line width of the unbroadened lines (*i.e.*,  $M_I^\beta = \pm 1$ , peak-to-peak in gauss), and  $I_u$  and  $I_b$  are the intensities of the theoretical unbroadened and observed broadened lines, respectively. Applying the Arrhenius rate equation,  $k = A \exp(-E_a/RT)$ , with the added assumption that both  $(a_1 - a_2)$  and  $\Delta H_u$  are temperature independent, we have the following equation

$$\ln(\sqrt{I_u/I_b} - 1) = \ln \left\{ 2.54 \times 10^6 \frac{(a_1 - a_2)^2}{(\Delta H)_u} \frac{1}{A} \right\} + \frac{E_a}{RT} \quad (12)$$

(13) J. H. Freed and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 326 (1963).

(9) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); (b) M. Barfield, *J. Phys. Chem.*, **74**, 621 (1970); (c) F. C. Adam and F. W. King, *J. Chem. Phys.*, **58**, 2446 (1973).

(10) R. W. Fessenden, *J. Chim. Phys. Physicochim. Biol.*, **61**, 1570 (1964).

(11) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

(12) (a) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971). (b) We have assumed a planar configuration for the tertiary radical sites in VII, VIII, and IX, although there is disagreement on this point. See D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 6241 (1972); M. C. R. Symons, *Tetrahedron Lett.*, 207 (1973); D. Griller and K. U. Ingold, private communication; H. Paul and H. Fischer, private communication.

**Table III.** Rotational Barriers for Carbon-Carbon Single Bonds in Alkyl Radicals

Radical	Bond of rotation	Barrier, kcal mol <sup>-1</sup>	Method
(CH <sub>3</sub> ) <sub>2</sub> ĊCH <sub>2</sub> C(CH <sub>3</sub> )=CH <sub>2</sub>	C <sub>β</sub> -C <sub>γ</sub>	3.5 ± 0.5 <sup>a</sup>	Line shape, relaxation matrix theory
ĊH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	C <sub>α</sub> -C <sub>β</sub>	0.2 <sup>b</sup>	a <sub>β</sub> (T), classical treatment
(CH <sub>3</sub> ) <sub>2</sub> ĊCH(CH <sub>3</sub> ) <sub>2</sub>	C <sub>α</sub> -C <sub>β</sub>	1.2 <sup>c</sup>	a <sub>β</sub> (T), quantum mechanical
(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>2</sub> CH <sub>3</sub>	C <sub>α</sub> -C <sub>β</sub>	0.6 <sup>c</sup>	a <sub>β</sub> (T), quantum mechanical
CH <sub>3</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	C <sub>α</sub> -C <sub>β</sub>	0.3 <sup>c</sup>	a <sub>β</sub> (T), quantum mechanical
CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	C <sub>α</sub> -C <sub>β</sub>	0.4 <sup>c</sup>	a <sub>β</sub> (T), quantum mechanical
ĊH <sub>2</sub> OH	C <sub>α</sub> -O	3.1 <sup>c</sup>	Line shape, density matrix theory
ĊH <sub>2</sub> C(=O)CH <sub>3</sub>	C <sub>α</sub> -CO	4.0 <sup>c</sup>	Line shape, density matrix theory
ĊH <sub>2</sub> C(=O)C(CH <sub>3</sub> ) <sub>3</sub>	C <sub>α</sub> -CO	9.4 <sup>d</sup>	Line shape, modified Bloch equation
(CH <sub>3</sub> ) <sub>2</sub> ĊC(=O)CH <sub>3</sub>	C <sub>α</sub> -CO	9.6 ± 1.2 <sup>e</sup>	Line shape, density matrix theory
CH <sub>2</sub> =CHĊCH <sub>2</sub> X	C <sub>α</sub> '-C <sub>β</sub>	10.5 ± 2 <sup>e</sup>	Line shape, density matrix theory
X = SCH <sub>3</sub>		3.3 <sup>f</sup>	Line shape, density matrix theory
= SnR <sub>3</sub>		4.8	
= SiR <sub>3</sub>		3.1	
= CH <sub>2</sub> CH <sub>3</sub>		2 ± 1	

<sup>a</sup> This work. <sup>b</sup> Reference 10. <sup>c</sup> Reference 12. <sup>d</sup> Reference 16a. <sup>e</sup> Reference 16b. <sup>f</sup> T. Kawamura, P. Meakin, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 8065 (1972).

An activation energy of  $3.5 \pm 0.5$  kcal mol<sup>-1</sup> is obtained from the plot of  $\log(\sqrt{I_u/I_b} - 1)$  vs.  $1/T$  as shown in Figure 6. The linearity of the graph observed over a fairly wide temperature range (-35 to -100°) provides strong support for the broadening in the spectra to be due to the two-jump process presented in eq 9, in which conformations VIII and VIII' have the same lifetimes.<sup>14</sup>

The preexponential factor  $A$  for the process was calculated to be  $10^{13.0}$  sec<sup>-1</sup> based on the spectrum observed at -160° for the (partial) slow exchange limit. This value compares with  $10^{12.4}$  for rotation about a single bond according to transition state theory,<sup>15</sup> and  $10^{12.9}$  and  $10^{12.6}$  for rotations in the acetyl and hydroxymethyl radicals, respectively, by line-shape analysis.<sup>12,16</sup> Interestingly, the magnitude of the barrier-to-rotation in V is comparable to that of  $4 \pm 0.5$  kcal mol<sup>-1</sup> obtained from infrared studies for methallyl chloride, which has roughly the same steric requirements.<sup>17</sup>

**Barriers-to-Rotation in Free Radicals.** There are as yet only a limited number of radicals in which rotational barriers have been reported, some of which are listed in Table III.

The reported barriers-to-rotation about carbon-carbon single bonds are usually low, even for the sterically hindered 2,3-dimethyl-2-butyl radical listed in Table III. The exceptionally high barrier for the acetyl radical is probably due to the partial double bond character<sup>16a</sup> of the C<sub>α</sub>-C<sub>β</sub> bond (analogous to the allyl radical), which has recently received support from <sup>13</sup>C and <sup>17</sup>O studies in the α-cyclohexanonyl radical.<sup>16b</sup>

Essentially two methods have been used to determine barriers-to-rotation in alkyl radicals from esr data.<sup>14</sup> In rotations about the C<sub>α</sub>-C<sub>β</sub> bond, the experimental temperature dependence of  $a_\beta$  has been fitted to a theoretical one using either a quantum mechanical or classical averaging of the proton coupling

(14) For a review, see K. S. Chen and N. Hirota in "Investigation of Rates and Mechanisms," Part II, Chapter 13, G. G. Hammes, Ed., Wiley-Interscience, New York, N. Y., 1973.

(15) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941, p 175 ff.

(16) (a) G. Golde, K. Mobius, and W. Kaminski, *Z. Naturforsch., Part A*, **24**, 1214 (1969); (b) D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, *J. Amer. Chem. Soc.*, **95**, 4057 (1973).

(17) F. Northam, J. Oliver, and G. A. Crowder, *J. Mol. Spectrosc.*, **25**, 436 (1968).

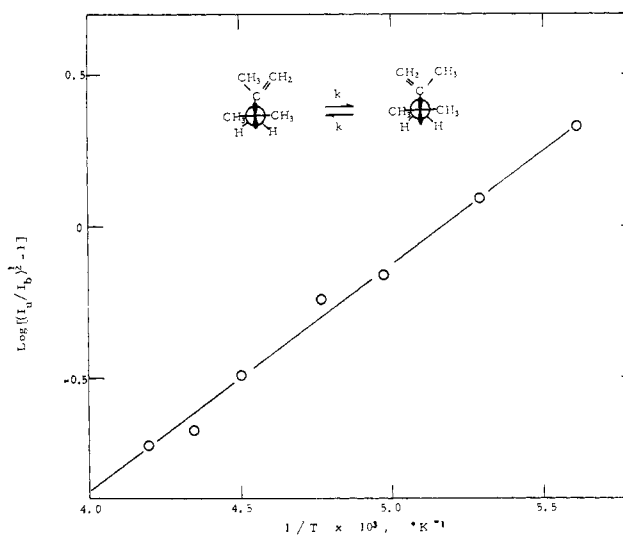


Figure 6. Activation parameters for hindered internal rotation in the 1,1,3-trimethylallylcarbonyl radical.

constants.<sup>10-12,18</sup> Alternatively, the temperature dependence of line shapes due to selective broadening has been analyzed using the density matrix method,<sup>11</sup> the modified Bloch equations,<sup>16a</sup> or the relaxation matrix theory.<sup>13</sup> There are difficulties in the first method which have been brought out by the observation of hindered internal rotation about the C<sub>β</sub>-C<sub>γ</sub> bond in the 1,1,3-trimethylallylcarbonyl radical and has caused us to reexamine a similar situation in the parent allylcarbonyl radical.

The esr spectrum of the allylcarbonyl radical is shown in Figure 7, together with modulation diagrams clearly showing selective line broadening due to (i) hindered rotation about the C<sub>α</sub>-C<sub>β</sub> bond (out-of-phase alternating line-width effect)<sup>6</sup> and (ii) hindered rotation about the C<sub>β</sub>-C<sub>γ</sub> bond (in-phase alternating line-width effect).<sup>19</sup> The same line-broadening behavior can be observed in the spectrum of the *n*-propyl radical,<sup>11</sup> as well as those of β-methoxyethyl, γ-halopropyl, and δ-ketoalkyl radicals.<sup>20</sup>

(18) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

(19) G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967); P. D. Sullivan and J. R. Bolton, *ibid.*, **73**, 4387 (1969).

(20) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6485, 7695 (1972); **95**, 2635 (1973).

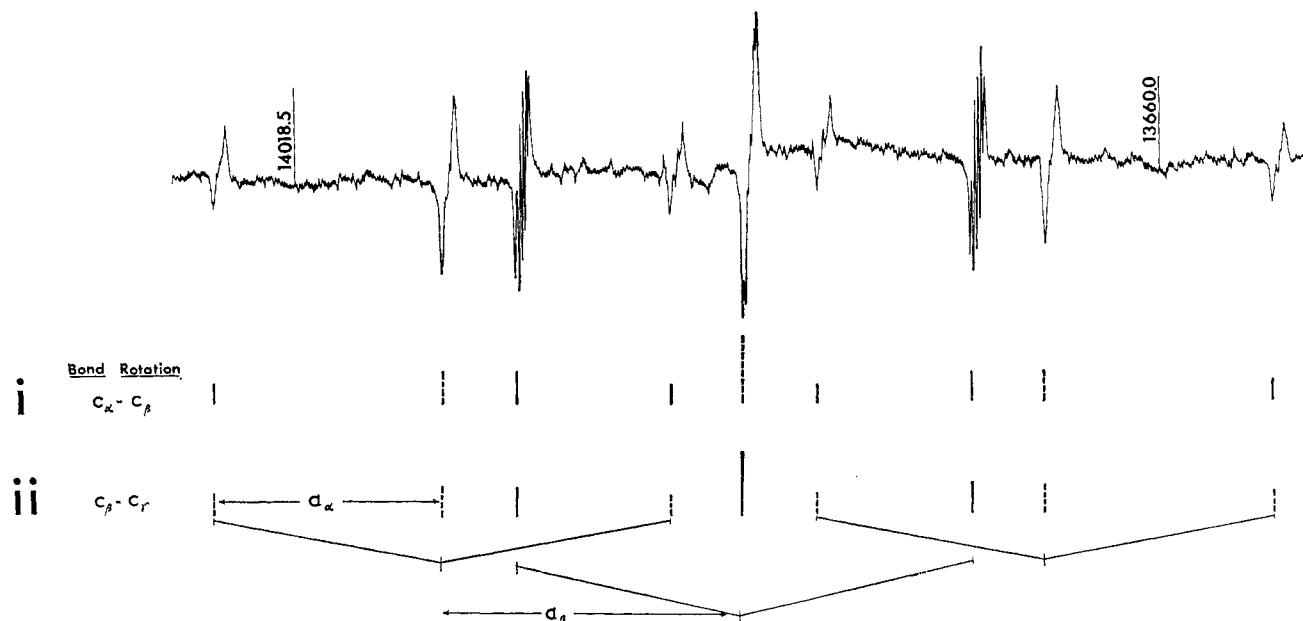
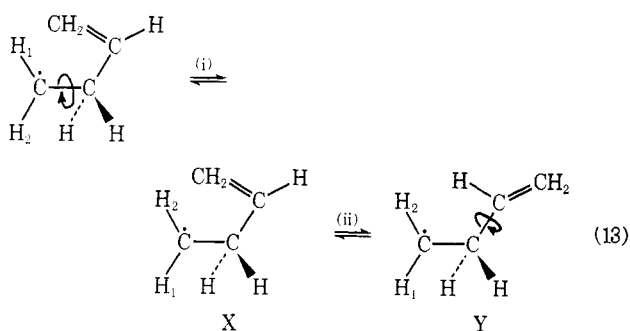


Figure 7. Selective line broadening in the esr spectrum of the allylcarbinyl radical at  $-115^\circ$  showing the stick spectra for (i) out-of-phase line-width effect in the  $\alpha$ -proton splitting, and (ii) in-phase line-width effect in the  $\beta$ -proton splitting. Solid and dotted lines are for unbroadened and broadened lines, respectively.



For these radicals, at least two processes given in eq 14 and 15 contribute to the temperature dependence of  $a_\beta$

$$a_\beta = A + B \cos^2 \theta \quad (14)$$

$$a_\beta = p_X a_\beta(X) + p_Y a_\beta(Y) \quad (15)$$

where  $p_X$  and  $p_Y$  are the populations and  $a_\beta(X)$  and  $a_\beta(Y)$  are the  $\beta$ -proton splittings in conformers X and Y, respectively. Neglect of the latter may have contributed to the imperfect fitting of the temperature dependence of  $a_\beta$  by either the classical or quantum mechanical treatment,<sup>10-12</sup> and thus may have led to an imprecise value of the barrier.<sup>21</sup>

The determination of barrier heights by line-shape analysis circumvents this difficulty, since specific lines in the spectrum can be selected to reflect the proper modulation as indicated by (i) or (ii) in Figure 7. Unfortunately, we were unable in this study to obtain barriers for allylcarbinyl or *n*-propyl radicals by line-shape analysis due to the insensitivity of the signal heights<sup>22</sup> within the limitations of the signal to noise ratio in the experimental spectra of these radicals. Hopefully, methods can be developed so that radicals

can be generated in sufficiently higher concentration in order to effect a significant improvement of the signal to noise ratio and enable us to determine the barriers for the two processes separately.

Recent *ab initio* calculations give varying values to barrier heights. A relatively high value of 4.8 kcal mol<sup>-1</sup> has been calculated for the rotation barrier of a methyl group about the  $C_\beta-C_\gamma$  bond in the *n*-propyl radical,<sup>23</sup> although a low barrier ( $\sim 100$  cal mol<sup>-1</sup>) has been calculated for the  $C_\alpha-C_\beta$  bond.<sup>24</sup> A barrier of 2.1 kcal mol<sup>-1</sup> has been calculated for rotation about the central  $C_\beta-C_\gamma$  bond in the allylcarbinyl radical,<sup>25</sup> but a symmetric conformation about the  $C_\alpha-C_\beta$  bond was used which is at variance with the conclusion based on the esr results.

Esr studies provide a convenient method for the study of barriers-to-hindered internal rotations in radicals. Barriers-to-rotations have also been obtained for molecules by the use of nmr, ir, and microwave techniques.<sup>26</sup> At the present time, insufficient accurate data are available to compare the magnitudes of the barriers in radicals and molecules. Therefore, evidence cannot yet be adduced that the radical can be used simply as a "spin probe" for the determination of the barrier for a molecule of similar structure.

## Summary and Conclusions

Hydrogen abstraction from 1,1,2,2-tetramethylcyclopropane by *tert*-butoxy radical occurs at one of the methyl groups to afford the ring-opened 1,1,3-trimethylallylcarbinyl radical. The isomeric 2,2,3,3-tetramethylcyclopropyl radical can be generated independently and shown not to be an intermediate, nor does it un-

(23) Y. Ellinger, A. Rassat, R. Subra, and G. Berthier, *J. Amer. Chem. Soc.*, **95**, 2372 (1973).

(24) L. Radom, J. Paviot, J. A. Pople, and P. v. R. Schleyer, private communication.

(25) W. J. Hehre, *J. Amer. Chem. Soc.*, **95**, 2643 (1973).

(26) For a review, see G. J. Karabatsos and D. J. Fenoglio, *Top. Stereochem.*, **5**, 167 (1970).

(21) Other difficulties include the uses of a proper potential function and values of  $A$  and  $B$ .

(22) Due to small values of the difference ( $a_1 - a_2$ ) or the activation energy.

dergo allylic isomerization to the 2,4-dimethyl-3-penten-2-yl radical. The 1,1,3-trimethylallylcarbonyl radical V exists in a symmetric conformation about the  $C_\alpha-C_\beta$  bond similar to the *tert*-amyl radical. The pronounced out-of-phase broadening observed in the esr spectrum of V is attributed to hindered internal rotation about the  $C_\beta-C_\gamma$  bond. A barrier of  $3.5 \text{ kcal mol}^{-1}$  has been calculated from the line shapes using the relaxation matrix theory and compared to other literature values. Difficulties in applying the temperature dependence of  $a_\beta$  to obtain barrier heights for alkyl radicals are pointed out.

## Experimental Section

**Esr Measurements.** The modified Varian X-band spectrometer, microwave frequency measurements, light source, and sample tubes are as described previously.<sup>11,20</sup>

To minimize the error in the  $g$ -value determinations, all measurements were made on spectra recorded on the same day for increasing magnetic field. Perylene cation radical ( $g = 2.00258$ )<sup>27</sup> was used as a standard in the configuration employed. The accuracy of the measurements is estimated as  $\pm 0.00003$ . The temperature in the tube was calibrated with a thermocouple and accurate to  $\pm 5^\circ$ .

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

**Materials.** 1,1,2,2-Tetramethylcyclopropane obtained from the Chemical Samples Co. was prepared by zinc dust reduction of 2,4-dibromo-2,4-dimethylpentane and contained less than 1% 2,3,3-trimethyl-1-butene as the only detectable impurity by gas chromatography. The nmr spectrum of tetramethylcyclopropane in  $\text{CCl}_4$  showed two singlet resonances at  $\delta$  0.23 and 1.21 ppm with the relative intensity ratio of 1:6, respectively.

4-Bromo-2,4-dimethyl-1-pentene was prepared from 20 g of 4-hydroxy-2,4-dimethyl-1-butene (Chemical Samples Co.) and 8 ml of pyridine in 60 ml of absolute ether. A solution of 6.1 ml of phosphorus tribromide in 20 ml of ether was added dropwise with stirring. The mixture was stirred at room temperature for 4 hr, and then poured onto ice and worked up to afford 12.5 g (40%) of 4-bromo-2,4-dimethyl-1-pentene, bp  $30-31^\circ$  (23 mm).<sup>28</sup>

2,2,3,3-Tetramethylcyclopropanecarboxylic acid was prepared from the copper-catalyzed reaction of tetramethylethylene and ethyl diazoacetate<sup>29</sup> and converted to the *tert*-butyl perester via the acid chloride.<sup>30</sup>

**Acknowledgment.** We wish to thank Dr. R. G. Salomon for the preparation of the perester and the National Science Foundation for financial support.

(28) M. A. Cheltzova, E. A. Chernyshev, and A. D. Petrov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 459 (1955).

(29) (a) R. G. Salomon and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 3300 (1973); (b) A. P. Mescheryakov and I. E. Dolgii, *Izv. Akad. Nauk SSSR, Khim. Nauk*, 931 (1960).

(30) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

## Optical Activity and Conformation of the Cation Carrier X537A

S. R. Alpha and A. H. Brady\*<sup>1</sup>

*Contribution from the Departments of Pharmacology, Medicine, and Biochemistry, University of Miami School of Medicine, Miami, Florida 33152. Received March 13, 1973*

**Abstract:** The polycyclic polyether antibiotic X537A exhibits strong optical activity in the presence of several amines and monovalent and divalent metals but weak optical activity when free in aqueous ethanol. In lipid solvents like heptane, X537A again shows optical activity similar to that seen in the presence of a metal ion. Since the two chromophores of particular interest, salicylic acid ( $\sim 245$  and  $308 \text{ nm}$ ) and a ketone ( $\sim 290 \text{ nm}$ ), are themselves symmetric, the induced optical activity associated with these absorption bands reflects changes in asymmetry arising from the repositioning of neighboring asymmetric centers. These changes in optical activity can be correlated quite well with the presence of a disordered structure in aqueous ethanol and a cyclic conformation in heptane and in the presence of a complexing cation. Thermodynamic arguments are presented to explain the temperature dependence of the circular dichroism. The changes in circular dichroism of free X537A in heptane seen with increasing temperature are consistent again with the unfolding of a cyclic conformation. The circular dichroism of cation complexes in absolute ethanol become more intense with increasing temperature, the opposite of that seen with free X537A in heptane. This behavior appears to indicate that competition of polar solvent for the polar interior of the cyclic structure diminishes with increasing temperature, thereby leaving a tighter metal ion complex.

Measurements of circular dichroism have facilitated resolution of the solution conformation of a number of cation carriers including gramicidin A,<sup>2,3</sup> enniatin,<sup>4</sup> valinomycin,<sup>4</sup> and antamanide.<sup>5</sup> In each of

these molecules changes in the intensities of optically active amide transitions accompanied the complexation of predominantly monovalent cations. In an attempt to extend our knowledge of these lipid soluble ion carriers we investigated the optical activity of the polyether antibiotic X537A, which, unlike the above molecules, also strongly complexes divalent cations.<sup>6</sup> Crystalline structures of the barium and silver salts of X537A are

(1) Department of Medicine.

(2) V. T. Ivanov, A. I. Miroshnikov, N. D. Abdullaev, L. B. Senyavina, S. F. Arkhipova, N. N. Uvarova, K. Kh. Kholikulina, V. F. Bystrov, and Yu. A. Ovchinnikov, *Biochem. Biophys. Res. Commun.*, **42**, 654 (1971).

(3) B. E. Isbell, *FEBS (Fed. Eur. Biochem. Soc.) Lett.*, **25**, 192 (1972).

(4) M. M. Shemyakin, Yu. A. Ovchinnikov, V. T. Ivanov, U. K. Antonov, E. I. Vinogradova, A. M. Shkrob, G. G. Malenkov, A. V. Evstratov, I. A. Laine, E. I. Melnik, and I. D. Ryabova, *J. Membrane Biol.*, **1**, 402 (1969).

(5) D. W. Urry, J. D. Glickson, D. F. Mayers, and J. Haider, *Biochemistry*, **11**, 487 (1972).

(6) S. M. Johnson, J. Herrin, S. J. Liu, and I. C. Paul, *Chem. Commun.*, 72 (1970).