

unit model JES-VT-3 and read off a calibration chart obtained with a thermocouple inside a solvent-containing dummy nmr tube. Checks on the accuracy of the calibration curve were made repeatedly and are believed accurate to within  $\pm 2^\circ$ . Deuterium decoupling was effected by means of the JEOL hetero spin decoupler Model JNM-SD-HC.

Mass spectra were performed on a Hitachi-Perkin-Elmer mass spectrometer Model RMU-6-D operating at 70 and 12.5 eV.

The theoretical spectra were generated by a CDC 6600 computer coupled to a Calcomp plotter.

**2,2,4,4,6,6,8,8-Octadeuterio-1,5-cyclooctanediol (6).** 1,5-Cyclooctanediol<sup>11</sup> (5, 5.0 g) was stirred for 12 hr at room temperature with 0.075 g of potassium carbonate dissolved in 42 ml of deuterium oxide. Fifteen extractions with 15-ml portions of chloroform were combined, dried with magnesium sulfate, and stripped of their solvent. After two additional similar exchanges using 20 ml of fresh deuterium oxide each time, the solid product isolated showed essentially complete deuteration as revealed from its greatly simplified pmr spectrum in  $\text{CDCl}_3$  which consists of a singlet at  $\delta$  2.10 in accord with that expected for 1,5-cyclooctanediol- $d_8$  (6).

**cis- and trans-1,5-Cyclooctanediol- $d_8$  (7 and 8).** 1,5-Cyclooctanediol- $d_8$  (11.0 g) was reduced with lithium aluminum hydride following the procedure described by Allinger and Maul<sup>11</sup> to give 9.0 g of a viscous oil after vaporation of the ether. Chromatography on 300 g of activity II alumina using ether and then 1% methanol-ether as eluent gave some fractions which crystallized on standing. These crystals were collected and recrystallized from ether-pentane to give about 1.0 g of *cis*-1,5-cyclooctanediol- $d_8$  (7), mp 68–70° (lit.<sup>12</sup> *cis*-1,5-cyclooctanediol, mp 73.8–74.8°). The pmr spectrum of 7 in  $\text{CDCl}_3$  confirmed its identity: singlet (two protons) at  $\delta$  1.90 which disappeared on adding  $\text{D}_2\text{O}$  and an AB quartet (four protons) centered at  $\delta$  1.65, and a singlet (two protons) at  $\delta$  3.80.

Fractions eluted with 20% methanol-ether afforded a viscous oil which did not crystallize on standing. Two successive chromatographies of this residue on activity II alumina using methanol-ether as eluent with increasing proportion of methanol gave more *cis*-diol- $d_8$  and fractions ( $\sim 0.5$  g) of an oil identified as *trans*-1,5-

cyclooctanediol- $d_8$  (8)<sup>12</sup> by its pmr spectrum: singlet (four protons) at  $\delta$  1.62, singlet (two protons) at  $\delta$  3.80, and a singlet (two protons) at  $\delta$  2.20 which disappeared on adding  $\text{D}_2\text{O}$ . Additional proof of this structure is provided later from its diacetate (10). (Note: attempts were not made to maximize the yields of each diol since only a small quantity was required for the next reaction.)

**cis-1,5-Diacetoxycyclooctane- $d_8$  (9).** *cis*-1,5-Cyclooctanediol- $d_8$  (7) (0.20 g) and 10 ml of acetyl chloride were placed in a dry flask protected with a calcium chloride tube. The mixture was stirred overnight at room temperature. Ether (100 ml) was then added followed by 50 ml of water. The aqueous phase was extracted three times with 50 ml of ether. The combined ether solutions were washed successively with a solution of sodium bicarbonate and water until neutral and the ether was evaporated. The liquid residue was purified by preparative vpc using a SF-96 column at 200°. A 6% solution in chlorodifluoromethane was then prepared, degassed, and sealed. The pmr spectrum described in the text (Figure 2) is in accord with structure 9. Mass spectral analysis at low ionization potential gave the following isotopic distribution:  $d_8 = 21\%$ ,  $d_7 = 68\%$ ,  $d_6 = 11\%$ .

**trans-1,5-Diacetoxycyclooctane- $d_8$  (10).** *trans*-1,5-Cyclooctanediol- $d_8$  (8) (0.20 g) was treated with acetyl chloride as described above to give a product which was purified by preparative vpc. A 6% solution in chlorodifluoromethane gave the pmr spectrum shown in Figure 1 which together with the mass spectral analysis supports structure 10. The following isotopic composition was calculated from the mass spectrum at low ionization potential:  $d_8 = 21\%$ ,  $d_7 = 68\%$ ,  $d_6 = 11\%$ .

Although this product is pure diacetate, it is not all *trans* as revealed from its pmr spectrum at  $-135^\circ$  (Figure 1) where the labeled peak indicates that a small percentage of *cis*-DAC- $d_8$  is also present in solution. This therefore indicates that the chromatographic separation provided the starting *trans*-diol- $d_8$  at a purity above 90%.

**Acknowledgment.** We are indebted to Mr. R. Mayer for technical assistance during the course of this work, to Mr. M. Bernard for writing the computer plotting program and to Dr. T. Schaefer for a communication on the use of the DNMR program. We are grateful to the National Research Council of Canada for financial assistance and to the Quebec Government for a scholarship to R. P.

(11) N. L. Allinger and J. J. Maul, *Tetrahedron*, **24**, 4257 (1968). We are indebted to Badische Anilin und Soda Fabrick, West Germany, for a sample of 5-hydroxycyclooctanone.

(12) A. C. Cope and A. Fournier, Jr., *J. Amer. Chem. Soc.*, **79**, 3896 (1957).

## Effects of Halogen Substitution on Alkyl Radicals. Conformational Studies by Electron Spin Resonance

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**Abstract:** The esr spectra of a variety of alkyl and allyl radicals with halogen substituents are examined in solution. The hyperfine splitting due to the  $\beta$  protons and their temperature dependence, as well as selective line broadening effects in the esr spectra, are used to deduce the conformational changes in alkyl radicals as they are affected by halogen substitution. Chlorine and bromine exert a particularly noticeable influence when located in the  $\beta$  and  $\gamma$  positions. The conformational effects of substitution further along the alkyl chain are not observed. The esr spectra of the  $\gamma$ -chloro and  $\gamma$ -bromopropyl radicals show an unusual alternation of line widths in which the hyperfine splittings of the  $\beta$  protons undergo in-phase modulation. The  $\beta$ -bromoallyl radical is tentatively identified (with the bromine splitting), but the esr spectra of  $\beta$ -bromoalkyl and iodoalkyl radicals have not been observed. Product studies of reactions carried out in the spectrometer show that the  $\beta$ -bromoethyl radical is particularly unstable.

Halogen substituents are particularly noteworthy in their influence on the stereochemistry and kinetics of various homolytic reactions. The presence of bromine in the  $\beta$  position is especially conspicuous

and the effect has also been noted for iodine in the  $\gamma$  position.<sup>1</sup> Generally, the influence of the halogen

(1) (a) P. S. Skell, *Chem. Soc., Spec. Publ.*, **19**, 131 (1965); (b) D. D. Tanner, H. Yabuuchi, and E. V. Blackburn, *J. Amer. Chem. Soc.*, **93**,

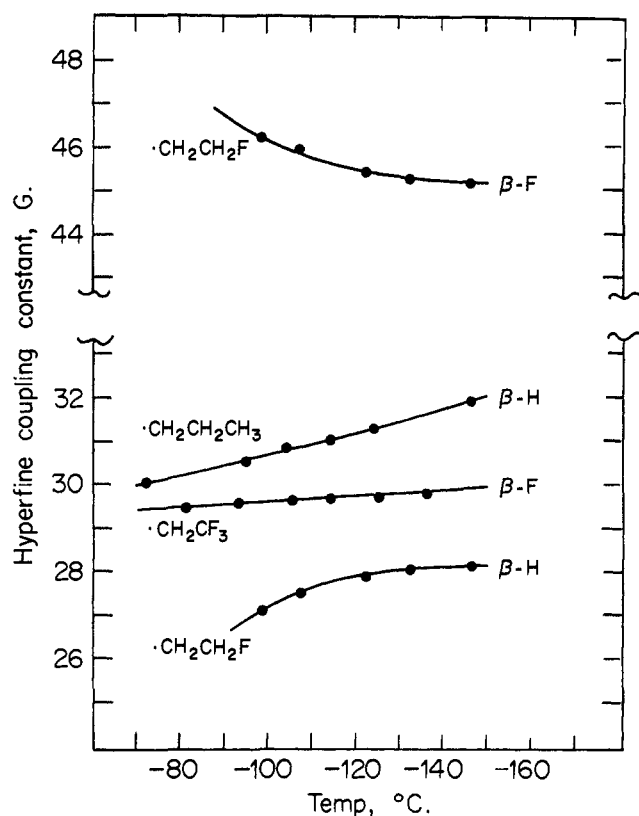


Figure 1. Temperature dependence of the  $\beta$ -hyperfine splittings in  $\beta$ -fluoroethyl,  $\beta,\beta,\beta$ -trifluoroethyl, and propyl radicals in cyclopropane solutions.

appears to decrease with distance from the radical center and the trend is  $F < Cl < Br < I$ . Various forms of halogen bridging have been qualitatively invoked to account for these observations.

Electron spin resonance (esr) is an effective tool for the study of the conformations of a variety of free radicals. The technique has been greatly aided by the development of procedures for the production of specific alkyl radicals in sufficiently high concentrations in solution to examine over a range of temperatures.<sup>2</sup> We employed these methods to examine the effects of halogen substitution on the conformations of a series of transient alkyl radicals in order to provide some indication of the interaction between the halogen nucleus and the radical center. In this study, the halogen substituents are successively moved from the  $\beta$  to  $\gamma$  positions and further along the alkyl chain.

## Results and Discussion

**$\beta$ -Halogen-Substituted Alkyl Radicals.** The  $\beta$ -fluoroethyl radical was generated by a procedure<sup>3</sup> involving the reaction of  $\beta$ -fluoroethyl bromide with triethylsilyl radicals. The hyperfine splitting constants (hfs) of

4801 (1971); D. D. Tanner, M. W. Mosher, N. C. Das, and E. V. Blackburn, *ibid.*, **93**, 5846 (1971); (c) W. C. Danen and R. C. Winter, *ibid.*, **93**, 716 (1971); (d) J. K. Kochi and D. M. Singleton, *ibid.*, **90**, 1582 (1968); J. K. Kochi and D. M. Singleton, *J. Org. Chem.*, **33**, 1027 (1968); (e) D. G. Korzan, F. Chen, and C. Ainsworth, *Chem. Commun.*, 1053 (1971); J. G. Traynham and W. G. Hines, *J. Amer. Chem. Soc.*, **90**, 5208 (1968).

(2) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, **24**, 147 (1970).

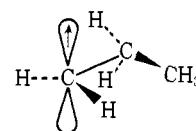
(3) (a) A. Hudson and R. A. Jackson, *Chem. Commun.*, 1327 (1969); (b) A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Lett.*, **5**, 552 (1970); (c) A. Hudson and K. D. J. Root, *Advan. Magn. Resonance*, **5**, 1 (1971).

Table I. ESR Parameters of Alkyl and  $\beta$ -Haloalkyl Radicals

Radical	$T$ , °C	$\langle g \rangle^a$	G		X	$\langle A_X \rangle$
$\cdot\text{CH}_2\text{CH}_2\text{X}$			$\langle A_{\alpha\text{-H}} \rangle$	$\langle A_{\beta\text{-H}} \rangle$		
$\cdot\text{CH}_2\text{CH}_3$	-180	2.00260 <sup>b</sup>	22.38	26.87		
$\cdot\text{CH}_2\text{CH}_2\text{CH}_3$	-130	2.00265	22.10	31.12	$\text{CH}_3$	0.27 <sup>c</sup>
$\cdot\text{CH}_2\text{CH}_2\text{F}$	-122	2.00249	22.15	27.92	$^{19}\text{F}$	45.44
$\cdot\text{CH}_2\text{CHF}_2^d$	-60	<i>e</i>	23.4	12.3	$^{19}\text{F}$	49.5
$\cdot\text{CH}_2\text{CF}_3$	-125	2.00225	23.78		$^{19}\text{F}$	29.78
$\cdot\text{CH}_2\text{CH}_2\text{Cl}$	-120	2.00214	21.75	10.20	$^{35}\text{Cl}$	18.78
					$^{37}\text{Cl}$	15.65

<sup>a</sup> Corrected to second order with respect to hyperfine interactions. <sup>b</sup> R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963). <sup>c</sup> Proton. <sup>d</sup> Reference 3c. <sup>e</sup> Not determined.

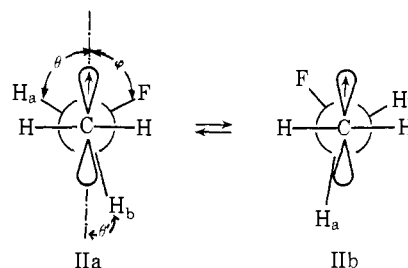
the  $\alpha$  protons given in Table I were invariant between  $-98$  and  $-146^\circ$ . The trend of the temperature-dependent hfs of the  $\beta$  protons shown in Figure 1 is diametrically opposed to that of the  $\beta$  fluorine. The slopes and curvatures of these plots indicate, furthermore, that both hfs are rapidly approaching limiting values at the lowest temperature studied ( $-146^\circ$ ). This behavior differs strongly from that of the  $\beta$  hfs of the *n*-propyl radical or *n*-butyl radical in the same temperature range. The quantitative analysis of the temperature dependence of the hfs has been used to assign I as the preferred conformation of the *n*-propyl radical.<sup>4</sup> Conformation I is also consistent with the



I

observed alternating line-width effect in the esr spectrum of the *n*-propyl radical in which the central lines (corresponding to  $M_I = 0$ ) of the triplets for the  $\alpha$  protons are selectively broadened. The latter is associated with the modulation of the hfs of the  $\alpha$  protons as a result of hindered rotation around the  $\text{C}_\alpha\text{-C}_\beta$  bond.<sup>4</sup>

In the  $\beta$ -fluoroethyl radical, on the other hand, Figure 1 clearly shows that the hyperfine splitting constant of the  $\beta$  protons attains an *upper limiting* value [ $A_{\beta\text{-H}}(\text{limit}) \cong 28$  G] at the lowest temperatures studied. Significantly, the temperature-dependent hfs of the  $\beta$  protons follows a diametrically opposed trend from that of the  $\beta$  fluorine, which reaches a *lower limiting* value [ $A_{\beta\text{-F}}(\text{limit}) \cong 45$  G] at the same temperatures. We deduce that at the lower temperature limit, the  $\beta$ -fluoroethyl radical is undergoing rapid exchange between conformations IIa and IIb. The angles  $\theta$  and



IIa

IIb

(4) (a) R. W. Fessenden, *J. Chim. Phys.*, **61**, 1570 (1964); (b) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971); (c) P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, **75**, 3438 (1971); (d) T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972).

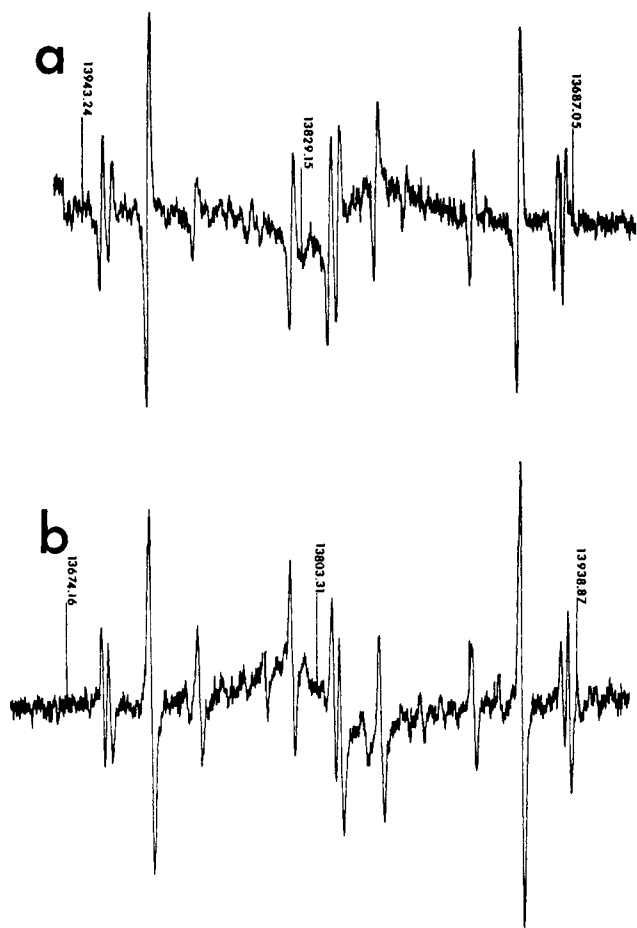


Figure 2. ESR spectra of the  $\beta$ -fluoroethyl radical in cyclopropane solution at (a)  $-98^\circ$ , (b)  $-132^\circ$ . Only the central portion of each spectrum is shown. Proton nmr field markers are in kHz.

$\theta'$  which describe the dihedral angles between the pair of  $C_\beta$ - $H_\beta$  bonds and the odd electron orbital at the  $\alpha$  carbon in these equivalent conformations can be obtained from the general expression<sup>5</sup>

$$\theta = \cos^{-1}(A_\beta Q/A_\alpha B)^{1/2} \quad (1)$$

where  $|B/Q| = 2.401$ , by invoking a simple  $\cos^2 \theta$  dependence of the  $\beta$ -proton coupling

$$A_\beta = A + B\rho \cos^2 \theta \quad (2)$$

and the McConnell relation from the  $\alpha$ -proton splitting

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

Equation 2 (with  $A = 0$ ) is the same relationship commonly applied to other alkyl radicals, including those with electronegative  $\beta$  substituents such as nitrogen and oxygen.<sup>2</sup> Under these conditions the value of approximately 28 G represents the average of the splittings by the pair of inequivalent  $\beta$  protons, from which we deduce that  $\theta = 70^\circ$  and  $\theta' = 10^\circ$  as shown in II. Furthermore, such a conformation places the  $\beta$  fluorine at approximately  $\varphi = 50^\circ$  from the plane of the p orbital, if it is assumed that the  $\beta$ -carbon center retains its tetrahedral configuration.

The esr spectrum of the  $\beta$ -fluoroethyl radical between  $-98$  and  $-146^\circ$  (the highest and lowest temperatures

(5) T. Kawamura and J. K. Kochi, *J. Organometal. Chem.*, **30**, C8 (1971); T. Kawamura, M. Ushio, T. Fujimoto, and T. Yonezawa, *J. Amer. Chem. Soc.*, **93**, 908 (1971).

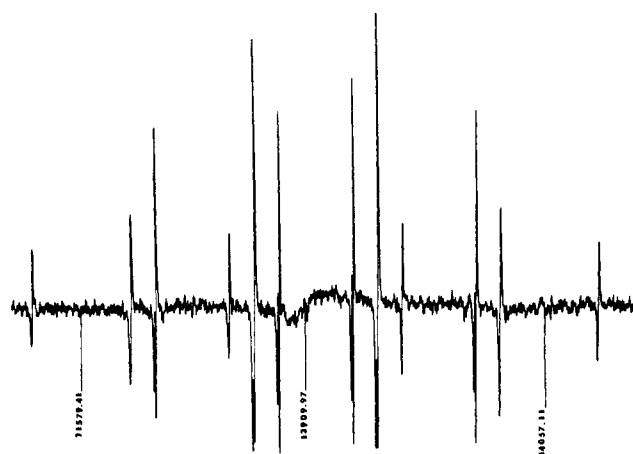
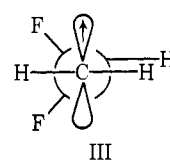


Figure 3. ESR spectrum of the  $\beta,\beta,\beta$ -trifluoroethyl radical in cyclopropane solution at  $-128^\circ$  showing resolved second-order splittings. Proton field markers are in kHz.

studied) shows no significant amount of selective line broadening (Figure 2). The latter would pertain if the barrier between the two equivalent conformations IIa and IIb is sufficiently low, so that the rate of interconversion is larger than the difference of the hyperfine frequencies. The low barrier between conformations IIa and IIb implied by such a ready interconversion indicates that the fluorine nucleus spends most of its time in either of two equivalent magnetic environments, which is tantamount to fluorine always located in a conformation at  $\varphi \cong \pm 50^\circ$ .

The introduction of three fluorines in the  $\beta$  position removes the asymmetry about the  $C_\alpha$ - $C_\beta$  bond, and all three fluorines are magnetically equivalent in the  $\beta,\beta,\beta$ -trifluoroethyl radical (Figure 3) over the temperature range studied. The temperature dependence of the hfs of the quartet splitting of the three fluorines is also plotted in Figure 1 for comparison with that of the single fluorine in the  $\beta$ -fluoroethyl radical. In contrast to the latter, the  $\beta,\beta,\beta$ -trifluoroethyl radical exhibits an almost temperature-independent value of  $A_F$  much like the behavior of  $A_{\beta-H}$  observed for the ethyl radical.<sup>4a</sup> Since methyl groups attached to  $\alpha$ -carbon atoms represent limiting cases of free rotation, we deduce that the values of  $A_F$  obtained for the  $\beta,\beta,\beta$ -trifluoroethyl radical at these temperatures are also close to the free rotation limit.

The esr parameters for the  $\beta,\beta$ -difluoroethyl radical given in Table I were recently reported at one temperature.<sup>3c</sup> Pending temperature dependence studies, if we again take eq 1 to represent the angular dependence of the single  $\beta$  proton, we conclude that it lies close to the nodal plane. The two fluorines would then be equivalently displaced from the plane of the p orbital by approximately  $30^\circ$ , as shown in conformation III.



The angular dependence of the hfs for  $\beta$  fluorines should be deduced from their locations in conformations II and III for  $\beta$ -fluoroethyl and  $\beta,\beta$ -difluoroethyl radicals,

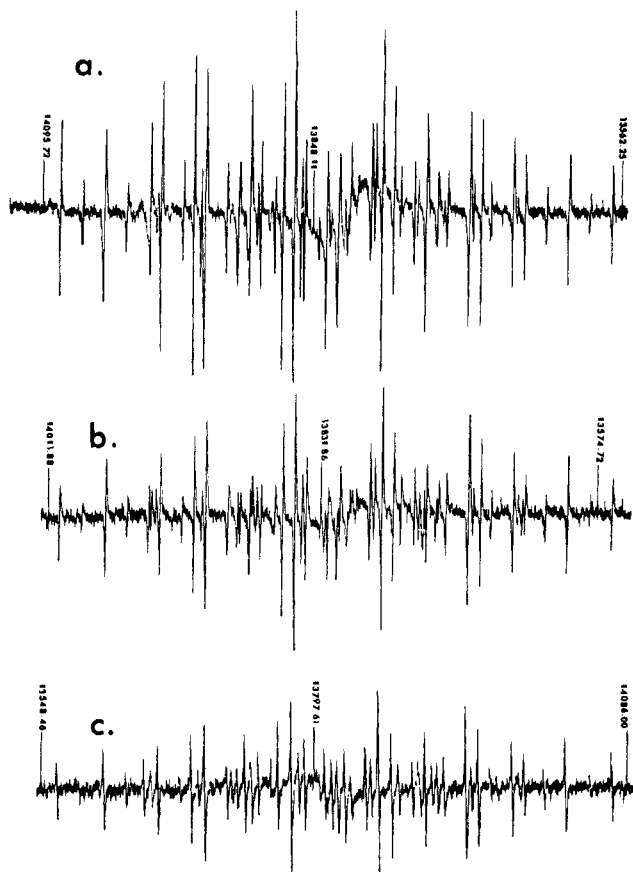


Figure 4. Electron spin resonance spectrum of  $\beta$ -chloroethyl radicals in cyclopropane solution showing the temperature dependence of the hyperfine splitting by  $\beta$  protons,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , at (a)  $-144^\circ$ , (b)  $-125^\circ$ , and (c)  $-117^\circ$ . Proton nmr field markers are in kHz.

respectively, together with the free rotation limit obtained from  $\beta,\beta,\beta$ -trifluoroethyl radical. It is apparent, however, that a simple relationship in the same form of eq 1 is inapplicable. For example, in the simplest case,  $B$  is not even constant since it varies from 110 to 67 to 58 G for the monofluoro-, difluoro-, and trifluoroethyl radicals, respectively, based on the conformations deduced from the  $\beta$  proton hfs and that of the free rotation limit and  $A = 0$ . The discrepancy is even larger for  $A \neq 0$ . The most obvious sources of the discrepancy lie in the assumptions that  $B$  is constant and the configuration about the  $\beta$ -carbon atom remains unchanged with fluorine substitution. Significant changes in the structure of the ethyl backbone are indeed indicated by the other esr parameters given in Table I. Thus, the value of the hfs for the  $\alpha$  protons increases with successive substitution of fluorines, and more significantly the  $g$  factor decreases. Both trends are contrary to those observed in alkyl radicals. The value of the  $g$  factor lower than that of alkyl radicals is also observed in the  $\beta$ -chloroethyl radical (*vide infra*). An analysis of the  $g$  factor of the  $\beta$ -chloroethyl radical indicates the participation of p-p homoconjugation between the radical site and the  $\beta$  chlorine.<sup>6</sup> Such

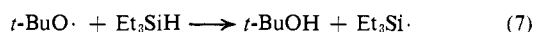
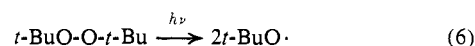
(6) (a) T. Kawamura, D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 1752 (1972); (b) within experimental error the  $\alpha$  and  $\beta$  proton hfs of the radical containing  $^{37}\text{Cl}$  are the same as those for  $^{35}\text{Cl}$  and show the same temperature dependence. The experimental ratio of the hfs  $^{35}\text{Cl}/^{37}\text{Cl} = 1.20 \pm 0.01$  is that expected from the moment ratio of 1.2014.

an interaction could also lead to a distortion of the  $\beta$  carbon in fluoroethyl radicals. At this juncture we must conclude that the angular dependence of the  $\beta$ -F splittings and the mechanism of interaction in these radicals are still unclear.<sup>7</sup> We hope that *ab initio* molecular orbital calculations<sup>8a</sup> presently in progress will help to clarify the problem.

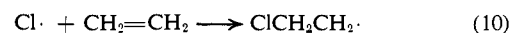
The  $\beta$ -chloroethyl radical was readily generated by a variety of photolytic procedures. Thus, the esr spectrum of the  $\beta$ -chloroethyl radical shown in Figure 4 was produced by irradiation of  $\beta$ -chloropropionyl peroxide or  $\beta$ -chloropropionyl *tert*-butyl perester in cyclopropane solutions at various temperatures<sup>9</sup>



The same spectra<sup>3b</sup> were obtained by the photolysis of a mixture of di-*tert*-butyl peroxide (DTPB), triethylsilane, and  $\beta$ -chloroethyl bromide. Alternatively, chloro-



rine atoms generated from hydrogen chloride (eq 9)



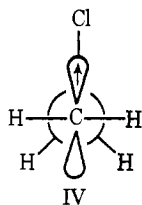
can be added to ethylene. The last method afforded spectra with the best signal-to-noise ratios. The hfs of the  $\alpha$  protons did not vary with temperature. The hfs of the  $\beta$  protons, however, is unusually small and decreases with temperature, as illustrated in Figure 5. Under the same conditions, the hfs of the  $\beta$  chlorine ( $^{35}\text{Cl}$ ) increases (Figure 5), and from the curvature of the plot we deduce that limiting values of both  $A_{\beta\text{-H}}$  and  $A_{\text{Cl}}$  are attained at approximately  $-160^\circ$ . No evidence of selective line broadening was observed in the esr spectra (Figure 4) taken over this temperature range. These results are consistent with a symmetric conformation IV.<sup>3b</sup>

The magnitude of the hfs for the  $\beta$  protons, however, is much too small even if the radical is *locked* in this conformation. If a  $\cos^2 \theta$  relationship holds for  $A_{\beta\text{-H}}$ , a value of 13.5 G is expected.<sup>4b</sup> Lower values of  $A_{\beta\text{-H}}$

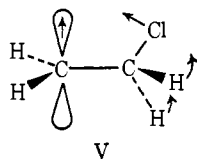
(7) (a) G. R. Underwood, V. L. Vogel, and I. Krefting, *J. Amer. Chem. Soc.*, **92**, 5019 (1970); J. L. Gerlock, E. G. Janzen, and J. K. Ruff, *ibid.*, **92**, 2558 (1970); K. Klabunde, *ibid.*, **92**, 2427 (1970); M. Iwasaki, *ibid.*, **92**, 6438 (1970); E. G. Janzen, B. R. Knauer, J. L. Gerlock, and K. L. Klabunde, *J. Phys. Chem.*, **74**, 2037 (1970); E. T. Strom and A. L. Bluhm, *ibid.*, **74**, 2036 (1970); W. R. Knolle and J. R. Bolton, *J. Amer. Chem. Soc.*, **91**, 5411 (1969); D. Kosman and L. M. Stock, *ibid.*, **92**, 409 (1970); K. Morokuma, *ibid.*, **91**, 5412 (1969); A. Hudson and J. W. E. Lewis, *Mol. Phys.*, **19**, 241 (1970); F. G. Herring, W. C. Lin, and M. R. Mustafa, *J. Magn. Resonance*, **2**, 9 (1970); C. Chachaty, A. Forchioni, and M. Shiotani, *Can. J. Chem.*, **48**, 435 (1970); M. Iwasaki, S. Noda, and K. Toriyama, *Mol. Phys.*, **18**, 201 (1970); P. H. H. Fischer and J. P. Colpa, *Z. Naturforsch. A*, **24**, 1980 (1969); (b) for a summary also see B. C. Gilbert, *Annu. Rep. Chem. Soc. B*, **67**, 23 (1970); (c) the  $g$  factor of the  $\beta$ -fluoroethyl radical is significantly smaller than that of the alkyl analogs. It is even smaller in  $\beta,\beta,\beta$ -trifluoroethyl radical.

(8) (a) Cf. L. Radom, J. A. Pople, V. Buss, and P. Schleyer, *J. Amer. Chem. Soc.*, **93**, 6987 (1971); (b) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y. 1970; (c) for example, for the strong effect of the trifluoromethyl group see C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Amer. Chem. Soc.*, **94**, 1451 (1972).

(9) Cf. J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).

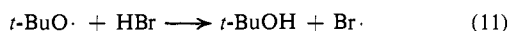


would result if the  $\beta$  protons were displaced toward the nodal plane of the p orbital (see V). Thus, to ac-

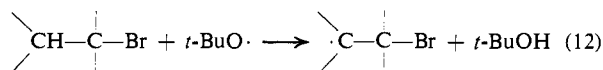


count for the observed value of  $A_{\beta-H}$ , a distortion of 25–30° is required by an INDO molecular orbital calculation using an ethyl radical as a simple model.<sup>4b</sup> Such a distortion no doubt is highly exaggerated since it is obtained by assuming only tetrahedral changes at the  $\beta$  carbon and neglecting the electronic effects of chlorine. It also suffers from assumptions inherent in the INDO approximation.<sup>5b</sup> Nonetheless, the conclusion that the chlorine nucleus is displaced toward the radical center in this radical appears inescapable. The enhanced interaction between the orbitals on chlorine and the radical center on carbon is also manifested by a  $g$  factor which is significantly less than that of other alkyl radicals. The delocalization of the odd electron has been attributed to p-p homoconjugation with the lone pair orbital on chlorine.<sup>6</sup>

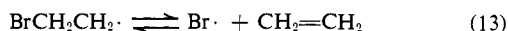
The  $\beta$ -bromoethyl radical was examined by the same procedures used with the chloro analog. Thus,  $\beta$ -bromopropionyl peroxide and the *tert*-butyl perester were photolyzed in a variety of solvents and over a wide range of temperatures (*cf.* eq 4 and 5). Various vicinal dibromides derived from ethylene, propylene, isobutylene, butene-2, cyclohexene (*cis* and *trans* adducts), and styrene were also treated with triethylsilyl and tributylstannyl radicals (*cf.* eq 6–8). Bromine atoms derived from the reaction of hydrogen bromide and *tert*-butoxy radicals from photolysis of di-*tert*-butyl peroxide (*cf.* eq 9 and 11) were added to ethylene. Finally, *tert*-butoxy radicals were photochemically gen-



erated in the presence of various alkyl halides such as *n*-propyl bromide, isobutyl bromide, and  $\beta$ -phenethyl bromide to abstract a  $\beta$  hydrogen (eq 12). None of



these procedures afforded an esr spectrum of a species which could be attributed to a bromoalkyl radical. The failure to observe  $\beta$ -bromoalkyl radicals is partly due to its extreme instability (eq 13),<sup>10</sup> which was deter-



mined in the following manner.

(10) (a) *Cf.* R. K. Friedlina, U. N. Kost, and M. Y. Kherlina, *Russ. Chem. Rev.*, **31**, 1 (1962); (b) W. O. Haag and E. I. Heiba, *Tetrahedron Lett.*, 3683 (1965); (c) W. Thaler, *Meth. Free Radical Chem.*, **2**, 121 (1969).

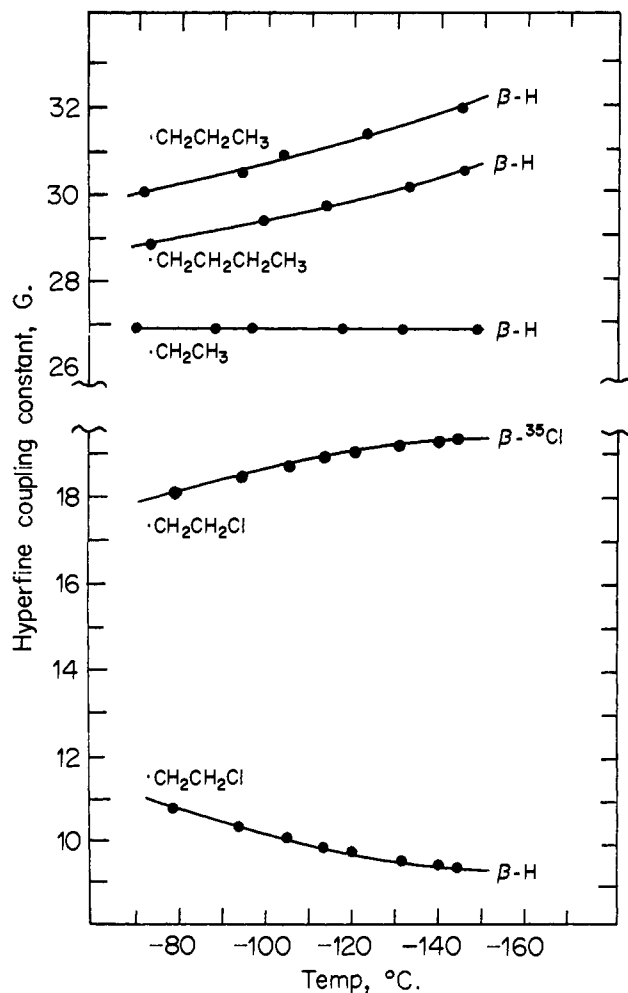
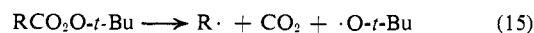


Figure 5. Temperature dependence of the hyperfine splittings of the  $\beta$  chlorine and the  $\beta$  protons in the  $\beta$ -chloroethyl radical in cyclopropane solution. Comparison with ethyl, *n*-propyl, and *n*-butyl radicals.

Previous studies<sup>11</sup> showed that photolysis of diacyl peroxides and peresters produced carbon dioxide with quantum yields of 2 and 1, respectively (eq 14 and 15).



The alkyl radicals subsequently suffer cage combination and disproportionation or reaction with solvent. The results given in Table II with ethyl radical generated from the photolysis of propionyl peroxide (run 1) show for comparison that the same processes occur in the spectrometer. The esr spectrum of the ethyl radical can be readily obtained under these conditions. Furthermore, the ethyl radicals are trapped by 1,3-butadiene (run 2), since the esr spectrum of the adduct can be observed and the analysis of products shows the absence of ethane and ethylene (butane is largely a cage product and, therefore, not scavenged or detected by esr).<sup>11</sup> Experimentally it is difficult to carry out photolysis quantitatively in the cavity of the spectrometer, but reactions carried out to various conversions show little difference (Table II, run 1). The yields given in Table II thus should be based on the conversion to carbon dioxide (eq 14 and 15).

(11) R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 4395, 5175 (1970).

**Table II.** ESR Spectra and Products from the Photolysis of Acyl and Bromoacyl Peroxides

Run	Peroxide	Solvent <sup>a</sup>	T, °C	Products, mmol <sup>b</sup>				Radical <sup>c</sup> obsd
				CO <sub>2</sub>	CH <sub>2</sub> =CH <sub>2</sub>	CH <sub>3</sub> CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	
1a	[CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> ] <sub>2</sub>	A	-88	0.46	0.11 (24)	0.05 (10)	0.13 (56)	CH <sub>3</sub> CH <sub>2</sub> ·
1b	[CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> ] <sub>2</sub>	A	-88	0.85	0.18 (21)	0.09 (11)	0.25 (59)	CH <sub>3</sub> CH <sub>2</sub> ·
2	[CH <sub>3</sub> CH <sub>2</sub> CO <sub>2</sub> ] <sub>2</sub>	A, B	-88	0.75	0.01 (1)	0.01 <sup>d</sup>	0.09 (24)	CH <sub>3</sub> CH <sub>2</sub> · + Et-C <sub>4</sub> H <sub>9</sub> ·
3	[BrCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> ] <sub>2</sub>	A	-88	0.23	0.11 (48)	<0.01	e	None
4	[BrCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> ] <sub>2</sub>	C	-89	0.59	0.31 (53)	<0.01	e	None
5	[BrCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> ] <sub>2</sub>	A, B	-88	0.48	0.25 (52)	<0.01	e	None
6	[BrCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> ] <sub>2</sub>	Bu <sub>3</sub> SnH, A	-88	0.64	0.06 (10)	0.36 (56)	e	None
7	BrCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> -O- <i>t</i> -Bu	A	-119	0.41	0.21 (51)	<0.01	e	None
8	BrCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> -O- <i>t</i> -Bu	C	-117	0.37	0.20 (54)	<0.01	e	None

<sup>a</sup> A, cyclopropane; B, 1,3-butadiene; C, isobutylene; Bu<sub>3</sub>SnH, tri-*n*-butylstannane. <sup>b</sup> Yields in mmol, those in parentheses based on CO<sub>2</sub> liberated. <sup>c</sup> ESR spectrum of radical observed; none indicates no ESR spectrum observed. <sup>d</sup> Adducts not identified. <sup>e</sup> No vinyl bromide or ethyl bromide detected.

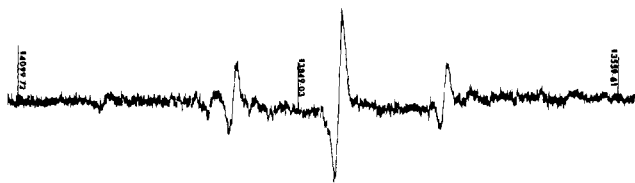
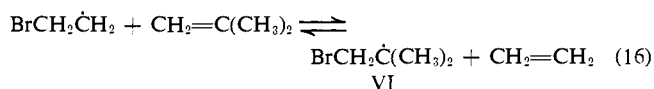


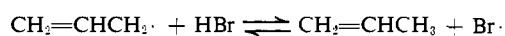
Figure 6. Selective line broadening in spectrum of the  $\gamma$ -bromopropyl radical at  $-123^\circ$  in cyclopropane solution.

The photolysis of  $\beta$ -bromopropionyl peroxide and perester was also carried out in the spectrometer to sufficiently high conversions at low temperature to enable the examination of the products of photolysis and the ESR spectrum simultaneously. Under these conditions a high yield of ethylene was formed (Table II, runs 3 and 4) and did not decrease appreciably at lower temperatures. Furthermore the presence of 1,3-butadiene (run 5) as a radical trap had little effect, under conditions in which it was highly effective in trapping ethyl radical from propionyl peroxide (run 2). Tri-*n*-butylstannane was effective in intercepting the bromoethyl radical, which was reduced further to ethane (run 6). The radical chain decomposition of diacyl peroxides by trialkylstannanes has been recently discussed.<sup>12</sup> Finally, the bromoethyl radical was generated in the presence of isobutylene as solvent to optimize formation of the adduct VI which is favored by a factor of 825,000 ( $40^\circ$ )<sup>13</sup> over the  $\beta$ -bromoethyl radical if equilibrium 16 obtains by dissociation and readdition of bromine atoms.



Our inability to observe the ESR spectra of  $\beta$ -bromoalkyl radicals *in solution* does not indicate that such is not possible. For example, the ESR spectra of  $\beta$ -bromo and iodoalkyl radicals were recently obtained in frozen solution at  $77^\circ\text{K}$  by  $^{60}\text{Co}$   $\gamma$ -radiolysis.<sup>14</sup> Unfortunately, the proton hyperfine splittings were not resolved under these conditions and the radical species

could not be positively identified. However, large  $\beta$ -bromine and iodine splittings were apparently indicated. These results contrast with the early report of the observation of  $\beta$ -bromoalkyl radicals from the photolysis of HBr and alkenes also in the "glassy" state at  $77^\circ\text{K}$ ,<sup>15</sup> which have been discounted by later analysis.<sup>16,17</sup> The paramagnetic species were ascribed to allylic radicals generated by hydrogen abstraction. Interestingly, photolysis of a mixture of HBr and propylene or butene with di-*tert*-butyl peroxide in cyclopropane solutions at temperatures as low as  $-150^\circ$  did not afford any ESR spectrum of the allylic radical obtained in the absence of HBr.<sup>2</sup> The latter is probably due to the reversibility



which is slow in the glass state, since the corresponding study with HCl does afford allylic radicals.

**$\gamma$ -Halogen-Substituted Alkyl Radicals.** In addition to their instability, our failure to observe the ESR spectra of  $\beta$ -bromoalkyl radicals in solution may be due to anisotropic effects present in these radicals, which may broaden the lines to a point beyond detection. However, the presence of a bromine substituent in an alkyl radical itself is insufficient to account for our inability to record the ESR spectra of  $\beta$ -bromoalkyl radicals. Thus, the ESR spectrum of the  $\gamma$ -bromopropyl radical (Table III) was obtained by either photolysis of  $\gamma$ -bromobutyryl peroxide (as well as the *tert*-butyl perester) or by reaction of triethylsilyl radicals with 1,3-dibromopropane.

The ESR spectrum of the *3-fluoropropyl* radical is similar to that of the *n*-butyl radical<sup>2,4</sup> and showed the same temperature-dependent behavior (Table III and Figure 8). Thus, at lower temperatures the central lines ( $M_1 = 0$ ) of the triplet corresponding to the  $\beta$  protons broadened and had reduced peak-to-peak amplitudes, in contrast to the selective line broadening of the  $\alpha$  protons in the *n*-propyl radical.<sup>4</sup>

The ESR spectrum of the  $\gamma$ -bromopropyl radical, on the other hand, showed a unique alternating line-width behavior.

The spectrum shown in Figure 6 consists of the expected triplets of triplets from splitting by the  $\alpha$  and

(12) J. L. Brokenshire and K. U. Ingold, *Int. J. Chem. Kinet.*, **3**, 343 (1971).

(13) (a) P. I. Abell, *Trans. Faraday Soc.*, **60**, 2214 (1964); (b) W. Thaler, *ibid.*, **60**, 186 (1964).

(14) A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.*, **93**, 7330 (1971).

(15) P. I. Abell and L. H. Piette, *ibid.*, **84**, 916 (1962).

(16) M. C. R. Symons, *J. Phys. Chem.*, **67**, 1566 (1963); cf. C. U. Morgan and K. J. White, *J. Amer. Chem. Soc.*, **92**, 3309 (1970).

(17) P. B. Ayscough, "Electron Spin Resonance in Chemistry," Methuen, Ltd., London, 1967, p 378.

Table III. ESR Parameters of Haloalkyl Radicals in Solution

Radical	$T$ , °C	$\langle g \rangle^a$	$A_{\alpha-H}$	$A_{\beta-H}$	$A_{\gamma-H}$
$\text{CH}_2\text{CH}_2\text{CH}_3$	-130	2.00265	22.10	31.12	0.27
$\text{CH}_2\text{CH}_2\text{CH}_2\text{OAc}$	-124	2.00265	22.29	29.10	0.75
$\text{CH}_2\text{CH}_2\text{CH}_2\text{F}$	-126	2.00269	22.31	28.19	0.50 <sup>b</sup>
$\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	-125	2.00271	22.36	27.74	0.85
$\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	-120	2.00368	22.28	27.17	n.r.
$\text{CH}_2\text{CH}_2\text{CCl}_3$	-128	2.00366	22.30	22.30	
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	-119	2.00265	21.94	29.73	0.72
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	-119	2.00267	22.34	29.46	0.69
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	-114	2.00274	22.11	29.89	nr
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	-125	2.00266	22.10	29.99	0.69
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	-122	2.00269	22.87	29.98	nr
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	-130	2.00265	21.98	29.97	0.70
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	-129	2.00266	22.05	30.11	0.68

<sup>a</sup> Corrected for second-order effects; hfs in gauss; nr = not resolved. <sup>b</sup>  $A_{\gamma-F} = 1.00$ .

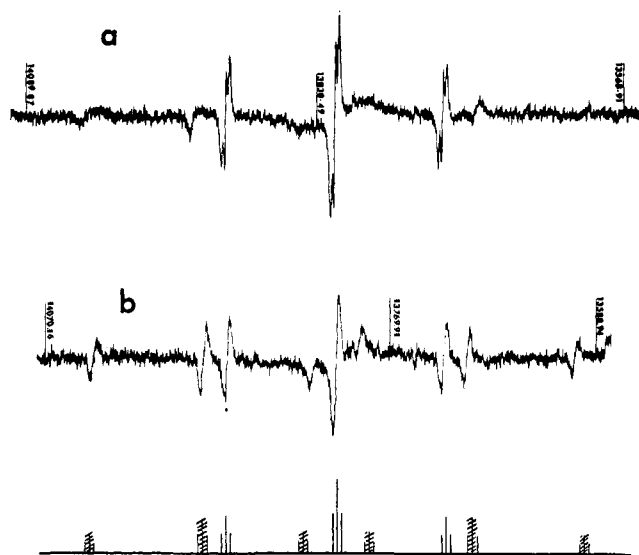


Figure 7. Temperature dependence of the selective broadening of lines in the esr spectrum of the  $\gamma$ -chloropropyl radical at (a)  $-132^\circ$  and (b)  $-94^\circ$  in cyclopropane solutions. The shaded portions of the stick spectrum correspond to the lines broadened by the *in-phase* modulation of the  $M_I = \pm 1$  of the  $\beta$  protons.

$\beta$  protons, but the outer lines (corresponding to  $M_I = \pm 1$ ) of the triplet for the  $\beta$  protons are broadened to a point where they almost disappear at this temperature ( $-123^\circ$ ).

A similar selective broadening of lines occurs in the esr spectrum of the  $\gamma$ -chloropropyl radical in Figure 7, which illustrates the dramatic effect of temperature. The onset of line broadening also occurs approximately at the same temperature (*ca.*  $-100^\circ$ ) that the hfs of both the  $\beta$  protons increased markedly as shown in Figure 8. The magnitude of the  $\gamma$  proton hfs also shows a distinct change at this temperature. Above  $-100^\circ$  the  $\gamma$  hfs is very small and the lines are not readily resolved, but below this temperature the  $\gamma$  hfs increases from 0.15 to 0.60 G and the individual components are easily identified. As the temperature was lowered beyond  $-150^\circ$  the "broadened" lines began to sharpen again. Unfortunately, we were unable to lower the temperature sufficiently to allow observation of normal peak-to-peak amplitudes. The temperature dependence of the hfs for the  $\beta$  protons of the *n*-butyl and  $\gamma$ -fluoropropyl radicals is included in Figure 8 for comparison.

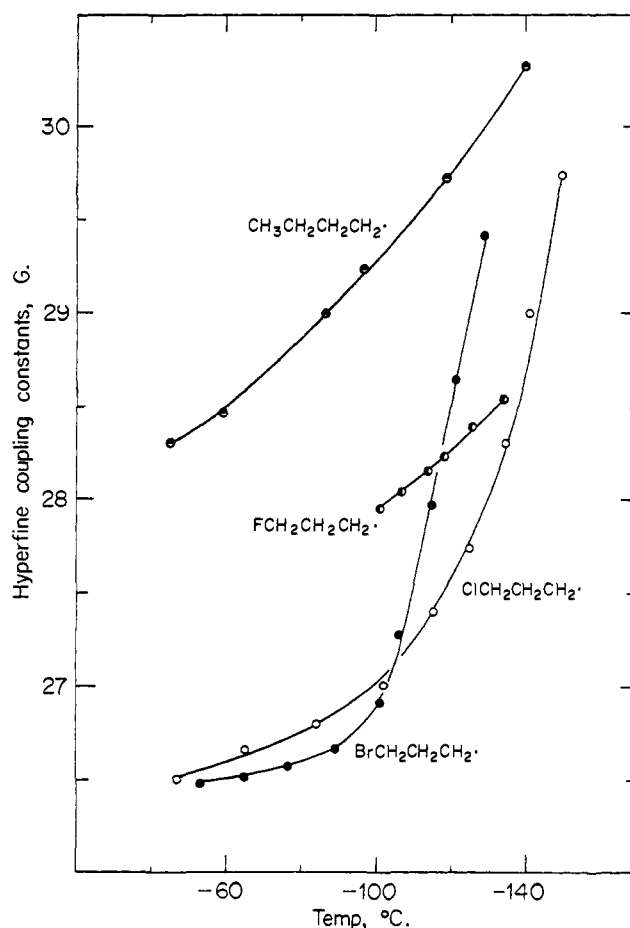


Figure 8. Temperature dependence of the hfs of the  $\beta$  protons in  $\gamma$ -fluoropropyl (○),  $\gamma$ -chloropropyl (●),  $\gamma$ -bromopropyl (●), and *n*-butyl radicals (○).

The rather unusual alternation of line widths is observed only in the spectra of  $\gamma$ -chloro and  $\gamma$ -bromopropyl radicals, and is clearly associated with an *in-phase* modulation of the  $\beta$  hfs. For example, if the two  $\beta$  hydrogens have hfs which are instantaneously equivalent at all times but modulated between two or more limiting values, the line widths would be proportional to  $(\bar{M}_H)^2$ .<sup>15</sup> The latter would lead to selective broadening of only the "outer" pairs of lines of the triplet corresponding to the  $\beta$  proton and is indicated by the shaded portions of

(15) There are a few previous examples of this line-width effect: G. K. Fraenkel, *J. Phys. Chem.*, **71**, 139 (1967); P. D. Sullivan and J. R. Bolton, *ibid.*, **73**, 4387 (1969).

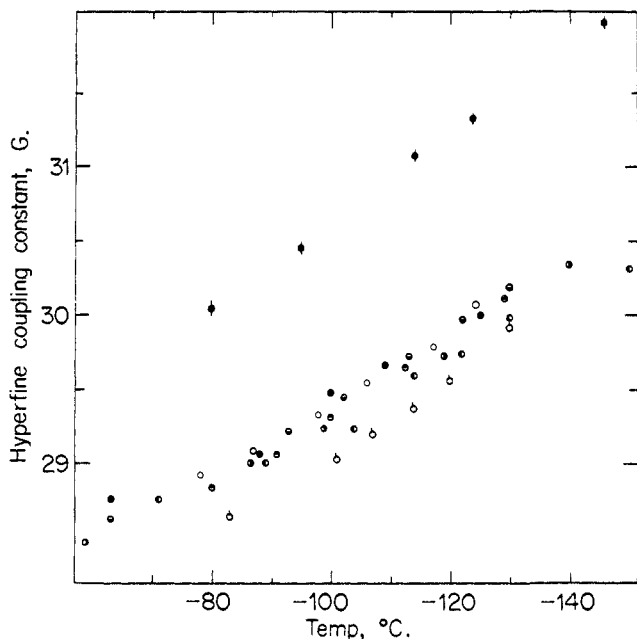
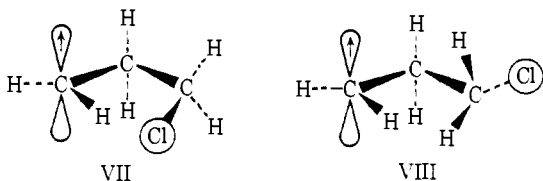


Figure 9. Temperature dependence of the hfs due to the  $\beta$  protons in 4-bromopropyl ( $\circ$ ), 5-bromopentyl ( $\square$ ), 6-bromohexyl ( $\triangle$ ), 4-chloropropyl ( $\diamond$ ), *n*-propyl ( $\bullet$ ), *n*-butyl ( $\blacksquare$ ), *n*-pentyl ( $\blacktriangle$ ), and *n*-octyl ( $\blacklozenge$ ) radicals in cyclopropane solutions.

the "stick" spectrum in Figure 7. This line-width effect is related to asymmetry around the  $C_\beta-C_\gamma$  bond since the esr spectrum of the  $\gamma,\gamma,\gamma$ -trichloropropyl radical is invariant between  $-20$  and  $-160^\circ$ . Furthermore, the esr parameters listed in Table III also indicate that the effect of halogen diminishes abruptly as the alkyl chain is lengthened.

We associate the magnitude and the change of the hfs as well as the occurrence of line broadening particularly at lower temperatures with unique conformational changes in the  $\gamma$ -chloro and  $\gamma$ -bromopropyl radicals. Two such conformations which are consistent with these observations are shown by VII and VIII.

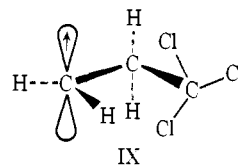


We also attribute the unusually high values of the  $g$  factors of the  $\gamma$ -chloropropyl and (especially) the  $\gamma$ -bromopropyl radical to the delocalization of the odd electron onto halogen orbitals. A hyperconjugative interaction is possible, but such a mechanism is not in accord with conformations VII or VIII. It may, however, reflect a slight tilting of the chlorine out of the nodal plane by rotation about the  $C_\beta-C_\gamma$  bond. The latter is consistent with the preferred conformation of the  $\gamma,\gamma,\gamma$ -trichloropropyl radical, as indicated by the trend toward decreasing hfs for the  $\beta$  protons (*vide infra*).<sup>19</sup> The  $g$  factor of the  $\gamma,\gamma,\gamma$ -trichloropropyl rad-

(19) (a) Although unresolved, we judge from the significantly broader lines that the chlorine splitting in  $\gamma,\gamma,\gamma$ -trichloropropyl radical is also larger than that of  $\gamma$ -chloropropyl radical. (b) Interestingly, chemical studies show that there is no stereospecificity in the addition of trichloromethyl radicals (as bromotrichloromethane) to *cis*- and *trans*-butene-2. Therefore, any conformational equilibration of the intermediate adduct radical is faster than chain transfer [P. S. Skellern and R. C. Woodworth, *J. Amer. Chem. Soc.*, 77, 4638 (1955)].

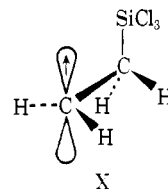
ical is also significantly larger than that of the monochloro analog.

Interestingly, the hfs of the  $\alpha$  and  $\beta$  protons in the  $\gamma,\gamma,\gamma$ -trichloropropyl radical both have the same value. The esr spectrum of this radical showed no dramatic line-width effect and remained a quintet with the intensity of lines in a ratio 1:4:6:4:1 between  $-20$  and  $-160^\circ$ . The relatively broad lines ( $\Delta H_{ms} \sim 1$  G) could have obscured small changes in hfs. Of the two explanations for this coincidence, we disfavor the possibility that the two pairs of protons are equivalent, since it would involve bridging by the  $Cl_3C$  group, for which there is no compelling evidence. It is more likely that the two hfs are accidentally equivalent as a result of the decreased value of the  $\beta$  hfs caused by displacement of the bulky  $\gamma$  carbon from the nodal plane<sup>19</sup> (IX). A



similar trend in  $\beta$  hfs is observed in *n*-propyl ( $A_{\beta-H} = 31.12$  G), *n*-butyl ( $A_{\beta-H} = 29.73$  G), and  $\gamma,\gamma$ -dimethylbutyl ( $A_{\beta-H} = 24.71$  G) radicals.

Furthermore, replacement of the  $\gamma$  carbon in the propyl radical with silicon is known to alter its conformation to a symmetric one.<sup>4b-d</sup> The esr spectrum of the  $\beta$ -trichlorosilylethyl radical which is the silicon analog of the  $\gamma,\gamma,\gamma$ -trichloropropyl radical can be readily observed when trichlorosilyl radicals generated from  $Cl_3SiH$  and di-*tert*-butyl peroxide are added to ethylene. The values of the  $\alpha$  ( $A_{\alpha-H} = 21.83$  G) and the  $\beta$  proton ( $A_{\beta-H} = 17.22$  G) splittings are clearly distinguished, and this radical ( $g = 2.00365$  at  $-128^\circ$ ) exists in conformation X similar to other  $\beta$ -silyl-substituted alkyl



radicals. Moreover, the sizable  $\gamma$ -chlorine splittings ( $A_{\gamma-Cl} \cong 1.0$  G) support this conformation.

$\delta$ ,  $\epsilon$ , and  $\omega$  Halogen-Substituted Alkyl Radicals. The 4-chlorobutyl, 4-bromobutyl, 5-bromopentyl, and 6-bromohexyl radicals were generated from the corresponding organic bromides and triethylsilyl radicals. The esr spectra of these radicals together with the hydrocarbon analogs were observed between  $-40$  and  $-150^\circ$ . The hyperfine splitting constants and the  $g$  factors are also tabulated in Table III and the temperature-dependent  $\beta$  hfs are plotted in Figure 9. The esr spectrum of each of these radicals was characterized by the selective broadening of the central line ( $M_I = 0$ ) of the triplet splitting of the  $\beta$  protons which appeared with reduced peak-to-peak amplitude as the temperature was lowered. This alternating line-width effect was observed previously in the esr spectrum of the *n*-butyl radical,<sup>8</sup> although terminal substitution by halogen caused the onset of broadening to occur at temperatures approximately  $20^\circ$  higher than that in the unsubstituted analog.

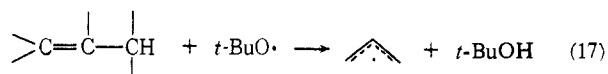


The unbroadened lines became more narrow as the temperature was lowered

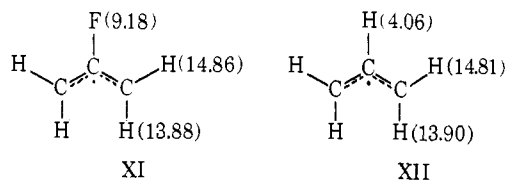
For the series of radicals 4-bromobutyl, 5-bromopentyl, and 6-bromohexyl, the unbroadened lines also became progressively sharper as the bromine was moved away from the radical center, as shown in Figure 10. The line widths of the 6-bromohexyl are also compared to those of the *n*-butyl radical at the same temperature.

It is clear from Figure 9 that halogen substitution beyond the  $\gamma$  carbon does not significantly affect the temperature dependence of the  $\beta$  hfs of alkyl radicals. Furthermore, the *g* factor and line-width effect indicate that there is little influence exerted by a halogen substituent on the conformation at the  $\alpha$ ,  $\beta$ , and  $\gamma$  carbon atoms of an alkyl chain. Thus, any interaction between the *p* orbital on carbon and the halogen drops off rapidly if substitution occurs beyond the  $\gamma$  carbon atom.

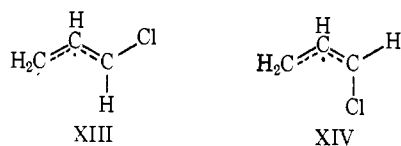
**$\beta$  Halogen-Substituted Allyl Radicals.** Allyl radicals are readily generated for esr study by abstraction of hydrogen from alkenes by *tert*-butoxy radicals generated photochemically from di-*tert*-butyl peroxide.<sup>20</sup> We examined a number of halogenated propenes to study



the esr of haloallyl radicals. Initial observations<sup>21</sup> showed that 2-fluoropropene gave rise to 2-fluoroallyl radical XI, the proton hfs of which were comparable to those of allyl radical XII.



Photolysis of mixtures of DTBP and allyl chloride produced a weak complex esr spectrum, probably due to radicals XIII and XIV. The analysis of the spectrum



was unfortunately discouraged by the multiplicity of doublet splittings (64) expected. When allyl bromide was employed, only a weak spectrum of allyl radical was obtained, the formation of which we attribute to transfer of bromine from allyl bromide to the bromo analogs of XIII and XIV. An alternative path involving bromine transfer directly to *tert*-butoxy radicals is without precedent.

Photolysis of a mixture of DTBP and 2-chloropropene afforded no spectra over a wide range of temperatures. However, a strong esr spectrum ( $g = 2.00316$ ) was observed when 2-bromopropene was treated similarly. The hyperfine splitting consisted of two doublets (17.14 and 10.60 G) and a quartet (2.35 G) which varied little with temperature. The sharp lines of the spectrum ( $\Delta H_{\text{mls}} \approx 0.010$  G) suggest that the paramagnetic species

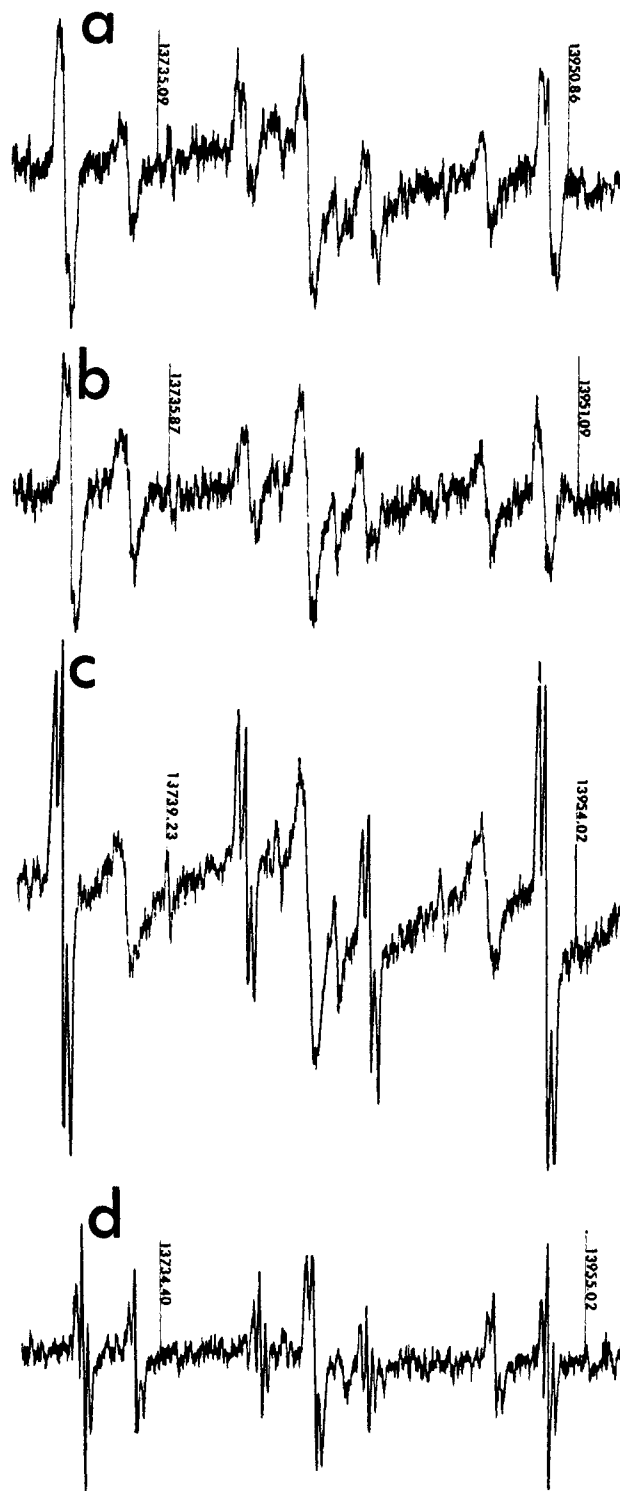


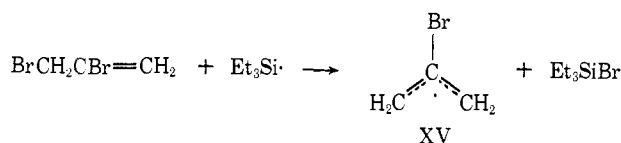
Figure 10. General line broadening effects in the esr spectra of bromoalkyl radicals in comparison to the *n*-butyl radical in cyclopropane solutions: (a)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  at  $-84^\circ$ ; (b)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  at  $-87^\circ$ ; (c)  $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  at  $-89^\circ$ ; (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot$  at  $-85^\circ$ .

does not contain bromine, but its identity is uncertain at present.

The photolysis of a mixture of 2,3-dibromopropene, triethylsilane, and DTBP at temperatures above  $-90^\circ$  produced a weak spectrum which was broadened and unresolved at lower temperatures. The weak spectrum consisted of two triplets (14.0 and 13.5 G), each line of which was further split into four lines of equal amplitude

(20) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **90**, 7157 (1968).  
 (21) P. J. Krusic and J. K. Kochi, unpublished observations.

and separated by 1.35 G. We tentatively assign this spectrum to the 2-bromoallyl radical XV, the small



1:1:1:1 quartet splitting being due to the bromine nucleus. The low  $g$  factor ( $2.00181 \pm 0.00005$ ) for this radical suggests an interaction between the odd electron and the bromine orbitals, resulting in a large negative contribution to the  $g$  factor.

Until recently, aromatic iminoxy, nitronyl, and carbonyl nitroxide radicals were the only species in which hyperfine splitting by bromine had been observed.<sup>22</sup> Due to the large quadrupole moments of both bromine isotopes, the presence of a bromine nucleus close to the radical center in a  $\pi$  radical may give rise to line broadening and anisotropy. Ullman<sup>22c</sup> has pointed out that the failure to observe bromine hyperfine splitting may be due to fluctuations in the electric field gradient at the bromine nucleus, causing nuclear spin relaxation at rates greater than the hyperfine splitting and leading to spectral averaging of the nuclear spin states.

In those radicals in which an extensive  $\pi$  system is present, back-bonding of the symmetric  $d$  orbitals on bromine with the  $\pi$  system or nonbonded interactions (e.g., with nitroxyl oxygen) may be sufficient to partially offset the nuclear field gradient caused by the halogen  $\sigma$  bond. Our failure to observe the esr spectrum of  $\beta$ -bromoalkyl radicals may be related to line broadening in the absence of these interactions. Further studies on these systems are desirable.

#### Conformational Effects of Halogen on Alkyl Radicals.

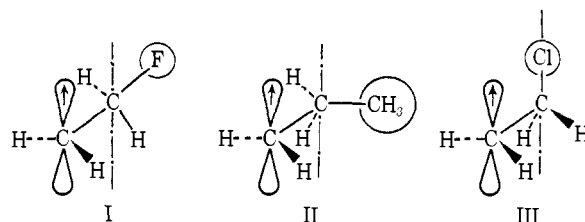
Esr studies show that chlorine located in the  $\beta$  and  $\gamma$  positions has a profound effect on the conformation of the alkyl chain. Analysis of the  $g$  factor indicates that  $p$ - $p$  homoconjugation from the radical center to chlorine is a significant mechanism for interaction in the  $\beta$ -chloroethyl radical.<sup>23</sup> The shift in the  $g$  factor of the  $\beta$ -fluoroethyl radical is less than that of the  $\beta$ -chloroethyl radical (Table I). Thus, the magnitude of the  $p$ - $p$  homoconjugation in this radical, previously proposed by Lossing<sup>24</sup> and by Iwasaki<sup>25</sup> on the basis of single crystal studies, is smaller than the interaction in the  $\beta$ -chloroethyl radical. Interestingly, the conformation I adopted by the  $\beta$ -fluoroethyl radical is also intermediate between that of the  $n$ -propyl radical II and the  $\beta$ -chloroethyl radical III. Since equilibrium conformations in an alkyl chain result from a delicate balance between steric repulsions and electron delocalization, the trend toward greater eclipsing of the halogen in proceeding from fluorine to chlorine is, thus, a manifestation of an increasing interaction between the odd electron orbital and the halogen, and is consistent with the

(22) (a) W. M. Fox and W. A. Waters, *J. Chem. Soc., London*, 4628 (1965); (b) R. O. C. Norman and B. C. Gilbert, *J. Phys. Chem.*, **71**, 14 (1967); *J. Chem. Soc. B*, 981 (1967); *ibid.*, 123 (1968); (c) E. F. Ullman, L. Call, and J. Osiecki, *J. Org. Chem.*, **35**, 3623 (1970); (d) A. J. Holman and M. S. Perkins, *Chem. Commun.*, 244 (1971).

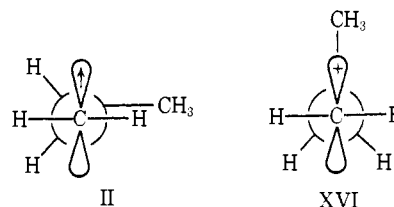
(23) The hyperconjugative interaction with the  $\beta$  chlorine cannot be simply computed from the value of the chlorine hfs and the contact term for chlorine, since the  $s$  character of the C-Cl  $\sigma$  and  $\sigma^*$  orbitals is unknown. The contact term for <sup>35</sup>Cl is 1672 G.

(24) R. J. Lossing, *J. Chem. Phys.*, **47**, 3634 (1967).

(25) M. Iwasaki, *Mol. Phys.*, **20**, 503 (1970); *J. Amer. Chem. Soc.*, **92**, 6348 (1970).



higher rotational barrier in the  $\beta$ -chloroethyl radical.<sup>26</sup> An analogous conformational distinction is shown between the  $n$ -propyl radical II and the cation XVI. Re-



cent calculations<sup>27</sup> show that the stable conformation of the  $n$ -propyl cation (in contrast to that of the  $n$ -propyl radical) is one in which the methyl group eclipses the  $p$  orbital. The rotational barriers are also substantially higher (2.5 vs. 0.4 kcal/mol),<sup>4c,5a</sup> which can be ascribed to stabilization of the cation by hyperconjugative effects.

#### Experimental Section

Esr spectra were taken with a modified Varian X-band spectrometer utilizing 100-kHz modulation. The microwave bridge was designed around a three-port ferrite circulator. A backward diode (Philco L4154B) was employed as detector in conjunction with a low-noise, wide-band preamplifier (Philco P301). The latter was provided with an impedance-matching input circuit and a simple dc circuit to monitor the crystal current by means of a sensitive galvanometer. The input transformer was wound in a ferrite pot core (Ferroxcube, Inc.) and was carefully shielded with many layers of high magnetic permeability foil. An attenuator was placed before the tunable detector mount and was used during tuning to avoid excess microwave power on the detector. The field of a Varian V3600 12-in. magnet was swept very linearly by a Varian V3508 magnet flux stabilizer and slow-sweep unit. The spectral scans were accurately calibrated by means of a field marker operating in conjunction with a Harvey-Wells G502 nmr gaussmeter and a Hewlett-Packard frequency counter. The field marker causes the superposition of markers at accurately known field values directly onto the spectral record. We wish to thank Dr. Paul J. Krusic for invaluable assistance and advice during the construction of the spectrometer.

The microwave frequency was determined directly using a Hewlett-Packard 5255A frequency converter and a Hewlett-Packard X281A microwave adapter in conjunction with a Hewlett-Packard 5248L frequency counter. The  $g$  factors were determined with the perylene cation radical ( $g = 2.00258$ )<sup>28</sup> as a daily standard in the configuration employed. A correction, usually  $5 \times 10^{-5}$ , was made to the measured values. The accuracy of such measurements is thought to be  $\pm 0.00003$ , and  $g$  factors made under these conditions were in agreement with those obtained by Fessenden and Schuler.<sup>29</sup> In most cases hfs were determined by positioning each line precisely,

(26) Although the esr spectrum of the  $\beta$ -bromoethyl radical in solution is still unavailable to us, we would speculate from the trend established for  $\beta$ -methyl-,  $\beta$ -fluoro-, and  $\beta$ -chloroethyl radicals and the  $\gamma$ -substituted (including bromo) propyl radicals that it would exist in an eclipsed conformation similar to III. The extent of "bridging" in  $\beta$ -bromoalkyl radicals must await a determination of the proton hfs [cf. also, C. Ronneau, J. P. Soumillion, P. Dejaifve, and A. Bruylants, *Tetrahedron Lett.*, 317 (1972)].

(27) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 6380 (1970).

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

(29) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

applying second-order corrections,<sup>30</sup> and then recomputing the distance between each line.

The light source, variable temperature equipment, and the sample tubes are as described previously.<sup>4b</sup> The temperature in the tube was calibrated with a thermocouple and accurate to  $\pm 5^\circ$ . The photolyses were carried out in typical cases as follows.

For the photolysis of diacyl peroxides or acyl peresters<sup>8</sup> a small amount of the peroxide (*ca.* 100 mg) was dissolved in a relatively large volume (15:1) of cyclopropane or cyclopropane-ethane mixtures. For diacyl peroxides it was also possible to employ diethyl ether or ether-pentane mixtures as solvent to enable lower temperatures to be obtained before crystallization became a problem.

For photolytic reduction of alkyl halides,<sup>3a</sup> equal volumes of di-*tert*-butyl peroxide and triethylsilane were diluted with sufficient cyclopropane (and ethane) to give a final ratio of approximately 1:1:1:4. A correspondingly smaller amount of dibromoalkanes was used. The halide was usually the bromide, but chlorides could also be used. In the latter case, good spectra of alkyl radicals could only be observed at certain temperatures, above and below which the spectrum of triethylsilyl radicals was also observed. In some experiments the triethylsilane was replaced by tri-*n*-butylstannane and an alkyl iodide employed.

For the addition of chlorine atoms to alkenes, the samples contained a small amount of di-*tert*-butyl peroxide, a very small amount of anhydrous HCl, and roughly equal amounts of cyclopropane and ethane. Larger amounts of HCl lead to a diminution of the intensity of the spectrum. In order to prevent premature thermal additions from occurring, the HCl was kept apart from the alkene by interposing a layer of cyclopropane during the preparation of the sample. The same procedure was used for HBr.

All samples were thoroughly degassed using a freeze-pump-thaw cycle. When spectra were weak or not observed, the amounts of

the various components were varied to obtain optimum concentrations.

**Materials.** Di-*tert*-butyl peroxide was obtained from Shell Chemical Co., washed, and redistilled at reduced pressure prior to use. The  $\beta$ -chloro and  $\beta$ -bromopropionyl peroxides and peresters were prepared by a procedure described previously.<sup>31</sup> The  $\gamma$ -chloro and  $\gamma$ -bromobutyryl peroxides and peresters were synthesized by Mr. Y. D. Tang and the *tert*-butyl  $\gamma,\gamma,\gamma$ -trichlorobutyryl perester was kindly donated by Dr. L. K. Montgomery.

Triethylsilane, 1-bromo-3-fluoropropane, 1,3-diiodopropane, 1,1,1-trichloro-3-bromopropane, 1-bromo-4-chlorobutane, 1,5-diiodopentane, and 1,6-dibromohexane were obtained from Columbia Organic Chemicals Co. 1,2-Dibromoethane and 1-bromo-3-chloropropane were kindly donated by the Dow Chemical Co. 1,3-Dibromopropane, 1,4-dibromobutane, and 1,5-dibromopentane were obtained from Distillation Products Industries (Eastman Kodak). 1-Bromo-2-chloroethane and *n*-propyl iodide were from Matheson Coleman and Bell, 1,4-diiodobutane came from City Chemical Co., 2-bromopropene was from J. T. Baker Co., 2,3-dibromopropene came from Aldrich Chemical Co., and 1,1,1-trifluoro-2-bromoethane was from Pierce Chemical Co. 1-Bromo-2-fluoroethane was prepared from 2-fluoroethanol (Columbia Organic Chemical Co.) and phosphorus tribromide; bp  $71-73^\circ$  (lit.  $71-72^\circ$ ).<sup>32</sup>

The procedure for quantitative analysis of carbon dioxide, ethane, ethylene, and butane was described previously.<sup>31</sup>

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(31) J. K. Kochi, *J. Amer. Chem. Soc.*, **85**, 1958 (1963).

(32) F. W. Hoffman, *J. Org. Chem.*, **15**, 425 (1950).

(30) R. W. Fessenden, *J. Chem. Phys.*, **37**, 747 (1962).

## Synthesis and Thermal Rearrangement of the 2-Azabicyclo[3.1.0]hex-3-ene Ring System<sup>1</sup>

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**Abstract:** The 2-azabicyclo[3.1.0]hex-3-ene ring system has been prepared. Heating *N*-carbomethoxy-2-azabicyclo[3.1.0]hex-3-ene in the gas phase at  $285^\circ$  gave only *N*-carbomethoxy-1,2-dihydropyridine. Studies on the 6,6-dideuterio derivative **17** and the results of an attempt to prepare the *N*-methyl derivative **25** suggest that a dipolar species analogous to **15** is involved in the thermal reactions of this ring system. In contrast, the thermal rearrangement of *N*-carbomethoxy-6-carbomethoxy-2-azabicyclo[3.1.0]hex-3-ene gave dihydropyridine **30**. This result is not consistent with a dipole intermediate but is consistent with **5b** undergoing a cycloreversion to give **29** which cyclizes to the observed dihydropyridine. The thermal rearrangements of the 2-azabicyclo[3.1.0]hex-3-ene ring systems are discussed in terms of the ability of substituents at position 6 to interact with one of the highest occupied molecular orbitals of the cyclopropane ring.

Heterocycles can be related to carbocycles by either substituting unsaturated nitrogen ( $-N=$ ) for unsaturated carbon ( $-CH=$ ) or by substituting saturated nitrogen ( $-NH-$ ) for saturated carbon ( $-CH_2-$ ). Paquette and coworkers have, in recent years, synthesized the aza analogs of cyclooctatetraene, semibullvalene, and bullvalene which are representatives of the former type of substitution.<sup>2</sup> They have observed

that these molecules display some fascinating chemistry and their studies have given chemists a more complete understanding of the chemical reactivity of unsaturated heterocyclic molecules.

Substitution of saturated nitrogen ( $-NH-$ ) for a saturated carbon ( $-CH_2-$ ) is particularly interesting since the lone pair of electrons on nitrogen can interact with unsaturated centers. Heterocycles of this latter type have the ability to be more extensively conjugated and contain two additional  $\pi$  electrons compared to the analogous carbocyclic system.

The 2-azabicyclo[3.1.0]hex-3-ene ring system (**1**) can be related to bicyclo[3.1.0]hex-2-ene (**2**) in the above

(1) Portions of this work have been published in preliminary form: F. W. Fowler, *Angew. Chem., Int. Ed. Engl.*, **10**, 135 (1971); *Chem. Commun.*, 1359 (1969).

(2) For a recent review of this work see L. A. Paquette, *Angew. Chem., Int. Ed. Engl.*, **10**, 11 (1971).