

# Rearrangements and Conformations of Chloroalkyl Radicals by Electron Spin Resonance

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**Abstract:** A variety of alkyl radicals containing one or more chlorine atoms substituted in the  $\alpha$ ,  $\beta$ , and  $\gamma$  positions are generated for esr study. The migration of chlorine from the  $\beta$  to  $\alpha$  position occurs readily if the centers are tertiary and primary, respectively, but no rearrangements are observed from more remote positions regardless of the pattern of substitution. The configuration at the radical center of  $\alpha,\alpha$ -dichloroalkyl radicals is intermediate between the highly pyramidal  $\alpha,\alpha$ -difluoro and the planar  $\alpha,\alpha$ -dimethyl analogs, and its effect on the conformation about the  $C_\alpha-C_\beta$  bond is discussed. Bridging by a  $\beta$ -chloro substituent is less in radicals with pyramidal configurations, and dynamic conformational effects can be observed by the selective line broadening in the esr spectra.  $\gamma,\gamma,\gamma$ -Trihalo substitution causes alterations in the stable conformation of primary alkyl radicals according to their size, but there is little evidence for 1,3 bridging of chlorine. The effect of chlorine substitution in the  $\alpha$  and  $\gamma$  positions is more akin to that of a methyl group rather than fluorine and suggests that size is a more important influence than electronegativity. The effect of chlorine diminishes beyond the  $\gamma$  position. The additions of methyl, trifluoromethyl, and trichloromethyl radicals to ethylene are compared.

Halogen substitution can cause substantial conformational and conformational changes in alkyl radicals and plays an important role in determining the course of a number of free radical reactions.<sup>1-3</sup> The effects of fluorine substitution in the  $\alpha$ ,  $\beta$ , and  $\gamma$  positions of alkyl radicals have been examined by electron spin resonance (esr) in previous studies.<sup>4,5</sup> Our primary objective in these studies is to employ information obtainable by esr to augment and extend conclusions based on chemical and other types of information.

Fluorine differs from the other halogens in its small size and high electronegativity. The latter has a particularly marked effect in inducing a pyramidal configuration at the radical site in  $\alpha$ -fluoroalkyl radicals.<sup>6,7</sup> The electronegativity of chlorine, however, like bromine and iodine, is significantly smaller than that of fluorine. Chlorine substituents should, thus, provide an additional probe for the esr study of transient alkyl radicals. Sterically, chlorine is about the same size as a methyl group and its electronegativity is larger. Finally, line broadening in the esr spectra of chloroalkyl radicals is not expected to be as serious an impediment as it is in the spectra of bromine or iodine analogs due to the lower nuclear quadrupole moments of <sup>35</sup>Cl and <sup>37</sup>Cl. Indeed, reasonably well-resolved esr spectra of stable chlorophenylmethyl radicals as well as transient chloroalkyl radicals have been previously obtained in solution.<sup>8-10</sup>

A chlorine atom substituted in the  $\beta$  position of an alkyl radical has been shown to have a particularly marked effect on the conformational properties.<sup>1,9-11</sup> Furthermore, the rapid rate of chlorine migration to the radical center in the  $\beta$ -chloroisobutyl radical (estimated as  $10^{10} \text{ sec}^{-1}$  at  $50^\circ\text{C}$ )<sup>11</sup> is highly indicative of the lability of the C-Cl bond in  $\beta$ -chloroalkyl radicals, and it is supported by esr studies.<sup>10a, 12</sup>

In this paper, we wish to employ esr studies to probe further the chlorine migration in a series of homologous chloroalkyl radicals and to couple these to a chemical study.<sup>14</sup> The effects of  $\alpha,\alpha$ -dichloro substitution on the configuration of the radical site and on the conformation of chloroalkyl radicals are compared to the  $\alpha,\alpha$ -difluoro and  $\alpha,\alpha$ -dimethyl analogs.

## Results and Discussion

**Formation and Rearrangement of Chloroalkyl Radicals.** The 1,2 migration of chlorine in  $\beta$ -chloroisobutyl radical to the tertiary isomer occurs even at temperatures as low as  $-130^\circ$ .<sup>10a, 13</sup>



Similarly, the  $\beta,\beta,\beta$ -trichloroethyl radical generated by hydrogen abstraction from 1,1,1-trichloroethane or

199 (1969); (c) for a recent study of bromine-containing radicals in the solid state, see S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J. Amer. Chem. Soc.*, **95**, 605 (1973); for iodine, see G. W. Neilson and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 717 (1973).

(10) (a) K. S. Chen, I. H. Elson, and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 5341 (1973); (b) T. Kawamura, D. J. Edge, and J. K. Kochi, *ibid.*, **94**, 1752 (1972).

(11) (a) P. S. Skell, R. R. Pavlis, D. C. Lewis, and K. J. Shea, *J. Amer. Chem. Soc.*, **95**, 6735 (1973); (b) for  $\gamma$ -alkyl radicals, see K. J. Shea and P. S. Skell, *ibid.*, **95**, 6728 (1973).

(12) After the initial report<sup>10a</sup> was completed, an independent study by Cooper, Hudson, and Jackson<sup>13</sup> appeared which is in substantial agreement.

(13) J. Cooper, A. Hudson, and R. A. Jackson, *Tetrahedron Lett.*, 831 (1973).

(14) The lack of long range interactions in haloalkyl radicals deduced from chemical studies has been discussed by (a) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967); (b) V. Jaacks and F. R. Mayo, *J. Amer. Chem. Soc.*, **87**, 3371 (1965); (c) D. Y.-H. Tang, Ph.D. Thesis, Indiana University, 1974, to be published with L. K. Montgomery.

(1) P. S. Skell and K. J. Shea, "Free Radicals," Wiley, New York, N. Y., 1973, Chapter 26.

(2) L. Kaplan, "Bridged Free Radicals," Marcel Dekker, New York, N. Y., 1972.

(3) A. P. Stefani, *Fluorine Chem. Rev.*, **5**, 115 (1971).

(4) A. Hudson and K. D. J. Root, *Advan. Magn. Resonance*, **5**, 1 (1971).

(5) (a) K. S. Chen, P. J. Krusic, P. Meakin, and J. K. Kochi, to be submitted for publication; (b) D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 6485 (1972).

(6) (a) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965); (b) cf. also, L. Pauling, *ibid.*, **51**, 2767 (1969).

(7) M. Iwasaki, *Fluorine Chem. Rev.*, **5**, 1 (1971).

(8) (a) J. Sinclair and D. Kivelson, *J. Amer. Chem. Soc.*, **90**, 5074 (1968); (b) W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 4625 (1964).

(9) (a) A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Lett.*, **5**, 552 (1970); (b) A. Hudson and H. A. Hussain, *Mol. Phys.*, **16**,

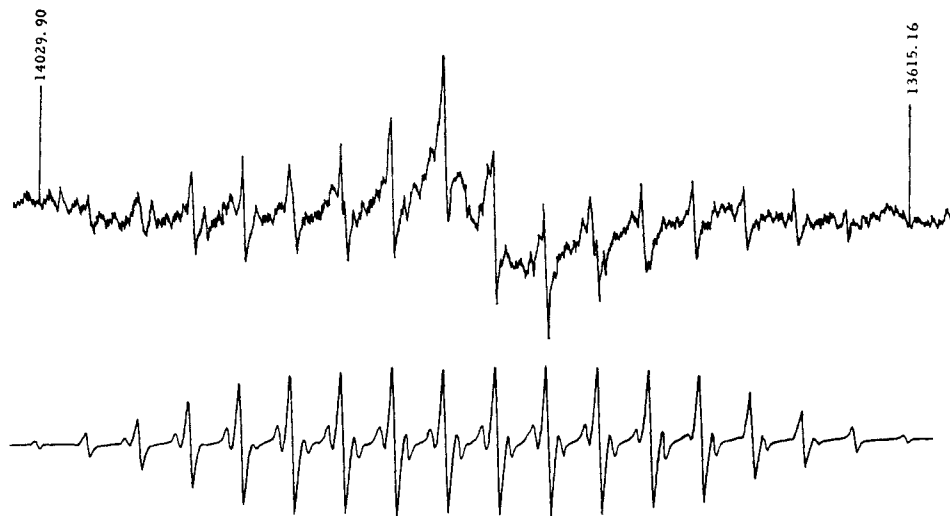
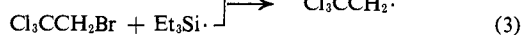
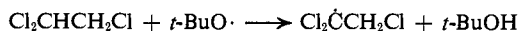


Figure 1. ESR spectrum of the 1,1,2-trichloroethyl radical in cyclopropane solution at  $-140^\circ$ . The simulated spectrum includes  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  in natural abundances for the 2 chlorine, but only  $^{35}\text{Cl}$  is included for the 1,1-dichloro groups. Proton nmr fieldmarkers are in kHz.

bromine transfer from 2,2,2-trichloroethyl bromide in eq 2 and 3, respectively, rearranges rapidly to the  $\alpha,\alpha,\beta$ -trichloroethyl radical.<sup>15,16</sup> Thus, the esr spectrum of



the  $\beta,\beta,\beta$ -trichloroethyl radical could not be observed even at  $-140^\circ$ . Only the esr spectrum of  $\alpha,\alpha,\beta$ -trichloroethyl radical shown in Figure 1 was obtained and verified by producing the radical by an independent procedure involving hydrogen abstraction from 1,1,2-trichloroethane by photochemically generated *tert*-butoxy radical.

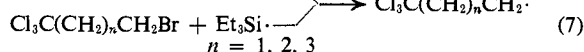
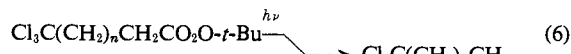


Homologation drastically reduces the ability of chlorine to migrate in alkyl radicals. Thus, the esr spectrum observed during bromine transfer from 3-chloro-3-methylbutyl bromide in eq 5 consisted of a



triplet (22.19 G) of triplets (25.64 G) undoubtedly associated with the splittings due to the  $\alpha$  and  $\beta$  protons, respectively, in the unrearranged  $\gamma$ -chloroisoamyl radical.

A series of homologous  $\omega,\omega,\omega$ -trichloroalkyl radicals was also generated by two independent procedures involving (a) the photolysis of the *tert*-butylperoxy esters<sup>15</sup> in eq 6 or (b) bromine transfer from the corresponding alkyl bromides (eq 7). In every case, only the



esr spectrum of the unrearranged radical was observed

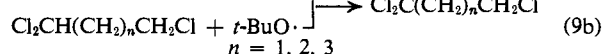
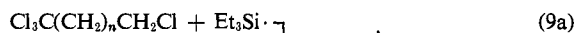
(15) (a) Cf. J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, No. 24, 147 (1970); (b) cf. A. Hudson and R. A. Jackson, *J. Chem. Soc., Chem. Commun.*, 1323 (1969).

(16) Other examples of 1,2-chlorine rearrangements have been reported previously by chemical studies: (a) A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, *Dokl. Akad. Nauk SSSR*, 81, 199 (1951); (b) W. H. Urry and J. R. Eiszner, *J. Amer. Chem. Soc.*, 74, 5822 (1952).

even at temperatures as high as  $+20^\circ$  in pentane or ether solutions. It is interesting to note that in reaction 7 the spectrum of the primary radical (corresponding to bromine transfer) was the sole species observed. In order to ensure that the spectra of the rearranged  $\alpha,\alpha$ -dichloroalkyl radicals were properly iden-



tified, they were generated by two alternate procedures. Treatment of the  $\alpha,\alpha,\alpha,\omega$ -tetrachloroalkane with photochemically generated triethylsilyl radicals in eq 9a afforded the same spectrum as that obtained from the reaction of *tert*-butoxy radicals with the corresponding  $\alpha,\alpha,\omega$ -trichloroalkane in eq 9b. The spectrum of a



single predominate species in both reactions suggests a high degree of selectivity in each. Thus, neither the spectrum of the isomeric radical obtained by transfer of the primary chlorine in eq 9a nor the spectrum of the secondary radical  $\text{Cl}_2\text{CH}(\text{CH}_2)\dot{\text{C}}\text{HCl}$  in eq 9b was observed under these conditions.

The foregoing esr studies exclude the nonvicinal 1,3-, 1,4-, or 1,5-chlorine migration in alkyl radicals as a facile process, despite the apparently favorable driving force incorporated into our systems. Chemical studies which could be carried out at higher temperatures also support these conclusions.<sup>14</sup> Conceptually, chlorine migration may be viewed in extreme situations as either a cage elimination readdition process or an intramolecular chlorine abstraction. These processes differ primarily in the degree to which the chlorine bond breaking or bond making process, respectively, has progressed in the transition state. The lability of only that chlorine (and bromine) located in the  $\beta$  position of alkyl radicals,<sup>5b,10a,11,13</sup> and the inertness of  $\gamma$ ,  $\delta$ , and  $\epsilon$  chlorines suggest that chlorine migration in alkyl radicals derives driving force from a bond breaking contribution.<sup>17</sup>

(17) This situation is in strong contrast to migration of hydrogen in alkyl radicals, since there are no examples of 1,2 shifts, but a number of 1,5 rearrangements have been observed.<sup>18</sup>

(18) J. W. Wilt, ref 1, Chapter 8.

Table I. ESR Parameters for  $\alpha,\alpha$ -Dichloroalkyl Radicals in Cyclopropane Solution

Radical	T, °C	$\langle g \rangle$	—Hyperfine splitting, G—		
			$a_{\alpha\alpha}$	$a_{H\beta}$	$a_{\alpha\beta}$
$\dot{H}CCl_2^a$			3.5 <sup>b</sup>		
			20.5 <sup>c</sup>		
$CH_3\dot{C}Cl_2$	-108	2.00727	4.34 <sup>b</sup>	19.70	
$CH_3CH_2\dot{C}Cl_2$	-112	2.00711	4.54 <sup>b</sup>	15.42	
$ClCH_2\dot{C}Cl_2$	-140	2.00634	5.72 <sup>b</sup>	5.72	17.16 <sup>f</sup>
$HOCH_2\dot{C}Cl_2^a$	-60		4.1 <sup>b</sup>	13.4	
$Cl(CH_2)_2\dot{C}Cl_2$	-112	2.00689	3.75 <sup>b</sup>	16.81	
$Cl(CH_2)_3\dot{C}Cl_2$	-119	2.00713	4.30 <sup>b</sup>	16.02	
$Cl(CH_2)_4\dot{C}Cl_2$	-117	2.00711	4.30 <sup>b</sup>	16.04	
$CH_2\dot{C}(CH_3)_2$	-113	2.00270		22.93	
$CH_3\dot{C}F_2$	-78	2.00361	94.01 <sup>d</sup>	13.99	
$CH_3CH_2\dot{C}(CH_3)_2$	-117	2.00278	22.80 <sup>e</sup>	17.94	
$ClCH_2\dot{C}(CH_3)_2$	-129	2.00359	21.24 <sup>e</sup>	6.18	21.24 <sup>f</sup>
$ClCH_2\dot{C}F_2$	-48	2.00501	83.59 <sup>d</sup>	2.04	8.41 <sup>f</sup>

<sup>a</sup> From A. Hudson and K. D. J. Root, *Advan. Magn. Resonance*, **5**, 1 (1971). <sup>b</sup>  $\alpha\text{-}^{35}\text{Cl}$ . <sup>c</sup>  $\alpha\text{-H}$ . <sup>d</sup>  $\alpha\text{-F}$ . <sup>e</sup>  $\alpha\text{-CH}_3$ . <sup>f</sup>  $\beta\text{-}^{35}\text{Cl}$ .

The latter is also consistent with the stable eclipsed conformations of  $\beta$ -chloroalkyl radicals in which hyperconjugative and homoconjugative interactions<sup>10</sup> of the  $\beta$  chlorine with the radical center are possible (*vide infra*). Thus, it is not surprising that the higher chloroalkyl analogs do not exist (*vide infra*) in comparable conformations which optimize interactions between the chlorine substituent and the radical center. On the other hand, the incipient formation of a carbon-halogen bond implicit in an intramolecular chlorine abstraction is not particularly favored in alkyl radicals due to the relatively low carbon-halogen bond strengths.<sup>19</sup>

#### Effect of $\alpha,\alpha$ -Dichloro Substitution on Alkyl Radicals.

**I. Configuration at the Radical Site.** The esr parameters for representative  $\alpha,\alpha$ -dichloroalkyl radicals are collected in Table I, together with the  $\alpha,\alpha$ -difluoro and  $\alpha,\alpha$ -dimethyl analogs for comparison. The  $\alpha$ -chlorine hyperfine splittings remain relatively constant at about 4 G throughout the series of  $\alpha,\alpha$ -dichloroalkyl radicals examined. The magnitude of the splitting, however, depends on the number of chlorines, as shown by comparison of  $\dot{C}Cl_3$ ,  $CH_3\dot{C}Cl_2$ , and  $(CH_3)_2\dot{C}Cl$  in which  $a_{\alpha^{35}\text{Cl}}$  is 6.25, 4.2, and 2.3 G, respectively.<sup>21</sup> The increasing trend in the chlorine splitting with chlorine substitution has been attributed to an increasing pyramidal configuration induced by the electronegative chlorine, similar to that observed with  $\alpha$ -fluorine substitution.<sup>6</sup> It is interesting to note in this regard that the chlorine splitting in  $\alpha$ -chloro- $\alpha,\alpha$ -di-*tert*-butylmethyl radical is also 2.26 G,<sup>22</sup> despite the highly congested radical center.

The large carbon-13 hyperfine splitting of 114 G in  $\dot{C}Cl_3$  is consistent with a pyramidal radical with  $\angle Cl-C-Cl$  of 116°,<sup>23</sup> which is in reasonable agreement with a value of 114.3° calculated by the INDO method.<sup>24,24a</sup>

(19) Such a formulation suggests the possibility of nonvicinal chlorine migration in metal-centered radicals such as  $\omega$ -chloroalkylsilyl radicals  $Cl(CH_2)_n SiR_2$  in which transition state contributions for chlorine bond making are greater. The rarity of hydrogen migrations<sup>20</sup> in silyl radicals represents the opposed situation.

(20) H. Sakurai, ref 1, Chapter 25.

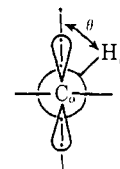
(21) J. Cooper, A. Hudson, and R. A. Jackson, *Mol. Phys.*, **23**, 209 (1972).

(22) (a) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6459 (1973); (b) private communication. (b) The esr spectrum of  $CF_3CH_2\dot{C}H_2$  has also been independently examined by D. Griller and K. U. Ingold, to be published.

(23) C. Hesse, N. Leray, and J. Roncin, *Mol. Phys.*, **22**, 137 (1971).

The configuration at the radical site of  $CH_3\dot{C}Cl_2$  is not known. However, it has been suggested that  $(CH_3)_2\dot{C}Cl$  has a planar configuration, based on a comparison of the methyl splitting with that in the *tert*-butyl radical.<sup>21</sup> Although there is some current controversy, the magnitude of the nonplanarity in *tert*-butyl radical is probably less than a degree.<sup>25</sup> The chlorine splitting suggests a value of  $\angle ClCCl$  in  $CH_3\dot{C}Cl_2$  which is intermediate between 116° in  $\dot{C}Cl_3$  and 120° in  $(CH_3)_2\dot{C}Cl$ .

**II. Conformation about the  $C_\alpha$ - $C_\beta$  Bond.** The esr parameters for alkyl radicals, particularly the magnitude and the temperature dependence of the  $\beta$ -proton hyperfine splittings, are valuable probes for establishing conformations.<sup>26</sup> If  $\theta$  describes the dihedral angle between the  $\beta$ -CH bond and the p orbital at the radical

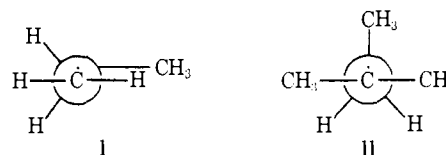


center at  $C_\alpha$ , then the hyperfine splitting for the  $\beta$  proton is given by eq 10, where  $A_H$  and  $B_H$  are constants

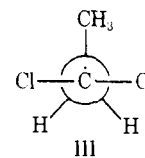
$$a_{H\beta}(T) = A_H + B_H \cos^2 \theta \quad (10)$$

with values of about 2 and 50 G, respectively, for the ethyl radical.

Thus, the decrease in  $a_{H\beta}$  of 31 G for the *n*-propyl radical (which has a negative temperature dependence,  $da_{H\beta}/dT$ ) to 18 G for the *tert*-amyl radical (with a positive temperature dependence) is associated with a change in the stable equilibrium conformation from I to II, respectively, largely due to steric effects imposed



by the two  $\alpha$ -methyl groups.<sup>27,28</sup> The similarity of  $a_{H\beta} = 15$  G in  $CH_3CH_2\dot{C}Cl_2$  to that in the *tert*-amyl radical suggests that it favors a similar conformation III.



(24) H. G. Benson and A. Hudson, *Theor. Chim. Acta*, **23**, 259 (1971).

(24a) NOTE ADDED IN PROOF. A recent electron diffraction study of trichloromethyl and tribromomethyl radicals in the gas phase indicates pyramidal structures which are not significantly different from a tetrahedral configuration. T. L. Leggett and D. A. Kohl, *J. Chem. Phys.*, in press. We wish to thank Dr. Kohl for these results prior to publication.

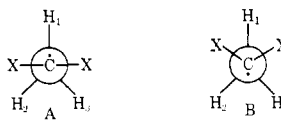
(25) For the configuration of the *tert*-butyl radical, see D. E. Wood, L. F. Williams, R. F. Sprecher, and W. A. Lathan, *J. Amer. Chem. Soc.*, **94**, 6241 (1972); M. C. R. Symons, *Tetrahedron Lett.*, 207 (1973); ref 22; H. Paul and H. Fischer, *Helv. Chem. Acta*, **56**, 1575 (1973).

(26) (a) R. W. Fessenden, *J. Chim. Phys. Physicochim. Biol.*, **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) K. S. Chen and J. K. Kochi, *J. Amer. Chem. Soc.*, **96**, 794 (1974).

(27) K. S. Chen, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 7036 (1973).

(28) Cf.  $\alpha$ -*tert*-butyl substitution by G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 3422 (1973).

Table II. ESR Parameters for  $\alpha,\alpha$ -Disubstituted Ethyl Radicals in a Frozen Conformation by INDO-MO (Effect of Nonplanarity at the Radical Center)

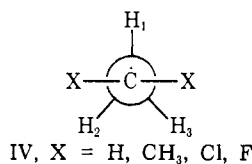


Parameters <sup>a</sup> and hfs (G)	A, X = H	A, X = CH <sub>3</sub>	B, X = Cl	B, <sup>c</sup> X = F	A, <sup>d</sup> X = F
$\angle C_\beta C_\alpha X_\alpha$ , deg	120	120	120	115	120
$\angle X_\alpha C_\alpha X_\alpha$ , deg	120	120	118	106	120
$r(C_\alpha-C_\beta)$ , Å	1.40			1.51	1.50
$a_{H_1}$	53.41	44.6 <sup>b</sup>	43.5 <sup>b</sup>	37.21	49.90
$a_{H_2} = a_{H_3}$	14.69	12.1 <sup>b</sup>	7.8 <sup>b</sup>	2.92	13.51
$a_{H_2,3}/a_{H_1}$	0.27	0.27	0.18	0.078	0.27
$1/3[a_{H_1} + a_{H_2} + a_{H_3}]$	27.60	22.93	19.70	14.31	25.64
$a_X$	-20.36			93.69	49.89

<sup>a</sup>  $r(C_\alpha-H_\alpha) = 1.08$ ,  $r(C_\alpha-F_\alpha) = 1.35$ ,  $r(C_\beta-H_\beta) = 1.08$ ,  $C_\beta =$  tetrahedral. <sup>b</sup> See text. <sup>c</sup> Structure Va. <sup>d</sup> Structure Vb.

isosteric radicals are not directly comparable, since they differ in the configuration at the radical site.

In order to determine the effects of  $\alpha$  substitution in the conformation, it would be highly desirable to know the splittings of each  $\beta$  proton in conformations of the  $\alpha$ -methyl-, chloro- and fluoro-substituted ethyl radicals, which are hypothetically frozen as shown in conformation IV.



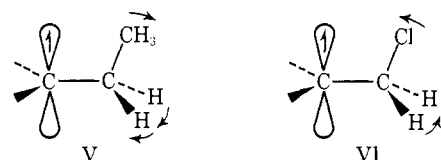
The configuration Va of  $CH_3\dot{C}F_2$  in Table II was determined by the INDO method in which the calculated proton and fluorine hyperfine splittings were optimized with respect to the experimental values.<sup>29</sup> Comparison with the planar model Vb shows that the proton splitting decreases and the fluorine splitting increases in the expected manner with an increasing pyramidal configuration. Indeed, the ratio of the calculated hyperfine splittings for  $H_1$  and  $H_{2,3}$  is strongly dependent on the degree of bending at the radical center.

The calculated ratio for  $a_{H_{2,3}}/a_{H_1}$  of 0.27 in Table II is the same for the ethyl and planar difluoroethyl radicals. We assume for other radicals that the ratio is determined by the degree of bending at the radical site. The individual proton splittings in Table II for the *tert*-butyl radical were obtained by fitting the experimental value of the methyl splitting of 22.9 G =  $1/3\sum a_{H_i}$  and  $a_{H_{2,3}}/a_{H_1} = 0.27$ . The splittings for  $CH_3\dot{C}Cl_2$  were determined in a similar manner using  $a_{H_{2,3}}/a_{H_1} = 0.18$ , determined<sup>29</sup> from a value of an assumed  $\angle ClCCl$  of 118°.

The hyperfine splitting of 12 G calculated for the two equivalent  $\beta$  protons,  $H_2$  and  $H_3$ , in the *tert*-amyl radical frozen in conformation II is significantly smaller than the experimental value. The difference is even greater in the  $\alpha,\alpha$ -dichloropropyl radical. It is possible, of course, that both of these radicals are far removed from the low-temperature limit.<sup>26b</sup> The discrepancy, however, appears to be more than a reasonable extrapolation would allow. Alternatively, a distortion in these radicals at  $C_\beta$  as in V, moving the  $\beta$ -methyl group away

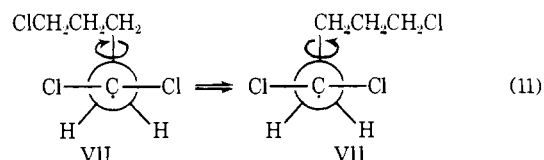
(29) K. S. Chen and J. K. Kochi, *Chem. Phys. Lett.*, **23**, 233 (1973).

and the pair of  $\beta$  protons toward the p orbital at the radical site, could account for the larger experimental values of  $a_{H\beta}$ .<sup>30</sup>



The latter possibility is not without some merit, since previous studies<sup>10,31</sup> showed that  $\beta$ -chloroalkyl radicals exist in the stable conformation VI in which distortion at  $C_\beta$  places the chlorine closer to the radical center. The concomitant displacement of  $H_\beta$  toward the nodal plane as shown in VI causes values of  $a_{H\beta}$  to be lower than the calculated value based on an undistorted conformation. The magnitude of the difference (which is 5.5 G (14.7–9.2) in  $ClCH_2\dot{C}H_2$  and 5.9 G (12.1–6.2) in  $ClCH_2\dot{C}(CH_3)_2$ ) partly reflects the distortion at  $C_\beta$  and the extent of bridging by  $\beta$  chlorine in these radicals. A pyramidal configuration at  $C_\alpha$ , however, appears to diminish bridging by chlorine since the small discrepancy between the experimental and calculated values of 0.9 G (2.9–2.0) for  $a_{H\beta}$  in  $ClCH_2\dot{C}F_2$  and 2.1 G (7.8–5.7) for  $ClCH_2\dot{C}Cl_2$  suggests only a limited distortion at  $C_\beta$  in radicals with pyramidal centers.

The magnitude of  $a_{H\beta}$  and the absence of selective line broadening in the esr spectrum of  $CH_3CH_2\dot{C}Cl_2$  (at temperatures as low as  $-130^\circ$ ) is consistent with conformation III and free rotation of the methyl group about the  $C_\beta-C_\gamma$  bond. The latter, however, is inhibited by homologation and the selective line width effect showing out-of-phase modulation of the  $\beta$ -proton splittings in the spectrum of  $Cl(CH_2)_4\dot{C}Cl_2$  can be attributed to the dynamic process illustrated in eq 11.



Spectra of the analogous  $Cl(CH_2)_2\dot{C}Cl_2$  and  $Cl(CH_2)_3\dot{C}Cl_2$

(30) (a) A somewhat analogous distortion at  $C_\beta$  was previously suggested for the isobutyl radical;<sup>26c</sup> (b) nonplanarity at  $C_\alpha$  could also decrease  $a_{H\beta}$  (*vide supra*).

(31) I. Biddles and A. Hudson, *Chem. Phys. Lett.*, **18**, 45 (1973).

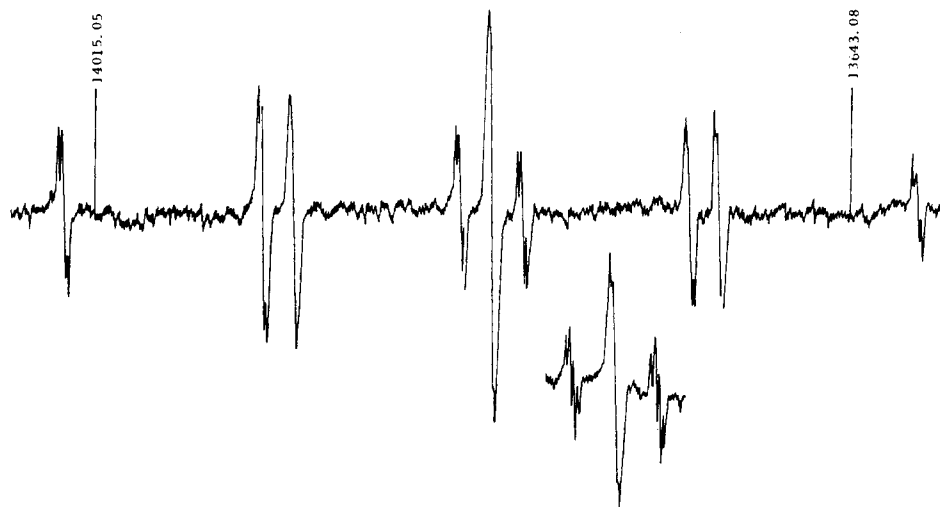


Figure 2. ESR spectrum of the 3,3,3-trifluoropropyl radical in cyclopropane solution at  $-136^\circ$ . The inset shows central multiplet under higher resolution. Proton nmr field markers are in kHz.

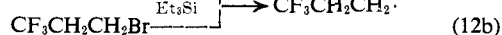
Table III. ESR Parameters of  $\omega,\omega,\omega$ -Trihaloalkyl Radicals in Cyclopropane Solution

Radical	$T, ^\circ\text{C}$	$\langle g \rangle$	Hyperfine splitting, G			
			$a_{X\alpha}$	$a_{H\beta}$	$a_{H\gamma}$	$a_{X\gamma}$
$\text{Cl}_3\text{CCH}_2\dot{\text{C}}\text{H}_2$	-93	2.00369	22.46	22.46		<0.3
$\text{Cl}_3\text{C}(\text{CH}_2)_2\dot{\text{C}}\text{H}_2$	-89	2.00269	22.33	28.67	0.90	
$\text{Cl}_3\text{C}(\text{CH}_2)_3\dot{\text{C}}\text{H}_2$	-97	2.00270	22.11	29.39	0.91	
$\text{Cl}_3\text{CCH}_2\dot{\text{C}}(\text{CH}_3)_2^a$	-100	2.00343	23.52 <sup>e</sup>	11.61		<0.1
$\text{Cl}_3\text{CCH}_2\dot{\text{C}}(t\text{-Bu})_2^a$	+20	2.0034		10.68		2.1
$\text{Cl}_3\text{SiCH}_2\dot{\text{C}}\text{H}_2^b$	-128	2.00365	21.83	17.22		$\sim 1.0$
$\text{Cl}_3\text{SiCH}_2\dot{\text{C}}(t\text{-Bu})_2^a$	+20	2.0030		14.58		2.2
$\text{Cl}(\text{CH}_3)_2\text{CCH}_2\dot{\text{C}}\text{H}_2$	-101	2.00284	22.19	25.64		N.R.
$(\text{CH}_3)_3\text{CCH}_2\dot{\text{C}}\text{H}_2$	-93	2.00280	22.06	24.70		
$\text{F}_3\text{CCH}_2\dot{\text{C}}\text{H}_2$	-128	2.00262	22.92	26.62 <sup>f</sup>		0.35
$\text{F}_3\text{CCH}_2\dot{\text{C}}(t\text{-Bu})_2^a$	+20	2.0026		12.16		0.90
$\text{Cl}(\text{CH}_2)_2\dot{\text{C}}\text{H}_2^b$	-125	2.00271	22.36	27.74	0.85	N.R.
$\text{F}(\text{CH}_2)_2\dot{\text{C}}\text{H}_2^b$	-126	2.00269	22.31	28.19	0.50	1.00
$\text{CH}_3(\text{CH}_2)_2\dot{\text{C}}\text{H}_2^c$	-119	2.00265	21.94	29.73	0.72	

<sup>a</sup> From ref 22. <sup>b</sup> From ref 5b. <sup>c</sup> From ref 26b. <sup>d</sup> We wish to thank Dr. I. H. Elson for this measurement. <sup>e</sup> Methyl septet. N.R. = not resolved. <sup>f</sup>  $a_{H\beta} = 26.30$  G at  $-120^\circ$  from ref 22a.

$\dot{\text{C}}\text{Cl}_2$  show the same selective line broadening behavior at these temperatures. Moreover, the similar values of  $a_{H\beta}$ , for the homologous series  $\text{Cl}(\text{CH}_2)_n\dot{\text{C}}\text{Cl}_2$  shown in Table I, indicate that all of these  $\alpha,\alpha$ -dichloroalkyl radicals exist in conformations similar to III and VII and that the effect of the lone chlorine located at the  $\gamma$  position or further along the chain is small. Finally, the effect of the electronegativity of an  $\alpha$  substituent on conformation and bridging was discussed earlier relative to  $\alpha$ -fluorine.<sup>29</sup>

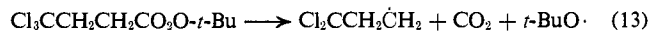
**The Effects of  $\gamma,\gamma,\gamma$ -Trihalo Substitution on Alkyl Radicals.** The esr spectrum of the  $\gamma,\gamma,\gamma$ -trifluoropropyl radical can be observed when trifluoromethyl radicals are generated from *tert*-butyl peroxy trifluoroacetate or trifluoromethyl iodide in the presence of ethylene as shown in Figure 2. The same species can be generated by bromine transfer from 3,3,3-trifluoro-



propyl bromide with triethylsilyl radicals. The spectrum showed no selective line broadening over the temperature range studied between  $-40$  and  $-140^\circ$ .

We were unable to observe the addition of either methyl or trichloromethyl radicals from *tert*-butyl-

peroxy acetate and bromotrichloromethane, respectively, to ethylene under the same conditions. The trichloromethyl adduct, however, was generated independently from *tert*-butylperoxy  $\gamma,\gamma,\gamma$ -trichloropropionate in cyclopropane, *n*-pentane, and ether solutions between  $+25$  and  $-160^\circ$ . The esr spectrum was re-



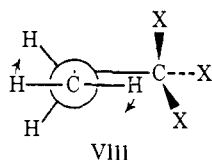
markably invariant under these conditions showing only a quintet splitting with the intensity of lines approximately in a ratio of 1:4:6:4:1. There was no selective line broadening, and the  $\gamma$ -chlorine splitting could not be resolved (<0.3 G) under any condition. We conclude from the absence of deuterium scrambling in the product  $[\text{Cl}_3\text{CH}_2\text{CD}_2\text{H}]$ , derived from the decomposition of  $\text{Cl}_3\text{CCH}_2\text{CD}_2\text{CO}_2\text{-}t\text{-Bu}$ ,<sup>14c</sup> that all of the proton splittings are accidentally equivalent in  $\text{Cl}_3\text{CCH}_2\dot{\text{C}}\text{H}_2$ .

Table III lists the esr parameters from a series of  $\gamma,\gamma,\gamma$ -trihalo-substituted alkyl radicals and some related analogs. The unusually large  $g$  factor for  $\text{Cl}_3\text{CCH}_2\dot{\text{C}}\text{H}_2$  is consistent with the relatively large spin-orbit coupling constant of chlorine ( $\xi_p = 587 \text{ cm}^{-1}$ ).

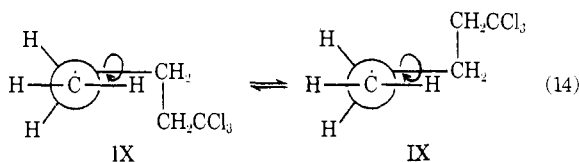
A single  $\gamma$ -X substituent is insufficient to effect any major change in the equilibrium conformation as indi-

cated by the similar values of  $a_{H\beta}$  for the series of radicals  $X(CH_2)_2\dot{C}H_2$ , in which  $X = CH_3, F,$  and  $Cl$  as listed in Table III.

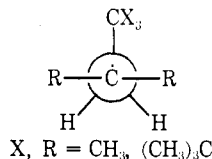
On the other hand, in the series of related  $\gamma,\gamma,\gamma$ -tri-substituted ethyl radicals,  $X_3CCH_2\dot{C}H_2$ , in which  $X$  is  $H, F, CH_3,$  and  $Cl$ , the value of the  $\beta$ -proton coupling constants at  $-130^\circ$  decreases roughly from 31, 27, 25, to 23 G, respectively. There is an apparent trend of  $a_{H\beta}$  with the size of  $X$  but none with the electronegativity, as also shown by  $a_{H\beta} = 25$  G for the unsymmetrically substituted  $Cl(CH_3)_2CCH_2\dot{C}H_2$ . Since the  $n$ -propyl radical prefers conformation I,<sup>26</sup> the trend toward decreasing values of  $a_{H\beta}$  in the series above may be ascribed to conformations in which the  $\gamma$  carbon is increasingly displaced from the nodal plane due to steric interaction with the *syn*- $H_\alpha$  as is depicted in VIII.<sup>32</sup> It



follows that removal of the  $Cl_3C-$  group further along the chain by homologation, as in  $Cl_3C(CH_2)_2\dot{C}H_2$  and  $Cl_3C(CH_2)_3\dot{C}H_2$ , would decrease these nonbonded interactions, and  $a_{H\beta}$  indeed increases substantially for these radicals as shown in Table III. However, steric differences between  $Cl_3C(CH_2)_2\dot{C}H_2$  and  $Cl_3C(CH_2)_3\dot{C}H_2$  can be observed in the esr spectra. Thus, the spectrum of  $Cl_3C(CH_2)_2\dot{C}H_2$  shows no or little selective line broadening, whereas the spectrum of  $Cl_3C(CH_2)_3\dot{C}H_2$  shows out-of-phase modulation of  $a_{H\beta}$  (*i.e.*, selective broadening of the  $M_T = 0$  lines due to the  $\beta$ -proton splittings). The dynamic process shown in eq 14 can account for the selective line width effect.



Encumbering the radical center in primary  $n$ -alkyl radicals with  $\alpha,\alpha$ -dimethyl<sup>26,27</sup> or di-*tert*-butyl groups<sup>22</sup> alters the stable conformation from VIII to X. The



values of  $a_{H\beta}$  in the range 11–15 G for the  $\gamma,\gamma,\gamma$ -tri-substituted radicals listed in Table III are comparable to 18 G in the *tert*-amyl radical.<sup>33</sup> Accompanying this change in conformation there is also a significant increase in all the hyperfine splittings by the various  $\gamma$ -X substituents (*i.e.*,  $X = F$  from 0.35 to 0.90 G;  $X = Cl$

(32) The value of  $a_{H\beta}$  in these radicals follows a negative temperature dependence.<sup>26</sup>

(33) The somewhat smaller values of  $a_{H\beta}$  for  $CX_3CH_2\dot{C}(t-Bu)_2$  compared to  $CH_3CH_2\dot{C}(CH_3)_2$  appear to contradict the earlier conclusion regarding distortion at  $C_\beta$  in *tert*-amyl radicals. However, the former species are highly congested, and it is not, *a priori*, obvious what the distortions (such as bending at  $C_\alpha$ ) may be. The same ambiguity applies to  $Cl_3CCH_2\dot{C}(CH_3)_2$ .

from  $<0.3$  to 2.1 G, etc.). The increase in the magnitude of the long range splittings is highly reminiscent of the similar change in a series of bridged  $\beta$ -chloroalkyl radicals.<sup>10</sup>

## Conclusions

In chloroalkyl radicals, migration of chlorine from the  $\beta$  to  $\alpha$  carbon is facile, provided they differ in the degree of substitution. No evidence for 1,3, 1,4, or 1,5 shift of chlorine was found in alkyl radicals. The pattern suggests, however, that nonvicinal migration of chlorine may occur to a heteroatom center. The configuration at the radical center of  $\alpha,\alpha$ -dichloroalkyl radicals is significantly less pyramidal than the  $\alpha,\alpha$ -difluoro analogs but not planar as in alkyl radicals. The effect of  $\alpha,\alpha$ -dichloro substitution on the conformation of alkyl radicals is similar to that effected by  $\alpha,\alpha$ -dimethyl substitution, and substituents on  $C_\beta$  occupy an eclipsed conformation relative to the p orbital at the radical center. A single  $\gamma$  chlorine has little influence on the conformation of alkyl radicals but the effect of  $\gamma,\gamma,\gamma$ -trichloro substitution is noticeable although not sufficient to alter the basic conformation about the  $C_\alpha-C_\beta$  bond.

## Experimental Section

**Materials.** Di-*tert*-butyl peroxide from Shell Chemical Co. was treated with aqueous ferrous sulfate, washed repeatedly with water, dried over molecular sieve, and distilled *in vacuo*. Triethylsilane was obtained from Pierce Chemical Co. and bis(trifluoromethyl) peroxide from PCR, Inc. Cyclopropane was from Matheson Gas Co.

The 2,2,2-trichloroethanol, 3,3,3-trichloropropyl bromide, and 1,1-dichloro-1-propene were obtained from Columbia Organic Chemicals Co. 1,1,1-Trichloroethane was obtained from Matheson Coleman and Bell. 1-Chloro-3,3-dimethylbutane was obtained from Aldrich Chemical Co. 1-Bromo-3-methyl-2-butene was obtained from Chemical Samples Co.

**2,2,2-Trichloroethyl bromide** was prepared by a two-step synthesis. Several attempts to prepare the bromide using standard procedures involving dry hydrogen bromide, phosphorus tribromide, and thionyl bromide were unsuccessful.

**A. 2,2,2-Trichloroethyl Triflate.** A 200-ml, three-necked, round-bottomed flask was fitted with a stirrer, a pressure-equalizing dropping funnel, and a nitrogen inlet tube. About 9.0 g (60 mmol) of 2,2,2-trichloroethanol, 7.0 g (64 mmol) of lutidine, and 90 ml of pentane were added to the flask. The solution was cooled to  $-10^\circ$ , and 17.0 g (60 mmol) of triflic anhydride in 10 ml of pentane was added dropwise. A white precipitate formed, and the mixture was stirred for 1 hr. The reaction mixture was filtered through anhydrous magnesium sulfate. The pentane was removed on a rotary evaporator, affording 12.5 g (75%) of the crude triflate: nmr ( $CDCl_3$ )  $\delta$  4.82 (s) ppm. The product was used without further purification.

**B. 2,2,2-Trichloroethyl Bromide.** A solution of 11.3 g (0.04 mol) of 2,2,2-trichloroethyl triflate, 17 g (0.3 mol) of lithium bromide, 60 ml of hexamethylphosphoric triamide, and 5 ml of water was stirred at  $80^\circ$  for 10 hr. The solution was poured into 300 ml of water. The product was taken up in pentane, and the aqueous layer was extracted several times with pentane. The pentane extracts were combined, dried, and filtered. The pentane was removed and the residual material was distilled. About 5.1 g (60%) of 2,2,2-trichloroethyl bromide, bp  $32-34^\circ$  (5 mm), was obtained: nmr ( $CDCl_3$ )  $\delta$  4.25 (s) ppm; mass spectrum  $M^+ m/e$  211.8409 (calcd for  $C_2H_2BrCl_3$ , 211.8385).

**1,1,1-Trichloropropane** was prepared following the general method of Levine and Cass.<sup>34</sup> Freshly distilled (bp  $77^\circ$ ) 1,1-dichloro-1-propene (50.5 g, 0.50 mol) was placed in a 300-ml, round-bottomed flask and cooled to  $-15^\circ$ . About 2.5 g of anhydrous aluminum chloride was added. Dry hydrogen chloride was bubbled into the vigorously stirred slurry for 4 hr. The

(34) A. A. Levine and O. W. Cass, U. S. Patent 2179218 (1940); *Chem. Abstr.*, 34, 1336 (1940).

mixture was poured into ice water. The organic layer was separated, washed with water, and dried over anhydrous calcium chloride. The reaction products were separated on a spinning band column. Pure 1,1,1-trichloropropane was obtained in 12% (8.9 g) yield: bp 105–107° (lit.<sup>1</sup> bp 106–107°); nmr (CDCl<sub>3</sub>) δ 1.29 (t, 3 H), 2.68 (q, 2 H) ppm.

**3,3,3-Trifluoropropyl bromide** was prepared using a modification of the general procedure of Henne and Nager.<sup>35</sup> A 50-ml, two-necked flask was fitted with a pressure-equalizing dropping funnel and a reflux condenser. The reflux condenser was connected in series to two cold traps, one maintained at 0° and the other at –78°. Antimony(III) fluoride (3.6 g, 20 mmol) and antimony(V) fluoride (2.0 g, 9.2 mmol) were placed in the reaction flask, and 10 ml of methylene chloride was added. The mixture was cooled to 0° and stirred with a magnetic stirring bar. 3,3,3-Trichloro-1-bromopropane (4.54 g, 20 mmol) was added dropwise, and the mixture was stirred for 3 hr. About 0.5 ml of concentrated hydrochloric acid was added, and the reaction mixture was steam distilled. The organic portion of the distillate was separated, dried over magnesium sulfate, and redistilled. Slightly more than 1 g (max yield 28%) of 3,3,3-trifluoropropyl bromide, bp 57–59° (lit.<sup>36</sup> bp 62–62.5°), which was contaminated with methylene chloride, was obtained: nmr (CDCl<sub>3</sub>) δ 3.48 (t, 2 H), 2.74 (q of t, 2 H) ppm.

**1-Bromo-3-chloro-3-methylbutane.** Twenty milliliters (0.2 mol) of concentrated hydrochloric acid and 15 g (0.1 mol) of 1-bromo-3-methyl-2-butene were stirred at room temperature for 8 hr. The mixture was extracted several times with ether. The combined extracts were dried over anhydrous magnesium sulfate and filtered. Fractional distillation afforded 12 g (64% yield) of 1-bromo-3-chloro-3-methylbutane: bp 73–74°; nmr (CDCl<sub>3</sub>) δ 1.58 (s, 6 H), 2.18 (t, 2 H), 3.66 (t, 2 H) ppm; M<sup>+</sup> – Cl *m/e* 150.9961 (calcd 150.9946), M<sup>+</sup> too weak to measure conveniently.

**1,1,1,3-Tetrachloropropane** was prepared by a modification of an existing procedure<sup>33</sup> involving the radical chain addition of carbon tetrachloride to ethylene. A 500-ml, three-necked, round-bottomed flask was fitted with a stirrer, a condenser, and a gas dispersion tube. Carbon tetrachloride (350 ml, 560 g, 4 mol) and 2 g of benzoyl peroxide were placed in the flask. Ethylene was passed slowly into the solution through the gas dispersion tube, and the solution was heated at 80° for 36 hr. The carbon tetrachloride was removed by distillation and the residue was distilled at reduced pressure. A fraction with bp 50–65° (30 mm) was collected. Redistillation of this fraction at atmospheric pressure afforded 8 g of 1,1,1,3-tetrachloropropane: bp 155–156° (lit.<sup>37</sup> bp 155°); nmr (CDCl<sub>3</sub>) δ 3.04–3.24 (mult, 2 H) and 3.72–3.90 (mult, 2 H) ppm.

**1,1,1,4-Tetrachlorobutane** was prepared by a multistep synthesis.

A. **4,4,4-Trichlorobutanoic acid** was synthesized by a known procedure.<sup>38</sup> Starting from 420 g (8.0 mol) of freshly distilled acrylonitrile, 1050 g (8.8 mol) of chloroform, and 160 g (4.0 mol) of sodium hydroxide pellets, 205 g (13%) of 4,4,4-trichlorobutanoic acid, mp 55° (lit.<sup>38</sup> 55°), was obtained.

B. **Methyl 4,4,4-trichlorobutanoate** was obtained in 92% yield by the Fischer esterification of 4,4,4-trichlorobutanoic acid in methylene chloride: bp 78° (8 mm) (lit.<sup>39</sup> 78–80° (8 mm)).

C. **4,4,4-Trichloro-1-butanol** was obtained by the reduction of methyl 4,4,4-trichlorobutanoate in 89% yield: bp 89° (4 mm) (lit.<sup>40</sup> bp 89° (4 mm)); nmr (CDCl<sub>3</sub>) δ 1.9–2.2 (complex mult, 2 H), 2.72–2.88 (complex mult, 2 H), 2.94 (s, 1 H), 3.68–3.83 (t, 2 H) ppm.

D. **1,1,1,4-Tetrachlorobutane.** A 300-ml, three-necked, round-bottomed flask was fitted with a dropping funnel, a reflux condenser, a thermometer, and a magnetic stirring bar. Freshly distilled thionyl chloride (33 g, 0.28 mol) was added dropwise to a stirred solution of 24 g (0.135 mol) of 4,4,4-trichloro-1-butanol. The solution was maintained below 10° during the addition and stirred overnight at room temperature. Excess thionyl chloride was destroyed by slowly adding 100 g of crushed ice. About 80 ml of methylene chloride was added. The organic layer was separated,

and washed twice with two 50-ml portions of water, and two 50-ml portions of 10% sodium carbonate. The solution was dried over anhydrous magnesium sulfate, and the methylene chloride was removed on a rotary evaporator. Distillation afforded 25.3 g (95%) of 1,1,1,4-tetrachlorobutane: bp 86–87° (20 mm) (lit.<sup>41</sup> 86.8–87.1° (20 mm)); nmr (CDCl<sub>3</sub>) δ 2.3 (mult, 2 H), 2.7–2.9 (mult, 2 H), 3.62 (mult, 2 H) ppm.

**1,1,1,5-Tetrachloropentane** was prepared by a five-step sequence.

A. **5,5,5-Trichloropentanitrile** was prepared utilizing the general procedure of Nesmeyanov, Zakharkin, and Freidlina.<sup>42</sup> 1,1,1,4-Tetrachlorobutane (19.6 g, 0.10 mol), 6.4 g (0.13 mol) of sodium cyanide, 1 g of potassium iodide, 11 ml of water, and 80 ml of ethanol were refluxed for 12 hr. The ethanol was removed by distillation, and 35 ml of water was added. An oil separated. The aqueous layer was extracted with three 60-ml portions of benzene. The combined extracts were dried over anhydrous magnesium sulfate and the benzene was removed on a rotary evaporator. Distillation of the residue afforded 16.1 g (89%) of 5,5,5-trichloropentanitrile: bp 87–90° (0.7 mm) (lit.<sup>43</sup> bp 250°, dec); nmr (CDCl<sub>3</sub>) δ 1.96–2.32 (mult, 2 H), 2.42–2.58 (unsym t, 2 H), 2.74–2.94 (mult, 2 H) ppm.

B. **5,5,5-Trichloropentanoic Acid.** About 47 g (0.3 mol) of 5,5,5-trichloropentanitrile, 200 ml of acetic acid, 90 ml of concentrated hydrochloric acid, and 70 ml of water were refluxed for 10 hr. Most of the water and acetic acid was removed at reduced pressure, and 100 ml of water was added. The mixture was extracted four times with chloroform. About 37 g (60%) of crude acid was obtained from the chloroform solution. Recrystallization from pentane afforded 32 g (52%) of 5,5,5-trichloropentanoic acid, mp 63.5–64° (lit.<sup>44</sup> mp 64°).

C. **The remaining three steps** were similar to those used for the preparation of 1,1,1,4-tetrachlorobutane, methyl 5,5,5-trichloropentanoate (90%), 5,5,5-trichloro-1-pentanol (85%), and 1,1,1,5-tetrachloropentane (91%): bp 204–205° (lit.<sup>45</sup> bp 206°); nmr (CDCl<sub>3</sub>) δ 1.9 (mult, 4 H), 2.6–2.8 (mult, 2 H), 3.6 (t, 2 H) ppm.

**The α,α,α,ω-tetrachloroalkanes** were prepared from α,α,α,ω-tetrachloroalkanes employing the general procedure of Kuivila and Menapace.<sup>46</sup>

A. **1,1,3-Trichloropropane.** 1,1,1,3-Tetrachloropropane (2.2 g, 12 mmol) was added dropwise to a stirred solution of 0.22 g (6 mmol) of lithium aluminum hydride and 3 drops of *n*-butyltin trichloride in 15 ml of ether. The solution was refluxed for 5 hr. About 15 ml of ice-cold 10% sulfuric acid solution was added dropwise with cooling. The organic layer was separated and the aqueous layer was extracted with two 15-ml portions of ether. The combined ether layers were dried. Distillation afforded 1.3 g (75%) of 1,1,3-trichloropropane, bp 49–50° (20 mm) (lit.<sup>47</sup> bp 51–53° (21 mm)).

**1,1,4-Trichlorobutane** and **1,1,5-trichloropentane** were prepared in a similar manner (90 and 85%, respectively).

The preparation of the chlorine-containing peresters used in this study are described separately.<sup>14</sup>

**Esr Measurements.** The modified Varian X-band spectrometer, microwave frequency measurements, light source, and sample tubes are as described previously.<sup>5b</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>48</sup> was used as a standard in the configuration employed. The accuracy of the measurements is estimated as ±0.00003. Hyperfine splittings were corrected for second-order shifts and confirmed by computer simulation.

The photolyses of peresters were carried out in an approximately 0.5 *M* solution in cyclopropane. For photolytic reductions, equal

(41) H. C. Brown and A. B. Ash, *J. Amer. Chem. Soc.*, **77**, 4019 (1955).

(42) A. N. Nesmeyanov, L. I. Zakharkin, and R. K. Freidlina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **35** (1955).

(43) Shell Internationale Research Maatschappij, N. V.; *Chem. Abstr.*, **64**, 19429 g; British Patent 1024398 (1966).

(44) K. Saotome and T. Yamazaki, *Bull. Chem. Soc. Jap.*, **36**, 1264 (1963).

(45) V. A. Sidnev, V. A. Shershnev, O. L. Anupyl'd, and B. A. Dogadkin, *Kauch. Rezina*, **25** (2), 15 (1966).

(46) H. G. Kuivila and L. W. Menapace, Jr., *J. Org. Chem.*, **28**, 2165 (1963).

(47) T. Asahara, M. Seno, and C. C. Wu, *Kogyo Kagaku Zasshi*, **72** (18), 1818 (1969).

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

(35) A. L. Henne and M. Nager, *J. Amer. Chem. Soc.*, **73**, 1042 (1951).

(36) E. T. McBee, H. B. Hass, W. G. Toland, Jr., and A. Truchan, *Ind. Eng. Chem.*, **39**, 420 (1947).

(37) M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Amer. Chem. Soc.*, **69**, 1100 (1947).

(38) H. A. Bruson, W. Niederhauser, T. Riener, and W. F. Hester, *J. Amer. Chem. Soc.*, **67**, 601 (1945).

(39) M. M. Brubaker, U. S. Patent 2680763 (1954); *Chem. Abstr.*, **49**, 6991 (1955).

(40) M. S. Matta, Ph.D. Thesis, Indiana University, 1966.

volumes of the chlorides (or bromochlorides), di-*tert*-butyl peroxide, and triethylsilane were diluted with sufficient cyclopropane to give a final ratio of approximately 1:1:1:4 (v/v).

All samples were thoroughly degassed using a freeze-pump-thaw cycle. When spectra were of low intensity, the relative amounts of the reactants were varied to maximize the signal.

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## $(CCH_3)_6^{2+}$ , an Unusual Dication<sup>1,2</sup>

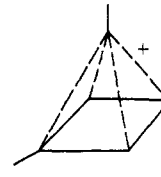
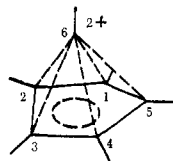
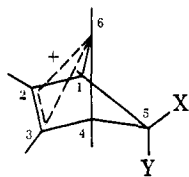
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**Abstract:** The  $(CCH_3)_6^{2+}$  dication (**2**) has been prepared in strongly acidic solution from a variety of precursors. Several reactions of this species are reported. A number of possible structures for the dication are considered and found to be not in agreement with the structure of the quenching products and/or the pmr spectrum. Two alternatives remain for further consideration: a rapid degenerate rearrangement of structures **5** and the nonclassical structure **2**, involving a hexacoordinated carbon atom. Pmr and cmr spectral data, the rates of deuterium exchange and of carbonylation, and the thermal stability together with the reported *ab initio* calculations provide strong evidence for the nonclassical structure **2**.

The idea that in some cations the carbon atom might have a coordination number higher than four was first suggested by Wilson<sup>3a</sup> and was later developed by Winstein.<sup>3b,c</sup> Nonclassical ions with a pentacoordinated carbon atom like norbornyl and norbornenyl cations have become common phenomena in the literature since then. Examples of ions with an electronic structure strongly related to that of the norbornenyl cation are the nonclassical 1,2,3,4,5,6-hexamethylbicyclo[2.1.1]hexenyl cations **1**.<sup>4</sup> These ions are im-

bond.<sup>4,5</sup> Examples of more extended delocalization are found in the larger aromatic and homoaromatic cations, but in these cases the coordination number of carbon does not exceed 4.<sup>3c</sup> In recent literature, however, one encounters some nonclassical ions in which a description in terms of a two-electron, three-center bond was judged to be not adequate and a more complex electronic structure was proposed. Among these is the  $(CH)_5^+$  cation proposed by Stohrer and Hoffmann<sup>6</sup> to have a square-pyramidal configuration **3** involving a



- a, X = H; Y = CH<sub>3</sub>  
 b, X = CH<sub>3</sub>; Y = H  
 c, X = CH<sub>3</sub>; Y = Cl  
 d, X = CH<sub>3</sub>; Y = Br  
 e, X = OH; Y = CH<sub>3</sub>  
 f, X = CH<sub>3</sub>; Y = OCH<sub>3</sub>

portant in this context as precursors and intermediates in the preparation and reactions of the title compound, dication **2**. In **1** and in the norbornenyl cation there is not much charge delocalization toward the bridgehead carbon atoms and therefore the electronic structure can be described making use of a two-electron, three-center

pentacoordinated carbon atom. Recent calculations<sup>7</sup> agree with these results insofar that **3** is considered to be an energy minimum. Experimental evidence concerning this type of ion was obtained in the case of the dimethyl-substituted species **4**<sup>8</sup> and some bishomo- $(CH)_5^+$  cations.<sup>9</sup>

In the case of dication **2** one deals with an analogous delocalized electronic structure; this time, however, a hexacoordinated carbon atom is involved. Hexa-

(1) Chemistry and spectroscopy in strongly acidic solutions XL. For part XXXIX, see ref 2a.

(2) For preliminary communications, see (a) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1665 (1973); (b) *ibid.*, 3747 (1973).

(3) (a) T. P. Nevell, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939); (b) S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, 71, 2953 (1949); (c) for a review, see S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 1411 (1969).

(4) H. Hogeveen and P. W. Kwant, *J. Amer. Chem. Soc.*, 95, 7315 (1973).

(5) S. Yoneda, Z. Yoshida, and S. Winstein, *Tetrahedron*, 28, 2395 (1972).

(6) W. D. Stohrer and R. Hoffmann, *J. Amer. Chem. Soc.*, 94, 1661 (1972).

(7) (a) H. Kollmar, H. O. Smith, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 95, 5834 (1973); (b) M. J. S. Dewar and R. C. Haddon, *ibid.*, 95, 5836 (1973); (c) W. J. Hehre and P. v. R. Schleyer, *ibid.*, 95, 5837 (1973).

(8) (a) S. Masamune, M. Sakai, and H. Ona, *J. Amer. Chem. Soc.*, 94, 8955 (1972); (b) S. Masamune, M. Sakai, H. Ona, and A. L. Jones, *ibid.*, 94, 8956 (1972).

(9) (a) H. Hart and M. Kuzuya, *J. Amer. Chem. Soc.*, 94, 8958 (1972); (b) S. Masamune, M. Sakai, A. V. Kemp-Jones, H. Ona, A. Venot, and T. Nakushima, *Angew. Chem.*, 85, 829 (1973); (c) H. Hart and M. Kuzuya, *Tetrahedron Lett.*, 4123 (1973).