In summary, ion cyclotron resonance spectroscopy has again proven itself well suited to the determination of the structure of organic ions. In this case it has proven itself capable of the detection of mechanistically different pathways giving rise to ions of identical mass but different structure.

Experimental Section[12]

***n*-Pentyl Thiovinyl Ether (Ia).** The sodium salt of 2-mercaptoethanol, prepared by treatment of 2-mercaptoethanol with sodium hydride in dry DMF, was heated with 1 equiv of *n*-pentyl bromide for 2 hr. The solution was cooled and the solvent removed by distillation. Water was added and the mixture was extracted with ether. The ether layer was dried over sodium sulfate and the ether removed *in vacuo*. The crude product in ether was refluxed overnight with excess phosphorus tribromide. Water was added and the ether layer was separated. The ether layer was washed with water and sodium bicarbonate solution, dried, and evaporated. An ether solution of 2-*S*-(*n*-pentyl)mercaptoethyl bromide was treated overnight at 25° with a 4 molar excess of 1,5-diazabicyclo[4.3.0]non-5-ene. The reaction mixture was extracted with excess saturated sodium bicarbonate and dried over sodium sulfate and the ether evaporated *in vacuo*. *n*-Pentyl thiovinyl ether was purified by preparative glc.

Deuterium Labeled *n*-Pentyl Thiovinyl Ethers: 1,1-d_2 **(Ib)**; 2,2-d_2 **(Ic)**; 3,3-d_2 **(Id)**; 4,4-d_2 **(Ie)**; 5,5,5-d_3 **(If)**. *n*-Pentyl-1,1-d_2, -2,2-d_2, -3,3-d_2, and -4,4-d_2 alcohols were previously described.[1] *n*-Pentyl-5,5,5-d_3 alcohol was prepared by reduction of acetic acid-d_4 with lithium aluminum hydride. The bromide was prepared by reaction with triphenylphosphine and bromine.[13] Alkylation of the ethyl-2,2,2-d_3 bromide thus formed with sodio diethyl malonate followed by saponification and decarboxylation yielded butyric-4,4,4-d_3 acid. Reduction of the acid with lithium aluminum hydride and formation of the bromide as above yielded the labeled butyl bromide, which was converted by carbonation of its Grignard complex to valeric-5,5,5-d_3 acid. Reduction with lithium aluminum hydride then formed *n*-pentyl-5,5,5-d_3 alcohol. Treatment of the labeled alcohols with phosphorus tribromide formed the labeled bromides. The latter were transformed into the labeled *n*-pentyl thiovinyl ethers as described above for the preparation of unlabeled *n*-pentyl thiovinyl ether. Per cent deuterium incorporation (compound, position, per cent): Ib, 1, 92.5% d_2, 7.5% d_1; Ic, 2, 100% d_2; Id, 3, 97% d_2, 3% d_1; Ie, 4, 91.5% d_2, 8.5% d_1; If, 5, 95% d_3, 5% d_2.

***n*-Pentyl-3,3,5,5-d_4 Thiovinyl Ether (Ig).** Methylmalonic acid was exchanged with deuterium oxide and decarboxylated thermally to yield propionic-2,2-d_2 acid. Reduction of the acid with lithium aluminum deuteride yielded 1,1,2,2-tetradeuteriopropanol. Treatment of the alcohol with triphenylphosphine and bromine[13] yielded 1-bromo-1,1,2,2-tetradeuteriopropane which was homologated with sodio diethyl malonate. The 3,3,5,5-tetradeuteriopentanol was transformed to *n*-pentyl-3,3,5,5-d_4 thiovinyl ether (Ig) as previously described for the labeled pentyl thiovinyl ethers (Ib–f). Mass spectral analysis showed an isotopic composition of 77% d_4 and 23% d_3.

Cyclobutanethiol (III).[14] Cyclobutanone was reduced with lithium aluminum hydride to yield cyclobutanol which was transformed into cyclobutyl tosylate by the procedure of Brown and Han.[15] The tosylate and thiourea were refluxed in ethanol overnight to form the thiouronium salt. Treatment of the thiouronium salt with aqueous sodium hydroxide yielded cyclobutanethiol which was purified by glc.

2,4-Dideuterio-2,4-dimethylthietane (VI). Acetylacetone was reduced with sodium borodeuteride to yield 2,4-dideuterio-2,4-pentanediol.[16] The cyclic carbonate of the diol was prepared by heating the diol with diethyl carbonate and a catalytic amount of sodium. Heating the cyclic carbonate with potassium thiocyanate[7] at 165° under nitrogen yielded 2,4-dideuterio-2,4-dimethylthietane (92% d_2, 8% d_1) which was purified by glc.

***n*-Pentyl Thiovinyl-2′,2′-d_2 Ether (VIII).** Reaction of the sodio salt of ethyl 2-mercaptoacetate with *n*-pentyl bromide in DMF yielded ethyl 2-*S*-(*n*-pentyl)mercaptoacetate which was reduced with lithium aluminum deuteride to yield 2-*S*-(*n*-pentyl)mercaptoethyl-2,2-d_2 alcohol. Conversion of this alcohol to *n*-pentyl thiovinyl-2′,2′-d_2 ether (VIII) through the corresponding bromide followed the procedures for Ia.

The preparations of 1-methylcyclobutanol and heptan-4-one-3,3,5,5-d_4 were described in an earlier paper.[5] Cyclobutanethiol-*S*-d_1 was prepared in the inlet system of the icr spectrometer by exchange with D_2O.

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[12] The basic spectrometer used in this study is the Varian V-5900 spectrometer fitted with a dual inlet system. The spectrometer, the method, and applications of single and double resonance have been described.[6] Mass spectra were run on an MS-9 mass spectrometer by Mr. R. Ross. We wish to thank Mr. John Garcia for technical assistance with the icr spectrometer.

[13] G. A. Wiley, A. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964).

[14] H. E. Gunning, U. S. Patent 3230161 (1966).

[15] H. C. Brown and G. Han, *J. Amer. Chem. Soc.*, **78**, 2735 (1956).

[16] J. Dale, *J. Chem. Soc.*, 910 (1961).

Bridging in β-Chloroalkyl Radicals by Electron Spin Resonance

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Contribution from the Chemistry Department, Indiana University, Bloomington, Indiana 47401. *Received March 12, 1973*

Abstract: Chlorine bridging in alkyl radicals is examined by esr for a series of methyl substituted β-chloroethyl radicals in solution. The criterion for bridging in these radicals is considered as restricted rotation about the C_α–C_β bond and distortion at C_β which places the eclipsed chlorine atom closer to the p orbital at the radical center. Analysis of isotropic esr *g* values and temperature-dependent chlorine-35 and proton hyperfine splittings indicates that all these β-chloroalkyl radicals exist in stable conformations consisting of chlorine in asymmetric bridges. Bridging is promoted by methyl groups, but counteracting steric effects prevent the tetramethyl analog from achieving a symmetric bridged structure. The facile 1, 2 migration of chlorine in the β-chloroisobutyl radical to the tertiary isomer is reported.

Stabilization of alkyl radicals and stereoselectivity in homolytic reactions due to bridging and anchimeric assistance by heteroatom substituents are subjects which have been discussed at length and are of current chemical interest.[1] Halogens are foremost among these substituents, particularly when they are bromine or chlorine located in the β position relative to the radical center. Since the effects have been exerted in free-radical additions to alkenes as well as substitution into and elimination from alkyl derivatives, the problem is largely associated with the structure of the β-haloalkyl radicals formed as intermediates in these reactions.

The electron spin resonance (esr) spectra of these interesting radicals offer the most direct approach to examining their structure and conformation.[2] Unfortunately, the β-bromoethyl radical is too unstable in solution even at $-120°$ to observe by esr.[3] How-

$$BrCH_2CH_2\cdot \longrightarrow Br\cdot + CH_2{=}CH_2$$

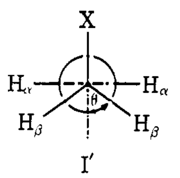
ever, the examination of partially resolved anisotropic spectra of haloalkyl radicals obtained in frozen solutions by ^{60}Co γ-radiolysis suggests rather large β-bromine and β-iodine splittings,[4] although the absence of proton hyperfine splittings precludes a definite assignment.

The well-resolved esr spectrum of the β-chloroethyl radical $ClCH_2\dot{C}H_2$ obtained in solution shows some unusual features relative to other β-substituted ethyl radicals.[2,5] Thus, the β-chloroethyl radical is characterized by an isotropic g factor which is smaller than that generally obtained for alkyl radicals. The negative shift ($\Delta g = -0.00046$) was attributed to the delocalization of the odd electron from the radical center onto the lone-pair orbital on chlorine.[6] Furthermore, the triplet splitting from the β protons in the β-chloroethyl radicals is quite small (9 G), and shows a temperature dependence ($da_{H\beta}/dT = +2.2 \times 10^{-2}$ G deg^{-1}) which is opposite to that of the ^{35}Cl splitting ($da_{Cl}/dT = -1.9 \times 10^{-2}$ G deg^{-1}).

The isotropic hyperfine coupling constant $a_{H\beta}$ of a β hydrogen in an alkyl radical depends strongly on its orientation relative to the free-radical center. The angular dependence of $a_{H\beta}$ can be approximated by eq 1, where θ is the dihedral angle between the β carbon–

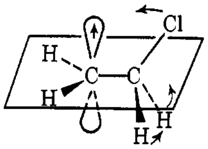
$$a_{H\beta} = A + B\cos^2\theta \qquad (1)$$

hydrogen bond and the p orbital at the radical center.[7] We assume that a similar angular dependence of a_{Cl} applies to β chlorine.



I′

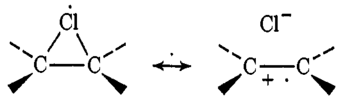
An INDO MO calculation indicates that a minimum value of $a_{H\beta} = 13.5$ G is obtained in a β-substituted ethyl radical $\dot{C}H_2CH_2X$ when it exists in the symmetric conformation I′.[8] However, the low-temperature limit for $a_{H\beta}$ of the β-chloroethyl radical is actually less than the predicted minimum. Such a result can be accommodated by a distortion at C_β which moves H_β closer to the nodal plane, since the sign of the coupling constant due to hyperconjugation is positive while that contribution from spin polarization is negative.[2] The distortion in I also places chlorine closer to the p orbital at the radical center.



I

Thus, the magnitudes of the β proton and the chlorine-35 splittings together with their temperature dependences indicate that the most stable conformation of the β-chloroethyl radical is I, in which the chlorine is positioned directly behind the p orbital at the radical center and optimally located to interact with it. The chlorine atom in I, however, is not symmetrically placed between C_α and C_β, since the methylene groups remain inequivalent. Nonetheless, homoconjugation and hyperconjugation described above may be considered as bridging in the broadest sense.[9]

The attractive possibility yet remains for a symmetrically bridged species II, especially if charge-transfer contributions (IIb) were optimized, *e.g.*



IIa IIb

Indeed, nucleophilic solvation of chlorine atoms with arenes has the character of charge-transfer complexes.[10,11]

$$[Cl\cdot ArH \longleftrightarrow Cl^{-}ArH\cdot^{+}]$$

Since methyl substituents help to stabilize cation radicals of alkenes,[12] it appeared to us that methyl groups on C_α and C_β of β-chloroalkyl radicals would optimize bridging by chlorine. With this in mind, we report in this paper the esr studies of a series of β-chloroalkyl radicals and our deductions about their structure and conformation.

Results and Discussion

Formation of β-Chloroalkyl Radicals. The β-chloroalkyl radicals were generated in solution for esr study by (a) addition of chlorine atom to the alkene (eq 2) or (b) halogen atom abstraction from the β-chloroalkyl

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[1] (a) P. S. Skell, "Free Radicals," Wiley-Interscience, New York, N. Y., 1973, Chapter 26; (b) L. Kaplan, "Bridged Free Radicals," Marcel Dekker, New York, N. Y., 1972; (c) J. G. Trayham, E. E. Green, Y.-S. Lee, F. Schweinsberg, and C.-E. Low, *J. Amer. Chem. Soc.*, **94**, 6552 (1972); (d) P. S. Skell and K. J. Shea, *ibid.*, **94**, 6550 (1972); **95**, 283 (1973); (e) C. Ronneau, J.-P. Soumillion, P. Dejaifve, and A. Bruylants, *Tetrahedron Lett.*, 317 (1972); (f) W. C. Danen and R. L. Winter, *J. Amer. Chem. Soc.*, **93**, 716 (1971); (g) D. D. Tanner, H. Yabuuchi, and E. V. Blackburn, *ibid.*, **93**, 4802 (1971).

[2] Partly published in preliminary form: T. Kawamura, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 1752 (1972).

[3] D. J. Edge and J. K. Kochi, *ibid.*, **94**, 6485 (1972).

[4] A. R. Lyons and M. C. R. Symons, *ibid.*, **93**, 7330 (1971).

[5] A. J. Bowles, A. Hudson, and R. A. Jackson, *Chem. Phys. Lett.*, **5**, 552 (1970).

[6] Homoconjugation between the nonbonding orbitals on chlorine and the radical center was described.[2] We were unable at that time to assess the importance of a hyperconjugative delocalization onto the C–Cl σ orbital (which would contribute a positive Δg change).

[7] (a) R. W. Fessenden, *J. Chim. Phys. Physicochim. Biol.*, **61**, 1570 (1964); (b) J. K. Kochi and P. J. Krusic, *Chem. Soc., Spec. Publ.*, No. **24**, 147 (1970).

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

[9] R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *ibid.*, **94**, 6221 (1972).

[10] G. A. Russell, *ibid.*, **79**, 2977 (1957); **80**, 4987 (1958).

[11] R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969.

[12] R. M. Dessau, *J. Amer. Chem. Soc.*, **92**, 6356 (1970).

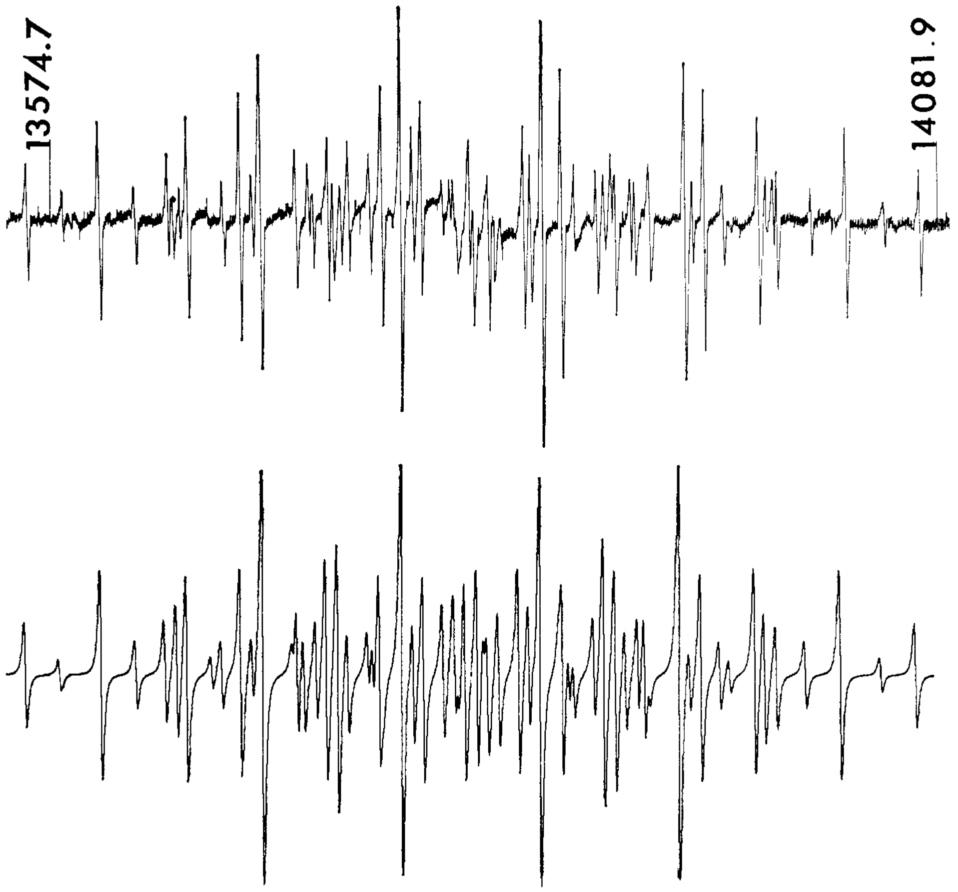
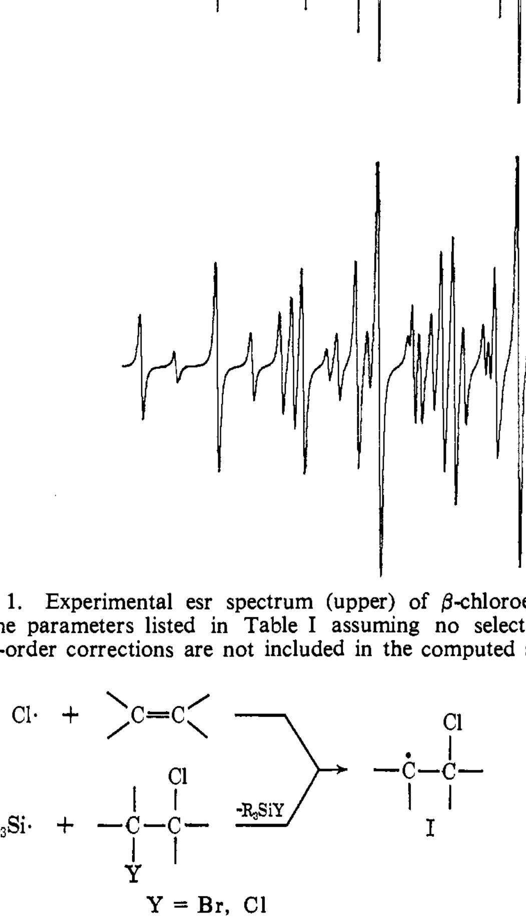


Figure 1. Experimental esr spectrum (upper) of β-chloroethyl radical in solution at −125°. The lower spectrum was computed from the parameters listed in Table I assuming no selective line broadening and includes ^{35}Cl and ^{37}Cl in natural abundances. Second-order corrections are not included in the computed spectrum.

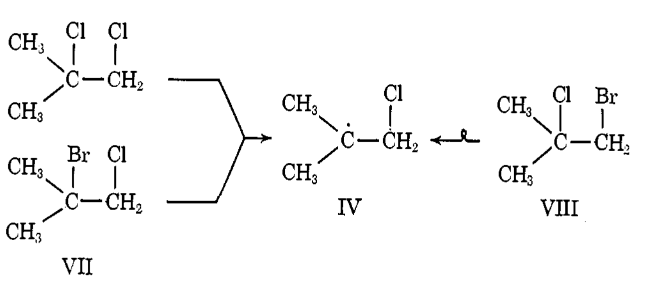


(2)

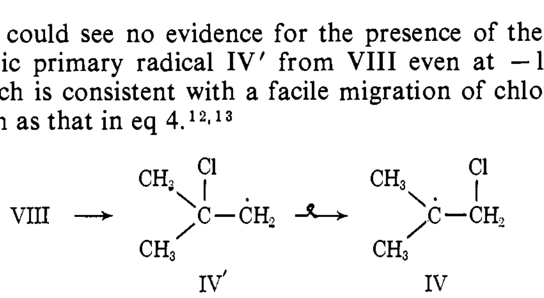
(3)

halide with silyl radical (eq 3). Chlorine atom and silyl radical were generated *in situ* from hydrogen chloride and triethylsilane, respectively, by reaction with photochemically generated *tert*-butoxy radicals.[3]

Addition was the method of choice for the production of β-chloroethyl radical I (Figure 1), but with other alkenes the process suffered in competition with allylic hydrogen abstraction. The α-methyl- (III), α,α-dimethyl- (IV), α,α,β-trimethyl- (V), and α,α,β,β-tetramethyl-β-chloroethyl (VI) radicals were generated from the corresponding dichlorides (Y = Cl). The α,α-dimethyl-β-chloroethyl radical (IV) was also generated from either isomeric bromo chloride, VII or VIII.



We could see no evidence for the presence of the isomeric primary radical IV′ from VIII even at −130°, which is consistent with a facile migration of chlorine, such as that in eq 4.[12,13]



(4)

The esr parameters for these β-chloroalkyl radicals are listed in Table I, and they were all verified by computer simulation of the spectra. Interestingly, the septet splitting due to two equivalent α-methyl protons in IV (Figure 2) was accidentally the same as the 1:1:1:1 splitting of chlorine-35 over a range of temperatures from −78 to −129°. In order to ensure that the spectrum observed for the tetramethyl analog VI was not due to the observation of only the central portion of a symmetrical radical with four equivalent methyl groups, both simulated spectra are compared with the experimental one in Figure 3. The experimental and calculated esr spectra of the α,α,β-trimethyl-β-chloroethyl radical V are shown in Figure 4.

Criterion for Bridging in β-Chloroalkyl Radicals. Bridging in the β-chloroalkyl radicals implies an energy minimum at the symmetric conformation imposed by *restricted rotation* about the C_α–C_β bond. If θ describes the dihedral angle between the C_β–Cl bond and the p orbital at the radical center, then θ =

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(13) P. S. Juneja and E. Hodnett, *ibid.*, **89**, 5685 (1967).

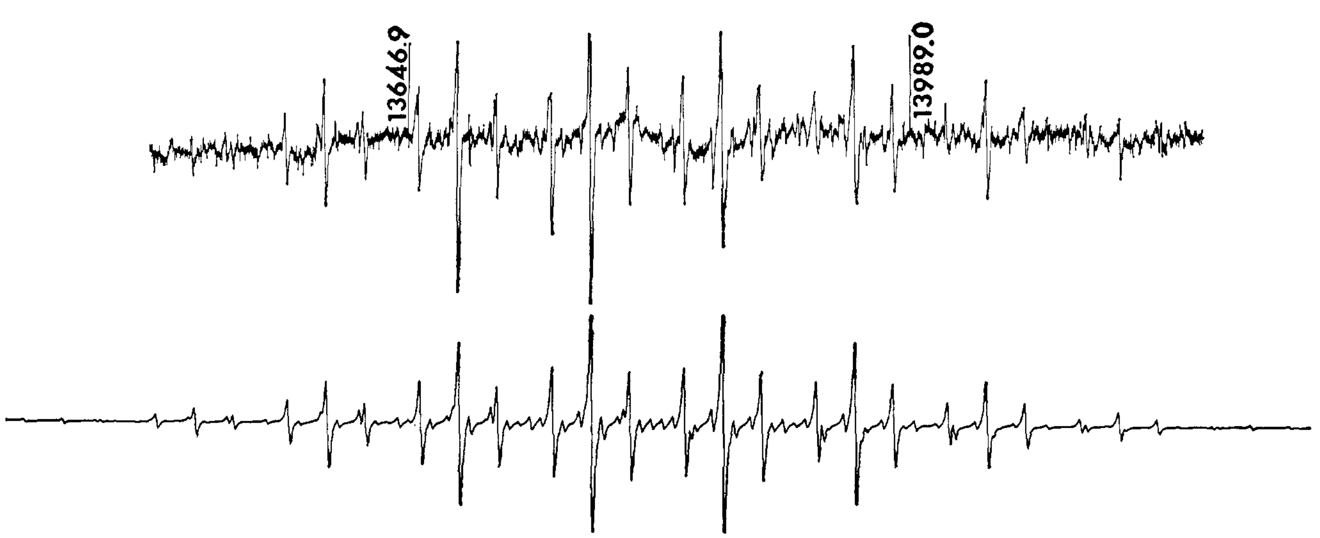


Figure 2. Esr spectrum (upper) of α,α-dimethyl-β-chloroethyl radical in solution at $-108°$. The simulated spectrum (lower) includes ^{35}Cl and ^{37}Cl in natural abundances. Proton nmr field markers are in kHz.

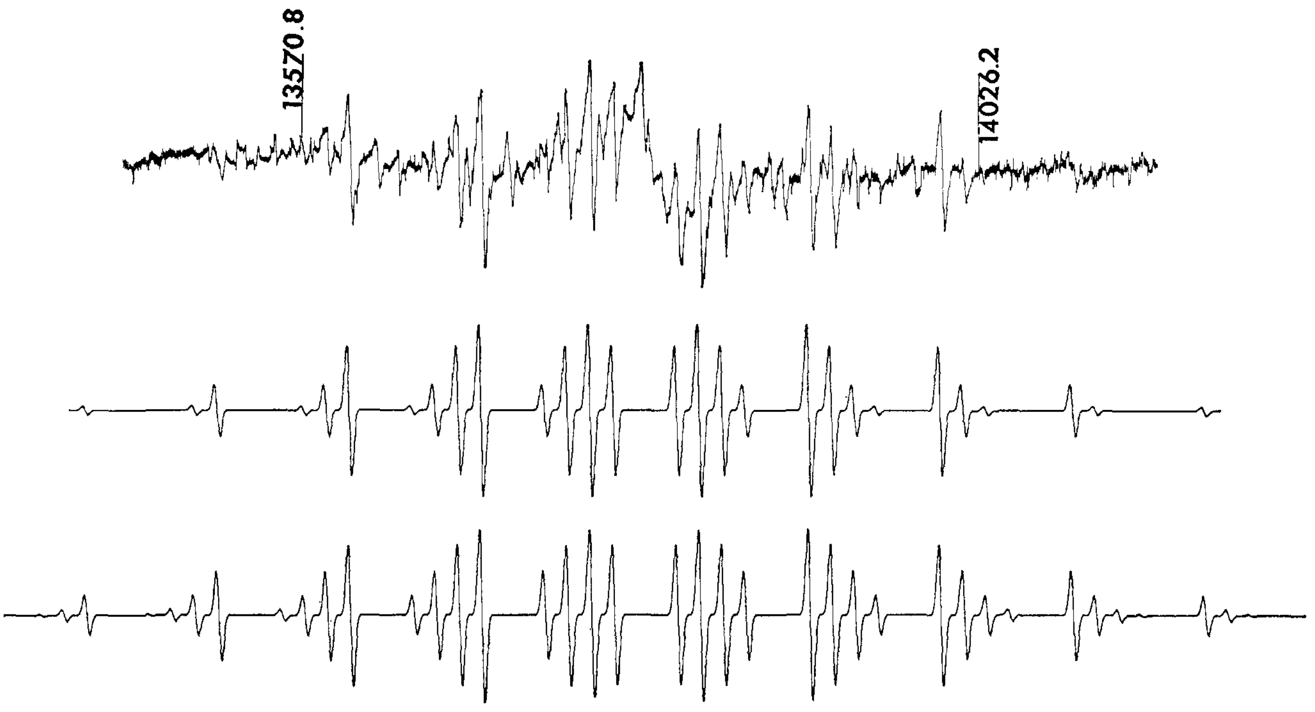
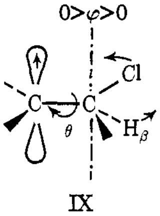


Figure 3. Esr spectrum (upper) of $\alpha,\alpha,\beta,\beta$-tetramethyl-$\beta$-chloroethyl radical in solution at $-127°$ carried out at relatively high modulation to optimize S/N. The simulated spectra represent: (middle) two equivalent α-methyl groups, and (lower) four equivalent methyl groups using parameters in Table I and employing Gaussian line shapes (^{35}Cl isotope only).

0 is optimum for the bridged structure. Bridging also implies *distortion* at C_β which moves the chlorine atom closer to the p orbital, and H_β closer to the nodal plane.



IX

If φ describes the angle through which the Cl–C_β bond must be moved to become perpendicular to the C_α–C_β bond, then $\varphi_0 = +19.5°$ applies to the undistorted configuration. In the following discussion, the values of $a_{H\beta}$ and the g factor given in Table I will be used to deduce changes in φ due to distortion, as a result of increasing the number of methyl groups on the β-chloroethyl radical. Secondly, the selective line broadening in the esr spectra of these radicals, together with a_{Cl} and $a_{H\beta}$, will be used to probe θ as a result of conformational changes about the C_α–C_β bond.

Distortion of β-Chloroalkyl Radicals at C_β. The unusually small value of $a_{H\beta}$ in the β-chloroethyl radical, which was ascribed to distortion at C_β moving H_β closer to the nodal plane (see IX), *decreases* even *further* with increasing methyl substitution as shown in Figure 5.

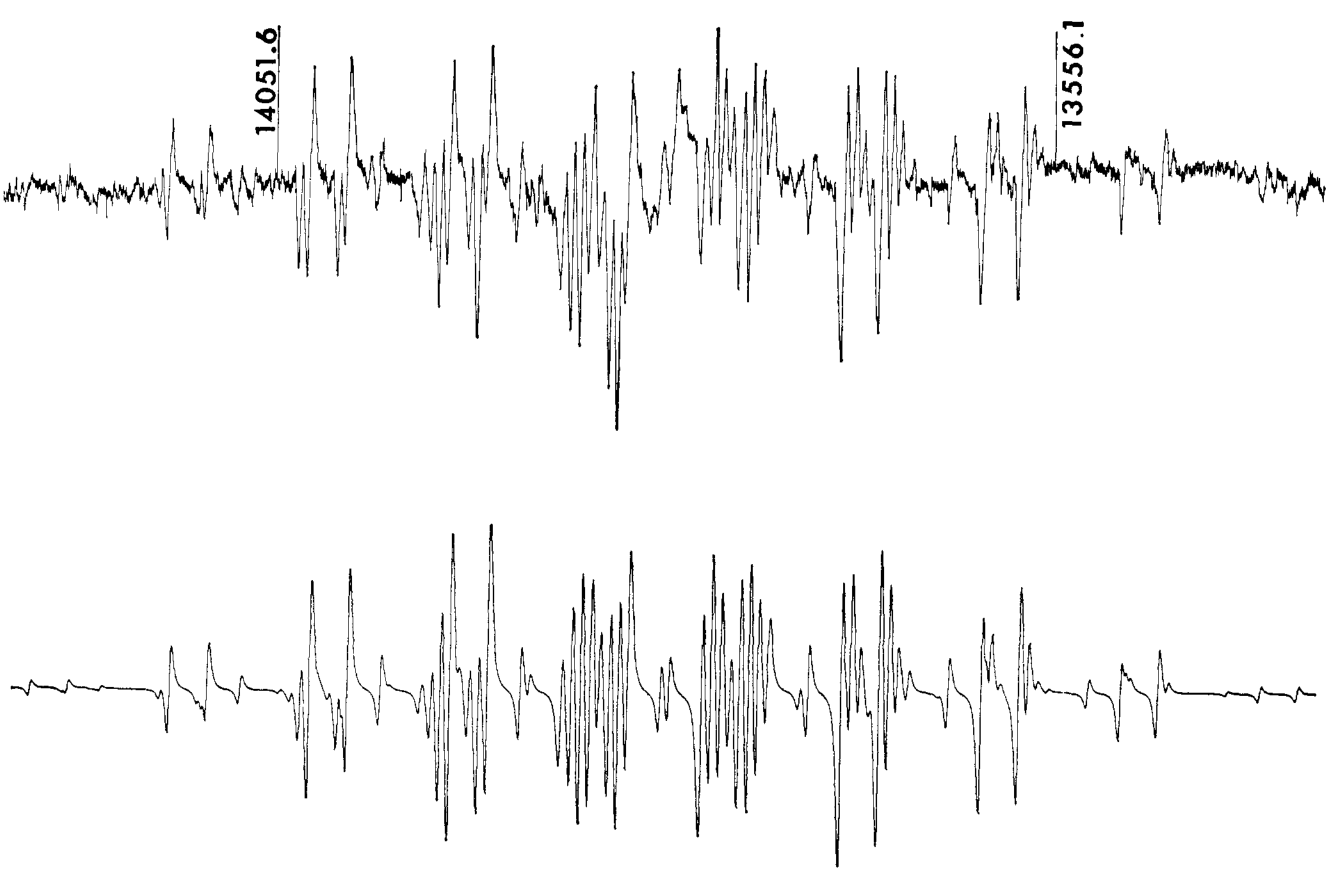


Figure 4. Esr spectrum (upper) of α,α,β-trimethyl-β-chloroethyl radical in solution at −121°. The simulated spectrum (lower) includes ^{35}Cl and ^{37}Cl in natural abundances. Proton nmr field markers are in kHz.

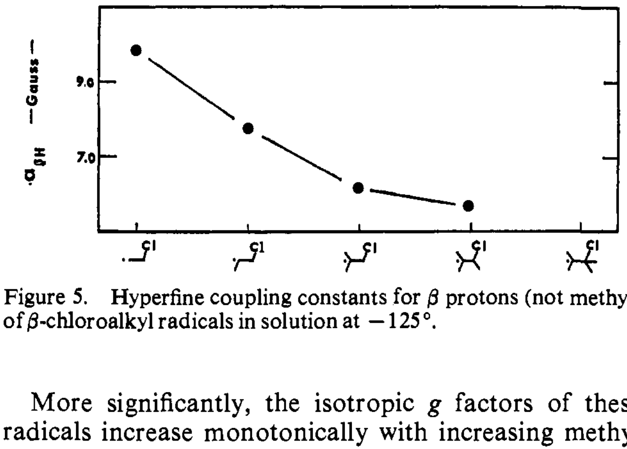


Figure 5. Hyperfine coupling constants for β protons (not methyl) of β-chloroalkyl radicals in solution at −125°.

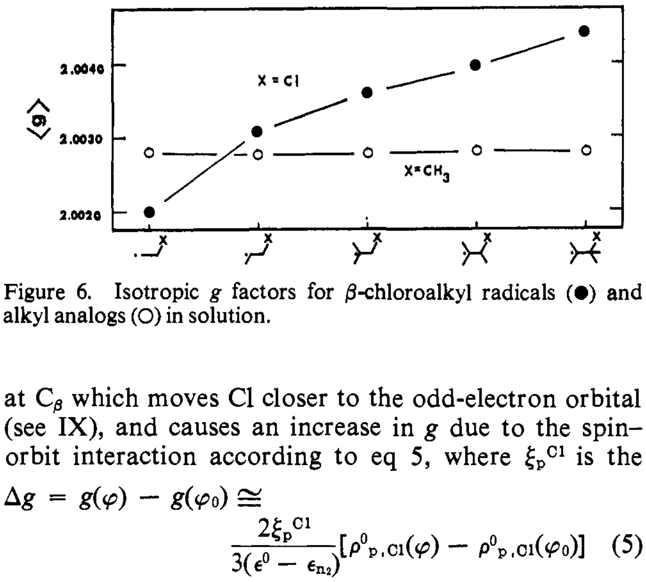


Figure 6. Isotropic g factors for β-chloroalkyl radicals (●) and alkyl analogs (○) in solution.

More significantly, the isotropic g factors of these radicals increase monotonically with increasing methyl substitution as shown in Figure 6. The changes in g factors (Δg) for β-chloroalkyl radicals are in striking contrast to Δg of the hydrocarbon analogs (in which CH_3 replaces Cl), whose g factors are almost invariant with methyl substitution (Figure 6). The increase in Δg is also most readily accounted for by the distortion at C_β which moves Cl closer to the odd-electron orbital (see IX), and causes an increase in g due to the spin–orbit interaction according to eq 5, where ξ_p^{Cl} is the

$$\Delta g = g(\varphi) - g(\varphi_0) \cong \frac{2\xi_p^{Cl}}{3(\epsilon^0 - \epsilon_{n_2})}[\rho^0_{p,Cl}(\varphi) - \rho^0_{p,Cl}(\varphi_0)] \quad (5)$$

$$\rho^0_{p,Cl}(\varphi) = \rho^{*0}_{p,Cl}(\cos\varphi - \sin\varphi)^2$$

Table I. Esr Parameters for β-Chloroalkyl Radicals

Radical	Temp, °C	Coupling constants, G ^{35}Cl	H_α	H_β	α-CH_3[a]	⟨g⟩ ±0.00003
$\dot{C}H_2CH_2Cl$	−125	18.78[b]	21.75	10.20		2.00199
$CH_3\dot{C}HCH_2Cl$	−127	19.89	20.70	7.79	24.03	2.00306
$CH_3\dot{C}HCH(CH_3)Cl$	−120	18.83	20.16	9.40	23.60	2.00303
$(CH_3)_2\dot{C}CH_2Cl$	−129	21.24[c]		6.18	21.24	2.00359
$(CH_3)_2\dot{C}CH(CH_3)Cl$	−121	19.43[d]		5.72	21.04	2.00395
$(CH_3)_2\dot{C}C(CH_3)_2Cl$	−129	17.30			20.89	2.00442

[a] β-CH_3 unresolved. [b] $a(^{37}Cl)$ = 15.65 G. [c] $a(^{37}Cl)$ = 17.63 G. [d] $a(^{37}Cl)$ = 16.30 G.

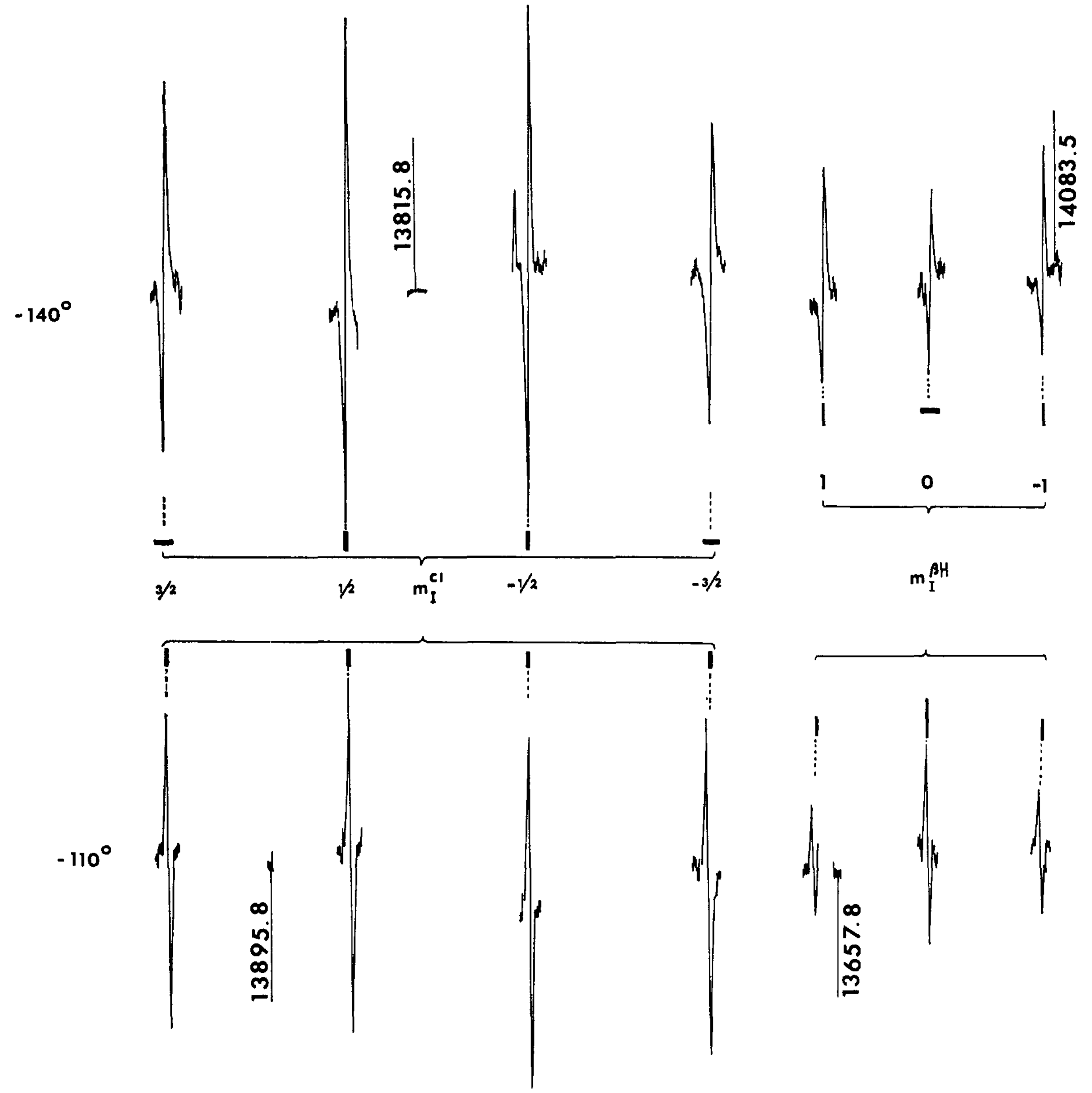


Figure 7. Temperature variation of the esr spectrum of the β-chloroethyl radical in solution, showing only the undisturbed 1:1:1:1 ^{35}Cl splitting and the 1:2:1 β-proton splitting. To emphasize line broadening (shown by —), other features of the spectrum were obliterated. Proton nmr field markers are in kHz.

spin–orbit coupling constant (587 cm^{-1}) of the chlorine p orbital, $\varphi_0 = 19.5°$ is the undistorted configuration, and ϵ^0 and ϵ_{n_2} are the energies of the odd-electron and nonbonding orbitals, respectively. $\rho^{*0}_{p,Cl}$ is the odd-electron density on the p orbitals of chlorine in the configuration $\varphi = 0°$, and has a lower limit of 0.1 based on the observed splitting and the atomic splitting of chlorine-35 (see Appendix).

Table II. Angular Dependence of Δg due to Distortion in β-Chloroalkyl Radicals

φ (deg)	Distortion (deg)	$\Delta g^a \times 10^5$
19.45	0	0
14.45	5	35
9.45	10	73
4.45	15	113
0.45	19	150

[a] According to eq 5, see structure IX.

The change in g caused by distortion at C_β is listed in Table II as a function of the angle φ through which the chlorine must be moved.

Table II shows a trend for Δg to parallel distortion at C_β, which is consistent with the prior conclusion based on the observed β-proton splittings, namely, distortion at C_β increases with increasing methyl substitution.

An alternative change in the *dihedral* angle θ between the odd-electron orbital and the C_β–Cl bond causes little or no alteration in the g values.[14]

Hindered Rotation about the C_α–C_β in Chloroalkyl Radicals. The esr spectrum of the β-chloroethyl radicals shows a temperature-dependent variation in line widths within the multiplicities of $M_I^{\beta H}$ ($M_I = 0$ lines broadened) and M_I^{Cl} ($M_I = \pm {}^3/_2$ broader than

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(14) The g factors for alkyl radicals with β-oxygen substituents are invariant with conformation [although the spin–orbit coupling constant for oxygen (ξ_p = 151 cm^{-1}) is about a fourth that of chlorine: D. J. Edge and J. K. Kochi, *J. Amer. Chem. Soc.*, **95**, 2635 (1973)].

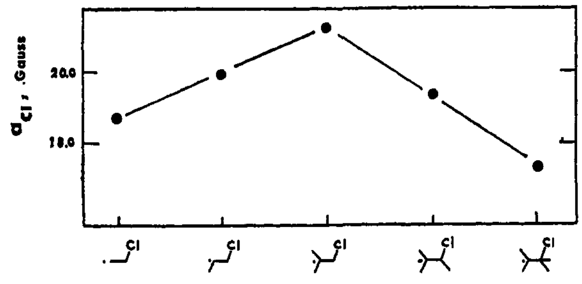
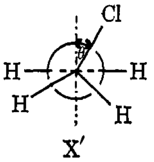


Figure 8. Hyperfine coupling constants for ^{35}Cl in β-chloroalkyl radicals in solution at −125°.

±½ lines).[15] Figure 7 illustrates how these selective line broadenings can be attributed to the temperature-dependent modulations of $a_{\beta H}$ and a_{Cl}. Torsional motion of the type shown below is also consistent with the temperature dependence of the β proton and chlorine-35 hyperfine splittings discussed earlier (*cf.* eq 1).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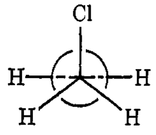
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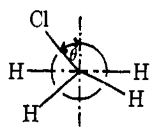
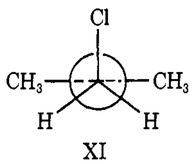
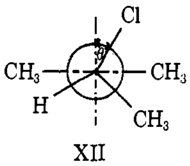

X′

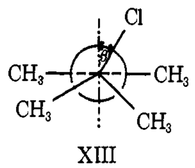
The barrier E_a for the torsional motion shown above may be estimated by eq 6 which is based on the relaxation matrix theory[16] applicable to the fast exchange limit with the assumption that the signal heights are inversely proportional to the squares of the total line widths. I_u and I_b are the signal heights of the theoretical unbroadened and the observed broadened lines. The activation energy for hindered rotation about the C_α–C_β bond in X estimated by this procedure is 4 kcal/mol.[17]

$$\log\,[(I_u/I_b)^{1/2} - 1] = \log C + E_a/2.3RT \qquad (6)$$

As methyl groups are substituted at C_α and C_β in the β-chloroethyl radical, two effects are noted. First, the chlorine-35 splitting reaches a *maximum* at the α,α-dimethyl analog IV as shown in Figure 8. The ^{35}Cl splitting in IV shows almost no temperature dependence (Figure 9), and there is no evidence for selective line broadening in the spectrum (Figure 2). Clearly, the α,α-dimethyl-β-chloroethyl radical is in a "locked" conformation XI. Further substitution of methyl groups at C_β causes an increase in the torsional angle θ as manifested in the trimethyl analog XII by the decreased values of a_{Cl} (Figure 8) and $a_{\beta H}$ (Table I). Finally, the even lower value of a_{Cl} in the tetramethyl analog XIII suggests a further increase in θ. We also infer from the limiting slopes[8,18] of da_{Cl}/dT in Figure 9 that barriers to hindered rotation about the C_α–C_β bonds increase with methyl substitution.


XI


XII


XIII

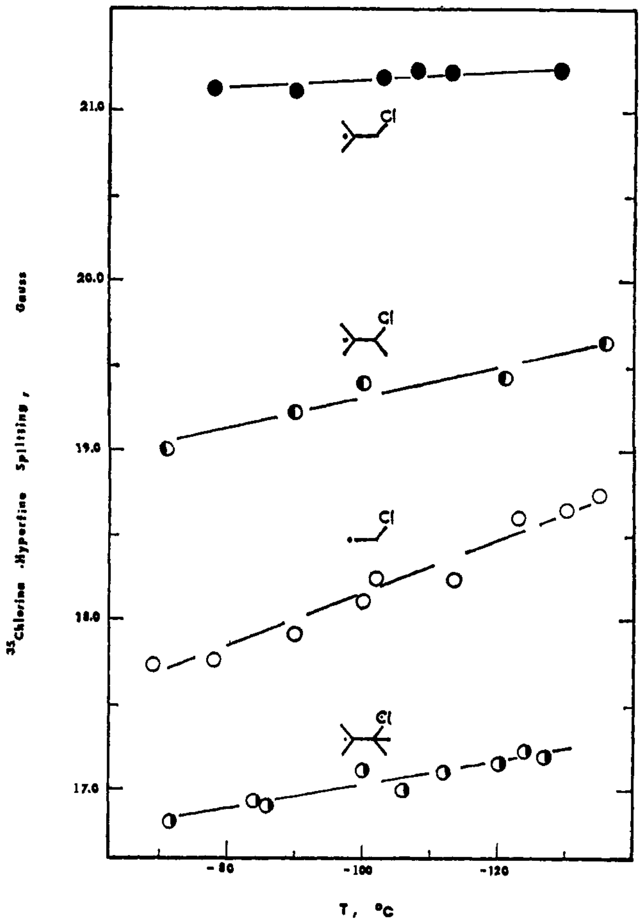


Figure 9. Temperature dependence of the ^{35}Cl hyperfine coupling constants for β-chloroalkyl radicals in solution.

The differences in the conformations XI, XII, and XIII are governed by counterbalancing steric effects between methyl groups on C_α and C_β. Similar differences are observed in the hydrocarbon analogs (in which CH_3 replaces Cl),[19] the esr parameters of which are listed in Table III and the conformations depicted below.

Table III. Esr Parameters for Methyl Substituted Alkyl Radicals

Alkyl radical	Sol-vent[a]	Temp, °C	Coupling constants, G α-H	β-H	α-CH$_3$	⟨g⟩ ± 0.00003
$\dot{C}H_2CH_3$	E	−99	22.28	[27.00]		2.00278
$\dot{C}H_2CH_2CH_3$	E	−108	22.13	31.17		2.00282
$CH_3\dot{C}HCH_3$	E	−99	21.97	[24.68]		2.00273
$(CH_3)_2\dot{C}CH_3$	P	−117			22.78	2.00276
$(CH_3)_2\dot{C}CH_2CH_3$	C	−117		17.94	22.80	2.00278
$(CH_3)_2\dot{C}CH(CH_3)_2$	C	−116		9.20	22.91	2.00278
$(CH_3)_2\dot{C}C(CH_3)_3$	C	−124			22.83	2.00282

[a] C = cyclopropane, P = *n*-pentane, E = ether.

The symmetric conformation XIV of the *tert*-amyl radical is based on the magnitude of $a_{H\beta}$ (18 G) and its

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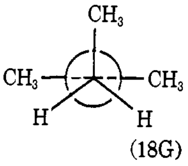
(15) Previously we noted[2] no dramatic line-width variations in the spectra. Closer scrutiny shown in Figure 7 reveals broadening if signal *heights* are considered.

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

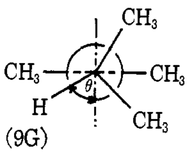
(17) This value compares with the extraordinarily high barrier of 16 kcal mol^{-1} based on INDO MO calculations: I. Biddles and A. Hudson, *Chem. Phys. Lett.*, 18, 45 (1973).

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

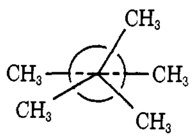
(19) Compare the barriers to hindered rotation of propane and ethyl chloride: J. Dale, *Tetrahedron*, 22, 3373 (1966).



XIV



XV

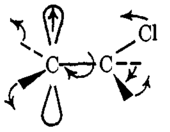


XVI

positive temperature dependence ($\mathrm{d}a_{\mathrm{H}\beta}/\mathrm{d}T = +6 \times 10^{-3}$ G deg^{-1}), as well as the absence of selective line broadening in the spectrum.[8] The presence of an additional β-methyl group alters the conformation to XV[18] as shown by the greatly reduced value of $a_{\mathrm{H}\beta}$ (9.2 G), and it is in accord with minimization of steric effects. On the same basis, we expected θ in the β,β,β-trimethyl analog XVI to decrease relative to XV and show inequivalence of three of the nine γ protons. Unfortunately, the γ-proton splittings in XVI were unresolved at −120°. Interestingly, the barrier to hindered rotation in *tert*-amyl radical XIV (620 cal mol^{-1}) is expectedly lower than that of XV (1200 cal mol^{-1}),[18] and higher than the barrier for isobutyl radical (300 cal mol^{-1}).[7a]

Conclusion

The α,α-dimethyl-β-chloroethyl radical IV, of all the methyl analogs of the β-chloroethyl radical, exists in the most symmetric conformation XI, since steric effects are minimal and the chlorine is well disposed to interact with the odd-electron orbital. Increasing methyl substitution in XII and XIII leads to greater distortion at C_β, but is obtained at the expense of steric interactions which increase the dihedral angle θ. Thus, these counterbalancing effects shown in XVII prevent the attainment of a truly symmetrical chlorine-bridged structure.



XVII

Experimental Section

Materials. Di-*tert*-butyl peroxide was obtained from Shell Chemical Co., washed, and redistilled at reduced pressure prior to use. Triethylsilane was obtained from Columbia Chemicals Co., refluxed over molecular sieves, and redistilled prior to use. 1-Bromo-2-chloroethane and 1,2-dichloropropane were obtained from Matheson Coleman and Bell.

1-Bromo-2-chloro-2-methylpropane and **2-bromo-1-chloro-2-methylpropane** were kindly donated by Professor P. S. Skell. Both samples were gc pure: nmr δ 2.25 (s), 4.22 (s), and 2.42 (s), 4.48 (s) ppm, respectively.

2,3-Dichloro-2-methylbutane was prepared by a modification of the method of Montgomery and Matt.[20] Dry chlorine was bubbled into a solution of isobutene (6 g 0.11 mol) in 25 ml of dimethylformamide at −60° in the dark until a light green coloration remained in the solution. The reaction mixture was then poured into water. The organic layer was removed, washed with 10% sodium carbonate solution and water, and then dried over magnesium sulfate. Distillation at atmospheric pressure gave 6.8 g (48%) of 1,2-dichloro-2-methylpropane, bp 104–105° (lit. bp 107°). The material was gc pure: mnr δ 1.65 (s), 3.70 (s) ppm.

2,3-Dichloro-2-methylbutane was prepared from 2-methyl-2-butene (7 g, 0.10 mol) as described above. In this case, reduced pressure distillation gave 9.9 g (70%) of 2,3-dichloro-2-methylbutane, bp 48–49° (55 mm). The material was gc pure: nmr δ 2.05 (s), 2.07 (d), 2.14 (s), 4.62 (q) ppm.

2,3-Dichloro-2,3-dimethylbutane was prepared from 2,3-dimethyl-2-butene (7.1 g, 0.08 mol) as described above. The product, a white crystalline solid, was obtained by addition of water to the reaction mixture and extracting with pentane. After washing with 10% sodium carbonate and water the product was recrystallized from pentane to afford 8.3 g (63%): mp 160–163° (lit. mp 164°); nmr δ 2.23 (s) ppm.

2-Bromo-2,3,3-trimethylbutane. 2,3,3-Trimethyl-2-butanol (4.5 g, 0.043 mol) was dissolved in 25 ml of dry ether. The solution was stirred and saturated with dry hydrogen bromide gas. The mixture was stoppered and left to stand overnight. The solution was then washed successively with 10% sodium bicarbonate and water, and dried over magnesium sulfate. After the ether was removed, traces of alcohol were eliminated by passing a pentane solution of the white crystalline solid down an alumina column to give 6.0 g (86%) of the pure product: nmr δ 1.12 (s), 1.79 (s) ppm.

Esr Measurements. The modified Varian X-band spectrometer, microwave frequency measurements, light source, and sample tubes are as described previously.[3,8]

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)[21] was used as 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.

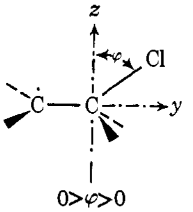
For photolytic reductions, equal volumes of the dichlorides (or bromochlorides), di-*tert*-butyl peroxide, and triethylsilane were diluted with sufficient cyclopropane to give a final ratio of approximately 1:1:1:4 (v/v).

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.

Acknowledgment. We wish to thank the National Science Foundation for generous financial support of this work and Dr. P. S. Skell for stimulating our interest in the chlorine migration and kindly supplying samples of the bromochloroisobutanes.

Appendix

The symmetric conformation I was used in the calculation of the change in g (Δg) due to distortion at C_β in which chlorine moves by an angle φ from its regular undistorted (tetrahedral) position (φ = +19.5°). The configuration at C_α was assumed to be planar for all the radicals.[22]



The isotropic g factors of β-chloroalkyl radicals can be expressed by eq 7 according to Stone's theory,[23]

$$g = g_e + \sum_s \Delta g_s = g_e + \sum_i \Delta g_i + \sum_j \Delta g_j \qquad (7)$$

where g_e is the free-spin value, and i and j sum over the σ orbitals and the chlorine lone pairs as well as

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(20) L. K. Montgomery and J. W. Matt, *J. Amer. Chem. Soc.*, **89**, 6556 (1967).

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

(22) 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), for disagreement on this point.

(23) A. J. Stone, *Proc. Roy. Soc., Ser. A*, **271**, 424 (1963); *Mol. Phys.*, **6**, 509 (1963); **7**, 311 (1964).

the d orbitals, respectively.

$$\sum_i \Delta g_i = \Delta g_{\mathrm{hc}} + \Delta g_{\beta\mathrm{Cl}}$$

and

$$\sum_j \Delta g_j = \Delta g_{\mathrm{n_1,Cl}} + \Delta g_{\mathrm{n_2,Cl}} + \Delta g_{\mathrm{d,Cl}}$$

$$\Delta g_{\mathrm{s}}^{\mathrm{zz}} = 2\sum_{\mathrm{ns}} \frac{\sum_{\mathrm{ks}} \langle X_{\mathrm{ks}}{}^{0}|\mathrm{l}_{\mathrm{ks}}{}^{\mathrm{z}}|X_{\mathrm{ks}}{}^{(\mathrm{ns})}\rangle \sum_{\mathrm{k's}} \xi_{\mathrm{k's}} \langle X_{\mathrm{k's}}{}^{(\mathrm{ns})}|\mathrm{l}_{\mathrm{k's}}{}^{\mathrm{z}}|X_{\mathrm{k's}}{}^{0}\rangle}{\epsilon^0 - \epsilon_{\mathrm{ns}}} \quad (8)$$

where

$$\Delta g_{\mathrm{s}} = {}^1/_3\Delta g_{\mathrm{s}}^{\mathrm{xx}} + {}^1/_3\Delta g_{\mathrm{s}}^{\mathrm{yy}} + {}^1/_3\Delta g_{\mathrm{s}}^{\mathrm{zz}}$$

The term ns sums over all the orbitals belonging to the group s, ks sums over atoms of the group s,$\psi_{\mathrm{ns}} = \Sigma_{\mathrm{ks}} X_{\mathrm{ks}}{}^{(\mathrm{ns})}$, ϵ^0 and ϵ_{ns} are the energies of the odd-electron orbital and ns orbitals, respectively, **l** is the angular momentum operator, and ξ is the spin–orbit coupling constant.

The contribution from the odd electron distributed on the hydrocarbon framework is given by Δg_{hc}. This term can be assumed to be invariant with changes in φ, since g factors are invariant for hydrocarbon analogs (Table III) and the value of ξ_{p} for carbon (28 cm^{-1}) is much smaller than that for chlorine (586 cm^{-1}). $\Delta g_{\beta\mathrm{Cl}}$ is the contribution from the odd electron distributed on the σ and σ^* orbitals of the C$_\beta$–Cl bond. The angular dependence of this term is unimportant due to the similar energy differences between $\epsilon^0 - \epsilon_\sigma$ and $\epsilon_{\sigma^*} - \epsilon^0$.[24] $\Delta g_{\mathrm{n_1,Cl}}$ is the contribution from the odd electron distributed on the chlorine nonbonding orbital which is parallel to the nodal plane of the odd electron p orbital. This term will depend on changes in the torsional dihedral angle θ, but will depend less on the changes in φ. $\Delta g_{\mathrm{d,Cl}}$ is the contribution from the odd electron distributed onto the chlorine d orbitals. It is given[2] by $4\xi_{\mathrm{d}}\rho_{\mathrm{d}}/(\epsilon^0 - \epsilon_{\mathrm{d}})$. This term is not important due to the small value of ϵ_{d} (8 cm^{-1}). Furthermore, if all five d orbitals are considered degenerate, $\Delta g_{\mathrm{d,Cl}}$ will be nearly invariant with changes in φ.

The most important term that emerges as a result of distortion at C$_\beta$ is that due to contributions ($\Delta g_{\mathrm{n_2,Cl}}$) from the odd electron distributed on to the chlorine nonbonding orbital which is directed toward the half-filled p orbital on C$_\alpha$. The optimum configuration of orbitals for this interaction, together with the small energy difference ($\epsilon^0 - \epsilon_{\mathrm{ns}}$),[24] contribute to the importance of this term as φ is varied. The change in g is obtained from eq 8 as

$$\Delta g_{\mathrm{n_2,Cl}} \cong \frac{2}{3}\frac{1}{\epsilon^0 - \epsilon_{\mathrm{n_2}}} \epsilon_{\mathrm{p}}{}^{\mathrm{Cl}} \rho^0{}_{\mathrm{p,Cl}}(\varphi) \quad (9)$$

where

$$\rho^0{}_{\mathrm{p,Cl}}(\varphi) = \rho^{0*}{}_{\mathrm{p,Cl}}(\cos\varphi - \sin\varphi)^2 \quad (10)$$

$\rho^{0*}{}_{\mathrm{p,Cl}}$ is the spin density on the chlorine p orbitals in the configuration $\varphi = 0°$. It can be estimated from the observed isotropic splitting and the atomic splitting of chlorine with the assumption, *i.e.*, $\rho^0{}_{\mathrm{p,Cl}}(\varphi = 19.45°) = (3)(20)/1640 = 0.037$ in which 1640 G is the atomic splitting of the chlorine atom, 20 G is the observed chlorine splitting, and 3 takes into account the ratio of the number of p orbitals relative to the s orbital of the same principal quantum number. It follows from eq 10 that $\rho^{0*}{}_{\mathrm{p,Cl}} \cong 0.1$, and then

$$\Delta g = g(\varphi) - g(\varphi_0) \cong \frac{2}{3}\frac{1}{\epsilon^0 - \epsilon_{\mathrm{n_2}}} \xi_{\mathrm{p}}{}^{\mathrm{Cl}}[\rho^0{}_{\mathrm{p,Cl}}(\varphi) - \rho^0{}_{\mathrm{p,Cl}}(\varphi_0)] \quad (5)$$

where $\varphi_0 = 19.45°$ refers to the undistorted configuration.

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(24) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970); D. C. Frost and C. A. McDowell, *Proc. Roy. Soc., Ser. A*, **241**, 194 (1957).