

UNSYMMETRICAL HALOGEN BRIDGING AND RADICAL REARRANGEMENTS:

THE ESR SPECTRA OF β -CHLOROALKYL RADICALS.

by J. Cooper, A. Hudson and R.A. Jackson

School of Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, Sussex, U.K.

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The question of bridging in β -substituted alkyl radicals continues to excite debate.^{1,2} Direct observation of potentially bridged species by e.s.r. is of particular value in providing evidence for or against the bridging hypothesis. Following the successful observation of the 2-chloroethyl radical³, we have used steady-state photolysis to obtain hyperfine coupling constants (table) for several related β -chloroalkyl radicals. In addition a number of radical re-arrangements have been observed which are believed to proceed via halogen bridging

The hyperfine coupling constants for $\dot{\text{C}}\text{H}_2\text{CH}_2\text{Cl}$ are consistent with an unsymmetrically bridged structure in which the chlorine atom eclipses the odd electron orbital; the suggestion³ that there is some distortion from a regular tetrahedral geometry at the β -carbon atom is supported by INDO calculations.⁴ The increase in a_{β}^{Cl} and the decrease in a_{β}^{H} , found on introduction of α -methyl substituents indicates an increased preference for the "bridged" conformation in $\dot{\text{C}}\text{HMeCH}_2\text{Cl}$ and $\dot{\text{C}}\text{Me}_2\text{CH}_2\text{Cl}$. A similar effect is found⁵ on comparing $\dot{\text{C}}\text{H}_2\text{CH}_2\text{F}$ ($a_{\beta}^{\text{H}} = 27.4$, $a^{\text{F}} = 47.8\text{G}$ at -60°) and $\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{F}$ ($a_{\beta}^{\text{H}} = 15.9$, $a^{\text{F}} = 85.3\text{G}$ at -60°). This behaviour is probably due to a combination of electronic and steric interactions. The latter are presumably responsible for the decrease in a_{β}^{Cl} found in $\dot{\text{C}}\text{Me}_2\text{CHMeCl}$ and $\dot{\text{C}}\text{Me}_2\text{CMe}_2\text{Cl}$ as β -methyl substituents are introduced. In contrast substitution by α -chlorine atoms leads to a much more marked decrease in a_{β}^{Cl} than would be expected in terms of spin delocalisation onto the α -chlorine. It would thus appear that the tendency for "bridging" and hence the barrier to internal rotation is reduced in $\dot{\text{C}}\text{HClCMe}_2\text{Cl}$ and $\dot{\text{C}}\text{Cl}_2\text{CH}_2\text{Cl}$. We suggest this behaviour is

connected with the known pyramidal character of α -chloroalkyl radicals⁶. Bending at the radical centre and introduction of σ -character into the odd electron orbital would be expected to reduce both hyperconjugation⁷ and p-p homoconjugation⁸ which are believed to be important in these systems. In contrast to the behaviour of a_{β}^H and a_{β}^{Cl} in the other radicals, the small chlorine splitting of 3.5G in $\text{CH}_2\text{SiMe}_2\text{Cl}$ is temperature independent; there is apparently relatively free internal rotation in the silicon containing radical. This is consistent with the idea that hyperconjugation is important in determining the strong conformational preferences found in the carbon radicals; such a mechanism will be less important for an Si-Cl bond because it is stronger than C-Cl and also because a silicon-carbon double bond is less favoured than a carbon-carbon double bond.

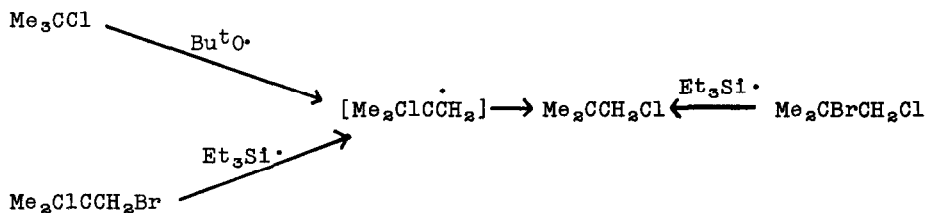
Table.

The hyperfine coupling constants (G) of some β -chloroalkyl radicals.

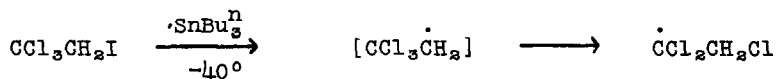
Radical	Temp. °C	a_{α}^H	a_{β}^H	a_{β}^{Cl}	a_{α}^{Me}	a_{α}^{Cl}
$\dot{\text{C}}\text{H}_2\text{CH}_2\text{Cl}$	-60	21.5	11.5	17.4	-	-
$\dot{\text{C}}\text{HMeCH}_2\text{Cl}$	-92	20.9	8.2	19.6	24.1	-
$\dot{\text{C}}\text{Me}_2\text{CH}_2\text{Cl}$	-100	-	6.5	21.4	21.4	-
$\dot{\text{C}}\text{Me}_2\text{CHMeCl}$	-60	-	6.0	19.4	21.3	-
$\dot{\text{C}}\text{Me}_2\text{CMe}_2\text{Cl}$	-50	-	-	17.4	21.1	-
$\dot{\text{C}}\text{HClCMe}_2\text{Cl}$	-60	19.9	-	13.4	-	3.0
$\dot{\text{C}}\text{Cl}_2\text{CH}_2\text{Cl}$	-40	-	10.5	10.5	-	3.5
$\dot{\text{C}}\text{H}_2\text{SiMe}_2\text{Cl}$	-60	21.0	-	3.5	-	$a_{\beta}^{Me} = 0.65$

We have been unsuccessful in attempts to observe $\dot{\text{C}}\text{H}_2\text{CMe}_2\text{Cl}$; even at -120° it rapidly rearranges to a tertiary radical (scheme 1). This type of rearrangement has been proposed previously⁹ to account for the chlorination products of t-butyl halides and to explain an e.s.r. spectrum observed⁷ in the radiolysis of t-butyl chloride. Similarly the radicals $\text{CCl}_2\dot{\text{C}}\text{H}_2$ (scheme 2) and $\text{MeCH}\dot{\text{C}}\text{Me}_2\text{Cl}$ rearranged too rapidly for us to detect their e.s.r. spectra. However $\text{CHClCMe}_2\dot{\text{C}}\text{H}$ shows no tendency to rearrange. The rapidity of these rearrangements implies a low activation energy and appears more consistent with an intramolecular reaction (with a "bridged" transition state) than with an

elimination/addition mechanism.



Scheme 1.



Scheme 2.

The hyperfine coupling constants in the mono- β -chloroalkyl radicals indicate the "bridging" is unsymmetrical with an essentially planar geometry at the radical carbon. The available evidence suggests some deformation at the β -carbon atom; the magnitude of such distortions is not yet established.

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