Electron Spin Resonance Evidence for Greatly Enhanced Hyperconjugation in Radicals Containing Tin, Phosphorus, and Arsenic

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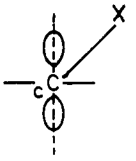
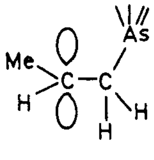
Summary Direct e.s.r. evidence for strong hyperfine interaction with phosphorus, arsenic, or tin atoms β to radical centres is presented, which is linked with the large rate enhancements detected by others when such groups are β to aromatic ring systems; the interaction is shown to be hyperconjugative rather than to involve outer *d* orbitals.

ELECTRON spin resonance spectroscopy has provided important evidence in favour of the concept usually described as hyperconjugation.[1,2] Attention has been primarily directed towards β-proton interaction, although there is good evidence in favour of the involvement of the σ-electrons of β-carbon and β-nitrogen atoms.[1] The extent of the interaction depends strongly upon the angle (θ) between the axis of the half-filled (or vacant, for carbonium ions) p-orbital and the direction of the C–X bond, where X is the β-substituent [see (I)], being a maximum when θ is zero.[3] The measured hyperfine coupling to the β-substituents has two major contributory factors, real delocalisation, and spin-polarisation, only the former being structurally significant. For β-protons held in the ideal position ($\theta = 0$), proton coupling is about 50 G, and probably about half of this arises from delocalisation.[2] This corresponds to a transfer of about 5% spin density. For β-carbon or -nitrogen, the isotropic hyperfine coupling is not a direct measure of spin-density in the σ-bond, but if one assumes sp^3 hybridisation, a rough estimate can be obtained. Commonly, the isotropic coupling corresponds to about 1% spin in the s-orbital of the β-atom.[1] Optimisation of the bond angle would increase this, but allowance must again be made for spin-polarisation. Thus the effects for protons and first-row atoms seem to be comparable.

It was suggested some time ago[4] that if a given β-group had a preferred hyperconjugative interaction, it would be expected to have a preference for the $\theta = 0$ conformation. A hint that this could arise is to be found in e.s.r. results assigned to radical (II),[5] in that the ^{1}H coupling to the β-methylene protons was unusually low. This is diagnostic of a preferred conformation such as to maximise overlap with the C–As σ-bond. Recently liquid-phase e.s.r. data have been described which show that a similar preference obtains for β-silicon groups.[6]



(I)



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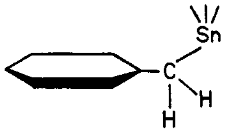

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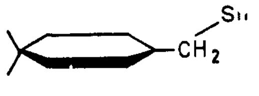

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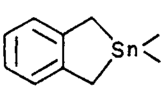

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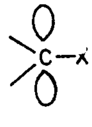

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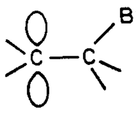


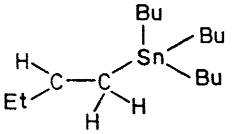
(VII)

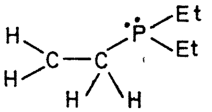
TABLE. *E.s.r. parameters for various alkyl radicals containing* Sn, P, *or* As *in the β position*

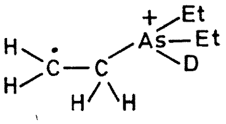
Radical	Hyperfine tensor (in G)[a]			Orbital populations (%)[b]	
	$A_{\parallel}$	$A_{\perp}$	A_{iso}	a_s^2	a_p^2
(A)	A_{av}	(^{117}Sn+^{119}Sn)	*ca.* 420[c]	*ca.* 5·7	
(B)	295	*ca.* 230	*ca.* 251[c,d]	*ca.* 6·9	*ca.* 22
(C)	*ca.* 162[d]			*ca.* 4·7	
(D)	260	221[c,d]	234	6·9	*ca.* 15

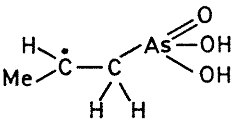
[a] All g-values ~ free spin. [b] Calculated for unit population of Hartree–Fock atomic wave functions of Froese. [c] Radicals with these parameters could not be detected in irradiated methyl derivatives. [d] ^{1}H coupling resolved; $a^{\alpha H} \sim 20\ G\ a^{\beta H} \sim 14$.

By far the most convincing evidence that a marked delocalisation involving the σ-electrons of the β-group is responsible for this preferred conformation comes from the greatly enhanced isotropic coupling to the β-atom (Table). We have confirmed the tentative assignment[5] for n-propanearsonic acid and find that the coupling to ^{75}As is almost, though not quite, isotropic at 77 K. The isotropic coupling can be translated into an approximate s-orbital spin-density (by dividing by the calculated atomic value of 3415 G)[7] of *ca.* 6·9%. The anisotropy is small, but as indirect or through-space contributions are negligible, a rough estimate of the 4p-orbital contribution can also be obtained. The value of *ca.* 15% agrees with the concept that the effect stems from interaction with the σ-electrons linking the β-group to the radical framework. A variety of similar radicals have been prepared containing β-phosphorus, -arsenic, and -tin (Table) and in all cases there is a very large, almost isotropic, interaction with the nucleus of the β-atom.


(A)


(B)


(C)


(D)

This important result should have wide mechanistic repercussions, and indeed some have already been discovered, largely by Traylor and his co-workers.[8] They found that groups such as SnR$_3$, suitably placed in aromatic compounds (III), greatly enhanced the rates of electrophilic substitution, and postulated that intermediates such as (IV) were strongly stabilised by the type of interaction clearly established by our results. Furthermore, when the β-substituent is constrained into the radical plane, as in (V), this rate enhancement was lost. In our view, our results rule out the postulate that $p(\pi)$–$d(\pi)$ interaction is responsible for the observed phenomena.[6] It could be argued that there is a greatly enhanced spin-polarisation occurring for the σ-electrons in the C–X bonds, but when X is α to the radical centre (VI), no such increased polarisation is detected. Indeed, the extent of such polarisation is remarkably constant, giving close to (−) 1% spin-density in the s-orbital of atom X.[9]

Finally, we suggest that the unusual steric requirements of radicals such as (VII) can best be understood in terms of this phenomenon. Preliminary e.s.r. results for such radicals seem to accord well with this suggestion; these results will be reported in full elsewhere.

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