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DIRECTIVE EFFECTS OF SUBSTITUENTS CH_2X IN AROMATIC ELECTROPHILIC SUBSTITUTIONS

M.C.R. Symons
Department of Chemistry, The University, Leicester, LE1 7RH.

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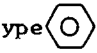
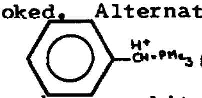
Attention has been called to the unsatisfactory nature of the present theory underlying the rate and *ortho*-*para* directing effects of positively charged groups such as $-PR_3^+$ and $-AsR_3^+$ in compounds of the type $-CH_2-X$, towards electrophilic substitution.[1] Because of their positive charges, these groups are expected to be deactivating and *meta*-directing, as indeed is the case for $X = NMe_3^+$, for example. In fact, they strongly favour *para*-substitution, and the partial rate factors show that they induce a relatively high reactivity in the *para*-position.

It seems[1] that these *para*-directing effects are usually ascribed to the effect of group X upon the extent to which the $-CH_2$ group can undergo hyperconjugative electron release, structures such as  (I) being invoked. Alternatively, contributions from structures such as  (II) involving incipient utilisation of the 3*d* phosphorus orbitals, might help to explain the observed behaviour.[2]

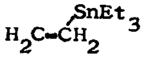
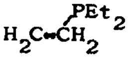
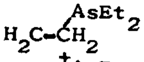
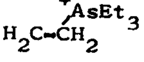
We have found that radicals such as $H_2\dot{C}-CH_2(AsEt_3)^+$ and $H_2\dot{C}-CH_2(SnEt_3)$ have e.s.r. spectra which are characterised by a very large, almost isotropic hyperfine coupling to the heavy-atom nucleus.[3] The magnitude of the β-proton coupling shows that there is a fixed conformation in which the C-X bond is in a plane at right-angles to the radical plane, favouring maximum overlap between the $2p_z$ orbital on carbon and the C-X σ-orbital.[3]

Greek Beta

Greek Sigma

These results link with kinetic studies on $Ar-CH_2-SnR_3$ and related molecules[4] which have been interpreted in terms of hyperconjugative electron release from the C-X σ-bond.[4] I suggest that a similar interaction occurs for $-CH_2PMe_3^+$ and $-CH_2AsMe_3^+$ substituents, *despite their positive charges*, and that this is primarily responsible for the enhanced sensitivity of the *para*-position in $ArCH_2X$ compounds. In the Table I quote calculated isotropic spin-densities;[5] the total delocalisation is generally about three times larger, but the *p*-contribution is difficult to estimate accurately. There is a clear fall on going from $-SnR_3$ to $-AsR_3^+$, but results for the corresponding silicon compounds seem to suggest that on going from $-SiR_3$ to $-PR_3^+$ there is very little change in the extent of the interaction.

TABLE Isotropic Hyperfine Coupling to Group X in Radicals R_2C-CR_2X together with estimated Spin-Densities (Isotropic) on X(a_s^2)

Material	Radical	Hyperfine Coupling to X(G)	^1H Hyperfine Coupling (G)		a_s^2
		A_{iso}	Hα	Hβ	
$SnEt_4$	 $H_2C-CH_2SnEt_3$	409	~20	13	5.6
PEt_3	 $H_2C-CH_2PEt_2$	251	~15		6.9
$AsEt_3$	 $H_2C-CH_2AsEt_2$	230	~15		6.7
$AsEt_4I$	 $H_2C-CH_2\overset{+}{A}sEt_3$	126.7	20	14	3.7

The strongly preferred conformation suggests that a considerable stabilisation is achieved by this mechanism which will, I suspect, outweigh the retarding effect of the charge. $-CH_2Hal$ groups should behave qualitatively in the manner described above. Thus we have found, for chloride, bromide and iodide, in the radicals $R_2\dot{C}-CR_2Hal$ a large isotropic hyperfine interaction to halogen, which increased through the series, and the same strongly preferred orientation.[6] In fact, β-Cl, Br, or I groups do have a marked o,p-directing effect.[1]

Thus it seems likely that hyperconjugation is indeed involved, but not that involving C–H bonds, as in I, because these are thought to be constrained into a position of poor overlap. Rather, the interaction is thought to involve the C–X bonds, as  (III).

The idea that phosphorus 3*d*- or arsenic 4*d*-orbitals are involved is rendered most improbable by the results for radicals of general structure $H_2\dot{C}-PR_3^+$ or $H_2\dot{C}AsR_3^+$. These show virtually no reduction in spin-density on carbon ($\sim$100%) and a ^{31}P or ^{75}As hyperfine interaction equal only to that predicted for spin-polarisation of the C–P or C–As σ-electrons. Thus direct evidence shows that in the ground-state of these radicals such interaction is negligible.

References

1. F. De Sarlo, G. Grynkiewicz, A. Ricci and J.H. Ridd, J. Chem. Soc. (B), 719 (1971).
2. F.L. Riley and E. Rothstein, J. Chem. Soc., 3872 (1964).
3. A.R. Lyons and M.C.R. Symons, Chem. Comm., 1068 (1971).

4. W. Hanstein, H.J. Berwin and T.G. Traylor, *J. Amer. Chem. Soc.*, **92**, 7476 (1970).

5. P.W. Atkins and M.C.R. Symons, The Structure of Inorganic Radicals, Elsevier, Amsterdam, 1967.

6. A.R. Lyons and M.C.R. Symons, *J. Amer. Chem. Soc.*, to be published.