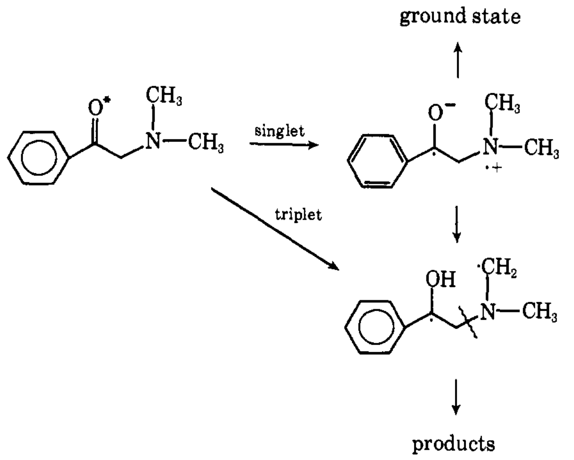


Whatever the exact mechanism, type II photoelimination of α-dialkylamino phenyl, biphenyl, and naphthyl ketones[6] is, for the present,[13] best interpreted as arising from their lowest n,π^* singlets and not from comparably reactive n,π^* or π,π^* triplets.

Acknowledgment. This work was supported by grants from the National Science Foundation and from the Alfred P. Sloan Foundation. We thank Professor Padwa for a preprint and for several discussions.

[13] See P. de Mayo, *Accounts Chem. Res.*, 4, 41 (1971), footnote 10.

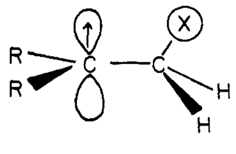
[14] Alfred P. Sloan Fellow, 1968–1972.

Peter J. Wagner,*[14] Thomas Jellinek
Chemistry Department, Michigan State University
East Lansing, Michigan 48823
Received August 14, 1971

Halogen Atom Additions to Olefins. An Electron Spin Resonance Study of the Intermediates

Sir:

Krusic and Kochi[1] have recently shown that radicals of type I, having β substituents (X) such as $-SiR_3$, $-SnR_3$, and $-SR$, exist in a strongly preferred conformation in which the group X sits above the radical plane so that overlap between the p_z orbital of the unpaired electron and the C–X σ bond is a maximum. Independently we have made similar observations, including also β groups $-PR_2$, $-PR_3^+$, $-AsR_2$, and $-AsR_3^+$, and in addition we have shown that there is a remarkably strong hyperfine interaction with the heavy atom (Sn, P, As) which shows that the unpaired electron is considerably delocalized onto group X.[2] Some pertinent results are included in Table I.



I

Table I. Esr Parameters for Radicals of Structure I at 77°K

Group X	System irradiated	Isotropic hyperfine coupling to X, G	Coupling to ^{1}H: α H	Coupling to ^{1}H: β H
$SnEt_3$	$SnEt_4 + \gamma$	409 ($^{117}Sn/^{119}Sn$)	~20	13
$AsEt_3^+$	$AsEt_4I + \gamma$	127 (^{75}As)	20	14
AsO_3H	$n\text{-}PrAsO_3H + \gamma$	232 (^{75}As)	20	11
Cl	$(CD_3)_3CCl + \gamma$	34 (^{35}Cl)^{a,b}	~2.8 (^2H)^c	
Br	$Me_3CBr + \gamma$	280 (^{81}Br)^b	~12.5	
Br	$CH_2{=}CH_2 + Br_2 + uv$	250 ($^{81}Br/^{79}Br$)	Not resolved	
I	$Me_3Cl + \gamma$	~400 (^{127}I)	Not resolved	
I	$CH_2{=}CH_2 + I_2 + uv$	~400 (^{127}I)	Not resolved	

[a] Strongly temperature dependent. [b] Considerable error because there are no well-defined || and ⊥ features. [c] Results for $(CH_3)_3CCl$ uncertain because the main features were hidden by those for $(CH_3)_3\dot{C}$ radicals.

We have now extended these studies to include compounds in which X is Cl, Br, or I and find, again, a very large hyperfine interaction with the halogen nucleus. In all three cases exposure of the *tert*-butyl halide (chosen because of the absence of α protons) to ^{60}Co γ rays at 77°K gave radicals of type I (X = hal), characterized by very large splittings between the components associated with hyperfine coupling to the halogen nuclei. A typical spectrum is given in Figure 1.

Most of the other alkyl halides which we have used, with the notable exception of the methyl compounds, had esr spectra after irradiation, containing evidence for the formation of radicals of type I, although in many instances the lines were partially obscured by stray features from other radicals, such as hal_2^- and $R_2\dot{C}$–hal.

Similar radicals have been prepared by exposing frozen solutions containing ethylene and bromine or iodine to ultraviolet light, as indicated in Table I. In addition to the large, almost isotropic, coupling to halogen, there was evidence on some or all of the main lines of proton hyperfine coupling, although in most cases this was too complex to allow complete analysis. However, as with the compounds of groups IV and V,[1,2] the smaller splitting always seemed to be close to 13 G, which strongly suggests structure I with the same preferred conformation. A β-proton coupling of this magnitude is diagnostic of such a conformation.[1,2]

The isotropic coupling can be used to estimate an approximate spin density in the valence s orbital of the halogen atoms (Table II). (We reject the idea that the outer vacant s orbital is involved to any major extent, because the spin density on halogen would then be near to unity, which is clearly not the case.[3]) The

Table II. Derived Atomic Populations for β Substituents in Radicals of Type I

Group X	Orbital populations, %^{a}: s	p^b	p/s
$SnEt_3$	5.6		
$AsEt_3^+$	3.7	~13	~3.5
AsO_3H	6.7	~14	~2.1
Cl	2.5	~8	~3.2
Br	3.4	~12	~3.5
I	5.5		

[a] Calculated from atomic values based upon the best available wavefunctions [calculated from the data of C. Froese, *J. Chem. Phys.*, **45**, 1417 (1966)]. [b] Based on the maximum anisotropy; very approximate values.

---

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

[2] A. R. Lyons and M. C. R. Symons, *Chem. Commun.*, in press.

[3] K. V. S. Rao and M. C. R. Symons, *ibid.*, 268 (1971).

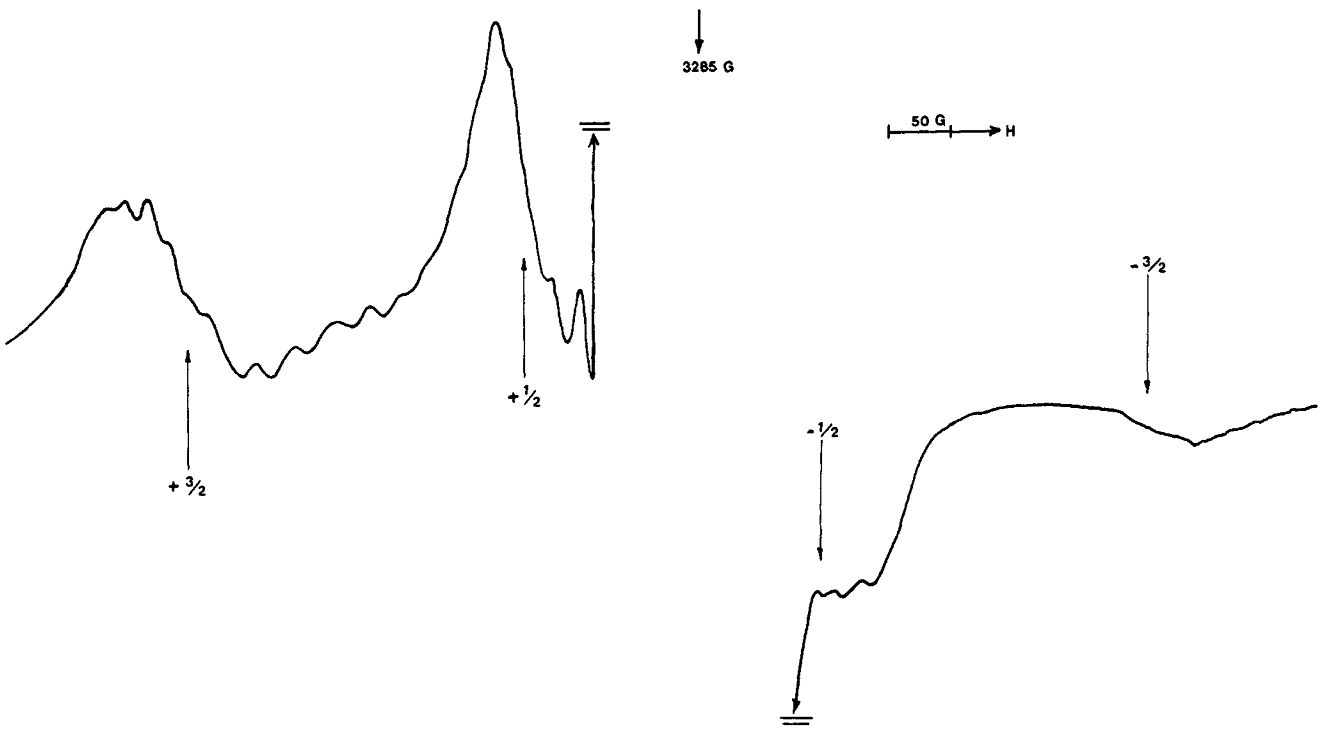


Figure 1. Esr spectrum for *n*-butyl bromide after exposure to γ rays at 77 °K, showing hyperfine features assigned to the radical $CH_3CH_2\dot{C}HCH_2Br$. Central features from other species are omitted for clarity.

anisotropies detected, though small, correspond to about three times as much valence p character, which strongly suggests that it is the C–X σ bonds which are involved in the delocalization mechanism, as is implied by the preferred conformation and required by the theory of hyperconjugation.

The s character on halogen increases steadily from chlorine to iodine. This probably reflects the increasing availability of the valence s orbitals for bonding in this sequence. We stress that hyperfine interaction to β-fluorine atoms, which has received a great deal of recent attention,[4,5] is negligibly small when compared with the present phenomena. Furthermore, it seems most likely that a different mechanism is involved.[4]

The results for the group IV compounds have close links with the very interesting studies of Traylor and his coworkers,[6] who have shown that the electrophilic reactivity of aromatic compounds containing $-CH_2X$ substituents is greatly enhanced, provided that the X group is free to adopt conformations comparable with I. Similarly, our present results shed light upon the problem of the stereochemistry of halogen addition to olefins. Clearly, if structure I is strongly favored energetically, further addition is likely to be trans to the group X.

The results for *tert*-butyl bromide, whose spectra were relatively well resolved, rule out the anticipated structure $H_2\dot{C}C(Me)_2Br$, which would only be expected to have two strongly interacting protons. The structure is probably $Me_2\dot{C}CH_2Br$, with eight almost equivalent protons, but, if this is the case, the methyl proton coupling is smaller than usual. This could be taken to indicate a more symmetrical bridged structure.[7]

The best results for the chloro compounds were obtained with $(CD_3)_3CCl$ (Table I). Again, the number of lines obtained on each main feature (≥ 13) requires us to postulate a 1,2 migration of the chlorine atom.[8]

---

(4) M. Iwasaki, *Mol. Phys.*, 20, 503 (1971).

(5) G. R. Underwood, V. L. Vogel, and I. Krefting, *J. Amer. Chem. Soc.*, **92**, 5019 (1970).

(6) W. Hanstein, H. J. Berwin, and T. G. Traylor, *ibid.*, **92**, 7476 (1970).

(7) It seems probable that the unidentified species in irradiated butyl bromide mentioned by M. L. Bonin, M. A. Bonin, and F. Williams [*J. Chem. Phys.*, 54, 2641 (1971)] is the radical $CH_3CH_2\dot{C}HCH_2Br$.

(8) A referee has drawn our attention to recent work of A. J. Bowles, A. Hudson, and R. A. Jackson [*Chem. Phys. Lett.*, **5**, 552 (1970)] who detected the radical H_2CCH_2Cl in fluid solution. Their results show clearly that the structure is asymmetric and that the chlorine atom is locked in the position indicated in I. Their isotropic coupling to ^{35}Cl (17.4 G) is, however, considerably smaller than ours for the $(CD_3)_2\dot{C}CD_2Cl$ radical. This difference arises partly because the coupling is strongly temperature dependent, decreasing on warming above 77 °K, and possibly because there is a large error in our measurement which arises because the tensor components in the solid-state spectra overlap considerably.

A. R. Lyons, M. C. R. Symons*

Department of Chemistry, The University
Leicester, LE1 7RH, England

Received September 20, 1971

Thallium in Organic Synthesis. XXVIII. Selective Oxidation of Acetylenes to Carboxylic Acids, Acyloins, Benzils, and Arylacetic Acids with Thallium(III) Nitrate[1,2]

Sir:

Although one of the classic reactions of acetylene chemistry is mercury(II) salt catalyzed hydration of the C≡C bond, there is only one report on the analogous reaction of acetylenes with isoelectronic thallium(III) salts.[3] In view of the marked differences in the reac-

---

(1) Part XXVII: A. McKillop, B. P. Swann, and E. C. Taylor, *J. Amer. Chem. Soc.*, **93**, 4919 (1971).

(2) We gratefully acknowledge partial financial support of this work by Eli Lilly and Co., Indianapolis, Ind.

(3) S. Uemura, R. Kitoh, K. Fujita, and K. Ichikawa, *Bull. Chem. Soc. Jap.*, **40**, 1499 (1967).