Journal of Organometallic Chemistry, 182 (1979) 333—344

ADDUCTS OF SILYL, GERMYL AND STANNYL RADICALS WITH HETEROCYCLIC α-DIKETONES: AN ELECTRON SPIN RESONANCE INVESTIGATION

ANGELO ALBERTI *, GIORGO MARTELLI,

Laboratorio dei Composti del Carbonio Contenenti Eteroatomi, C.N.R., Via Tolara di Sotto 89, 40064 Ozzano Emilia (Bo) (Italy)

ANDREW HUDSON *,

School of Molecular Sciences, University of Sussex, Brighton, BN1 9QJ (Great Britain)

GIAN FRANCO PEDULLI *

Istituto Chimico dell'Università, Via Ospedale 72, 09100 Cagliari (Italy)

MARCELLO TIECCO,

Istituto di Chimica, Facoltà di Farmacia, Via del Liceo, 06100 Perugia (Italy)

and FRANCESCO CIMINALE

Istituto di Chimica Organica dell'Università, Viale Amendola 173, 70126 Bari (Italy)

(Received June 8th, 1979)

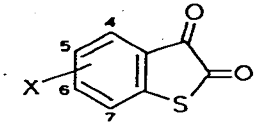
Summary

Hyperfine coupling constants are reported for adducts of silyl, germyl and stannyl radicals with a series of substituted benzo[*b*]thiophen-2,3-diones (Ia—Ip), benzo[*b*]furan-2,3-dione (II), ninhydrin (III), and thieno[3,2-*b*]thiophen-2,3-dione (IV). The conformational and electronic properties of these radicals are compared with those of similar adducts formed by diaryl ketones.

Photolytically or thermally produced Group IVB metal-centred radicals add to the carbon—oxygen double bond of ketones to give paramagnetic adducts of general formula $R'RC^{\cdot}OMR_3$ (M = Si, Ge, Sn) [1]. Addition to α-diketones occurs even more readily giving relatively persistent radicals [1b,2], which can be characterised by e.s.r. spectroscopy.

With ketones as substrates, the e.s.r. spectra of the adducts establish that [3]: (i) the hyperfine splitting constants of the metals indicate that the organometallic groups sit above the plane of the sp^2 hybrids centred on the carbonyl carbon; (ii) the spin-density distribution in the substrate moiety is hardly affected by the nature of the metal atom of the entering group.

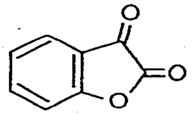
Since with α-diketones both the conformational preference and the electronic effects of the organometallic groups seemed to be remarkably different from those of the similar adducts of ketones, we undertook an e.s.r. investigation using as substrates the diones (I)—(IV), with the aim of gaining a better insight into the structure and electronic properties of their adducts with $R_3M^\bullet$ radicals.



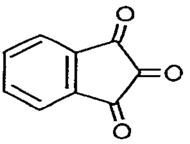
(I)

(Ia); X = H
(Ib); X = 5-Me
(Ic); X = 7-Me
(Id); X = 5-F
(Ie); X = 6-F
(If); X = 7-F
(Ig); X = 5-Cl
(Ih); X = 6-Cl
(Ii); X = 7-Cl
(Ij); X = 5-Br
(Il); X = 6-Br
(Im); X = 7-Br
(In); X = 5-I
(Io); X = 6-I
(Ip); X = 7-I

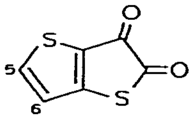
We also report, for comparison, experimental data for the hydrogen adducts and radical anions of (I)—(IV) and for the alkali-metal ion-pairs of (Ia).



(II)



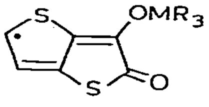
(III)



(IV)

Results and discussion

The hyperfine splitting constants of the adducts and of the radical anions from I—IV are reported in Tables 1, 2 and 3. The assignment to the various positions in the case of benzo[*b*]thiophen-2,3-dione (Ia) was made by comparison with the data for the substituted derivatives Ib—Ip, and in the radicals from benzo[*b*]furan-2,3-dione (II) by analogy with Ia. With ninhydrin (III) the non-equivalence of the couplings at the 5 and 6 protons indicate that addition of the organometallic radical occurs at either of the 1 or 3 carbonyl groups and therefore the assignment parallels that given for Ia. The larger splitting in the adducts of thieno[3,2-*b*]thiophen-2,3-dione (IV), has been assigned to proton 5 on the basis of structure A.



(A)

TABLE 1

HYPERFINE SPLITTING CONSTANTS (G) FOR THE RADICAL ADDUCTS FROM Ia—Ip

Compound	Solvent	MR_3	a_4	a_5	a_6	a_7	a_M	g
Ia	$HSiPH_3$	$SiPh_3$	3.92	1.27	4.67	1.35	—	2.0039
	$HSiEt_3$	$SiEt_3$	3.79	1.26	4.40	1.36	—	
	$HGePh_3$	$GePh_3$	3.70	1.20	4.30	1.30	—	2.0040
	$HSnPh_3$	$SnPh_3$	3.33	1.10	3.81	1.10	1.08	2.0038
	Sn_2Me_6	$SnMe_3$	3.45	1.10	3.93	1.20	1.59	
	[a]	H	3.50	1.16	4.21	1.20	1.16	
	Toluene [b]	H	3.86	1.23	4.47	1.32	1.76	2.0039
Ib	$HSiPh_3$	$SiPh_3$	3.80	1.19 [c]	4.70	1.40	—	
	$HGePh_3$	$GePh_3$	3.60	1.15 [c]	4.32	1.30	—	
	[a]	H	3.57	1.14 [c]	4.25	1.27	1.15	
Ic	$HSiPh_3$	$SiPh_3$	3.90	1.27	4.55	1.33 [c]	—	
	$HGePh_3$	$GePh_3$	3.63	1.22	4.24	1.27 [c]	—	
	$HSnPh_3$	$SnPh_3$	3.45	1.10	3.76	1.14 [c]	1.35	
	[a]	H	3.60	1.20	4.22	1.25 [c]	1.17	
	$HSiPh_3$	H	3.82	1.25	4.38	1.30 [c]	1.70	
Id	$HSiPh_3$	$SiPh_3$	3.69	3.35 [d]	4.66	1.40	—	
	$HGePh_3$	$GePh_3$	3.55	3.22 [d]	4.32	1.32	—	
	$HSnPh_3$	$SnPh_3$	3.32	3.03 [d]	3.86	1.19	1.25	
	[a]	H	3.53	3.19 [d]	4.21	1.29	0.98	
	$HSiPh_3$	H	3.70	3.42 [d]	4.57	1.40	1.40	
Ie	$HSiPh_3$	$SiPh_3$	3.96	1.16	11.46 [d]	1.32	—	
	$HGePh_3$	$GePh_3$	3.73	1.11	10.44 [d]	1.24	—	
	$HSnPh_3$	$SnPh_3$	3.33	1.05	9.08 [d]	1.05	n.r.	
	[a]	H	3.75	1.20	10.08 [d]	1.20	0.89	
	$HSiPh_3$	H	3.91	1.14	11.16 [d]	1.30	1.48	
If	$HSiPh_3$	$SiPH_3$	3.98	1.33	4.59	3.98 [d]	—	
	$HGePh_3$	$GePh_3$	3.78	1.24	4.30	3.78 [d]	—	
	$HSnPh_3$	$SnPh_3$	3.35	1.05	3.75	3.35 [d]	1.40	
	[a]	H	3.66	1.19	4.14	3.66 [d]	1.19	
	Toluene [b]	H	3.91	1.30	4.42	3.91 [d]	1.75	
Ig	$HSiPh_3$	$SiPh_3$	3.81	0.16 [e]	4.64	1.38	—	
	$HGePh_3$	$GePh_3$	3.63	0.15 [e]	4.29	1.29	—	
	$HSnPh_3$	$SnPh_3$	3.35	<0.15 [e]	3.83	1.15	1.59	
	[a]	H	3.65	~0.1 [e]	4.30	1.17	1.17	
Ih	$HSiPh_3$	$SiPh_3$	3.92	1.32	0.59—0.42 [e]	1.40	—	
	$HGePh_3$	$GePh_3$	3.73	1.30	0.44 [e]	1.30	—	
	[a]	H	3.70	1.25	0.40	1.25	0.85	
Ii	$HSiPh_3$	$SiPh_3$	3.95	1.31	4.60	0.18 [e]	—	
	$HGePh_3$	$GePh_3$	3.73	1.24	4.26	0.17 [e]	—	
	$HSnPh_3$	$SnPh_3$	3.33	1.05	3.72	<0.1 [e]	1.45	
	[a]	H	3.62	1.21	4.15	0.19 [e]	0.88	
Ij	$HGePh_3$	$GePh_3$	3.66	—	4.30	1.27	—	
Il	$HGePh_3$	$GePh_3$	3.65	1.20	—	1.30	—	
	$HGePh_3$	H	3.83	1.35	—	1.35	1.47	
Im	$HGePh_3$	$GePh_3$	3.68	1.20	4.23	—	—	
In	$HGePh_3$	$GePh_3$	3.71	—	4.34	1.29	—	
Io	$HGePh_3$	$GePh_3$	3.66	1.24	—	1.24	—	
Ip	$HGePh_3$	$GePh_3$	3.71	1.20	4.26	—	—	

[a] 1/1(v/v) mixture of *i*-propanol and HMPTA. [b] Toluene + 2,6-di-t-butylphenol. [c] Splitting from three equivalent hydrogen atoms. [d] Splitting from one fluorine atom. [e] Splitting from one chlorine atom.

TABLE 2

HYPERFINE SPLITTING CONSTANTS (G) FOR THE RADICAL ADDUCTS FROM II—IV

Compound	Solvent	MR_3	a_4	a_5	a_6	a_7	a_M
II	$HSiPh_3$	$SiPh_3$	4.17	1.27	5.05	1.47	—
	$HGePh_3$	$GePh_3$	3.99	1.22	4.72	1.34	—
	Sn_2But_6	$SnBut_3$	3.92	1.23	4.49	1.23	3.33
	[a]	H	4.09	1.26	4.74	1.36	0.81
III	[b]	$SiPh_3$	3.89	1.09	4.44	1.22	—
	[b]	$GePh_3$	3.65	1.09	4.08	1.09	—
IV	$HSiPh_3$	$SiPh_3$		6.34	1.39		—
	$HGePh_3$	$GePh_3$		5.95	1.32		—
	$HSnPh_3$	$SnPh_3$		5.26	1.15		0.25
	[a]	H		6.03	1.30		1.01

[a] 1/1(v/v) mixture of *i*-propanol and HMPTA. [b] 1/1(v/v) mixture of benzene and DTBP containing some $HSiPh_3$ ($HGePh_3$).

Information on the structure of the radical adducts is provided by the hyperfine splittings of the aromatic protons. These constants, as shown in the Tables, are always larger than in the corresponding radical anions. A similar behaviour was also found in the related radicals from diaryl ketones [1d,3] and can be

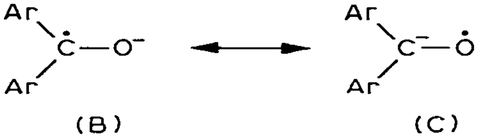
TABLE 3

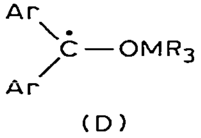
HYPERFINE SPLITTING CONSTANTS (G) FOR THE RADICAL ANIONS FROM Ia, Ib, Ic, If, Ig, Ii, II AND III, AND FOR THE RADICAL ION PAIRS FROM Ia, III AND IV

Compound	Solvent	Counterion	a_4	a_5	a_6	a_7	$a_{count.}$
Ia	DMSO [a]	free ion	2.43	0.70	2.86	0.82	—
	[c]	free ion	2.71	0.85	3.07	0.94	—
	DME	Li	2.53	0.75	2.95	0.87	0.44
	DME	Na	2.45	0.74	2.85	0.86	0.50
	DME	K	2.47	0.74	2.87	0.86	—
Ib	DMSO	free ion	2.41	0.73 [d]	2.74	0.82	—
	[c]	free ion	2.70	0.82 [d]	3.03	0.96	—
Ic	DMSO	free ion	2.30	0.70	2.69	0.83 [d]	—
	[c]	free ion	2.56	0.80	2.91	0.93 [d]	—
If	DMSO	free ion	2.40	0.68	2.76	2.31 [e]	—
Ig	DMSO	free ion	2.54	~0.1 [f]	2.91	0.82	—
Ii	DMSO	free ion	2.36	0.68	2.87	0.13 [f]	—
Il	DMSO [a]	free ion	3.04	0.91	3.44	0.91	—
III	DMSO	free ion	0.93	1.02	1.02	0.93	—
	[b]	$SnBut_3$	0.45	0.81	0.81	0.45	1.75
IV	Sn_2Me_6	$SnMe_3$		3.88	0.93		1.05
	Sn_2Bu_6	$SnBu_3$		3.80	0.91		1.45

[a] See ref. 4. [b] 1/1(v/v) mixture of benzene and DTBP containing some Sn_2But_6. [c] a 1/1/1 mixture of DME, MeOH and MeO^-Na^+. [d] Splitting from three equivalent hydrogen atoms. [e] Splitting from one fluorine atom. [f] Splitting from one chlorine atom.

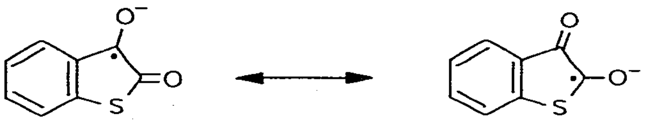
explained in terms of the resonance structures which can be written for the anions (B and C) for the adducts D.


(B) (C)


(D)

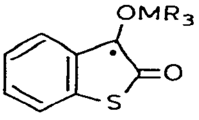
On this basis smaller couplings to the nuclei of the aryl rings attached to the carbonyl carbon are expected for the anions where the structure in which the unpaired electron is delocalized onto the oxygen atom (C) contributes considerably to the mesomeric system. Preferential stabilization of structure B, and therefore increase of spin density on Ar, occurs in the ion pairs because of the complexation of the alkali cation by the oxygen atom or in protic solvents, such as MeOH, because of hydrogen bonding to the carbonyl group. In the organometallic or hydrogen adducts of ketones only structure D contributes to the mesomeric system if resonance forms involving charge separation are neglected, thus accounting for the larger hyperfine splittings from the aryl ring protons.

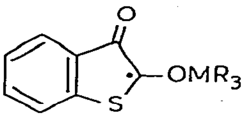
With the radicals from α-diones I—IV, besides the above mentioned effect, there is a second reason why the adducts show larger proton splittings than the related radical anions. In the anions the negative charge can be formally located on either of the two carbonyl oxygens (see structures B and F), the two situations are characterized by very different spin density distributions.


(E) (F)

In fact, a number of mesomeric structures in which the unpaired electron is delocalized into the condensed ring can be written starting from E, while in F the unpaired electron is essentially confined to the two carbonyl groups. In the anions the resulting spin density distribution will then be a weighted average of these two limiting cases, one with high and the other with low spin density in the aromatic ring. On the other hand in the adducts from the same α-diketones, the addition of the MR_3 group amy take place at either of the two oxygen atoms giving rise to two different isomers. These are expected to show large or small proton splittings depending on whether radical attack occurs at the carbonyl group in position 3 or 2 respectively.

Since we always detected only one isomer, the much higher values of the proton splittings for the adducts can be accounted for if the stable isomer is the one in which the entering group is bonded to the carbonyl oxygen adjacent to the aromatic ring (G).


(G)


(H)

The stability of isomer G can be accounted for in terms of resonance stabilization resulting from the larger extension of its mesomeric system.

The detection of only one e.s.r. spectrum for the adducts from I—IV could be alternatively explained by assuming that both isomers are present, but that the migration rate of the entering group from one carbonyl to the other is fast enough, in the e.s.r. time scale, to produce averaging of the spectra of G and H. Such a process has been actually detected in the organometallic adducts of some symmetric α-diketones like benzil [6], acenaphthaquinone (1c) and benzo(2,1-*b*;3,4-*b*′)dithiophen-4,5-dione [7] for which both the slow and fast exchange limits are accessible. However, the related activation energies are so large that complete averaging occurs, at least for the silyl derivatives, only at elevated temperatures ($T > 200°$C), Since in the present case, even by lowering the temperature to below —50° C, no spectral variations were detected, the latter interpretation can be rejected and we may be reasonably confident that the observed spectrum belongs to isomer G.

The magnitude and the temperature dependence of the hyperfine splitting at the metal atom may also provide useful information on the conformational preference of the entering group. With alkali ion pairs the transmission of spin density from the π-MO containing the unpaired electron the valence orbitals of the cation may occur through direct electron transfer [8] or via indirect spin polarization due to σ—π exchange [9]. The first mechanism operates only when the cation is out of the molecular plane and gives rise to a positive metal coupling. The second mechanism, on the other hand, is particularly effective when the cation is in the molecular plane and gives negative splitting constants. The relative location of the alkali metal with respect to the organic substrate may then be established in the ion-pairs from a knowledge of the sign of the hyperfine splitting at the cation.

A way of determining this sign is to measure its temperature dependence. It seems to be generally accepted that the temperature coefficient $\mathrm{d}a_M/\mathrm{d}T$ is always positive [10] since at higher temperature the increased out of plane vibrations of the alkali counterion make the direct mechanism of spin transfer more effective. Therefore a_M will be positive or negative depending on whether its magnitude $|a_M|$, which is actually measured in the e.s.r. experiment, increases or decreases with increasing temperature.

Similar considerations apply also to the hydroxy proton splitting in the hydrogen adducts. As far as the organometallic adducts are concerned, we were able to measure only the coupling at tin. In this case the transmission of spin density to the metal atom may be more complex than with alkali cations if there is some degree of π-bonding between the organic moiety and the organometallic group. However, the similarity of the tin splittings in the adducts and in the ion-pair of IV seems to indicate that π-interactions are small and we assume that direct transfer and spin polarization are still the more important mechanisms.

The temperature dependence of the Li, Na, H and Sn splittings measured in the various radicals from Ia are plotted in Figure 2. In all other cases, although no accurate measurements have been made, the observed trends of a_M against T are practically the same as for Ia, thus suggesting that the preferred position of the metal or hydrogen atom is scarcely dependent on the nature of the

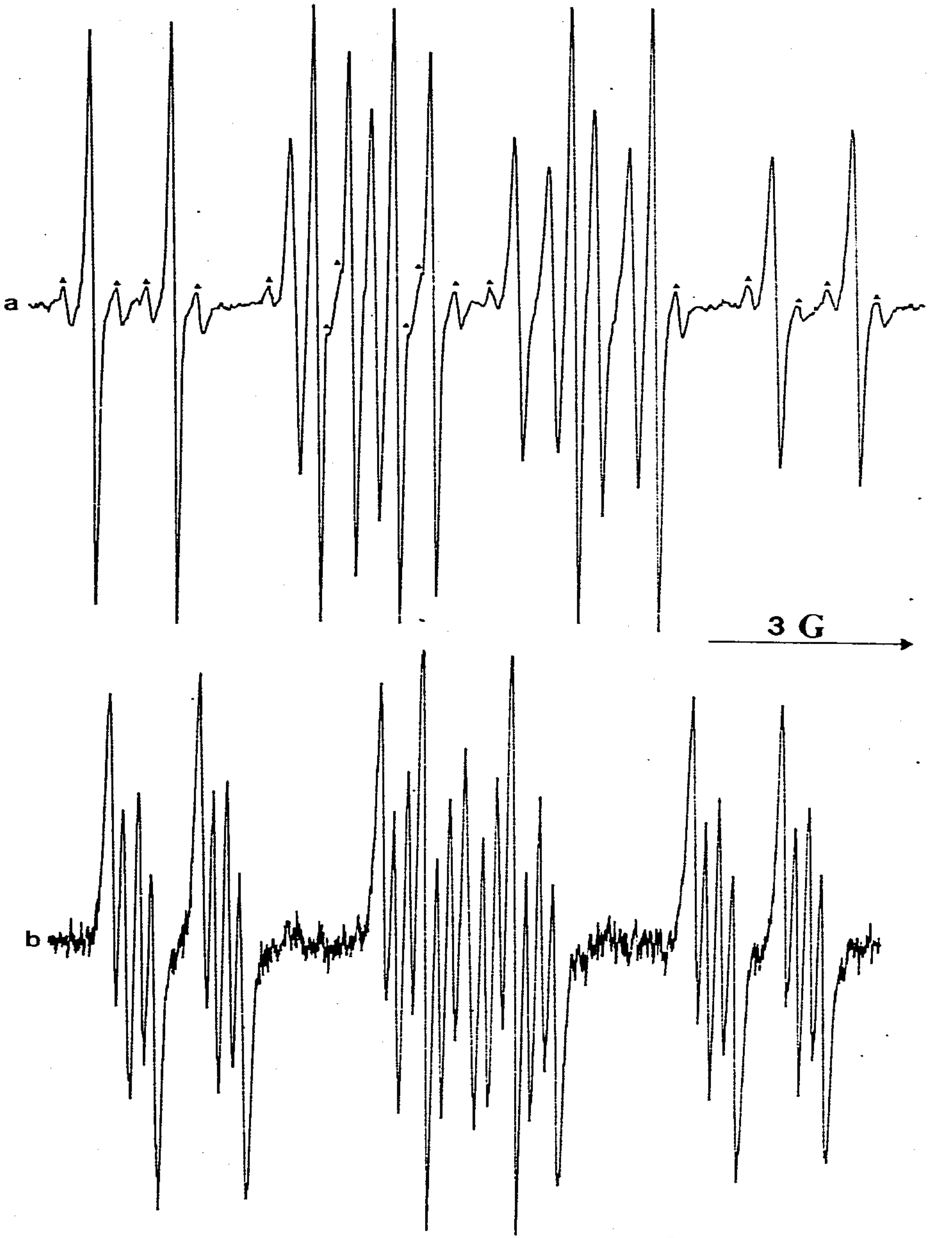


Fig. 1. (a) E.s.r. spectrum of the triphenyltin adduct of Id at 80° C. The larger width of some of the lines is due to presence of the fluorine atom in position 5. Some of the tin satellites (average of the ^{117}Sn and ^{119}Sn isotopes) are clearly visible (▲). (b) E.s.r. spectrum of the triphenylsilyl adduct of Ii at 80° C. The smaller quartet splitting is due to ^{35}Cl and ^{37}Cl.

organic moiety. With the potassium ion pair no alkali coupling was observed. Figure 2 shows that in every case the hyperfine splittings decrease on raising the temperature, the temperature coefficient being larger for H and Sn than for the alkali cations. On the basis of our previous considerations, we may infer that these constants are all negative and, therefore, that both ion-pairs and

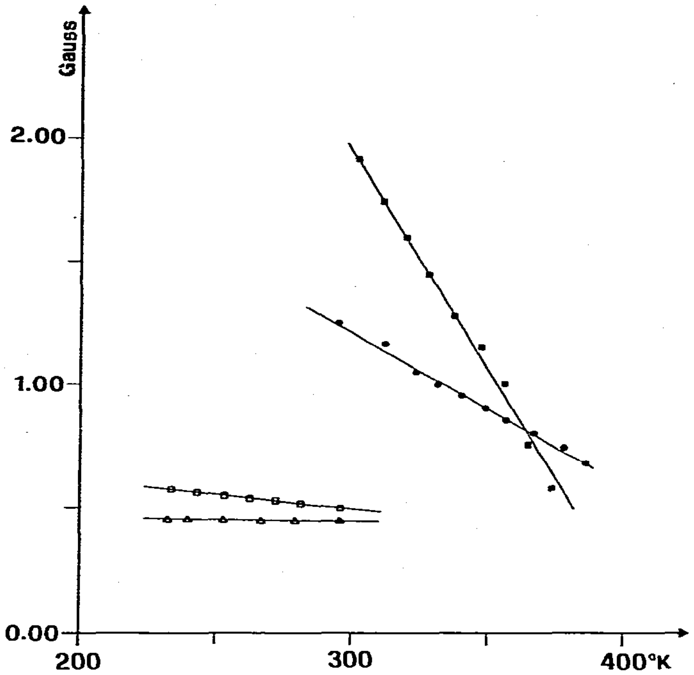


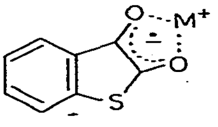
Fig. 2. Temperature dependence of a_{Na} (□) and a_{Li} (△) in the alkali ion pairs from Ia, and a_H (●) and a_{Sn} (■) in the hydroxyl and triphenyltin adducts to the same compound.

adducts adopt a conformation with the metal in the plane of the organic molecule.

With silicon and germanium no metal satellites were observed despite the good quality of the e.s.r. spectra, suggesting that the ^{29}Si and ^{73}Ge splittings are negligibly small in this case, in contrast to the values of ca. 6—7 G and ca. 4—5 G respectively, measured in the non-planar adducts of ketones [3]. This implies that in the silyl and germyl derivatives the metal atom is also coplanar with the organic molecule.

The different conformational preference of the adducts of diones and ketones is also indicated by the values of the *g*-factors which are practically independent of the nature of the entering group in the former derivatives while they show significant variations in the latter ones as a consequence of delocalization of the unpaired electron into metal orbitals (σ—π hyperconjugation or *p*—*d* homoconjugation [3,11].

Planarity is not unexpected for the alkali ion-pairs, as it is known that with dione systems chelated complexes are usually obtained [12,13]. We thus propose structure K for these species.

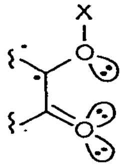


M = Li, Na, K

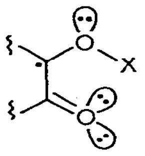
(K)

Consistent with this interpretation, are the observations that $a_{Li} = a_{Na}$ and $a_K = 0$, and that the lithium and sodium splittings are scarcely temperature dependent [13].

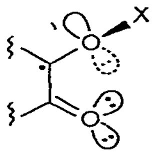
For the hydroxyl radicals, planarity is also predictable by analogy with results for the related adducts with ketones. However, with the diketones the proton may be located on the same or on the opposite side of the second oxygen atom.



(L)



(M)



(N)

X = H, MR$_3$

We believe that the first hypothesis is more likely for the following reasons: (i) conformation M should be stabilized by intramolecular hydrogen bonding; (ii) conformation L should be destabilized by the σ nonbonded interaction between the hybrid in-plane oxygen lone pairs [14].

Preferential stabilization of the planar conformation in the organometallic adducts of diones is, on the other hand, peculiar for these systems since in the same radicals from ketones the MR$_3$ group sits above the molecular plane with the O—M bond eclipsing the $2p_z$ orbital of the adjacent carbon atom. Destabilization of the orthogonal conformation N may, in this case, result from the σ nonbonded interaction between the $2p$ and hybrid lone-pairs of the oxygen atoms, and from some kind of bonding interaction between the metal and the second oxygen (structure M). The latter interaction is presumably of some importance in the tin adducts, since this metal may give pentacoordinated complexes [2]. Conformation L should be characterized by higher energy for the same reasons as discussed in the case of the hydroxyl radicals.

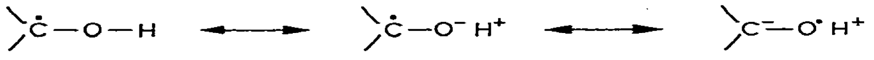
Effect of the entering groups and of the substituents on the spin density distribution

An examination of Tables 1 and 2 shows that the proton hyperfine splittings of the radical adducts decrease following the order

$SiR_3 > GeR_3 > SnR_3$

A reduction of spin density in the condensed ring denotes a greater ability of the entering group to release electrons. Actually the limiting case of complete electron transfer to the organic substrate is represented by the radical anions of I—IV where the smaller hyperfine couplings are observed. The increasing electron-releasing power on going from Si to Ge and Sn is consistent with the greater metallic character of Group IVB elements on descending the Periodic Table. The strong tendency of stannyl radicals to take part in electron-transfer is further demonstrated by the formation of radical ion-pairs in the reaction of Sn$^\bullet$Bu$^t_3$ with III. It is worth pointing out that the spin density variations as a function of the entering group are much larger than in the non-planar adducts of diarylketones where σ—π conjugation between the metal—oxygen bond and the π system may occur.

For most of the derivatives the Tables give also data for the hydrogen adducts measured in a 1/1 mixture of i-propanol and HMPTA; good quality e.s.r. spectra are easily obtained in this solvent. Under these conditions the condensed ring splittings seem to suggest that in the above sequence the hydrogen atom is located between the germyl and stannyl groups. It is however the polar nature of the solvent employed together with the acidic character of the OH proton which leads to the misleading conclusion that the silyl and, to a lesser extent, the germyl groups behave as electron-acceptors with respect to hydrogen. Polar solvents can stabilize resonance structures involving charge separation such as P and Q, thus inducing a decrease in spin density at the condensed ring atoms.



(O) (P) (Q)

In order to overcome this effect we generated the adducts of Ia and of some of its substituted derivatives by photolysis in the apolar solvent toluene containing a small amount of 2,6-di-t-butylphenol [15]. The corresponding data, together with those obtained by photolyzing some of the compounds in $HSiPh_3$, show that the condensed ring splittings in the hydroxyl radicals are intermediate between those of the $SiPh_3$ and $SiEt_3$ adducts. We therefore deduce that the electron releasing or accepting character of SiR_3 groups is very small and mainly determined by the nature of the R substituent.

Substitution of oxygen (II) or of a carbonyl group (III) for sulphur in I has the effect of respectively increasing and decreasing the proton hyperfine splittings. As far as II is concerned, this behaviour is in line with the results for other radicals from heteroaromatic compounds containing sulphur or oxygen atoms and is usually explained in terms of the greater electronegativity of the latter [16]. With ninhydrin III the presence of an additional carbonyl group increases the extension of the conjugative system and some reduction of the coupling constants in the condensed ring is to be expected.

Halogen substitution of the ring protons, on the other hand, has little effect on the spin density distribution, the most significant change being observed with fluorine. Carbon spin density, ρ_c, deduced from proton splittings can therefore be used to discuss halogen coupling in the same positions. The ratio a_{Hal}/a_H can then be used to check whether the empirical relationship (1) can give a useful prediction of the halogen splitting.

$$a_{Hal} = Q_{eff}^{Hal}\,\rho_c^{\pi} \qquad (1)$$

Three series of radical adducts were studied with halogen substituents in the 5, 6 or 7 positions. These positions are predicted by McLachlan calculations to bear negative, positive and negative spin density, respectively. With bromine and iodine derivatives the coupling to the halogens was never resolved. Since the spectral lines were broader than in the other adducts this can be attributed to the strong quadrupolar relaxation of these nuclei [17]. However, fluorine and chlorine splittings could be measured in almost every case and the values of a_{Hal}/a_H determined. For a given ring position this ratio is reasonably constant for the three series of substituted compounds but there is a significant difference from one position to another. The averaged ratios a_F/a_H are 2.69 ± 0.06, 2.41 ± 0.03 and 2.95 ± 0.09 for the 5, 6 and 7 substituted derivatives, while for chlorine a_{Cl}/a_H is 0.12 ± 0.02, 0.10 ± 0.01 and 0.14 ± 0.02 respectively. If we assume $Q^H = -25$ G, Q^F_{eff} is calculated to be 67, 60 and 74 G. Equation 1 therefore has only a rough predictive value. This is not entirely unexpected since previous work [18,19] has established that a_F is dependent on both ρ_F and ρ_C; eq. 1 will only be valid of ρ_F/ρ_C is constant for different positions. Data on chlorine containing radicals is more limited. The present results indicate that similar considerations apply to chlorine hyperfine splittings.

Experimental

Compounds (Ia), [4] (II), [4] (Ib—Ip) [5] were prepared as described elsewhere, while ninhydrin (III), hexamethylphosphotriamide (HMPTA), 2,6-di-t-butylphenol, triphenylsilane, triphenylgermane, triphenylstannane, hexamethylditin and hexa-n-butylditin were commercial products.

The radical adducts were produced by photolysis of a melt of the appropriate dione and organometallic reagent. Details are given in previous papers [1c,3]. Hydrogen abstraction from the silicon or germanium hydride by the $^3n,\pi$ excited state of the dione has been proposed as the initiating step of the reaction. This is in agreement with the fact that in the photo-reaction with some of the examined compounds, besides the expected addition products, substantial amounts of the corresponding hydrogen adducts were detected, mainly at lower temperature.

Irradiation of solutions of (III) or (IV) in Sn_2Me_6 or Sn_2Bu_6, instead of leading to the expected radical adducts, gave e.s.r. spectra which are probably best thought of as due to radical ion-pairs with the trialkyltin cation acting as the positive counterion.

Irradiation of melts or of di-t-butylperoxide (DTBP) solutions of the bromine or iodine substituted derivatives of (I) afforded the radical adducts of benzo[*b*]thiophen-2,3-dione (Ia) as the result of photolytic cleavage of the carbon—halogen bond. However by simply heating a molten mixture of the halogenated diones with Ph_3GeH the corresponding radical adducts could be obtained. Although the e.s.r. spectra of these derivatives show no resolvable coupling to Br or I, the large linewidths and the values of the proton splittings are consistent with the structures of the starting products.

The e.s.r. spectra were recorded on a Varian E-104 spectrometer equipped with standard variable temperature accessories. Temperatures were measured by means of a copper-constantan thermocouple placed inside the sample tube.

The g-factors for the organometallic and hydrogen adducts of (Ia), reported in Table 1, were measured using a solid sample of DPPH ($g = 2.0037$) as a standard.

Acknowledgement

Two of us (A.A. and A.H.) are grateful to the North Atlantic Treaty Organisation for the award of a collaborative research grant.

References

1 (a) A.R. McIntosh and J.K.S. Wan, Mol. Phys., 22 (1971) 183; (b) J. Cooper, A. Hudson and R.A. Jackson, J. Chem. Soc. Perkin II, (1973) 1933; (c) A. Alberti and A. Hudson, J. Chem. Soc. Perkin II, (1978) 1098; (d) A. Alberti and A. Hudson, J. Organometal. Chem., 164 (1979) 219; (e) W.P. Neumann, B. Schroeder and M. Ziebarth, Justus Liebigs Ann. Chem., (1975) 2279; (f) H. Hillgartner, B. Schroeder and W.P. Neumann, J. Organometal. Chem., 42 (1972) C83.
2 B. Schroeder, W.P. Neumann and H. Hillgartner, Chem. Ber., 107 (1974) 3494.
3 A. Alberti, M. Guerra and G.F. Pedulli, J. Chem. Soc. Perkin II, in press.
4 G.A. Russell, C.L. Myers, P. Bruni, F.A. Neugebauer and R. Blankespoor, J. Amer. Chem. Soc., 92 (1970) 2762.
5 (a) F. Ciminale, G. Bruno, L. Testaferri, C. Martelli and M. Tiecco, J. Org. Chem., in press; (b) F. Ciminale and M. Tiecco, to be published.
6 A. Alberti and A. Hudson, Chem. Phys. Lett., 48 (1977) 331.
7 A. Alberti, A. Hudson and G.F. Pedulli, to be published.
8 S. Aono and K. Oohashi, Progr. Theor. Phys., 30 (1963) 162.
9 M.C.R. Symons, Nature, 224 (1969) 685.
10 E. de Boer, Rec. Trav. Chim. Pays-Bas, 84 (1965) 609; S.A. Al-Baldawi and T.E. Gough, Can. J. Chem., 48 (1970) 2798.
11 T. Kawamura and J.K. Kochi, J. Amer. Chem. Soc., 94 (1972) 648.
12 G.A. Russell and D.F. Lawson, J. Amer. Chem. Soc., 94 (1972) 1699.
13 G.F. Pedulli, A. Alberti, L. Testaferri and M. Tiecco, J. Chem. Soc. Perkin II, (1974) 1701.
14 N.D. Epiotis, W.R. Cherry, S. Schaik, A.L. Yates and F. Bernardi, Structural Theory of Organic Chemistry, Springer-Verlag, Berlin, 1977.
15 A.I. Prokofiev, N.N. Bubnov, S.P. Solodovnikov and M.I. Kabachnik, Tetrahedron Lett., (1973) 2479.
16 E.T. Strom and G.A. Russell, J. Amer. Chem. Soc., 87 (1965) 3326.
17 A. Hudson and R.F. Treweek, J. Chem. Soc. Faraday II, (1976) 855.
18 A. Hudson and K.J. Root, Advan. Mag. Res., 5 (1971) 1.
19 H.G. Benson, A. Hudson and J.W.E. Lewis, Mol. Phys., 21 (1971) 935.