

## SPIN ADDUCTS OF GROUP IVB ORGANOMETALLIC RADICALS WITH THIOKETONES. AN ESR STUDY

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### Summary

The radical adducts resulting from the reaction between Group IVB organometallic radicals  $\cdot\text{MR}_3$  ( $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ ;  $\text{R} = \text{alkyl or aryl}$ ) and a number of thioketones of the chromone and flavone series have been investigated by ESR spectroscopy. The spectral parameters obtained for these species have been compared with those of similar adducts of the corresponding ketones. Both classes of radicals adopt an orthogonal conformation, and the differences between the former and the latter paramagnetic species can be accounted for by the different electronegativity of oxygen and sulphur. The effects of substitution of the heterocyclic oxygen with a sulphur or selenium atom on the spin density distribution are likewise explained. INDO calculations have been carried out on the model systems  $\cdot\text{CH}_2\text{XSiH}_3$  ( $\text{X} = \text{O}, \text{S}$ ).

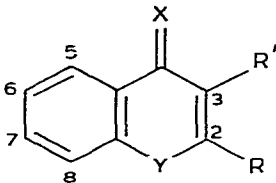
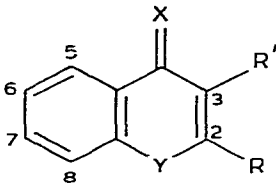
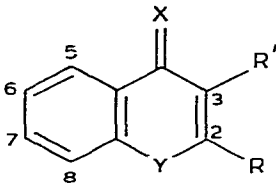
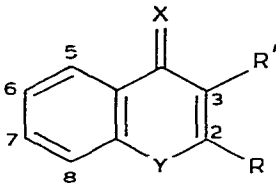
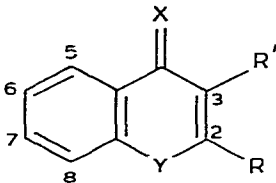
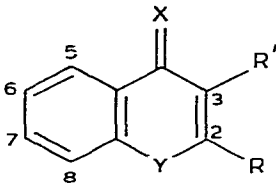
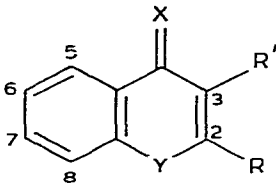
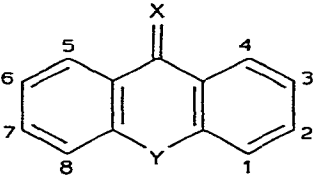
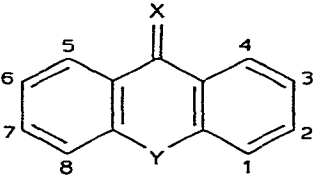
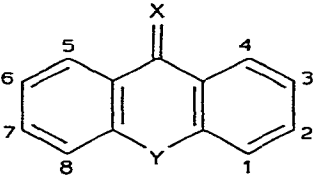
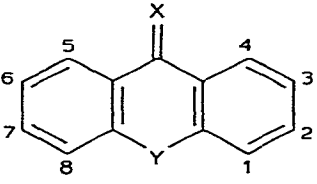
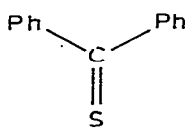
### Introduction

Persistent organometallic radicals can be readily produced by reaction of photolytically generated  $\cdot\text{SiR}_3$ ,  $\cdot\text{GeR}_3$ , and  $\cdot\text{SnR}_3$  radicals with thioketones. The addition occurs at the thiocarbonyl sulphur with formation of a sulphur–metal bond and a radical centre at the carbon atom. Thus the  $\text{C}=\text{S}$  double bond acts as a spin trap, behaving like the  $\text{C}=\text{O}$  bond of carbonyl derivatives. However, while adducts with the latter compounds have been widely investigated, only a few

examples of adducts between metal-centred radicals and thiocarbonyl compounds are described in the literature.

Scaiano and Ingold [1] reported that adducts bearing hindering substituents in the proximity of the radical centre adopt the conformation where the S—M bond is eclipsed with the  $2p_z$  orbital of carbon. In a recent paper [2] we have shown that the same conformation is preferred also in the absence of bulky substituents adjacent to the thiocarbonyl group, indicating that electronic rather than steric interactions are responsible for the orthogonal geometry.

With the aim of obtaining a better understanding of the electronic and stereochemical properties of this class of radicals, we have collected experimental data on the paramagnetic adducts resulting from the reaction of triphenylsilyl, triphenylgermyl, and triphenylstannyl radicals with 4 H-benzopyran-4-thione, 4 H-benzothiapyran-4-thione, 9 H-xanthen-9-thione, 9 H-thioxanthen-9-thione, 9 H-selenaxanthen-9-thione, thiobenzophenone and, for comparative purposes, with the corresponding ketones. The examined compounds are listed below.

	X	Y	R	R'
	O	O	H	H
	S	O	H	H
	O	S	H	H
	S	S	H	H
	O	O	Ph	H
	O	S	Ph	H
	O	O	H	Ph
	S	O		
	S	S		
	O	Se		
	S	Se		
				

INDO molecular orbital calculations have also been performed on model systems, and the results are discussed.

## Experimental

The investigated ketones were prepared by standard methods. The thio-ketones were obtained by reaction of the ketones with either HCl and  $H_2S$  in alcoholic solution [3] or with  $P_2S_5$  in xylene [4]. All the organometallic compounds were commercially available and were used without further purification.

The adducts were produced by photolysis with a high pressure mercury lamp of solutions of the substrates containing also ditert-butyl peroxide and the appropriate triphenyl or trialkylsilane, germanium hydride, or tin hydride. (The mechanism of formation of the paramagnetic species has been discussed by other authors [5].)

In the case of several of the thioketones the adducts are also formed in the absence of ditert-butyl peroxide. In these cases hydrogen abstraction from the metal hydride is believed to involve the photoexcited states  $n, \pi^*$  for ketones and  $\pi, \pi^*$  for the thioketones [2,6]. The hydrogen adducts formed in the primary step of the reaction are not sufficiently long lived for observation under the conditions used. Trialkylstannyl radicals may also be generated by thermal cleavage of the tin-tin bond of the parent hexaalkyldistannanes.

It should also be noted that the tin adducts of thiobenzophenone can also be produced simply by mixing the thioketone with hexabutyliditin in tert-butylbenzene at room temperature. A charge-transfer mechanism is believed to be responsible for the formation of the radical.

Attempts to generate organometallic adducts from thiofluorenone were unsuccessful since simply heating this compound in tert-butylbenzene gave an ESR spectrum characterized by the following hyperfine splitting constants: 3.50 G (1 H), 3.15 G (2 H), 0.77 G (3 H), 0.56 G (1 H). The same spectrum was obtained also in the presence of the metal hydrides and ditert-butyl peroxide. Thermal self reaction of thiofluorenone leading to fluorenylidene, 9,9'-epidithiodifluorenyl-(9,1') and rubicene was reported in the early sixties [7]. The detection of an ESR signal under similar experimental conditions suggests that this reaction may be a radical process.

The ESR spectra were recorded at temperatures ranging between 30°C and 150°C, high temperature enhancing the intensity of the ESR signals in several cases. The  $g$  factors were measured relative to a sample of solid DPPH ( $g = 2.0037$ ).

## Results and discussion

In almost all cases the reaction of compounds I–XII with photolytically generated  $\cdot MR_3$  radicals gave the expected spin adducts as the only detectable paramagnetic species. An exception is provided by 4 H-benzopyran-4-thione, the ESR spectra of which are characterized by the appearance of a second radical shortly after the start of the UV irradiation. Because of the fast formation of the latter species we were unable to record a spectrum attributable to the spin adduct between II and  $\cdot SiPh_3$ ; a spectrum assigned to the adduct of  $\cdot GePh_3$  with II was recorded, but within a few minutes it was replaced by that of the second radical. The spectra of the undesired species can be interpreted in terms of the coupling between the unpaired electron and six different protons, exactly as for the correct adducts, although the hyperfine splittings are ca. 30% larger. We are unable to suggest a reasonable structure which would account for the spectra of these species\*.

\* The hyperfine splitting constants for these radicals are:

II +  $\cdot SiPh_3$ : 12.30 G (1 H), 5.00 G (1 H), 4.28 G (1 H), 1.31 G (2 H), 0.25 G (1 H).

II +  $\cdot GePh_3$ : 11.55 G (1 H), 4.94 G (1 H), 4.16 G (1 H), 1.30 G (2 H), 0.40 G (1 H).

TABLE I  
ESR SPECTRAL PARAMETERS FOR THE PARAMAGNETIC ORGANOMETALLIC ADDUCTS FROM COMPOUNDS I-VII (COUPLING CONSTANTS IN GAUSS)

Compound	Radical	MR <sub>3</sub>	$a_2$	$a_3$	$a_5$	$a_6$	$a_7$	$a_8$	$g$	T (°C)
I	Ia	SiPh <sub>3</sub>	9.80	2.26	3.19	<0.05	3.19	0.54	2.0038	Room
I	Ib	GePh <sub>3</sub>	9.76	2.26	3.21	<0.05	3.21	0.59	2.0032	Room
I	Ic	SnPh <sub>3</sub>	9.45	2.18	3.22	<0.05	3.22	0.55	2.0028	Room
I	Id	SnBu <sub>3</sub>	9.50	2.25	3.30	<0.05	3.30	0.57	—	Room
II	IIfa	GePh <sub>3</sub>	8.62	2.00	2.89	0.32	2.66	0.50	—	Room
III	IIIa	SiPh <sub>3</sub>	9.38	2.60	2.80	0.30	2.60	0.50	2.0043	95
III	IIIb	GePh <sub>3</sub>	9.40	2.65	2.85	0.25	2.65	0.56	2.0041	55
III	IIIc	SnPh <sub>3</sub>	9.28	2.70	2.70	0.20	2.70	0.55	2.0037	55
IV	IVa	SiPh <sub>3</sub>	8.60	2.30	2.50	~0.40	2.50	~0.40	2.0048	Room
IV	IVb	GePh <sub>3</sub>	8.35	2.33	2.45	0.42	2.45	0.42	—	Room
IV	IVc	SnPh <sub>3</sub>	8.40	2.38	2.38	0.40	2.38	0.40	—	Room
IV	IVd	SnBu <sub>3</sub>	8.45	2.50	2.50	n.r.	2.50	n.r.	2.0042	Room
V	Va	SiPh <sub>3</sub>	{ 2.88(1 H) 2.54(2 H) 0.89(2 H)	2.35	2.59	<0.05	2.42	0.31	—	120
V	Vb	GePh <sub>3</sub>	{ 2.87(1 H) 2.55(2 H) 0.89(2 H)	2.14	2.49	<0.05	2.26	0.26	—	120
VI	VIa	SiPh <sub>3</sub>	{ 2.38(1 H) 2.19(2 H) 0.81(2 H)	2.03	2.80	0.18	2.06	0.37	—	100
VI	VIb	GePh <sub>3</sub>	{ 2.47(1 H) 2.25(2 H) 0.82(2 H)	1.96	2.77	0.13	1.98	0.35	—	100
VII	VIIa	SiPh <sub>3</sub>	9.30	—	3.04	<0.05	3.04	0.45	2.0032	180
VII	VIIb	GePh <sub>3</sub>	9.25	—	3.11	<0.05	3.11	0.44	2.0031	150
VII	VIIc	SnPh <sub>3</sub>	9.21	—	3.11	<0.05	3.11	0.40	2.0024	80

TABLE 2

ESR SPECTRAL PARAMETERS FOR THE PARAMAGNETIC ORGANOMETALLIC ADDUCTS FROM COMPOUNDS VIII—XI (COUPLING CONSTANTS IN GAUSS)

Compound	Radical	MR <sub>3</sub>	a <sub>1,8</sub>	a <sub>2,7</sub>	a <sub>3,6</sub>	a <sub>4,5</sub>	a <sub>M</sub>	g	T(°C)
VIII	VIIIa	SiPh <sub>3</sub>	0.76	3.11	0.76	3.54	—	2.0032	40
VIII	VIIIb	GePh <sub>3</sub>	0.72	3.07	0.72	3.51	—	2.0031	40
VIII	VIIIc	SnMe <sub>3</sub>	0.80	3.30	0.80	3.30	106.0 <sup>a, c</sup> 111.0 <sup>b, c</sup>	2.0025	Room
VIII	VIII d	SnBu <sub>3</sub>	0.75	3.10	0.75	3.50	93.0 <sup>a</sup> 97.5 <sup>b</sup>	—	Room
IX	IXa	SiPh <sub>3</sub>	0.89	2.91	0.89	3.32	—	2.0039	Room
IX	IXb	GePh <sub>3</sub>	0.85	3.34	1.05	3.70	—	2.0037	Room
IX	IXc	SnMe <sub>3</sub>	0.86	3.00	0.86	3.20	91.6 <sup>a</sup> 95.7 <sup>b</sup>	—	Room
IX	IXd	SnBu <sub>3</sub>	0.90	3.00	0.90	3.20	79.1 <sup>a</sup> 82.7 <sup>b</sup>	2.0036	Room
X	Xa	SiPh <sub>3</sub>	0.96	3.32	1.14	3.72	7.24 <sup>d</sup>	2.0059	Room
X	Xb	GePh <sub>3</sub>	0.92	3.30	1.13	3.66	5.08 <sup>e</sup>	2.0057	Room
X	Xc	SnPh <sub>3</sub>	0.88	3.34	1.08	3.63	98.0 <sup>a</sup> 102.6 <sup>b</sup>	2.0050	Room
X	Xd	SnMe <sub>3</sub>	0.91	3.33	1.09	3.69	84.9 <sup>a</sup> 88.9 <sup>b</sup>	2.0051	Room
XI	XIa	SiPh <sub>3</sub>	0.96	2.96	0.96	3.36	—	2.0070	Room
XI	XIb	GePh <sub>3</sub>	0.94	2.92	0.94	3.32	—	2.0069	Room
XI	XIc	SnMe <sub>3</sub>	0.92	3.00	0.92	3.20	86.0 <sup>a</sup> 90.0 <sup>b</sup>	2.0069	Room
XI	XI d	SnBu <sub>3</sub>	1.00	3.00	1.00	3.20	75.0 <sup>a</sup> 78.5 <sup>b</sup>	2.0069	Room

<sup>a</sup> a<sup>117</sup>Sn, <sup>b</sup> a<sup>119</sup>Sn, <sup>c</sup> Additional decet of 0.15 G, <sup>d</sup> a<sup>29</sup>Si, <sup>e</sup> a<sup>73</sup>Ge.

The ESR spectral parameters of the adducts from I—XII are listed in Tables 1—3. The proton hyperfine splittings for the radicals from VIII—XI and XII were assigned by analogy with data for related derivatives [8]. For the adducts from 4 H-benzopyran-4-one (I) the assignment was made on the basis of McLachlan spin density calculations, which were performed by using the parameters:  $h_O = 2.0$ ,  $k_{CO} = 1.0$  for the heterocyclic and  $h_O = 2.8$ ,  $k_{CO} = 1.6$  [9] for the ketyl oxygen. For radicals from II—VII a similar spin density

TABLE 3

ESR SPECTRAL PARAMETERS FOR THE PARAMAGNETIC ORGANOMETALLIC ADDUCTS FROM THIOBENZOPHENONE XII (COUPLING CONSTANTS IN GAUSS)

Compound	Radical	MR <sub>3</sub>	a <sub>O</sub>	a <sub>m</sub>	a <sub>p</sub>	a <sub>M</sub>	g	T(°C)
XII	XIIa	SiPh <sub>3</sub>	2.90	1.20	3.16	11.2 <sup>c</sup>	2.0033	25—100
XII	XIIb	GePh <sub>3</sub>	2.90	1.20	3.16	5.94 <sup>d</sup>	2.0033	25—100
XII	XIIc	SnMe <sub>3</sub>	3.00	1.15	3.00	80.2 <sup>a, e</sup> 83.7 <sup>b, e</sup>	2.0036	25
XII	XII d	SnBu <sub>3</sub>	3.00	1.20	3.00	68.7 <sup>a</sup> 71.2 <sup>b</sup>	—	25
XII	XIIe	SnPh <sub>3</sub>	3.00	1.25	3.00	100.9 <sup>a</sup> 105.6 <sup>b</sup>	—	25
XII	XII f	CH <sub>3</sub>	2.78	1.15	3.06	1.15(3 H)	2.0032	25

<sup>a</sup> a<sup>117</sup>Sn, <sup>b</sup> a<sup>119</sup>Sn; <sup>c</sup> a<sup>29</sup>Si; <sup>d</sup> a<sup>73</sup>Ge; <sup>e</sup> additional decet of 0.13 G.

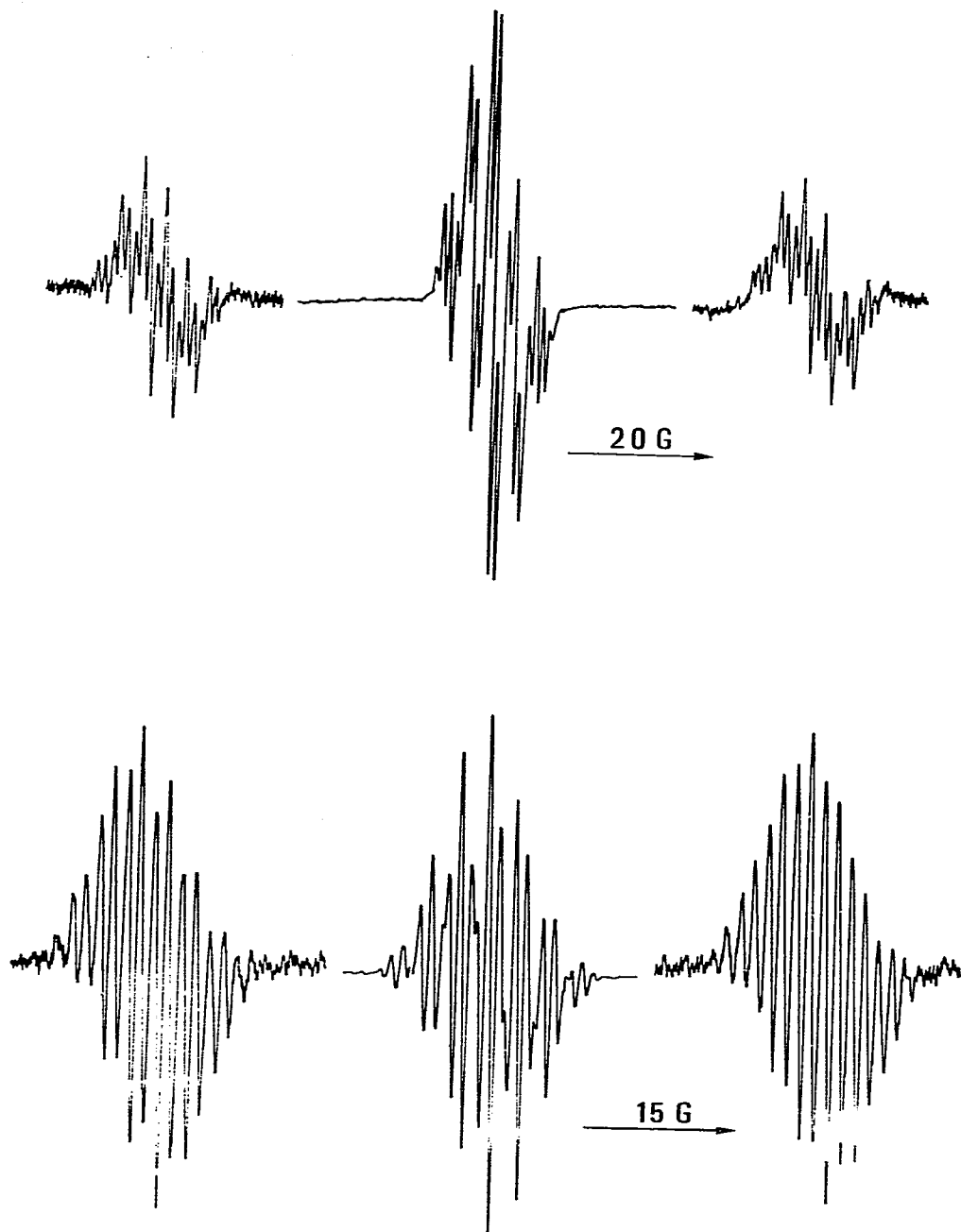


Fig. 1. Room temperature ESR spectra of the radical adducts of 9 H-selenaxanthen-9-thione with  $^{119}\text{SnMe}_3$  radicals (upper spectrum), and of thiobenzophenone with  $^{119}\text{SnBu}_3$  radicals (lower spectrum).

distribution was assumed. It should be pointed out that the assignments of slightly different proton couplings given in Table 1 may be interchanged. The hyperfine splittings at the nuclei in low natural abundance, viz  $^{13}\text{C}$  (1.1%),  $^{29}\text{Si}$  (4.7%),  $^{73}\text{Ge}$  (7.6%),  $^{117}\text{Sn}$  (7.7%) and  $^{119}\text{Sn}$  (8.7%), could be readily assigned

from the relative intensities of the satellite lines.

Information on the preferred geometry adopted by the  $\text{MR}_3$  group with respect to the plane defined by the  $\pi$  system can be obtained both from the magnitude of the hyperfine splittings at the metal atoms and by the trends in the  $g$  factors. It has been shown in previous papers that the organometallic adducts of ketones adopt the equilibrium conformation in which the O—M bond eclipses the  $2p_z$  orbital of the radical carbon centre. In this conformation large metal splittings are expected, as this geometrical arrangement allows spin density to be transferred from the  $\pi$  system to the metal atom through direct orbital overlap. In the present cases the large couplings at  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$ , which could be measured for several tin adducts, as well as the few examples of  $^{29}\text{Si}$  and  $^{73}\text{Ge}$  splittings, are consistent with the above geometry. In the adducts from thioketones the metal splittings are even larger than in those from ketones.

The same configurational preference is also suggested by the decrease in the  $g$  factor with increasing atomic number of the metal within the series of adducts originated from the same diamagnetic precursor. This trend is common to other organometallic radicals adopting the eclipsed geometry [10], whereas  $g$  factors are practically independent of the size of the metal atom in planar adducts, as it is for the organometallic adducts of  $\alpha$ -diketones [11].

The variations of the ring proton splittings upon substitution of sulphur or selenium for oxygen in the examined radical adducts provide information on the relative electronic properties of these Group VI elements.

We first consider the effect exerted by the heteroatoms when they are part of the heterocyclic ring. As will be seen from Tables 1 and 2, substitution of the ring oxygen by sulphur produces a redistribution of spin density which parallels that observed in the corresponding adducts from  $\gamma$ -pyrones and  $\gamma$ -thiapyrones [2], and can be similarly explained in terms of the greater electronegativity of oxygen than of sulphur. The practical invariance of the proton couplings in the sulphur and selenium derivatives is not surprising in view of the small electronegativity difference between these two elements.

A similar effect is also produced by replacement of an organometalloxy by an organometalthio group, that is upon substitution of the exocyclic oxygen atom. Again, in the sulphur derivatives the aromatic proton splittings are smaller than in their oxygen-containing analogues, implying that sulphur substitution favours spin transfer from the  $\pi$ -system to the organometallic group.

Because of the eclipsed geometry adopted by the oxygen—metal or sulphur—metal bonds, several orbitals of the organometallic fragment have the correct symmetry for interacting with the singly occupied MO (SOMO) of  $\pi$  symmetry; these are the lone pair  $n_X$  of the X atom ( $X = \text{O}, \text{S}$ ), and the bonding  $\sigma_{X-M}$  and antibonding  $\sigma_{X-M}^*$  orbitals of the X—M bonds. In Fig. 2 is shown a schematic diagram of these possible orbital interactions.

A reduction of spin density on the  $\pi$  system may be the result of electron transfer from the radical carbon centre to the  $\text{XMR}_3$  group, the orbital behaving as acceptor for the unpaired electron, in this case the  $\sigma_{X-M}^*$  vacant orbital, as suggested [2] in a previous paper. However, the decrease of spin density on the unsaturated carbons might also originate in the opposite effect, i.e. electron transfer to the  $\pi$  system from either the  $n_X$  lone pair or the  $\sigma_{X-M}$

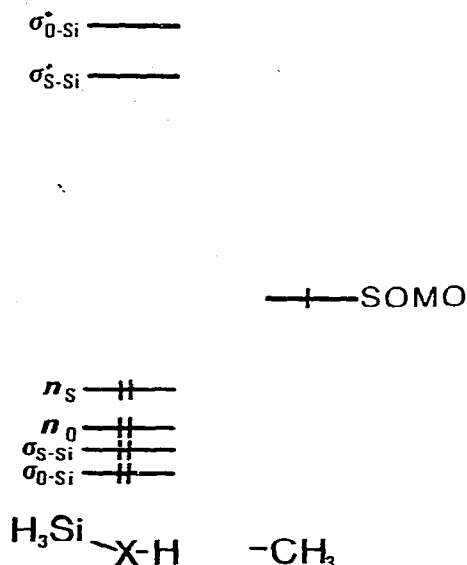
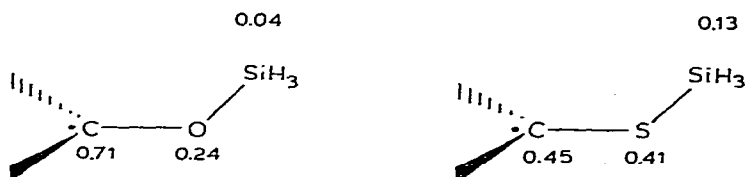


Fig. 2. Schematic interaction diagram between the orbitals of the two fragments  $-CH_3$  and  $-XSiH_3$ , where  $X = O, S$ . An orthogonal conformation for  $\cdot CH_2XSiH_3$  is assumed.

bonding orbital. The importance of these effects will be the greater the smaller is the energy gap between the SOMO and the appropriate orbital of the substituent group. Since in the metalthio adducts both the lone pair and the  $\sigma_{X-M}$  and  $\sigma_{X-M}^*$  orbitals are closer to the SOMO than the corresponding orbitals of the metalloxy group, we expect the spin density on the  $\pi$  system to be smaller in the former derivatives, in agreement with experiment.

This expectation is substantiated by INDO [12] calculations performed on the model systems  $\cdot CH_2OSiH_3$  and  $\cdot CH_2SSiH_3$  assuming the following standard geometrical parameters:  $r(CH) = 1.09 \text{ \AA}$ ,  $r(CO) = 1.394 \text{ \AA}$ ,  $r(CS) = 1.815 \text{ \AA}$ ,  $r(OSi) = 1.633 \text{ \AA}$ ,  $r(SSi) = 2.15 \text{ \AA}$ ,  $r(SiH) = 1.48 \text{ \AA}$ ,  $\angle COSi = 120^\circ$ , and  $\angle CSSi = 120^\circ$ . The calculations suggest that the spin density at the radical carbon centre should be smaller in the sulphur derivatives than in their oxygen analogues, as indicated by the spin density values set out below:



The form of the molecular orbital containing the unpaired electron, which is more localized on oxygen or sulphur than on silicon, also suggests that the contribution of the  $n_X$  lone pair to the SOMO is larger than that of the  $\sigma_{X-Si}$  bonding and  $\sigma_{X-Si}^*$  antibonding orbitals. It thus seems that the variations in the spin density distribution on passing from an oxygen- to the corresponding sulphur-



containing radical can be explained essentially in terms of the lower electronegativity of the sulphur atom, independent of the molecular geometry.

Finally, although the formation of the radical anions of flavones by polarographic methods has been reported [13] and their intermediacy inferred [14] in the photochemical dimerization of their parent compounds, the organometallic adducts with compounds V, VI and VII studied in this work are, to the best of our knowledge, the only radical species from either flavone (or thiaflavone) or iso-flavone which have been detected by ESR spectroscopy. By comparison with the ESR spectral data of the paramagnetic species from I and III, it can be seen that the presence of a phenyl substituent in position 3 in the radicals from iso-flavone has little effect on the spin density distribution within the rest of the molecule, only inducing a slight decrease of the h.f.s. constant at the proton in the adjacent position 2. In contrast, in the adducts from V and VI the phenyl ring is attached to a position characterized by a high spin density. It then produces a significant decrease of more or less all the proton couplings of the chromone skeleton, and shows relatively large splittings at the *ortho*, *meta*, and *para* protons. This indicates that conjugation is possible between the benzopyrone moiety and the phenyl ring, whose rotation must be unhindered, as is the case for the diamagnetic precursors [15] of these radicals.

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