

An ESR Study of some Group IVB Radical Adducts with Aromatic Ketones

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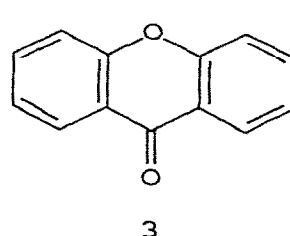
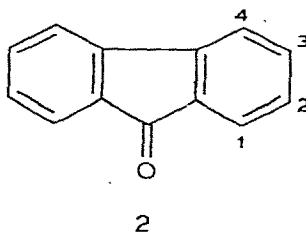
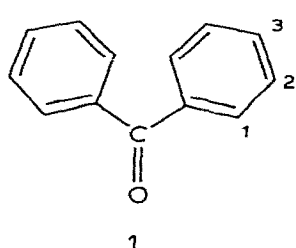
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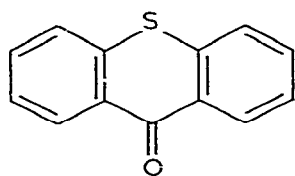
(Received September 26th, 1978)

Summary

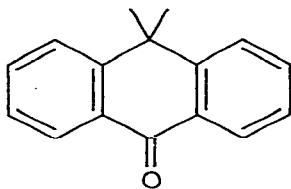
Hyperfine coupling constants are reported for the paramagnetic adducts of silyl, germyl and stannyl radicals with five aromatic ketones. The spin distribution in these systems is compared with the H atom adducts and analogous hydrocarbon radicals. The large  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  satellite splittings observed in the stannyl adducts indicate that these radicals exist in a conformation with the O - Sn bond orthogonal to the  $\pi$ -system. The ESR spectrum of the previously unknown anthronyl radical has been recorded and analysed.

Several recent publications have dealt with the interaction of Group IVB free radicals with compounds containing carbon-oxygen double bonds [1], especially  $\alpha$ -diketones and quinones [2,3,4]. In the present paper we report detailed ESR results for the adducts of silicon, germanium and tin-centred radicals with a series of structurally related aromatic ketones, benzophenone (1), fluorenone (2), xanthone (3), thioxanthone (4) and anthrone (5). The observed radicals can all be represented by the basic structure (6) when X is  $\text{OMR}_3$  ( $M = \text{Si, Ge, Sn}$ ) and the aryl groups may be linked in the ortho positions (e.g. by O, S,  $\text{CH}_2$ ). The spin density distribution in these systems is compared with the H atom adducts

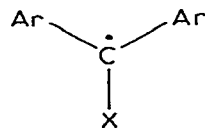




4



5



6

(X=OH) and the hydrocarbon radicals (X=H). To facilitate this comparison we have prepared the previously unknown H atom adduct of anthrone and the anthronyl radical (7).

### Results and Discussion

As outlined previously [4] the adducts formed by benzophenone and fluorenone are readily prepared by U. V. irradiation of a melt of the ketone with the Group IVB precursor, in the present instance triphenyl silane, triphenylgermane or hexamethylditin. The stannyl adducts were found to exhibit a large coupling to  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  not observed in earlier work. These splittings are an order of magnitude larger than the tin coupling constants found in adducts with  $\alpha$ -diketones [4]. Similar methods were successful for xanthone and thioxanthone. However the spectra of the tin adducts were markedly improved by performing the reactions in benzene. The figure shows the well resolved spectrum of the  $\text{SnMe}_3$ -xanthone adduct which, in addition to the expected ring proton couplings, also shows a decet from the nine methyl protons. The tin and germanium adducts of anthrone were also easily observable but we were unable to obtain a satisfactory spectrum of the  $\text{SiPh}_3$  adduct; the signals were too weak and short-lived for analysis. Difficulty in obtaining a silyl adduct was also found [4] in earlier work with p-benzoquinone. All the coupling constants are summarised in Table 1.

The H-atom adducts of 1-4 have been reported by Wilson [6] who photolysed the ketones in ethanol and similar solvents. This method does not work for anthrone but we were able to obtain an ESR spectrum by photolysing a solution of the ketone in hexamethylphosphoramide containing triphenylgermane. For comparative purposes we have also prepared the other H-adducts in HMPA since the splittings are solvent dependent. As is well established [6], the hydroxyl splitting in the ketyls is also temperature dependent. For 1, 3, 4 and 5 the temperature dependence is positive but in fluorenone ketyl the splitting decreases in magnitude with increasing temperature and becomes zero at  $210^\circ$ . The hydroxyl splitting is therefore positive for all the adducts except that from

Table 1

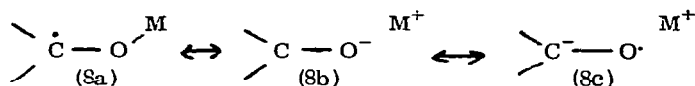
Hyperfine coupling constants (G) for the adduct radicals

Ketone	X	$a_1$	$a_2$	$a_3$	$a_4$	$a_M$	T(°C)
<u>1</u>	OSiPh <sub>3</sub>	3.20	1.25	3.55		7.10 [5]	130
	OGepH <sub>3</sub>	3.16	1.22	3.55			130
	OSnMe <sub>3</sub>	3.10	1.20	3.50		87.3 (117) 91.4 (119)	80
	OH	3.16	1.20	3.56		3.10	100
<u>2</u>	OSiPh <sub>3</sub>	3.53	0.80	3.81	0.80		240
	OGepH <sub>3</sub>	3.40	0.80	3.72	0.80		210
	OSnMe <sub>3</sub>	3.20	0.75	3.57	0.75	70.9 (117) 74.2 (119)	120
	OH	3.15	0.82	3.58	0.76	0.50	100
<u>3</u>	OSiPh <sub>3</sub>	3.55	0.95	3.87	0.65		180
	OGepH <sub>3</sub>	3.55	0.93	3.85	0.62		100
	OSnMe <sub>3</sub>	3.64	0.94	3.88	0.53	91.2 (117) 95.5 (119) $a_{Me}=0.07$	60
	OH	3.75	0.99	3.96	0.58	2.72	100
<u>4</u>	OSiPh <sub>3</sub>	3.35	1.05	3.70	0.85		120
	OGepH <sub>3</sub>	3.35	1.05	3.67	0.85		100
	OSnMe <sub>3</sub>	3.40	1.06	3.71	0.79	86.7 (117) 90.7 (119) $a_{Me}=0.06$	50
	OH	3.44	1.11	3.77	0.84	4.30	100
<u>5</u>	CGepH <sub>2</sub>	3.45	1.10	3.78	1.10	$a_{CH_2}=13.00$	80
	OSnMe <sub>3</sub>	3.45	1.10	3.78	1.10	$a_{CH_2}=12.88$	110
	OH	3.48	1.14	3.90	1.14	3.54 $a_{CH_2}=13.10$	210

2. This suggests that the barrier to internal rotation of the hydroxyl group is highest in fluorenone ketyl. It is interesting to note that the fluorenone - trimethyltin adduct exhibits a smaller tin splitting than the other systems. The large tin coupling constants found in the ketone adducts, compared with the small values found [4] for o-quinones and  $\alpha$ -diketones, almost certainly arise from conformational differences. The tin atom is  $\beta$  to the radical

centre and its splitting is expected to show a strong angular dependence. In the present instance steric hindrance forces the organometallic group into an out-of-plane position with the Sn-O bond perpendicular to the  $\pi$ -system. This maximises hyperconjugative interactions and leads to a large hyperfine splitting. Molecular models support this conclusion. The variation in the tin-splittings probably reflects changes in the spin density on the radical centre since they were found to exhibit only a small temperature dependence consistent with a high barrier to internal rotation.

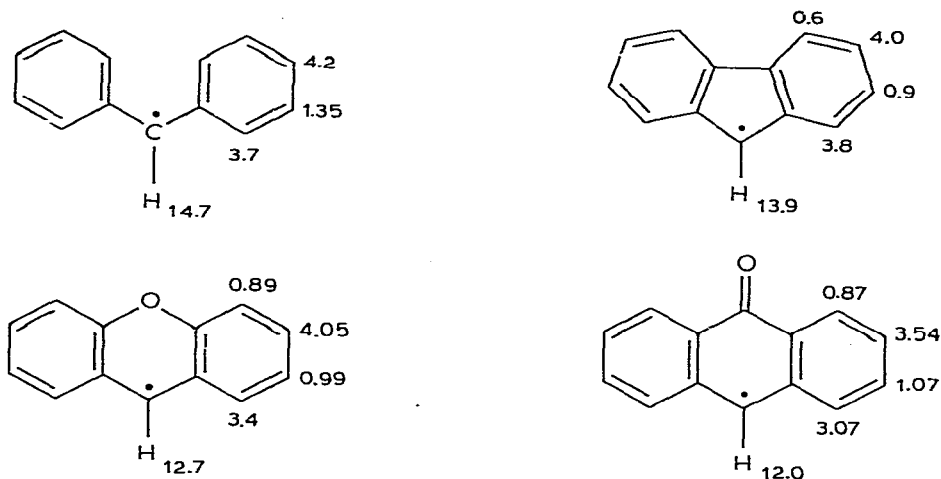
The most noticeable feature of the proton coupling constants collected in table 1 is that, with the exception of fluorenone, they are insensitive to the nature of the organometallic substituent. This is in contrast with the results of earlier studies [1-4] which have generally shown a reduction in proton splittings on going from Si - Pb indicating a reduction in spin density on the radical carbon. It has been argued that this arises from a redistribution of spin density within the carbonyl group, consistent with increased ionic character for the oxygen-metal bond. In valence bond terms this corresponds to increased participation of the ionic forms (8b) and (8c) in the resonance hybrid. In the aromatic ketyls steric hindrance twists the O-M bond out of plane and  $\pi$ -delocalisation onto oxygen



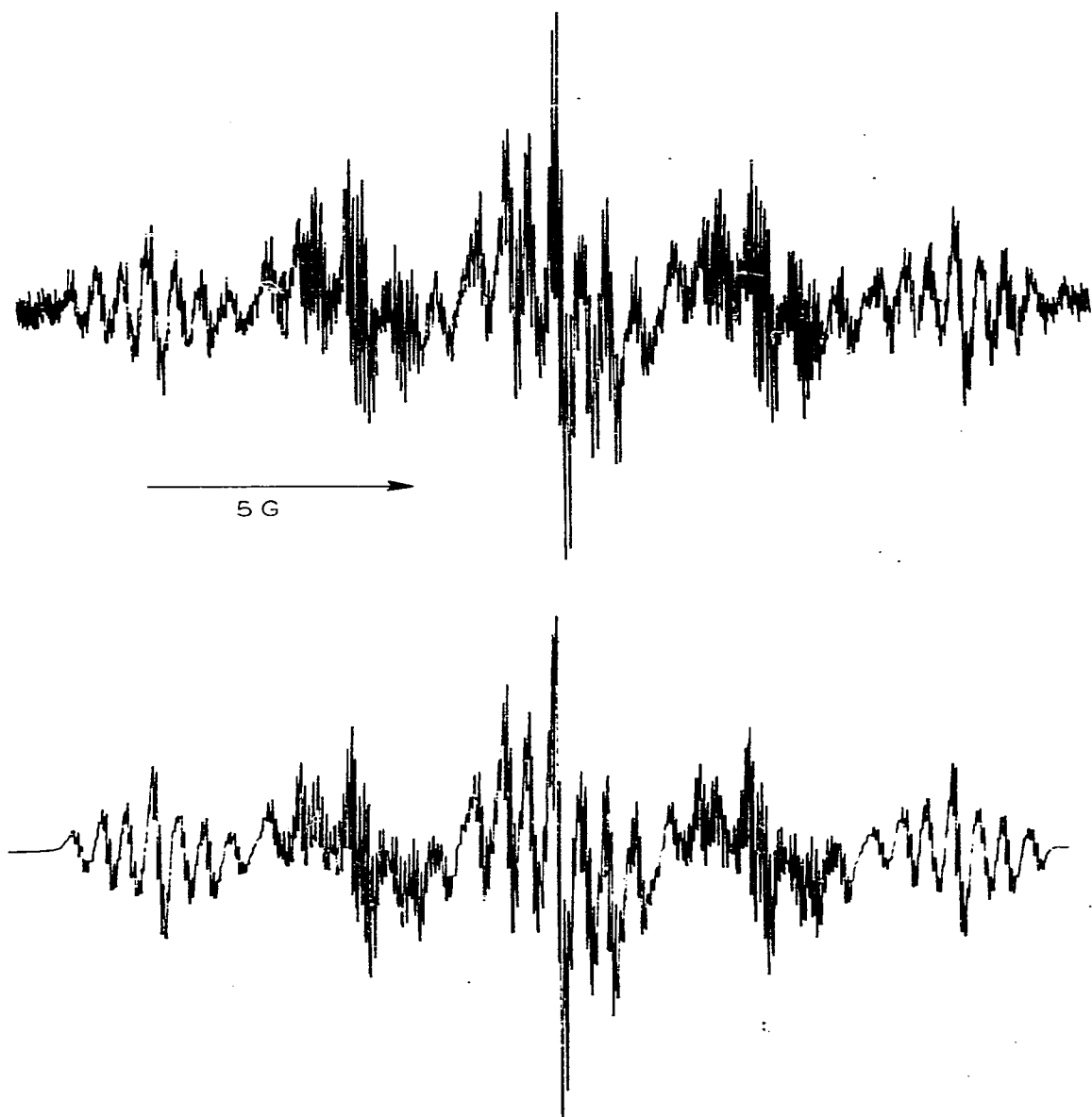
is inhibited. The spin distribution is then essentially independent of the nature of M.

Table 2

Hyperfine splitting constants (G) for the hydrocarbon radicals:



(7)



The ESR spectrum of the adduct formed by xanthone and  $\cdot\text{SnMe}_3$  together with a computer simulation.

The extent of spin-delocalisation onto M by hyperconjugation seems to be roughly constant on going down the group. The  $^{29}\text{Si}$  [5] and  $^{117,119}\text{Sn}$  coupling constants for 1 correspond to comparable spin densities in the 3s and 5s orbitals of Si and Sn respectively (ca. 0.005).

The small variation in coupling constants found for 2 might arise from a lower barrier to rotation for the  $\text{OMR}_3$  group and less steric hindrance. This is consistent with the reduced  $^{117}, ^{119}\text{Sn}$  hyperfine interaction and also the increased barrier to rotation of the OH group away from the planar conformation (vide supra). The spin density distribution in the various aromatic systems 1-5 is similar in the OH and  $\text{OMR}_3$  adducts to that in the parent hydrocarbon radicals diphenylmethyl [7], fluorenyl [8], and xanthyl [9]. With the exception of benzophenone and diphenylmethyl, there are ambiguities in the assignment of the various triplet splittings. We have assumed in table 1 that  $a_1 < a_3$  and  $a_4 < a_2$  but this is by no means certain. Indeed Wilson [6] in his work on xanthone and thioxanthone proposed a reversal in the assignment on changing oxygen to sulphur but we do not find his argument persuasive.

Previous attempts to study the spin distribution in anthrone by preparing the radical anion [10] have failed and it seemed worthwhile obtaining a spectrum of the anthronyl radical 7. We eventually achieved this by photolysing a saturated solution of anthrone in a 1:1 mixture of benzene and di-*t*-butyl peroxide at  $80^\circ\text{C}$ . The expected 162 line spectrum was computer simulated to give the coupling constants in table 2. where we have also included some analogous hydrocarbon radicals. The most interesting conclusion is that anthronyl is best regarded as a hydrocarbon radical rather than the alternative phenoxy structure in which the odd electron is localised on oxygen. The 12G coupling from the hydrogen attached to the radical centre corresponds to a spin density of ca. 0.5 at that position. The carbonyl bridge in anthronyl has only a slightly greater effect on the spin distribution than the oxygen bridge in xanthyl.

### Experimental

The ESR spectra were obtained on a Varian E104A spectrometer as described previously [4]. Computer simulations were performed with a Digico Micro 16 computer on-line to a Varian E3 spectrometer.

### Acknowledgement

We thank the SRC for a grant towards the purchase of the E104A spectrometer and NATO for the award of a collaborative research grant.

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