

AN ESR INVESTIGATION ON GROUP IVB ORGANOMETALLOXY- AND ORGANOMETALTHIO-PYRYL AND THIAPYRYL RADICALS

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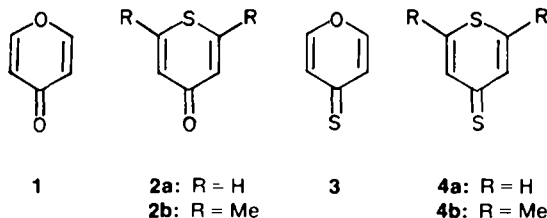
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Abstract—The spin adducts of triphenylsilyl, triphenylgermyl and triphenylstannyl radicals with γ -pyrone, γ -thiopyrone, thia- γ -pyrone and thia- γ -thiopyrone have been studied by ESR spectroscopy. The spectral parameters indicate that these radicals adopt the conformation where the O-M or S-M bonds are eclipsed with the $2p_z$ orbital of the γ -carbon, despite the absence of hindering substituent groups in proximity of the radical centre.

The electronic effects of sulphur and oxygen on the spin density distribution are also discussed.

The reactivity of C=O double bonds towards addition of Group IVB organometallic radicals has been widely exploited during recent years to generate a variety of spin adducts from dialkyl- or diaryl-ketones, α -diketones and quinones.¹⁻³ Even though the C=S double bond of thioketones is also known to be a good trap for metal centered radicals, there are only few ESR spectroscopic studies on the resulting adducts.⁴ No comparative investigations of organometallic radicals from ketones and the related thioketones have been reported.

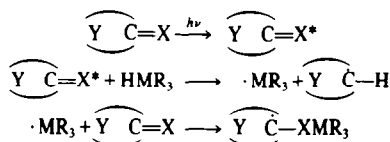
For this reason we have examined the addition reaction of Group IVB radicals with the carbonyl and thio-carbonyl compounds (1-4):



EXPERIMENTAL

The adducts have been produced at slightly below room temp by photolysing with a high pressure mercury lamp (1kW) degassed solns of the appropriate substrate in butylbenzene containing triphenylsilane, triphenylgermanium hydride or triphenyltin hydride; with ketones 1 and 2 the addition of di-*t*-butylperoxide (DTBP) was found to enhance the stationary concentration of the radicals.

The formation of the adducts may be explained according to the following reaction sequence:



The photoexcited state giving hydrogen abstraction from the triphenylmetal hydride is the $^3(n, \pi^*)$ for the ketones (1 and 2). For the thiones (3 and 4), the $^1(\pi, \pi^*)$ seems more probable in view of the inefficiency of the low-lying triplet.⁵

The hydrogen adducts formed in the primary step of the reaction are not sufficiently long lived to be observed under the experimental conditions used.

The ESR lines of the organometallic adducts were sharp but not intense enough to allow the detection of the metal satellites. Only in the case of trimethylstannylthio- γ -thiapyryl generated by irradiation of a toluene solution of hexamethylditin and (4) the tin splitting could be measured as 108.4 G for ^{117}Sn and 113.3 G for ^{119}Sn .

The investigated ketones and thioketones were prepared according to standard procedures,⁶ while the organometallic compounds were all commercially available.

RESULTS AND DISCUSSION

The hyperfine splittings and g values of the organometallic radicals from (1-4) are listed in Table 1. The assignment of the proton couplings to the ring positions is straightforward for the Me substituted derivatives and can be safely transferred to the unsubstituted radicals.

It has been shown in previous studies that the adducts of both ketones and thioketones with Group IVB radicals adopt the geometry placing the R_3M group in the eclipsed position with respect to the symmetry axis of the $2p_z$ orbital on the carbon radical centre,^{2,3} this behaviour being imputed to a concomitance of electronic and steric effects. Also for the present radicals, despite the absence of crowding groups in the neighbourhood of the γ -carbon, the spectral parameters are consistent with the same non planar conformation. In fact in the series of both radicals from ketones and thioketones the g -factors decrease with increasing atomic number of the metal as in other cases where the conformational preference of similar adducts could be determined from the values of the metal hyperfine splittings.² In the second place the g -factors are much lower than in the corresponding radical anions⁷ and practically identical for the adducts

Table I. ESR spectral parameters of the adducts between compounds 1-4 and organometallic ($R_3M\cdot$) radicals measured *ca.* 0°. Coupling constants are expressed in Gauss

Compound	MR_3	$a_{2,6}$	$a_{3,5}$	g
(I)	SiPh ₃	8.25	1.97	2.0036
	GePh ₃	8.16	1.99	2.0034
	SnPh ₃	8.06	1.98	2.0031
(IIa)	SiPh ₃	7.33	2.21	2.0049
	GePh ₃	7.11	2.21	2.0047
	SnPh ₃	7.13	2.23	2.0043
(IIb)	SiPh ₃	7.10 (2 Me)	2.28	2.0046
	GePh ₃	7.08 (2 Me)	2.30	2.0044
	SnPh ₃	7.11 (2 Me)	2.28	2.0040
(III)	SiPh ₃	7.29	1.67	2.0036
	GePh ₃	7.33	1.63	2.0035
	SnPh ₃	7.28	1.66	2.0029
(IVa)	SiPh ₃	6.70	1.95	2.0052
	GePh ₃	6.65	1.95	2.0049
	SnPh ₃	6.61	1.96	2.0045
	SnMe ₃	6.75	2.01	--
(IVb)	SiPh ₃	6.23 (2 Me)	2.03	2.0047
	GePh ₃	6.19 (2 Me)	2.05	2.0046
	SnBu ₃	6.23 (2 Me)	2.11	2.0044

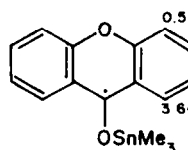
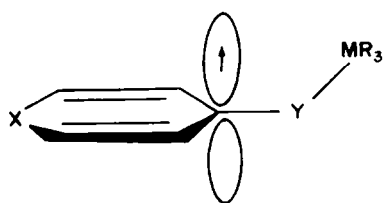
$$a(^{117}\text{Sn}) = 108.4 \text{ G}, a(^{119}\text{Sn}) = 113.3 \text{ G}$$

of ketones and thioketones. This provides evidence that the delocalisation of the unpaired electron on the oxygen or sulphur π lone pairs of the carbonyl or thiocarbonyl functions is negligible and therefore is consistent with a non planar geometry. Finally the magnitude of the tin splitting measured in the trimethyltin adduct of 4 is such that it can be accounted for only by a direct spin transfer mechanism which again can be operative only in the eclipsed conformation where the $2p_z$ orbital of the ring γ -carbon overlaps with the X-MR₃ bond.

The experimental data provide also useful information on the relative electronic effect of the organometalloy and organometalithio groups. The comparison of the spectral parameters for the related radicals with oxygen and sulphur containing substituents shows that the proton splittings are lower in the latter case. This means that sulphur substitution favours electron transfer from the pyryl or thiapyryl moiety to the substituent. Since, as discussed previously, the radical adducts adopt the eclipsed conformation depicted below, the only important interaction which may originate this effect is that between the unpaired electron in the singly-occupied π MO (SOMO) and the σ^* vacant orbital in the Y-MR₃ bond.

In the radical anions of substituted benzenes this interaction has been shown to be responsible for the electron acceptor character of the Y-R (Y = O, S) groups when the molecular geometry is such that overlap between SOMO and σ_{YR}^* orbital may occur.⁸ It has also been shown that this interaction is larger for thio than for oxy groups because the σ_{SR}^* orbital is lower in energy than σ_{OR}^* and therefore closer to the SOMO.

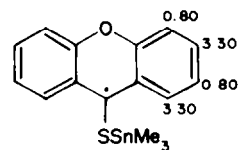
Thus, in the present case, we also propose a similar interpretation to explain the larger electron transfer to the metalthio substituent. In principle, evidence for the correctness of this hypothesis could be provided by the knowledge of the metal hyperfine splitting in related metaloxy and metalthio derivatives. However these splittings could not be measured, except in one case, because of the low stability of the radical adducts. Since a greater stability can be obtained by increasing the extension of the conjugative system, we generated the adducts between trimethyltin radicals and xanthen-9-one and xanthen-9-thione. In both cases, in fact, we have been able to measure the coupling at the Sn atom as shown below.



(0.07, 9H)

$$a(^{117}\text{Sn}) = 91.2 \text{ G}$$

$$a(^{119}\text{Sn}) = 95.5 \text{ G}$$



(0.15, 9H)

$$a(^{117}\text{Sn}) = 106.0 \text{ G}$$

$$a(^{119}\text{Sn}) = 111.0 \text{ G}$$

Also for these adducts the proton splittings decrease on going from the organometalloxy to the organometalthio derivative while, correspondingly, the a_{Sn} coupling becomes larger. The latter finding is therefore indicative of a stronger hyperconjugative interaction with the SMR_3 group, and is consistent with the above explanation. The present data seem also to suggest that this interaction is mostly determined by the nature of the X atom i.e. oxygen or sulphur, rather than of the metal.

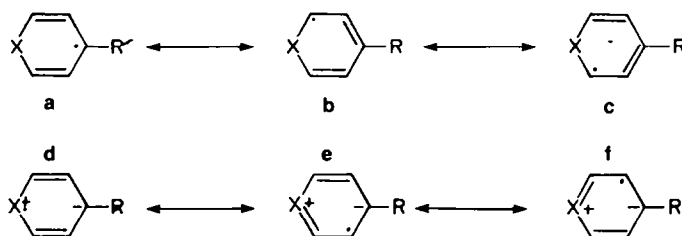
As far as the effect of the heterocyclic oxygen or sulphur is concerned, the observed trend of the proton hyperfine splittings is consistent with the greater electronegativity of oxygen. Actually the lower value of the proton splittings in the thiapyryl radicals, which reflects a reduction of spin density on the ring carbons, can be easily rationalised in terms of the mesomeric structures (a-c) and (d-f) which can be written for these systems.⁹

Actually the limiting structures involving charge separation (d-f) are expected to be more important in the

also a redistribution of the spin density itself which privileges carbons 3 and 5 at the expenses of carbons 2 and 6.

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thiapyryl than in the pyryl radicals because of the greater electronegativity of oxygen with respect to sulphur. The consequent larger delocalisation of the unpaired electron on sulphur with respect to oxygen implies not only an overall reduction of spin density on the ring carbons, but

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