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TEMPERATURE DEPENDENT REACTION PATHWAYS IN THE ADDITION OF SILYL, GERMYL, STANNYL AND PLUMBYL RADICALS TO MALEIC ANHYDRIDE AND RELATED COMPOUNDS: AN ESR STUDY

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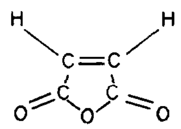
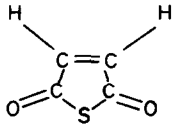
Abstract—The addition of Group IVB organometallic radicals to maleic anhydride, maleic thioanhydride, maleimide and N-methyl maleimide has been investigated by ESR spectroscopy. For Si and Ge centred radicals the reaction pathway has been found to be temp dependent, the addition of the organometallic radical occurring at the CC double bond at lower temps and at either of the two CO groups at higher temps. For Sn and Pb centred radicals only the latter spin adducts could be detected even at low temp.

The addition of Group IVB metal-centred radicals to a variety of compounds containing C=C, C=O, and other multiple bonds has been the subject of numerous ESR studies. In compounds containing more than one type of multiple bond alternative pathways for radical addition can lead to different paramagnetic intermediates readily distinguishable by ESR. An early example[1] involved the reaction of triethylsilyl radicals with isopropenyl acetate: only the radical formed by addition to the C=C bond was detected at −40°. Acetylacetone reacts with silyl radicals to give the O- adduct of the enol form[2] but triphenylstannyl radicals are "trapped" by the diketone.[3] Most of the work has been performed at room temperature or below under continuous UV photolysis. We have shown that in many cases low temperatures are not an essential requirement for the observation of transient radicals. Good quality ESR spectra can be obtained by thermolysis and/or photolysis at temperatures of 100° or higher.[4] The nature of the radicals detected may be dependent on temperature, e.g. in the thermolysis of azodicarboxylates.[5]

Maleic anhydride(I), maleic thioanhydride(II), maleimide(III) and N-methyl maleimide(IV) are examples of molecules where addition can occur to either a C=C or C=O bond. The photochemistry of these molecules has been the subject of several ESR investigations[6–8] but the only organometallic species which has been reported is the triphenylstannyl adduct to the CO group of I.[8]


(I)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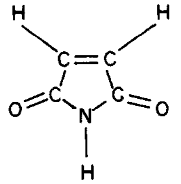
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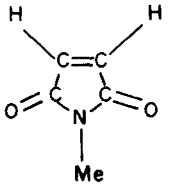
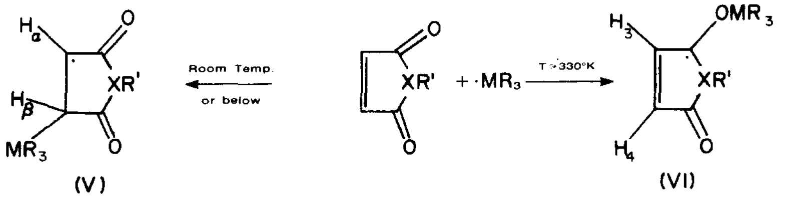

(IV)

We have performed a systematic investigation of the reactions of silyl, germyl, stannyl and plumbyl radicals with I–IV. For silyl and germyl radicals the species observed at low temperatures (25° or below) are consistent with addition to C=C, V, but at higher temperatures (60°–150°) the ESR spectra indicate addition to C=O, VI. For stannyl and plumbyl radicals we were only able to observe adducts of type VI. It would appear that the reaction pathway is kinetically controlled at low temperatures but thermodynamically controlled at high temperatures.



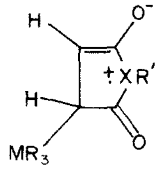
(V) (VI)

(where R′ = H, Me when X = N)

RESULTS

Compounds I–IV react with photochemically generated silyl or germyl radicals below 300°K to give ESR spectra consisting of two large doublets, which we assign to structure V. The coupling constants (Table 1) are similar to those of the known H atom adducts which have been produced by photolysis of the anhydrides or imides in polar solvents.[6–8] We were however unable to obtain a spectrum attributable to the silyl adduct of IV.

An interesting feature in the coupling constants of adducts V is the trend towards lower values of a_H^{β} on going from Si to Ge-containing species. This trend parallels that found for similarly substituted β-Et radicals[9] and appears to be characteristic of this kind of organometallic spin adduct. A similar reduction of the β-proton splitting occurs when O is replaced by N or S atoms in the 5-membered ring. This is likely the result of a partial delocalization of the unpaired electron



(VII)

Table 1. ESR spectral parameters for radical adducts of general structure V

X	R'	MR_3	a_H^{α}	a_H^{β}	a_X	$a_{R'}$
O	--	H[◇]	20.4	34.0(2H)	---	---
O	--	$SiPh_3$	18.6	32.1	---	---
O	--	$GePh_3$	17.9	28.4	---	---
S	--	$SiPh_3$	17.3	28.4	---	---
S	--	$GePh_3$	16.5	23.9	---	---
N	H	H[#]	20.6	29.6(2H)	0.4	1.4
N	H	$SiPh_3$	18.9	29.6	<0.5	1.0
N	H	$GePh_3$	18.4	26.3	<0.5	0.9
N	Me	$GePh_3$	18.2	23.2	<0.5	1.1

[◇] Ref. 7 and 8.

[#] Ref. 6.

Table 2. ESR spectral parameters for radical adducts of general structure VI

X	R'	MR	a_{H_3}	a_{H_4}	a_X	$a_{R'}$	a_M	*g*
O	--	H	3.23	9.17	----	----	0.73[◇]	2.0035
O	--	$SiPh_3$	1.42	9.94	----	----	----	2.0035
O	--	$GePh_3$	2.22	9.62	----	----	----	2.0034
O	--	$SnPh_3$	2.75	9.42	----	----	----	2.0033
O	--	$SnBu_3$	2.96	9.20	----	----	----	2.0033
O	--	$PbPh_3$	3.96	8.46	----	----	----	2.0026
S	--	$SiPh_3$	0.29	9.06	----	----	----	----
S	--	$GePh_3$	0.82	8.68	----	----	----	----
S	--	$SnPh_3$	1.46	8.37	----	----	----	----
S	--	$PbPh_3$	2.59	7.59	----	----	----	----
N	H	$SiPh_3$	1.45	8.92	2.16	<0.3	----	----
N	H	$GePh_3$	2.35	8.48	2.35	<0.3	----	----
N	H	$SnPh_3$	2.67	8.03	2.40	<0.3	----	----
N	H	$PbPh_3$	3.73	7.45	2.60	<0.3	----	----
N	Me	$SiPh_3$	1.79	8.50	2.11	0.3(3H)	----	----
N	Me	$GePh_3$	2.21	8.43	2.21	0.4(3H)	----	----
N	Me	$SnBu_3$	3.30	8.29	2.60	0.7(3H)	----	----

[◇] At room temperature

on the ring heteroatom due to polar structures such as VII, whose importance is expected to increase with increasing electronegativity differences between O and X.

When the temperature is raised above 30° the spectra of radicals V decrease in intensity and are replaced by a new series of spectra, characterised by a doublet splitting of *ca* 8–10 G and a small doublet of 1–4 G, which we assign to VI. These are the only species detectable above 60° and can be seen up to *ca* 150°. The coupling constants (Table 2) are comparable in magnitude with those of the H atom adduct of I.[7] As an example, the spectrum obtained from a melt of $GePh_3H$ and IV at 373°K is shown in Fig. 1.

Compared with Si and Ge, the reaction of stannyl and plumbyl radicals with I–IV is less straightforward. At high temperatures spectra consistent with the expected adducts VI are formed, but no adducts of type V were detected at low temperatures. In fact the spectra of type VI were observable at lower temperatures than those of the Si or Ge analogues. Moreover below room temperature the spectra of the Sn adducts were complicated by the presence of other unidentified species and by an apparent selective line broadening effect.

DISCUSSION

The marked temperature dependence of the reaction pathway found in the reactions of Group IVB radicals with maleic anhydride and its analogues demonstrates the value of performing experiments over as wide a range of temperature as possible. In some of the systems studied there is in fact a range of temperature where no radicals are detectable by ESR. The spectrum of V disappears and VI does not appear until the temperature has been raised by another 30°.

To understand our observations it is necessary to consider the thermodynamic and kinetic factors involved. Of the two possible radical adducts we would expect VI to be the more stabilized. Firstly it is an allylic type system and secondly the M–O bond strengths are greater than those of the corresponding M–C bonds. On the other hand the radical centre in V is probably only stabilized to a small extent by the adjacent CO group. The fact that we see VI rather than V at high temperatures is consistent with these considerations.

Furthermore there is evidence that the activation energy for addition to C=O is higher than for C=C. For example in the addition of silyl radicals to formate esters, ESR spectra of both the adduct and the free silyl radical are detected at low temperatures, whereas only the adduct is seen at high temperatures.[1,2] In contrast the addition of stannyl radicals to C=C double bonds is fast at low temperatures but becomes reversible at ambient temperature;[10] our inability to see a stannyl adduct of type V at −50° suggests that such a species, if formed, is of low stability. In view of the high electron affinity of I–IV, it is possible that the unidentified species found in the reactions with hexabutylditin at low temperatures are formed by a charge-transfer reaction, rather than by radical addition.

Adducts of type V could not be detected also in the case of triphenyllead radicals; the available data on the

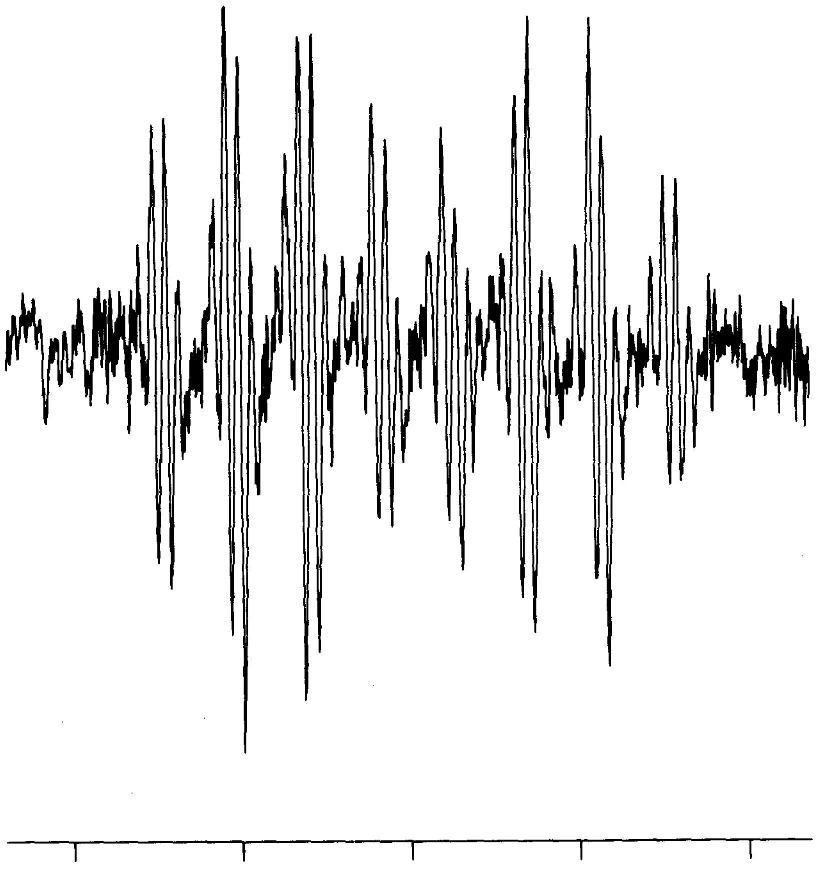


Fig. 1. ESR spectrum of radical VI (X = N, R′ = Me, $MR_3 = GePh_3$) at 373°K. Marks are at 5.0 G spacing.

addition of Pb-centred radicals to alkenes suggest that this may be due to the relatively high endothermicity of this reaction.[10]

The addition of stannyl and plumbyl radicals to the CO group to give VI appears to be more "facile" than the corresponding reactions involving silyl or germyl radicals. This may be connected, as suggested by Wan,[8] with stabilization of the adducts by coordination of the metal with the adjacent ring O atom. However the presence of an adjacent O does not appear to play a vital role, as stannyl radicals do add to one of the CO groups of *p*-benzoquinone to give a detectable ESR spectrum, provided the temperature is raised to 80°.[11]

EXPERIMENTAL

All of the compounds used were commercial samples apart from II which was prepared by a lit method.[12] The radicals were generated by photolysis of the reactants in solns of t-butylbenzene and di-t-butylperoxide 2/1 (v/v). $SiPh_3H$, $GePh_3H$, $SnPh_3H$, $(Bu_3S_n)_2$, and $(Ph_3Pb)_2$ were used as sources of the organometallic radicals. In a few cases better spectra were obtained at high temps by melting a mixture of the anhydride or imide with the organometallic hydride.

A 1 kW high pressure mercury lamp was used for photolysis. ESR spectra were recorded on a Bruker ER-200 spectrometer as previously described.[4]

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