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REGIOSELECTIVE ADDITION REACTION OF GROUP IVB ORGANOMETALLIC RADICALS TO 2,6-DIMETHOXYBENZOQUINONE AND TO SOME SUBSTITUTED PYRAZINES: AN ELECTRON SPIN RESONANCE STUDY

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Summary

The results of an ESR study on the spin adducts derived from the reaction between $\cdot MR_3$ organometallic radicals (M = Si, Ge, Sn, Pb) and 2,6-dimethoxybenzoquinone are reported. For the two heavier Group IVB elements two isomeric radical adducts have been detected, whereas only the less hindered isomer could be observed with silicon or germanium centred radicals.

The results of a similar investigation on the adducts with pyrazine and some of its derivatives are also reported.

Introduction

Addition of transient Group IVB organometallic radicals to the carbonyl oxygen of quinones [1] and to the nitrogen of pyridines [2,3] is known to give persistent paramagnetic adducts which have been widely studied by ESR spectroscopy. Since quinones have two sites susceptible to radical attack, i.e. the two carbonyl groups, the formation of isomeric spin adducts is possible whenever they are made different by unsymmetrical substitution. Although a large variety of quinones have been investigated, there have been only a few studies on unsymmetrical derivatives. These include toluquinone [4], 2,6-dimethylbenzoquinone [5,6] and 2,6-di-t-butylbenzoquinone [6,7], which upon reaction with $\cdot MR_3$ radicals (M = Si, Ge, Sn, Pb) gave only the less hindered isomeric adduct, with the possible exception of the triphenylsilyl adduct of 2,6-di-t-butylbenzoquinone for which the detection by ESR of both isomers has been claimed [6]. On the other hand, the two isomeric forms were unambiguously observed for the Group IVB organometallic spin adducts of 3-meth-

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ylthieno[3,2-b]thiophen-2,5-dione and of benzo[1,2-b;5,4-b′]dithiophen-4,8-dione [5], where the steric crowding at both sites of attack is less serious.

In principle, substitution of alkyls with other groups containing electron-rich atoms capable of coordinating the metal of the attacking radical should induce a stabilization of the most hindered isomer and thus make it detectable [8]. To check whether this is the case we have investigated the addition reaction of triphenylsilyl, triphenylgermyl, tributylstannyl and triphenylplumbyl radicals to 2,6-dimethoxybenzoquinone.

This study was extended to pyrazine and some of its derivatives symmetrically and unsymmetrically substituted with respect to the two heterocyclic nitrogens, namely tetramethyl-, 2,6-dimethyl-, 2-chloro-, and 2,6-dichloro-pyrazine.

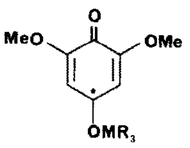
Results and discussion

2,6-Dimethoxybenzoquinone (I)

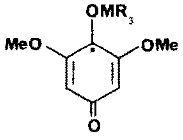
The photoreaction of triphenylsilyl and of triphenylgermyl radicals with 2,6-dimethoxybenzoquinone in t-butylbenzene gives intense and well resolved ESR spectra. In contrast tributylstannyl and triphenylplumbyl radicals under similar condiions give rise to rather weak signals, whose intensity can be substantially enhanced by adding a few drops of hexamethylphosphoric triamide (HMPTA). In the case of the two lighter Group IVB elements the spectra are symmetric and, even at high amplification, indicative of the presence of a single paramagnetic species, showing, beside the coupling with the hydrogens of the methoxy groups, a ca. 1 G triplet splitting due to the two ring protons (see Table 1). With tin and lead centred radicals two species are observed, differing drastically both in their relative concentrations and in the magnitudes of the ring proton coupling, i.e. ca. 0.1 G for the most abundant radical and ca. 3.8 G for the other; satellite lines due to $^{117/119}$Sn and ^{207}Pb were also observable for the former species. As an example, in Fig. 1 is shown the ESR spectrum obtained by reacting hexaphenyldilead with the title quinone, together with its computer simulation.

Since both the number of coupled nuclei and the magnitude of the hyperfine splitting constants are consistent with the structure of the starting quinone, the observed spectra can be safely assigned to the corresponding organometallic adducts.

The identification of the two isomeric radicals can be done straightforwardly on the basis of the ring proton splittings, which should be comparable for the less hindered isomer (A) with $a_{2,6}$ (0.3–0.7 G) and for the more crowded isomer (B) with



(A)



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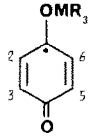
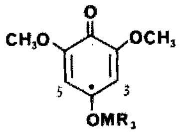


(C)

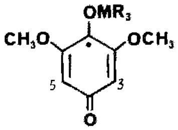
$a_{3,5}$ (4.5–5.8 G) measured in the related organometallic adducts (C) of benzoquinone [4]. It can be therefore concluded that for M = Si or Ge only isomer A is formed, and that for M = Sn or Pb isomer A is predominant but that ca. 17% of isomer B is also present.

TABLE I

HYPERFINE SPLITTING CONSTANTS, THEIR TEMPERATURE COEFFICIENTS, *g* VALUES AND ISOMER RATIOS FOR THE ORGANOMETALLIC ADDUCTS OF 2,6-DIMETHOXYBENZOQUINONE[a]



(A)



(B)

MR_3	Solvent	T (K)	Isomer	$a_{3,5}$	$da_{3,5}/dT$	a_{Me}	da_{Me}/dT	a_M	da_M/dT	g	B/A ratio
$SiPh_3$	BB	296	A	1.11	1.0	1.11	−1.1	–	–	2.0049	< 0.02
$GePh_3$	BB	296	A	0.93	0.4	1.06	−1.2	–	–	2.0048	< 0.02
$SnBu_3$	BB/HMPTA	373	A	0.16	> 0	0.69	−1.6	5.3[b]	–	2.0046	0.20
	(8/1)		B	3.89	1.4	0.40	−1.0	–	–	2.0045	
$PbPh_3$	BB/HMPTA	363	A	< 0.1	–	0.73	−1.5	10.12	36	2.0039	0.19
	(8/1)		B	3.79	–	0.41	–	–	–	2.0032	

[a] All couplings are expressed in Gauss; da/dT are given in mG K^{-1}; BB = t-butylbenzene. [b] At 333 K.

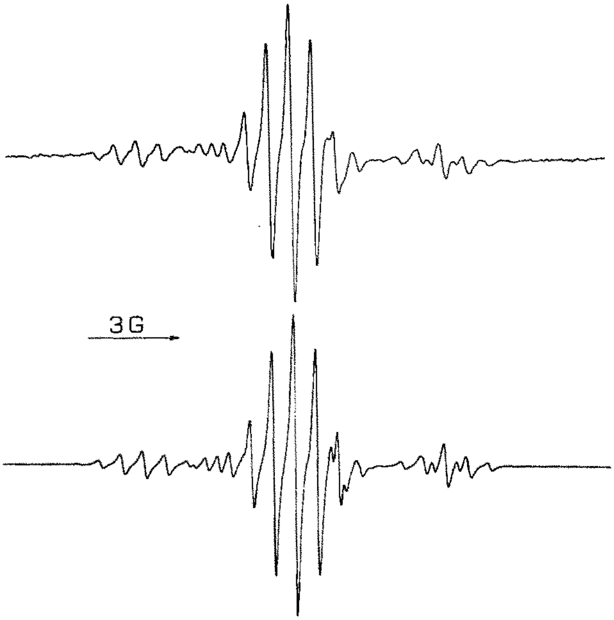


Fig. 1. Experimental (top) and computer simulated (bottom) ESR spectrum of the triphenylplumbyl adduct of I at 363 K.

These results indicate that the regioselectivity of the addition of silyl and germyl radicals to the less hindered carbonyl group is dictated by the steric hindrance exerted by the 2- and 6-methoxy substituents in the neighborhood of the other carbonyl. In the stannyl and plumbyl adducts the presence of also a small amount of isomer B might be the result of either a decrease of the steric repulsion due to the longer metal–oxygen bonds, or a partial stabilization arising from a coordination of the metal atom by the lone pair of a methoxy oxygen. It seems that the former possibility can be discarded in view of previous results for the analogous adducts from 2,6-dimethylbenzoquinone [5,6] and toluquinone [4], where the more crowded isomer was never observed. Since the claimed detection of both isomers in the triphenylsilyl adduct of 2,6-di-t-butylbenzoquinone [6] contrasts with the latter findings, given the larger bulk of t-butyl with respect to methyl, we reinvestigated the addition of $\cdot MR_3$ radicals (M = Si, Ge, Sn, Pb) to this quinone, but in no case were we able to obtain evidence for the presence of a second isomer, even at very high signal amplification.

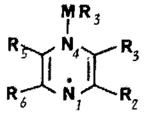
The more likely explanation for the formation of B when M = Sn, Pb is that coordination by one of the adjacent oxygen atoms plays an important role in its stabilization, this being in line with the greater metallic character of the heavier elements of Group IVB. However, since the ESR parameters for adducts B are indicative of the magnetic equivalence of protons 3 and 5 and of the methoxy groups, a rapid (on the ESR time scale) exchange of coordination from one to the other methoxy oxygen must also be assumed.

Pyrazines (II–VI)

It has been shown in previous papers that Group IVB radicals can add across the

TABLE 2

ESR PARAMETERS FOR THE GROUP IVB ORGANOMETALLIC ADDUCTS OF PYRAZINES II–VI [a]



Compound	Solvent	MR$_3$	$a_{N(1)}$	$a_{N(4)}$	$a_{2,6}$	$a_{3,5}$	a_{other}	g	T (K)
II	B	SiPh$_3$	7.25	4.84	0.28	5.86	–	2.0033$_5$	298
II	B	GePh$_3$	7.28	6.37	0.51	5.49	–	2.0033$_7$	298
III	BB	SiPh$_3$	6.10	3.75	0.90 (6H)	6.10 (6H)	–	–	298
IV	BB	SiPh$_3$	6.55	5.02	0.16 (6H)	5.74	–	2.0034$_6$	298
IV	BB	SiEt$_3$	6.45	5.50	< 0.1 (6H)	5.50	–	2.0034$_7$	298
IV	BB	GePh$_3$	6.46	6.46	< 0.05 (6H)	5.42	1.48 (^{13}C) 4.06 (^{13}C) 6.76 (^{13}C)	2.0034$_7$	298
V	BP	SiPh$_3$	6.90	5.30	0.68 (^{35}Cl) 0.74 (1H)	4.72 (1H) 6.78 (1H)	–	2.0033$_2$	418
V	BP	GePh$_3$	6.76	6.66	0.64 (^{35}Cl) 1.08 (1H)	4.22 (1H) 6.20 (1H)	–	–	393
VI	BP	SiPh$_3$	6.77	5.66	0.57 (2^{35}Cl)	5.66	–	2.0037	413
VI	BP	GePh$_3$	6.70	7.12	0.55 (2^{35}Cl)	5.16	–	–	413

[a] B = benzene; BB = t-butylbenzene; BP = biphenyl. All couplings are expressed in Gauss.

carbon–nitrogen bond of heteroaromatic bases as pyridines [2,3]. On this basis pyrazine is expected to be a good trap for organometallic radicals, and as for quinones, its two sites of attack can be made unequivalent by unsymmetrical substitution.

With the purpose of investigating the regioselectivity of the addition reaction of Group IVB radicals to these substrates, we extended the ESR study to use pyrazine (II) and its tetramethyl (III), 2,6-dimethyl (IV), 2-chloro (V) and 2,6-dichloro (VI) derivatives.

Silicon and germanium centred radicals proved to add readily to compounds II–VI with the exception of III which reacted with silyl but not with germyl radicals. With the chloropyrazines V and VI, rather drastic conditions had to be used to produce the adducts, since sufficiently intense ESR signals could be observed only at ca. 400 K. With all the investigated pyrazines we were unable to observe any stannyl or plumbyl adduct even at high temperature.

Table 2 lists the hyperfine splitting constants and *g* factors for the observed radicals. In contrast to the adducts obtained from quinones the assignment of the coupling constants is not straightforward, owing to the presence of two nitrogen atoms exhibiting similar splittings. One of these is practically independent of the nature of the entering MR_3 group, while the other is always ca. 1.4 G larger in the germyl than in the corresponding silyl adduct. Since a similar variation is also shown by the Group IVB adducts of pyridines [3], we assign the latter coupling to the trivalent nitrogen.

The ESR spectra of the unsymmetrically substituted adducts from IV–VI show that only one of the two possible isomeric radicals is formed, although the presence of traces of the second isomer cannot be excluded because of the rather complex spectral pattern characteristic of these species. The observed adduct can be unambiguously identified on the basis of the hyperfine splittings of the protons at the unsubstituted positions; these are expected to be in the range 5 to 6 G if the entering $\cdot MR_3$ radical attacks the less hindered nitrogen, and less than 1 G in the other case. The data of Table 2 clearly indicate that the less crowded isomer is formed in all instances, including the relatively more favorable case of the adduct from the monosubstituted 2-chloropyrazine.

It therefore appears that steric repulsion effects represent the only important factor in determining the regioselectivity of the attack of the organometallic radical toward the less crowded nitrogen, whether the substituent is a methyl group or an electron-rich chlorine atom. It is not possible to establish whether the lack of a stabilizing interaction of silicon or germanium with the chlorines is due to the poor coordinating ability of these two elements or to the strain in the resulting four-membered ring. In this respect it is unfortunate that the reaction with tin and lead centred radicals does not lead to any detectable paramagnetic species, in view of the greater ability of the latter two metals to undergo coordination by suitable elements.

Experimental

All of the compounds used were commercial samples. The radicals were generated by photolysis of the reactants in benzene or t-butylbenzene solutions containing some di-t-butylperoxide. $SiPh_3H$, $GePh_3H$, $(Bu_2Sn)_2$ and $(Ph_3Pb)_2$ were used as sources of $\cdot MR_3$ radicals. In the case of compounds V and VI the photolysis was carried out in molten biphenyl.

A 1 kW high pressure mercury lamp was used as a source of UV light, while the spectra were recorded on a Bruker ER-200 spectrometer.

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