Free Radical Adducts of Tri(cyclohexyl)plumbyl Radicals with α-Dicarbonyl Compounds †

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The addition of lead-centred radicals to five α-dicarbonyl compounds has been investigated by e.s.r. In a number of cases satellite hyperfine lines from ^{207}Pb have been detected. The structures of the adduct radicals are discussed in terms of their e.s.r. spectra; comparison is made with analogous adducts formed by other group 4B radicals.

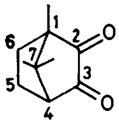
SEVERAL recent publications[1-4] have been concerned with the e.s.r. spectra of transient species formed by the reactions of group 4B metal-centred radicals with carbonyl compounds. It has been established[2] that the ease of addition falls in the order $R_3Si\cdot > R_3Ge\cdot > R_3Sn\cdot$ for a given carbonyl compound and in the order α-diketones > oxalates > ketones > trifluoroacetates > formates > acetates for a given group 4B radical. In comparison, lead-containing species have received little attention. No e.s.r. signals were detected when trimethylplumbyl radicals were generated in the presence of acetone or benzophenone.

The non-formation of adducts of trialkylplumbyl radicals with ketones may be attributed to the weakness of the Pb–O bond. Addition should be easier to carbonyl compounds which give a resonance-stabilized adduct radical. We have recently reported the detection of a paramagnetic adduct in the reaction of tri(cyclohexyl)plumbyl radicals with diethyl mesoxalate,[5] and now present the results of an investigation of the interaction of this Pb-centred radical with the α-dicarbonyl compounds camphorquinone, norcamphorquinone, ethyl pyruvate, biacetyl, and benzil. We have also studied the addition of silyl and stannyl radicals to the first three of these compounds, since these reactions have not been reported previously.

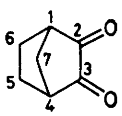
Camphorquinone.—The e.s.r. spectrum obtained from camphorquinone (1) and tri(cyclohexyl)plumbyl radicals was computer-simulated using the values $a_5(exo) = a_6(exo) = 3.14$, $a_4 = 2.51$, and a_7 (*anti*-methyl) $= 0.70$ G. It was very similar in appearance to the spectrum of the semidione radical anion in dimethyl sulphoxide.[6] In addition satellite peaks from ^{207}Pb ($I = \frac{1}{2}$; 21.1%) were apparent, with a coupling constant of 6.2 G. This indicates that the lead-containing moiety is involved in the radical either as a contact ion-pair or chelated by the oxygen atoms of the semidione.

A similar but less well resolved spectrum was observed with tri-n-butylstannyl radicals [$a_5(exo) = a_6(exo) = 2.65$, $a_4 = 3.55$, a_7(*anti*-methyl) $= 0.65$ G], but satellite peaks from ^{117}Sn and ^{119}Sn were not identified. In contrast triethylsilyl radicals gave an intense and complex e.s.r. signal. We have been unable to analyse this in detail but believe it to arise from a mixture of radicals produced by unsymmetrical addition of $Et_3Si\cdot$ to each carbonyl group.

Norcamphorquinone.—This compound (2) proved less reactive than camphorquinone towards group 4B radicals, and although reactions with Si, Sn, and Pb species all gave e.s.r. signals, only that of the plumbyl adduct has been analysed. We find $a_1 = a_4 = a_5(exo) = a_6(exo) = 2.7$ and $a_7(anti) = 6.3$ G; *cf.* 2.49 and 6.47 G for the semidione in dimethyl sulphoxide. Our assignment of the coupling constants for both (1) and (2) is based on Russell and Chang's work on the semidiones.[6]



(1)



(2)

Ethyl Pyruvate.—The reactions of this compound with group 4B radicals have not been investigated previously. As expected, this α-oxo-ester is more reactive than ketones or oxalates, but not as reactive as α-diketones. All the group 4B radicals gave e.s.r. spectra consisting of a large quartet and a small triplet splitting which we attribute to the ketone carbonyl adducts (**3**; X = MR_3). The hyperfine coupling constants are given in Table 1.

TABLE 1

Hyperfine coupling constants (G) for adducts of group 4B radicals with ethyl pyruvate

	$a^{H}_{CH_3}$	$a^{H}_{OCH_2}$	
$\cdot SiEt_3$	17.9	1.2	
$\cdot GeBu_3^n$	15.87	1.3	
$\cdot SnBu_3^n$	14.8	0.9	
$\cdot Pb(C_6H_{11})_3$	12.7	1.5	
·H* *cis*	16.74	1.51	2.23 †
trans	16.41	1.17	1.92

* In propan-2-ol. † Hydroxy-proton.

The silyl adduct was only observed below −30 °C. Above this temperature the spectrum was obscured by a similar signal with an additional doublet splitting due to the hydrogen atom adduct (**3**; X = H). This radical, formed by photochemical reaction of pyruvate with a hydrogen-donating solvent, has been studied by several

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† No reprints available.

[1] A. Hudson and R. A. Jackson, *Chem. Comm.*, 1969, 1323; A. J. Bowles, A. Hudson, and R. A. Jackson, *J. Chem. Soc.* (*B*), 1971, 1947.

[2] J. Cooper, A. Hudson, and R. A. Jackson, *J.C.S. Perkin II*, 1973, 1933.

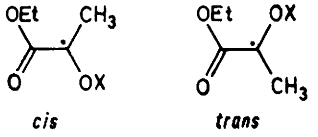
[3] B. Schroeder, W. P. Neumann, and H. Hillgartner, *Chem. Ber.*, 1974, **107**, 3494.

[4] P. J. Krusic, K. S. Chen, P. Meakin, and J. K. Kochi, *J. Phys. Chem.*, 1974, 2036.

[5] G. N. Coppin, A. Hudson, R. A. Jackson, and N. P. C. Simmons, *J. Organometallic Chem.*, 1977, **131**, 371.

[6] G. A. Russell and K. Y. Chang, *J. Amer. Chem. Soc.*, 1965, **87**, 4381.

authors.[7-9] The most detailed interpretation is that of Fessenden and his co-workers,[9] who showed that under high resolution the e.s.r. spectrum of the system in propan-2-ol could be assigned to *cis*- and *trans*-isomers (3; X = H) present in roughly equal amounts. We have included their results in Table 1 for comparison with those for the metal adducts. The spectra of the latter also show clear indications that they arise from a superposition of two isomers, although we have not been able to obtain sufficient resolution to measure separate coupling constants for each conformer. By analogy with the hydrogen adduct, we anticipate that any differences will be small in comparison with the variation in coupling constants amongst Si, Ge, Sn, and Pb, which is our main concern.



(3)

Biacetyl.—This diketone reacts with silyl and germyl radicals to give unsymmetrical adducts with e.s.r. spectra consisting of a quartet of quartets.[2] However, with stannyl radicals one observes a septet from six equivalent protons and a coupling constant close to that of the semidione radical anion; hyperfine satellites from ^{117}Sn and ^{119}Sn are readily detectable. The adduct with tri-n-butylstannyl radicals exhibits linewidth alternation, suggesting a dynamic migration of the tin moiety between the two oxygen atoms.[2] However, with trimethylstannyl radicals no linewidth effect was reported,[3] and a symmetrical *cis*-chelate structure is indicated. It is possible that a symmetrical structure is too sterically hindered to form the potential minimum in the case of tri-n-butylstannyl.

For tri(cyclohexyl)plumbyl radicals with biacetyl we observed a weak e.s.r. spectrum which at −20 °C consisted of a quartet of quartets (8.6 and 2.8 G), indicating an unsymmetrical adduct with migration of the organometallic group slow on the e.s.r. timescale. The difference between the quartet splittings is considerably less than with the triethylsilyl (15.6 and 1.7 G) and tri-n-butylgermyl (14.3 and 2.0 G) adducts.

The formation of an unsymmetrical adduct is probably connected with the bulky nature of the tri(cyclohexyl)plumbyl radical.

Benzil.—At room temperature or below, benzil, like biacetyl, forms an unsymmetrical adduct with triethylsilyl radicals but a symmetrical adduct with trimethylstannyl[3] and tri-n-butylstannyl.[2] We have recently found that germyl radicals occupy an intermediate position. At low temperatures hyperfine coupling is observed to only one phenyl group but at high temperatures migration of the trialkylgermyl group between the two oxygen atoms leads to a time-averaged spectrum with coupling to both rings. A similar effect is found with the silyl adducts but with an increased activation energy. A full account of the lineshapes and kinetics of these dynamic systems has been presented elsewhere.[10]

Tri(cyclohexyl)plumbyl radicals react with benzil in dioxan–benzene at 20 °C to give a spectrum similar in appearance to that of the stannyl adducts but with increased linewidths. The spectrum could be analysed in terms of a 0.95 G septet, a 0.45 G quintet, and a lead satellite splitting of 5.9 G. The proton splittings, assigned to six *ortho*- and *para*-positions and four *meta*-positions, are very close to those in the tri-n-butylstannyl adduct (1.0 and 0.5 G) and in the radical anion. On lowering the temperature to −30 °C some linewidth alternation was apparent, but it was not possible to obtain spectra over a wide enough range of temperatures to study this in any detail.

DISCUSSION

We have established that lead-centred radicals add to α-diketones to give intermediates detectable by e.s.r. Addition has also been observed to an α-oxo-ester (ethyl pyruvate) but no signals were recorded with diethyl oxalate. Plumbyl radicals are therefore less reactive than stannyl radicals, which do add to oxalates.[2] The decreasing reactivity towards carbonyl compounds of group 4B radicals in the series from Si to Pb is illustrated in Table 2.

TABLE 2

Comparison of reactivities * of radicals $R_3M\cdot$ with carbonyl compounds [a]

	$Et_3Si\cdot$	$(Me_3Si)_3Si\cdot$	$Et_3Ge\cdot$	$Bu_3Sn\cdot$	$(C_6H_{11})_3Pb\cdot$
$(MeCO)_2$	+	+	+	+	+
$(CO_2Et)_2$	+	±	±	+	0
Me_2CO	+	±	±	+	0
$CF_3\cdot CO_2Et$	+	−	−	0 [b]	
HCO_2Me	±		−	0	
$MeCO_2Me$	−				

* +, adduct seen; −, $R_3M\cdot$ seen; 0, nothing seen [$Bu_3Sn\cdot$, $(C_6H_{11})_3Pb$, and $Me_3Pb\cdot$ are not expected to be visible].

[a] Results from ref. 2 except for $(C_6H_{11})_3Pb\cdot$. [b] $CF_3\cdot CO_2$ Me. [c] $Me_3Pb\cdot$ used.

The comparison of lead with the other group 4B elements is most straightforward for ethyl pyruvate; in each case a similar spectrum was observed. The most obvious feature is the systematic decrease in methyl proton splitting on going down the group, indicating a reduction in spin density on the radical carbon atom. Similar trends are also apparent in the other series but these are complicated by the effects of migration of the organometallic group and steric effects. The bulky nature of the tri(cyclohexyl)plumbyl group probably accounts for the detection of unsymmetrical adducts in situations where tin forms symmetrical species.

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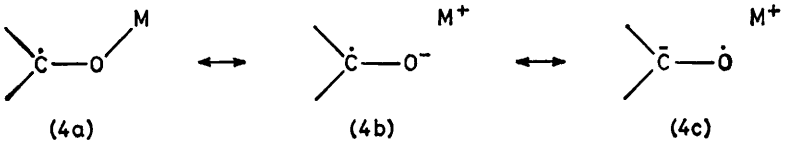
[7] T. Fujisawa, B. M. Monroe, and G. S. Hammond, *J. Amer. Chem. Soc.*, 1970, **92**, 542.

[8] N. H. Anderson, A. J. Dobbs, D. J. Edge, R. O. C. Norman, and P. R. West, *J. Chem. Soc.* (*B*), 1971, 491.

[9] A. Samuni, D. Behar, and R. W. Fessenden, *J. Phys. Chem.*, 1973, **77**, 777.

[10] A. Alberti and A. Hudson, *Chem. Phys. Letters*, 1977, **48**, 331.

The diminished proton coupling constants can be regarded as arising from a redistribution of spin density within the carbonyl group, consistent with increased ionic character for the oxygen–metal bond. In valence-bond terms we can represent this by increased participation of the ionic forms (4b) and (4c) in the resonance hybrid. Any contributions from (4c) will decrease the spin density on the carbon atom. There are obvious analogies with the well documented effects of solvent and ion-pairing on the coupling constants of ketyls [11] and isoelectronic nitroxide radicals.[12]



The ionic nature of the lead adducts is reflected in the coupling constants of the camphorquinone and norcamphorquinone radicals, which are very close to those of the corresponding semidiones. However, the detection of lead hyperfine satellites indicates that the organometallic group is involved in the observed radical and that the reaction is not simply one of electron transfer. Either a tight (contact) ion-pair or a chelated complex is consistent with the available data. Neumann and his co-workers [3] favour a chelated structure for the benzil–trimethylstannyl adduct because the tin hyperfine coupling exhibits no marked temperature dependence. The tri(cyclohexyl)plumbyl–benzil adduct shows evidence of line-broadening, suggesting a dynamic equilibrium with a time-averaged symmetrical structure, but the spectrum could not be obtained over a wide enough range of temperatures to examine this point in detail.

EXPERIMENTAL

The e.s.r. spectra were recorded with a Varian E3 spectrometer, with variable temperature accessory. Samples were irradiated *in situ* with an Osram 250 W high-pressure mercury lamp and quartz lens system.

Camphorquinone, norcamphorquinone, and hexa(cyclohexyl)diplumbane were prepared by standard procedures. All other compounds used were obtained commercially.

Samples containing triethylsilane or hexa-n-butyldistannane were a mixture of group 4B compound with di-t-butyl peroxide in the ratio 1 : 2 (v/v), with approximately 5—10 mg of carbonyl compound per ml of the above mixture. For reactions involving plumbyl radicals most samples were dissolved in benzene or toluene with proportions of dilead to carbonyl compound *ca.* 3 : 1 (w/w), and 5 mg of carbonyl compound per ml of solvent.

[7/500 *Received*, 21*st March*, 1977]

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[11] P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, 1963, 5412; R. Wilson, *J. Chem. Soc.* (*B*), 1968, 84.

[12] R. Brière, H. Lemaire, and A. Rassat, *Bull. Soc. chim. France*, 1965, 3273.