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Preliminary communication

ELECTRON SPIN RESONANCE SPECTRA AND STRUCTURES OF THE BUTYLCHLOROTIN DERIVATIVES OF BUTANE-2,3-SEMIDIONE, $Bu_nCl_{3-n}SnOCMeCMeO^{\bullet}$

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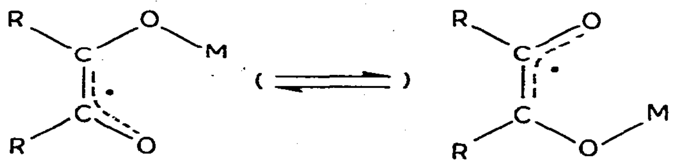
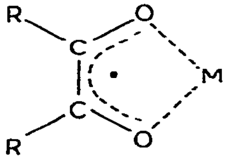
Summary

The ESR spectra of the radicals $Bu_nCl_{3-n}SnOCMeCMeO^{\bullet}$ are interpreted to imply that when $n = 0$ or 1, the biacetyl acts as a *cis*-bidentate ligand. When $n = 2$ it is (probably *cis*) monodentate. When $n = 3$ it can act as both a *cis*- and a *trans*-monodentate ligand; the former is rapidly fluxional and the latter is more slowly fluxional on the ESR time scale.

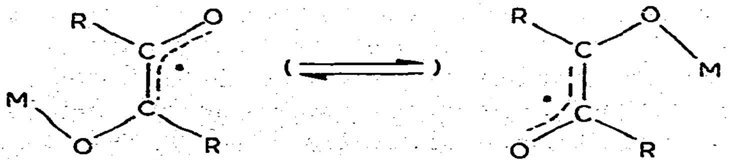
The metallic derivatives of semidiones have been studied extensively [1]; the various structures which have been considered to be important in non-polar solvents are illustrated in formulae I—V.



(I) (II)



(III)



(IV) (V)

It is usually assumed that the ESR spectra of the rapidly equilibrating monodentate *cis*-derivatives I and II would be indistinguishable from that of the static bidentate derivative III and that the two groups R in III would be magnetically equivalent. We show here that neither assumption necessarily holds when M represents a metal carrying further ligands. The structure III can then lack C_{2v} symmetry and the ESR spectra can distinguish between these various possible structures; we illustrate this for the case of the butylchlorotin derivatives of biacetyl.

The radicals were generated in the ESR cavity by the reactions shown in equations 1 [2], 2, and 3 [3,4].

$$\mathrm{Bu}_n\mathrm{Cl}_{3-n}\mathrm{SnC_5H_5} \rightarrow \mathrm{C_5H_5}^{\bullet} + \mathrm{Bu}_n\mathrm{Cl}_{3-n}\mathrm{Sn}^{\bullet} \xrightarrow{\mathrm{O{=}CMeCMe{=}O}}$$

$$(n = 0\text{—}3) \qquad \mathrm{Bu}_n\mathrm{Cl}_{3-n}\mathrm{SnOCMeCMeO}^{\bullet} \qquad (1)$$

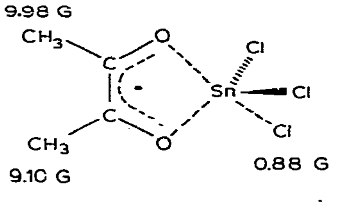
$$\mathrm{Bu}_n\mathrm{Cl}_{3-n}\mathrm{SnOCHMeCMe{=}O} \xrightarrow{t\text{-BuO}^{\bullet}} \mathrm{Bu}_n\mathrm{Cl}_{3-n}\mathrm{SnOCMeCMeO}^{\bullet} \qquad (2)$$

$$(n = 1\text{—}3)$$

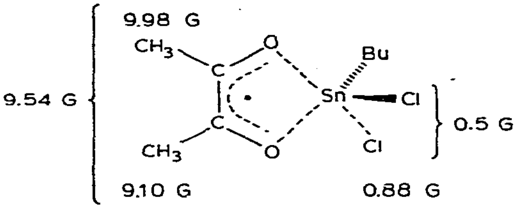
$$\mathrm{Bu_3SnSnBu_3} + \mathrm{O{-}CMe{=}CMe{=}O} \xrightarrow{h\nu} \mathrm{Bu_3SnOCMeCMeO}^{\bullet} \qquad (3)$$

When $n = 0$—2, concordant results were always obtained from reactions 1 and 2, but when $n = 3$, the spectra of the radicals depended on their source.

At −20°C, the spectrum of the radical $\mathrm{Cl_3SnOCMeCMeO}^{\bullet}$ showed hyperfine coupling to two non-equivalent methyl groups, and one unique chlorine atom. Among the structures I—V, this is best compatible with structure III in which the chlorine occupies an apical site at approximately trigonal bipyramidal tin, and the biacetyl moiety bridges apical and equatorial positions, as shown in VI.



(VI)



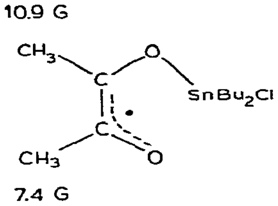
(VII)

Above about +10°C, the spectrum changed but became too weak to analyse in detail.

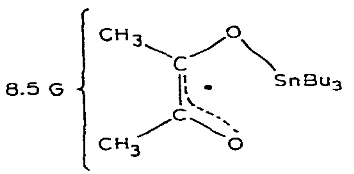
Similarly at low temperature, the spectrum of the radical $\mathrm{BuCl_2SnOCMeCMeO}^{\bullet}$ showed the presence of two non-equivalent methyl groups and one unique chlorine atom, as shown in VII, but at +20°C, the spectrum showed two equivalent methyl groups and two equivalent chlorine atoms. We conclude that in the structures VI and VII, positional exchange occurs between the ligands about the tin above +20°C, to render the methyl and chloro groups equivalent on the ESR time scale; in VI, the coupling by three chlorine atoms (75% $^{35}\mathrm{Cl}$, 25% $^{37}\mathrm{Cl}$, both with $I = 3/2$) renders the spectrum too complicated to be readily interpreted.

Structures VI and VII are important in that they can be regarded as models for the intermediates involved in homolytic substitution at a tin centre.

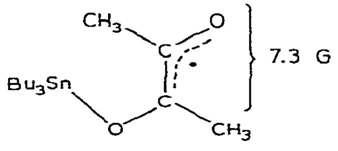
In contrast, the radical $Bu_2ClSnOCMeCMeO^{\bullet}$ over the range of temperature which could be covered (−50 to 0°C) showed the presence of two non-equivalent methyl groups, and no hyperfine coupling to chlorine. This would be compatible with either a monodentate or bidentate structure, but the absence of chlorine coupling, and the larger difference between the coupling constants of the two methyl groups seems best ascribed to the monodentate *cis*-structure VIII. This would be reasonable in view of the drop in Lewis acidity as the chloro ligands are replaced by alkyl groups*.



(VIII)



(IX)



(X)

The various routes to the radicals $Bu_3SnOCMeCMeO^{\bullet}$ showed the spectra of two radicals whose relative concentrations were dependent on the source and the temperature. One spectrum consisted of a regular septet, a(6H) 8.5 G, with a(^{119}Sn) varying from 11.0 G at −110°C to 8.5 G at +20°C. The second, with a slightly higher g-value, showed a(6H) 7.3 G [3,4] but it had such a severe alternating line width effect that it often appeared as a doublet with separation 14.6 G**. Structure III would not show an alternating line width effect, it seems unlikely that a(^{119}Sn) in III should be strongly temperature dependent, and the Bu_3SnO group is less prone to 5-coordination than Bu_2ClSnO. We therefore assign the former of these two septets to the rapidly equilibrating structures I $\rightleftharpoons$ II as shown in IX***, in which hyperconjugative coupling to tin would increase at low temperature.

The spectrum with a(6H) 7.3 G, showing a pronounced alternating line width effect, would then be ascribed to the more slowly equilibrating structure X.

Acknowledgement

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*For example, in $Bu_2ClSnOMe$, the dimer is in equilibrium with the monomer in dilute solution [6].

**A similar alternating line width effect is observed in the spectrum of IV $\rightleftharpoons$ V (M = H) in aqueous solution at pH 2 [7].

***Similarly, in the adducts of tin radicals with 3,6-di-t-butyl-o-benzoquinone, the R_3Sn group appears to be more mobile than the R_2SnCl group [8—11].

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