Photolysis of Cyclopentadienyltin Compounds: a New Source of Tin-centred Radicals

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Summary η^1-Cyclopentadienyltin(IV) compounds and bis-(η^5-cyclopentadienyl)tin(II) are photolysed to give the cyclopentadienyl radical, and the former process provides a useful new route to tin(III) radicals.

Recent work has shown that whereas the diamagnetic metallocenes, $(\eta^5\text{-}C_5H_5)_2M$ (M = Fe, Ru, or Co$^+$) are photostable,[1] the alkylmetallocenes of the titanium group, $(\eta^5\text{-}C_5H_5)_2MR_2$ (M = Ti, Zr, or Hf)[2] and $(\eta^5\text{-}C_5H_5)_3ThPr^i$[3] are photolysed with homolysis of the metal–alkyl σ-bond. We report here that, in contrast, both $\eta^1\text{-}C_5H_5Sn^{IV}$ and $\eta^5\text{-}C_5H_5Sn^{II}$ compounds are readily photolysed with preferential loss of the cyclopentadienyl group, and that the former reaction provides a useful new route to a series of Sn^{III} radicals.

If the $\eta^1\text{-}C_5H_5$ compounds $(C_5H_5)_4Sn$, $(C_5H_5)_2SnBu_2$, $C_5H_5SnBu_3$, and $(C_5H_5)_3SnCl$ are photolysed in an inert solvent in the cavity of an e.s.r. spectrometer, they all show a strong spectrum of the cyclopentadienyl radical $C_5H_5\cdot$, a(5H) 5·9 G (*e.g.*, Figure 1). No spectrum of the butyl radical could be detected with the compounds $(C_5H_5)_2SnBu_2$ and $C_5H_5SnBu_3$.

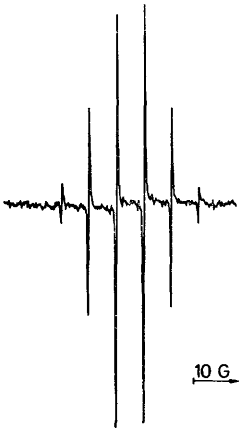

Figure 1. E.s.r. spectrum of the cyclopentadienyl radical formed by the photolysis of tricyclopentadienyltin chloride in cyclopentane at −60 °C.

The e.s.r. spectra of non-persistent tin(III) radicals in solution are difficult to observe, and attempts to use the high power conditions necessary were unsuccessful with the present compounds because the spectrum of the cyclopentadienyl radical, which overlies that of the tin radicals, is difficult to saturate. However, all these systems show the characteristic reactions of tin(III) radicals. For example, photolysis of $(C_5H_5)SnBu_3$ in ethylene as solvent shows the spectrum of the β-tributylstannylethyl radicals, $Bu_3SnCH_2CH_2\cdot$, $a(2H_\alpha)$ 19·6, $a(2H_\beta)$ 16·0 G at −90 °C, and photolysis in the presence of alkyl bromides shows the characteristic spectra of the corresponding alkyl radicals. The reactions which are involved are illustrated in equations (1)—(3).

$$\eta^1\text{-}C_5H_5SnR_3 \xrightarrow{h\nu} C_5H_5\cdot + \cdot SnR_3 \qquad (1)$$

$$R_3Sn\cdot + CH_2{=}CH_2 \rightleftharpoons R_3SnCH_2CH_2\cdot \qquad (2)$$

$$R_3Sn\cdot + R'Br \rightarrow R_3SnBr + R'\cdot \qquad (3)$$

In reaction (3), unless the concentration of the alkyl bromide is very low, the spectrum of the cyclopentadienyl radical is broadened presumably by an exchange process, and the spectrum of the radical $R'\cdot$ can be observed in isolation. An example with an intermediate concentration of ethyl bromide is shown in Figure 2.

Reagents of this type provide a useful alternative to the hexa-alkylditins[4] for the photolytic generation of $R_3Sn\cdot$ radicals, and should make accessible for the first time a variety of other radicals $X_3Sn\cdot$, as the precursors $C_5H_5\text{-}SnX_3$ can readily be prepared by reaction (4).

$$(C_5H_5)_4Sn + 3HX \rightarrow C_5H_6 + C_5H_5SnX_3 \qquad (4)$$

E.s.r. experiments with the π-bonded compound $(\eta^5\text{-}C_5H_5)_2Sn^{II}$ are less convenient because it is only slightly soluble in non-polar solvents, and a yellow solid separates during photolysis. However, photolysis of a solution in toluene again gave a spectrum of the cyclopentadienyl

FIGURE 2. E.s.r. spectrum of the ethyl radical formed by the photolysis of tributyl(cyclopentadienyl)tin in the presence of ethyl bromide in cyclopropane at −90 °C. The broadened lines of the cyclopentadienyl radical in the centre of the spectrum are lost if the concentration of ethyl bromide is increased.

radical, but now the addition of ethyl bromide served only to broaden the spectrum, and no signals due to the ethyl radical could be detected. We conclude that again photolysis results in cleavage of the cyclopentadienyl group from tin [equation (5)], but the fate of the Sn^I radical is uncertain.

$$(\eta^5\text{-}C_5H_5)_2Sn^{II} \rightarrow C_5H_5Sn\cdot + C_5H_5\cdot \qquad (5)$$

This reaction is parallel to the photolysis of the σ-bonded sterically-hindered dialkyltin compound $[(Me_3Si)_2CH]_2Sn^{II}$ which has been studied by Lappert and his co-workers,[5] but in that case only the spectrum of the persistent tin(III) radical $[(Me_3Si)_2CH]_3Sn\cdot$ is observed; again the fate of the Sn^I fragment is unknown.

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