Chemistry of Organoditins. Trapping of Radicals Generated from Organic Halides[1]

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Summary Triphenyltin and tri-n-butyltin radicals generated photochemically from the corresponding hexaorganoditins abstract halogen atoms from alkyl halides; the fate of these alkyl radicals can be modified by the nature and concentration of hydrogen atom donors present.

We have shown previously that the reduction of organic halides by organotin hydrides proceeds by a free-radical chain mechanism, the propagating steps of which are generally considered to be those in equations (1) and (2).[2,3] This reaction has proved to be useful in the study of free radicals because of its convenience and the normally high yield of reduction products.[4] The rate of reaction (2) is fairly insensitive to the nature of R· and k_1 is *ca.* 10^6 l mol^{-1} s^{-1} [5] Because of the high value of this rate constant

$$\text{Sn}\cdot + \text{R–X} \xrightarrow{k_t} \text{SnX} + \text{R}\cdot \tag{1}$$

$$\text{R}\cdot + \text{SnH} \xrightarrow{k_1} \text{Sn}\cdot + \text{R–H} \tag{2}$$

$$\text{R}\cdot \xrightarrow{k_r} \text{R}'\cdot \tag{3}$$

$$\text{R}'\cdot + \text{SnH} \xrightarrow{k_2} \text{Sn}\cdot + \text{R}'\text{H} \tag{4}$$

certain free radicals can be trapped, equation (2), in competition with secondary transformations, equation (3), and their rates can thus be estimated from the amounts of R–H and R′–H formed.[4,5] However, if the rate of the secondary transformation of R· is slow ($k_r << k_1$ [SnH]) it cannot be detected. In order to detect such a process the trapping agent must be less reactive than the organotin hydride. This requires generation of the organotin radicals from some source other than the hydride. We report herein that organotin radicals generated from organoditins can be used for this purpose.

Organoditins react with organic halides thermally,[6] under catalysis by peroxides[6a] and copper metal,[7] and under photoinitiation.[8] Reaction takes place readily upon irradiation of a mixture of a simple organic halide with an organoditin in a Pyrex vessel, and in a hydrogen donor solvent, the major reaction is that shown in equation (4). Results

$$\text{Sn–Sn} + 2\,\text{RX} \xrightarrow{\text{R}'\text{H}} 2\,\text{SnX} + 2\,\text{RH} \tag{4}$$

from experiments with hexaphenylditin and 1-iodo-octane in diethyl ether, with concentrations of reactants of *ca.* 0·1—2M are in the Table. In these reactions all the ditin and >98% of the iodide were consumed. 85—88% of the octyl fragments were found as n-octane, the major product, and as oct-1-ene.† However, the proportion of the latter decreases from 17·5 to 6·2% in the three experiments as the proportion of ether in the reaction mixture increases, and this is accompanied by an increase in the proportion of n-octane. Thus, most of the octyl radicals formed in the reaction undergo hydrogen abstraction at the expense of fragmentation and coupling,‡ and this process becomes even more predominant as the proportion of ether in the reaction mixture increases. This suggests that most of the hydrogen abstraction occurs from the ether, as would be expected, although some could occur from hydrocarbon and iodide. When tri-n-butyltin hydride was allowed to react with 1-iodoheptane, hept-1-ene was not detected among the products.[2] The presence of phenyl radicals in the reaction mixture is indicated by the formation of small amounts of iodobenzene and benzene, presumably by abstraction of iodine from the iodo-octane and of hydrogen from alkyl groups. The phenyl radicals are probably formed by the fragmentation (5) of triphenyltin radicals. This fragmentation is characteristic of the photoinduced reactions of

$$\text{Ph}_3\text{Sn}\cdot \rightarrow \text{Ph}_2\text{Sn} + \text{Ph}\cdot \tag{5}$$

hexaphenylditin and of hexa-n-butylditin with organic halides.§ It has also been observed in the photolysis of tetraphenyltin, and has been attributed to the intermediacy of 'hot' triphenyltin radicals.[9] This question will be considered more explicitly elsewhere.

TABLE

Photoinduced reaction of hexaphenylditin with 1-iodo-octane[a,b]

Experiment	1	2	3
Reactants (mmol)			
Et_2O	1·35	6·88	18·9
$Ph_3SnSnPh_3$	0·521	0·584	0·750
n-$C_8H_{17}I$	1·10	1·25	1·35
n-$C_8H_{17}I$ consumed	0·954	0·990	·0992
Products (mmol)			
Oct-1-ene	0·167	0·090	0·062
n-C_8H_{18}	0·642	0·780	0·815
C_6H_6	trace	0·026	0·083
PhI	trace	0·010	0·026

[a] Irradiation for 24 h in Pyrex vessels. All the ditin was consumed in these experiments.

In an experiment under the same conditions as those described above 1,3-di-iodopropane (1·57 mmol) and hexa-n-butylditin (1·50 mmol) were irradiated in benzenethiol (11·7 mmol). The C_3 products found were 1-iodopropane (87%) and propane (6·7%), indicating that the predominant

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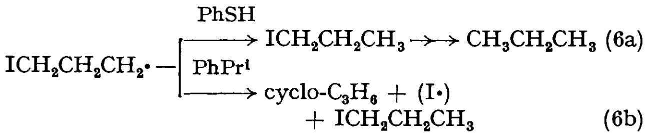
† The products of the reactions described in this report were characterized by gas chromatographic retention times as well as by i.r. and/or n.m.r. spectroscopy.

‡ Hexadecane would be expected as a product of coupling of octyl radicals.

§ The fact that such products are not normally observed in photoinduced reactions of organotin hydrides with organic halides may indicate that the mechanisms of the reactions differ.

fate of the initially formed iodopropyl radicals was that shown in equation (6a); they were effectively trapped by reaction with the efficient hydrogen atom donor, PhSH.



$$ICH_2CH_2CH_2\cdot - \begin{cases} \xrightarrow{PhSH} ICH_2CH_2CH_3 \rightarrow\rightarrow CH_3CH_2CH_3 & (6a)\\ \xrightarrow{PhPr^i} \text{cyclo-}C_3H_6 + (I\cdot) + ICH_2CH_2CH_3 & (6b)\end{cases}$$

On the other hand, when the less efficient hydrogen donor, cumene (9·51 mmol) was allowed to react with the di-iodide (1·26 mmol) and hexa-n-butylditin (1·26 mmol) 1-iodopropane (26%), cyclopropane (23·5%), and only a trace of propane were produced.¶ In this case the iodopropyl radical has a long enough lifetime to form cyclopropane by a probable intramolecular S_H reaction in competition with hydrogen abstraction from solvent, equation (6b).

The above reactions show that the lifetimes of organic free radicals generated by reaction with organotin radicals originating from ditins can be controlled by varying the nature and concentration of hydrogen atom donors. This technique complements the use of organotin hydrides, and extends the range of secondary transformations of the radicals which can be studied to those with smaller rate constants. Because the reactions are initiated photochemically they can be examined over a wide range of temperatures, and it should be possible to obtain relative activation parameters for the competing processes, and to exert additional control over the course of the overall reaction. Indeed hexa-n-butylditin has been used as a source of free radicals for use in a novel method for determination of relative activation energies for various RX compounds in reaction (1) by a novel e.s.r. technique.[10] Other e.s.r. studies have also been conducted using ditins as the source of free radicals.[11]

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¶ Other reaction products included n-butane, but-1-ene and tri-n-butylstannylphenylthiostannane.

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