Homolytic Substitution at Tin by the Succinimidyl Radical

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Summary *N*-Bromosuccinimide readily reacts with tetra-alkyltin compounds by a free-radical chain mechanism involving bimolecular homolytic substitution by the succinimidyl radical at tin in one of the propagation steps.

AN INCREASING number of organometallic reactions are being recognised to follow a mechanism involving bimolecular homolytic substitution (S_H2) at the metallic centre (Equation 1).[1]

$$X\cdot + MR_n \rightarrow R\cdot + XMR_{n-1} \quad (1)$$

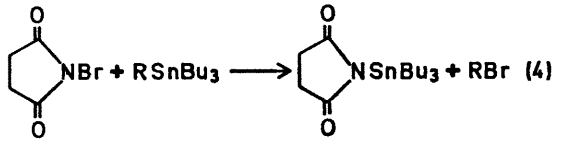
There are few unambiguous examples of an S_H2 reaction occurring at a tin centre, and no quantitative data pertaining to the rate of such a process is available. For example, homolytic substitution at tin is probably involved in the photoinitiated reactions of a hexa-alkylditin with trifluoroiodomethane[2] or with oxygen.[3] Triethyltin benzoate is a product of the thermal decomposition of benzoyl peroxide in the presence of tetraethyltin, and this was interpreted in terms of S_H2 attack of a benzoyloxy radical at tin.[4]

$$(PhCO_2)_2 \rightarrow 2PhCO_2\cdot \quad (2)$$

$$PhCO_2\cdot + SnEt_4 \rightarrow PhCO_2SnEt_3 + Et\cdot \quad (3)$$

We now report that *N*-bromosuccinimide reacts with tetra-n-butyltin and with benzyltri-n-butyltin by a free-radical chain mechanism involving bimolecular homolytic substitution by the succinimidyl radical at the tin centre.

N-Bromosuccinimide reacts with tetrabutyltin in acetone at 35° to give butyl bromide (quantitatively) and *N*-tributylstannyl succinimide† (Equation 4; R = Bu); only



(4)

† The stannylsuccinimide has also been prepared by azeotropic dehydration of a mixture of bistributyltin oxide and succinimide in toluene; satisfactory analyses, and n.m.r., and i.r. spectra have been obtained.

one group is cleaved, even in the presence of a three-fold excess of *N*-bromosuccinimide. The reaction was studied preparatively, and followed kinetically by n.m.r. spectroscopy by integrating the signal of the α-methylene protons of butyl bromide.

Initially, the reaction was first-order with respect to tetrabutyltin (0·05—0·40M), and independent of *N*-bromosuccinimide (0·125—1·00M). At any stage, the reaction could be initiated by t-butyl hyponitrite, and totally inhibited by galvinoxyl (or oxygen); the induction period was then proportional to the galvinoxyl concentration, and if it is assumed that one molecule of inhibitor removes one chain-carrying radical[5] the rate of initiation, R_i, could be derived from the expression

$$R_i = [\text{galvinoxyl}]_{t=0}/\text{induction period.}$$

The overall rate of there action was shown to be proportional to $(R_i)^{\frac{1}{2}}$.

$$\text{Initiation} \rightarrow \text{S}\cdot \text{ (Rate } R_i) \quad (5)$$

$$\text{Propagation} \quad \text{S}\cdot + \text{RSnBu}_3 \xrightarrow{k_6} \text{SSnBu}_3 + \text{R}\cdot \quad (6)$$

$$\text{R}\cdot + \text{SBr} \xrightarrow{k_7} \text{RBr} + \text{S}\cdot \quad (7)$$

$$\text{Termination} \quad 2\text{S}\cdot \xrightarrow{2k_8} \quad (8)$$

$$\text{S}\cdot + \text{R}\cdot \xrightarrow{2k_9} \quad (9)$$

$$\text{S}\cdot = \text{succinimidyl} \quad 2\text{R}\cdot \xrightarrow{2k_{10}} \quad (10)$$

(8), (9), (10): non-radical products

These results are compatible with the overall reaction scheme shown in Equations (5)—(10) (R = Bu), in which the rate-determining propagating step is the displacement of a butyl radical from tetrabutyltin by a succinimidyl radical (Equation 6), and termination is solely by the bimolecular self-reaction of succinimidyl radicals (Equation 8), the other possible termination processes being insignificant at the concentrations studied.

Application of the steady-state approximation to this reaction scheme gives

$$\frac{\text{d[BuBr]}}{\text{d}t} = \frac{-\text{d[Bu}_3\text{SnR]}}{\text{d}t} = k_6\left(\frac{R_i}{2k_8}\right)^{\frac{1}{2}}[\text{Bu}_3\text{SnR}] \quad (11)$$

The value of $k_6/(2k_8)^{\frac{1}{2}}$ can then be derived, and if termination is assumed to occur at a limiting rate,[5] with $2k_8$ equal to approximately 2×10^9 l mole^{-1}sec^{-1}, a rough value for k_6 of 8×10^3 l mole^{-1}sec^{-1} at 35° is obtained.

A similar study was carried out with benzyltributyltin, when the benzyl group was cleaved selectively and quantitatively (Equation 4; R = $PhCH_2$), reflecting its greater stability as a radical. The reaction could again be initiated with t-butyl hyponitrite, but galvinoxyl was ineffective as an inhibitor; the reaction could be inhibited by 2,6-di-t-butyl-4-methoxyphenol, but reliable values of R_i could not be obtained because the phenol reacted rapidly with *N*-bromosuccinimide.

At low concentrations of $PhCH_2SnBu_3$ (< 0·25M), the reaction was first-order with respect to the benzyltributyltin, and zero-order with respect to *N*-bromosuccinimide; the mechanism under these conditions is therefore similar to that for tetrabutyltin in which termination occurs exclusively by the combination of two succinimidyl radicals (Equation 8).

At high concentrations (>0·50M), however, the reaction is zero-order in benzyltributyltin, and first-order with respect to *N*-bromosuccinimide; termination is now by the combination of two benzyl radicals (Equation 10; R = $PhCH_2$), and the overall rate equation assumes the form

$$\frac{\text{d[PhCH}_2\text{Br]}}{\text{d}t} = \frac{-\text{d[PhCH}_2\text{SnBu}_3\text{]}}{\text{d}t} = k_7\left(\frac{R_i}{2k_{10}}\right)^{\frac{1}{2}} \times [N\text{-bromosuccinimide}] \quad (12)$$

As R_i could not be determined directly, the value of k_6 for benzyltributyltin was determined by competition experiments with tetrabutyltin and benzyltributyltin, whence k_6 for benzyltributyltin was estimated to be about $1{\cdot}2 \times 10^5$ l mole^{-1}sec^{-1}, and k_7, the rate of abstraction of bromine from *N*-bromosuccinimide by the benzyl radical, to be about 6×10^5 l mole^{-1}sec^{-1}, both at 35°, again assuming diffusion control of the termination processes.[5]

It has been reported previously that *N*-bromosuccinimide reacts with tetraphenyltin in refluxing carbon tetrachloride to give bromobenzene, and some evidence for a rapidly hydrolysed *N*-triphenylstannylsuccinimide was found.[6] More recently a similar reaction between *N*-bromosuccinimide and trimethyl-*p*-tolyltin has been reported in which the *p*-tolyl group was selectively cleaved.[7] For none of these reactions was the mechanism discussed, and indeed heterolytic (electrophilic) cleavage of the arylcarbon–tin bond is a possibility in these cases.

Although it was originally suggested that the succinimidyl radical was involved in allylic bromination by *N*-bromosuccinimide, this was later shown to be incorrect,[8] and the only clear demonstration of its involvement as a chain-carrying species (in the oxidation of 1-phenylethanol) was obtained recently.[9]

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