Homolytic Organometallic Reactions. Part VIII.[1,2] Kinetics of the Homolytic Reaction between *N*-Halogenosuccinimides and Tetra-alkyltins

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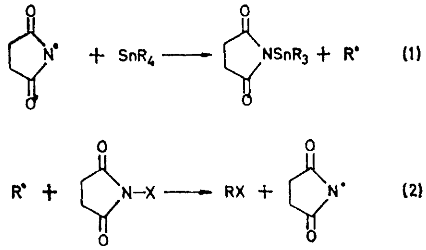
N-Halogenosuccinimides react with tetra-alkyltins by a radical chain mechanism to give the corresponding alkyl halides and *N*-trialkylstannylsuccinimides. Rate constants for the homolytic attack of the succinimidyl radical at the tin centre have been measured, and interpreted in terms of steric hindrance towards the formation of a 5-co-ordinate transition state, and of electronic stabilisation of the displaced radical. Rate constants for the abstraction of chlorine, bromine, or iodine from the corresponding *N*-halogenosuccinimide by benzyl and propyl radicals have also been determined.

It is well established that the N–X bond (X = halogen) in *N*-halogenosuccinimides can react by both homolytic and heterolytic mechanisms. Bromodehydrogenation at allylic or benzylic carbon by *N*-bromosuccinimide is a radical chain process, which was originally believed to involve hydrogen abstraction by the succinimidyl radical,[3] but it is now generally accepted that bromine atoms are the attacking species.[4] The only reaction in which the succinimidyl radical has been established to be a chain-carrying species appears to be the oxidation of 1-phenylethanol to acetophenone by *N*-iodosuccinimide.[5]

Kupchik and Lanigan[6] reported that tetraphenyltin reacts with *N*-bromosuccinimide to give bromobenzene and, probably, *N*-triphenylstannylsuccinimide. This might be represented as a radical chain process involving bimolecular substitution by the succinimidyl radical at the tin atom [equations (1) and (2); R = Ph, X = Br], and it was to examine this possibility that the present work was started.



We find that phenyltin compounds react in all probability by a polar process, but that tetra-alkyltins do react homolytically by equations (1) and (2) (R = alkyl, X = Cl, Br, or I).† Absolute rate constants for the S_H2 reaction (1) have been obtained for a variety of alkyl groups, R, and relative (and one absolute) rate constants for the halogen-abstraction reaction (2) (X = Cl, Br, or I).

EXPERIMENTAL

N.m.r. spectra were recorded at 35°, using a Perkin-Elmer R12 60 MHz spectrometer. G.l.c. analyses were carried out with a Perkin-Elmer F11 instrument, with a 2 m column of 15% squalane on Chromosorb B, balanced against an Antarox 6 column, at 90—140°.

Reactants.—Tetra-alkyltins were either commercial products (B.D.H. or K. and K.), or were prepared from the appropriate Grignard reagent and tin tetrachloride or trialkyltin chloride. They were distilled under reduced pressure, and, before use, were degassed under reduced pressure and flushed with nitrogen. Benzyltributyltin showed b.p. 192—194° at 24 mmHg, τ 3·05 (5H, s, C_6H_5), 7·05 (2H, s, $PhCH_2$), and 8·1–9·5 (27H, Bu_3Sn).

The *N*-halogenosuccinimides were commercial products which were recrystallised from dioxan or toluene before use, and stored under nitrogen.

Products.—The alkyl halides were identified by g.l.c. N.m.r. spectra showed that the yields of alkyl halides were always >90% and, from the reactions of tetrapropyltin, tetrabutyltin, and benzyltributyltin, >95%. *N*-Tributylstannylsuccinimide was identified by comparison with an authentic sample which was prepared as follows.

A mixture of bis(tributyltin) oxide (18 g) and succinimide (6 g) in toluene (60 ml) was heated under a Dean and Stark water separator. After 2 h, the solvent was removed under reduced pressure, leaving a white, moisture-sensitive solid, which was recrystallised from pentane at −80° to give N-*tributylstannylsuccinimide*, τ (acetone) 7·15 (4H, s, C_2H_4) and 8·1—9·3 (27H, Bu_3Sn) (Found: C, 49·3; H, 8·1; N, 3·4. $C_{16}H_{31}NO_2Sn$ requires C, 49·5; H, 8·1; N, 3·6%).

Kinetics.—Reactions were carried out at 35°, the temperature of the n.m.r. thermostat. Acetone was used as a solvent because the *N*-halogenosuccinimides were sufficiently soluble, and the n.m.r. signals of the α-CH_2 group in the alkyl halides which are formed are separated, to high field, from the ^{13}C-coupling satellite of the solvent.

Inhibition and Initiation.—Stock solutions of the tetra-alkyltin and the *N*-halogenosuccinimide were mixed in an n.m.r. tube as described below, and treated with a trace

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† We use the shorthand NCS, NBS, and NIS for the three respective *N*-halogenosuccinimides, and NXS when the particular halogen is not specified.

[1] Part VII, A. G. Davies, D. Griller, and B. P. Roberts, *J.C.S. Perkin II*, 1972, 993.

[2] A preliminary account of some of the present work was published by A. G. Davies, B. P. Roberts, and J. M. Smith, *Chem. Comm.*, 1970, 557.

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[4] References are given by G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 401.

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(1—5 mole %) of galvinoxyl * when the reaction was proceeding steadily. The formation of the alkyl halide was monitored by n.m.r.

The reactions of all the tetra-alkyltins, but not of tributylphenyltin, showed the presence of distinct induction periods, indicating that a radical chain mechanism was followed. The induction period was proportional to the concentration of galvinoxyl, and the rate of initiation was derived from the expression [galvinoxyl]/induction period. With benzyltributyltin, the reaction was too fast to give measurable values of the rate of initiation; 4-methoxy-2-t-butylphenol, 6-methoxy-2,4-di-t-butylphenol, and 6-methyl-2,4-di-t-butylphenol gave longer induction periods than did galvinoxyl, but the effect was not clear cut enough for quantitative measurements.

Rates of initiation were varied by injecting 60 µl of a stock acetone solution of di-t-butyl hyponitrite into 0·60 ml of the reaction mixture. For example, to give a molar ratio of initiator to tetra-alkyltin of 1 : 20 for a 0·600M solution of tetra-n-propyltin, the concentration of the stock solution of initiator was 3M (0·014 g in 0·25 ml).

The Reaction of Tetra-n-propyltin with N-*Bromosuccinimide*.—This illustrates the direct determination of the rate of the S_H2 process. *N*-Bromosuccinimide (0·03200 g) was weighed into an n.m.r. tube which was then repeatedly evacuated and flushed with nitrogen, then sealed with a rubber serum cap. Degassed acetone (0·30 ml) was added by syringe, followed by 0·30 ml of a solution of tetra-n-propyltin (0·60M) in degassed acetone, to give initial concentrations of tetra-n-propyltin (0·300M) and *N*-bromosuccinimide (0·300M).

The course of the reaction was followed by monitoring the n.m.r. signal of the α-methylene group of the n-propyl bromide which was formed. The initial gradient of the curve so obtained gave the initial rate of the reaction. Rates of initiation were determined as described above. Several experiments were carried out with varying concentrations of reagents, to establish the order with respect to each component. The range of concentration of the *N*-halogenosuccinimides which could be studied was limited by their solubilities.

Competition between Tetra-n-propyl- and Tetra-n-butyl-tin for N-*Bromosuccinimide*.—This illustrates the procedure for determining relative rates of the S_H2 reactions of the two tetra-alkyltins. Solutions of the two tetra-alkyltins were prepared in acetone. Aliquot portions of each organotin were then injected into a nitrogen-filled flask, and a deficiency of *N*-bromosuccinimide in acetone was added to the stirred mixture. The reaction was allowed to proceed to completion overnight. Next day, the relative concentration of the two alkyl halides which were formed were determined by g.l.c.

Competition between N-*Chloro-*, N-*Bromo-, and* N-*Iodosuccinimide for Tetra-n-propyltin*.—This illustrates the method for determining the relative rate of abstraction of the different halogens for the alkyl radical. A mixture of tetra-n-propyltin (0·025M) and *N*-chloro-, *N*-bromo-, and *N*-iodo-succinimide (each 0·25M) in acetone was allowed to react to completion, and the products were analysed by g.l.c.

RESULTS

At 35°, in acetone, tetra-alkyltins react with *N*-chloro-, *N*-bromo-, and *N*-iodo-succinimide in a 1 : 1 stoicheiometry, to give the appropriate alkyl halide and *N*-trialkylstannylsuccinimide, according to equation (3), in yields >90%. Under no conditions could a second alkyl group be caused to react.

$$R_4Sn + (CH_2CO)_2NX \longrightarrow RX + (CH_2CO)_2NSnR_3 \quad (3)$$

Under the same conditions, benzyltributyltin gave only benzyl halide, and tributylphenyltin only halogenobenzene, together with *N*-tributylstannylsuccinimide.

All the reactions except that of tributylphenyltin were susceptible to inhibition by galvinoxyl (1—5 mole %), and to acceleration by di-t-butyl hyponitrite (5 mole %) or phenylazotriphenylmethane (1—5 mole %); with this one aromatic exception, all therefore proceed by a radical chain process. A reasonable mechanism for this is given in equations (4)—(9).

The alternative of a chain carried by the radicals X• and R₃Sn• is rejected principally because (*a*) the kinetics would be dependent on the nature of X, which is not observed under our normal conditions; (*b*) there is no clear precedent for the S_H2 reaction at saturated carbon, which would be implied; and (*c*) iodine atoms are known not to react with tetra-alkyltins.

$$\begin{array}{llr}
\text{Initiation} & \longrightarrow (CH_2CO)_2N^{\bullet}\ (\text{Rate } R_i) & (4)\\
\text{Propagation} & (CH_2CO)_2N^{\bullet} + SnR_4 \longrightarrow (CH_2CO)_2NSnR_3 + R^{\bullet} & (5)\\
 & R^{\bullet} + (CH_2CO)_2NX \longrightarrow RX + (CH_2CO)_2N^{\bullet} & (6)
\end{array}$$

$$\begin{array}{llr}
\text{Termination} & 2(CH_2CO)_2N^{\bullet} \xrightarrow{2k_7} \quad \left.\begin{array}{l}\\ \\ \\ \end{array}\right\} & (7)\\
 & (CH_2CO)_2N^{\bullet} + R^{\bullet} \xrightarrow{k_8} \quad \longrightarrow \text{inactive products} & (8)\\
 & 2R^{\bullet} \xrightarrow{k_9} & (9)
\end{array}$$

If the chain is long and termination is solely by the self-reaction of two succinimidyl radicals, the rate of the overall reaction will be given by equation (10). If, on the other hand, termination is by the self-reaction of two alkyl radicals [equation (9)], we have equation (11).

$$\frac{d[RX]}{dt} = k_5[R_4Sn]\left(\frac{R_i}{2k_7}\right)^{\frac{1}{2}} \quad (10)$$

$$\frac{d[RX]}{dt} = k_6[NXS]\left(\frac{R_i}{2k_9}\right)^{\frac{1}{2}} \quad (11)$$

Between these two extremes, the kinetics will be described by a more complex expression involving both k_5 and k_6, [R₄Sn] and [NXS], and all three termination rate constants k_7, k_8, and k_9.

The reaction of *N*-bromosuccinimide with tetra-n-propyl- and tetra-n-butyl-tin in acetone was followed at 35° by monitoring the n.m.r. spectrum of the alkyl bromide which was formed. Rates of initiation were varied by adding di-t-butyl hyponitrite or phenylazotriphenylmethane, and were measured using galvinoxyl as an inhibitor. In the concentration ranges (Pr_4Sn) = 0·075—0·60M, [NBS] = 0·10—0·30M, and [Bu_4Sn] = 0·05—0·50M, [NBS] = 0·125—0·75M, and with R_i in the range 1·67—5·95 × 10^5 l mol^{-1} s^{-1}, both reactions followed the kinetics described by equation (10). If the rate constant for the self-reaction of succinimidyl radicals ($2k_7$) is assumed to be approximately 2 × 10^9 l mol^{-1} s^{-1},[7] the values of k_5 for the S_H2 reaction of succinimidyldealkylation at tin, given in Table 1, can be derived.

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* Phenothiazine, 4-methoxy-2-t-butylphenol, and methoxy-2,6-di-t-butylphenol gave incomplete inhibition, and appeared to react with *N*-bromosuccinimide. Galvinoxyl did not react on the time scale of the experiments described here.

At values of $[R_4Sn] > 1{\cdot}0$M, the overall rate of the reaction tended to become independent of $[R_4Sn]$, indicating that termination reactions involving alkyl radicals by reactions (8) and (9) were becoming important.

In the absence of an added initiator, the rates of the self-initiation of the reactions of tetra-n-propyl- and tetra-n-butyl-tin appear to be constant at *ca.* 2×10^{-5} l mol^{-1} s^{-1}, independent of the concentration of the *N*-bromosuccinimide or tetra-alkyltin. The overall rate of the reaction of *N*-bromosuccinimide with benzyltributyltin was too fast for accurate inhibition periods to be measured with galvinoxyl, but, if it can be assumed that the same constant rate of self-initiation (2×10^5 l mol^{-1} s^{-1}) holds, the value of k_5 for benzyltributyltin which is listed in Table 1 can be derived for the range $[PhCH_2SnBu_3] = 0{\cdot}025$—$0{\cdot}20$M, and $[NBS] = 0{\cdot}50$—$0{\cdot}75$M. This assumption is justified by the fact that the same value of k_5 is obtained by an independent competition method described below.

TABLE 1

Rate constants (at 35°, acetone solvent) for reaction (5)

R_4Sn	NXS	k_5/l mol^{-1} s^{-1}
By direct measurement [a]		
Pr_4Sn	NBS	4×10^3
Bu_4Sn	NBS	8×10^3
$PhCH_2SnBu_3$	NBS	$1{\cdot}3 \times 10^5$
By competition with Pr_4Sn [b]		
Me_4Sn	NIS	$1{\cdot}4 \times 10^5$
Et_4Sn	NBS	$3{\cdot}5 \times 10^4$
	NIS	4×10^4
Bu_4Sn	NBS	4×10^3
$Bu^s{}_4Sn$	NBS	8×10^2
By competition with Bu_4Sn [c]		
$PhCH_2SnBu_3$	NBS	$1{\cdot}2 \times 10^5$

[a] Assuming $2k_7 = 2 \times 10^9$ l mol^{-1} s^{-1}. [b] Taking $k_5(Pr_4Sn) = 4 \times 10^3$ l mol^{-1} s^{-1}. [c] Taking $k_5(Bu_4Sn) = 8 \times 10^3$ l mol^{-1} s^{-1}.

If the concentration of benzyltributyltin is increased, the kinetic behaviour becomes more complicated until at $[PhCH_2SnBu_3] = 0{\cdot}40$—$0{\cdot}75$M and $[NBS] = 0{\cdot}075$—$0{\cdot}20$M reaction (6) rather than reaction (5) becomes rate limiting and the kinetics are described by equation (11). If $2k_9$ for the benzyl radical is taken to be 2×10^9 l mol^{-1} s^{-1},[7,8] the value of k_6, the rate constant for the abstraction of bromide from *N*-bromosuccinimide by the benzyl radical at 35°, can be derived (see Table 2).

TABLE 2

Relative rate constants (at 35°, acetone solvent) for reaction (6)

R•	NCS	NBS	NIS
$PhCH_2$•	(1)	7 [a]	22
Pr•	(1)	7·3	22

[a] By direct measurement, $k_6 = 5 \times 10^6$ l mol^{-1} s^{-1}.

The relative reactivities of the compounds Et_4Sn, $Pr^n{}_4Sn$, $Bu^n{}_4Sn$, $Bu^n{}_4Sn$, and $PhCH_2SnBu_3$ (this last in the lower concentration range defined above) towards the succinimidyl radical were then determined by causing each to compete with tetra-n-propyltin (or, in one case, tetra-n-butyltin) for reaction with a deficiency of *N*-bromo- or *N*-iodo-succinimide, and the two halides produced, RX and R′X, were analysed by g.l.c. If the initial concentrations of R_4Sn and R'_4Sn were large enough to be sensibly constant throughout the reaction, equation (12) will hold.

$$k_5/k'_5 = [RX][R'_4Sn]/[R'X][R_4Sn] \qquad (12)$$

Absolute values of k'_5 can then be obtained by using the value of k_5 for tetra-n-propyltin (or tetra-n-butyltin) which was derived above. The results are given in Table 1; it will be seen that, as required by the mechanism of equations (4)—(9), the same value of k'_5 for tetraethyltin is obtained in its reaction with either *N*-bromo- or *N*-iodo-succinimide.

Relative reactivities of *N*-chloro-, *N*-bromo-, and *N*-iodo-succinimide toward alkyl radicals were obtained by causing a mixture of two, or all three, of these to react with benzyltributyltin or tetrapropyltin, and analysing the alkyl halides which were formed by n.m.r. and/or g.l.c. The results are given in Table 2.

DISCUSSION

Apart from halogenodealkylation,[9] there appears to be little precedent for an S_H2 dealkylation at a tin centre. Razuvaev and his colleagues[10] have shown that thermolysis of t-butyl peroxybenzoate in the presence of tetraethyltin gives some triethyltin benzoate, but this could conceivably arise through induced decomposition of the peroxide by a triethylstannyl radical. If di-t-butyl peroxide is photolysed at or below room temperature in the presence of a tetra-alkyltin, the only species that can be observed by e.s.r. result from abstraction of hydrogen from the alkyl group by the t-butoxyl radical.*[11] Similarly, photolytic generation of the dimethylaminyl radical from tetramethyltetrazene in the presence of a tetra-alkyltin gives no indication of substitution at the tin centre.

The N–H bond energy in succinimide has been estimated to be as high as 100 kcal mol^{-1},[12] compared with *ca.* 86 kcal mol^{-1} for dimethylamine.[13] If the N–Sn bond energy in *N*-trialkylstannylsuccinimide is similarly high compared with that in trialkyltin dimethylamide, this could account for the relatively high reactivity of the succinimidyl radical.†

The succinimidyldealkylation reaction could proceed by either a stepwise or a synchronous process, *i.e.* the

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* However, homolytic alkoxydealkylation of organotin halides and carboxylates, R_nSnX_{4-n} (n = 1—3), can readily be observed.[11b] The factors which determine the reactivity of functional organotin compounds are under investigation.

† Attempts to observe succinimidyl radicals by e.s.r. spectroscopy by, *inter alia*, the photolysis of t-butyl succinimideperoxycarboxylate, or of a mixture of di-t-butyl peroxide and tetramethyl succinimide in 2,2,5,5-tetramethyltetrahydrofuran, have so far been unsuccessful. We are grateful to Dr. M. J. Perkins, and to Dr. D. G. Morris, for the gift of these chemicals.

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[11] (*a*) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1969, **91**, 6161; (*b*) J. C. Scaiano, unpublished work.

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species (I) could be either an intermediate or an activated complex.

$$(CH_2CO)_2N^{\bullet} + SnR_4 \xrightarrow{a} \underset{\text{(I)}}{[(CH_2CO)_2\dot{N}SnR_4]} \xrightarrow{b} (CH_2CO)_2NSnR_3 + R^{\bullet}$$

Intermediates analogous to (I) have been identified by e.s.r. in reactions of compounds of phosphorus[14] and of arsenic,[15] and there is some evidence for their involvement in the alkoxydealkylation of alkyltin halides and carboxylates.[11b]

The results summarised in Table 1 appear to favour the interpretation that (I) is a transition state.

First, there is a general decrease in reactivity in the sequence $Me_4Sn > Et_4Sn > Pr^n{}_4Sn$, $Bu^n{}_4Sn > Bu^s{}_4Sn$. Some of this difference, particularly that between the first two members, may be due to a difference in the strengths of the N–Sn bonds which are being formed, but the general trend suggests that the larger alkyl groups provide steric hindrance to the formation of the five co-ordinate species (I). If this species is an intermediate and not a transition state, its formation rather than its breakdown must be rate controlling. Steric hindrance towards S_H2 reactions has already been identified in the homolytic dealkylation of alkylboranes.

Second, benzyltributyltin reacts to give cleavage of essentially only the benzyl–tin bond, and has a reactivity some 15 times greater than that of tetrabutyltin. The selectivity can clearly be associated with stabilisation of the incipient benzyl radical by resonance as the benzyl–tin bond is cleaved. If the combined steric and polar effects of the benzyl and butyl groups are similar, the high overall reactivity implies that the cleavage of this benzyl–tin bond must be involved in the rate-controlling stage; if species (I) is an intermediate (formed irreversibly) and not a transition state, its breakdown and not its formation must now be rate controlling. Such a change in the energy profile between tetra-n-butyltin and benzyltributyltin seems rather unlikely, suggesting that species (I) may be a transition state rather than intermediate.

The data in Table 2 shows that the ease of the abstraction of a halogen atom from a *N*-halogenosuccinimide increases in the sequence $Cl < Br < I$, as would be expected; if anything, the propyl radical is more selective than the benzyl radical. If it is accepted that the reaction between *N*-bromosuccinimide and benzyltributyltin has a rate of initiation of 2×10^5 l mol^{-1} s^{-1} (see above), the value of k_6 of 5×10^5 l mol^{-1} s^{-1} for the rate of abstraction of bromine by the benzyl radical, is obtained; the corresponding rate constants for the abstract of chlorine and of iodine are therefore 7×10^4 and 2×10^6 l mol^{-1} s^{-1} respectively.

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