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CHEMISTRY OF ORGANODITINS

II*. THE FREE RADICAL CHAIN REACTION BETWEEN *N*-CHLOROSUCCINIMIDE AND HEXAALKYLDITINS

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SUMMARY

The reaction of *N*-chlorosuccinimide with hexaalkylditins has been examined. The reaction has been found to be subject to catalysis by molecular oxygen, and to inhibition by galvinoxyl. A free radical chain mechanism is proposed in which one propagating step involves attack upon the ditin by *N*-succinimidyl radicals, and another involves attack upon the chlorine atom of the *N*-chlorosuccinimide molecule by organotin radicals. Evidence is also presented that dimethylamino radicals from decomposition of 1,1,4,4-tetramethyl-2-tetrazine participate in a homolytic displacement upon the tin radical of hexamethylditin. On the other hand, the trimethyltin radicals do not appear to attack the nitrogen of the tetramethylhydrazine.

Investigations in these laboratories have shown that alkyl[2a] and acyl halides[2b–d] react with organotin hydrides by a free radical chain mechanism of which the chain carrying steps are generally assumed to be reactions 1 and 2.

$$R_3Sn\cdot + R'X \rightarrow R_3SnX + R'\cdot \quad (1)$$

$$R'\cdot + R_3SnH \rightarrow R'H + R_3Sn\cdot \quad (2)$$

Reaction 1 serves as an excellent source of free radicals from halides[3]. It has also been shown that organoditins react with organic halides photochemically to form products whose formation is attributable to the involvement of reaction 1[4]. Thus, it appeared to be of interest to ascertain whether the reaction of organotin hydrides or organoditins with *N*-haloamides would produce neutral nitrogen-centered free radicals via reaction 3. Preliminary experiments showed that *N*-haloamides did indeed react

$$Sn\cdot + R_2NX \rightarrow SnX + R_2N\cdot \quad (3)$$

rapidly and exothermally with both tributyltin hydride and with hexabutylditin.

There has been considerable interest in the succinimidyl radical over past decade, particularly since it was shown that it is not an intermediate in allylic brominations by *N*-bromosuccinimide (NBS)[5] as had been assumed previously. Estimates of

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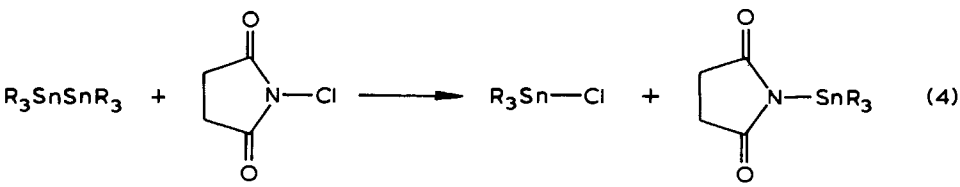
* For part I see ref. 1a.

its resonance energy over that of its nonparamagnetic precursor have decreased from 17 (ref. 6) or 30 kcal/mole[7] to virtually zero[8] in recent years. However, evidence of varying force is available for its intermediacy in several reactions: rearrangement of NBS to β-bromopropionyl isocyanate[9]; addition of NBS to olefins[10]; bromination of benzyl *p*-bromophenyl ether with NBS[11]: decarboxylation of t-butyl *N*-succinimide percarboxylate[8,12]; reaction of NBS with tetraalkyltins[13★]; and the oxidation of 1-phenylethanol with *N*-iodosuccinimide[14]. Electron spin resonance has been used with the aid of the spin traps 2-methyl-2-nitrosopropane[15a] and t-butylmethylene nitrone[15b] to provide evidence for formation of the radical from *N*-bromosuccinimide[15a,b] and from t-butyl *N*-succinimidyl percarboxylate[15b].

RESULTS AND DISCUSSION

Because of the wide interest in succinimidyl radicals we chose for initial detailed study the reaction between hexabutylditin and *N*-chlorosuccinimide (NCS). The reaction proceeded quantitatively as shown in eq. 4. Products were characterized by GLPC retention times, spectral properties and independent synthesis[16]. Solvents such as heptane, chloroform or bromoform could be used.



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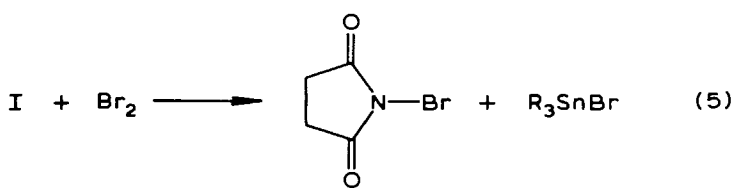
(I)

NBS reacted in the same way, but faster. The *N*-trimethyltin succinimide reacts rapidly and quantitatively with bromine (eq. 5).



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Rate Studies. Although a detailed quantitative kinetic study of reaction 4 leading to explicit rate laws was not carried out, a considerable amount of mechanistic information was obtained by study of the effects of reaction parameters on concentration *vs.* time profiles. The ultraviolet spectral data presented in the Experimental show that the extinction coefficient at 242 nm of hexabutyltin is about fifty times larger than that of the other species of the reaction. Rates were followed spectrophotometrically at this wavelength.

★ For reviews on S_{H2} reactions see ref. 13c

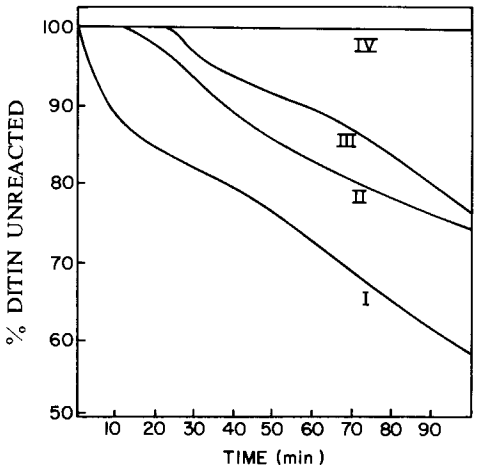
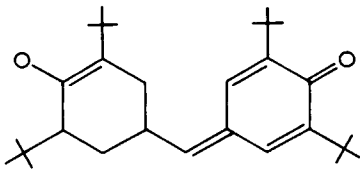


Fig. 1. Concentration-time profiles for reaction of hexabutylditin and *N*-chlorosuccinimide in chloroform at 25° I "Normal" reaction II Purged with argon III 1 9 mole % galvinoxyl added IV 1 9 mole % galvinoxyl added and purged with argon

Figure 1 shows concentration *vs.* time profiles for typical experiments in chloroform as solvent at 25°. In the experiments represented by profile I solutions of the reactants were equilibrated at 25°, mixed and transferred to a conventional square capped UV cell, which was then placed in the spectrophotometer for reading of absorbance. The profile shows an initial rapid consumption of ditin which slows down rapidly; after about 20% reaction the slope increases slightly and then resumes with a steady decrease, giving the profile a sigmoid character. In other experiments the slopes could not be reproduced quantitatively. However, the shape of the profile and the changes in slope at about 25% reaction could be reproduced. In the experiment represented by profile II the solutions of reactants were purged with argon before mixing. Now the reaction showed an induction period of about fifteen minutes and then proceeded in a manner characteristic of a free radical chain reaction. This profile could be reproduced in detail with reasonable accuracy. The difference in shapes of the two profiles can be explained if it be assumed that the reaction is catalyzed by oxygen (see below). Profile II represents a reaction in which insufficient oxygen is present to catalyze the reaction initially, but oxygen gradually diffuses into the cell, is dissolved, and initiates the reaction when its concentration reaches a certain level. Profile I represents a reaction in which enough oxygen is present to initiate reaction at a high rate. This oxygen is consumed rapidly and falls to a low concentration, and the reaction rate decreases; then diffusion of oxygen, which has lagged behind consumption, raises its concentration to the steady state concentration determined by the rates of consumption and diffusion.

Profile III represents a reaction in which 1.9 mole percent of the highly efficient free radical trap galvinoxyl[2] was present*, but unpurged reactant solutions were used. Now an induction period of about 25 minutes is observed. The greater slope after the induction period than in profile II suggests that the solution still

* Galvinoxyl is an efficient scavenger of organotin radicals[17]



(II) (†=t-Bu)

contains oxygen. The similarity between profile I and profile III after about 30 minutes supports this view. The experiment represented by profile IV differed from the preceding one only in that the reactant solutions were purged with nitrogen before mixing. No change in ditin concentration was observed during 3 hours.

These observations lead us to conclude that we are dealing with a free radical chain reaction. Eqns. 6–11 represent reasonable elementary steps. A novel aspect of this scheme is that termination reaction 9 leads to one of the reactants, and 11 leads to the major product of the reaction; hence the occurrence of these reactions cannot be detected by examination of the products.

$$R_3SnSnR_3 + \text{initiator} \rightarrow R_3Sn\cdot + R_3Sn\text{-initiator} \quad (6)$$

$$R_3Sn\cdot + R'_2NX \rightarrow R_3SnX + R'_2N\cdot \quad (7)$$

$$R'_2N\cdot + R_3SnSnR_3 \rightarrow R'_2NSnR_3 + R_3Sn\cdot \quad (8)$$

$$2\,R_3Sn\cdot \rightarrow R_3SnSnR_3 \quad (9)$$

$$2\,R'_2N\cdot \rightarrow R'_2NNR'_2 \quad (10)$$

$$R'_2N\cdot + R_3Sn\cdot \rightarrow R'_2NSnR_3 \quad (11)$$

Initiation. It is clear from the data represented in Fig. 1 that the reaction can be initiated by molecular oxygen. However, it seemed of interest to ascertain whether

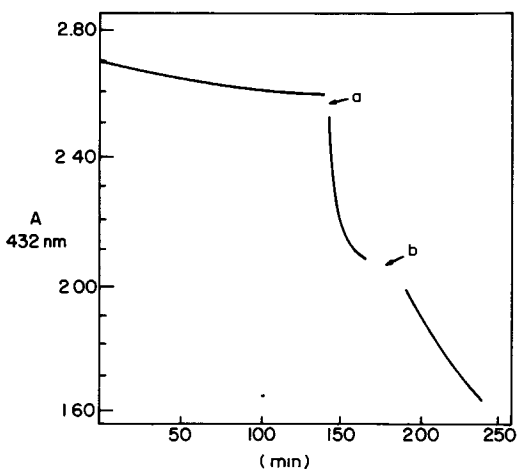


Fig 2 Reaction of hexamethylditin and *N*-chlorosuccinimide in chloroform at 25°, in presence of 0 3 mole % galvinoxyl, degassed. At (a) Nitrogen containing 0 2% O_2 added (b) Nitrogen containing 1 0 mole % O_2 added

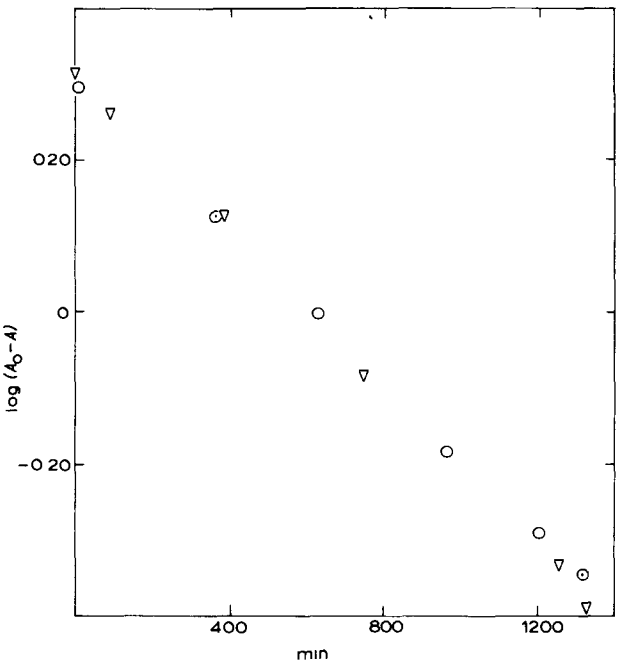


Fig. 3. Reaction of hexabutylditin and galvinoxyl at 25° in chloroform △, c_0 (ditin), 3.92×10^{-2}, c_0 (galvinoxyl), 1.33×10^{-5}; ○, c_0 (ditin), 9.68×10^{-3}, c_0 (galvinoxyl), 1.27×10^{-5} (all molar).

spontaneous initiation could be induced. Only a few cases of this phenomenon have been reported[18]. Reactions involving ca. 0.01 *M* NCS and hexamethylditin, and ca 10^{-5} *M* galvinoxyl were carried out. The solutions of the reactants in chloroform were thoroughly degassed before mixing. The rate of disappearance of galvinoxyl was followed by measuring the absorbance at 432 nm. The results of a typical experiment are represented in Fig. 2. The first segment of the curve represents reaction between galvinoxyl and solvent. This was confirmed by separate experiments in which it was shown that the slow reaction which occurred when hexabutylditin and galvinoxyl were dissolved in chloroform had a rate independent of the concentration of ditin (See Fig. 3). Thus, the spontaneous initiation, if it occurs, does so at a rate slower than the reaction of galvinoxyl with solvent. The effect of oxygen is again dramatically demonstrated in the figure. At 140 min nitrogen containing 1% of air was introduced, leading to the precipitous increase in the rate of consumption of galvinoxyl. At 170 min the reaction mixture was frozen, evacuated, and warmed to 25°. Now nitrogen containing 5% of air was introduced; and the resulting increased rate of consumption of galvinoxyl is shown in the third segment of the plot.

Propagation. As neither NCS nor galvinoxyl reacts with oxygen it is clear that initiation by oxygen is the result of reaction with ditin, presumably to form organotin and peroxyorganotin radicals. Galvinoxyl, in turn, reacts with the organotin radicals to inhibit the reaction. The most likely product would be *o*-trimethyltin galvinoxyl. Hexamethylditin (0.124 mmole) and galvinoxyl (0.237 mmole) were dissolved in 1 ml chloroform and irradiated in a Pyrex vessel until the initial intense absorption of

TABLE 1

THE NMR SPECTRUM OF THE PRODUCTS OF THE REACTION OF HEXAMETHYLDITIN AND GALVINOXYL IN CHLOROFORM AT 25° TMS AS INTERNAL STANDARD RATIO 1/2 (ditin/galvinoxyl)

δ(ppm)	Multiplet	Assignment	J(Hz)[a]	Area	Relative area
	broad				
1 38	singlet	t-Bu		132	4 1
0 37	singlet	Me_3Sn-O-	54, 56	23 5	
0 20	singlet	$Me_3SnSnMe_3$	46, 48	3 5	1
0.07	singlet	(Me_3Sn–C)	51, 53	5.0	

[a] ^{117}Sn–H and ^{119}Sn–H, respectively

galvinoxyl at 432 nm (ε1.57 × 10^5) was replaced by one at 395 nm (ε2.9 × 10^4). Data on the high-field portion of the NMR spectrum are given in Table 1. The broad singlet at δ1.38 is assigned to the protons of the four t-butyl groups of the galvinoxyl moiety. The ratio of these to the trimethyltin protons should be 3.8 according to the stoichiometry used in the reaction; the value found is 4.1. The resonance at δ0.20 was shown to be due to unreacted hexamethylditin. The singlet at δ0.37 is characteristic of a trimethyltin group bound to an electronegative element such as oxygen. The peak at δ0.07 has not been explicitly assigned, but is probably due to a trimethyltin group bound to carbon. When equimolar amounts of ditin and galvinoxyl were used in another experiment one-half of the ditin was unreacted as revealed by the fact that the area of the peak at δ0.20 equalled the sum of the areas of the peaks at δ0.37 and 0.07, but the intensity of that at δ0.20 indicated that only a half of the ditin had reacted.

Thus the stoichiometry of the reaction between ditin and galvinoxyl is represented by eq. 12.

$$2\ \mathrm{Gal} + R_3SnSnR_3 \rightarrow 2\ \mathrm{GalSnR_3} \qquad (12)$$

When a chloroform solution 1.97 *M* in hexamethylditin, 1.32 *M* in NCS, and 1.32 *M* in galvinoxyl was allowed to react for 24 h, the mixture showed a maximum at 395 nm of intensity expected on the basis of the preceding experiment, assuming the reaction of eq. 13. The NMR spectrum showed the resonances listed in Table 2.

$$3/2\ Me_3SnSnMe_3 + \mathrm{NCS} + \text{galvinoxyl} \rightarrow Me_3SnCl + \mathrm{galSnMe_3} + \underset{H_2C-CO}{\overset{H_2C-CO}{\diagdown\!\diagup}}\!\!>\!NSnMe_3 \quad (\mathrm{NSnS}) \qquad (13)$$

The assignments of the high-field resonances is straightforward with the exception that there is only a single peak for the trimethyltin protons at δ0.56 with *J* (^{117}Sn–H) 56.2 Hz. This is undoubtedly due to rapid exchange of the trimethyltin group between chlorine, nitrogen and oxygen in the products. The individual chemical shifts for the products are (in Hz upfield from chloroform): Me_3SnCl, 395.7; >NSnS, 399.7; $\mathrm{galSnMe_3}$, 409.2. Rapid exchange would give a shift which is the simple average of these, 401.0 Hz. The observed value is 401.3 ± 0.5 Hz.

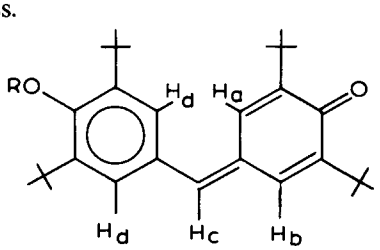
TABLE 2

THE NMR SPECTRUM OF THE REACTION PRODUCT OF *N*-CHLOROSUCCINIMIDE AND HEXAMETHYLDITIN CONTAINING GALVINOXYL IN CHLOROFORM, TMS AS INTERNAL STANDARD

δ(ppm)	*Multiplet*	*Assignment*	$J(^{117}Sn-^{119}Sn)$ *(Hz)*	*Analysis H(%) Found*	*Calc.*
2.62	singlet	$-CH_2$ of succinimidyl		4	4
1 38	broad singlet	t-Bu of galvinoxyl		32	36
0 56	singlet	Me_3Sn–(O-Cl-N)	56 2, 58 4	29	27
0 20	singlet	$Me_3SnSnMe_3$	46, 48	3 5	0
0.07[a]	singlet	(Me_3Sn-C)			

[a] This resonance, if present, is masked by the trimethyltin satellites The integrated intensity is definitely less than 0 5

Further evidence for rapid exchange was obtained as follows. A chloroform solution containing trimethyltin chloride and *N*-succinimidyltrimethyltin showed the trimethyltin proton resonance at δ0.616 and the methylene proton resonance of the succinimidyl ring at δ2.62. To this was added solution containing the product of reaction of hexamethylditin and galvinoxyl. (See Table 2). The resulting solution showed a new trimethyltin proton resonance at δ0.584; those at δ0.616 and 0.37 were missing. The intensity of the new resonance relative to the succinimide methylene proton resonance was increased. The resonance at δ0.20 due to hexamethylditin was unchanged indicating that this compound did not engage in the rapid exchange process.



(III , R = Me_3Sn)
(IV , R = H)

The most reasonable structure for the major product of the reaction between hexamethylditin and galvinoxyl is III. This compound showed λ_{max} at 395 nm ($\varepsilon 3.0 \times 10^4$) and at 263 nm ($\varepsilon 7.5 \times 10^3$). It was treated with acetic acid and then with potassium fluoride. Trimethyltin fluoride precipitated. The resulting solution yielded IV with λ_{max} at 395 nm ($\varepsilon 2.1 \times 10^4$) and at 263 nm ($\varepsilon 7.5 \times 10^3$). This compound had an infrared spectrum identical to that of an authentic sample prepared by the reduction of galvinoxyl with hydroquinone[19]. Its NMR parameters are shown in Table 3.

TABLE 3

THE NMR SPECTRUM OF THE ACETOLYSIS PRODUCT OF THE TRIMETHYLTIN GALVINOXYL REACTION IN CCl_4 (TMS as Internal Standard)

δ(ppm)	*Multiplet*	*Assignment*	*Integrated area*	*Relative area*
7 44	broad singlet	H_a or H_b	19	1
7 20	singlet	H_d	33	2
6.99	broad singlet	H_b or H_a	17	1
6 84	broad singlet	H_c	17	1
5.36	singlet	H_c[a]	17	1
1.45	singlet	H_b or $H_{b'}$	680	40
1.28	singlet	$H_{b'}$ or H_b		

[a] This singlet is broadened and shifted about 4.5 cps downfield upon the addition of 1 drop of pyridine This is consistent with structure IV.

The above observations are consistent with the involvement of organotin radicals as intermediates in the reaction of ditins with NCS. They function as chain carriers by abstraction of halogen atoms from nitrogen as shown in eq. 7. Abstraction of chlorine from nitrogen is much faster than abstraction of chlorine from carbon[20] because the reaction of ditin with NCS goes quantitatively in chloroform. This is consistent with the greater strength of the C–Cl bond (~80 kcal/mole) than that of the N–Cl bond (~45 kcal/mole)[21].

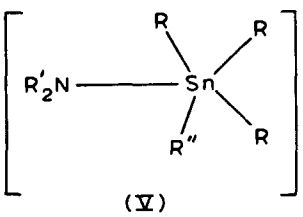
The second chain propagating reaction, eq. 8, is a homolytic displacement on tin, examples of which have been reported in recent years[13a]. Among the radicals involved have been stannoxy[22], acyloxy[23], trifluoromethyl[24] (or the iodine atom[24b]), and *N*-succinimidyl[13]. Such reactions appear to be fairly common at elements having empty *p* orbitals (boron) or *d* orbitals (tin).

The most compelling evidence for homolytic substitution on tin by the succinimidyl radical was provided by Davies, Roberts and Smith[13] who studied the products and kinetics of the reaction of *N*-bromosuccinimide with tetraalkyltins. They proposed as chain propagating steps reactions 14 and 15[27].

$$R'_2N\cdot + n\text{-}Bu_3SnR'' \rightarrow n\text{-}Bu_3SnNR'_2 + R''\cdot \quad (14)$$

$$R''\cdot + R'_2NBr \rightarrow R''Br + R'_2N\cdot \quad (15)$$

If species V is a transition state in a one-step substitution one would expect reaction 8 to be faster than 14 inasmuch as the $R_3Sn–SnR_3$ bond is weaker than the $R_3Sn–C$



(V)

bond by about 12 kcal/mole[25b]. We sought a direct demonstration of the occurrence of reaction 8, but a suitable precursor of the succinimidyl radicals could not be obtained under appropiate conditions. Hence, we turned to an alternative radical, $(CH_3)_2N\cdot$ which can be obtained by the photochemical decomposition of tetramethyl-2-tetrazene, eq. 16[25].

$$(CH_3)_2N{-}N{=}N{-}N(CH_3)_2 \xrightarrow{h\nu} 2(CH_3)_2N\cdot + N_2$$

When the tetrazene was decomposed photolytically in octane the rate of nitrogen evolution followed the path represented by line I of Fig. 4. Tetramethylhydrazine was identified as the product formed by coupling of the dimethylamino radicals. When the experiment was repeated in the presence of hexamethylditin the rate of nitrogen evolution was slightly slower (line II of Fig. 3). No tetramethylhydrazine was formed.

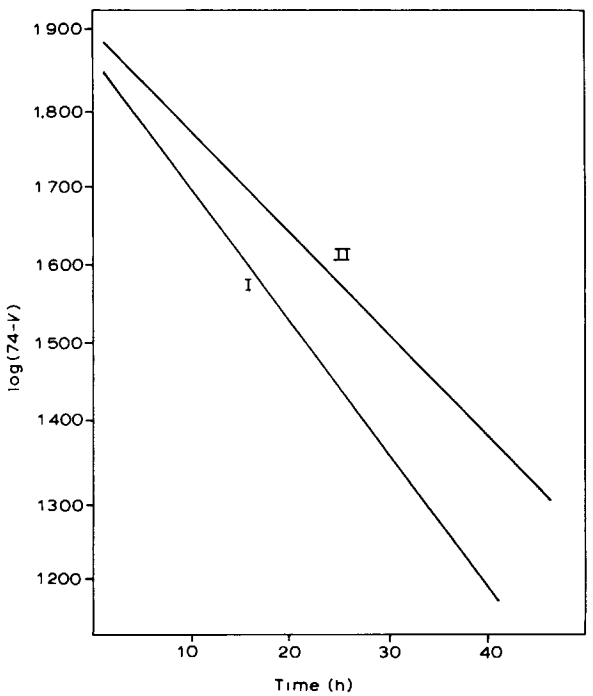


Fig 4. I, rate of nitrogen evolution in photolysis of 1,1,4,4-tetramethyl-2-tetrazene, II, rate of nitrogen evolution in photolysis of 1,1,4,4-tetramethyl-2-tetrazene in presence of 96 mole % hexamethylditin. (solvent chloroform)

The product in the octane solution hydrolyzed rapidly upon exposure to atmospheric moisture to form dimethylamine and trimethyltin hydroxide. The precursor of these compounds is undoubtedly dimethylaminotrimethyltin, formed via reactions 17 and 18. Two conclusions may be drawn from these results: (a) dimethylamino radicals participate in homolytic substitution at tin; (b) trimethyltin radicals do not participate in homolytic substitution on nitrogen; otherwise the presence of hexamethylditin

would have accelerated the decomposition of the tetramethyltetrazine*.

$$(CH_3)_2N\cdot + (CH_3)_3SnSn(CH_3)_3 \rightarrow (CH_3)_2NSn(CH_3)_3 + (CH_3)_3Sn\cdot \quad (17)$$

$$(CH_3)_2N\cdot + (CH_3)_3Sn\cdot \rightarrow (CH_3)_2NSn(CH_3)_3 \quad (18)$$

At first glance this conclusion appears to be puzzling in light of the elegant work of Neumann which indicates quite clearly that organotin radicals can, indeed, attack either of the terminal nitrogen atoms of triazenes**. Those which are designated as $S_H2\gamma$, eq. 19, can be easily rationalized on the basis of the ready attack by the organotin radical at a nitrogen bearing a double bond,

$$Ar\overset{\curvearrowright}{N}=N-N\begin{matrix}R'\cdot\\R\end{matrix} \rightarrow Ar-\underset{\displaystyle R_3Sn}{N}-\dot{N}-N\begin{matrix}R'\\R\end{matrix} \rightarrow Ar-\underset{\displaystyle R_3Sn}{N}-N=N-R + R'\cdot \rightarrow \text{products} \quad (19)$$

and accommodation of the unpaired electron on the adjacent nitrogen atom, thus avoiding the necessity of using an antibonding orbital of the nitrogen atom attacked, a process which would undoubtedly have extremely high activation energy. This latter would account for the fact that compounds in which R′· (*e.g.* benzyl) is a relatively stable radical undergo the reaction designated $S_H\alpha$ more readily than those which form less stable radicals (*e.g.* methyl). This implies a substantial degree of breaking of the N–R′ bond in the transition state.

Termination. As pointed out at the outset, the only termination reaction whose presence might be verified by product analysis is reaction 10, the coupling of succinimidyl radicals to form *N,N*-bissuccinimide. No traces of this compound could be detected, nor were any products which might result from rearrangement of the succinimidyl radical to the γ-propionyl isocyanate radical[8,9]. If this type of product is, in fact, completely absent our reaction has the novel characteristic of being a free radical chain reaction in which the termination products cannot be found explicitly in the product.

The reactions of *N*-halosuccinimides with tetraalkyltins, on the one hand, as reported by Davies and his colleagues[13a], and with hexaalkylditins, on the other, as reported above show two striking differences. Whereas (Fig. 2) the reaction with ditin is powerfully catalyzed by oxygen, the reactions with tetraalkyltins are inhibited by the same reagent. Since alkyl radicals are involved in the tetraalkyltin reactions, it is most probable that the function of oxygen is to trap these intermediates. On the other hand, it initiates reaction by attack on a tin atom of the ditin to give species VI which may be a transition state or an intermediate[22–24].

$$R_3Sn-\underset{\displaystyle O-O}{\dot{S}nR_3} \qquad \text{(VI)}$$

Another difference lies in the fact that dimethylimino radicals generated from

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* For another reaction which may involve homolytic displacement on tin by the succinimidyl radical see ref 26.

** The structure V is written as a reversibly formed intermediate However, the greater reaction rate when R′· is a stable radical could suggest that the species is actually a transition state If it is an intermediate then substituents which form stable free radicals appear to play a special role in its stabilization by, for example, hyperconjugation or equivalent mechanism. Also see text

tetramethyltetrazine are completely trapped in the presence of hexamethylditin to form dimethylaminotrimethyltin, but escape reaction with tetraalkyltins[13a]. The simplest interpretation is that the weakness of the Sn–Sn bond is such that displacement of $R_3Sn\cdot$ occurs easily whereas displacement of $R\cdot$ has an activation energy which is so high that this process cannot compete with coupling of the amino radicals.

Other N-haloamides. That the reaction between ditins and haloamides in general may be of synthetic value was shown by preliminary experiments carried out with the following compounds and hexabutyltin: *N*-chlorosuccinimide; *N*,*p*-dichloroacetanilide; *N*-chloro-*p*-nitroacetanilide (reaction with N–Cl in preference of reduction of the nitro group) and *N*-chloroacetanilide. The products were not fully characterized.

The procedure used in the reaction of hexabutylditin with *N*′,*p*-dichloroacetanilidide, described in the Experimental section, is representative of the general characteristics of these reactions.

EXPERIMENTAL

Materials. The hexaalkyditins were prepared by the reaction of trialkyltinlithium with the corresponding halide[29]. *N*-Chlorosuccinimide (m.p. 148–150°) was prepared by the reaction of t-butylhypochlorite with succinimide in methanol[4], as were the *N*-chloroamides. Chloroform used was Baker's reagent grade, containing 0.25% by weight of ethanol as stabilizer.

NMR spectra were recorded with a Varian A-60A spectrometer. Infrared spectra were recorded on a Beckman IR8 or IR10 spectrophotometer. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer. Kinetic measurements were made with a Beckman DU spectrophotometer. GLPC analyses were performed with an F&M model 5750 gas chromatograph using helium as the carrier gas.

Reaction of hexabutylditin and N-bromosuccinimide in heptane. A three-necked 50 ml flask fitted with a reflux condensor, and a serum cap was flushed with nitrogen, charged with a suspension of 0.889 g. (5.02 mmoles) of *N*-bromosuccinimide in 20 ml of heptane. The heptane was heated to reflux and 1.450 g (2.50 mmoles) of hexabutylditin in 2 ml of heptane was added with a syringe through the serum cap. Refluxing was continued for 2 h, whence the solution was cooled and the succinimide and unreacted *N*-bromosuccinimide were removed by filtration. The NMR spectrum of the filtrate showed the expected patterns for tributyltin bromide and heptane plus a small singlet at δ2.47, which was enhanced by addition of authentic *N*-tributyltin succinimide prepared by the method of Davies, Mitchell and Symes[30].

Reaction of hexabutylditin and N-bromosuccinimide in bromoform at room temperature. To a flask equipped with a magnetic stirrer and a serum cap was added 15 ml of bromoform and 1.3 g (7.2 mmole) of *N*-bromosuccinimide. To the stirred suspension was added 4.2 g (7.2 mmole) of hexabutylditin. The solid *N*-bromosuccinimide immediately dissolved and a highly exothermic reaction ensued. When the reaction was over, and the reaction mixture cooled to room temperature the solvent was removed at reduced pressure. GLPC on 10% carbowax 20 M at 30° indicated that methylene bromide was not present. The residue of the vacuum distillation was *N*-tributyltin succinimide and tributyltin bromide as confirmed by titration of the residue with bromine which yielded *N*-bromosuccinimide (1.1 g, 85%) m.p 179–180°,

recrystallized from acetone–petroleum ether (5/95, v/v) at −78°, and tributyltin bromide.

The reaction of N-tributyltin succinimide and bromine. To 5.0 g (12.9 mmole) *N*-tributyltin succinimide in 5 ml of bromoform bromine was added until the solution did not discharge the color. The bromoform was removed under vacuum, the residue washed with petroleum ether, and after recrystallization from acetone: petroleum ether, (5/95, v/v) at −78°C yielded 2.1 g (90%) *N*-bromosuccinimide, m.p. 178–180°. The identification was confirmed by comparison of the m.p. and infrared spectrum to that of authentic *N*-bromosuccinimide and by reaction with potassium iodide to form iodine.

The reaction of hexabutylditin and N-bromosuccinimide. To 0.65 g (3.6 mmole) of *N*-bromosuccinimide in a 10 ml flask was added 2.1 g (3.6 mmole) of hexabutylditin. An immediate exothermic reaction ensued. After the flask cooled to room temperature, the infrared spectrum was taken. It was very similar to that of authentic *N*-tributyltin succinimide showing common bands at 2930, 2850, 1665, $(\nu(C{=}O))^{cm^{-1}}$ and in the fingerprint region.

The reaction of hexabutyltin and N-chlorosuccinimide in methylene chloride and chloroform. To 15 ml of $CHCl_3$ (or CH_2Cl_2) in a 25 ml round bottom flask was added 0.480 g (3.6 mmole) of *N*-chlorosuccinimide and 2.1 g (3.6 mmole) of hexabutylditin. There was a short induction period and then an exothermic reaction took place. Examination of the NMR spectrum showed the singlet at δ2.74 (NCS) replaced by a singlet at δ2.52 (*N*-tributyltin succinimide). Comparison of the intensities of these two peaks indicated greater than 95% conversion of *N*-chlorosuccinimide to *N*-tributyltin succinimide.

The reaction of hexabutylditin and N,p-dichloroacetanilide in CCl_4. To 3.0 ml of CCl_4 in 10 ml round bottom flask, was added 0.25 g (1.5 mmole) of *N,p*-dichloroacetanilide and 0.85 g (1.5 mmole) of hexabutylditin; the flask was immediately stoppered. An exothermic reaction took place which was over in a few minutes. The flask was opened in a nitrogen filled dry box and a sample withdrawn for NMR analysis. Comparison of the intensities of the singlet at δ 2.04 (CH_3 of *N*, *p*-dichloroacetanilide) and δ1.75 (CH_3 of *N*-tributyltin, *p*-chloroacetanilide) indicated essentially complete conversion of *N*-haloamide to tin amide.

Concentration vs. time profiles. The reaction of hexabutylditin and N-chlorosuccinimide at 25.0° C in chloroform. Spectral parameters are shown in Table 4. The solutions of the starting material were purged with argon in the experiments described in Fig. 1, 2 and 4. In the other experiments, this procedure was omitted. The following is a representative procedure. Into separate compartments of a two compartment vessel were placed 2.00 ml of a 2.48×10^{-4} *M* ditin solution (4.968 mmole) and 2.00 ml of a 2.58×10^{-4} *M* *N*-chlorosuccinimide solution (5.168 mmole). The vessel was flushed for about a second with argon, capped and placed in a water bath maintained at 25.00°C ± 0.01° for twenty minutes to effect equilibration. The vessel was inverted and shaken vigorously, a sample withdrawn to fill a 1 cm absorption cell, and the absorbance change at 242 nm followed with a Beckman DU, the cell compartment of which was kept at 25 ± 0.10°.

The reaction of hexamethylditin and galvinoxyl. (a) In 1 ml of chloroform, 100.5 mg galvinoxyl (0.237 mmole) and 41.2 mg hexamethylditin (0.124 mmole) were dissolved. The dark black-brown solution was irradiated in a pyrex vessel with a

100 watt mercury lamp for 24 h at 40°C. (b) Concurrently in 1.0 ml of chloroform, 100.2 mg (0.237 mmole) of galvinoxyl and 82.4 mg (0.250 mmole) of hexamethylditin were irradiated under the same conditions. After irradiation, aliquots were withdrawn from both (a) and (b), diluted and the UV spectra recorded. A small (0.15) absorbance at 432 nm indicated the complete disappearance of galvinoxyl and the strong absorbance at λ_{max} 375 nm (ε 2.9×10^4) was indicative of the trimethyltin-galvinoxyl coupling product. The NMR spectral data are presented in Table 1.

Acetolysis of the trimethyltin-galvinoxyl product. The chloroform solution (a) in the reaction of hexamethylditin and galvinoxyl was concentrated to heavy oil which was diluted to 75 ml with tetrahydrofuran. To this was added 5.0 ml of acetic acid followed by 4 g of potassium fluoride. The precipitate which formed which was separated by filtration. The filtrate was concentrated under vacuum to a heavy oil, which solidified on scratching. The solid was air-dried and 9.6 mg (1.64×10^{-2} mmole) was dissolved in 10.00 ml of chloroform. The concentration was reduced to 4.37×10^{-5} *M* by dilution with chloroform and the UV and visible spectra recorded. The NMR spectrum was recorded in CCl_4, and is presented in Table 3. The infrared spectrum showed bands at 3600, 2940–2850, 1607, 1580 and 1550 cm^{-1}.

TABLE 4

EXTINCTION COEFFICIENTS OF REACTANTS AND PRODUCTS AT 242 NM IN CHLOROFORM SOLUTION

Compound	*Concentration*	*A*(242 *nm*)	ε(242 *nm*)[a] (M^{-1} cm^{-1})
$(Bu_3Sn)_2$	1.34×10^{-4}	1.217	0.909×10^4
$(Bu_3Sn)_2$	1.007×10^{-4}	0.989	0.982×10^4
$(Bu_3Sn)_2$	6.716×10^{-5}	0.697	1.04×10^4
$(Bu_3Sn)_2$	2.489×10^{-5}	0.353	1.422×10^4
N-chlorosuccinimide	1.00×10^{-3}	0.180	1.80×10^2
	5.00×10^{-3}	0.880	1.76×10^2
Bu_3SnCl	1.00×10^{-3}	0.17	1.70×10^2
N-tributyltin succinimide	1.0×10^{-3}	0.20	2.0×10^2
Galvinoxyl			2.67×10^2
Bu_3Sn-Gal[b]			7.88×10^3

[a] Path length = 1 cm. [b] Galvinoxyl-tin radical coupling product.

The reduction of galvinoxyl by hydroquinone[19]. To 224.8 mg (0.532 mmole) of galvinoxyl in 20 ml of ether was added with stirring 29.3 mg (0.266 mmole) of hydroquinone. The color immediately changed from dark brown to red. The ether solution was concentrated to a heavy oil and the quinone removed by sublimation. The heavy red oil solidified on standing. The infrared spectrum was identical in all respects to that obtained in the previous experiment.

The rate of disappearance of galvinoxyl in the reduction of hexaalkylditin and N-chlorosuccinimide. The reaction vessel is shown in Fig. 5. Into the separate chambers of the vessel were pipetted 1.00 ml of 4.817×10^{-1} *M* hexabutylditin, 2.00 ml of 2.457×10^{-1} *M N*-chlorosuccinimide and 0.40 ml of 2.8×10^{-4} *M* galvinoxyl, followed by 6.60 ml chloroform distributed among the three chambers. The absorption cell

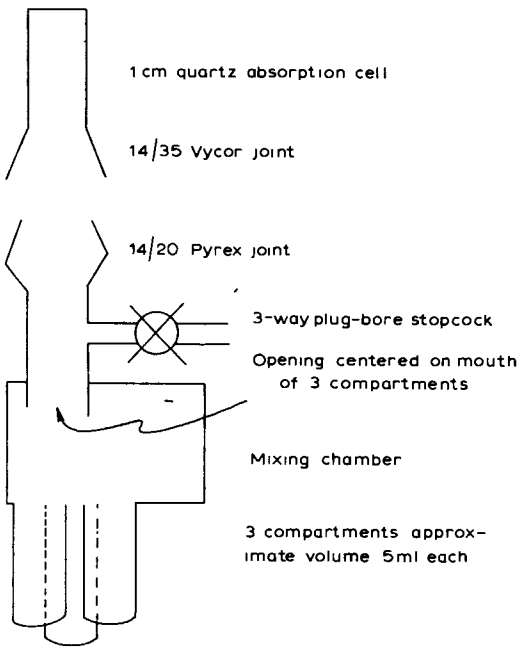

Fig. 5. Reaction vessel used for measurement of rate of disappearance of galvinoxyl in the presence of hexamethylditin and *N*-chlorosuccinimide.

was attached, and the lower half of the vessel immersed in a dry ice–acetone bath. Three freeze-pump-thaw cycles were performed and the vessel was equilibrated to 25.00°C. The vessel was inverted, pouring the contents of each compartment into the mixing chamber and shaken vigorously; the absorption cell was filled and the cell inserted into the DU, which was modified with a boxed opaque cell compartment to accommodate the size of the vessel. The rate of decrease in absorbance at 432 nm was followed. The control reaction (containing only ditin, solvent and galvinoxyl) was performed in an analogous manner.

The reaction of hexamethylditin and N-chlorosuccinimide in the presence of galvinoxyl and oxygen. This experiment was performed in the same way as the previous experiment; however, the reaction system was subjected to six freeze-pump-thaw cycles, equilibrated to 25.00°C and the absorbance recorded for 140 min. During this period, there was very little decrease in absorbance at 432 nm. The vessel was filled with an atmosphere made by mixing 1 ml of air with 99 ml of nitrogen in a gas burette (0.2% oxygen). The absorbance change was again recorded at intervals. After 170 minutes had passed (from original zero time), the system was frozen, evacuated, thawed, equilibrated in the thermostat bath for 15 min and filled with an atmosphere made by mixing 5 ml of air and 95 ml of nitrogen in a gas burette. Absorbance and time were again recorded until 240 minutes had passed from the original zero time. These data are recorded in Fig. 2.

The preparation of 1,1,4,4,-*tetramethyl*-2-*tetrazene**. Into 1 liter of water in a

* This procedure was adapted from that used for the preparation of 1,1,4,4-tetraphenyltetrazine [31]

3-neck round bottom flask fitted with an addition funnel (500 ml) was added 12 g (0.20 moles) of 1,1-dimethylhydrazine. To the aqueous solution was added 63 ml of concentrated hydrochloric acid (11.8 *N*). The solution was stirred and cooled in an ice bath. When the temperature reached 0°C, a solution of 11.5 g $KMnO_4$, in 500 ml of water was added dropwise such that the temperature did not go above 2°C. The permanganate color was immediately discharged upon addition. After all the permanganate was added (1.5 h), the solution was allowed to warm up to room temperature and made just basic to litmus with NaOH. The turbid solution was extracted with five 100 ml portions of pentane. The pentane solution was concentrated by distillation through a glass column packed with glass helices. A steam bath was used to remove the pentane at the lowest feasible temperature. The concentrate was subjected to vacuum distillation from room temperature to −78°C at 160 mm to remove the remaining pentane. The tetrazene was then vacuum distilled trap to trap at 1 mm Hg, yielding 5.8 g. (50%). The NMR spectrum in CCl_4 showed a singlet at δ2.72, the infrared showed strong absorptions at 2960, 2865, 2795, 1450 and 993 cm^{-1} with medium intensity bands at 1266, 1240, 1131, 810 cm^{-1}. The ultraviolet spectrum in ethanol gave λ_{max} 277 nm ($\varepsilon 9 \times 10^3$) with a shoulder at 248 nm. The reported ultraviolet spectrum gave λ_{max} 277 nm (ε 8.98 × 10^3)[29].

The photolysis of 1,1,4,4-*tetramethyl*-2-*tetrazene in chloroform.* Into a 5.00 ml volumetric flask, 352.9 mg (3.04 mmoles) of 1,1,4,4-tetramethyl-2-tetrazene was weighted and diluted to the mark with chloroform. The solution was transferred to a pyrex photolysis tube, the tube connected to a gas burette, and the solution irradiated for 70 h with a 100 watt mercury vapor lamp. The evolution of nitrogen was measured with time. The data are presented as a log function in Fig. 3, line I.

The photolysis of 1,1,4,4-*tetramethyl*-2-*tetrazene in chloroform in the presence of hexamethylditin.* Into a 5.00 ml volumetric flask, 353.0 mg (3.04 mmole) of 1,1,4,4-tetramethyl-2-tetrazene was weighed along with 974.3 mg (2.99 mmole) of hexamethylditin. The mixture was diluted to the mark with chloroform and photolyzed as in the previous experiment. The data are presented as a log function in Fig. 3, line II.

The photolysis of 1,1,4,4-*tetramethyl*-2-*tetrazene in octane.* This experiment was performed in an identical fashion to the previous experiments except that octane was used as a solvent. After photolysis for 72 h, tetramethylhydrazine formed a separate layer in the photolysis tube and was characterized by IR.

The photolysis of 1,1,4,4-*tetramethyl*-2-*tetrazene in octane in the presence of hexamethylditin.* By the same procedure as the previous experiments, 361.0 mg (3.11 mmoles) of 1,1,4,4-tetramethyl-2-tetrazene and 973.2 mg (2.99 mmoles) of hexamethylditin were photolyzed in octane. As the photolysis continued, a solid product began to precipitate, the amount of which increased with time. This product was removed by filtration. It sublimed at 80–85° and decomposed on heating to 120° in a sealed tube. Treatment with potassium fluoride in acetic acid precipitated trimethyltin fluoride (decomposed without melting above 98°C), indicating that the original solid product was trimethyl hydroxide. Examination of the octane solution by GLPC on UCW-98 on Chromosorb P at 100° isothermal showed that no tetramethylhydrazine was formed in this reaction. Extraction of the octane solution with 2 ml of water and treatment of the extract with ethanolic picric acid yielded dimethylammonium picrate, m.p. 156–158° (lit.[35] 158°), infrared bands 3200–3015, 2700–2300, 1610, 1510, 1540 cm^{-1}. This indicates that trimethyltin dimethylamide

was formed in the photolysis. The isolated products, trimethyltin hydroxide and dimethylamine, resulted from hydrolysis on exposure to the atmosphere.

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